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First P*,S-bidentate diamidophosphite ligand in Pd-catalyzed asymmetric reactions

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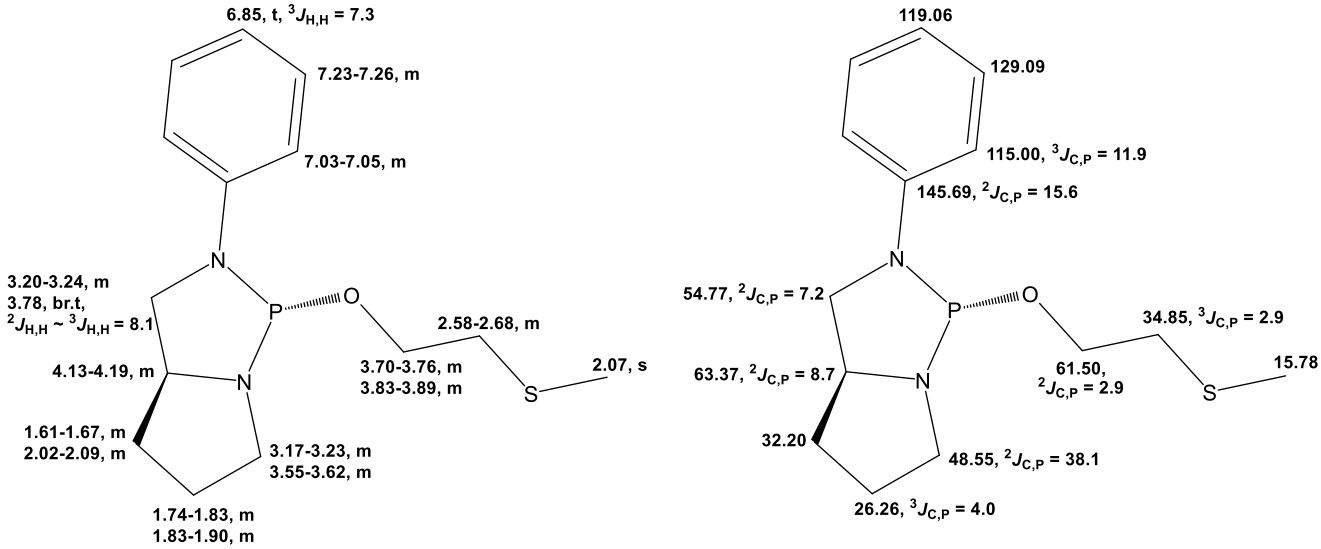


Figure S1 Full assignment of all H-1 and C-13 resonances for ligand **1**.

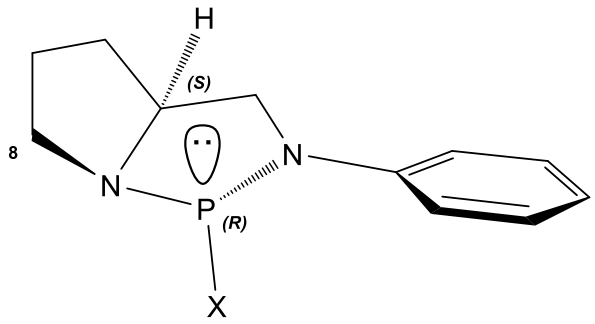


Figure S2 Stereochemistry of the phosphabicyclic part in ligand **1** (X - exocyclic substituent).

Table S1 Pd-catalyzed enantioselective allylic alkylation of substrate **2a** with dimethyl malonate using known P*-mono, P*,P- and P*,N-bidentate diamidophosphites and novel P*,S-bidentate diamidophosphite **1** (precatalyst – $[Pd(\pi\text{-allyl})Cl]_2$).

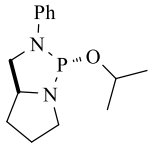
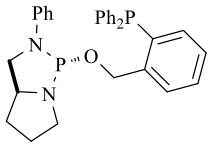
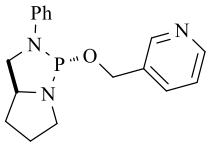
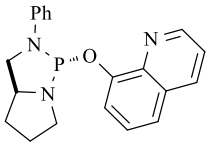
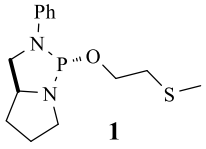
Ligand					 **1**
ee, maximum value (%)	70 (*S*) [S1]	70 (*S*) [S2]	80 (*S*) [S3]	85 (*S*) [S4]	86 (*S*)
Conversion (%)	16	62	96	100	100

Table S2 Pd-catalyzed allylic amination of substrate **2a** with pyrrolidine. [a]

Entry	**1** : Pd	Solvent	Conversion (%)	*ee* (%) [b,c]
1	1 : 1	THF	100	73 (*R*)
2	2 : 1	THF	100	70 (*R*)
3	1 : 1	CH_2Cl_2	100	31 (*R*)
4	2 : 1	CH_2Cl_2	100	11 (*R*)

[a] Reaction conditions: 2 mol% of $[Pd(\pi\text{-allyl})Cl]_2$, 20 °C, 48 h.
[b] The conversion of substrate **2a** and enantiomeric excess of **4** were determined by HPLC (Daicel Chiralcel OD-H, $C_6H_{14}/Pr^iOH/Et_2NH$ = 200:1:0.1, 0.4 ml min^{-1}, 254 nm, *t*(*R*) = 10.5 min, *t*(*S*) = 11.6 min).
[c] The absolute configuration was assigned by comparison of the HPLC retention times reported in the literature.[S2]

Table S3 Pd-catalyzed allylic amination of substrate **2a** with diethyl (aminomethyl)phosphonate. [a]

Entry	**1** : Pd	Solvent	Conversion (%)	*ee* (%) [b,c]
1	1 : 1	THF	64	51 (II)
2	2 : 1	THF	71	68 (II)
3	1 : 1	CH_2Cl_2	73	57 (II)
4	2 : 1	CH_2Cl_2	86	75 (II)

[a] Reaction conditions: 2 mol% of $[Pd(\pi\text{-allyl})Cl]_2$, 20 °C, 48 h.
[b] Conversion of substrate **2a** and enantiomeric excess of product **5** were determined by HPLC (Kromasil 5-CelluCoat, C_6H_{14}/Pr^iOH = 98:2, 1.5 ml min^{-1}, 254 nm, *t*(I) = 21.2 min, *t*(II) = 24.6 min).
[c] The absolute configuration of the product **7** was not assigned.

Table S4 Pd-catalyzed allylation of substrate **6** with ethyl 2-oxocyclopentane-1-carboxylate (**7a**). [a]

Entry	**1** : Pd	Conversion (%)	*ee* (%) [b,c]
1	1 : 1	100	52 (*S*)
2	2 : 1	100	62 (*S*)

[a] Reaction conditions: 2 mol% of $[Pd(\pi\text{-allyl})Cl]_2$, BSA, $Zn(OAc)_2$, toluene, 20 °C, 48 h.
[b] The conversion of substrate **6** and enantiomeric excess of **8a** were determined by HPLC (Daicel Chiralcel OD-H, C_6H_{14}/Pr^iOH = 99:1, 0.6 ml min^{-1}, 254 nm, *t*(*R*) = 22.9 min, *t*(*S*) = 25.7 min).
[c] The absolute configuration was assigned by comparison of the HPLC retention times reported in the literature.[S5]

Table S5 Pd-catalyzed allylation of substrate **6** with ethyl 2-oxocyclohexane-1-carboxylate (**7b**). [a]

Entry	**1** : Pd	Conversion (%)	*ee* (%) [b,c]
1	1 : 1	73	47 (*S*)
2	2 : 1	100	76 (*S*)

[a] Reaction conditions: 2 mol% of $[Pd(\pi\text{-allyl})Cl]_2$, BSA, $Zn(OAc)_2$, toluene, 20 ^{0}C, 48 h.
[b] The conversion of substrate **6** and enantiomeric excess of **8b** were determined by HPLC (Kromasil 5-CelluCoat, C_6H_{14}/Pr^iOH = 95:5, 0.4 ml min^{-1}, 254 nm, *t*(*R*) = 13.8 min, *t*(*S*) = 15.7 min).
[c] The absolute configuration was assigned by comparison of the HPLC retention times reported in the literature.[S5]

Table S6 Pd-catalyzed allylation of substrate **6** with ethyl 2-acetamido-3-oxobutanoate (**9**). [a]

Entry	**1** : Pd	Conversion (%)	*ee* (%) [b,c]
1	1 : 1	100	49 (*R*)
2	2 : 1	100	55 (*R*)
3	2 : 1	100	54 (*R*) [d]

[a] Reaction conditions: 2 mol% of $[Pd(\pi\text{-allyl})Cl]_2$, BSA, KOAc, toluene, 20 °C, 48 h.
[b] The conversion of substrate **6** and enantiomeric excess of **10** were determined by HPLC (Daicel Chiralcel OD-H, C_6H_{14}/Pr^iOH = 85:15, 0.8 ml min^{-1}, 254 nm, *t*(*S*) = 9.7 min, *t*(*R*) = 10.4 min).
[c] The absolute configuration was assigned by comparison of the HPLC retention times reported in the literature.[S6]
[d] With $Zn(OAc)_2$.

Experimental Section

General Remarks. ^{31}P, ^{1}H, and ^{13}C NMR spectra were recorded with Varian Inova 500 spectrometer at 202.33, 499.86 and 125.70 MHz, respectively; 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 APT, ^{1}H-^{1}H COSY, ^{1}H-^{1}H NOESY, ^{1}H-^{13}C HSQC and ^{1}H-^{13}C HMBC experiments taking into account the published data.[S1,S3,S4,S7] 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 analyzer.

All reactions were carried out in anhydrous solvents under dry argon. Phosphorylating reagent (5*S*)-2-chloro-3-phenyl-1,3-diaza-2-phosphabicyclo[3.3.0]octane was obtained as published.[S1] The starting substrates *rac*-(*E*)-1,3-diphenylallyl acetate (**2a**) and *rac*-(*E*)-1,3-diphenylallyl ethyl carbonate (**2b**), precatalyst [Pd(π-allyl)Cl]$_2$, N-nucleophile diethyl (aminomethyl)phosphonate, C-nucleophile ethyl 2-acetamido-3-oxobutanoate (**9**) and NaB[$C_6H_3(CF_3)_2$-3,5]$_4$ were synthesized following the known procedures.[S8] Catalytic studies of asymmetric alkylation of **2a,b** with dimethyl malonate and amination of **2a** with pyrrolidine and diethyl (aminomethyl)phosphonate; alkylation of cinnamyl acetate (**6**) with ethyl 2-oxocyclopentane-1-carboxylate (**7a**), ethyl 2-oxocyclohexane-1-carboxylate (**7b**) and ethyl 2-acetamido-3-oxobutanoate (**9**), determination of the conversion of substrates **2a,b** and **6**, and enantiomeric excesses of products **3**, **4**, **5**, **8a,b**, and **10** were performed as earlier described.[S1-S3,S5,S6,S7a,S9]

2-(Methylthio)ethan-1-ol, dimethyl malonate, BSA, pyrrolidine, triethylamine, cinnamyl acetate (**6**), ethyl 2-oxocyclopentane-1-carboxylate (**7a**) and ethyl 2-oxocyclohexane-1-carboxylate (**7b**) were purchased from Fluka and Aldrich.

(2*R*,5*S*)-2-(2-methylthioethoxy)-3-phenyl-1,3-diaza-2-phosphabicyclo[3.3.0]octane (1). To a vigorously stirred solution of phosphorylating agent (0.48 g, 2 mmol) and Et_3N (0.56 ml, 4 mmol) in toluene (15 ml), 2-(methylthio)ethan-1-ol (0.18 g, 2 mmol) was added in one portion at 20 °C. The reaction mixture was stirred at 20 °C for 24 h and passed through a short column filled with SiO_2/Al_2O_3. The filtrate was concentrated under reduced pressure (40 Torr) and the residue was dried in vacuum (1 Torr). The product **1** was purified by flash chromatography on SiO_2 (eluent — toluene) and bulb-to-bulb vacuum distillation. Yield 0.41 g (69%), clear oil, bp 245-246 °C (bath, 1 Torr). ^{1}H NMR (499.9 MHz, $CDCl_3$, ambient temperature): δ = 1.61-1.67 (m, 1H; C$\underline{H}_2$), 1.74-1.83 (m, 1H; NCH$_2$C$\underline{H}_2$), 1.83-1.90 (m, 1H; NCH$_2$C$\underline{H}_2$), 2.02-2.09 (m, 1H; C$\underline{H}_2$), 2.07 (s, 3H; CH_3), 2.58-2.68 (m, 2H; SCH_2), 3.17-3.23 (m, 1H; NC$\underline{H}_2$CH$_2$), 3.20-3.24 (m, 1H; NC$\underline{H}_2$CH), 3.55-3.62 (m, 1H; NC$\underline{H}_2$CH$_2$), 3.70-3.76 (m, 1H; $POCH_2$), 3.78 (br.t, ^{2}J(H,H) ~ ^{3}J(H,H) ~ 8.1 Hz, 1H; NC$\underline{H}_2$CH), 3.83-

3.89 (m, 1H; $POCH_2$), 4.13-4.19 (m, 1H; $NCH_2C\underline{H}$), 6.85 (t, ^3J(H,H) = 7.3 Hz, 1H; CH_{para}), 7.03-7.05 (m, 2H; CH_{ortho}), 7.23-7.26 (m, 2H; CH_{meta}) ppm. $^{13}C\{^1H\}$ NMR (125.7 MHz, $CDCl_3$, ambient temperature): δ = 15.78 (s; $\underline{C}H_3$), 26.26 (d, ^3J(C,P) = 4.0 Hz; $NCH_2\underline{C}H_2$), 32.20 (s; $\underline{C}H_2$), 34.85 (d, ^3J(C,P) = 2.9 Hz; SCH_2), 48.55 (d, ^2J(C,P) = 38.1 Hz; $N\underline{C}H_2CH_2$), 54.77 (d, ^2J(C,P) = 7.2 Hz; $N\underline{C}H_2CH$), 61.50 (d, ^2J(C,P) = 2.9 Hz; $POCH_2$), 63.37 (d, ^2J(C,P) = 8.7 Hz; $NCH_2\underline{C}H$), 115.00 (d, ^3J(C,P) = 11.9 Hz; CH_{ortho}), 119.06 (s; CH_{para}), 129.09 (s; CH_{meta}), 145.69 (d, ^2J(C,P) = 15.6 Hz; CNP), ppm. $^{31}P\{^1H\}$ NMR (202.36 MHz, $CDCl_3$, ambient temperature): δ = 123.07 (s) ppm.Anal. Calcd for $C_{14}H_{21}N_2OPS$: C, 56.74; H, 7.14; N, 9.45. Found: C, 56.94; H, 7.19; N, 9.34.

Pd-catalyzed asymmetric allylic alkylation of (*E*)-1,3-diphenylallyl acetate (2a) or (*E*)-1,3-diphenylallyl ethyl carbonate (2b) with dimethyl malonate. A solution of $[Pd(\pi\text{-allyl})Cl]_2$ (0.0019 g, 0.005 mmol) and ligand **1** (0.003 g, 0.01 mmol or 0.006 g, 0.02 mmol) in the appropriate solvent (1.5 ml) was stirred for 40 min (in the experiment carried out with $NaB[C_6H_3(CF_3)_2\text{-}3,5]_4$, this compound (0.011 g, 0.012 mmol) was added). The appropriate substrate (0.25 mmol) was added and the solution was stirred for 15 min. Dimethyl malonate (0.05 ml, 0.44 mmol), BSA (0.11 ml, 0.44 mmol), and KOAc (0.002 g) (or LiOAc, 0.0014 g) or dimethyl malonate (0.05 ml, 0.44 mmol) and Cs_2CO_3 (0.163 g, 0.5 mmol) were added. The reaction mixture was stirred for 48 h, diluted with CH_2Cl_2 or THF (2 ml), and filtered through a thin layer of SiO_2. The filtrate was evaporated at reduced pressure (40 Torr) and dried in vacuum (10 Torr, 12 h) affording a residue containing (*E*)-dimethyl 2-(1,3-diphenylallyl)malonate (**3**).[S10] 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 chiral HPLC analysis.

Pd-catalyzed asymmetric allylic amination of *rac*-(*E*)-1,3-diphenylallyl acetate (2a) with pyrrolidine. A solution of $[Pd(\pi\text{-allyl})Cl]_2$ (0.0019 g, 0.005 mmol) and ligand **1** (0.003 g, 0.01 mmol or 0.006 g, 0.02 mmol) in the appropriate solvent (1.5 ml) was stirred for 40 min. *rac*-(*E*)-1,3-Diphenylallyl acetate (0.05 ml, 0.25 mmol) was added and the solution was stirred for 15 min, then freshly distilled pyrrolidine (0.06 ml, 0.75 mmol) was added. The reaction mixture was stirred for 48 h, diluted with CH_2Cl_2 or THF (2 ml), and filtered through a thin layer of SiO_2. The filtrate was evaporated at reduced pressure (40 Torr) and dried in vacuum (10 Torr, 12 h) affording a residue containing (*E*)-1-(1,3-diphenylallyl)pyrrolidine (**4**).[S11] 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 chiral HPLC analysis.

Pd-catalyzed asymmetric allylic amination of *rac*-(*E*)-1,3-diphenylallyl acetate (2a) with diethyl (aminomethyl)phosphonate. A solution of $[Pd(\pi\text{-allyl})Cl]_2$ (0.0019 g, 0.005 mmol) and ligand **1** (0.003 g, 0.01 mmol or 0.006 g, 0.02 mmol) in the appropriate solvent (1.5 ml) was stirred for 40 min. *rac*-(*E*)-1,3-Diphenylallyl acetate (0.05 ml, 0.25 mmol) was added and the solution was stirred for 15 min, then diethyl (aminomethyl)phosphonate (0.05 g, 0.3 mmol) was added. The reaction mixture was stirred for 48 h, diluted with CH_2Cl_2 or THF (2 ml), and filtered through a thin layer of SiO_2. The filtrate was evaporated at reduced pressure (40 Torr) and dried in vacuum (10 Torr, 12 h) affording a residue containing diethyl (*E*)-(((1,3-diphenylallyl)amino)methyl)phosphonate (**5**).[S12] 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 chiral HPLC analysis.

Pd-catalyzed asymmetric allylic alkylation of cinnamyl acetate (6) with ethyl 2-oxocyclopentane-1-carboxylate (7a) or ethyl 2-oxocyclohexane-1-carboxylate (7b). A solution of $[Pd(\pi\text{-allyl})Cl]_2$ (0.0019 g, 0.005 mmol) and ligand **1** (0.003 g, 0.01 mmol or 0.006 g, 0.02 mmol) in toluene (1.5 ml) was stirred for 40 min. Cinnamyl acetate (**6**) (0.04 ml, 0.25 mmol) was added and the solution was stirred for 15 min. β-Keto ester **7a** or **7b** (0.375 mmol), BSA (0.25 ml, 1 mmol) and $Zn(OAc)_2$ (0.005 g) were added. The reaction mixture was stirred for 48 h, diluted with toluene (2 ml) and filtered through a thin layer of SiO_2. The filtrate was evaporated at reduced pressure (40 Torr) and dried in vacuum (10 Torr, 12 h) affording a residue containing ethyl 1-cinnamyl-2-oxocyclopentane-1-carboxylate (**8a**) or ethyl 1-cinnamyl-2-oxocyclohexane-1-carboxylate (**8b**).[S5a,b,S13] 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.

Pd-catalyzed asymmetric allylic alkylation of cinnamyl acetate (6) with ethyl 2-acetamido-3-oxobutanoate (9). A solution of $[Pd(\pi\text{-allyl})Cl]_2$ (0.0019 g, 0.005 mmol) and ligand **1** (0.003 g, 0.01 mmol or 0.006 g, 0.02 mmol) in toluene (1.5 ml) was stirred for 40 min. Cinnamyl acetate (**6**) (0.04 ml, 0.25 mmol) was added and the solution was stirred for 15 min. Compound **9** (0.07 g, 0.375 mmol), BSA (0.25 ml, 1 mmol) and KOAc (0.003 g) or $Zn(OAc)_2$ (0.005 g) were added. The reaction mixture was stirred for 48 h, diluted with toluene (2 ml) and filtered through a thin layer of SiO_2. The filtrate was evaporated at reduced pressure (40 Torr) and dried in vacuum (10 Torr, 12 h) affording a residue containing ethyl (*R*,*E*)-2-acetamido-2-acetyl-5-phenylpent-4-enoate (**10**).[S9a] 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.

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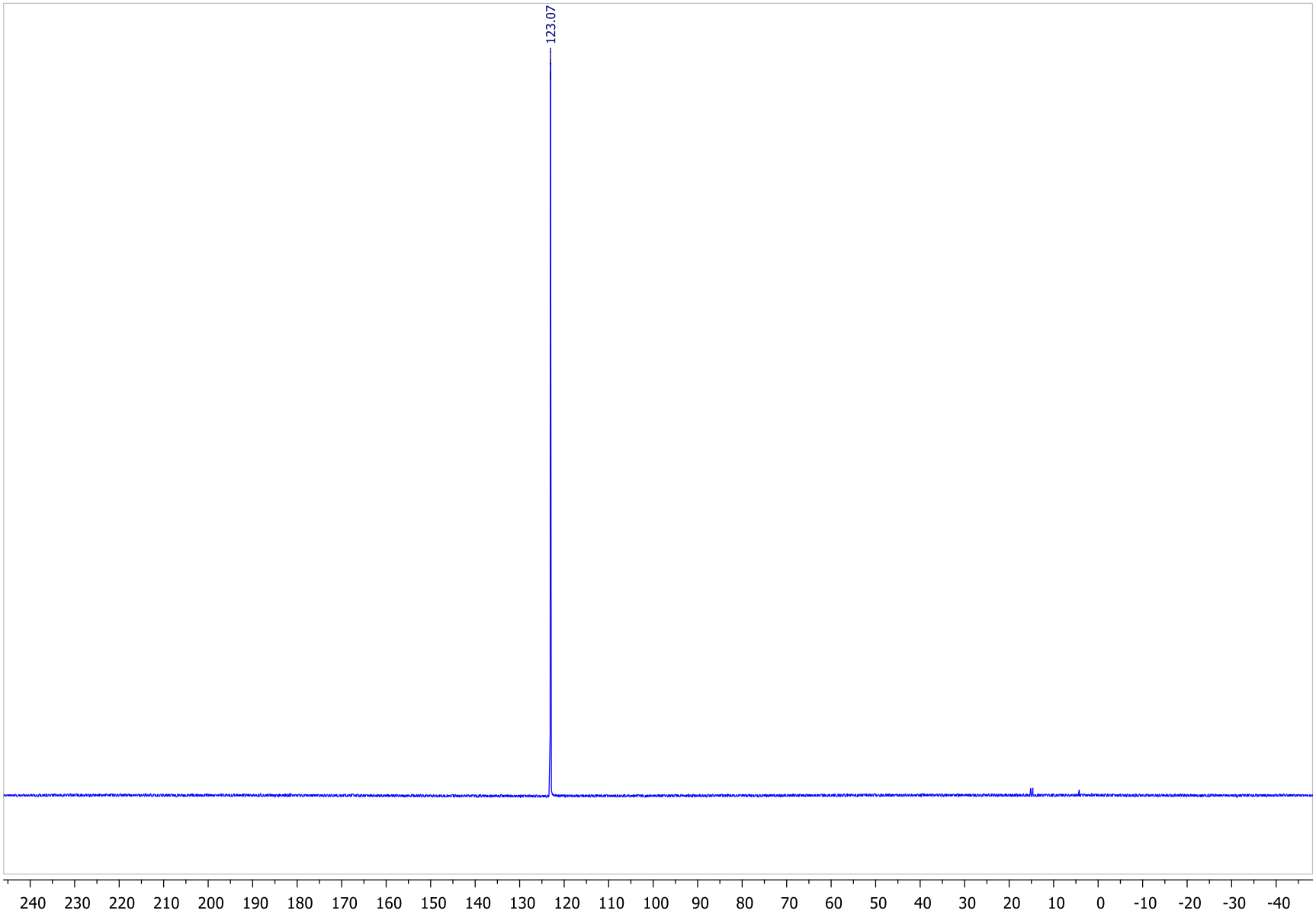

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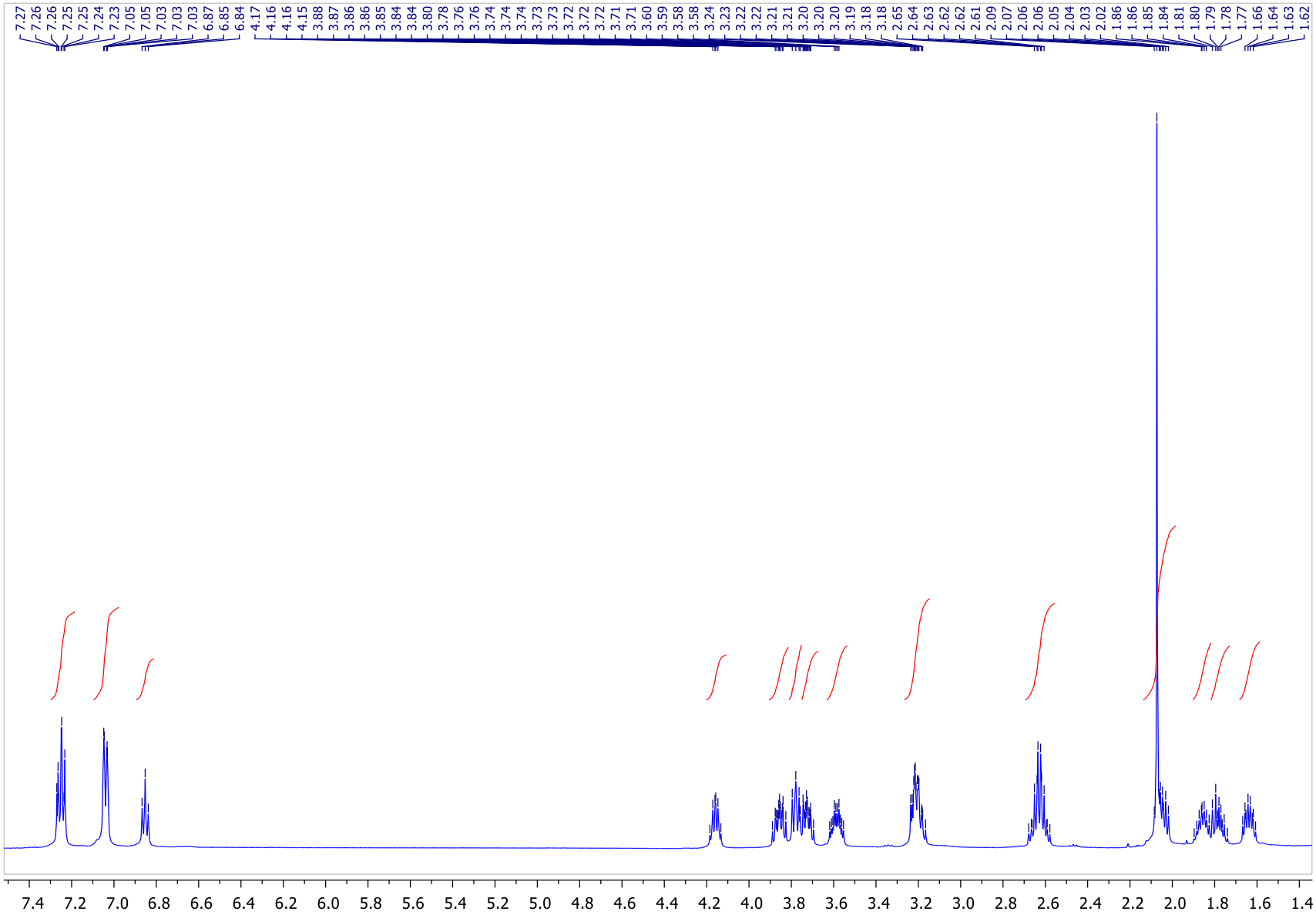

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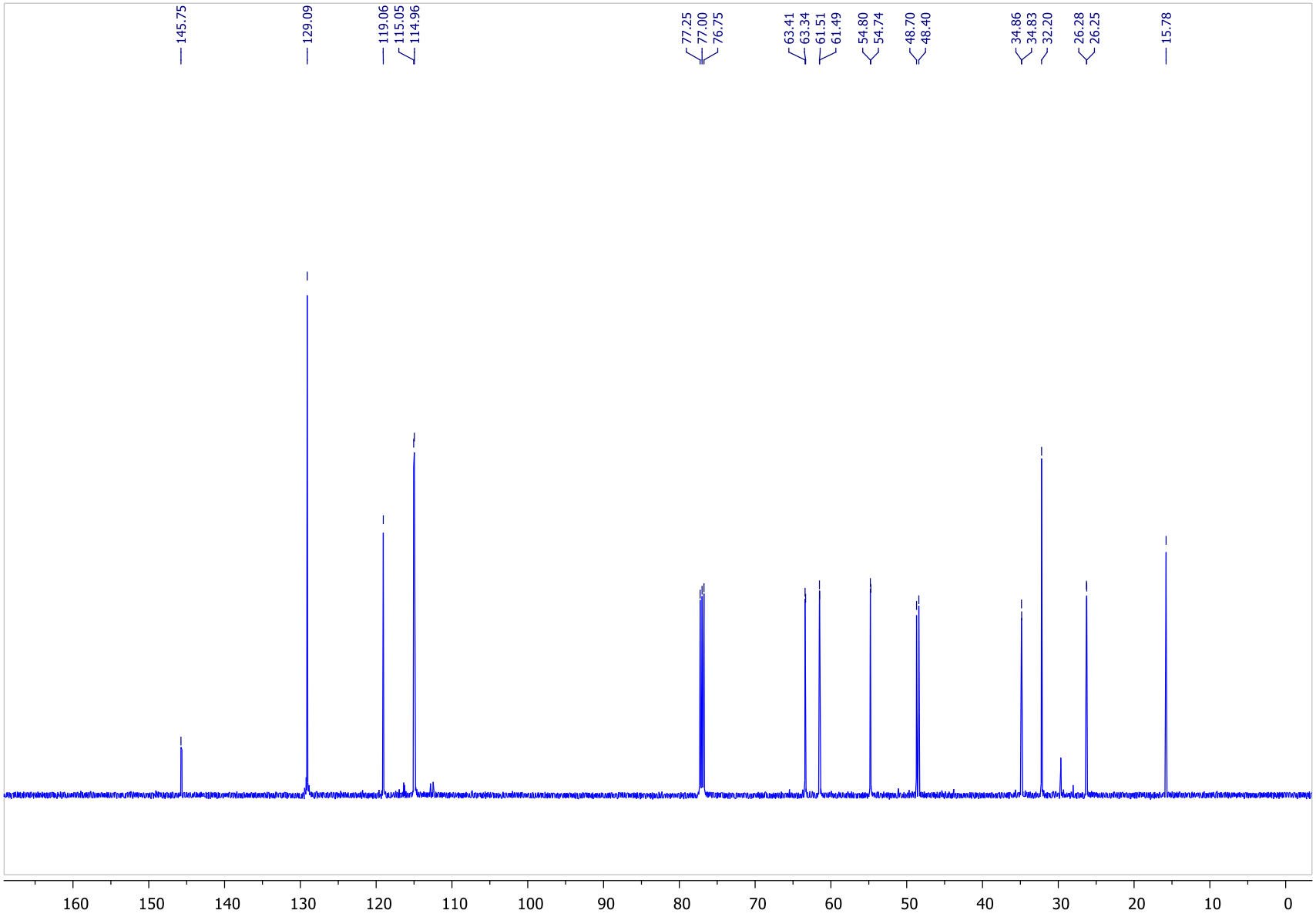
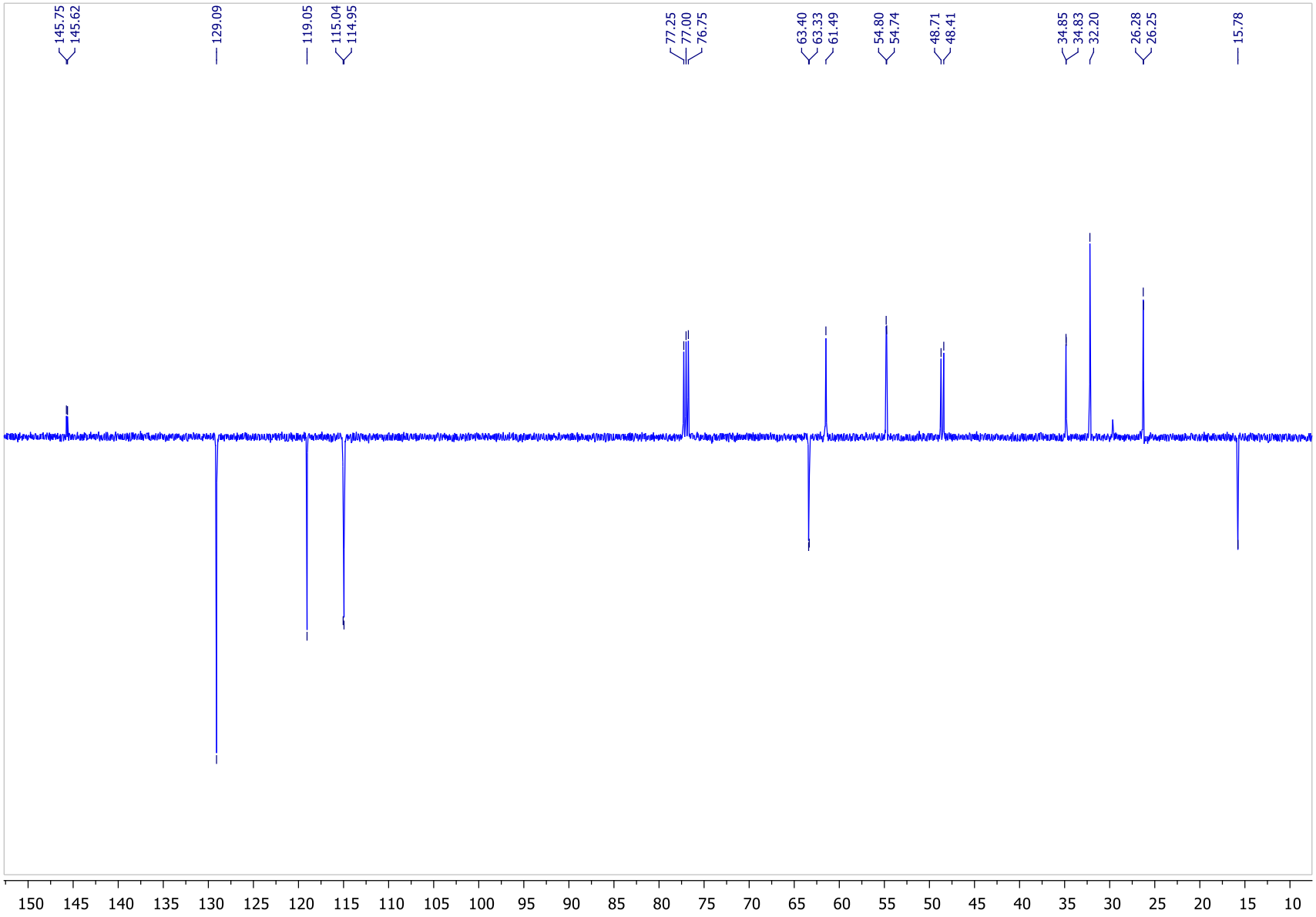
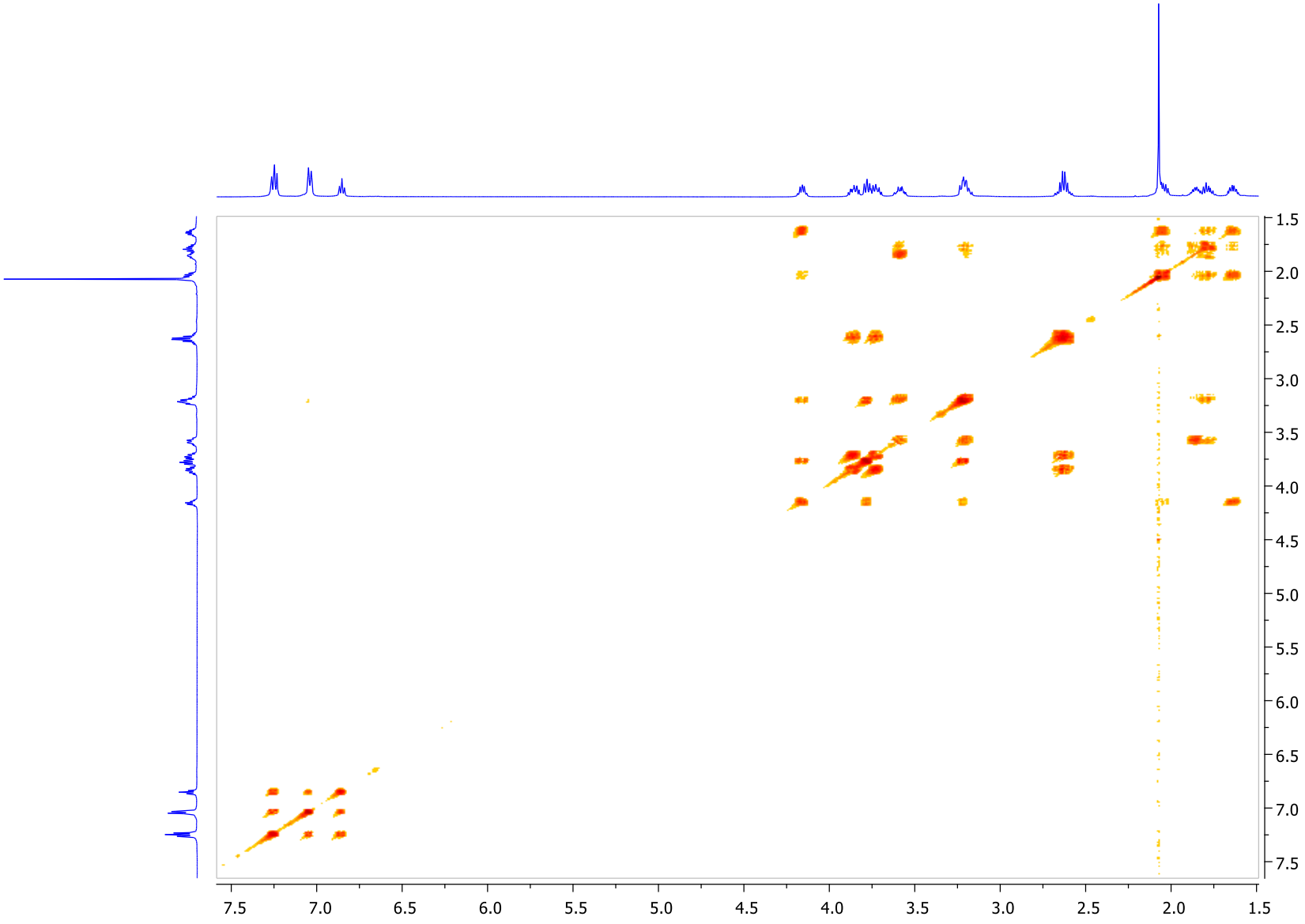


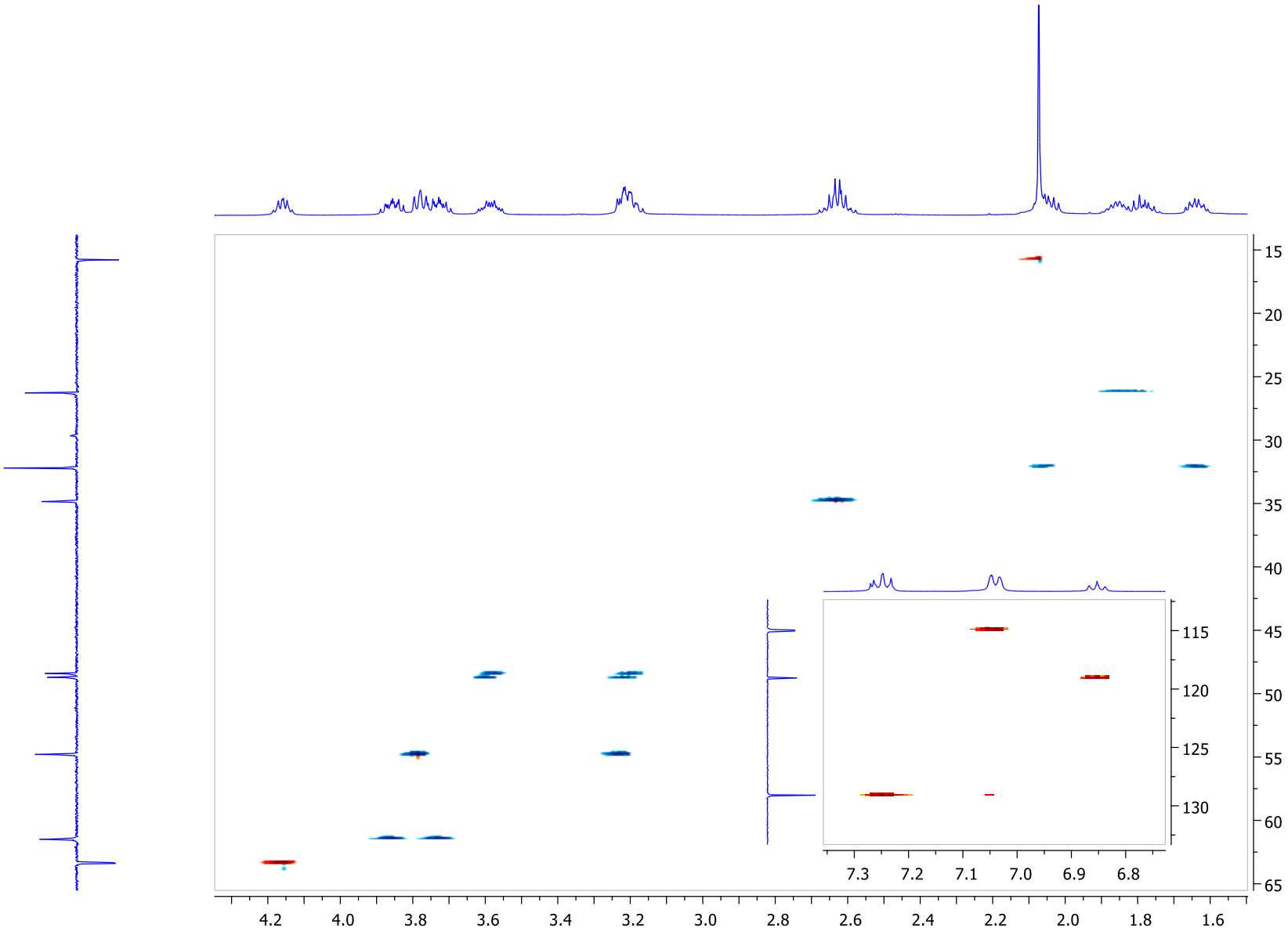
Ligand 1, $^{13}C\{H\}$ ($CDCl_3$, 125.69 MHz)



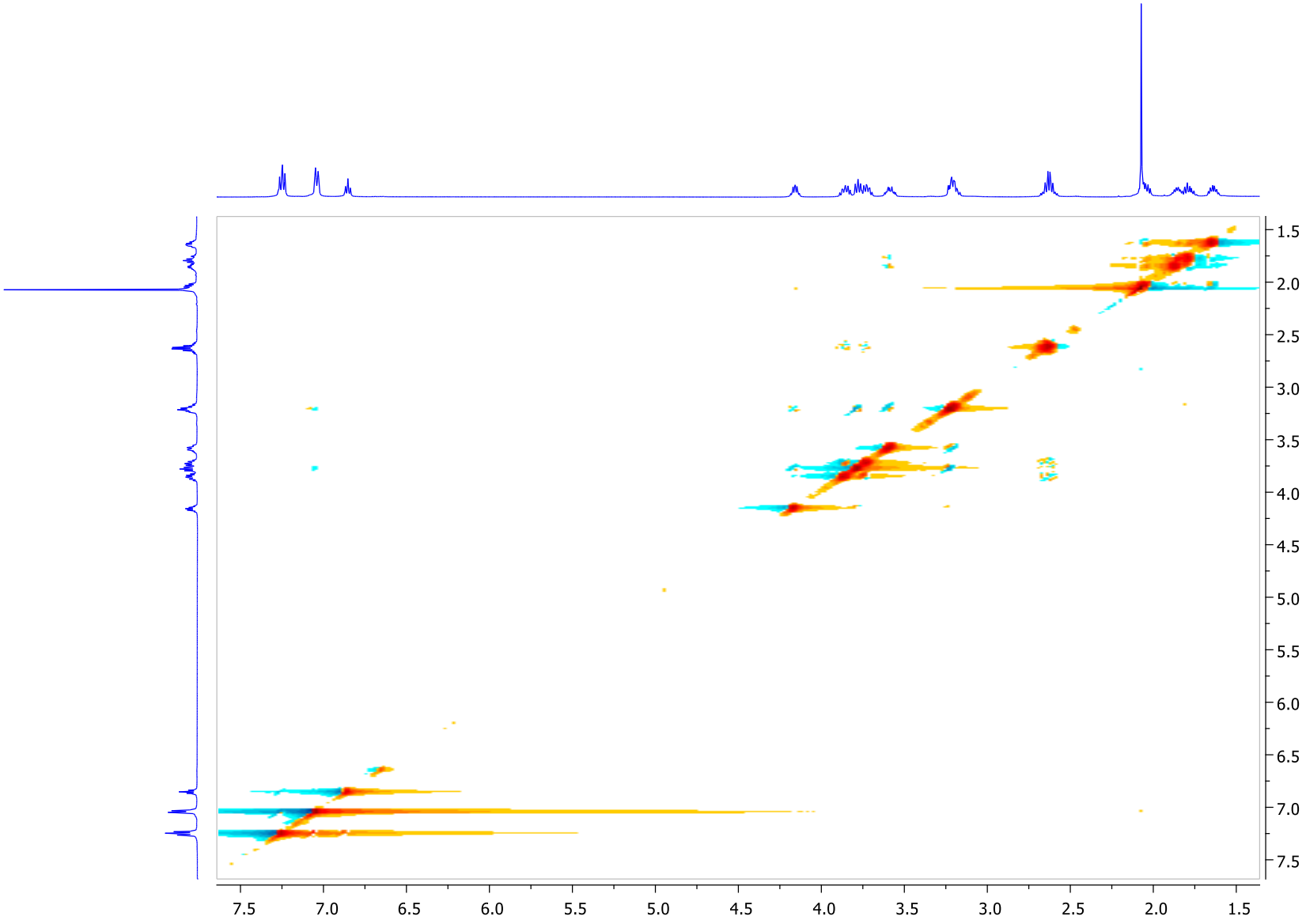
Ligand 1, ^{13}C APT ($CDCl_3$, 125.690 MHz)



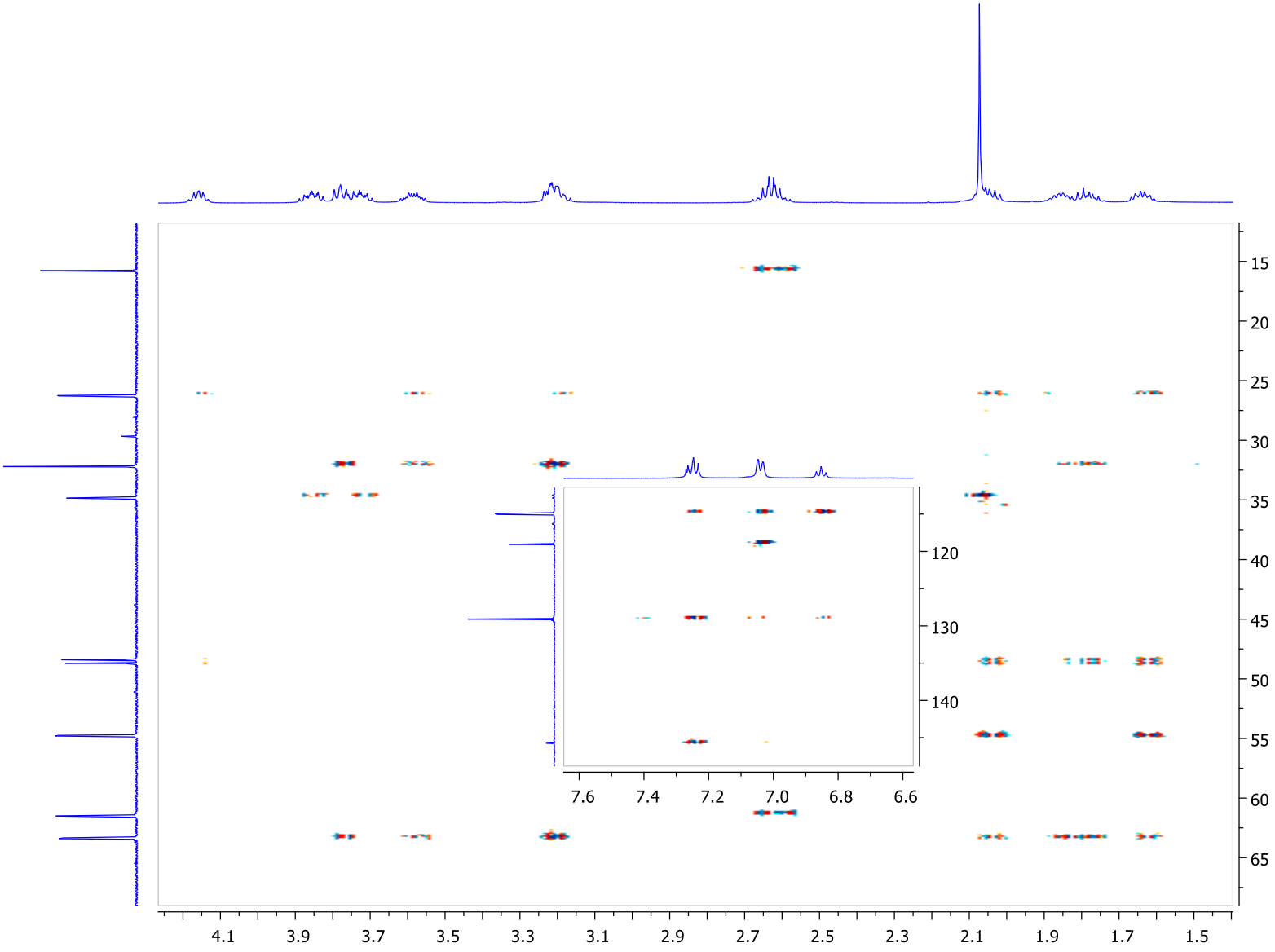
Ligand 1, ^{1}H-^{1}H COSY



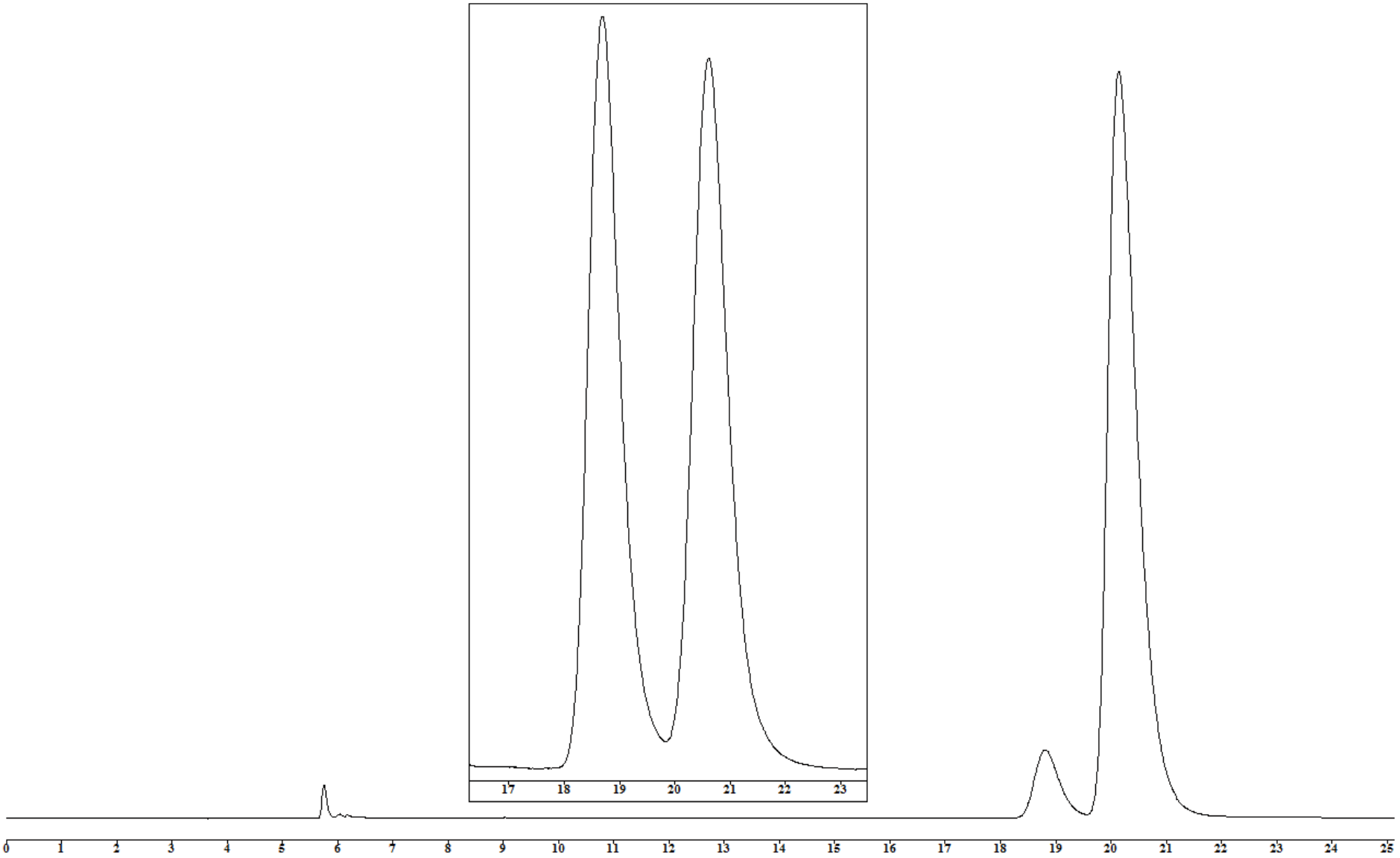
Ligand 1, ^{1}H-^{13}C HSQC



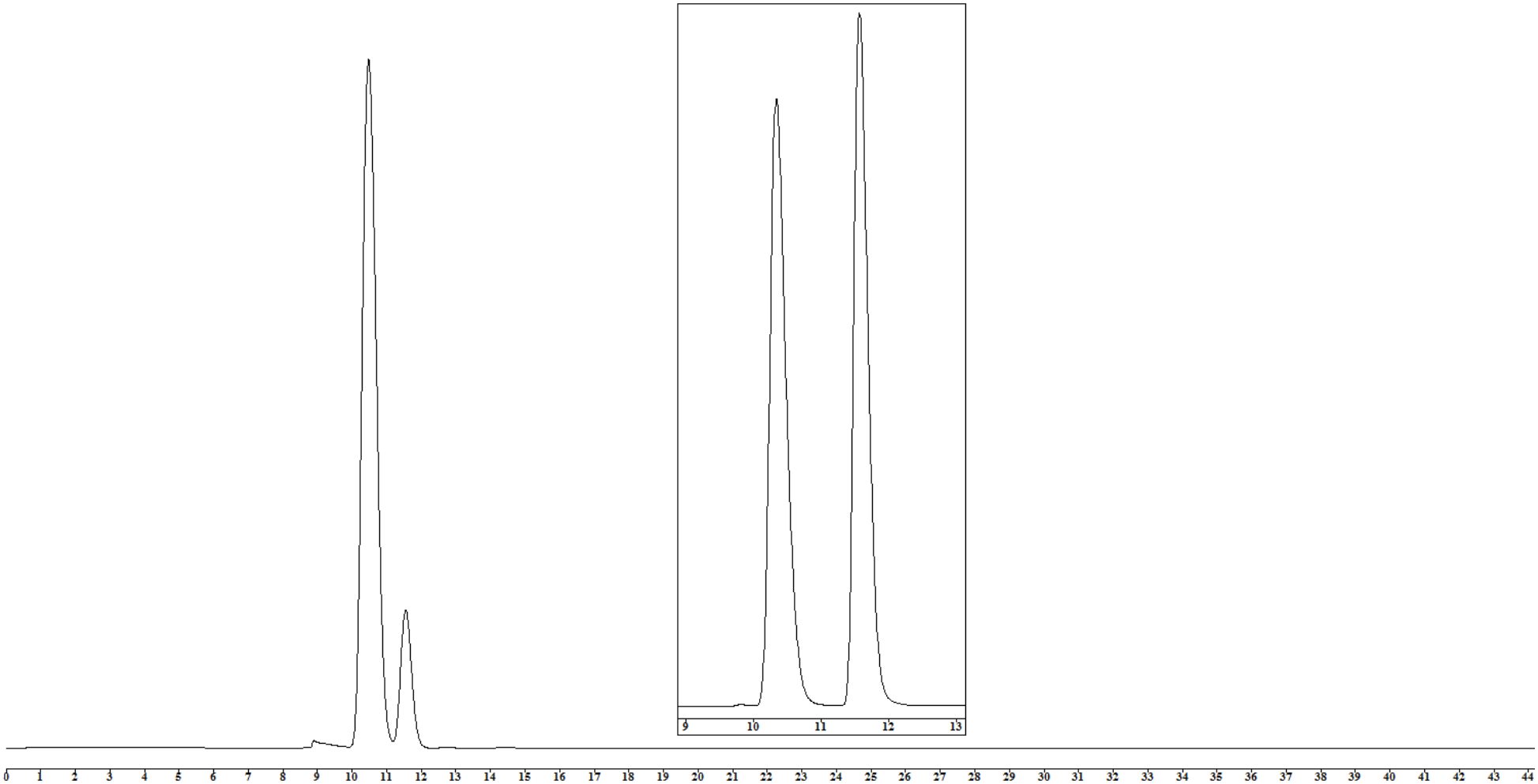
Ligand 1, ^{1}H,^{1}H NOESY



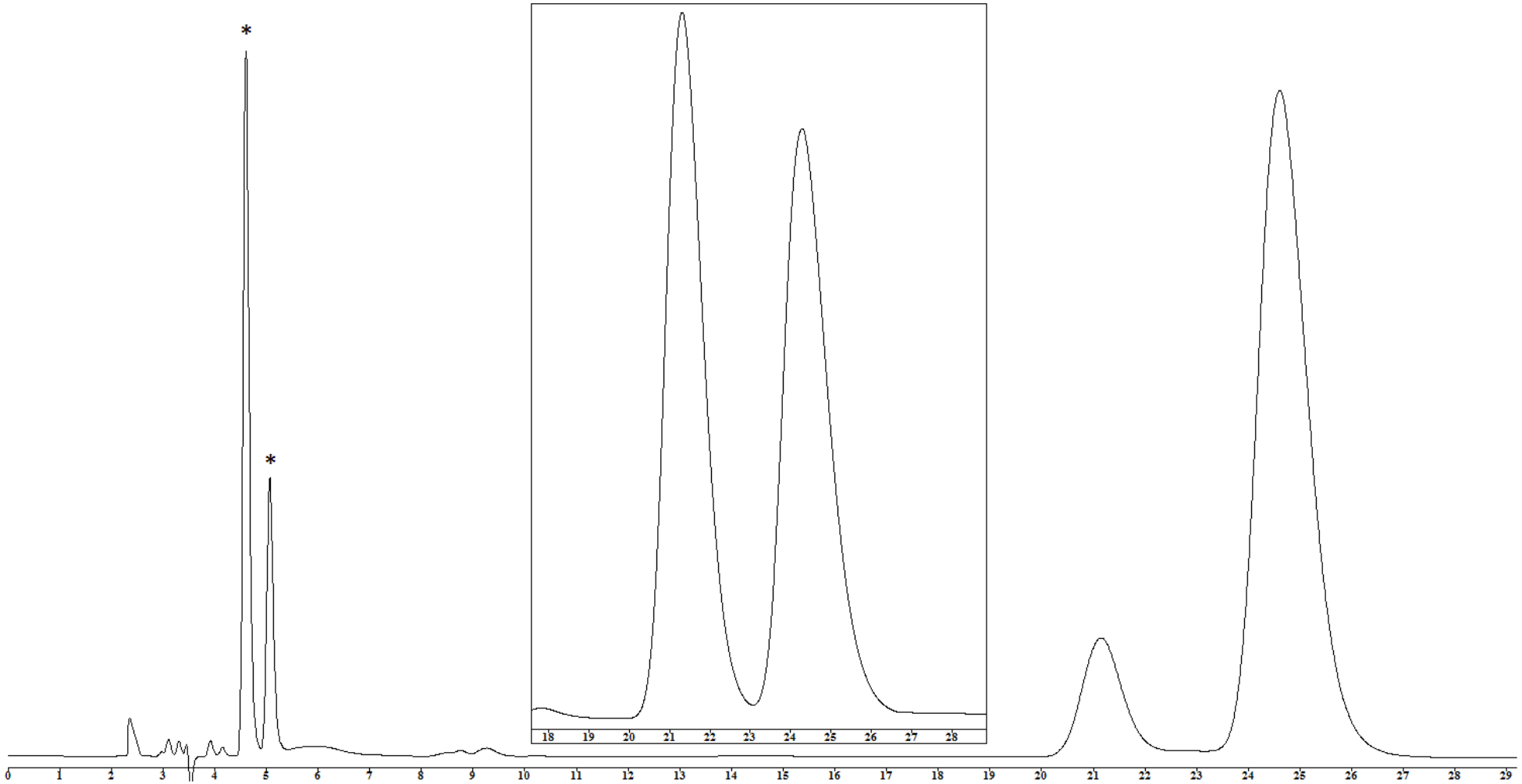
Ligand 1, ^{1}H-^{13}C HMBC



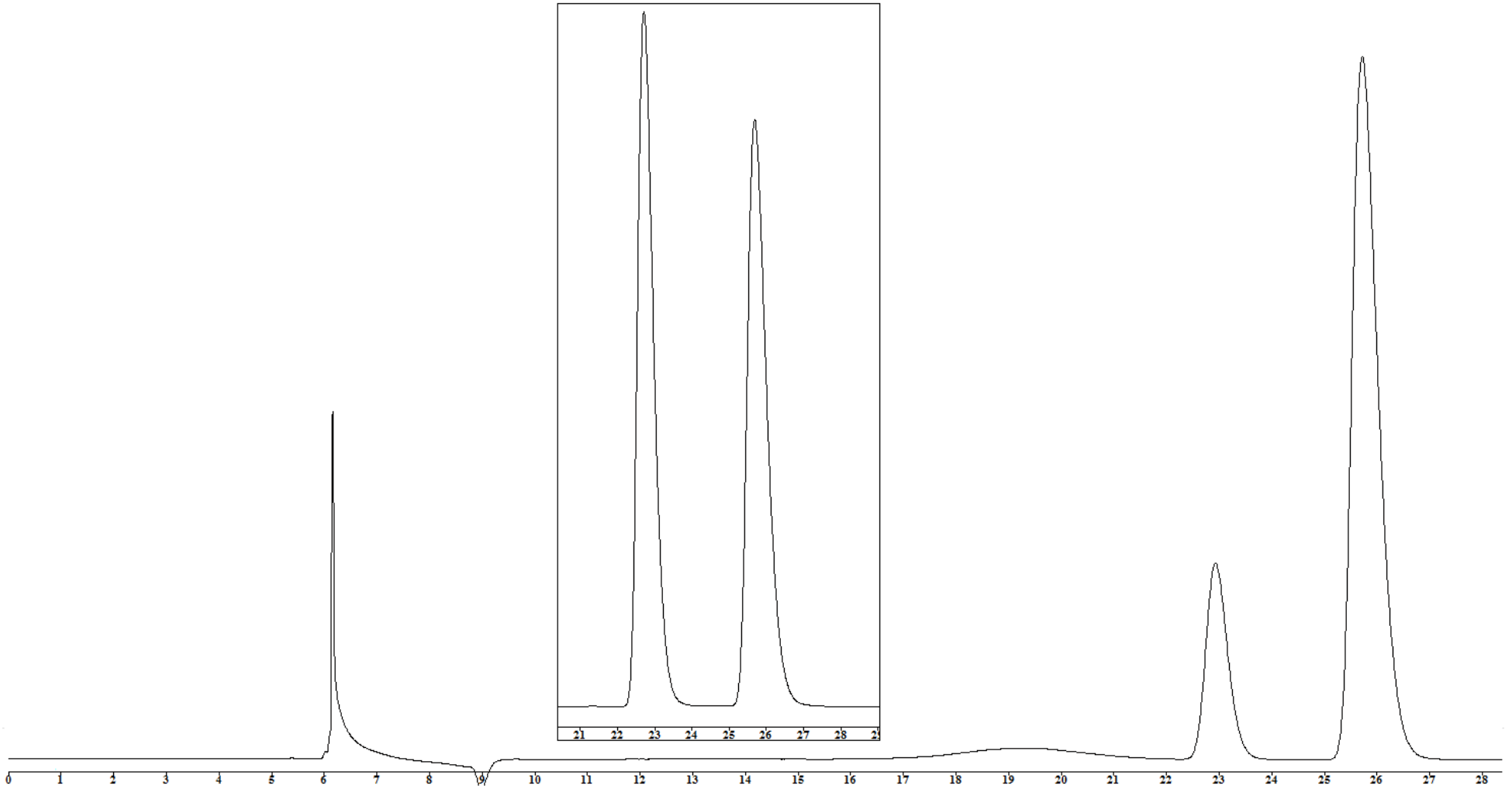
Chiral HPLC trace for the Pd-catalyzed asymmetric allylic alkylation of 2a with dimethyl malonate (entry 7 in Table 1) and for a racemic mixture of 3 (in the frame).



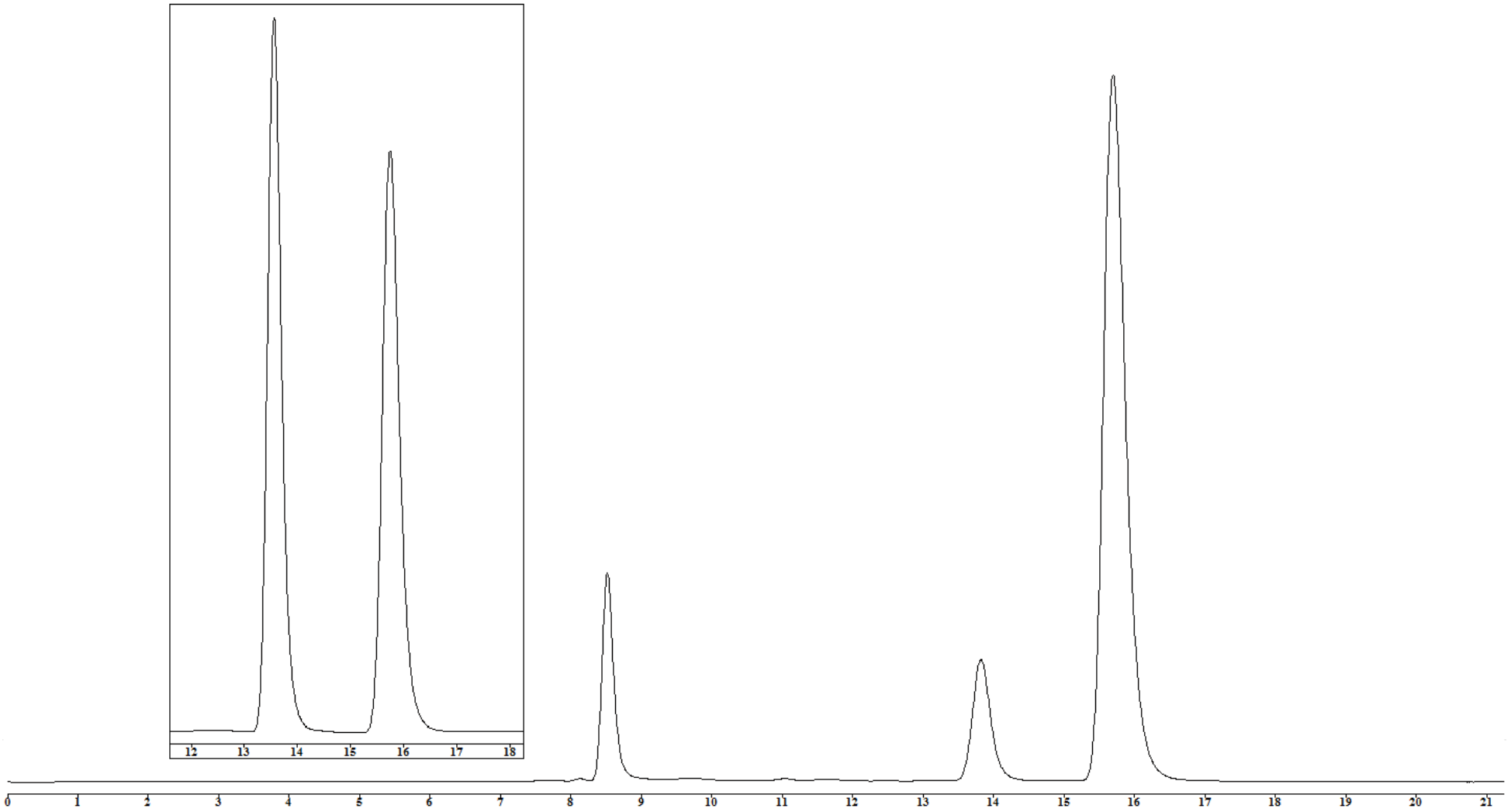
Chiral HPLC trace for the Pd-catalyzed asymmetric allylic amination of 2a with pyrrolidine (entry 1 in Table S2) and for a racemic mixture of 4 (in the frame).



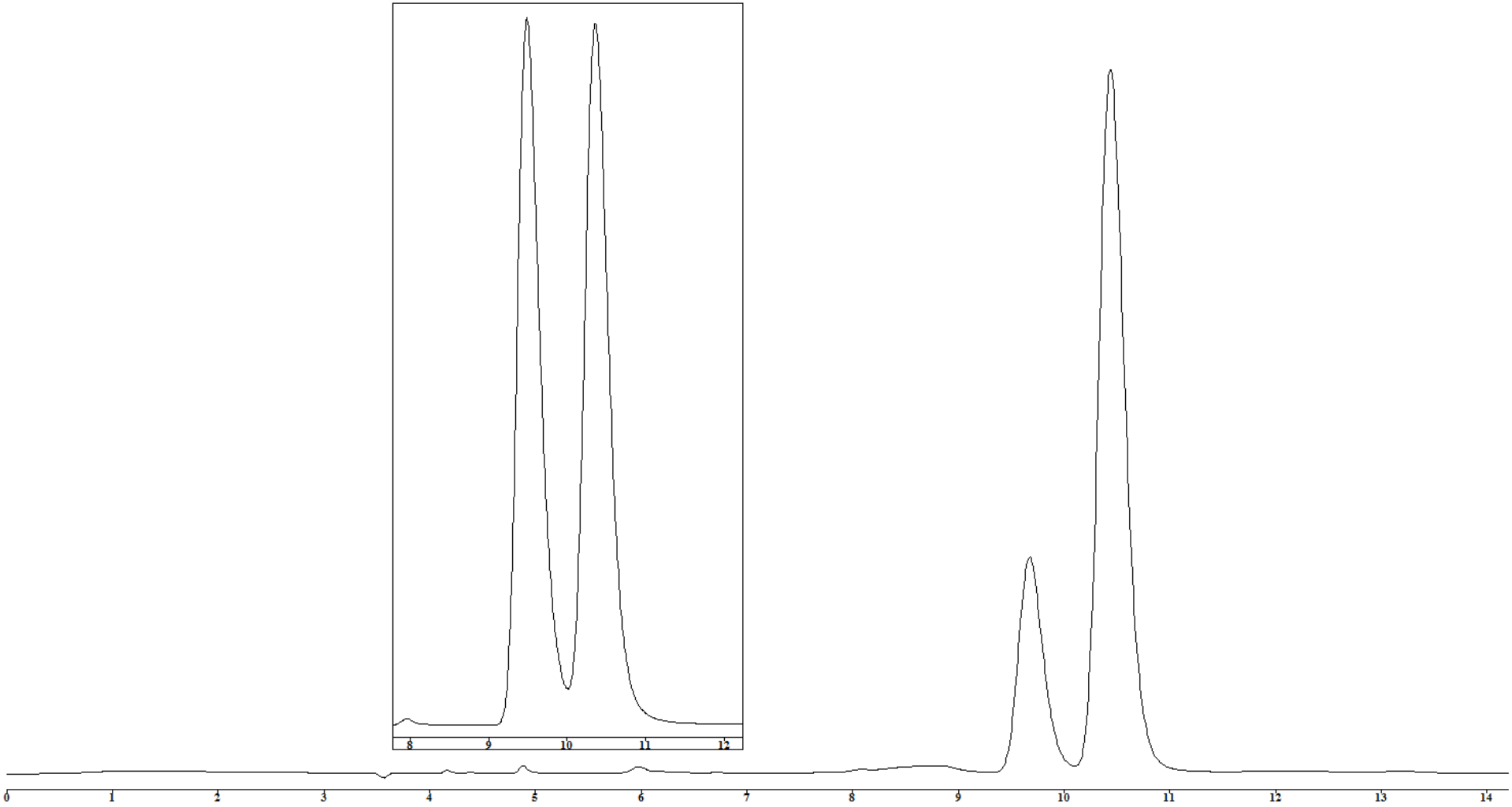
Chiral HPLC trace for the Pd-catalyzed asymmetric allylic amination of 2a with diethyl (aminomethyl)phoshonate (entry 4 in Table S3) and for a racemic mixture of 5 (in the frame).
* starting substrate **2a**



Chiral HPLC trace for the Pd-catalyzed asymmetric allylic alkylation of 6 with 7a (entry 2 in Table S4) and for a racemic mixture of 8a (in the frame).



Chiral HPLC trace for the Pd-catalyzed asymmetric allylic alkylation of 6 with 7b (entry 2 in Table S5) and for a racemic mixture of 8b (in the frame).



Chiral HPLC trace for the Pd-catalyzed asymmetric allylic alkylation of 6 with 9 (entry 2 in Table S6) and for a racemic mixture of 10 (in the frame).