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Novel BIPHEN H2 based P,S-bidentate phosphoramidite ligand in palladium-catalyzed asymmetric allylation

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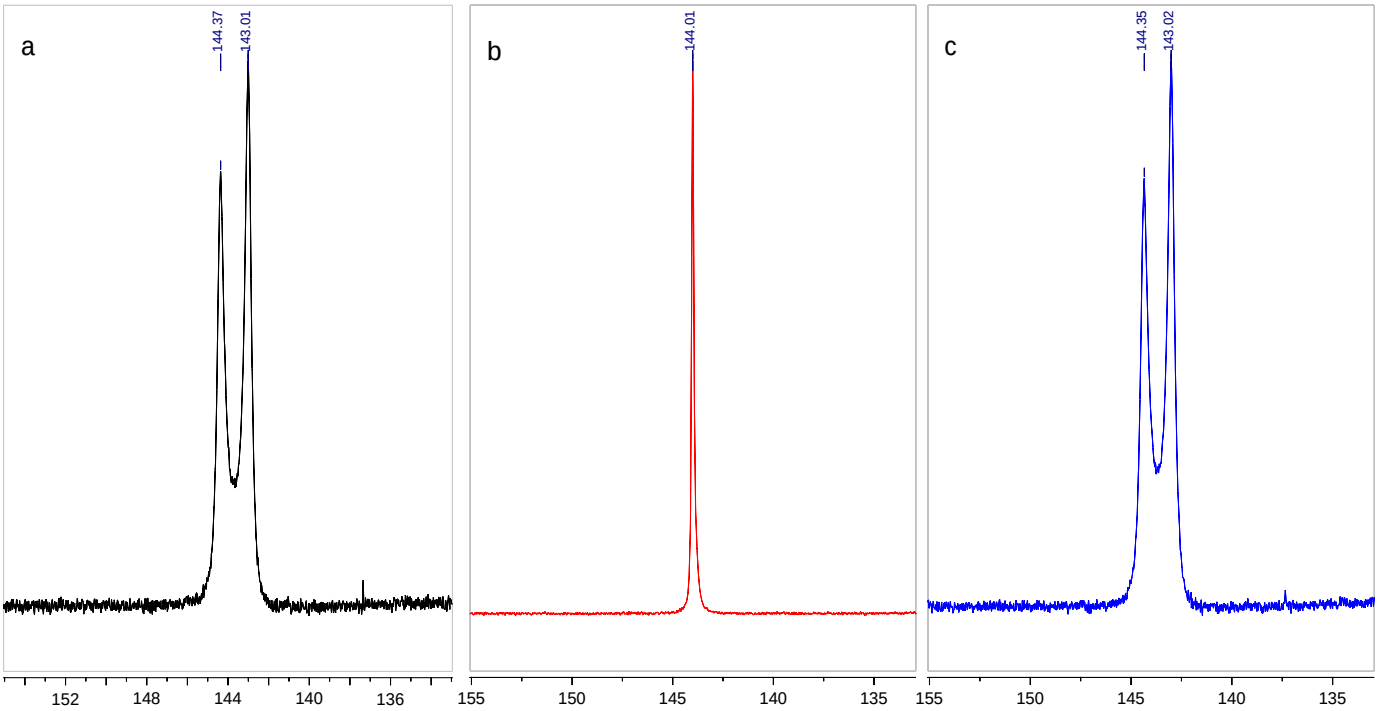


Figure S1 Temperature dependence of the ^{31}P NMR spectra of ligand **1** in d_8 –toluene medium: *a*, at 25 °C; *b*, at 100 °C and *c*, over again at 25 °C.

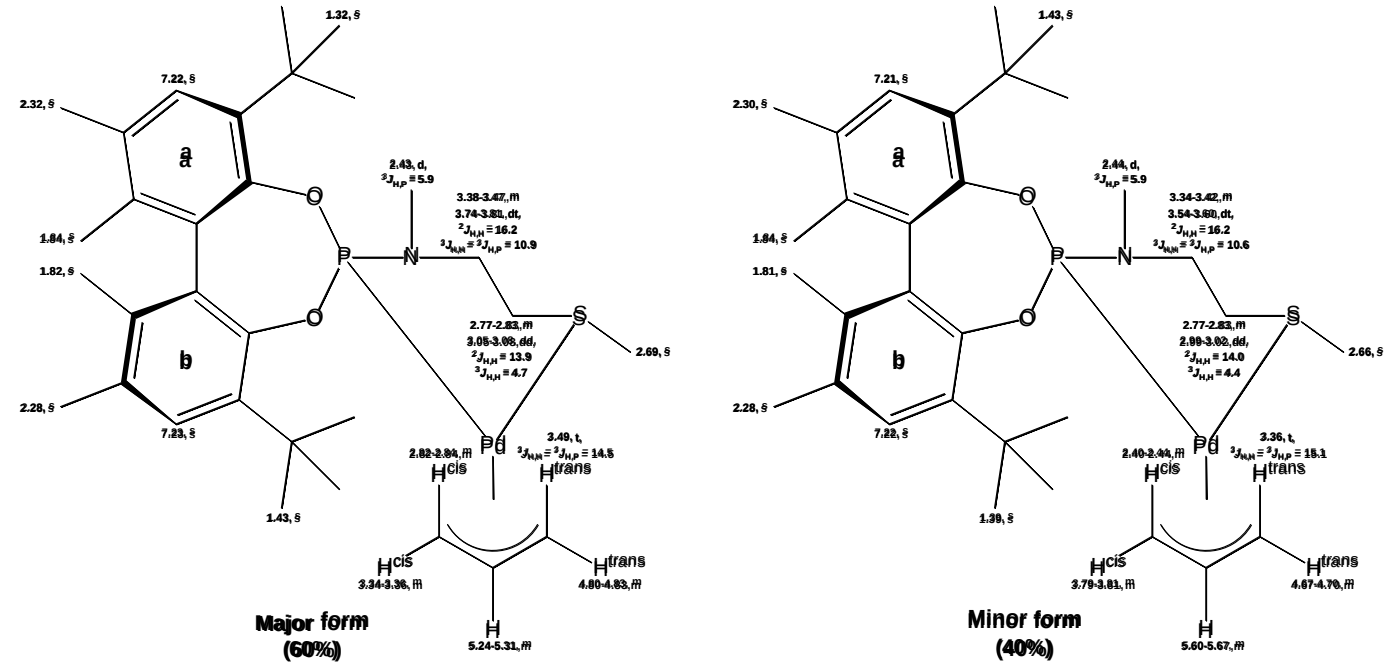


Figure S2 Full assignment of all H-1 resonances for complex **2**.

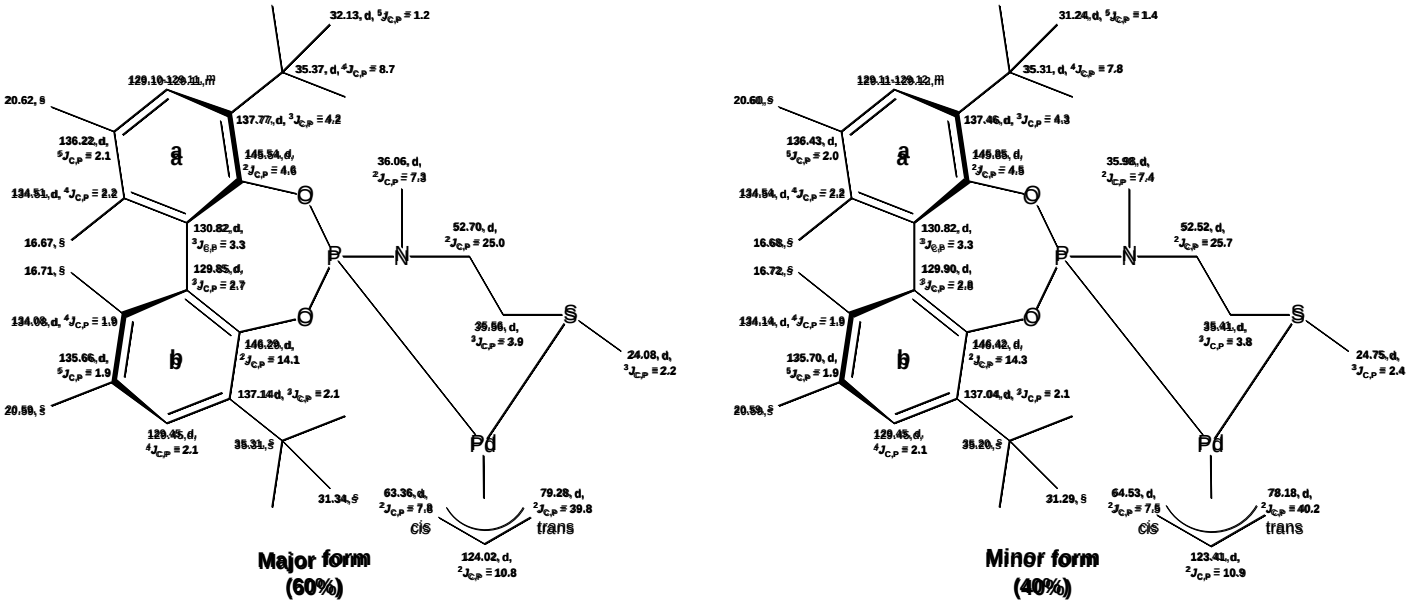


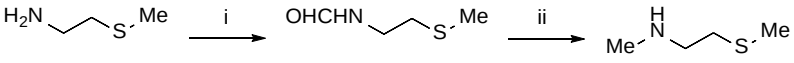
Figure S3 Full assignment of all C-13 resonances for complex **2**.

Experimental Section

General Remarks. ^{31}P, ^{13}C and ^{1}H NMR spectra were recorded with Bruker Avance 400 (400.1 MHz for ^{1}H), Bruker Avance 600 (242.9 MHz for ^{31}P, 150.9 MHz for ^{13}C and 600.1 MHz for ^{1}H) and Varian Inova 500 (202.3 MHz for ^{31}P, 125.7 MHz for ^{13}C and 499.8 MHz for ^{1}H) instruments; the chemical shifts are given in the δ scale relative to 85% H_3PO_4 in D_2O and Me_4Si, respectively. ^{1}H and ^{13}C NMR signals were attributed using DEPT, ^{13}C-^{1}H HSQC, ^{13}C-^{1}H HMBC, ^{1}H-^{1}H COSY and ^{1}H-^{1}H NOESY experiments. Enantiomeric analysis of the products of catalytic reactions was performed with a Staier HPLC system. Elemental analysis was carried out on a Carlo Erba EA1108 CHNS-O CHN analyzer. Mass spectra were recorded with Bruker Daltonix UltrafleXtreme instrument, positive-ion mode using reflection mode with 20 MV voltage.

All reactions were carried out in anhydrous solvents under dry argon. Starting (*E*)-1,3-diphenylallyl acetate (**3a**), (*E*)-1,3-diphenylallyl ethyl carbonate (**3b**), 2-diethoxyphosphoryl-1-phenylallyl acetate (**6**) and precatalyst $[Pd(\pi\text{-allyl})Cl]_2$ were prepared following the known procedures.[S1] Pd-catalyzed allylic alkylation of **3a,b** with dimethyl malonate, di-*tert*-butyl malonate and dibenzyl malonate, theirs amination with pyrrolidine and phthalimide, allylic amination of **6** with aniline were performed according to the appropriate procedures.[S1c,S2]

(R_a)-BIPHEN H2, dimethyl malonate, di-*tert*-butyl malonate, dibenzyl malonate, *N*,*O*-bis(trimethylsilyl) acetamide (BSA), triethylamine, pyrrolidine, phthalimide and aniline were purchased from Fluka and Aldrich.



Scheme S1 *Reagents and conditions*: i, HCO_2Et, reflux; ii, $LiAlH_4$, THF.

***N*-(2-Methylthioethyl)formamide.** A solution of 2-(methylthio)ethan-1-amine (3.72 ml, 40 mmol) in ethyl formate (30 ml) was refluxed for 6 h. The resulting solution was concentrated under reduced pressure (40 Torr), and the residue was purified by bulb-to-bulb vacuum distillation. Yield 4.43 g (93%), light yellow oil, b.p. 149-150 °C (bath, 3 Torr). ^{1}H NMR (400.1 MHz, $CDCl_3$, 27 °C): δ = 2.11 (s, 3H; CH_3), 2.64-2.68 (m, 2H; CH_2), 3.49-3.53 (m, 2H; CH_2), 6.13 (br.s, 1H; NH), 8.19 (s, 1H; CHO) ppm. Calcd for C_4H_9NOS: C, 40.31; H, 7.61; N, 11.75. Found: C, 40.44; H, 7.66; N, 11.81.

***N*-Methyl-2-(methylthio)ethan-1-amine.** To a cold suspension of $LiAlH_4$ (1.71 g, 45 mmol) in THF (50 ml), *N*-(2-(methylthio)ethyl)formamide (3.58 g, 30 mmol) was added. 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. Yield 3.0 g (95%), colorless oil, b. p. 150 °C (bath, 6 Torr). ^{1}H NMR (400.1 MHz, $CDCl_3$, 27 °C): δ = 1.65 (br.s, 1H; NH), 2.06 (s, 3H; CH_3), 2.41 (s, 3H; CH_3), 2.62 (t, ^{3}J(H,H) = 6.4 Hz, 2H; CH_2), 2.75 (t, ^{3}J(H,H) = 6.4 Hz, 2H; CH_2) ppm. Calcd for $C_4H_{11}NS$: C, 45.67; H, 10.54; N, 13.31. Found: C, 45.85; H, 10.60; N, 13.20.

(R_a)-6-[*N*-Methyl-*N*-(2-methylthioethyl)amino]-4,8-di-*tert*-butyl-1,2,10,11-tetramethyldibenzo-[*d,f*][1,3,2]dioxaphosphepine (1). To a vigorously stirred suspension of (R_a)-BIPHEN H2 (0.89 g, 2.5 mmol) in PCl_3 (5 ml, 57.5 mmol), *N*-methyl-2-pyrrolidone (0.01 g, 0.1 mmol) was added, and the mixture was refluxed for 2 h until homogenous. The PCl_3 excess was removed under reduced pressure (40 Torr), the residue was dried in vacuum (30 min, 10^{-3} Torr) to remove the PCl_3 traces and then dissolved in toluene (15 ml). The obtained vigorously stirred solution was treated with Et_3N (0.7 ml, 5 mmol) and *N*-methyl-2-(methylthio)ethan-1-amine (0.26 g, 2.5 mmol) at 20 °C. The reaction mixture was stirred for 24 h at 20 °C, then heated to 40 °C, stirred at this temperature for 1 h, and cooled to 20 °C. The resulting suspension was filtered through a short plug of Al_2O_3/SiO_2, the column was washed twice with toluene (15 ml), and the solvent was evaporated under reduced pressure (40 Torr). The obtained substance was dried in vacuum (10^{-3} Torr). Yield 1.12 g (92%), white powder. ^{1}H NMR (600.1 MHz, d_8 –toluene, 100 °C): δ = 1.44 (br.s, 9 H), 1.53 (br.s, 9 H), 1.68 (br.s, 3 H), 1.74 (br.s, 3 H), 1.81 (br.s, 3 H), 2.00-2.17 (br.m, 7 H), 2.22-2.43 (br.m, 4 H), 2.75-3.03 (br.m, 2 H), 7.14 (br.s, 2H) ppm. ^{13}C{^{1}H} NMR (125.7 MHz, $CDCl_3$, ambient temperature): δ = 14.81 (br.s; $CH_2S\underline{C}H_3$), 16.32 (s; CH_3), 16.56 (s; CH_3), 20.24 (s; CH_3), 20.31 (s; CH_3), 30.94 (s; CH_3(*t*-Bu)), 31.40 (s; CH_3(*t*-Bu)), 31.44 (s; CH_3(*t*-Bu)), 32.27, (br.s; $\underline{C}H_2SCH_3$), 34.63 (s; C(*t*-Bu)), 34.73 (s; C(*t*-Bu)), 48.08 (br.s; $\underline{C}H_2NCH_3$), 127.62 (s; CH(Ar)), 127.86 (br.s; CH(Ar)), 130.67 (s; C(Ar)), 130.95 (d, ^{3}J(C,P) = 2.5 Hz; C(Ar)), 131.81 (s; C(Ar)), 131.83 (d, ^{3}J(C,P) = 4.3 Hz; C(Ar)), 133.90 (s; C(Ar)), 134.55 (s; C(Ar)), 136.96 (br.s; C(Ar)), 137.96 (d, ^{3}J(C,P) = 2.7 Hz; C(Ar)), 146.53 (d, ^{2}J(C,P) = 5.3 Hz; C(Ar)), 147.42 (br.s; C(Ar)) ppm. ^{31}P{^{1}H} NMR (242.9 MHz, d_8 –toluene, 25 °C): δ = 143.02 (br.s), 144.35 (br.s), ppm. Calcld. for $C_{28}H_{42}NO_2PS$: C, 68.96; H, 8.68; N, 2.87. Found: C, 69.21; H, 8.75; N, 2.80.

[Pd(π-allyl)(1)]BF_4 (2). A solution of ligand **1** (98 mg, 0.2 mmol) in THF (2 ml) was added dropwise over 30 min to a stirred solution of [Pd(π-allyl)Cl]$_2$ (37 mg, 0.1 mmol) in THF (1 ml) at 20 °C. The mixture was stirred at 20 °C for 1 h. Solid $AgBF_4$ (39 mg, 0.2 mmol) was added to the resulting solution, and the mixture was stirred at 20 °C for 1.5 h. The precipitate of the complex and AgCl was separated by centrifugation and washed with THF (2 x 10 mL). The crude material was dissolved in CH_2Cl_2, and then the precipitate of AgCl was separated by centrifugation. The solvent was removed in vacuum (40 Torr), and the product was dried in air and in vacuum (10^{-3} Torr). White powder, yield 130 mg (90%). ^{1}H NMR (600.1 MHz, CD_2Cl_2, 25 °C): δ = 1.32 (s, 9H; CH_3(*t*-Bu)^{a}), 1.43 (s, 9H; CH_3(*t*-Bu)^{b}), 1.82 (s, 3H; $CCH_3{}^{b}$), 1.84 (s, 3H; $CCH_3{}^{a}$), 2.28 (s, 3H; $CHCC\underline{H}_3{}^{b}$), 2.32 (s, 3H; $CHCC\underline{H}_3{}^{a}$), 2.43 (d, ^{3}J(H,P) = 5.9 Hz, 3H; $CH_2NC\underline{H}_3$), 2.69 (s, 3H; $CH_2SC\underline{H}_3$), 2.77-2.83 (m, 1H; $C\underline{H}_2SCH_3$), 2.82-2.84 (m, 1H; $CH_2(allyl_{anti})^{cis}$), 3.05-3.08 (dd,

^{2}J(H,H) = 13.9 Hz, ^{3}J(H,H) = 4.7 Hz, 1H; C$\underline{H}_2$SCH$_3$), 3.34-3.36 (m, 1H; CH$_2$(allyl$_{syn}$)^{cis}), 3.38-3.47 (m, 1H; C$\underline{H}_2$NCH$_3$), 3.49 (t, ^{3}J(H,H) = ^{3}J(H,P) =14.5 Hz, 1H; CH$_2$(allyl$_{anti}$)^{trans}), 3.74-3.81 (dt, (d, ^{2}J(H,H) = 16.2 Hz, ^{3}J(H,H) = ^{3}J(H,P) =10.9 Hz, 1H; C$\underline{H}_2$NCH$_3$), 4.80-4.83 (m, 1H; CH$_2$(allyl$_{syn}$)^{trans}), 5.24-5.31 (m, 1H; CH(allyl)), 7.22 (s, 1H; C$\underline{H}$CCH$_3^{a}$), 7.23 (s, 1H; C$\underline{H}$CCH$_3^{b}$) (major form), 1.39 (s, 9H; CH$_3$(*t*-Bu)^{b}), 1.43 (s, 9H; CH$_3$(*t*-Bu)^{a}), 1.81 (s, 3H; CCH$_3^{b}$), 1.84 (s, 3H; CCH$_3^{a}$), 2.28 (s, 3H; CHCC$\underline{H}_3^{b}$), 2.30 (s, 3H; CHCC$\underline{H}_3^{a}$), 2.40-2.44 (m, 1H; CH$_2$(allyl$_{anti}$)^{cis}), 2.44 (d, ^{3}J(H,P) = 5.9 Hz, 3H; CH$_2$NC$\underline{H}_3$), 2.66 (s, 3H; CH$_2$SC$\underline{H}_3$), 2.77-2.83 (m, 1H; C$\underline{H}_2$SCH$_3$), 2.99-3.02 (dd, (d, ^{2}J(H,H) = 14.0 Hz, ^{3}J(H,H) = 4.4 Hz, 1H; C$\underline{H}_2$SCH$_3$), 3.34-3.42 (m, 1H; C$\underline{H}_2$NCH$_3$), 3.36 (t, ^{3}J(H,H) = ^{3}J(H,P) =15.1 Hz, 1H; CH$_2$(allyl$_{anti}$)^{trans}), 3.54-3.60 (dt, (d, ^{2}J(H,H) = 16.2 Hz, ^{3}J(H,H) = ^{3}J(H,P) =10.6 Hz, 1H; C$\underline{H}_2$NCH$_3$), 3.79-3.81 (m, 1H; CH$_2$(allyl$_{syn}$)^{cis}), 4.67-4.70 (m, 1H; CH$_2$(allyl$_{syn}$)^{trans}), 5.60-5.67 (m, 1H; CH(allyl)), 7.21 (s, 1H; C$\underline{H}$CCH$_3^{a}$), 7.22 (s, 1H; C$\underline{H}$CCH$_3^{b}$) (minor form) ppm. ^{13}C{^{1}H} NMR (150.9 MHz, CD_2Cl_2, 25 °C): δ = 16.67 (s; C$\underline{C}$H$_3^{a}$), 16.71 (s; C$\underline{C}$H$_3^{b}$), 20.59 (s; CHC$\underline{C}$H$_3^{b}$), 20.62 (s; CHC$\underline{C}$H$_3^{a}$), 24.08 (d, ^{3}J(C,P) = 2.2 Hz; CH$_2$S$\underline{C}$H$_3$), 31.34 (s; CH$_3$(*t*-Bu)^{b}), 32.13 (d, ^{5}J(C,P) = 1.2 Hz; CH$_3$(*t*-Bu)^{a}), 35.31 (s; C(*t*-Bu)^{b}), 35.37 (d, ^{4}J(C,P) = 8.7 Hz; C(*t*-Bu)^{a}), 35.56, (d, ^{3}J(C,P) = 3.9 Hz; $\underline{C}$H$_2$SCH$_3$), 36.06 (d, ^{2}J(C,P) = 7.3 Hz; CH$_2$N$\underline{C}$H$_3$), 52.70 (d, ^{2}J(C,P) = 25.0 Hz; $\underline{C}$H$_2$NCH$_3$), 63.36 (d, ^{2}J(C,P) = 7.8 Hz; CH$_2$(allyl)^{cis}), 79.28 (d, ^{2}J(C,P) = 39.8 Hz; CH$_2$(allyl)^{trans}), 124.02 (d, ^{2}J(C,P) = 10.8 Hz; CH(allyl)), 129.10-129.11 (m; $\underline{C}$HCCH$_3^{a}$), 129.45 (d, ^{4}J(C,P) = 2.1 Hz; $\underline{C}$HCCH$_3^{b}$), 129.85 (d, ^{3}J(C,P) = 2.7 Hz; C^{b}), 130.82 (d, ^{3}J(C,P) = 3.3 Hz; C^{a}), 134.08 (d, ^{4}J(C,P) = 1.9 Hz; $\underline{C}$CH$_3^{b}$), 134.51 (d, ^{4}J(C,P) = 2.2 Hz; $\underline{C}$CH$_3^{a}$), 135.66 (d, ^{5}J(C,P) = 1.9 Hz; CH$\underline{C}$CH$_3^{b}$), 136.22 (d, ^{5}J(C,P) = 2.1 Hz; CH$\underline{C}$CH$_3^{a}$), 137.14 (d, ^{3}J(C,P) = 2.1 Hz; *t*-Bu$\underline{C}^{b}$), 137.77 (d, ^{3}J(C,P) = 4.2 Hz; *t*-Bu$\underline{C}^{a}$), 145.54 (d, ^{2}J(C,P) = 4.6 Hz; O$\underline{C}^{a}$), 146.29 (d, ^{2}J(C,P) = 14.1 Hz; O$\underline{C}^{b}$) (major form), 16.68 (s; C$\underline{C}$H$_3^{a}$), 16.72 (s; C$\underline{C}$H$_3^{b}$), 20.59 (s; CHC$\underline{C}$H$_3^{b}$), 20.60 (s; CHC$\underline{C}$H$_3^{a}$), 24.75 (d, ^{3}J(C,P) = 2.4 Hz; CH$_2$S$\underline{C}$H$_3$), 31.24 (d, ^{5}J(C,P) = 1.4 Hz; CH$_3$(*t*-Bu)^{a}), 31.29 (s; CH$_3$(*t*-Bu)^{b}), 35.20 (s; C(*t*-Bu)^{b}), 35.31 (d, ^{4}J(C,P) = 7.8 Hz; C(*t*-Bu)^{a}), 35.41, (d, ^{3}J(C,P) = 3.8 Hz; $\underline{C}$H$_2$SCH$_3$), 35.98 (d, ^{2}J(C,P) = 7.4 Hz; CH$_2$N$\underline{C}$H$_3$), 52.52 (d, ^{2}J(C,P) = 25.7 Hz; $\underline{C}$H$_2$NCH$_3$), 64.53 (d, ^{2}J(C,P) = 7.5 Hz; CH$_2$(allyl)^{cis}), 78.18 (d, ^{2}J(C,P) = 40.2 Hz; CH$_2$(allyl)^{trans}), 123.41 (d, ^{2}J(C,P) = 10.9 Hz; CH(allyl)), 129.11-129.12 (m; $\underline{C}$HCCH$_3^{a}$), 129.45 (d, ^{4}J(C,P) = 2.1 Hz; $\underline{C}$HCCH$_3^{b}$), 129.90 (d, ^{3}J(C,P) = 2.8 Hz; C^{b}), 130.82 (d, ^{3}J(C,P) = 3.3 Hz; C^{a}), 134.14 (d, ^{4}J(C,P) = 1.9 Hz; $\underline{C}$CH$_3^{b}$), 134.54 (d, ^{4}J(C,P) = 2.2 Hz; $\underline{C}$CH$_3^{a}$), 135.70 (d, ^{5}J(C,P) = 1.9 Hz; CH$\underline{C}$CH$_3^{b}$), 136.43 (d, ^{5}J(C,P) = 2.0 Hz; CH$\underline{C}$CH$_3^{a}$), 137.04 (d, ^{3}J(C,P) = 2.1 Hz; *t*-Bu$\underline{C}^{b}$), 137.46 (d, ^{3}J(C,P) = 4.3 Hz; *t*-Bu$\underline{C}^{a}$), 145.85 (d, ^{2}J(C,P) = 4.5 Hz; O$\underline{C}^{a}$), 146.42 (d, ^{2}J(C,P) = 14.3 Hz; O$\underline{C}^{b}$) (minor form) ppm. ^{31}P{^{1}H} NMR (242.9 MHz, $CDCl_3$, 25 °C): δ = 127.65 (s) (major form), 128.07 (s) (minor form) ppm. MALDI-TOF MS (*m/z*, Da): [Pd(π-allyl)(**1**)]$^{+}$ = 634. Calcd. for $C_{31}H_{47}BF_4NO_2PPdS$: C 51.57, H 6.56, N 1.94. Found C 51.72, H 6.60, N 1.88.

Palladium-catalyzed asymmetric allylic alkylation of (*E*)-1,3-diphenylallyl acetate (3a) with malonates: A solution of $[Pd(\pi\text{-allyl})Cl]_2$ (1 mg, 0.0025 mmol) and ligand **1** (2.4 mg, 0.005 mmol or 4.8 mg, 0.01 mmol) in appropriate solvent (1.5 ml) was stirred for 40 min or the cationic complex **2** (3.6 mg, 0.005 mmol) was dissolved in the appropriate solvent (1.5 ml). (*E*)-1,3-Diphenylallyl acetate (**3a**) (0.05 ml, 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 (2 mg) were added. The mixture was stirred at ~20°C for 24 h, diluted with CH_2Cl_2 (2 ml) and filtered through a thin layer of SiO_2. The filtrate was evaporated under reduced pressure (40 Torr) and dried in vacuum (10^{-3} Torr) affording a residue containing dimethyl (*E*)-2-(1,3-diphenylallyl)malonate (**4a**), di-*tert*-butyl (*E*)-2-(1,3-diphenylallyl)malonate (**4b**) or dibenzyl (*E*)-2-(1,3-diphenylallyl)malonate (**4c**).[S3] In order to evaluate *ee* and conversion, the obtained residue was dissolved in an appropriate eluent mixture (8 ml) and the sample was taken for HPLC analysis.

Palladium-catalyzed asymmetric allylic amination of (*E*)-1,3-diphenylallyl acetate (3a) or (*E*)-1,3-diphenylallyl ethyl carbonate (3b) with pyrrolidine and phthalimide: A solution of $[Pd(\pi\text{-allyl})Cl]_2$ (1 mg, 0.0025 mmol) and ligand **1** (2.4 mg, 0.005 mmol or 4.8 mg, 0.01 mmol) in the appropriate solvent (1.5 ml) was stirred for 40 min, or cationic complex **2** (3.6 mg, 0.005 mmol) was dissolved in the appropriate solvent (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) or phthalimide (45 mg, 0.3 mmol) and K_2CO_3 (83 mg, 0.6 mmol) were added. The mixture was stirred at ~20°C for 24 h, diluted with CH_2Cl_2 (2 ml) and filtered through a thin layer of SiO_2. The filtrate was evaporated under reduced pressure (40 Torr) and dried in vacuum (10^{-3} Torr) affording a residue containing (*E*)-1-(1,3-diphenylallyl)pyrrolidine (**5a**) or (*E*)-2-(1,3-diphenylallyl)isoindoline-1,3-dione (**5b**).[S2c,S4] In order to evaluate *ee* and conversion, the obtained residue was dissolved in an appropriate eluent mixture (8 ml), and the sample was taken for HPLC analysis.

Palladium-catalyzed asymmetric allylic amination of 2-diethoxyphosphoryl-1-phenylallyl acetate with aniline: A solution of $[Pd(\pi\text{-allyl})Cl]_2$ (1 mg, 0.0025 mmol) and ligand **1** (2.4 mg, 0.005 mmol or 4.8 mg, 0.01 mmol) in CH_2Cl_2 (1.5 ml) was stirred for 40 min. Alternatively, cationic complex **2** (3.6 mg, 0.005 mmol) was dissolved in CH_2Cl_2 (1.5 ml). 2-Diethoxyphosphoryl-1-phenylallyl acetate (**6**) (80 mg, 0.25 mmol) was added, and the solution was stirred for 15 min, then freshly distilled aniline (0.05 ml, 0.5 mmol) and K_2CO_3 (69 mg, 0.5 mmol) were added. The mixture was stirred at ~20°C 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 (**7**), diethyl (*E*)-(1-phenyl-3-(phenylamino)prop-1-en-2-yl)phosphonate (**8**) and (*E*)-2-(diethoxyphosphoryl)-3-phenylallyl acetate (**9**).[S1c] Conversion of **6** and the **7**/**8**/**9** ratio 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 the sample was taken for HPLC analysis.

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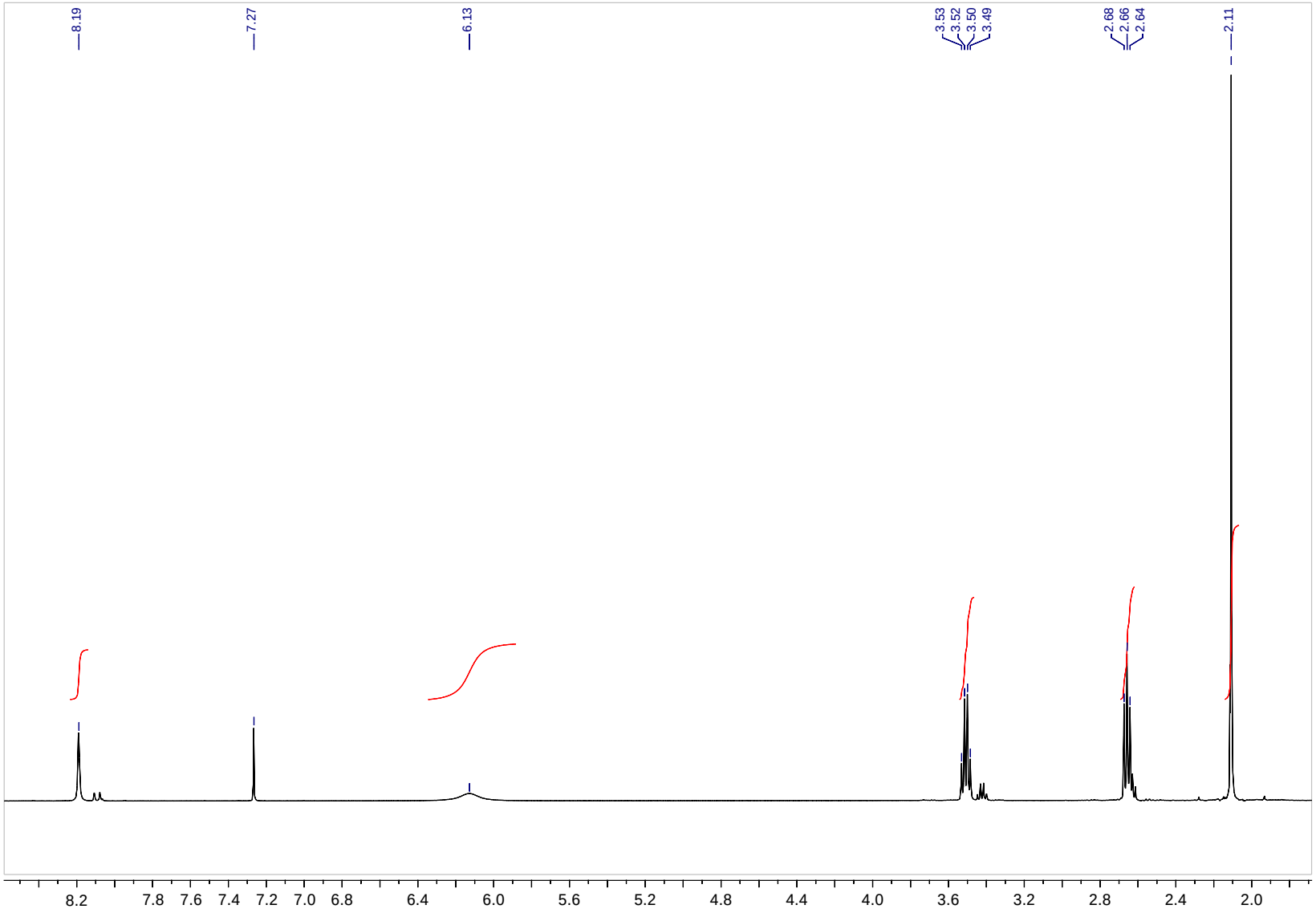
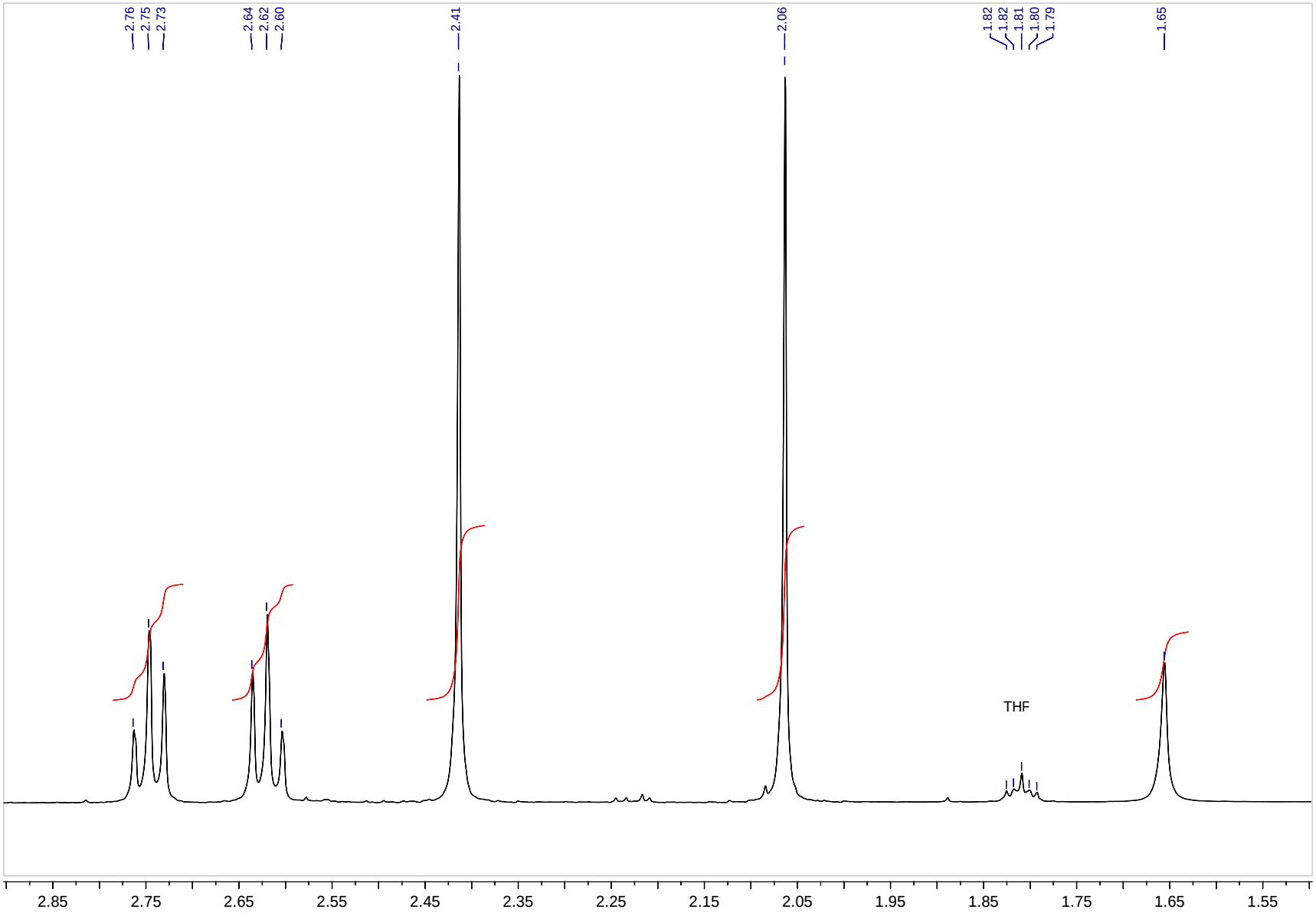
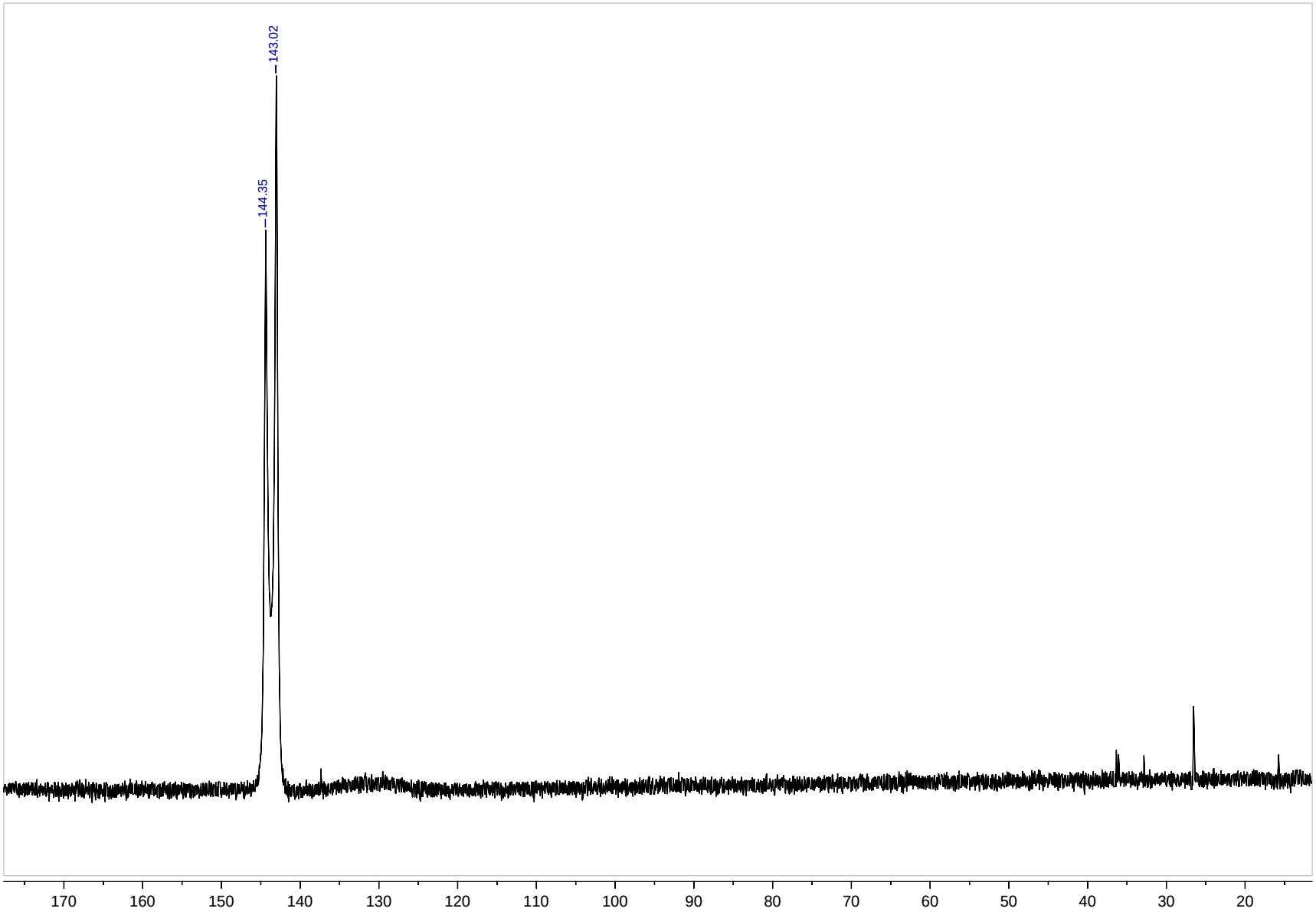


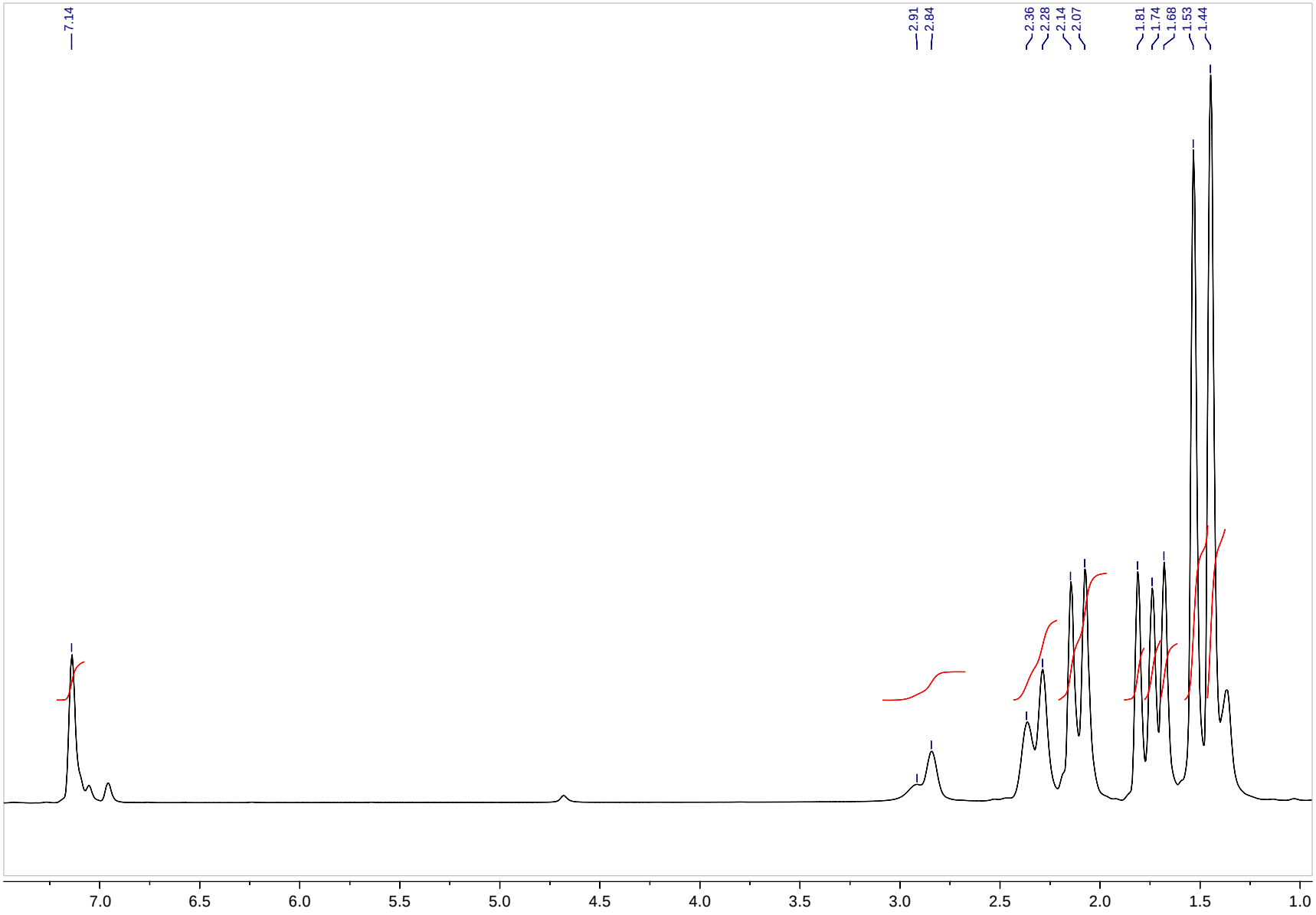
***N*-(2-Methylthioethyl)formamide, ^{1}H (400.1 MHz, $CDCl_3$, 27 °C)**



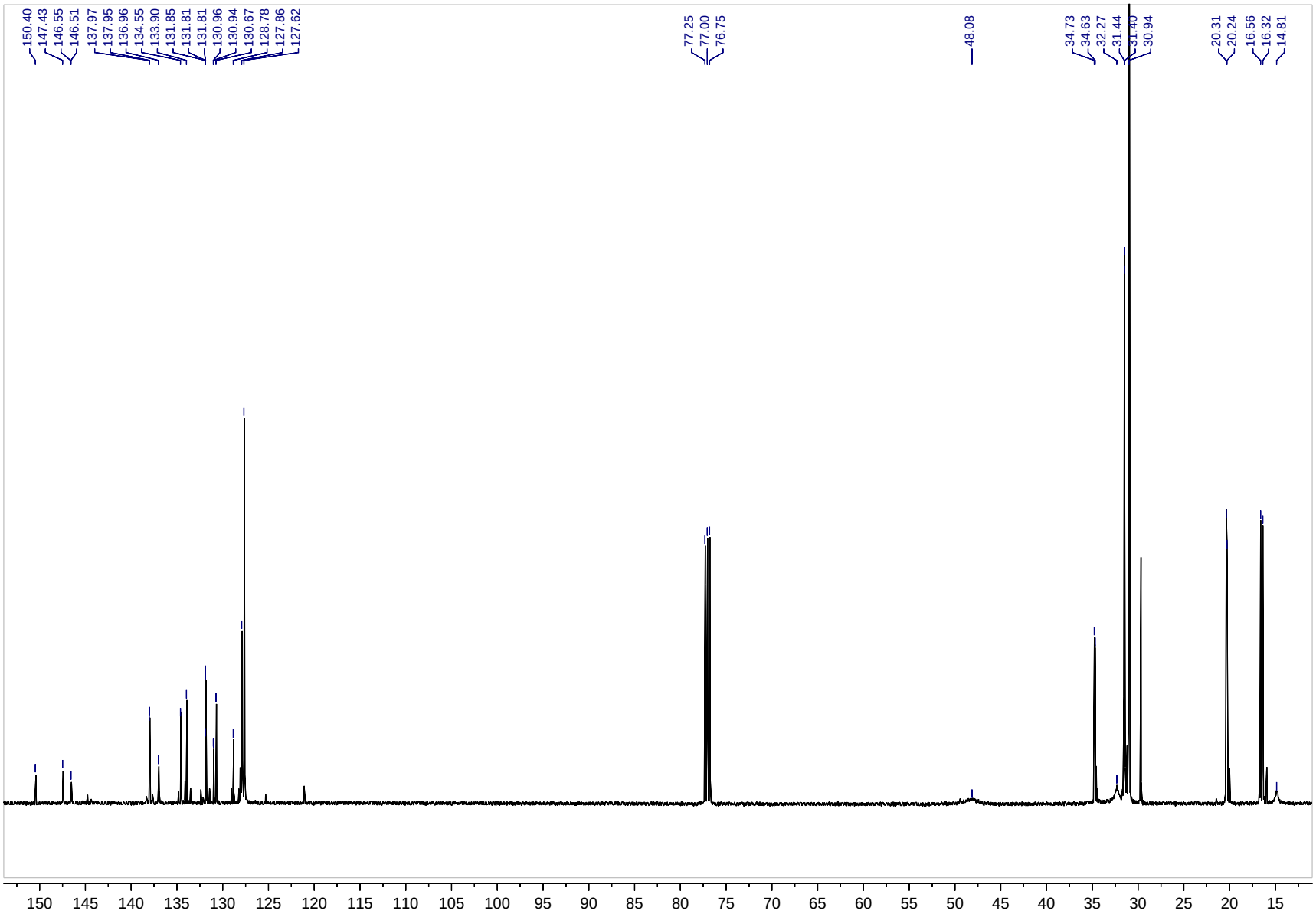
***N*-Methyl-2-(methylthio)ethan-1-amine, ^{1}H (400.1 MHz, $CDCl_3$, 27 °C)**



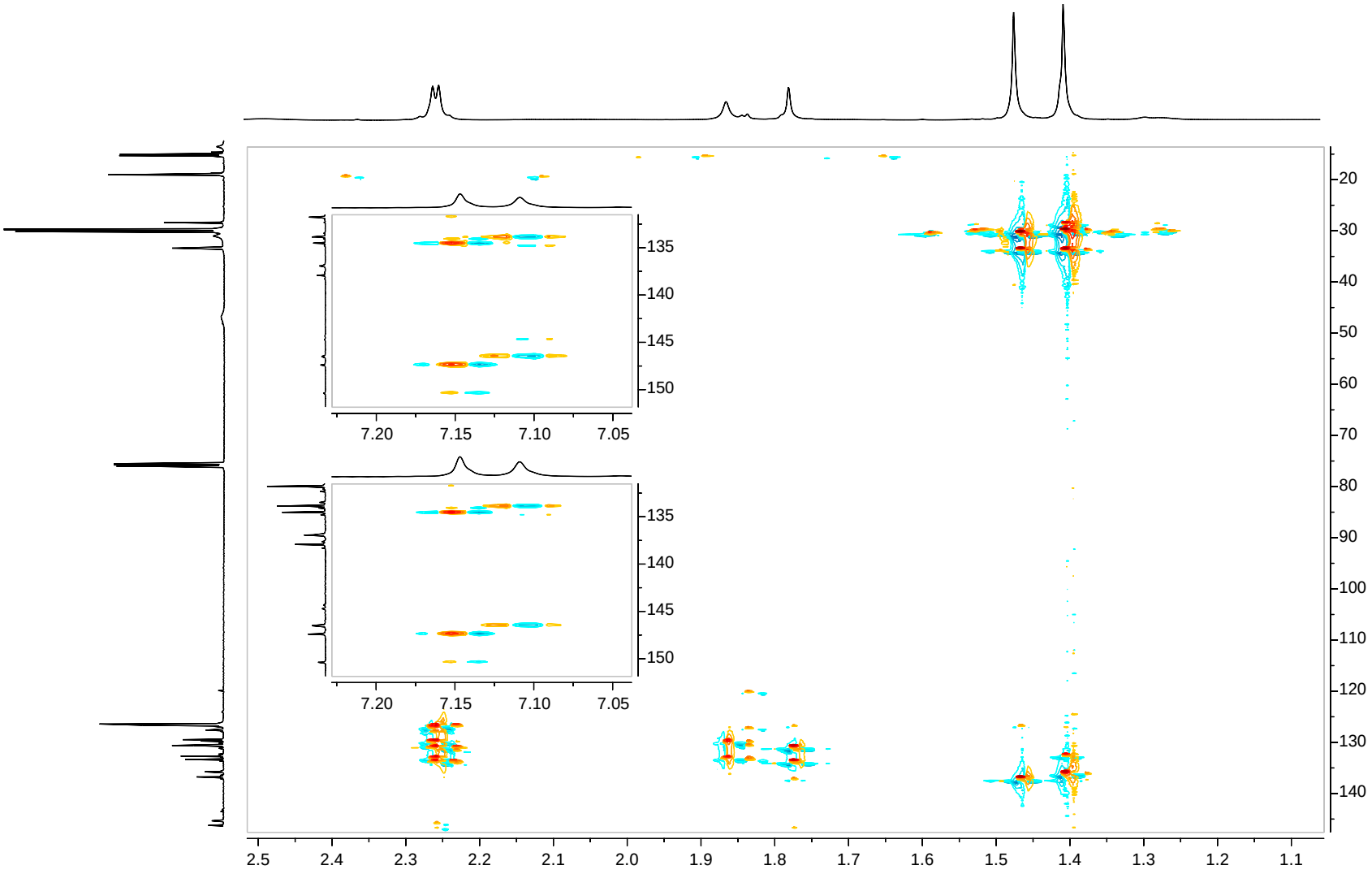
Ligand 1, $^{31}P\{H\}$ (242.9 MHz, d_8 –toluene, 25 °C)



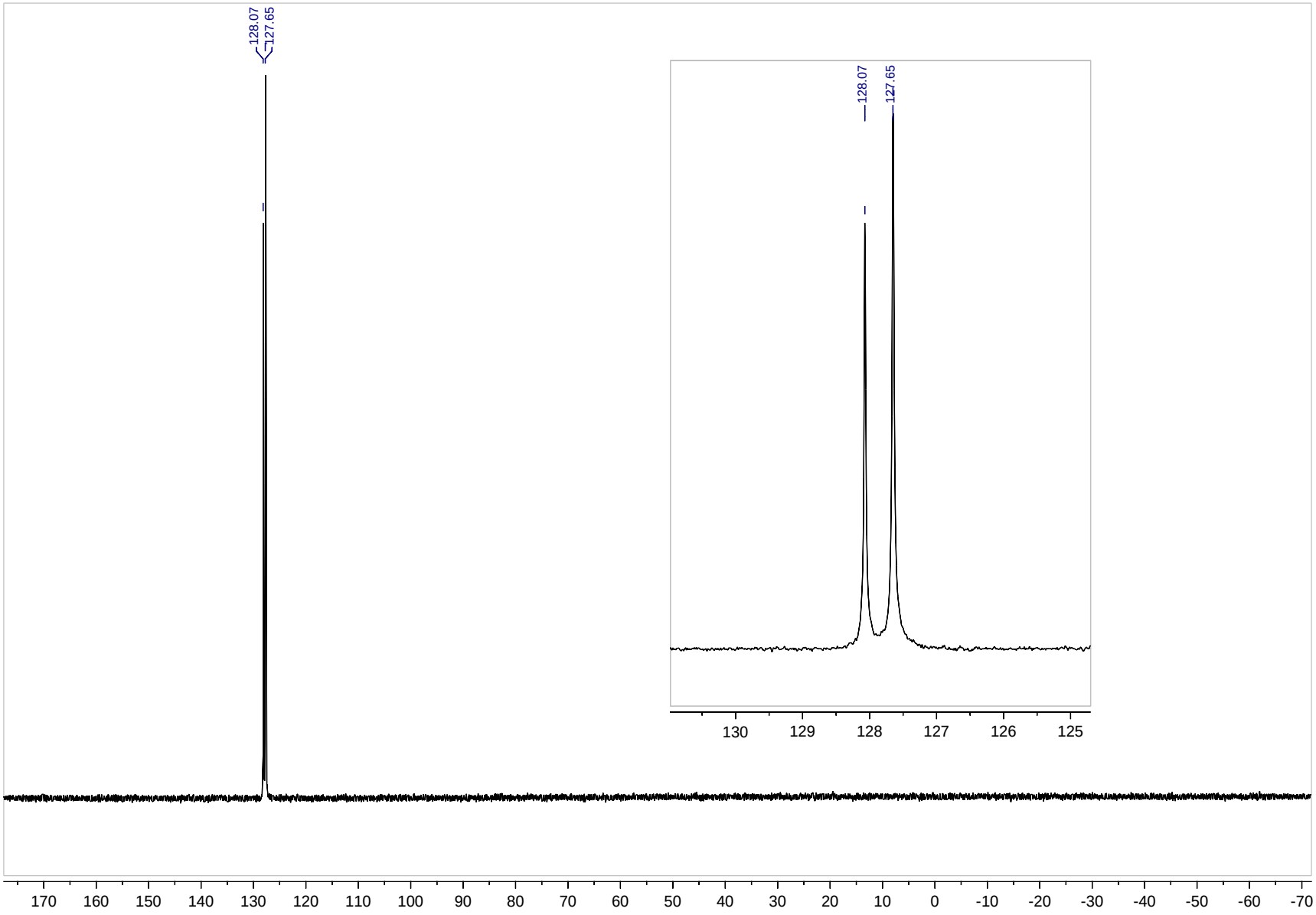
Ligand 1, ^{1}H (600.1 MHz, d_8 –toluene, 100 °C)



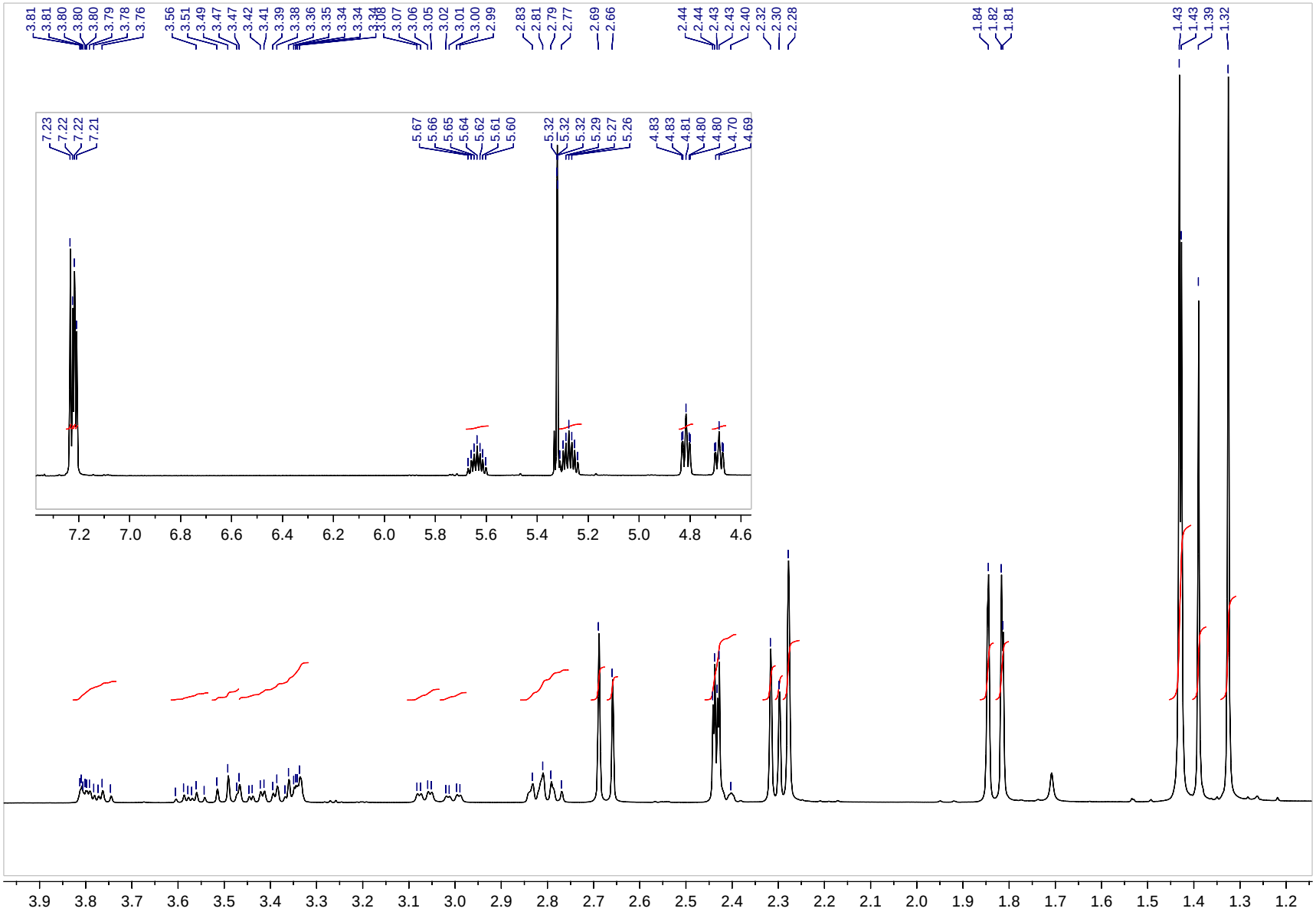
Ligand 1, $^{13}C\{H\}$ (125.69 MHz, $CDCl_3$, ambient temperature)



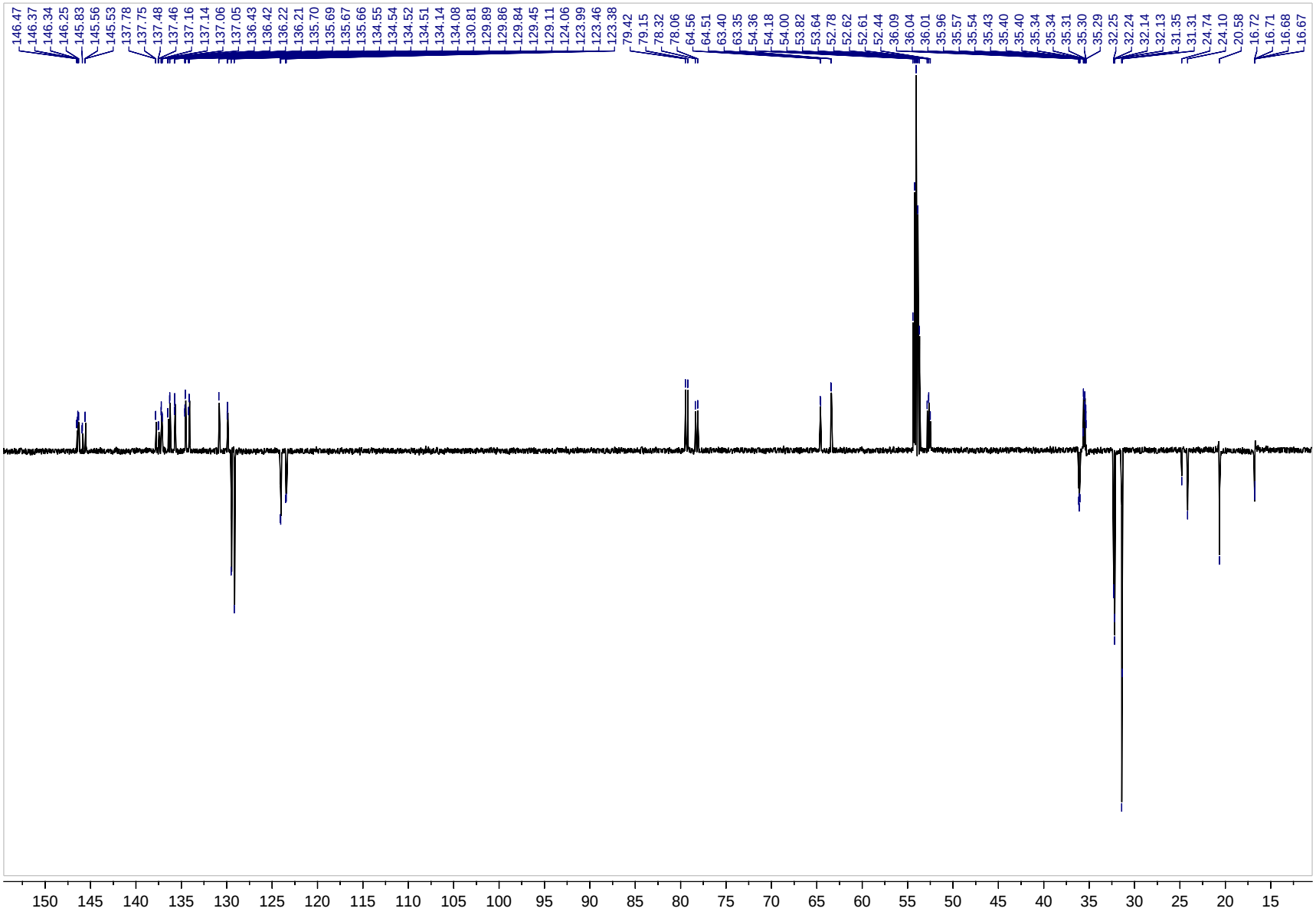
Ligand 1, ^{1}H-^{13}C HMBC



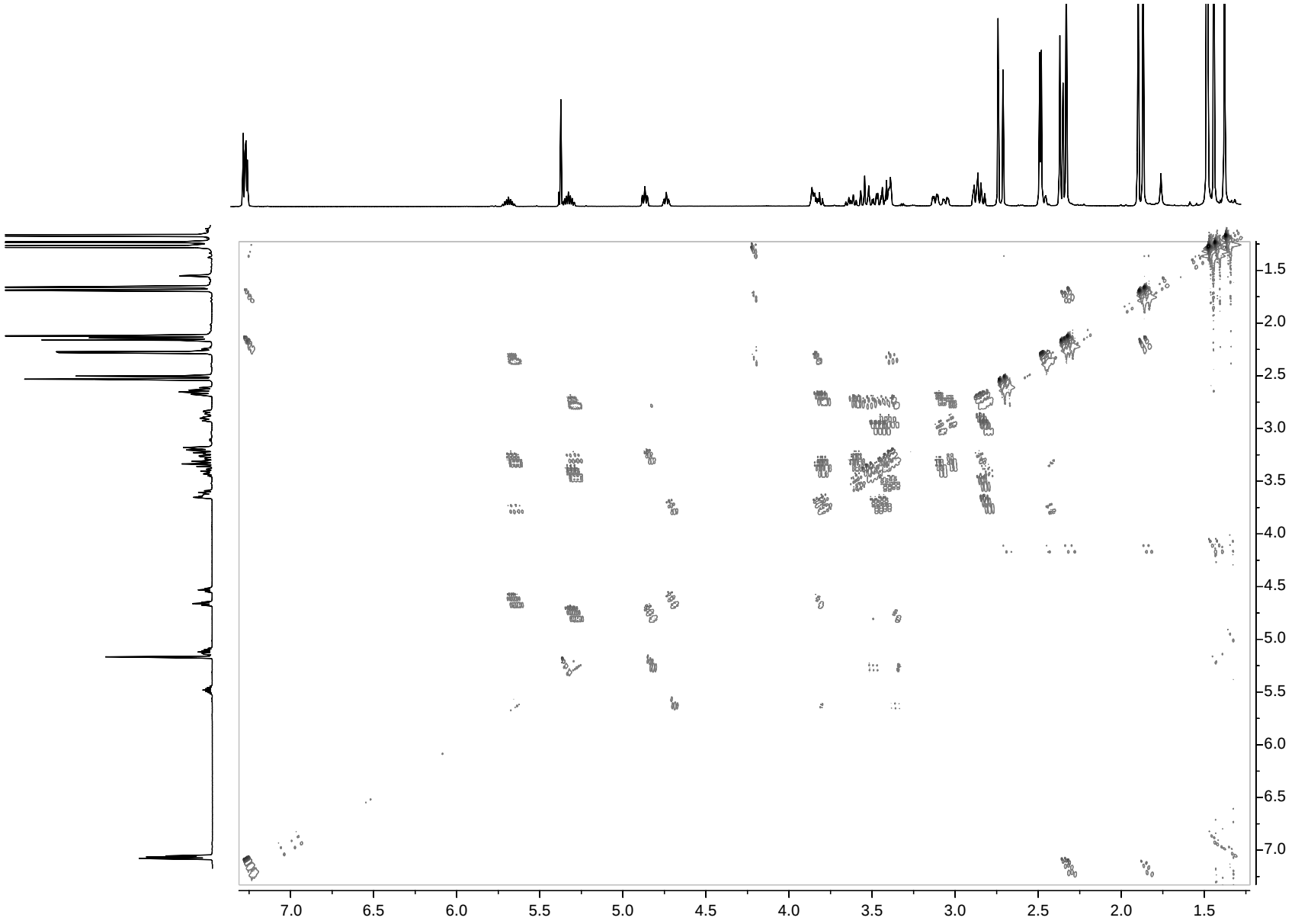
Complex 2, $^{31}P\{H\}$ (242.9 MHz, $CDCl_3$, 25 °C)



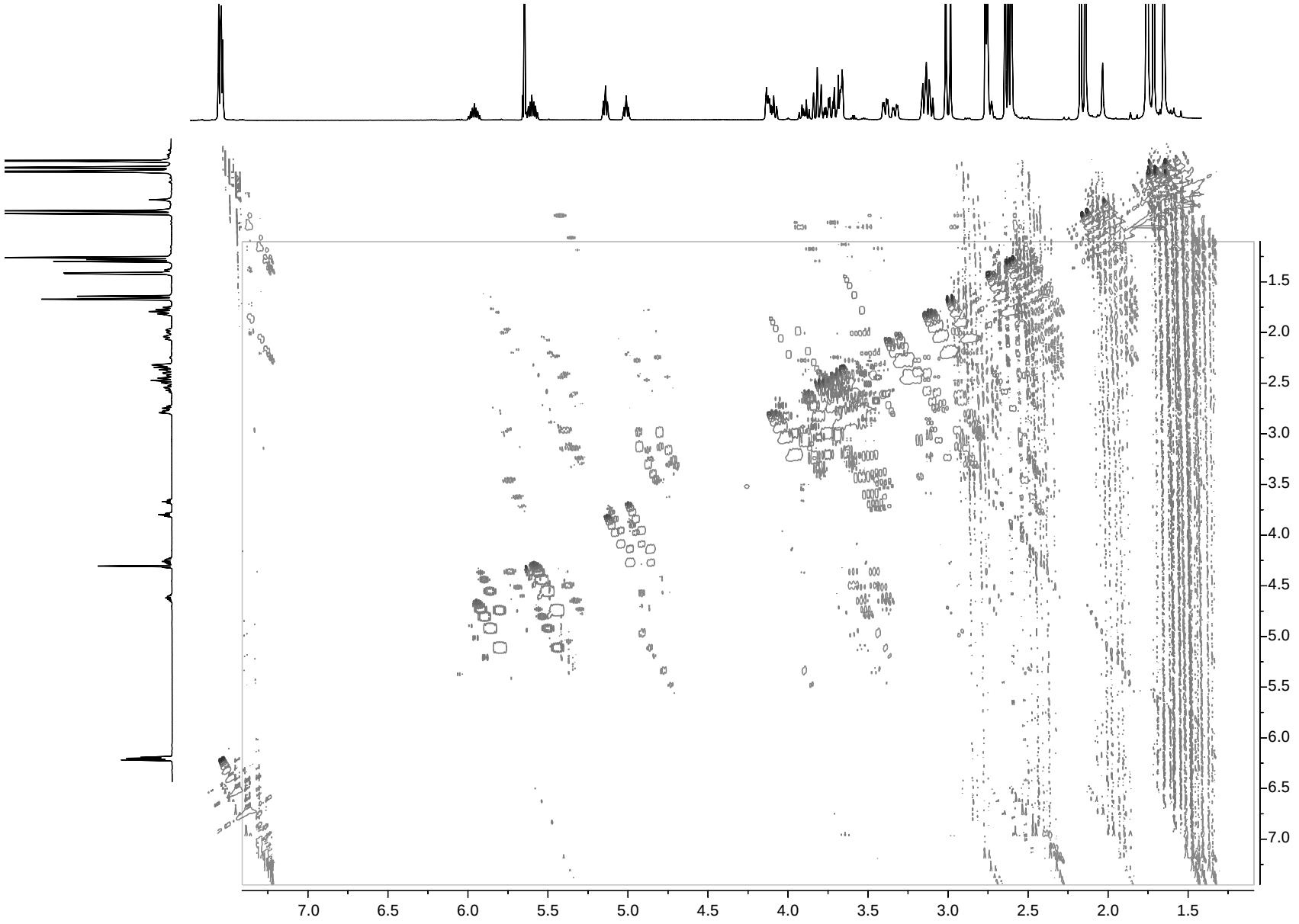
Complex 2, ^{1}H (600.1 MHz, $CDCl_3$, 25 °C)



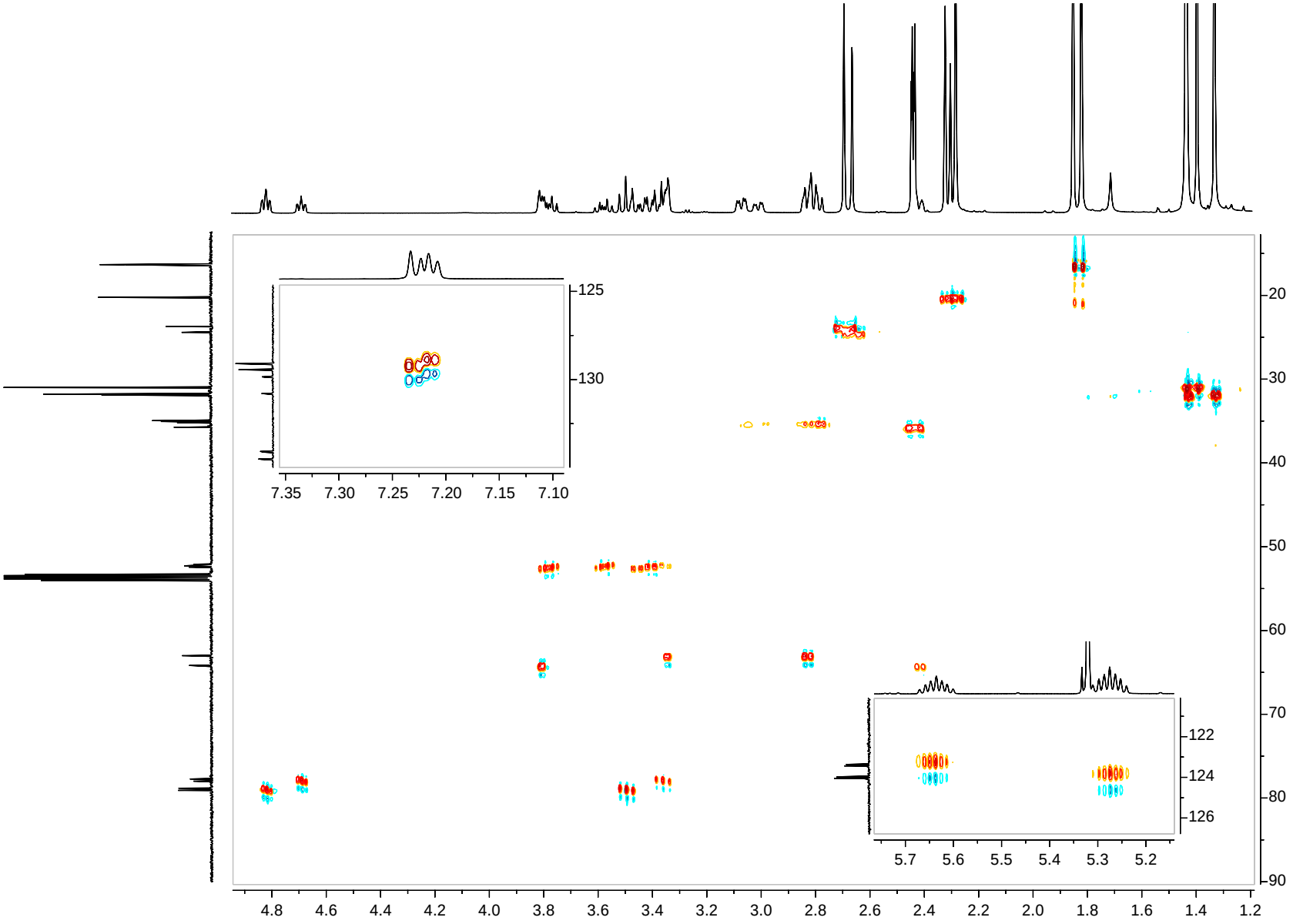
Complex 2, ^{13}C DEPT (150.9 MHz, $CDCl_3$, 25 °C)



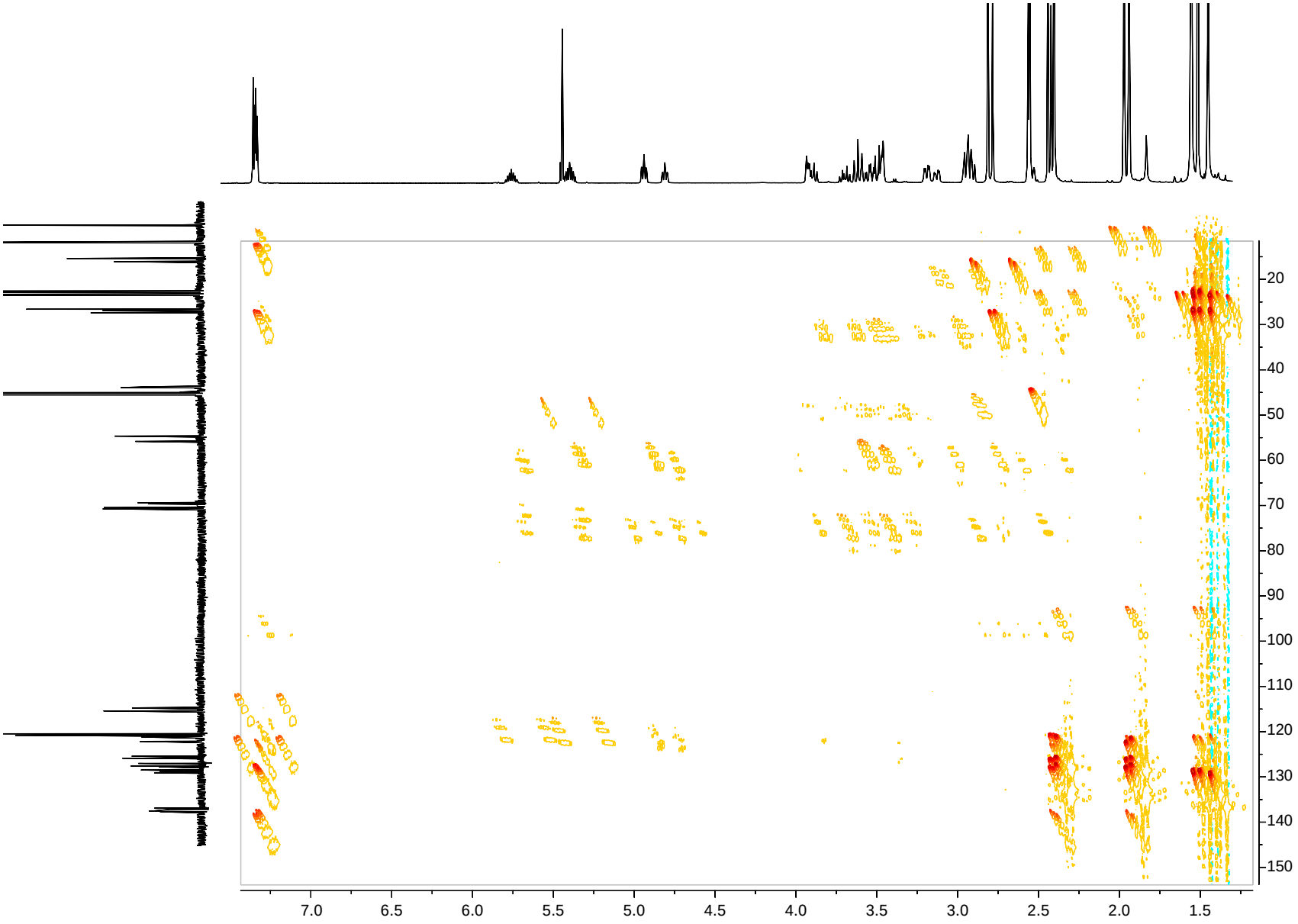
Complex 2, ^{1}H-^{1}H COSY



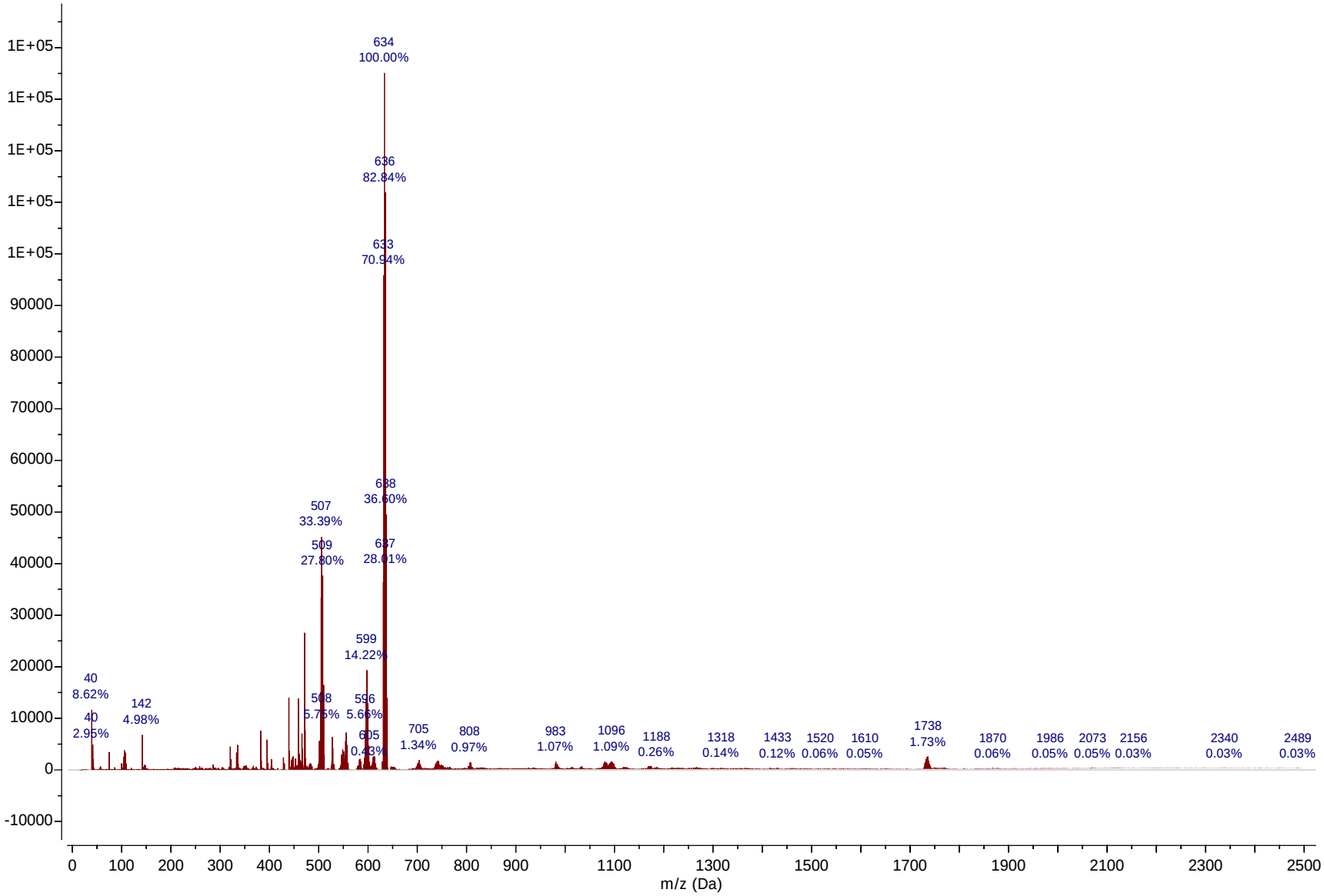
Complex 2, ^{1}H,^{1}H NOESY



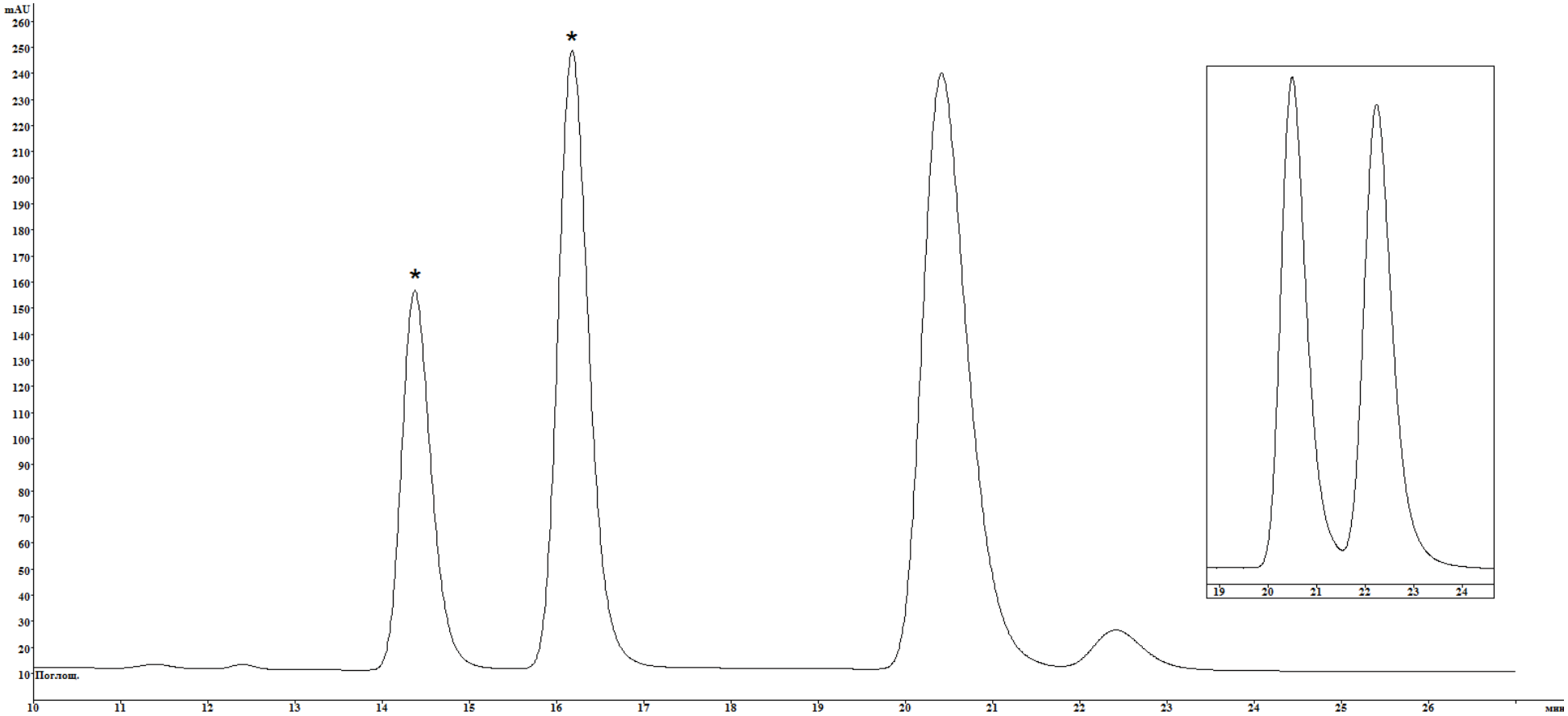
Complex 2, ^{1}H-^{13}C HSQC



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

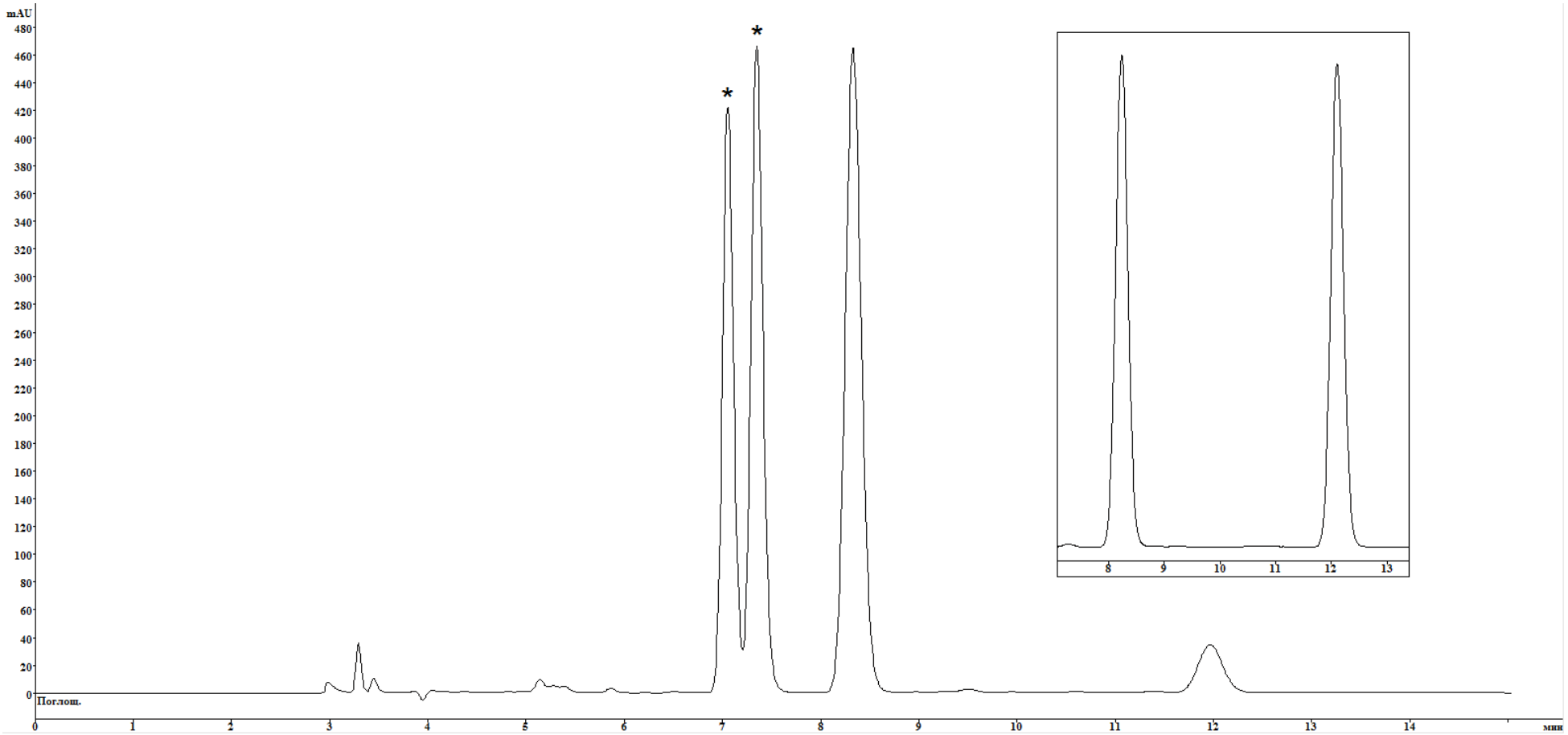


Complex 2, MALDI-TOF MS



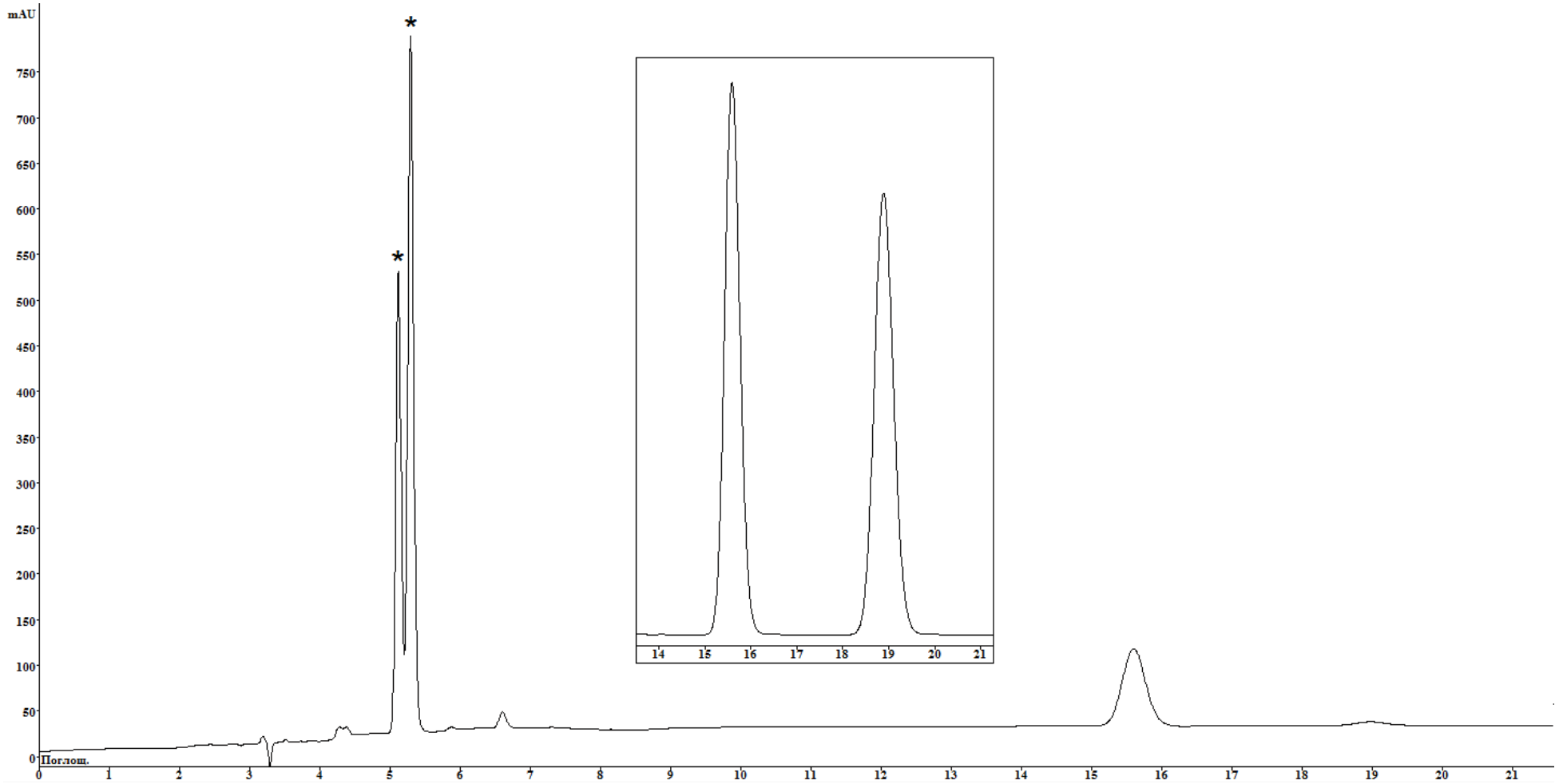
Chiral HPLC trace for the Pd-catalyzed asymmetric allylic alkylation of 3a with dimethyl malonate (entry 3 in Table 1) and for a racemic mixture of 4a (in the frame).

* starting substrate **3a**



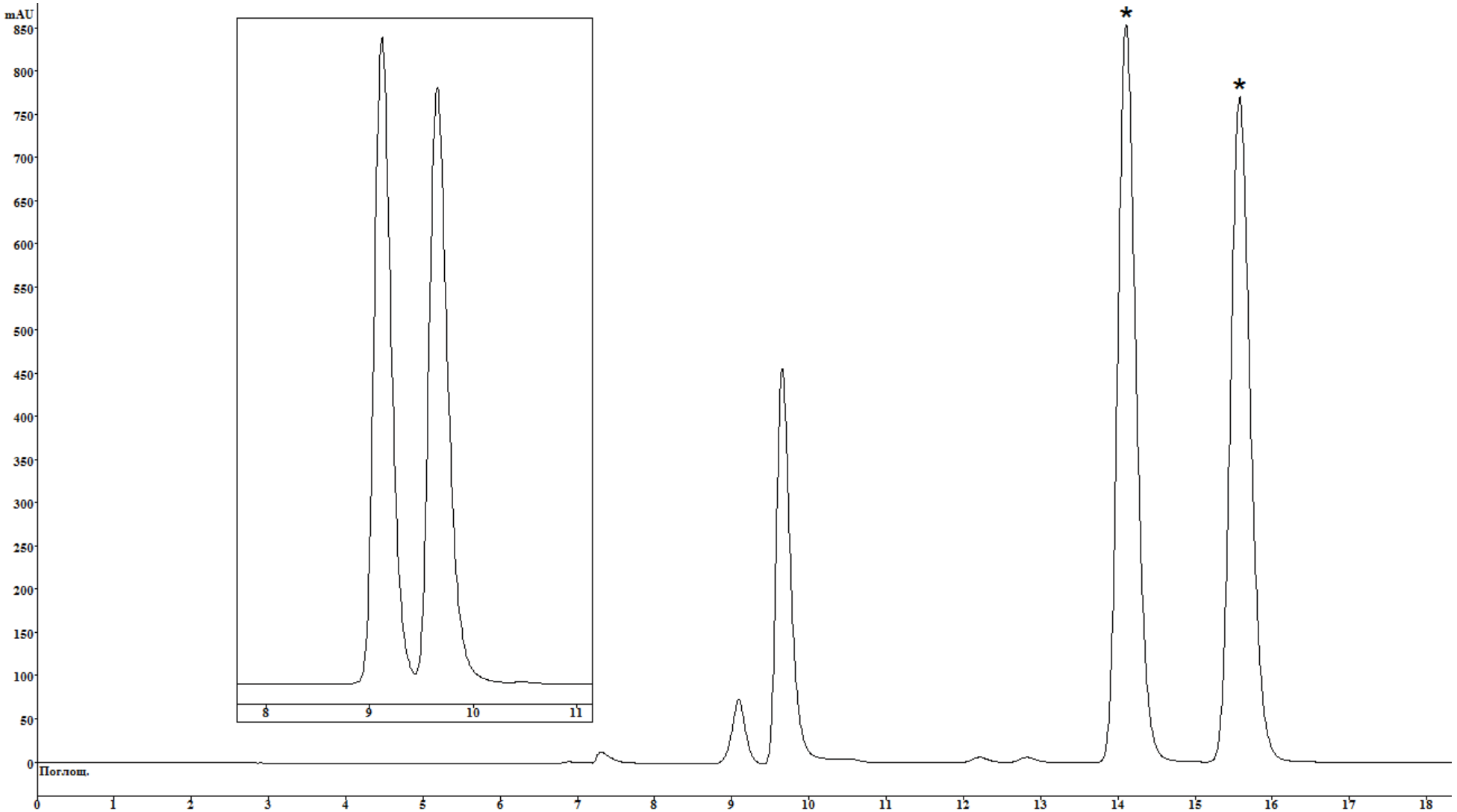
Chiral HPLC trace for the Pd-catalyzed asymmetric allylic alkylation of 3a with di-*tert*-butyl malonate (entry 9 in Table 1) and for a racemic mixture of 4b (in the frame).

* starting substrate **3a**



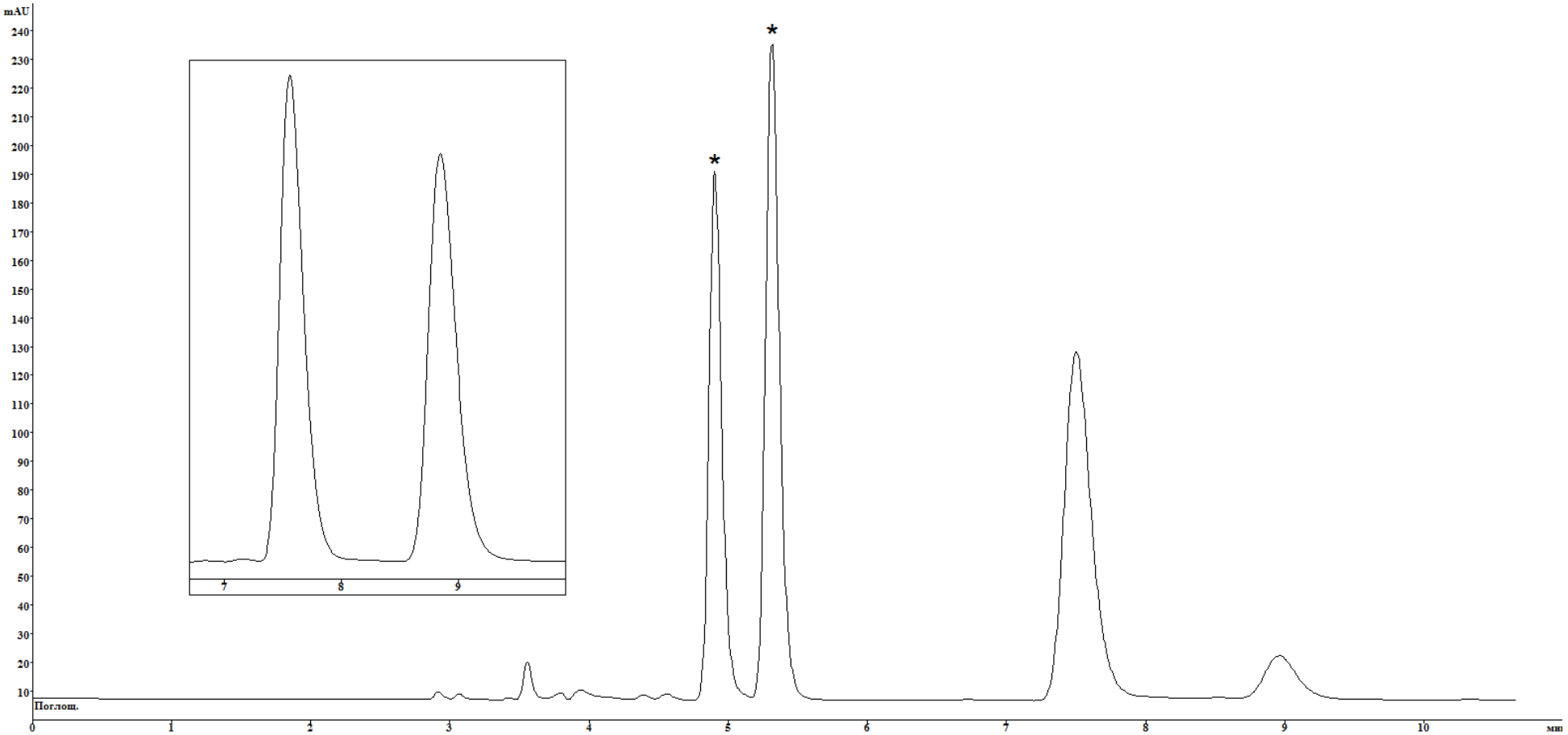
Chiral HPLC trace for the Pd-catalyzed asymmetric allylic alkylation of 3a with dibenzyl malonate (entry 14 in Table 1) and for a racemic mixture of 4c (in the frame).

* starting substrate **3a**



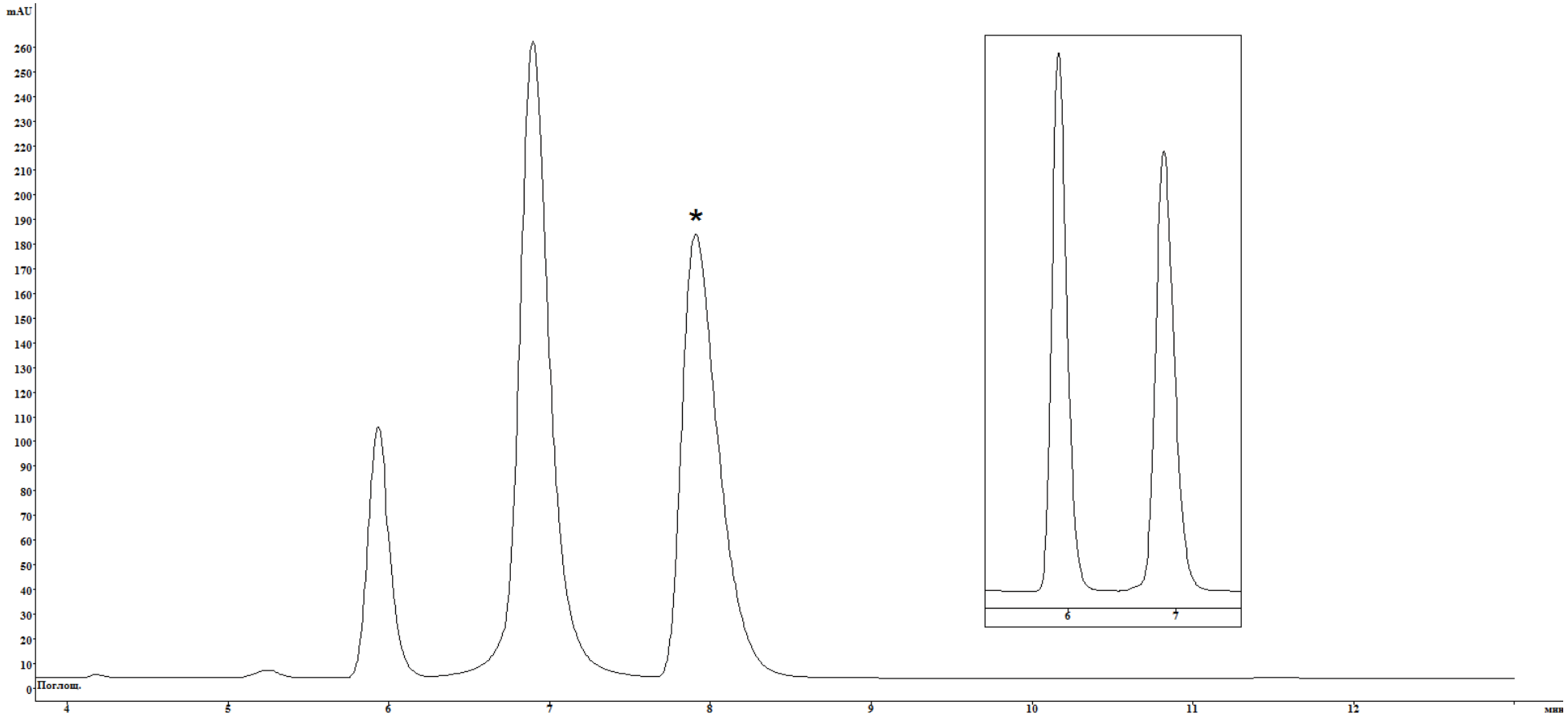
Chiral HPLC trace for the Pd-catalyzed asymmetric allylic amination of 3a with pyrrolidine (entry 5 in Table 2) and for a racemic mixture of 5a (in the frame).

* starting substrate **3a**



Chiral HPLC trace for the Pd-catalyzed asymmetric allylic amination of 3a with phthalimide (entry 10 in Table 2) and for a racemic mixture of 5b (in the frame).

* starting substrate **3a**



Chiral HPLC trace for the Pd-catalyzed allylic amination of substrate 6 with aniline (entry 3 in Table 3) and for a racemic mixture of 7 (in the frame).

* product **8**