

Light-driven C–O coupling of carboxylic acids and alkyl halides over a Ni single-atom catalyst

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Supplementary Information

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1. Materials and methods

Material synthesis. All reagents for the synthetic part of the work were purchased from commercial suppliers and used directly without any further purification. $\text{Ni}_{\text{SA}}-\text{nCN}_x$ was prepared through a modified published procedure.^{1–3} In brief, graphitic carbon nitride (gCN_x) was first prepared using dicyanamide as a source of carbon and nitrogen. In a typical experiment, dicyanamide (10 g) was placed in an alumina crucible and heated in air at 550 °C for 3 h, at a heating rate of 10 °C min⁻¹. To prepare the nanosheets, gCN_x (750 mg) was thinly spread out in the alumina combustion boat, making good contact with air, and then heated at 520 °C for 4.5 h, using a heating rate of 2 °C min⁻¹. A pale-yellow powdered material was obtained. The nanosheets of carbon nitride were used as such as a photoactive support for the dispersion of the nickel single atoms. Specifically, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in (Millipore) water (140 mg, 14 mL) was added dropwise to nCN_x (350 mg) and the resultant suspension was sonicated for 30 min, and then left for 12 h under ambient conditions. Sodium borohydride (NaBH_4 , 1.05 g) was dissolved in Millipore water (5 mL) and was added dropwise to the stirring suspension. The mixture was stirred for a further 12 h at 80 °C, followed by twenty runs (1 min each) of rapid microwave heating (LG, power 1000 W). The resultant solid was redispersed in Millipore water, filtered, washed with plenty of water and ethanol, and left to dry in the oven at 55 °C for 3 h. The final material was denoted as “ $\text{Ni}_{\text{SA}}-\text{nCN}_x$ ”, and its single site nature was confirmed through in-depth characterization, in accordance with the published findings.

Material characterization. Powder X-ray diffraction (XRD) patterns were collected on a PANalytical X'Pert PRO MPD diffractometer equipped with an X'Celerator detector and with iron-filtered $\text{Co K}\alpha$ (40 kV, 30 mA, $\lambda = 0.1789$ nm) radiation. using a 0.01° s⁻¹ (2 θ) scanning speed. The angular range of measurement was set as 2 θ = 5°–60°, with a step size of 0.01°. The Ni content was determined by inductively coupled plasma mass spectrometry (ICP-MS) on an Agilent 7700x (Agilent, Japan). A weighted amount of sample from the catalyst (0.01 mg) was digested in nitric acid using a microwave. Elemental C, N, and H analysis was accomplished by combustion using a Vario Micro device. High-resolution transmission electron microscopy (HRTEM) images were obtained over a Titan G2 60-300 microscope (FEI), equipped with an X-FEG-type emission gun operating at 300 kV. High-angle annular dark-field detector (HAADF) scanning transmission electron microscopy (STEM)

analysis was conducted over a Titan G2 60-300 microscope (FEI), equipped with HAADF detector 3000 (Fisihone). Nitrogen physisorption was performed on a Micromeritics ASAP 3020 instrument (Micromeritics, Atlanta) at $-196\text{ }^{\circ}\text{C}$. Before the measurement, the samples (ca. 20–40 mesh) were degassed at $150\text{ }^{\circ}\text{C}$ for 24 h. The specific surface area was determined by the Brunauer–Emmett–Teller (BET) method using the adsorption branch in the p/p_0 range of 0.05–0.35. X-ray photoelectron spectroscopy (XPS) measurements were carried out in a custom-designed UHV system working at the base pressure of 1×10^{-9} mbar and equipped with an electron analyzer (EA125 Omicron) and an X-ray source (DAR400 Omicron). The powder samples were suspended in methanol and drop-cast on metal support to obtain a homogeneous film. Once dried, the sample was introduced in an ultrahigh-vacuum system and left outgassing overnight. Photoemission spectra were acquired at room temperature in normal emission. The spectra were analyzed using the XPSPEAK software using Voigt functions and subtracting a Shirley background. X-ray absorption spectroscopy (XAS) at the Ni K edge was recorded at the SuperXAS beamline of the Swiss Light Source (Paul Scherrer Institut, Villigen, Switzerland). Measurements were performed ex situ in transmission mode on pellets, and a Ni foil was measured simultaneously for absolute energy calibration. The quick-EXAFS (QEXAFS) method was used to collect 100 spectra in 100 s, which were then merged. Athena and Artemis from the Demeter software package were used for data analysis.⁴ The fit of the EXAFS spectra was performed by using, for the path description, a structure in which Ni is hosted in a dicarbon vacancy in carbon nitride, following an approach already employed for a Cu single-atom catalyst.⁵ The amplitude reduction factor was calculated from EXAFS fits of the NiO reference material. The infrared (IR) spectra were acquired in diffuse reflectance mode (DRIFT) using a Bruker Vector 22 FTIR spectrometer equipped with a Mercury-Cadmium-Telluride detector. Before starting the IR experiments, 100 μL of a 0.2 M water solution of pyrrolidine-2-carboxylic acid were deposited on 20 mg of catalyst powder. Subsequently, the powder was dried at room temperature for 6 h. Each spectrum was collected by averaging 128 acquisitions at 2 cm^{-1} spectral resolution. The reflectance data were successively converted in pseudo-absorbance (*i.e.*, $A = -\log R$, where R is the measured reflectance).

Photocatalytic experiments. $\text{Ni}_{\text{SA-nCN}_x}$ (5 mg), *N*-Boc-L-proline (0.45 mmol, 1.5 equiv), K_2CO_3 (0.6 mmol, 2.0 equiv), solvent (3 mL), and a magnetic stirrer bar were transferred into a 4 mL vial equipped with a screw cap

rubber septum, which in-turn functioned as the batch photoreactor. The reaction mixture was degassed by bubbling a N₂ stream for 15 min at 0 °C. Then, 1-bromo-3-phenylpropane (0.30 mmol, 1.0 equiv) was added dropwise into the solution. Photocatalytic batch experiments were carried out using a PhotoCube™ reactor (ThalesNano Inc.), and an irradiation time of 8 h (unless otherwise stated). The preliminary product analysis was conducted using ¹H and ¹³C NMR spectroscopy. Essentially, the reaction mixture was filtered through a PTFE syringe filter (0.45 µm) and concentrated in vacuo; ¹H and ¹³C NMR spectroscopic analysis were performed on a Bruker DPX 400 spectrometer at 298 K. To quantify the conversion of the limiting reagent (*i.e.*, the 1-bromo-3-phenylpropane) after the reaction, a 30 µL aliquot of the solution was taken from the batch photoreactor and diluted with 2.97 mL of MeCN, filtered, and then analyzed via high-performance liquid chromatography (HPLC). Conversion of 1-bromo-3-phenylpropane was deduced using an Agilent 1200 instrument, with an ultraviolet-visible detector (G1315D) set at 210 nm. Samples and standards (5 µL) were injected directly onto a 250 mm × 4.6 mm Hypersil GOLD™ aQ 5 µm 175 Å column purchased from Thermo Scientific. The mobile phase was comprised of a 60/40 MeCN/H₂O mixture with a total flow rate of 0.7 mL min⁻¹ at 40 °C. When conducting the analysis, one hour of equilibration was required before the first sample injection. Initially, 1-bromo-3-phenylpropane was analyzed in isolation, to identify the respective retention time on the chromatogram (*N*-Boc-L-proline was not visible at the available detection wavelength). A standard calibration curve of 1-bromo-3-phenylpropane (*i.e.*, the limiting reagent) was produced (Supplementary Information, Fig. S9); this allowed for the concentration of alkyl halide in the reaction aliquot to be deduced, and hence, for the starting material conversion and reaction rate to be computed. It should be noted that this analytical protocol was implemented based on the observation that the metallaphotocatalysed reaction led to the generation of a sole product, *i.e.* the corresponding ester.

For the substrate scope, purification of the crude product was afforded through an extraction process, in which ethyl acetate (15 mL ×3) and water (15 mL) were employed. Organic solutions were collected and concentrated under reduced pressure on a Büchi rotary evaporator using a water bath.

For experiments invoking the use of alternative catalytic systems, the same reaction vial (with 1-bromo-3-phenylpropane as the alkyl halide) was adopted, as previously described, but the following quantities of the homogeneous photocatalyst and/or homogeneous nickel catalyst (plus ligating agent) were employed: Ir[dF(CF₃)ppy]₂(dtbbpy)PF₆ (0.02 equiv), NiCl₂•glyme (0.1 equiv), 4,4'-di-methoxy-2,2'-bipyridyl (0.1 equiv), in

accordance with the published procedure.^{6,7} For the semi-heterogeneous system involving gCN_x, 5 mg of the photocatalyst was used and the aforementioned quantities of the homogeneous nickel catalyst (plus ligating agent).

For the recovery and reutilization of the catalyst, after completion of the reaction involving 1-bromo-3-phenylpropane, the mixture was first filtered through a Millipore filtration setup (using a 0.45 µm PTFE membrane filter). The recovered material was then rinsed under vacuum with water and acetone, and dried overnight at 45 °C.

Theoretical calculations. Density Functional Theory (DFT) calculations were performed with the VASP code.^{8,9} H(1s), C(2s,2p), N(2s,2p), Br(4s,4p), and Ni(3d,4s) electrons were treated explicitly, and the interaction between the inner electrons and the nuclei was treated with the Projector Augmented Wave method.^{10,11} The exchange-correlation functional proposed by Perdew, Burke, and Ernzerhof (PBE) was adopted.¹² In some cases (vide infra), single point calculations on top of PBE results were done with the hybrid functional HSE06 to improve the electronic structure description.^{13,14} The long-range dispersion was added to the potential according to Grimme's DFT+D3 scheme with a Becke-Johnson damping function.^{15,16} Structure relaxations were performed at the Γ point with a cutoff of 400 eV recurring to a conjugated gradient algorithm. Spin-polarization effects were included in all calculations. Dipole and quadrupole corrections to the total energy were applied along the non-periodic direction for all calculations on slab models. A vacuum region of at least 1.5 nm was included along the non-periodic direction in the supercell, to avoid spurious interactions between a replica of the slab models. The carbon nitride nanosheets have been modelled assuming a corrugated heptazine structure.^{5,17–19} Gibbs free energy profiles have been determined by adopting the computational approach pioneered by Nørskov and co-workers,^{20,21} to study reactions involving gas-phase molecules,^{22–27} where we added the standard entropies of gas species to the calculated DFT energies. The entropy of all gas species involved in the reaction cycle have been taken from the literature.²⁸

2. Tables

Table S1. Compositional and textural characterization of the gCN_x, nCN_x, and Ni_{SA}-nCN_x samples.

Sample	C ^a / wt. %	N ^a / wt. %	H ^a / wt. %	C:N ^a / -	Ni ^b / wt. %	S _{BET} ^c / m ² g ⁻¹
gCN _x	31.39	47.30	2.34	0.66	-	11.8
nCN _x	32.15	47.92	2.12	0.67	-	27.9
Ni _{SA} -nCN _x	32.46	48.16	2.38	0.67	7.4	29.7

^a CHNS data (*note*: total wt.% falls below 100% due to the presence of oxygen-containing defects and oxygen-containing adsorbates); ^b ICP-OES data; ^c BET to the N₂ isotherm collected at 77 K.

3. Figures

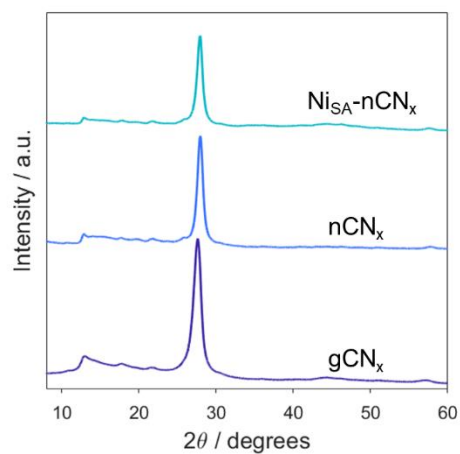


Fig. S1. Wide-angle X-ray diffraction patterns of gCN_x , nCN_x , and $\text{Ni}_{\text{SA}}\text{-nCN}_x$.

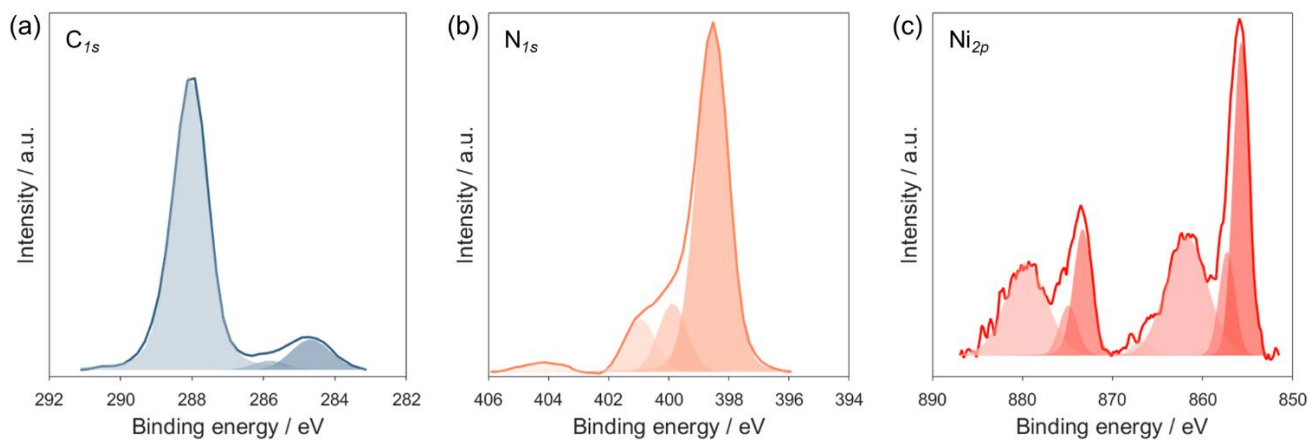


Fig. S2. High-resolution C 1s, N 1s, and Ni 2p X-ray photoelectron spectroscopy of $\text{Ni}_{\text{SA}}\text{-nCN}_x$.

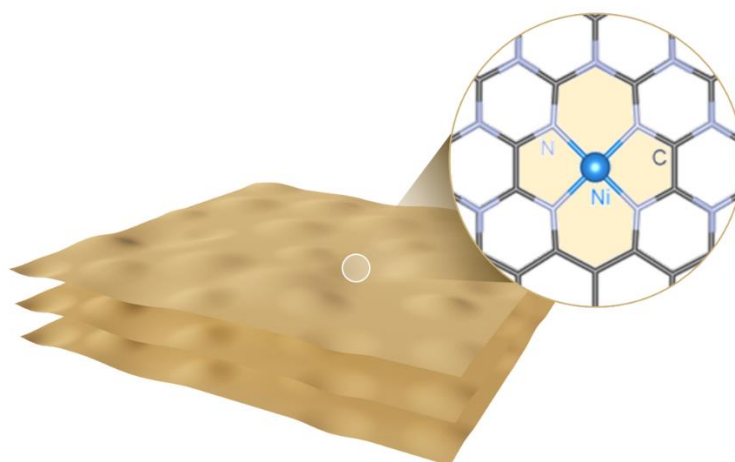


Fig. S3. Alternative symmetric motif, envisaging the Ni atom surrounded by four N atoms in a square planar coordination, within a di-carbon vacancy of carbon nitride.

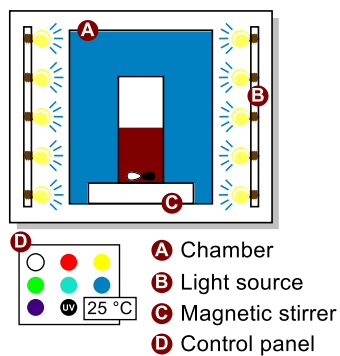


Fig. S4. Scheme and photograph of the ThalesNano PhotoCube™ reactor.

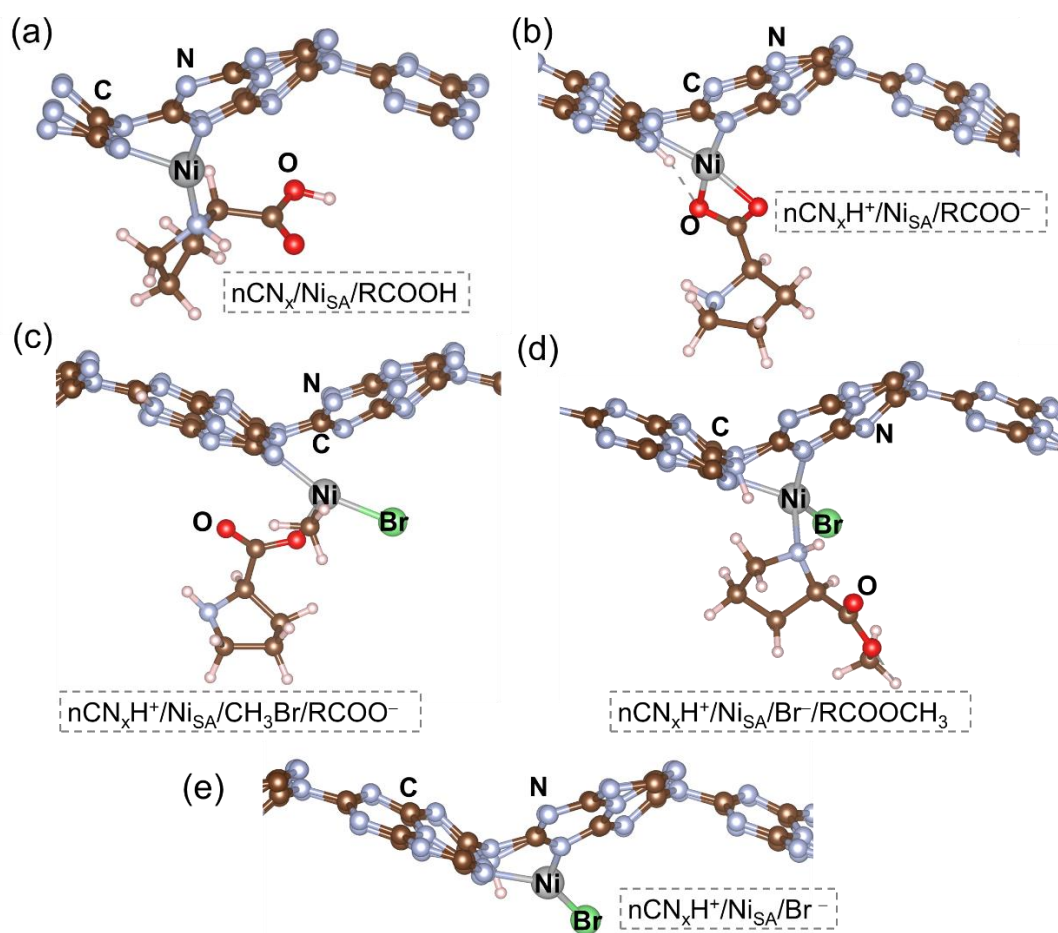


Fig. S5. (a) – (e); ball-and-stick models of the optimized molecular intermediates in DFT simulations.

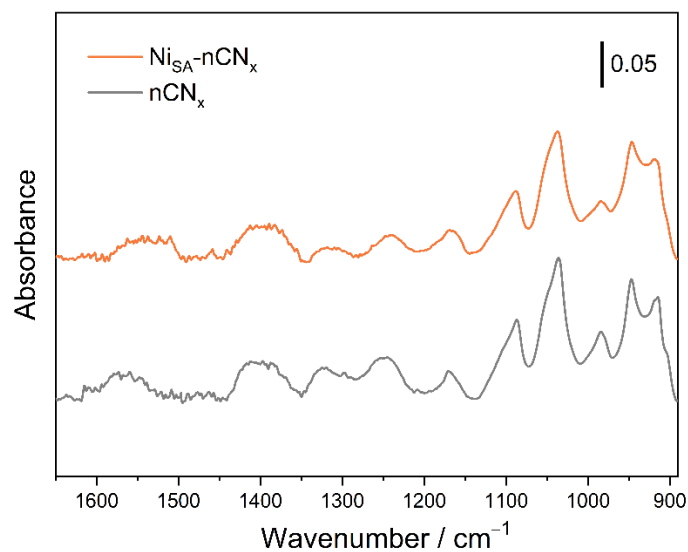


Fig. S6. DRIFT spectra of pyrrolidine-2-carboxylic acid adsorbed on nCN_x and Ni_{SA}-nCN_x. The DRIFT spectrum of the same sample contacted only with water has been subtracted from both spectra.

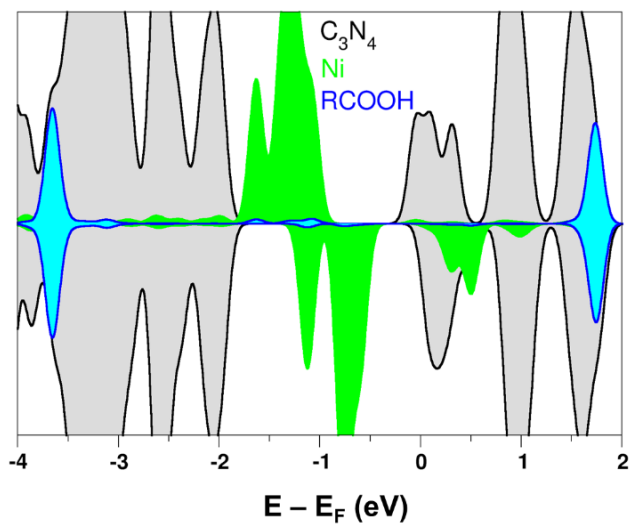


Fig. S7. Projected Density of States (DOS) plot of RCOOH on the Ni_{SA}-nCN_x material.

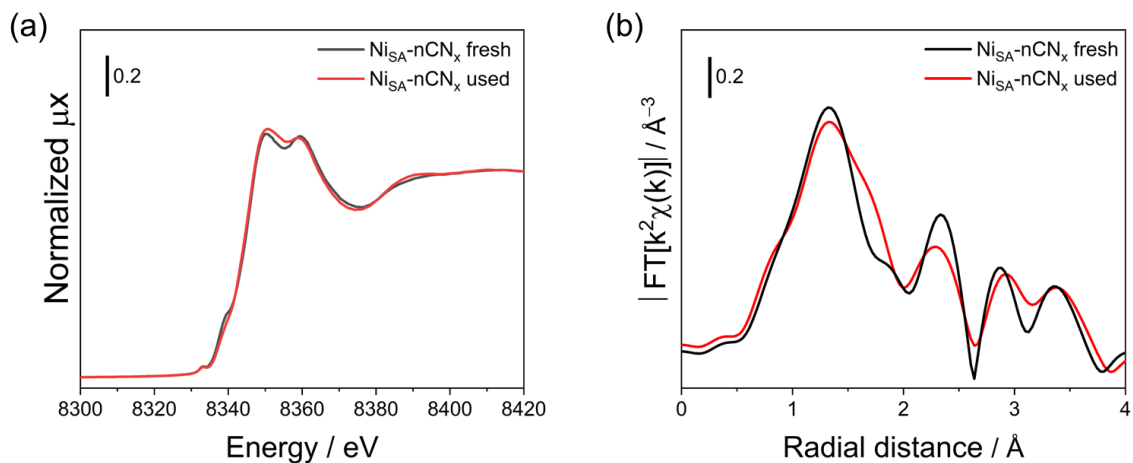


Fig. S8. (a) XANES and (b) EXAFS spectra for the *fresh* and *used* $\text{Ni}_{\text{SA-nCN}_x}$ catalyst.

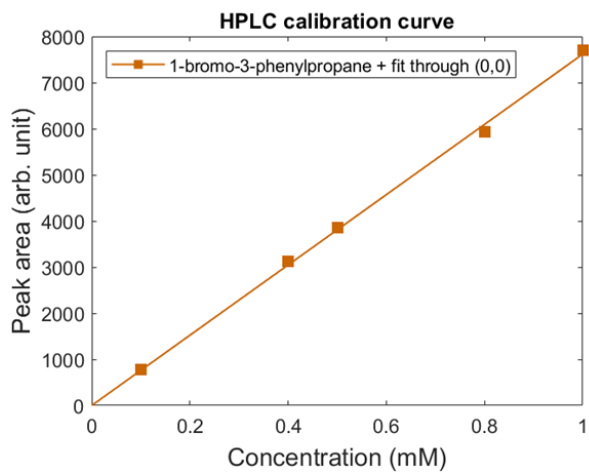
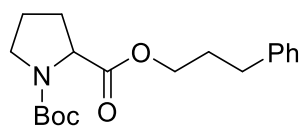


Fig. S9. High-performance liquid chromatography calibration curve for the model alkyl halide, 1-bromo-3-phenylpropane, produced using a UV-Vis detector set at 210 nm.

4. Product characterization

Note: For ^{13}C NMR, where visible, minor rotamer peaks are included in parenthesis.

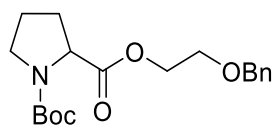


1-(tert-butyl)-2-(3-phenylpropyl)pyrrolidine-1,2-dicarboxylate (±1): colorless oil,

70 mg (isolated yield: 70%).

^1H NMR (400 MHz, CDCl_3): δ 7.25 – 7.15 (m, 2H), 7.10 (t, 3H), 4.25 – 4.16 (dd, 1H), 4.12 – 3.99 (m, 2H), 3.53 – 3.23 (m, 2H), 2.64 – 2.52 (t, 2H), 2.36–2.09 (m, 1H), 1.99 – 1.70 (m, 5H), 1.33 (s, 9H).

^{13}C NMR (101 MHz, CDCl_3): δ 173.22 (173.02), 154.40 (153.83), 140.95 (141.23), 128.47, 125.96, 79.83 (79.70), 64.16, 59.20, 46.34, 32.10, 30.95 (30.26), 28.35, 24.34, 23.62.

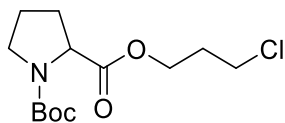


2-((benzyloxy)methyl)-1-(tert-butyl)pyrrolidine-1,2-dicarboxylate (±2): yellowish oil,

85.5 mg (isolated yield: 85%).

^1H NMR (400 MHz, CDCl_3): δ 7.28 – 7.18 (m, 5H), 4.47 (s, 2H), 4.34 – 4.09 (m, 3H), 3.64 – 3.53 (m, 2H), 3.50 – 3.16 (m, 2H), 2.22 – 2.05 (m, 1H), 1.97 – 1.69 (m, 3H), 1.32 (s, 9H).

^{13}C NMR (101 MHz, CDCl_3): δ 173.18 (172.89), 153.80 (154.40), 137.82 (138.01), 128.41, 127.65, 79.84 (79.71), 73.09, 67.96 (67.85), 63.89, 59.10 (58.84), 46.33 (46.56), 30.91, 29.95 (29.67), 28.43 (28.31), 24.27, 23.57.

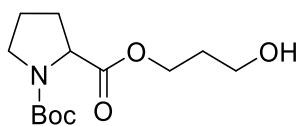


1-(tert-butyl)-2-(3-chloropropyl)pyrrolidine-1,2-dicarboxylate (±3): yellowish oil,

53.4 mg (isolated yield: 61%).

¹H NMR (400 MHz, CDCl₃): δ 4.30 – 4.01 (m, 3H), 3.58 – 3.16 (m, 3H), 2.23 – 2.08 (m, 1H), 2.08 – 1.99 (m, 5H), 1.34 (s, 10H).

¹³C NMR (101 MHz, CDCl₃): δ 173.03 (172.80), 154.34 (153.72), 79.82, 61.54 (61.29) 59.06 (58.83), 46.52 (46.29), 30.89, 29.92, 28.38 (28.29), 24.31, 23.57.

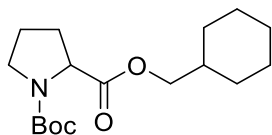


1-(tert-butyl)-2-(3-hydroxypropyl)pyrrolidine-1,2-dicarboxylate (±4): yellowish

oil, 44.6 mg (isolated yield: 54%).

¹H NMR (400 MHz, CDCl₃): δ 4.27 – 4.11 (m, 2H), 3.62 (t, 2H), 3.52 – 3.26 (m, 2H), 2.57 (s, 1H) 2.22 – 2.04 (m, 2H), 1.98 – 1.72 (m, 5H), 1.37 (s, 9H).

¹³C NMR (101 MHz, CDCl₃): δ 172.62 (172.48), 153.56 (152.85), 79.89, 61.05 (60.92), 57.96 (58.19), 45.33 (45.63), 30.76 (30.67), 29.90, 28.94 (28.67), 27.42 (27.32), 23.38, 22.59.

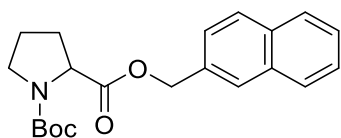


1-(tert-butyl)-2-(cyclohexylmethyl)pyrrolidine-1,2-dicarboxylate (±5): yellowish oil,

83.1 mg (isolated yield: 89%).

¹H NMR (400 MHz, CDCl₃): δ 4.21 (m, 1H), 3.86 (m, 2H), 3.55 – 3.17 (m, 2H), 2.28 – 1.99 (m, 1H), 1.99 – 1.73 (m, 2H), 1.62 (m, 6H), 1.37 (s, 9H), 1.13 (m, 4H), 0.98 – 0.68 (m, 2H).

¹³C NMR (101 MHz, CDCl₃): δ 173.27 (173.00), 153.84 (154.32), 79.78, 69.97, 59.23 (59.83), 46.48 (46.28), 37.09, 31.42, 29.99 (29.60), 28.30, 26.28, 25.59, 24.26, 23.57.

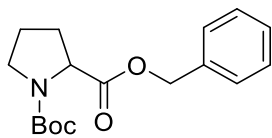


1-(tert-butyl)-2-(naphthalen-2-ylmethyl)pyrrolidine-1,2-dicarboxylate (±6):

colorless oil, 72.4 mg (isolated yield: 68%).

¹H NMR (400 MHz, CDCl₃): 7.74 (m, 4H), 7.47 – 7.34 (m, 3H), 5.47 – 5.01 (m, 2H), 4.27 – 4.15 (m, 1H), 3.59 – 3.21 (m, 2H), 2.27 – 2.01 (m, 1H), 1.99 – 1.64 (m, 3H), 1.27 (s, 9H).

¹³C NMR (101 MHz, CDCl₃): δ 173.09 (172.87), 153.83 (154.46), 133.20 (133.11), 128.46, (128.31), 128.00, 127.69, 127.60, (127.18), 126.36, (126.19), 125.91, (125.76), 79.89, 66.76, 59.23 (58.97), 46.59 (46.36), 30.91, 29.93, 28.47, 28.23, 24.33.

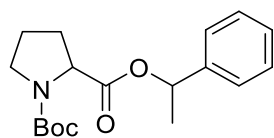


2-benzyl 1-(tert-butyl)pyrrolidine-1,2-dicarboxylate (±7): colorless oil, 55.3 mg

(isolated yield: 60%).

¹H NMR (400 MHz, CDCl₃): δ 7.30 – 7.21 (m, 5H), 5.08 (m, 2H), 4.3-4.191 (m, 1H), 3.54 – 3.21 (m, 2H), 2.22 – 2.03 (m, 1H), 1.98 – 1.68 (m, 3H), 1.24 (s, 9H).

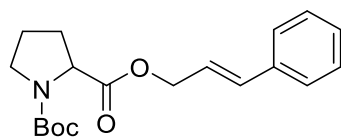
¹³C NMR (101 MHz, CDCl₃): δ 173.04 (172.79), 153.80 (154.42), 135.70 (135.92), 128.59 (128.47), 128.47 (128.34), 128.09 (127.98), 79.98 (79.76), 66.61, 59.18 (58.92), 46.33 (46.55), 30.89, 29.89 (29.69), 28.44 (28.24), 24.30, 23.60.



1-(tert-butyl)-2-(1-phenylethyl)pyrrolidine-1,2-dicarboxylate (±8): yellowish oil, 58.6 mg (isolated yield: 61%).

¹H NMR (400 MHz, CDCl₃): δ 7.34 – 7.08 (m, 5H), 5.84 (m, 1H), 4.22 (m, 1H), 3.54 – 3.22 (m, 2H), 2.24 – 2.00 (m, 1H), 1.93 – 1.68 (m, 3H), 1.53 – 1.46 (d, 3H) 1.25 (s, 9H).

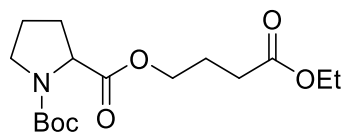
¹³C NMR (101 MHz, CDCl₃): δ 172.32, (172.27), 153.83 (154.33), 141.28 (141.68), 128.49 (128.40), 127.94 (127.72), 126.17 (126.00), 79.82, 72.78 (72.68), 59.22 (58.91), 46.51 (46.32), 30.87 (30.77), 28.24 (28.43), 24.30 (24.19), 23.49, 22.28 (22.07).



1-(tert-butyl)-2-cinnamylpyrrolidine-1,2-dicarboxylate (±9): colorless oil, 72.6 mg (isolated yield: 84%).

¹H NMR (400 MHz, CDCl₃): δ 7.30 (d, 2H), 7.20 (dt, 3H), 6.59 (d, 1H), 6.19 (dq, 1H), 4.79 – 4.61 (m, 2H), 4.27 – 4.15 (m, 1 H), 3.56 – 3.25 (m, 2H), 2.26 – 1.99 (m, 1H), 2.00 – 1.68 (m, 3H), 1.34 (s, 9H).

¹³C NMR (101 MHz, CDCl₃): δ 173.04 (172.76), 153.81 (154.43), 136.07 (136.40), 134.72 (134.07), 128.61, 128.18 (127.98), 126.63, 122.78 (123.09), 79.89, 65.43, 59.22 (58.93), 46.35 (46.58), 30.92, 29.94 (29.69) 28.45 (28.30), 23.59, 23.65.

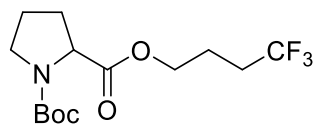


1-(tert-butyl)-2-(4-ethoxy-4-oxobutyl)pyrrolidine-1,2-dicarboxylate (±10):

yellowish oil, 92.6 mg (isolated yield: 94%).

¹H NMR (400 MHz, CDCl₃): δ 4.32 – 4.16 (m, 1H), 4.16 – 3.85 (m, 3H), 3.61 – 3.26 (m, 2H), 2.29 – 2.04 (m, 3H), 2.02 – 1.75 (m, 5H), 1.49 – 1.32 (d, 9H), 1.23 (t, *J* = 7.1 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃): δ 173.08, (172.83), 172.56, 154.33, (153.73), 79.81 (79.68), 63.80, 60.46 (60.35), 59.08 (58.83), 46.50 (46.28), 30.88 (30.60), 29.91, 28.38 (28.28), 24.04 (23.57), 14.16 (s).

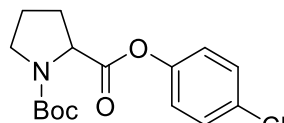


1-(tert-butyl)-2-(4,4,4-trifluorobutyl)pyrrolidine-1,2-dicarboxylate (±11):

colorless oil, 83.1 mg (isolated yield: 85%).

¹H NMR (400 MHz, CDCl₃): δ 4.24 (dd, *J* = 8.6, 3.0 Hz, 1H), 4.20 – 4.04 (m, 2H), 3.54 – 3.26 (m, 2H), 2.27 – 2.02 (m, 3H), 1.97 – 1.72 (m, 5H), 1.45 – 1.27 (m, 9H).

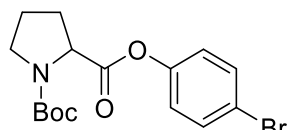
¹³C NMR (101 MHz, CDCl₃): δ 173.01 (172.88), 154.37 (153.70), 126.84 (q, *J* = 276.1), 79.91 (79.82), 63.00, 59.02 (58.85), 46.53 (46.31), 30.91 (30.72), 30.43 (29.93), 28.30, 24.36, 23.57, 21.59.



1-(tert-butyl) 2-(4-chlorophenyl) pyrrolidine-1,2-dicarboxylate (±12)

¹H NMR (400 MHz, CDCl₃): δ 7.36 – 7.32 (m, 2H), 7.08 – 7.04 (m, 2H), 4.53 – 4.41 (m, 1H), 3.67 – 3.42 (m, 2H), 2.45 – 2.30 (m, 1H), 2.19 – 2.14 (m, 1H), 2.10 – 1.91 (m, 2H), 1.49 – 1.44 (m, 9H).

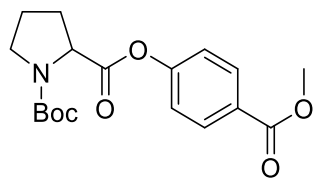
¹³C NMR (100 MHz, CDCl₃): δ 171.5, 153.6, 149.0, 131.2, 129.5, 122.6, 80.2, 59.1, 46.4, 30.0, 28.4, 24.5.



2-(4-bromophenyl) 1-(tert-butyl) pyrrolidine-1,2-dicarboxylate (±13)

¹H NMR (400 MHz, CDCl₃): 7.52 – 7.47 (m, 2H), 7.01 – 6.99 (m, 2H), 4.55 – 4.40 (m, 1H), 3.67 – 3.41 (m, 2H), 2.40 – 2.28 (m, 1H), 2.17 – 2.10 (m, 1H), 2.08 – 1.92 (m, 2H), 1.46 (m, 9H).

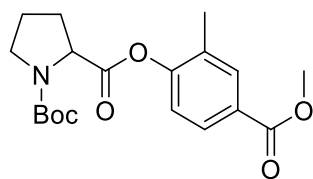
¹³C NMR (100 MHz, CDCl₃): δ 171.2, 153.9, 149.7, 132.4, 123.0, 118.9, 80.1, 59.1, 46.5, 30.5, 28.3, 23.9.



1-(tert-butyl) 2-(4-(methoxycarbonyl)phenyl) pyrrolidine-1,2-dicarboxylate (±14)

¹H NMR (400 MHz, CDCl₃): δ 7.58 – 7.46 (m, 1H), 7.36 – 7.33 (m, 1H), 7.15 – 7.08 (m, 1H), 7.01 – 6.89 (m, 1H), 4.37 – 4.26 (m, 1H), 3.74 (s, 3H), 3.49 – 3.31 (m, 2H), 2.42 – 2.30 (m, 1H), 2.20 – 2.15 (m, 1H), 2.15 – 1.90 (m, 2H), 1.51 – 1.48 (m, 9H).

¹³C NMR (100 MHz, CDCl₃): δ 171.11, 154.4, 153.6, 134.7, 129.9, 121.3, 80.2, 59.1, 46.5, 29.9, 28.4, 26.6, 24.2.

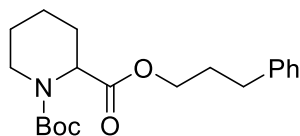


1-(tert-butyl) 2-(4-(methoxycarbonyl)-2-methylphenyl) pyrrolidine-1,2-

dicarboxylate (±15)

¹H NMR (400 MHz, CDCl₃): 7.49 – 7.45 (m, 2H), 6.73 – 6.62 (m, 2H), 4.14 – 4.26 (m, 1H), 3.62 (s, 3H), 3.18 – 3.33 (m, 2H), 2.25 – 2.13 (m, 1H), 2.12 – 1.94 (m, 1H), 1.94 – 1.77 (m, 2H), 1.49 – 1.48 (m, 9H).

¹³C NMR (100 MHz, CDCl₃): δ 171.4, 166.0, 153.6, 150.5, 131.7, 129.5, 127.0, 125.7, 122.4, 80.3, 59.1, 52.3, 46.4, 31.0, 28.3, 23.7, 14.9.

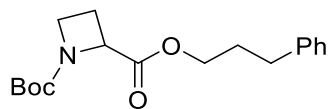


1-(tert-butyl)-2-(3-phenylpropyl)piperidine-1,2-dicarboxylate (±16): yellowish oil,

74 mg (isolated yield: 71%).

¹H NMR (400 MHz, CDCl₃): δ 7.20 (t, *J* = 7.3 Hz, 2H), 7.15 – 7.05 (m, 3H), 4.75 (m, 1H), 3.99 (m, 3H), 3.02 – 2.73 (m, 1H), 2.66 – 2.54 (t, 2H), 2.11 (m, 1H), 1.97 – 1.80 (m, 2H), 1.59 (tt, *J* = 6.0, 3.6 Hz, 3H), 1.49 – 1.28 (m, 9H) 1.21 – 1.11 (m, 1H).

¹³C NMR (101 MHz, CDCl₃): δ 171.96, 155.94 (155.45), 141.05, 128.44, 126.06, 79.90, 64.21, 54.96, 53.87, 42.15, 41.14, 32.14, 30.34, 28.39, 26.82, 24.84.

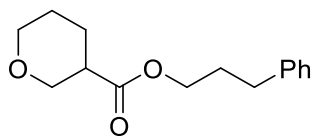


1-(tert-butyl)-2-(3-phenylpropyl)azetidine-1,2-dicarboxylate (±17): yellowish

oil, 88.3 mg (isolated yield: 92%).

¹H NMR (400 MHz, CDCl₃): δ 7.20 (dd, *J* = 9.7, 5.3 Hz, 2H), 7.11 (dd, *J* = 10.0, 4.4 Hz, 3H), 4.53 (dd, *J* = 9.2, 5.3 Hz, 2H), 4.17 – 4.04 (m, 1H), 3.95 (td, *J* = 8.5, 6.3 Hz, 1H), 3.81 (td, *J* = 8.5, 5.6 Hz, 1H), 2.66 – 2.56 (t, 2H), 2.49 – 2.34 (m, 1H), 2.15 – 2.01 (m, 1H), 1.97 – 1.84 (m, 2H), 1.34 (s, 9H).

¹³C NMR (101 MHz, CDCl₃): δ 171.46, 155.37, 141.01, 128.43, 126.05, 79.95, 64.35, 60.59, 47.54, 32.03, 30.20, 28.31.

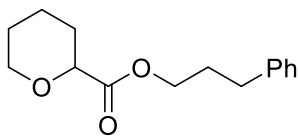


3-phenylpropyl tetrahydro-2H-pyran-3-carboxylate, (±18): yellowish oil, 76.8 mg

(isolated yield: 99%).

¹H NMR (400 MHz, CDCl₃): δ 7.23 – 7.17 (m, 2H), 7.14 – 7.06 (m, 3H), 4.07 – 3.98 (t, 2H), 3.97 – 3.88 (m, 1H), 3.74 (dt, *J* = 7.7, 3.6 Hz, 1H), 3.50 (dd, *J* = 11.3, 9.2 Hz, 1H), 3.36 (ddd, *J* = 11.3, 9.9, 3.2 Hz, 1H), 2.64 – 2.58 (m, 2H), 2.51 (ddd, *J* = 14.0, 8.7, 4.1 Hz, 1H), 2.00 – 1.83 (m, 3H), 1.74 – 1.45 (m, 3H).

¹³C NMR (101 MHz, CDCl₃): δ 173.04, 141.12, 128.47, 128.40, 126.05, 69.02, 68.15, 63.79, 41.72, 32.18, 30.19, 25.96, 24.81.

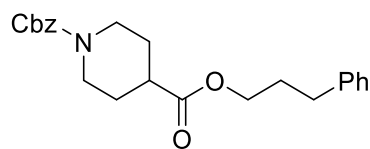


3-phenylpropyl tetrahydro-2H-pyran-2-carboxylate (±19): yellowish oil, 68.4 mg

(isolated yield: 71%).

¹H NMR (400 MHz, CDCl₃): δ 7.33 – 7.26 (m, 2H), 7.23 – 7.16 (m, 3H), 4.20 (t, *J* = 6.6 Hz, 2H), 4.14 – 4.08 (m, 1H), 4.00 (dd, *J* = 10.3, 2.7 Hz, 1H), 3.52 (td, *J* = 11.2, 2.5 Hz, 1H), 2.74 – 2.66 (t, 2H), 2.07 – 1.85 (m, 4H), 1.73 – 1.51 (m, 4H).

¹³C NMR (101 MHz, CDCl₃): δ 171.69, 141.05, 128.41, 126.04, 76.23, 68.14, 64.22, 32.07, 30.15, 28.95, 25.31, 22.93.

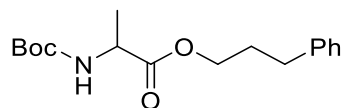


1-benzyl-4-(3-phenylpropyl)piperidine-1,4-dicarboxylate (20): colorless oil,

96.1 mg (isolated yield: 84%).

¹H NMR (400 MHz, CDCl₃): δ 7.32 – 7.02 (m, 10H), 5.04 (s, 2H), 4.04 (m, 5H), 2.84 (t, *J* = 11.6 Hz, 2H), 2.65 – 2.52 (m, 2H), 2.36 (tt, *J* = 10.9, 3.9 Hz, 1H), 1.96 – 1.71 (m, 4H), 1.67 – 1.47 (m, 2H).

¹³C NMR (101 MHz, CDCl₃): δ 174.30, 162.54, 155.18, 141.07, 136.80, 128.49, 128.46, 128.37, 127.99, 127.85, 67.10, 63.91, 43.26, 40.96, 36.42, 32.18, 31.39, 30.16, 27.91.

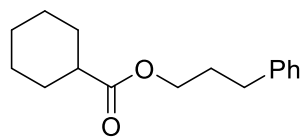


3-phenylpropyl-(tert-butoxycarbonyl)alaninate (±21): yellowish oil, 80.1 mg

(isolated yield: 87%).

¹H NMR (400 MHz, CDCl₃): δ 7.30 (t, *J* = 7.3 Hz, 2H), 7.21 (dd, *J* = 12.2, 4.6 Hz, 3H), 5.21 – 5.02 (m, 1H), 4.33 (s, 1H), 4.25 – 4.08 (t, 2H), 2.78 – 2.65 (t, 2H), 2.00 (dq, *J* = 13.5, 6.6 Hz, 2H), 1.47 (s, 9H), 1.40 (d, *J* = 7.2 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃): δ 173.37, 155.12, 140.99, 128.31, 126.08, 79.77, 64.56, 49.28, 32.06, 30.14, 28.35, 19.09.

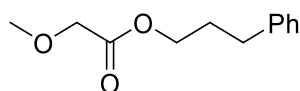


3-phenylpropylcyclohexanecarboxylate (22): yellowish oil, 38.3 mg (isolated yield:

52%).

¹H NMR (400 MHz, CDCl₃): δ 7.23 – 7.15 (m, 2H), 7.11 (dd, *J* = 10.0, 4.4 Hz, 3H), 4.00 (t, *J* = 6.5 Hz, 2H), 2.67 – 2.54 (t, 2H), 2.22 (tt, *J* = 11.2, 3.7 Hz, 1H), 1.93 – 1.79 (m, 4H), 1.75 – 1.62 (m, 2H), 1.60 – 1.51 (m, 1H), 1.45 – 1.30 (m, 2H), 1.27 – 1.07 (m, 4H).

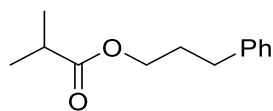
¹³C NMR (101 MHz, CDCl₃): δ 176.11, 141.29, 128.43, 125.99, 63.39, 43.28, 32.20, 30.33, 29.17, 25.80, 25.41.



3-phenylpropyl-2-methoxyacetate (23): yellowish oil, 15.6 mg (isolated yield: 25%).

¹H NMR (400 MHz, CDCl₃): δ 7.23 – 7.17 (m, 2H), 7.14 – 7.06 (m, 3H), 4.11 (t, *J* = 6.6 Hz, 2H), 3.93 (s, 2H), 3.37 (s, 3H), 2.62 (t, *J* = 7.0 Hz, 2H), 1.97 – 1.85 (m, 2H).

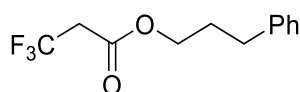
¹³C NMR (101 MHz, CDCl₃): δ 170.29, 141.00, 128.48, 128.37, 126.08, 69.83, 64.22, 59.37, 32.13, 30.12.



3-phenylpropylisobutyrate (24): yellowish oil, 13.6 mg (isolated yield: 22%).

¹H NMR (400 MHz, CDCl₃): δ 7.24 – 7.16 (m, 2H), 7.11 (dd, *J* = 9.7, 4.3 Hz, 3H), 4.01 (t, *J* = 6.5 Hz, 2H), 2.64 – 2.58 (m, 2H), 2.47 (hept, *J* = 7.0 Hz, 1H), 1.92 – 1.84 (m, 2H), 1.10 (d, *J* = 7.0 Hz, 6H).

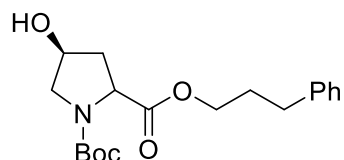
¹³C NMR (101 MHz, CDCl₃): δ 177.15, 141.27, 128.44, 128.40, 126.00, 63.54, 34.06, 32.19, 30.30, 19.02.



3-phenylpropyl-3,3,3-trifluoropropanoate (25): yellowish oil, 7.4 mg (isolated yield: 10%).

¹H NMR (400 MHz, CDCl₃): δ 7.23 – 7.18 (m, 2H), 7.11 (dd, *J* = 12.6, 7.1 Hz, 3H), 4.10 (t, 2H), 3.31 (s, 2H), 2.67 – 2.54 (m, 2H), 1.98 – 1.85 (m, 2H).

¹³C NMR (101 MHz, CDCl₃): δ 166.58, 140.97, 128.48, 128.39, 126.07, 64.85, 41.60, 32.02, 29.88, 29.70.

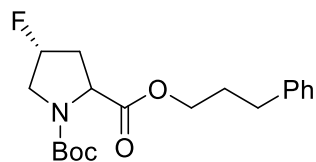


1-(tert-butyl)-2-(3-phenylpropyl)-(4S)-4-hydroxypyrrolidine-1,2-dicarboxylate

(±26): yellowish oil, 101.4 mg (isolated yield: 97%).

¹H NMR (400 MHz, DMSO-*d*₆): δ 7.28 (t, *J* = 7.5 Hz, 2H), 7.25 – 7.14 (m, 3H), 5.01 (s, 1H), 4.24 (ddd, *J* = 13.1, 9.0, 4.2 Hz, 2H), 4.11 – 3.91 (m, 2H), 3.51 (dt, *J* = 10.7, 5.2 Hz, 1H), 3.23 – 3.10 (m, 1H), 2.71 – 2.58 (t, 2H), 2.34 (tdd, *J* = 13.9, 9.0, 5.3 Hz, 1H), 1.97 – 1.79 (m, 3H), 1.37 (s, 9H).

¹³C NMR (101 MHz, DMSO-*d*₆): δ 172.62 (172.36), 154.00 (153.48), 141.73 (141.60), 128.83 (128.76), 126.33 (126.28), 79.25 (79.17), 68.99 (68.09), 63.99 (63.79), 57.97 (57.80), 54.71 (54.27), 38.31 (s), 31.73 (31.69), 31.22, 28.55 (28.37).

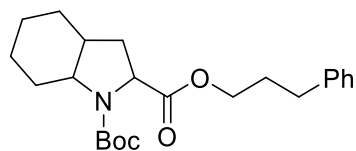


1-(tert-butyl)-2-(3-phenylpropyl)-(4R)-4-fluoropyrrolidine-1,2-dicarboxylate

(±27): yellowish oil, 92.81 mg (isolated yield: 88%).

¹H NMR (400 MHz, CDCl₃): δ 7.18 (dd, *J* = 13.5, 10.4 Hz, 2H), 7.11 (t, *J* = 9.5 Hz, 3H), 5.18-5.04 (two broad s, 1H), 4.36 (dt, *J* = 30.4, 8.3 Hz, 1H), 4.10 (t, *J* = 6.7 Hz, 2H), 3.78 (m, 1H), 3.64 – 3.41 (m, 1H), 2.69 – 2.39 (m, 3H), 2.11 – 1.84 (m, 3H), 1.36 (s, 9H).

¹³C NMR (101 MHz, CDCl₃): δ 172.64 (172.45), 154.13 (153.61), 141.17 (140.85), 128.51 (128.34), 126.15, 125.99, 92.34 (d, *J* = 82.9 Hz), 90.56 (d, *J* = 82.9 Hz), 80.58 (80.46), 64.58, 57.74 (57.50), 53.40, 53.17 (53.09), 52.86, 37.73 (37.50), 36.79 (36.57), 32.13 (32.03), 30.18 (30.11), 28.37 (28.26).



1-(tert-butyl)-2-(3-phenylpropyl)-octahydro-1*H*-indole-1,2-dicarboxylate

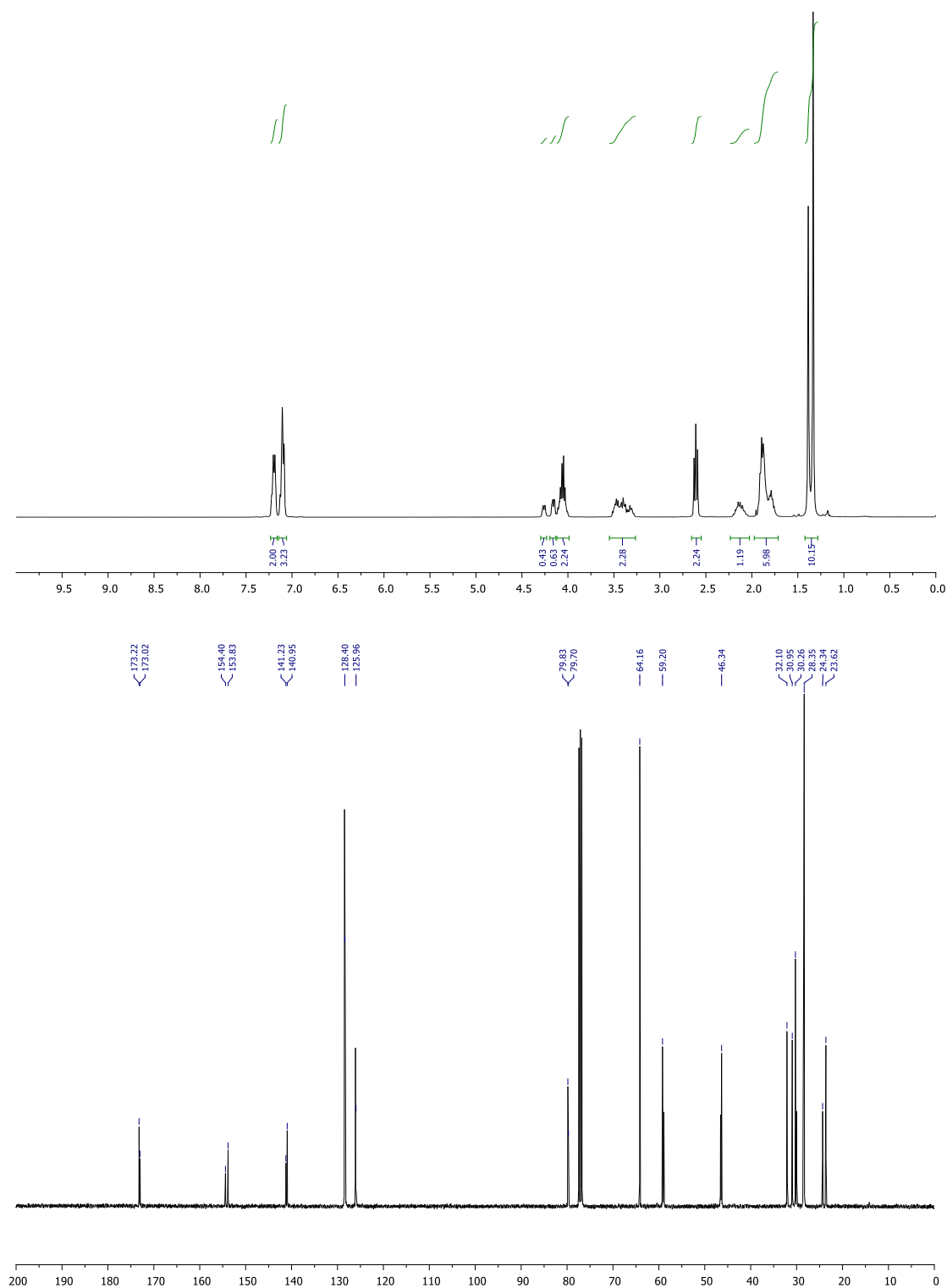
(±28): yellowish oil, 106.2 mg (isolated yield: 91%).

¹H NMR (400 MHz, CDCl₃): δ 7.19 (d, *J* = 7.3 Hz, 2H), 7.10 (t, *J* = 8.0 Hz, 3H), 4.26 – 4.00 (m, 3H), 3.83 – 3.58 (m, 1H), 2.62 (t, *J* = 7.8 Hz, 2H), 2.21 (dd, *J* = 18.3, 12.0 Hz, 1H), 2.13 – 1.82 (m, 5H), 1.69 – 1.47 (m, 3H), 1.34 (m, 11H), 1.28 – 0.99 (m, 2H).

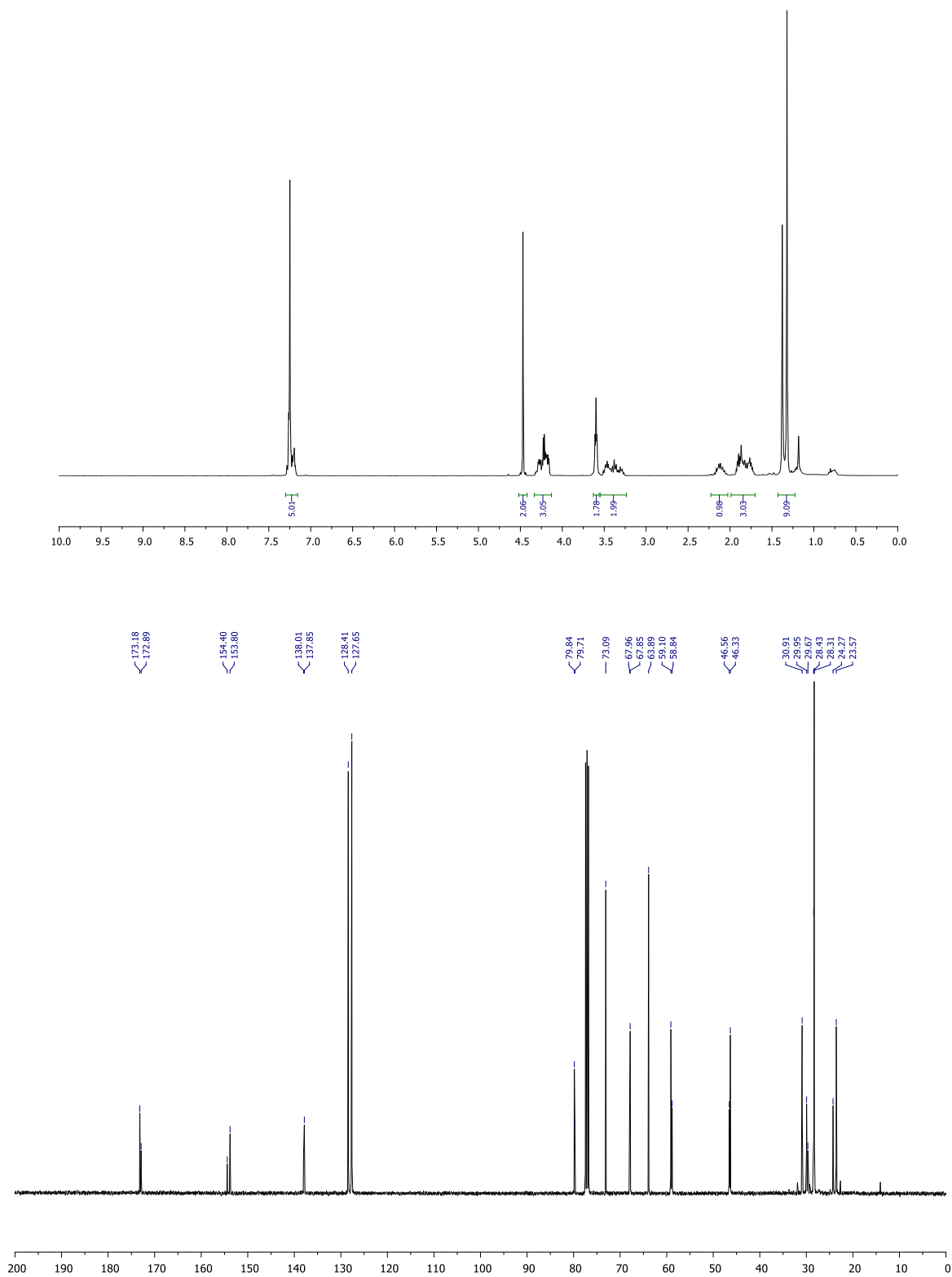
¹³C NMR (101 MHz, CDCl₃): δ 173.52 (173.23), 154.03 (153.33), 141.36 (141.04), 128.48 (128.41), 126.08 (125.93), 79.65 (79.47), 64.13, 59.49 (59.13), 57.44 (57.13), 37.06 (s), 36.44 (32.64), 32.18 (31.72), 30.34 (s), 28.50 (28.37), 27.92 (27.55), 25.94 (25.86), 23.85 (23.68), 20.62.

5. NMR spectra of purified products

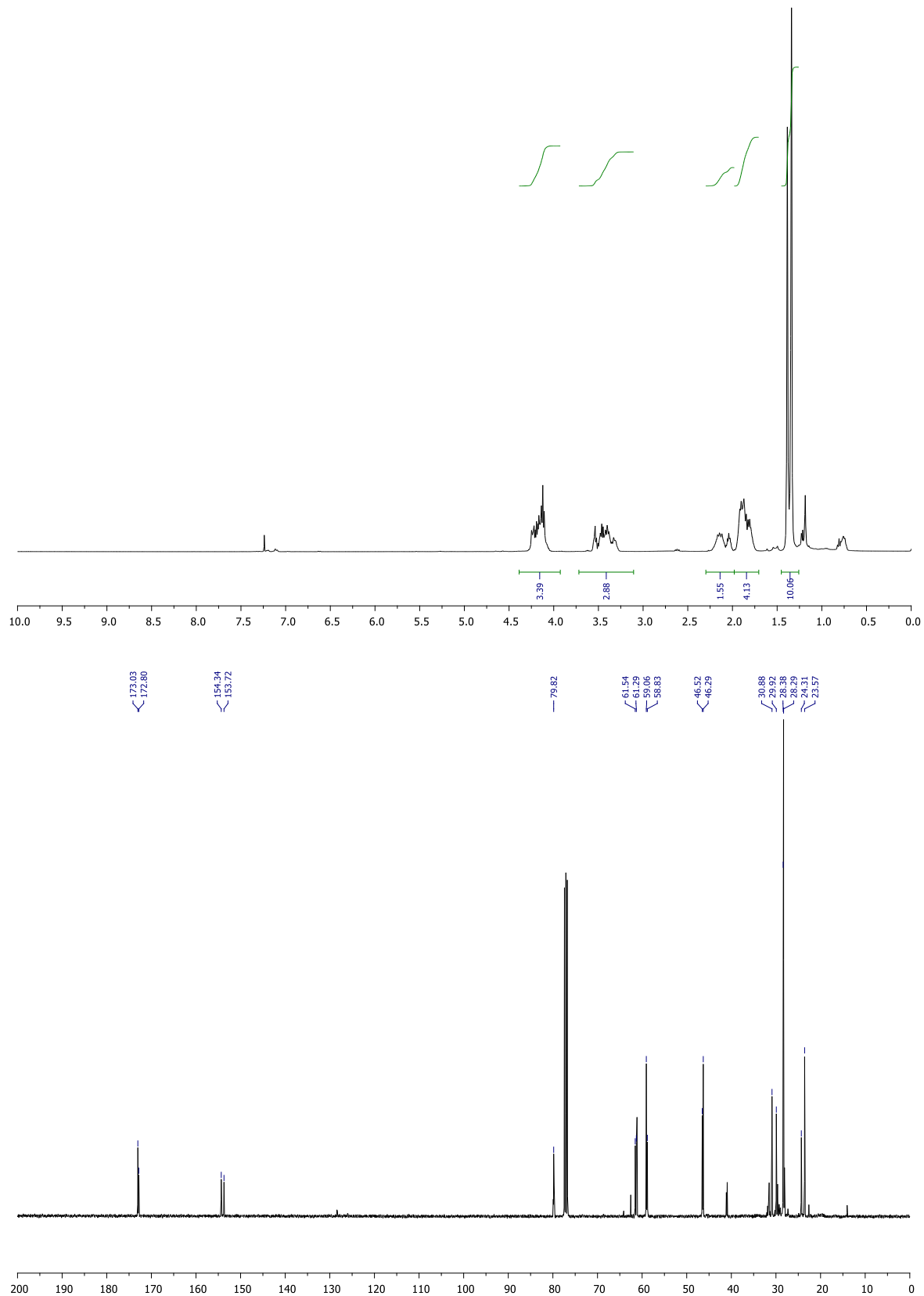
1-(tert-butyl)-2-(3-phenylpropyl)pyrrolidine-1,2-dicarboxylate (± 1)



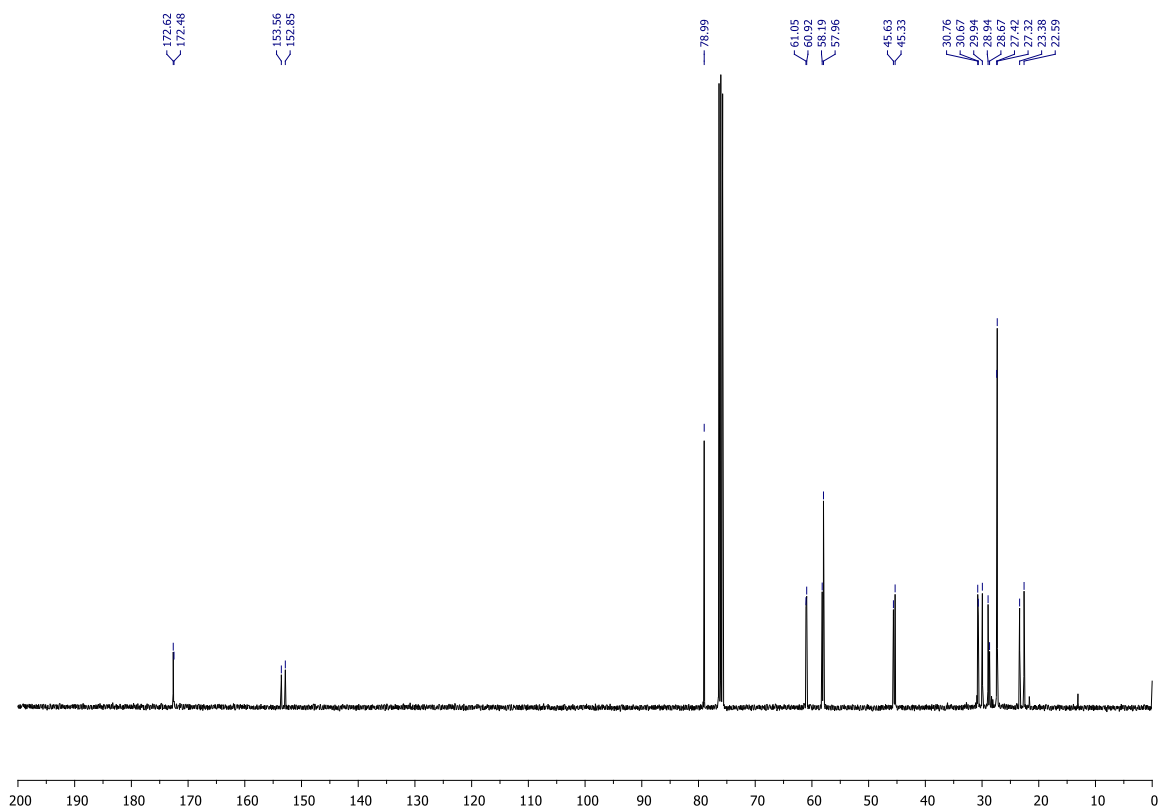
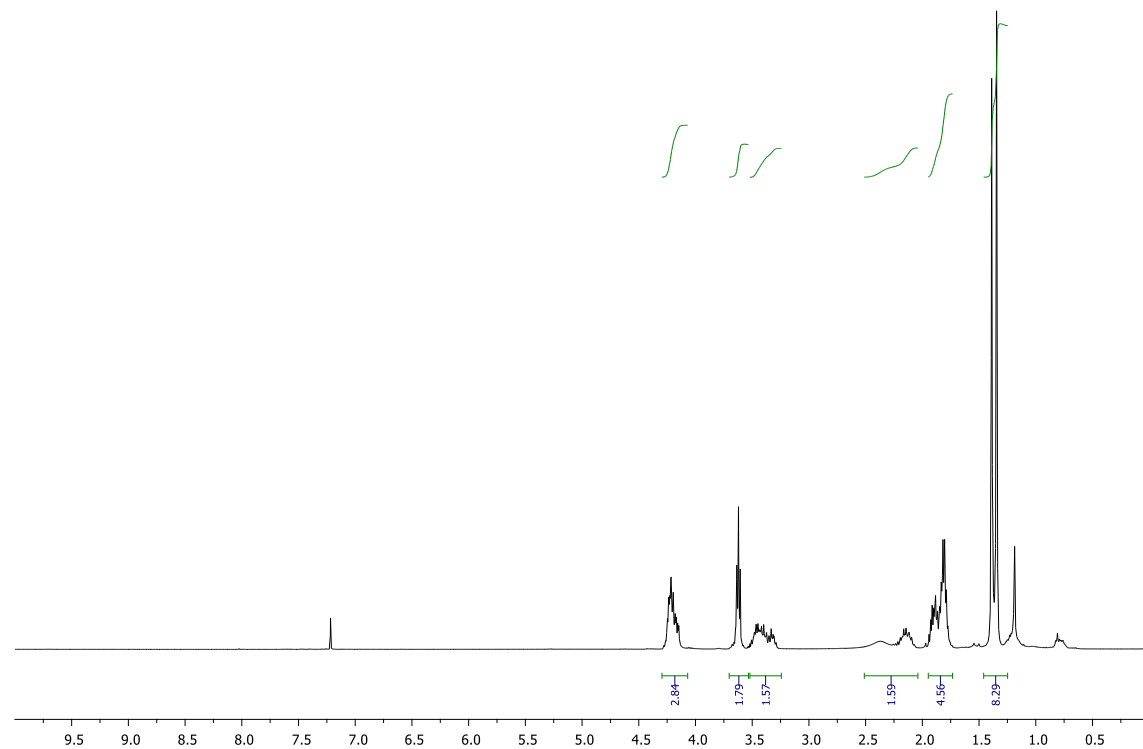
2-((benzyloxy)methyl)-1-(tert-butyl)pyrrolidine-1,2-dicarboxylate (± 2)



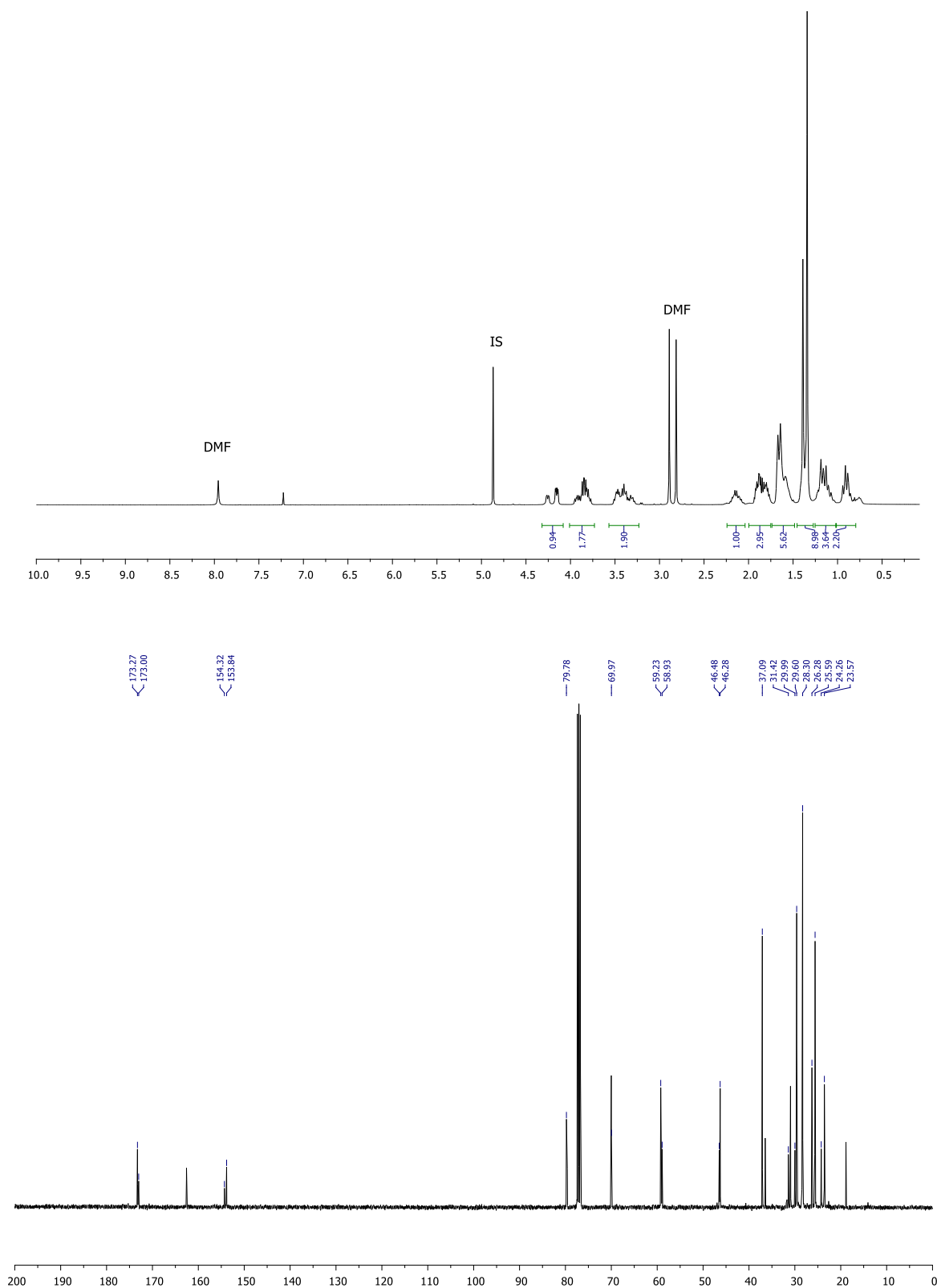
1-(tert-butyl)-2-(3-chloropropyl)pyrrolidine-1,2-dicarboxylate (± 3)



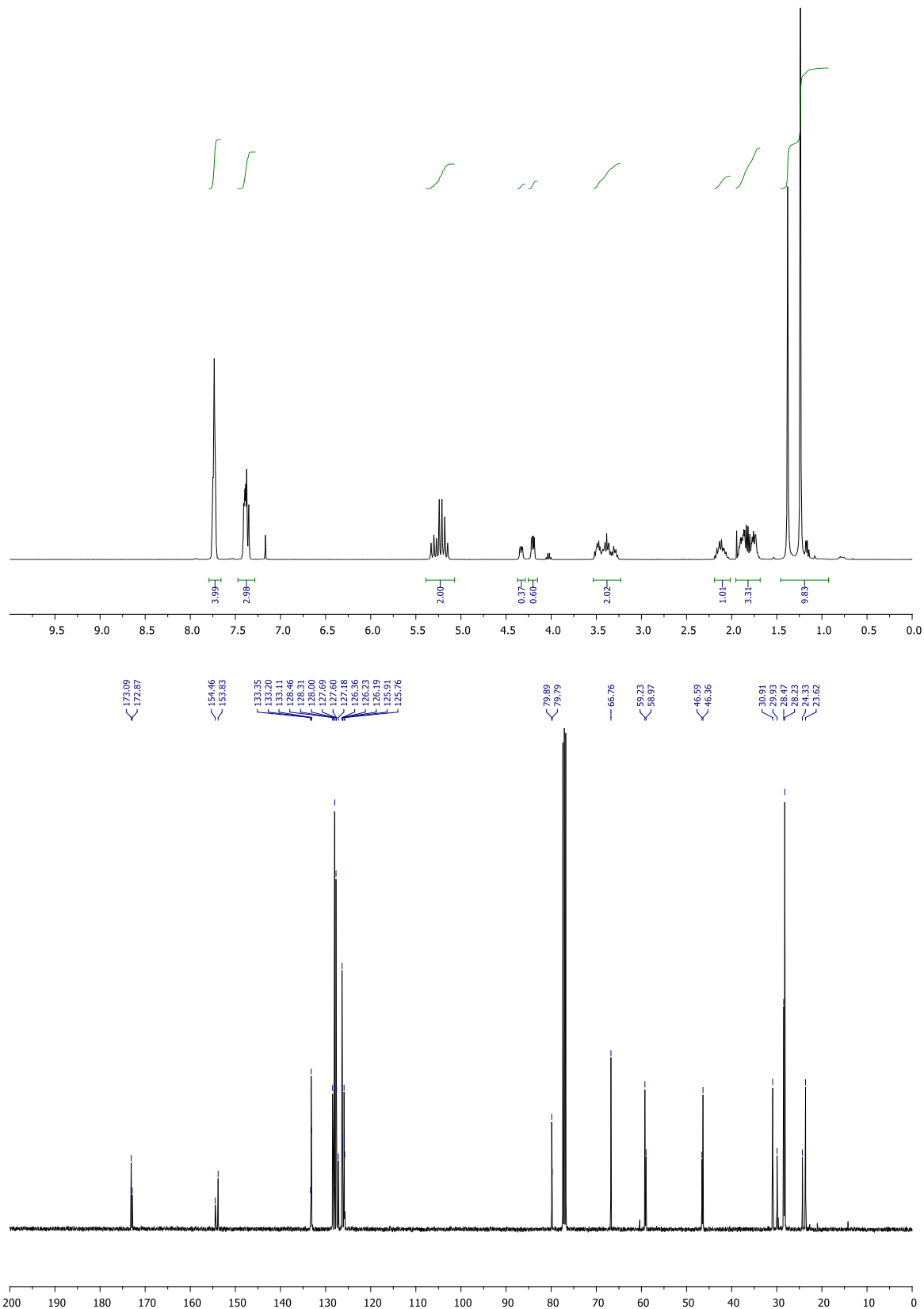
1-(tert-butyl)-2-(3-hydroxypropyl)pyrrolidine-1,2-dicarboxylate (± 4)



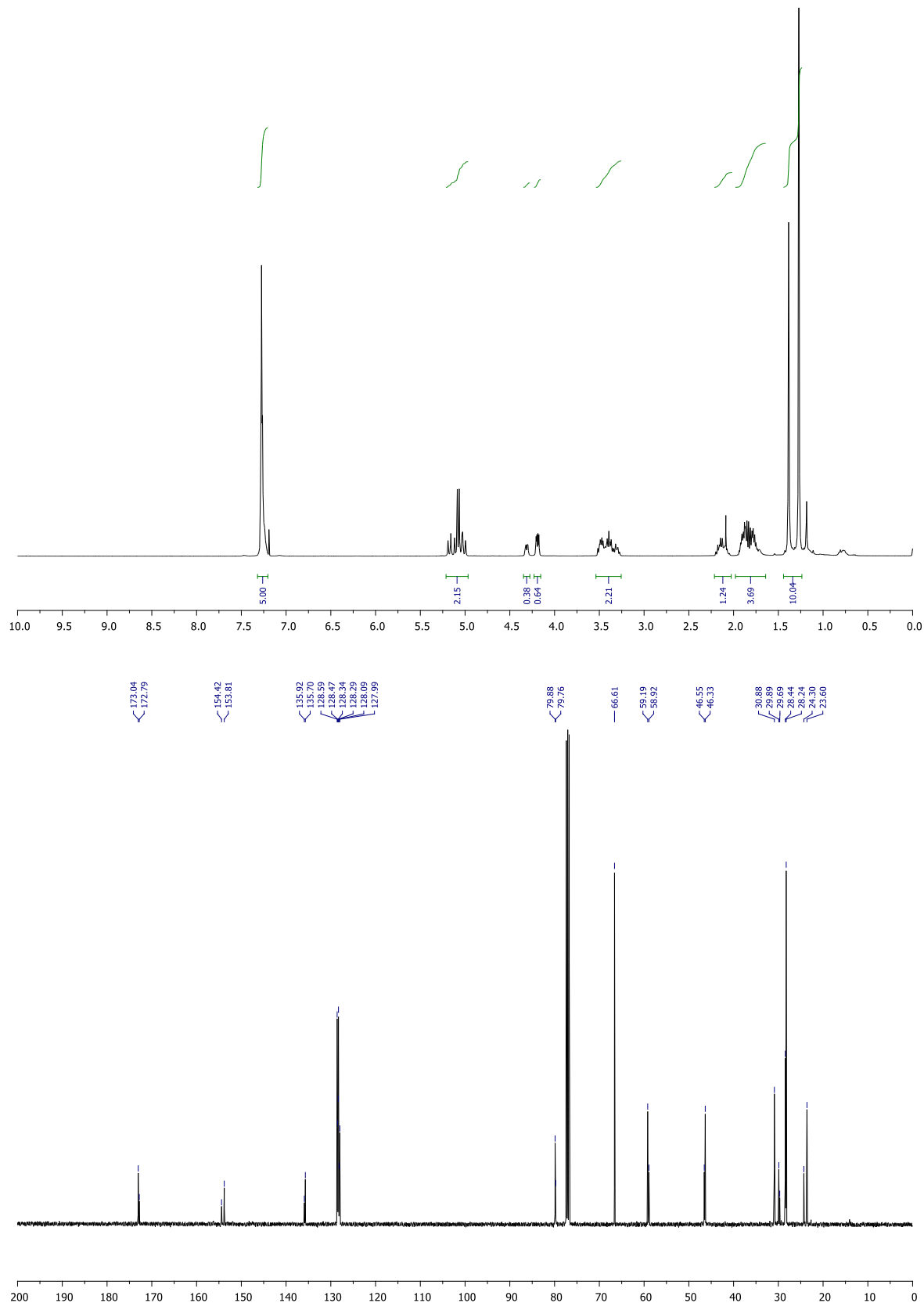
1-(tert-butyl)-2-(cyclohexylmethyl)pyrrolidine-1,2-dicarboxylate (± 5)



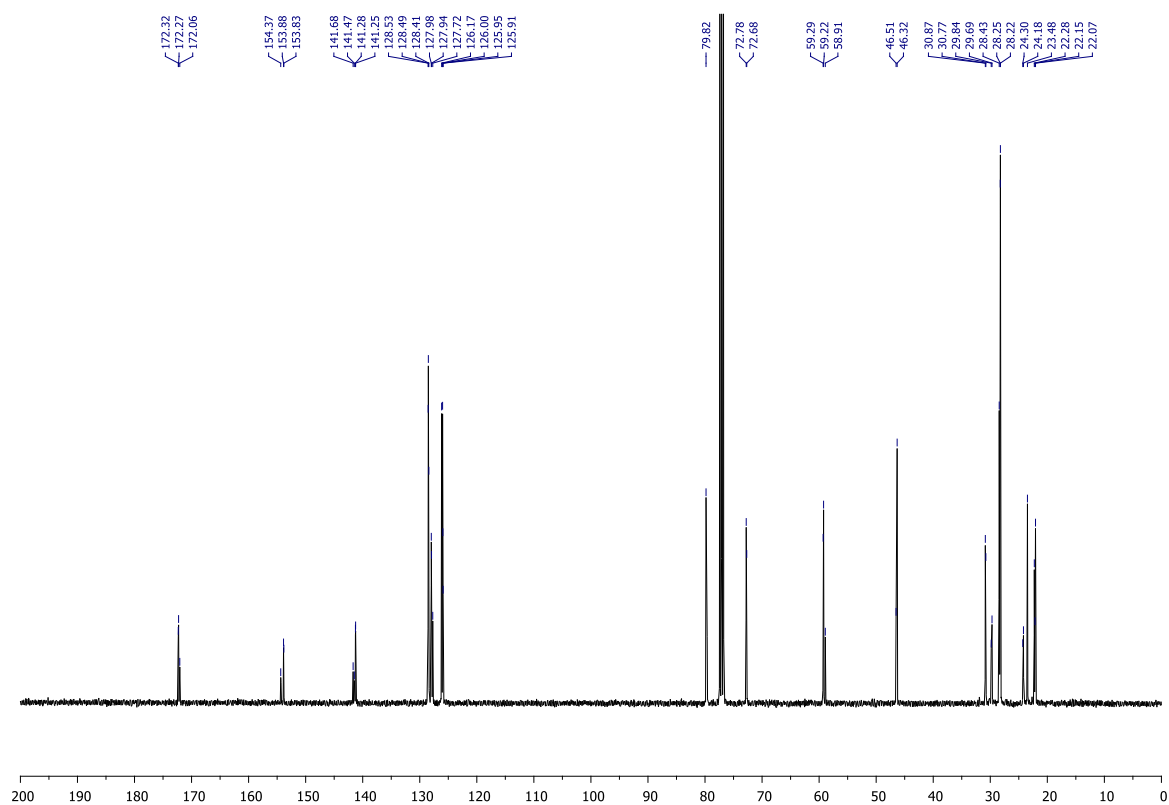
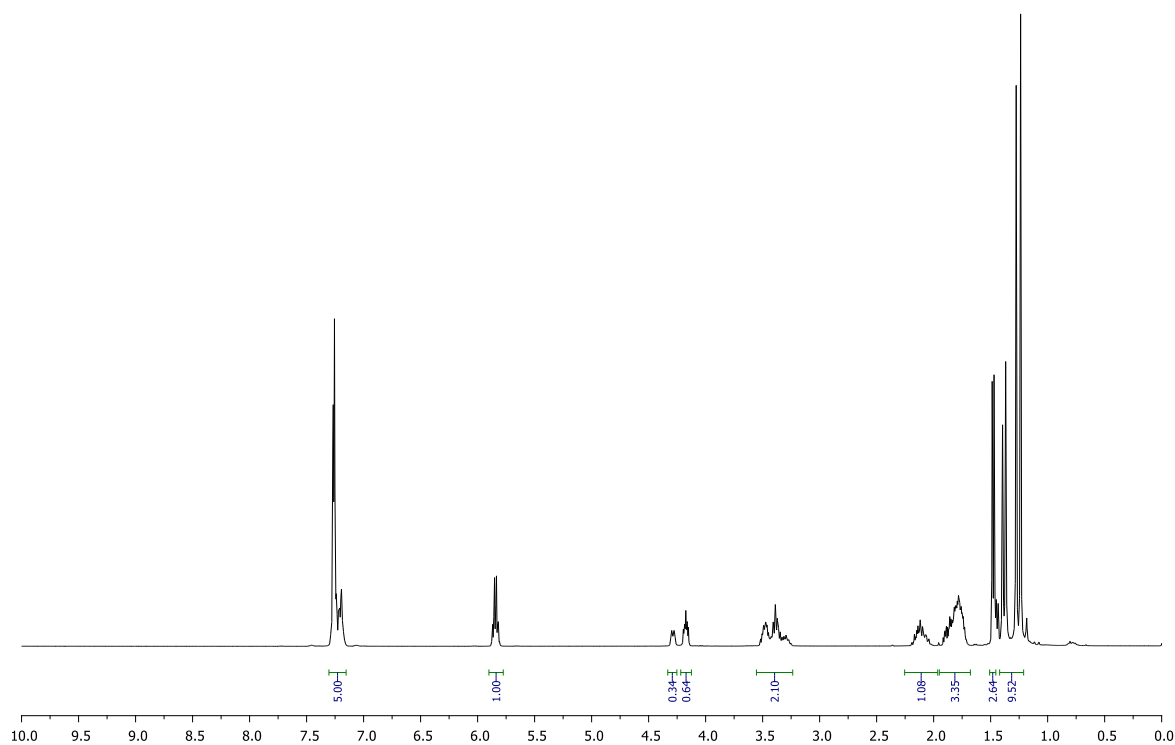
1-(tert-butyl)-2-(naphthalen-2-ylmethyl)pyrrolidine-1,2-dicarboxylate (± 6)



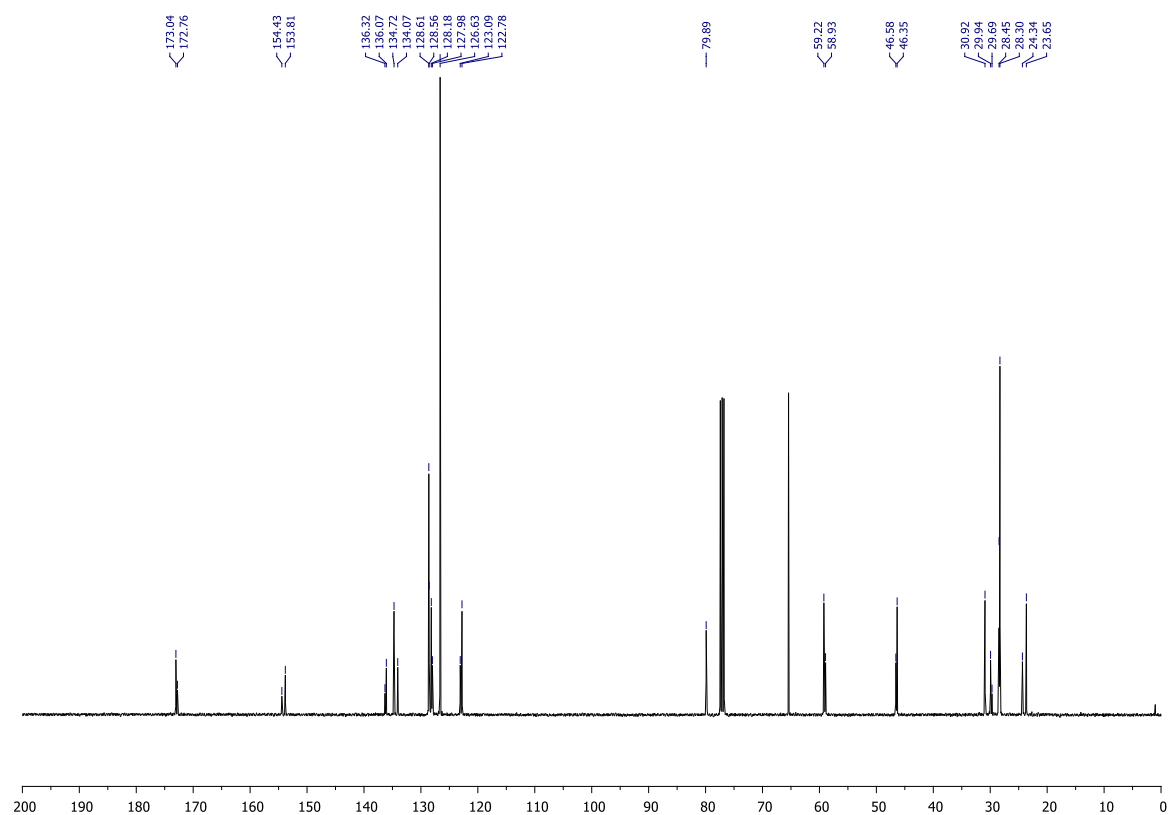
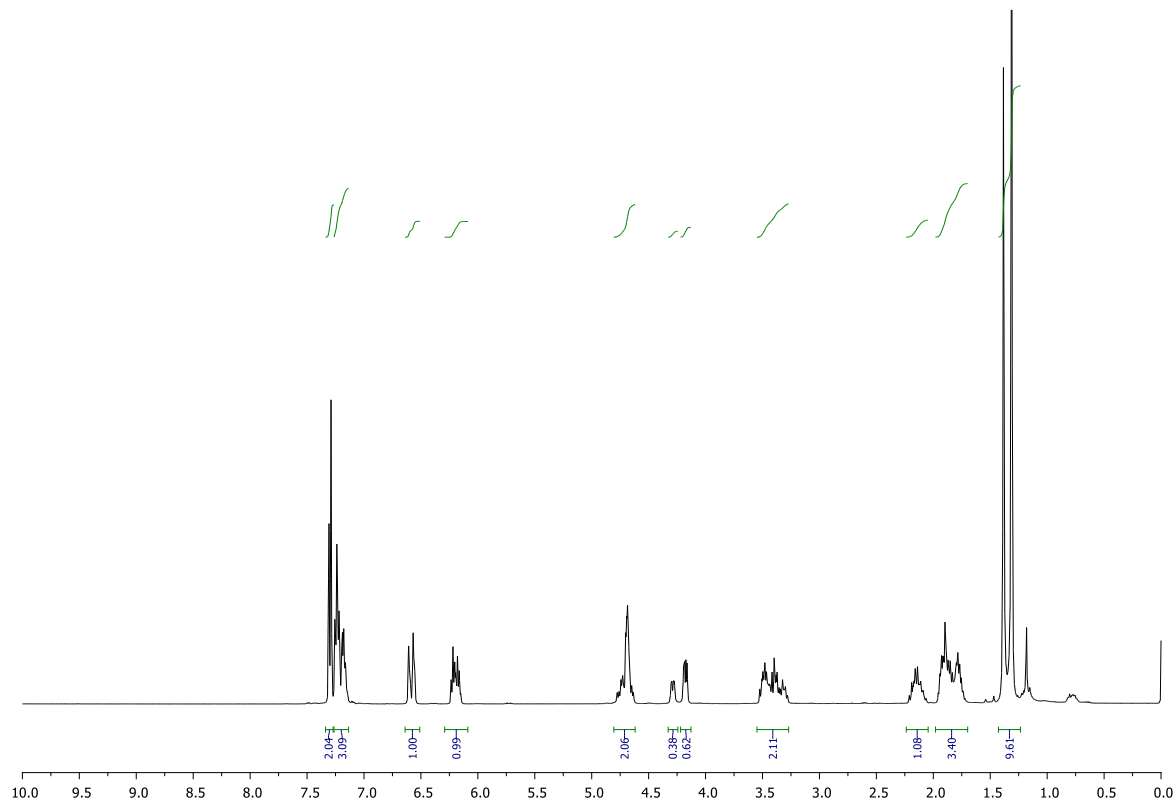
2-benzyl 1-(tert-butyl)pyrrolidine-1,2-dicarboxylate ($\pm$ 7)



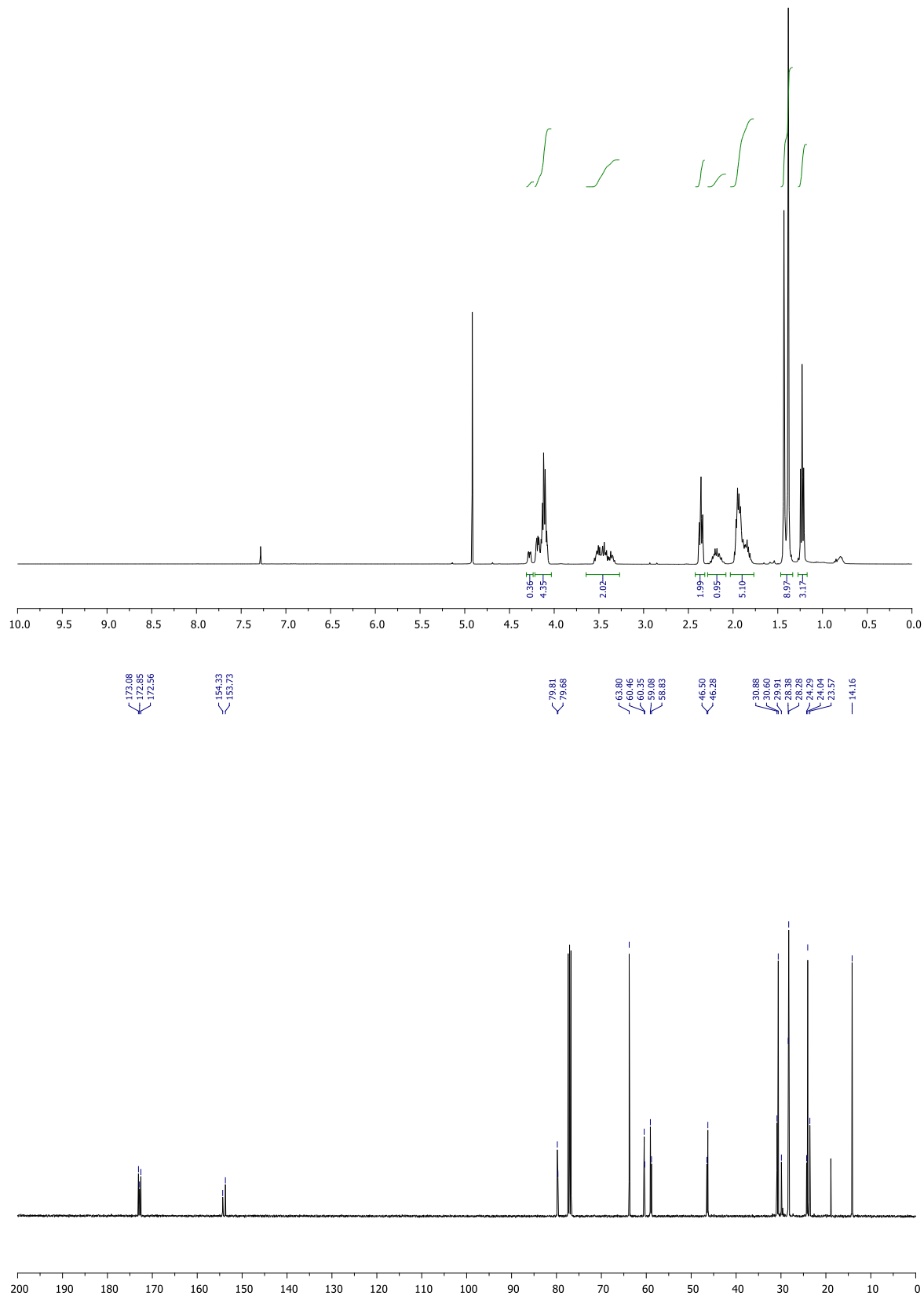
1-(tert-butyl)-2-(1-phenylethyl)pyrrolidine-1,2-dicarboxylate (± 8)



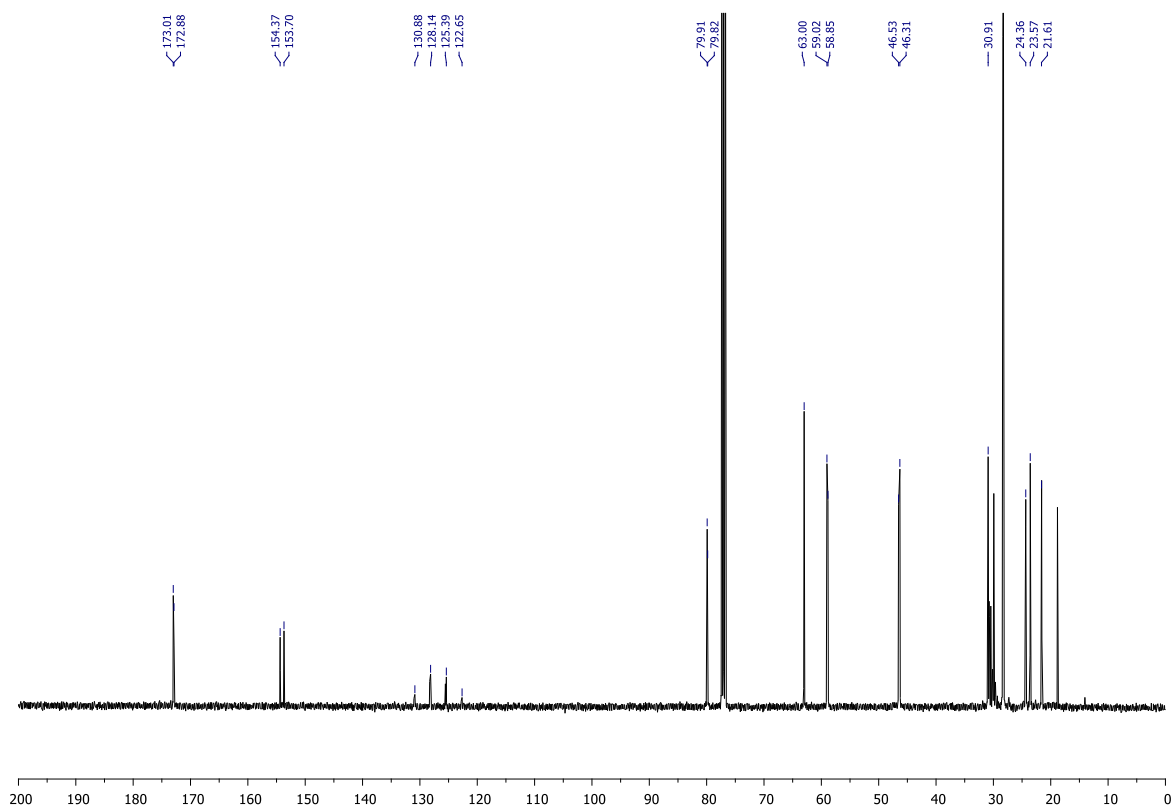
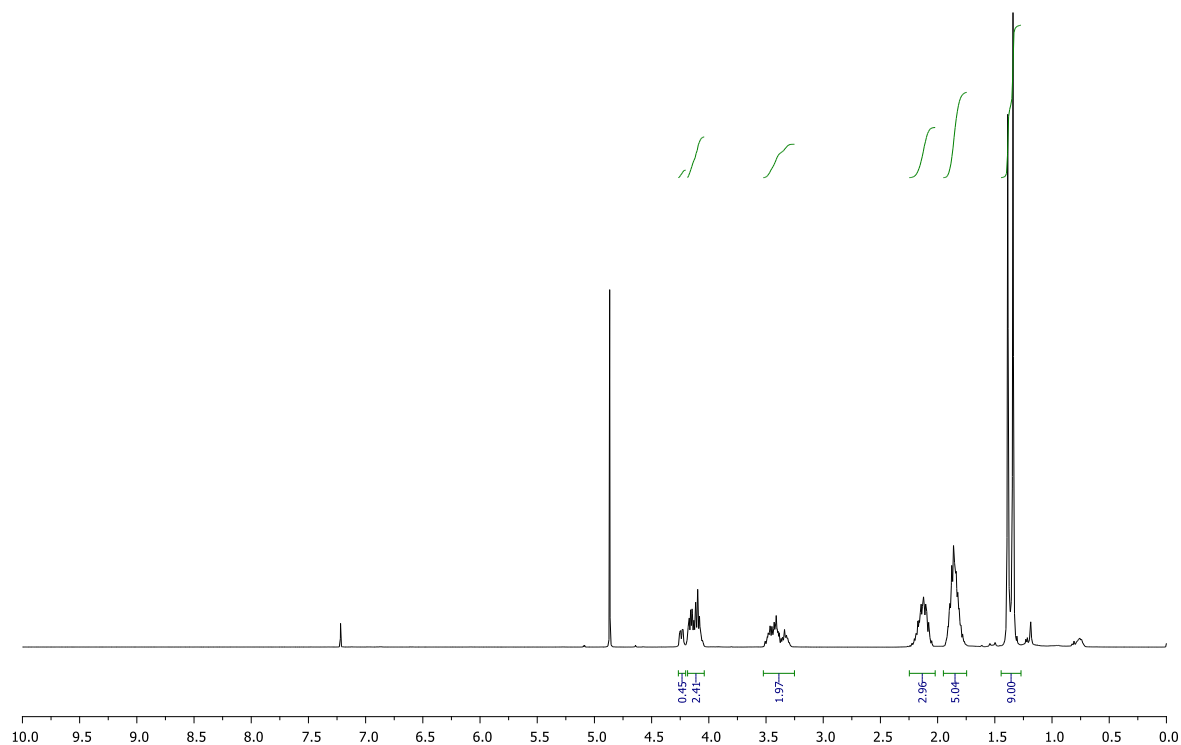
1-(tert-butyl)-2-cinnamylpyrrolidine-1,2-dicarboxylate ($\pm$ 9)



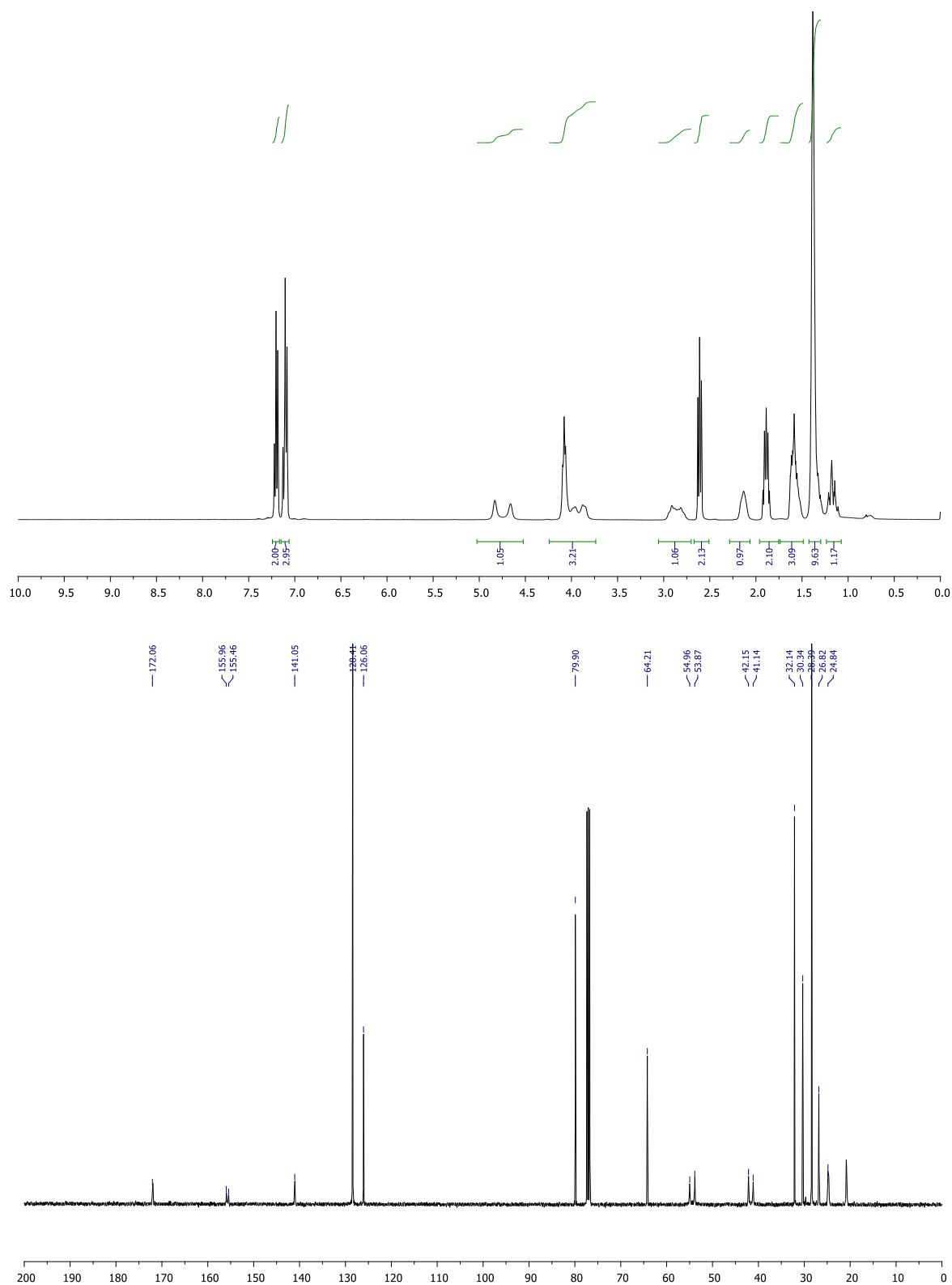
1-(tert-butyl)-2-(4-ethoxy-4-oxobutyl)pyrrolidine-1,2-dicarboxylate (± 10)



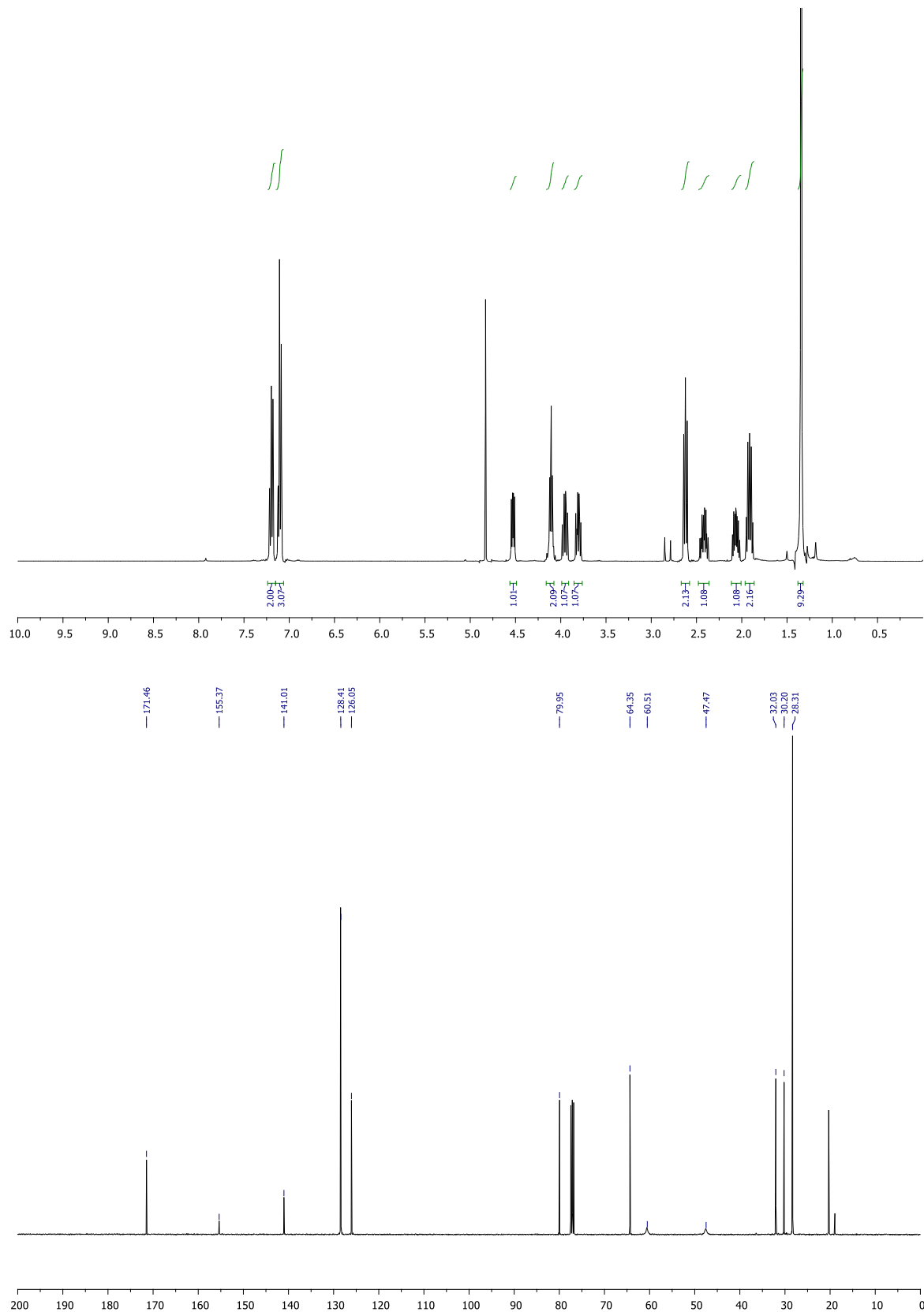
1-(tert-butyl)-2-(4,4,4-trifluorobutyl)pyrrolidine-1,2-dicarboxylate (± 11)



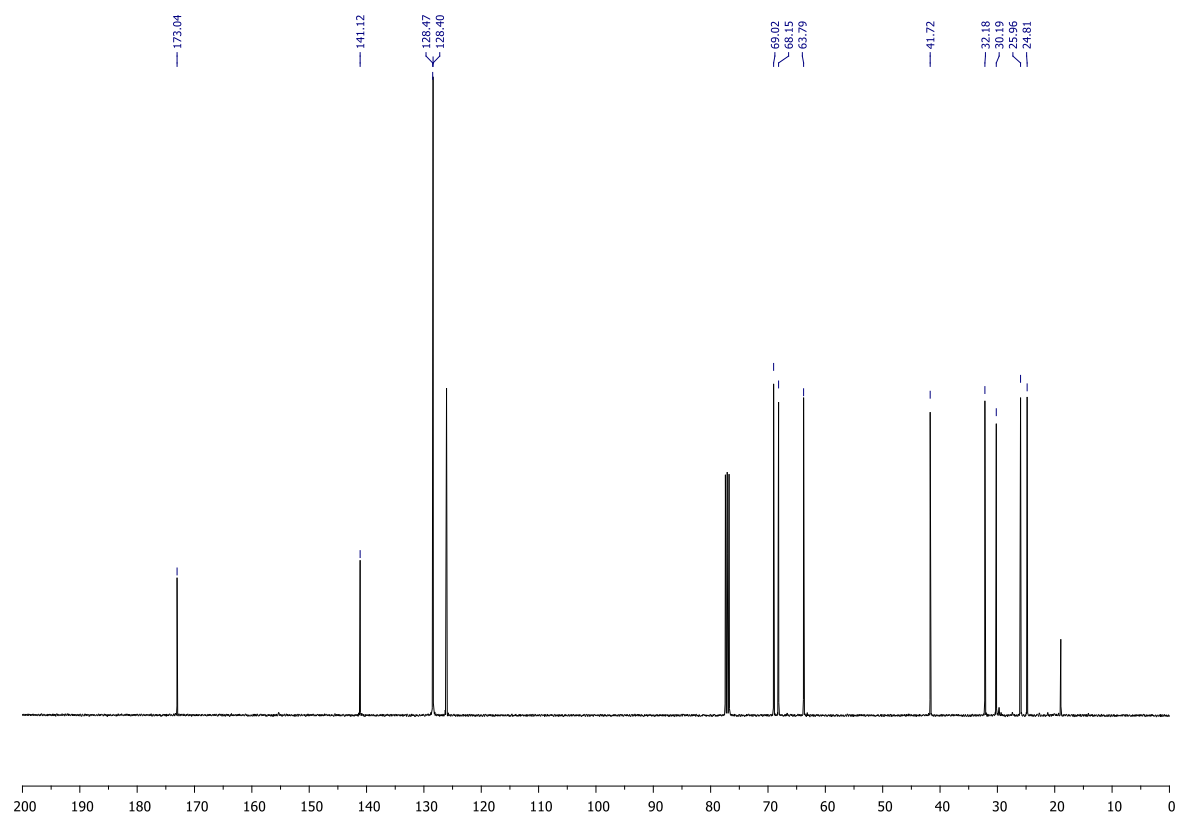
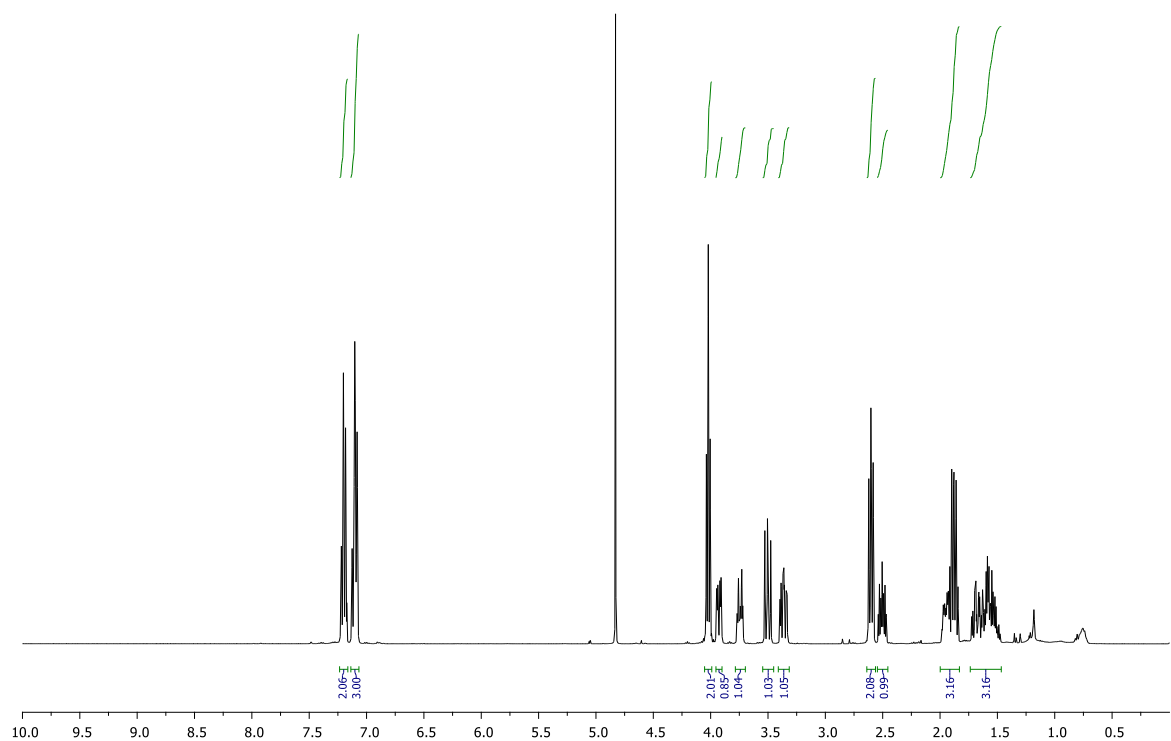
1-(tert-butyl)-2-(3-phenylpropyl)piperidine-1,2-dicarboxylate (± 16)



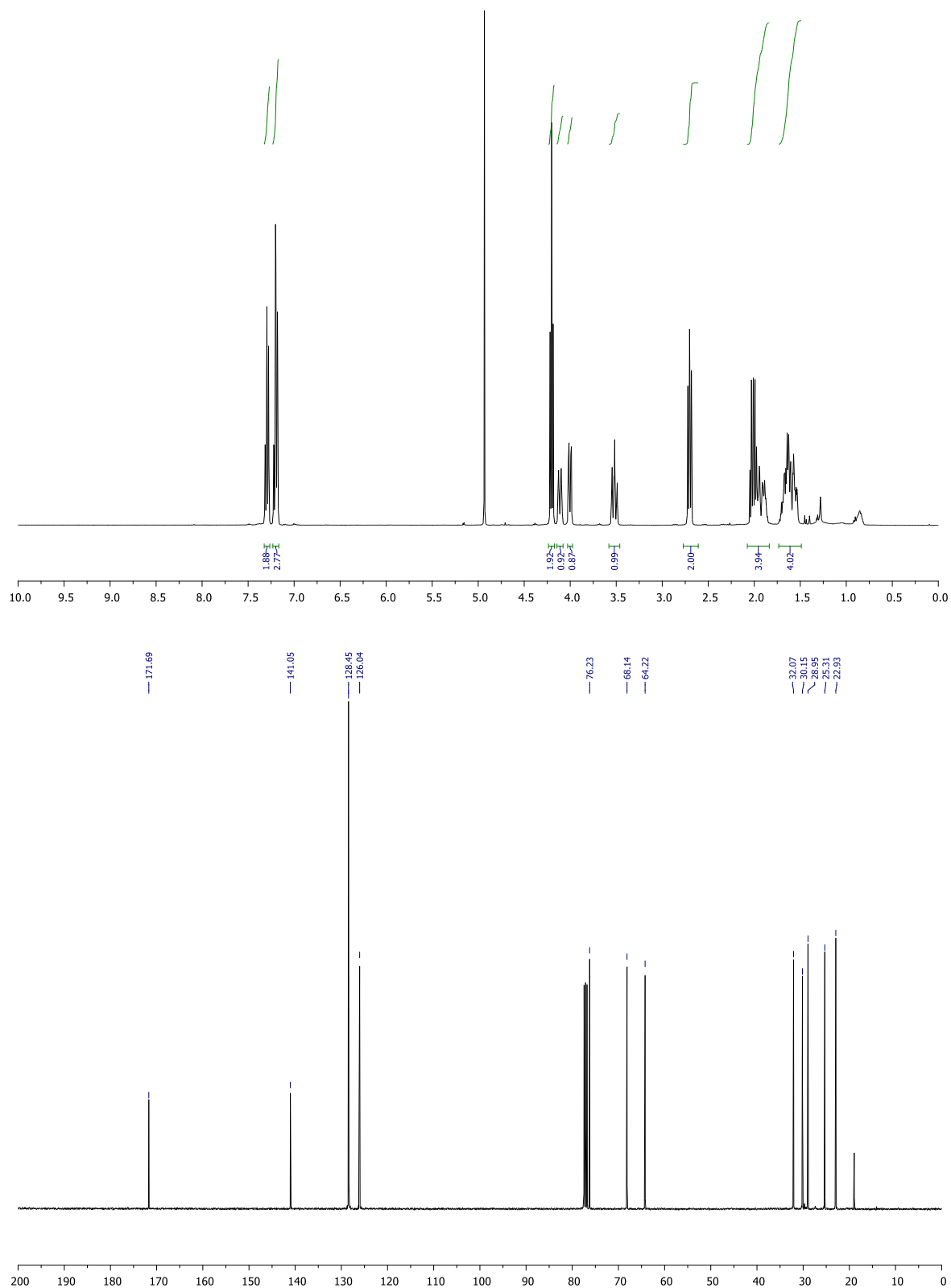
1-(tert-butyl)-2-(3-phenylpropyl)azetidine-1,2-dicarboxylate (± 17)



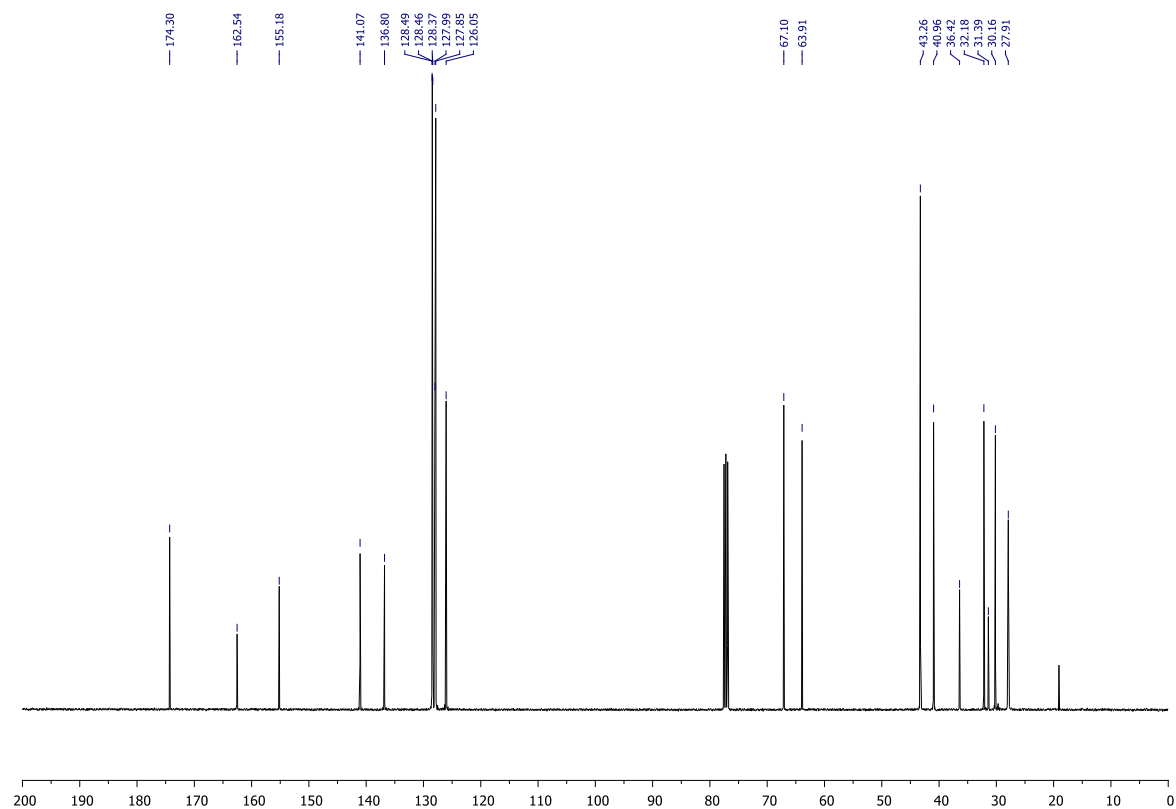
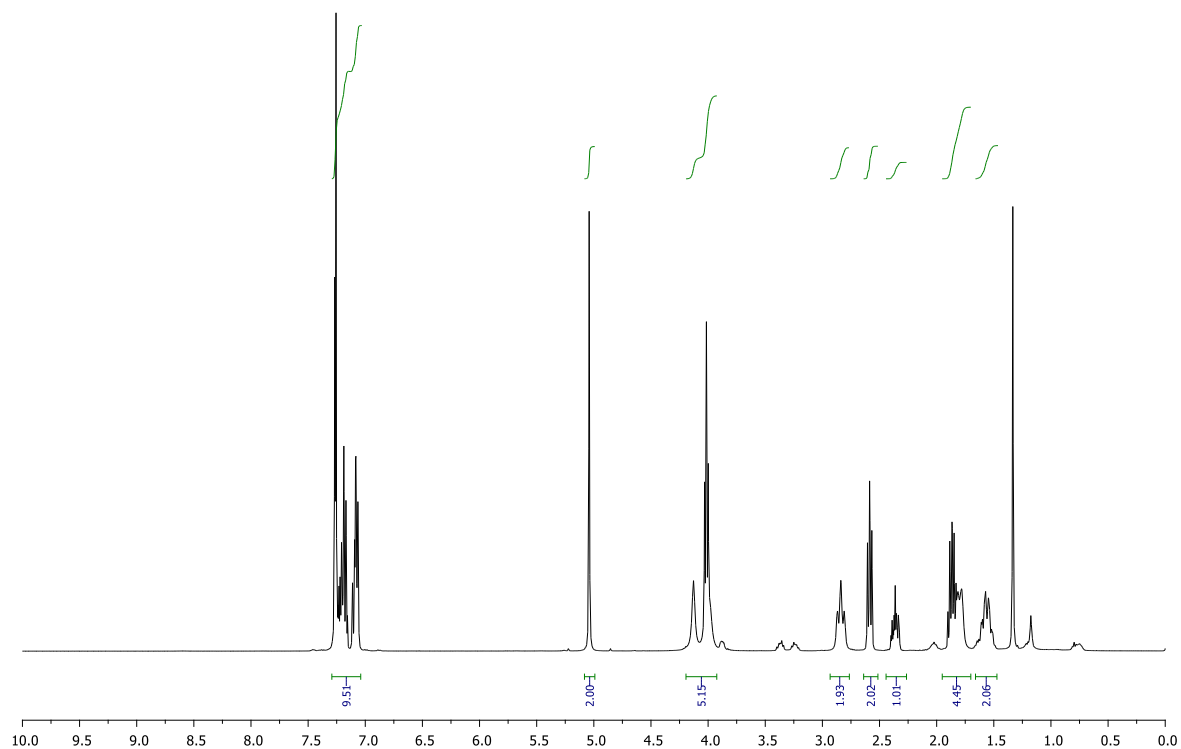
3-phenylpropyltetrahydro-2H-pyran-3-carboxylate ($\pm$ 18)



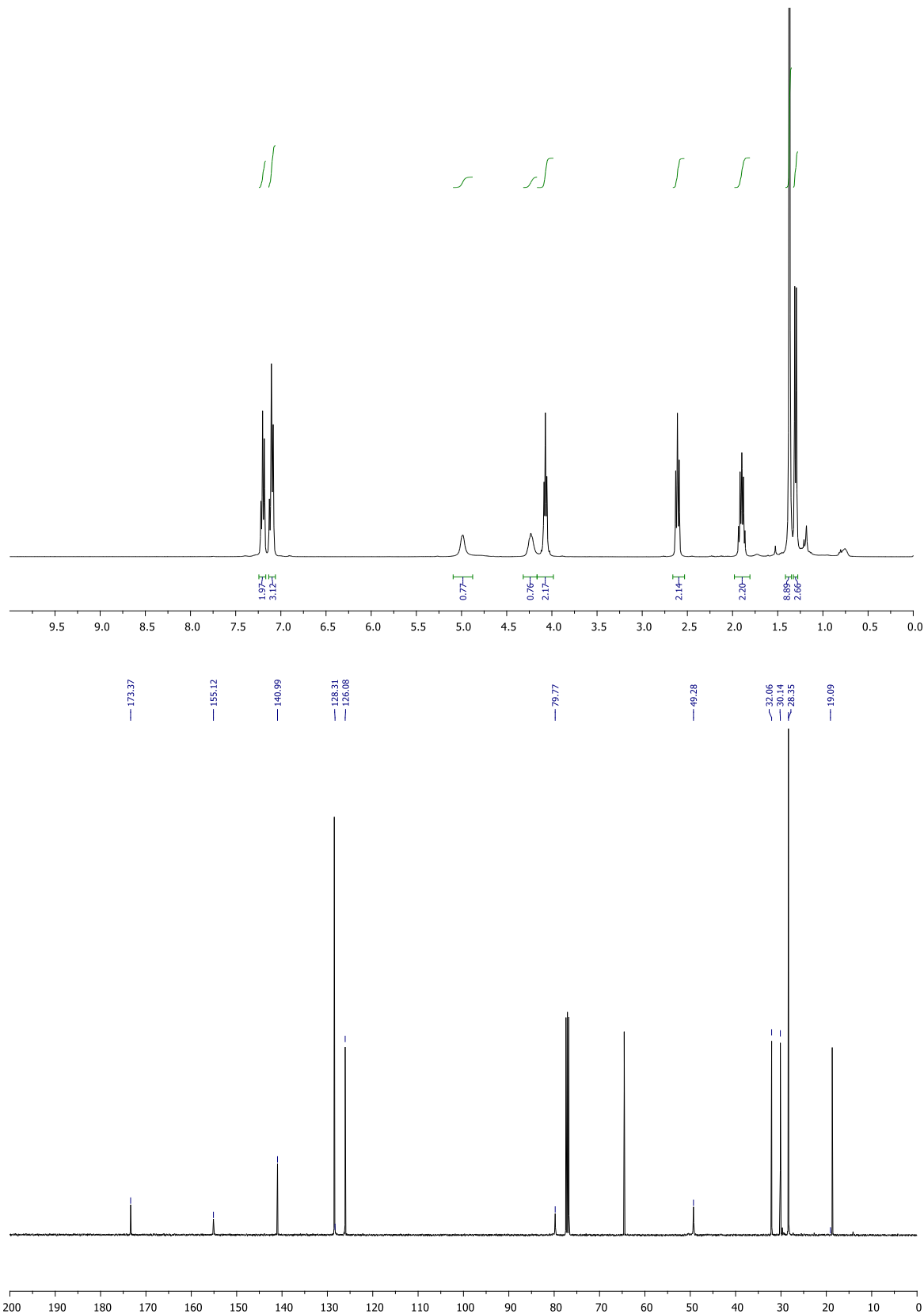
3-phenylpropyltetrahydro-2H-pyran-2-carboxylate ($\pm$ 19)



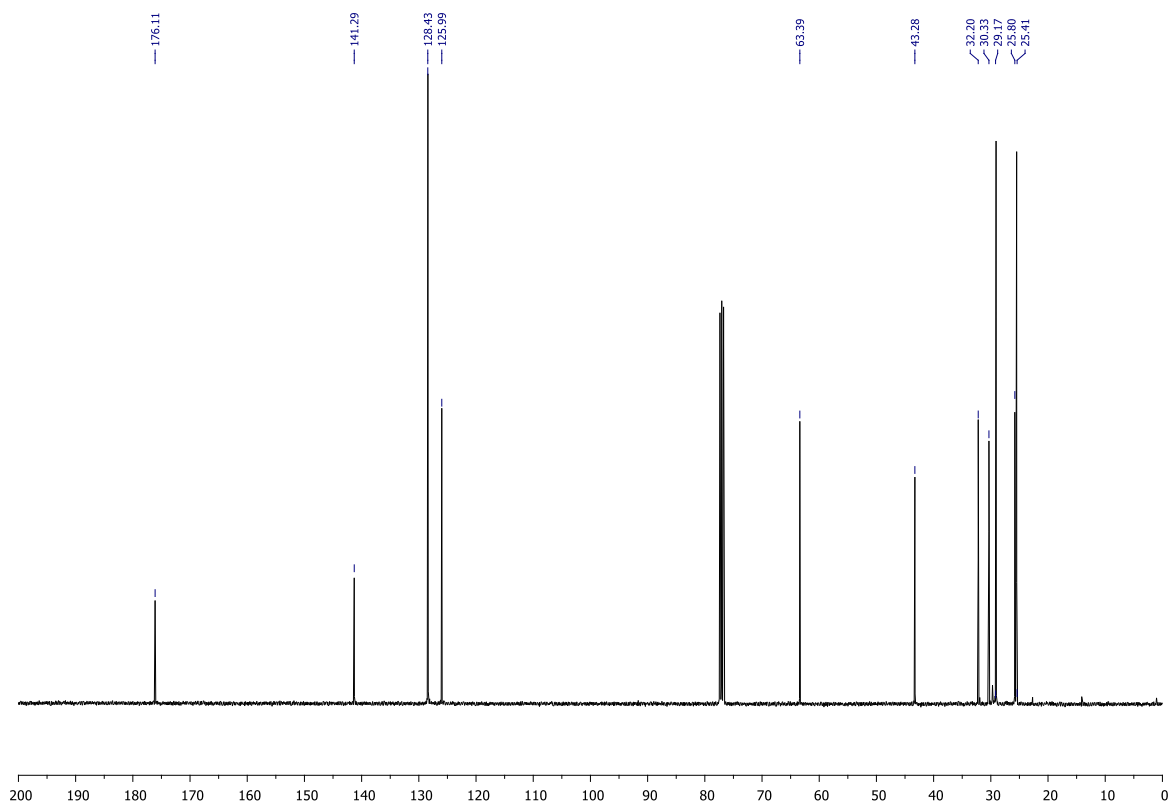
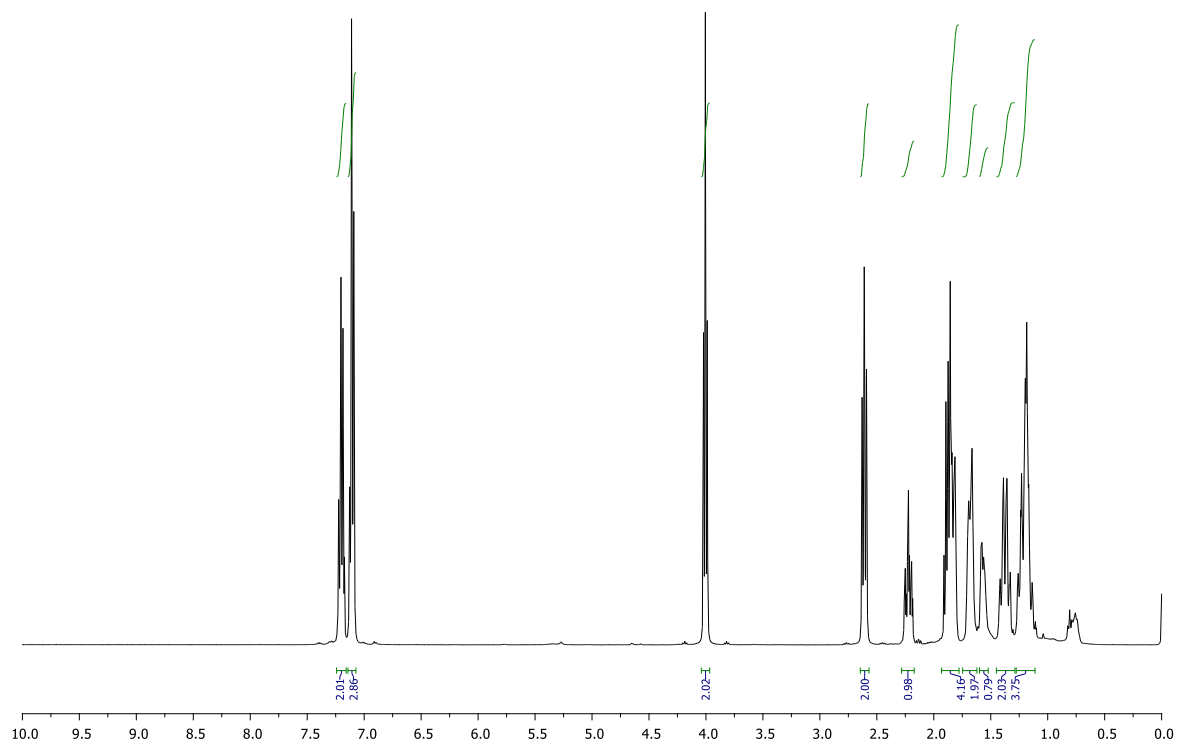
1-benzyl-4-(3-phenylpropyl)piperidine-1,4-dicarboxylate (20)



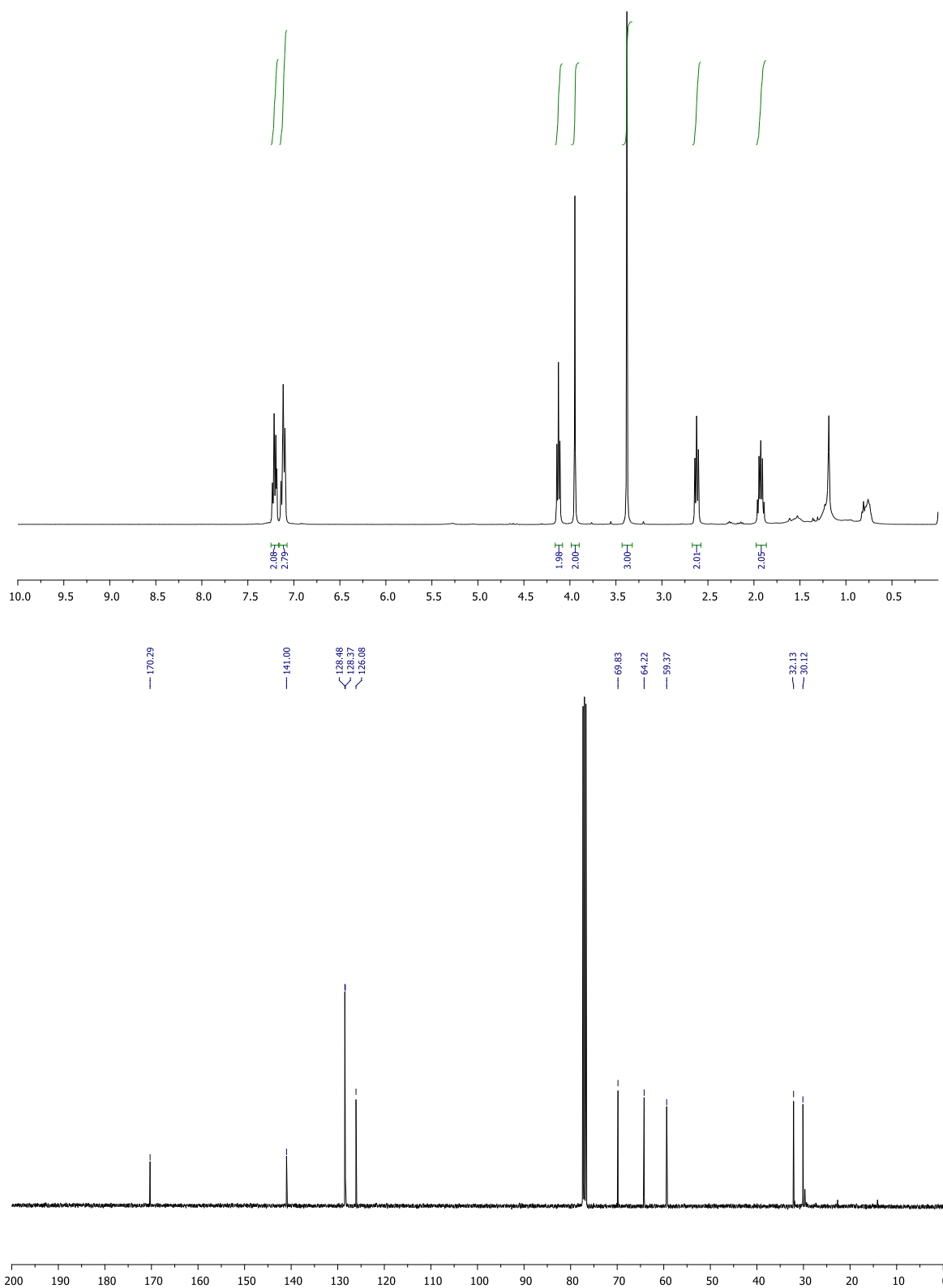
3-phenylpropyl-(tert-butoxycarbonyl)alaninate (± 21)



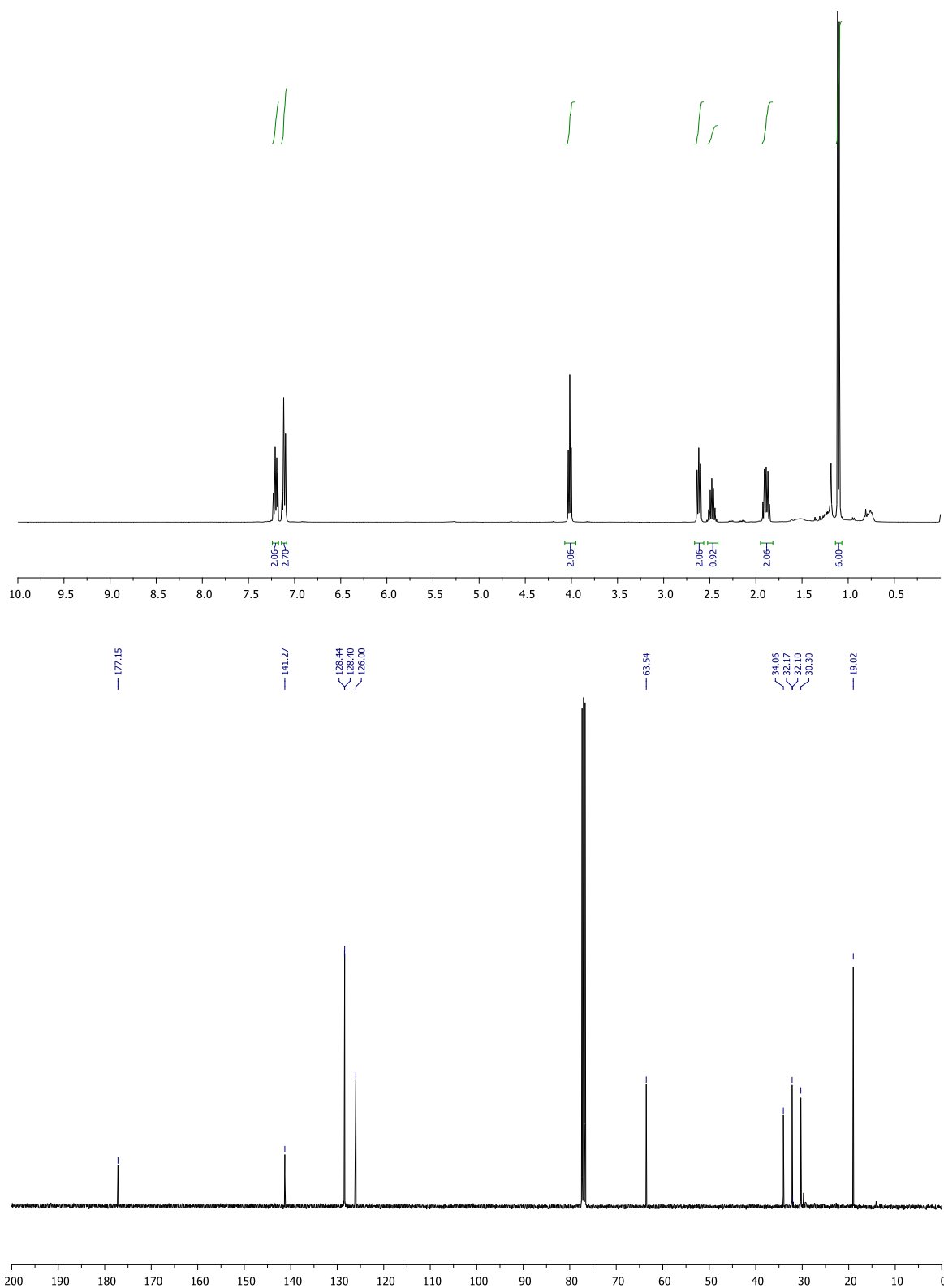
3-phenylpropylcyclohexanecarboxylate (22)



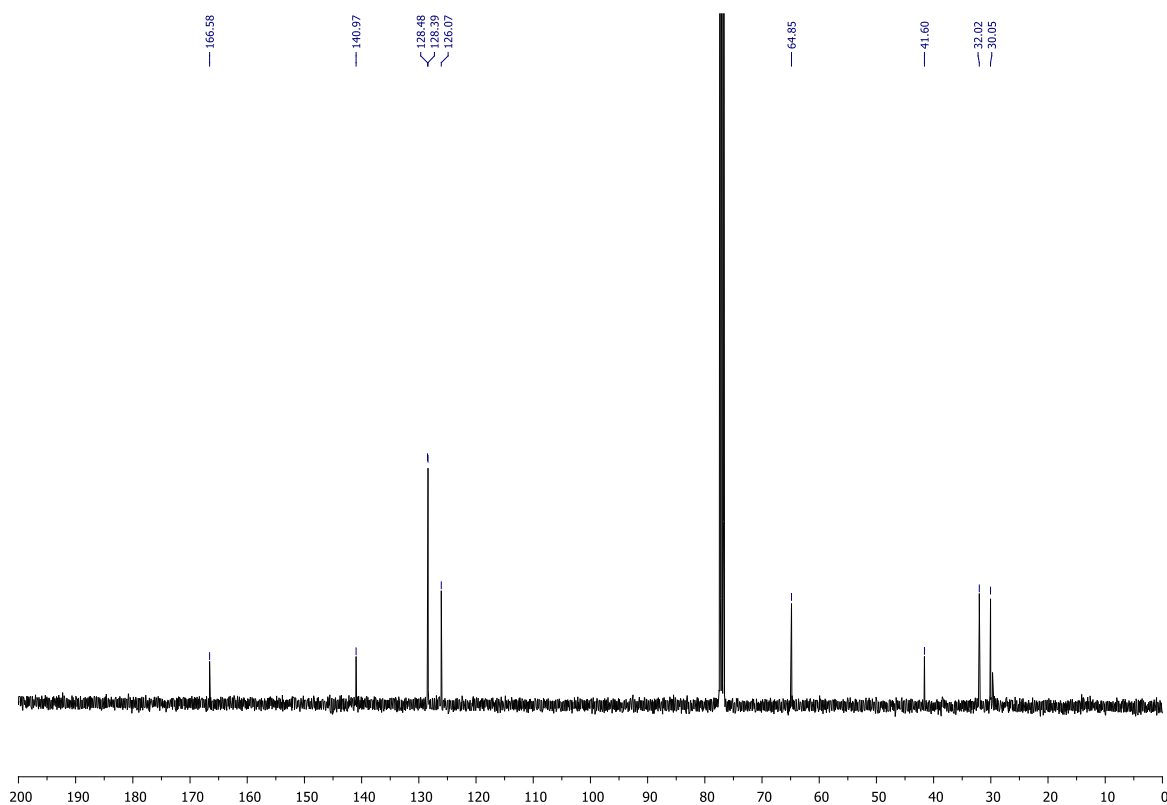
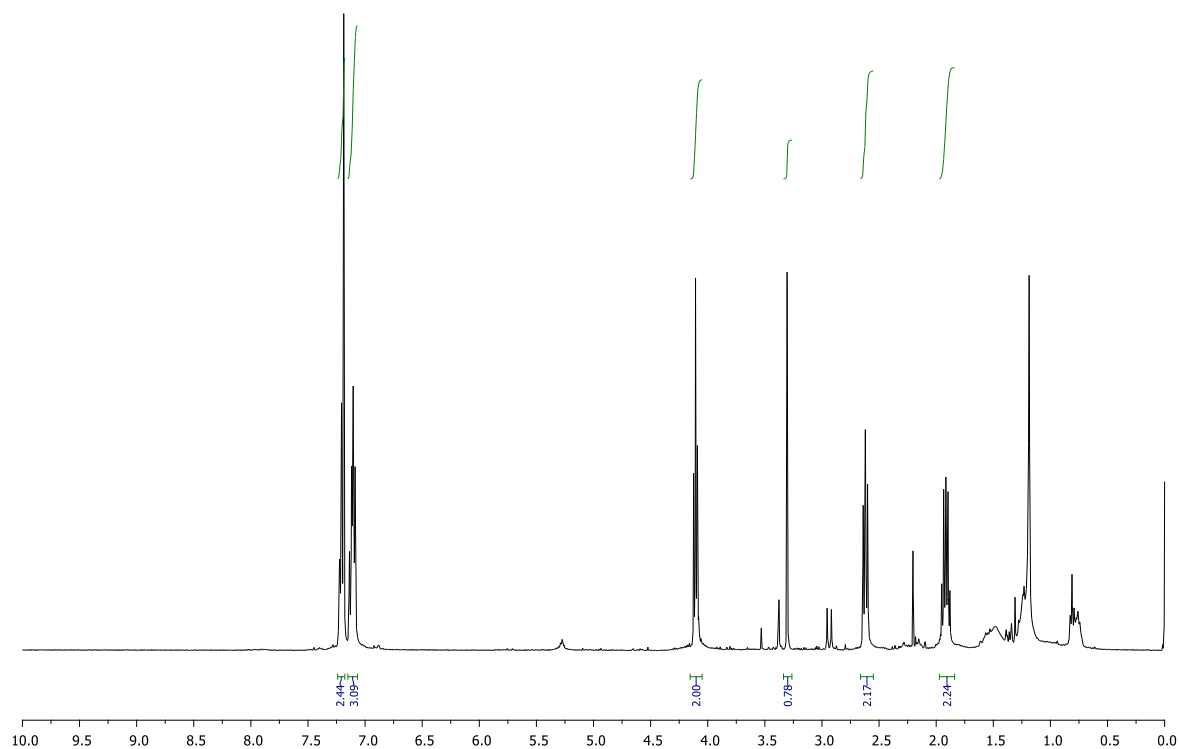
3-phenylpropyl-2-methoxyacetate (23)



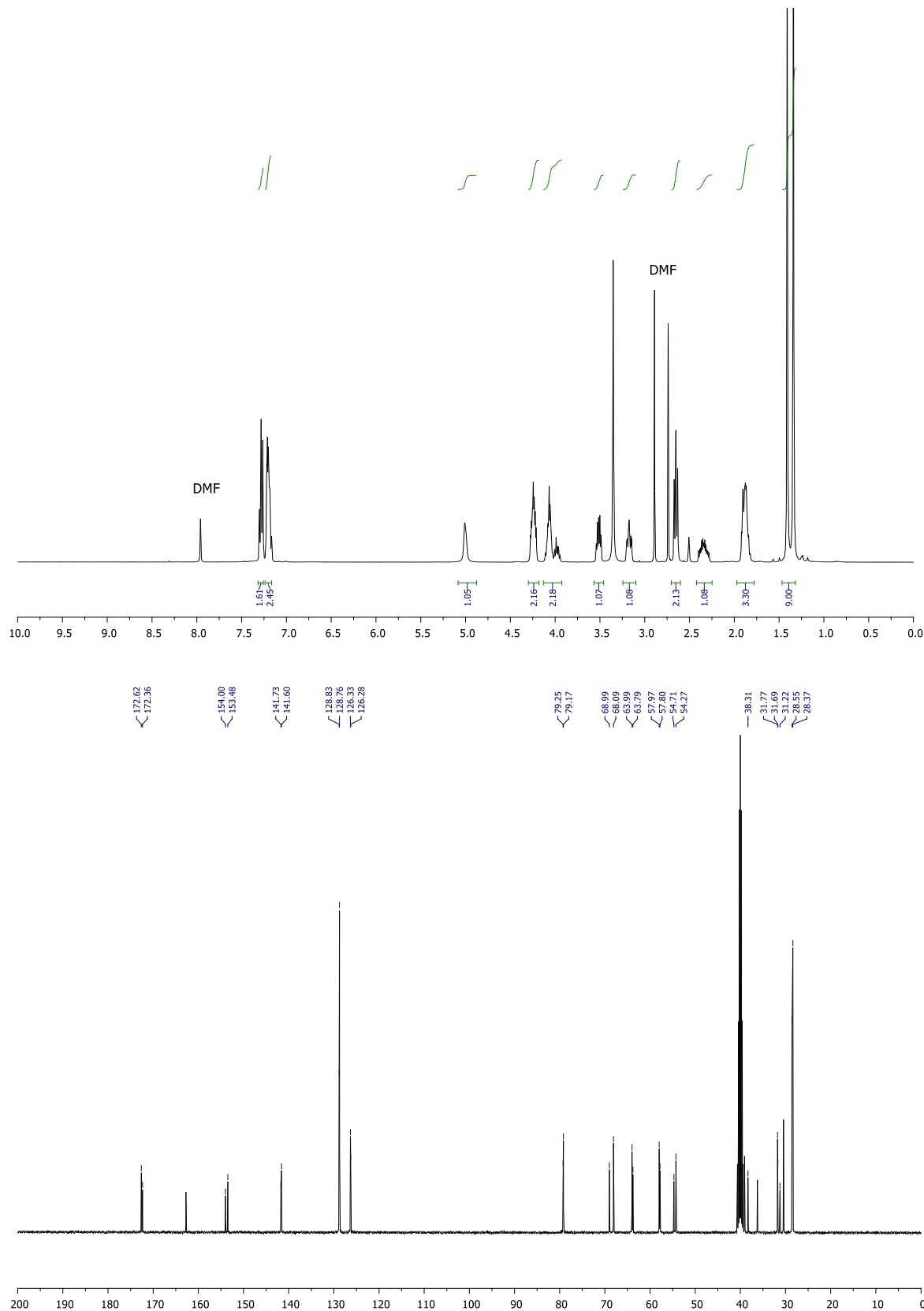
3-phenylpropylisobutyrate (24)



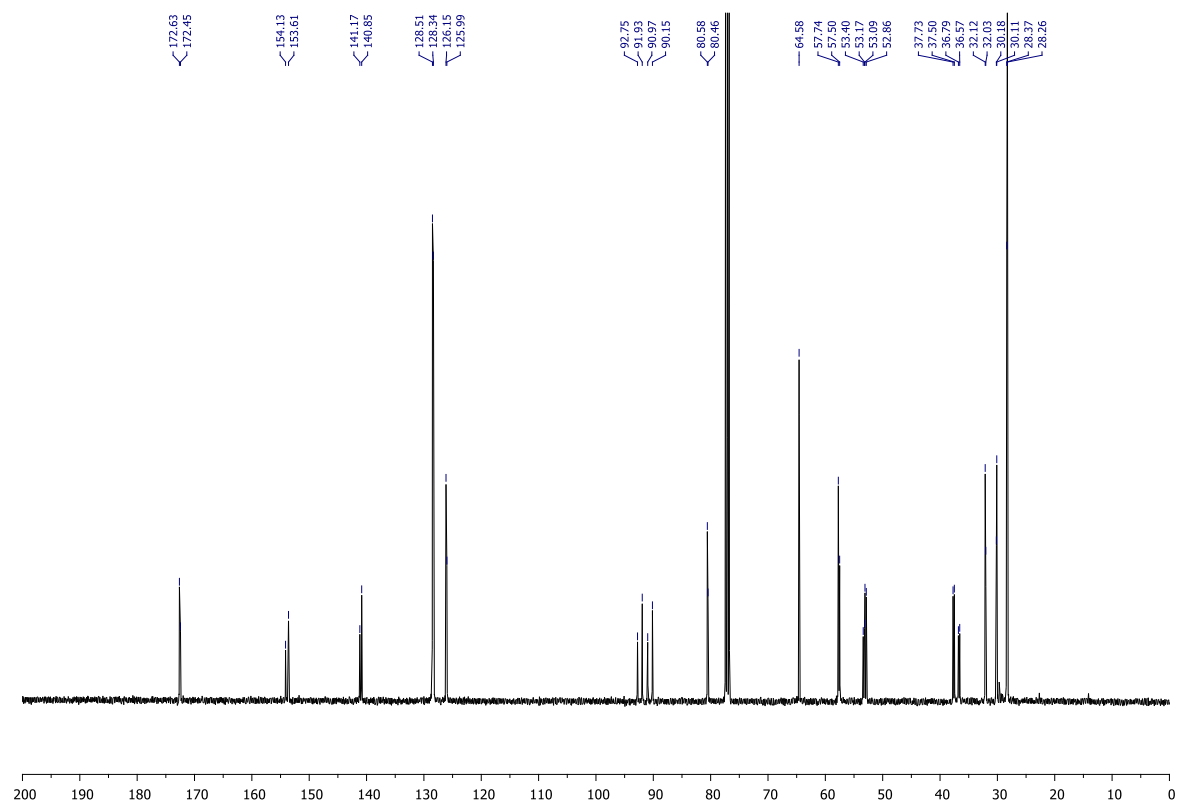
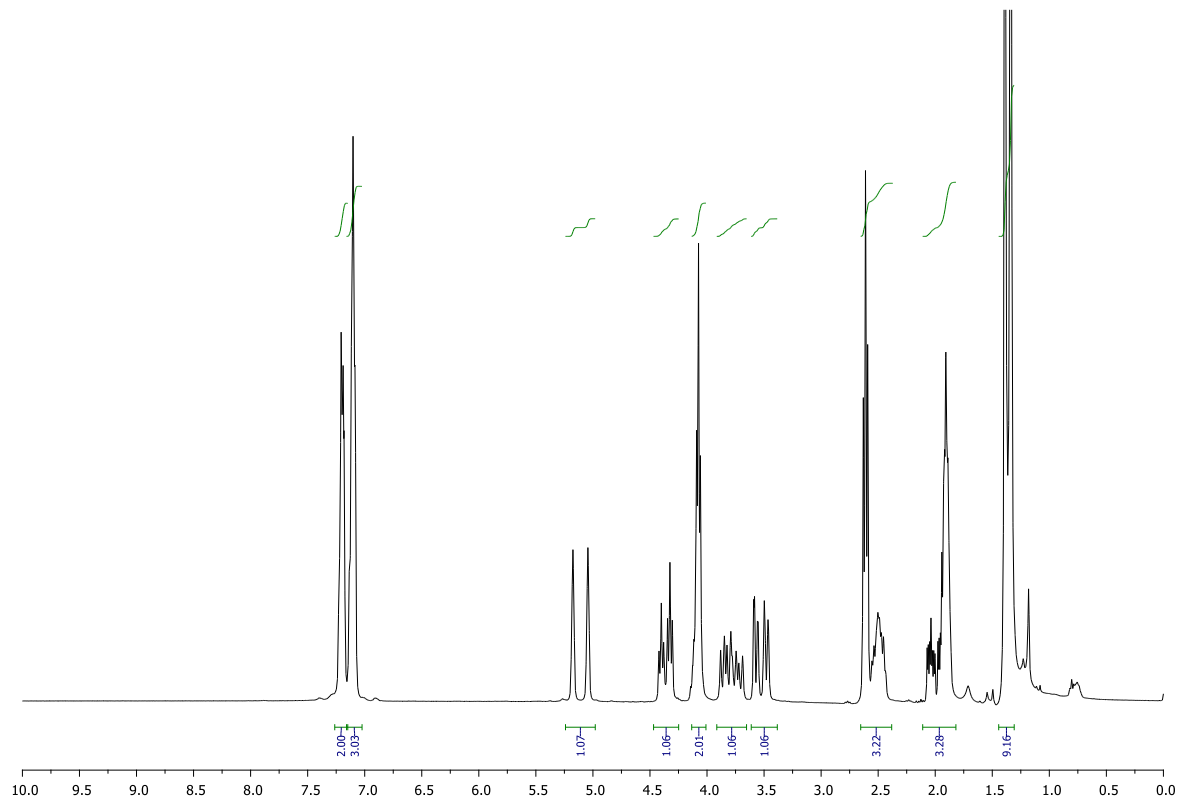
3-phenylpropyl-3,3,3-trifluoropropanoate (25)



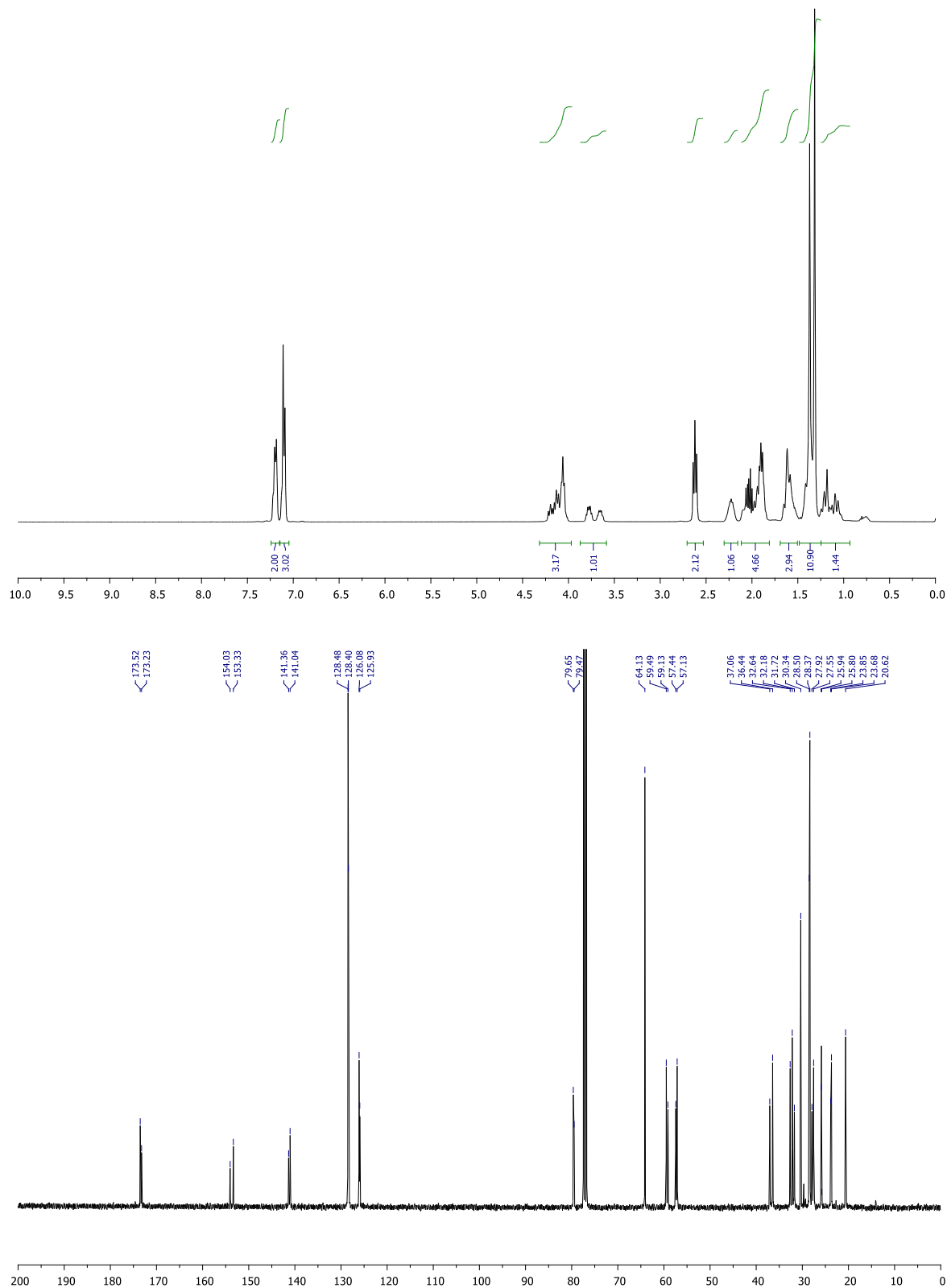
1-(tert-butyl)-2-(3-phenylpropyl)-(4S)-4-hydroxypyrrolidine-1,2-dicarboxylate (± 26)



1-(tert-butyl)-2-(3-phenylpropyl)-(4*R*)-4-fluoropyrrolidine-1,2-dicarboxylate (±27)



1-(tert-butyl)-2-(3-phenylpropyl)-octahydro-1*H*-indole-1,2-dicarboxylate (±28):



6. References

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End of Supplementary Information.