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Chiral inducers with (1*R*,2*R*)-1,2-diaminocyclohexane core for organo- and metallocatalysis

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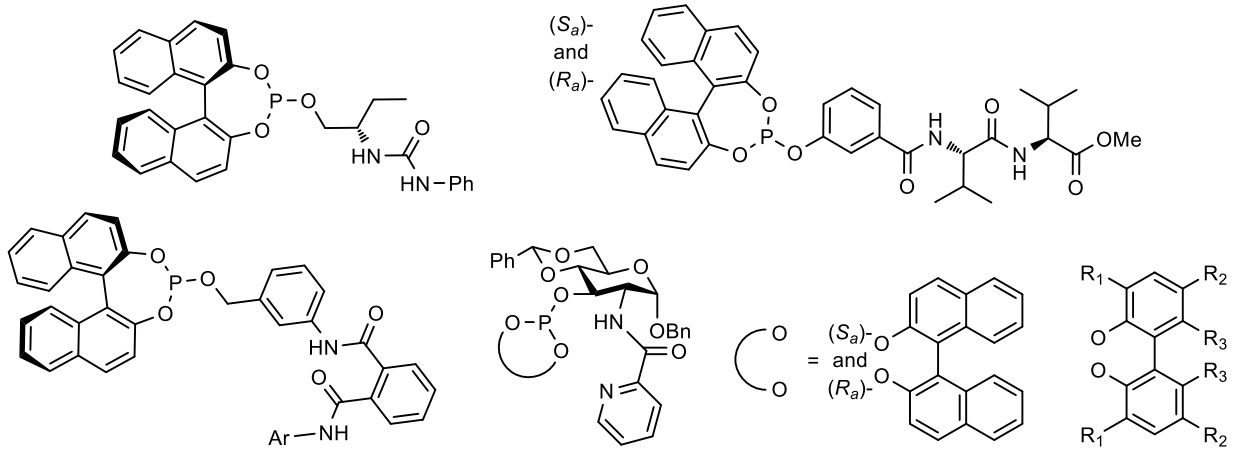

Figure S1. Phosphite ligands based on hydroxyl-containing amides.

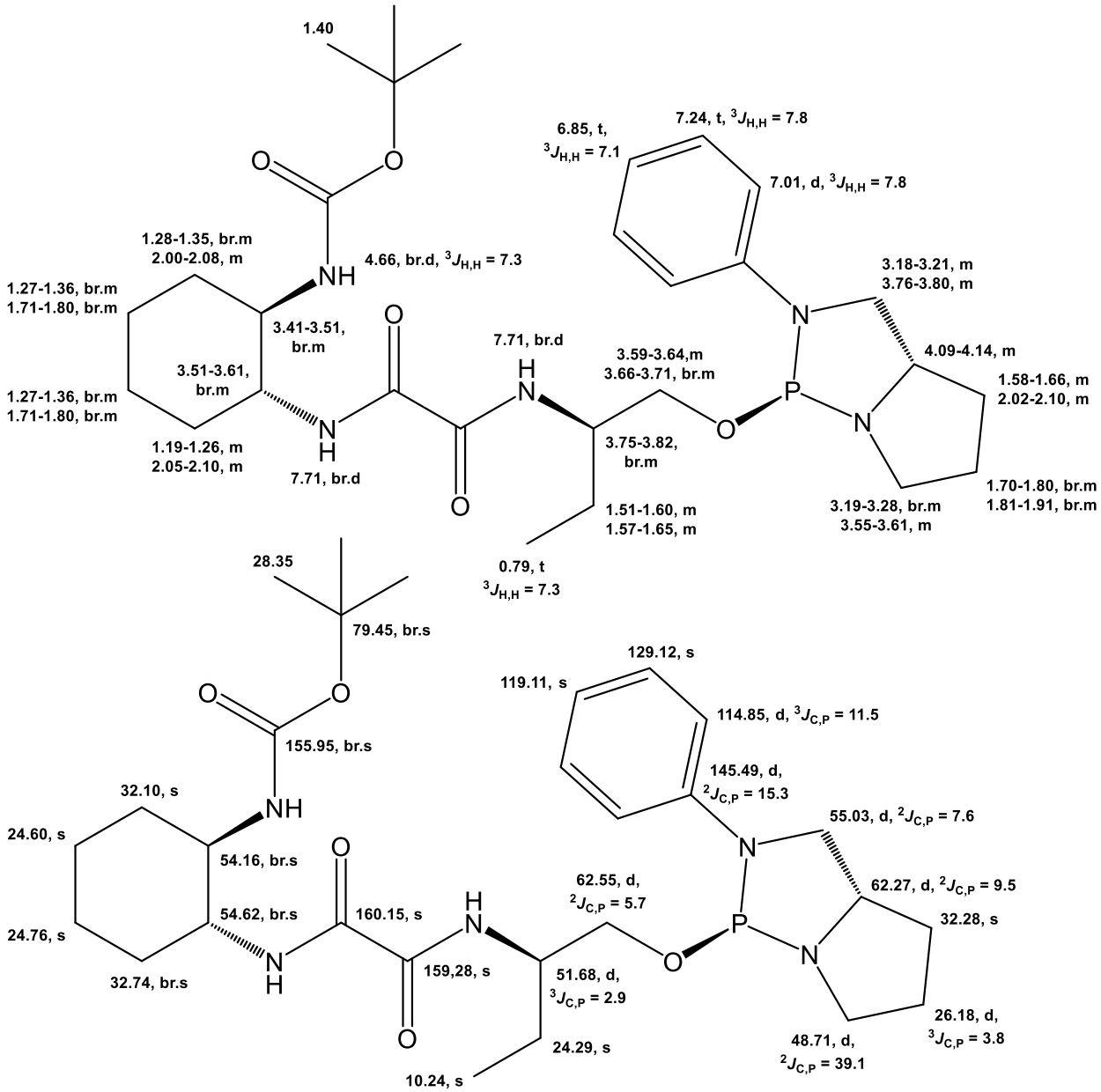

Figure S2. Full assignment of all H-1 and C-13 resonances for ligand 1.

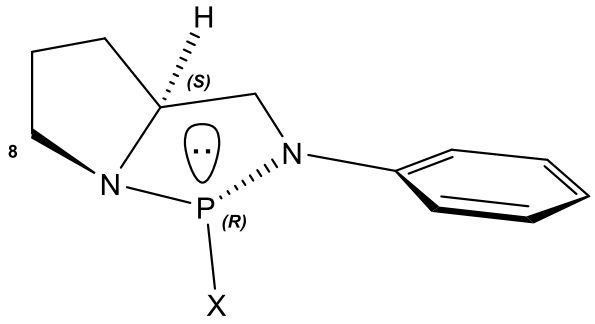

Figure S3. Stereochemistry of the phosphabicyclic part in ligand 1 (X is exocyclic substituent).

Table S1. Pd-catalyzed allylic alkylation of substrate **5** with dimethyl malonate. [a]

Entry	**1**/Pd	Solvent	Conversion (%)	*ee* (%) [b]
1	1:1	THF	95	88 (*S*)
2	2:1	THF	100	93 (*S*)
3	1:1	CH_2Cl_2	100	97 (*S*)
4	2:1	CH_2Cl_2	100	98 (*S*)

[a] Reaction conditions: 2 mol% of $[Pd(allyl)Cl]_2$, *N*,*O*–bis(trimethylsilyl)acetamide (BSA), K_2CO_3, 20 °C, 48 h.
[b] Conversion of substrate **5** and enantiomeric excess of product **6** were determined by HPLC (Kromasil 5-CelluCoat, C_6H_{14}—Pr^iOH (99 : 1), 0.6 ml × min^{-1}, 254 нм, *t*(*R*) = 21.0 min, *t*(*S*) = 22.7 min).

Table S2. Pd-catalyzed allylic amination of substrate **5** with pyrrolidine. [a]

Entry	**1**/Pd	Solvent	Conversion (%)	*ee* (%) [b]
1	1:1	THF	98	94 (*R*)
2	2:1	THF	100	94 (*R*)
3	1:1	CH_2Cl_2	100	85 (*R*)
4	2:1	CH_2Cl_2	100	85 (*R*)

[a] Reaction conditions: 2 mol% of $[Pd(allyl)Cl]_2$, 20 °C, 48 h.
[b] Conversion of substrate **5** and enantiomeric excess of product **7** were determined by HPLC (Daicel Chiralcel OD-H, C_6H_{14}—Pr^iOH (200 : 1), 0.3 ml × min^{-1}, 254 нм, *t*(*R*) = 17.3 min, *t*(*S*) = 19.2 min).

Table S3. Pd-catalyzed allylic amination of substrate **5** with diethyl (aminomethyl)phosphonate. [a]

Entry	**1**/Pd	Solvent	Conversion (%)	*ee* (%) [b]
1	1:1	THF	33	88 (II)
2	2:1	THF	72	94 (II)
3	1:1	CH_2Cl_2	60	96 (II)
4	2:1	CH_2Cl_2	88	94 (II)

[a] Reaction conditions: 2 mol% of $[Pd(allyl)Cl]_2$, 20 °C, 48 h.
[b] Conversion of substrate **5** and enantiomeric excess of product **8** were determined by HPLC (Kromasil 5-CelluCoat, C_6H_{14}—Pr^iOH (98 : 2), 1.5 ml × min^{-1}, 254 нм, *t*(I) = 19.5 min, *t*(II) = 21.5 min).

Table S4. Pd-catalyzed allylation of ethyl 2-oxocyclohexane-1-carboxylate (**9**) with cinnamyl acetate (**10**). [a]

Entry	**1**/Pd	Conversion (%)	*ee* (%) [b]
1	1:1	26	64 (*S*)
2	2:1	100	81 (*S*)

[a] Reaction conditions: 2 mol% of $[Pd(allyl)Cl]_2$, BSA, $Zn(OAc)_2$, toluene, 20 °C, 48 h.
[b] Conversion of substrate **10** and enantiomeric excess of product **11** were determined by HPLC (Kromasil 5-CelluCoat, C_6H_{14}—Pr^iOH (95: 5), 0.4 ml × min^{-1}, 254 нм, *t*(*R*) = 14.5 min, *t*(*S*) = 16.7 min).

Table S5. Rh-catalyzed hydrogenation of substrate **12**. [a]

Entry	Precatalyst	**1**/Rh	*ee* (%) [b]
1	$[Rh(COD)_2]BF_4$	1:1	59 (*R*)
2	$[Rh(COD)_2]BF_4$	2:1	43 (*R*)
3	$[Rh(COD)_2]B[C_6H_3(CF_3)_2\text{-}3,5]_4$	1:1	78 (*R*)
4	$[Rh(COD)_2]B[C_6H_3(CF_3)_2\text{-}3,5]_4$	2:1	72 (*R*)

[a] Reaction conditions: 1 mol% of $[Rh(COD)_2]X$, CH_2Cl_2, 1.5 atm. H_2, 20 °C, 24 h.
[b] Conversion of substrate **12** and enantiomeric excess of product **13** were determined by HPLC (Daicel Chiralcel OD-H, C_6H_{14}—Pr^iOH (80 : 20), 0.6 mL × min^{-1}, 215 нм, *t*(*R*) = 9.1 min, *t*(S) = 11.1 min).

Table S6. Rh- and Ir-catalyzed hydrosilylation of substrate **14** with diphenylsilane. [a]

Entry	Precatalyst	**1**/M	Yield (%)	*ee* (%) [b]
1	$[Rh(COD)Cl]_2$	1:1	55	32 (*R*)
2	$[Rh(COD)Cl]_2$	2:1	42	26 (*R*)
3	$[Ir(COD)Cl]_2$	1:1	28	28 (*R*)
4	$[Ir(COD)Cl]_2$	2:1	26	10 (*R*)

[a] Reaction conditions: 0.5 mol% of $[M(COD)Cl]_2$, toluene, 20 °C, 48 h.
[b] Enantiomeric excess of product **15** were determined by HPLC (Daicel Chiralcel OD-H, C_6H_{14}—Pr^iOH (99: 1), 0.75 mL × min^{-1}, 200 нм, *t*(*R*) = 20.5 min, *t*(*S*) = 23.5 min).

Table S7. Organocatalytic reduction of substrate **14** with trichlorosilane. [a]

Entry	Solvent	Yield (%)	*ee* (%) [b]
1	$CHCl_3$	90	50 (*S*)
2	CH_2Cl_2	88	36 (*S*)

[a] Reaction conditions: 10 mol% of **2**, 0 ^{0}C, 24 h.
[b] Enantiomeric excess of product **15** were determined by HPLC (Daicel Chiralcel OD-H, C_6H_{14}—Pr^iOH (99: 1), 0.75 mL × min^{-1}, 200 нм, *t*(*R*) = 20.5 min, *t*(*S*) = 23.5 min).

Experimental Section

General Remarks. ^{31}P, ^{1}H, and ^{13}C NMR spectra were recorded with Bruker Avance 400 (working frequencies of 161.98, 400.13, and 100.61 MHz, respectively) and Varian Inova 500 (working frequencies of 202.33, 499.8 and 125.69 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 and ^{1}H-^{13}C HSQC experiments taking into accounts the published data.[S1] 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.

All reactions were carried out in anhydrous solvents under dry argon. Ethyl 2-(((1*R*,2*R*)-2-((*tert*-butoxycarbonyl)amino)cyclohexyl)amino)-2-oxoacetate (**3**), as well as phosphorylating reagent – (5*S*)-2-chloro-3-phenyl-1,3-diaza-2-phosphabicyclo[3.3.0]octane (**4**) were obtained as published.[S2,S1a] The starting substrates – (*E*)-1,3-diphenylallyl acetate (**5**), methyl (*Z*)-2-acetamido-3-phenylacrylate (**12**) and (*E*)-*N*-(4-methoxyphenyl)-1-phenylethan-1-imine (**14**), N-nucleophile diethyl (aminomethyl)phosphonate, as well as precatalysts $[Pd(allyl)Cl]_2$, $[Rh(COD)_2]BF_4$, $[Rh(COD)_2]B[C_6H_3(CF_3)_2\text{-}3,5]_4$, $[Rh(COD)Cl]_2$ and $[Ir(COD)Cl]_2$ were synthesized following the known procedures.[S3] Catalytic studies of asymmetric alkylation of substrate **5** with dimethyl malonate and its amination with pyrrolidine and diethyl (aminomethyl)phosphonate, allylation of compound **9** with substrate **10**, asymmetric hydrogenation of substrate **12**, asymmetric reduction of substrate **14** with trichlorosilane and diphenylsilane, determination of the conversion of substrates **5, 10** and **12**, and enantiomeric excesses of products **6**, **7**, **8**, **11**, **13** and **15** were performed as earlier described.[S1a,S4,S3c]

(*R*)-2-Aminobutan-1-ol, trichlorosilane, diphenylsilane, dimethyl malonate, BSA, pyrrolidine, triethylamine, ethyl 2-oxocyclohexane-1-carboxylate (**9**) and cinnamyl acetate (**10**) were purchased from Fluka and Aldrich.

***N*-[(1*R*,2*R*)-2-(*tert*-Butoxycarbonylamino)cyclohexyl]-*N'*-[(1*R*)-1-(hydroxymethyl)-propyl]oxalamide (2).** To a vigorously stirred solution of compound **3** (1.57 g, 5 mmol) in toluene (5 mL), (*R*)-2-aminobutan-1-ol (0.45 g, 5 mmol) was added in one portion at 20 °C. The mixture was then heated to boiling point, refluxed for 2 h and allowed to cool to 20 °C. The precipitated product was filtered off, washed with diethyl ether (2 × 10 ml) and dried in vacuum (1 Torr). Yield 1.66 g (93%), white powder, m. p. 225-226 °C. Anal. Calcd for $C_{17}H_{31}N_3O_5$: C, 57.12; H, 8.74; N, 11.76. Found: C, 57.27; H, 8.80; N, 11.59. ^{1}H NMR (499.6 MHz, DMSO-d_6, *J*/Hz): δ = 0.80 (t, 3 H, CH_{3Me}, $^{3}J_{H,H}$ = 7.3), 1.14–1.5 (m, 2 H CH_{2Cy} and CH_{2Cy}), 1.25–1.35 (m, 1 H CH_{2Cy}), 1.34–1.34 (m, 1 H CH_{2Cy}), 1.33 (s, 9 H, $(CH_3)_{3Bu^t}$), 1.37–1.47 (m, 1 H, CH_2CH$_3$,), 1.55–1.68 (m, 1 H, CH_2CH$_3$) , 1.59–1.69 (br.m, 2 H, CH_{2Cy} and CH_{2Cy}), 1.75–1.82 (m, 2 H, CH_{2Cy} and CH_{2Cy}), 3.28–3.34 (m, 1 H,

C*H*$_2$OH), 3.36–3.45 (m, 3 H, CH$_{Cy}$N, CH$_{Cy}$N and C*H*$_2$OH), 3.56–3.65 (br.m, 1 H, CHN), 4.68 (t, 1 H, CH$_2$O*H*, $^3J_{H,H}$ = 5.4), 6.60 (br.d, 1 H, CH$_{Cy}$N*H*) 8.16 (br.d, 1 H, CHN*H*), 8.21 (br.d, 1 H, CH$_{Cy}$N*H*). ^{13}C NMR (125.70 MHz, DMSO-*d*$_6$): δ = 10.26 (s, CH$_{3Me}$), 23.15 (s, CH$_2$), 24.12 (s, CH$_{2Cy}$), 24.37 (s, CH$_{2Cy}$), 27.99 (s, (*C*H$_3$)$_3$C), 31.03 (s, CH$_{2Cy}$), 31.55 (br.s, CH$_{2Cy}$), 52.14 (br.s, CH$_{Cy}$N), 52.83 (s, CHN), 54.09 (br.s, CH$_{Cy}$N), 62.21 (s, CH$_2$OH), 77.59 (s, (CH$_3$)$_3$*C*), 155.57 (br.s, (O)C=O), 159.43 (s, C=O), 159.47 (s, C=O).

(2*R*,5*S*)-2-{(2*R*)-[(1*R*,2*R*)-2-(*tert*-Butoxycarbonylamino)cyclohexylamino]-2-ethyl-4,5-dioxo-3-azapent-1-yloxy}-3-phenyl-1,3-diaza-2-phosphabicyclo[3.3.0]octane (1). To a vigorously stirred solution of phosphorylating agent **4** (0.48 g, 2 mmol) and Et$_3$N (0.56 ml, 4 mmol) in toluene (15 ml), compound **2** (0.72 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$_2$O$_3$. The filtrate was concentrated in vacuum (40 Torr) and the residue was dried in vacuum (1 Torr). The product **1** was purified by flash chromatography on SiO$_2$ (eluent — toluene). Yield 0.91 g (81%), white powder, m.p. 105-106 °C. Anal. Calcd for C$_{28}$H$_{44}$N$_5$O$_5$P: C, 59.88; H, 7.90; N, 12.47. Found: C, 60.14; H, 7.97; N, 12.58.

Pd-catalyzed allylic alkylation of (*E*)-1,3-diphenylallyl acetate (5) with dimethyl malonate. A solution of [Pd(allyl)Cl]$_2$ (0.0019 g, 0.005 mmol) and ligand **1** (0.0056 g, 0.01 mmol or 0.0112 g, 0.02 mmol) in the appropriate solvent (1.5 mL) was stirred for 40 min. (*E*)-1,3-Diphenylallyl acetate (0.05 ml, 0.25 mmol) was added and the solution stirred for 15 min. Dimethyl malonate (0.05 ml, 0.44 mmol), BSA (0.11 ml, 0.44 mmol), and potassium acetate (0.002 g) were added. The reaction mixture was stirred for 48 h, diluted with CH$_2$Cl$_2$ 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 (**6**). 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 allylic amination of (*E*)-1,3-diphenylallyl acetate (5) with pyrrolidine. A solution of [Pd(allyl)Cl]$_2$ (0.0019 g, 0.005 mmol) and ligand **1** (0.0056 g, 0.01 mmol or 0.0112 g, 0.02 mmol) in the appropriate solvent (1.5 mL) was stirred for 40 min. (*E*)-1,3-Diphenylallyl acetate (0.05 ml, 0.25 mmol) was added and the solution stirred for 15 min, then freshly distilled pyrrolidine (0.06 ml, 0.75 mmol) was added. The reaction mixture was stirred for 48 h, diluted with CH$_2$Cl$_2$ 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 (**7**). 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 allylic amination of (*E*)-1,3-diphenylallyl acetate (5) with diethyl (aminomethyl)phosphonate. A solution of [Pd(allyl)Cl]$_2$ (0.0019 g, 0.005 mmol) and ligand **1** (0.0056 g, 0.01 mmol or 0.0112 g, 0.02 mmol) in the appropriate solvent (1.5 ml) was stirred for 40

min. (*E*)-1,3-Diphenylallyl acetate (0.05 ml, 0.25 mmol) was added and the solution 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 (**8**). 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 allylation of ethyl 2-oxocyclohexane-1-carboxylate (9) with cinnamyl acetate (10). A solution of $[Pd(allyl)Cl]_2$ (0.0019 g, 0.005 mmol) and ligand **1** (0.0056 g, 0.01 mmol or 0.0112 g, 0.02 mmol) in toluene (1.5 mL) was stirred for 40 min. Cinnamyl acetate (0.04 ml, 0.25 mmol) was added and the solution stirred for 15 min. Ethyl 2-oxocyclohexane-1-carboxylate (0.06 mL, 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-oxocyclohexanecarboxylate (**11**). 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.

Rh-catalyzed hydrogenation of methyl (*Z*)-2-acetamido-3-phenylacrylate (12). A solution of $[Rh(COD)_2]X$ (X = BF_4, $B[C_6H_3(CF_3)_2\text{-}3,5]_4$) (0.0025 mmol) and ligand **1** (0.0014 g, 0.0025 mmol or 0.0028 g, 0.005 mmol) in CH_2Cl_2 (2 ml) was stirred for 40 min. Then (*Z*)-methyl 2-acetamido-3-phenylacrylate (0.055 g, 0.25 mmol) was added. Catalytic vessel containing the resulting solution was filled with hydrogen to a pressure of 1.5 atm and the reaction mixture was stirred for 24 h. The solvent was evaporated at reduced pressure (40 Torr), the residue was dissolved in diethyl ether (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 methyl acetylphenylalaninate (**13**). 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.

Rh- and Ir-catalyzed hydrosilylation of (*E*)-*N*-(4-methoxyphenyl)-1-phenylethan-1-imine (14) with diphenylsilane. A solution of $[Ir(COD)Cl]_2$ or $[Rh(COD)Cl]_2$ (0.005 mmol) and ligand **1** (0.0056 g, 0.01 mmol or 0.0112 g, 0.02 mmol) in toluene (5 ml) was stirred for 40 min. Substrate **14** (0.23 g, 1 mmol) was added and the solution stirred for 15 min at 0 °C, then pre-cooled to 0 °C H_2SiPh_2 (0.38 ml, 2 mmol) was added dropwise over 5 min. The reaction mixture was stirred at 20 °C for 48 h, cooled to 0 °C, quenched with MeOH (1 mL) and stirred for 30 min at 0 °C. 1 *M* HCl (5 mL) was added, the reaction mixture was stirred at 20 °C for 1 h, diluted with H_2O (50 ml), 3 *M* NaOH (20 ml) and extracted with CH_2Cl_2 (3 x 50 ml). The combined organic layers were dried over Na_2SO_4 and filtered through a short plug of SiO_2. The filtrate was evaporated at reduced pressure (40 Torr) and the obtained residue was purified by flash chromatography on SiO_2 (eluent — hexane–

EtOAc (95:5)). The ^{1}H NMR spectrum of **15** was in complete correspondence with published data.[3c] Enantiomeric excess of product **15** were determined by HPLC on chiral stationary phase.

Organocatalytic reduction of (*E*)-*N*-(4-methoxyphenyl)-1-phenylethan-1-imine (14) with trichlorosilane. To a vigorously stirred solution of the substrate **14** (0.045 g, 0.2 mmol) and organocatalyst **2** (0.0072 g, 0.02 mmol) in the appropriate solvent (1.5 ml) a solution of trichlorosilane (0.04 ml, 0.4 mmol) in the appropriate solvent (0.5 ml) was added dropwise at 0 °C. The reaction mixture was stirred at 0 °C for 24 h, quenched with a saturated aqueous solution of $NaHCO_3$ (3 ml), stirred for 5 min and extracted with CH_2Cl_2 (3 x 5 ml). The combined organic layers were washed with brine (2 x 2 ml), dried over Na_2SO_4 and filtered through a short plug of SiO_2. The filtrate was evaporated at reduced pressure (40 Torr) and the obtained residue was purified by flash chromatography on SiO_2 (eluent — hexane–EtOAc (95 : 5)). The ^{1}H NMR spectrum of **15** was in complete correspondence with published data.[3c] Enantiomeric excess of product **15** were determined by HPLC on chiral stationary phase.

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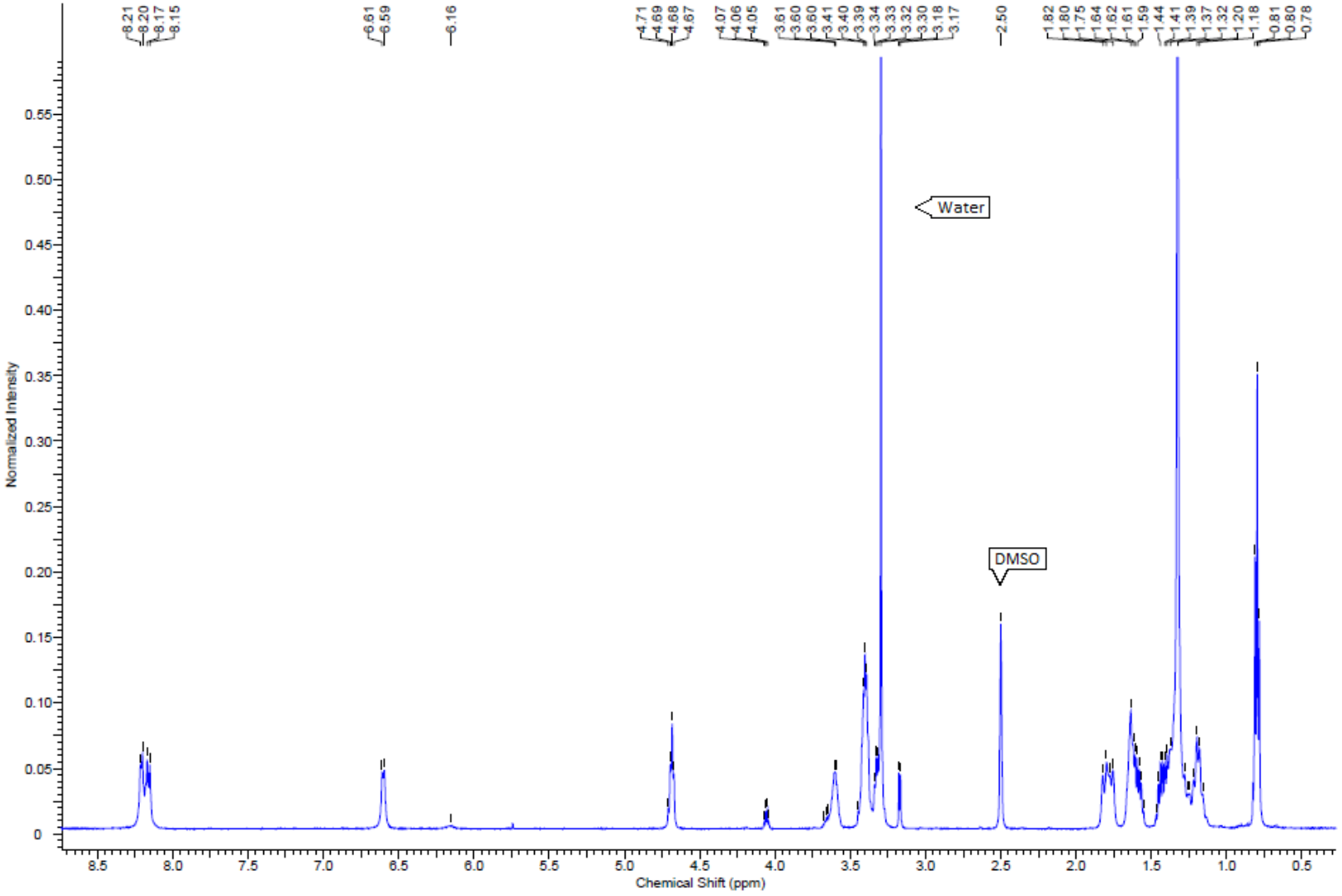
Oxalamide 2, ^{1}H (DMSO-d_6, 499.86 MHz)



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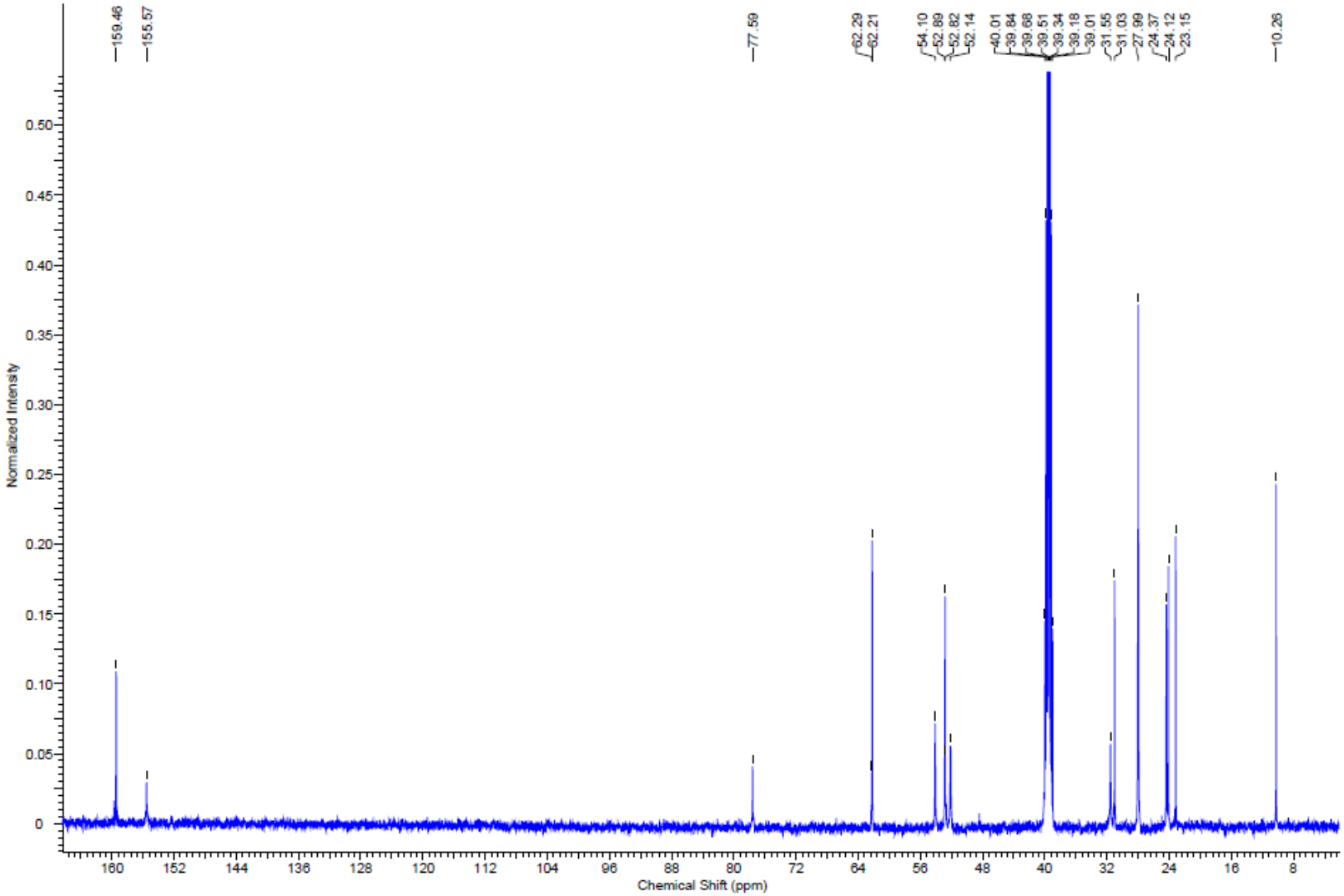
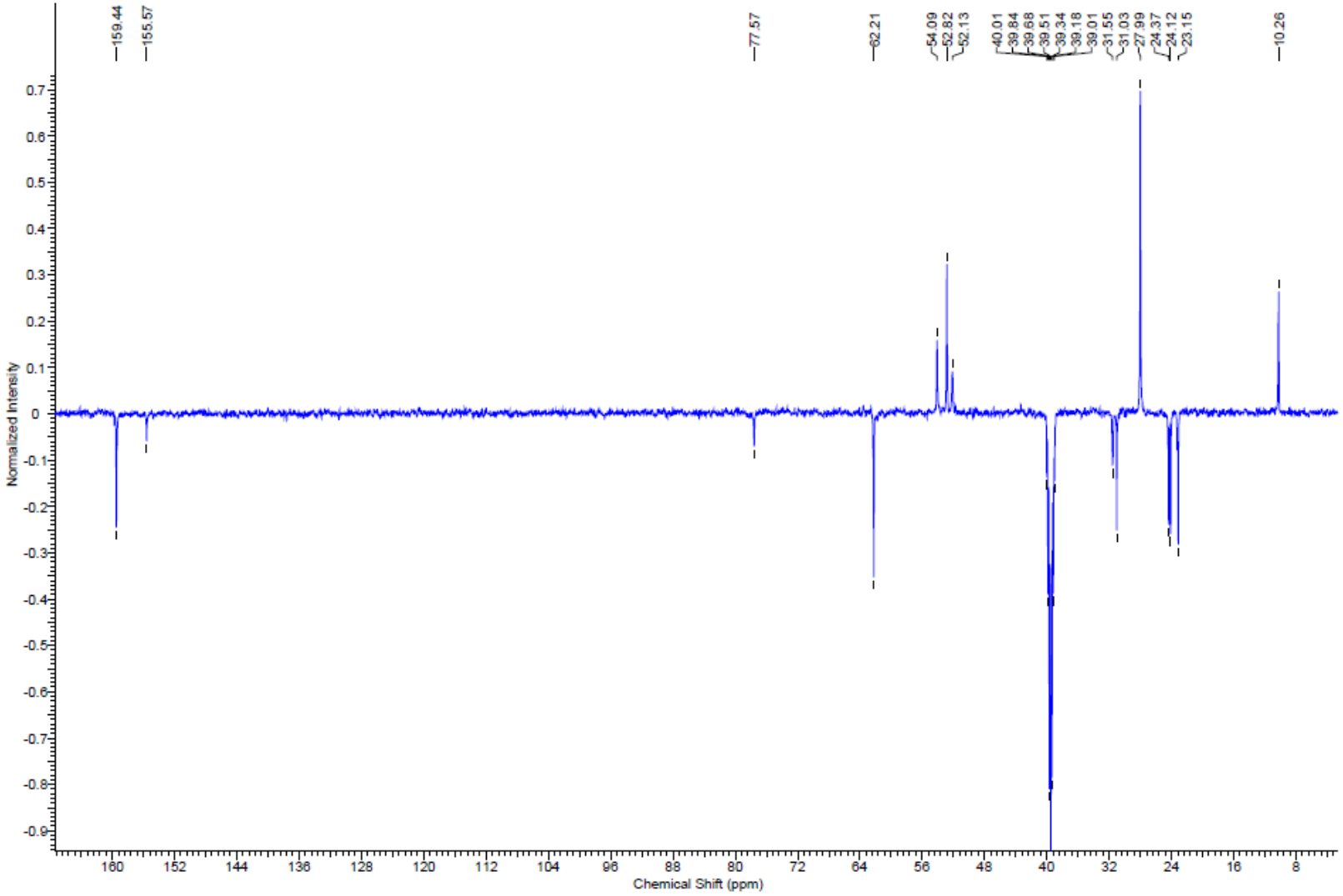
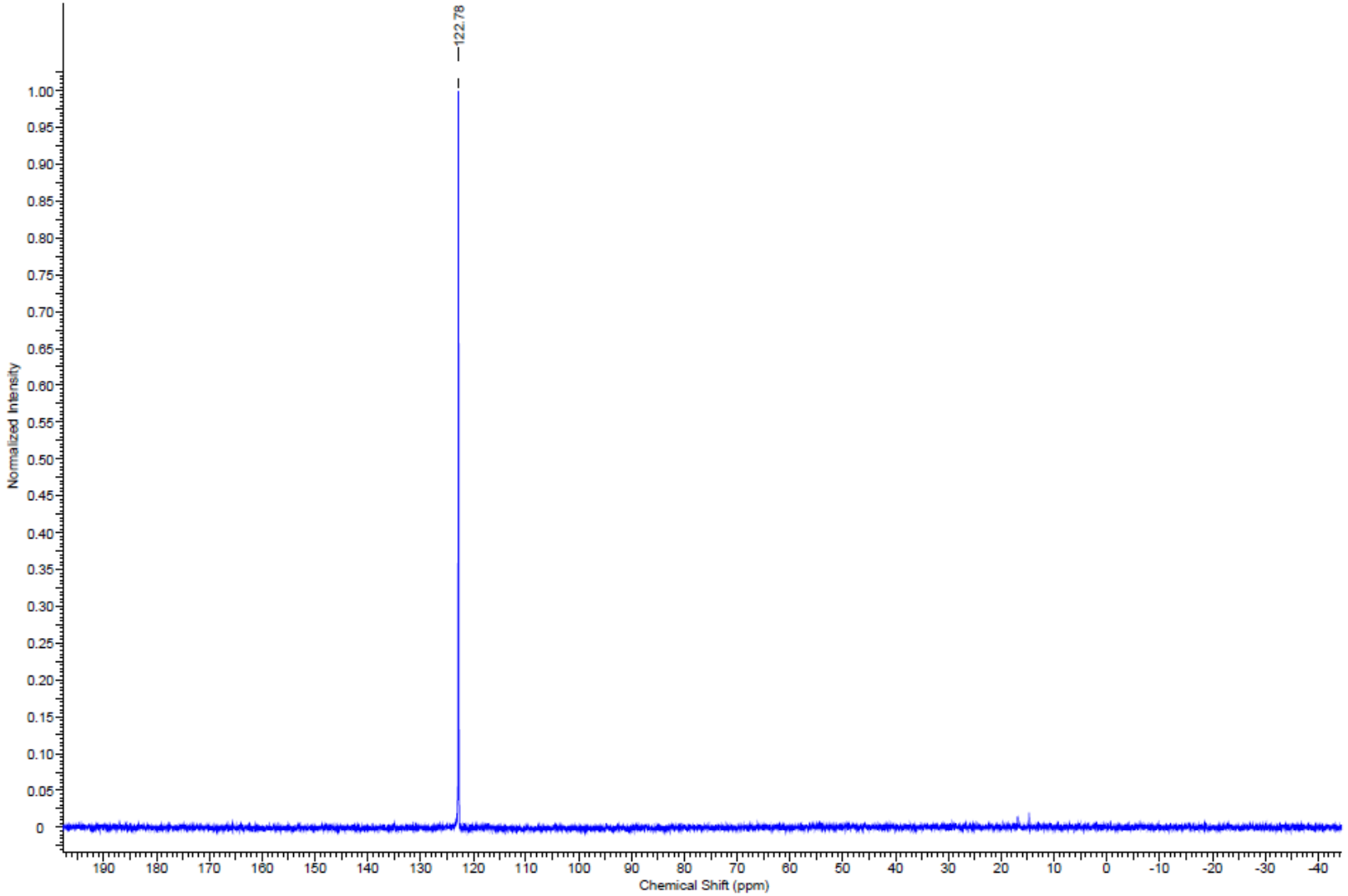


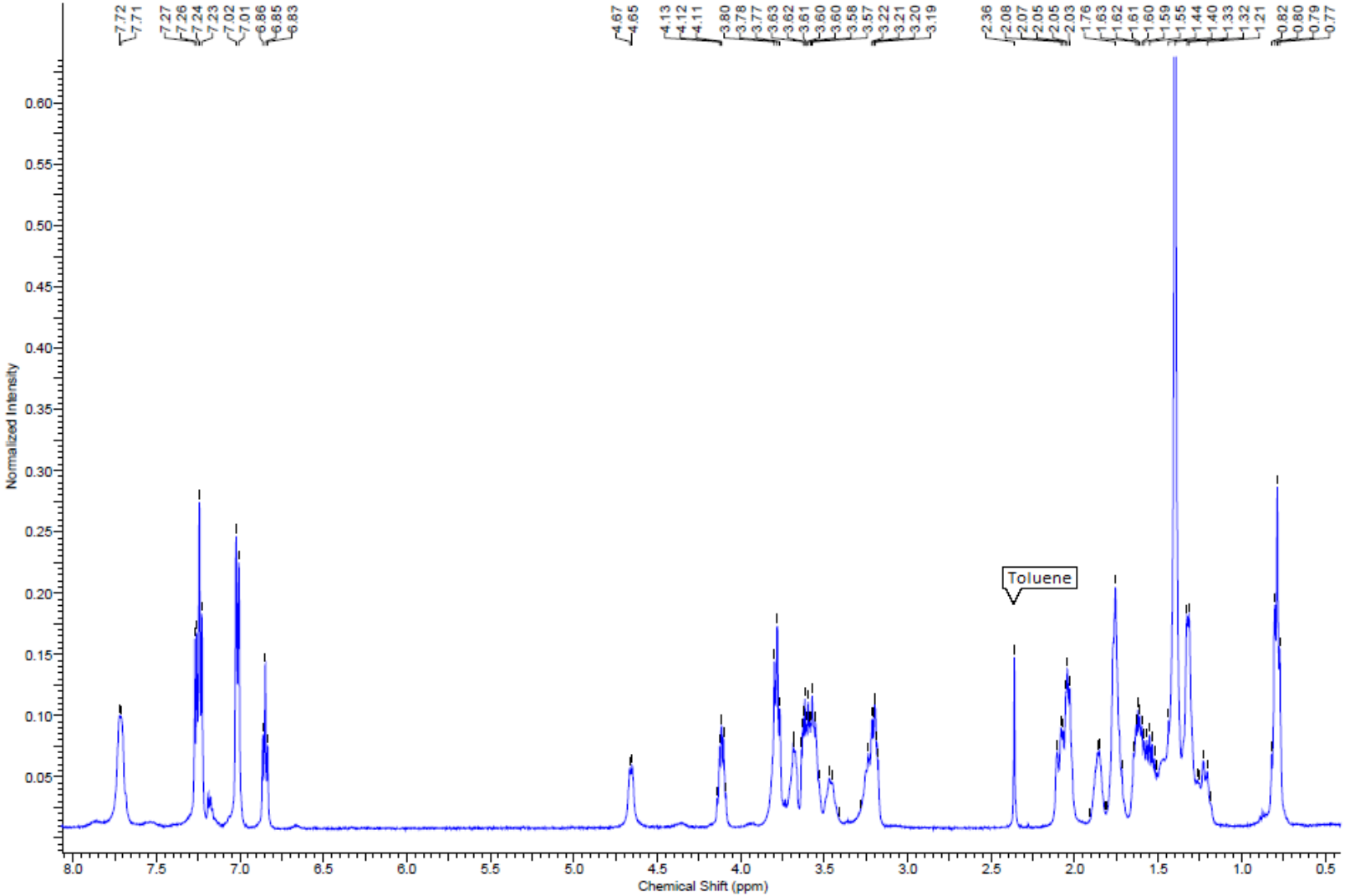
Oxalamide 2, ^{13}C APT (DMSO-d_6, 125.70 MHz)



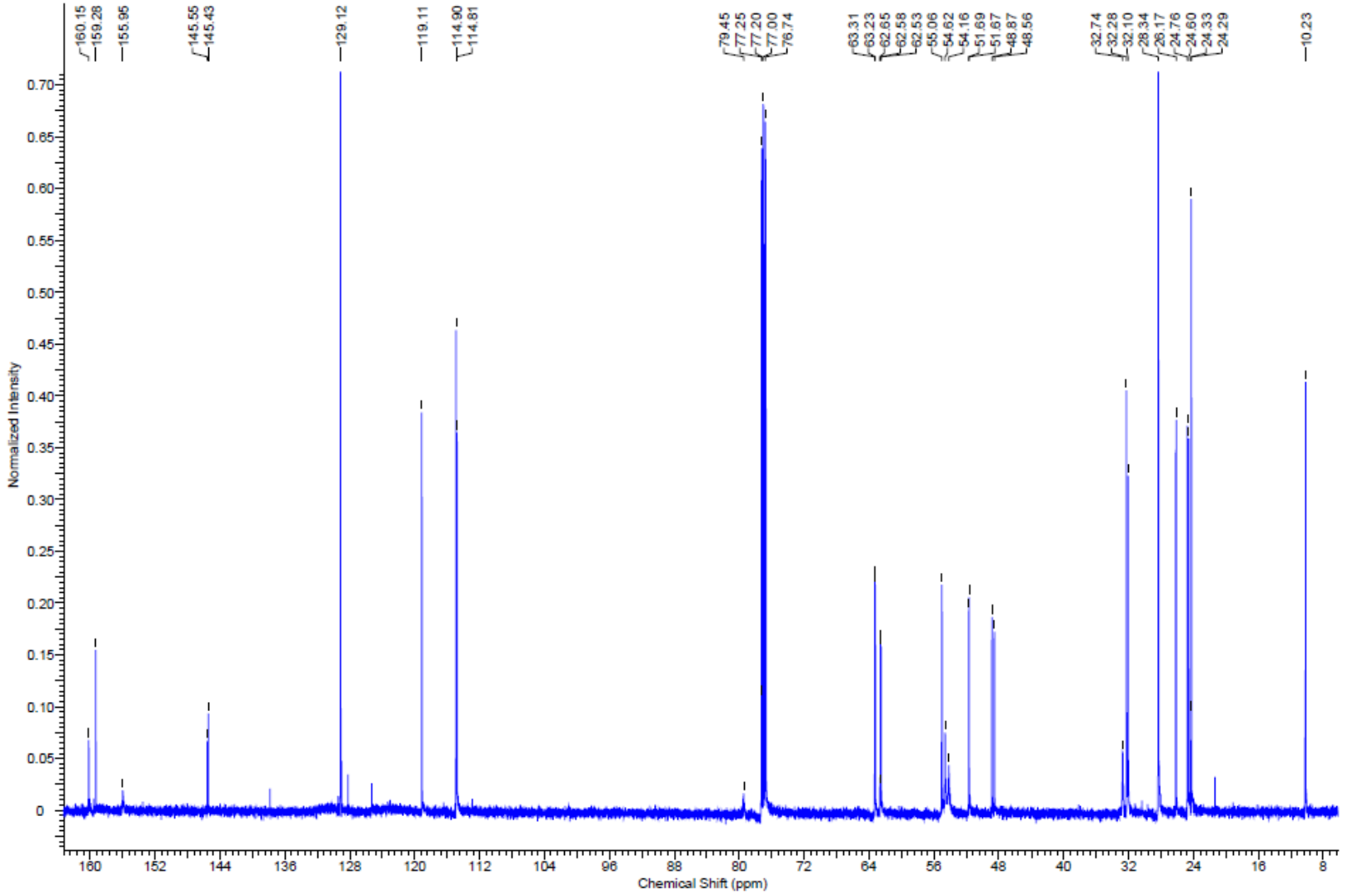
Ligand 1, $^{31}P\{H\}$ ($CDCl_3$, 202.36 MHz)



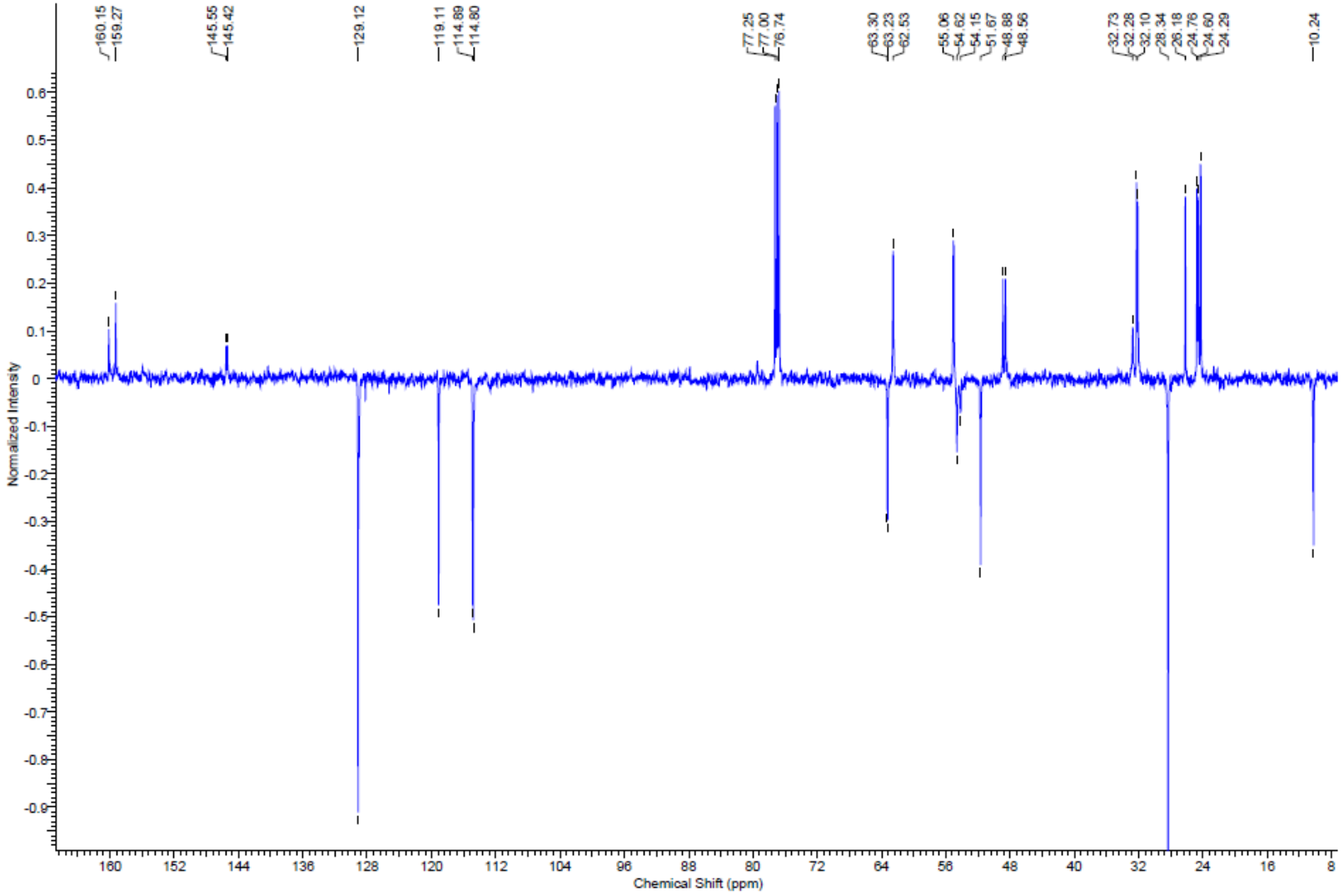
Ligand 1, ^{1}H ($CDCl_3$, 499.86 MHz)



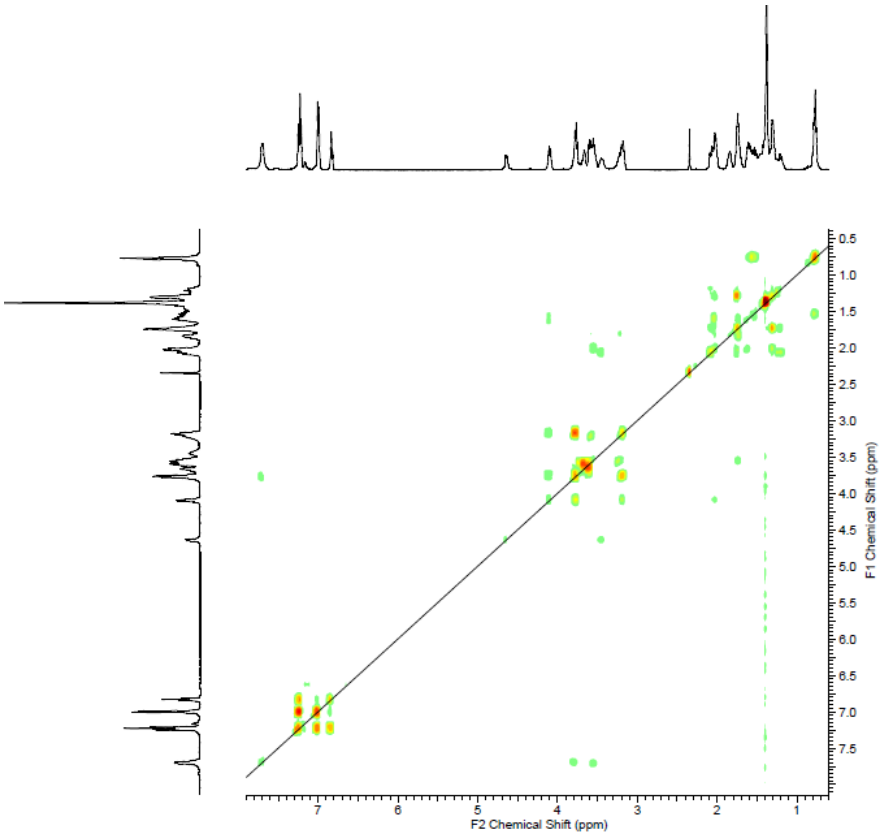
Ligand 1, $^{13}C\{H\}$ ($CDCl_3$, 125.70 MHz)



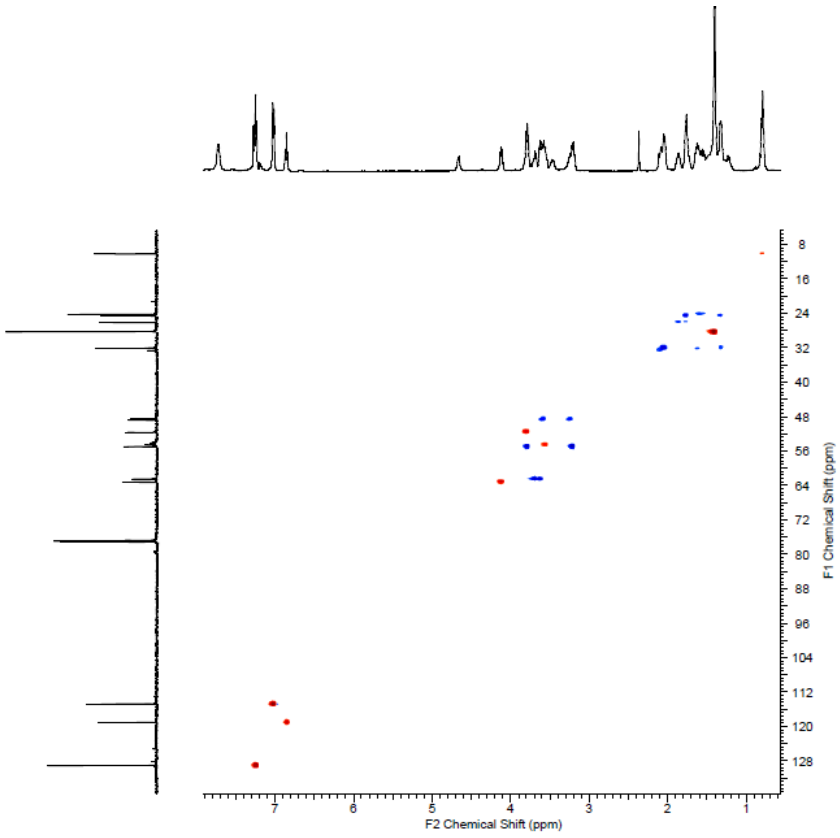
Ligand 1, ^{13}C APT ($CDCl_3$, 125.70 MHz)



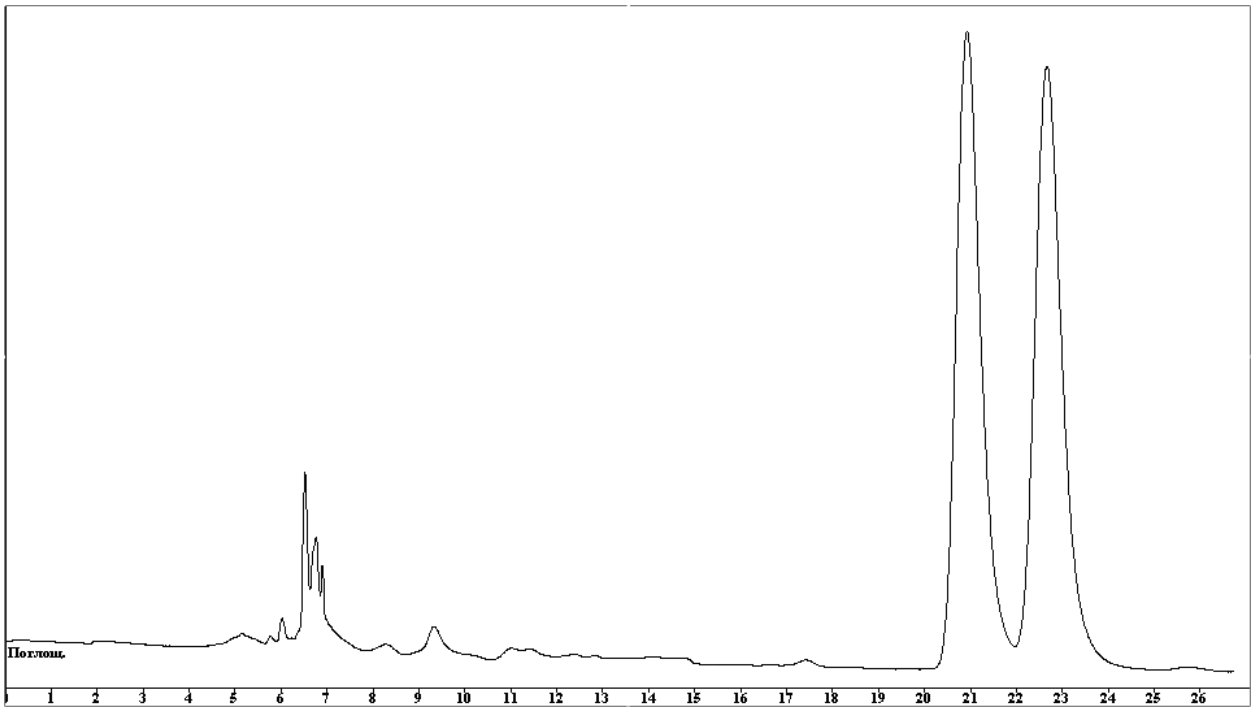
Ligand 1, ^{1}H-^{1}H COSY



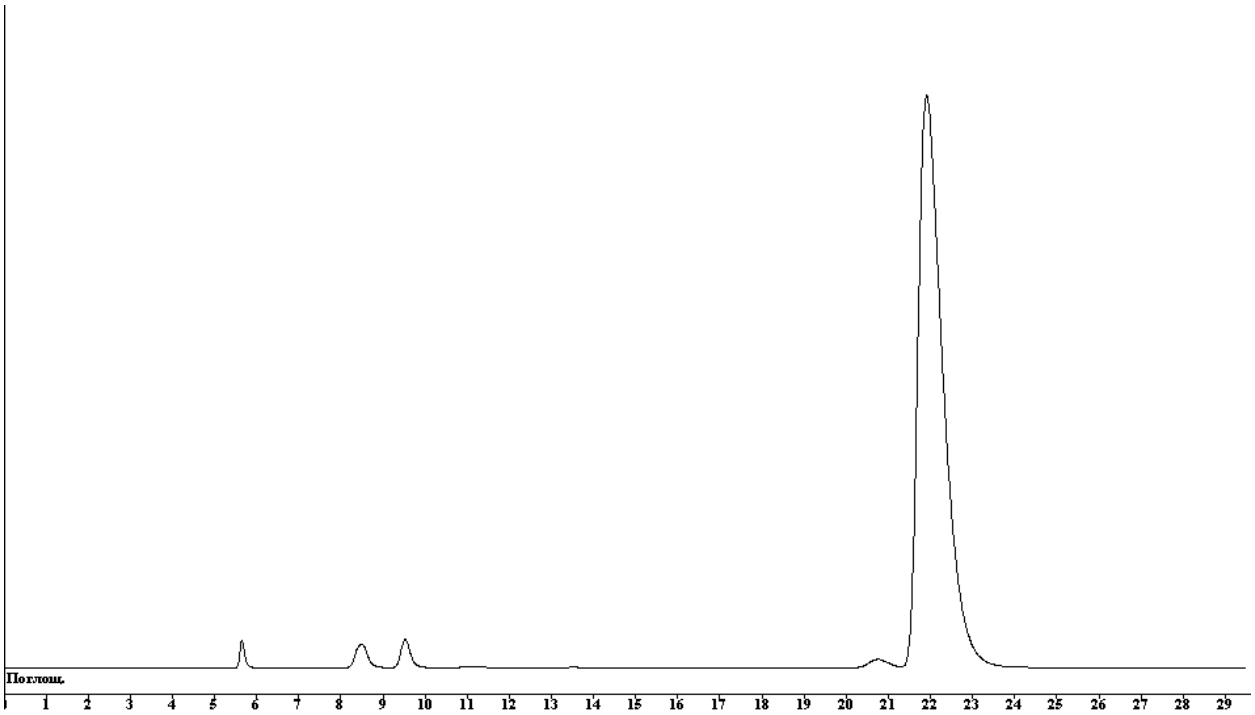
Ligand 1, ^{1}H-^{13}C HSQC



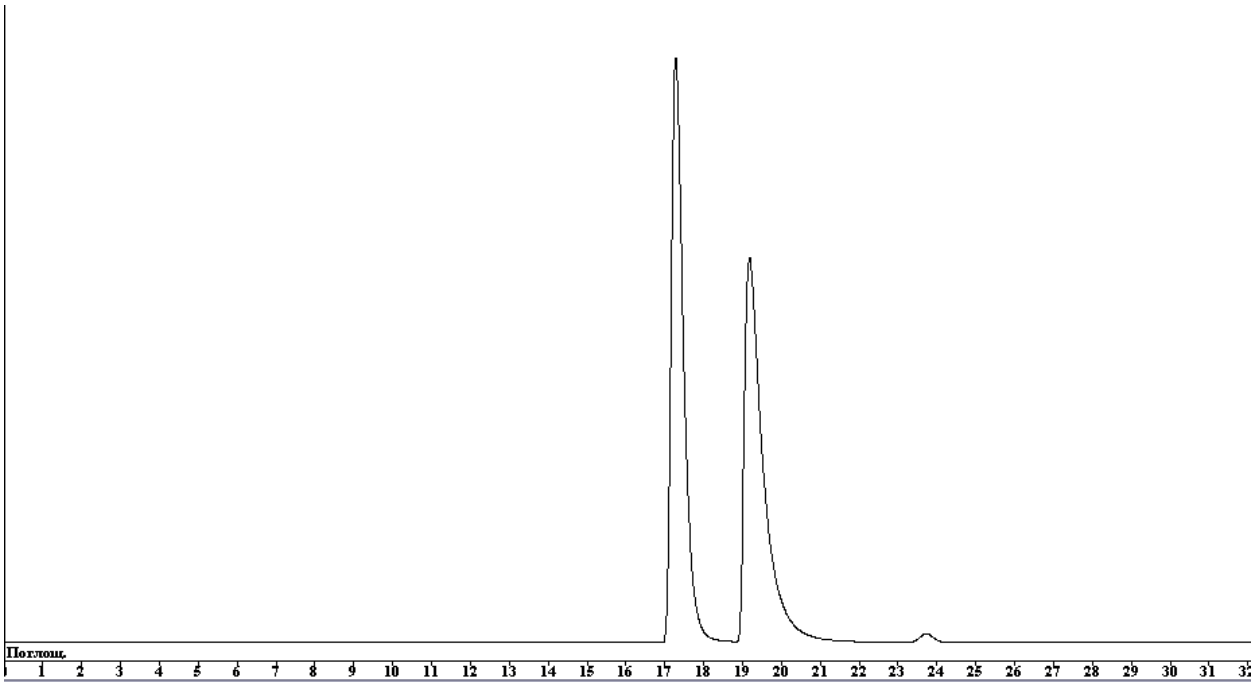
Chiral HPLC trace for racemic product 6



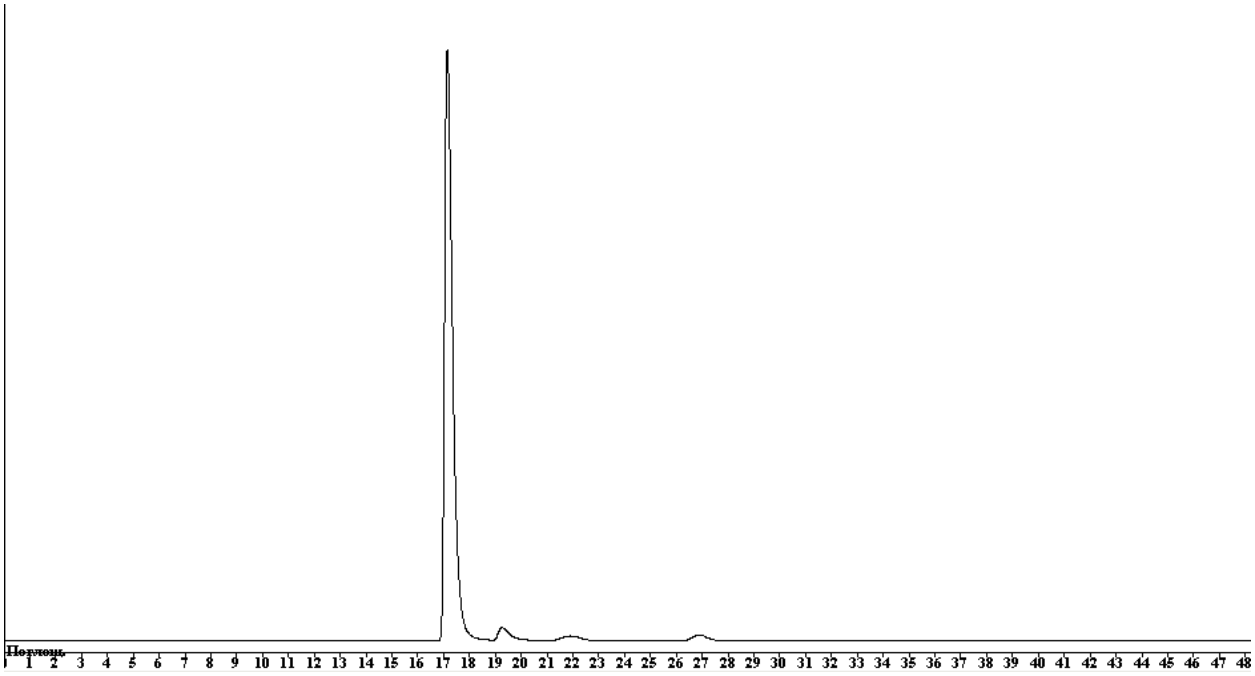
Chiral HPLC trace for enantio-enriched product 6 (Table S1, entry 4)



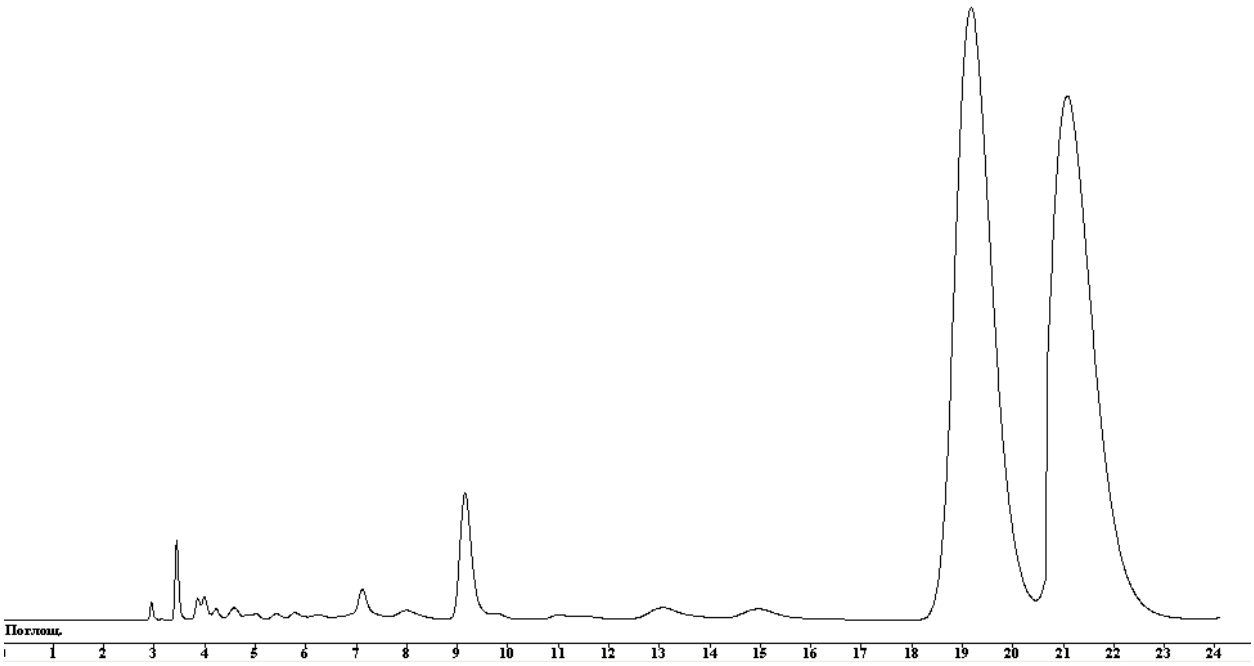
Chiral HPLC trace for racemic product 7



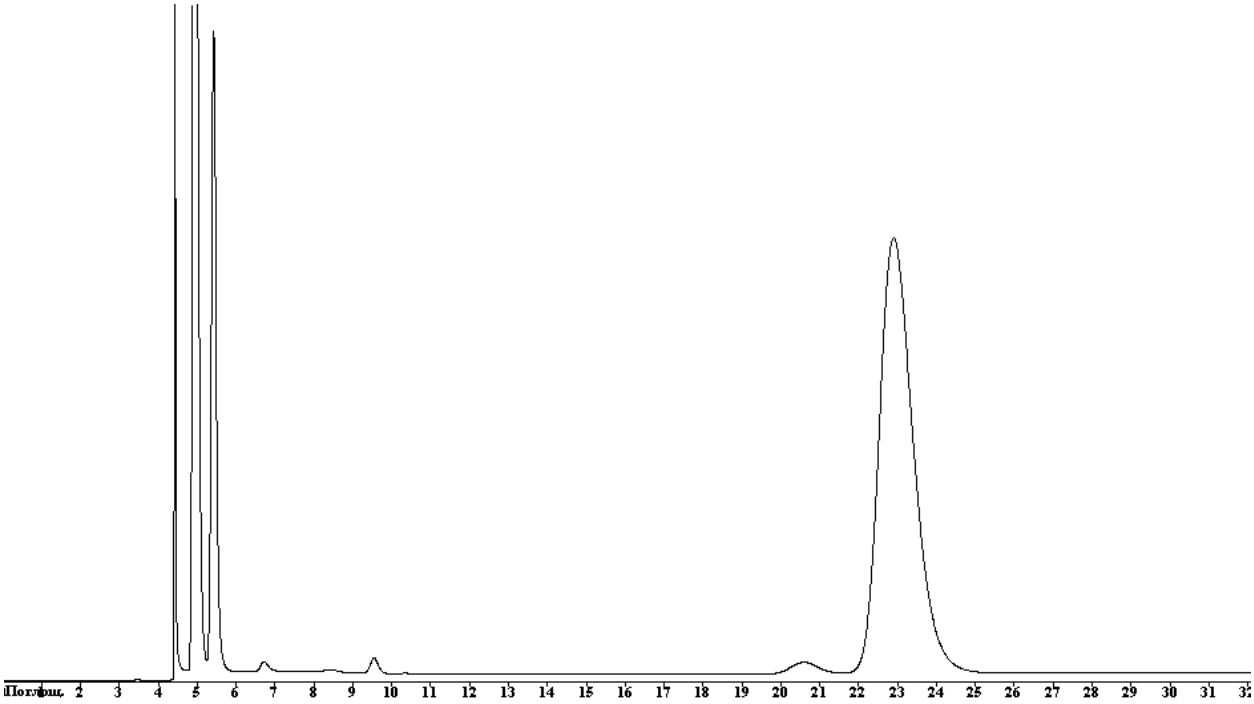
Chiral HPLC trace for enantio-enriched product 7 (Table S2, entry 2)



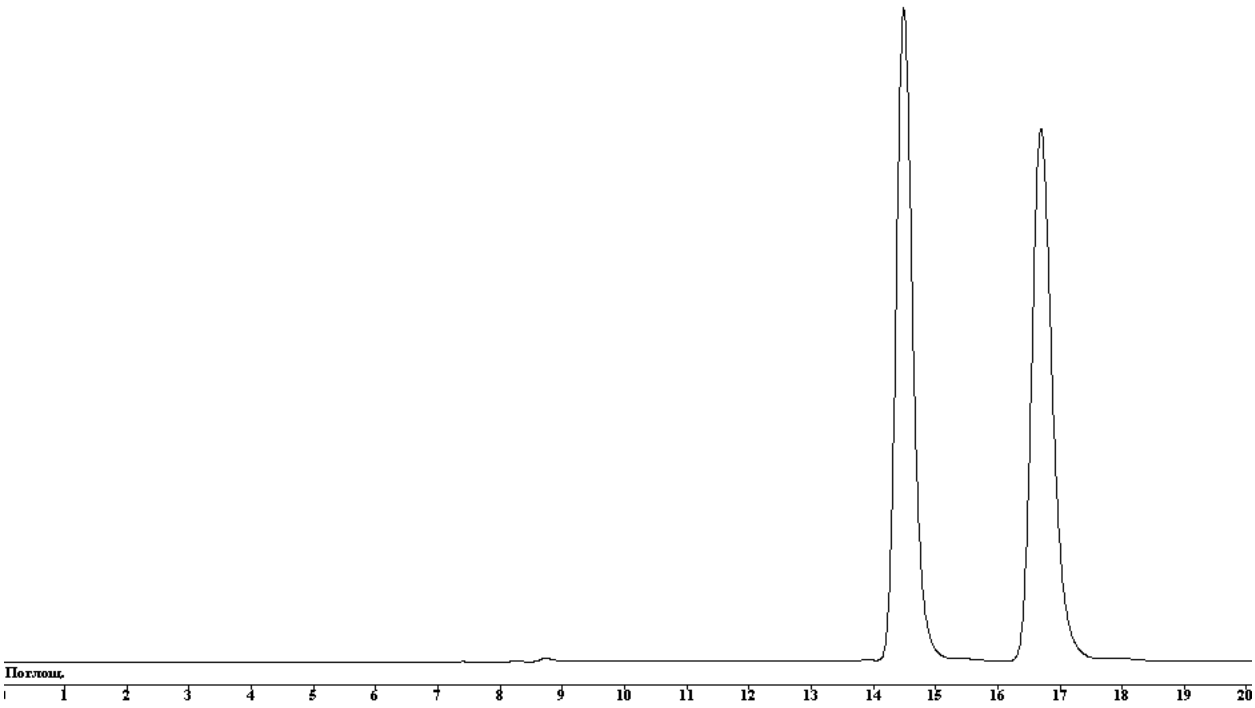
Chiral HPLC trace for racemic product 8



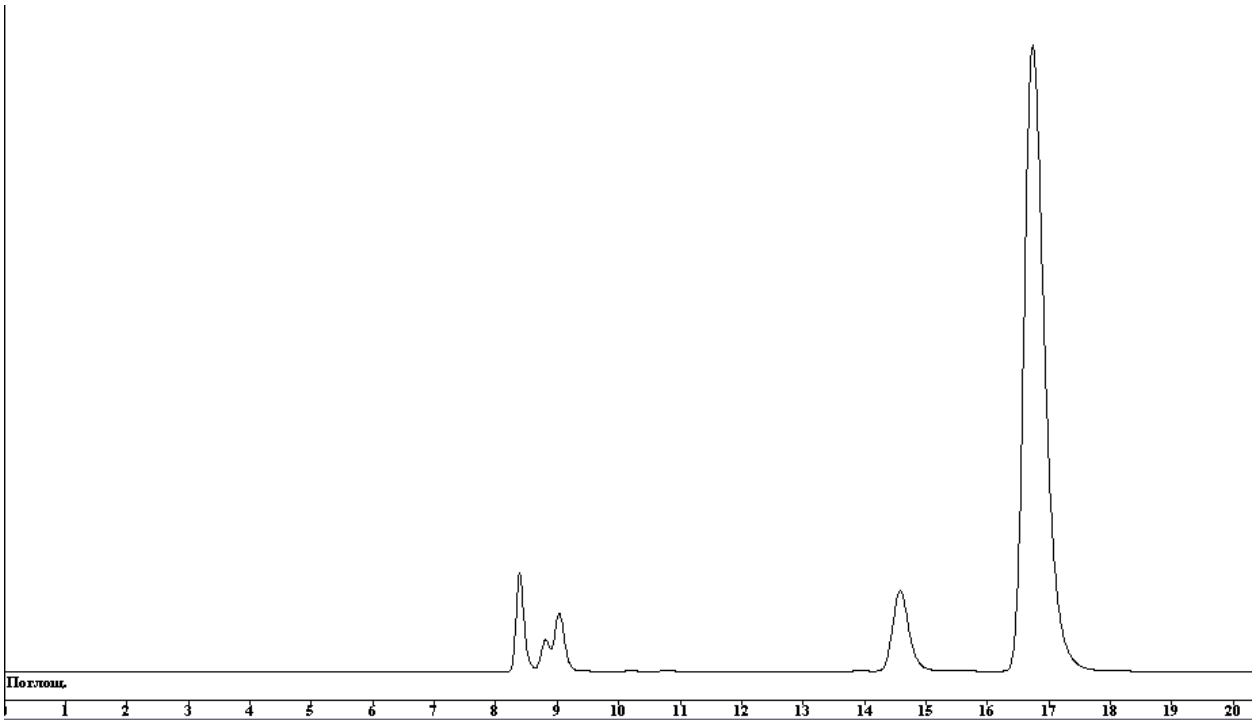
Chiral HPLC trace for enantio-enriched product 8 (Table S3, entry 3)



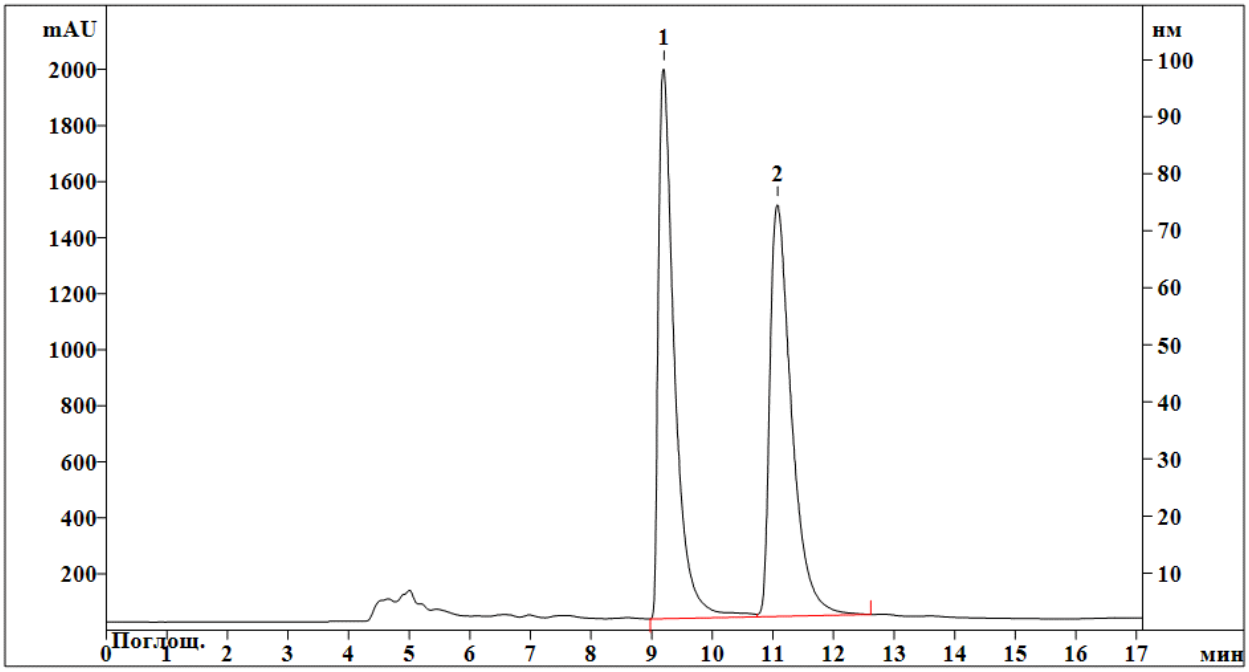
Chiral HPLC trace for racemic product 11



Chiral HPLC trace for enantio-enriched product 11 (Table S4, entry 2)



Chiral HPLC trace for racemic product 13



Chiral HPLC trace for enantio-enriched product 13 (Table S5, entry 3)