Amine Adducts of Triallylborane As Highly Reactive Allylborating Agents For Cu(I)-Catalyzed Allylation of Chiral Sulfinylimines

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Supporting Information

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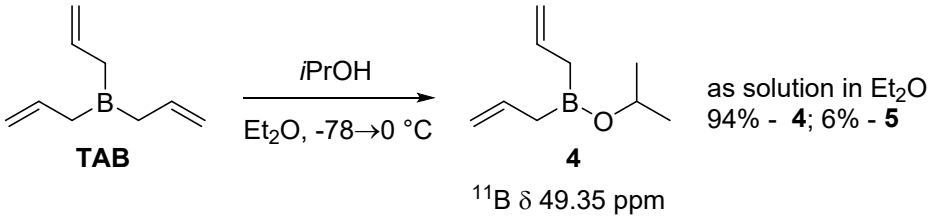
General. All manipulations with sensitive to air compounds were carried out under inert atmosphere of dry Ar by Schlenk technique[1]. NMR spectra were recorded on Bruker Avance 400, Varian Inova 400, and Bruker Avance 300 instruments. UV-Vis spectra were recorded on Shimadzu UV-1800 scanning double beam spectrophotometer with quartz cuvettes with an optical path length of 1.00 cm. Column chromatography was carried out using silica gel 60–230 mesh (Merck) and automated flash chromatograph Biotage Isolera Prime (UV detector) with silica loaded cartridges Varian SuperFlash SF-15 and Buchi GraceResolve. Thin layer chromatography was run on Alugram SilG/UV_{254} (Macherey-Nagel) or TLC Silica gel 60 F_{254} (Merck). Preparative thin layer chromatography was run on PTLC Silica gel 60 F_{254} 0.5 mm (Merck). Visualization of spots on TLC plate was accomplished with UV light or by staining in I_2 chamber, and after removing of I_2 by heat gun TLC plate was immersed in $KMnO_4$ solution. Melting points were measured on a Stuart SMP10 (uncorrected) and Büchi B-540 (corrected) capillary melting point apparats. All melting points were determined in opened capillary tubes. Optical rotation was measured on Perkin Elmer 341 polarimeter. Elemental analyses were conducted in laboratory of microanalysis of INEOS RAS. HPLC analysis was run on chiral columns Kromasil 5-TBB; Kromasil 3-AmyCoat; Chiracel OD-H; Chiralpak AS-H and ASTEC ChiraleDEX. Solutions for kinetic experiments were thermostated by Fisher Isotemp 1013s thermostat. Slow addition of alcohol solution was run by NE-300 Just Infusion™ Syringe Pump.

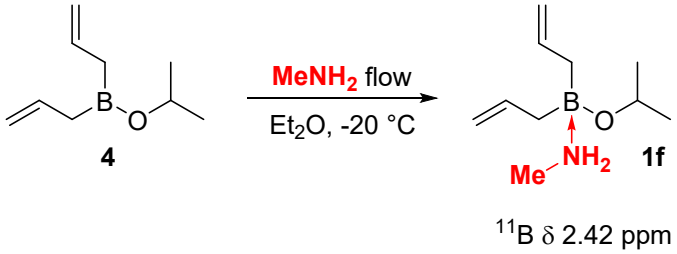
Reagents and solvents. All reagents and solvents if it not stated are commercially available and used without any treatment. Triallylborane was synthesized by procedure.[2] Amine adducts of triallylborane were prepared as earlier described.[3,4] Ellman's imines were synthesized by modified procedure.[5] Racemic homoallylamines were synthesized as earlier described.[6] Potassium *tert*-butoxide (Acros Organics®) was sublimated at T = 173 °C (0.76 Torr). Cuprous(I) chloride was prepared by literature procedure.[7] Copper(II) fluoride dihydrate was obtained by described method.[8] 1,3-*bis*(2,4,6-Trimethylphenyl)imidazolinium chloride was synthesized as described.[9] $(MesCu)_5$*PhMe was synthesized by described procedure.[10]
Acetonitrile HPLC (Baker®) was degassed under Ar atmosphere for synthesis of CuCl complexes. THF was freshly distilled over LAH. Anhydrous *i*PrOH HPLC (Scharlau®) was degassed under Ar atmosphere for measuring of allylation reaction rate constants.

Synthesis of diallyl(isopropoxy)borane (4).



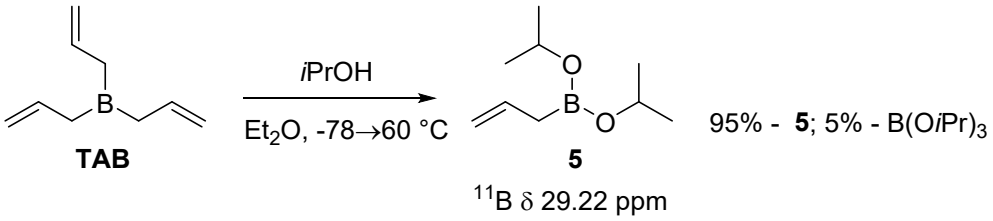
To a solution of triallylborane (1.37 g/1.76 ml, 10.2 mmol) in Et_2O (15 ml) under Ar atmosphere at -78 °C was added dropwise a solution of *i*PrOH (0.601g/0.765 ml, 10 mmol) in Et_2O (1 ml) and the mixture was stirred for 10 min followed by gradual warming of the reaction solution to 0 °C to give ethereal solution of **4**. Consistency and purity of **4** in the ethereal solution was confirmed by ^{11}B NMR (128 MHz, Et_2O): δ 49.35 ppm.

Preparation of methylamine adduct of diallyl(isopropoxy)borane (1f).



Through the ethereal solution of borinane **4** chilled to -20 °C a flow of dry methylamine was passed for 15 min, after then the volatiles were removed under reduced pressure of water-jet pump (15 mmHg) to give crude **1f** (1.75 g, 96%) as a white solid, melting below 0 °C. For the use in the kinetics study crude **1f** was recrystallized from *n*-pentane at -23 °C and stored at this temperature. Upon dissolution in the neat *i*PrOH at 25 °C **1f** is decomposed on 40% for 15 min, however addition of (~2 equiv.) of methylamine (as 6M sol. in *i*PrOH) to **1f** stabilizes the adduct, giving satisfactory NMR spectra in C_6D_6. There are shown several NMR spectra of **1f** (the same solution of **1f** with and without $MeNH_2$ additive) to demonstrate dynamic behavior of the adduct and the stabilization effect of methylamine additive. Signals of $MeNH_2$ and *i*PrOH are overlapping with signals of the corresponding groups in **1f**. ^1H NMR (400 MHz, C_6D_6 with 2 equiv. of $MeNH_2$ in *i*PrOH): δ 6.18 (ddd, J = 22.1, 15.2, 8.2 Hz, 2H, CH=); 4.89 (d, J = 12.3 Hz, 4H, CH_2=); 3.97–3.77 (m, 1H, OC<u>H</u>); 1.94 (s, 3H, Me); 1.43 (d, J = 7.8 Hz, 4H, CH_2B); 1.14 (d, J = 6.3 Hz, 6H, <u>Me</u>$_2$CHO) ppm. Overlapping signals are given in bold, ^{13}C NMR (101 MHz, C_6D_6 with 2 equiv. of $MeNH_2$ in *i*PrOH): δ 143.2 (2C), 110.6 (2C), **63.3**, 29.2 (2C, br., <u>C</u>H_2B), **27.0**, **25.7** (2C) ppm. ^{11}B NMR (128 MHz, C_6D_6 with 2 equiv. of $MeNH_2$ in *i*PrOH): δ 2.42 ppm.

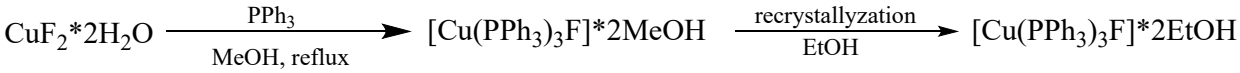
Synthesis of allyl(diisopropoxy)borane (5)



To a solution of **TAB** (3.87 g, 5.0 ml, 29.0 mmol) in Et_2O (10 ml) cooled to -78 °C under Ar was added dropwise a solution of *i*PrOH (4.17 g, 5.31 ml, 69.6 mmol) in Et_2O (5 ml). The mixture was stirred at this temperature for 30 min then it was allowed to warm to rt and the solution was left for 16 h. Then ether was distilled off under gentle heating on an oil bath and the residue consisting of borinane **4** and boronate **5** were heated up to 60 °C for 30 min. A progress of the reaction was monitored by ^{11}B NMR until disappearance of **4**. Then mixture was distilled under reduced pressure of water-jet pump to give boronate **5** (3.6 g, 73%) as colorless liquid, b.p. 50 °C (15 mmHg) with admixture of B(O*i*Pr)$_3$. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.88 (ddt, *J* = 17.3, 10.1, 7.4 Hz, 1H, CH=), 4.99–4.78 (m, 2H, CH_2=), 4.38 (spt, *J* = 6.2 Hz, 2H, 2OC<u>H</u>Me$_2$), 1.68 (d, *J* = 7.5 Hz, 2H, CH_2B), 1.14 (d, *J* = 6.3 Hz, 12H, 2OCH<u>Me$_2$</u>) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ 135.9, 113.9, 65.4, 24.6, 20.7 (br., CH_2B) ppm. ^{11}B (128 MHz, $CDCl_3$) δ 29.22 ppm. **Spectral data coincide with the literature[11].**

Synthesis of copper(I) complexes

Synthesis of *tris*(triphenylphosphine)copper(I)fluoride*2ethanol [Cu-1]



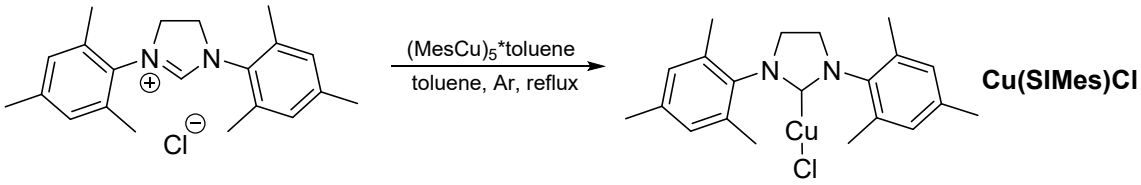
Copper(II) fluoride dihydrate (0.69 g, 5 mmol) was mixed with PPh_3 (4.59 g, 17.5 mmol, 3.5 equiv.) in MeOH (50 ml), and the suspension was heated at reflux for 2 hours. The mixture was cooled down to room temperature and filtrated through the pad of Celite®. The filtrate was evaporated to volume apprx. 20 ml, and left in refrigerator. The precipitated crystals were filtered off and recrystallized twice from hot ethanol that furnished **[Cu-1]** (1.87 g, 39%) as colorless crystals, m.p. 167-169 °C (ethanol). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.38-7.30 (m, 27H, Ph), 7.26-7.21 (m, 18H, Ph), 3.72 (q, 4H, *J* = 9.4 Hz, $CH_3C\mathbf{H_2}OH$), 2.48 (br.s, 2H, $CH_3CH_2O\mathbf{H}$), 1.25 (t, 6H, *J* = 9.3 Hz, $C\mathbf{H_3}CH_2OH$) ppm. ^{31}P NMR ($CDCl_3$, 121 MHz): δ -3.97 ppm. UV spectrum λ, nm (ε, $cm^{-1}M^{-1}$): 260 (30600). **NMR spectra coincide with the literature data[12].**

Synthesis of *bis*(triphenylphosphine)-copper(I)-*bis*(μ_2-ethoxy)-difluoroborate [Cu-2]

$$CuF_2{*}2H_2O + 2\ PPh_3 + 2\ TABDMA \xrightarrow[AllNH_2,\ EtOH,\ 60°C,\ Ar]{} [(PPh_3)_2Cu(\mu_2\text{-}OEt)_2BF_2]$$

To copper(II) fluoride dihydrate (0.20 g, 1.45 mmol) abs. ethanol (12 ml), allylamine (2 ml) were added under Ar atm. and the mixture was heated up to 60 °C. PPh_3 (0.76 g, 2.9 mmol) and TABDMA **1c** (0.52 g, 2.9 mmol) were added to the formed dark-blue solution that led to gradual change of the color to yellow during 15 minutes with simultaneous evolution of propylene gas. The solution was centrifuged from unreacted CuF_2 followed by the evaporation of volatiles under reduced pressure. In order to remove impurity of allylamine the solution was evaporated trice with ethanol. The formed oil was recrystallized from hot ethanol to give **[Cu-2]** (0.47 g, 45%) as beige crystals, m.p. 183-184 °C dec. (ethanol). Due to the dynamic behavior of $[(EtO)_2BF_2]^-$ in $CDCl_3$ solution ^{1}H NMR spectrum contains two different signals in 1:3 ratio. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38–7.23 (m, 30H, Ar), 3.71 and 3.61 (both q, 4H, J = 7.0 Hz, $OC\mathbf{H_2}CH_3$), 1.24 and 0.82 (both t, 6H, J = 7.0 Hz, $OCH_2C\mathbf{H_3}$) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 133.9, 132.8 (br.), 130.0, 128.7, 57.5, 18.2 ppm. ^{31}P NMR (121 MHz, $CDCl_3$) δ -3.21 ppm. ^{11}B NMR spectrum contains two signals in 8:1 ratio. ^{11}B NMR (128 MHz, $CDCl_3$) δ 1.59 and 0.37 (both t, J = 27.3 Hz) ppm. ^{19}F NMR contains two signals in 1:3 ratio, ^{19}F NMR (282 MHz, $CDCl_3$) δ -151.96 (br.), -156.06 (br.) ppm. UV spectrum λ, nm (ε, $cm^{-1}M^{-1}$): 260 (21900). Anal. Calcd. for $C_{40}H_{40}BCuF_2O_2P_2$ (727.06): C, 66.08; H, 5.55; Cu, 8.74; found: C, 66.11; H, 5.64; Cu, 8.50.

Synthesis of [1,3-b*is*(2,4,6-trimethylphenyl)-2-imidazolidinylidene]copper(I)chloride [Cu-4]



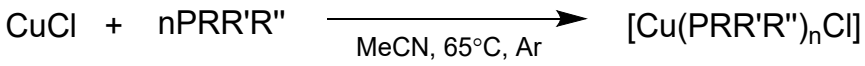
To a mixture of imidazolium salt (0.20 g, 0.58 mmol) in degassed toluene (2 ml) was added $(MesCu)_5$*PhMe (0.12 g, 0.116 mmol) and the mixture was stirred under reflux for 30 min. The resulting solution was filtered; the filtrate was evaporated to dryness under reduced pressure. The solid was taken up in DCM, passed through the pad of SuperCel Hyflo, evaporated and the residue was recrystallized from a mixture DCM/*n*-pentane to give **[Cu-4]** (216 mg, 92%) as white crystals, m.p 259-260 °C (DCM/*n*-pentane). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.95 (s, 4H, Ar), 3.95 (s, 4H, $CH_{2(imidaz.)}$), 2.31 (s, 12H, Me), 2.30 (s, 6H, Me) ppm. UV spectrum λ, nm (ε, $cm^{-1}M^{-1}$): 258 (12800). **NMR spectra coincide with the literature data[13].**

***bis*(1,2-*bis*(Diphenylphosphino)ethane)copper(I) tetrafluoroborate [Cu-5]**

CuF_2*2H_2O (0.138 g, 1.0 mmol) and CsF (0.304 g, 2.0 mmol) were suspended in MeOH (20 ml) with allylamine (5 ml) and heated up to 60 °C with the formation of dark blue solution. To this solution cooled to rt TABDMA **1c** (0.269 g, 1.5 mmol) and dppe (0.800 g, 2 mmol) were added. Resulting light yellow solution was evaporated, and the residual oil was recrystallized from EtOAc to give **[Cu-5]** (0.38 g, 40%) as colorless crystals, m.p. 248-250 °C (EtOAc). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.35-7.31 (m, 8H, Ar), 7.20-7.15 (m, 32H, Ar), 2.43 (br.s, 8H, CH_2) ppm. ^{31}P NMR ($CDCl_3$, 121 MHz): δ +7.05 (br.) ppm. UV spectrum λ, nm (ε, $cm^{-1}M^{-1}$): 265 (27100). **NMR spectra coincide with the literature data[14].**

General procedure of synthesis of cuprous(I) chloride complexes

Cuprous(I) chloride (9.9 mg, 0.1 mmol) was dissolved in degassed MeCN (3 ml), phosphine ligand was added (1, 2 or 3 equiv. according to a formula of complex), and the suspension was refluxed under Ar atm. for 30 min. The mixture was cooled down to room temperature, evaporated and crystals were dried in vacuum and stored under Ar in a dark glass container. Yields were quantitative; some complexes crystallized as MeCN solvates.



***tris*(Triphenylphosphine)copper(I)chloride $Cu(PPh_3)_3Cl*MeCN$ [Cu-3]**

Colorless crystals, m.p. 168-170°C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.32-7.28 (m, 27H, Ar), 7.20-7.17 (m, 18H, Ar), 2.00 (s, 3H, MeCN) ppm. ^{31}P NMR ($CDCl_3$, 121 MHz): δ -4.66 ppm. UV spectrum λ, nm (ε, $cm^{-1}M^{-1}$): 259 (30300). **NMR spectra coincide with the literature data[15].**

***bis*[(1,1'-*bis*(Diphenylphosphino)ferrocene)copper(I)chloride] $[Cu(dppf)Cl]_2$ [Cu-6]**

A solution of dppf (277 mg, 0.5 mmol) in DCM (5 ml) was added to a solution of CuCl (49.5 mg, 0.5 mmol) in MeCN (15 ml) and stirred for 15 min, followed by evaporation of the resulting suspension. The complex was crystallized by adding MeCN to the saturated solution in $CHCl_3$. Yellowish-orange crystals, m.p. 254°C dec., ($CHCl_3$/MeCN). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.70 (m, 16H, Ar), 7.37 (m, 24H, Ar), 4.33 (br.s, 8H, Cp), 4.20 (br.s, 8H, Cp) ppm. ^{31}P NMR ($CDCl_3$, 121 MHz): δ -19.10 ppm. UV spectrum λ, nm (ε, $cm^{-1}M^{-1}$): 257 (18400). **NMR spectra coincide with the literature data[16].**

***tris*(Tri-(*o*-tolyl)phosphine)copper(I)chloride $Cu(P(oTol)_3)_3Cl$ [Cu-7]**

Colorless crystals, m.p. 222-224°C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.34-7.26 (m, 18H, Ar), 7.10 (t, 9H, *J* = 7.3 Hz, Ar), 6.79 (t, 9H, *J* = 7.1 Hz, Ar), 2.50 (s, 27H, Me) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz): δ 143.1 and 142.8 (d, *J* = 21.7 Hz), 133.2 and 133.1 (d, *J* = 2.9 Hz), 131.3 (br.), 130.84 and 130.78 (d, *J* = 6.0 Hz), 129.7, 126.42 and 126.39 (d, *J* = 3.6 Hz), 22.1 and 22.0 (d, *J* = 18.4 Hz) ppm. ^{31}P NMR ($CDCl_3$, 162 MHz): δ -24.26 ppm. UV spectrum λ, nm (ε, $cm^{-1}M^{-1}$): 275 (37000). Anal. Calcd. for $C_{63}H_{63}ClCuP_3$ (1012.11): C, 74.76; H, 6.27; Cl, 3.50; found: C, 74.66; H, 6.26; Cl, 3.69.

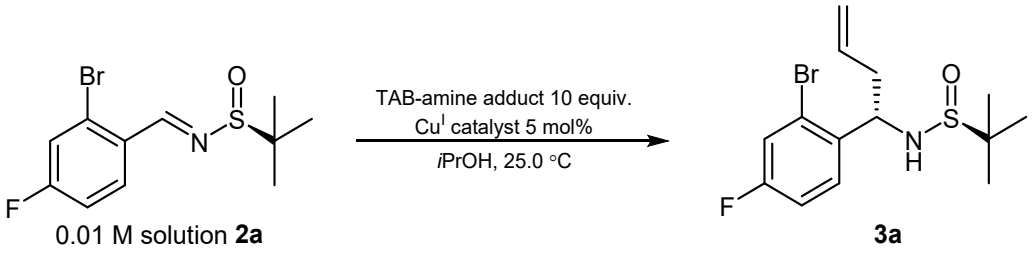
***tris*(Methyldiphenylphosphine)copper(I)chloride Cu(PPh_2Me)$_3$Cl [Cu-8]**

Colorless crystals, light-sensitive, m.p. 164-165 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.30-7.26 (m, 18H, Ar), 7.20-7.15 (m, 12H, Ar), 1.56 (s, 9H, Me) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz): δ 136.8 and 136.6 (*J* = 21.2 Hz), 132.3 and 132.2 (*J* = 12.2 Hz), 129.0, 128.3 (br.), 13.1 and 13.0 (*J* = 12.3 Hz) ppm. ^{31}P NMR ($CDCl_3$, 121 MHz): δ -19.24 ppm. UV spectrum λ, nm (ε, $cm^{-1}M^{-1}$): 250 (21200). Anal. Calcd. for $C_{39}H_{39}ClCuP_3$ (699.66): C, 66.95; H, 5.62; Cl, 5.07; found: C, 66.94; H, 5.77; Cl, 5.05.

[(4,5-*bis*(Diphenylphosphino)-9,9-dimethylxanthene)copper(I)chloride] [Cu(XantPhos)Cl] [Cu-9]

Colorless crystals, m.p. 347-349°C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.59 (d, 2H, *J* = 7.8 Hz, Ar), 7.47 (q, 8H, *J* = 6.3 Hz, Ar), 7.38-7.33 (m, 5H, Ar), 7.29-7.26 (m, 8H, Ar), 7.15 (t, 2H, *J* = 7.7 Hz, Ar), 6.62 (m, 2H, Ar), 1.74 and 1.71 (both s, 6H, Me) ppm. ^{31}P NMR ($CDCl_3$, 162 MHz): δ -17.72 ppm. UV spectrum λ, nm (ε, $cm^{-1}M^{-1}$): 272 (19700). **NMR spectra coincide with the literature data[17].**

Procedure for determination of reaction rate constants



0.01 M solution **2a** **3a**

Before experiment conduction a series of standard solutions in *i*PrOH were prepared: Ellman's imine **2a** (0.04 M), TABMA **1a** (0.2 M), Cu^{I} catalyst **[Cu-1]** (0.002 M) and AcOH (0.01 M). It is recommended to prepare standard 0.2 M solutions of AAT in alcohols only before conduction of kinetic experiment and do not store for a long time without amine additive. In some cases, the solution of Cu^{I} catalyst (it's better to grind crystals to powder) should be preheated to be completely dissolved in *i*PrOH. All standard solutions were preliminarily cooled down to

temperature of an experiment. Vials (*circa* 7-10 pcs.) were filled with 3.0 ml of 0.01 M AcOH solution and stoppered with caps with rubber gasket to avoid the evaporation of solvent. Immediately before experiment vials were opened. To the temperature controlled jacketed flask (cooling agent was aqueous ethylene glycol) charged with magnetically stirred solution of 200 µl of 0.04 M imine **2a** and 200 µl of 0.002 M **[Cu-1]**, 400 µl of 0.2 M **1a** solution was added and simultaneously keep track of time with a stopwatch after addition **1a** solution. Every 15 seconds 50 µl aliquot was taken from the reaction mixture and quenched in 3.0 ml 0.01 M AcOH solution in vial. After taking of 7-10 aliquots all vials were stoppered and shaken up. The zero-point solution (t = 0th second) was prepared by mixing of 200 µl of 0.04 M **2a** solution, 200 µl of 0.002 M **[Cu-1]** solution and 400 µl of *i*PrOH; from this solution a 50 µl aliquot was taken and also dissolved in 3.0 ml 0.01 M AcOH solution in vial. For the resulting solutions of quenched and diluted reaction mixture UV spectra were recorded (λ = 235-360 nm, quartz cuvettes with optical path 1.00 cm, the reference solution is 0.01 M AcOH in *i*PrOH). The absorbance at λ = 307 nm was logged, and imine **2a** concentration was calculated by next formula based on Bouguer-Beer-Lambert law:

$$C_{imine} = C_{dil.} * k_{dil.} = \frac{A^{307}}{\varepsilon_{imine}^{307} * l} * \frac{V_{dilution} + V_{aliquot}}{V_{aliquot}} = \frac{A^{307}}{8425\ M^{-1}cm^{-1} * 1.00\ cm} * 3.$$

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The rate constant was calculated as pseudo-first order reaction law approximation (excess of *i*PrOH and **1a**, concentration of catalyst **[Cu-1]** not change), the observed allylation rate constant was determined by plot logarithm of concentration **2a** versus time:

$$Rate\ of\ allylation = -\frac{dC(2a)}{dt} = k_{eff} * [2a]^1 * [1a]^1 * [Cu-1]^1 * [iPrOH]^1 \approx k_{obs}[2a]^1;$$

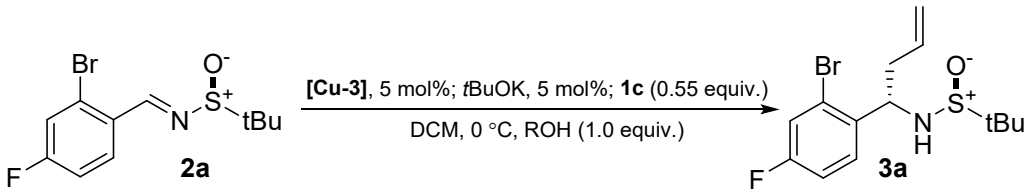
$$k_{obs} = -\frac{1}{t} * \ln\left(\frac{[2a]_t}{[2a]_0}\right).$$

The average error of this kinetic experiment procedure is 7%. Measurement error of reaction rate constant is calculated by next formula (S_x - standard deviation, t_s – Student's factor at p = 0.95):

$$\pm\Delta = S_x * t_s = \sqrt{\frac{\sum_{i=1}^{N}\left(lnC_i - \bar{lnC}\right)^2}{n(n-1)}} * t_s.$$

Optimization of the yield and diastereoselectivity of Ellman's imine allylation

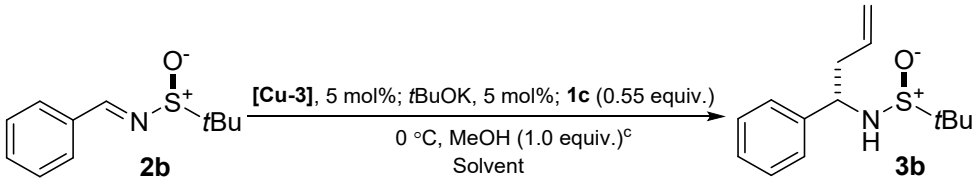
Table S1. Influence of the alcohol on the diastereoselectivity of the allylation



Alcohol	Conv. **2a**, %[a]	*de*, %[c]
MeOH	90	>98
MeOH	100[b]	>99
EtOH	90	>97
*i*PrOH	90	98
*t*BuOH	67	96
$MeOCH_2CH_2OH$	87	95
$tBuMe_2SiOH$	90	95

Addition of 1M alcohol sol. in THF for 30 min;
[a] by ^1H NMR; [b] conversion and *de* were obtained for addition of 1M alcohol sol. in THF for 1 h; [c] by chiral HPLC of *N*-Boc-homoallylamine

Table S2. Influence of the solvents on the yield and diastereoselectivity of the allylation

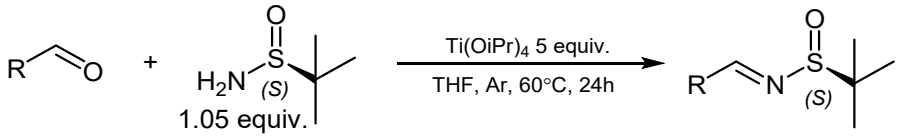


Solvent	Conv. **2b**, %[d]	*de*, %[e]
DCM[a]	77	96
DCM	78	95
THF	99	95
DME	99	95
*i*PrOAc	99	95
Et_3N	80	94
EtOAc	79	94
DMSO[b]	58	94

Dioxane[b]	99	93
DMA	69	93
MeCN	38	92
PhMe	53	92
Et_2NH	91	89

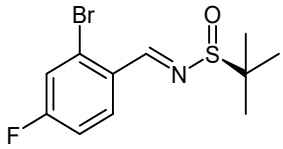
[a] with additive of 3 equiv. Et_3N; [b] reaction was run at 25 °C; [c] Addition of 1M MeOH sol. in THF for 30 min; [d] by ^1H NMR; [e] by chiral HPLC of the phenyl-*N*-Boc-homoallylamine.

Procedure for synthesis of Ellman's imines (2a-2w)



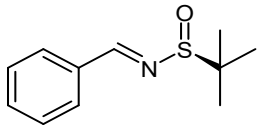
A 50 ml flask was charged with an aldehyde (5.0 mmol), (*S*)-2-methyl-2-propanesulfinamide (0.64 g, 5.25 mmol) and Ti(O*i*Pr)$_4$ (7.1 g, 7.4 mL, 25.0 mmol) in THF (8 mL) under Ar atm. The flask was stoppered and the solution was left on a water bath at 60 °C for 24 h. The resulting mixture was poured into water (50 mL), stirred for 15 min, then filtered through the pad of Hyflo® Super-Cell® and the filter-cake was washed with DCM. The filtrate was diluted with water (50 mL) and extracted with DCM (20 mL x 3). The combined organic extracts were dried over K_2CO_3, evaporated on a rotary evaporator. The purification method is described in detail in the substance resume, basically, flash chromatography is used.

(*S*,*E*)-*N*-(2-Bromo-4-fluorobenzylidene)-2-methylpropane-2-sulfinamide (2a)



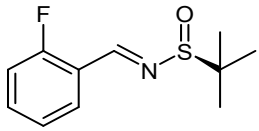
The purification by flash chromatography with gradient elution gives white solid. Yield: 91%, m.p. 47-49 °C (hexane), R_f 0.55 (hexane/EtOAc, 4:1). ^1H NMR ($CDCl_3$, 400 MHz): δ 8.90 (s, 1H, CH=N), 8.07 (td, 1H, *J* = 6.4 Hz, *J* = 1.5 Hz, Ar), 7.38 (dd, 1H, *J* = 8.0 Hz, *J* = 1.7 Hz, Ar), 7.12 (td, 1H, *J* = 8.1 Hz, *J* = 1.9 Hz, Ar), 1.26 (s, 9H, *t*Bu) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz): δ 165.9 and 163.3 (d, J_{CF} = 259.6 Hz), 161.0, 131.4 and 131.4 (d, J_{CF} = 8.8 Hz), 129.6 and 129.5 (d, J_{CF} = 3.7 Hz), 127.2 and 127.1 (d, J_{CF} = 10.0 Hz), 121.0 and 120.8 (d, J_{CF} = 25.0 Hz), 115.7 and 115.5 (d, J_{CF} = 21.4 Hz), 58.1, 22.8 (3C) ppm. UV spectrum λ, nm (ε, $cm^{-1}M^{-1}$): 210 (18550), 256 (9000), 281 (8000), 297 (7890). **NMR spectra coincide with the literature data[18].**

(*S*,*E*)-*N*-Benzylidene-2-methylpropane-2-sulfinamide (2b)



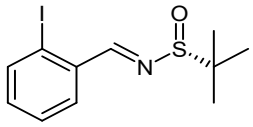
The purification by flash chromatography with gradient elution gives lemon-yellow oil. Yield: 88%, R_f 0.48 (hexane/EtOAc, 4:1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.57 (s, 1H, CH=N), 7.83 (d, 2H, *J* = 6.8 Hz, Ar), 7.52-7.44 (m, 3H, Ar), 1.25 (s, 9H, *t*Bu) ppm. UV spectrum λ, nm (ε, $cm^{-1}M^{-1}$): 198 (18070), 249 (9050), 275 (8310). **NMR spectrum coincides with the literature data[19].**

(*S*,*E*)-*N*-(2-Fluorobenzylidene)-2-methylpropane-2-sulfinamide (2c)



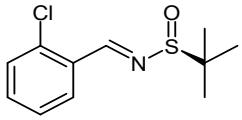
The purification by flash chromatography with gradient elution gives yellow oil. Yield: 83%, R_f 0.55 (hexane/EtOAc, 4:1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.89 (s, 1H, CH=N), 7.99 (t, 1H, *J* = 7.4 Hz, Ar), 7.52-7.47 (m, 1H, Ar), 7.23 (t, 1H, *J* = 7.5 Hz, Ar), 7.14 (t, 1H, *J* = 9.4 Hz, Ar), 1.26 (s, 9H, *t*Bu) ppm. UV spectrum λ, nm (ε, $cm^{-1}M^{-1}$): 197 (18750), 244 (10640), 299 (8750). **NMR spectrum coincides with the literature data[20].**

(*R*,*E*)-*N*-(2-Iodobenzylidene)-2-methylpropane-2-sulfinamide (2d)



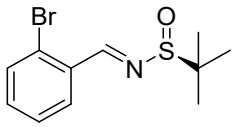
The synthesis was carried out using (*R*)-2-methyl-2-propanesulfinamide instead of (*S*)-2-methyl-2-propanesulfinamide. The purification by flash chromatography with gradient elution gives yellow solid. Yield: 95%, m.p. 76-77 °C (hexane), R_f 0.49 (hexane/EtOAc, 4:1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.77 (s, 1H, CH=N), 7.99 (d, 1H, *J* = 7.7 Hz, Ar), 7.93 (d, 1H, *J* = 7.8 Hz, Ar), 7.42 (t, 1H, *J* = 7.4 Hz, Ar), 7.17 (t, 1H, *J* = 7.9 Hz, Ar), 1.27 (s, 9H, *t*Bu) ppm. UV spectrum λ, nm (ε, $cm^{-1}M^{-1}$): 224 (16240), 254 (7420), 262 (7390), 287 (7710), 306 (7690). **NMR spectrum coincides with the literature data[21].**

(*S*,*E*)-*N*-(2-Chlorobenzylidene)-2-methylpropane-2-sulfinamide (2e)



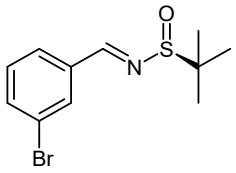
The purification by flash chromatography with gradient elution gives lemon-yellow oil. Yield: 94%, R_f 0.53 (hexane/EtOAc, 4:1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.04 (s, 1H, CH=N), 8.06 (d, 1H, *J* = 7.8 Hz, Ar), 7.46-7.41 (m, 2H, Ar), 7.37-7.33 (m, 1H, Ar), 1.28 (s, 9H, *t*Bu) ppm. UV spectrum λ, nm (ε, $cm^{-1}M^{-1}$): 210 (18480), 249 (8830), 300 (7570). **NMR spectrum coincides with the literature data[22].**

(*S*,*E*)-*N*-(2-Bromobenzylidene)-2-methylpropane-2-sulfinamide (2f)



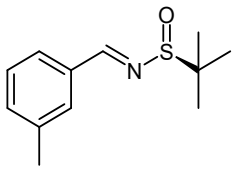
The purification by flash chromatography with gradient elution gives yellow oil. Yield: 85%, R_f 0.41 (hexane/EtOAc, 4:1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.95 (s, 1H, CH=N), 8.01 (dd, 1H, *J* = 7.6, 1.1 Hz, Ar), 7.61 (d, 1H, *J* = 7.7 Hz, Ar), 7.37 (t, 1H, *J* = 7.2 Hz, Ar), 7.32 (td, *J* = 7.7, 1.1 Hz, Ar), 1.25 (s, 9H, *t*Bu) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz): δ 162.2, 133.7, 133.4, 132.9, 129.7, 127.8, 126.5, 58.1, 22.8 (3C) ppm. UV spectrum λ, nm (ε, $cm^{-1}M^{-1}$): 209 (17630), 254 (8330), 301 (7620). **NMR spectra coincide with the literature data[23].**

(*S*,*E*)-*N*-(3-Bromobenzylidene)-2-methylpropane-2-sulfinamide (2g)



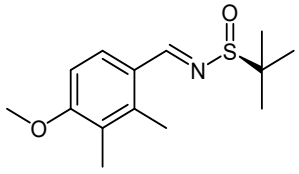
The purification by flash chromatography with gradient elution gives white solid. Yield: 96%, m.p. 34-35 °C (hexane), R_f 0.42 (hexane/EtOAc, 4:1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.50 (s, 1H, CH=N), 8.00 (s, 1H, Ar), 7.72 (d, 1H, *J* = 7.6 Hz, Ar), 7.62 (d, 1H, *J* = 8.0 Hz, Ar), 7.34 (t, 1H, *J* = 7.8 Hz, Ar), 1.25 (s, 9H, *t*Bu) ppm. UV spectrum λ, nm (ε, $cm^{-1}M^{-1}$): 215 (22200), 249 (8740), 278 (7550), 299 (7820). **NMR spectrum coincides with the literature data[24].**

(*S*,*E*)-2-Methyl-*N*-(3-methylbenzylidene)propane-2-sulfinamide (2h)



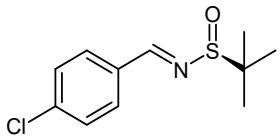
The purification by flash chromatography with gradient elution gives light-yellow liquid. Yield: 84%, R_f 0.47 (hexane/EtOAc, 4:1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.54 (s, 1H, CH=N), 7.66-7.62 (m, 2H, Ar), 7.37-7.30 (m, 2H, Ar), 2.40 (s, 3H, *m*-Me), 1.25 (s, 9H, *t*Bu) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz): 163.0, 138.9, 134.2, 133.4, 129.8, 129.0, 127.0, 57.8, 22.7 (3C), 21.4 ppm. UV spectrum λ, nm (ε, $cm^{-1}M^{-1}$): 208 (21190), 253 (9690), 274 (9780), 294 (9820). **NMR spectra coincide with the literature data[25].**

(*S*,*E*)-*N*-(4-Methoxy-2,3-dimethylbenzylidene)-2-methylpropane-2-sulfinamide (2i)



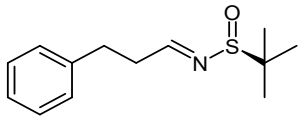
The purification by flash chromatography with gradient elution gives white solid. Yield: 81%, m.p. 115-116 °C (hexane), R_f 0.33 (hexane/EtOAc, 4:1), $[\alpha]_D^{25}$ +48.2 (*c* 1.0, $CHCl_3$). ^1H NMR ($CDCl_3$, 400 MHz): δ 8.83 (s, 1H, CH=N), 7.82 (d, 1H, *J* = 8.7 Hz, Ar), 6.79 (d, 1H, *J* = 8.6 Hz, Ar), 3.86 (s, 3H, OMe), 2.50 (s, 3H, *m*-Me), 2.19 (s, 3H, *o*-Me), 1.24 (s, 9H, *t*Bu) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz): δ 161.6, 160.6, 139.8, 128.9, 125.9, 125.6, 108.0, 57.5, 55.7, 22.7 (3C), 15.5, 11.8 ppm. UV spectrum λ, nm (ε, $cm^{-1}M^{-1}$): 208 (16520), 233 (13610), 310 (18830). Anal. Calcd. for $C_{14}H_{21}NO_2S$ (267.39): C, 62.89; H, 7.92; N, 5.24; found: C, 62.68; H, 7.86; N, 5.14.

(*S*,*E*)-*N*-(4-Chlorobenzylidene)-2-methylpropane-2-sulfinamide (2j)



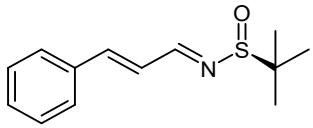
The purification by flash chromatography with gradient elution gives yellowish-brown solid. Yield: 92%, m.p. 44-46 °C (hexane), R_f 0.45 (hexane/EtOAc, 4:1). ^1H NMR ($CDCl_3$, 400 MHz): δ 8.53 (s, 1H, CH=N), 7.77 (d, 2H, *J* = 8.1 Hz, Ar), 7.43 (d, 2H, *J* = 8.0 Hz, Ar), 1.24 (s, 1H, *t*Bu) ppm. UV spectrum λ, nm (ε, $cm^{-1}M^{-1}$): 199 (18280), 257 (12460), 275 (11160). **NMR spectrum coincides with the literature data[19].**

(*S*,*E*)-2-Methyl-*N*-(3-phenylpropylidene)propane-2-sulfinamide (2k)



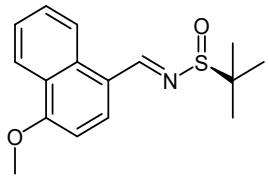
The purification by flash chromatography with gradient elution gives light yellow oil. Yield: 89%, R_f 0.48 (hexane/EtOAc, 2:1). ^1H NMR ($CDCl_3$, 400 MHz): δ 8.11 (t, 1H, *J* = 4.2 Hz, CH=N), 7.31-7.27 (m, 2H, Ar), 7.22-7.18 (m, 3H, Ar), 2.99-2.95 (m, 2H, Ph-C**H**$_2$-CH$_2$), 2.89-2.84 (m, 2H, Ph-CH$_2$-C**H**$_2$), 1.13 (s, 9H, *t*Bu) ppm. UV spectrum λ, nm (ε, $cm^{-1}M^{-1}$): 247 (4950). **NMR spectrum coincides with the literature data[26].**

(*S*)-2-Methyl-*N*-((1*E*,2*E*)-3-phenylallylidene)propane-2-sulfinamide (2l)



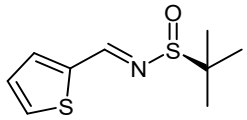
The purification by flash chromatography with gradient elution gives lemon-yellow solid. Yield: 91%, m.p. 62-63 °C (hexane), R_f 0.44 (hexane/EtOAc, 2:1). ^1H NMR ($CDCl_3$, 400 MHz): δ 8.37 (d, 1H, *J* = 9.2 Hz, CH=N), 7.55-7.53 (m, 2H, Ar), 7.39 (m, 3H, Ar), 7.22 (d, 1H, *J* = 15.3 Hz, Ph-C**H**=CH), 7.08 (dd, 1H, *J* = 9.2, 15.9 Hz, Ph-CH=C**H**), 1.23 (s, 9H, *t*Bu) ppm. UV spectrum λ, nm (ε, $cm^{-1}M^{-1}$): 204 (12160), 226 (11300), 307 (25060). **NMR spectrum coincides with the literature data[27].**

(*S*,*E*)-*N*-((4-Methoxynaphthalen-1-yl)methylene)-2-methylpropane-2-sulfinamide (2m)



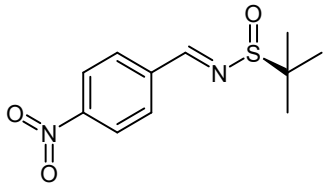
After the evaporation the residue was recrystallized from hexane/EtOAc (8:1) solution, that gave beige solid. Yield: 83%, m.p. 129-130 °C (hexane/EtOAc, 8:1), R_f 0.34 (hexane/EtOAc, 2:1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.19 (d, 1H, *J* = 8.6 Hz, Ar), 8.96 (s, 1H, CH=N), 8.35 (d, 1H, *J* = 8.3 Hz, Ar), 7.94 (d, 1H, *J* = 8.1 Hz, Ar), 7.65 (t, 1H, *J* = 8.1 Hz, Ar), 7.56 (t, 1H, *J* = 7.5 Hz, Ar), 6.88 (d, 1H, *J* = 8.2 Hz, Ar), 4.06 (s, 3H, OMe), 1.31 (s, 9H, *t*Bu) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz): 162.4, 159.5, 135.2, 132.4, 128.7, 126.0, 125.8, 124.8, 122.7, 122.6, 103.5, 57.5, 56.0, 22.7 (3C) ppm. UV spectrum λ, nm (ε, $cm^{-1}M^{-1}$): 240 (29280), 343 (19920). **NMR spectra coincide with the literature data[28].**

(*S*,*E*)-2-Methyl-*N*-(thiophen-2-ylmethylene)propane-2-sulfinamide (2n)



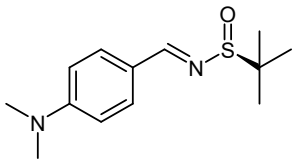
After the evaporation the residue was recrystallized from hexane that gave beige solid. Yield: 85%, m.p. 85-86 °C (hexane), R_f 0.46 (hexane/EtOAc, 2:1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.67 (s, 1H, CH=N), 7.59 (dd, 1H, *J* = 4.8, 1.0 Hz, Ar), 7.53 (dd, 1H, *J* = 3.5, 1.1 Hz, Ar), 7.14 (td, 1H, *J* = 3.8, 1.2 Hz, Ar), 1.24 (s, 9H, *t*Bu) ppm. UV spectrum λ, nm (ε, $cm^{-1}M^{-1}$): 215 (3400), 263 (8840), 312 (12680). **NMR spectrum coincides with the literature data[29].**

(*S*,*E*)-2-Methyl-*N*-(4-nitrobenzylidene)propane-2-sulfinamide (2o)



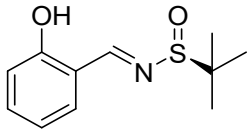
After the evaporation the residue was dissolved in ethyl acetate, sedimentated by hexane addition and filtered. Filtration gave pure pale yellow solid. Yield: 90%, m.p. 139-140 °C (hexane), R_f 0.38 (hexane/EtOAc, 2:1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.67 (s, 1H, CH=N), 8.34 (d, 2H, *J* = 8.6 Hz, Ar), 8.03 (d, 2H, *J* = 8.6 Hz, Ar), 1.29 (s, 9H, *t*Bu) ppm. UV spectrum λ, nm (ε, $cm^{-1}M^{-1}$): 270 (8940), 318 (9900). **NMR spectrum coincides with the literature data[29].**

(*S*,*E*)-*N*-(4-(Dimethylamino)benzylidene)-2-methylpropane-2-sulfinamide (2p)



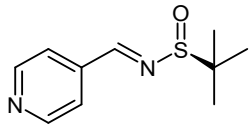
The residue was purified by flash chromatography with gradient elution and recrystallized from hexane that gave yellow solid. Yield: 83%, m.p. 96-97 °C (hexane), R_f 0.32 (hexane/EtOAc, 2:1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.43 (s, 1H, CH=N), 7.72 (d, 2H, *J* = 8.6 Hz, Ar), 6.70 (d, 2H, *J* = 8.6 Hz, Ar), 3.06 (s, 6H, NMe_2), 1.23 (s, 9H, *t*Bu) ppm. UV spectrum λ, nm (ε, $cm^{-1}M^{-1}$): 240 (9280), 354 (36420). **NMR spectrum coincides with the literature data[29].**

(*S*,*E*)-*N*-(2-Hydroxybenzylidene)-2-methylpropane-2-sulfinamide (2q)



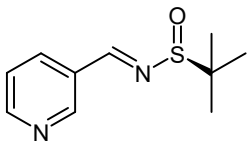
The compound was purified by flash chromatography with gradient elution that gave white solid. Yield: 86%, R_f 0.36 (hexane/EtOAc, 4:1), m.p. 87-89 °C (hexane). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 11.02 (s, 1H, OH), 8.68 (s, 1H, CH=N), 7.47-7.40 (m, 2H, Ar), 7.01-6.96 (m, 2H, Ar), 1.25 (s, 9H, *t*Bu) ppm. UV spectrum λ, nm (ε, $cm^{-1}M^{-1}$): 214 (21300), 269 (10250), 291 (9430), 330 (8940). **NMR spectrum coincides with the literature data[30].**

(*S*,*E*)-2-Methyl-*N*-(pyridin-4-ylmethylene)propane-2-sulfinamide (2r)



The residue was purified by flash chromatography with gradient elution. Recrystallization from hexane gave white solid. Yield: 78%, R_f 0.44 (hexane/EtOAc, 1:1), m.p. 47-48 °C (hexane). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.77 (dd, 2H, *J* = 1.5 Hz, *J* = 4.2 Hz, Ar), 8.57 (s, 1H, CH=N), 7.67 (dd, 2H, *J* = 1.6 Hz, *J* = 2.8 Hz, Ar), 1.26 (s, 9H, *t*Bu) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz): δ 161.4, 151.0 (2C), 140.2, 122.5 (2C), 58.5, 22.8 (3C) ppm. UV spectrum λ, nm (ε, $cm^{-1}M^{-1}$): 227 (12470), 285 (6800). **NMR spectra coincide with the literature data[31].**

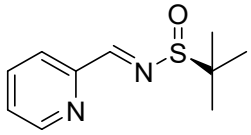
(*S*,*E*)-2-Methyl-*N*-(pyridin-3-ylmethylene)propane-2-sulfinamide (2s)



The residue was purified by flash chromatography with gradient elution and solution in hexane was washed with small amount of $NaHSO_3$ solution to remove the impurity of aldehyde, dried

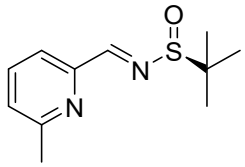
with K_2CO_3 and evaporated that gave yellow oil. Yield: 87%, R_f 0.48 (hexane/EtOAc, 1:1). ^1H NMR ($CDCl_3$, 400 MHz): δ 8.96 (d, 1H, *J* = 1.3 Hz, Ar), 8.66 (dd, 1H, *J* = 4.8, 1.5 Hz, Ar), 8.58 (s, 1H, CH=N), 8.10 (dt, 1H, *J* = 6.3, 1.6 Hz, Ar), 7.35 (dd, 1H, *J* = 7.9, 4.5 Hz, Ar), 1.20 (s, 9H, *t*Bu) ppm. UV spectrum λ, nm (ε, $cm^{-1}M^{-1}$): 234 (12420), 282 (7380). **NMR spectrum coincides with the literature data[27].**

(*S*,*E*)-2-Methyl-*N*-(pyridin-2-ylmethylene)propane-2-sulfinamide (2t)



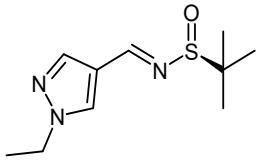
The compound was purified by flash chromatography with gradient elution that gave yellow oil. Yield: 94%, R_f 0.37 (hexane/EtOAc, 1:1). ^1H NMR ($CDCl_3$, 400 MHz): δ 8.72 (d, 1H, *J* = 4.3 Hz, Ar), 8.67 (s, 1H, CH=N), 7.99 (d, 1H, *J* = 7.8 Hz, Ar), 7.79 (td, 1H, *J* = 7.7, 1.2 Hz, Ar), 7.39-7.36 (m, 1H, Ar), 1.25 (s, 9H, *t*Bu) ppm. UV spectrum λ, nm (ε, $cm^{-1}M^{-1}$): 238 (6840), 284 (6600). **NMR spectrum coincides with the literature data[29].**

(*S*,*E*)-2-Methyl-*N*-((3-methylpyridin-2-yl)methylene)propane-2-sulfinamide (2u)



The residue was purified by flash chromatography with gradient elution. Recrystallization from hexane gave white solid. Yield: 84%, R_f 0.39 (hexane/EtOAc, 2:1), m.p. 58-59 °C (hexane), $[\alpha]_D^{25}$ +190.6 (*c* 1.0, $CHCl_3$). ^1H NMR ($CDCl_3$, 400 MHz): δ 8.62 (s, 1H, CH=N), 7.79 (d, 1H, *J* = 7.7 Hz, Ar), 7.64 (t, 1H, *J* = 7.7 Hz, Ar), 7.21 (d, 1H, *J* = 7.6 Hz, Ar), 2.56 (s, 3H, Me), 1.22 (s, 9H, *t*Bu) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz): δ 164.0, 159.1, 151.9, 137.0, 125.7, 120.1, 58.0, 24.4, 22.7 (3C) ppm. UV spectrum λ, nm (ε, $cm^{-1}M^{-1}$): 198 (20800), 242 (6170), 293 (8980). Anal. Calcd. for $C_{11}H_{16}N_2OS$ (224.322): C, 58.90; H, 7.19; N, 12.49; found: C, 58.74; H, 7.19; N, 12.41.

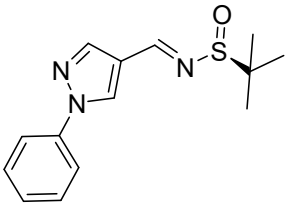
(*S*,*E*)-*N*-((1-Ethyl-1*H*-pyrazol-4-yl)methylene)-2-methylpropane-2-sulfinamide (2v)



The compound was purified by flash chromatography with gradient elution that gave yellow oil. Yield: 95%, R_f 0.50 (hexane/EtOAc, 1:1). ^1H NMR ($CDCl_3$, 400 MHz): δ 8.44 (s, 1H, CH=N), 7.86 (s, 1H, Ar), 7.81 (s, 1H, Ar), 4.17 (q, 2H, *J* = 7.3 Hz, C**H**$_2$-CH_3), 1.49 (t, 2H, *J* = 7.2 Hz,

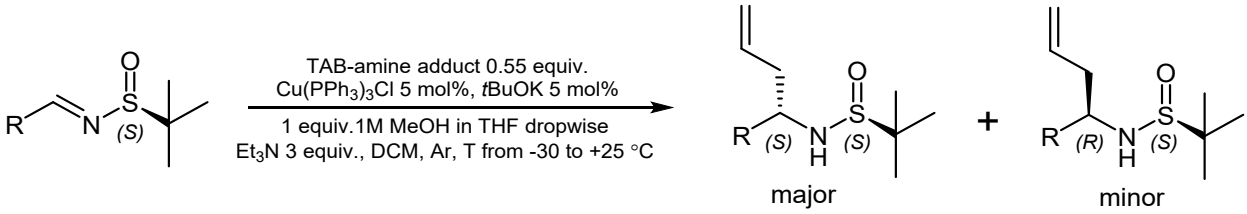
CH_2-C**H**$_3$), 1.17 (s, 9H, *t*Bu) ppm. UV spectrum λ, nm (ε, $cm^{-1}M^{-1}$): 206 (8260), 283 (12220). **NMR spectrum coincides with the literature data[5].**

(*S*,*E*)-2-Methyl-*N*-((1-phenyl-1*H*-pyrazol-4-yl)methylene)propane-2-sulfinamide (2w)



The residue was purified by flash chromatography with gradient elution. Recrystallization from hexane/*i*Pr_2O gave white solid. Yield: 85%, m.p. 67-68°C (hexane/*i*Pr_2O), R_f 0.27 (hexane/EtOAc, 2:1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.57 (s, 1H, CH=N), 8.33 (s, 1H, CH_{pyr}), 8.11 (s, 1H, CH_{pyr}), 7.71 (d, 2H, *J* = 7.8 Hz, Ph), 7.48 (t, 2H, *J* = 7.4 Hz, Ph), 7.35 (t, 1H, *J* = 7.7 Hz, Ph), 1.24 (s, 9H, *t*Bu) ppm. UV spectrum λ, nm (ε, $cm^{-1}M^{-1}$): 196 (28440), 294 (21060). **NMR spectrum coincides with the literature data[5].**

Procedure for allylation of Ellman's imines 2a-w and synthesis of 3a-w



A 25 ml 2-necks pear-shaped flask was charged with an Ellman's imine (0.32 mmol), catalyst $Cu(PPh_3)_3Cl$ **[Cu-3]** (14.4 mg, 0.016 mmol, 5 mol%) and a magnetic stirrer bar. The flask was stoppered, evacuated and filled with Ar atm. 3 times. Then, to the catalyst and substrate mixture, DCM (1 ml) was added, and the flask was immersed in a cooling bath. To the cooled stirred solution, sublimated solid *t*BuOK (1.8 mg, 0.016 mmol, 5 mol%) or 0.8M *t*BuOK stock solution in THF (20 µl, 0.016 mmol) was added. [*All amount of tBuOK has to be entered into the solution that led to the color change from almost colorless to light yellow or bright orange*] Further, 3 equiv. of Et_3N (134 µl, 97.2 mg, 0.96 mmol) and 0.55 equiv. (0.66 equiv. for **2b**, **2h**, **2i**, **2m**, **2n** and **2p**) of the corresponding adduct was added (see **Table S3**). The reaction mixture was stirred for indicated Time A. Then 1 equiv. of 1M solution of MeOH (13 µl, 10.2 mg, 0.32 mmol) in anhydrous THF (307 µl) was added by slow injection through the septum by Syringe Pump over Time B. When alcohol solution was completely added, the mixture was stirred for extra Time C. The end of the reaction was controlled by the disappearance of imine on TLC, other eye-visible sign of the reaction progress is slow disappearing of yellow color (or change of orange color to yellow in case of pyridinic substrates **2r-u**). The reaction was quenched with 5 equiv. of glacial

AcOH (92 µl, 96 mg, 1.6 mmol) followed by evaporation. All substrates except pyridinic type (**2a-q, 2v-w**) were workuped as follows. After evaporation the resulting oil was dissolved in a mixture of Et_2O and K_2CO_3 aq. solution and stirred for 30 min, during that time the aqueous layer became blue-colored. Etheral layer was separated and aqueous one extracted several times. The combined extracts were dried over K_2CO_3 and evaporated.

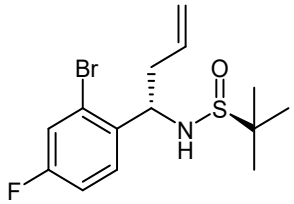
To the pyridinic substrates (**2r-u**) after evaporation of solvent, EDTA (60 mg, 0.2 mmol), K_2CO_3 (1.36 g, 10 mmol), H_2O (5 ml) and EtOAc (3 ml) were added and the mixture was stirred for 30 min. The organic extract was separated, dried over K_2CO_3 and evaporated.

The ratio of diastereomeric allylated amides **3a,b** can be determined by proton NMR spectra. However at high ratios of diastereomers, precise analysis of reaction mixtures was hampered by small impurities. Chromatography purification of the reaction mixtures will change the authentic diastereomers ratio and has to be avoided. It is more accurate to transform diastereomers into enantiomers, having uniform chemical and physical properties followed by analysis using chiral HPLC. In our case the full procedure for analysis includes a standard desulfination of crude homoallylamides with HCl/MeOH sol.,[32] followed by treatment of the formed homoallylamines hydrochlorides by the Boc-anhydride in the presence of Et_3N in THF thus preparing *N*-Boc-homoallylamines as a mixture of enantiomers. The completeness of the desulfination of amides was controlled by TLC, making concentrated (overloaded) spot on TLC plate to see any traces of starting amide. Corresponding racemates for chiral HPLC analysis were synthesized *via* three component aminoallylation of carbonyl compounds[3] followed by the *N*-Boc-acylation of *rac*-homoallylamines.

Table S3. Reaction conditions for different adducts application (variations №1-4).

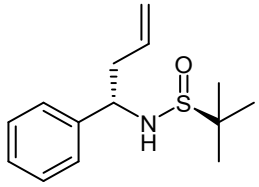
№	T, °C	Cooling bath	TAB adduct	**Time A** (stirring w\o MeOH), min	**Time B** (MeOH addition), min	**Time C** (post addition), min
1	25	Water	**1a**	5	5	5
2	0	Ice/water	**1c**	15	30	30
3	-15	$(CH_2OH)_2/N_{2liq.}$	**1d**	30	60	60
4	-30	$(CH_2OH)_{2aq.}/N_{2liq.}$		120	120	180

(*S*)-*N*-((*S*)-1-(2-Bromo-4-fluorophenyl)but-3-en-1-yl)-2-methylpropane-2-sulfinamide (3a)



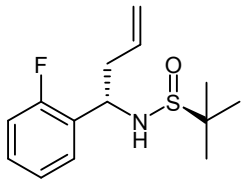
The substance was obtained by variation method №2 (**Table S3**). The compound was purified by flash chromatography with gradient elution (hexane/EtOAc from 8:1 to 1:1) that gave white solid. Yield: 95%, *de* > 99%, R_f 0.42 (hexane/EtOAc, 1:1), m.p. 79-80 °C (hexane), $[\alpha]_D^{25}$ +5.7 (*c* 1.0, $CHCl_3$). ^1H NMR ($CDCl_3$, 400 MHz): δ 7.39 (dd, 1H, *J* = 8.7, 6.0 Hz, Ar), 7.29 (dd, 1H, *J* = 8.2, 2.5 Hz, Ar), 7.04 (td, 1H, *J* = 8.4, 2.5 Hz, Ar), 5.70-5.60 (m, 1H, CH=), 5.10-5.06 (m, 2H, CH_2=), 4.84 (q, 1H, *J* = 6.2 Hz, CHAr), 3.76 (d, 1H, *J* = 5.7 Hz, NH), 2.65-2.54 (m, 2H, CH_2), 1.19 (s, 9H, *t*Bu) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz): δ 162.8 and 160.3 (d, J_{CF} = 251.8 Hz), 136.91 and 136.88 (d, J_{CF} = 3.5 Hz), 133.2, 129.9 and 129.8 (d, J_{CF} = 8.6 Hz), 123.3 and 123.2 (d, J_{CF} = 9.4 Hz), 120.4 and 120.2 (d, J_{CF} = 24.4 Hz), 119.2, 115.0 and 114.8 (d, J_{CF} = 21.2 Hz), 56.8, 56.5, 40.5, 22.7 (3C) ppm. UV spectrum λ, nm (ε, $cm^{-1}M^{-1}$): 269 (806), 276 (725). Anal. Calcd. for $C_{14}H_{19}BrFNOS$ (348.27): C, 48.28; H, 5.50; N, 4.02; found: C, 48.11; H, 5.71; N, 3.91.

(*S*)-2-Methyl-*N*-((*S*)-1-phenylbut-3-en-1-yl)propane-2-sulfinamide (3b)



The substance was obtained by variation method №2 (**Table S3**). The compound was purified by flash chromatography with gradient elution (hexane/EtOAc from 8:1 to 1:1) that gave white solid. Yield: 95%, *de* 96%, R_f 0.30 (hexane/EtOAc, 1:1), m.p. 83-84°C (hexane). ^1H NMR ($CDCl_3$, 400 MHz): δ 7.32-7.26 (m, 5H, Ar), 5.65-5.55 (m, 1H, CH=), 5.05-5.00 (m, 2H, CH_2=), 4.44 (br.s, 1H, CHAr), 3.52 (br.s, 1H, NH), 2.77-2.70 (m, 1H, C**H**$_a$H$_b$), 2.58-2.51 (m, 1H, CH$_a$**H**$_b$), 1.21 (s, 9H, *t*Bu) ppm. UV spectrum λ, nm (ε, $cm^{-1}M^{-1}$): 258 (152). **NMR spectrum coincides with the literature data[33].**

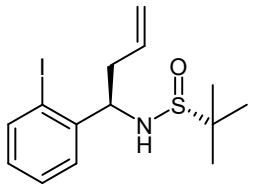
(*S*)-*N*-((*S*)-1-(2-Fluorophenyl)but-3-en-1-yl)-2-methylpropane-2-sulfinamide (3c)



The substance was obtained by variation method №2 (**Table S3**). The compound was purified by flash chromatography with gradient elution (hexane/EtOAc from 8:1 to 1:1) that gave yellow oil. Yield: 90%, *de* >99%, R_f 0.35 (hexane/EtOAc, 1:1). ^1H NMR ($CDCl_3$, 400 MHz): δ 7.33 (td, 1H, *J* = 8.6, 1.1 Hz, Ar), 7.28-7.22 (m, 1H, Ar), 7.12 (td, 1H, *J* = 7.5, 1.0 Hz, Ar), 7.06-7.01 (m, 1H, Ar), 5.71-5.61 (m, 1H, CH=), 5.08-5.03 (m, 2H, CH_2=), 4.70-4.65 (dd, 1H, *J* = 13.6, 6.8 Hz, CHAr), 3.68 (d, 1H, *J* = 6.5 Hz, NH), 2.73-2.66 (m, 1H, C**H**$_a$H$_b$), 2.60-2.53 (m, 1H, CH$_a$**H**$_b$),

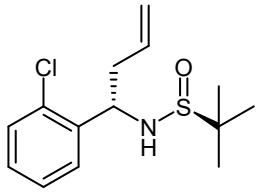
1.21 (s, 9H, *t*Bu) ppm. UV spectrum λ, nm (ε, $cm^{-1}M^{-1}$): 262 (866), 268 (774). **NMR spectrum coincides with the literature data[34].**

(*R*)-*N*-((*R*)-1-(2-Iodophenyl)but-3-en-1-yl)-2-methylpropane-2-sulfinamide (3d)



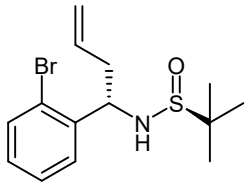
Since the imine configuration **2d** was (*R*) the reaction product **3d** was (*R,R*)-isomer. The substance was obtained by variation method №2 (**Table S3**). The compound was purified by flash chromatography with gradient elution (hexane/EtOAc from 8:1 to 1:1) that gave yellow oil. Yield: 93%, *de* >99%, R_f 0.36 (hexane/EtOAc, 1:1), $[\alpha]_D^{25}$ -13.5 (*c* 0.2, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.82 (d, 1H, *J* = 7.7 Hz, Ar), 7.37-7.33 (m, 2H, Ar), 6.98-6.94 (m, 1H, Ar), 5.74-5.63 (m, 1H, CH=), 5.10-5.07 (m, 2H, CH_2=), 4.73 (q, 1H, *J* = 6.1 Hz, CHAr), 3.76 (d, 1H, *J* = 5.1 Hz, NH), 2.60 (m, 1H, CH_aH_b), 1.19 (s, 9H, *t*Bu) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz): δ 143.6, 139.8, 133.4, 129.4, 128.5, 128.3, 118.9, 99.5, 61.5, 56.4, 40.6, 22.7 (3C) ppm. UV spectrum λ, nm (ε, $cm^{-1}M^{-1}$): 258 (833). Anal. Calcd. for $C_{14}H_{20}INOS$ (377.28): C, 44.57; H, 5.34; N, 3.71; found: C, 44.53; H, 5.41; N, 3.76.

(*S*)-*N*-((*S*)-1-(2-Chlorophenyl)but-3-en-1-yl)-2-methylpropane-2-sulfinamide (3e)



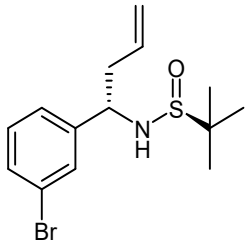
The substance was obtained by variation method №3 (**Table S3**). The compound was purified by flash chromatography with gradient elution (hexane/EtOAc from 8:1 to 1:1) that gave light yellow oil. Yield: 90%, *de* 98%, R_f 0.15 (hexane/EtOAc, 2:1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.40 (dd, 1H, *J* = 7.6, 1.1 Hz, Ar), 7.33 (dd, 1H, *J* = 7.8, 1.0 Hz, Ar), 7.28-7.24 (m, 1H, Ar), 7.19 (td, 1H, *J* = 7.6, 1.5 Hz, Ar), 5.65 (ddt, 1H, *J* = 17.1, 9.2, 7.1 Hz, CH=), 5.08-5.05 (m, 2H, CH_2=), 4.90 (q, 1H, *J* = 6.2 Hz, CHAr), 3.77 (d, 1H, *J* = 5.7 Hz, NH), 2.68-2.56 (m, 1H, CH_aH_b), 1.19 (s, 9H, *t*Bu) ppm. UV spectrum λ, nm (ε, $cm^{-1}M^{-1}$): 267 (233). **NMR spectrum coincides with the literature data[32].**

(*S*)-*N*-((*S*)-1-(2-Bromophenyl)but-3-en-1-yl)-2-methylpropane-2-sulfinamide (3f)



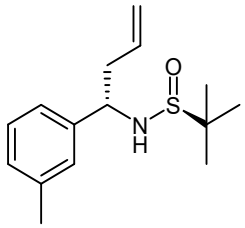
The substance was obtained by variation method №3 (**Table S3**). The compound was purified by flash chromatography with gradient elution (hexane/EtOAc from 8:1 to 1:1) that gave light yellow oil. Yield: 88%, *de* 98%, R_f 0.33 (hexane/EtOAc, 1:1), $[\alpha]_D^{25}$ +7.1 (*c* 0.2, $CHCl_3$). ^1H NMR ($CDCl_3$, 400 MHz): δ 7.54 (d, 1H, *J* = 8.0 Hz, Ar), 7.40 (d, 1H, *J* = 7.7 Hz, Ar), 7.32 (t, 1H, *J* = 7.4 Hz, Ar), 7.13 (t, 1H, *J* = 7.5 Hz, Ar), 5.73-5.62 (m, 1H, CH=), 5.10-5.07 (m, 2H, CH_2=), 4.89 (q, 1H, *J* = 6.1 Hz, CHAr), 3.80 (br.d, 1H, *J* = 5.4 Hz, NH), 2.63 (m, 2H, CH_aH_b), 1.20 (s, 9H, *t*Bu) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz): δ 140.9, 133.5, 133.3, 129.2, 128.8, 127.7, 123.4, 118.9, 57.3, 56.5, 40.5, 22.7 (3C) ppm. UV spectrum λ, nm (ε, $cm^{-1}M^{-1}$): 258 (274). Anal. Calcd. for $C_{14}H_{20}BrNOS$ (330.28): C, 50.91; H, 6.10; N, 4.24; found: C, 51.02; H, 6.18; N, 4.05.

(*S*)-*N*-((*S*)-1-(3-Bromophenyl)but-3-en-1-yl)-2-methylpropane-2-sulfinamide (3g)



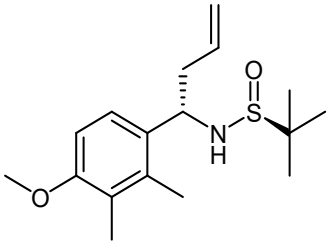
The substance was obtained by variation method №3 (**Table S3**). The compound was purified by flash chromatography with gradient elution (hexane/EtOAc from 8:1 to 1:1) that gave white solid. Yield: 89%, *de* 98%, R_f 0.20 (hexane/EtOAc, 2:1), m.p. 57-58 °C (hexane). ^1H NMR ($CDCl_3$, 400 MHz): δ 7.52 (t, 1H, Ar), 7.48 (dt, 1H, *J* = 7.6, 1.8 Hz, Ar), 7.33-7.28 (m, 2H, Ar), 5.71-5.60 (m, 1H, CH=), 5.13-5.09 (m, 2H, CH_2=), 4.47 (dd, 1H, *J* = 11.2, 5.9 Hz, CHAr), 3.57 (d, 1H, *J* = 4.0 Hz, NH), 2.81-2.74 (m, 1H, C**H$_a$**H$_b$), 2.62-2.55 (m, 1H, CH$_a$**H$_b$**), 1.29 (s, 9H, *t*Bu) ppm. UV spectrum λ, nm (ε, $cm^{-1}M^{-1}$): 268 (244). **NMR spectrum coincides with the literature data[32].**

(*S*)-2-Methyl-*N*-((*S*)-1-(*m*-tolyl)but-3-en-1-yl)propane-2-sulfinamide (3h)



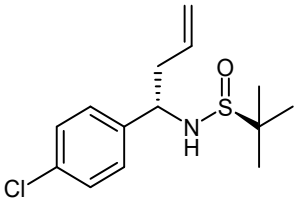
The substance was obtained by variation method №3 (Table S1). The compound was purified by flash chromatography with gradient elution (hexane/EtOAc from 8:1 to 1:1) that gave yellow oil. Yield: 91%, *de* 97%, R_f 0.38 (hexane/EtOAc, 1:1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.24-7.20 (m, 1H, Ar), 7.12-7.07 (m, 3H, Ar), 5.60 (ddt, 1H, *J* = 17.2, 10.1, 7.0 Hz, CH=), 5.05-4.99 (m, 2H, CH_2=), 4.41-4.37 (m, 1H, CHAr), 3.49 (d, 1H, *J* = 3.2 Hz, NH), 2.75-2.68 (m, 1H, C**H**$_a$H$_b$), 2.57-2.49 (m, 1H, CH$_a$**H**$_b$), 2.34 (s, 3H, *m*-Me), 1.21 (s, 9H, *t*Bu) ppm. UV spectrum λ, nm (ε, $cm^{-1}M^{-1}$): 265 (329). **NMR spectrum coincides with the literature data[35].**

(*S*)-*N*-((*S*)-1-(4-Methoxy-2,3-dimethylphenyl)but-3-en-1-yl)-2-methylpropane-2-sulfinamide (3i)



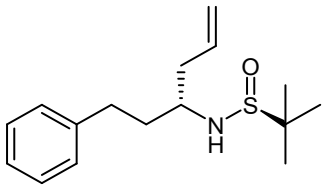
The substance was obtained by variation method №4 (**Table S3**). The compound was purified by flash chromatography with gradient elution (hexane/EtOAc from 8:1 to 1:1) that gave light yellow oil. Yield: 93%, *de* 98%, R_f 0.20 (hexane/EtOAc, 2:1), $[\alpha]_D^{25}$ +46.2 (*c* 0.6, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.18 (d, 1H, *J* = 8.6 Hz, Ar), 6.72 (d, 1H, *J* = 8.6 Hz, Ar), 5.62 (ddt, 1H, *J* = 17.1, 10.3, 7.1 Hz, CH=), 5.08-4.99 (m, 2H, CH_2=), 4.69 (td, 1H, *J* = 6.8, 3.2 Hz, CHAr), 3.78 (s, 3H, *p*-OMe), 3.46 (d, 1H, *J* = 3.3 Hz, NH), 2.73-2.66 (m, 1H, C**H**$_a$H$_b$), 2.60-2.53 (m, 1H, CH$_a$**H**$_b$), 2.25 (s, 3H, *m*-Me), 2.14 (s, 3H, *o*-Me), 1.18 (s, 9H, *t*Bu) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz): δ 156.7, 135.7, 134.3, 131.6, 125.3, 124.6, 118.0, 107.7, 55.7, 55.4, 54.1, 40.7, 22.7 (3C), 15.3, 12.2 ppm. UV spectrum λ, nm (ε, $cm^{-1}M^{-1}$): 275 (1125), 283 (1112). Anal. Calcd. for $C_{17}H_{27}N_2OS$ (309.47): C, 65.98; H, 8.79; N, 4.53; found: C, 65.84; H, 8.74; N, 4.47.

(*S*)-*N*-((*S*)-1-(4-Chlorophenyl)but-3-en-1-yl)-2-methylpropane-2-sulfinamide (3j)



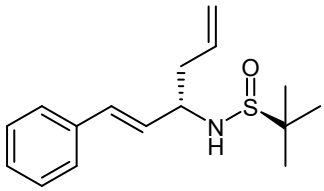
The substance was obtained by variation methodic №3 (**Table S3**). The compound was purified by flash chromatography with gradient elution (hexane/EtOAc from 8:1 to 1:1) that gave yellow oil. Yield: 96%, *de* 98%, R_f 0.20 (hexane/EtOAc, 2:1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.31-7.24 (m, 4H, Ar), 5.63-5.52 (m, 1H, CH=), 5.04-5.00 (m, 1H, CH_2=), 4.41 (q, 1H, *J* = 3.2 Hz, CHAr), 3.51 (d, 1H, *J* = 2.3 Hz, NH), 2.73-2.67 (m, 1H, C**H**$_a$H$_b$), 2.53-2.46 (m, 1H, CH$_a$**H**$_b$), 1.20 (s, 9H, *t*Bu) ppm. UV spectrum λ, nm (ε, $cm^{-1}M^{-1}$): 267 (155), 313 (54). **NMR spectrum coincides with the literature data[34].**

(*S*)-2-Methyl-*N*-((*R*)-1-phenylhex-5-en-3-yl)propane-2-sulfinamide (3k)



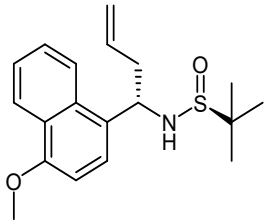
Because of the changing of priority of substituents in **3k** according to *R,S*-nomenclature the sign of the configuration of newly formed chiral center now is *R*. The substance was obtained by variation method №4 (**Table S3**). The compound was purified by flash chromatography with gradient elution (hexane/EtOAc from 8:1 to 1:1) that gave yellow oil. Yield: 93%, *de* 95%, R_f 0.19 (hexane/EtOAc, 2:1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.30-7.26 (m, 2H, Ar), 7.22-7.16 (m, 3H, Ar), 5.82-5.72 (m, 1H, CH=), 5.12-5.08 (m, 2H, CH_2=), 3.35 (q, 1H, *J* = 6.1 Hz, CHN), 3.15 (d, 1H, *J* = 3.9 Hz, NH), 2.73 (t, 2H, *J* = 7.1 Hz, Ph**CH$_2$**CH$_2$), 2.33 (m, 2H, **CH$_2$**-CH=CH$_2$), 1.91 (q, 2H, *J* = 7.0 Hz, PhCH$_2$**CH$_2$**), 1.19 (s, 9H, *t*Bu) ppm. UV spectrum λ, nm (ε, $cm^{-1}M^{-1}$): 258 (363). **NMR spectrum coincides with the literature data[34].**

(*S*)-2-Methyl-*N*-((*S,E*)-1-phenylhexa-1,5-dien-3-yl)propane-2-sulfinamide (3l)



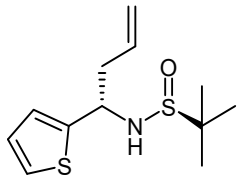
The substance was obtained by variation method №3 (**Table S3**). The compound was purified by flash chromatography with gradient elution (hexane/EtOAc from 8:1 to 1:1) that gave lemon-yellow oil. Yield: 95%, *de* 98%, R_f 0.26 (hexane/EtOAc, 2:1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.39-7.37 (m, 2H, Ar), 7.32-7.28 (m, 2H, Ar), 7.25-7.21 (m, 1H, Ar), 6.61 (d, 1H, *J* = 15.9 Hz, Ph-**CH**=CH), 6.21 (dd, 1H, *J* = 15.9, 7.3 Hz, Ph-CH=**CH**), 5.80 (ddt, 1H, *J* = 14.6, 9.9, 7.1 Hz, CH=), 5.16-5.10 (m, 2H, CH_2=), 4.04 (pent, 1H, *J* = 6.3 Hz, CHN), 3.33 (d, 1H, *J* = 5.2 Hz, NH), 2.56-2.41 (m, 2H, CH$_a$H$_b$), 1.22 (s, 9H, *t*Bu) ppm. UV spectrum λ, nm (ε, $cm^{-1}M^{-1}$): 201 (16940), 254 (9220). **NMR spectrum coincides with the literature data[36].**

(*S*)-*N*-((*S*)-1-(4-Methoxynaphthalen-1-yl)but-3-en-1-yl)-2-methylpropane-2-sulfinamide (3m)



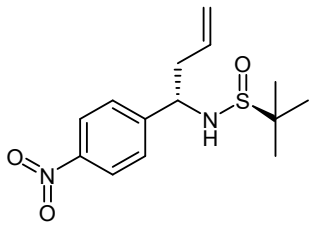
The substance was obtained by variation method №4 (**Table S3**). The compound was purified by flash chromatography with gradient elution (hexane/EtOAc from 8:1 to 1:1) that gave yellow oil. Yield: 70%, *de* 97%, R_f 0.32 (hexane/EtOAc, 1:1), $[\alpha]_D^{25}$ +3.4 (*c* 0.5, $CHCl_3$). ^1H NMR ($CDCl_3$, 400 MHz): δ 8.33 (d, 1H, *J* = 8.3 Hz, Ar), 8.14 (d, 1H, *J* = 8.5 Hz, Ar), 7.57-7.46 (m, 3H, Ar), 6.80 (d, 1H, *J* = 8.1 Hz, Ar), 5.69 (ddt, 1H, *J* = 14.1, 10.0, 7.0 Hz, CH=), 5.18 (br.s, 1H, CHAr), 5.13-5.03 (m, 2H, CH_2=), 3.97 (s, 3H, OMe), 3.75 (d, *J* = 2.8 Hz, NH), 2.87 (m, 2H, CH_aH_b), 1.18 (s, 9H, *t*Bu) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz): δ 155.3, 134.3, 131.8, 128.5, 126.9, 125.9, 125.2, 125.1, 123.0, 122.8, 118.3, 103.0, 55.9, 55.5, 53.7, 40.2, 22.7 (3C) ppm. UV spectrum λ, nm (ε, $cm^{-1}M^{-1}$): 212 (25860), 236 (18350), 299 (4590). Anal. Calcd. for $C_{19}H_{25}NO_2S$ (331.47): C, 68.85; H, 7.60; N, 4.23; found: C, 68.87; H, 7.64; N, 4.17.

(*S*)-2-Methyl-*N*-((*S*)-1-(thiophen-2-yl)but-3-en-1-yl)propane-2-sulfinamide (3n)



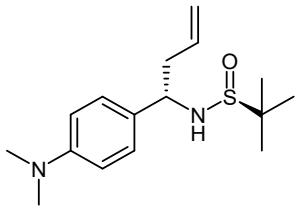
The substance was obtained by variation method №4 (**Table S3**). The compound was purified by flash chromatography with gradient elution (hexane/EtOAc from 8:1 to 1:1) that gave light yellow oil. Yield: 94%, *de* 98%, R_f 0.43 (hexane/EtOAc, 1:1), $[\alpha]_D^{25}$ +11.3 (*c* 0.4, $CHCl_3$). ^1H NMR ($CDCl_3$, 400 MHz): δ 7.18 (d, 1H, *J* = 5.0 Hz, thiophene), 7.00 (d, 1H, *J* = 3.1 Hz, thiophene), 6.90 (t, 1H, *J* = 4.5 Hz, thiophene), 5.66 (ddt, 1H, *J* = 14.1, 10.1, 7.0 Hz, CH=), 5.08-5.02 (m, 2H, CH_2=), 4.68 (q, 1H, *J* = 6.1 Hz, CHN), 3.58 (d, 1H, *J* = 4.3 Hz, NH), 2.77-2.70 (m, 1H, C**H**$_a$H$_b$), 2.59-2.52 (m, 1H, CH$_a$**H**$_b$), 1.17 (s, 9H, *t*Bu) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz): 145.6, 133.5, 126.7, 125.4, 124.9, 118.5, 56.1, 54.6, 41.9, 22.6 (3C) ppm. UV spectrum λ, nm (ε, $cm^{-1}M^{-1}$): 234 (7200), 325 (130). Anal. Calcd. for $C_{12}H_{19}NOS_2$ (257.41): C, 55.99; H, 7.44; N, 5.44; found: C, 56.04; H, 7.47; N, 5.51.

(*S*)-2-Methyl-*N*-((*S*)-1-(4-nitrophenyl)but-3-en-1-yl)propane-2-sulfinamide (3o)



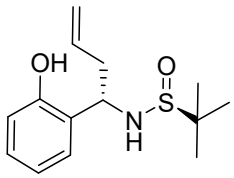
The substance was obtained by variation method №3 (**Table S3**). The compound was purified by flash chromatography with gradient elution (hexane/EtOAc from 8:1 to 1:1) that gave orange solid. Yield: 51%, *de* 98%, R_f 0.27 (hexane/EtOAc, 1:1), m.p. 88-90°C (EtOAc), $[\alpha]_D^{25}$ +0.9 (*c* 0.5, $CHCl_3$). ^1H NMR ($CDCl_3$, 400 MHz): δ 8.16 (d, 2H, *J* = 8.5 Hz, Ar), 7.49 (d, 2H, *J* = 8.5 Hz, Ar), 5.57 (ddt, 1H, *J* = 14.2, 10.2, 7.1 Hz, CH=), 5.06-5.01 (m, 2H, CH_2=), 4.53 (q, 1H, *J* = 6.0 Hz, CHAr), 3.69 (d, 1H, *J* = 4.9 Hz, NH), 2.74-2.67 (m, 1H, C**H$_a$**H$_b$), 2.58-2.51 (m, 1H, CH$_a$**H$_b$**), 1.20 (s, 9H, *t*Bu) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz): δ 149.4, 147.4, 132.7, 128.2 (2C), 123.9 (2C), 119.4, 58.3, 56.5, 41.3, 22.6 (3C) ppm. UV spectrum λ, nm (ε, $cm^{-1}M^{-1}$): 273 (9660). Anal. Calcd. for $C_{14}H_{20}N_2O_3S$ (296.39): C, 56.73; H, 6.80; N, 9.45; found: C, 56.61; H, 6.71; N, 9.29.

(*S*)-*N*-((*S*)-1-(4-(Dimethylamino)phenyl)but-3-en-1-yl)-2-methylpropane-2-sulfinamide (3p)



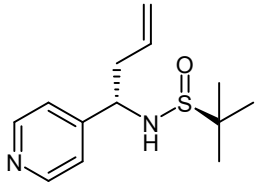
The substance was obtained by variation method №3 (**Table S3**). The compound was purified by flash chromatography with gradient elution (hexane/EtOAc from 8:1 to 1:1) that gave yellow oil. Total yield: 74%, *de* 85%, R_f 0.33 (hexane/EtOAc, 1:1), though diastereomers were not separated by TLC, major isomer was separated by the flash chromatography, $[\alpha]_D^{25}$ +97.3 (*c* 0.1, $CHCl_3$). ^1H NMR ($CDCl_3$, 400 MHz): δ 7.18 (d, 2H, *J* = 8.6 Hz, Ar), 6.69 (d, 2H, *J* = 8.6 Hz, Ar), 5.62 (ddt, 1H, *J* = 17.2, 10.2, 7.0 Hz, CH=), 5.05-4.98 (m, 2H, CH_2=), 4.38-4.34 (m, 1H, CHAr), 3.39 (d, 1H, *J* = 2.8 Hz, NH), 2.94 (s, 6H, NMe_2), 2.76-2.69 (m, 1H, C**H$_a$**H$_b$), 2.55-2.48 (m, 1H, CH$_a$**H$_b$**), 1.21 (s, 9H, *t*Bu) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz): δ 150.2, 134.5, 129.5, 128.2 (2C), 117.8, 112.5 (2C), 58.0, 55.8, 41.0, 40.6, 22.8 (3C) ppm. UV spectrum λ, nm (ε, $cm^{-1}M^{-1}$): 261 (13900), 305 (2190), 398 (410). Anal. Calcd. for $C_{16}H_{26}N_2OS$ (294.46): C, 65.26; H, 8.90; N, 9.51; found: C, 65.17; H, 8.91; N, 9.44.

(*S*)-*N*-((*S*)-1-(2-Hydroxyphenyl)but-3-en-1-yl)-2-methylpropane-2-sulfinamide (3q)



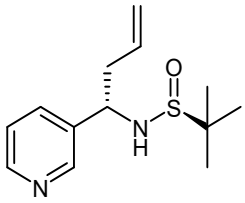
The substance was obtained by variation method №3 (**Table S3**). The isolation of the allylated product **3q** was accomplished according to general procedure, however instead of K_2CO_3 saturated solution $NaHCO_3$ was used, and the organic extracts were dried over Na_2SO_4. The compound was purified by flash chromatography with gradient elution (hexane/EtOAc from 8:1 to 1:1) that gave white solid. Yield: 86%, *de* >99%, R_f 0.30 (hexane/EtOAc, 1:1), m.p. 82-83°C (hexane), $[\alpha]_D^{25}$ -11.3 (*c* 0.3, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.17 (s, 1H, OH), 6.98 (d, 1H, *J* = 7.1 Hz, Ar), 6.75 (t, 1H, *J* = 7.2 Hz, Ar), 6.68 (t, 1H, *J* = 7.2 Hz, Ar), 6.23 (d, 1H, *J* = 7.8 Hz, Ar), 5.71 (ddt, 1H, *J* = 17.2, 10.3, 7.1 Hz, CH=), 5.22 (d, 1H, *J* = 9.1 Hz, NH), 5.05-4.98 (m, 2H, CH_2=), 4.20 (q, 1H, *J* = 8.2 Hz, CHAr), 2.76-2.68 (m, 1H, C**H**$_a$H$_b$), 2.56-2.50 (m, 1H, CH$_a$**H**$_b$), 1.29 (s, 9H, *t*Bu) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz): δ 154.9, 135.7, 128.9, 127.8, 127.3, 118.9, 117.0, 116.7, 62.8, 56.7, 41.0, 22.9 (3C) ppm. UV spectrum λ, nm (ε, cm^{-1}M^{-1}): 273 (2340). Anal. Calcd. for $C_{14}H_{21}NO_2S$ (267.39): C, 62.89; H, 7.92; N, 5.24; found: C, 62.78; H, 7.99; N, 5.20.

(*S*)-2-Methyl-*N*-((*S*)-1-(pyridin-4-yl)but-3-en-1-yl)propane-2-sulfinamide (3r)



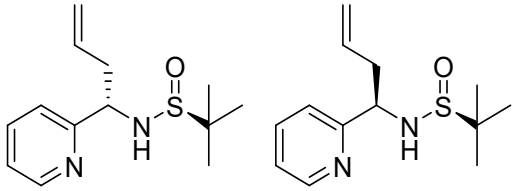
The substance was obtained by variation method №3 (**Table S3**). The compound was purified by flash chromatography with gradient elution (from EtOAc to EtOAc/MeOH 8:1) that gave dark yellow oil. Yield: 83%, *de* 78%, R_f 0.41 (EtOAc/MeOH 8:1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.59 (d, 2H, *J* = 5.5 Hz, Ar), 7.27 (d, 2H, *J* = 5.5 Hz, Ar), 5.64-5.54 (m, 1H, CH=), 5.09-5.04 (m, 2H, CH_2=), 4.46 (q, 1H, *J* = 6.1 Hz, CHAr), 3.60 (d, 1H, *J* = 5.0 Hz, NH), 2.73-2.66 (m, 1H, C**H**$_a$H$_b$), 2.59-2.52 (m, 1H, CH$_a$**H**$_b$), 1.23 (s, 9H, *t*Bu) ppm. UV spectrum λ, nm (ε, cm^{-1}M^{-1}): 257 (901). **NMR spectrum coincides with the literature data[37].**

(*S*)-2-Methyl-*N*-((*S*)-1-(pyridin-3-yl)but-3-en-1-yl)propane-2-sulfinamide (3s)



The substance was obtained by variation method №3 (**Table S3**). The compound was purified by flash chromatography with gradient elution (from EtOAc to EtOAc/MeOH 8:1) that gave orange solid. Yield: 65%, *de* 98%, R_f 0.41 (EtOAc/MeOH, 8:1), m.p. 95-97 °C (EtOAc), $[\alpha]_D^{25}$ +36.5 (*c* 1.0, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.45-8.40 (m, 2H, Ar), 7.59 (d, 1H, *J* = 7.4 Hz, Ar), 7.19-7.16 (m, 1H, Ar), 5.57-5.47 (m, 1H, CH=), 4.97-4.92 (m, 2H, CH_2=), 4.38 (q, 1H, *J* = 5.0 Hz, CHAr), 3.81 (d, 1H, *J* = 3.8 Hz, NH), 2.69-2.63 (m, 1H, C**H$_a$**H$_b$), 2.50-2.43 (m, 1H, CH$_a$**H$_b$**), 1.12 (s, 9H, *t*Bu) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz): δ 149.0, 148.7, 137.4, 134.9, 132.9, 123.4, 118.9, 56.5, 56.1, 40.9, 22.5 (3C) ppm. UV spectrum λ, nm (ε, $cm^{-1}M^{-1}$): 261 (1005). Anal. Calcd. for $C_{13}H_{20}N_2OS$ (252.38): C, 61.87; H, 7.99; N, 11.10; found: C, 61.75; H, 7.84; N, 11.04.

(*S*)-2-Methyl-*N*-((*S*)-1-(pyridin-2-yl)but-3-en-1-yl)propane-2-sulfinamide ((*S*$_s$,*S*)-3t) and (*R*)-2-methyl-*N*-((*S*)-1-(pyridin-2-yl)but-3-en-1-yl)propane-2-sulfinamide ((*S*$_s$,*R*)-3t)



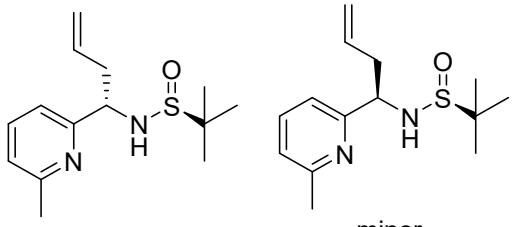
The substances were obtained by variation method №2 (**Table S3**). The compound **3t** was purified by flash chromatography with gradient elution that gave yellow oil. Total yield: 94%, *de* 17%, R_f 0.15 (EtOAc). The impurity of phosphine was removed by acid-base extraction with transformation first **3t** into HCl-salt followed by the extraction of aqueous sol. with Et_2O impurity. To aqueous layer excess of 20% solution NaOH was added and **3t** was extracted by Et_2O, dried over K_2CO_3 and evaporated. The diastereomers were separated by PTLC in MeCN. Both diastereomers slowly oxidize on air. UV spectrum λ, nm (ε, $cm^{-1}M^{-1}$): 261 (1142).

Major isomer (*S*$_s$,*S*)-**3t**: Yellow oil, R_f 0.18 (MeCN), $[\alpha]_D^{25}$ +39.5 (*c* 0.5, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.55 (d, 1H, *J* = 4.5 Hz, Ar), 7.64 (td, 1H, *J* = 7.7, 1.6 Hz, Ar), 7.27 (d, 1H, *J* = 6.6 Hz, Ar), 7.17 (dd, 1H, *J* = 7.0, 5.2 Hz, Ar), 5.70 (ddt, 1H, *J* = 14.1, 9.4, 7.0 Hz, CH=), 5.05-5.01 (m, 2H, CH_2=), 4.84 (d, 1H, *J* = 6.7 Hz, NH), 4.49 (q, 1H, *J* = 6.6 Hz, CHAr), 2.59 (m, 1H, CH$_a$H$_b$), 1.26 (s, 9H, *t*Bu) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz): δ 160.6, 149.2,

136.7, 134.1, 122.5, 122.0, 118.1, 60.1, 56.3, 42.3, 22.9 (3C) ppm. **NMR spectra coincide with the literature data[38].**

Minor isomer (S_s,*R*)-**3t**: Yellow oil, R_f 0.11 (MeCN), $[\alpha]_D^{25}$ +80.9 (*c* 0.5, $CHCl_3$). ^1H NMR ($CDCl_3$, 400 MHz): δ 8.56 (d, 1H, *J* = 4.6 Hz, Ar), 7.65 (td, 1H, *J* = 7.7, 1.6 Hz, Ar), 7.27 (d, 1H, *J* = 7.9 Hz, Ar), 7.18 (dd, 1H, *J* = 7.2, 5.1 Hz, Ar), 5.68 (ddt, 1H, *J* = 14.4, 10.1, 7.2 Hz, CH=), 5.14-5.09 (m, 1H, CH_2=), 4.56 (q, 1H, *J* = 6.3 Hz, CHAr), 4.05 (d, 1H, *J* = 4.7 Hz, NH), 2.76-2.64 (m, 2H, CH_aH_b), 1.18 (s, 9H, *t*Bu) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz): δ 160.8, 149.4, 136.7, 133.9, 122.6, 122.1, 119.3, 59.4, 56.1, 42.0, 22.7 (3C) ppm. Anal. Calcd. for $C_{13}H_{20}N_2OS$ (252.38): C, 61.87; H, 7.99; N, 11.10; found: C, 61.74; H, 8.01; N, 10.91.

(*S*)-2-Methyl-*N*-((*S*)-1-(6-methylpyridin-2-yl)but-3-en-1-yl)propane-2-sulfinamide ((*S*$_s$,*S*)-3u) and (*S*)-2-methyl-*N*-((*R*)-1-(6-methylpyridin-2-yl)but-3-en-1-yl)propane-2-sulfinamide ((*S*$_s$,*R*)-3u)

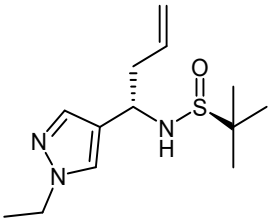


The substances were obtained by variation method №3 (**Table S3**). The compound **3u** was purified by flash chromatography with gradient elution that gave yellow oil. Total yield: 89%, *de* 29%, R_f 0.23 (EtOAc). The diastereomers were separated by PTLC in MeCN. Both diastereomers slowly oxidize on air. UV spectrum λ, nm (ε, $cm^{-1}M^{-1}$): 265 (4540).

Major isomer (S_s,*S*)-**3u**: Yellow oil, R_f 0.24 (MeCN), $[\alpha]_D^{25}$ +24.6 (*c* 0.6, $CHCl_3$). ^1H NMR ($CDCl_3$, 400 MHz): δ 7.50 (t, 1H, *J* = 7.0 Hz, Ar), 7.02 (dd, 2H, *J* = 21.9, 7.5 Hz, Ar), 5.69 (ddt, 1H, *J* = 17.3, 10.3, 7.0 Hz, CH=), 5.10 (br.s, 1H, NH), 5.03-4.99 (m, 2H, CH_2=), 4.44 (q, 1H, *J* = 6.5 Hz, CHAr), 2.56 (m, 2H, CH_aH_b), 2.50 (s, 3H, Me), 1.24 (s, 9H, *t*Bu) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz): δ 159.6, 157.6, 137.0, 134.3, 122.0, 118.8, 117.9, 59.7, 56.2, 42.2, 24.4, 22.9 (3C) ppm. Anal. Calcd. for $C_{14}H_{22}N_2OS$ (266.40): C, 63.12; H, 8.32; N, 10.52; found: C, 62.98; H, 8.34; N, 10.34.

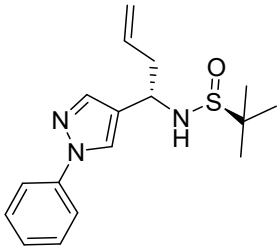
Minor isomer (S_s,*R*)-**3u**: White solid, R_f 0.15 (MeCN), m.p. 84-86°C (hexane), $[\alpha]_D^{25}$ +121.0 (*c* 0.4, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.51 (t, 1H, Ar), 7.03 (dd, 2H, Ar), 5.69 (ddt, 1H, CH=), 5.14-5.08 (m, 2H, CH_2=), 4.51 (q, 1H, CHAr), 4.09 (d, 1H, NH), 2.74-2.58 (m, 2H, CH_aH_b), 2.51 (s, 3H, 6-Me), 1.18 (s, 9H, *t*Bu) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz): δ 160.2, 158.2, 136.7, 134.2, 122.0, 119.1, 118.7, 59.3, 56.1, 42.2, 24.5, 22.7 (3C) ppm. Anal. Calcd. for $C_{14}H_{22}N_2OS$ (266.40): C, 63.12; H, 8.32; N, 10.52; found: C, 63.19; H, 8.35; N, 10.48.

(*S*)-*N*-((*S*)-1-(1-Ethyl-1*H*-pyrazol-4-yl)but-3-en-1-yl)-2-methylpropane-2-sulfinamide (3v)



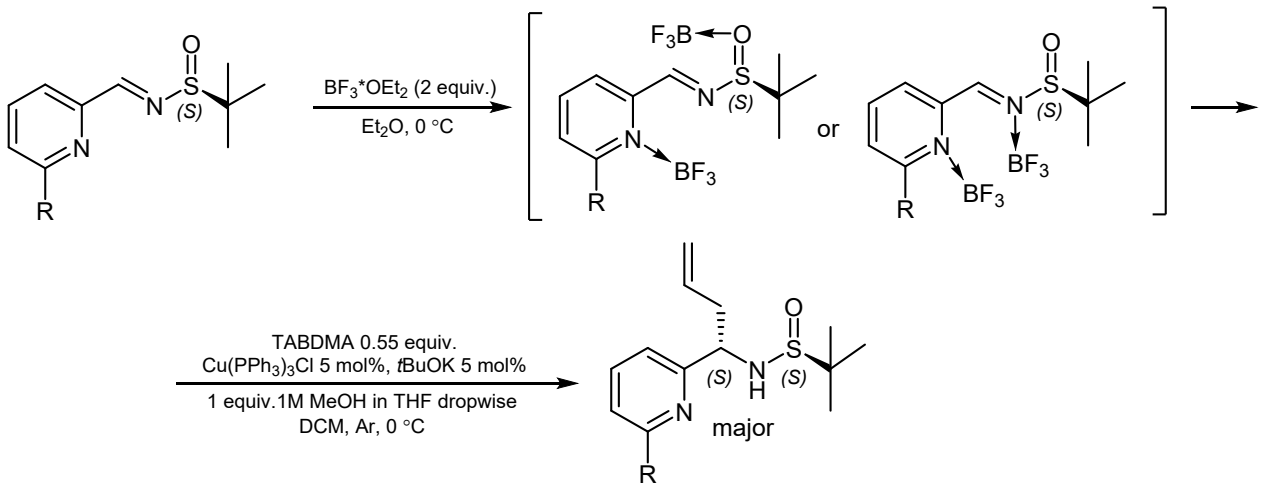
The substance was obtained by variation method №3 (**Table S3**). The compound was purified by flash chromatography with gradient elution (from EtOAc to EtOAc/MeOH 1:1) that gave yellow oil. Yield: 73%, *de* 93%, R_f 0.23 (EtOAc). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.46 (s, 1H, Ar), 7.43 (s, 1H, Ar), 5.78-5.68 (m, 1H, CH=), 5.11-5.06 (m, 2H, CH_2=), 4.44 (q, 1H, *J* = 6.3 Hz, CHN), 4.11 (q, 2H, *J* = 7.3 Hz, C**H**$_2$CH$_3$), 3.34 (d, 1H, *J* = 5.4 Hz, NH), 2.65-2.53 (m, 2H, CH_aH_b), 1.45 (t, 3H, *J* = 7.3 Hz, CH$_2$C**H**$_3$), 1.20 (s, 9H, *t*Bu) ppm. UV spectrum λ, nm (ε, $cm^{-1}M^{-1}$): 269 (830). **NMR spectrum coincides with the literature data[5].**

(*S*)-2-Methyl-*N*-((*S*)-1-(1-phenyl-1*H*-pyrazol-4-yl)but-3-en-1-yl)propane-2-sulfinamide (3w)



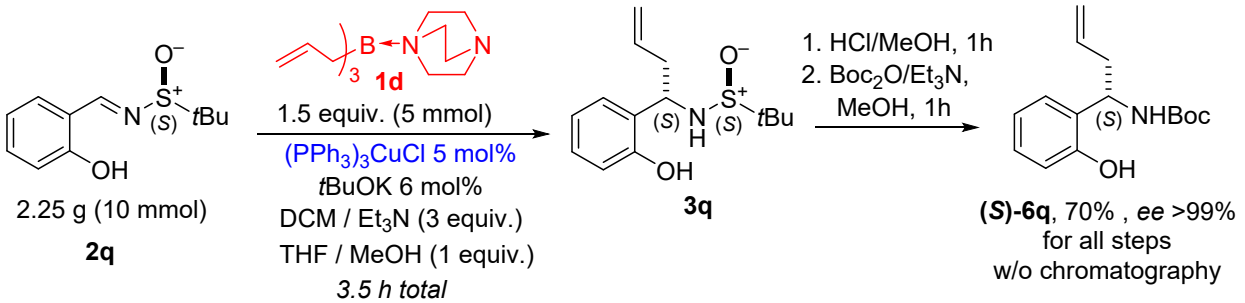
The substance was obtained by variation methodic №3 (**Table S3**). The compound was purified by flash chromatography with gradient elution (from hexane to EtOAc) that gave yellow oil. Yield: 92%, *de* 92%, R_f 0.26 (hexane/EtOAc, 1:1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.03 (s, 1H, CH_{pyr}), 7.68 (s, 2H, Ph), 7.66 (s, 1H, CH_{pyr}), 7.43 (t, 2H, *J* = 7.4 Hz, Ph), 7.27 (t, 1H, *J* = 7.4 Hz, Ph), 5.84-5.74 (m, 1H, CH=), 5.17-5.11 (m, 2H, CH_2=), 4.55 (unresolved t, 1H, CHAr), 3.43 (br.s, 1H, NH), 2.73-2.61 (m, 2H, CH_aH_b), 1.24 (s, 9H, *t*Bu) ppm. UV spectrum λ, nm (ε, $cm^{-1}M^{-1}$): 261 (16180). **NMR spectrum coincides with the literature data[5].**

Modified procedure for allylation of 2-pyridinic Ellman's imines (2t,u)



A 25 ml 2-necks pear-shaped flask was charged with a solution of **2t** or **2u** (1.0 mmol) in Et_2O (2 ml) under Ar atm., cooled to 0 °C and BF_3*OEt_2 (248 µl, 2.0 equiv.) was added dropwise with stirring to produce light orange precipitate. The suspension was stirred for 30 minutes, after that solvent was evaporated under reduced pressure and the flask was refilled with Ar. To the solid was added $Cu(PPh_3)_3Cl$ **[Cu-3]** (44.3 mg, 0.05 mmol, 5 mol%), followed by DCM (3 ml), and the resulting solution was cooled to 0 °C in an ice bath. To the stirred solution 0.8M *t*BuOK stock solution in THF (62.5 µl, 0.05 mmol) was added followed by TABDMA **1c** (179 mg, 0.55 mmol). To the reaction mixture 1M solution of MeOH in anhydrous THF (1.0 ml, 1.0 mmol) was slowly injected through the septum by Syringe Pump over 30 minutes. After the completion of the addition, the mixture was stirred for 30 minutes and quenched with glacial AcOH (286 µl, 5.0 mmol). After evaporated the residue was treated with a mixture of EDTA (180 mg, 0.6 mmol), K_2CO_3 (4.08 g, 30 mmol), H_2O (15 ml) and EtOAc (9 ml) with stirred for 30 min. The organic layer was separated, aqueous layer was extracted by EtOAc (3x9 ml), and combined extracts were dried over K_2CO_3 and evaporated. Determination of *de* was conducted by the analysis of NMR spectra of the crude reaction mixture (for **3t** R = H, *de* = 82%; for **3u** R = Me, *de* = 90%), yields were 32% and 36% correspondingly.

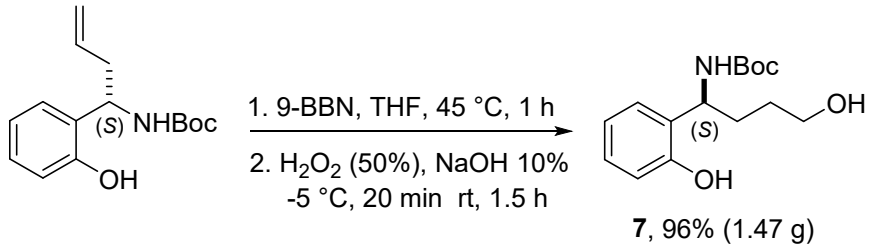
Gram-Scale Allylation of Salicylic imine 2q for synthesis of 7.



Imine **2q** (2.25 g, 10.0 mmol), catalyst **[Cu-3]** (0.442 g, 0.5 mmol) was dissolved in DCM (17 ml) under Ar and to the solution at -10 °C was injected solution of *t*BuOK (0.8 M in THF, 0.63

ml, 0.5 mmol) giving an orange colored solution. The mixture was cooled to -15 °C, Et_3N (3.02 g, 4.18 ml, 30.0 mmol) and adduct **1d** (1.23 g, 5.0 mmol) were added followed by stirring for 1.5 h at this temperature. To the formed mixture was added via syringe pump a solution of MeOH (0.32 g, 0.4 ml, 10.0 mmol) in THF (8 ml) for 1 h and after completion of the addition the mixture was stirred for another 1 h followed by quenching with AcOH (3.0 ml, 50.0 mmol) at -20 °C, diluted with EtOAc (15 ml) and a mixture of solution of K_2CO_3 and 25% aq.NH_3 for copper extraction. Organic layer was separated and washed with a mixture of brine with 25% aq.NH_3 several times until blue coloration is disappeared. The resulting extract was dried over $MgSO_4$, evaporated to give crude **3q**. The resulting oil was dissolved in MeOH (10 ml) and treated with 4M HCl in dioxane (12.0 ml, 48.0 mmol), the progress of the reaction was monitored by TLC. After completion of the deprotection MeOH was evaporated under reduced pressure. The residue was dissolved in water (15 ml) and extracted with DCM (7 ml x 5). Water was removed under reduced pressure to give semisolid of homoallylamine hydrochloride. It was dissolved in MeOH (10 ml) with Et_3N (3.53 g, 4.9 ml, 35.0 mmol) and Boc_2O (3.27 g, 15.0 mmol) was added portionwise. Self-heating reaction was quickly developed and the Boc-protection was cleanly completed within 1 h. The solvent was evaporated to dryness and the residue was suspended in a mixture Et_2O/*n*-hexane, filtered and washed with $NaCl_{sat.}$ two times, dried over Na_2SO_4 and concentrated under redued pressure. During the concentration crystalline solid was precipitated, the resulting suspension was chilled to 0 °C, filtered and washed with chilled (-10 °C) *n*-hexane to give **(*S*)-6q** (1.84 g, 70%) as beige solid, m.p. 129-130 °C (*n*-hexane), $[\alpha]_D^{20}$ -55.9 (C 1.0, $CHCl_3$), HPLC: *ee* >99%. (Description of NMR spectra see for ***rac*-6q**).

***tert*-Butyl *N*-[(*S*)-4-Hydroxy-1-(2-hydroxyphenyl)butyl]carbamate (7)**

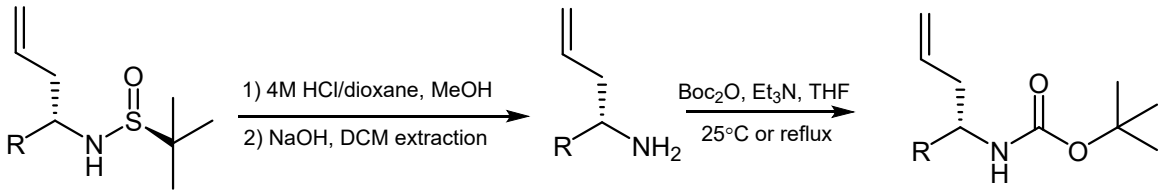


7, 96% (1.47 g)
$[\alpha]_D^{20}$ -48.9 (*C* 1, $CHCl_3$)
lit.$[\alpha]_D^{20}$ -33.6 (*C* 0.24, $CHCl_3$)
for *ee* 90%

To a solution of **(*S*)-6q** (1.45 g, 5.5 mmol) in THF (10 ml) was added solid 9-BBN (1.71 g, 14.0 mmol) at 15 °C and the suspension was stirred for 20 min until complete dissolution with evolution of hydrogen. The solution was heated at 45 °C for 1 h until no more starting material was visible on TLC (EtOAc/*n*-hexane, 1:1). The reaction mixture was cooled to -5 °C, NaOH 10% (14 g, 35.0 mmol) was added and H_2O_2 (50%) (2.86 g, 2.39 ml, 42.0 mmol) was injected by

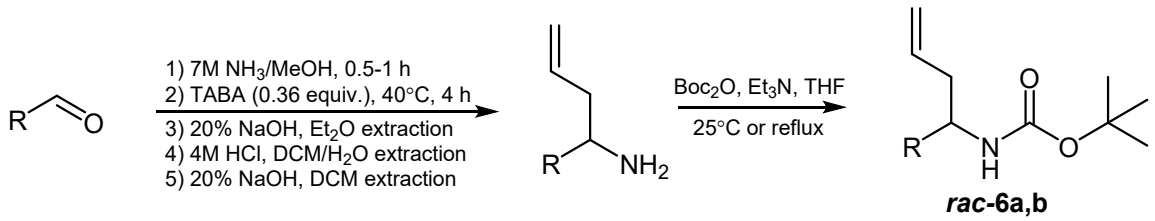
dropwise at -5-+5 °C with intense stirring. After complete addition the mixture was stirred at ambient temperature for 1.5 h. The reaction mixture was diluted with water and EtOAc. Aqueous layer was extracted with EtOAc (10 ml x 3), combined extracts were washed with $NaCl_{sat}$, dried over $MgSO_4$, filtered, evaporated and subjected to FC (EtOAc/*n*-hexane in gradient 12% to 100%) to give **7** (1.48 g, 96%) as viscous transparent mass, $[\alpha]_D^{20}$ -48.9 (C 1.0, $CHCl_3$), (lit.[39] $[\alpha]_D^{20}$ -33.6 (C 0.24, $CHCl_3$), R_f 0.27 (EtOAc/n-hexane, 1:1). ^1H NMR ($CDCl_3$, 400 MHz): δ 7.07 (t, *J* = 7.3 Hz, 2H, both *m*-CH), 6.81 (t, *J* = 8.0 Hz, 2H, *o,p*-CH), 5.57 (br. s, 3H, 2OH and NH), 4.78 (br. s, 1H, CHNH), 3.64 (t, *J* = 6.0 Hz, 2H, CH_2OH), 1.90 (dd, *J* = 14.2, 7.0 Hz, 2H, CH_2CHNH), 1.68–1.48 (m, 2H, CH_2CH_2OH), 1.42 (s, 9H, *t*Bu). ^{13}C NMR ($CDCl_3$, 101 MHz): δ 157.0 (C=O), 154.6 (C-OH), 128.5 2C (m-CH), 127.2(C), 120.1(*p*-CH), 116.9 (*o*-CH), 80.5 ($OCMe_3$), 62.3 (CH_2OH), 50.6 br. (CHNH), 31.5 (CH_2CHNH), 29.4 (CH_2CH_2OH, 28.5 3C (3Me). **NMR spectra coincides with the literature data.[39]**

General procedure for synthesis of *N*-Boc-amides for chiral HPLC analysis



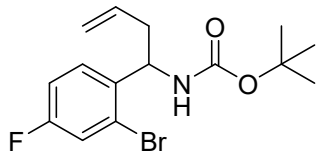
A 5 ml flask was charged with the mixture of allylated compounds (~0.15 mmol), dissolved in MeOH (0.15 ml) and stirred with 4 equiv. of 4M HCl solution in dioxane (0.15 ml, 0.6 mmol) at r.t. for 1 hour. The hydrolysis was controlled by the disappearing of allylated sulfonamide on TLC (hexane/EtOAc, 1:1), after that the solution was evaporated. The hydrochloride salt was dissolved in water (3 ml) and extracted with DCM (3x3 ml) to remove all organic impurities. The water layer was treated with 20% NaOH solution (0.15 ml, 0.9 mmol) and homoallylamine was extracted with DCM (3x3 ml). The organic layer was dried with K_2CO_3 and evaporated. The amine was dissolved in THF (0.5 ml), Boc_2O (0.038 ml, 1.1 equiv., 0.165 mmol) and Et_3N (0.021 ml, 1.0 equiv., 0.15 mmol) were added. The solution was refluxed for 30 min until the desired amine converted into Boc-amide. The progress of the reaction was monitored by TLC (hexane/EtOAc, 4:1). For the pyridinic and salicylic amines the reaction with Boc_2O was conducted at r.t. The resulting solution of *N*-Boc-amide was evaporated, purified by flash chromatography and subjected to chiral HPLC analysis. The conditions of chiral chromatography are indicated in the chromatography section.

General procedure for synthesis of racemic *N*-Boc-homoallylamides as HPLC standards (6a-w).



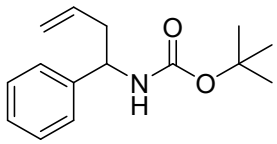
Carbonyl compound (1.0 mmol) was dissolved in 7 M NH_3 solution in MeOH (4 mmol), and the solution was stirred for 30 min, after then TABA **1b** (0.36 mmol) was added, and the resulting mixture was left for 4 h at 40 °C. The reaction was monitored by ^{1}H and ^{11}B NMR. After the imine's signals were disappeared the reaction mixture was concentrated on the Rotavapor under reduced pressure. The residue was treated with 20% NaOH and extracted with Et_2O (8 ml x 3). The combined extracts were washed with alkaline NaCl sol., dried over K_2CO_3, filtered. To the etheral extracts was added 4 M HCl in dioxane (1.0-1.5 mmol), the precipitated hydrochloride salt was collected by filtration, washed with Et_2O and dried in vacuum. Pyridinic homoallylamines were treated with oxalic acid solution in MeOH instead of HCl. Next, homoallylamine hydrochloride or oxalate salt was treated by 20% NaOH and corresponding amine was extracted by DCM (8 ml x 3), dried over K_2CO_3, and organic extracts were evaporated. The amine was dissolved in THF (5 ml), Boc_2O (0.25 ml, 1.1 equiv., 1.1 mmol) and Et_3N (0.14 ml, 1.0 mmol) were added. The solution was refluxed for 30 min until disappiarence of the homoallylamine. A progress of the reaction was monitored by TLC (hexane/EtOAc, 4:1). For the pyridinic and salicylic homoallylamines the reaction with Boc_2O was conducted at r.t. The solution of *N*-Boc-amide was evaporated again, and purified by flash chromatography.

***tert*-Butyl-(1-(2-bromo-4-fluorophenyl)but-3-en-1-yl)carbamate (*rac*-6a)**



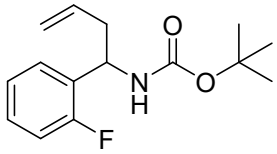
White solid, R_f 0.32 (hexane/EtOAc, 8:1). Proton NMR spectrum contains signals of two rotamers 2.5:1. First meaning is for major rotamer. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.28 (dd, 1H, J = 8.2, 2.5 Hz, Ar), 7.24 (br.s, 1H, Ar), 7.01 (td, 1H, J = 8.4, 2.4 Hz, Ar), 5.73-5.63 (m, 1H, CH=), 5.16-5.12 (m, 2H, CH_2=), 5.02 (br.s, 2H, CHAr and NH), 2.52 (br.s, 1H, C$\mathbf{H_a}$$CH_b$), 2.39 (br.s, 1H, CH_aC$\mathbf{H_b}$), 1.40 and 1.27 (both br.s, 9H, *t*Bu) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz): δ 162.6 and 160.1 (J_{CF} = 249.7 Hz), 155.0, 137.6 and 137.5 (J_{CF} = 6.2 Hz), 133.4, 128.2 and 128.1 (J_{CF} = 8.8 Hz), 122.7 and 122.6 (J_{CF} = 4.9 Hz), 120.5 and 120.3 (J_{CF} = 22.4 Hz), 119.0, 114.8 and 114.6 (J_{CF} = 21.4 Hz), 80.0, 53.0, 39.6, 28.4 (3C) ppm. UV spectrum λ, nm (ε, $cm^{-1}M^{-1}$): 268 (1026), 275 (963). Anal. Calcd. for $C_{15}H_{19}BrFNO_2$ (344.22): C, 52.34; H, 5.56; N, 4.07; found: C, 52.22; H, 5.67; N, 4.00.

***tert*-Butyl-(1-phenylbut-3-en-1-yl)carbamate (*rac*-6b)**



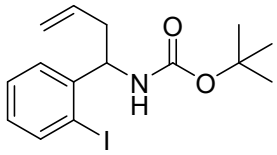
White solid, R_f 0.39 (hexane/EtOAc, 8:1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.34-7.31 (m, 2H, Ar), 7.27-7.24 (m, 3H, Ar), 5.73-5.63 (m, 1H, CH=), 5.13-5.06 (m, 2H, CH_2=), 4.86 (br.s., 1H, NH), 4.73 (br.s., 1H, CHAr), 2.52 (s, 2H, CH_aH_b), 1.41 (s, 9H, *t*Bu) ppm. UV spectrum λ, nm (ε, $cm^{-1}M^{-1}$): 258 (218). **NMR spectrum coincides with the literature data[40].**

***tert*-Butyl-(1-(2-fluorophenyl)but-3-en-1-yl)carbamate (*rac*-6c)**



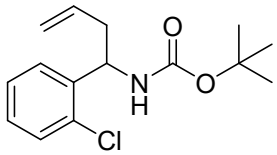
White solid, R_f 0.40 (hexane/EtOAc, 8:1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.24-7.19 (m, 2H, Ar), 7.08 (t, 1H, *J* = 7.5 Hz, Ar), 7.04-6.99 (m, 1H, Ar), 5.72-5.61 (m, 1H, CH=), 5.11-5.04 (m, 2H, CH_2=), 4.95 (br.d, 2H, *J* = 5.4 Hz, CHAr and NH), 2.52 (br.s, 2H, CH_aH_b), 1.41 (s, 9H, *t*Bu) ppm. UV spectrum λ, nm (ε, $cm^{-1}M^{-1}$): 262 (545). **NMR spectrum coincides with the literature data[41].**

***tert*-Butyl-(1-(2-iodophenyl)but-3-en-1-yl)carbamate (*rac*-6d)**



White solid, R_f 0.30 (hexane/EtOAc, 8:1). Proton NMR spectrum contains signals of two rotamers 1.5:1. First meaning is for major rotamer. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.81 (d, 1H, *J* = 7.8 Hz, Ar), 7.31 (t, 1H, *J* = 7.6 Hz, Ar), 7.23 (br.s, 1H, Ar), 6.93 (t, 1H, *J* = 7.6 Hz, Ar), 5.77-5.67 (m, 1H, CH=), 5.18-5.12 (m, 2H, CH_2=), 5.04 (br.d, 1H, *J* = 5.6 Hz, CHAr), 4.93 and 4.81 (both br.s, 1H, NH), 2.53-2.36 (m, 2H, CH_aH_b), 1.41 and 1.25 (s, 9H, *t*Bu) ppm. ^{13}C NMR spectrum contains signals of rotamers. ^{13}C NMR ($CDCl_3$, 101 MHz): 155.0, (145.4 and 144.5), (140.0 and 139.7), 133.6, 128.9, 128.4, 126.6, 118.8, 98.6, 79.8, (59.2 and 57.8), 39.9, 28.4 (3C). UV spectrum λ, nm (ε, $cm^{-1}M^{-1}$): 225 (749). Anal. Calcd. for $C_{15}H_{20}INO_2$ (373.23): C, 48.27; H, 5.40; N, 3.75; found: C, 48.20; H, 5.45; N, 3.73.

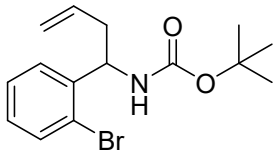
***tert*-Butyl-(1-(2-chlorophenyl)but-3-en-1-yl)carbamate (*rac*-6e)**



White solid, R_f 0.34 (hexane/EtOAc, 8:1). Proton NMR spectrum contains signals of two rotamers 2.5:1. First meaning is for major rotamer. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.38-7.18 (m,

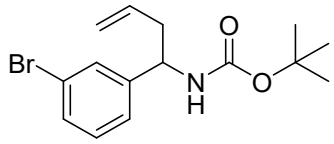
4H, Ar), 5.79-5.65 (m, 1H, CH=), 5.19-5.13 (m, 4H, CH_2= and CHAr and NH), 2.54 (br.d, 2H, *J* = 29.2 Hz, CH_aH_b), 1.45 and 1.29 (both s, 9H, *t*Bu) ppm. UV spectrum λ, nm (ε, $cm^{-1}M^{-1}$): 265 (310). **NMR spectrum coincides with the literature data[42].**

***tert*-Butyl-(1-(2-bromophenyl)but-3-en-1-yl)carbamate (*rac*-6f)**



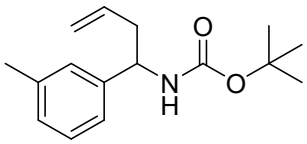
White solid, R_f 0.40 (hexane/EtOAc, 4:1). Proton NMR spectrum contains signals of two rotamers 3:1. First meaning is for major rotamer. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.54 (d, 1H, *J* = 7.3 Hz, Ar), 7.27 (m, 2H, Ar), 7.11 (m, 1H, Ar), 5.77-5.67 (m, 1H, CH=), 5.18-5.13 (m, 2H, CH_2=), 5.05 (br.s, 2H, CHAr and NH), 2.57 (br.s, 1H, C**H$_a$**H$_b$), 2.44 (br.s, 1H, CH$_a$**H$_b$**), 1.42 and 1.27 (both br.s, 9H, *t*Bu) ppm. UV spectrum λ, nm (ε, $cm^{-1}M^{-1}$): 264 (152). **NMR spectrum coincides with the literature data[43].**

***tert*-Butyl-(1-(3-bromophenyl)but-3-en-1-yl)carbamate (*rac*-6g)**



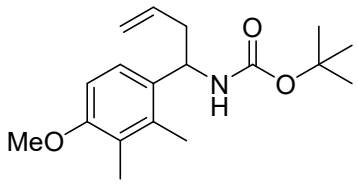
Colorless oil, R_f 0.39 (hexane/EtOAc, 8:1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.40 (s, 1H, Ar), 7.38-7.36 (m, 1H, Ar), 7.19 (d, 2H, *J* = 4.8 Hz, Ar), 5.64 (ddt, 1H, *J* = 17.2, 10.2, 7.1 Hz, CH=), 5.15-5.10 (m, 2H, CH_2=), 4.87 (br.s, 1H, CH), 4.70 (br.s, 1H, NH), 2.50-2.47 (m, 2H, CH_aH_b), 1.42 (s, 9H, *t*Bu) ppm. UV spectrum λ, nm (ε, $cm^{-1}M^{-1}$): 267 (277). **NMR spectrum coincides with the literature data[44].**

***tert*-Butyl-(1-(m-tolyl)but-3-en-1-yl)carbamate (*rac*-6h)**



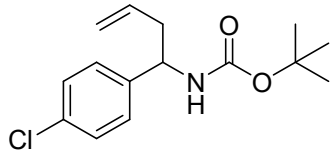
White solid, R_f 0.46 (hexane/EtOAc, 8:1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.21 (t, 1H, *J* = 7.6 Hz, Ar), 7.20-7.07 (m, 3H, Ar), 5.68 (ddt, 1H, *J* = 14.3, 9.6, 6.9 Hz, CH=), 5.13-5.06 (m, 2H, CH_2=), 4.86 (br.s, 1H, CHAr), 4.70 (br.s, 1H, NH), 2.51 (br.s, 2H, CH_aH_b), 2.34 (s, 3H, m-Me), 1.42 (s, 9H, *t*Bu) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz): 155.3, 142.5, 138.2, 134.3, 128.5, 128.0, 127.2, 123.3, 118.2, 79.6, 54.2, 41.4, 28.5 (3C), 21.6 ppm. UV spectrum λ, nm (ε, $cm^{-1}M^{-1}$): 264 (246). Anal. Calcd. for $C_{16}H_{23}NO_2$ (261.37): C, 73.53; H, 8.87; N, 5.36; found: C, 73.41; H, 8.90; N, 5.34.

***tert*-Butyl-(1-(4-methoxy-2,3-dimethylphenyl)but-3-en-1-yl)carbamate (*rac*-6i)**



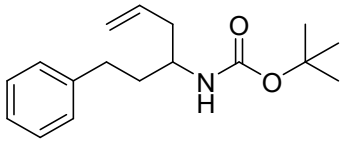
White solid, R_f 0.27 (hexane/EtOAc, 8:1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.04 (d, 1H, *J* = 8.6 Hz, Ar), 6.70 (d, 1H, *J* = 8.5 Hz, Ar), 5.76-5.66 (m, 1H, CH=), 5.14-5.05 (m, 2H, CH_2=), 4.97 (br.s., 1H, NH), 4.78 (br.s, 1H, CHAr), 3.80 (s, 3H, OMe), 2.47 (br.s., 2H, CH_aH_b), 2.26 (s, 3H, Me), 2.16 (s, 3H, Me), 1.41 (s, 9H, *t*Bu) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz): 156.6, 155.2, 135.6, 134.7, 132.6, 125.7, 123.0, 117.9, 107.7, 79.4, 55.6, 50.5, 40.6, 28.5 (3C), 15.2, 12.2. UV spectrum λ, nm (ε, $cm^{-1}M^{-1}$): 274 (1220). Anal. Calcd. for $C_{18}H_{27}NO_3$ (305.42): C, 70.79; H, 8.91; N, 4.59; found: C, 70.65; H, 8.99; N, 4.51.

***tert*-Butyl-(1-(4-chlorophenyl)but-3-en-1-yl)carbamate (*rac*-6j)**



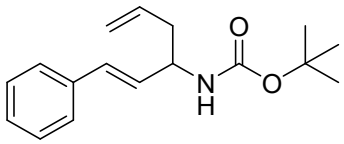
White solid, R_f 0.41 (hexane/EtOAc, 8:1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.29 (d, 2H, *J* = 8.1 Hz, Ar), 7.19 (d, 2H, *J* = 8.3 Hz, Ar), 5.69-5.59 (m, 1H, CH=), 5.13-5.08 (m, 2H, CH_2=), 4.85 (br.s, 1H, CHAr), 4.69 (br.s, 1H, NH), 2.47 (s, 2H, CH_aH_b), 1.40 (s, 9H, *t*Bu) ppm. UV spectrum λ, nm (ε, $cm^{-1}M^{-1}$): 221 (2409), 267 (84). **NMR spectrum coincides with the literature data[45].**

***tert*-Butyl-(1-phenylhex-5-en-3-yl)carbamate (*rac*-6k)**



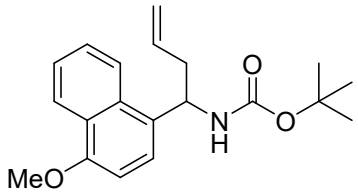
White solid, R_f 0.38 (hexane/EtOAc, 8:1). Proton NMR spectrum contains signals of two rotamers 11:1. First meaning is for major rotamer. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.30-7.28 (m, 2H, Ar), 7.19-7.17 (m, 2H, Ar), 5.77 (m, 1H, CH=), 5.10-5.06 (m, 2H, CH_2=), 4.39 (d, 1H, *J* = 7.9 Hz, CH) and 4.17 (br.s, 1H, CH), 3.72 and 3.55 (both br.s, 1H, NH), 2.74-2.59 (m, 2H, PhC$\mathbf{H_2}$$CH_2$), 2.32-2.18 (m, 2H, $PhCH_2C\mathbf{H_2}$), 1.85-1.76 (m, 1H, C$\mathbf{H_a}H_b$), 1.71-1.61 (m, 1H, $CH_a\mathbf{H_b}$), 1.45 (s, 9H, *t*Bu) ppm. UV spectrum λ, nm (ε, $cm^{-1}M^{-1}$): 261 (228). **NMR spectrum coincides with the literature data[42].**

***tert*-Butyl-(E)-(1-phenylhexa-1,5-dien-3-yl)carbamate (*rac*-6l)**



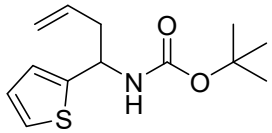
Light-beige solid, R_f 0.39 (hexane/EtOAc, 8:1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.37-7.21 (m, 5H, Ar), 6.51 (d, 1H, *J* = 15.9 Hz, ArC**H**=CH), 6.13 (dd, 1H, *J* = 15.9, 5.9 Hz, Ar-CH=C**H**), 5.85-5.75 (m, 1H, CH=), 5.17-5.11 (m, 2H, CH_2=), 4.60 (br.s., 1H, NH), 4.38 (br.s., 1H, CH-N), 2.39 (br.s., 2H, CH_aH_b), 1.46 (s, 9H, *t*Bu) ppm. UV spectrum λ, nm (ε, $cm^{-1}M^{-1}$): 252 (18960). **NMR spectrum coincides with the literature data[42].**

***tert*-Butyl-(1-(4-methoxynaphthalen-1-yl)but-3-en-1-yl)carbamate (*rac*-6m)**



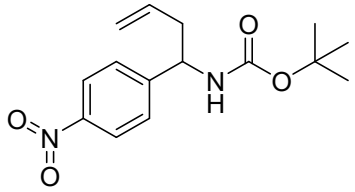
White solid, R_f 0.25 (hexane/EtOAc, 8:1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.31 (d, 1H, *J* = 8.2 Hz, Ar), 8.07 (br.d, 1H, *J* = 7.6 Hz, Ar), 7.50 (t, 1H, *J* = 7.0 Hz, Ar), 7.48 (t, 1H, *J* = 7.8 Hz, Ar), 7.33 (d, 1H, *J* = 8.0 Hz, Ar), 6.77 (d, 1H, *J* = 7.8 Hz, Ar), 5.81-5.71 (m, 1H, CH=), 5.48 (br.s, 1H, CHAr), 5.18-5.07 (m, 2H, CH_2=), 4.89 (br.s, 1H, NH), 3.99 (s, 3H, OMe), 2.70 (br.d, 2H, *J* = 17.1 Hz, CH_aH_b), 1.43 (s, 9H, *t*Bu) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz): δ 155.3, 155.1, 134.6, 132.0, 131.5, 129.7, 126.9, 126.1, 125.1, 123.0, 122.8, 117.9, 103.0, 79.5, 55.6, 49.8, 40.3, 28.5 (3C) ppm. UV spectrum λ, nm (ε, $cm^{-1}M^{-1}$): 212 (28950), 236 (22120), 298 (5420). Anal. Calcd. for $C_{20}H_{25}NO_3$ (327.42): C, 73.37; H, 7.70; N, 4.28; found: C, 73.20; H, 7.83; N, 4.22.

***tert*-Butyl-(1-(thiophen-2-yl)but-3-en-1-yl)carbamate (*rac*-6n)**



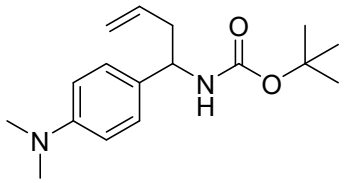
White solid, R_f 0.43 (hexane/EtOAc, 8:1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.19 (s, 1H, CH_{thioph}), 6.94 (s, 2H, CH_{thioph}), 5.82-5.69 (m, 1H, CH=), 5.18-5.09 (m, 2H, CH_2=), 5.03 (br.s, 1H, CHAr), 4.84 (br.s, 1H, NH), 2.61 (br.s, 2H, CH_aH_b), 1.44 (s, 9H, *t*Bu) ppm. UV spectrum λ, nm (ε, $cm^{-1}M^{-1}$): 234 (7350). **NMR spectrum coincides with the literature data[44].**

***tert*-Butyl-(1-(4-nitrophenyl)but-3-en-1-yl)carbamate (*rac*-6o)**



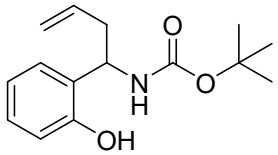
Light yellow solid, R_f 0.16 (hexane/EtOAc, 8:1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.19 (d, 2H, *J* = 8.0 Hz, Ar), 7.43 (d, 2H, *J* = 8.1 Hz, Ar), 5.68-5.58 (m, 1H, CH=), 5.16-5.12 (m, 2H, CH_2=), 4.97 (br.s., 1H, NH), 4.79 (br.s., 1H, CHAr), 2.49 (br.s., 2H, CH_aH_b), 1.40 (s, 9H, *t*Bu) ppm. UV spectrum λ, nm (ε, $cm^{-1}M^{-1}$): 274 (3510). **NMR spectrum coincides with the literature data[39].**

tert-Butyl-(1-(4-(dimethylamino)phenyl)but-3-en-1-yl)carbamate (*rac*-6p)



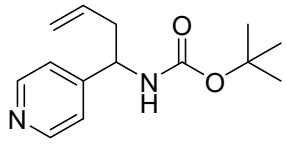
White solid, m.p. 113-114 °C (hexane), R_f 0.36 (hexane/EtOAc, 4:1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.14 (d, 2H, *J* = 8.3 Hz, Ar), 6.71 (d, 2H, *J* = 8.4 Hz, Ar), 5.70 (ddt, *J* = 14.1, 10.1, 7.0 Hz, CH=), 5.11-5.03 (m, 2H, CH_2=), 4.81 (br.s, 1H, CHAr), 4.65 (br.s, 1H, NH), 2.93 (s, 6H, NMe_2), 2.52 (br.s, 2H, CH_aH_b), 1.42 (s, 9H, *t*Bu) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz): 155.3, 149.8, 134.7, 130.3, 127.3 (2C), 117.7, 112.8 (2C), 79.3, 53.7, 41.2, 40.8, 28.5 (3C) ppm. UV spectrum λ, nm (ε, $cm^{-1}M^{-1}$): 200 (25500), 259 (19750), 303 (2230). Anal. Calcd. for $C_{17}H_{26}N_2O_2$ (290.41): C, 70.31; H, 9.02; N, 9.65; found: C, 70.22; H, 9.07; N, 9.55.

tert-Butyl-(1-(2-hydroxyphenyl)but-3-en-1-yl)carbamate (*rac*-6q)



Reaction of amine with Boc_2O was carried out at r.t. The substance was purified by PTLC (hexane/EtOAc, 4:1) giving white solid. R_f 0.16 (hexane/EtOAc, 8:1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.53 (br.s, 1H, OH), 7.11-7.07 (m, 2H, Ar), 6.85-6.81 (m, 2H, Ar), 5.73 (ddt, 1H, *J* = 13.9, 10.1, 6.9 Hz, CH=), 5.40-5.06 (m, 3H, CH_2= and CHAr), 4.89 (br.s, 1H, NH), 2.62-2.59 (m, 2H, CH_aH_b), 1.46 (s, 9H, *t*Bu) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz): δ 157.2, 154.8, 134.7, 128.7, 128.0, 126.6, 120.0, 117.9, 117.1, 80.8, 49.0, 38.7, 28.5 (3C) ppm. UV spectrum λ, nm (ε, $cm^{-1}M^{-1}$): 273 (3180), 331 (260). **NMR spectra coincide with the literature data[46].**

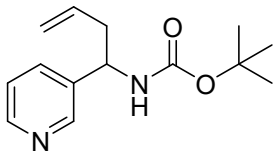
tert-Butyl-(1-(pyridin-4-yl)but-3-en-1-yl)carbamate (*rac*-6r)



Reaction of amine with Boc_2O was carried out at r.t. After protection of amine group, the reaction mixture was dissolved in hexane/EtOAc = 1:1, extracted with saturated K_2CO_3 solution, dried with K_2CO_3 and evaporated. The residue was purified by flash chromatography that gave brown oil, R_f 0.31 (hexane/EtOAc, 1:1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.54 (br.s, 2H, Ar), 7.21 (d, 2H, *J* = 4.6 Hz, Ar), 5.66-5.56 (m, 1H, CH=), 5.17 (d, 1H, *J* = 6.8 Hz, NH), 5.12-5.08 (m, 2H, CH_2=), 4.71 (br.s, 1H, CH), 2.46 (br.s, 2H, CH_aH_b), 1.39 (s, 9H, *t*Bu) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz): 155.2, 152.5, 149.3 (2C), 132.8, 121.6 (2C), 119.3, 80.1, 53.3, 40.5, 28.4

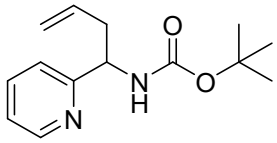
(3C) ppm. UV spectrum λ, nm (ε, $cm^{-1}M^{-1}$): 255 (1710). Anal. Calcd. for $C_{14}H_{20}N_2O_2$ (248.33): C, 67.72; H, 8.12; N, 11.28; found: C, 67.55; H, 8.34; N, 11.20.

tert-Butyl-(1-(pyridin-3-yl)but-3-en-1-yl)carbamate (_rac_-6s)



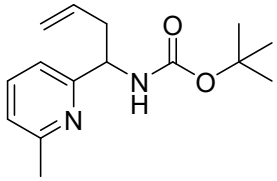
Reaction of amine with Boc_2O was carried out at r.t. After protection of amine group, the reaction mixture was dissolved in hexane/EtOAc = 1:1, washed with saturated K_2CO_3 solution, organic extracts were dried with K_2CO_3 and evaporated. The residue was purified by flash chromatography that gave beige solid, R_f 0.44 (hexane/EtOAc, 1:1). ^1H NMR ($CDCl_3$, 400 MHz): δ 8.49 (d, 2H, *J* = 29.8 Hz, Ar), 7.58 (d, 1H, *J* = 7.8 Hz, Ar), 7.24-7.21 (m, 1H, Ar), 5.66-5.56 (m, 1H, CH=), 5.34 (br.s., 1H, CHAr), 5.07-5.03 (m, 2H, CH_2=), 4.71 (br.s., 1H, NH), 2.46 (br.s, 2H, CH_aH_b), 1.34 (s, 9H, *t*Bu) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz): 155.2, 147.8, 147.6, 138.5, 134.7, 133.1, 123.6, 119.0, 79.8, 52.1, 40.8, 28.3 (3C) ppm. UV spectrum λ, nm (ε, $cm^{-1}M^{-1}$): 261 (2220). Anal. Calcd. for $C_{14}H_{20}N_2O_2$ (248.33): C, 67.72; H, 8.12; N, 11.28; found: C, 67.69; H, 8.15; N, 11.20.

tert-Butyl-(1-(pyridin-2-yl)but-3-en-1-yl)carbamate (_rac_-6t)



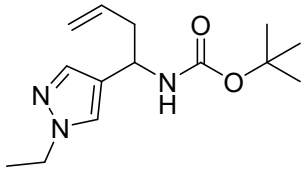
Reaction of amine with Boc_2O was carried out at r.t. White solid, R_f 0.22 (hexane/EtOAc, 4:1). Proton NMR spectrum contained signals of two rotamers 6:1. First meaning is for major rotamer. ^1H NMR ($CDCl_3$, 400 MHz): δ 8.48 (d, 1H, *J* = 4.7 Hz, Ar), 7.56 (td, 1H, *J* = 7.6, 1.2 Hz, Ar), 7.15 (d, 1H, *J* = 7.8 Hz, Ar), 7.11-7.08 (m, 1H, Ar), 5.73 (br.d, 1H, *J* = 6.8 Hz, NH) and 5.33 (br.s, 1H, NH), 5.66-5.55 (m, 1H, CH=), 4.98-4.77 (m, 2H, CH_2=), 4.76 (q, 1H, *J* = 6.9 Hz, CH) and 4.62 (br.s, 1H, CH), 2.53 (t, 2H, *J* = 6.6 Hz, CH_aH_b), 1.36 and 1.31 (both s, 9H, *t*Bu) ppm. ^{13}C NMR spectrum contains signals of rotamers. ^{13}C NMR ($CDCl_3$, 101 MHz): δ 160.1, 155.4, 149.13 and 149.09, 136.5 and 136.4, 133.8, 122.20, 121.9, 118.2 and 118.0 and 117.8, 79.2, 55.0 and 54.9, 40.9 and 40.8 and 40.7, 28.4 (3C) ppm. UV spectrum λ, nm (ε, $cm^{-1}M^{-1}$): 260 (2970). **NMR spectra coincide with the literature data[47].**

tert-Butyl-(1-(3-methylpyridin-2-yl)but-3-en-1-yl)carbamate (_rac_-6u)



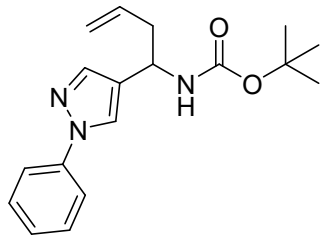
Reaction of amine with Boc_2O was carried out at r.t. White solid, R_f 0.44 (hexane/EtOAc, 4:1). Proton NMR spectrum contained signals of two rotamers 5:1. First meaning is for major rotamer. ^1H NMR ($CDCl_3$, 400 MHz): δ 7.50 (t, 1H, *J* = 7.7 Hz, Ar), 6.99 (t, 2H, *J* = 8.0 Hz, Ar), 5.77 and 5.34 (both br.s, 1H, NH), 5.65 (ddt, 1H, *J* = 17.3, 10.2, 7.1 Hz, CH=), 5.03-4.99 (m, 2H, CH_2=), 4.75 (q, 1H, *J* = 7.1 Hz, CH) and 4.63 (br.s, 1H, CH), 2.57 (t, 2H, *J* = 6.8 Hz, CH_aH_b), 2.53 (s, 3H, Me), 1.43 and 1.37 (both br.s, 9H, *t*Bu) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz): 159.19, 157.96, 155.45, 136.86, 134.16, 121.92, 118.84, 117.95, 79.29, 54.98, 41.09, 28.51 (3C), 24.40 ppm. UV spectrum λ, nm (ε, $cm^{-1}M^{-1}$): 264 (4000). Anal. Calcd. for $C_{15}H_{22}N_2O_2$ (262.35): C, 68.67; H, 8.45; N, 10.68; found: C, 68.60; H, 8.53; N, 10.62.

tert-Butyl-(1-(1-ethyl-1H-pyrazol-4-yl)but-3-en-1-yl)carbamate (*rac*-6v)



Pale yellow oil, R_f 0.23 (hexane/EtOAc, 2:1). ^1H NMR ($CDCl_3$, 400 MHz): δ 7.40 (s, 1H, Ar), 7.30 (s, 1H, Ar), 5.78-5.68 (m, 1H, CH=), 5.12-5.06 (m, 2H, CH_2=), 4.74 (br.s., 2H, CH and NH), 4.12 (q, 2H, *J* = 7.3 Hz, C**H$_2$**-CH_3), 2.50 (br.s., 2H, CH_aH_b), 1.45 (t, 3H, *J* = 7.3 Hz, CH_2-C**H$_3$**), 1.41 (s, 9H, *t*Bu) ppm. UV spectrum λ, nm (ε, $cm^{-1}M^{-1}$): 340 (86). **NMR spectrum coincides with the literature data[5].**

tert-Butyl-(1-(1-phenyl-1H-pyrazol-4-yl)but-3-en-1-yl)carbamate (*rac*-6w)



White solid, R_f 0.28 (hexane/EtOAc, 4:1). ^1H NMR ($CDCl_3$, 400 MHz): δ 7.83 (s, 1H, CH_{pyr}), 7.66 (s, 1H, CH_{pyr}), 7.63 (s, 2H, Ph), 7.43 (t, 2H, *J* = 7.8 Hz, Ph), 7.27 (t, 1H, *J* = 7.4 Hz, Ph), 5.79 (ddt, 1H, *J* = 17.1, 10.1, 7.0 Hz, CH=), 5.18-5.11 (m, 2H, CH_2=), 4.82 (br.s, 2H, CHN and NH), 2.64-2.52 (m, 2H, CH_aH_b), 1.45 (s, 9H, *t*Bu) ppm. UV spectrum λ, nm (ε, $cm^{-1}M^{-1}$): 261 (10890). **NMR spectrum coincides with the literature data[5].**

Quantum-Chemical Calculations

To account for nucleophilicity of the amine after dissociation, we have computed reaction energies (total and Gibbs free ones) for the following reaction for complexes **1a-f**:

$All_3B{\leftarrow}NR_3 + iPrOH \rightarrow All_3B + iPrOH{\ldots}NR_3$

$All_2B(OiPr){\leftarrow}NH_2Me + iPrOH \rightarrow All_2B(OiPr) + iPrOH{\ldots}NH_2Me$

Starting geometries were constructed by hand starting from the lowest-energy conformer of All_3B (Figure S1).

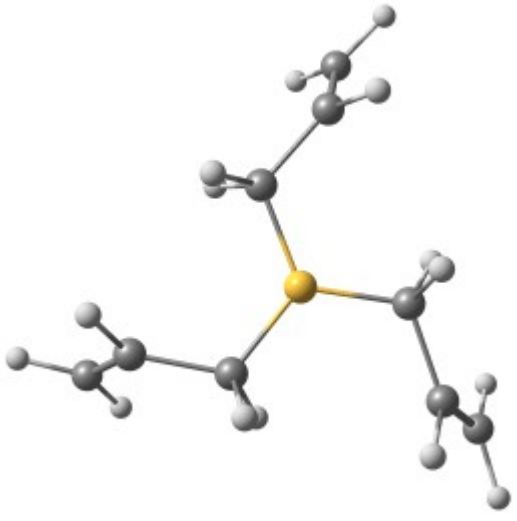


Figure S1. Lowest-energy conformer of All_3B.

The constructed structures were optimized at PBE0[48]-D4[49]/def2SVP[50]/CPCM[51](*i*PrOH) level of theory in Orca[52] 5.0.4 program package. Harmonic frequencies were computed for all structures to ensure that they correspond to local minima and estimate their Gibbs free energies at 298 °K using quasiharmonic correction[53]. The considered molecules and their energies are provided in Table S3; their geometries are available in StatPoints.xyz file in **SI**.

Table S4. Total and Gibbs free energies of all the computed molecules.

Molecule	**Total energy, Ha**	**Quasi-harmonic Gibbs free energy, Ha**
All_3B	-376.059	-375.883
$All_2B(OiPr)$	-452.434	-452.229
*i*PrOH_NH_3	-250.463	-250.350
*i*PrOH_$NHMe_2$	-328.921	-328.754
*i*PrOH_NH_2Me	-289.690	-289.549
*i*PrOH_DABCO	-538.721	-538.465
All_3B*NH_3	-432.557	-432.339
$All_3B*NHMe_2$	-511.012	-510.739
All_3B*NH_2Me	-471.785	-471.540
$All_2B(OiPr)*NH_2Me$	-548.143	-547.872
All_3B*DABCO	-720.807	-720.446
*i*PrOH	-193.997	-193.917

X-ray crystallography general view

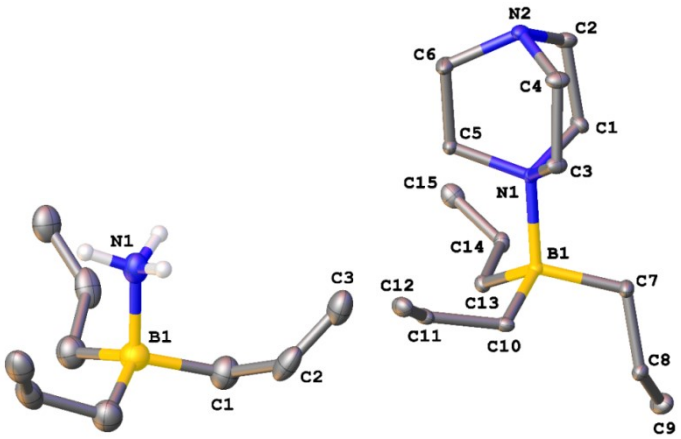


Figure S2. General view of **1b** (left) and **1d** (right). Hydrogen atoms except those of the NH_3 groups in **1b** are omitted, other atoms are shown as thermal ellipsoids at 20% probability level. Hydrogen atoms except those of the NH_3 groups in **1b** are omitted. Minor components of the disordered allyl groups in **1d** are not shown.

Table S5. Selected bond length in triallylborane of ammonia **1b** and DABCO **1d** adducts

Compound	B-N, Å	B-C^{sp3}_{allyl}, Å	C^{sp3}_{allyl}-C^{sp2}, Å	C^{sp2}_{allyl}-C^{sp2}_{allyl}, Å
TABA **1b**	1.638(15)	1.636(8)	1.521(10)	1.308(10)
TABDABCO **1d**	1.691(3)	1.627(3)	1.495(3)	1.310(3)

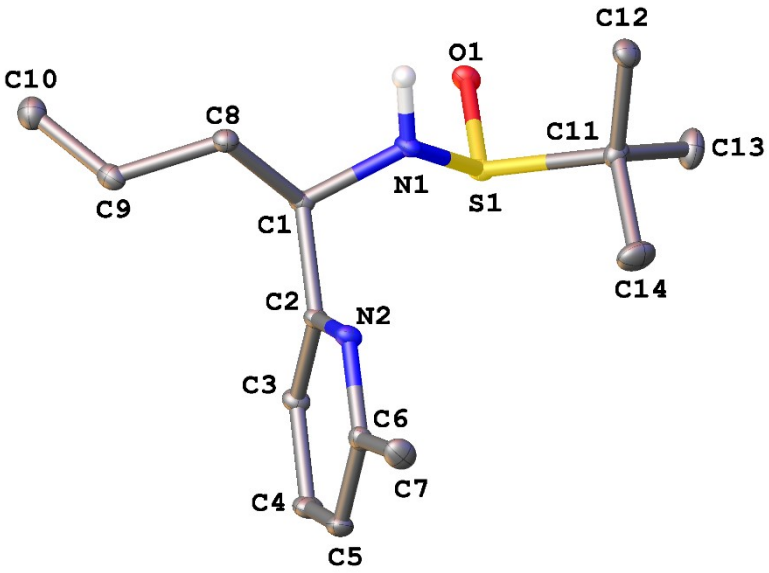


Figure S3. General view of minor isomer **3u**. Hydrogen atoms except those of the NH group are omitted, other atoms are shown as thermal ellipsoids at 30% probability level. Selected bond lengths (Å): N1-C11.488(2), C1-C21.519(3), C1-C81.532(3), C8-C91.496(3), C9-C101.316(3), N1-S11.6657(16), S1-O1 1.5004(13), S1-C111.844(2).

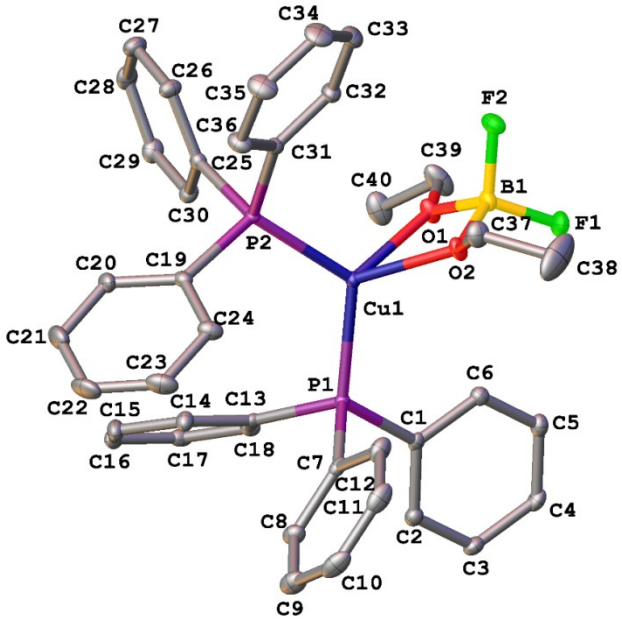


Figure S4. General view of **[Cu-2]**. Hydrogen atoms are omitted, other atoms are shown as thermal ellipsoids at 30% probability level. Selected bond lengths (Å): Cu(1)-O(1) 2.1108(16), Cu(1)-O(2) 2.1735(17), Cu(1)-P(1) 2.2279(7), Cu(1)-P(2) 2.2336(7).

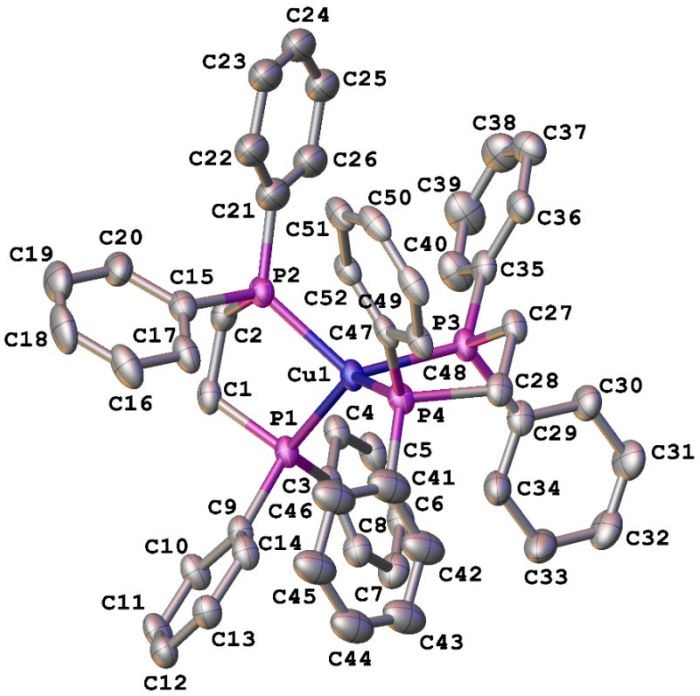


Figure S5. General view of **[Cu-5]**. Tetrafluoroborate anions and hydrogen atoms are omitted, other atoms are shown as thermal ellipsoids at 30% probability level. Selected bond lengths (Å): Cu(1)-P(1) 2.2914(17), Cu(1)-P(2) 2.2585(2), Cu(1)-P(3) 2.2869(18), Cu(1)-P(4) 2.2855(19).

X-Ray crystallography experimental section

X-ray diffraction data for **1b** were collected at 100 K on the 'Belok/RSA' beamline (λ = 0.96990 Å) of the Kurchatov Synchrotron Radiation Source using a Rayonix SX165 detector. In total, 720 frames were collected with an oscillation range of 1.0° in the φ-scanning mode using two different orientations for the crystal. The semi-empirical correction for absorption was applied using the *Scala* program[54].The data were indexed and integrated using the utility *iMOSFLM* from the CCP4 software suite. The data for **[Cu-2]** and **[Cu-5]** were collected at 100 K on a four-circle Rigaku Synergy S diffractometer equipped with a HyPix6000HE area-detector (Cu$K\alpha$-radiation, graphite monochromator, shutterless φ- and ω-scanning mode) and integrated and corrected for absorption by the *CrysAlisPro* program[55]. The data for **1d** and **3u** were collected at 100 K with a Bruker Quest D8 CMOS diffractometer using graphite monochromated Mo-Kα radiation (lλ = 0.71073 Å, ω-scans). All structures were solved using intrinsic phasing with the ShelXT[56] structure solution program and refined by a full-matrix least-squares technique on F^2

with anisotropic displacement parameters for all non-hydrogen atoms. In the case of **[Cu-5]**, all attempts to model and refine positions of solvate molecules were unsuccessful; therefore, their contribution to the total scattering was removed by using *SQUEEZE* option in PLATON15[57]. The hydrogen atoms of the NH_3-group in **1b** were located in the difference-Fourier maps and included in the refinement with fixed positional and isotropic displacement parameters [U_{iso}(H) = 1.5U_{eq}(N)]. The other hydrogen atoms were placed in calculated positions and refined within riding model with fixed isotropic displacement parameters [U_{iso}(H) = 1.2U_{eq}(C) for the other groups]. Crystal data and structure refinement parameters are given in **Tables S6**. Calculations for **1b**, **1d** and **3u** were carried out using the Olex2 program[58], those for **[Cu-2]** and **[Cu-5]**, using the SHELXTL program[54]. Crystallographic data have been deposited with the Cambridge Crystallographic Data Center, **CCDC 2288950** (**1b**), **CCDC 2288951** (**1d**), **CCDC 2288952** (**3u**), **CCDC 2298366** (**[Cu-2]**), and **CCDC 2298367** (**[Cu-5]**). Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk or www.ccdc.cam.ac.uk).

Table S6. Crystal data and structure refinement parameters for **1b**, **1d**, **3u**, **[Cu-2]**, **[Cu-5]**.

	1b	**1d**	**3u**	**[Cu-2]**	**[Cu-5]**
Empirical formula	$C_9H_{18}BN$	$C_{15}H_{27}BN_2$	$C_{14}H_{22}N_2OS$	$C_{40}H_{40}BCuF_2O_2P_2$	$C_{52}H_{48}BCuF_4P_4$
Formula weight	151.05	246.19	266.39	727.02	947.14
T, °K	100	100	100	100	100
Crystal system	Trigonal	Orthorhombic	Monoclinic	Orthorhombic	Monoclinic
Space group	R3	$P2_12_12_1$	$P2_1$	*P*ca2_1	*P*2_1/n
Z	3	4	2	4	4
a, Å	10.5689(15)	8.6952(2)	10.7916(4)	22.02359(16)	14.0344(3)
b, Å	10.5689(15)	10.1193(2)	6.2242(2)	9.06591(6)	18.8088(3)
c, Å	8.3975(17)	17.1397(4)	11.7768(4)	18.14329(10)	18.9839(4)
α, °	90	90	90	90	90
β, °	90	90	108.897(2)	90	90.5447(19)
γ, °	120	90	90	90	90
V, Å^3	812.3(3)	1508.11(6)	748.40(5)	3622.56(4)	5010.96(17)

D_{calc} (g cm^{-1})	0.926	1.084	1.182	1.333	1.255
Linear absorption, μ (cm^{-1})	1.11	0.62	2.08	2.043	2.214
F(000)	252	544	288	1512	1960
$2\theta_{max}$, °	70	58	58	79.884	79.673
Reflections measured	2089	20204	9895	30742	47124
Independent reflections	596	4000	3943	5494	10502
Observed reflections [$I > 2\sigma(I)$]	416	3582	3721	5437	7727
Parameters	35	180	167	435	475
R1	0.0750	0.0485	0.0316	0.0275	0.1164
wR2	0.1792	0.1240	0.0767	0.0741	0.2470
GOF	0.941	1.045	1.039	1.032	1.031
$\Delta\rho_{max}$/ $\Delta\rho_{min}$ (e Å^{-3})	0.151/-0.291	0.208/-0.183	0.288/-0.195	0.300/-0.424	1.746/-0.817

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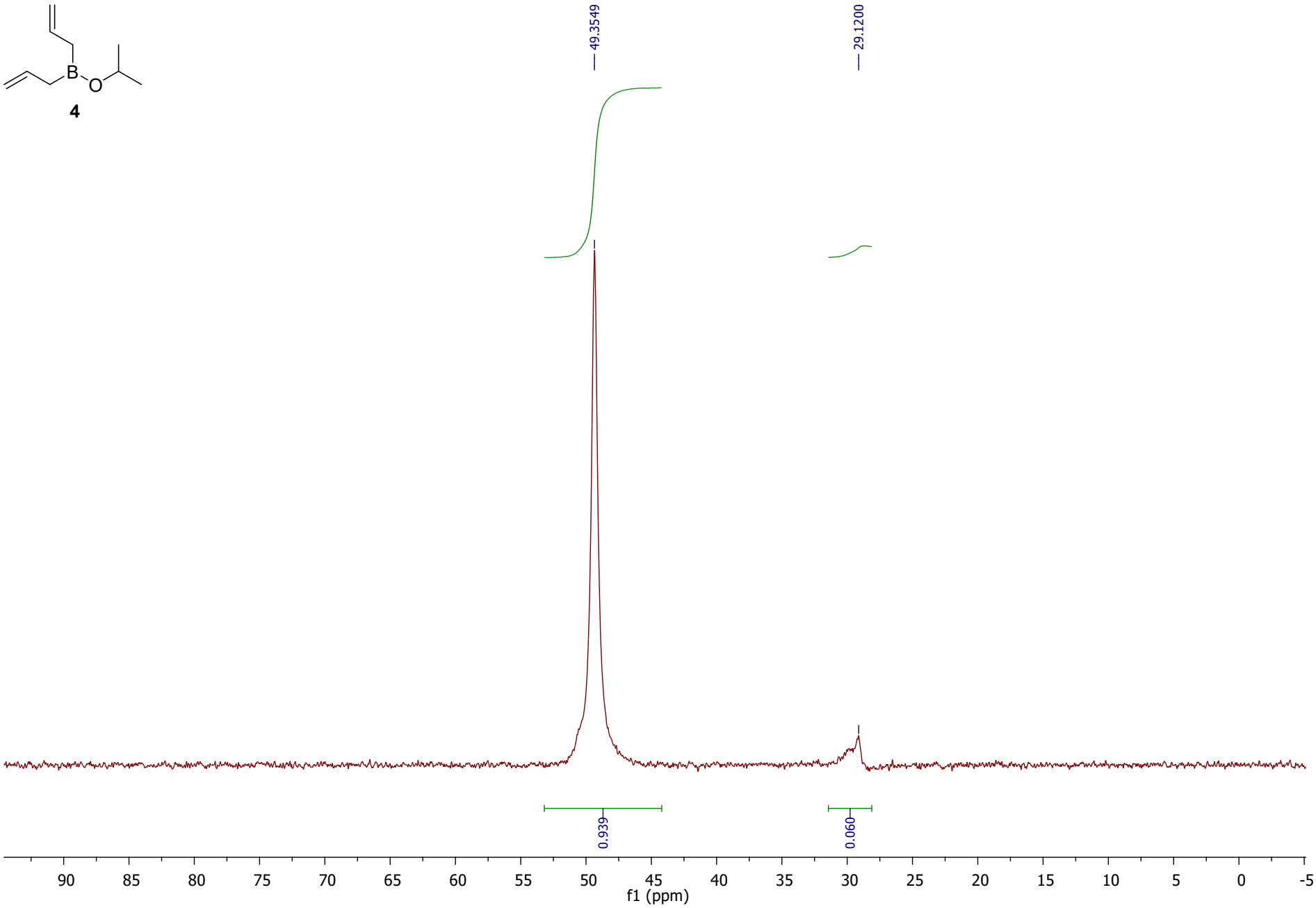
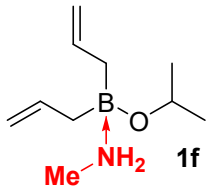
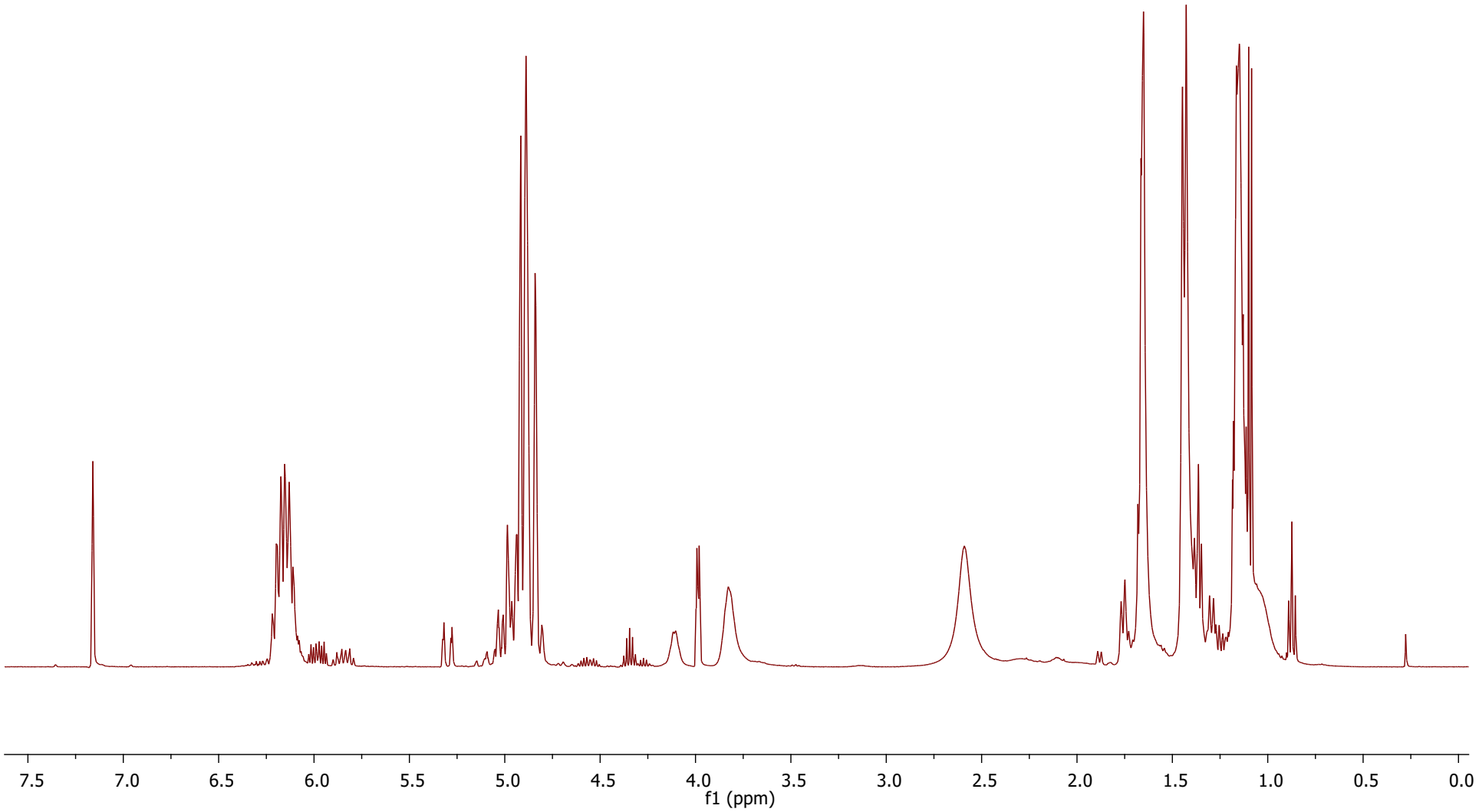
Diallyl(isopropoxy)borane **4**. ^{11}B NMR (128 MHz) as ethereal solution, purity 94%. Admixture of allyl(diisopropoxy)borane **5** (6%).



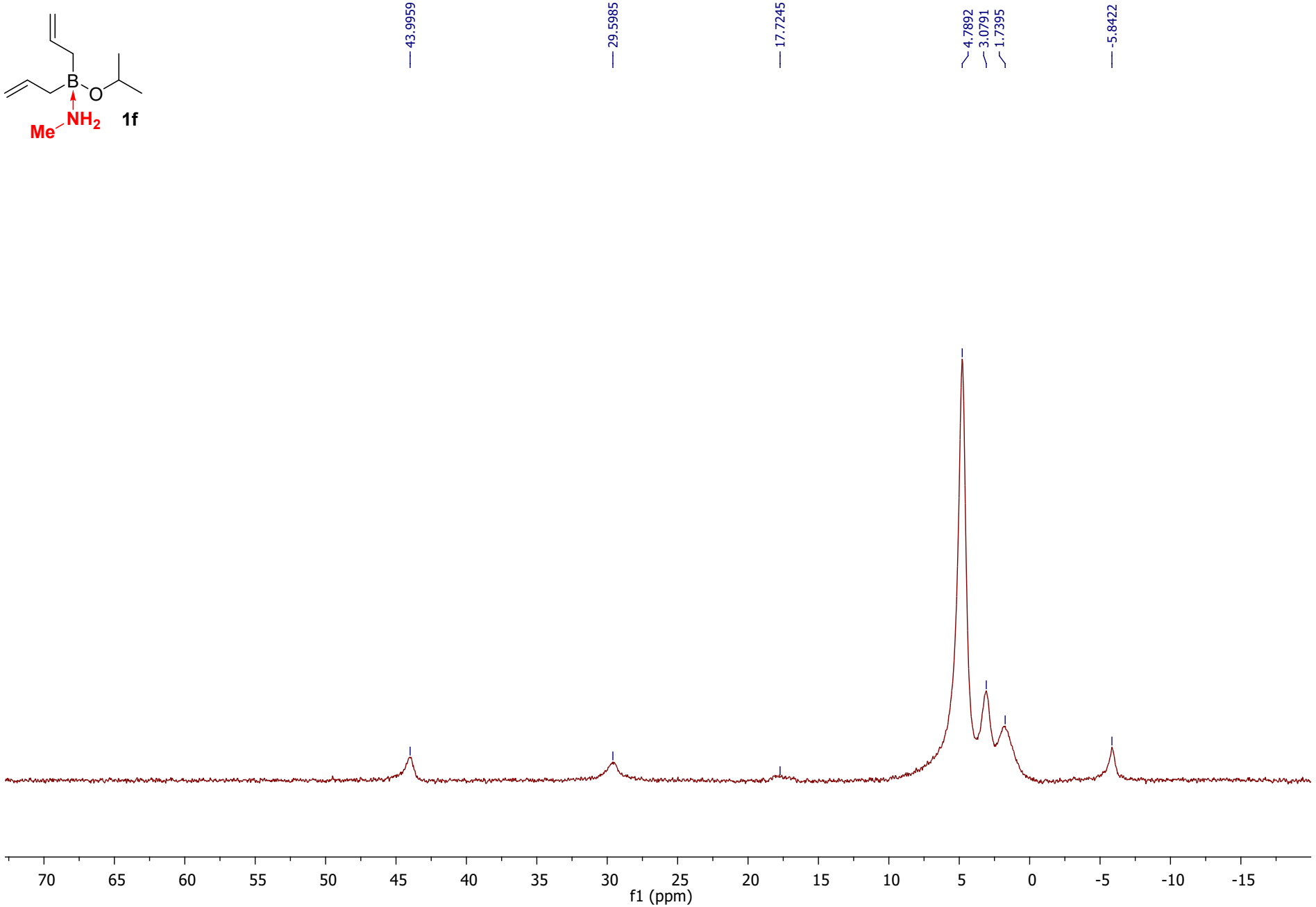
Methylamine adduct **1f.** ^{1}H NMR (400 MHz, C_6D_6) without additives.



1f

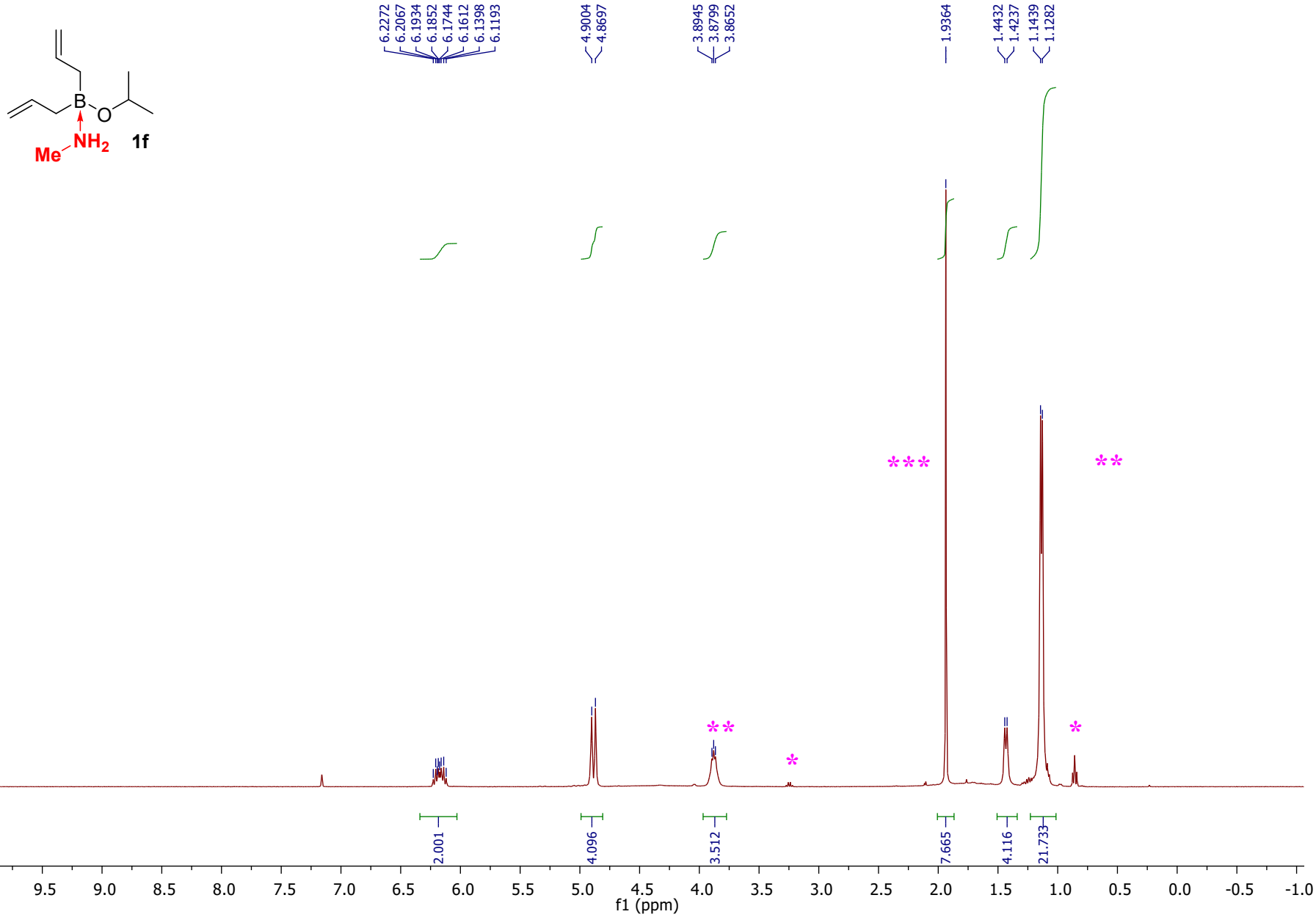


Methylamine adduct **1f.** ^{11}B NMR (128 MHz, C_6D_6) without additives.

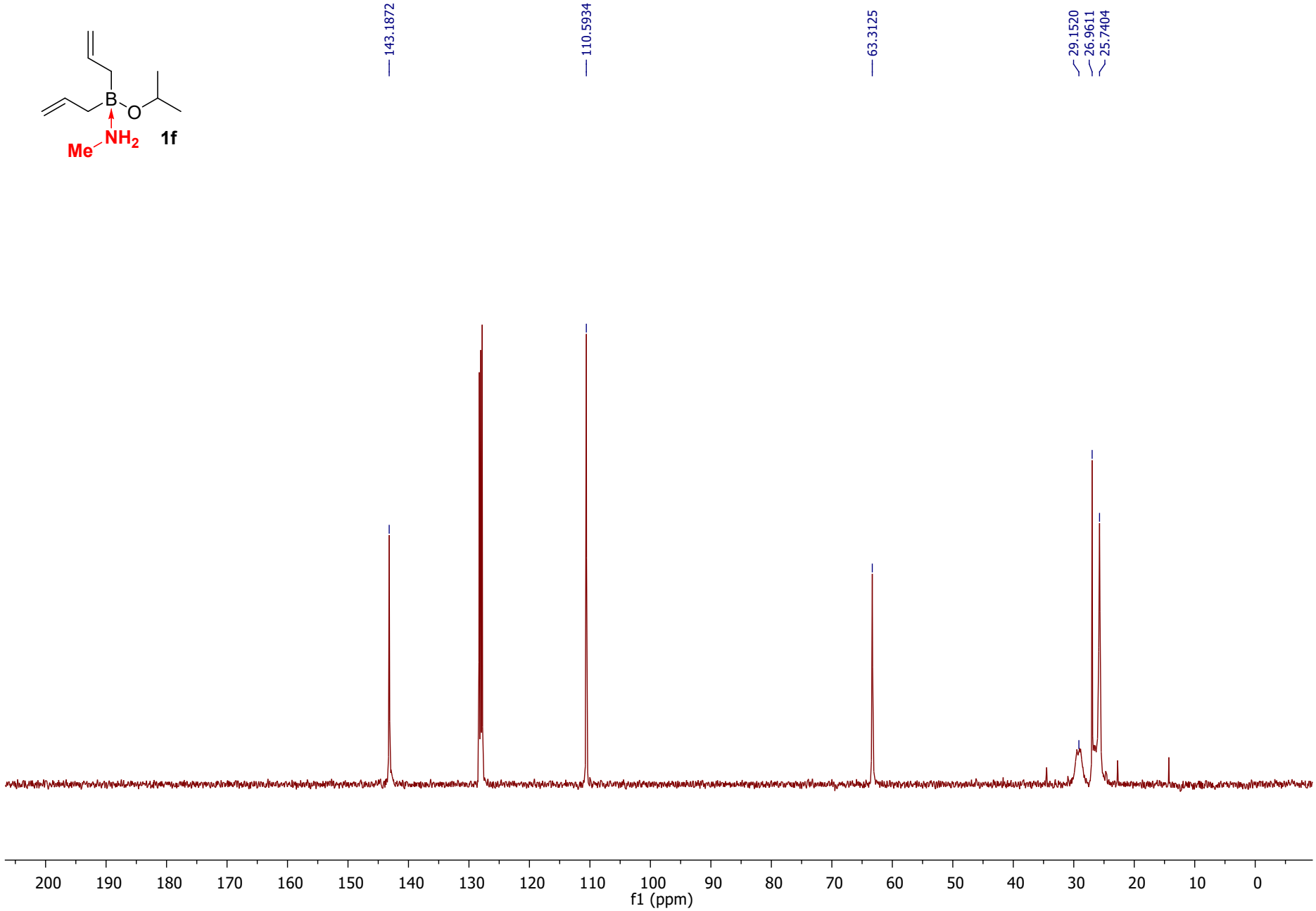


Methylamine adduct **1f.** ^{1}H NMR (400 MHz, C_6D_6) with addition of 1.5 equiv. of $MeNH_2$ in *i*PrOH for stabilization).

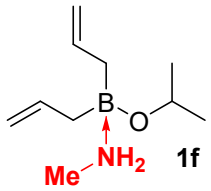
Admixtures of * - Et_2O; ** - *i*PrOH; *** - $MeNH_2$.



Methylamine adduct **1f.** ^{13}C NMR (101 MHz, C_6D_6) with addition of 1.5 equiv. of $MeNH_2$ in *i*PrOH for stabilization)..

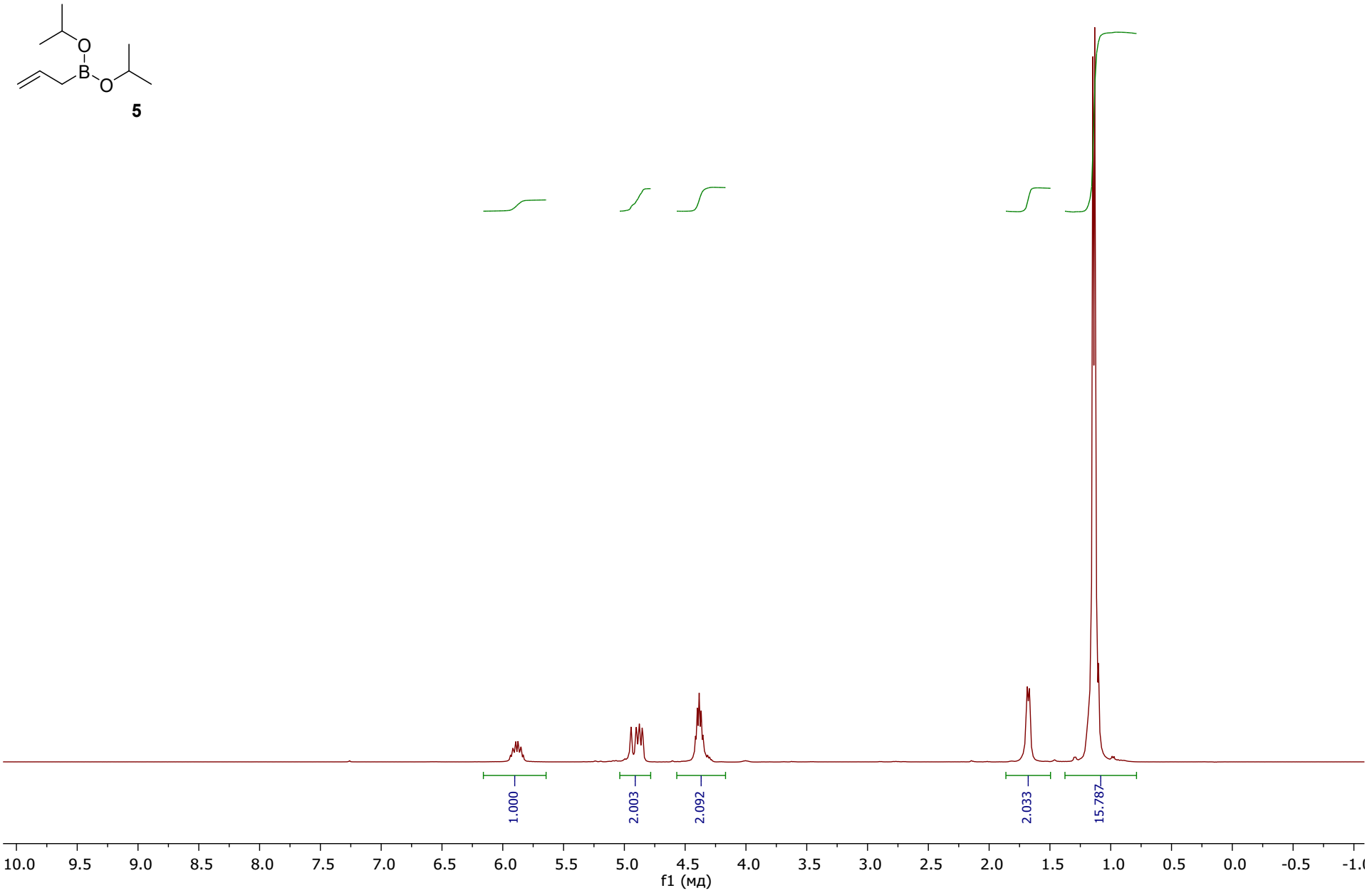


Methylamine adduct **1f.** ^{11}B NMR (128 MHz, C_6D_6) with addition of 2 equiv. of $MeNH_2$ in *i*PrOH for stabilization.

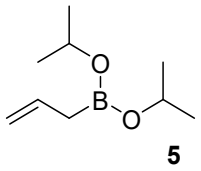


1f

Allyl(diisopropoxy)borane **5**. ^{1}H (400 MHz, $CDCl_3$).

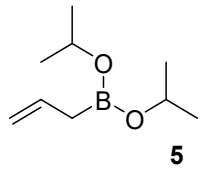


Allyl(diisopropoxy)borane **5**. ^{11}B (128 MHz, $CDCl_3$); admixture of $B(OiPr)_3$ 4.8%.



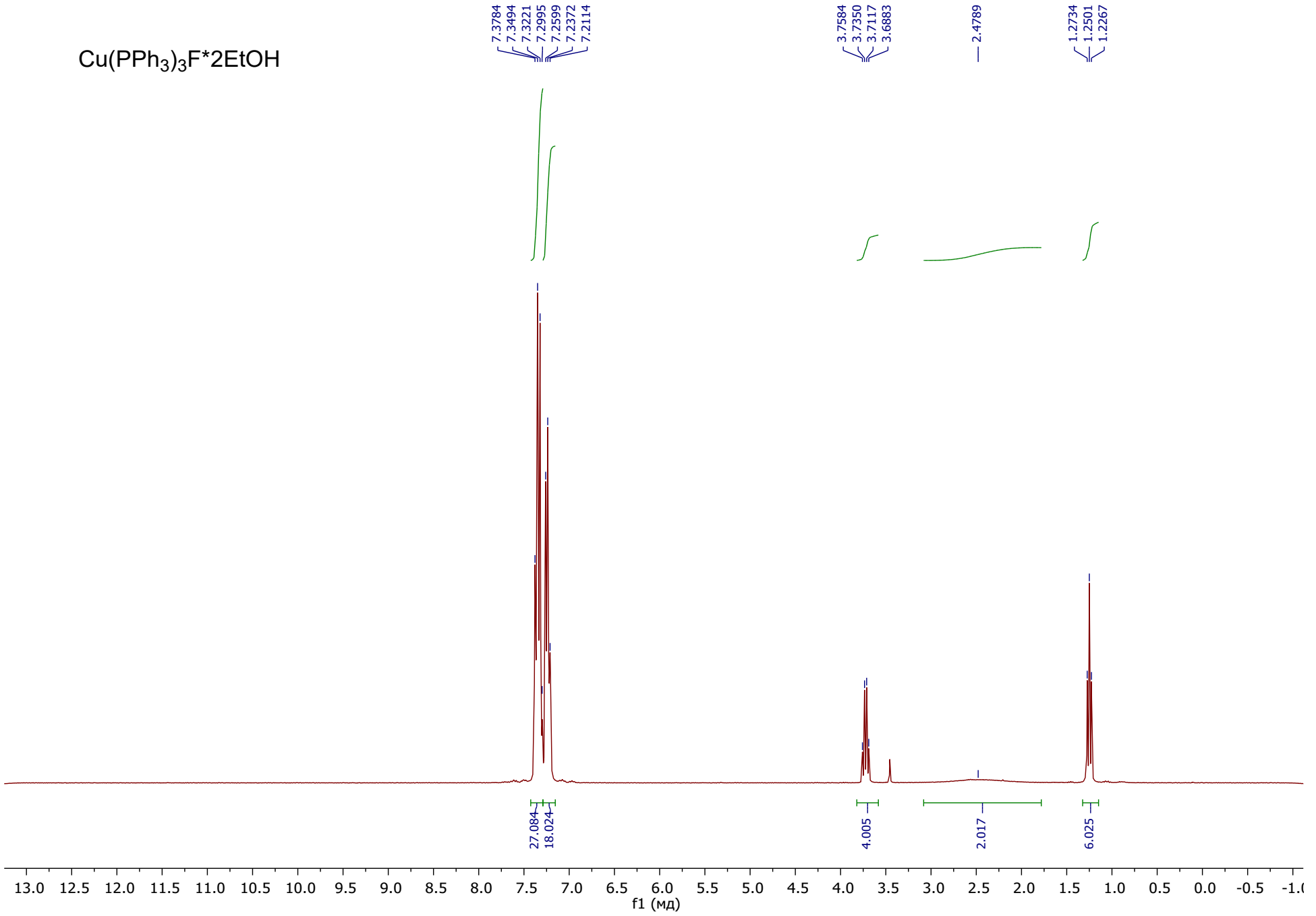
5

Allyl(diisopropoxy)borane **5**. ^{13}C (101 MHz, $CDCl_3$); admixture of $B(OiPr)_3$.

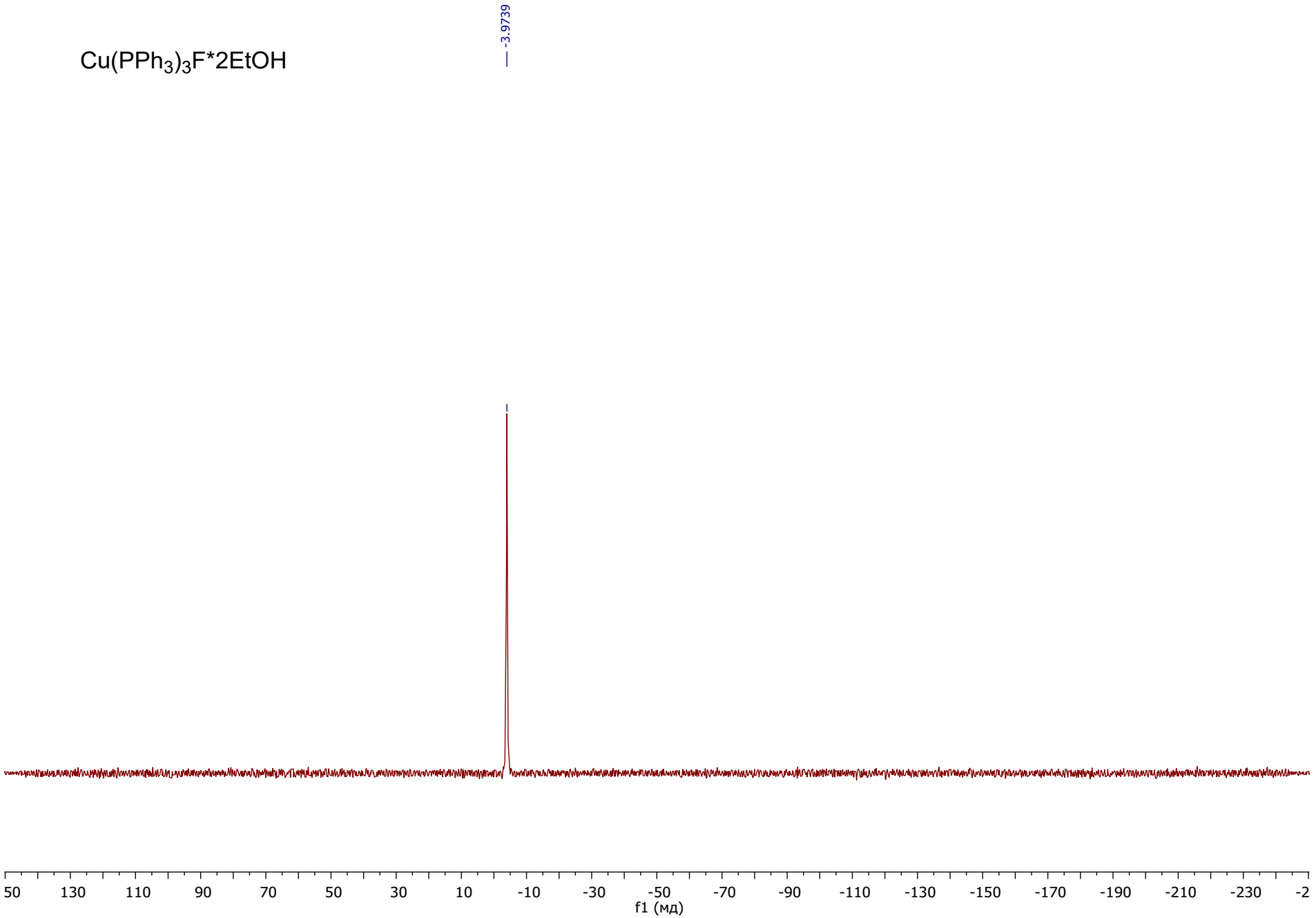


5

^{1}H NMR ($CDCl_3$, 400 MHz) **[Cu-1]**

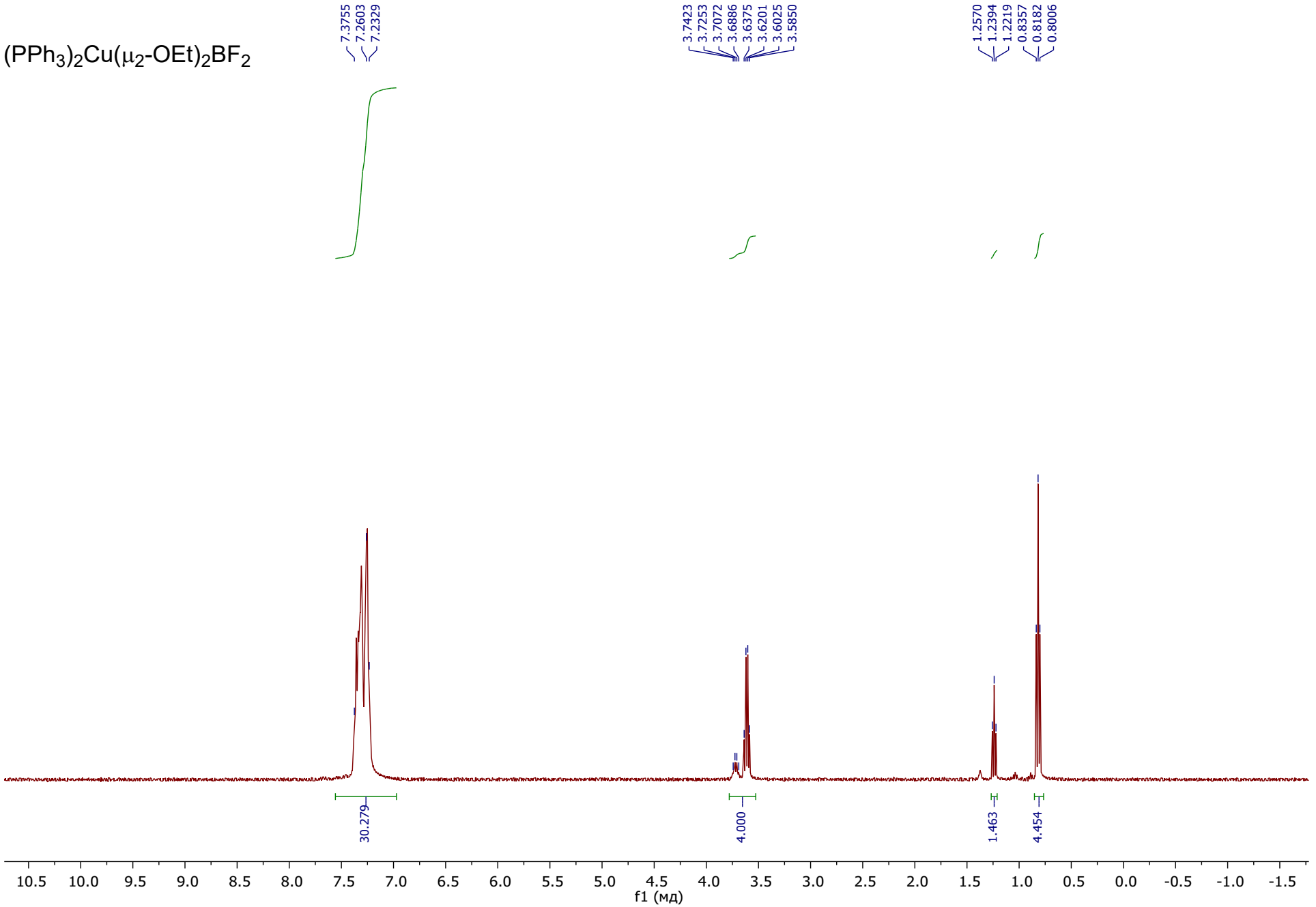


^{31}P NMR ($CDCl_3$, 121 MHz) **[Cu-1]**



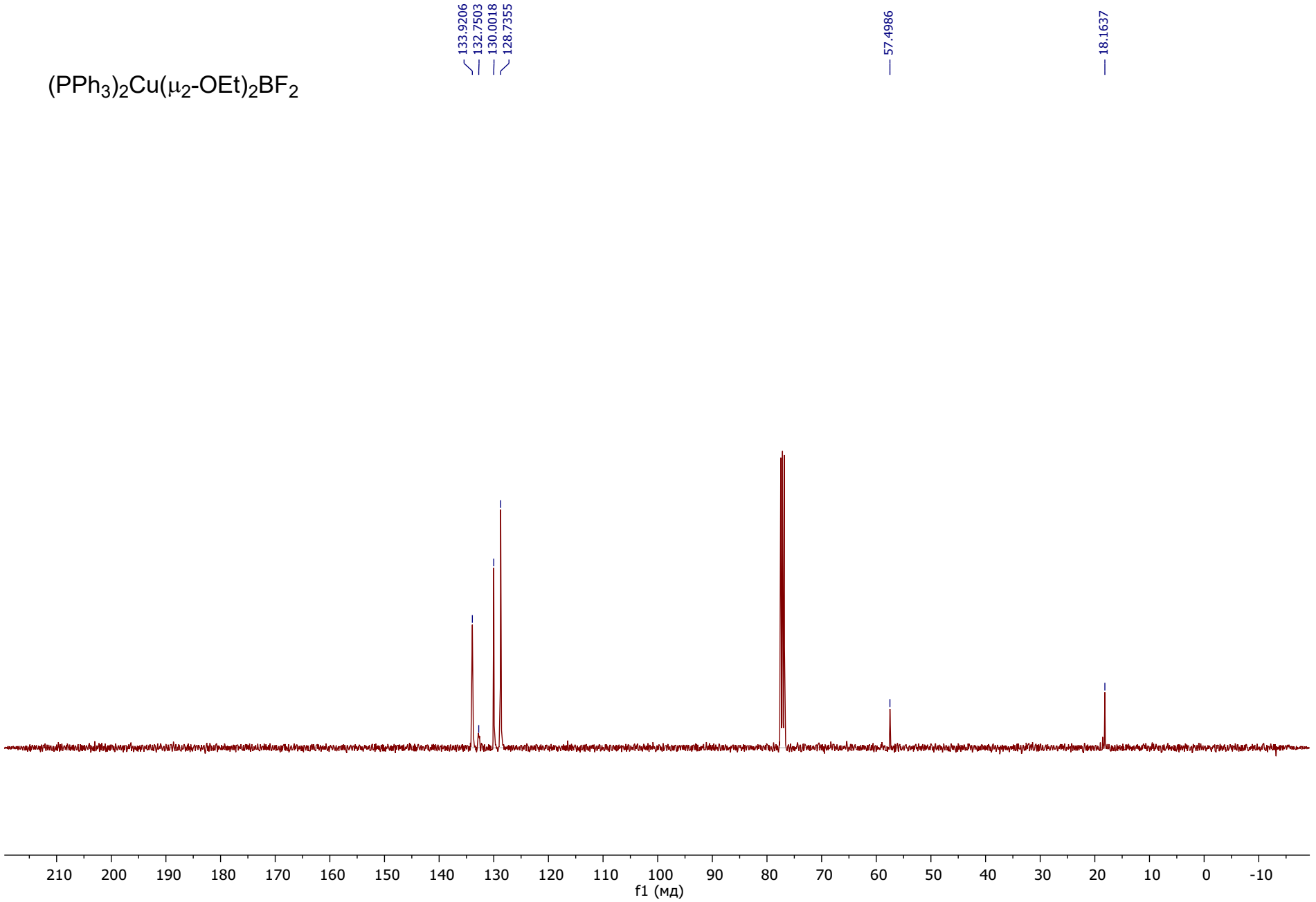
^{1}H NMR ($CDCl_3$, 400 MHz) **[Cu-2]**

$(PPh_3)_2Cu(\mu_2\text{-}OEt)_2BF_2$



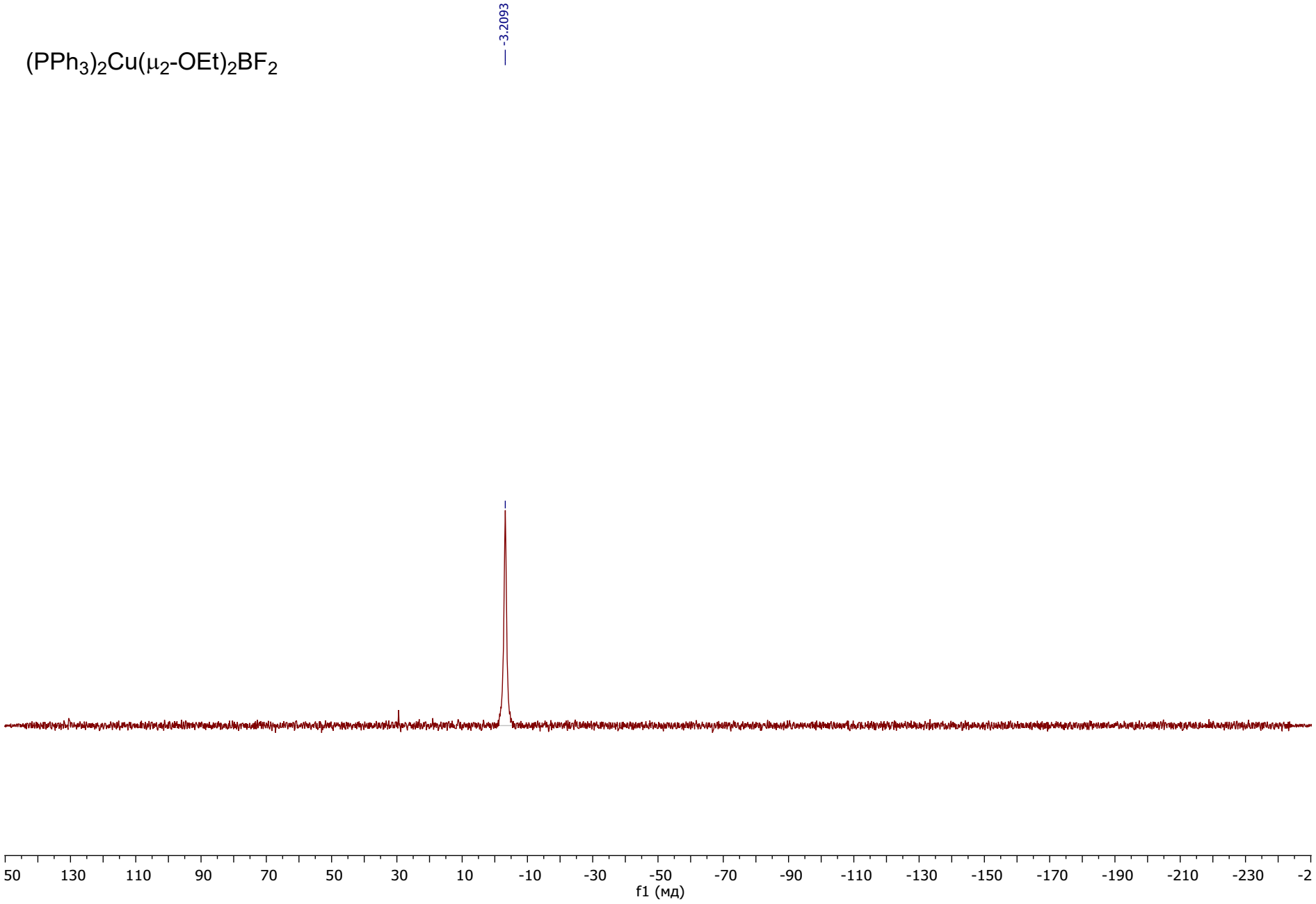
^{13}C NMR ($CDCl_3$, 101 MHz) **[Cu-2]**

$(PPh_3)_2Cu(\mu_2\text{-}OEt)_2BF_2$



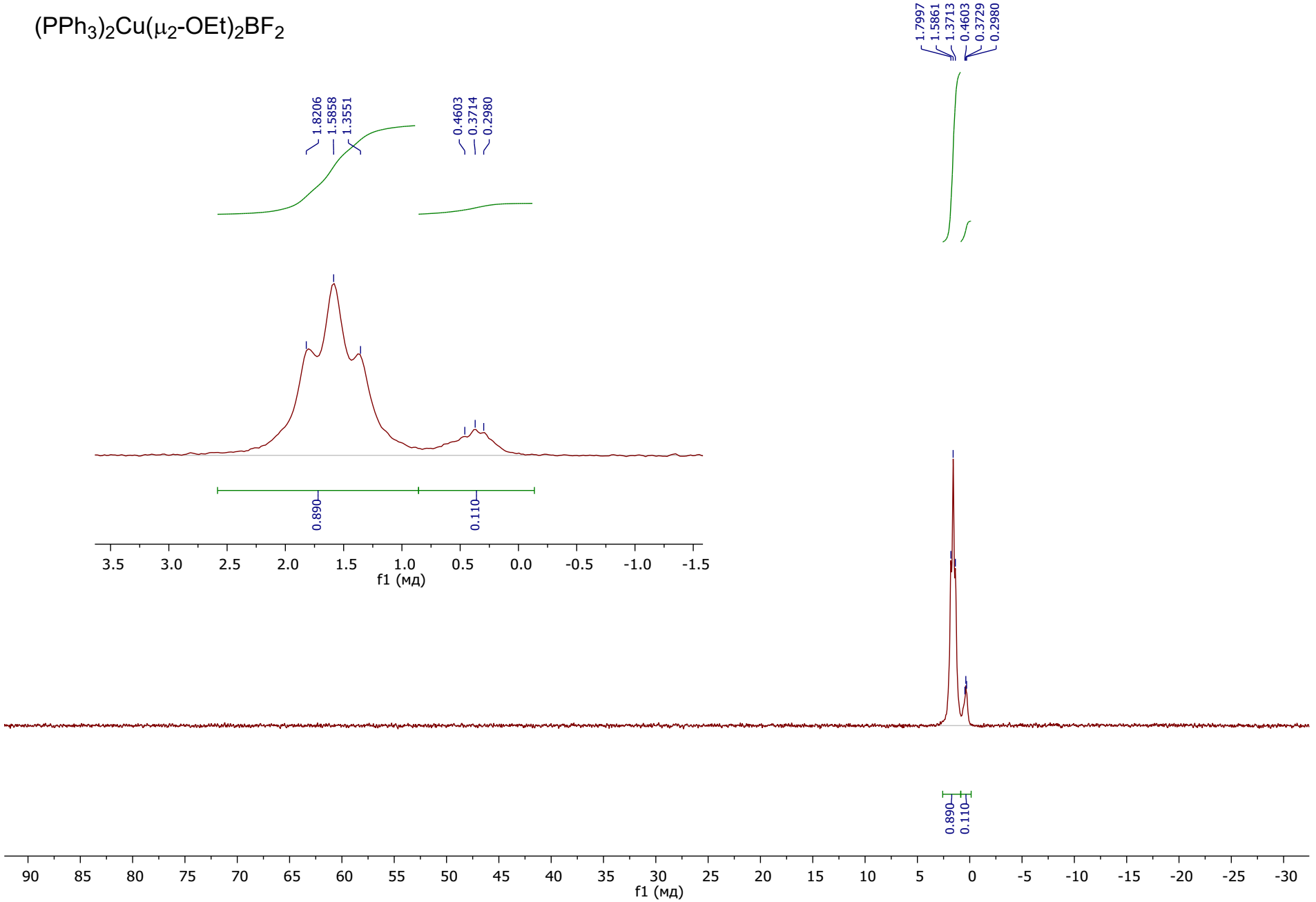
^{31}P NMR ($CDCl_3$, 121 MHz) **[Cu-2]**

$(PPh_3)_2Cu(\mu_2\text{-}OEt)_2BF_2$



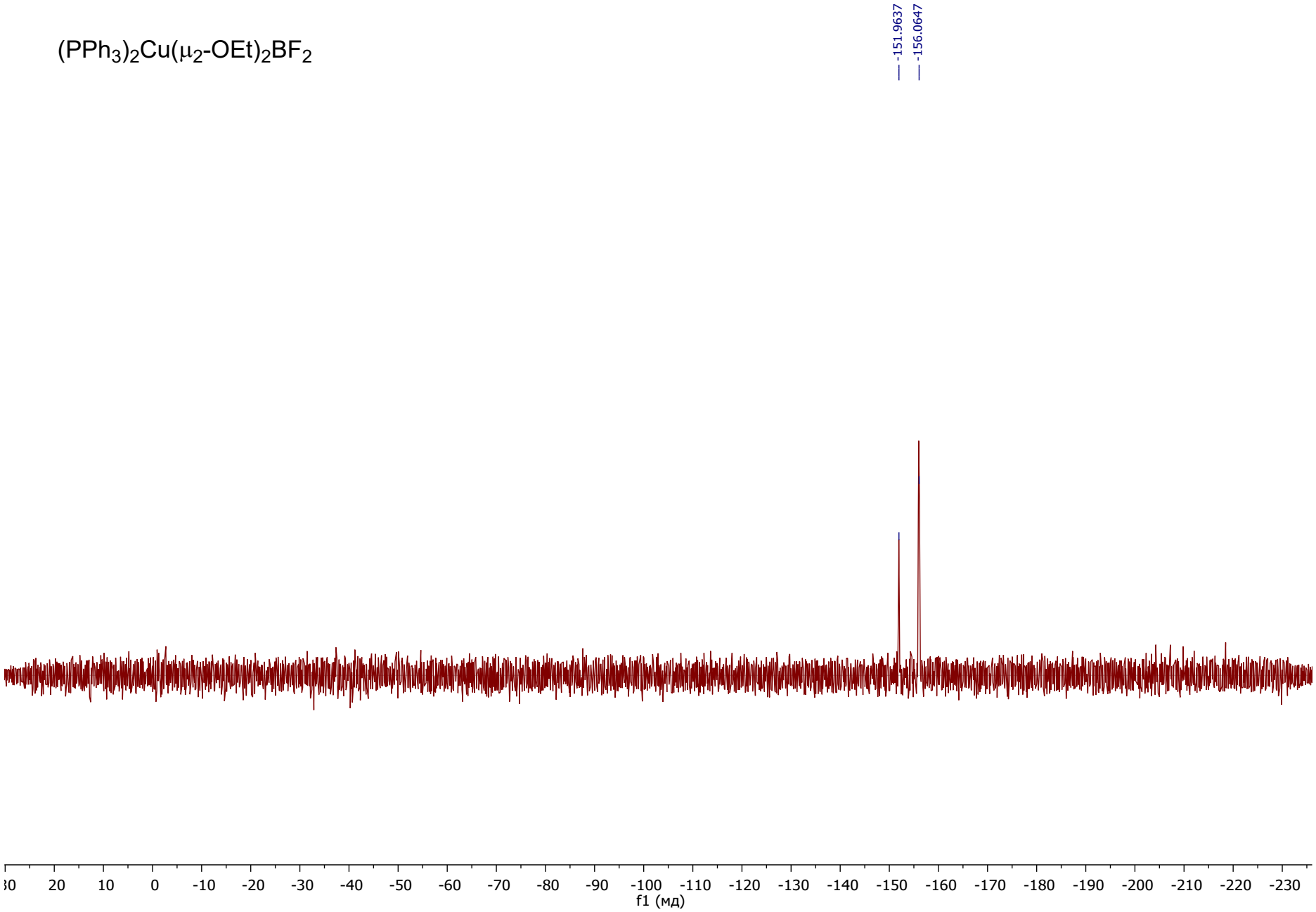
^{11}B NMR ($CDCl_3$, 128 MHz) **[Cu-2]**

$(PPh_3)_2Cu(\mu_2\text{-}OEt)_2BF_2$

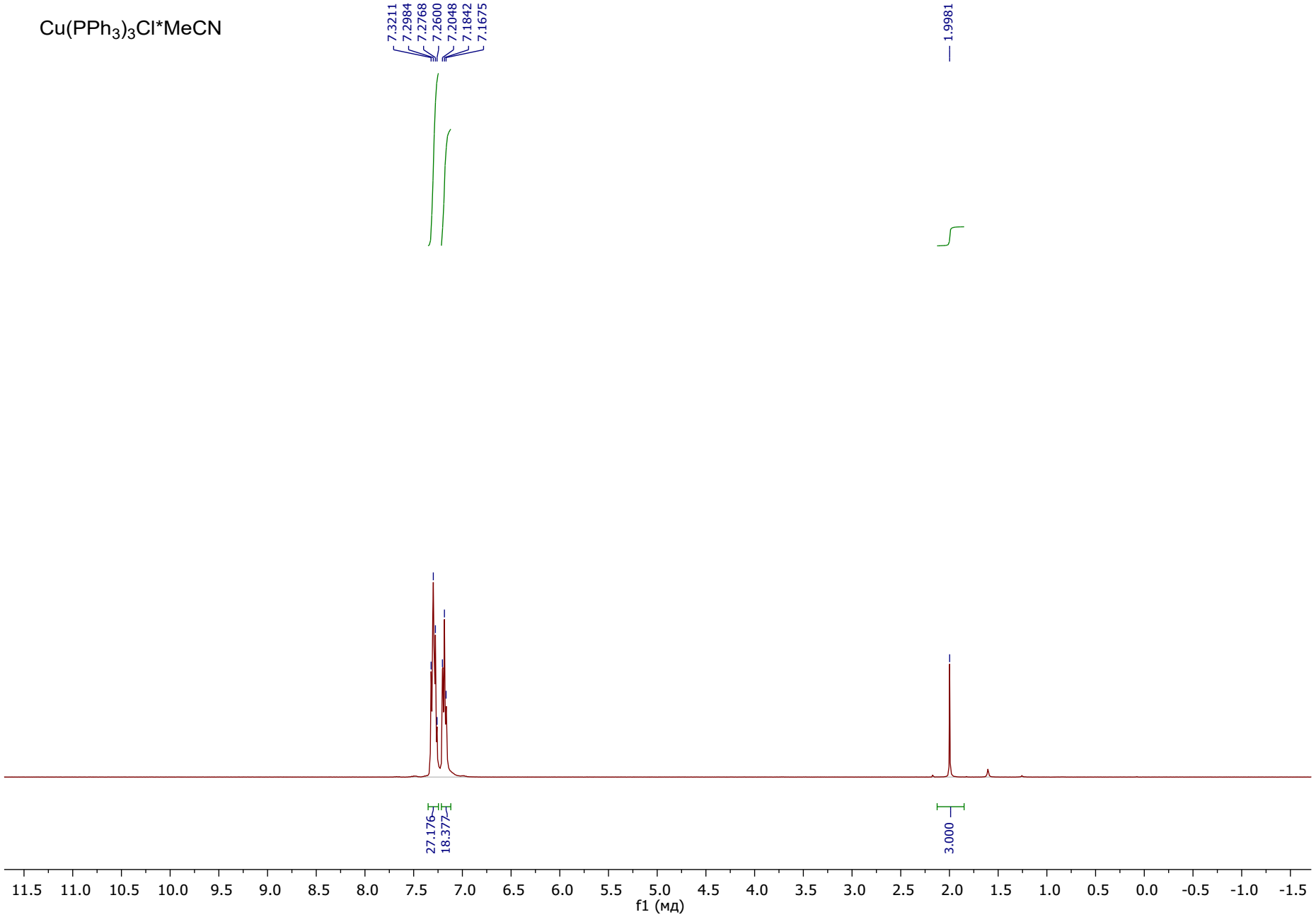


^{19}F NMR ($CDCl_3$, 282 MHz) **[Cu-2]**

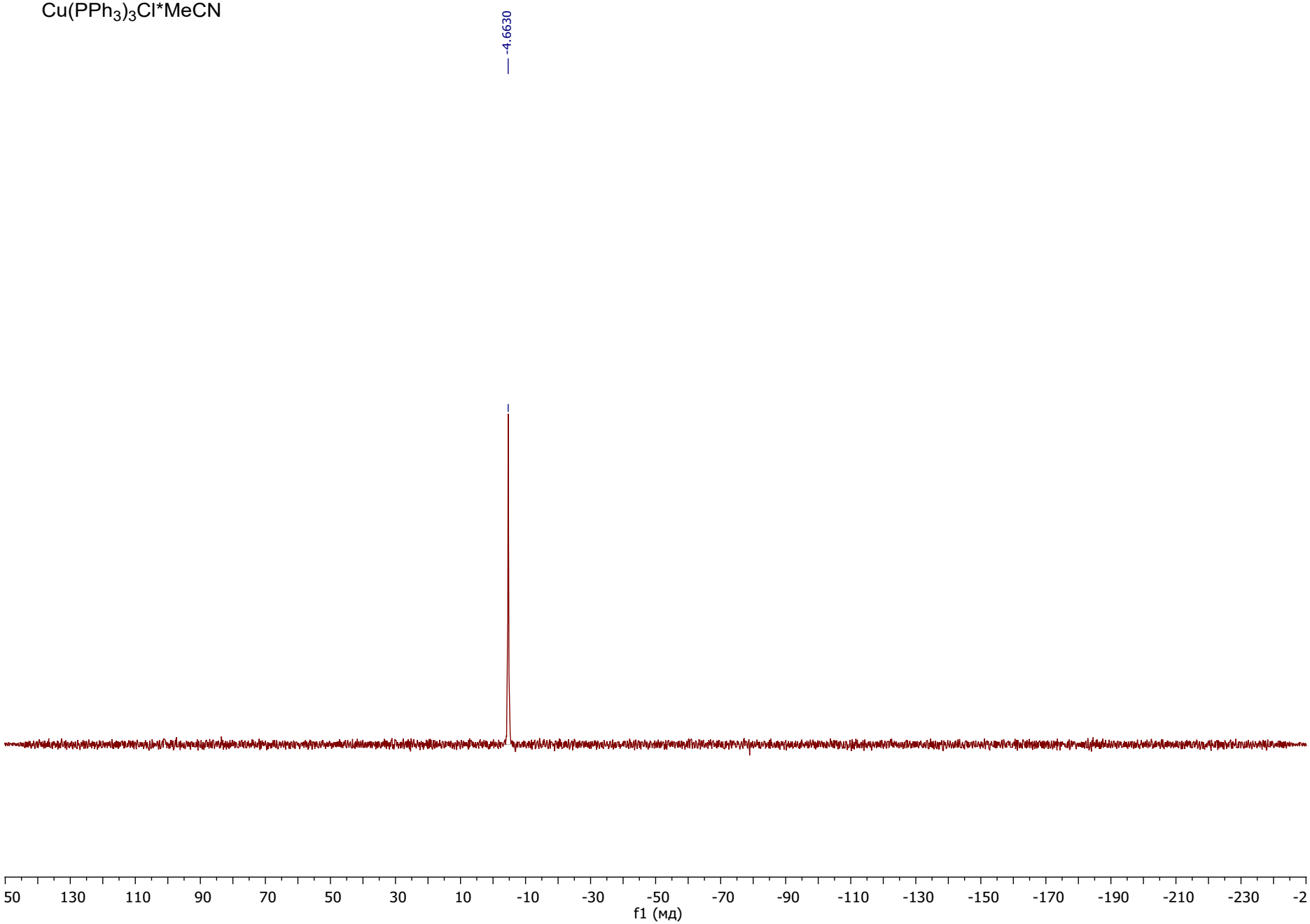
$(PPh_3)_2Cu(\mu_2\text{-}OEt)_2BF_2$



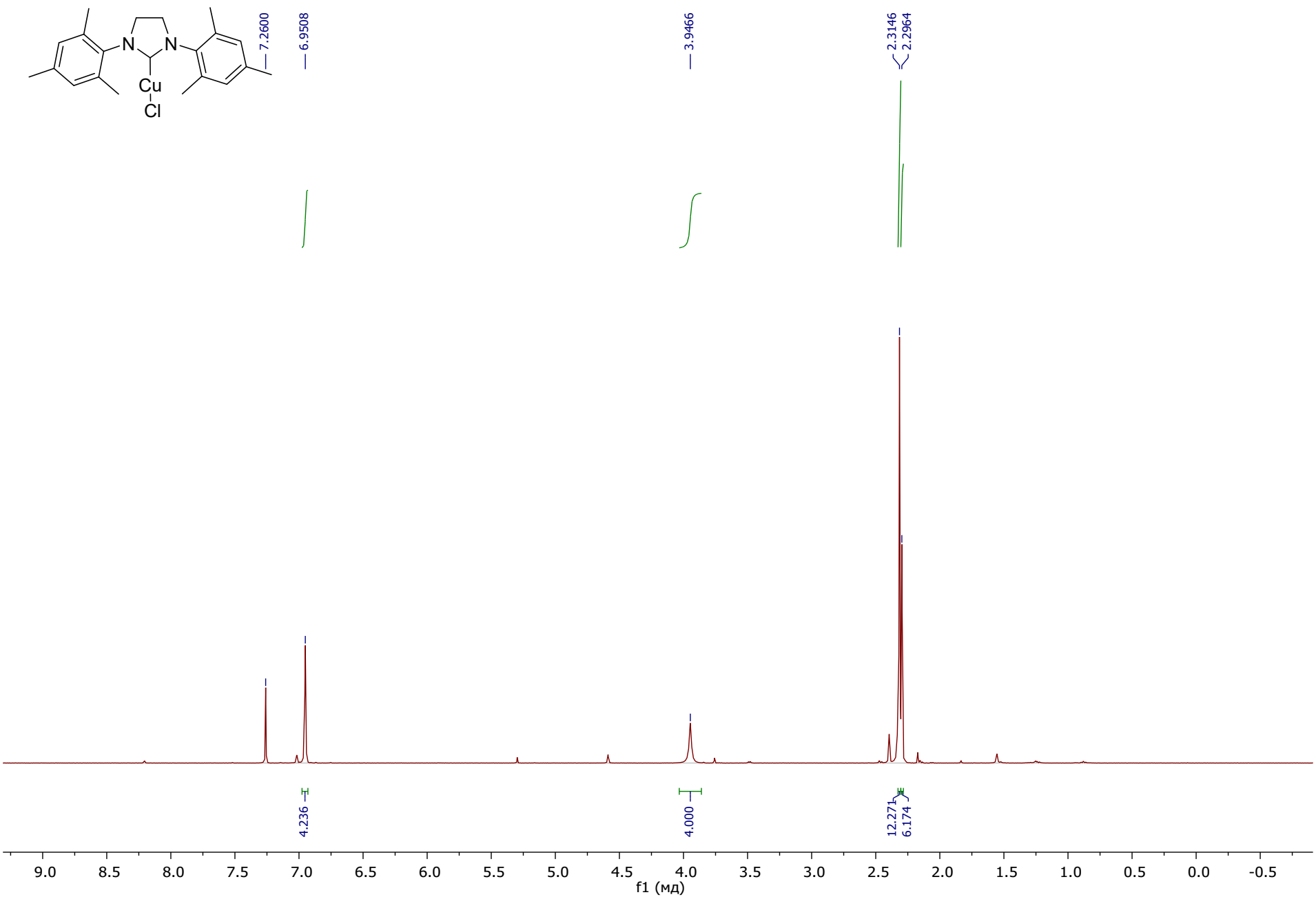
^{1}H NMR ($CDCl_3$, 400 MHz) **[Cu-3]**



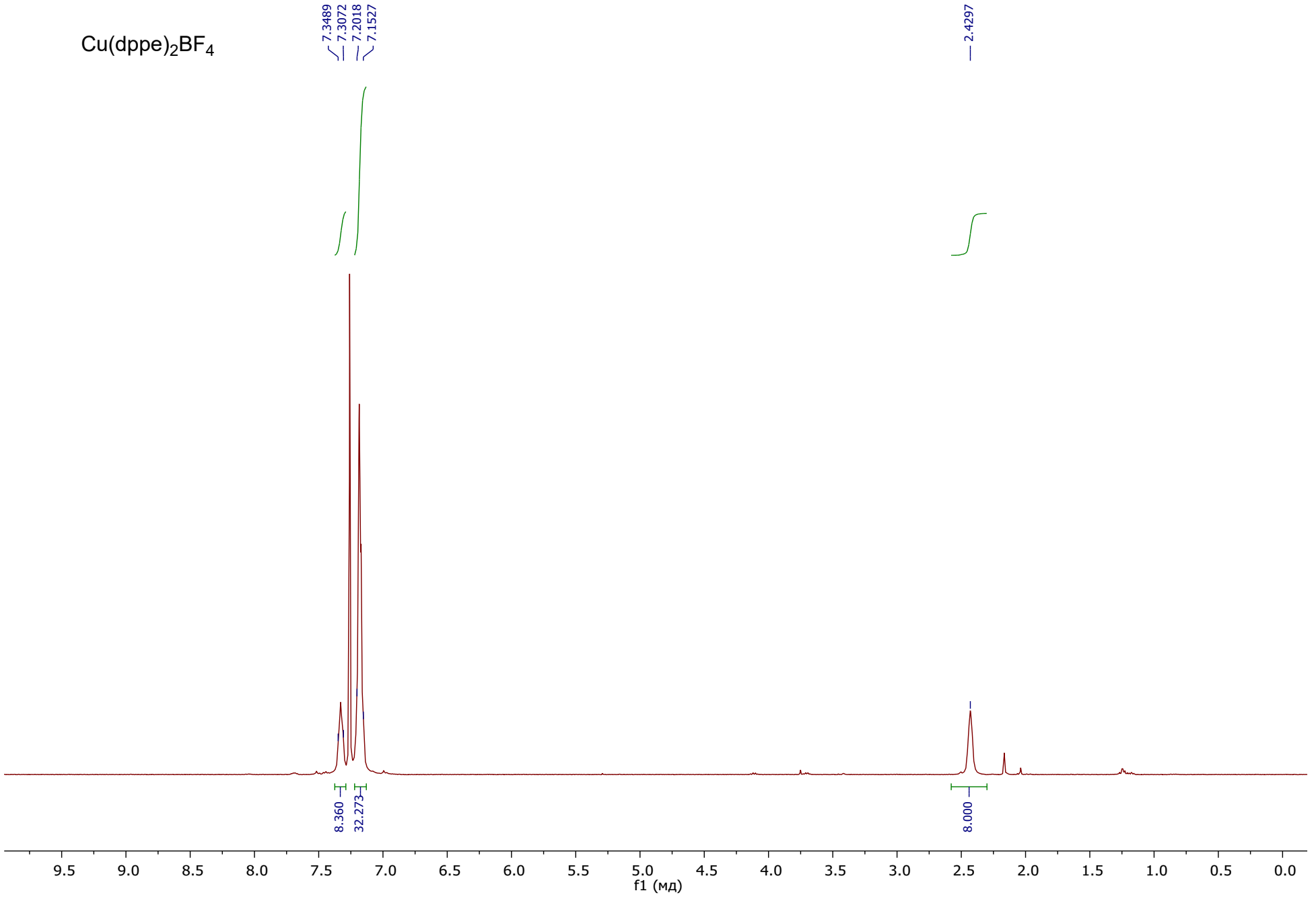
^{31}P NMR ($CDCl_3$, 121 MHz) **[Cu-3]**



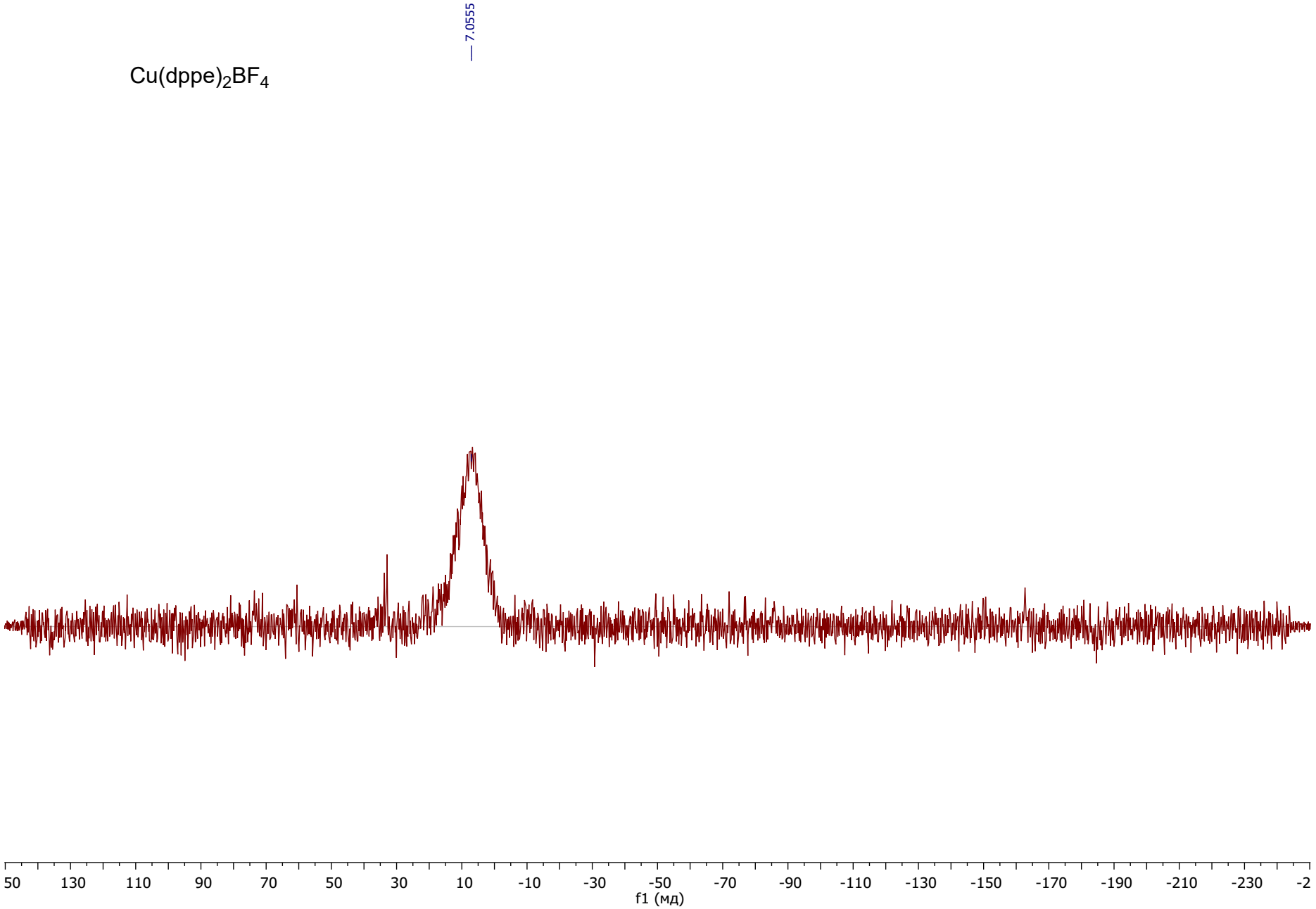
^{1}H NMR ($CDCl_3$, 400 MHz) **[Cu-4]**



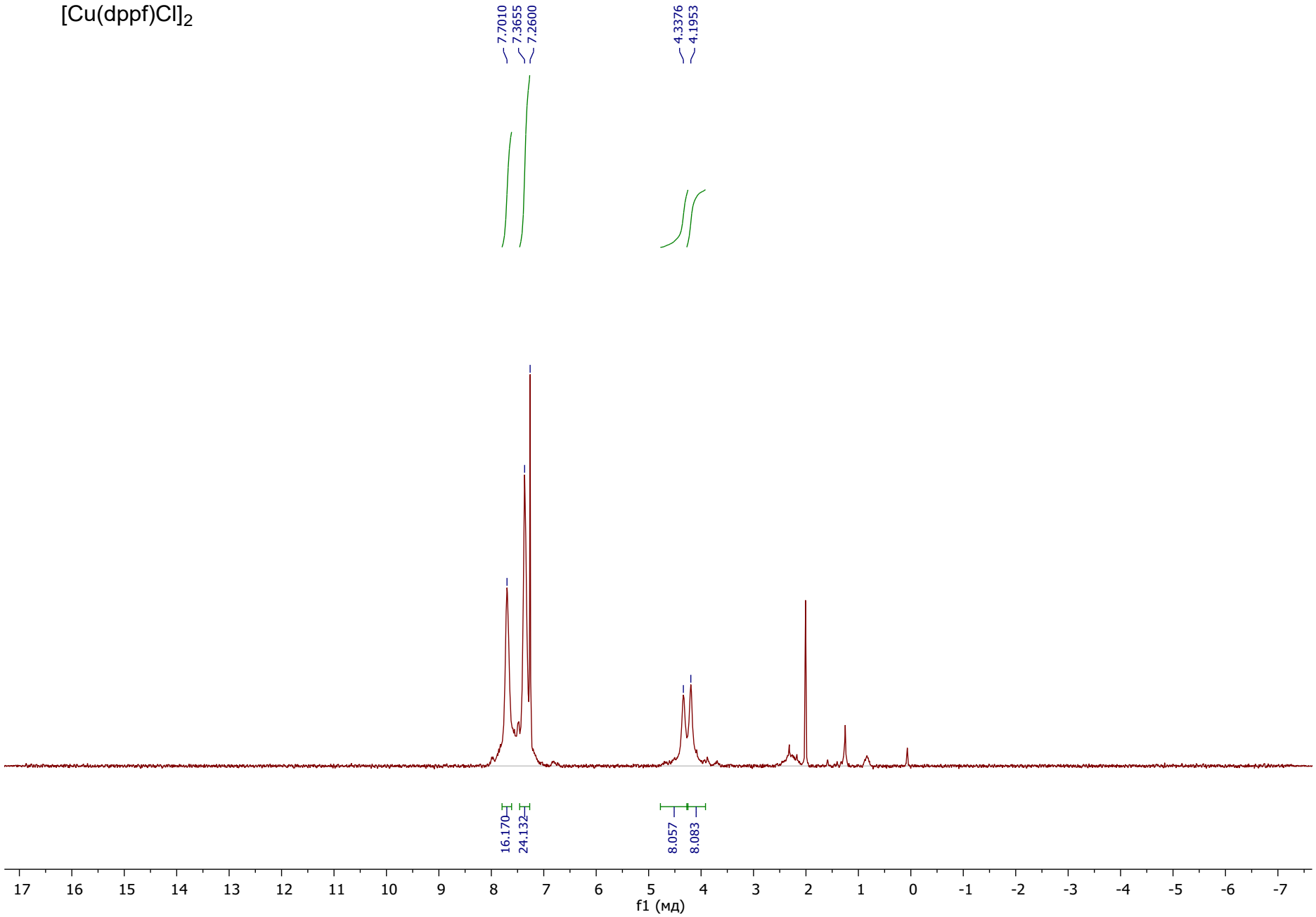
^{1}H NMR ($CDCl_3$, 400 MHz) **[Cu-5]**



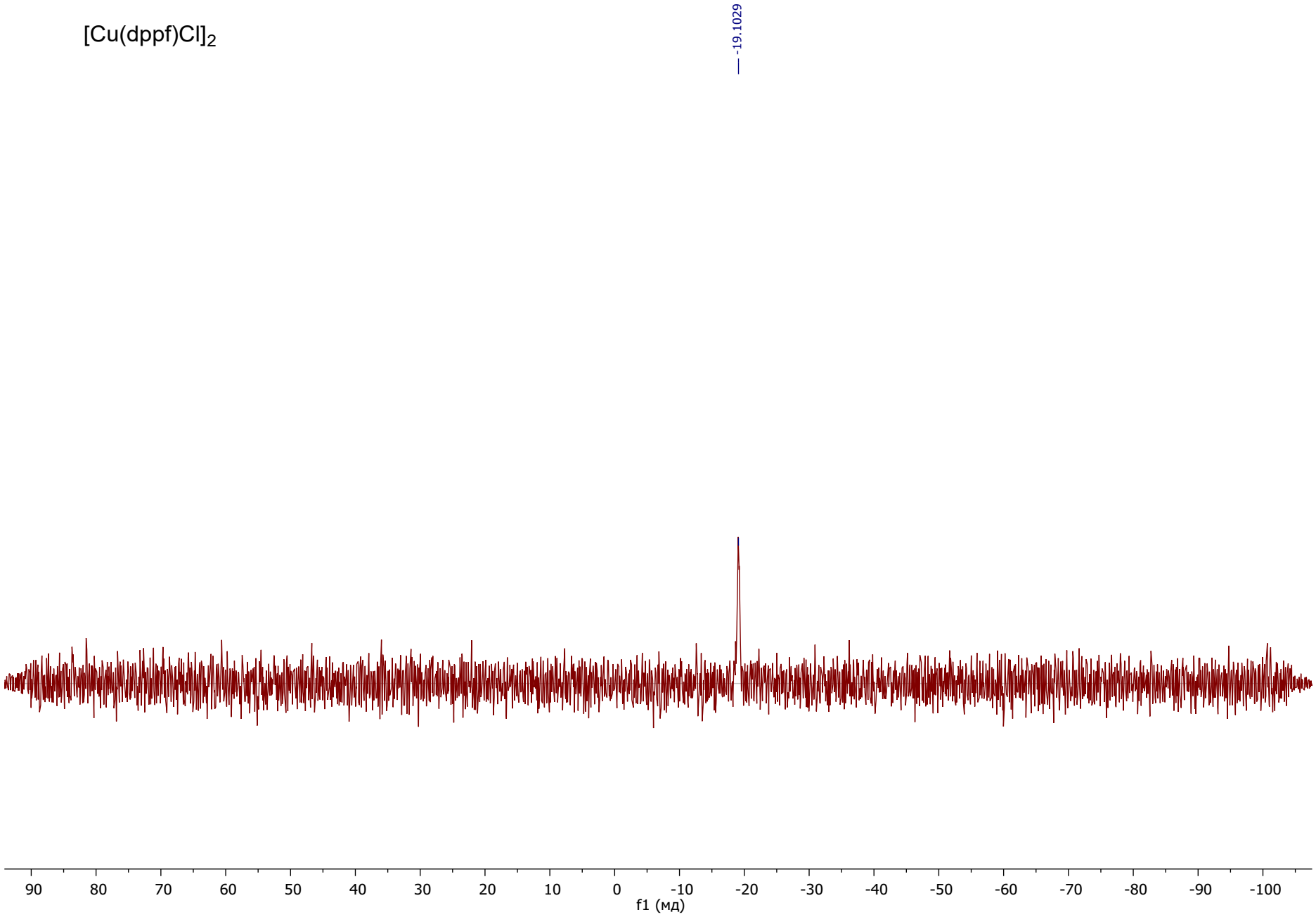
^{31}P NMR ($CDCl_3$,121 MHz) **[Cu-5]**



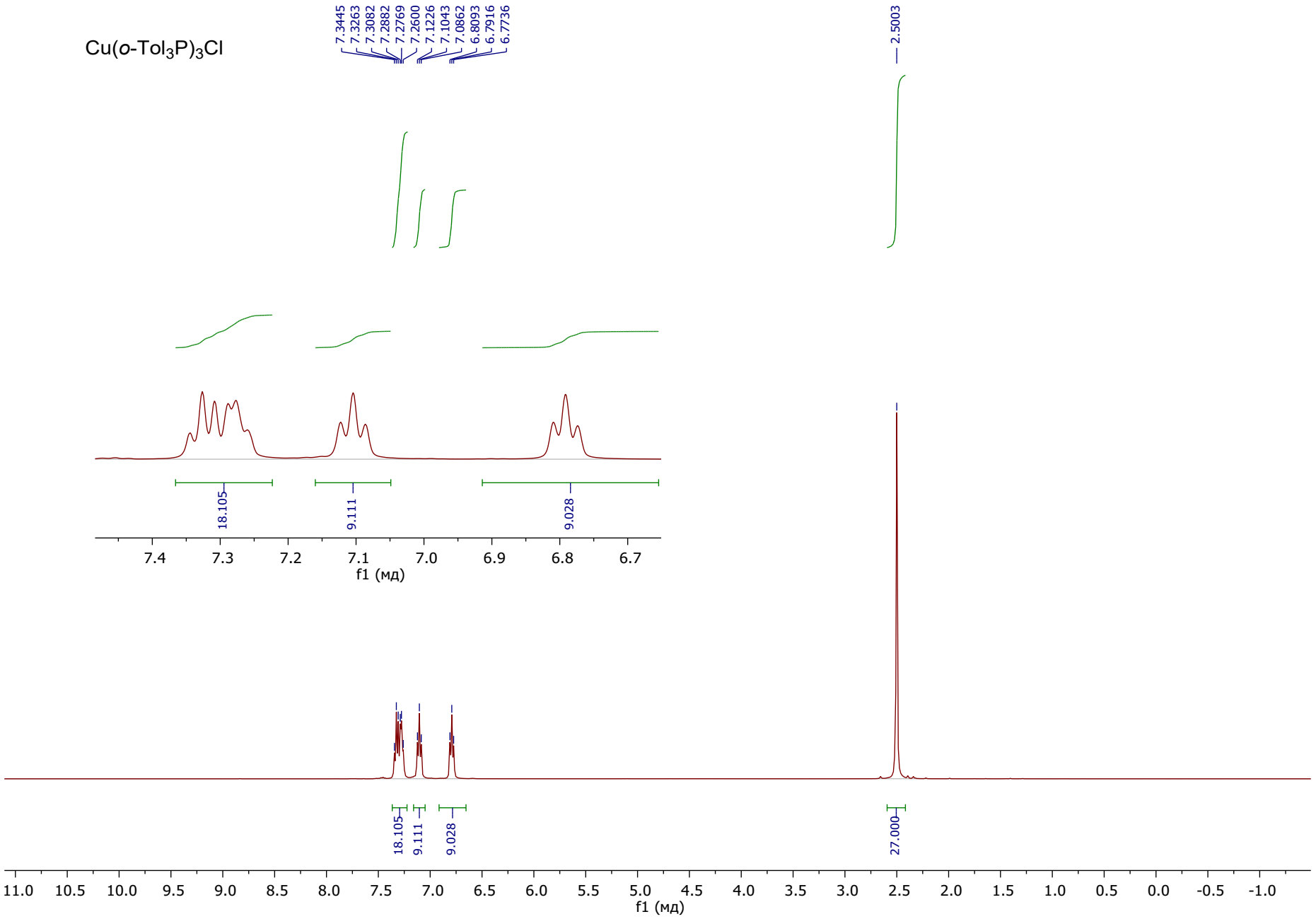
^{1}H NMR ($CDCl_3$, 400 MHz) **[Cu-6]**



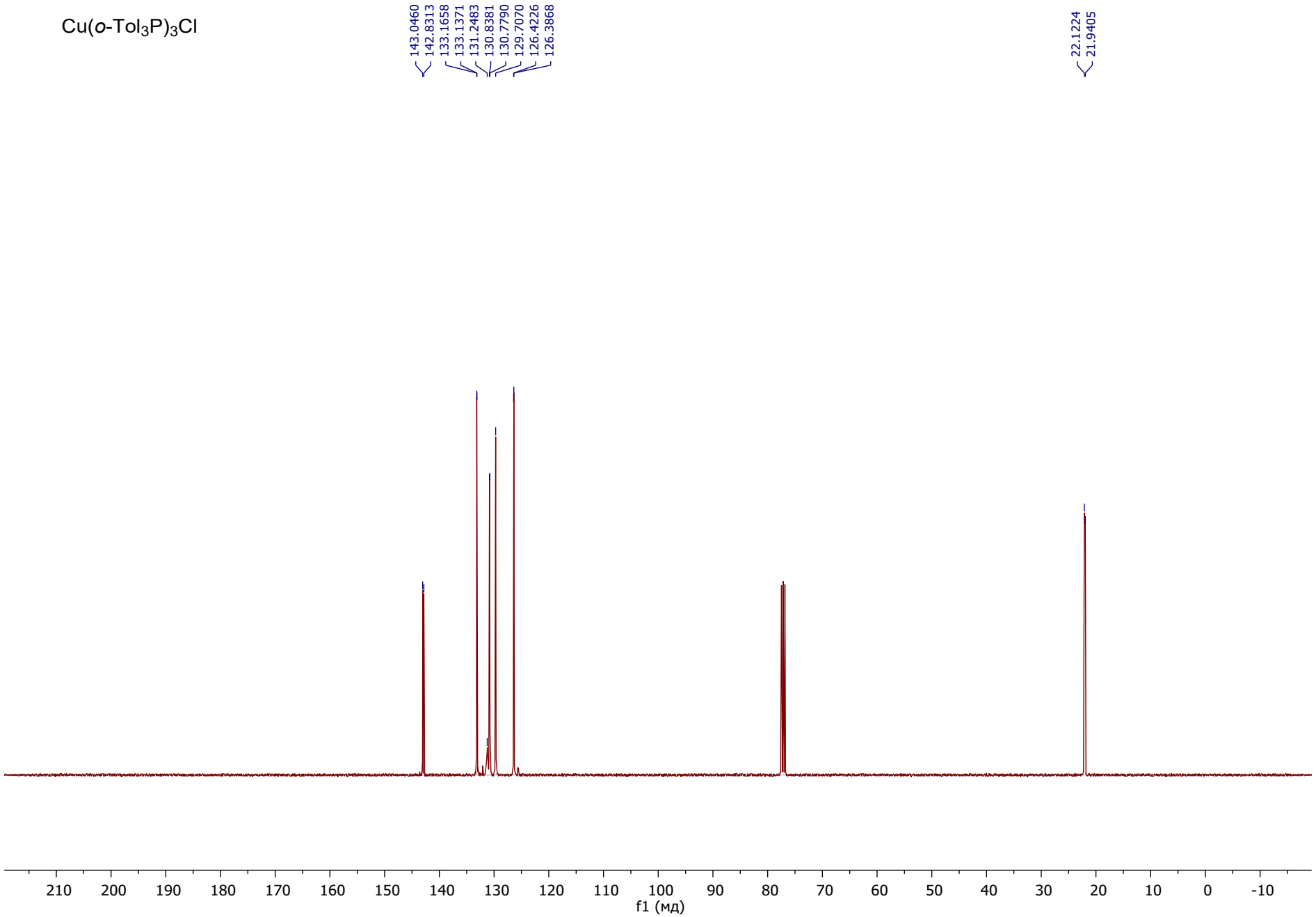
^{31}P NMR ($CDCl_3$, 121 MHz) **[Cu-6]**



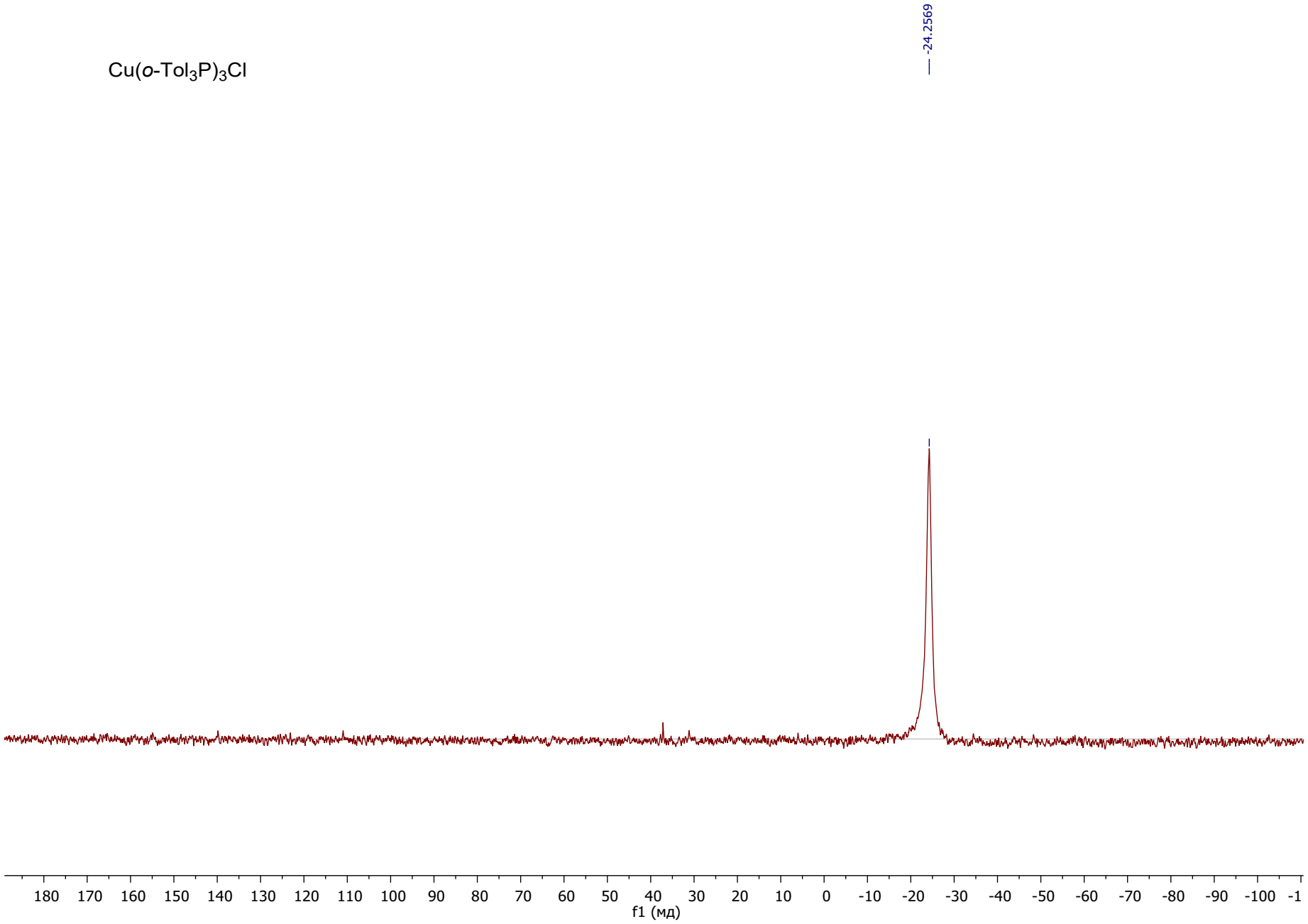
^{1}H NMR ($CDCl_3$, 400 MHz) **[Cu-7]**



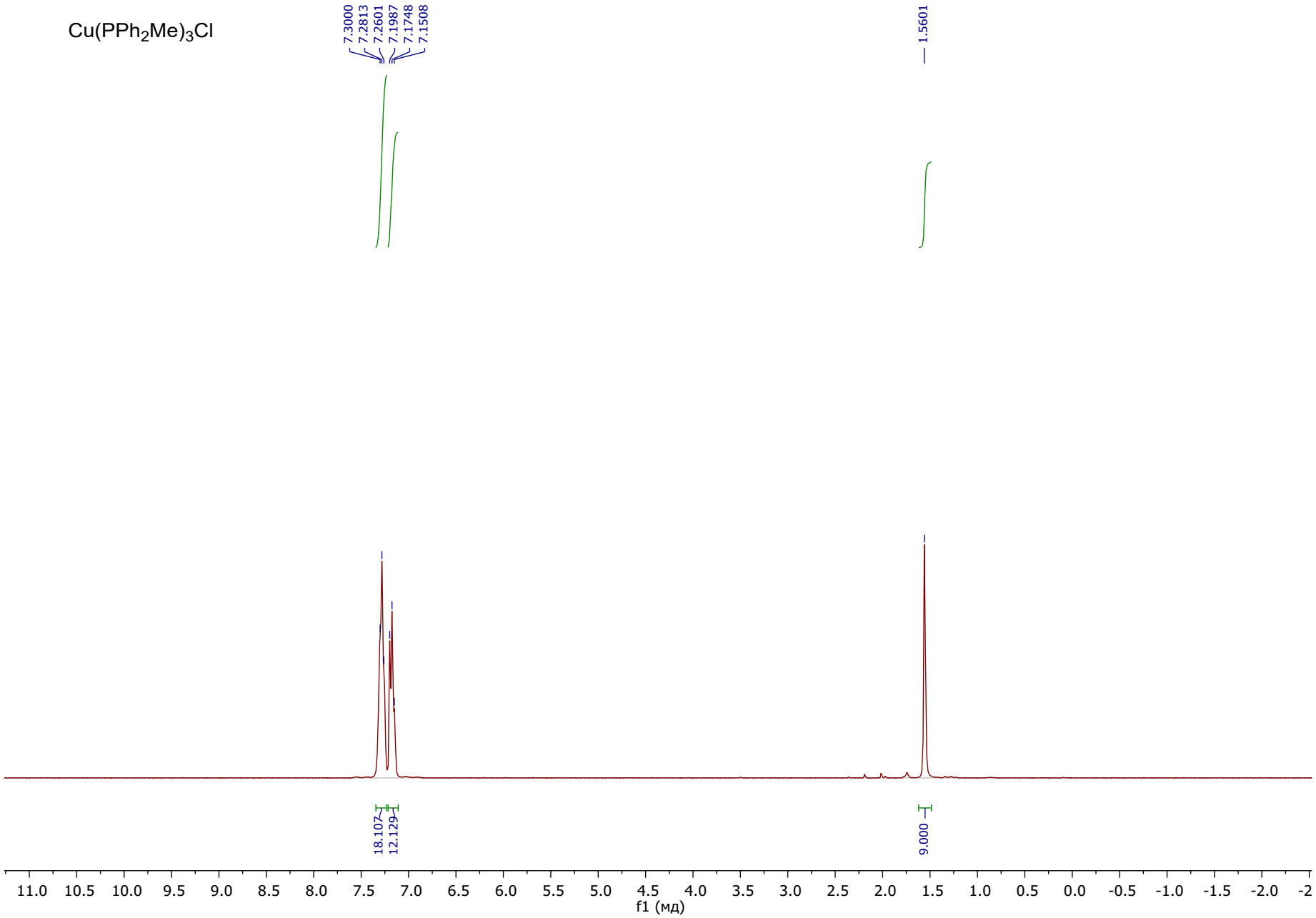
^{13}C NMR ($CDCl_3$, 101 MHz) **[Cu-7]**



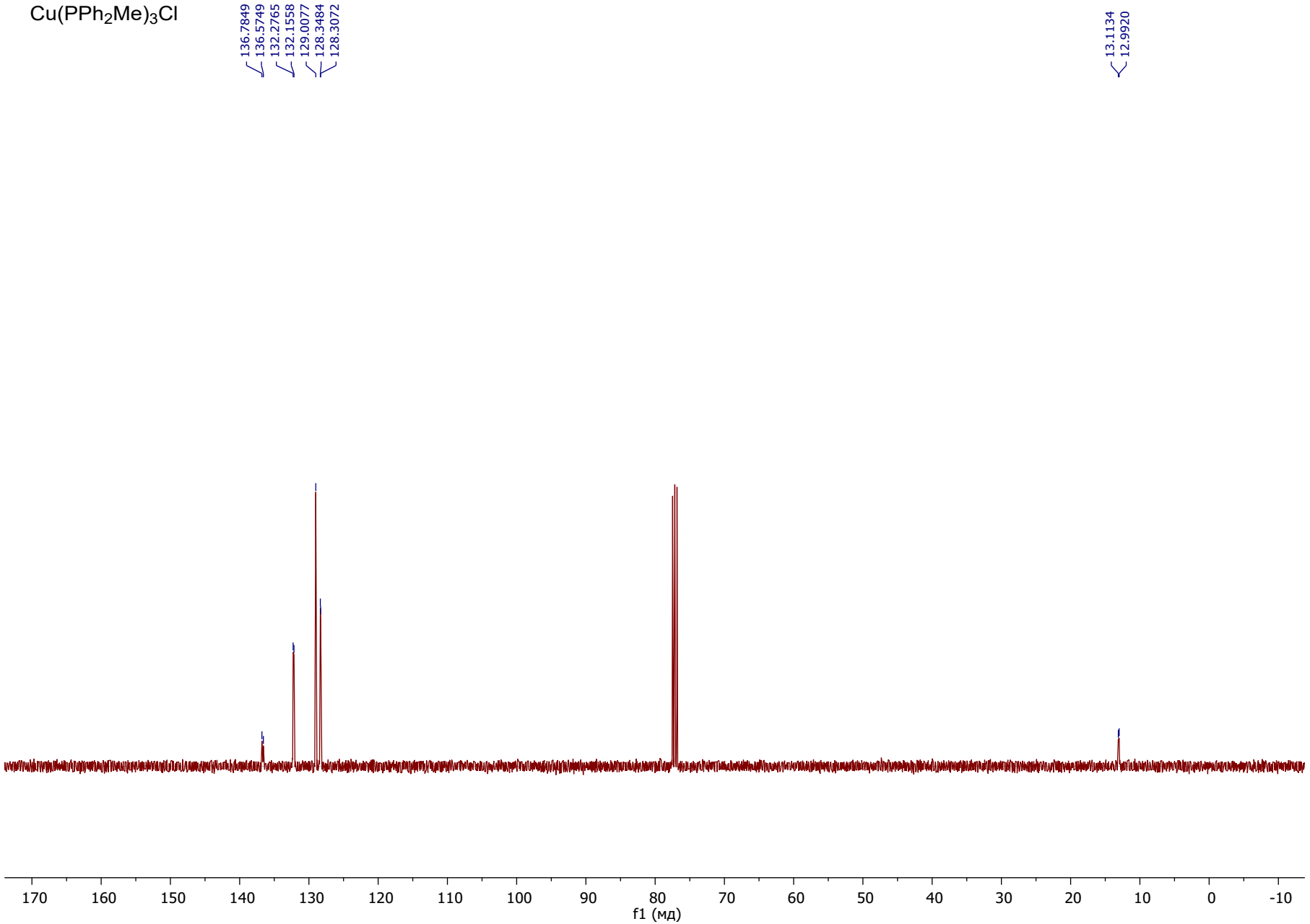
^{31}P NMR ($CDCl_3$, 162 MHz) **[Cu-7]**



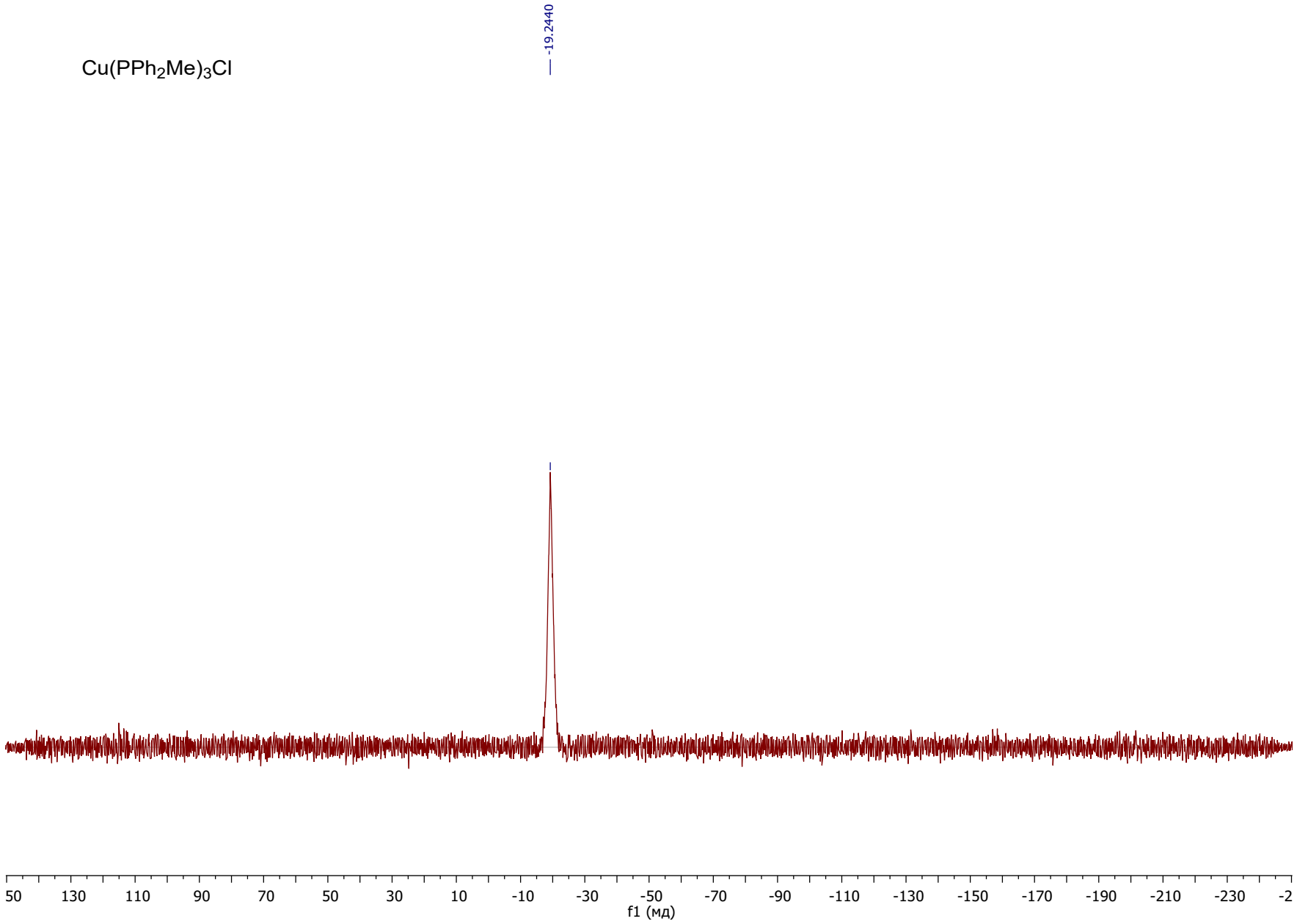
^{1}H NMR ($CDCl_3$, 400 MHz) **[Cu-8]**



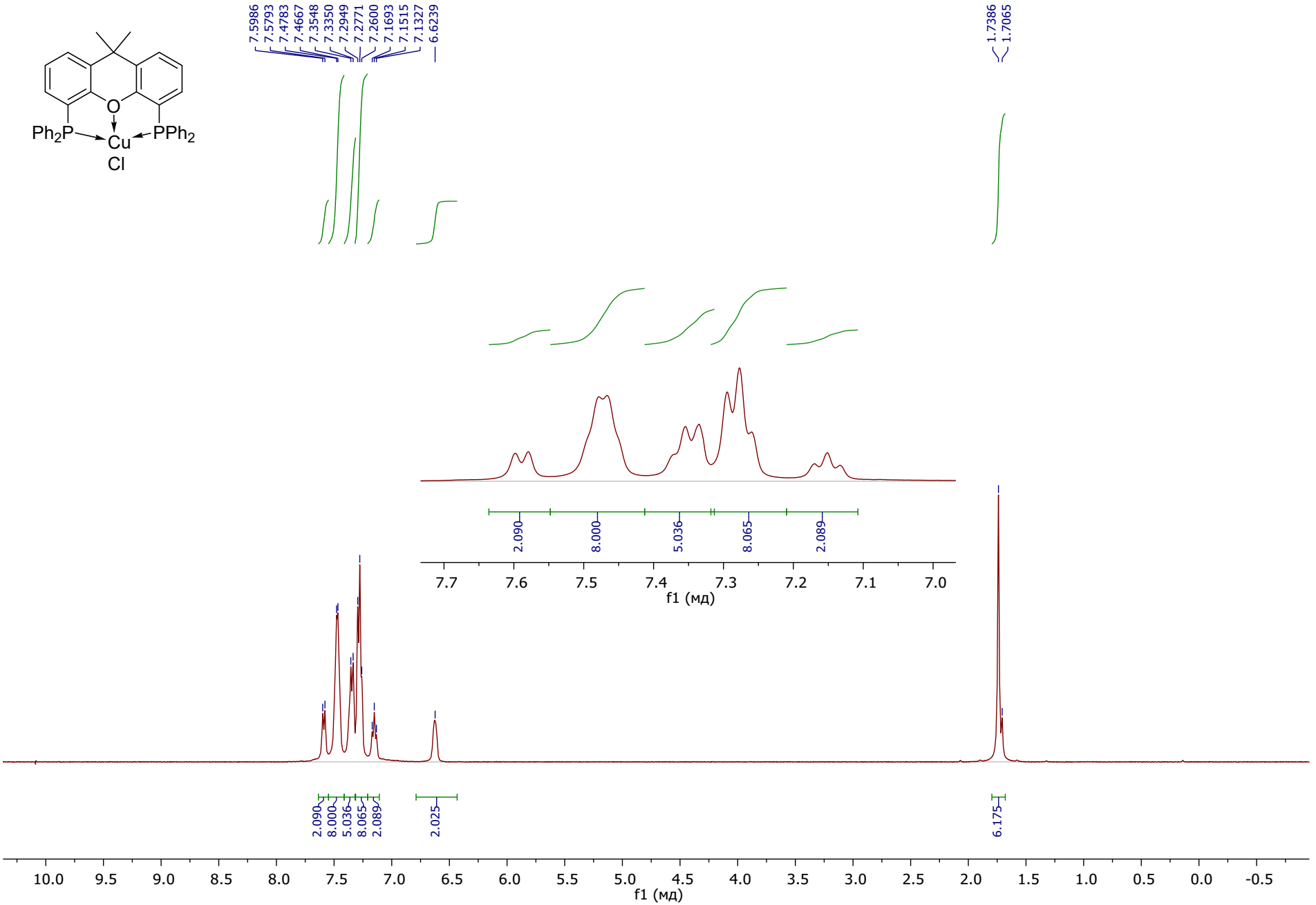
^{13}C NMR ($CDCl_3$, 101 MHz) **[Cu-8]**



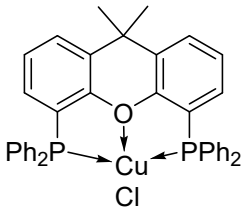
^{31}P NMR ($CDCl_3$, 121 MHz) **[Cu-8]**



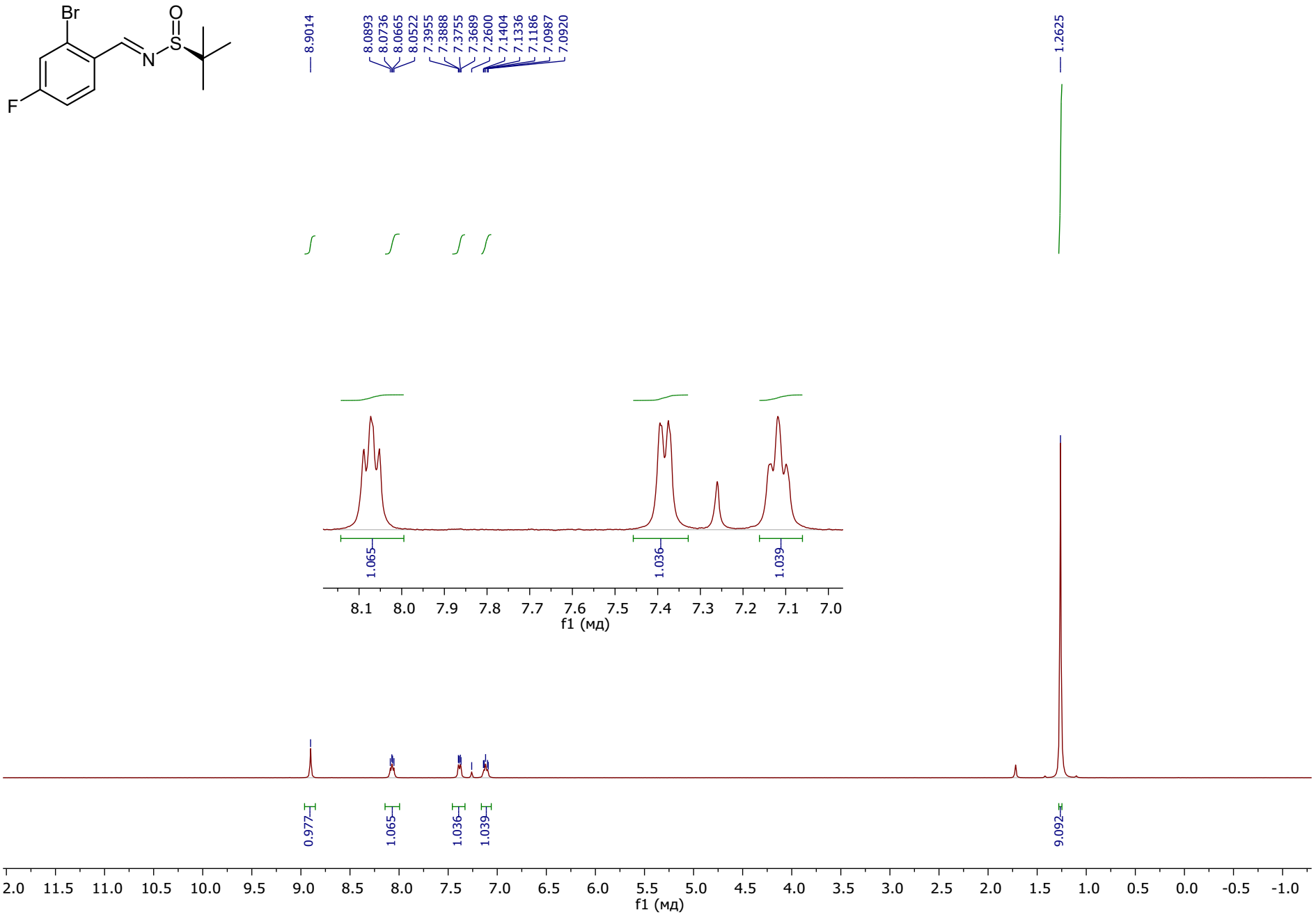
^{1}H NMR ($CDCl_3$, 400 MHz) **[Cu-9]**



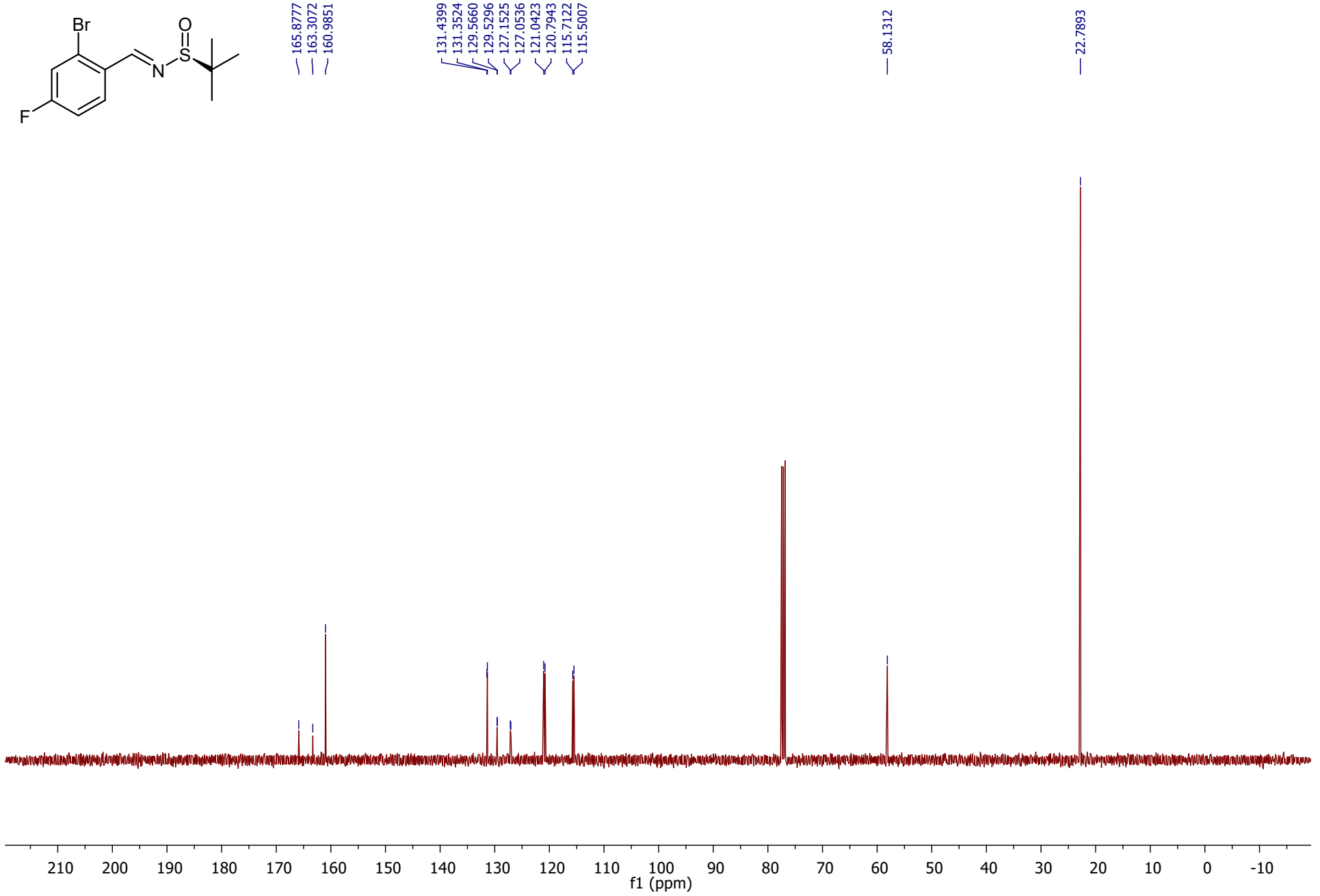
^{31}P NMR ($CDCl_3$, 162 MHz) **[Cu-9]**



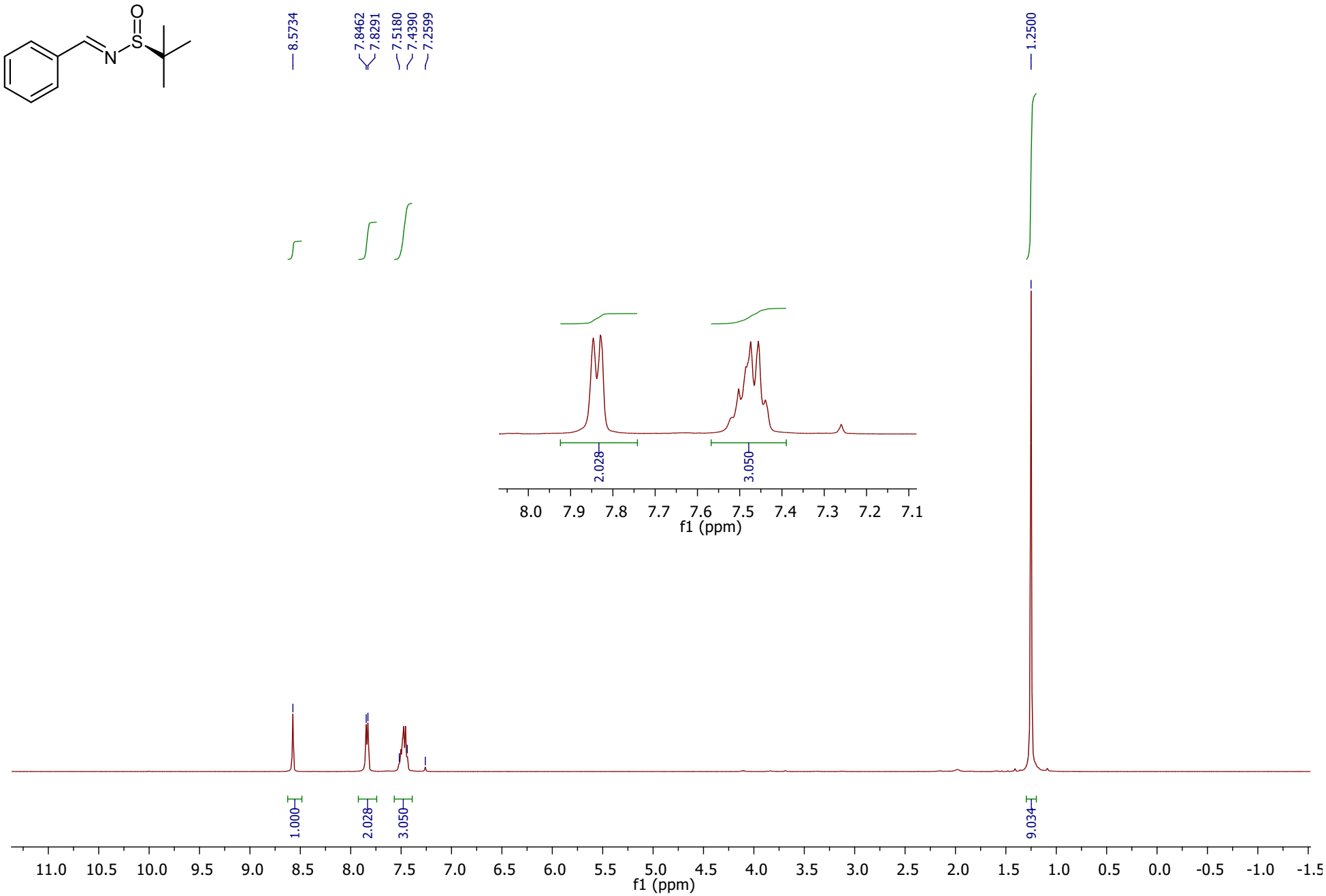
^{1}H NMR ($CDCl_3$, 400 MHz) **2a**



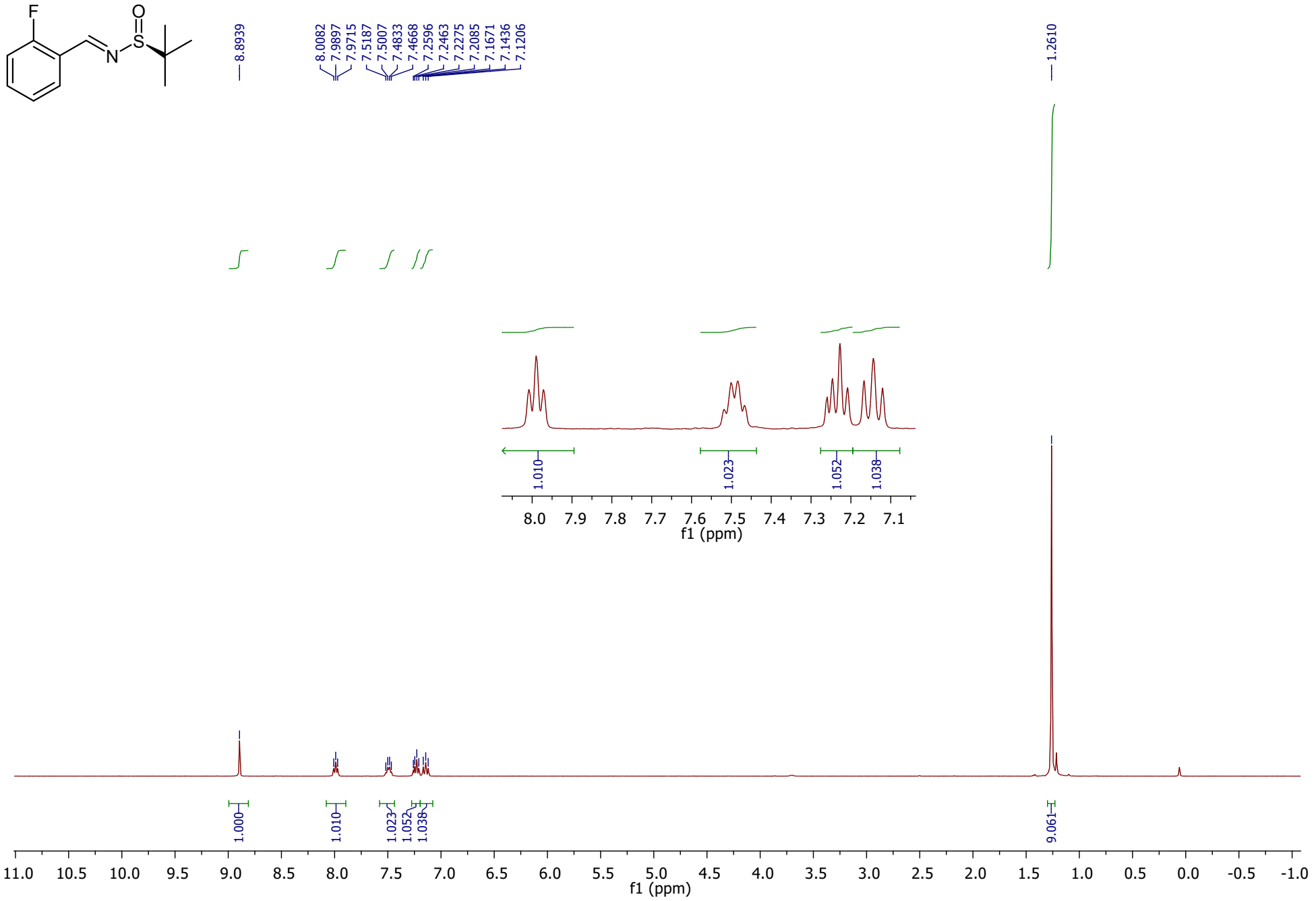
^{13}C NMR ($CDCl_3$, 101 MHz) **2a**



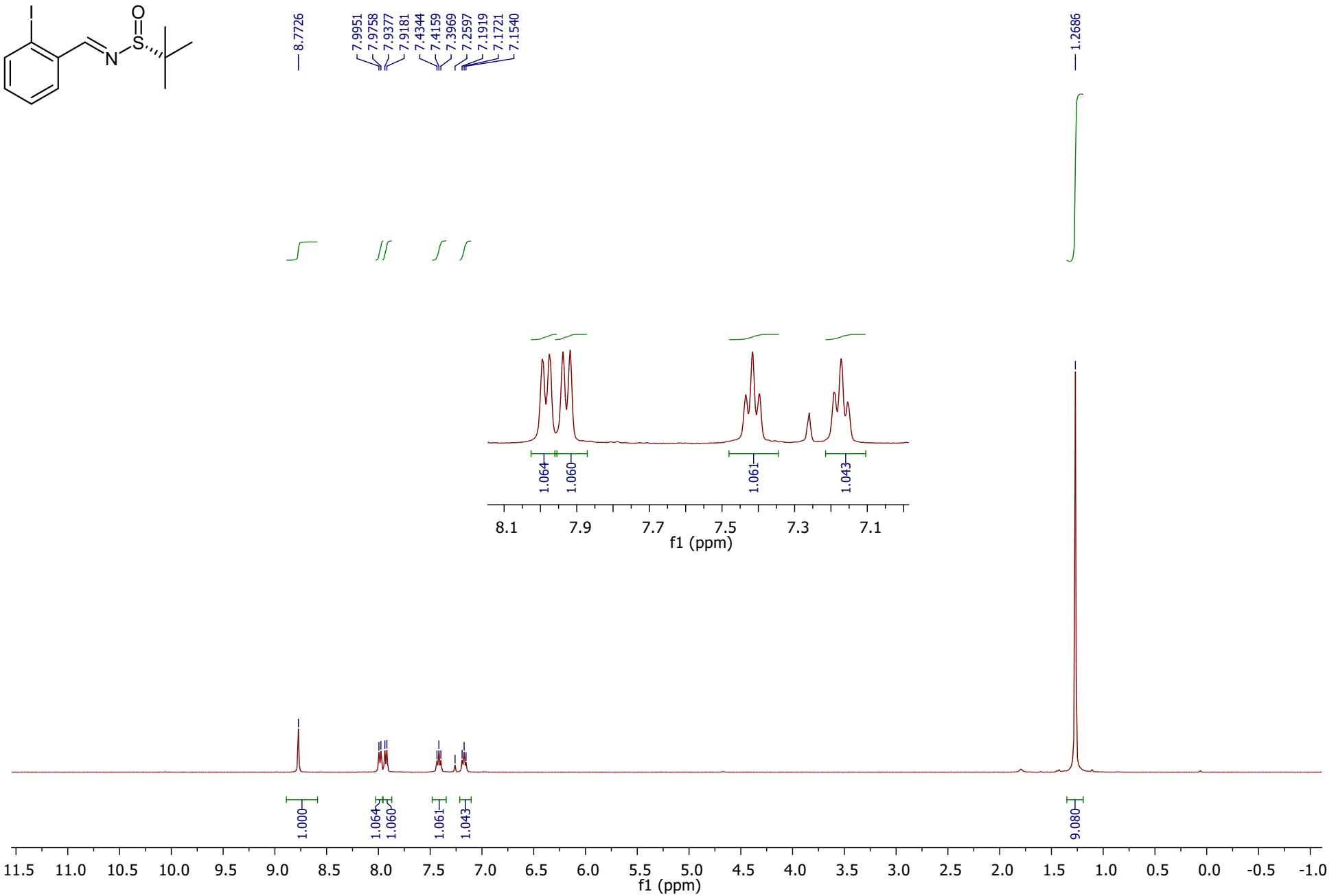
^{1}H NMR ($CDCl_3$, 400 MHz) **2b**



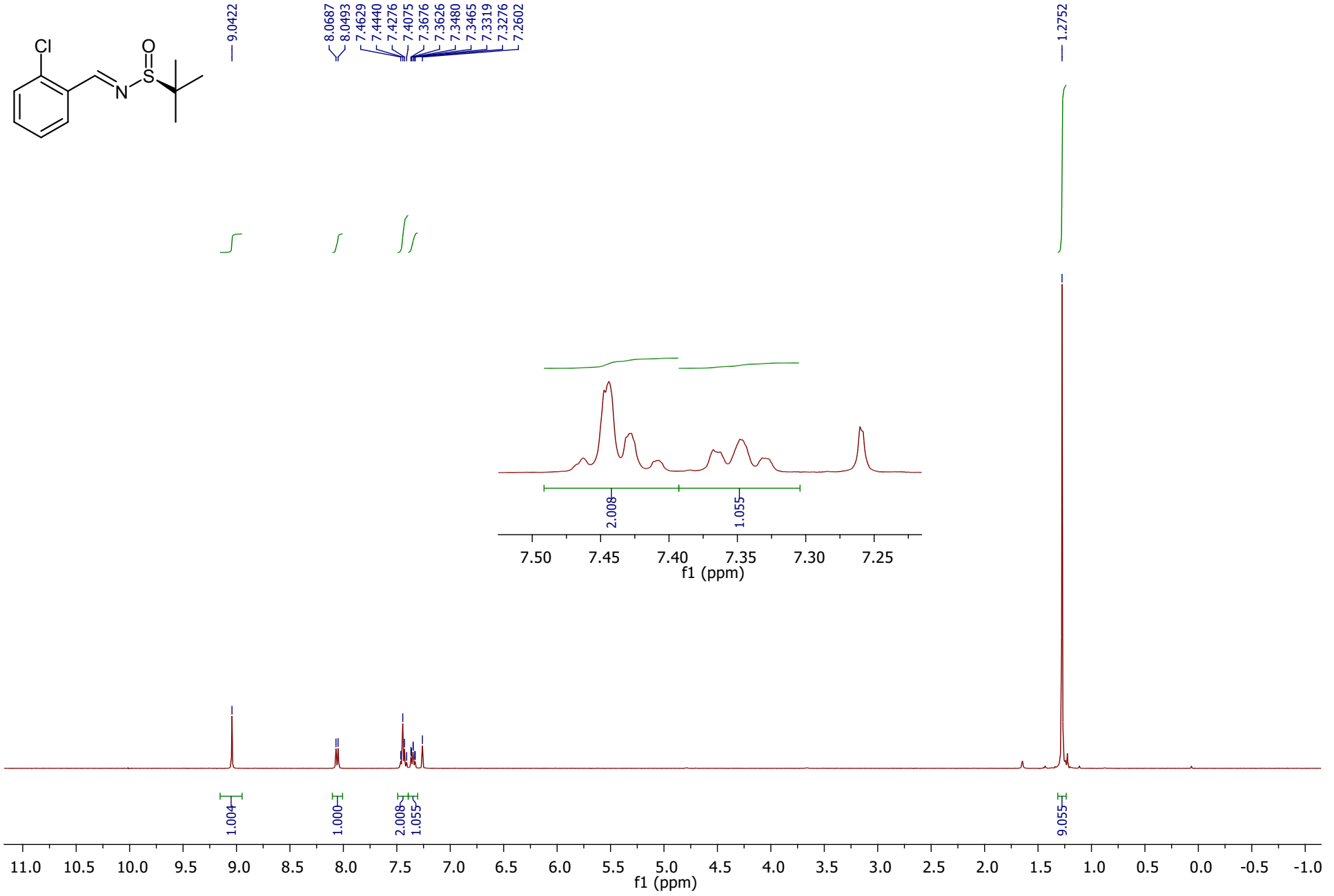
^{1}H NMR ($CDCl_3$, 400 MHz) **2c**



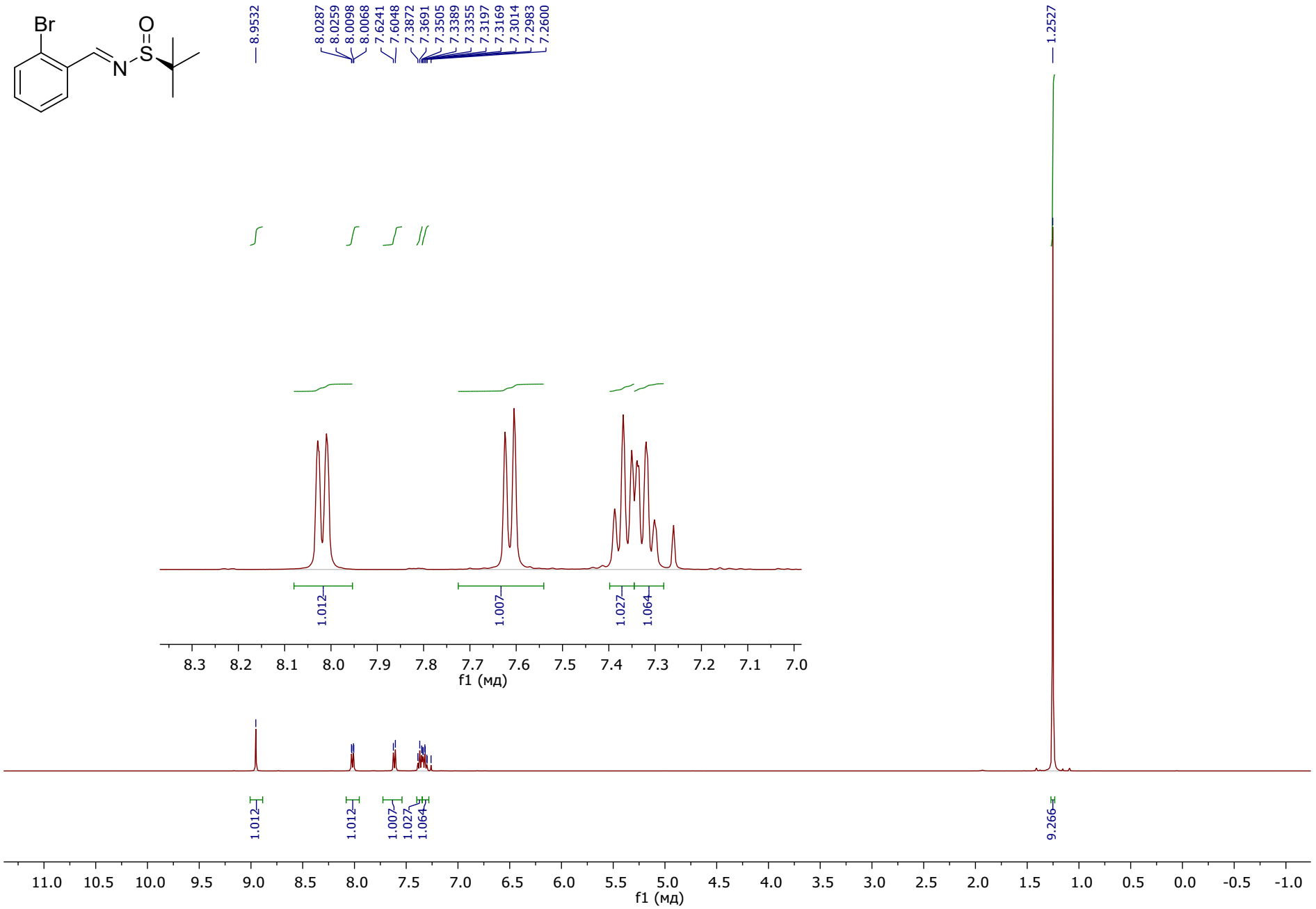
^{1}H NMR ($CDCl_3$, 400 MHz) **2d**



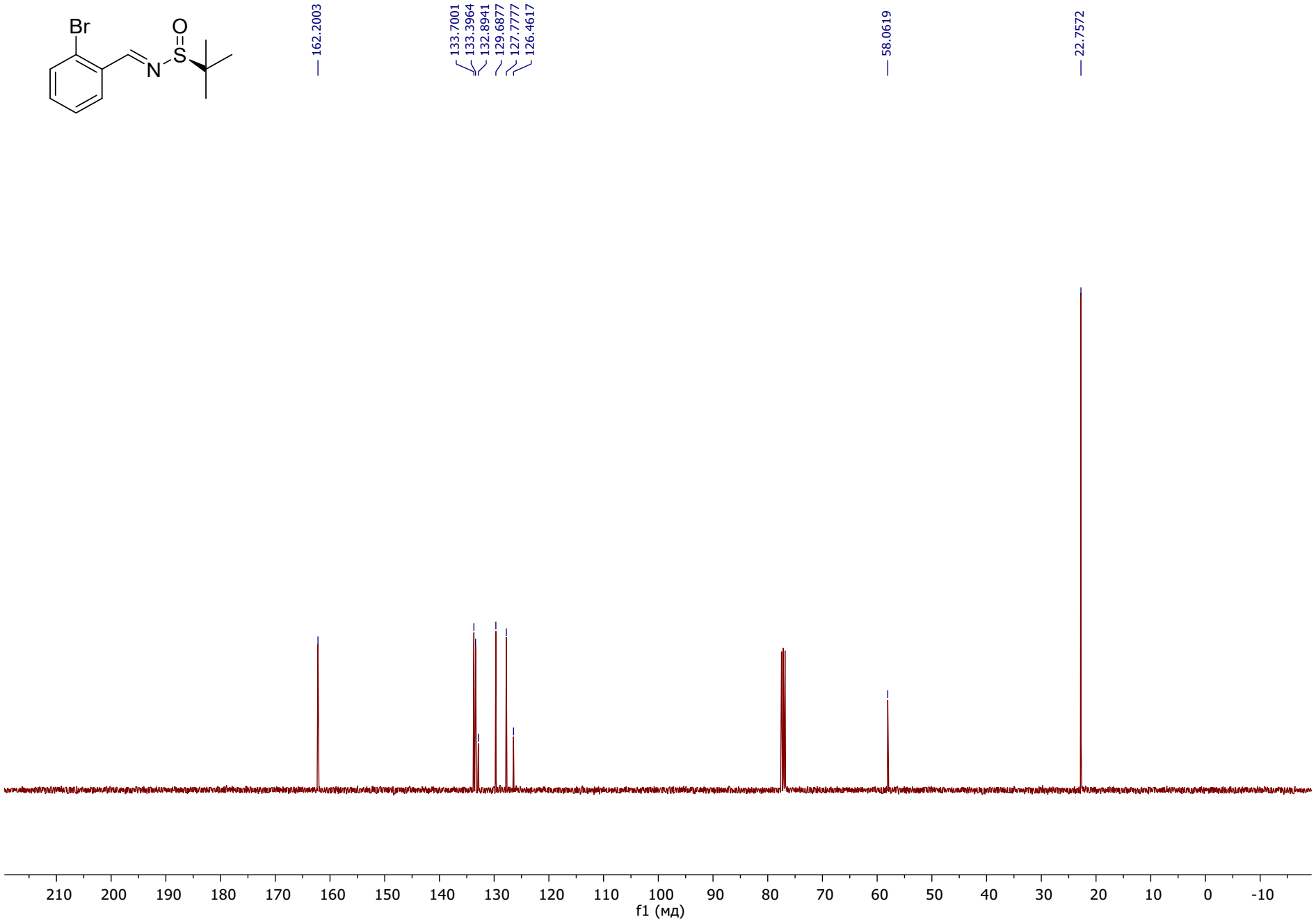
^{1}H NMR ($CDCl_3$, 400 MHz) **2e**



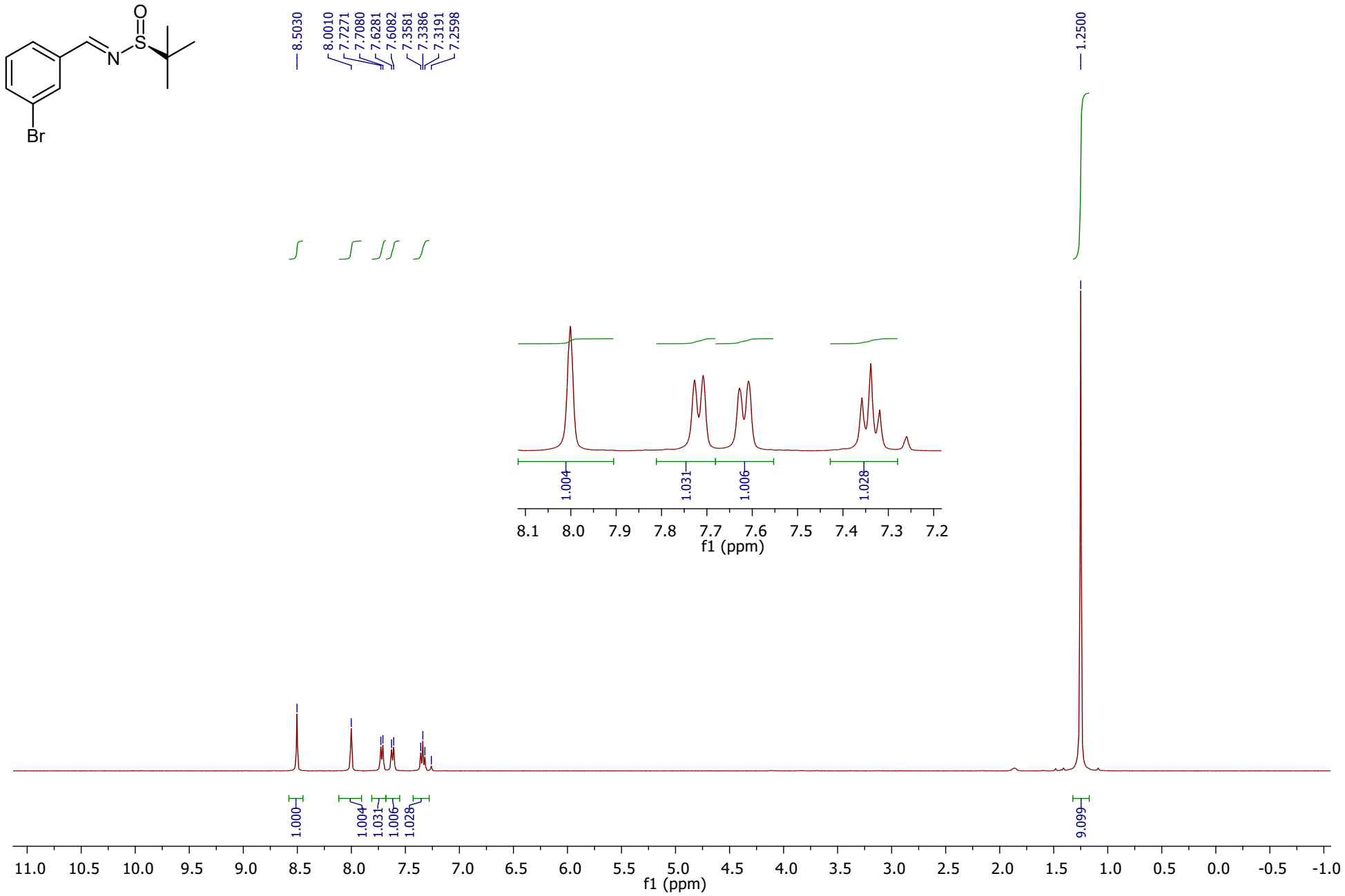
^{1}H NMR ($CDCl_3$, 400 MHz) **2f**



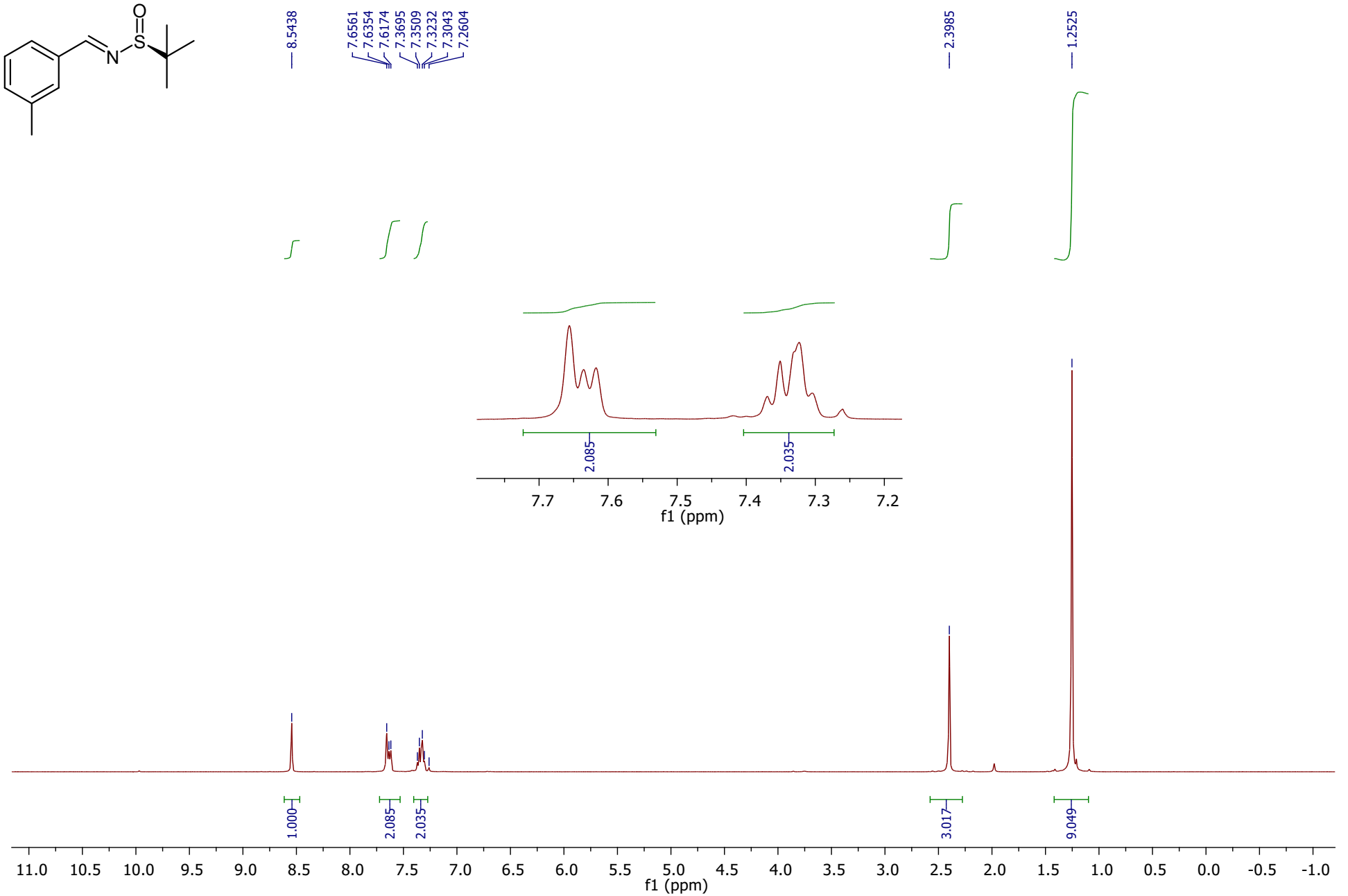
^{13}C NMR ($CDCl_3$, 101 MHz) **2f**



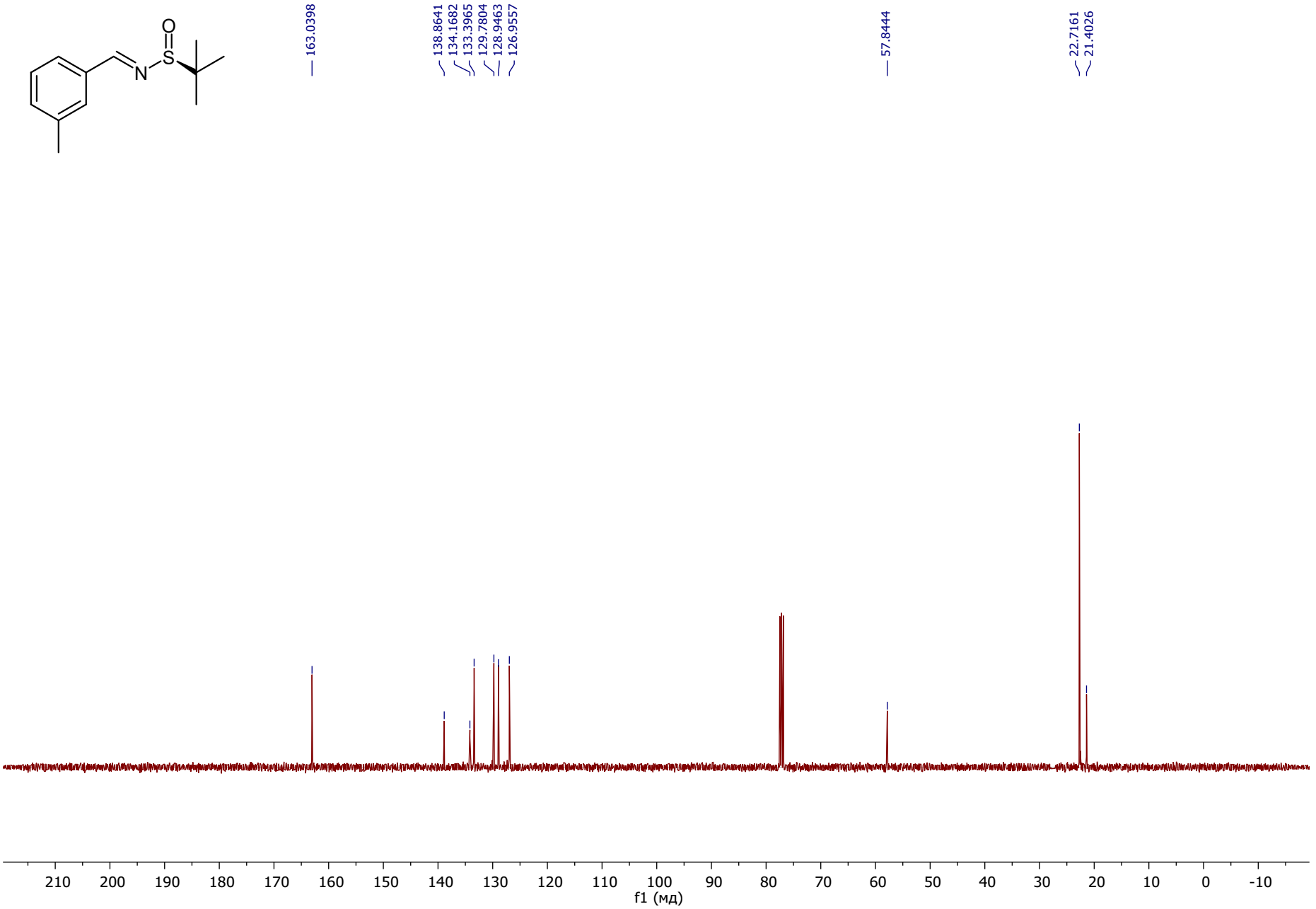
^{1}H NMR ($CDCl_3$, 400 MHz) **2g**



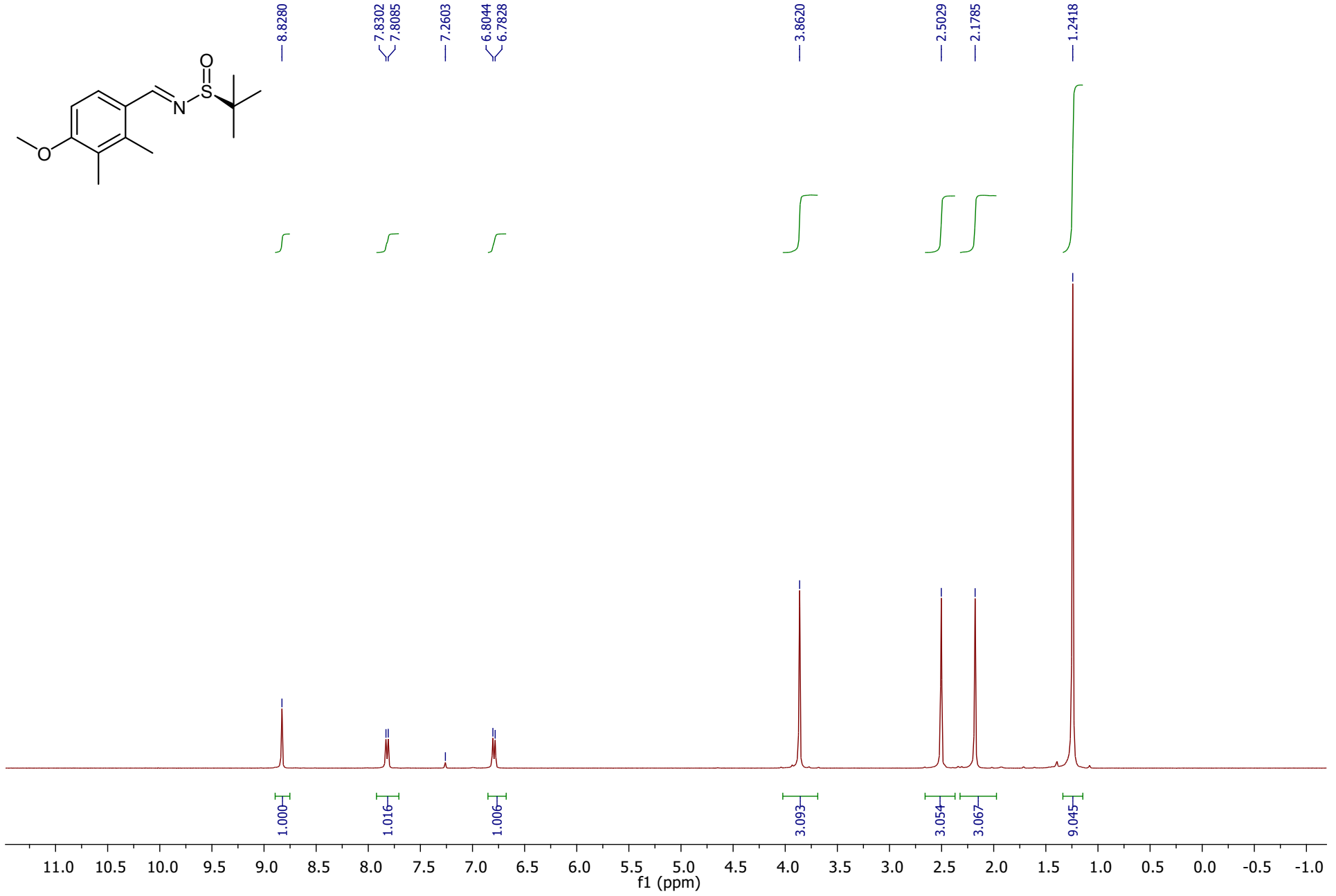
^{1}H NMR ($CDCl_3$, 400 MHz) **2h**



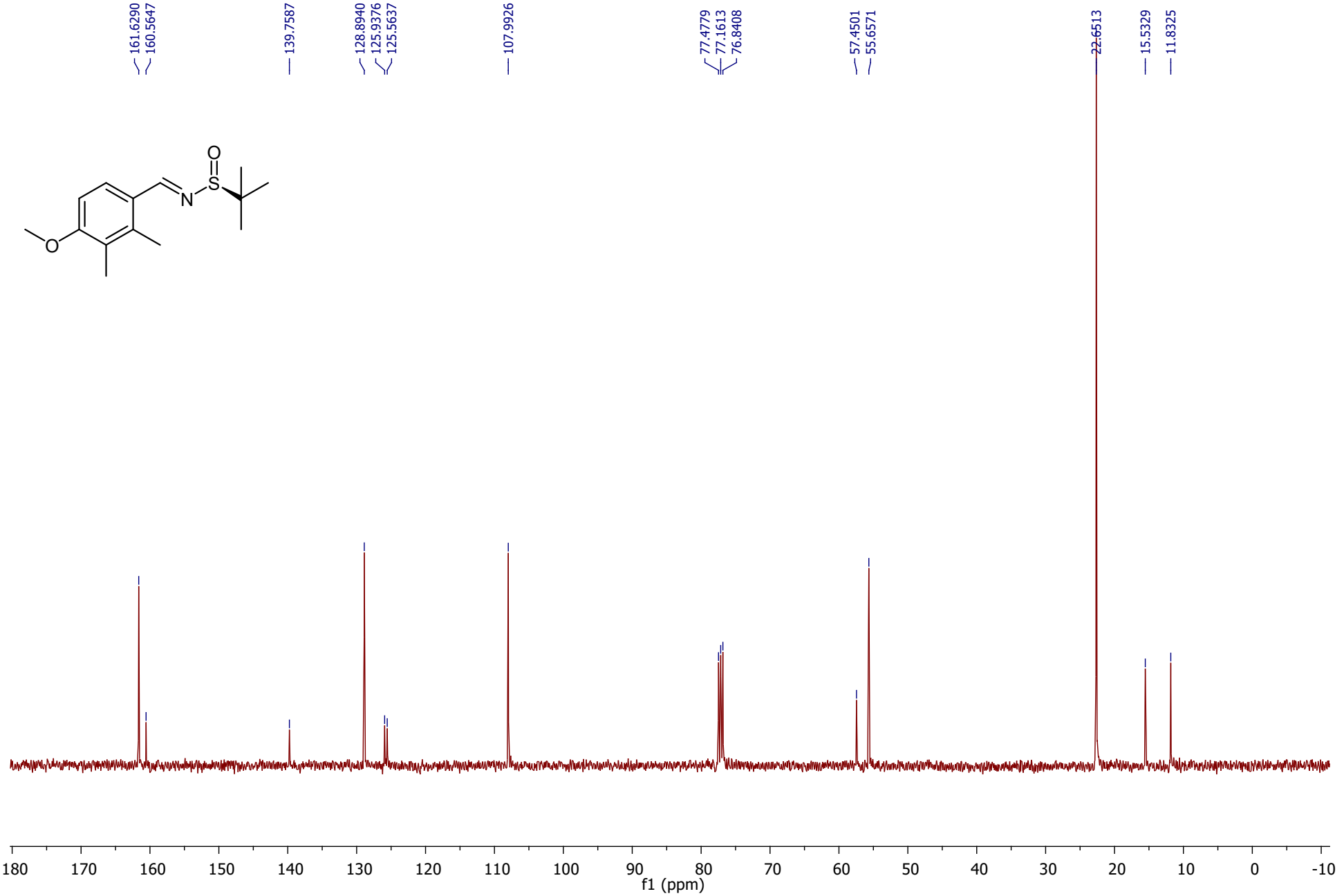
^{13}C NMR ($CDCl_3$, 101 MHz) **2h**



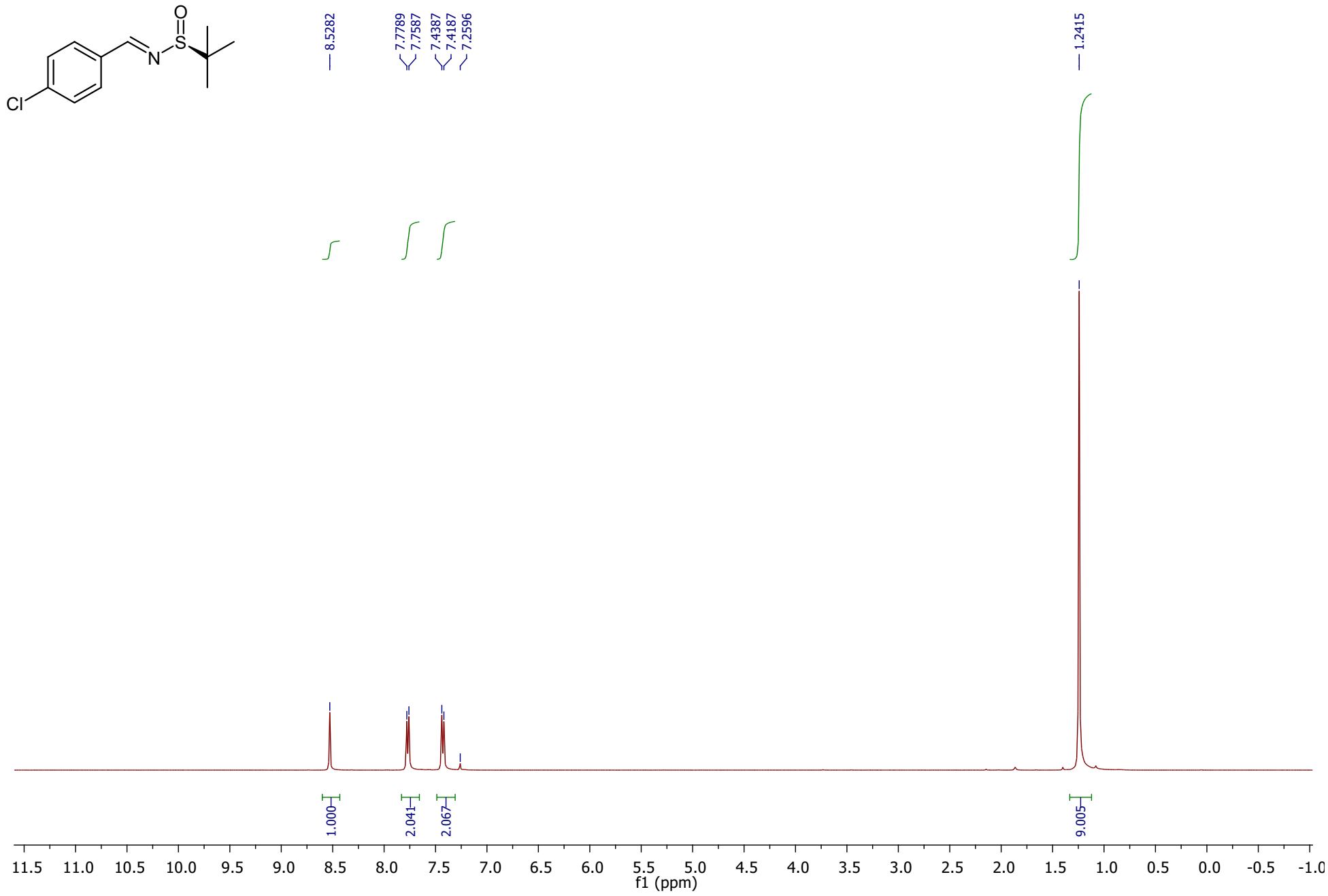
^{1}H NMR ($CDCl_3$, 400 MHz) **2i**



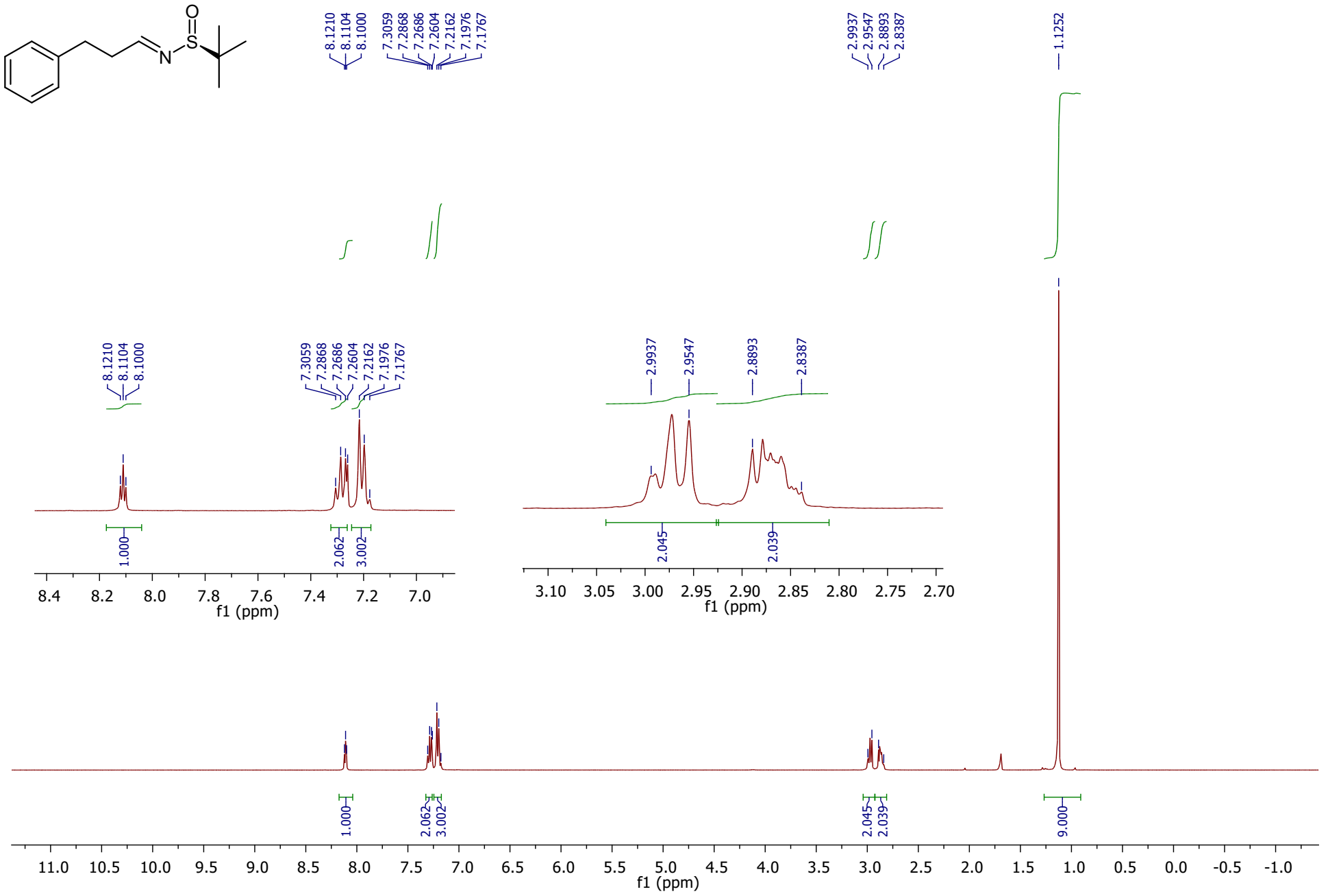
^{13}C NMR ($CDCl_3$, 101 MHz) **2i**



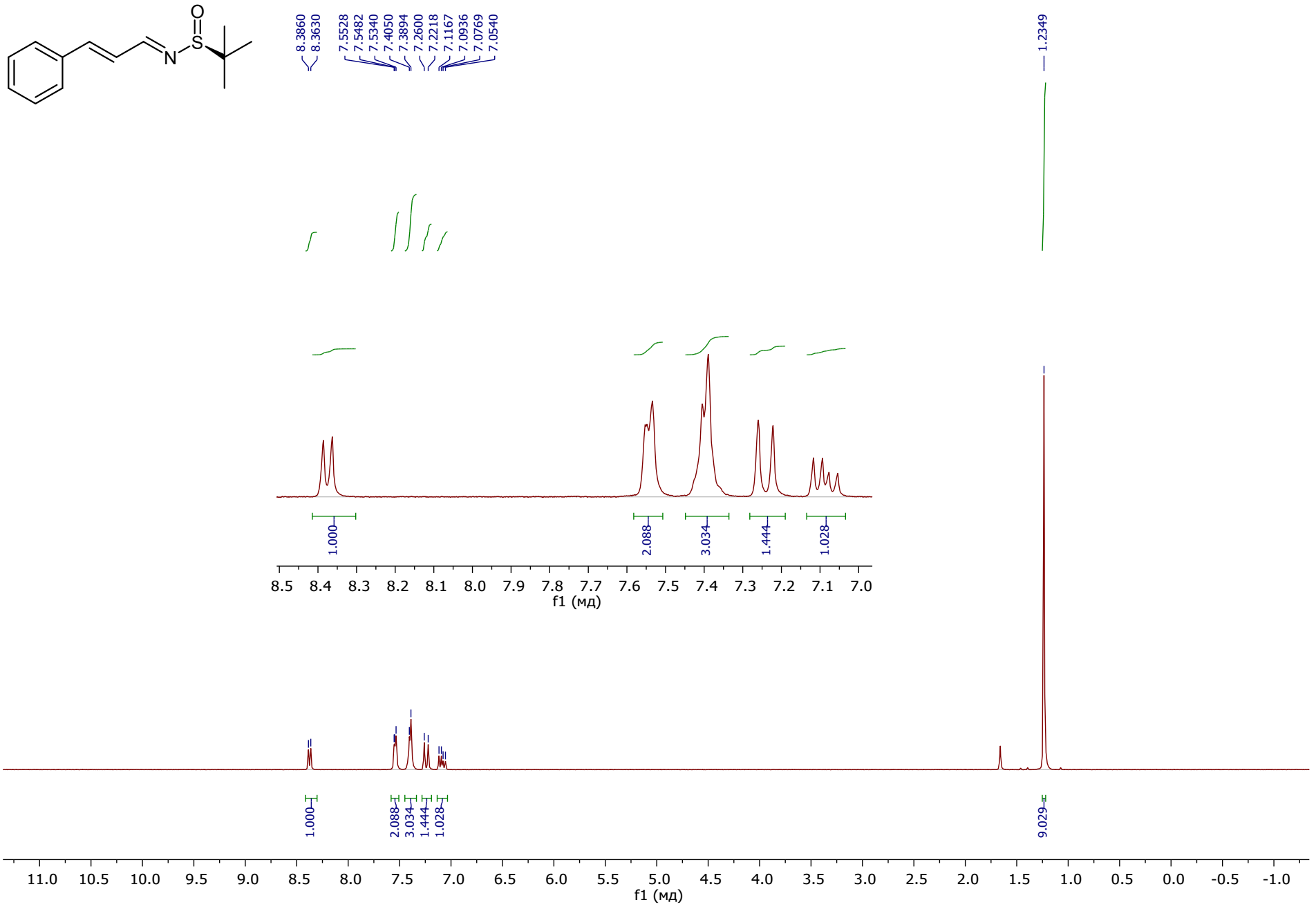
^{1}H NMR ($CDCl_3$, 400 MHz) **2j**



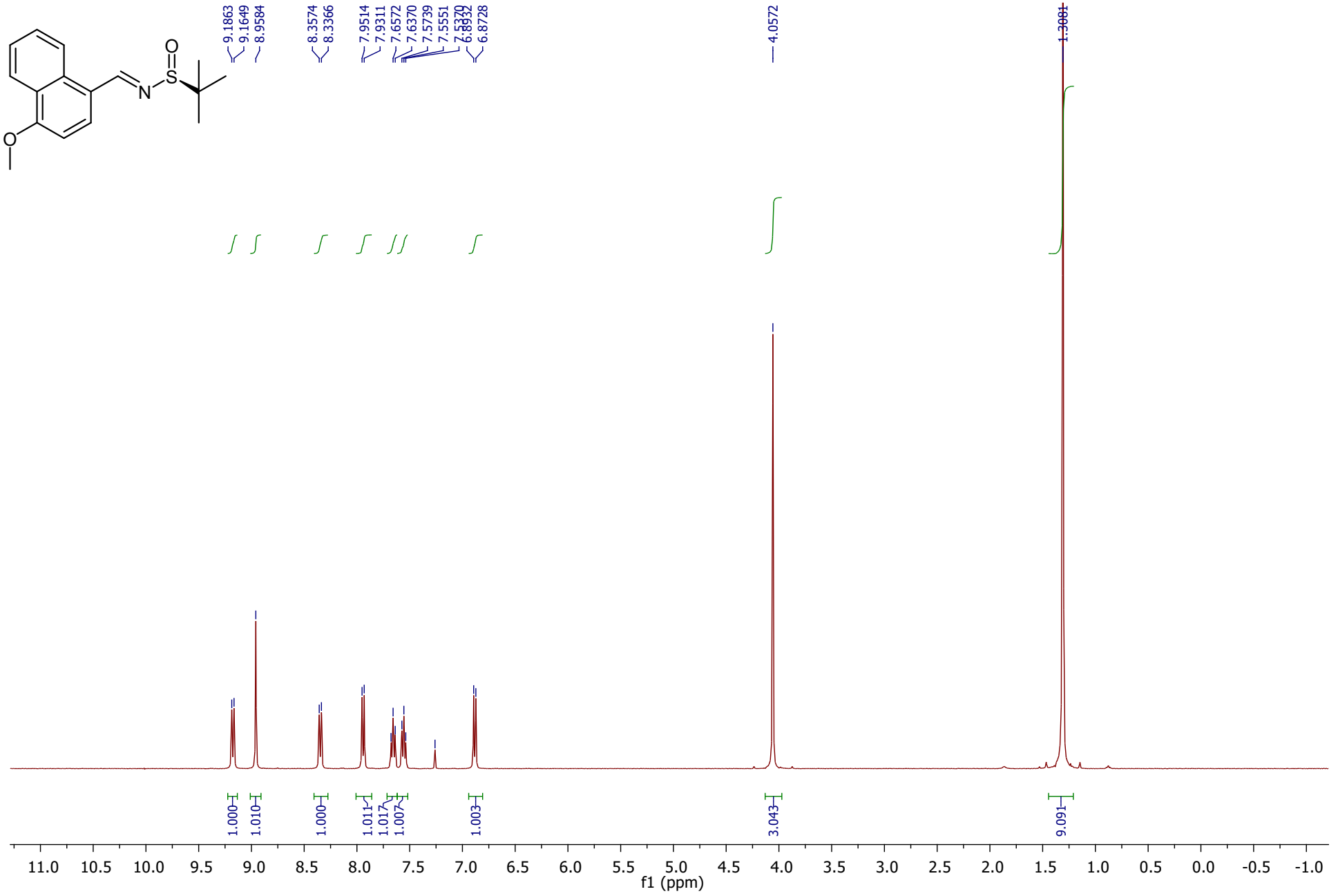
^{1}H NMR ($CDCl_3$, 400 MHz) **2k**



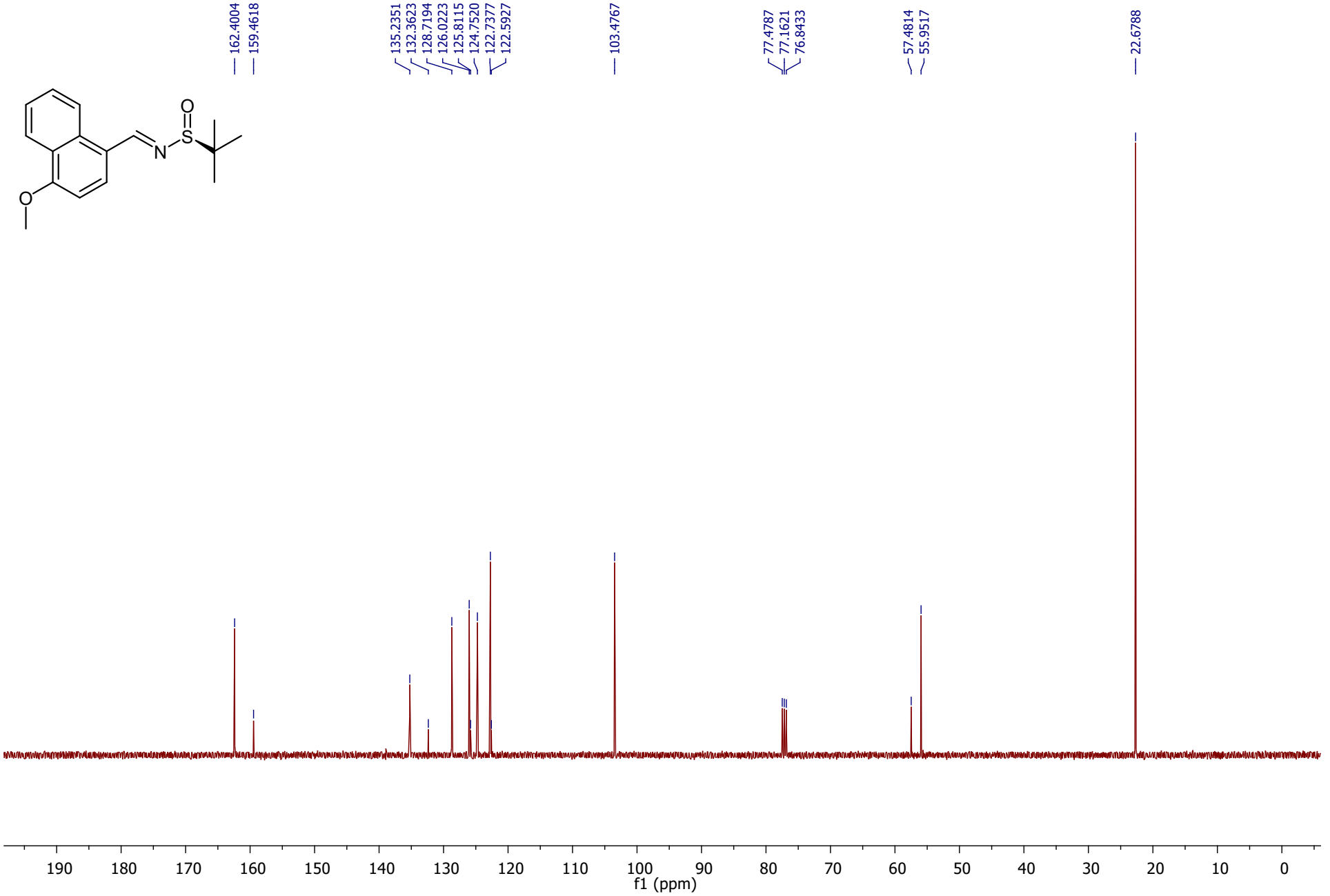
^{1}H NMR ($CDCl_3$, 400 MHz) **2l**



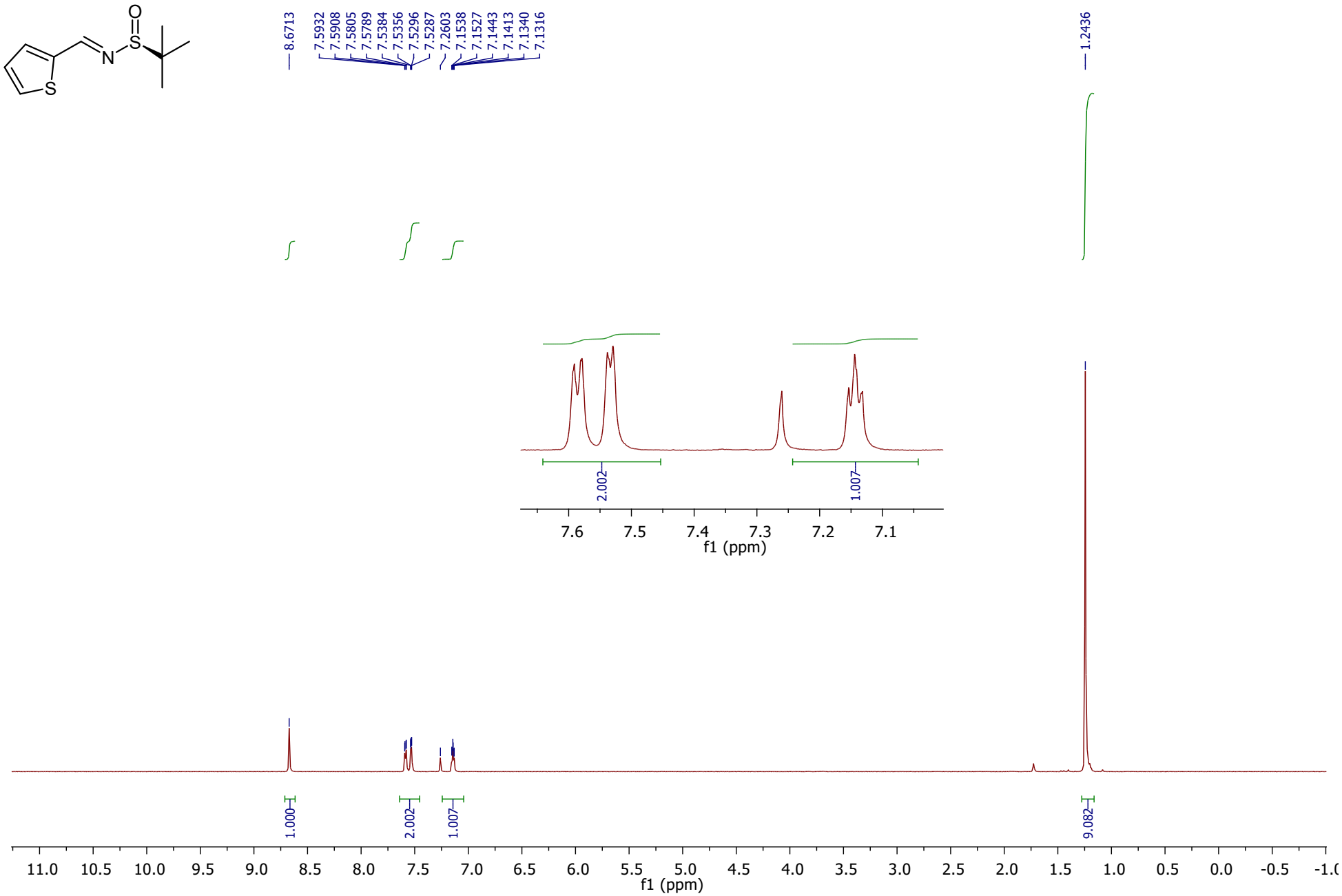
^{1}H NMR ($CDCl_3$, 400 MHz) **2m**



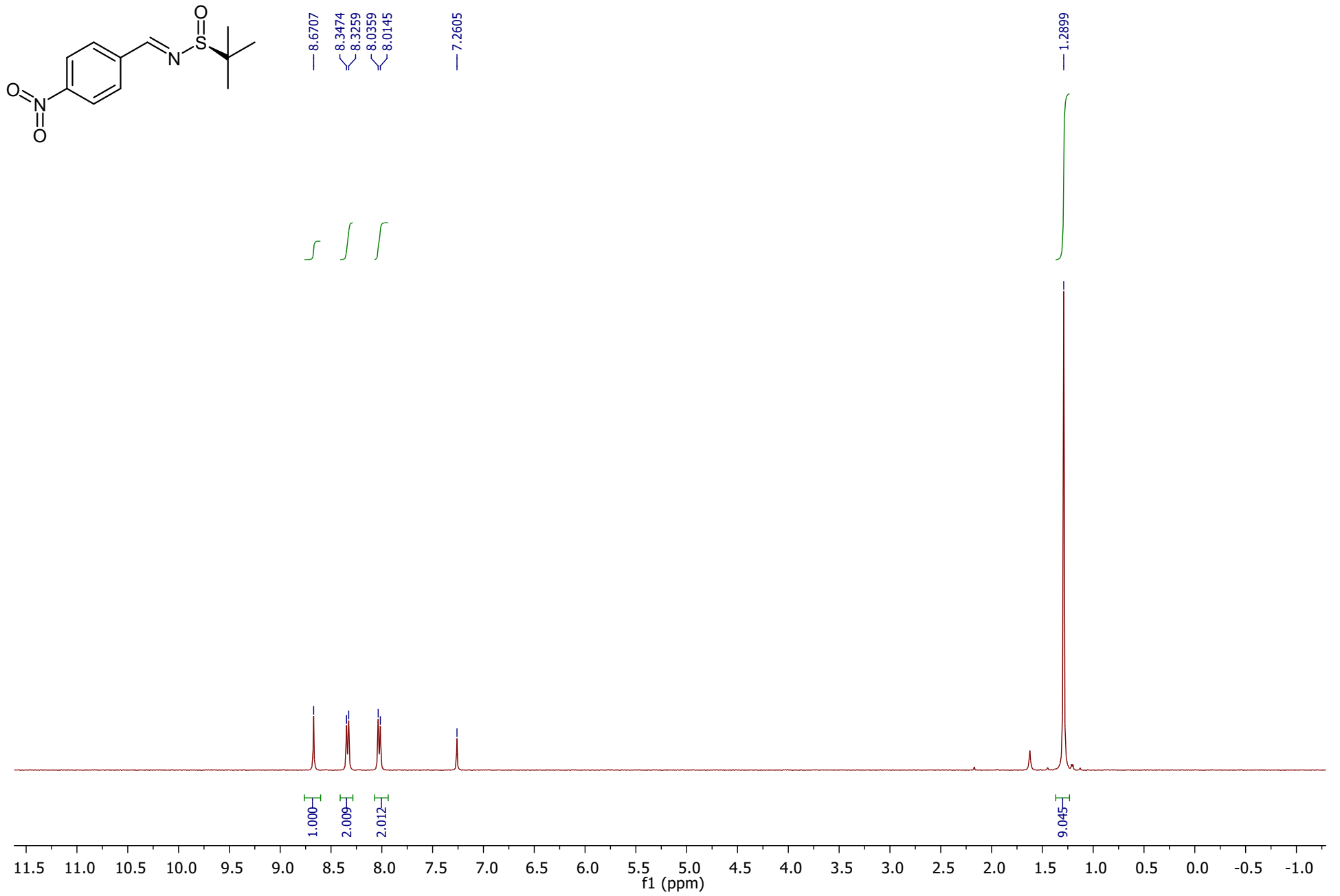
^{13}C NMR ($CDCl_3$, 101 MHz) **2m**



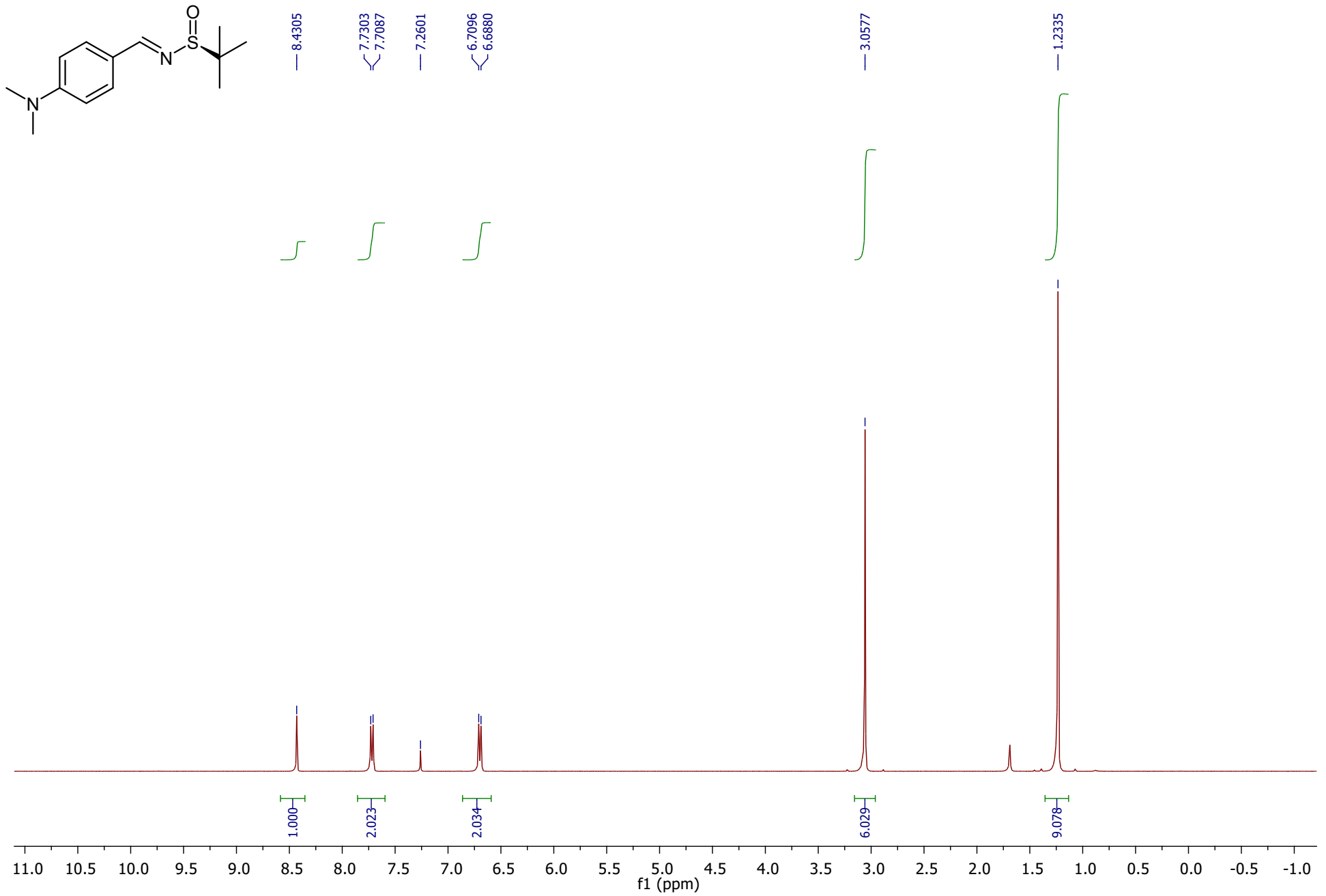
^{1}H NMR ($CDCl_3$, 400 MHz) **2n**



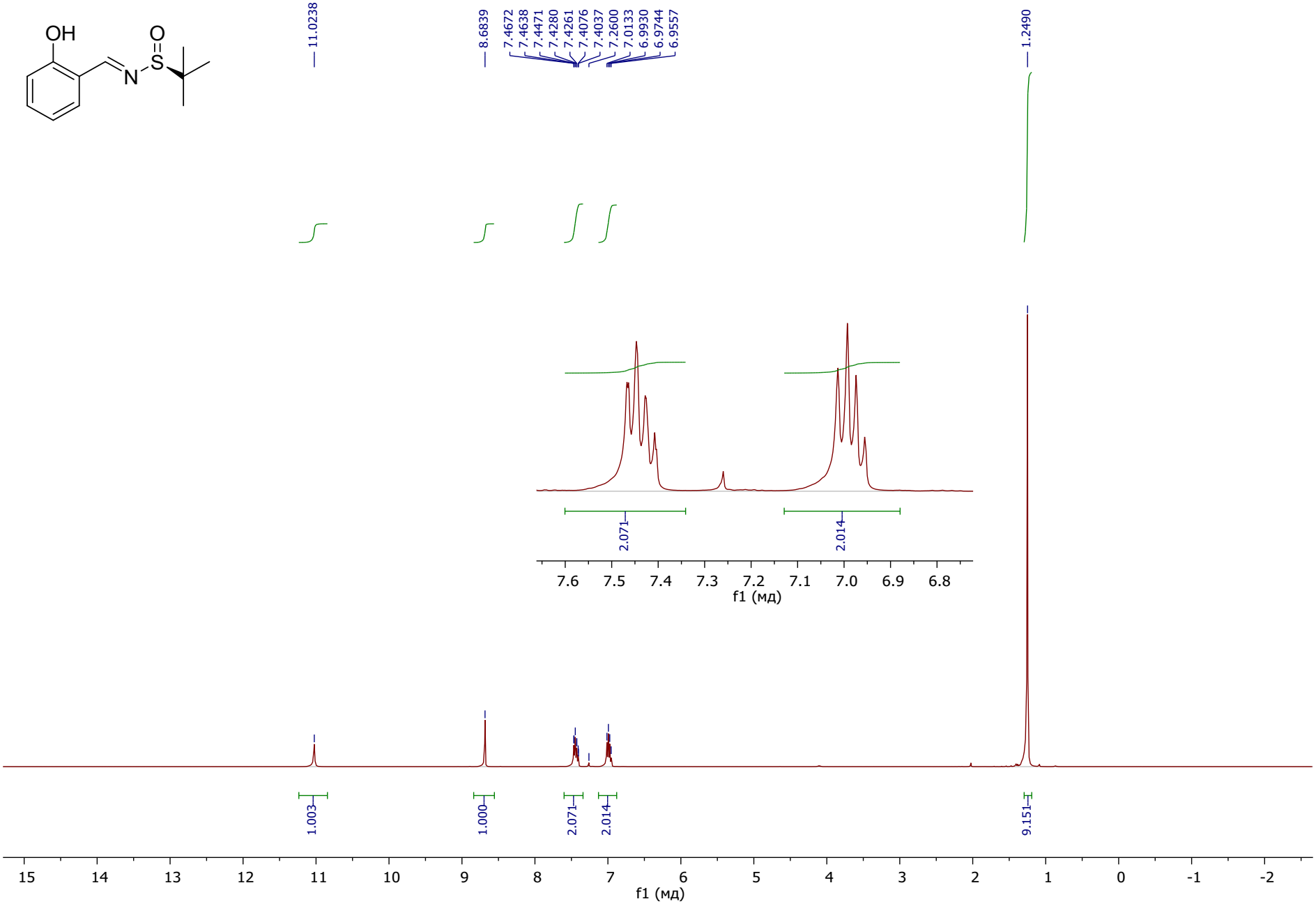
^{1}H NMR ($CDCl_3$, 400 MHz) **2o**



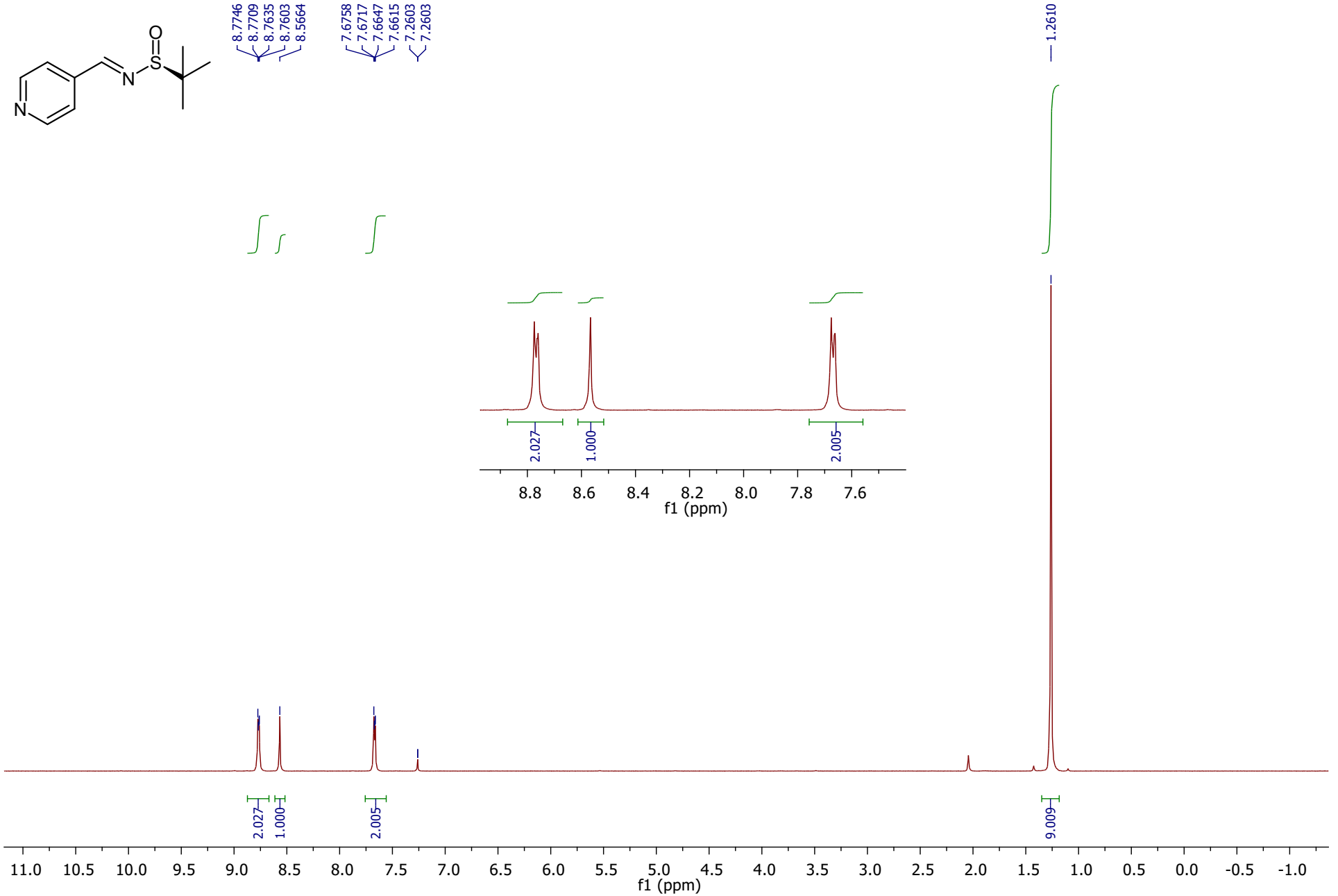
^{1}H NMR ($CDCl_3$, 400 MHz) **2p**



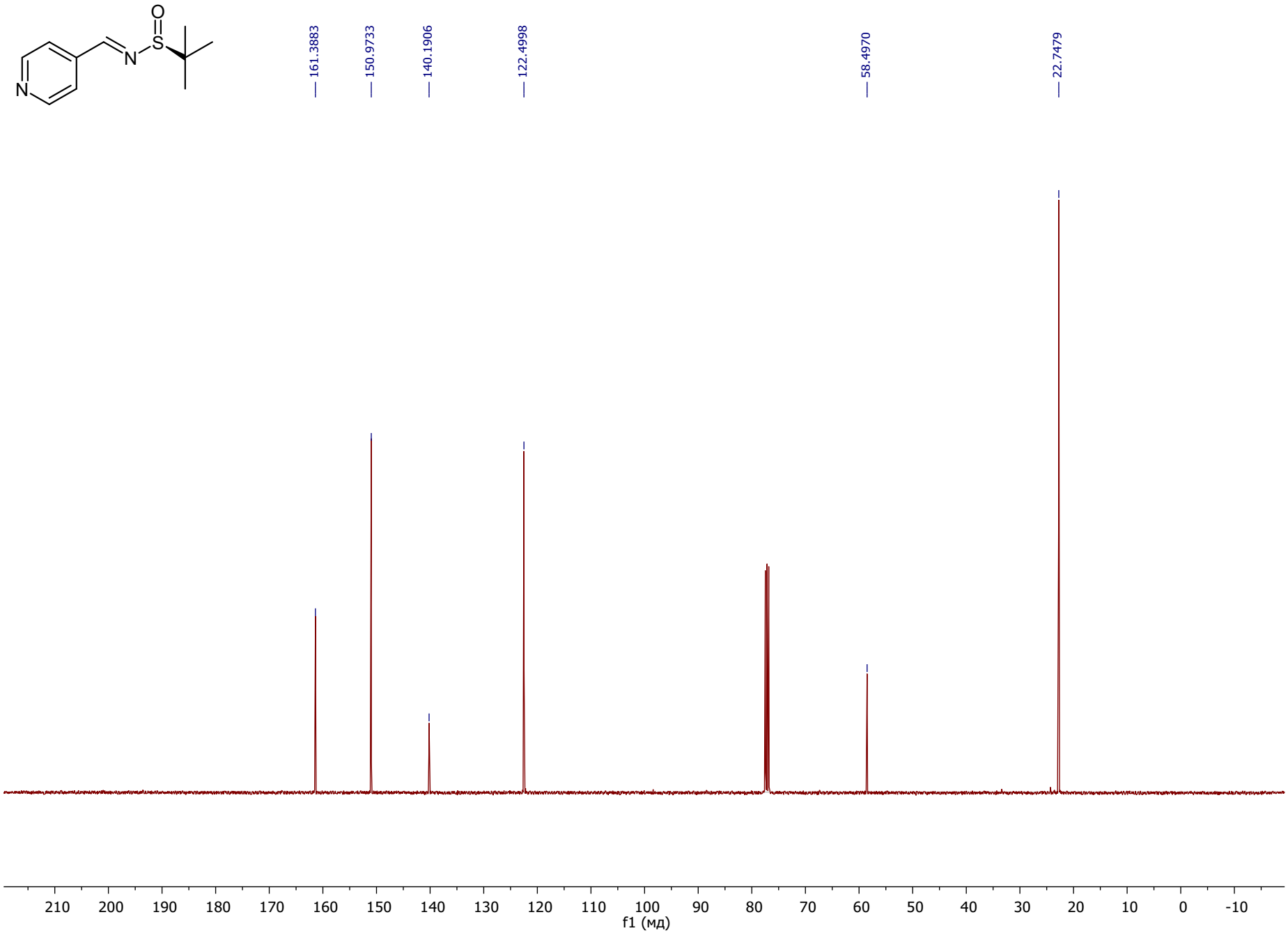
^{1}H NMR ($CDCl_3$, 400 MHz) **2q**



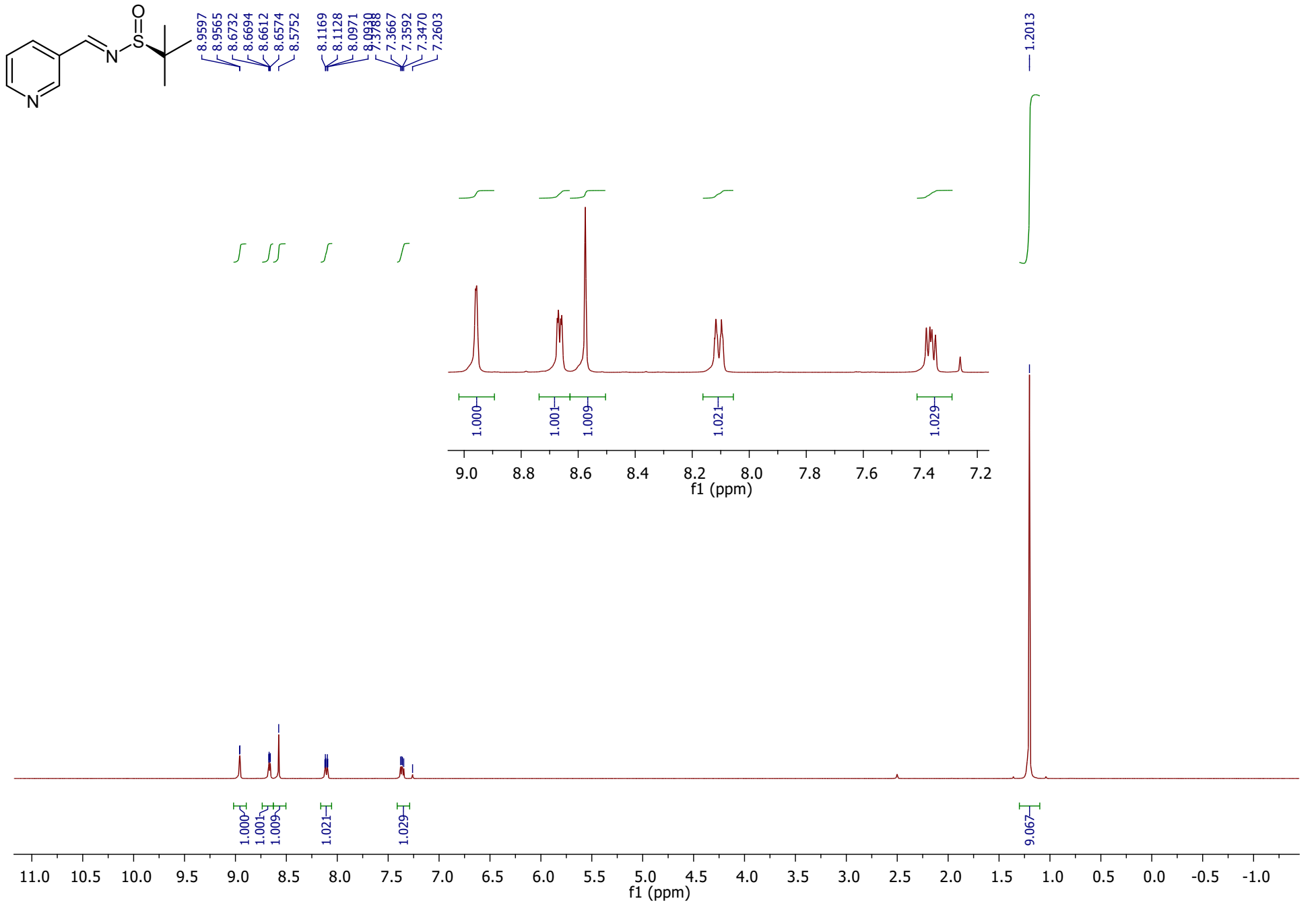
^{1}H NMR ($CDCl_3$, 400 MHz) **2r**



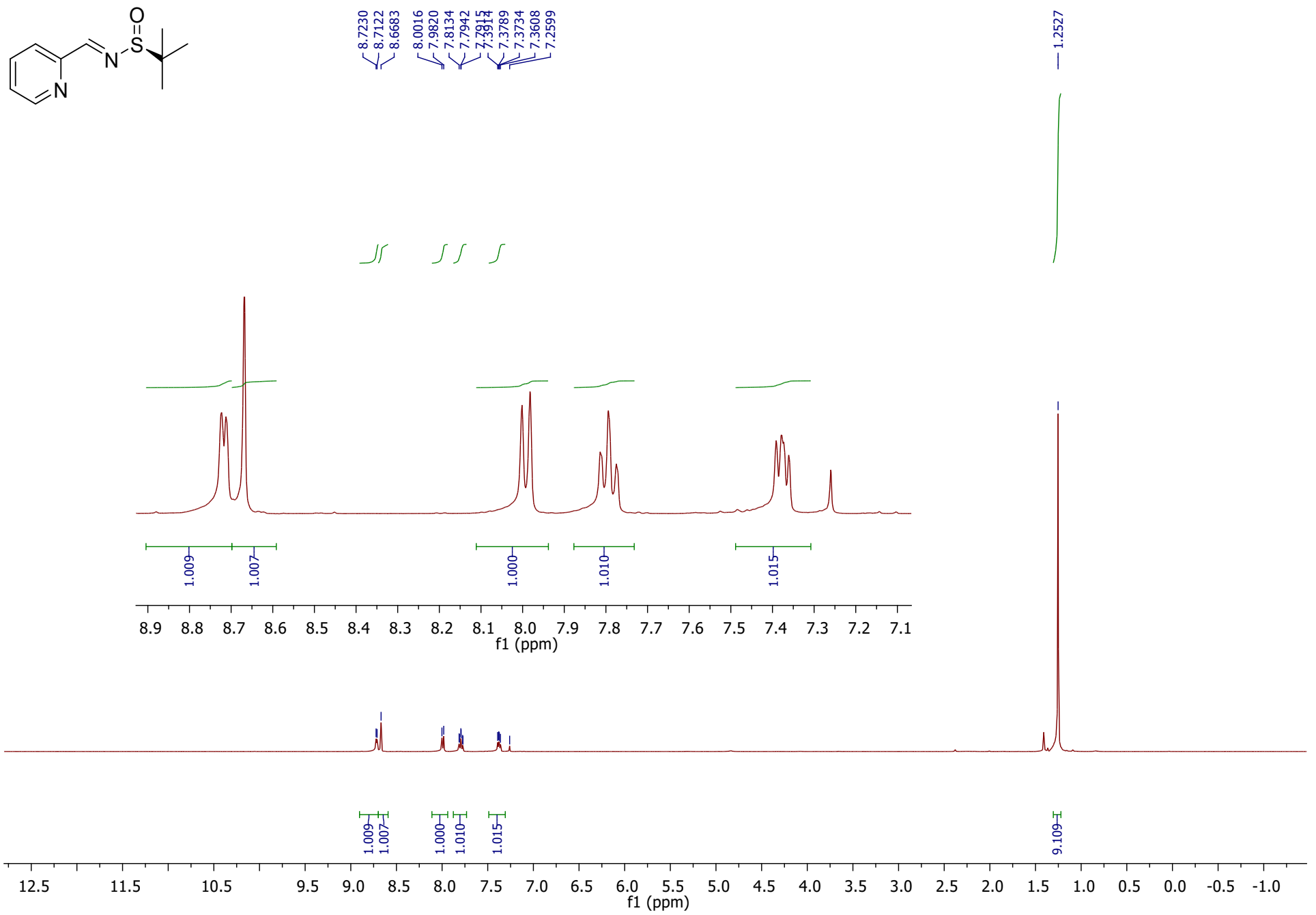
^{13}C NMR ($CDCl_3$, 101 MHz) **2r**



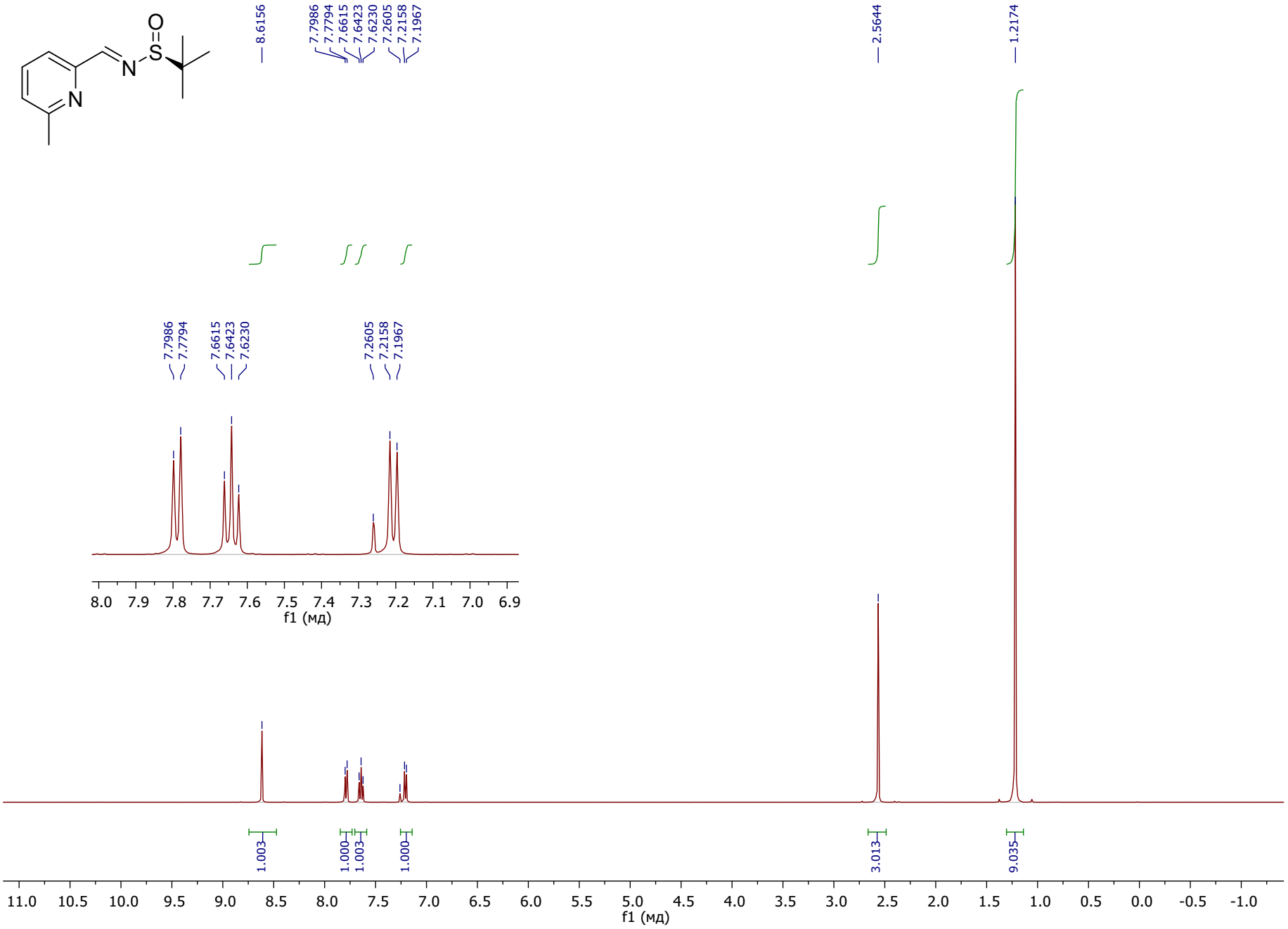
^{1}H NMR ($CDCl_3$, 400 MHz) **2s**



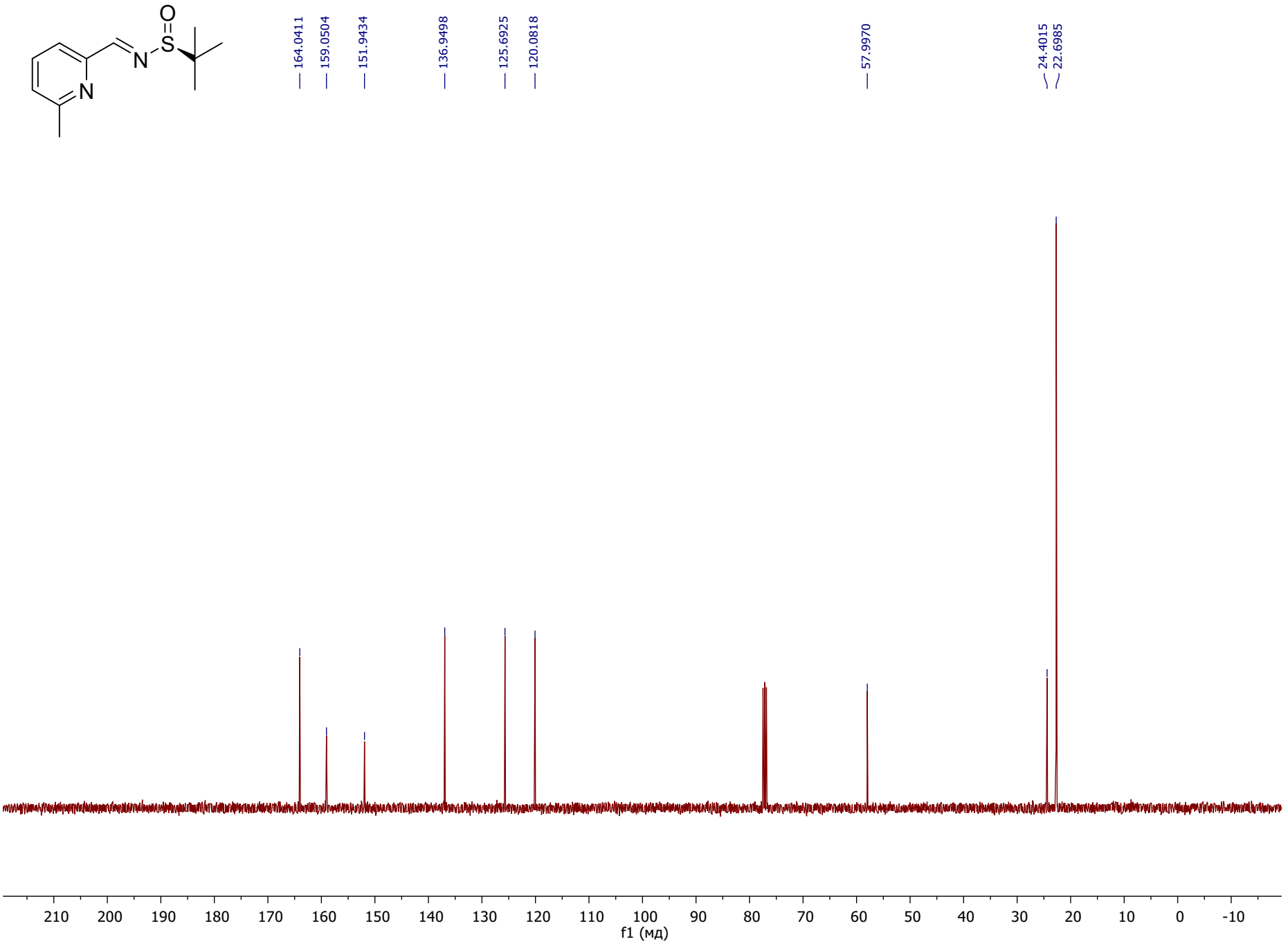
^{1}H NMR ($CDCl_3$, 400 MHz) **2t**



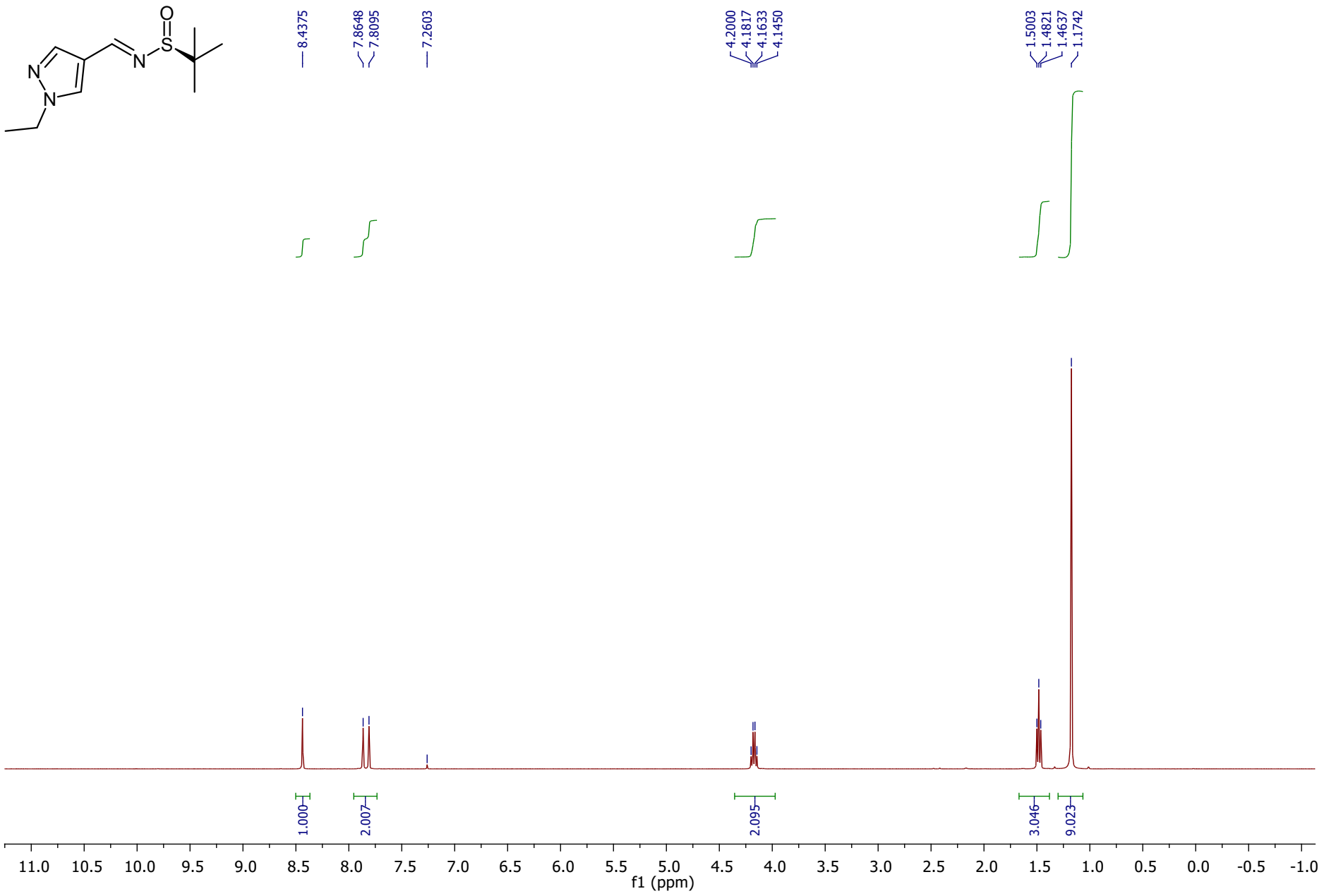
^{1}H NMR ($CDCl_3$, 400 MHz) **2u**



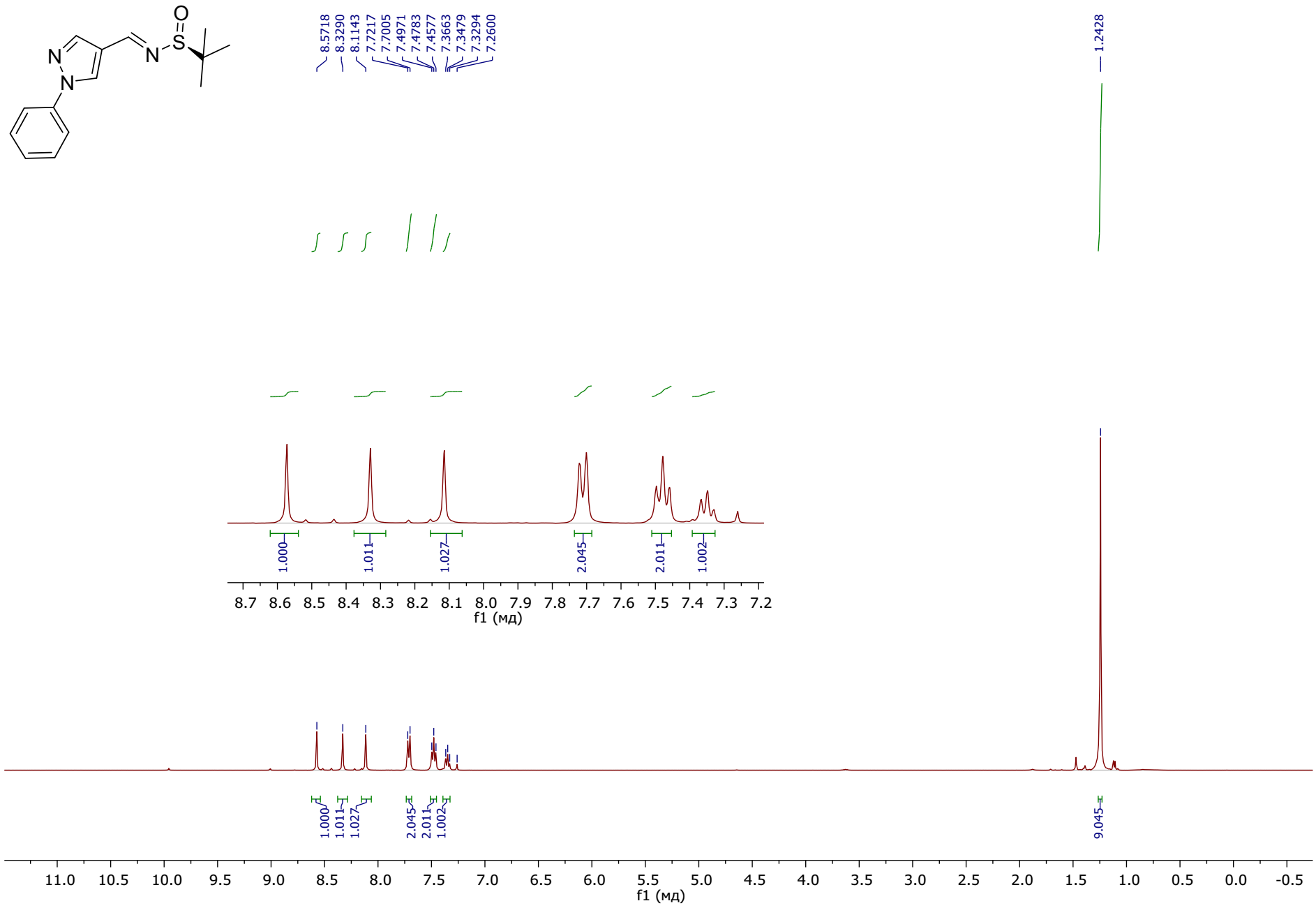
^{13}C NMR ($CDCl_3$, 101 MHz) **2u**



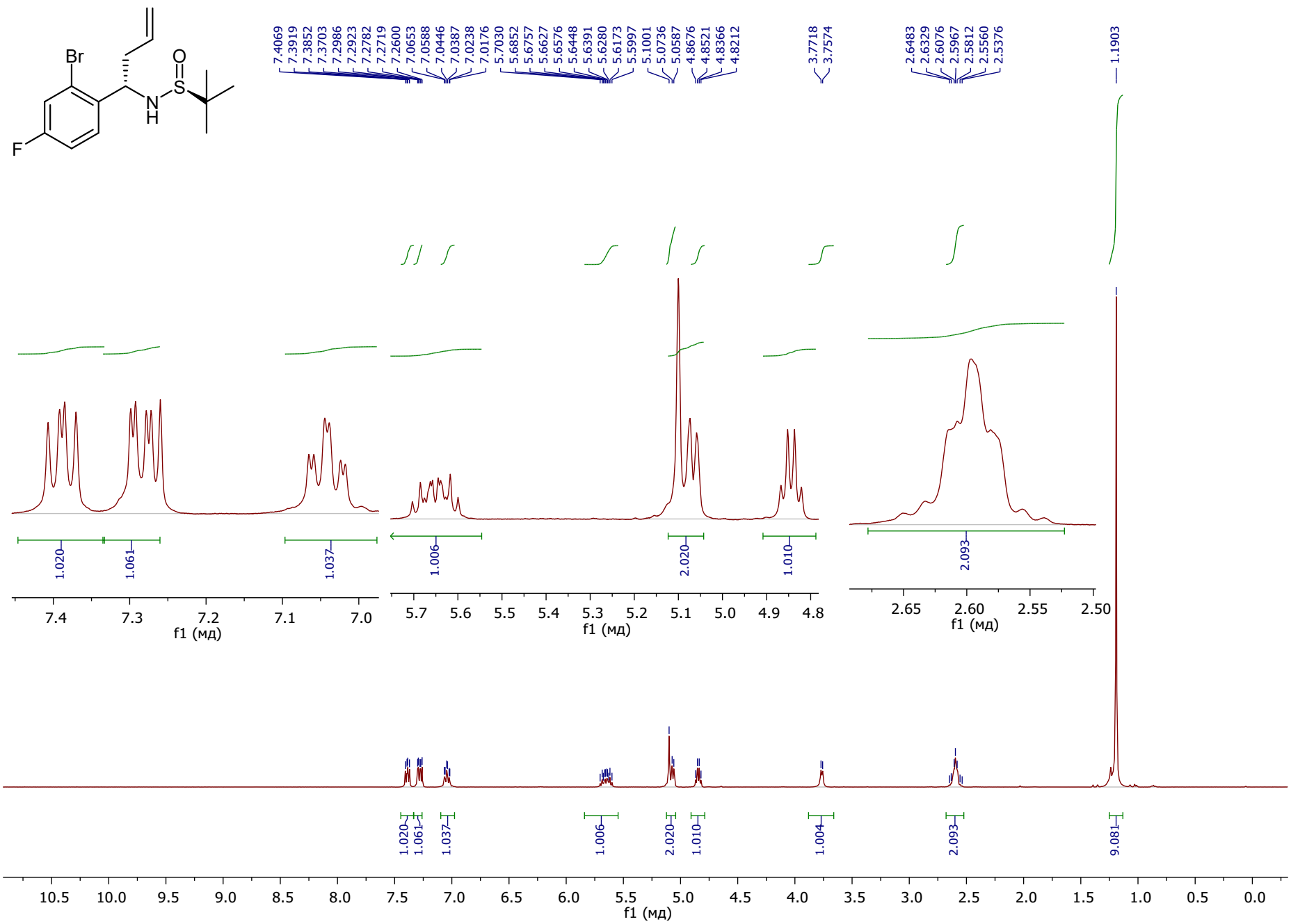
^{1}H NMR ($CDCl_3$, 400 MHz) **2v**



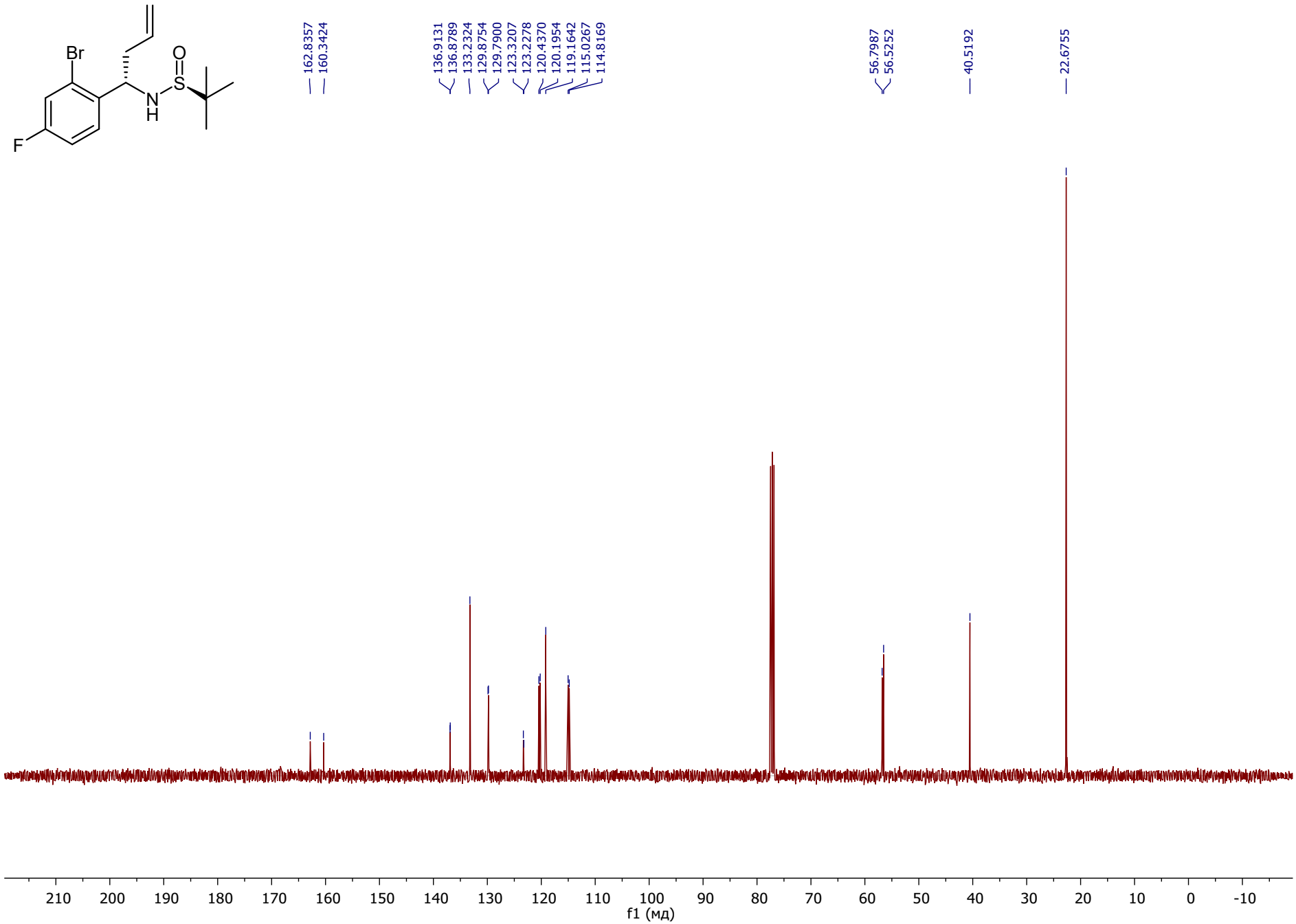
^{1}H NMR ($CDCl_3$, 400 MHz) **2w**



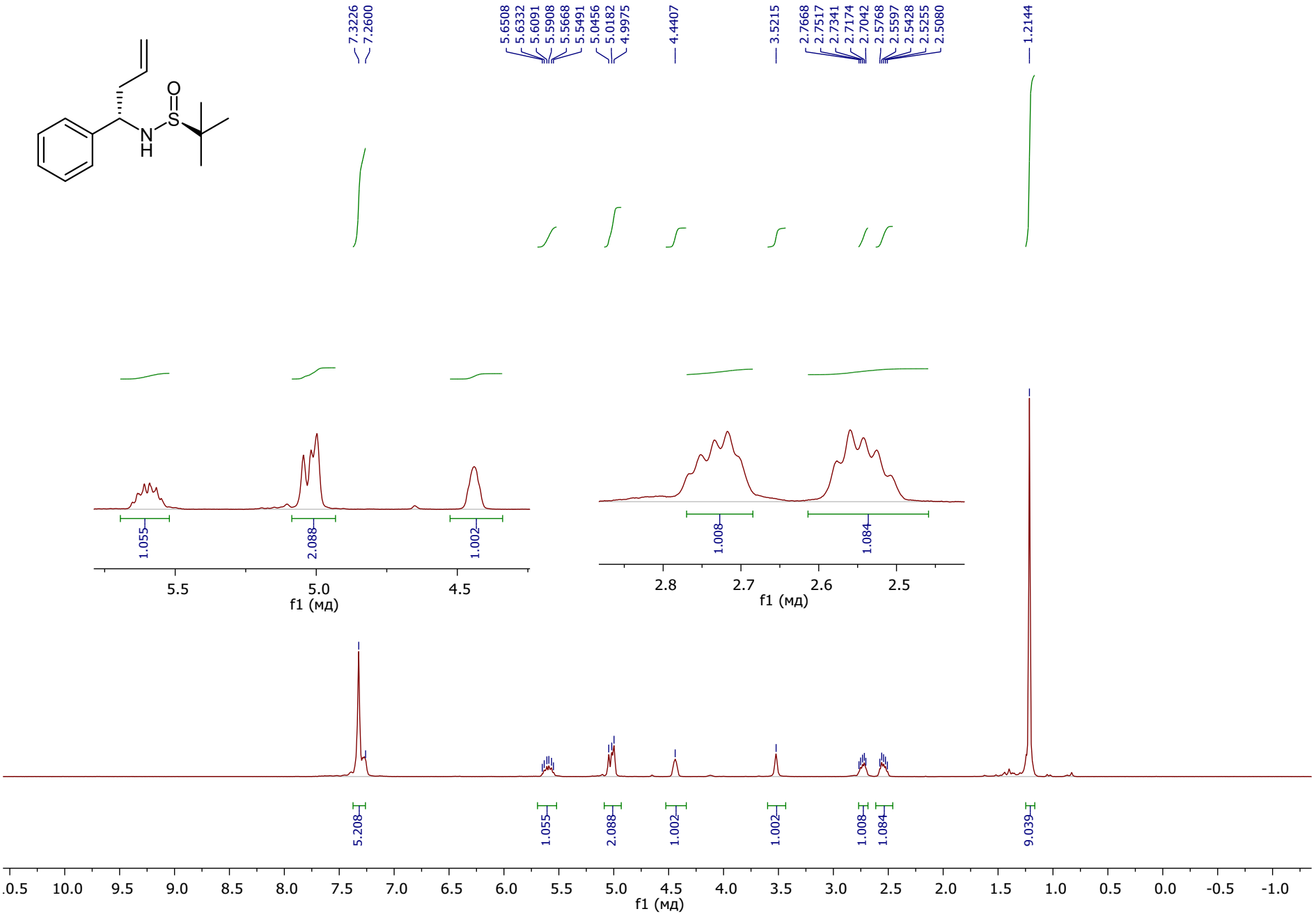
^{1}H NMR ($CDCl_3$, 400 MHz) **3a**



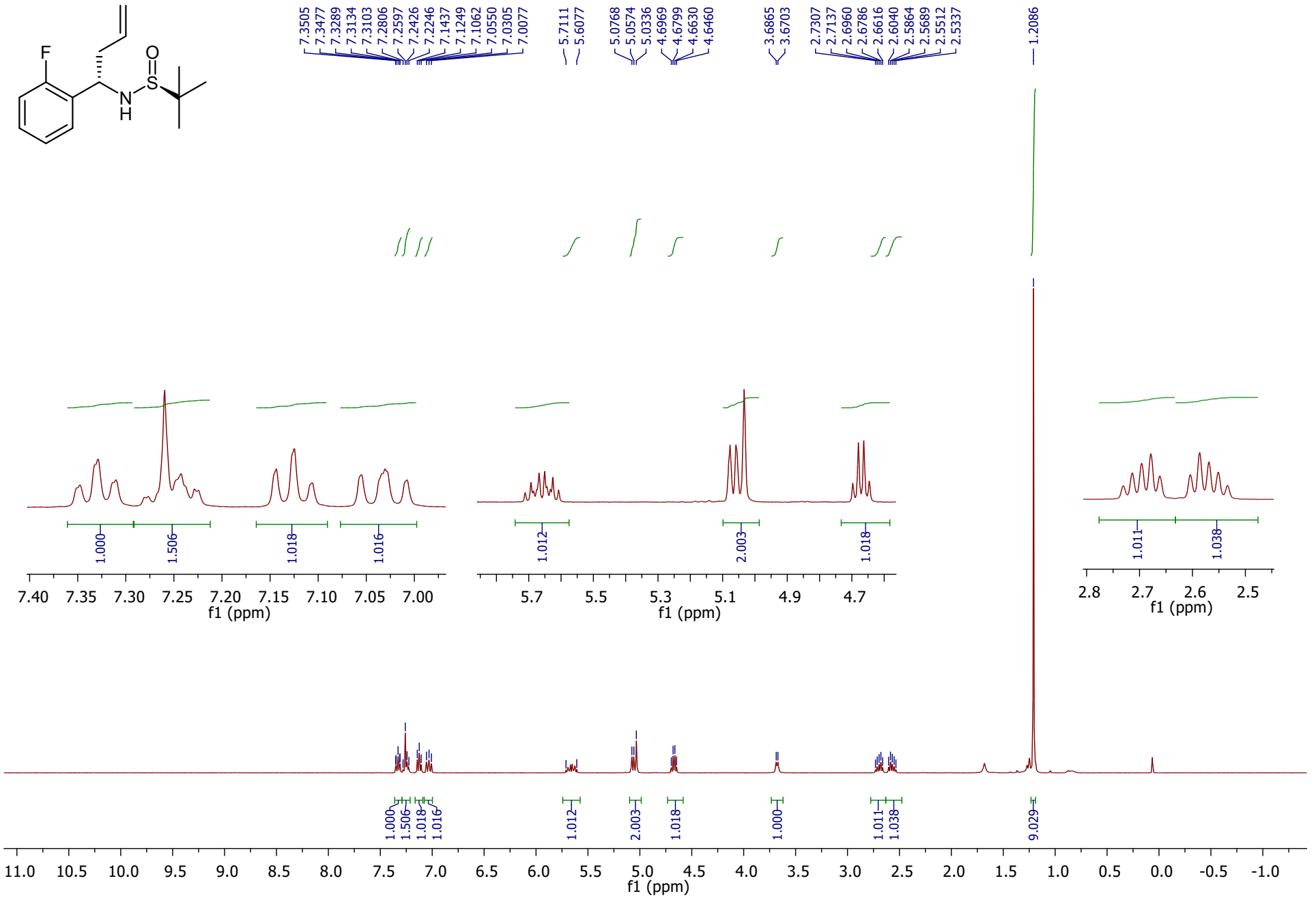
^{13}C NMR ($CDCl_3$, 101 MHz) **3a**



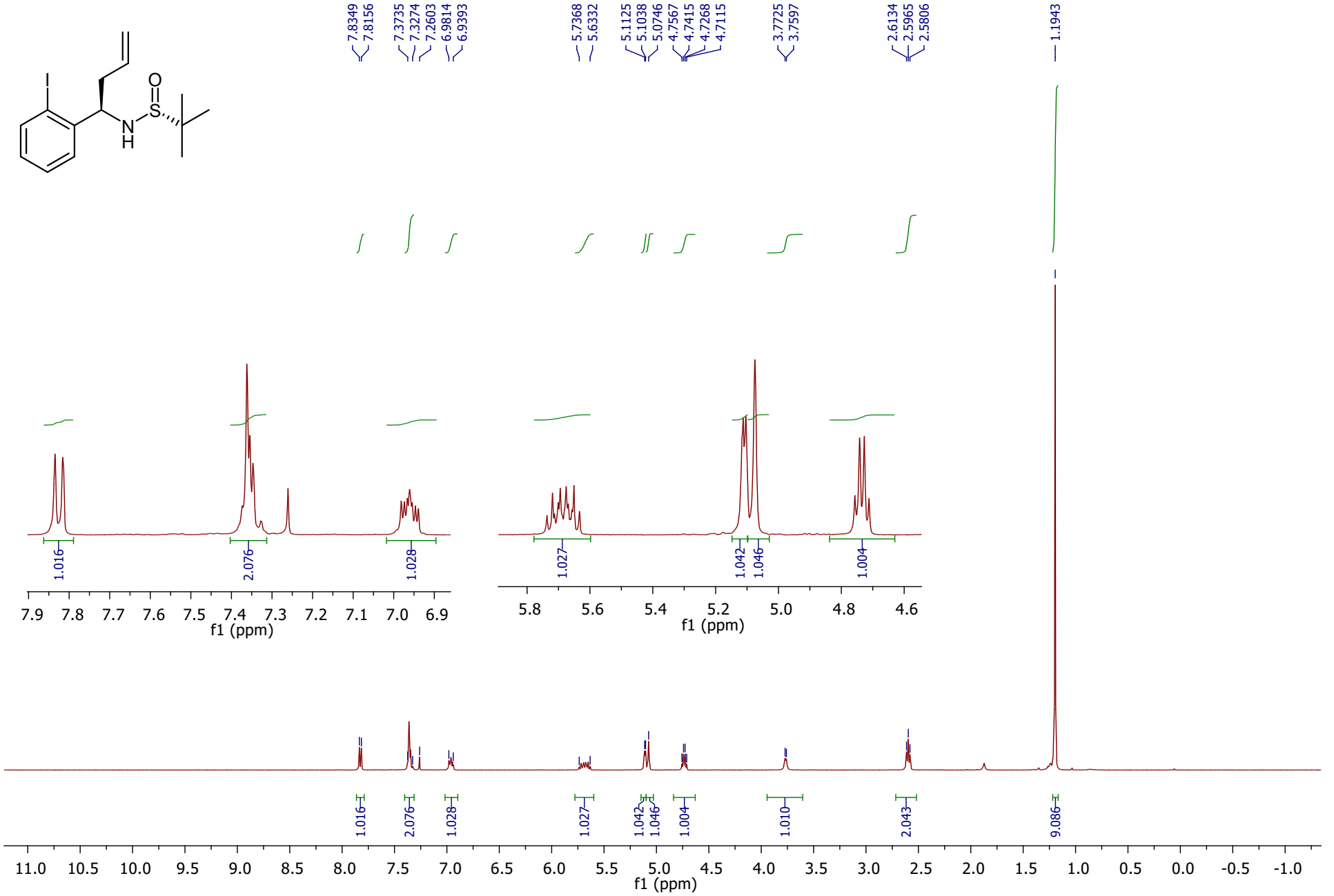
^{1}H NMR ($CDCl_3$, 400 MHz) **3b**



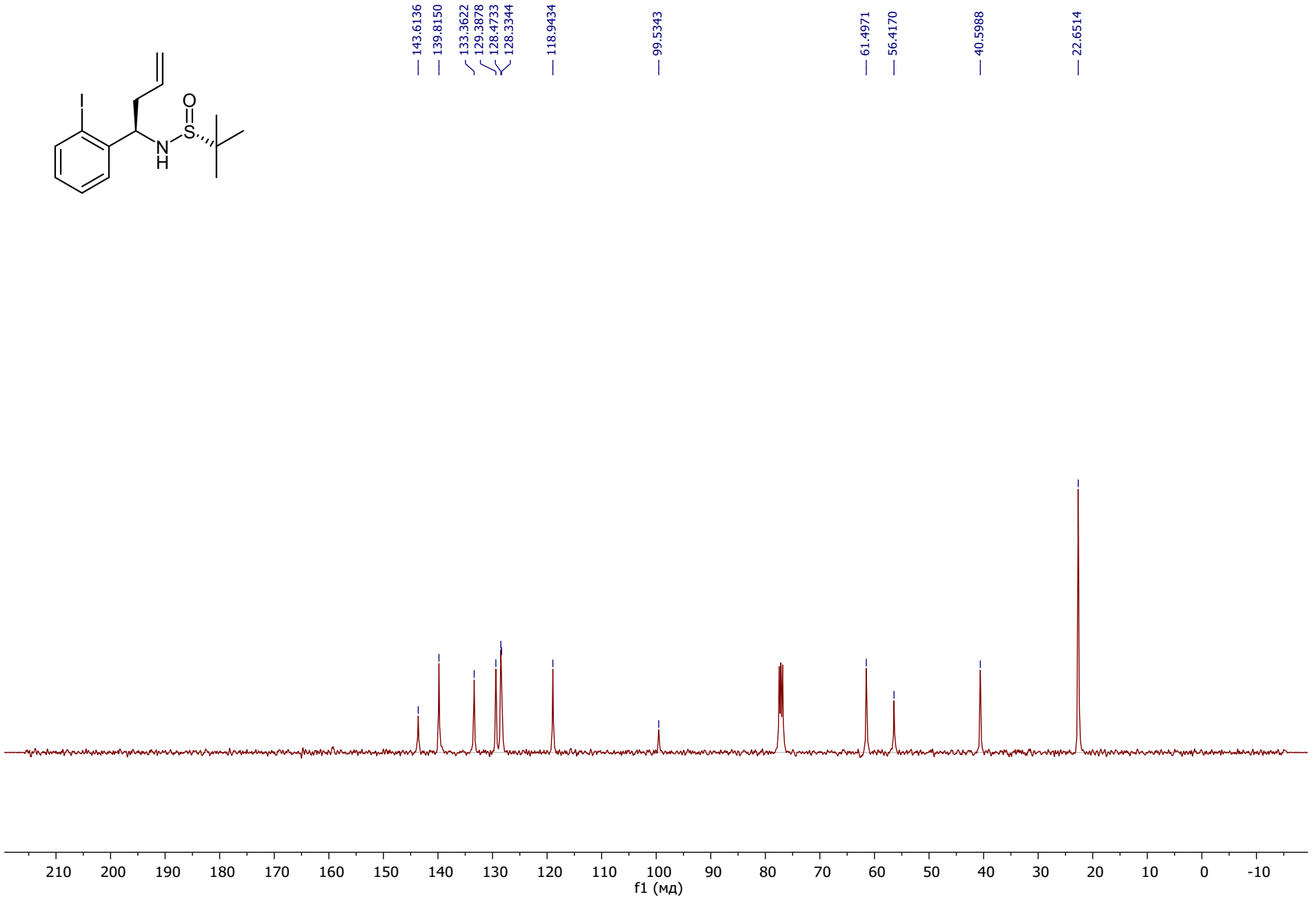
^{1}H NMR ($CDCl_3$, 400 MHz) **3c**



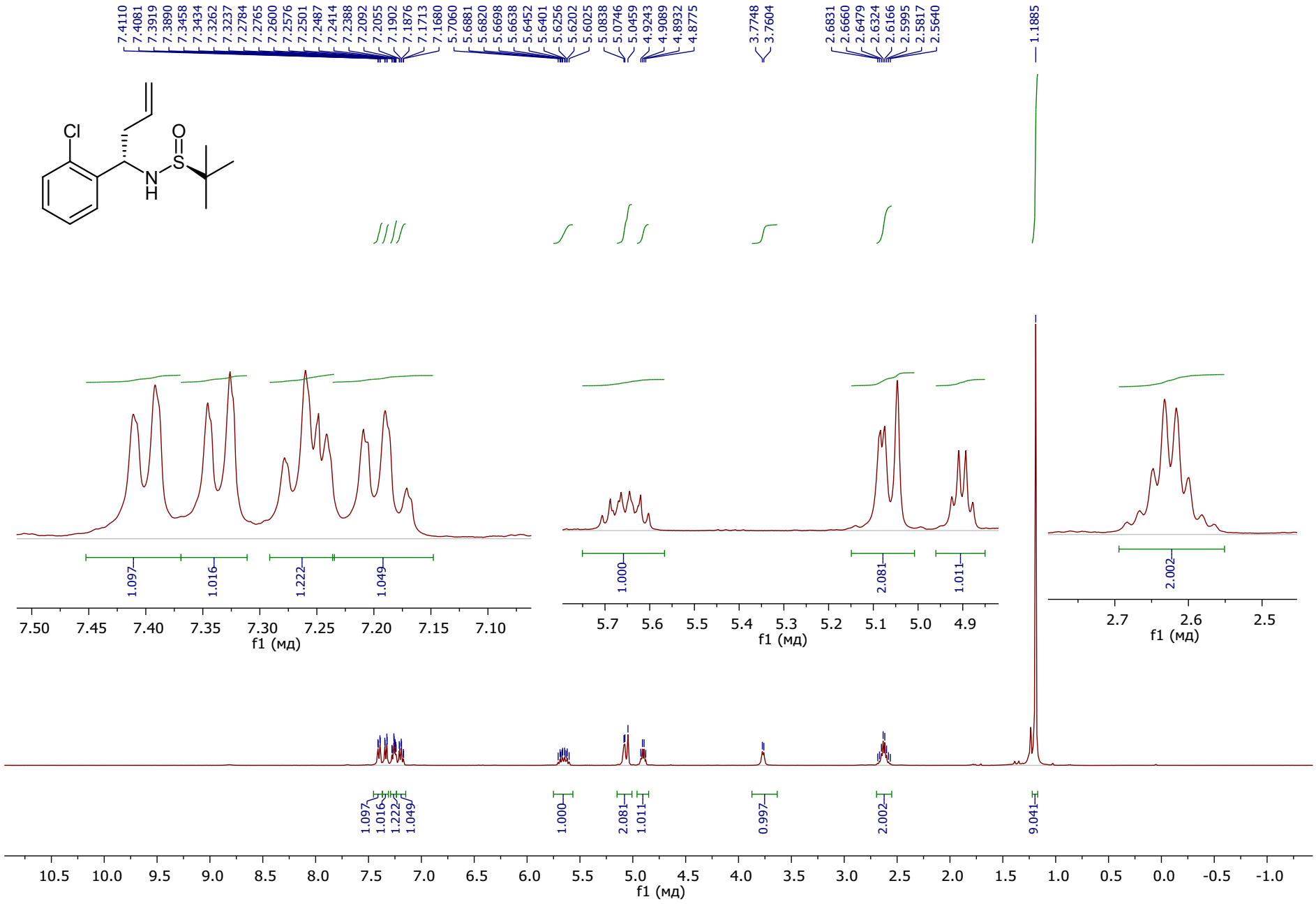
^{1}H NMR ($CDCl_3$, 400 MHz) **3d**



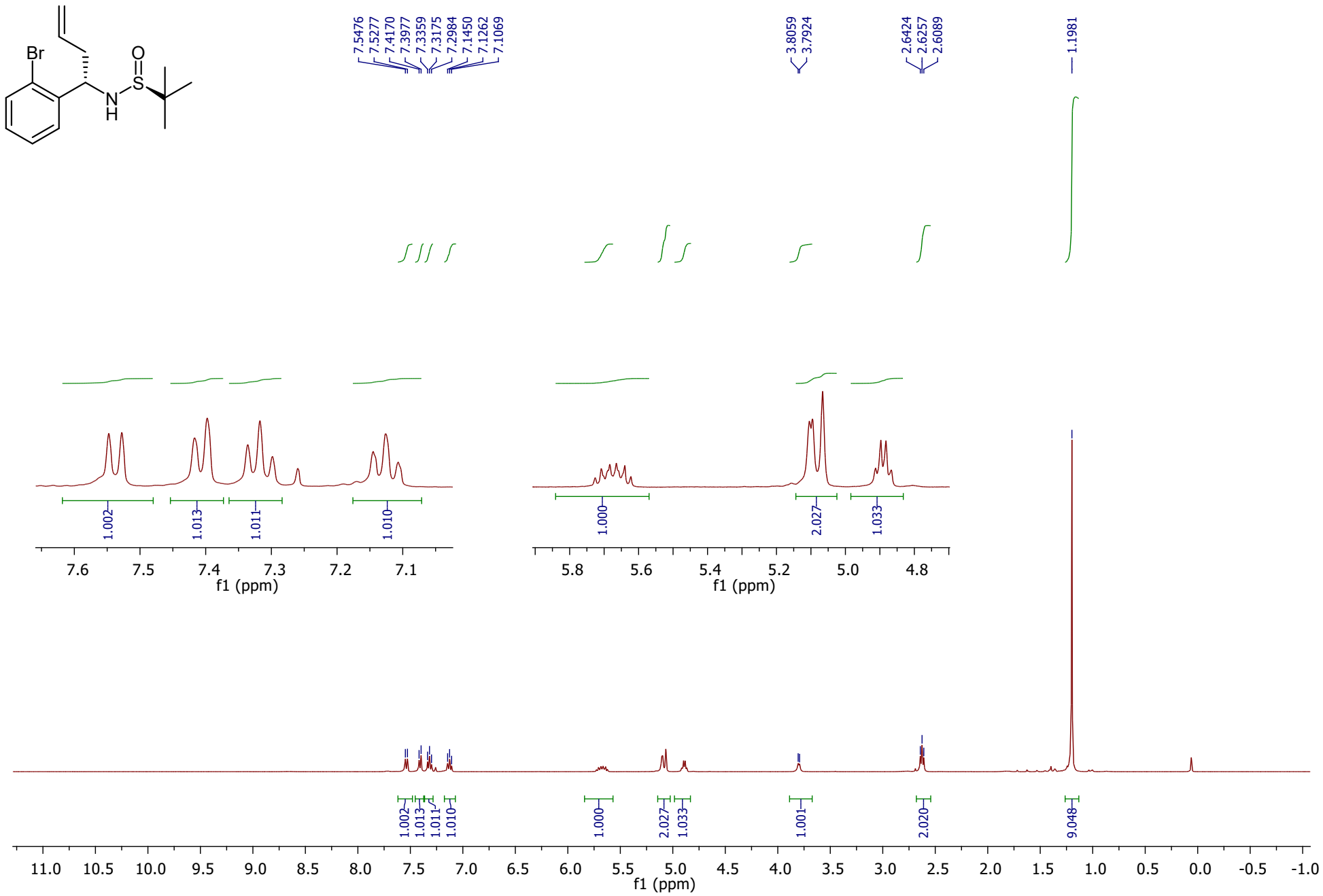
^{13}C NMR ($CDCl_3$, 101 MHz) **3d**



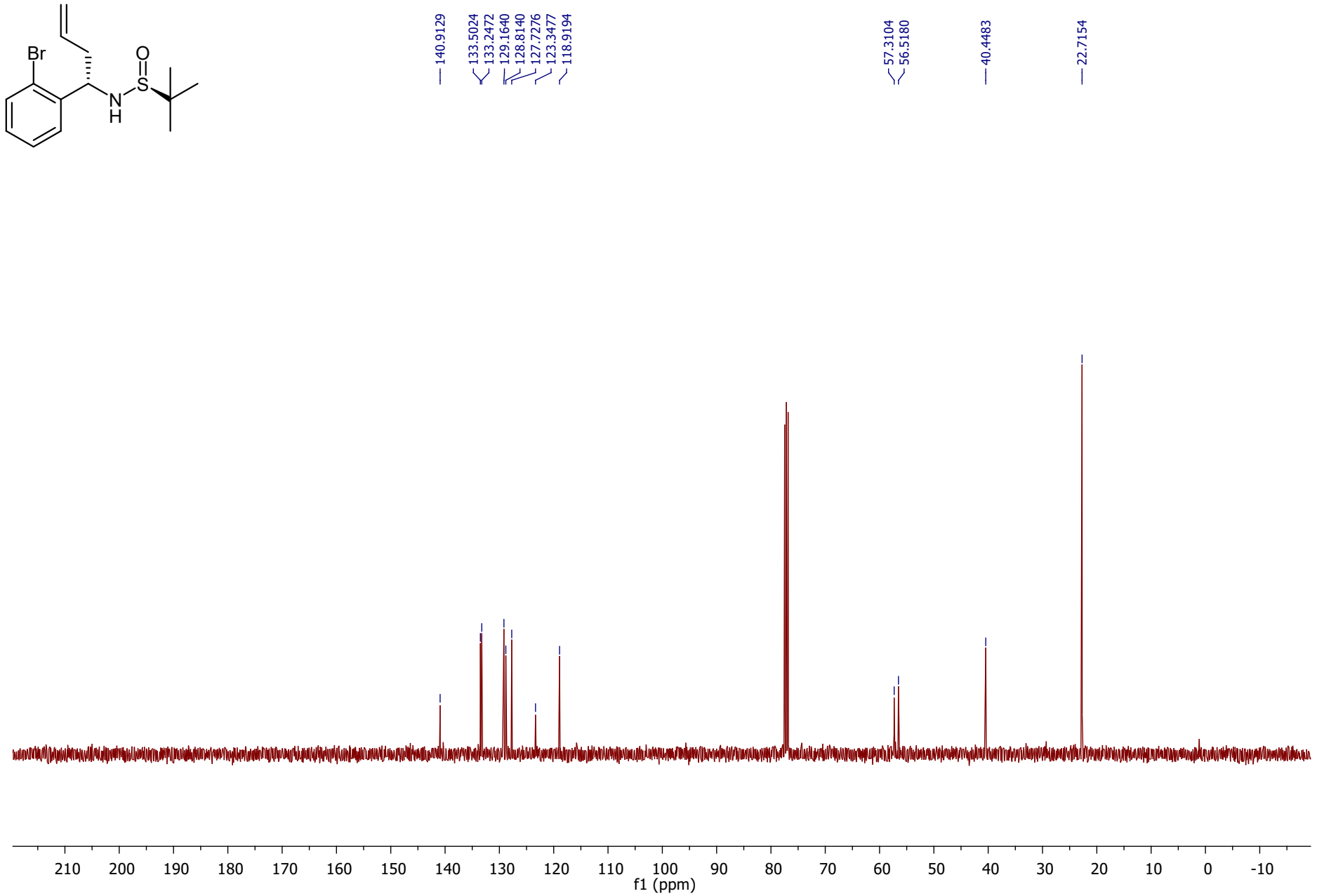
^{1}H NMR ($CDCl_3$, 400 MHz) **3e**



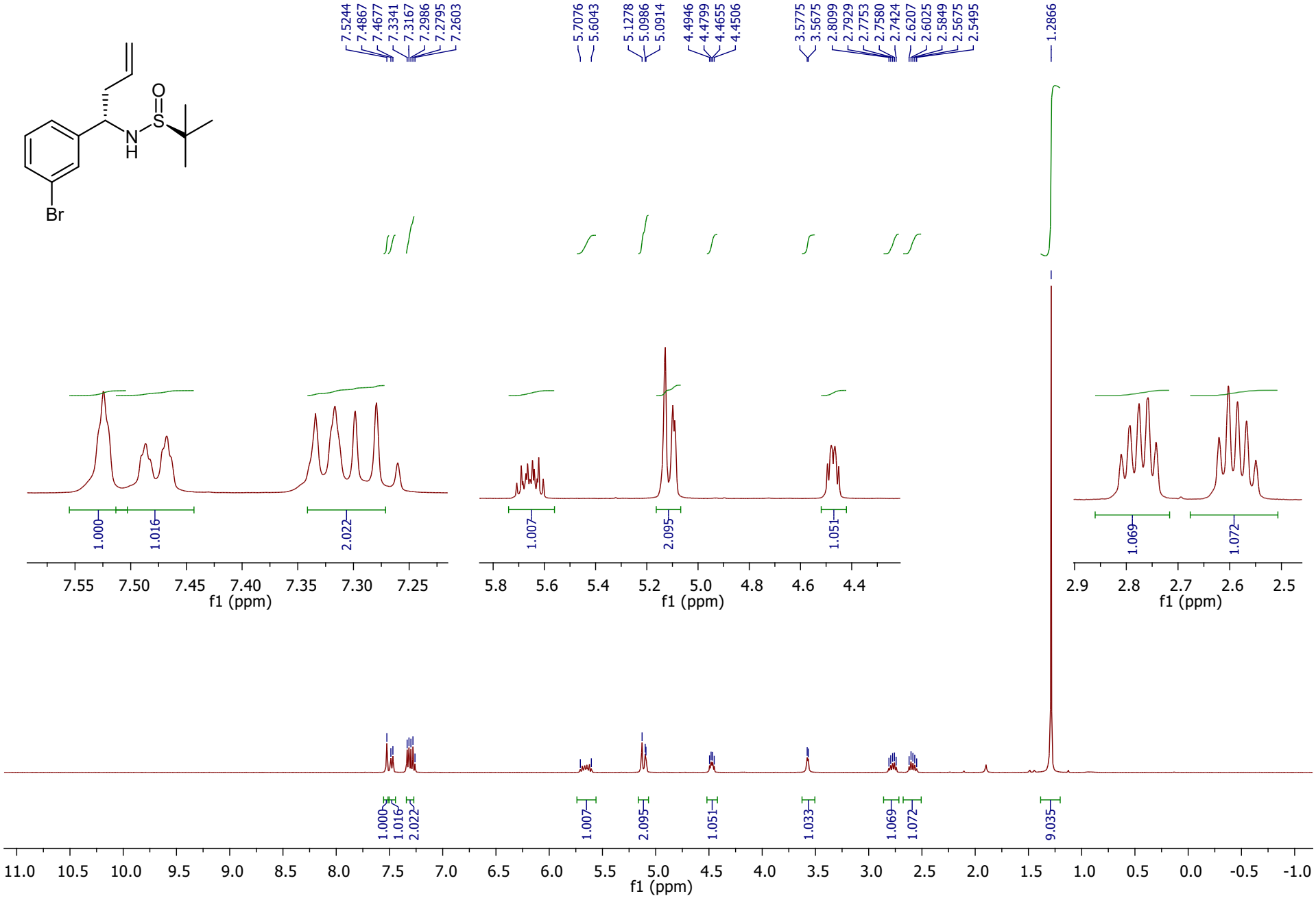
^{1}H NMR ($CDCl_3$, 400 MHz) **3f**



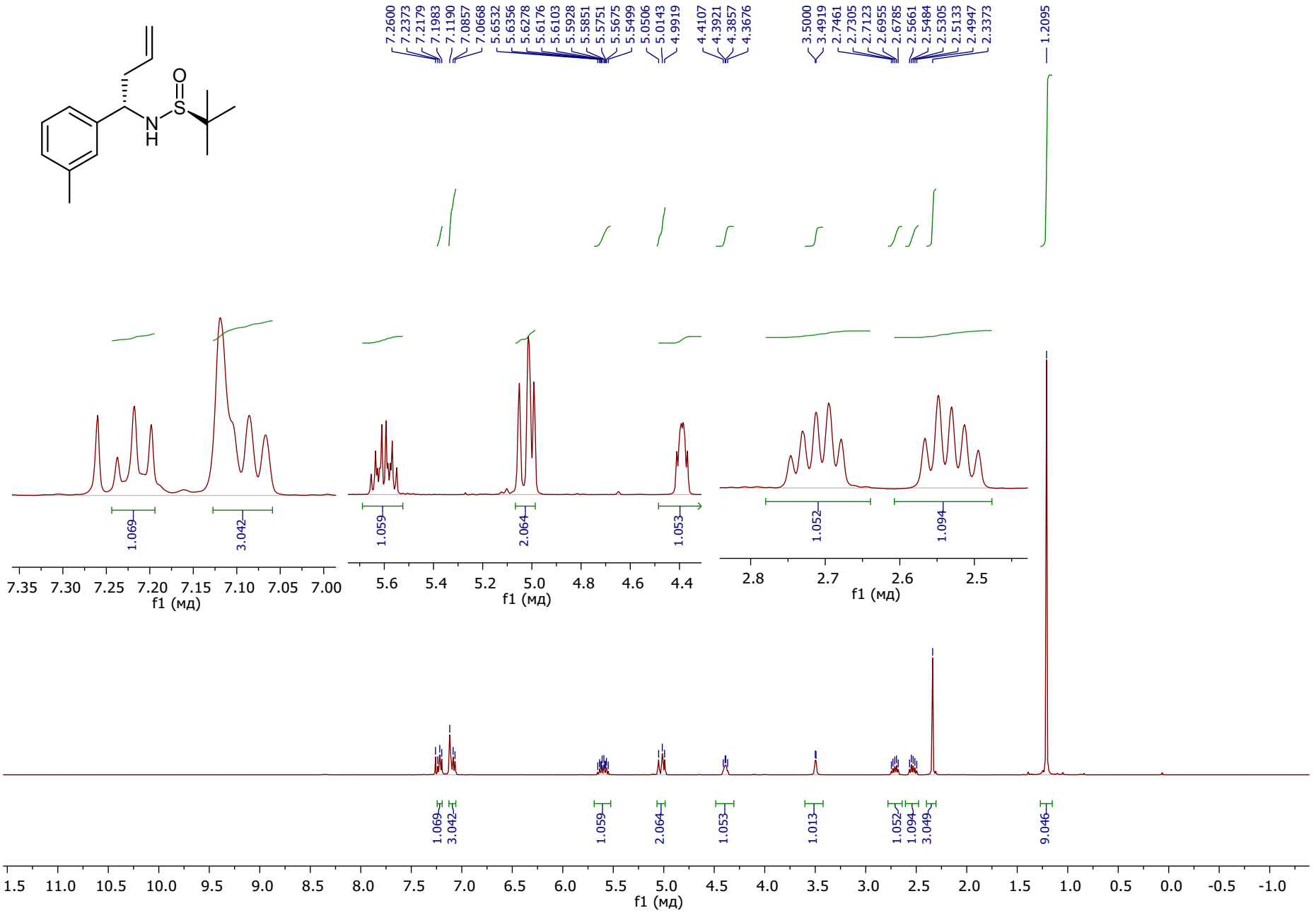
^{13}C NMR ($CDCl_3$, 101 MHz) **3f**



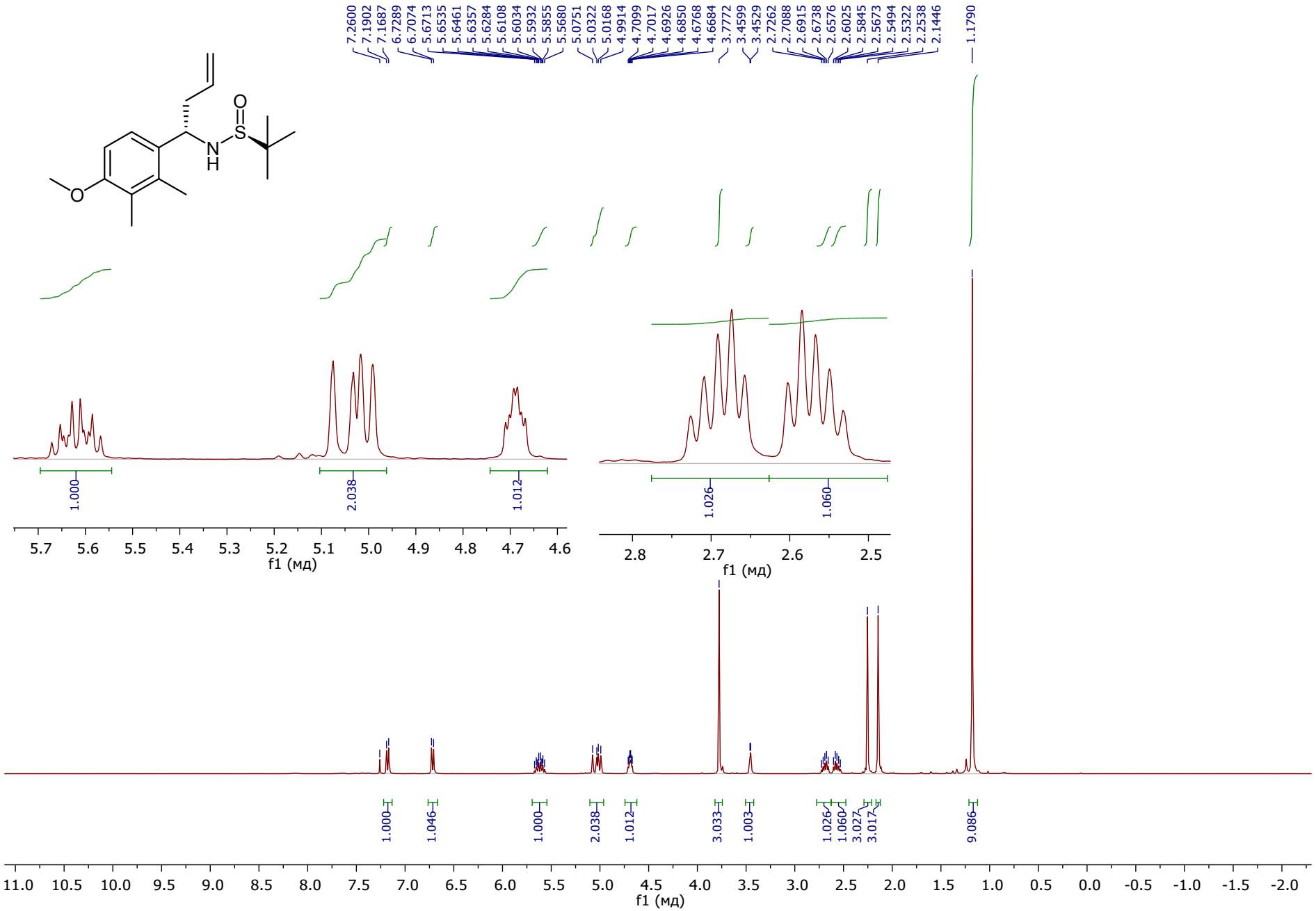
^{1}H NMR ($CDCl_3$, 400 MHz) **3g**



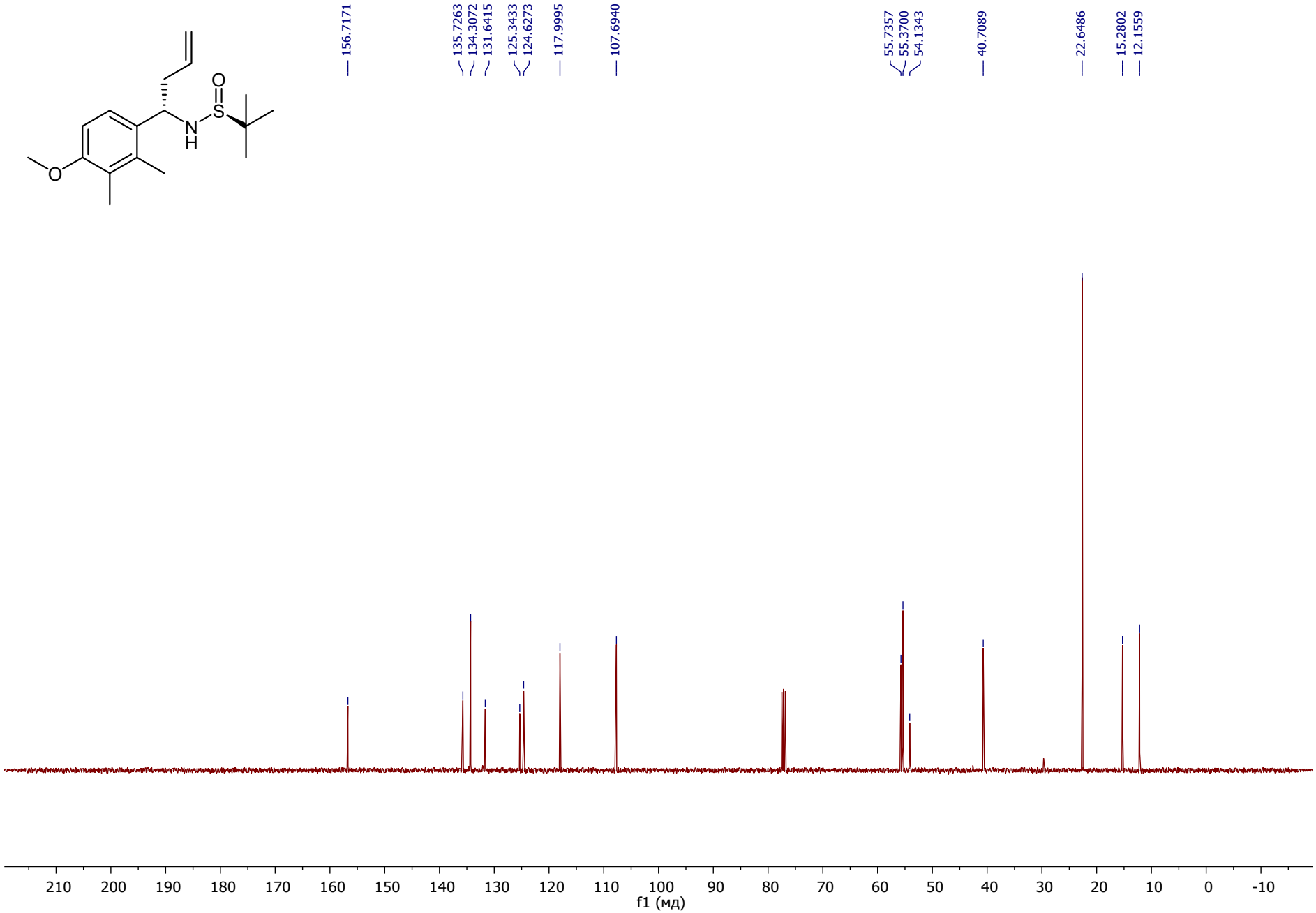
^{1}H NMR ($CDCl_3$, 400 MHz) **3h**



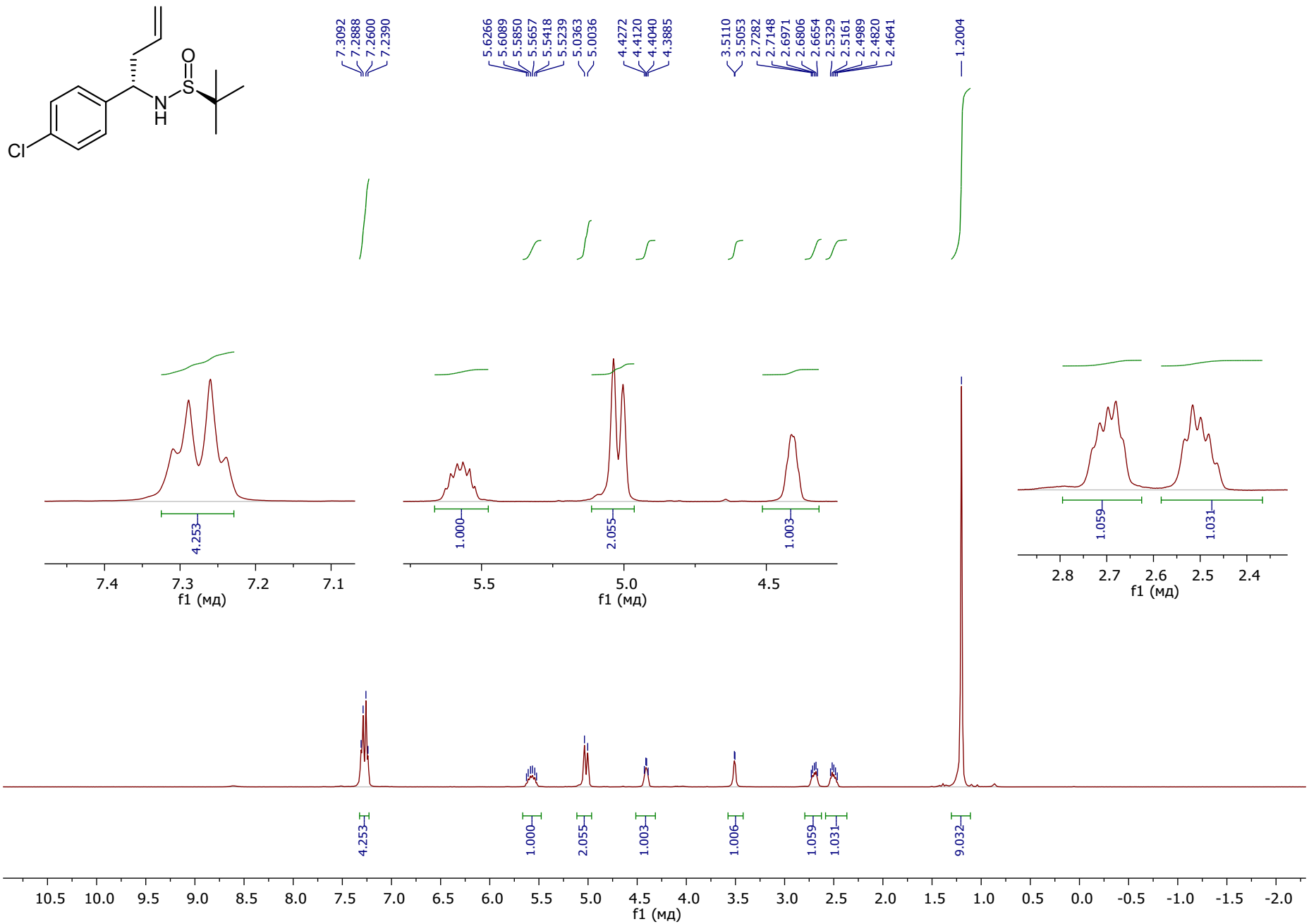
^{1}H NMR ($CDCl_3$, 400 MHz) **3i**



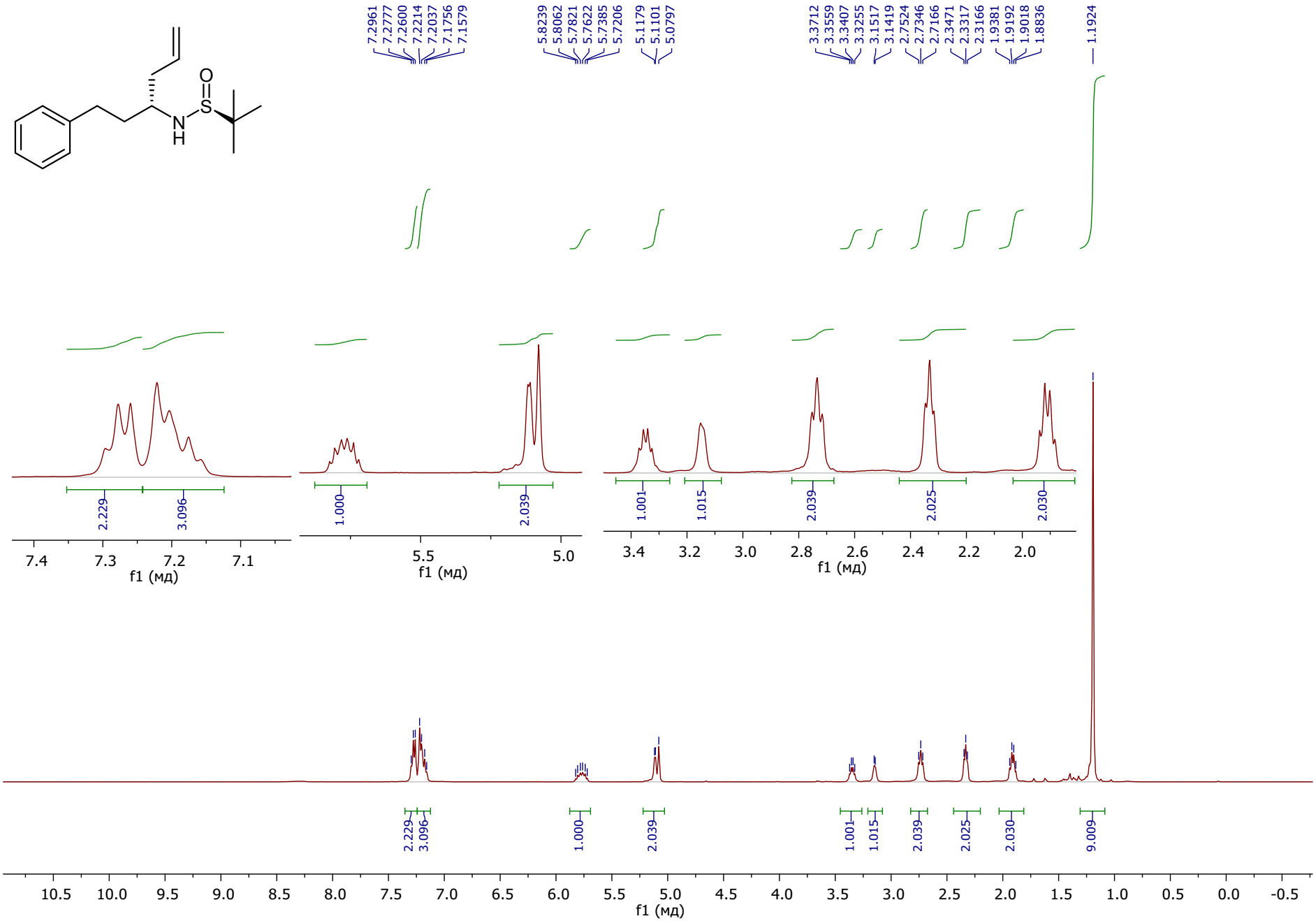
^{13}C NMR ($CDCl_3$, 101 MHz) **3i**



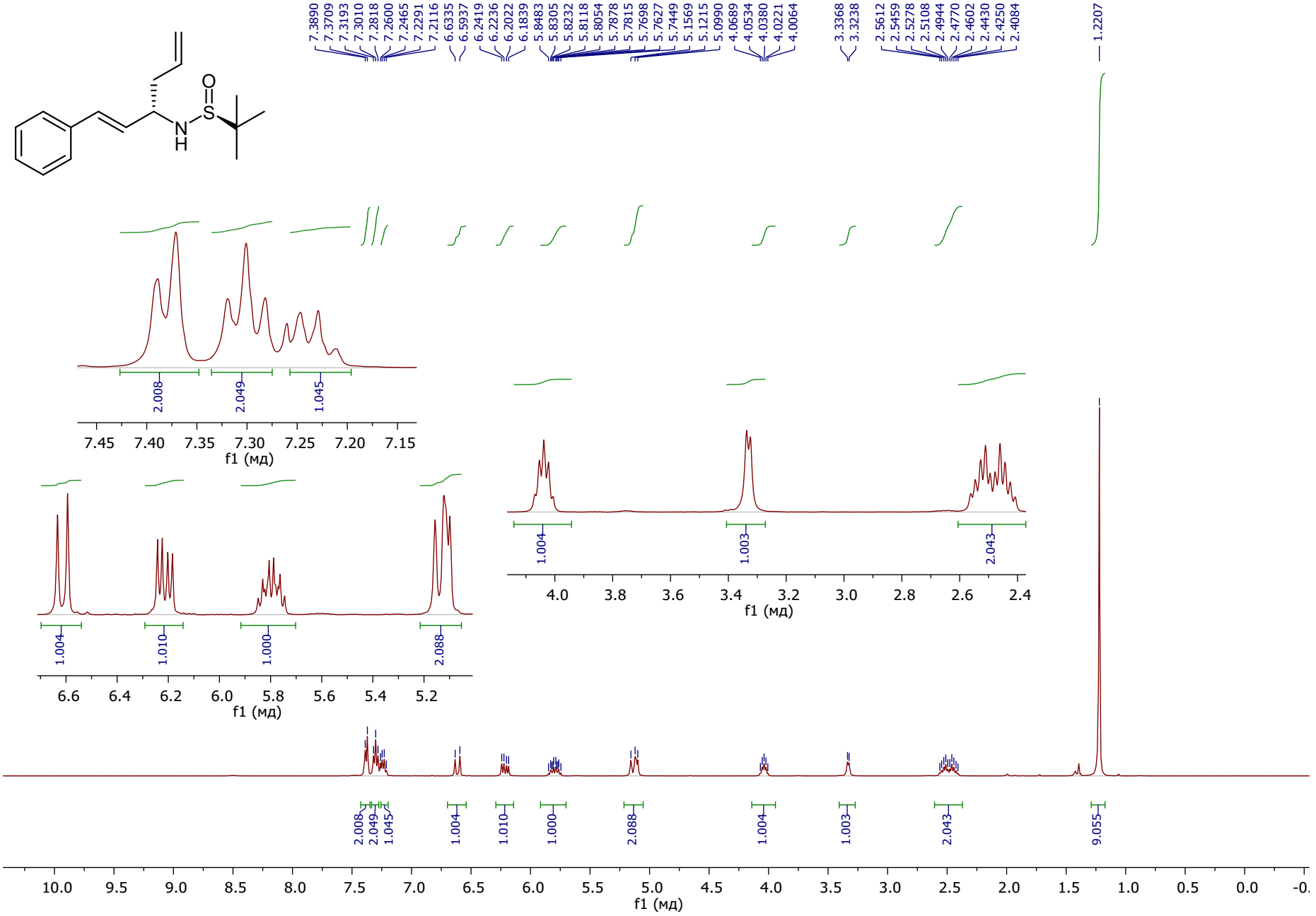
^{1}H NMR ($CDCl_3$, 400 MHz) **3j**



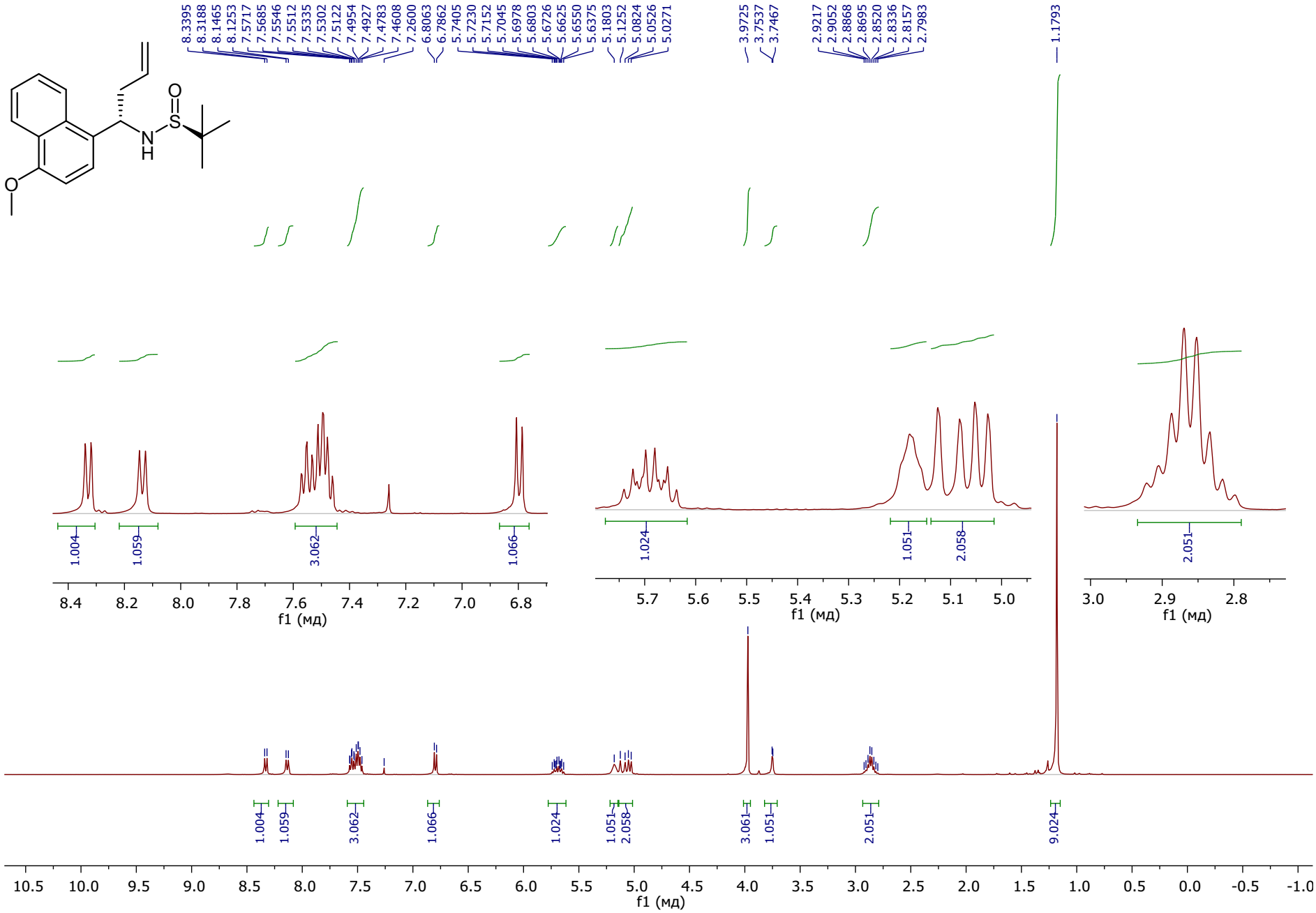
^{1}H NMR ($CDCl_3$, 400 MHz) **3k**



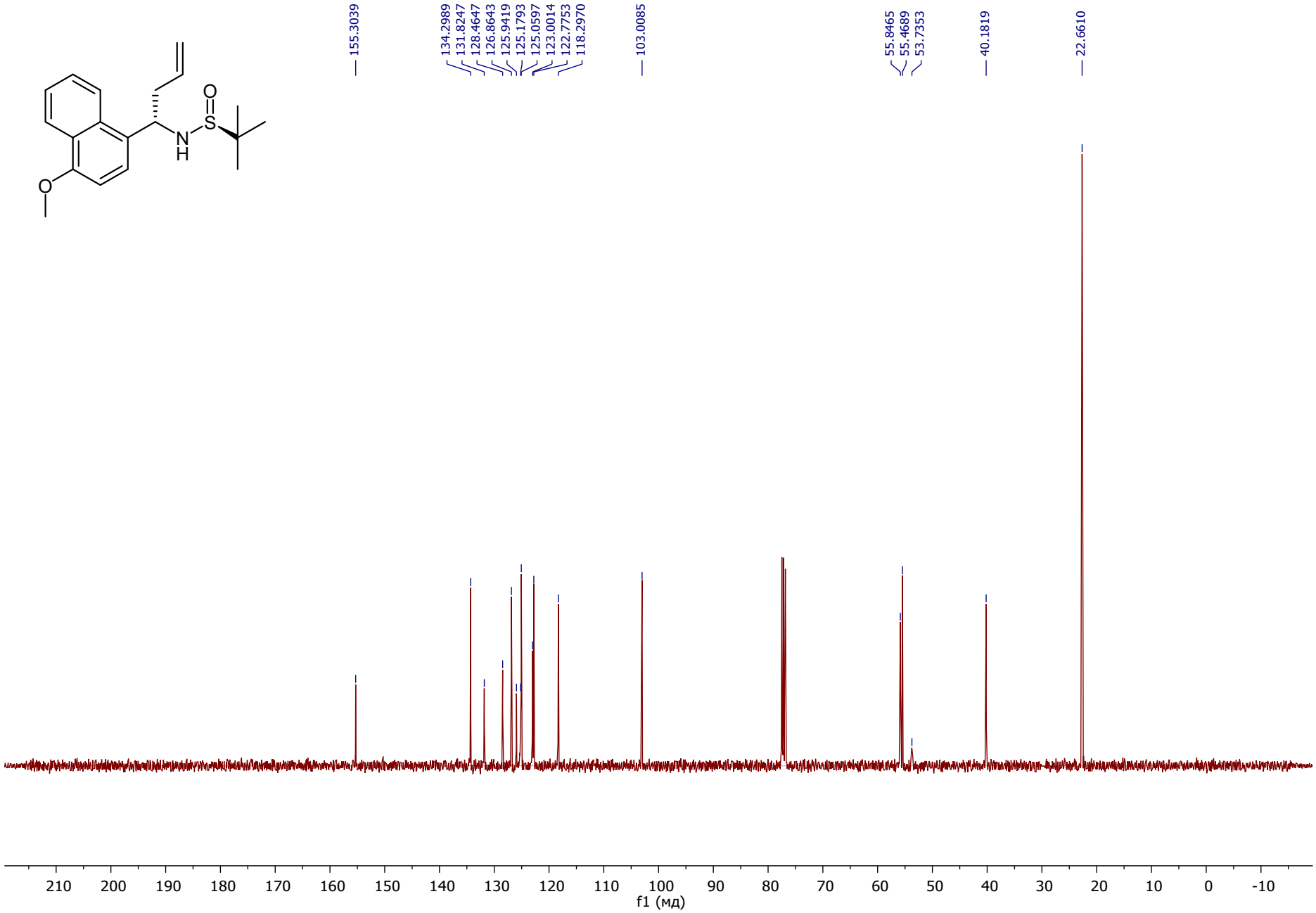
^{1}H NMR ($CDCl_3$, 400 MHz) **3l**



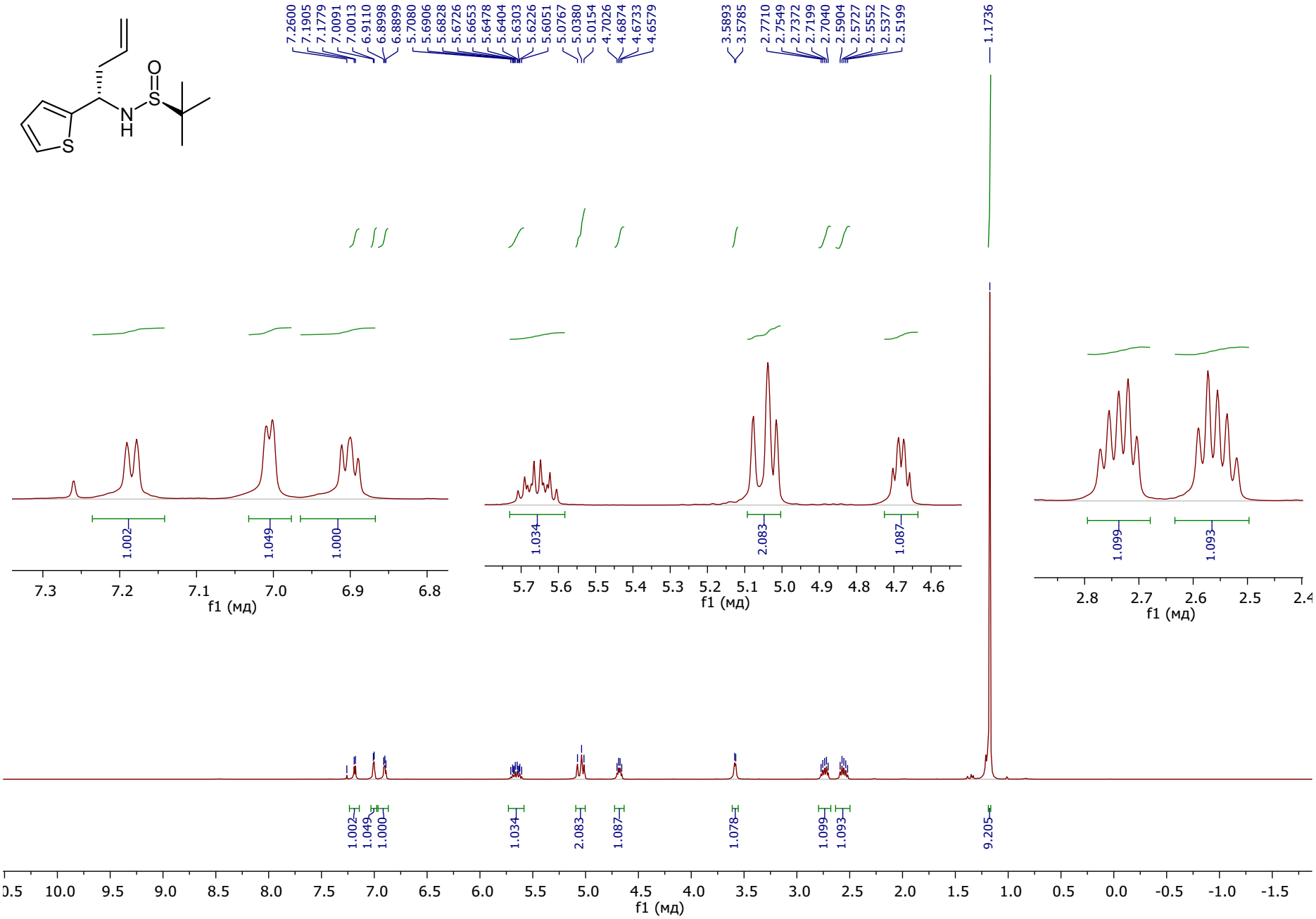
^{1}H NMR ($CDCl_3$, 400 MHz) **3m**



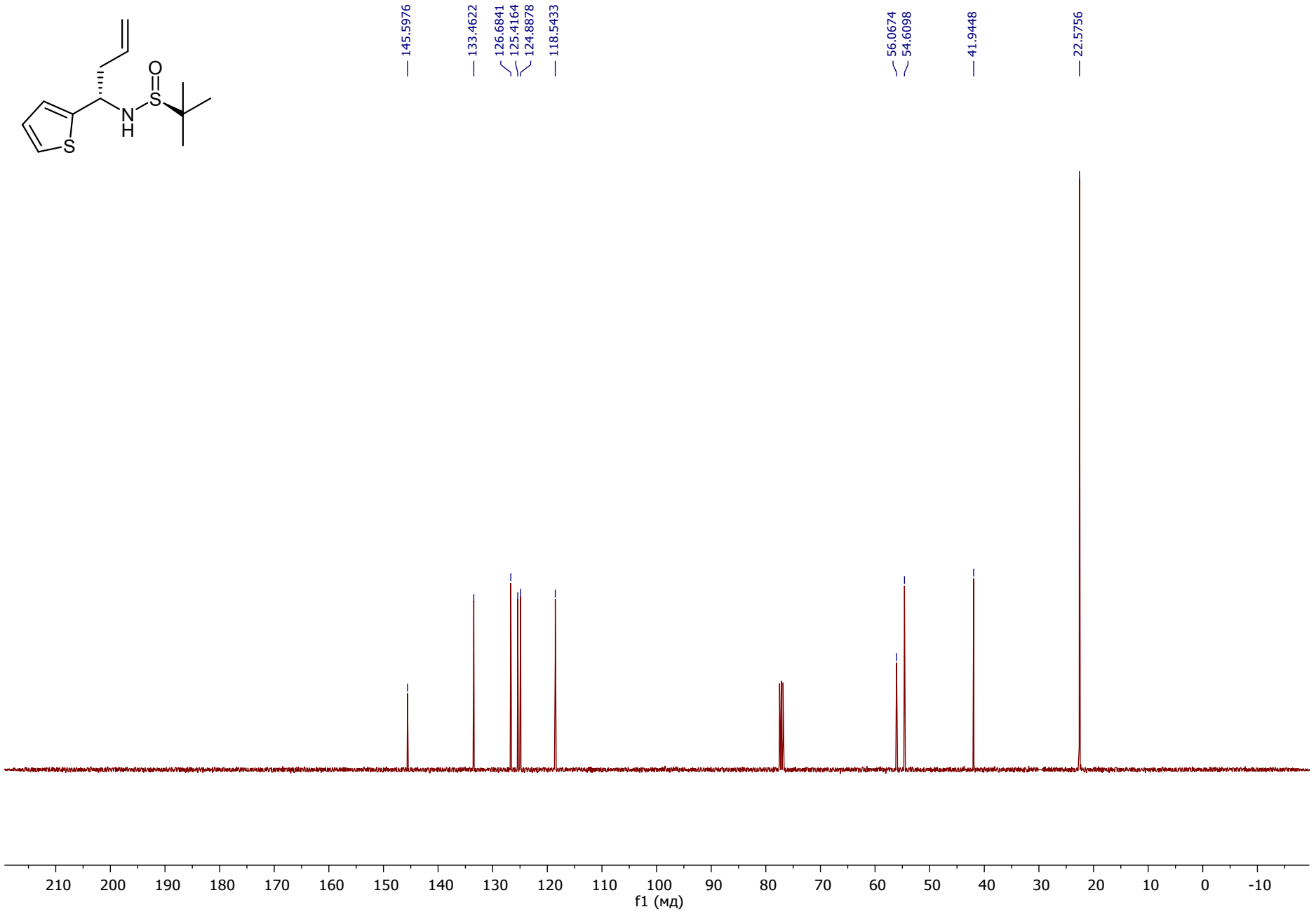
^{13}C NMR ($CDCl_3$, 101 MHz) **3m**



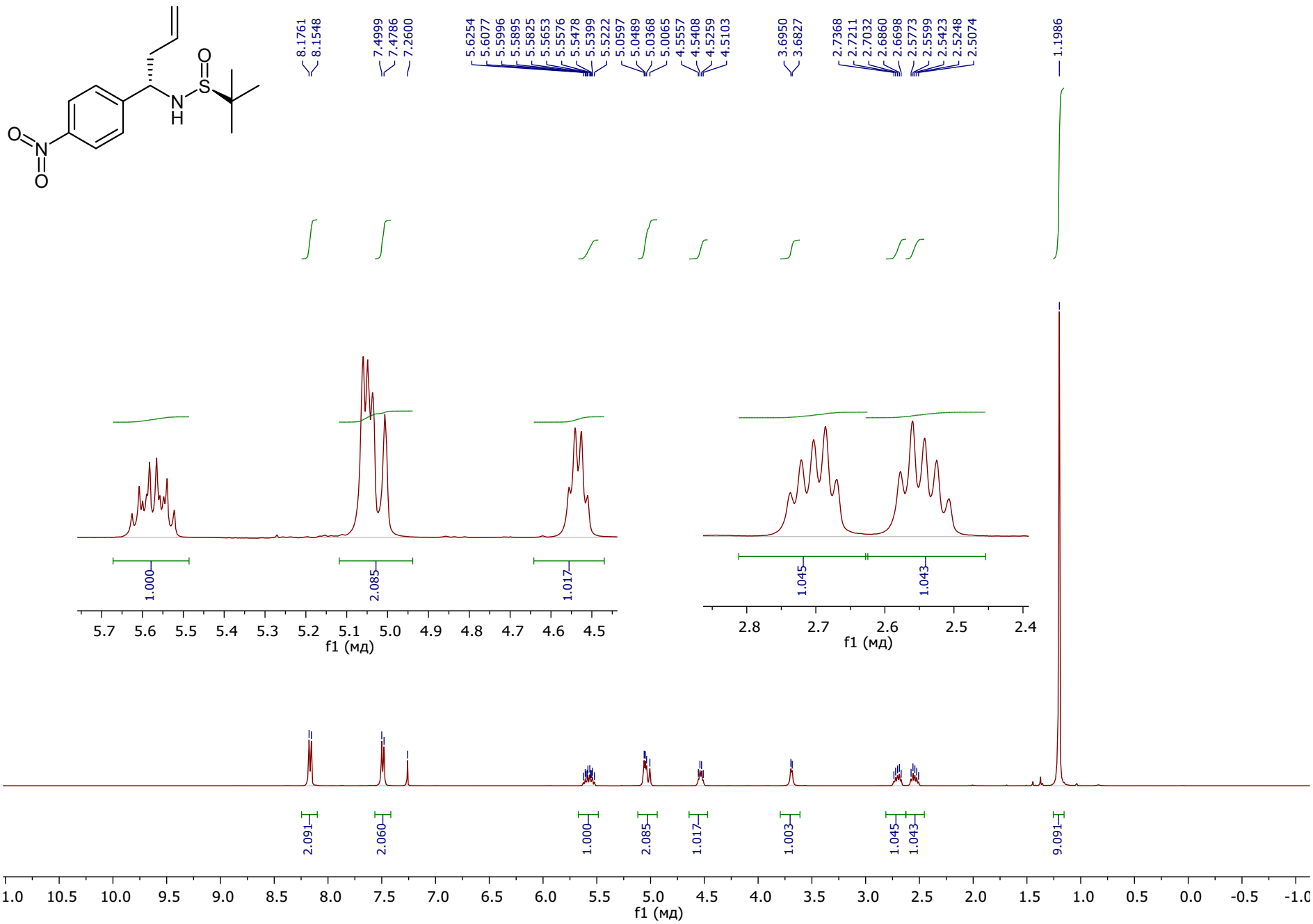
^{1}H NMR ($CDCl_3$, 400 MHz) **3n**



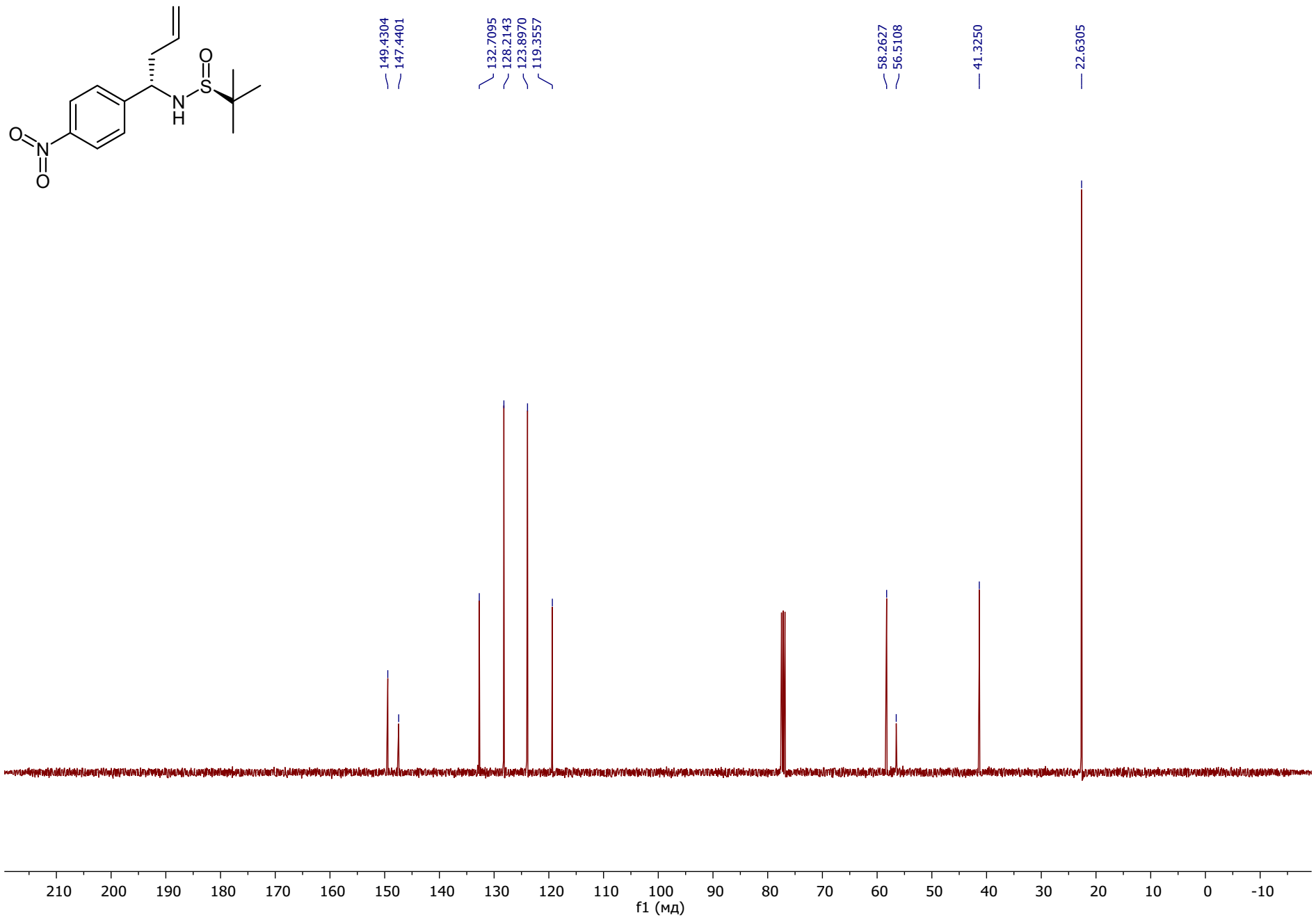
^{13}C NMR ($CDCl_3$, 101 MHz) **3n**



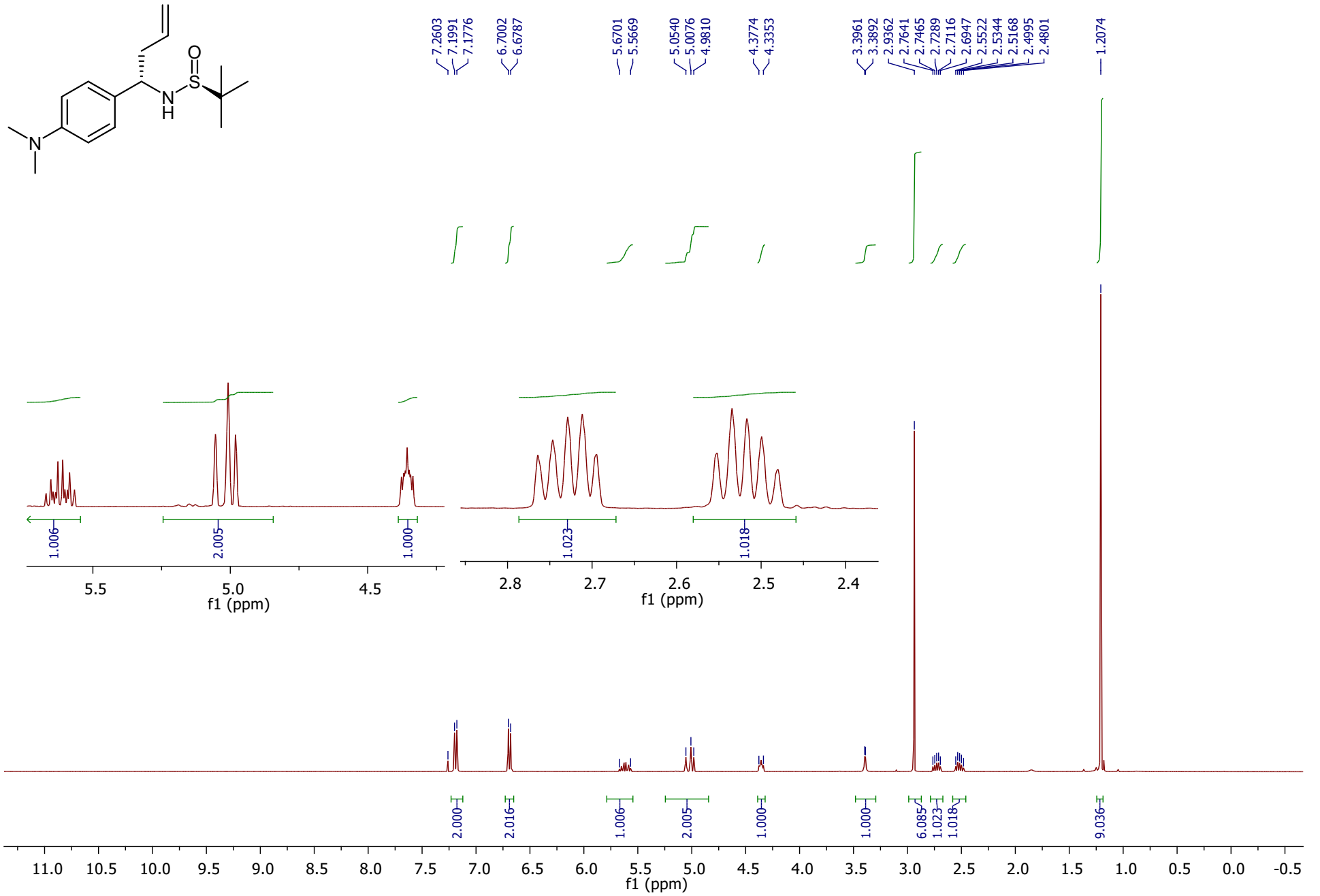
^{1}H NMR ($CDCl_3$, 400 MHz) **3o**



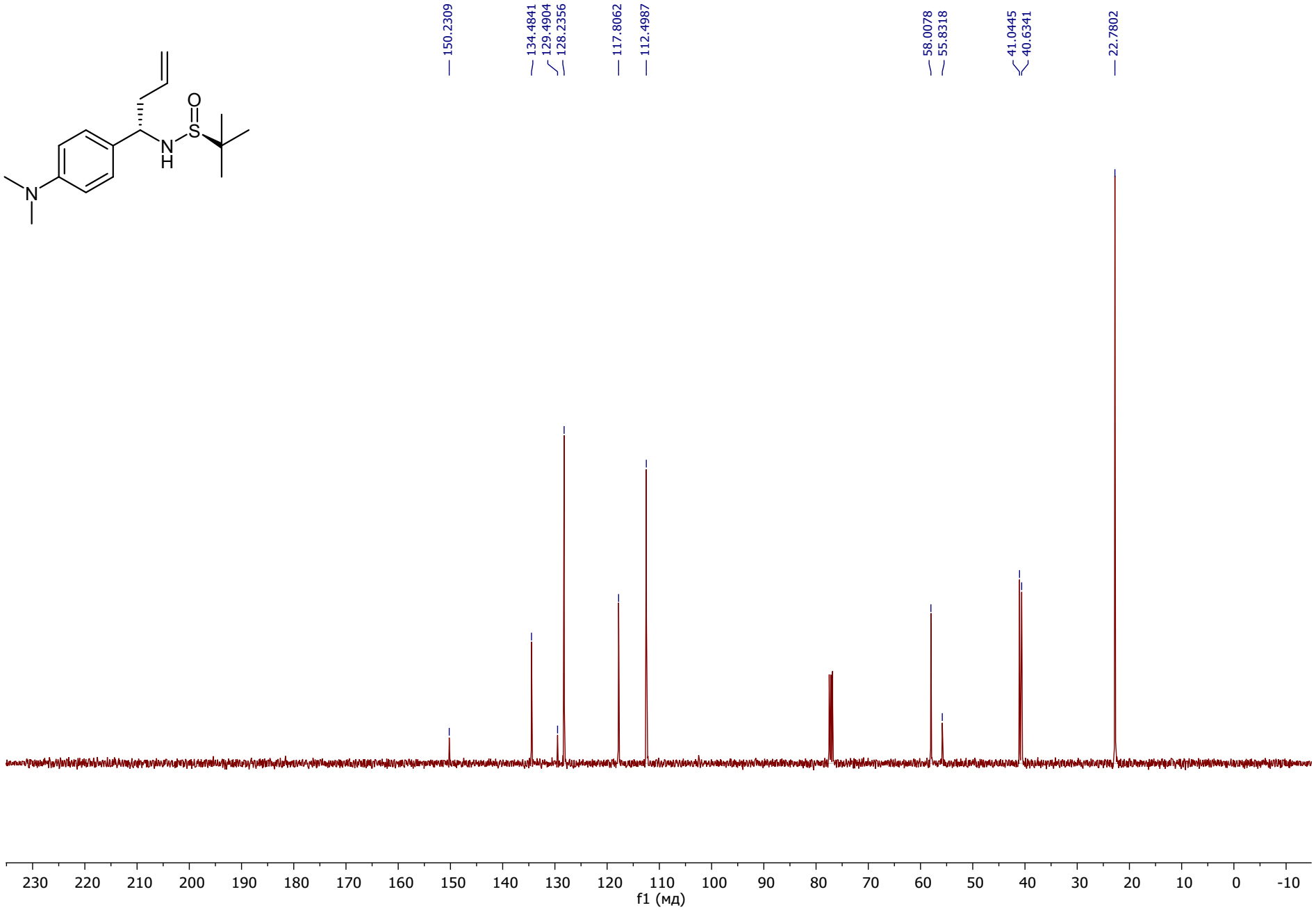
^{13}C NMR ($CDCl_3$, 101 MHz) **3o**



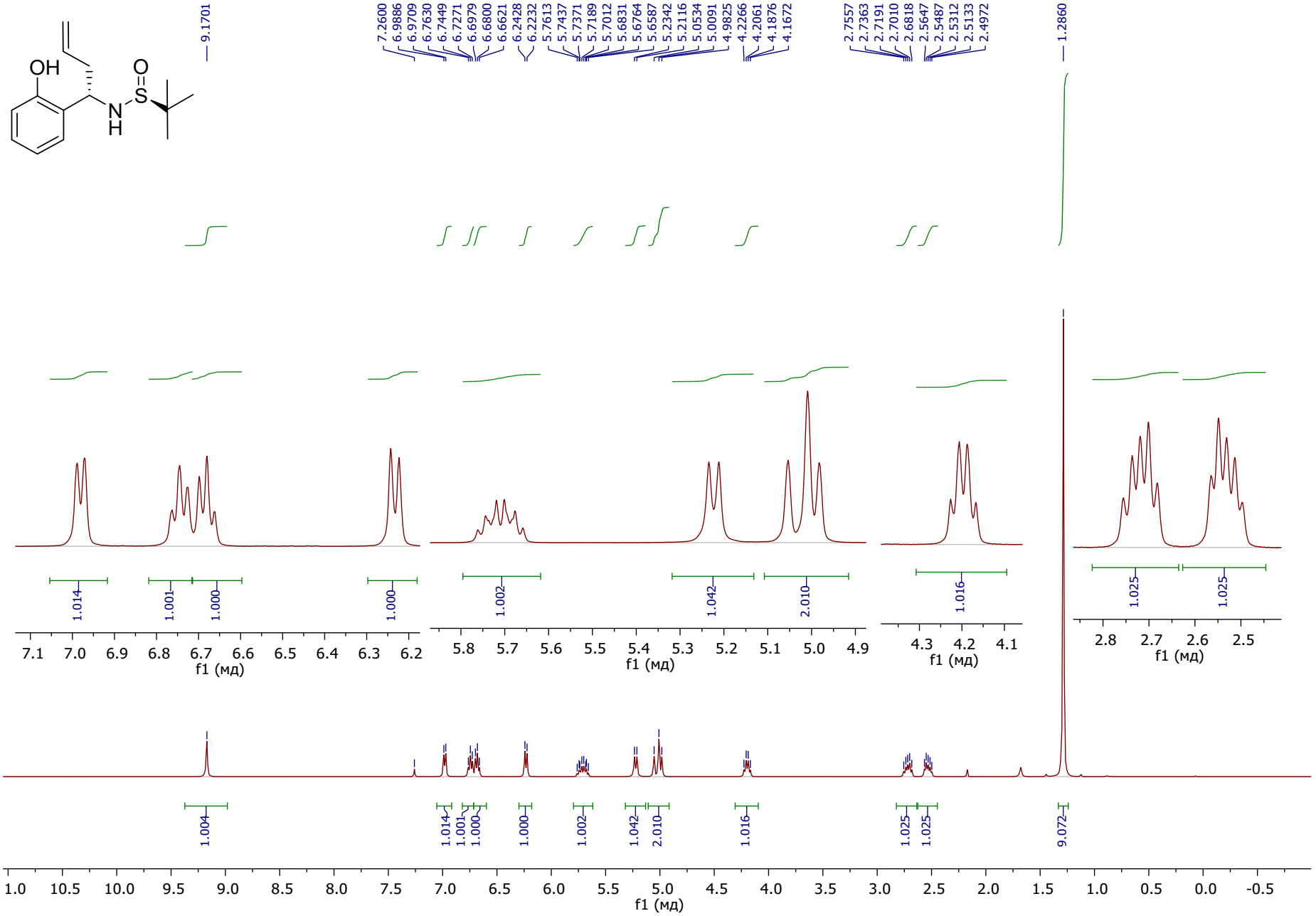
^{1}H NMR ($CDCl_3$, 400 MHz) **3p**



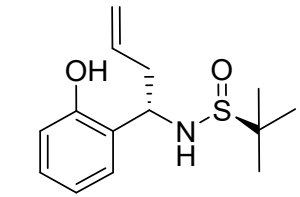
^{13}C NMR ($CDCl_3$, 101 MHz) **3p**



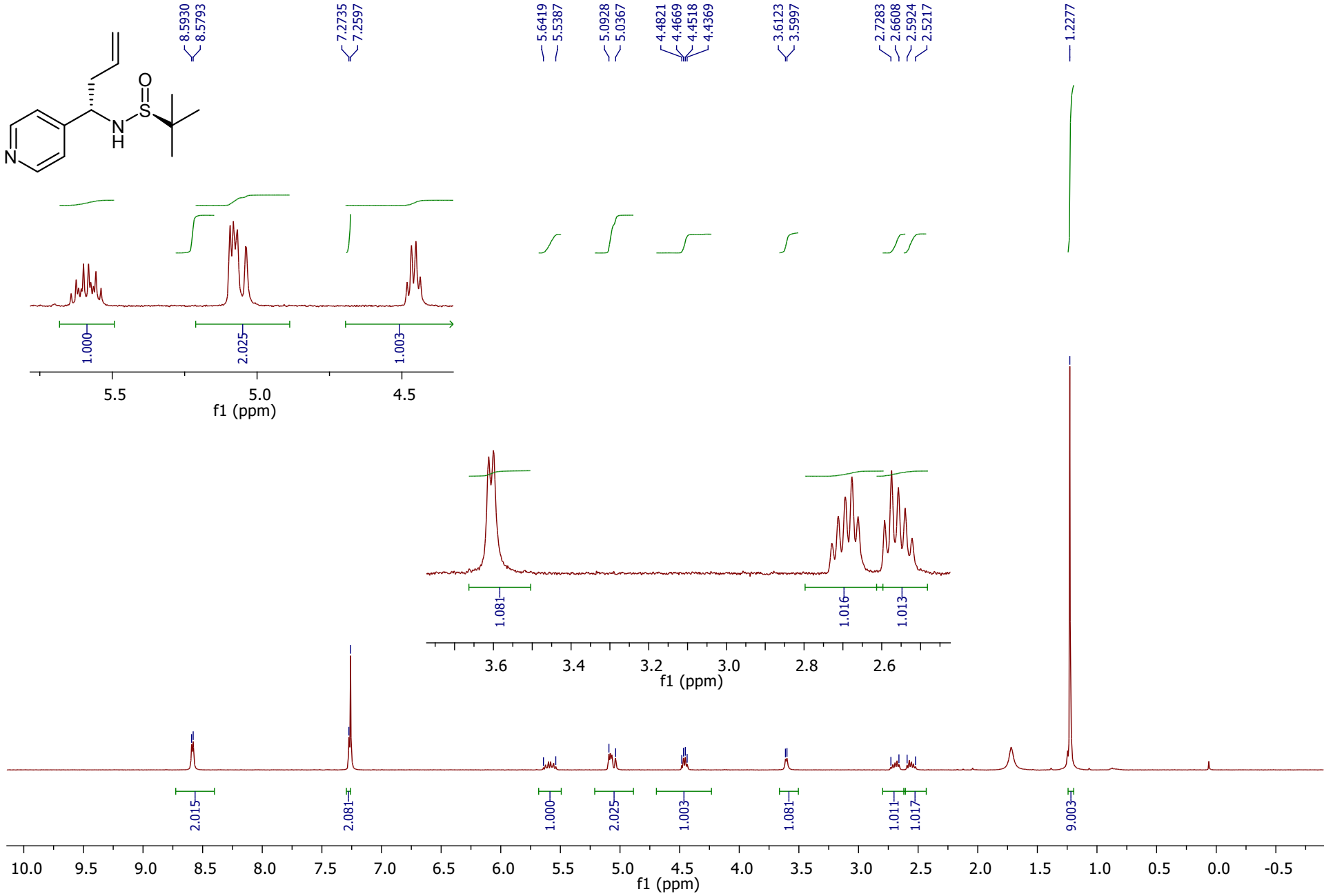
^{1}H NMR ($CDCl_3$, 400 MHz) **3q**



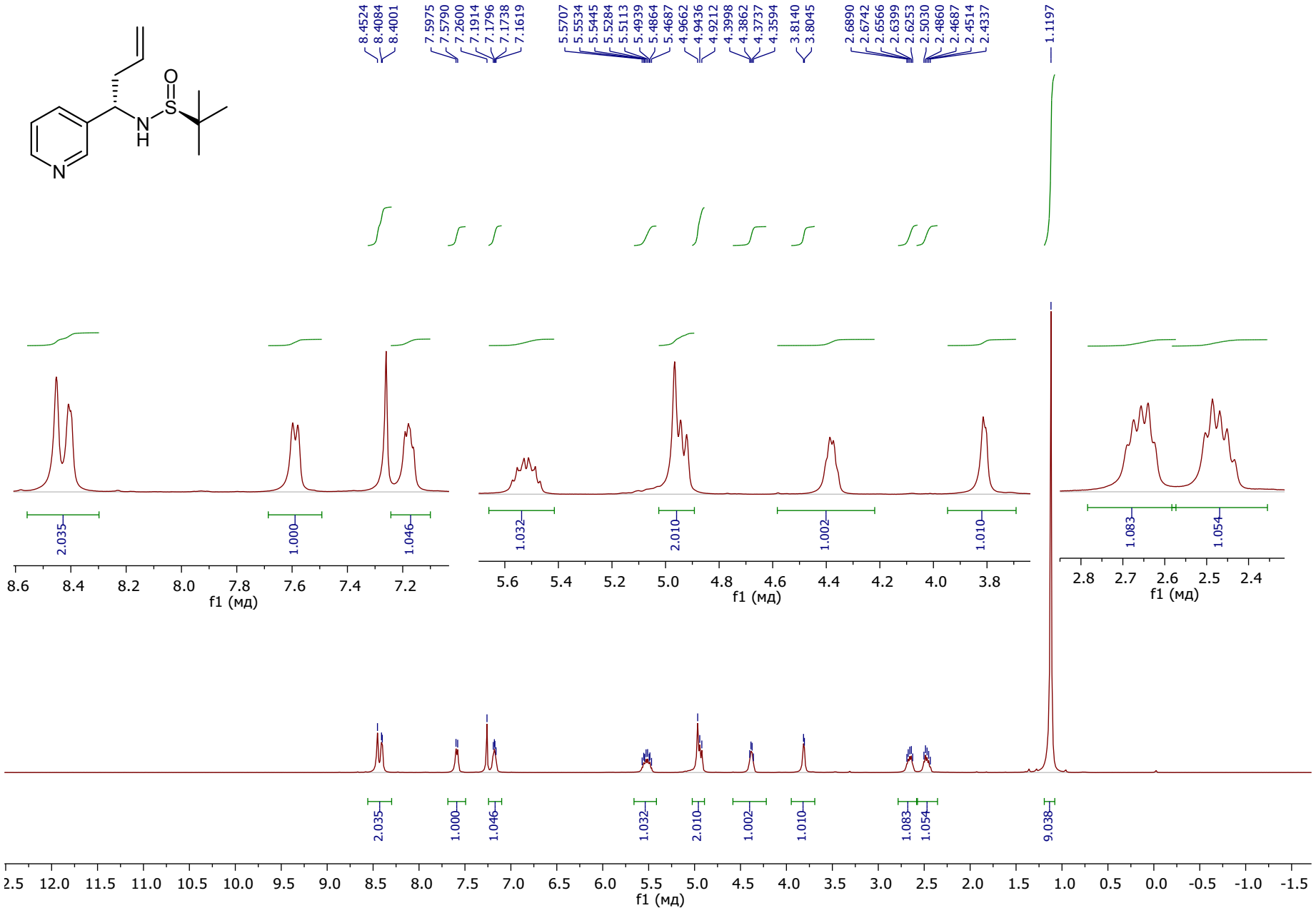
^{13}C NMR ($CDCl_3$, 101 MHz) **3q**



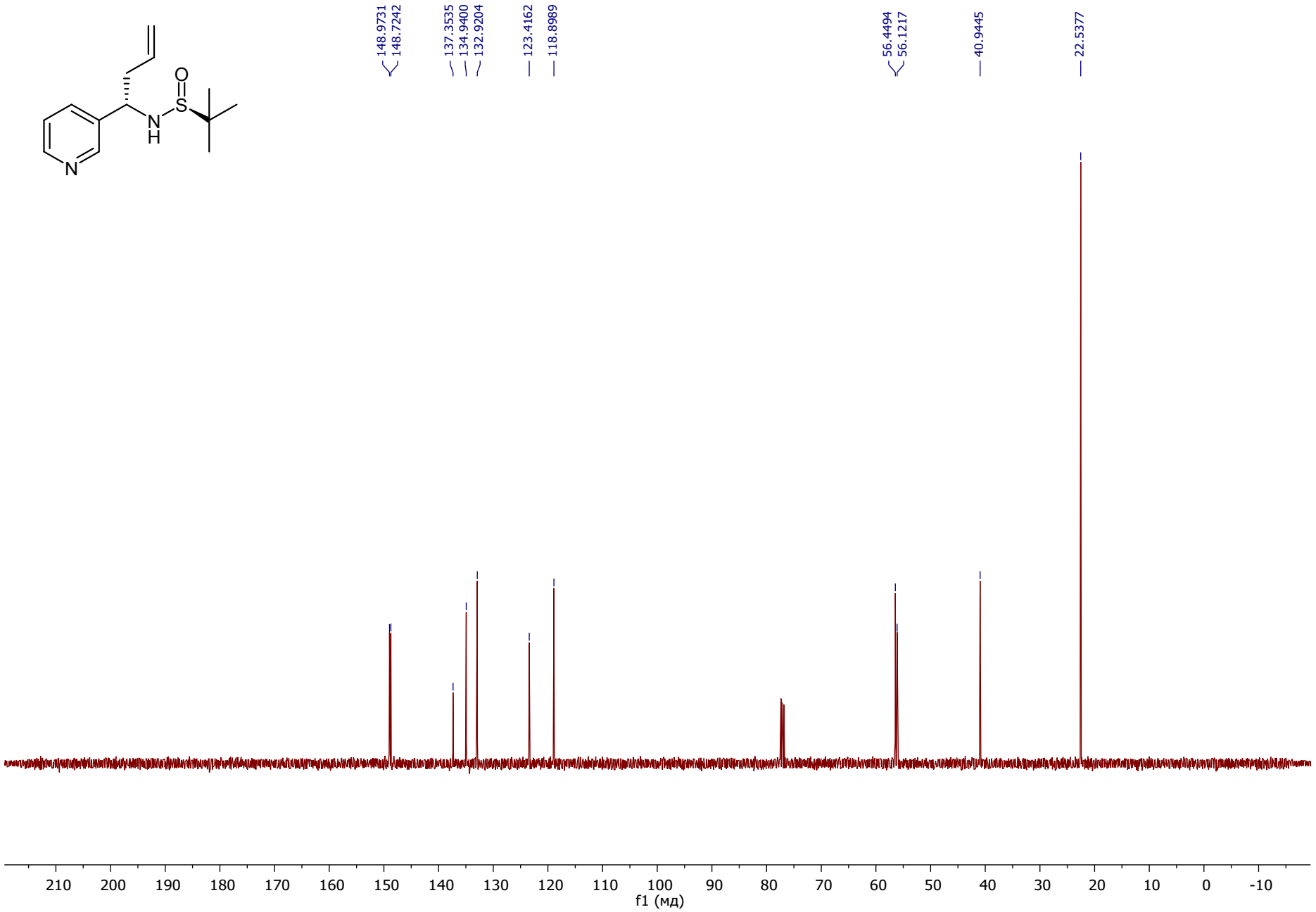
^{1}H NMR ($CDCl_3$, 400 MHz) **3r**



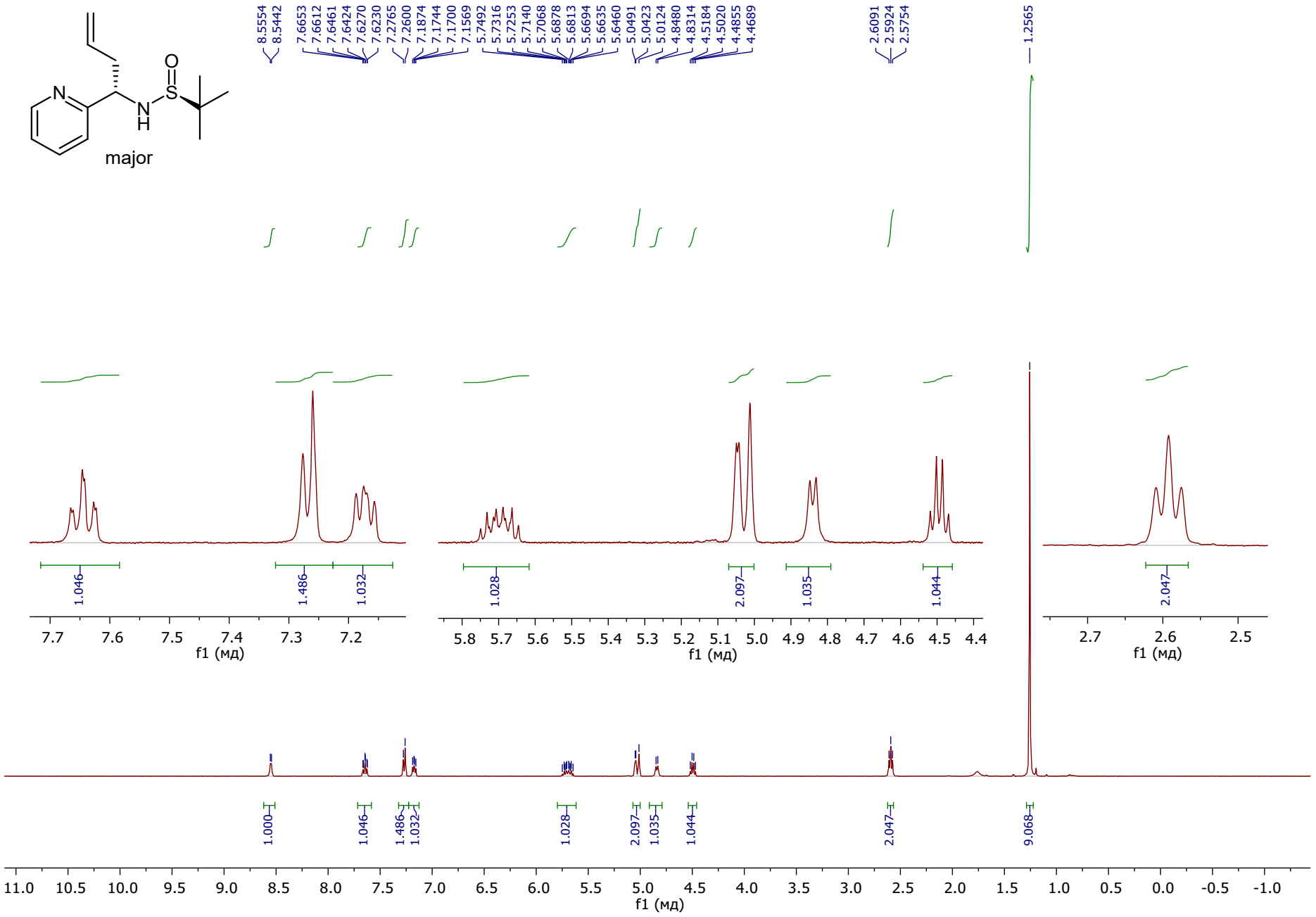
^{1}H NMR ($CDCl_3$, 400 MHz) **3s**



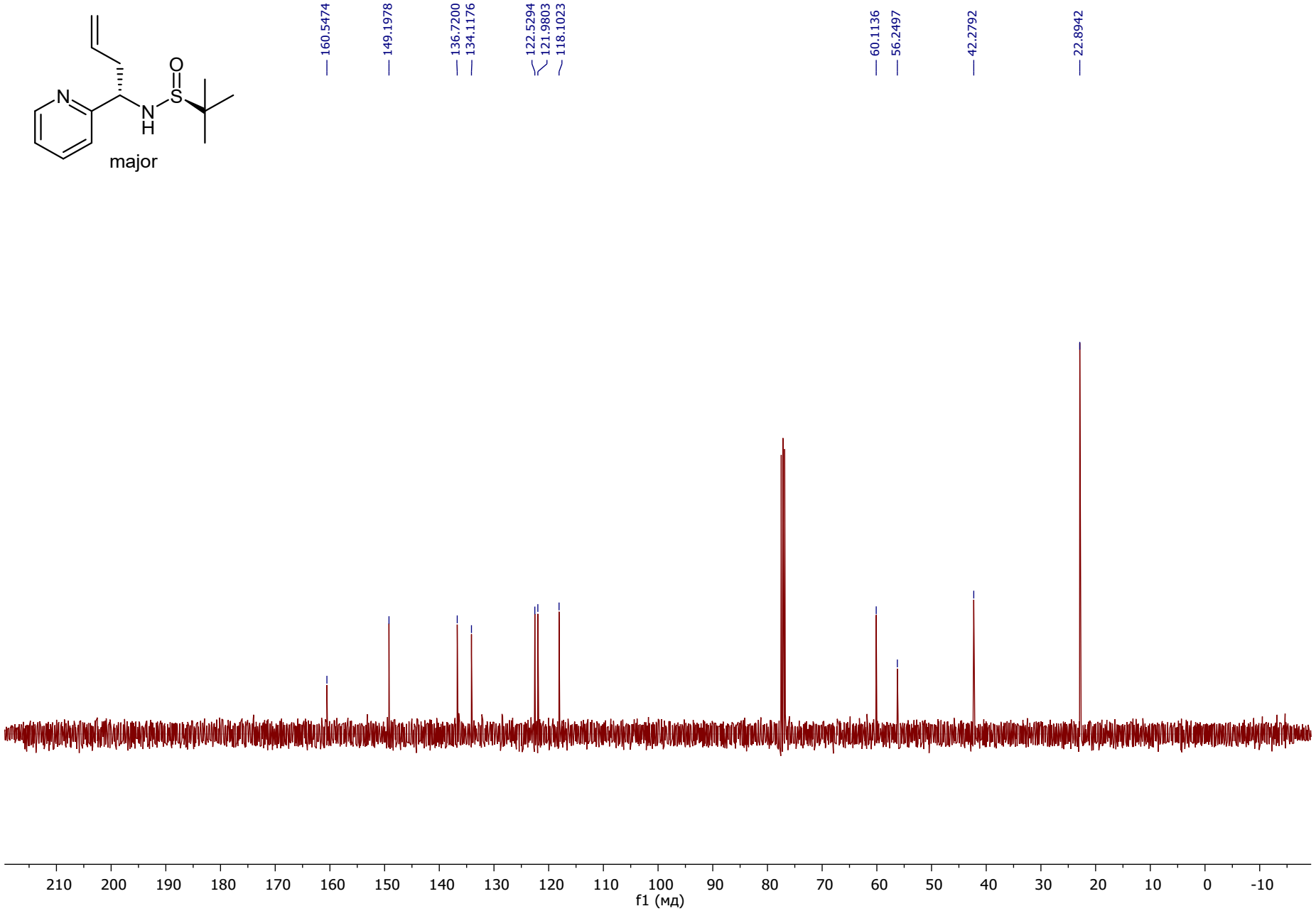
^{13}C NMR ($CDCl_3$, 101 MHz) **3s**



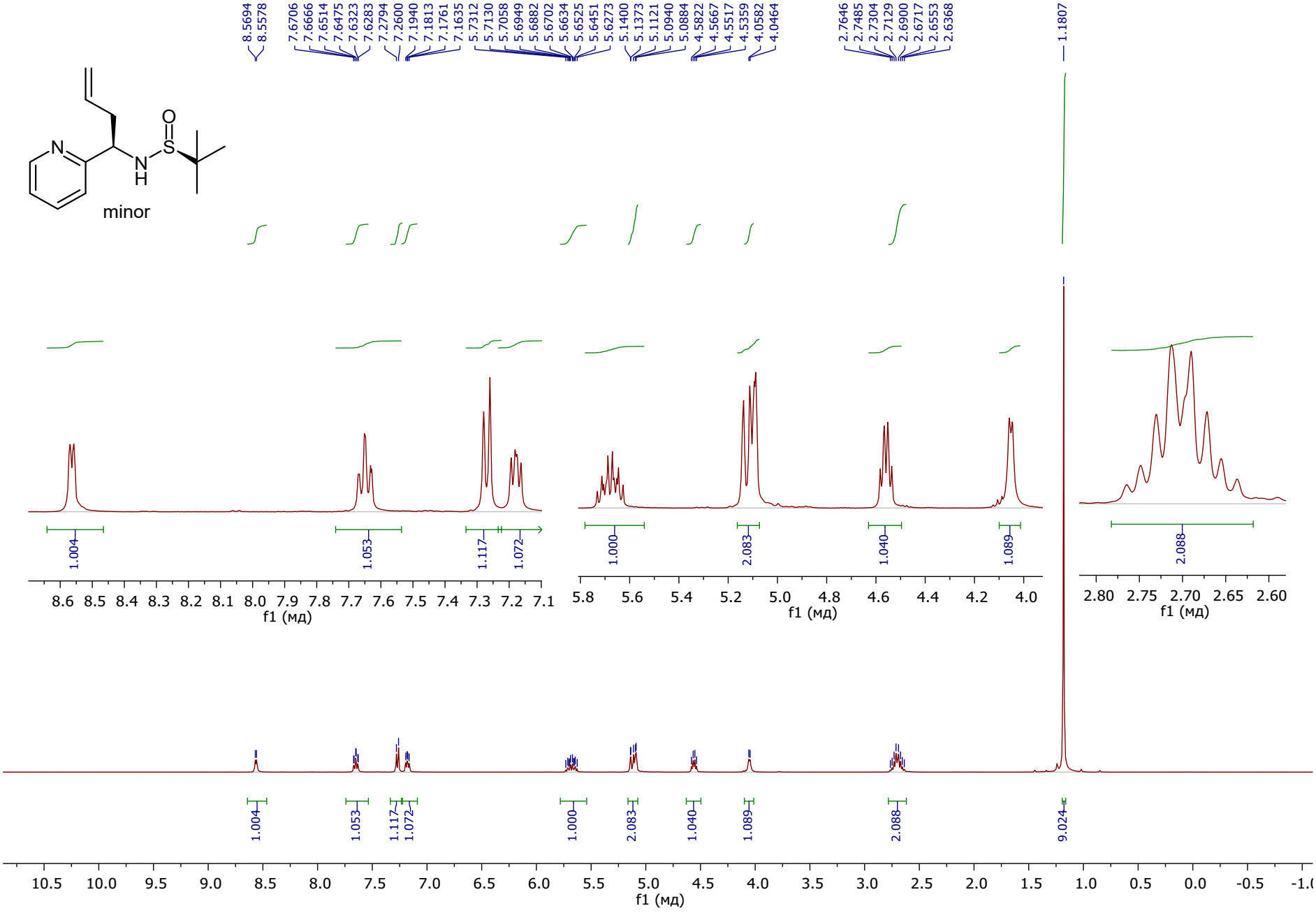
^{1}H NMR ($CDCl_3$, 400 MHz) **(S_s,*S*)-3t**



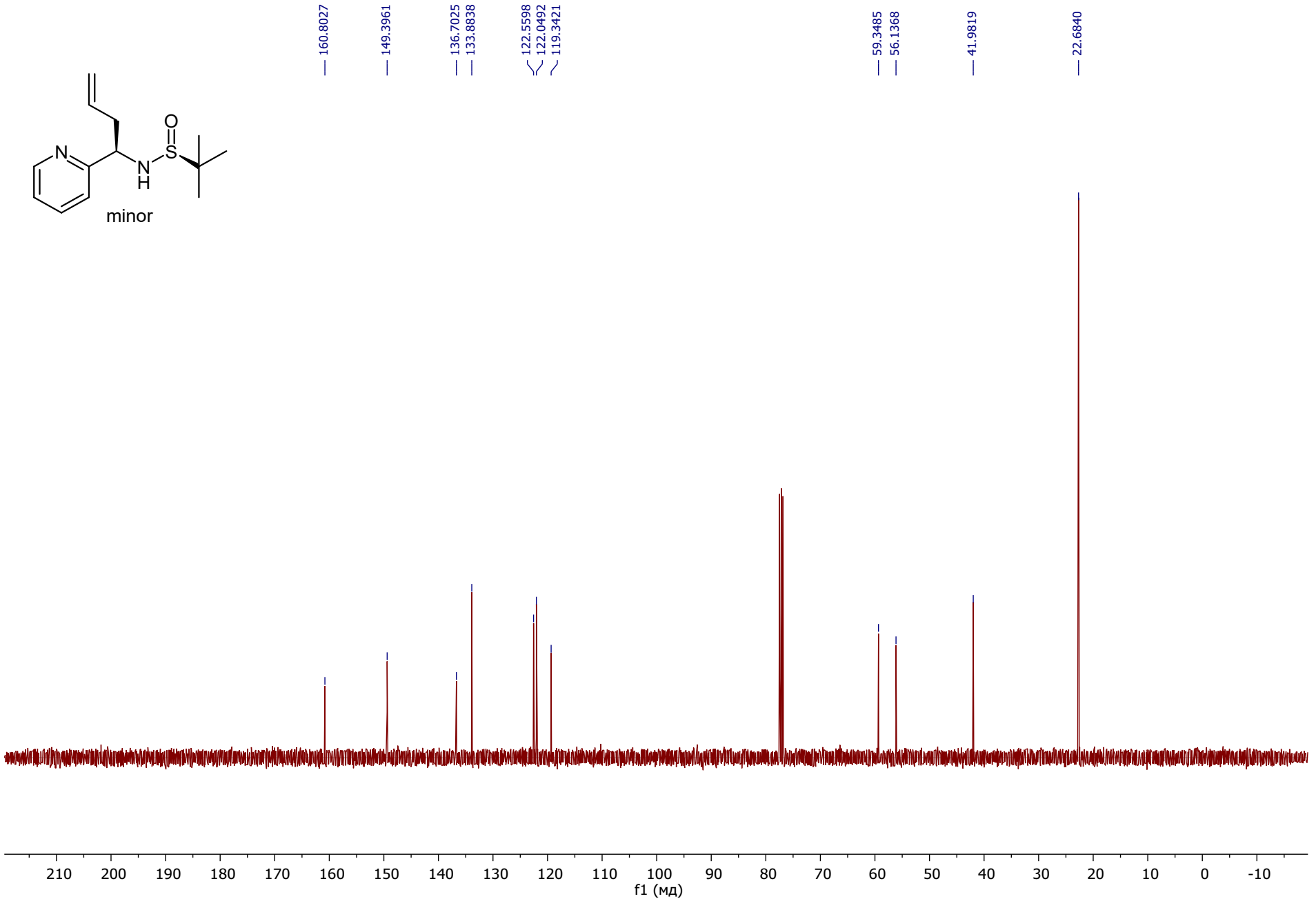
^{13}C NMR ($CDCl_3$, 101 MHz) **(S_s,*S*)-3t**



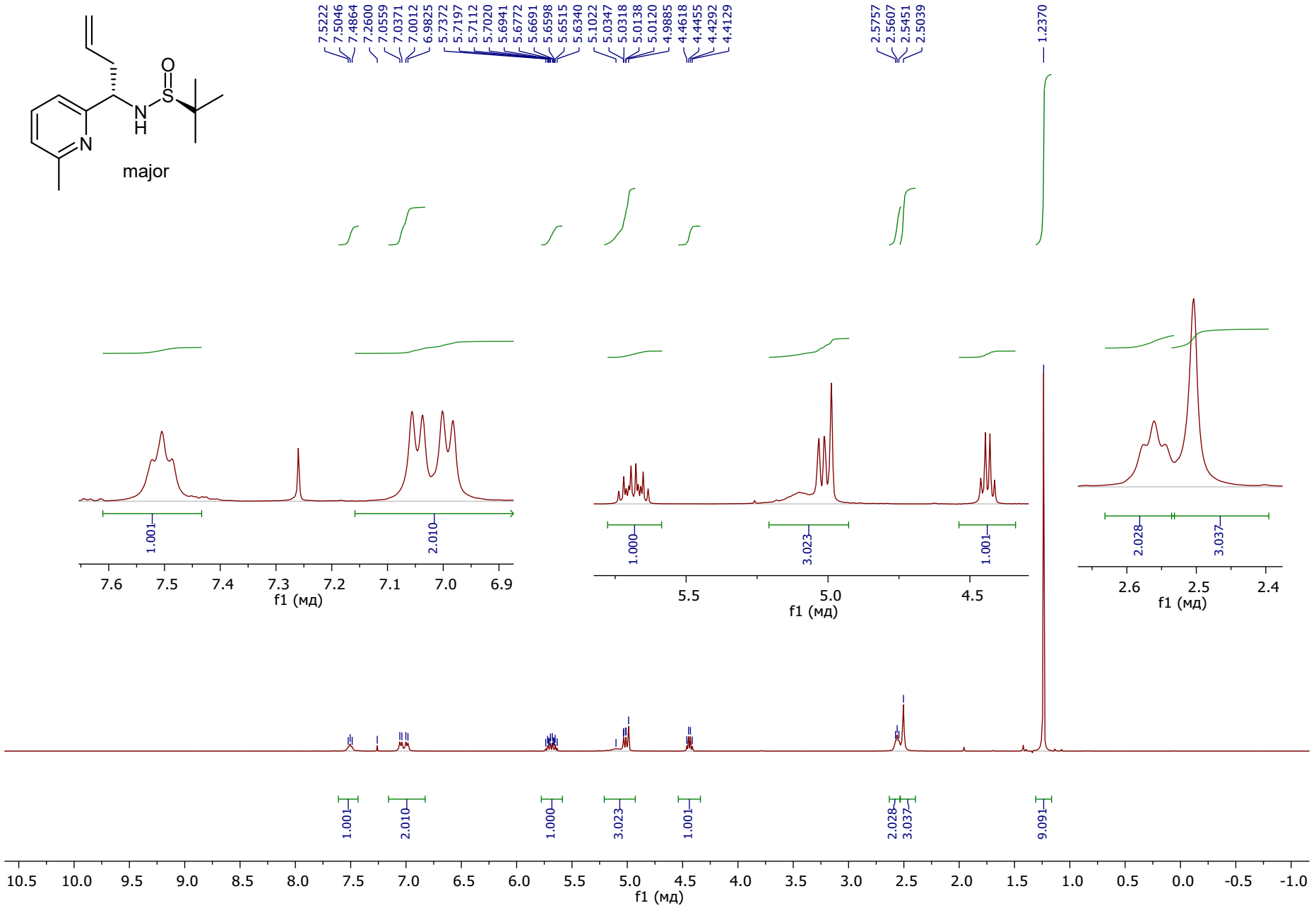
^{1}H NMR ($CDCl_3$, 400 MHz) **(S_s,*R*)-3t**



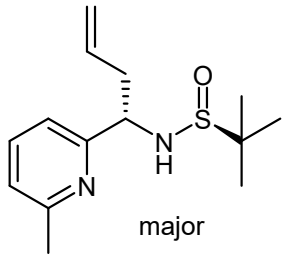
^{13}C NMR ($CDCl_3$, 101 MHz) **(S_s,*R*)-3t**



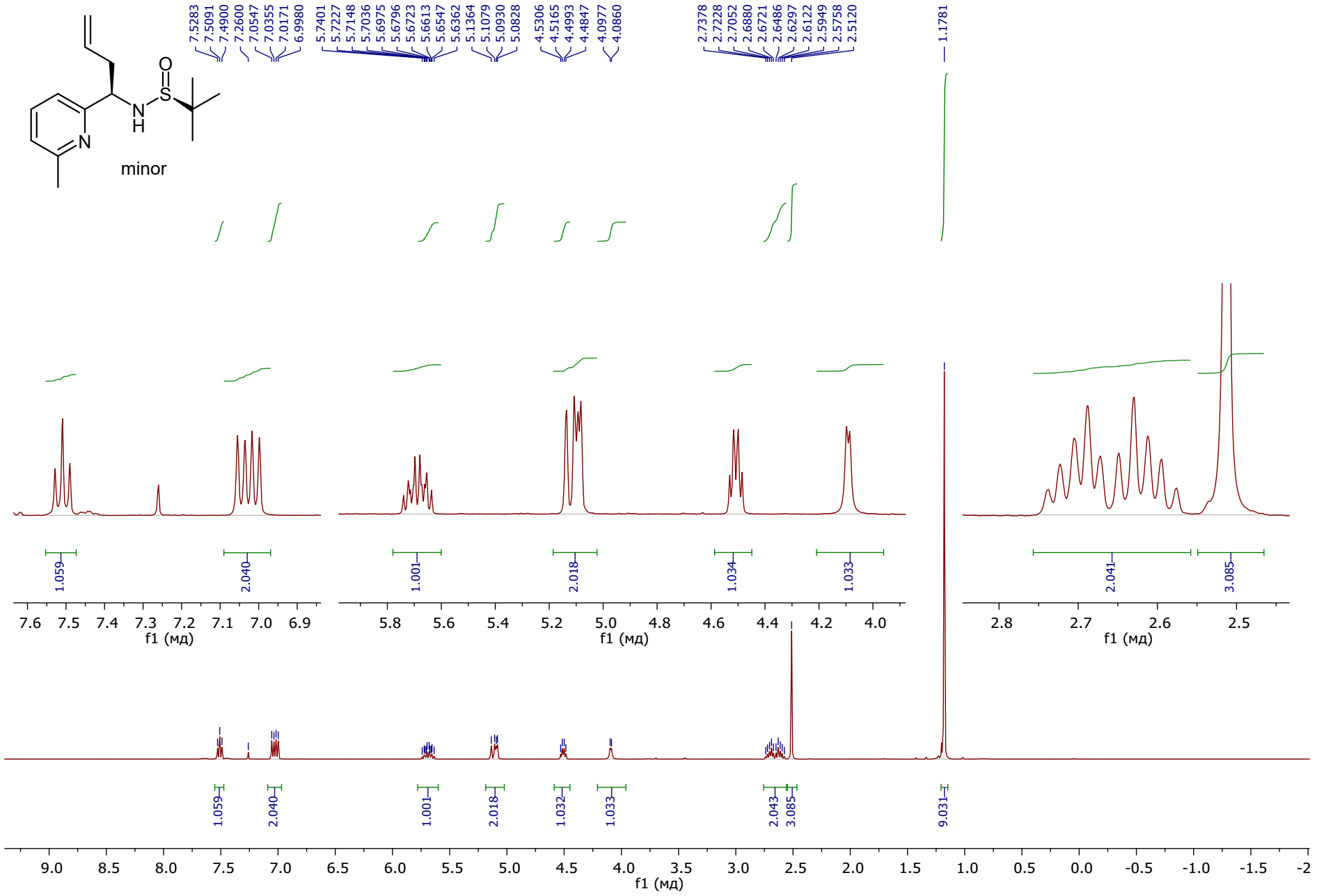
^{1}H NMR ($CDCl_3$, 400 MHz) **(S_s,*S*)-3u**



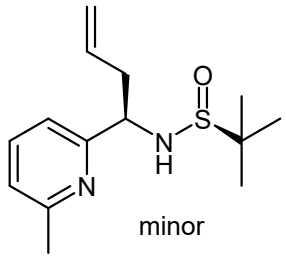
^{13}C NMR ($CDCl_3$, 101 MHz) **(S_s,*S*)-3u**



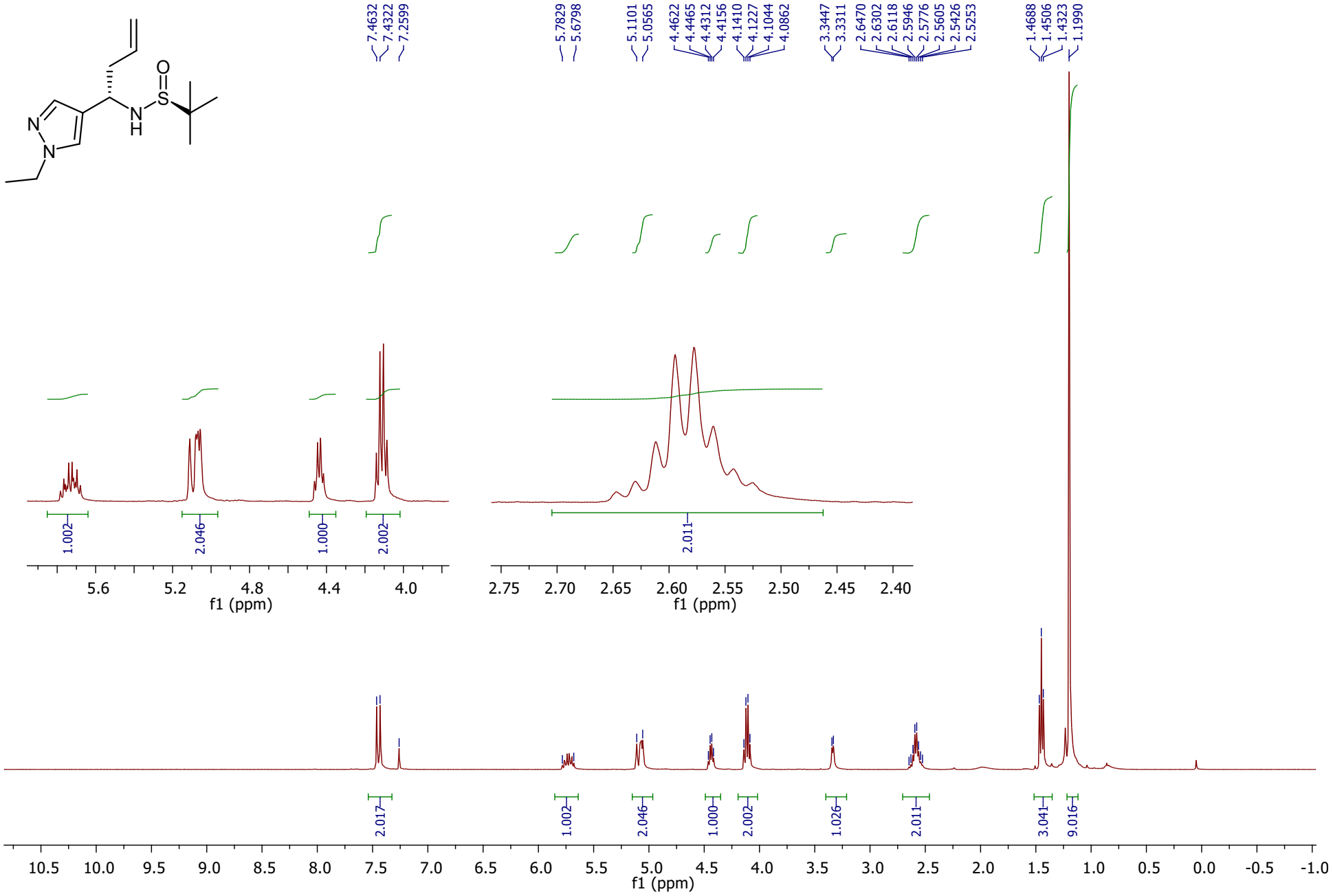
^{1}H NMR ($CDCl_3$, 400 MHz) **(S_s,*R*)-3u**



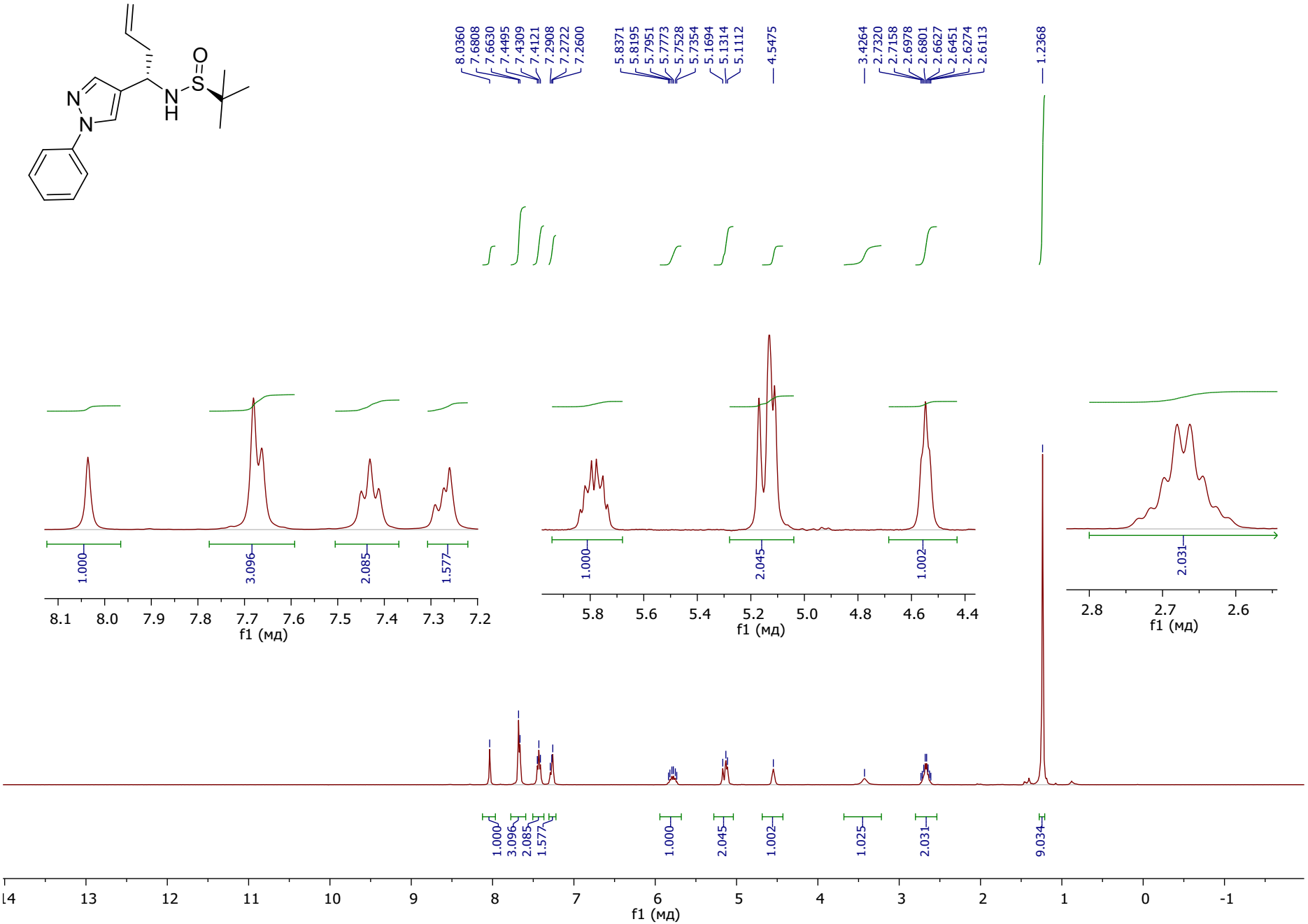
^{13}C NMR ($CDCl_3$, 101 MHz) **(S_s,*R*)-3u**



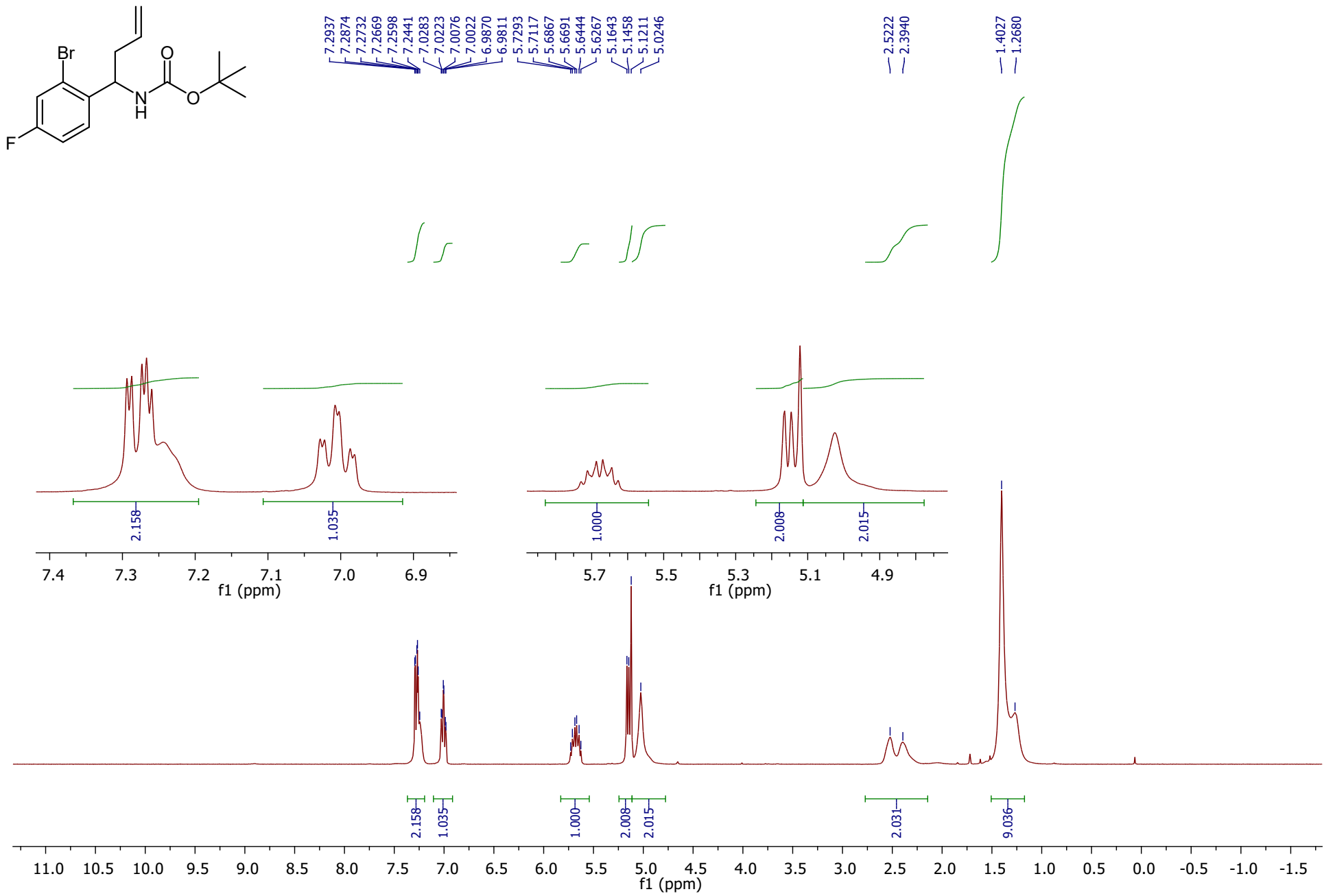
^{1}H NMR ($CDCl_3$, 400 MHz) **3v**



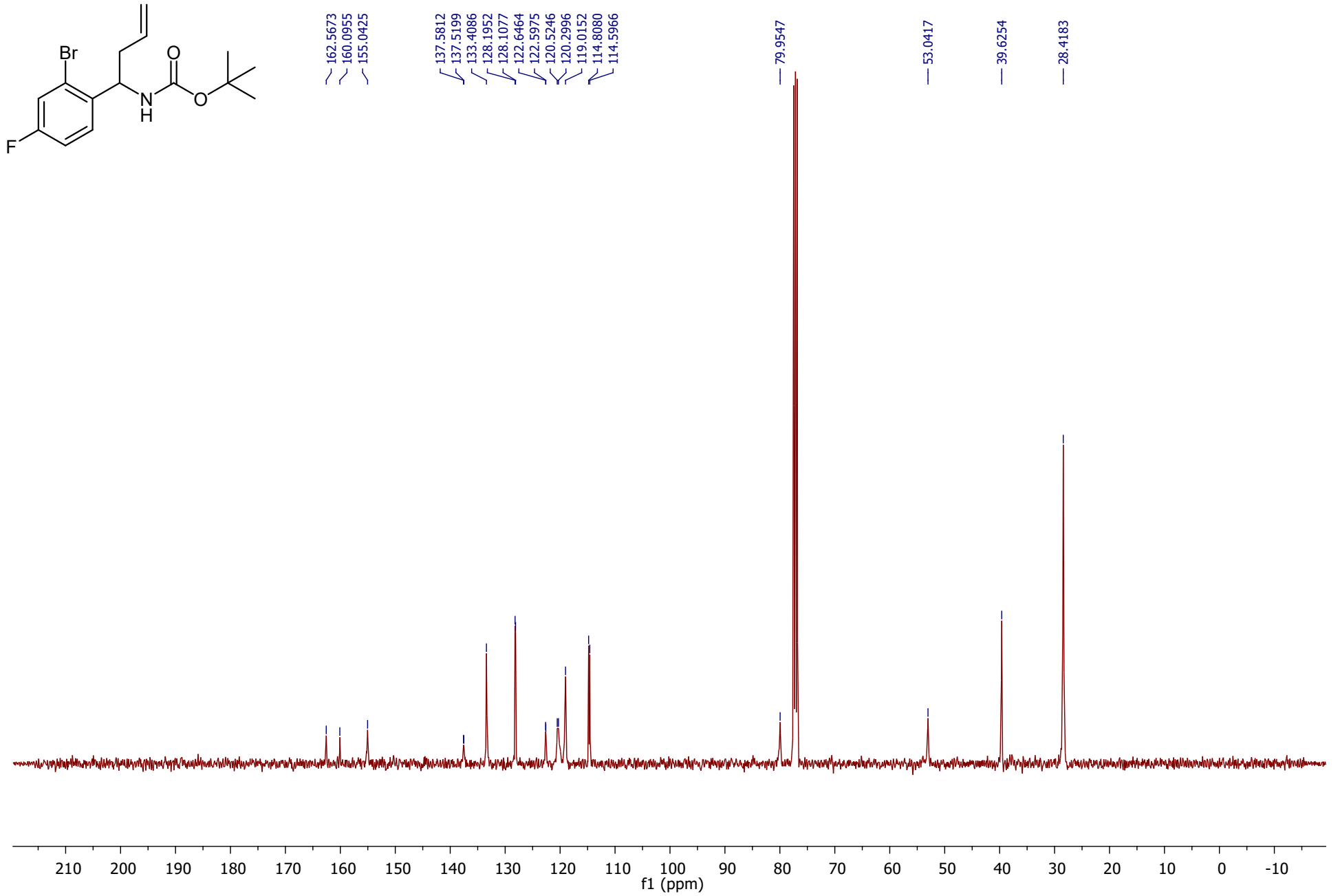
^{1}H NMR ($CDCl_3$, 400 MHz) **3w**



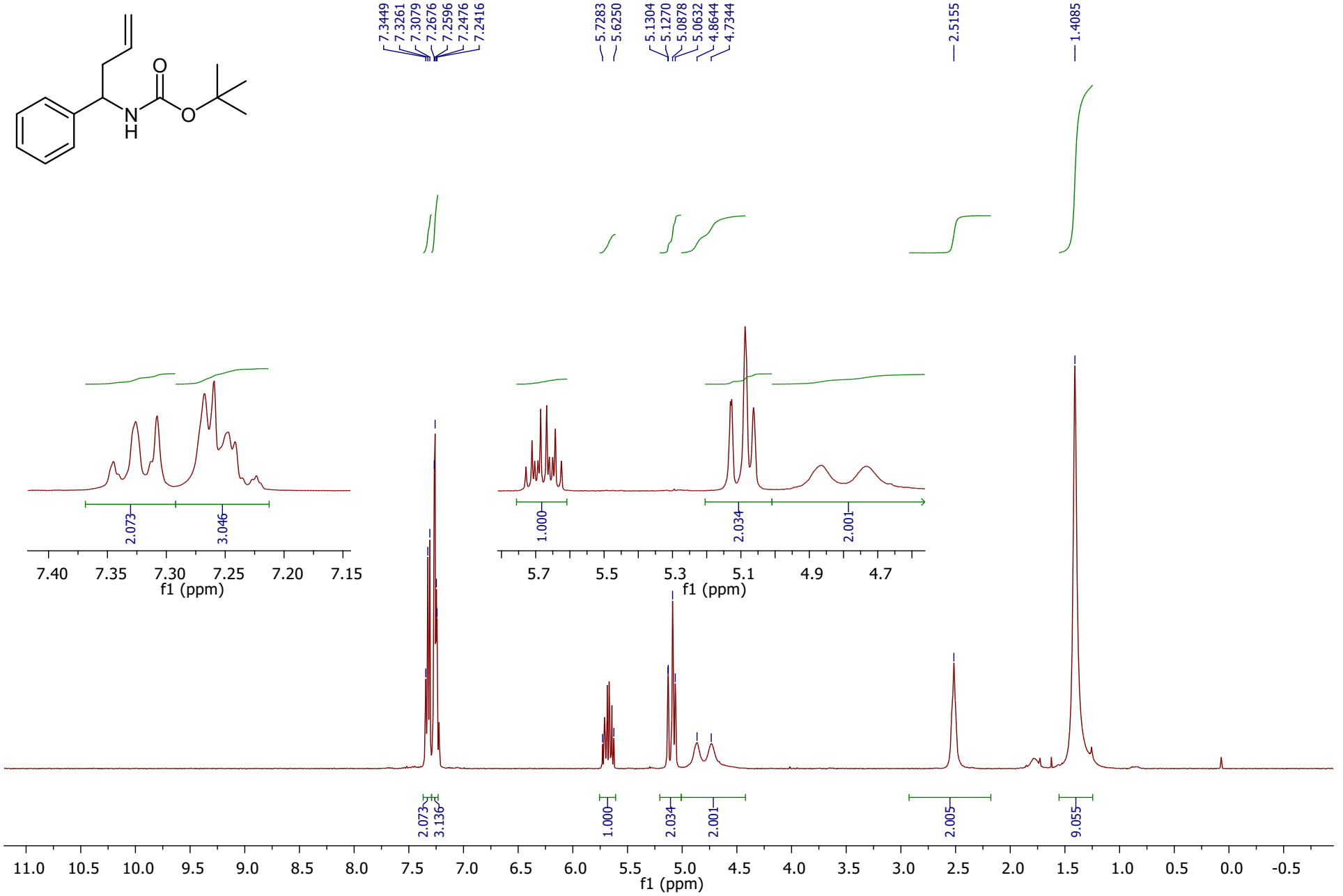
^{1}H NMR ($CDCl_3$, 400 MHz) **6a**



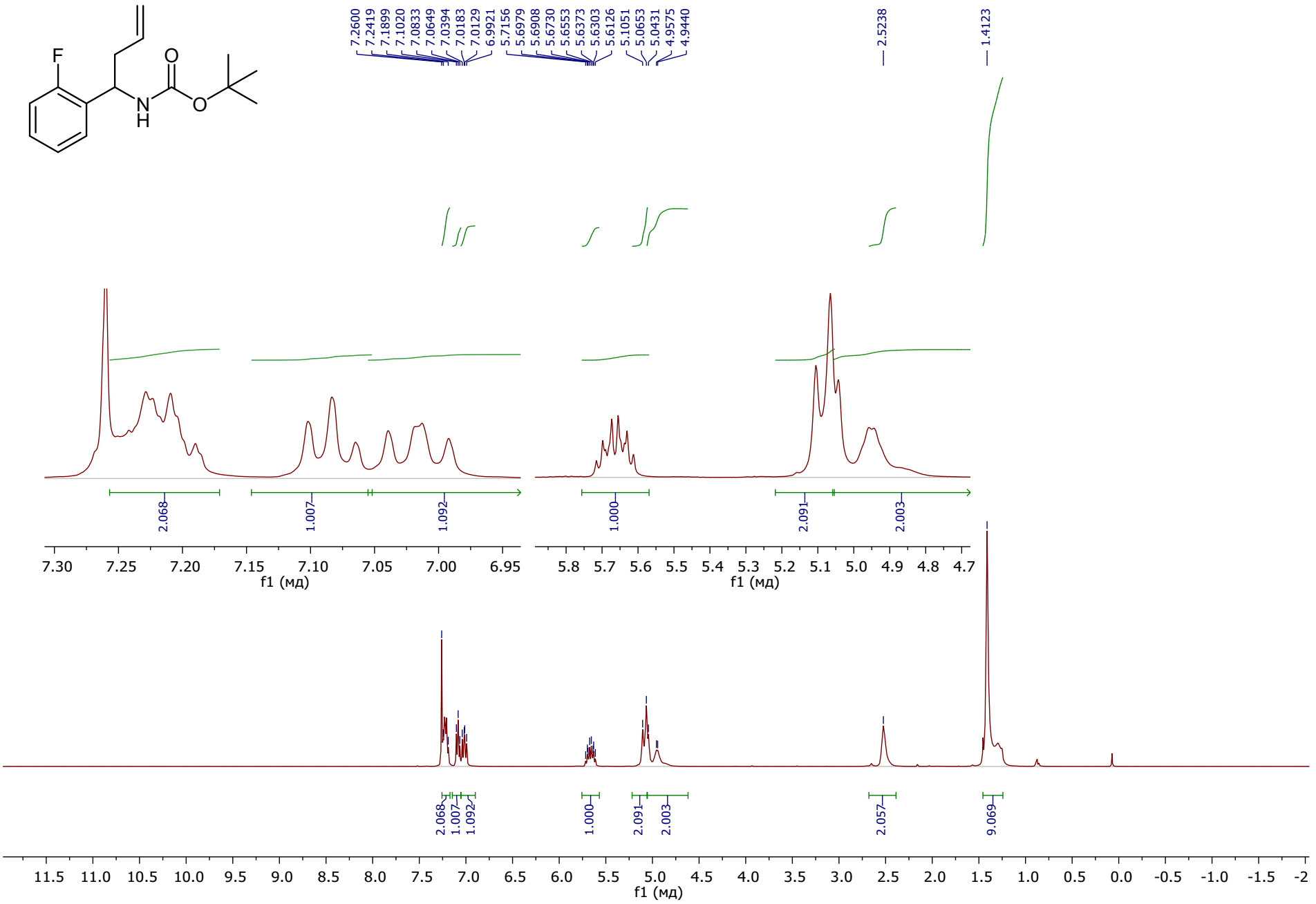
^{13}C NMR ($CDCl_3$, 101 MHz) **6a**



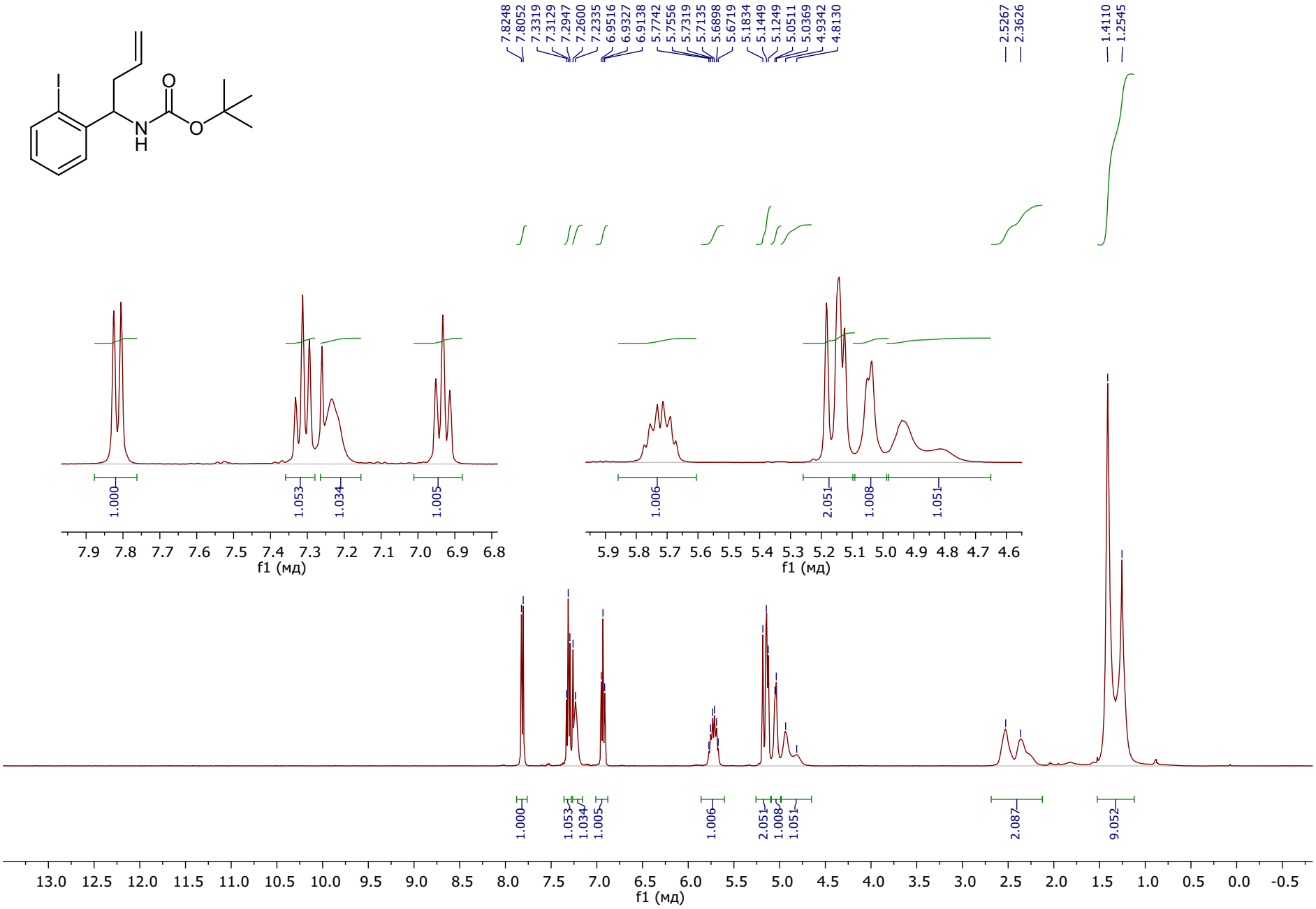
^{1}H NMR ($CDCl_3$, 400 MHz) **6b**



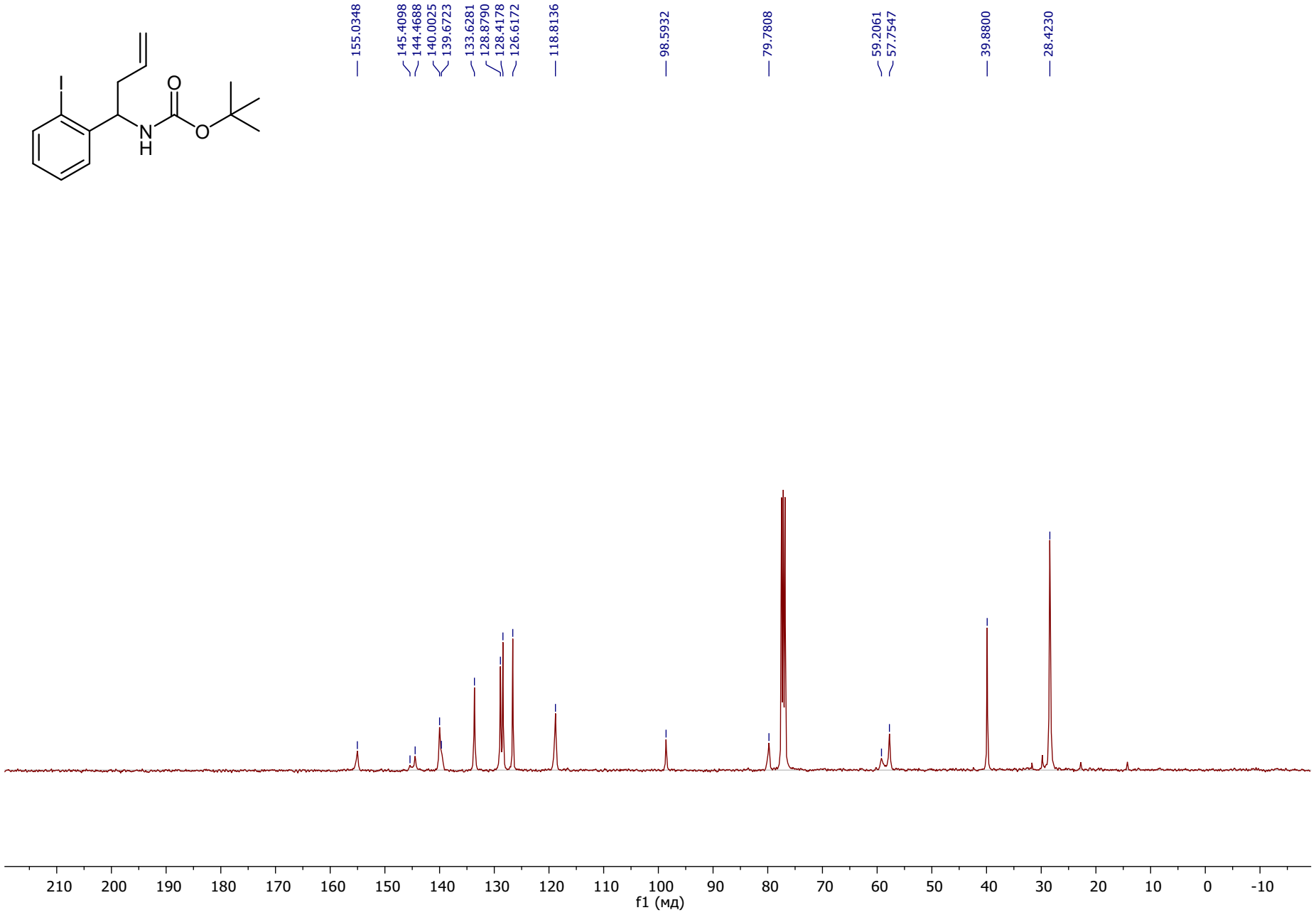
^{1}H NMR ($CDCl_3$, 400 MHz) **6c**



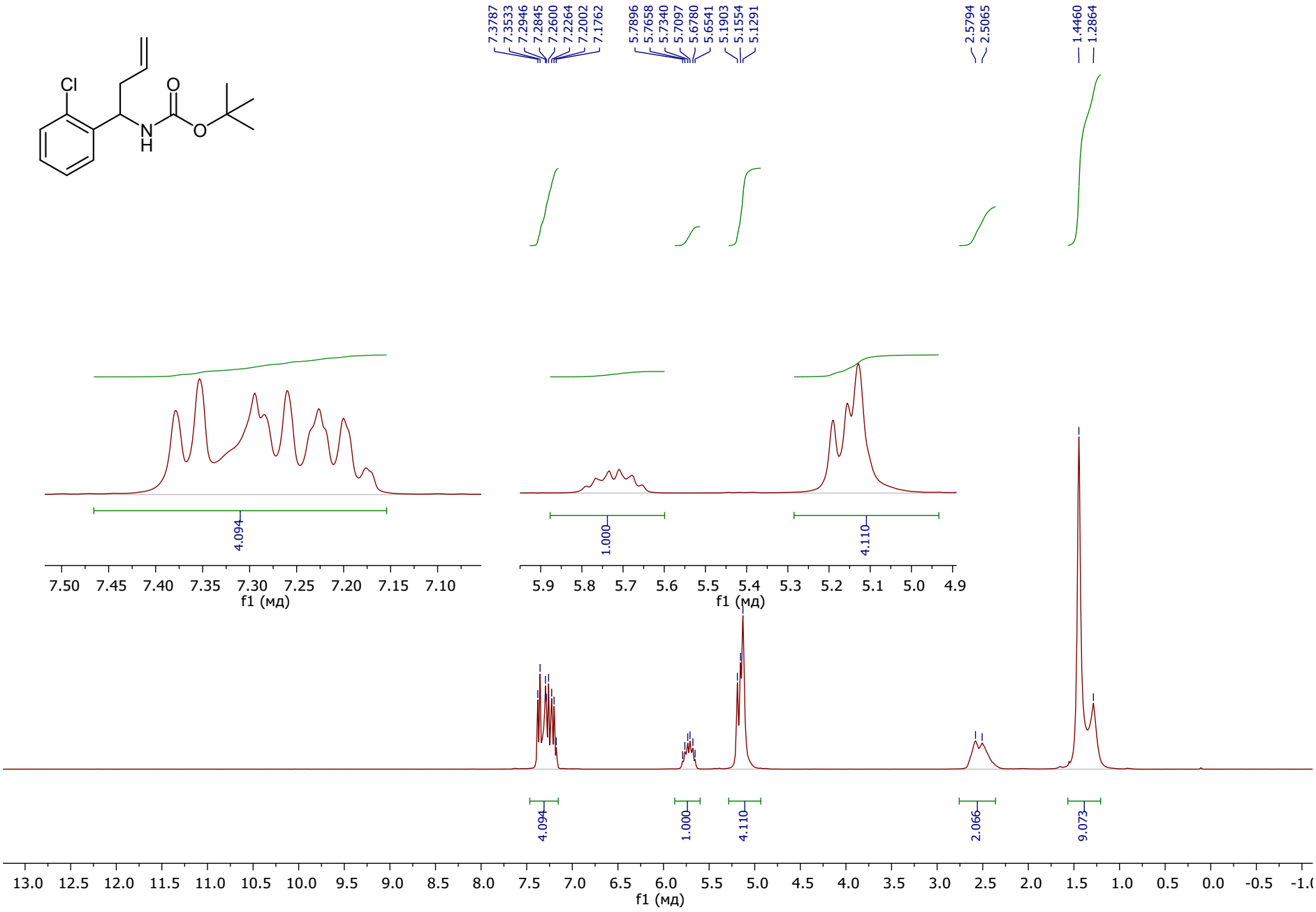
^{1}H NMR ($CDCl_3$, 400 MHz) **6d**



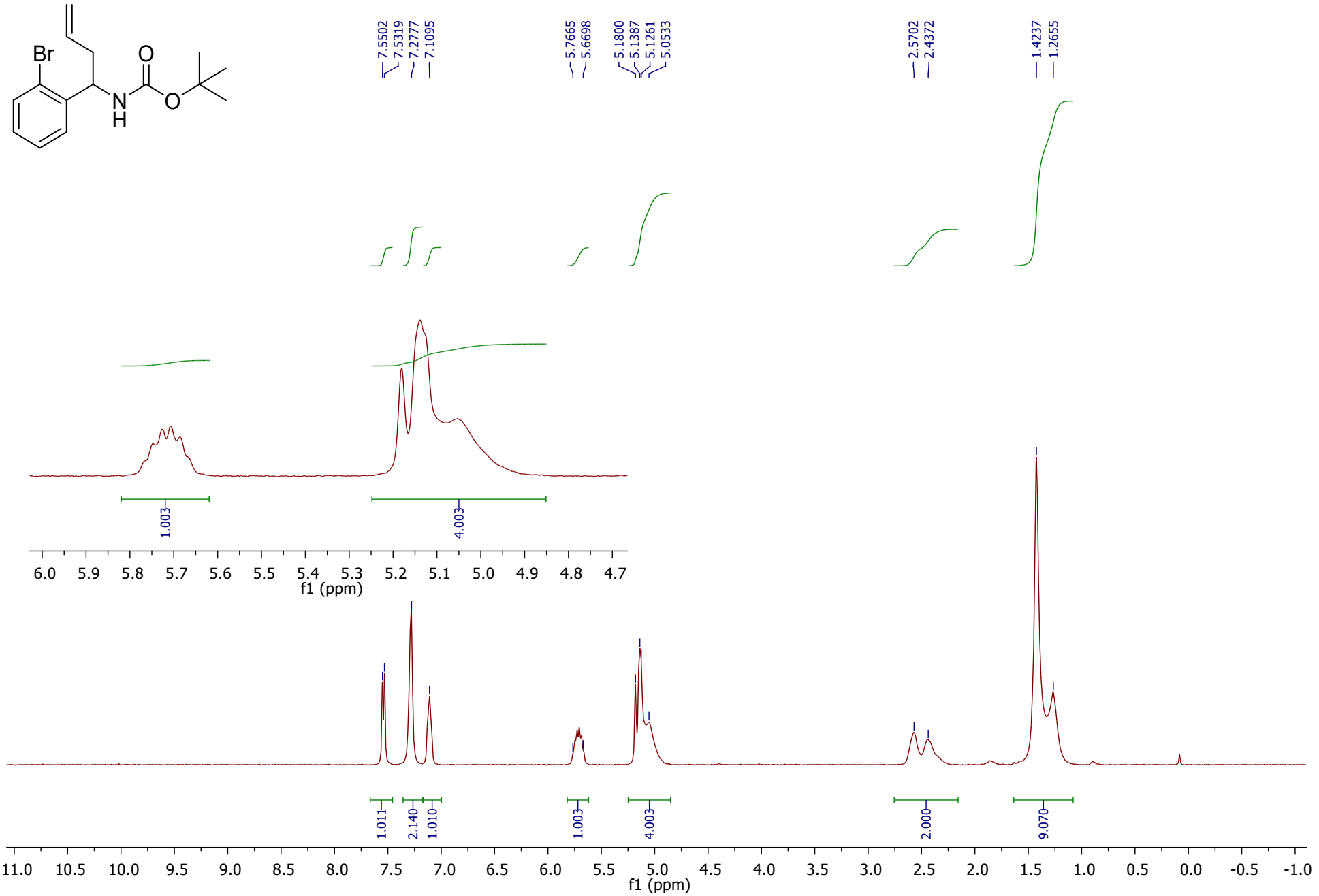
^{13}C NMR ($CDCl_3$, 101 MHz) **6d**



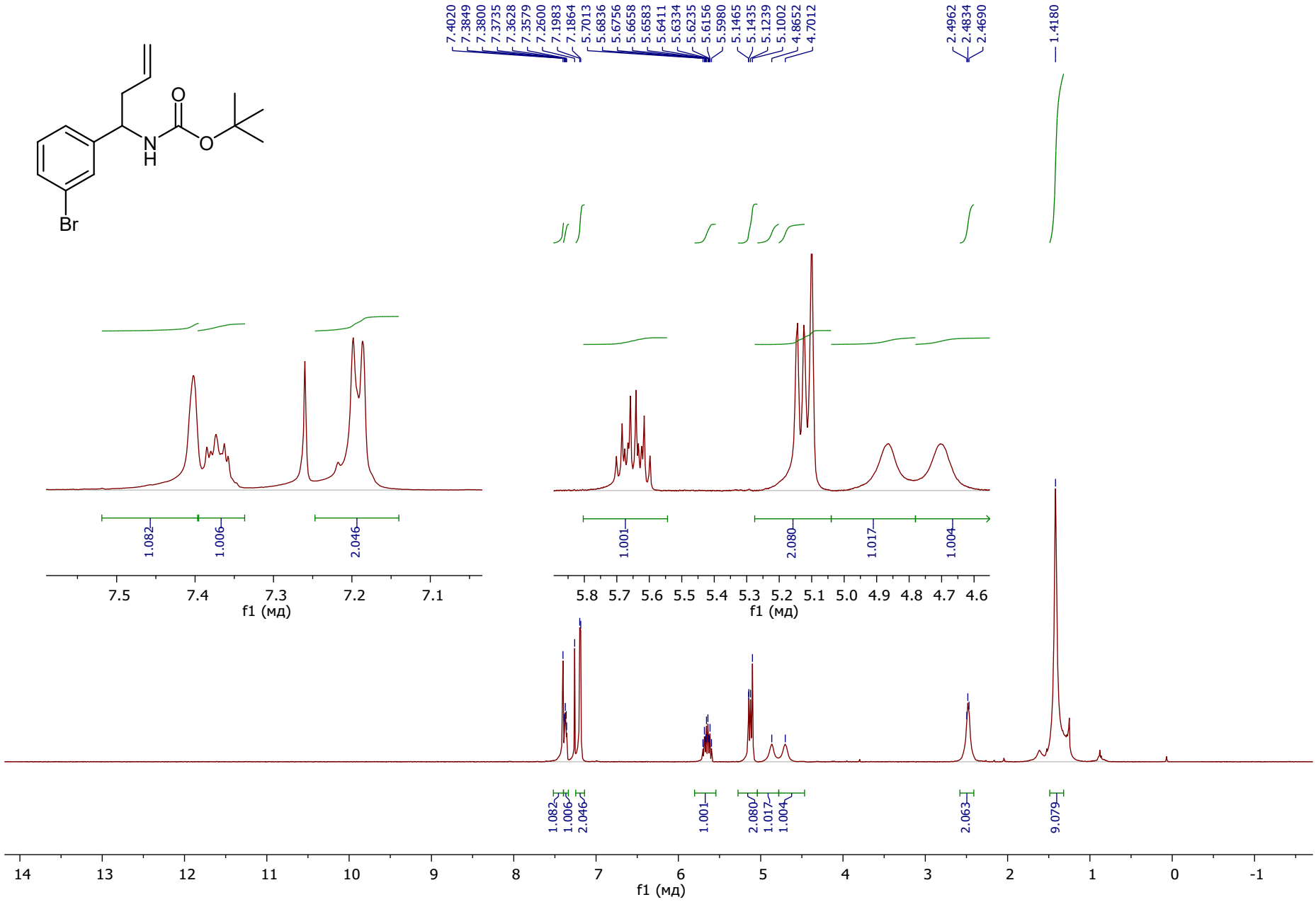
^{1}H NMR ($CDCl_3$, 400 MHz) **6e**



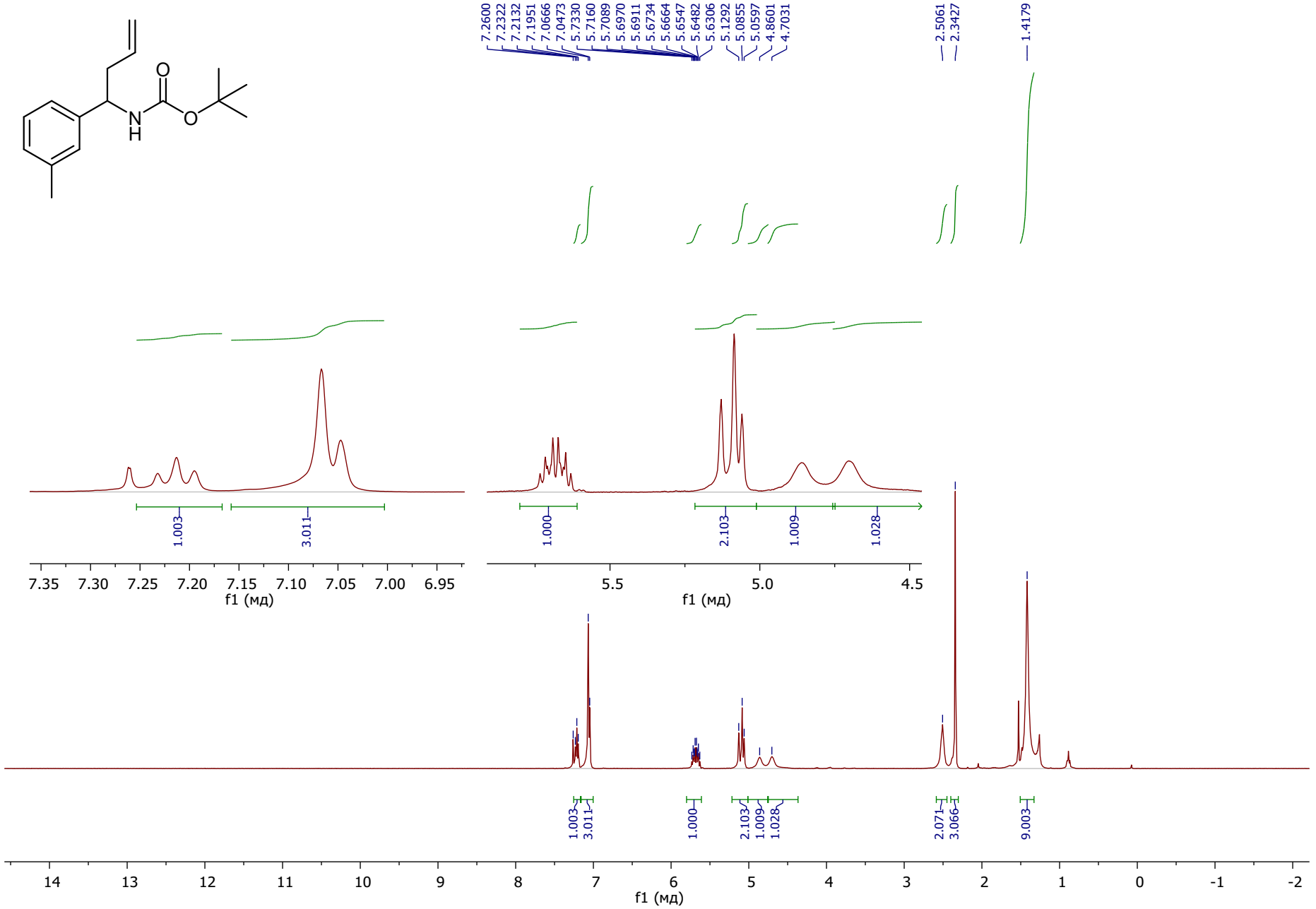
^{1}H NMR ($CDCl_3$, 400 MHz) **6f**



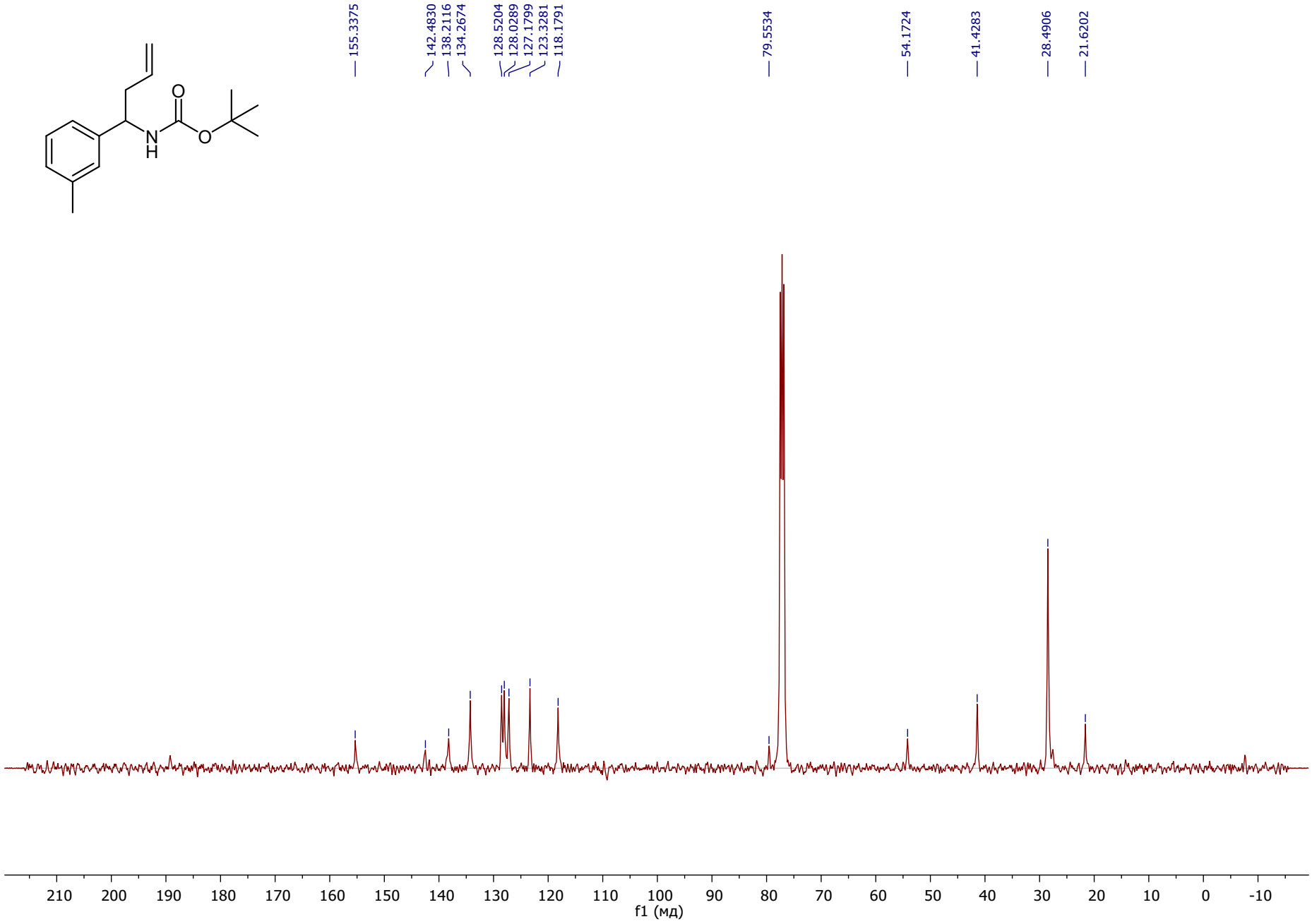
^{1}H NMR ($CDCl_3$, 400 MHz) **6g**



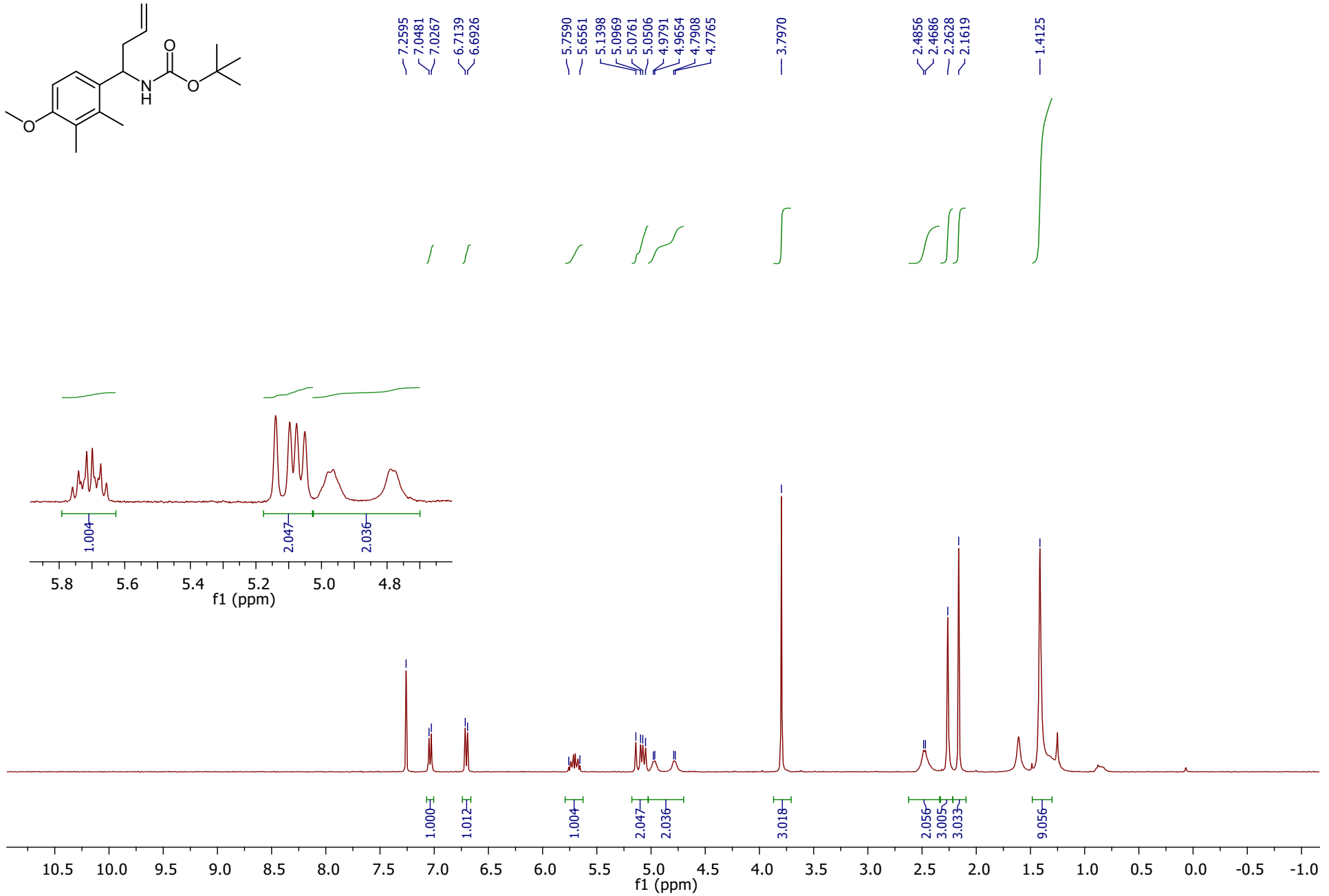
^{1}H NMR ($CDCl_3$, 400 MHz) **6h**



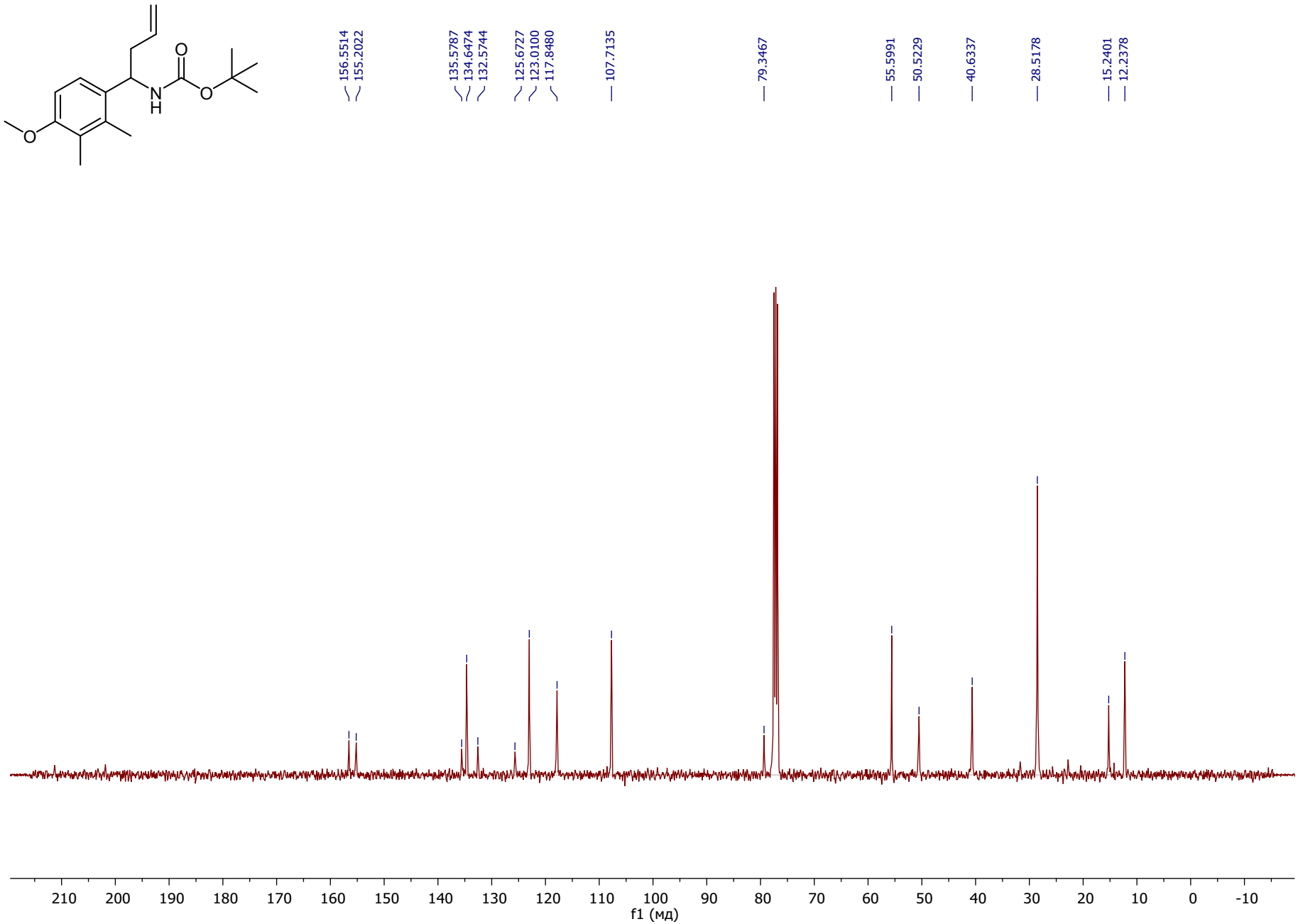
^{13}C NMR ($CDCl_3$, 101 MHz) **6h**



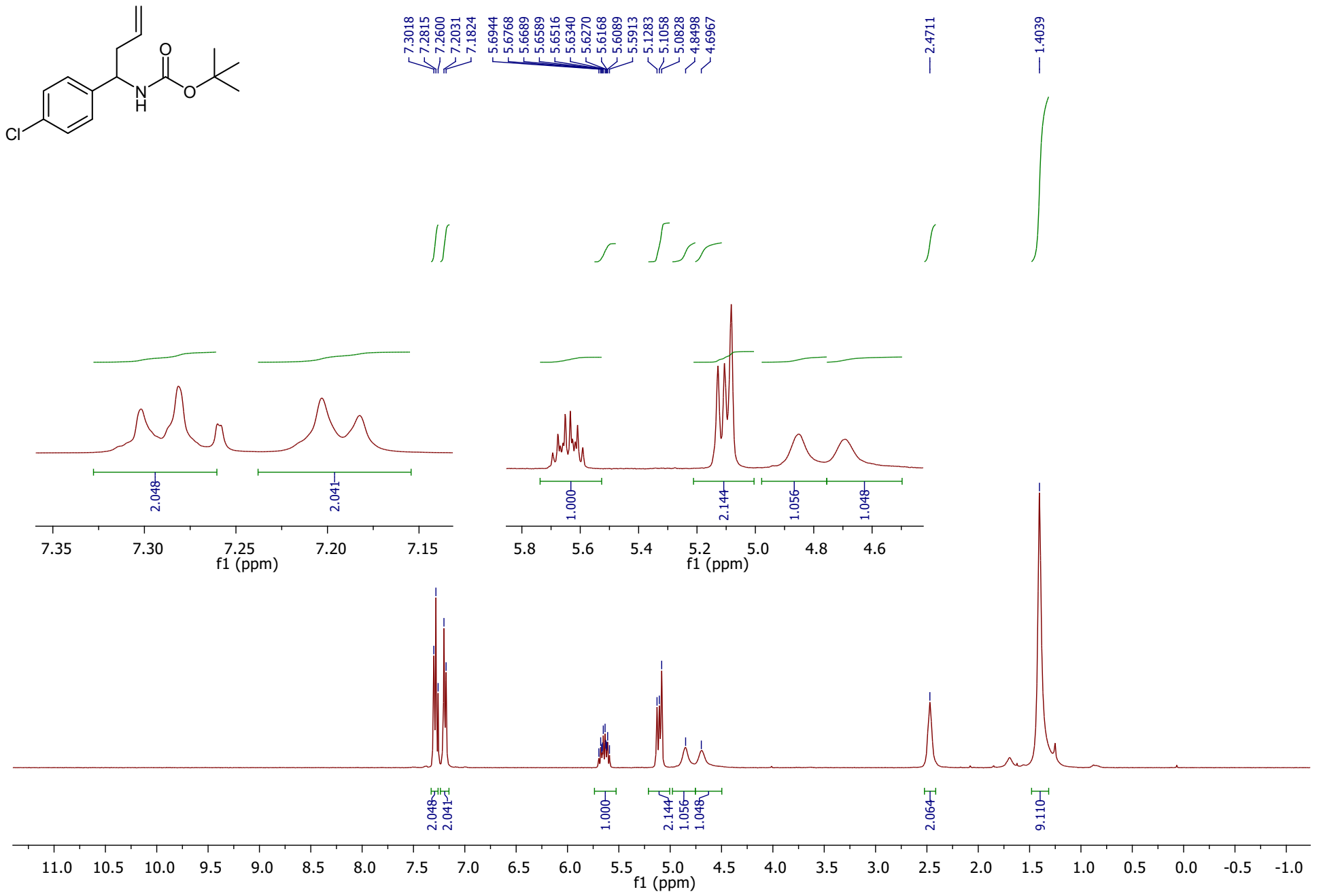
^{1}H NMR ($CDCl_3$, 400 MHz) **6i**



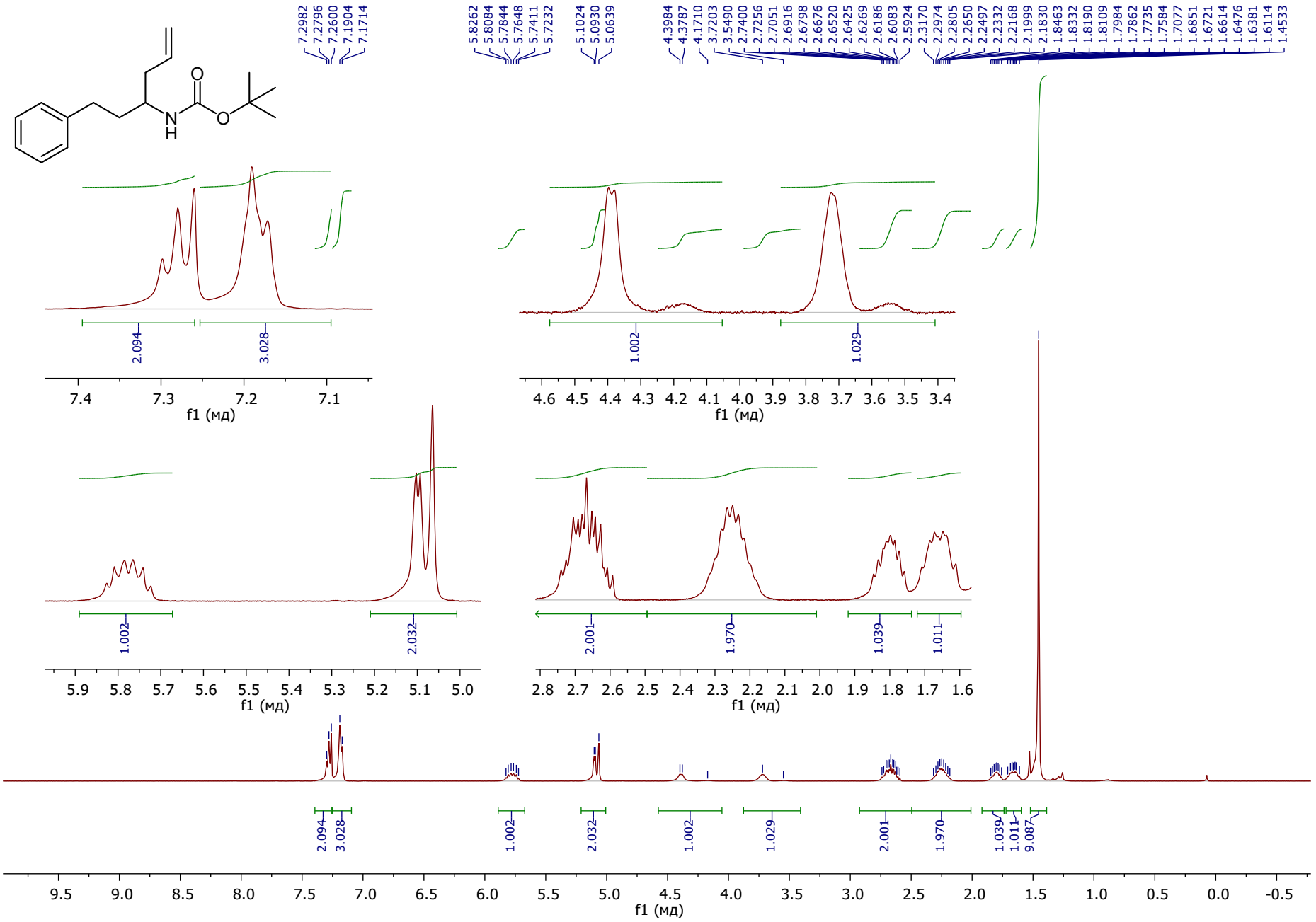
^{13}C NMR ($CDCl_3$, 101 MHz) **6i**



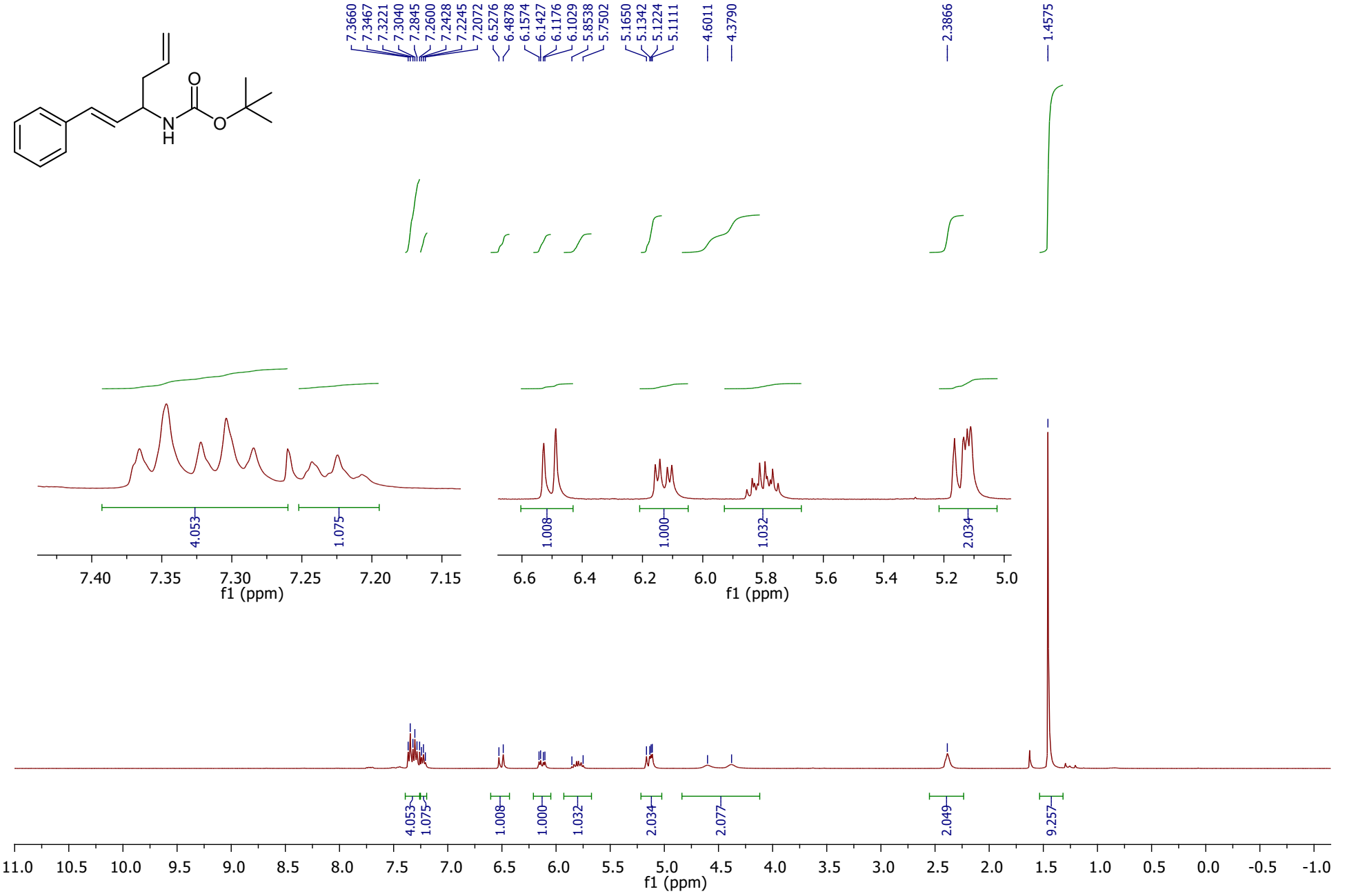
^{1}H NMR ($CDCl_3$, 400 MHz) **6j**



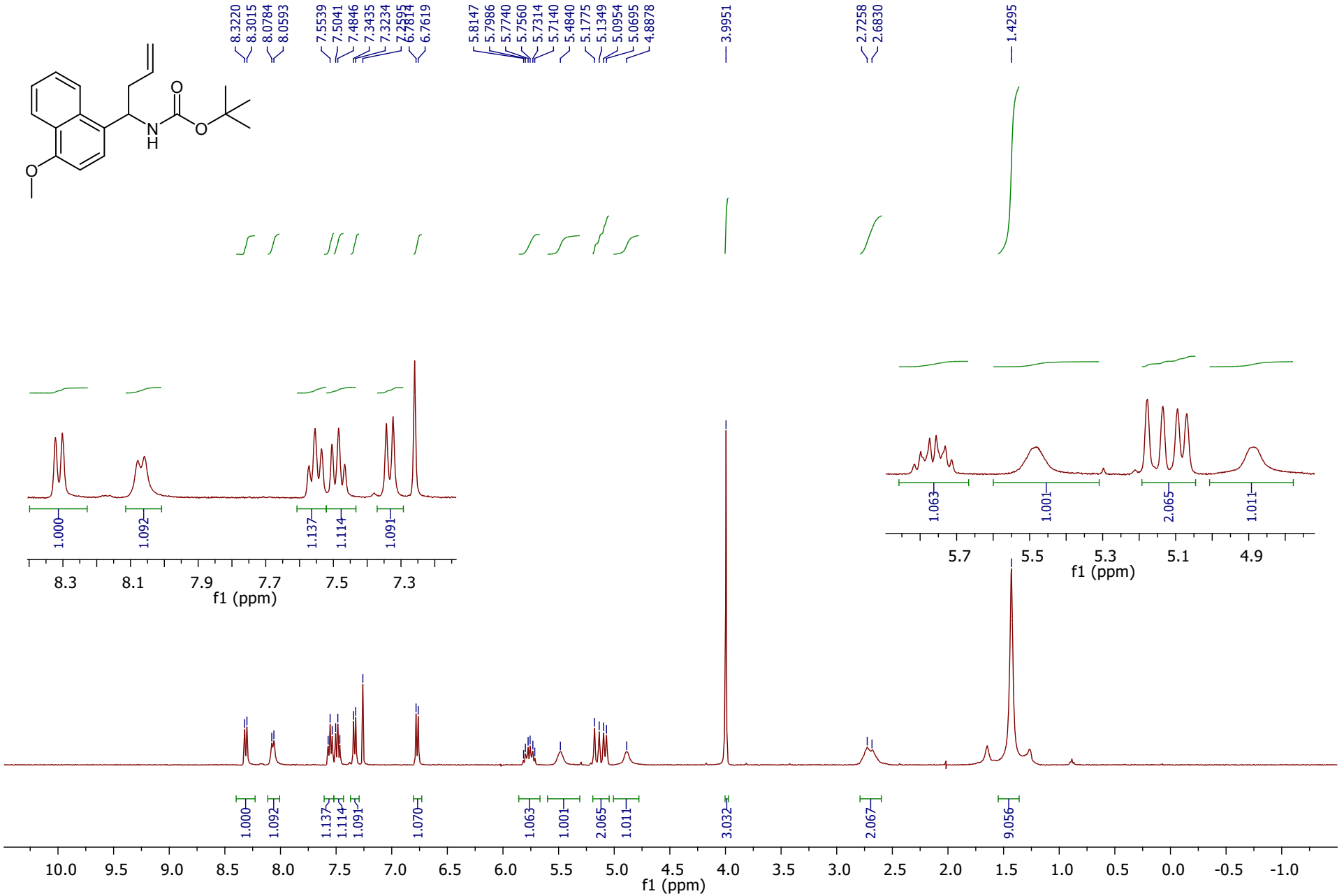
^{1}H NMR ($CDCl_3$, 400 MHz) **6k**



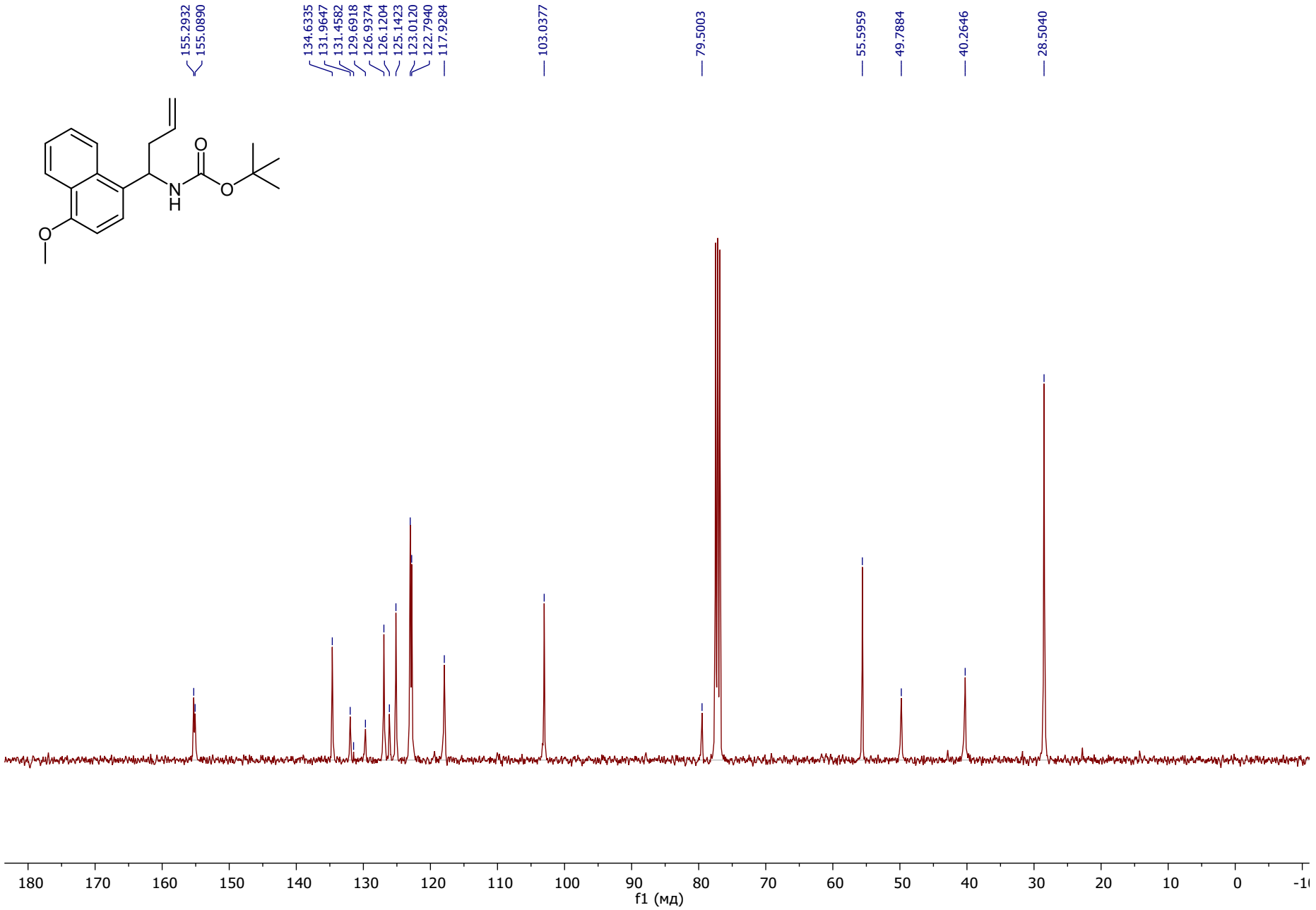
^{1}H NMR ($CDCl_3$, 400 MHz) **6l**



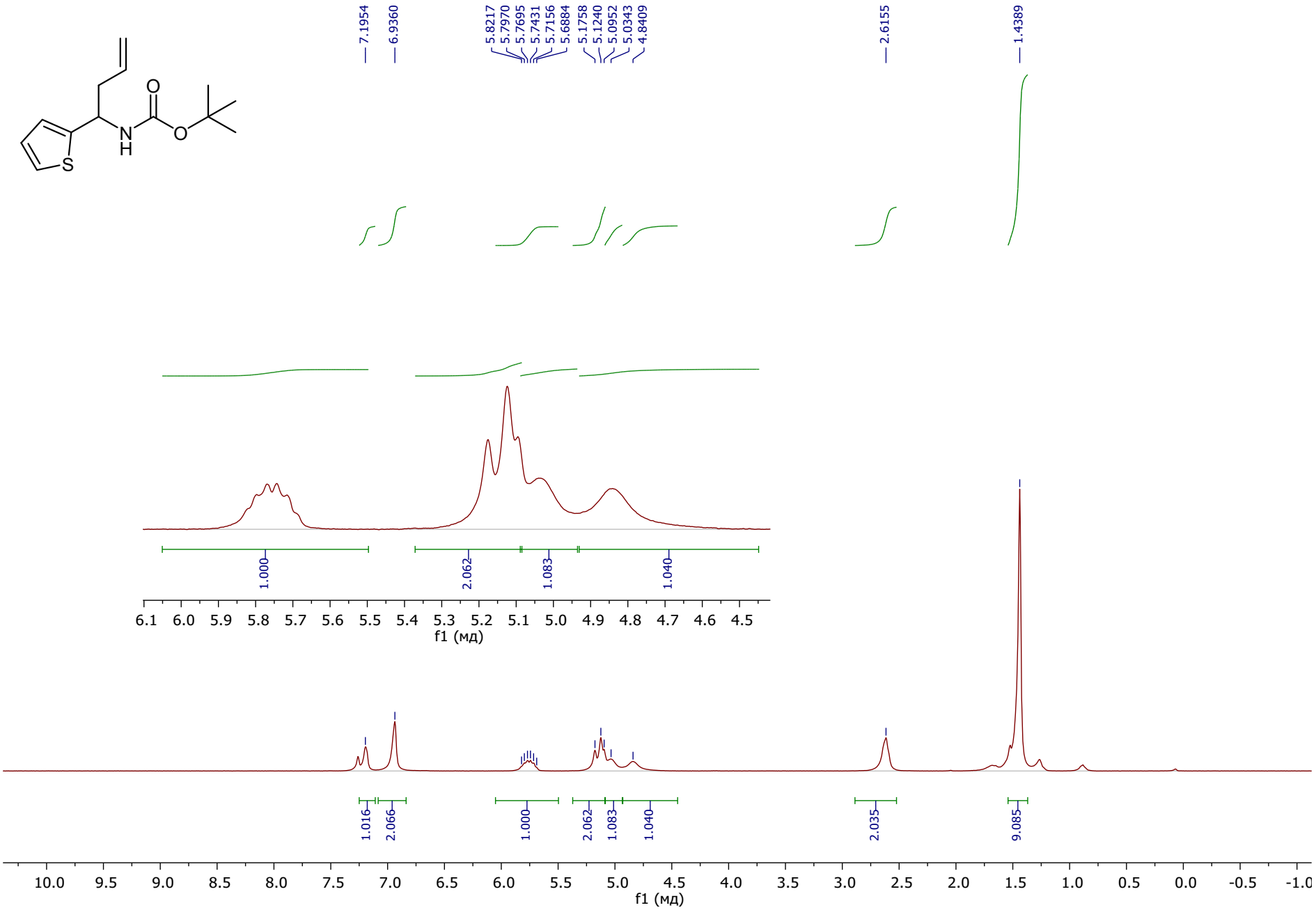
^{1}H NMR ($CDCl_3$, 400 MHz) **6m**



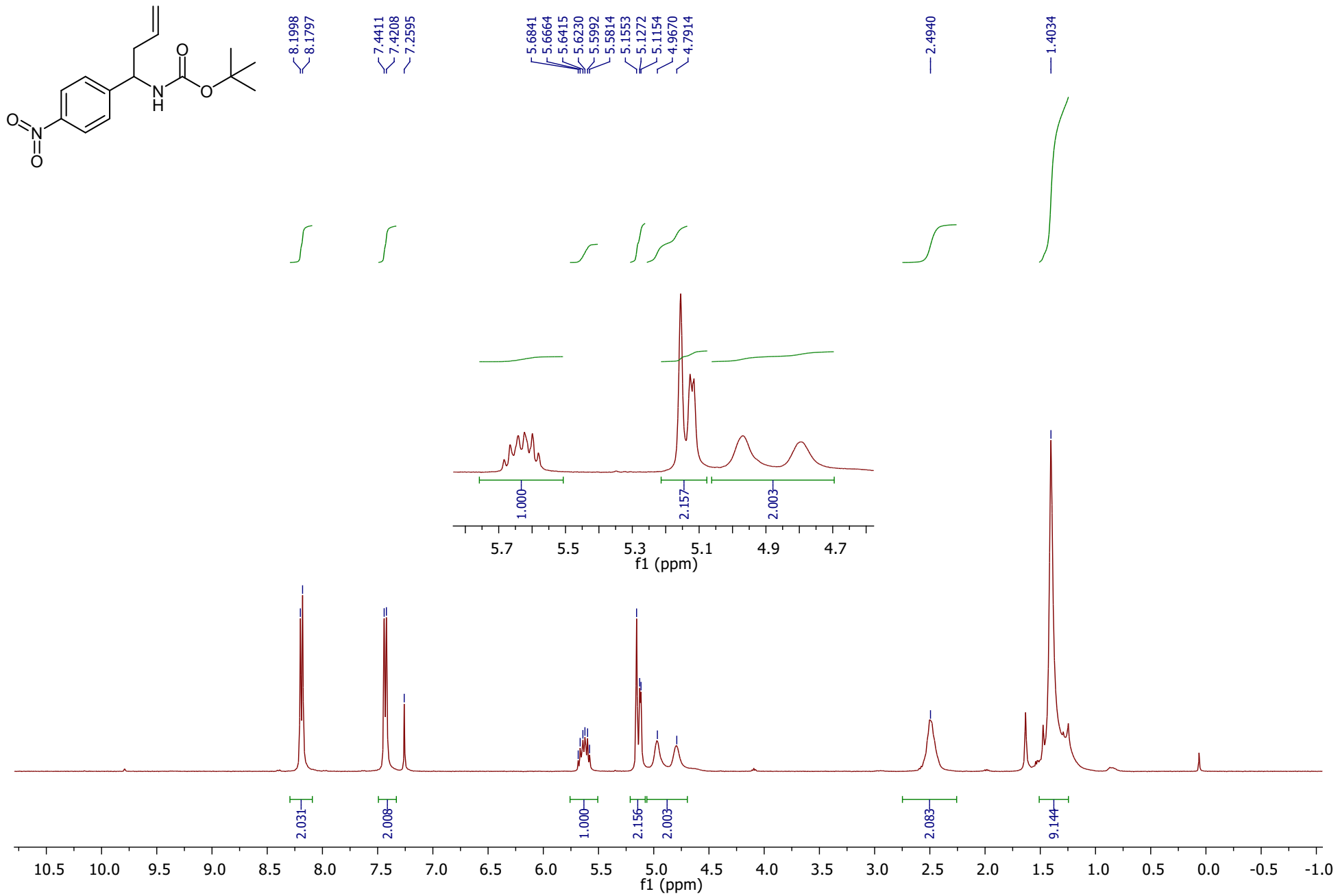
^{13}C NMR ($CDCl_3$, 101 MHz) **6m**



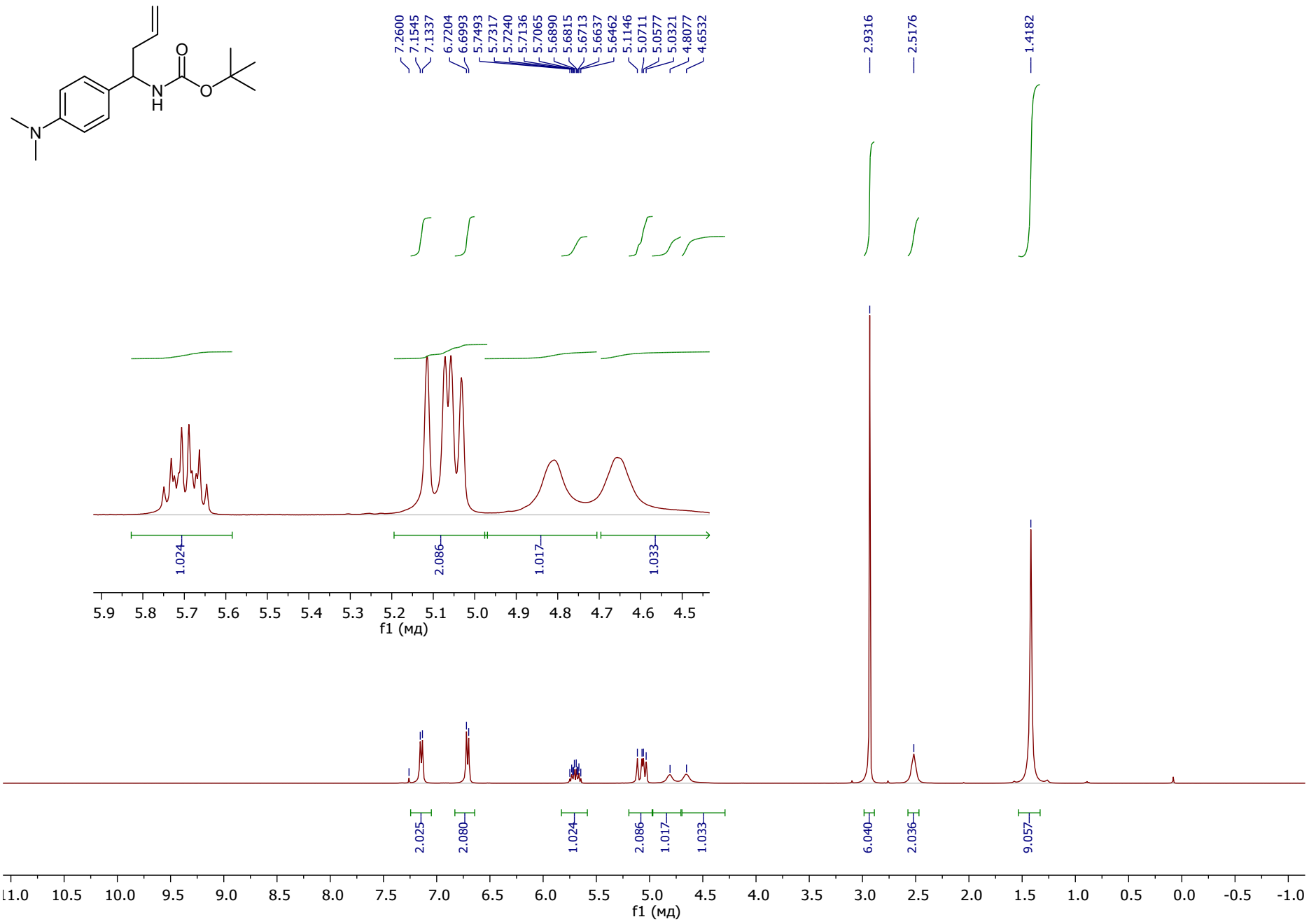
^{1}H NMR ($CDCl_3$, 400 MHz) **6n**



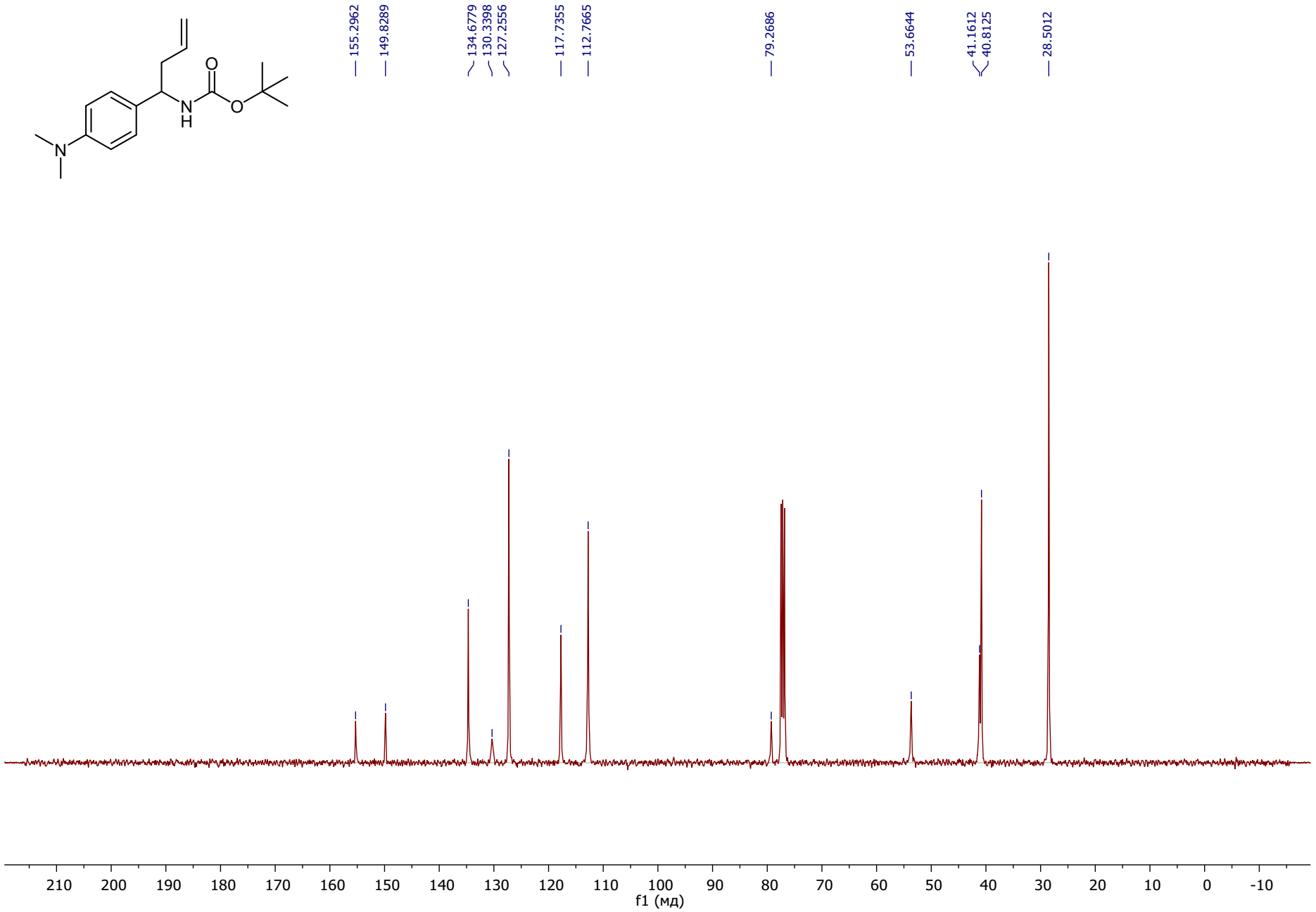
^{1}H NMR ($CDCl_3$, 400 MHz) **6o**



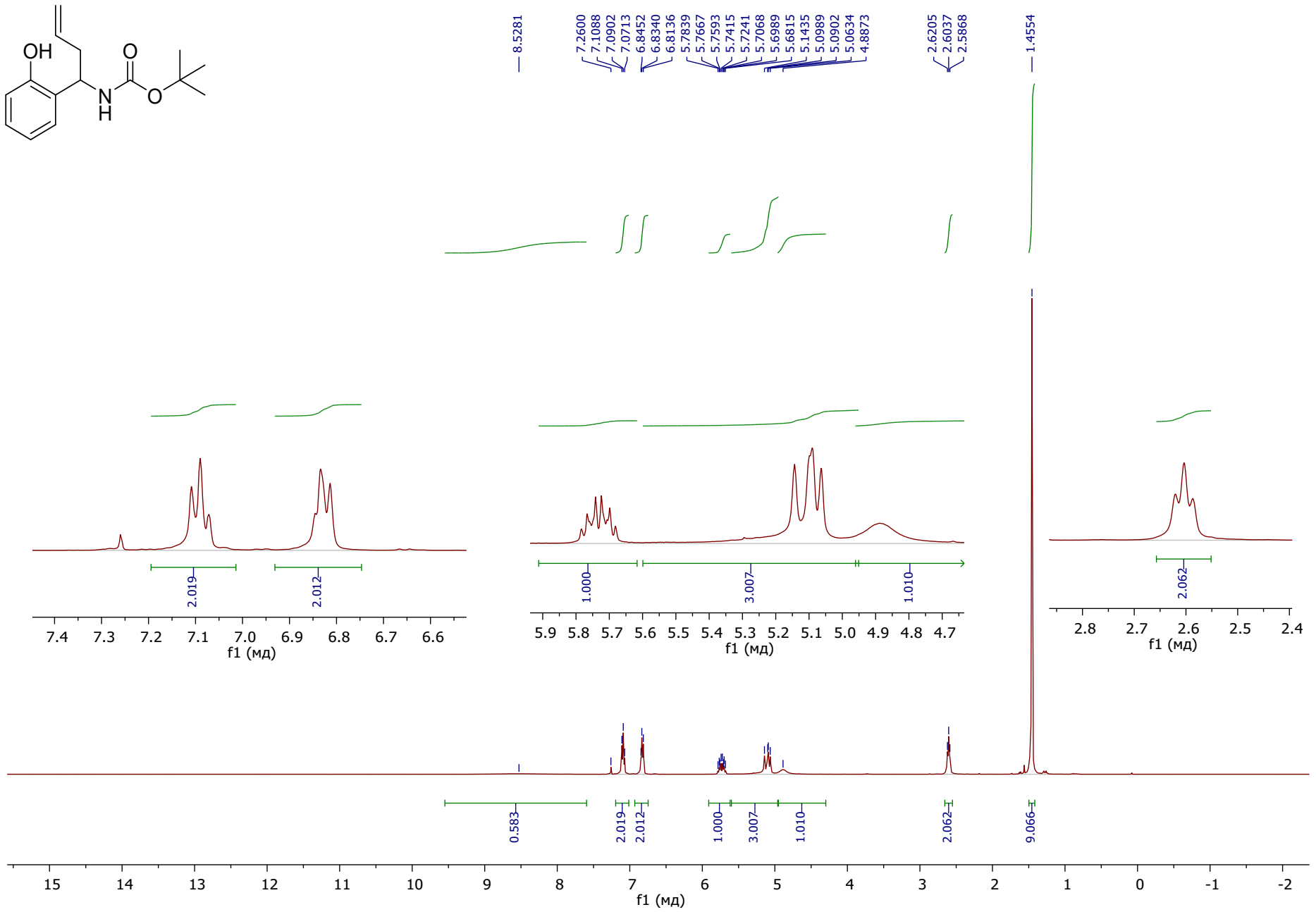
^{1}H NMR ($CDCl_3$, 400 MHz) **6p**



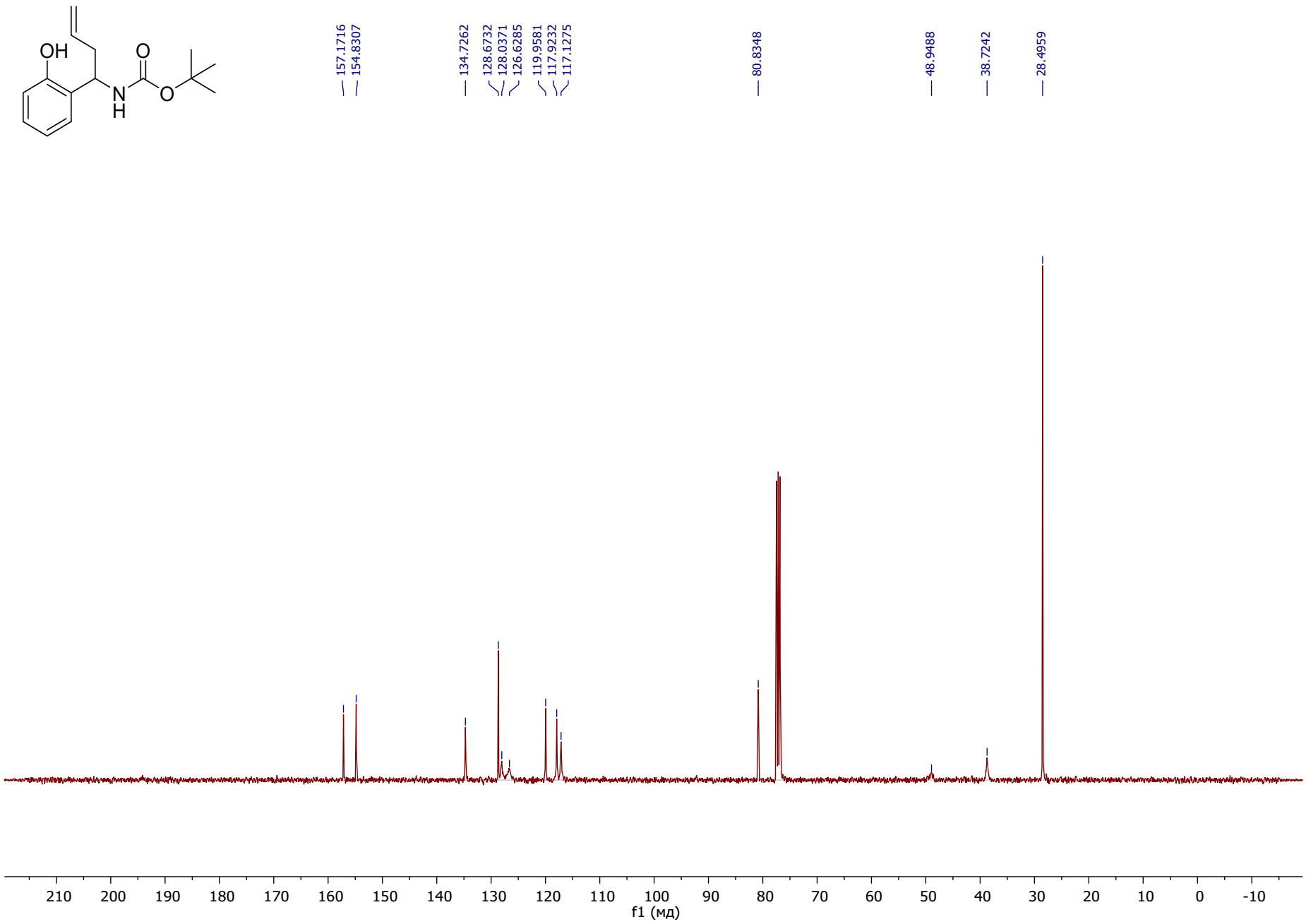
^{13}C NMR ($CDCl_3$, 101 MHz) **6p**



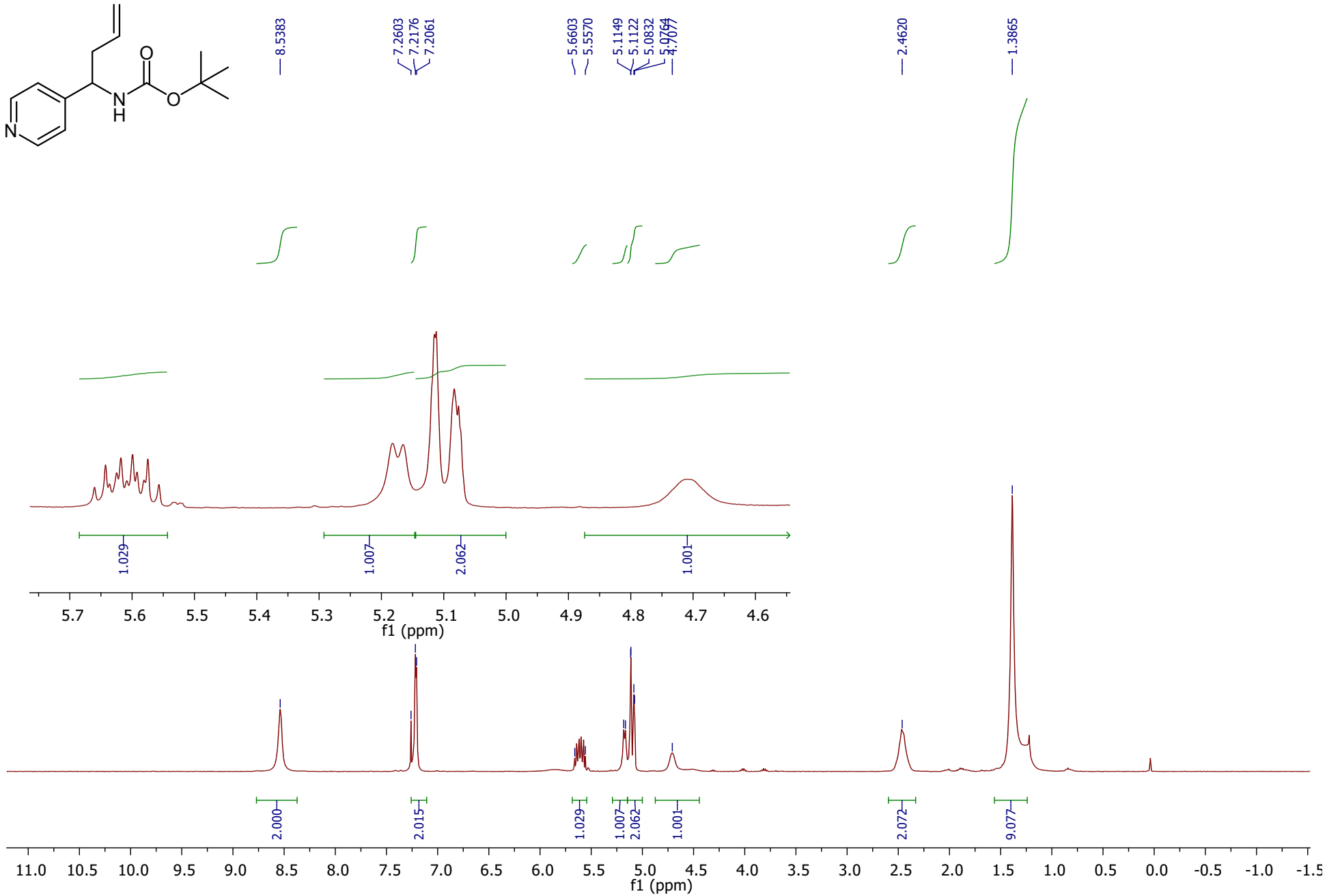
^{1}H NMR ($CDCl_3$, 400 MHz) **6q**



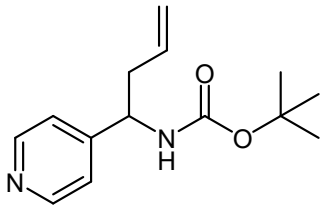
^{13}C NMR ($CDCl_3$, 101 MHz) **6q**



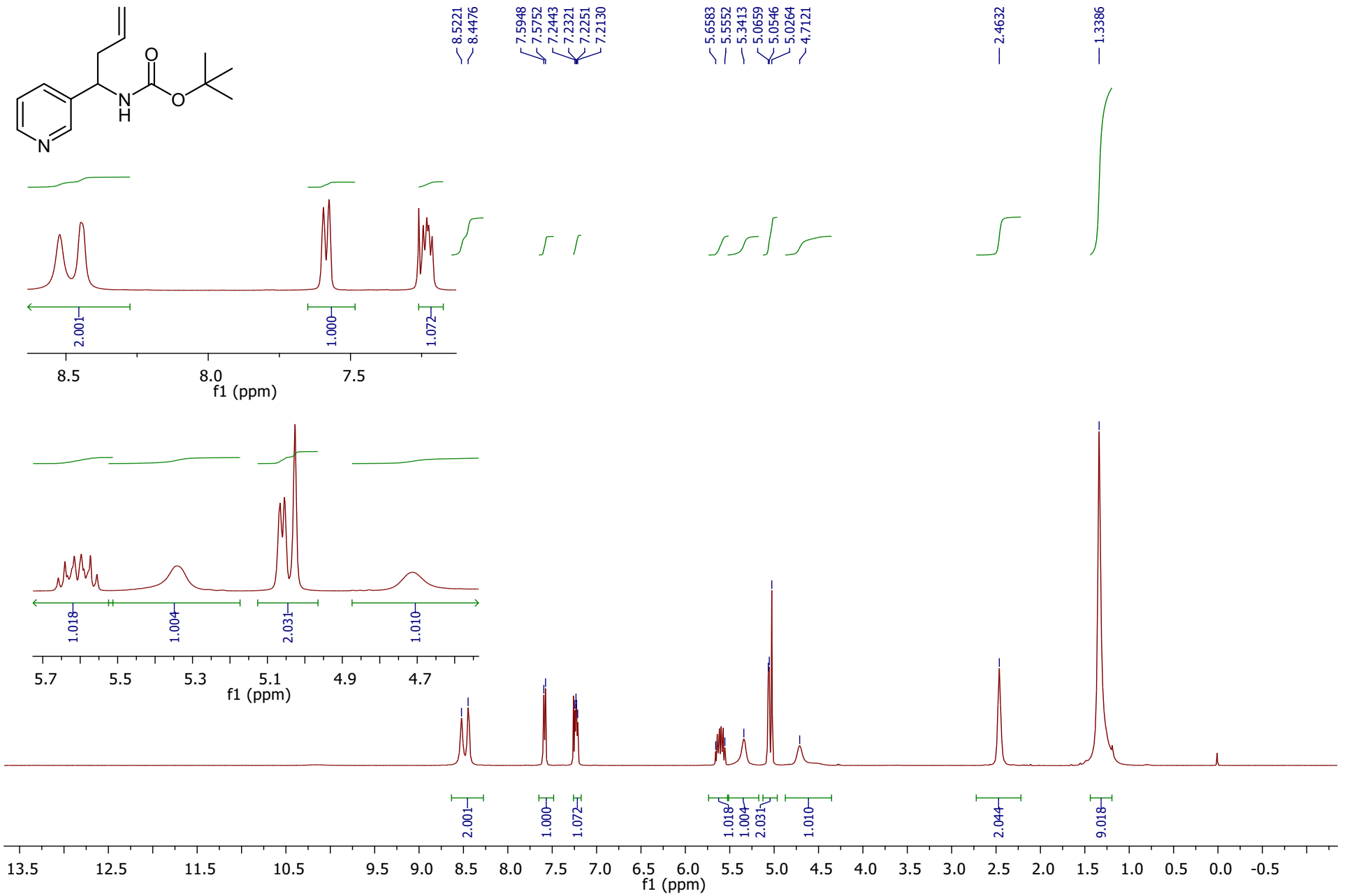
^{1}H NMR ($CDCl_3$, 400 MHz) **6r**



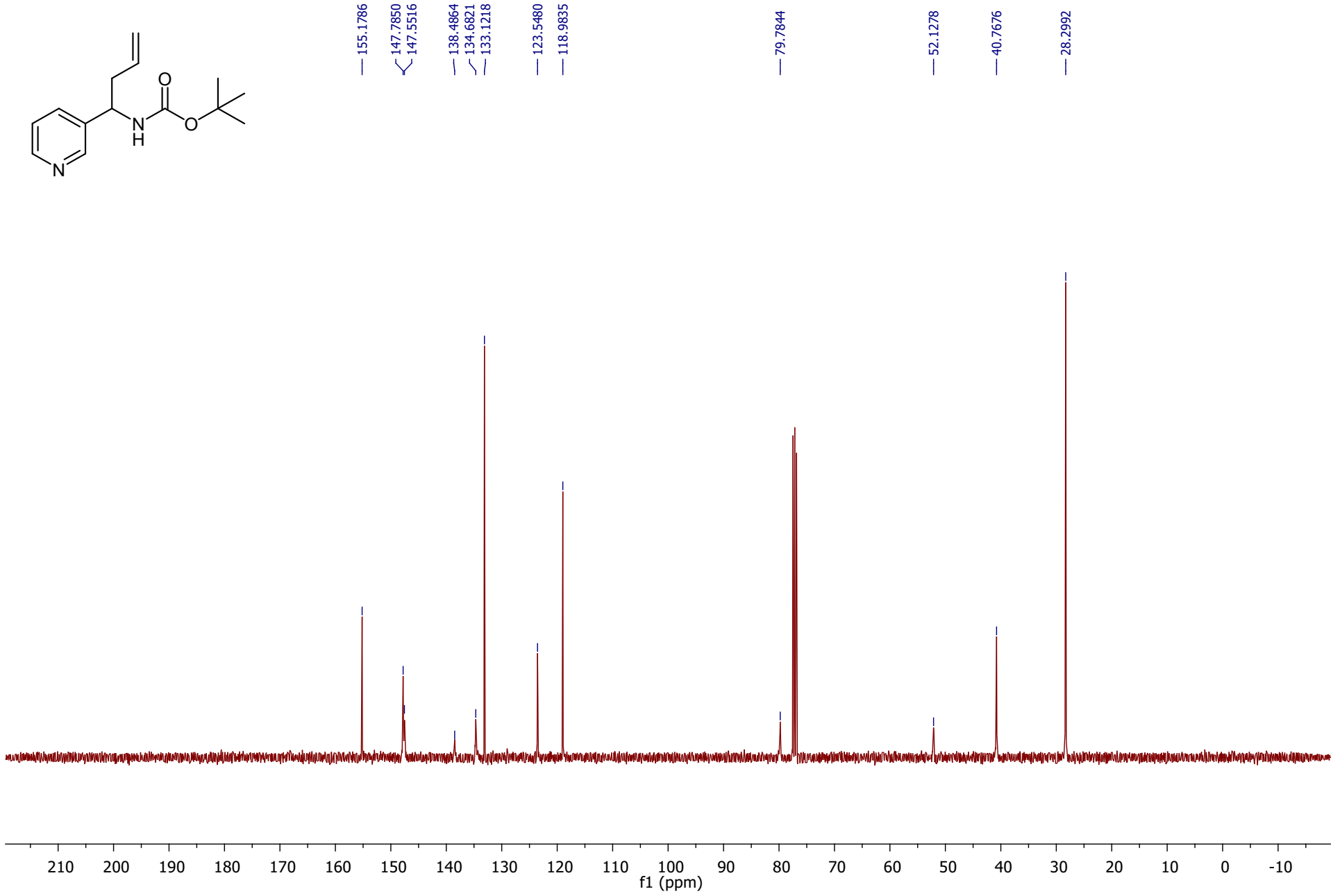
^{13}C NMR ($CDCl_3$, 101 MHz) **6r**



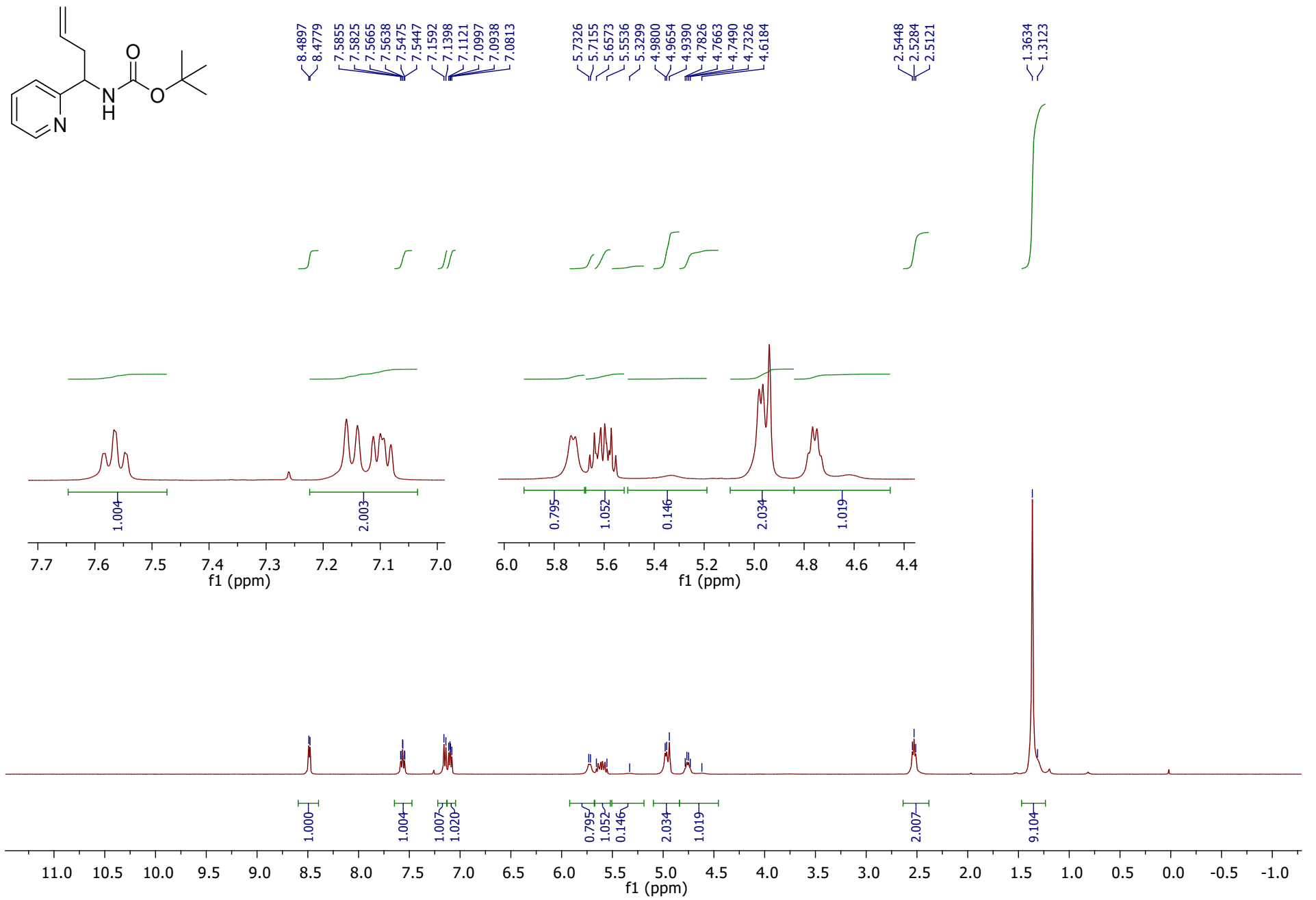
^{1}H NMR ($CDCl_3$, 400 MHz) **6s**



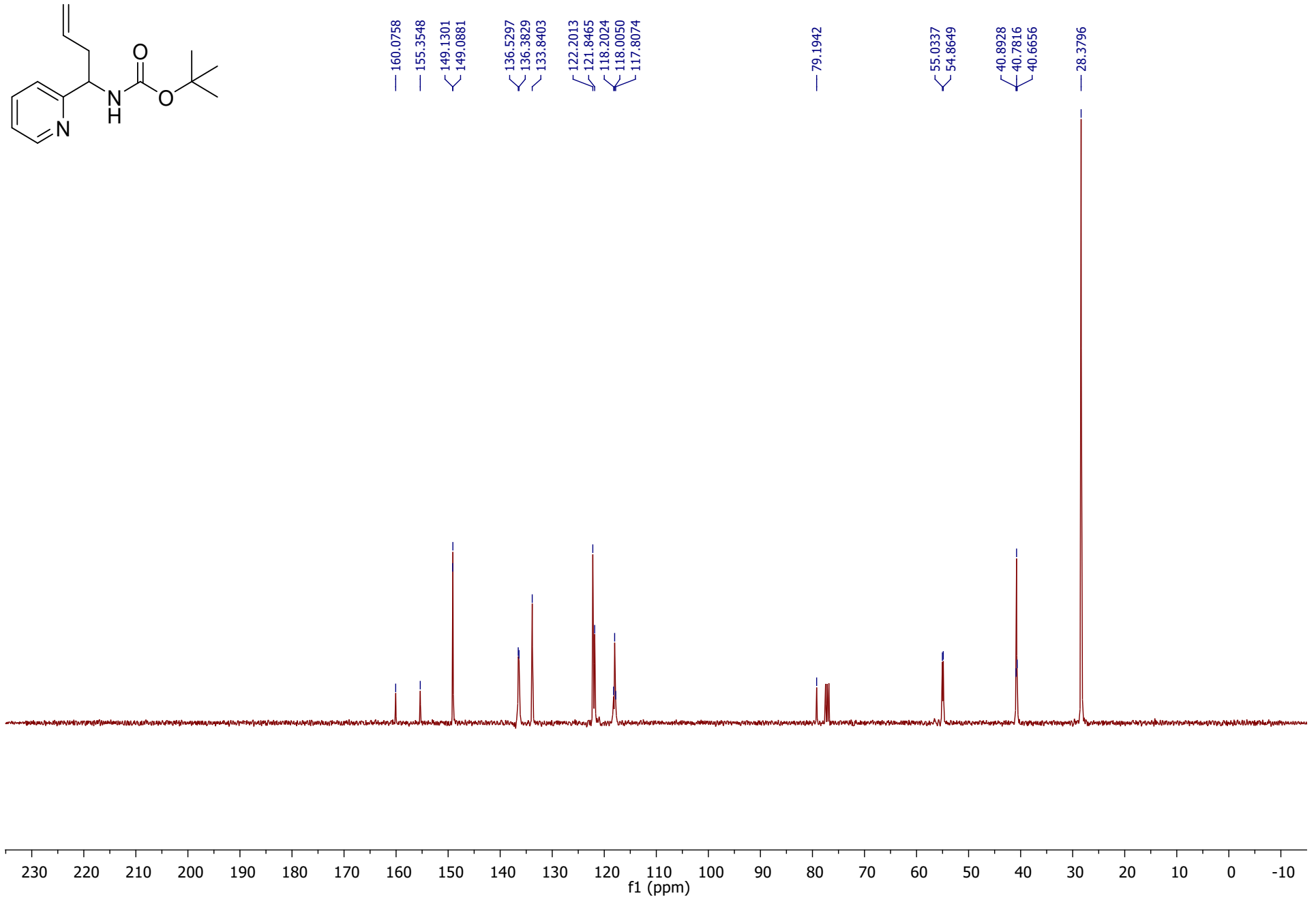
^{13}C NMR ($CDCl_3$, 101 MHz) **6s**



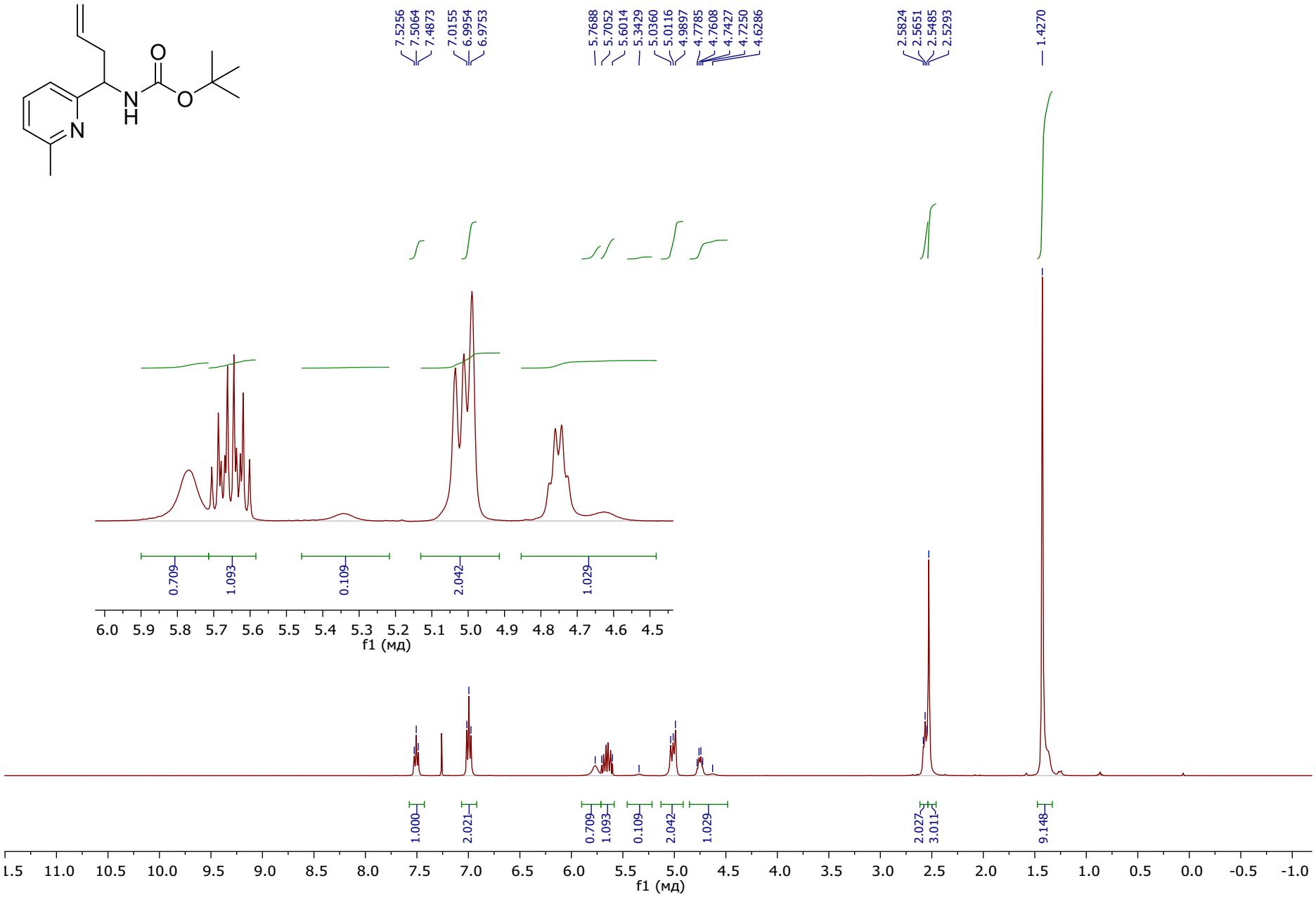
^{1}H NMR ($CDCl_3$, 400 MHz) **6t**



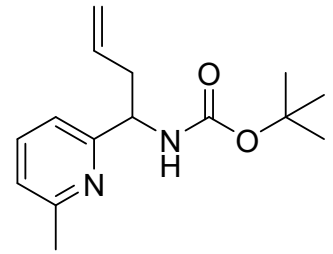
^{13}C NMR ($CDCl_3$, 101 MHz) **6t**



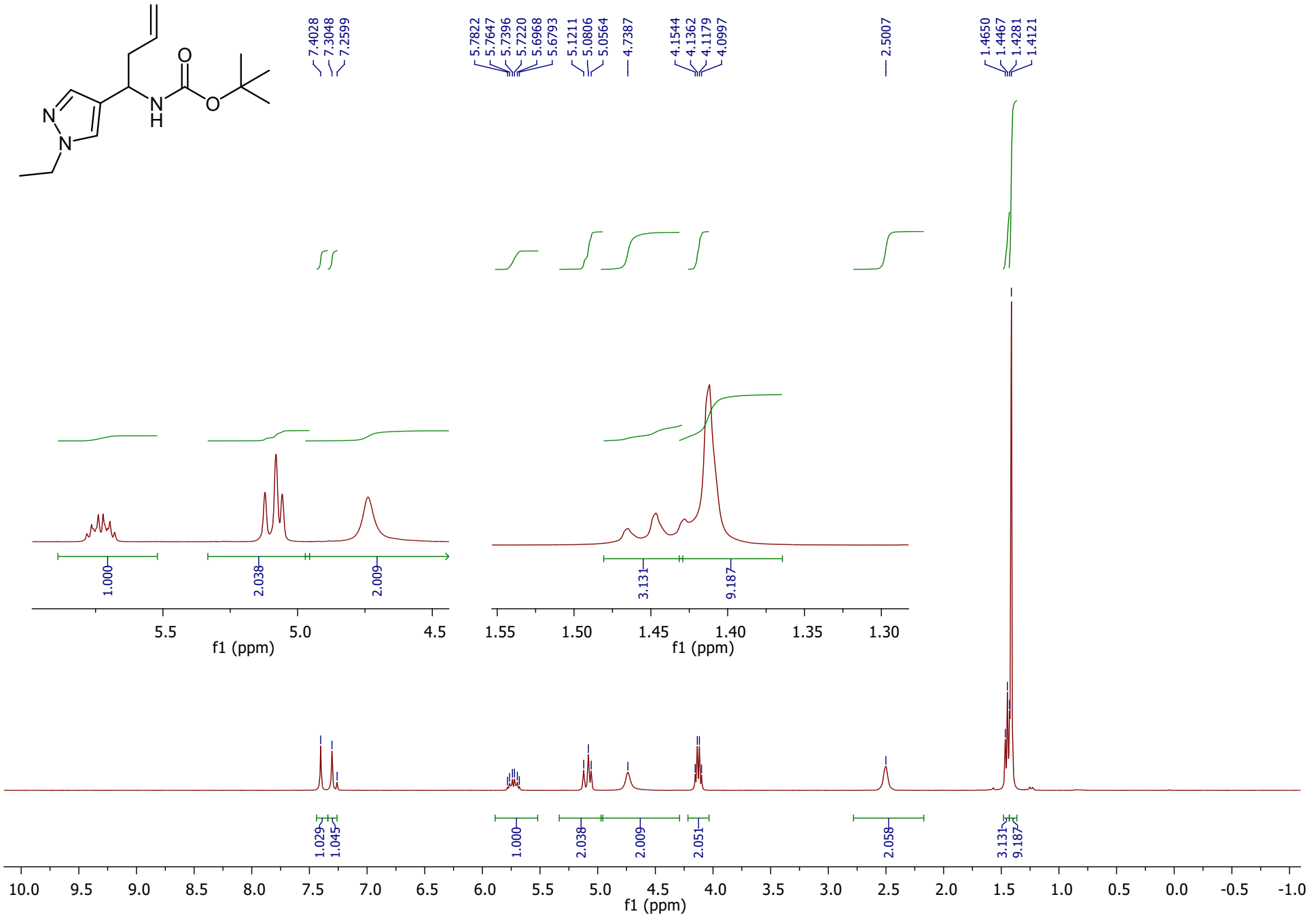
^{1}H NMR ($CDCl_3$, 400 MHz) **6u**



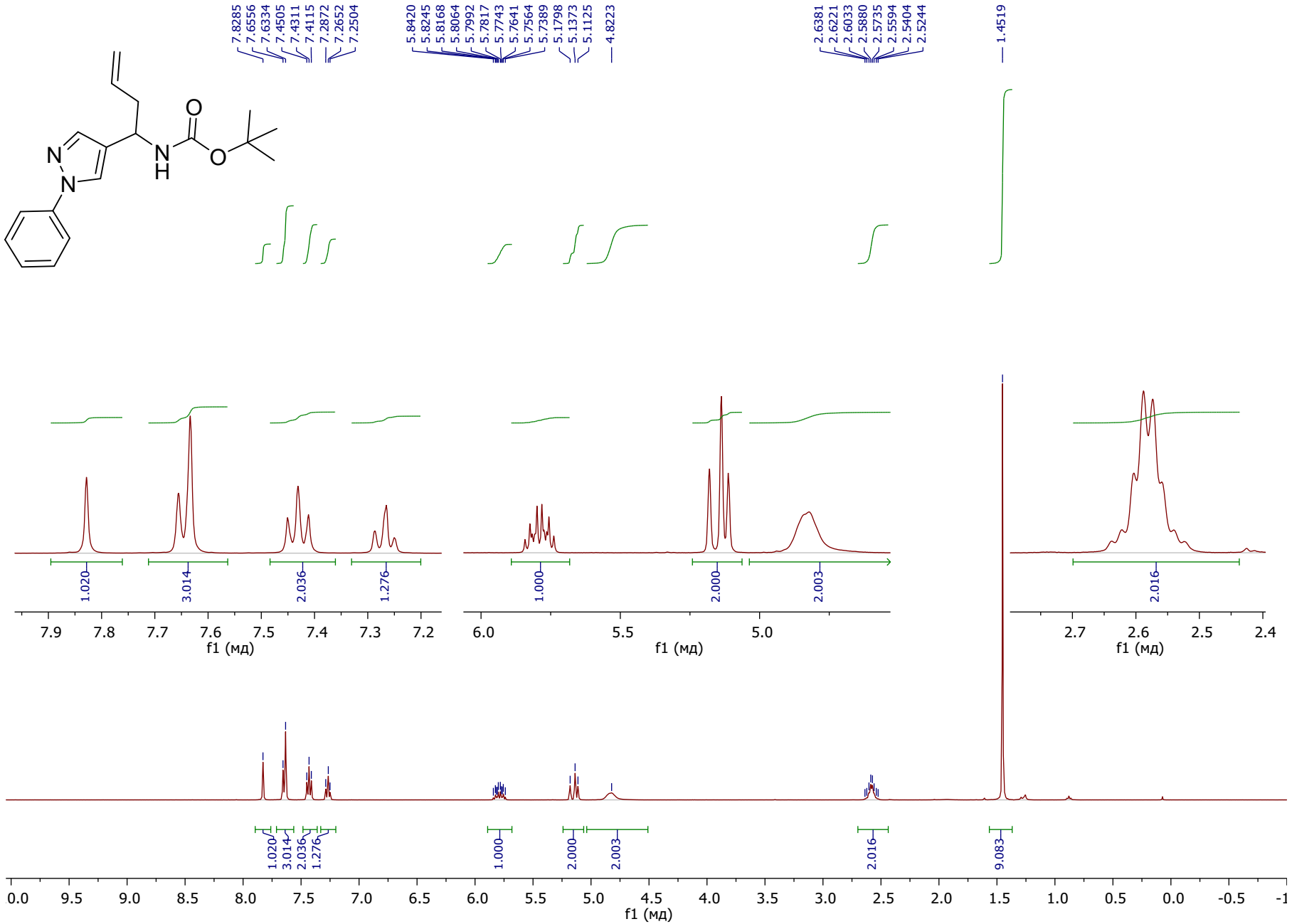
^{13}C NMR ($CDCl_3$, 101 MHz) **6u**



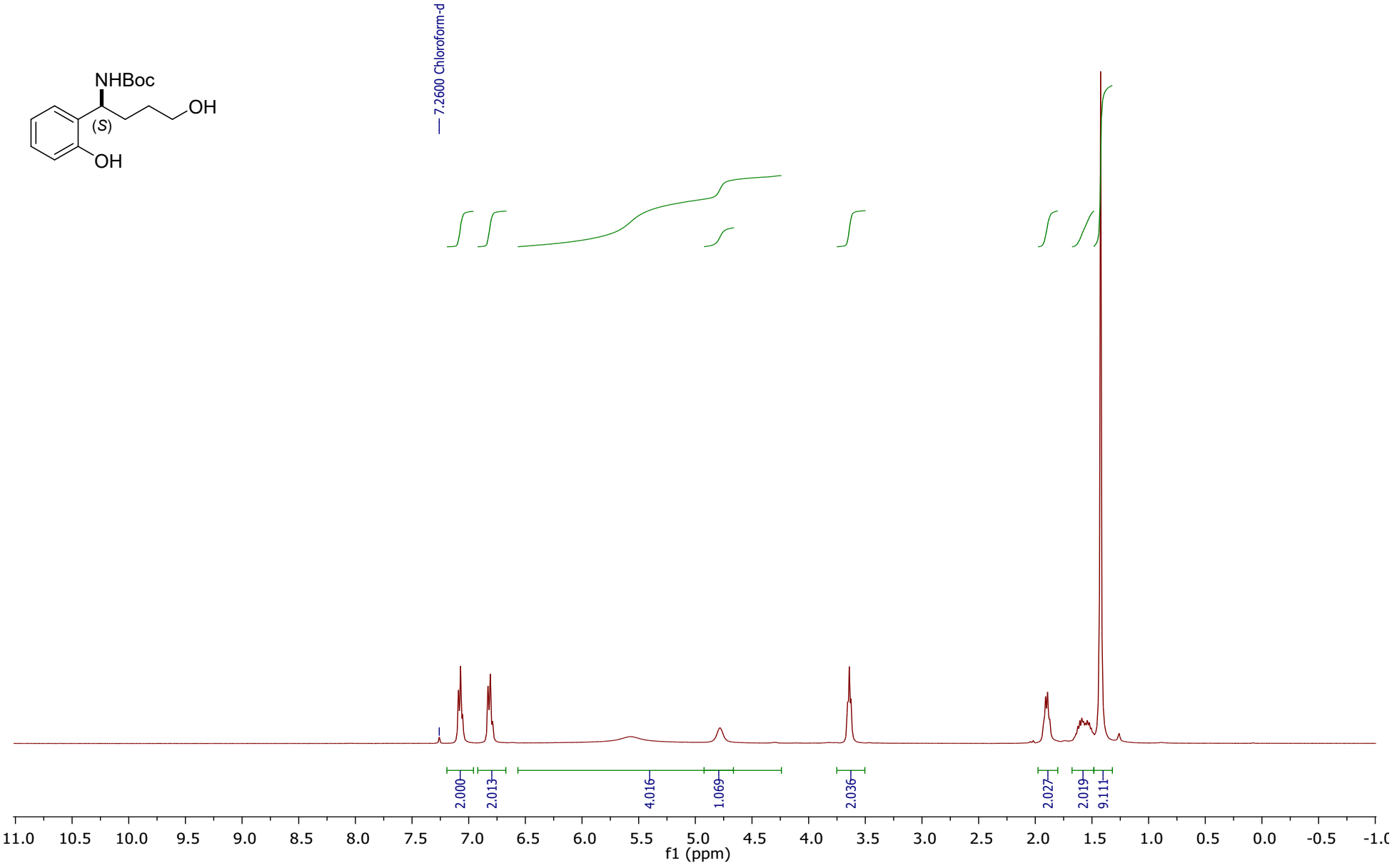
^{1}H NMR ($CDCl_3$, 400 MHz) **6v**



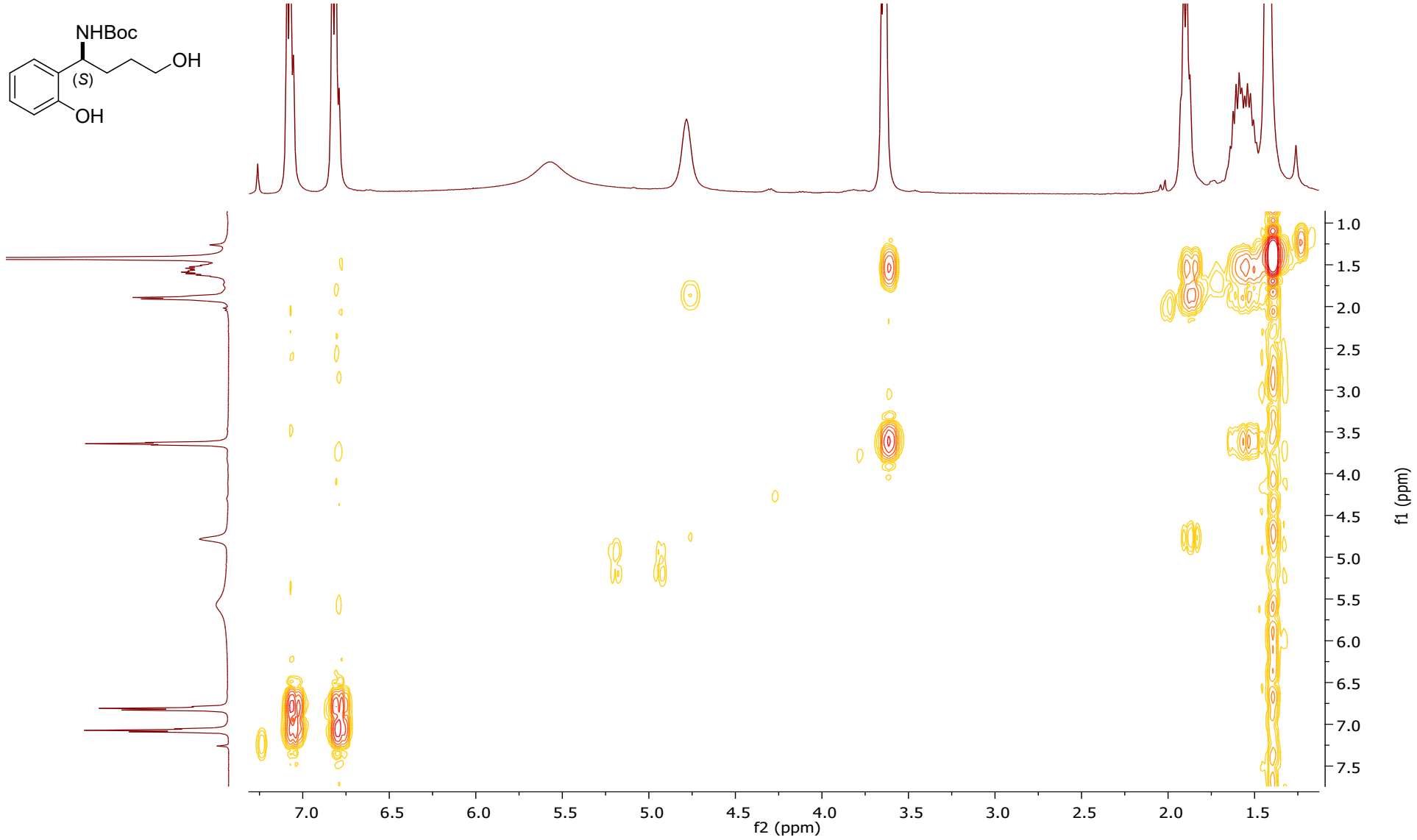
^{1}H NMR ($CDCl_3$, 400 MHz) **6w**



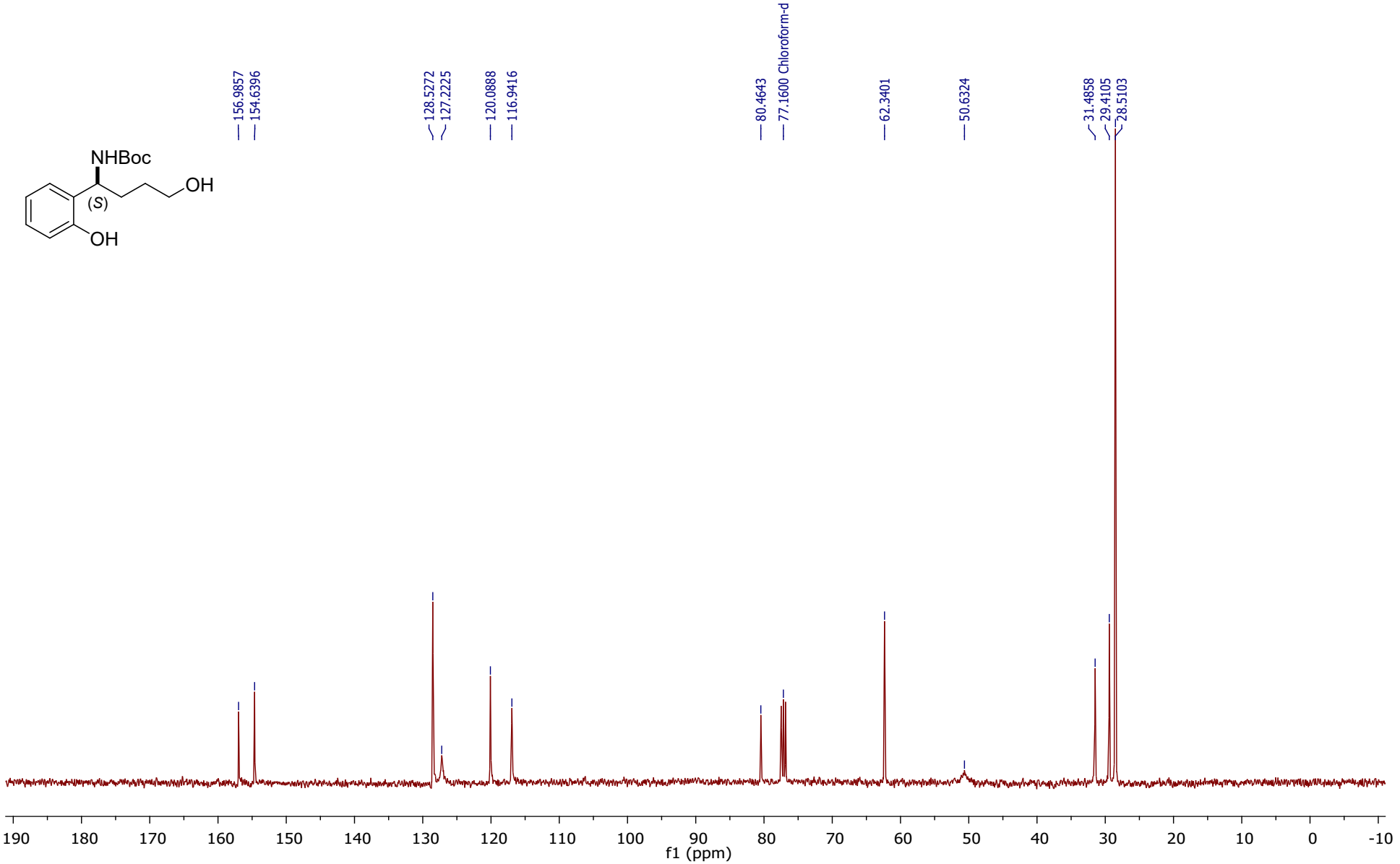
^{1}H NMR ($CDCl_3$, 400 MHz) **7**



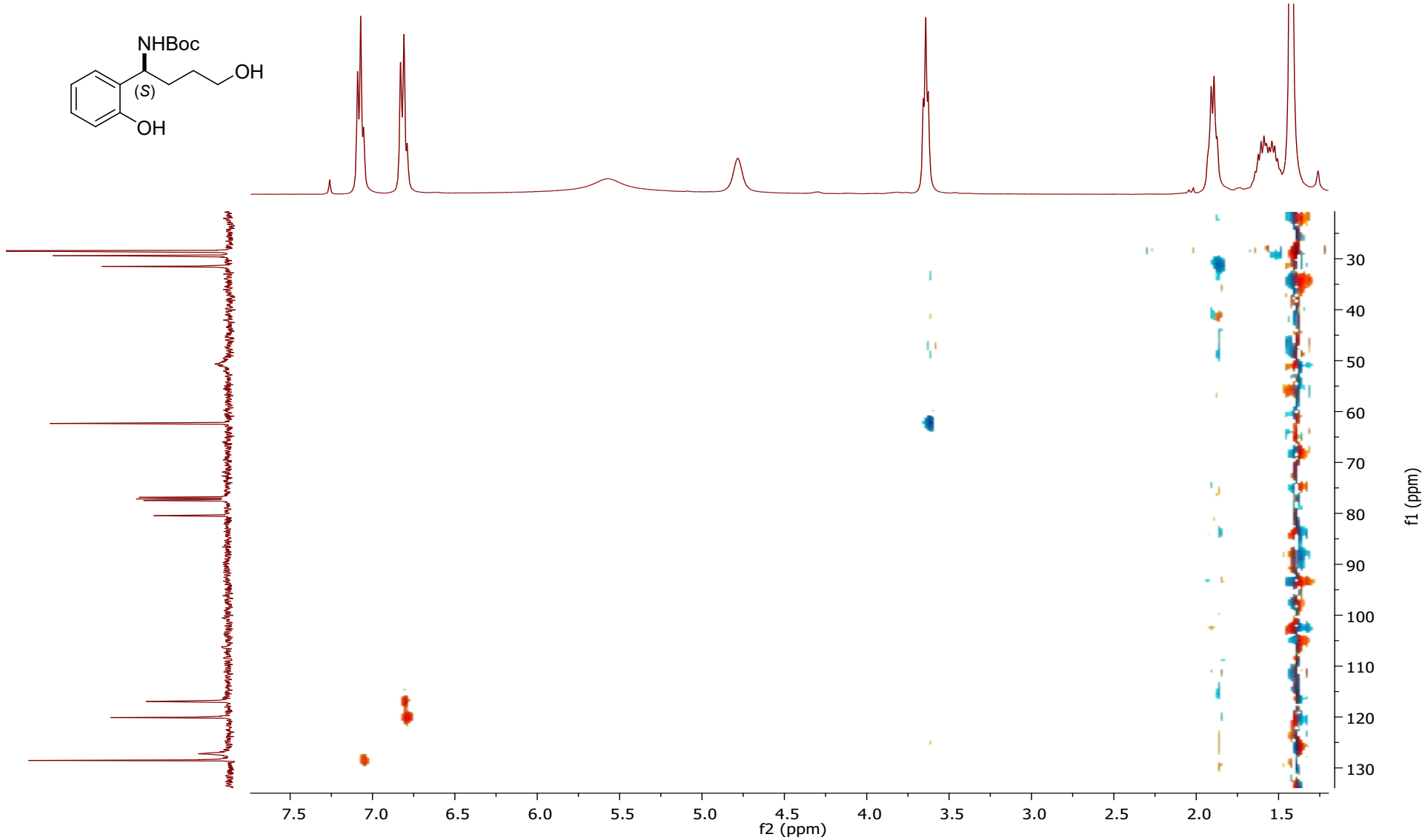
^{1}H-^{1}H COSY NMR **7**



^{13}C NMR ($CDCl_3$, 101 MHz) **7**

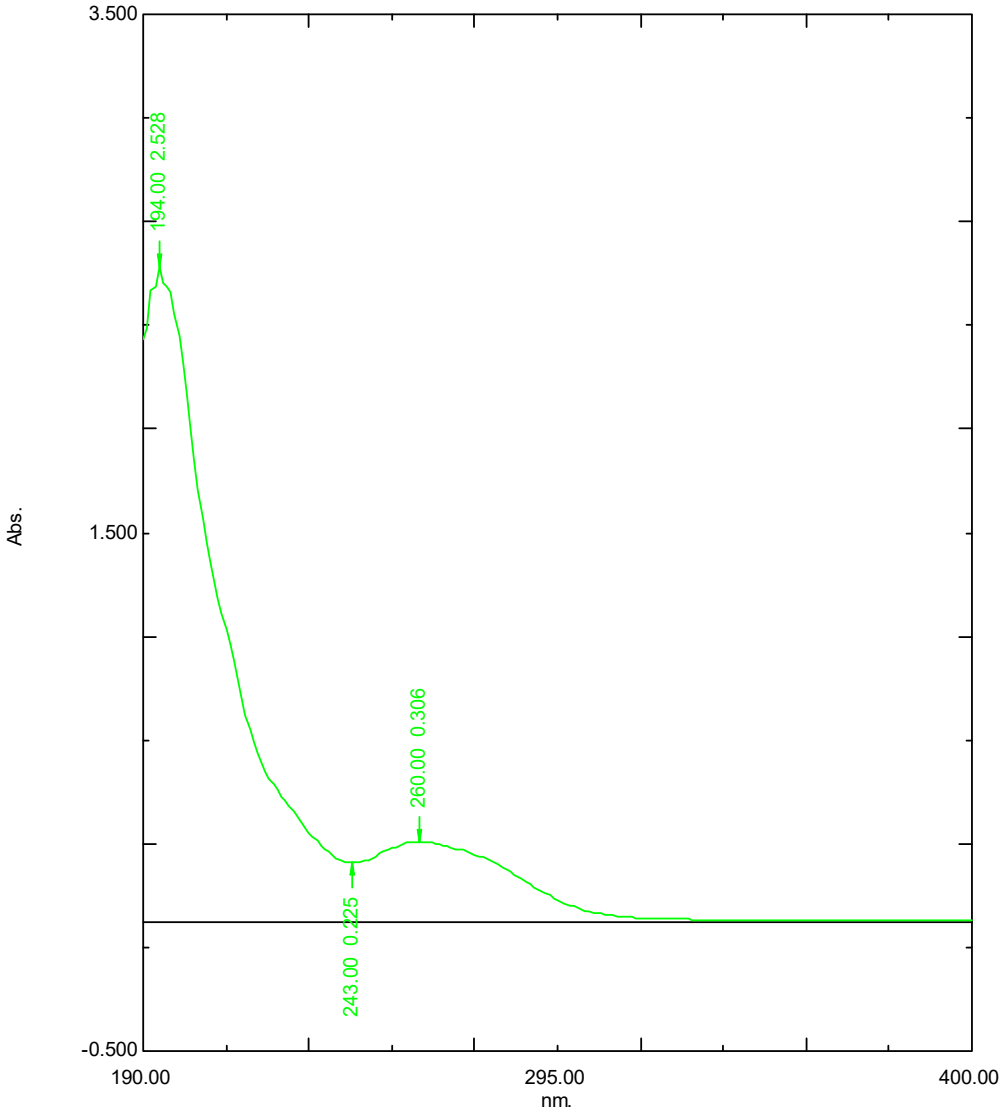


HSQC (^{13}C-^{1}H) **7**


NHBoc
OH
(S)
OH
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
f2 (ppm)
30
40
50
60
70
80
90
100
110
120
130
f1 (ppm)

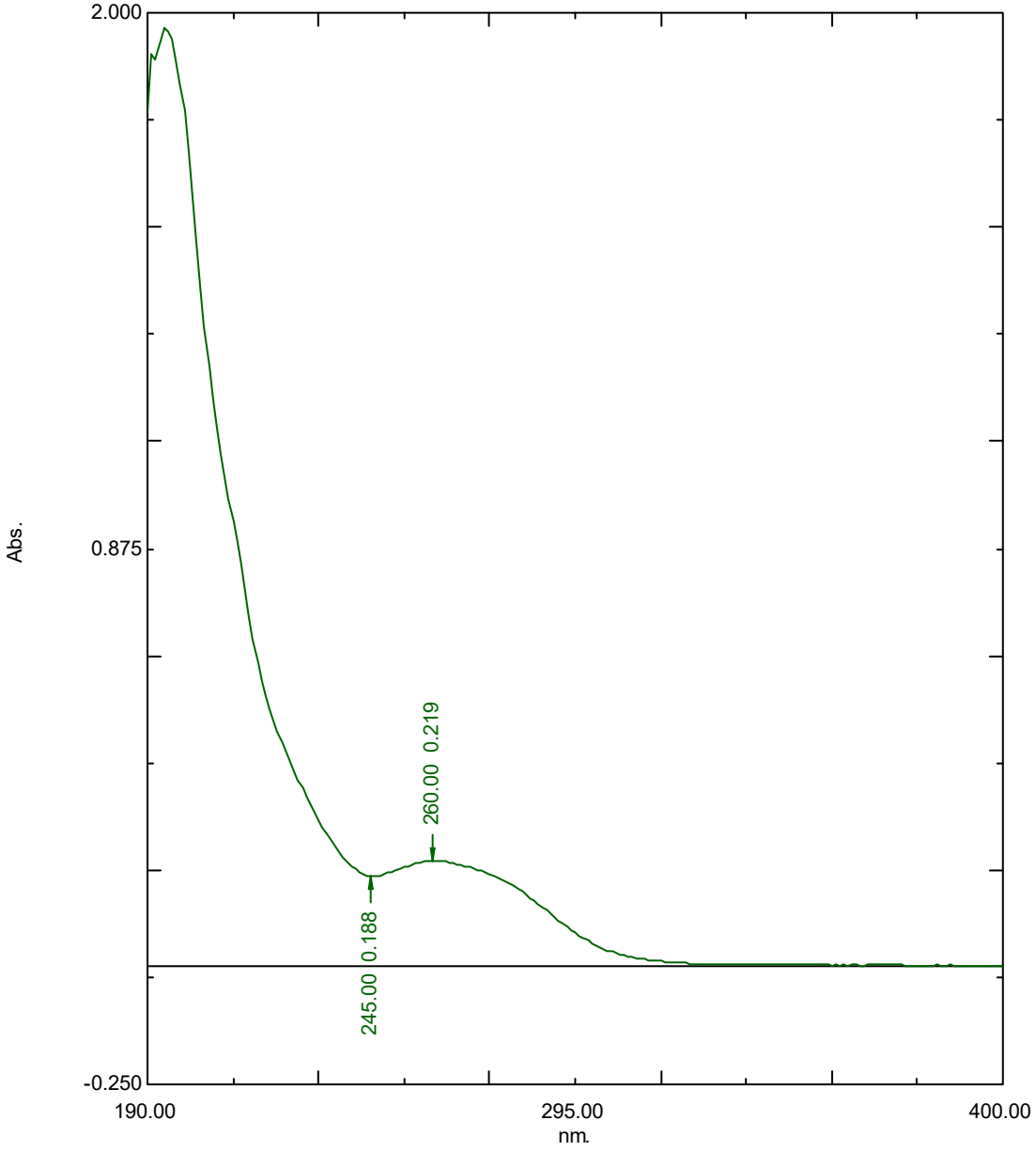
UV absorbance (MeCN, 1.0×10^{-5}M) **[Cu-1]**

$Cu(PPh_3)_3F*2EtOH$



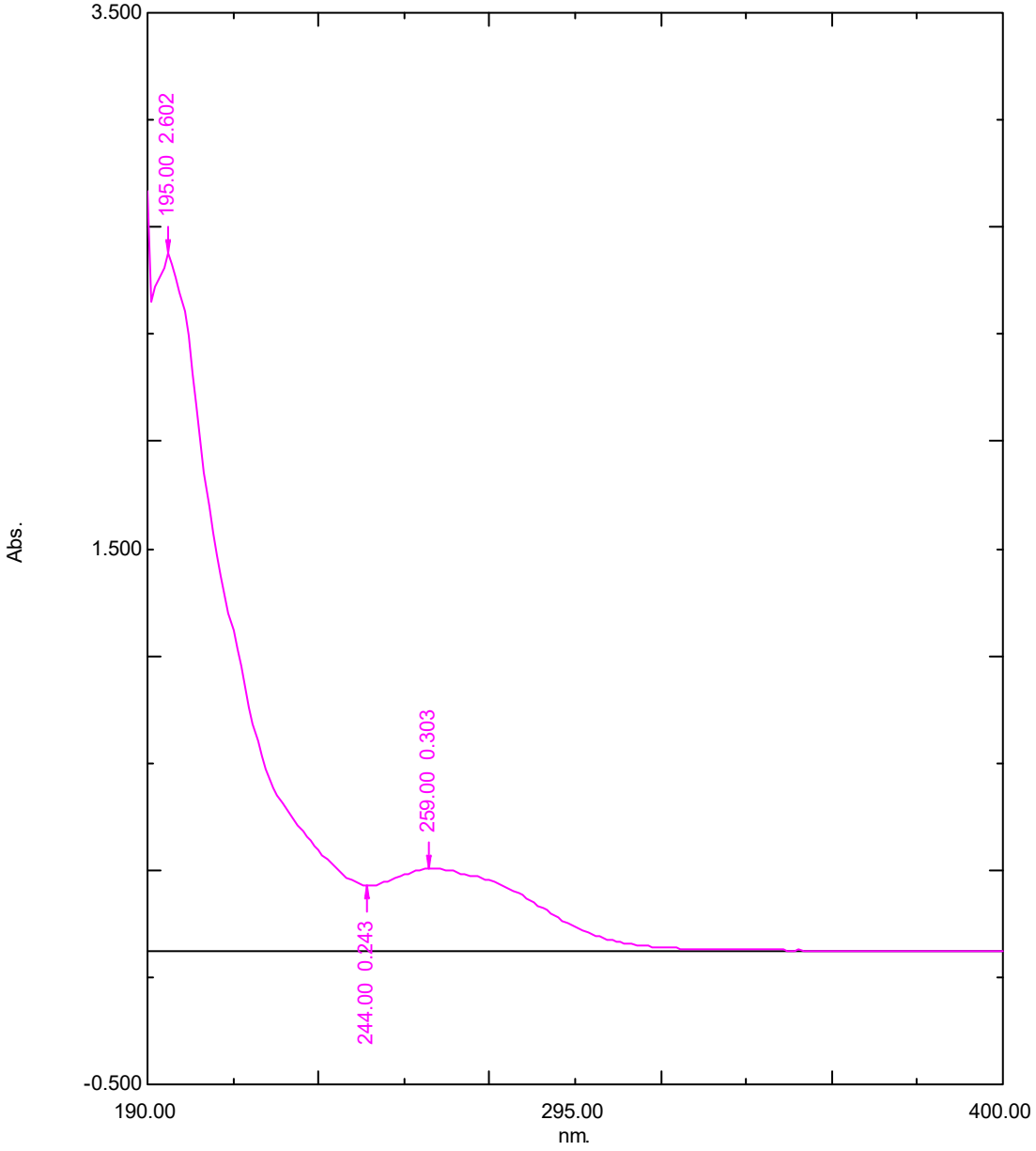
UV absorbance (MeCN, 1.0×10^{-5}M) **[Cu-2]**

$(PPh_3)_2Cu(OEt)_2BF_2$



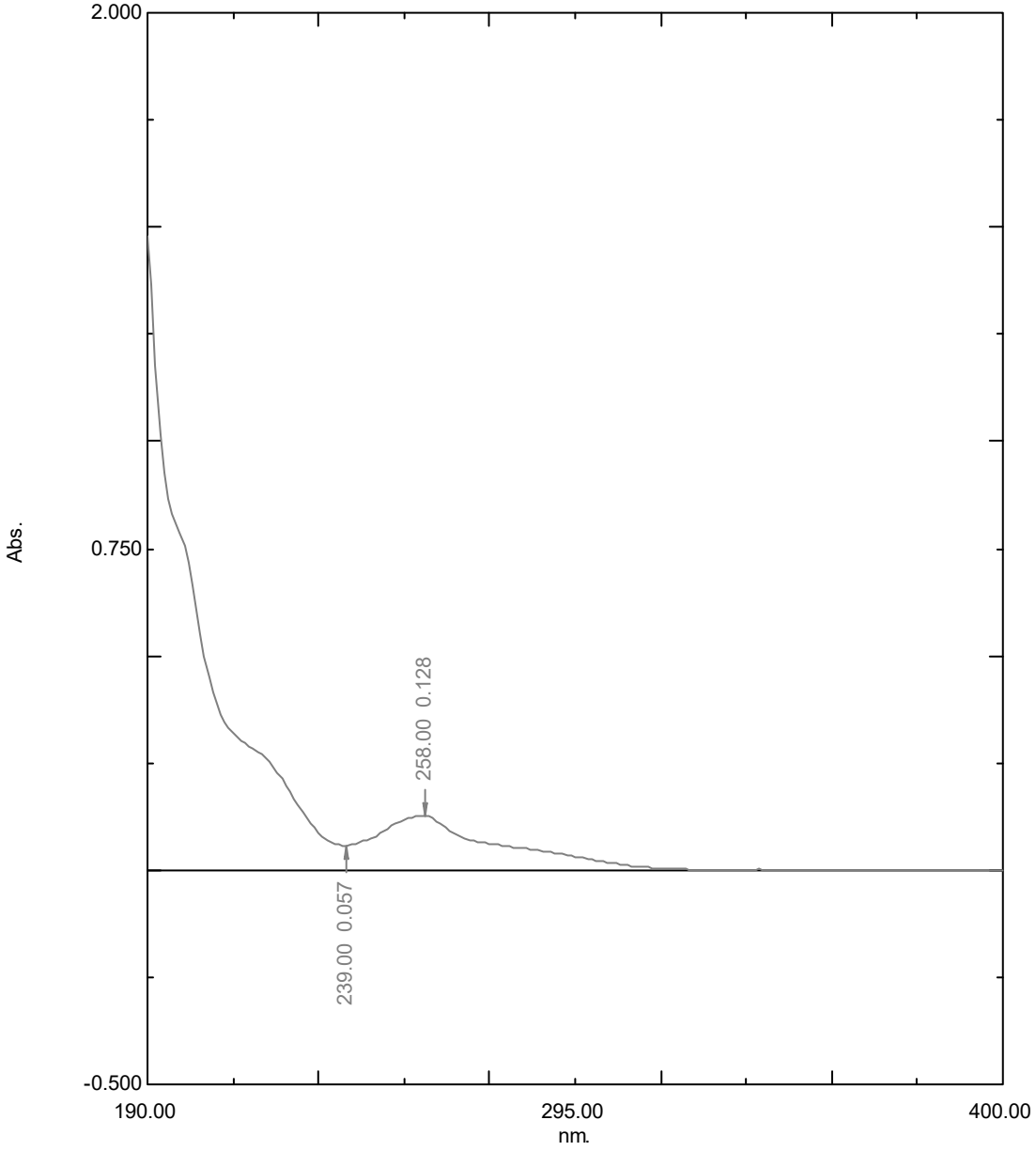
UV absorbance (MeCN, 1.0×10^{-5}M) **[Cu-3]**

$Cu(PPh_3)_3Cl$*MeCN



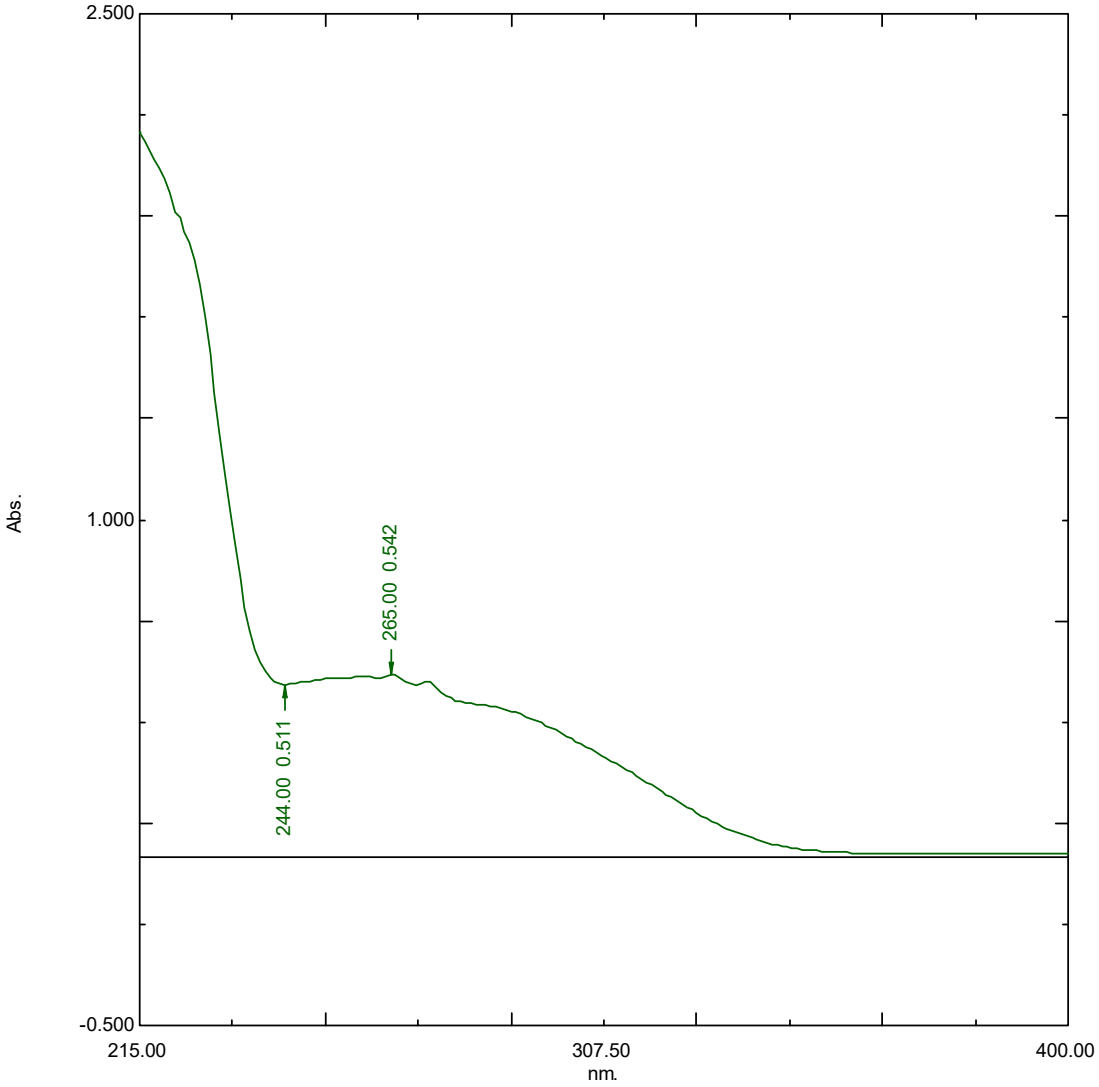
UV absorbance (MeCN, 1.0×10^{-5}M) **[Cu-4]**

Cu(SiMes)Cl



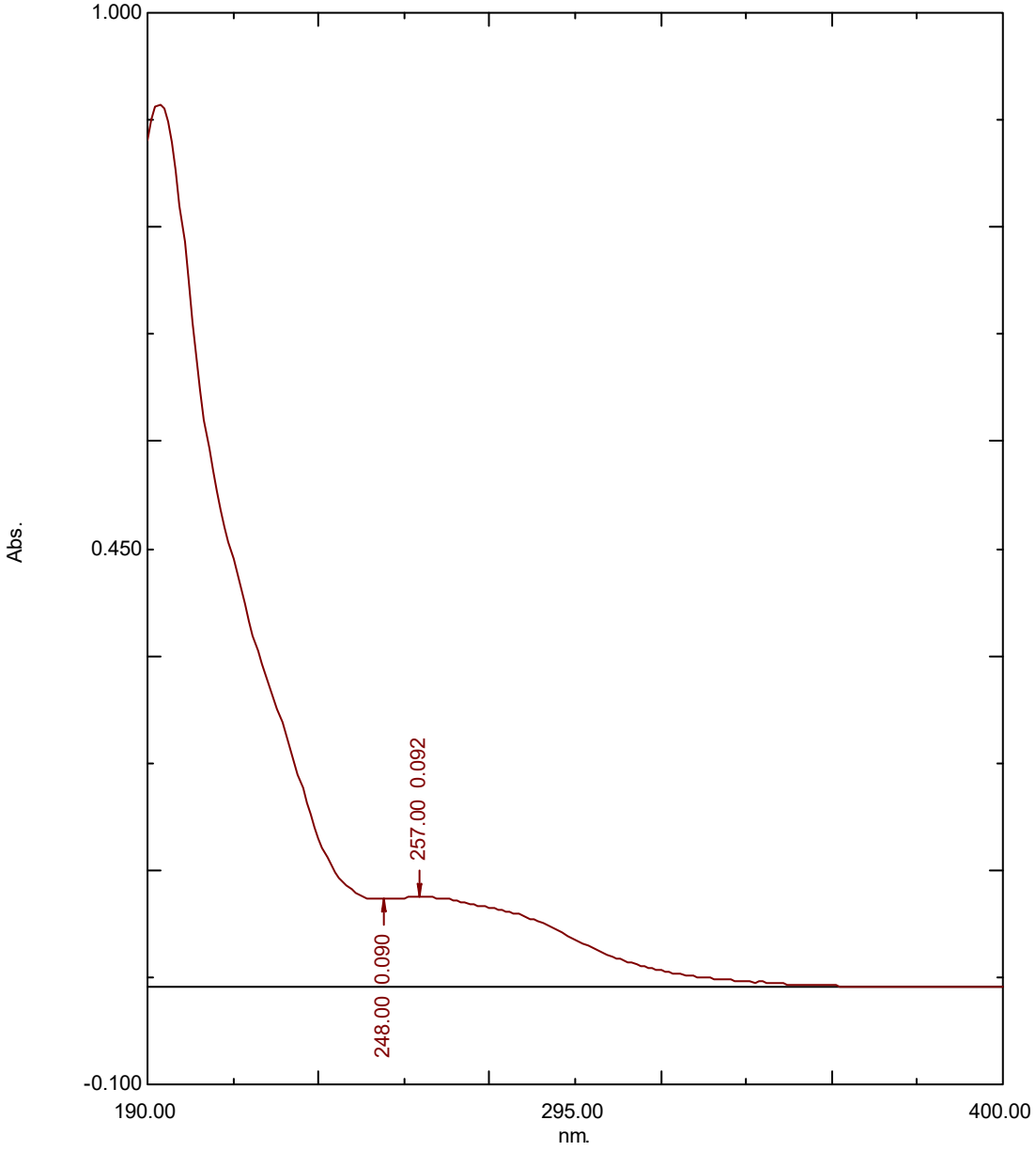
UV absorbance (MeCN, 2.0×10^{-5}M) **[Cu-5]**

$Cu(dppe)_2BF_4$



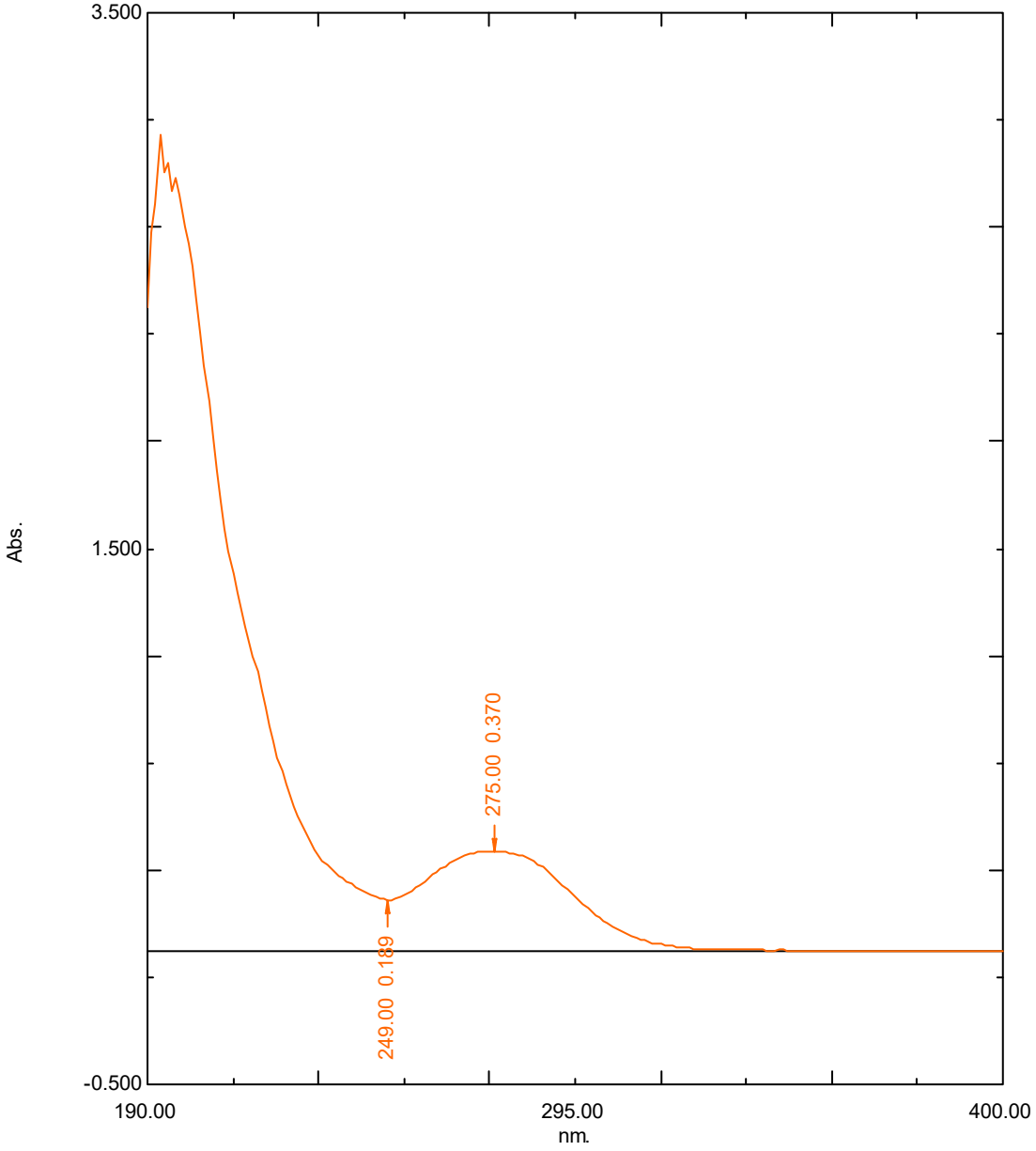
UV absorbance (MeCN, 0.5×10^{-5}M) **[Cu-6]**

$[Cu(dppf)Cl]_2$



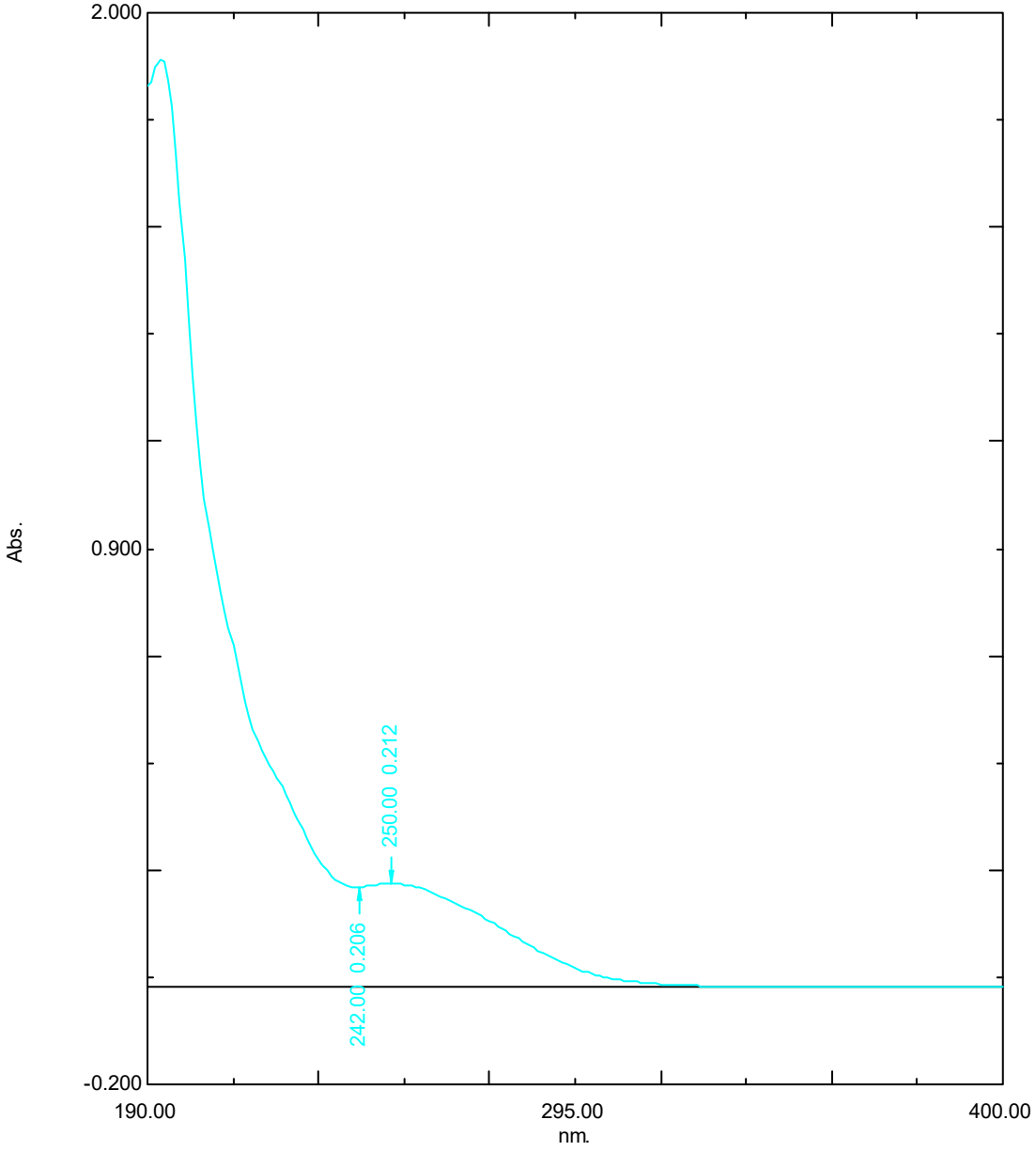
UV absorbance (MeCN, 1.0×10^{-5}M) **[Cu-7]**

$Cu(o\text{Tol}_3P)_3Cl$



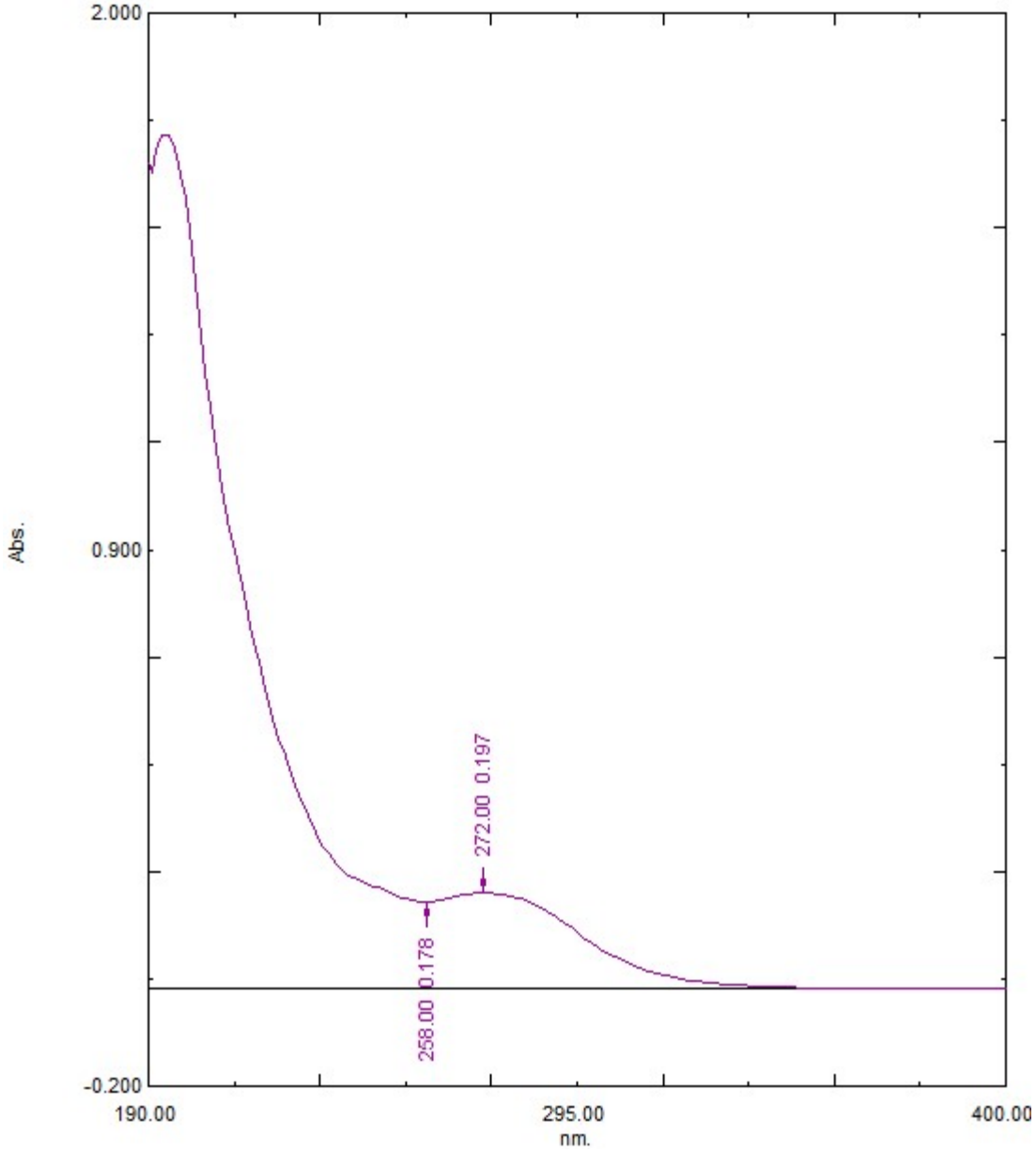
UV absorbance (MeCN, 1.0×10^{-5}M) **[Cu-8]**

$Cu(Ph_2MeP)_3Cl$

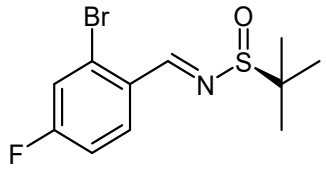


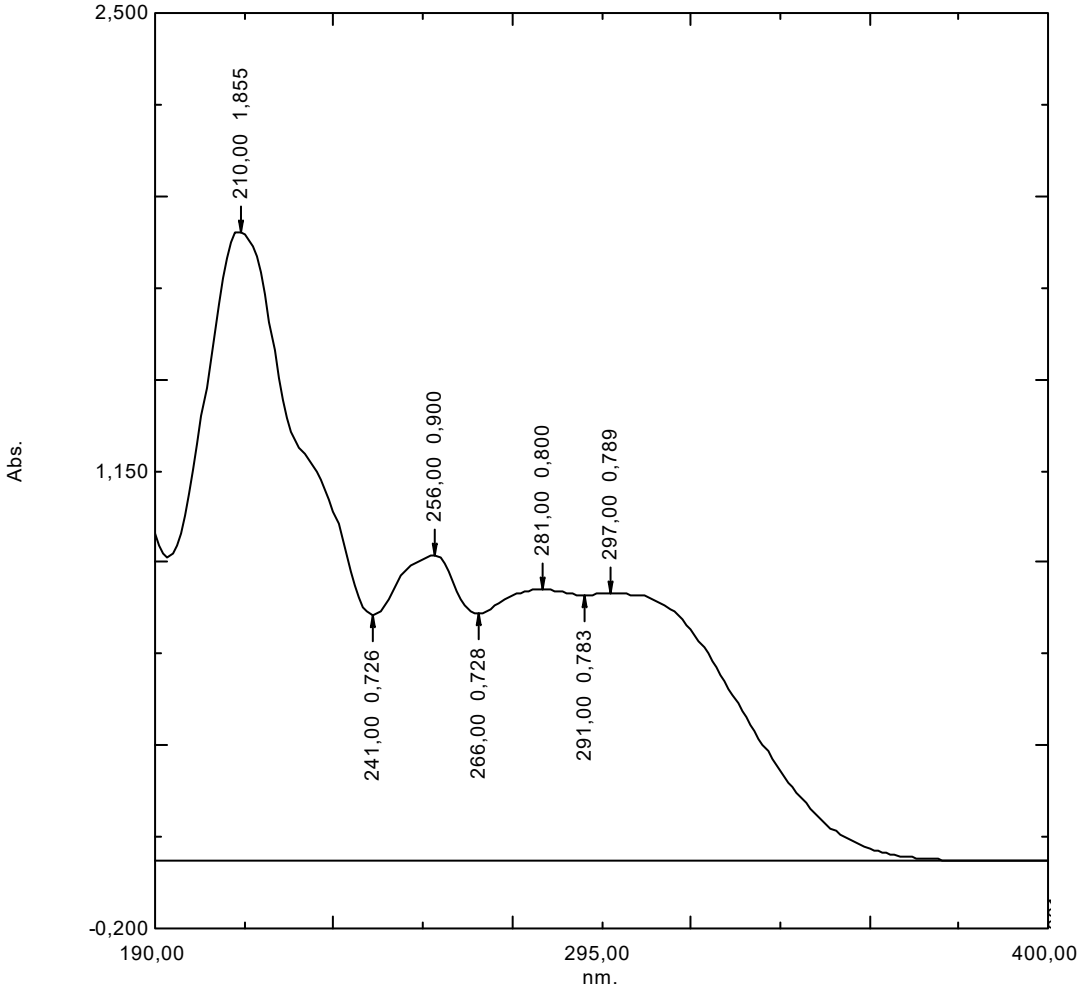
UV absorbance (MeCN, 1.0x10^{-5}M) **[Cu-9]**

Cu(XantPhos)Cl

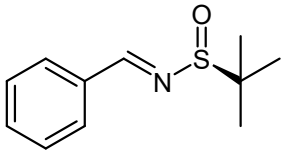


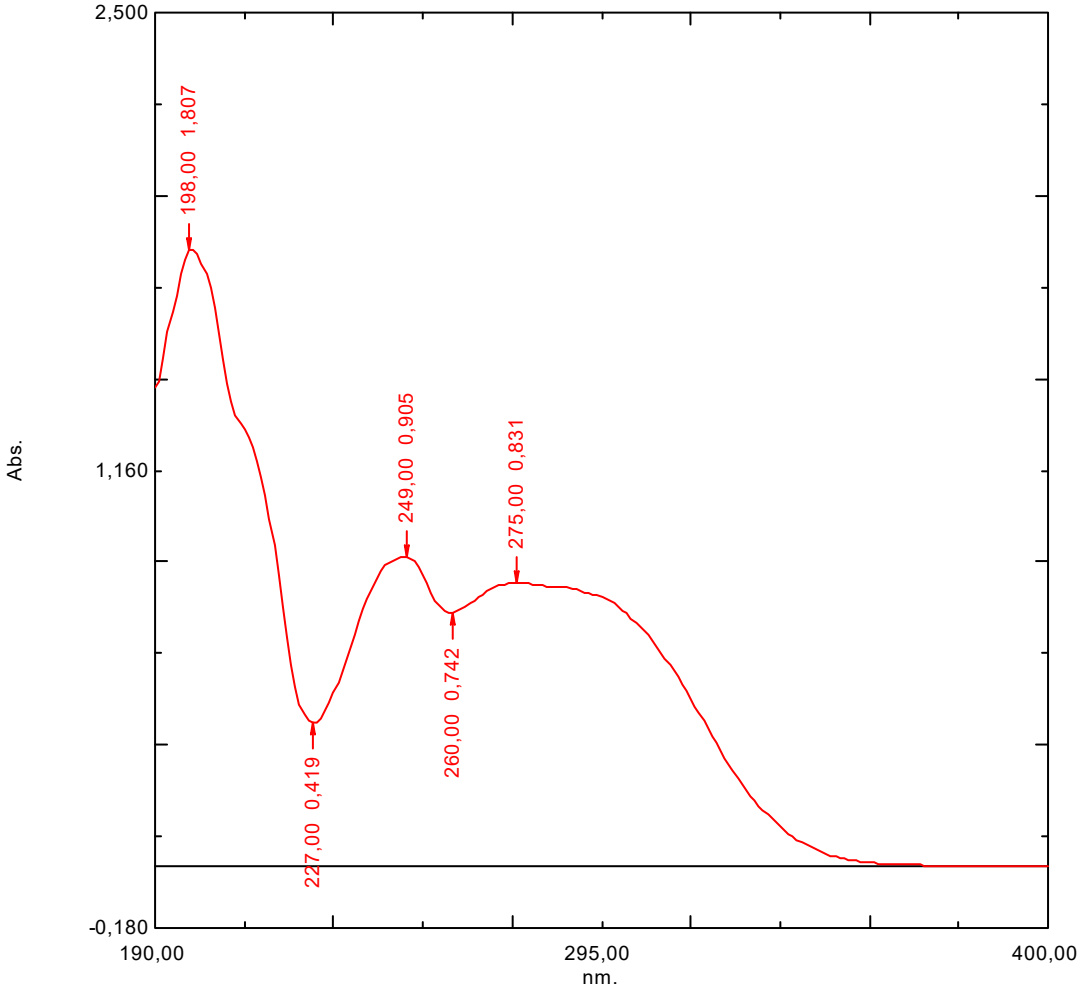
UV absorbance (MeCN, 1.0×10^{-4}M) **2a**



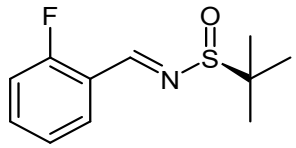


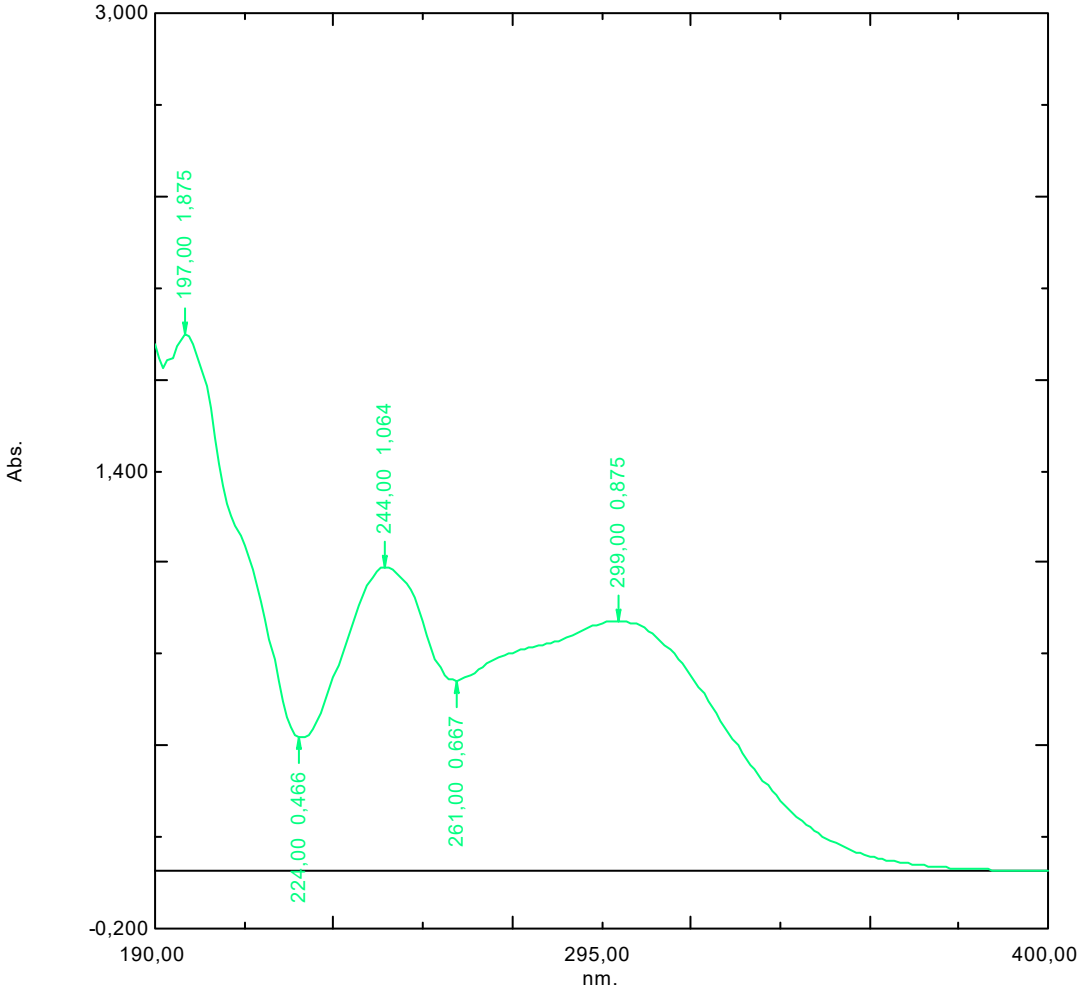
UV absorbance (MeCN, 1.0x10^{-4}M) **2b**



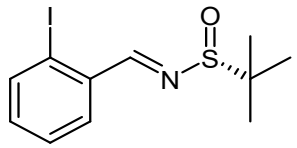


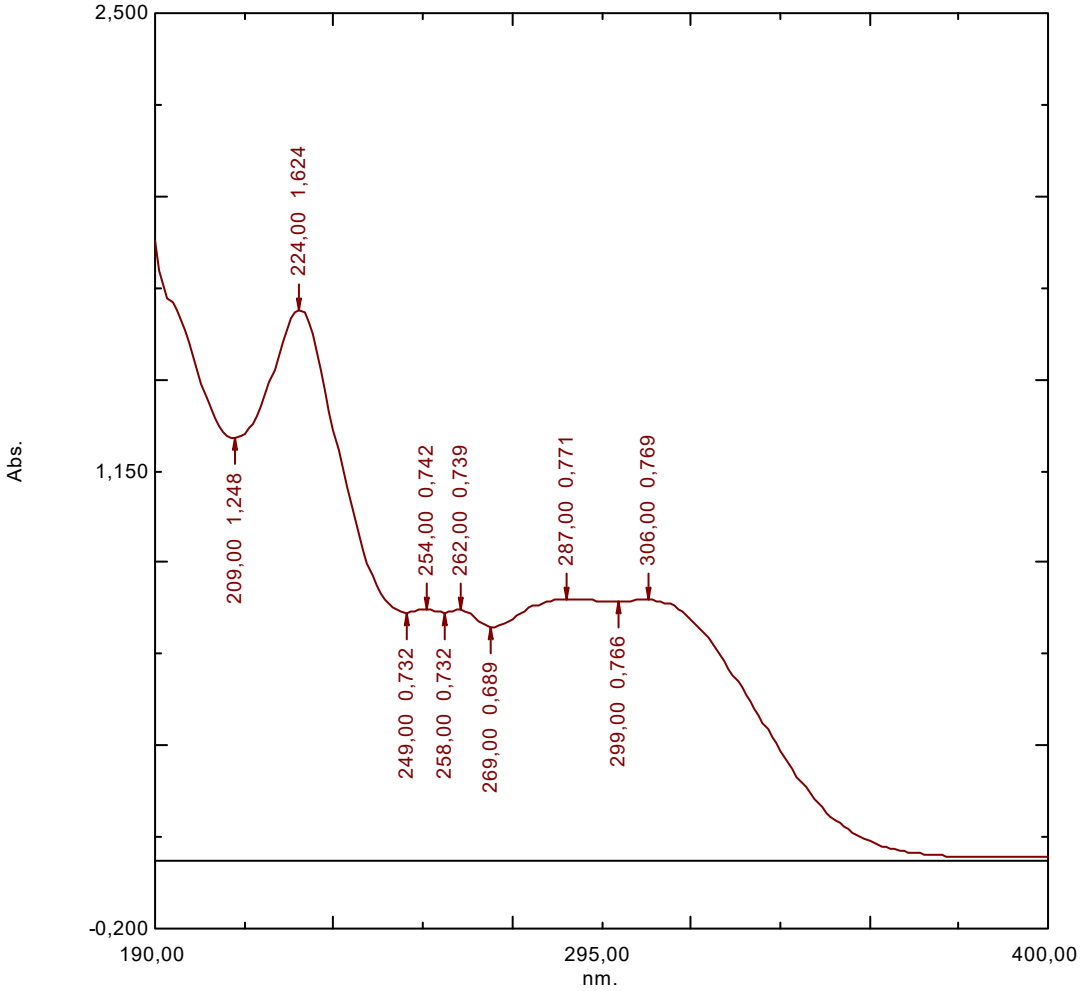
UV absorbance (MeCN, 1.0x10^{-4}M) **2c**



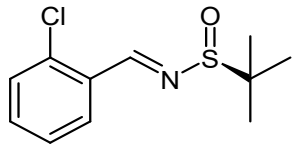


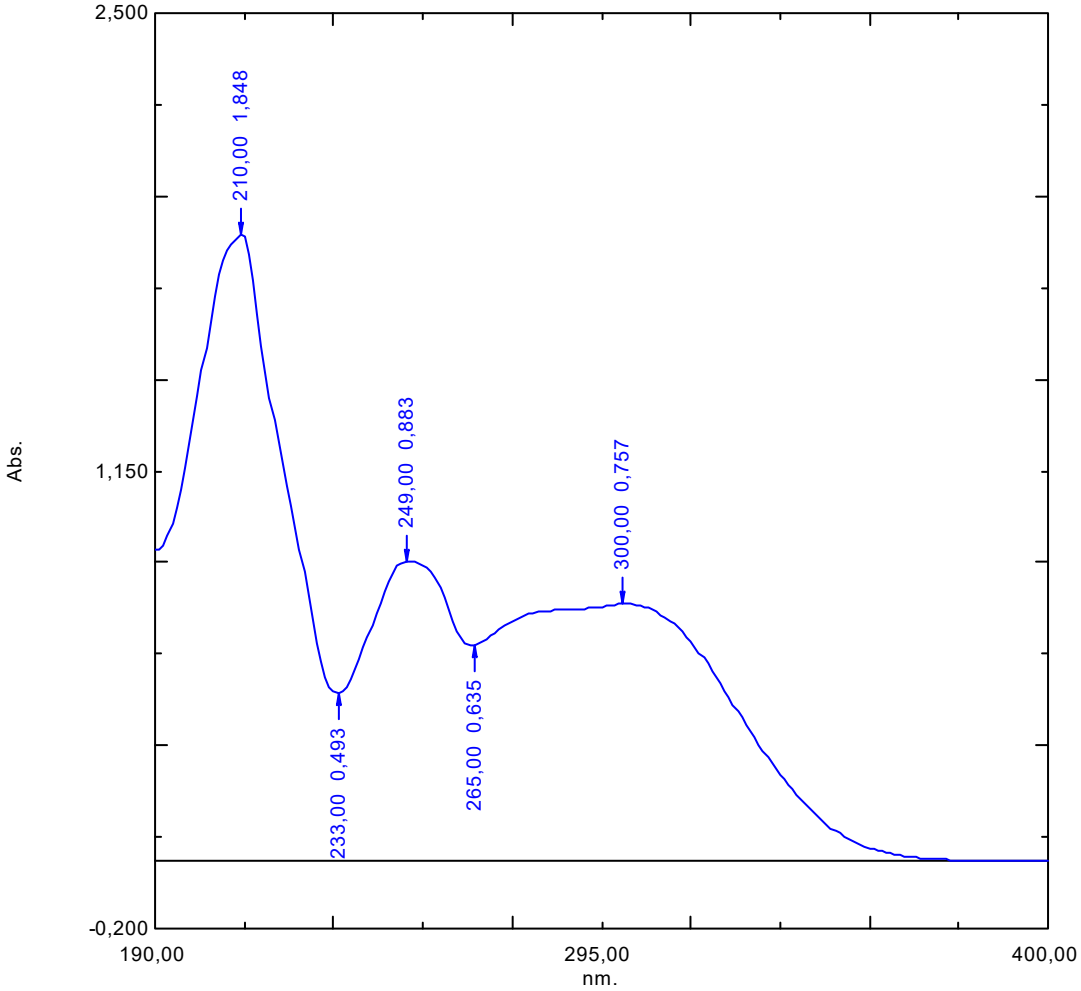
UV absorbance (MeCN, 1.0x10^{-4}M) **2d**



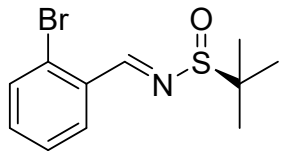


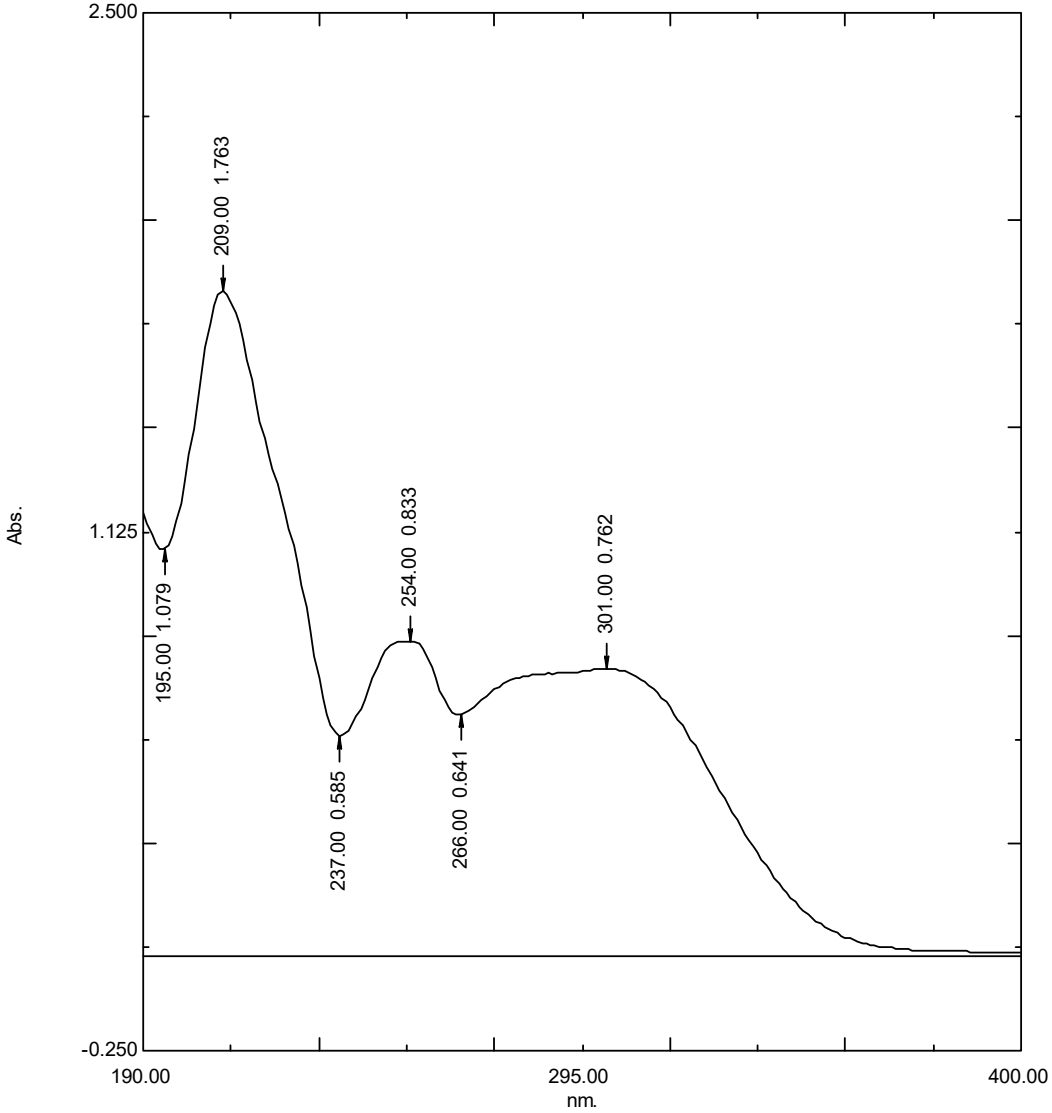
UV absorbance (MeCN, 1.0x10^{-4}M) **2e**



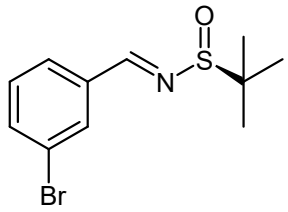


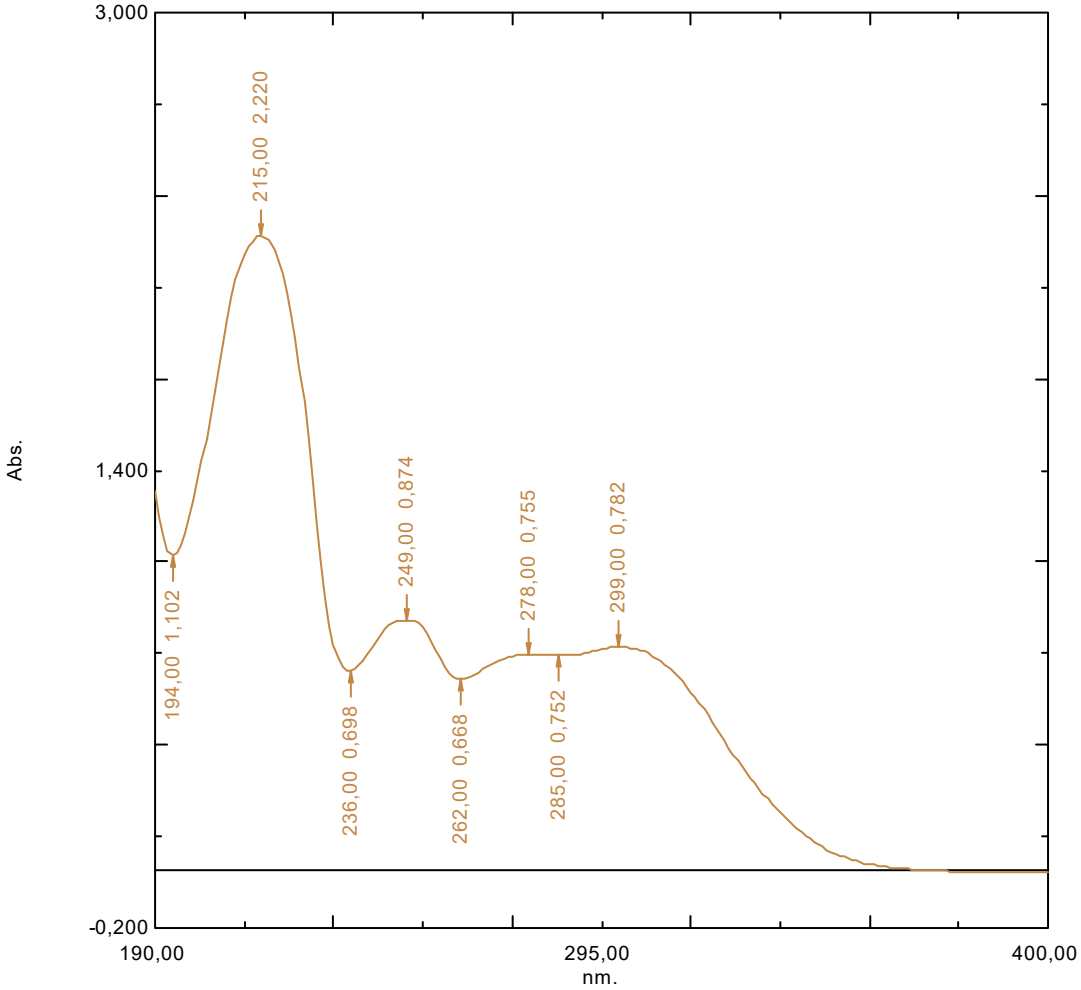
UV absorbance (MeCN, 1.0x10^{-4}M) **2f**



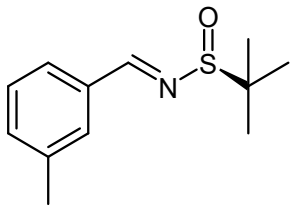


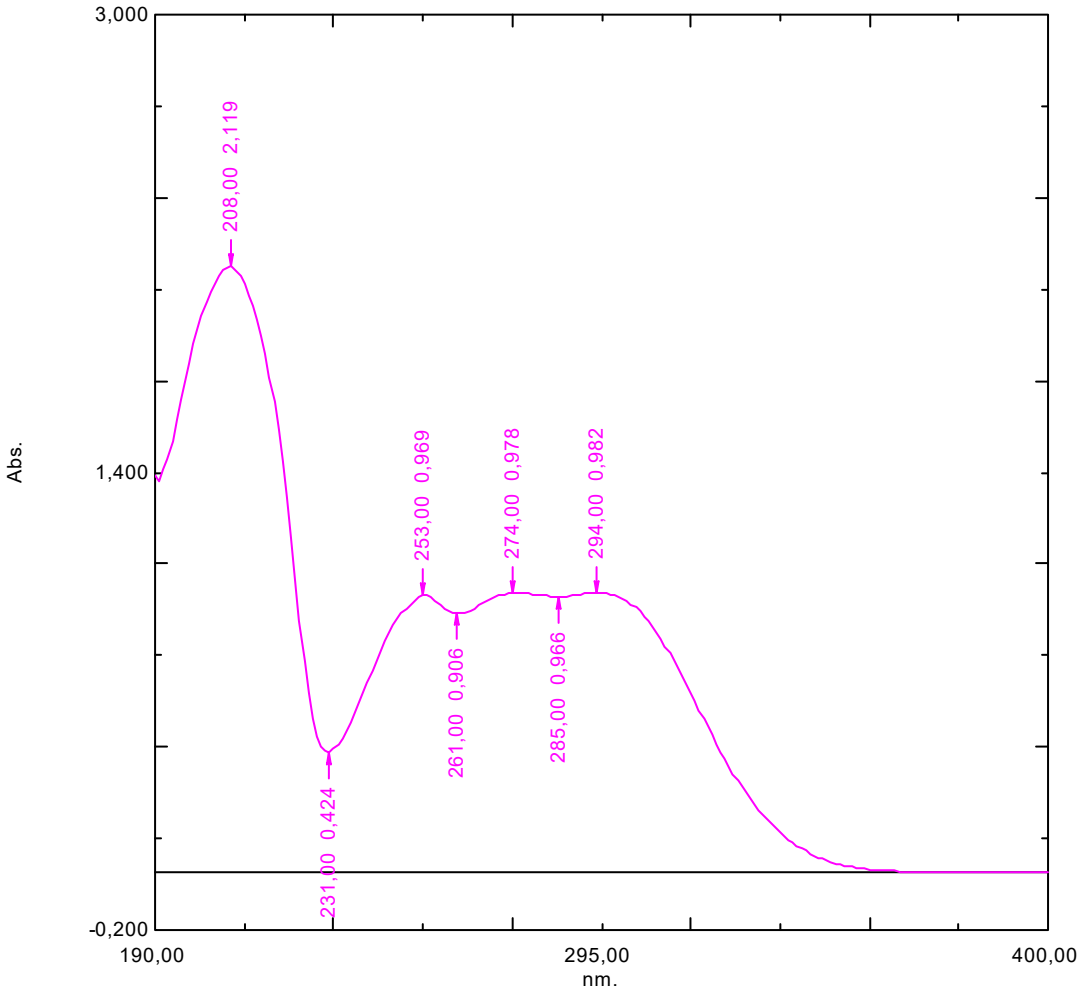
UV absorbance (MeCN, 1.0×10^{-4}M) **2g**



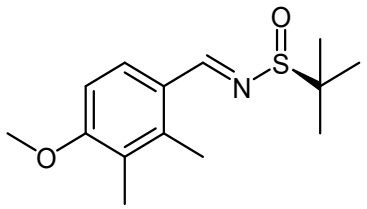


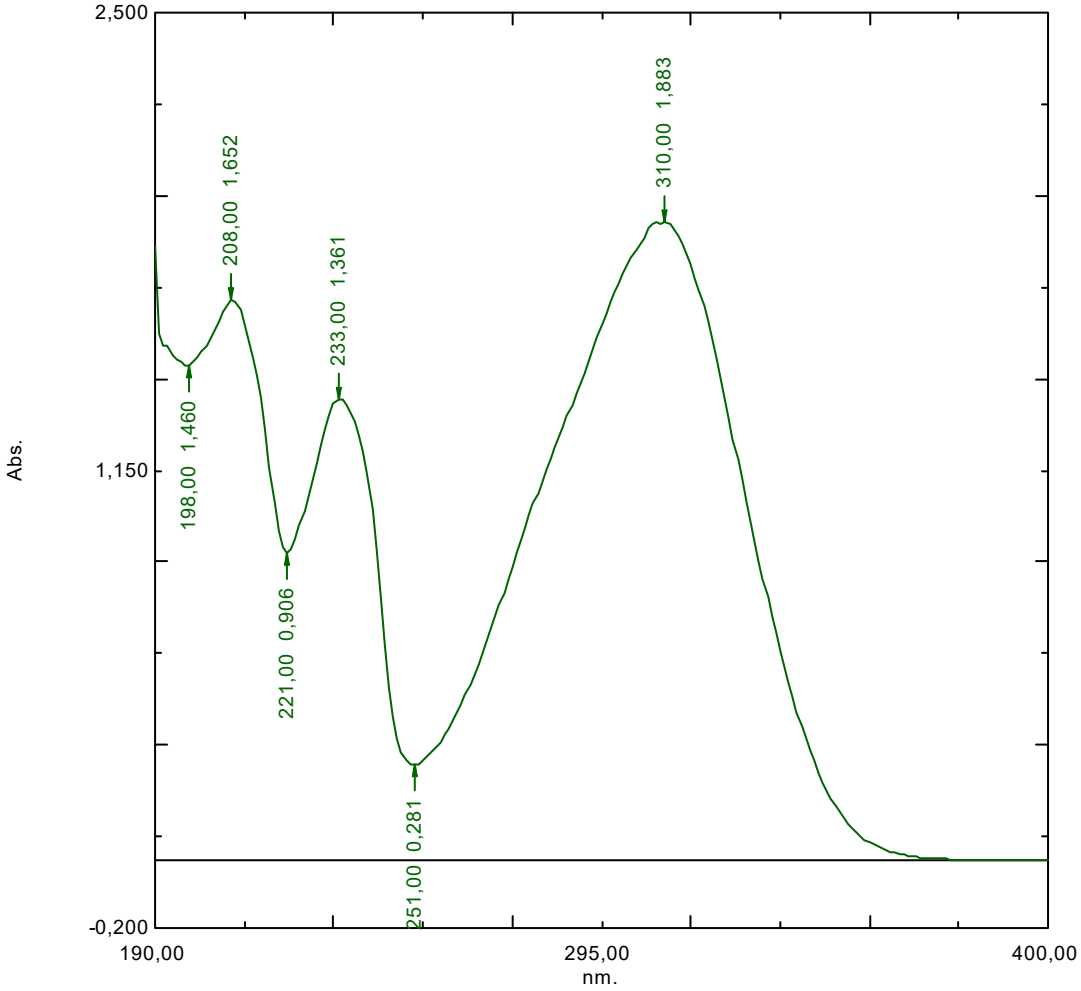
UV absorbance (MeCN, 1.0x10^{-4}M) **2h**



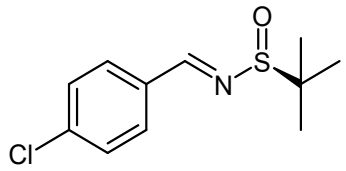


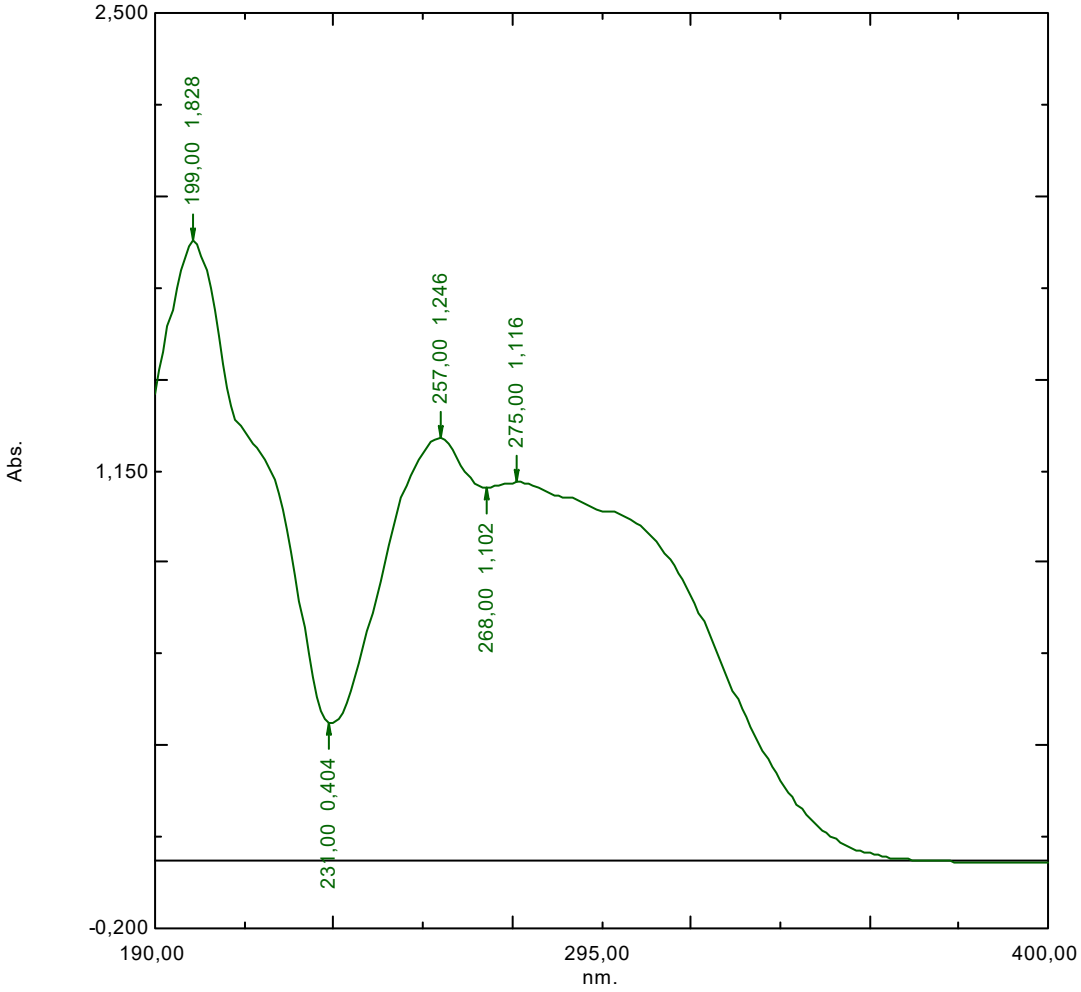
UV absorbance (MeCN, 1.0x10^{-4}M) **2i**



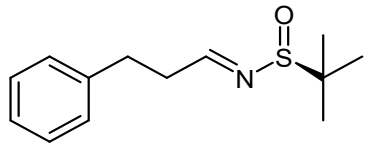


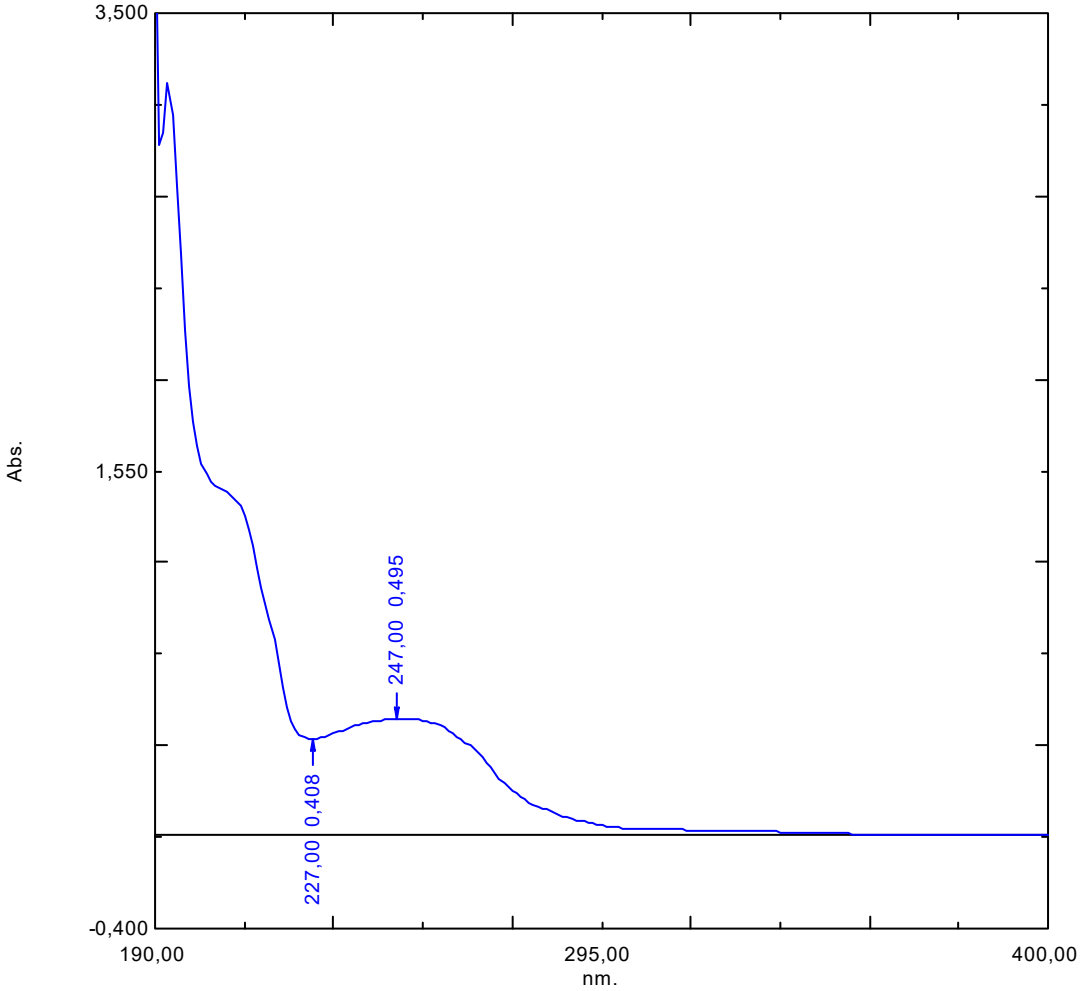
UV absorbance (MeCN, 1.0x10^{-4}M) **2j**



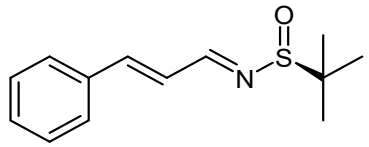


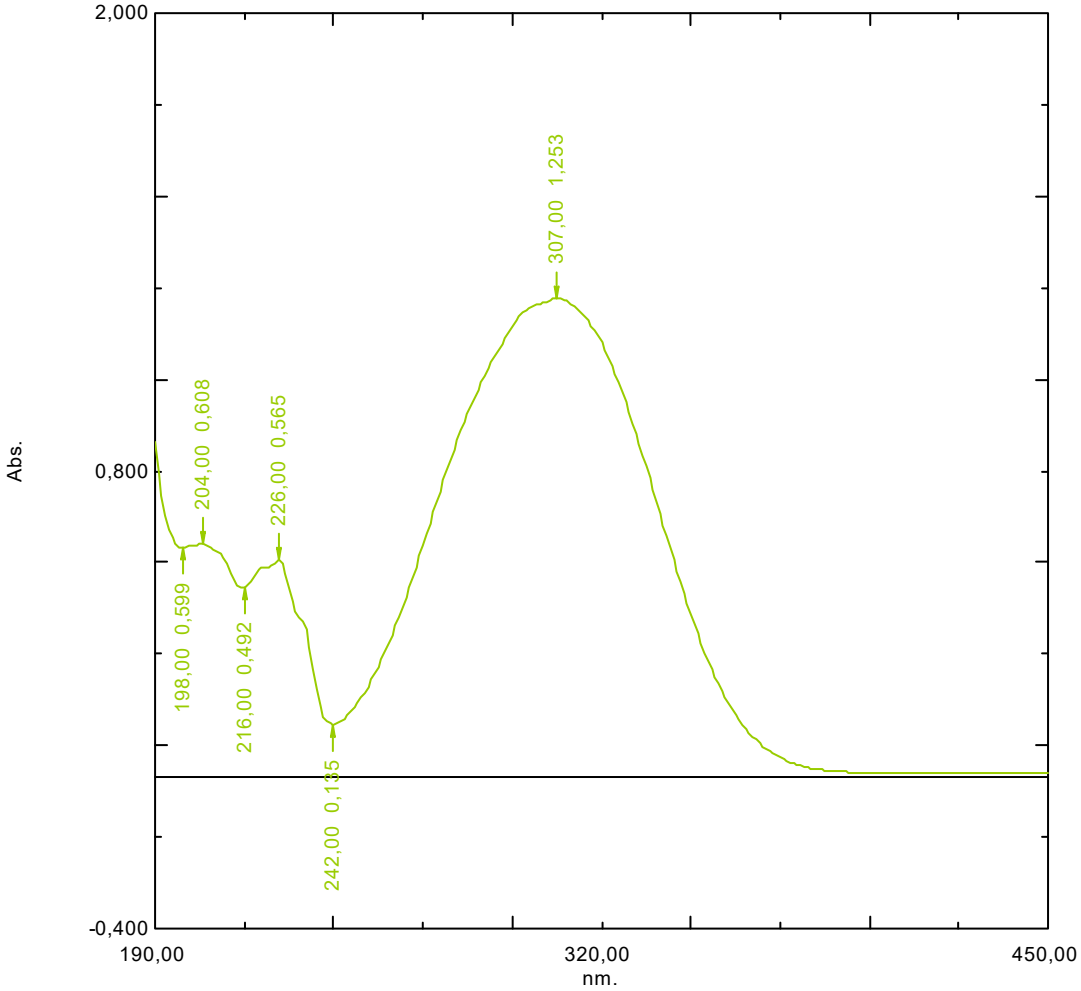
UV absorbance (MeCN, 1.0x10^{-4}M) **2k**



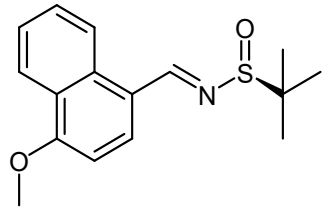


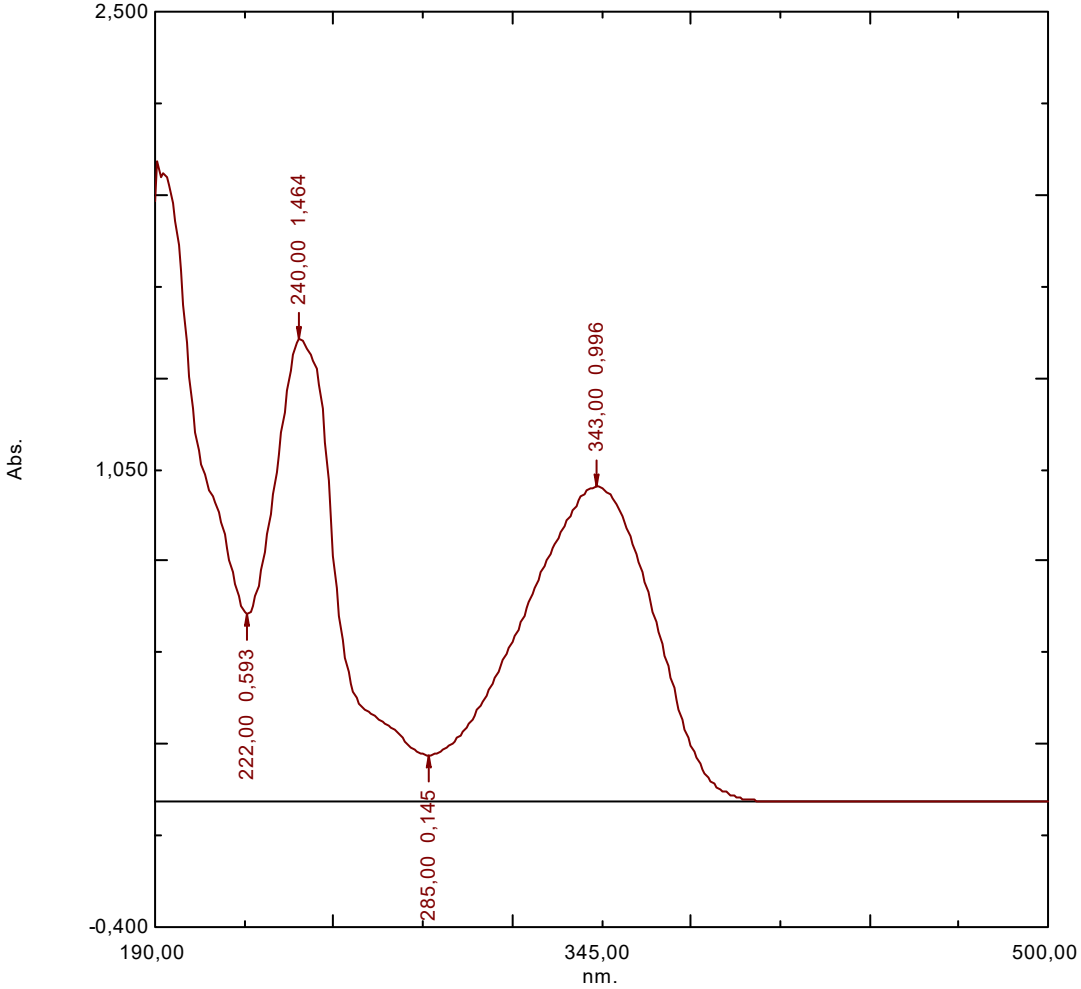
UV absorbance (MeCN, $0.5x10^{-4}$M) **2l**



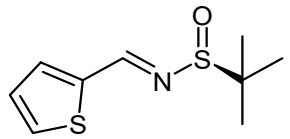


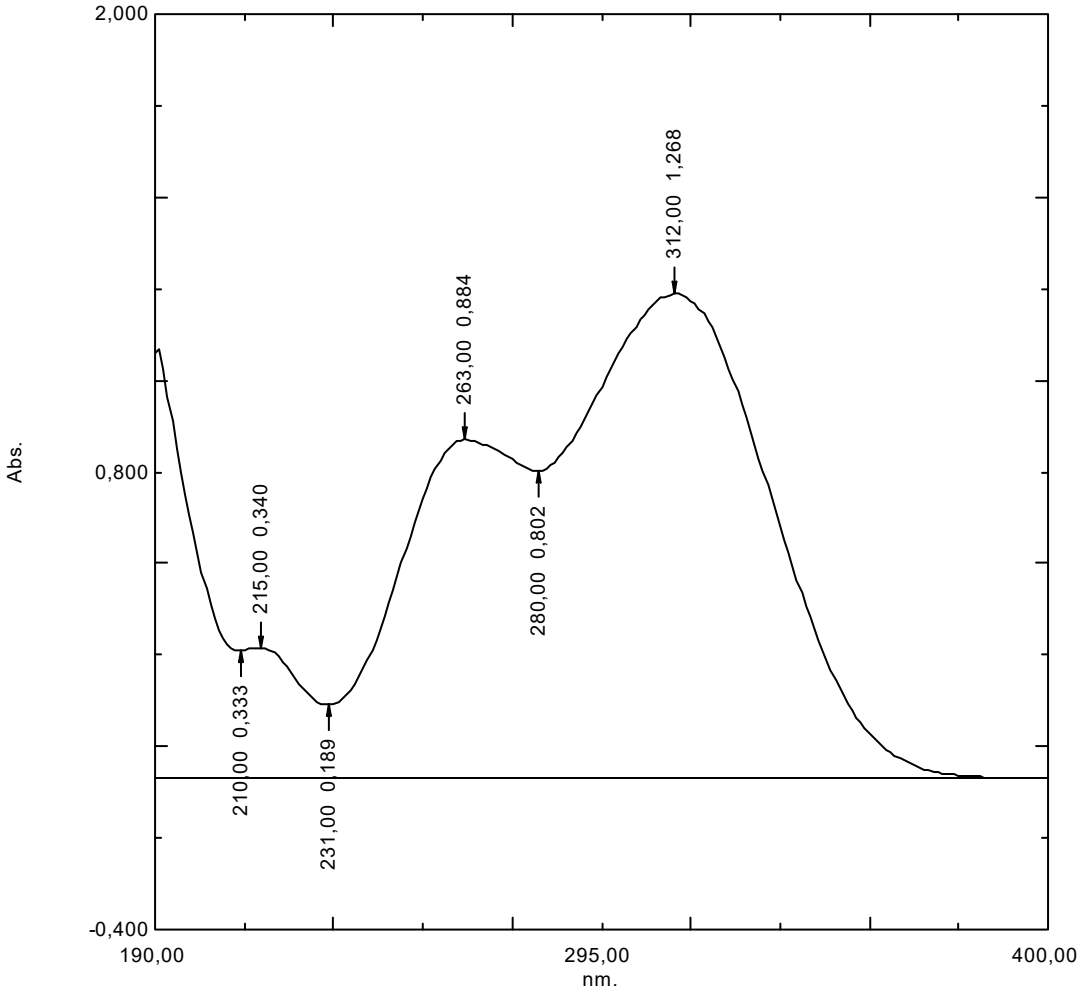
UV absorbance (MeCN, $0.5x10^{-4}$M) **2m**



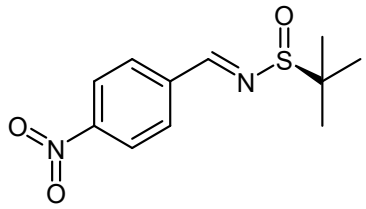


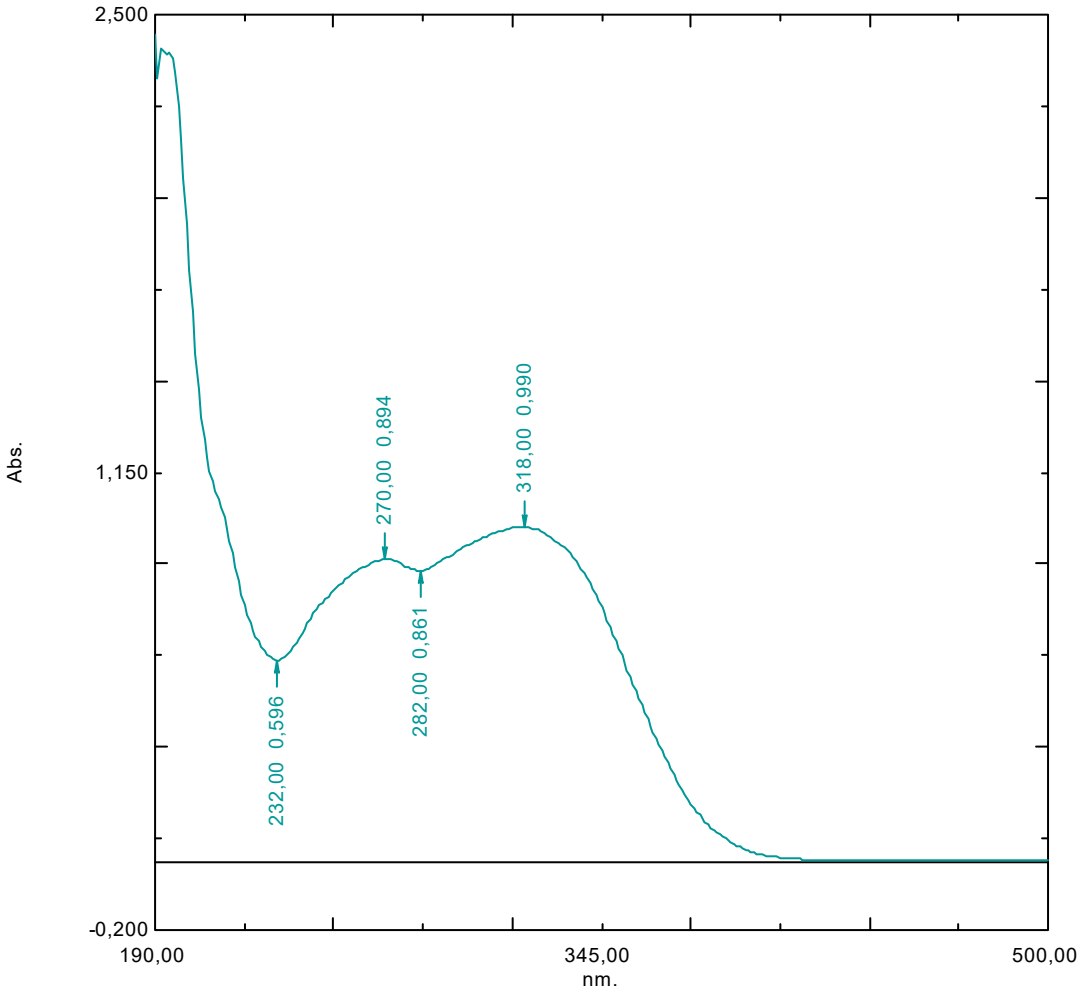
UV absorbance (MeCN, 1.0x10^{-4}M) **2n**



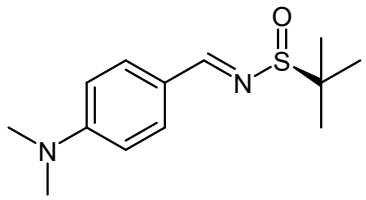


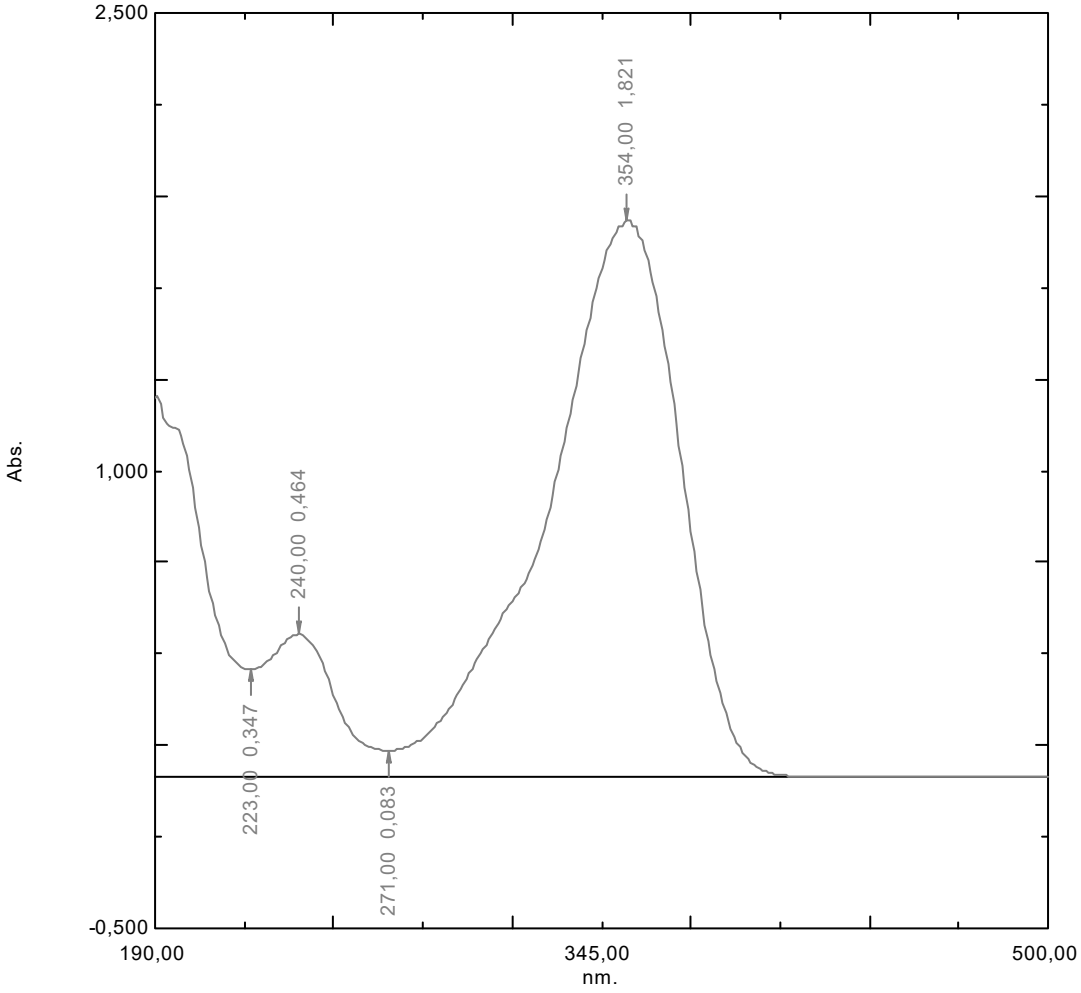
UV absorbance (MeCN, 1.0×10^{-4}M) **2o**



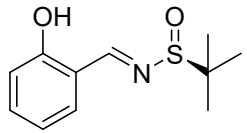


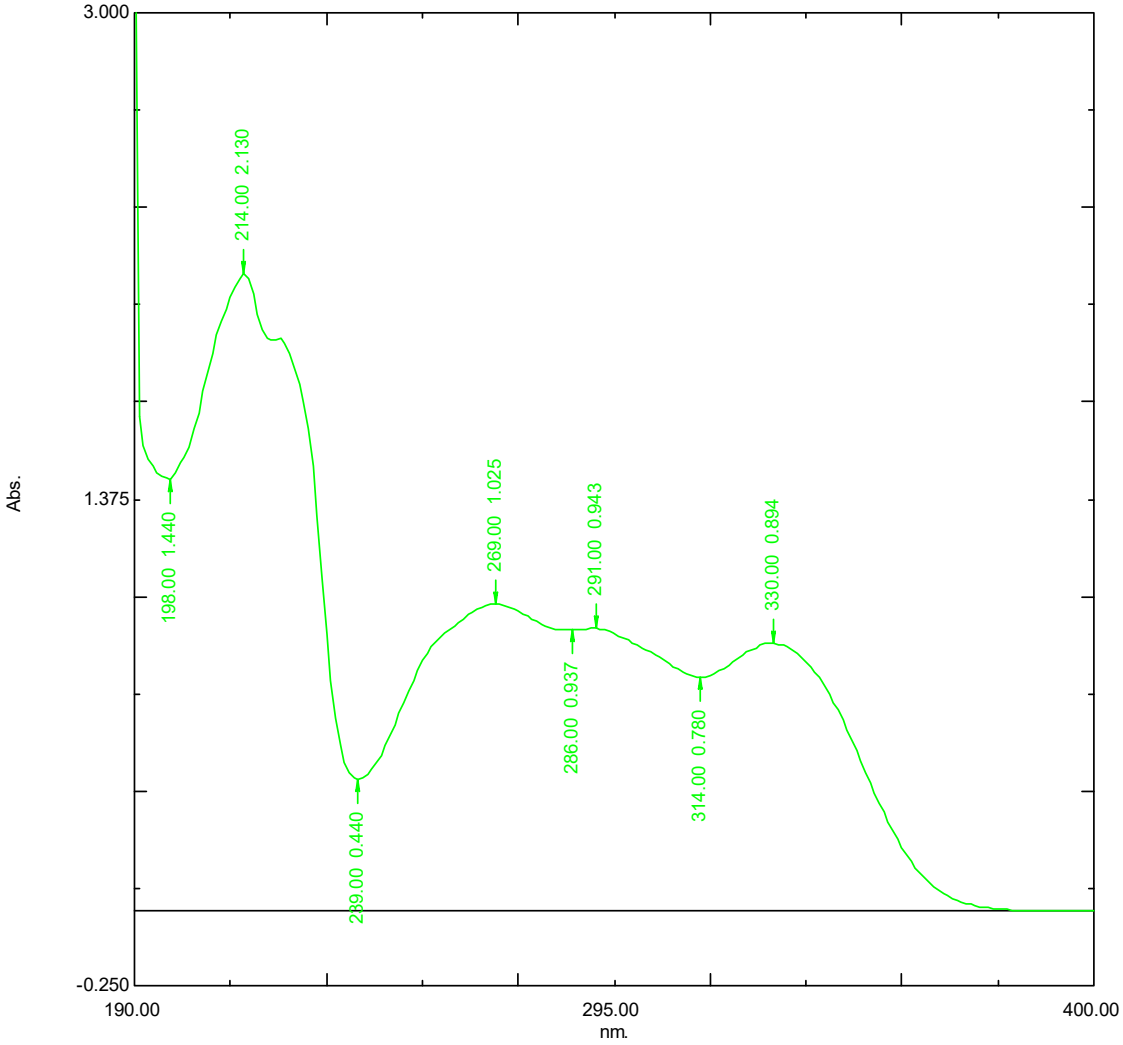
UV absorbance (MeCN, 0.5x10^{-4}M) **2p**



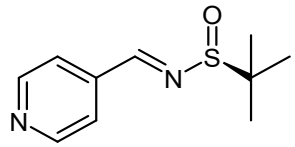


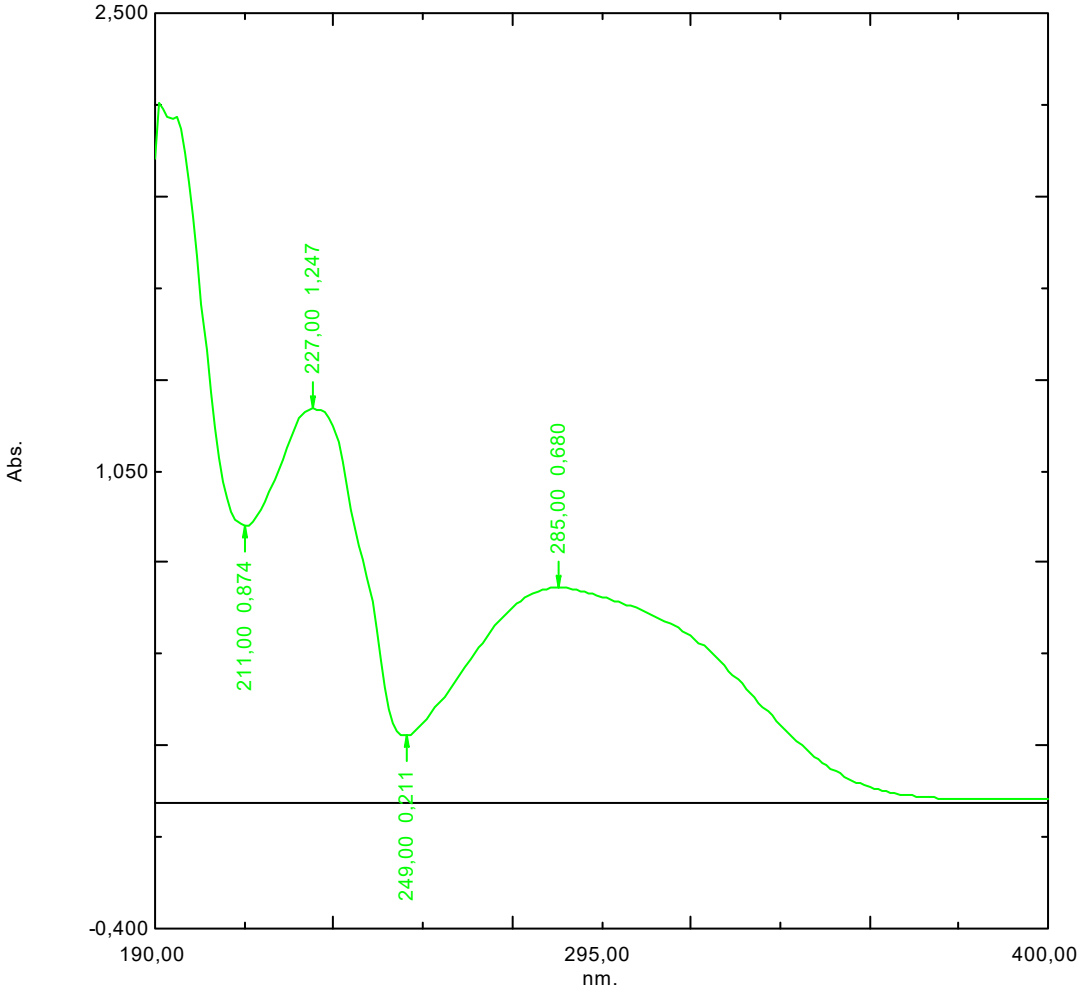
UV absorbance (MeCN, 1.0×10^{-4}M) **2q**



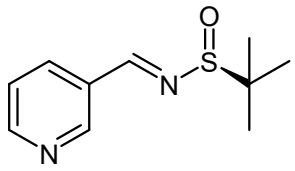


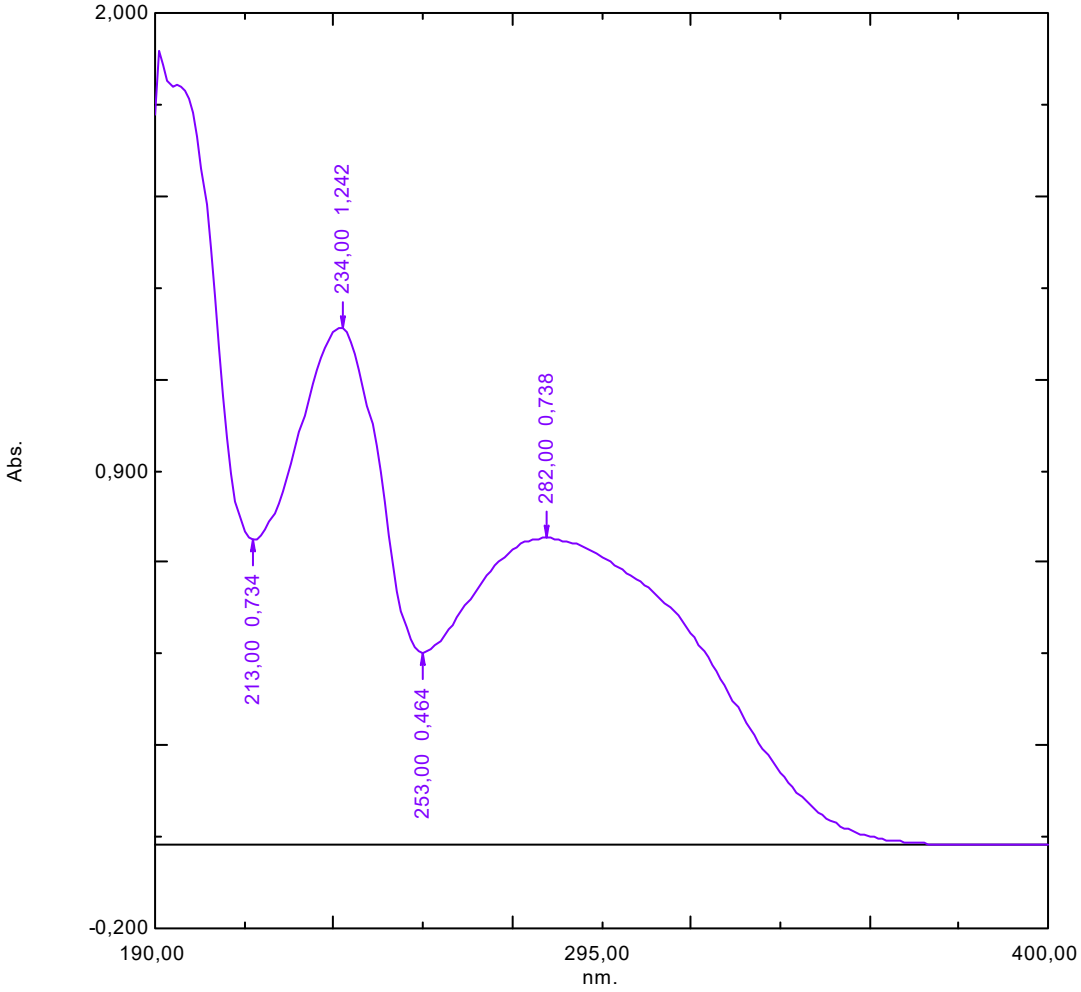
UV absorbance (MeCN, 1.0×10^{-4}M) **2r**



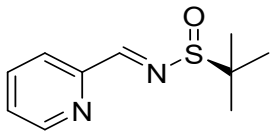


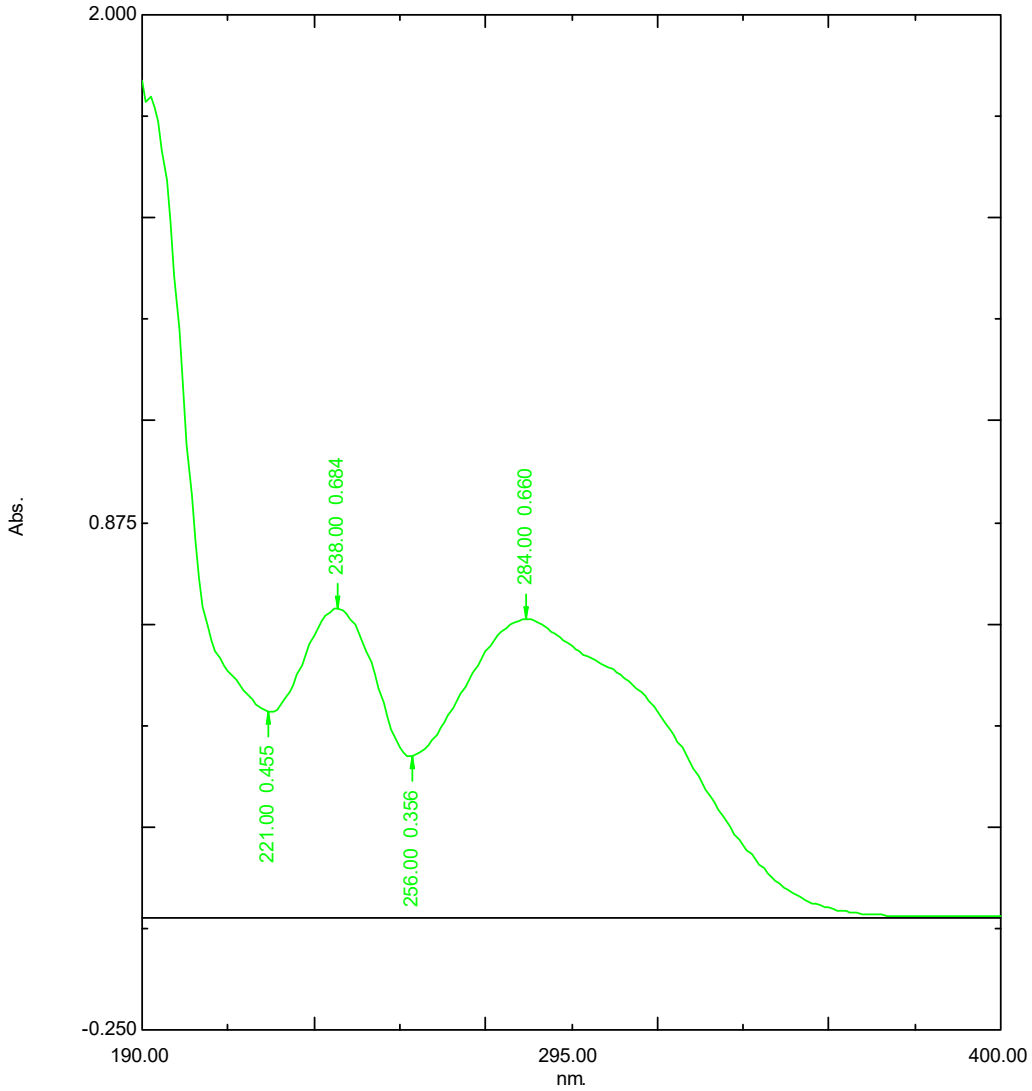
UV absorbance (MeCN, 1.0x10^{-4}M) **2s**



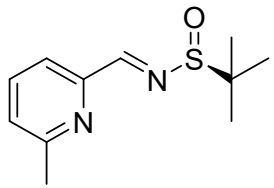


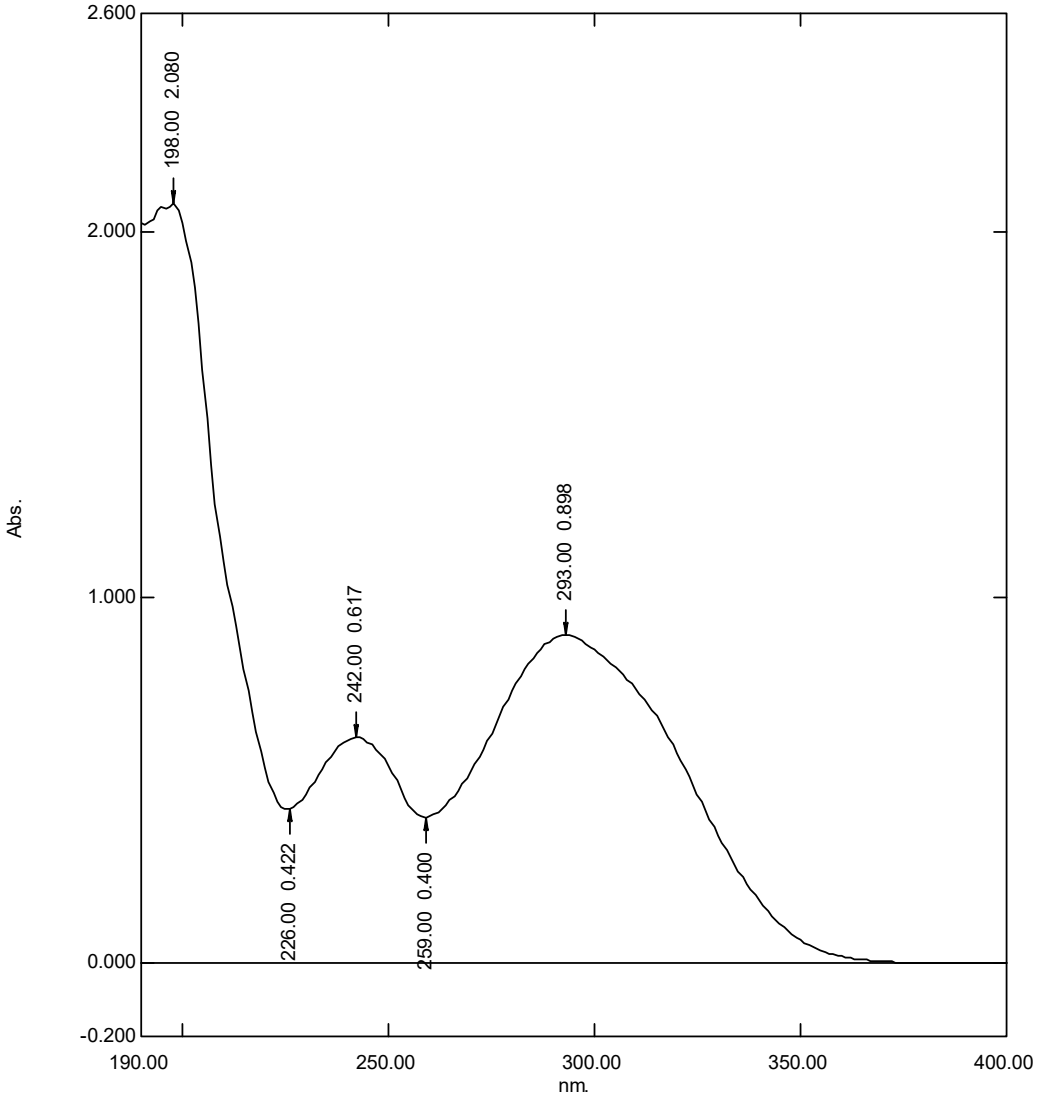
UV absorbance (MeCN, 1.0×10^{-4}M) **2t**



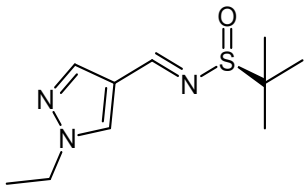


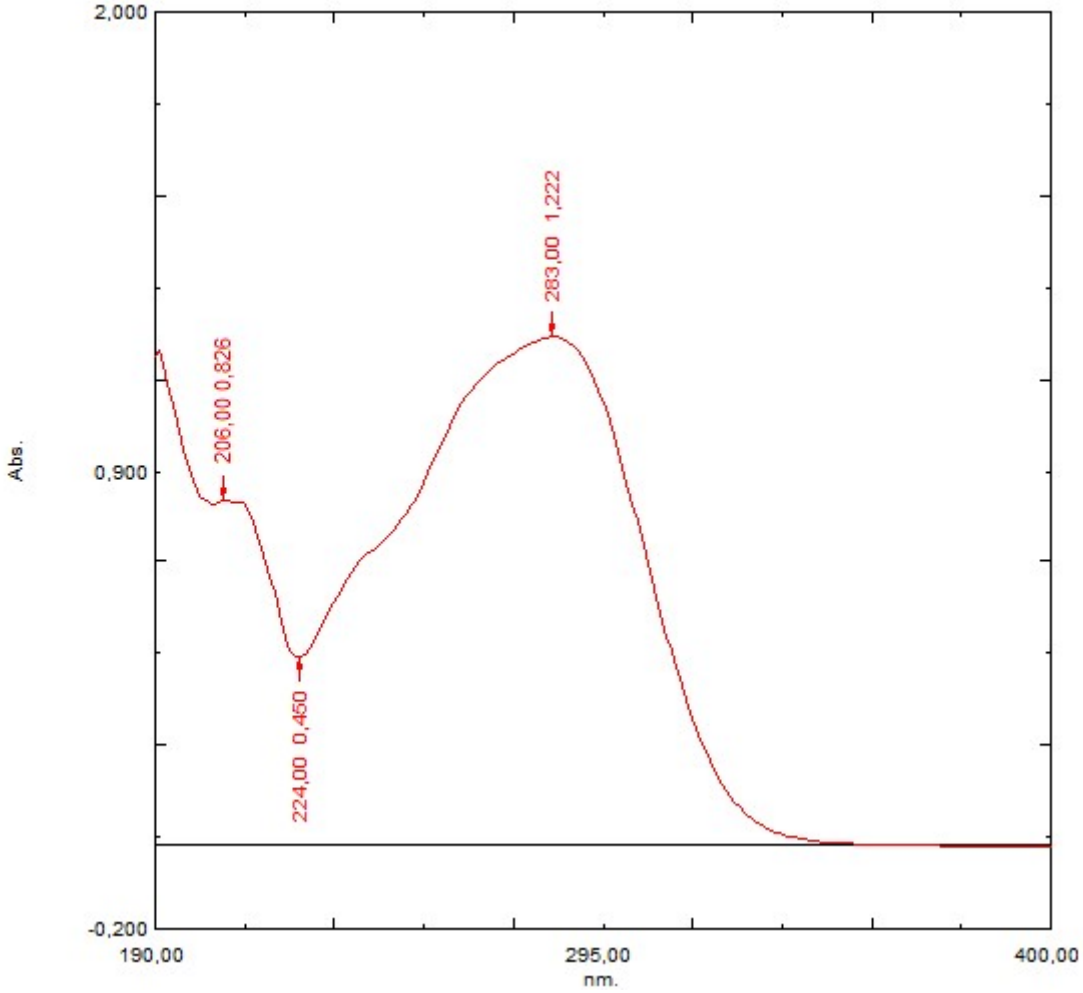
UV absorbance (MeCN, 1.0x10^{-4}M) **2u**



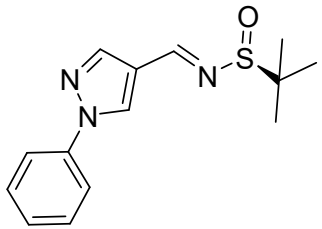


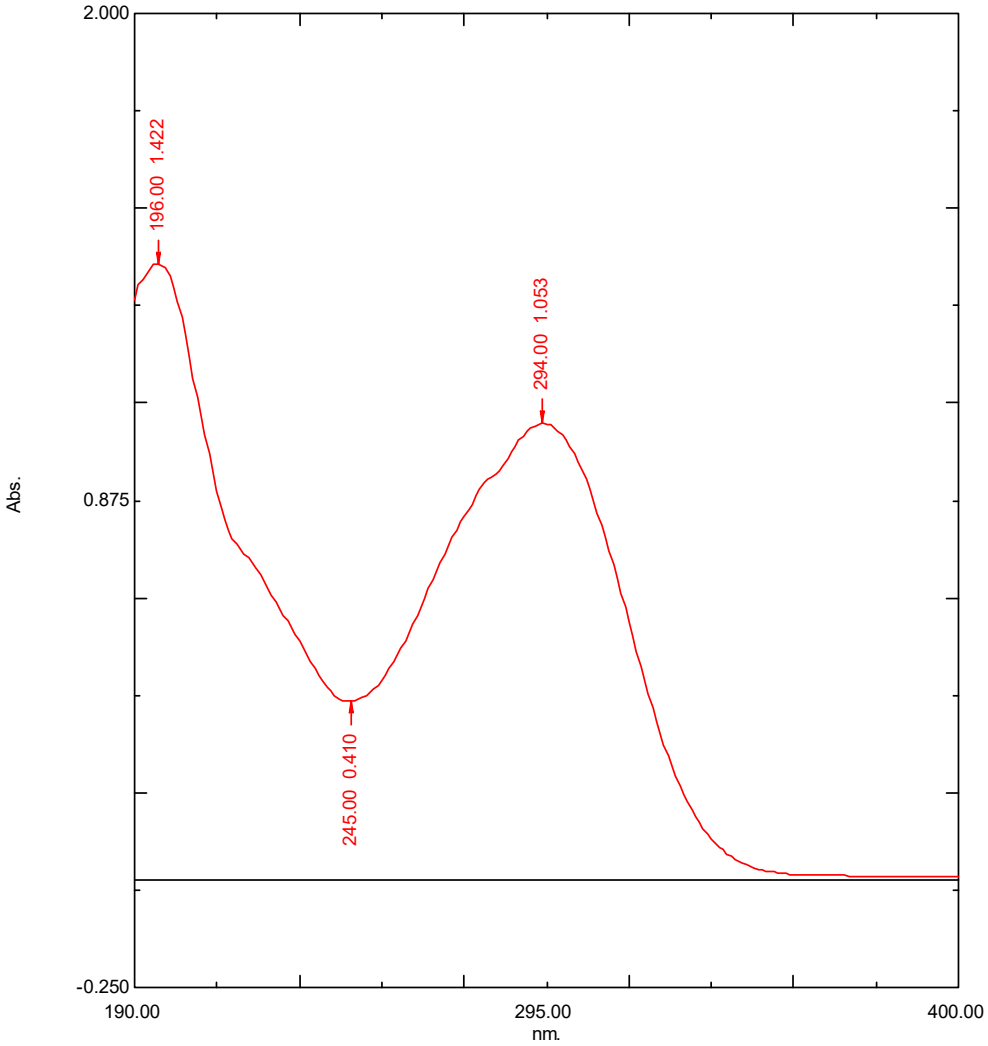
UV absorbance (MeCN, 1.0x10^{-4}M) **2v**



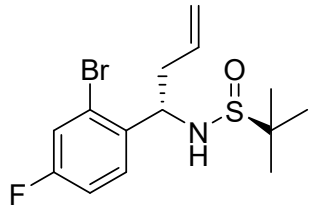


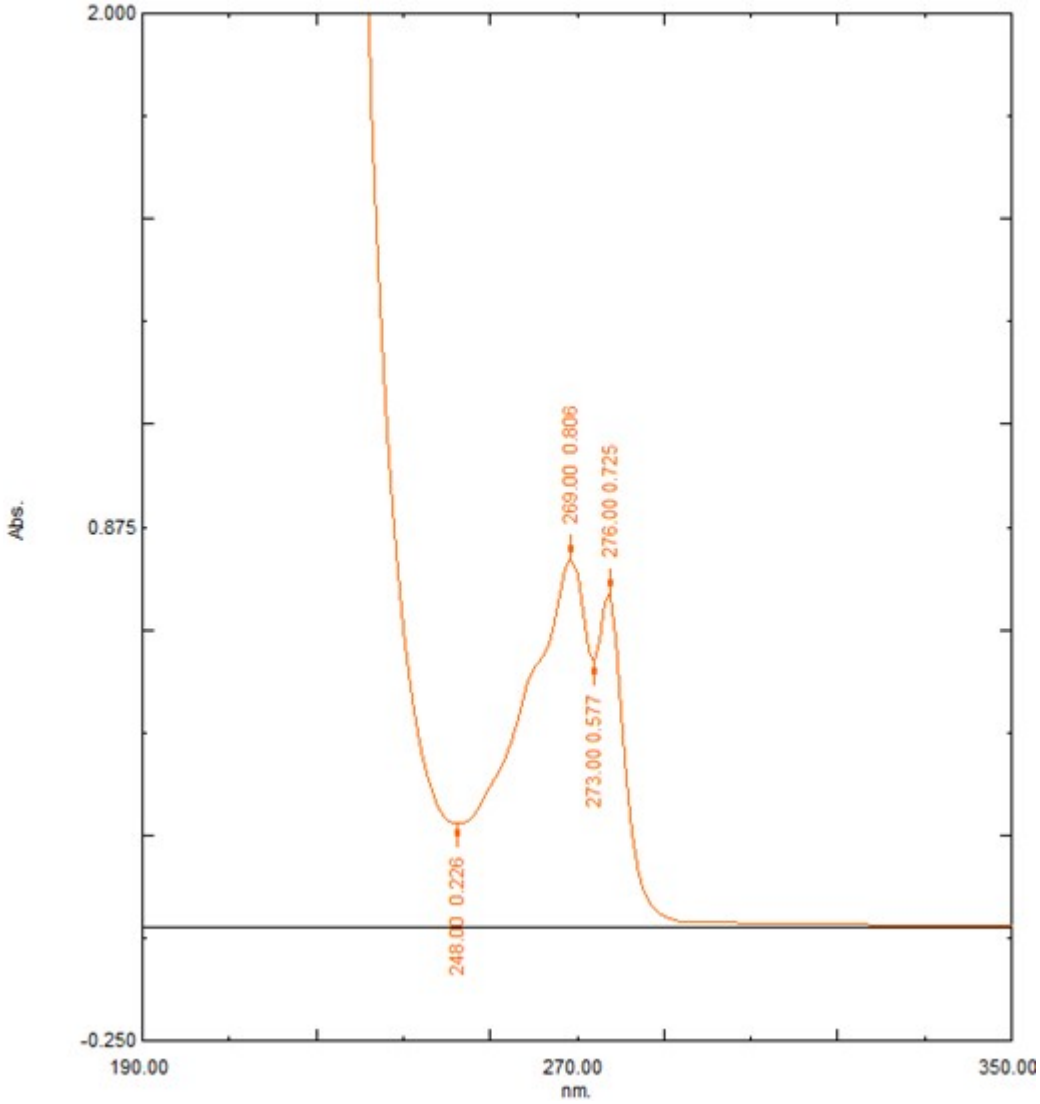
UV absorbance (MeCN, 0.5×10^{-4}M) **2w**



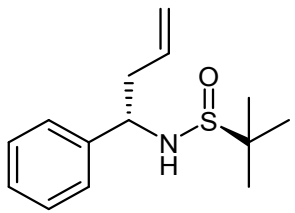


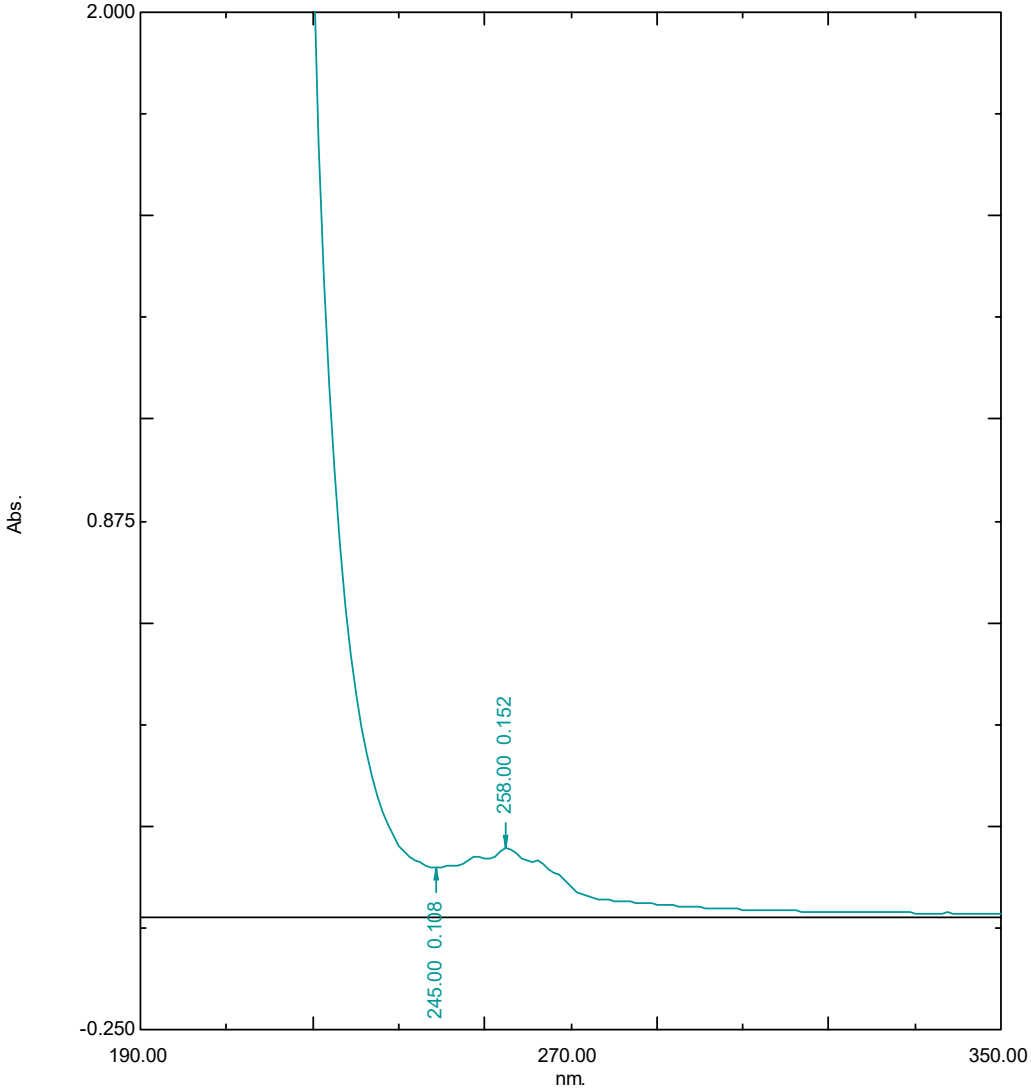
UV absorbance (MeCN, 1.0×10^{-3}M) **3a**



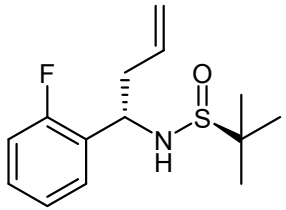


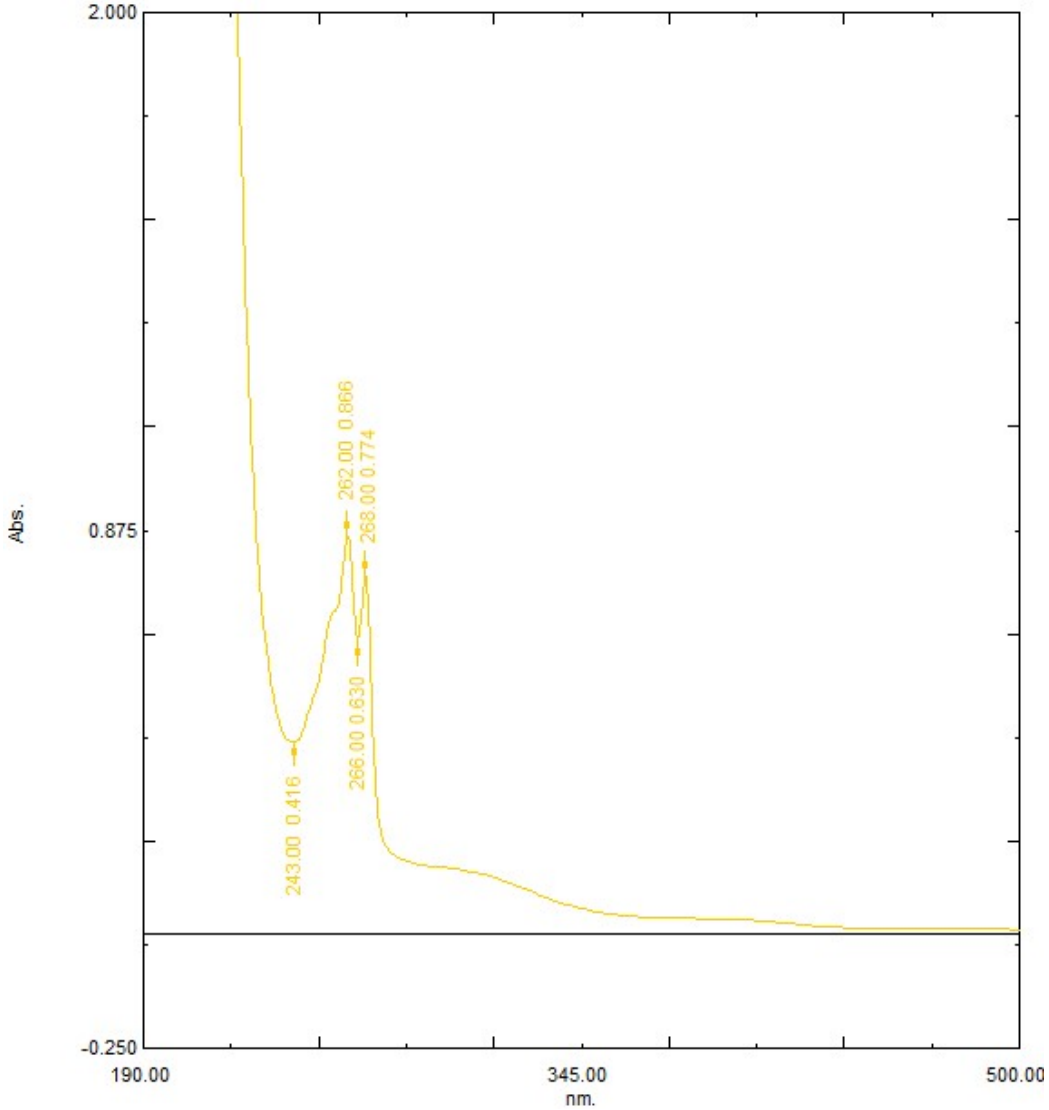
UV absorbance (MeCN, 1.0×10^{-3}M) **3b**



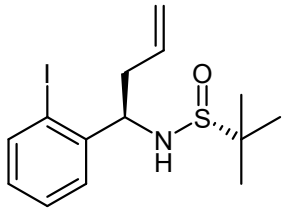


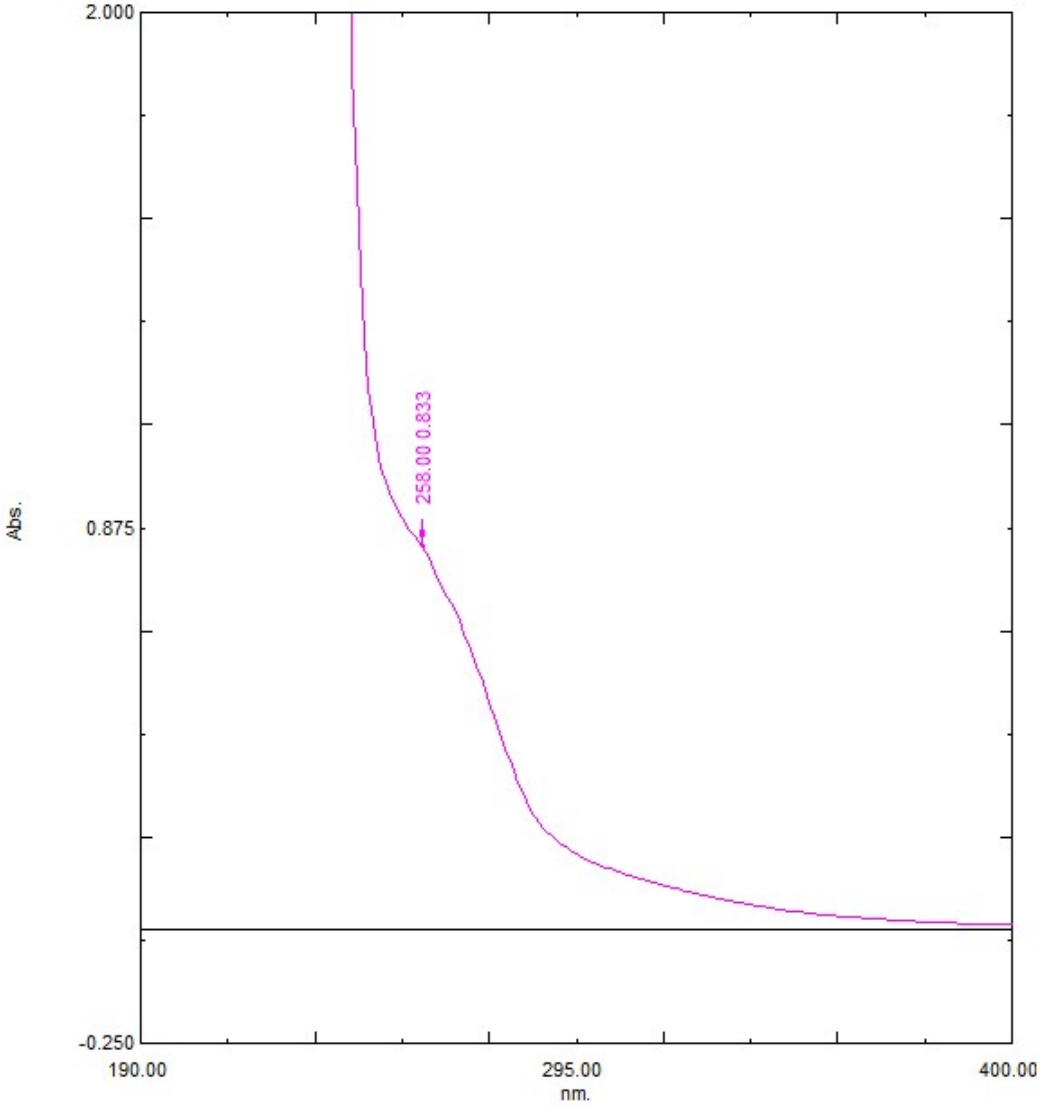
UV absorbance (MeCN, 1.0×10^{-3}M) **3c**



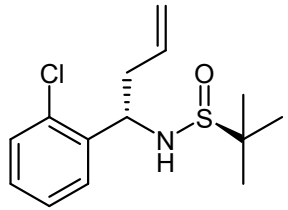


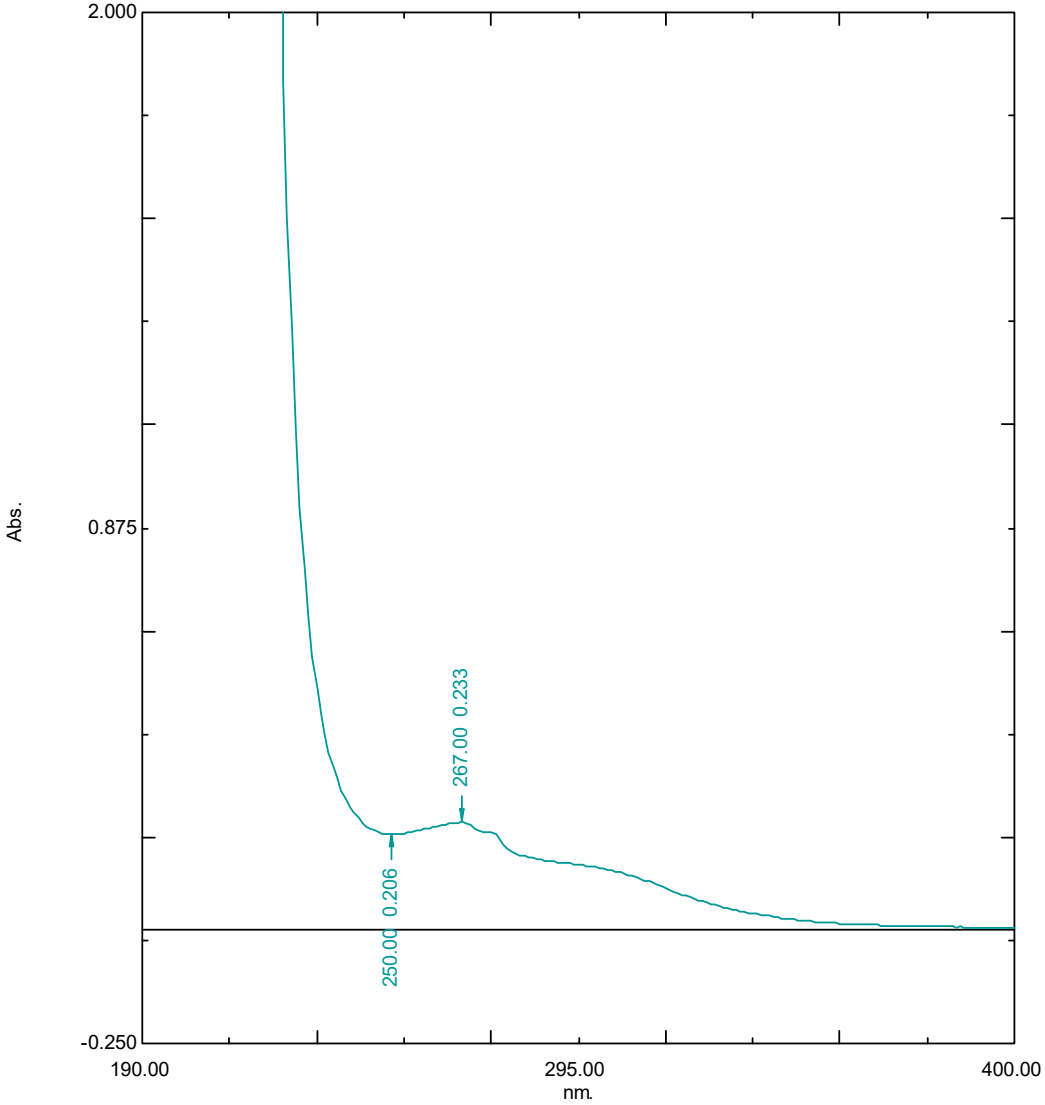
UV absorbance (MeCN, 1.0×10^{-3}M) **3d**



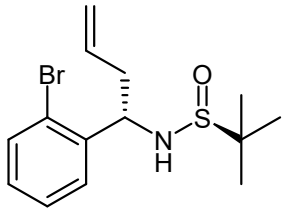


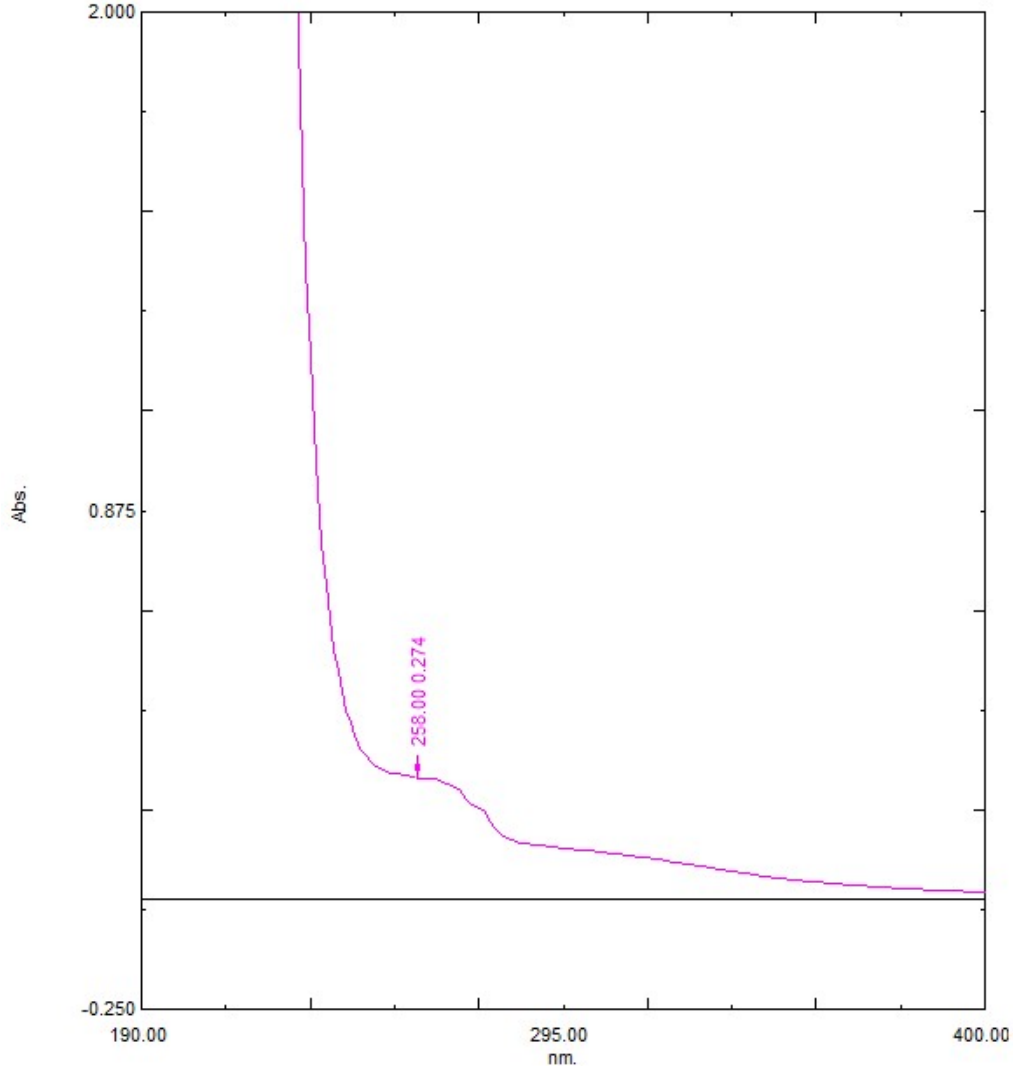
UV absorbance (MeCN, 1.0×10^{-3}M) **3e**



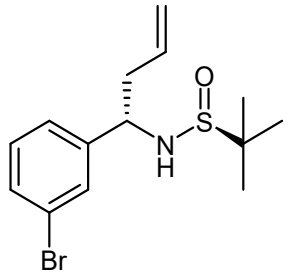


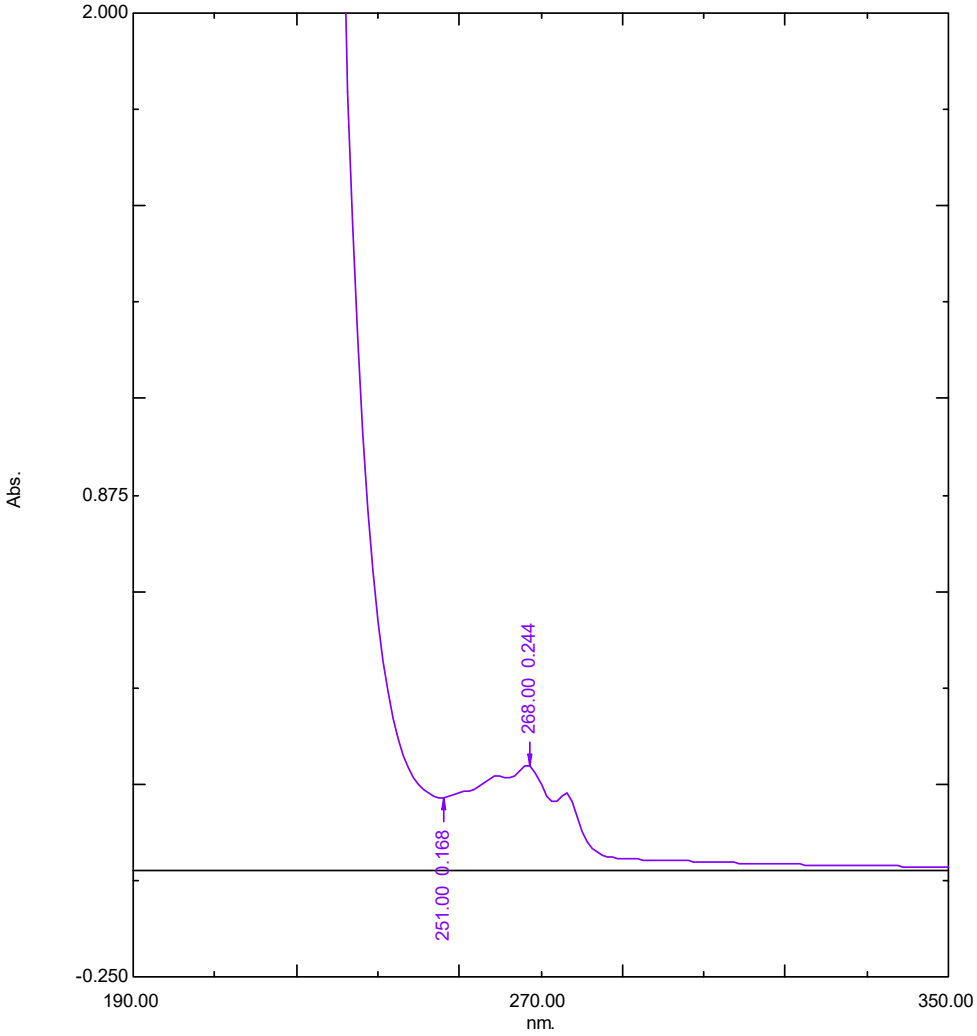
UV absorbance (MeCN, 1.0×10^{-3}M) **3f**



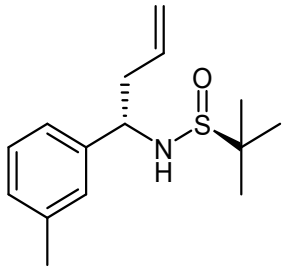


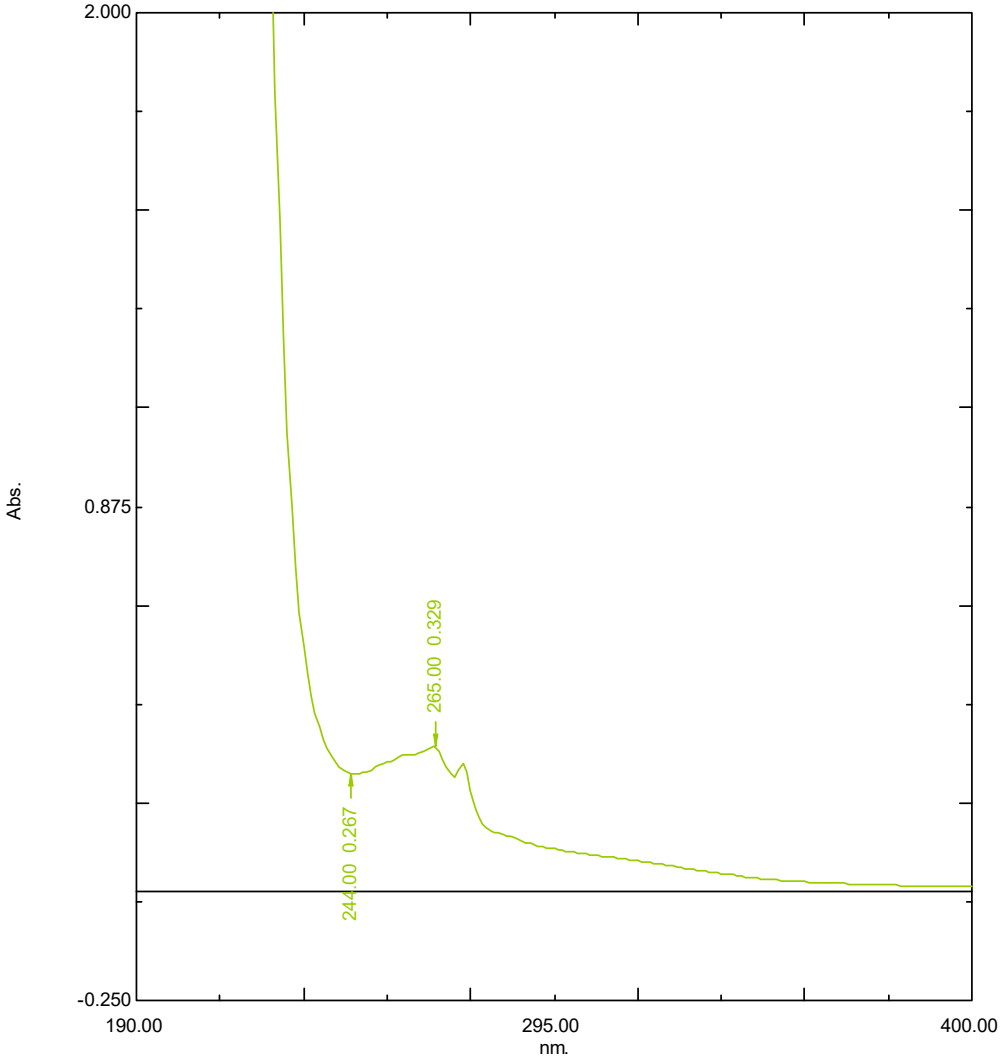
UV absorbance (MeCN, 1.0×10^{-3}M) **3g**



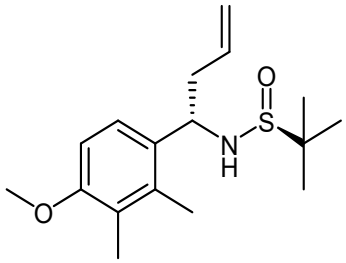


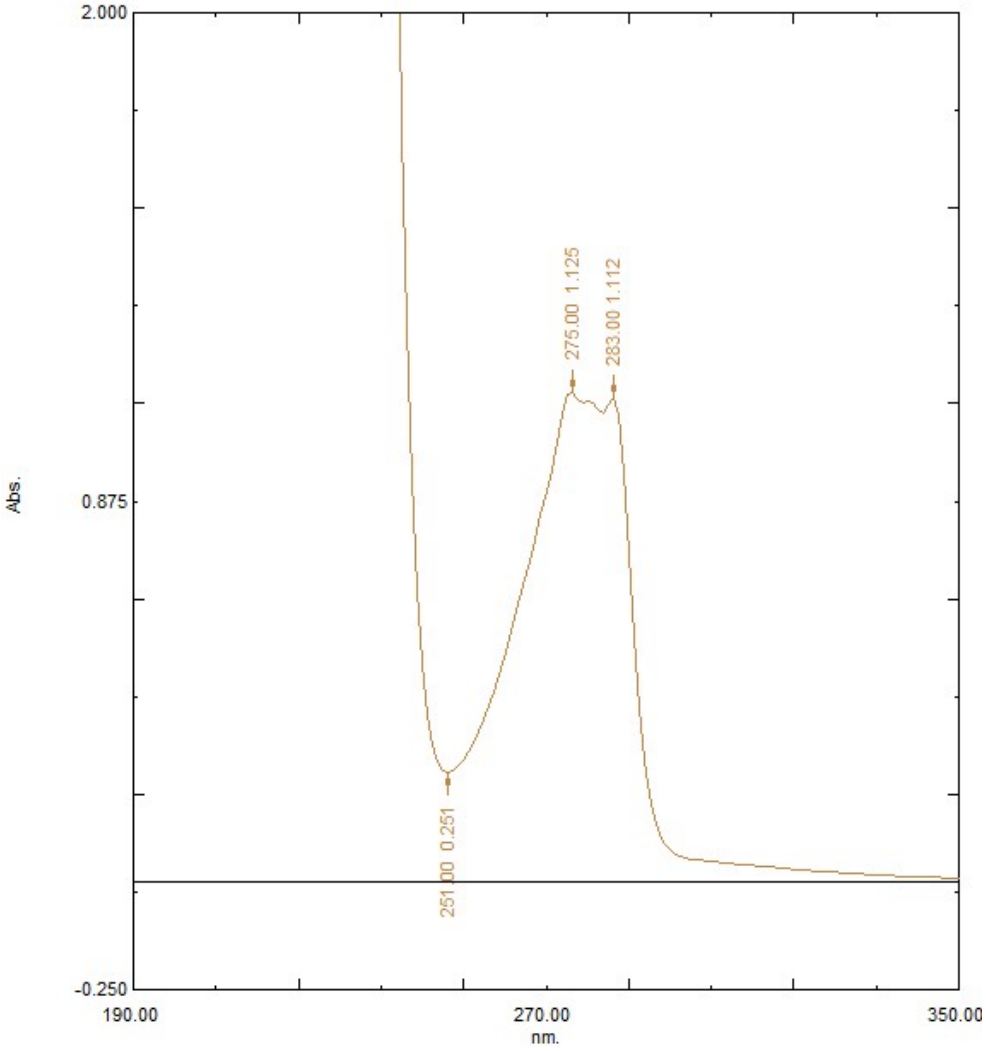
UV absorbance (MeCN, 1.0×10^{-3}M) **3h**



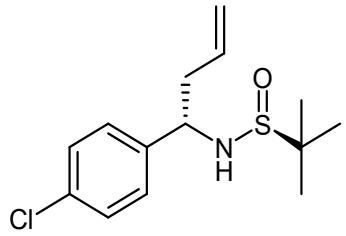


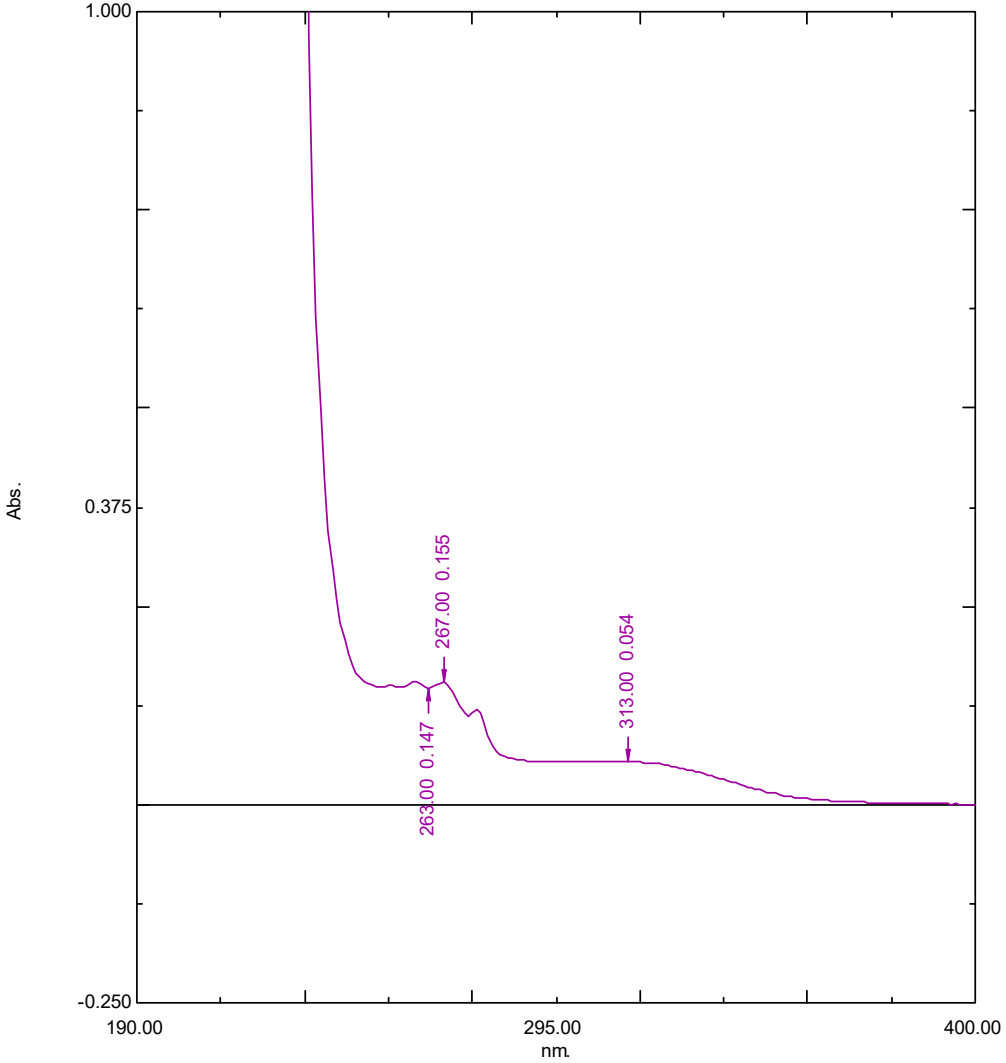
UV absorbance (MeCN, 1.0×10^{-3}M) **3i**



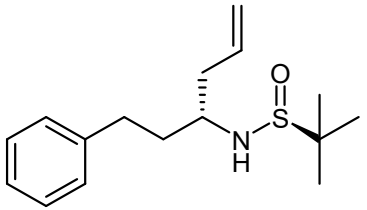


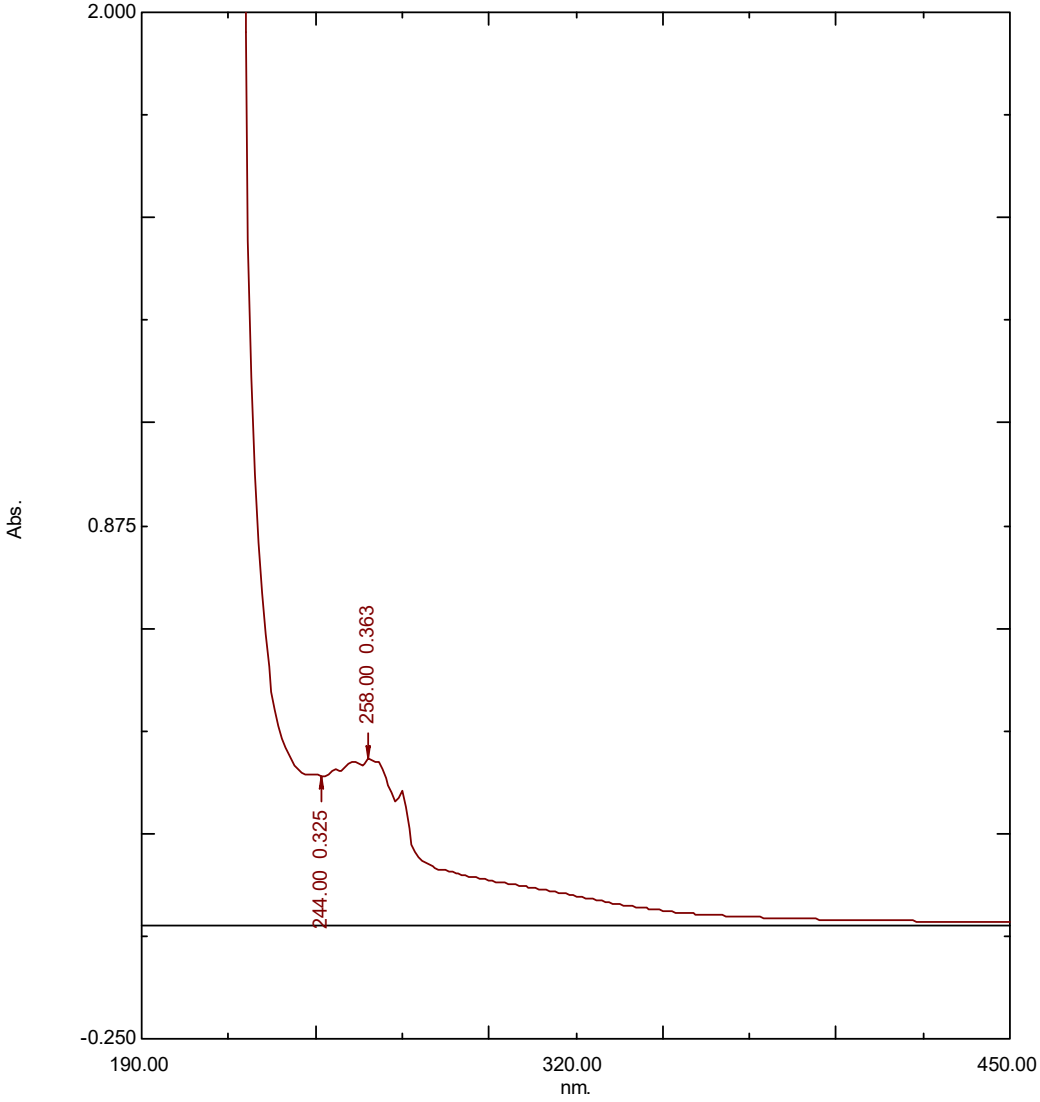
UV absorbance (MeCN, 1.0×10^{-3}M) **3j**



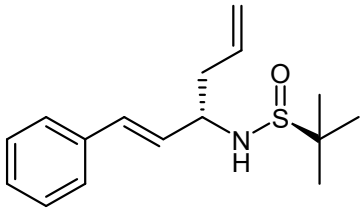


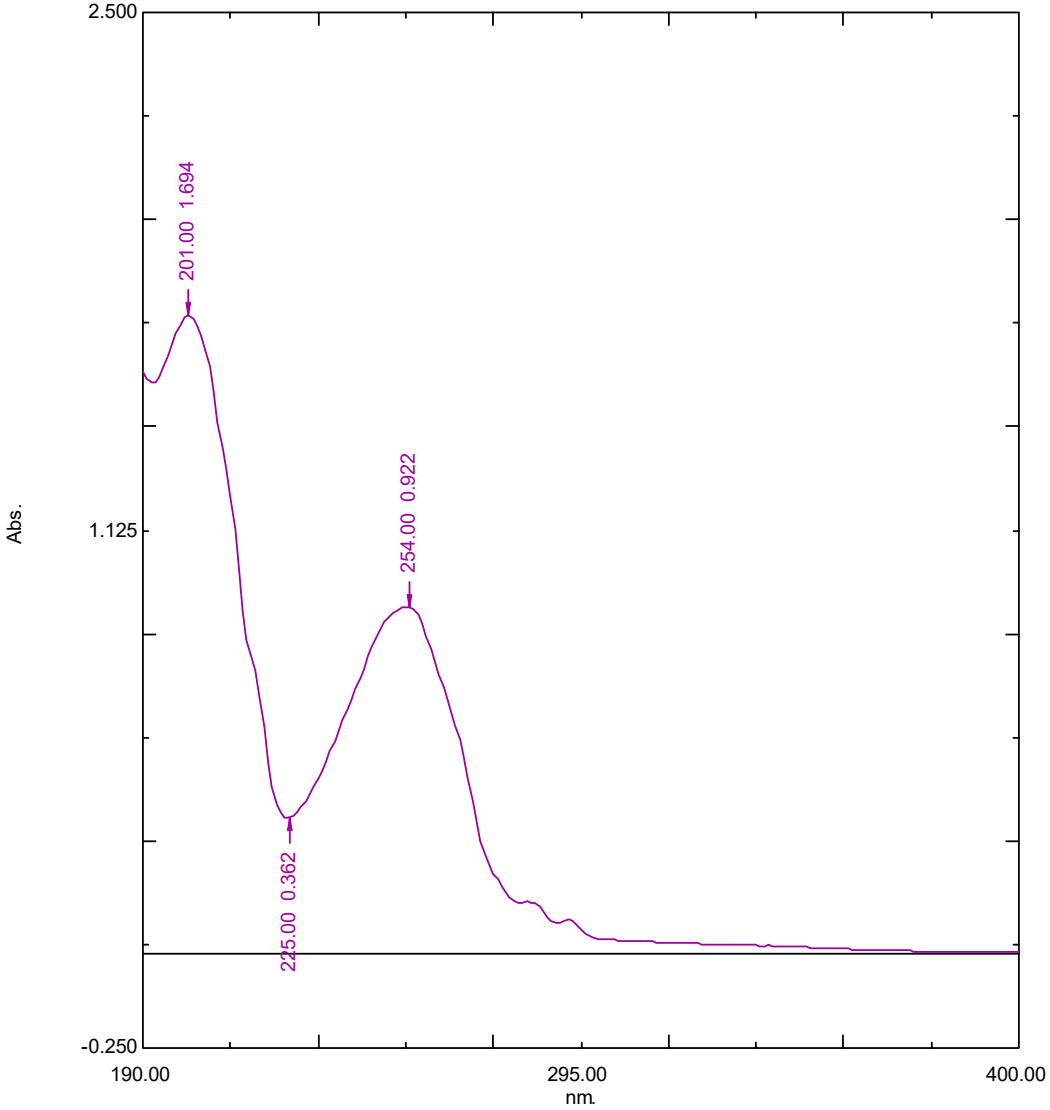
UV absorbance (MeCN, 1.0×10^{-3}M) **3k**



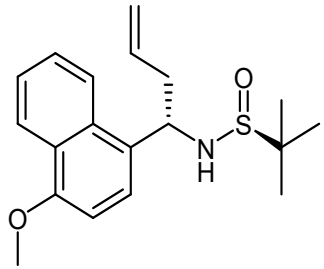


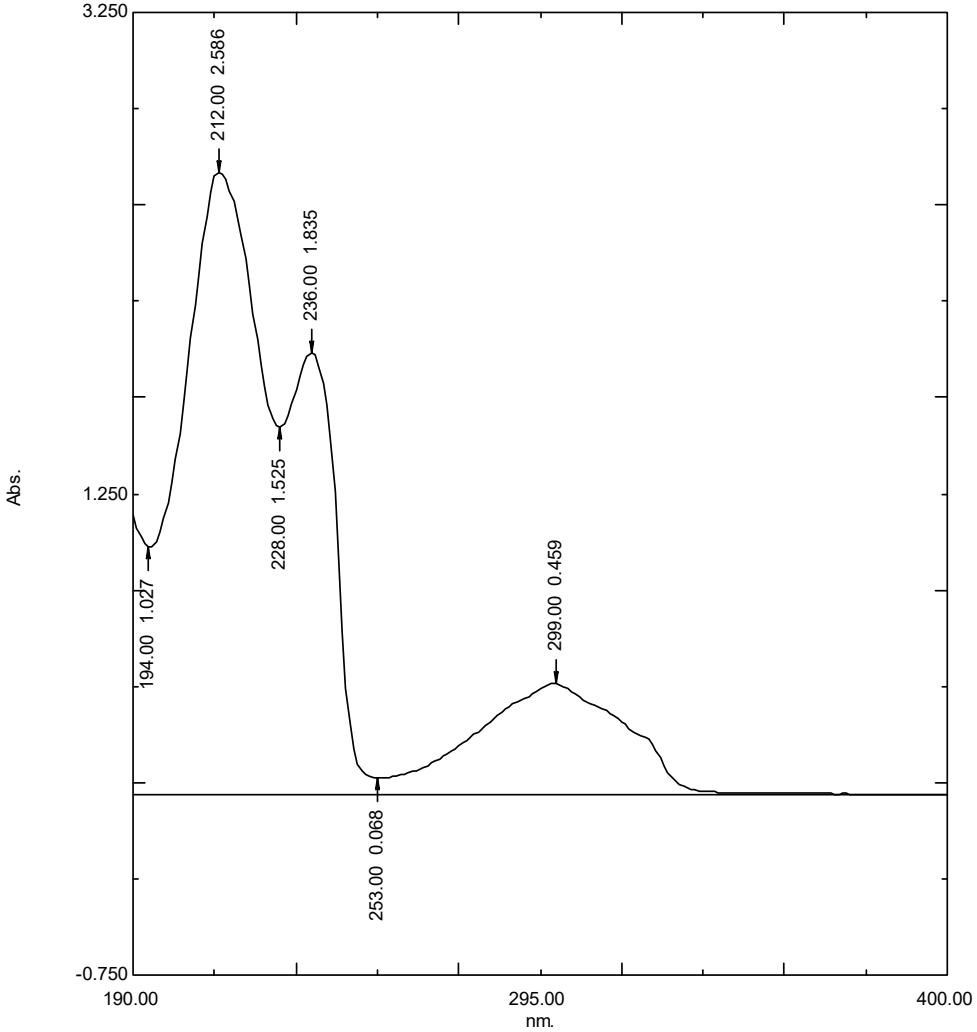
UV absorbance (MeCN, 1.0×10^{-4}M) **3l**



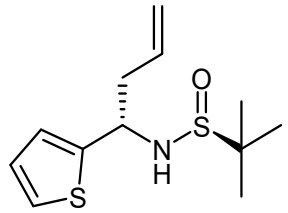


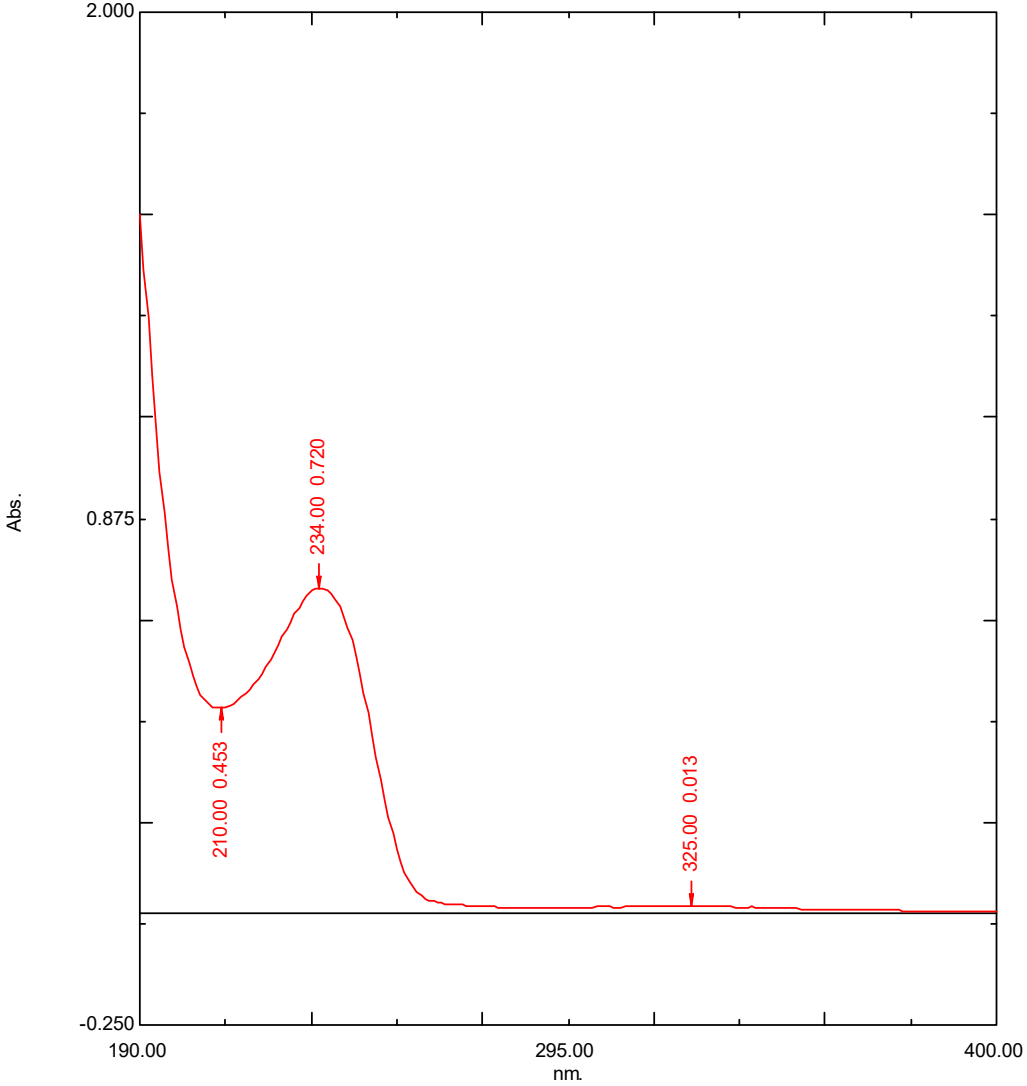
UV absorbance (MeCN, 1.0x10^{-4}M) **3m**



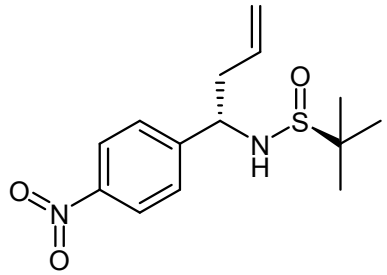


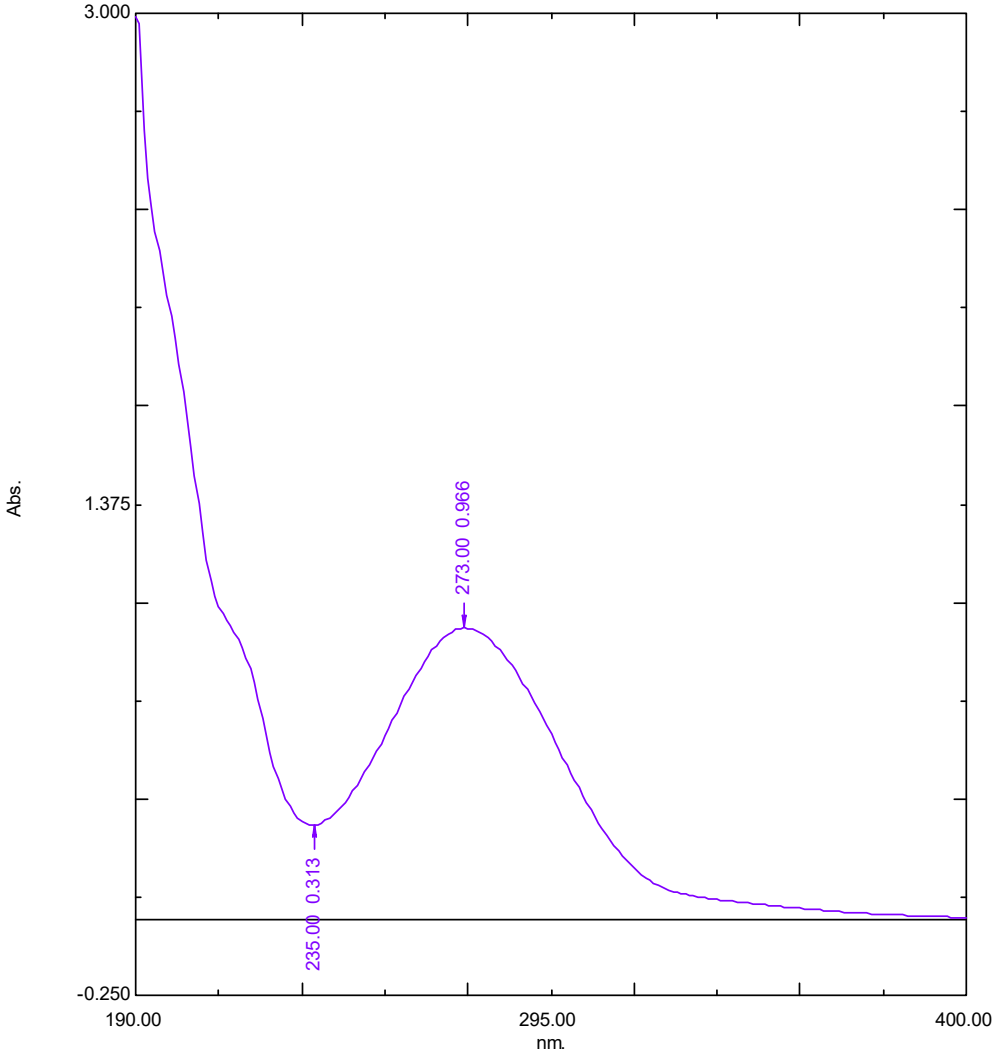
UV absorbance (MeCN, 1.0×10^{-4}M) **3s**



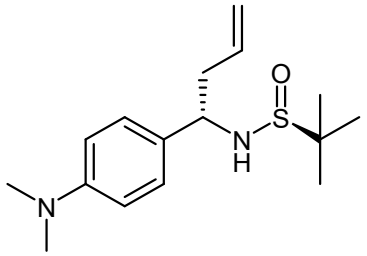


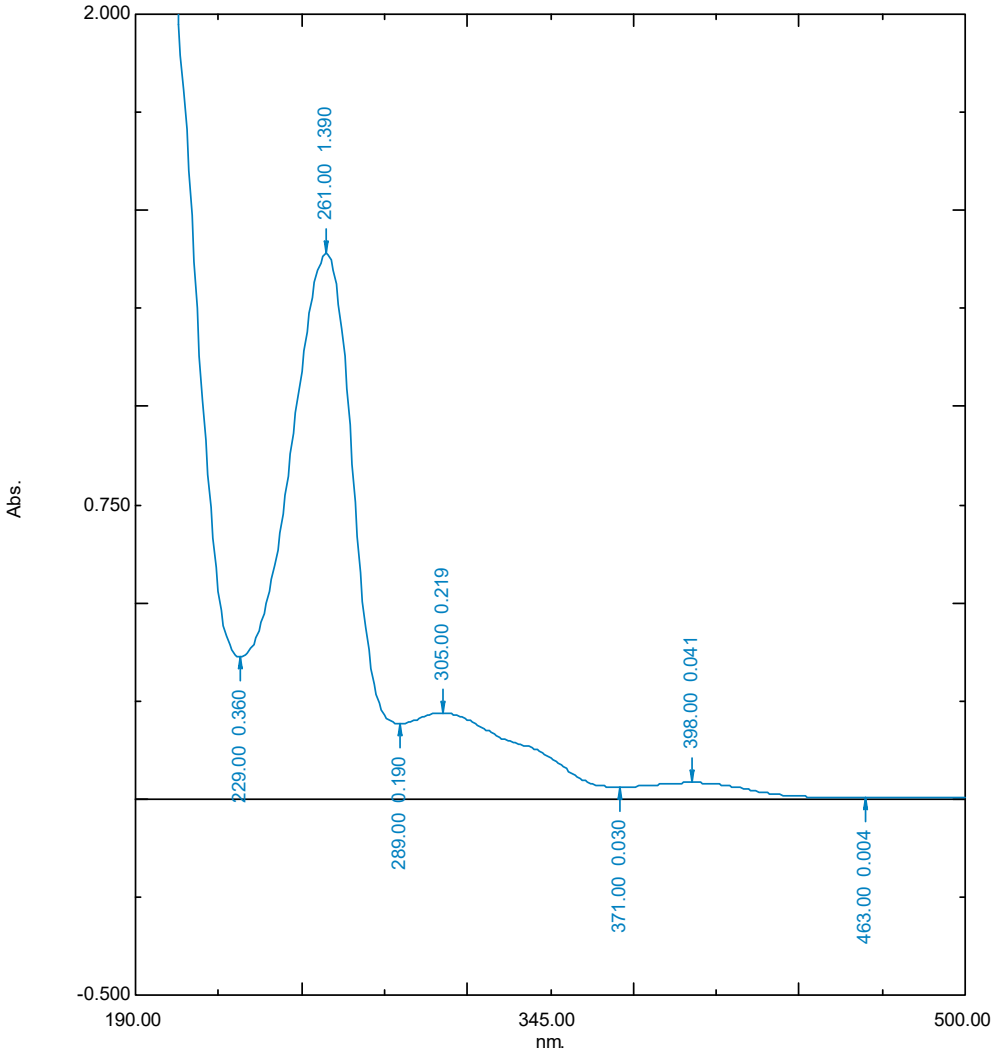
UV absorbance (MeCN, 1.0×10^{-4}M) **3o**



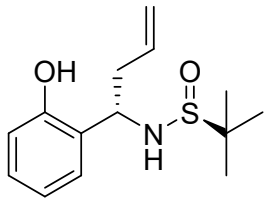


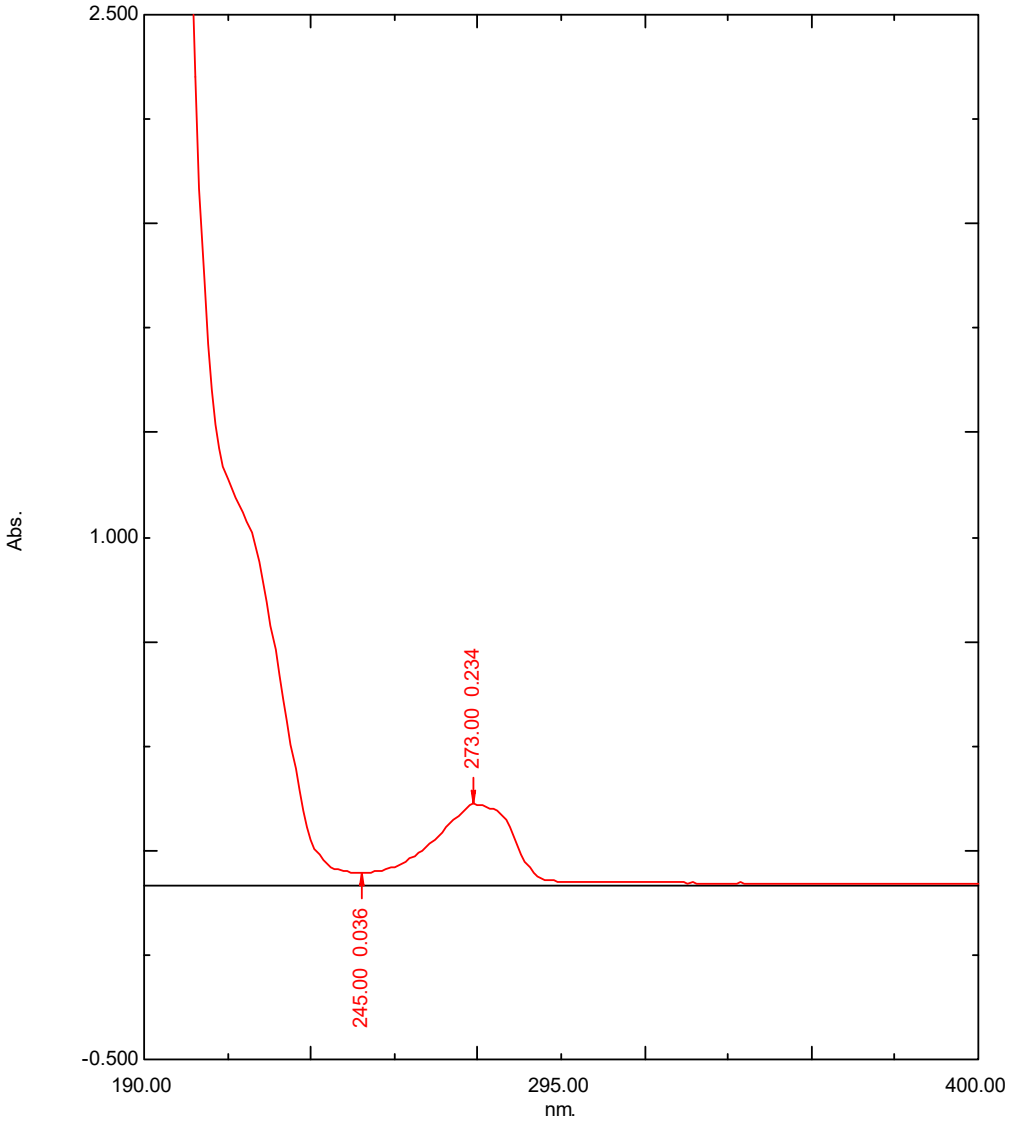
UV absorbance (MeCN, 1.0×10^{-4}M) **3p**



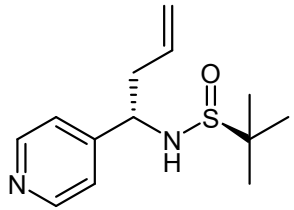


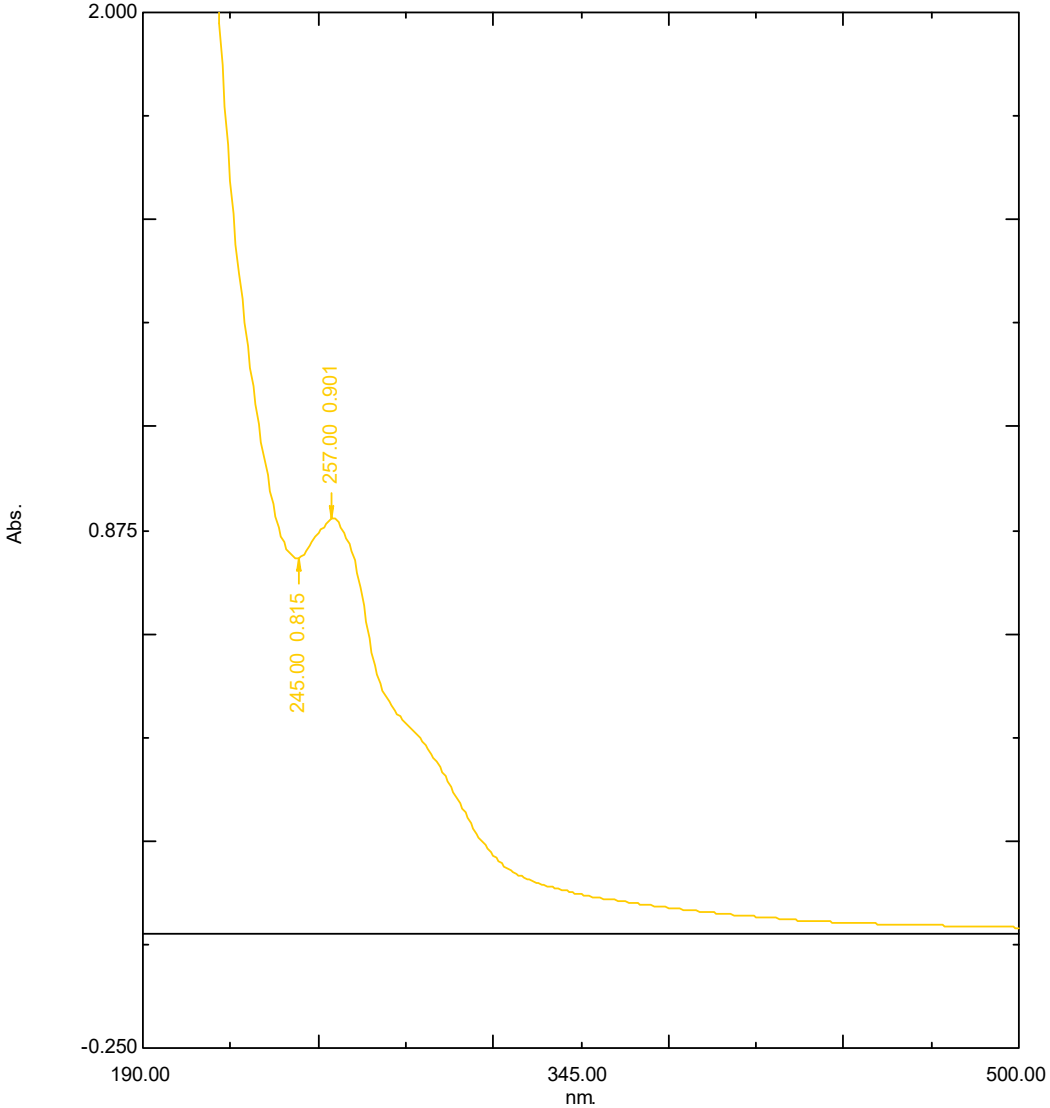
UV absorbance (MeCN, 1.0×10^{-4}M) **3q**



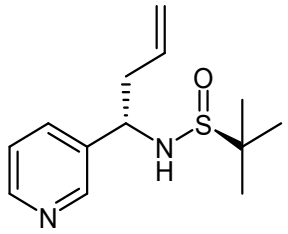


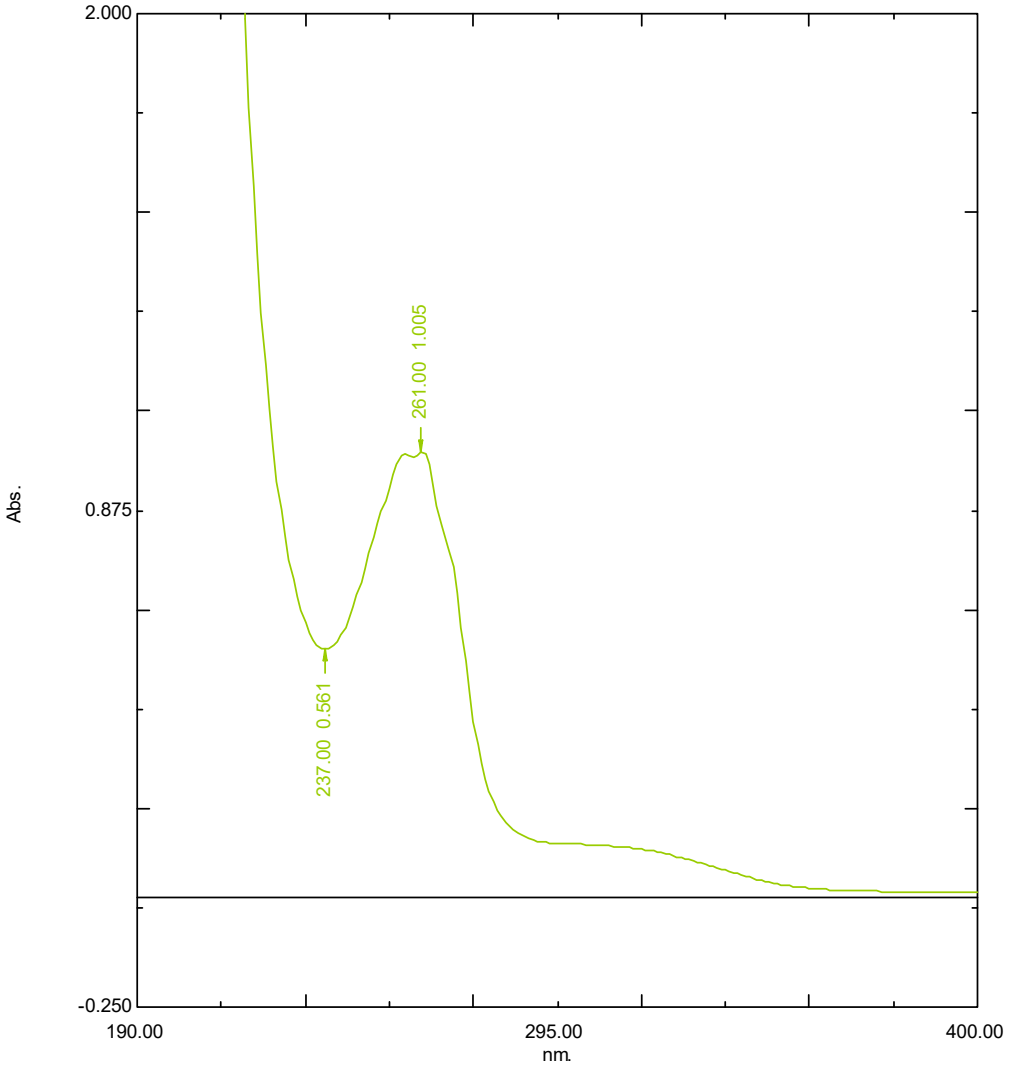
UV absorbance (MeCN, 1.0×10^{-3}M) **3r**



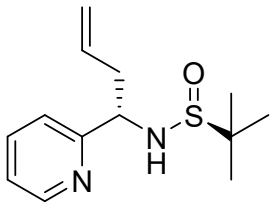


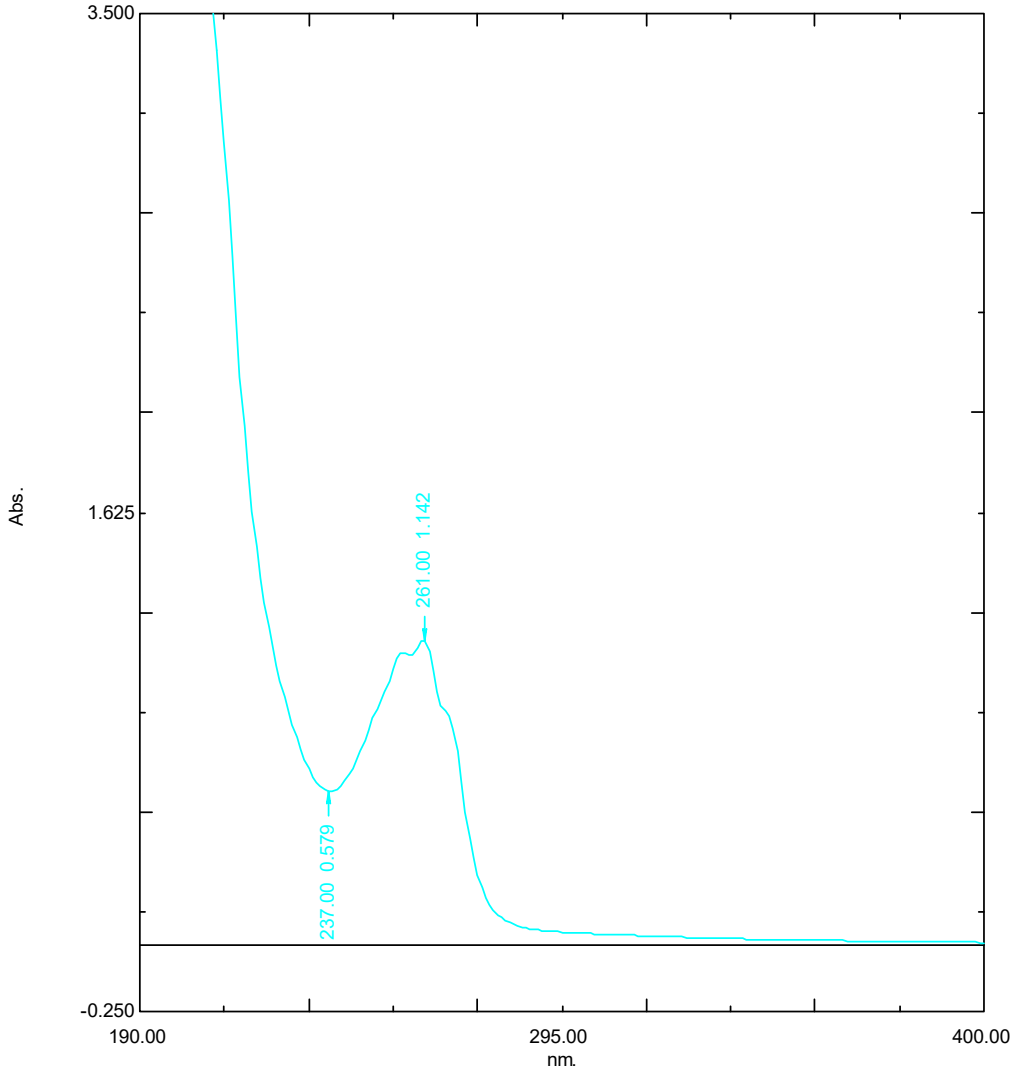
UV absorbance (MeCN, 1.0x10^{-3}M) **3s**



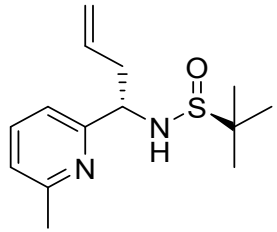


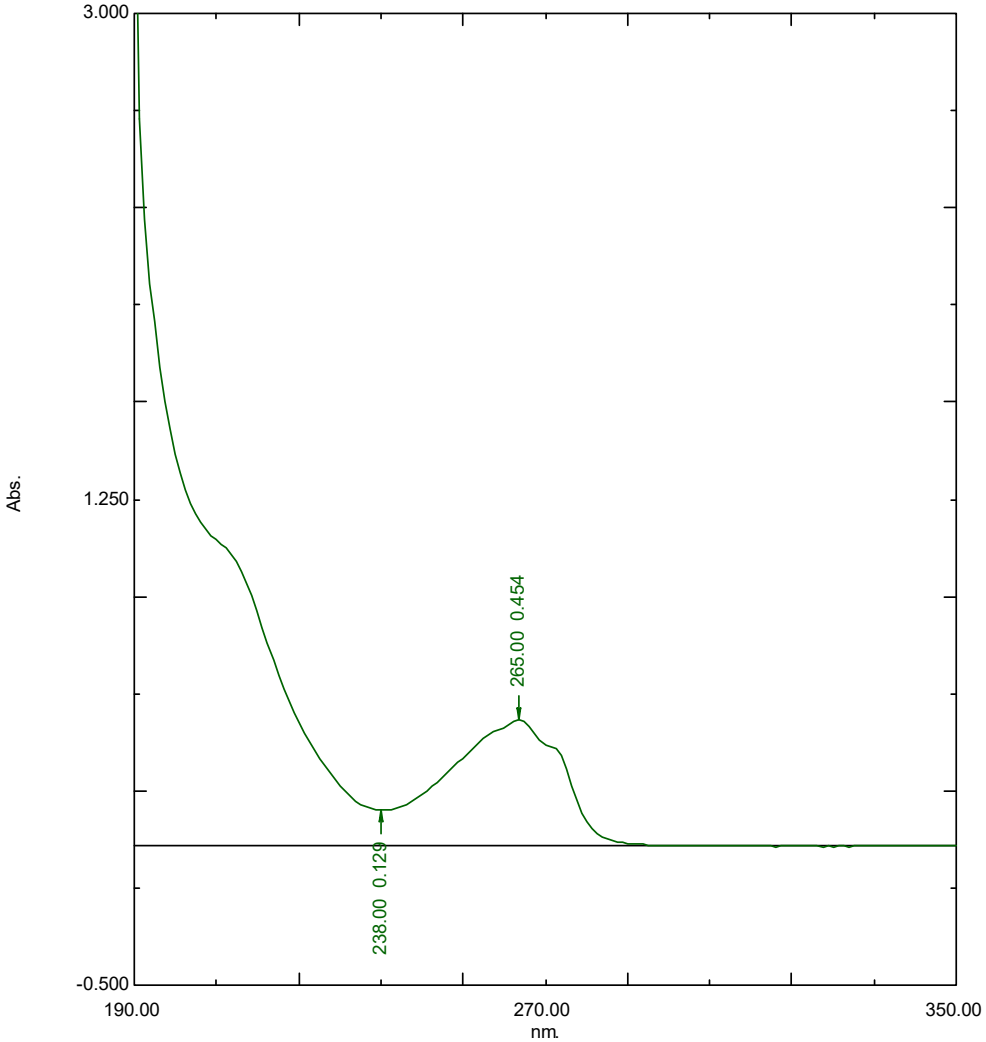
UV absorbance (MeCN, 1.0×10^{-3}M) **3t**



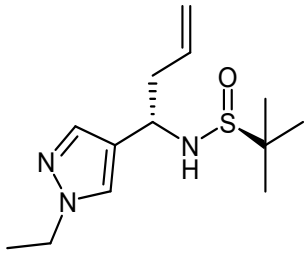


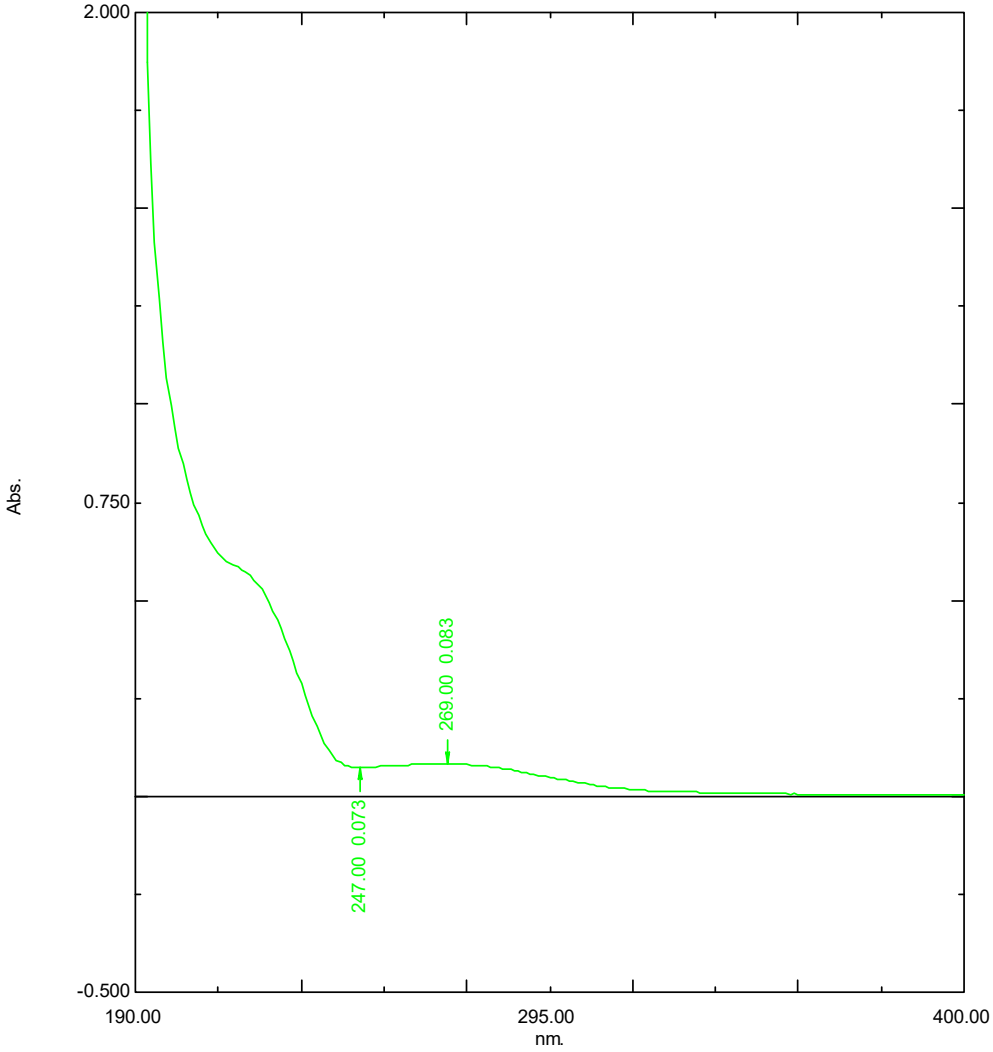
UV absorbance (MeCN, 1.0×10^{-4}M) **3u**



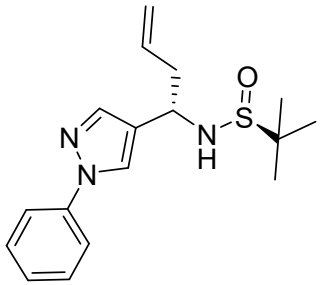


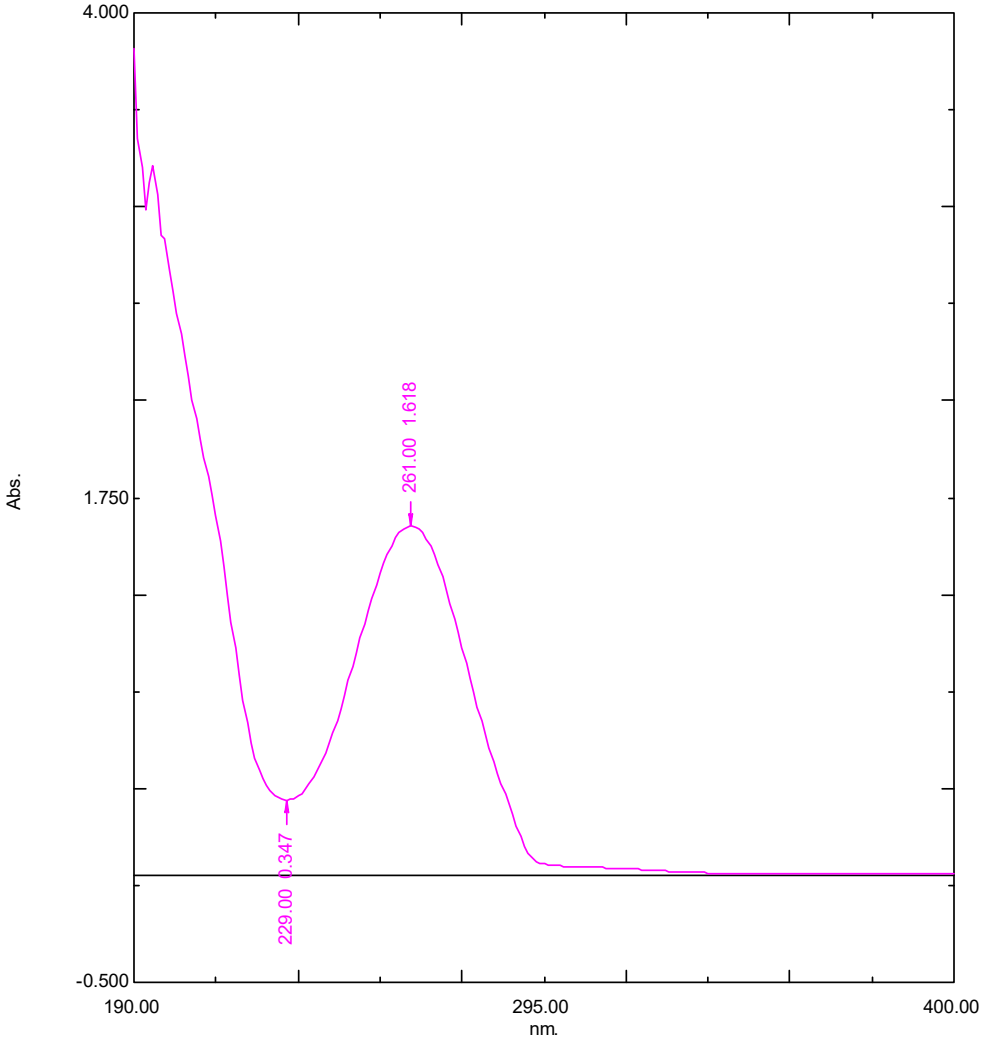
UV absorbance (MeCN, 1.0×10^{-4}M) **3v**



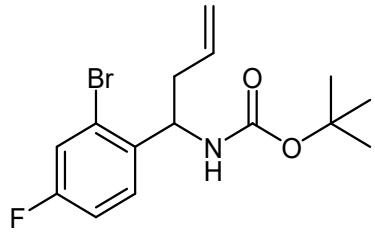


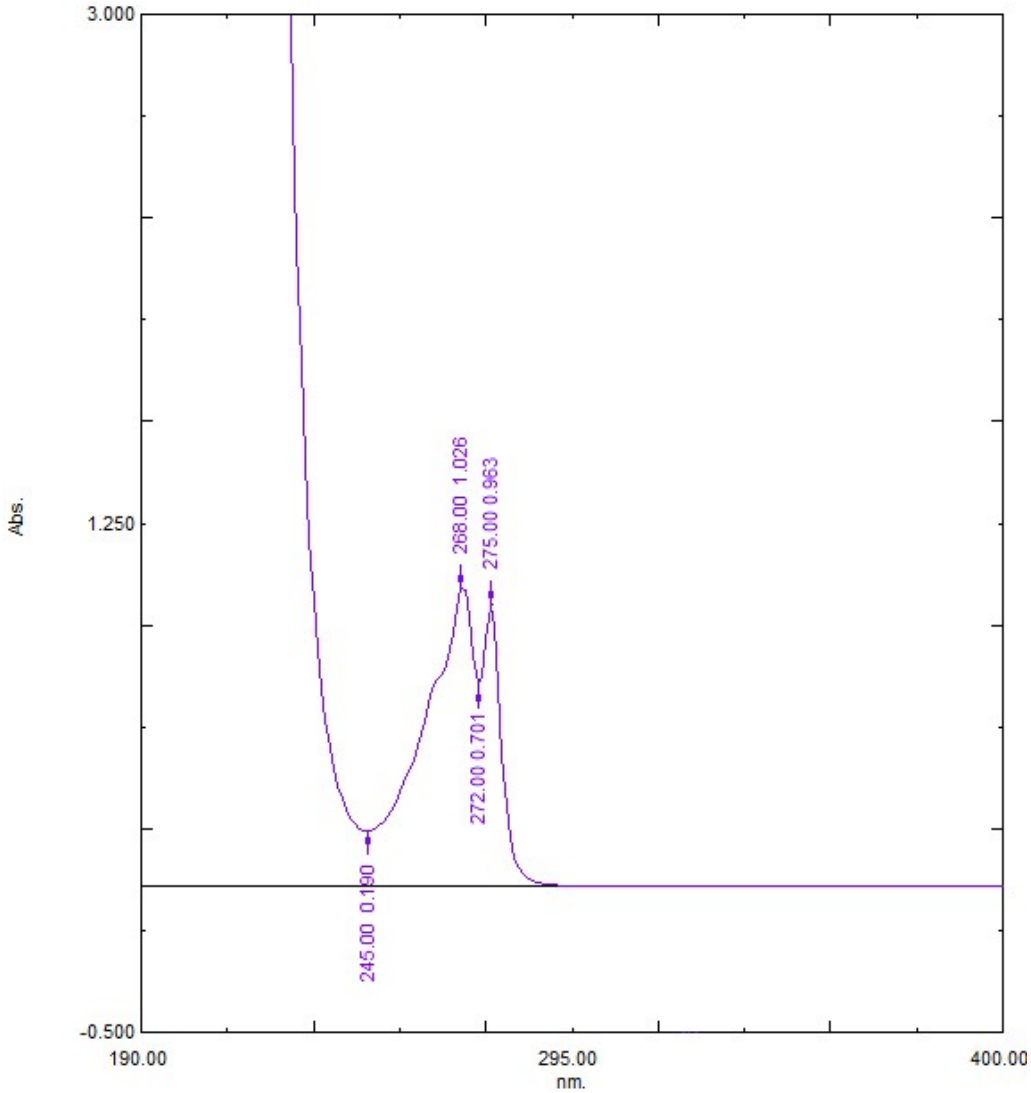
UV absorbance (MeCN, 1.0x10^{-4}M) **3w**



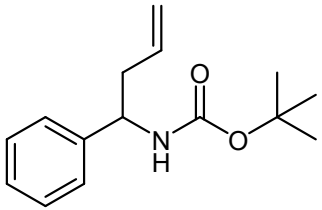


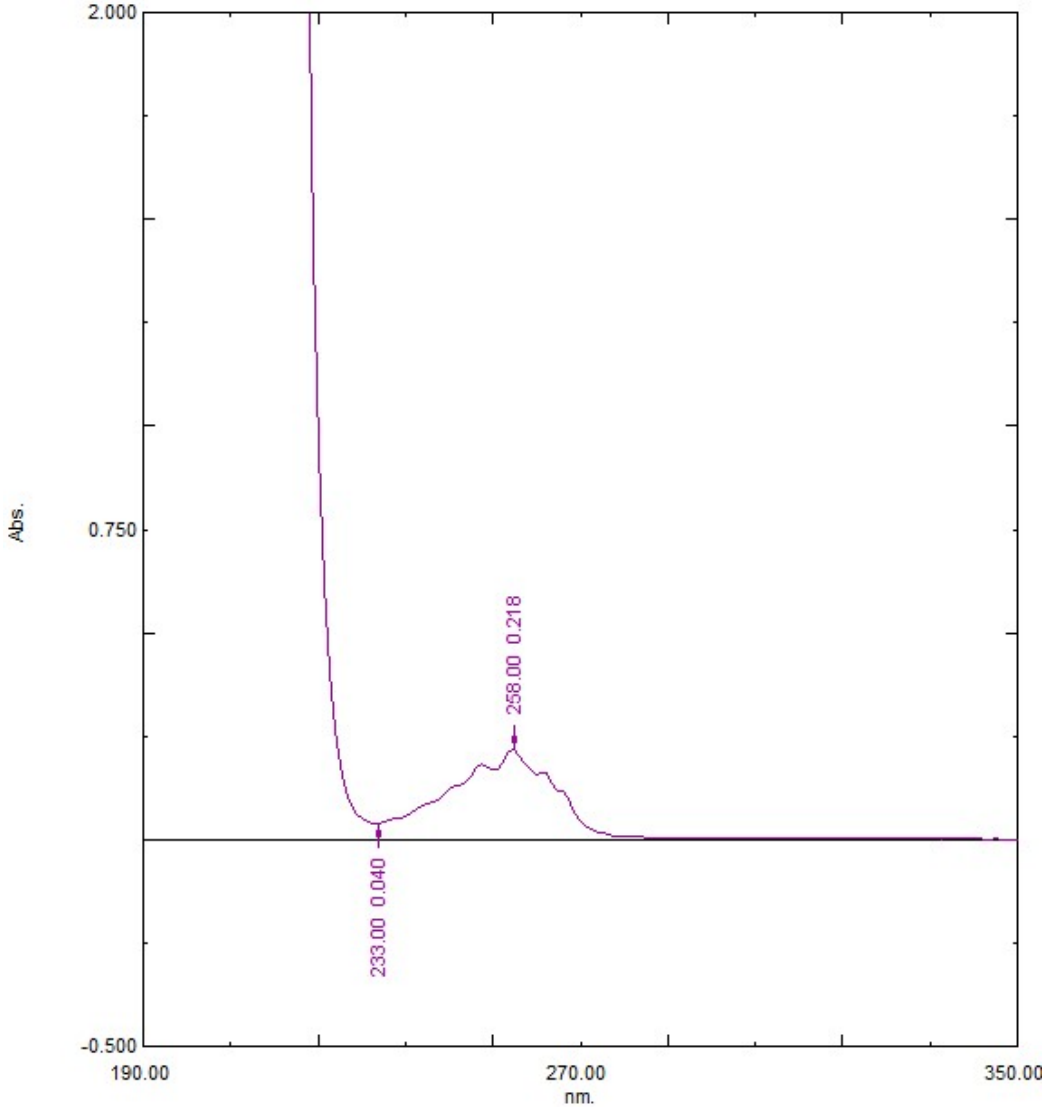
UV absorbance (MeCN, 1.0×10^{-3}M) **6a**



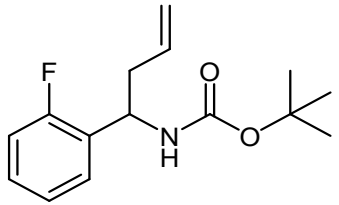


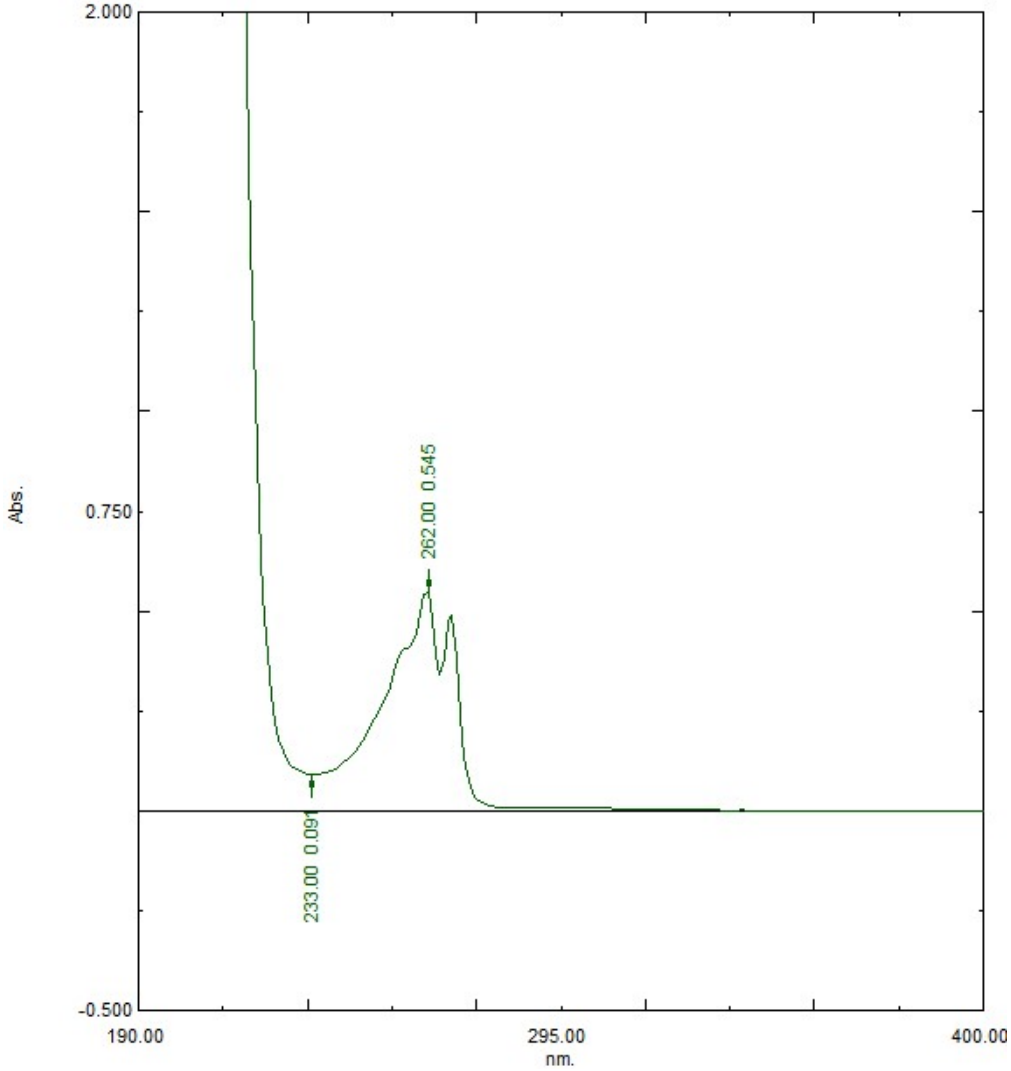
UV absorbance (MeCN, 1.0×10^{-3}M) **6b**



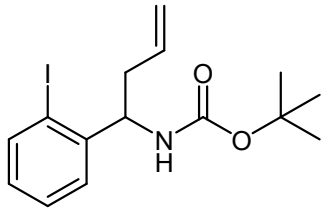


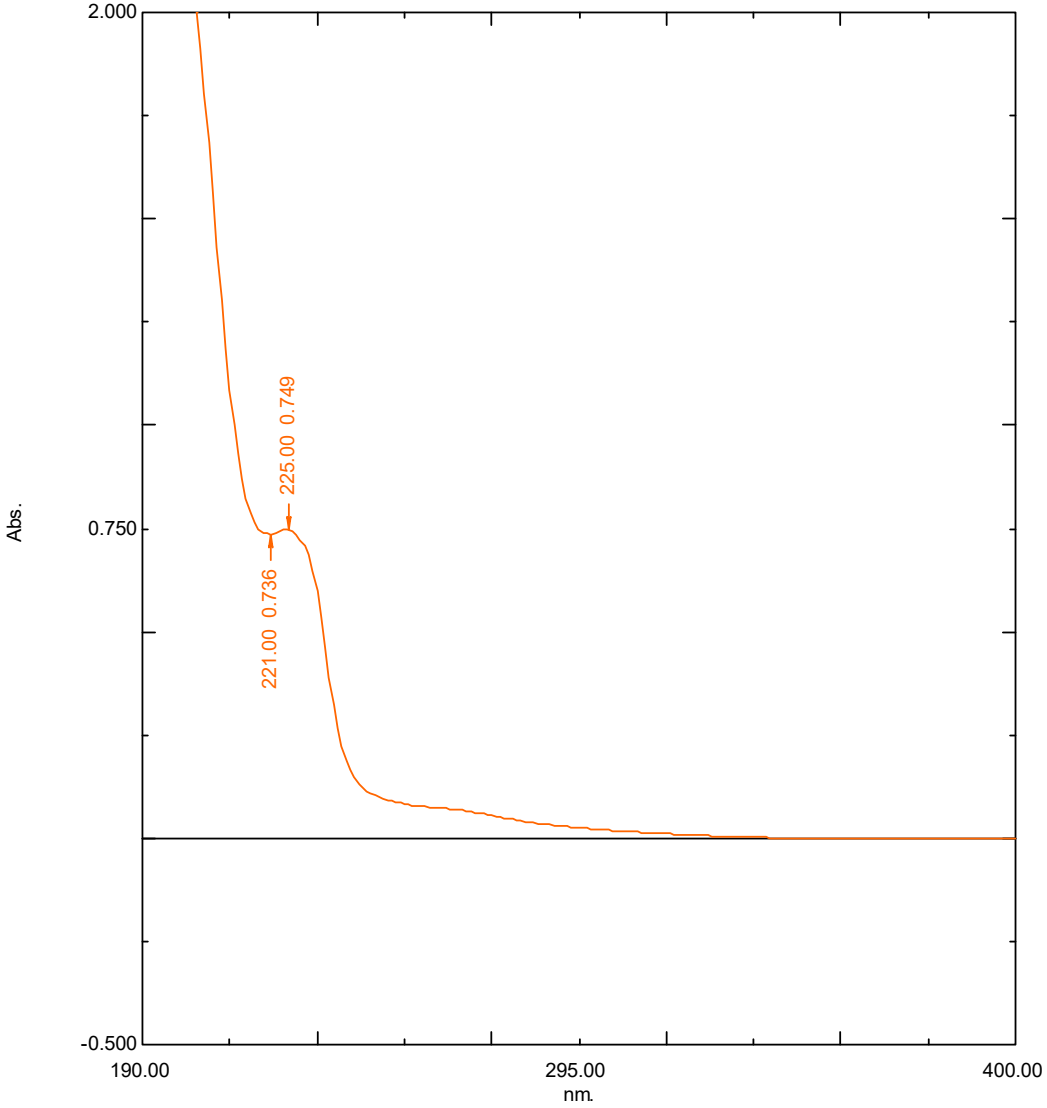
UV absorbance (MeCN, 1.0×10^{-3}M) **6c**



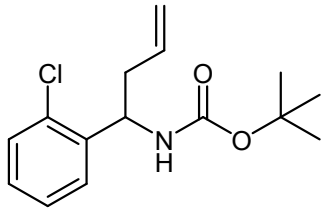


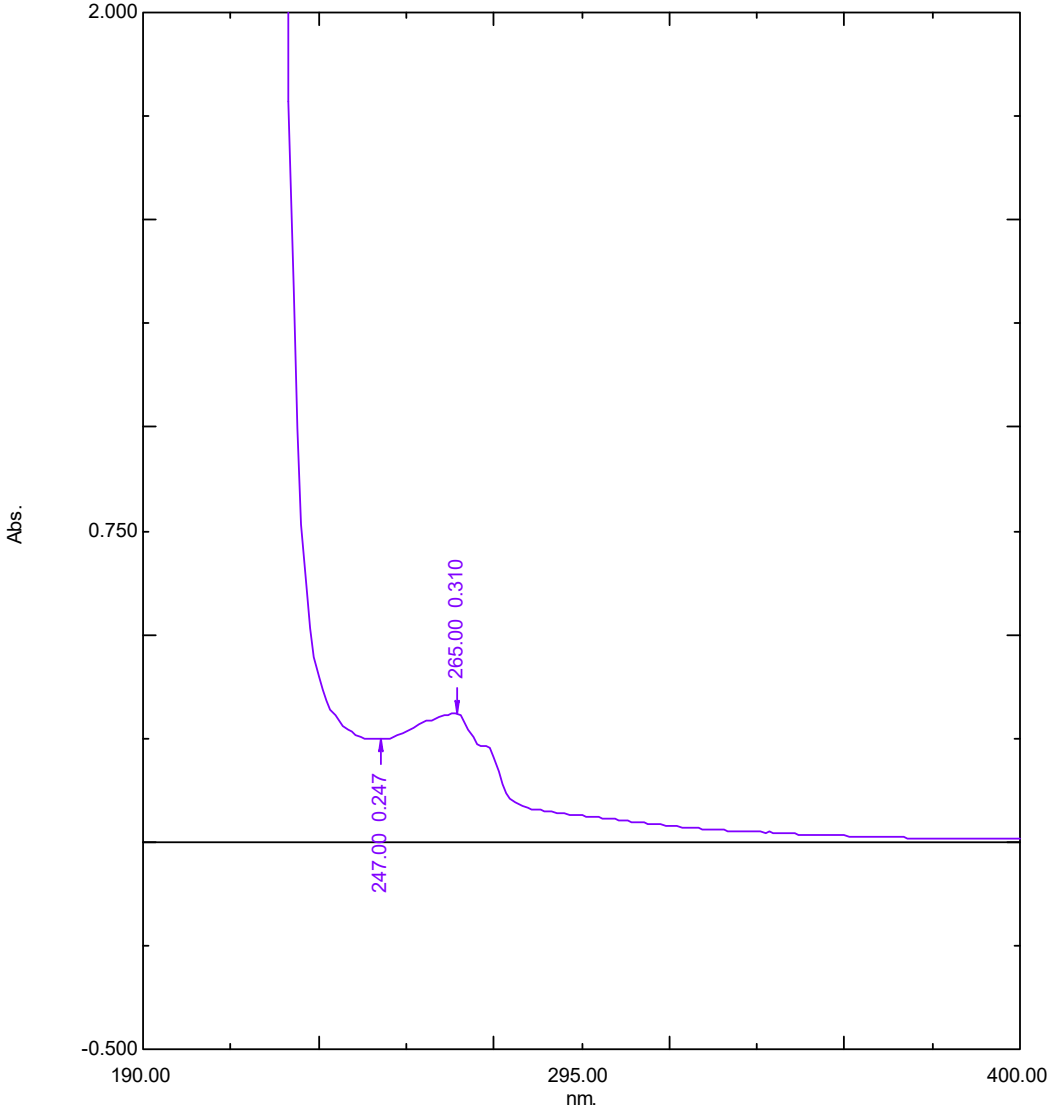
UV absorbance (MeCN, 1.0×10^{-4}M) **6d**



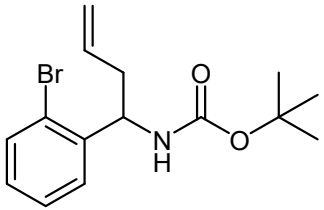


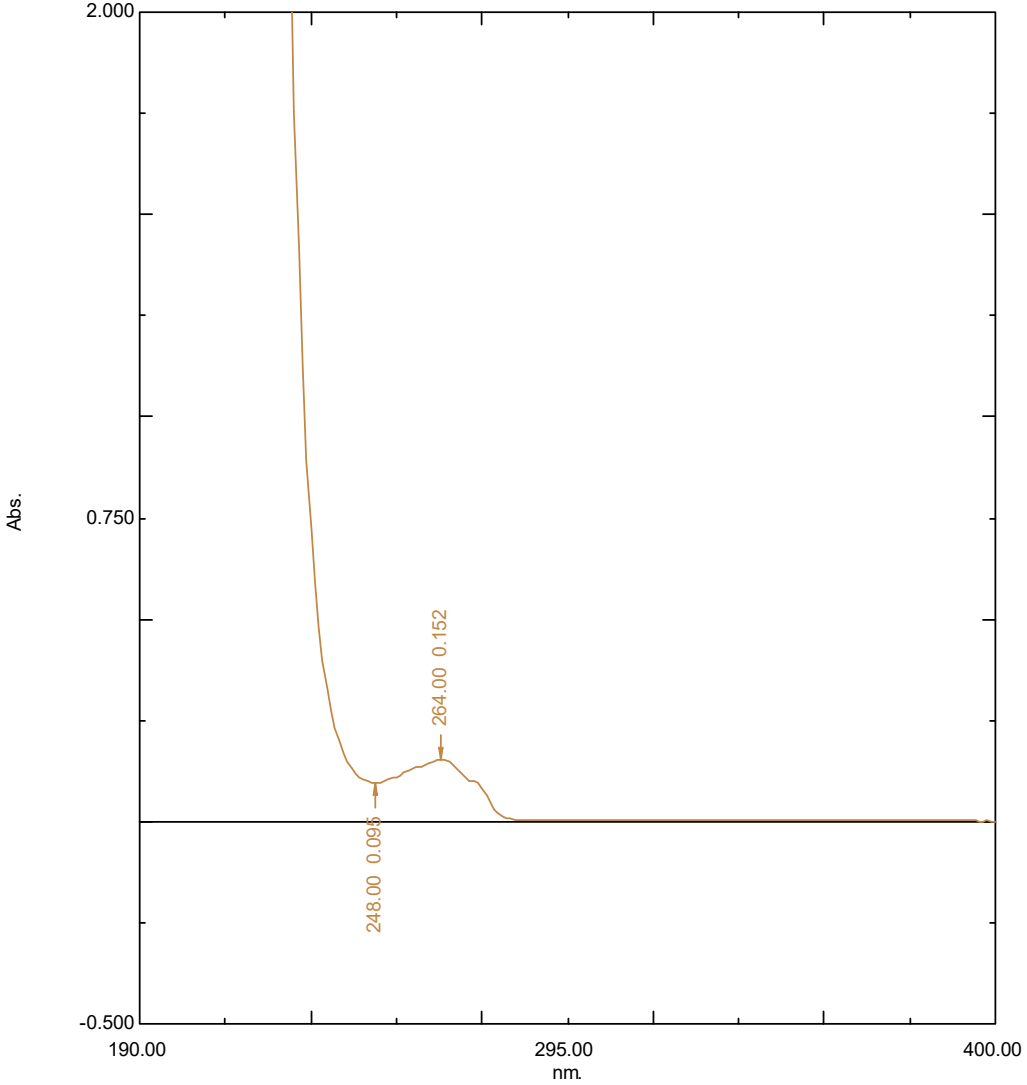
UV absorbance (MeCN, 1.0×10^{-3}M) **6e**



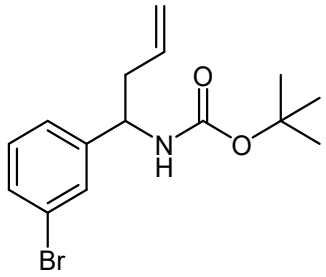


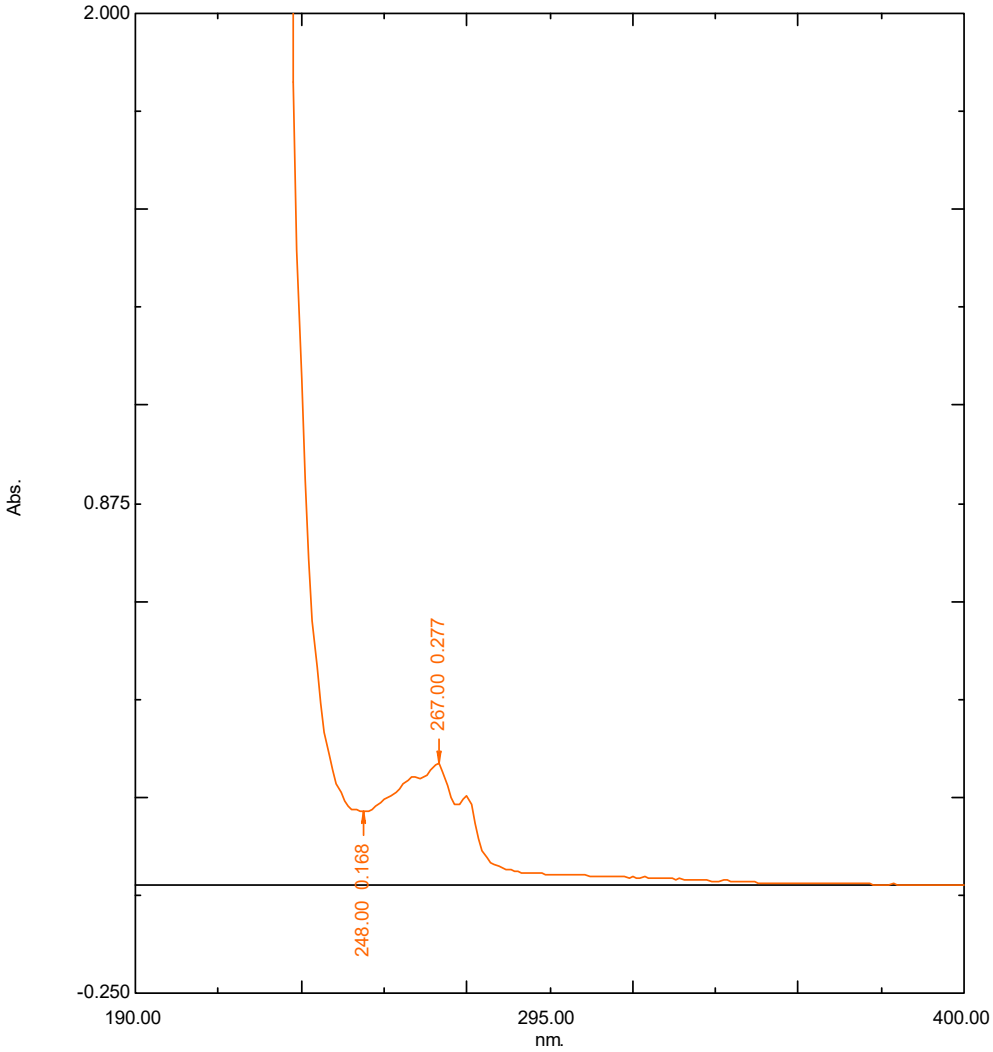
UV absorbance (MeCN, 1.0×10^{-3}M) **6f**



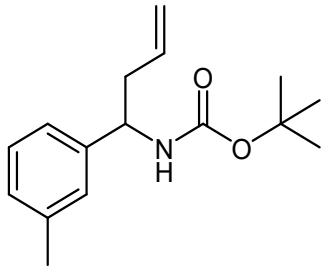


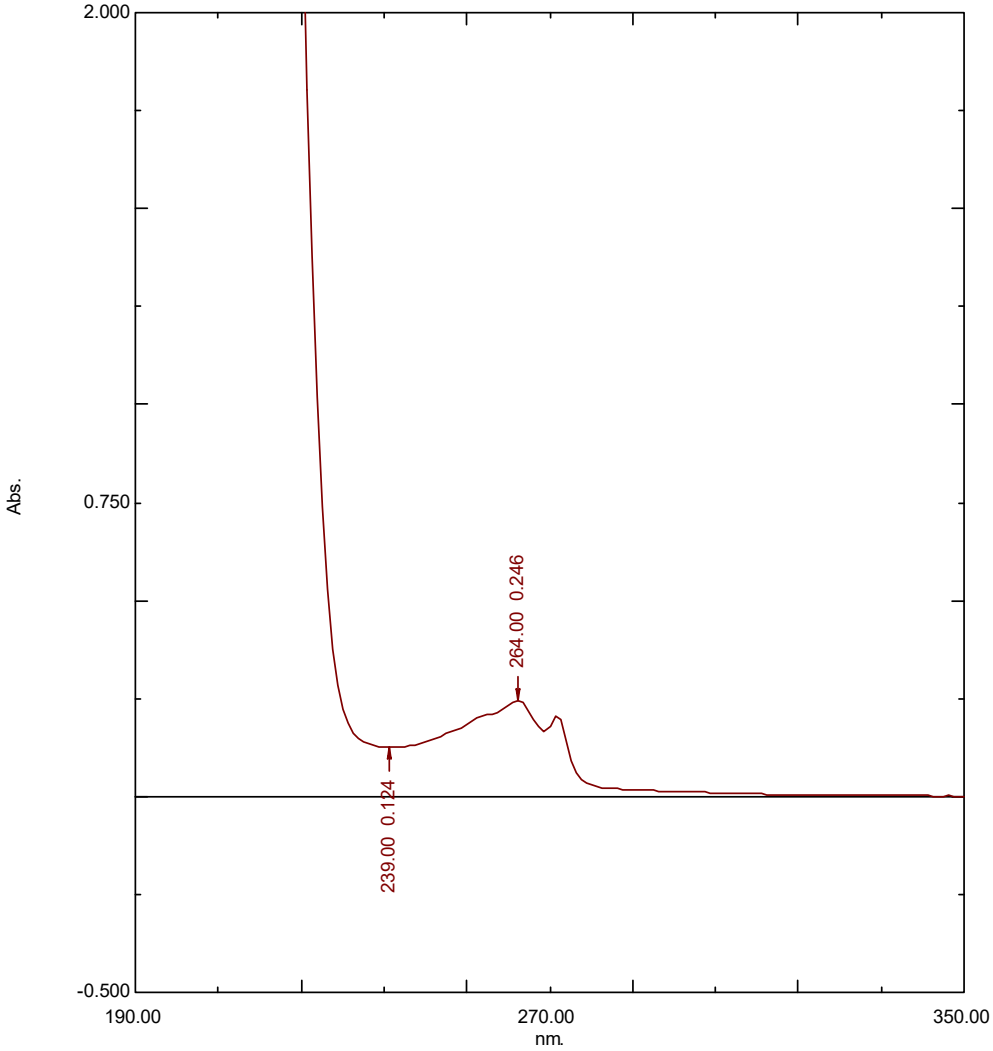
UV absorbance (MeCN, 1.0×10^{-3}M) **6g**



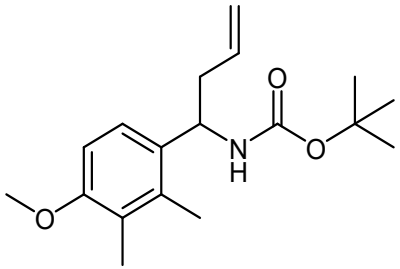


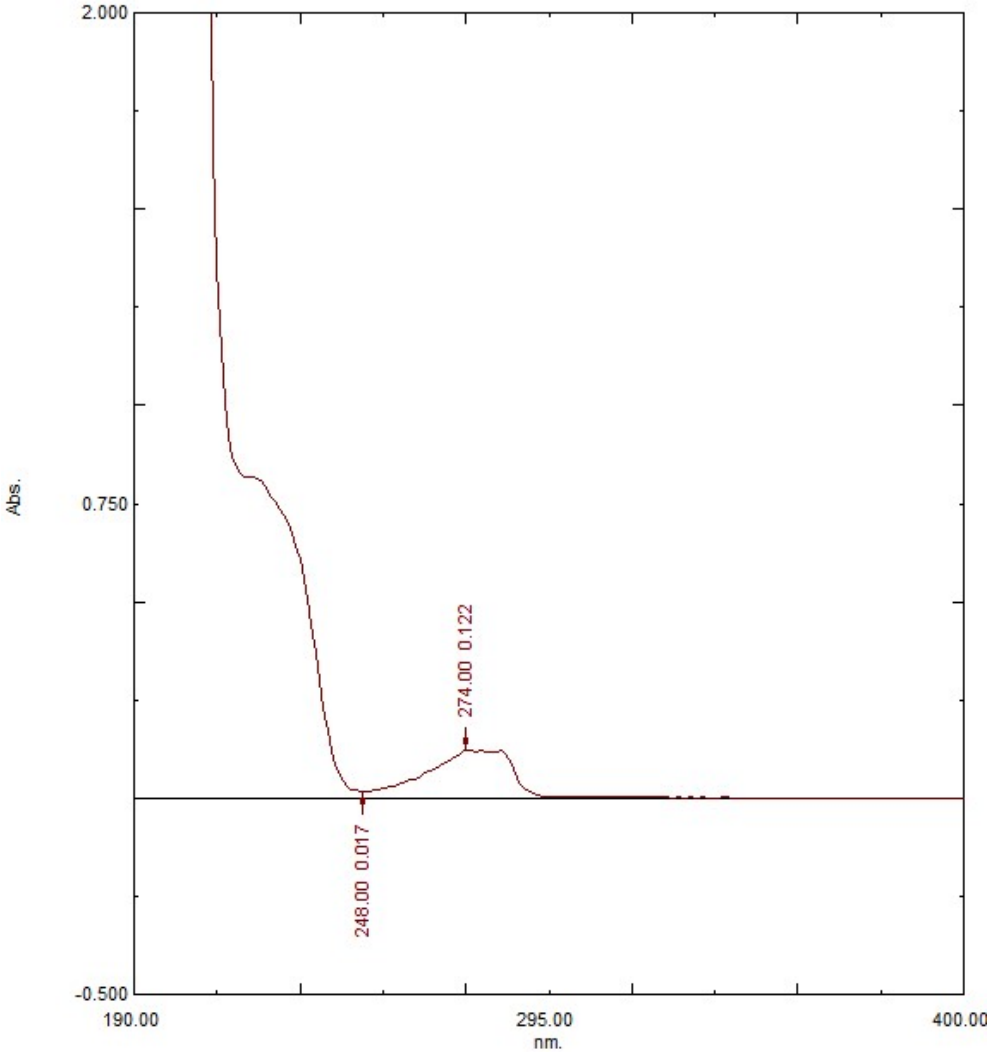
UV absorbance (MeCN, 1.0×10^{-3}M) **6h**



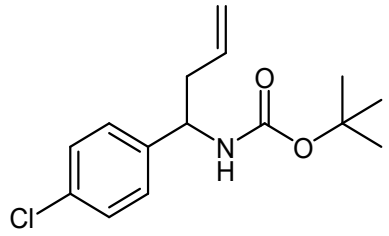


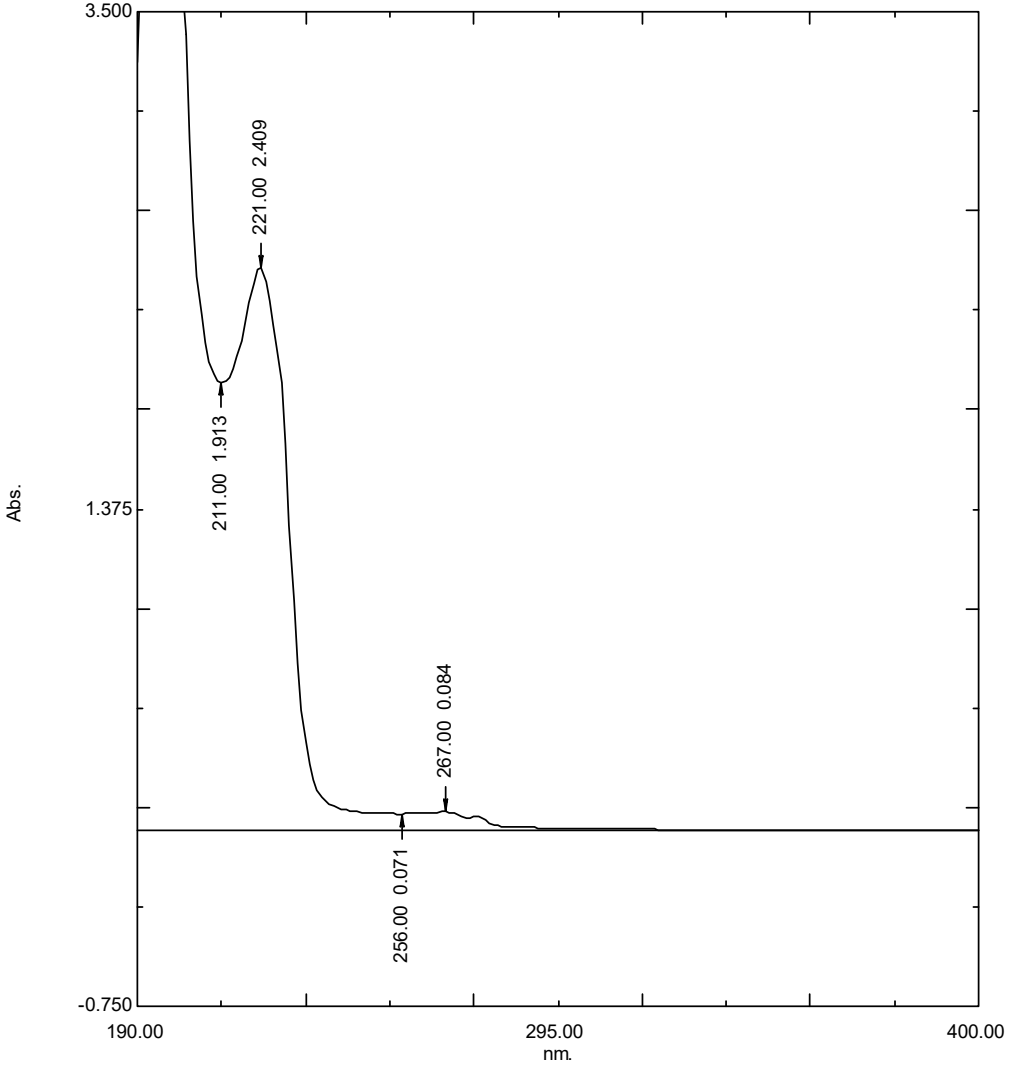
UV absorbance (MeCN, 1.0×10^{-4}M) **6i**



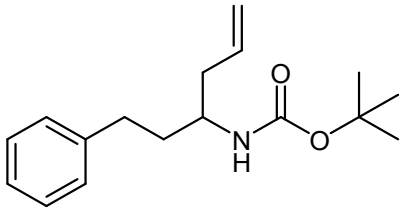


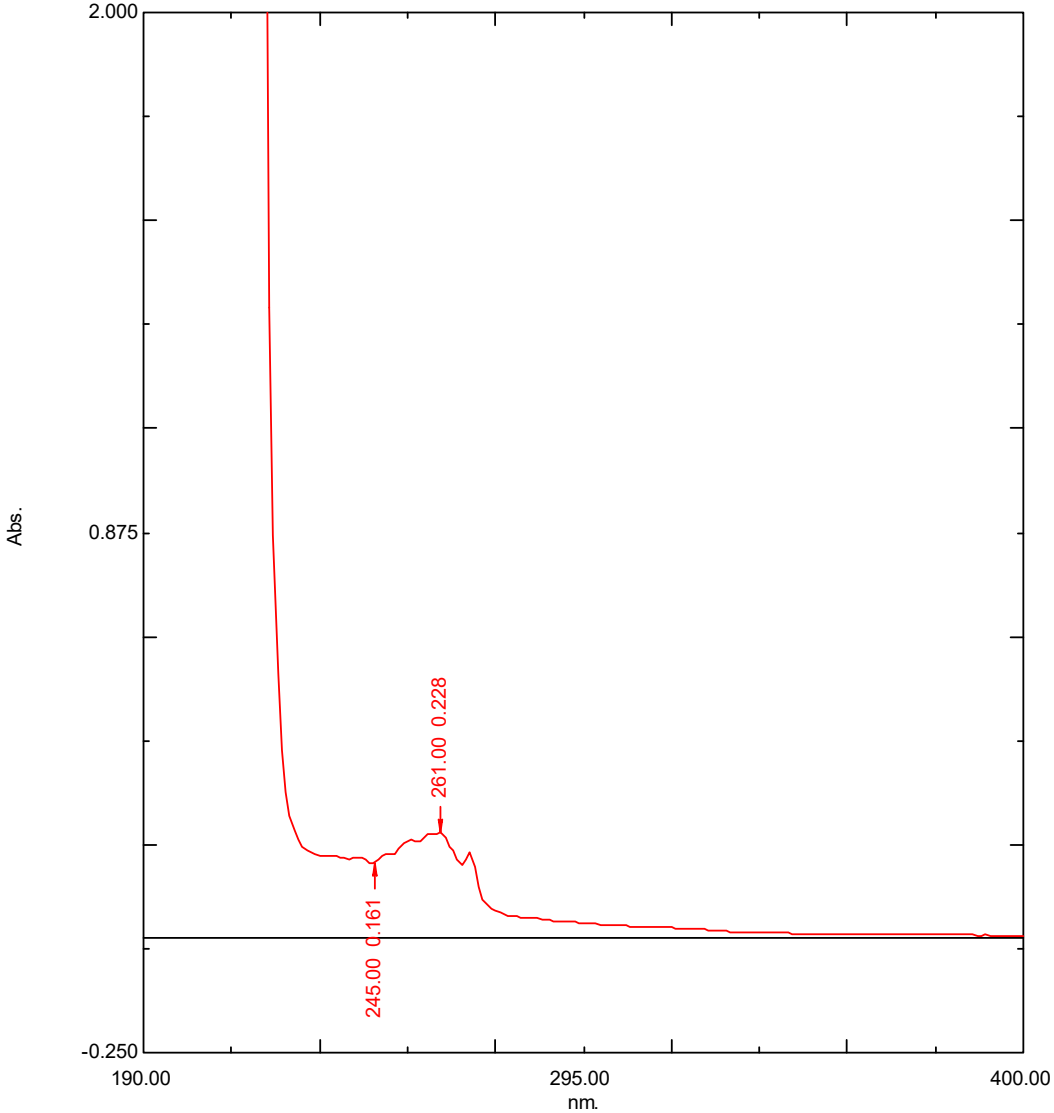
UV absorbance (MeCN, 1.0×10^{-3}M) **6j**



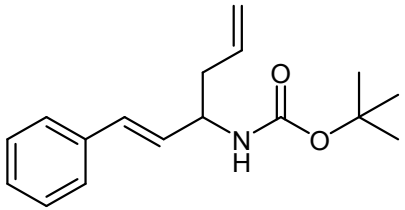


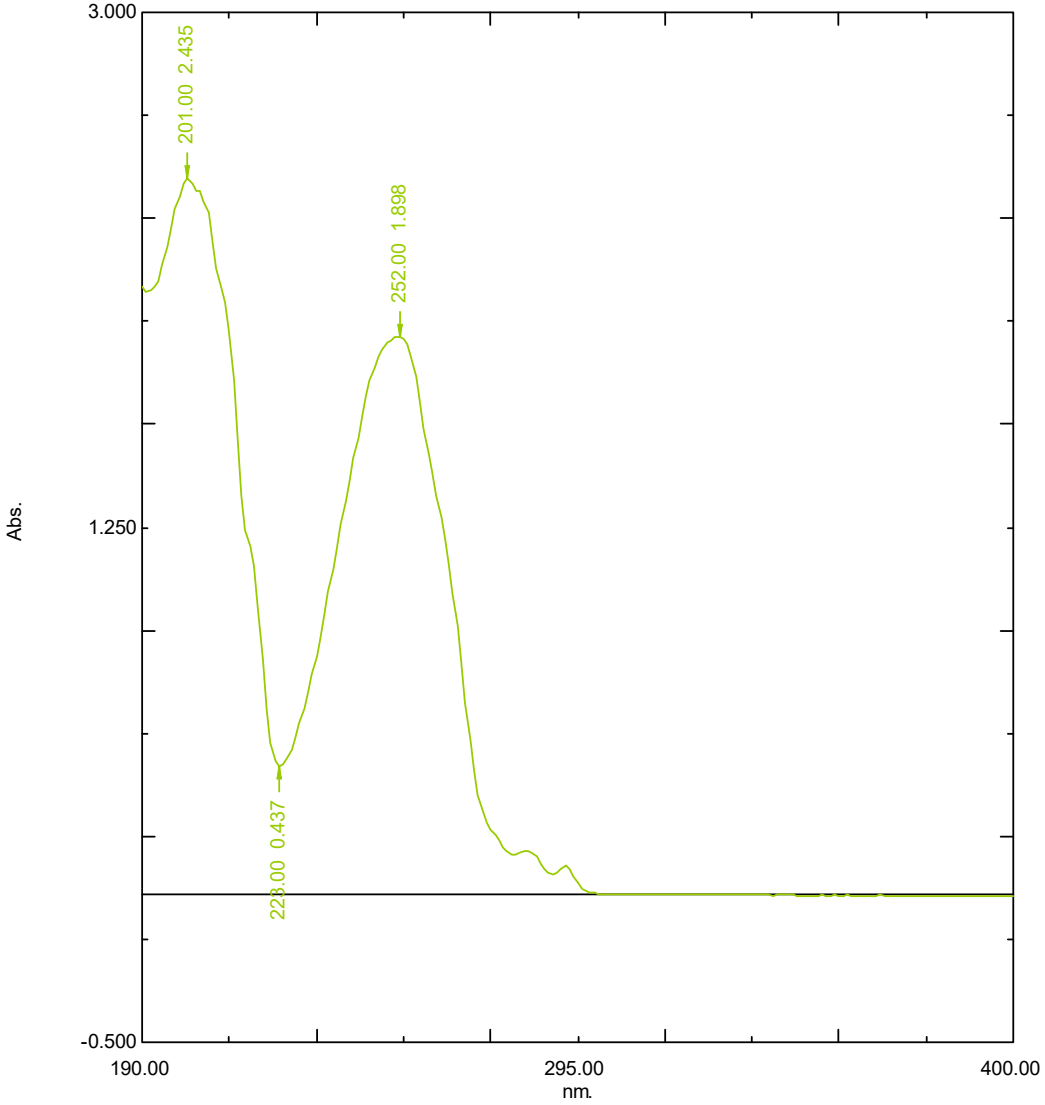
UV absorbance (MeCN, 1.0×10^{-3}M) **6k**



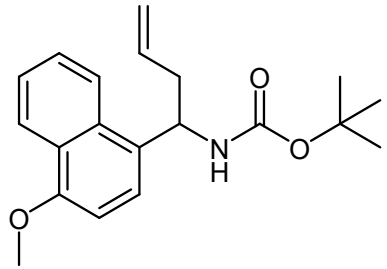


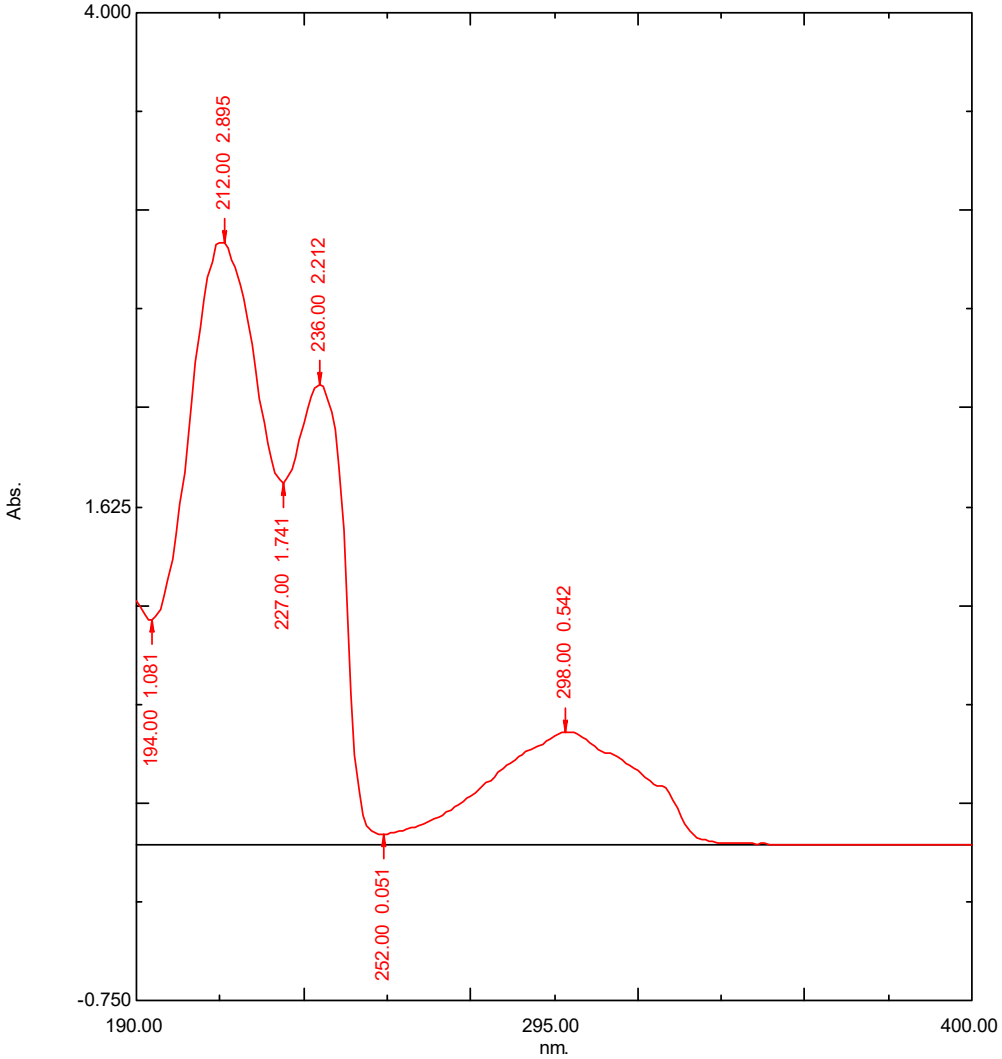
UV absorbance (MeCN, 1.0×10^{-4}M) **6l**



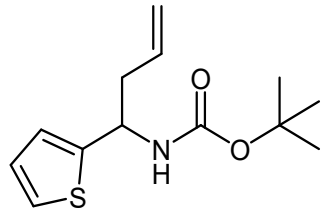


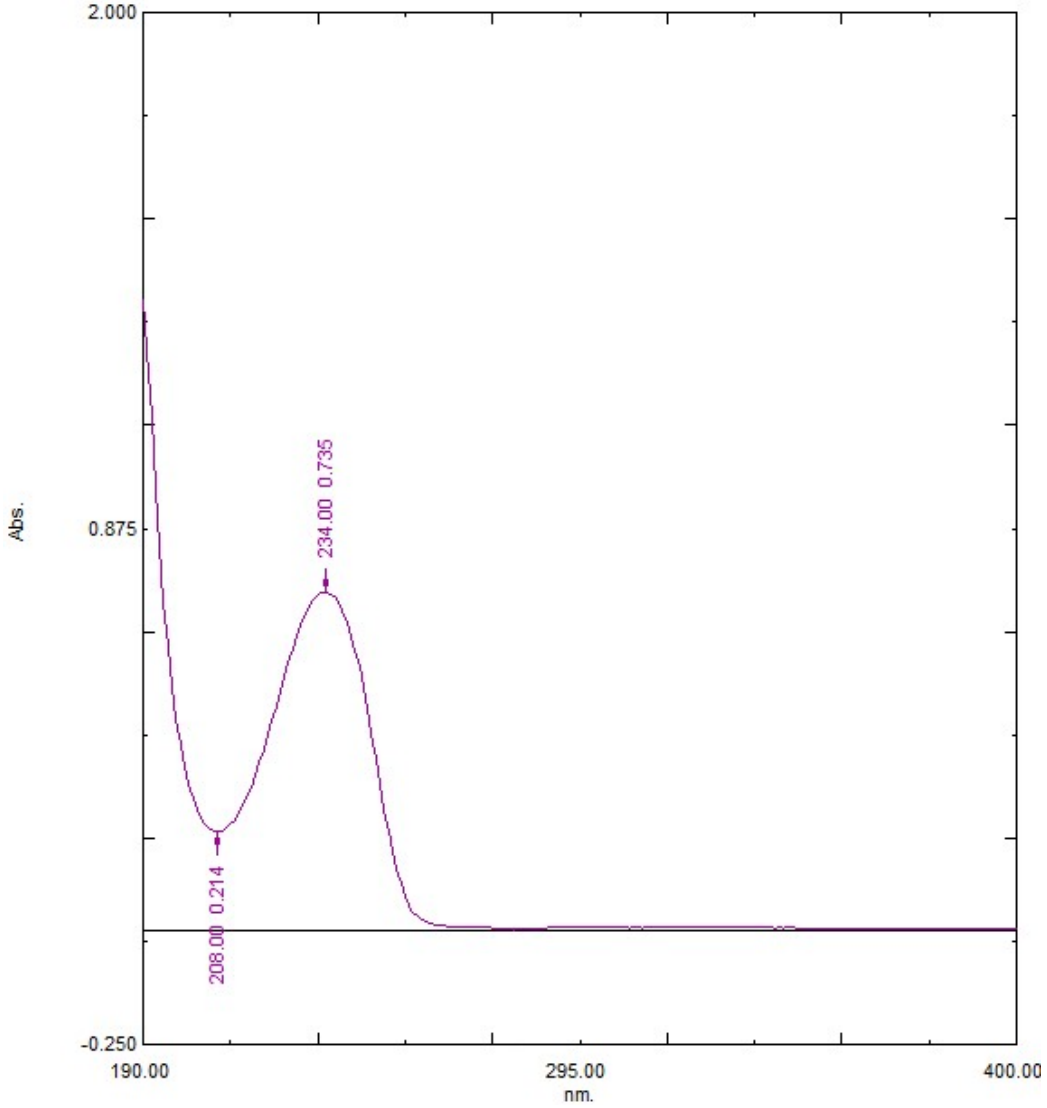
UV absorbance (MeCN, 1.0x10^{-4}M) **6m**



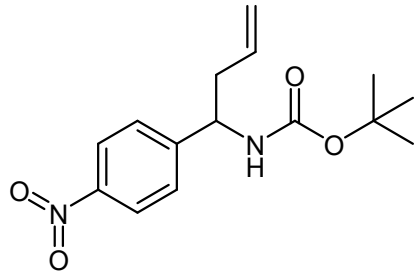


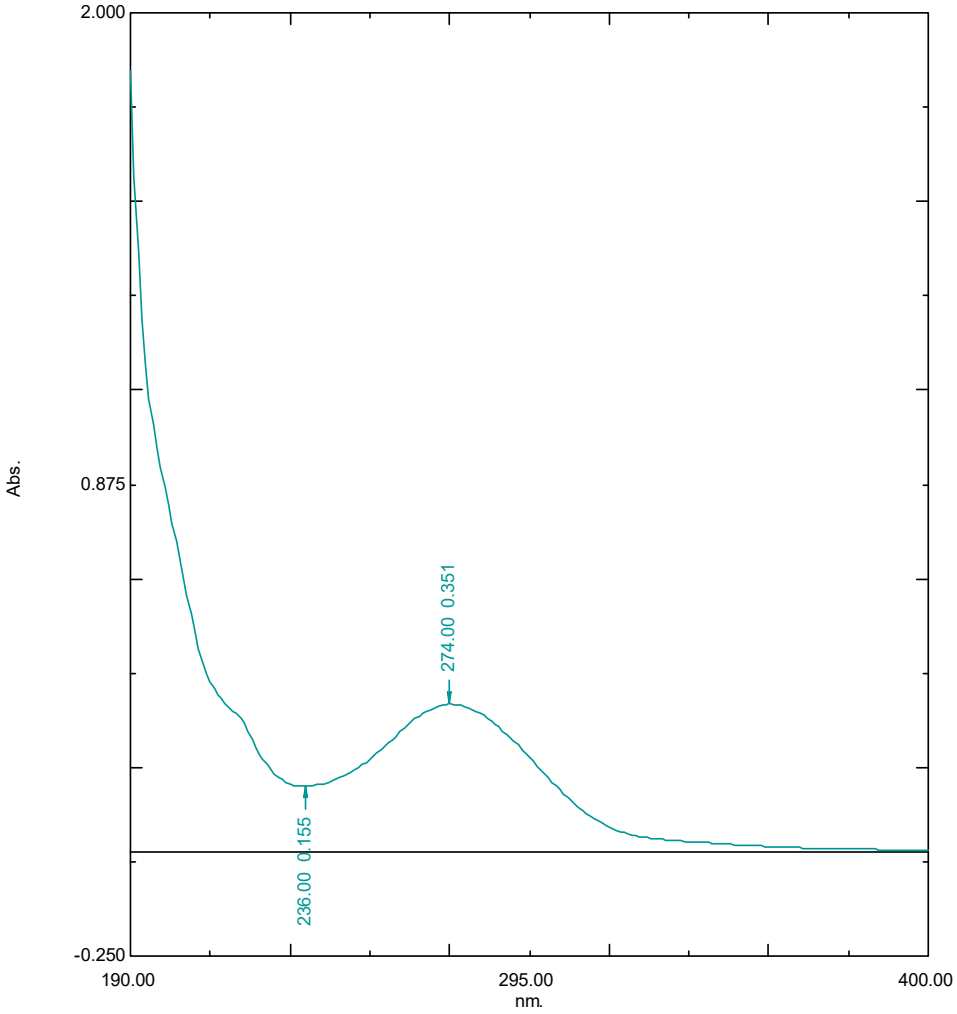
UV absorbance (MeCN, 1.0×10^{-4}M) **6n**



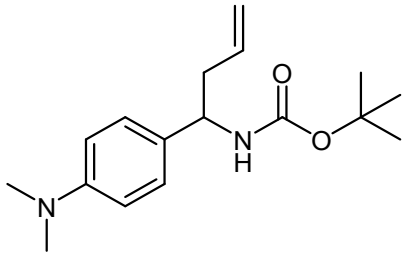


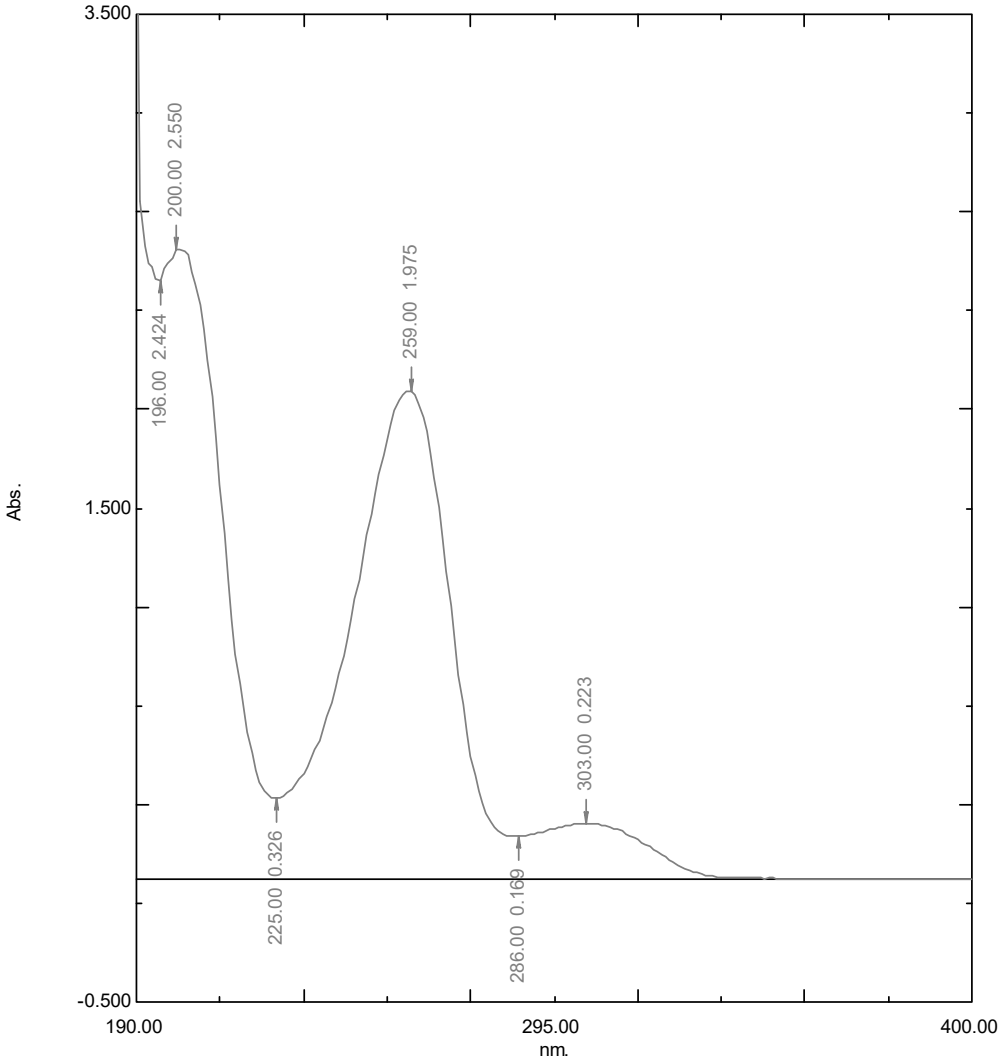
UV absorbance (MeCN, 1.0×10^{-4}M) **6o**



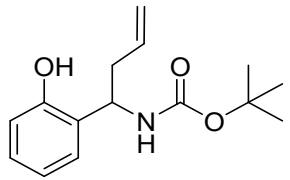


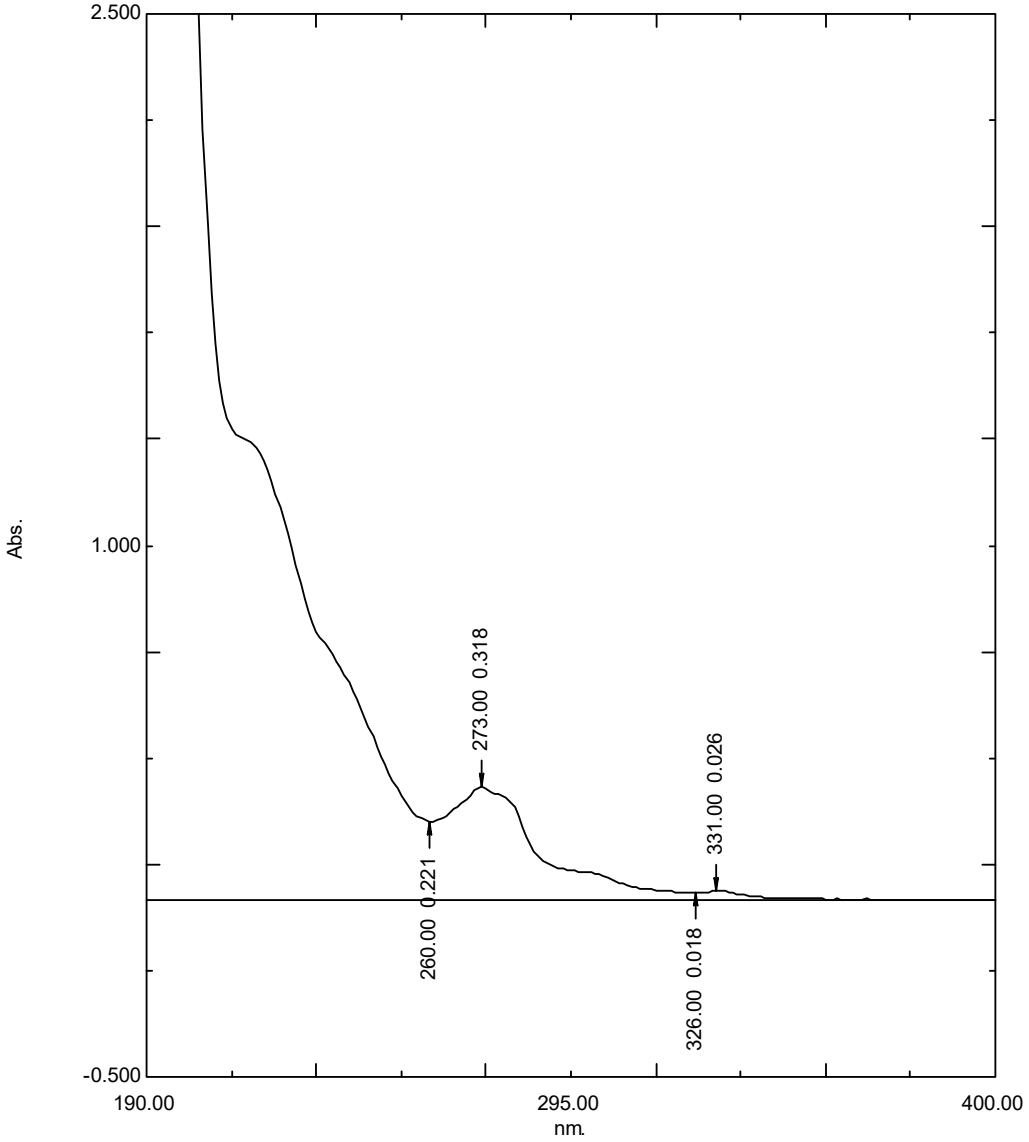
UV absorbance (MeCN, 1.0x10^{-4}M) **6p**



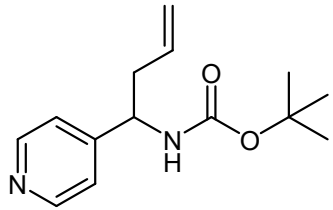


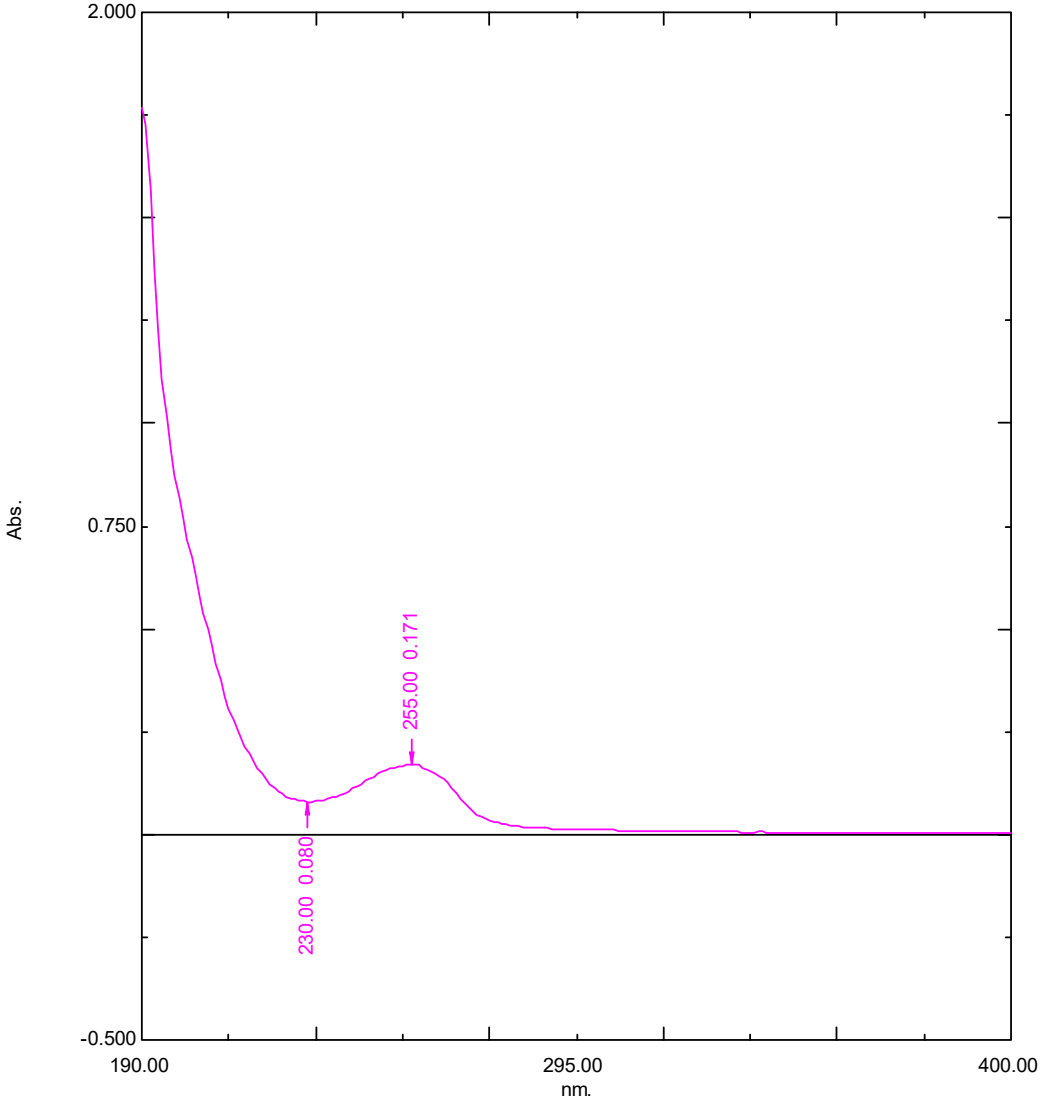
UV absorbance (MeCN, 1.0×10^{-4}M) **6q**



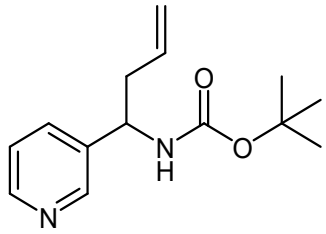


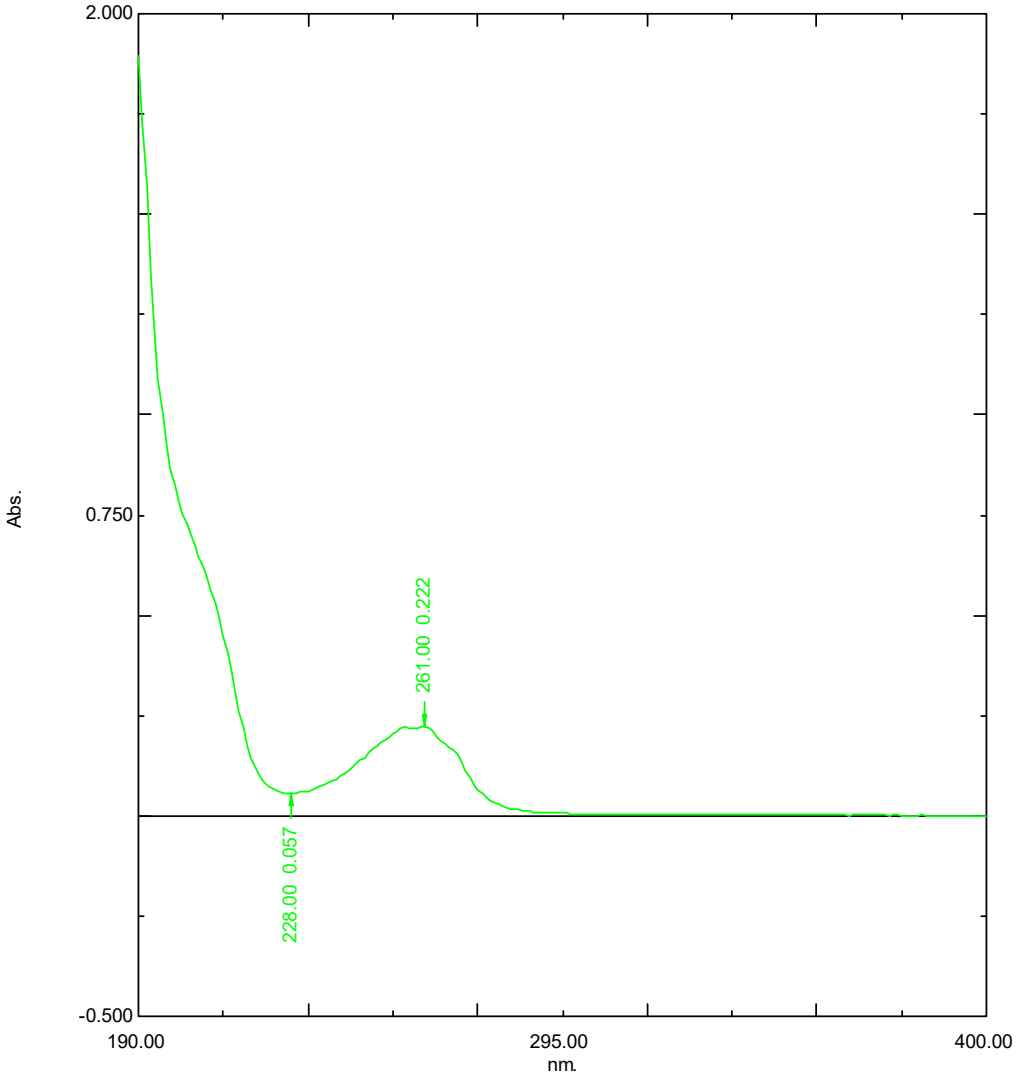
UV absorbance (MeCN, 1.0×10^{-4}M) **6r**



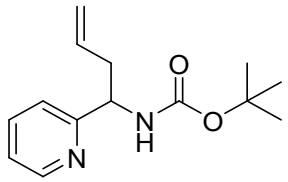


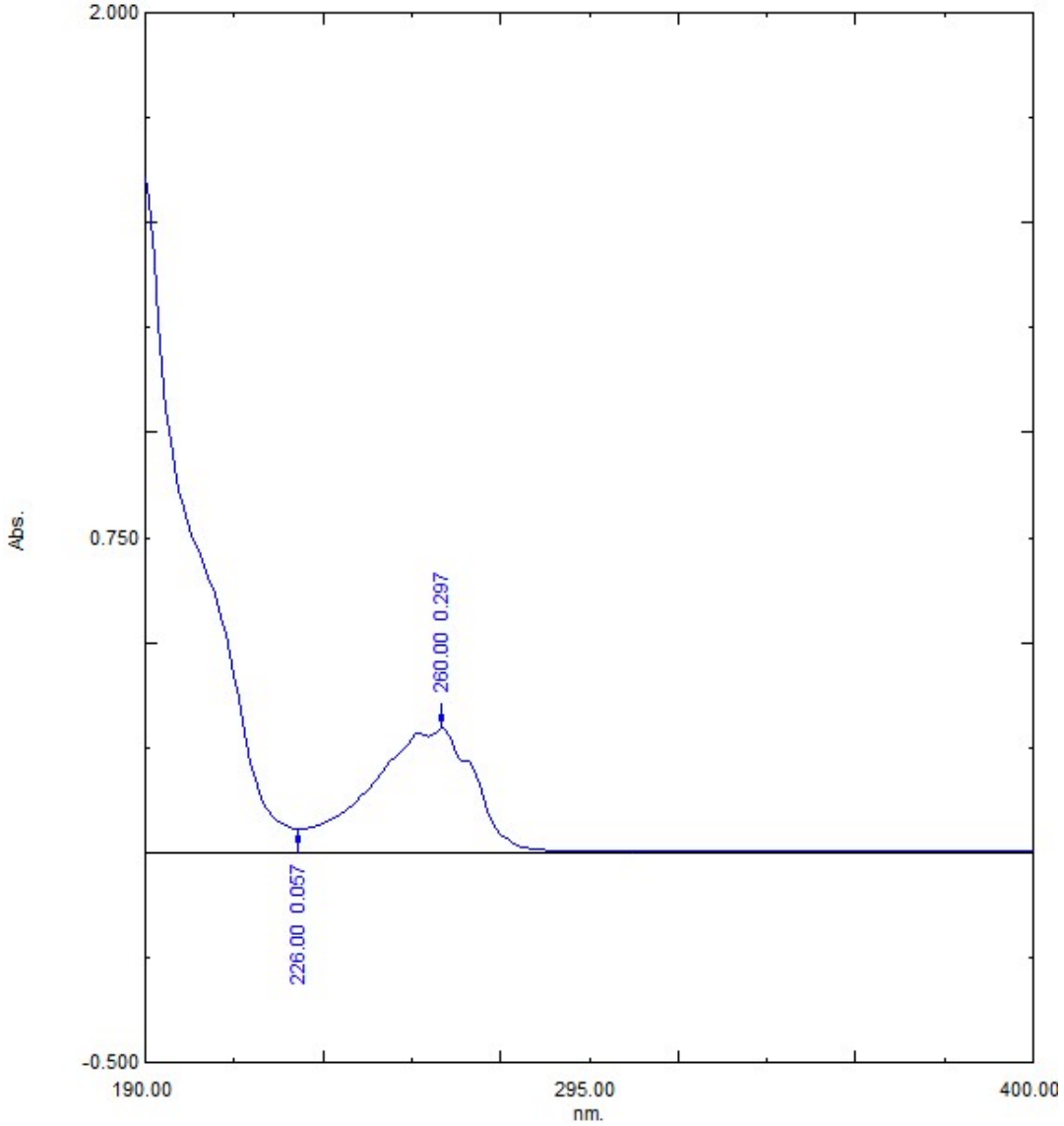
UV absorbance (MeCN, 1.0×10^{-4}M) **6s**



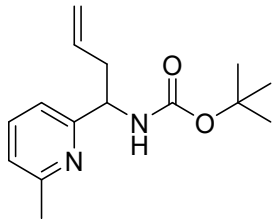


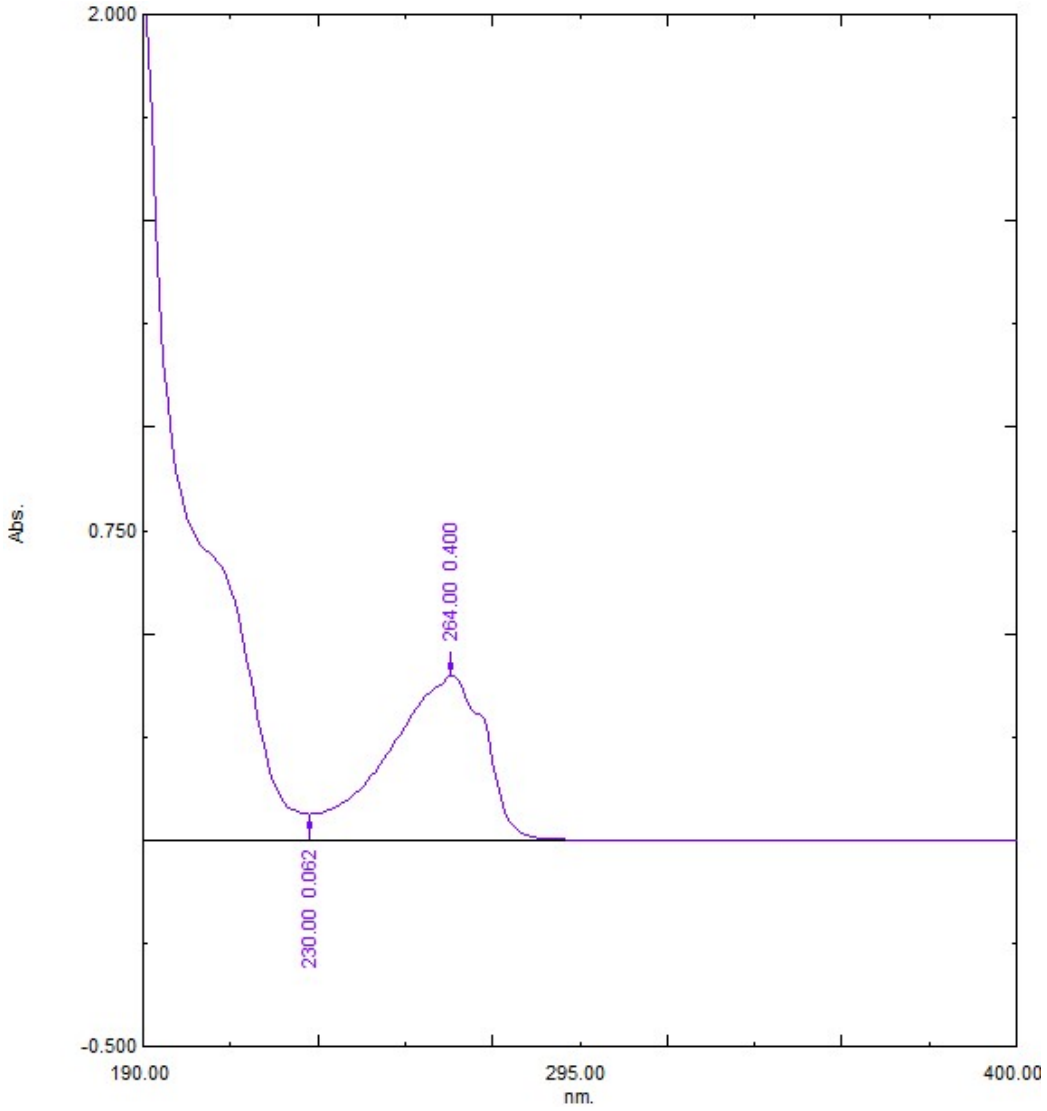
UV absorbance (MeCN, 1.0×10^{-4}M) **6t**



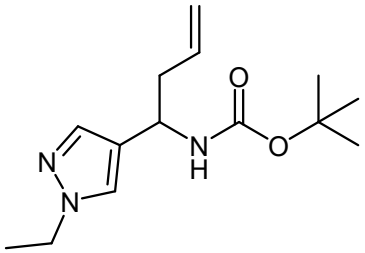


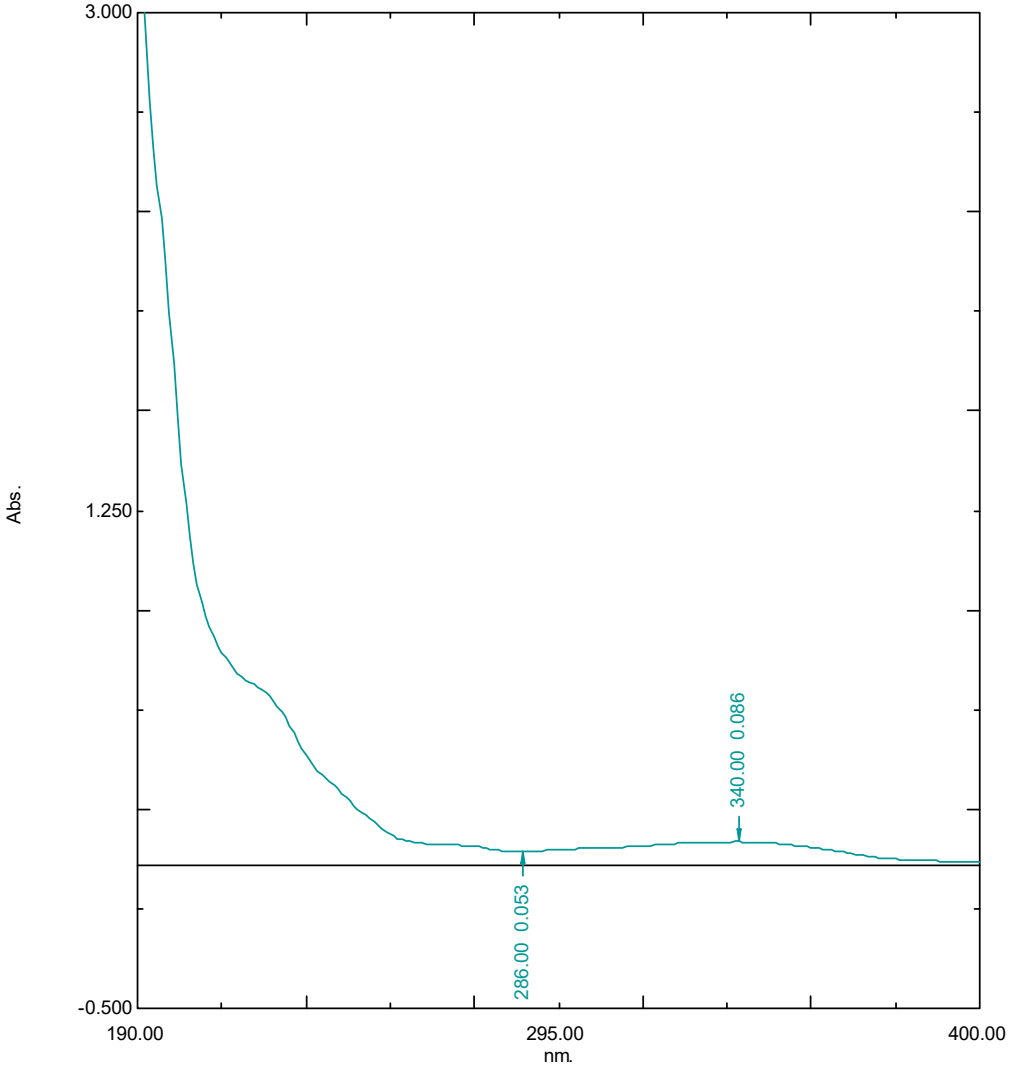
UV absorbance (MeCN, 1.0×10^{-4}M) **6u**



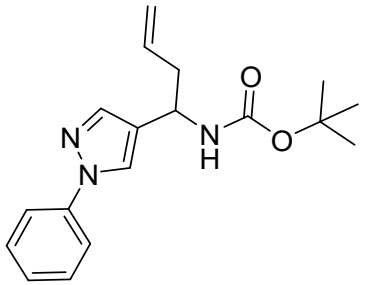


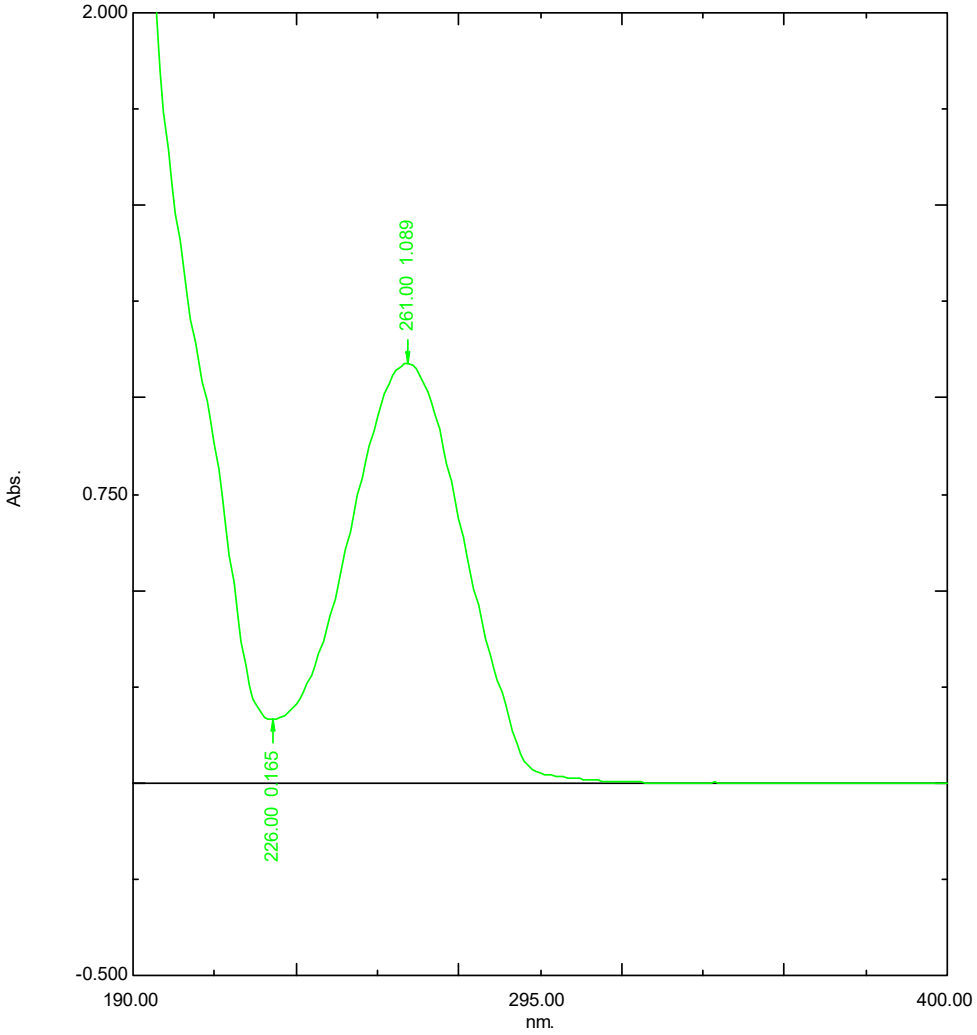
UV absorbance (MeCN, 1.0×10^{-3}M) **6v**



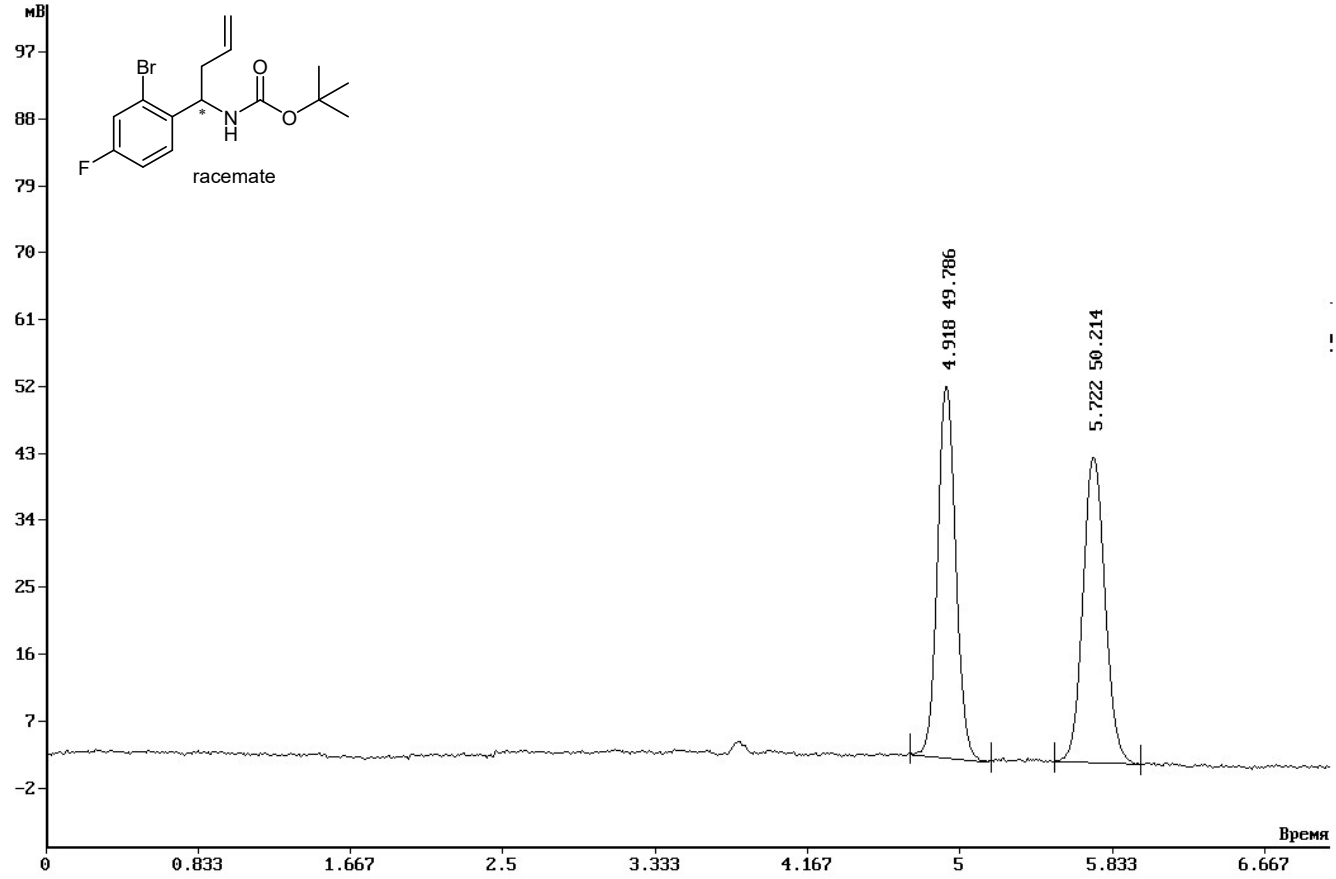


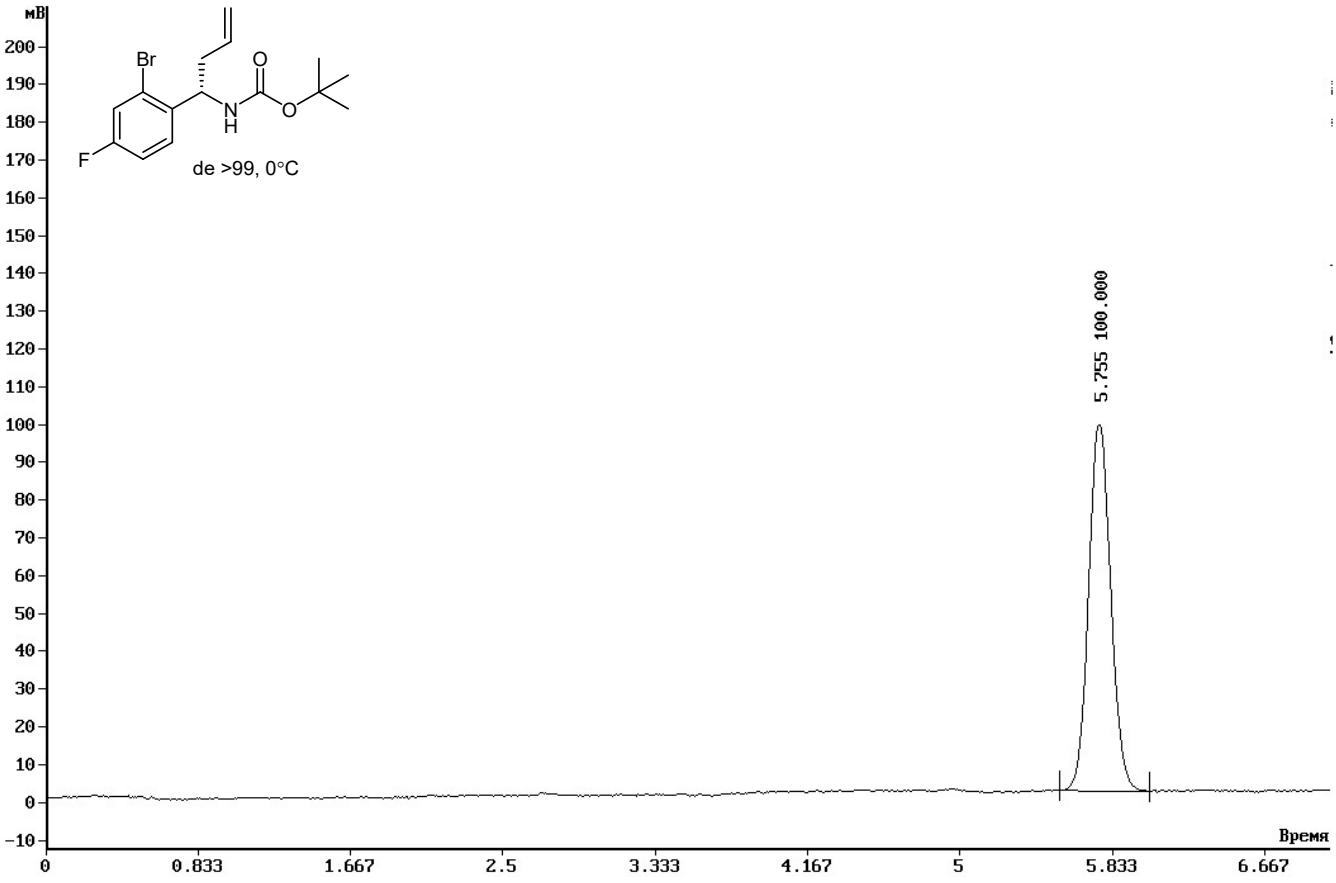
UV absorbance (MeCN, 1.0×10^{-4}M) **6w**



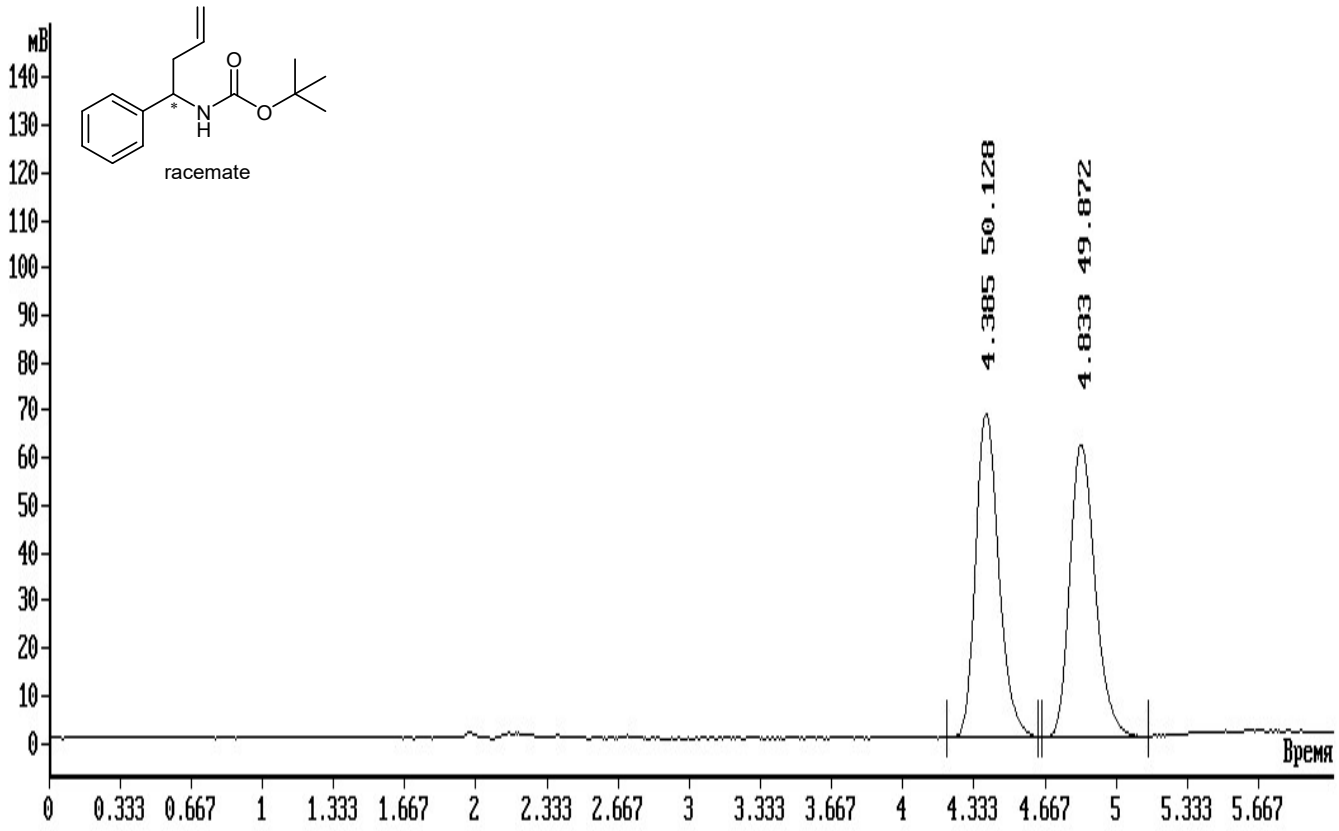


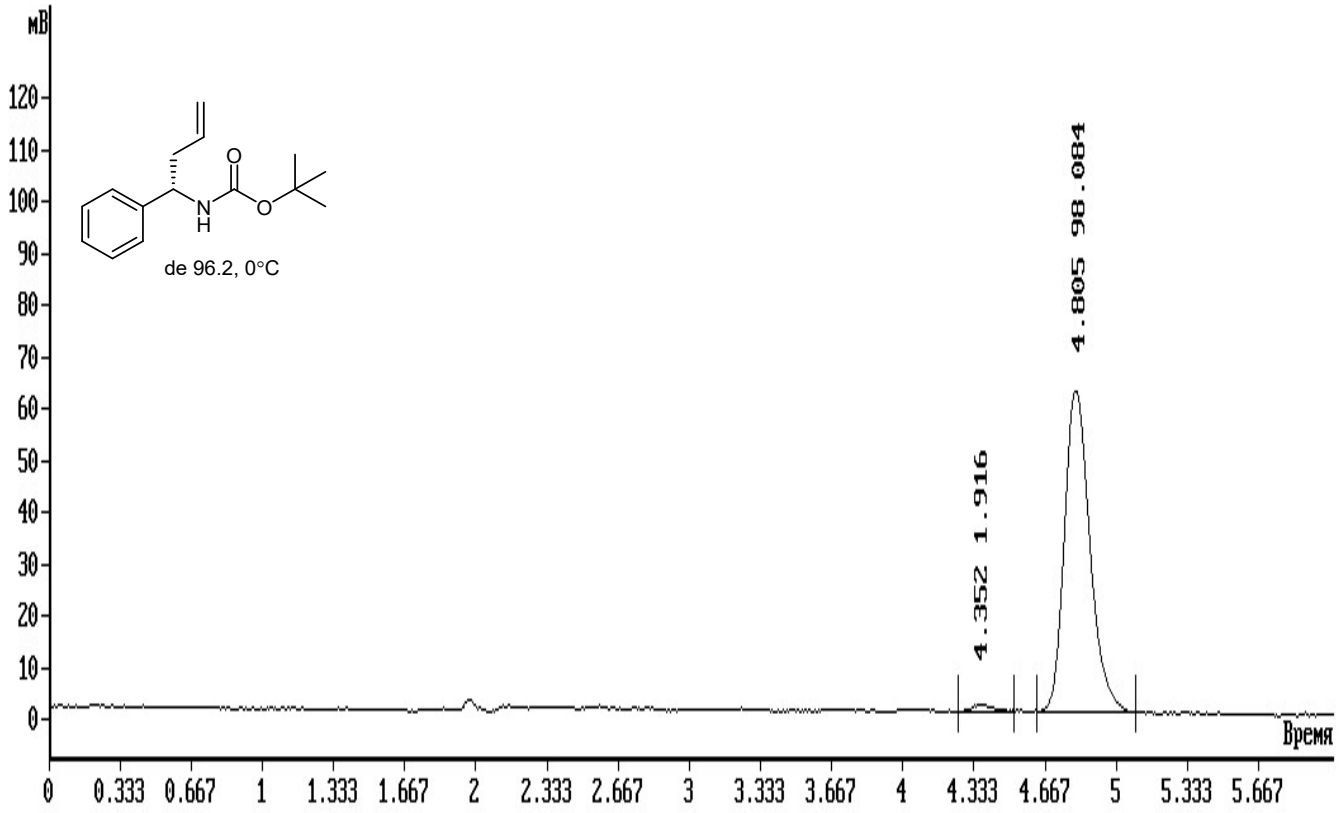
Enantiomeric analysis of *tert*-butyl (*S*)-(1-(2-bromo-4-fluorophenyl)but-3-en-1-yl)carbamate (6a).
Column Kromasil 5-TBB (250x4.6mm, 5μm), eluent *n*-C_6H_{14}/*iso*-PrOH = 95/5, flow rate 1.0 ml/min, UV 220 nm.





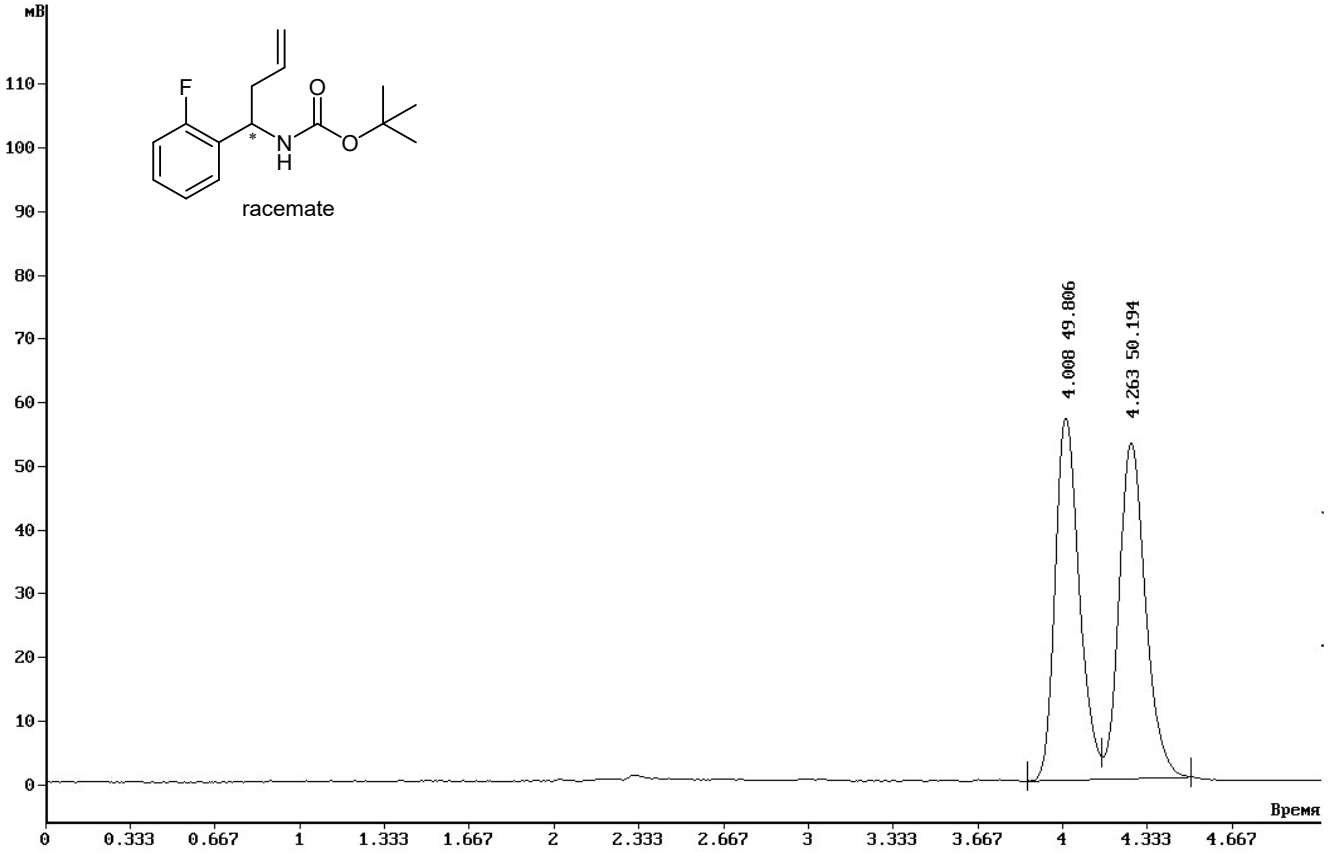
Enantiomeric analysis of *tert*-butyl (*S*)-(1-phenyl-but-3-en-1-yl)carbamate (6b).
Column Kromasil 3-AmyCoat (150x4.6mm, 5μm), eluent *n*-C_6H_{14}/*iso*-PrOH = 95/5, flow rate 1.0 ml/min, UV 220 nm.

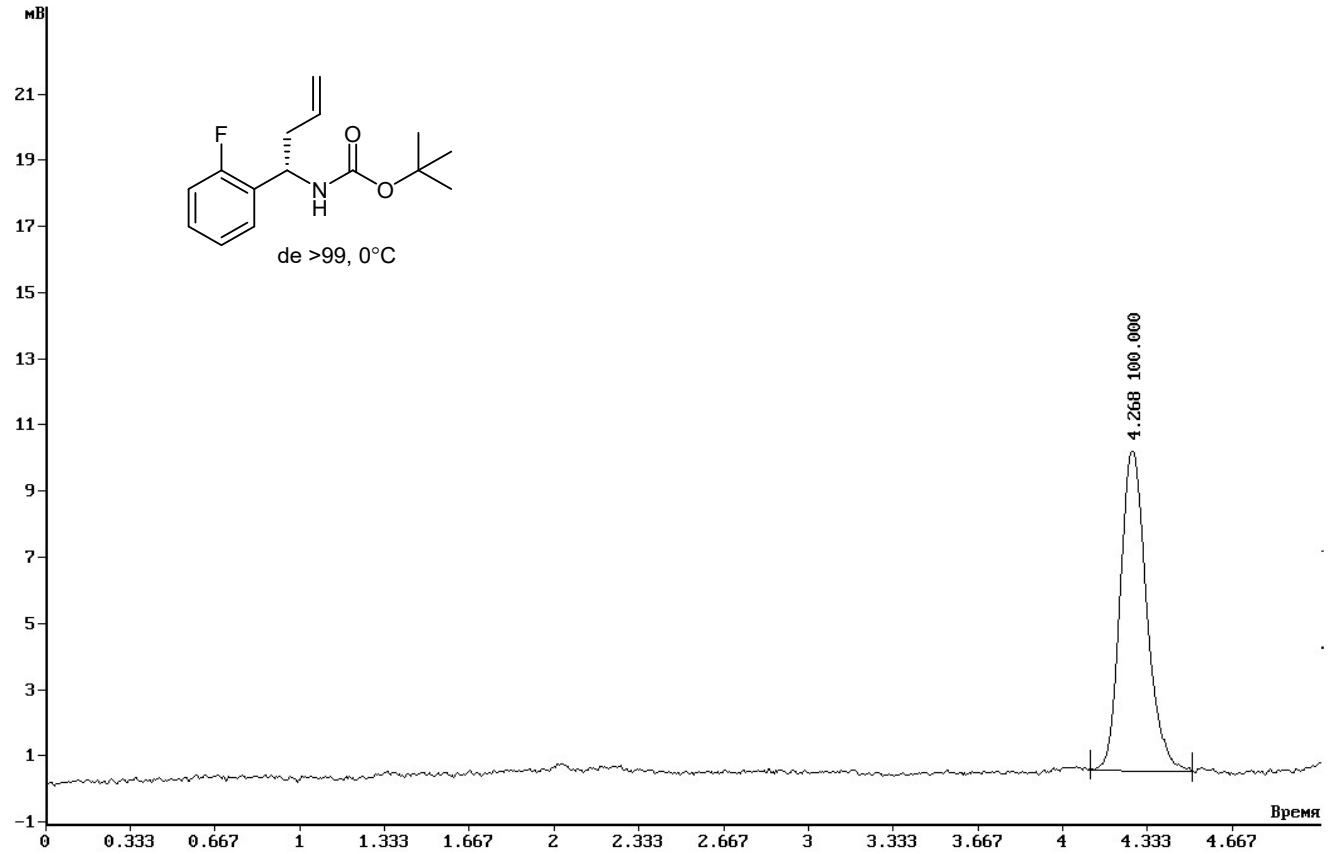




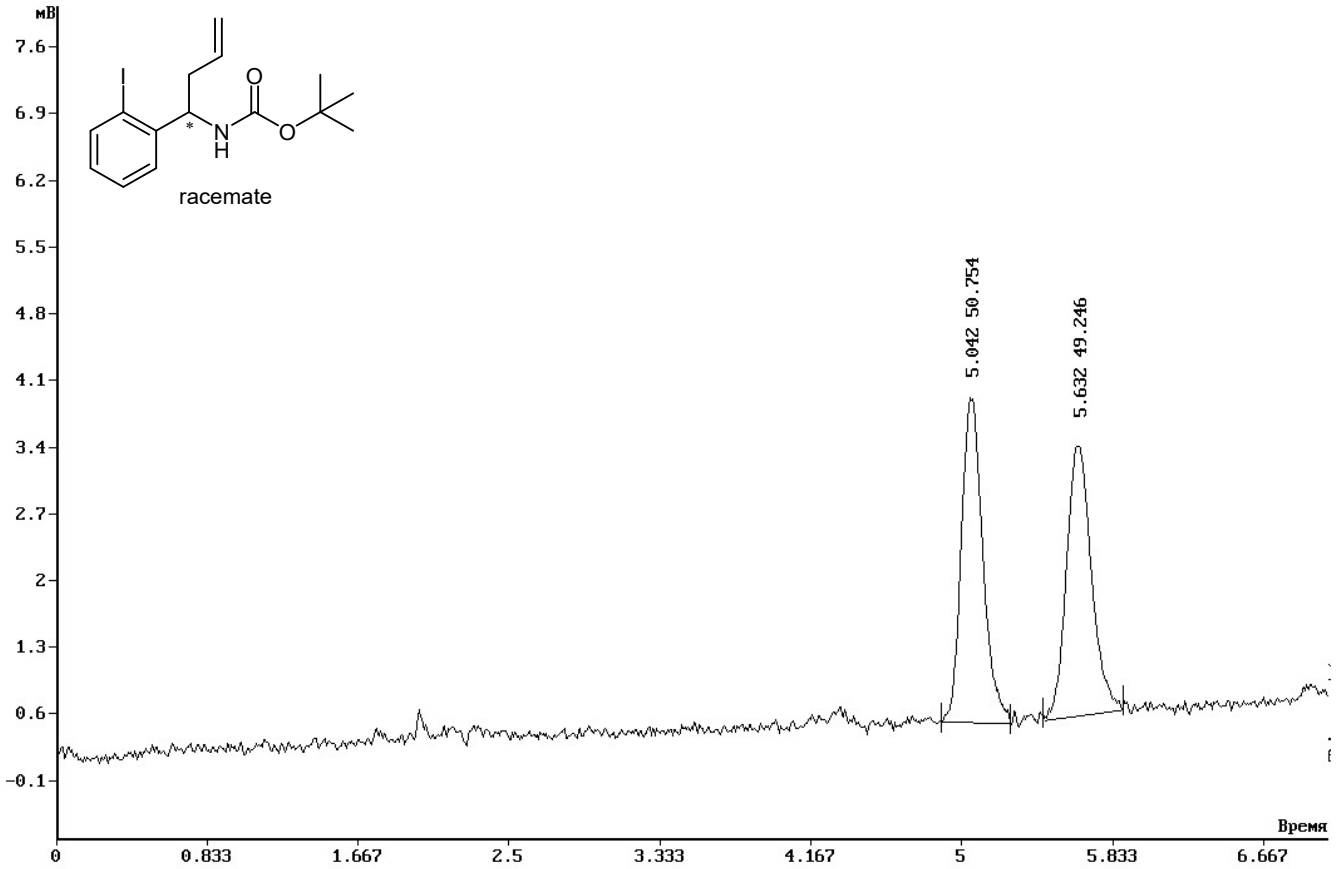
Enantiomeric analysis of *tert*-butyl (*S*)-(1-(2-fluorophenyl)but-3-en-1-yl)carbamate (6c).

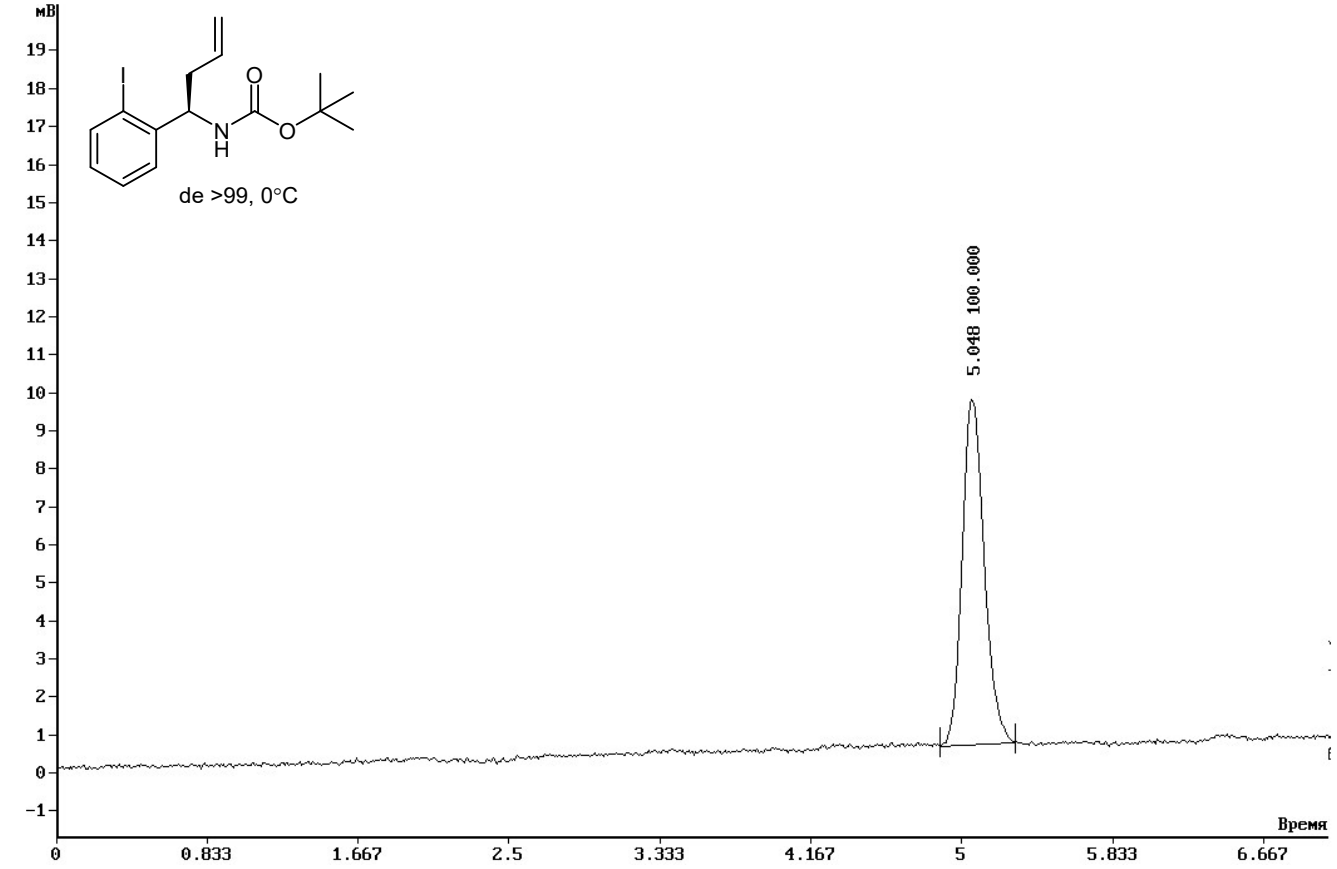
Column Kromasil 3-AmyCoat (150x4.6mm, 5μm), eluent *n*-C_6H_{14}/*iso*-PrOH = 95/5, flow rate 1.0 ml/min, UV 260 m.



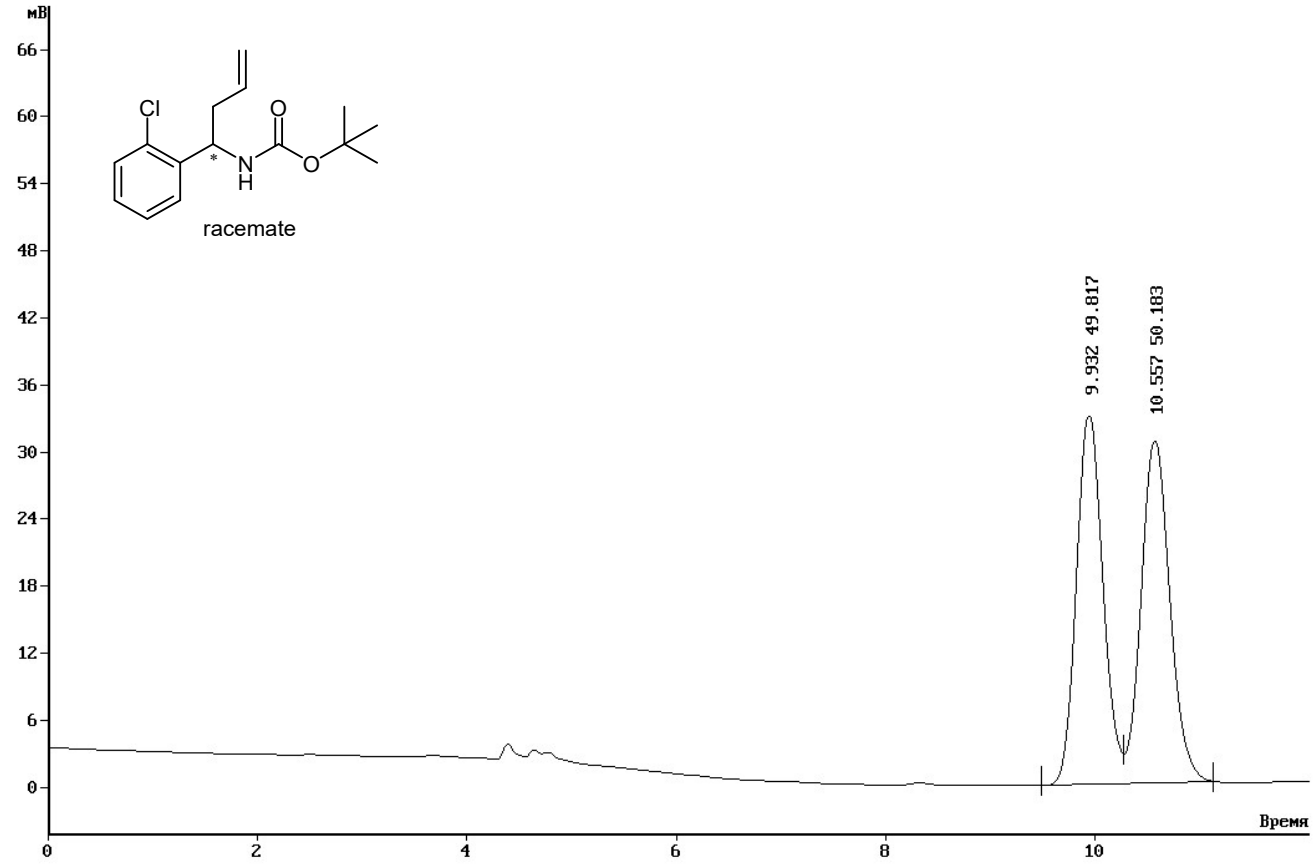


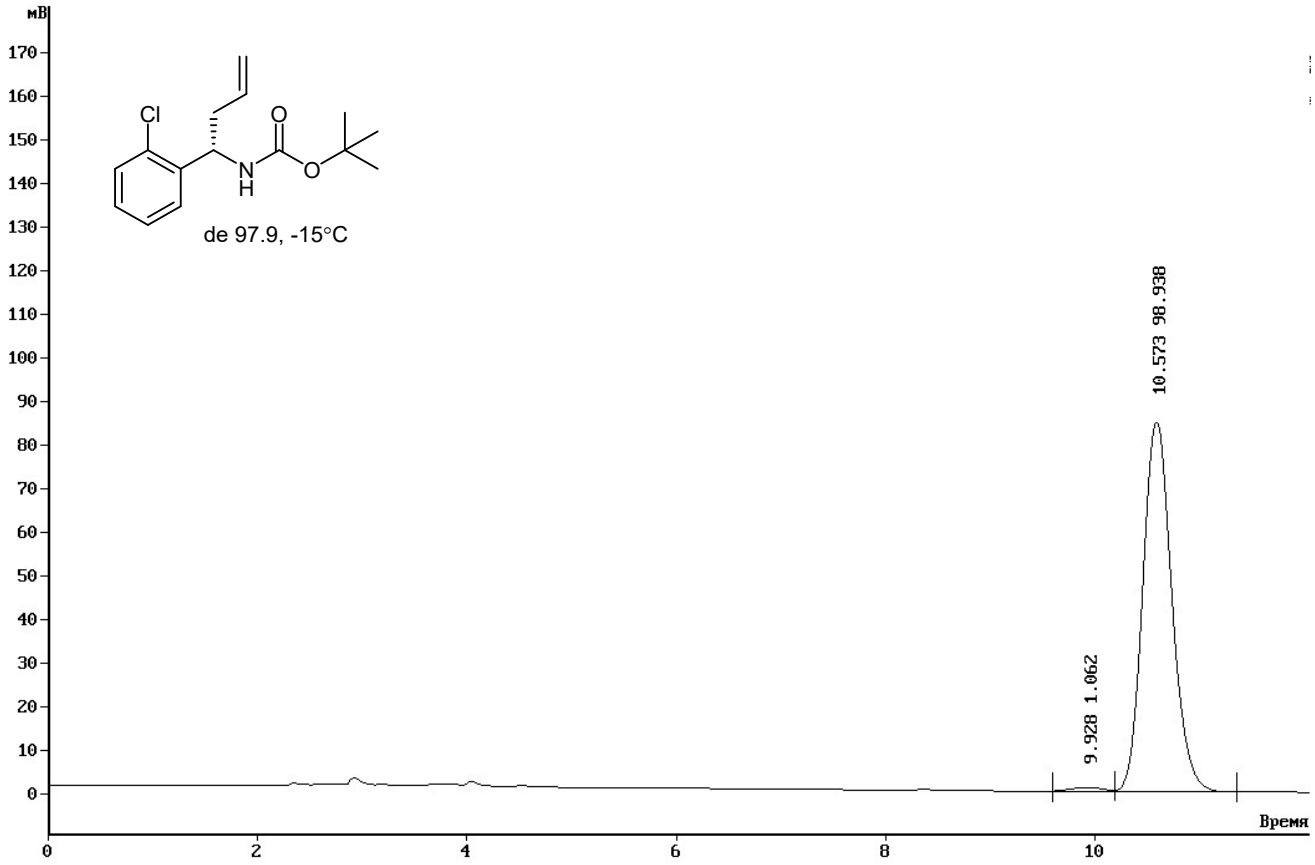
Enantiomeric analysis of *tert*-butyl (*R*)-(1-(2-iodophenyl)but-3-en-1-yl)carbamate (6d).
Column Kromasil 3-AmyCoat (150x4.6mm, 5μm), eluent *n*-C_6H_{14}/*iso*-PrOH = 95/5, flow rate 1.0 ml/min, UV 260 nm.



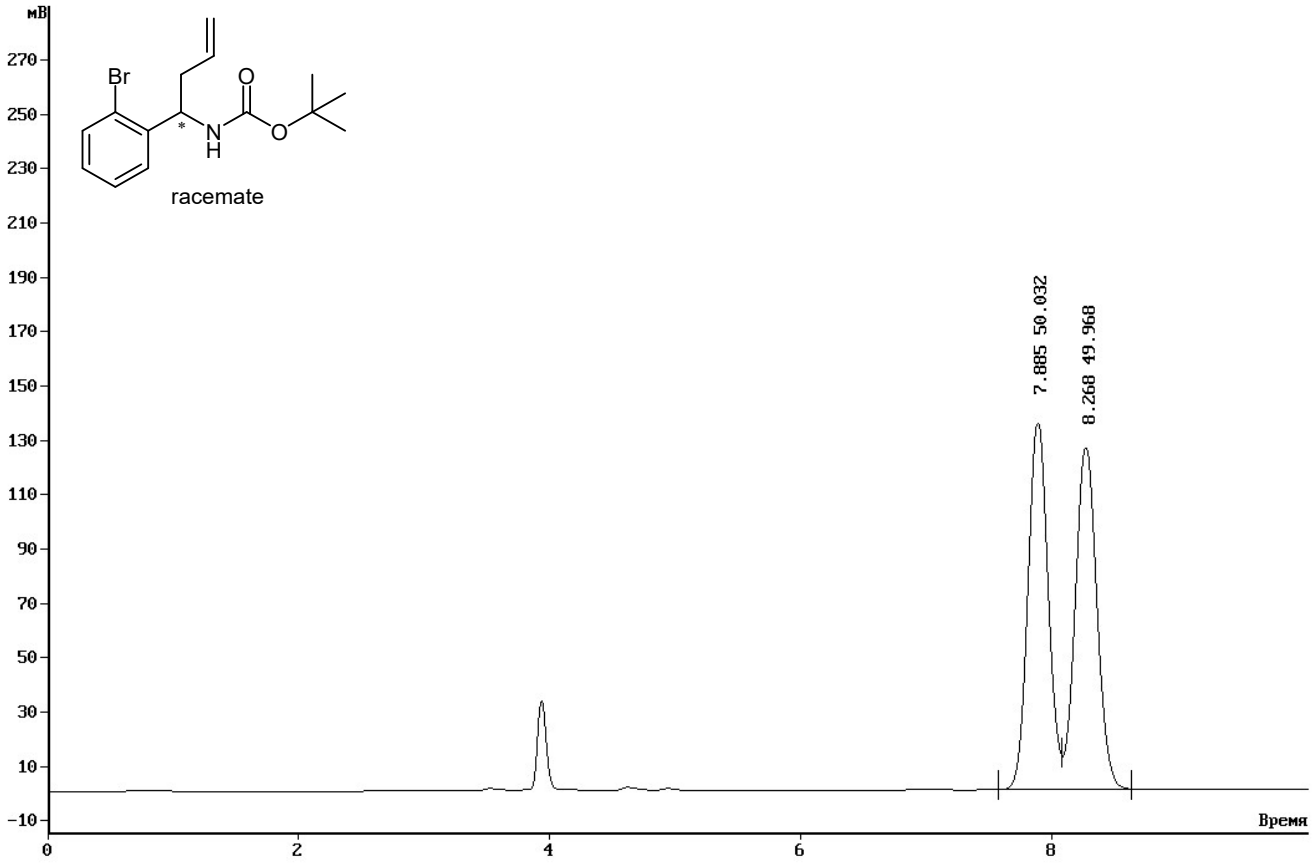


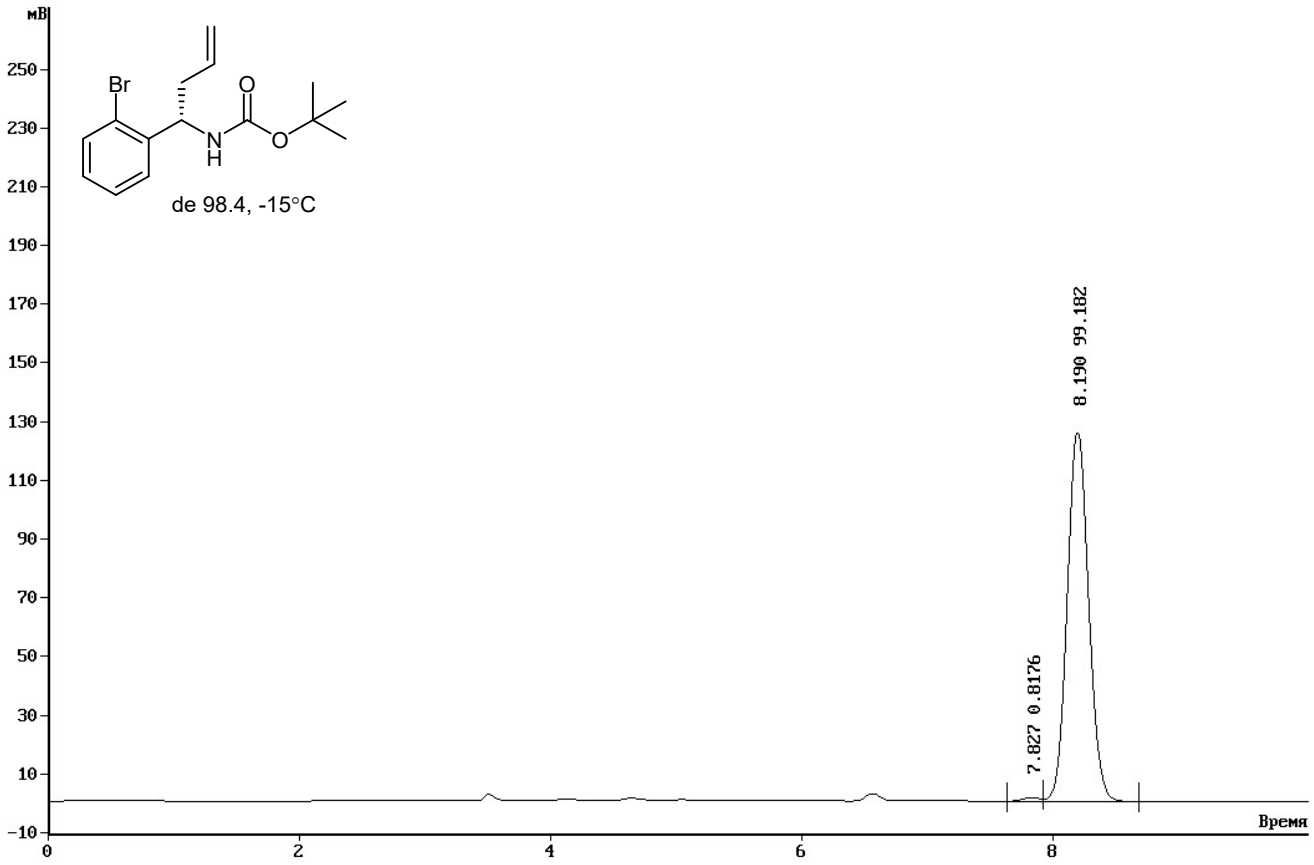
Enantiomeric analysis of *tert*-butyl (*S*)-(1-(2-chlorophenyl)but-3-en-1-yl)carbamate (6e).
Column Kromasil 3-AmyCoat (150x4.6mm, 5μm), eluent *n*-C_6H_{14}/*iso*-PrOH = 98/2, flow rate 0.75 ml/min, UV 220 nm.



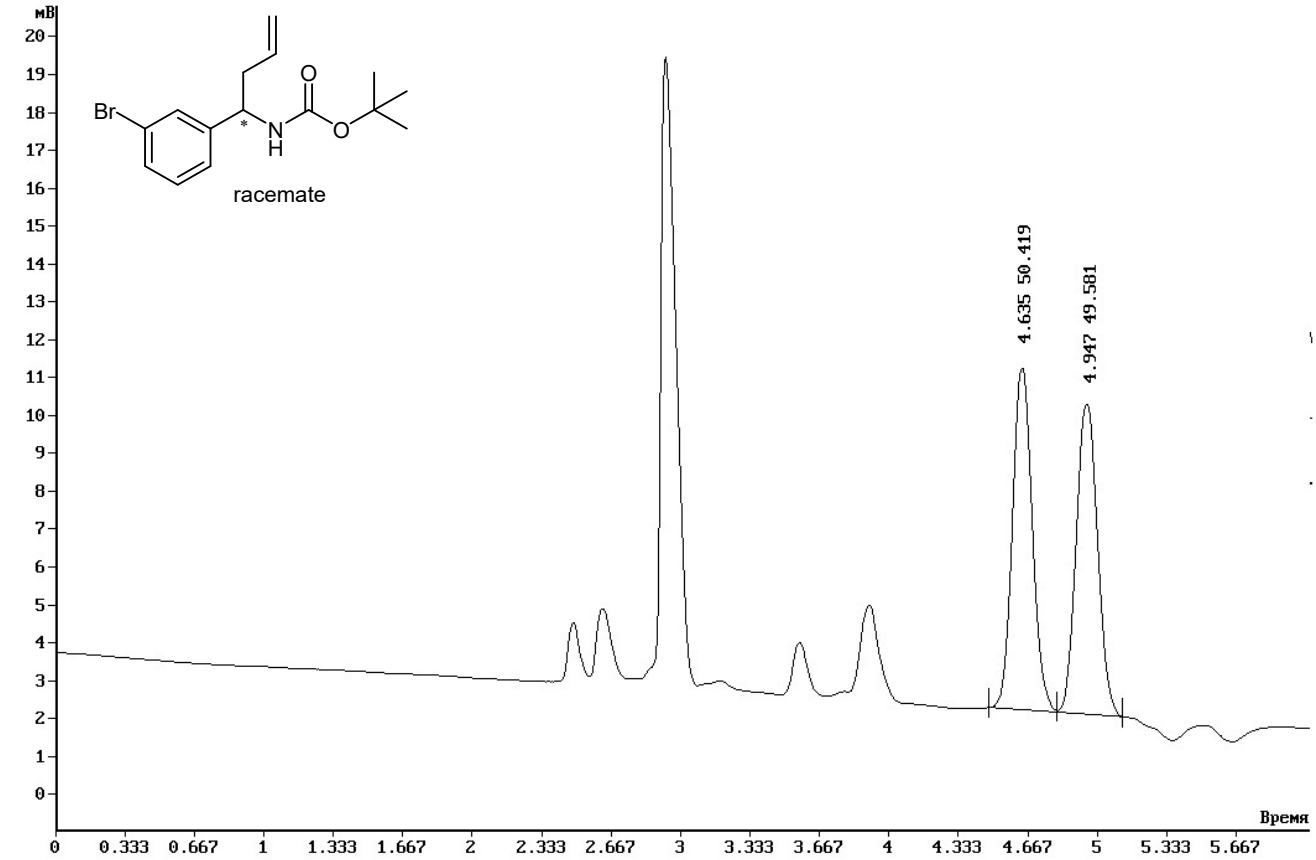


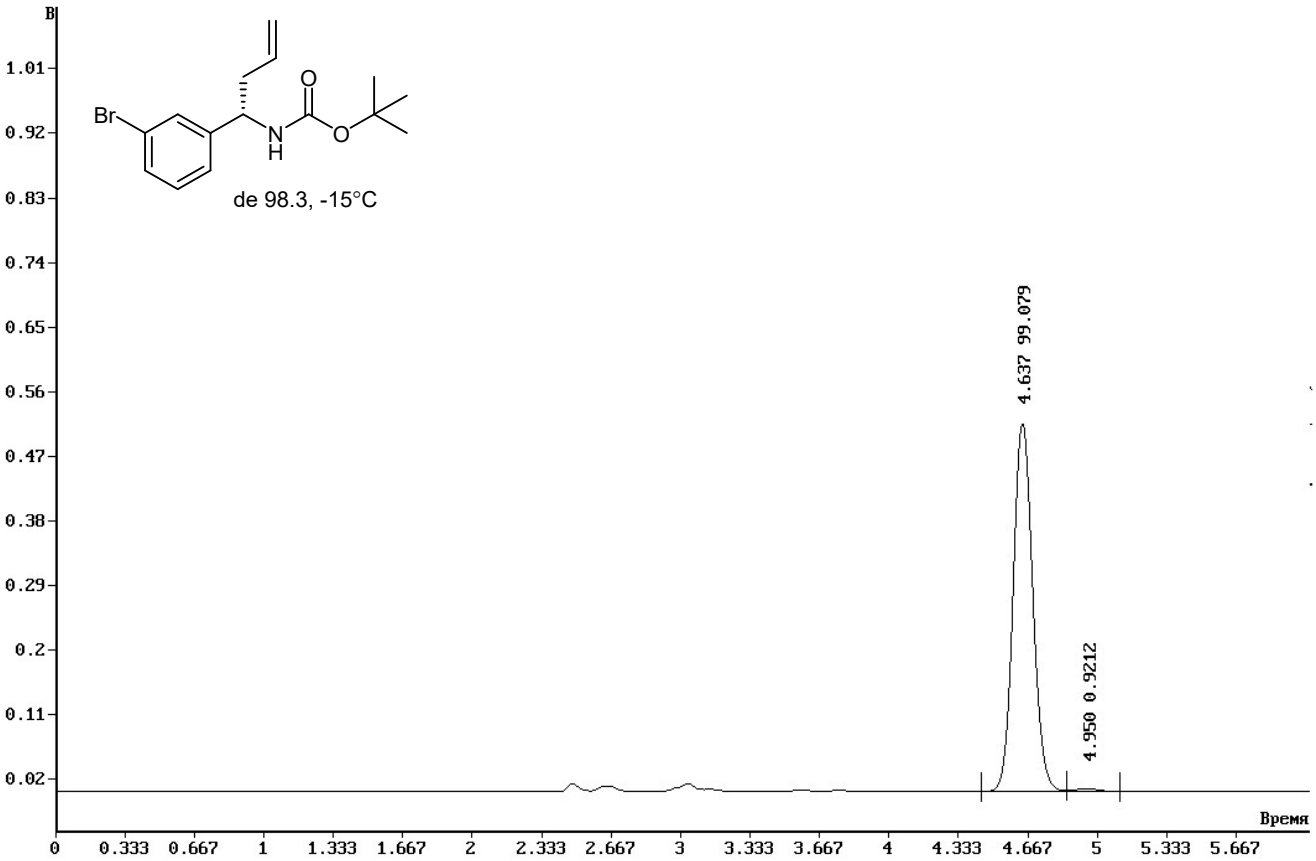
Enantiomeric analysis of *tert*-butyl (*S*)-(1-(2-bromophenyl)but-3-en-1-yl)carbamate (6f).
Column Kromasil 5-TBB (250x4.6mm, 5μm), eluent *n*-C_6H_{14}/*iso*-PrOH = 98/2, flow rate 0.75 ml/min, UV 220 nm.



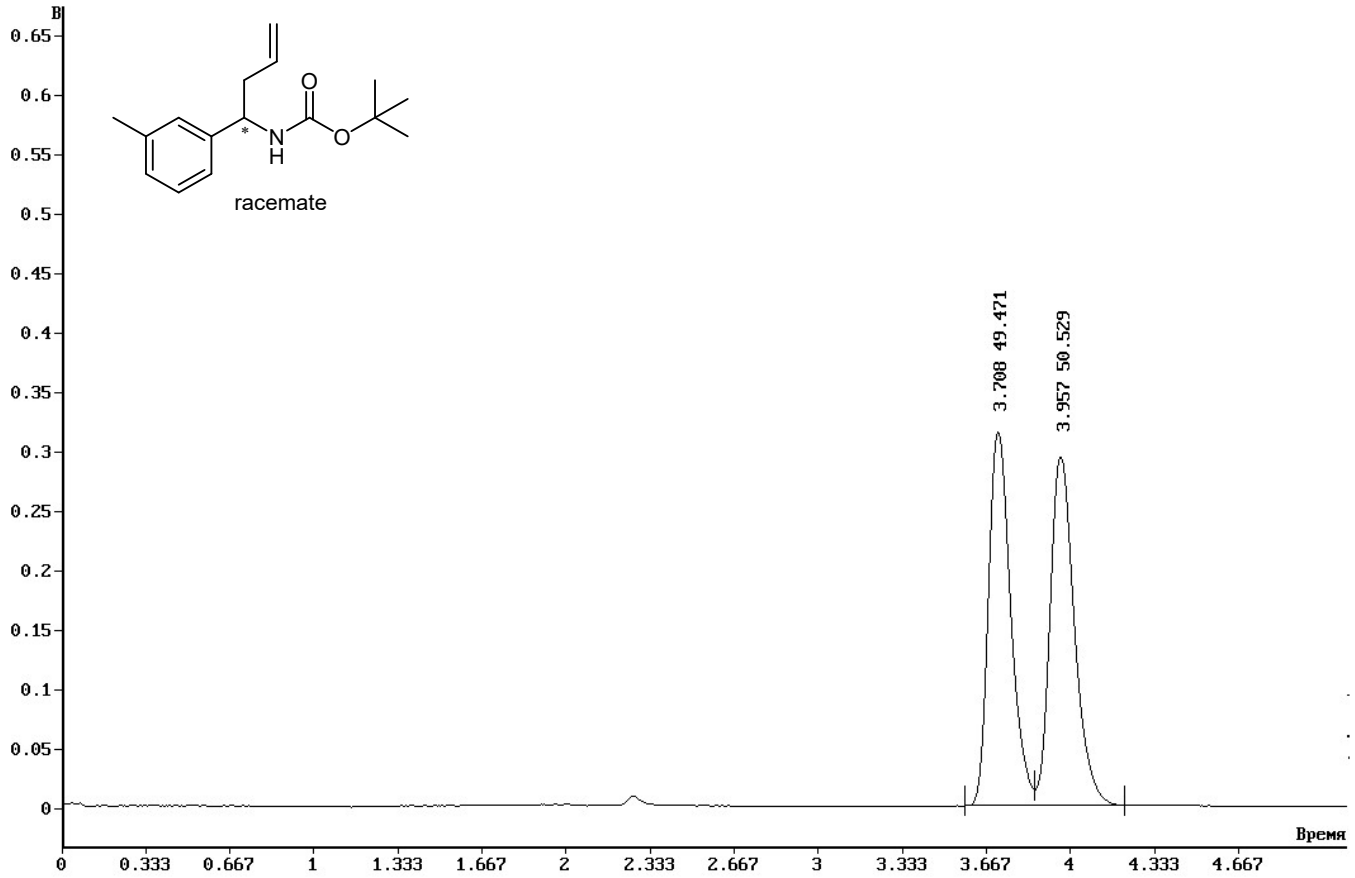


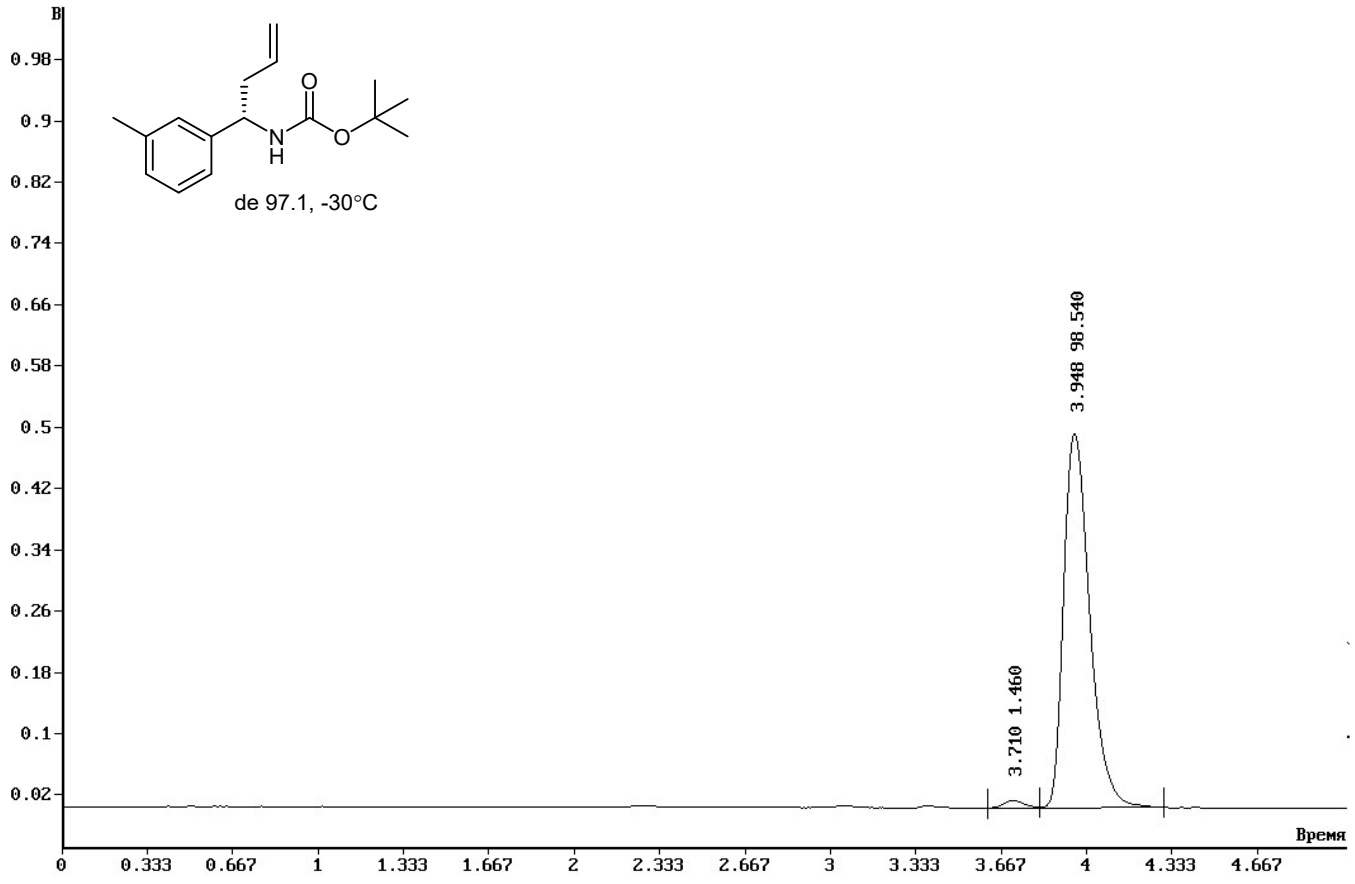
Enantiomeric analysis of *tert*-butyl (*S*)-(1-(3-bromophenyl)but-3-en-1-yl)carbamate (6g).
Column Kromasil 5-TBB (250x4.6mm, 5μm), eluent *n*-C_6H_{14}/*iso*-PrOH = 95/5, flow rate 1.0 ml/min, UV 220 nm.



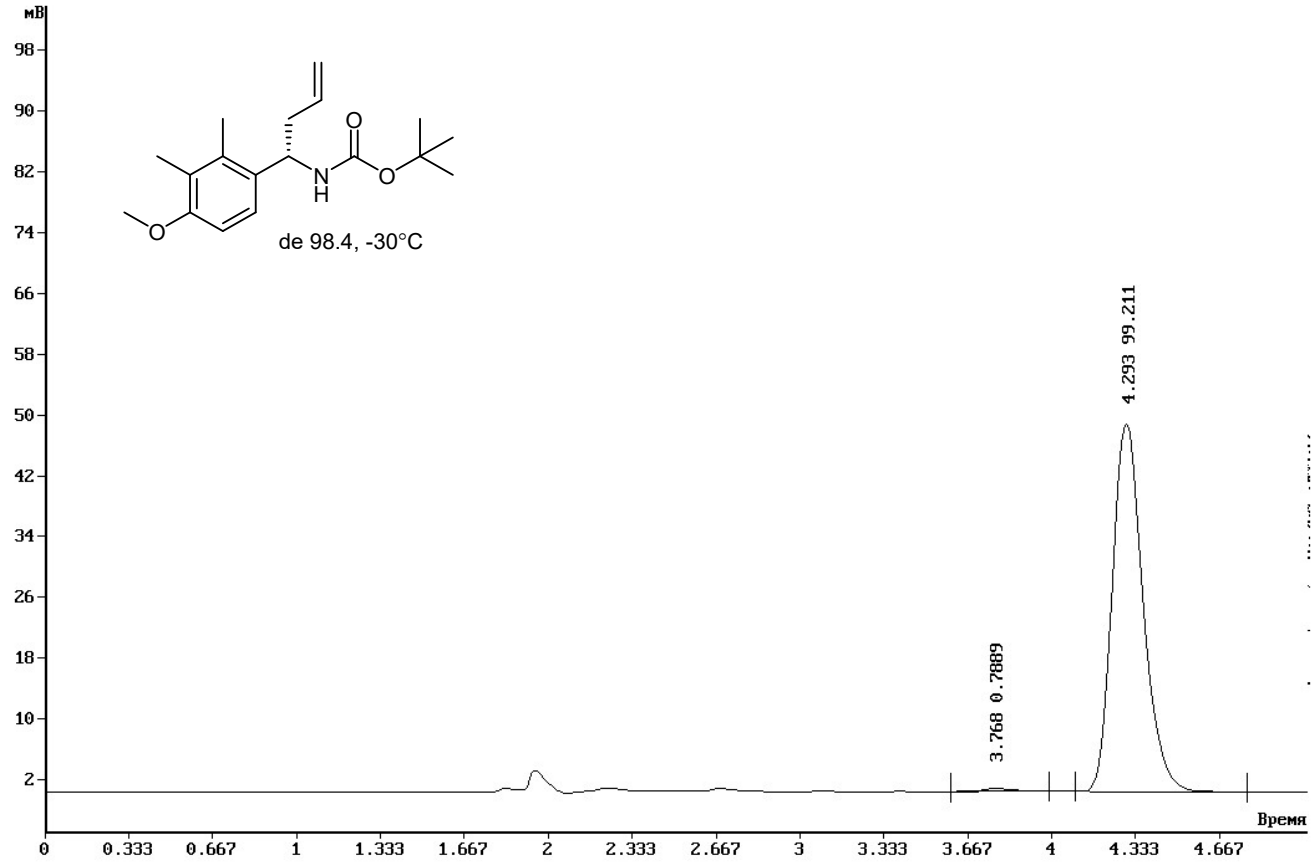


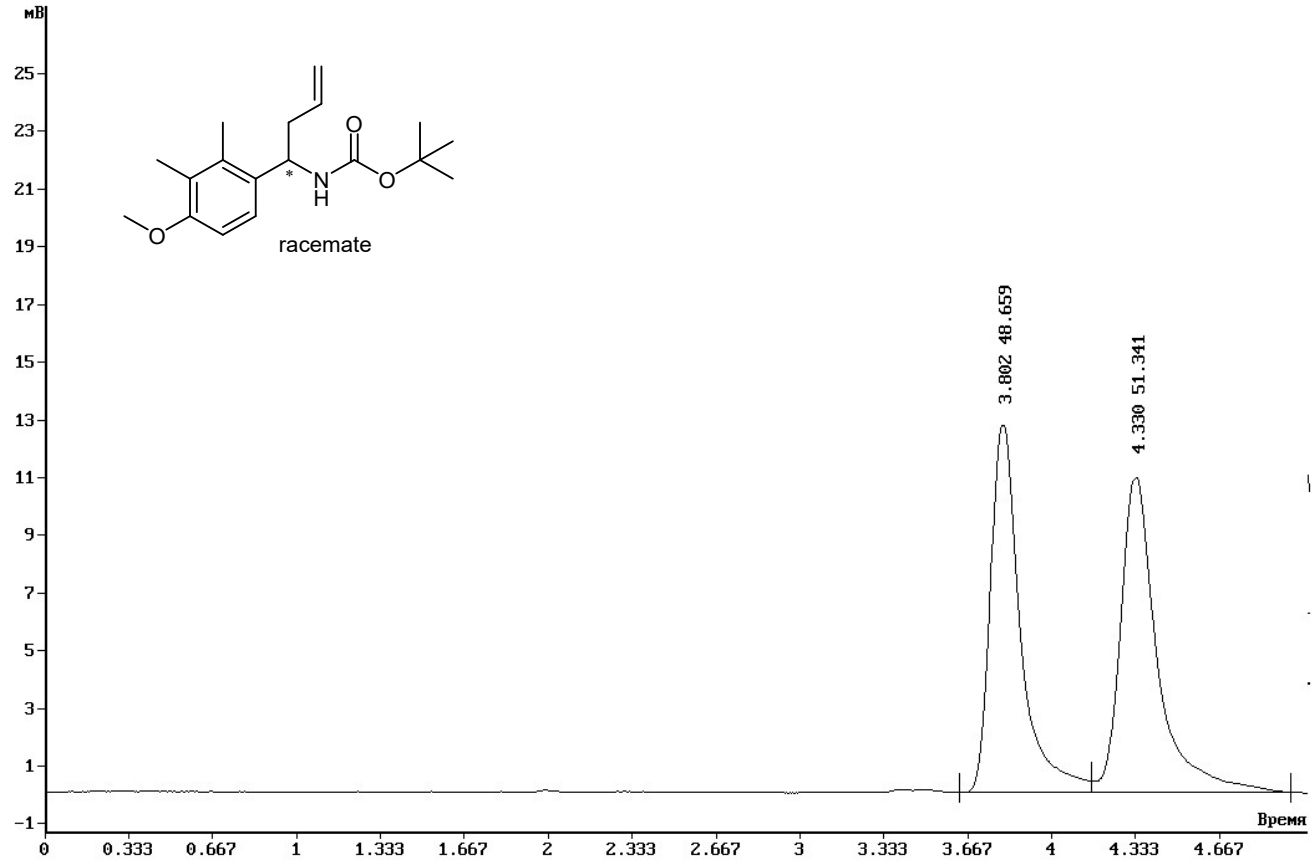
Enantiomeric analysis of *tert*-butyl (*S*)-(1-(m-tolyl)but-3-en-1-yl)carbamate (6h).
Column Kromasil 3-AmyCoat (150x4.6mm, 5μm), eluent *n*-C_6H_{14}/*iso*-PrOH = 95/5, flow rate 1.0 ml/min, UV 220 nm.





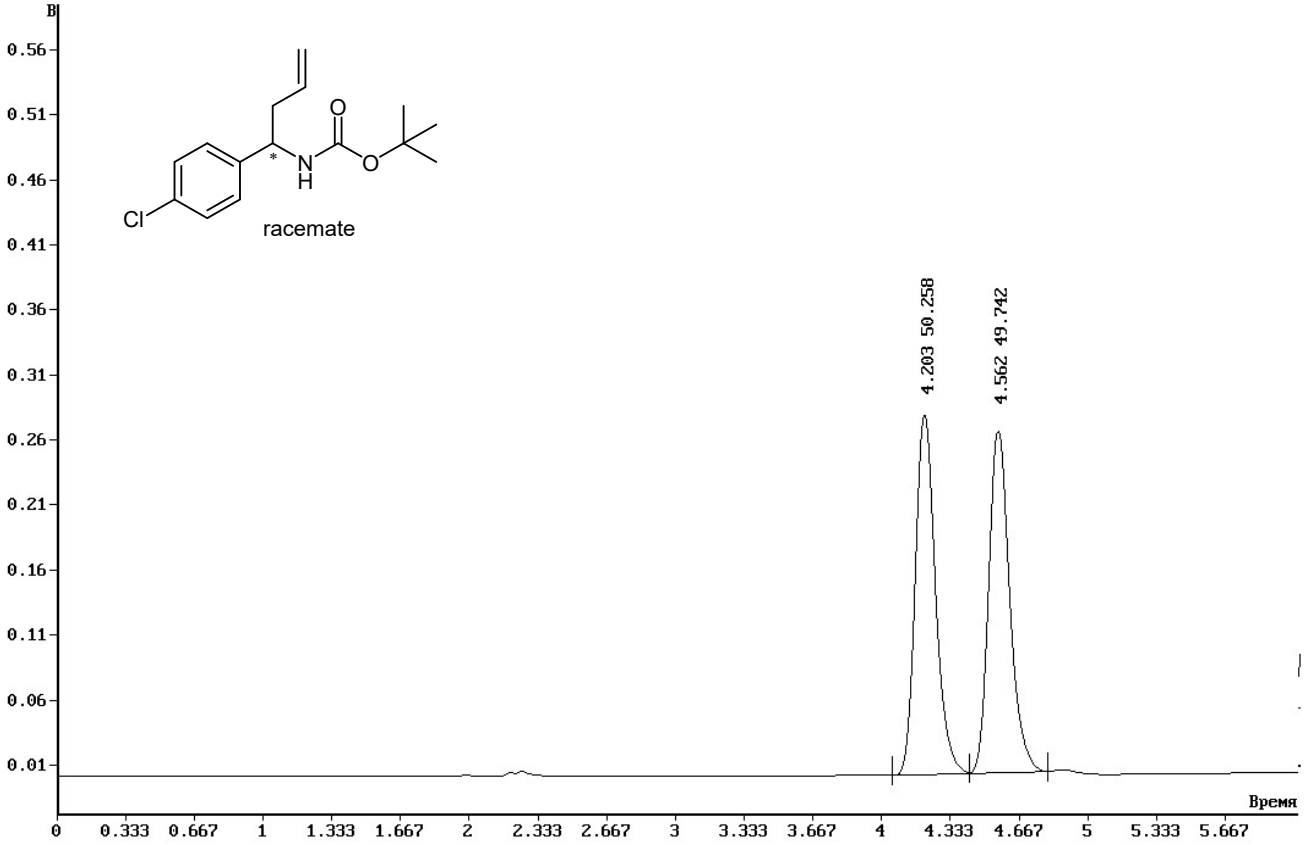
Enantiomeric analysis of *tert*-butyl (*S*)-(1-(4-methoxy-2,3-dimethylphenyl)but-3-en-1-yl)carbamate (6i). Column Kromasil 3-AmyCoat (150x4.6mm, 5μm), eluent *n*-C_6H_{14}/*iso*-PrOH = 95/5, flow rate 1.0 ml/min, UV 260 nm.

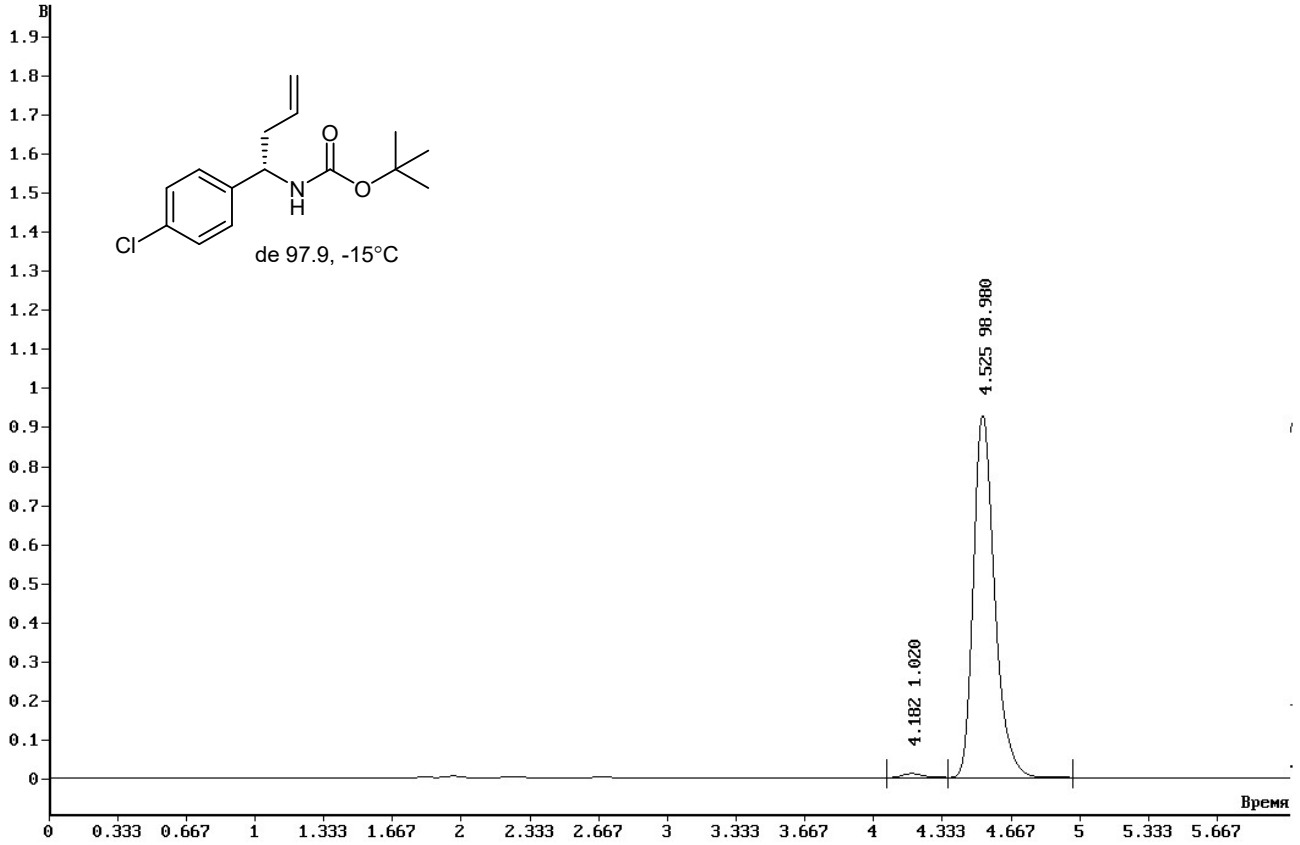




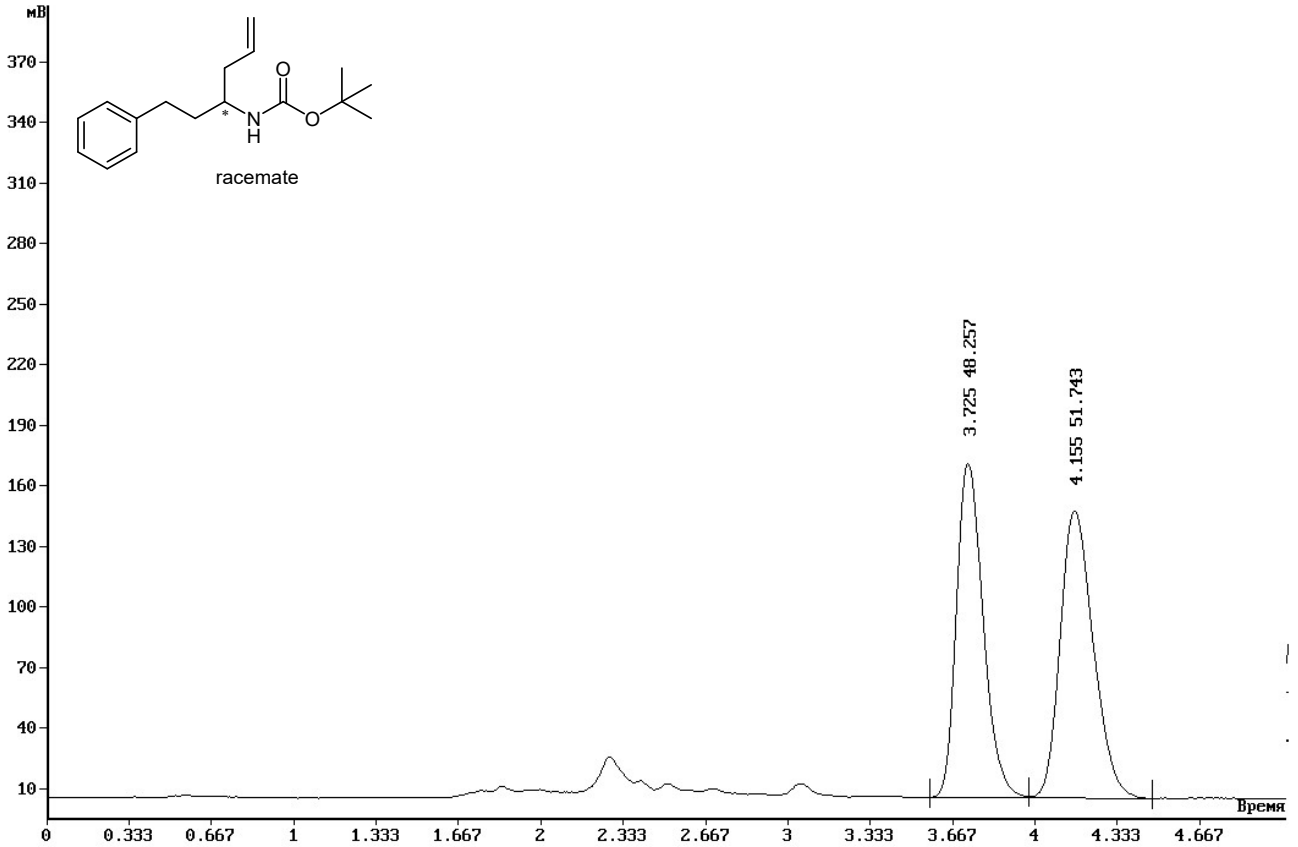
Enantiomeric analysis of *tert*-butyl (*S*)-(1-(4-chlorophenyl)but-3-en-1-yl)carbamate (6j).

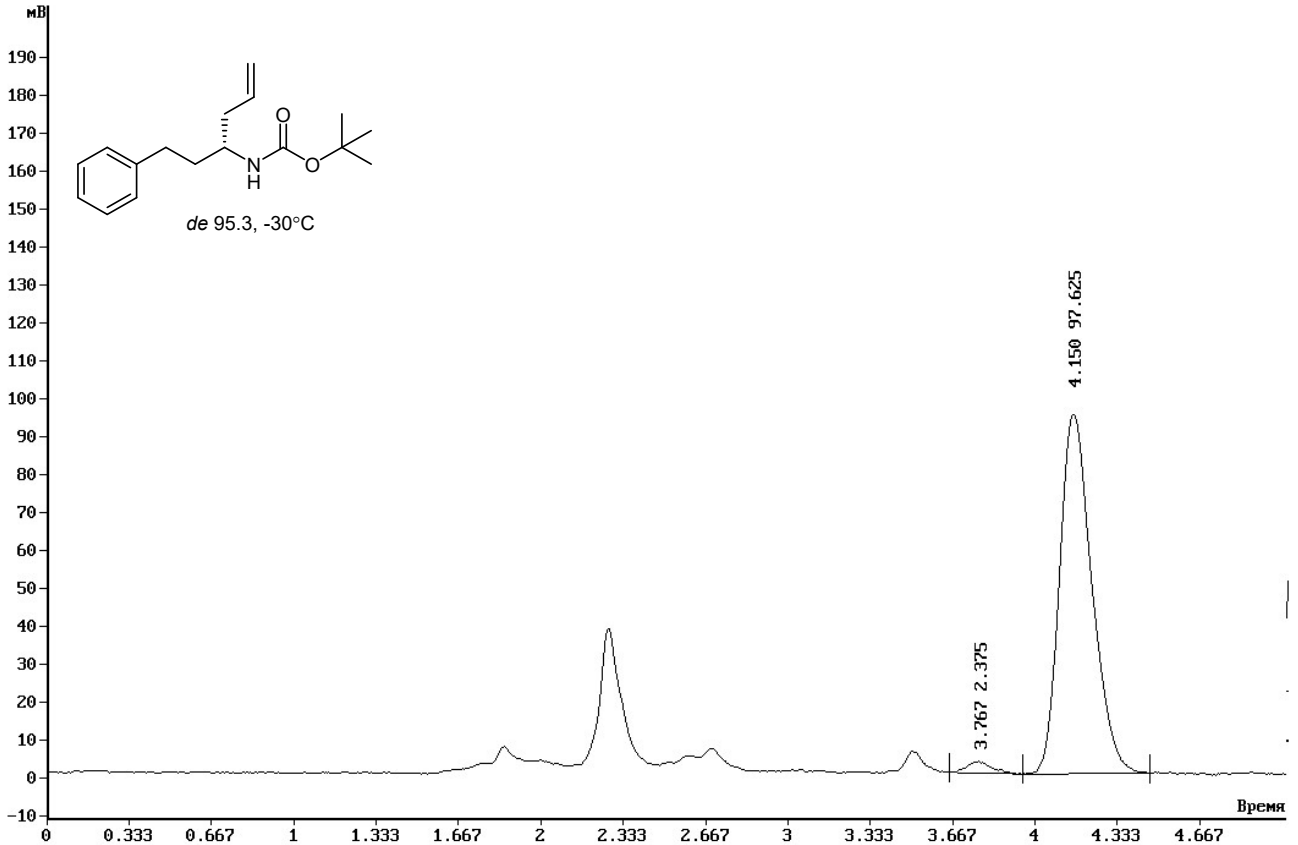
Column Kromasil 3-AmyCoat (150x4.6mm, 5µm), eluent *n*-C_6H_{14}/*iso*-PrOH = 95/5, flow rate 1.0 ml/min, UV 220 nm.





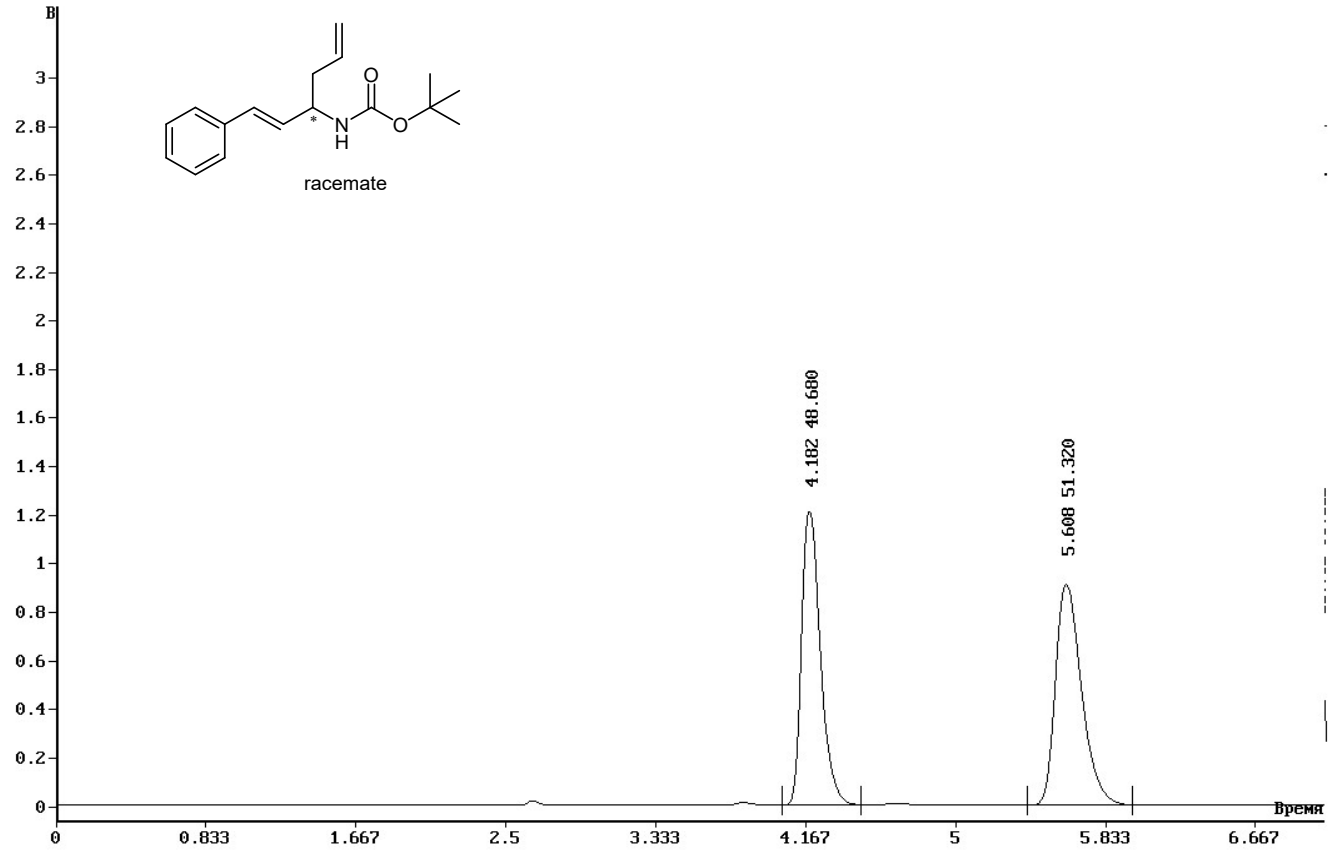
Enantiomeric analysis of *tert*-butyl (*R*)-(1-phenylhex-5-en-3-yl)carbamate (6k).
Column Kromasil 3-AmyCoat (150x4.6mm, 5μm), eluent *n*-C_6H_{14}/*iso*-PrOH = 95/5, flow rate 1.0 ml/min, UV 220 nm.

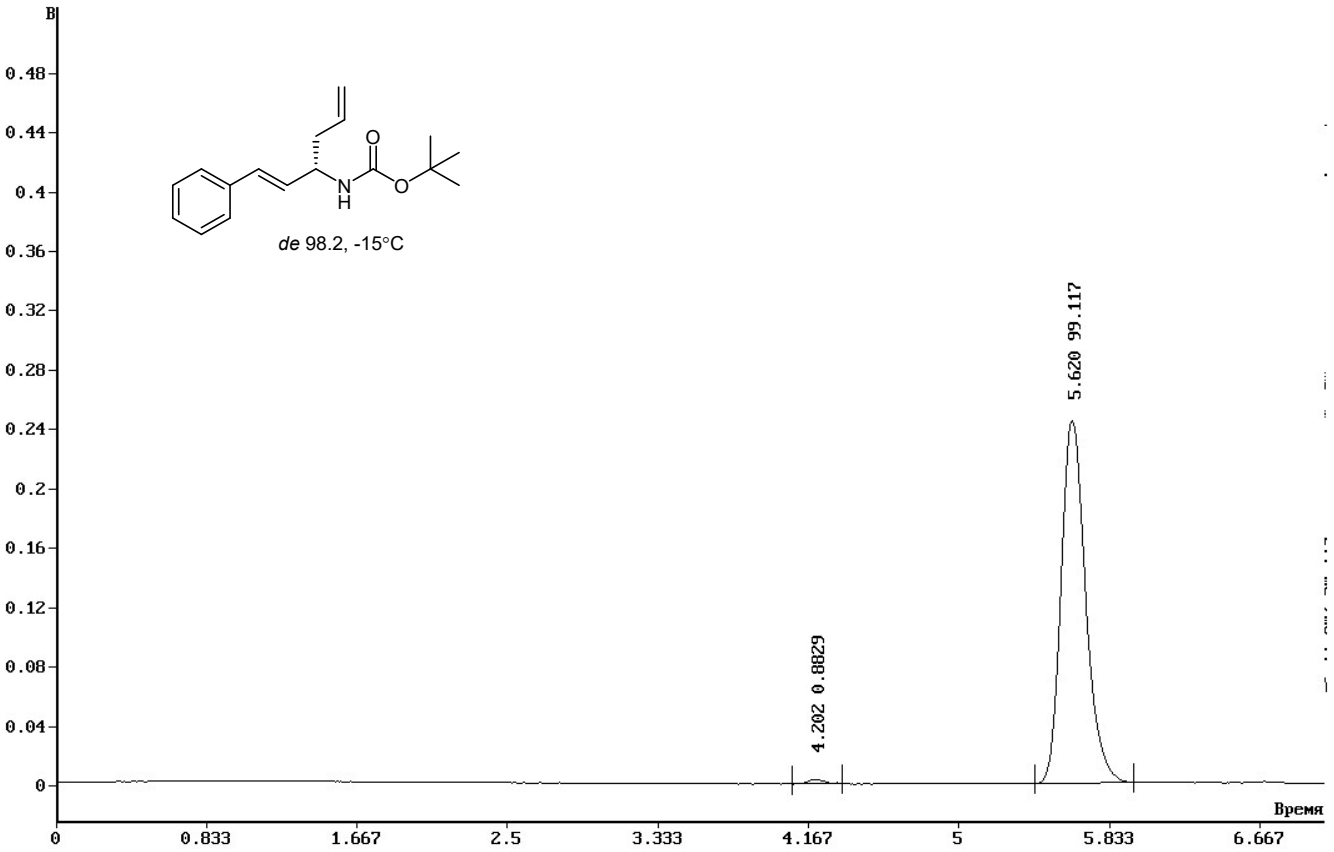




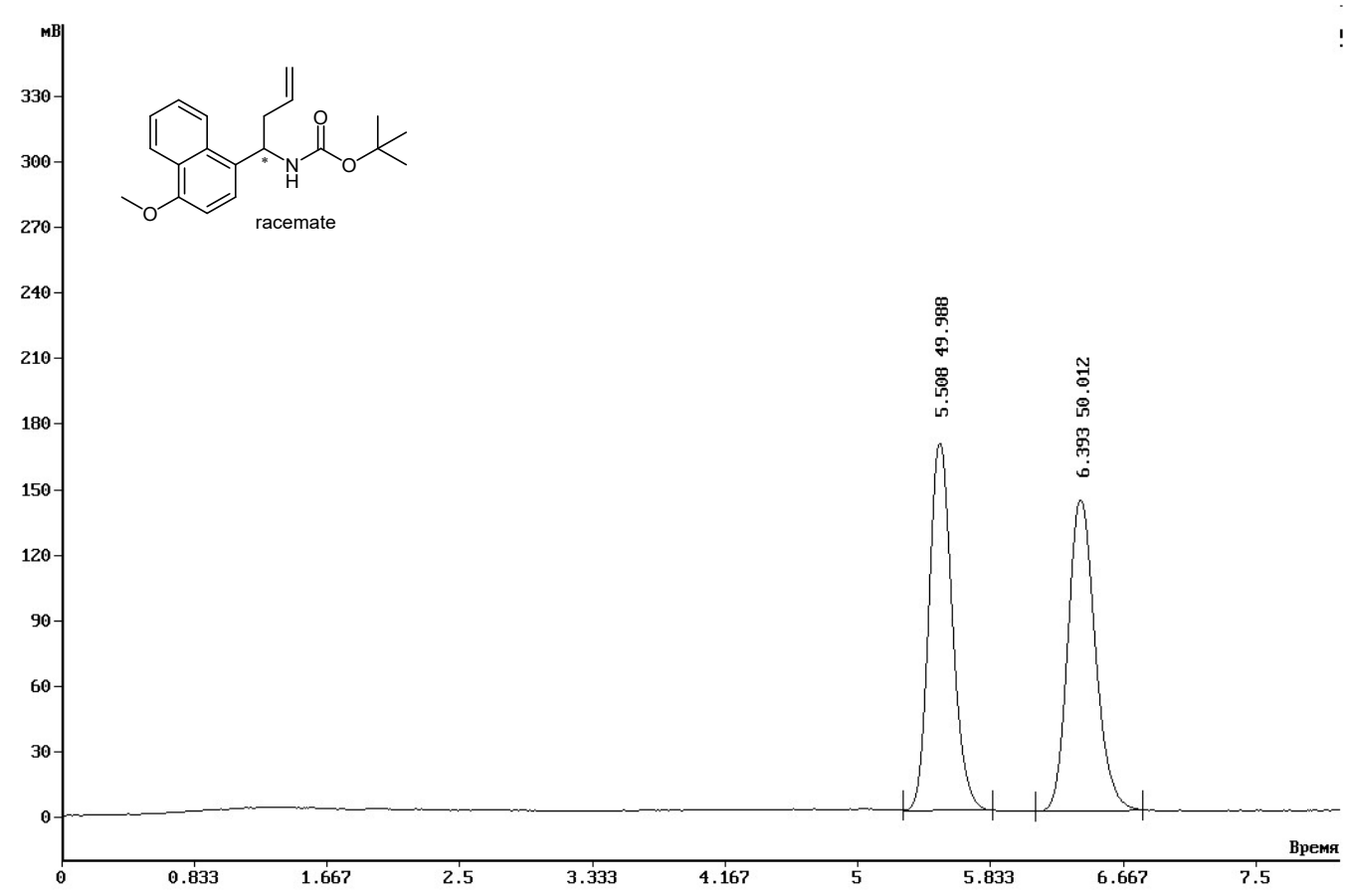
Enantiomeric analysis of *tert*-butyl (*S,E*)-(1-phenylhexa-1,5-dien-3-yl)carbamate (6l).

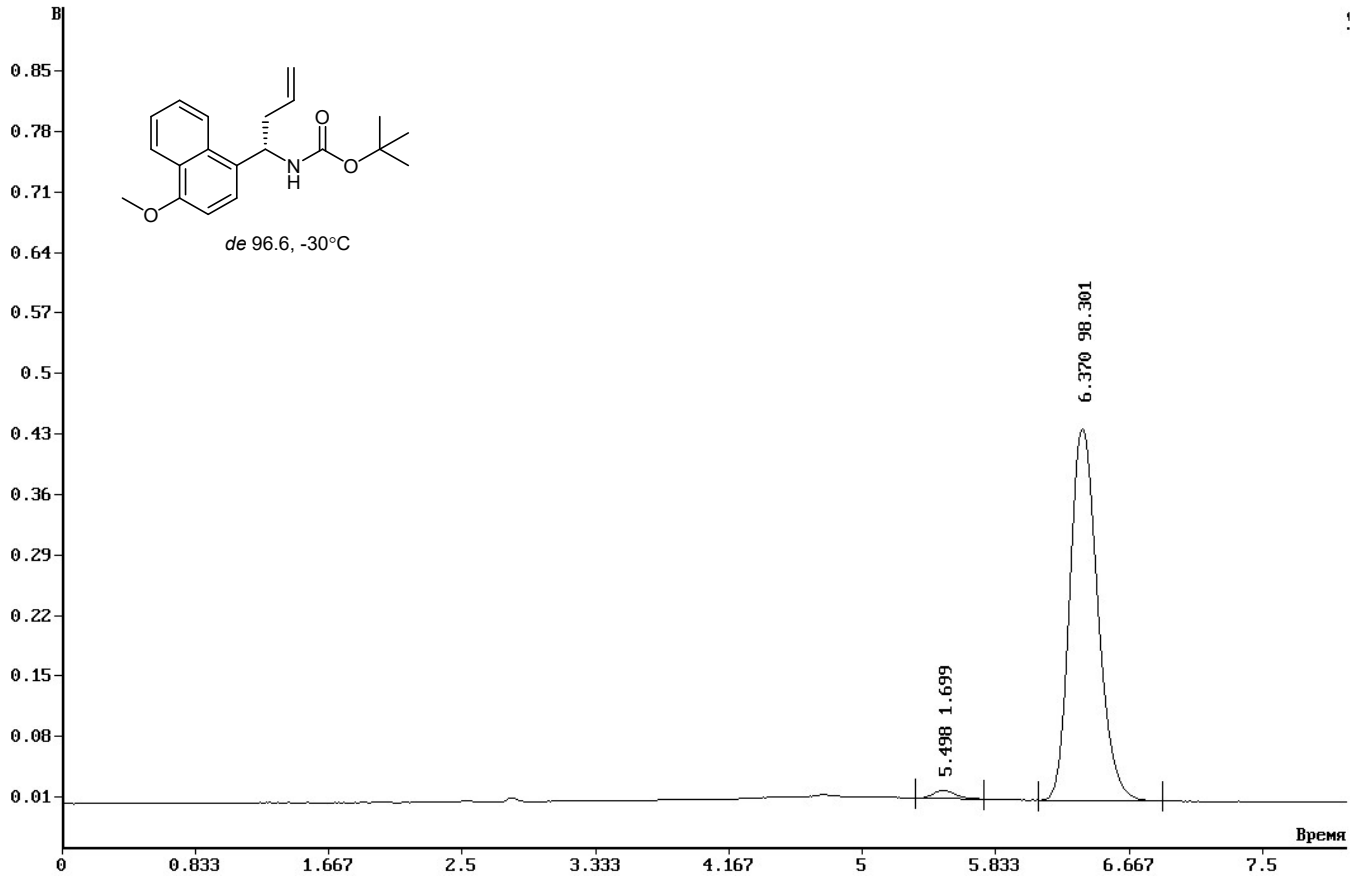
Column Kromasil 3-AmyCoat (150x4.6mm, 5μm), eluent *n*-C_6H_{14}/*iso*-PrOH = 95/5, flow rate 1.0 ml/min, UV 256 nm.



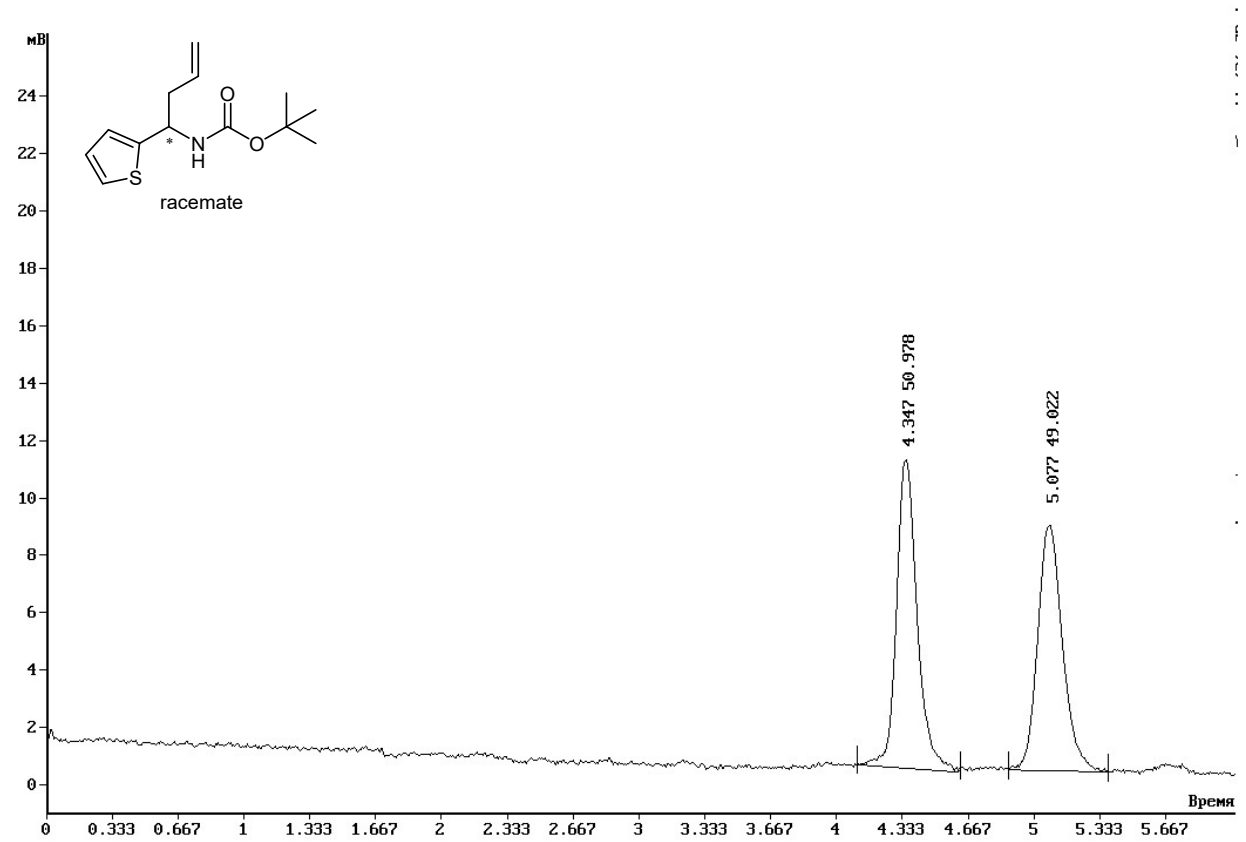


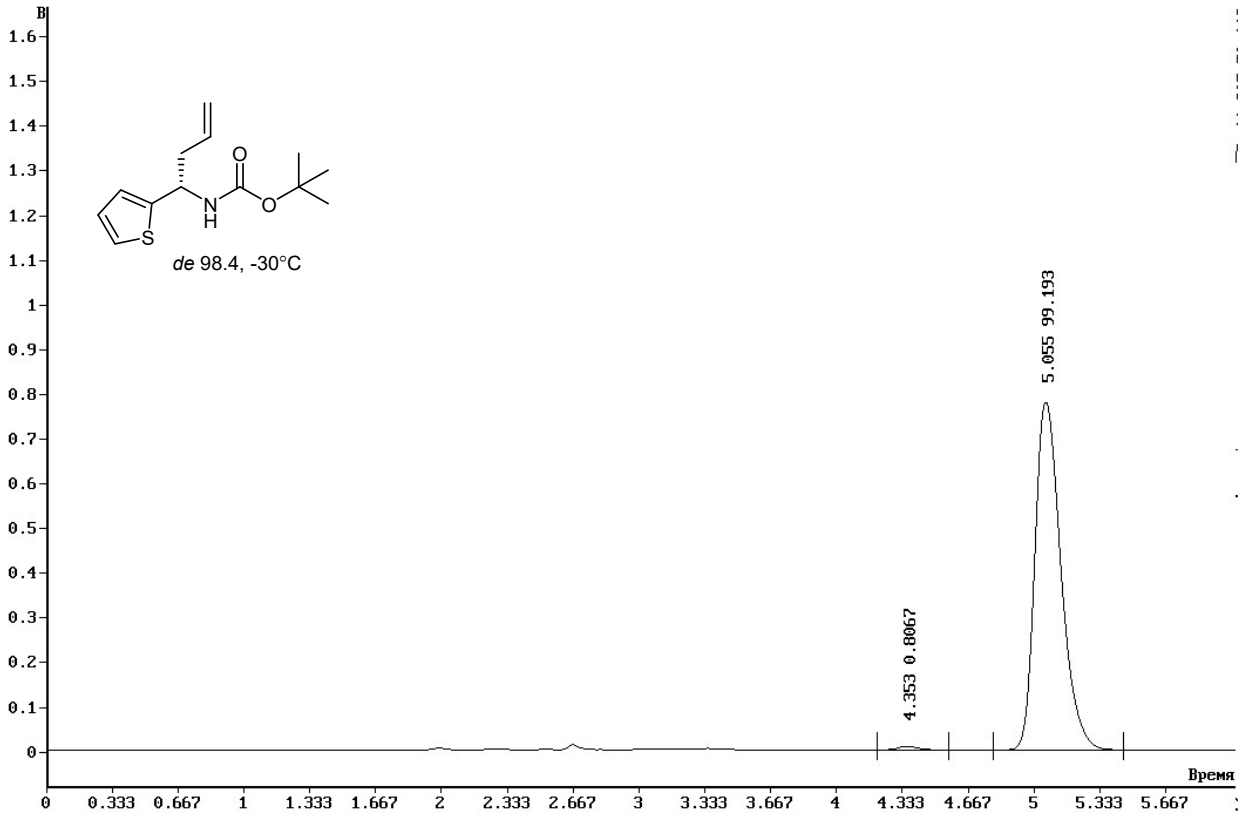
Enantiomeric analysis of *tert*-butyl (*S*)-(1-(4-methoxynaphthalen-1-yl)but-3-en-1-yl)carbamate (6m).
Column Kromasil 3-AmyCoat (150x4.6mm, 5µm), eluent *n*-C_6H_{14}/*iso*-PrOH = 95/5, flow rate 1.0 ml/min, UV 220 nm.



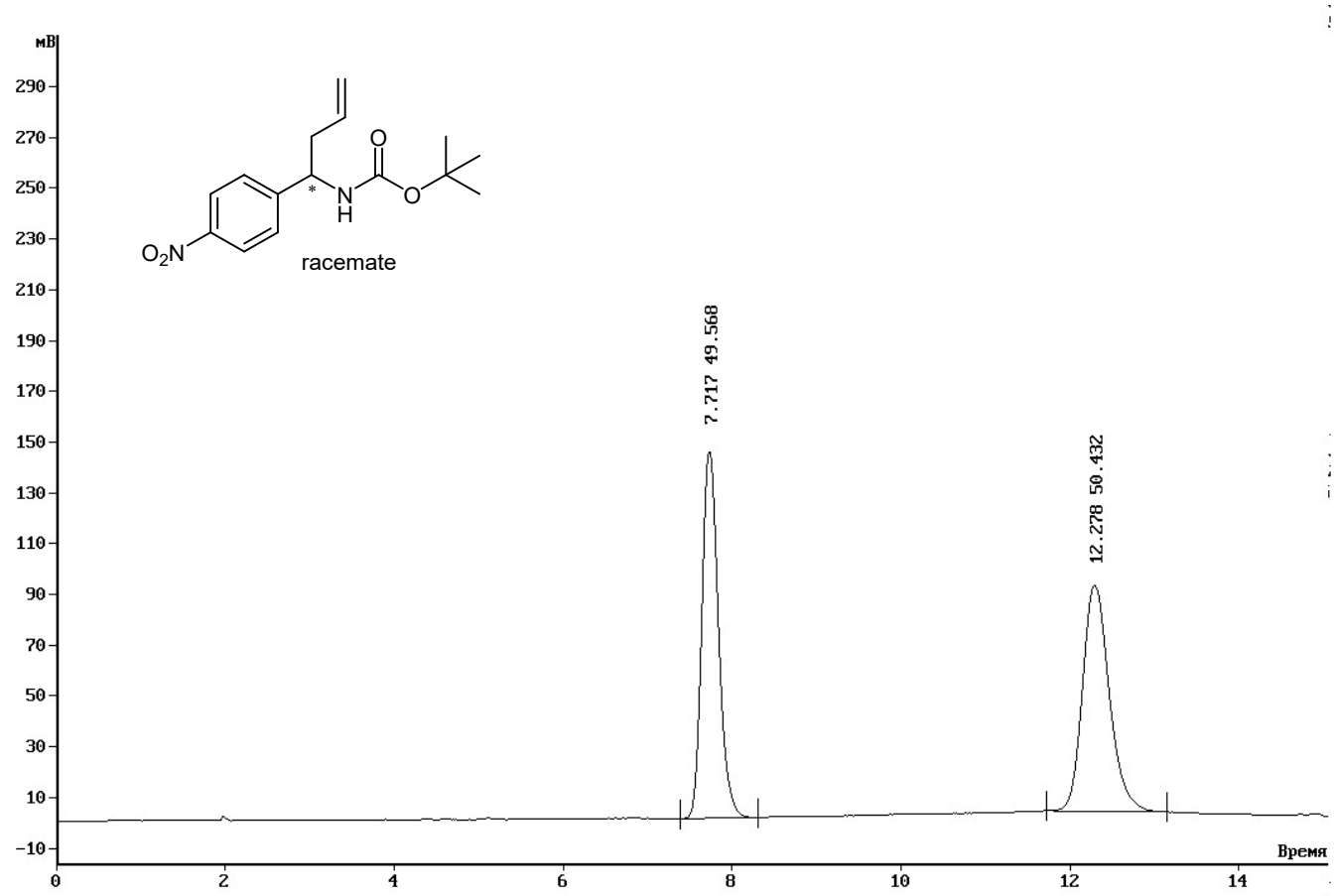


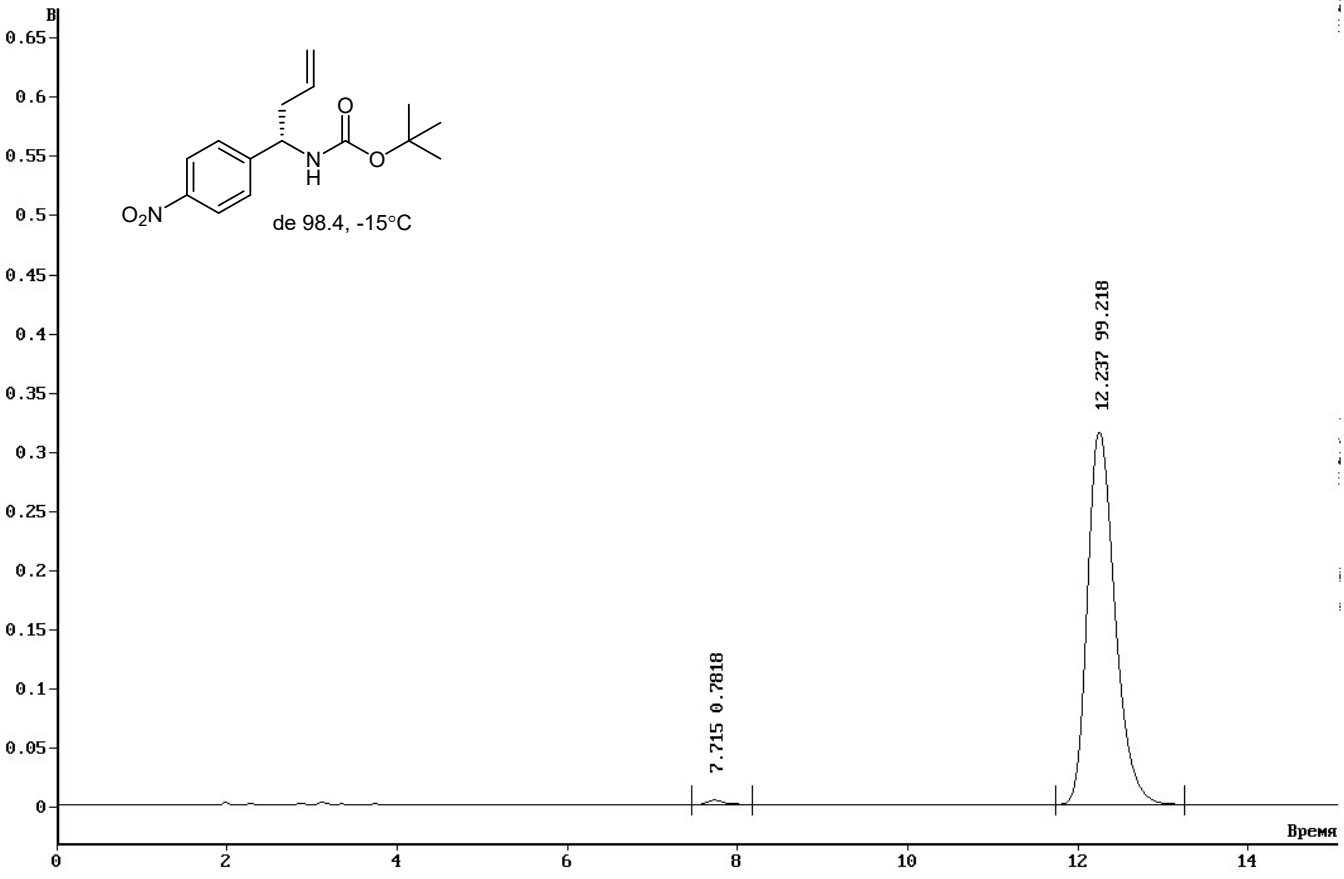
Enantiomeric analysis of *tert*-butyl (*S*)-(1-(thiophen-2-yl)but-3-en-1-yl)carbamate (6n).
Column Kromasil 3-AmyCoat (150x4.6mm, 5μm), eluent *n*-C_6H_{14}/*iso*-PrOH = 95/5, flow rate 1.0 ml/min, UV 233 nm.





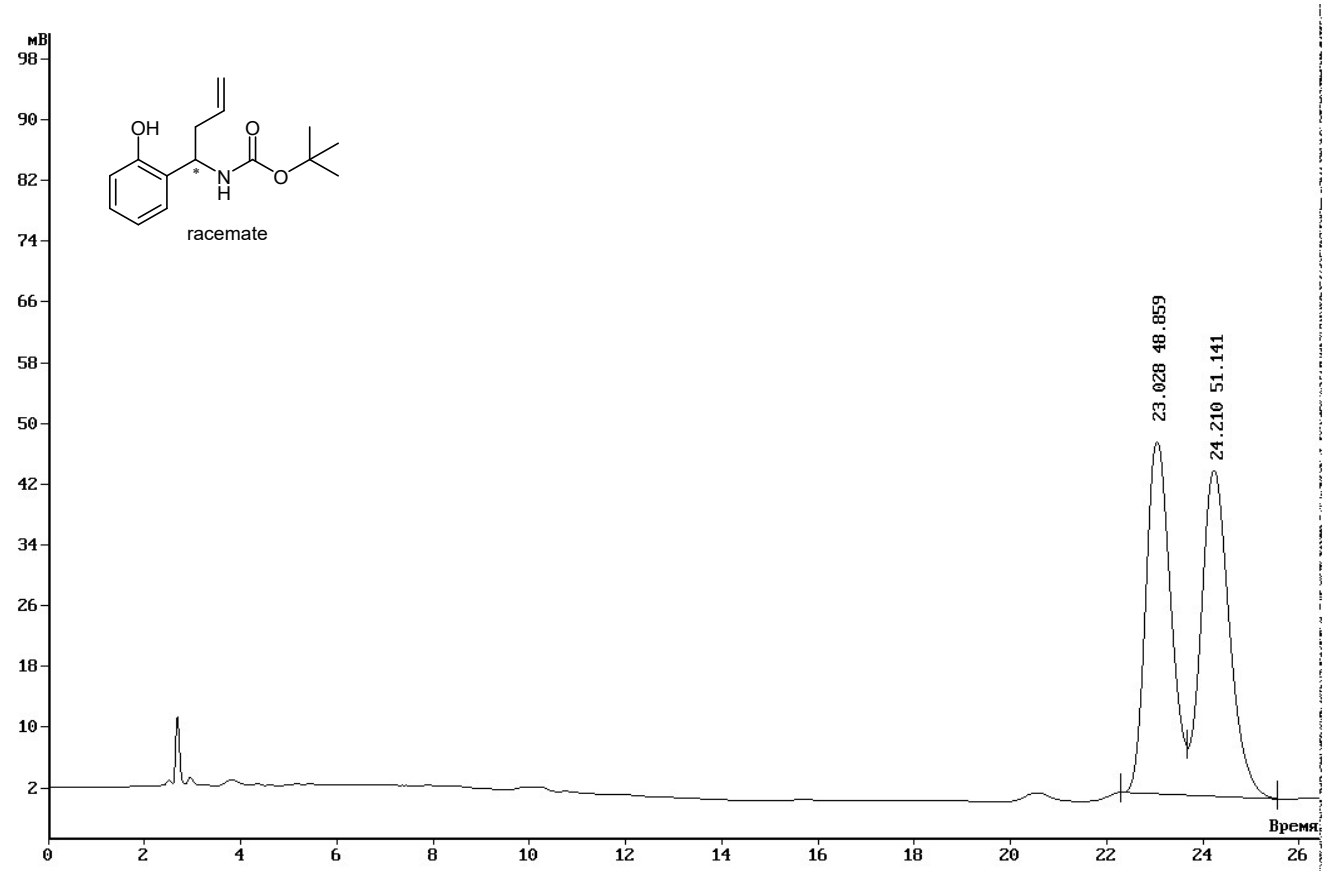
Enantiomeric analysis of *tert*-butyl (*S*)-(1-(4-nitrophenyl)but-3-en-1-yl)carbamate (6o).
Column Kromasil 3-AmyCoat (250x4.6mm, 5μm), eluent *n*-C_6H_{14}/*iso*-PrOH = 95/5, flow rate 1.0 ml/min, UV 220 nm.

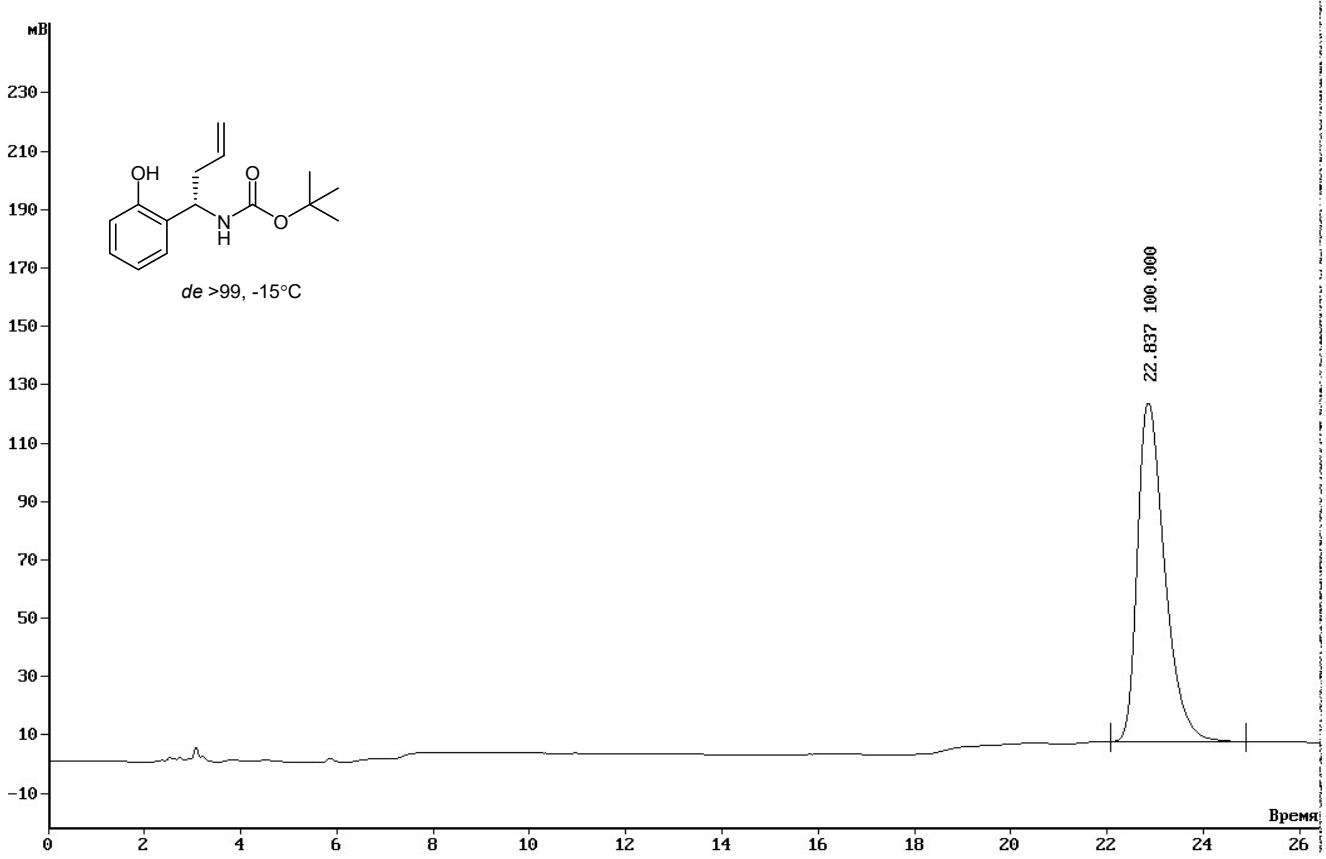




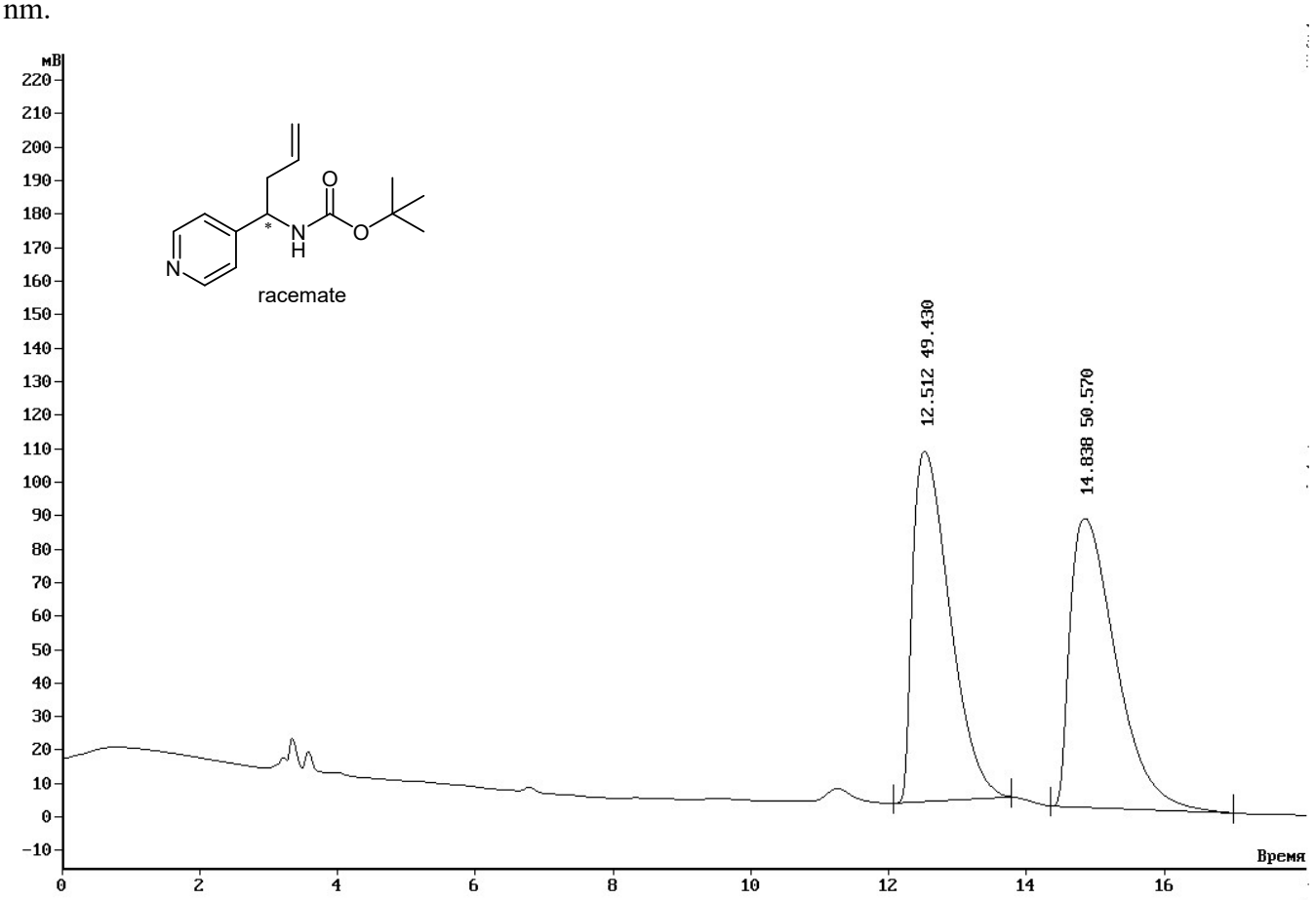
Enantiomeric analysis of *tert*-butyl (*S*)-(1-(2-hydroxyphenyl)but-3-en-1-yl)carbamate (6q).

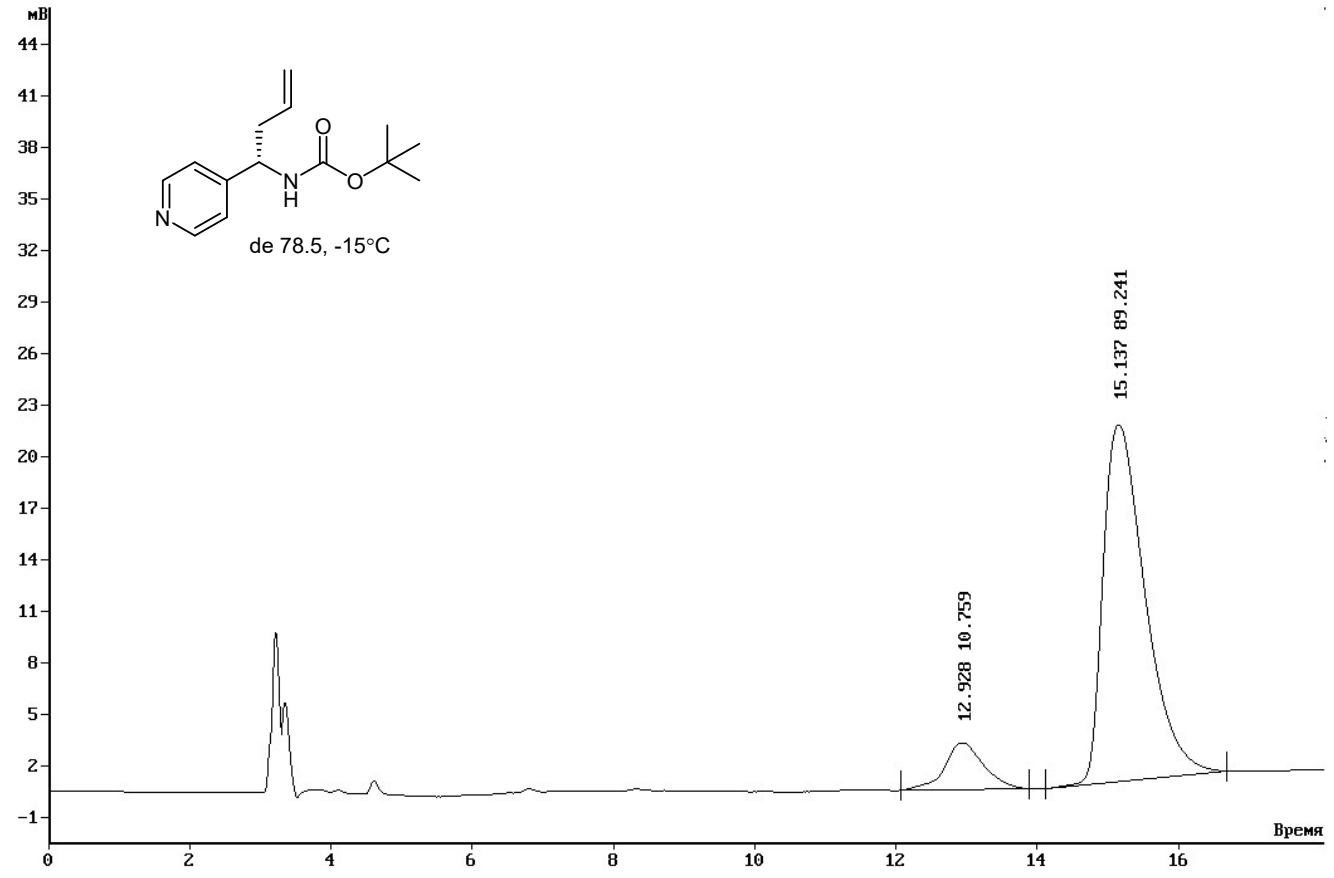
Column Kromasil 3-AmyCoat (150x4.6mm, 5μm), eluent *n*-C_6H_{14}/*iso*-PrOH = 98/2, flow rate 0.75 ml/min, UV 220 nm.



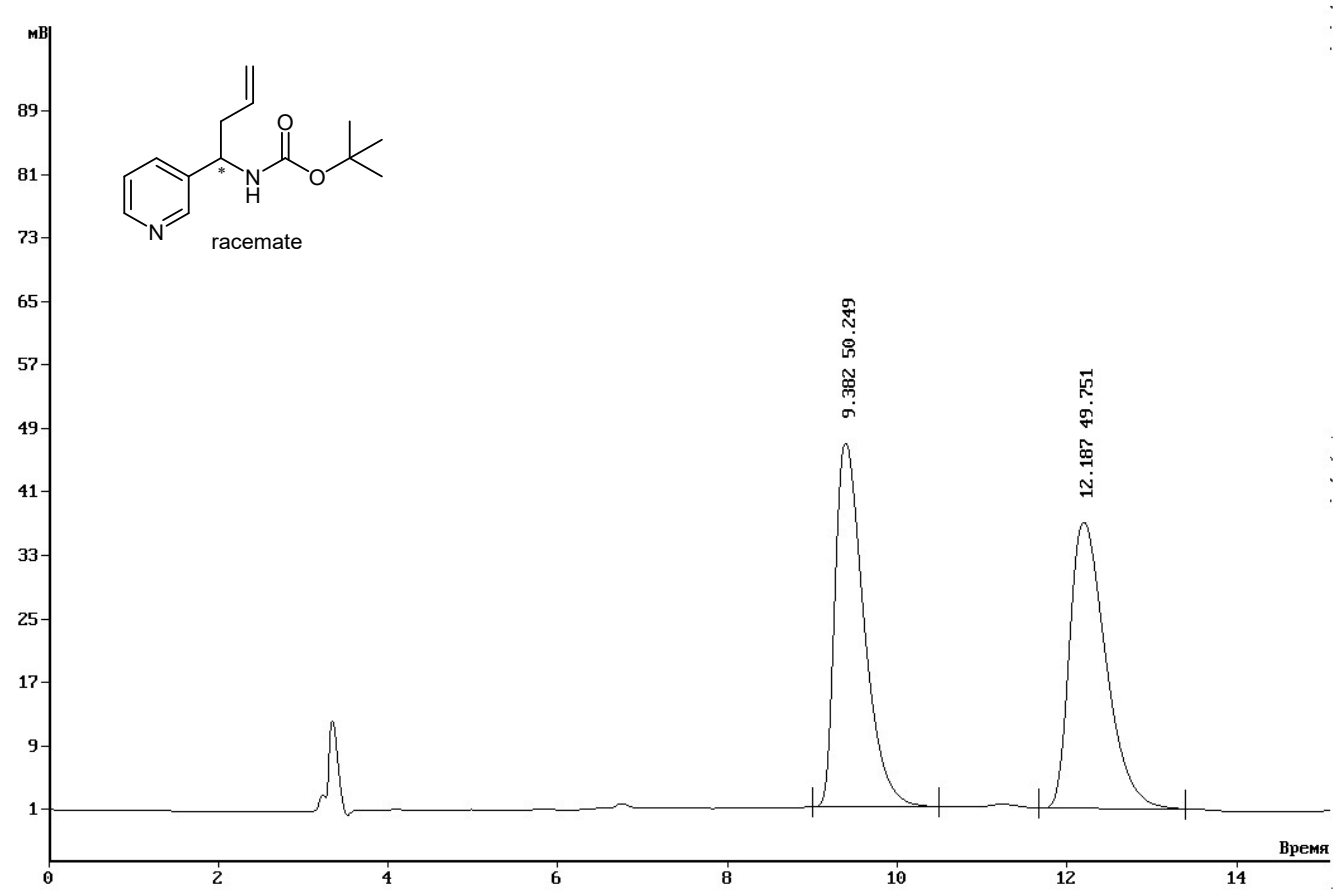


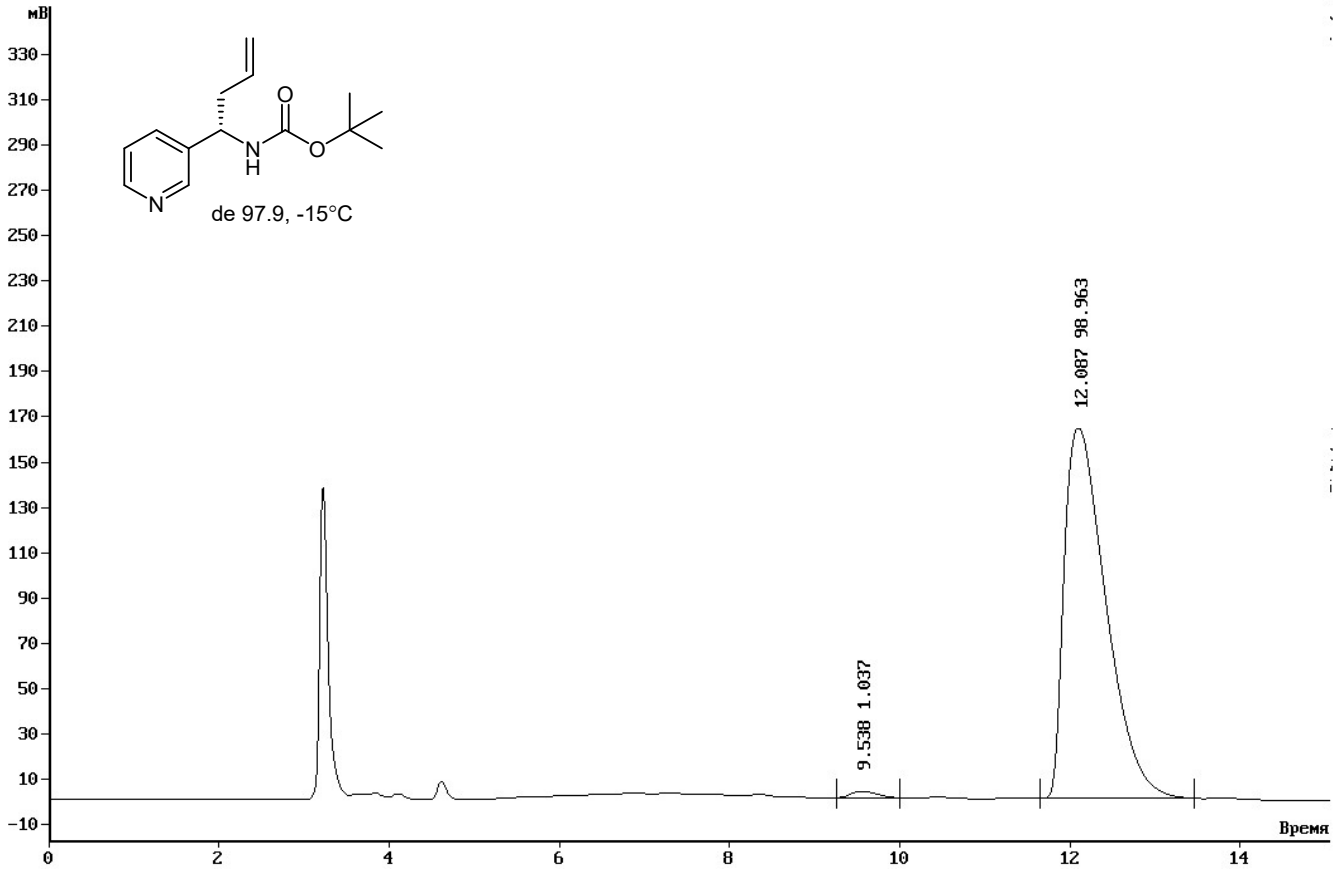
Enantiomeric analysis of *tert*-butyl (*S*)-(1-(pyridin-4-yl)but-3-en-1-yl)carbamate (6r).
Column Chiralpak AS-H (250x4.6mm, 5μm), eluent *n*-C_6H_{14}/*iso*-PrOH = 95/5, flow rate 1.0 ml/min, UV 220 nm.



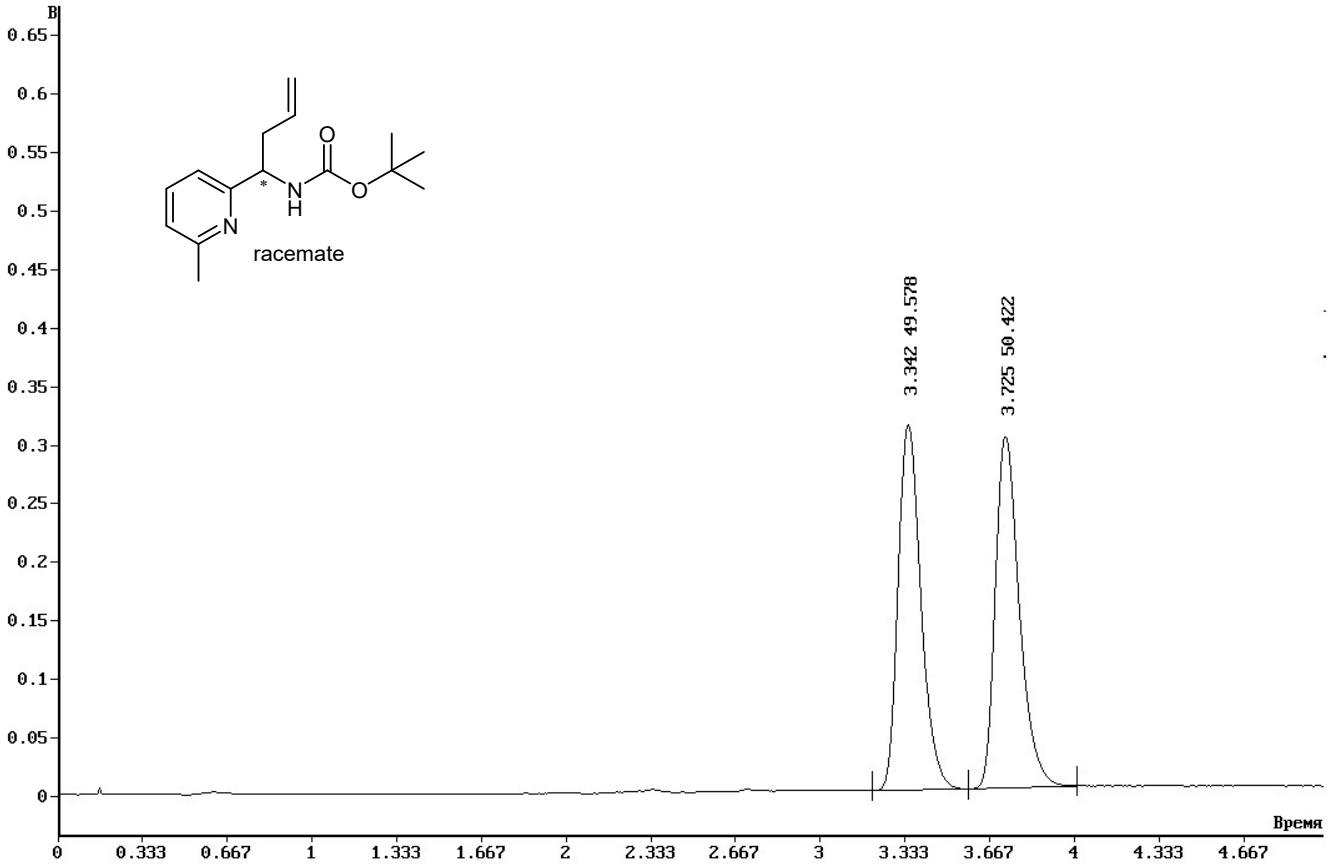


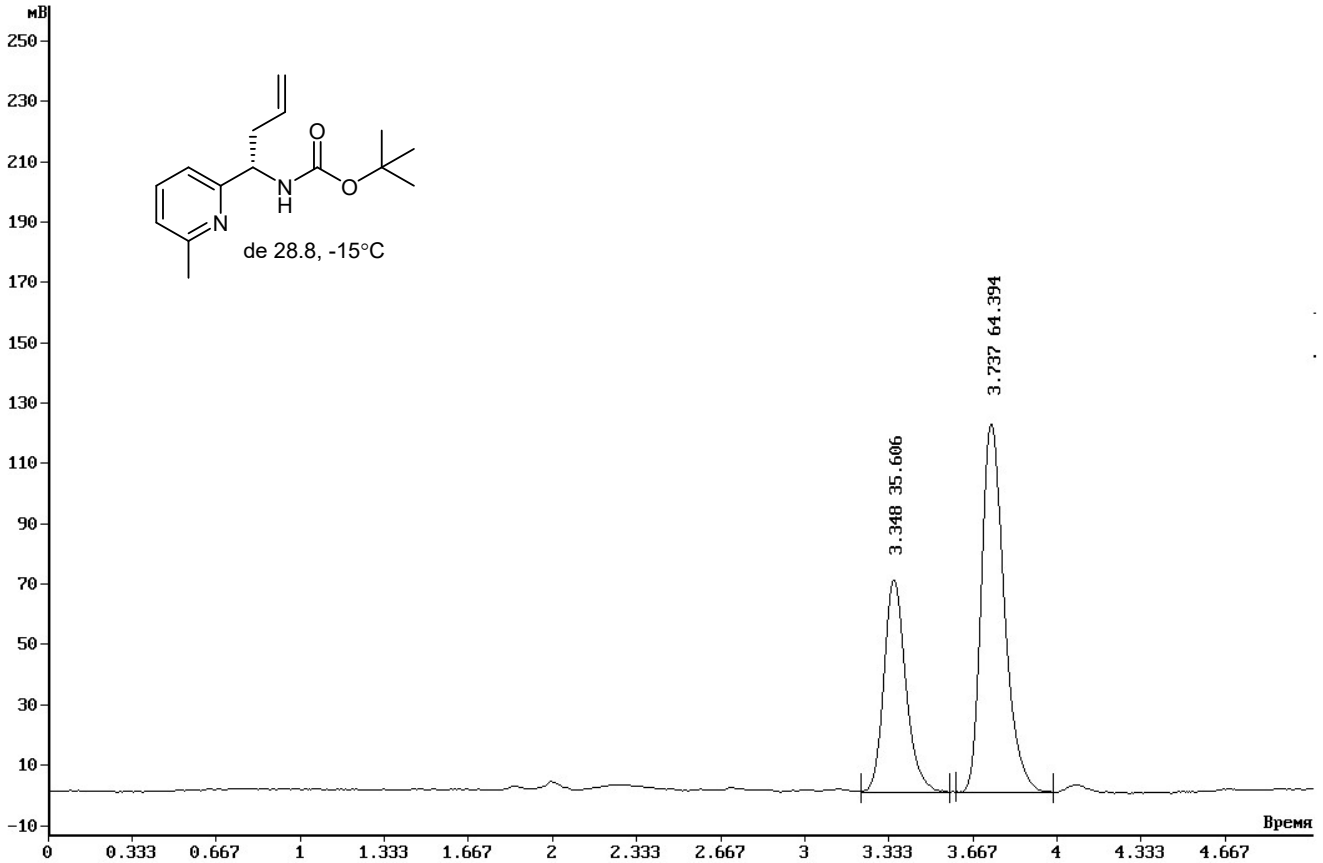
Enantiomeric analysis of *tert*-butyl (*S*)-(1-(pyridin-3-yl)but-3-en-1-yl)carbamate (6s).
Column Chiralpak AS-H (250x4.6mm, 5μm), eluent *n*-C_6H_{14}/*iso*-PrOH = 95/5, flow rate 1.0 ml/min, UV 220 nm.





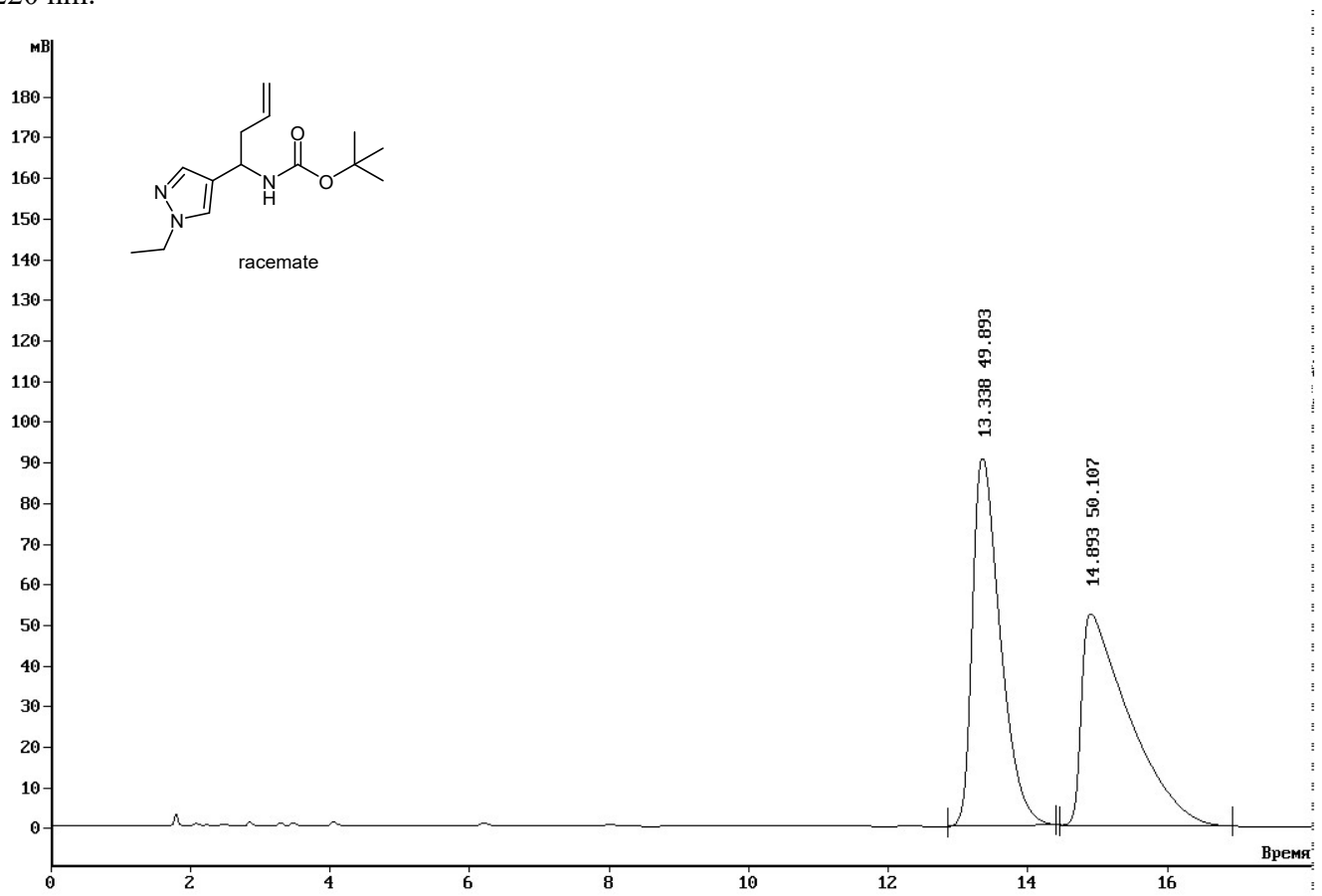
Enantiomeric analysis of *tert*-butyl (*S*)-(1-(6-methylpyridin-2-yl)but-3-en-1-yl)carbamate (6u).
Column Kromasil 3-AmyCoat (150x4.6mm, 5μm), eluent *n*-C_6H_{14}/*iso*-PrOH = 95/5, flow rate 1.0 ml/min, UV 220 nm.

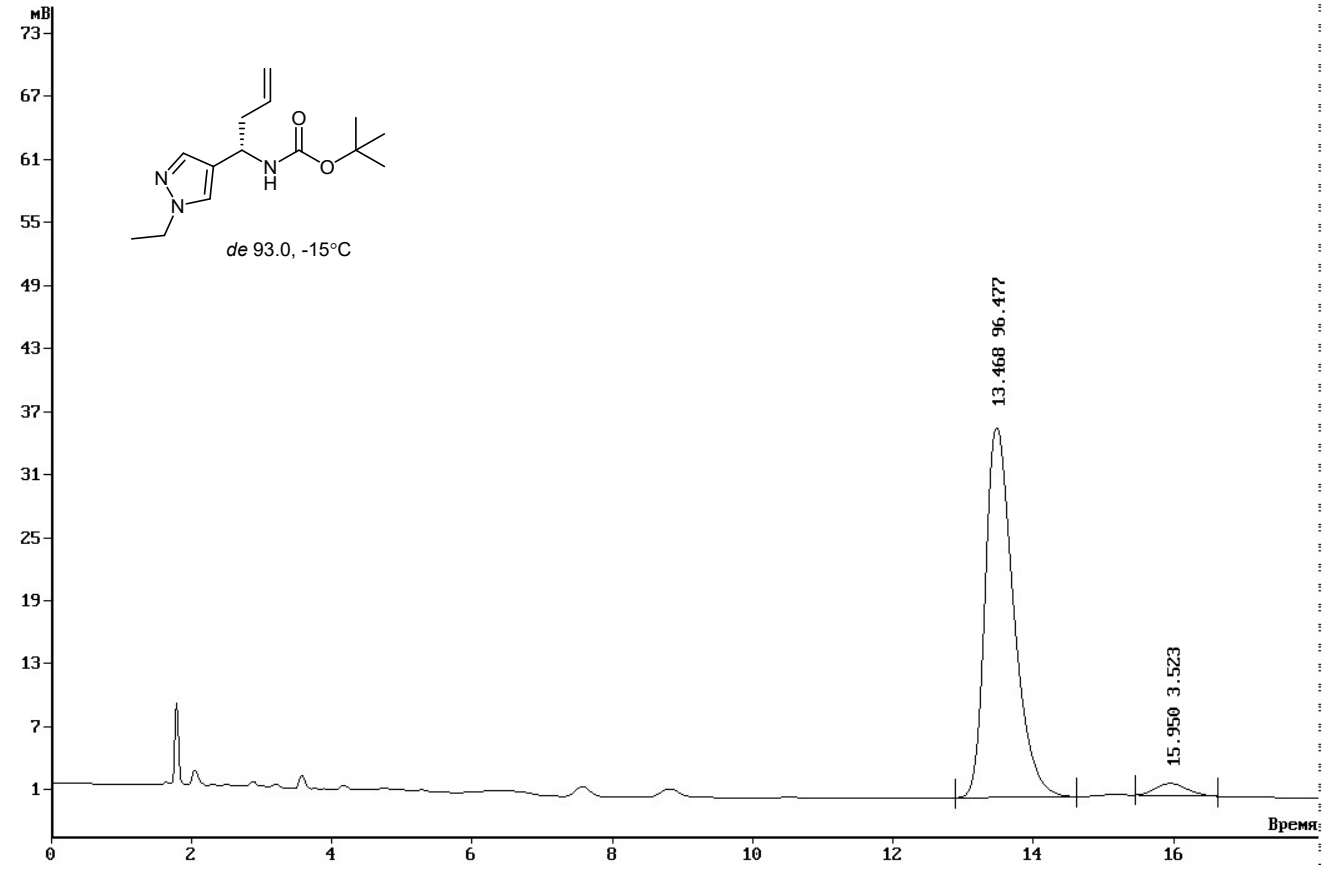




Enantiomeric analysis of *tert*-butyl (*S*)-(1-(1-ethyl-1*H*-pyrazol-4-yl)but-3-en-1-yl)carbamate (6v).

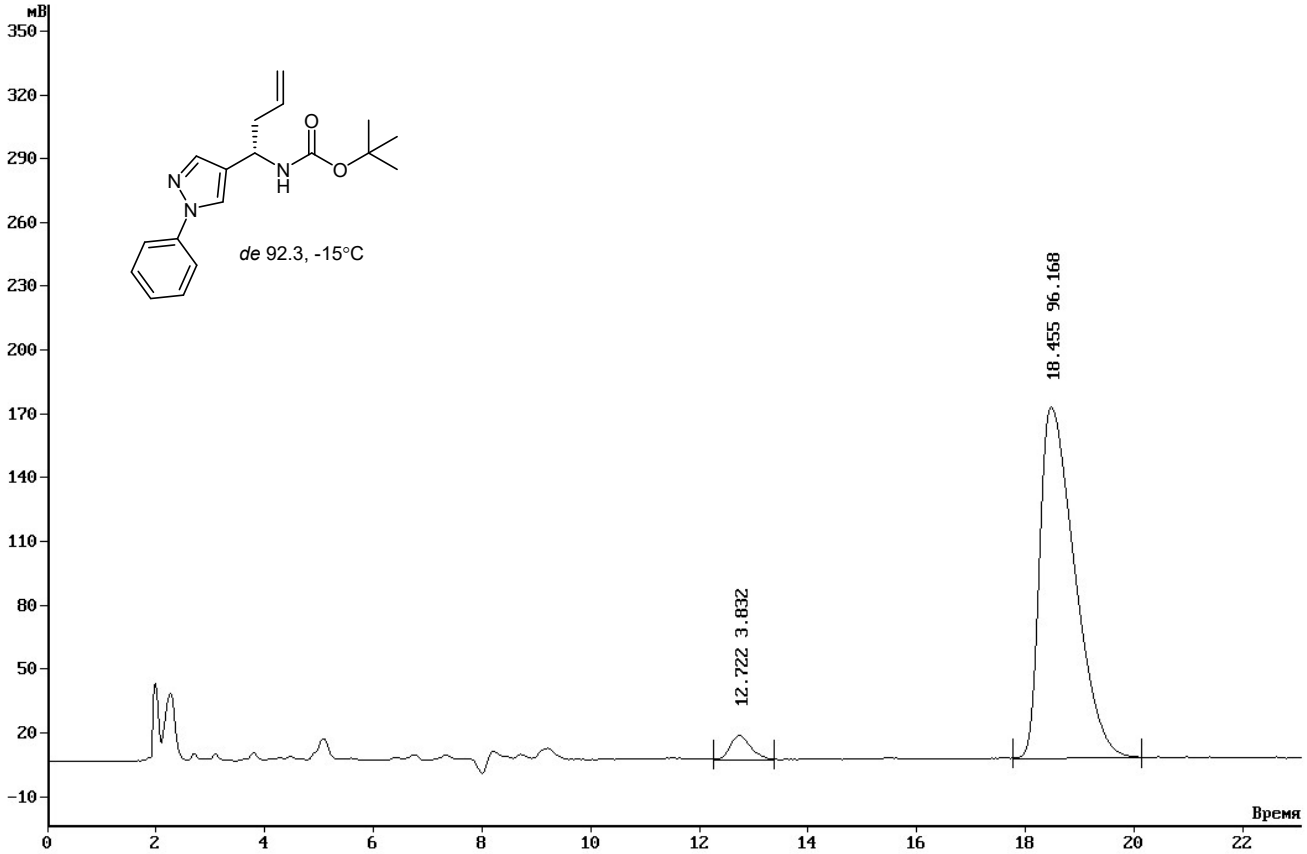
Column ASTEC ChiraleDEX (150x4.6mm, 5µm), eluent *n*-C_6H_{14}/*iso*-PrOH = 98/2, flow rate 1.0 ml/min, UV 220 nm.

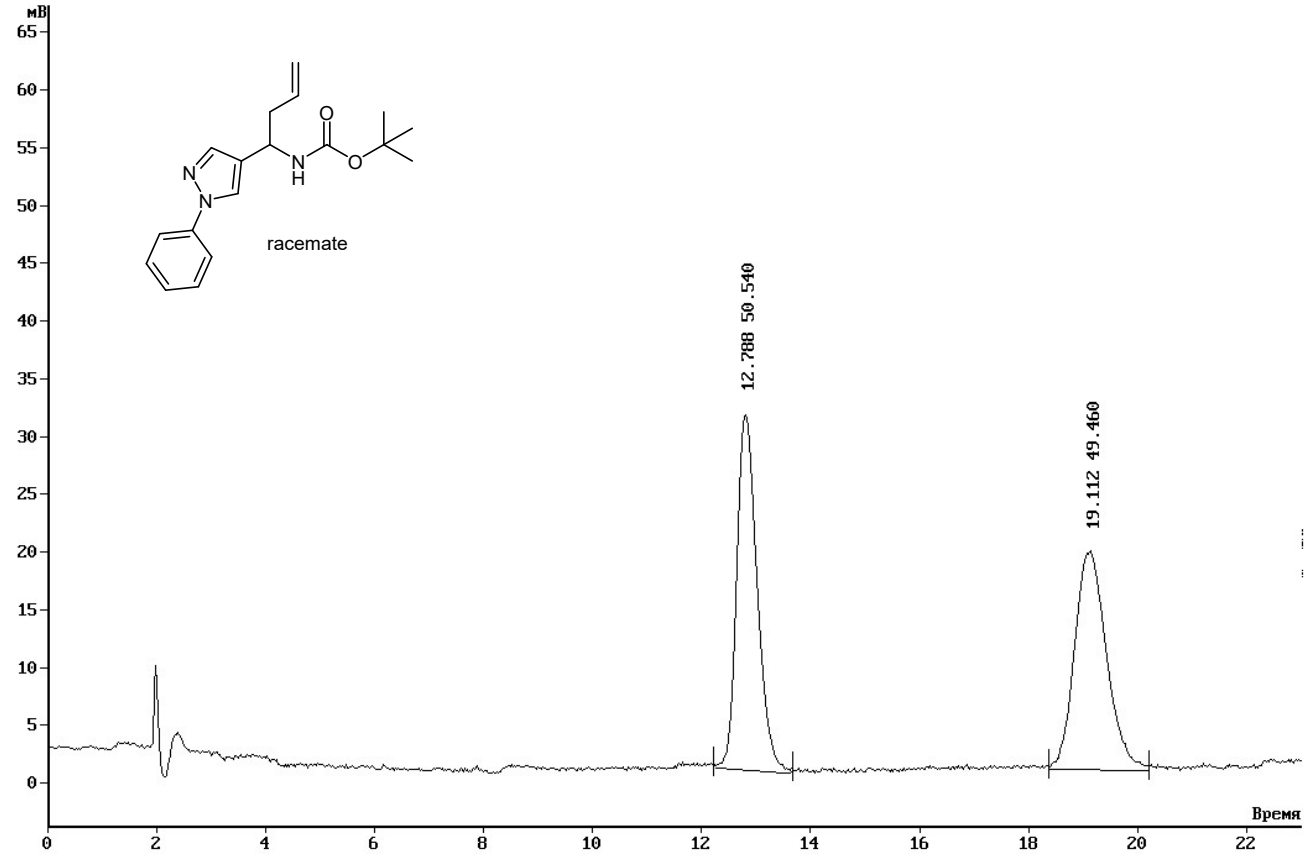




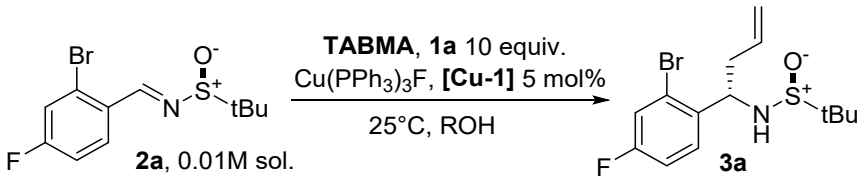
Enantiomeric analysis of *tert*-butyl (*S*)-(1-(1-phenyl-1*H*-pyrazol-4-yl)but-3-en-1-yl)carbamate (6w).

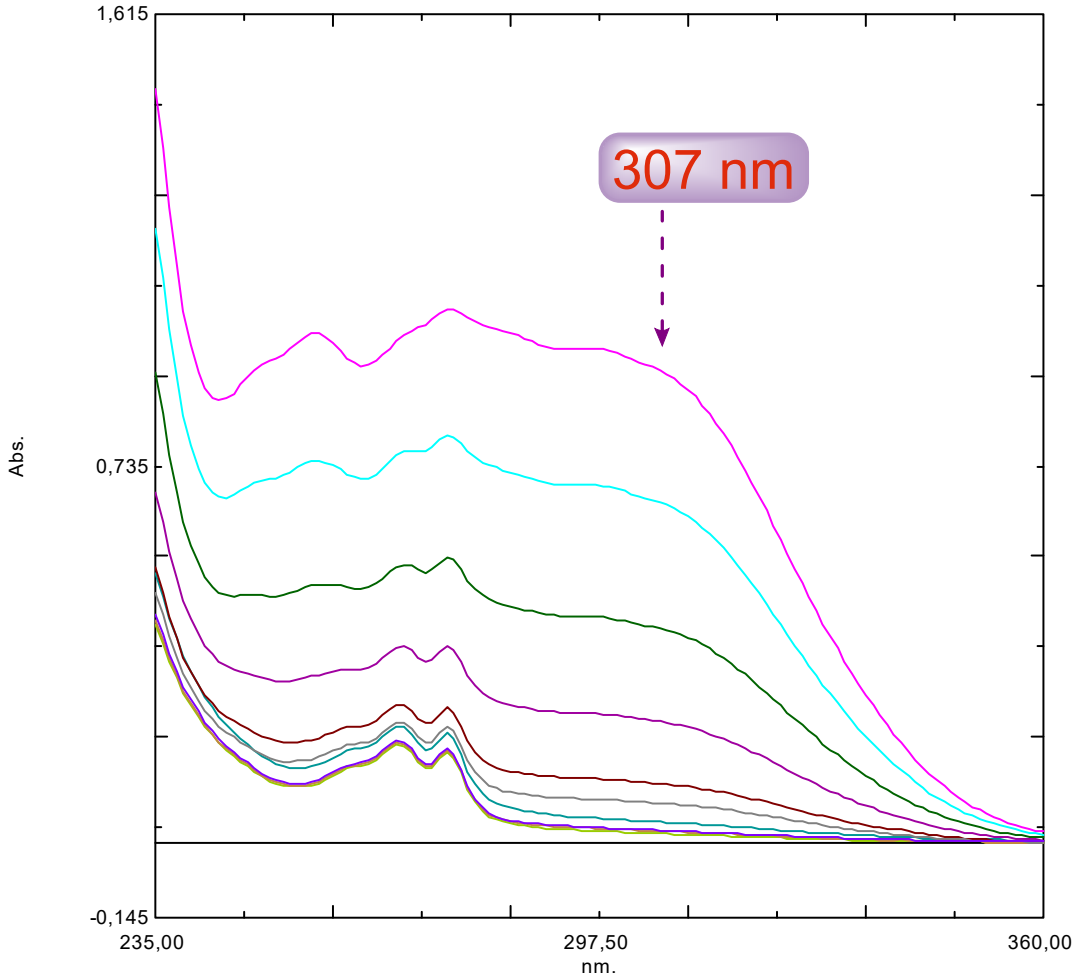
Column Kromasil 3-AmyCoat (150x4.6mm, 5μm), eluent *n*-C_6H_{14}/*iso*-PrOH = 95/5, flow rate 1.0 ml/min, UV 220 nm.





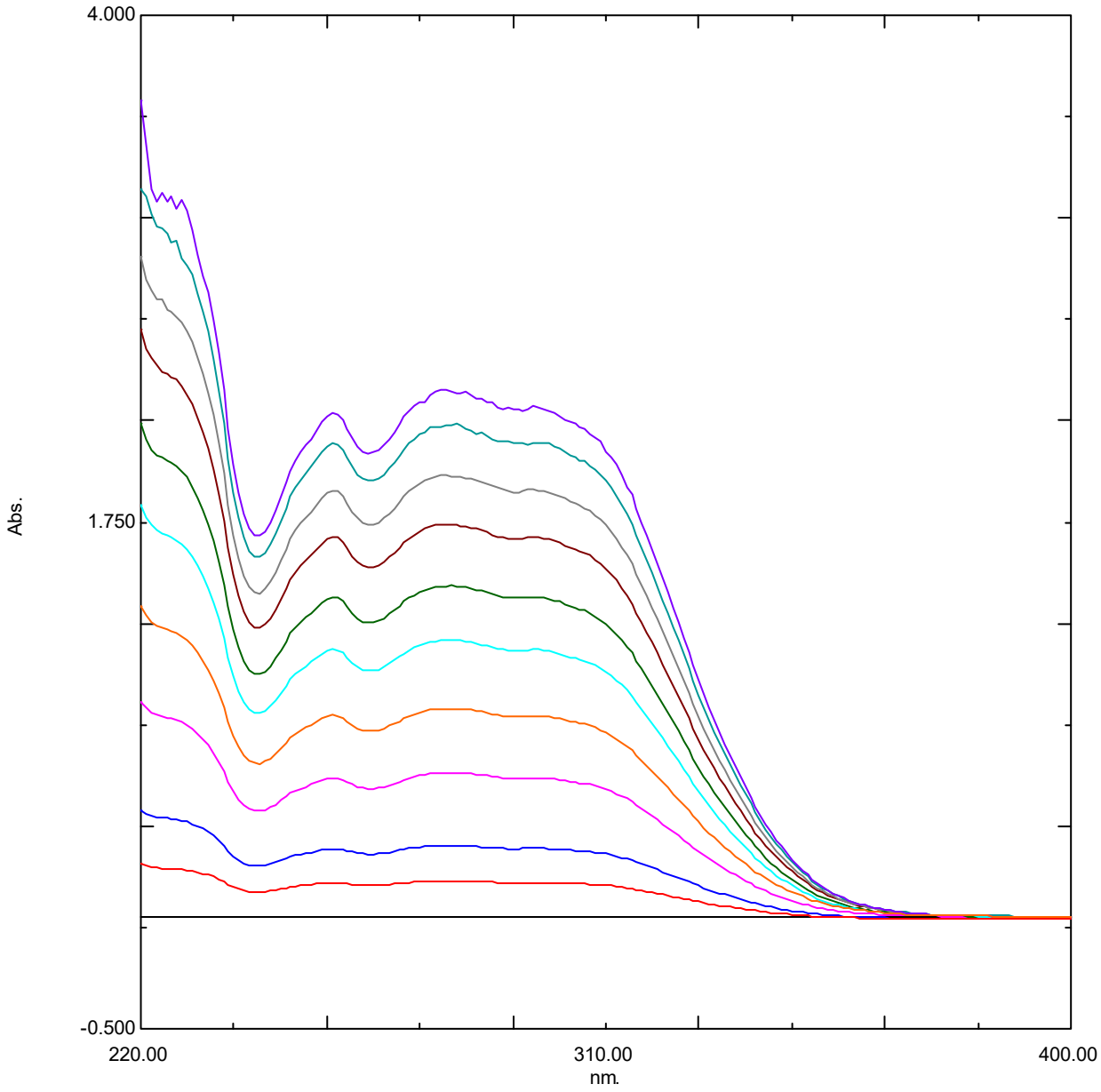
Rate constant determination tables and plots

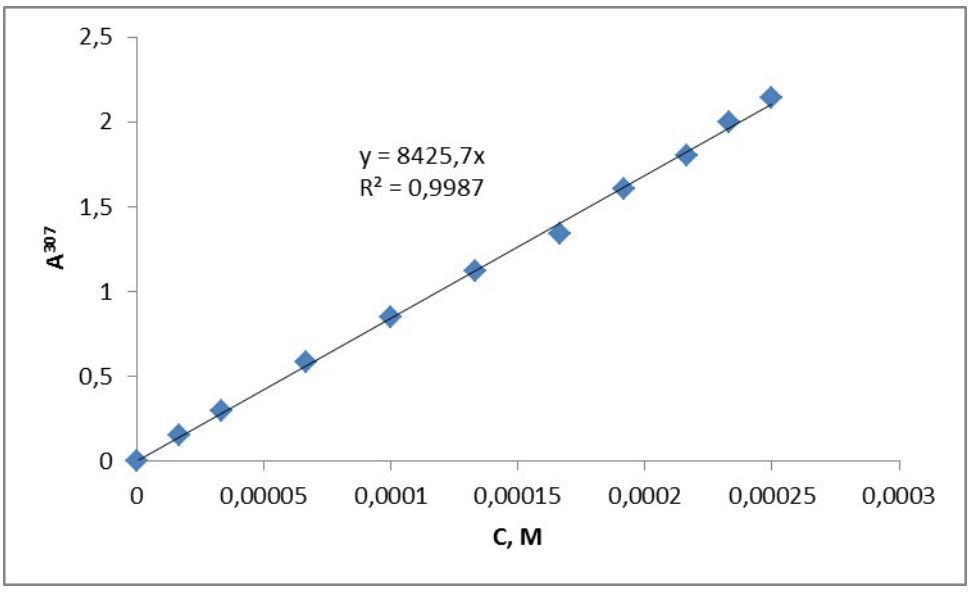




Calibration curve of imine 2a in *i*PrOH

№	C, μM	A^{307}
0	0	0
1	16.7	0.153
2	33.3	0.298
3	66.7	0.584
4	100.0	0.845
5	133.3	1.123
6	166.7	1.343
7	191.7	1.603
8	216.7	1.801
9	233.3	1.997
10	250.0	2.139





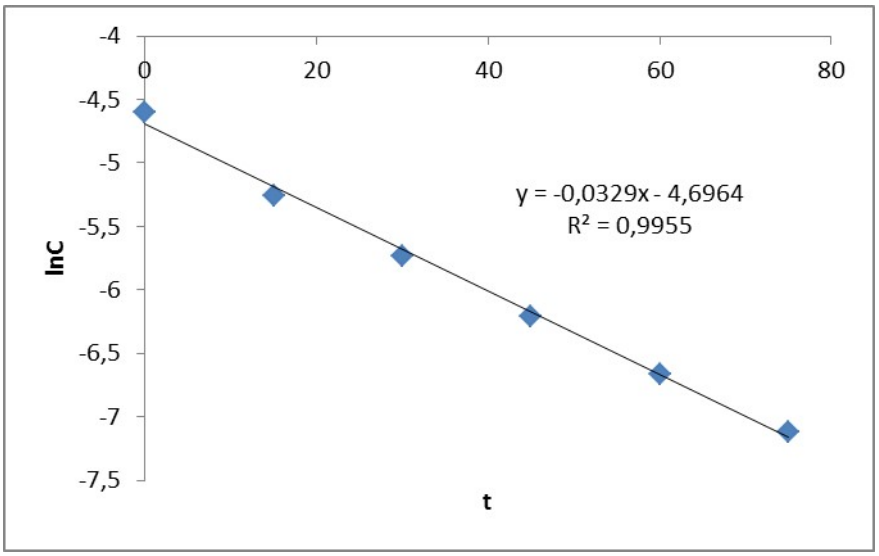
$\varepsilon^{307} = 8425 \pm 225\ cm^{-1}M^{-1}$

Rate constants of allylation of imine 2a with 1a in alcohols (Table 1 of the main text)

- **2-Propanol**

Conditions of experiment: 2Br-4F-Ph Ellman's imine **2a** (200 µl, 0.04 M), 5 mol% $Cu(PPh_3)_3F*2EtOH$ **[Cu-1]** (200 µl, 0.002 M), 10 eq. TABMA **1a** (400 µl, 0.2 M), solvent – *i*PrOH, T = 25.0 °C.

№	A^{307}	t, sec	c, M	lnC
0	1,386	0	0,0100	-4,6017
1	0,718	15	0,0052	-5,2594
2	0,449	30	0,0033	-5,7288
3	0,278	45	0,0020	-6,2082
4	0,177	60	0,0013	-6,6597
5	0,112	75	0,0008	-7,1173
6	0,047	**900**	0,0003	-7,9857

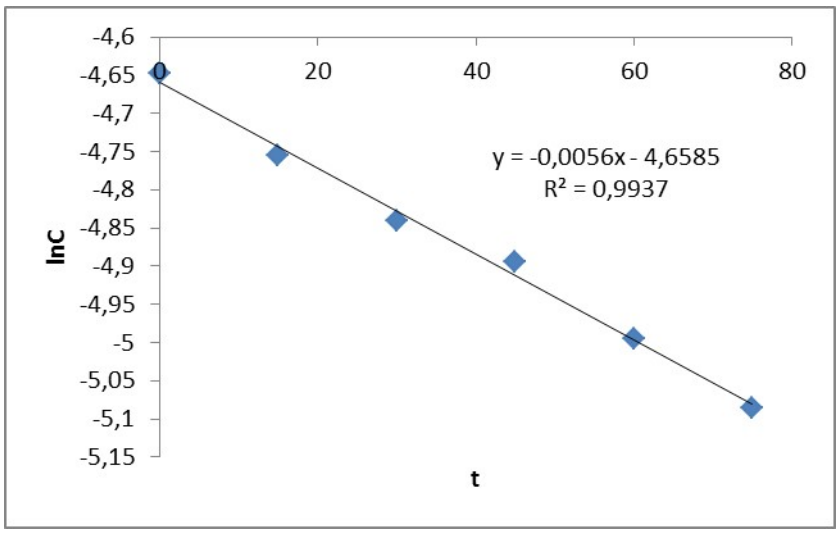


$k_{obs} = 32.9 \pm 2.2 \times 10^{-3} s^{-1}$

- ***tert*-Buthanol**

Conditions of experiment: 2Br-4F-Ph Ellman's imine **2a** (200 µl, 0.04 M), 5 mol% $Cu(PPh_3)_3F*2EtOH$ **[Cu-1]** (200 µl, 0.002 M), 10 eq. TABMA **1a** (400 µl, 0.2 M), solvent – *t*BuOH, T = 25.0 °C.

№	A^{307}	t, sec	c, M	lnC
0	1,323	0	0,0096	-4,6482
1	1,189	15	0,0086	-4,7550
2	1,091	30	0,0079	-4,8410
3	1,035	45	0,0075	-4,8937
4	0,936	60	0,0068	-4,9942
5	0,855	75	0,0062	-5,0847
6	0,689	**900**	0,0050	-5,3006

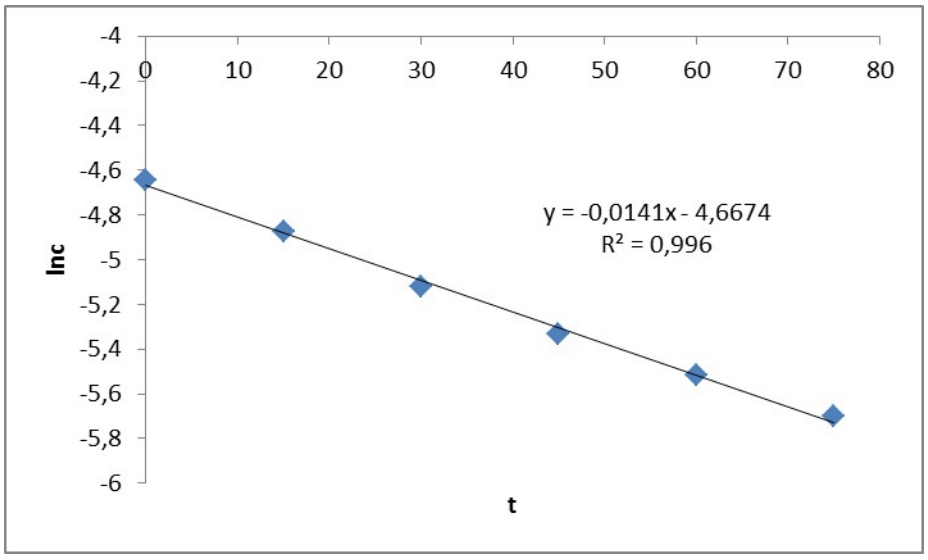


$k_{obs} = 5.6 \pm 0.6 \times 10^{-3} s^{-1}$

- **Ethanol**

Conditions of experiment: 2Br-4F-Ph Ellman's imine **2a** (200 µl, 0.04 M), 5 mol% $Cu(PPh_3)_3F*2EtOH$ **[Cu-1]** (200 µl, 0.002 M), 10 eq. TABMA **1a** (400 µl, 0.2M), solvent – EtOH, T = 25.0 °C.

№	A^{307}	t, sec	c, M	lnC
0	1,331	0	0,0096	-4,6422
1	1,055	15	0,0076	-4,8745
2	0,826	30	0,0060	-5,1192
3	0,667	45	0,0048	-5,3331
4	0,556	60	0,0040	-5,5151
5	0,463	75	0,0034	-5,6981
6	0,095	**900**	0,0007	-7,2820

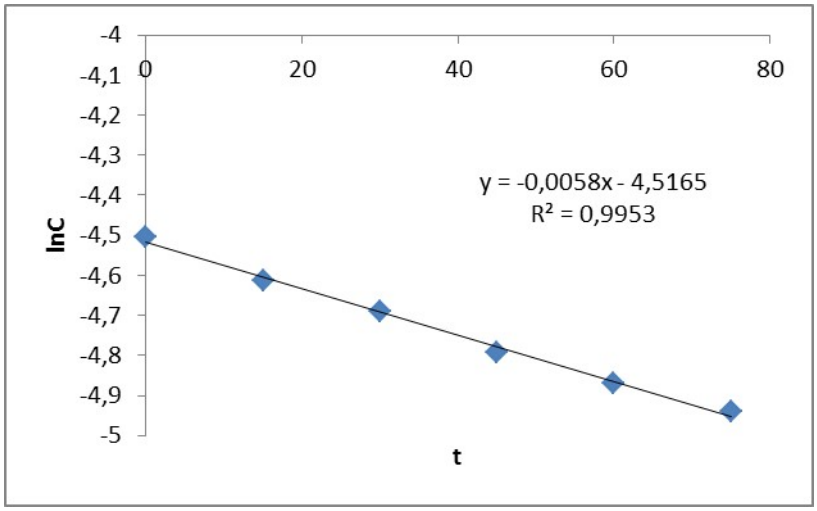


$k_{obs} = 14.1 \pm 1.1 \times 10^{-3} s^{-1}$

- **Methanol**

Conditions of experiment: 2Br-4F-Ph Ellman's imine **2a** (200 µl, 0.04 M), 5 mol% $Cu(PPh_3)_3F*2EtOH$ **[Cu-1]** (200 µl, 0.002 M), 10 eq. TABMA **1a** (400 µl, 0.2M), solvent – MeOH, T = 25.0 °C.

№	A^{307}	t, sec	c, M	lnC
0	1,529	0	0,0111	-4,5035
1	1,371	15	0,0099	-4,6125
2	1,269	30	0,0092	-4,6899
3	1,146	45	0,0083	-4,7918
4	1,061	60	0,0077	-4,8689
5	0,989	75	0,0072	-4,9391
6	0,407	**900**	0,0029	-5,8270



$k_{obs} = 5.8 \pm 0.5 \times 10^{-3} s^{-1}$

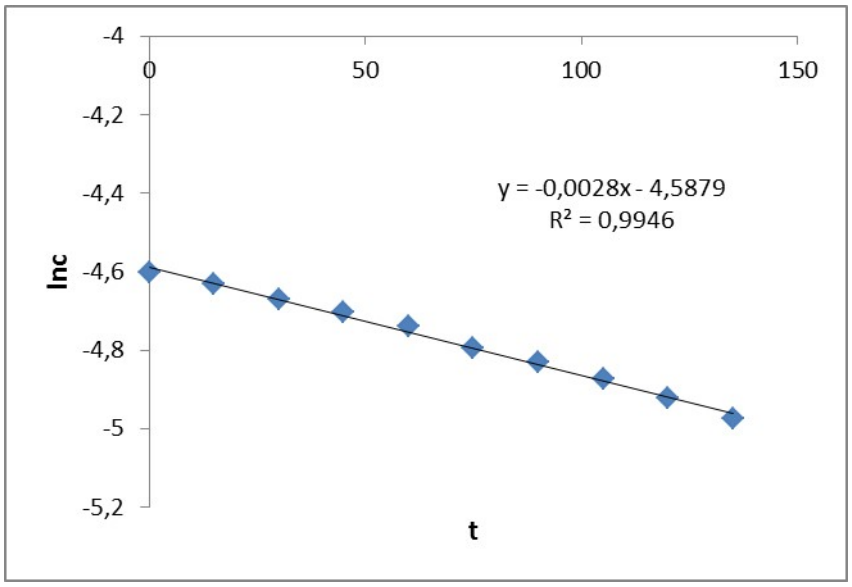
Determination of order allylation reaction of imine 2a on catalyst [Cu-1]

- **0.5 mol% of [Cu-1]**

Conditions of experiment: 2Br-4F-Ph Ellman's imine **2a** (200 µl, 0.04 M), 0.5 mol% $Cu(PPh_3)_3F*2EtOH$ **[Cu-1]** (200 µl, 0.002 M), 10 eq. TABMA **1a** (400 µl, 0.2 M), solvent – *i*PrOH, T = 25.0 °C.

№	A^{307}	t, sec	c, M	lnC
0	1,385	0	0,0100	-4,6024
1	1,344	15	0,0097	-4,6324
2	1,294	30	0,0094	-4,6703
3	1,251	45	0,0091	-4,7041
4	1,207	60	0,0087	-4,7399
5	1,144	75	0,0083	-4,7936
6	1,102	90	0,0080	-4,831
7	1,056	105	0,0076	-4,8736

8	1,005	120	0,0073	-4,9231
9	0,953	135	0,0069	-4,9762

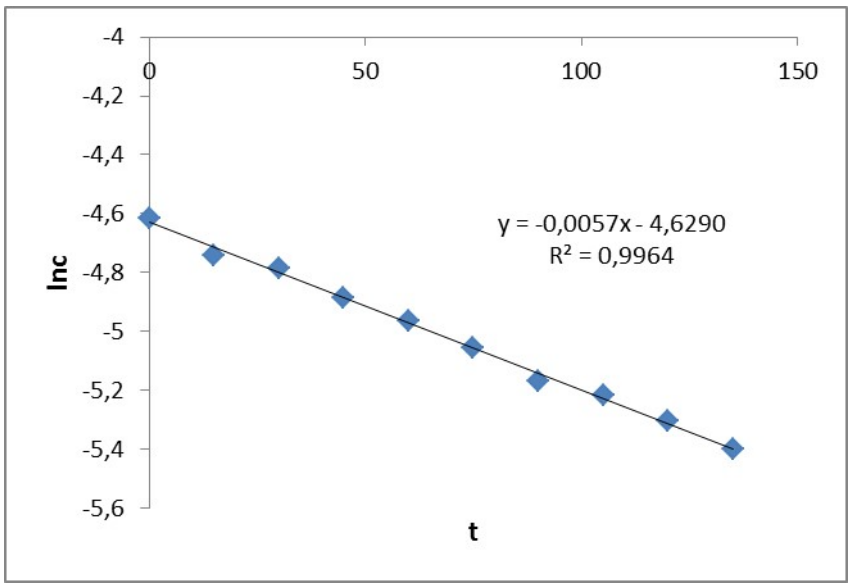


$k_{obs} = 2.8 \pm 0.2 \times 10^{-3} s^{-1}$

- **1 mol% of [Cu-1]**

Conditions of experiment: 2Br-4F-Ph Ellman's imine **2a** (200 µl, 0.04 M), 1 mol% $Cu(PPh_3)_3F*2EtOH$ **[Cu-1]** (200 µl, 0.002 M), 10 eq. TABMA **1a** (400 µl, 0.2 M), solvent – *i*PrOH, T = 25.0 °C.

№	A^{307}	t, sec	c, M	lnC
0	1,369	0	0,0099	-4,6140
1	1,204	15	0,0087	-4,7424
2	1,154	30	0,0084	-4,7849
3	1,042	45	0,0075	-4,8869
4	0,964	60	0,0070	-4,9647
5	0,879	75	0,0064	-5,0571
6	0,785	90	0,0057	-5,1702
7	0,748	105	0,0054	-5,2184
8	0,686	120	0,0050	-5,3050
9	0,623	135	0,0045	-5,4013

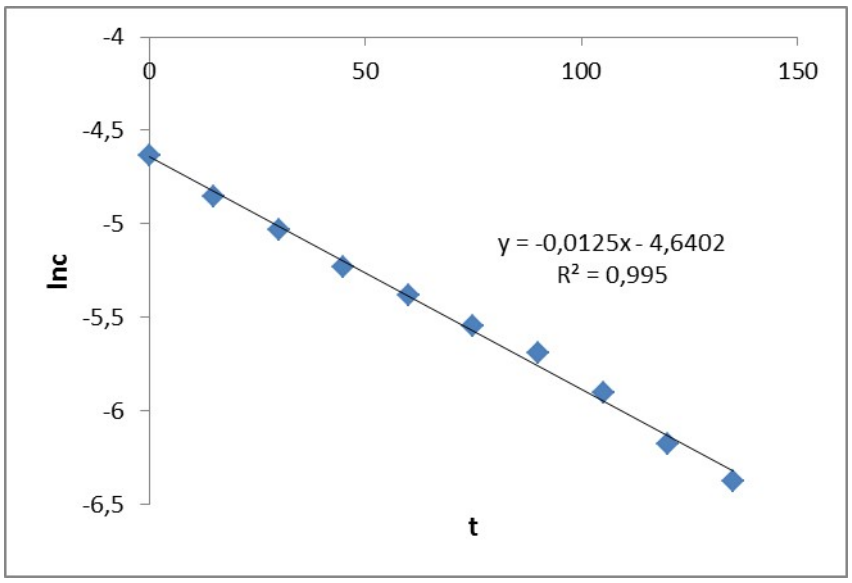


$k_{obs} = 5.7 \pm 0.3 \times 10^{-3} s^{-1}$

- **2 mol% of [Cu-1]**

Conditions of experiment: 2Br-4F-Ph Ellman's imine **2a** (200 µl, 0.04 M), 2 mol% $Cu(PPh_3)_3F*2EtOH$ **[Cu-1]** (200 µl, 0.002 M), 10 eq. TABMA **1a** (400 µl, 0.2 M), solvent – *i*PrOH, T = 25.0 °C.

№	A^{307}	t, sec	c, M	lnC
0	1,345	0	0,0097	-4,6317
1	1,075	15	0,0078	-4,8558
2	0,903	30	0,0065	-5,0301
3	0,741	45	0,0054	-5,2278
4	0,634	60	0,0046	-5,3838
5	0,538	75	0,0039	-5,5480
6	0,465	90	0,0034	-5,6938
7	0,378	105	0,0027	-5,9009
8	0,287	120	0,0021	-6,1764
9	0,234	135	0,0017	-6,3805

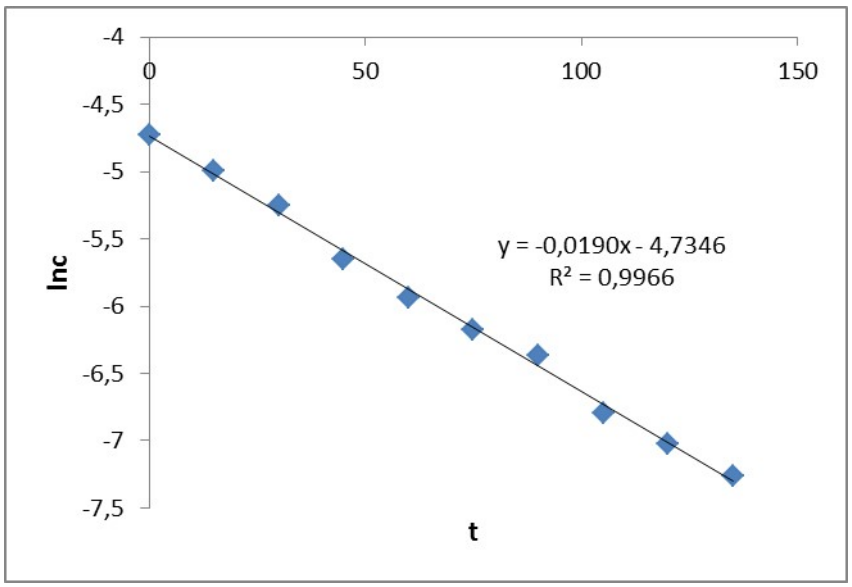


$k_{obs} = 12.5 \pm 0.7 \times 10^{-3} s^{-1}$

- **3 mol% of [Cu-1]**

Conditions of experiment: 2Br-4F-Ph Ellman's imine **2a** (200 µl, 0.04 M), 3 mol% $Cu(PPh_3)_3F*2EtOH$ **[Cu-1]** (200 µl, 0.002 M), 10 eq. TABMA **1a** (400 µl, 0.2 M), solvent – *i*PrOH, T = 25.0 °C.

№	A^{307}	t, sec	c, M	lnC
0	1,225	0	0,0089	-4,7251
1	0,932	15	0,0067	-4,9985
2	0,721	30	0,0052	-5,2552
3	0,487	45	0,0035	-5,6476
4	0,363	60	0,0026	-5,9414
5	0,287	75	0,0021	-6,1764
6	0,237	90	0,0017	-6,3678
7	0,154	105	0,0011	-6,7989
8	0,123	120	0,0009	-7,0237
9	0,097	135	0,0007	-7,2611

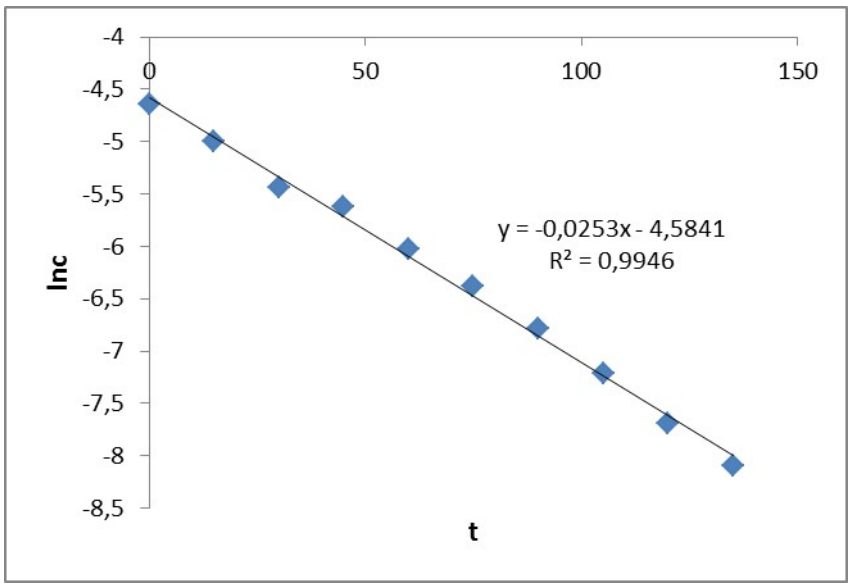


$k_{obs} = 19.0 \pm 0.9 \times 10^{-3} s^{-1}$

- **4 mol% of [Cu-1]**

Conditions of experiment: 2Br-4F-Ph Ellman's imine **2a** (200 µl, 0.04 M), 4 mol% $Cu(PPh_3)_3F*2EtOH$ **[Cu-1]** (200 µl, 0.002 M), 10 eq. TABMA **1a** (400 µl, 0.2 M), solvent – *i*PrOH, T = 25.0 °C.

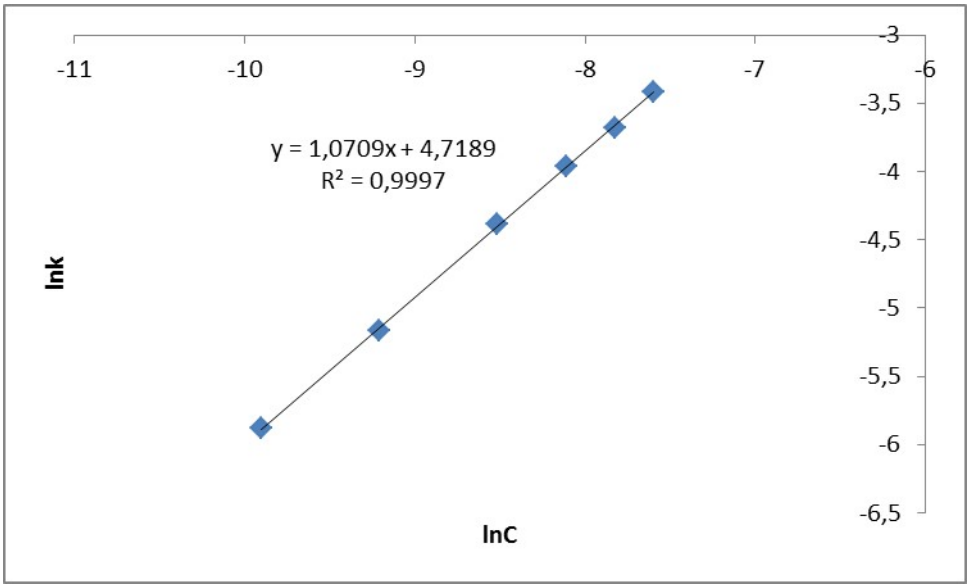
№	A^{307}	t, sec	c, M	lnC
0	1,324	0	0,0096	-4,6474
1	0,931	15	0,0067	-4,9996
2	0,597	30	0,0043	-5,4439
3	0,499	45	0,0036	-5,6232
4	0,332	60	0,0024	-6,0307
5	0,235	75	0,0017	-6,3763
6	0,157	90	0,0011	-6,7796
7	0,102	105	0,0007	-7,2109
8	0,063	120	0,0005	-7,6927
9	0,042	135	0,0003	-8,0982



$k_{obs} = 25.3 \pm 1.5 \times 10^{-3} s^{-1}$

- **Determination of [Cu-1] order in the allylation reaction**

C, M	lnC	k, s^{-1}	lnk
0,0005	-7,6009	0,0329	-3,41428
0,0004	-7,82405	0,0253	-3,67695
0,0003	-8,11173	0,0190	-3,96332
0,0002	-8,51719	0,0125	-4,38203
0,0001	-9,21034	0,0057	-5,16729
0,00005	-9,90349	0,0028	-5,87814



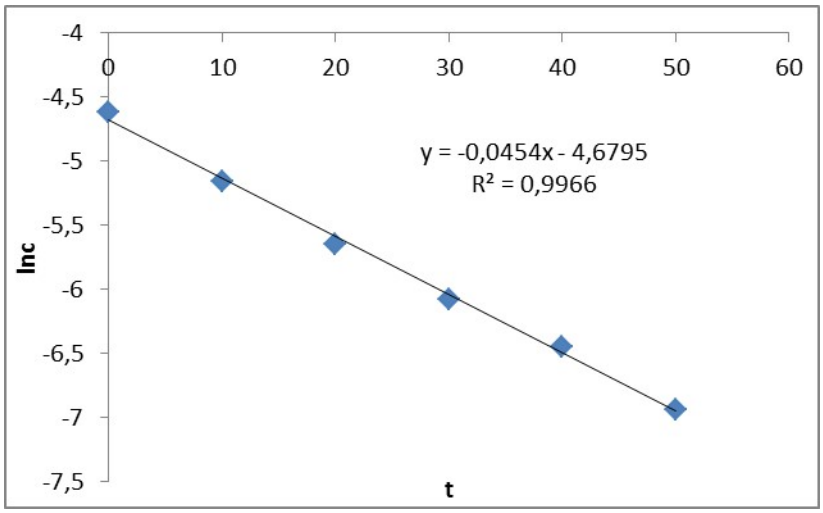
Reaction has the 1st order on the **[Cu-1]** catalyst.

Rate constants of allylation of imine 2a with different triallylborane-amine adducts 1b-1d in isopropyl alcohol (Scheme 6 of the main text)

- **Triallylborane-ammonia adduct (1b)**

Conditions of experiment: 2Br-4F-Ph Ellman's imine **2a** (200 µl, 0.04 M), 5 mol% $Cu(PPh_3)_3F*2EtOH$ **[Cu-1]** (200 µl, 0.002 M), 10 eq. TABA **1b** (400 µl, 0.2 M), solvent – *i*PrOH, T = 25.0 °C.

№	A^{307}	t, sec	c, M	lnC
0	1,365	0	0,0099	-4,6169
1	0,794	10	0,0057	-5,1588
2	0,485	20	0,0035	-5,6517
3	0,317	30	0,0023	-6,0769
4	0,219	40	0,0016	-6,4468
5	0,134	50	0,0010	-6,9380



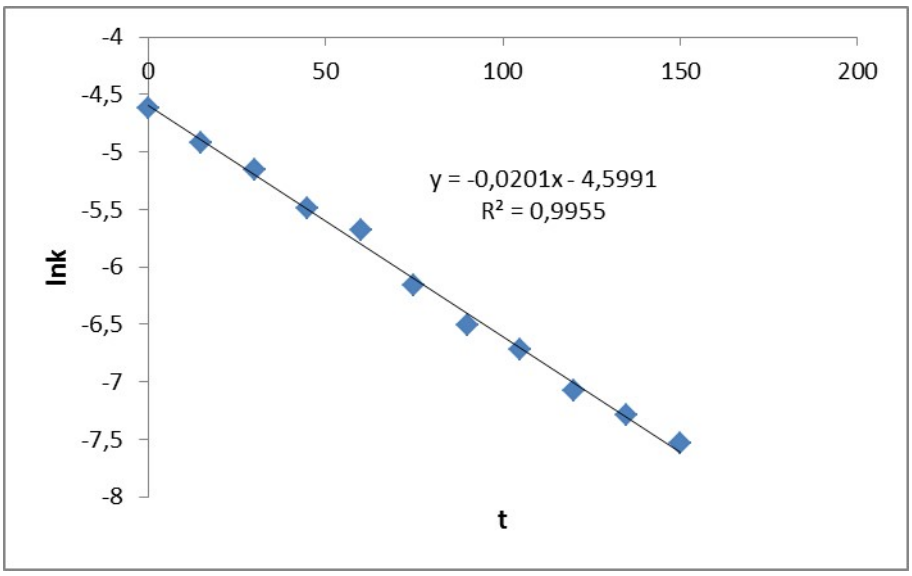
$k_{obs} = 45.4 \pm 3.4 \times 10^{-3} s^{-1}$

- **Triallylborane-dimethylamine adduct (1c)**

Conditions of experiment: 2Br-4F-Ph Ellman's imine **2a** (200 µl, 0.04 M), 0.5 mol% $Cu(PPh_3)_3F*2EtOH$ **[Cu-1]** (200 µl, 0.002 M), 10 eq. TABDMA **1c** (400 µl, 0.2 M), solvent – *i*PrOH, T = 25.0 °C.

№	A^{307}	t, sec	c, M	lnC
0	1,364	0	0,0099	-4,6177
1	1,005	15	0,0073	-4,9231
2	0,800	30	0,0058	-5,1512
3	0,568	45	0,0041	-5,4937
4	0,473	60	0,0034	-5,6767
5	0,293	75	0,0021	-6,1557
6	0,206	90	0,0015	-6,5080
7	0,166	105	0,0012	-6,7239
8	0,116	120	0,0008	-7,0822

9	0,094	135	0,0007	-7,2925
10	0,074	150	0,0005	-7,5318



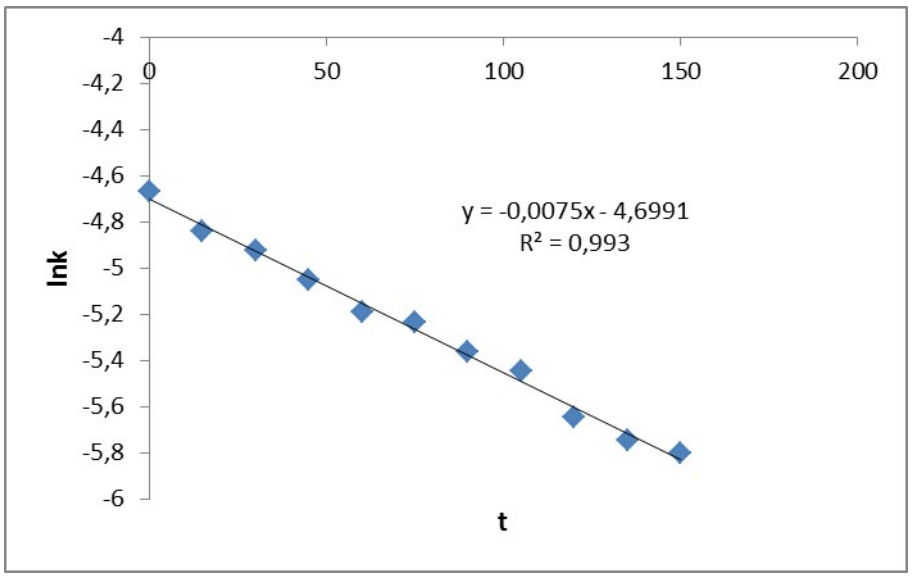
k_{obs} = 20.1 ± 1.0 x $10^{-3}s^{-1}$ (at 0.5 mol% of **[Cu-1]**)

$k_{calculated}$ = 201 ± 10 x $10^{-3}s^{-1}$ (at 5 mol% of **[Cu-1]**)

- **Triallylborane-1,4-diazabicyclo[2.2.2]octane adduct (1c)**

Conditions of experiment: 2Br-4F-Ph Ellman's imine **2a** (200 µl, 0.04 M), 0.05 mol% $Cu(PPh_3)_3F*2EtOH$ **[Cu-1]** (200 µl, 0.002 M), 10 eq. TABDABCO **1d** (400 µl, 0.2M), solvent – *i*PrOH, T = 25.0 °C.

№	A^{307}	t, sec	c, M	lnC
0	1,300	0	0,0094	-4,6657
1	1,091	15	0,0079	-4,8410
2	1,004	30	0,0073	-4,9241
3	0,885	45	0,0064	-5,0503
4	0,771	60	0,0056	-5,1882
5	0,737	75	0,0053	-5,2333
6	0,648	90	0,0047	-5,3619
7	0,597	105	0,0043	-5,4439
8	0,489	120	0,0035	-5,6435
9	0,442	135	0,0032	-5,7445
10	0,417	150	0,0030	-5,8028



k_{obs} = 7.5 ± 0.5 x $10^{-3}s^{-1}$ (at 0.05 mol% of **[Cu-1]**)

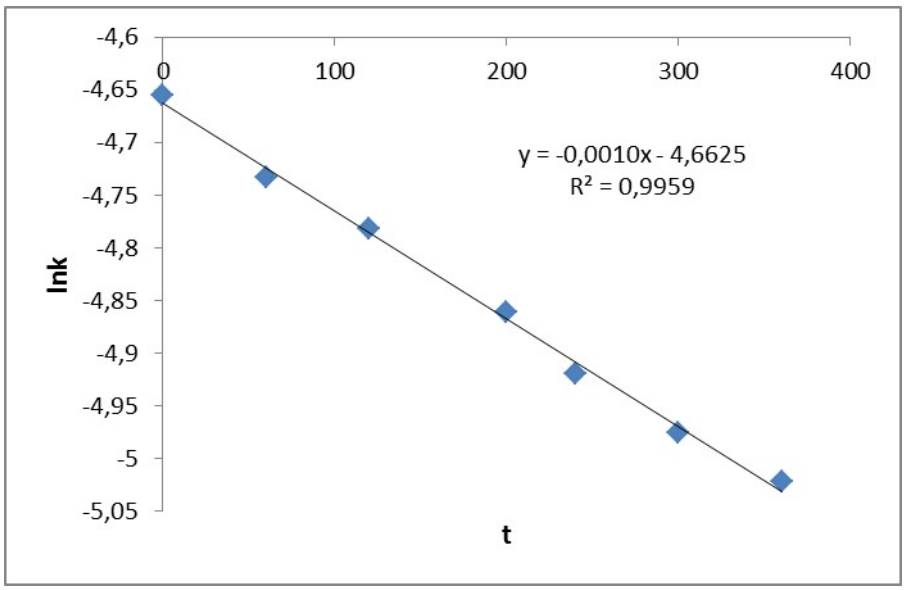
$k_{calculated}$ = 750 ± 50 x $10^{-3}s^{-1}$ (at 5 mol% of **[Cu-1]**)

The dependence of the allylation reaction rate with triallylborane-methylamine adduct 1a on the temperature

- **T = 10.0 °C (283.1 °K)**

Conditions of experiment: 2Br-4F-Ph Ellman's imine **2a** (200 µl, 0.04 M), 5 mol% $Cu(PPh_3)_3F$*2EtOH **[Cu-1]** (200 µl, 0.002 M), 10 eq. TABMA **1a** (400 µl, 0.2M), solvent – *i*PrOH, T = 10.0 °C.

№	A^{307}	t, sec	c, M	lnC
0	1,314	0	0,0095	-4,6550
1	1,215	60	0,0088	-4,7333
2	1,158	120	0,0084	-4,7814
3	1,069	200	0,0077	-4,8614
4	1,009	240	0,0073	-4,9191
5	0,954	300	0,0069	-4,9752
6	0,911	360	0,0066	-5,0213

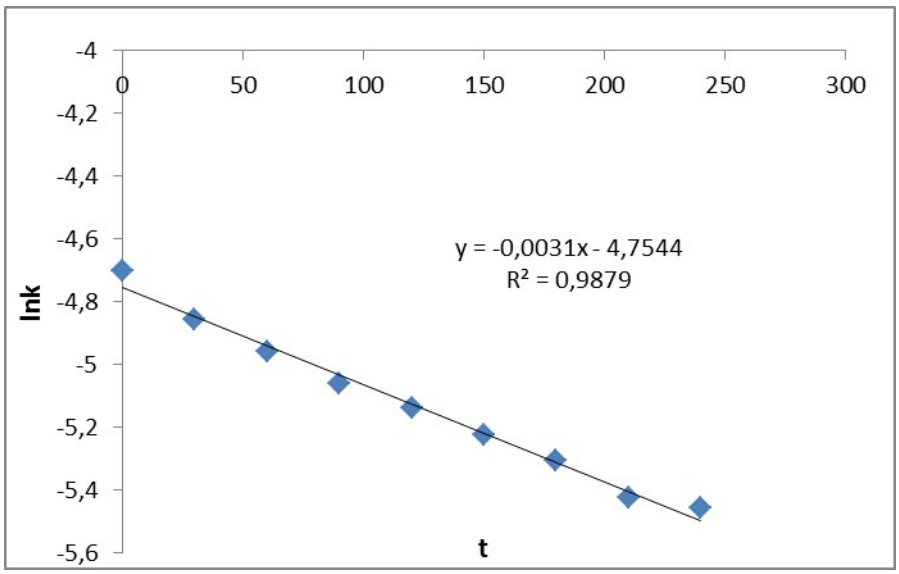


$k_{obs} = 1.0 \pm 0.1 \times 10^{-3} s^{-1}$

- **T = 15.0 °C (288.1 °K)**

Conditions of experiment: 2Br-4F-Ph Ellman's imine **2a** (200 µl, 0.04 M), 5 mol% $Cu(PPh_3)_3F*2EtOH$ **[Cu-1]** (200 µl, 0.002 M), 10 eq. TABMA **1a** (400 µl, 0.2M), solvent – *i*PrOH, T = 15.0 °C.

№	A^{307}	t, sec	c, M	lnC
0	1,254	0	0,0091	-4,7017
1	1,072	30	0,0078	-4,8586
2	0,969	60	0,0070	-4,9596
3	0,876	90	0,0063	-5,0605
4	0,809	120	0,0059	-5,1400
5	0,745	150	0,0054	-5,2225
6	0,685	180	0,0050	-5,3064
7	0,610	210	0,0044	-5,4224
8	0,590	240	0,0043	-5,4557

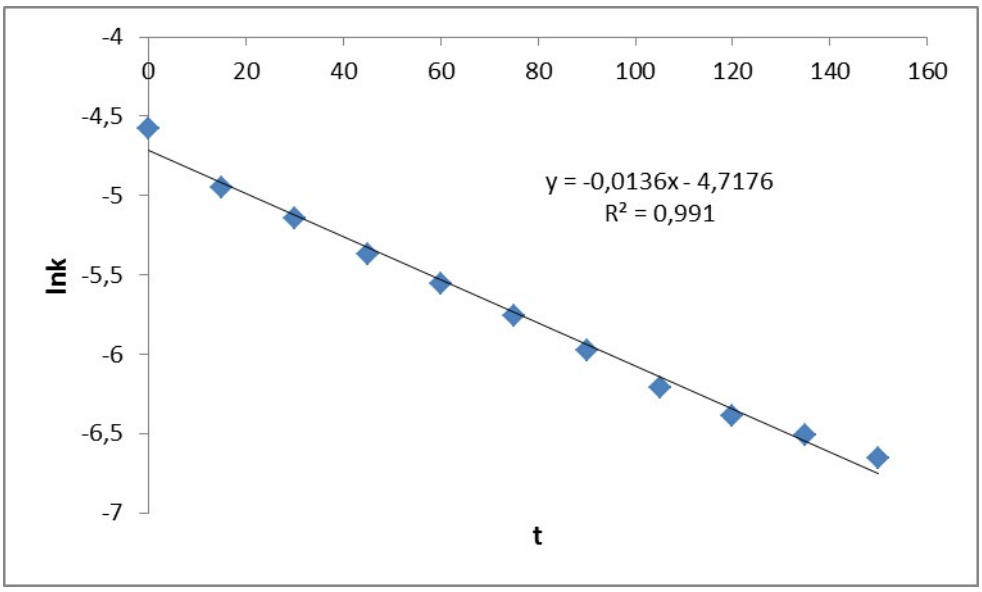


$k_{obs} = 3.1 \pm 0.3 \times 10^{-3} s^{-1}$

- **T = 20.0 °C (293.1 °K)**

Conditions of experiment: 2Br-4F-Ph Ellman's imine **2a** (200 µl, 0.04 M), 5 mol% $Cu(PPh_3)_3F*2EtOH$ **[Cu-1]** (200 µl, 0.002 M), 10 eq. TABMA **1a** (400 µl, 0.2M), solvent – *i*PrOH, T = 20.0 °C.

№	A^{307}	t, sec	c, M	lnC
0	1,415	0	0,0102	-4,5810
1	0,975	15	0,0071	-4,9534
2	0,803	30	0,0058	-5,1475
3	0,641	45	0,0046	-5,3728
4	0,535	60	0,0039	-5,5536
5	0,436	75	0,0032	-5,7582
6	0,350	90	0,0025	-5,9779
7	0,278	105	0,0020	-6,2082
8	0,232	120	0,0017	-6,3891
9	0,206	135	0,0015	-6,5080
10	0,177	150	0,0013	-6,6597

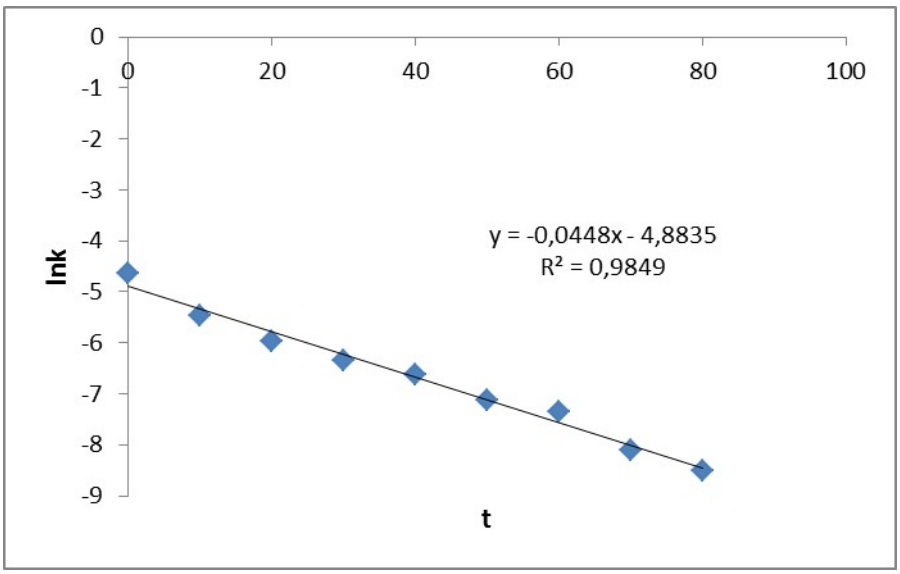


$k_{obs} = 13.6 \pm 1.0 \times 10^{-3} s^{-1}$

- **T = 30.0 °C (303.1 °K)**

Conditions of experiment: 2Br-4F-Ph Ellman's imine **2a** (200 µl, 0.04 M), 5 mol% $Cu(PPh_3)_3F$*2EtOH **[Cu-1]** (200 µl, 0.002 M), 10 eq. TABMA **1a** (400 µl, 0.2M), solvent – *i*PrOH, T = 30.0 °C.

№	A^{307}	t, sec	c, M	lnC
0	1,334	0	0,0097	-4,6399
1	0,584	10	0,0042	-5,4659
2	0,354	20	0,0026	-5,9665
3	0,245	30	0,0018	-6,3346
4	0,185	40	0,0013	-6,6155
5	0,112	50	0,0008	-7,1173
6	0,089	60	0,0006	-7,3472
7	0,042	70	0,0003	-8,0982
8	0,028	80	0,0002	-8,5036

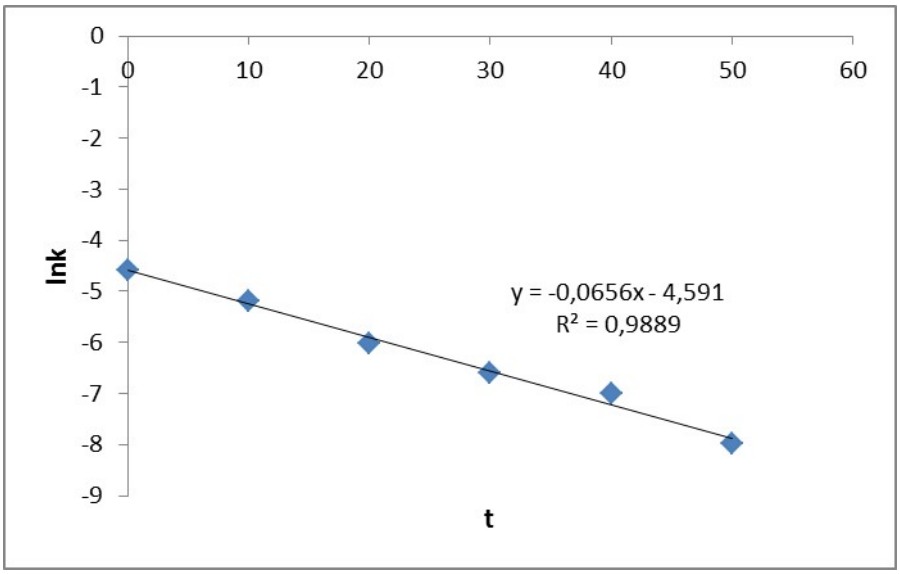


$k_{obs} = 44.8 \pm 4.8 \times 10^{-3} s^{-1}$

- **T = 35.0 °C (308.1 °K)**

Conditions of experiment: 2Br-4F-Ph Ellman's imine **2a** (200 µl, 0.04 M), 5 mol% $Cu(PPh_3)_3F*2EtOH$ **[Cu-1]** (200 µl, 0.002 M), 10 eq. TABMA **1a** (400 µl, 0.2M), solvent – *i*PrOH, T = 35.0 °C.

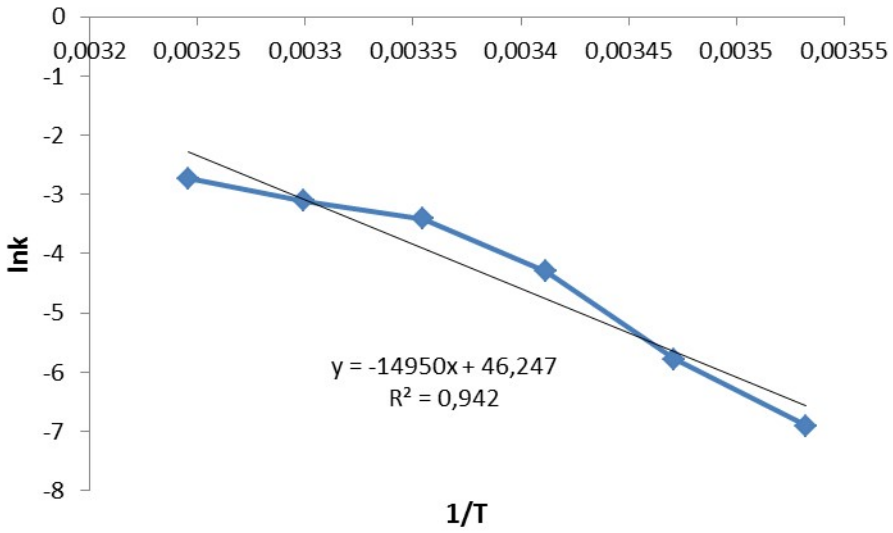
№	A^{307}	t, sec	c, M	lnC
0	1,394	0	0,0101	-4,5959
1	0,776	10	0,0056	-5,1817
2	0,333	20	0,0024	-6,0277
3	0,188	30	0,0014	-6,5994
4	0,127	40	0,0009	-6,9917
5	0,047	50	0,0003	-7,9857



$k_{obs} = 65.6 \pm 8.9 \times 10^{-3} s^{-1}$

- **Graph of dependence logarithmic allylation reaction rate versus inverse of the temperature**

T, °C	T, °K	k, s^{-1}	1/T	lnk
10.0	283,1	0,0010	0,00353	-6,9078
15.0	288,1	0,0031	0,00347	-5,7764
20.0	293,1	0,0136	0,00341	-4,2977
25.0	298,1	0,0329	0,00335	-3,4143
30.0	303,1	0,0448	0,00330	-3,1055
35.0	308,1	0,0656	0,00325	-2,7242



$E_{a(obs.)}$ = 124 ± 40 kJ/mol

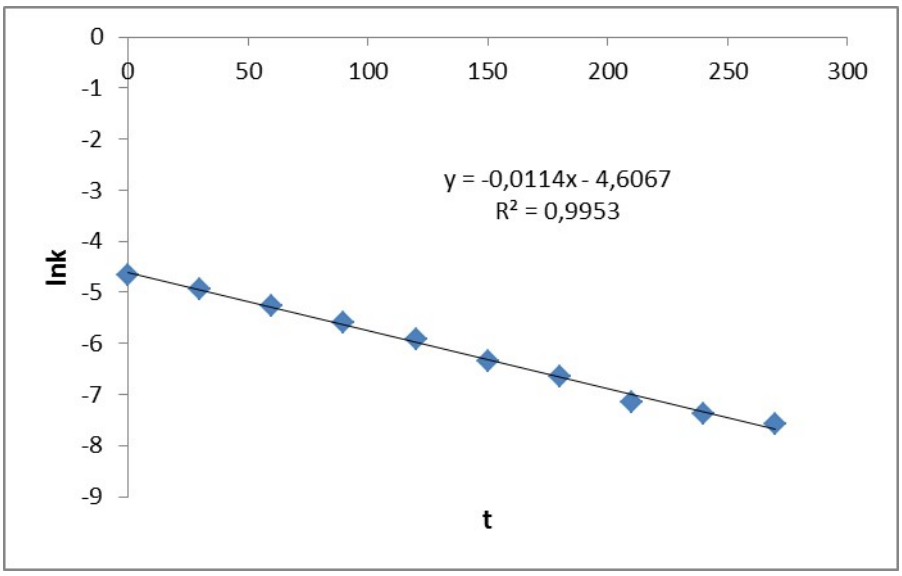
Rate constants of allylation of imine 2a with intermediate (diallyl)isopropoxyborinane-methylamine adduct 1f and allyl(diisopropoxy)borane 5 in isopropyl alcohol (Scheme 7 of the main text)

- **Allyl(diisopropoxy)borane (5)**

Conditions of experiment: 2Br-4F-Ph Ellman's imine **2a** (200 µl, 0.04 M), 5 mol% $Cu(PPh_3)_3F$*2EtOH **[Cu-1]** (200 µl), 10 eq. $AllB(OiPr)_2$ **5** (400 µl, 0.2 M), solvent – *i*PrOH, T = 25.0 °C.

№	A^{307}	t, sec	c, M	lnC
0	1,301	0	0,0094	-4,665
1	0,991	30	0,0072	-4,9371
2	0,723	60	0,0052	-5,2524
3	0,511	90	0,0037	-5,5995
4	0,376	120	0,0027	-5,9063

5	0,242	150	0,0018	-6,3469
6	0,179	180	0,0013	-6,6485
7	0,108	210	0,0008	-7,1537
8	0,086	240	0,0006	-7,3815
9	0,070	270	0,0005	-7,5873

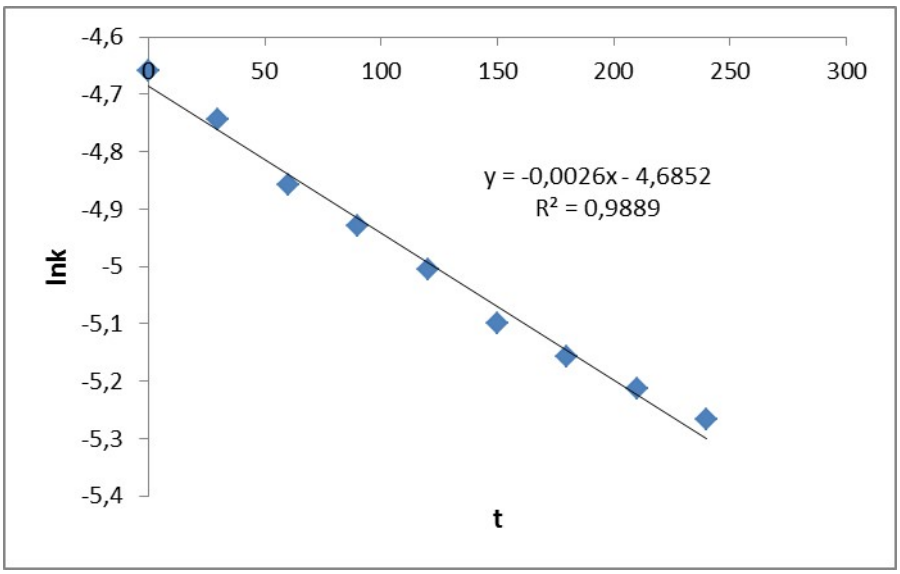


$k_{obs} = 11.4 \pm 0.6 \times 10^{-3} s^{-1}$

- **Allyl(diisopropoxy)borane (5) with addition of $MeNH_2$**

Conditions of experiment: 2Br-4F-Ph Ellman's imine **2a** (200 µl, 0.04 M), 5 mol% $Cu(PPh_3)_3F$*2EtOH **[Cu-1]** (200 µl), 10 eq. $AllB(OiPr)_2$ **5** + 10 eq. $MeNH_2$ (400 µl, 0.2 M), solvent – *i*PrOH, T = 25.0 °C. $MeNH_2$ was added as 6 M solution in iPrOH.

№	A^{307}	t, sec	c, M	lnC
0	1,310	0	0,0095	-4,6581
1	1,201	30	0,0087	-4,7449
2	1,073	60	0,0078	-4,8576
3	0,999	90	0,0072	-4,9291
4	0,925	120	0,0067	-5,006
5	0,843	150	0,0061	-5,0989
6	0,795	180	0,0058	-5,1575
7	0,752	210	0,0054	-5,2131
8	0,713	240	0,0052	-5,2664

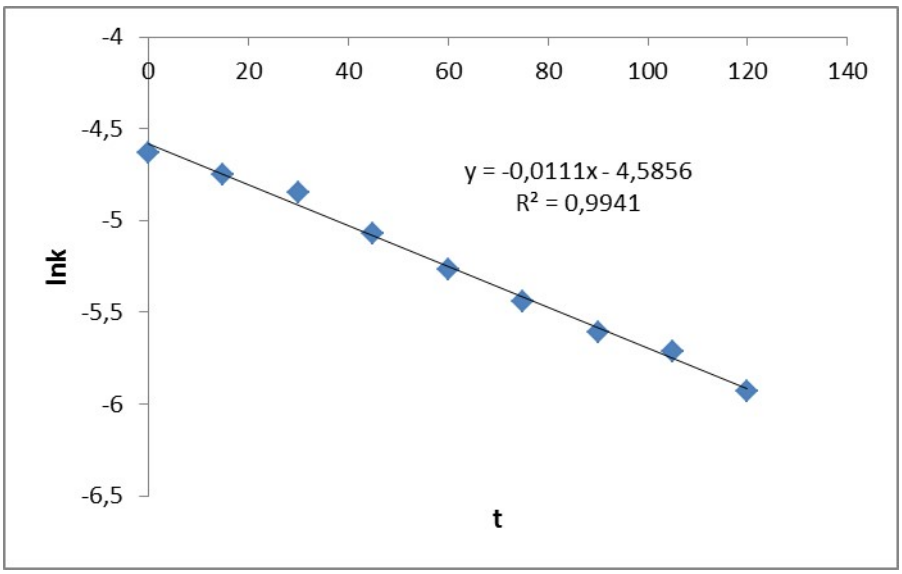


$k_{obs} = 2.6 \pm 0.2 \times 10^{-3} s^{-1}$

- **Allyl(diisopropoxy)borane (5) with addition of Et_3N**

Conditions of experiment: 2Br-4F-Ph Ellman's imine **2a** (200 µl, 0.04 M), 5 mol% $Cu(PPh_3)_3F$*2EtOH **[Cu-1]** (200 µl), 10 eq. $AllB(OiPr)_2$ **5** + 10 eq. Et_3N (400 µl, 0.2 M), solvent – *i*PrOH, T = 25.0 °C.

№	A^{307}	t, sec	c, M	lnC
0	1,350	0	0,0098	-4,6280
1	1,195	15	0,0087	-4,7499
2	1,080	30	0,0078	-4,8511
3	0,868	45	0,0063	-5,0696
4	0,711	60	0,0051	-5,2692
5	0,597	75	0,0043	-5,4439
6	0,505	90	0,0037	-5,6113
7	0,456	105	0,0033	-5,7133
8	0,367	120	0,0027	-5,9305

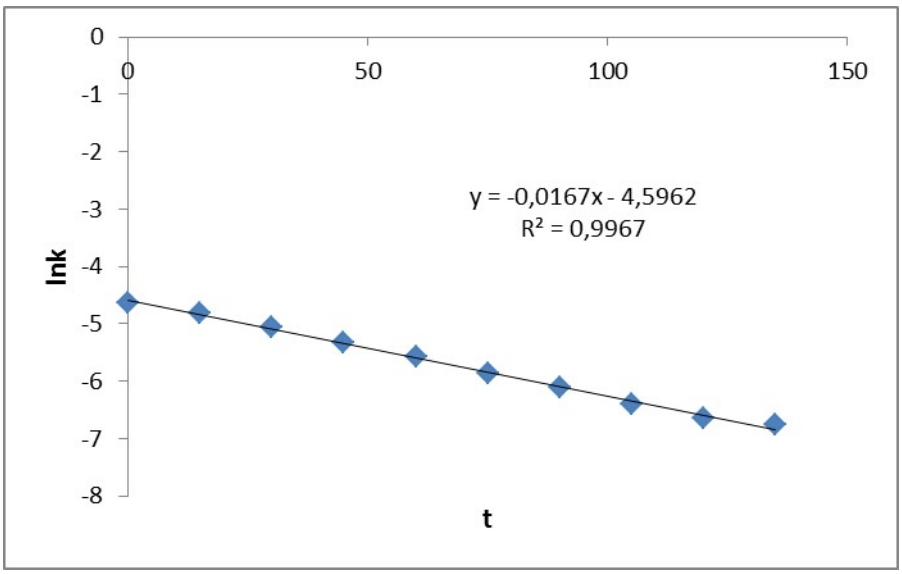


$k_{obs} = 11.1 \pm 0.7 \times 10^{-3} s^{-1}$

- **Allyl(diisopropoxy)borane (5) with addition of DABCO**

Conditions of experiment: 2Br-4F-Ph Ellman's imine **2a** (200 µl, 0.04 M), 5 mol% $Cu(PPh_3)_3F*2EtOH$ **[Cu-1]** (200 µl), 10 eq. $AllB(OiPr)_2$ **5** + 10 eq. DABCO (400 µl, 0.2 M), solvent – *i*PrOH, T = 25.0 °C.

№	A^{307}	t, sec	c, M	lnC
0	1,350	0	0,0098	-4,6280
1	1,110	15	0,0080	-4,8237
2	0,871	30	0,0063	-5,0662
3	0,666	45	0,0048	-5,3346
4	0,529	60	0,0038	-5,5649
5	0,389	75	0,0028	-5,8723
6	0,305	90	0,0022	-6,1155
7	0,228	105	0,0017	-6,4065
8	0,181	120	0,0013	-6,6373
9	0,160	135	0,0012	-6,7607

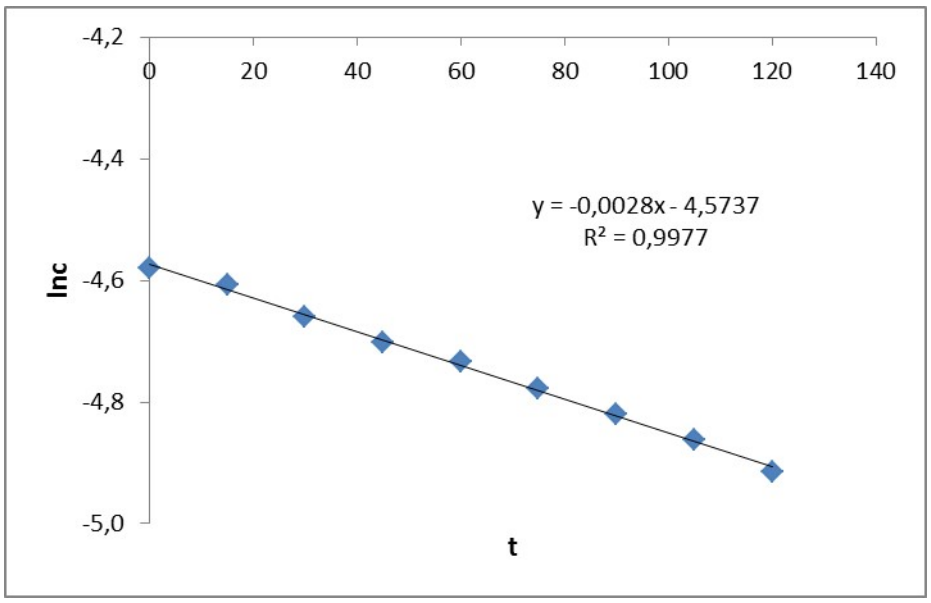


$k_{obs} = 16.7 \pm 0.8 \times 10^{-3} s^{-1}$

- **Allylboronic acid pinacol ester**

Conditions of experiment: 2Br-4F-Ph Ellman's imine **2a** (200 µl, 0.04 M), 5 mol% $Cu(PPh_3)_3F*2EtOH$ **[Cu-1]** (200 µl), 10 eq. AllBPin (400 µl, 0.2 M), solvent – *i*PrOH, T = 25.0 °C.

№	A^{307}	t, sec	c, M	lnC
0	1.417	0	0.0103	-4.5795
1	1.377	15	0.0100	-4.6082
2	1.307	30	0.0095	-4.6604
3	1.253	45	0.0091	-4.7025
4	1.214	60	0.0088	-4.7342
5	1.161	75	0.0084	-4.7788
6	1.114	90	0.0081	-4.8201
7	1.069	105	0.0077	-4.8614
8	1.014	120	0.0073	-4.9142

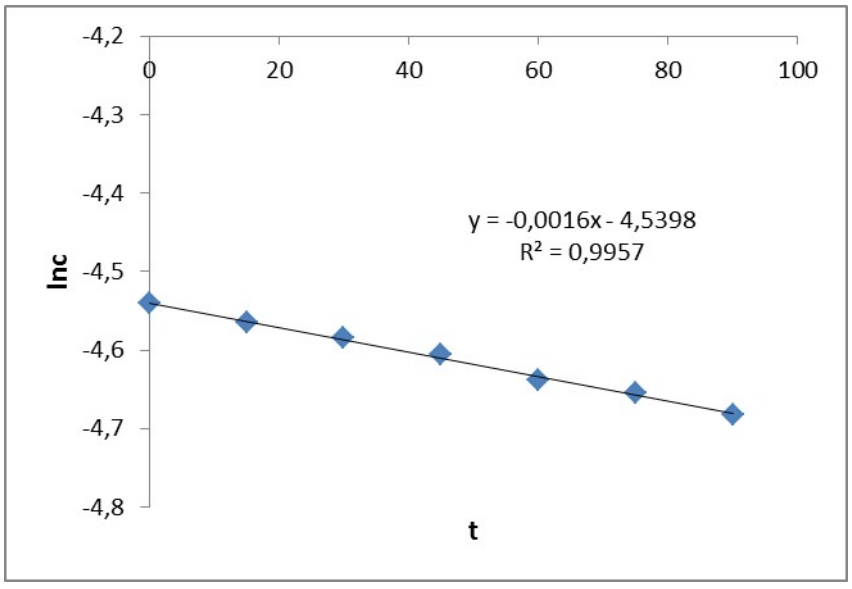


$k_{obs} = 2.8 \pm 0.1 \times 10^{-3} s^{-1}$

- **(Diallyl)isopropoxyborinane-methylamine adduct (1f) without copper(I) catalyst**

Conditions of experiment: 2Br-4F-Ph Ellman's imine **2a** (200 µl, 0.04 M), no catalyst - *i*PrOH (200 µl), 10 eq. DABMA(O*i*Pr) **1f** (400 µl, 0.2 M), solvent – *i*PrOH, T = 25.0 °C.

№	A^{307}	t, sec	c, M	lnC
0	1,474	0	0,0107	-4,5401
1	1,437	15	0,0104	-4,5655
2	1,409	30	0,0102	-4,5852
3	1,380	45	0,0100	-4,606
4	1,335	60	0,0097	-4,6392
5	1,315	75	0,0095	-4,6542
6	1,278	90	0,0093	-4,6828

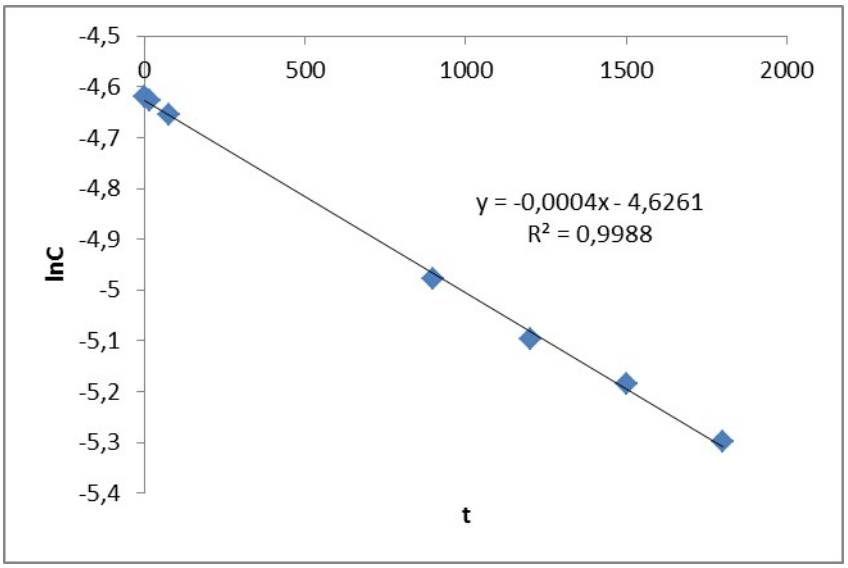


$k_{obs} = 1.6 \pm 0.1 \times 10^{-3} s^{-1}$

- **(Diallyl)isopropoxyborinane-methylamine adduct (1f) without copper(I) catalyst and with addition of $MeNH_2$**

Conditions of experiment: 2Br-4F-Ph Ellman's imine **2a** (200 µl, 0.04 M), no catalyst - *i*PrOH (200 µl), 10 eq. DABMA(O*i*Pr) **1f** +20 eq $MeNH_2$ (400 µl, 0.2 M), solvent – *i*PrOH, T = 25.0 °C.

№	A^{307}	t, sec	c, M	lnC
0	1,361	0	0,0099	-4,6199
1	1,350	15	0,0098	-4,6280
2	1,314	75	0,0095	-4,6550
3	0,952	900	0,0069	-4,9773
4	0,845	1200	0,0061	-5,0965
5	0,773	1500	0,0056	-5,1856
6	0,691	1800	0,0050	-5,2977



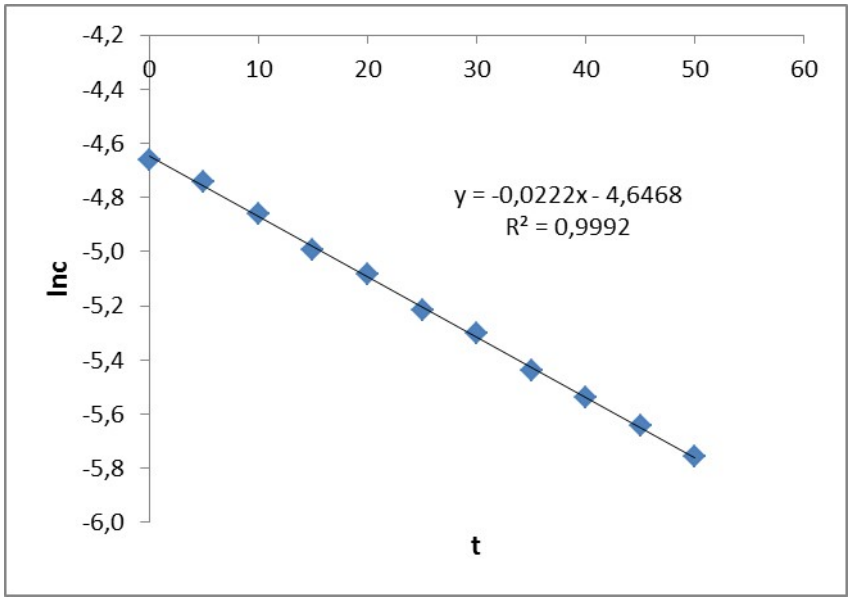
$k_{obs} = 0.37 \pm 0.02 \times 10^{-3} s^{-1}$

- **(Diallyl)isopropoxyborinane-methylamine adduct (1f) with copper(I) catalyst**

Conditions of experiment: 2Br-4F-Ph Ellman's imine **2a** (200 µl, 0.04 M), 0.05 mol% $Cu(PPh_3)_3F*2EtOH$ **[Cu-1]** (200 µl, 0.002 M), 10 eq. DABMA(O*i*Pr) **1f** (400 µl, 0.2M) + 400 µl of *i*PrOH, solvent – *i*PrOH, T = 25.0 °C.

№	A^{307}	t, sec	c, M	lnC
0	1,308	0	0,0095	-4,6596
1	1,203	5	0,0087	-4,7433
2	1,069	10	0,0077	-4,8614
3	0,938	15	0,0068	-4,9921
4	0,857	20	0,0062	-5,0824
5	0,751	25	0,0054	-5,2144

6	0,688	30	0,0050	-5,3021
7	0,601	35	0,0044	-5,4372
8	0,543	40	0,0039	-5,5387
9	0,489	45	0,0035	-5,6435
10	0,436	50	0,0032	-5,7582



k_{obs} = 22.2 ± 0.5 x $10^{-3}s^{-1}$ (at 0.05 mol% of **[Cu-1]** with 1.5 times dilution)

k_{obs} = 33.3 ± 0.8 x $10^{-3}s^{-1}$ (at 0.05 mol% of **[Cu-1]** without 1.5 times dilution)

$k_{calculated}$ = 3330 ± 75 x $10^{-3}s^{-1}$ (at 5 mol% of **[Cu-1]** without 1.5 times dilution)

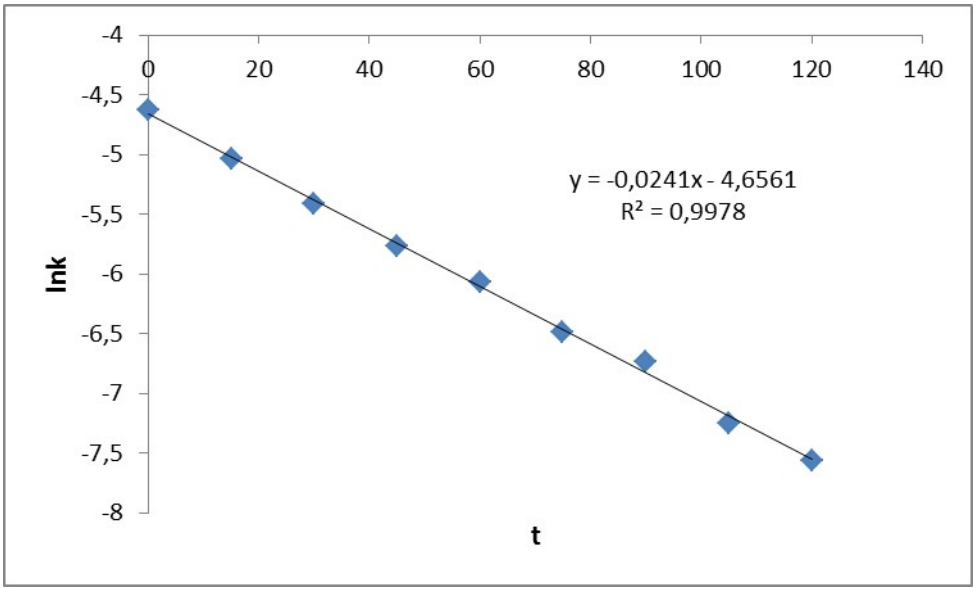
Rate constants of allylation of imine 2a with triallylborane-methylamine adduct 1a in isopropyl alcohol with addition of $MeNH_2$ (Figure 3 of the main text)

- **Addition of 0.25 eq. of $MeNH_2$**

Conditions of experiment: 2Br-4F-Ph Ellman's imine **2a** (200 µl, 0.04 M), 5 mol% $Cu(PPh_3)_3F$*2EtOH **[Cu-1]** (200 µl, 0.002 M), 10 eq. TABMA **1a** + 0.25 eq. $MeNH_2$ (400 µl, 0.2 M), solvent – *i*PrOH, T = 25.0 °C. $MeNH_2$ was added as 6 M solution in *i*PrOH.

№	A^{307}	t, sec	c, M	lnC
0	1,354	0	0,0098	-4,6250
1	0,893	15	0,0065	-5,0413
2	0,616	30	0,0045	-5,4126
3	0,432	45	0,0031	-5,7674
4	0,321	60	0,0023	-6,0644
5	0,210	75	0,0015	-6,4887
6	0,164	90	0,0012	-6,7360

7	0,098	105	0,0007	-7,2509
8	0,072	120	0,0005	-7,5592

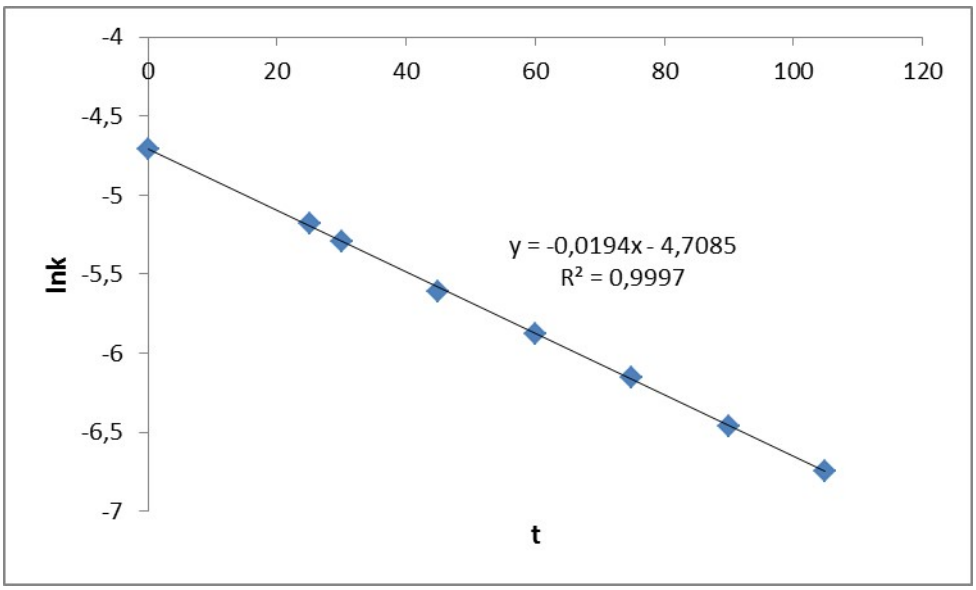


$k_{obs} = 24.1 \pm 1.0 \times 10^{-3} s^{-1}$

- **Addition of 0.5 eq. of $MeNH_2$**

Conditions of experiment: 2Br-4F-Ph Ellman's imine **2a** (200 µl, 0.04 M), 5 mol% $Cu(PPh_3)_3F*2EtOH$ **[Cu-1]** (200 µl, 0.002 M), 10 eq. TABMA **1a** + 0.5 eq. $MeNH_2$ (400 µl, 0.2 M), solvent – *i*PrOH, T = 25.0 °C. $MeNH_2$ was added as 6 M solution in *i*PrOH.

№	A^{307}	t, sec	c, M	lnC
0	1,245	0	0,0090	-4,7089
1	0,777	25	0,0056	-5,1804
2	0,696	30	0,0050	-5,2905
3	0,507	45	0,0037	-5,6073
4	0,388	60	0,0028	-5,8748
5	0,294	75	0,0021	-6,1523
6	0,216	90	0,0016	-6,4606
7	0,162	105	0,0012	-6,7482

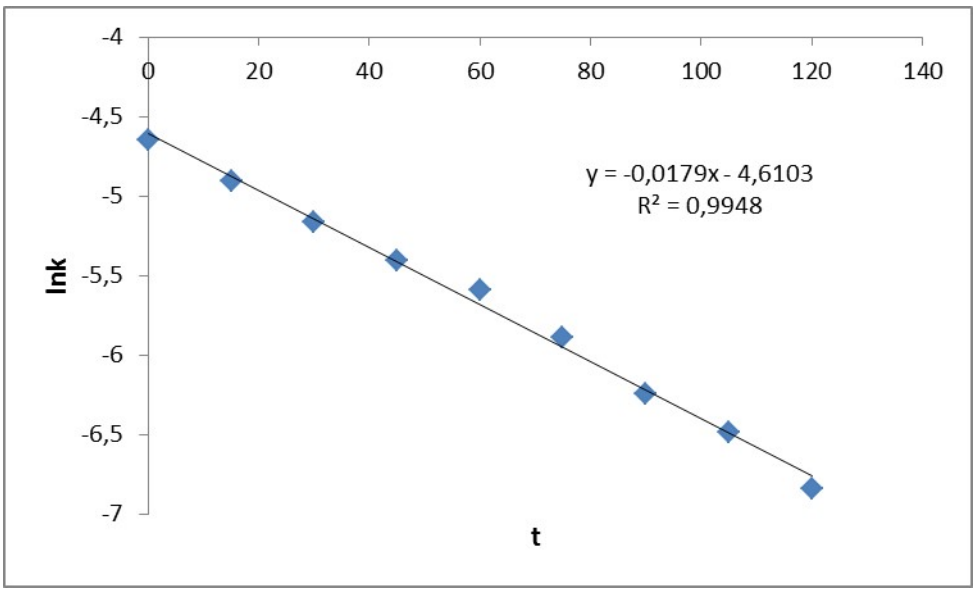


$k_{obs} = 19.4 \pm 0.3 \times 10^{-3} s^{-1}$

- **Addition of 1 eq. of $MeNH_2$**

Conditions of experiment: 2Br-4F-Ph Ellman's imine **2a** (200 µl, 0.04 M), 5 mol% $Cu(PPh_3)_3F*2EtOH$ **[Cu-1]** (200 µl, 0.002 M), 10 eq. TABMA **1a** + 1 eq. $MeNH_2$ (400 µl, 0.2 M), solvent – *i*PrOH, T = 25.0 °C. $MeNH_2$ was added as 6 M solution in *i*PrOH.

№	A^{307}	t, sec	c, M	lnC
0	1,326	0	0,0096	-4,6459
1	1,020	15	0,0074	-4,9083
2	0,787	30	0,0057	-5,1676
3	0,620	45	0,0045	-5,4061
4	0,516	60	0,0037	-5,5897
5	0,382	75	0,0028	-5,8904
6	0,267	90	0,0019	-6,2486
7	0,211	105	0,0015	-6,4840
8	0,148	120	0,0011	-6,8386

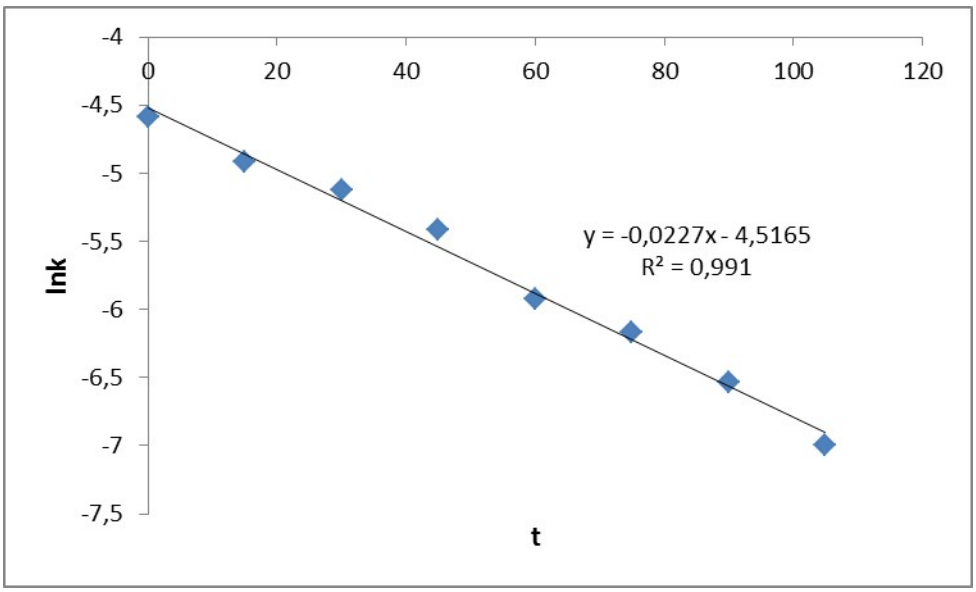


$k_{obs} = 17.9 \pm 0.8 \times 10^{-3} s^{-1}$

- **Addition of 2 eq. of $MeNH_2$**

Conditions of experiment: 2Br-4F-Ph Ellman's imine **2a** (200 µl, 0.04 M), 5 mol% $Cu(PPh_3)_3F*2EtOH$ **[Cu-1]** (200 µl, 0.002 M), 10 eq. TABMA **1a** + 2 eq. $MeNH_2$ (400 µl, 0.2 M), solvent – *i*PrOH, T = 25.0 °C. $MeNH_2$ was added as 6 M solution in *i*PrOH.

№	A^{307}	t, sec	c, M	lnC
0	1,401	0	0,0101	-4,5909
1	1,012	15	0,0073	-4,9162
2	0,825	30	0,0060	-5,1205
3	0,613	45	0,0044	-5,4175
4	0,371	60	0,0027	-5,9196
5	0,289	75	0,0021	-6,1694
6	0,200	90	0,0014	-6,5375
7	0,126	105	0,0009	-6,9996

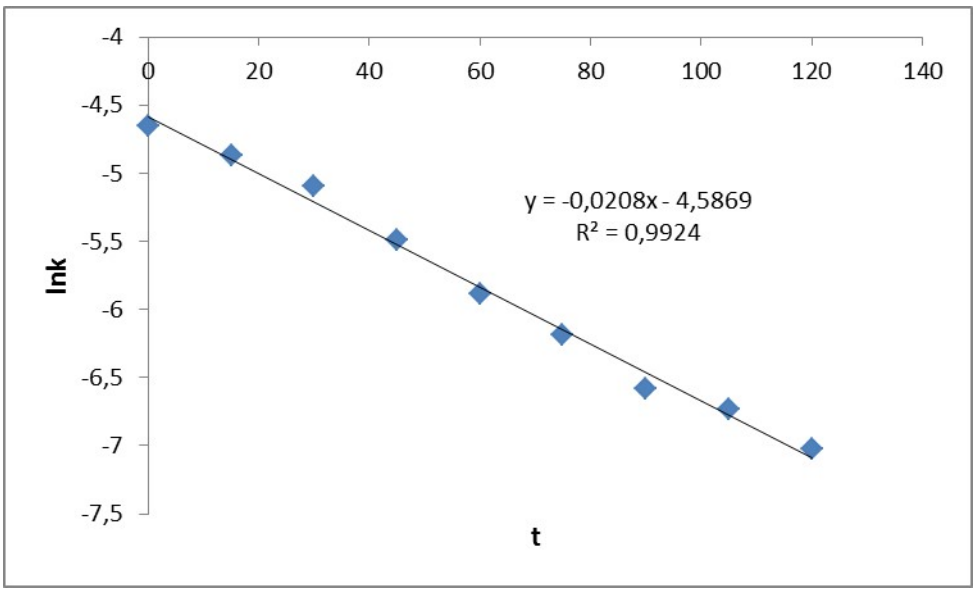


$k_{obs} = 22.7 \pm 1.6 \times 10^{-3} s^{-1}$

- **Addition of 3 eq. of $MeNH_2$**

Conditions of experiment: 2Br-4F-Ph Ellman's imine **2a** (200 µl, 0.04 M), 5 mol% $Cu(PPh_3)_3F*2EtOH$ **[Cu-1]** (200 µl, 0.002 M), 10 eq. TABMA **1a** + 3 eq. $MeNH_2$ (400 µl, 0.2 M), solvent – *i*PrOH, T = 25.0 °C. $MeNH_2$ was added as 6 M solution in *i*PrOH.

№	A^{307}	t, sec	c, M	lnC
0	1,311	0	0,0095	-4,6573
1	1,063	15	0,0077	-4,8670
2	0,847	30	0,0061	-5,0941
3	0,568	45	0,0041	-5,4937
4	0,384	60	0,0028	-5,8852
5	0,283	75	0,0020	-6,1904
6	0,191	90	0,0014	-6,5836
7	0,164	105	0,0012	-6,7360
8	0,123	120	0,0009	-7,0237

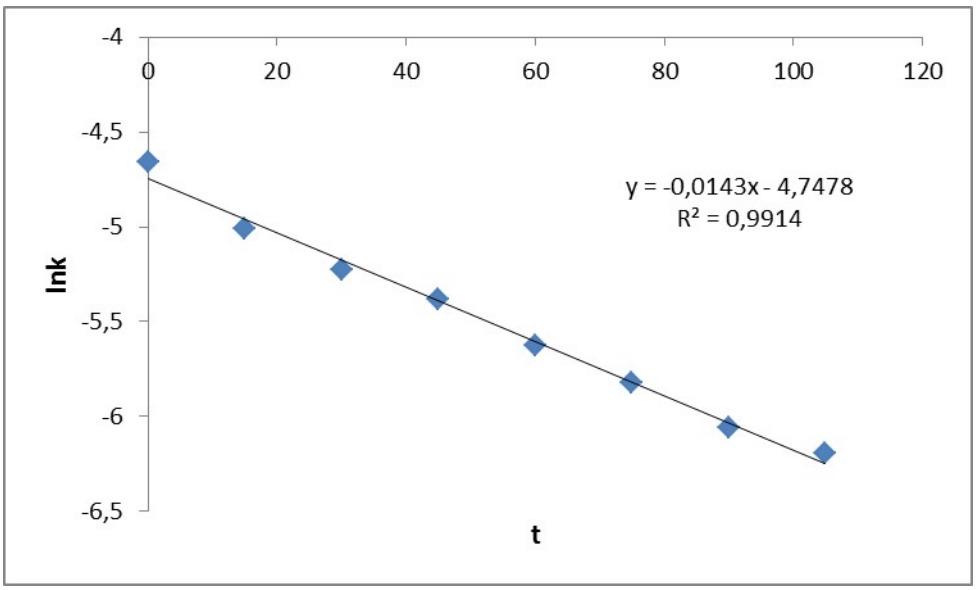


$k_{obs} = 20.8 \pm 1.6 \times 10^{-3} s^{-1}$

- **Addition of 5 eq. of $MeNH_2$**

Conditions of experiment: 2Br-4F-Ph Ellman's imine **2a** (200 µl, 0.04 M), 5 mol% $Cu(PPh_3)_3F*2EtOH$ **[Cu-1]** (200 µl, 0.002 M), 10 eq. TABMA **1a** + 5 eq. $MeNH_2$ (400 µl, 0.2 M), solvent – *i*PrOH, T = 25.0 °C. $MeNH_2$ was added as 6 M solution in *i*PrOH.

№	A^{307}	t, sec	c, M	lnC
0	1,308	0	0,0095	-4,6596
1	0,920	15	0,0067	-5,0115
2	0,743	30	0,0054	-5,2251
3	0,634	45	0,0046	-5,3838
4	0,499	60	0,0036	-5,6232
5	0,408	75	0,0030	-5,8246
6	0,324	90	0,0023	-6,0551
7	0,283	105	0,0020	-6,1904

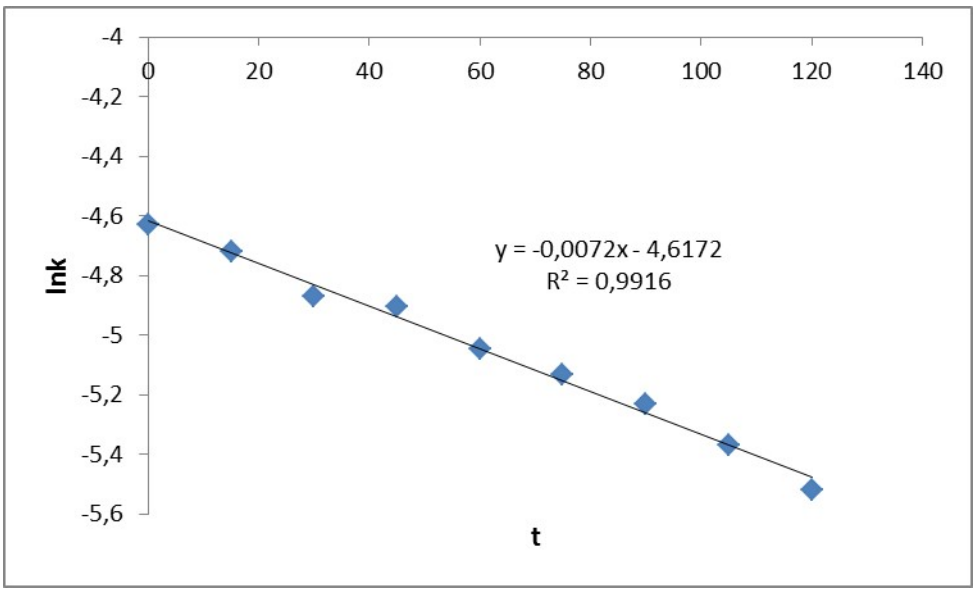


$k_{obs} = 14.3 \pm 1.3 \times 10^{-3} s^{-1}$

- **Addition of 10 eq. of $MeNH_2$**

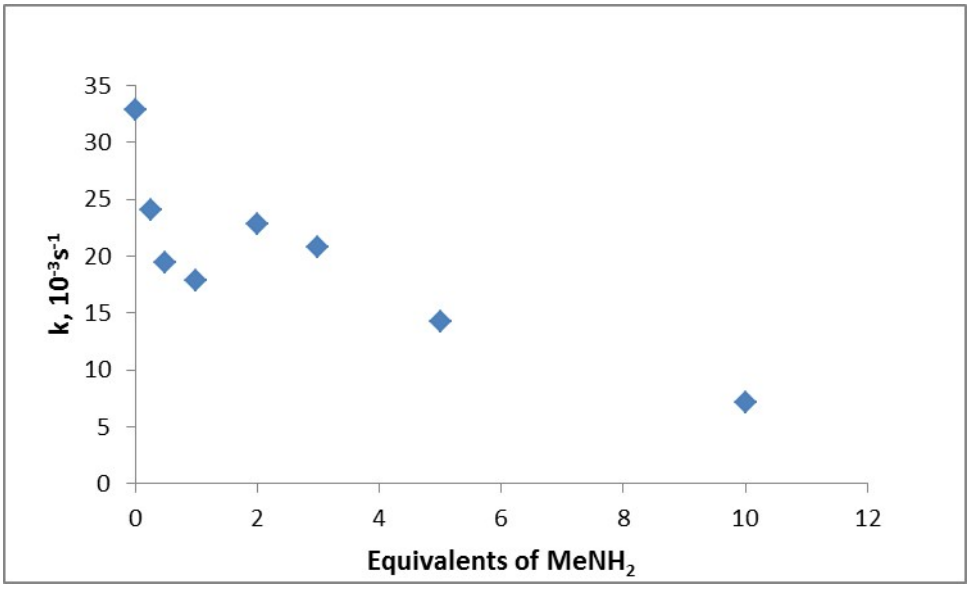
Conditions of experiment: 2Br-4F-Ph Ellman's imine **2a** (200 µl, 0.04 M), 5 mol% $Cu(PPh_3)_3F*2EtOH$ **[Cu-1]** (200 µl, 0.002 M), 10 eq. TABMA **1a** + 10 eq. $MeNH_2$ (400 µl, 0.2 M), solvent – *i*PrOH, T = 25.0 °C. $MeNH_2$ was added as 6 M solution in *i*PrOH.

№	A^{307}	t, sec	c, M	lnC
0	1,347	0	0,0098	-4,6302
1	1,229	15	0,0089	-4,7219
2	1,061	30	0,0077	-4,8689
3	1,023	45	0,0074	-4,9053
4	0,886	60	0,0064	-5,0491
5	0,814	75	0,0059	-5,1339
6	0,738	90	0,0053	-5,2319
7	0,642	105	0,0046	-5,3713
8	0,553	120	0,0040	-5,5205



$k_{obs} = 7.2 \pm 0.5 \times 10^{-3} s^{-1}$

- **Dependence of the observed allylation rate on methylamine additive**



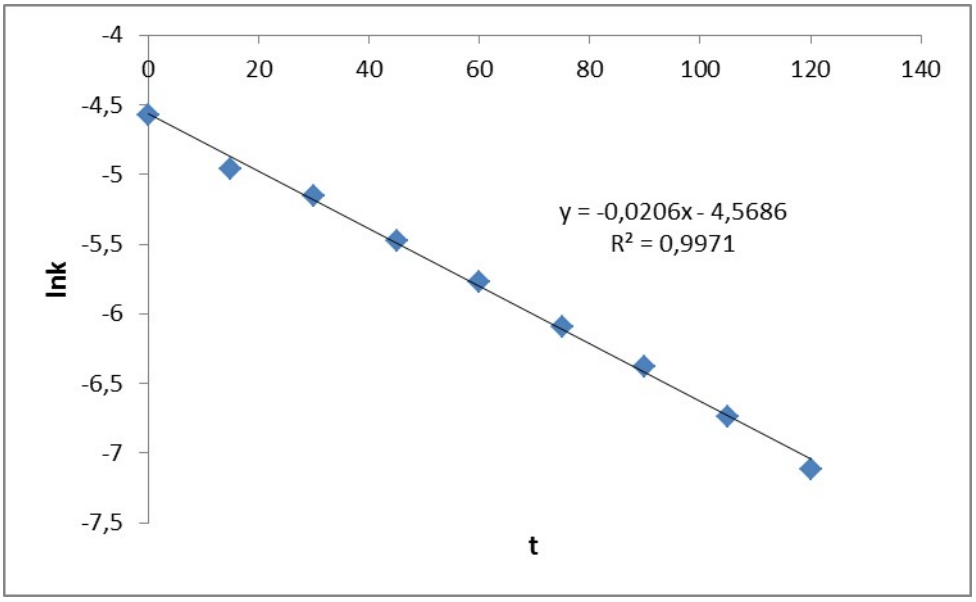
Rate constants of allylation of imine 2a with triallylborane-methylamine adduct 1a in isopropyl alcohol with addition of Et_3N (Figure 3 of the main text)

- **Addition of 2 eq. of Et_3N**

Conditions of experiment: 2Br-4F-Ph Ellman's imine **2a** (200 µl, 0.04 M), 5 mol% $Cu(PPh_3)_3F$*2EtOH **[Cu-1]** (200 µl, 0.002 M), 10 eq. TABMA **1a** + 2 eq. Et_3N (400 µl, 0.2 M), solvent – *i*PrOH, T = 25.0 °C.

№	A^{307}	t, sec	c, M	lnC
0	1,425	0	0,0103	-4,5739
1	0,971	15	0,0070	-4,9575
2	0,794	30	0,0057	-5,1588

3	0,580	45	0,0042	-5,4728
4	0,431	60	0,0031	-5,7697
5	0,311	75	0,0023	-6,0960
6	0,234	90	0,0017	-6,3805
7	0,164	105	0,0012	-6,7360
8	0,112	120	0,0008	-7,1173

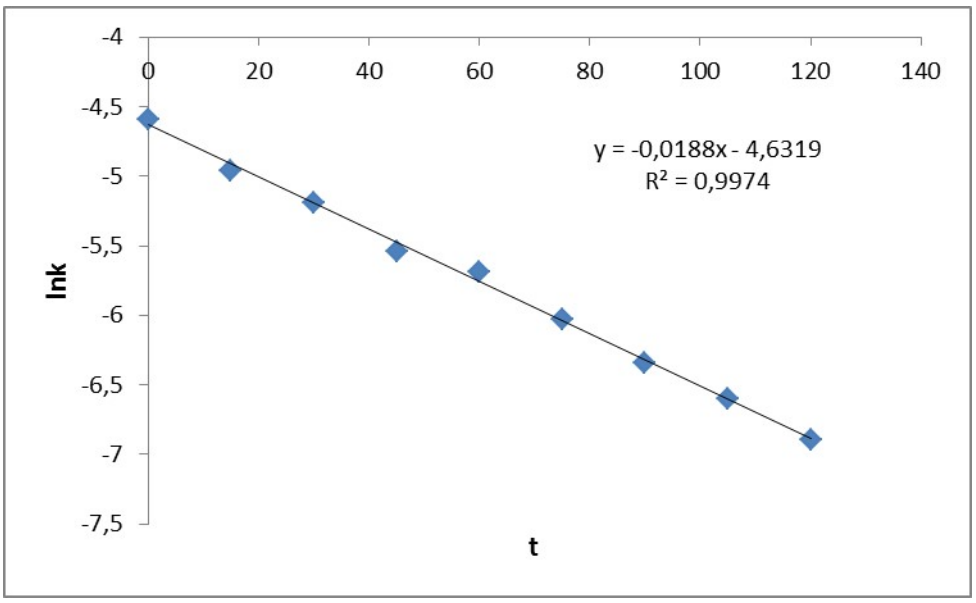


$k_{obs} = 20.6 \pm 1.0 \times 10^{-3} s^{-1}$

- **Addition of 5 eq. of Et_3N**

Conditions of experiment: 2Br-4F-Ph Ellman's imine **2a** (200 µl, 0.04 M), 5 mol% $Cu(PPh_3)_3F*2EtOH$ **[Cu-1]** (200 µl, 0.002 M), 10 eq. TABMA **1a** + 5 eq. Et_3N (400 µl, 0.2 M), solvent – *i*PrOH, T = 25.0 °C.

№	A^{307}	t, sec	c, M	lnC
0	1,396	0	0,0101	-4,5945
1	0,971	15	0,0070	-4,9575
2	0,769	30	0,0056	-5,1907
3	0,543	45	0,0039	-5,5387
4	0,467	60	0,0034	-5,6895
5	0,331	75	0,0024	-6,0337
6	0,243	90	0,0018	-6,3428
7	0,188	105	0,0014	-6,5994
8	0,140	120	0,0010	-6,8942

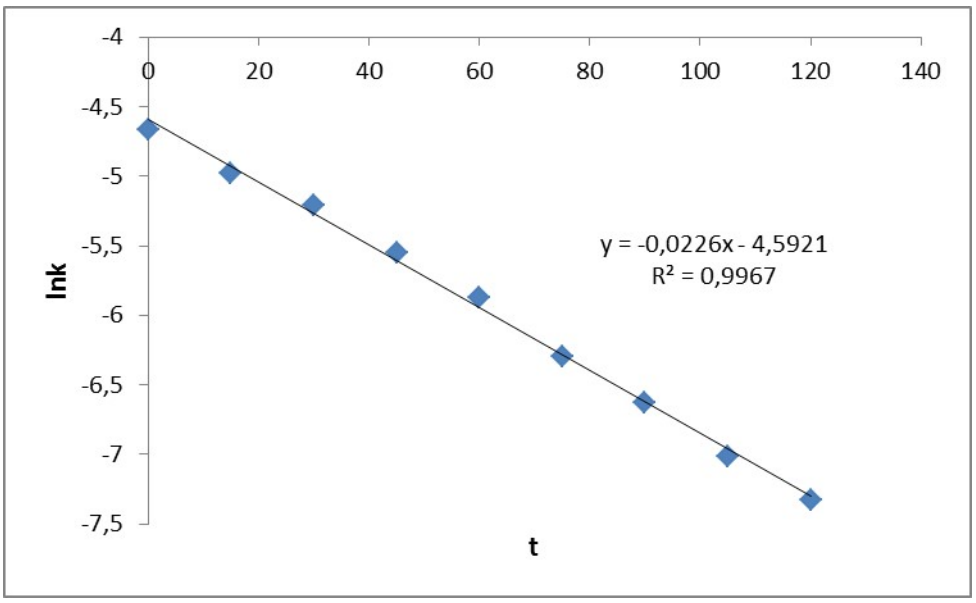


$k_{obs} = 18.8 \pm 0.9 \times 10^{-3} s^{-1}$

- **Addition of 8 eq. of Et_3N**

Conditions of experiment: 2Br-4F-Ph Ellman's imine **2a** (200 µl, 0.04 M), 5 mol% $Cu(PPh_3)_3F*2EtOH$ **[Cu-1]** (200 µl, 0.002 M), 10 eq. TABMA **1a** + 8 eq. Et_3N (400 µl, 0.2 M), solvent – *i*PrOH, T = 25.0 °C.

№	A^{307}	t, sec	c, M	lnC
0	1,304	0	0,0094	-4,6626
1	0,952	15	0,0069	-4,9773
2	0,754	30	0,0055	-5,2104
3	0,539	45	0,0039	-5,5461
4	0,387	60	0,0028	-5,8774
5	0,255	75	0,0018	-6,2946
6	0,183	90	0,0013	-6,6264
7	0,124	105	0,0009	-7,0156
8	0,091	120	0,0007	-7,3250

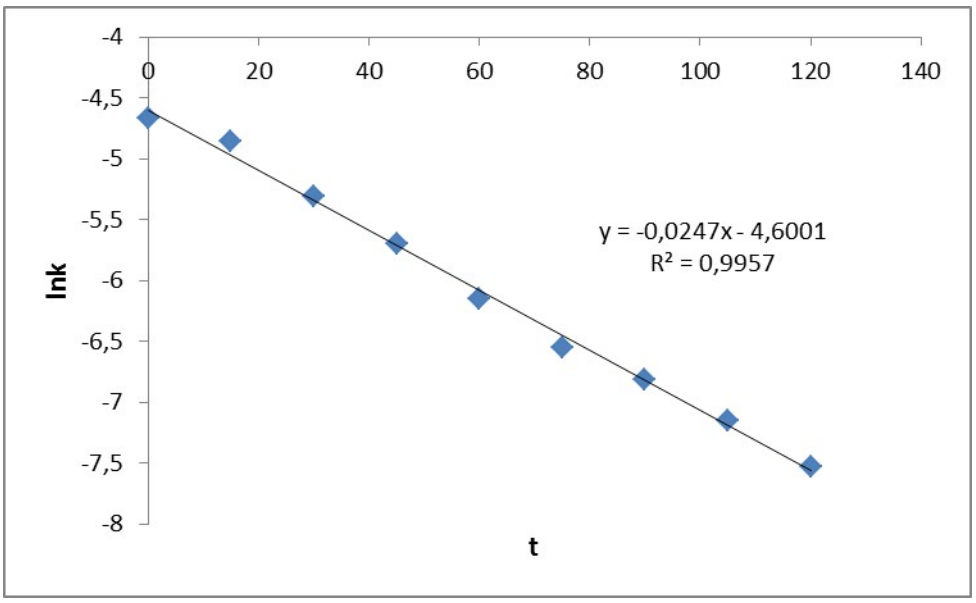


$k_{obs} = 22.6 \pm 1.2 \times 10^{-3} s^{-1}$

- **Addition of 9 eq. of Et_3N**

Conditions of experiment: 2Br-4F-Ph Ellman's imine **2a** (200 µl, 0.04 M), 5 mol% $Cu(PPh_3)_3F*2EtOH$ **[Cu-1]** (200 µl, 0.002 M), 10 eq. TABMA **1a** + 9 eq. Et_3N (400 µl, 0.2 M), solvent – *i*PrOH, T = 25.0 °C.

№	A^{307}	t, sec	c, M	lnC
0	1,304	0	0,0094	-4,6626
1	1,076	15	0,0078	-4,8548
2	0,680	30	0,0049	-5,3137
3	0,462	45	0,0033	-5,7003
4	0,294	60	0,0021	-6,1523
5	0,197	75	0,0014	-6,5526
6	0,152	90	0,0011	-6,8120
7	0,108	105	0,0008	-7,1537
8	0,074	120	0,0005	-7,5318

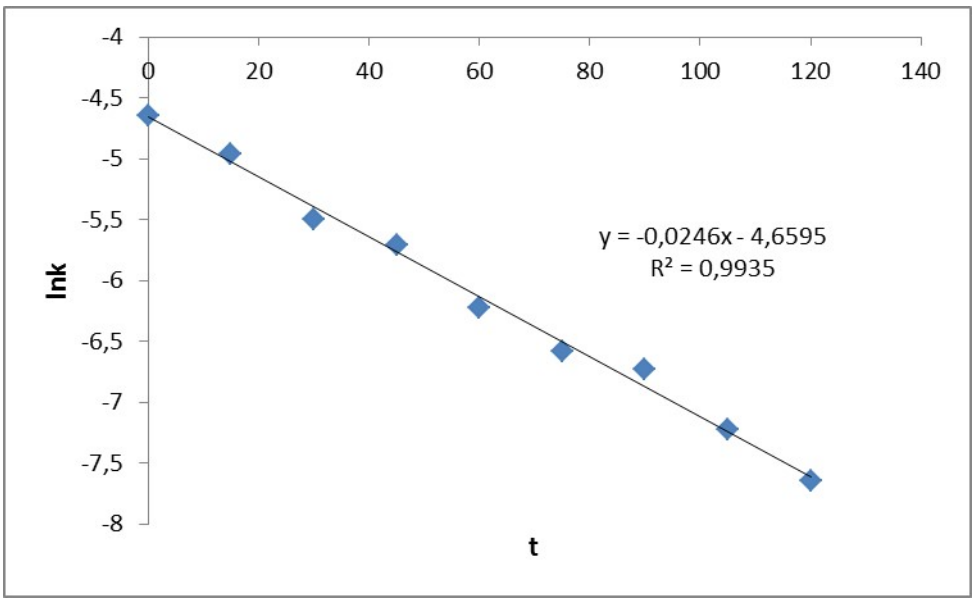


$k_{obs} = 24.7 \pm 1.5 \times 10^{-3} s^{-1}$

- **Addition of 10 eq. of Et_3N**

Conditions of experiment: 2Br-4F-Ph Ellman's imine **2a** (200 µl, 0.04 M), 5 mol% $Cu(PPh_3)_3F*2EtOH$ **[Cu-1]** (200 µl, 0.002 M), 10 eq. TABMA **1a** + 10 eq. Et_3N (400 µl, 0.2 M), solvent – *i*PrOH, T = 25.0 °C.

№	A^{307}	t, sec	c, M	lnC
0	1,326	0	0,0096	-4,6459
1	0,971	15	0,0070	-4,9575
2	0,567	30	0,0041	-5,4955
3	0,456	45	0,0033	-5,7133
4	0,274	60	0,0020	-6,2227
5	0,192	75	0,0014	-6,5783
6	0,165	90	0,0012	-6,7299
7	0,101	105	0,0007	-7,2207
8	0,066	120	0,0005	-7,6462

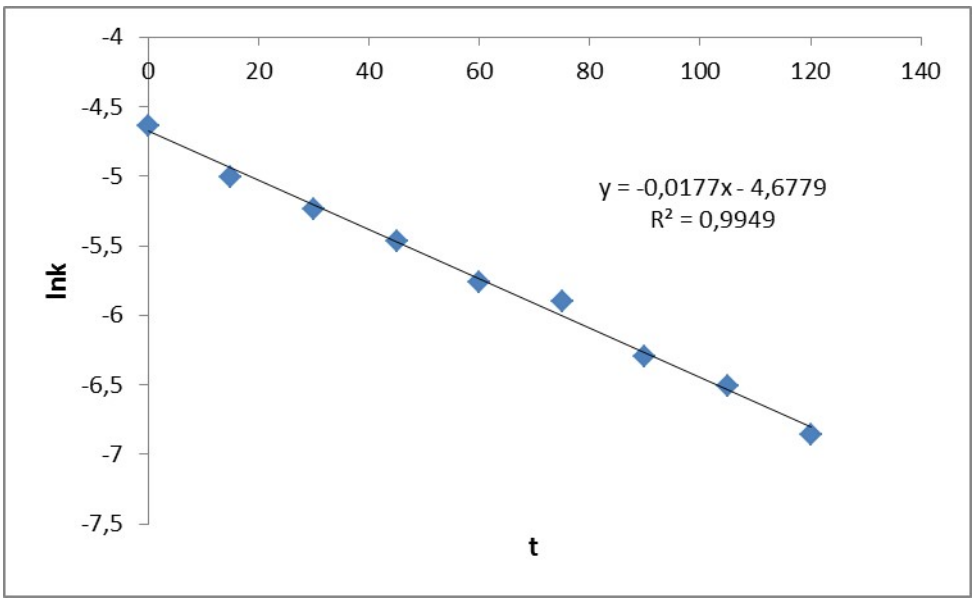


$k_{obs} = 24.6 \pm 1.8 \times 10^{-3} s^{-1}$

- **Addition of 20 eq. of Et_3N**

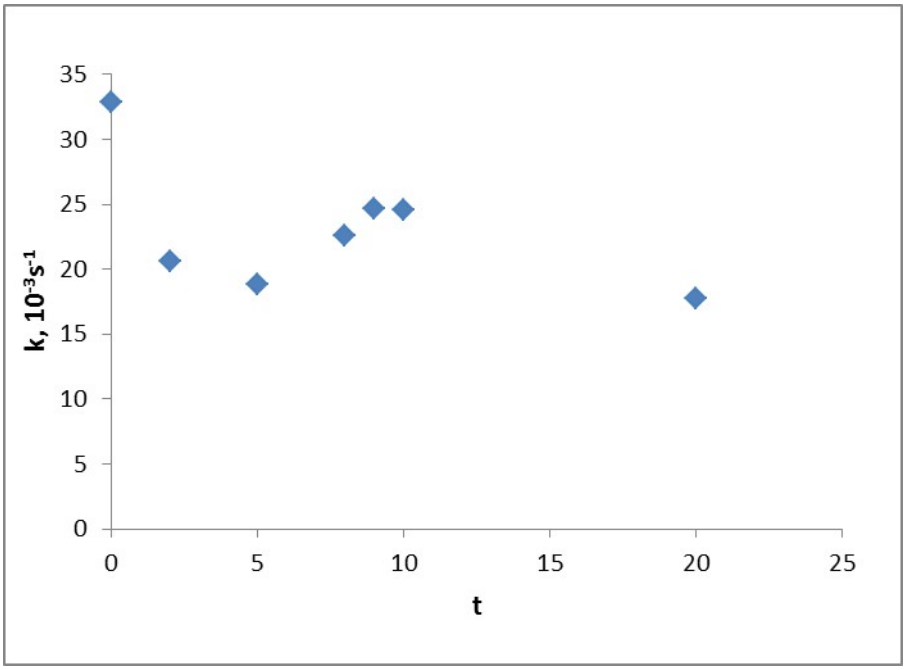
Conditions of experiment: 2Br-4F-Ph Ellman's imine **2a** (200 µl, 0.04 M), 5 mol% $Cu(PPh_3)_3F*2EtOH$ **[Cu-1]** (200 µl, 0.002 M), 10 eq. TABMA **1a** + 20 eq. Et_3N (400 µl, 0.2 M), solvent – *i*PrOH, T = 25.0 °C.

№	A^{307}	t, sec	c, M	lnC
0	1,334	0	0,0097	-4,6399
1	0,928	15	0,0067	-5,0028
2	0,736	30	0,0053	-5,2346
3	0,582	45	0,0042	-5,4694
4	0,434	60	0,0031	-5,7628
5	0,378	75	0,0027	-5,9009
6	0,254	90	0,0018	-6,2985
7	0,205	105	0,0015	-6,5128
8	0,145	120	0,0010	-6,8591



$k_{obs} = 17.7 \pm 1.1 \times 10^{-3} s^{-1}$

- **Dependence of the observed allylation rate on Et_3N additive**



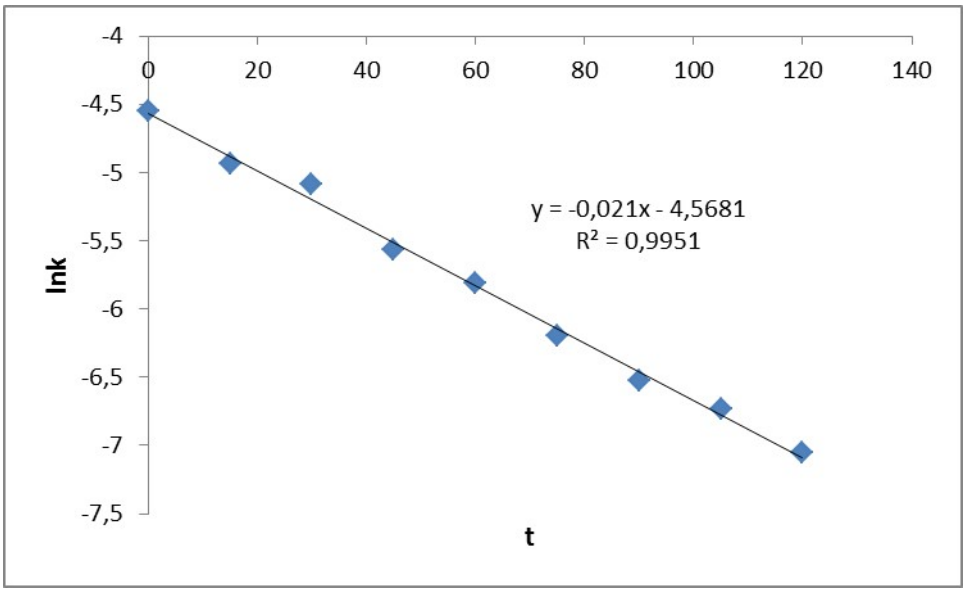
Rate constants of allylation of imine 2a with triallylborane-methylamine adduct 1a in isopropyl alcohol with addition of DABCO (Figure 3 of the main text)

- **Addition of 5 eq. of DABCO**

Conditions of experiment: 2Br-4F-Ph Ellman's imine **2a** (200 µl, 0.04 M), 5 mol% $Cu(PPh_3)_3F*2EtOH$ **[Cu-1]** (200 µl, 0.002 M), 10 eq. TABMA **1a** + 5 eq. DABCO (400 µl, 0.2 M), solvent – *i*PrOH, T = 25.0 °C.

№	A^{307}	t, sec	c, M	lnC
0	1,466	0	0,0106	-4,5455

1	0,989	15	0,0072	-4,9391
2	0,851	30	0,0062	-5,0894
3	0,529	45	0,0038	-5,5649
4	0,415	60	0,0030	-5,8076
5	0,282	75	0,0020	-6,1939
6	0,202	90	0,0015	-6,5276
7	0,165	105	0,0012	-6,7299
8	0,120	120	0,0009	-7,0483

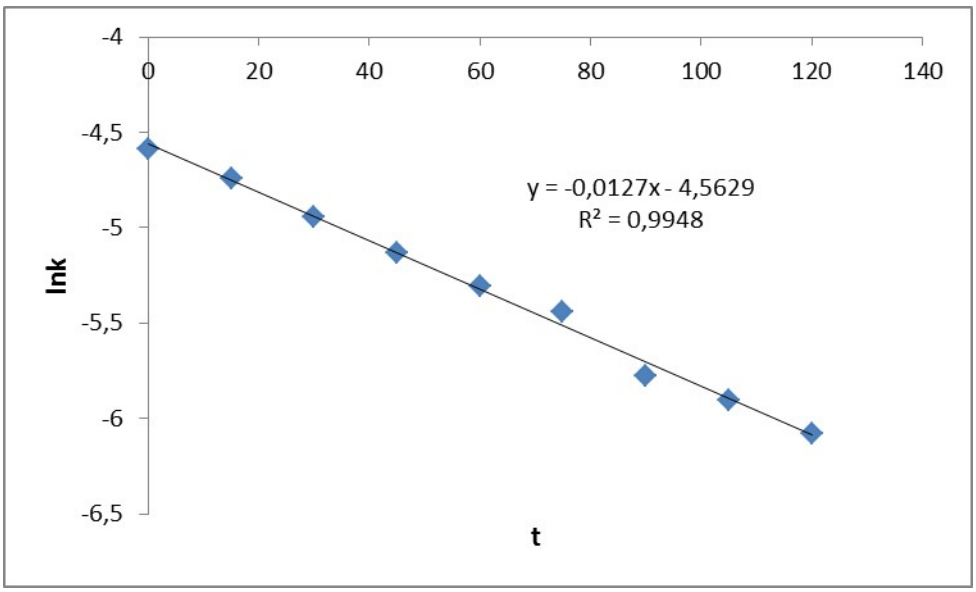


$k_{obs} = 21.0 \pm 1.3 \times 10^{-3} s^{-1}$

- **Addition of 10 eq. of DABCO**

Conditions of experiment: 2Br-4F-Ph Ellman's imine **2a** (200 µl, 0.04 M), 5 mol% $Cu(PPh_3)_3F*2EtOH$ **[Cu-1]** (200 µl, 0.002 M), 10 eq. TABMA **1a** + 10 eq. DABCO (400 µl, 0.2 M), solvent – *i*PrOH, T = 25.0 °C.

№	A^{307}	t, sec	c, M	lnC
0	1,402	0	0,0102	-4,5902
1	1,207	15	0,0087	-4,7399
2	0,983	30	0,0071	-4,9452
3	0,814	45	0,0059	-5,1339
4	0,683	60	0,0049	-5,3093
5	0,598	75	0,0043	-5,4422
6	0,429	90	0,0031	-5,7744
7	0,376	105	0,0027	-5,9063
8	0,316	120	0,0023	-6,0801

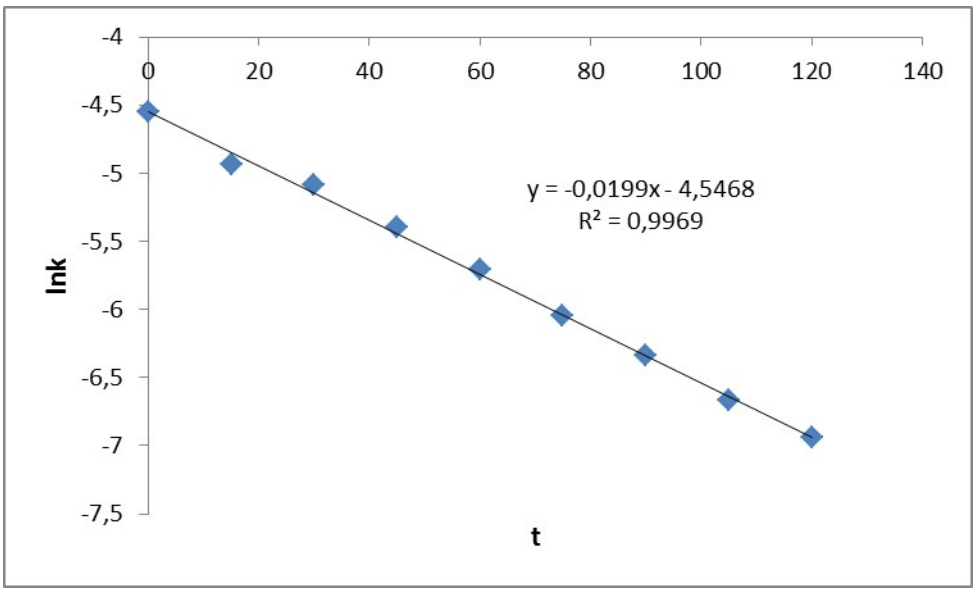


$k_{obs} = 12.7 \pm 0.8 \times 10^{-3} s^{-1}$

- **Addition of 20 eq. of DABCO**

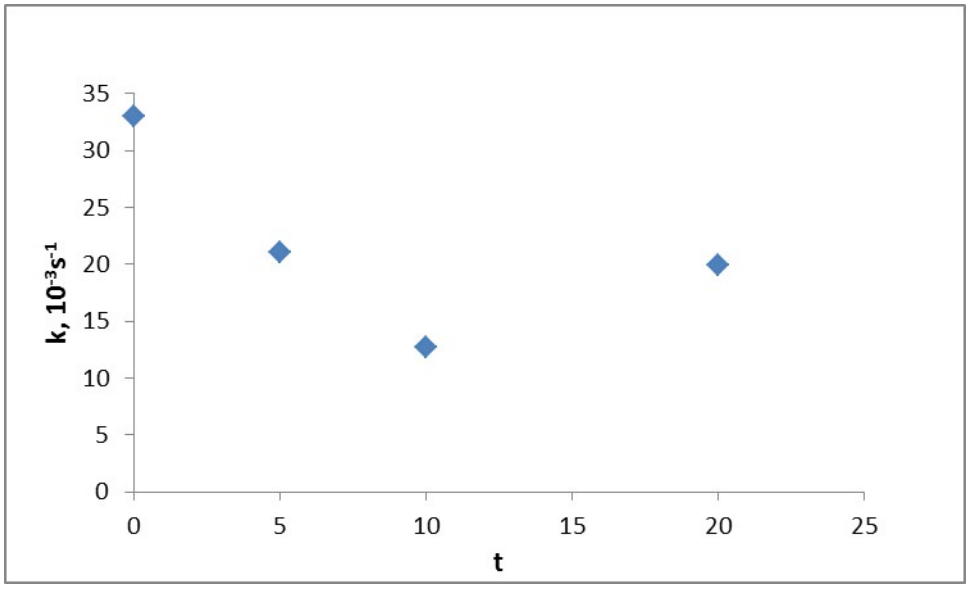
Conditions of experiment: 2Br-4F-Ph Ellman's imine **2a** (200 µl, 0.04 M), 5 mol% $Cu(PPh_3)_3F*2EtOH$ **[Cu-1]** (200 µl, 0.002 M), 10 eq. TABMA **1a** + 20 eq. DABCO (400 µl, 0.2 M), solvent – *i*PrOH, T = 25.0 °C.

№	A^{307}	t, sec	c, M	lnC
0	1,466	0	0,0106	-4,5455
1	0,989	15	0,0072	-4,9391
2	0,851	30	0,0062	-5,0894
3	0,629	45	0,0046	-5,3917
4	0,457	60	0,0033	-5,7112
5	0,326	75	0,0024	-6,0489
6	0,244	90	0,0018	-6,3387
7	0,175	105	0,0013	-6,6711
8	0,134	120	0,0010	-6,9380



$k_{obs} = 19.9 \pm 1.0 \times 10^{-3} s^{-1}$

- **Dependence of the observed allylation rate on DABCO additive**



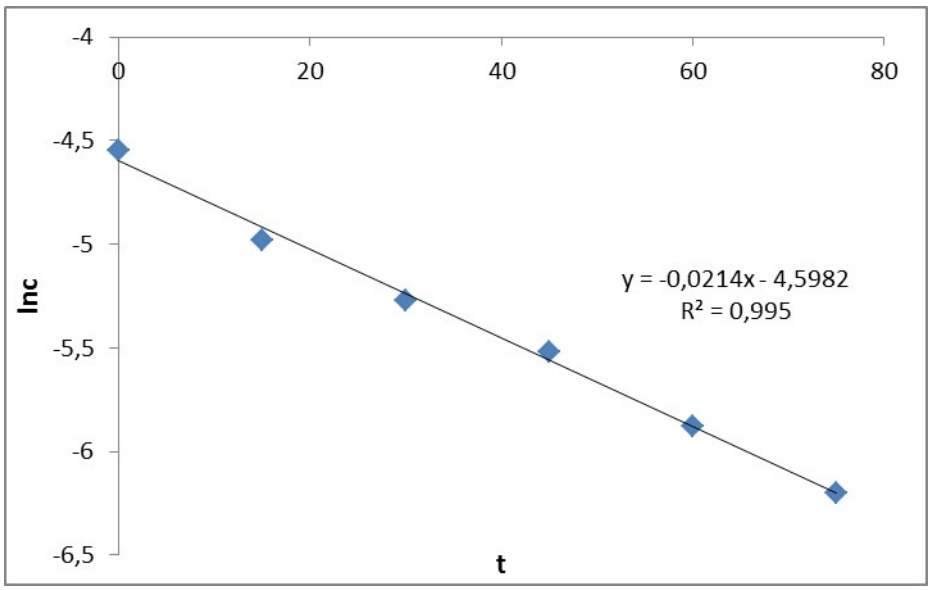
Rate constants of allylation of imine 2a with triallylborane-methylamine adduct 1a in isopropyl alcohol with addition of PPh_3 (Figure 4 of the main text)

- **Addition of 1 eq. of PPh_3**

Conditions of experiment: 2Br-4F-Ph Ellman's imine 2**a** (200 µl, 0.04 M), 5 mol% $Cu(PPh_3)_3F*2EtOH$ **[Cu-1]** + 5 mol% PPh_3 (200 µl, 0.002 M), 10 eq. TABMA **1a** (400 µl, 0.2 M), solvent – *i*PrOH, T = 25.0 °C.

№	A^{307}	t, sec	c, M	lnC
0	1,465	0	0,0106	-4,5462
1	0,948	15	0,0069	-4,9815
2	0,711	30	0,0051	-5,2692

3	0,553	45	0,0040	-5,5205
4	0,386	60	0,0028	-5,8800
5	0,280	75	0,0020	-6,2011

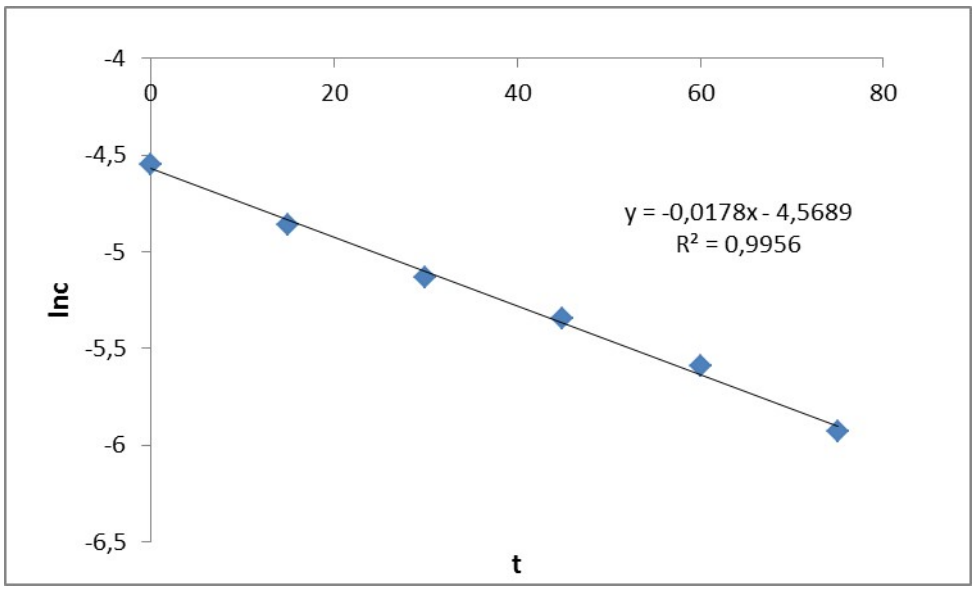


$k_{obs} = 21.4 \pm 0.5 \times 10^{-3} s^{-1}$

- **Addition of 2 eq. of PPh_3**

Conditions of experiment: 2Br-4F-Ph Ellman's imine **2a** (200 µl, 0.04 M), 5 mol% $Cu(PPh_3)_3F*2EtOH$ **[Cu-1]** + 10 mol% PPh_3 (200 µl, 0.002 M), 10 eq. TABMA **1a** (400 µl, 0.2 M), solvent – *i*PrOH, T = 25.0 °C.

№	A^{307}	t, sec	c, M	lnC
0	1,465	0	0,0106	-4,5462
1	1,069	15	0,0077	-4,8614
2	0,813	30	0,0059	-5,1351
3	0,660	45	0,0048	-5,3436
4	0,514	60	0,0037	-5,5936
5	0,367	75	0,0027	-5,9305

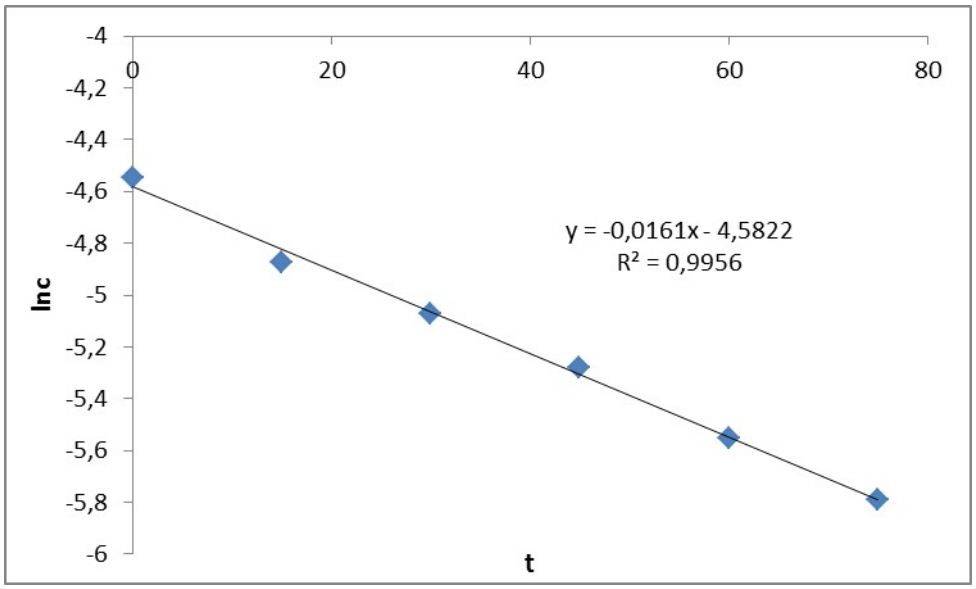


$k_{obs} = 17.8 \pm 0.3 \times 10^{-3} s^{-1}$

- **Addition of 3 eq. of PPh_3**

Conditions of experiment: 2Br-4F-Ph Ellman's imine **2a** (200 µl, 0.04 M), 5 mol% $Cu(PPh_3)_3F*2EtOH$ **[Cu-1]** + 15 mol% PPh_3 (200 µl, 0.002 M), 10 eq. TABMA **1a** (400 µl, 0.2 M), solvent – *i*PrOH, T = 25.0 °C.

№	A^{307}	t, sec	c, M	lnC
0	1,465	0	0,0106	-4,5462
1	1,056	15	0,0076	-4,8736
2	0,864	30	0,0063	-5,0743
3	0,702	45	0,0051	-5,2819
4	0,536	60	0,0039	-5,5517
5	0,423	75	0,0031	-5,7885



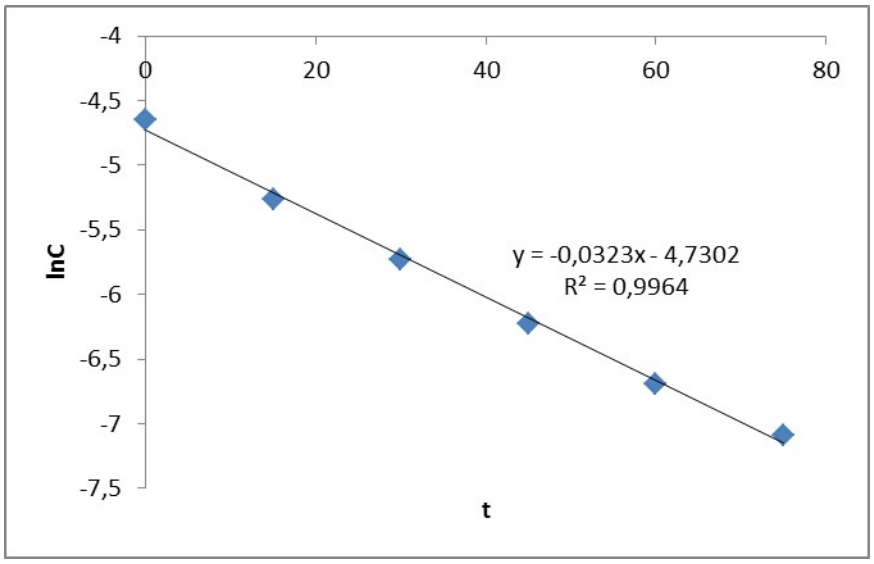
$k_{obs} = 16.1 \pm 0.3 \times 10^{-3} s^{-1}$

Rate constants of allylation of imine 2a with triallylborane-methylamine adduct 1a in isopropyl alcohol with using of different copper catalysts (Table 3 of the main text)

- ***bis*(Triphenylphosphine)-copper(I)-bis(μ$_2$-ethoxy)-difluoroborate [Cu-2]**

Conditions of experiment: 2Br-4F-Ph Ellman's imine **2a** (200 μl, 0.04 M), 5 mol% $Cu(PPh_3)_2BF_2(OEt)_2$ **[Cu-2]** (200 μl, 0.002 M), 10 eq. TABMA **1a** (400 μl, 0.2M), solvent – *i*PrOH, T = 25.0 °C.

№	A^{307}	t, sec	c, M	lnC
0	1,316	0	0,0095	-4,6535
1	0,717	15	0,0052	-5,2608
2	0,447	30	0,0032	-5,7333
3	0,274	45	0,0020	-6,2227
4	0,172	60	0,0012	-6,6883
5	0,115	75	0,0008	-7,0909



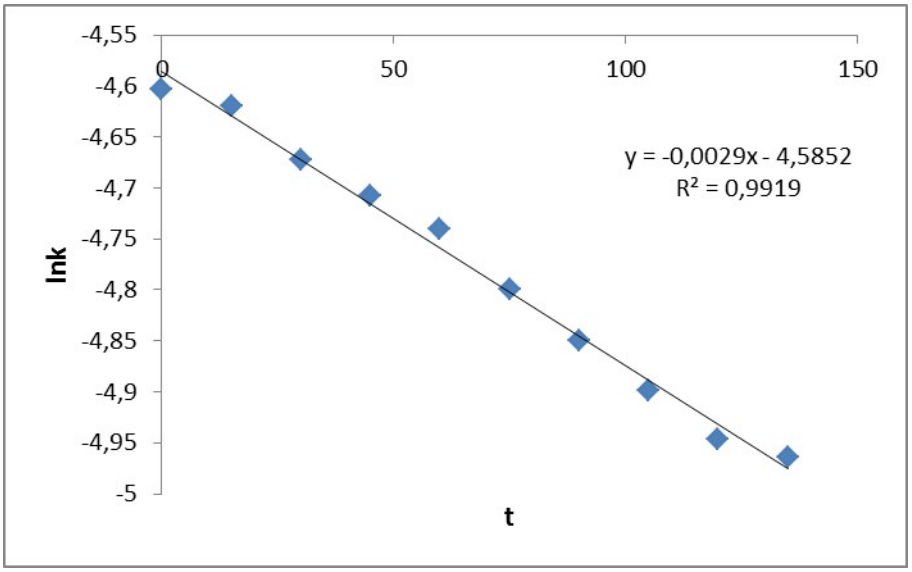
$k_{obs} = 32.3 \pm 2.5 \times 10^{-3} s^{-1}$

- ***tris*-(Triphenylphosphine)copper(I)chloride*acetonitrile [Cu-3]**

Conditions of experiment: 2Br-4F-Ph Ellman's imine **2a** (200 μl, 0.04 M), 5 mol% $Cu(PPh_3)_3Cl$*MeCN **[Cu-3]** (200 μl, 0.002 M), 10 eq. TABMA **1a** (400 μl, 0.2M), solvent – *i*PrOH, T = 25.0 °C.

№	A^{307}	t, sec	c, M	lnC
0	1,384	0	0,0100	-4,6031
1	1,361	15	0,0099	-4,6199
2	1,291	30	0,0093	-4,6727
3	1,247	45	0,0090	-4,7073
4	1,207	60	0,0087	-4,7399
5	1,137	75	0,0082	-4,7997
6	1,082	90	0,0078	-4,8493

7	1,030	105	0,0075	-4,8985
8	0,982	120	0,0071	-4,9462
9	0,965	135	0,0070	-4,9637

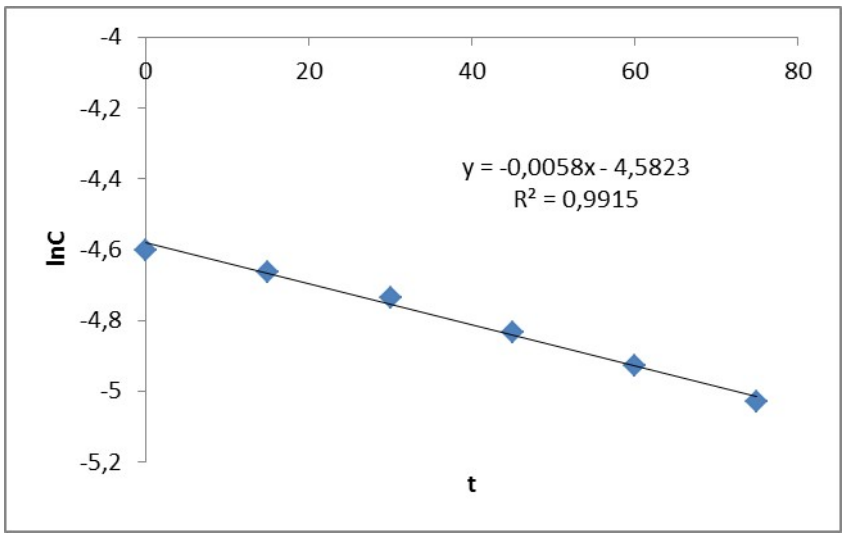


$k_{obs} = 2.9 \pm 0.2 \times 10^{-3} s^{-1}$

- **[1,3-b*is*(2,4,6-Trimethylphenyl)-2-imidazolidinylidene]copper(I)chloride [Cu-4]**

Conditions of experiment: 2Br-4F-Ph Ellman's imine **2a** (200 µl, 0.04 M), 5 mol% (SiMes)CuCl **[Cu-4]** (200 µl, 0.002 M), 10 eq. TABMA **1a** (400 µl, 0.2M), solvent – *i*PrOH, T = 25.0 °C.

№	A^{307}	t, sec	c, M	lnC
0	1,385	0	0,0100	-4,6024
1	1,303	15	0,0094	-4,6634
2	1,212	30	0,0088	-4,7358
3	1,100	45	0,0080	-4,8328
4	0,998	60	0,0072	-4,9301
5	0,903	75	0,0065	-5,0301
6	0,114	**900**	0,0008	-7,0996

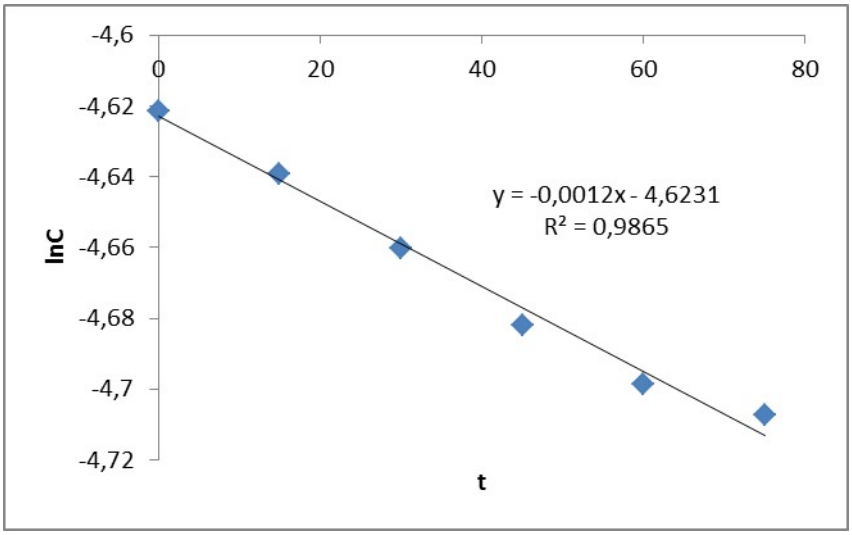


$k_{obs} = 5.8 \pm 0.7 \times 10^{-3} s^{-1}$

- ***bis*(1,2-*bis*(diphenylphosphaneyl)ethane)copper(I)tetrafluoroborate [Cu-5]**

Conditions of experiment: 2Br-4F-Ph Ellman's imine **2a** (200 µl, 0.04 M), 5 mol% $Cu(DPPE)_2BF_4$ **[Cu-5]** (200 µl, 0.002 M), 10 eq. TABMA **1a** (400 µl, 0.2 M), solvent – *i*PrOH, T = 25.0 °C.

№	A^{307}	t, sec	c, M	lnC
0	1,359	0	0,0098	-4,6213
1	1,335	15	0,0097	-4,6392
2	1,307	30	0,0095	-4,6604
3	1,279	45	0,0093	-4,6820
4	1,258	60	0,0091	-4,6986
5	1,247	75	0,0090	-4,7073
6	1,023	**900**	0,0074	-4,9053

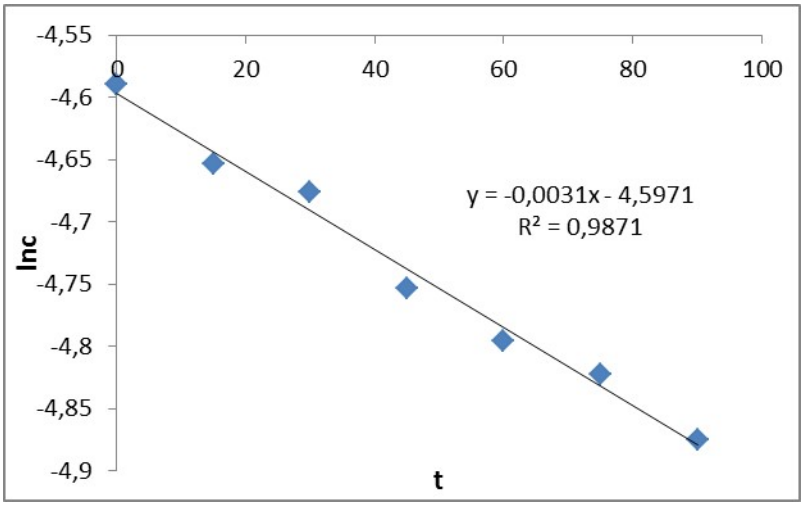


$k_{obs} = 1.2 \pm 0.2 \times 10^{-3} s^{-1}$

- **Addition of 2 eq. of $MeNH_2$ to [Cu-5]-catalyzed allylation reaction**

Conditions of experiment: 2Br-4F-Ph Ellman's imine **2a** (200 µl, 0.04 M), 5 mol% $Cu(DPPE)_2BF_4$ **[Cu-5]** (200 µl, 0.002 M), 10 eq. TABMA **1a** + 2 eq. $MeNH_2$ (400 µl, 0.2 M), solvent – *i*PrOH, T = 25.0 °C. $MeNH_2$ was added as 6 M solution in *i*PrOH.

№	A^{307}	t, sec	c, M	lnC
0	1,403	0	0,0102	-4,5895
1	1,316	15	0,0095	-4,6535
2	1,286	30	0,0093	-4,6765
3	1,191	45	0,0086	-4,7533
4	1,141	60	0,0083	-4,7962
5	1,111	75	0,0080	-4,8228
6	1,054	90	0,0076	-4,8755
7	1,024	**900**	0,0074	-4,9044

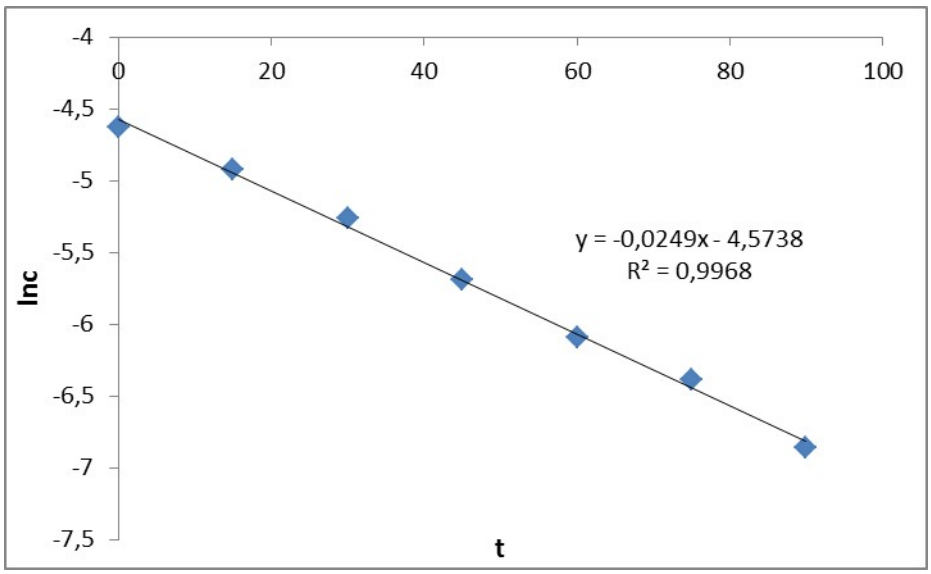


$k_{obs} = 3.1 \pm 0.5 \times 10^{-3} s^{-1}$

- **Addition of 0.5 eq. of *t*BuOK to [Cu-5]-catalyzed allylation reaction**

Conditions of experiment: 2Br-4F-Ph Ellman's imine **2a** (200 µl, 0.04 M), 5 mol% $Cu(DPPE)_2BF_4$ **[Cu-5]** (200 µl, 0.002 M), 10 eq. TABMA **1a** + 0.5 eq. *t*BuOK (400 µl, 0.2M), solvent – *i*PrOH, T = 25.0 °C.

№	A^{307}	t, sec	c, M	lnC
0	1,348	0	0,0098	-4,6295
1	1,006	15	0,0073	-4,9221
2	0,713	30	0,0052	-5,2664
3	0,466	45	0,0034	-5,6917
4	0,311	60	0,0023	-6,0960
5	0,233	75	0,0017	-6,3848
6	0,145	90	0,0010	-6,8591
7	0,031	**900**	0,0002	-8,4019

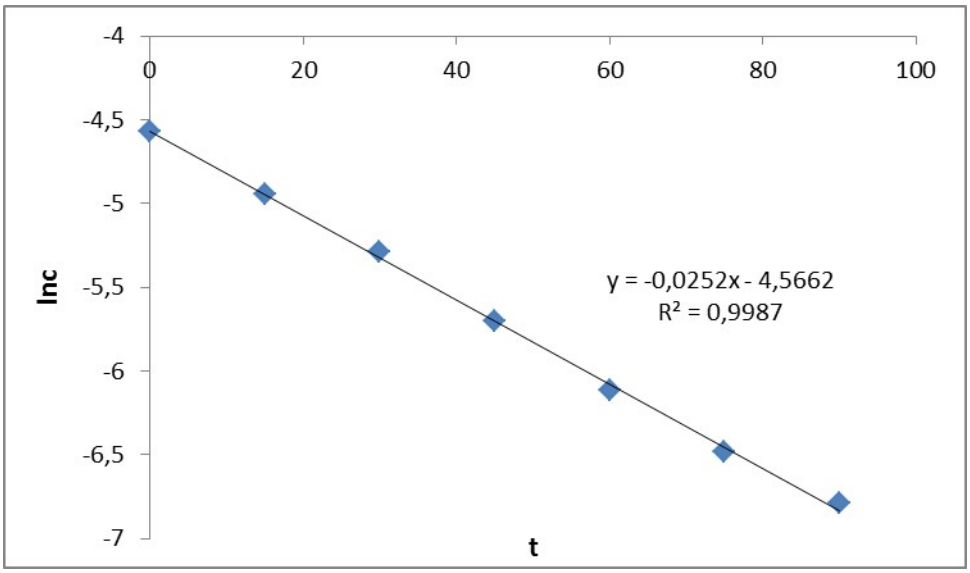


$k_{obs} = 24.9 \pm 1.0 \times 10^{-3} s^{-1}$

- **Addition of 0.5 eq. of *t*BuOK to [Cu-1]-catalyzed allylation reaction**

Conditions of experiment: 2Br-4F-Ph Ellman's imine **2a** (200 µl, 0.04 M), 5 mol% $Cu(PPh_3)_3F*2EtOH$ **[Cu-1]** (200 µl, 0.002 M), 10 eq. TABMA **1a** + 0.5 eq. *t*BuOK (400 µl, 0.2M), solvent – *i*PrOH, T = 25.0 °C.

№	A^{307}	t, sec	c, M	lnC
0	1,435	0	0,0104	-4,5669
1	0,983	15	0,0071	-4,9452
2	0,697	30	0,0050	-5,2891
3	0,461	45	0,0033	-5,7024
4	0,304	60	0,0022	-6,1188
5	0,212	75	0,0015	-6,4793
6	0,155	90	0,0011	-6,7924

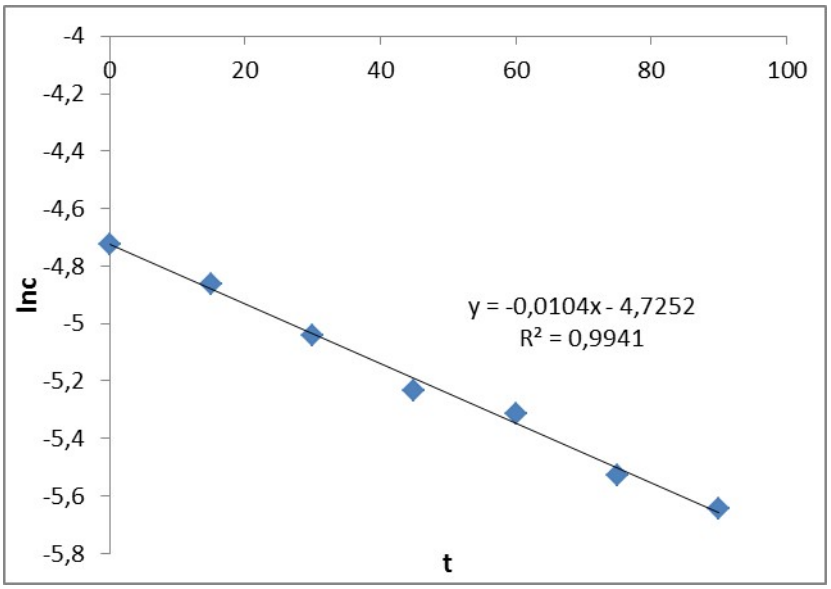


$k_{obs} = 25.2 \pm 0.8 \times 10^{-3} s^{-1}$

- **Addition of 2 eq. of *t*BuOK to [Cu-5]-catalyzed allylation reaction**

Conditions of experiment: 2Br-4F-Ph Ellman's imine **2a** (200 µl, 0.04 M), 5 mol% $Cu(DPPE)_2BF_4$ **[Cu-5]** (200 µl, 0.002 M), 10 eq. TABMA **1a** + 2 eq. *t*BuOK (400 µl, 0.2 M), solvent – *i*PrOH, T = 25.0 °C.

№	A^{307}	t, sec	c, M	lnC
0	1,228	0	0,0089	-4,7227
1	1,065	15	0,0077	-4,8651
2	0,892	30	0,0065	-5,0424
3	0,738	45	0,0053	-5,2319
4	0,681	60	0,0049	-5,3123
5	0,548	75	0,0040	-5,5296
6	0,489	90	0,0035	-5,6435
7	0,104	**780**	0,0008	-7,1886



$k_{obs} = 10.4 \pm 0.9 \times 10^{-3} s^{-1}$

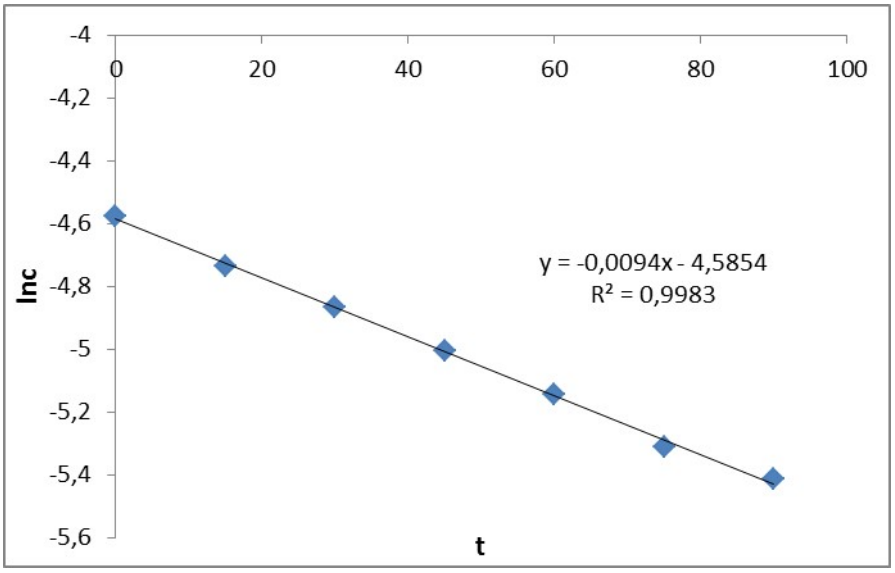
Rate constants of [Cu-5]-catalyzed allylation of imine 2a with triallylborane-methylamine adduct 1a in isopropyl alcohol with addition of tBuOK (Figure 5 and Table 3 of the main text)

- **Addition of 0.1 eq. of *t*BuOK**

Conditions of experiment: 2Br-4F-Ph Ellman's imine **2a** (200 µl, 0.04 M), 5 mol% $Cu(DPPE)_2BF_4$ **[Cu-4]** (200 µl, 0.002 M), 10 eq. TABMA **1a** + 0.1 eq. *t*BuOK (400 µl, 0.2M), solvent – *i*PrOH, T = 25.0 °C.

№	A^{307}	t, sec	c, M	lnC
0	1,422	0	0,0103	-4,5760
1	1,209	15	0,0088	-4,7383

2	1,065	30	0,0077	-4,8651
3	0,926	45	0,0067	-5,0050
4	0,805	60	0,0058	-5,1450
5	0,682	75	0,0049	-5,3108
6	0,614	90	0,0044	-5,4158
7	0,036	900	0,0003	-8,2523

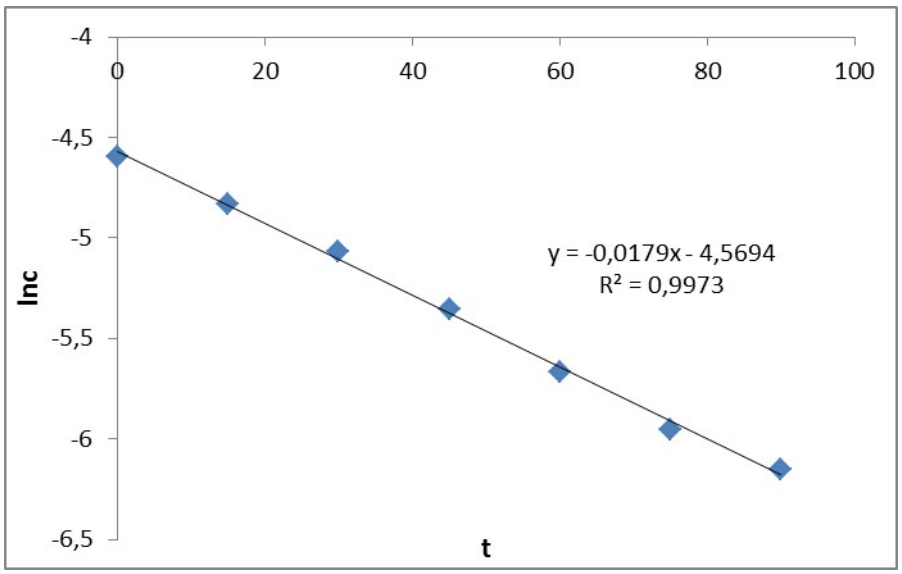


$k_{obs} = 9.4 \pm 0.4 \times 10^{-3} s^{-1}$

- **Addition of 0.3 eq. of *t*BuOK**

Conditions of experiment: 2Br-4F-Ph Ellman's imine **2a** (200 µl, 0.04 M), 5 mol% $Cu(DPPE)_2BF_4$ **[Cu-4]** (200 µl, 0.002 M), 10 eq. TABMA **1a** + 0.3 eq. *t*BuOK (400 µl, 0.2M), solvent – *i*PrOH, T = 25.0 °C.

№	A^{307}	t, sec	c, M	lnC
0	1,396	0	0,0101	-4,5945
1	1,101	15	0,0080	-4,8319
2	0,868	30	0,0063	-5,0696
3	0,653	45	0,0047	-5,3543
4	0,479	60	0,0035	-5,6641
5	0,358	75	0,0026	-5,9553
6	0,294	90	0,0021	-6,1523
7	0,050	**840**	0,0004	-7,9238

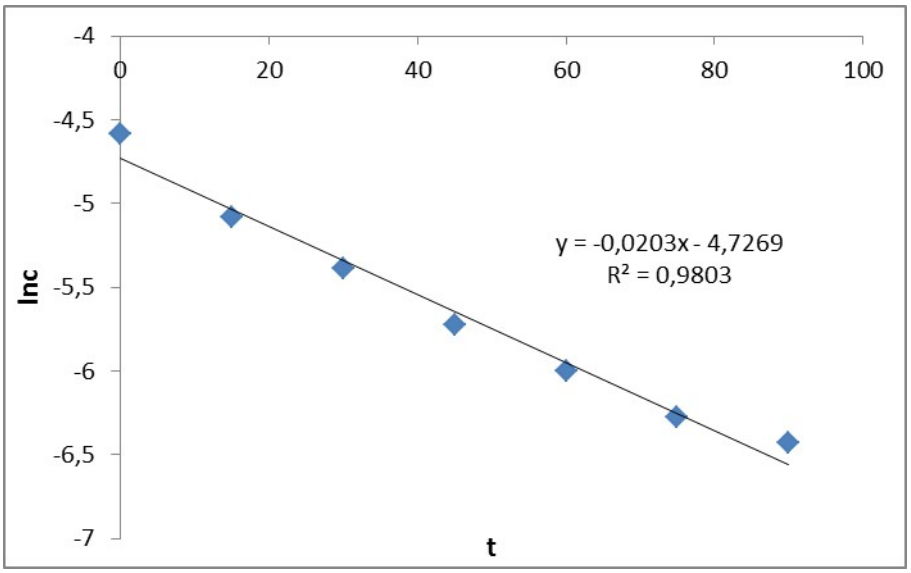


$k_{obs} = 17.9 \pm 1.0 \times 10^{-3} s^{-1}$

- **Addition of 0.4 eq. of *t*BuOK**

Conditions of experiment: 2Br-4F-Ph Ellman's imine **2a** (200 µl, 0.04 M), 5 mol% $Cu(DPPE)_2BF_4$ **[Cu-4]** (200 µl, 0.002 M), 10 eq. TABMA **1a** + 0.4 eq. *t*BuOK (400 µl, 0.2M), solvent – *i*PrOH, T = 25.0 °C.

№	A^{307}	t, sec	c, M	lnC
0	1,409	0	0,0102	-4,5852
1	0,857	15	0,0062	-5,0824
2	0,630	30	0,0046	-5,3901
3	0,452	45	0,0033	-5,7222
4	0,341	60	0,0025	-6,0040
5	0,259	75	0,0019	-6,2790
6	0,223	90	0,0016	-6,4287

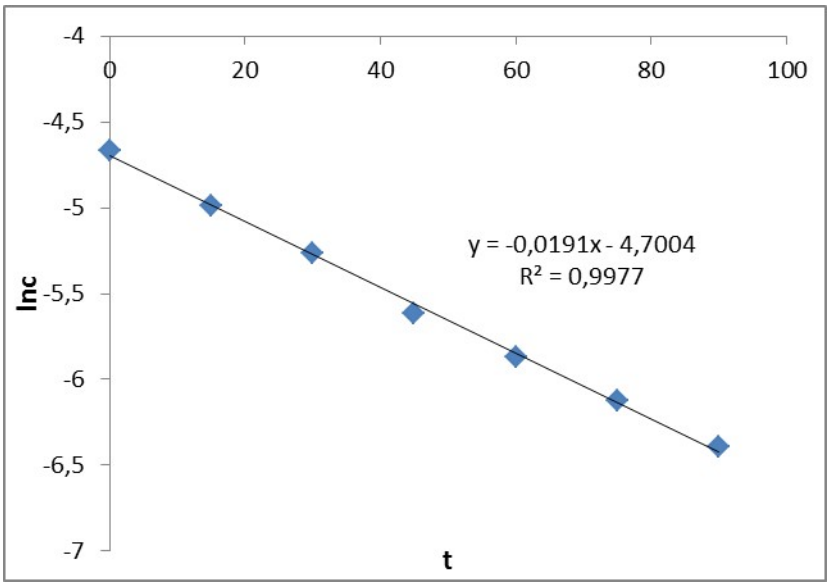


$k_{obs} = 20.3 \pm 3.2 \times 10^{-3} s^{-1}$

- **Addition of 1 eq. of *t*BuOK**

Conditions of experiment: 2Br-4F-Ph Ellman's imine **2a** (200 µl, 0.04 M), 5 mol% $Cu(DPPE)_2BF_4$ **[Cu-5]** (200 µl, 0.002 M), 10 eq. TABMA **1a** + 1 eq. *t*BuOK (400 µl, 0.2 M), solvent – *i*PrOH, T = 25.0 °C.

№	A^{307}	t, sec	c, M	lnC
0	1,294	0	0,0094	-4,6703
1	0,940	15	0,0068	-4,9900
2	0,712	30	0,0052	-5,2678
3	0,504	45	0,0036	-5,6133
4	0,391	60	0,0028	-5,8671
5	0,302	75	0,0022	-6,1254
6	0,232	90	0,0017	-6,3891
7	0,046	**1080**	0,0003	-8,0072



$k_{obs} = 19.1 \pm 1.0 \times 10^{-3} s^{-1}$

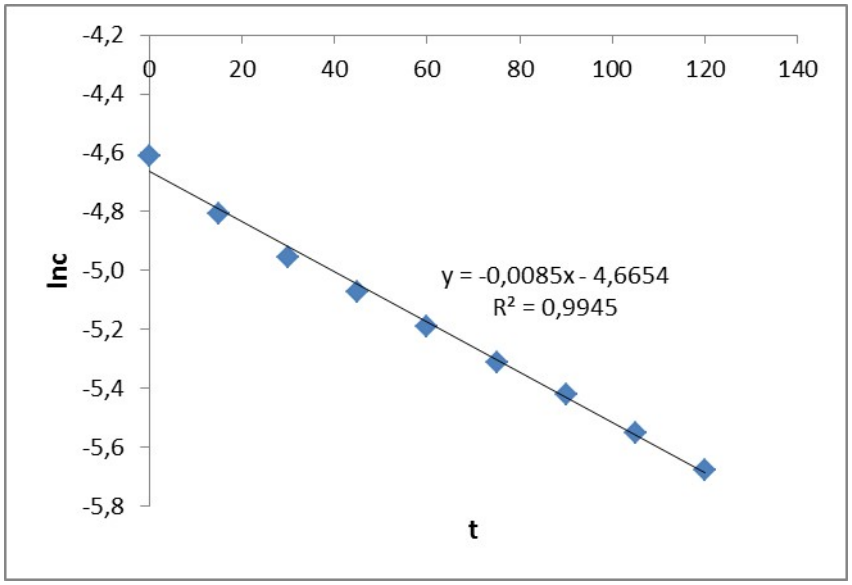
Rate constants of [Cu-3]-catalyzed allylation of imine 2a with triallylborane-methylamine adduct 1a in isopropyl alcohol with addition of tBuOK (Figure 5 of the main text)

- **Addition of 0.1 eq. of *t*BuOK**

Conditions of experiment: 2Br-4F-Ph Ellman's imine **2a** (200 µl, 0.04 M), 5 mol% $Cu(PPh_3)_3Cl$*MeCN **[Cu-3]** (200 µl, 0.002 M), 10 eq. TABMA **1a** + 0.1 eq. *t*BuOK (400 µl, 0.2 M), solvent – *i*PrOH, T = 25.0 °C.

№	A^{307}	t, sec	c, M	lnC
0	1,374	0	0,0099	-4,6104
1	1,130	15	0,0082	-4,8059
2	0,975	30	0,0071	-4,9534
3	0,866	45	0,0063	-5,0720

4	0,769	60	0,0056	-5,1907
5	0,681	75	0,0049	-5,3123
6	0,611	90	0,0044	-5,4207
7	0,537	105	0,0039	-5,5498
8	0,473	120	0,0034	-5,6767

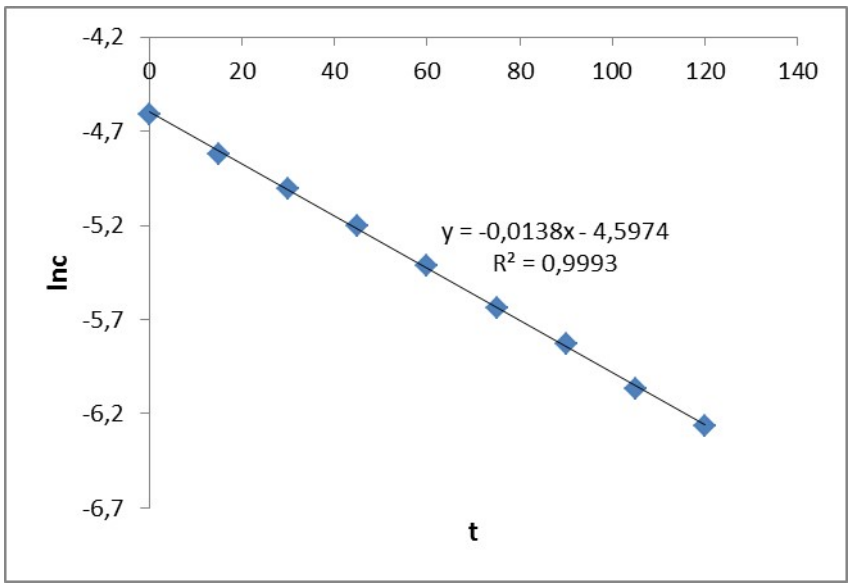


$k_{obs} = 8.5 \pm 0.6 \times 10^{-3} s^{-1}$

- **Addition of 0.2 eq. of *t*BuOK**

Conditions of experiment: 2Br-4F-Ph Ellman's imine **2a** (200 µl, 0.04 M), 5 mol% $Cu(PPh_3)_3Cl$*MeCN **[Cu-3]** (200 µl, 0.002 M), 10 eq. TABMA **1a** + 0.2 eq. *t*BuOK (400 µl, 0.2 M), solvent – *i*PrOH, T = 25.0 °C.

№	A^{307}	t, sec	c, M	lnC
0	1,374	0	0,0099	-4,6104
1	1,114	15	0,0081	-4,8201
2	0,927	30	0,0067	-5,0039
3	0,762	45	0,0055	-5,1999
4	0,615	60	0,0045	-5,4142
5	0,493	75	0,0036	-5,6353
6	0,406	90	0,0029	-5,8295
7	0,319	105	0,0023	-6,0706
8	0,263	120	0,0019	-6,2637

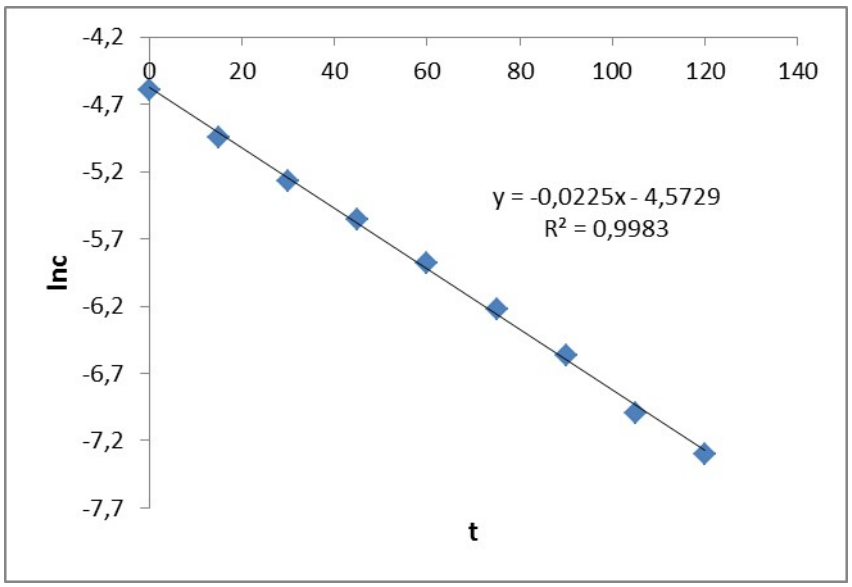


$k_{obs} = 13.8 \pm 0.3 \times 10^{-3} s^{-1}$

- **Addition of 0.5 eq. of *t*BuOK**

Conditions of experiment: 2Br-4F-Ph Ellman's imine **2a** (200 µl, 0.04 M), 5 mol% $Cu(PPh_3)_3Cl$*MeCN **[Cu-3]** (200 µl, 0.002 M), 10 eq. TABMA **1a** + 0.5 eq. *t*BuOK (400 µl, 0.2 M), solvent – *i*PrOH, T = 25.0 °C.

№	A^{307}	t, sec	c, M	lnC
0	1,402	0	0,0102	-4,5902
1	0,986	15	0,0071	-4,9422
2	0,712	30	0,0052	-5,2678
3	0,534	45	0,0039	-5,5554
4	0,387	60	0,0028	-5,8774
5	0,275	75	0,0020	-6,2191
6	0,194	90	0,0014	-6,5680
7	0,127	105	0,0009	-6,9917
8	0,093	120	0,0007	-7,3032

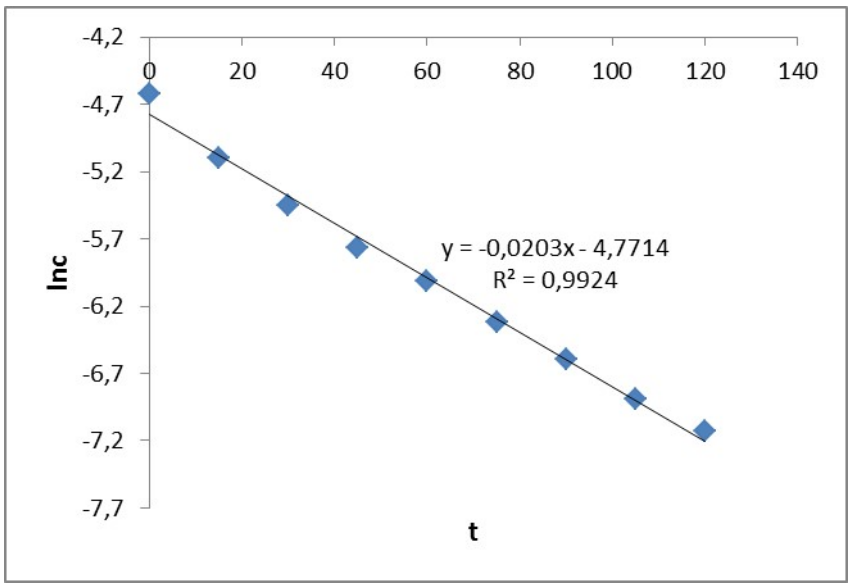


$k_{obs} = 22.5 \pm 0.8 \times 10^{-3} s^{-1}$

- **Addition of 1 eq. of *t*BuOK**

Conditions of experiment: 2Br-4F-Ph Ellman's imine **2a** (200 µl, 0.04 M), 5 mol% $Cu(PPh_3)_3Cl$*MeCN **[Cu-3]** (200 µl, 0.002 M), 10 eq. TABMA **1a** + 1 eq. *t*BuOK (400 µl, 0.2 M), solvent – *i*PrOH, T = 25.0 °C.

№	A^{307}	t, sec	c, M	lnC
0	1,358	0	0,0098	-4,6221
1	0,842	15	0,0061	-5,1001
2	0,594	30	0,0043	-5,4490
3	0,432	45	0,0031	-5,7674
4	0,337	60	0,0024	-6,0158
5	0,249	75	0,0018	-6,3184
6	0,189	90	0,0014	-6,5941
7	0,140	105	0,0010	-6,8942
8	0,111	120	0,0008	-7,1263

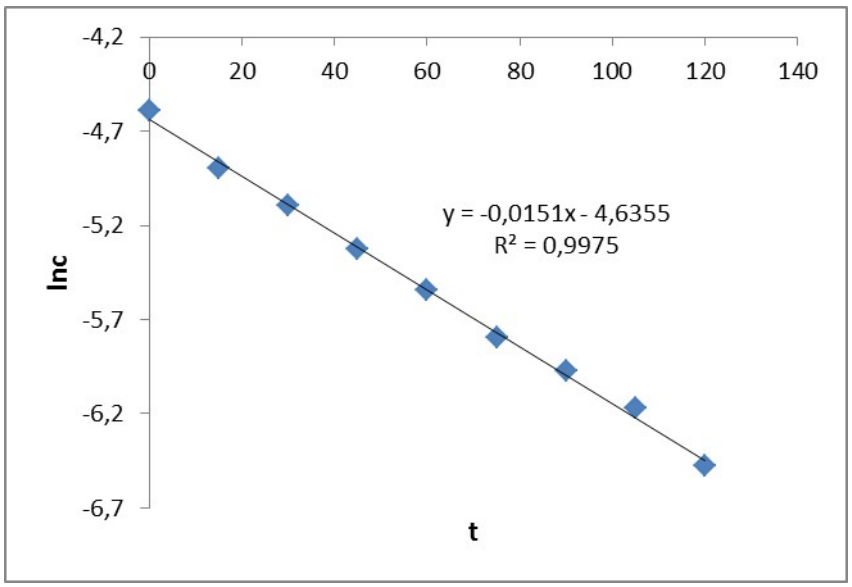


$k_{obs} = 20.3 \pm 1.5 \times 10^{-3} s^{-1}$

- **Addition of 2 eq. of *t*BuOK**

Conditions of experiment: 2Br-4F-Ph Ellman's imine **2a** (200 µl, 0.04 M), 5 mol% $Cu(PPh_3)_3Cl$*MeCN **[Cu-3]** (200 µl, 0.002 M), 10 eq. TABMA **1a** + 2 eq. *t*BuOK (400 µl, 0.2 M), solvent – *i*PrOH, T = 25.0 °C.

№	A^{307}	t, sec	c, M	lnC
0	1,398	0	0,0101	-4,5930
1	1,034	15	0,0075	-4,8947
2	0,849	30	0,0061	-5,0918
3	0,670	45	0,0049	-5,3286
4	0,539	60	0,0039	-5,5461
5	0,419	75	0,0030	-5,7980
6	0,351	90	0,0025	-5,9751
7	0,289	105	0,0021	-6,1694
8	0,213	120	0,0015	-6,4745



$k_{obs} = 15.1 \pm 0.7 \times 10^{-3} s^{-1}$