Supporting Information

TADDOLs-based group of *P,S*-bidentate phosphoramidite ligands in palladium-catalyzed asymmetric allylic substitution

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

X-ray data was collected by using STOE diffractometer Pilatus100K detector, focusing mirror collimation Cu Kα (1.54086 Å) radiation, rotation method mode. STOE X-AREA software was used for cells refinement and data reduction. Data collection and image processing was performed with X-Area 1.67 (STOE & Cie GmbH, Darmstadt, Germany, 2013). Intensity data were scaled with LANA (part of X-Area) in order to minimize differences of intensities of symmetry-equivalent reflections (multi-scan method). The structures were solved and refined with SHELX[1] program. The non-hydrogen atoms were refined by using the anisotropic full matrix least-square procedure. Molecular geometry calculations were performed with the SHELX program, and the molecular graphics were prepared by using DIAMOND[2] software. The crystal data one can see in the Table S1 and can be obtained, free of charge, from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

All reactions were carried out under a dry argon atmosphere in flame-dried glassware and in freshly dried and distilled solvents. 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: ((4*R*,5*R*)-2,2-dimethyl-1,3-dioxolane-4,5-diyl)bis(diphenylmethanol) (**1a**) and ((4R,5*R*)-2-phenyl-1,3-dioxolane-4,5-diyl)bis(diphenylmethanol) (**1b**),[3] ((4*R*,5*R*)-2,2-dimethyl-1,3-dioxolane-4,5-diyl)bis(bis(4-(*tert*-

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butyl)phenyl)methanol) (**1c**),[4] ((4*R*,5*S*)-5-(hydroxymethyl)-2,2-dimethyl-1,3-dioxolan-4-yl)diphenylmethanol (**1d**),[5] *N*-methyl-2-(methylthio)ethan-1-amine (**2a**),[6] *N*-methylbutan-1-amine (**5**),[7] (*S*)-*N*-methyl-1-phenyl-2-(phenylthio)ethan-1-amine (**7**),[8] (*S*)-1-phenyl-*N*-(2-(phenylthio)ethyl)ethan-1-amine (**8**),[9] (*S*)-2-((phenylthio)methyl)pyrrolidine (**9**),[8] $[Pd(allyl)Cl]_2$ and (*E*)-1,3-diphenylallyl acetate (**10a**),[10] (*E*)-1,3-diphenylallyl ethyl carbonate (**10b**),[11] cinnamyl methyl carbonate (**12b**),[12] ethyl 2-acetamido-3-oxobutanoate (**15**)[13] and 2-(diethoxyphosphoryl)-1-phenylallyl acetate (**19**),[14] ligands $\mathbf{L_{A,B}}$.[15]

Pd-catalyzed allylic alkylation of (*E*)-1,3-diphenylallyl acetate (**10a**) and (*E*)-1,3-diphenylallyl ethyl carbonate (**10b**) with dimethyl malonate, di-*tert*-butyl malonate and dibenzyl malonate, their amination with pyrrolidine, allylic alkylation of cinnamyl acetate (**12a**) and cinnamyl methyl carbonate (**12b**) with ethyl 2-oxocyclohexane-1-carboxylate (**13**) and ethyl 2-acetamido-3-oxobutanoate (**15**), allylic alkylation of cinnamyl methyl carbonate (**12b**) with 2,5-dimethylpyrrole (**17**), allylic amination of 2-(diethoxyphosphoryl)-1-phenylallyl acetate (**19**) with aniline were performed according to the appropriate procedures.[14,16]

Thiophenol, 2-chloroacetamide, 2-mercapto-*N*-phenylacetamide (**S3**), 3-(methylthio)propan-1-amine (**S5**), 2-(*tert*-butylthio)-*N*-methylethan-1-amine (**2b**), 2-(methylthio)ethan-1-amine (**3a**), 2-(methylthio)ethan-1-ol (**6**), dimethyl malonate, di-*tert*-butyl malonate, dibenzyl malonate, BSA (*N*,*O*-bis(trimethylsilyl)acetamide), cinnamyl acetate (**12a**), ethyl 2-oxocyclohexane-1-carboxylate (**13**) and 2,5-dimethylpyrrole (**17**) were purchased from Aldrich and Acros Organics.

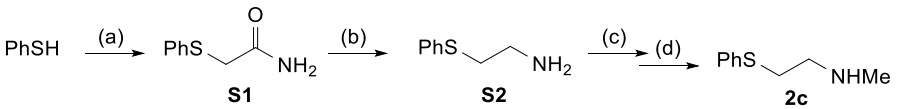
EXPERIMENTAL SECTION

Procedure for the Preparation of Thioether-amine 2c: 2-(Phenylthio)acetamide (**S1**). To a stirred solution of thiophenol (2.19 mL, 21.4 mmol) in methanol (25 mL) was added sodium methylate (1.16 g, 21.4 mmol) and 2-chloroacetamide (2 g, 21.4 mmol). Within 5 min, a precipitate of NaCl falls out. The reaction mixture was brought to a boil, cooled to 20 °C and H_2O (30 mL) was added. The resulting mixture was evaporated to half and extracted with $CHCl_3$ (3 x 30 mL). The combined organic phase was washed with 2 M NaOH, water and brine, dried over $MgSO_4$, filtered, and concentrated under vacuum (40 Torr). The product **S1** was obtained as white crystals, yield 3.19 g (89 %). The NMR spectra corresponds to the one described in the literature.[17]

2-(Phenylthio)ethan-1-amine (**S2**). $NaBH_4$ (3.59 g, 95 mmol) was added to a vigorously stirred solution of **S1** (3.18 g, 19 mmol) in THF (60 mL) at 0 °C. Then, a solution of I_2 (11.17 g, 44 mmol) in THF (30 mL) was added within 30 min at 0 °C. The reaction mixture was stirred for 2 h at 20 °C and boiled for 24 h. Then the mixture was quenched with methanol (60 mL) at 0 °C and concentrated under vacuum (40 Torr). The resulting residue was refluxed with 5 M KOH (60 mL) for 6 h. The mixture was cooled to 20 °C and the product was extracted with CH_2Cl_2 (4 x 50 mL). The combined extract was washed with brine, dried over Na_2SO_4, filtered and concentrated under vacuum (40 Torr). The product was distilled in the vacuum. Colorless oil, yield 1.95 g, (67 %). Bp 64–65 °C (0.2 torr). The NMR spectra corresponds to the one described in the literature.[18]

A solution of **S2** (1.95 g, 12.7 mmol) in ethyl formate (12 mL) was refluxed for 6 h and concentrated under reduced pressure (40 Torr). The *N*-formyl derivative of **S2** was obtained as beige powder, yield 2.28 g (99%).

N-Methyl-2-(phenylthio)ethan-1-amine (**2c**). To a vigorously stirred cold suspension of $LiAlH_4$ (0.38 g, 9.9 mmol) in THF (20 mL) the crude *N*-(2-(phenylthio)ethyl)formamide (1.2 g, 6.6 mmol) was added portionwise. The resulting mixture was allowed to warm up to room temperature, refluxed for 6 h and quenched with 0.7 mL H_2O and 0.13 g KOH at 0 °C. The reaction mixture was then shortly heated up to boiling point, cooled down to room temperature and filtered. The filter cake was washed with THF (25 mL) and CH_2Cl_2 (2 × 15 mL), the combined filtrates were concentrated under reduced pressure (40 Torr). The product was distilled in the vacuum. Colorless oil, yield 0.92 g, (83 %). Bp 68–70 °C (0.2 Torr). The NMR spectra corresponds to the one described in the literature.[19]



a) NaOMe, MeOH, $ClCH_2C(O)NH_2$; b) $NaBH_4$, I_2, THF; c) HCO_2Et, reflux; d) $LiAlH_4$, THF.

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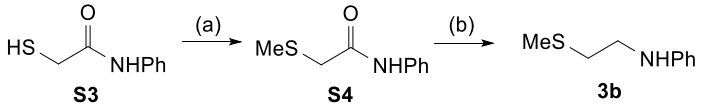
EXPERIMENTAL SECTION

Procedure for the Preparation of Thioether-amine 3b: 2-(Methylthio)-*N*-phenylacetamide (**S4**). To a stirred solution of 2-mercapto-*N*-phenylacetamide (**S3**) (4.0 g, 24 mmol) in methanol (60 mL) was added NaOH (1.0 g, 25 mmol). The reaction mixture was stirred for 10 min and methyl iodide (1.57 mL, 25 mmol) was added at 0 °C. The resulting mixture was stirred overnight at 20 °C, concentrated under vacuum (40 Torr) and the obtained residue was dissolved in H_2O (50 mL). The product was extracted with ethyl acetate (3 x 40 mL), the combined organic phase was dried over Na_2SO_4, filtered and concentrated under vacuum (40 Torr). The compound **S4** was obtained as beige powder, yield 4.0 g (92%). The NMR spectra corresponds to the one described in the literature.[20]

N-(2-(methylthio)ethyl)aniline (**3b**). To a vigorously stirred cold suspension of $LiAlH_4$ (1.26 g, 33 mmol) in THF (60 mL) the compound **S4** (4.0 g, 22 mmol) was added portionwise. The resulting mixture was allowed to warm up to room temperature, refluxed for 8 h and quenched with 2.38 mL H_2O and 0.43 g KOH at 0 °C. The reaction mixture was then shortly heated up to boiling point, cooled down to room temperature and filtered. The filter cake was washed with THF (40 mL) and CH_2Cl_2 (2 × 25 mL), the combined filtrates were concentrated under reduced pressure (40 Torr). The obtained residue was purified by column chromatography on SiO_2 (petroleum ether/ethyl acetate 10/1). The product was obtained as yellowish viscous oil, yield 2.8 g (76 %). The NMR spectra corresponds to the one described in the literature.[21]



S3 **S4** **3b**

a) NaOH, CH_3I, MeOH; b) $LiAlH_4$, THF.

Procedure for the Preparation of Thioether-amine 4: A solution of 3-(methylthio)propan-1-amine (**S5**) (4.49 mL, 40 mmol) in ethyl formate (30 mL) was refluxed for 6 h and concentrated under reduced pressure (40 Torr). The residue was purified by bulb-to-bulb vacuum distillation (b. p. 156-157 °C, bath, 3 Torr) to give *N*-formyl derivative of **S5** as clear oil.

To a vigorously stirred cold suspension of $LiAlH_4$ (1.71 g, 45 mmol) in THF (50 mL) the crude *N*-(3-(methylthio)propyl)formamide (4.0 g, 30 mmol) was added portionwise. The resulting mixture was allowed to warm up to room temperature, refluxed for 6 h and quenched with 3.3 mL H_2O and 0.59 g KOH at 0 °C. The reaction mixture was then shortly heated up to boiling point, cooled down to room temperature and filtered. The filter cake was washed with THF (50 mL) and CH_2Cl_2 (2 × 30 mL), the combined filtrates were concentrated under reduced pressure (40 Torr) and the residue was purified by bulb-to-bulb vacuum distillation.

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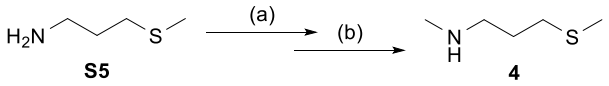

a) HCO_2Et, reflux; b) $LiAlH_4$, THF.

N-Methyl-3-(methylthio)propan-1-amine (**4**): Colorless oil, yield 3.08 g (86 %). Bp 162–163 °C (bath, 6 Torr). ^{1}H NMR (400.1 MHz, $CDCl_3$, 25 ^{o}C): δ 0.97 (br.s, 1H; NH), 1.77 (m, 2H; CH_2), 2.09 (s, 3H; CH_3), 2.42 (s, 3H; CH_3), 2.54 (t, ^3J(H,H) = 7.3 Hz, 2H; CH_2), 2.66 (t, ^3J(H,H) = 7.0 Hz, 2H; CH_2). $C_5H_{13}NS$ (119.08): calcd. C, 50.37; H, 10.99; N, 11.75; found C, 50.51; H, 11.04; N, 11.70.

General Procedure for the Preparation of Ligands: A solution of the appropriate (*R,R*)- or (*S,S*)-diol **1a-d** (4.0 mmol) in THF (30 mL) was added dropwise at - 10 °C over 10 min to a vigorously stirred solution of PCl_3 (0.37 mL, 4.2 mmol) and Et_3N (1.17 mL, 8.4 mmol) in THF (12 mL). The reaction mixture was brought to 20°C and allowed to stir for 2 h. Solid Et_3N·HCl was filtered off, and the filtrate was concentrated in vacuum (40 Torr). The residue was triturated in pentane and dried in vacuum (10^{-3} Torr) for 8 h.

The relevant compound **2-9** (2 mmol) was added at 20 °C in one portion to a vigorously stirred solution of the appropriate phosphorylating reagent (2 mmol) and Et_3N (0.56 mL, 4 mmol) in toluene (15 mL). The reaction mixture was stirred during 24 h at 20°C and filtered through a short column with SiO_2/Al_2O_3, the column was washed with toluene (2 x 20 mL), and the solvent was evaporated under reduced pressure (40 Torr). Products were additionally purified by flash chromatography on SiO_2 (toluene). The obtained ligands were dried in vacuum (10^{-3} Torr) for 8 h.

(3a*R*,8a*R*)-6-[*N*-methyl-2-(methylthio)ethan-1-amino]-2,2-dimethyl-4,4,8,8-tetraphenyltetrahydro-[1,3]dioxolo[4,5-*e*][1,3,2]dioxaphosphepin (**L1a**): Yellowish powder, yield 0.66 g (55 %). ^{1}H NMR (499.9 MHz, $CDCl_3$): δ 0.29 (s, 3H; CH_3), 1.25 (s, 3H; CH_3), 2.04 (s, 3H; CH_3), 2.55-2.62 (ddd, $^2J_{H,H}$ = 13.3 Hz, $^3J_{H,H}$ = 8.8 Hz, $^3J_{H,H}$ = 6.5 Hz, 1H; CH_2S), 2.63-2.69 (ddd, $^2J_{H,H}$ = 13.3 Hz, $^3J_{H,H}$ = 8.4 Hz, $^3J_{H,H}$ = 6.7 Hz, 1H; CH_2S), 2.78 (d, $^3J_{H,P}$ = 8.4 Hz, 3H; NCH_3), 3.22-3.29 (m, 2H; NCH_2), 4.82 (d, $^3J_{H,H}$ = 8.5 Hz, 1H; OCH), 5.16 (dd, $^3J_{H,H}$ = 8.5 Hz, $^4J_{H,P}$ = 3.2 Hz, 1H; OCH), 7.15-7.35 (m, 12H; CH(Ph)), 7.40 (d, $^3J_{H,H}$ = 7.6 Hz, 2H; CH(Ph)), 7.46 (d, $^3J_{H,H}$ = 7.6 Hz, 2H; CH(Ph)), 7.59 (d, $^3J_{H,H}$ = 7.6 Hz, 2H; CH(Ph)), 7.73 (d, $^3J_{H,H}$ = 7.6 Hz, 2H; CH(Ph)). ^{13}C{^{1}H} NMR (125.7 Hz, $CDCl_3$): δ 15.64 (s; SCH_3), 25.62 (s; CCH_3), 27.65 (s; CCH_3), 32.24 (d, $^2J_{C,P}$ = 14.1 Hz; NCH_3), 33.29 (d, $^3J_{C,P}$ = 4.3 Hz; CH_2S), 48.87 (d, $^2J_{C,P}$ = 27.3 Hz; NCH_2), 81.65 (d, $^2J_{C,P}$ = 8.0 Hz; CPh_2), 82.38 (d, $^3J_{C,P}$ = 20.1 Hz; OCH), 82.49 (d, $^3J_{C,P}$ = 3.1 Hz; OCH), 82.50 (s; CPh_2), 111.93 (s; $\underline{C}(CH_3)_2$), 127.22 (s; CH(Ph)), 127.24 (s; CH(Ph)), 127.31 (s; CH(Ph)), 127.40 (s; CH(Ph)), 127.41 (s; CH(Ph)), 127.54 (s; CH(Ph)), 127.60 (s; CH(Ph)), 127.84 (s; CH(Ph)), 128.19 (s; CH(Ph)), 129.03 (s; CH(Ph)), 129.07 (s; CH(Ph)), 129.18 (s; CH(Ph)), 141.95 (s; C(Ph)), 142.38 (d; $^3J_{C,P}$ = 1.9 Hz, C(Ph)), 146.73 (d, $^3J_{C,P}$ = 1.9 Hz;

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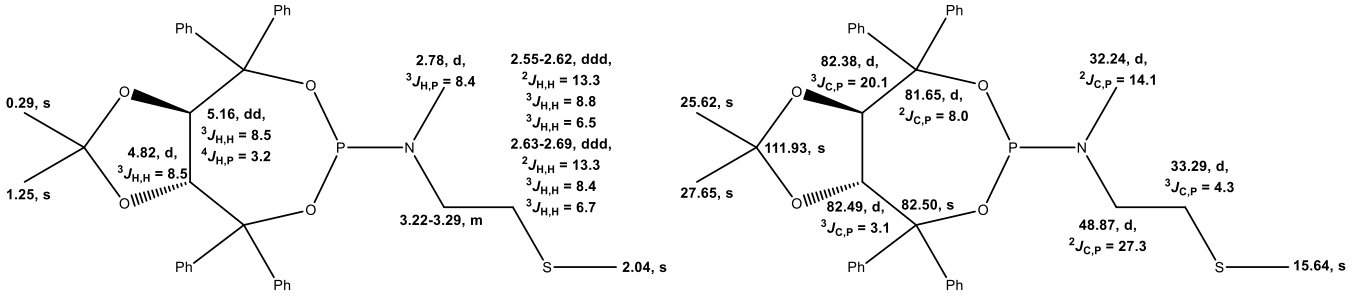
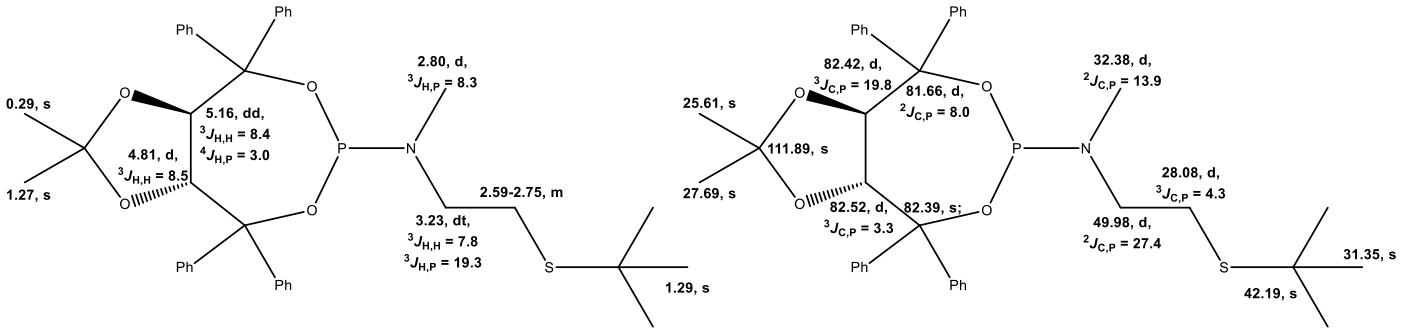
C(Ph)), 147.07 (s; C(Ph)). $^{31}P\{^{1}H\}$ NMR (202.4 Hz, $CDCl_3$): δ 139.91 (s). $C_{35}H_{38}NO_4PS$ (599.23): calcd. C, 70.10; H, 6.39; N, 2.34; found C, 70.35; H, 6.46; N, 2.26.



^{1}H (left) and $^{13}C\{^{1}H\}$ (right) NMR Signal Assignment for **L1a**.

(3a*R*,8a*R*)-6-[2-(*tert*-butylthio)-*N*-methylethan-1-amino]-2,2-dimethyl-4,4,8,8-tetraphenyltetrahydro-[1,3]dioxolo[4,5-*e*][1,3,2]dioxaphosphepin (**L1b**): White powder, yield 1.26 g (98 %). ^{1}H NMR (499.9 MHz, $CDCl_3$): δ 0.29 (s, 3H; CH_3), 1.27 (s, 3H; CH_3), 1.29 (s, 9H, $C(CH_3)_3$), 2.59-2.75 (m, 2H; CH_2S), 2.80 (d, $^{3}J_{H,P}$ = 8.3 Hz, 3H; NCH_3), 3.23 (dt, $^{3}J_{H,P}$ = 19.3 Hz, $^{3}J_{H,H}$ = 7.8 Hz, 2H; NCH_2), 4.81 (d, $^{3}J_{H,H}$ = 8.5 Hz, 1H; CH), 5.16 (dd, $^{3}J_{H,H}$ = 8.4 Hz, $^{4}J_{H,P}$ = 3.0 Hz, 1H; CH), 7.11-7.33 (m, 12H; CH(Ph)), 7.40 (d, $^{3}J_{H,H}$ = 7.4 Hz, 2H; CH(Ph)), 7.46 (d, $^{3}J_{H,H}$ = 7.5 Hz, 2H; CH(Ph)), 7.59 (d, $^{3}J_{H,H}$ = 7.5 Hz, 2H; CH(Ph)), 7.74 (d, $^{3}J_{H,H}$ = 7.5 Hz, 2H; CH(Ph)). $^{13}C\{^{1}H\}$ NMR (125.7 Hz, $CDCl_3$): δ 25.45 (s; CCH_3), 27.52 (s; CCH_3), 27.92 (d, $^{3}J_{C,P}$ = 4.5 Hz; CH_2S), 31.20 (s; $C(\underline{C}H_3)_3$), 32.22 (d, $^{2}J_{C,P}$ = 14.2 Hz; NCH_3), 42.02 (s; $\underline{C}(CH_3)_3$), 49.82 (d, $^{2}J_{C,P}$ = 27.4 Hz; NCH_2), 81.50 (d, $^{2}J_{C,P}$ = 8.0 Hz; CPh_2), 82.22 (s; CPh_2), 82.26 (d, $^{3}J_{C,P}$ = 19.9 Hz; OCH), 82.43 (d, $^{3}J_{C,P}$ = 3.6 Hz; OCH), 111.73 (s; $\underline{C}(CH_3)_2$), 127.20 (s; CH(Ph)), 127.26 (s; CH(Ph)), 127.33 (s; CH(Ph)), 127.40 (s; CH(Ph)), 127.42 (s; CH(Ph)), 127.57 (s; CH(Ph)), 127.59 (s; CH(Ph)), 127.85 (s; CH(Ph)), 128.23 (s; CH(Ph)), 129.05 (s; CH(Ph)), 129.09 (s; CH(Ph)), 129.24 (s; CH(Ph)), 141.99 (s; C(Ph)), 142.43 (s; C(Ph)), 146.74 (s; C(Ph)), 147.12 (s; C(Ph)). $^{31}P\{^{1}H\}$ NMR (202.4 Hz, $CDCl_3$): δ 139.85 (s) ppm. $C_{38}H_{44}NO_4PS$ (641.27): calcd. C, 71.11; H, 6.91; N, 2.18; found C, 71.34; H, 7.01; N, 2.24.



^{1}H (left) and $^{13}C\{^{1}H\}$ (right) NMR Signal Assignment for **L1b**.

(3a*R*,8a*R*)-6-[*N*-methyl-2-(phenylthio)ethan-1-amino]-2,2-dimethyl-4,4,8,8-tetraphenyltetrahydro-[1,3]dioxolo[4,5-*e*][1,3,2]dioxaphosphepin (**L1c**): White powder, yield 1.03 g (78 %). ^{1}H NMR (499.9 MHz, $CDCl_3$): δ 0.29 (s, 3H; CH_3), 1.25 (s, 3H; CH_3), 2.79 (d, $^{3}J_{H,P}$ = 8.4 Hz, 3H; NCH_3), 2.98-3.12 (m, 2H; CH_2S),

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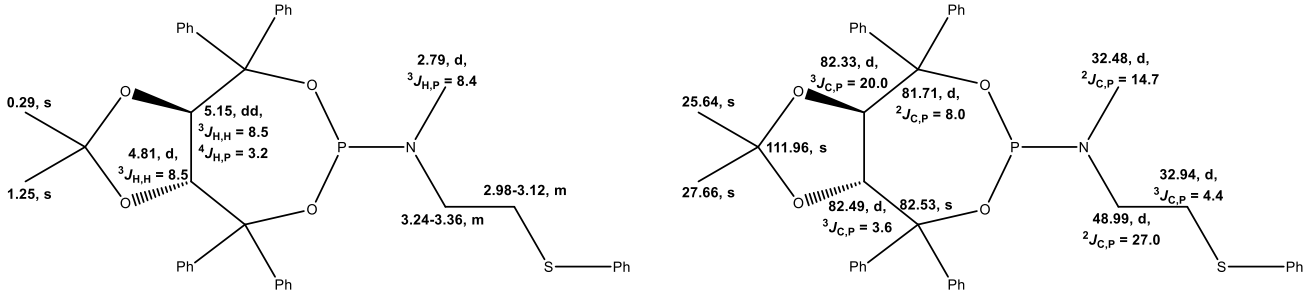
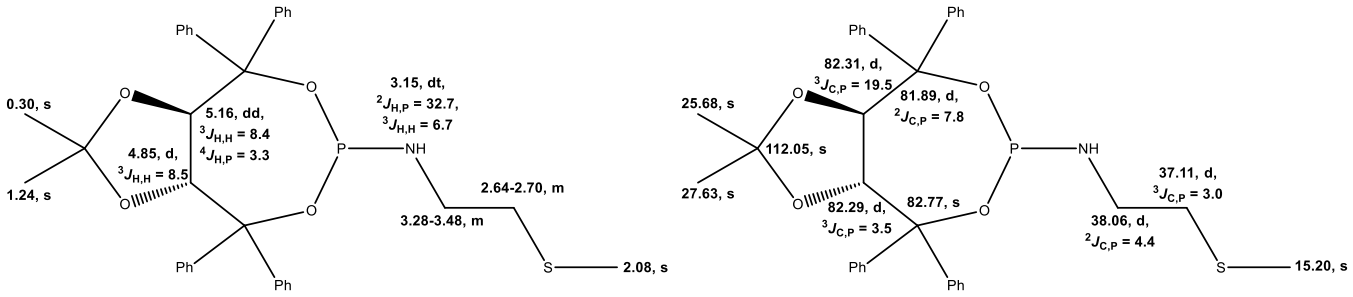
3.24-3.36 (m, 2H; NCH_2), 4.81 (d, $^3J_{H,H}$ = 8.5 Hz, 1H; CH), 5.15 (dd, $^3J_{H,H}$ = 8.5 Hz, $^4J_{H,P}$ = 3.2 Hz, 1H; CH), 7.15-7.35 (m, 17H; CH(Ph)), 7.36 (d, $^3J_{H,H}$ = 7.7 Hz, 2H; CH(Ph)), 7.45 (d, $^3J_{H,H}$ = 7.7 Hz, 2H; CH(Ph)), 7.58 (d, $^3J_{H,H}$ = 7.6 Hz, 2H; CH(Ph)), 7.72 (d, $^3J_{H,H}$ = 7.6 Hz, 2H; CH(Ph)). $^{13}C\{^1H\}$ NMR (125.7 Hz, $CDCl_3$): δ 25.64 (s; CCH_3), 27.66 (s; CCH_3), 32.48 (d, $^2J_{C,P}$ = 14.7 Hz; NCH_3), 32.94 (d, $^3J_{C,P}$ = 4.4 Hz; CH_2S), 48.99 (d, $^2J_{C,P}$ = 27.0 Hz; NCH_2), 81.71 (d, $^2J_{C,P}$ = 8.0 Hz; CPh_2), 82.33 (d, $^3J_{C,P}$ = 20.0 Hz; OCH), 82.49 (d, $^3J_{C,P}$ = 3.6 Hz; OCH), 82.53 (s; CPh_2), 111.96 (s; $\underline{C}(CH_3)_2$), 126.16 (s; CH(Ph)), 127.23 (s; CH(Ph)), 127.27 (s; CH(Ph)), 127.31 (s; CH(Ph)), 127.42 (s; CH(Ph)), 127.43 (s; CH(Ph)), 127.58 (s; CH(Ph)), 127.64 (s; CH(Ph)), 127.88 (s; CH(Ph)), 128.25 (s; CH(Ph)), 129.05 (s; CH(Ph)), 129.08 (s; CH(Ph)), 129.20 (s; CH(Ph)), 129.54 (s; CH(Ph)), 136.36 (s; C(Ph)), 141.91 (s; C(Ph)), 142.36 (d; $^3J_{C,P}$ = 1.9 Hz, C(Ph)), 146.72 (d; $^3J_{C,P}$ = 1.9 Hz, C(Ph)), 147.04 (s; C(Ph)). $^{31}P\{^1H\}$ NMR (202.4 Hz, $CDCl_3$): δ 140.03 (s). $C_{40}H_{40}NO_4PS$ (661.24): calcd. C, 72.60; H, 6.09; N, 2.12; found C, 72.92; H, 6.00; N, 2.01.



^1H (left) and $^{13}C\{^1H\}$ (right) NMR Signal Assignment for **L1c**.

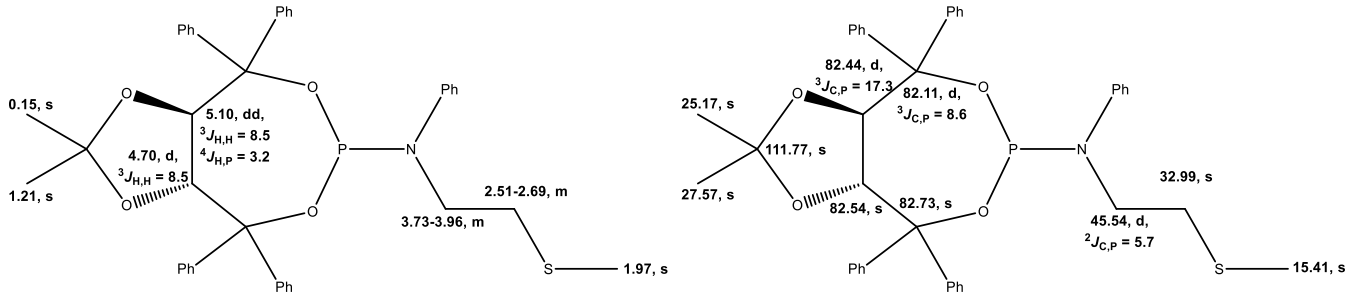
(3a*R*,8a*R*)-6-[2-(methylthio)ethan-1-amino]-2,2-dimethyl-4,4,8,8-tetraphenyltetrahydro-[1,3]dioxolo[4,5-*e*][1,3,2]dioxaphosphepin (**L1d**): White powder, yield 0.39 g (33 %). ^1H NMR (499.9 MHz, $CDCl_3$): δ 0.30 (s, 3H; CH_3), 1.24 (s, 3H; CH_3), 2.08 (s, 3H; CH_3), 2.64-2.70 (m, 2H; CH_2S), 3.15 (dt, $^2J_{H,P}$ = 32.7 Hz, $^2J_{H,H}$ = 6.7 Hz, 1H; NH), 3.28-3.48 (m, 2H; NCH_2), 4.85 (d, $^3J_{H,H}$ = 8.5 Hz, 1H; OCH), 5.16 (dd, $^3J_{H,H}$ = 8.4 Hz, $^4J_{H,P}$ = 3.3 Hz, 1H; OCH), 7.16-7.36 (m, 12H; CH(Ph)), 7.40 (d, $^3J_{H,H}$ = 7.7 Hz, 2H; CH(Ph)), 7.47 (d, $^3J_{H,H}$ = 7.8 Hz, 2H; CH(Ph)), 7.60 (d, $^3J_{H,H}$ = 7.8 Hz, 2H; CH(Ph)), 7.72 (d, $^3J_{H,H}$ = 7.7 Hz, 2H; CH(Ph)). $^{13}C\{^1H\}$ NMR (125.7 Hz, $CDCl_3$): δ 15.20 (s; SCH_3), 25.68 (s; CCH_3), 27.63 (s; CCH_3), 37.11 (d, $^3J_{C,P}$ = 3.0 Hz; CH_2S), 38.06 (d, $^2J_{C,P}$ = 4.4 Hz; NCH_2), 81.89 (d, $^2J_{C,P}$ = 7.8 Hz; CPh_2), 82.29 (d, $^3J_{C,P}$ = 3.5 Hz; OCH), 82.31 (d, $^3J_{C,P}$ = 19.5 Hz; OCH), 82.77 (s; CPh_2), 112.05 (s; $\underline{C}(CH_3)_2$), 127.26 (s; CH(Ph)), 127.31 (s; CH(Ph)), 127.36 (s; CH(Ph)), 127.42 (s; CH(Ph)), 127.51 (s; CH(Ph)), 127.55 (s; CH(Ph)), 127.67 (s; CH(Ph)), 127.90 (s; CH(Ph)), 128.27 (s; CH(Ph)), 129.08 (s; CH(Ph)), 129.12 (s; CH(Ph)), 129.18 (s; CH(Ph)), 141.90 (d, $^3J_{C,P}$ = 1.9 Hz; C(Ph)), 142.31 (d, $^3J_{C,P}$ = 1.9 Hz; C(Ph)), 146.67 (d, $^3J_{C,P}$ = 1.9 Hz; C(Ph)), 146.90 (s; C(Ph)). $^{31}P\{^1H\}$ NMR (202.4 Hz, $CDCl_3$): δ 136.06 (s). $C_{34}H_{36}NO_4PS$ (585.21): calcd. C, 69.72; H, 6.20; N, 2.39; found C, 70.02; H, 6.29; N, 2.30.

EXPERIMENTAL SECTION



^{1}H (left) and ^{13}C{^{1}H} (right) NMR Signal Assignment for **L1d**.

(3a*R*,8a*R*)-6-[*N*-(2-(methylthio)ethyl)anilino]-2,2-dimethyl-4,4,8,8-tetraphenyltetrahydro-[1,3]dioxolo[4,5-*e*][1,3,2]dioxaphosphepin (**L1e**): White powder, yield 0.53 g (40 %). ^{1}H NMR (400.1 MHz, $CDCl_3$): δ 0.15 (s, 3H; CH_3), 1.21 (s, 3H; CH_3), 1.97 (s, 3H; CH_3), 2.51-2.69 (m; CH_2S), 3.73-3.96 (m, 2H; NCH_2), 4.70 (d, $^3J_{H,H}$ = 8.5 Hz, 1H; OCH), 5.10 (dd, $^3J_{H,H}$ = 8.5 Hz, $^4J_{H,P}$ = 3.2 Hz, 1H; OCH), 6.94 (t, $^3J_{H,H}$ = 7.2 Hz, 1H; CH(Ph)), 7.02 (t, $^3J_{H,H}$ = 7.9 Hz, 2H; CH(Ph)), 7.07-7.22 (m, 16H; CH(Ph)), 7.26-7.31 (m, 2H; CH(Ph)), 7.50 (d, $^3J_{H,H}$ = 7.2 Hz, 2H; CH(Ph)), 7.64 (d, $^3J_{H,H}$ = 7.5 Hz, 2H; CH(Ph)). ^{13}C{^{1}H} NMR (100.6 Hz, $CDCl_3$): δ 15.41 (s; SCH_3), 25.17 (s; CCH_3), 27.57 (s; CCH_3), 32.99 (s; CH_2S), 45.54 (d, $^2J_{C,P}$ = 5.7 Hz; NCH_2), 82.11 (d, $^2J_{C,P}$ = 8.6 Hz; CPh_2), 82.44 (d, $^3J_{C,P}$ = 17.3 Hz; OCH), 82.54 (s; OCH), 82.73 (s; CPh_2), 111.77 (s; $\underline{C}(CH_3)_2$), 123.27 (s; CH(Ph)), 123.40 (s; CH(Ph)), 127.14 (s; CH(Ph)), 127.21 (s; CH(Ph)), 127.46 (s; CH(Ph)), 127.60 (s; CH(Ph)), 127.73 (s; CH(Ph)), 128.14 (s; CH(Ph)), 128.31 (s; CH(Ph)), 128.68 (s; CH(Ph)), 128.73 (s; CH(Ph)), 129.00 (s; CH(Ph)), 141.24 (s; C(Ph)), 141.78 (s; C(Ph)), 143.98 (d; $^2J_{C,P}$ = 21.6 Hz; NC(Ph)), 146.01 (s; C(Ph)), 146.64 (s; C(Ph)). ^{31}P{^{1}H} NMR (162.0 Hz, $CDCl_3$): δ 137.04 (s). $C_{40}H_{40}NO_4PS$ (661.24): calcd. C, 72.60; H, 6.09; N, 2.12; found C, 72.74; H, 6.15; N, 2.18.



^{1}H (left) and ^{13}C{^{1}H} (right) NMR Signal Assignment for **L1e**.

(3a*R*,8a*R*)-6-[*N*-methyl-3-(methylthio)propan-1-amino]-2,2-dimethyl-4,4,8,8-tetraphenyltetrahydro-[1,3]dioxolo[4,5-*e*][1,3,2]dioxaphosphepin (**L1f**): White powder, yield 1.2 g (98 %). ^{1}H NMR (499.9 MHz, $CDCl_3$): δ 0.30 (s, 3H; CH_3), 1.25 (s, 3H; CH_3), 2.03 (s, 3H; CH_3), 1.75-1.86 (m, 2H; CH_2), 2.39-2.49 (m, 2H; CH_2S), 2.76 (d, $^3J_{H,P}$ = 7.8 Hz, 3H; NCH_3), 3.07-3.19 (m, 2H; NCH_2), 4.81 (d, $^3J_{H,H}$ = 8.5 Hz, 1H; OCH), 5.17 (dd, $^3J_{H,H}$ = 8.4 Hz, $^4J_{H,P}$ = 3.1 Hz, 1H; OCH), 7.16-7.31 (m, 12H; CH(Ph)), 7.40 (d, $^3J_{H,H}$ = 7.7 Hz, 2H; CH(Ph)), 7.45 (d, $^3J_{H,H}$ = 7.8 Hz, 2H; CH(Ph)), 7.58 (d, $^3J_{H,H}$ = 7.8 Hz, 2H; CH(Ph)), 7.73 (d,

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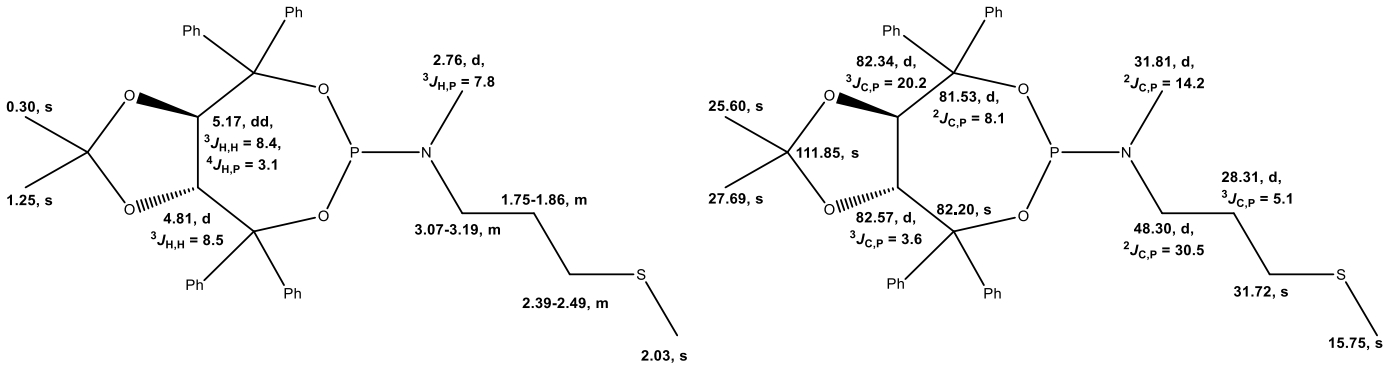
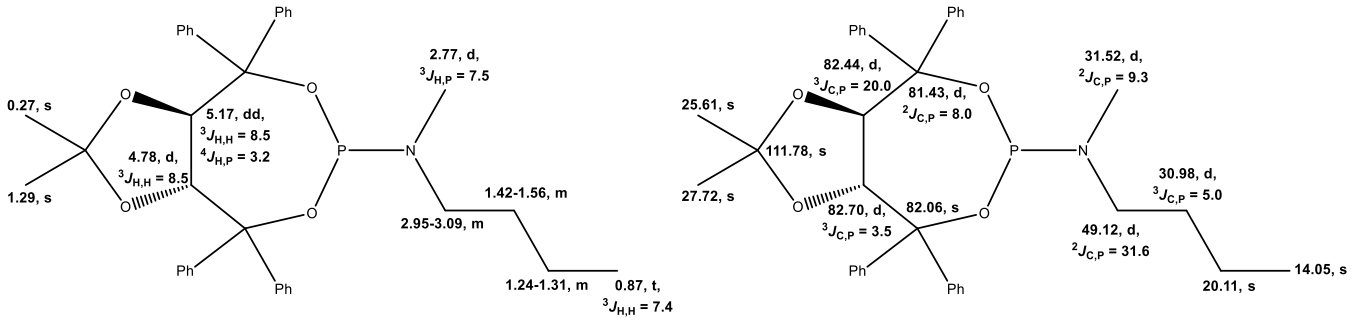
$^{3}J_{H,H}$ = 7.8 Hz, 2H; CH(Ph)). $^{13}C\{^{1}H\}$ NMR (125.7 Hz, $CDCl_3$): δ 15.75 (s; SCH_3), 25.60 (s; CCH_3), 27.69 (s; CCH_3), 28.31 (d, $^{3}J_{C,P}$ = 5.1 Hz; CH_2), 31.72 (s; CH_2S), 31.81 (d, $^{2}J_{C,P}$ = 14.2 Hz; NCH_3), 48.30 (d, $^{2}J_{C,P}$ = 30.5 Hz; NCH_2), 81.53 (d, $^{2}J_{C,P}$ = 8.1 Hz; CPh_2), 82.20 (s; CPh_2), 82.34 (d, $^{3}J_{C,P}$ = 20.2 Hz; OCH), 82.57 (d, $^{3}J_{C,P}$ = 3.6 Hz; OCH), 111.85 (s; $\underline{C}(CH_3)_2$), 127.18 (s; CH(Ph)), 127.20 (s; CH(Ph)), 127.23 (s; CH(Ph)), 127.33 (s; CH(Ph)), 127.41 (s; CH(Ph)), 127.59 (s; CH(Ph)), 127.60 (s; CH(Ph)), 127.83 (s; CH(Ph)), 129.04 (s; CH(Ph)), 129.06 (s; CH(Ph)), 129.25 (s; CH(Ph)), 142.04 (d, $^{3}J_{C,P}$ = 1.9 Hz; C(Ph)), 142.48 (d, $^{3}J_{C,P}$ = 1.9 Hz; C(Ph)), 146.82 (d, $^{3}J_{C,P}$ = 1.9 Hz; C(Ph)), 147.14 (s; C(Ph)). $^{31}P\{^{1}H\}$ NMR (202.4 Hz, $CDCl_3$): δ 140.21(s). $C_{36}H_{40}NO_4PS$ (613.24): calcd. C, 70.45; H, 6.57; N, 2.28; found C, 70.62; H, 6.61; N, 2.33.



^{1}H (left) and $^{13}C\{^{1}H\}$ (right) NMR Signal Assignment for **L1f**.

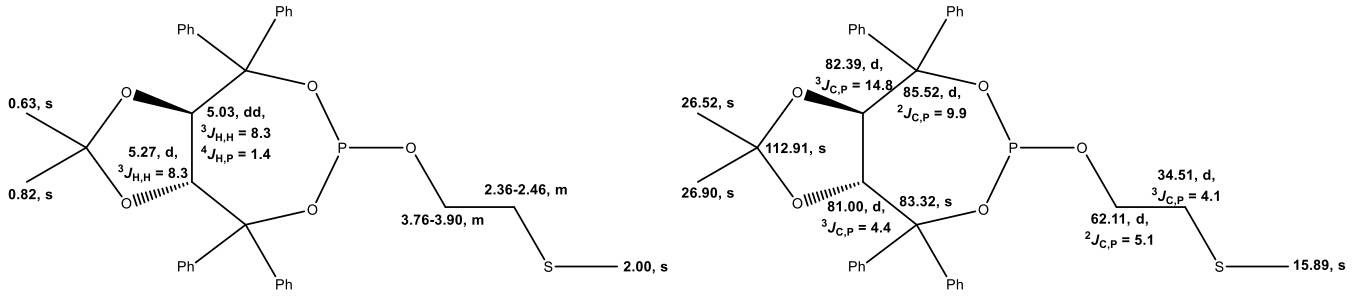
(3a*R*,8a*R*)-6-[*N*-methylbutan-1-amino]-2,2-dimethyl-4,4,8,8-tetraphenyltetrahydro-[1,3]dioxolo[4,5-*e*][1,3,2]dioxaphosphepin (**L1g**): White powder, yield 1.14 g (98 %). ^{1}H NMR (499.9 MHz, $CDCl_3$): δ 0.27 (s, 3H; CH_3), 0.87 (t, $^{3}J_{H,H}$ = 7.4 Hz, 3H; CH_3), 1.24-1.31 (m, 2H; CH_2), 1.42-1.56 (m, 2H; CH_2), 2.77 (d, $^{3}J_{H,P}$ = 7.5 Hz, 3H; NCH_3), 2.95-3.09 (m, 2H; NCH_2), 4.78 (d, $^{3}J_{H,H}$ = 8.5 Hz, 1H; OCH), 5.17 (dd, $^{3}J_{H,H}$ = 8.5 Hz, $^{4}J_{H,P}$ = 3.2 Hz, 1H; OCH), 7.14-7.32 (m, 12H; CH(Ph)), 7.41 (d, $^{3}J_{H,H}$ = 7.8 Hz, 2H; CH(Ph)), 7.47 (d, $^{3}J_{H,H}$ = 7.8 Hz, 2H; CH(Ph)), 7.59 (d, $^{3}J_{H,H}$ = 7.8 Hz, 2H; CH(Ph)), 7.75 (d, $^{3}J_{H,H}$ = 7.8 Hz, 2H; CH(Ph)). $^{13}C\{^{1}H\}$ NMR (125.7 Hz, $CDCl_3$): δ 14.05 (s; CH_3), 20.11 (s; CH_2), 25.61 (s; CCH_3), 27.72 (s; CCH_3), 30.98 (d, $^{3}J_{C,P}$ = 5.0 Hz; CH_2), 31.52 (d, $^{2}J_{C,P}$ = 9.3 Hz; NCH_3), 49.12 (d, $^{2}J_{C,P}$ = 31.6 Hz; NCH_2), 81.43 (d, $^{2}J_{C,P}$ = 8.0 Hz; CPh_2), 82.06 (s; CPh_2), 82.44 (d, $^{3}J_{C,P}$ = 20.0 Hz; OCH), 82.70 (d, $^{3}J_{C,P}$ = 3.5 Hz; OCH), 111.78 (s; $\underline{C}(CH_3)_2$), 127.12 (s; CH(Ph)), 127.15 (s; CH(Ph)), 127.22 (s; CH(Ph)), 127.35 (s; CH(Ph)), 127.47 (s; CH(Ph)), 127.53 (s; CH(Ph)), 127.56 (s; CH(Ph)), 127.79 (s; CH(Ph)), 128.16 (s; CH(Ph)), 129.06 (s; CH(Ph)), 129.08 (s; CH(Ph)), 129.28 (s; CH(Ph)), 142.22 (s; C(Ph)), 142.63 (d, $^{3}J_{C,P}$ = 1.9 Hz; C(Ph)), 146.96 (d, $^{3}J_{C,P}$ = 1.9 Hz; C(Ph)), 147.27 (s; C(Ph)). $^{31}P\{^{1}H\}$ NMR (202.4 Hz, $CDCl_3$): δ 139.80 (s). $C_{36}H_{40}NO_4P$ (581.27): calcd. C, 74.33; H, 6.93; N, 2.41; found C, 74.55; H, 7.00; N, 2.34.

EXPERIMENTAL SECTION



^{1}H (left) and ^{13}C{^{1}H} (right) NMR Signal Assignment for **L1g**.

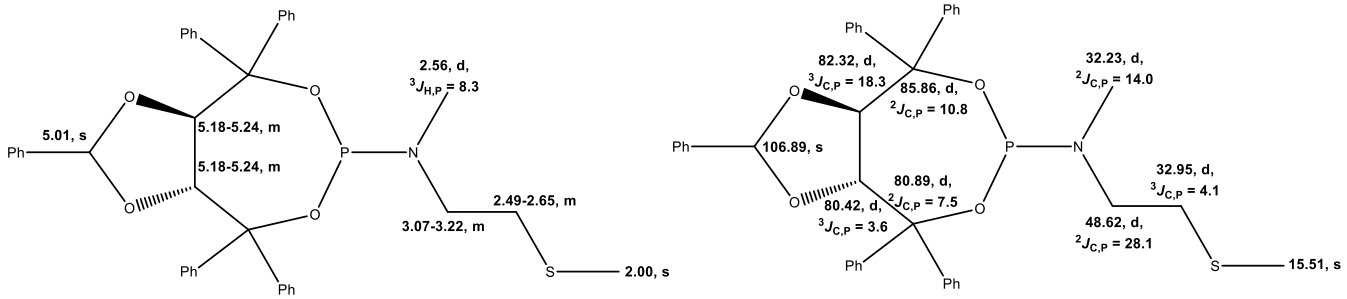
(3a*R*,8a*R*)-6-[2-(methylthio)ethoxy]-2,2-dimethyl-4,4,8,8-tetraphenyltetrahydro-[1,3]dioxolo[4,5-*e*][1,3,2]dioxaphosphepin (**L1h**): White powder, yield 1.15 g (98 %). ^{1}H NMR (499.9 MHz, $CDCl_3$): δ 0.63 (s, 3H; CH_3), 0.82 (s, 3H; CH_3), 2.00 (s, 3H; CH_3), 2.36-2.46 (m, 2H; CH_2S), 3.36-3.90 (m, 2H; NCH_2), 5.03 (dd, $^3J_{H,H}$ = 8.3 Hz, $^4J_{H,P}$ = 1.4 Hz, 1H; OCH), 5.27 (d, $^3J_{H,H}$ = 8.3 Hz; OCH), 7.13-7.36 (m, 12H; CH(Ph)), 7.39-7.58 (m, 8H; CH(Ph)). ^{13}C{^{1}H} NMR (125.7 Hz, $CDCl_3$): δ 15.89 (s; SCH_3), 26.52 (s; CCH_3), 26.90 (s; CCH_3), 34.51 (d, $^3J_{C,P}$ = 4.1 Hz; CH_2S), 62.11 (d, $^2J_{C,P}$ = 5.1 Hz; NCH_2), 81.00 (d, $^3J_{C,P}$ = 4.4 Hz; OCH), 82.39 (d, $^3J_{C,P}$ = 14.8 Hz; OCH), 83.32 (s; CPh_2), 85.52 (d, $^2J_{C,P}$ = 9.9 Hz; CPh_2), 112.91 (s; $\underline{C}(CH_3)_2$), 127.24 (s; CH(Ph)), 127.35 (s; CH(Ph)), 127.38 (s; CH(Ph)), 127.48 (s; CH(Ph)), 127.52 (s; CH(Ph)), 127.82 (s; CH(Ph)), 128.09 (s; CH(Ph)), 128.28 (s; CH(Ph)), 128.88 (s; CH(Ph)), 129.26 (s; CH(Ph)), 129.28 (s; CH(Ph)), 130.39 (s; CH(Ph)), 141.72 (d, $^3J_{C,P}$ = 2.9 Hz; C(Ph)), 141.76 (s; C(Ph)), 146.28 (s; C(Ph)), 146.53 (s; C(Ph)). ^{31}P{^{1}H} NMR (202.4 Hz, $CDCl_3$): δ 131.10 (s). $C_{34}H_{35}O_5PS$ (586.19): calcd. C, 69.61; H, 6.01; found C, 69.86; H, 6.08.

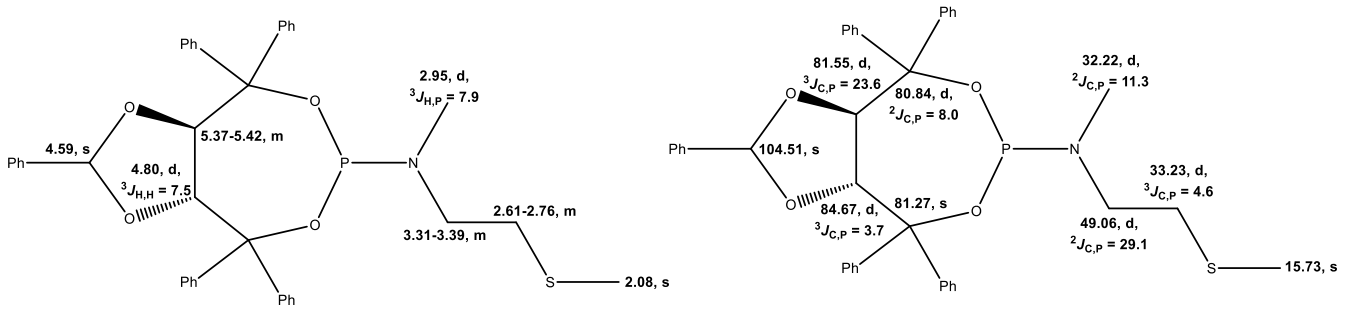


^{1}H (left) and ^{13}C{^{1}H} (right) NMR Signal Assignment for **L1h**.

(3a*R*,8a*R*)-6-[*N*-methyl-2-(methylthio)ethan-1-amino]- 2,4,4,8,8-pentaphenyltetrahydro-[1,3]dioxolo[4,5-*e*][1,3,2]dioxaphosphepin (**L2a**): White powder, yield 1.26 g (97 %). ^{1}H NMR (600.1 MHz, $CDCl_3$): δ 2.00 (s, 3H; CH_3), 2.49-2.65 (m, 2H; CH_2S), 2.56 (d, $^3J_{H,P}$ = 8.3, 3H; NCH_3), 3.07-3.22 (m, 2H; NCH_2), 5.18-5.24 (m, 2H; OCH) (major form), 2.08 (s, 3H; CH_3), 2.61-2.76 (m, 2H; CH_2S), 2.95 (d, $^3J_{H,P}$ = 7.9, 3H; NCH_3), 3.31-3.39 (m, 2H; NCH_2), 4.80 (d, $^3J_{H,H}$ = 7.5, 1H; OCH), 5.37-5.42 (m, 1H; OCH) (minor form), 6.75 (d, $^3J_{H,H}$ = 7.4 Hz; CH(Ph)), 7.16 (t, $^3J_{H,H}$ = 7.5 Hz; CH(Ph)), 7.39-7.19 (m; CH(Ph)), 7.42 (d, $^3J_{H,H}$ = 3.4 Hz; CH(Ph)), 7.46 (d, $^3J_{H,H}$ = 7.6 Hz; CH(Ph)), 7.56 (d, $^3J_{H,H}$ = 7.6 Hz; CH(Ph)), 7.60 (d, $^3J_{H,H}$ = 8.6 Hz;

CH(Ph)), 7.64 (t, $^{3}J_{H,H}$ = 8.3 Hz; CH(Ph)), 7.84 (d, $^{3}J_{H,H}$ = 7.2 Hz; CH(Ph)). $^{13}C\{^{1}H\}$ NMR (150.9 Hz, $CDCl_3$): δ 15.51 (s; SCH_3), 32.23 (d, $^{2}J_{C,P}$ = 14.0 Hz; NCH_2), 32.95 (d, $^{3}J_{C,P}$ = 4.1 Hz; CH_2S), 48.62 (d, $^{2}J_{C,P}$ = 28.1 Hz; NCH_2), 80.42 (d, $^{3}J_{C,P}$ = 3.6 Hz; OCH), 80.89 (d, $^{2}J_{C,P}$ = 7.5 Hz; CPh_2), 82.32 (d, $^{3}J_{C,P}$ = 18.3 Hz; OCH), 85.86 (d, $^{3}J_{C,P}$ = 10.8 Hz; CPh_2), 106.89 (s; CHPh) (major form), 15.73 (s; SCH_3), 32.22 (d, $^{2}J_{C,P}$ = 11.3 Hz; NCH_2), 33.23 (d, $^{3}J_{C,P}$ = 4.6 Hz; CH_2S), 49.06 (d, $^{2}J_{C,P}$ = 29.1 Hz; NCH_2), 80.84 (d, $^{2}J_{C,P}$ = 8.0 Hz; CPh_2), 81.27 (s; CPh_2), 81.55 (d, $^{3}J_{C,P}$ = 23.6 Hz; OCH), 84.67 (d, $^{3}J_{C,P}$ = 3.7 Hz; OCH), 104.51 (s; CHPh) (minor form), 125.45 (s; CH(Ph)), 126.97 (s; CH(Ph)), 127.12 (s; CH(Ph)), 127.17 (s; CH(Ph)), 127.32 (s; CH(Ph)), 127.34 (s; CH(Ph)), 127.36 (s; CH(Ph)), 127.44 (s; CH(Ph)), 127.47 (s; CH(Ph)), 127.51 (s; CH(Ph)), 127.54 (s; CH(Ph)), 127.68 (s; CH(Ph)), 127.74 (s; CH(Ph)), 127.84 (s; CH(Ph)), 127.94 (s; CH(Ph)), 128.11 (s; CH(Ph)), 128.14 (s; CH(Ph)), 128.18 (s; CH(Ph)), 128.25 (s; CH(Ph)), 128.29 (s; CH(Ph)), 128.32 (s; CH(Ph)), 128.34 (s; CH(Ph)), 128.38 (s; CH(Ph)), 128.46 (s; CH(Ph)), 128.57 (s; CH(Ph)), 128.83 (s; CH(Ph)), 128.87 (s; CH(Ph)), 129.18 (s; CH(Ph)), 129.66 (s; CH(Ph)), 129.72 (s; CH(Ph)), 135.92 (s; C(Ph)), 136.48 (s; C(Ph)), 138.02 (s; C(Ph)), 140.78 (s; C(Ph)), 140.84 (s; C(Ph)), 141.86 (s; C(Ph)), 141.91 (d, $^{3}J_{C,P}$ = 2.7 Hz; C(Ph)), 145.62 (d, $^{3}J_{C,P}$ = 1.3 Hz; C(Ph)), 145.80 (s; C(Ph)), 146.52 (s; C(Ph)),146.57 (s; C(Ph)). $^{31}P\{^{1}H\}$ NMR (242.9 Hz, $CDCl_3$): δ 140.92 (s) (major form), 145.05 (s) (minor form). $C_{39}H_{38}NO_4PS$ (647.23): calcd. C, 72.31; H, 5.91; N, 2.16; found C, 72.44; H, 5.85; N, 2.10.



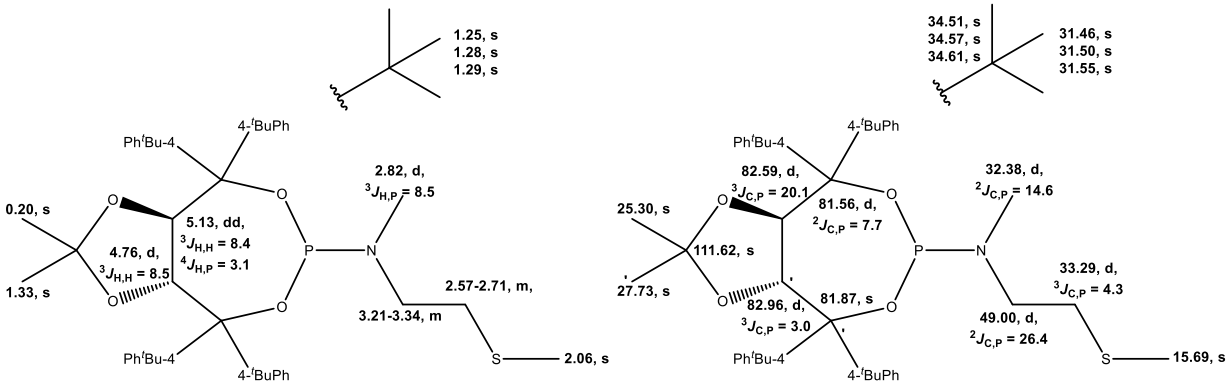


^{1}H (left) and $^{13}C\{^{1}H\}$ (right) NMR Signal Assignment for **L2a**.

(3a*R*,8a*R*)-6-[*N*-methyl-2-(methylthio)ethan-1-amino]-2,2-dimethyl-4,4,8,8-tetra(4-(*tert*-butyl)phenyl)tetrahydro-[1,3]dioxolo[4,5-*e*][1,3,2]dioxaphosphepin (**L2b**): White powder, yield 1.47 g

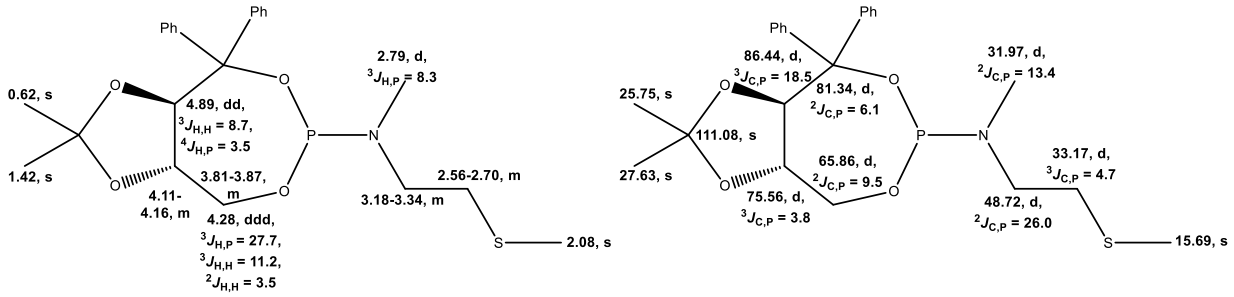
EXPERIMENTAL SECTION

(89 %). ^{1}H NMR (499.9 MHz, $CDCl_3$): δ 0.20 (s, 3H; CH_3), 1.25 (s, 9H; $C(CH_3)$), 1,28 (s, 9H; $C(CH_3)$), 1,29 (s, 18H; $C(CH_3)$), 1.33 (s, 3H; CH_3), 2.06 (s, 3H; CH_3), 2.57-2.71 (m, 2H; CH_2S), 2.82 (d, $^{3}J_{H,P}$ = 8.5 Hz, 3H; NCH_3), 3.21-3.34 (m, 2H; NCH_2), 4.76 (d, $^{3}J_{H,H}$ = 8.5 Hz; OCH), 5.13 (dd, $^{3}J_{H,H}$ = 8.4 Hz, $^{4}J_{H,P}$ = 3.1 Hz, 1H; OCH), 7.22-7.39 (m, 8H; CH(Ph)), 7.52 (d, $^{3}J_{H,H}$ = 8.3 Hz, 2H; CH(Ph)), 7.67 (d, $^{3}J_{H,H}$ = 8.4 Hz, 2H; CH(Ph)). $^{13}C\{^{1}H\}$ NMR (125.7 Hz, $CDCl_3$): δ 15.69 (s; SCH_3), 25.30 (s; CCH_3), 27.73 (s; CCH_3), 31.46 (s, $C(\underline{C}H_3)_3$), 31.50 (s, $C(\underline{C}H_3)_3$), 31.55 (s, $C(\underline{C}H_3)_3$), 32.38 (d, $^{2}J_{C,P}$ = 14.6 Hz; NCH_3), 33.29 (d, $^{3}J_{C,P}$ = 4.3 Hz; CH_2S), 34.52 (s, $\underline{C}(CH_3)_3$), 34.57 (s, $\underline{C}(CH_3)_3$), 34.61 (s, $\underline{C}(CH_3)_3$), 49.00 (d, $^{2}J_{C,P}$ = 26.4 Hz; NCH_2), 81.56 (d, $^{2}J_{C,P}$ = 7.7 Hz; CPh_2), 81.87 (s; CPh_2), 82.59 (d, $^{3}J_{C,P}$ = 20.1 Hz; OCH), 82.96 (d, $^{3}J_{C,P}$ = 3.0 Hz; OCH), 111.62 (s; $\underline{C}(CH_3)_2$), 124.06 (s; CH(Ph)), 124.26 (s; CH(Ph)), 124.49 (s; CH(Ph)), 124.66 (s; CH(Ph)), 125.03 (s; CH(Ph)), 125.25 (s; CH(Ph)), 125.64 (s; CH(Ph)), 126.70 (s; CH(Ph)), 126.79 (s; CH(Ph)), 126.94 (s; CH(Ph)), 127.05 (s; CH(Ph)), 128.07 (s; CH(Ph)), 128.52 (s; CH(Ph)), 128.55 (s; CH(Ph)), 128.64 (s; CH(Ph)), 128.91 (s; CH(Ph)), 139.32 (d; $^{3}J_{C,P}$ = 7.0 Hz, C(Ph)), 143.99 (d, $^{3}J_{C,P}$ = 1.2 Hz; C(Ph)), 149.61 (s; C(Ph)), 149.91 (s; C(Ph)), 150.07 (s; C(Ph)). $^{31}P\{^{1}H\}$ NMR (202.4 Hz, $CDCl_3$): δ 139.48 (s). $C_{51}H_{70}NO_4PS$ (823.48): calcd. C, 74.33; H, 8.56; N, 1.70; found C, 74.66; H, 8.70; N, 1.60.



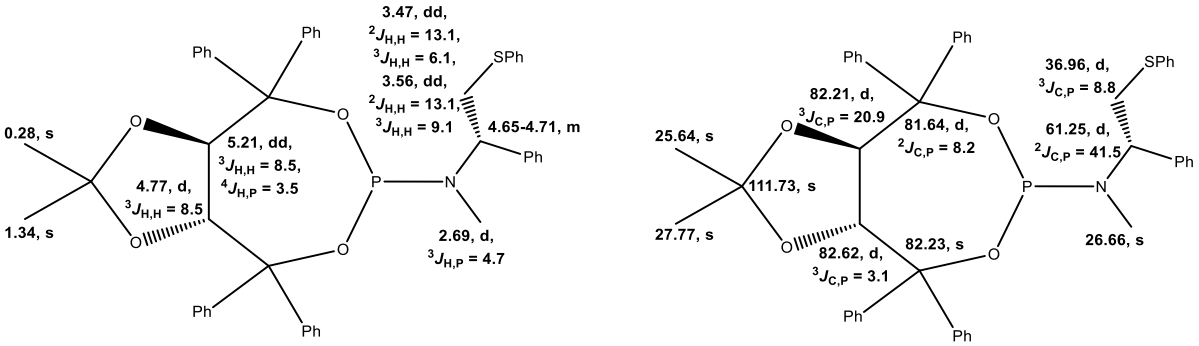
(3a*R*,8a*S*)-6-[*N*-methyl-2-(methylthio)ethan-1-amino]-2,2-dimethyl-4,4-diphenyltetrahydro-[1,3]dioxolo[4,5-*e*][1,3,2]dioxaphosphepin (**L2c**): White powder, yield 0.33 g (37 %). ^{1}H NMR (499.9 MHz, $CDCl_3$): δ 0.62 (s, 3H; CH_3), 1.42 (s, 3H; CH_3), 2.08 (s, 3H; CH_3), 2.56-2.70 (m, 2H; CH_2S), 2.79 (d, $^{3}J_{H,P}$ = 8.3 Hz, 3H; NCH_3), 3.18-3.34 (m, 2H; NCH_2), 3.81-3.87 (m, 1H; CH_2O), 4.10-4.16 (m, 1H; OCH), 4.27 (ddd, $^{3}J_{H,P}$ = 27.6 Hz, $^{3}J_{H,H}$ = 11.1 Hz, $^{2}J_{H,H}$ = 3.6 Hz, 1H; CH_2O), 4.89 (dd, $^{3}J_{H,H}$ = 8.7 Hz, $^{4}J_{H,P}$ = 3.6 Hz, 1H; OCH), 7.15-7.31 (m, 4H; CH(Ph)), 7.31-7.40 (m, 2H; CH(Ph)), 7.62 (d, $^{3}J_{H,P}$ = 7.6 Hz, 2H; CH(Ph)). $^{13}C\{^{1}H\}$ NMR (125.7 Hz, $CDCl_3$): δ 15.69 (s; SCH_3), 25.75 (s; CCH_3), 27.63 (s; CCH_3), 31.97 (d, $^{2}J_{C,P}$ = 13.4 Hz; NCH_3), 33.17 (d, $^{3}J_{C,P}$ = 4.7 Hz; CH_2S), 48.72 (d, $^{2}J_{C,P}$ = 26.0 Hz; NCH_2), 65.86 (d, $^{2}J_{C,P}$ = 9.5 Hz; CH_2O), 75.56 (d, $^{3}J_{C,P}$ = 3.8 Hz; OCH), 81.34 (d, $^{2}J_{C,P}$ = 6.1 Hz; CPh_2), 86.44 (d, $^{3}J_{C,P}$ = 18.5 Hz; OCH), 111.08 (s; $\underline{C}(CH_3)_2$), 127.04 (s; CH(Ph)), 127.15 (s; CH(Ph)), 127.25 (s; CH(Ph)), 127.70 (s; CH(Ph)), 128.23 (s; CH(Ph)), 128.73 (s; CH(Ph)), 141.51 (s; C(Ph)), 146.84 (s; $^{3}J_{H,H}$ = 7.8 Hz, C(Ph)). $^{31}P\{^{1}H\}$ NMR (202.4 Hz, $CDCl_3$): δ 146.56 (s). $C_{23}H_{30}NO_4PS$ (447.16): calcd. C, 61.73; H, 6.76; N, 3.13; found C, 62.03; H, 6.87; N, 3.00.

EXPERIMENTAL SECTION



^{1}H (left) and ^{13}C{^{1}H} (right) NMR Signal Assignment for **L2c**.

(3a*R*,8a*R*)-6-[(*S*)-*N*-methyl-1-phenyl-2-(phenylthio)ethan-1-amino]-2,2-dimethyl-4,4,8,8-tetraphenyltetrahydro-[1,3]dioxolo[4,5-*e*][1,3,2]dioxaphosphepin (**L3a**): White powder, yield 1.33 g (90 %). ^{1}H NMR (499.9 MHz, $CDCl_3$): δ 0.28 (s, 3H; CH_3), 1.34 (s, 3H; CH_3), 2.69 (d, $^3J_{H,P}$ = 4.7 Hz, 1H; NCH_3), 3.47 (dd, $^2J_{H,H}$ = 13.1 Hz, $^3J_{H,H}$ = 6.1 Hz, 1H; CH_2S), 3.56 (dd, $^2J_{H,H}$ = 13.1 Hz, $^3J_{H,H}$ = 9.1 Hz, 1H; CH_2S), 4.65-4.71 (m, 1H; CHPh), 4.77 (d, $^3J_{H,H}$ = 8.5 Hz, 1H; OCH), 5.21 (dd, $^3J_{H,H}$ = 8.5 Hz, $^4J_{H,P}$ = 3.5 Hz, 1H; OCH), 7.13-7.33 (m, 22H; CH(Ph)), 7.37 (d, $^3J_{H,H}$ = 7.6 Hz, 2H; CH(Ph)), 7.53 (d, $^3J_{H,H}$ = 7.8 Hz, 2H; CH(Ph)), 7.58 (d, $^3J_{H,H}$ = 7.7 Hz, 2H; CH(Ph)), 7.89 (d, $^3J_{H,H}$ = 7.5 Hz, 2H; CH(Ph)). ^{13}C{^{1}H} NMR (125.7 Hz, $CDCl_3$): δ 25.64 (s; CCH_3), 26.66 (s; NCH_3), 27.77 (s; CCH_3), 36.96 (d, $^3J_{C,P}$ = 8.8 Hz; CH_2), 61.25 (d, $^2J_{C,P}$ = 41.5 Hz; CHPh), 81.64 (d, $^2J_{C,P}$ = 8.2 Hz; CPh_2), 82.21 (d, $^3J_{C,P}$ = 20.9 Hz; OCH), 82.23 (s; CPh_2), 82.62 (d, $^3J_{C,P}$ = 3.1 Hz; OCH), 111.73 (s; $\underline{C}(CH_3)_2$), 126.19 (s; CH(Ph)), 127.10 (s; CH(Ph)), 127.21 (s; CH(Ph)), 127.36 (s; CH(Ph)), 127.52 (s; CH(Ph)), 127.63 (s; CH(Ph)), 127.75 (s; CH(Ph)), 127.82 (s; CH(Ph)), 128.07 (s; CH(Ph)), 128.10 (s; CH(Ph)), 128.37 (s; CH(Ph)), 129.09 (s; CH(Ph)), 129.21 (s; CH(Ph)), 129.25 (s; CH(Ph)), 129.39 (s; CH(Ph)), 129.73 (s; CH(Ph)),137.08 (s; C(Ph)), 140.44 (d, $^3J_{C,P}$ = 3.8 Hz; C(Ph)), 142.08 (s; C(Ph)), 142.52 (s; C(Ph)), 146.92 (d, $^3J_{C,P}$ = 1.1 Hz; C(Ph)), 147.17 (s; C(Ph)). ^{31}P{^{1}H} NMR (202.4 Hz, $CDCl_3$): δ 140.86 (s). $C_{46}H_{44}NO_4PS$ (737.27): calcd. C, 74.88; H, 6.01; N, 1.90; found C, 74.80; H, 6.05; N, 1.98

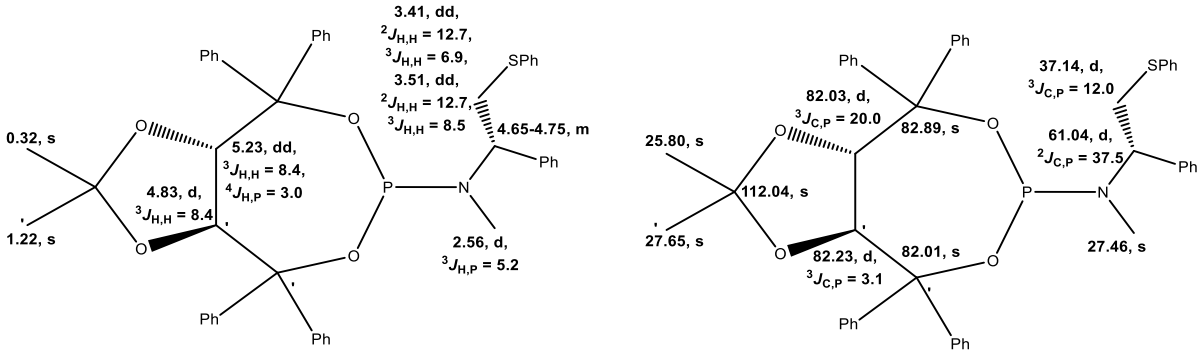


^{1}H (left) and ^{13}C{^{1}H} (right) NMR Signal Assignment for **L3a**.

(3a*S*,8a*S*)-6-[(*S*)-*N*-methyl-1-phenyl-2-(phenylthio)ethan-1-amino]-2,2-dimethyl-4,4,8,8-tetraphenyltetrahydro-[1,3]dioxolo[4,5-*e*][1,3,2]dioxaphosphepin (**L3b**): White powder, yield 1.03 g (70 %). ^{1}H NMR (499.9 MHz, $CDCl_3$): δ 0.32 (s, 3H; CH_3), 1.22 (s, 3H; CH_3), 2.56 (d, $^3J_{H,P}$ = 5.2 Hz, 1H; NCH_3), 3.41 (dd, $^2J_{H,H}$ = 12.7 Hz, $^3J_{H,H}$ = 6.9 Hz, 1H; CH_2S), 3.51 (dd, $^2J_{H,H}$ = 12.7 Hz, $^3J_{H,H}$ = 8.5 Hz, 1H; CH_2S), 4.65-

EXPERIMENTAL SECTION

4.75 (m, 1H; CHPh), 4.83 (d, $^{3}J_{H,H}$ = 8.4 Hz, 1H; OCH), 5.23 (dd, $^{3}J_{H,H}$ = 8.4 Hz, $^{4}J_{H,P}$ = 3.0 Hz, 1H; OCH), 7.10-7.36 (m, 22H; CH(Ph)), 7.37-7.45 (m, 4H; CH(Ph)), 7.67-7.75 (m, 4H; CH(Ph)). $^{13}C\{^{1}H\}$ NMR (125.7 Hz, $CDCl_3$): δ 25.80 (s; CCH_3), 27.46 (d, $^{3}J_{C,P}$ = 2.8 Hz; NCH_3), 27.65 (s; CCH_3), 37.14 (d, $^{3}J_{C,P}$ = 12.0 Hz; CH_2), 61.04 (d, $^{2}J_{C,P}$ = 37.5 Hz; CHPh), 82.01 (s; CPh_2), 82.03 (d, $^{3}J_{C,P}$ = 20.0 Hz; OCH), 82.23 (d, $^{2}J_{C,P}$ = 3.1 Hz; CPh_2), 82.89 (s; CPh_2), 112.04 (s; $\underline{C}(CH_3)_2$), 126.17 (s; CH(Ph)), 127.10 (s; CH(Ph)), 127.22 (s; CH(Ph)), 127.34 (s; CH(Ph)), 127.52 (s; CH(Ph)), 127.68 (s; CH(Ph)), 127.80 (s; CH(Ph)), 127.88 (s; CH(Ph)), 128.07 (s; CH(Ph)), 128.22 (s; CH(Ph)), 128.44 (s; CH(Ph)), 129.03 (s; CH(Ph)), 129.17 (s; CH(Ph)), 129.21 (s; CH(Ph)), 129.36 (s; CH(Ph)), 129.84 (s; CH(Ph)),136.85 (s; C(Ph)), 140.36 (s; C(Ph)), 142.06 (s; C(Ph)), 142.63 (s; C(Ph)), 146.82 (s; C(Ph)). $^{31}P\{^{1}H\}$ NMR (202.4 Hz, $CDCl_3$): δ 139.02 (s). $C_{46}H_{44}NO_4PS$ (737.27): calcd. C, 74.88; H, 6.01; N, 1.90; found C, 75.02; H, 6.08; N, 1.95.

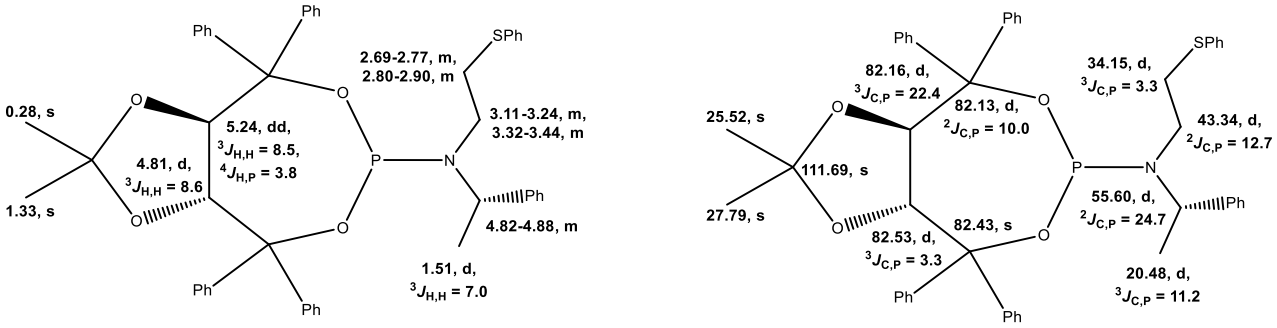


^{1}H (left) and $^{13}C\{^{1}H\}$ (right) NMR Signal Assignment for **L3b**.

(3a*R*,8a*R*)-6-[(*S*)-1-phenyl-*N*-(2-(phenylthio)ethyl)ethan-1-amino]-2,2-dimethyl-4,4,8,8-tetraphenyltetrahydro-[1,3]dioxolo[4,5-*e*][1,3,2]dioxaphosphepin (**L4a**): Yellowish powder, yield 1.23 g (82 %). ^{1}H NMR (499.9 MHz, $CDCl_3$): δ 0.28 (s, 3H; CH_3), 1.33 (s, 3H; CH_3), 1.51 (d, $^{3}J_{H,H}$ = 7.0 Hz, 3H; $C\underline{H}_3CH$), 2.69-2.77 (m, 1H; CH_2S), 2.80-2.90 (m, 1H; CH_2S), 3.11-3.24 (m, 1H; NCH_2), 3.32-3.44 (m, 1H; NCH_2), 4.82-4.88 (m, 1H; NCH_2), 4.81 (d, $^{3}J_{H,H}$ = 8.6 Hz, 1H; OCH), 5.24 (dd, $^{3}J_{H,H}$ = 8.5 Hz, $^{4}J_{H,P}$ = 3.8 Hz, 1H; OCH), 7.02 (d, $^{3}J_{H,H}$ = 7.7 Hz, 2H; CH(Ph)), 7.11-7.49 (m, 24H; CH(Ph)), 7.62 (d, $^{3}J_{H,H}$ = 7.8 Hz, 2H; CH(Ph)), 7.81 (d, $^{3}J_{H,H}$ = 7.8 Hz, 2H; CH(Ph)). $^{13}C\{^{1}H\}$ NMR (125.7 Hz, $CDCl_3$): δ 20.48 (d, $^{3}J_{C,P}$ = 11.2 Hz; $\underline{C}H_3CH$), 25.52 (s; CCH_3), 27.79 (s; CCH_3), 34.15 (d, $^{3}J_{C,P}$ = 3.3 Hz; CH_2), 43.34 (d, $^{2}J_{C,P}$ = 12.7 Hz; NCH_2), 55.60 (d, $^{2}J_{C,P}$ = 24.7 Hz; $\underline{C}$HPh), 82.13 (d, $^{2}J_{C,P}$ = 10.0 Hz; CPh_2), 82.16 (d, $^{3}J_{C,P}$ = 22.4 Hz; OCH), 82.43 (s; CPh_2), 82.53 (d, $^{3}J_{C,P}$ = 3.3 Hz; OCH), 111.69 (s; $\underline{C}(CH_3)_2$), 125.84 (s; CH(Ph)), 127.19 (s; CH(Ph)), 127.29 (s; CH(Ph)), 127.32 (s; CH(Ph)), 127.34 (s; CH(Ph)), 127.40 (s; CH(Ph)), 127.53 (s; CH(Ph)), 127.64 (s; CH(Ph)), 127.78 (s; CH(Ph)), 127.88 (s; CH(Ph)), 128.20 (s; CH(Ph)), 128.47 (s; CH(Ph)), 128.96 (s; CH(Ph)), 129.16 (s; CH(Ph)), 129.19 (s; CH(Ph)), 129.40 (s; CH(Ph)), 129.84 (s; CH(Ph)),136.19 (s; C(Ph)), 141.84 (s; C(Ph)), 142.49 (s; C(Ph)), 143.71 (d, $^{3}J_{C,P}$ = 3.5 Hz; C(Ph)), 146.74 (d, $^{3}J_{C,P}$ = 1.3 Hz; C(Ph)), 147.19 (s; C(Ph)). $^{31}P\{^{1}H\}$ NMR

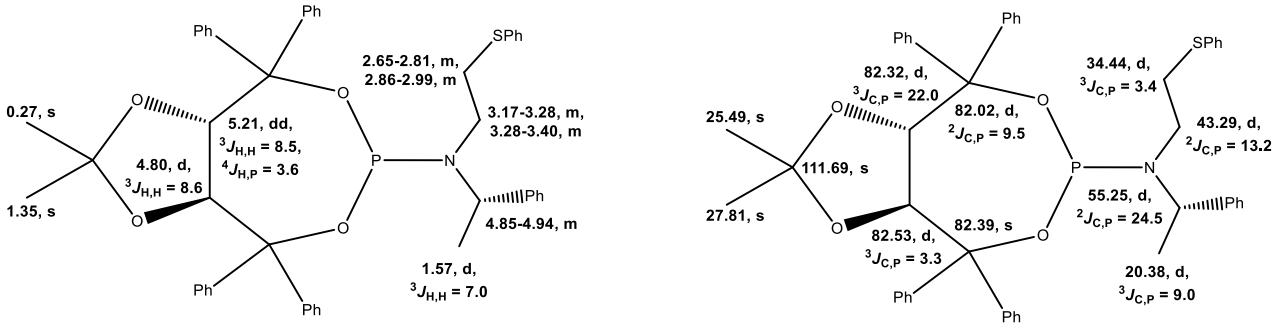
EXPERIMENTAL SECTION

(202.4 Hz, $CDCl_3$): δ 141.67 (s). $C_{47}H_{46}NO_4PS$ (751.29): calcd. C, 75.08; H, 6.17; N, 1.86; found C, 75.31; H, 6.10; N, 1.96.



^{1}H (left) and $^{13}C\{^1H\}$ (right) NMR Signal Assignment for **L4a**.

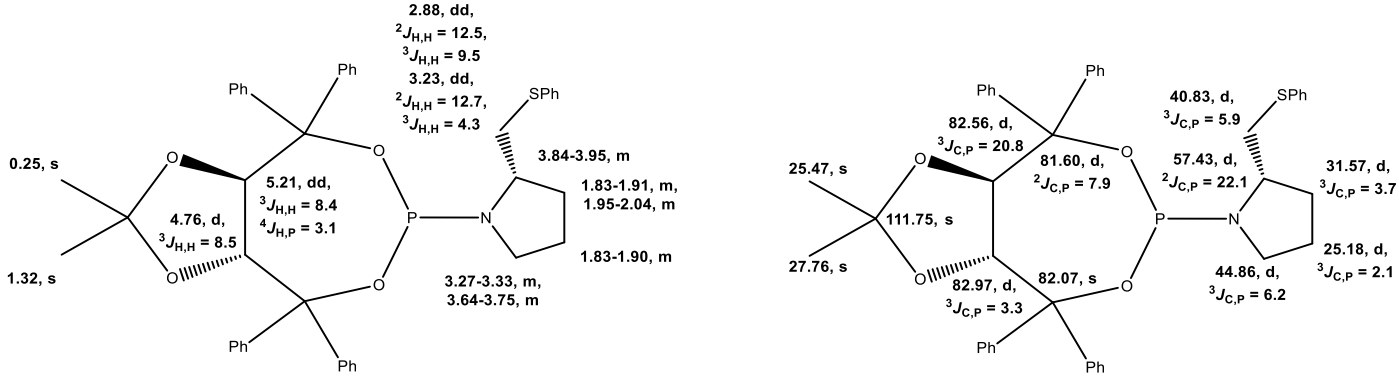
(3a*S*,8a*S*)-6-[(*S*)-1-phenyl-*N*-(2-(phenylthio)ethyl)ethan-1-amino]-2,2-dimethyl-4,4,8,8-tetraphenyltetrahydro-[1,3]dioxolo[4,5-*e*][1,3,2]dioxaphosphepin (**L4b**): White solid foam, yield 1.28 g (85 %). ^{1}H NMR (499.9 MHz, $CDCl_3$): δ 0.27 (s, 3H; CH_3), 1.35 (s, 3H; CH_3), 1.57 (d, $^3J_{H,H}$ = 7.0 Hz, 3H; $C\underline{H}_3CH$), 2.65-2.81 (m, 1H; CH_2S), 2.86-2.99 (m, 1H; CH_2S), 3.17-3.28 (m, 1H; NCH_2), 3.28-3.40 (m, 1H; NCH_2), 4.85-4.94 (m, 1H; NCH_2), 4.80 (d, $^3J_{H,H}$ = 8.6 Hz, 1H; OCH), 5.21 (dd, $^3J_{H,H}$ = 8.5 Hz, $^4J_{H,P}$ = 3.6 Hz, 1H; OCH), 7.04 (d, $^3J_{H,H}$ = 7.5 Hz; 2H; CH(Ph)), 7.09-7.41 (m, 24H; CH(Ph)), 7.44 (d, $^3J_{H,H}$ = 7.7 Hz, 2H; CH(Ph)), 7.62 (d, $^3J_{H,H}$ = 7.6 Hz, 2H; CH(Ph)), 7.78 (d, $^3J_{H,H}$ = 7.5 Hz, 2H; CH(Ph)). $^{13}C\{^1H\}$ NMR (125.7 Hz, $CDCl_3$): δ 20.38 (d, $^3J_{C,P}$ = 9.0 Hz; $C\underline{H}_3CH$), 25.49 (s; CCH_3), 27.81 (s; CCH_3), 34.44 (d, $^3J_{C,P}$ = 3.4 Hz; CH_2), 43.29 (d, $^2J_{C,P}$ = 13.2 Hz; NCH_2), 55.25 (d, $^2J_{C,P}$ = 24.5 Hz; $C\underline{H}Ph$), 82.02 (d, $^2J_{C,P}$ = 9.5 Hz; CPh_2), 82.32 (d, $^3J_{C,P}$ = 22.0 Hz; OCH), 82.39 (s; CPh_2), 82.53 (d, $^3J_{C,P}$ = 3.3 Hz; OCH), 111.69 (s; $\underline{C}(CH_3)_2$), 125.87 (s; CH(Ph)), 127.16 (s; CH(Ph)), 127.37 (s; CH(Ph)), 127.47 (s; CH(Ph)), 127.49 (s; CH(Ph)), 127.53 (s; CH(Ph)), 127.64 (s; CH(Ph)), 127.68 (s; CH(Ph)), 127.86 (s; CH(Ph)), 127.93 (s; CH(Ph)), 128.20 (s; CH(Ph)), 128.37 (s; CH(Ph)), 128.97 (s; CH(Ph)), 129.15 (s; CH(Ph)), 129.19 (s; CH(Ph)), 129.30 (s; CH(Ph)), 136.20 (s; C(Ph)), 141.77 (s; C(Ph)), 142.46 (s; C(Ph)), 143.40 (d, $^3J_{C,P}$ = 4.0 Hz; C(Ph)), 146.69 (d, $^3J_{C,P}$ = 1.5 Hz; C(Ph)), 147.29 (s; C(Ph)). $^{31}P\{^1H\}$ NMR (202.4 Hz, $CDCl_3$): δ 142.09 (s). $C_{47}H_{46}NO_4PS$ (751.29): calcd. C, 75.08; H, 6.17; N, 1.86; found C, 75.43; H, 6.29; N, 2.00.



^{1}H (left) and $^{13}C\{^1H\}$ (right) NMR Signal Assignment for **L4b**.

EXPERIMENTAL SECTION

(3a*R*,8a*R*)-6-[(*S*)-2-((phenylthio)methyl)pyrrolidino]-2,2-dimethyl-4,4,8,8-tetraphenyltetrahydro-[1,3]dioxolo[4,5-*e*][1,3,2]dioxaphosphepin (**L5a**): White powder, yield 1.35 g (98 %). ^{1}H NMR (499.9 MHz, $CDCl_3$): δ 0.25 (s, 3H; CH_3), 1.32 (s, 3H; CH_3), 1.83-1.90 (m, 2H; CH_2), 1.83-1.91 (m, 1H; CH_2), 1.95-2.04 (m, 1H; CH_2), 2.88 (dd, $^{2}J_{H,H}$ = 12.5 Hz, $^{3}J_{H,H}$ = 9.5 Hz, 1H; CH_2), 3.23 (dd, $^{2}J_{H,H}$ = 12.7 Hz, $^{3}J_{H,H}$ = 4.3 Hz, 1H; CH_2), 3.27-3.33 (m, 1H; CH_2), 3.64-3.75 (m, 1H; CH_2), 3.84-3.95 (m, 1H; NCH), 4.76 (d, $^{3}J_{H,H}$ = 8.5 Hz, 1H; OCH), 5.21 (dd, $^{3}J_{H,H}$ = 8.4 Hz, $^{4}J_{H,P}$ = 3.1 Hz, 1H; OCH), 7.10-7.31 (m, 16H; CH(Ph)), 7.35-7.48 (m, 5H; CH(Ph)), 7.56 (d, $^{3}J_{H,H}$ = 7.8, 2H; CH(Ph)), 7.78 (d, $^{3}J_{H,H}$ = 7.8, 2H; CH(Ph)). ^{13}C{^{1}H} NMR (125.7 Hz, $CDCl_3$): δ 25.18 (d, $^{3}J_{C,P}$ = 2.1 Hz; CH_2), 25.47 (s; CCH_3), 27.76 (s; CCH_3), 31.57 (d, $^{3}J_{C,P}$ = 3.7 Hz; CH_2), 40.83 (d, $^{3}J_{C,P}$ = 5.9 Hz; CH_2S), 44.86 (d, $^{3}J_{C,P}$ = 6.2 Hz; CH_2), 57.43 (d, $^{2}J_{C,P}$ = 22.1 Hz; NCH), 81.60 (d, $^{2}J_{C,P}$ = 7.9 Hz; CPh_2), 82.07 (s; CPh_2), 82.56 (d, $^{3}J_{C,P}$ = 20.8 Hz; OCH), 82.97 (d, $^{3}J_{C,P}$ = 3.3 Hz; OCH), 111.75 (s; $\underline{C}(CH_3)_2$), 125.87 (s; CH(Ph)), 127.18 (s; CH(Ph)), 127.27 (s; CH(Ph)), 127.32 (s; CH(Ph)), 127.35 (s; CH(Ph)), 127.43 (s; CH(Ph)), 127.56 (s; CH(Ph)), 127.65 (s; CH(Ph)), 127.81 (s; CH(Ph)), 128.03 (s; CH(Ph)), 128.26 (s; CH(Ph)), 128.98 (s; CH(Ph)), 129.00 (s; CH(Ph)), 129.03 (s; CH(Ph)), 129.22 (s; CH(Ph)), 129.25 (s; CH(Ph)), 130.39 (s; CH(Ph)), 137.03 (s; C(Ph)), 142.07 (d, $^{3}J_{C,P}$ = 1.5 Hz; C(Ph)), 142.47 (d, $^{3}J_{C,P}$ = 1.5 Hz; C(Ph)), 146.74 (d, $^{3}J_{C,P}$ = 1.6 Hz; C(Ph)), 147.21 (s; C(Ph)). ^{31}P{^{1}H} NMR (202.4 Hz, $CDCl_3$): δ 138.90 (s). $C_{42}H_{42}NO_4PS$ (687.26): calcd. C, 73.34; H, 6.15; N, 2.04; found C, 73.60; H, 6.22; N, 1.93.



^{1}H (left) and ^{13}C{^{1}H} (right) NMR Signal Assignment for **L5a**.

(3a*S*,8a*S*)-6-[(*S*)-2-((phenylthio)methyl)pyrrolidino]-2,2-dimethyl-4,4,8,8-tetraphenyltetrahydro-[1,3]dioxolo[4,5-*e*][1,3,2]dioxaphosphepin (**L5b**): White powder, yield 0.93 g (68 %). ^{1}H NMR (499.9 MHz, $CDCl_3$): δ 0.31 (s, 3H; CH_3), 1.25 (s, 3H; CH_3), 1.71-1.80 (m, 1H; CH_2), 1.82-1.91 (m, 2H; CH_2), 1.95-2.04 (m, 1H; CH_2), 2.76 (dd, $^{2}J_{H,H}$ = 12.6, $^{3}J_{H,H}$ = 10.2 Hz, 1H; CH_2), 3.19 (dd, $^{2}J_{H,H}$ = 12.6, $^{3}J_{H,H}$ = 3.0 Hz, 1H; CH_2), 3.37-3.45 (m, 2H; CH_2), 3.98-4.08 (m, 1H; NCH), 4.82 (d, $^{3}J_{H,H}$ = 8.5 Hz, 1H; OCH), 5.14 (dd, $^{3}J_{H,H}$ = 8.4 Hz, $^{4}J_{H,P}$ = 3.5 Hz, 1H; OCH), 7.11-7.30 (m, 17H; CH(Ph)), 7.35 (d, $^{3}J_{H,H}$ = 7.5, 2H; CH(Ph)), 7.45 (d, $^{3}J_{H,H}$ = 7.7, 2H; CH(Ph)), 7.59 (d, $^{3}J_{H,H}$ = 7.6, 2H; CH(Ph)), 7.72 (d, $^{3}J_{H,H}$ = 7.5, 2H; CH(Ph)). ^{13}C{^{1}H} NMR (125.7 Hz, $CDCl_3$): δ 25.04 (d, $^{3}J_{C,P}$ = 2.5 Hz; CH_2), 25.67 (s; CCH_3), 27.68 (s; CCH_3), 31.50 (d, $^{3}J_{C,P}$ = 3.3 Hz; CH_2), 40.14 (d, $^{3}J_{C,P}$ = 5.8 Hz; CH_2S), 45.13 (d, $^{3}J_{C,P}$ = 9.9 Hz; CH_2), 57.03 (d, $^{2}J_{C,P}$ = 19.1 Hz; NCH), 81.60 (d, $^{2}J_{C,P}$ = 8.4 Hz;

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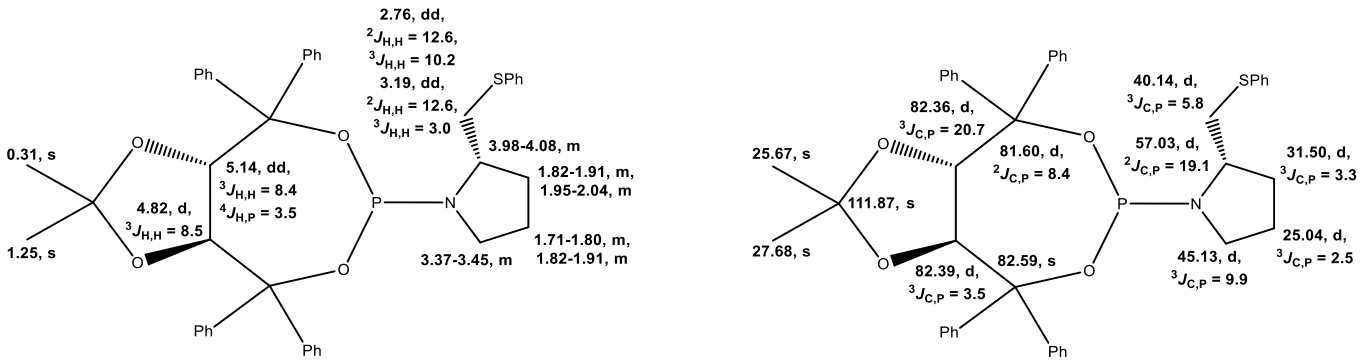
CPh_2), 82.36 (d, $^3J_{C,P}$ = 20.7 Hz; OCH), 82.39 (d, $^3J_{C,P}$ = 3.5 Hz; OCH), 82.59 (s; CPh_2), 111.87 (s; $\underline{C}(CH_3)_2$), 125.76 (s; CH(Ph)), 127.19 (s; CH(Ph)), 127.24 (s; CH(Ph)), 127.34 (s; CH(Ph)), 127.38 (s; CH(Ph)), 127.49 (s; CH(Ph)), 127.54 (s; CH(Ph)), 127.59 (s; CH(Ph)), 127.87 (s; CH(Ph)), 128.20 (s; CH(Ph)), 128.96 (s; CH(Ph)), 129.14 (s; CH(Ph)), 129.17 (s; CH(Ph)), 129.24 (s; CH(Ph)), 136.75 (s; C(Ph)), 142.01 (d, $^3J_{C,P}$ = 1.9 Hz; C(Ph)), 142.31 (s; C(Ph)), 146.82 (d, $^3J_{C,P}$ = 1.9 Hz; C(Ph)), 146.13 (s; C(Ph)). $^{31}P\{^1H\}$ NMR (202.4 Hz, $CDCl_3$): δ 139.76 (s). $C_{42}H_{42}NO_4PS$ (687.26): calcd. C, 73.34; H, 6.15; N, 2.04; found C, 73.54; H, 6.05; N, 2.14.



^1H (left) and $^{13}C\{^1H\}$ (right) NMR Signal Assignment for **L5b**.

EXPERIMENTAL SECTION

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

[Pd(allyl)(**L1a**)]BF_4: White powder, yield 15.3 mg (92%). ^{1}H NMR (500 MHz, CD_2Cl_2) **L1a**: δ 0.57 (s, 3H; CH_3), 0.60 (s, 3H; CH_3), 2.11 (d, $^3J_{H,P}$ = 6.9 Hz, 3H; CH_3), 2.65 (s, 3H; CH_3), 2.60-2.63 (br.m, 1H; CH_2), 2.87-2.90 (br.m, 1H; CH_2), 2.93-3.04 (m, 1H; CH_2), 3.71-3.78 (m, 1H; CH_2), 5.36 (d, $^3J_{H,H}$ = 7.9 Hz, 1H; CH), 5.44 (d, $^3J_{H,H}$ = 7.9 Hz, 1H; CH), 7.11-7.72 (m, 20H, CH(Ph)) (major form), 0.57 (s, 3H; CH_3), 0.60 (s, 3H; CH_3), 2.07 (d, $^3J_{H,P}$ = 6.8 Hz, 3H; CH_3), 2.66 (s, 3H; CH_3), 2.51-2.54 (br.m, 1H; CH_2), 2.90-3.01 (m, 1H; CH_2), 2.95-2.98 (br.m, 1H; CH_2), 3.43-3.52 (m, 1H; CH_2), 5.45 (d, $^3J_{H,H}$ = 8.0 Hz, 1H; CH), 5.36 (d, $^3J_{H,H}$ = 8.0 Hz, 1H; CH), 7.11-7.72 (m, 20H, CH(Ph)) (minor form); ***η*^{3}-allylic ligand**: δ 3.24 (dd, $^3J_{H,H}$ = 12.6 Hz, $^3J_{H,P}$ = 4.1 Hz, 1H; CH_2), 3.40 (t, $^3J_{H,H}$ = $^3J_{H,P}$ = 14.4 Hz, 1H; CH_2), 3.97 (d, $^3J_{H,H}$ = 6.8 Hz, 1H; CH_2), 4.48-4.51 (m, 1H;CH_2), 4.28-4.36 (m, 1H;CH) (allyl) (major form), 1.41 (dd, $^3J_{H,H}$ = 12.4 Hz, $^3J_{H,P}$ = 4.1 Hz, 1H; CH_2), 2.79 (t, $^3J_{H,H}$ = $^3J_{H,P}$ = 14.5 Hz, 1H; CH_2), 4.28-4.32 (m, 1H; CH_2), 4.50-4.53 (m, 1H;CH_2), 5.67-5.75 (m, 1H;CH) (minor form). ^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2) **L1a**: δ 24.96 (d, $^3J_{C,P}$ = 4.0 Hz; CH_3), 26.86 (s; CH_3), 26.88 (s; CH_3), 33.66 (d, $^2J_{C,P}$ = 7.8 Hz; CH_3), 34.31 (s; CH_2), 52.89 (d, $^2J_{C,P}$ = 31.3 Hz; CH_2), 80.78 (d, $^3J_{C,P}$ = 2.9 Hz; CH), 88.29 (s;CPh_2), 91.05 (d, $^2J_{C,P}$ = 20.0 Hz; CPh_2), 116.49 (s; CMe_2), (major form), 25.72 (d, $^3J_{C,P}$ = 4.8 Hz; CH_3), 26.80 (s; CH_3), 26.88 (s; CH_3), 33.42 (d, $^2J_{C,P}$ = 7.6 Hz; CH_3), 34.91 (s; CH_2), 52.71 (d, $^2J_{C,P}$ = 31.9 Hz; CH_2), 80.78 (d, $^3J_{C,P}$ = 2.9 Hz; CH), 80.93 (d, $^3J_{C,P}$ = 2.9 Hz; CH), 88.01 (s;CPh_2), 91.52 (d, $^2J_{C,P}$ = 20.2 Hz; CPh_2), 116.44 (s; CMe_2), (minor form), 127.61 (s; CH(Ph)), 127.68 (s; CH(Ph)), 127.93 (s; CH(Ph)), 127.95 (s; CH(Ph)), 127.98 (s; CH(Ph)), 128.06 (s; CH(Ph)), 128.08 (s; CH(Ph)), 128.40 (s; CH(Ph)), 128.48 (s; CH(Ph)), 128.51 (s; CH(Ph)), 128.59 (s; CH(Ph)), 128.63 (s; CH(Ph)), 128.66 (s; CH(Ph)), 128.68 (s; CH(Ph)), 129.17 (s; CH(Ph)), 129.20 (s; CH(Ph)), 129.34 (s; CH(Ph)), 129.40 (s; CH(Ph)), 129.48 (s; CH(Ph)), 129.58 (s; CH(Ph)), 129.82 (s; CH(Ph)), 129.96 (s; CH(Ph)), 140,36 (d, $^3J_{C,P}$ = 6.0 Hz; C(Ph)), 140,57 (d, $^3J_{C,P}$ = 6.2 Hz; C(Ph)), 140,92 (d, $^3J_{C,P}$ = 8.7 Hz; C(Ph)), 140,96 (d, $^3J_{C,P}$ = 8.7 Hz; C(Ph)), 143.97 (s; C(Ph), 144.20 (s; C(Ph), 144.44 (s; C(Ph), 145.29 (s; C(Ph); ***η*^{3}-allylic ligand**: 63.72 (d, $^2J_{C,P}$ = 8.5 Hz; CH_2), 79.21 (d, $^2J_{C,P}$ = 42.1 Hz; CH_2), 123.83 (d, $^2J_{C,P}$ = 10.6 Hz; CH) (major form), 62.94 (d, $^2J_{C,P}$ = 8.1 Hz; CH_2), 80.54 (d, $^2J_{C,P}$ = 42.0 Hz;

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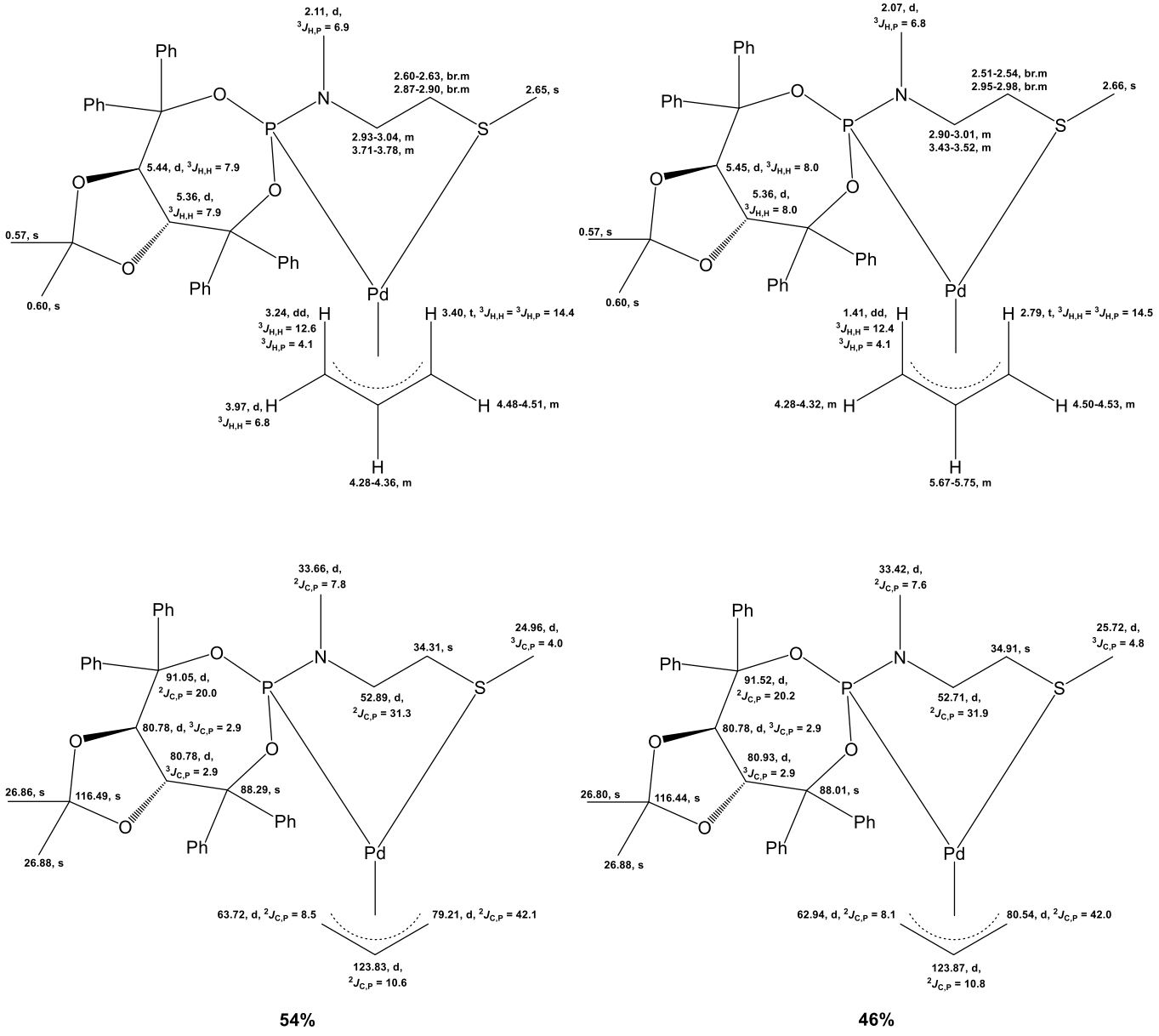
CH_2), 123.87 (d, $^2J_{C,P}$ = 10.8 Hz; CH) (minor form). $^{31}P\{^1H\}$ NMR (202 MHz, CD_2Cl_2): δ 105.57 (major form), 107.98 (minor form). $C_{38}H_{43}BF_4NO_4PPdS$ (833.17): calcd. C 54.72, H 5.20, N 1.68; found C 54.94, H 5.28, N 1.62. M/z = 746.1699 (calcd. 746.1680) Da for $[Pd(\mathbf{L1a})(allyl)]^+$.

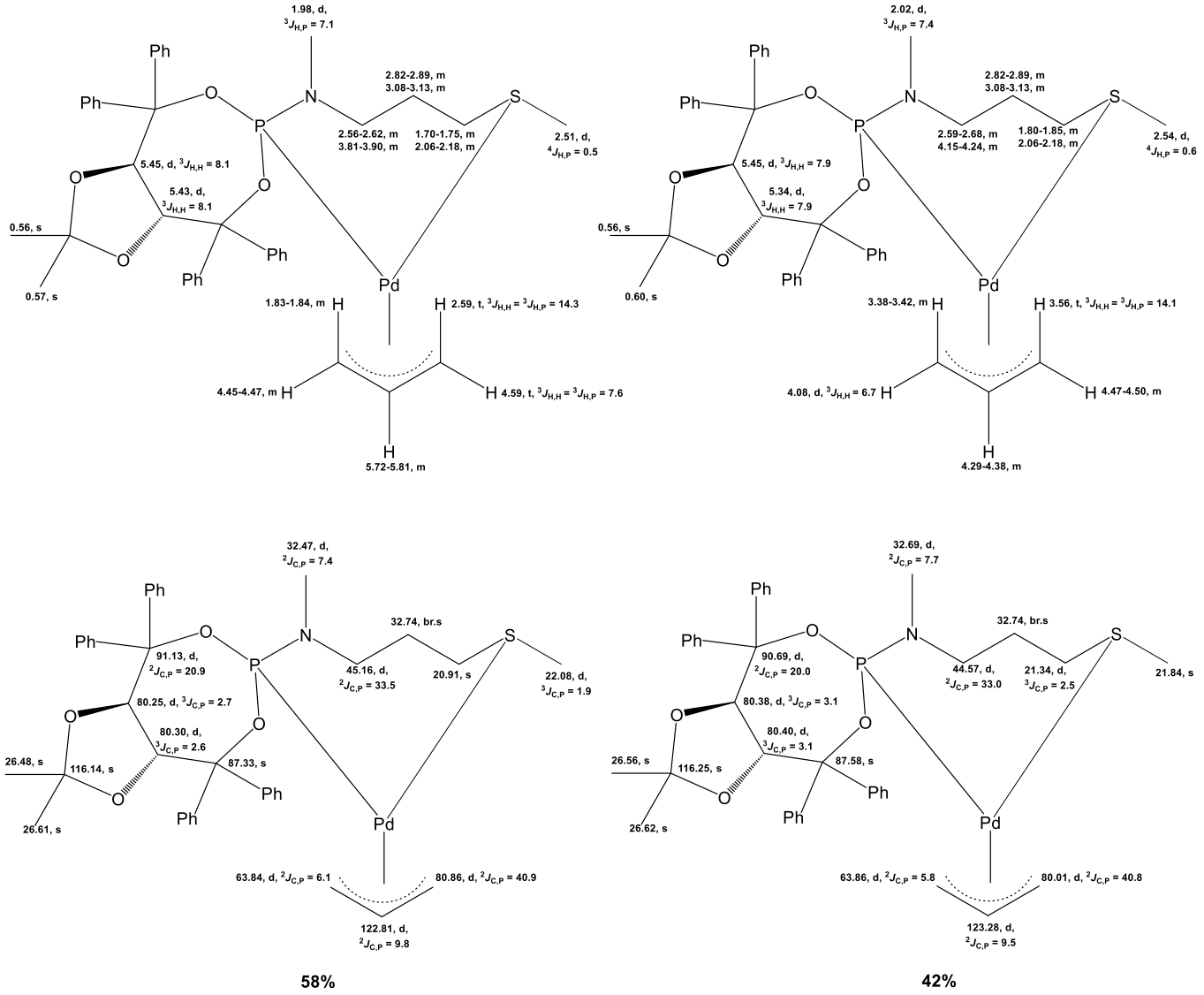


^1H (top) and $^{13}C\{^1H\}$ (bottom) NMR signal assignment for the major (left) and minor (right) diastereomers of $[Pd(allyl)(\mathbf{L1a})]BF_4$.

EXPERIMENTAL SECTION

[Pd(allyl)(**L1f**)]BF_4: White powder, yield 14.9 mg (88 %).^{1}H NMR (600 MHz, CD_2Cl_2) **L1f**: δ 0.56 (s, 3H; CH_3), 0.57 (s, 3H; CH_3), 1.98 (d, $^3J_{H,P}$ = 7.1 Hz, 3H; CH_3), 2.51 (d, $^4J_{H,P}$ = 0.5 Hz, 3H; CH_3), 1.70-1.75 (m, 1H; CH_2), 2.06-2.18 (m, 1H; CH_2), 2.56-2.62 (m, 1H; CH_2), 2.82-2.89 (m, 1H; CH_2), 3.08-3.13 (m, 1H; CH_2), 3.81-3.90 (m, 1H; CH_2), 5.43 (d, $^3J_{H,H}$ = 8.1 Hz, 1H; CH), 5.45 (d, $^3J_{H,H}$ = 8.1 Hz, 1H; CH), 7.22-7.63 (m, 20H, CH(Ph)) (major form), 0.56 (s, 3H; CH_3), 0.60 (s, 3H; CH_3), 2.02 (d, $^3J_{H,P}$ = 7.4 Hz, 3H; CH_3), 2.54 (d, $^4J_{H,P}$ = 0.6 Hz, 3H; CH_3), 1.80-1.85 (m, 1H; CH_2), 2.06-2.18 (m, 1H; CH_2), 2.59-2.68 (m, 1H; CH_2), 2.82-2.89 (m, 1H; CH_2), 3.08-3.13 (m, 1H; CH_2), 4.15-4.24 (m, 1H; CH_2), 5.34 (d, $^3J_{H,H}$ = 8.0 Hz, 1H; CH), 5.45 (d, $^3J_{H,H}$ = 8.0 Hz, 1H; CH), 7.22-7.63 (m, 20H, CH(Ph)) (minor form); ***η*^{3}-allylic ligand**: δ 1.83-1.84 (m, 1H; CH_2), 2.59 (t, $^3J_{H,H}$ = $^3J_{H,P}$ = 14.3 Hz, 1H; CH_2), 4.45-4.47 (m, 1H; CH_2), 4.59 (t, $^3J_{H,H}$ = $^3J_{H,P}$ = 7.6 Hz, 1H; CH_2), 5.72-5.81 (m, 1H;CH) (allyl) (major form), 3.38-3.42 (m, 1H; CH_2), 3.56 (t, $^3J_{H,H}$ = $^3J_{H,P}$ = 14.1 Hz, 1H; CH_2), 4.08 (d, $^3J_{H,H}$ = 6.7 Hz, 1H; CH_2), 4.47-4.50 (m, 1H;CH_2), 4.29-4.38 (m, 1H;CH) (minor form). $^{13}C\{^1H\}$ NMR (151 MHz, CD_2Cl_2) **L1f**: δ 22.08 (d, $^3J_{C,P}$ = 1.9 Hz; CH_3), 26.48 (s; CH_3), 26.61 (s; CH_3), 32.47 (d, $^2J_{C,P}$ = 7.4 Hz; CH_3), 20.91 (s; CH_2), 32.74 (br.s; CH_2), 45.16 (d, $^2J_{C,P}$ = 33.5 Hz; CH_2), 80.25 (d, $^3J_{C,P}$ = 2.7 Hz; CH), 80.30 (d, $^3J_{C,P}$ = 2.6 Hz; CH), 87.33 (s;CPh_2), 91.13 (d, $^2J_{C,P}$ = 20.9 Hz; CPh_2), 116.14 (s; CMe_2), (major form), 21.84 (s; CH_3), 26.56 (s; CH_3), 26.62 (s; CH_3), 32.69 (d, $^2J_{C,P}$ = 7.7 Hz; CH_3), 21.34 (d, $^3J_{C,P}$ = 2.5 Hz; CH_2), 32.74 (br.s; CH_2), 44.57 (d, $^2J_{C,P}$ = 33.0 Hz; CH_2), 80.38 (d, $^3J_{C,P}$ = 3.1 Hz; CH), 80.40 (d, $^3J_{C,P}$ = 3.1 Hz; CH), 87.58 (s;CPh_2), 90.69 (d, $^2J_{C,P}$ = 20.0 Hz; CPh_2), 116.25 (s; CMe_2), (minor form), 127.36 (s; CH(Ph)), 127.54 (s; CH(Ph)), 127.64 (s; CH(Ph)), 127.65 (s; CH(Ph)), 127.71 (s; CH(Ph)), 127.75 (s; CH(Ph)), 127.83 (s; CH(Ph)), 127.90 (s; CH(Ph)), 128.10 (s; CH(Ph)), 128.22 (s; CH(Ph)), 128.29 (s; CH(Ph)), 128.29 (s; CH(Ph)), 128.36 (s; CH(Ph)), 128.38 (s; CH(Ph)), 128.94 (s; CH(Ph)), 128.98 (s; CH(Ph)), 129.01 (s; CH(Ph)), 129.11 (s; CH(Ph)), 129.33 (s; CH(Ph)), 129.48 (s; CH(Ph)), 129.66 (s; CH(Ph)), 129.86 (s; CH(Ph)), 140,36 (d, $^3J_{C,P}$ = 6.3 Hz; C(Ph)), 140,40 (d, $^3J_{C,P}$ = 6.6 Hz; C(Ph)), 140,73 (d, $^3J_{C,P}$ = 8.3 Hz; C(Ph)), 140,89 (d, $^3J_{C,P}$ = 8.5 Hz; C(Ph)), 143.72 (s; C(Ph), 144.10 (s; C(Ph), 144.14 (d, $^3J_{C,P}$ = 1.2 Hz; C(Ph)), 144.75 (d, $^3J_{C,P}$ = 1.1 Hz; C(Ph)); ***η*^{3}-allylic ligand**: 63.84 (d, $^2J_{C,P}$ = 6.1 Hz; CH_2), 80.86 (d, $^2J_{C,P}$ = 40.9 Hz; CH_2), 122.81 (d, $^2J_{C,P}$ = 9.8 Hz; CH) (major form), 63.86 (d, $^2J_{C,P}$ = 5.8 Hz; CH_2), 80.01 (d, $^2J_{C,P}$ = 40.8 Hz; CH_2), 123.28 (d, $^2J_{C,P}$ = 9.5 Hz; CH) (minor form). $^{31}P\{^1H\}$ NMR (243 MHz, CD_2Cl_2): δ 115.84 (major form), 115.16 (minor form). $C_{39}H_{45}BF_4NO_4PPdS$ (847.19): calcd. C 55.24, H 5.35, N 1.65; found C 55.50, H 5.44, N 1.73. M/z = 760.1853 (calcd. 760.1836) Da for [Pd(**L1f**)(allyl)]$^+$.

EXPERIMENTAL SECTION



^{1}H (top) and ^{13}C{^{1}H} (bottom) NMR signal assignment for the major (left) and minor (right) diastereomers of [Pd(allyl)(**L1f**)]BF_4.

General procedure for the addition of the second equivalent of corresponding ligand to the solution of [Pd(allyl)(L)]BF_4 complexes. A solution of **L1a** or **L1f** (0.025 mmol) in CD_2Cl_2 (0.6 mL) was added to the appropriate [Pd(allyl)(**L**)]BF_4 complex sampled in a NMR tube (0.025 mmol). The resulting mixture was shacked and left overnight, then NMR-spectra were recorded.

Table S1. Crystal data and structure refinement for new compounds.

L1b		
CCDC number	2213985	
Empirical formula	$C_{76}H_{88}N_2O_8P_2S_2$	
Formula weight	1283.54	
Temperature	295(2) K	
Wavelength	1.54186 Å	
Crystal system	Triclinic	
Space group	P 1	
Unit cell dimensions	a = 9.4004(2) Å	α= 82.188(2)°.
	b = 9.4572(2) Å	β= 80.662(2)°.
	c = 22.4551(4) Å	γ = 60.1160(10)°.
Volume	1704.38(6) $Å^3$	
Z	1	
Density (calculated)	1.251 Mg/m^3	
Absorption coefficient	1.606 mm^{-1}	
F(000)	684	
Theta range for data collection	1.998 to 67.943°.	
Index ranges	-11<=h<=7, -11<=k<=10, -26<=l<=26	
Reflections collected	34079	
Independent reflections	8542 [R(int) = 0.0625]	
Completeness to theta = 67.686°	95.4 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8542 / 3 / 824	
Goodness-of-fit on F^2	1.020	
Final R indices [I>2sigma(I)]	R1 = 0.0477, wR2 = 0.1187	
R indices (all data)	R1 = 0.0551, wR2 = 0.1272	
Absolute structure parameter	-0.001(16)	
Extinction coefficient	0.0052(5)	
Largest diff. peak and hole	0.460 and -0.345 e. $Å^{-3}$	
[Pd(allyl)(**L1f**)]BF_4		
CCDC number	2308760	
Empirical formula	$C_{39}H_{45}BF_4NO_4PPdS$	
Formula weight	848.00	
Temperature	295(2) K	
Wavelength	1.54186 Å	

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Crystal system	Hexagonal	
Space group	P 64	
Unit cell dimensions	a = 29.2000(10) Å	α= 90°.
	b = 29.2000(10) Å	β= 90°.
	c = 10.1029(4) Å	γ = 120°.
Volume	7460.1(6) $Å^3$	
Z	6	
Density (calculated)	1.133 Mg/m^3	
Absorption coefficient	4.102 mm^{-1}	
F(000)	2616	
Theta range for data collection	3.027 to 55.802°.	
Index ranges	-31<=h<=25, -31<=k<=31, -6<=l<=10	
Reflections collected	32191	
Independent reflections	5314 [R(int) = 0.2007]	
Completeness to theta = 55.802°	99.4 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5314 / 346 / 431	
Goodness-of-fit on F^2	0.617	
Final R indices [I>2sigma(I)]	R1 = 0.0544, wR2 = 0.1327	
R indices (all data)	R1 = 0.2115, wR2 = 0.1613	
Absolute structure parameter	-0.05(2)	
Extinction coefficient	0.00139(10)	
Largest diff. peak and hole	0.304 and -0.336 e. $Å^{-3}$	

CATALYTIC RESULTS

Palladium-Catalyzed Asymmetric Allylic Alkylation of (*E*)-1,3-Diphenylallyl Acetate or (*E*)-1,3-Diphenylallyl Ethyl Carbonate with Dimethyl Malonate, Di-*tert*-butyl Malonate and Dibenzyl 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 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). The appropriate substrate (0.25 mmol) was added and the solution stirred for 15 min. The appropriate malonate (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 (**11a**), di-*tert*-butyl (*E*)-2-(1,3-diphenylallyl)malonate (**11b**) or dibenzyl (*E*)-2-(1,3-diphenylallyl)malonate (**11c**).[22] 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 or (*E*)-1,3-Diphenylallyl Ethyl Carbonate with Pyrrolidine: A solution of $[Pd(allyl)Cl]_2$ (0.001 g, 0.0025 mmol) and the appropriate ligand (0.005 mmol or 0.01 mmol) in 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). The appropriate substrate (0.25 mmol) was added and the solution stirred for 15 min, then freshly distilled pyrrolidine (0.06 mL, 0.75 mmol) was added. The reaction mixture was stirred for 24 h, diluted with CH_2Cl_2 (2 mL) and filtered through a thin layer of SiO_2. The filtrate was evaporated at reduced pressure (40 Torr) and dried in vacuum (10^{-3} Torr) affording a residue containing (*E*)-1-(1,3-diphenylallyl)pyrrolidine (**11d**).[23] In order to evaluate *ee* and conversion, the obtained residue was dissolved in an appropriate eluent mixture (8 mL) and a sample was taken for HPLC analysis.

Palladium-Catalyzed Asymmetric Allylic Alkylation of Cinnamyl Acetate or Cinnamyl Methyl Carbonate 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). The appropriate substrate (0.25 mmol) was added and the solution stirred for 15 min. β-Ketoether **13** (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 (**14**).[16c,d] 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.

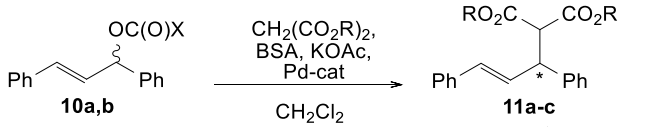
Palladium-Catalyzed Asymmetric Allylic Alkylation of Cinnamyl Acetate or Cinnamyl Methyl Carbonate with Ethyl 2-Acetamido-3-Oxobutanoate: A solution of $[Pd(allyl)Cl]_2$ (0.001 g, 0.0025 mmol) and the appropriate ligand (0.005 mmol or 0.01 mmol) in toluene (1.5 mL) was stirred for 40 min or the appropriate cationic complex (0.005 mmol) was dissolved in toluene (1.5 mL). The appropriate substrate (0.25 mmol) was added and the solution stirred for 15 min. α-Acetamido-β-Ketoether **15** (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 (**16**).[16e] 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 Methyl Carbonate with 2,5-Dimethylpyrrole: 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 methyl carbonate (0.05 g, 0.25 mmol) was added and the solution stirred for 15 min. Freshly distilled 2,5-dimethylpyrrole (**17**) (0.02 mL, 0.2 mmol) and Cs_2CO_3 (0.065 g, 0.2 mmol) were added. The reaction mixture was stirred for 24 h, precipitate was separated by centrifugation and solvent was removed in vacuum (40 Torr). The obtained residue was purified by flash chromatography on SiO_2: impurities were eluted with CH_2Cl_2 (5 mL), then the product was eluted with ethyl acetate (10 mL). The solvent was evaporated at reduced pressure (40 Torr) and dried in vacuum (10^{-3} Torr) affording 2-cinnamyl-2,5-dimethylpyrrole (**18**).[16f] In order to evaluate *ee*, the obtained product 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 (**19**) (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 (**20**), (*E*)-diethyl (1-phenyl-3-(phenylamino)prop-1-en-2-yl)phosphonate (**21**) and (*E*)-2-(diethoxyphosphoryl)-3-phenylallyl acetate (**22**).[14] Conversion of **19** and the ratio of **20**/**21**/**22** 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.

Table S2. Pd-catalyzed allylic alkylation of **10a,b** with dialkyl malonates. [a]



Entry	Substrate	Compound	L/Pd	Product	Conversion [%]	*Ee* [%] [b,c]
1	**10a**	**L1a**	1	**11a**	51	98 (*R*)
2	**10a**	**L1a**	2	**11a**	35	98 (*R*)
3	**10a**	**L1a**	1	**11a**	100	97 (*R*) [d]
4	**10a**	**L1a**	1	**11b**	73	99 (*R*)
5	**10a**	**L1a**	2	**11b**	15	99 (*R*)
6	**10a**	**L1a**	1	**11b**	100	97 (*R*) [d]
7	**10a**	**L1a**	1	**11c**	85	96 (*R*)
8	**10a**	**L1a**	2	**11c**	27	98 (*R*)
9	**10a**	**L1a**	1	**11c**	100	95 (*R*) [d]
10	**10b**	**L1a**	1	**11a**	75	87 (*R*)
11	**10b**	**L1a**	2	**11a**	52	97 (*R*)
12	**10b**	**L1a**	1	**11b**	74	93 (*R*)
13	**10b**	**L1a**	2	**11b**	22	98 (*R*)
14	**10b**	**L1a**	1	**11c**	100	89 (*R*)
15	**10b**	**L1a**	2	**11c**	59	92 (*R*)
16	**10a**	[Pd(allyl)(**L1a**)]BF_4	1	**11a**	76	97 (*R*)
17	**10b**	[Pd(allyl)(**L1a**)]BF_4	1	**11a**	73	92 (*R*)
18	**10a**	**L1b**	1	**11a**	74	76 (*R*)
19	**10a**	**L1b**	2	**11a**	24	87 (*R*)
20	**10a**	**L1c**	1	**11a**	100	92 (*R*)
21	**10a**	**L1c**	2	**11a**	14	87 (*R*)
22	**10a**	**L1d**	1	**11a**	81	90 (*R*)

CATALYTIC RESULTS

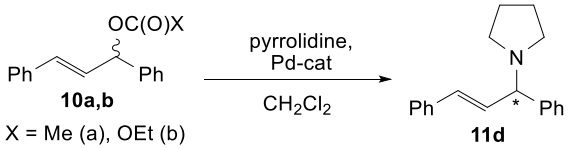
23	**10a**	**L1d**	2	**11a**	50	92 (*R*)
24	**10a**	**L1e**	1	**11a**	95	97 (*R*)
25	**10a**	**L1e**	2	**11a**	73	98 (*R*)
26	**10a**	**L1f**	1	**11a**	92	97 (*R*)
27	**10a**	**L1f**	2	**11a**	50	98 (*R*)
28	**10a**	[Pd(allyl)(**L1f**)]BF_4	1	**11a**	97	98 (*R*)
29	**10a**	**L1g**	1	**11a**	60	88 (*S*)
30	**10a**	**L1g**	2	**11a**	41	86 (*S*)
31	**10a**	**L1h**	1	**11a**	90	63 (*R*)
32	**10a**	**L1h**	2	**11a**	79	63 (*R*)
33	**10a**	**L2a**	1	**11a**	100	99 (*R*)
34	**10a**	**L2a**	2	**11a**	65	99 (*R*)
35	**10a**	**L2a**	1	**11b**	83	99 (*R*)
36	**10a**	**L2a**	2	**11b**	15	99 (*R*)
37	**10a**	**L2a**	1	**11c**	100	99 (*R*)
38	**10a**	**L2a**	2	**11**	28	98 (*R*)
39	**10a**	**L2b**	1	**11a**	100	78 (*R*)
40	**10a**	**L2b**	2	**11a**	60	64 (*R*)
41	**10a**	**L2c**	1	**11a**	100	96 (*R*)
42	**10a**	**L2c**	2	**11a**	100	98 (*R*)
43	**10a**	**L3a**	1	**11a**	100	21 (*S*)
44	**10a**	**L3a**	2	**11a**	45	17 (*S*)
45	**10a**	**L3b**	1	**11a**	100	88 (*S*)
46	**10a**	**L3b**	2	**11a**	100	89 (*S*)
47	**10a**	**L4a**	1	**11a**	100	21 (*R*)
48	**10a**	**L4a**	2	**11a**	98	29 (*R*)
49	**10a**	**L4b**	1	**11a**	95	7 (*S*)
50	**10a**	**L4b**	2	**11a**	97	6 (*S*)
51	**10a**	**L5a**	1	**11a**	100	44 (*R*)
52	**10a**	**L5a**	2	**11a**	34	37 (*R*)
53	**10a**	**L5b**	1	**11a**	100	95 (*S*)
54	**10a**	**L5b**	2	**11a**	100	94 (*S*)
55	**10a**	**L5b**	1	**11b**	100	95 (*S*)
56	**10a**	**L5b**	2	**11b**	100	94 (*S*)
57	**10a**	**L5b**	1	**11c**	100	95 (*S*)

CATALYTIC RESULTS

58	**10a**	**L5b**	2	**11c**	100	94 (*S*)
59	**10a**	$\mathbf{L_A}$	1	**11a**	40	81 (*S*)
60	**10a**	$\mathbf{L_A}$	2	**11a**	19	76 (*S*)
61	**10a**	$\mathbf{L_B}$	1	**11a**	68	82 (*R*)
62	**10a**	$\mathbf{L_B}$	2	**11a**	7	77 (*R*)
63	**10a**	(*S*)-$\mathbf{L_C}$	1	**11a**	100	87 (*S*) [e]
64	**10a**	(*S*)-$\mathbf{L_C}$	2	**11a**	100	79 (*S*) [e]
65	**10a**	(*R*)-$\mathbf{L_C}$	1	**11a**	27	2 (*S*) [e]
66	**10a**	(*R*)-$\mathbf{L_C}$	2	**11a**	15	12 (*S*) [e]

[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 substrates **10a,b** and enantiomeric excess of **11a** were determined by HPLC (Kromasil 5-CelluCoat, C_6H_{14}/*i*PrOH = 99/1, 0.6 mL/min, 254 nm, *t*(*R*) = 19.6 min, *t*(*S*) = 21.0 min); **11b** – (Daicel Chiralpak AD-H, C_6H_{14}/*i*PrOH = 95/5, 1.0 mL/min, 254 nm, *t*(*R*) = 9.2 min, *t*(*S*) = 12.8 min); **11c** – (Daicel Chiralpak AD-H, C_6H_{14}/*i*PrOH = 4/1, 1.0 mL/min, 254 nm, *t*(*R*) = 16.0 min, *t*(*S*) = 19.8 min) [c] The absolute configurations were assigned by comparison of the HPLC retention times reported in the literature.[16a,b,24] [d] At 40 °C for 12 h. [e] Ref.[25]

Table S3. Pd-catalyzed allylic amination of **10a,b** with pyrrolidine. [a]



Entry	Substrate	Compound	L/Pd	Conversion [%]	*Ee* [%] [b,c]
1	**10a**	**L1a**	1	21	56 (*S*)
2	**10a**	**L1a**	2	74	85 (*S*)
3	**10b**	**L1a**	1	77	75 (*S*)
4	**10b**	**L1a**	2	100	96 (*S*)
5	**10a**	[Pd(allyl)(**L1a**)]BF_4	1	24	58 (*S*)
6	**10b**	[Pd(allyl)(**L1a**)]BF_4	1	72	82 (*S*)
7	**10a**	**L1b**	1	17	60 (*S*)
8	**10a**	**L1b**	2	18	67 (*S*)
9	**10b**	**L1b**	1	100	16 (*S*)
10	**10b**	**L1b**	2	100	42 (*S*)
11	**10a**	**L1c**	1	15	43 (*S*)
12	**10a**	**L1c**	2	27	47 (*S*)
13	**10a**	**L1d**	1	49	74 (*S*)
14	**10a**	**L1d**	2	100	80 (*S*)
15	**10a**	**L1e**	1	14	65(*S*)

CATALYTIC RESULTS

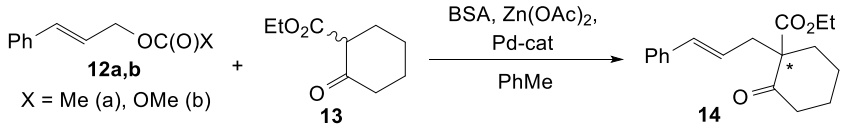
16	**10a**	**L1e**	2	20	91 (*S*)
17	**10b**	**L1e**	1	100	23 (*S*)
18	**10b**	**L1e**	2	100	52 (*S*)
19	**10a**	**L1f**	1	12	93 (*S*)
20	**10a**	**L1f**	2	34	96 (*S*)
21	**10a**	[Pd(allyl)(**L1f**)]BF_4	1	12	86 (*S*)
22	**10a**	**L1g**	1	17	22 (*S*)
23	**10a**	**L1g**	2	18	21 (*S*)
24	**10a**	**L1h**	1	58	65 (*S*)
25	**10a**	**L1h**	2	100	67 (*S*)
26	**10a**	**L2a**	1	100	96 (*S*)
27	**10a**	**L2a**	2	100	97 (*S*)
28	**10a**	**L2b**	1	14	46 (*S*)
29	**10a**	**L2b**	2	15	61 (*S*)
30	**10b**	**L2b**	1	100	48 (*S*)
31	**10b**	**L2b**	2	100	6 (*S*)
32	**10a**	**L2c**	1	86	76 (*S*)
33	**10a**	**L2c**	2	100	86 (*S*)
34	**10a**	**L3a**	1	22	41 (*S*)
35	**10a**	**L3a**	2	17	38 (*S*)
36	**10a**	**L3b**	1	20	27 (*R*)
37	**10a**	**L3b**	2	21	34 (*R*)
38	**10a**	**L4a**	1	3	19 (*S*)
39	**10a**	**L4a**	2	5	30 (*S*)
40	**10a**	**L4b**	1	4	9 (*R*)
41	**10a**	**L4b**	2	6	12 (*R*)
42	**10a**	**L5a**	1	6	40 (*R*)
43	**10a**	**L5a**	2	18	28 (*R*)
44	**10a**	**L5b**	1	39	96 (*R*)
45	**10a**	**L5b**	2	100	97 (*R*)
46	**10b**	**L5b**	1	100	77 (*R*)
47	**10b**	**L5b**	2	100	85 (*R*)
48	**10a**	$\mathbf{L_A}$	1	6	17 (*R*)
49	**10a**	$\mathbf{L_A}$	2	6	14 (*R*)
50	**10a**	$\mathbf{L_B}$	1	6	12 (*R*)

CATALYTIC RESULTS

51	**10a**	$\mathbf{L_B}$	2	7	6 (*R*)
52	**10a**	(*S*)-$\mathbf{L_C}$	1	28	28 (*R*) [d]
53	**10a**	(*S*)-$\mathbf{L_C}$	2	45	30 (*R*) [d]
54	**10a**	(*R*)-$\mathbf{L_C}$	1	12	10 (*S*) [d]
55	**10a**	(*R*)-$\mathbf{L_C}$	2	13	10 (*S*) [d]

[a] All reactions were carried out with 1 mol% of $[Pd(allyl)Cl]_2$ at room temperature for 24 h. [b] The conversion of substrates **10a,b** and enantiomeric excess of **11d** were determined by HPLC (Daicel Chiralcel OD-H, C_6H_{14}/*i*PrOH = 95/5, 0.4 mL/min, 254 nm, *t*(*R*) = 9.0 min, *t*(*S*) = 9.6 min). [c] The absolute configurations was assigned by comparison of the HPLC retention times reported in the literature.[16a,b,23b,26] [d] Ref.[25]

Table S4. Pd-catalyzed allylic alkylation of **12a,b** with **13**. [a]



Entry	Substrate	Compound	L/Pd	Conversion [%]	*Ee* [%] [b,c]
1	**12a**	**L1a**	1	23	81 (*R*)
2	**12a**	**L1a**	2	19	80 (*R*)
3	**12a**	**L1a**	1	46	65 (*R*) [d]
4	**12b**	**L1a**	1	32	75 (*R*)
5	**12b**	**L1a**	2	48	75 (*R*)
6	**12a**	[Pd(allyl)(**L1a**)]BF_4	1	16	81 (*R*)
7	**12a**	[Pd(allyl)(**L1a**)]BF_4	1	35	64 (*R*) [d]
8	**12b**	[Pd(allyl)(**L1a**)]BF_4	1	40	76 (*R*)
9	**12a**	**L1b**	1	38	56 (*R*)
10	**12a**	**L1b**	2	36	55 (*R*)
11	**12a**	**L1c**	1	72	78 (*R*)
12	**12a**	**L1c**	2	44	77 (*R*)
13	**12a**	**L1d**	1	13	70 (*R*)
14	**12a**	**L1d**	2	0	-
15	**12a**	**L1e**	1	100	80 (*R*)
16	**12a**	**L1e**	2	76	79 (*R*)
17	**12a**	**L1f**	1	74	37 (*R*)
18	**12a**	**L1f**	2	38	41 (*R*)
19	**12a**	[Pd(allyl)(**L1f**)]BF_4	1	97	23 (*R*)
20	**12a**	**L1g**	1	0	-
21	**12a**	**L1g**	2	0	-

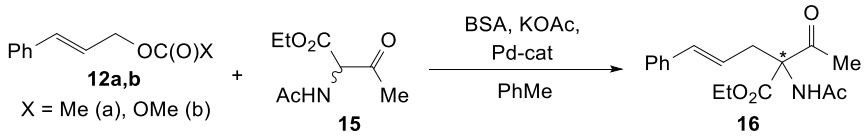
CATALYTIC RESULTS

22	**12a**	**L1h**	1	95	26 (*R*)
23	**12a**	**L1h**	2	80	22 (*R*)
24	**12a**	**L2a**	1	46	64 (*R*)
25	**12a**	**L2a**	2	36	67 (*R*)
26	**12a**	**L2b**	1	12	87 (*R*)
27	**12a**	**L2b**	2	21	91 (*R*)
28	**12b**	**L2b**	1	34	92 (*R*)
29	**12b**	**L2b**	2	38	94 (*R*)
30	**12a**	**L2c**	1	14	3 (*S*)
31	**12a**	**L2c**	2	23	2 (*S*)
32	**12a**	**L3a**	1	36	31 (*R*)
33	**12a**	**L3a**	2	30	28 (*R*)
34	**12a**	**L3b**	1	29	47 (*S*)
35	**12a**	**L3b**	2	38	53 (*S*)
36	**12a**	**L4a**	1	35	72 (*R*)
37	**12a**	**L4a**	2	49	74 (*R*)
38	**12a**	**L4b**	1	32	65 (*S*)
39	**12a**	**L4b**	2	77	66 (*S*)
40	**12a**	**L5a**	1	47	82 (*R*)
41	**12a**	**L5a**	2	32	80 (*R*)
42	**12a**	**L5b**	1	95	87 (*S*)
43	**12a**	**L5b**	2	99	87 (*S*)
44	**12b**	**L5b**	1	100	90 (*S*)
45	**12b**	**L5b**	2	100	88 (*S*)
46	**12a**	$\mathbf{L_A}$	1	0	-
47	**12a**	$\mathbf{L_A}$	2	0	-
48	**12a**	$\mathbf{L_B}$	1	4	61 (*R*)
49	**12a**	$\mathbf{L_B}$	2	0	-
50	**12a**	(*S*)-$\mathbf{L_C}$	1	0	- [e]
51	**12a**	(*S*)-$\mathbf{L_C}$	2	0	- [e]
52	**12a**	(*R*)-$\mathbf{L_C}$	1	0	- [e]
53	**12a**	(*R*)-$\mathbf{L_C}$	2	0	- [e]

[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 substrates **12a,b** and enantiomeric excess of **14** were determined by HPLC (Kromasil 5-CelluCoat, C_6H_{14}/*i*PrOH = 99/1, 1.0 mL/min, 254 nm, *t*(*R*) = 10.1 min, *t*(*S*) = 14.9 min). [c] The absolute

configuration was assigned by comparison of the HPLC retention times reported in the literature.[16a-d] [d] At 55 °C for 12 h. [e] Ref.[25]

Table S5. Pd-catalyzed allylic alkylation of **12a,b** with **15**. [a]



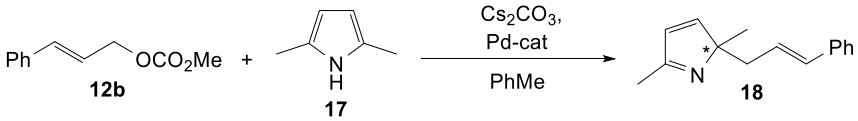
Entry	Substrate	Compound	L/Pd	Conversion [%]	*Ee* [%] [b,c]
1	**12a**	**L1a**	1	98	74 (*S*)
2	**12a**	**L1a**	2	20	66 (*S*)
3	**12a**	**L1a**	1	100	64 (*S*) [d]
4	**12a**	**L1a**	2	100	65 (*S*) [d]
5	**12b**	**L1a**	1	100	67 (*S*)
6	**12b**	**L1a**	2	78	67 (*S*)
7	**12a**	[Pd(allyl)(**L1a**)]BF_4	1	100	67 (*S*)
8	**12b**	[Pd(allyl)(**L1a**)]BF_4	1	100	66 (*S*)
9	**12a**	**L1b**	1	100	63 (*S*)
10	**12a**	**L1b**	2	70	63 (*S*)
11	**12a**	**L1c**	1	100	74 (*S*)
12	**12a**	**L1c**	2	92	73 (*S*)
13	**12a**	**L1d**	1	84	56 (*S*)
14	**12a**	**L1d**	2	100	55 (*S*)
15	**12a**	**L1e**	1	100	64 (*S*)
16	**12a**	**L1e**	2	100	71 (*S*)
17	**12a**	**L1f**	1	100	20 (*S*)
18	**12a**	**L1f**	2	33	20(*S*)
19	**12a**	[Pd(allyl)(**L1f**)]BF_4	1	100	23 (*S*)
20	**12a**	**L1g**	1	0	-
21	**12a**	**L1g**	2	0	-
22	**12a**	**L1h**	1	100	49 (*S*)
23	**12a**	**L1h**	2	88	48 (*S*)
24	**12a**	**L2a**	1	100	66 (*S*)
25	**12a**	**L2a**	2	32	69 (*S*)
26	**12a**	**L2b**	1	100	75 (*S*)
27	**12a**	**L2b**	2	100	76 (*S*)

CATALYTIC RESULTS

28	**12a**	**L2c**	1	100	18 (*S*)
29	**12a**	**L2c**	2	76	17 (*S*)
30	**12a**	**L3a**	1	52	8 (*S*)
31	**12a**	**L3a**	2	62	9 (*S*)
32	**12a**	**L3b**	1	84	50 (*R*)
33	**12a**	**L3b**	2	77	50 (*R*)
34	**12a**	**L4a**	1	96	36 (*S*)
35	**12a**	**L4a**	2	97	38 (*S*)
36	**12a**	**L4b**	1	100	17 (*R*)
37	**12a**	**L4b**	2	100	20 (*R*)
38	**12a**	**L5a**	1	100	27 (*S*)
39	**12a**	**L5a**	2	40	30 (*S*)
40	**12a**	**L5b**	1	100	66 (*R*)
41	**12a**	**L5b**	2	100	68 (*R*)
42	**12a**	**L_A**	1	0	-
43	**12a**	**L_A**	2	0	-
44	**12a**	**L_B**	1	11	47 (*S*)
45	**12a**	**L_B**	2	0	-

[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 substrates **12a,b** and enantiomeric excess of **16** were determined by HPLC (Daicel Chiralcel OD-H, C_6H_{14}/*i*PrOH = 85/15, 0.8 mL/min, 254 nm, *t*(*S*) = 9.7 min, *t*(*R*) = 10.6 min). [c] The absolute configuration was assigned by comparison of the HPLC retention times reported in the literature.[27] [d] In C_6H_6.

Table S6. Pd-catalyzed allylic alkylation of **12b** with **17**. [a]



Entry	Compound	L/Pd	Yield [%]	*Ee* [%] [b,c]
1	**L1a**	1	47	53 (*S*)
2	**L1a**	2	52	55 (*S*)
3	[Pd(allyl)(**L1a**)]BF_4	1	32	40 (*S*)
4	**L1b**	1	38	76 (*S*)
5	**L1b**	2	45	77 (*S*)
6	**L1c**	1	36	76 (*S*)
7	**L1c**	2	44	76 (*S*)
8	**L1d**	1	0	-

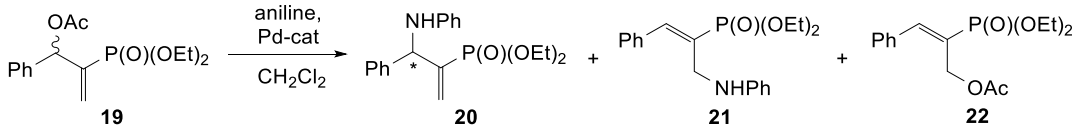
CATALYTIC RESULTS

9	**L1d**	2	0	-
10	**L1e**	1	62	82 (*S*)
11	**L1e**	2	73	73 (*S*)
12	**L1f**	1	41	65 (*S*)
13	**L1f**	2	37	22 (*S*)
14	[Pd(allyl)(**L1f**)]BF_4	1	30	47 (*S*)
15	**L1g**	1	0	-
16	**L1g**	2	0	-
17	**L1h**	1	0	-
18	**L1h**	2	0	-
19	**L2a**	1	25	50 (*S*)
20	**L2a**	2	30	51 (*S*)
21	**L2b**	1	0	-
22	**L2b**	2	0	-
23	**L2c**	1	0	-
24	**L2c**	2	0	-
25	**L3a**	1	0	-
26	**L3a**	2	0	-
27	**L3b**	1	0	-
28	**L3b**	2	0	-
29	**L4a**	1	53	52 (*S*)
30	**L4a**	2	55	56 (*S*)
31	**L4b**	1	0	-
32	**L4b**	2	0	-
33	**L5a**	1	48	55 (*S*)
34	**L5a**	2	50	60 (*S*)
35	**L5b**	1	45	71 (*R*)
36	**L5b**	2	57	91 (*R*)
37	**L5b**	2	73	89 (*R*) [d]
38	$\mathbf{L_A}$	1	0	-
39	$\mathbf{L_A}$	2	0	-
40	$\mathbf{L_B}$	1	9	13 (*S*)
41	$\mathbf{L_B}$	2	0	-

[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 **12b** and enantiomeric excess of **18** were determined by HPLC (Daicel Chiralpak AD-H, C_6H_{14}/*i*PrOH = 99/1, 1.0 mL/min, 254 nm, *t*(*S*) = 13.0 min, *t*(*R*) = 16.8 min). [c] The absolute

configuration was assigned by comparison of the HPLC retention times reported in the literature.[16f] [d] At 55 °C for 12 h.

Table S7. Pd-catalyzed allylic amination of **19** with aniline. [a]



19 **20** **21** **22**

Entry	Compound	L/Pd	Conversion [%]	20/21/22 [b]	*Ee* [%] [c,d]
1	**L1a**	1	100	92/8/0	58 (*R*)
2	**L1a**	2	100	89/11/0	52 (*R*)
3	[Pd(allyl)(**L1a**)]BF_4	1	100	100/0/0	59 (*R*)
4	**L1b**	1	95	84/16/0	76 (*R*)
5	**L1b**	2	95	78/22/0	75 (*R*)
6	**L1c**	1	100	74/26/0	37 (*R*)
7	**L1c**	2	100	90/10/0	17 (*R*)
8	**L1d**	1	62	62/27/11	50 (*R*)
9	**L1d**	2	0	-	-
10	**L1e**	1	100	100/0/0	29 (*R*)
11	**L1e**	2	100	97/3/0	24 (*R*)
12	**L1f**	1	100	95/5/0	73 (*R*)
13	**L1f**	2	100	97/3/0	73 (*R*)
14	[Pd(allyl)(**L1f**)]BF_4	1	100	26/74/0	16 (*R*)
15	**L1g**	1	0	-	-
16	**L1g**	2	0	-	-
17	**L1h**	1	100	72/18/10	19 (*R*)
18	**L1h**	2	100	85/15/0	20 (*R*)
19	**L2a**	1	0	-	-
20	**L2a**	2	100	82/18/0	52 (*R*)
21	**L2b**	1	100	63/37/0	0
22	**L2b**	2	100	21/79/0	0
23	**L2c**	1	100	45/55/0	11 (*R*)
24	**L2c**	2	100	63/37/0	12 (*R*)
25	**L3a**	1	100	100/0/0	92 (*S*)
26	**L3a**	2	100	100/0/0	92 (*S*)
27	**L3b**	1	100	80/20/0	71 (*S*)
28	**L3b**	2	100	86/14/0	64 (*S*)
29	**L4a**	1	100	100/0/0	84 (*S*)
30	**L4a**	2	100	99/1/0	83 (*S*)

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31	**L4b**	1	100	100/0/0	87 (*R*)
32	**L4b**	2	100	100/0/0	88 (*R*)
33	**L5a**	1	100	100/0/0	67 (*S*)
34	**L5a**	2	100	100/0/0	67 (*S*)
35	**L5b**	1	100	100/0/0	70 (*S*)
36	**L5b**	2	100	100/0/0	69 (*S*)
37	$\mathbf{L_A}$	1	90	37/58/5	13 (*S*)
38	$\mathbf{L_B}$	1	100	71/29/0	83 (*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 **19** and the ratio of **20/21/22** was determined by $^{31}P\{^1H\}$ NMR spectroscopy. [c] The enantiomeric excess of **20** was 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*) = 7.0 min). [d] The absolute configuration was assigned by comparison of the HPLC retention times reported in the literature.[14]

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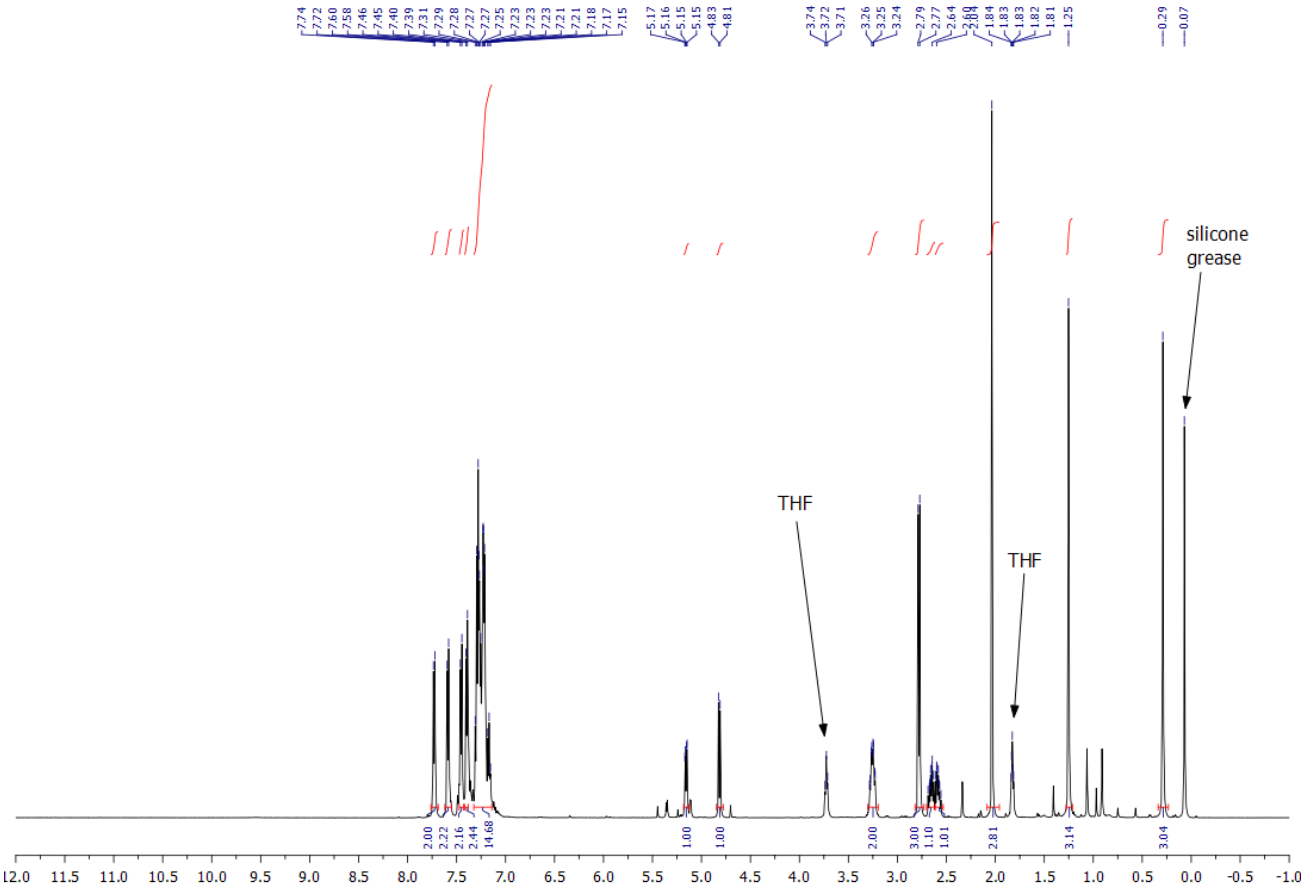
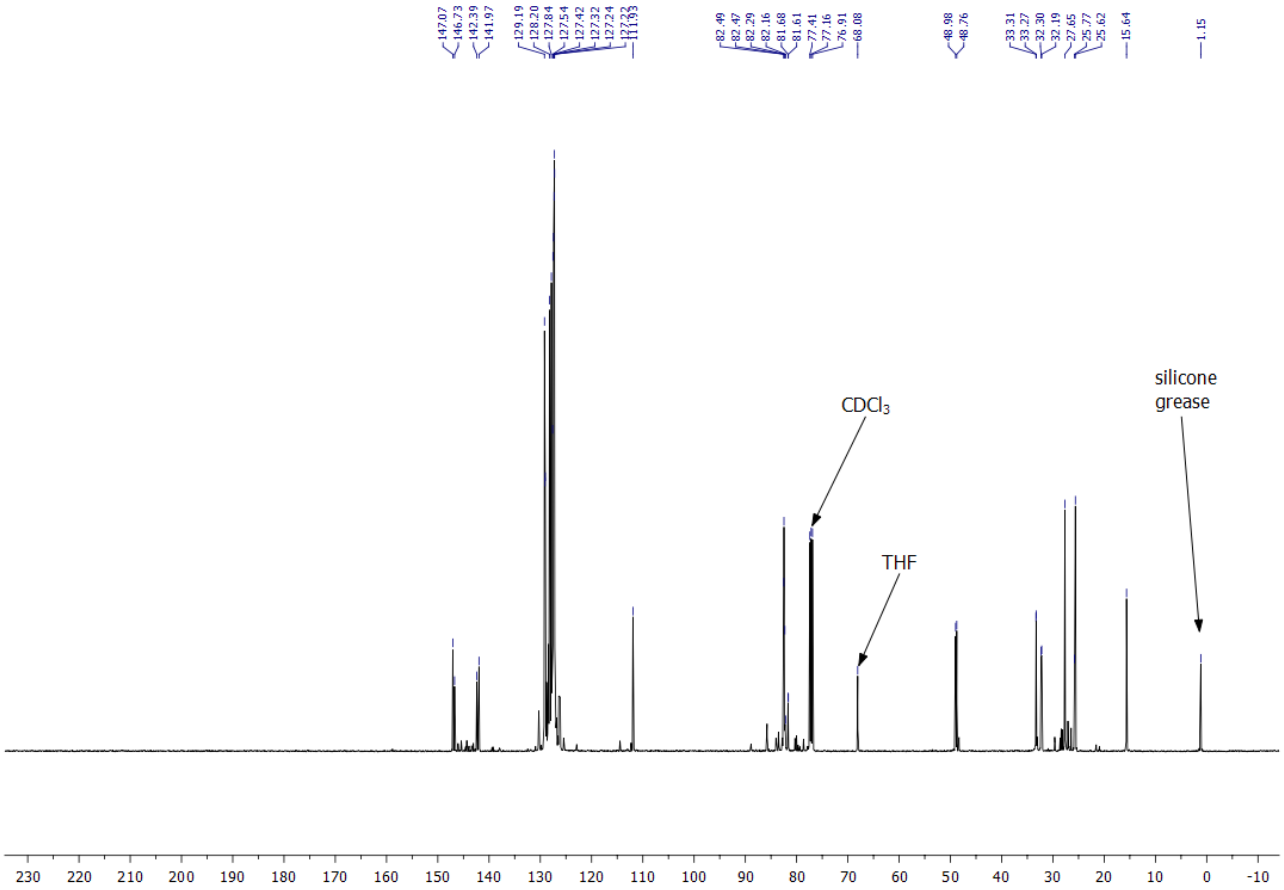
NMR AND MASS SPECTRA

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



L1a, ^{1}H spectrum.

NMR AND MASS SPECTRA



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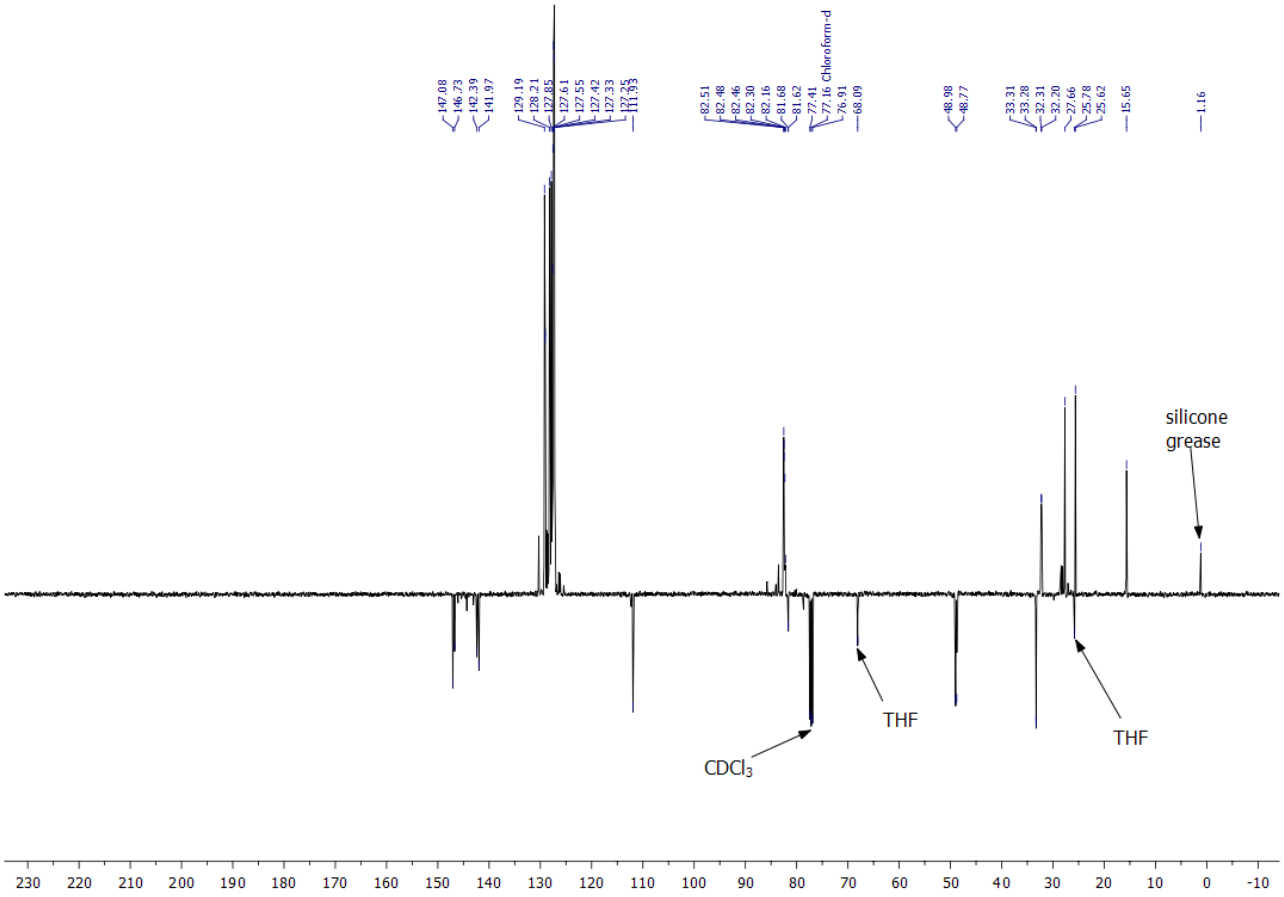
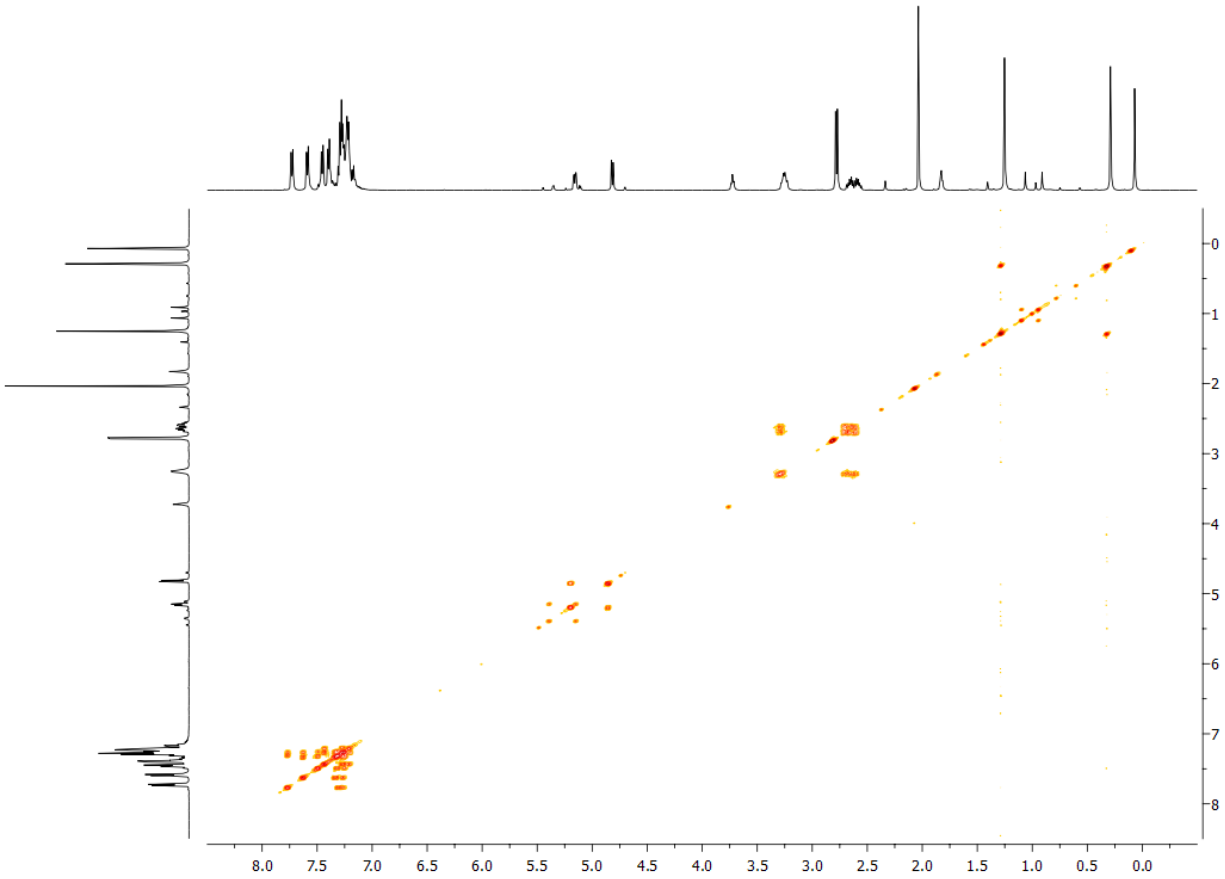


L1a, $^{13}C\{^{1}H\}$ APT spectrum.

NMR AND MASS SPECTRA



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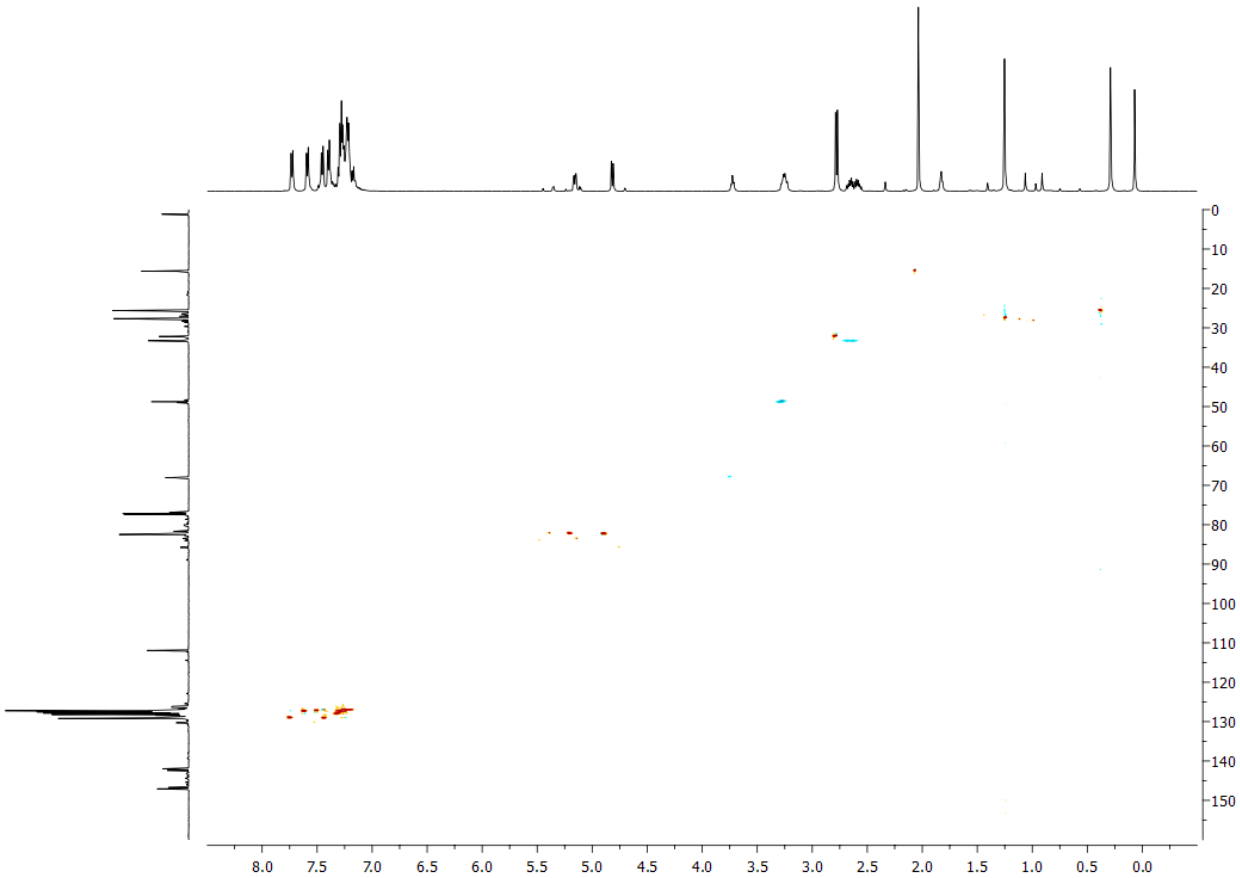
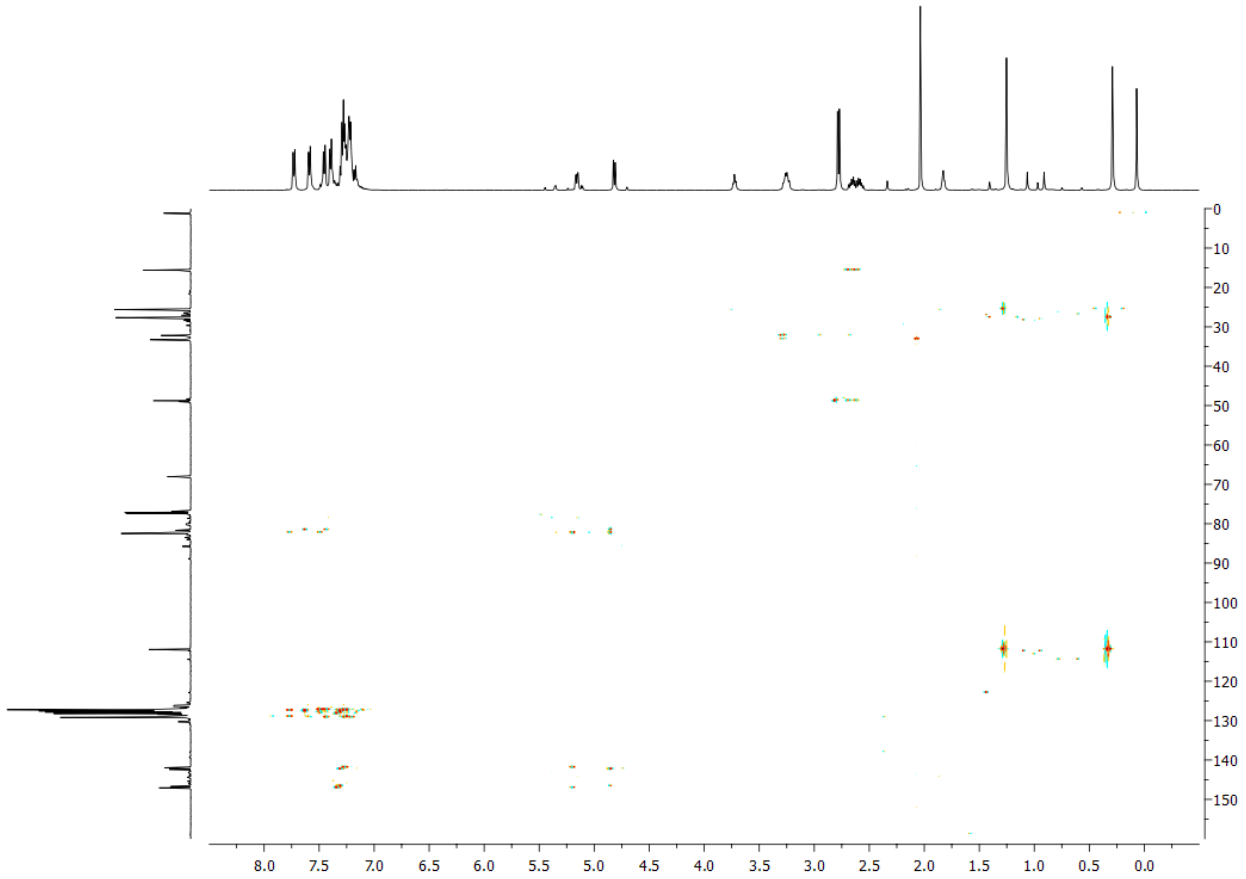


L1a, ^{1}H-^{13}C HSQC spectrum.

NMR AND MASS SPECTRA



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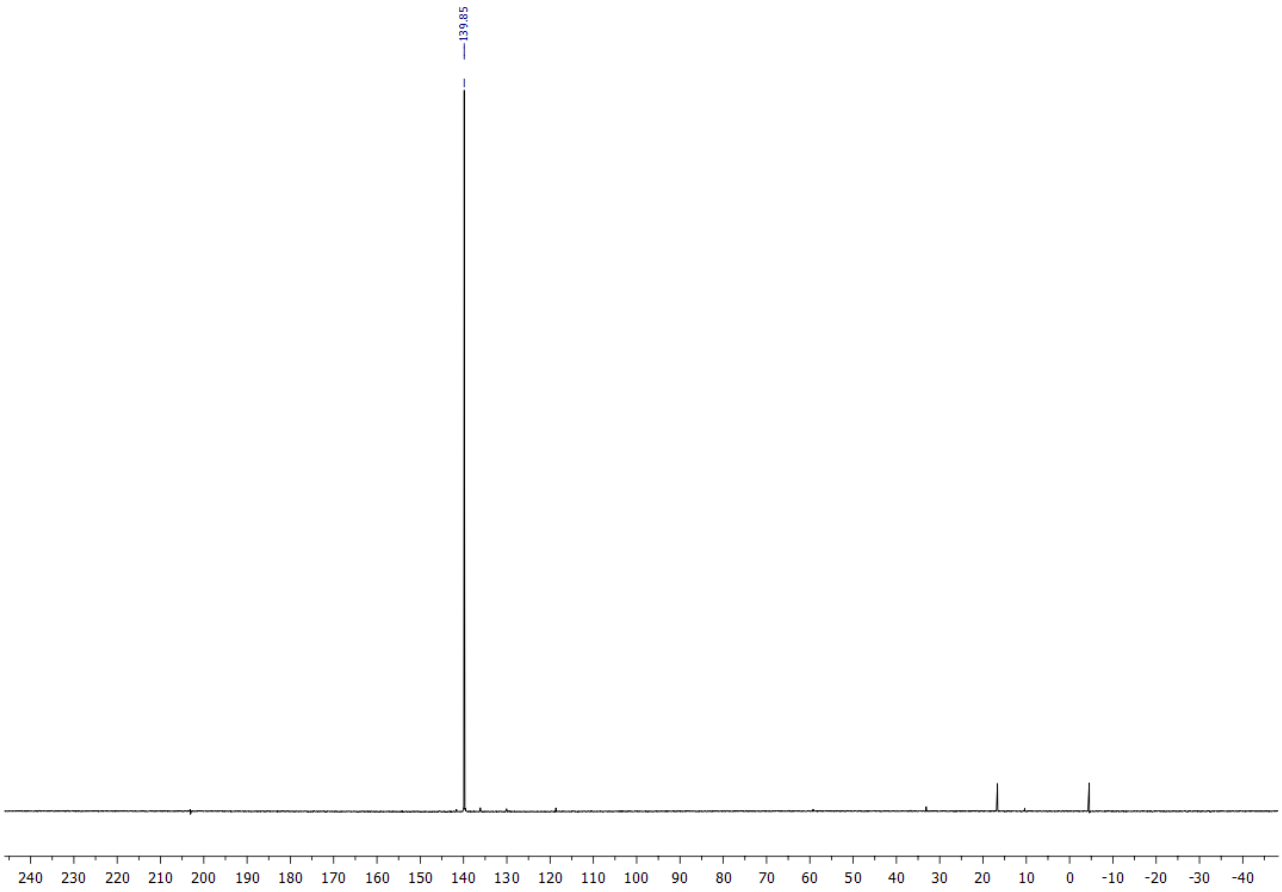
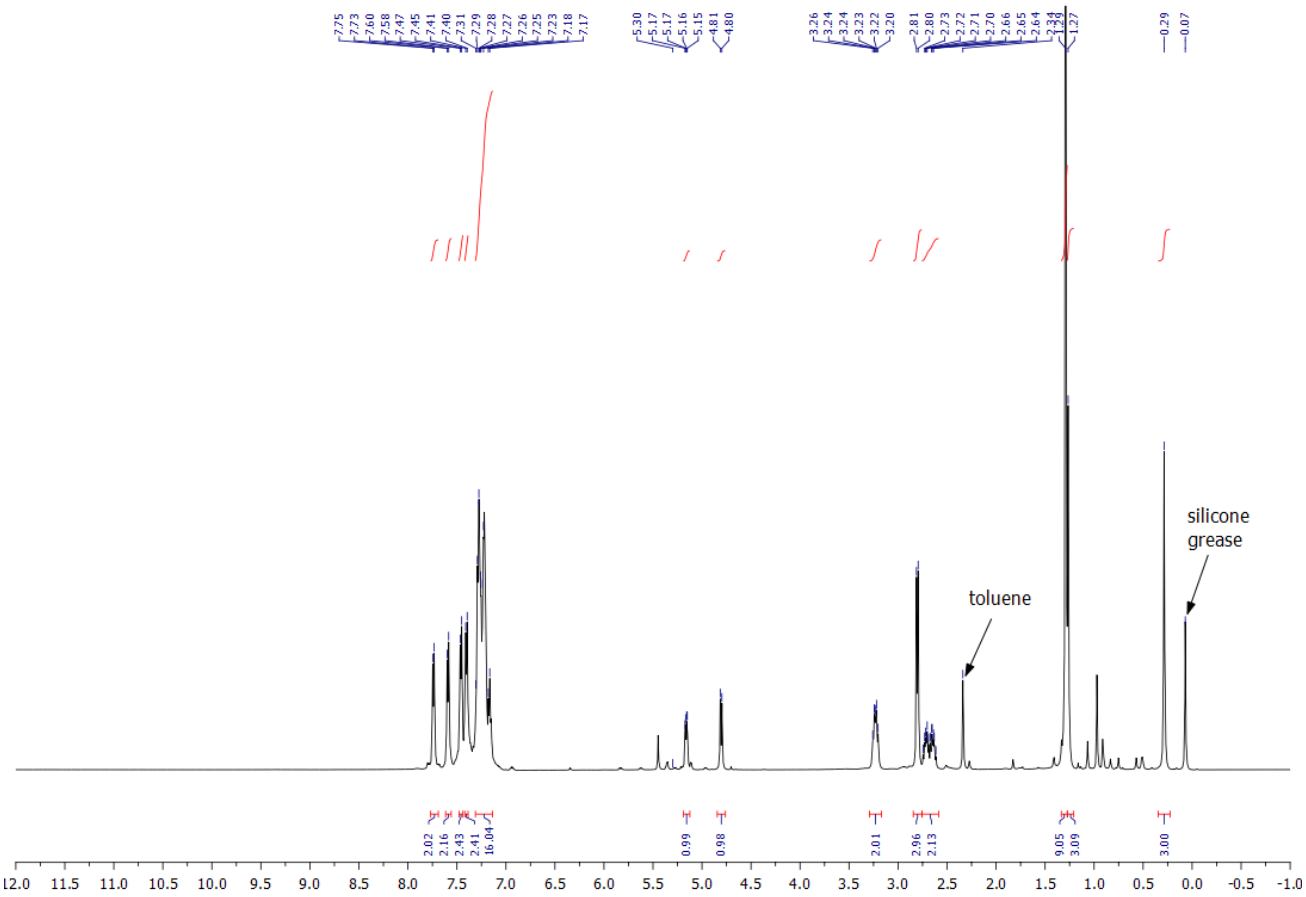
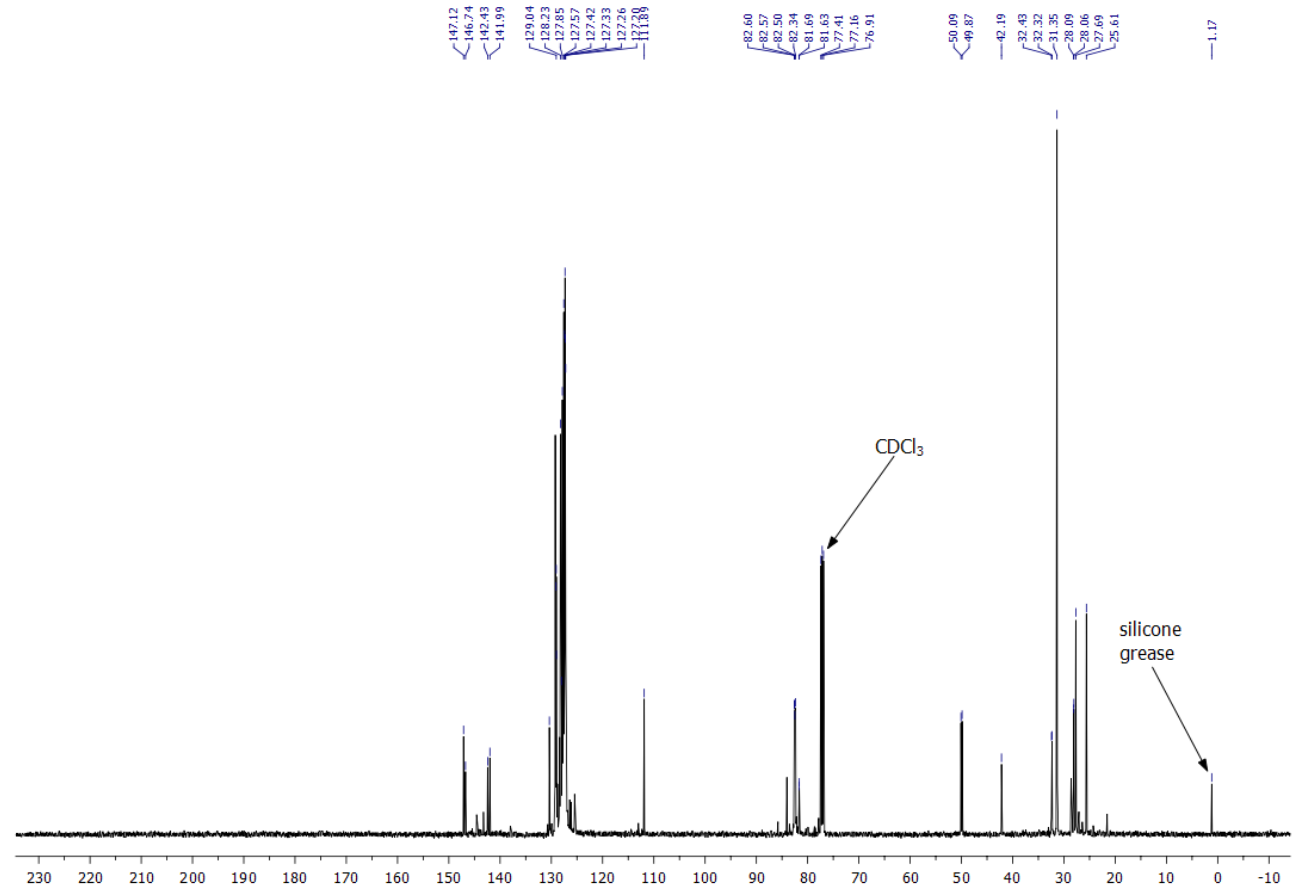


L1b, $^{31}P\{^{1}H\}$ spectrum.

NMR AND MASS SPECTRA

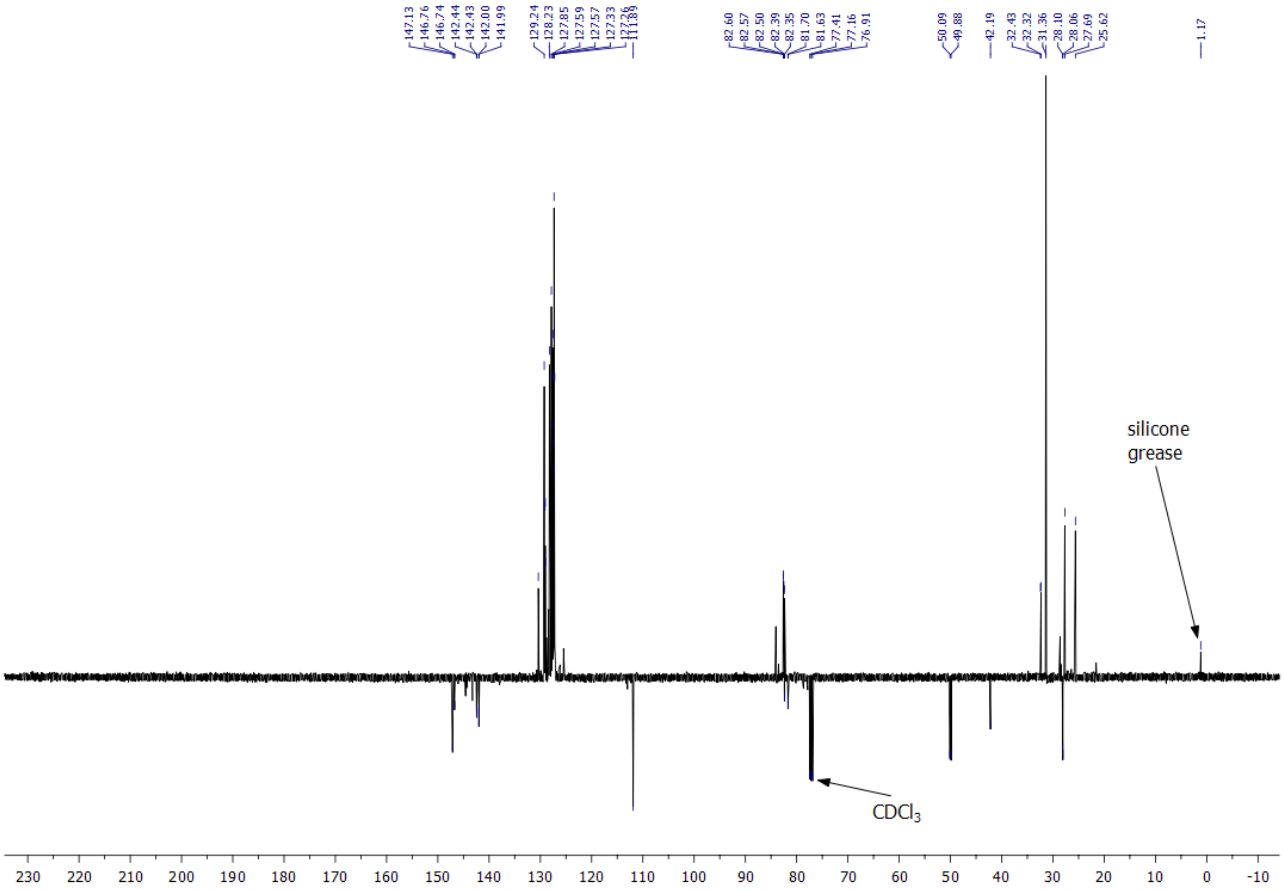


L1b, ^{1}H spectrum.

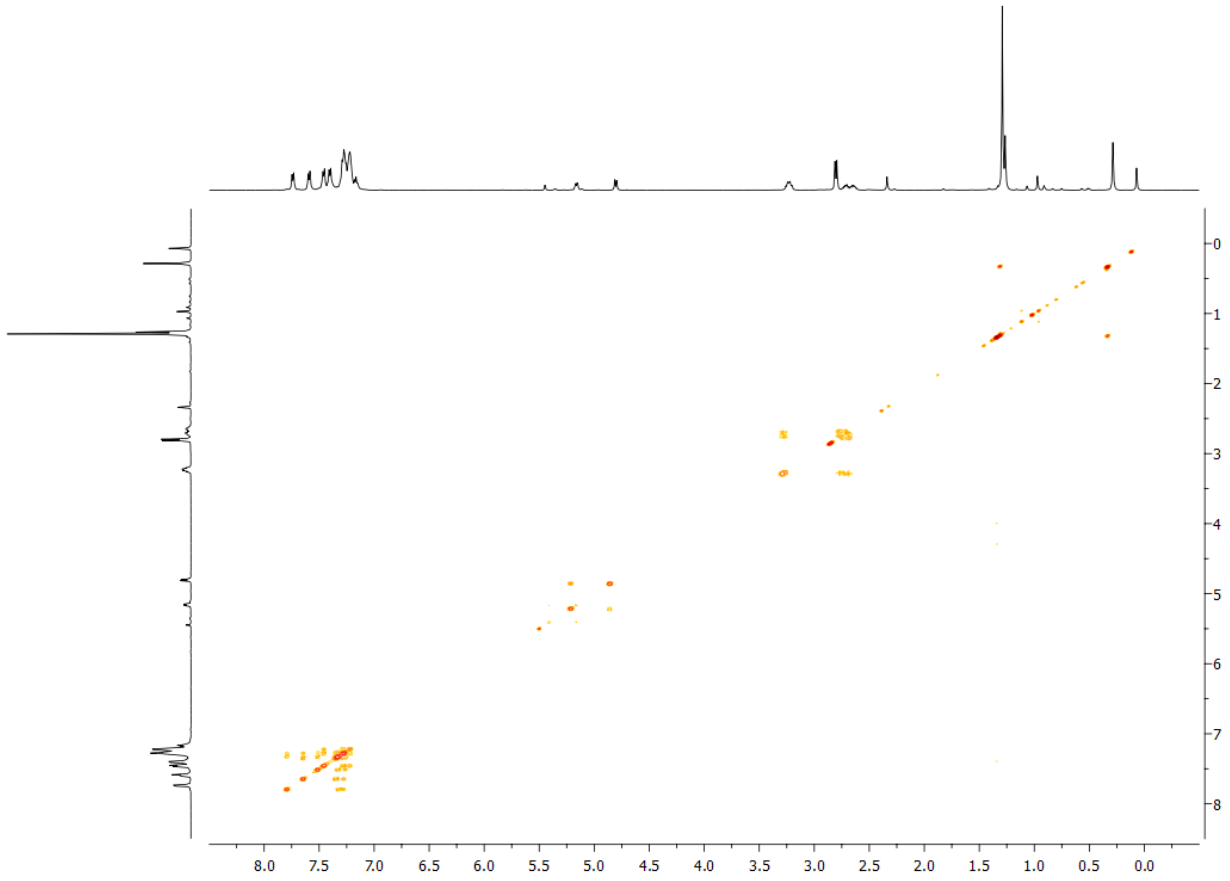


L1b, $^{13}C\{^{1}H\}$ spectrum.

NMR AND MASS SPECTRA



L1b, $^{13}C\{^{1}H\}$ APT spectrum.



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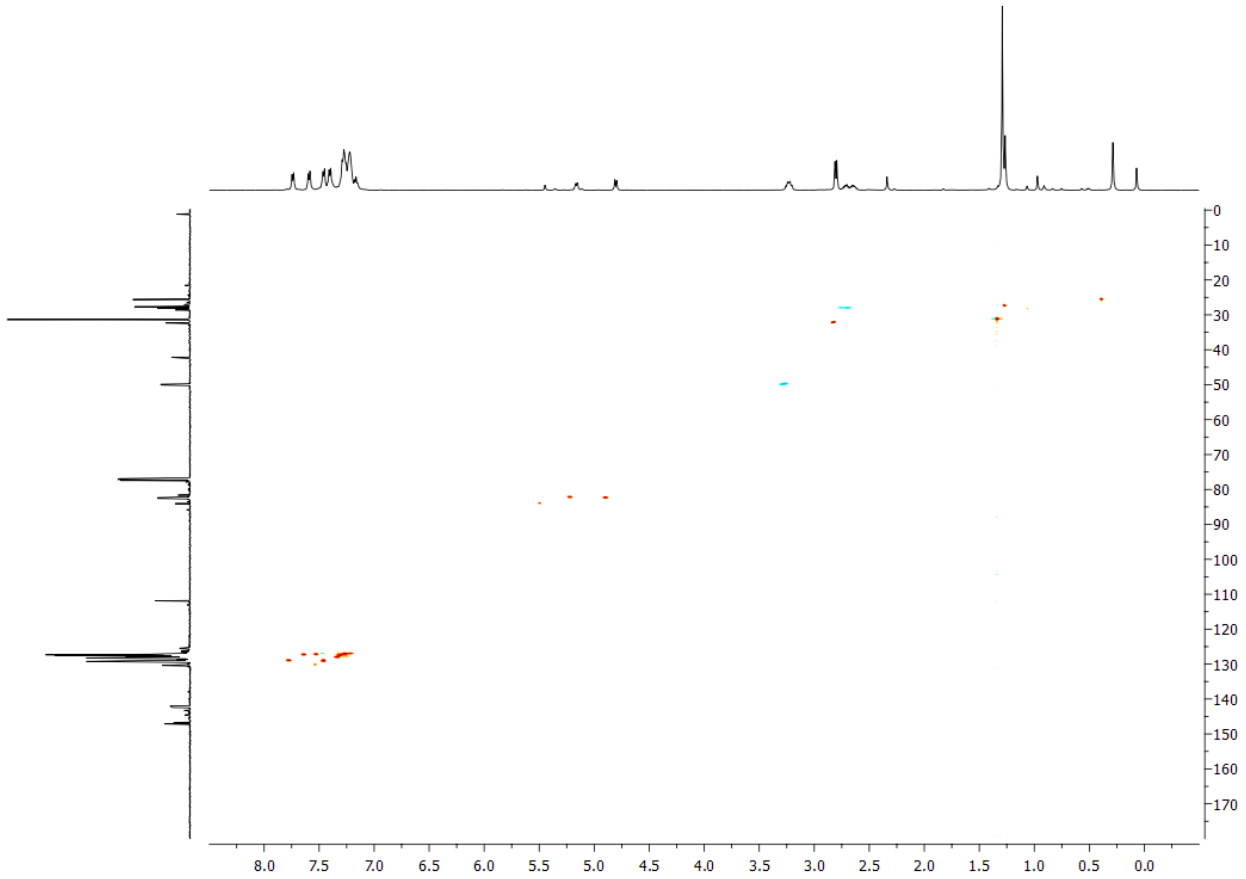

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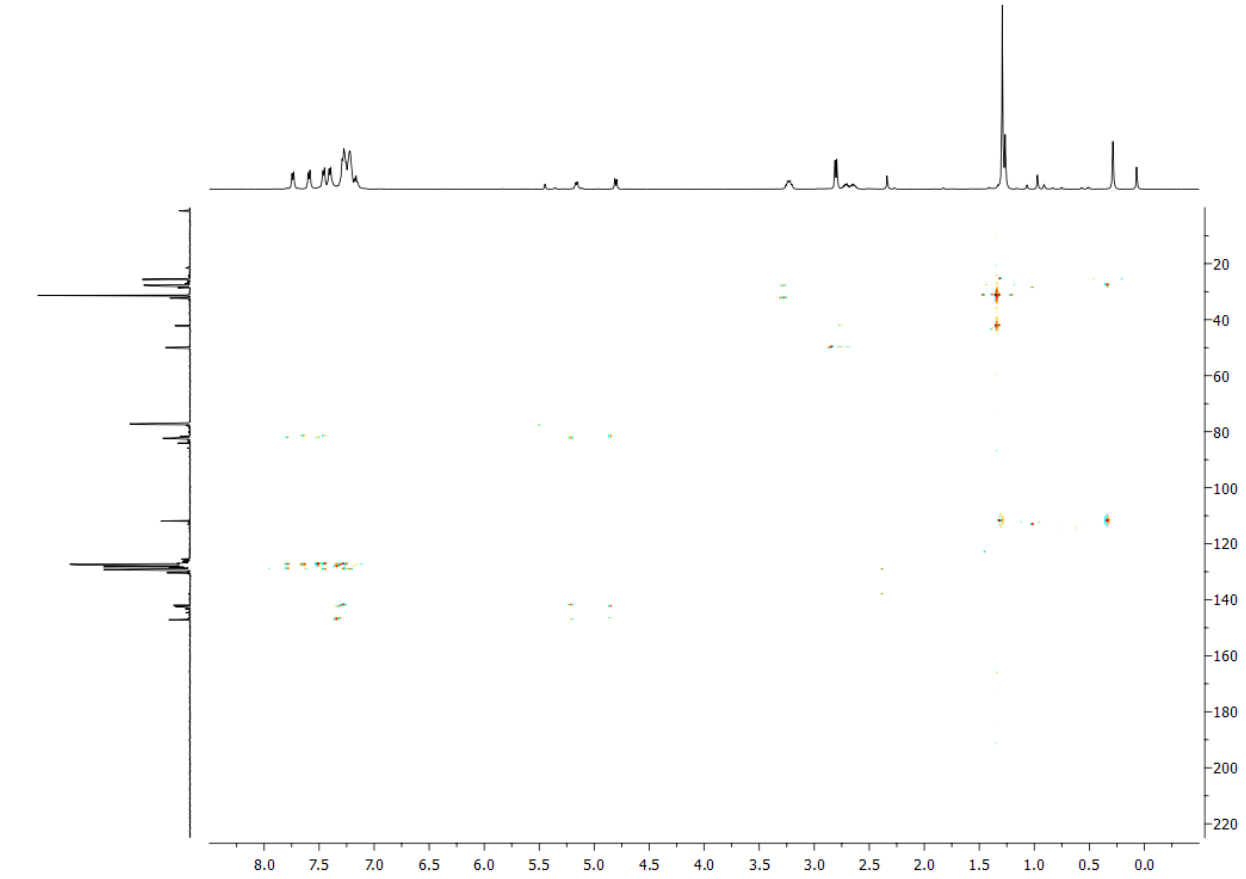
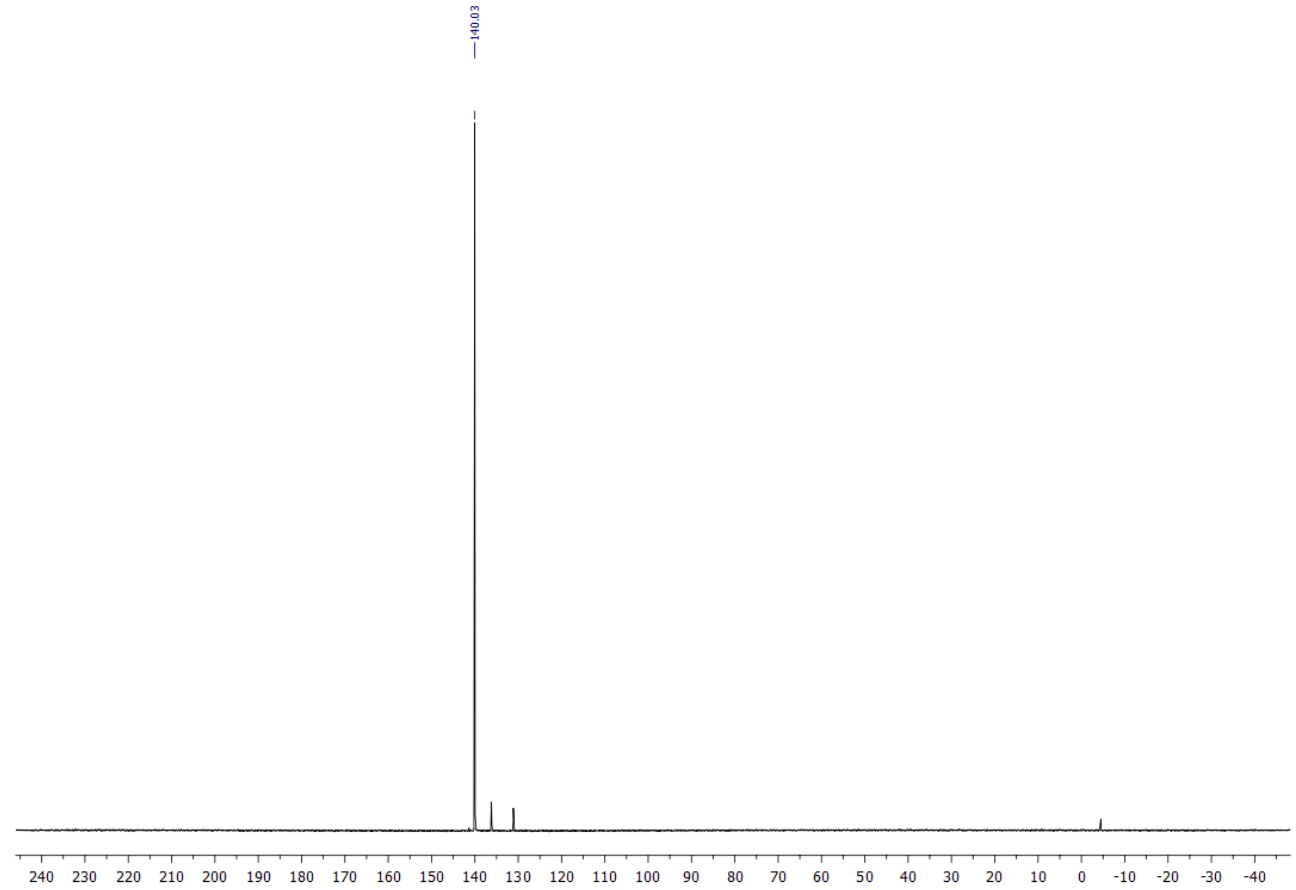
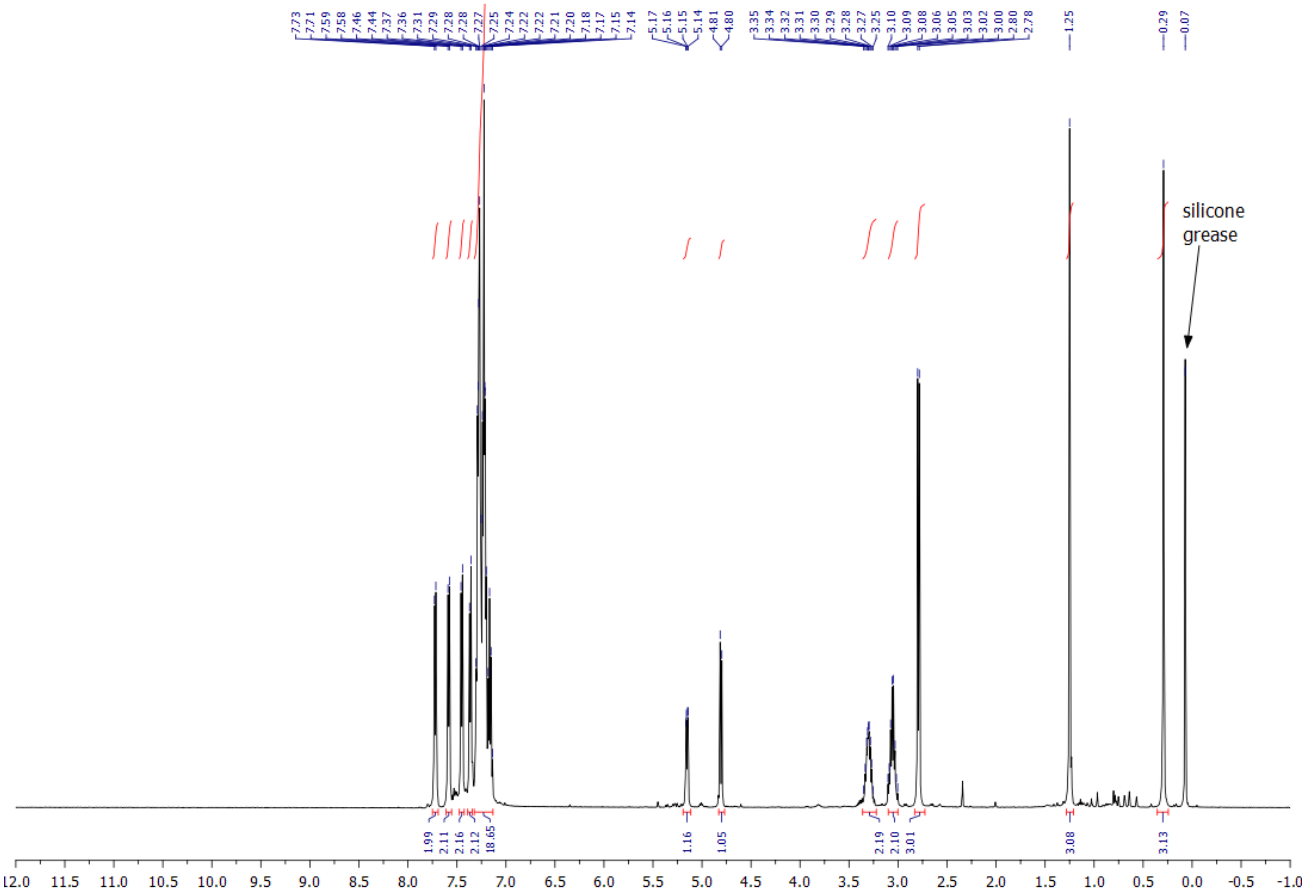


L1b, ^{1}H-^{13}C HMBC spectrum.

NMR AND MASS SPECTRA

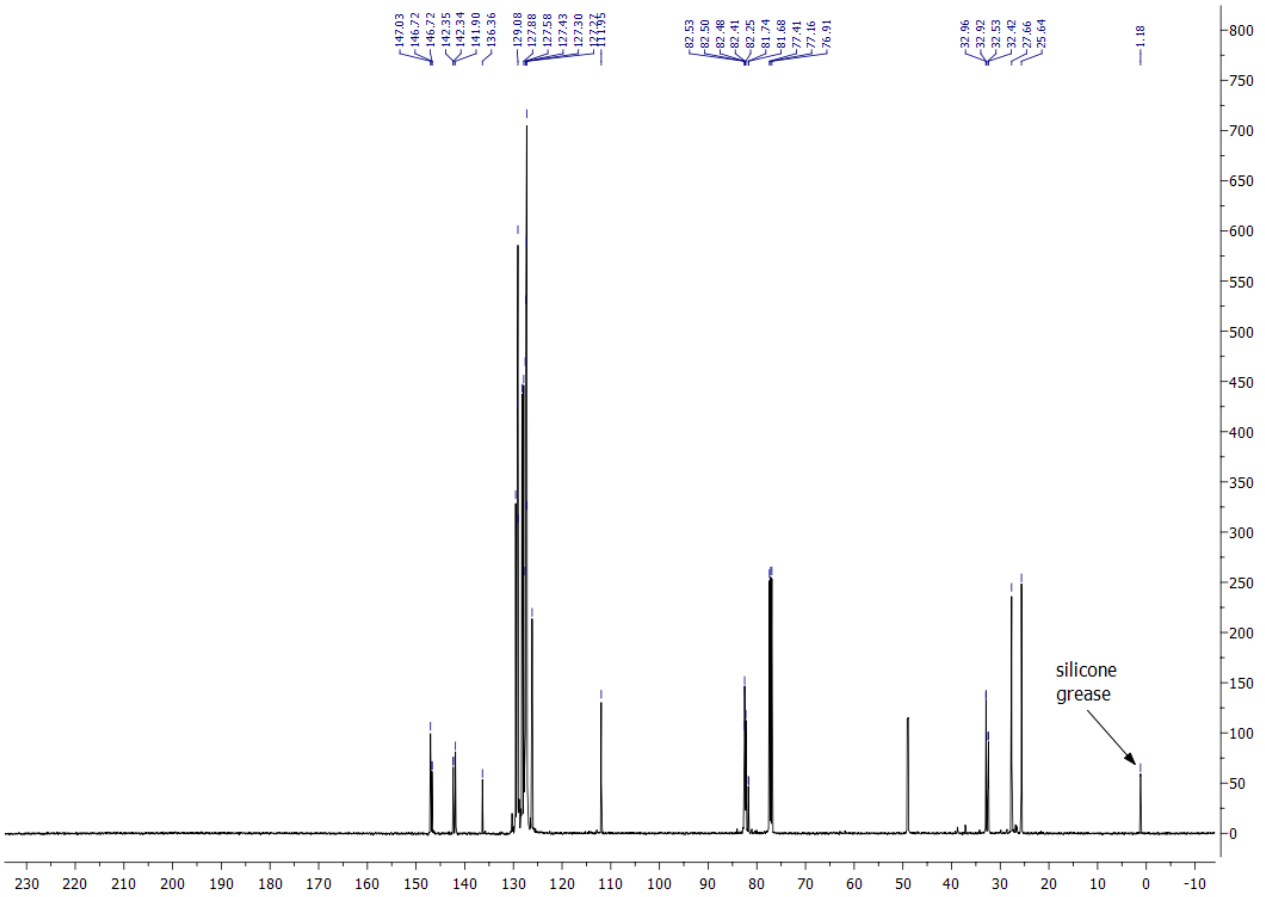


L1c, $^{31}P\{^{1}H\}$ spectrum.

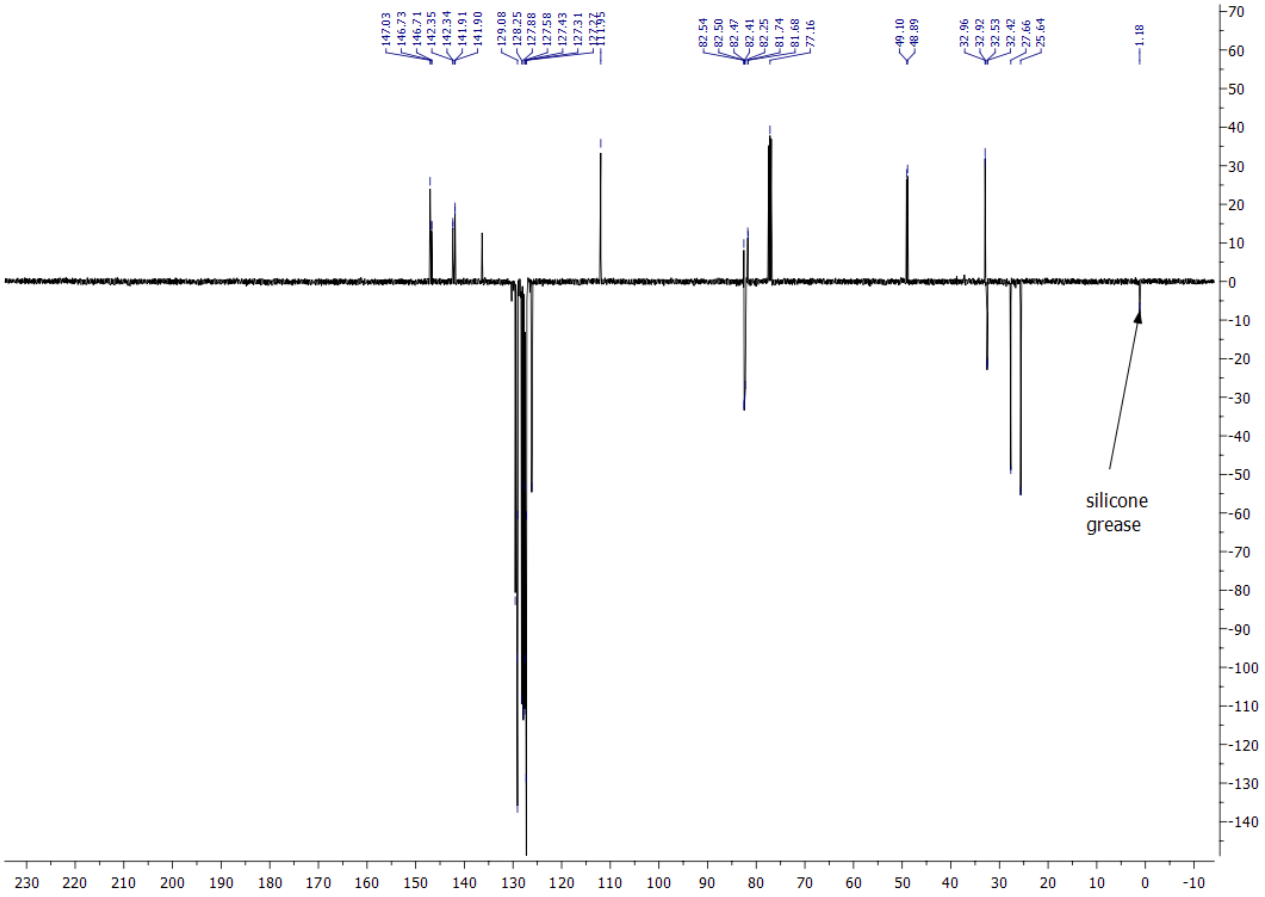


L1c, ^{1}H spectrum.

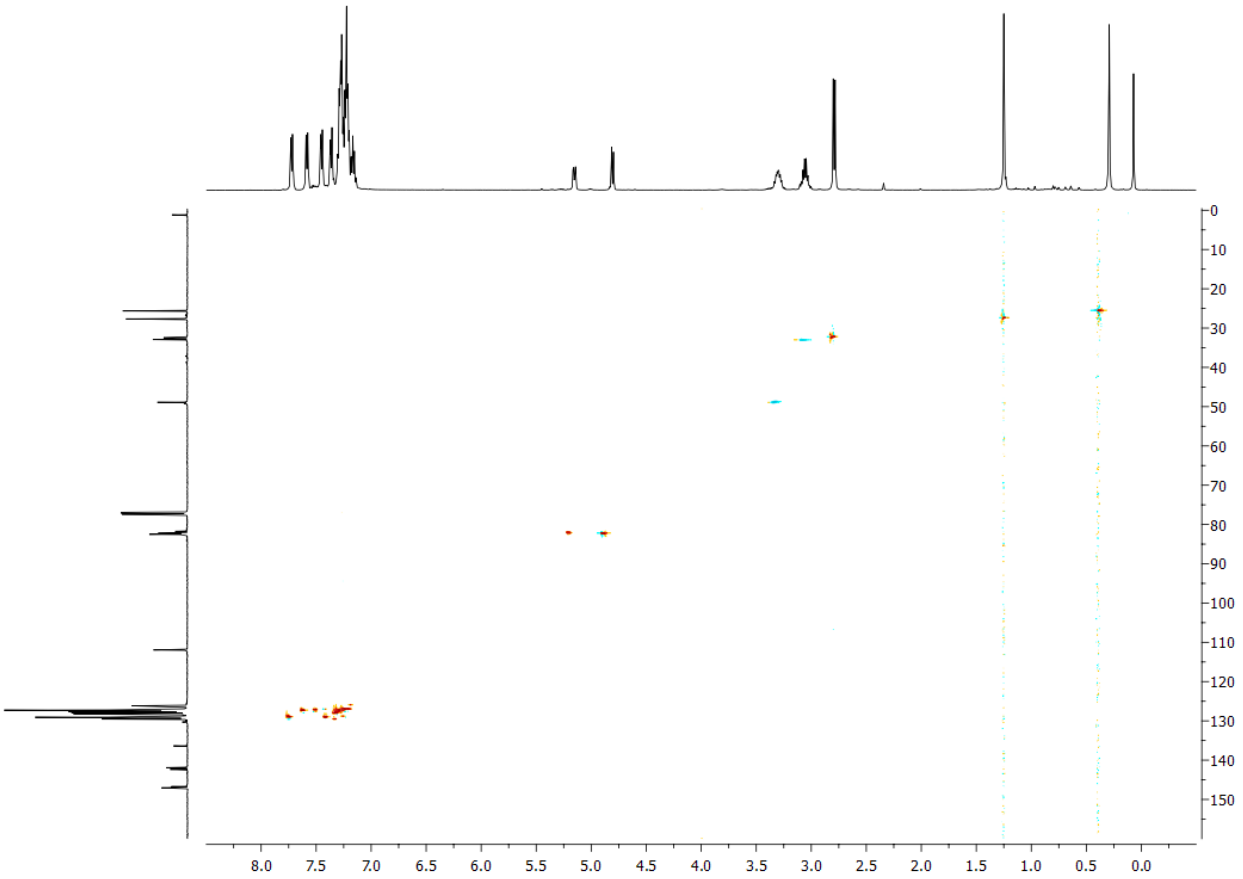
NMR AND MASS SPECTRA



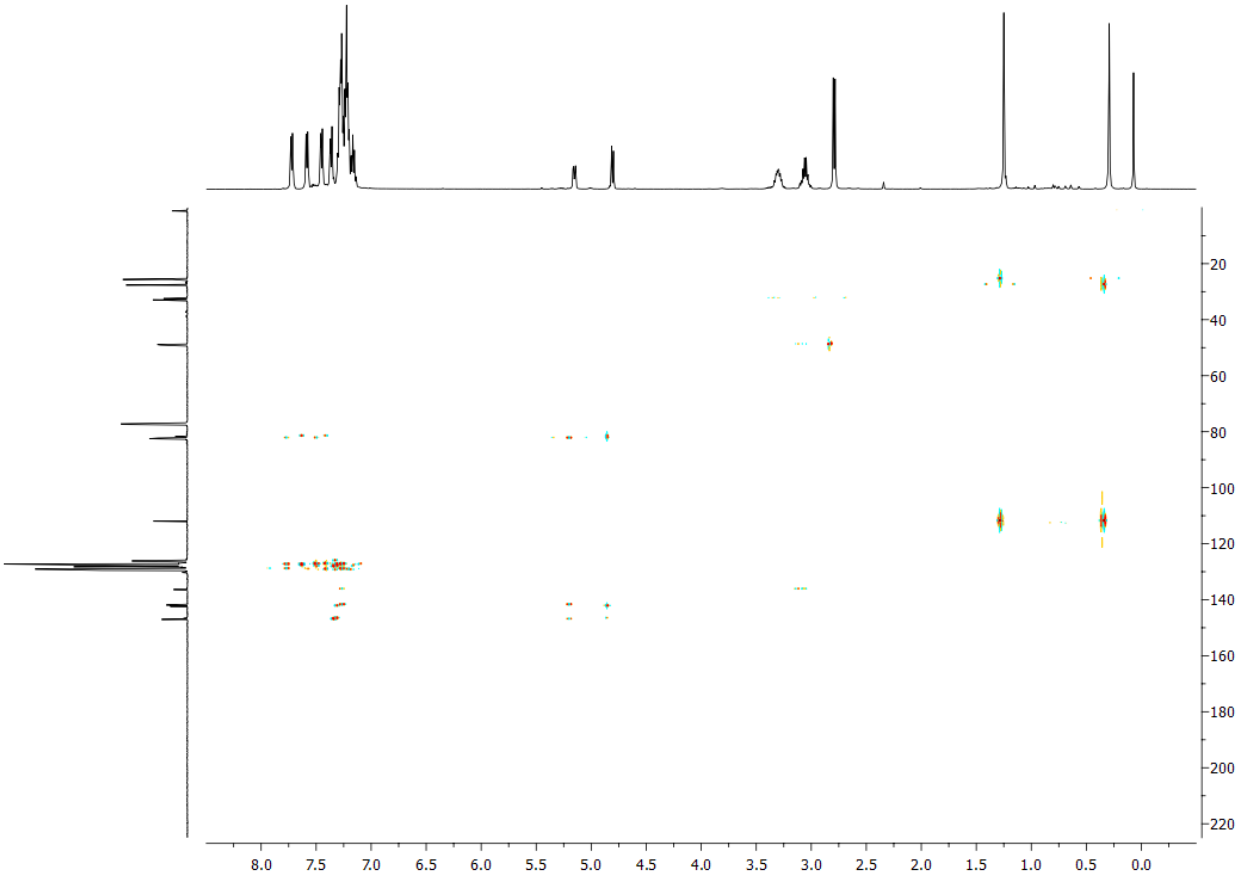
L1c, $^{13}C\{^{1}H\}$ spectrum.



L1c, $^{13}C\{^{1}H\}$ APT spectrum.

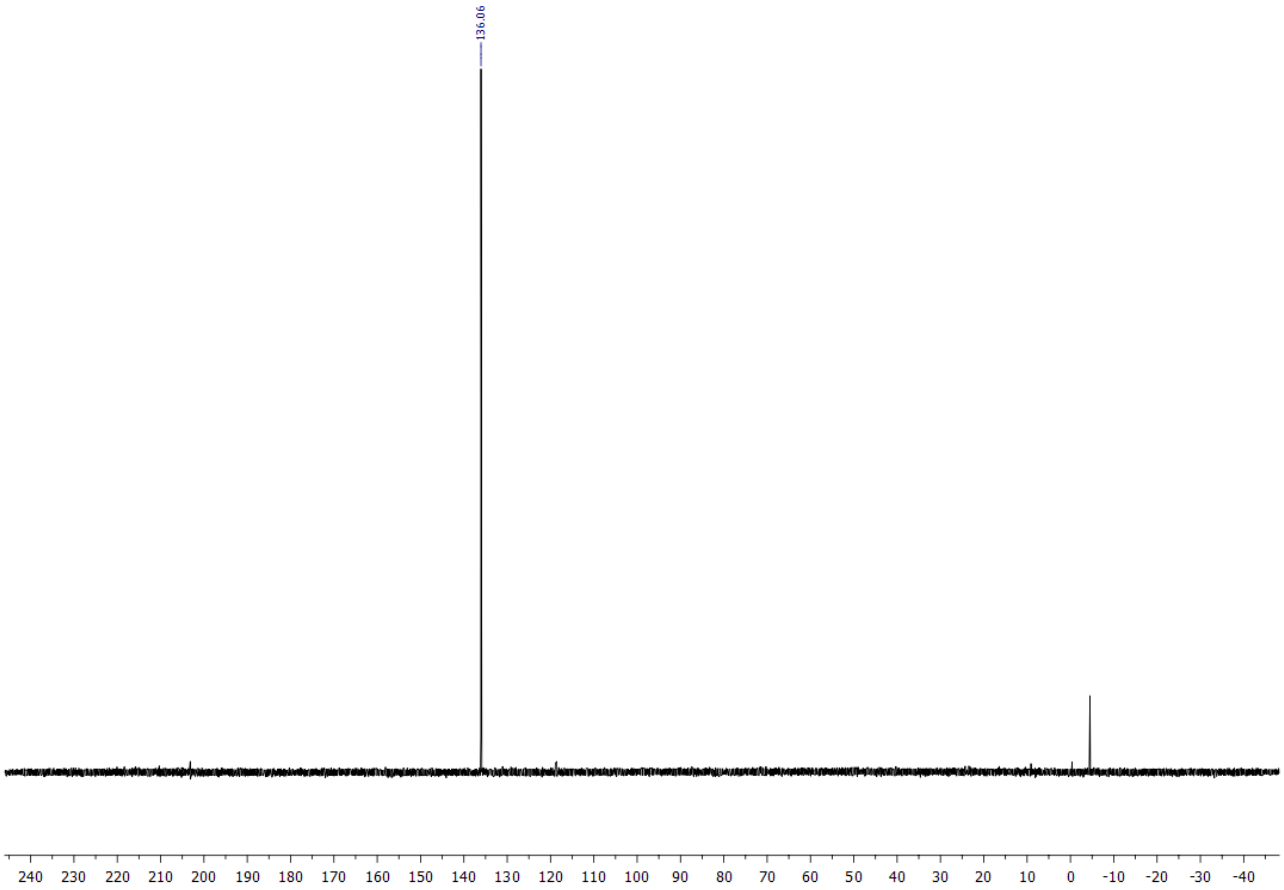


L1c, ^{1}H-^{13}C HSQC spectrum.

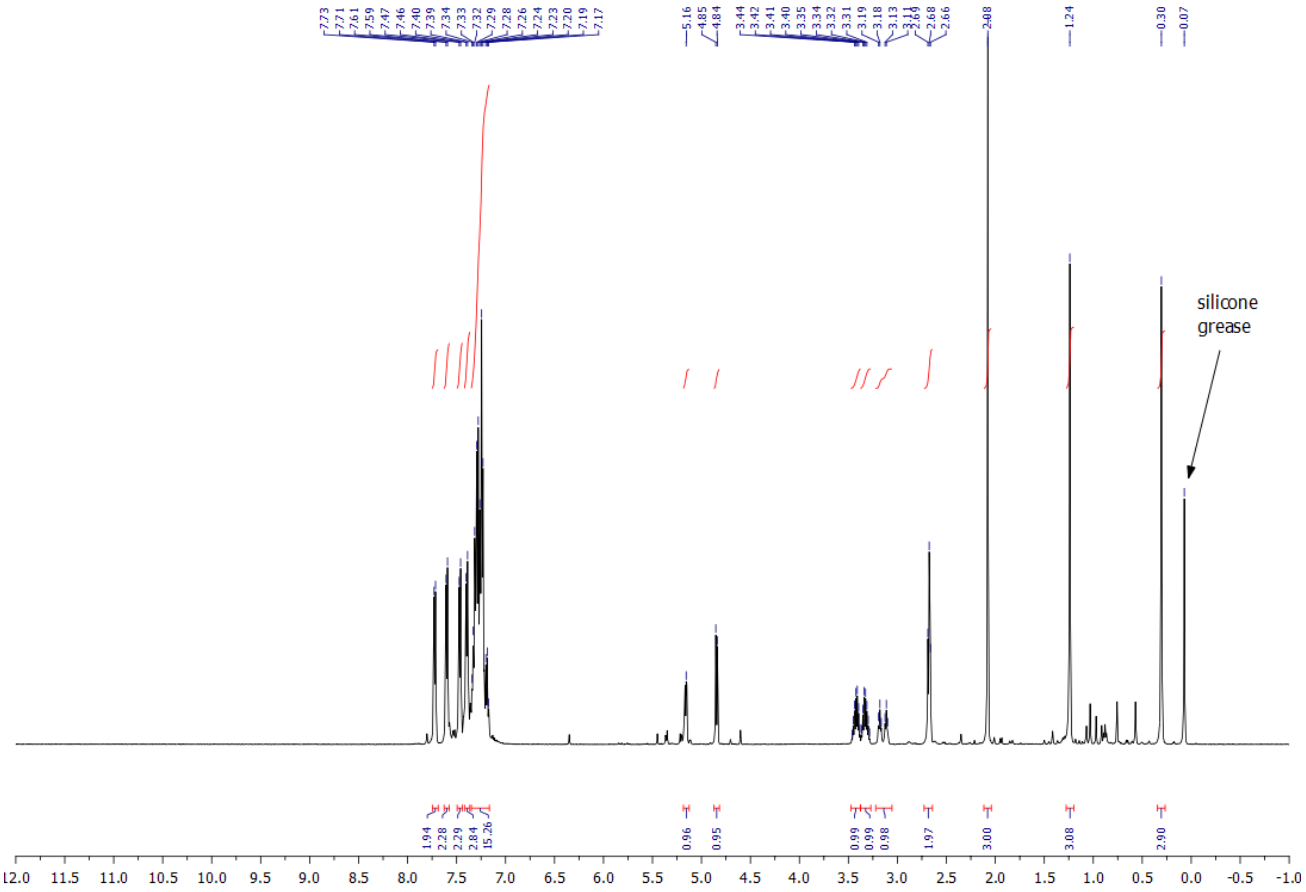


L1c, ^{1}H-^{13}C HMBC spectrum.

NMR AND MASS SPECTRA

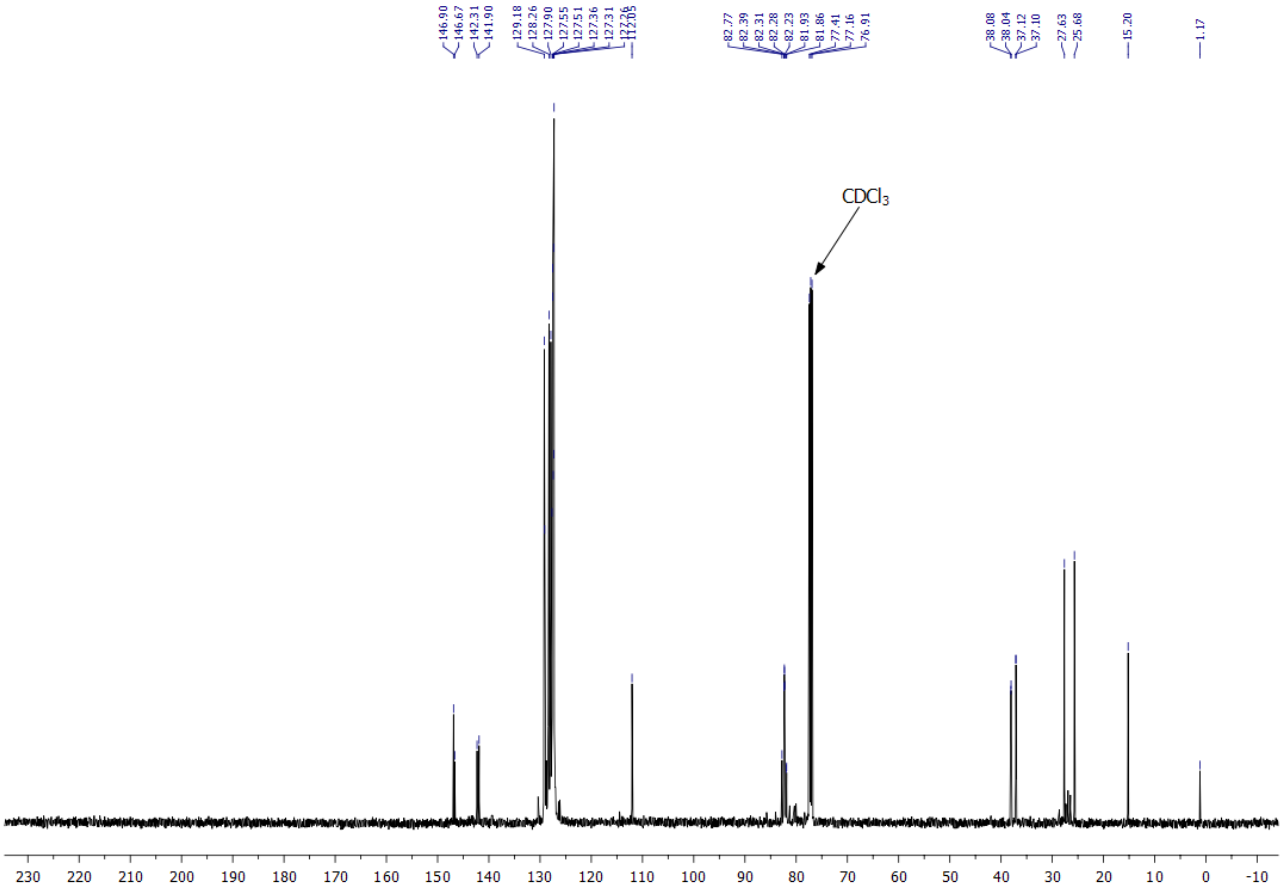


L1d, $^{31}P\{^{1}H\}$ spectrum.

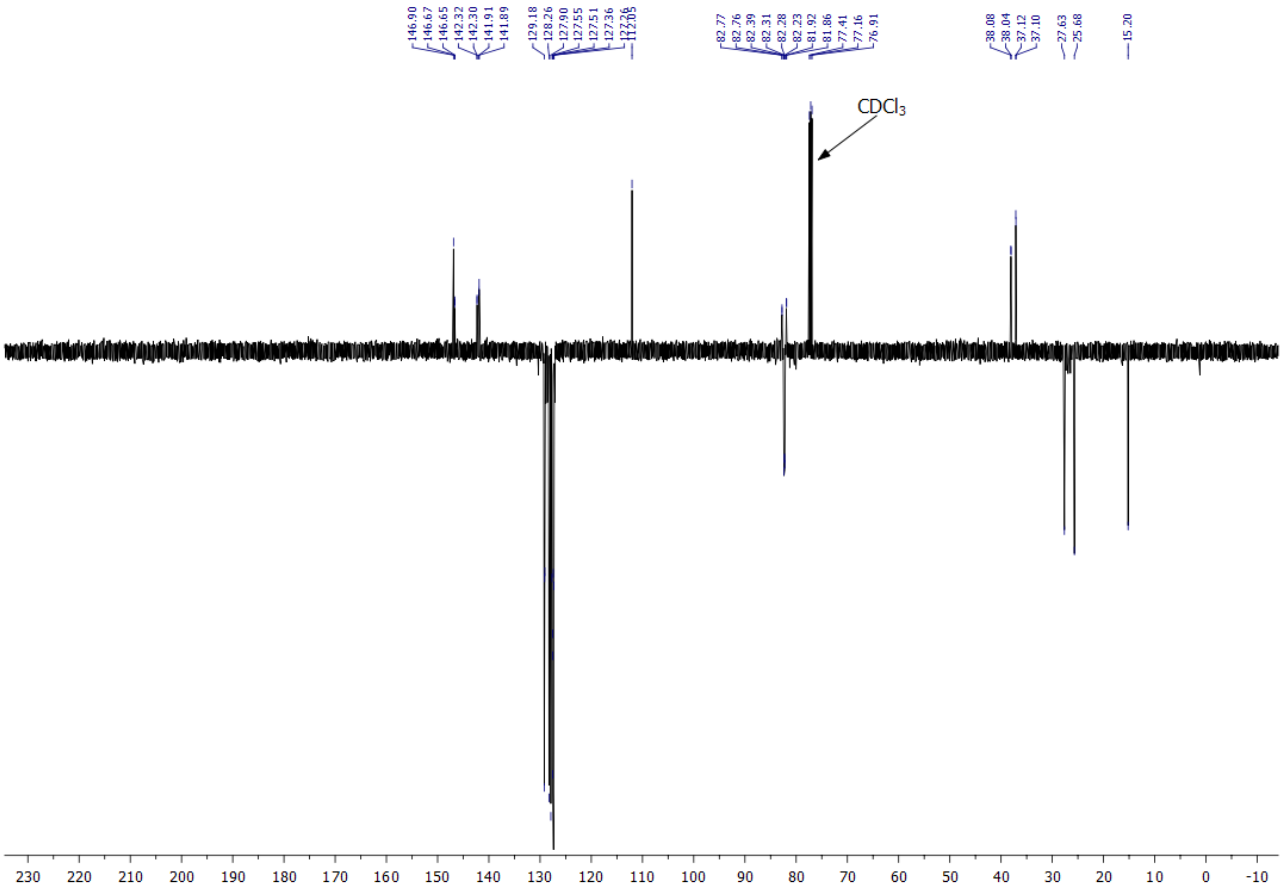


L1d, ^{1}H spectrum.

NMR AND MASS SPECTRA

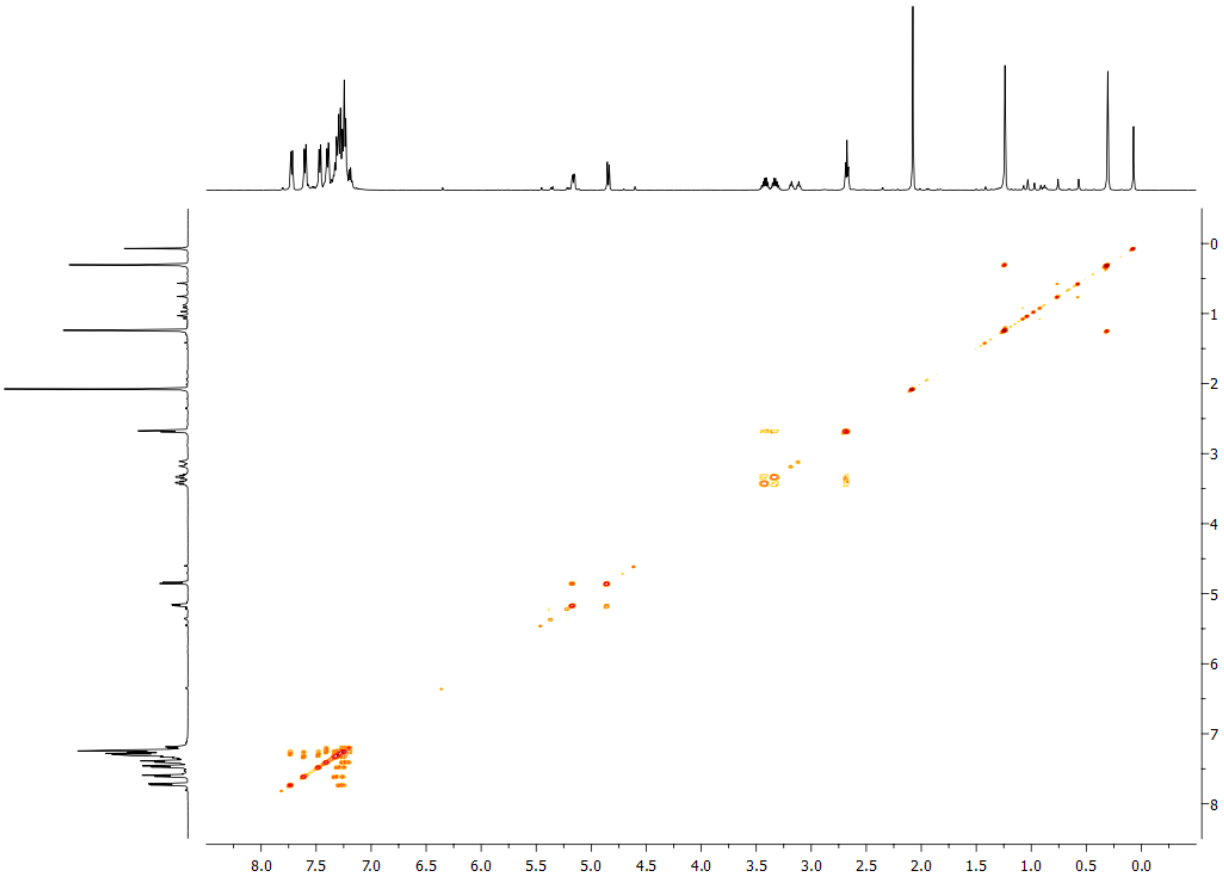


L1d, $^{13}C\{^{1}H\}$ spectrum.

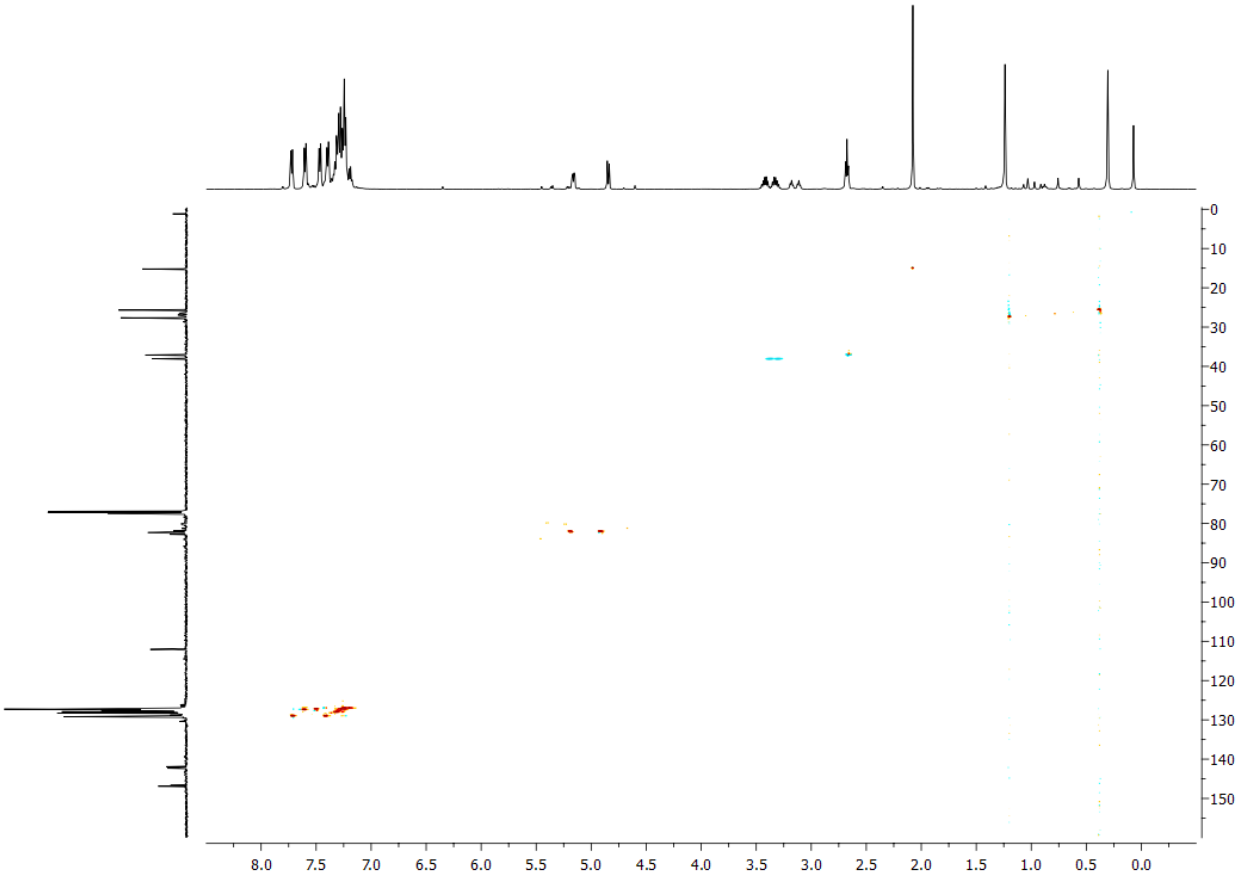


L1d, $^{13}C\{^{1}H\}$ APT spectrum.

NMR AND MASS SPECTRA

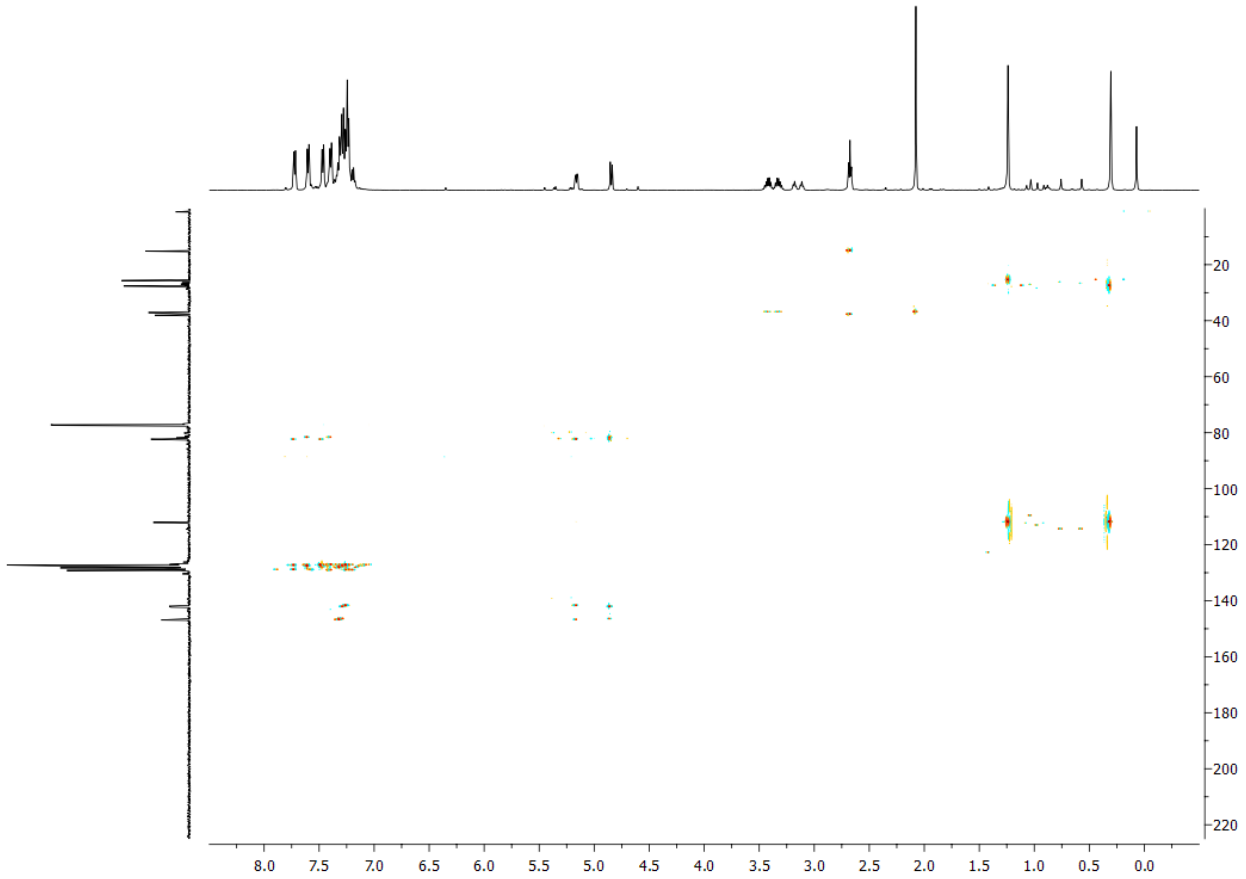


L1d, ^{1}H-^{1}H COSY spectrum.

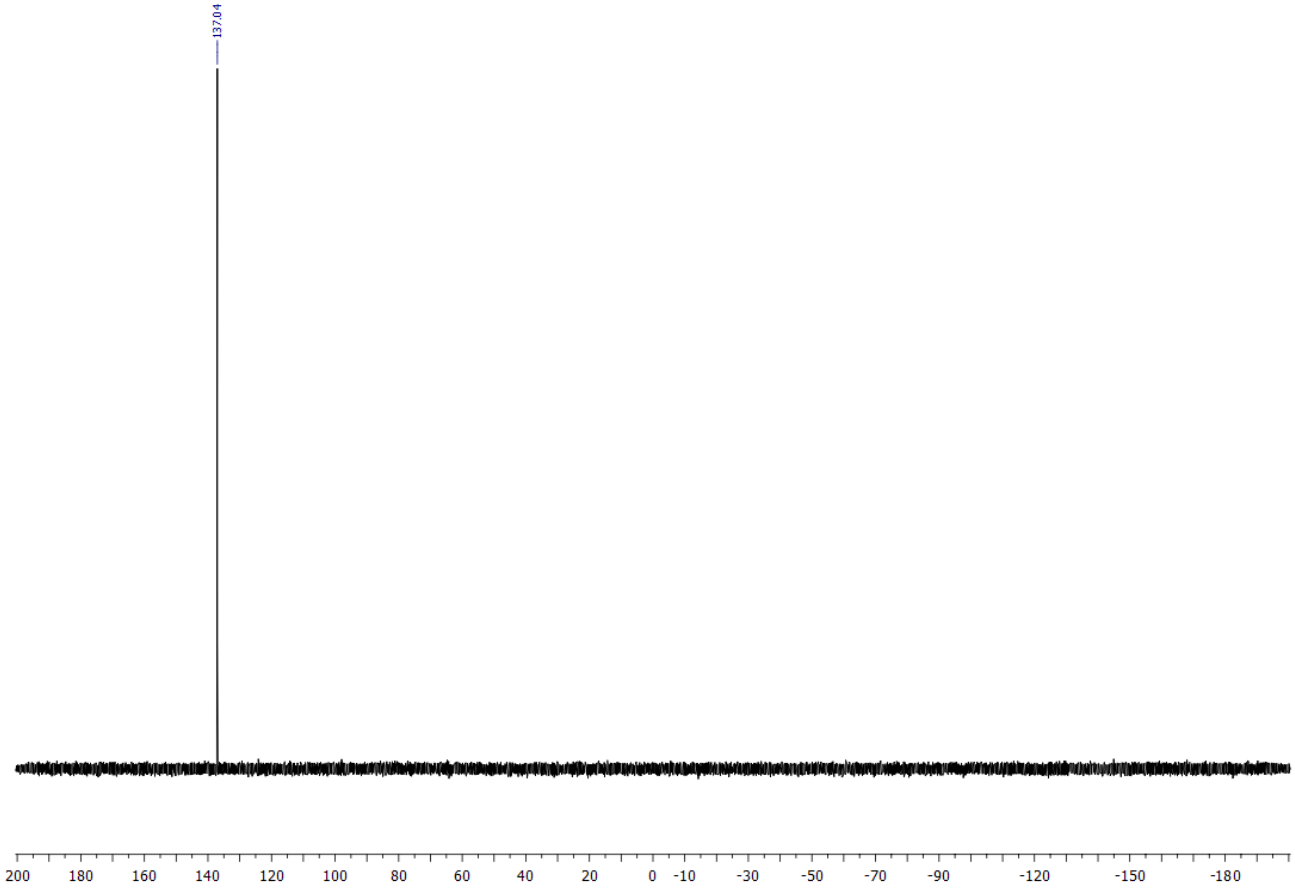


L1d, ^{1}H-^{13}C HSQC spectrum.

NMR AND MASS SPECTRA

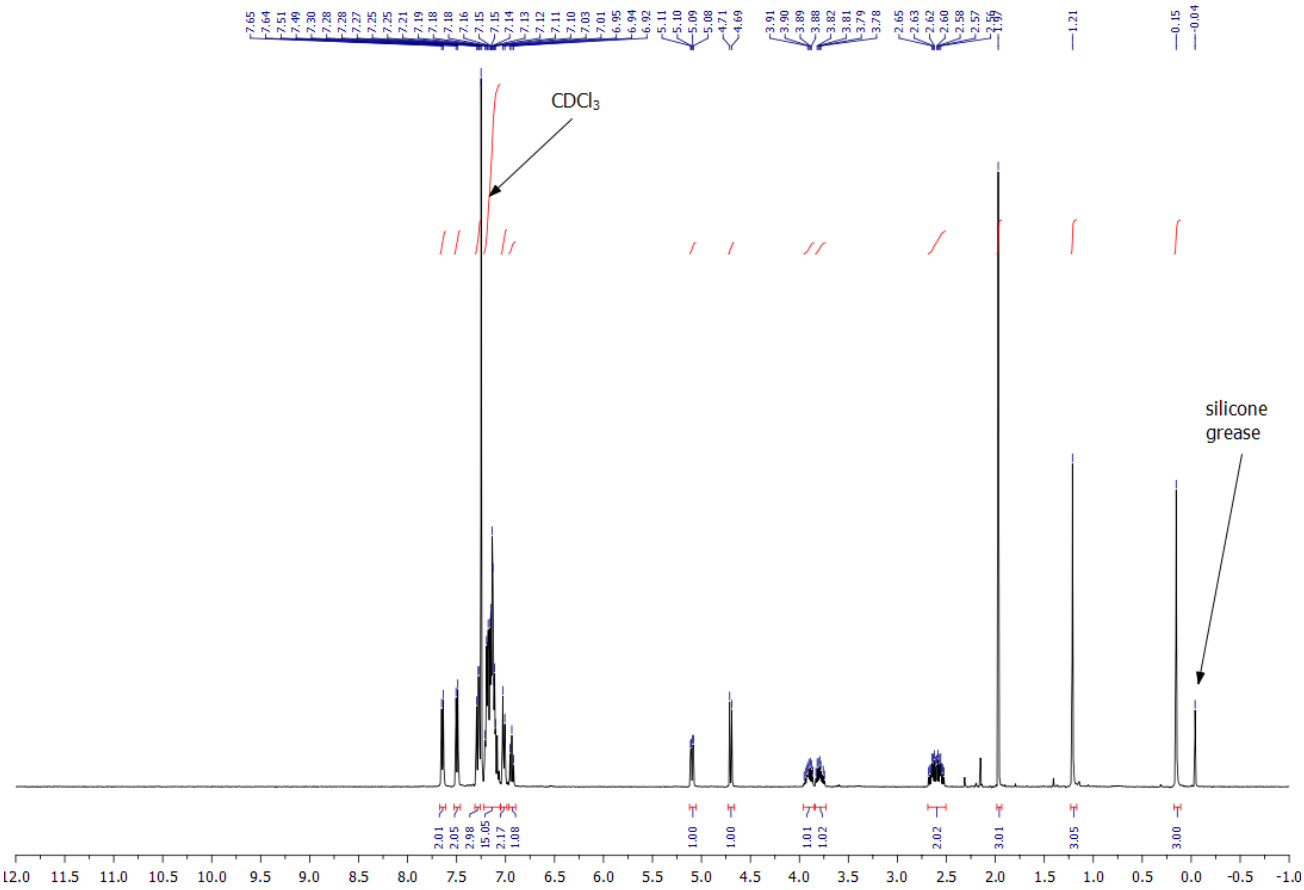


L1d, ^{1}H-^{13}C HMBC spectrum.

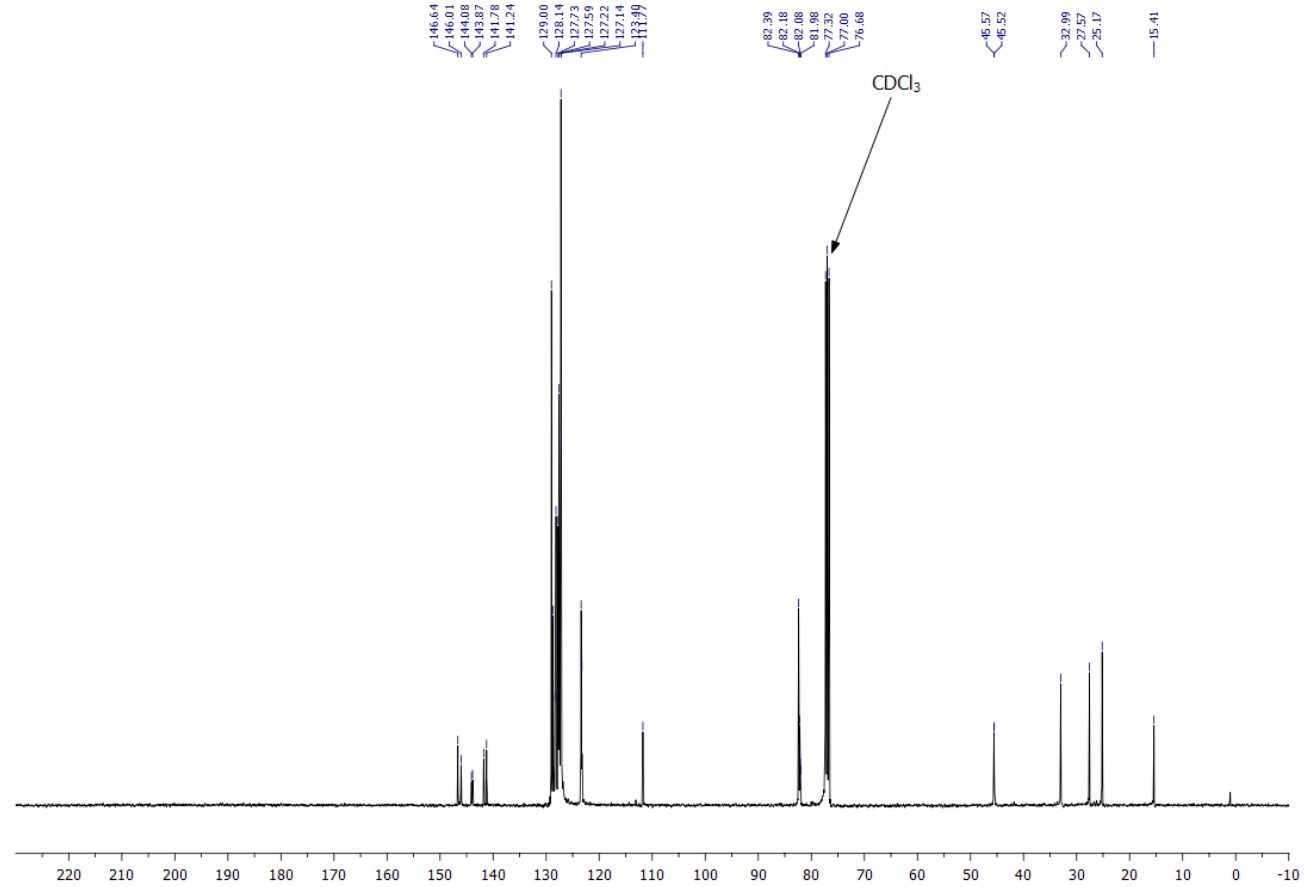


L1e, $^{31}P\{^{1}H\}$ spectrum.

NMR AND MASS SPECTRA

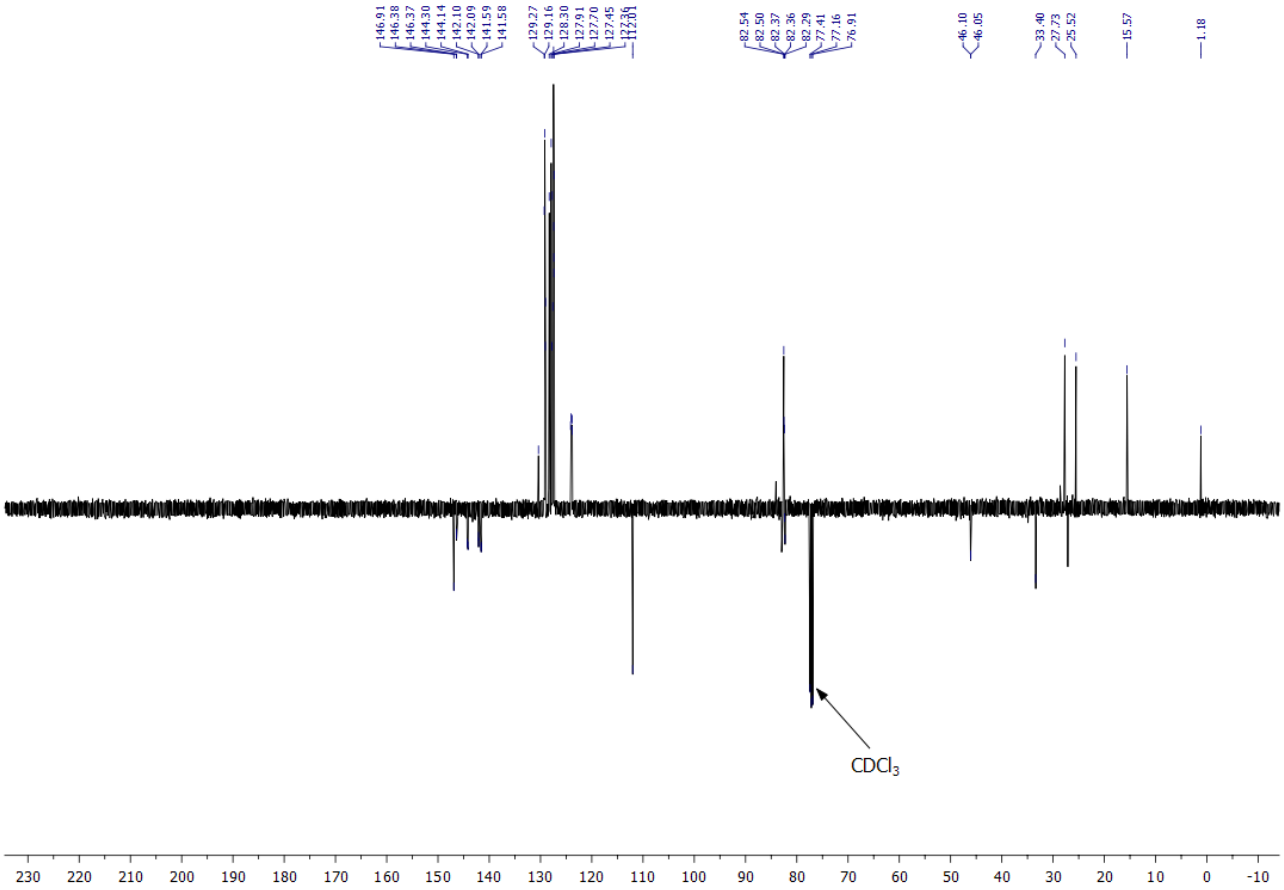


L1e, ^{1}H spectrum.

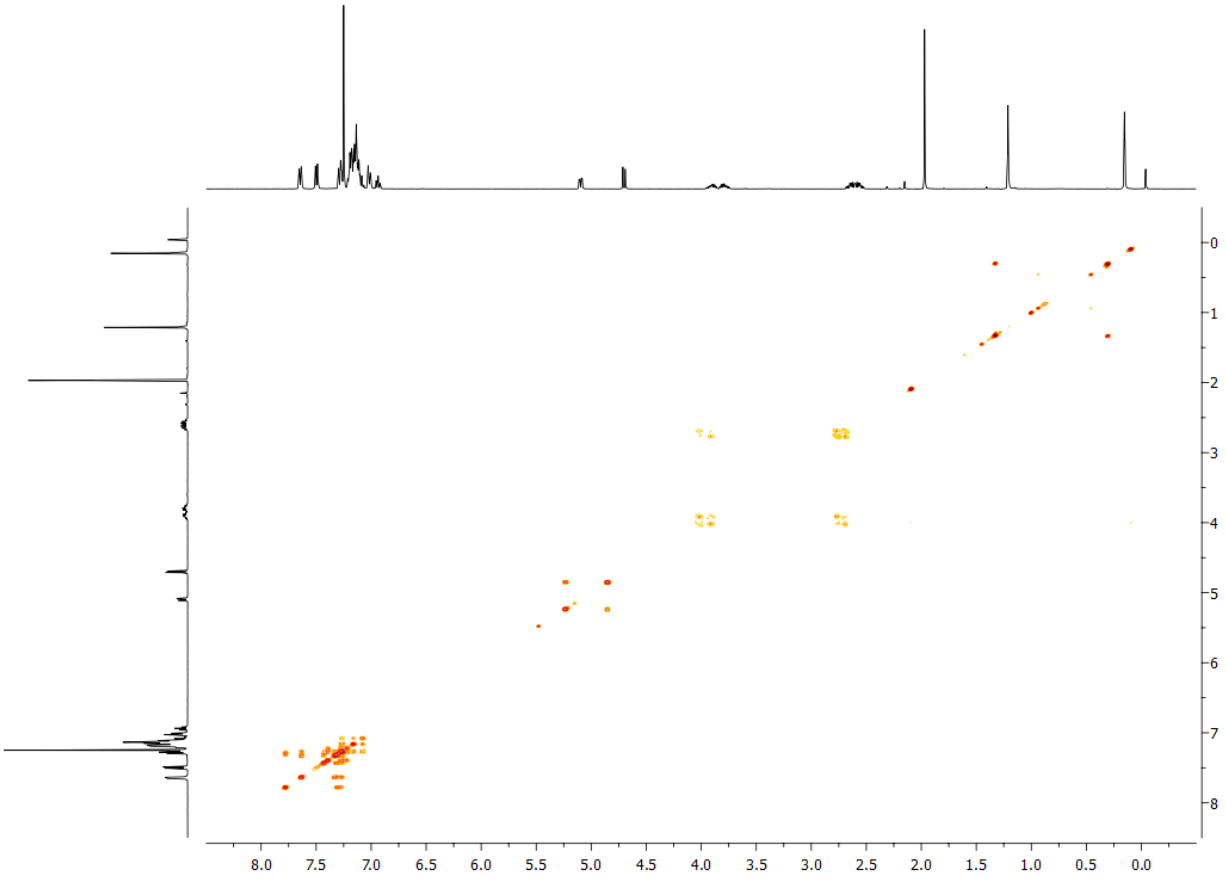


L1e, $^{13}C\{^{1}H\}$ spectrum.

NMR AND MASS SPECTRA

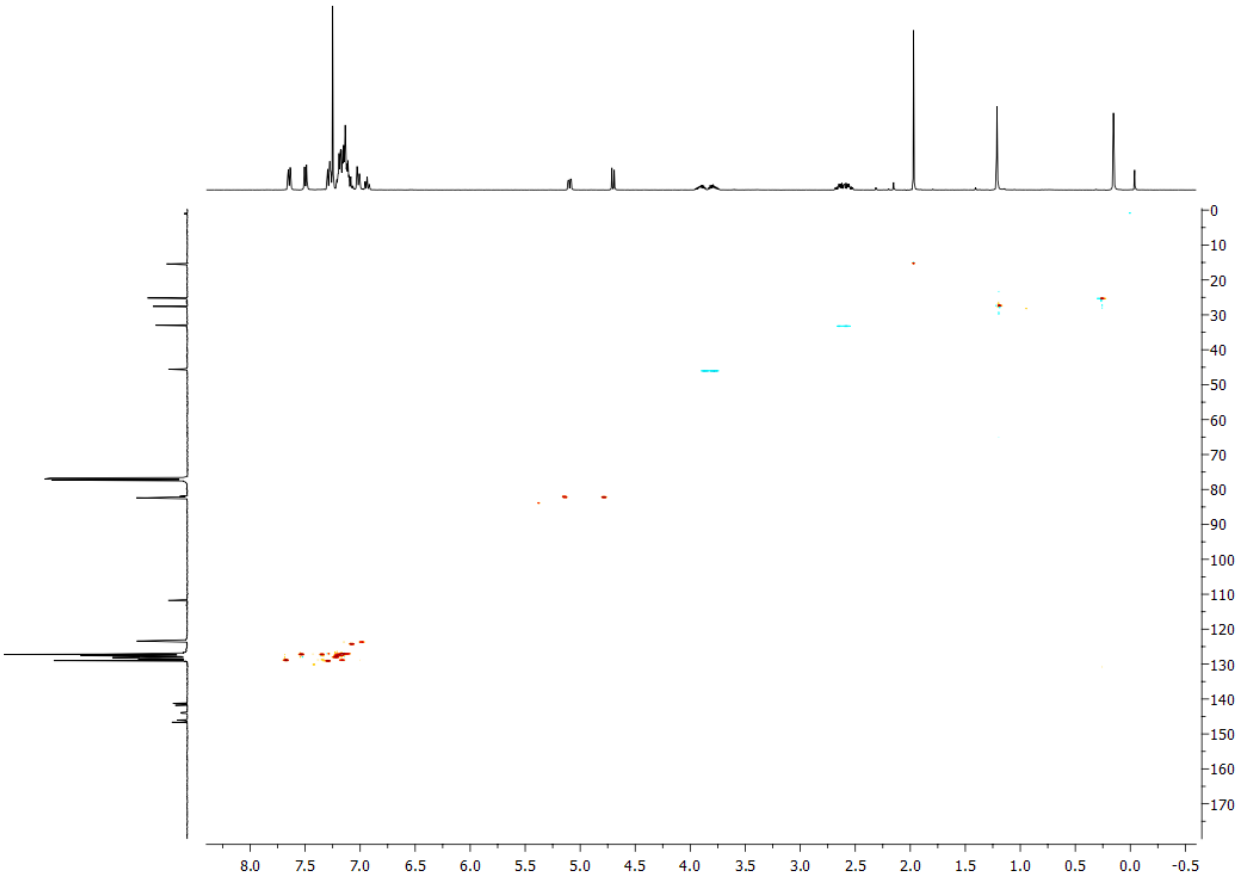


L1e, $^{13}C\{^{1}H\}$ APT spectrum.

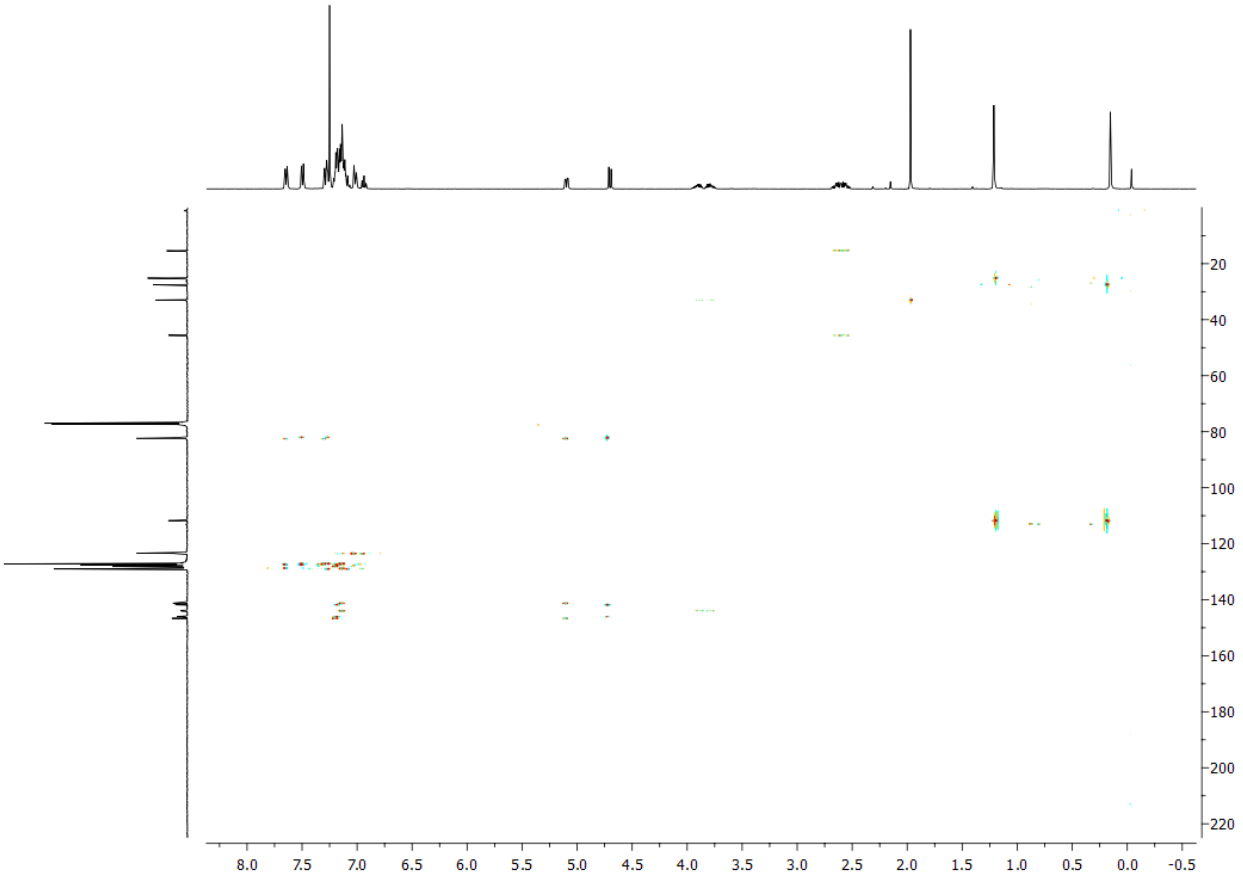


L1e, ^{1}H-^{1}H COSY spectrum.

NMR AND MASS SPECTRA



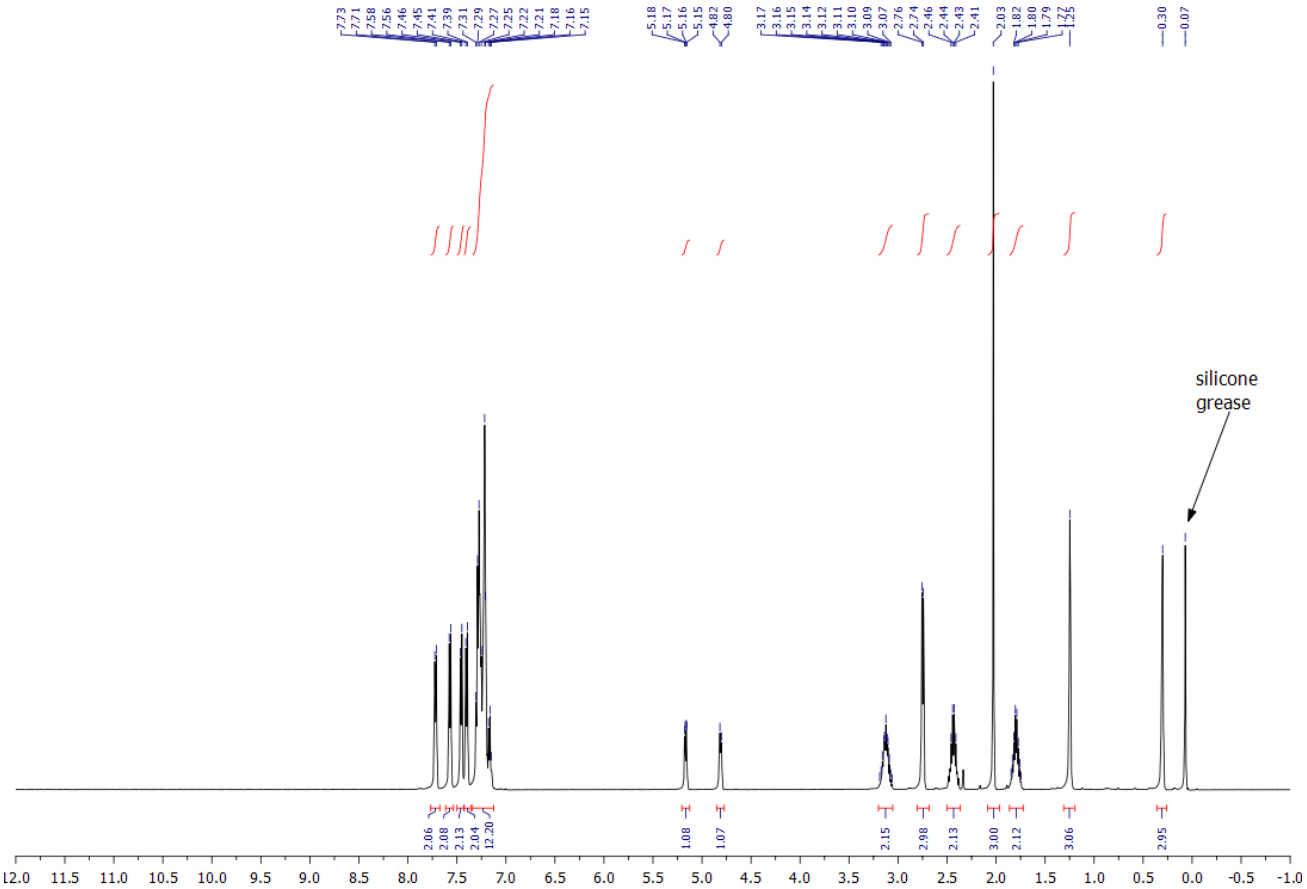
L1e, ^{1}H-^{13}C HSQC spectrum.



L1e, ^{1}H-^{13}C HMBC spectrum.

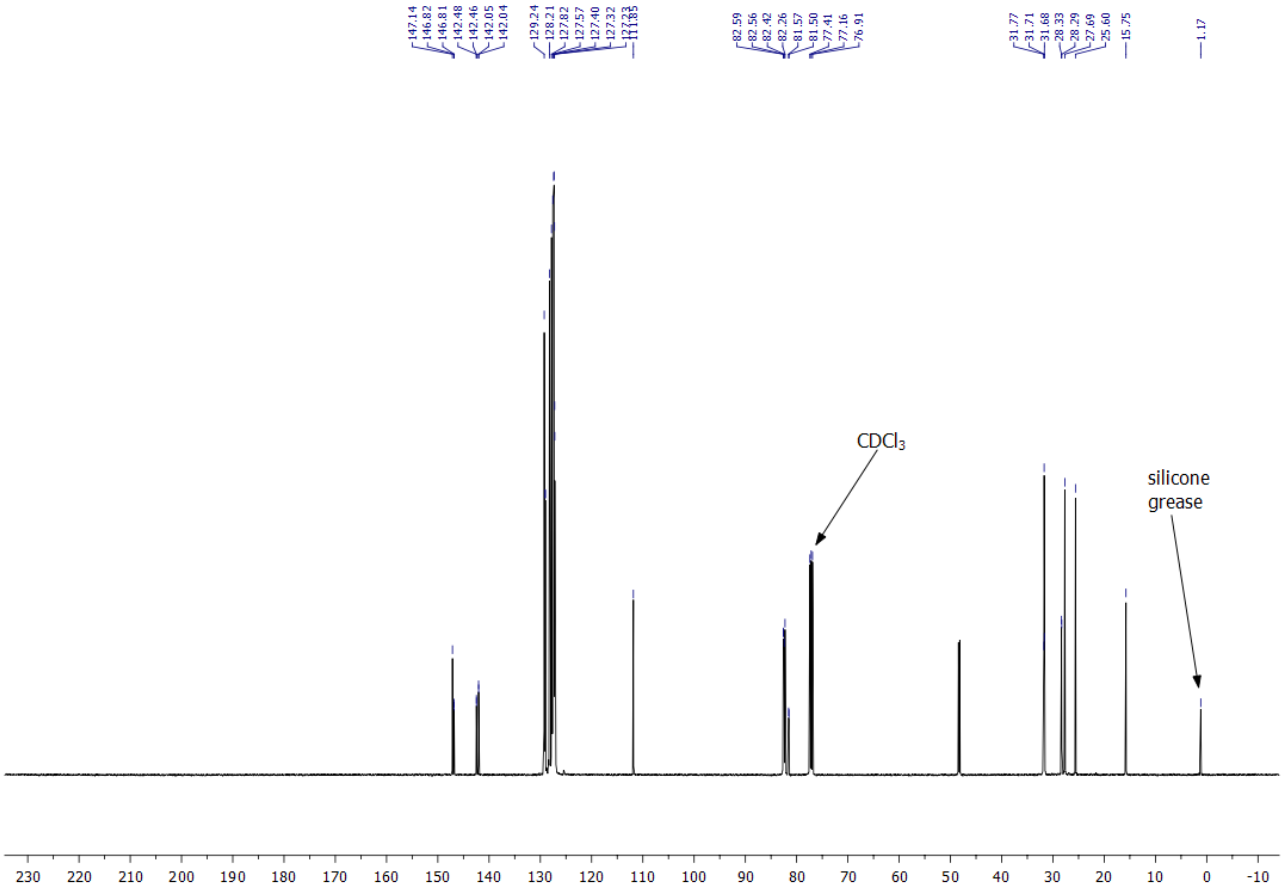
NMR AND MASS SPECTRA

L1f, $^{31}P\{^{1}H\}$ spectrum.

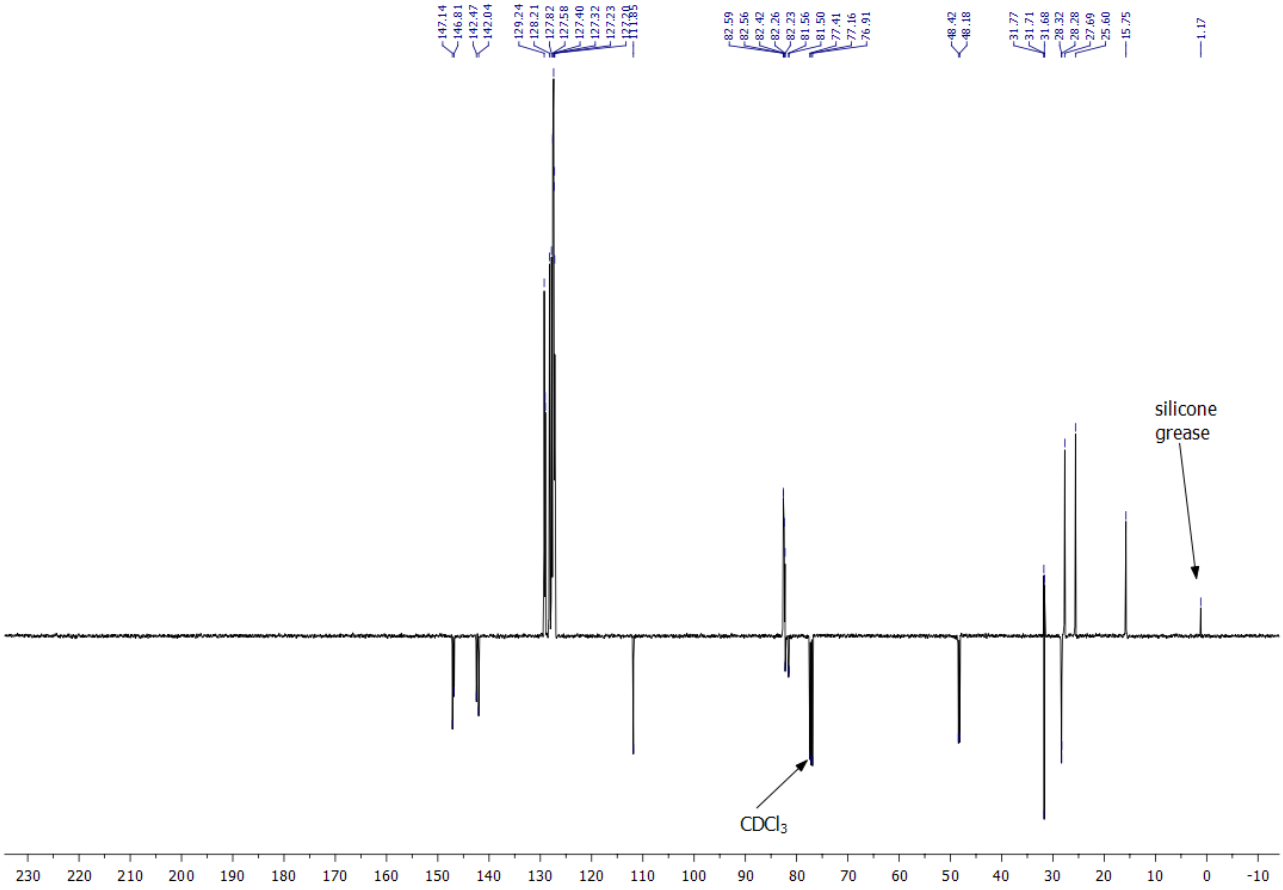


L1f, ^{1}H spectrum.

NMR AND MASS SPECTRA

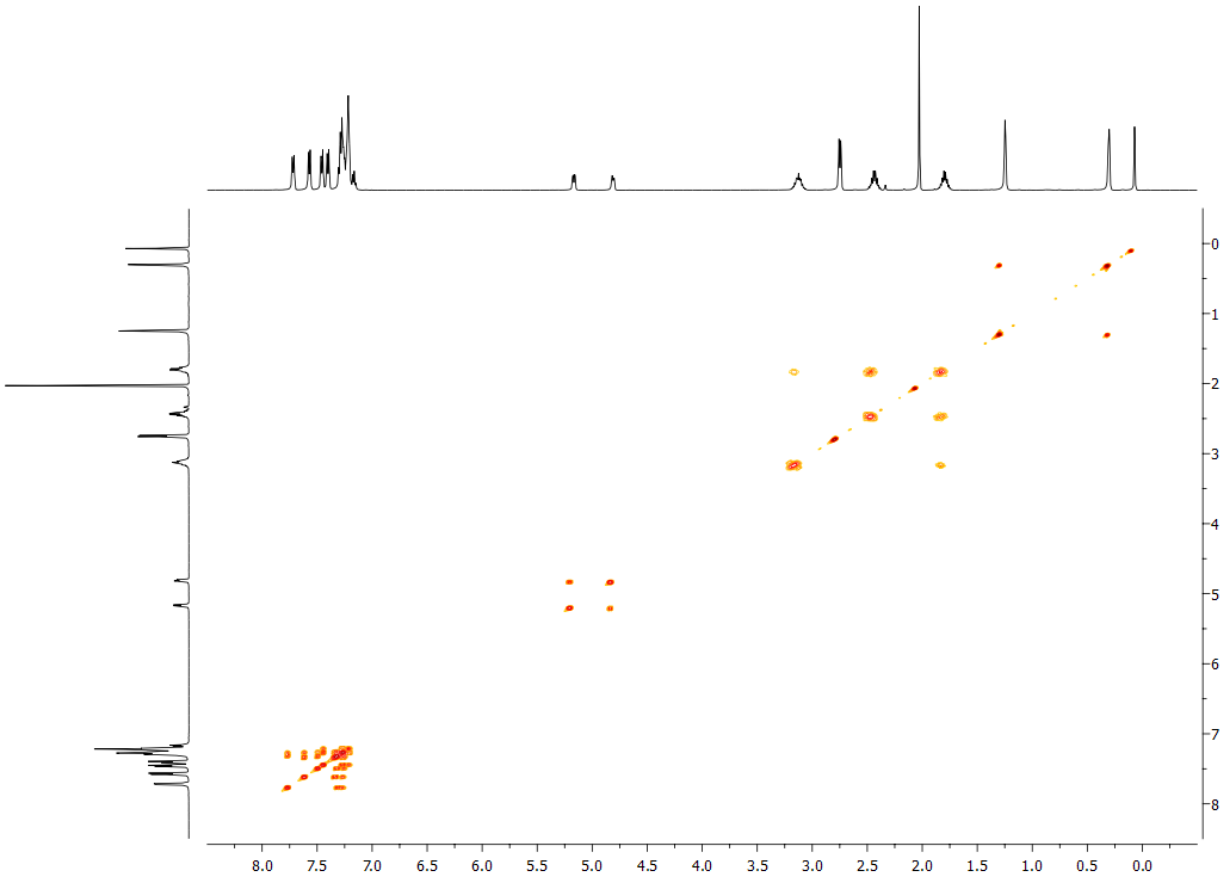


L1f, $^{13}C\{^{1}H\}$ spectrum.

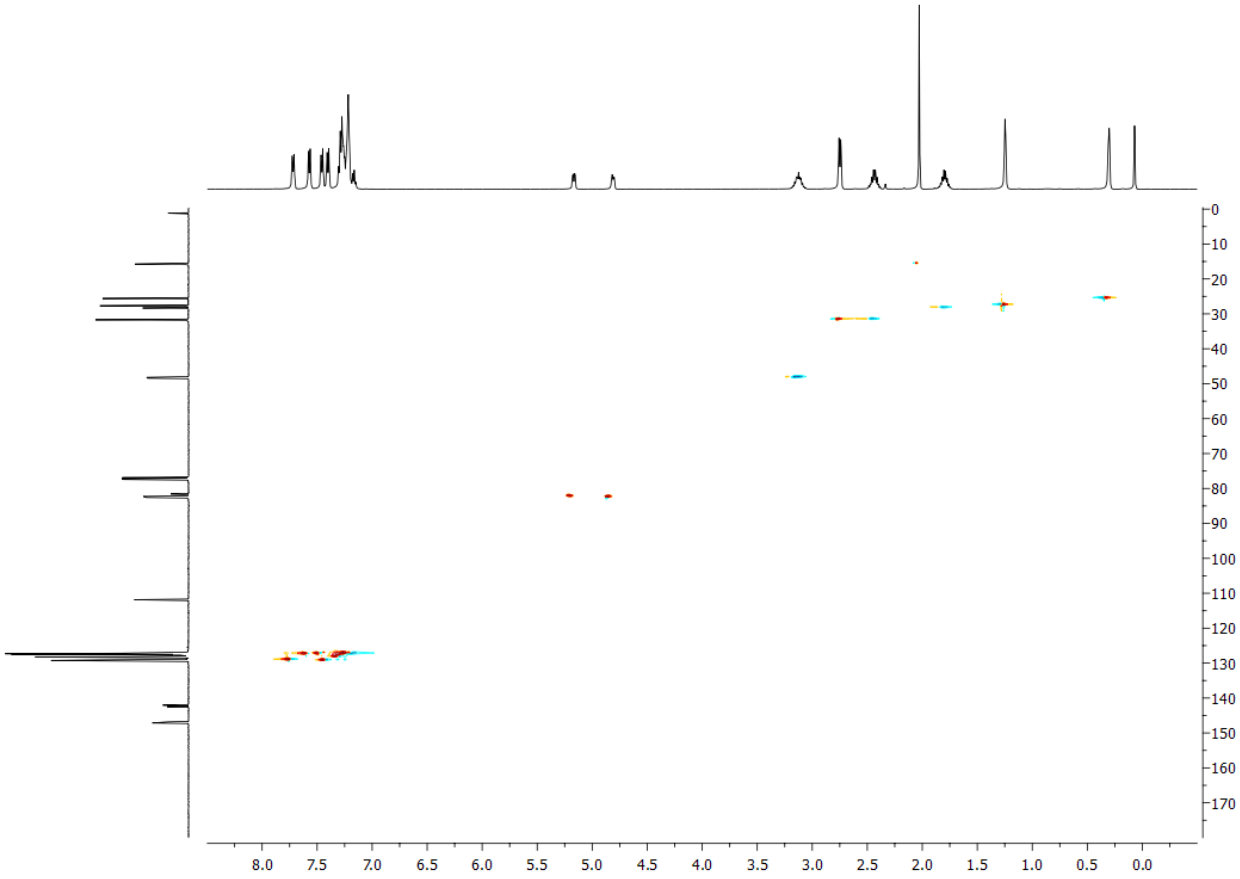


L1f, $^{13}C\{^{1}H\}$ APT spectrum.

NMR AND MASS SPECTRA

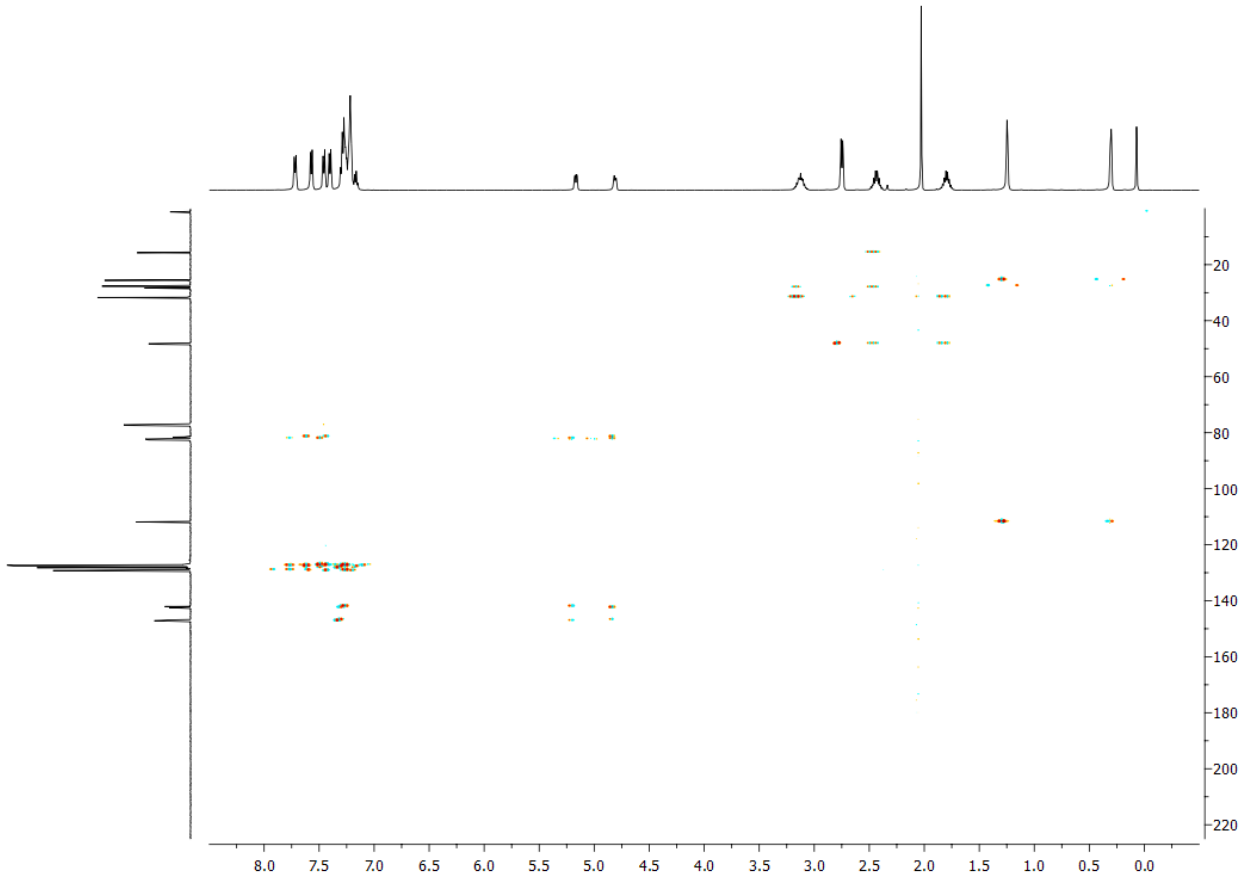


L1f, ^{1}H-^{1}H COSY spectrum.

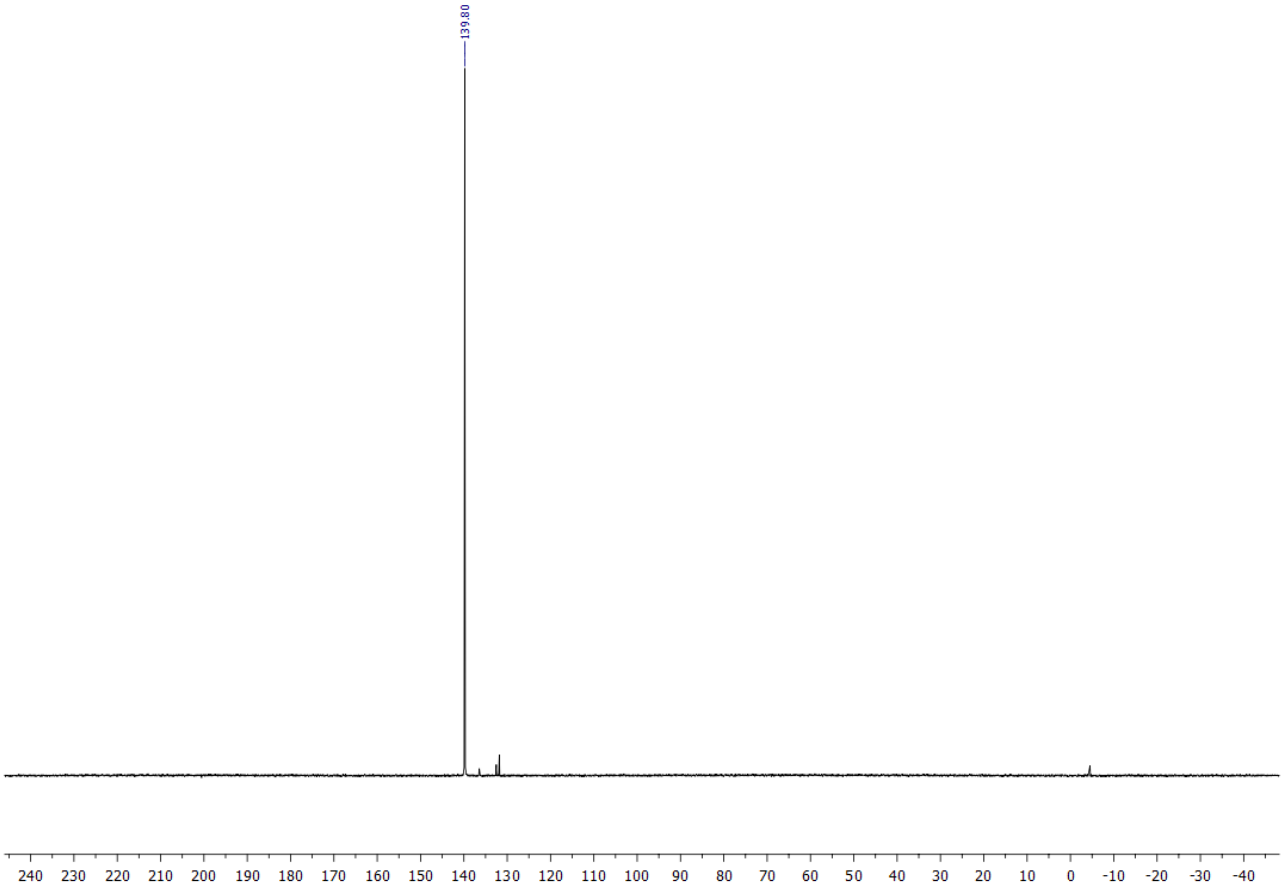


L1f, ^{1}H-^{13}C HSQC spectrum.

NMR AND MASS SPECTRA

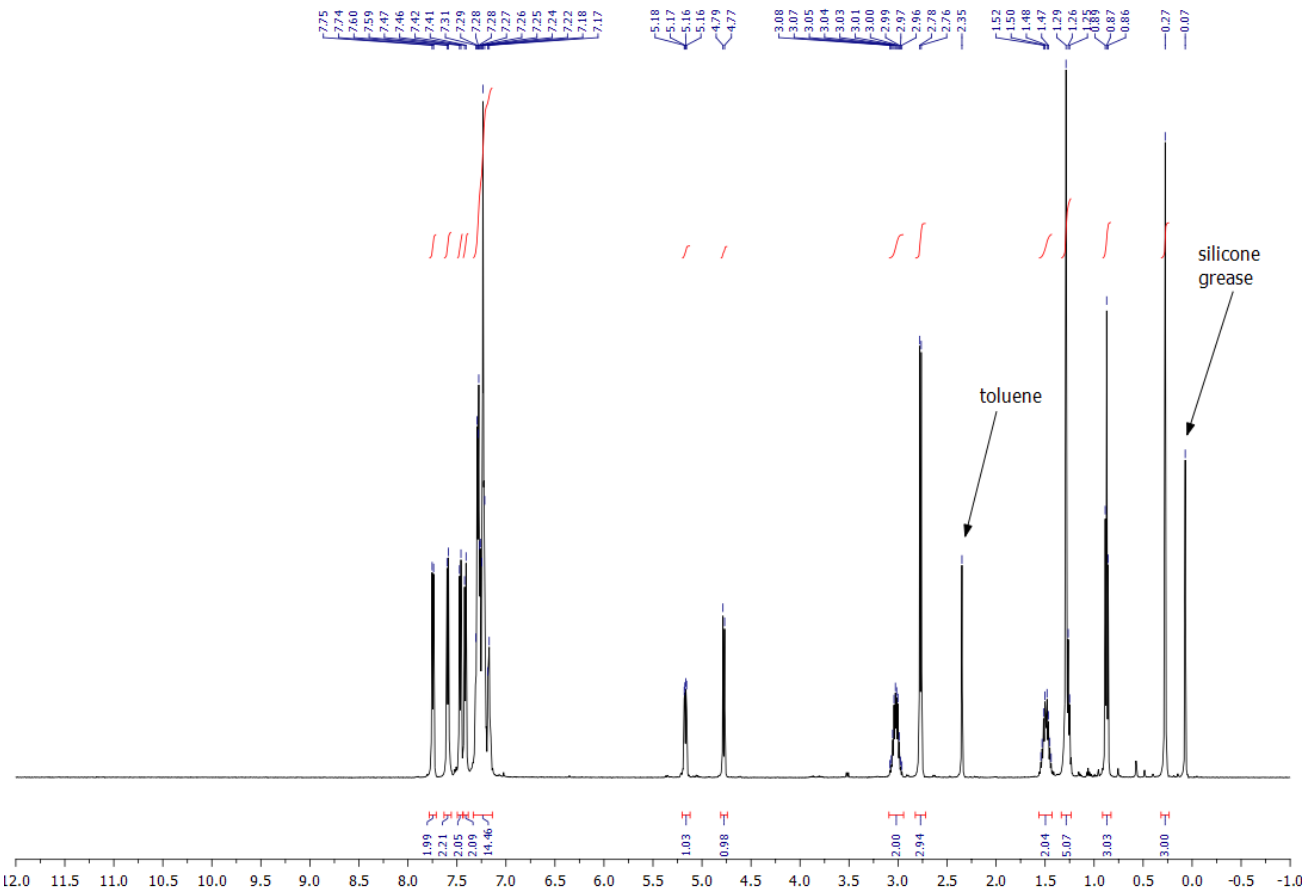


L1f, ^{1}H-^{13}C HMBC spectrum.

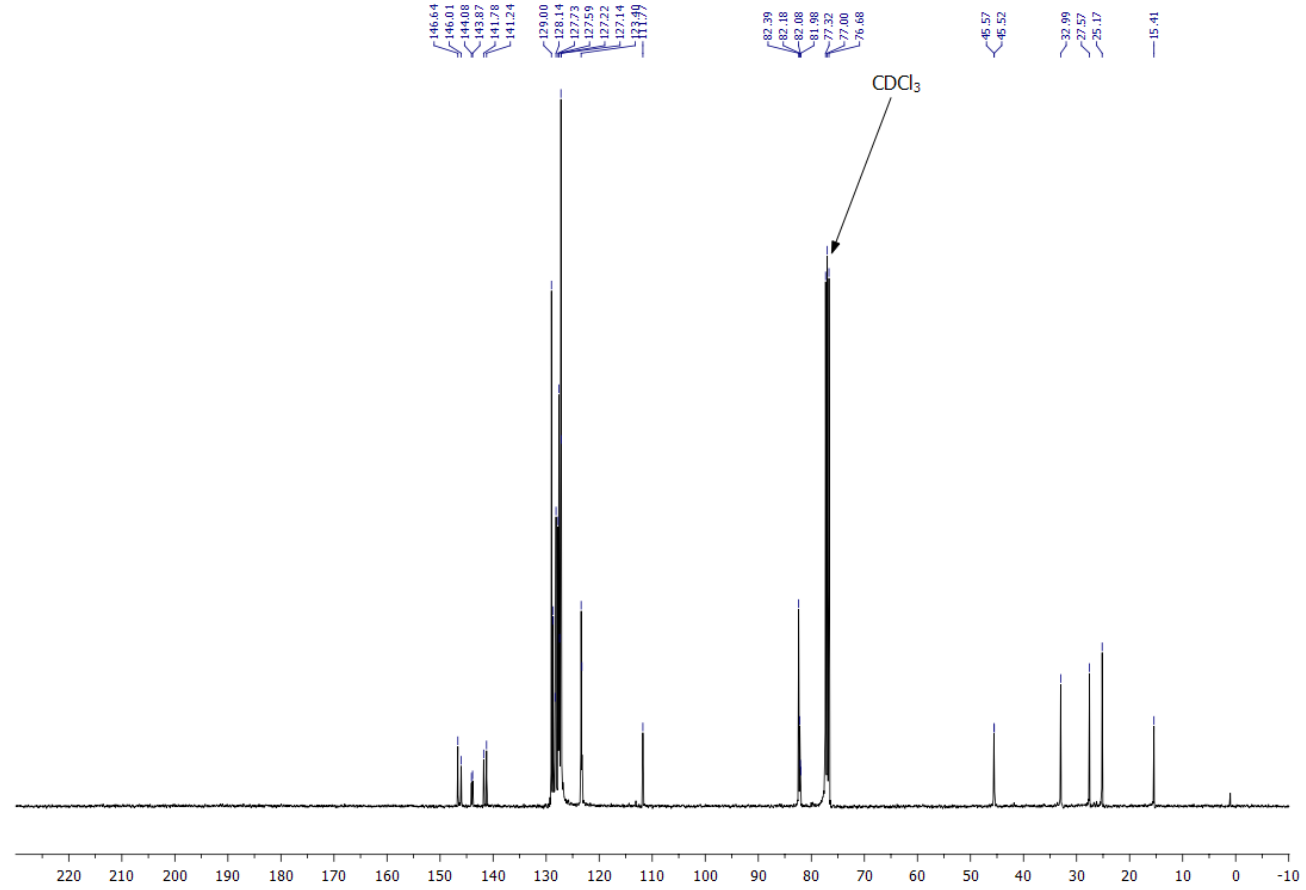


L1g, $^{31}P\{^{1}H\}$ spectrum.

NMR AND MASS SPECTRA

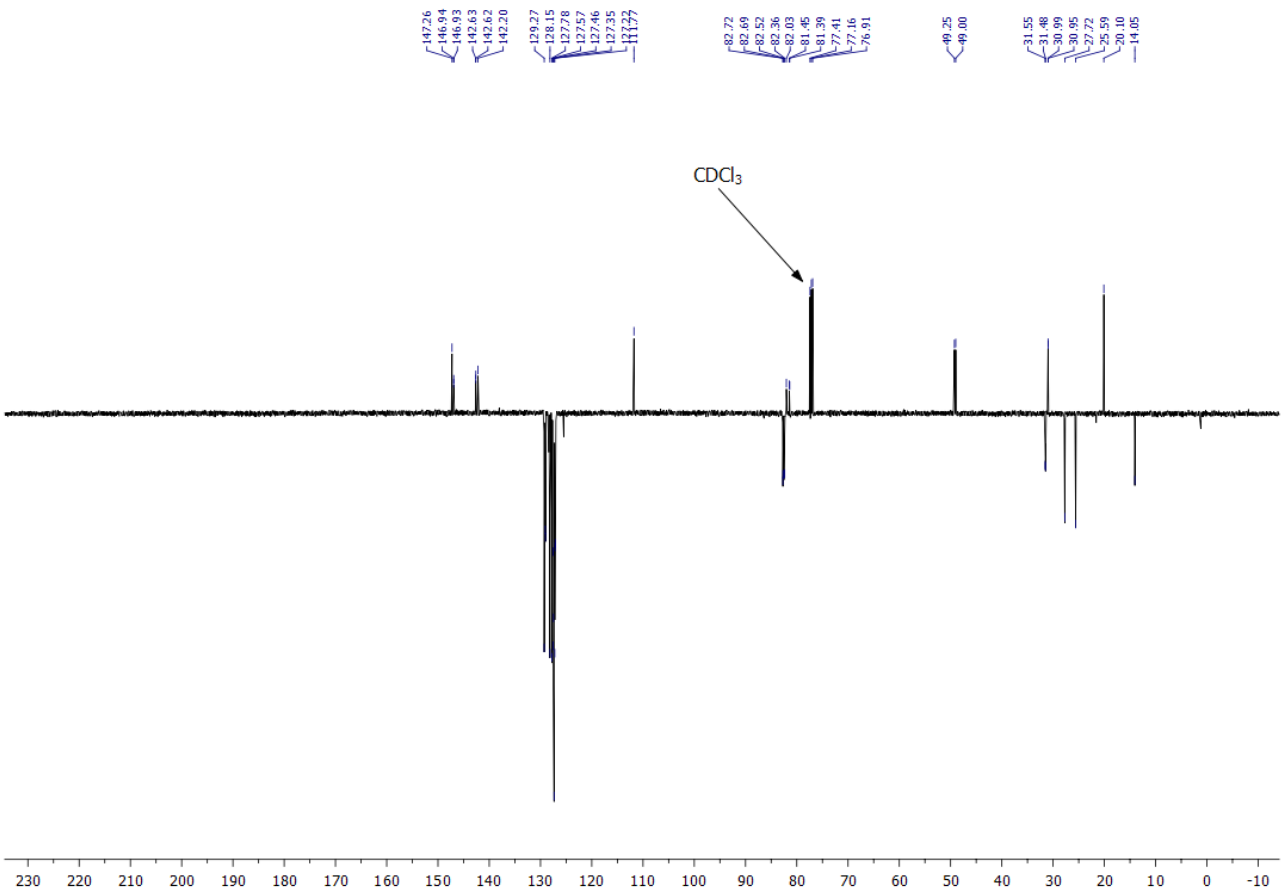


L1g, ^{1}H spectrum.

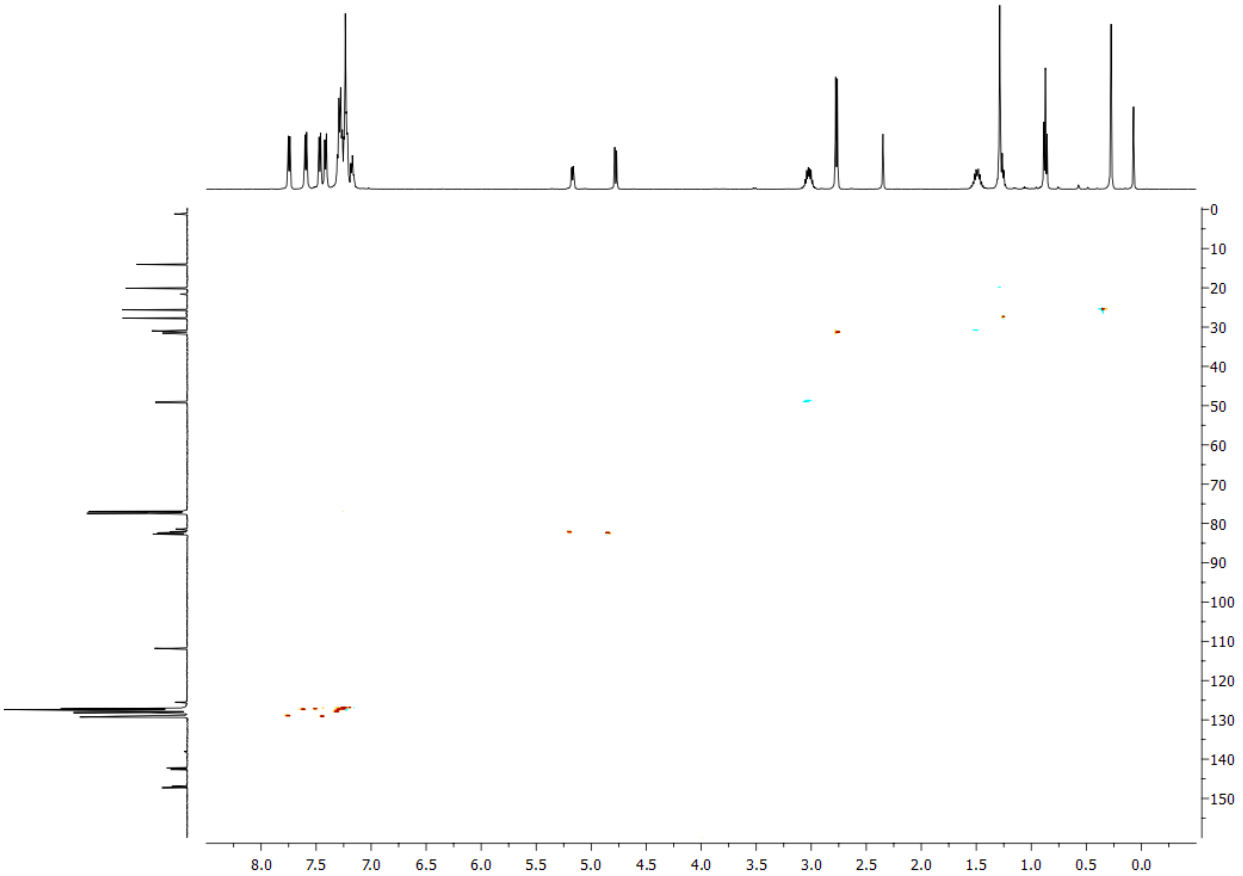


L1g, $^{13}C\{^{1}H\}$ spectrum.

NMR AND MASS SPECTRA

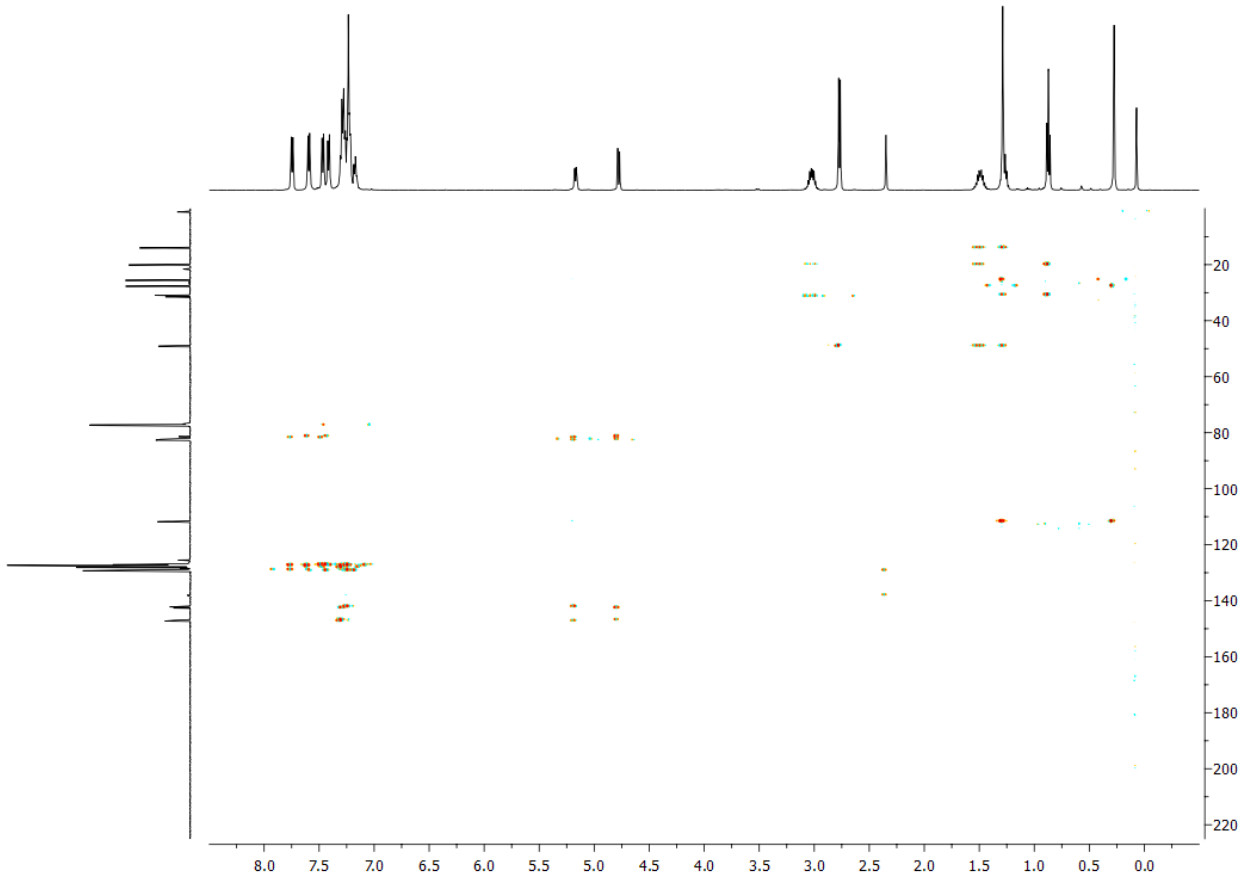


L1g, $^{13}C\{^{1}H\}$ APT spectrum.

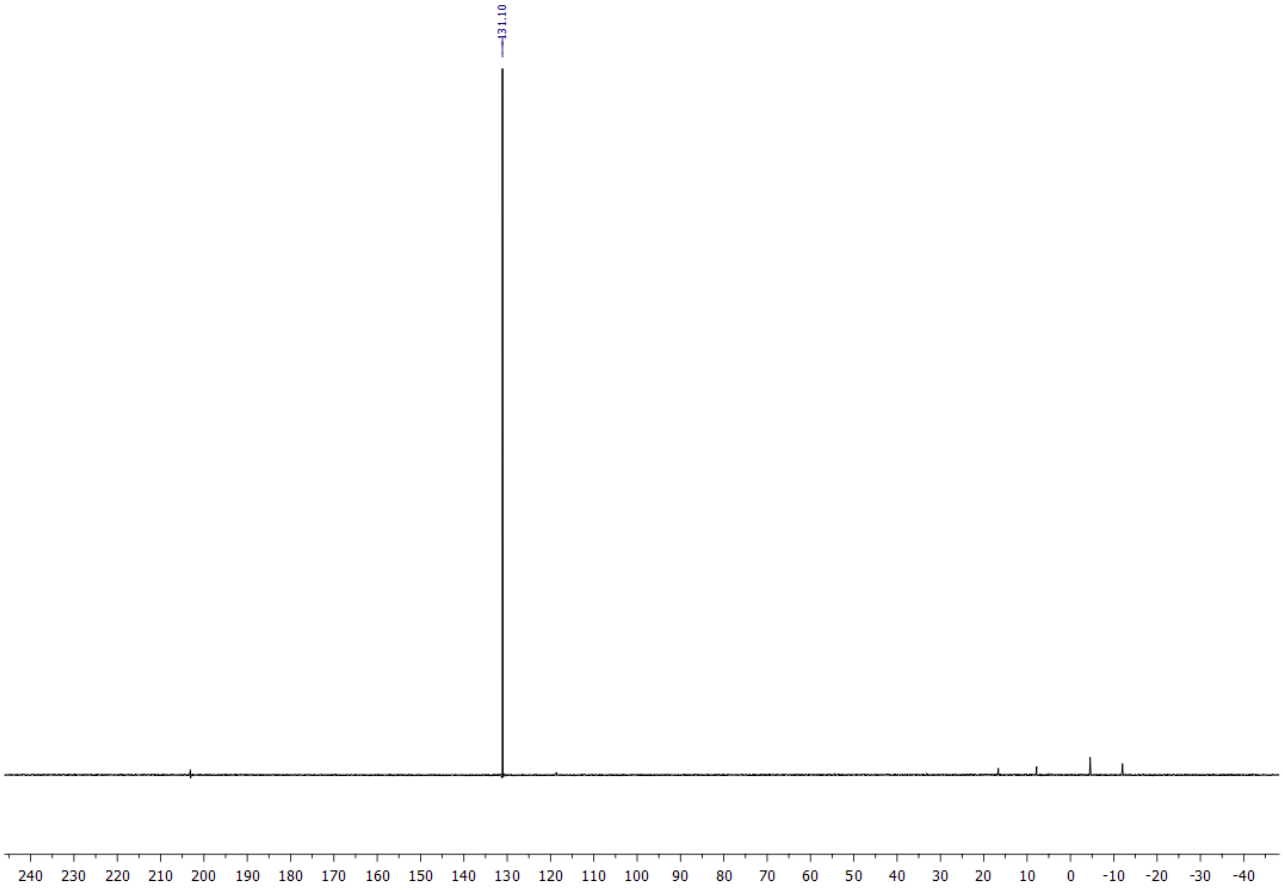


L1g, ^{1}H-^{13}C HSQC spectrum.

NMR AND MASS SPECTRA

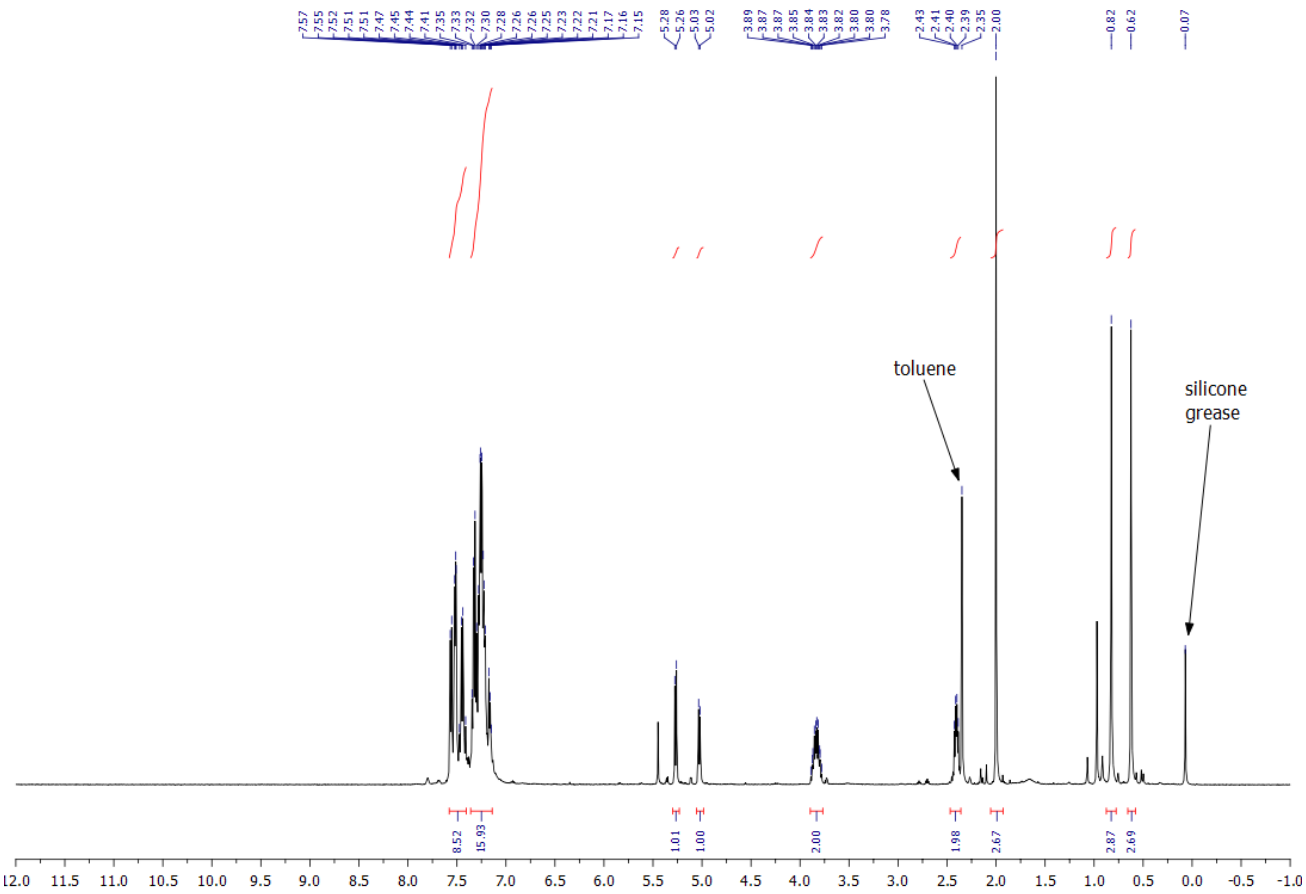


L1g, ^{1}H-^{13}C HMBC spectrum.

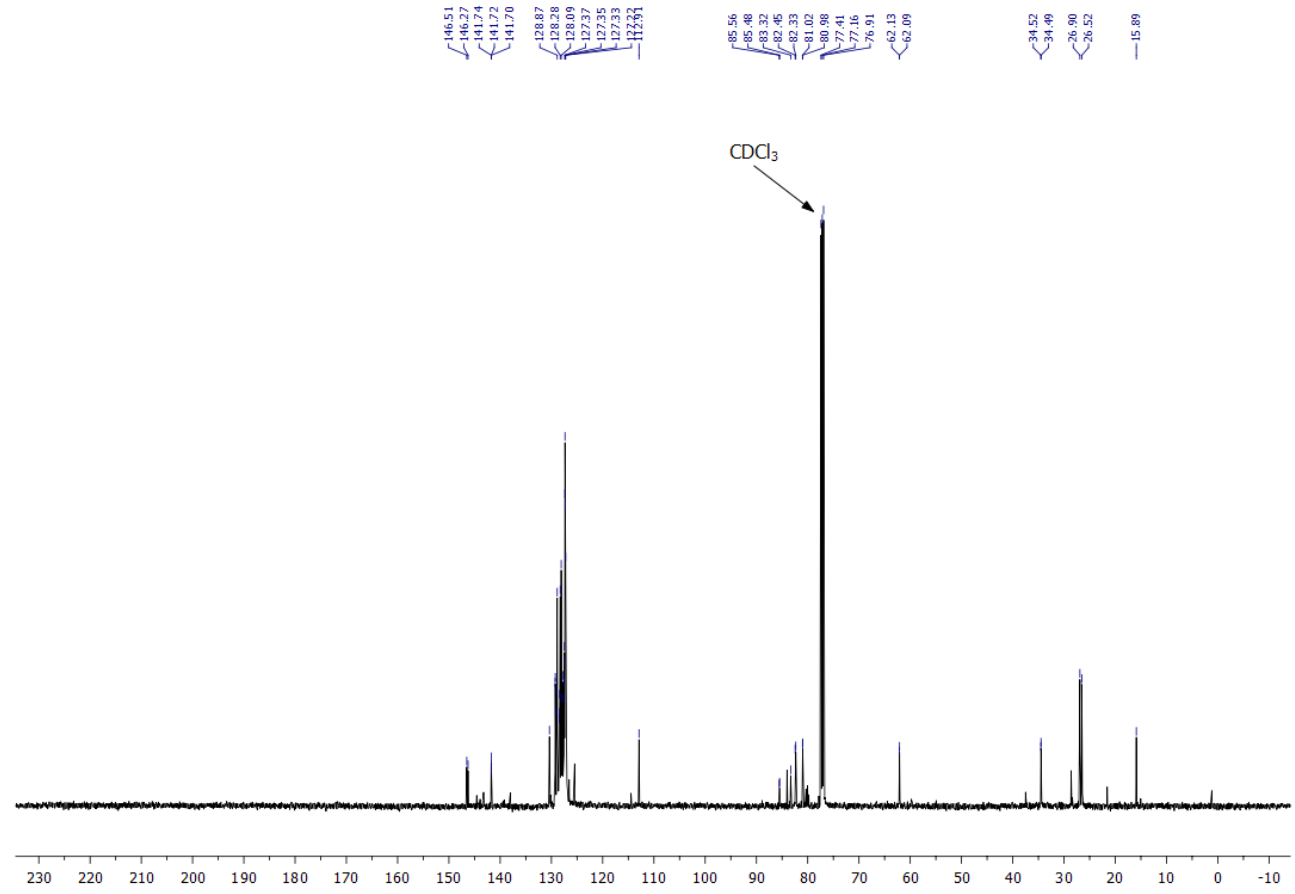


L1h, $^{31}P\{^{1}H\}$ spectrum.

NMR AND MASS SPECTRA

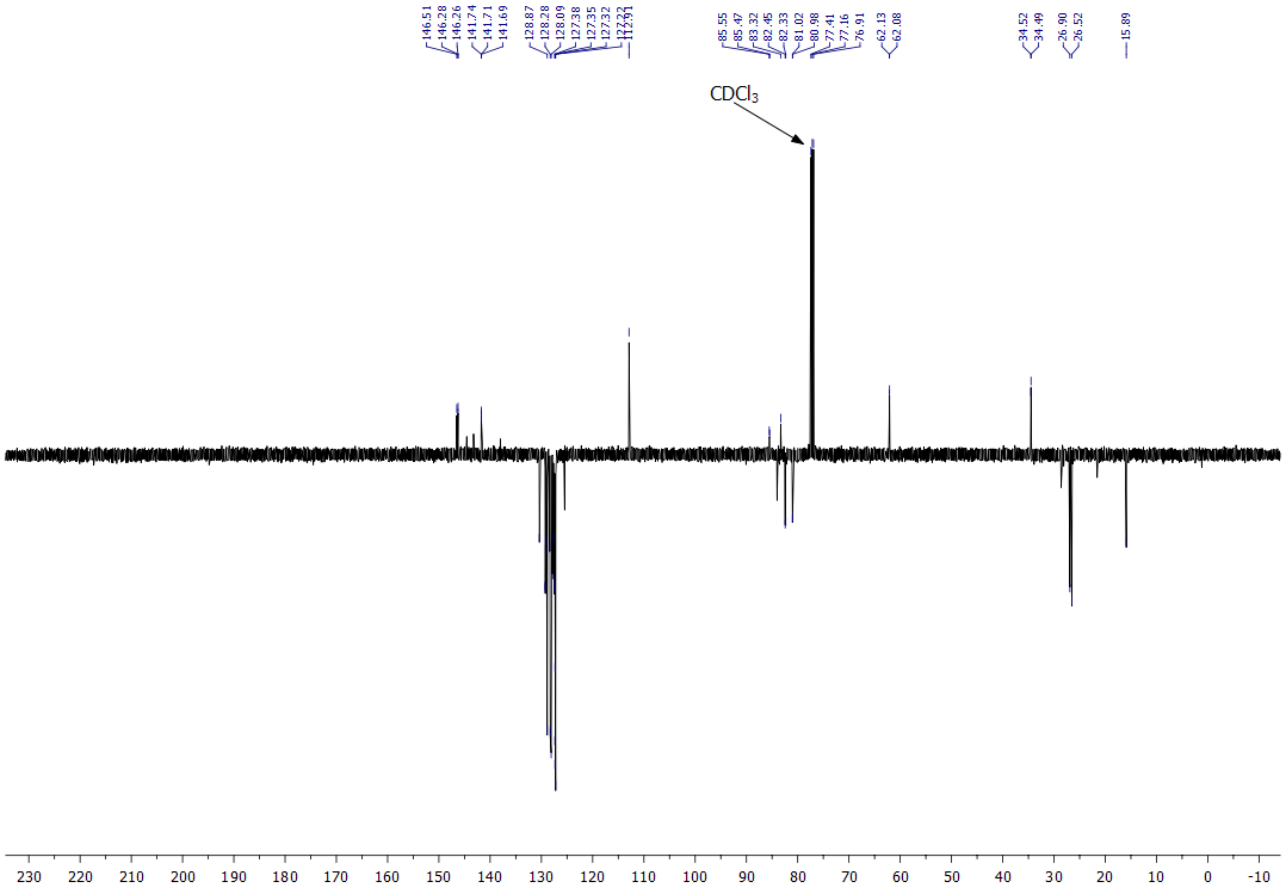


L1h, ^{1}H spectrum.

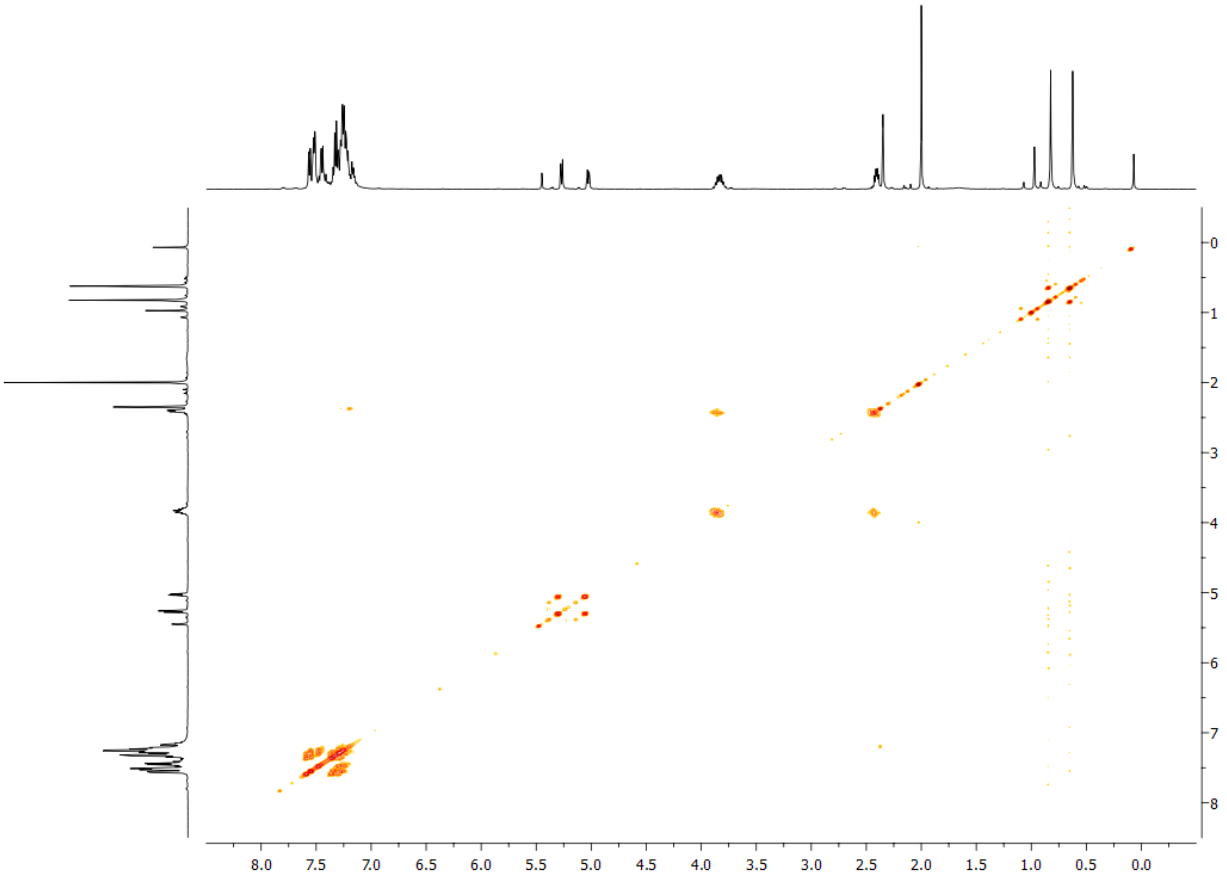


L1h, $^{13}C\{^{1}H\}$ spectrum.

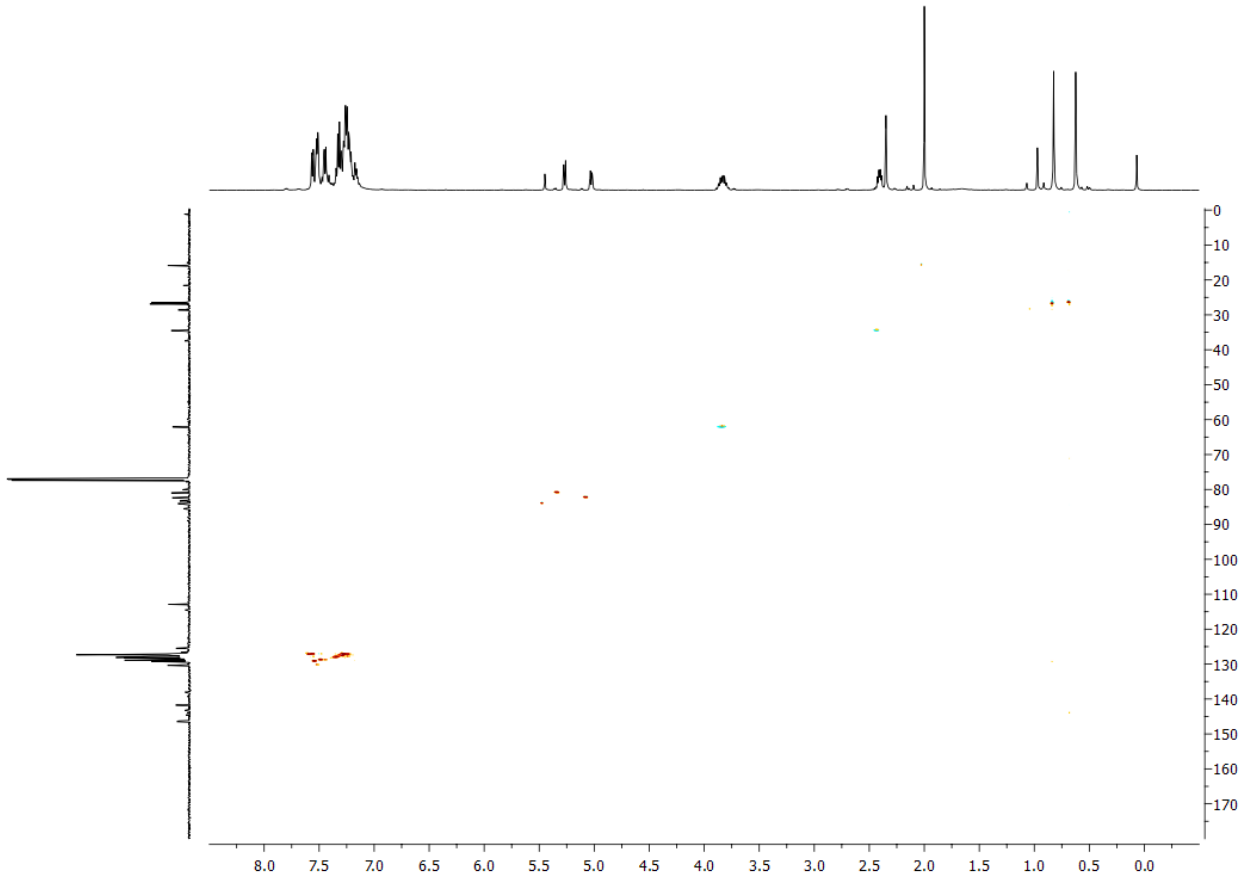
NMR AND MASS SPECTRA



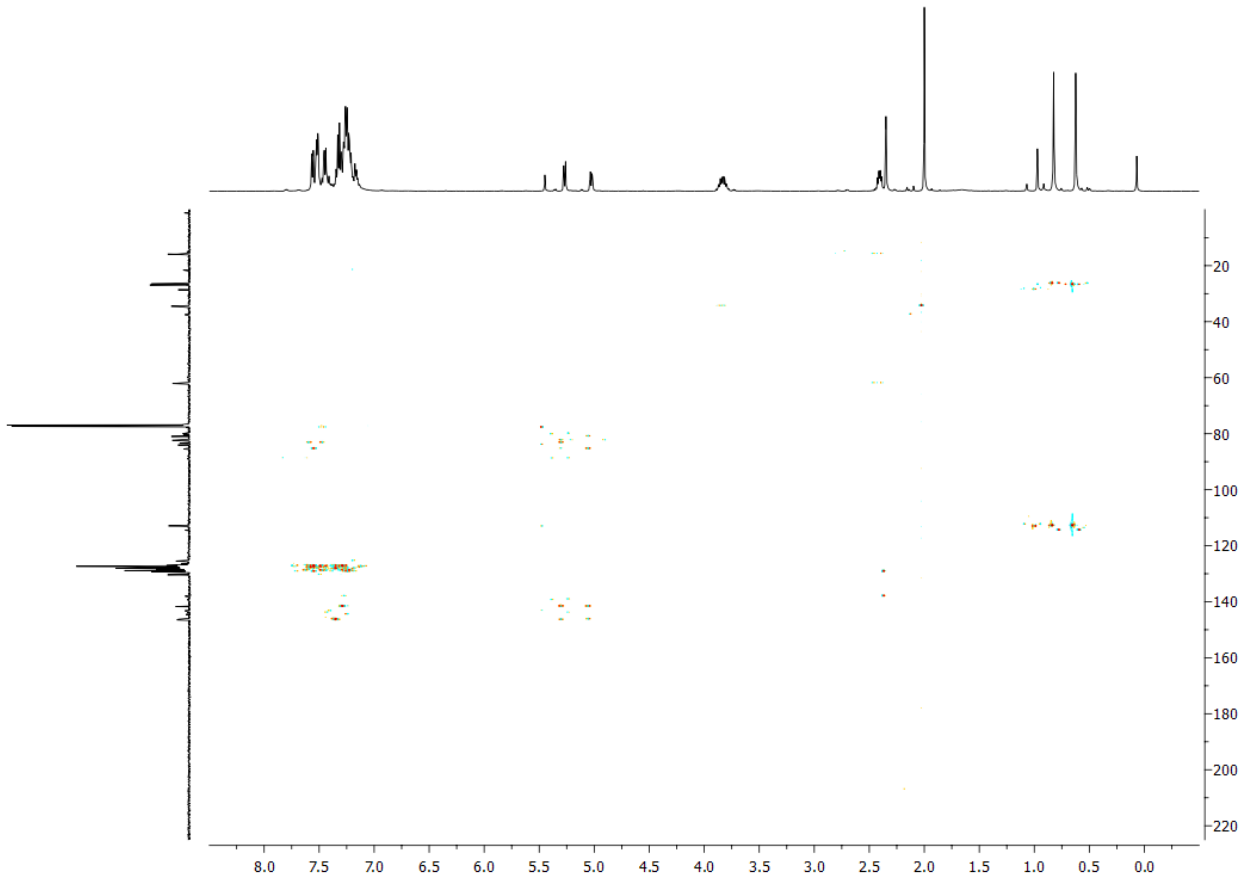
L1h, $^{13}C\{^{1}H\}$ APT spectrum.



L1h, ^{1}H-^{1}H COSY spectrum.

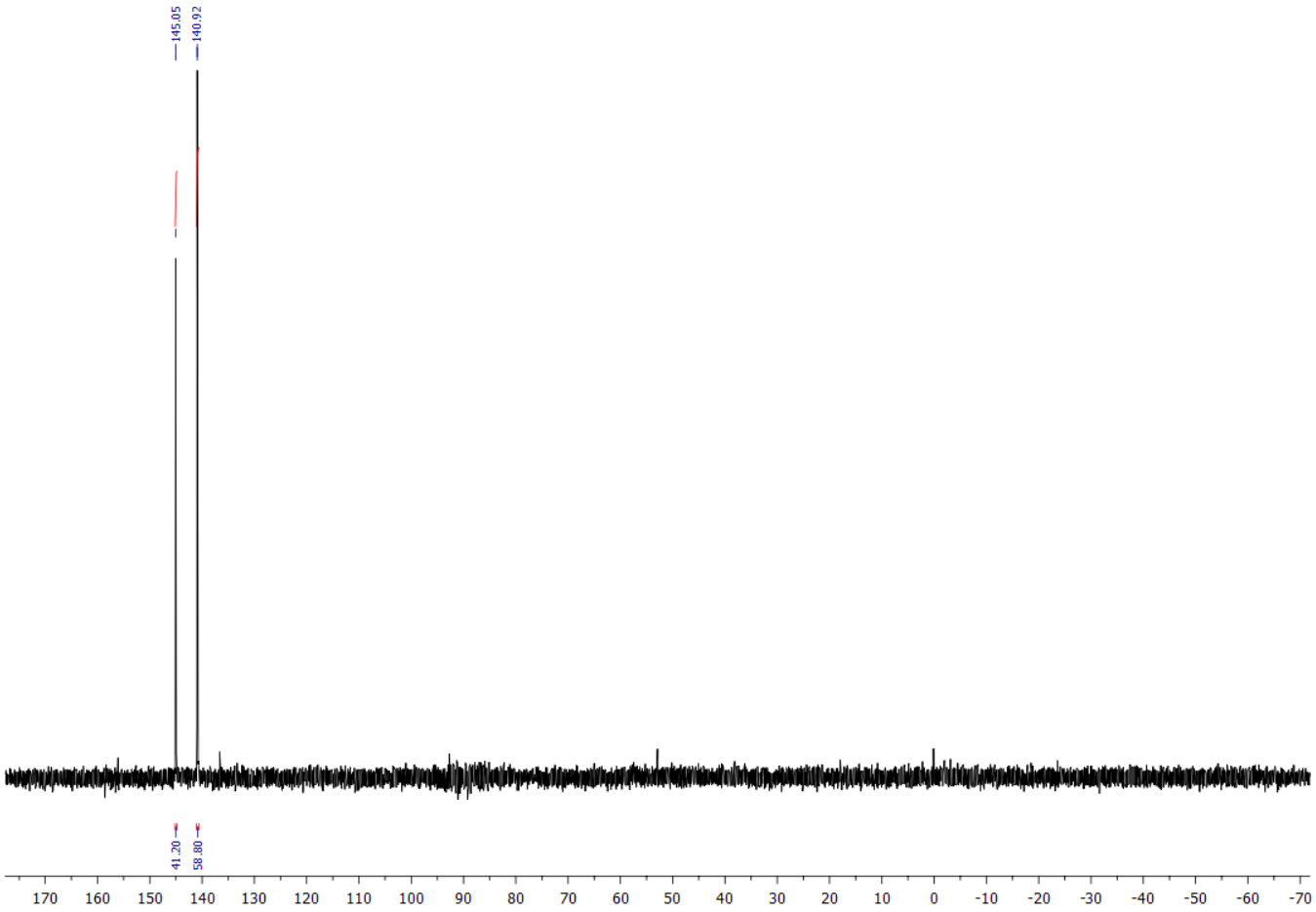


L1h, ^{1}H-^{13}C HSQC spectrum.

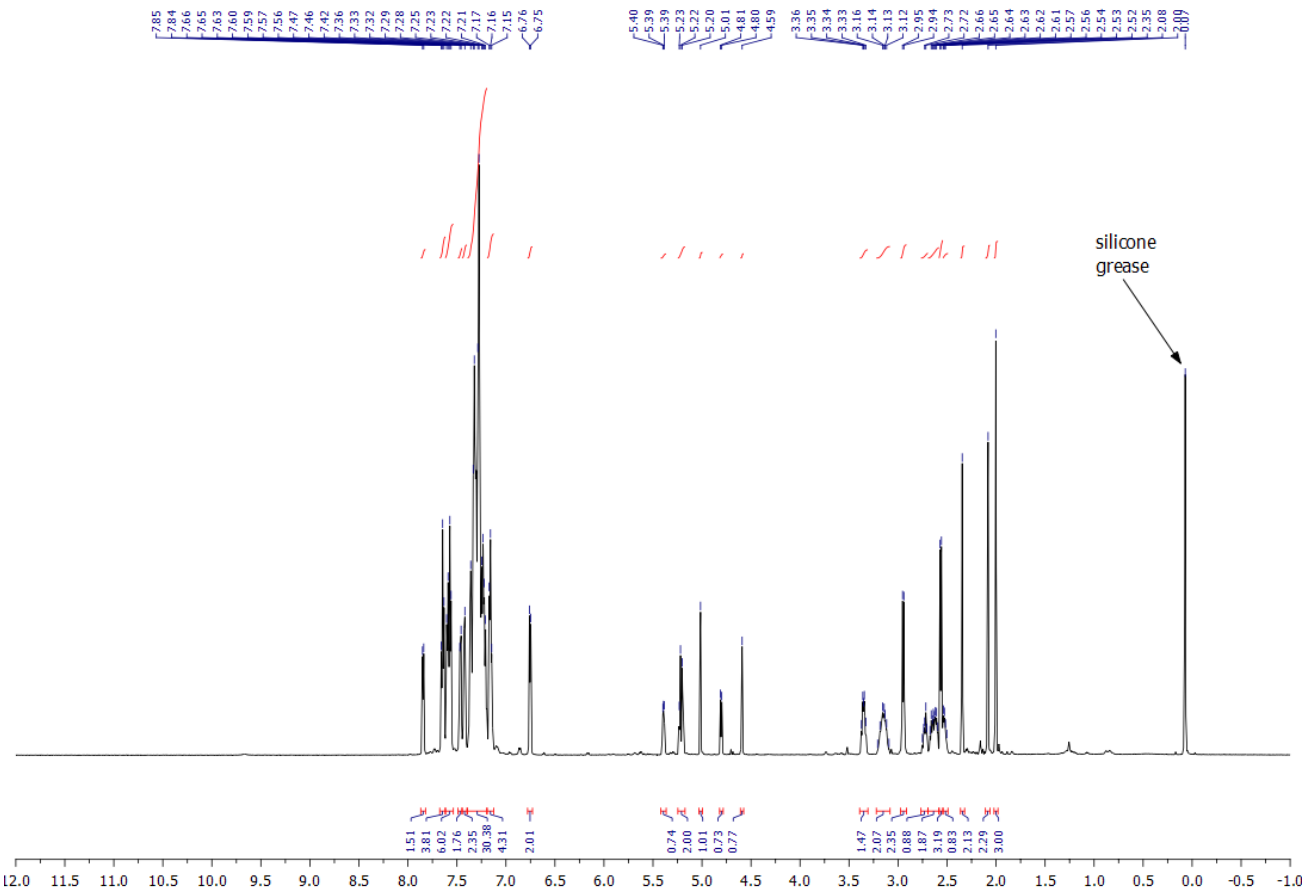


L1h, ^{1}H-^{13}C HMBC spectrum.

NMR AND MASS SPECTRA

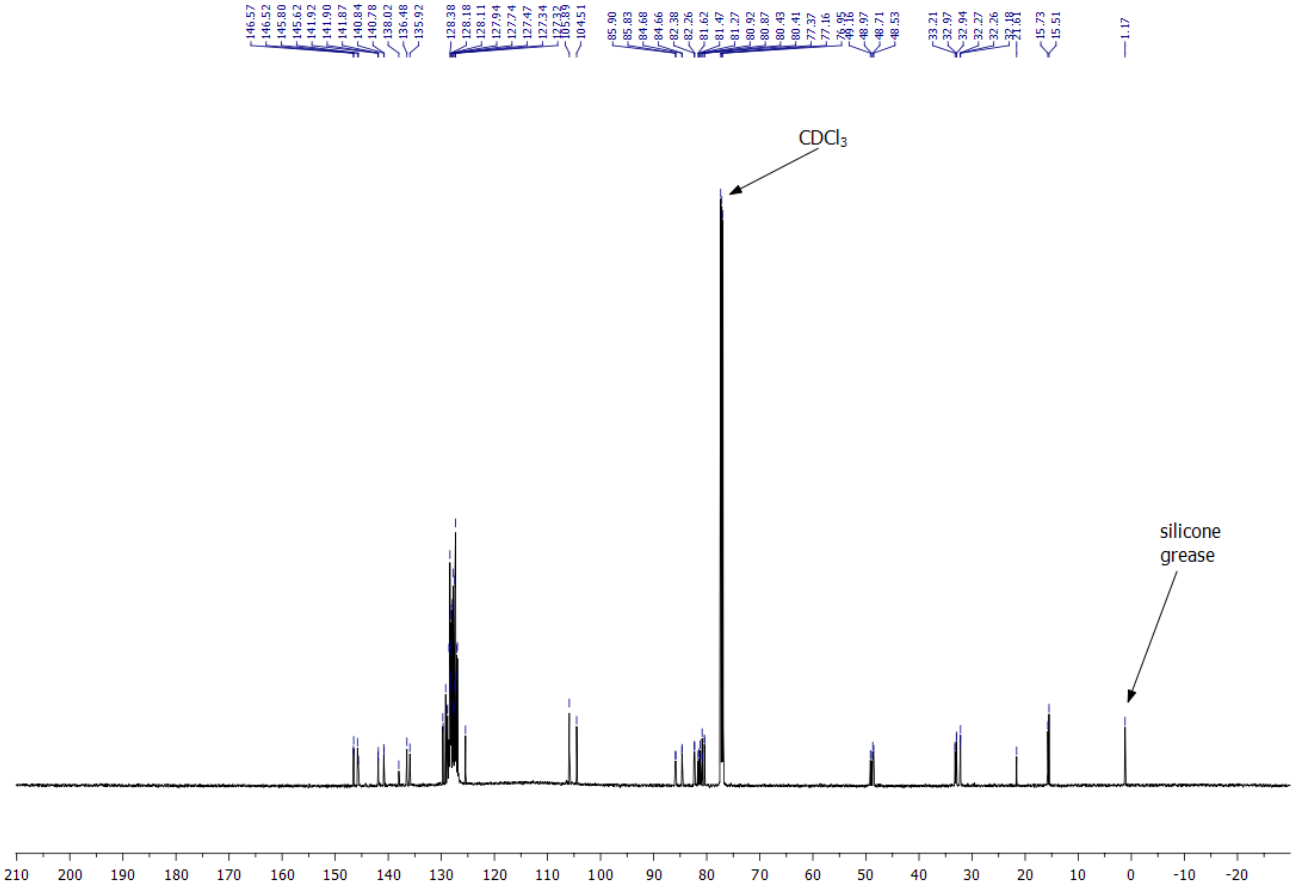


L2a, $^{31}P\{^{1}H\}$ spectrum.

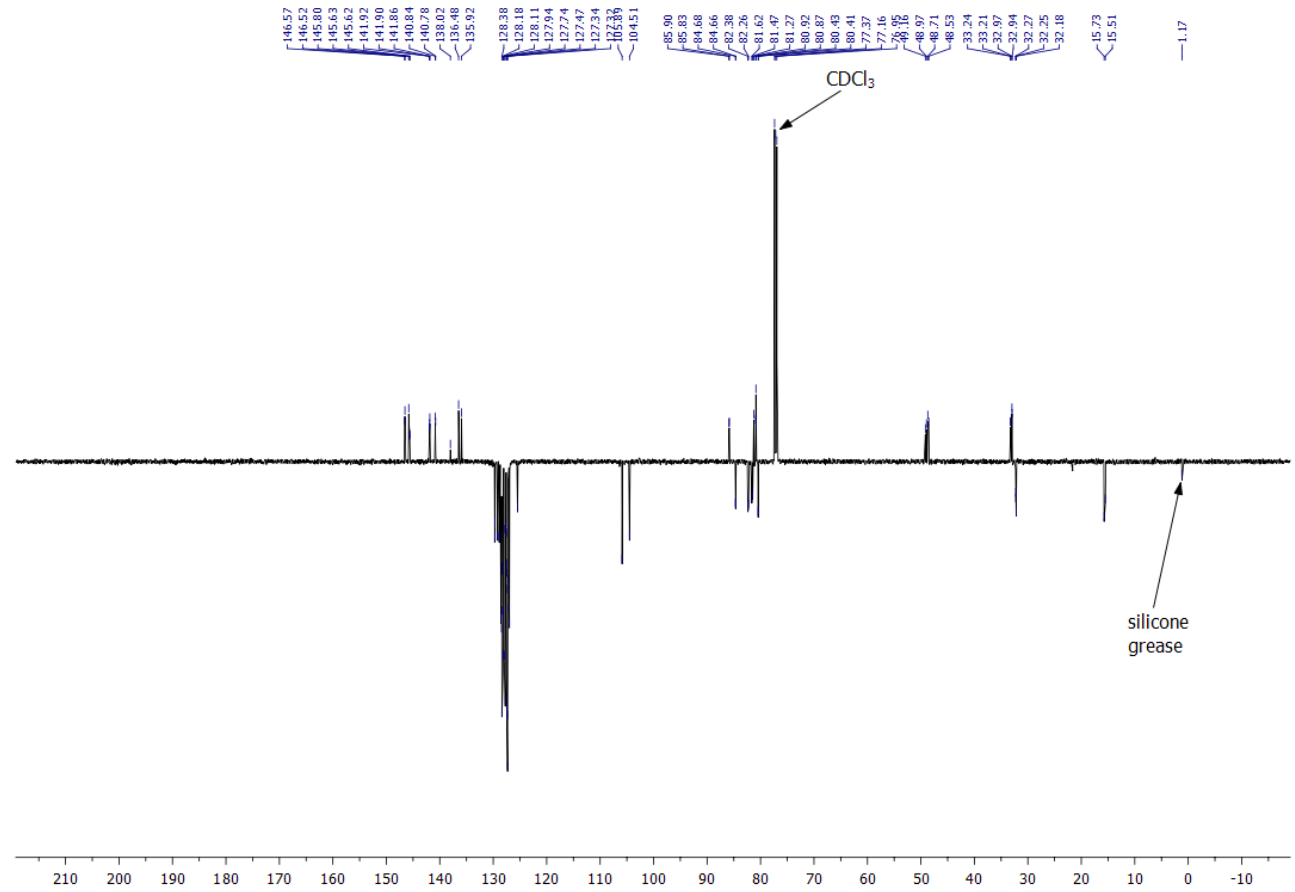


NMR AND MASS SPECTRA

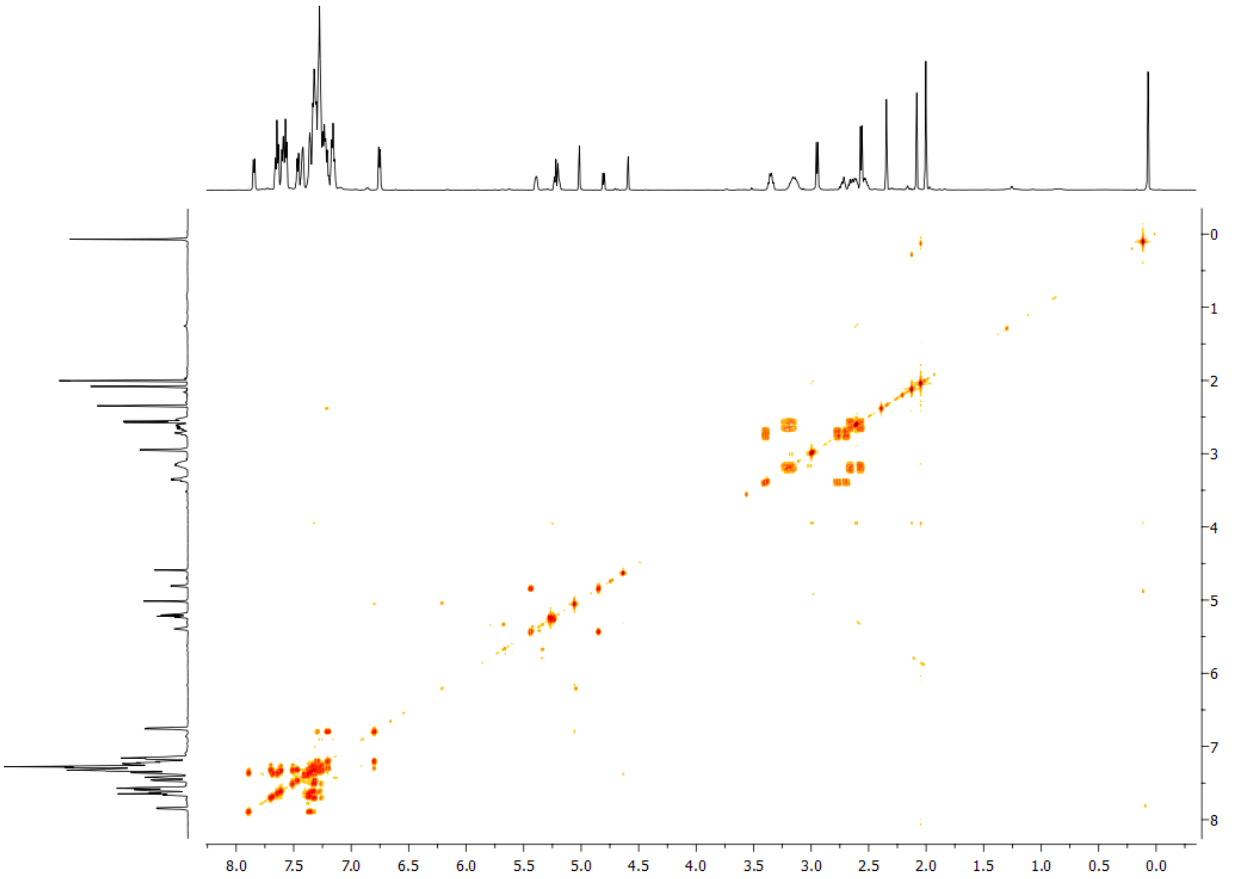
L2a, ^{1}H spectrum.



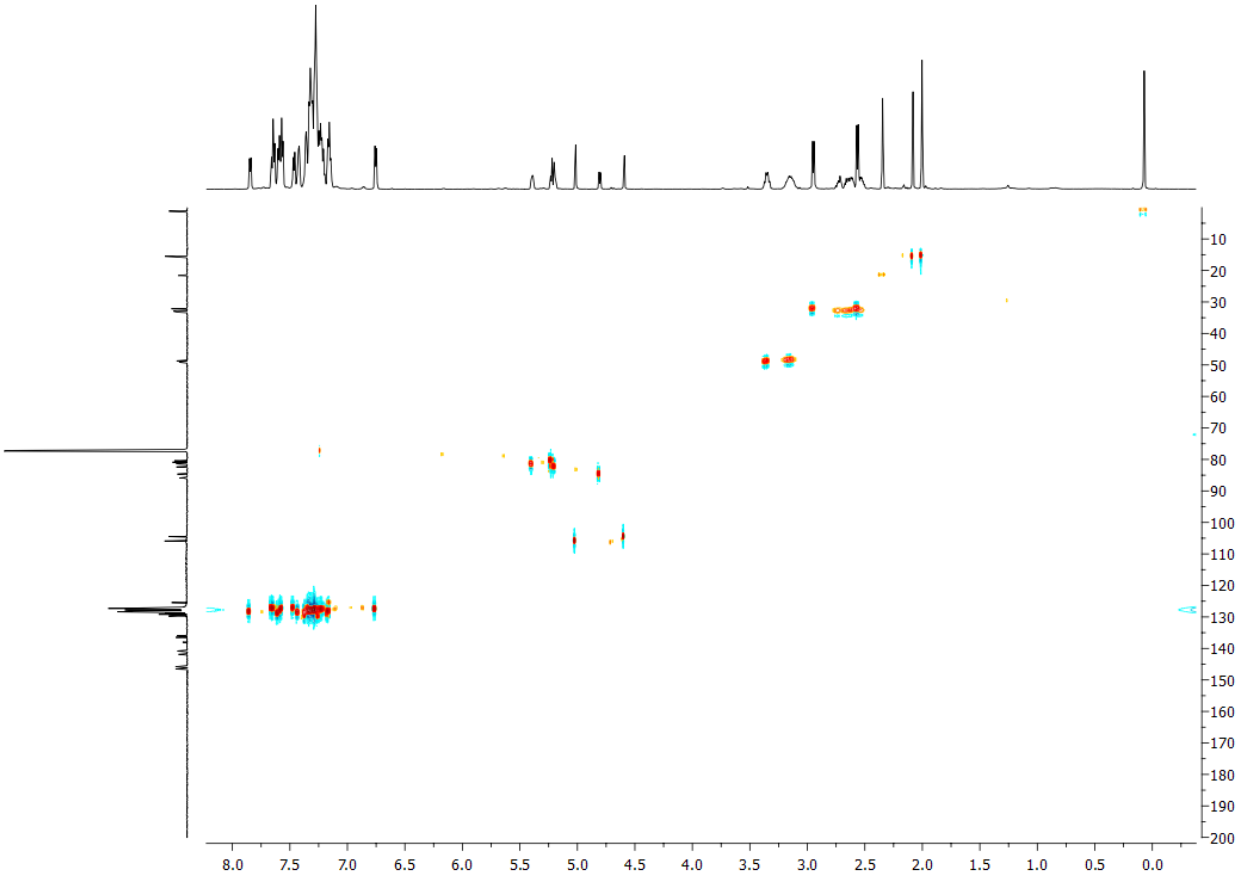
L2a, $^{13}C\{^{1}H\}$ spectrum.



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

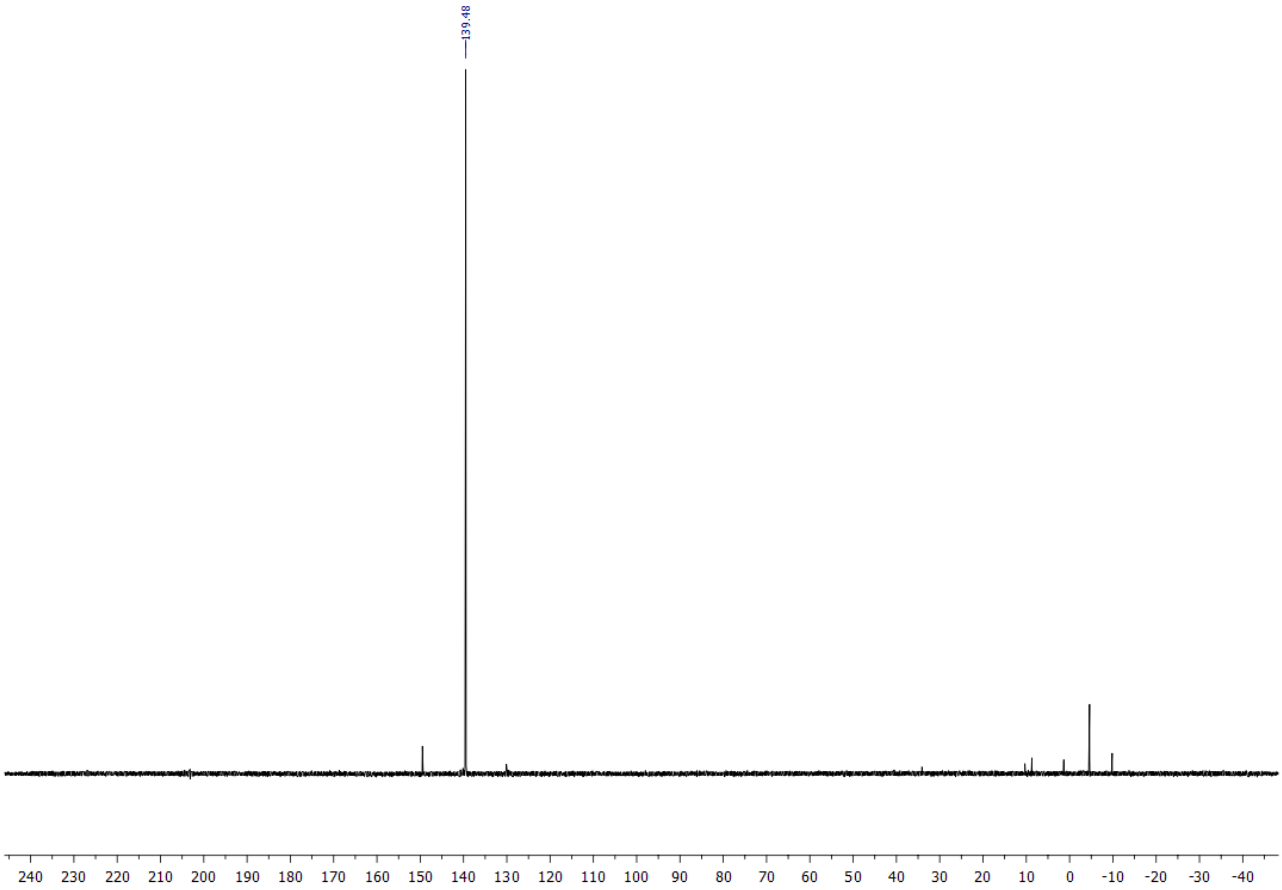


L2a, ^{1}H-^{1}H COSY spectrum.

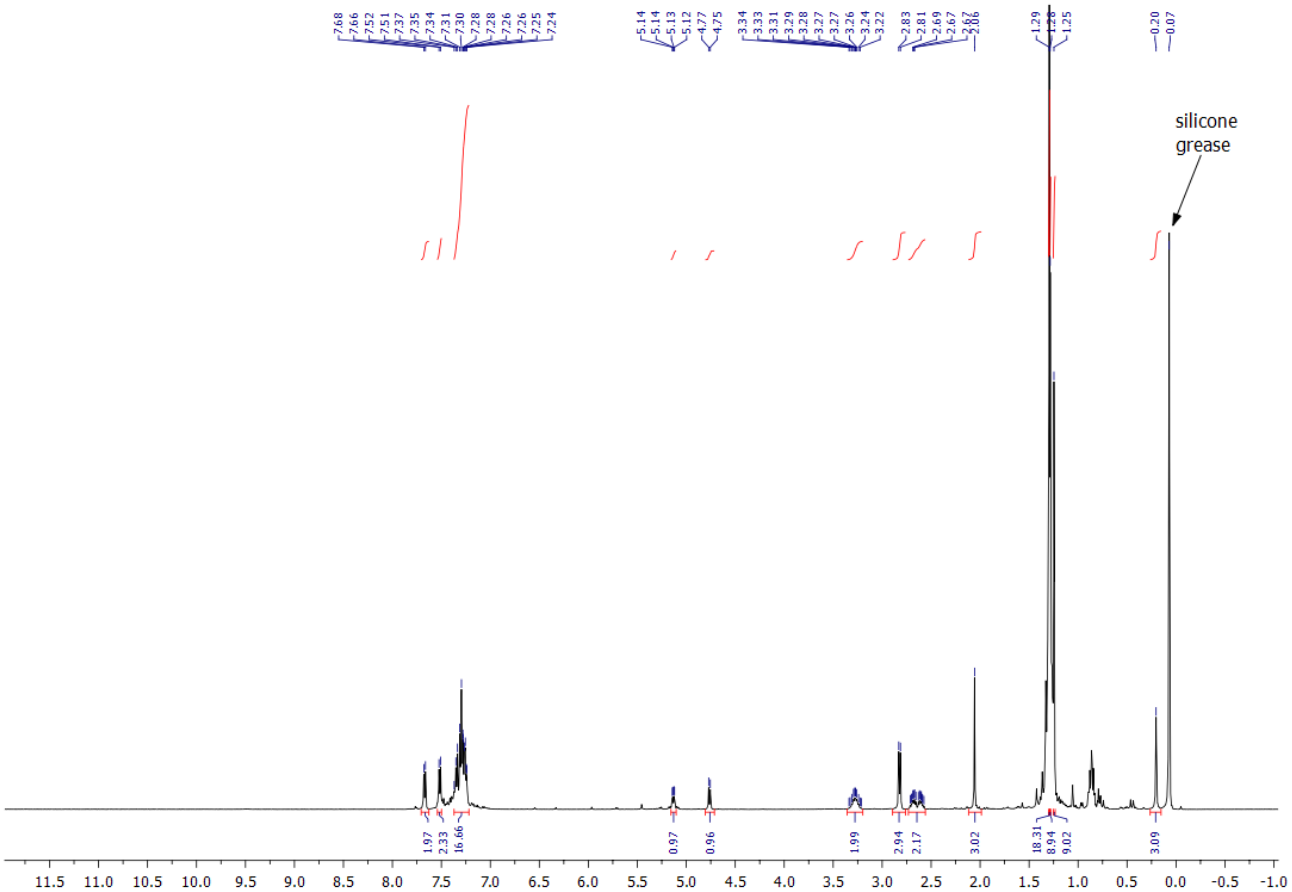


L2a, ^{1}H-^{13}C HSQC spectrum.

NMR AND MASS SPECTRA

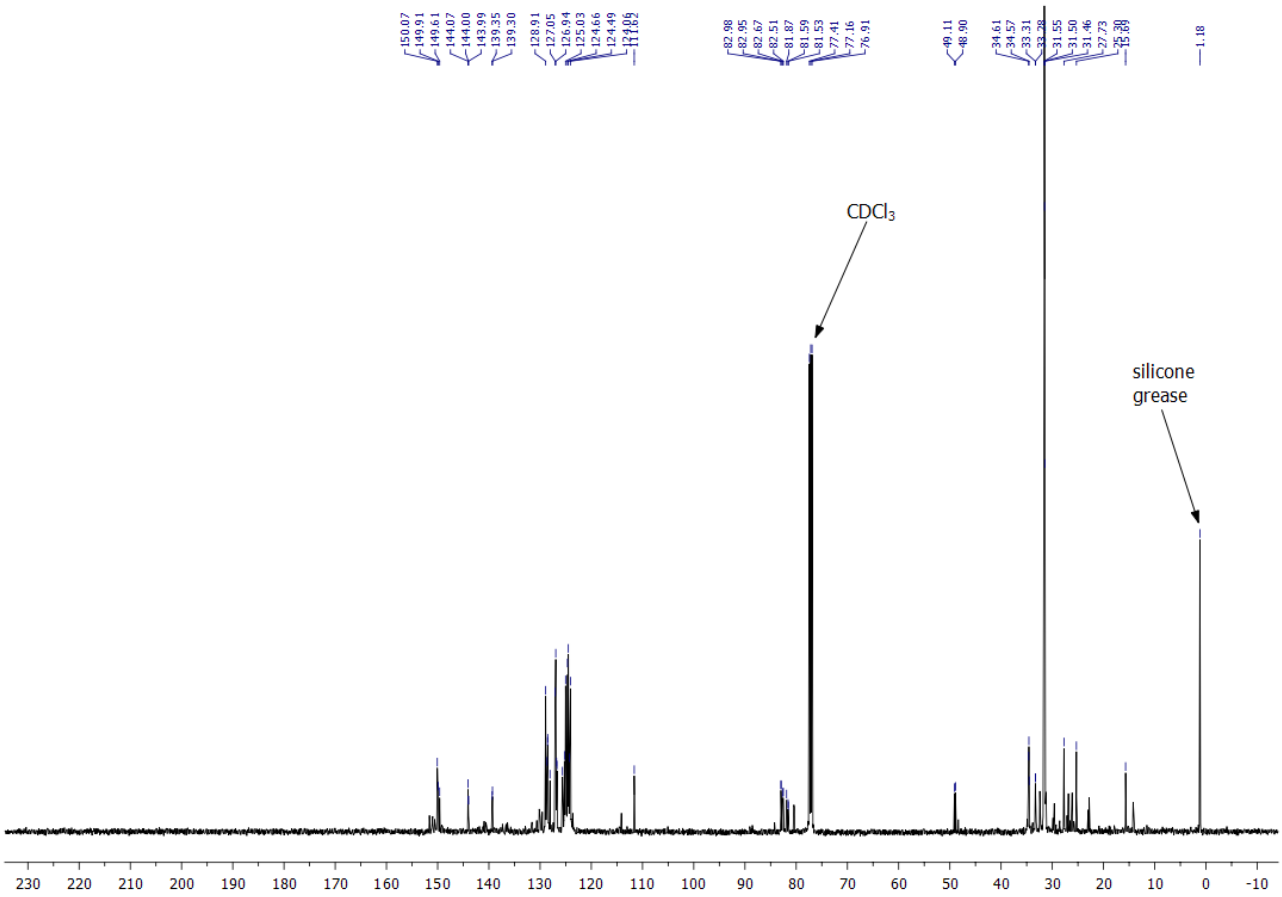


L2b, $^{31}P\{^{1}H\}$ spectrum.

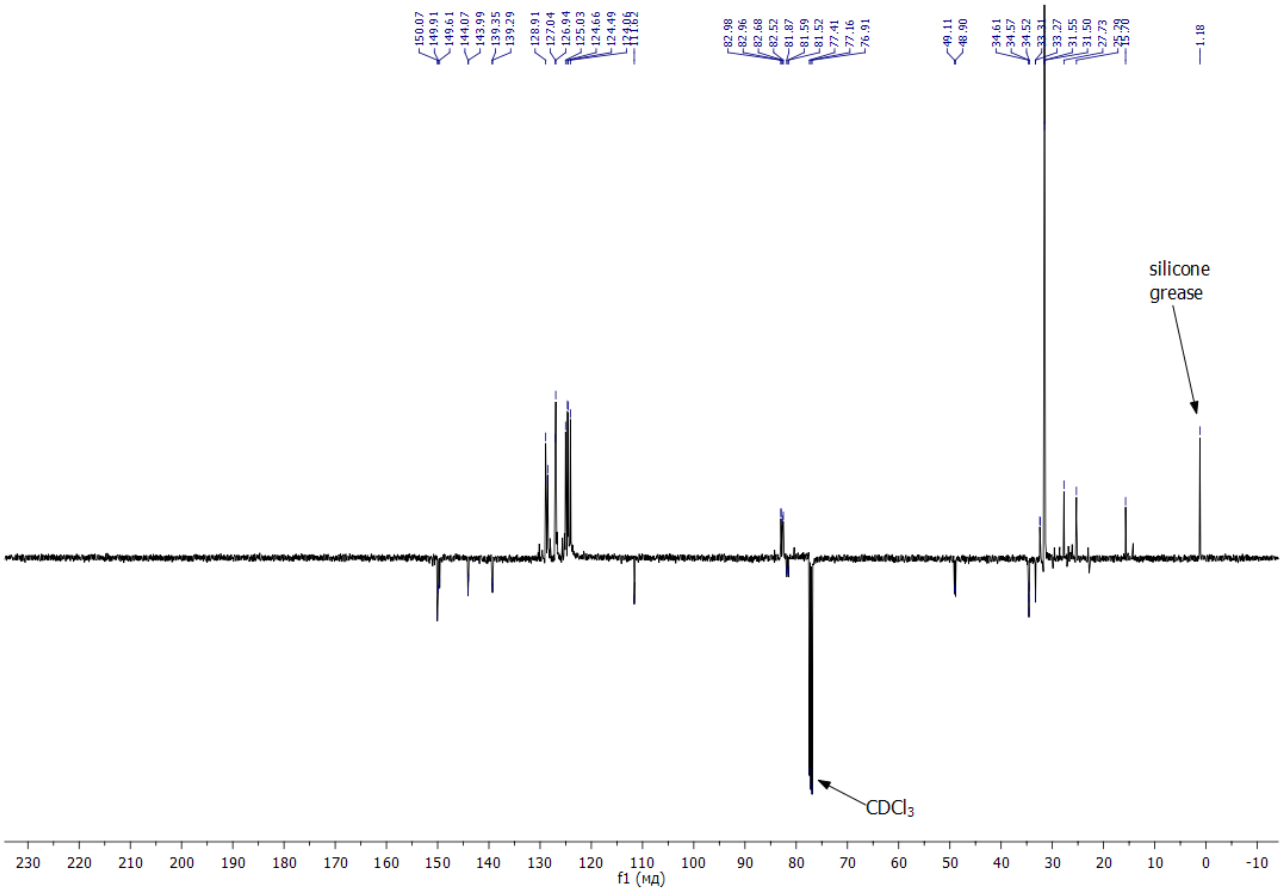


L2b, ^{1}H spectrum.

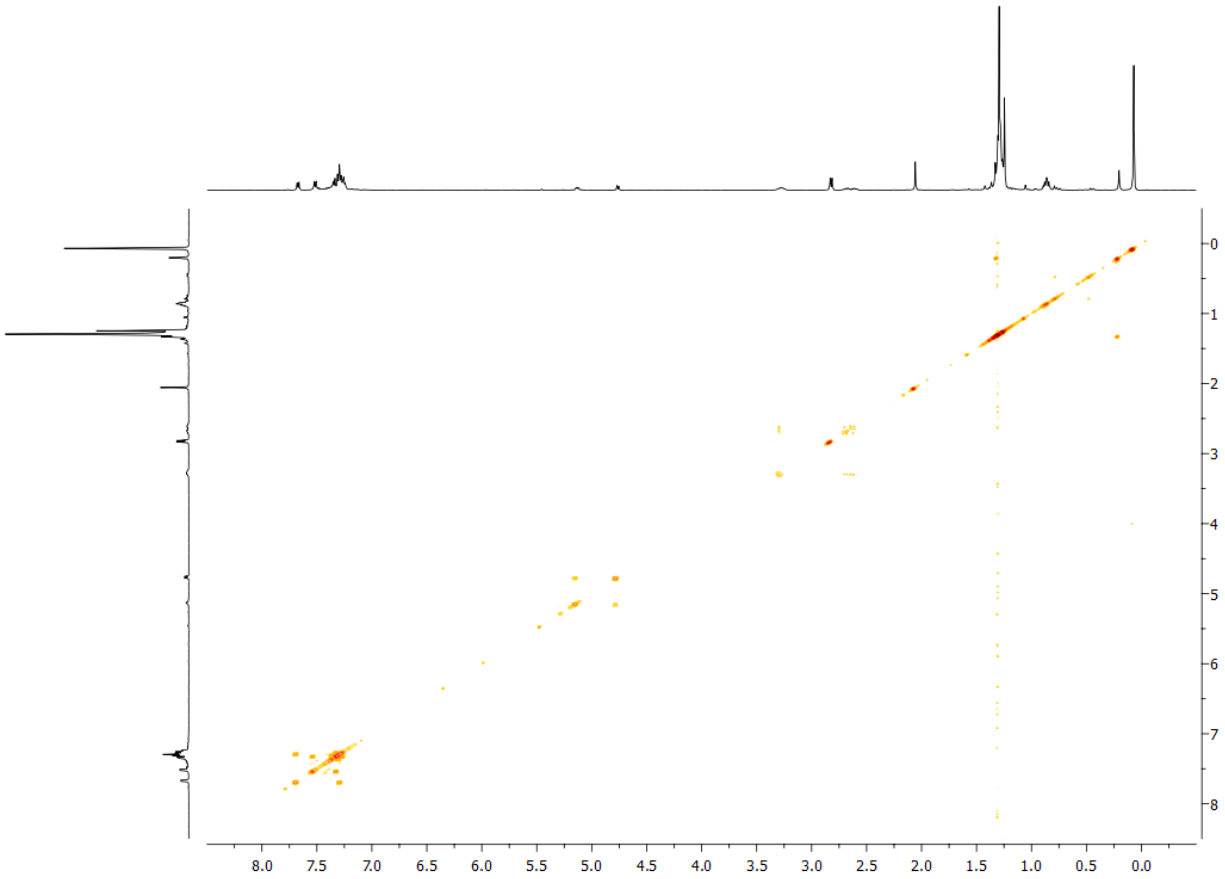
NMR AND MASS SPECTRA



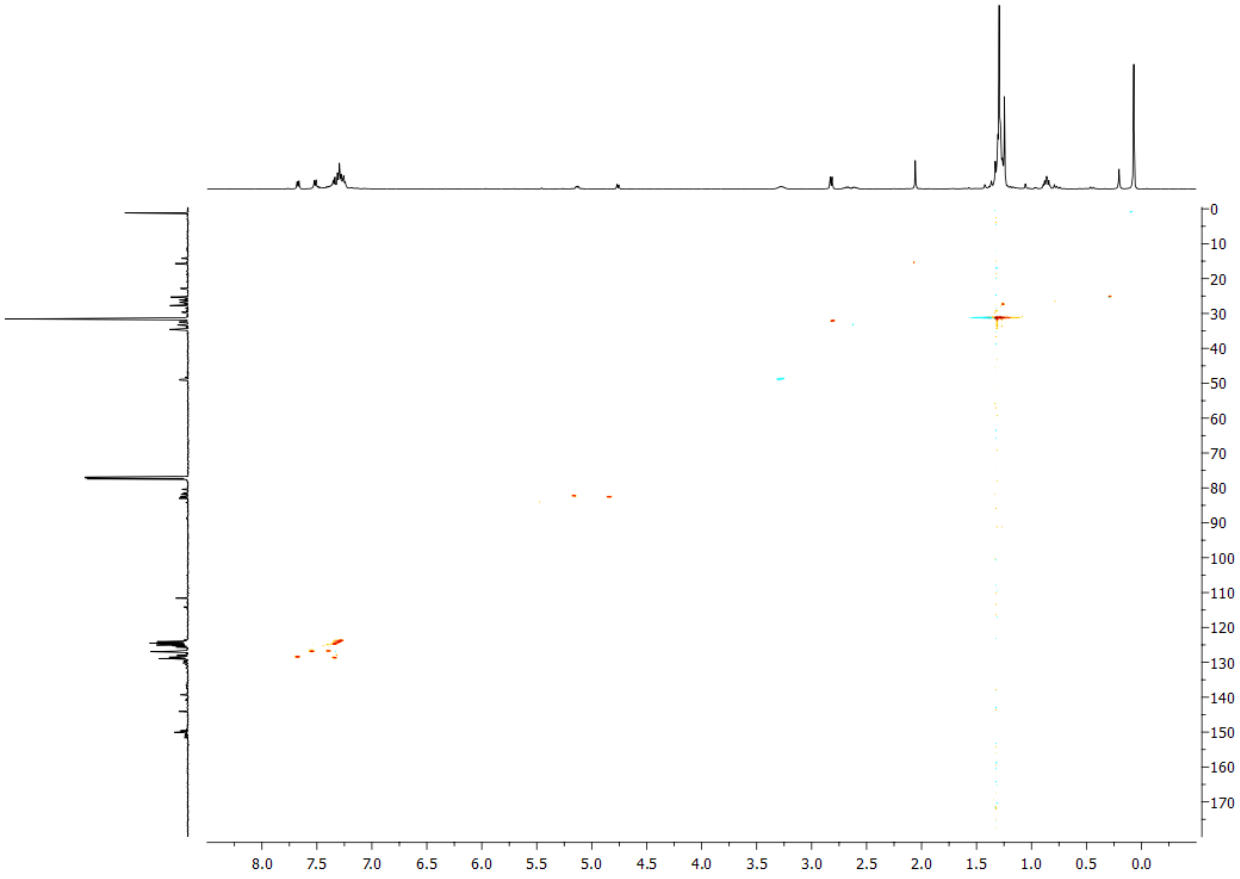
L2b, $^{13}C\{^{1}H\}$ spectrum.



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

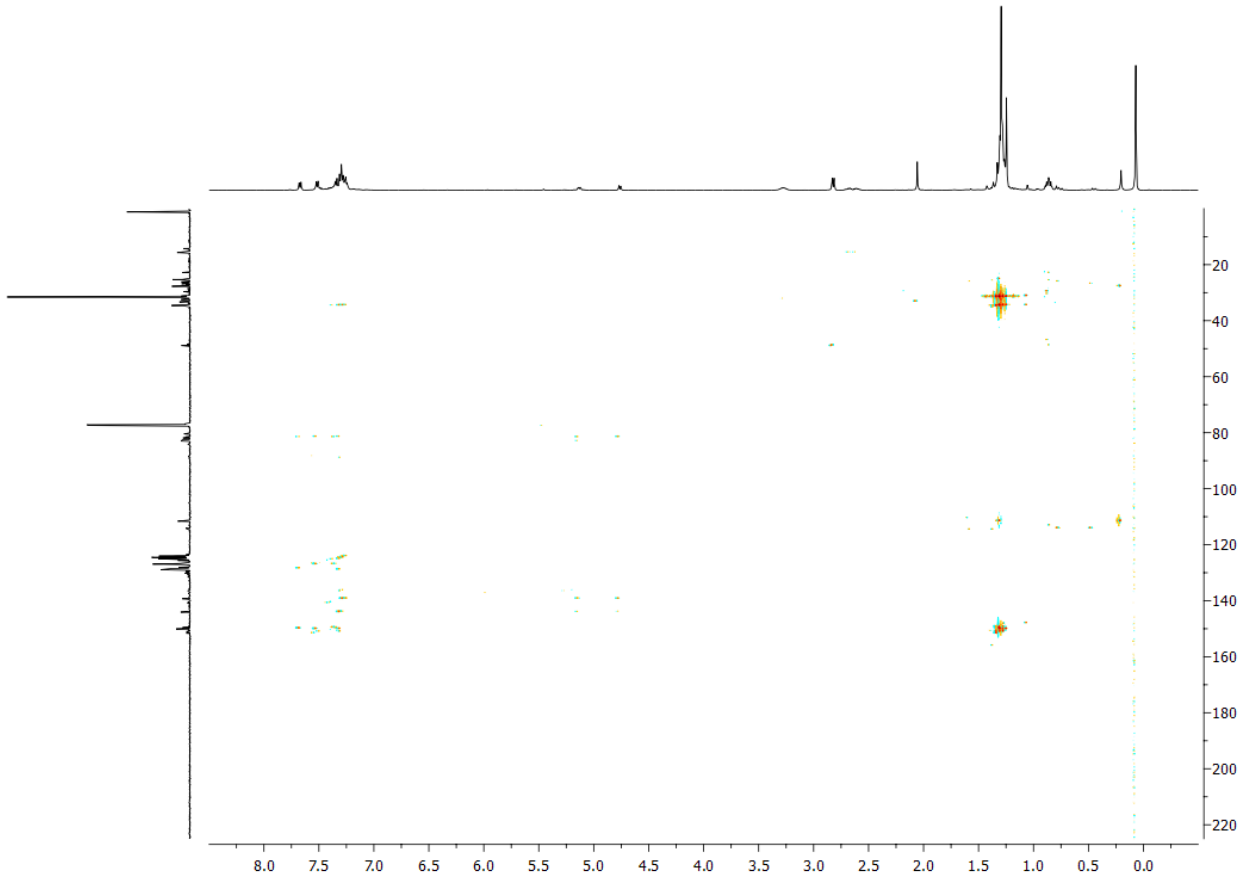


L2b, ^{1}H-^{1}H COSY spectrum.

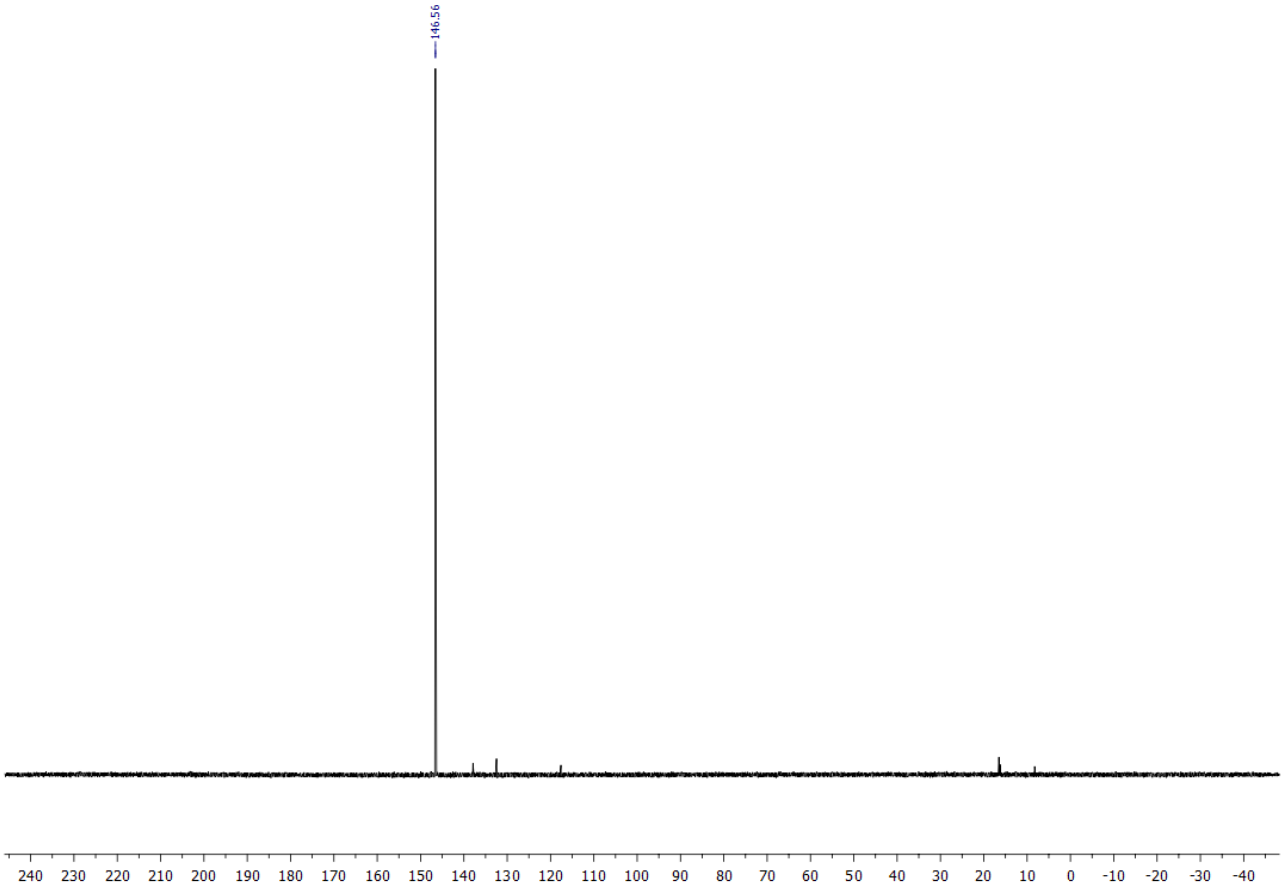


L2b, ^{1}H-^{13}C HSQC spectrum.

NMR AND MASS SPECTRA

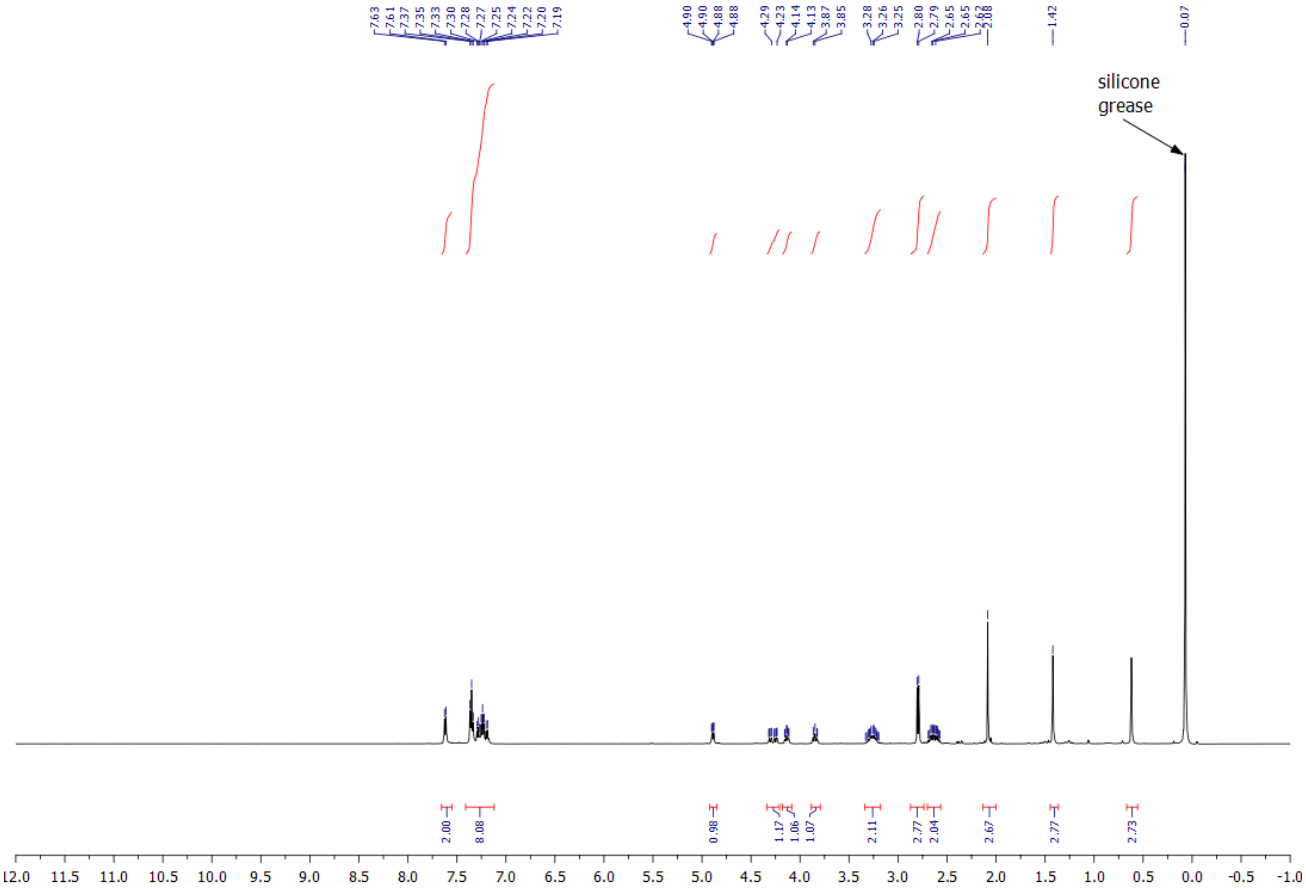


L2b, ^{1}H-^{13}C HMBC spectrum.

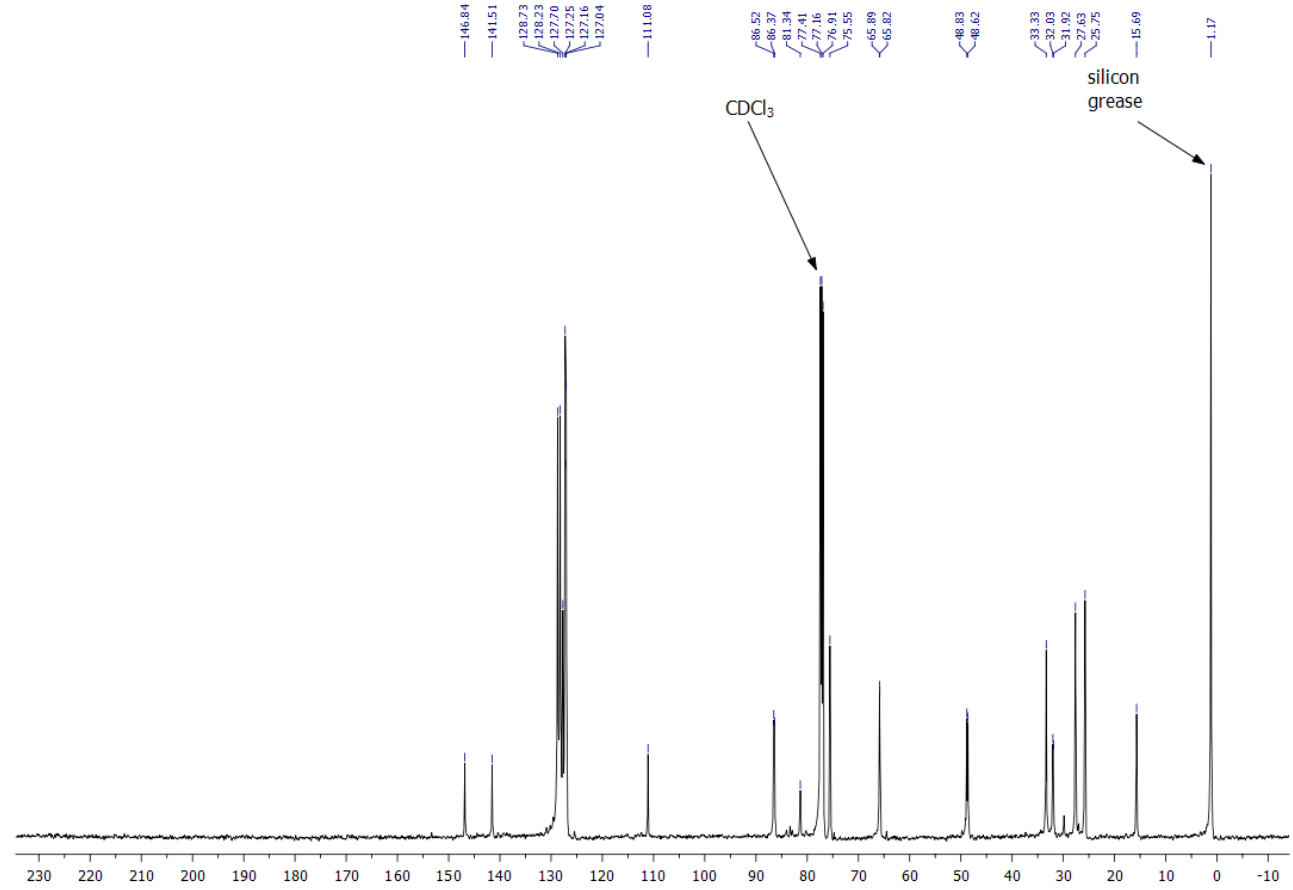


L2c, $^{31}P\{^{1}H\}$ spectrum.

NMR AND MASS SPECTRA

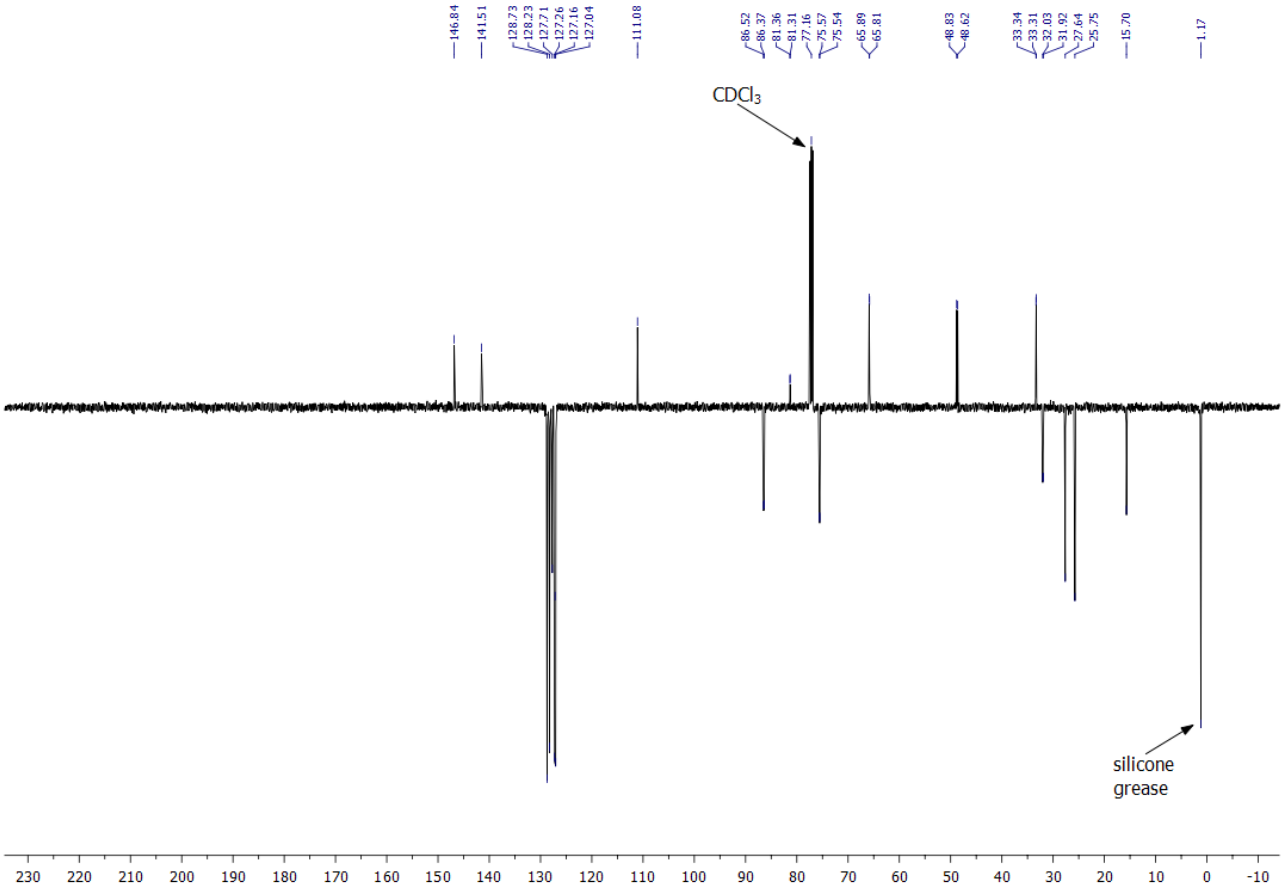


L2c, ^{1}H spectrum.

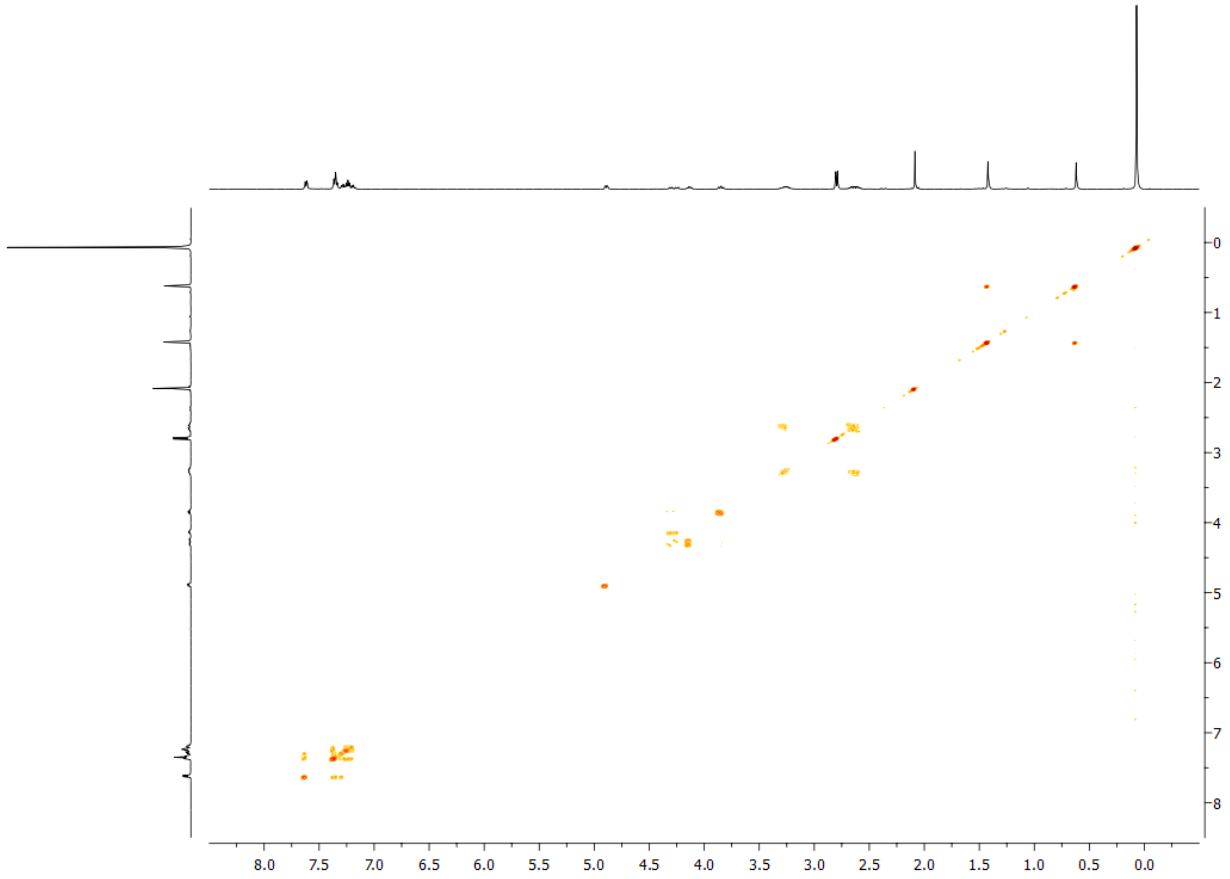


L2c, ^{13}C{^{1}H} spectrum.

NMR AND MASS SPECTRA

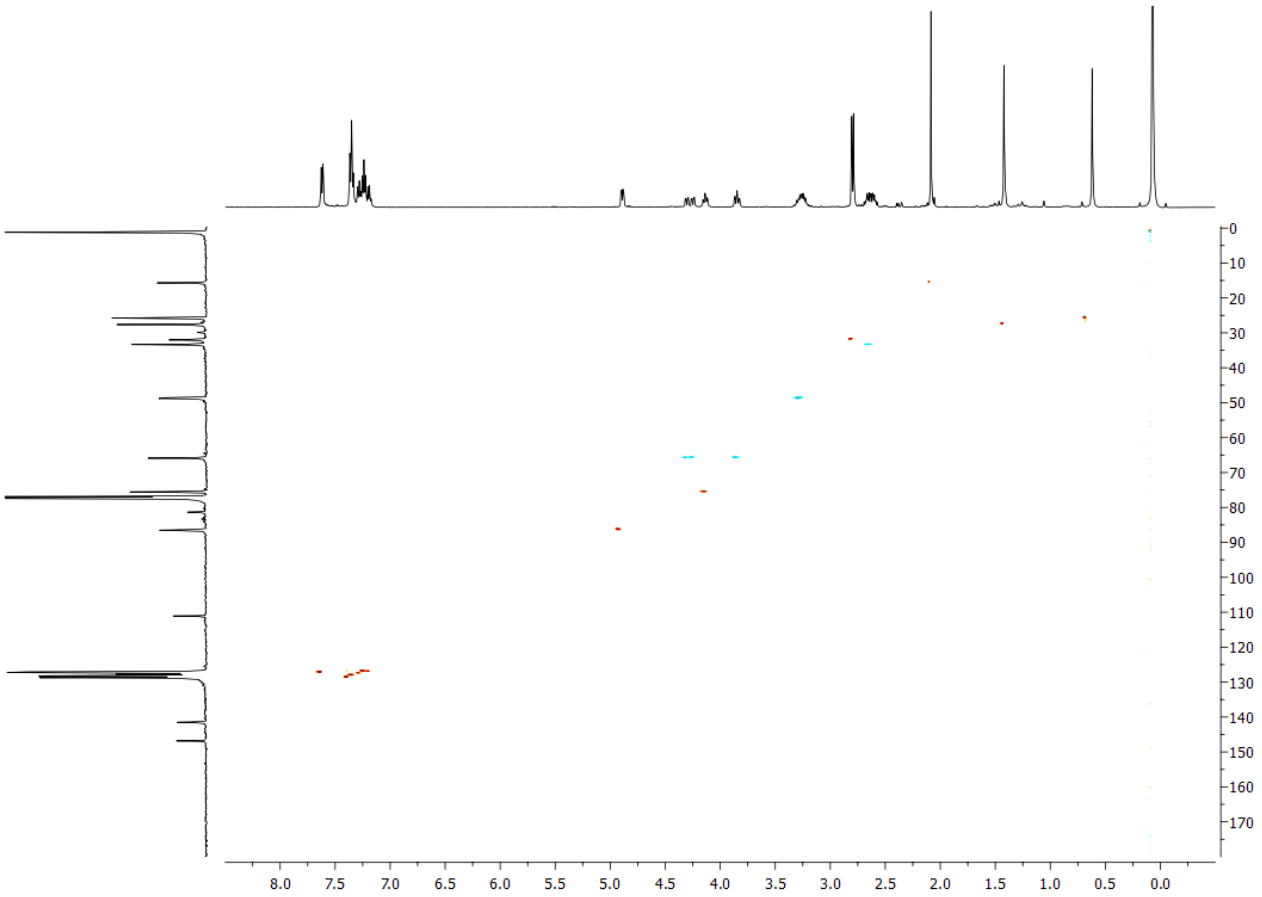


L2c, $^{13}C\{^{1}H\}$ APT spectrum.

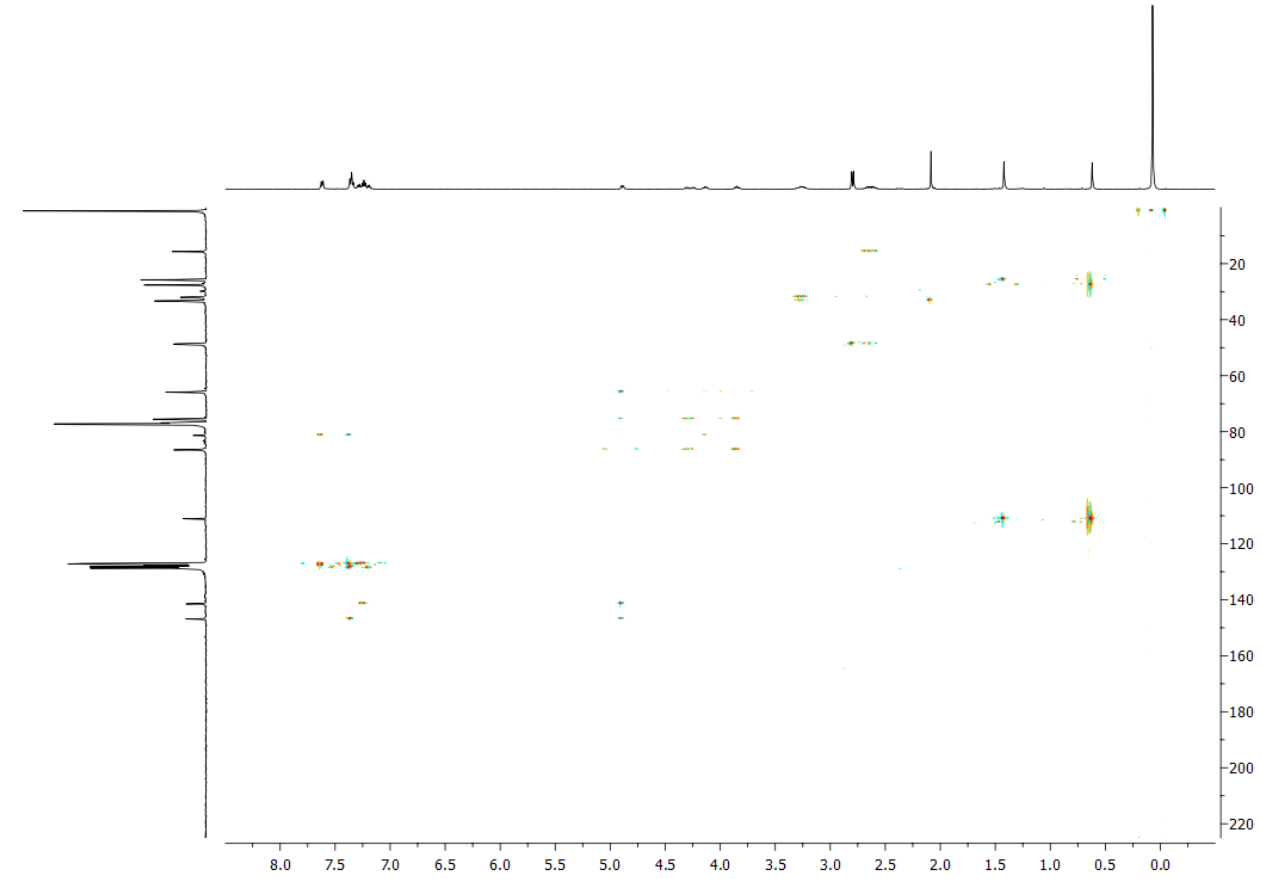


L2c, ^{1}H-^{1}H COSY spectrum.

NMR AND MASS SPECTRA



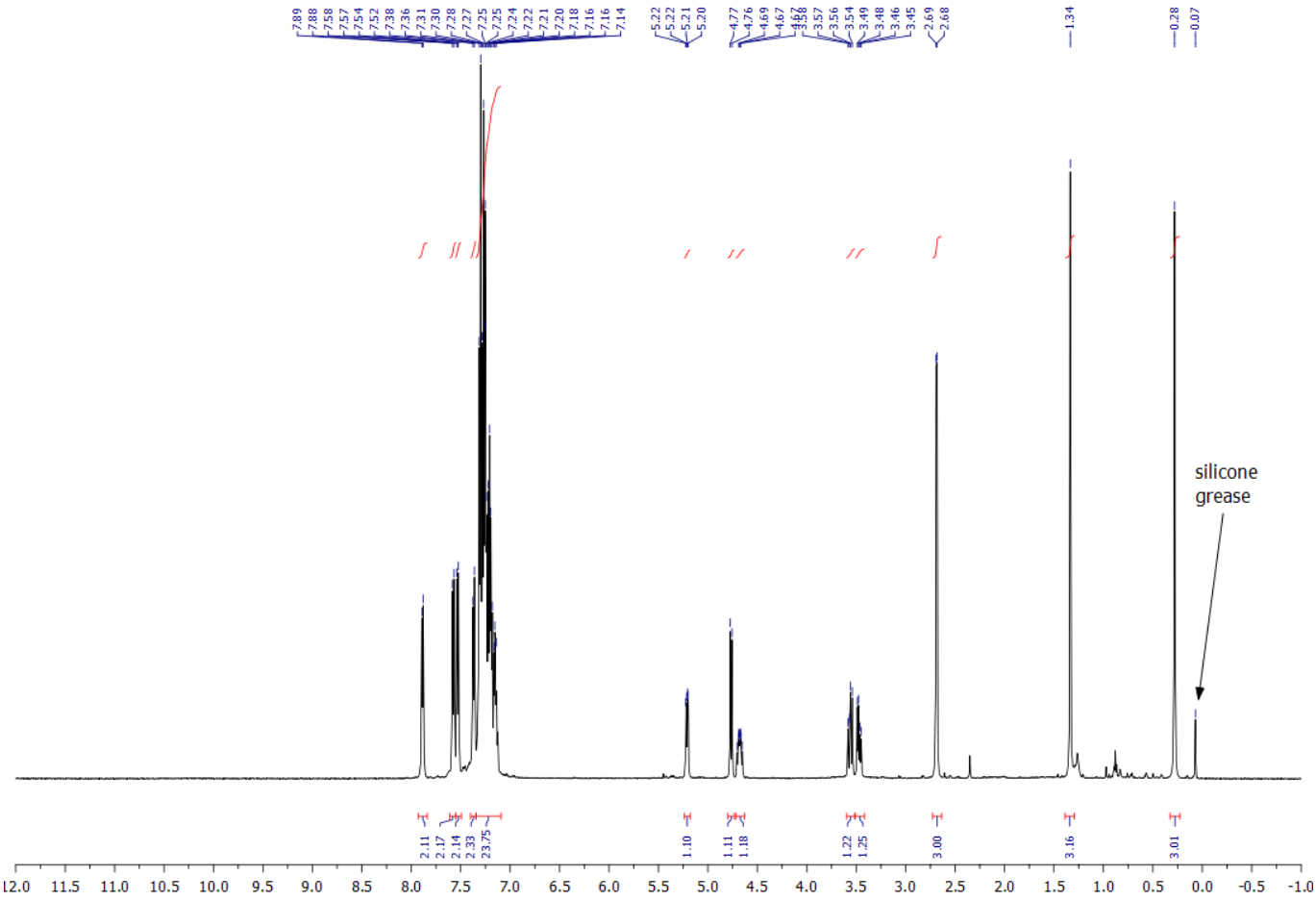
L2c, ^{1}H-^{13}C HSQC spectrum.



L2c, ^{1}H-^{13}C HMBC spectrum.

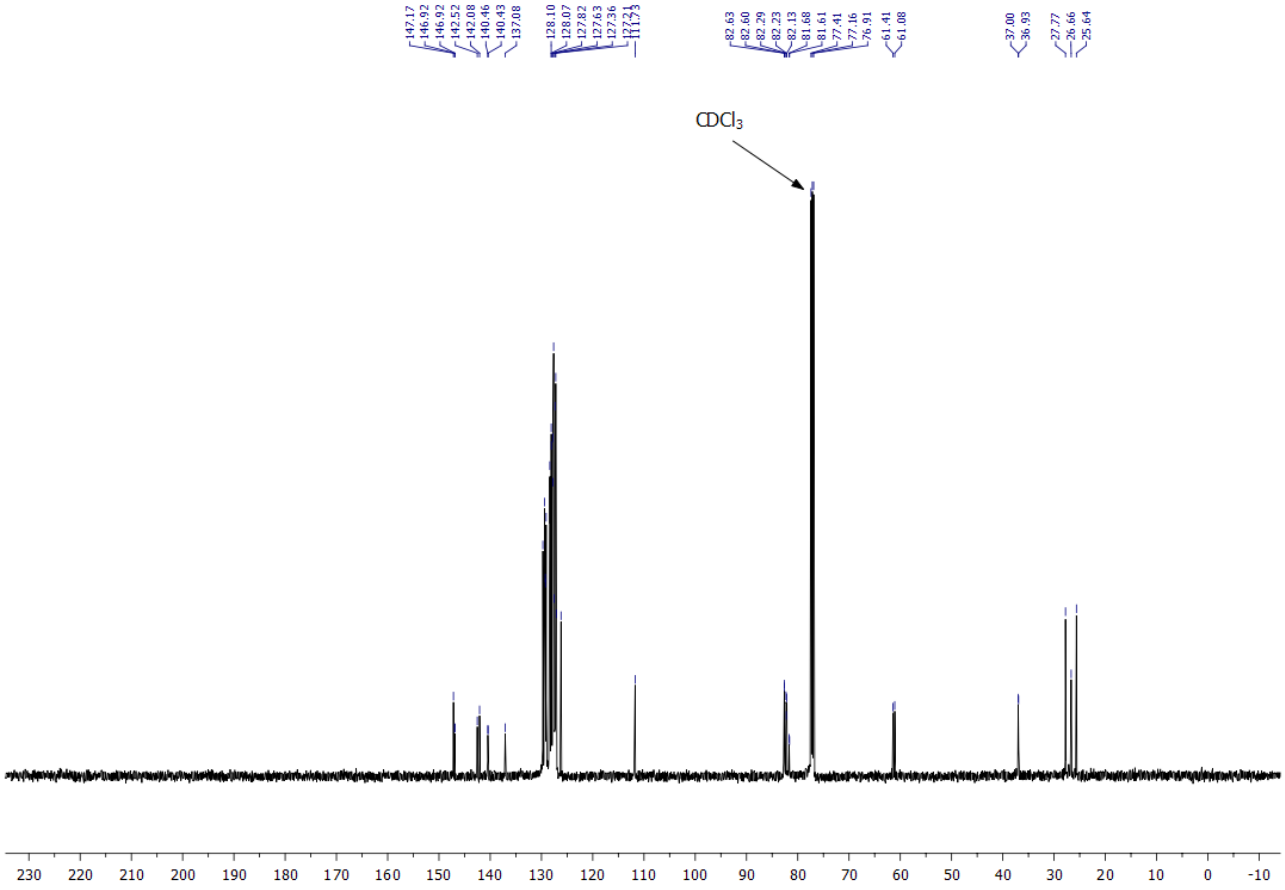
NMR AND MASS SPECTRA

L3a, $^{31}P\{^{1}H\}$ spectrum.

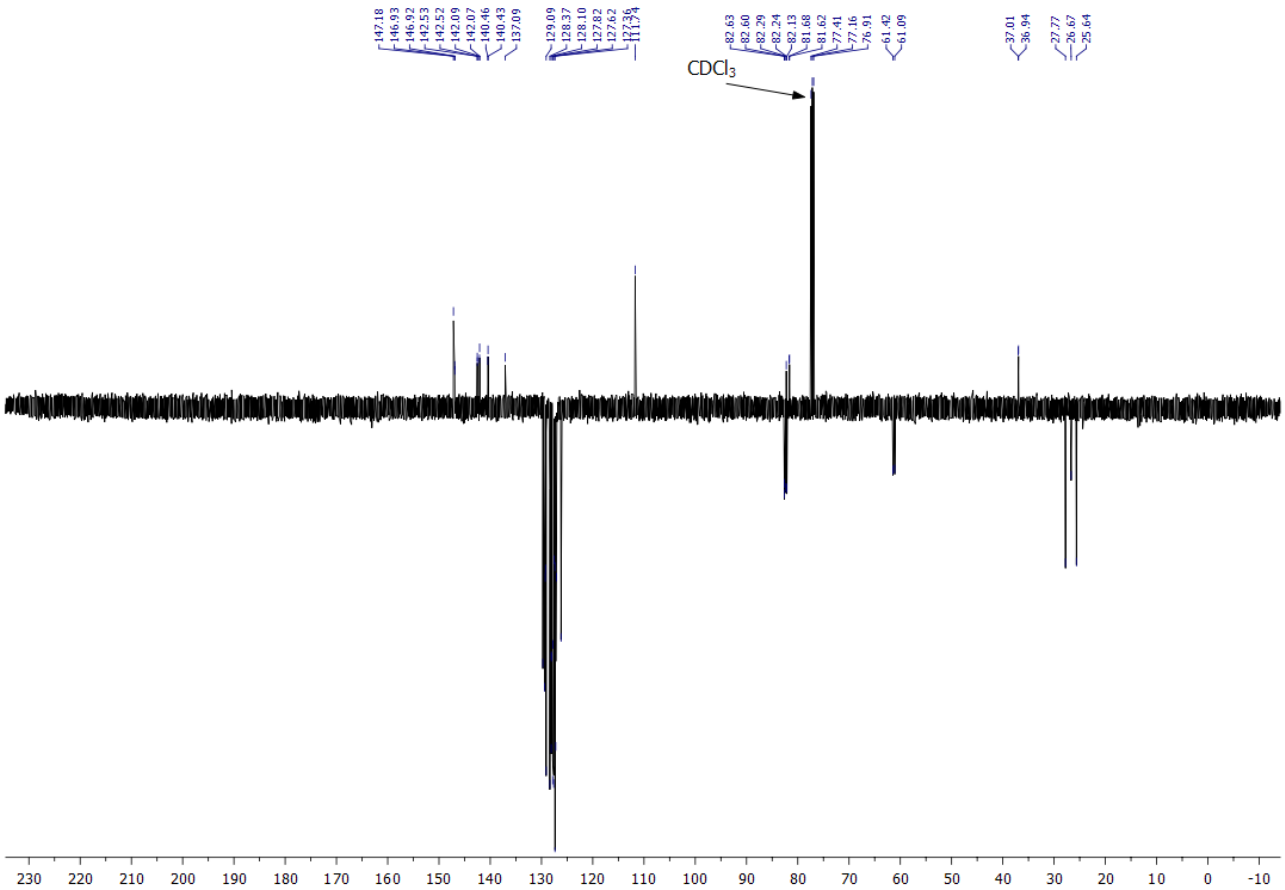


NMR AND MASS SPECTRA

L3a, ^{1}H spectrum.

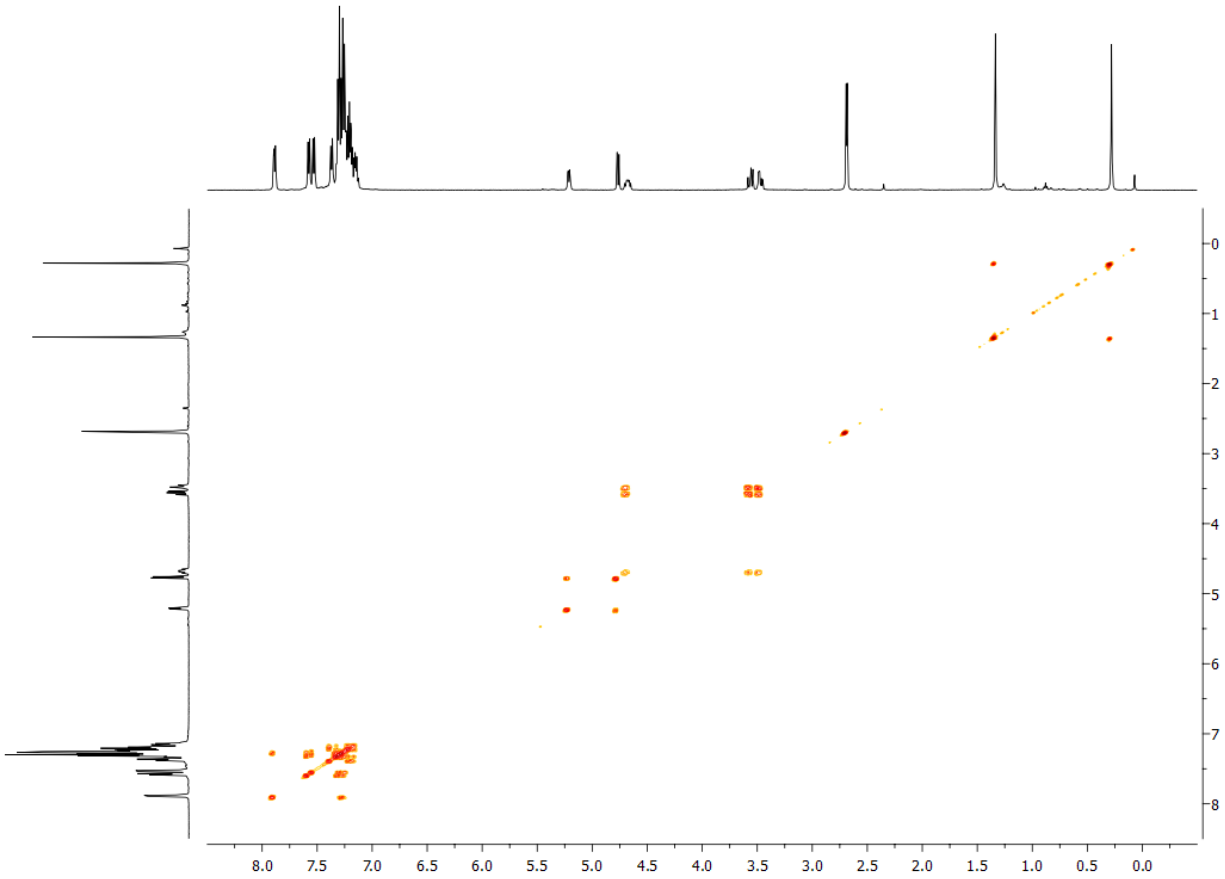


L3a, $^{13}C\{^{1}H\}$ spectrum.

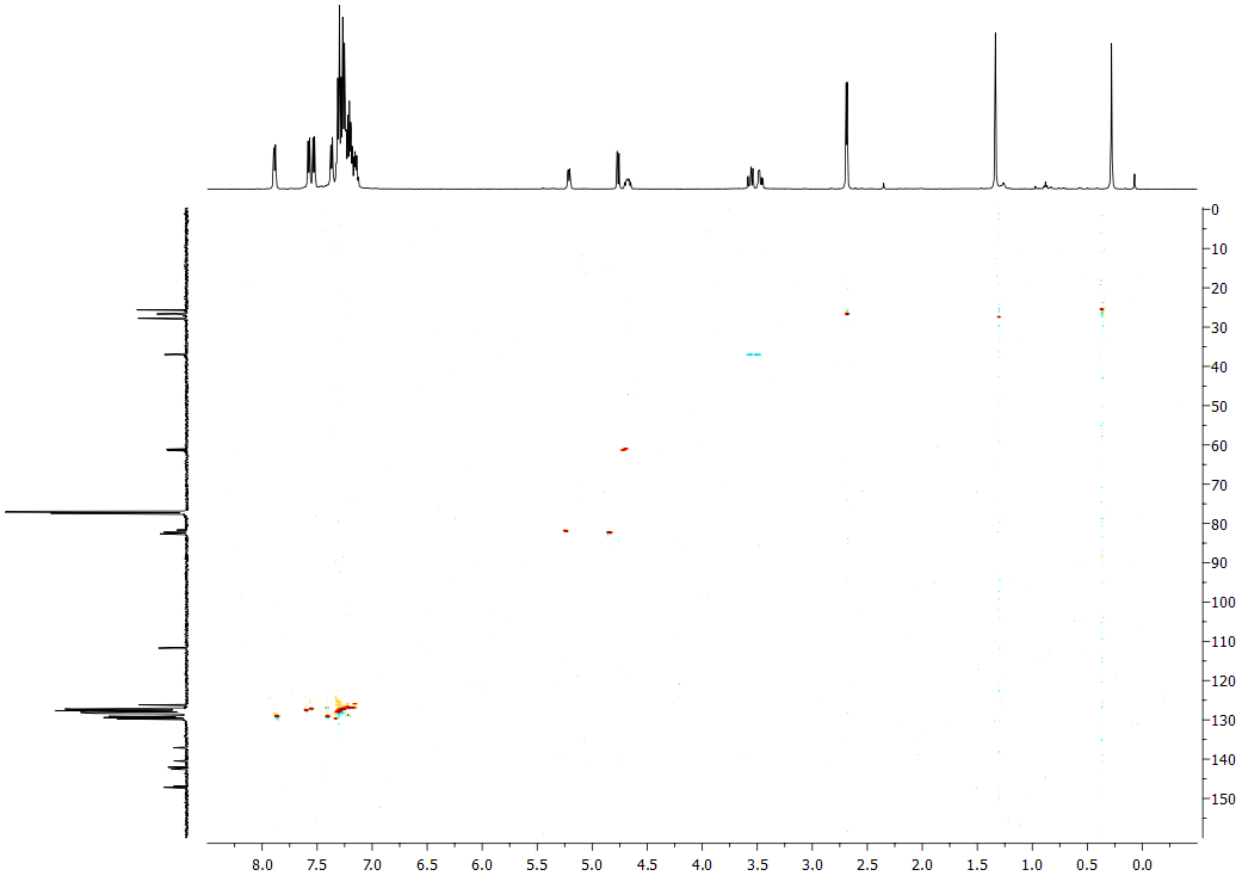


L3a, $^{13}C\{^{1}H\}$ APT spectrum.

NMR AND MASS SPECTRA

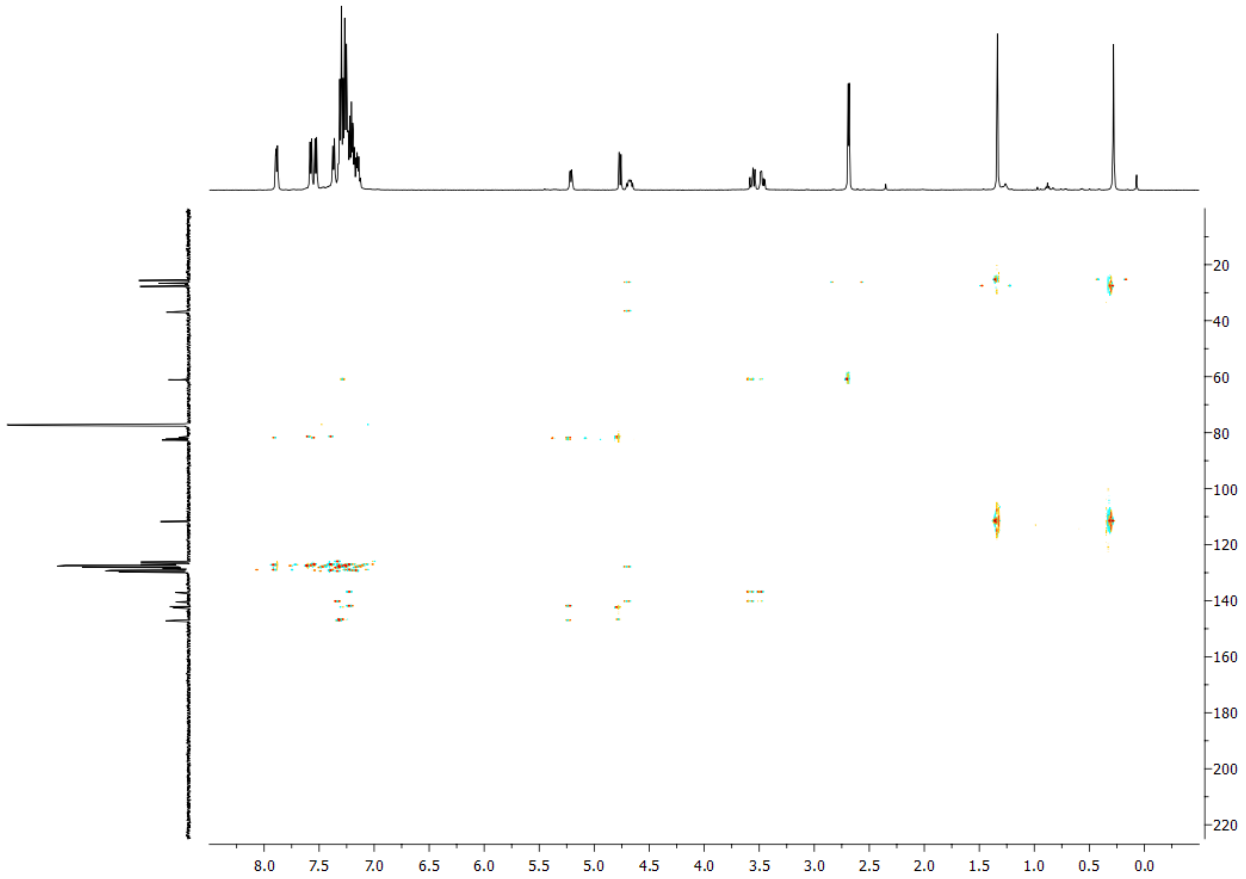


L3a, ^{1}H-^{1}H COSY spectrum.

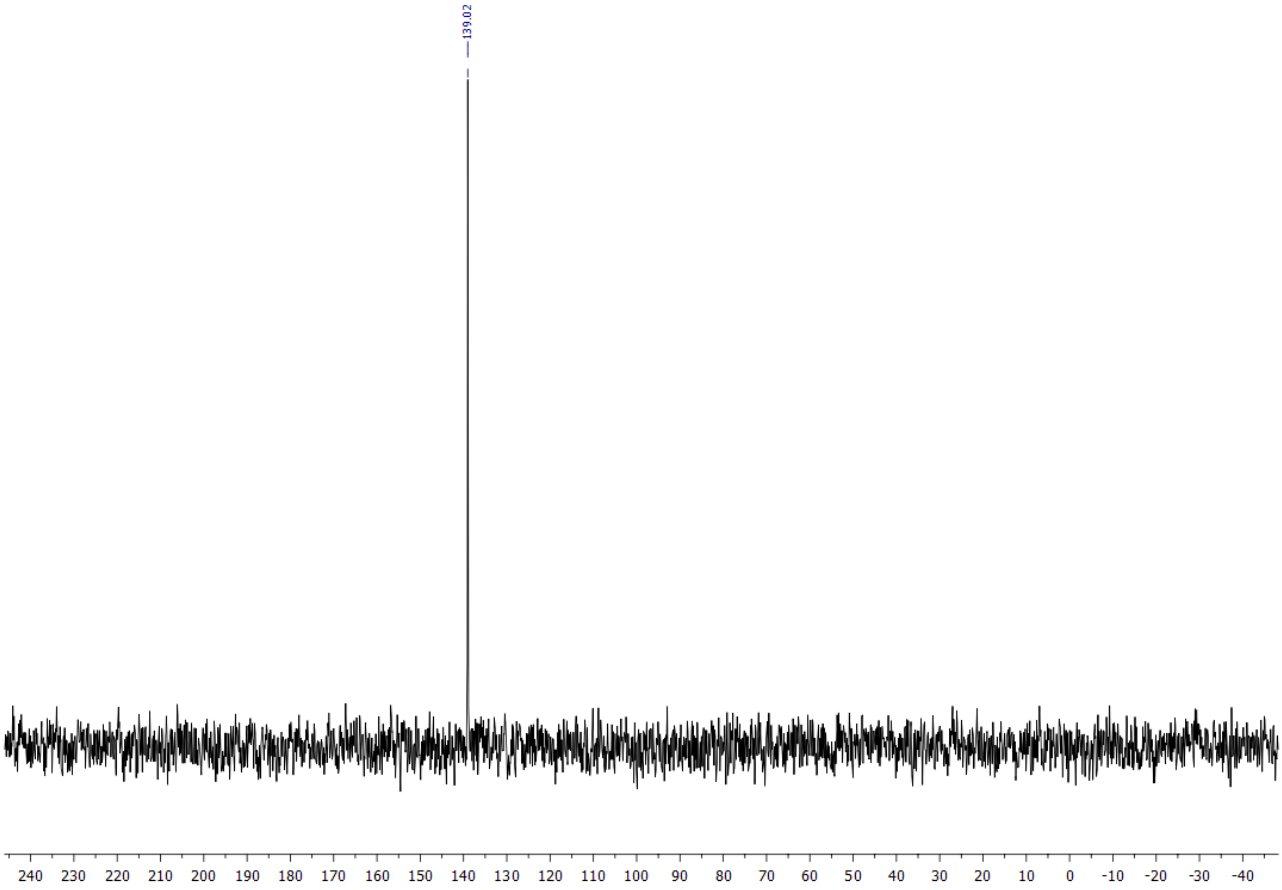


L3a, ^{1}H-^{13}C HSQC spectrum.

NMR AND MASS SPECTRA

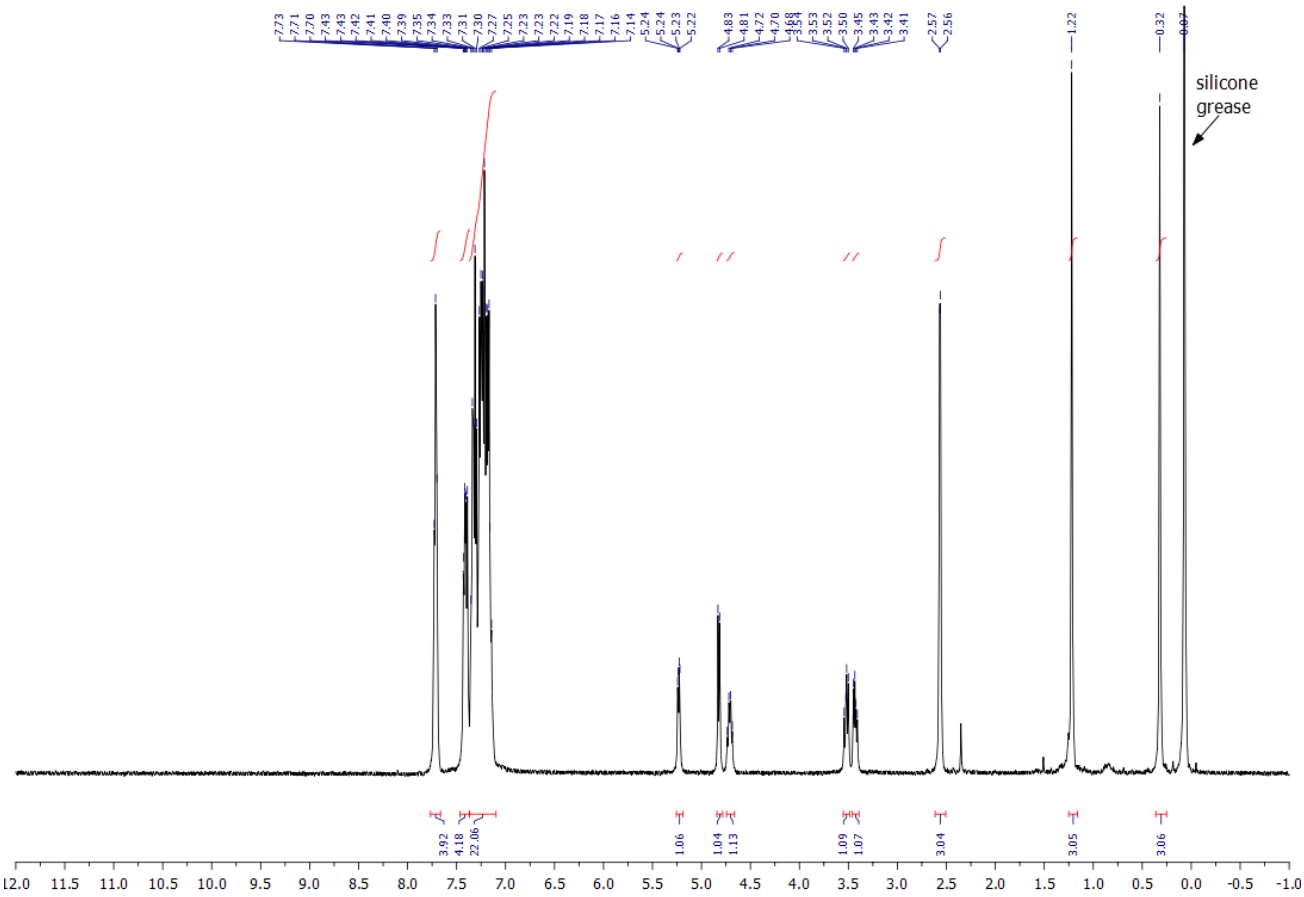


L3a, ^{1}H-^{13}C HMBC spectrum.

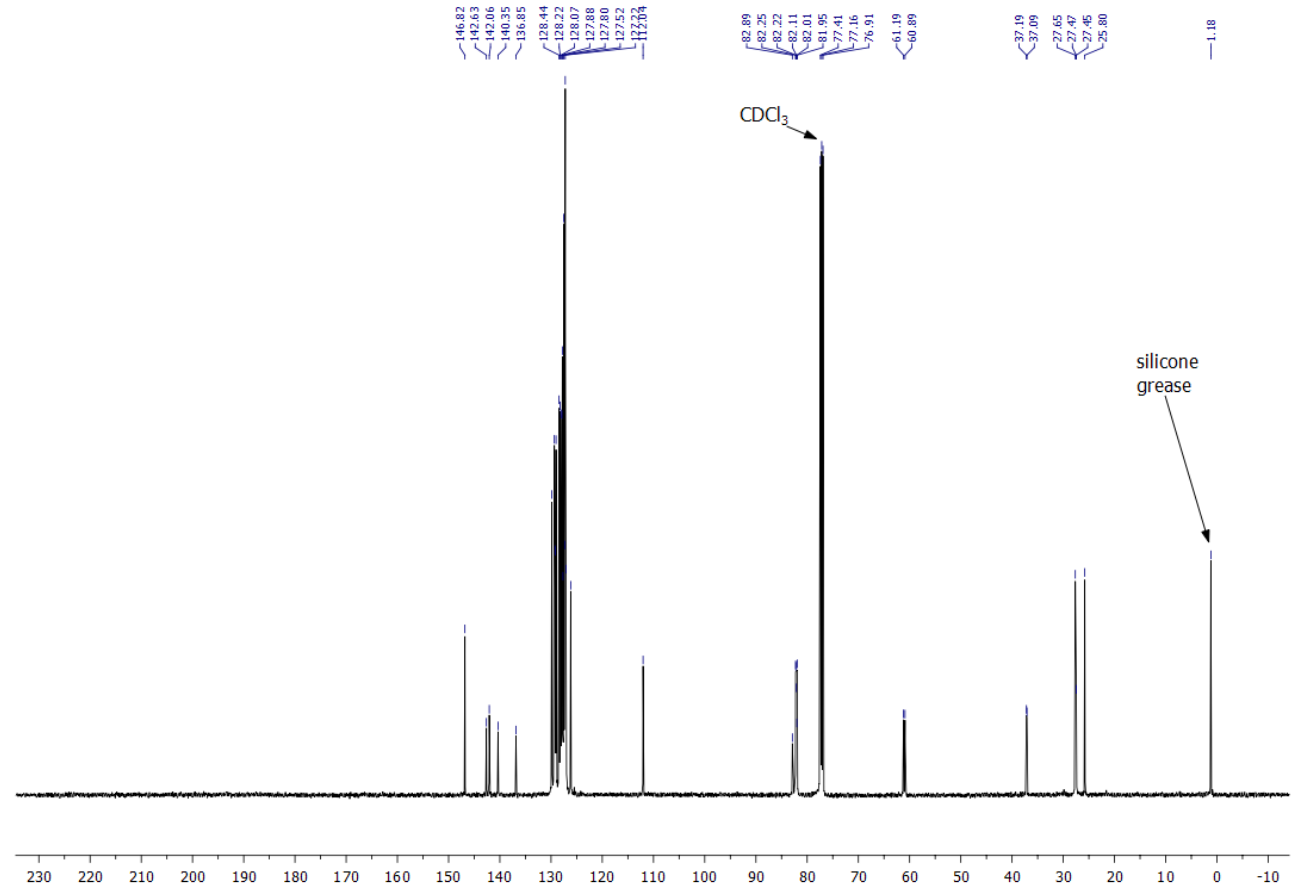


L3b, $^{31}P\{^{1}H\}$ spectrum.

NMR AND MASS SPECTRA

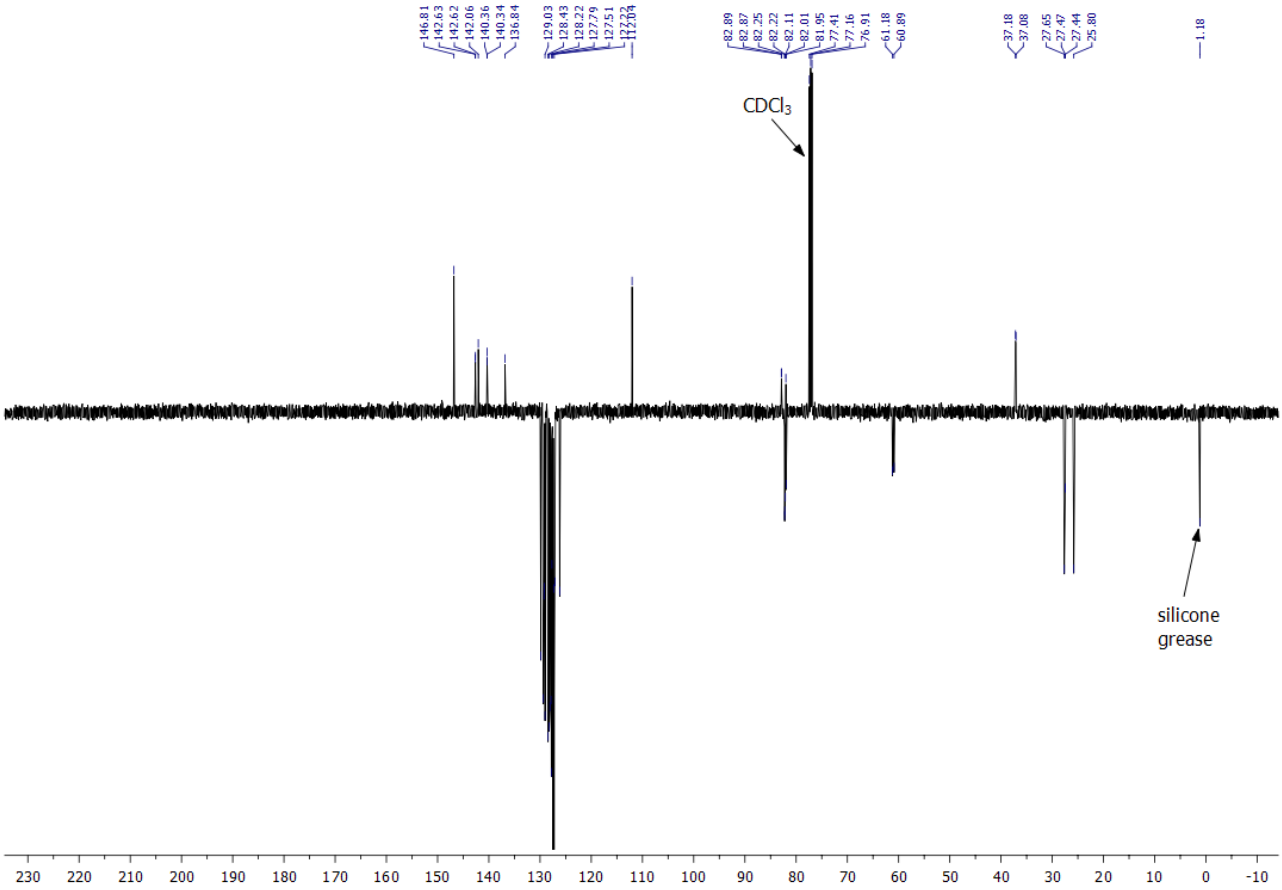


L3b, ^{1}H spectrum.

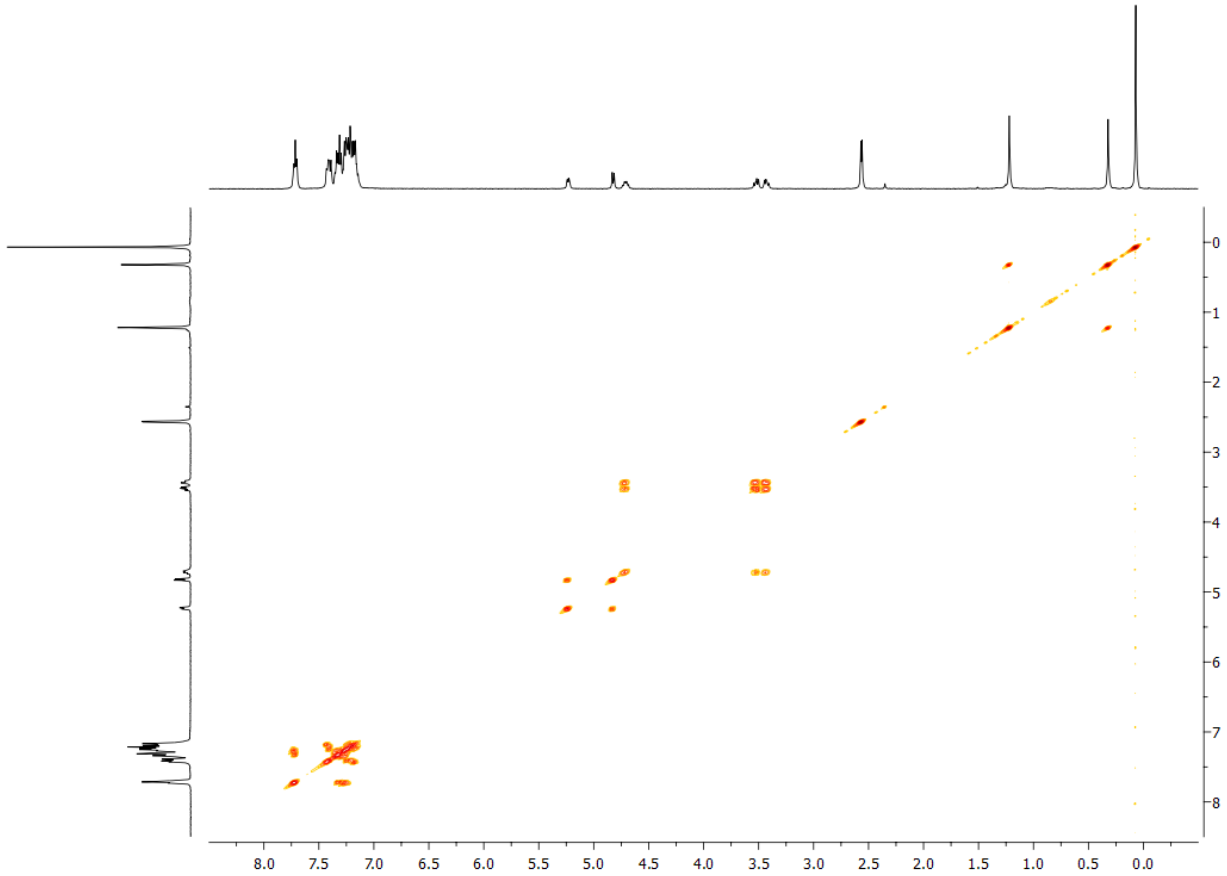


L3b, $^{13}C\{^{1}H\}$ spectrum.

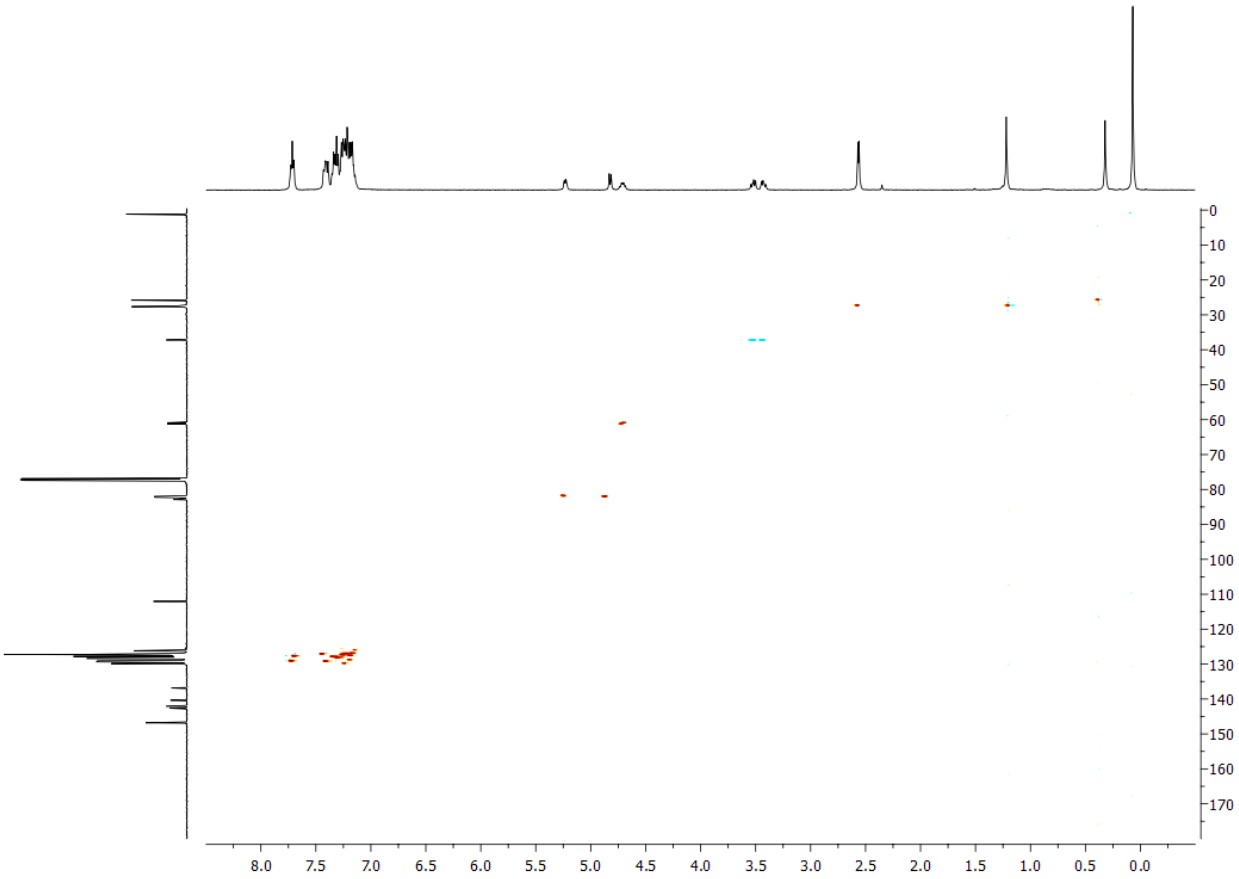
NMR AND MASS SPECTRA



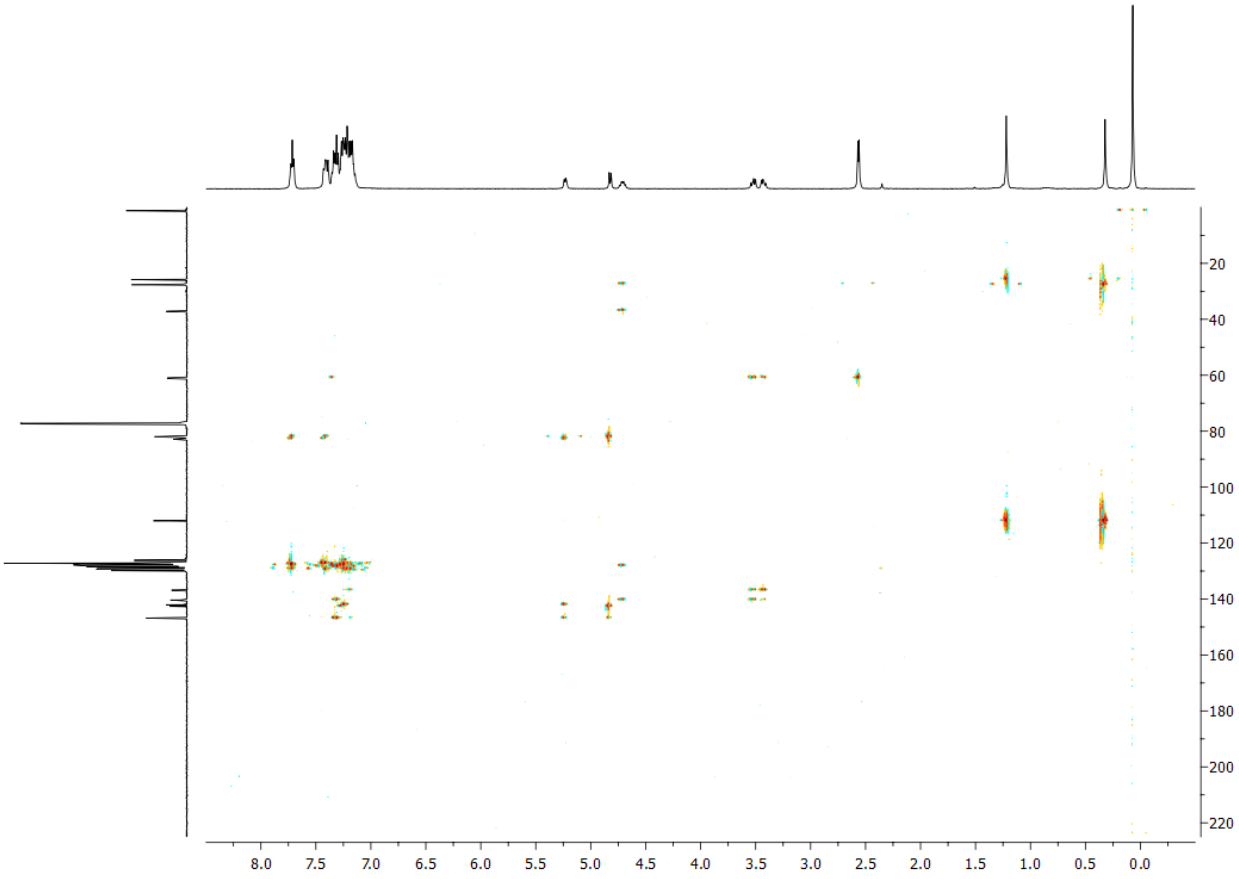
L3b, $^{13}C\{^{1}H\}$ APT spectrum.



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

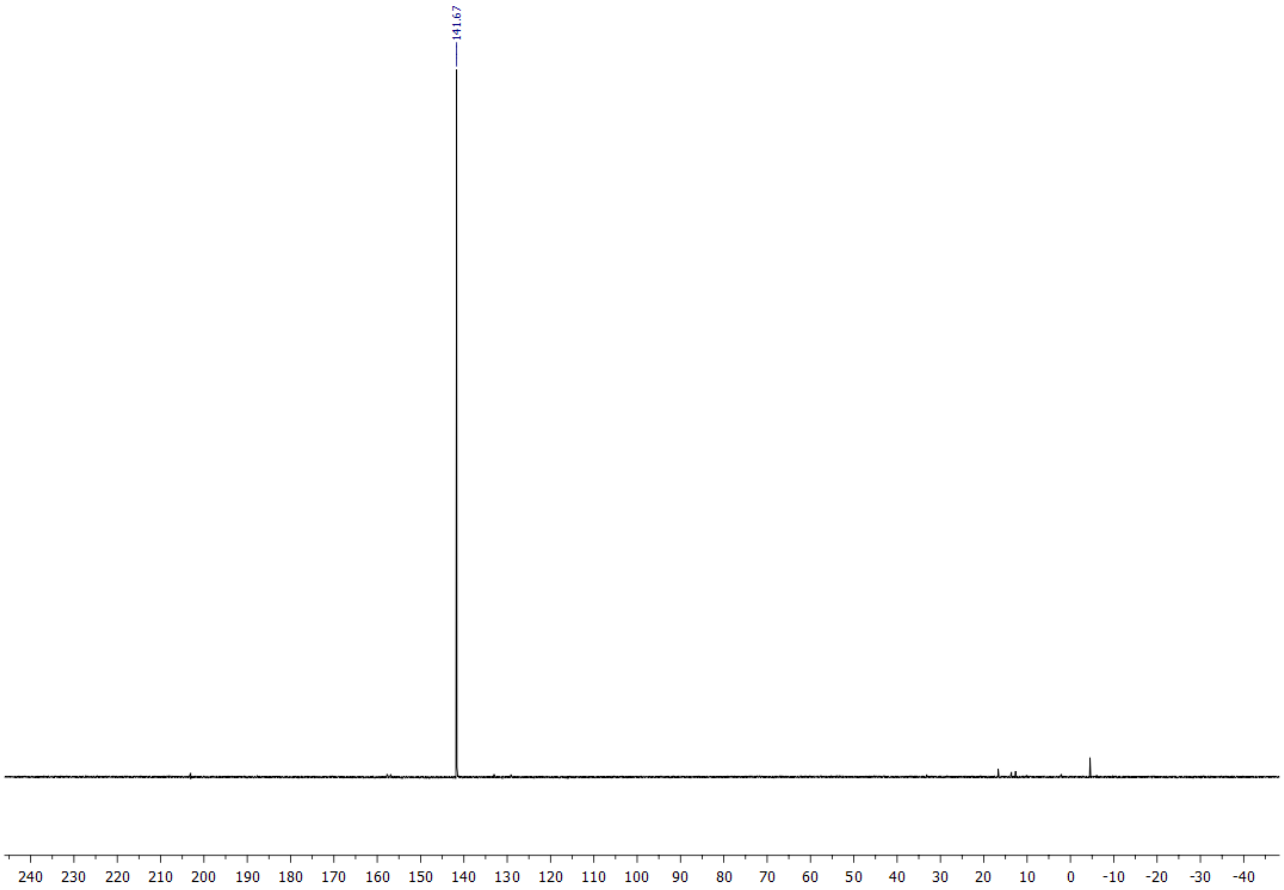


L3b, ^{1}H-^{13}C HSQC spectrum.

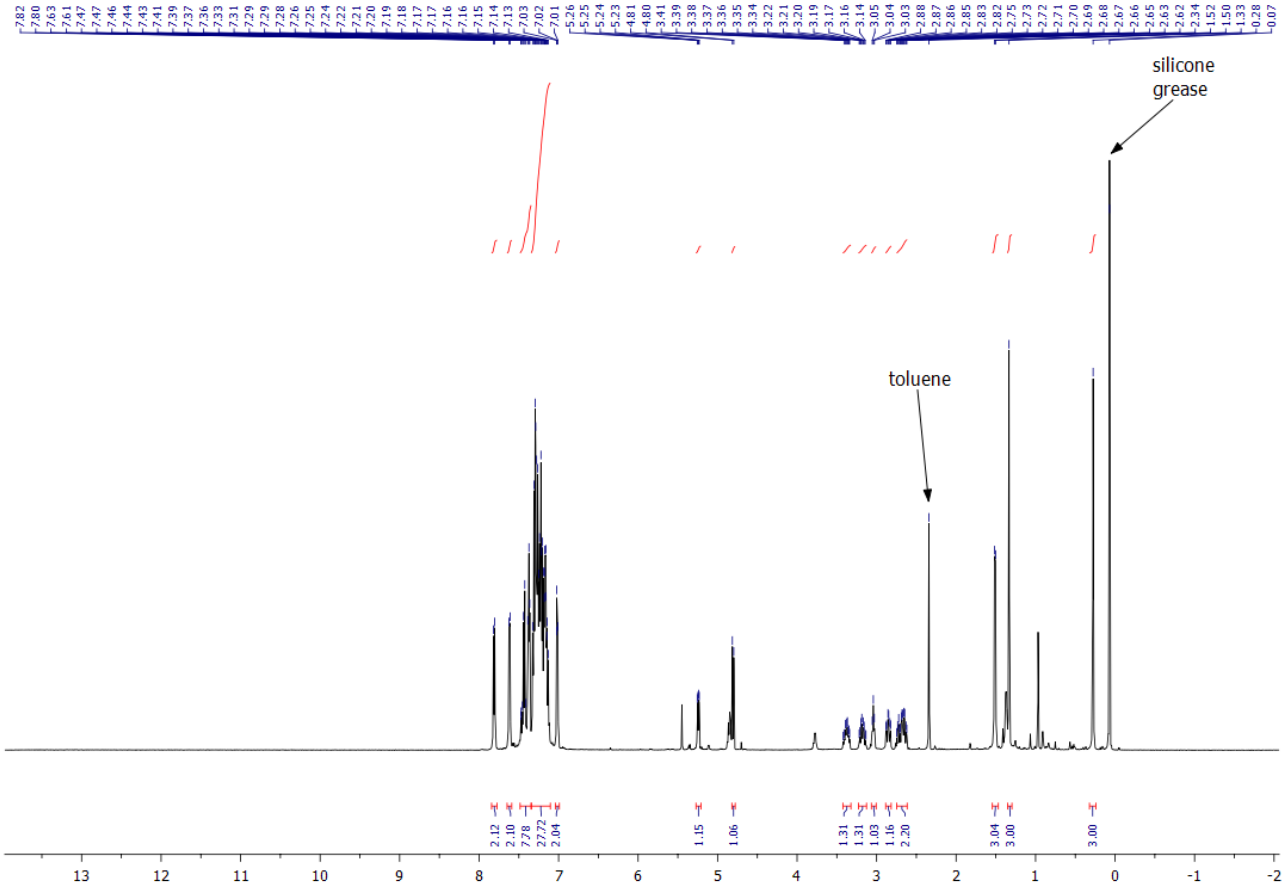


L3b, ^{1}H-^{13}C HMBC spectrum.

NMR AND MASS SPECTRA

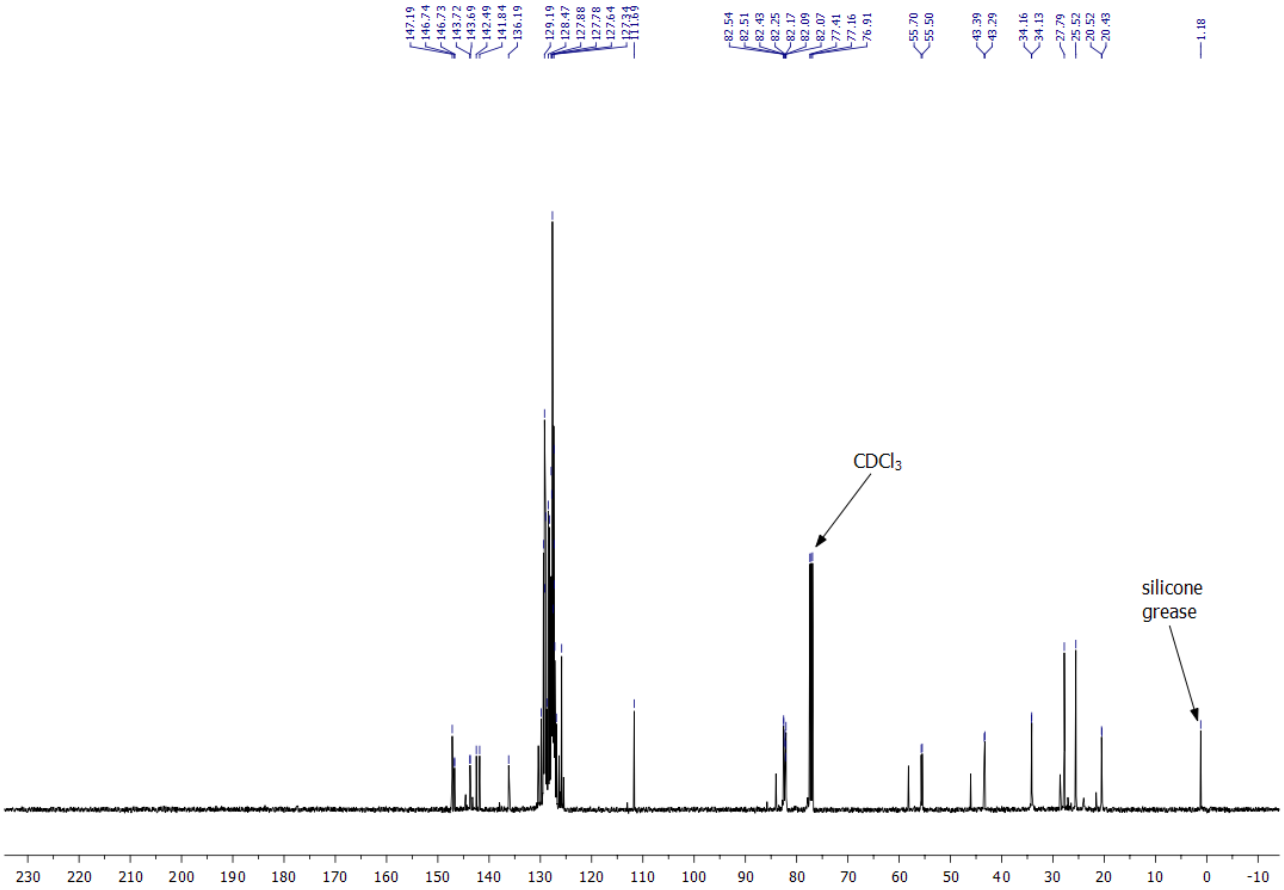


L4a, $^{31}P\{^{1}H\}$ spectrum.

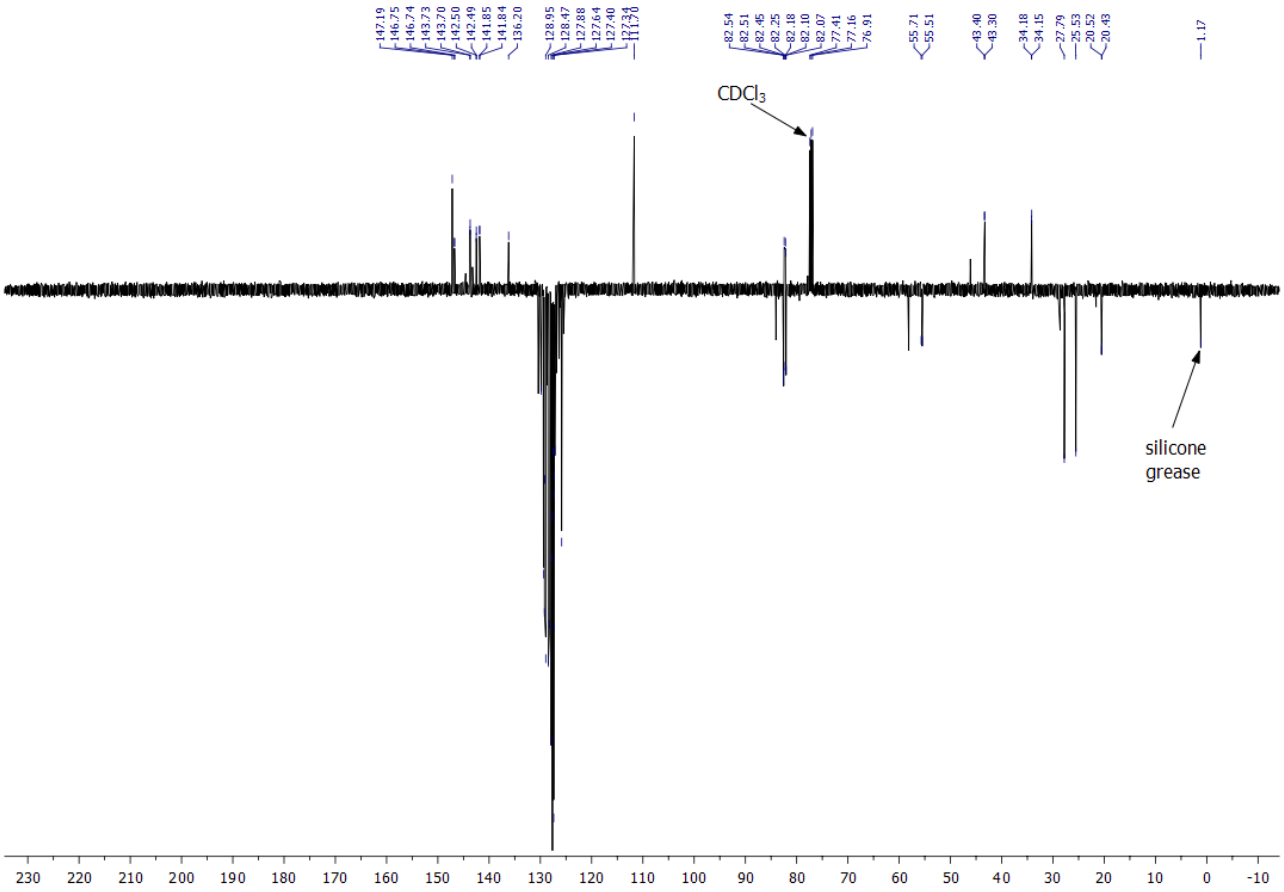


L4a, ^{1}H spectrum.

NMR AND MASS SPECTRA

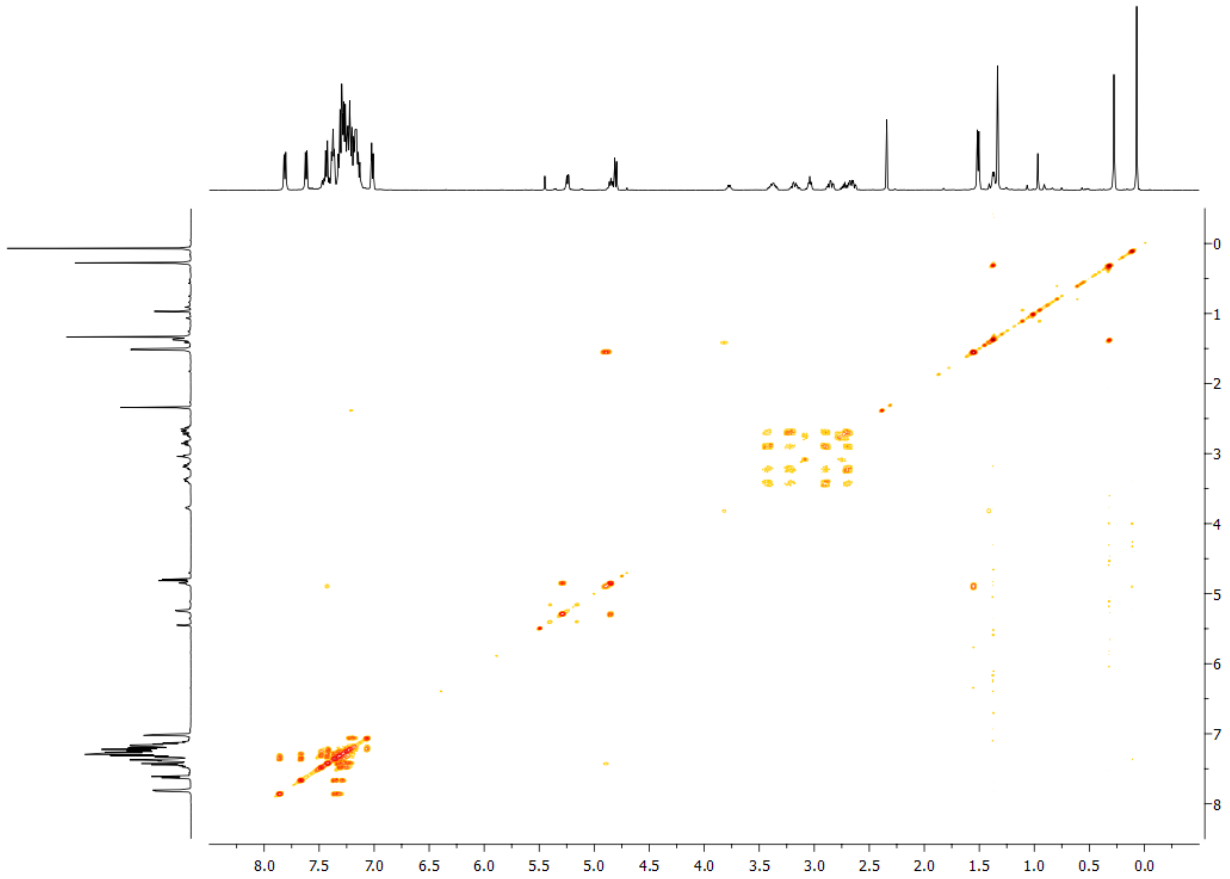


L4a, $^{13}C\{^{1}H\}$ spectrum.

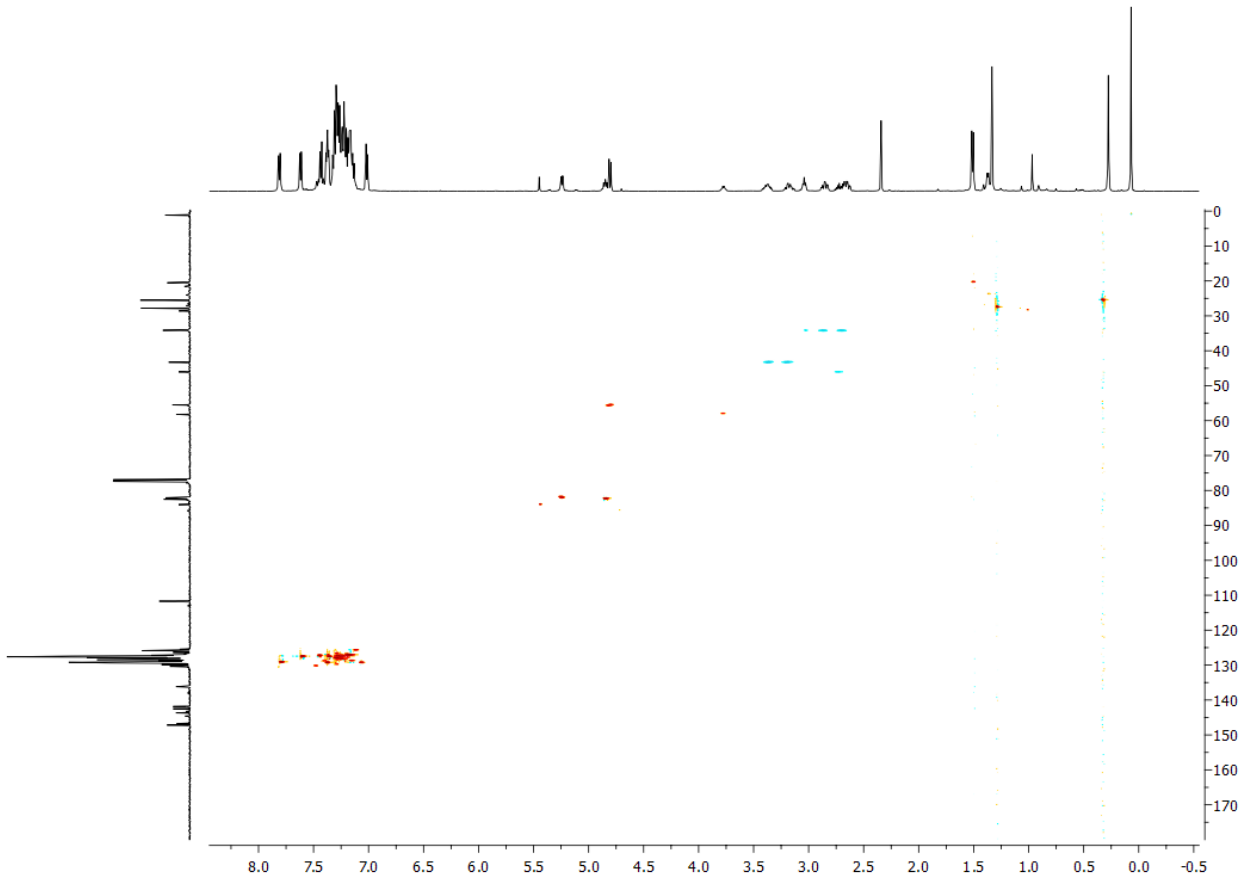


L4a, $^{13}C\{^{1}H\}$ APT spectrum.

NMR AND MASS SPECTRA

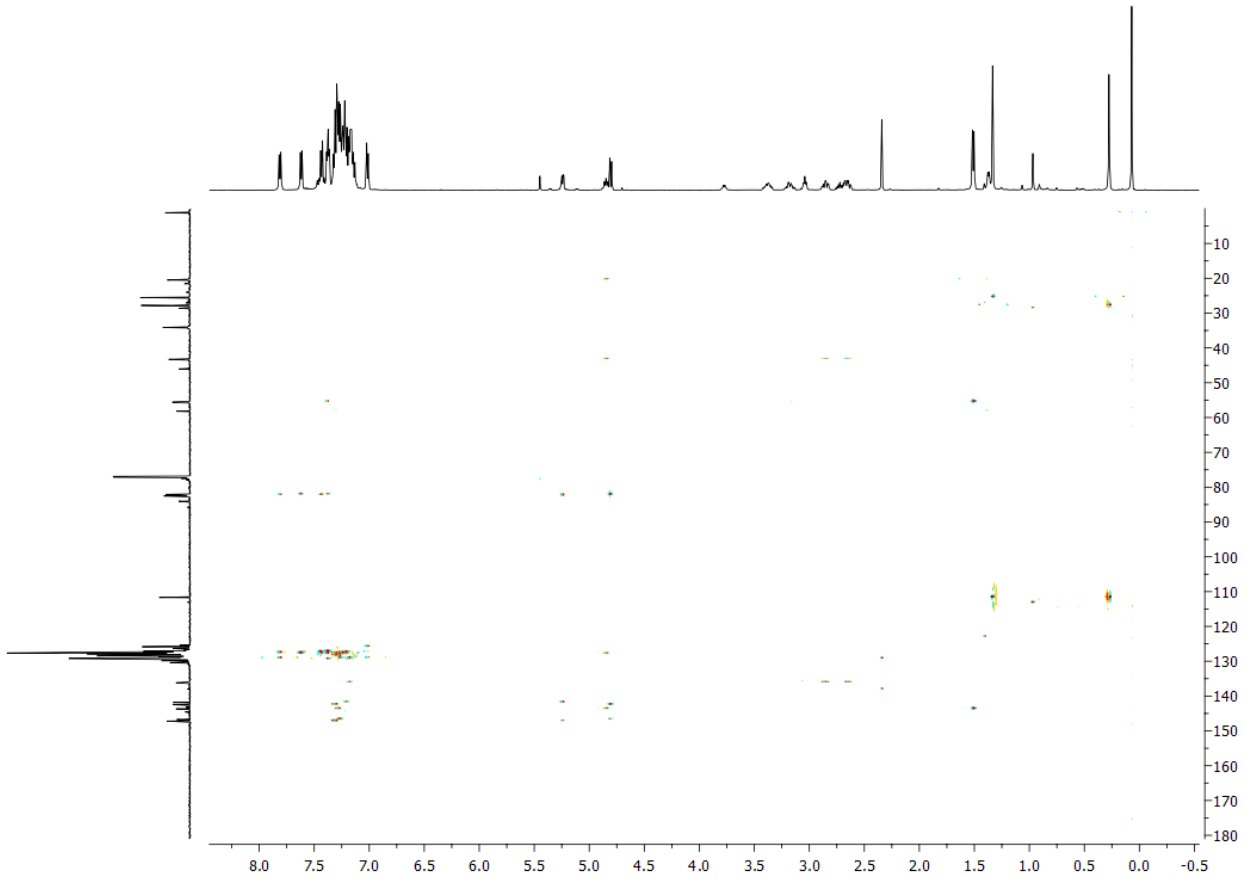


L4a, ^{1}H-^{1}H COSY spectrum.

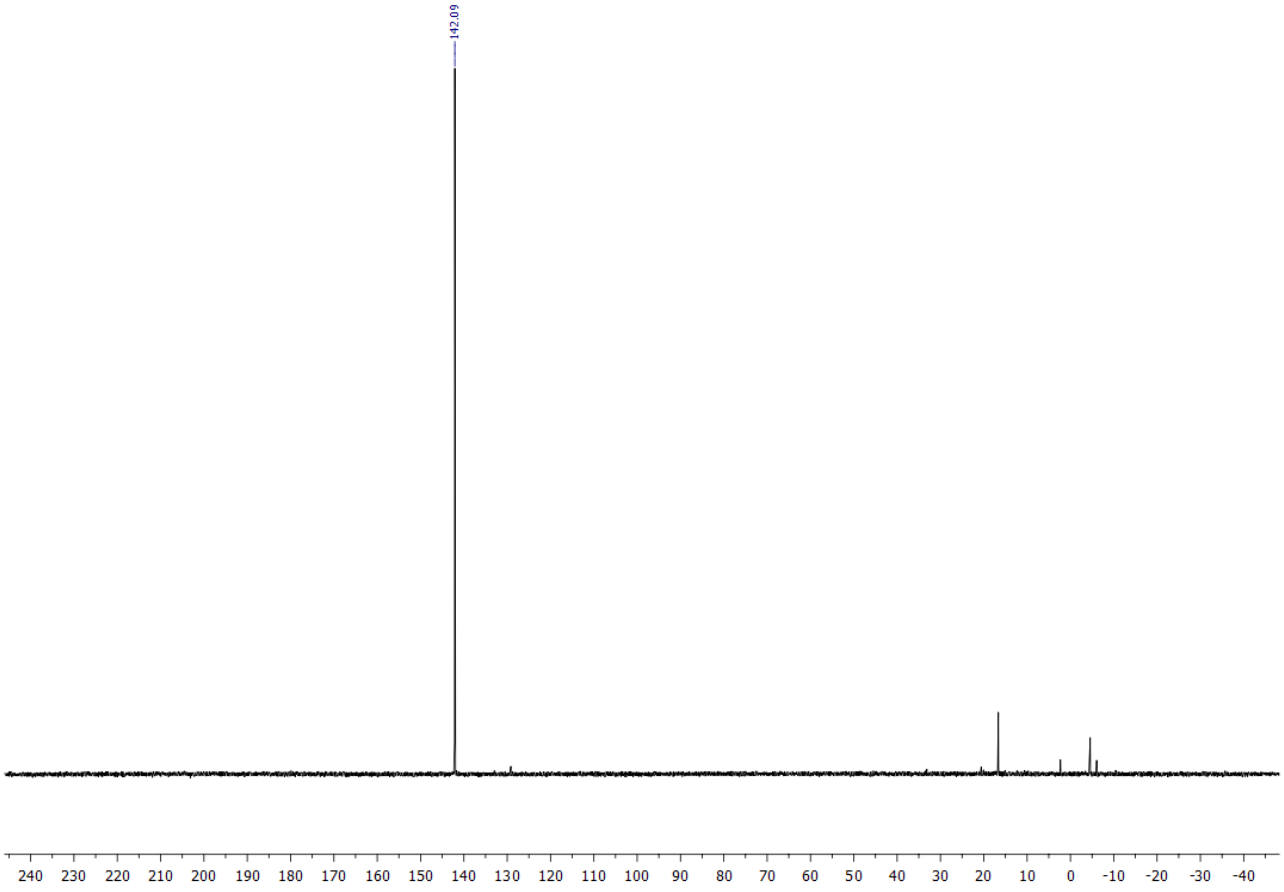


L4a, ^{1}H-^{13}C HSQC spectrum.

NMR AND MASS SPECTRA

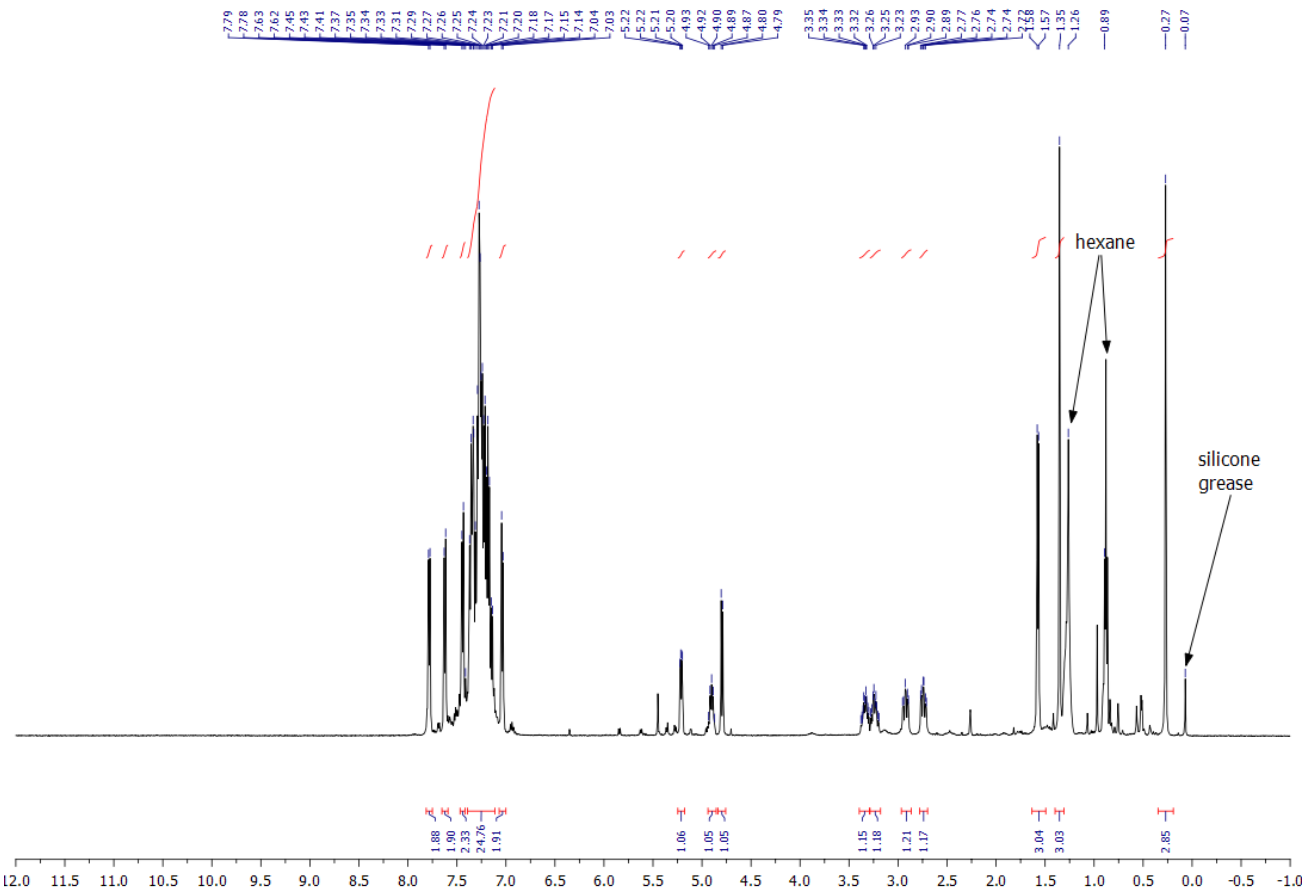


L4a, ^{1}H-^{13}C HMBC spectrum.

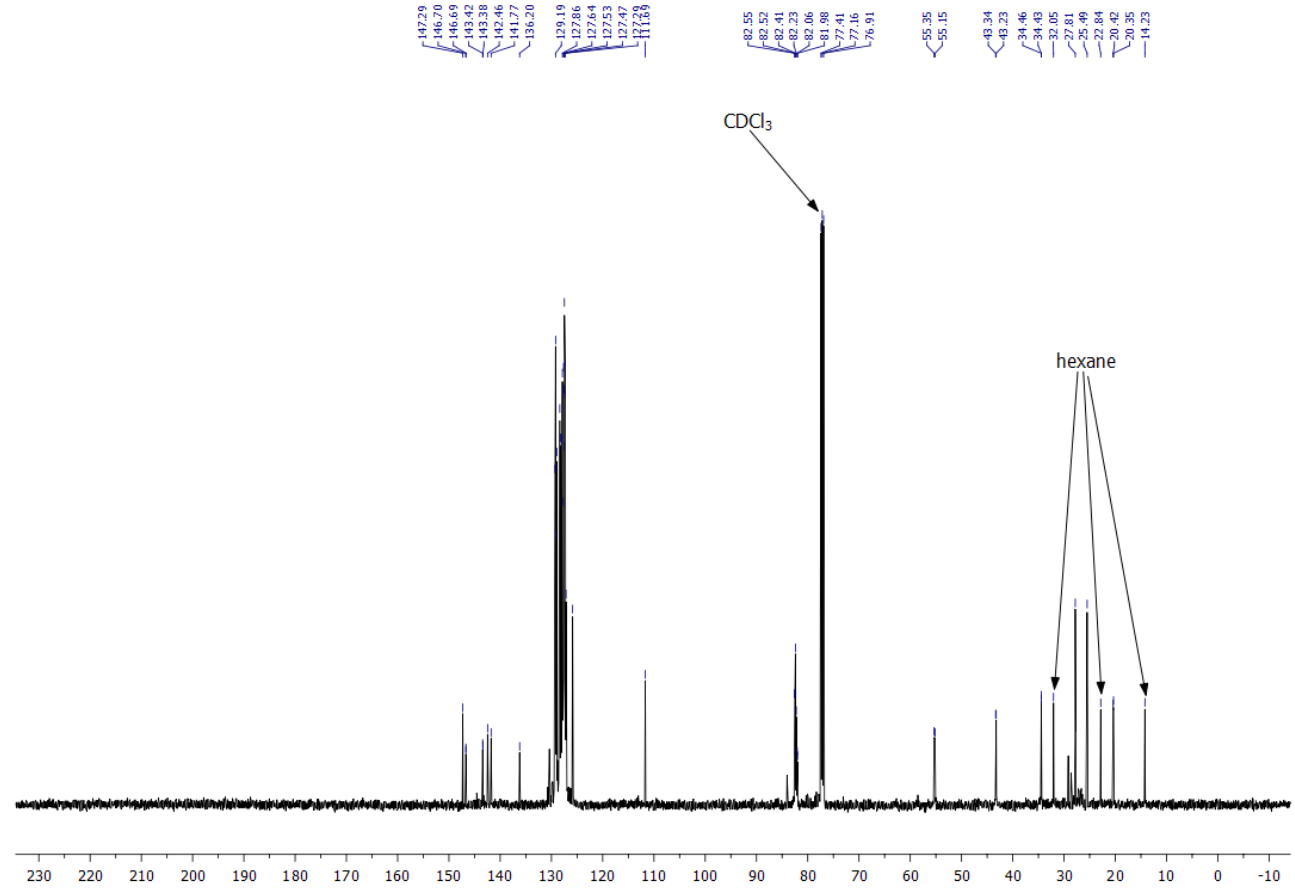


L4b, $^{31}P\{^{1}H\}$ spectrum.

NMR AND MASS SPECTRA

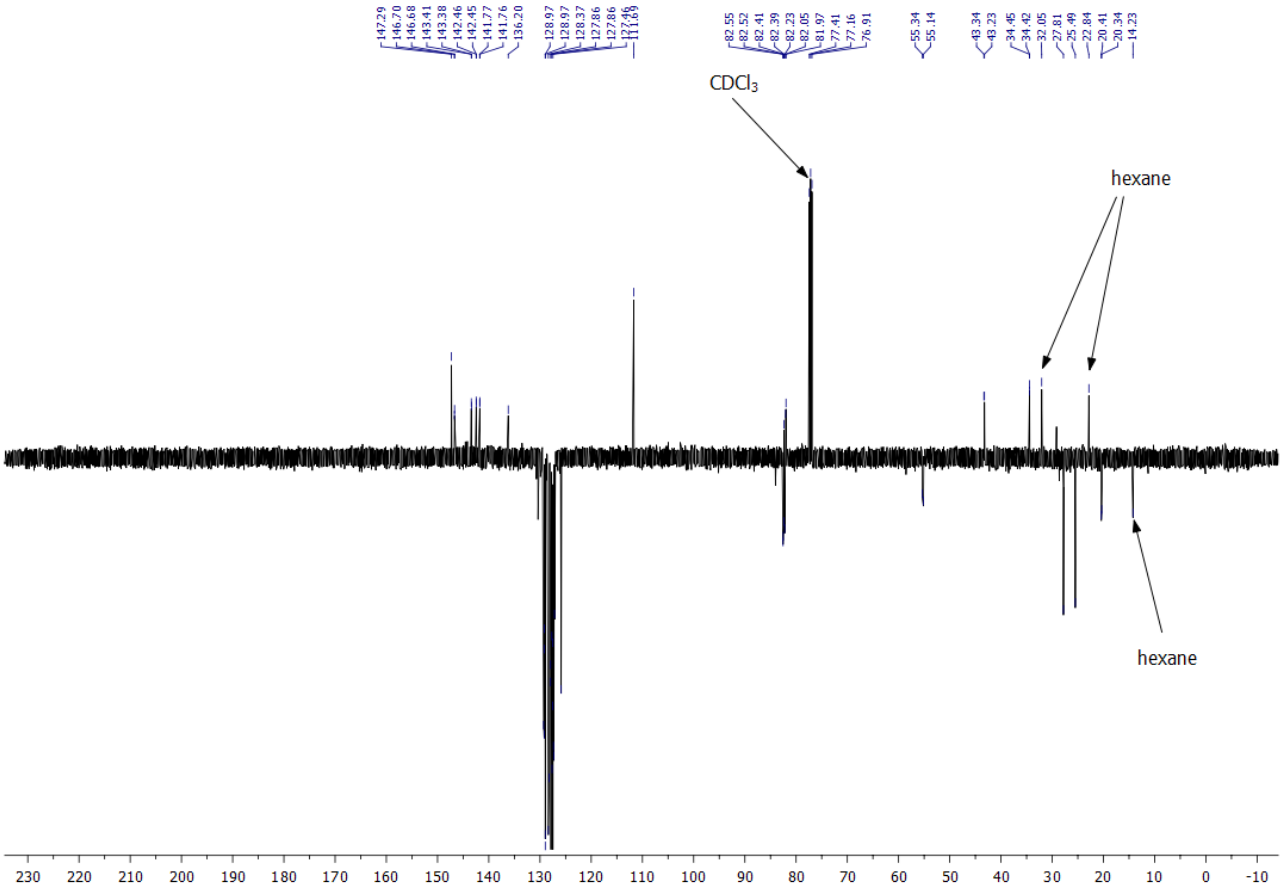


L4b, ^{1}H spectrum.

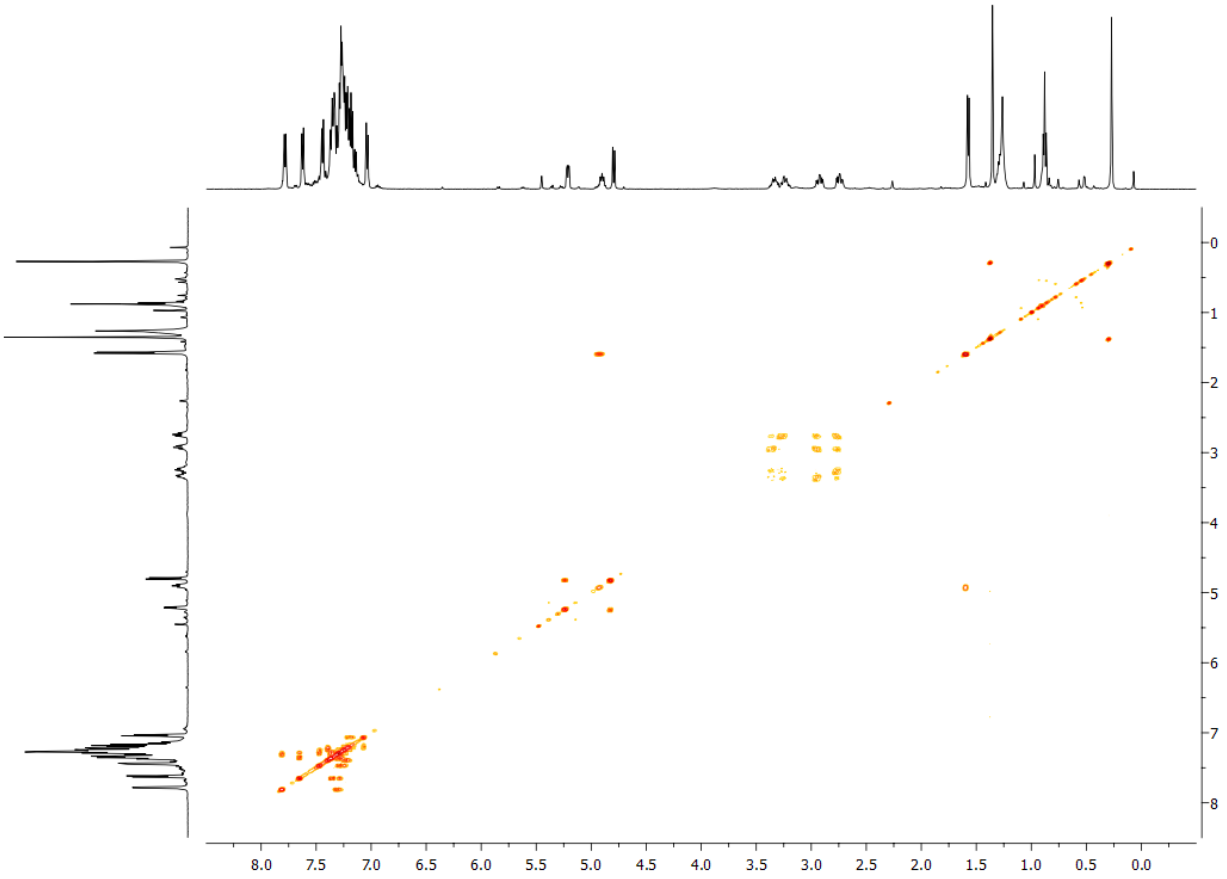


L4b, $^{13}C\{^{1}H\}$ spectrum.

NMR AND MASS SPECTRA

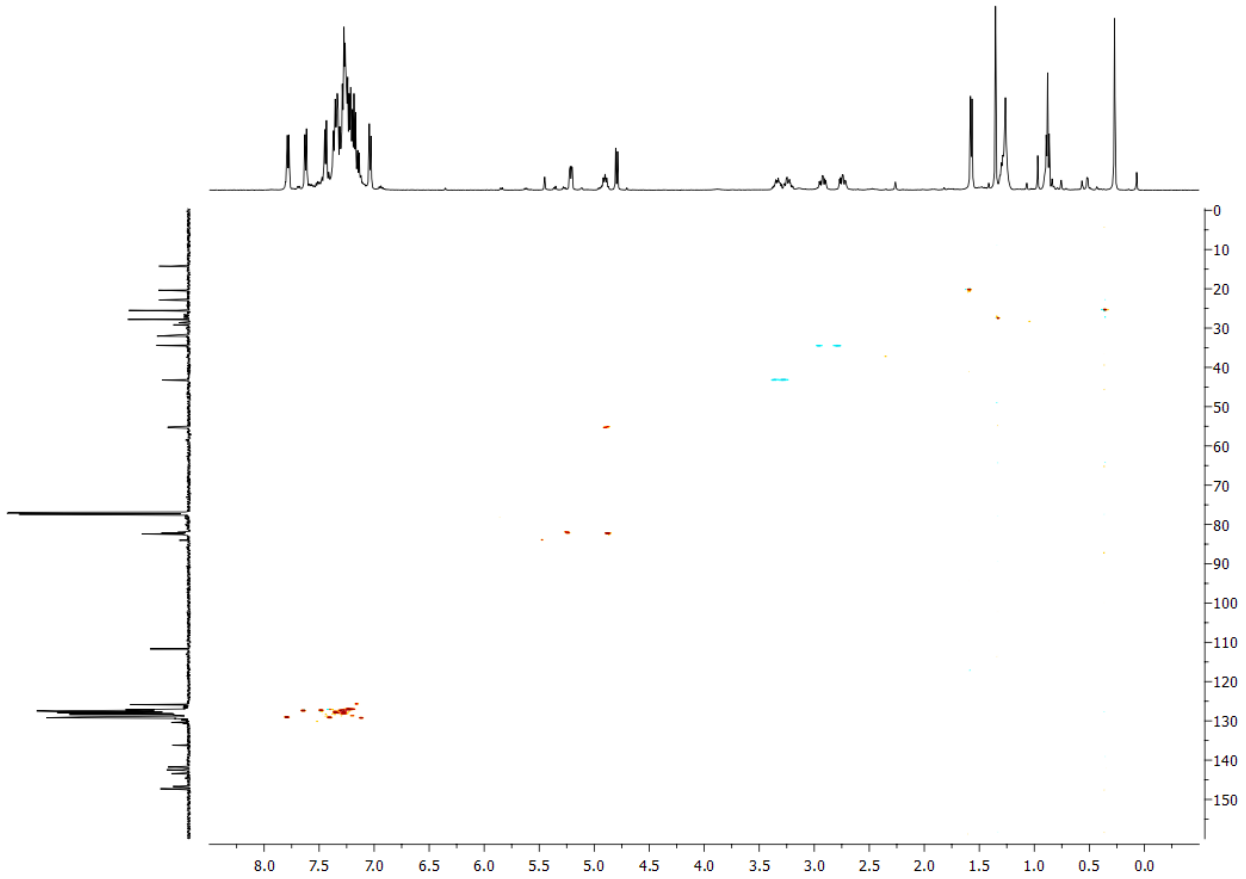


L4b, $^{13}C\{^{1}H\}$ APT spectrum.

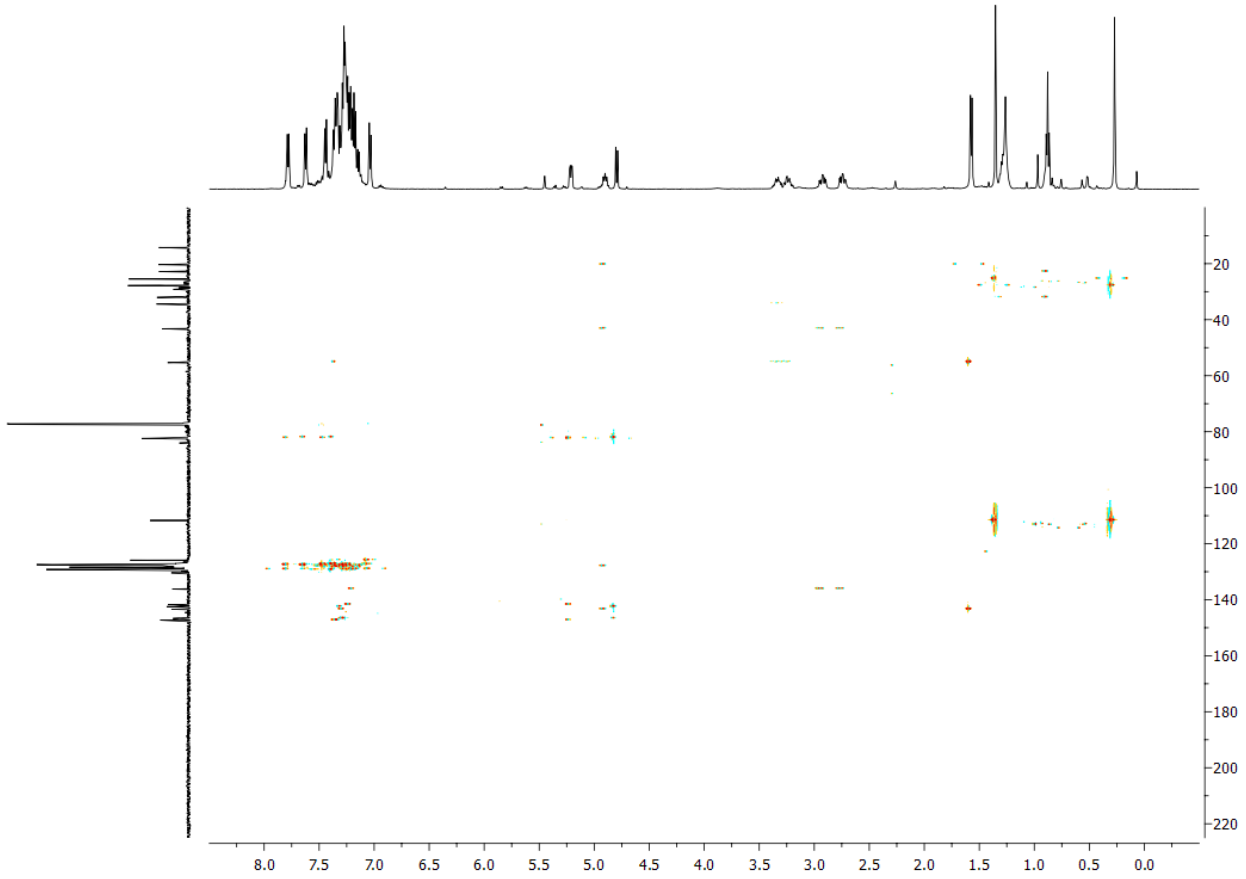


L4b, ^{1}H-^{1}H COSY spectrum.

NMR AND MASS SPECTRA

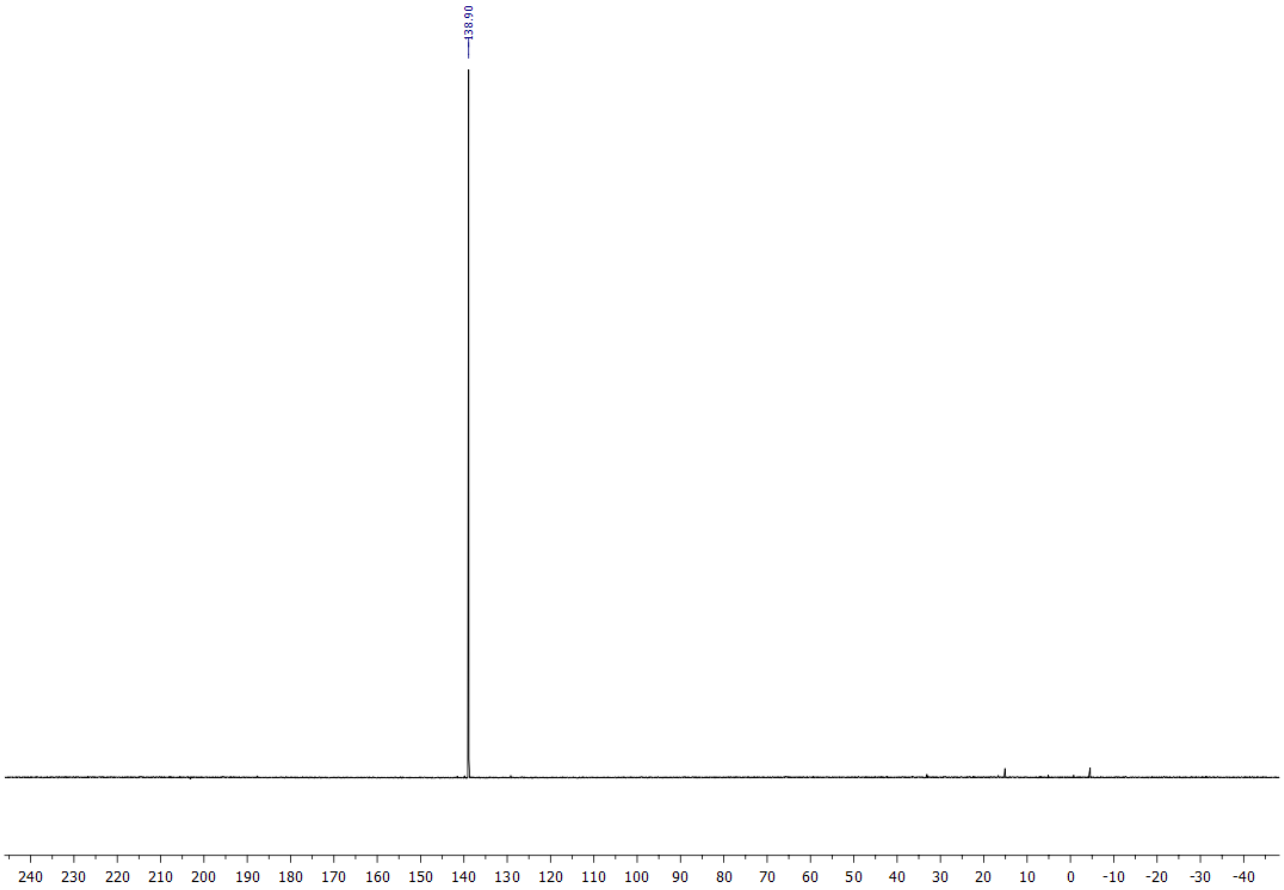


L4b, ^{1}H-^{13}C HSQC spectrum.

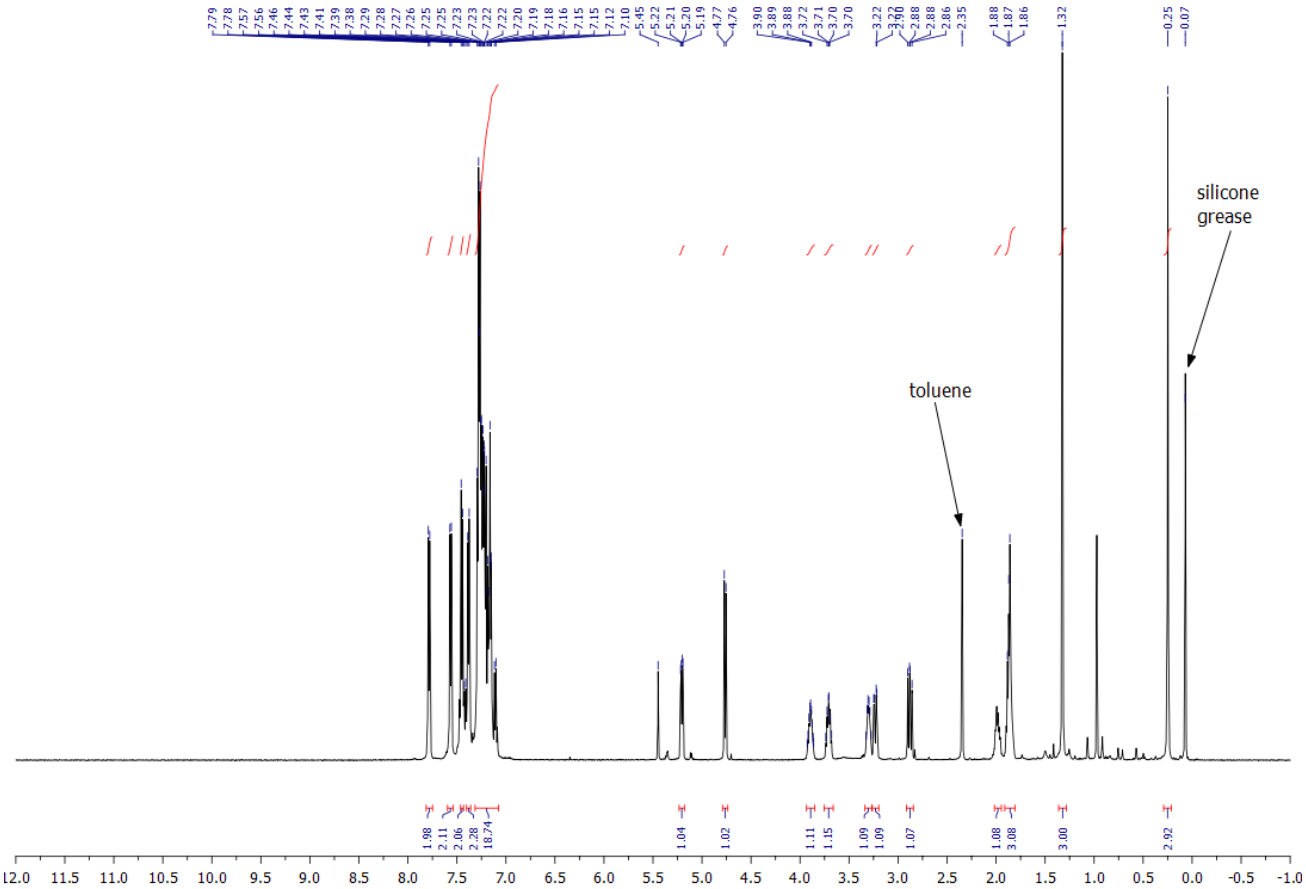


L4b, ^{1}H-^{13}C HMBC spectrum.

NMR AND MASS SPECTRA

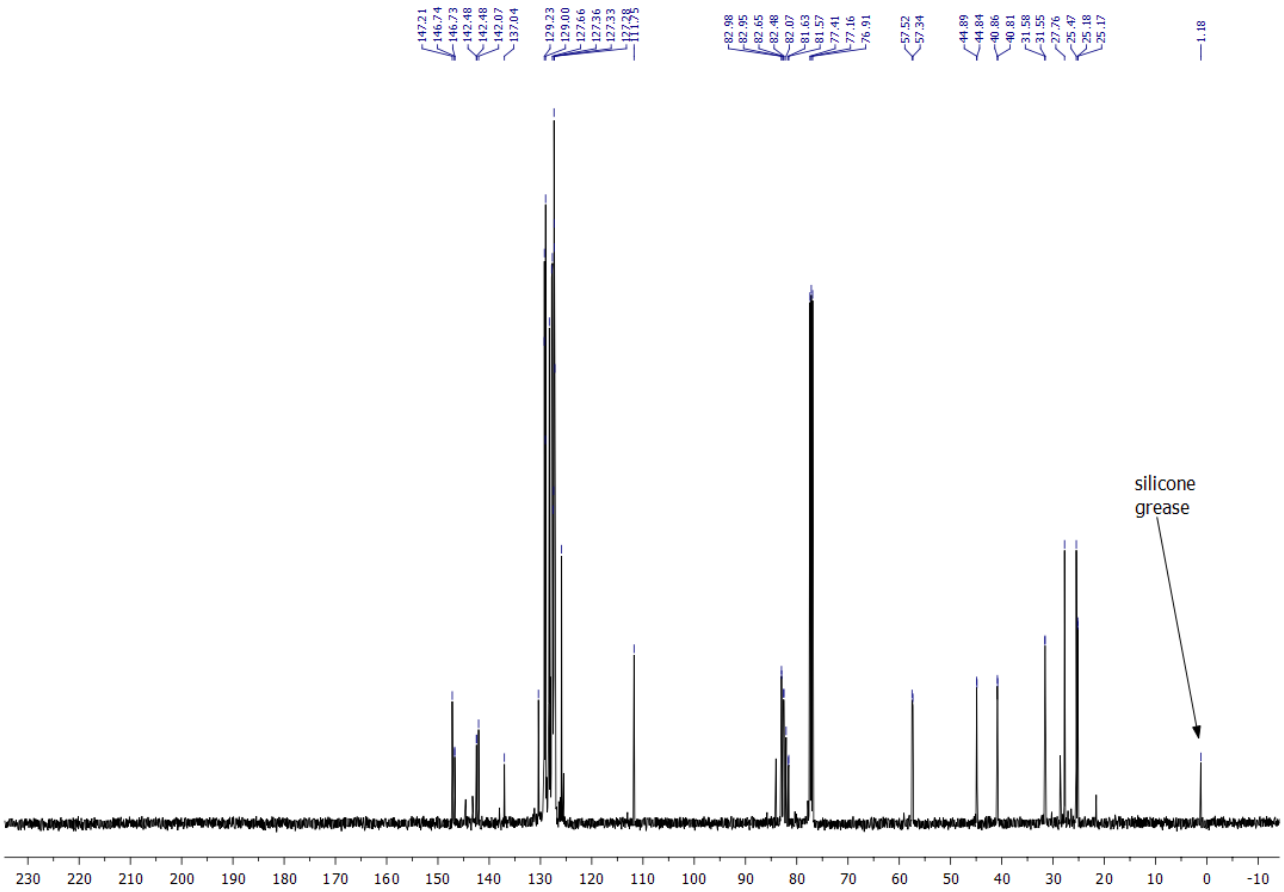


L5a, $^{31}P\{^{1}H\}$ spectrum.

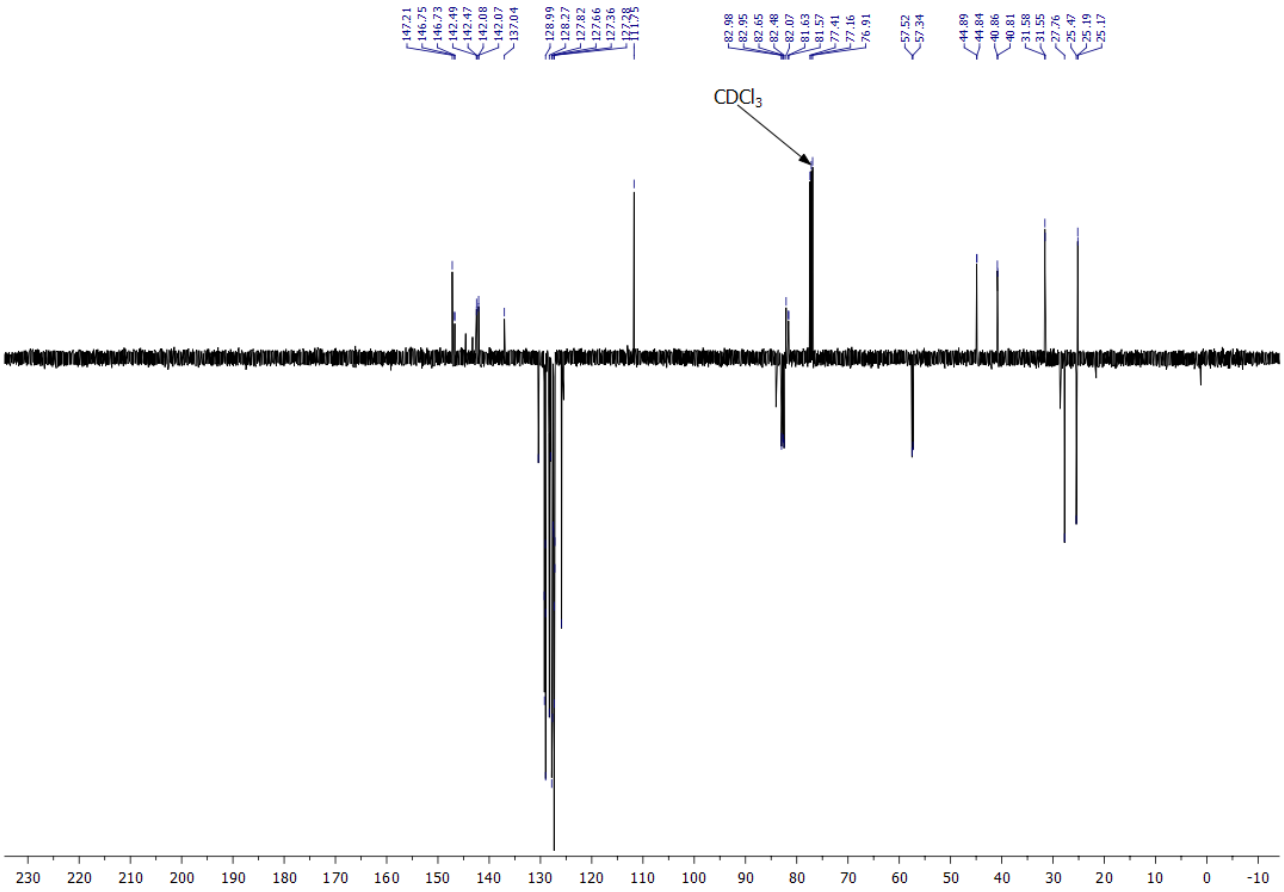


L5a, ^{1}H spectrum.

NMR AND MASS SPECTRA

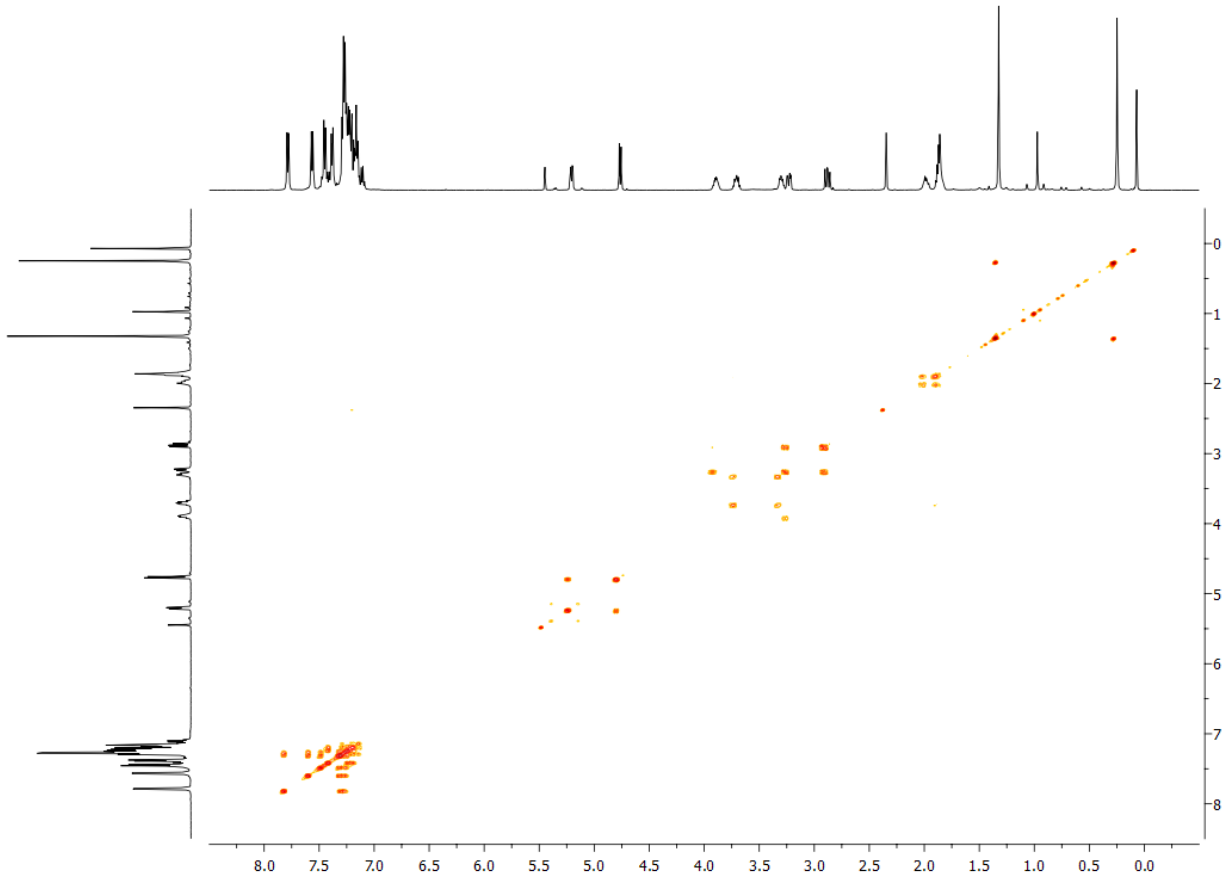


L5a, $^{13}C\{^{1}H\}$ spectrum.

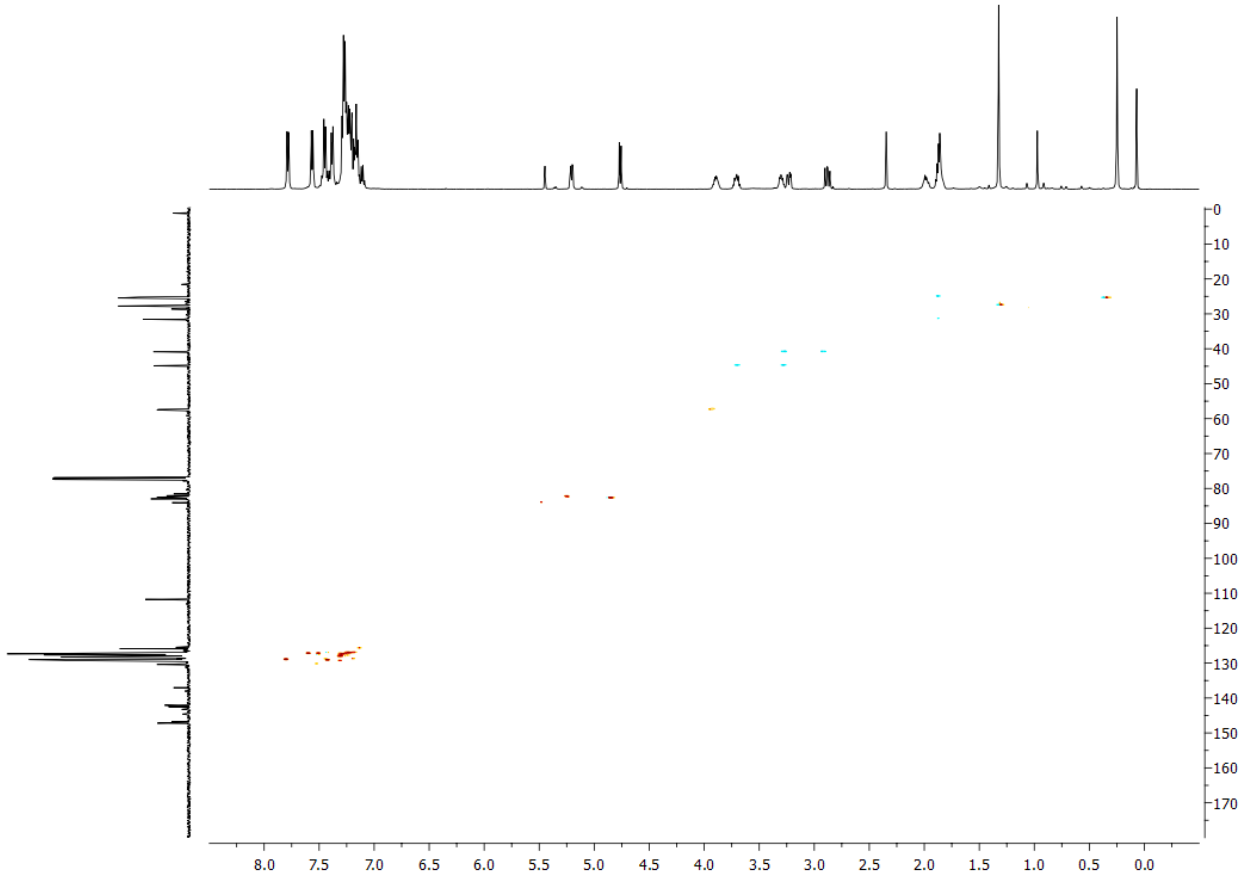


L5a, $^{13}C\{^{1}H\}$ APT spectrum.

NMR AND MASS SPECTRA

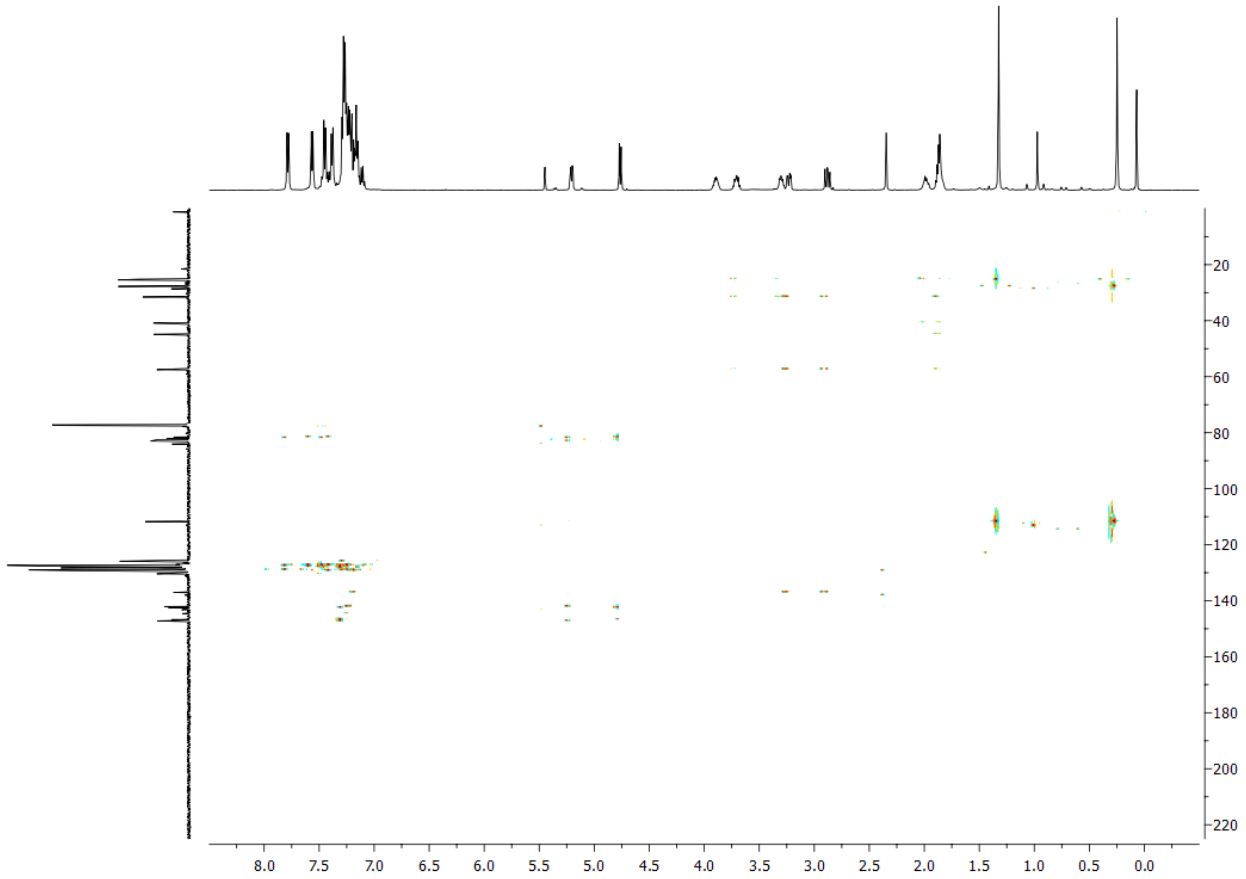


L5a, ^{1}H-^{1}H COSY spectrum.

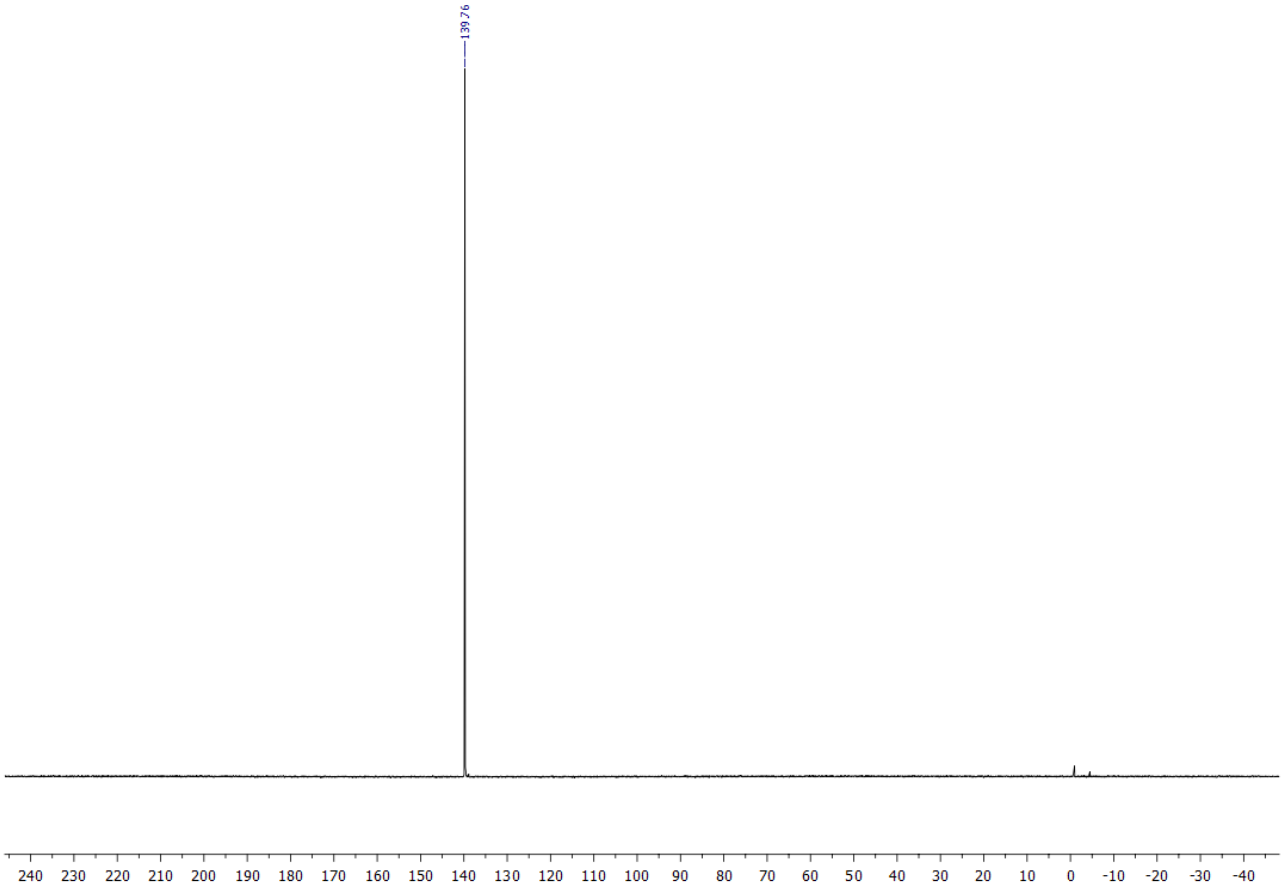


L5a, ^{1}H-^{13}C HSQC spectrum.

NMR AND MASS SPECTRA

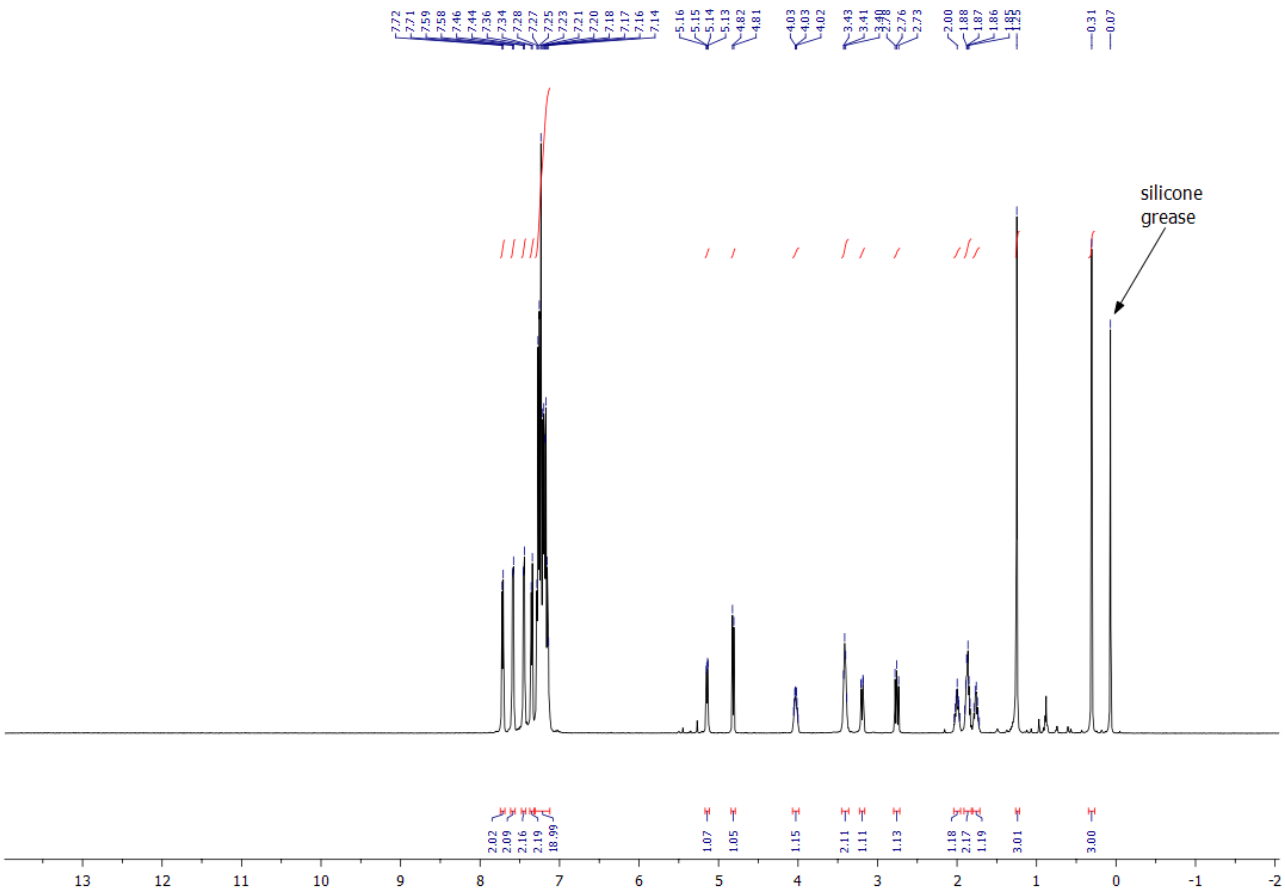


L5a, ^{1}H-^{13}C HMBC spectrum.

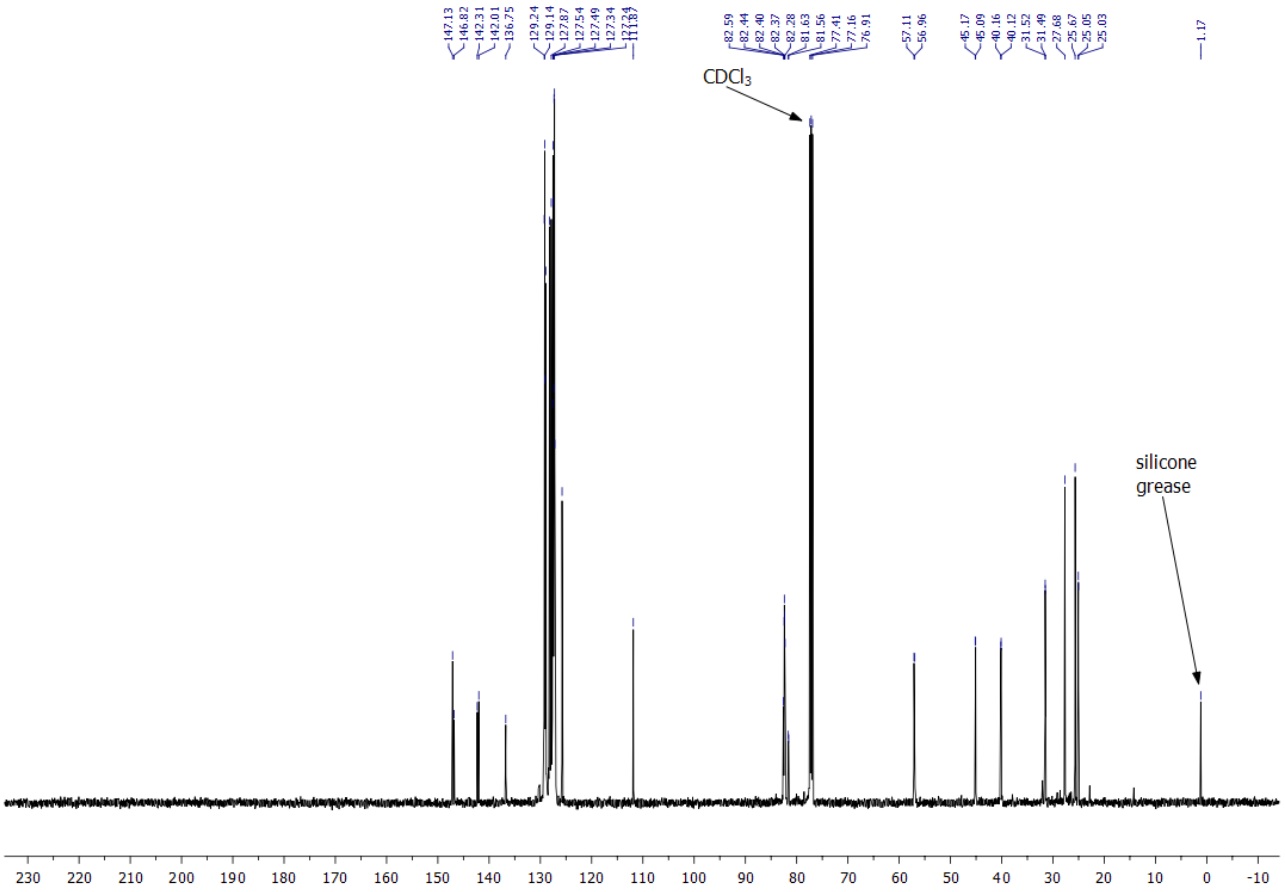


L5b, $^{31}P\{^{1}H\}$ spectrum.

NMR AND MASS SPECTRA

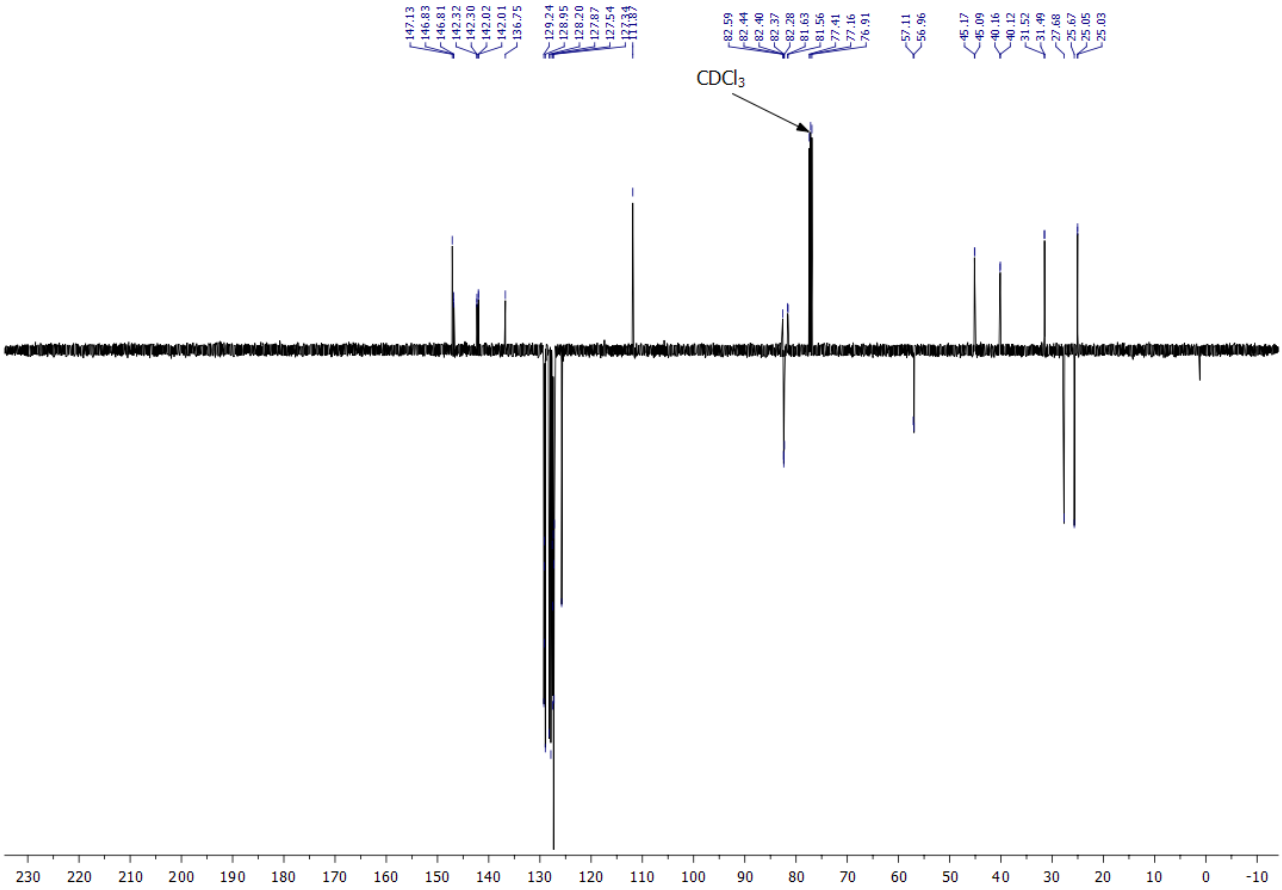


L5b, ^{1}H spectrum.

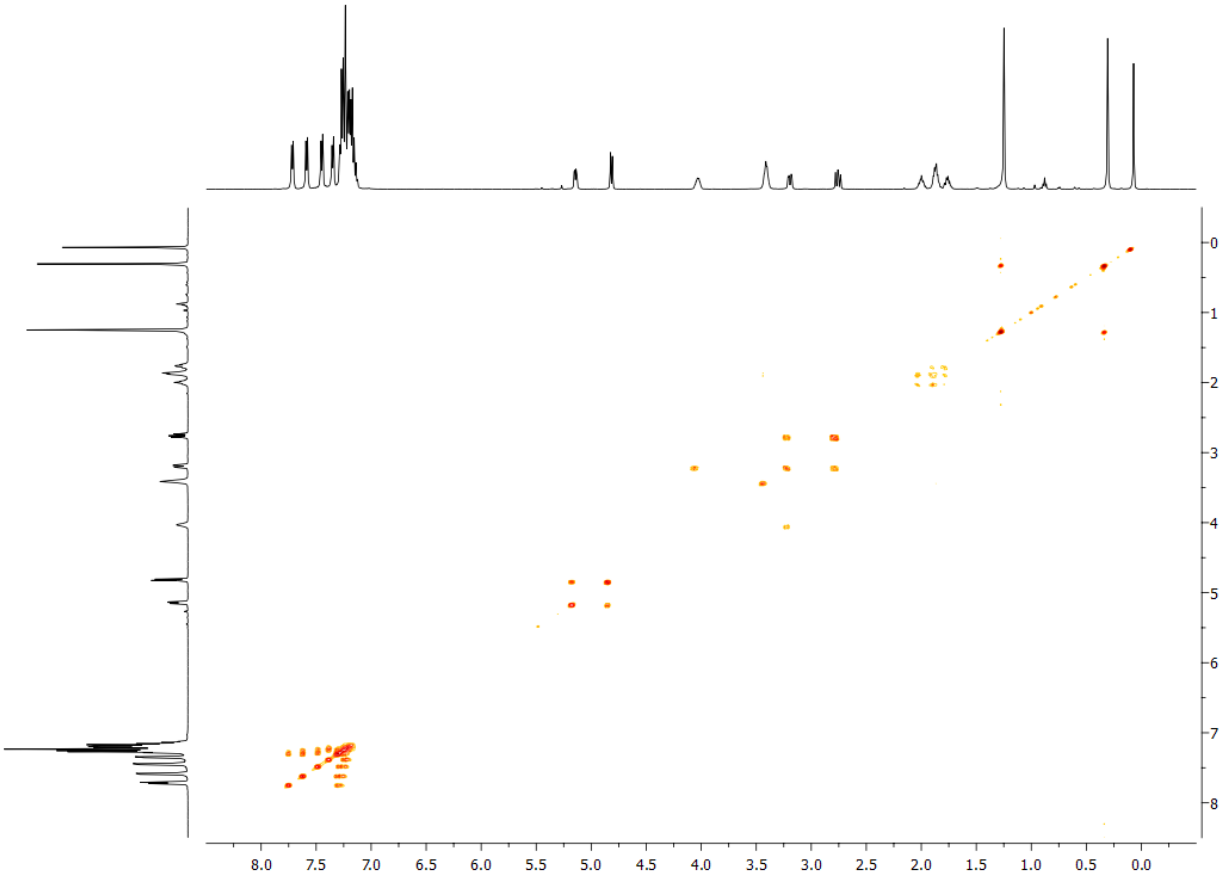


L5b, $^{13}C\{^{1}H\}$ spectrum.

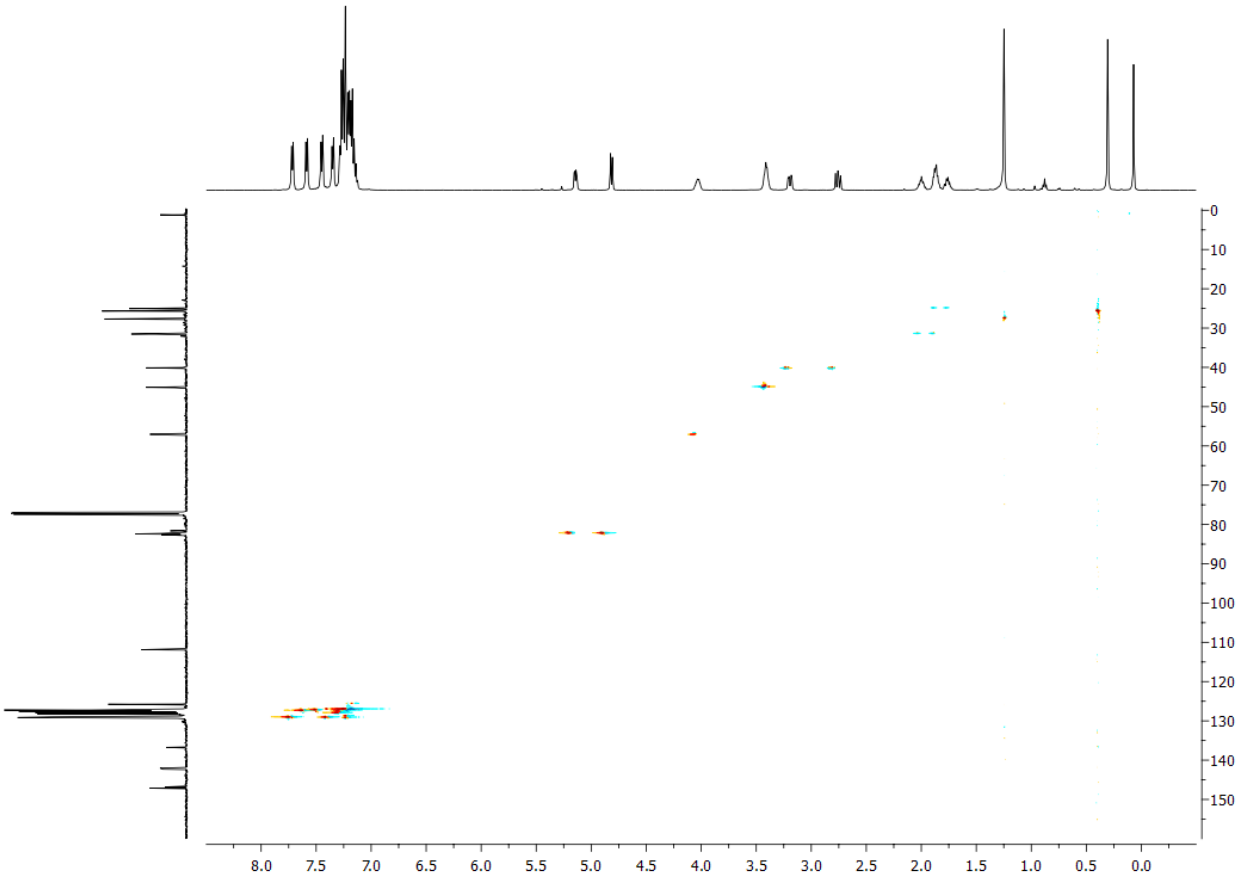
NMR AND MASS SPECTRA



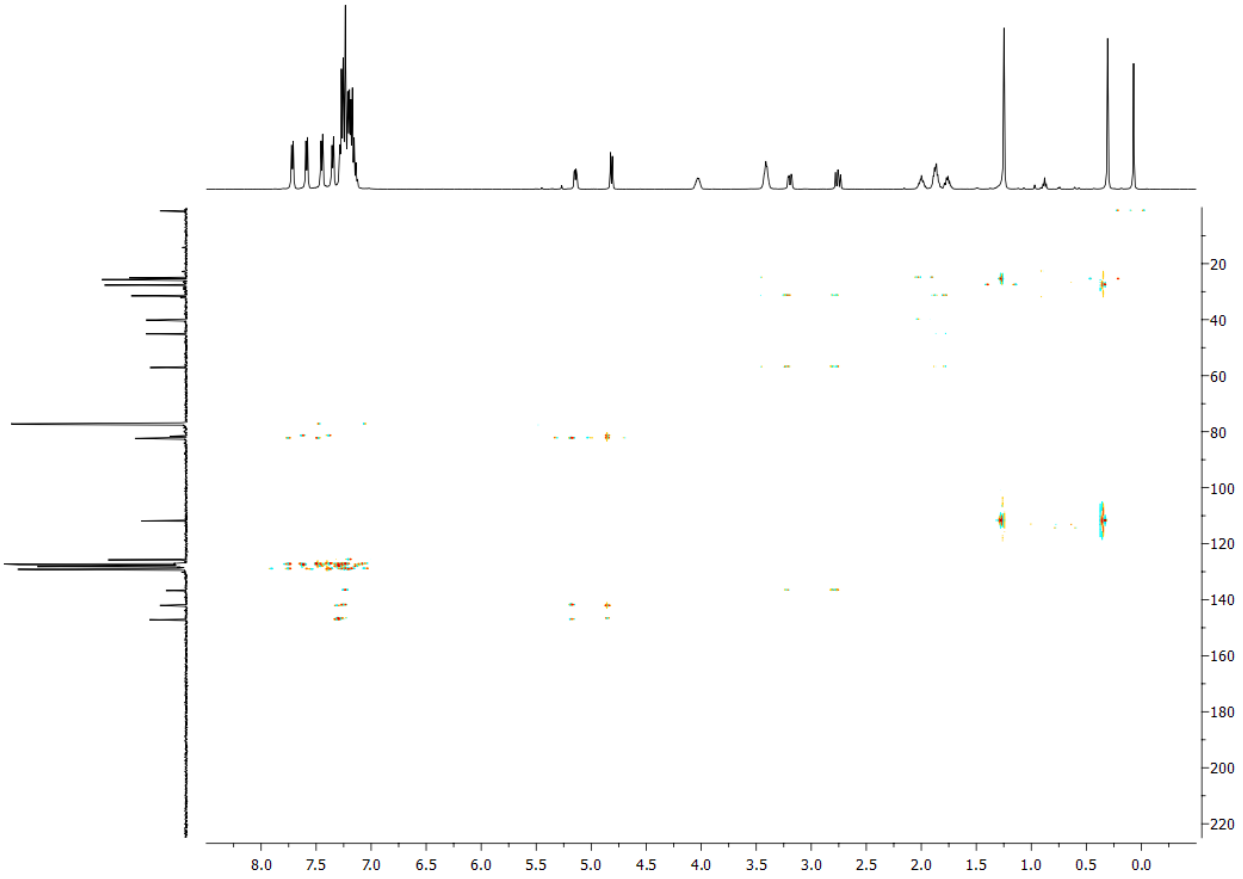
L5b, $^{13}C\{^{1}H\}$ APT spectrum.



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

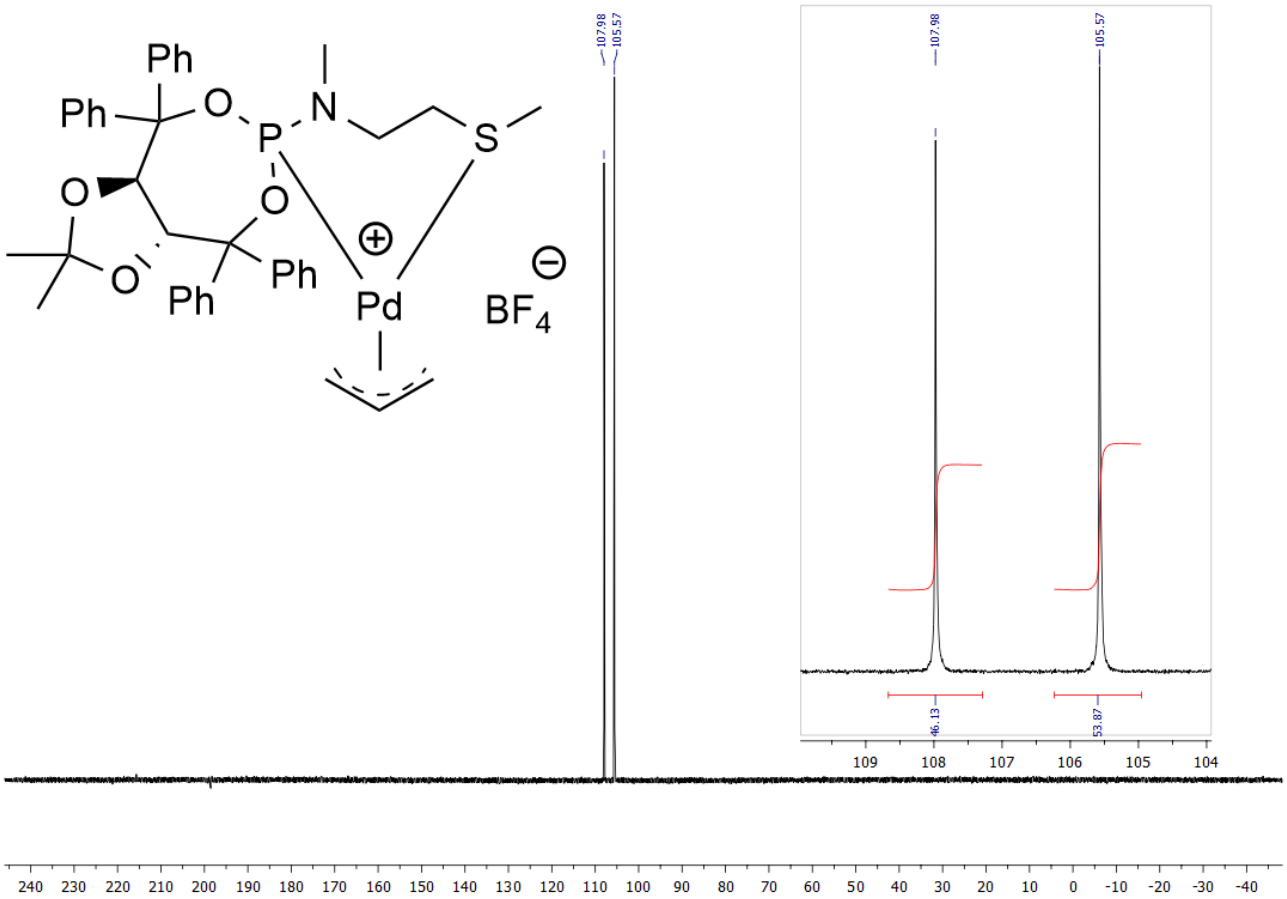


L5b, ^{1}H-^{13}C HSQC spectrum.

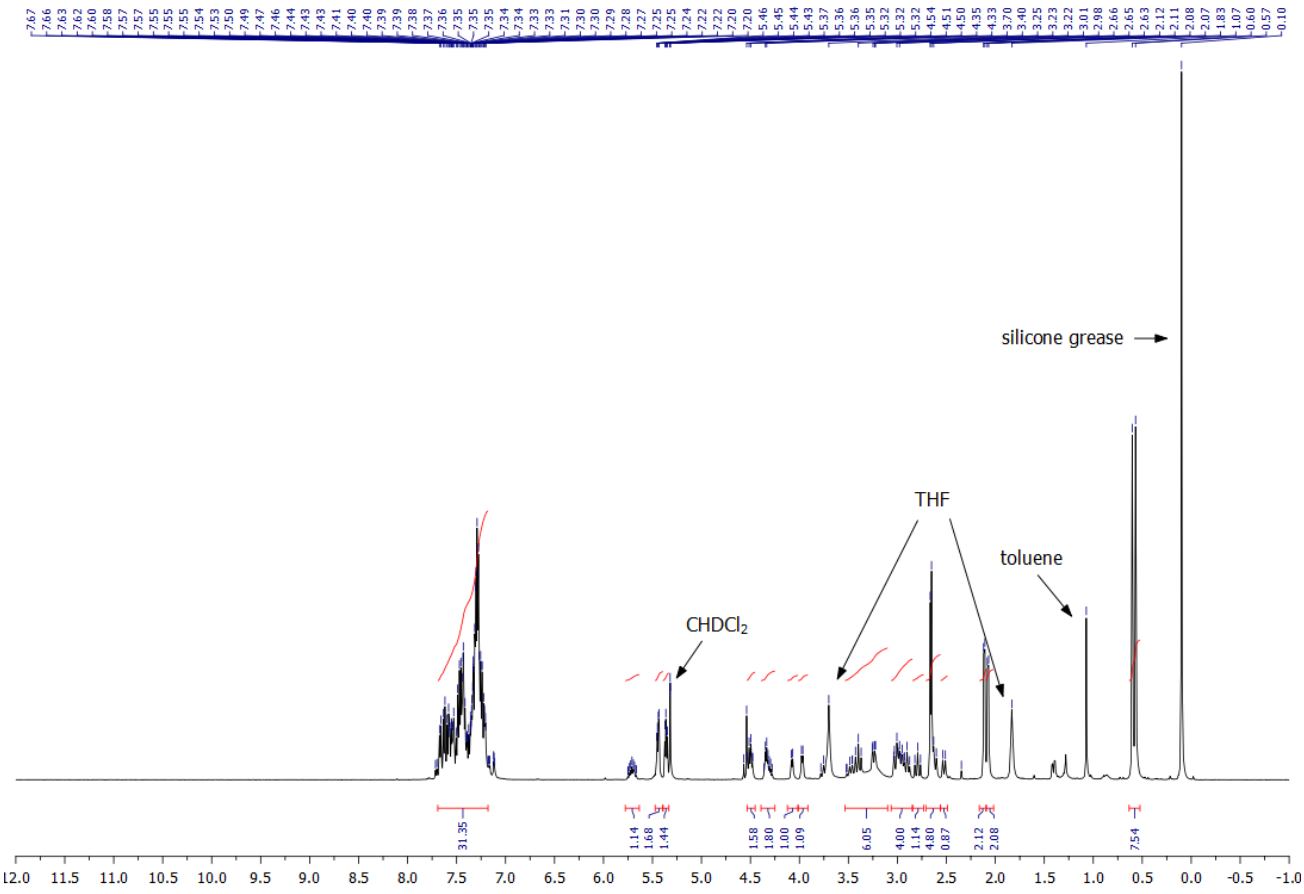


L5b, ^{1}H-^{13}C HMBC spectrum.

NMR AND MASS SPECTRA

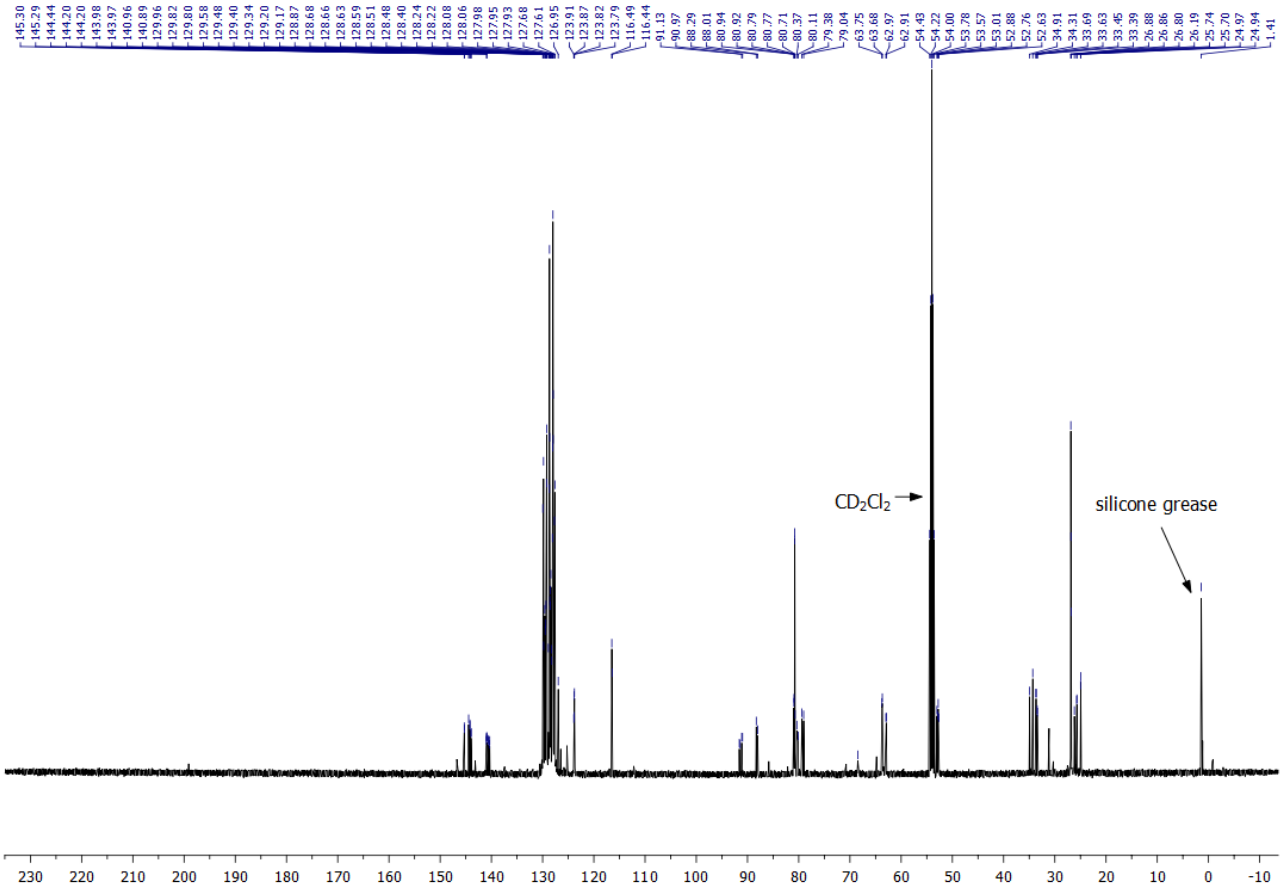


[Pd(allyl)(**L1a**)]BF_4, $^{31}P\{^1H\}$ spectrum.

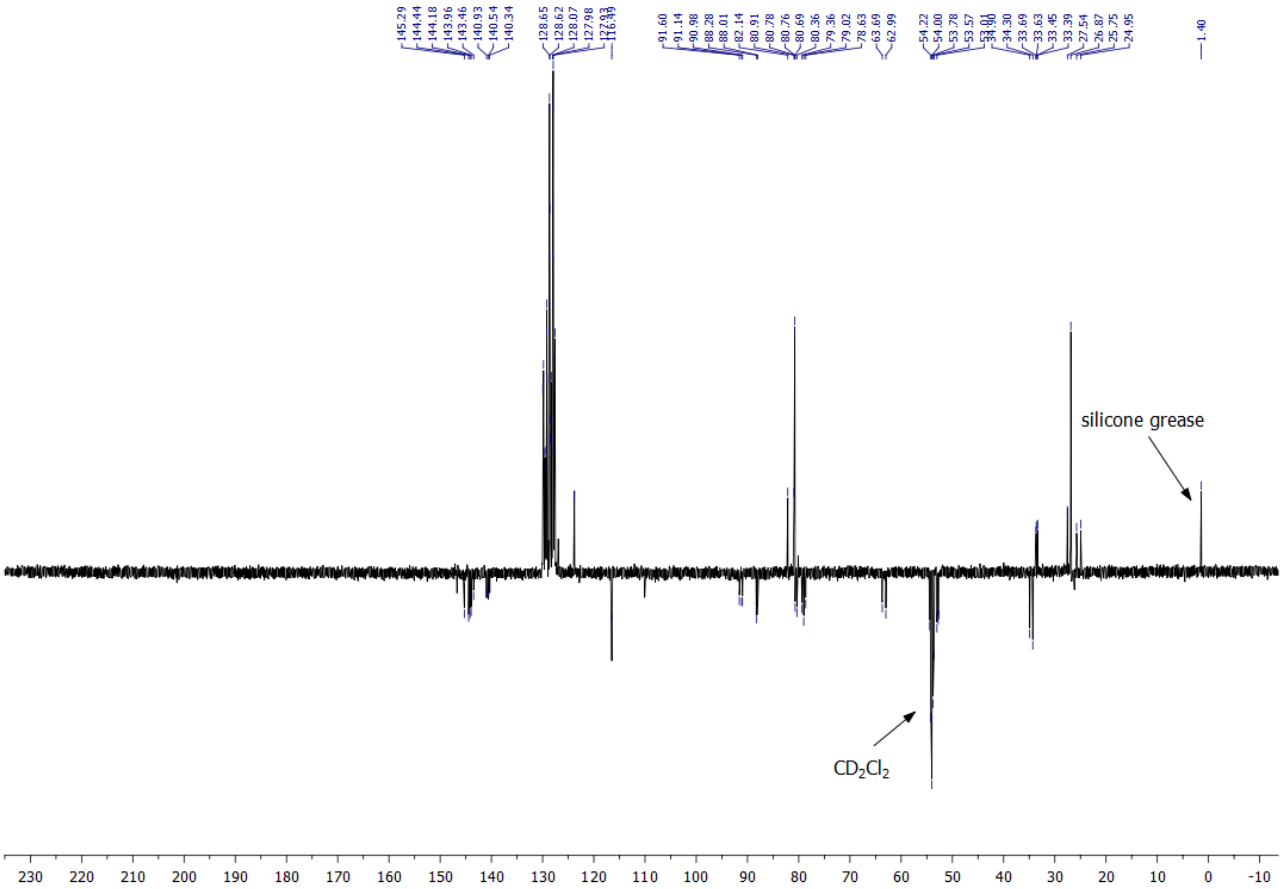


[Pd(allyl)(**L1a**)]BF_4, ^1H spectrum.

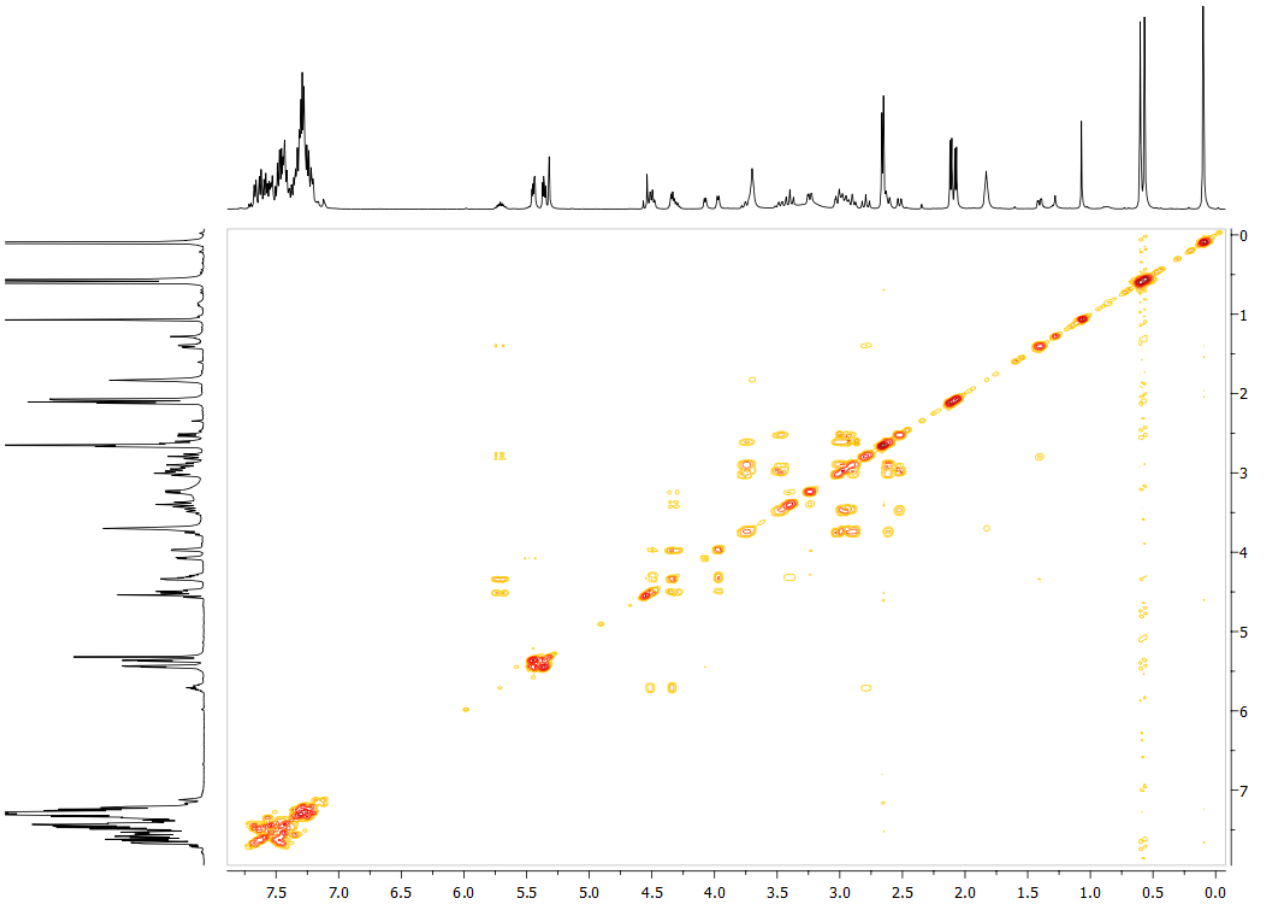
NMR AND MASS SPECTRA



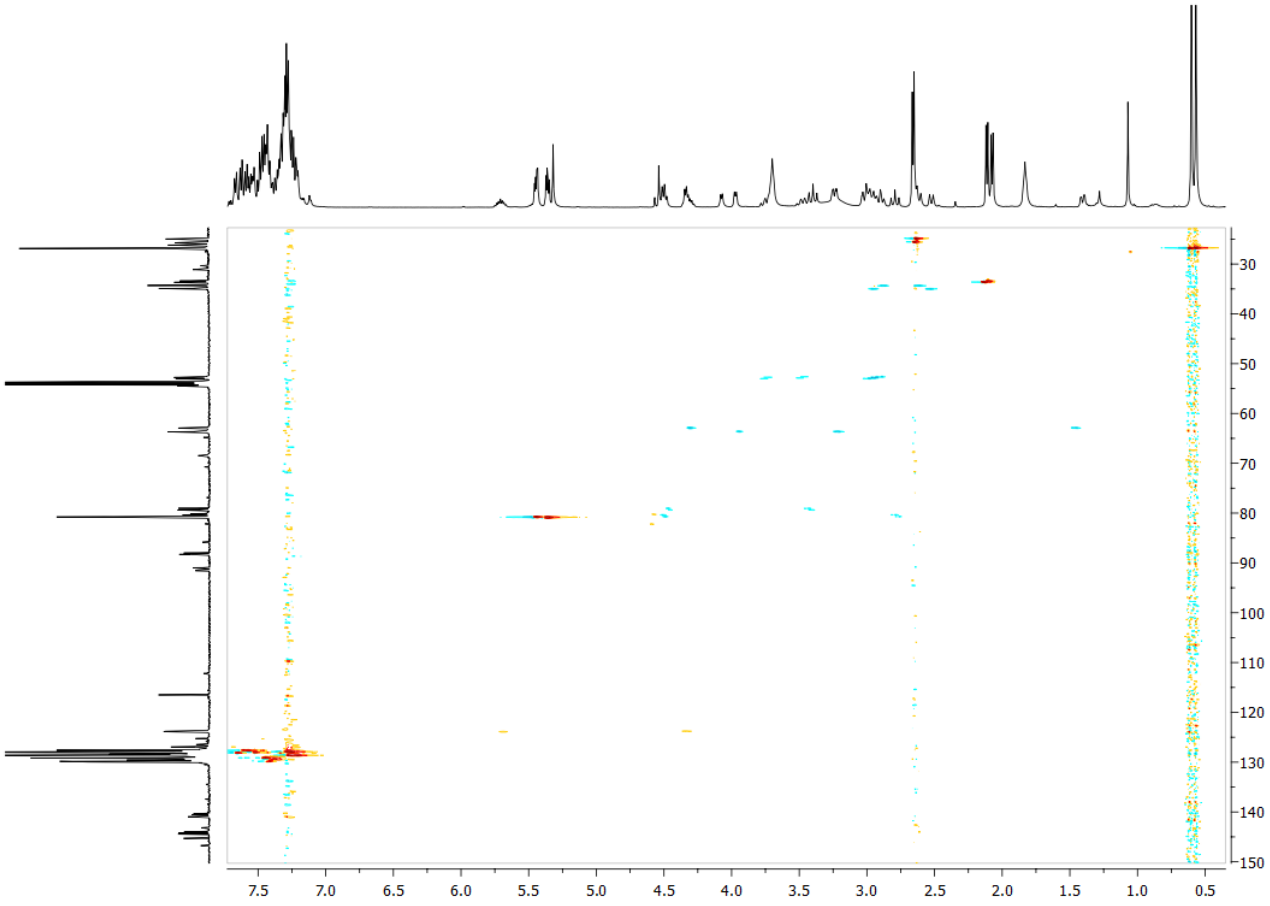
[Pd(allyl)(**L1a**)]BF_4, $^{13}C\{^1H\}$ spectrum.



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

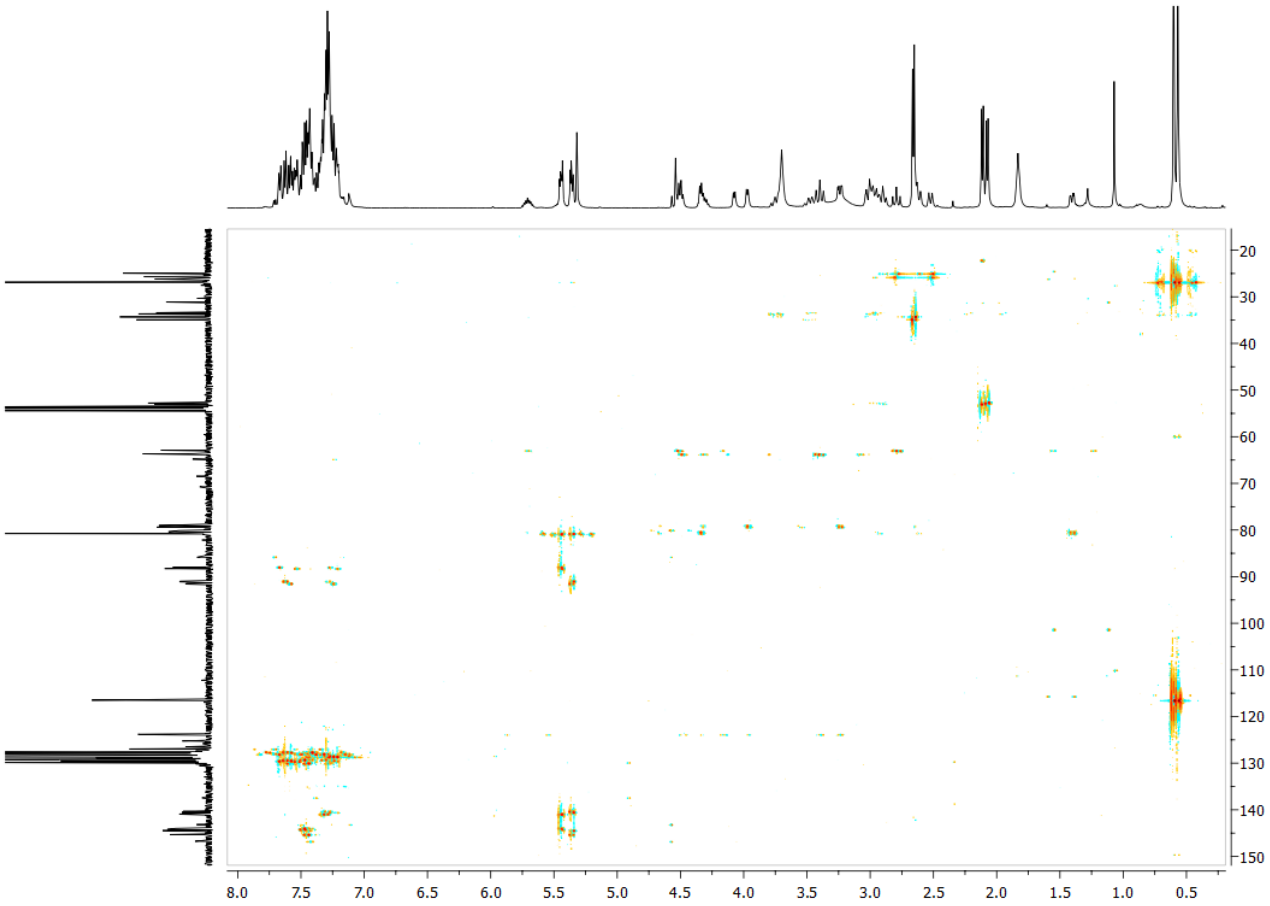


[Pd(allyl)(**L1a**)]BF_4, ^1H-^1H COSY spectrum.

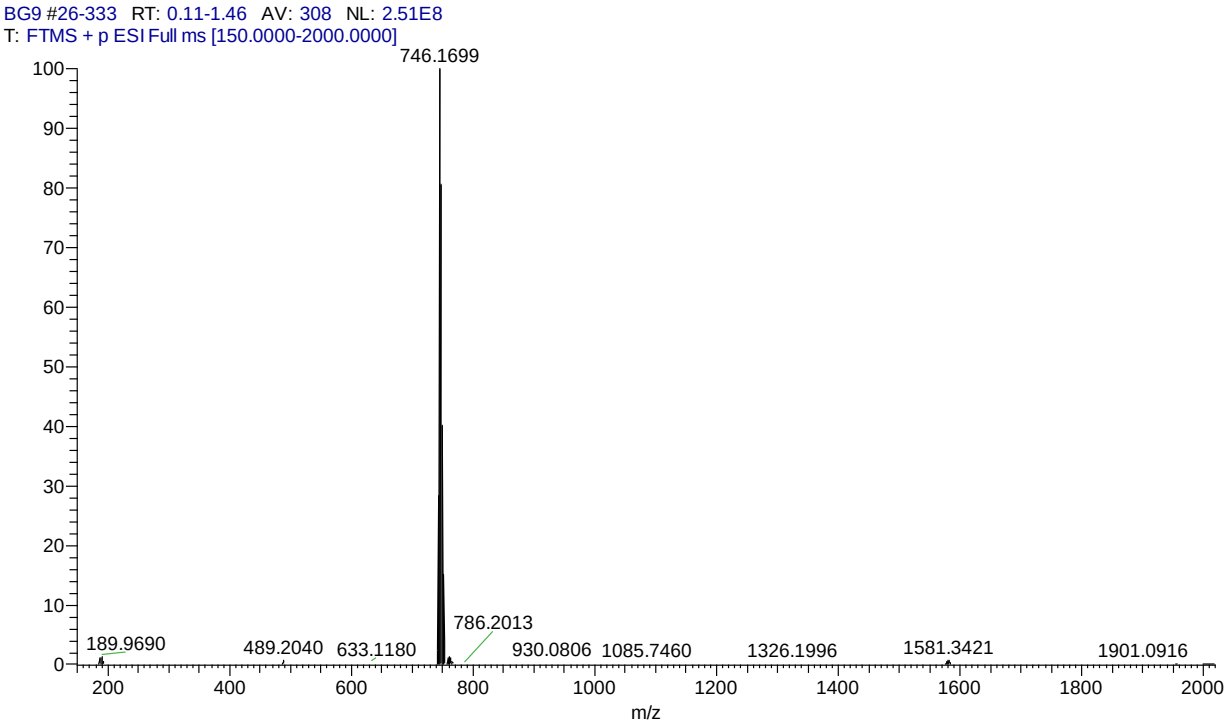


[Pd(allyl)(**L1a**)]BF_4, ^1H-^{13}C HSQC spectrum.

NMR AND MASS SPECTRA

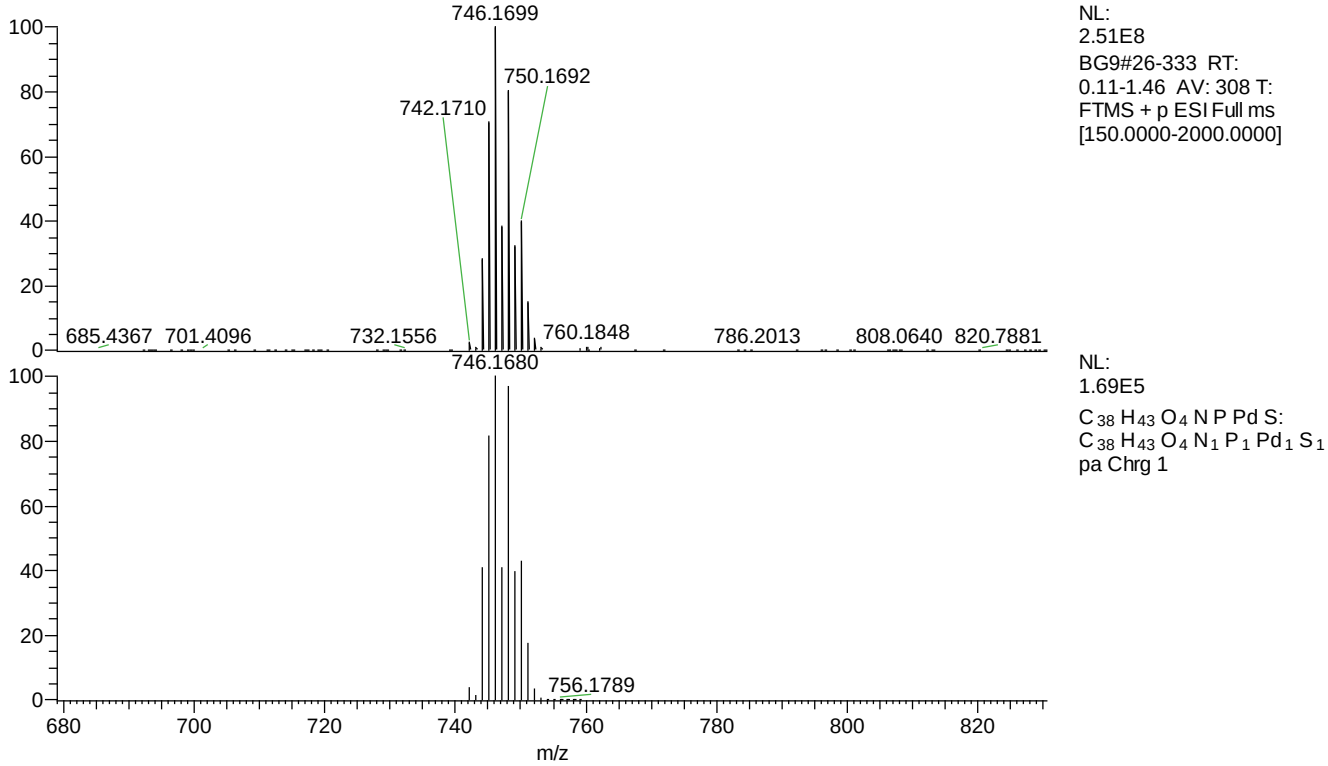


[Pd(allyl)(**L1a**)]BF_4, ^{1}H-^{13}C HMBC spectrum.

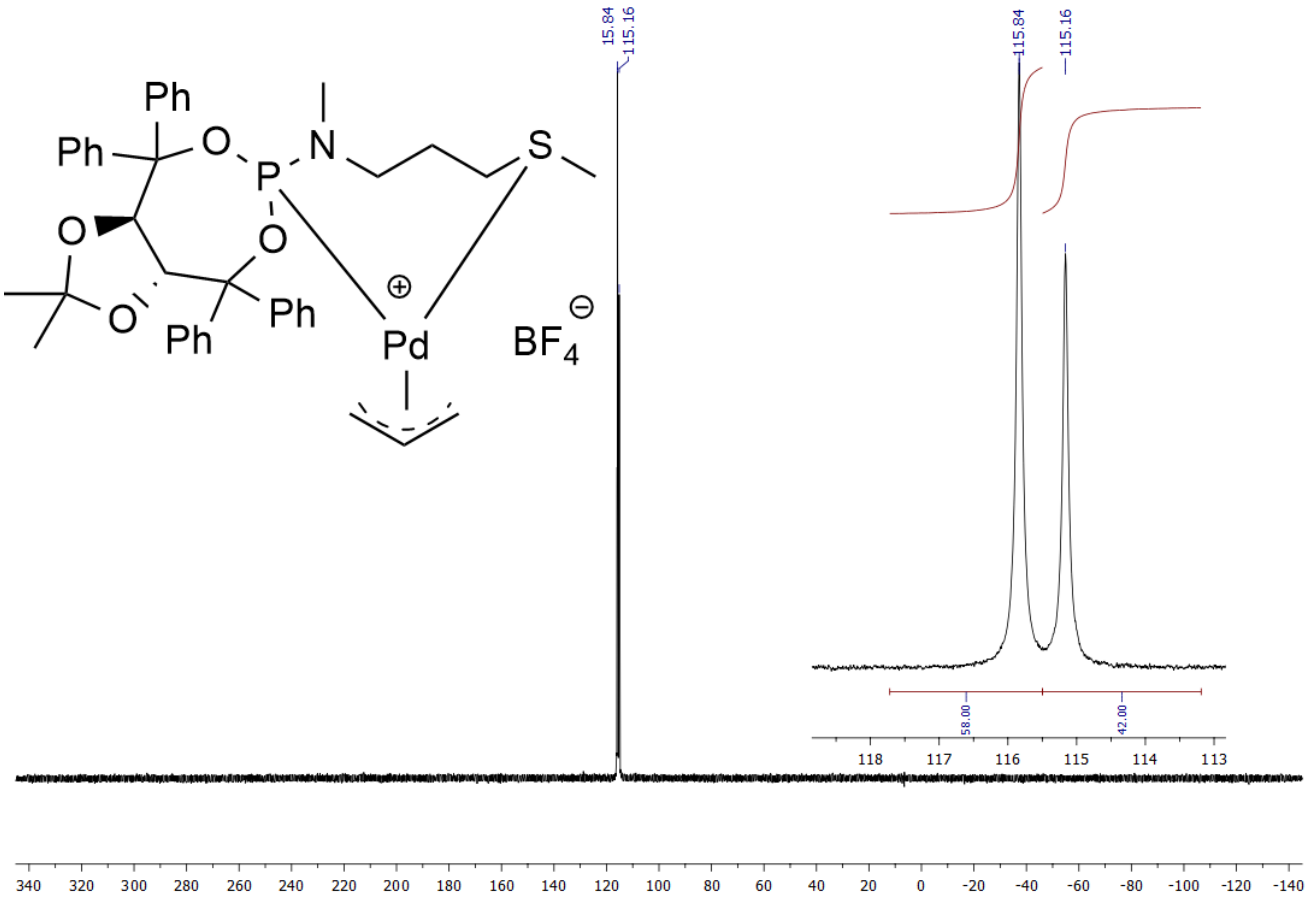


[Pd(allyl)(**L1a**)]BF_4, HRMS-spectrum (general view of the spectrum).

NMR AND MASS SPECTRA

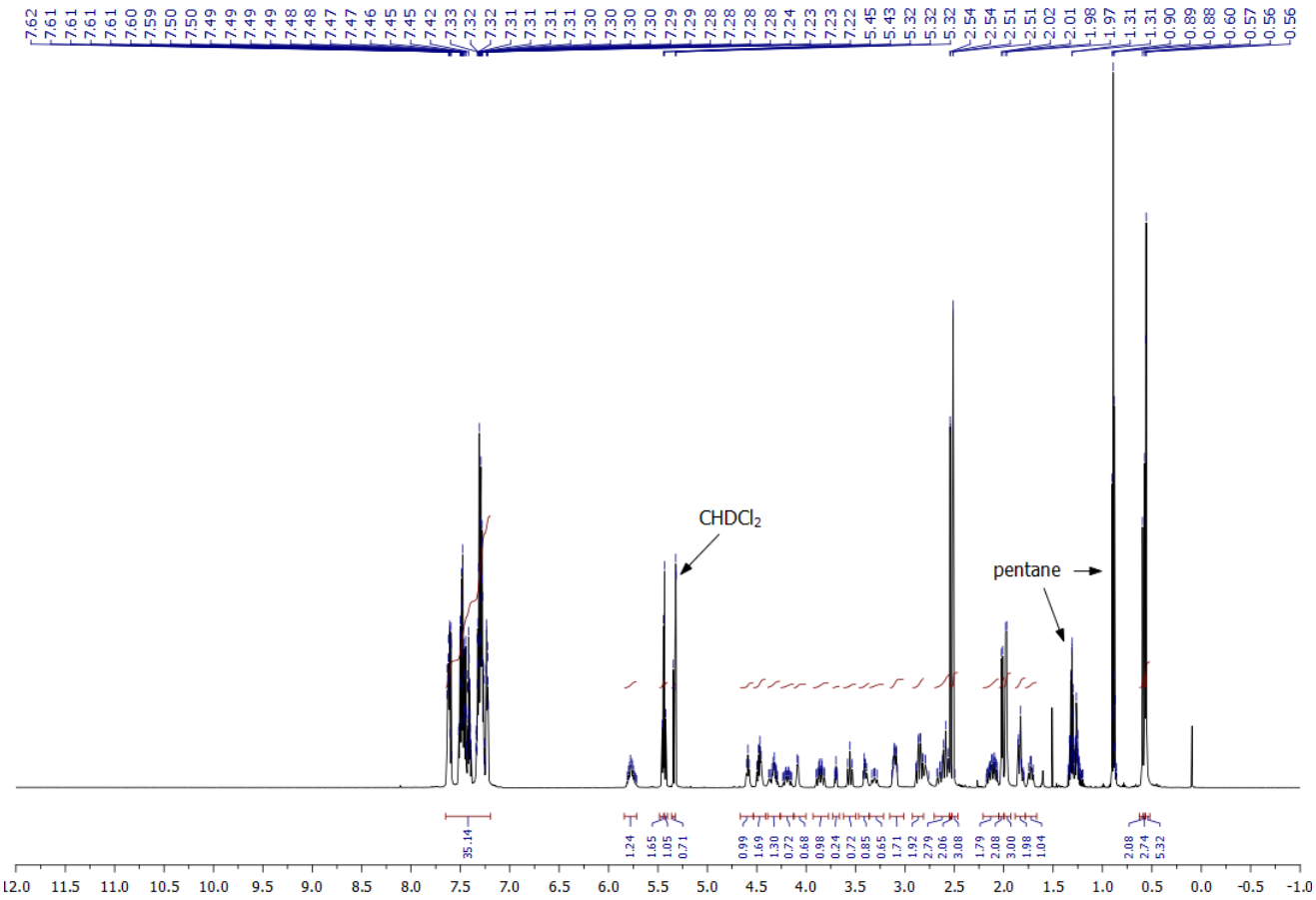


[Pd(allyl)(**L1a**)]$^{+}$, experimental (top) and calculated (bottom) peaks.

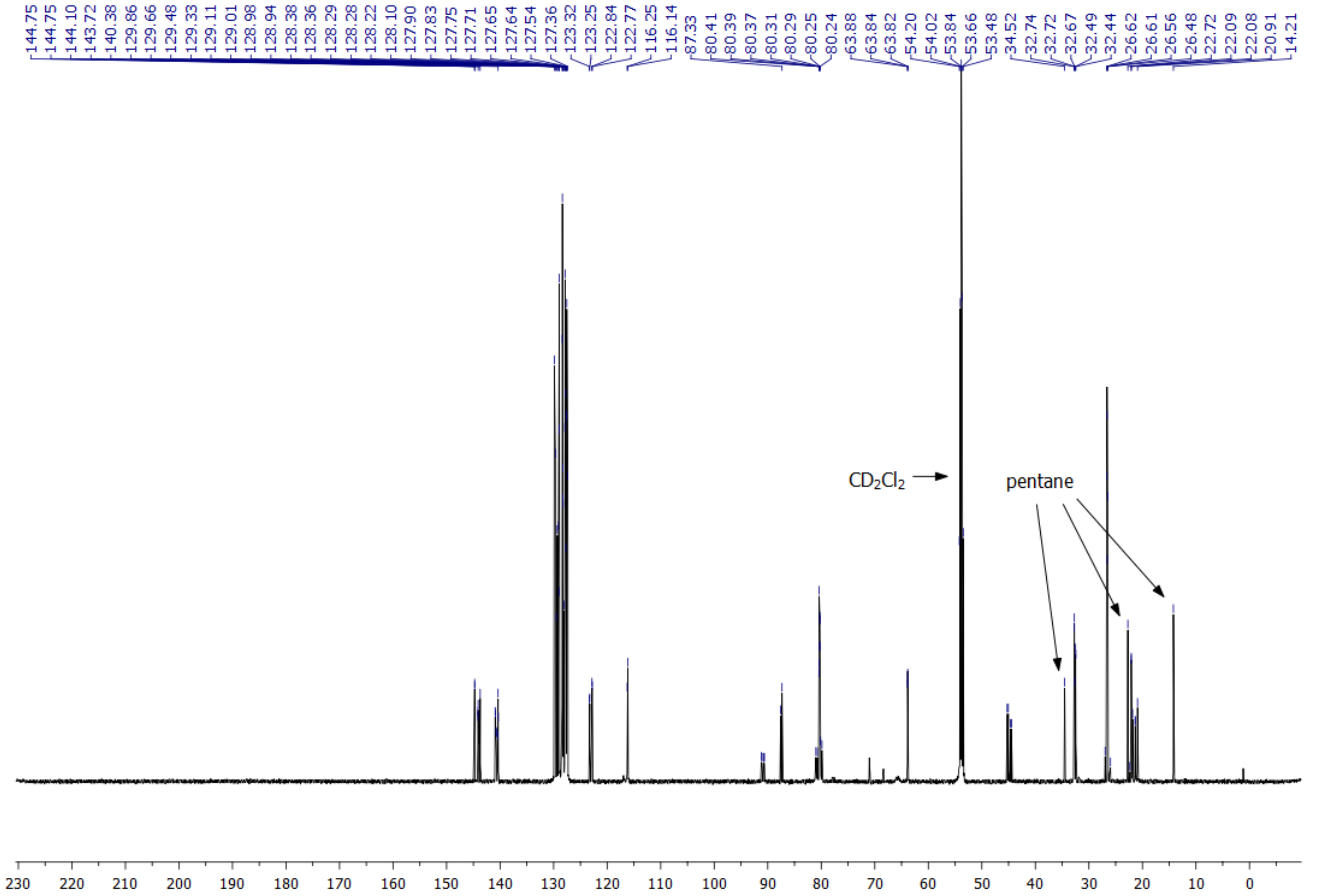


[Pd(allyl)(**L1f**)]BF_4, $^{31}P\{^{1}H\}$ spectrum.

NMR AND MASS SPECTRA

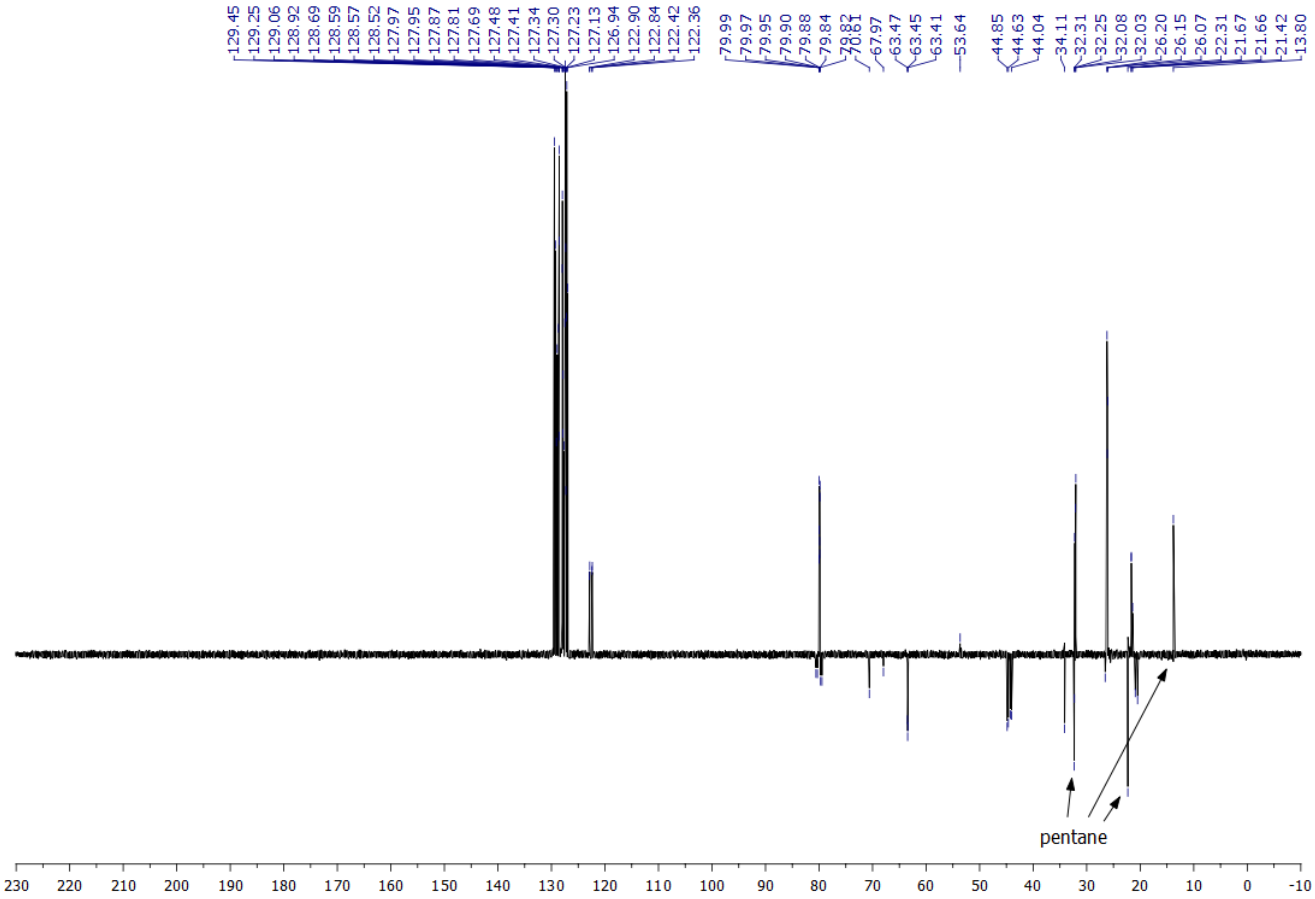


[Pd(allyl)(**L1f**)]BF_4, ^1H spectrum.

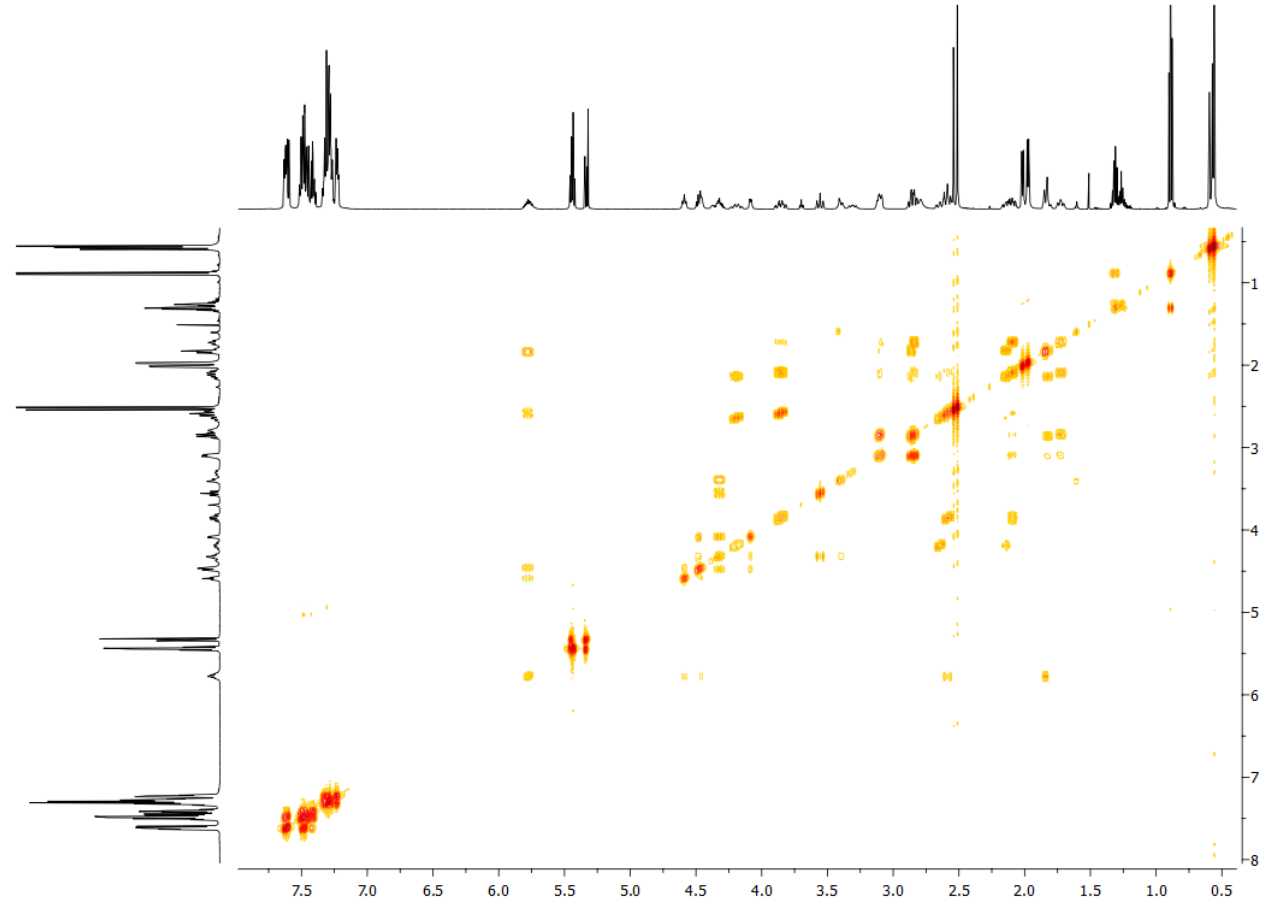


[Pd(allyl)(**L1f**)]BF_4, $^{13}C\{^1H\}$ spectrum.

NMR AND MASS SPECTRA

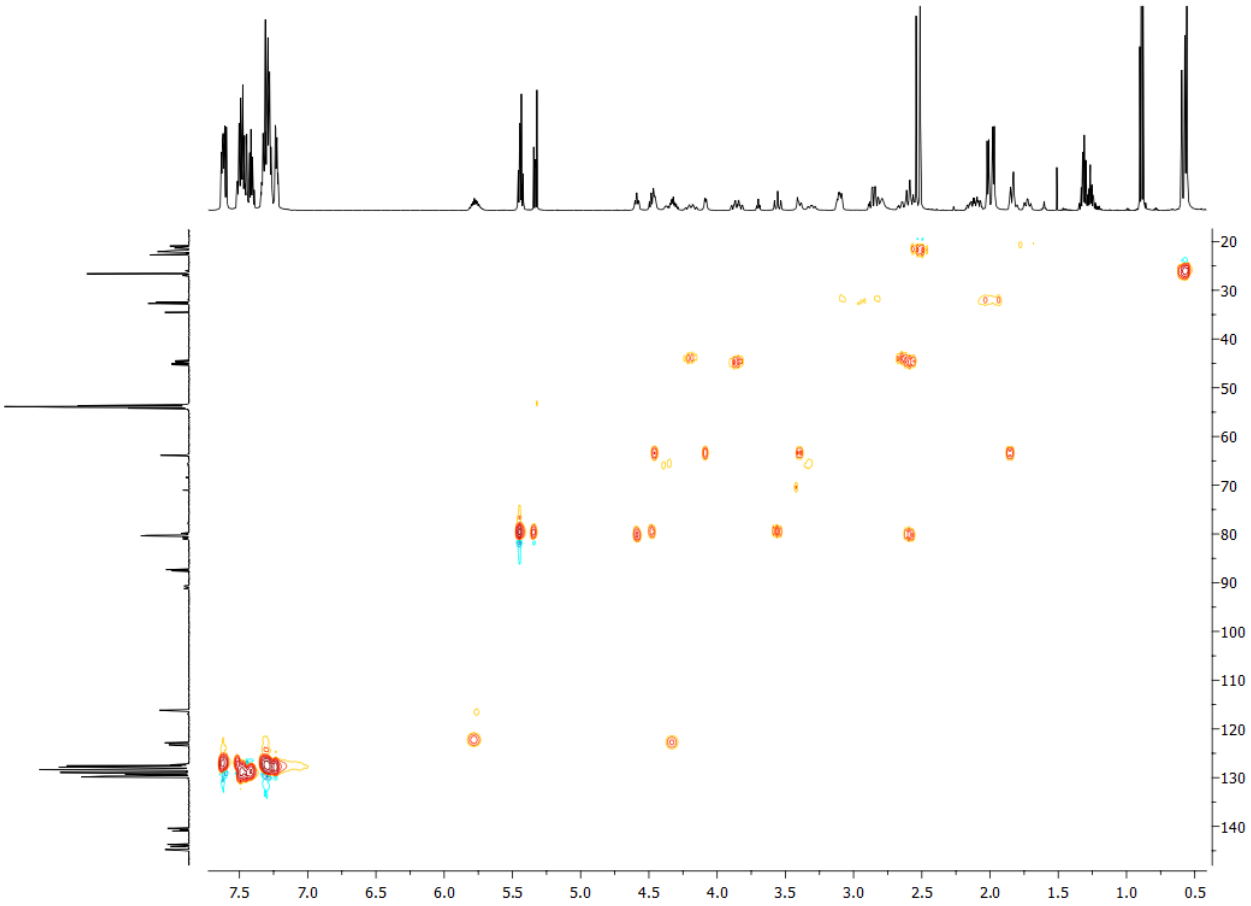


[Pd(allyl)(**L1f**)]BF_4, $^{13}C\{^1H\}$ DEPT spectrum.

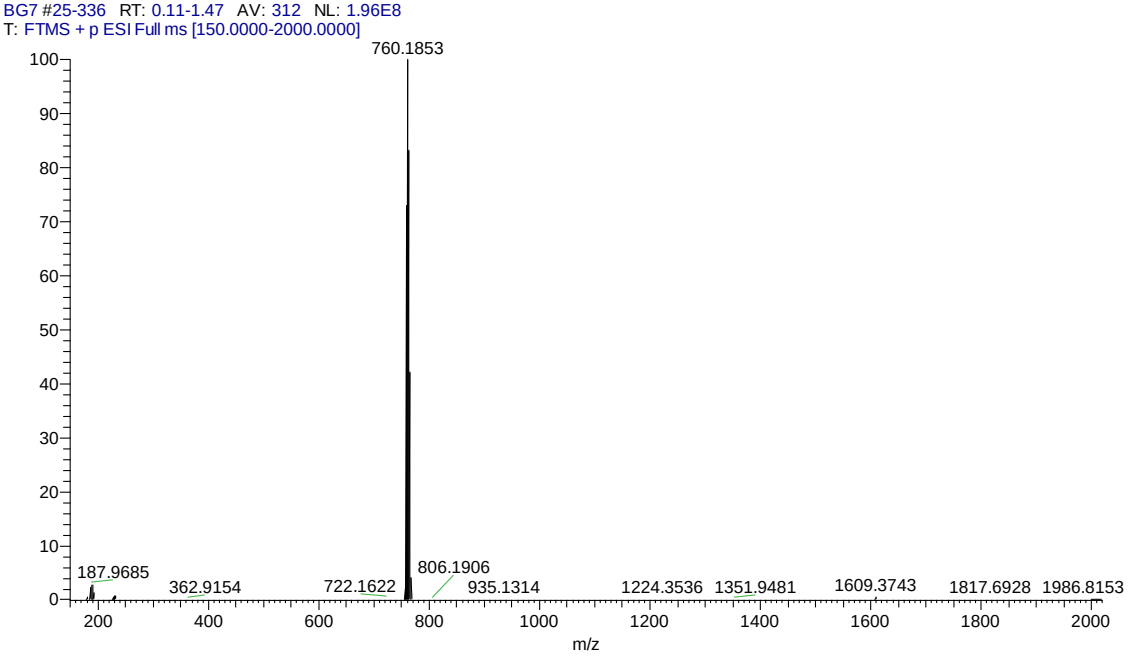


[Pd(allyl)(**L1f**)]BF_4, ^1H-^1H COSY spectrum.

NMR AND MASS SPECTRA

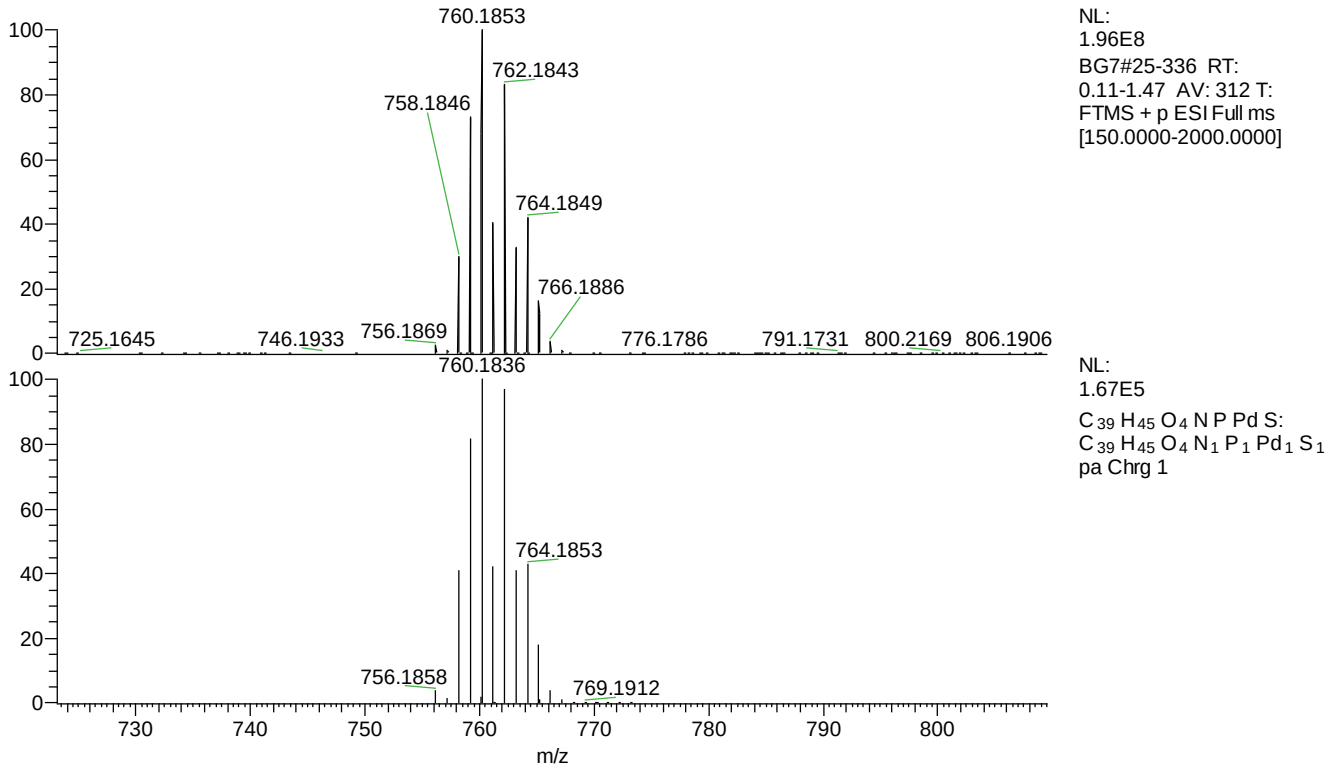


[Pd(allyl)(**L1f**)]BF_4, ^{1}H-^{13}C HSQC spectrum.

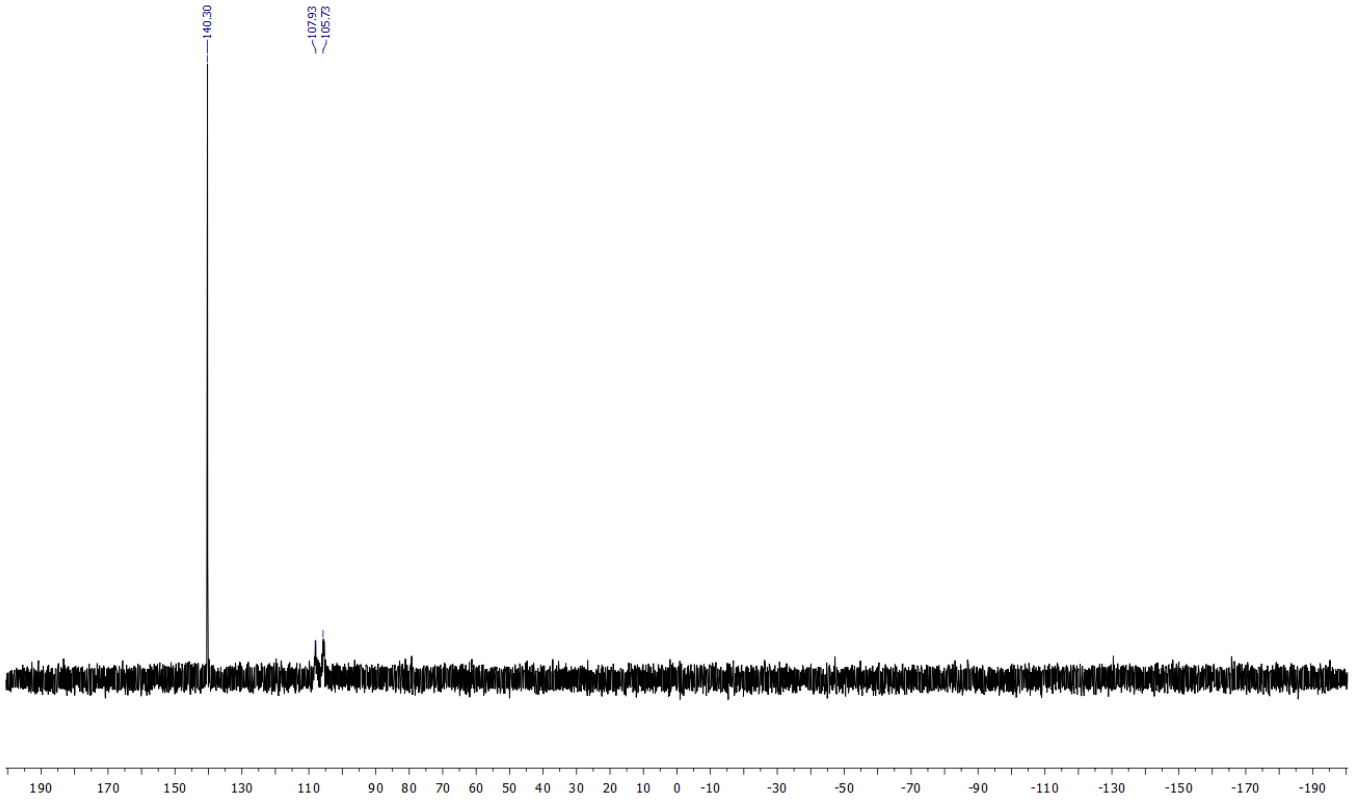


[Pd(allyl)(**L1f**)]BF_4, HRMS-spectrum (general view of the spectrum).

NMR AND MASS SPECTRA

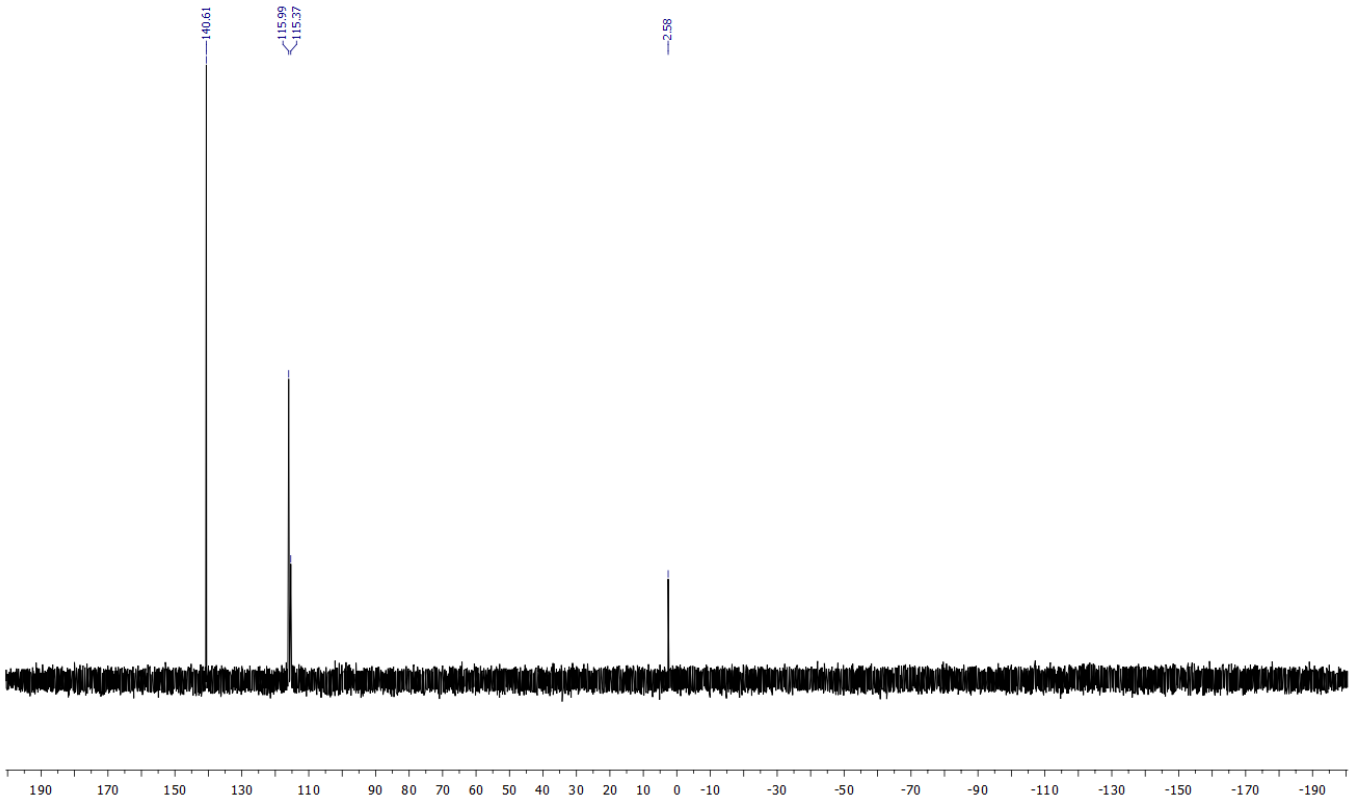


[Pd(allyl)(**L1f**)]$^{+}$, experimental (top) and calculated (bottom) peaks.



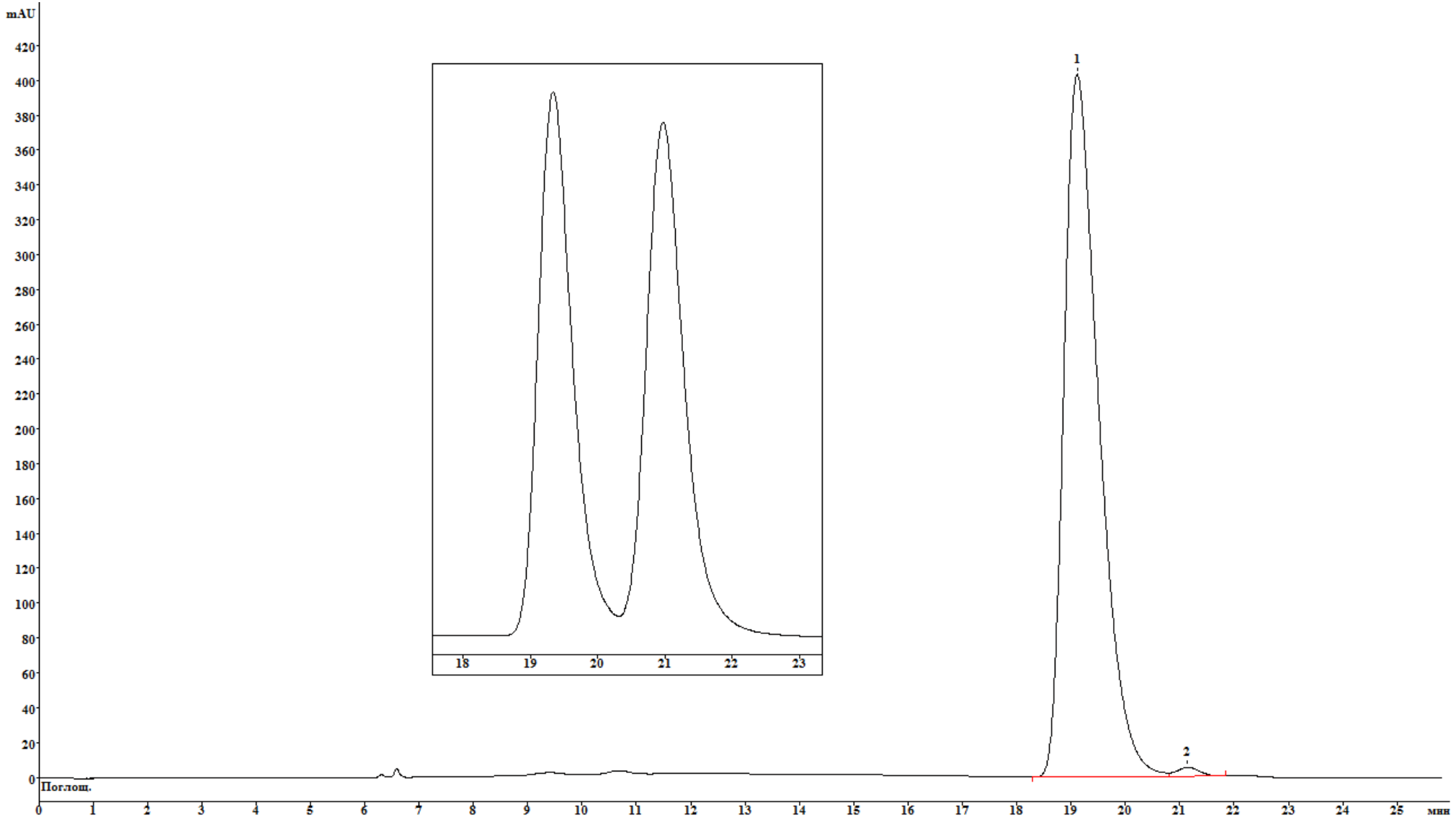
Mixture of **L1a** and [Pd(allyl)(**L1a**)]BF_4, $^{31}P\{^1H\}$ spectrum

NMR AND MASS SPECTRA



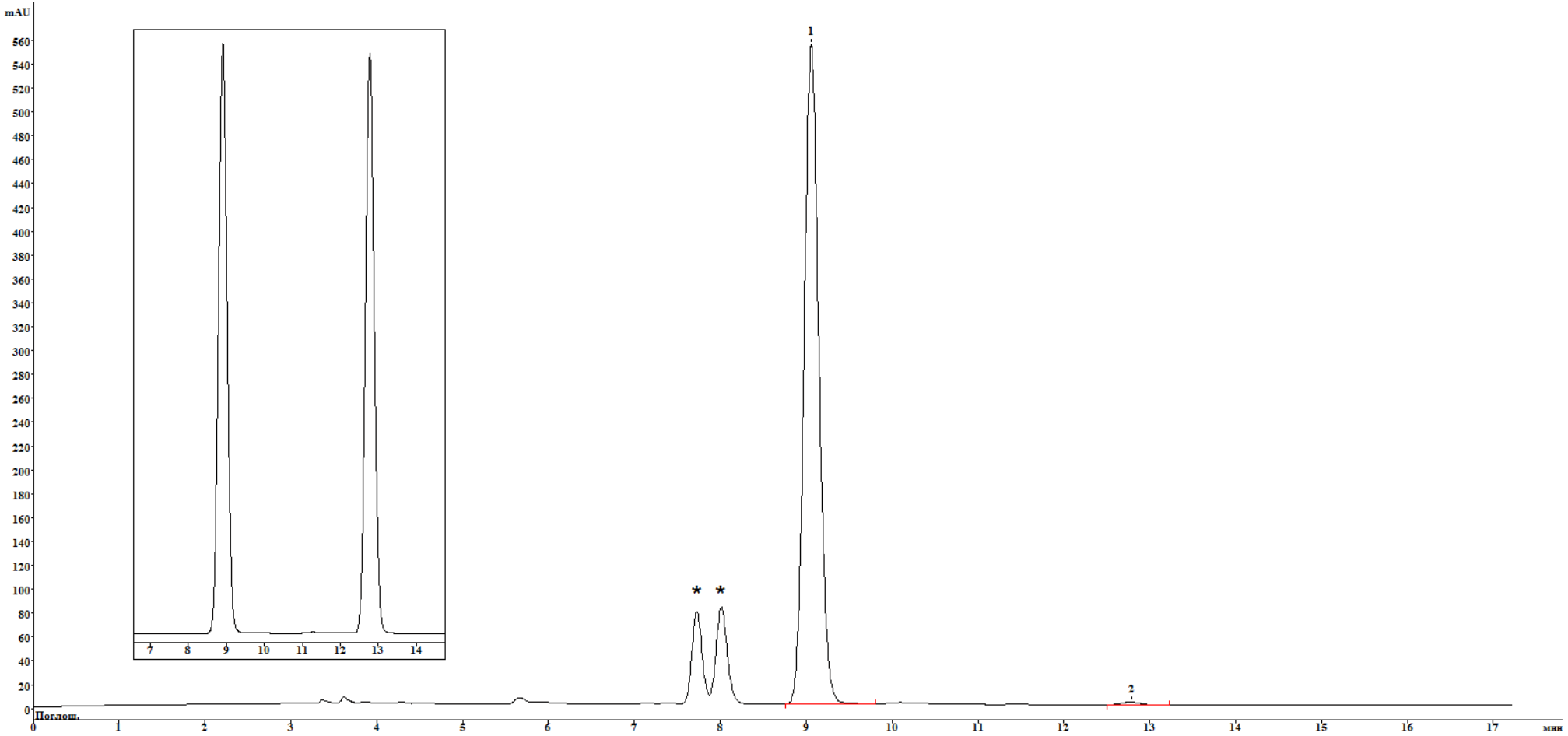
Mixture of **L1f** and [Pd(allyl)(**L1f**)]BF_4, $^{31}P\{^1H\}$ spectrum.

HPLC TRACES



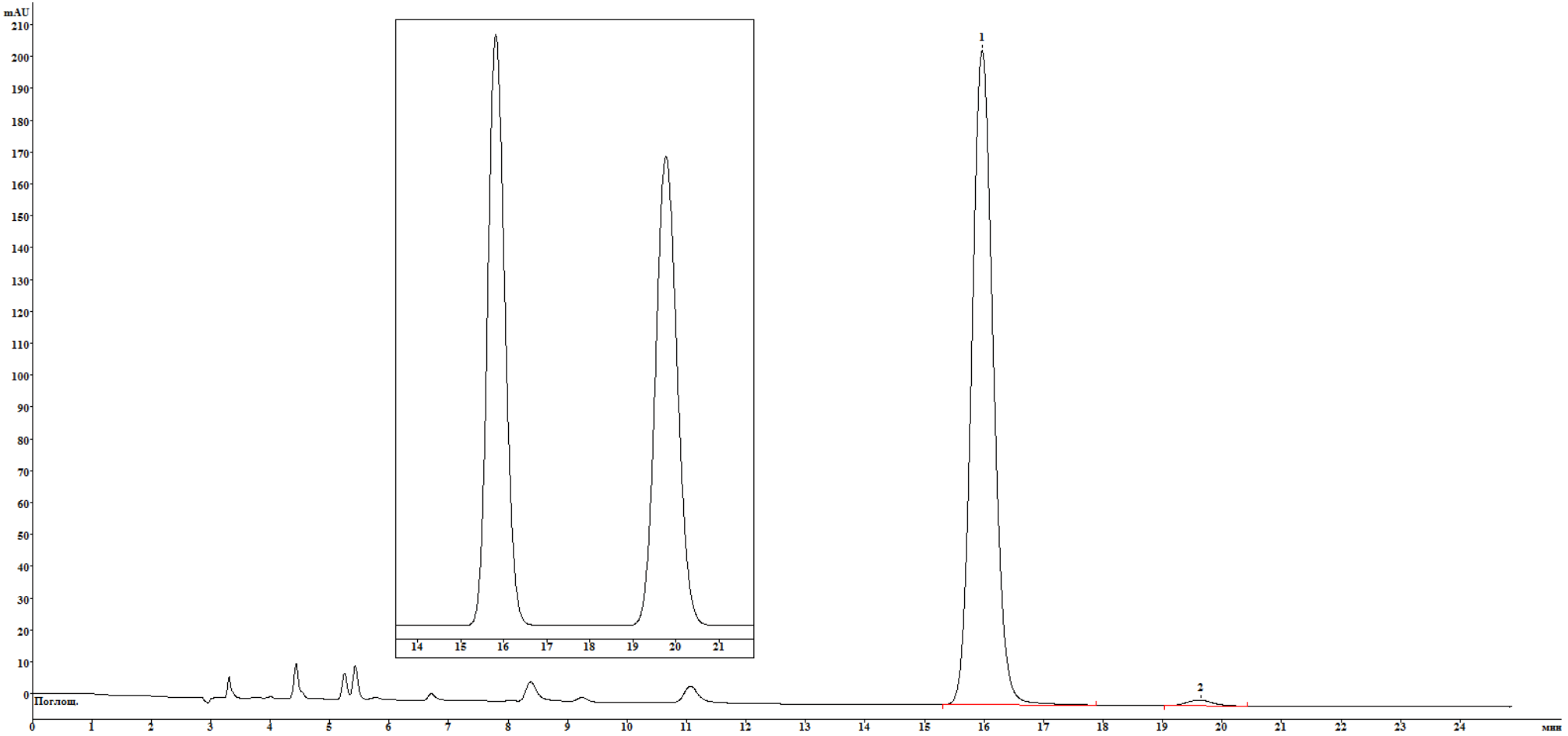
Chiral HPLC trace for the Pd-catalyzed asymmetric allylic alkylation of **10a** with dimethyl malonate (entry 33 in Table S2) and for a racemic mixture of **11a** (in the frame).

HPLC TRACES



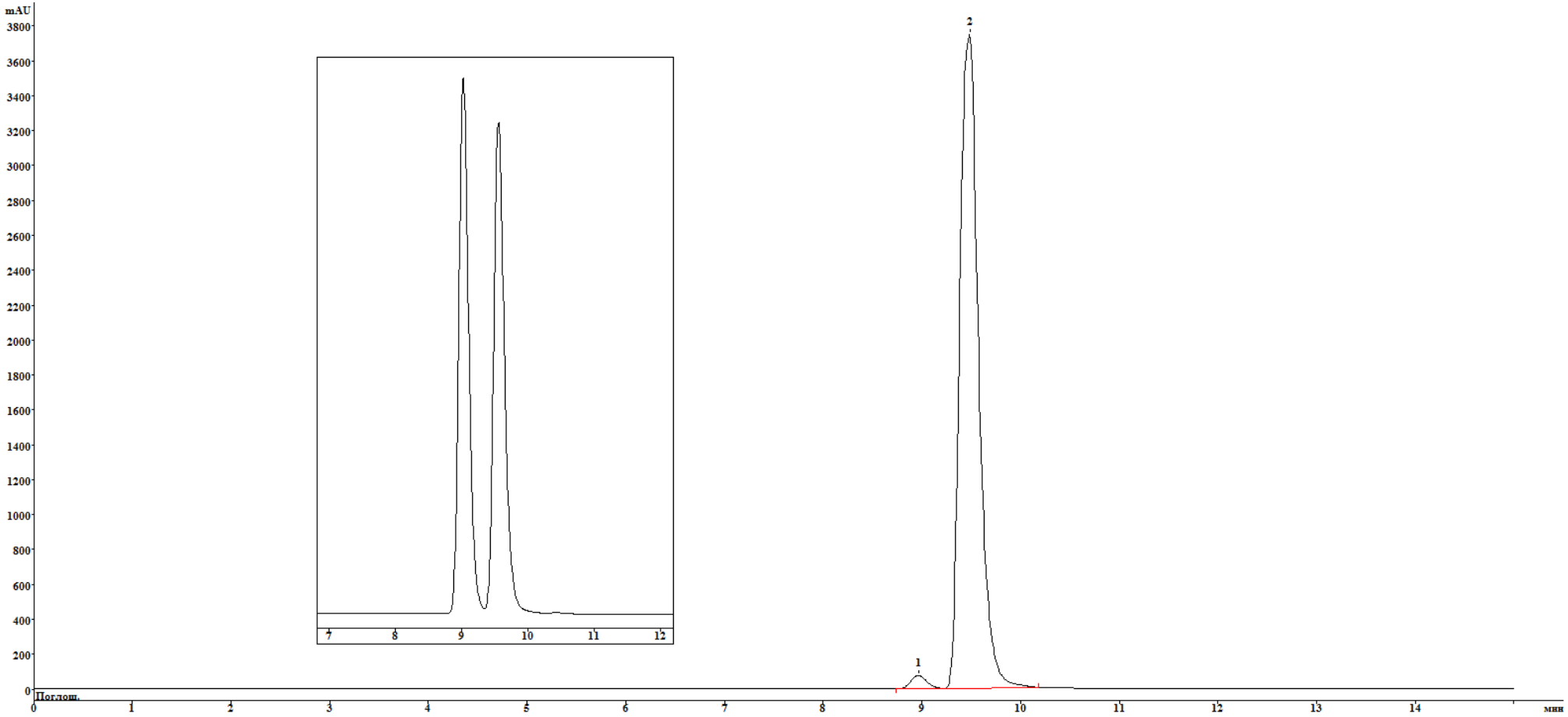
Chiral HPLC trace for the Pd-catalyzed asymmetric allylic alkylation of **10a** with di-*tert*-butyl malonate (entry 35 in Table S2) and for a racemic mixture of **11b** (in the frame).
* starting substrate 10a

HPLC TRACES



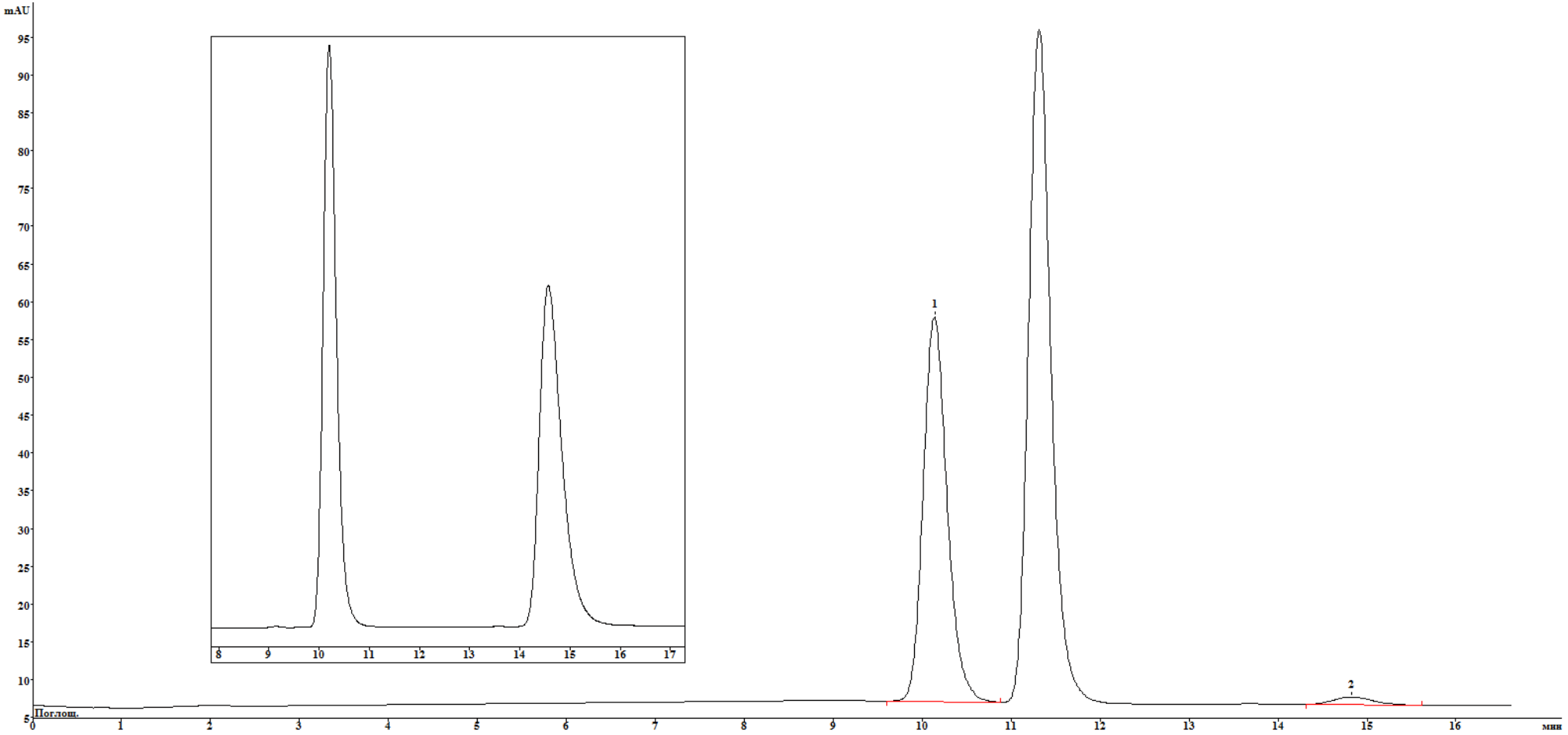
Chiral HPLC trace for the Pd-catalyzed asymmetric allylic alkylation of **10a** with dibenzyl malonate (entry 37 in Table S2) and for a racemic mixture of **11c** (in the frame).

HPLC TRACES



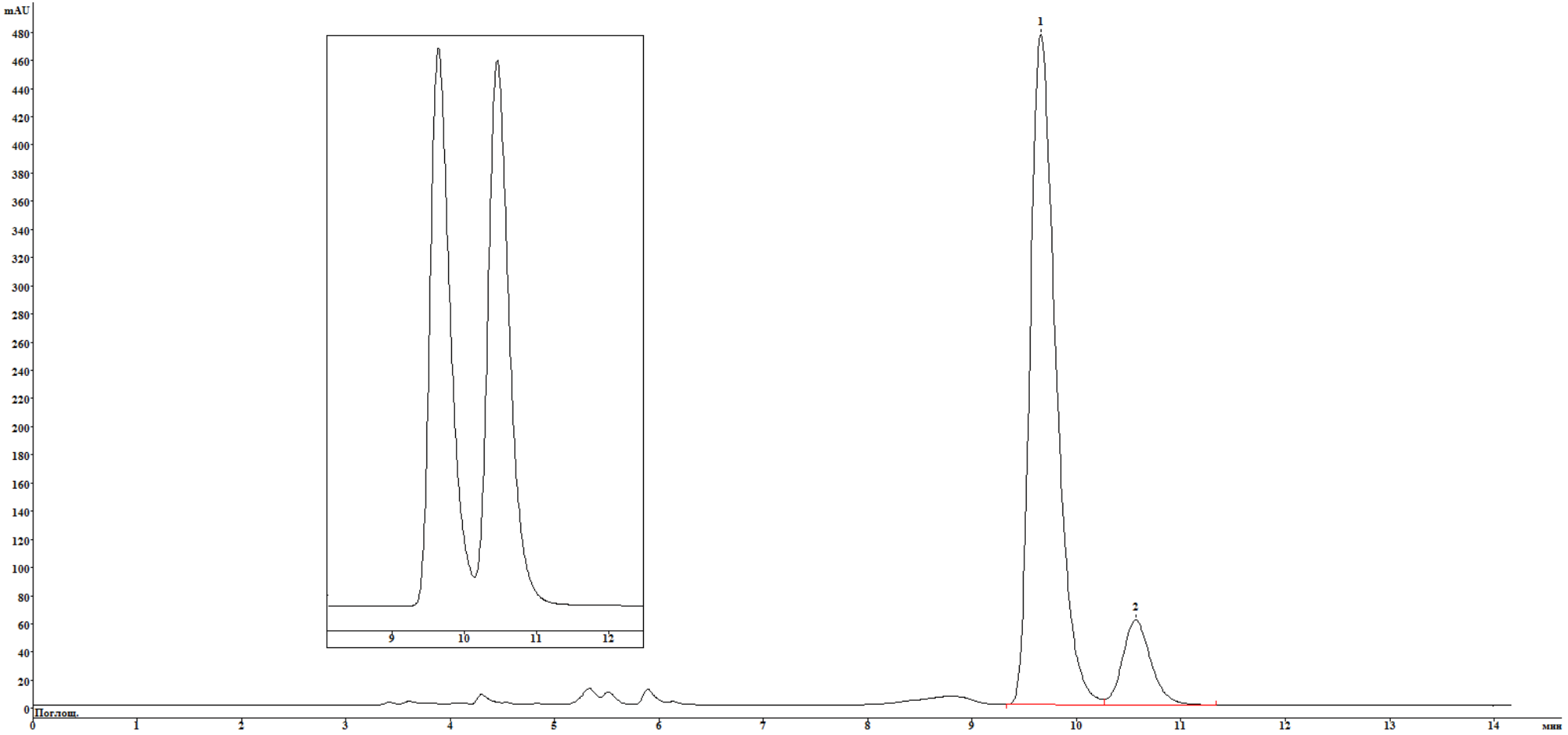
Chiral HPLC trace for the Pd-catalyzed asymmetric allylic amination of **10a** with pyrrolidine (entry 27 in Table S3) and for a racemic mixture of **11d** (in the frame).

HPLC TRACES



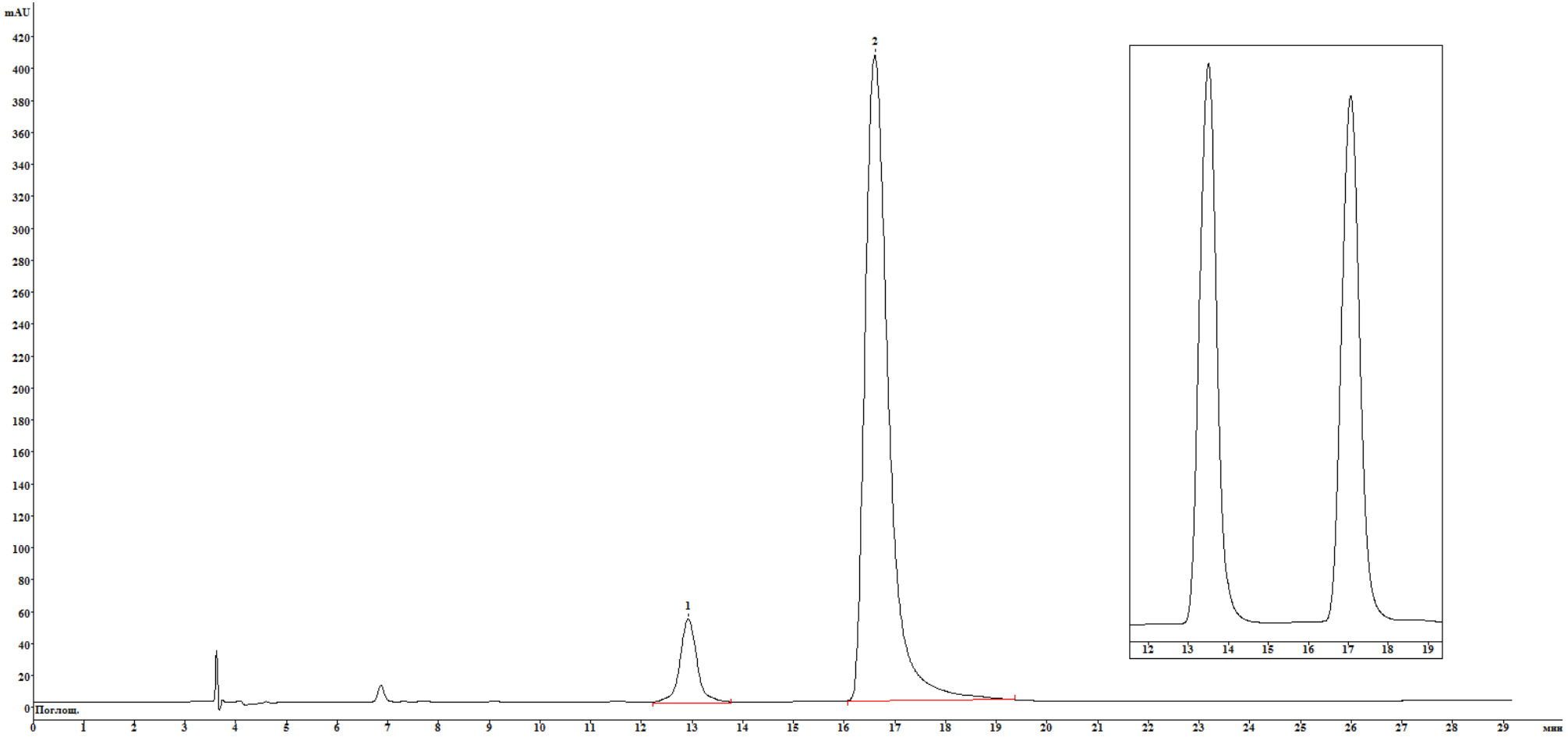
Chiral HPLC trace for the Pd-catalyzed asymmetric allylic alkylation of **12b** with ethyl 2-oxocyclohexane-1-carboxylate (entry 29 in Table S4) and for a racemic mixture of **14** (in the frame).

HPLC TRACES



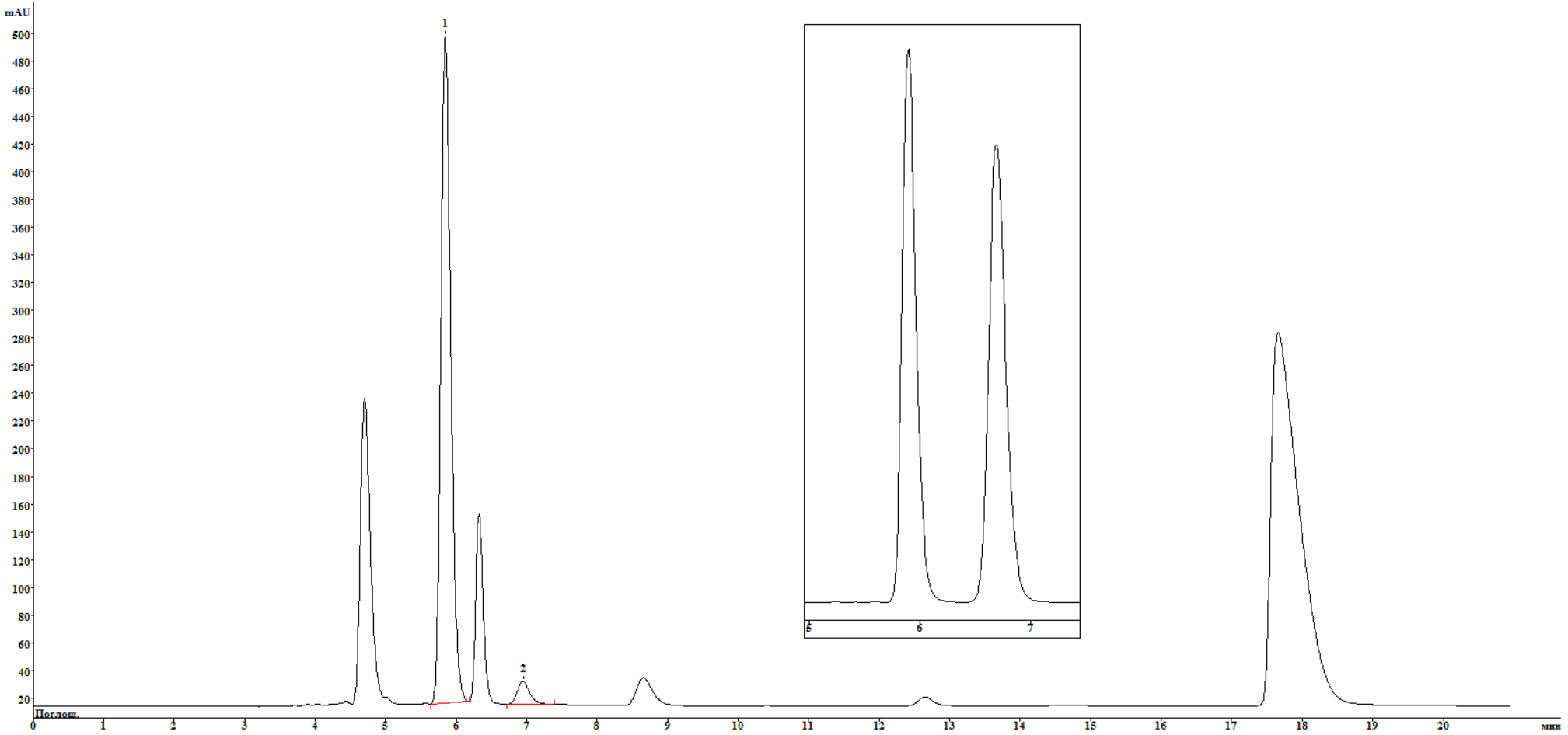
Chiral HPLC trace for the Pd-catalyzed asymmetric allylic alkylation of **12a** with ethyl 2-acetamido-3-oxobutanoate (entry 27 in Table S5) and for a racemic mixture of **16** (in the frame).

HPLC TRACES



Chiral HPLC trace for the Pd-catalyzed asymmetric allylic alkylation of **12b** with 2,5-dimethylpyrrole (entry 36 in Table S6) and for a racemic mixture of **18** (in the frame).

HPLC TRACES



Chiral HPLC trace for the Pd-catalyzed asymmetric allylic amination of **19** with aniline (entry 25 in Table S7) and for a racemic mixture of **20** (in the frame).