

Electronic Supplementary Information for

Rational investigations in the ring opening of cyclic carbonates by amines

M. Blain,^{a,b} L. Jean-Gérard,^a R. Auvergne,^b D. Benazet,^c S. Caillol,^{b,*} and B. Andrioletti^{a,*}

a ICBMS-UMR 5246 Université Claude Bernard-Lyon 1 Equipe de CAlyse, SYNthèse et Environnement (CASYEN) Domaine Scientifique de la Doua-Bât. Curien/CPE, 2^o étage aile C 43 Boulevard du 11 Novembre 1918, 69622 Villeurbanne Cedex-France.

b Ecole Nationale Supérieure de Chimie de Montpellier 8, Rue de l'Ecole Normale, 34296 Montpellier-France.

c JUXTA 5 rue de la Jalesie, BP 71039 25401 Audincourt cedex-France

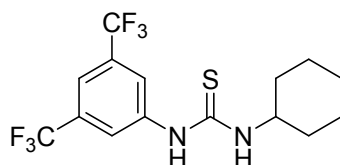
Content :

1. General information
2. Synthesis of catalysts, carbonates and carbamates
3. General procedure for the GC/MS quantitative analysis of the carbonate aminolysis
4. General procedure for the NMR analysis of the carbonate aminolysis
5. Examples and spectrum of quantitative analysis from the publication
6. ¹H NMR comparison of the aminolysis 1) in the presence of TBD (revealing traces of impurities), 2) using the thiourea as an organocatalyst.
7. ¹H and ¹³C NMR spectrum

1. General information

^1H and ^{13}C spectra were recorded on a Bruker ALS-300 or a Bruker ALS-400 spectrometers. The NMR chemical shifts are reported as δ in parts per million (ppm) relative to the traces of non-deuterated solvent (eg $\delta = 2.50$ ppm for $\text{d}_6\text{-DMSO}$ or $\delta = 7.26$ ppm for CDCl_3). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, br = broad), coupling constants (J) given in Hertz (Hz), integration and attribution. Low-resolution gas chromatography coupled with a mass spectrometry detector (GC-MS) was performed using a Shimadzu GCMS-QP2010S apparatus using a ZB5-HT column and helium as carrier gas. The quantitative GC-MS analyses were performed using an internal standard (diphenyl ether) and calibration charts. Flash column chromatographies were performed using normal phase silica gel (60 Å, particle size 40-63 μm) and monitored with thin-layer chromatographies using TLC plates GF254 purchased from Merck (0.25 mm). All the catalysts and IPDA were used as received. The thioureas were synthesized according to the reported literature procedure.¹ Propylene carbonate (PC) was purified by distillation. 4-(methoxymethyl)-1,3-dioxolan-2-one, 4,6-dimethyl-1,3-dioxan-2-one and 4-phenyl-1,3-dioxolan-2-one were synthesized according to the reported literature procedure.^{2,3}

2. Synthesis of catalysts, carbonates and carbamates



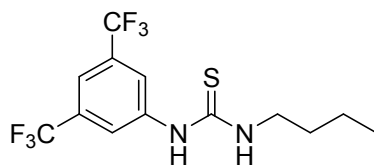
1-(3,5-bis(trifluoromethyl)phenyl)-3-cyclohexylthiourea was synthesized according to the literature procedure¹: At room temperature, cyclohexanamine (0.534 g, 5.39mmol) was added dropwise to a stirred solution of 3,5-bis(trifluoromethyl)phenyl isothiocyanate (1.500 g, 5.53 mmol) in THF (10 mL). After stirring for 4 h at room temperature, the solvent was evaporated. The white residue was recrystallized from chloroform to give **1-(3,5-bis(trifluoromethyl)phenyl)-3-cyclohexylthiourea** as a white powder. Yield: 1.76 g (88%).

^1H NMR ($\text{DMSO-}d_6$, 400 MHz): δ 7.42 (s , 1H, 4-ArH), 7.29 (s , 2H, 2,6-ArH), 6.82 (s , 1H, ArNH), 5.19 (s , 1H, CyNH), 4.40 ($br\ m$, 1H, NCyH), 1.91-0.86 (m , 10H, CyH).

^{13}C NMR ($\text{DMSO-}d_6$, 100 MHz): δ 179.2, 142.0, 130.1 (q , $J=33$ Hz), 123.3 (q , $J=273$ Hz), 121.7, 115.8, 52.3, 31.6, 25.1, 24.4.

^{19}F NMR ($\text{benzene-}d_6$, 376 MHz): δ -63.5 (s , CF_3).

Spectroscopic data were identical to those found in previous literature reports for this compound.¹



1-(3,5-bis(trifluoromethyl)phenyl)-3-butylthiourea was synthesized according to the literature procedure¹ : Butylamine (0.161g, 2.21 mmol) was added dropwise at room temperature to a stirred solution of 3,5-bis(trifluoromethyl)phenyl isothiocyanate (0.500 g, 1.84 mmol) in dry THF (5 mL). After the solution was stirred for 4 h at room temperature, the solvent was evaporated. The white residue was recrystallized from cyclohexane to give **1-(3,5-bis(trifluoromethyl)phenyl)-3-butylthiourea** as a white powder. Yield: 0.463g (77%).

m.p. = 101°C

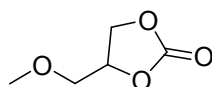
¹H NMR (DMSO-d₆, 400 MHz): δ 10.02 (*s*, 1H, ArNH), 8.23 (*s*, 1H, BuNH), 8.23 (*s*, 2H, 2,6-ArH), 7.71 (*s*, 1H, 4-ArH), 3.49 (*br m*, 2H, N-CH₂), 1.54 (*m*, 2H, CH₂), 1.33 (*m*, 2H, CH₂-CH₃), 0.90 (*t*, 3H, *J*=7.3 Hz, CH₃).

¹³C NMR (DMSO-d₆, 100 MHz): δ 180.4, 142.0, 130.2, 123.3, 121.7, 115.9, 43.6, 30.3, 19.6, 13.7.

¹³C NMR (DMSO-d₆, 100 MHz): δ 180.4, 142.0, 130.2 (*q*, *J*=33 Hz), 123.3 (*q*, *J*=273 Hz), 121.7, 115.9, 43.6, 30.3, 19.6, 13.7.

¹⁹F NMR (DMSO-d₆, 282 MHz): δ -61.67 (*s*, CF₃).

ESI-MS: calcd for [C₁₃H₁₅F₆N₂S (M + H⁺)] 345.0855, found 345.0853

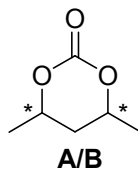


4-(methoxymethyl)-1,3-dioxolan-2-one : In a 50 mL round bottom flask at 0°C 4-(hydroxymethyl)-1,3-dioxolan-2-one (3.37 mL, 40 mmol) was added to a suspension of sodium hydride (60% w/w dispersion in mineral oil, 1.76g, 44 mmol) in dry THF (25 mL). After stirring at room temperature for 3 hours the mixture was cooled to 0°C and dimethyl sulfate (4.16mL, 44 mmol) was added. After stirring 15 hours at room temperature the mixture was quenched with water. The aqueous layer was extracted with EtOAc (4x100 mL). The combined organic phases were dried over MgSO₄, and concentrated under reduced pressure. The crude residue was purified on a silica gel column chromatography using EtOAc /Heptane (70:30) to give **4-(methoxymethyl)-1,3-dioxolan-2-one** as a colorless oil. Yield: 3.2g (60%).

¹H NMR (DMSO-d₆, 400 MHz): δ 4.92 (*m*, 1H, CH), 4.52 (*dd*, 1H, *J*=8.4Hz, *J*=8.4Hz, CH₂-OC=O), 4.25 (*dd*, 1H, *J*=8.3Hz, *J*=5.9Hz, CH₂-OC=O), 3.55 (*m*, 2H, CH₂-OMe), 3.31 (*s*, 3H, CH₃).

^{13}C NMR (DMSO- d_6 , 100 MHz): δ 155.0, 75.4, 71.4, 66.0, 58.7.

Spectroscopic data were identical to those found in previous literature reports for this compound.⁴

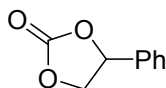


4,6-dimethyl-1,3-dioxan-2-one² : In a 250 mL round bottom flask at 0°C, dry pyridine (19 mL, 230 mmol) was added to a solution of 2,4-pentanediol (4.21 mL, 38 mmol) in dry CH_2Cl_2 (80 mL), followed by the dropwise addition of a solution of triphosgene (6.77g, 23mmol) in dry CH_2Cl_2 (40mL). The mixture was then slowly warmed up to room temperature. The reaction was quenched with a saturated NH_4Cl aqueous solution and the products were extracted with CH_2Cl_2 (5x25 mL). The combined organic layers were successively washed with 1M HCl (1x20mL), saturated NaHCO_3 solution (2x25 mL), brine, dried over Na_2SO_4 and concentrated under reduced pressure. The crude residue was purified on a silica gel column chromatography using EtOAc /Heptane (50:50) to give the combined diastereoisomers **A** and **B** of **4,6-dimethyl-1,3-dioxan-2-one** as a slightly yellow oil. Yield: 3.39 g (68%)

^1H NMR (DMSO- d_6 , 400 MHz): δ 4.72 (*m*, 2H, CH_A), 4.61 (*m*, 2H, CH_B), 2.14 (*ddd*, 1H, $J=14.1\text{Hz}$, $J=2.9\text{Hz}$, $J=2.9\text{Hz}$, $\text{CH}_{2\text{B}}$), 1.93 (*dd*, 2H, $J=5.5\text{Hz}$, $J=5.5\text{Hz}$, $\text{CH}_{2\text{A}}$), 1.52 (*ddd*, 1H, $J=14.1\text{Hz}$, $J=11.5\text{Hz}$, $J=2.9\text{Hz}$, $\text{CH}_{2\text{B}}$), 1.32 (*d*, 6H, $J=6.4\text{Hz}$, $\text{CH}_{3\text{A}}$), 1.27 (*d*, 6H, $J=6.3\text{Hz}$, $\text{CH}_{3\text{B}}$)

^{13}C NMR (DMSO- d_6 , 100 MHz): δ 148.6, 148.6, 75.0, 72.6, 35.4, 32.8, 20.7, 20.4.

Spectroscopic data were identical to those found in previous literature reports for this compound⁵.



4-phenyl-1,3-dioxolan-2-one³ : In a 270 mL reactor styrene oxide (6.0 g, 50 mmol) and LiBr (0.22 g, 2.5 mmol) were dissolved in DMF (100 mL). The atmosphere was replaced with CO_2 ($P=20$ bar). The solution was then allowed to stand at 80 °C with continuous stirring for 12 h. The reaction media was diluted with EtOAc (300mL), extracted several times with brine, dried over Na_2SO_4 and concentrated under reduced pressure. The crude residue was purified on a silica gel column chromatography using EtOAc /Heptane (25:75) to give **4-phenyl-1,3-dioxolan-2-one** as a white solid. Yield: 6.8g (83%).

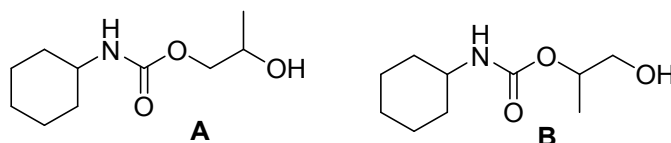
^1H NMR (DMSO- d_6 , 400 MHz): δ 7.55-7.35 (*m*, 5H, $\text{CH}_\text{aromatic}$), 5.86 (*dd*, 1H, $J=7.9$, $J=7.9$ Hz, CH), 4.89 (*dd*, 1H, $J=7.9$, $J=8.3$ Hz, CH_2), 4.42 (*dd*, 1H, $J=7.9$, $J=8.3$ Hz, CH_2).

^{13}C NMR (DMSO- d_6 , 100 MHz): δ 154.7, 136.2, 129.3, 128.9, 126.7, 77.8, 70.8.

Spectroscopic data were identical to those found in previous literature reports for this compound⁶.

General procedure for the synthesis of the carbamates

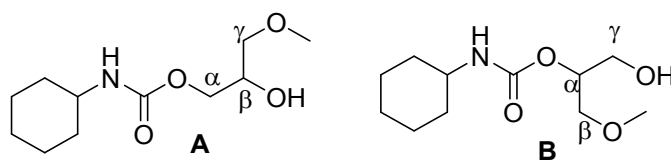
In a 10 mL reaction tube cyclohexanamine (2 equiv.) was added to the carbonate (1 equiv.). After stirring at 25°C for 15 hours the reaction mixture was purified on a silica gel column chromatography using EtOAc and Heptane to give the combined isomers.



The reaction was performed with cyclohexyl amine (600 μL , 5.21mmol) and propylene carbonate (220 μL , 2.59mmol). The reaction mixture was purified on a silica gel column chromatography using a gradient of EtOAc in Heptane (4:1 to 1:0) to give the combined isomers **2-hydroxypropyl cyclohexylcarbamate A** and **1-hydroxypropan-2-yl cyclohexylcarbamate B** (58:42) isolated as colorless oil. Global yield: 416 mg (80%).

^1H NMR (DMSO- d_6 + ϵ D $_2$ O, 300 MHz): δ 7.00 (*d*, 1H, J =7.82 Hz, NH_A), 6.91 (*d*, 1H, J =7.96 Hz, NH_B), 4.59 (*tdq*, 1H, J =6.39 Hz, J =6.22 Hz, $\text{CH}_3\text{-CH}_\text{B}$), 3.73 (*m*, 3H, $\text{CH}_3\text{-CH}_\text{A}$, $\text{O-CH}_2\text{A}$), 3.49-3.12 (*m*, 4H, $\text{HO-CH}_2\text{B}$, NCyH_{AB}), 1.80-0.95 (*m*, 20H, CyH_{AB}), 1.08 (*d*, 3H, J =6.39 Hz, CH_3B), 1.01 (*d*, 3H, J =6.01 Hz, CH_3A)

^{13}C NMR (DMSO- d_6 + ϵ D $_2$ O, 100 MHz): δ 155.7, 155.4, 70.7, 68.9, 64.5, 64.0, 49.5, 32.8, 25.3, 24.8, 20.1, 17.1

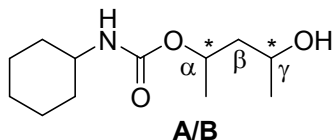


The reaction was performed with cyclohexyl amine (349 μL , 3.0mmol) and 4-(methoxymethyl)-1,3-dioxolan-2-one (0.200g, 1.5mmol). The reaction mixture was purified on a silica gel column chromatography using a gradient of EtOAc in Heptane (2:3 to 1:1) to give the combined isomers **2-hydroxy-3-methoxypropyl cyclohexylcarbamate A** and **1-hydroxy-3-methoxypropan-2-yl cyclohexylcarbamate B** (75:25) isolated as white powder. Global yield: 304mg (87%).

^1H NMR (DMSO- d_6 , 400 MHz): δ 7.06 (2H, NH_A , NH_B), 4.93 (*d*, 1H, J =5.2 Hz, OH_A), 4.77 (*t*, 1H, J =5.6Hz, OH_B), 4.67 (*m*, 1H, CH_B), 3.86 (*m*, 2H, $\text{CH}_{2\alpha\text{A}}$), 3.73 (*m*, 1H, CH_A), 3.50-

3.38 (*m*, 4H, CH_{2βB}, CH_{2γB}), 3.35-3.15 (*m*, 10H, CH_{3A,B}, CH_{2γA}, CH_{A,B-cyclohexyl}), 1.82-1.45 (*m*, 10H, CH_{2A,B-cyclohexyl}), 1.33-0.93 (*m*, 10H, CH_{2A,B-cyclohexyl}).

¹³C NMR (DMSO-d₆, 100 MHz): δ 155.4, 155.1, 73.9, 72.7, 71.2, 67.6, 65.3, 60.1, 58.5, 58.3, 49.4, 32.7, 25.2, 24.7.



The reaction was performed with cyclohexyl amine (0.2349g, 4.8mmol) and **4,6-dimethyl-1,3-dioxan-2-one** (0.3087g, 2.4mmol). The reaction mixture was purified on a silica gel column chromatography with EtOAc and heptane (70:30) to give the distinct diastereoisomers **A** and **B** of **4-hydroxypentan-2-yl cyclohexylcarbamate** (75:25) isolated as colorless liquids. Yield A: 199mg (36%), yield B: 333mg (60%).

4-hydroxypentan-2-yl cyclohexylcarbamate A

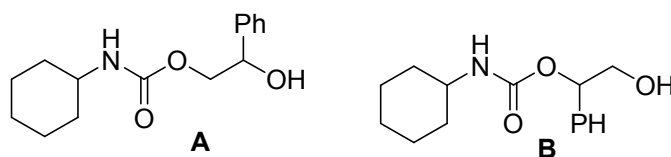
¹H NMR (DMSO-d₆, 400 MHz): δ 6.92 (*d*, 1H, *J*=5.2 Hz, NH), 4.76 (*m*, 1H, CH_α), 4.42 (*d*, 1H, *J*=4.9 Hz, OH), 3.63 (*m*, 1H, CH_γ), 3.21 (*m*, 1H, CH_{cyclohexyl}), 1.77-0.96 (*m*, 12H, CH_{2cyclohexyl}, CH_{2β}), 1.13 (*d*, 3H, *J*=6.24 Hz, CH_{3α}), 1.03 (*d*, 3H, *J*=6.18 Hz, CH_{3γ}).

¹³C NMR (DMSO-d₆, 100 MHz): δ 155.4, 67.4, 62.6, 49.3, 45.8, 32.7, 25.2, 24.7, 24.2, 21.2

4-hydroxypentan-2-yl cyclohexylcarbamate B

¹H NMR (DMSO-d₆, 400 MHz): δ 6.89 (*d*, 1H, *J*=7.9 Hz, NH), 4.76 (*m*, 1H, CH_α), 4.43 (*d*, 1H, *J*=4.9 Hz, OH), 3.63 (*m*, 1H, CH_γ), 3.21 (*m*, 1H, CH_{cyclohexyl}), 1.78-0.97 (*m*, 12H, CH_{2cyclohexyl}, CH_{2β}), 1.13 (*d*, 3H, *J*=6.22 Hz, CH_{3α}), 1.05 (*d*, 3H, *J*=6.14 Hz, CH_{3γ}).

¹³C NMR (DMSO-d₆, 100 MHz): δ 155.1, 67.5, 63.0, 49.3, 45.5, 32.8, 25.2, 24.7, 23.8, 20.0.



The reaction was performed with cyclohexyl amine (0.362g, 3.6mmol) and **4-phenyl-1,3-dioxolan-2-one** (0.300g, 1.83mmol). The reaction mixture was purified on a silica gel column chromatography using a gradient of EtOAc in Heptane (1:4 to 3:7) to give the distinct isomers **2-hydroxy-2-phenylethyl cyclohexylcarbamate A** and **1-hydroxy-2-phenylethyl cyclohexylcarbamate B** (60:40) isolated as white powders. Yield A: 257mg (53%), yield B: 171mg (35%)

2-hydroxy-2-phenylethyl cyclohexylcarbamate A

^1H NMR (DMSO- d_6 , 400 MHz): δ 7.40-7.21 (*m*, 5H, $\text{CH}_{\text{aromatic}}$), 7.07 (*d*, 1H, $J = 7.9$ Hz, NH), 5.48 (*d*, 1H, $J = 4.6$ Hz, OH), 4.73 (*m*, 1H, CH-OH), 3.97 (*d*, 2H, $J = 6$ Hz, CH_2), 3.23 (*m*, 1H, $\text{CH}_{\text{cyclohexyl}}$), 1.87-1.43 (*m*, 5H, $\text{CH}_{2\text{cyclohexyl}}$), 1.35-0.87 (*m*, 5H, $\text{CH}_{2\text{cyclohexyl}}$).

^{13}C NMR (DMSO- d_6 , 100 MHz): δ 155.3, 142.5, 128.0, 127.2, 126.3, 70.8, 68.6, 49.4, 32.6, 25.1, 24.7.

1-hydroxy-2-phenylethan-2-yl cyclohexylcarbamate B

^1H NMR (DMSO- d_6 , 400 MHz): δ 7.41-7.22 (*m*, 5H, $\text{CH}_{\text{aromatic}}$), 7.19 (*d*, 1H, $J = 7.9$ Hz, NH), 5.54 (*dd*, 1H, $J = 7.1$, $J = 4.8$ Hz, CH-Ph), 4.95 (*t*, $J = 5.6$, 1H, OH), 3.59 (*m*, 2H, $\text{CH}_2\text{-OH}$), 3.20 (*m*, 1H, $\text{CH}_{\text{cyclohexyl}}$), 1.874-1.43 (*m*, 5H, $\text{CH}_{2\text{cyclohexyl}}$), 1.37-0.96 (*m*, 5H, $\text{CH}_{2\text{cyclohexyl}}$).

^{13}C NMR (DMSO- d_6 , 100 MHz): δ 154.9, 139.5, 128.1, 127.5, 126.3, 75.9, 64.5, 49.4, 32.7, 25.1, 24.6.

3. General procedure for following the aminolysis of carbonates by GC/MS quantitative analysis

In a typical procedure, carbonate (1 equiv), amine (1 equiv) and diphenyl ether (0.4 equiv) internal standard) were stirred together for the appropriate amount of with the quantity of catalyst used in the table in an open air reaction tube maintained at the temperature shown in the table.

- General procedure for GC/MS analysis**

An aliquot of the reaction medium was dissolved in CH_2Cl_2 (1.5mL), then filtered on Na_2SO_4 and celite and analyzed by GC/MS.

GC column temperature program: 50 °C for 1 minutes followed by a ramp at 8 °C/min to 180°C followed by a ramp at 40 °C/min to 300°C (4.5 minutes)

The conversion of propylene carbonate was calculated using calibration curves of propylene carbonate with PhOPh as internal standard.

- General procedure for GC/MS analysis of samples containing Lewis acid**

The samples for the GC/MS analysis were prepared as follow: An aliquot of the reaction medium was quenched with a saturated NaHCO_3 aqueous solution (0.1mL), extracted twice with CH_2Cl_2 (1.5mL), then filtered on Na_2SO_4 , celite and analyzed by GC/MS.

GC column temperature program: 50 °C for 1 minutes followed by a ramp at 8 °C/min to 180°C followed by a ramp at 40 °C/min to 300°C (4.5 minutes)

The conversion of propylene carbonate was calculated using calibration curves of propylene carbonate with PhOPh as internal standard.

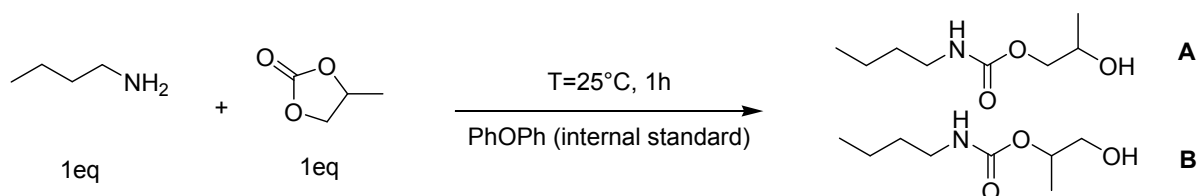
4. General procedure for following the aminolysis of carbonates by NMR

5. In a typical procedure, carbonate (1 equiv), amine (1 equiv) and diphenyl ether (0.4 equiv) internal standard) were stirred together for the appropriate amount of with the quantity of catalyst used in the table in an open air reaction tube maintained at 25°C.

The samples for NMR analysis were prepared as follow. A known quantity (~45mg) of the reaction mixture was introduced in an NMR tube together with a known quantity of a solution of acetonitrile (~5.9 g.L⁻¹) in DMSO-d₆ (~ 0.7 g) and analyzed by NMR.

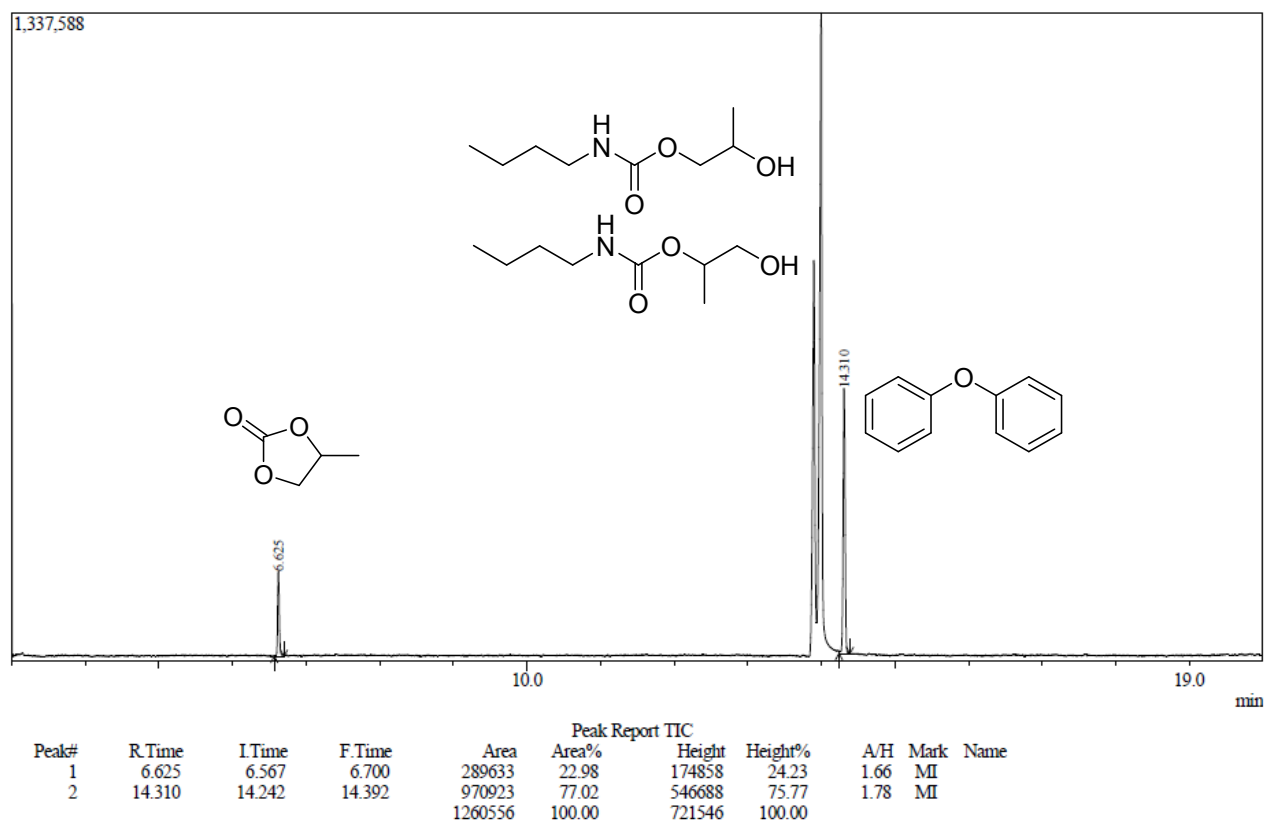
6. Examples and spectrum of quantitative analysis from the publication

Figure 1 Conversion of PC with butyl amine 1h



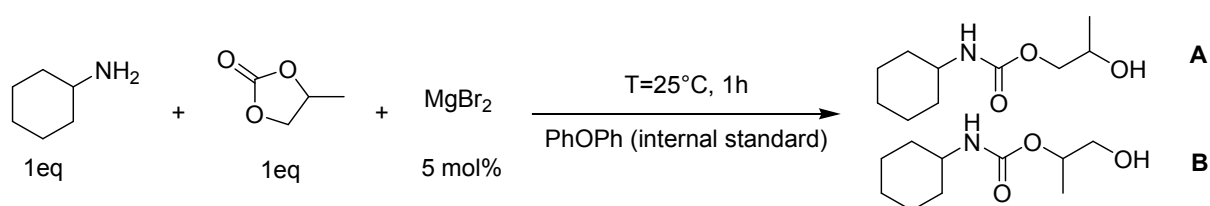
In an open air reaction tube were stirred together during 1h at 25°C propylene carbonate (220 μ L, 2.6 mmol), butyl amine (256 μ L, 2.6 mmol), PhOPh (0.0371g, 0.22mmol).

Procedure for GC/MS analysis



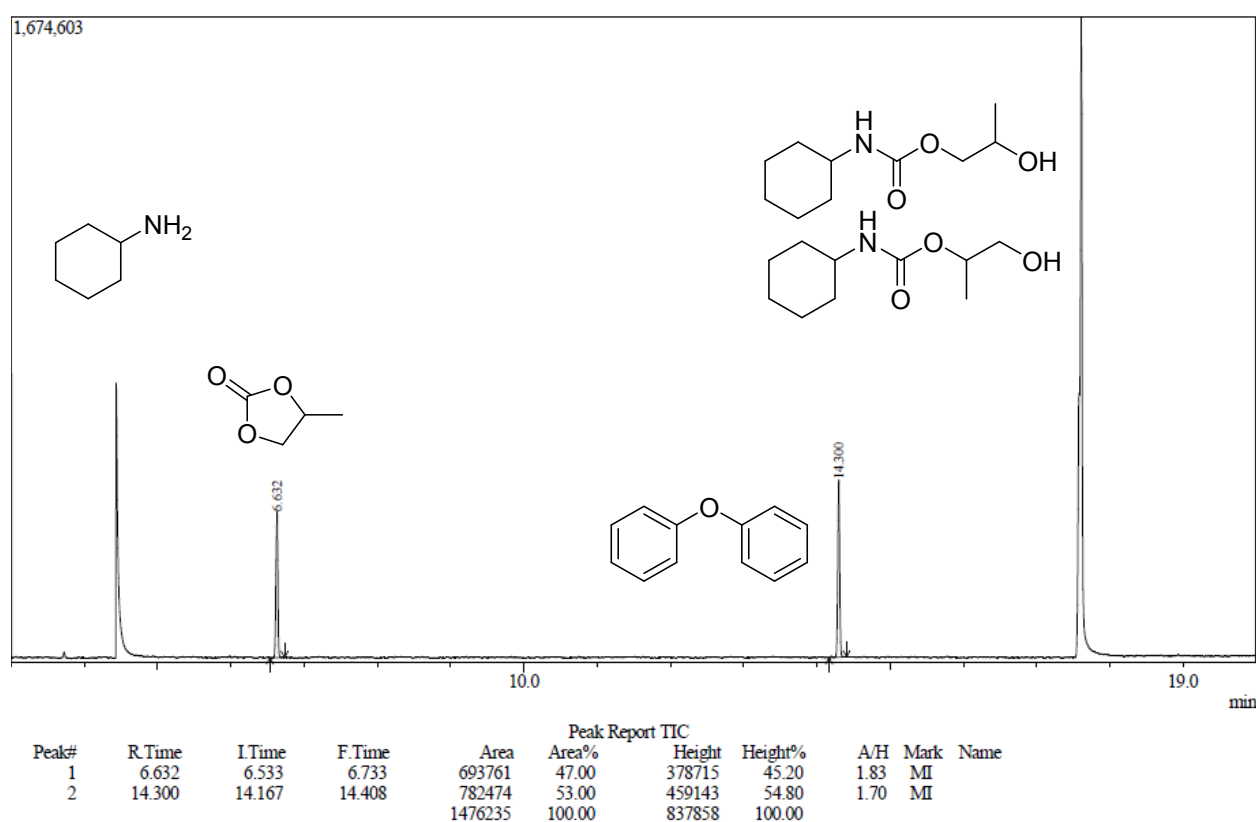
The calculated conversion of propylene carbonate is 80%.

Table 1 MgBr₂ catalyzed aminolysis of CP with cyclohexyl amine 1h



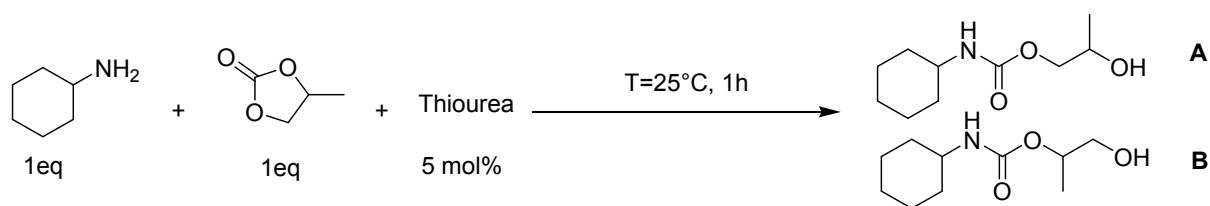
In an open air reaction tube were stirred together during 1h at 25°C propylene carbonate (220 μ L, 2.6 mmol), cyclohexyl amine (300 μ L, 2.6 mmol), PhOPh (0.0310g, 0.18mmol) and MgBr₂ (0.0239g, 0.13mmol).

Procedure for GC/MS analysis of samples containing Lewis acid



The calculated conversion of propylene carbonate is 51%.

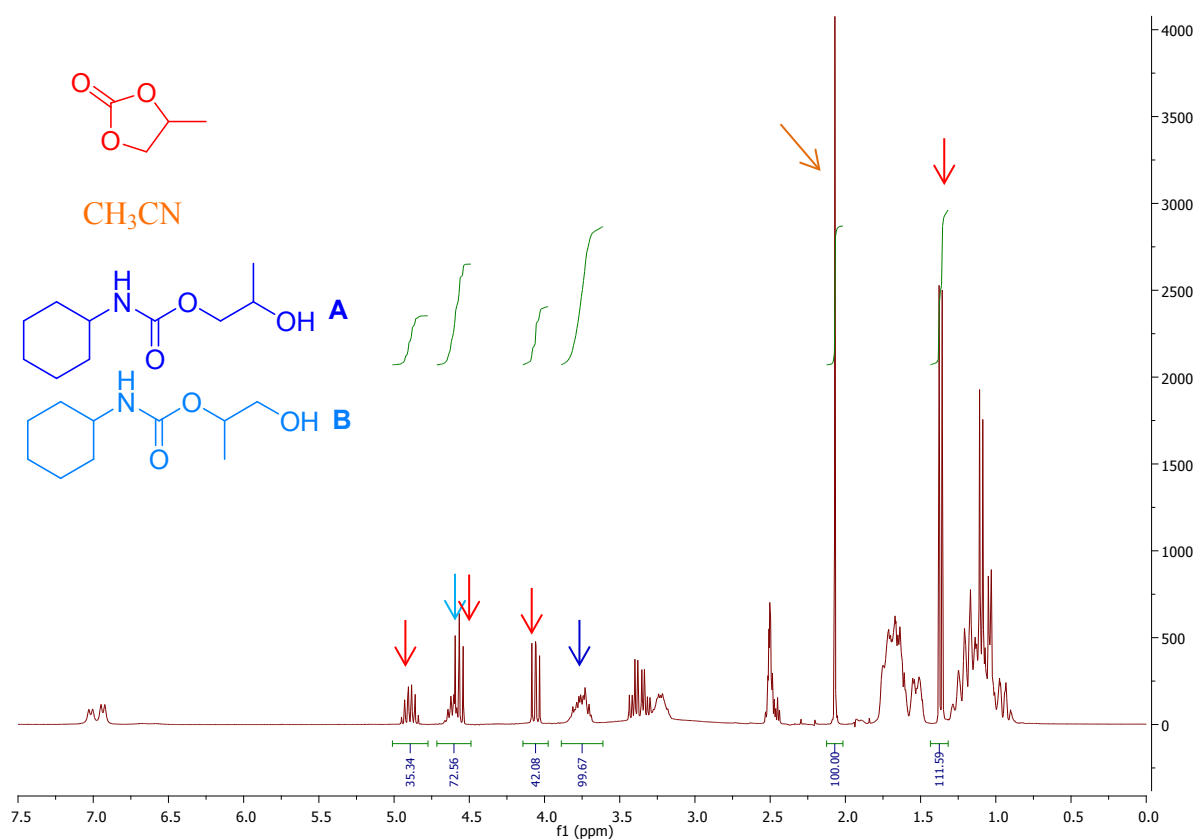
Table 2 Cyclohexyl thiourea catalyzes aminolysis of CP with cyclohexyl amine 1h



In an open air reaction tube were stirred together during 1h at 25°C propylene carbonate (220 μL , 2.6 mmol), cyclohexyl amine (300 μL , 2.6 mmol), cyclohexyl thiourea (0.0479g, 0.13mmol).

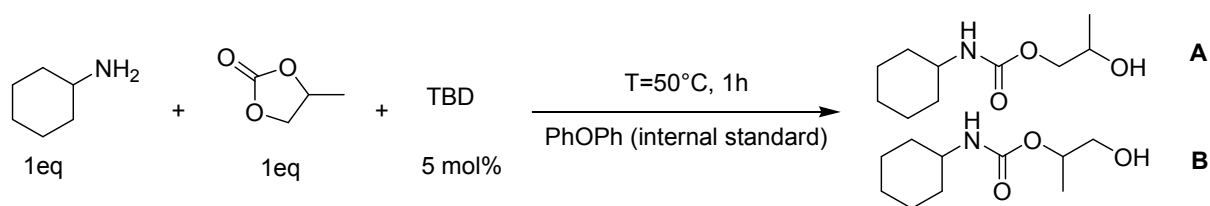
Procedure for NMR analysis

For the NMR analysis, 0.0448g of reaction media was introduced in an NMR tube as well as 0.7438g of a solution of acetonitrile (5.91 $\text{g}\cdot\text{L}^{-1}$) in DMSO- d_6



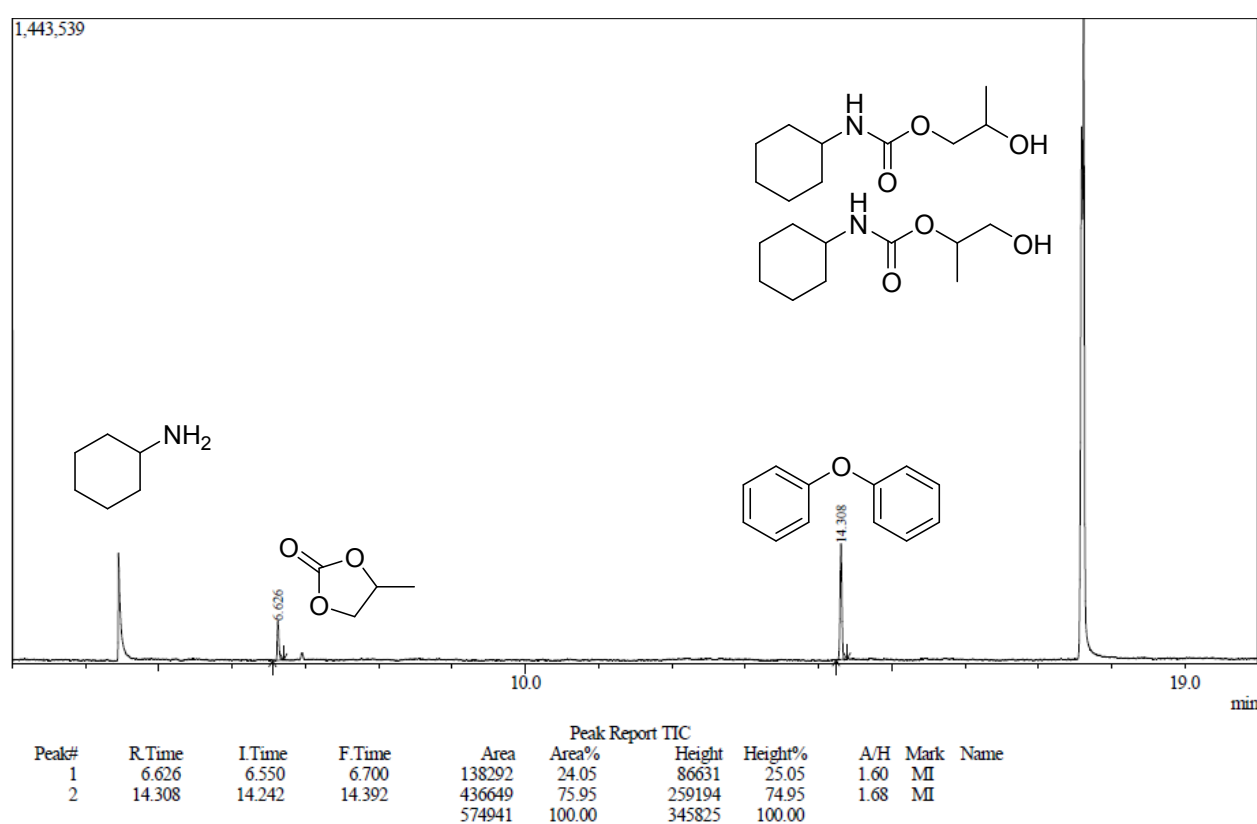
The calculated conversion of propylene carbonate is 66% and the ratio A:B is 45:55

Figure 2 Reaction of CP with the cyclohexyl amine at 50°C using TBD as catalyst 1h.



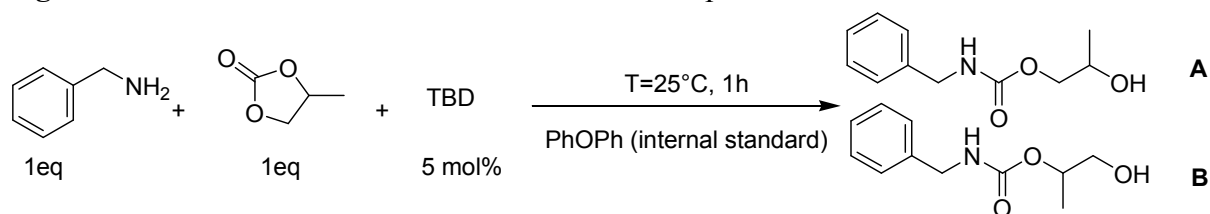
In an open air reaction tube were stirred together during 1h at 50°C propylene carbonate (220 μ L, 2.6 mmol), cyclohexyl amine (300 μ L, 2.6 mmol), PhOPh (0.0343g, 0.20mmol) and TBD (0.018g, 0.13mmol).

Procedure for GC/MS analysis



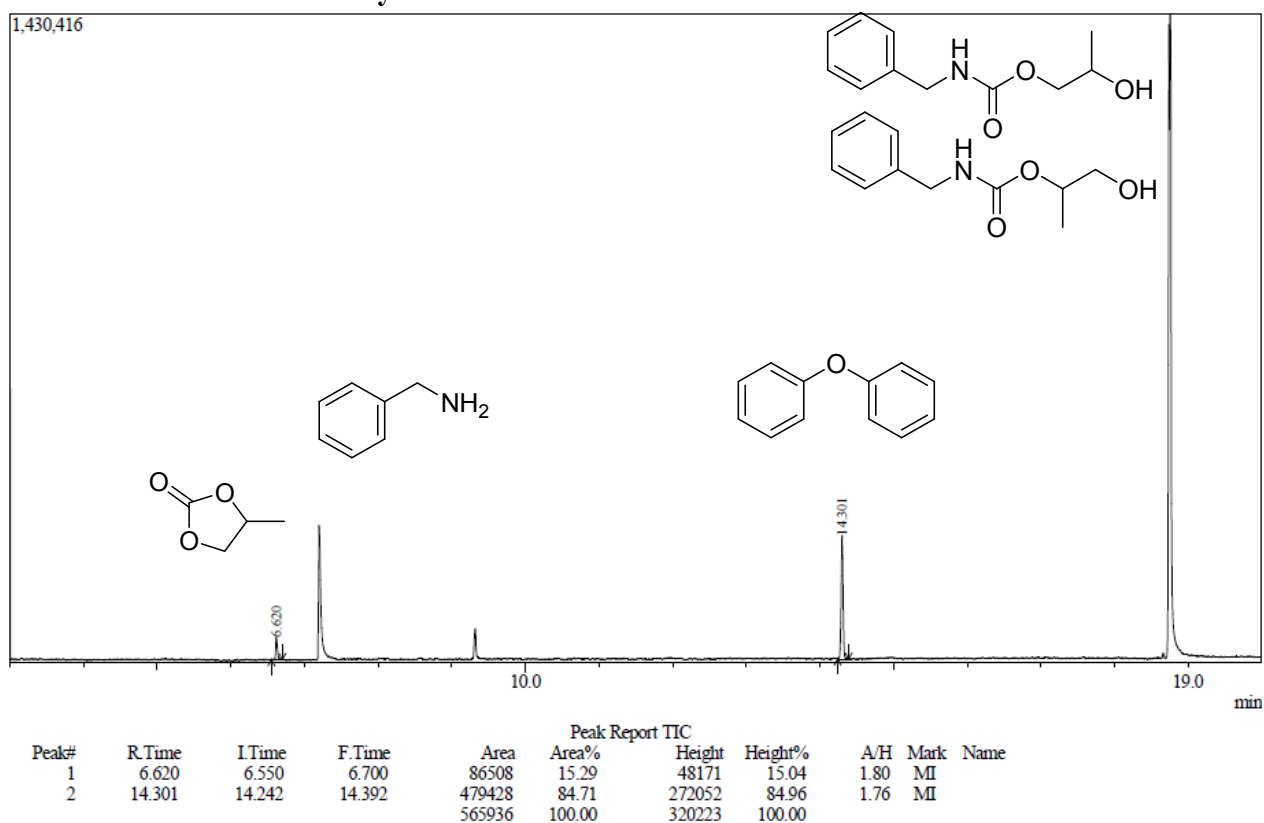
The calculated conversion of propylene carbonate is 80%.

Figure 4: Reaction of CP with different amines in the presence of TBD 1h



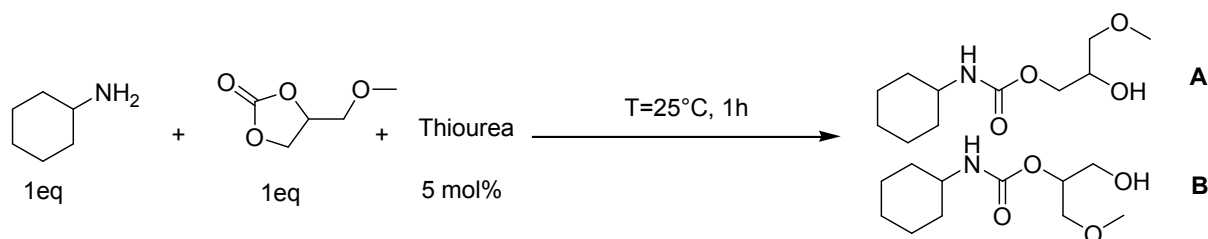
In an open air reaction tube were stirred together during 1h at 25°C propylene carbonate (220 μL , 2.6 mmol), cyclohexyl amine (322 μL , 2.6 mmol), PhOPh (0.0326g, 0.19mmol) and TBD (0.018g, 0.13mmol).

Procedure for GC/MS analysis



The calculated conversion of propylene carbonate is 94%.

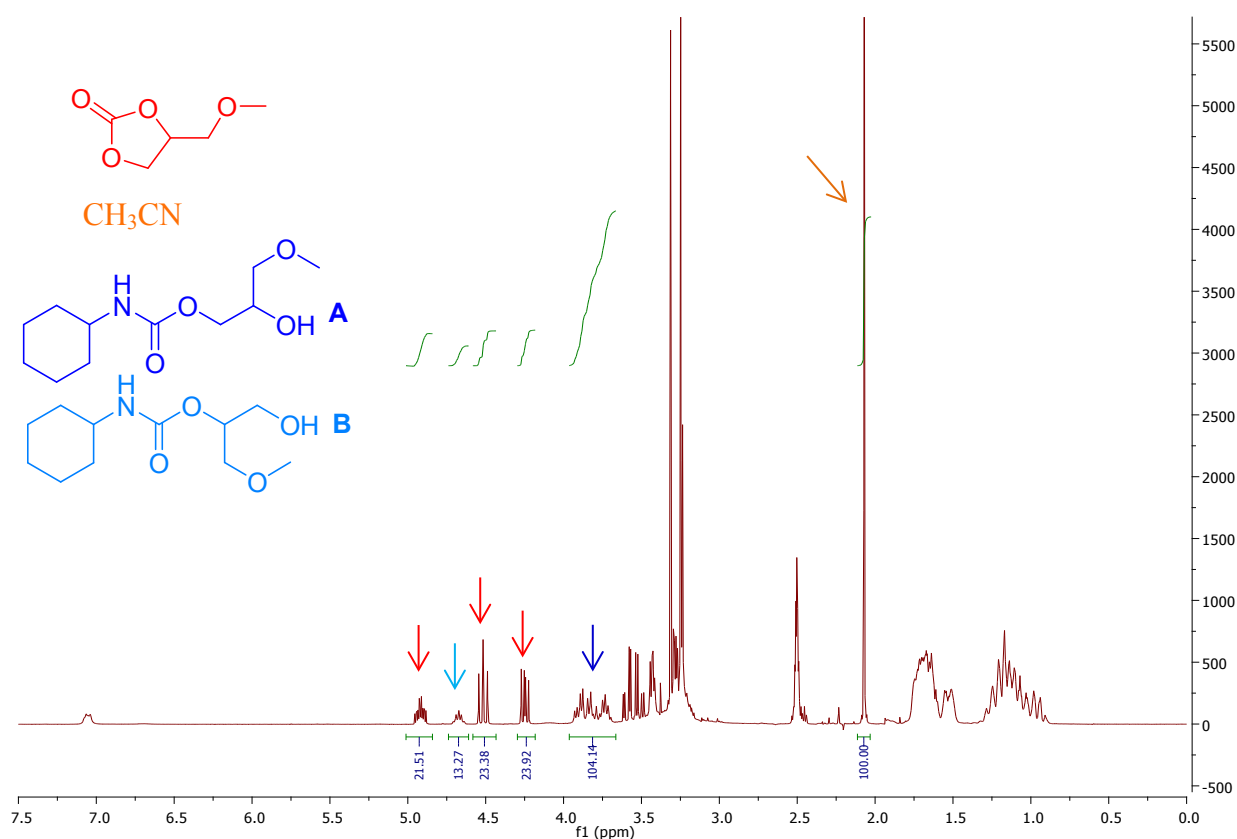
Figure 5: Cyclohexyl thiourea catalyzed aminolysis of 4-(methoxymethyl)-1,3-dioxolan-2-one with cyclohexyl amine 1h



In an open air reaction tube were stirred together during 1h at 25°C 4-(methoxymethyl)-1,3-dioxolan-2-one (0.3433g, 2.6 mmol), cyclohexyl amine (300 μ L, 2.6 mmol), cyclohexyl thiourea (0.0479g, 0.13mmol).

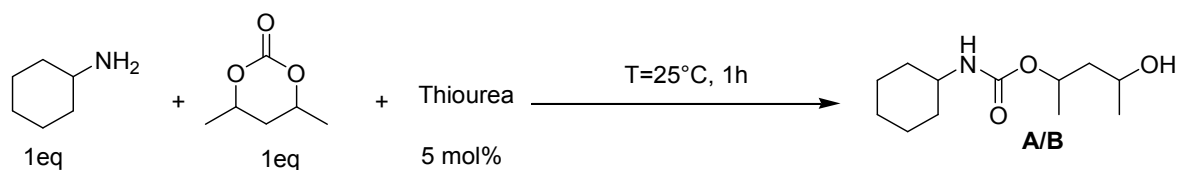
Procedure for NMR analysis

For the NMR analysis, 0.0316g of reaction media was introduced in an NMR tube as well as 0.6722g of a solution of acetonitrile (4.54 g.L⁻¹) in DMSO-d₆



The calculated conversion of 4-(methoxymethyl)-1,3-dioxolan-2-one is 68%

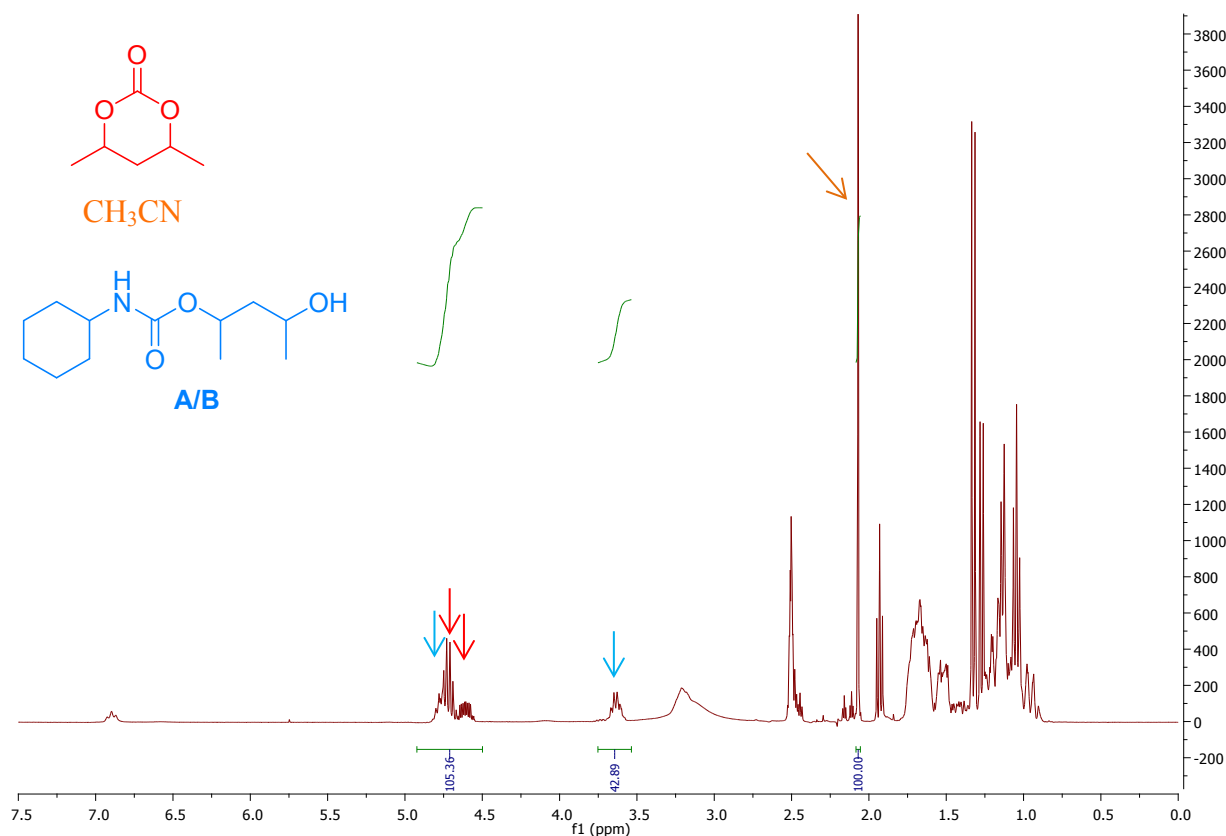
Figure 5: Cyclohexyl thiourea catalyzed aminolysis of 4,6-dimethyl-1,3-dioxan-2-one with cyclohexyl amine 1h



In an open air reaction tube were stirred together during 1h at 25°C, 4,6-dimethyl-1,3-dioxan-2-one (0.3381g, 2.6 mmol), cyclohexyl amine (300 μ L, 2.6 mmol), cyclohexyl thiourea (0.0479g, 0.13mmol).

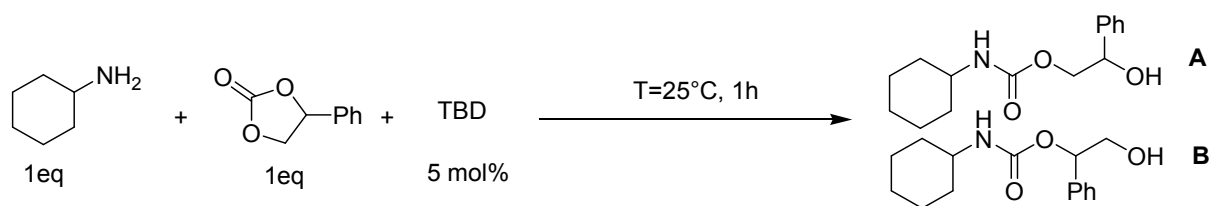
Procedure for NMR analysis

For the NMR analysis, 0.0286g of reaction media was introduced in an NMR tube as well as 0.5771g of a solution of acetonitrile (4.54 g.L⁻¹) in DMSO-d₆



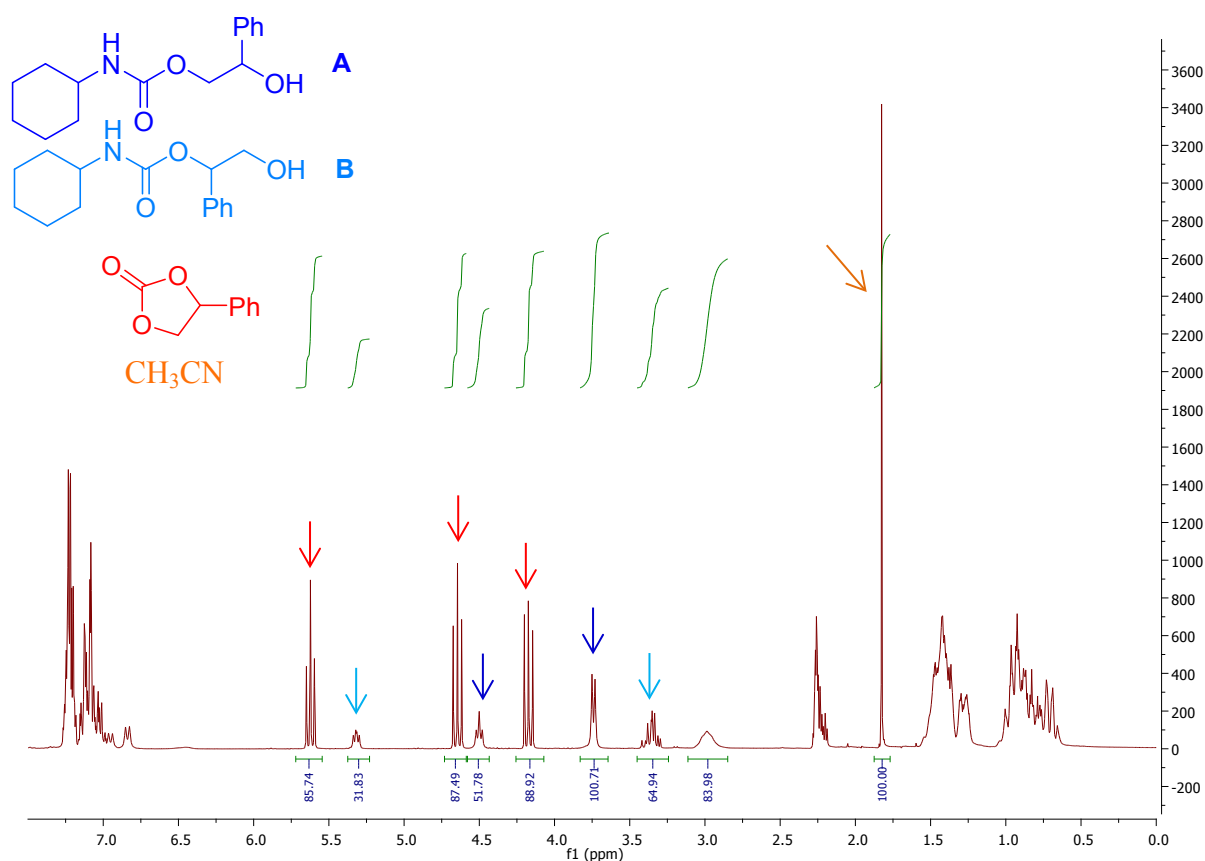
The calculated conversion of 4,6-dimethyl-1,3-dioxan-2-one is 57%

Figure 5: TBD catalyzed aminolysis of 4-phenyl-1,3-dioxolan-2-one with cyclohexyl amine 1h



In an open air reaction tube were stirred together for 1h at 25°C 4-phenyl-1,3-dioxolan-2-one (0.2132g, 1.3 mmol), cyclohexyl amine (150 μL , 1.3 mmol), TBD (9mg, 0.065mmol).

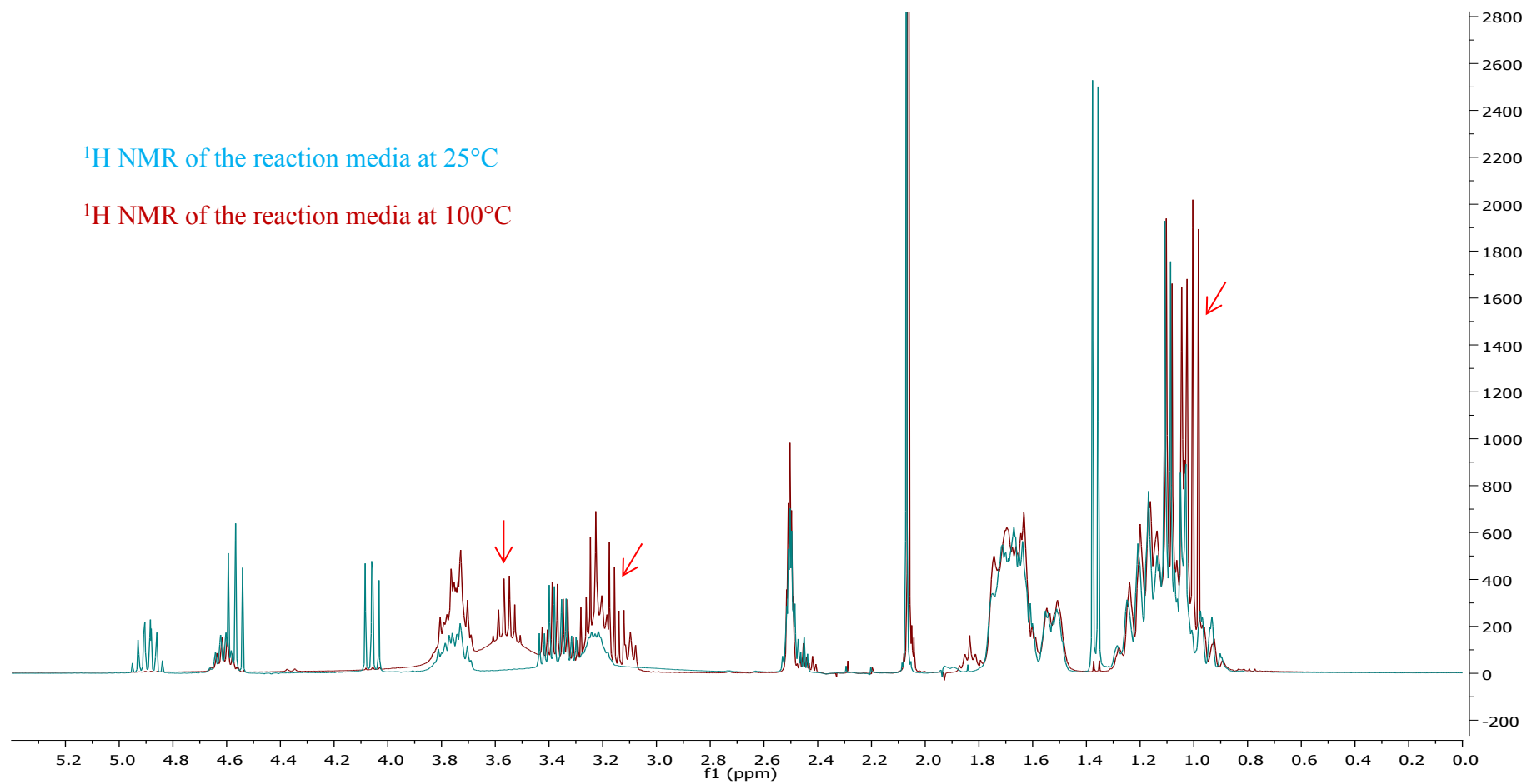
The samples for NMR analysis were prepared as follow. A precise quantity of a solution of acetonitrile ($\sim 2.7 \text{ g.L}^{-1}$) in DMSO- d_6 ($\sim 3 \text{ g}$) was introduced in the reaction tube and stirred affording a homogenous solution. Then a sample of this solution was analysed by NMR.



The calculated conversion of 4-phenyl-1,3-dioxolan-2-one is 63%

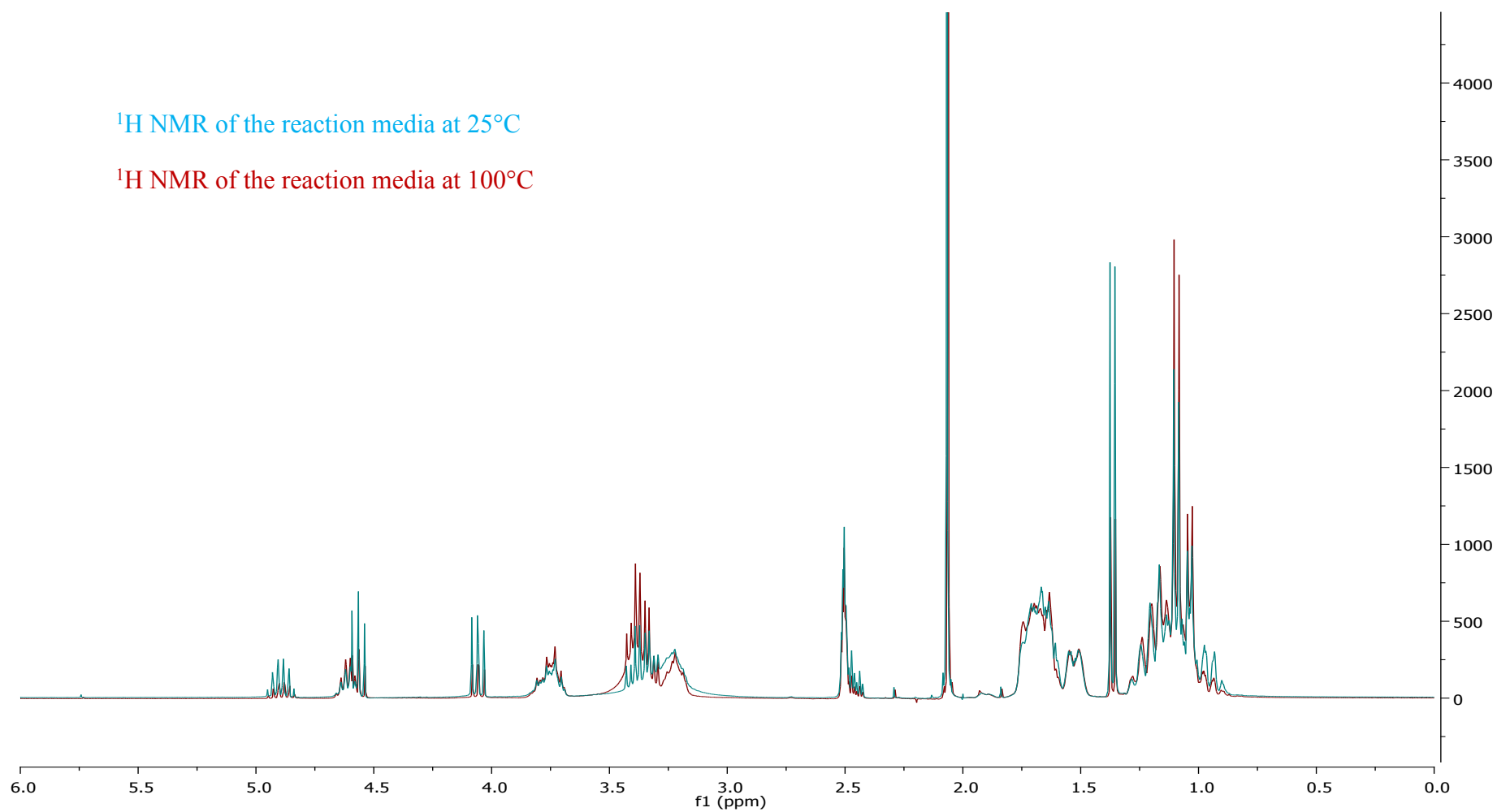
7. NMR ^1H evidencing the presence of impurities when TBD is used. Comparison with the thiourea.

Figure 2 Comparison of the reaction of CP with the cyclohexyl amine at 100°C and 25°C using TBD as catalyst 1h.



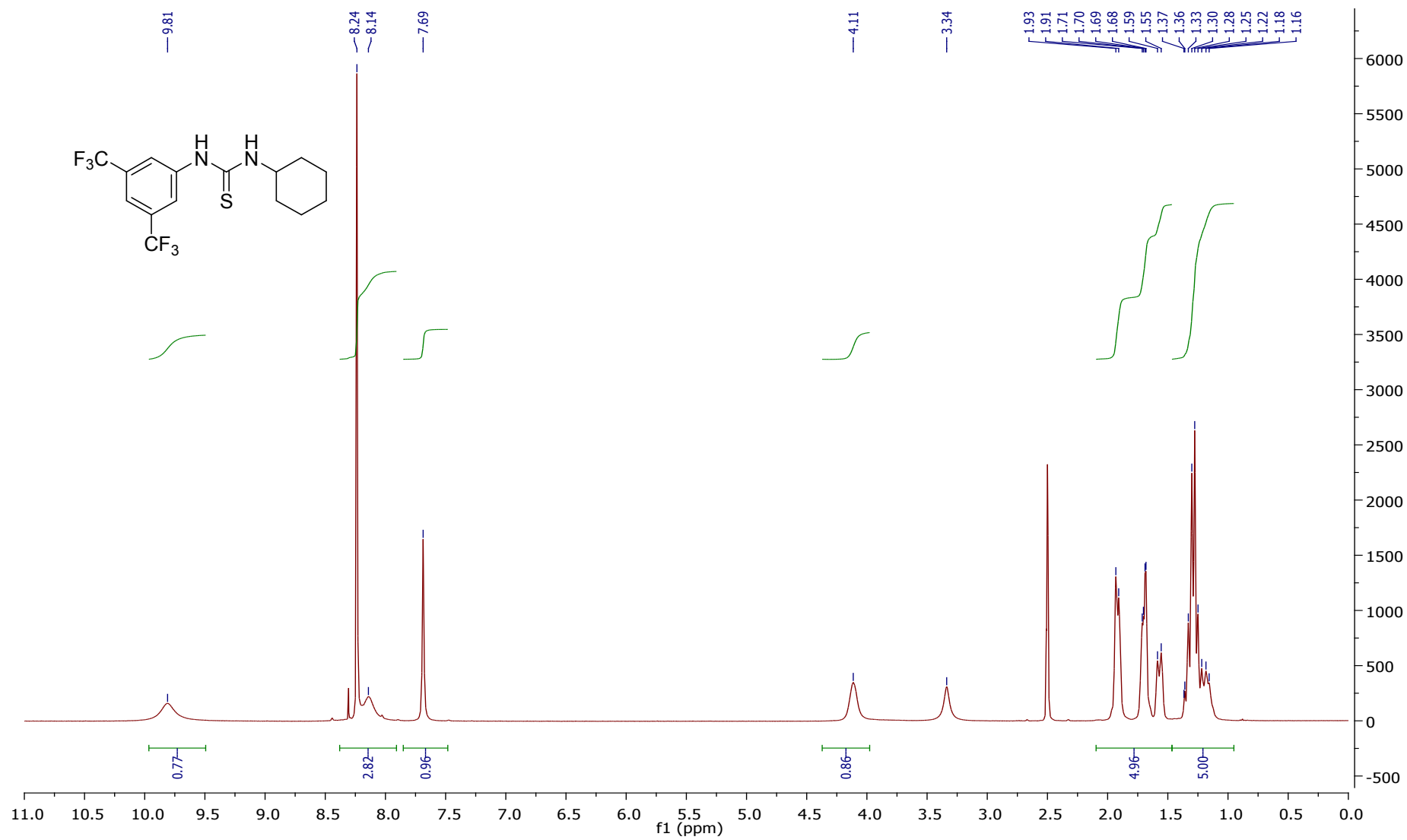
New signals corresponding to impurities have appeared.

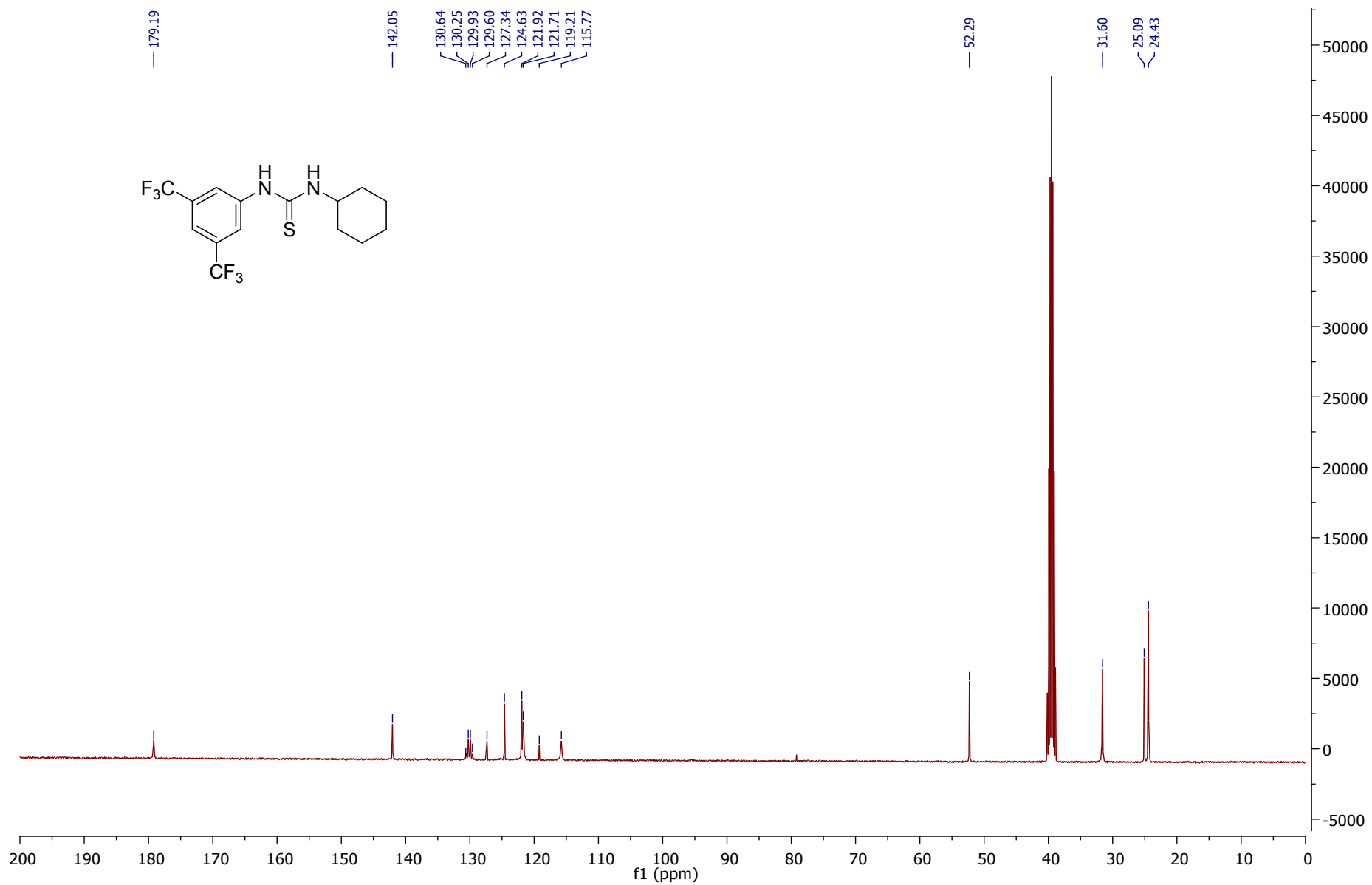
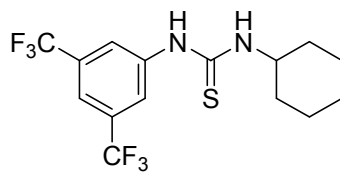
Figure 2 Comparison of the reaction of CP with the cyclohexyl amine at 100°C and 25°C using Thiourea as catalyst 1h.

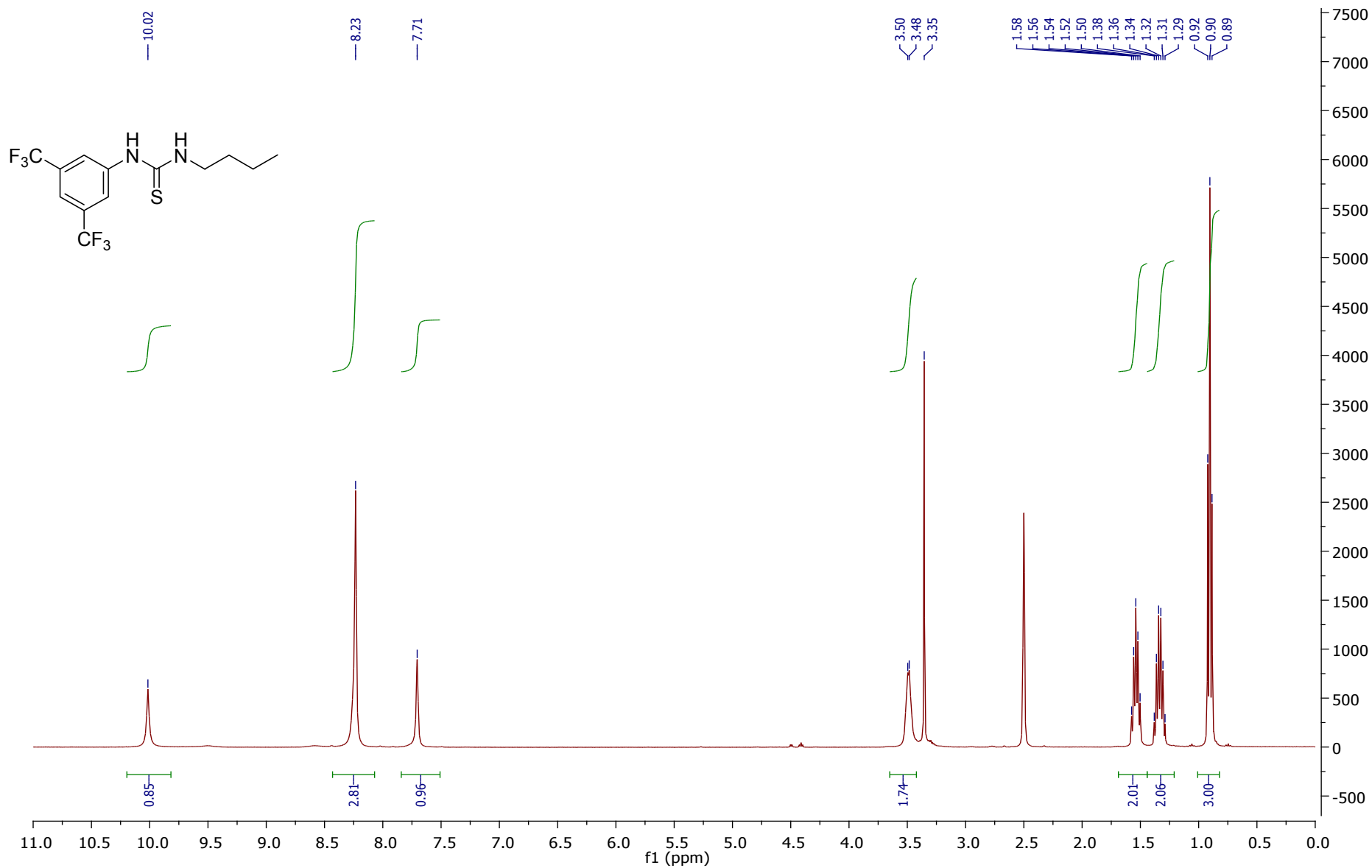


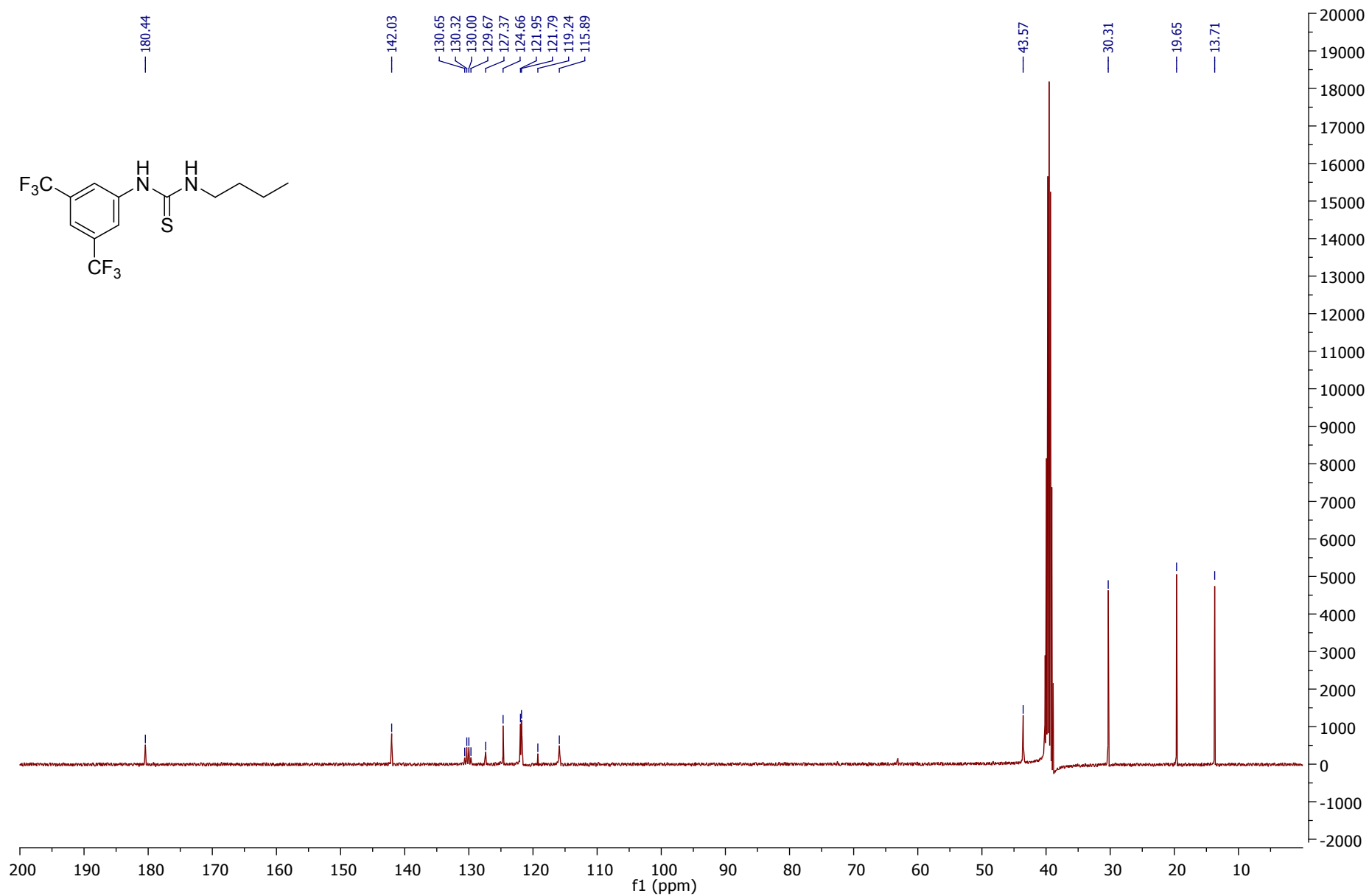
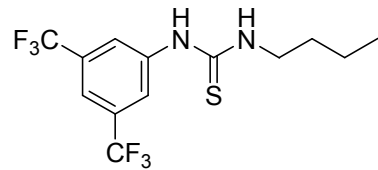
Absence of new signals.

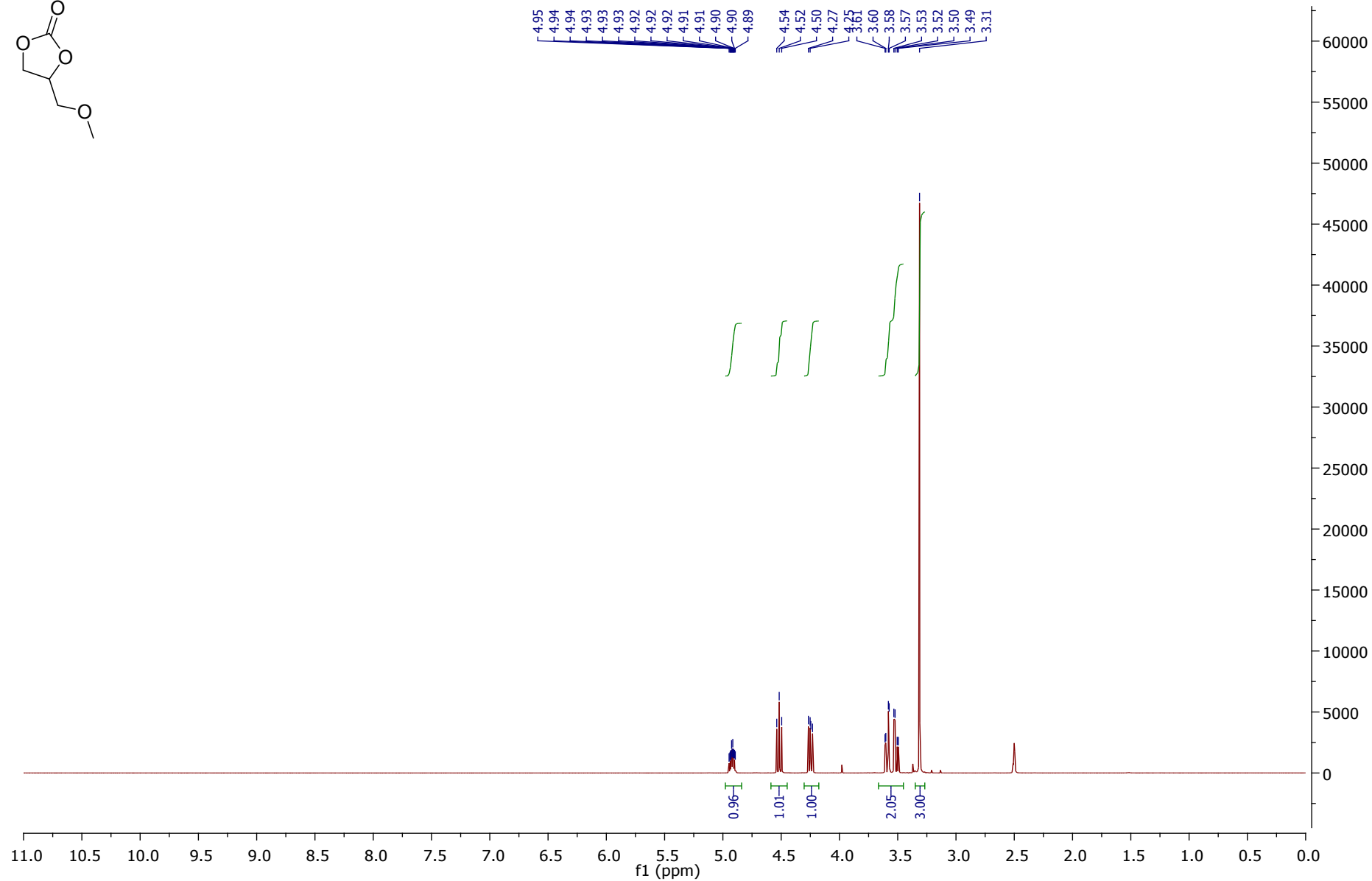
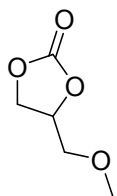
8. ^1H and ^{13}C NMR spectrum

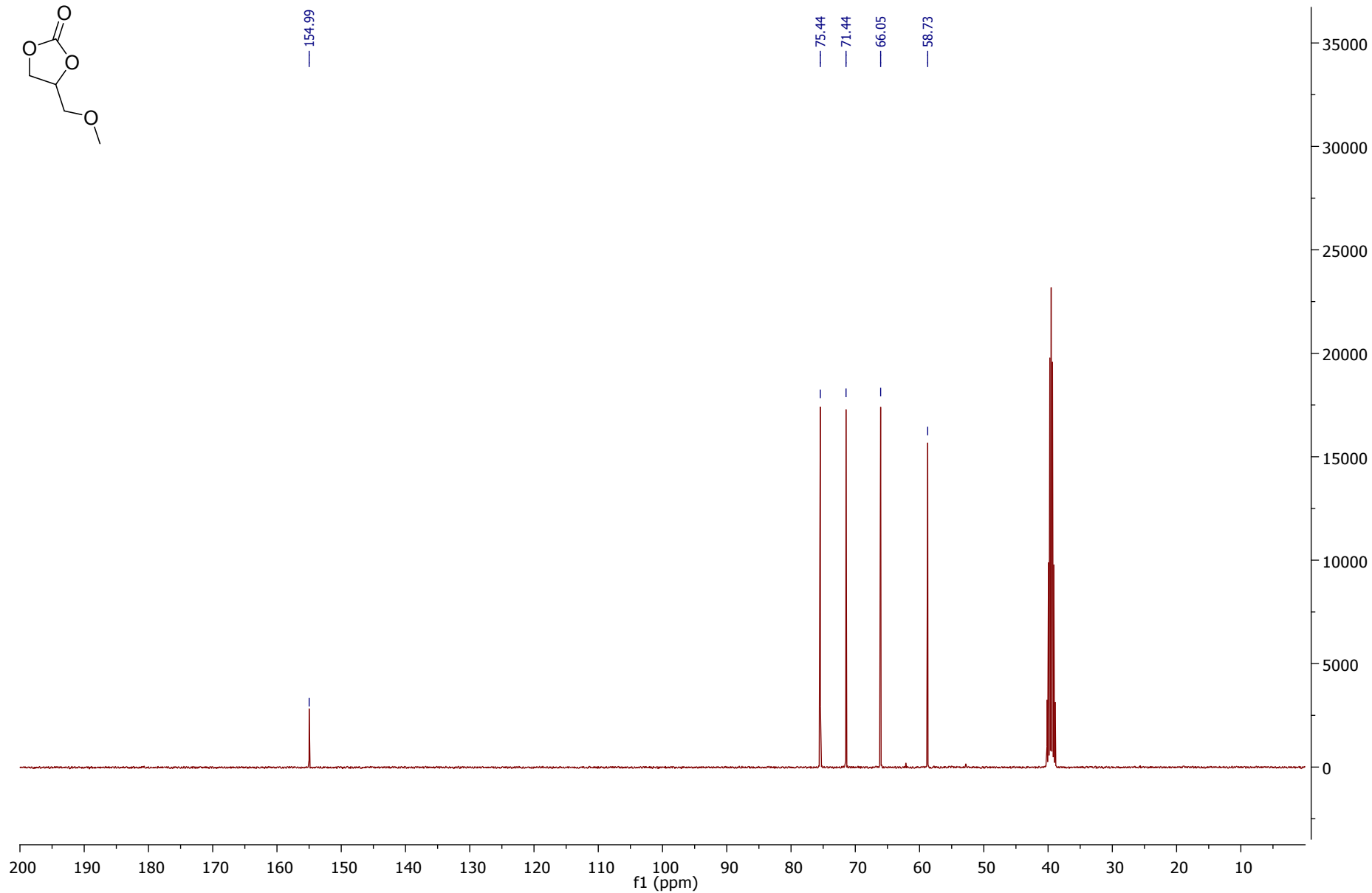
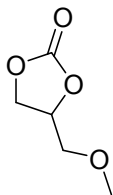


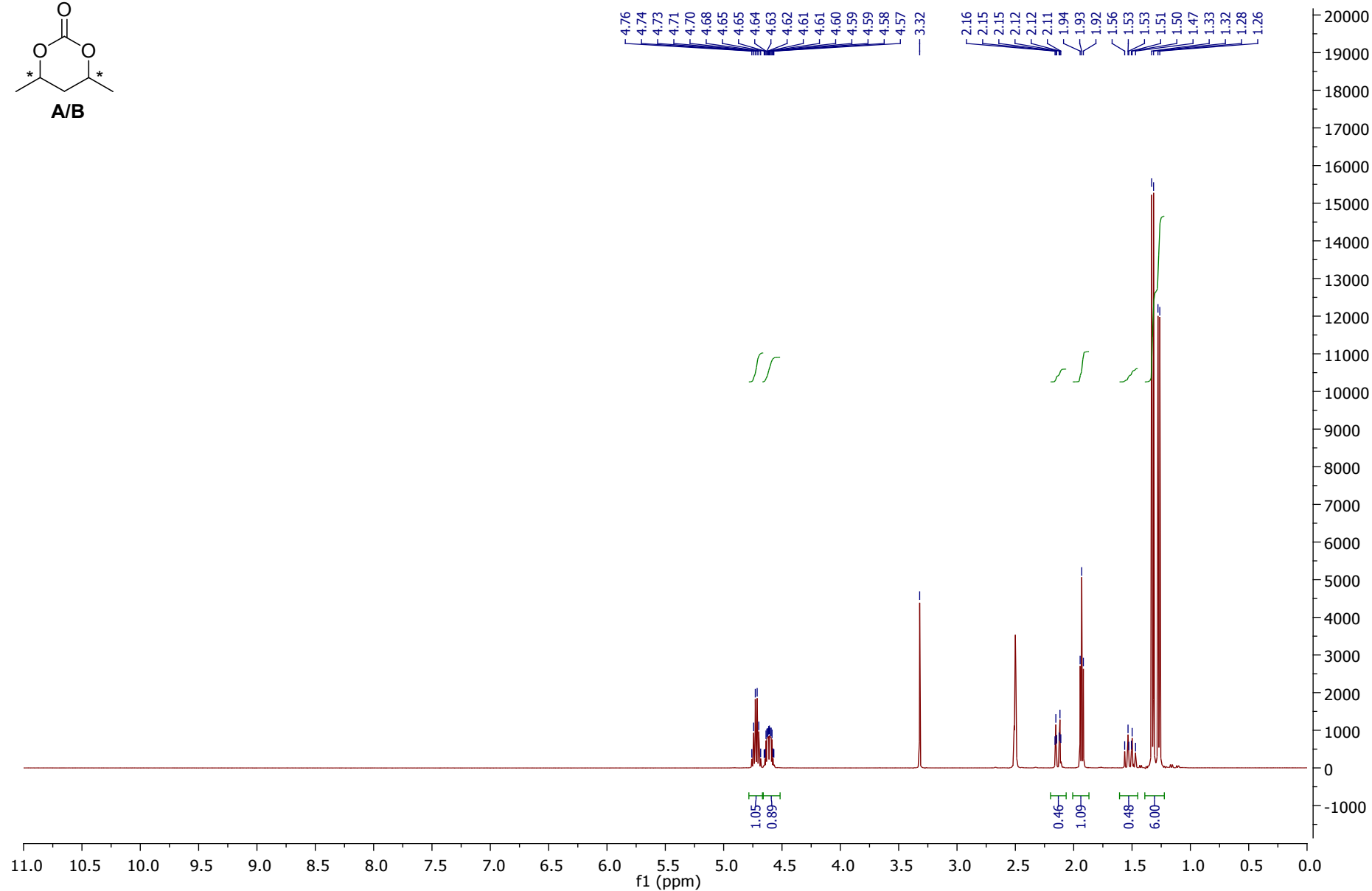
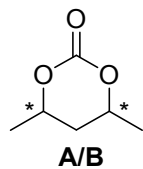


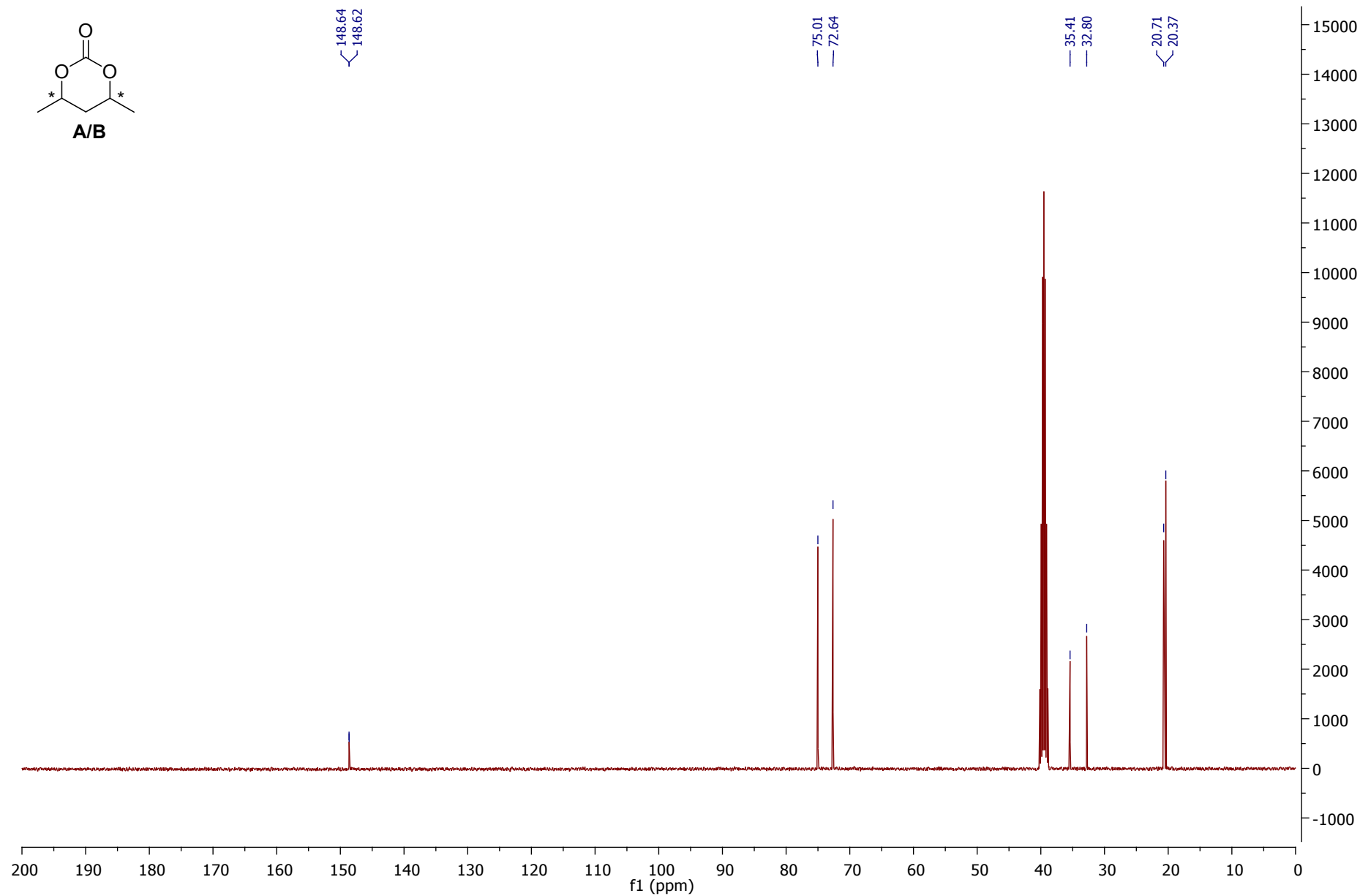
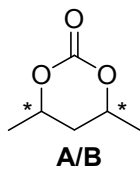


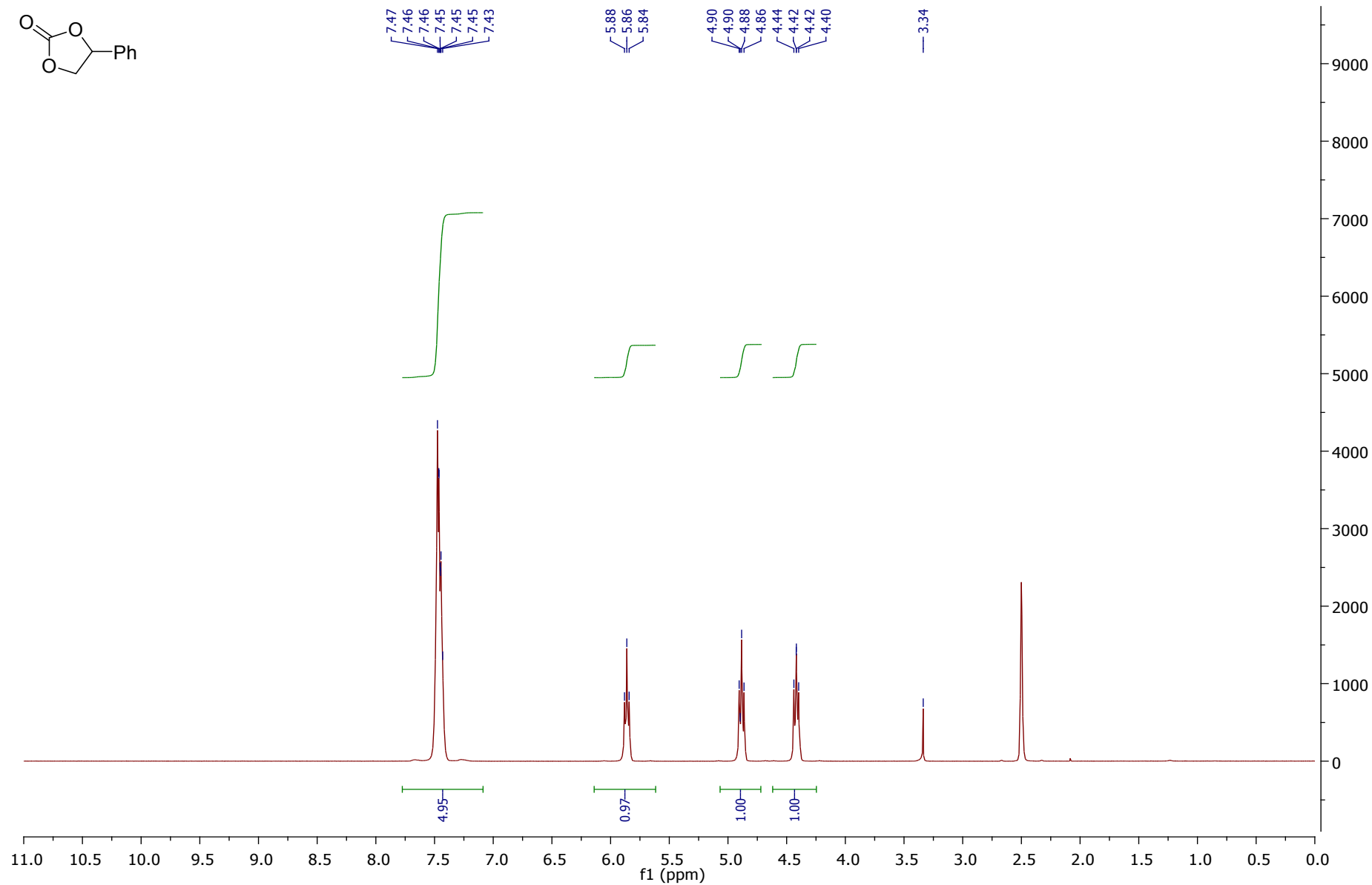
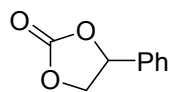


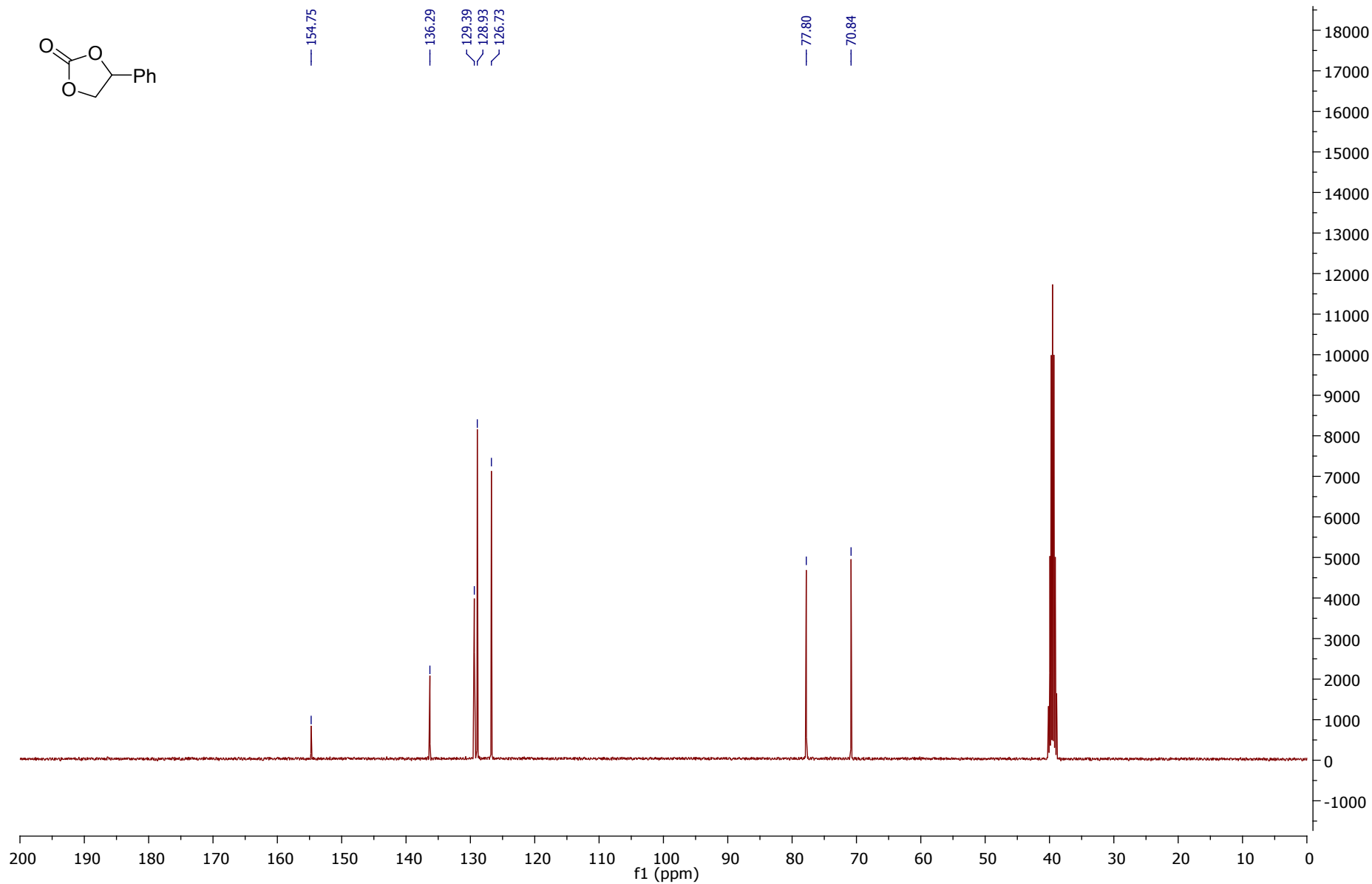
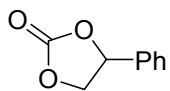


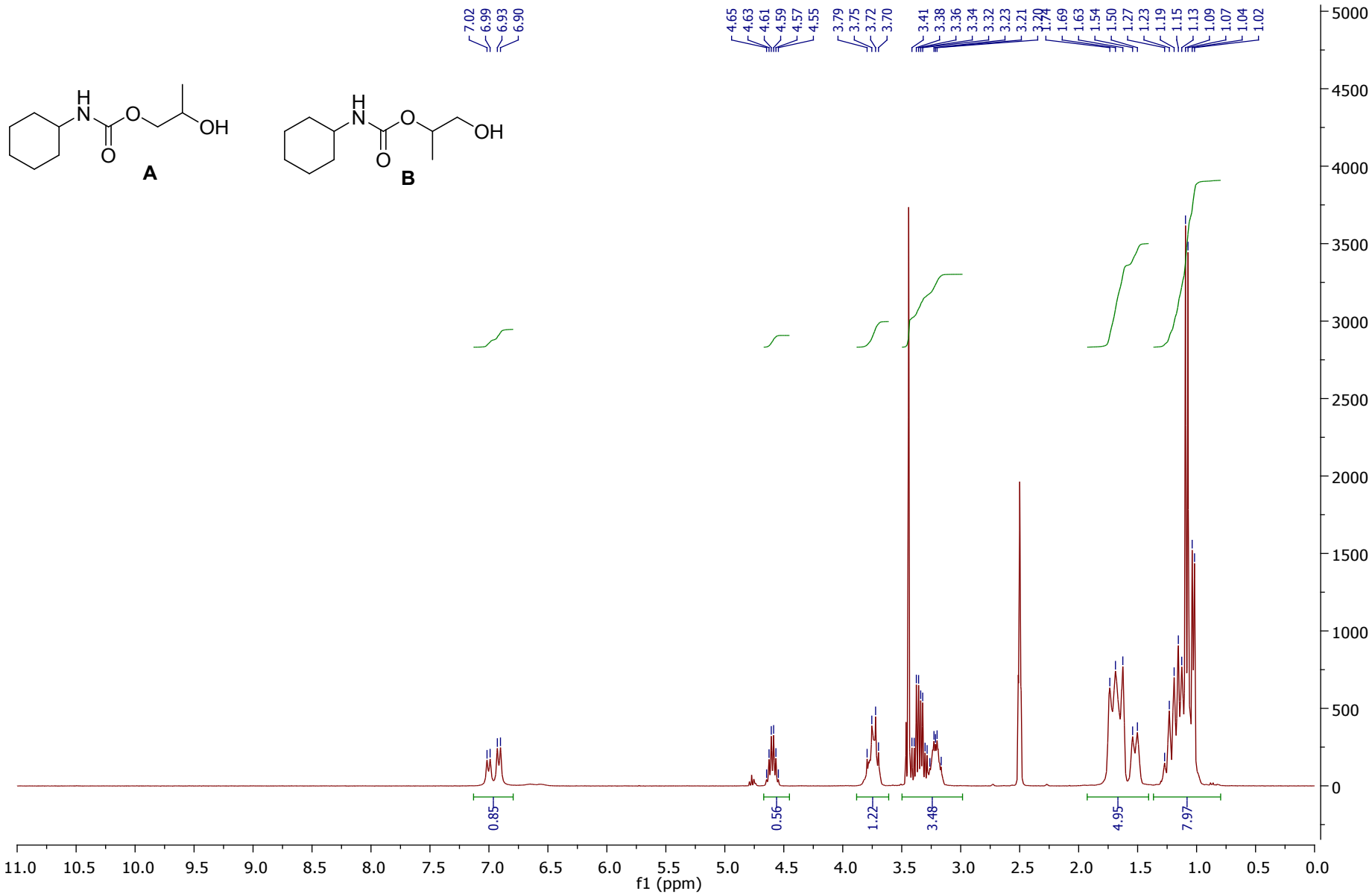


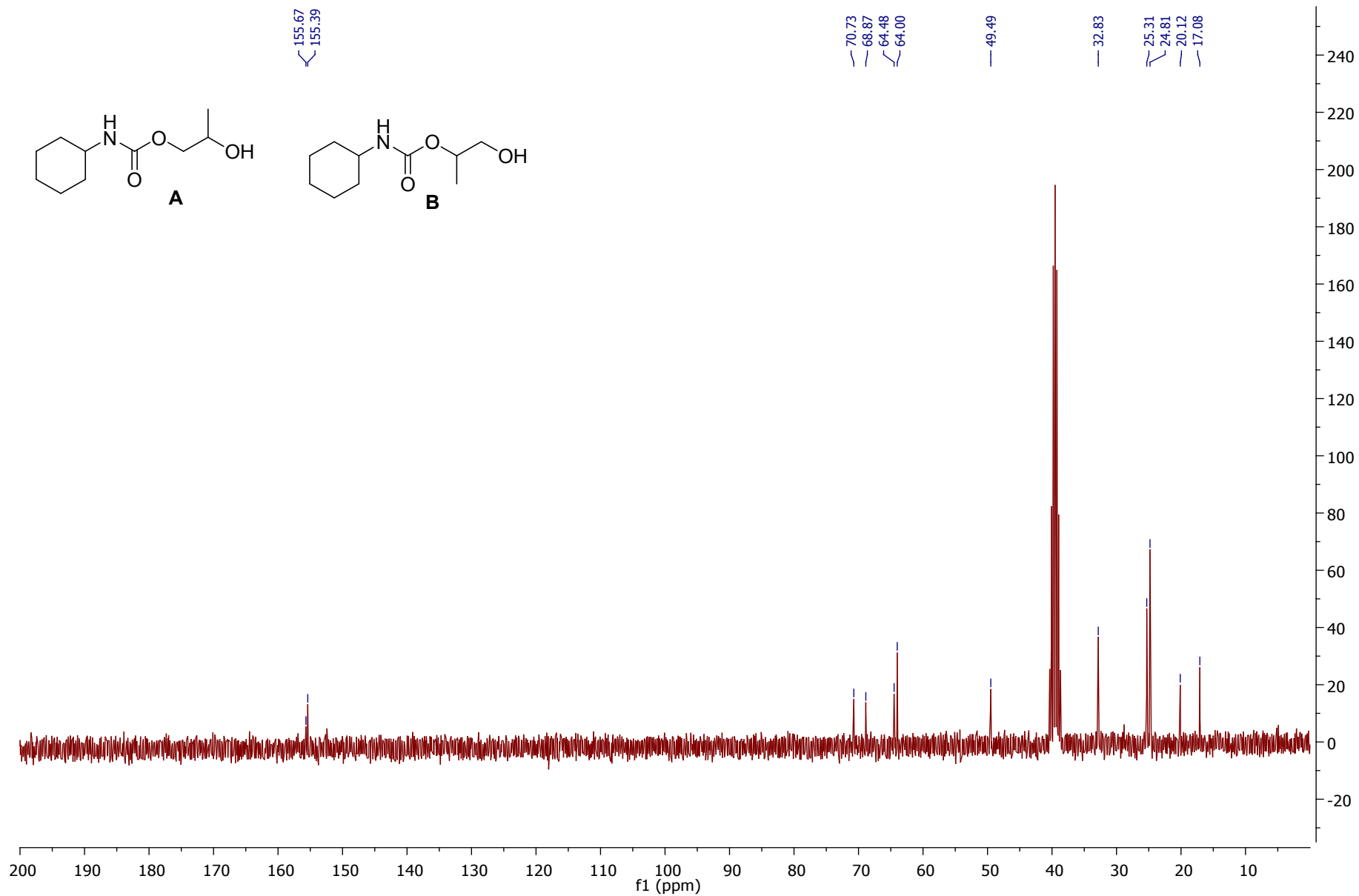


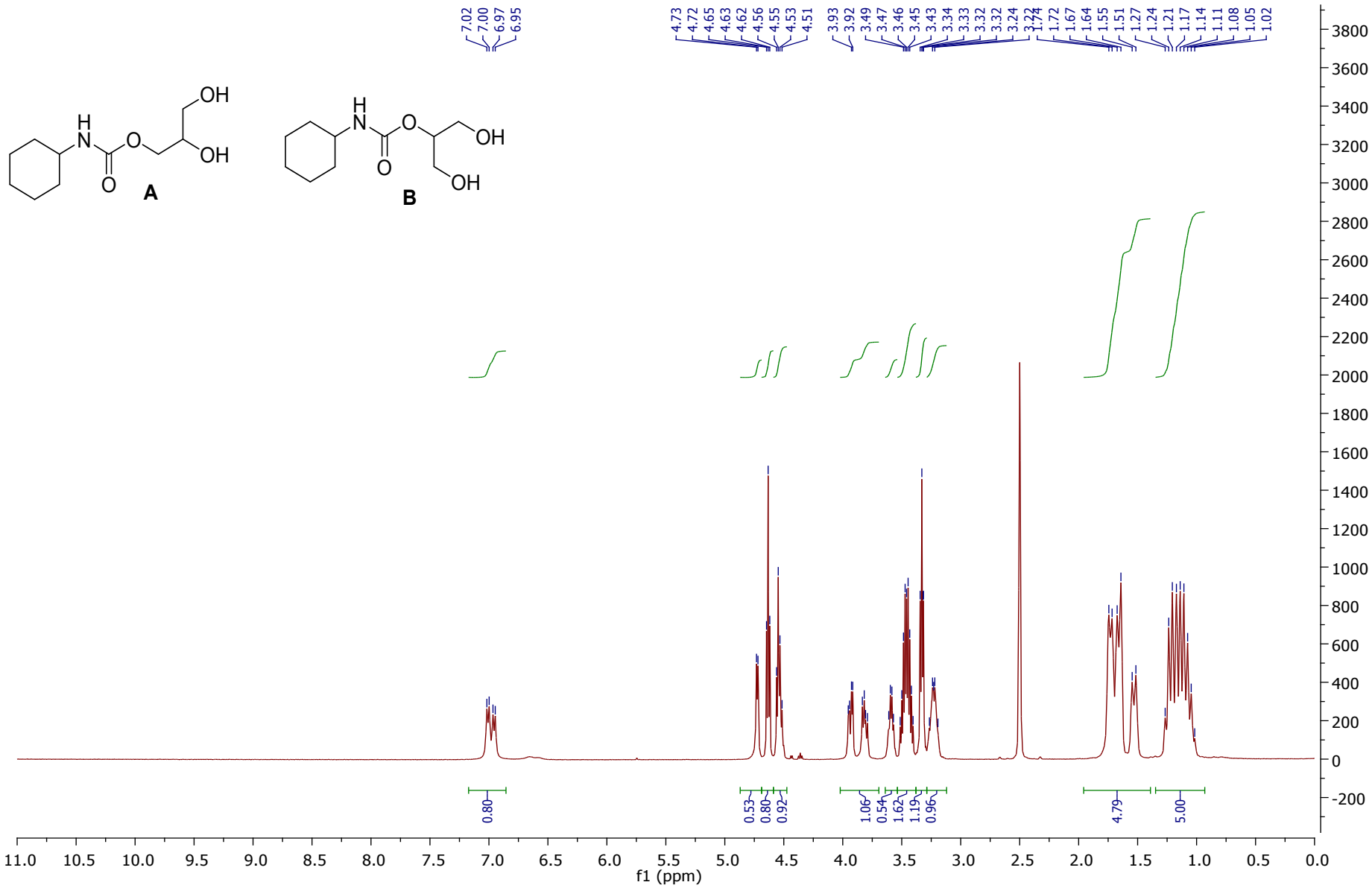


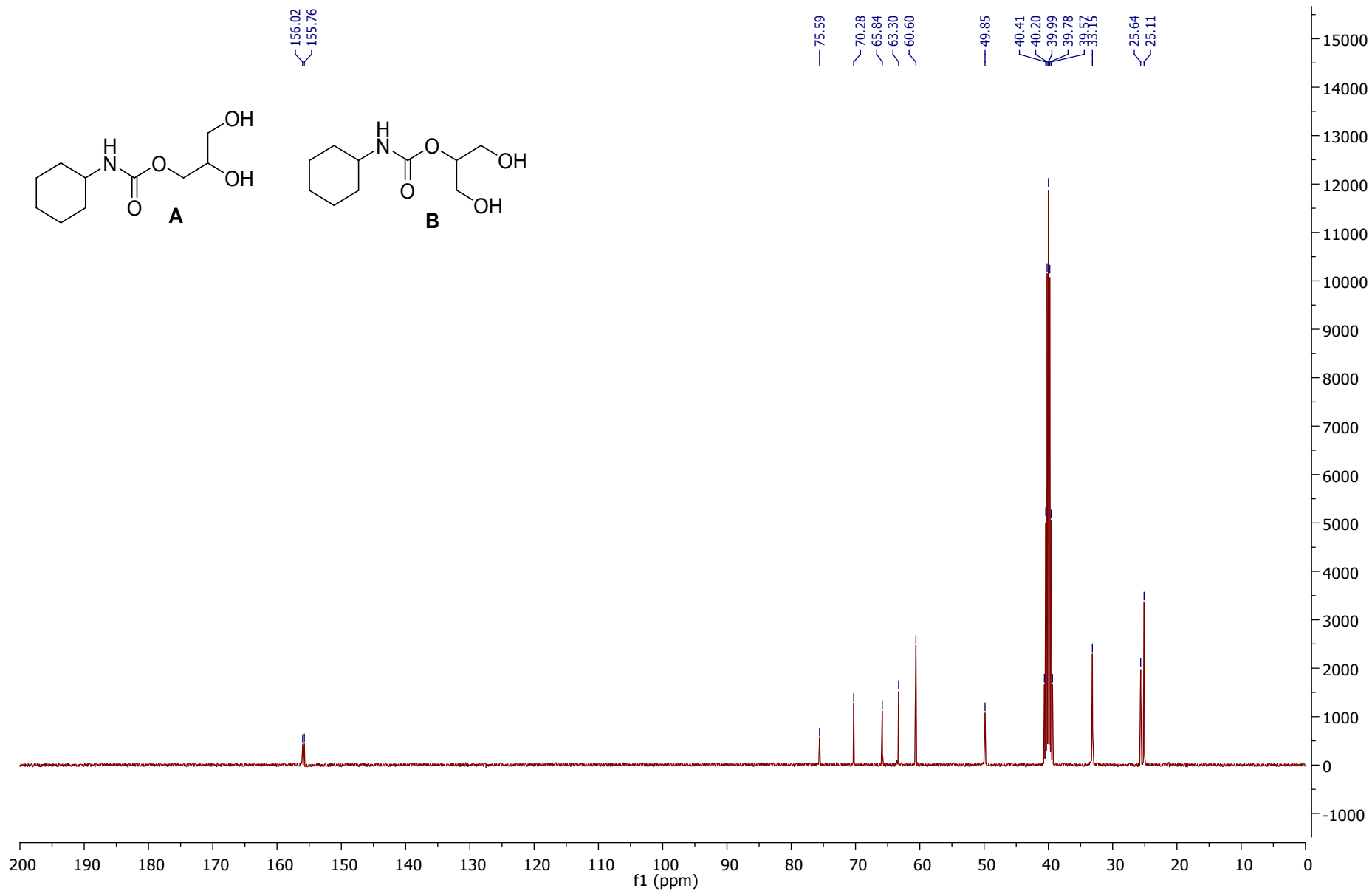


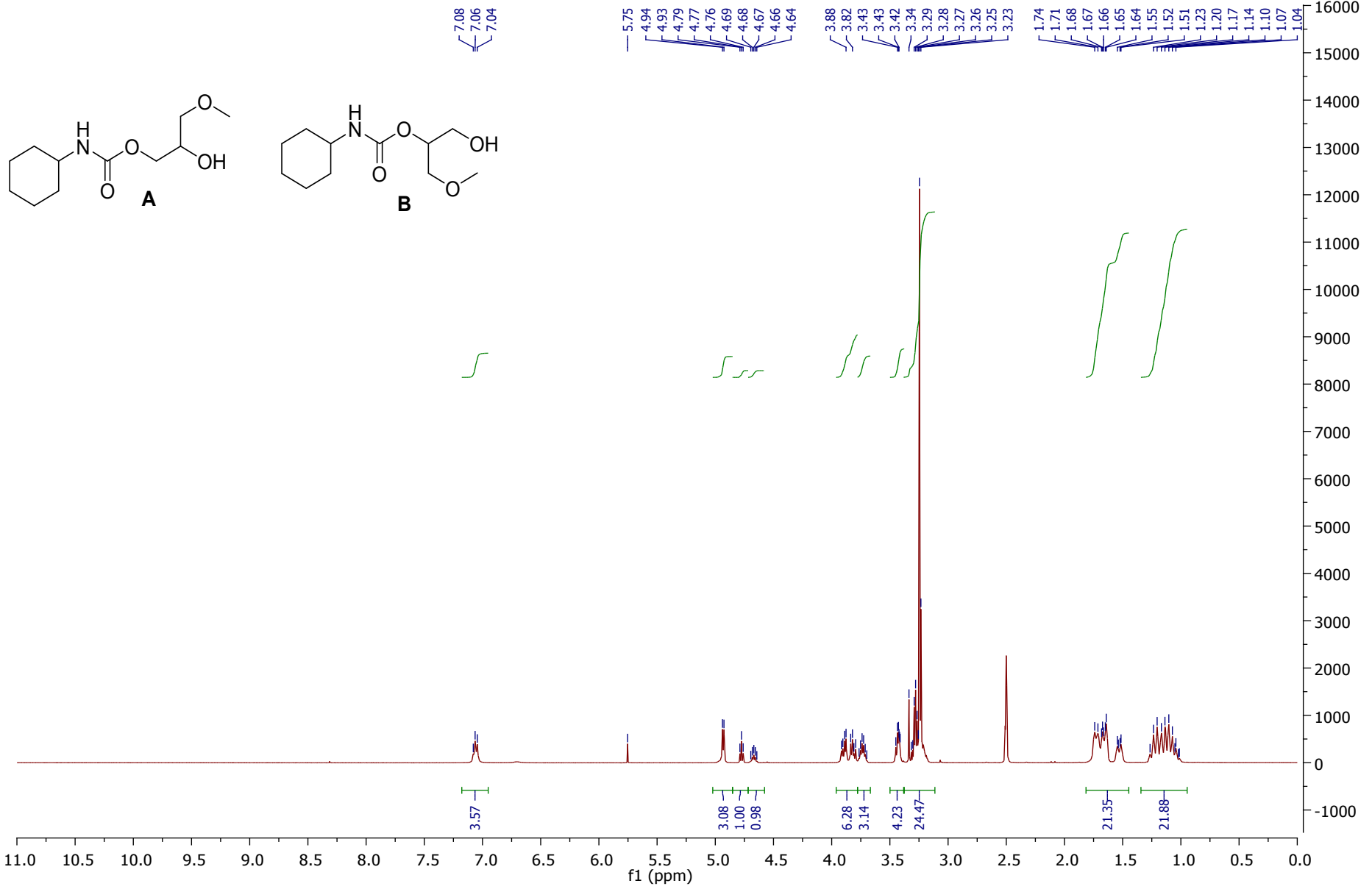


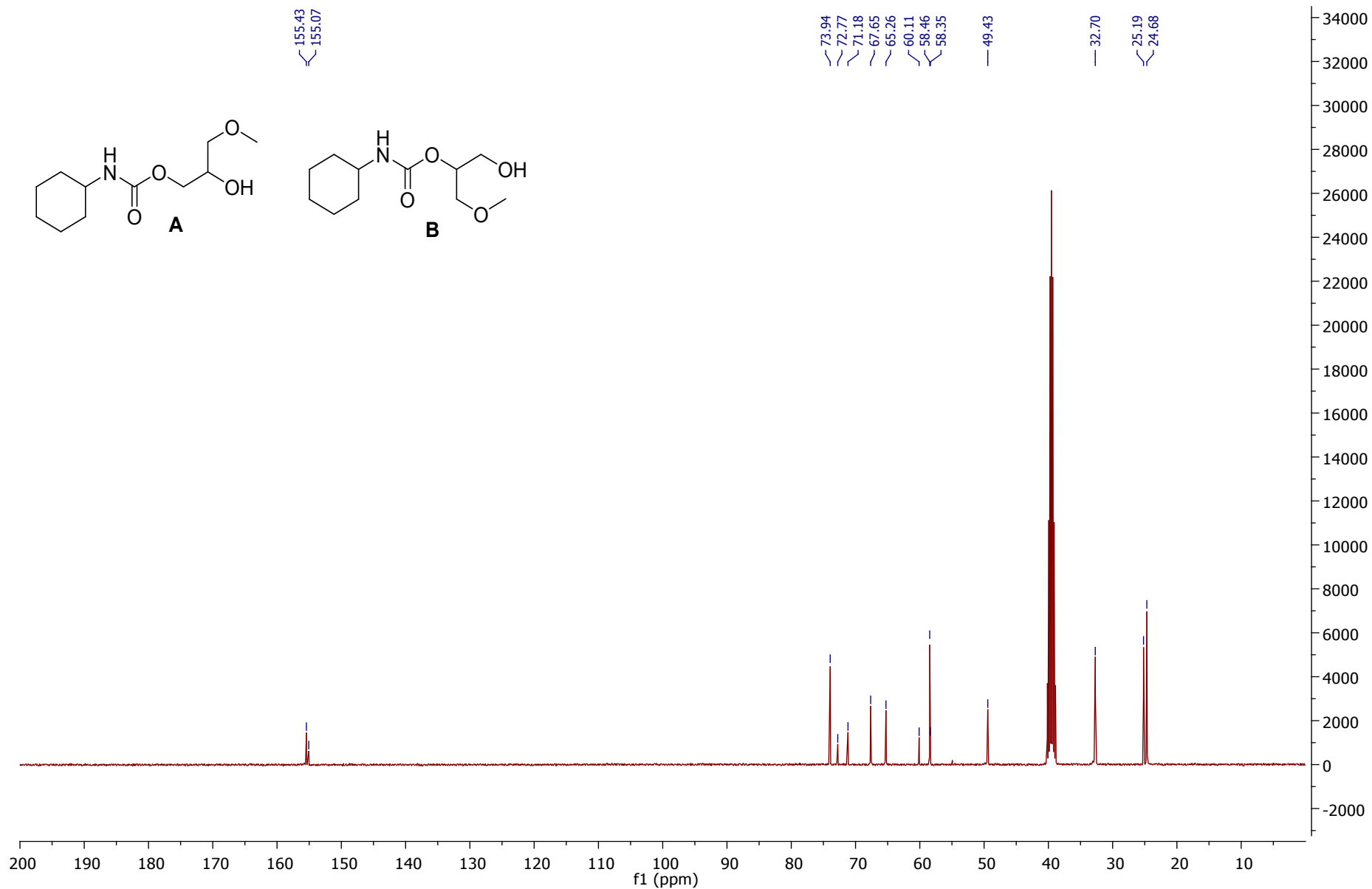


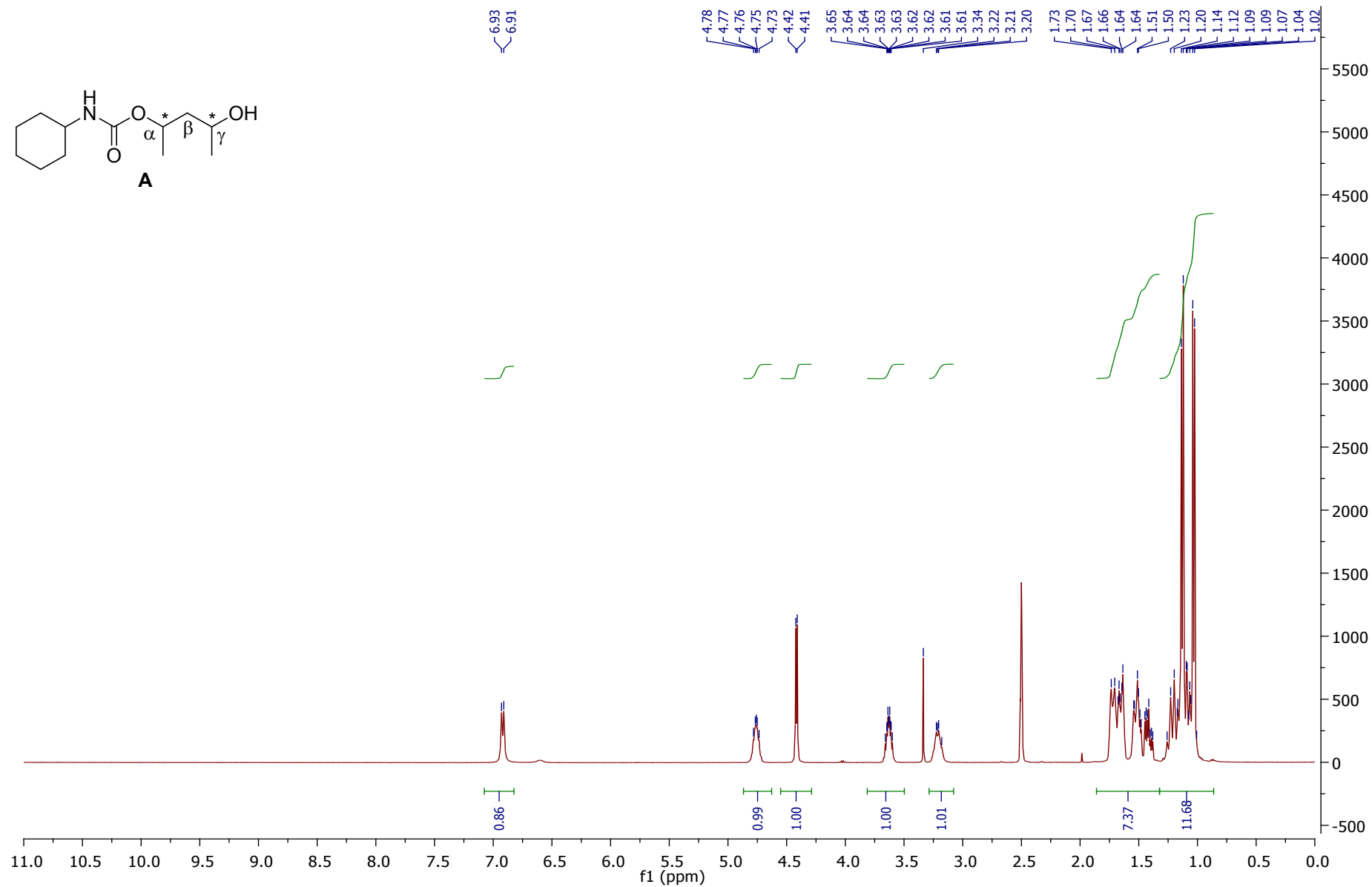
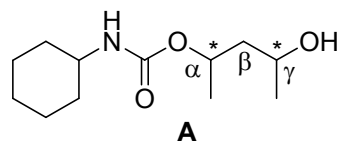


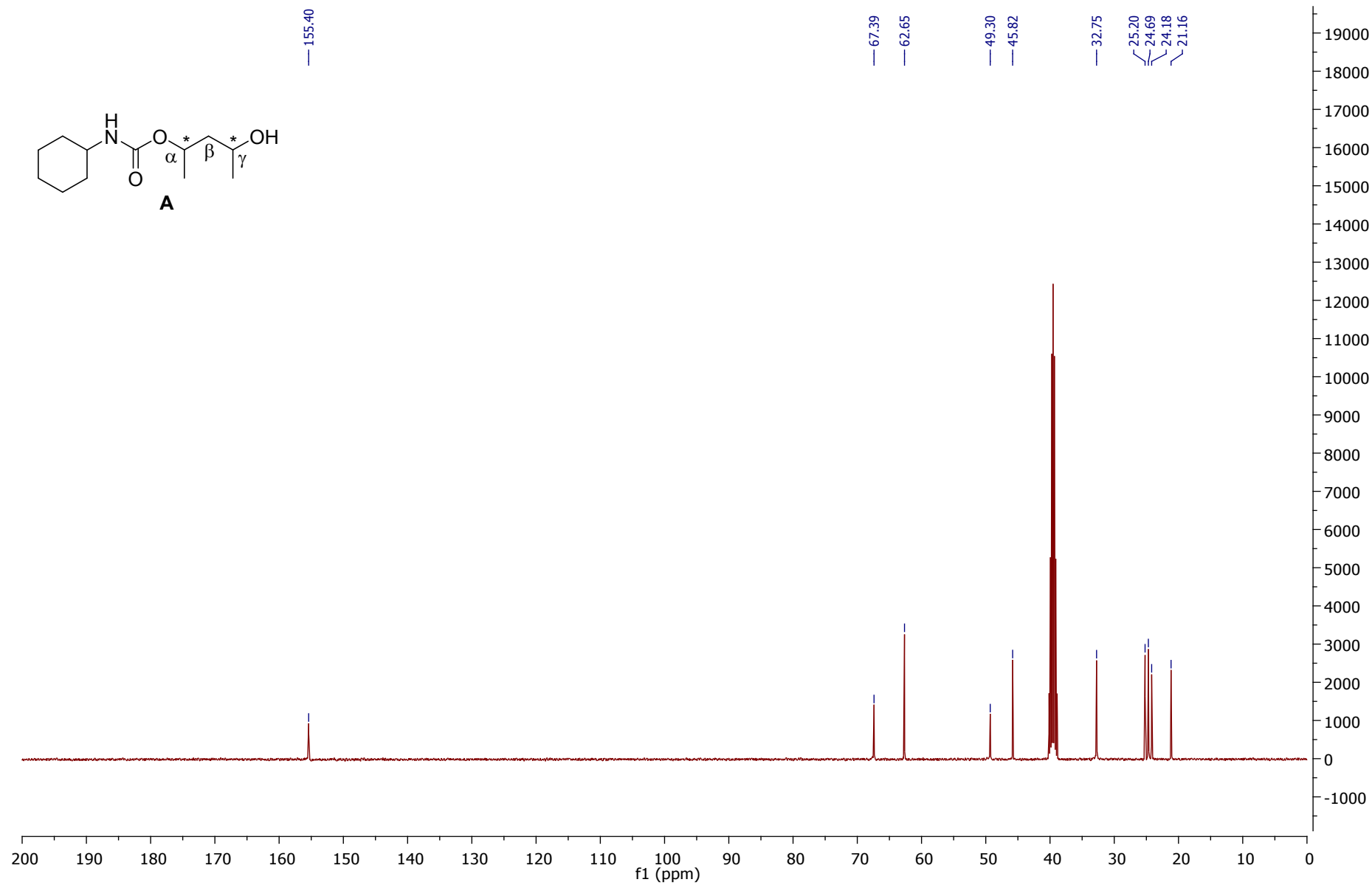
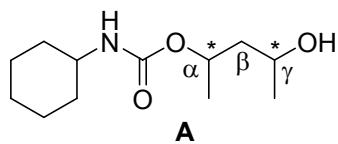


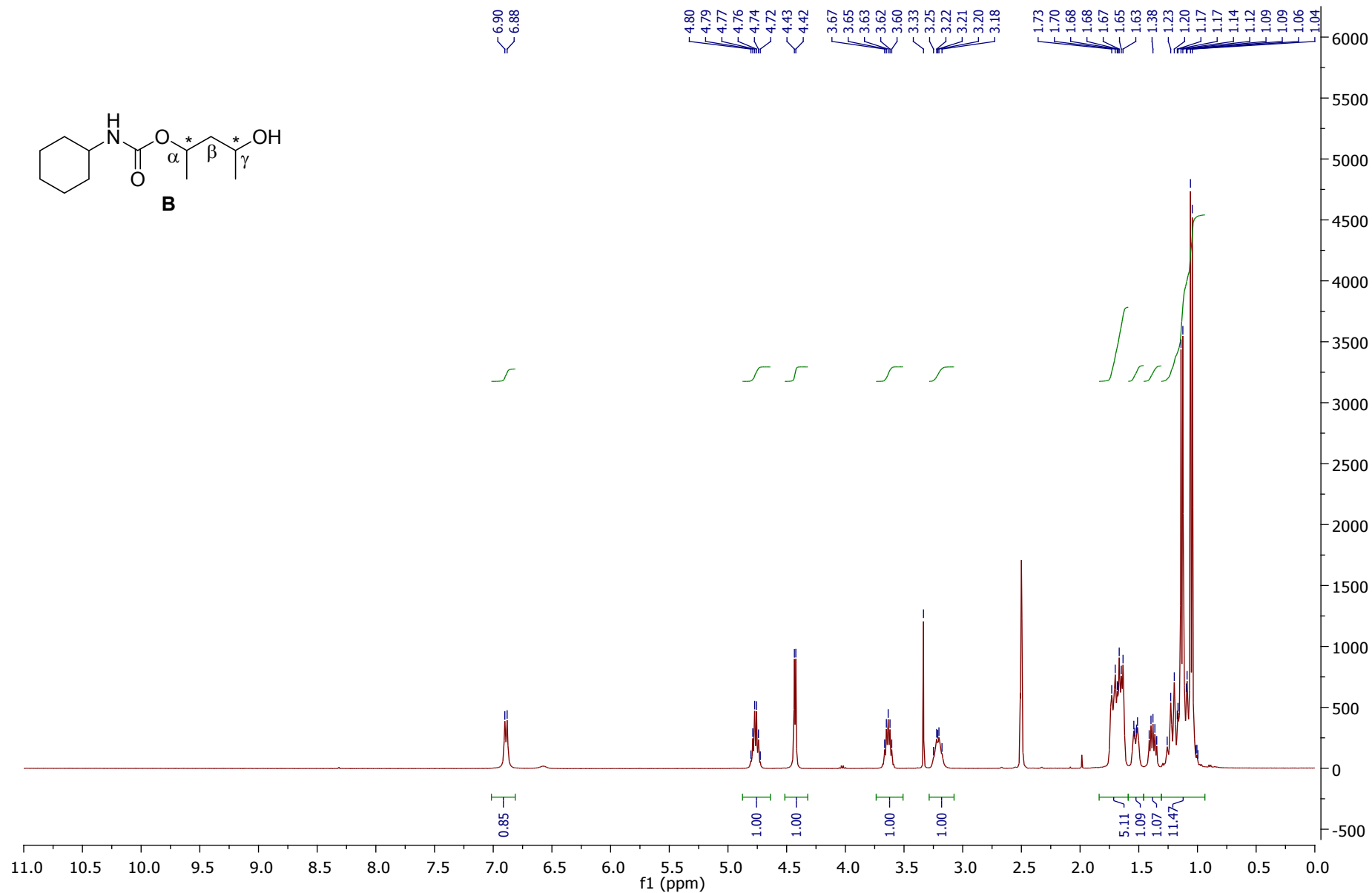
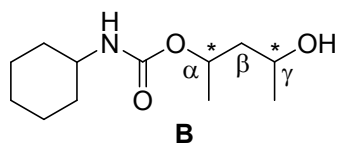


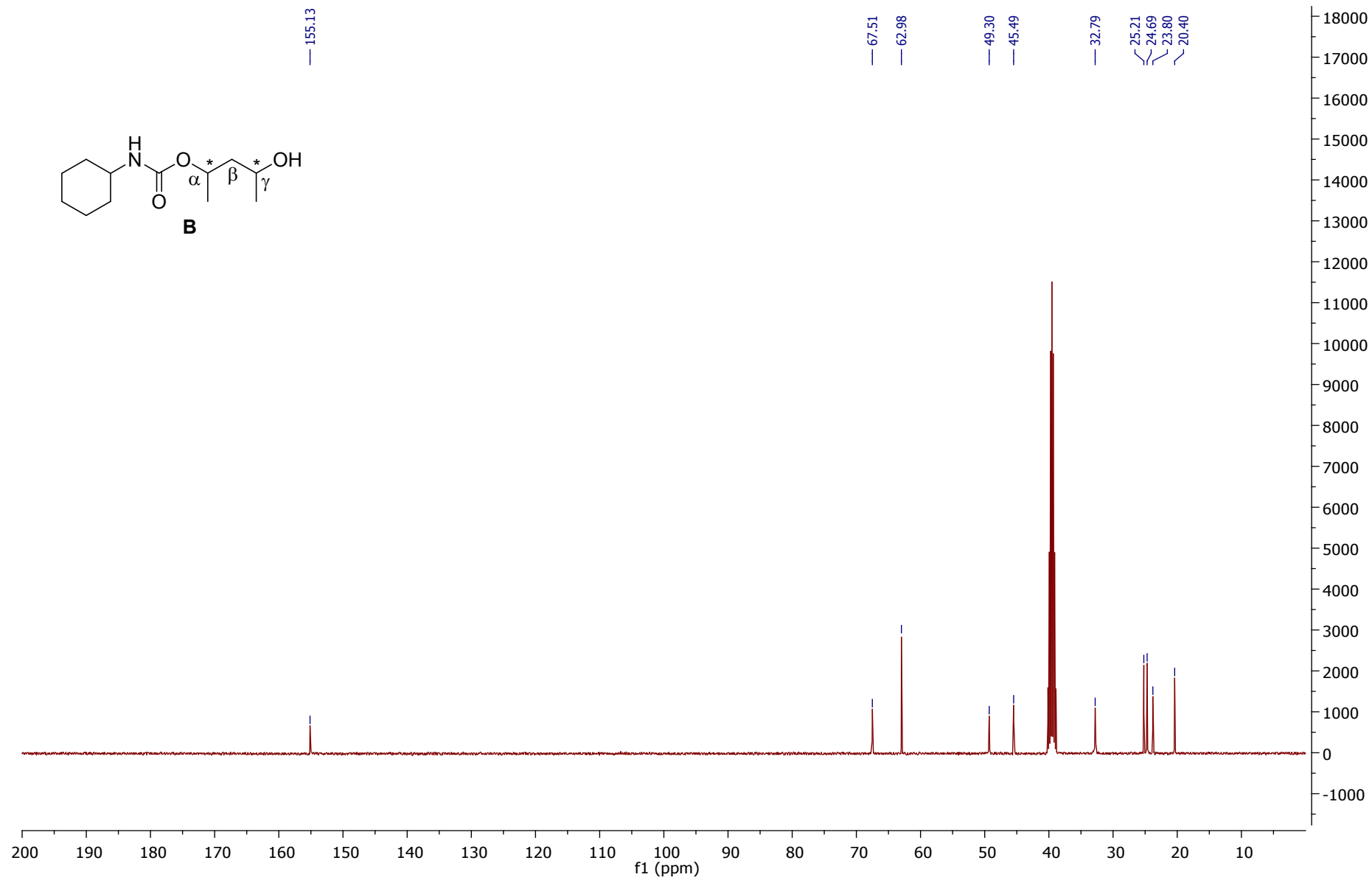
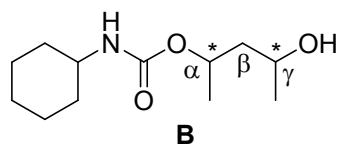


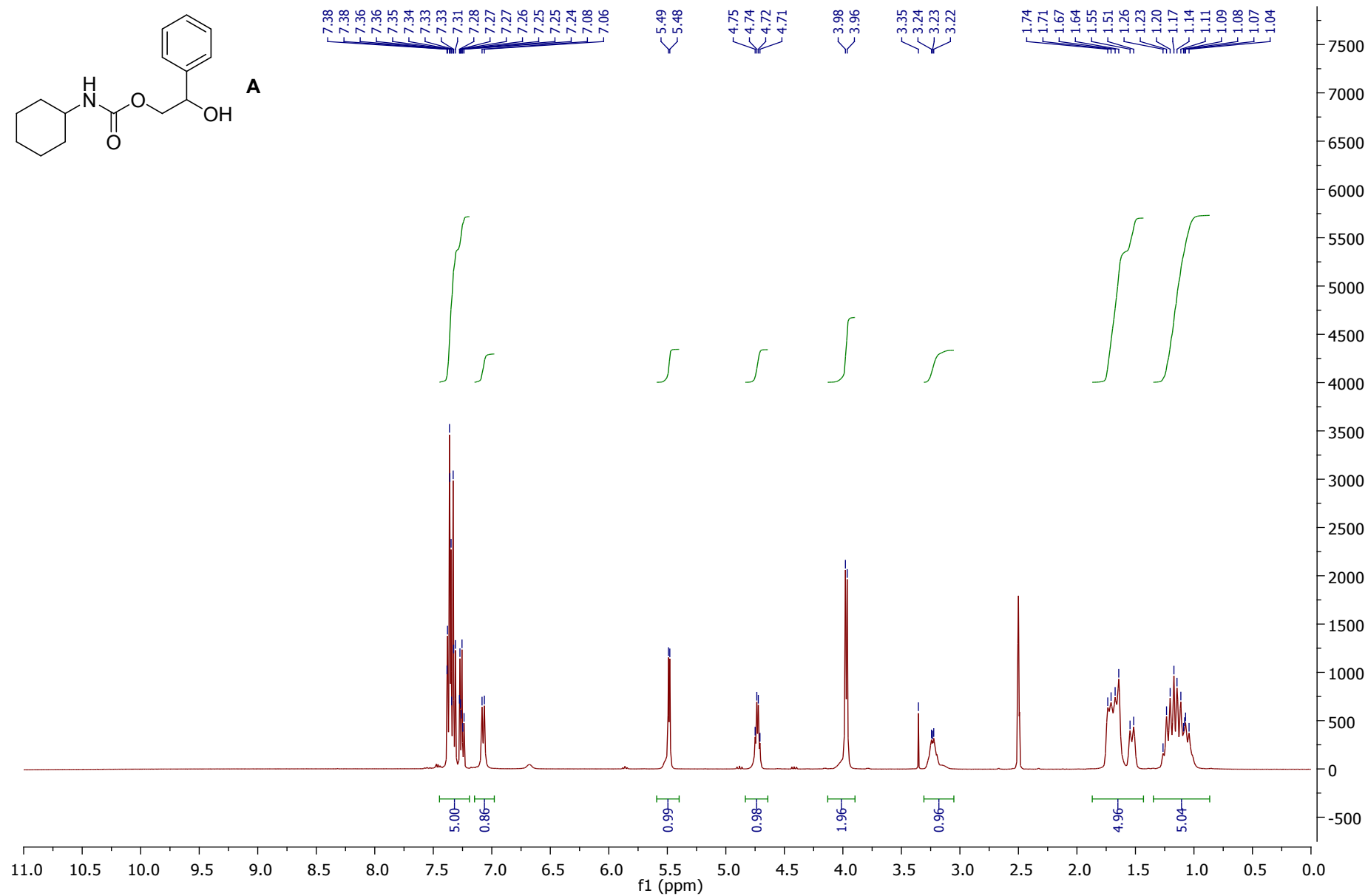
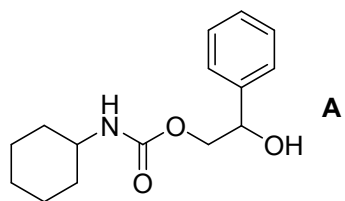


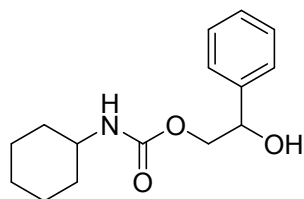




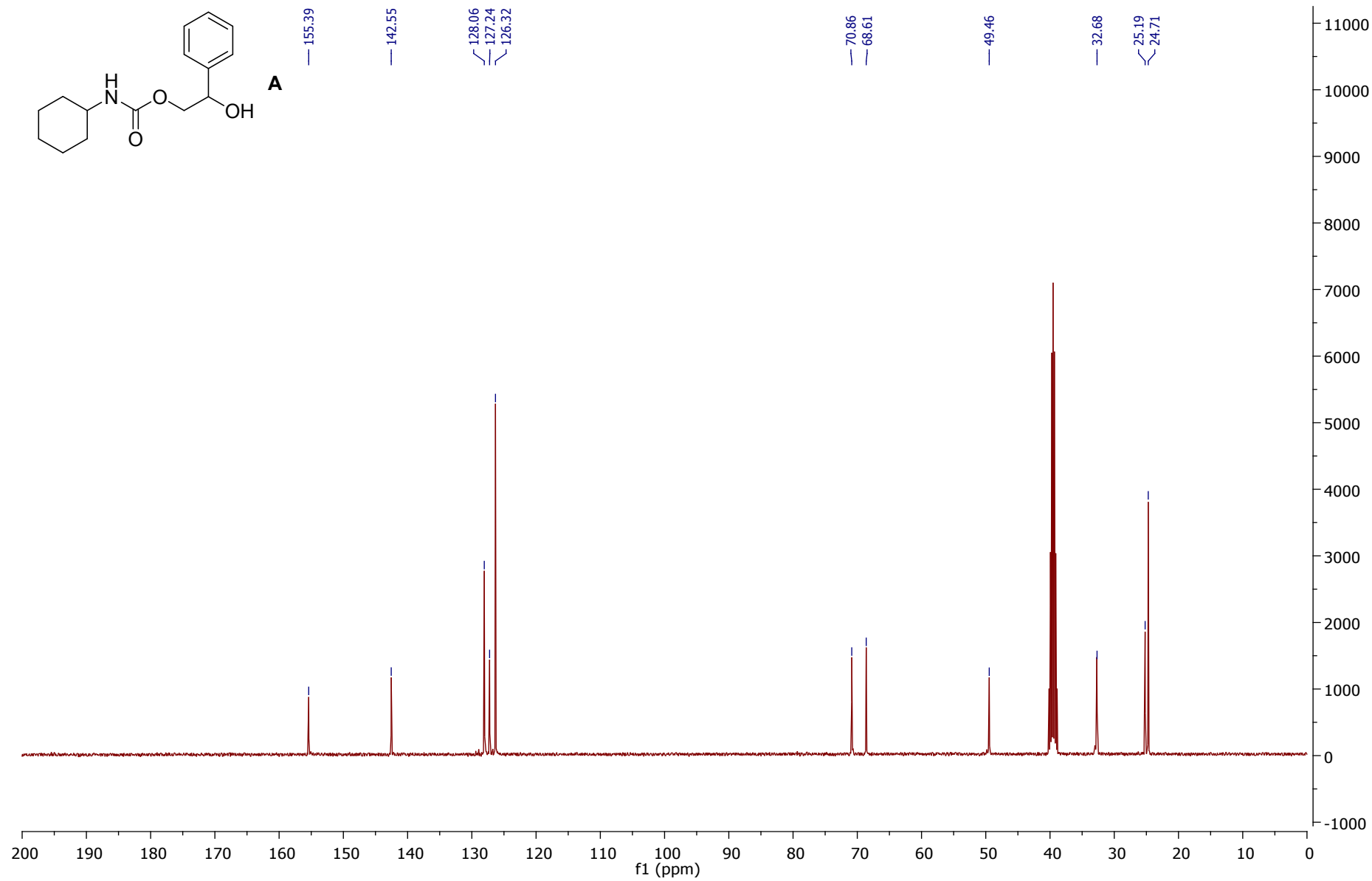


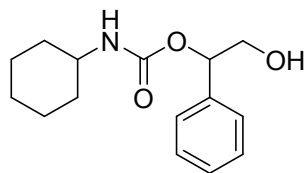




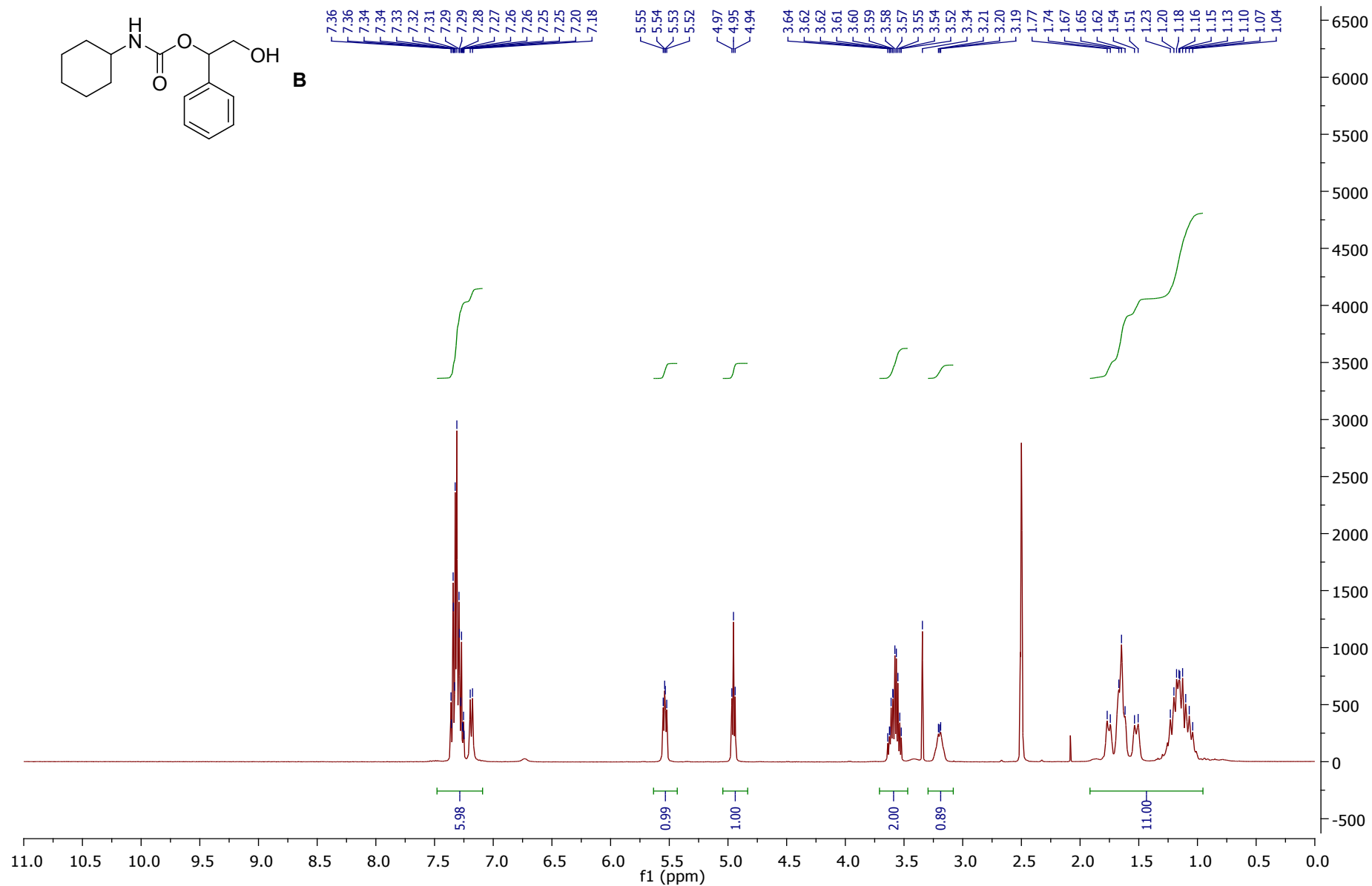


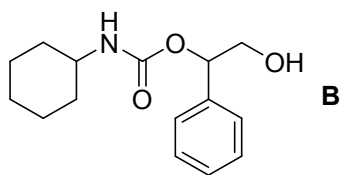
A



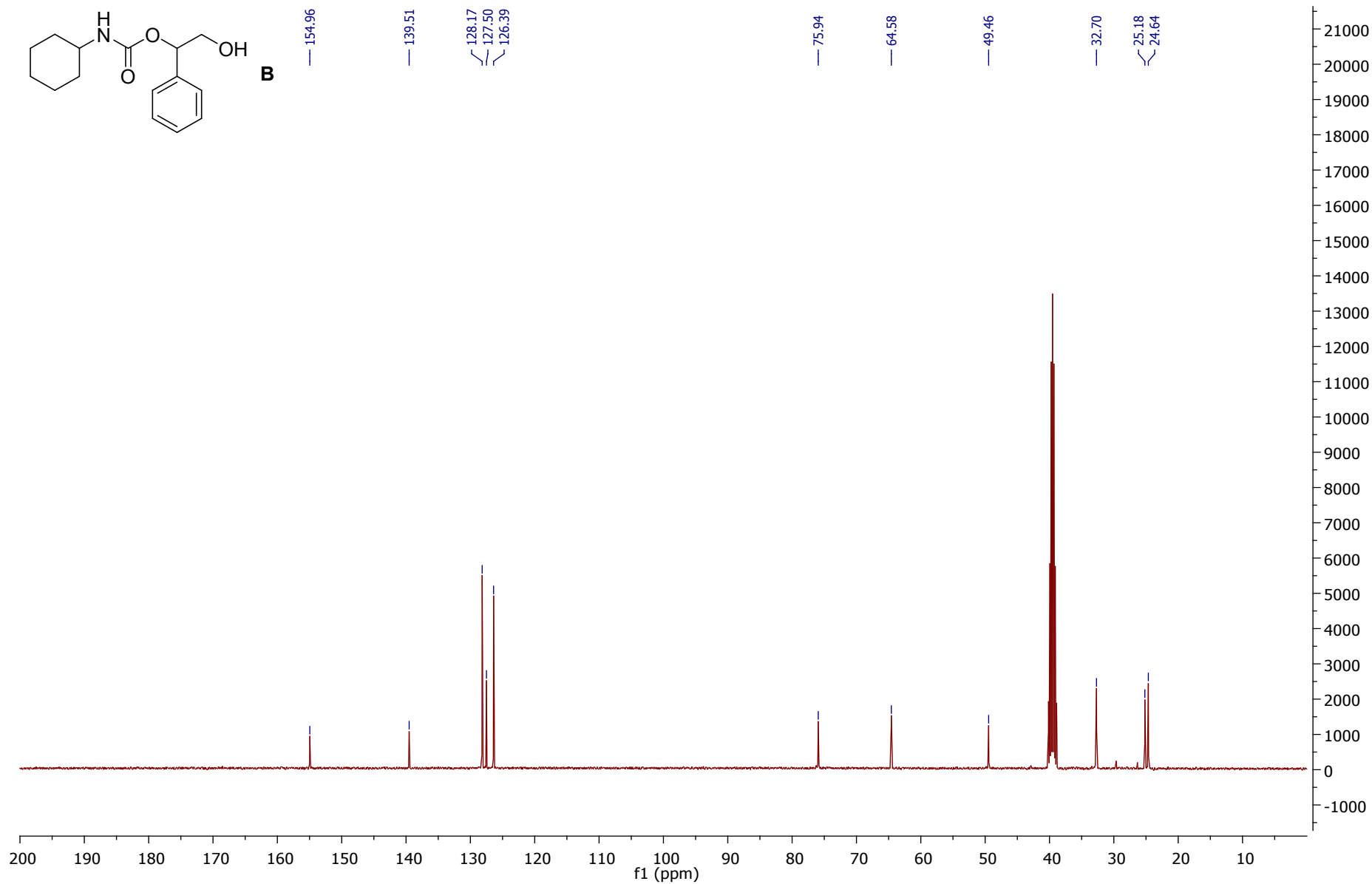


B





B



- (1) Pratt, R. C.; Lohmeijer, B. G. G.; Long, D. A.; Lundberg, P. N. P.; Dove, A. P.; Li, H.; Wade, C. G.; Waymouth, R. M.; Hedrick, J. L. *Macromolecules* **2006**, *39*, 7863–7871.
- (2) Nogawa, M.; Sugawara, S.; Iizuka, R.; Shimojo, M.; Ohta, H.; Hatanaka, M.; Matsumoto, K. *Tetrahedron* **2006**, *62*, 12071–12083.
- (3) Besse, V.; Foyer, G.; Auvergne, R.; Caillol, S.; Boutevin, B. *J. Polym. Sci. Part A Polym. Chem.* **2013**, 3284–3296.
- (4) Jeoshua, K.; Israel, R.; Shalom, S. *J. Chem. Soc. Perkin Trans. 2* **1972**, 2019–2025.
- (5) Reithofer, M. R.; Sum, Y. N.; Zhang, Y. *Green Chem.* **2013**, *15*, 2086–2090.
- (6) Huang, J.; Shi, M. *J. Org. Chem.* **2003**, *68*, 6705–6709.