Development and Applications of Heterogeneous Chiral Bifuncitonal Alkaloid-Thioureas as Recyclable Organocatalysts

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General Experimental Information

Solvents and chemicals were obtained from typical commercial vendors and were used as received, without any further purification. Starting materials were synthesized according to literature protocols.

Solvents for extraction, chromatography and crystallization were technical grade. All solvents used in reactions were treated with dry molecular sieves as specified in the literature.[1]

When required, chromatographic purification was performed by flash chromatography using commercial grades of silica gel finer than 230 mesh with pressure. Analytical thin-layer chromatography (TLC) was carried out using 60 F_{254} TLC aluminum plates. Compounds were visualized by means of UV or by using $KMnO_4$.

^{1}H, and ^{13}C-NMR spectra were recorded on a Bruker Avance 400 spectrometer instrument at room temperature, in $CDCl_3$ or acetone-d6 as a solvent, at 300 MHz and 75 MHz, respectively. Chemical shifts (δ) are reported in ppm relative to the residual solvent peak ($CDCl_3$, ^{1}H: 7.26 ppm; ^{13}C: 77.16 ppm. Acetone-d6 ^{1}H: 2.09 ppm; ^{13}C: 205.87, 30.60 ppm). External reference CFCl3 (δF = 0.0 ppm) is used for ^{19}F NMR spectra. Coupling constants (*J*) are reported in Hertz. ^{13}C NMR spectra were recorded in a broad band decoupled mode, and peak assignments were supported by Distortionless Enhanced Polarization Transfer (DEPT). Multiplicity is reported with the usual abbreviations.

High resolution mass spectra (HRMS) spectra were obtained by positive-ion electrospray ionization (ESI) using a LC-QTOF method. Data are reported in the form m/z (intensity relative to base = 100).

Chiral HPLC analysis was performed on a HPLC Agilent 1100/1200 Series system, with Chiracel® IA, Chiracel® IC and Chiracel® OD-H columns as stationary phases.

The absolute configuration was determined by comparison of chiral HPLC data with literature reports for compound **4a** and **6c**, and the absolute configurations of other compounds were assigned by analogy.[2,3]

The infrared spectra (FTIR) were registered using a Nicolet iS10 spectrophotometer (Thermo Scientific), using Smart iTR accessory (ATR) and reporting the value of the peaksin cm^{-1}. IR spectra were taken as neat solids.

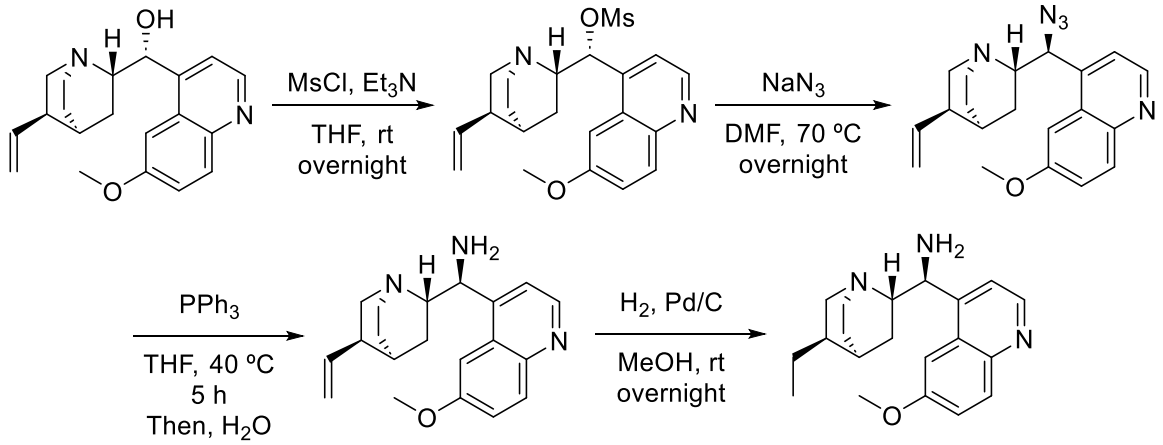
Elemental analysis was carried out according to the protocol described below. For calibration, five tin capsules were packed with acetanilide test samples of varying mass. The mass of samples was chosen so as to make the absolute content of the detected elements cover all their expected concentration range in the analyzed samples. Samples to be analyzed were placed in tin capsules, weighed and packed carefully. The prepared calibration and analysis samples were placed in the auto-sampler wherefrom they were periodically tipped into a vertical quartz reactor heated at a temperature of 980 °C with a constant flow of helium stream. A few seconds before introduction, the helium stream was enriched with high purity oxygen. The combustion gas mixture is driven through a chromium oxide zone to achieve a complete quantitative oxidation followed by a reduction step in a copper zone to reduce nitrogen oxides to nitrogen. The resulting components N_2, CO_2, H_2O are separated in a chromatographic column and detected by a thermo conductivity detector. The resulting signals, proportional to the amount of eluted gasses, are analyzed by Callidus® software which automatically provides the sample elemental composition report.

Orbital shakers IKA® KS 130 basic were used for all reactions involving the Merrifield resin derived polymer-supported catalysts.

Scanning electron microscopy (SEM) was used to study the morphology. A Hitachi TM3030Plus microscope (Tokyo, Japan), equipped with a secondary electron detector and an accelerating voltage of 15 kV, was employed. The samples were gold-coated prior to analysis. Morphological observations were also carried out using a Nikon Eclipse TS100 optical microscope equipped with a biocular head, Nikon C-W10 B/12 eyepieces, and an ELWD 0.3/OD75 objective lens. The internal calibration of the optical microscope was done using a Neubauer cell.

Synthesis and characterization of Merrifield-supported thiourea catalysts

Synthesis of cinchona alkaloid derived chiral amines:



General procedure is described for Quinine. The same procedures were used for other Quinidine, Cinchonine and Cinchonidine.

Step 1, alcohol mesylation: Quinine (1 equiv., 8.11 g, 25 mmol) was dissolved in a mixture of dry THF (50 mL) and Et_3N (3.6 equiv., 12.5 mL, 90 mmol). After cooling the resulting solution to 0 °C, methanesulfonyl chloride (1.8 equiv., 3.48 mL, 45 mmol) was added dropwise. The mixture was stirred at room temperature overnight. Afterwards, the reaction was quenched with water (40 mL) and extracted with DCM (3 x 60 mL). The combined organic extracts were dried over $MgSO_4$, filtered and the solvent was evaporated. The product was used directly in the next step without further purification.

Step 2, azide SN2: The crude mesylated alkaloid (1 equiv., 10.0 g, 25 mmol) was dissolved in in dry DMF (50 mL). The solution was cooled to 0 °C and NaN_3 (2 equiv., 3.25 g, 50 mmol) was added gradually in portions. The mixture was stirred at 70°C overnight and subsequently the reaction was quenched with water (40 mL) and extracted with ethyl acetate (3 x 60 mL). The organic layers were combined and washed with brine several times (15 x 50 mL) to remove DMF traces, dried over $MgSO_4$ and concentred under vacuum to afford the crude product, which was used in the next step without additional purification.

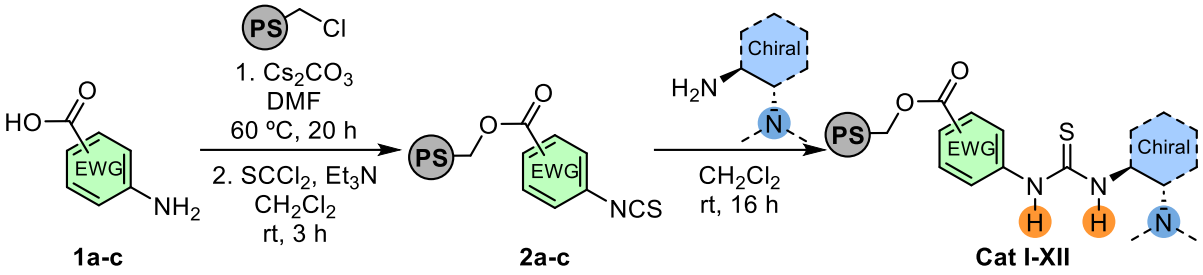
Step 3, Staudinger reaction: The crude azide (1 equiv., 8.74 g, 25 mmol) was dissolved in anhydrous THF (50 mL) under N_2 atmosphere and PPh_3 (1.05 equiv., 6.89 g, 26.25 mmol) was added in portions. The reaction mixture was stirred at 40 °C for 5h. Then, water (5 mL) was added and the mixture was stirred overnight at 40 °C. After solvent removal, the residue was dissolved in aqueous HCl (2N, 80 mL) and wash with DCM (3 x 60 mL). The aqueous layer was basified with NaOH 40 % and extracted with Et_2O (3 x 60 mL). The combined Et_2O phases were dried over $MgSO_4$, filtered and the solvent was evaporated to afford 5.73 g (71% from Quinine) of 9-amino-(9- deoxy)epiquinine as a yellow viscous oil.

Step 4, alkene reduction: 9-amino-(9- deoxy)epiquinine (1 equiv., 0.647 g, 2 mmol) was dissolved in MeOH (10 mL) and added to a solution of Pd on activated charcoal 10% (0.1 equiv., 0.21 g, 0.2 mmol) in MeOH (20 mL). The reaction mixture then purgued with H_2 and shaken overnight at 5 bar of H_2. The reaction mixture was filtered through a short pad of celite and washed with MeOH (3x30 mL) and

concentrated under reduced pressure to obtain 0.5 g (77%) (S)-((1S,2S,4S,5R)-5-ethylquinuclidin-2-yl)(6-methoxyquinolin-4-yl)methanamine as a dark viscous oil.

The reported data match the literature.[4]

General procedure for the synthesis of Merrifield-supported chiral catalysts I-XII:



The synthesis of catalysts **V** is used as example. Other thiourea catalysts were synthesized using analogous procedures. Squaramide catalyst **III** was synthesized following the procedure described in the literature.[5,6]

Step 1, PS-NH_2: Merrifield resin (1 equiv., 1 g, *f*= 1.6 mmol/g, 1.6 mmol) was swollen in dry DMF (6 mL) under N_2 atmosphere, stirring in an orbital shaker. Then, Cs_2CO_3 (1.5 equiv., 0.78 g, 2.4 mmol) and 4-amino-2-(trifluoromethyl)benzoic acid (1.5 equiv., 0.49 g, 2.4 mmol) were added to the previous suspension and the reaction mixture was shaken at room temperature for 1h and afterwards, at 65°C overnight. The resulting resin was allowed to cool down to room temperature, filtered and washed successively with water (60 mL), water/MeOH 1:1 (60 mL), MeOH/CH_2Cl_2 1:1 (60 mL) and (60 mL). The resin was dried overnight at 50°C.

Step 2, PS-NCS: PS-NH_2 (1 equiv., 0.9 g, 1.48 mmol) was swollen for 30 min in dry DCM. Then, Et_3N (4 equiv., 0.82 mL, 5.92 mmol) and thiophosgene (1.2 equiv., 0.14 mL, 1.77 mmol) were added dropwise to the suspension at room temperature under N_2 atmosphere. After 3h, the dark brown mixture was filtered and the resin was washed with DCM (60 mL), THF (60 mL) and DCM (60 mL). The resin was dried under vacuum for 30 min and used directly in the next step.

Step 3, Cat. V: PS-NCS (1 equiv., 0.7 g, 1.08 mmol) was pre-swollen in dry DCM for 30 min, and 9-amino-(9-deoxy)epiquinine (1.5 equiv., 0.52 g, 1.6 mmol) was subsequently added at room temperature. After shaking 16h, the dark brown reaction mixture was filtered and the resin was washed with DCM (60 mL), THF (60 mL) and DCM (60 mL). The resin was dried under vacuum for 12h.

The reported data match the literature.[7]

The catalyst loading of the resin was calculated based on the N elemental analysis by using the following formula:

$$f\left(\frac{mmol}{g}\right) = \frac{\%N\ x\ 1000}{number\ of\ N\ atoms\ x\ MW(N) x\ 100}$$

Elem. Anal. N: 5.04%.

f = 0.90 mmol/g

As-prepared catalyst

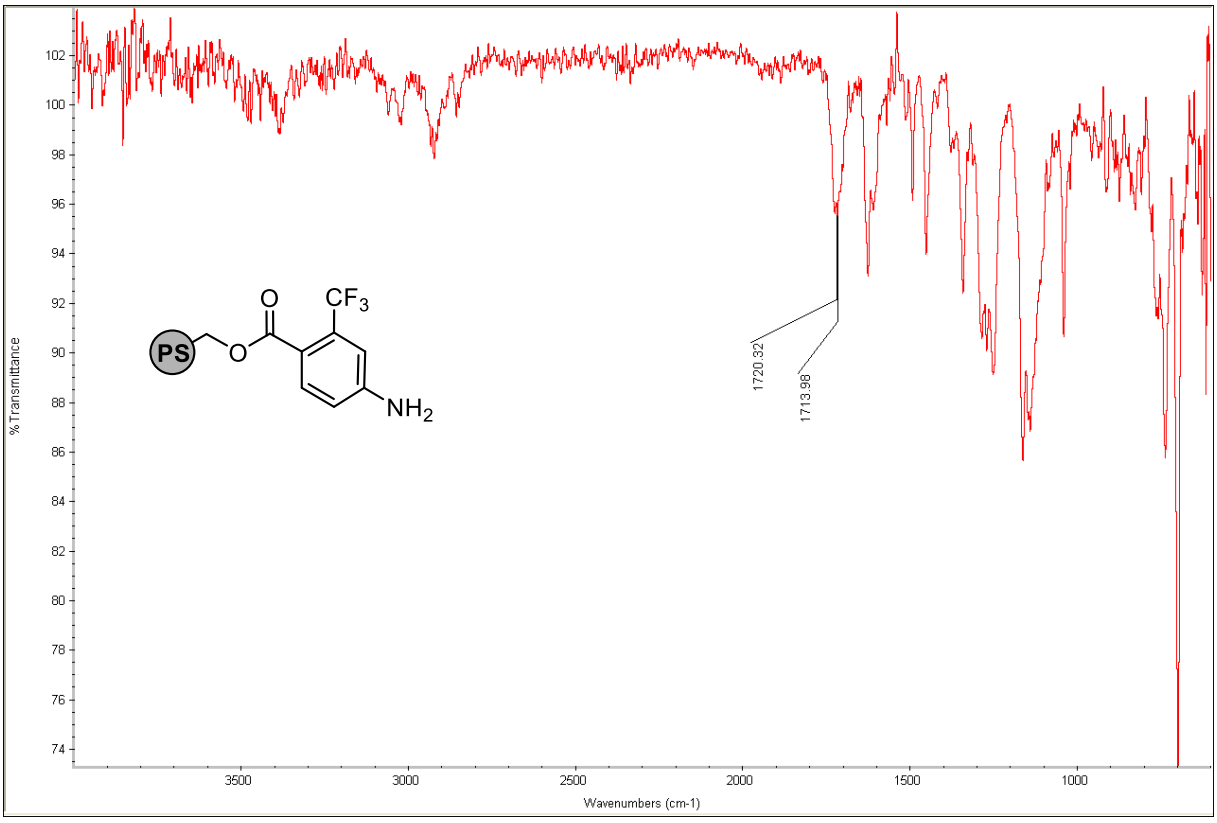


Figure S1. FTIR of the as-prepared **PS-NH$_2$**.

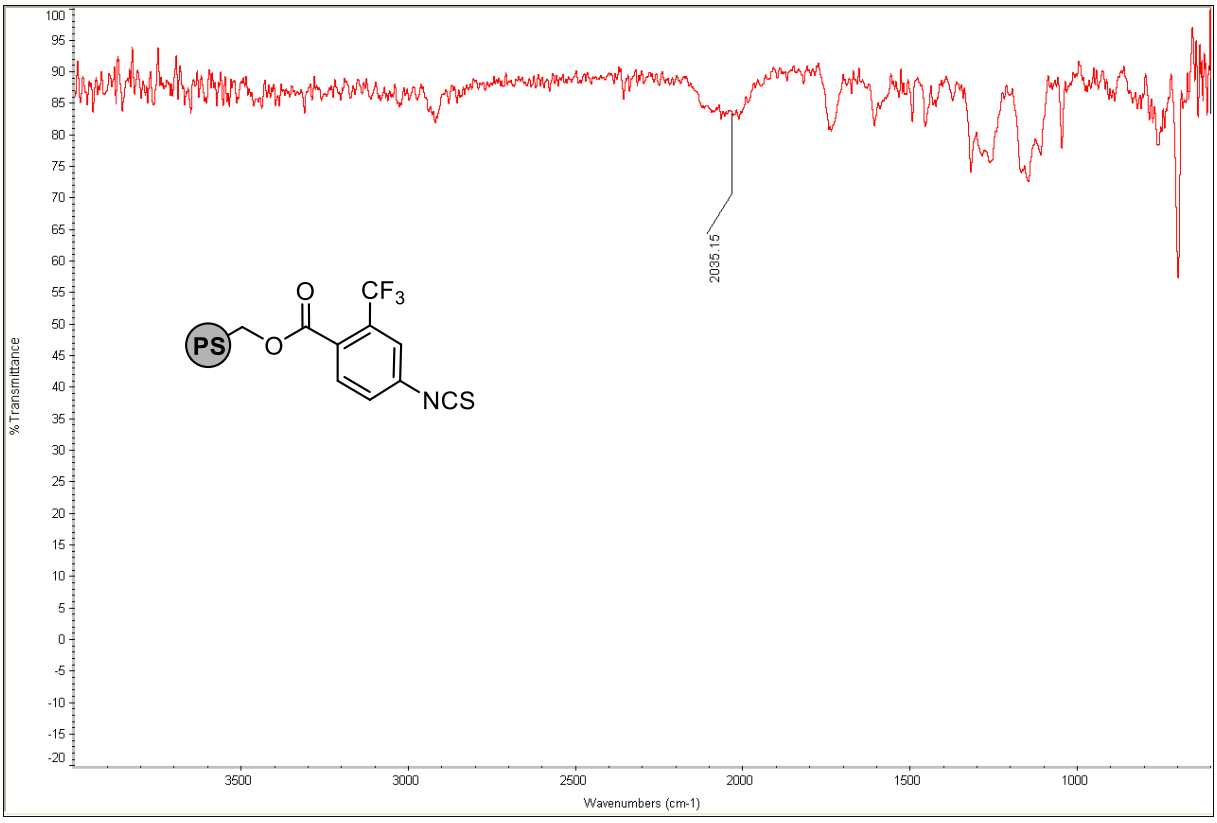


Figure S2. FTIR of the as-prepared **PS-NCS**.

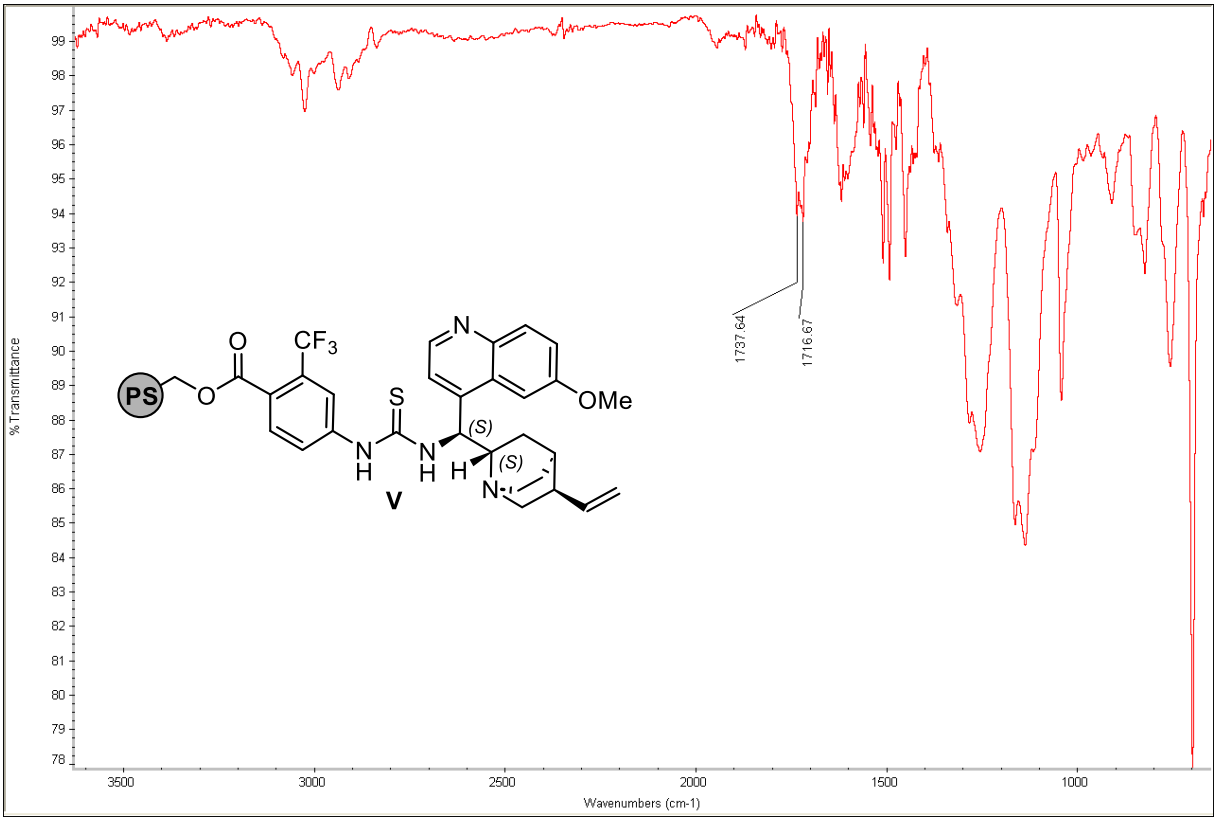


Figure S3. FTIR of the as-prepared catalyst **V**.

Used catalyst (aza-Henry reaction)

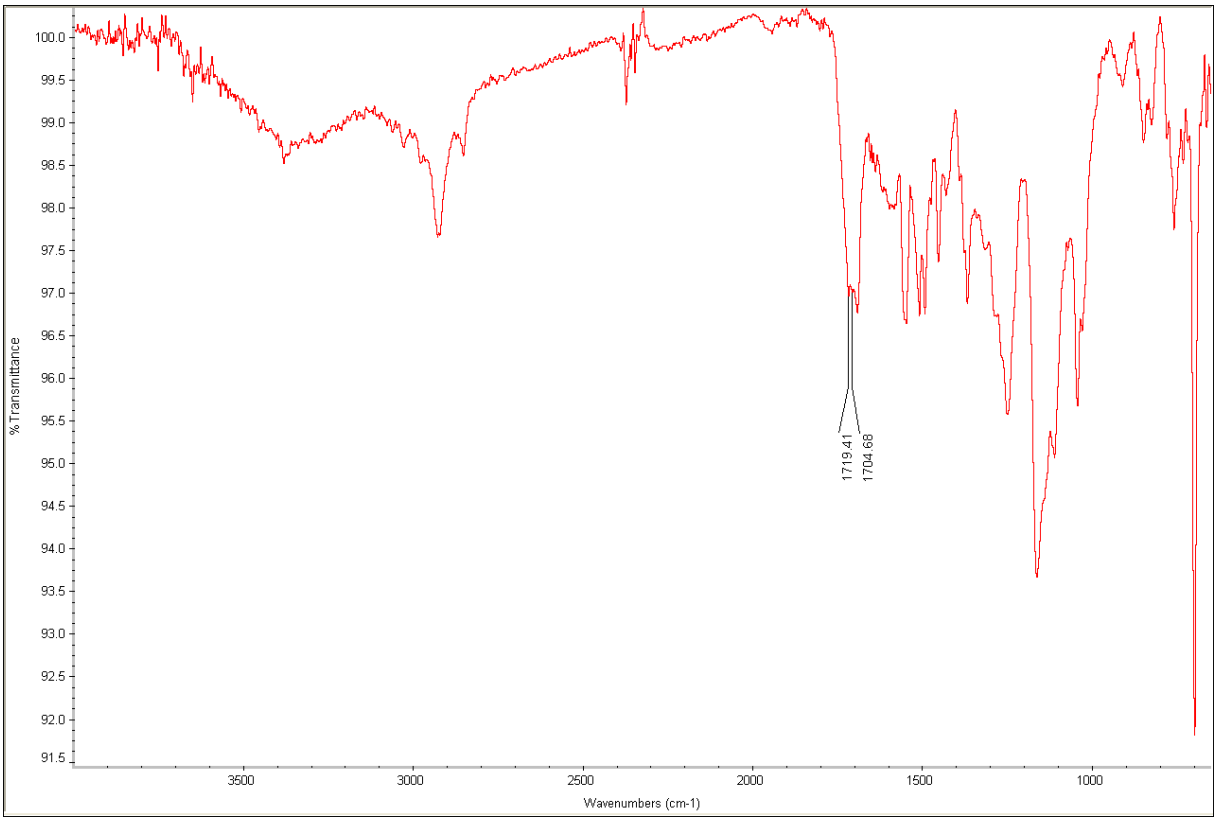


Figure S4. FTIR of catalyst **V** after 15 reaction cycles (aza-Henry reaction).

Used catalyst (Michael reaction)

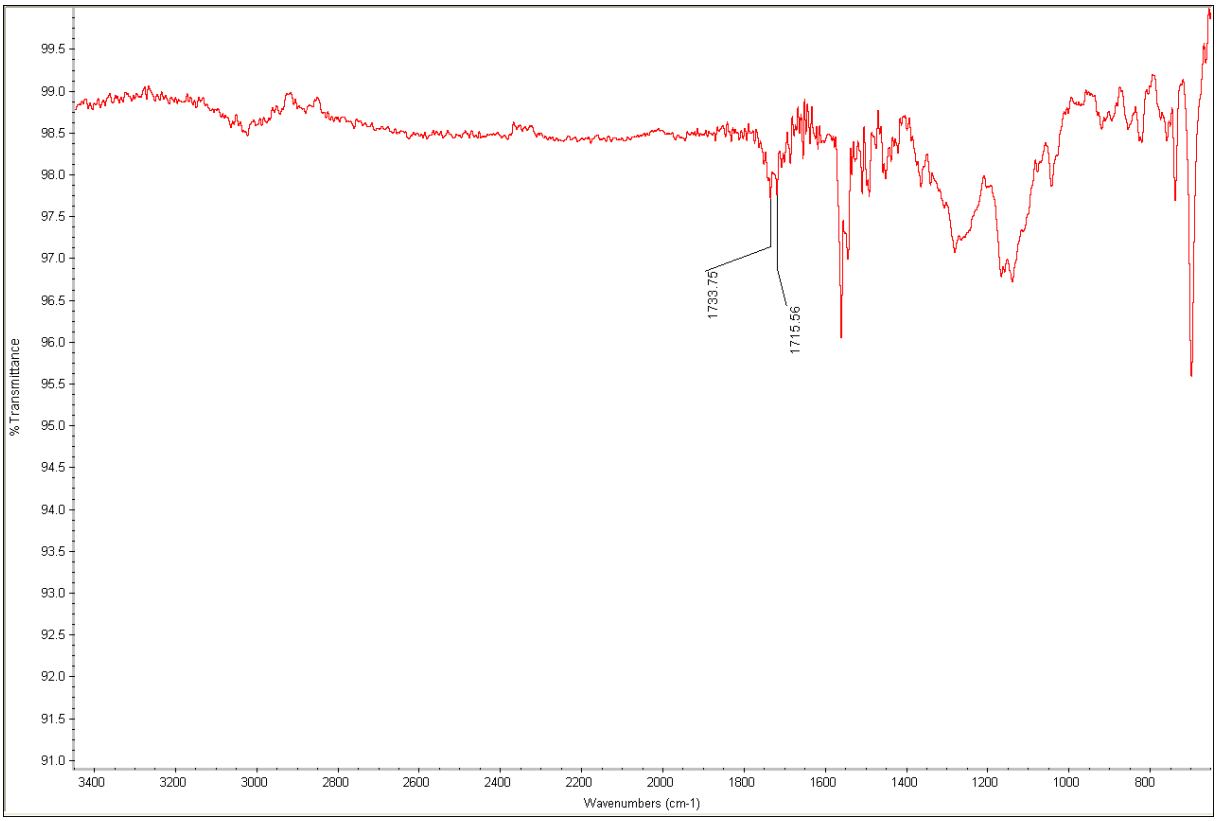


Figure S5. FTIR of catalyst **V** after 10 reaction cycles (Michael reaction).

As-prepared catalyst

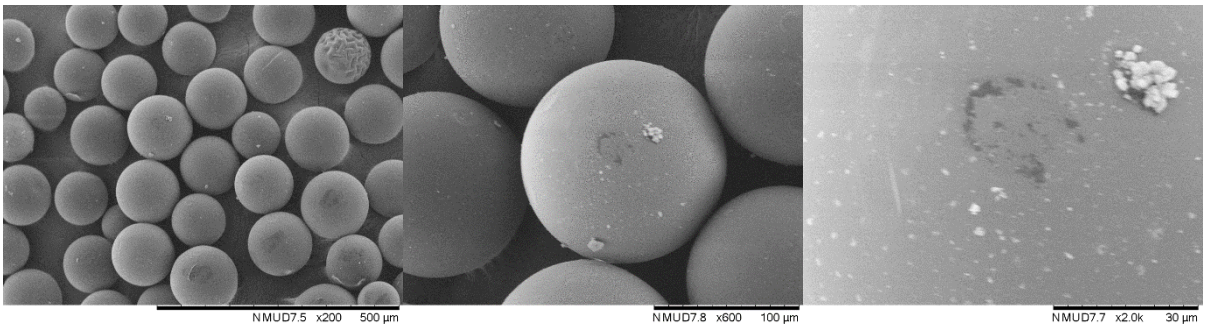


Figure S6. SEM images of the as-prepared catalyst **V**.

Used catalyst (aza-Henry reaction)

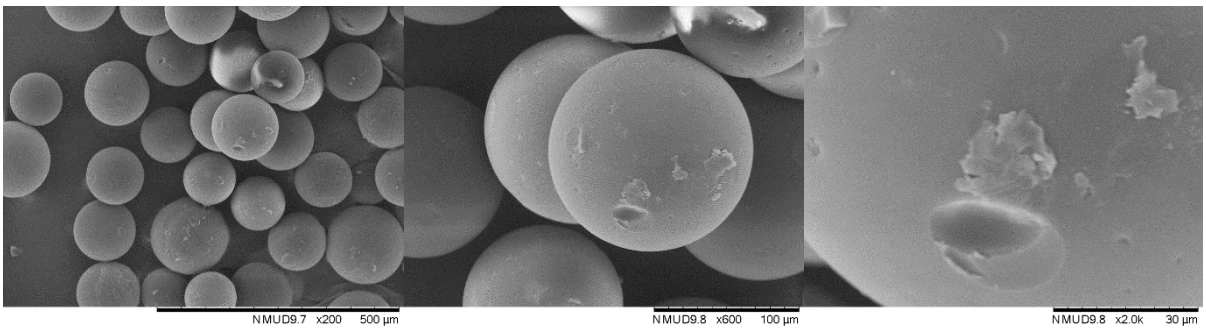


Figure S7. SEM images of catalyst **V** after 15 reaction cycles (aza-Henry reaction).

Used catalyst (Michael reaction)

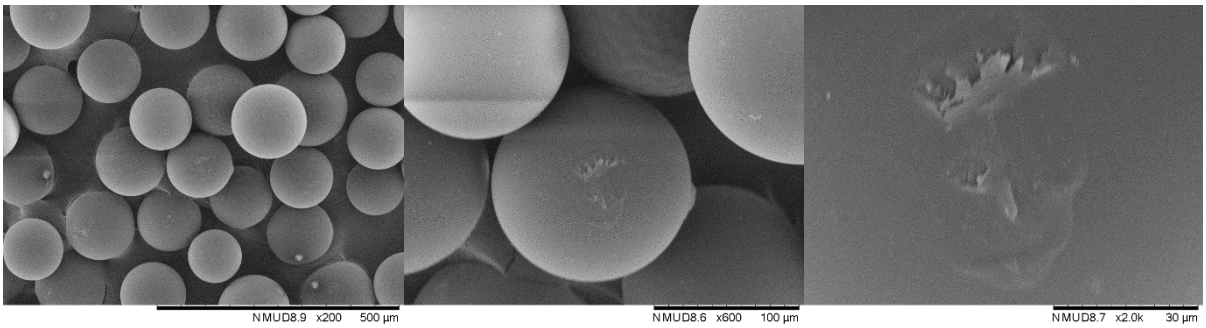


Figure S8. SEM images of catalyst **V** after 10 reaction cycles (Michael reaction).

As-prepared catalyst

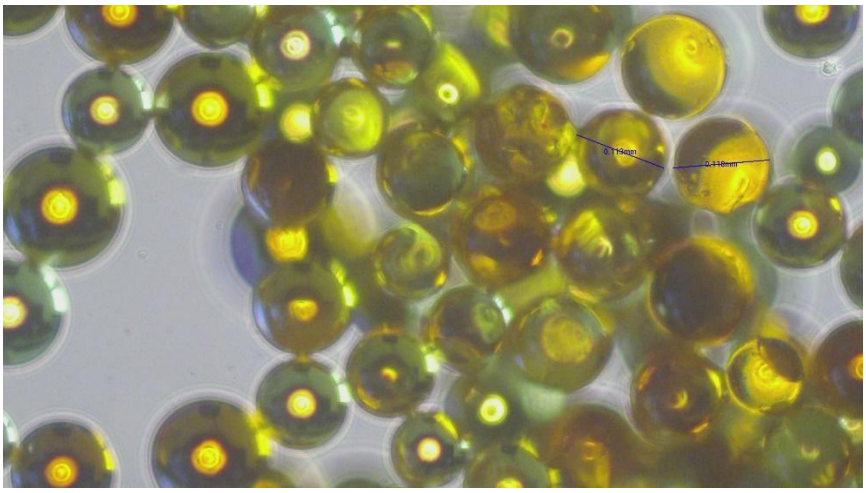


Figure S9. Optical microscope image of the as-prepared catalyst **V**.

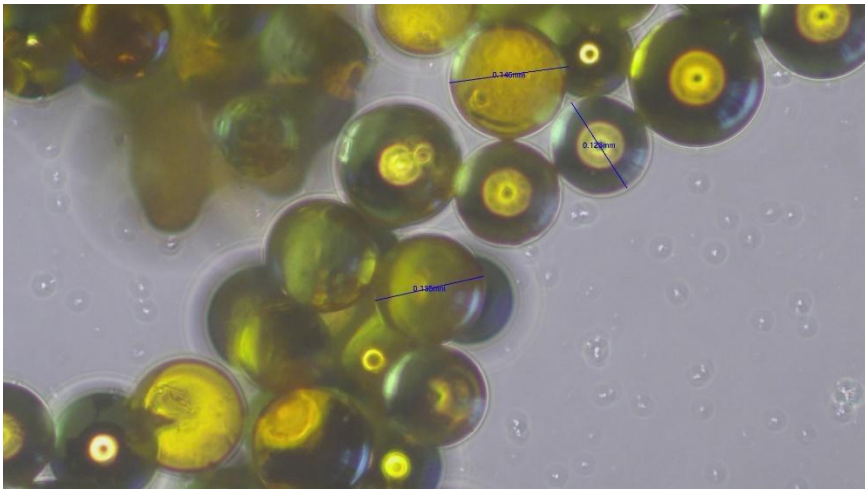


Figure S10. Optical microscope image of catalyst **V** after 15 reaction cycles (aza-Henry reaction).

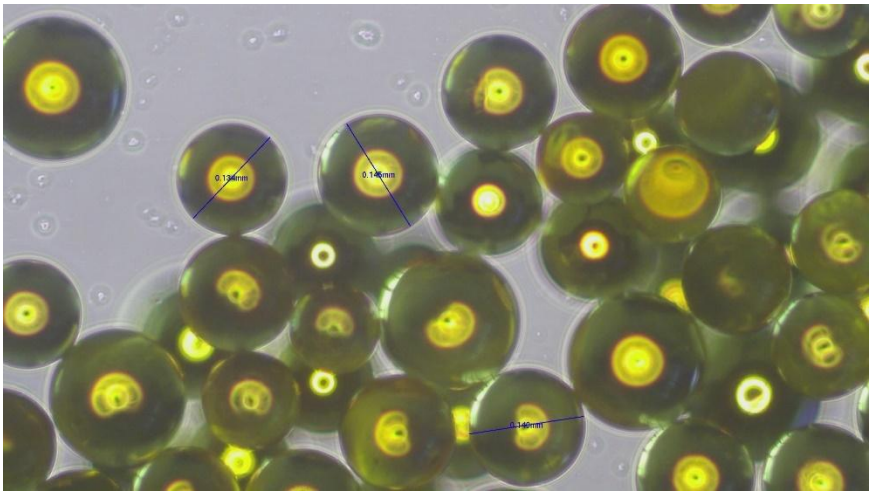


Figure S11. Optical microscope image of catalyst **V** after 10 reaction cycles (Michael reaction).

Reactor setup

All experiments involving the supported catalyst were conducted in filters so that, once the reaction was complete, the product and solvent could be easily separated from the catalyst (Figure S12). Additionally, an orbital shaker was used to stir the reactions, as magnetic stirrers were avoided to prevent mechanical degradation of the polymer-supported catalysts (Figure S13). High and low temperature experiments were carried out as shown (Figure S14).

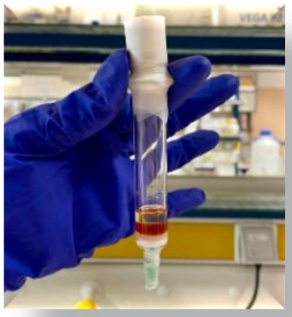


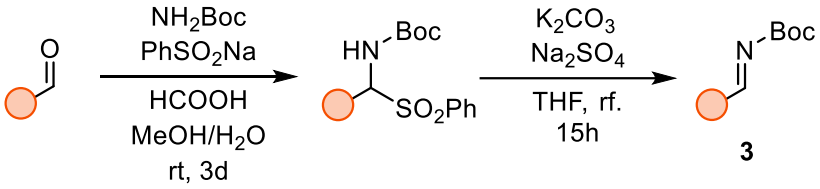
***Figure S12**. The filter where all the tests have been performed*

***Figure S13.** Orbital shaker used to stir the reaction at room temperature*

***Figure S14**. The setup for temperature optimization*

Synthesis and characterization of imines 3

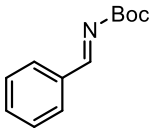
General procedure for the preparation of *N*-Boc imine:



Step 1, α-sulfonyl amine: A reaction mixture was prepared by combining benzaldehyde (1.5 equiv., 3.83 mL, 37.5 mmol), tert-butyl carbamate (1 equiv., 2.93 g, 25 mmol), sodium benzenesulfinate (2 equiv., 8.2 g, 50 mmol) and formic acid (4 equiv., 3.75 mL, 100mmol) in a solvent mixture of methanol (50 mL) and water (100 mL). The reaction was allowed to stir 3 days at room temperature, during which time the product precipitated as a white solid. It was isolated via Büchner funnel filtration and washed with water and diethyl ether. After drying in vacuum, the product was obtained as a white solid (6.6 g, 76%).

Step 2, N-Boc imine: A 100 mL round-bottom flask containing potassium carbonate (6.00 equiv., 4.14 g, 30.0 mmol) and sodium sulfate (5.00 equiv., 5 g, 5 mmol) was flame-dried under vacuum and cooled under an inert atmosphere. Subsequently, the corresponding sulfonyl amine (1 equiv., 1.19 g, 5 mmol) was added with dry THF (40 mL). The mixture was refluxed under N_2 for 15h. After cooling to room temperature, it was filtered and the solvent was evaporated to afford imines **3a-l** as an oil. The appearance of the oil varied in color depending on the nature of the substituent in the starting material. The crude imine was used directly in the step without further purification.[8]

Tert-butyl (*E*)-benzylidenecarbamate (3a)

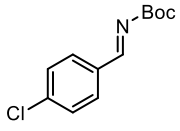


The general procedure was followed to afford 0.46 g (74 %) of the product as a white-yellow liquid. The reported data match the literature.[8]

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.86 (s, 1H), 7.90 (d, $^{3}J_{HH}$ = 9.6 Hz, 2H), 7.55 (t, 1H), 7.45 (t, $^{3}J_{HH}$ = 6.7 Hz, 2H), 1.58 (s, 9H).

^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ 169.7, 162.7, 134.2, 133.6, 130.3, 129.0, 82.4, 28.0.

Tert-butyl (*E*)-(4-chlorobenzylidene)carbamate (3b)

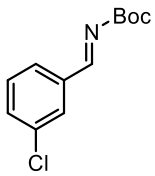


The general procedure was followed to afford 1.16 g (97 %) of the product as a white-yellow solid. The reported data match the literature.[8]

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.64 (s, 1H), 7.66 (d, $^{3}J_{HH}$ = 8.6 Hz, 2H), 7.25 (d, $^{3}J_{HH}$ = 8.5 Hz, 2H), 1.43 (s, 9H).

^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ 167.2, 161.6, 139.0, 132.0, 130.6, 128.6, 81.5, 27.3.

Tert-butyl (*E*)-(3-chlorobenzylidene)carbamate (3c)

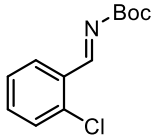


The general procedure was followed to afford 0.50 g (49 %) of the product as a white liquid. The reported data match the literature.[9]

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.79 (s, 1H), 7.94 (s, 1H), 7.74 (d, $^{3}J_{HH}$ = 7.8 Hz, 1H), 7.52 (d, $^{3}J_{HH}$ = 6.9 Hz, 1H), 7.40 (t, $^{3}J_{HH}$ = 7.8 Hz, 1H), 1.58 (s, 9H).

^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ 167.4, 161.7, 135.4, 134.7, 132.9, 129.8, 128.9, 128.2, 82.2, 27.5.

Tert-butyl (*E*)-(2-chlorobenzylidene)carbamate (3d)

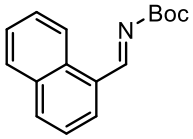


The general procedure was followed to afford 0.75 g (87 %) of the product as a white liquid. The reported data match the literature.[9]

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.25 (s, 1H), 8.16 (t, $^{3}J_{HH}$ = 8.0 Hz, 1H), 7.41 (t, 2H), 7.30 (t, $^{3}J_{HH}$ = 7.8 Hz, 1H), 1.57 (s, 9H).

^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ 165.4, 162.1, 137.6, 134.0, 131.1, 129.9, 128.9, 126.9, 82.4, 27.7.

Tert-butyl (*E*)-(naphthalen-1-ylmethylene)carbamate (3e)

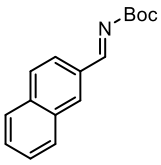


The general procedure was followed to afford 1.26 g (99 %) of the product as a yellow liquid. The reported data match the literature.[9]

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.53 (s, 1H), 8.93 (d, $^{3}J_{HH}$ =8.6 Hz, 1H), 8.16 (d, $^{3}J_{HH}$ = 7.3 Hz, 1H), 8.02 (d, $^{3}J_{HH}$ =8.3 Hz, 1H), 7.89 (d, $^{3}J_{HH}$ = 8.1 Hz, 1H), 7.63 (t, $^{3}J_{HH}$ = 7.8 Hz, 1H), 7.54 (d, $^{3}J_{HH}$ = 8.4 Hz, 2H), 1.64 (s, 9H).

^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ 169.0, 162.9, 134.3, 133.8, 132.0, 131.9, 129.3, 128.9, 128.2, 126.6, 125.2, 124.0, 82.3, 28.1.

Tert-butyl (*E*)-(naphthalen-2-ylmethylene)carbamate (3f)

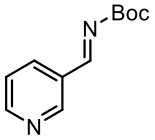


The general procedure was followed to afford 1.16 g (91 %) of the product as a white solid. The reported data match the literature.[10]

^{1}H NMR (400 MHz, $CDCl_3$) δ (s, 1H), 8.21 (d, 1H), 8.03 (d, $^{3}J_{HH}$ =8.6 Hz, 1H), 7.83 (t, $^{3}J_{HH}$ = 13.1 Hz, 3H), 7.50 (d, $^{3}J_{HH}$ = 14.6 Hz, 2H), 1.60 (s, 9H).

^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ 170.2, 163.1, 136.4, 134.5, 133.1, 132.2, 129.6, 129.2, 129.0, 128.3, 127.6, 124.3, 82.6, 28.4.

Tert-butyl (*E*)-(pyridin-3-ylmethylene)carbamate (3g)

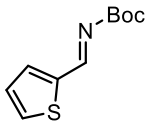


The general procedure was followed to afford 0.98 g (95 %) of the product as an orange liquid. The reported data match the literature.[9]

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.99 (s, 1H), 8.85 (d, $^{3}J_{HH}$ = 7.8 Hz, 1H), 8.75 (d, $^{4}J_{HH}$ = 4.8 Hz, 1H), 8.26 (dd, $^{3}J_{HH}$ = 8.0 Hz, $^{4}J_{HH}$ = 2.0 Hz, 1H), 7.39 (d, $^{3}J_{HH}$ = 7.1 Hz, 1H), 1.57 (s, 9H).

^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ 166.8, 162.1, 154.0, 152.3, 136.0, 130.0, 124.0, 83.0, 28.0.

Tert-butyl (*E*)-(thiophen-2-ylmethylene)carbamate (3h)

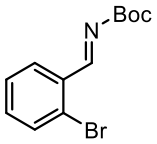


The general procedure was followed to afford 0.92 g (97 %) of the product as a brown liquid. The reported data match the literature.[10]

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.02 (s, 1H), 7.66 (d, $^{4}J_{HH}$ = 3.9 Hz, 1H), 7.62 (s, 1H), 7.15 – 7.10 (m, 1H), 1.52 (s, 9H).

^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ 163.5, 162.2, 140.3, 137.1, 134.2, 128.4, 82.1, 28.0.

Tert-butyl (*E*)-(2-bromobenzylidene)carbamate (3i)

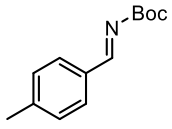


The general procedure was followed to afford 1.29 g (91 %) of the product as a white liquid. The reported data match the literature.[11]

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.15 (s, 1H), 8.12 (t, $^{3}J_{HH}$ = 9.6 Hz, 1H), 7.56 (t, $^{3}J_{HH}$ = 9.3 Hz, 1H), 7.32 (d, $^{3}J_{HH}$ = 9.5 Hz, 2H), 1.55 (s, 9H).

^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ 168.2, 162.5, 135.6, 134.7, 133.8, 133.0, 129.8, 128.1, 82.9, 28.3.

Tert-butyl (*E*)-(4-methylbenzylidene)carbamate (3j)

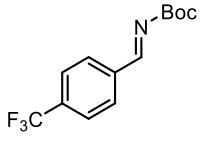


The general procedure was followed to afford 0.42 g (53 %) of the product as a yellow solid. The reported data match the literature.[8]

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.87 (s, 1H), 7.81 (d, $^{3}J_{HH}$ = 8.3 Hz, 2H), 7.27 (d, $^{3}J_{HH}$ = 8.1 Hz, 2H), 2.42 (s, 3H), 1.59 (s, 9H).

^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ 170.4, 163.2, 145.0, 132.0, 130.8, 130.1, 82.5, 28.4, 22.3.

Tert-butyl (*E*)-(4-(trifluoromethyl)benzylidene)carbamate (3k)



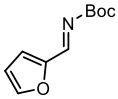
The general procedure was followed to afford 1.29 g (94 %) of the product as a white solid. The reported data match the literature.[8]

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.81 (s, 1H), 7.97 (d, $^{3}J_{HH}$ = 8.1 Hz, 2H), 7.68 (d, $^{3}J_{HH}$ = 8.1 Hz, 2H), 1.55 (s, 9H).

^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ 167.2 (s), 162.1 (s), 137.2 (s), 134.6 (q), 130.1 (s), 125.8 (s), 82.7 (s), 27.8 (s).

^{19}F {^{1}H} NMR (376 MHz, $CDCl_3$) δ -63.19.

Tert-butyl (*E*)-(furan-2-ylmethylene)carbamate (3l)



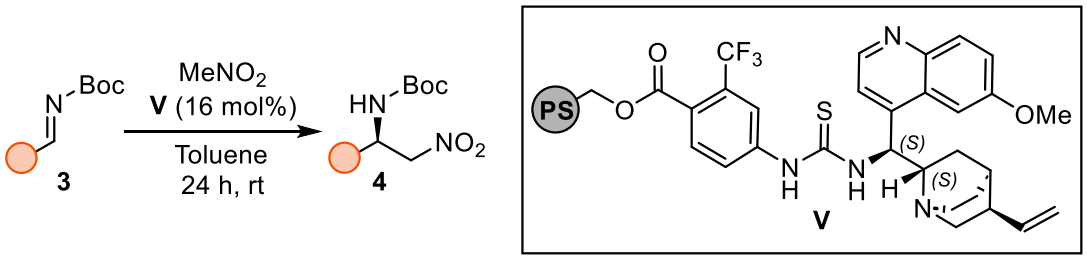
The general procedure was followed to afford 0.77 g (79 %) of the product as a brown liquid. The reported data match the literature.[10]

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.75 (s, 1H), 7.67 (s, 1H), 7.21 (d, $^{4}J_{HH}$ = 3.6 Hz, 2H), 6.58 (d, $^{4}J_{HH}$ = 1.9 Hz, 1H), 1.55 (s, 9H).

^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ 162.3, 157.6, 150.9, 148.2, 121.4, 113.1, 82.2, 28.0.

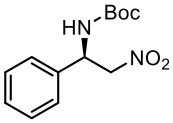
Synthesis and characterization of β-nitro amines 4

General procedure for the enantioselective aza-Henry reaction:



In a filtered tube were added a solution of the imine in toluene (1 equiv., 1 mL, 0.2 mmol, 0.2 M), the supported-catalyst (0.16 equiv., *f*= 0.7 mmol/g, 44.0 mg, 0.032 mmol) and nitromethane (5 equiv., 53 µL, 1 mmol). The tube was shaked at room temperature overnight. Afterward, the reaction mixture was filtered off and the supported catalyst was washed three times with DCM (2 mL). After evaporating the solvent, the reaction crude was purified by chromatography in hexane/EtOAc to afford aza-Henry adducts **4a-l**. Racemic products **4** were synthesized using trimethylamine (10 mol%) as the catalyst.[12]

Tert-butyl (*R*)-(2-nitro-1-phenylethyl)carbamate (4a)



The general procedure was followed to afford 50.0 mg (94%) of the product as a white solid. The reported data match the literature.[2]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.29 (m, 5H), 5.42 – 5.19 (m, 2H), 4.85 (s, 1H), 4.71 (dd, $^{3}J_{HH}$ = 12.6 Hz, $^{3}J_{HH}$ = 5.6 Hz, 1H), 1.44 (s, 9H).

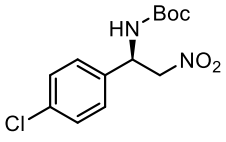
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ 154.9, 137.0, 129.4, 128.9, 126.5, 80.9, 79.0, 53.1, 28.4.

The absolute configuration of **4a** was determined by comparing the HPLC data with the literature:
HPLC (chiral): Chiralpak-IA, n-heptane/EtOH 98:2, 1.0 mL/min, 40 °C, detection at 230 nm. Residence time: 18.8 min (major), 20.7 (minor). 91:9 er.
Lit. for (*R*) isomer HPLC (chiral): Chiralpak IA, Hexanes/i-PrOH 90:10, 1.0 mL/min, temperature not specified, detection at 210 nm. Residence time: 12.0 min (major), 13.0 (minor).

The accumulated turnover number (TON) was calculated using the average yield of all the recycling tests for compound **4a**.

$$\mathrm{TON} = \frac{mmoles\ limiting\ reactant}{mmoles\ catalyst} \times yield = \frac{3.0}{0.032} \times 0.89 = 83.4$$

Tert-butyl (*R*)-(1-(4-chlorophenyl)-2-nitroethyl)carbamate (4b)



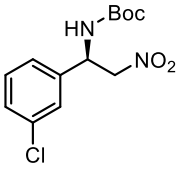
The general procedure was followed to afford 55.0 mg (93%) of the product as a white solid. The reported data match the literature.[2]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, $^3J_{HH}$ = 8.5 Hz, 2H), 7.27 (, $^3J_{HH}$= 9.0 Hz, 2H), 5.37 (s, 2H), 4.84 (s, 1H), 4.71 (d, $^3J_{HH}$ = 7.6 Hz, 1H), 1.46 (s, 9H).

^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ 154.8, 135.6, 134.8, 131.1, 129.5, 127.9, 78.8, 52.4, 28.4.

HPLC (chiral): Chiralpak-IA, n-heptane/EtOH 95:5, 1.0 mL/min, 40 °C, detection at 254 nm. Residence time: 10.65 min (major), 12.52 (minor). 86:14 er.

Tert-butyl (*R*)-(1-(3-chlorophenyl)-2-nitroethyl)carbamate (4c)



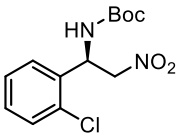
The general procedure was followed to afford 56.0 mg (93%) of the product as a white solid. The reported data match the literature.[13]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, $^2J_{HH}$ = 4.4 Hz, 1H), 7.36 (d, $^2J_{HH}$= 4.4 Hz, 1H), 7.30 (d, $^3J_{HH}$= 5.0 Hz, 2H), 5.73 (s, 1H), 4.88 - 4.80 (m, 1H), 1.43 (s, 9H), 1.25 (s, 2H).

^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ 132.8, 130.5, 130.2, 130.1, 128.2, 127.7, 83.6, 50.8, 29.9, 28.4.

HPLC (chiral): Chiralpak-IA, n-heptane/EtOH 99:1, 1.0 mL/min, 40 °C, detection at 230 nm. Residence time: 15.12 min (major), 16.77 (minor). 92:8 er.

Tert-butyl (*R*)-(1-(2-chlorophenyl)-2-nitroethyl)carbamate (4d)



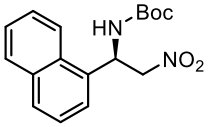
The general procedure was followed to afford 56.0 mg (93%) of the product as a white solid. The reported data match the literature.[14]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (dd, $^3J_{HH}$ = 5.9, $^4J_{HH}$ =3.4 Hz, 1H), 7.37 – 7.33 (m, 1H), 7.29 (dd, $^3J_{HH}$ = 5.9, $^4J_{HH}$ = 3.6 Hz, 2H), 5.73 (s, 2H), 4.94 – 4.68 (m, 2H), 1.43 (s, 9H).

^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ 154.7, 134.4, 132.7, 130.4, 130.0, 129.8, 128.2, 127.7, 80.9, 51.7, 28.4.

HPLC (chiral): Chiralpak-IA, n-heptane/EtOH 98:2, 1.0 mL/min, 40 °C, detection at 254 nm. Residence time: 13.94 min (major), 14.60 (minor). 86:14 er.

Tert-butyl (*R*)-(1-(naphthalen-1-yl)-2-nitroethyl)carbamate (4e)



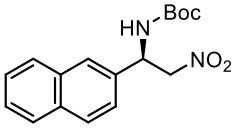
The general procedure was followed to afford 57.0 mg (90%) of the product as a white solid. The reported data match the literature.[2]

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, $^3J_{HH}$ = 8.6 Hz, 1H), 7.91 (d, $^3J_{HH}$ =9.9 Hz, 1H), 7.86 (dd, $^3J_{HH}$ =6.8, $^4J_{HH}$ =2.8 Hz, 1H), 7.62 (t, 1H), 7.55 (t, 1H), 7.46 (t, 2H), 6.28 (d, $^4J_{HH}$ = 6.6 Hz, 1H), 5.30 (s, 1H), 4.91 (s, 2H), 1.44 (s, 9H).

^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ 154.8, 134.2, 132.7, 130.4, 129.7, 129.4, 127.4, 126.4, 125.4, 123.4, 122.3, 80.9, 78.4, 49.4, 28.4.

HPLC (chiral): Chiralpak-IA, n-heptane/EtOH 99:1, 1.0 mL/min, 40 °C, detection at 254 nm. Residence time: 15.45 min (major), 19.64 (minor). 88:12 er.

Tert-butyl (*R*)-(1-(naphthalen-2-yl)-2-nitroethyl)carbamate (4f)



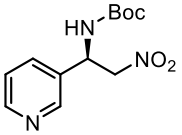
The general procedure was followed to afford 60.0 mg (95%) of the product as a white solid. The reported data match the literature.[13]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (t, 3H), 7.76 (s, 1H), 7.51 (d, $^3J_{HH}$ = 9.5 Hz, 2H), 7.40 (dd, $^3J_{HH}$ = 8.5 Hz, $^4J_{HH}$ = 2.0 Hz, 1H), 5.48 (d, 2H), 4.93 (s, 1H), 4.80 (dd, $^3J_{HH}$ = 12.7 Hz, $^4J_{HH}$ = 5.7 Hz, 1H), 1.45 (s, 9H).

^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ 154.8, 134.2, 133.3, 133.2, 129.3, 128.1, 127.7, 126.8, 126.6, 125.6, 123.8, 80.8, 78.9, 53.1, 28.3.

HPLC (chiral): Chiralpak-IA, n-heptane/EtOH 99:1, 1.0 mL/min, 40 °C, detection at 254 nm.
Residence time: 20.31 min (major), 24.57 (minor). 89:11 er.

Tert-butyl (*R*)-(2-nitro-1-(pyridin-3-yl)ethyl)carbamate (4g)



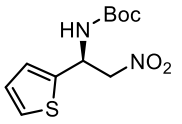
The general procedure was followed to afford 40.0 mg (75%) of the product as a white solid. The reported data match the literature.[14]

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60 (d, $^3J_{HH}$ = 8.0 Hz, 2H) , 7.65 (d, $^3J_{HH}$ = 8.0 Hz, 1H), 7.32 (dd, $^3J_{HH}$= 8.0 Hz, $^4J_{HH}$ =4.9 Hz, 1H), 5.42 (d, $^4J_{HH}$= 5.7 Hz, 2H), 4.89 (s, 1H), 4.75 (dd, $^3J_{HH}$ = 13.3 Hz, $^4J_{HH}$ =4.8 Hz, 1H), 1.44 (s, 9H).

^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ 154.8, 150.2, 148.3, 134.2, 132.9, 124.0, 81.3, 78.4, 51.0, 28.4.

HPLC (chiral): Chiralpak-IA, n-heptane/EtOH 90:10, 1.0 mL/min, 40 °C, detection at 210 nm.
Residence time: 10.90 min (major), 13.41 (minor). 94:6 er.

Tert-butyl (*R*)-(2-nitro-1-(thiophen-2-yl)ethyl)carbamate (4h)



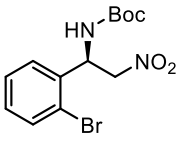
The general procedure was followed to afford 48.0 mg (90%) of the product as a white solid. The reported data match the literature.[15]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (dd, $^4J_{HH}$= 5.0, $^4J_{HH}$= 1.4 Hz, 1H), 6.98 (dd, $^3J_{HH}$ = 9.1 Hz, $^4J_{HH}$= 4.1 Hz, 2H) 5.66 – 5.58 (m, 1H), 5.33 (s, 1H), 4.89 (s, 1H), 4.75 (dd, $^3J_{HH}$ = 12.9 Hz, $^4J_{HH}$ =5.6 Hz, 1H), 1.45 (s, 9H).

^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ 155.0, 140.5, 127.8, 126.1, 125.7, 81.4, 79.1, 49.3, 28.7.

HPLC (chiral): Chiralpak-IA, n-heptane/EtOH 99:1, 1.0 mL/min, 40 °C, detection at 254 nm.
Residence time: 20.43 min (major), 22.73 (minor). 88:12 er.

Tert-butyl (*R*)-(1-(2-bromophenyl)-2-nitroethyl)carbamate (4i)



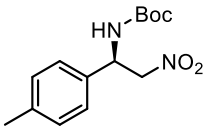
The general procedure was followed to afford 54.0 mg (80%) of the product as a white solid. The reported data match the literature.[16]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, $^3J_{HH}$ = 7.6 Hz, 1H), 7.36 – 7.32 (m, 2H), 7.23 – 7.18 (m, 1H), 5.73 (s, 2H), 4.91 – 4.67 (m, 2H), 1.43 (s, 9H).

^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ 154.64, 136.06, 133.72, 130.56, 130.24, 128.24, 128.04, 122.82, 80.92, 52.61, 28.36.

HPLC (chiral): Chiralpak-IA, n-heptane/EtOH 98:2, 1.0 mL/min, 40 °C, detection at 254 nm.
Residence time: 15.78 min (minor), 25.48 (major). 10:90 er.

Tert-butyl (*R*)-(1-(2-bromophenyl)-2-nitroethyl)carbamate (4j)



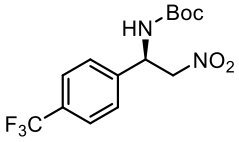
The general procedure was followed to afford 30.0 mg (54%) of the product as a white solid. The reported data match the literature.[14]

^{1}H NMR (400 MHz, Acetone-d6) δ 7.36 (d, $^3J_{HH}$ = 8.1 Hz, 2H), 7.20 (d, $^3J_{HH}$= 7.9 Hz, 2H), 6.80 (s, 1H), 5.44 (d, $^3J_{HH}$ = 7.4 Hz, 1H), 4.87 (d, $^3J_{HH}$ = 8.1 Hz, 2H), 2.31 (s, 3H), 1.38 (s, 9H).

^{13}C {^{1}H} NMR (101 MHz, Acetone-d6) δ 192.6, 155.9, 138.7, 136.7, 130.3, 127.7, 79.8, 53.8, 28.6, 21.2.

HPLC (chiral): Chiralpak-IA, n-heptane/EtOH 97:3, 1.0 mL/min, 40 °C, detection at 254 nm.
Residence time: 11.33 min (major), 12.76 (minor). 91:9 er.

Tert-butyl (*R*)-(2-nitro-1-(4-(trifluoromethyl)phenyl)ethyl)carbamate (4k)



The general procedure was followed to afford 44.0 mg (66%) of the product as a white solid. The reported data match the literature.[2]

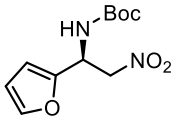
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, $^3J_{HH}$ = 8.4 Hz, 2H), 7.45 (d, $^3J_{HH}$= 8.4 Hz, 2H), 5.44 (s, 2H), 4.85 (s, 1H), 4.74 (s, 1H), 1.44 (s, 9H).

^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ 154.7(s), 141.1 (s), 131.1 (s), 126.9 (s), 126.3 (q, $^2J_{HH}$ = 4.0 Hz), 126.3 (s), 81.2 (s), 78.7 (s), 52.5 (s), 28.3 (s).

^{19}F {^{1}H} NMR (376 MHz, $CDCl_3$) δ -62.78.

HPLC (chiral): Chiralpak-IA, n-heptane/EtOH 97:3, 1.0 mL/min, 40 °C, detection at 254 nm.
Residence time: 13.45 min (major), 15.29 (minor). 62:38 er.

Tert-butyl (*R*)-(1-(furan-2-yl)-2-nitroethyl)carbamate (4l)



The general procedure was followed to afford 38.0 mg (75%) of the product as a white solid. The reported data match the literature.[2]

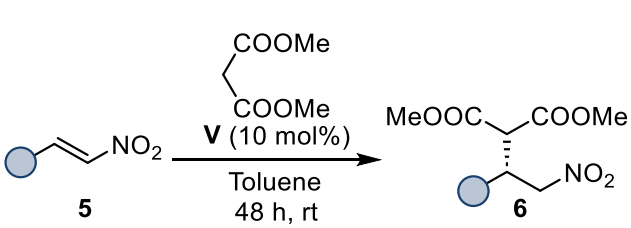
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (s, 1H), 6.32 (dd, $^3J_{HH}$ = 13.0 Hz, $^4J_{HH}$= 2.6 Hz, 2H), 5.51-5.22 (m, 2H), 4.83 (s, 1H), 4.72 (dd, $^3J_{HH}$ = 12.9 Hz, $^4J_{HH}$ =5.8 Hz, 1H), 1.45 (s, 9H).

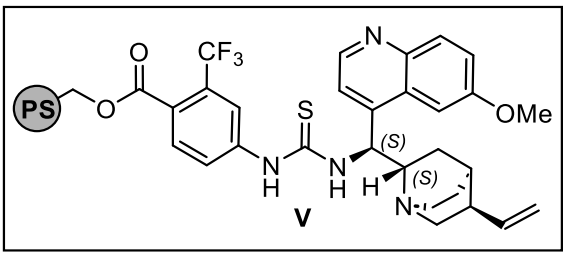
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ 154.8, 149.6, 143.0, 110.8, 107.9, 81.0, 76.7, 47.3, 28.4.

HPLC (chiral): Chiralpak-IA, n-heptane/EtOH 98:2, 1.0 mL/min, 40 °C, detection at 254 nm.
Residence time: 15.03 min (minor), 20.16 (major). 37:63 er.

Synthesis and characterization of Michael adducts 6

General procedure for the enantioselective Michael addition:

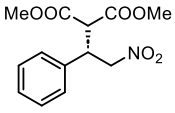




A solution of β-Nitrostyrene **5a** (1 equiv., 74.5 mg, 0.5 mmol) and dimethyl malonate (2 equiv., 114 µL, 1.0 mmol) in toluene (1.0 mL, 1 M) was added to a fritted tube containing the catalyst **V** (0.1 equiv., 74 mg, 0.05 mmol). The tube was then closed with a rubber septum and shaken at room temperature for 2 days. The reaction mixture was filtered off and the supported catalyst was washed three times with

DCM (2 mL). After evaporating the solvent, the reaction crude was purified by chromatography in Hexanes/EtOAc to afford Michael adduct **6a**. Racemic products **6** were synthesized using trimethylamine (10 mol%) as the catalyst.

(*S*)-dimethyl 2-(2-nitro-1-phenylethyl)malonate (6a)



The general procedure was followed to afford 116.0 mg (83%) of the product as a yellow solid. The reported data match the literature.[17]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.19 (m, 5H), 4.99 – 4.79 (m, 2H), 4.29 – 4.19 (m, 1H), 3.86 (d, $^3J_{HH}$ = 9.0 Hz, 1H), 3.76 (s, 3H), 3.56 (s, 3H).

^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ 168.0, 167.4, 136.3, 129.2, 128.6, 128.0, 77.5, 54.9, 53.2, 53.0, 43.1.

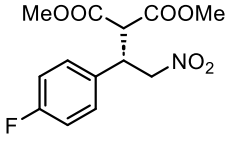
HPLC (chiral): Chiralpak-IA, n-heptane/EtOH 99:1, 1.0 mL/min, 40 °C, detection at 254 nm.

Residence time: 18.5 min (major), 26.8 (minor). 90:10 er.

The accumulated turnover number (TON) was calculated using the average yield of all the recycling tests for compound **6a**.

$$\mathrm{TON} = \frac{mmoles\ limiting\ reactant}{mmoles\ catalyst} \times yield = \frac{5.0}{0.05} \times 0.61 = 61.0$$

(S)-dimethyl 2-(1-(4-fluorophenyl)-2-nitroethyl)malonate (6b)



The general procedure was followed to afford 135.0 mg (90 %) of the product as a yellow solid. The reported data match the literature.[18]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 – 7.19 (m, 2H), 7.01 (t, $^3J_{HH}$ = 8.6 Hz, 2H), 4.93 – 4.80 (m, 2H), 4.26 – 4.20 (m, 1H), 3.82 (d, $^3J_{HH}$ = 9.1 Hz, 1H), 3.76 (s, 3H), 3.57 (s, 3H).

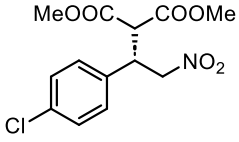
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ 168.1, 167.6, 164.2, 161.7, 130.2, 130.1 (d, $^3J_{HH}$ = 8.4 Hz), 116.6 (d, $^3J_{HH}$ = 21.4 Hz), 116.4, 55.1, 53.5, 53.3, 42.7.

^{19}F NMR (376 MHz, $CDCl_3$) δ -113.2.

HPLC (chiral): Chiralpak-IA, n-heptane/EtOH 99:1, 1.0 mL/min, 40 °C, detection at 254 nm.

Residence time: 26.6 min (major), 34.4 (minor). 92:8 er.

(S)-dimethyl 2-(1-(4-chlorophenyl)-2-nitroethyl)malonate (6c)



The general procedure was followed to afford 0.140 g (89%) of the product as a yellow solid. The reported data match the literature.[3]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (d, $^3J_{HH}$ = 8.6 Hz, 2H), 7.16 (d, $^3J_{HH}$ = 8.8 Hz, 2H), 4.91 – 4.77 (m, 2H), 4.23 – 4.15 (m, 1H), 3.81 (d, $^3J_{HH}$ = 9.1 Hz, 1H), 3.69 (s, 3H), 3.51 (s, 3H).

^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ 167.6, 167.0, 134.7, 134.1, 129.3, 129.1, 77.1, 54.4, 52.9, 52.8, 42.3.

HPLC (chiral): Chiralpak-IA, n-heptane/EtOH 99:1, 1.0 mL/min, 40 °C, detection at 254 nm.

Residence time: 30.4 min (major), 36.9 (minor). 90:10 er.

The absolute configuration of **6c** was determined by comparing the HPLC data with the literature:

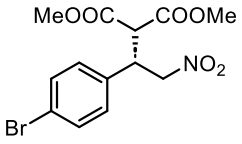
HPLC (chiral): Chiralpak-OD-H, n-heptane/EtOH 95:5, 1.0 mL/min, 40 °C, detection at 254 nm.

Residence time: 17.1 min (major), 20.3 (minor). 91:9 er.

Lit. for (*S*) isomer HPLC (chiral): Chiralcel-OD-H, Hexanes/i-PrOH 70:30, 1.0 mL/min, temperature not specified, detection at 220 nm.

Residence time: 10.2 min (major), 13.6 (minor).

(S)-dimethyl 2-(1-(4-bromophenyl)-2-nitroethyl)malonate (6d)



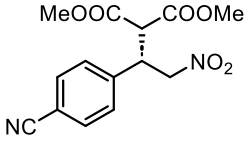
The general procedure was followed to afford 0.142 g (80%) of the product as a yellow solid. The reported data match the literature.[18]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, $^3J_{HH}$ = 8.0 Hz, 2H), 7.12 (d, $^3J_{HH}$ = 8.0 Hz, 2H), 4.97 – 4.77 (m, 2H), 4.28 – 4.13 (m, 1H), 3.82 (d, $^3J_{HH}$ = 9.0 Hz, 1H), 3.76 (s, 3H), 3.59 (s, 3H).

^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ 167.7, 167.2, 135.3, 132.3, 129.7, 122.7, 77.2, 54.6, 53.3, 53.1, 42.5.

HPLC (chiral): Chiralpak-IA, n-heptane/EtOH 99:1, 1.0 mL/min, 40 °C, detection at 254 nm. Residence time: 32.9 min (major), 39.9 (minor). 92:8 er.

(*S*)-dimethyl 2-(1-(4-cyanophenyl)-2-nitroethyl)malonate (6e)



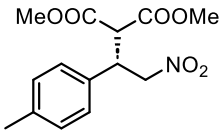
The general procedure was followed to afford 0.097 g (64%) of the product as a yellow solid. The reported data match the literature.[19]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, $^3J_{HH}$ = 8.1 Hz, 2H), 7.38 (d, $^3J_{HH}$ = 8.1 Hz, 2H), 5.01 – 4.82 (m, 2H), 4.37 – 4.22 (m, 1H), 3.85 (d, $^3J_{HH}$ = 8.8 Hz, 1H), 3.77 (s, 3H), 3.60 (s, 3H).

^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ 167.5, 166.9, 141.7, 132.9, 129.0, 118.2, 112.8, 76.8, 54.3, 53.4, 53.2, 42.9.

HPLC (chiral): Chiralpak-IC, n-heptane/EtOH 97:3, 1.0 mL/min, 40 °C, detection at 254 nm. Residence time: 61.6 min (major), 73.4 (minor). 88:12 er.

(*S*)-dimethyl 2-(2-nitro-1-(p-tolyl)ethyl)malonate (6f)



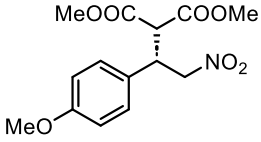
The general procedure was followed to afford 0.095 g (64%) of the product as a yellow solid. The reported data match the literature.[17]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 – 7.01 (m, 4H), 4.99 – 4.76 (m, 2H), 4.29 – 4.10 (m, 1H), 3.84 (d, $^3J_{HH}$ = 9.0 Hz, 1H), 3.75 (s, 3H), 3.57 (s, 3H), 2.30 (s, 3H).

^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ 168.0, 167.4, 138.3, 133.1, 129.8, 127.8, 77.7, 54.9, 53.2, 52.9, 42.7, 21.2.

HPLC (chiral): Chiralpak-IA, n-heptane/EtOH 99:1, 1.0 mL/min, 40 °C, detection at 254 nm. Residence time: 16.1 min (major), 19.8 (minor). 84:16 er.

(S)-dimethyl 2-(1-(4-methoxyphenyl)-2-nitroethyl)malonate (6g)



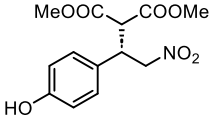
The general procedure was followed to afford 0.097 g (62%) of the product as a yellow liquid. The reported data match the literature.[17]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14 (d, $^3J_{HH}$ = 8.1 Hz, 2H), 6.83 (d, $^3J_{HH}$ = 8.1 Hz, 2H), 4.96 – 4.71 (m, 2H), 4.27 – 4.06 (m, 1H), 3.82 (d, $^3J_{HH}$ = 9.0 Hz, 1H), 3.80 – 3.68 (m, 6H), 3.57 (s, 3H).

^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ 168.0, 167.4, 159.6, 129.1, 128.0, 114.5, 77.8, 55.3, 55.0, 53.1, 53.0, 42.4.

HPLC (chiral): Chiralpak-IC, n-heptane/EtOH 97:3, 1.0 mL/min, 40 °C, detection at 254 nm. Residence time: 21.3 min (major), 25.0 (minor). 91:9 er.

(*S*)-dimethyl 2-(1-(4-hydroxyphenyl)-2-nitroethyl)malonate (6h)



The general procedure was followed to afford 0.112 g (76%) of the product as a yellow solid. The reported data match the literature.[20]

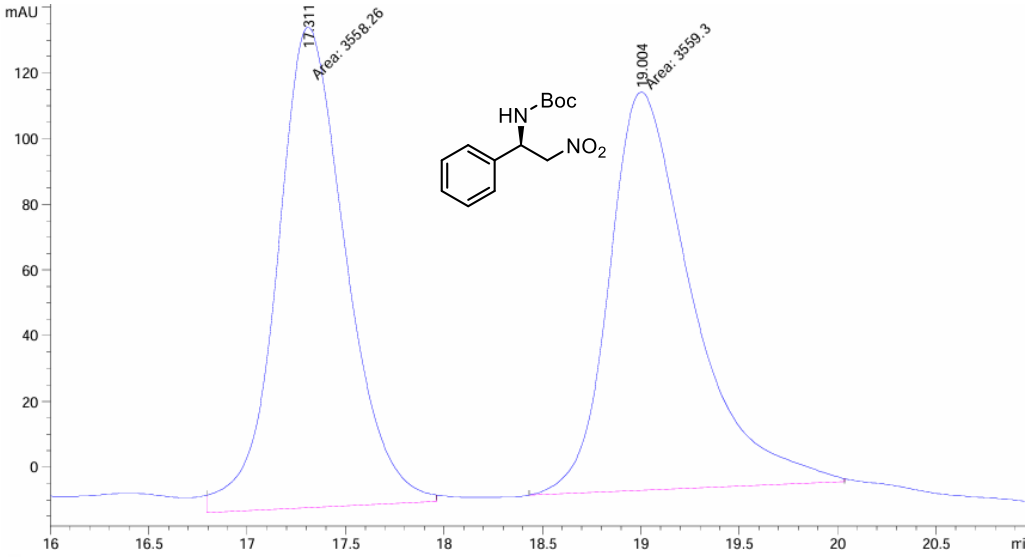
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.08 (d, $^3J_{HH}$ = 8.2 Hz, 2H), 6.73 (d, $^3J_{HH}$ = 8.0 Hz, 2H), 5.19 (s, 1H), 4.98 – 4.71 (m, 2H), 4.25 – 4.11 (m, 1H), 3.82 (d, $^3J_{HH}$ = 9.2 Hz, 1H), 3.76 (s, 3H), 3.57 (s, 3H).

^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ 168.0, 167.6, 155.8, 129.4, 128.0, 116.1, 77.8, 55.0, 53.2, 53.1, 42.45.

HPLC (chiral): Chiralpak-IC, n-heptane/EtOH 97:3, 1.0 mL/min, 40 °C, detection at 254 nm. Residence time: 48.1 min (major), 51.5 (minor). 88:12 er.

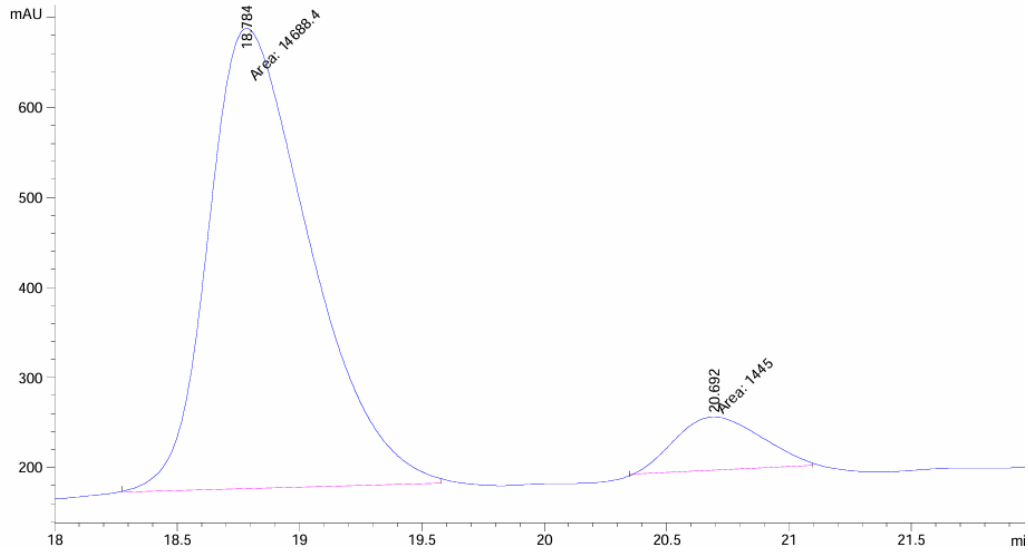
Chiral HPLC chromatograms of 4

Tert-butyl (*R*)-(2-nitro-1-phenylethyl)carbamate (4a)



Signal 1: DAD1 D, Sig=230,16 Ref=360,100

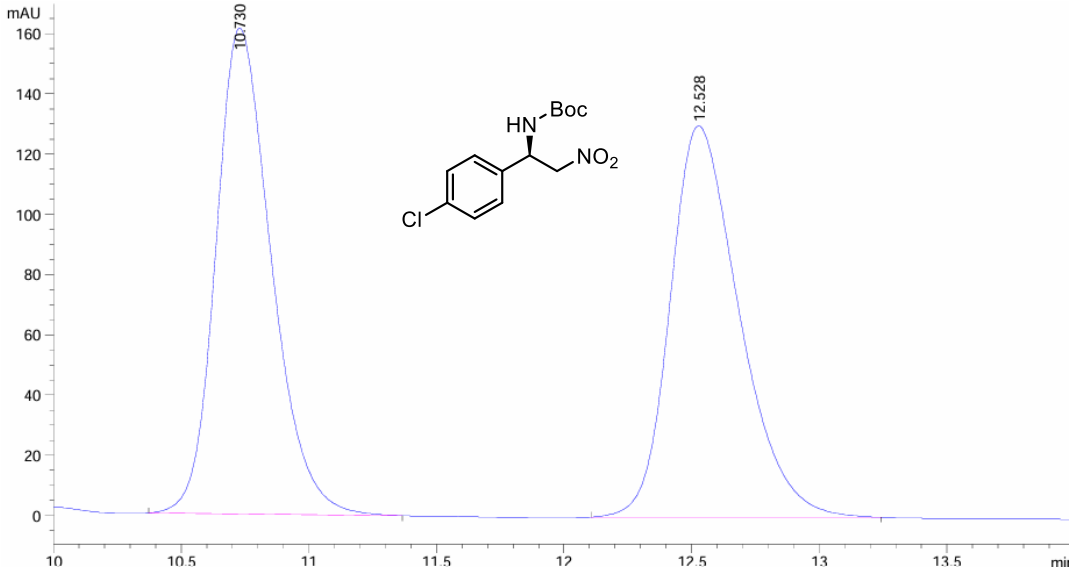
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.311	MM	0.4053	3558.25830	146.32263	49.9927
2	19.004	MM	0.4894	3559.29712	121.20937	50.0073
Totals :				7117.55542	267.53201	



Signal 1: DAD1 D, Sig=230,16 Ref=360,100

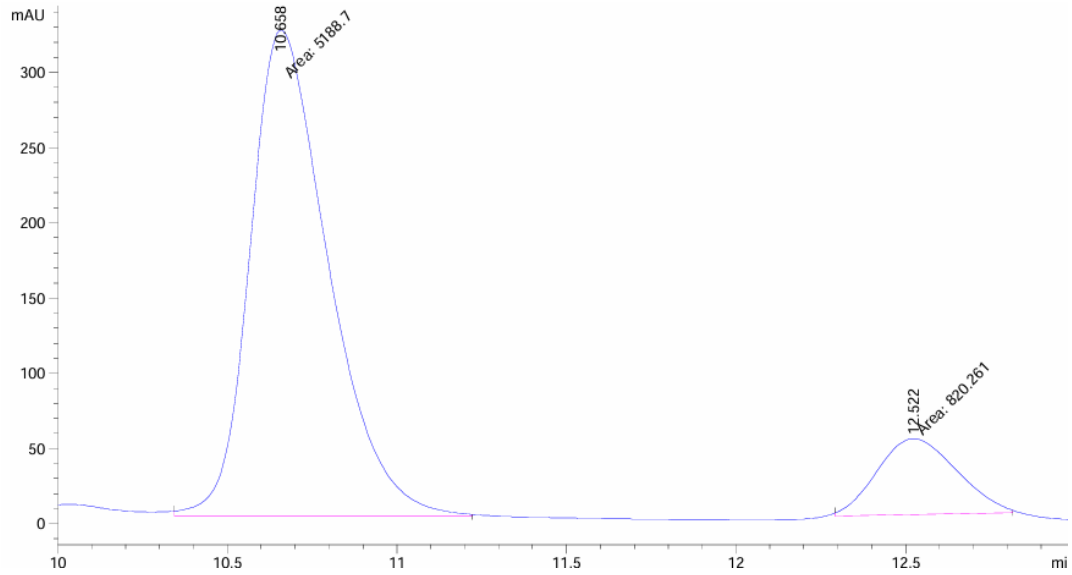
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.784	MM	0.4788	1.46884e4	511.30420	91.0434
2	20.692	MM	0.4056	1445.00256	59.37882	8.9566
Totals :				1.61334e4	570.68302	

Tert-butyl (*R*)-(1-(4-chlorophenyl)-2-nitroethyl)carbamate (4b)



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

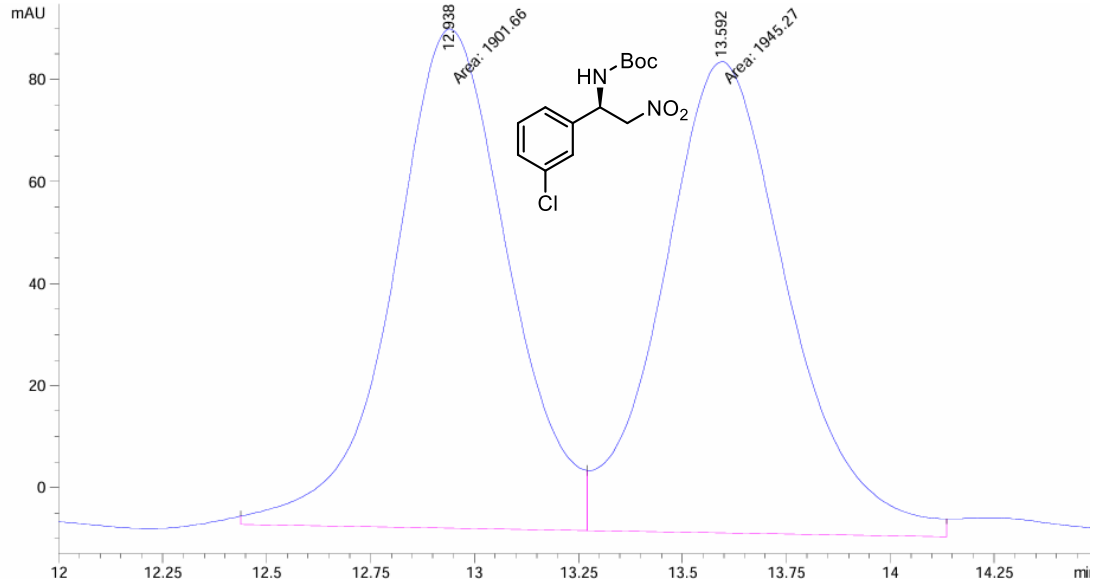
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.730	BB	0.2308	2443.55518	161.28192	49.7940
2	12.528	BB	0.2888	2463.77222	130.16356	50.2060
Totals :				4907.32739	291.44548	



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.658	MM	0.2677	5188.70068	323.03860	86.3494
2	12.522	MM	0.2713	820.26141	50.38549	13.6506
Totals :				6008.96210	373.42409	

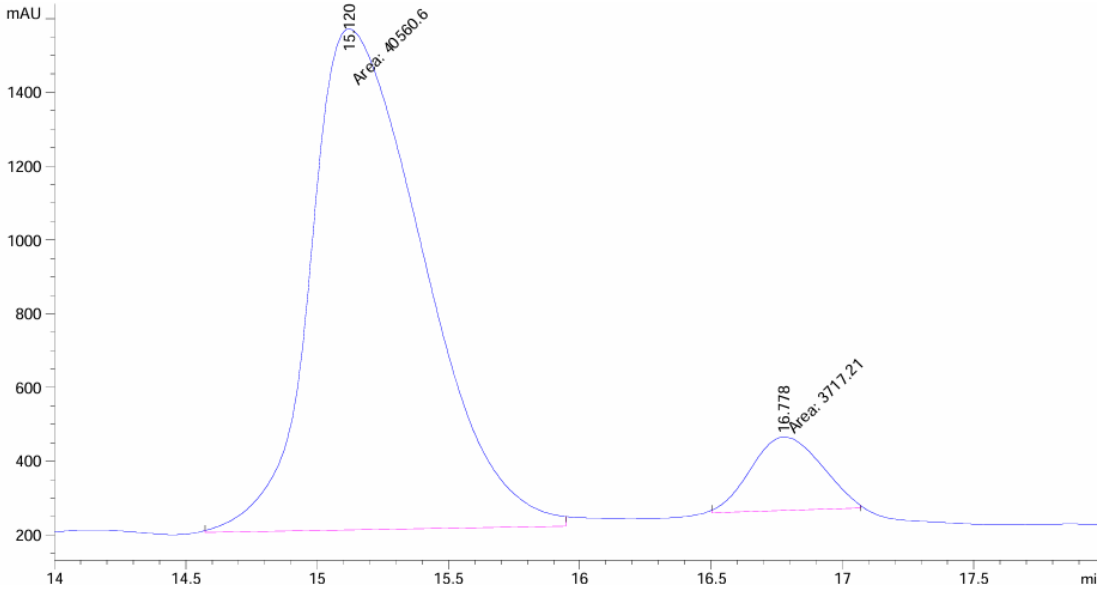
Tert-butyl (*R*)-(1-(3-chlorophenyl)-2-nitroethyl)carbamate (4c)



Signal 1: DAD1 D, Sig=230,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.938	MF	0.3241	1901.65735	97.79926	49.4332
2	13.592	FM	0.3513	1945.26550	92.28041	50.5668

Totals : 3846.92285 190.07967

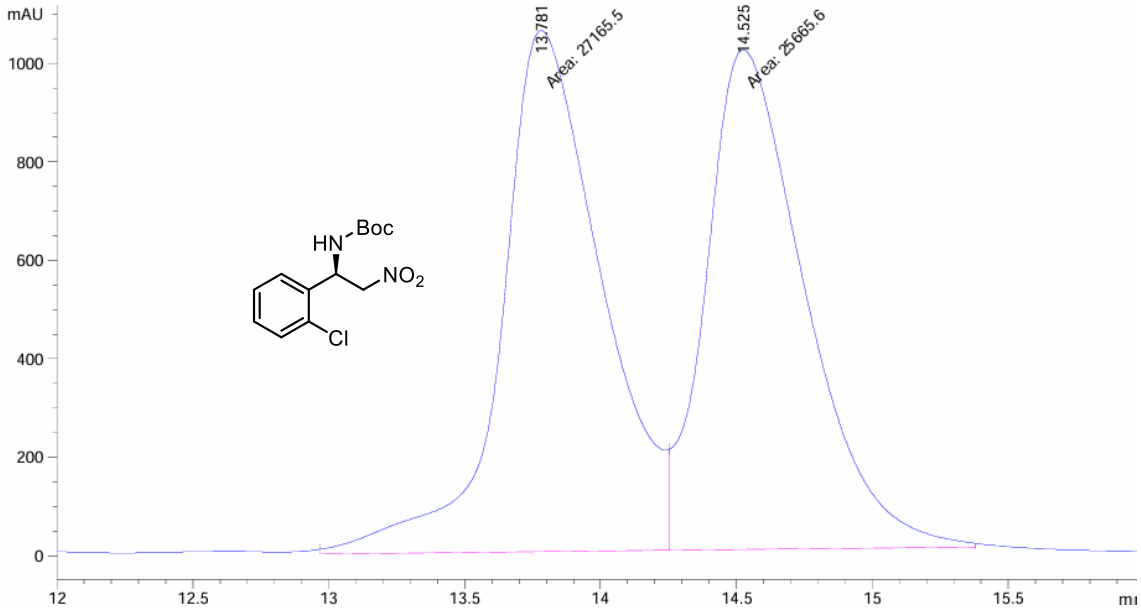


Signal 1: DAD1 D, Sig=230,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.120	MM	0.4976	4.05606e4	1358.56177	91.6048
2	16.778	MM	0.3107	3717.20703	199.42900	8.3952

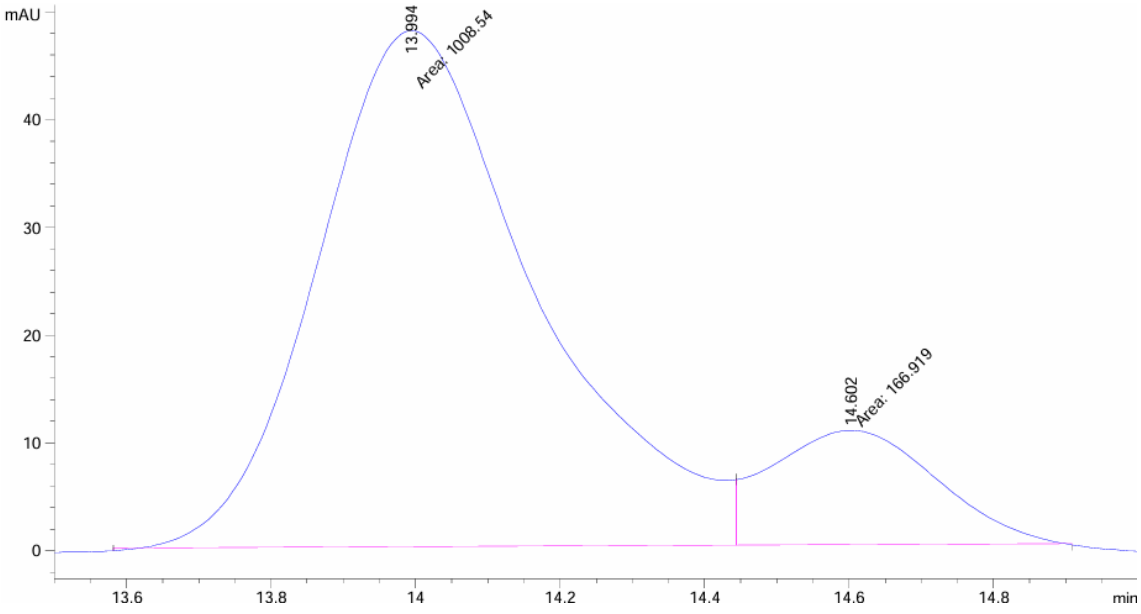
Totals : 4.42778e4 1557.99077

Tert-butyl (*R*)-(1-(2-chlorophenyl)-2-nitroethyl)carbamate (4d)



Signal 1: DAD1 D, Sig=230,16 Ref=360,100

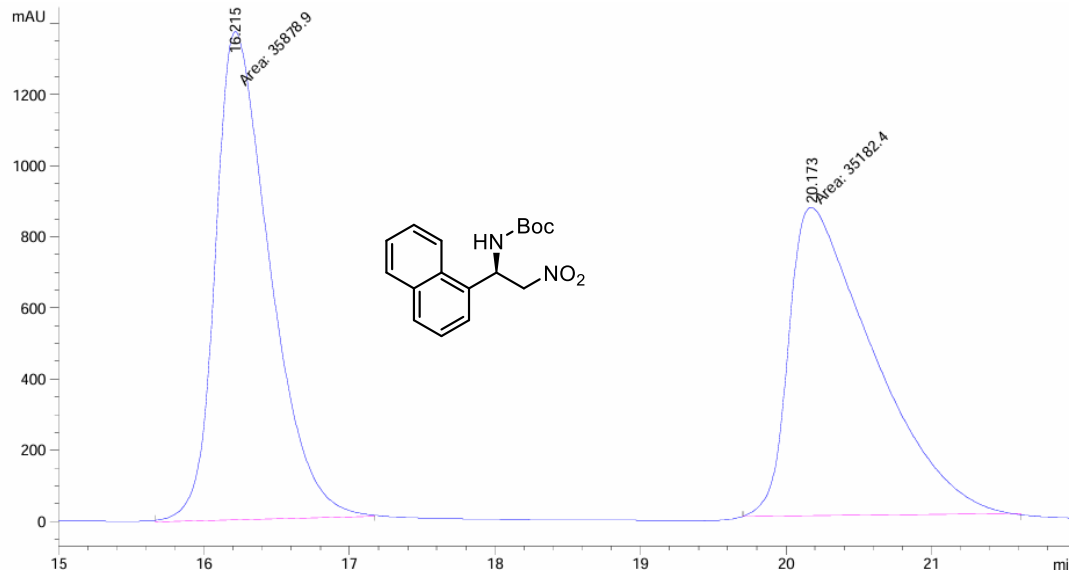
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.781	MF	0.4276	2.71655e4	1058.89563	51.4195
2	14.525	FM	0.4213	2.56656e4	1015.36279	48.5805
Totals :				5.28311e4	2074.25842	



Signal 1: DAD1 B, Sig=254,16 Ref=360,100

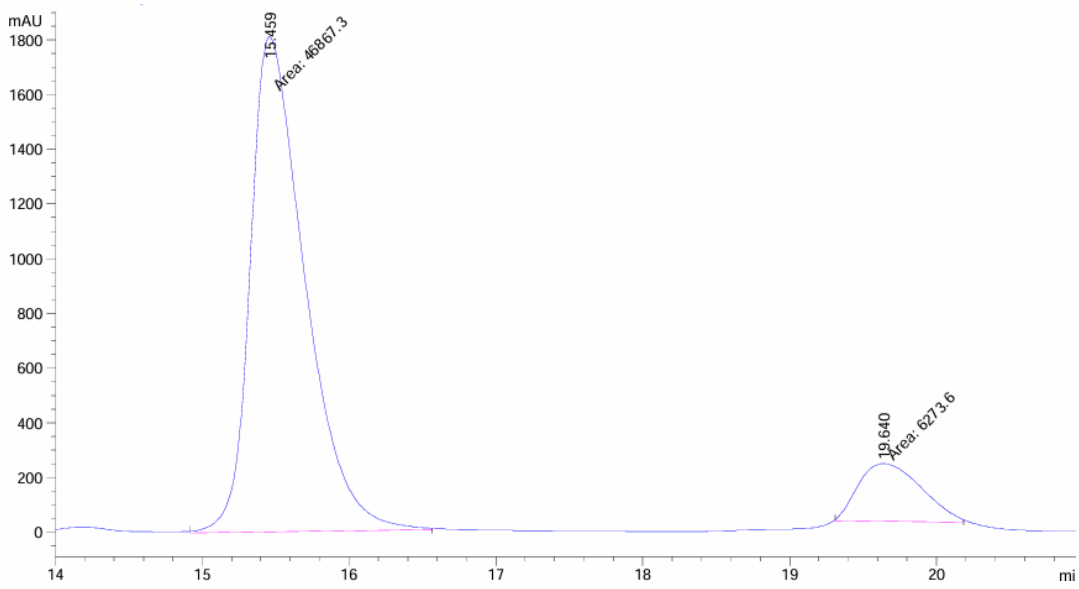
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.994	MF	0.3509	1008.54425	47.90654	85.7997
2	14.602	FM	0.2620	166.91896	10.61637	14.2003
Totals :				1175.46321	58.52291	

Tert-butyl (*R*)-(1-(naphthalen-1-yl)-2-nitroethyl)carbamate (4e)



Signal 1: DAD1 B, Sig=254,16 Ref=360,100

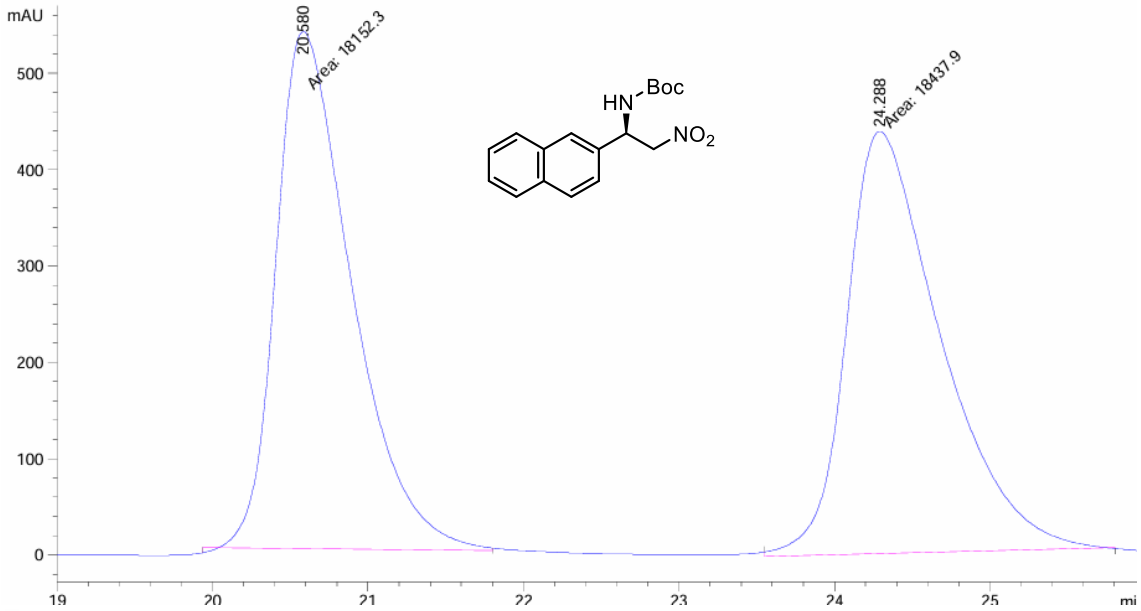
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.215	MM	0.4353	3.58789e4	1373.73767	50.4901
2	20.173	MM	0.6761	3.51824e4	867.30377	49.5099
Totals :				7.10613e4	2241.04144	



Signal 1: DAD1 B, Sig=254,16 Ref=360,100

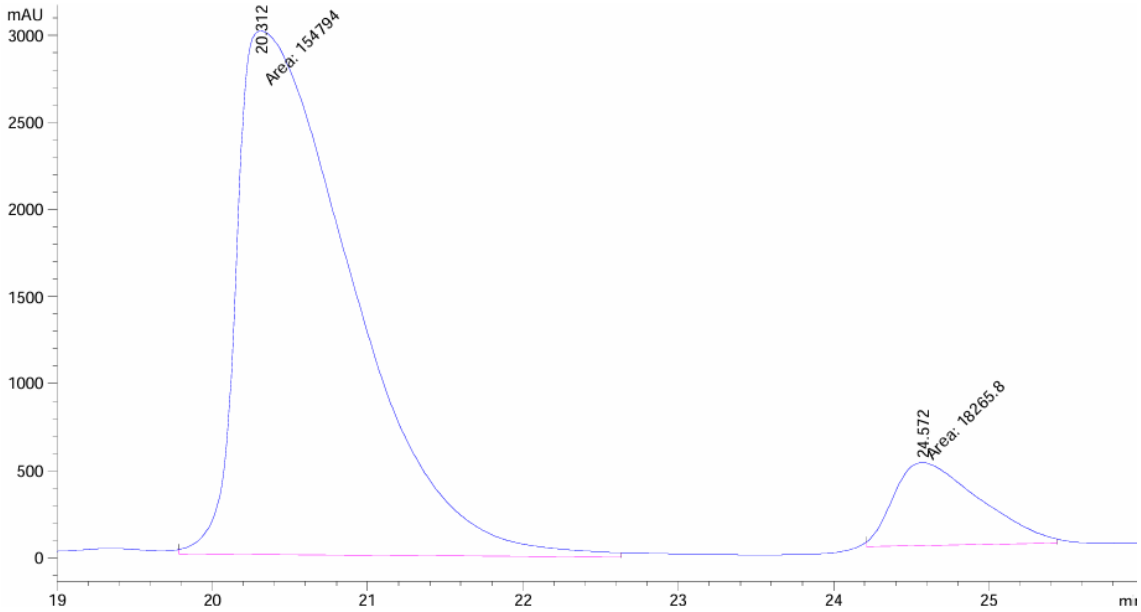
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.459	MM	0.4314	4.68673e4	1810.73157	88.1944
2	19.640	MM	0.4953	6273.59863	211.09323	11.8056
Totals :				5.31409e4	2021.82480	

Tert-butyl (*R*)-(1-(naphthalen-2-yl)-2-nitroethyl)carbamate (4f)



Signal 1: DAD1 B, Sig=254,16 Ref=360,100

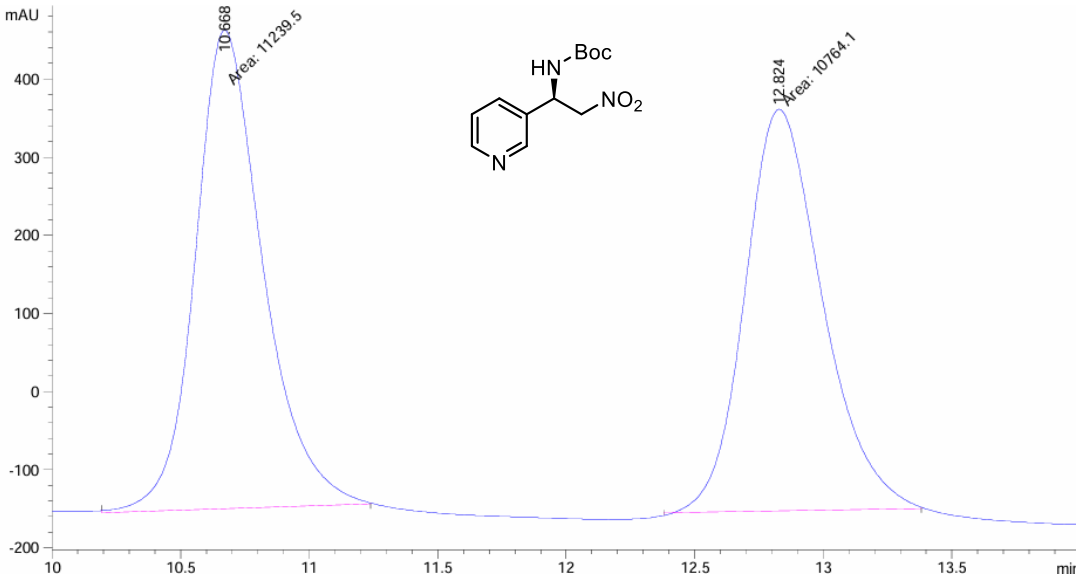
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.580	MM	0.5635	1.81523e4	536.86047	49.6097
2	24.288	MM	0.7011	1.84379e4	438.31787	50.3903
Totals :				3.65903e4	975.17834	



Signal 1: DAD1 B, Sig=254,16 Ref=360,100

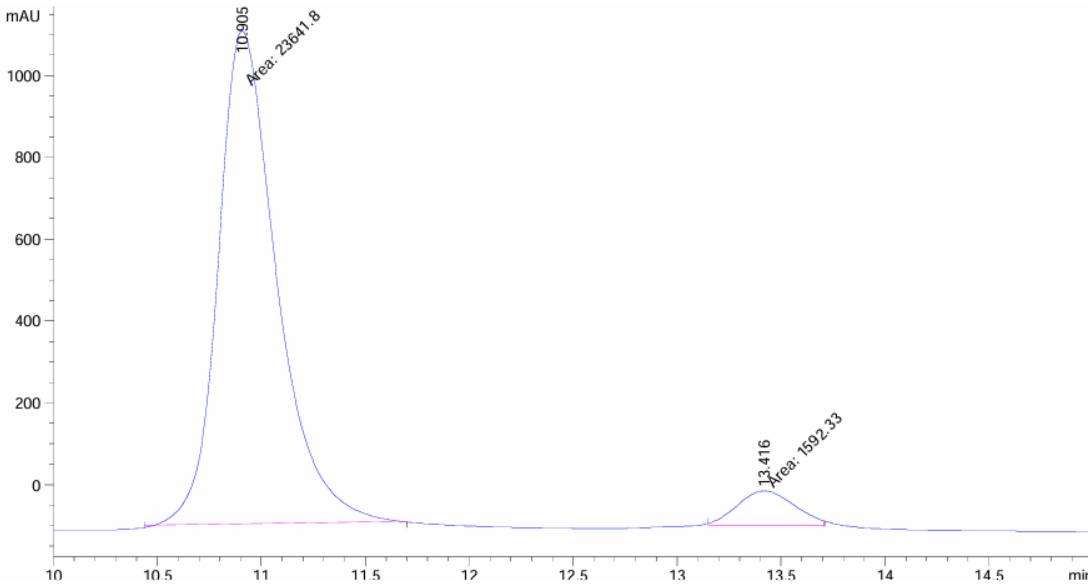
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.312	MM	0.8579	1.54794e5	3007.25537	89.4454
2	24.572	MM	0.6396	1.82658e4	475.93234	10.5546
Totals :				1.73060e5	3483.18771	

Tert-butyl (*R*)-(2-nitro-1-(pyridin-3-yl)ethyl)carbamate (4g)



Signal 1: DAD1 C, Sig=210,8 Ref=360,100

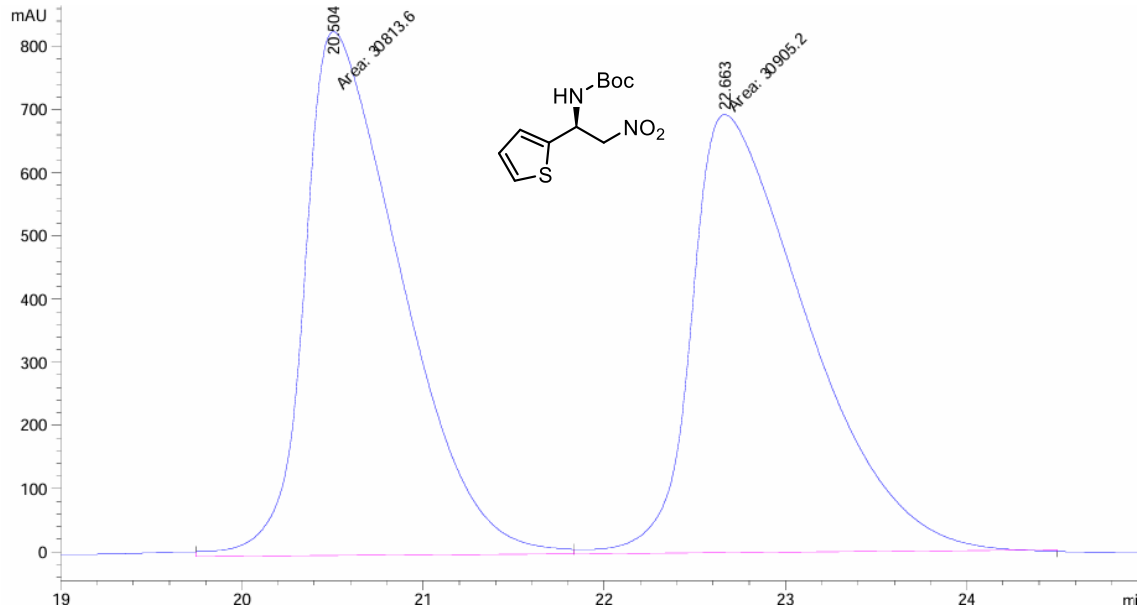
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.668	MM	0.3058	1.12395e4	612.61719	51.0805
2	12.824	MM	0.3492	1.07641e4	513.78003	48.9195
Totals :				2.20036e4	1126.39722	



Signal 1: DAD1 C, Sig=210,8 Ref=360,100

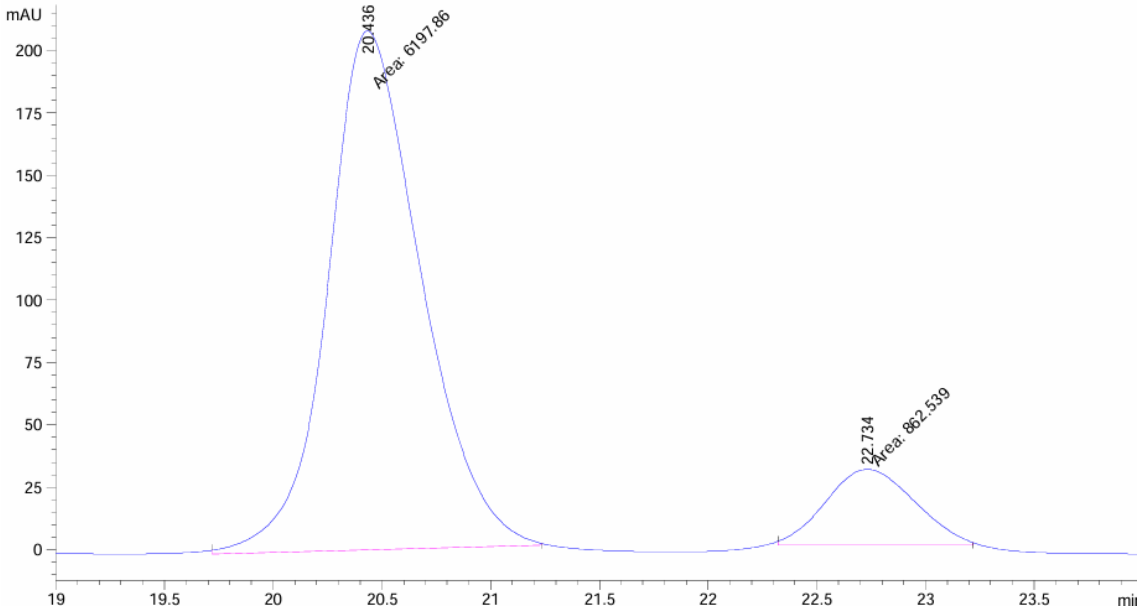
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.905	MM	0.3271	2.36418e4	1204.67261	93.6898
2	13.416	MM	0.3169	1592.33142	83.73948	6.3102
Totals :				2.52342e4	1288.41209	

Tert-butyl (*R*)-(2-nitro-1-(thiophen-2-yl)ethyl)carbamate (4h)



Signal 1: DAD1 B, Sig=254,16 Ref=360,100

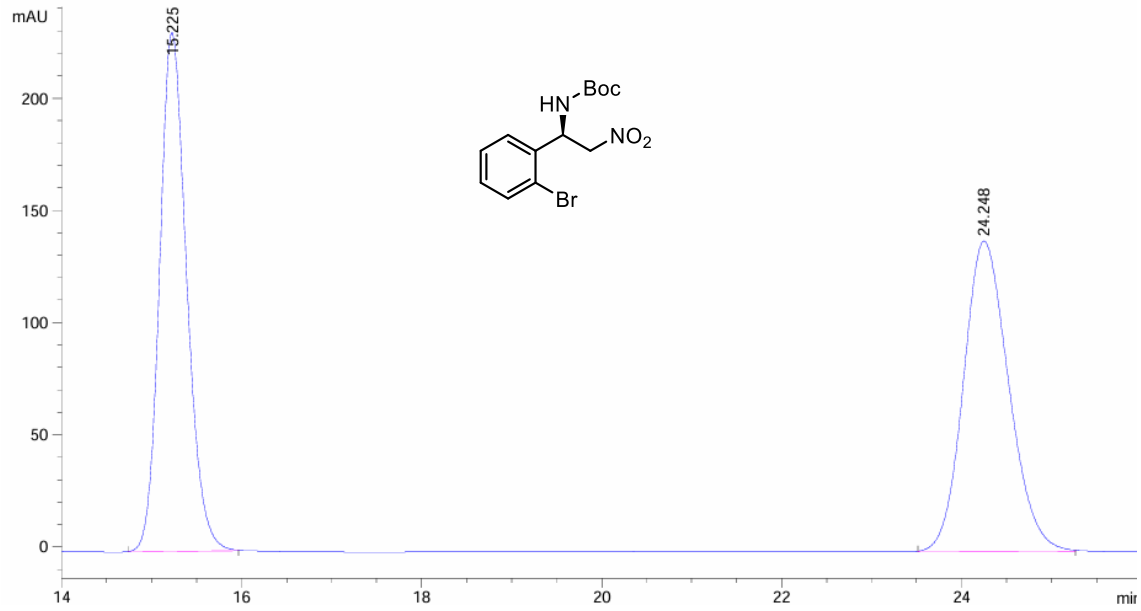
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.504	MF	0.6191	3.08136e4	829.49475	49.9258
2	22.663	FM	0.7427	3.09052e4	693.54529	50.0742
Totals :				6.17188e4	1523.04004	



Signal 1: DAD1 B, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.436	MM	0.4966	6197.85547	208.00462	87.7834
2	22.734	MM	0.4725	862.53937	30.42364	12.2166
Totals :				7060.39484	238.42826	

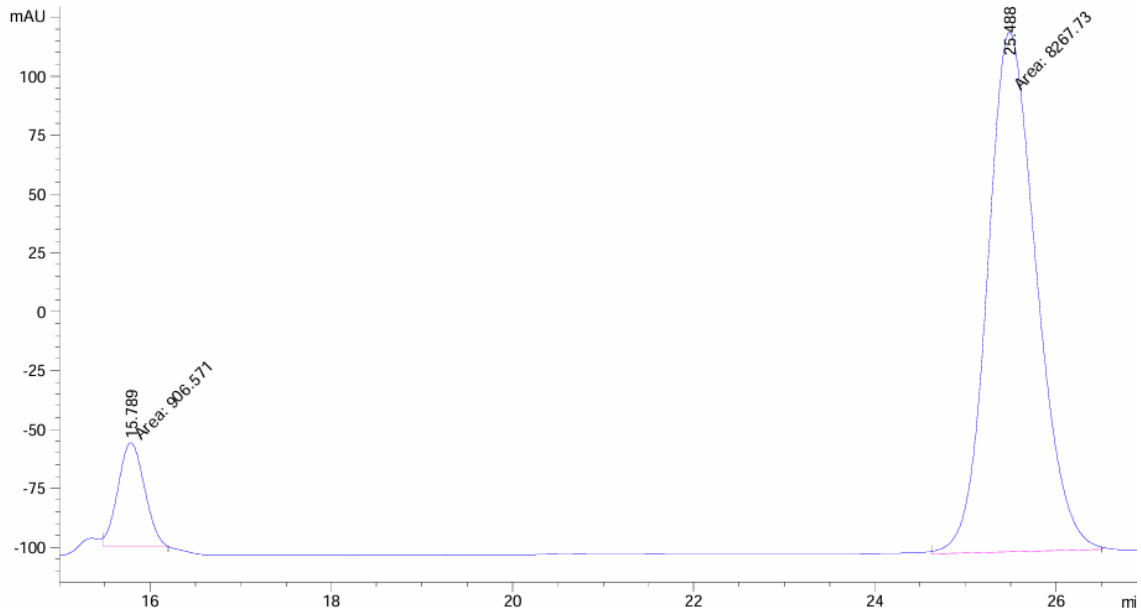
Tert-butyl (*R*)-(1-(2-bromophenyl)-2-nitroethyl)carbamate (4i)



Signal 1: DAD1 B, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.225	BB	0.3193	4821.98438	231.21657	49.9596
2	24.248	BB	0.5393	4829.78369	138.33565	50.0404

Totals : 9651.76807 369.55222

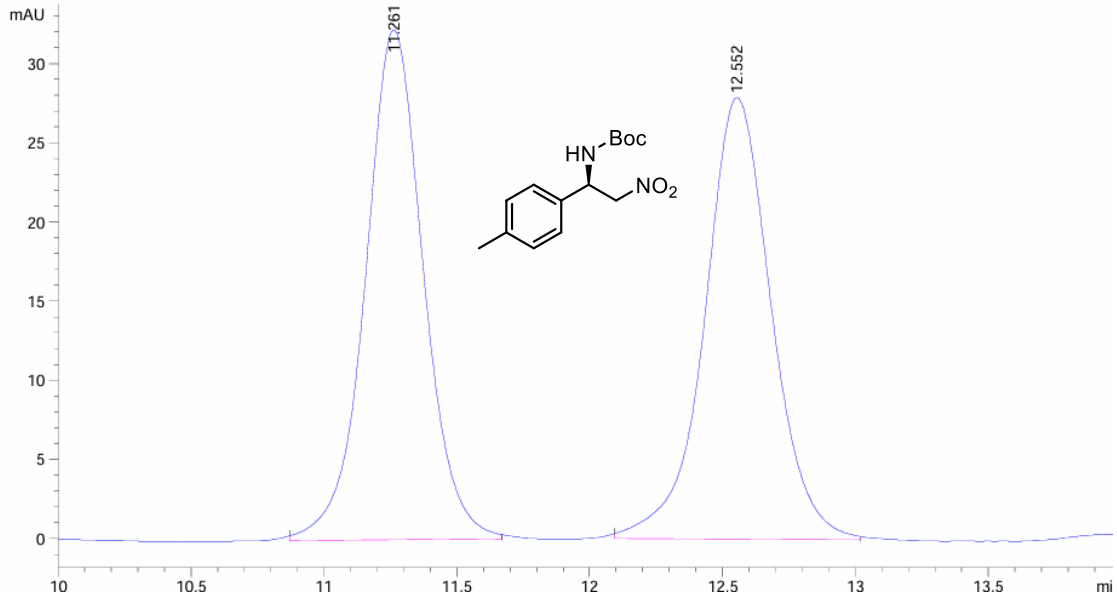


Signal 1: DAD1 B, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.789	MM	0.3414	906.57147	44.26062	9.8816
2	25.488	MM	0.6248	8267.72656	220.55910	90.1184

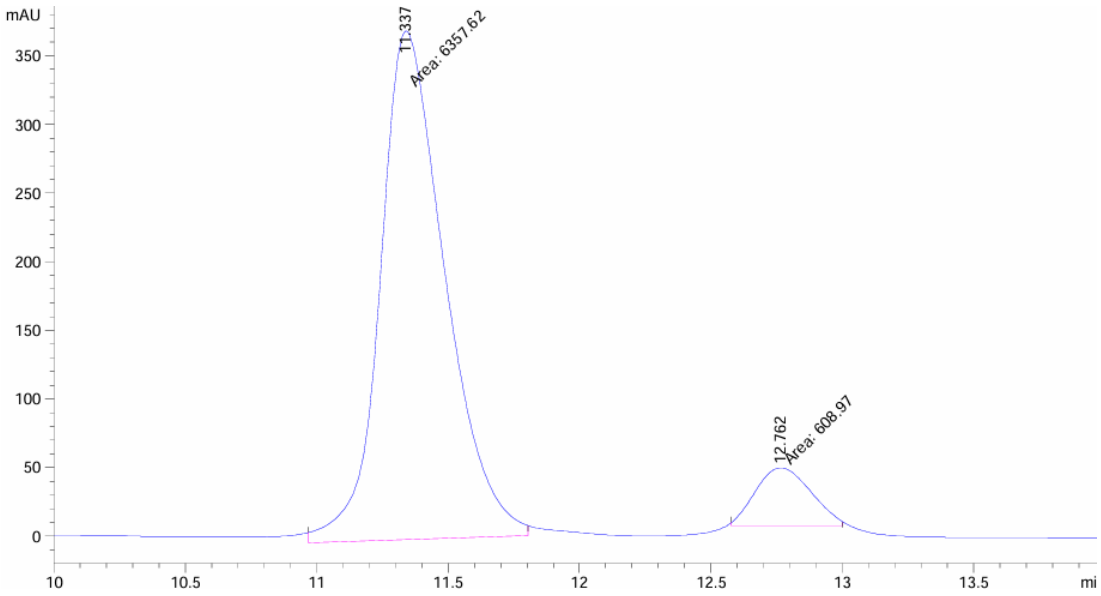
Totals : 9174.29803 264.81972

Tert-butyl (*R*)-(1-(2-bromophenyl)-2-nitroethyl)carbamate (4j)



Signal 1: DAD1 B, Sig=254,16 Ref=550,100

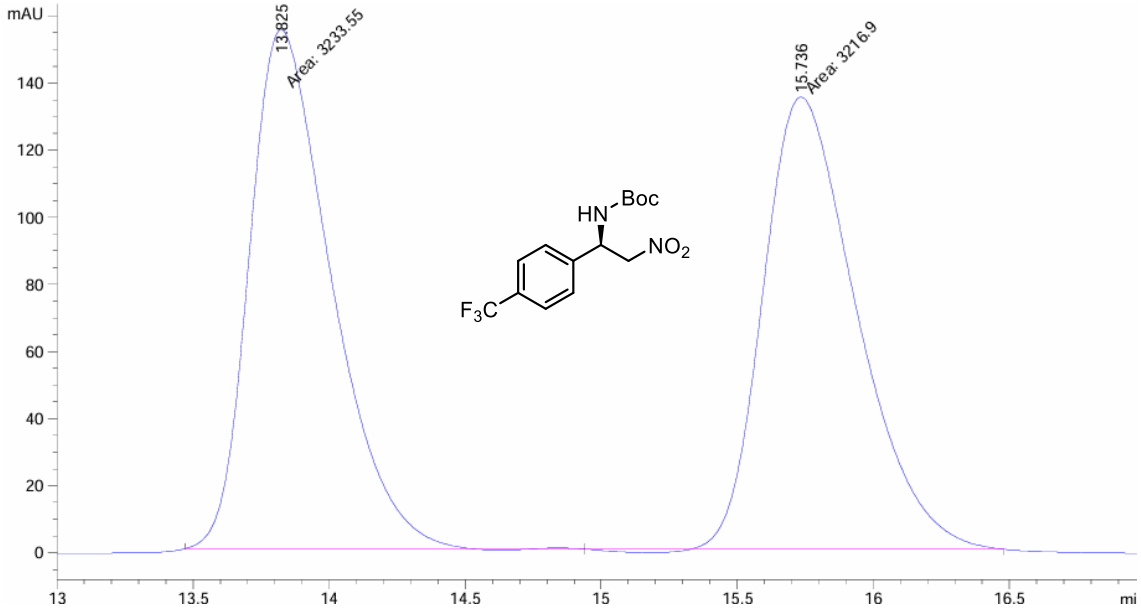
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.261	BB	0.2309	488.31039	32.21157	50.1146
2	12.552	BB	0.2633	486.07770	27.89753	49.8854
Totals :				974.38809	60.10910	



Signal 1: DAD1 A, Sig=254,4 Ref=550,99.7

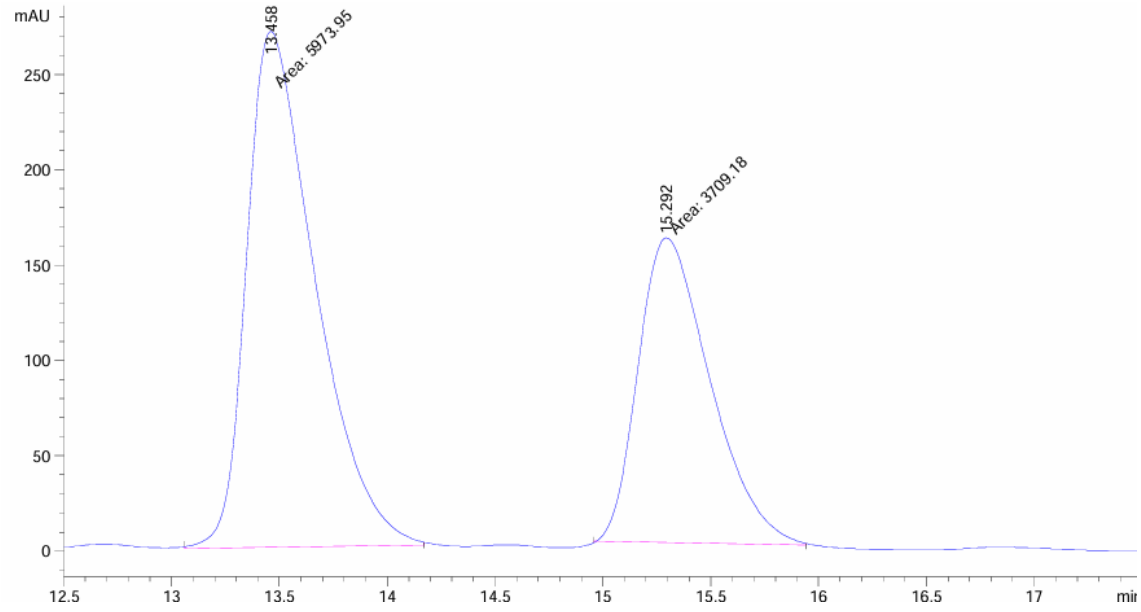
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.337	MM	0.2860	6357.62061	370.54602	91.2587
2	12.762	MM	0.2421	608.96997	41.92290	8.7413
Totals :				6966.59058	412.46892	

Tert-butyl (*R*)-(2-nitro-1-(4-(trifluoromethyl)phenyl)ethyl)carbamate (4k)



Signal 1: DAD1 B, Sig=254,16 Ref=550,100

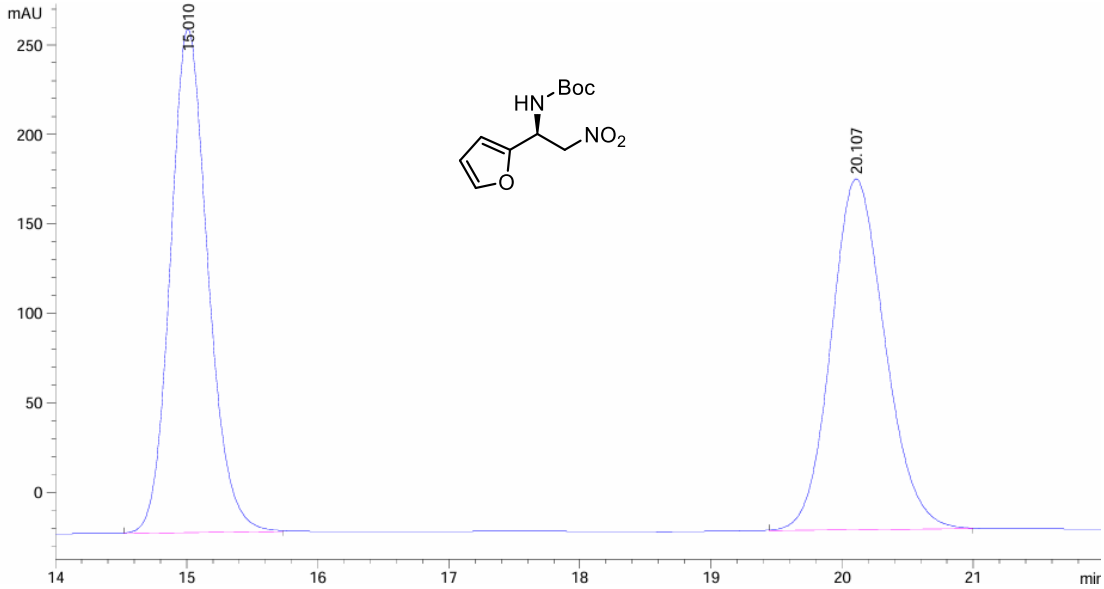
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.825	MF	0.3483	3233.54590	154.74586	50.1290
2	15.736	FM	0.3982	3216.89966	134.63853	49.8710
Totals :				6450.44556	289.38440	



Signal 1: DAD1 B, Sig=254,16 Ref=550,100

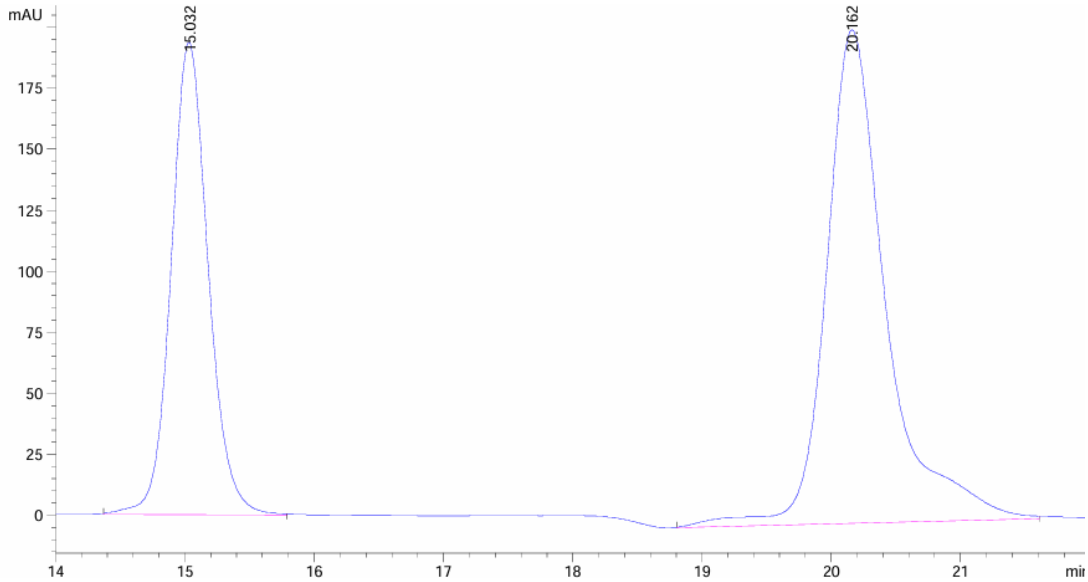
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.458	MM	0.3682	5973.95068	270.43240	61.6944
2	15.292	MM	0.3871	3709.17822	159.69753	38.3056
Totals :				9683.12891	430.12993	

Tert-butyl (*R*)-(1-(furan-2-yl)-2-nitroethyl)carbamate (4l)



Signal 1: DAD1 B, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.010	BB	0.3047	5614.80566	281.54291	50.0372
2	20.107	BB	0.4415	5606.45557	196.10039	49.9628
Totals :				1.12213e4	477.64330	

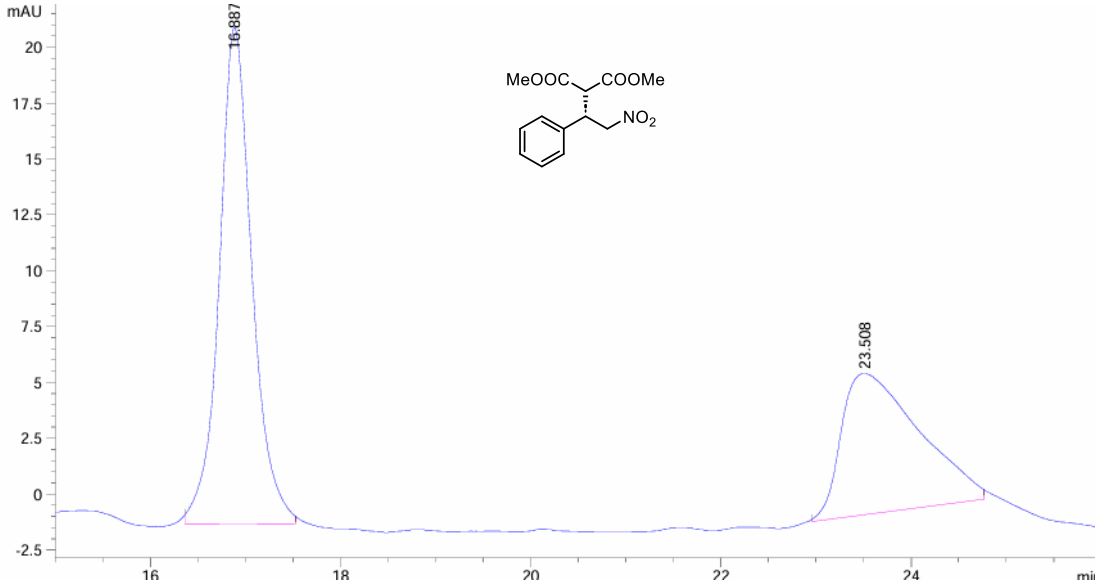


Signal 1: DAD1 B, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.032	BB	0.3055	3875.34839	193.62755	37.3029
2	20.162	BB	0.4778	6513.52832	202.19289	62.6971
Totals :				1.03889e4	395.82043	

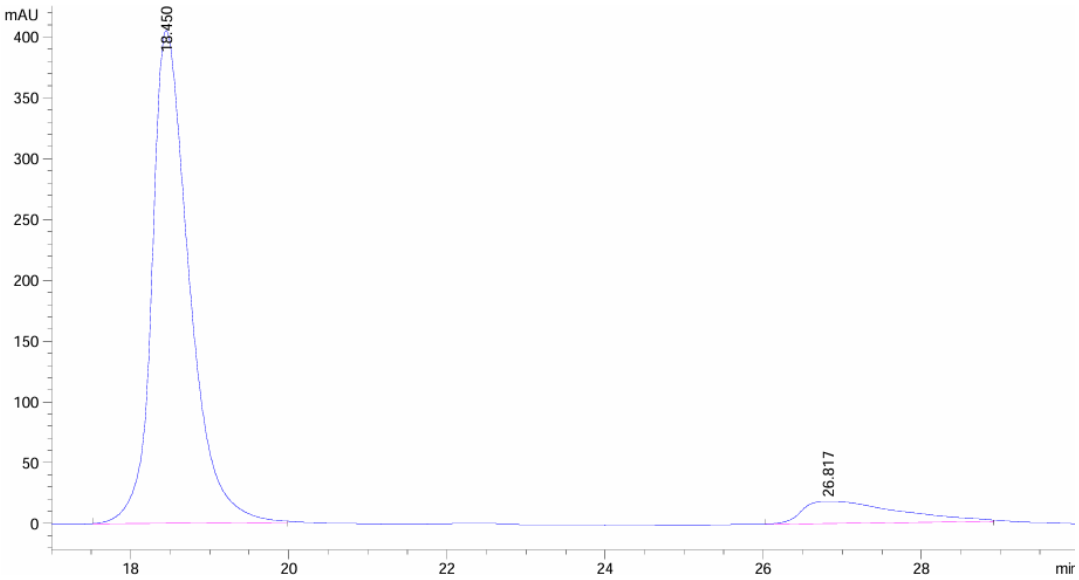
Chiral HPLC chromatograms of 6

(*S*)-dimethyl 2-(2-nitro-1-phenylethyl)malonate (6a)



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

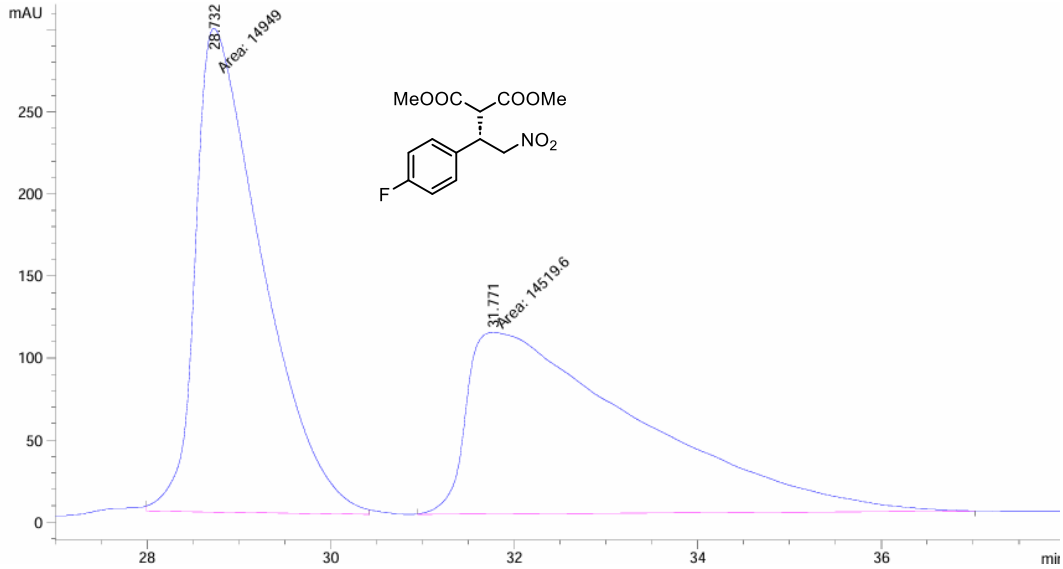
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.887	BB	0.3607	535.05011	22.23783	49.5488
2	23.503	MM	1.2590	544.79376	7.21205	50.4512
Totals :				1079.84387	29.44987	



Signal 1: DAD1 B, Sig=254,16 Ref=360,100

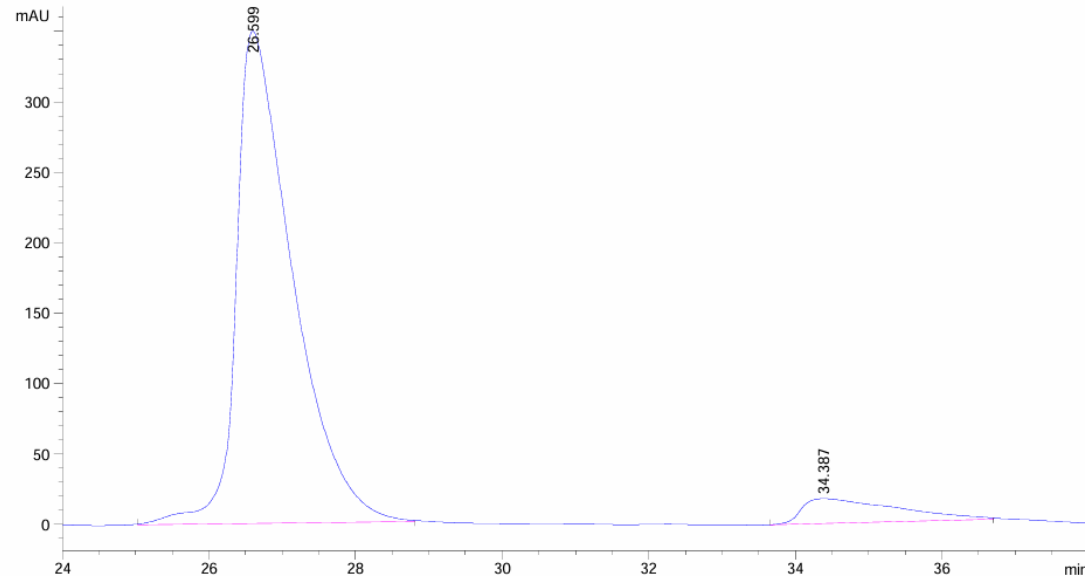
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.450	BB	0.4942	1.32816e4	405.38852	89.6975
2	26.817	BB	1.2262	1525.50781	18.23069	10.3025
Totals :				1.48071e4	423.61921	

(*S*)-dimethyl 2-(1-(4-fluorophenyl)-2-nitroethyl)malonate (6b)



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

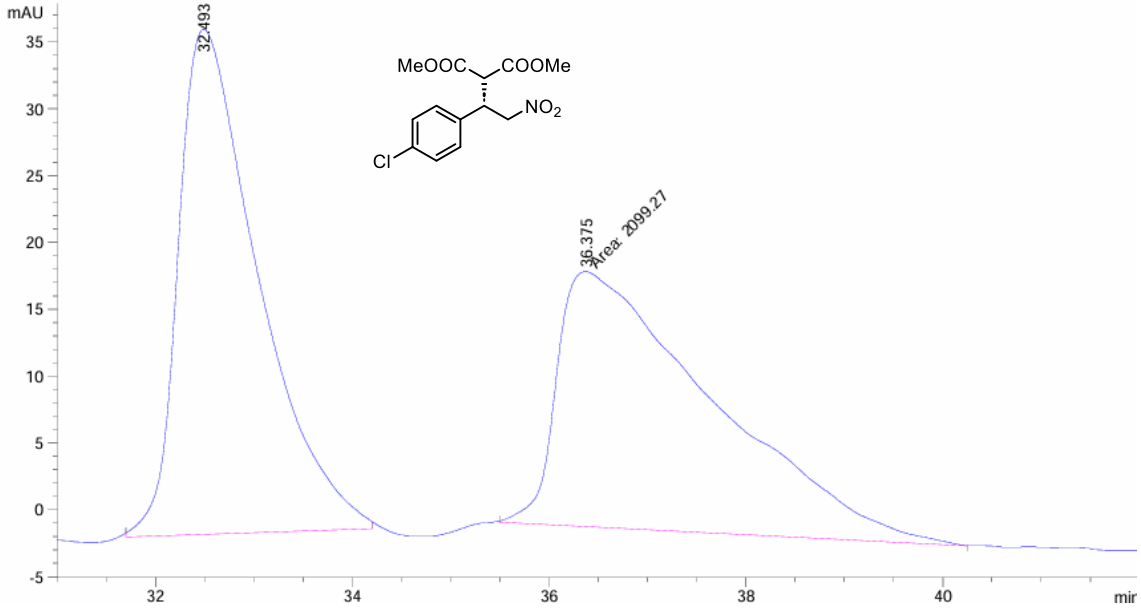
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	28.732	MM	0.8452	1.49490e4	294.78055	50.7286
2	31.771	MM	2.1865	1.45196e4	110.67889	49.2714
Totals :				2.94687e4	405.45944	



Signal 1: DAD1 B, Sig=254,16 Ref=360,100

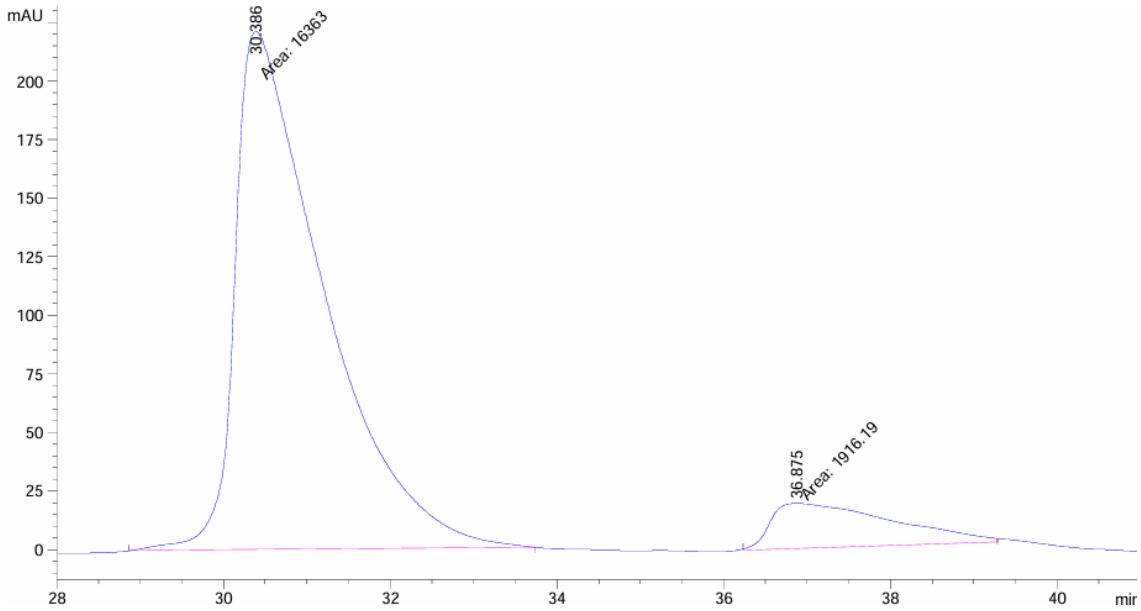
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	26.599	BB	0.8085	1.87842e4	349.78241	92.2168
2	34.387	BB	1.2584	1585.40247	17.60824	7.7832
Totals :				2.03696e4	367.39065	

(*S*)-dimethyl 2-(1-(4-chlorophenyl)-2-nitroethyl)malonate (6c)



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

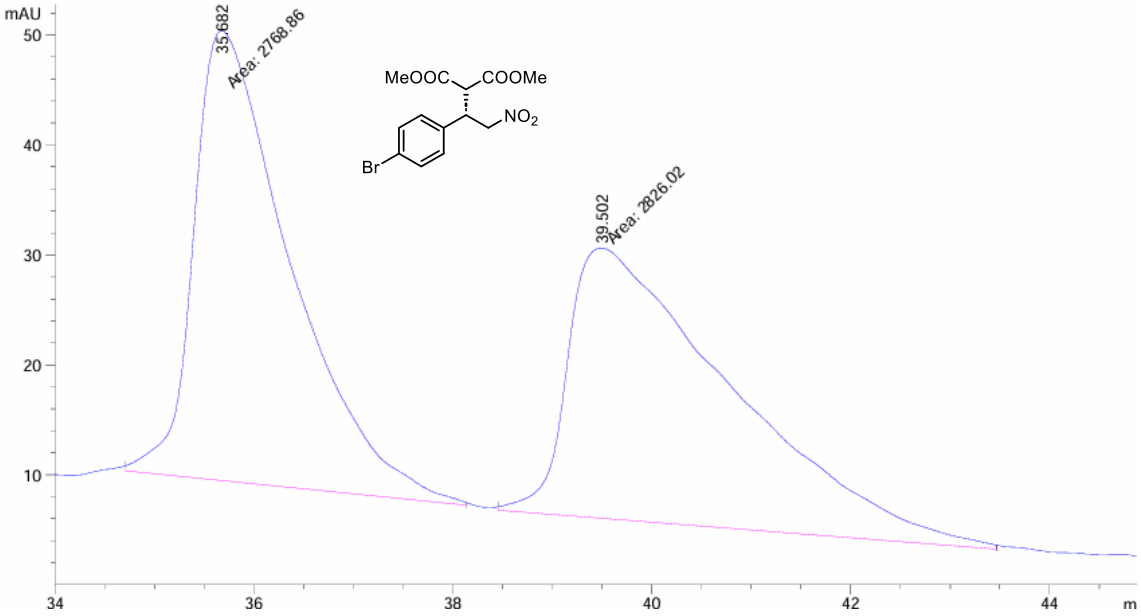
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	32.493	BB	0.8260	2130.01782	37.76342	50.3636
2	36.375	MM	1.8358	2099.26660	19.05853	49.6364
Totals :				4229.28442	56.82195	



Signal 1: DAD1 B, Sig=254,16 Ref=360,100

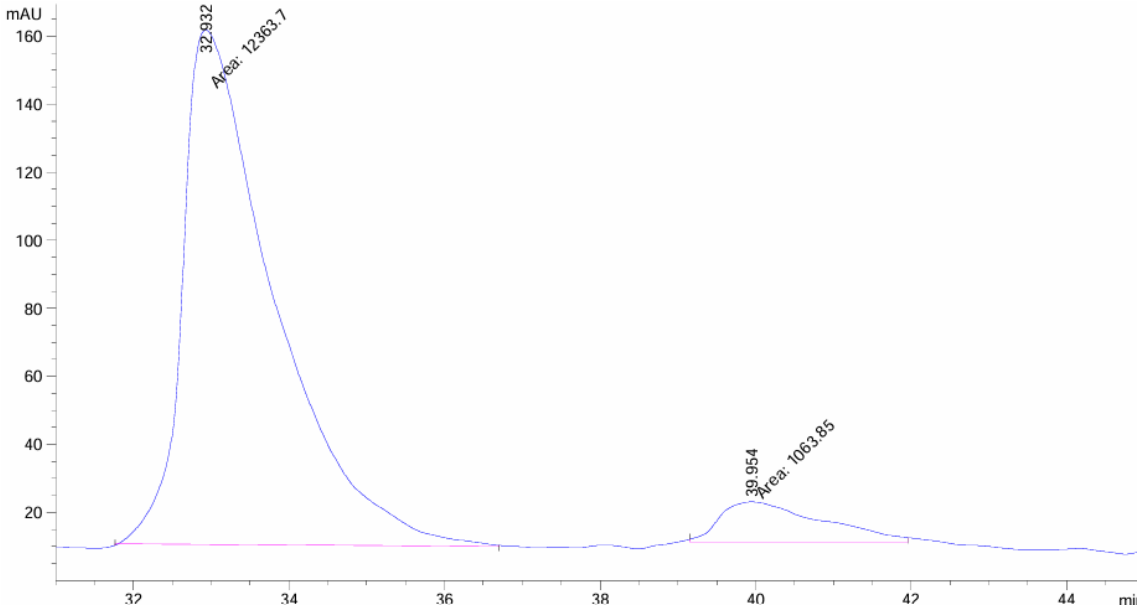
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	30.386	MM	1.2335	1.63630e4	221.08369	89.5171
2	36.875	MM	1.6546	1916.18994	19.30120	10.4829
Totals :				1.82792e4	240.38489	

(*S*)-dimethyl 2-(1-(4-bromophenyl)-2-nitroethyl)malonate (6d)



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

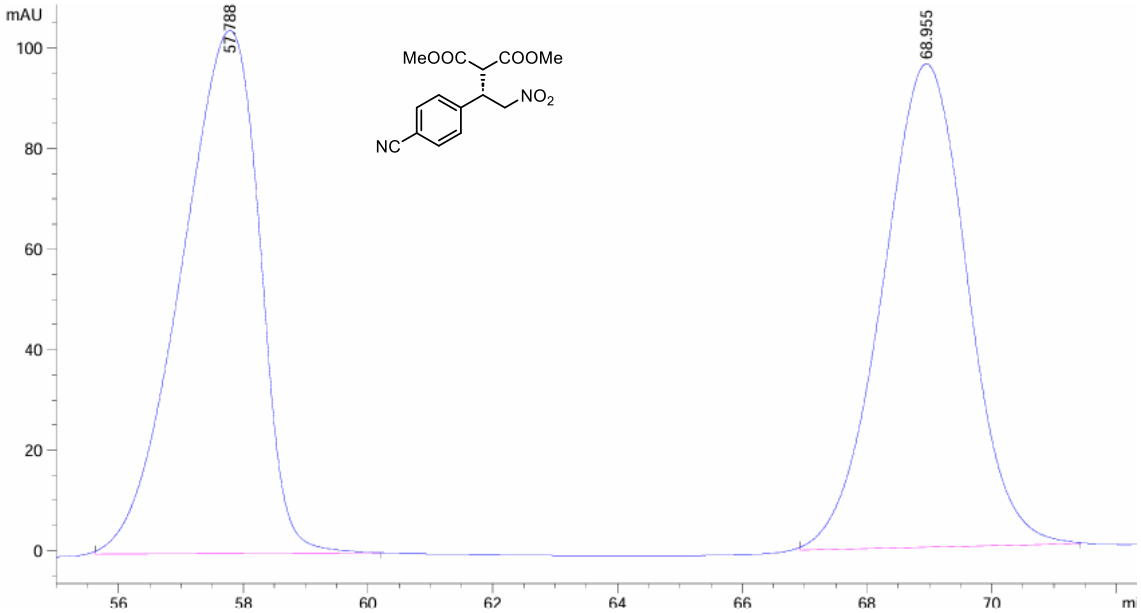
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	35.682	MM	1.1275	2768.85547	40.93092	49.4891
2	39.502	MM	1.9163	2826.02197	24.57929	50.5109
Totals :				5594.87744	65.51021	



Signal 1: DAD1 B, Sig=254,16 Ref=360,100

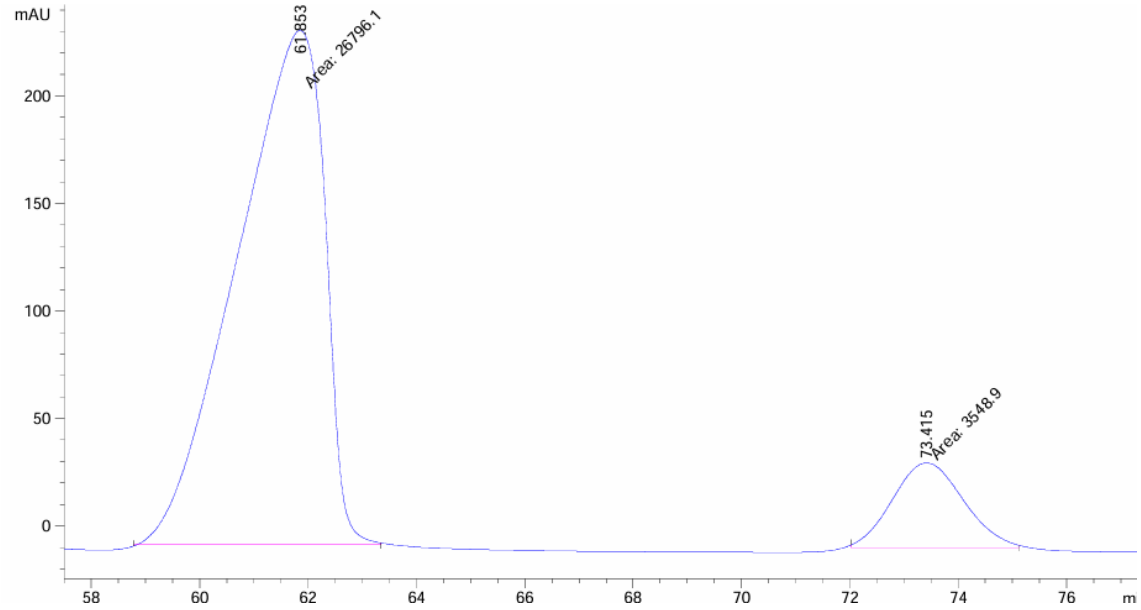
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	32.932	MM	1.3638	1.23637e4	151.09863	92.0771
2	39.954	MM	1.5060	1063.84729	11.77319	7.9229
Totals :				1.34276e4	162.87182	

(*S*)-dimethyl 2-(1-(4-cyanophenyl)-2-nitroethyl)malonate (6e)



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

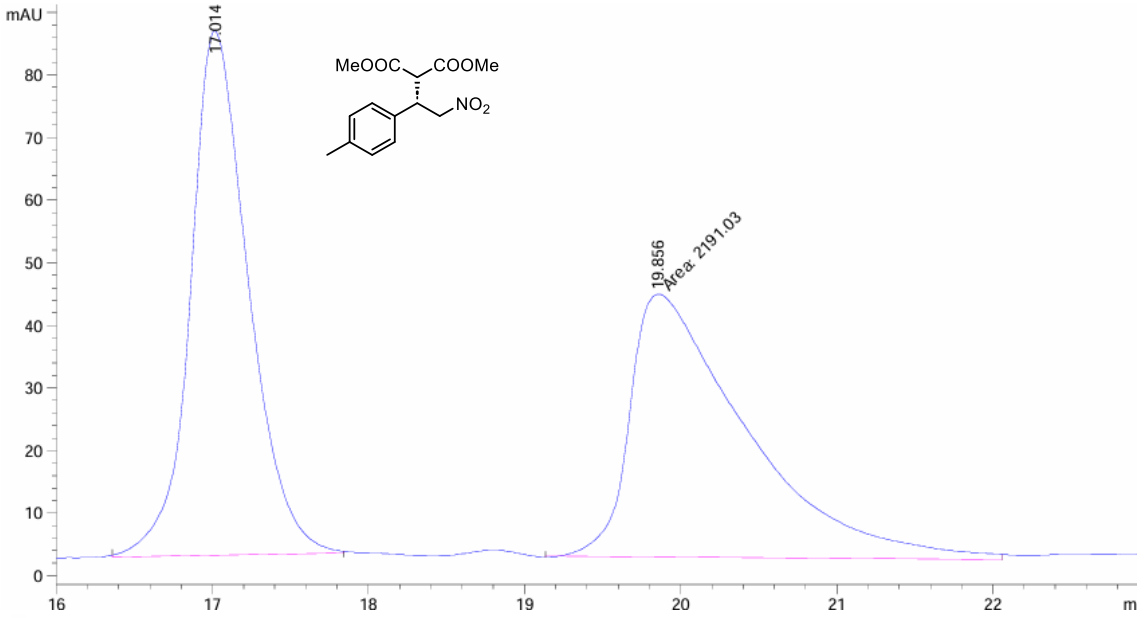
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	57.788	BB	1.3769	9072.02930	104.07824	49.9349
2	68.955	BB	1.4512	9095.68652	96.18860	50.0651
Totals :				1.81677e4	200.26684	



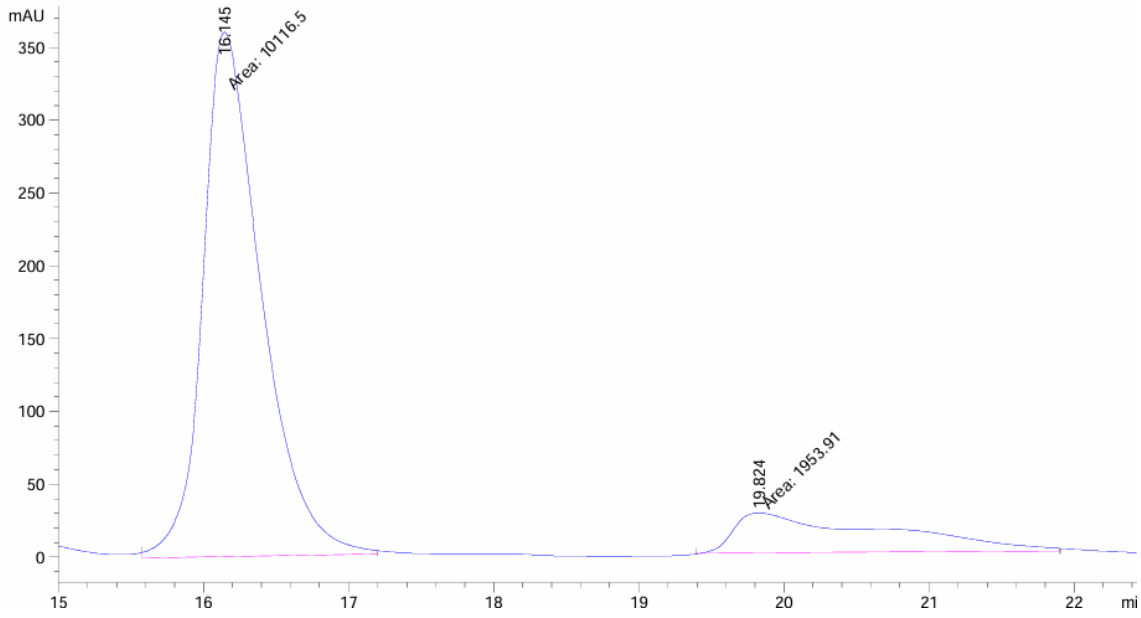
Signal 1: DAD1 B, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	61.853	MM	1.8680	2.67961e4	239.08089	88.3048
2	73.415	MM	1.5085	3548.89819	39.20918	11.6952
Totals :				3.03450e4	278.29007	

(*S*)-dimethyl 2-(2-nitro-1-(p-tolyl)ethyl)malonate (6f)



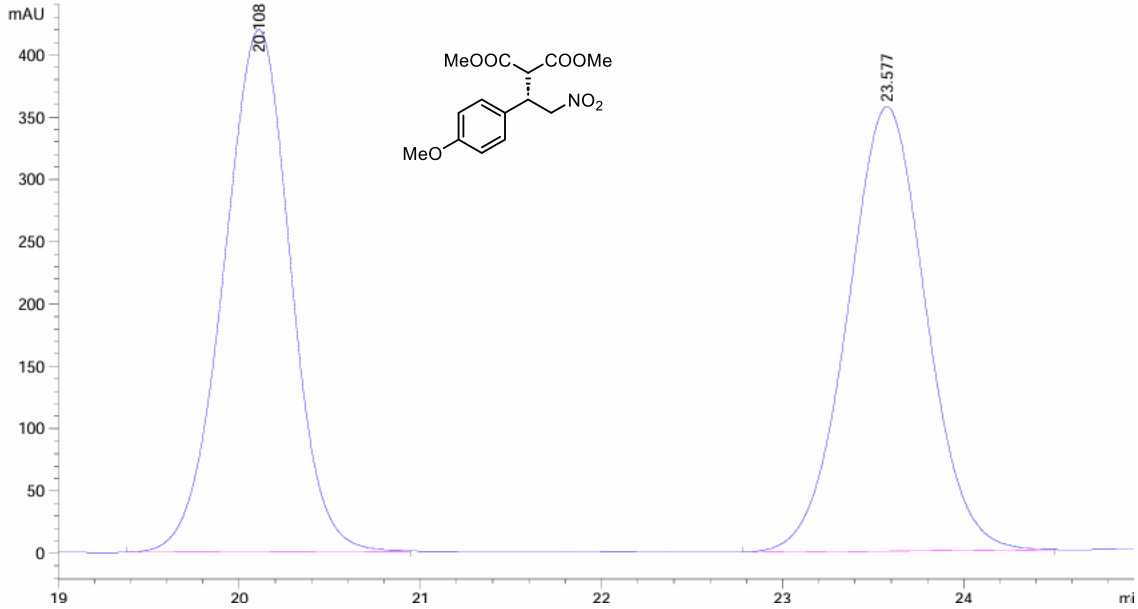
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.014	BB	0.3871	2163.00879	83.81332	49.6782
2	19.856	MM	0.8702	2191.03101	41.96473	50.3218
Totals :				4354.03979	125.77804	



Signal 1: DAD1 B, Sig=254,16 Ref=360,100

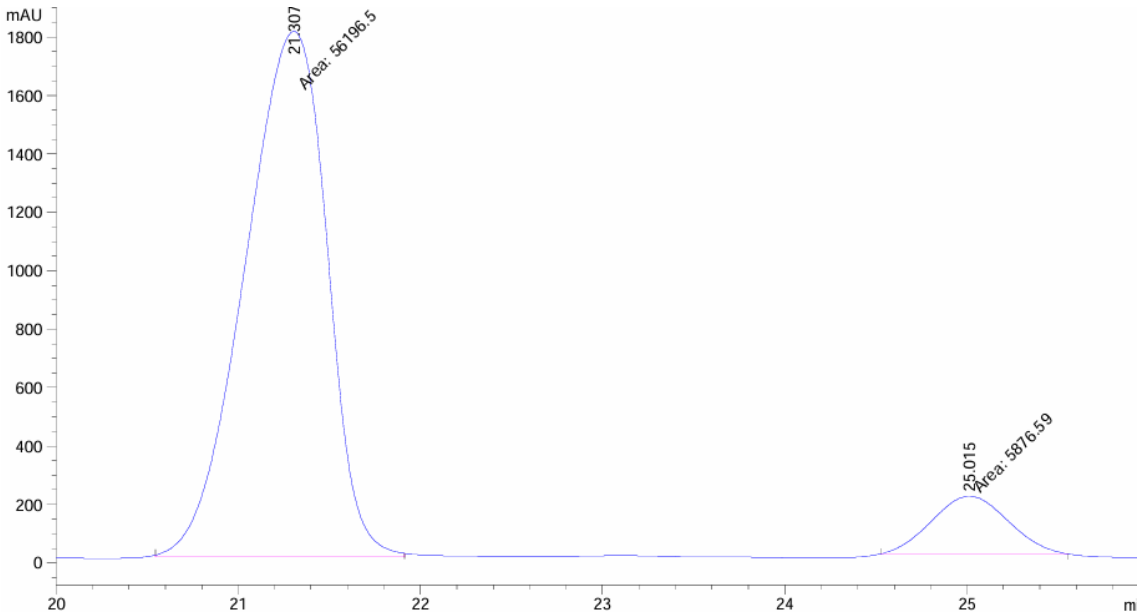
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.145	MM	0.4683	1.01165e4	360.00928	83.8124
2	19.824	MM	1.1887	1953.91248	27.39496	16.1876
Totals :				1.20705e4	387.40424	

(*S*)-dimethyl 2-(1-(4-methoxyphenyl)-2-nitroethyl)malonate (6g)



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

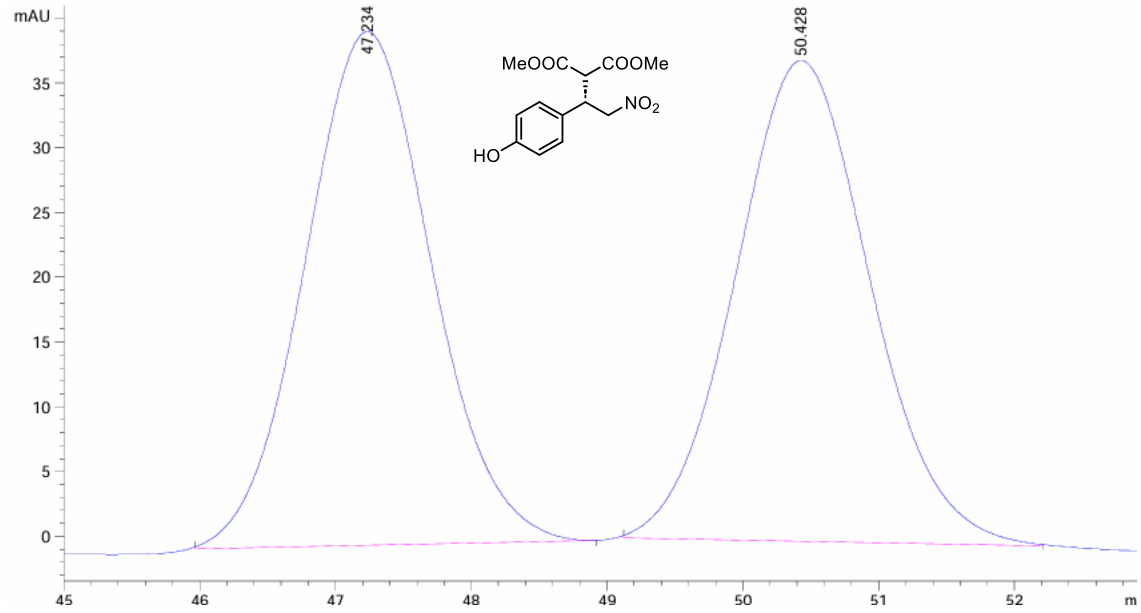
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.108	BB	0.3997	1.07658e4	419.02090	50.1148
2	23.577	BB	0.4646	1.07165e4	356.56686	49.8852
Totals :				2.14822e4	775.58777	



Signal 1: DAD1 B, Sig=254,16 Ref=360,100

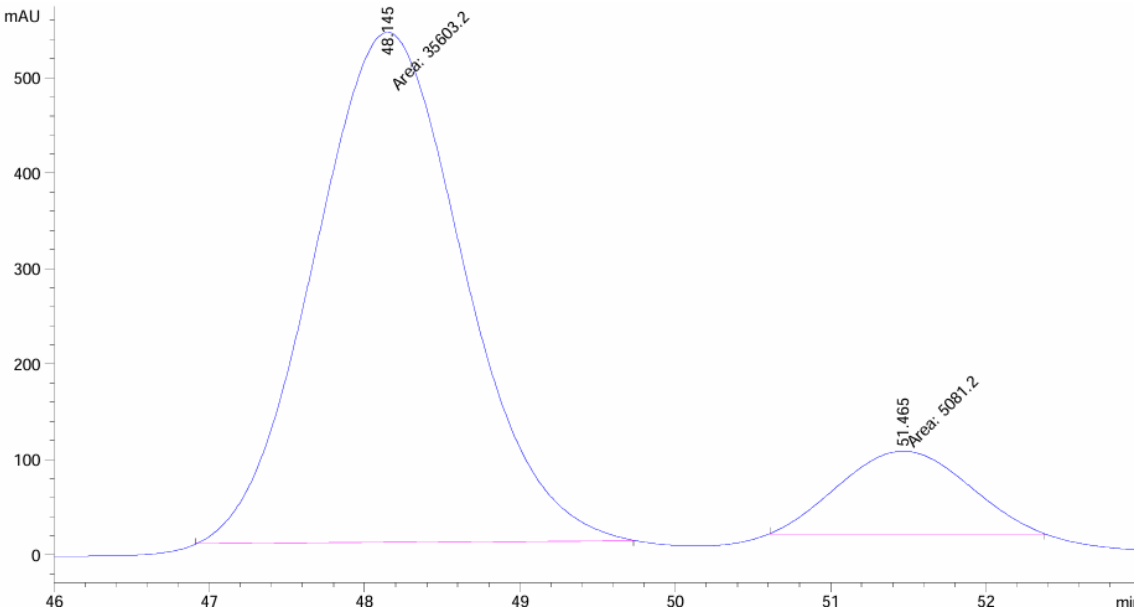
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.307	MM	0.5208	5.61965e4	1798.35657	90.5328
2	25.015	MM	0.4904	5876.58643	199.72989	9.4672
Totals :				6.20731e4	1998.08646	

(*S*)-dimethyl 2-(1-(4-hydroxyphenyl)-2-nitroethyl)malonate (6h)



Signal 1: DAD1 B, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	47.234	BB	1.0009	2560.21094	39.66983	50.0256
2	50.428	BB	1.0638	2557.59497	37.12057	49.9744
Totals :				5117.80591	76.79041	

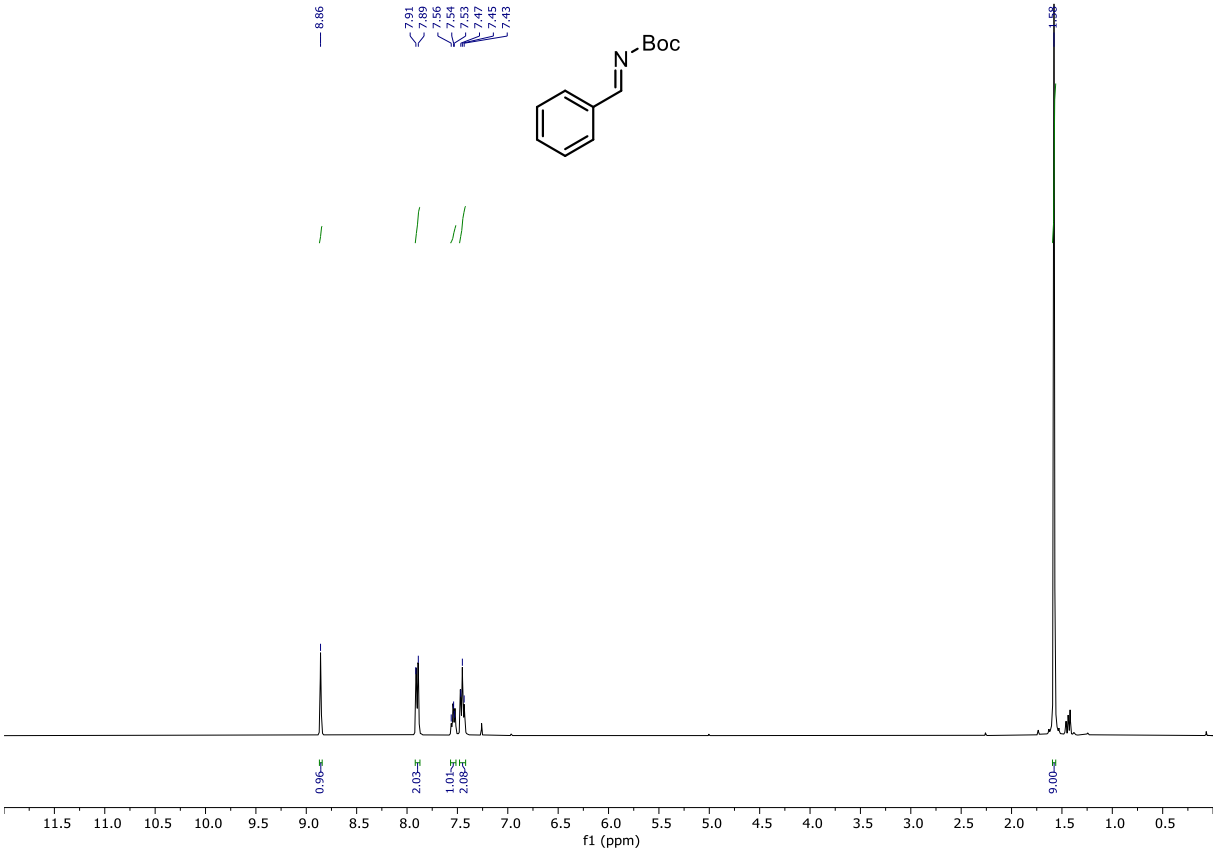


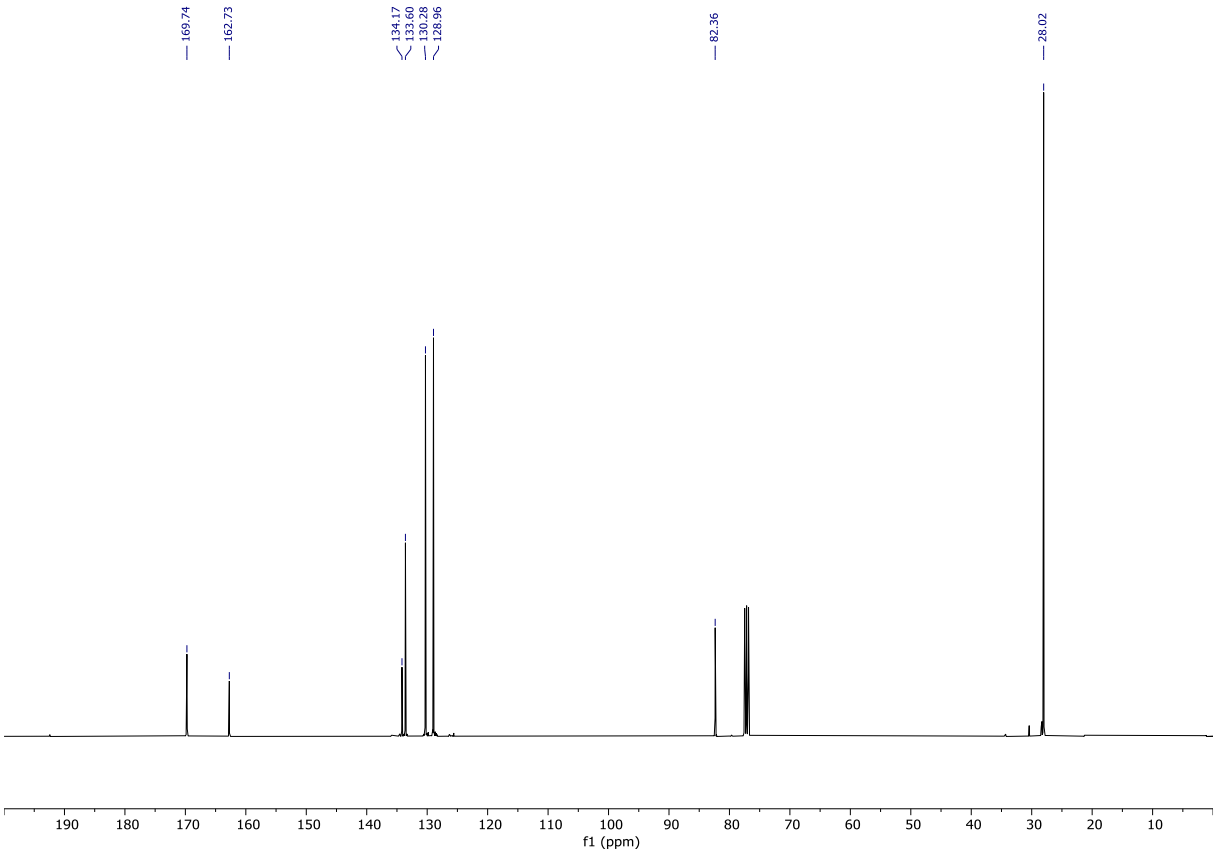
Signal 1: DAD1 B, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	48.145	MM	1.1110	3.56032e4	534.12360	87.5107
2	51.465	MM	0.9644	5081.19775	87.80897	12.4893
Totals :				4.06844e4	621.93256	

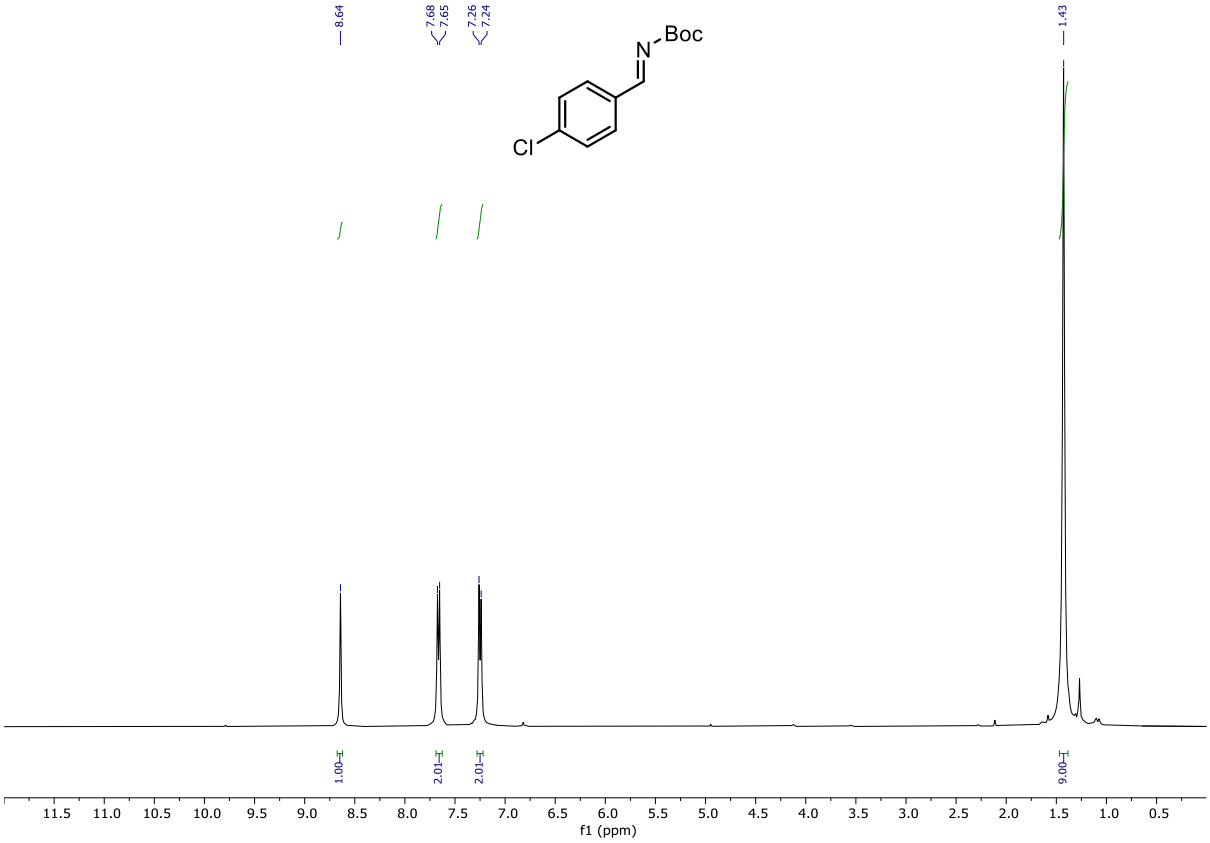
NMR spectra of 3

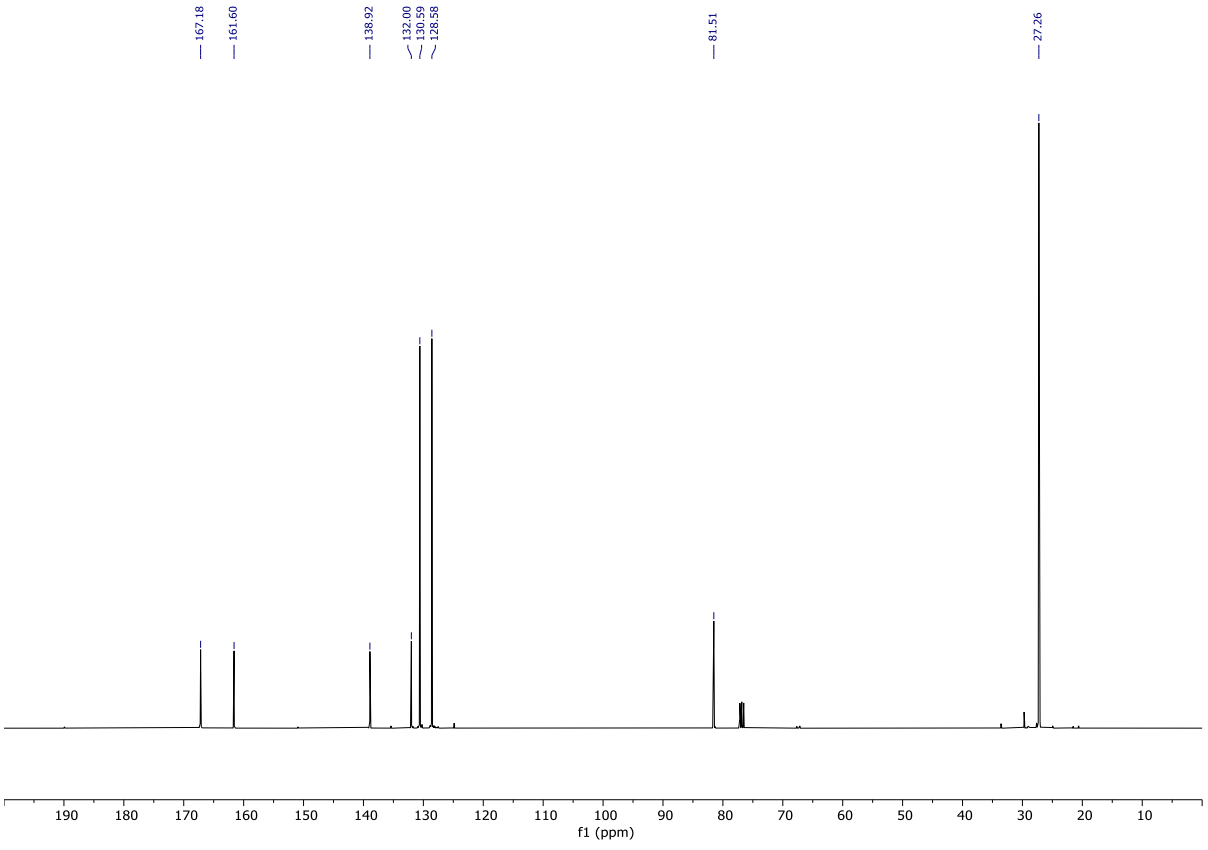
Tert-butyl (*E*)-benzylidenecarbamate (3a) ($CDCl_3$, ^1H 400 MHz, ^{13}C 101 MHz)



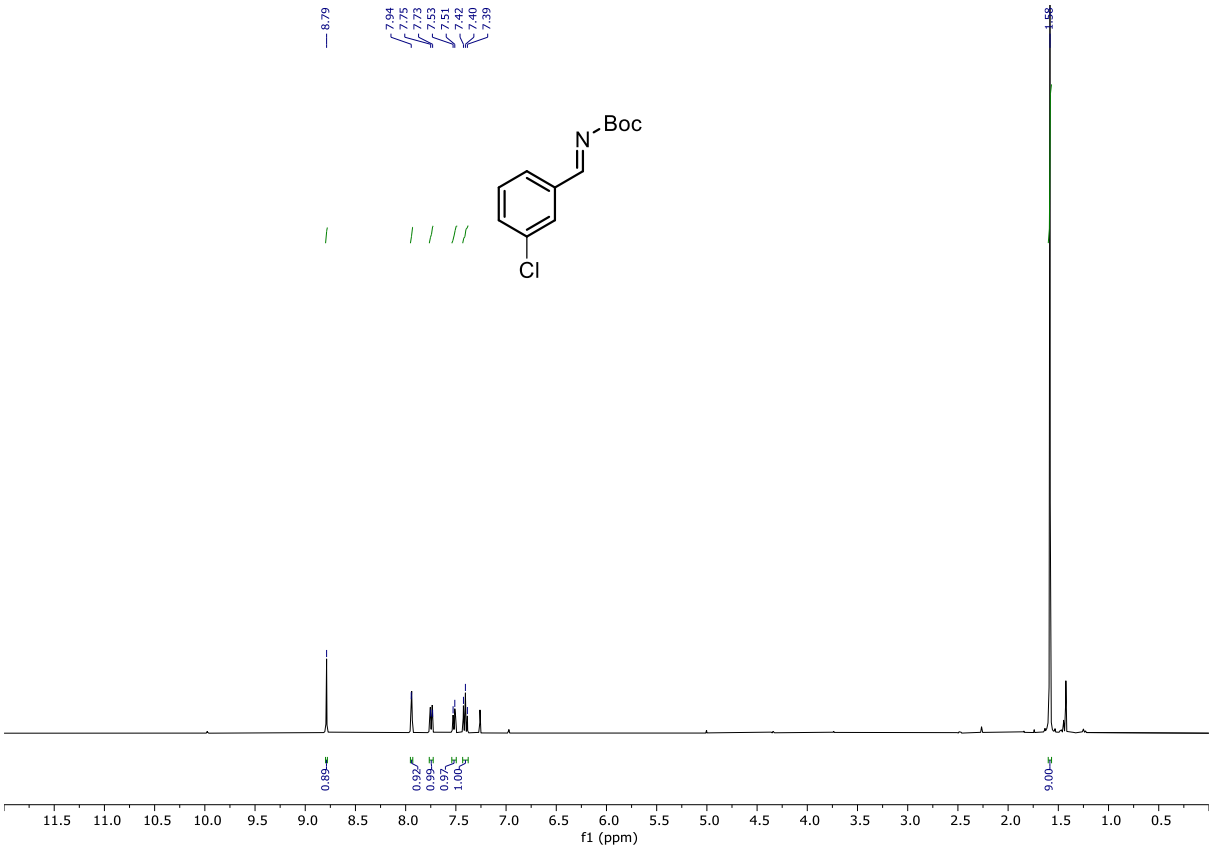


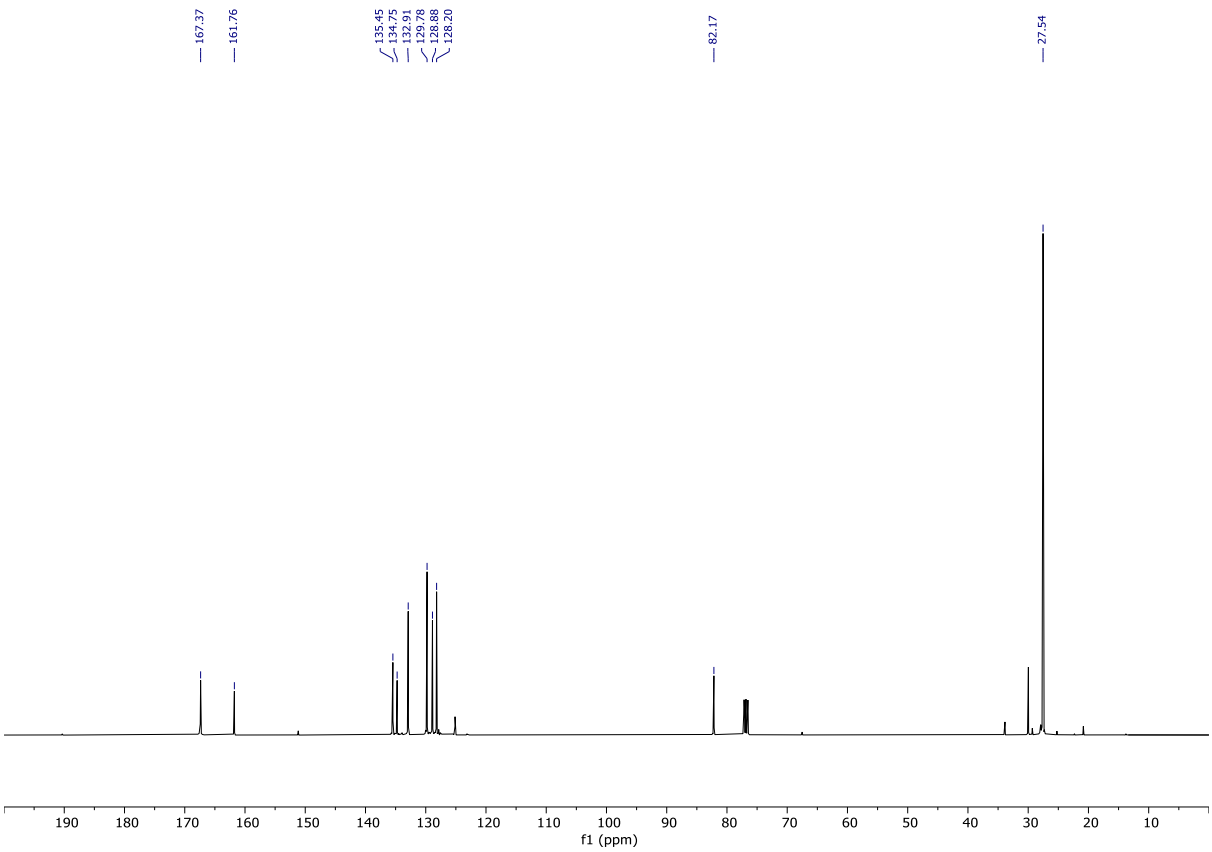
Tert-butyl (*E*)-(4-chlorobenzylidene)carbamate (3b) ($CDCl_3$, ^1H 400 MHz, ^{13}C 101 MHz)



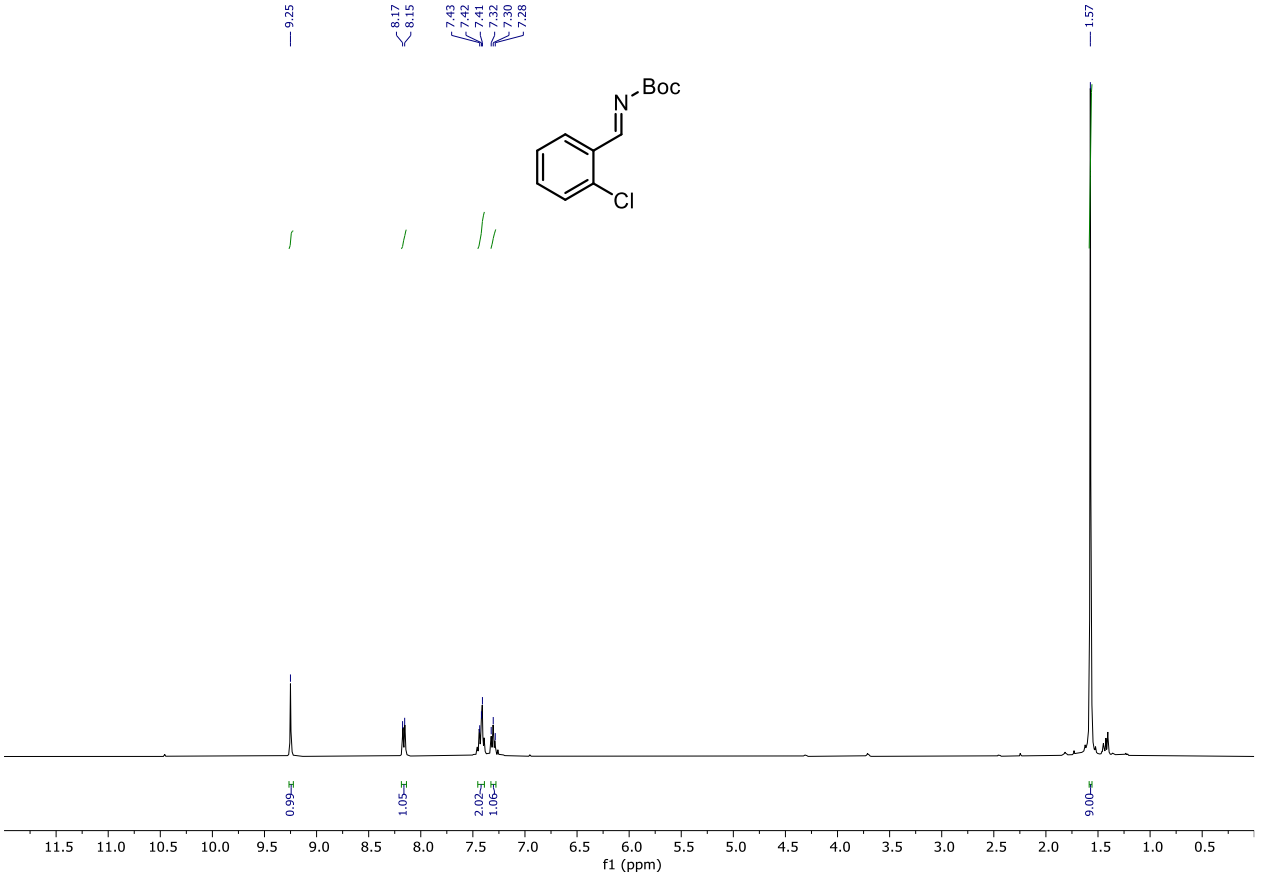


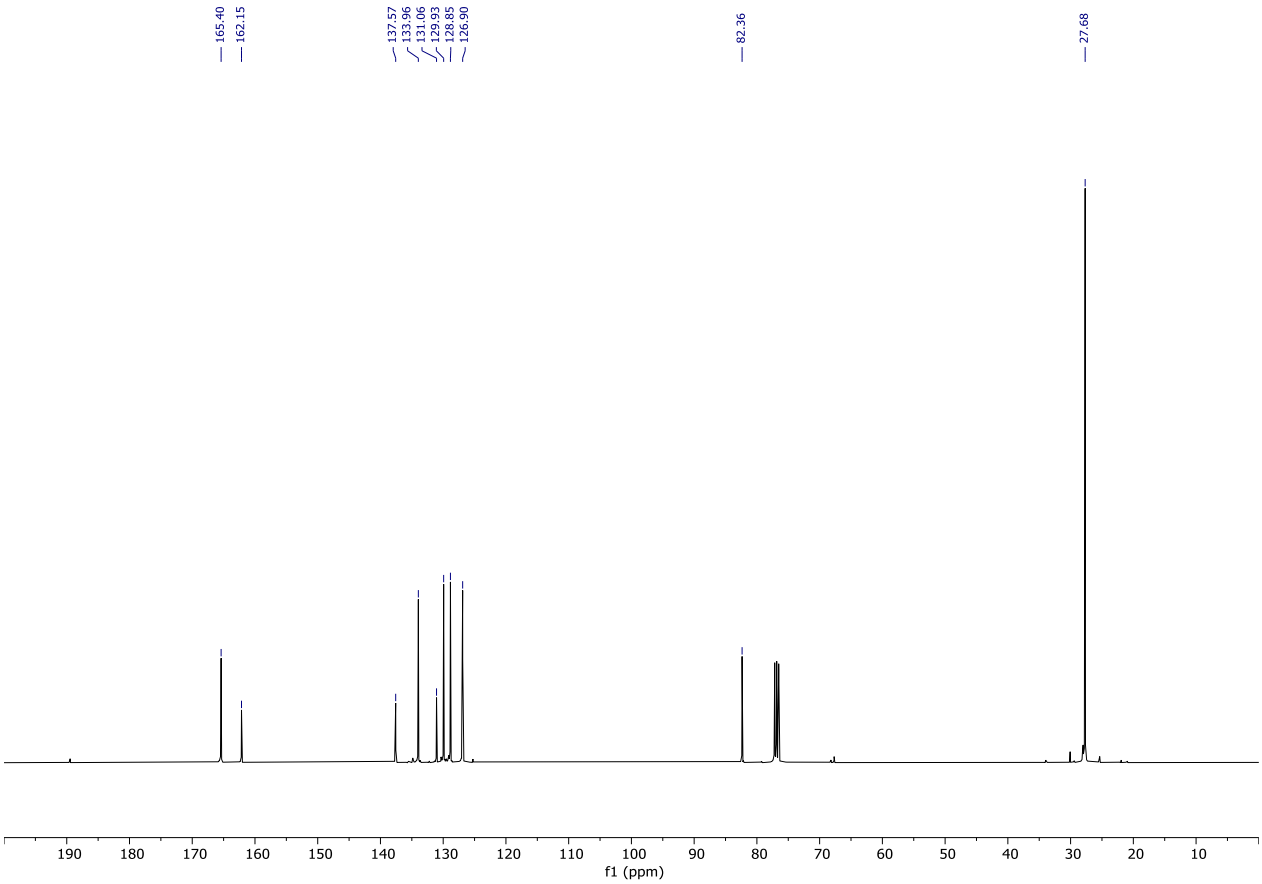
Tert-butyl *(E)*-(3-chlorobenzylidene)carbamate (3c) ($CDCl_3$, ^1H 400 MHz, ^{13}C 101 MHz)



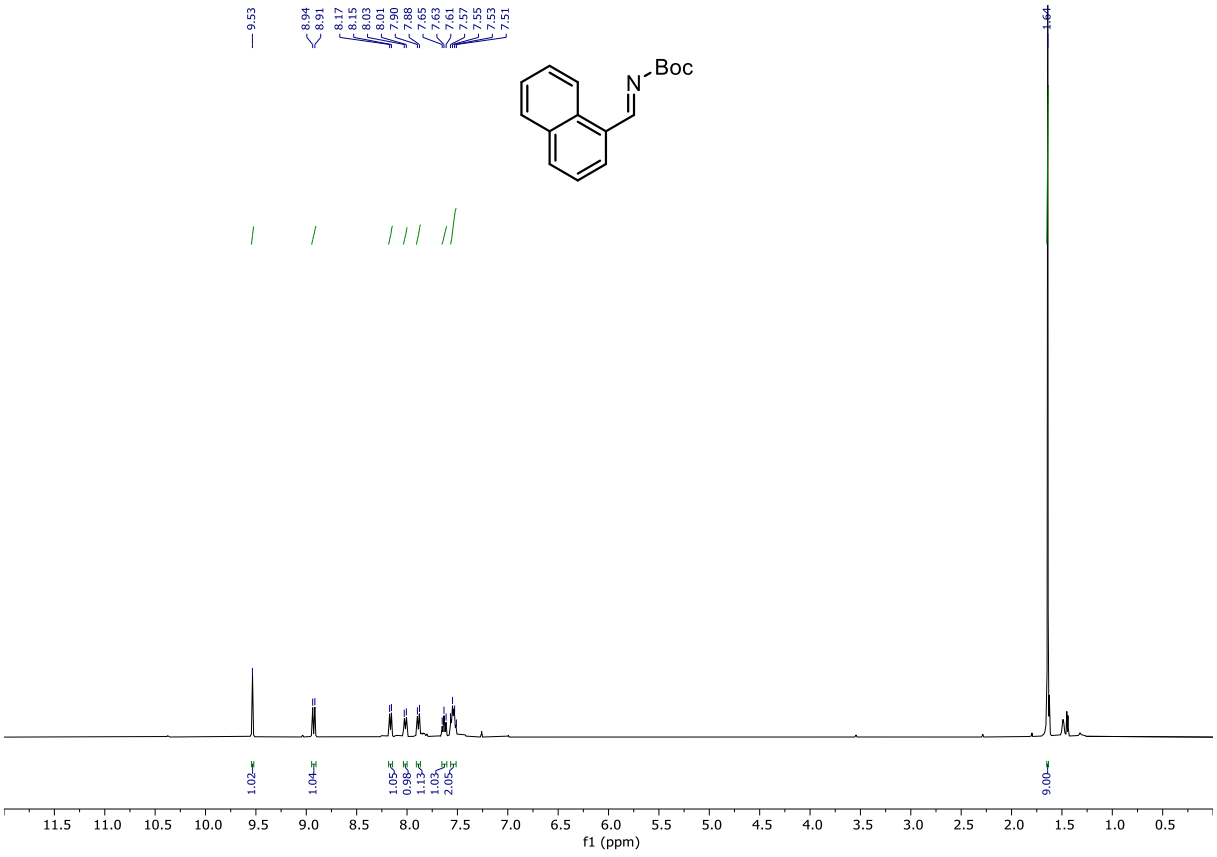


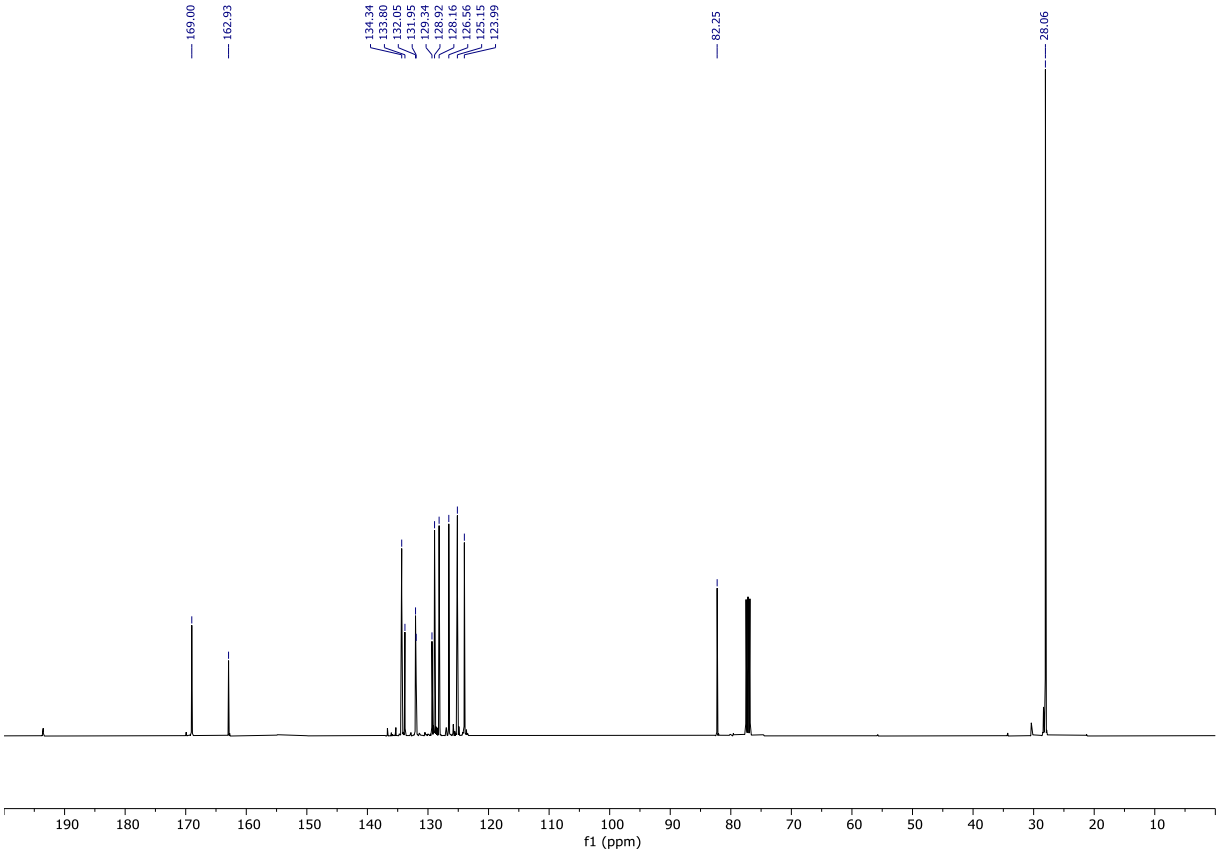
Tert-butyl (*E*)-(2-chlorobenzylidene)carbamate (3d) ($CDCl_3$, ^1H 400 MHz, ^{13}C 101 MHz)



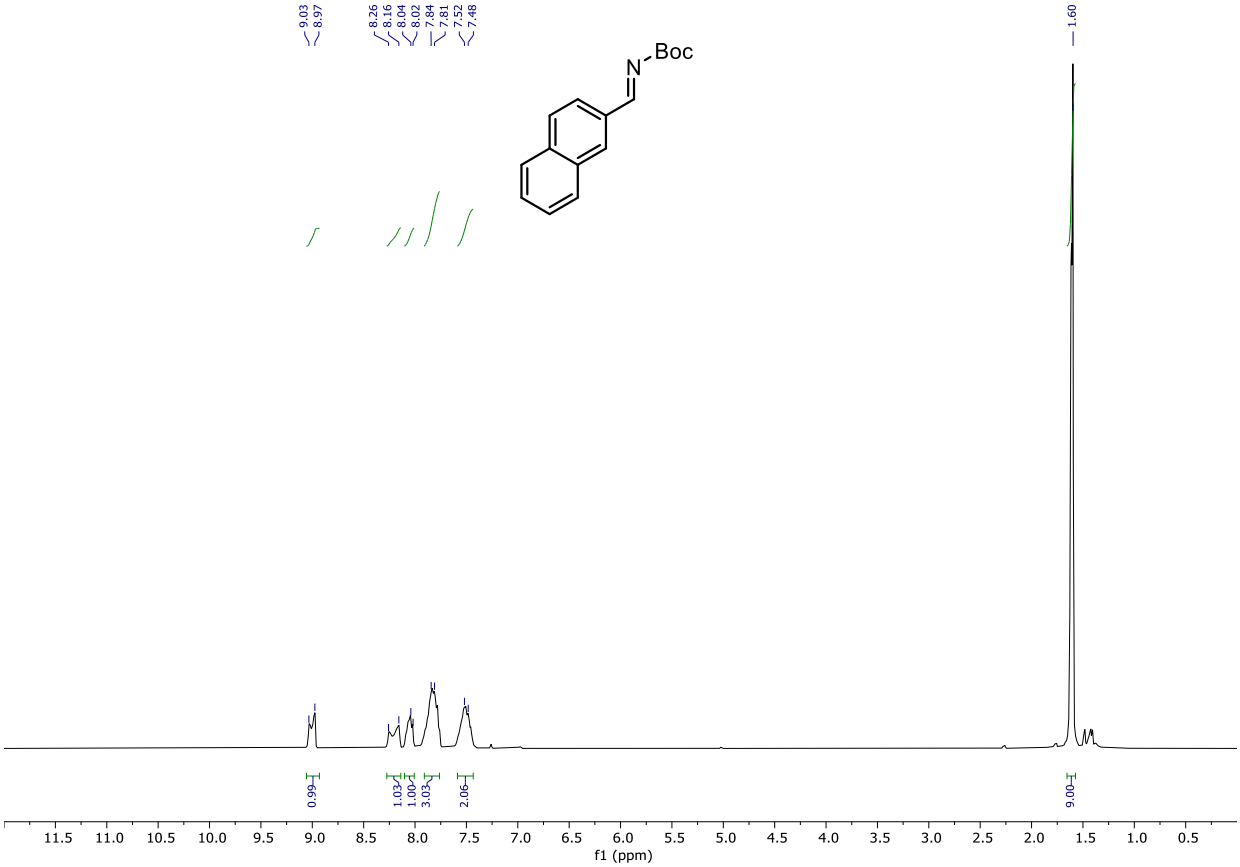


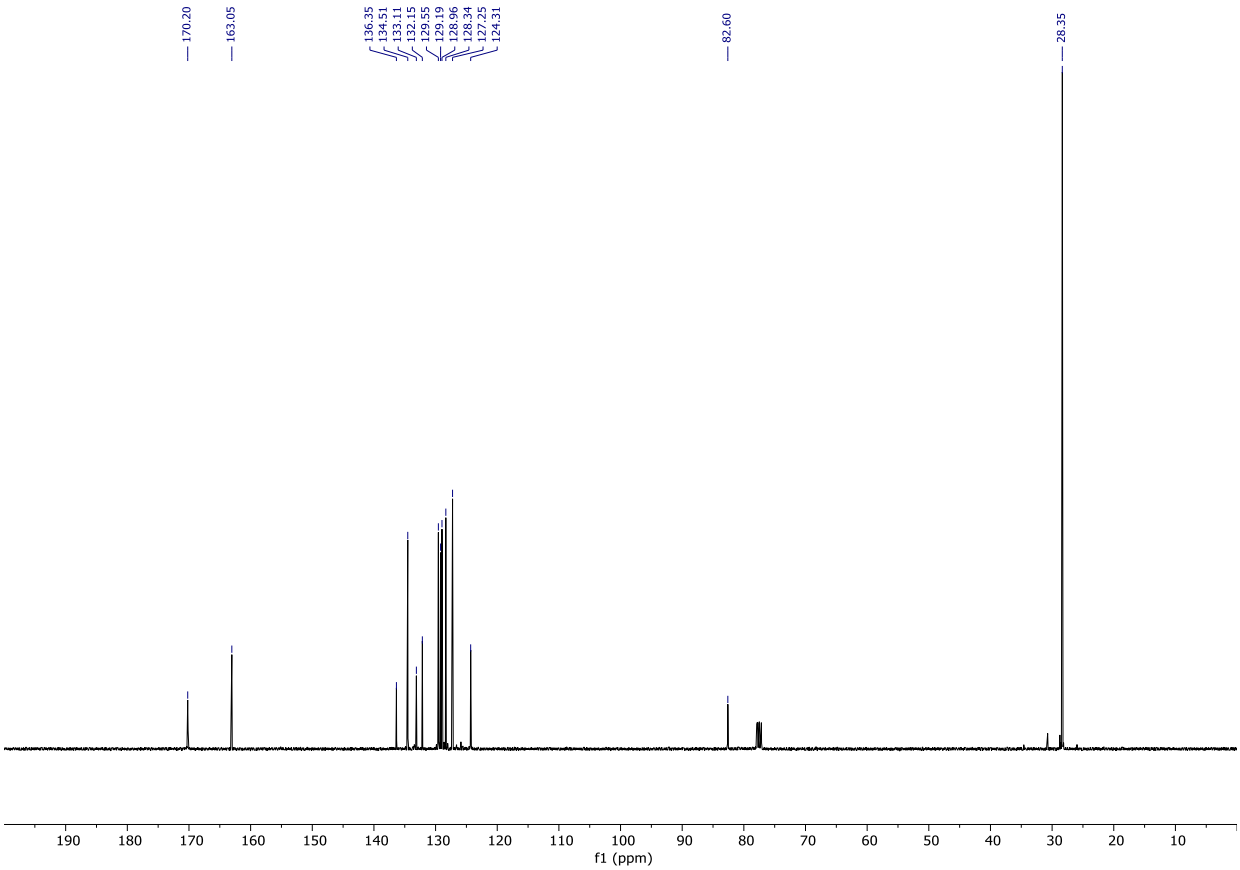
Tert-butyl (*E*)-(naphthalen-1-ylmethylene)carbamate (3e) ($CDCl_3$, ^1H 400 MHz, ^{13}C 101 MHz)



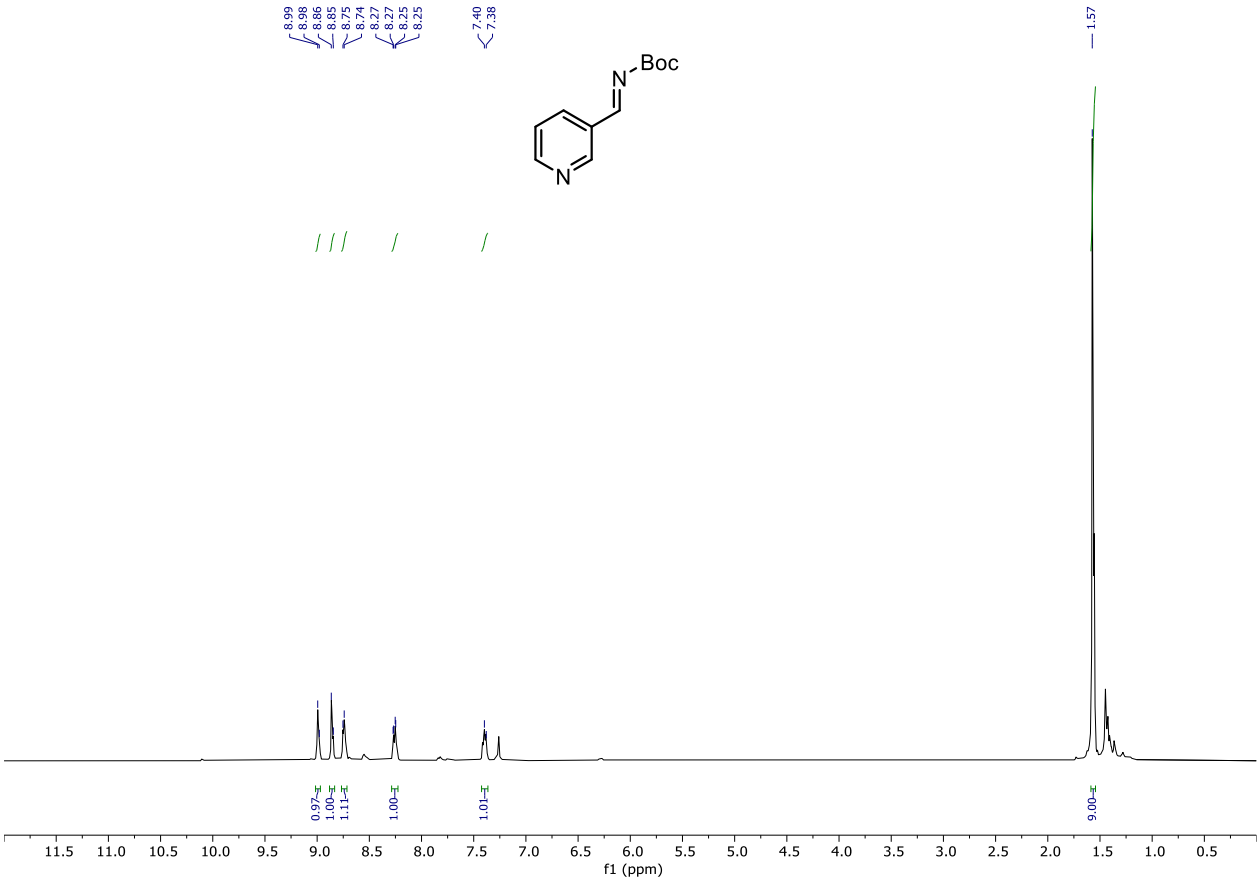


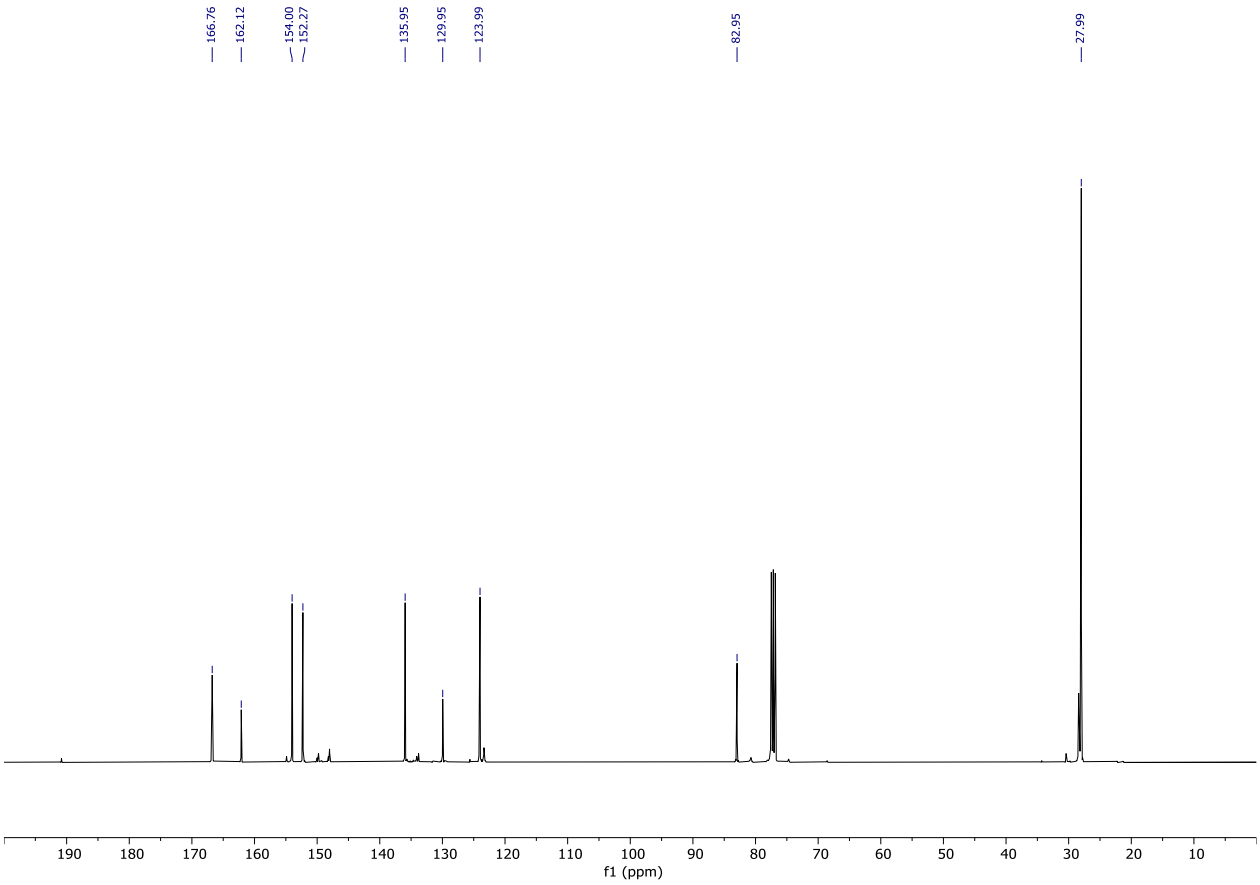
Tert-butyl (*E*)-(naphthalen-2-ylmethylene)carbamate (3f) ($CDCl_3$, ^1H 400 MHz, ^{13}C 101 MHz)



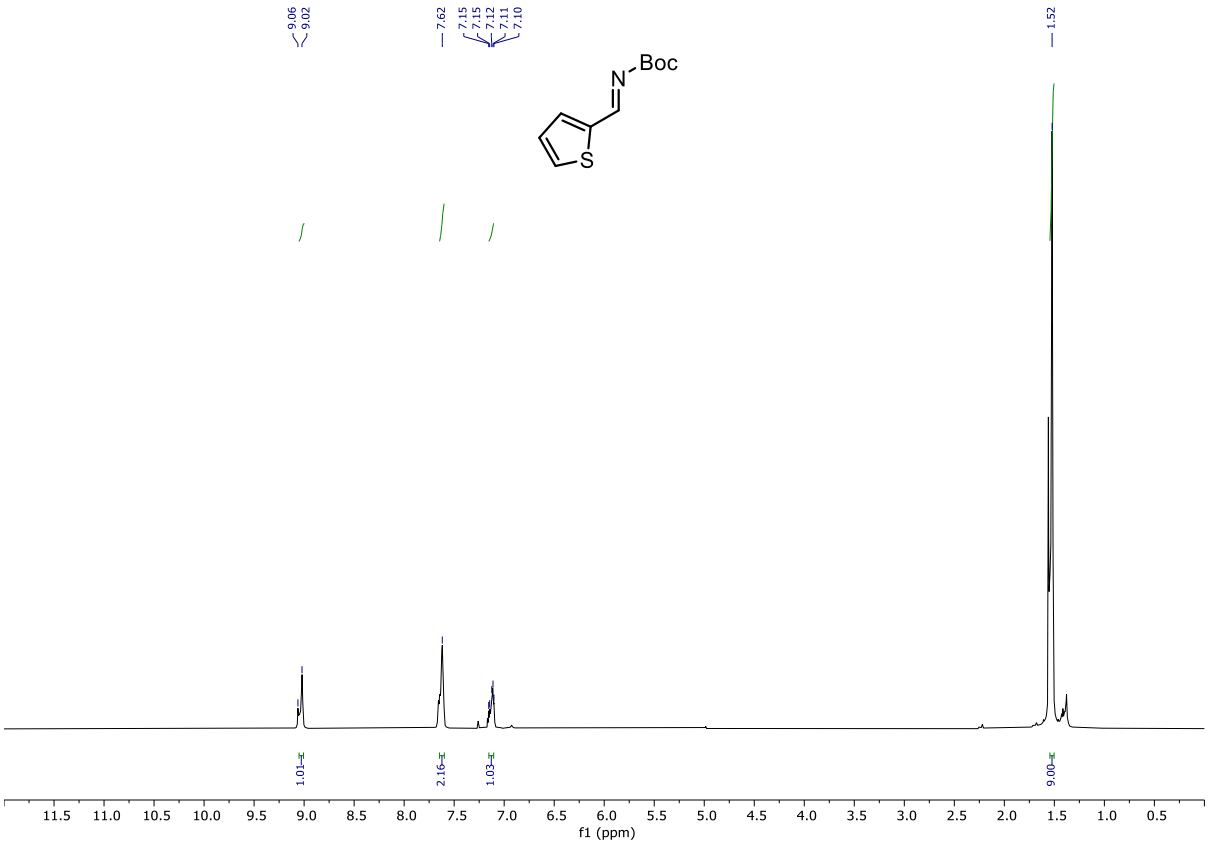


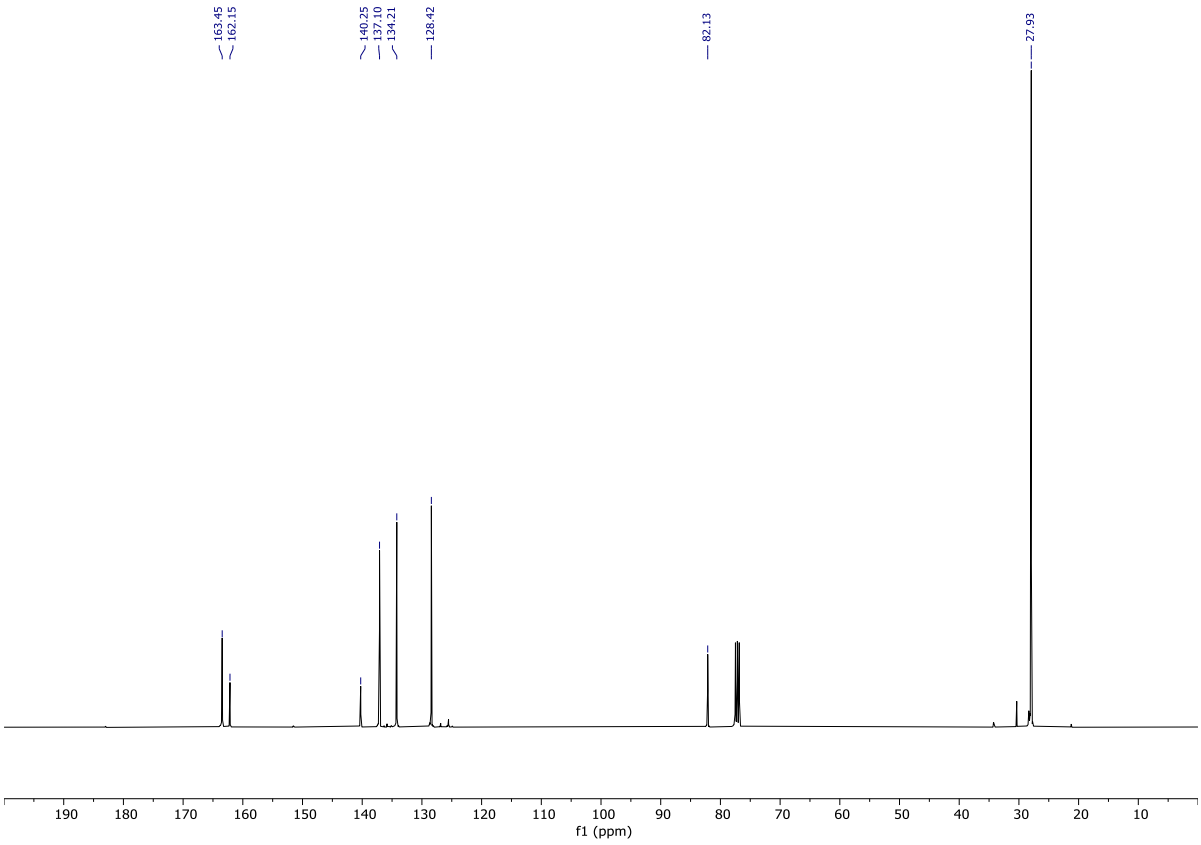
Tert-butyl (*E*)-(pyridin-3-ylmethylene)carbamate (3g) ($CDCl_3$, ^1H 400 MHz, ^{13}C 101 MHz)



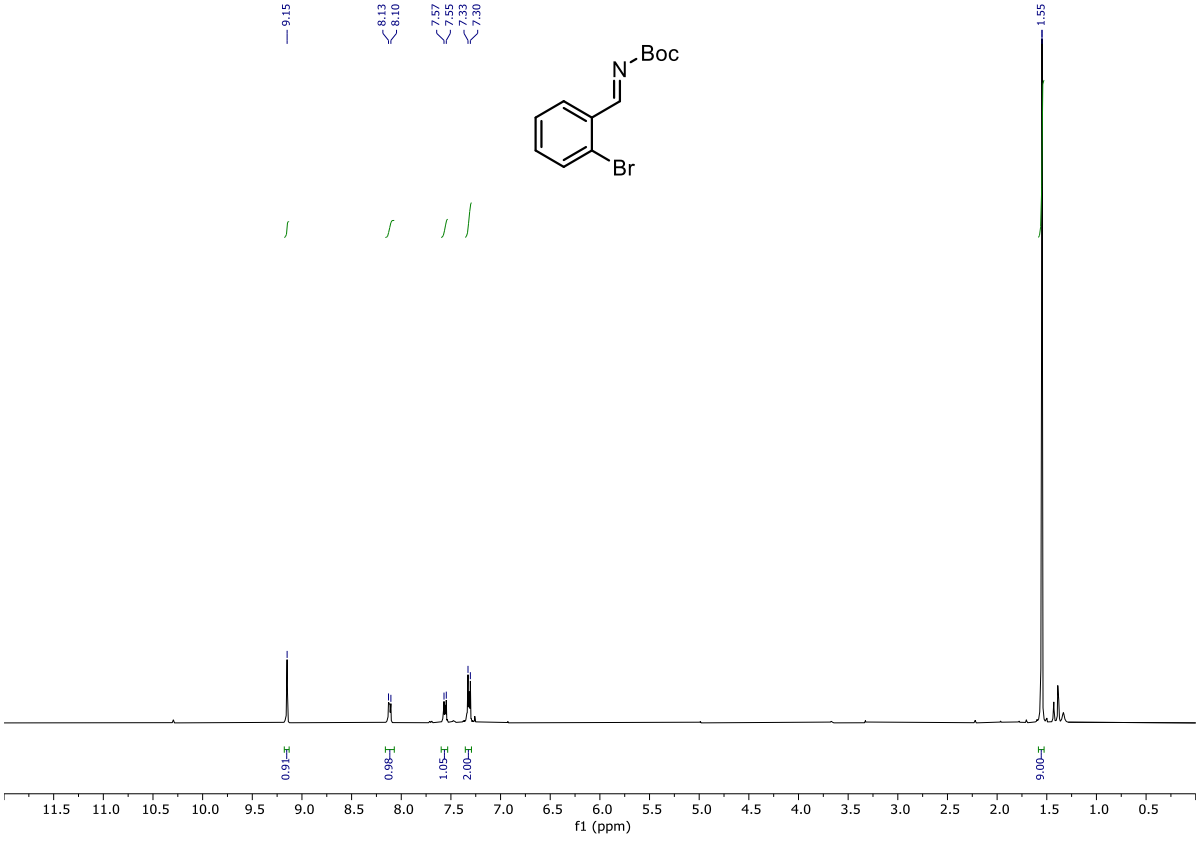


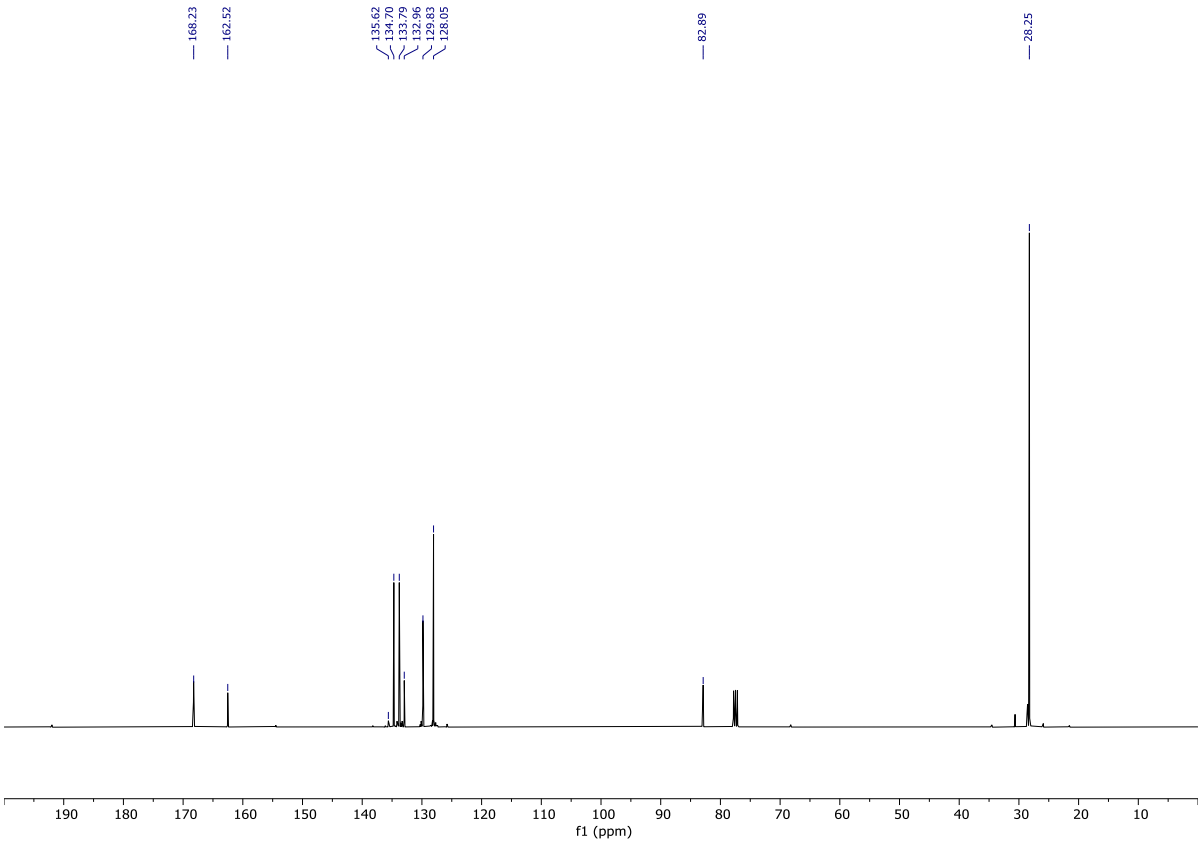
Tert-butyl (*E*)-(thiophen-2-ylmethylene)carbamate (3h) ($CDCl_3$, ^1H 400 MHz, ^{13}C 101 MHz)



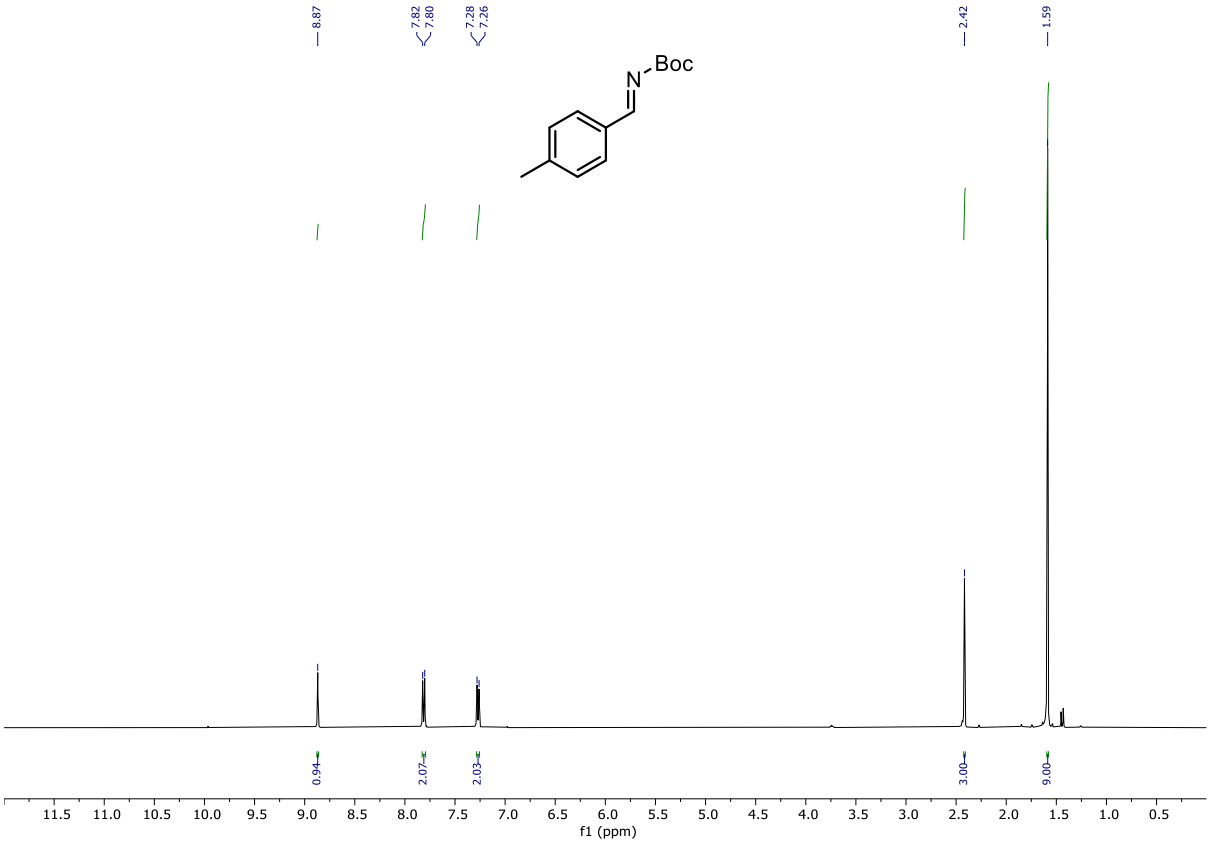


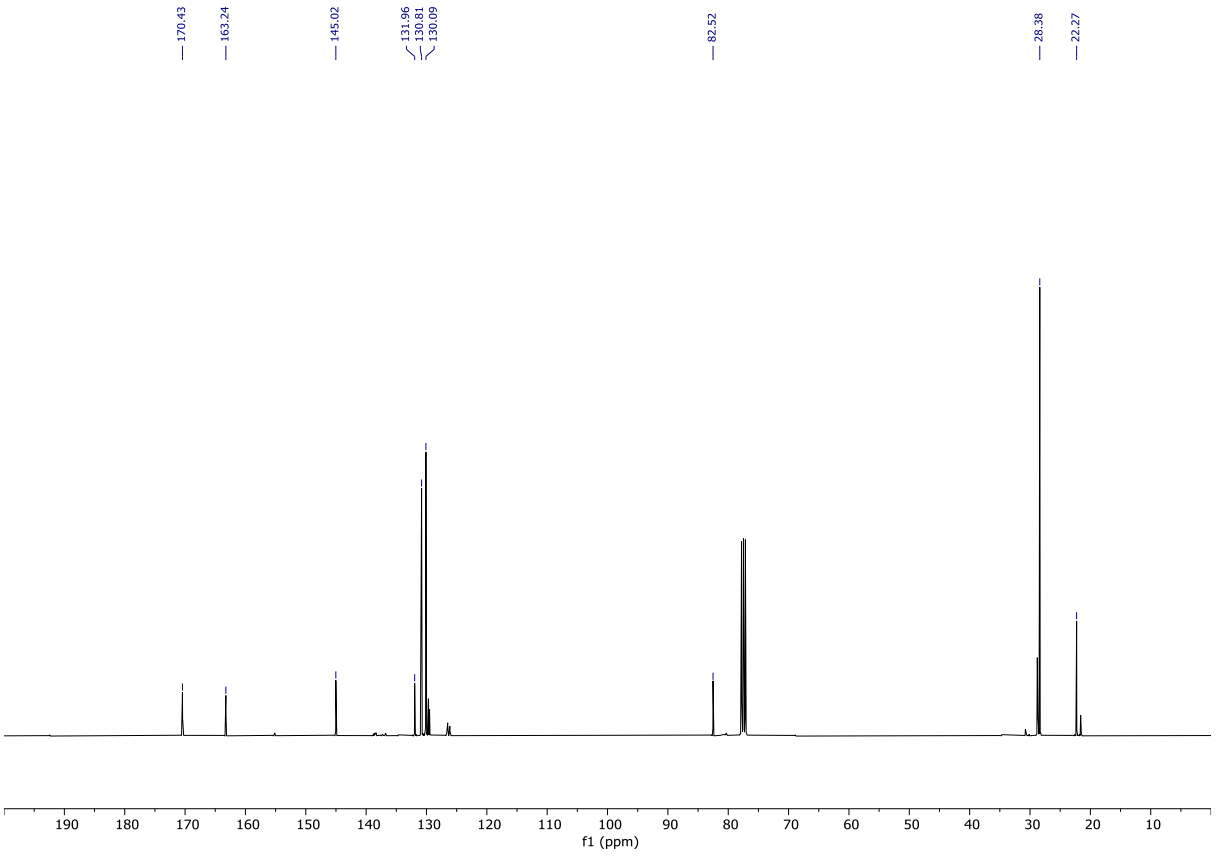
Tert-butyl (*E*)-(2-bromobenzylidene)carbamate (3i) ($CDCl_3$, ^1H 400 MHz, ^{13}C 101 MHz)



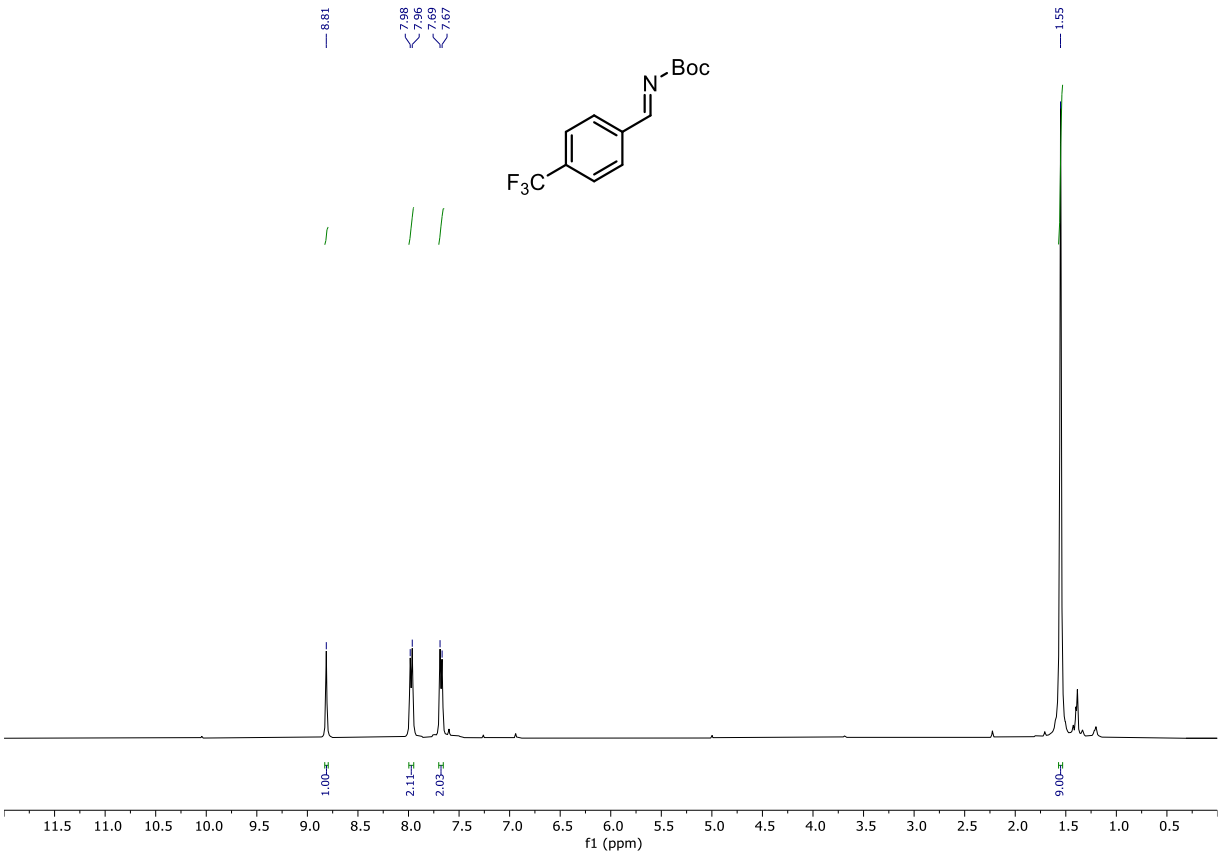


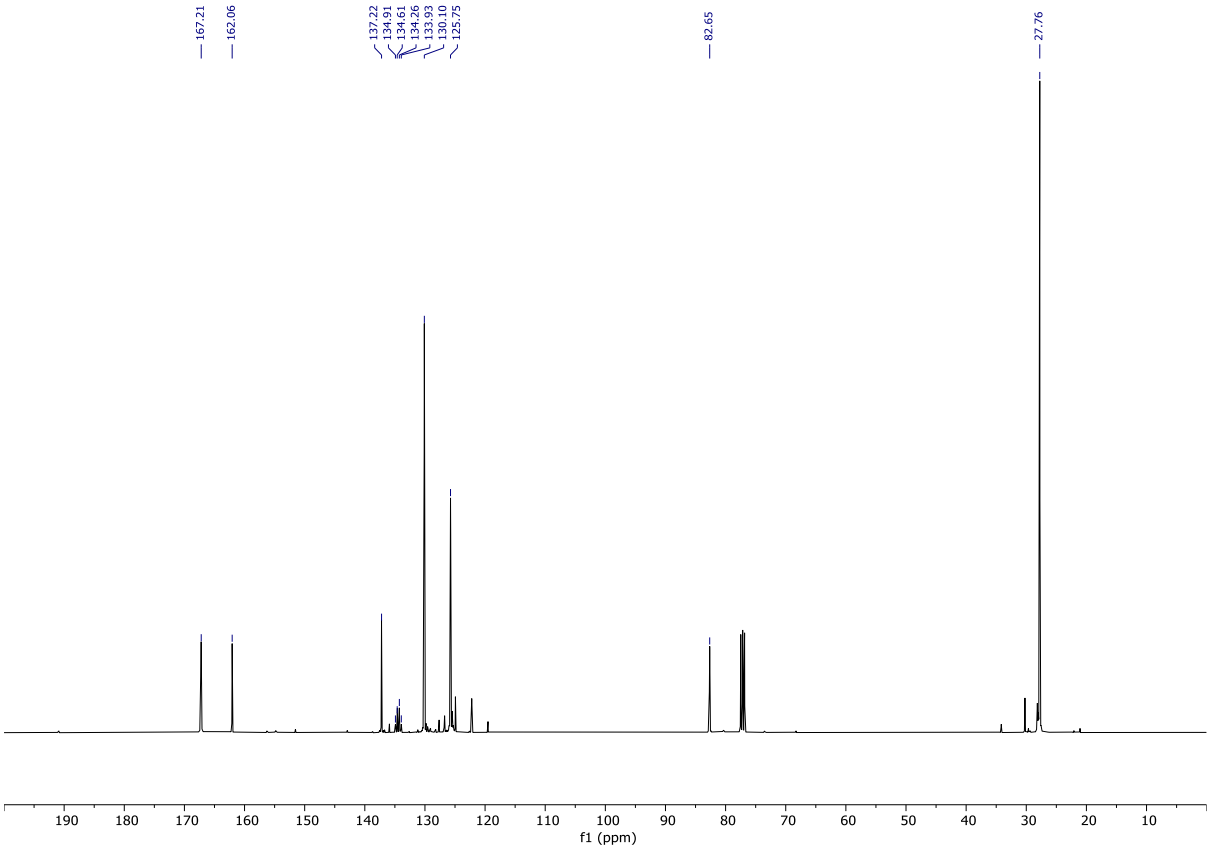
Tert-butyl (*E*)-(4-methylbenzylidene)carbamate (3j) ($CDCl_3$, ^1H 400 MHz, ^{13}C 101 MHz)

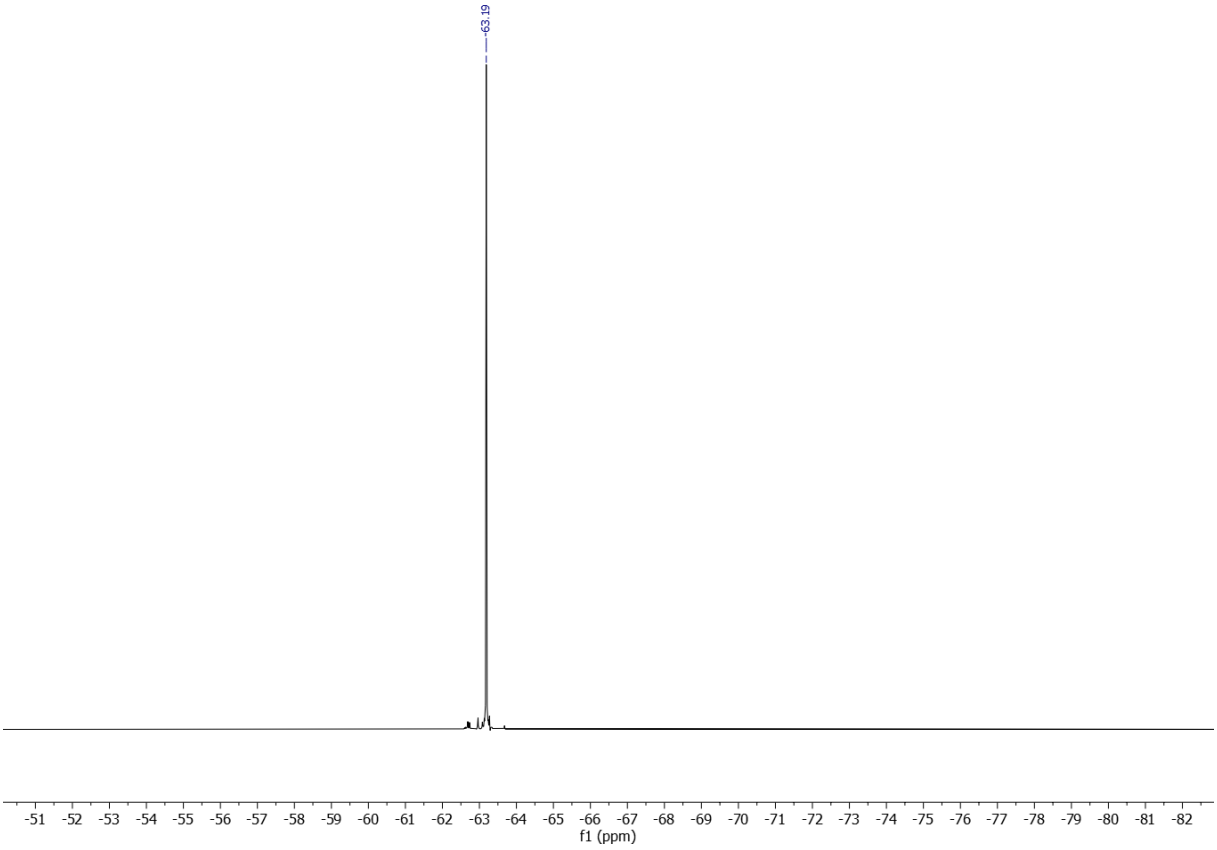




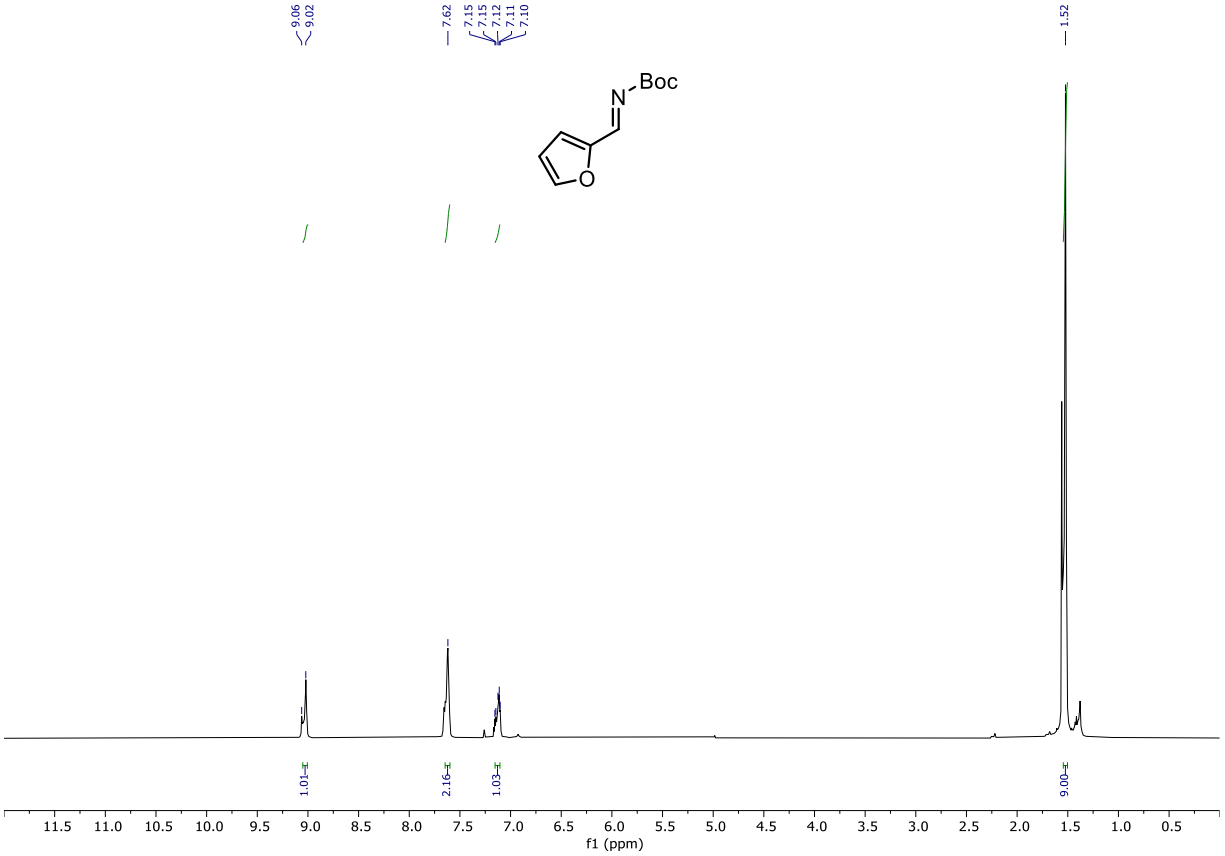
Tert-butyl (*E*)-(4-(trifluoromethyl)benzylidene)carbamate (3k) ($CDCl_3$, ^{1}H 400 MHz, ^{13}C 101 MHz, ^{19}F 376 MHz)

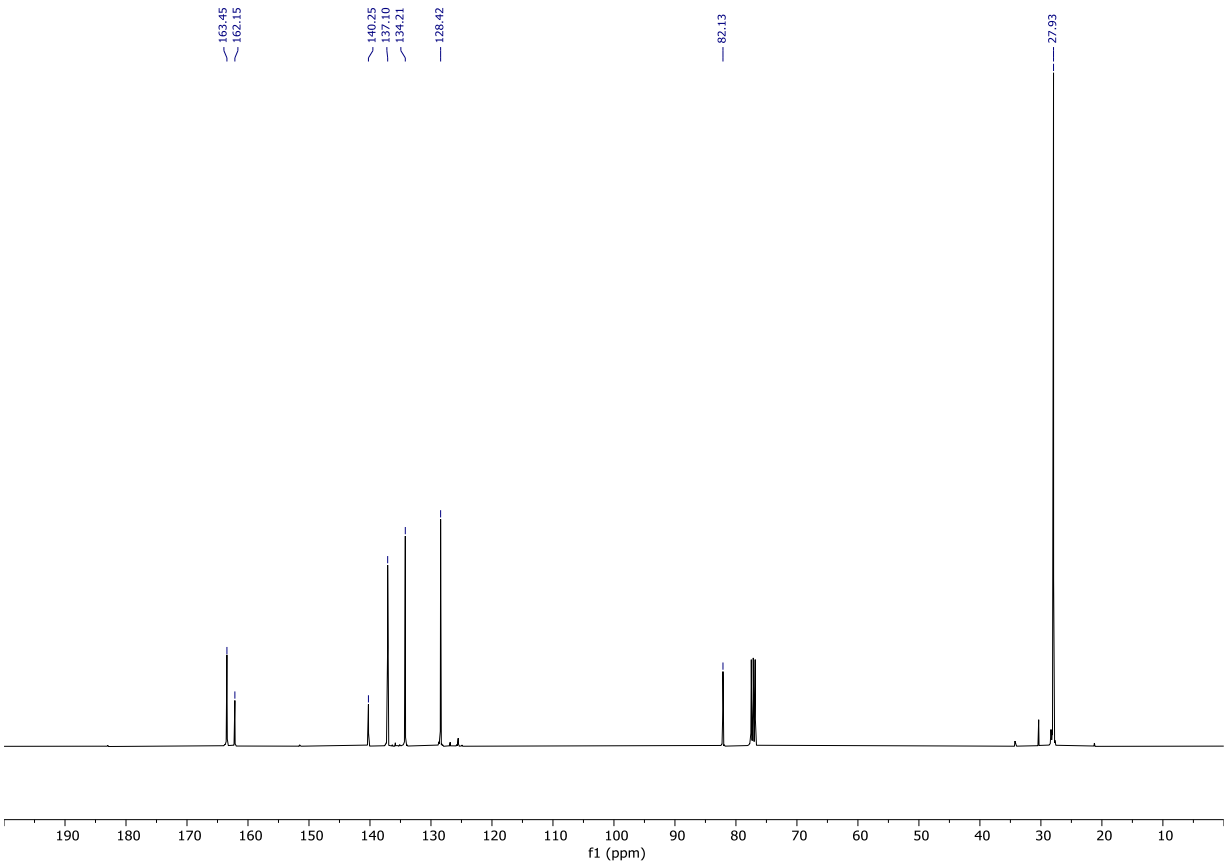

8.81
7.98
7.96
7.69
7.67
1.55
N
Boc
F3C
1.00
2.11
2.03
9.00
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


167.21
162.06
137.22
134.91
134.61
134.26
133.93
130.10
125.75
82.65
27.76
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


-63.19
-51 -52 -53 -54 -55 -56 -57 -58 -59 -60 -61 -62 -63 -64 -65 -66 -67 -68 -69 -70 -71 -72 -73 -74 -75 -76 -77 -78 -79 -80 -81 -82
f1 (ppm)

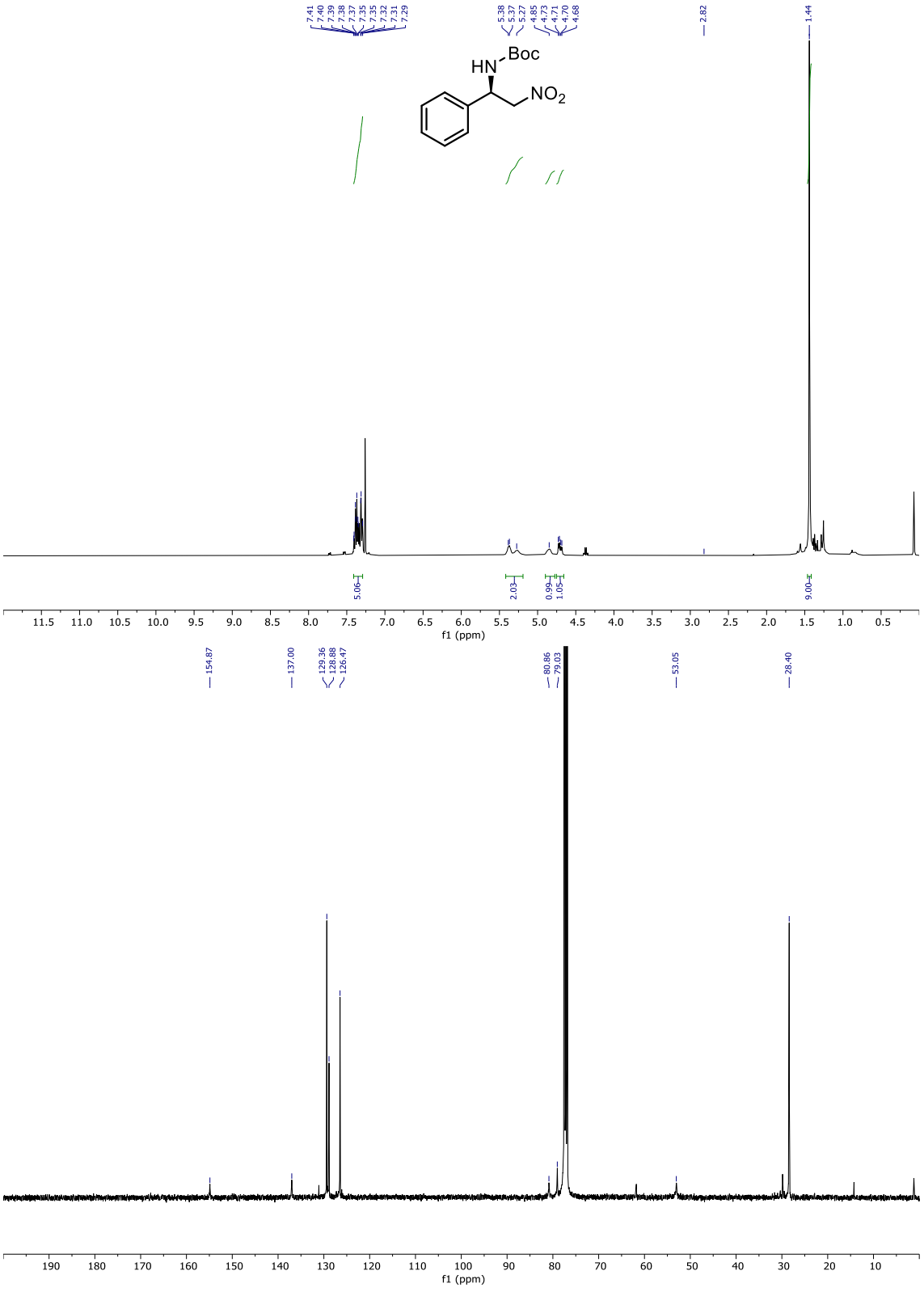
Tert-butyl (*E*)-(furan-2-ylmethylene)carbamate (3l) ($CDCl_3$, ^1H 400 MHz, ^{13}C 101 MHz)



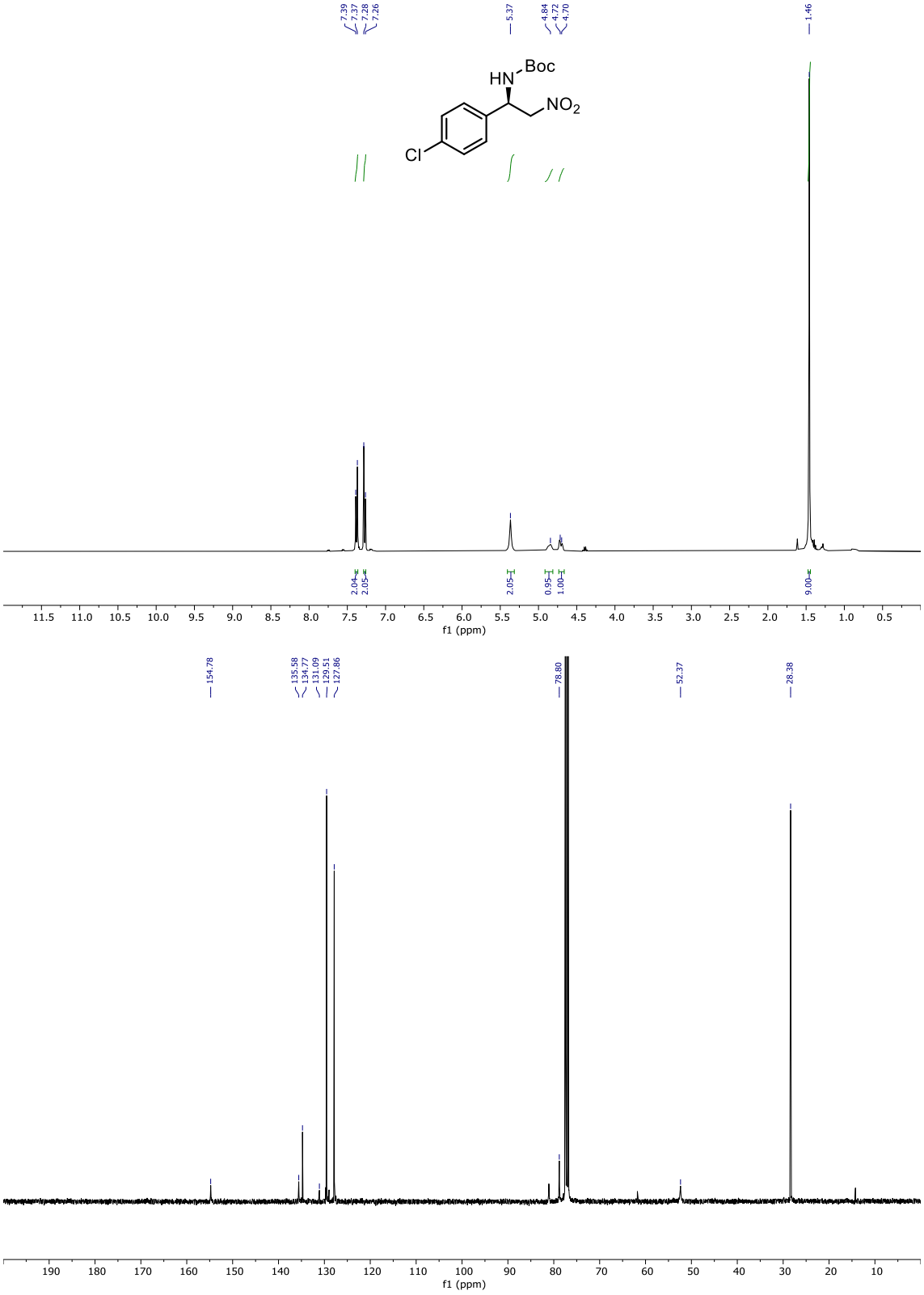


NMR spectra of 4

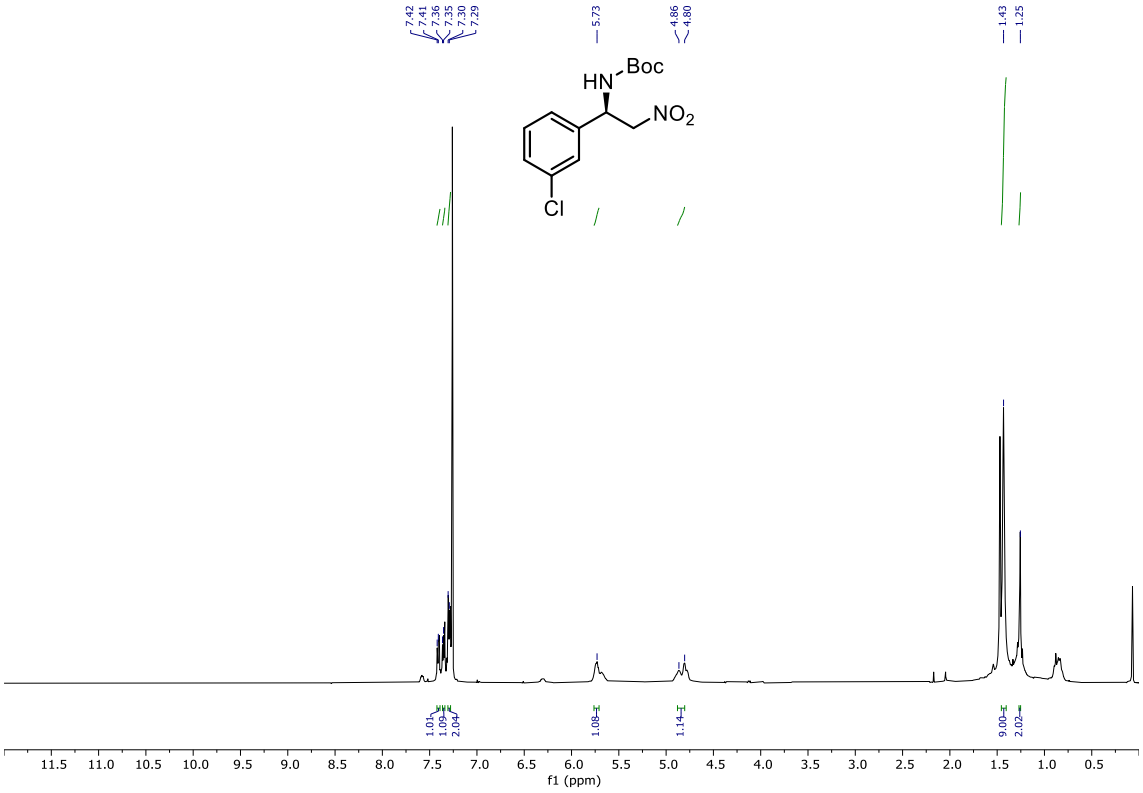
Tert-butyl (*R*)-(2-nitro-1-phenylethyl)carbamate (4a) ($CDCl_3$, ^1H 400 MHz, ^{13}C 101 MHz)

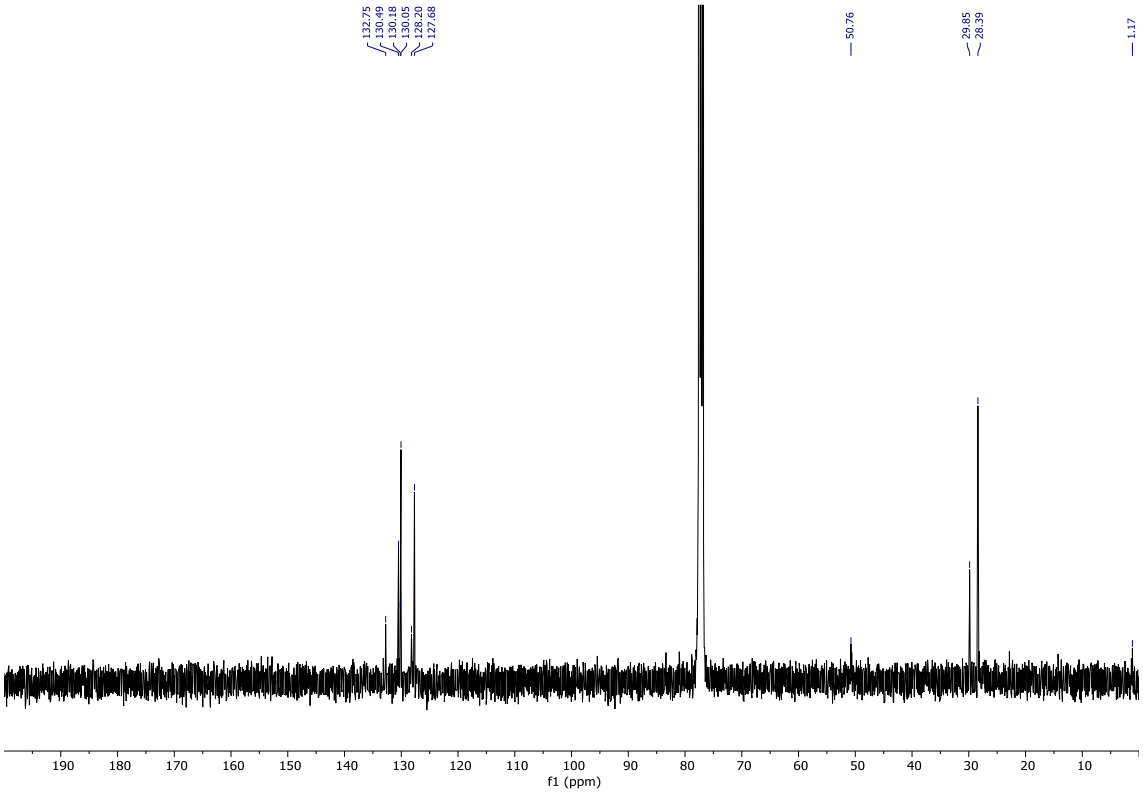


Tert-butyl (*R*)-(1-(4-chlorophenyl)-2-nitroethyl)carbamate (4b) ($CDCl_3$, ^1H 400 MHz, ^{13}C 101 MHz)

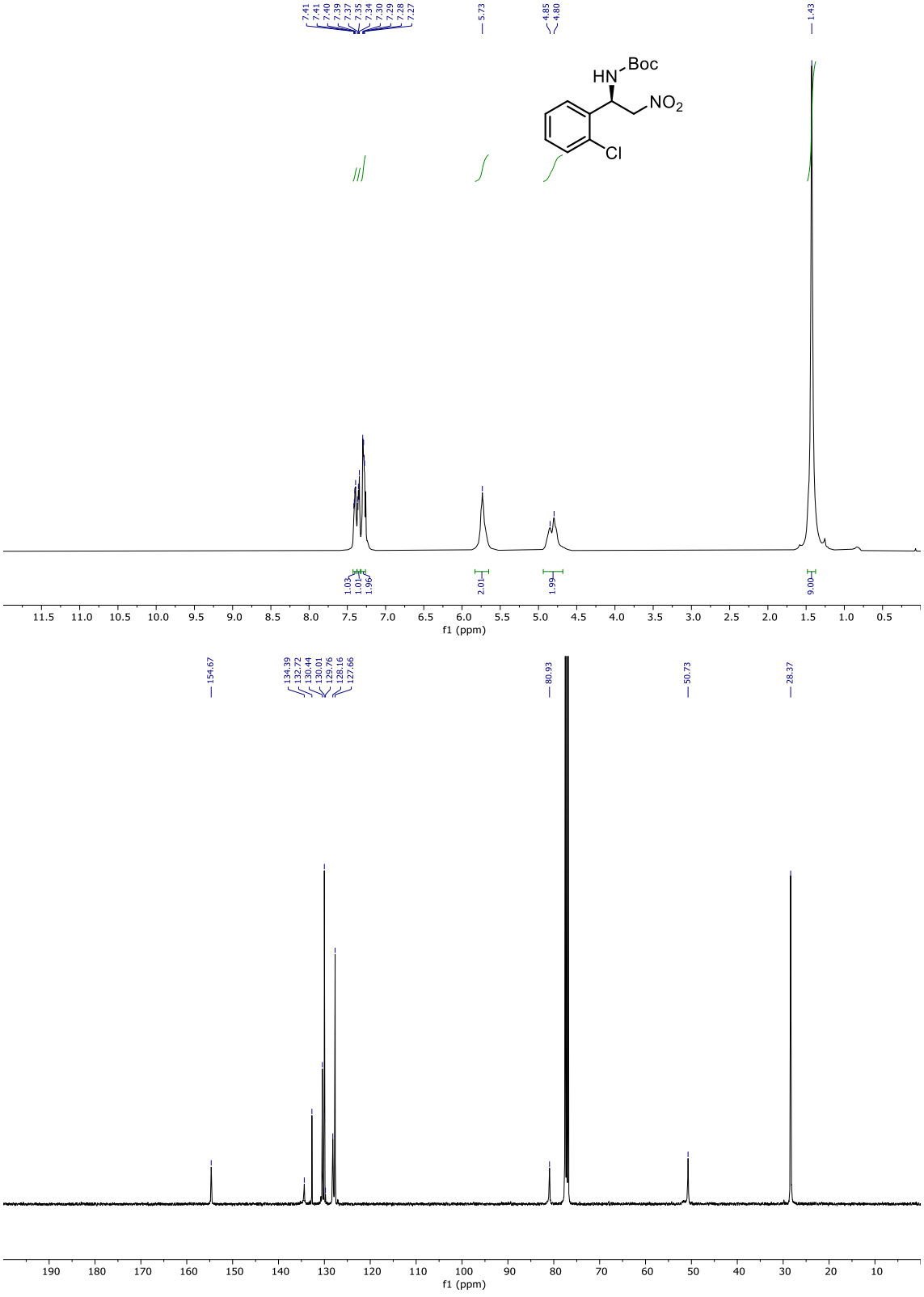


Tert-butyl (*R*)-(1-(3-chlorophenyl)-2-nitroethyl)carbamate (4c) ($CDCl_3$, ^1H 400 MHz, ^{13}C 101 MHz)

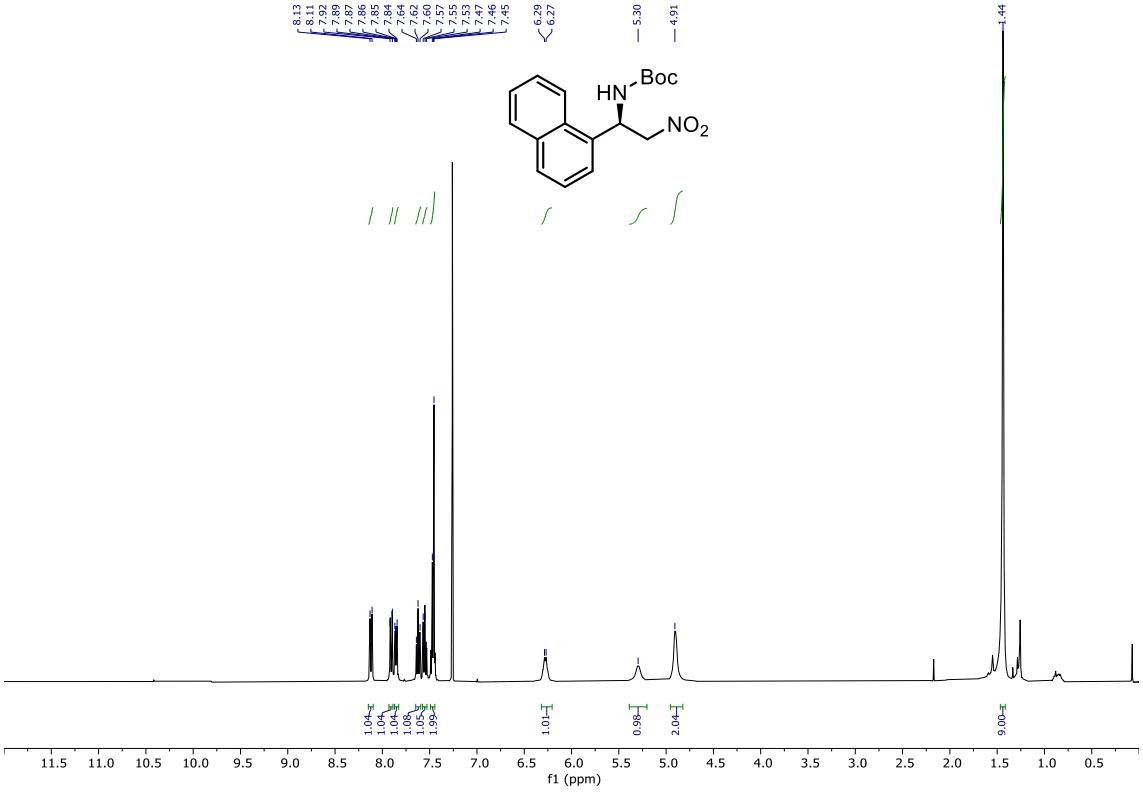


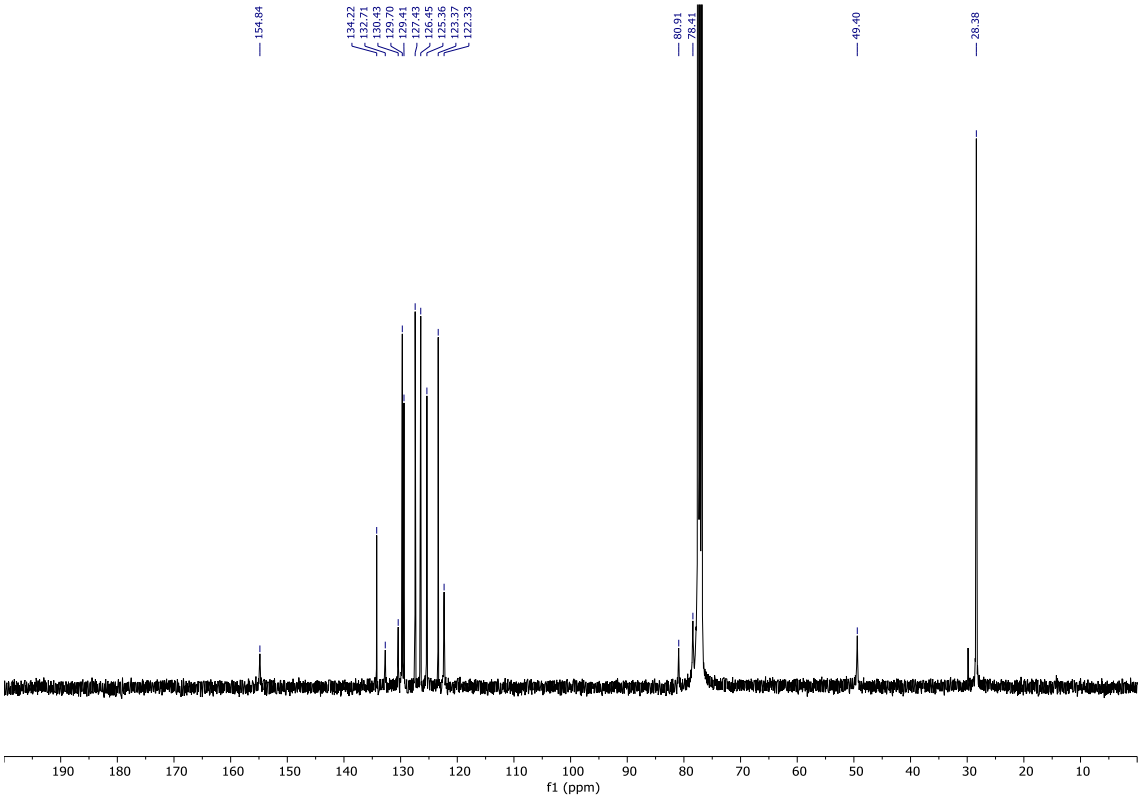


Tert-butyl (*R*)-(1-(2-chlorophenyl)-2-nitroethyl)carbamate (4d) ($CDCl_3$, ^1H 400 MHz, ^{13}C 101 MHz)

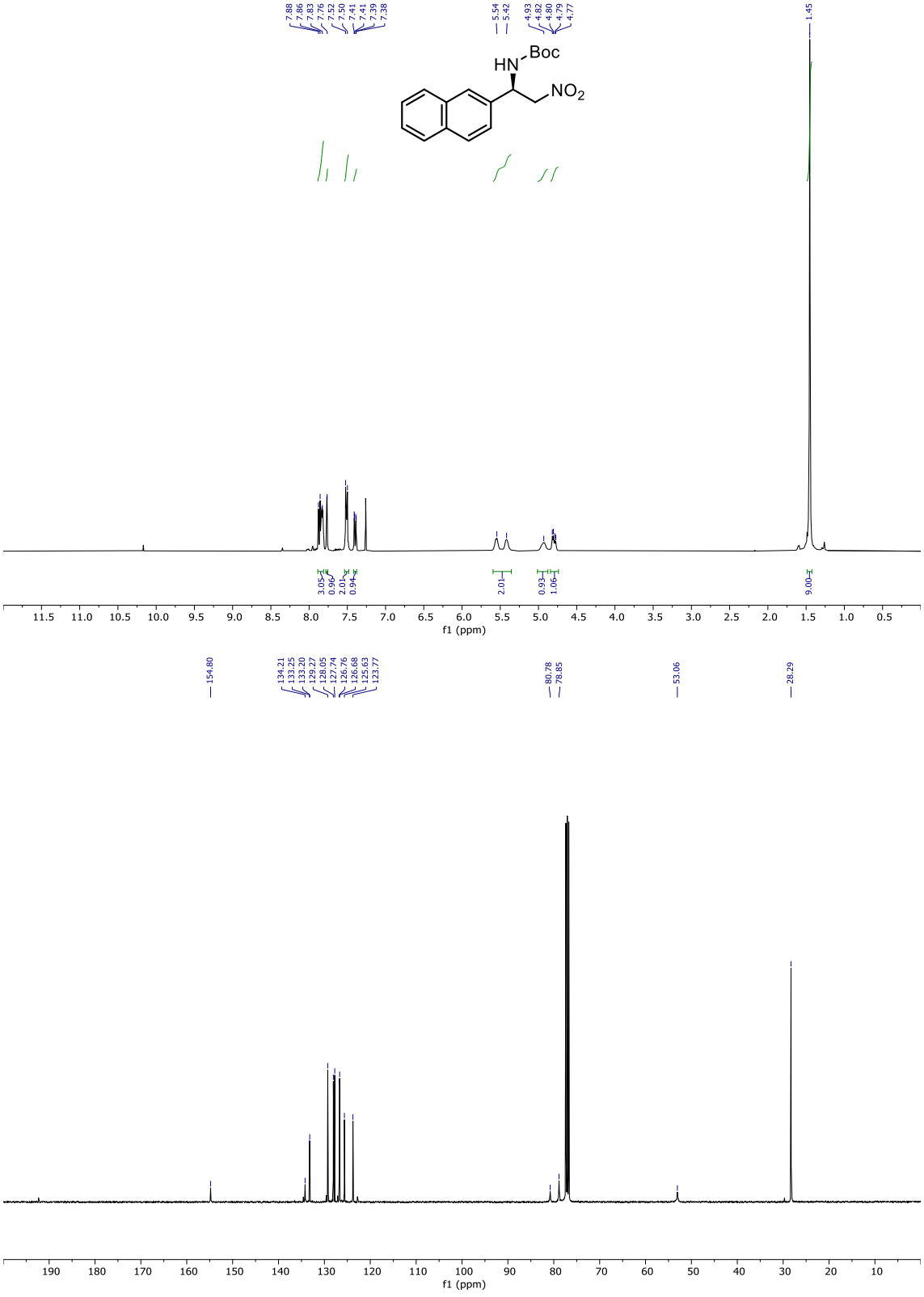


Tert-butyl (*R*)-(1-(naphthalen-1-yl)-2-nitroethyl)carbamate (4e) ($CDCl_3$, ^1H 400 MHz, ^{13}C 101 MHz)

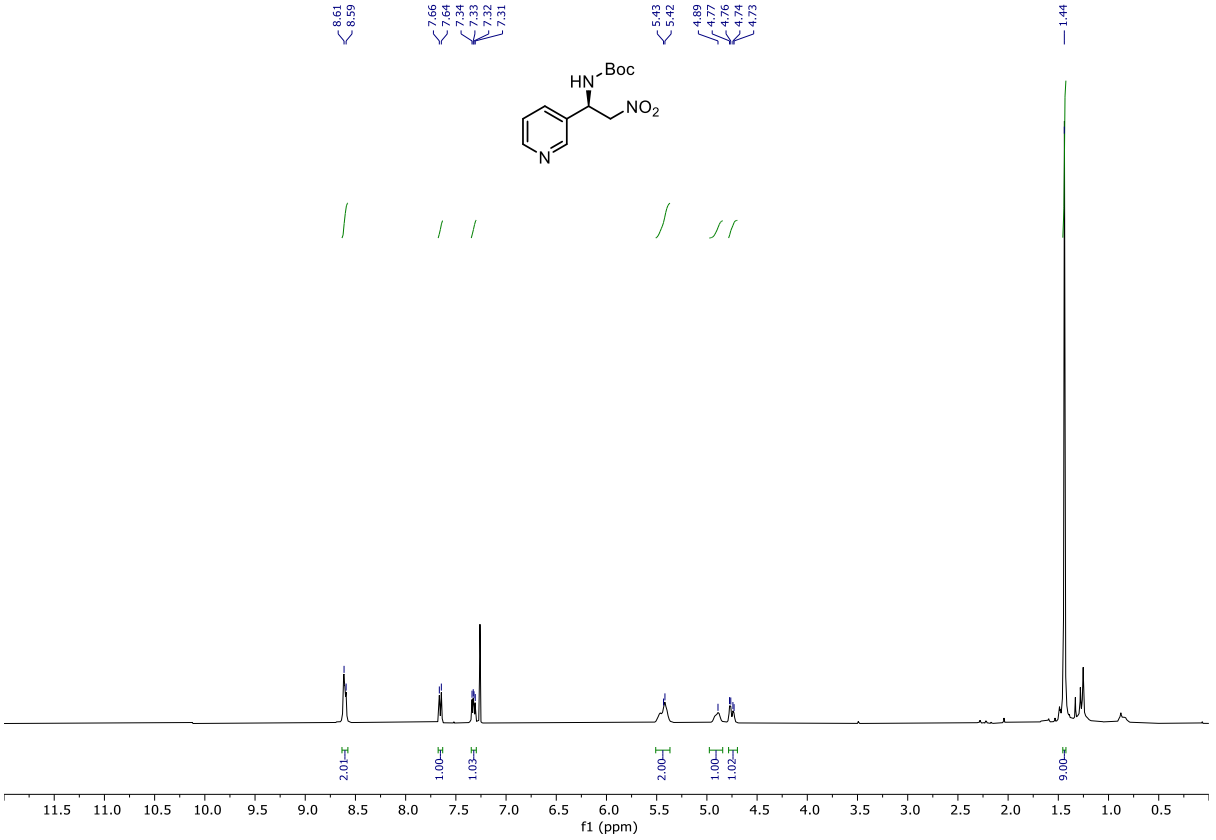


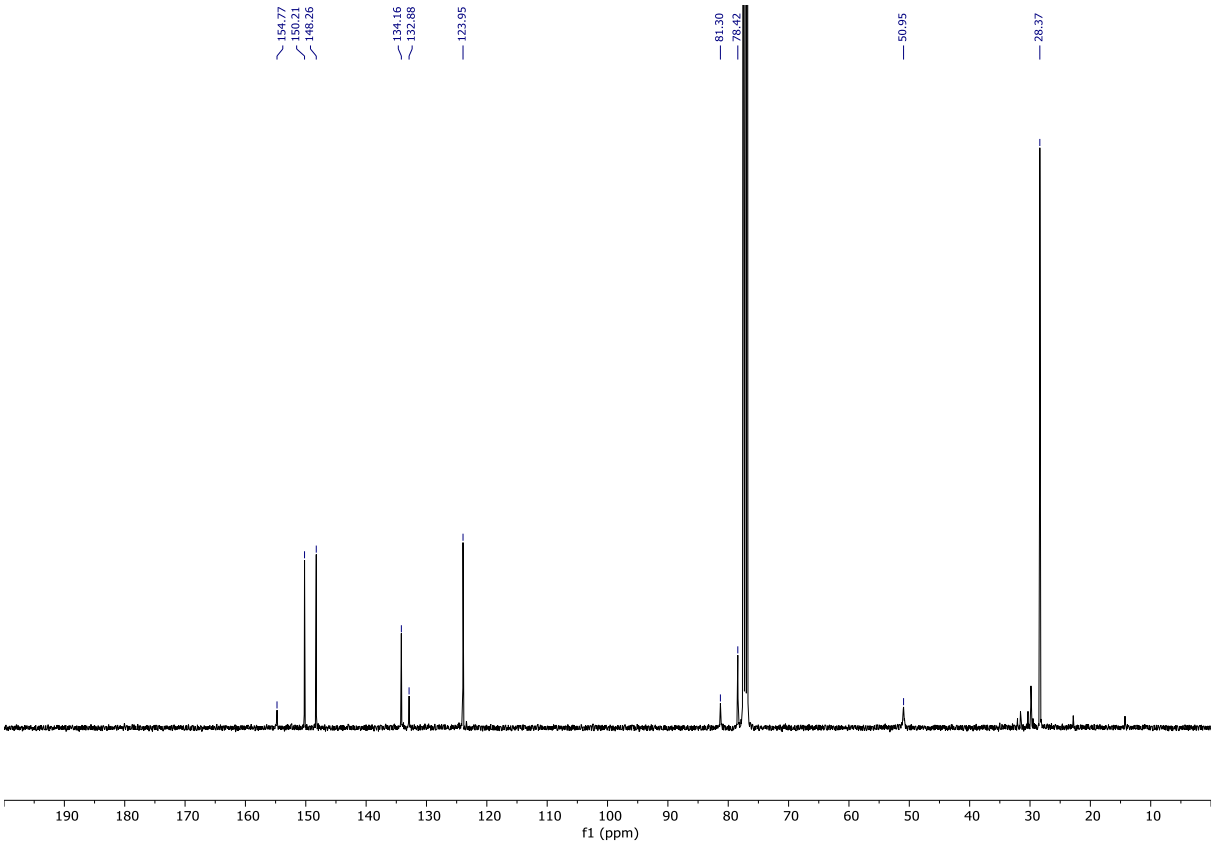


Tert-butyl (*R*)-(1-(naphthalen-2-yl)-2-nitroethyl)carbamate (4f) ($CDCl_3$, ^1H 400 MHz, ^{13}C 101 MHz)

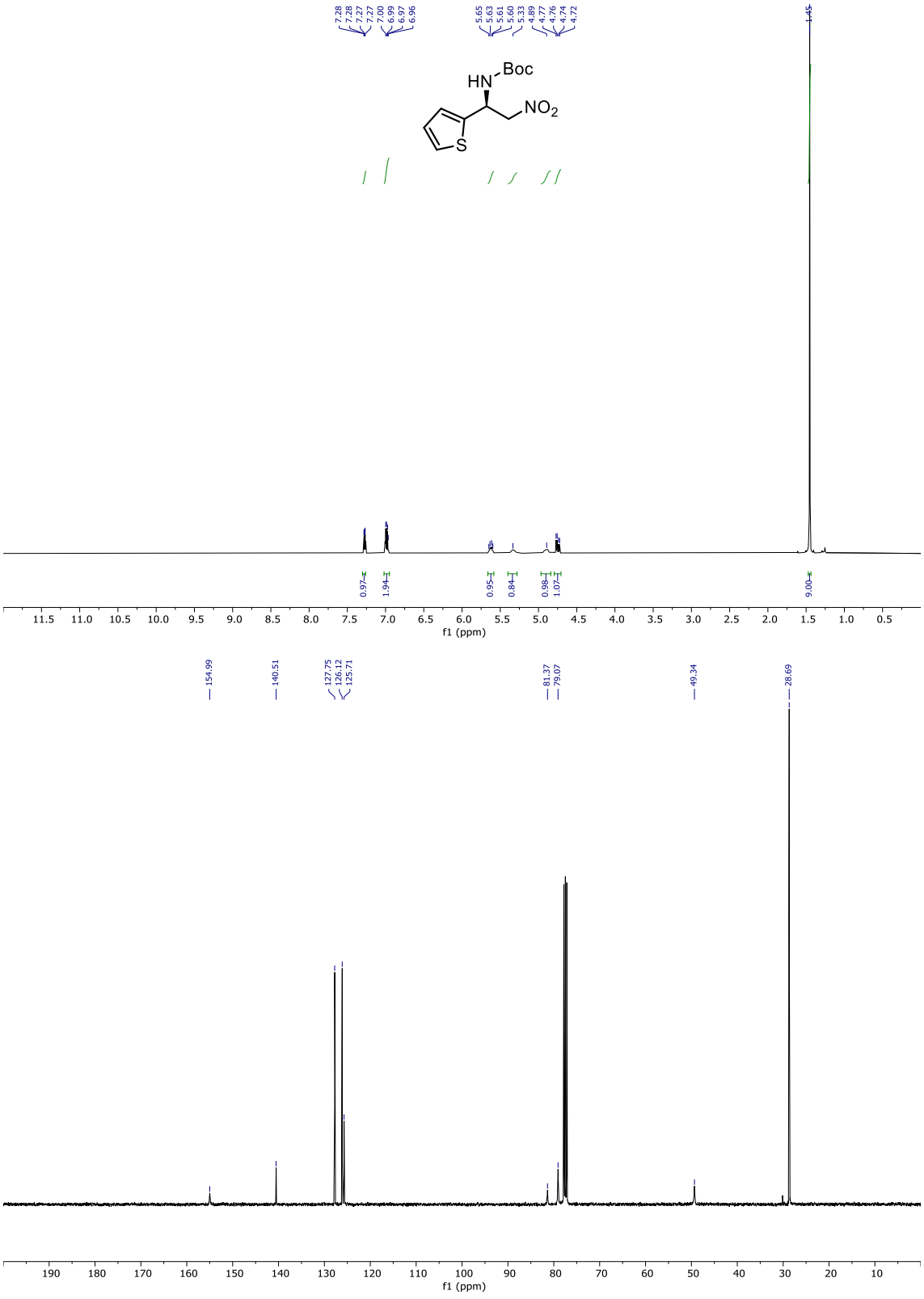


Tert-butyl (*R*)-(2-nitro-1-(pyridin-3-yl)ethyl)carbamate (4g) ($CDCl_3$, ^1H 400 MHz, ^{13}C 101 MHz)

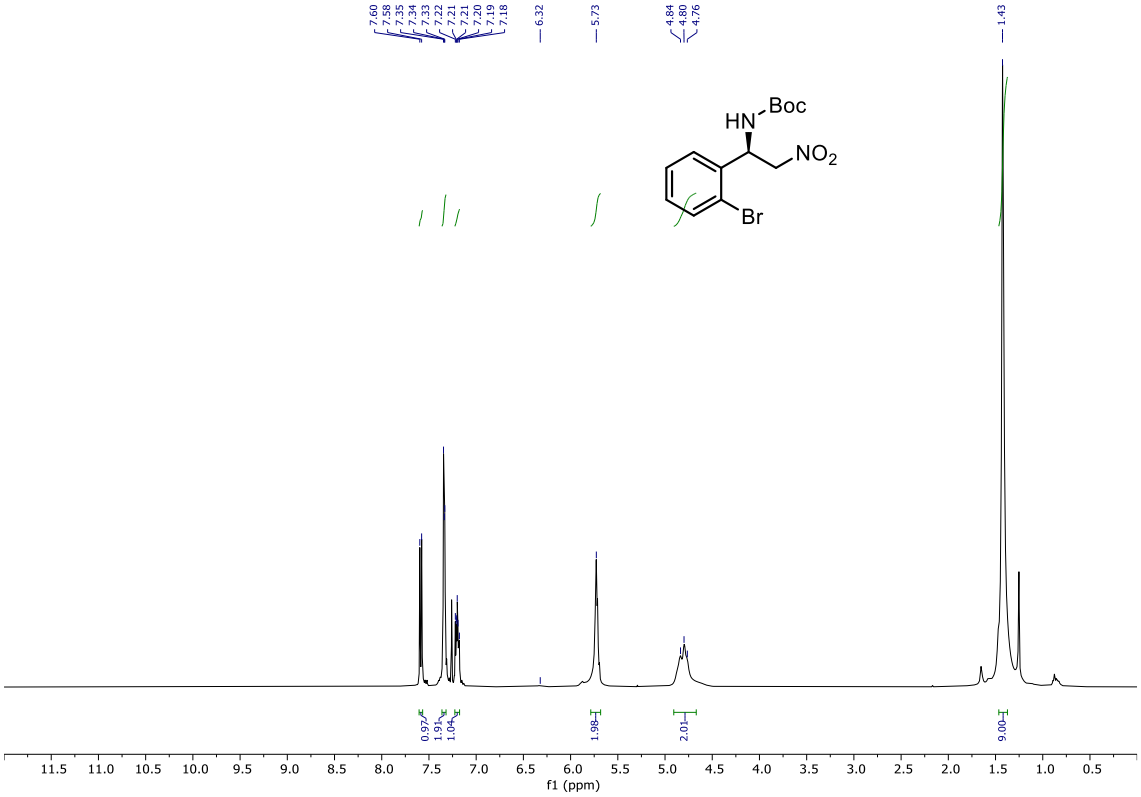


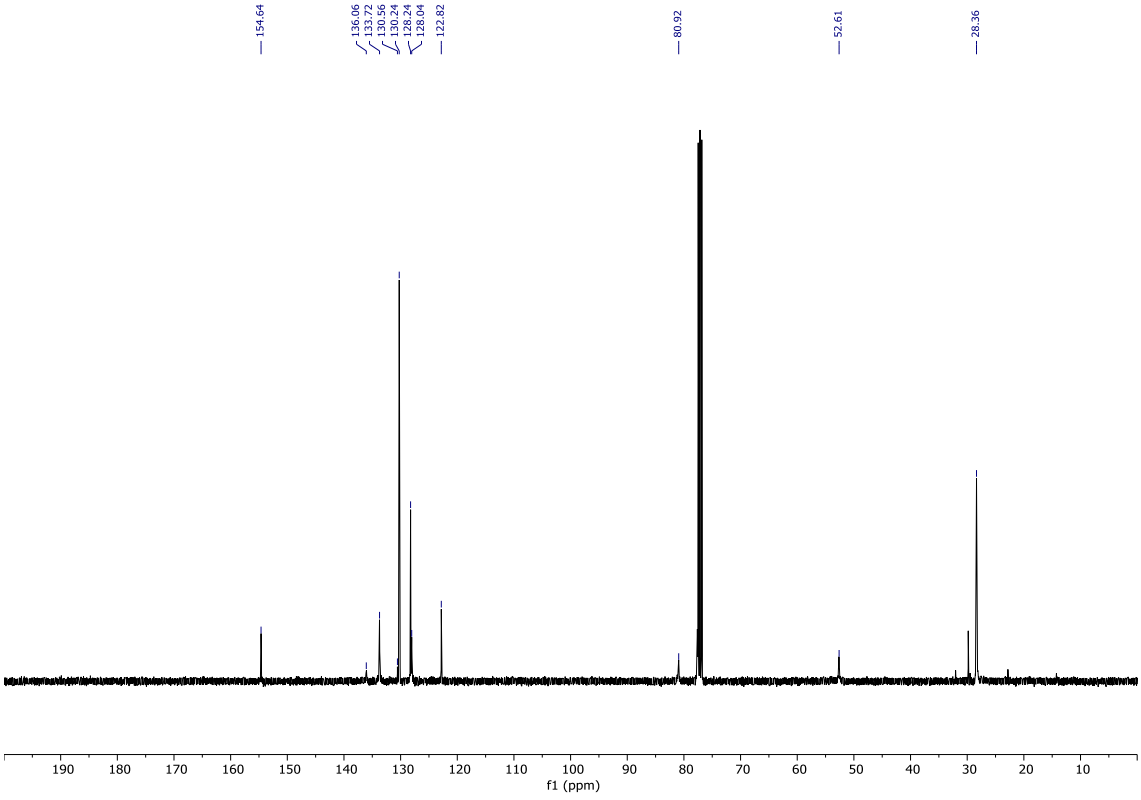


Tert-butyl (*R*)-(2-nitro-1-(thiophen-2-yl)ethyl)carbamate (4h) ($CDCl_3$, ^1H 400 MHz, ^{13}C 101 MHz)

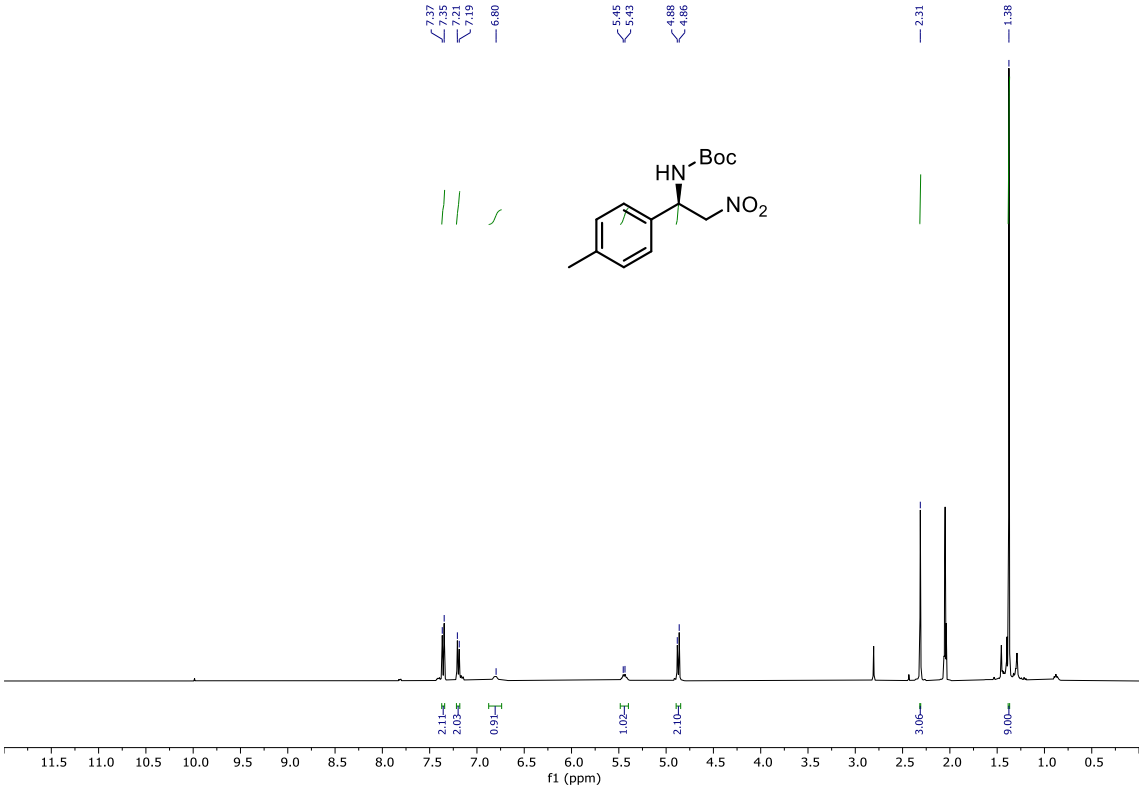


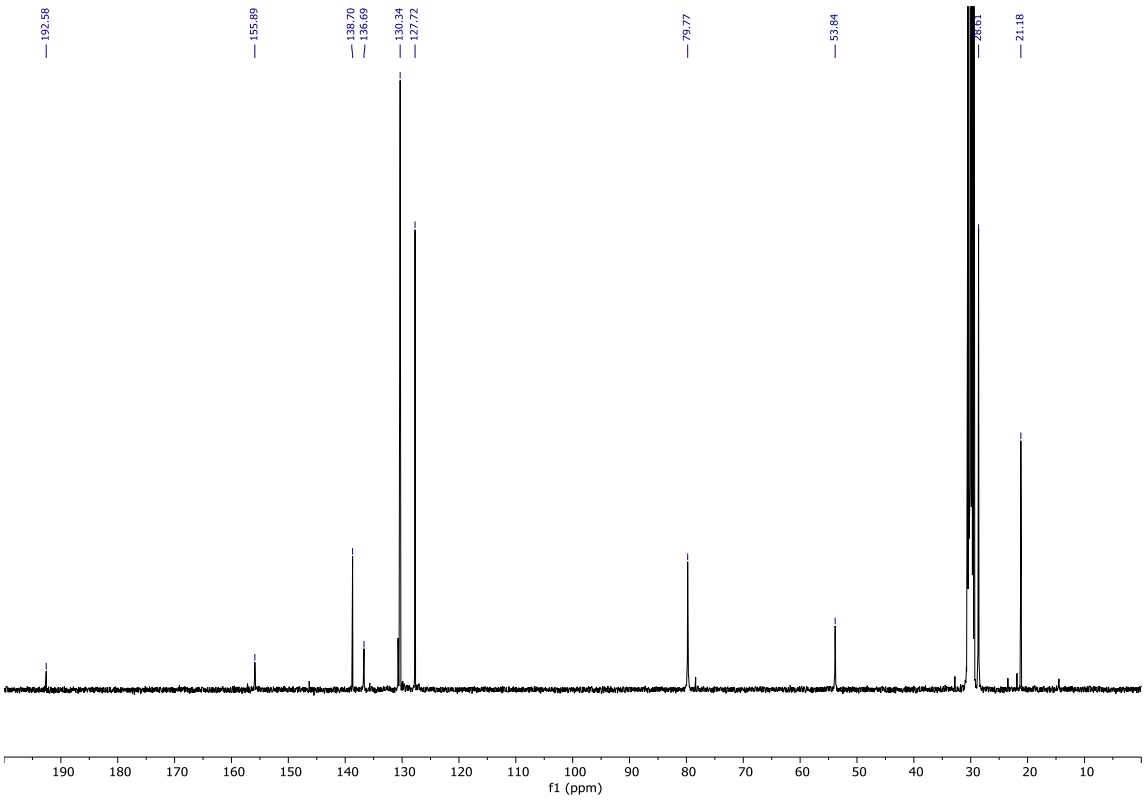
Tert-butyl (*R*)-(1-(2-bromophenyl)-2-nitroethyl)carbamate (4i) ($CDCl_3$, ^1H 400 MHz, ^{13}C 101 MHz)



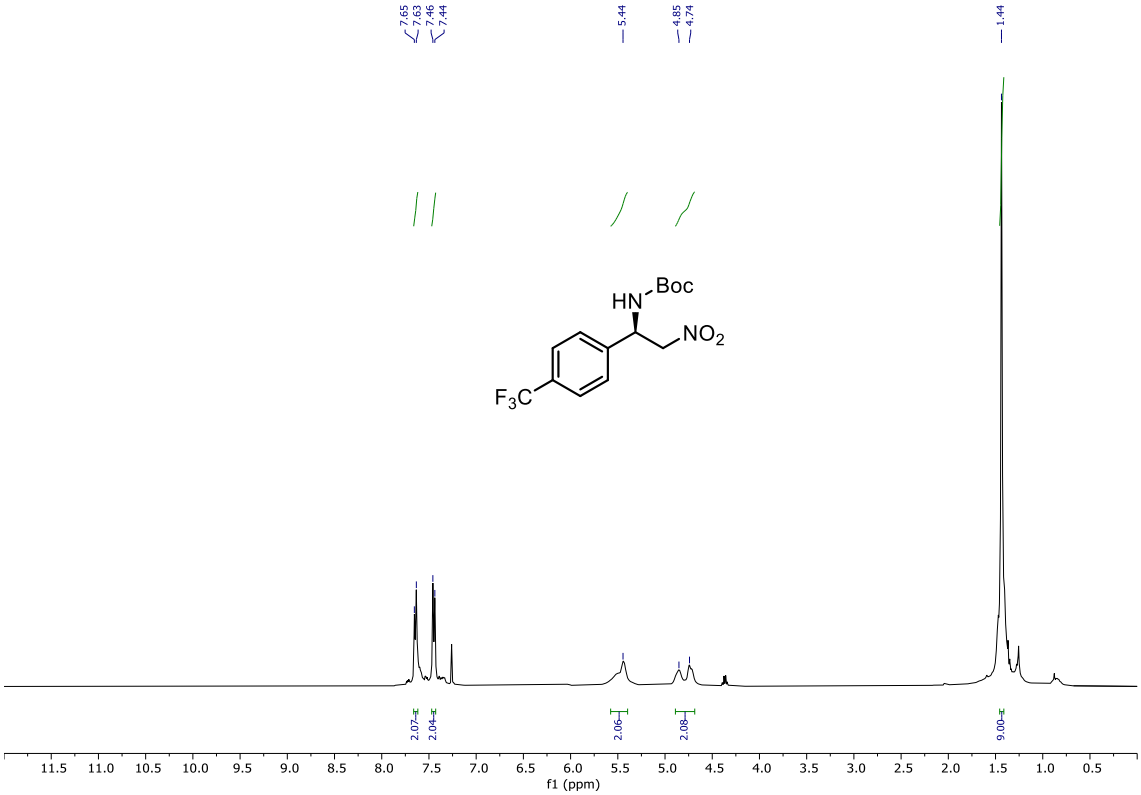


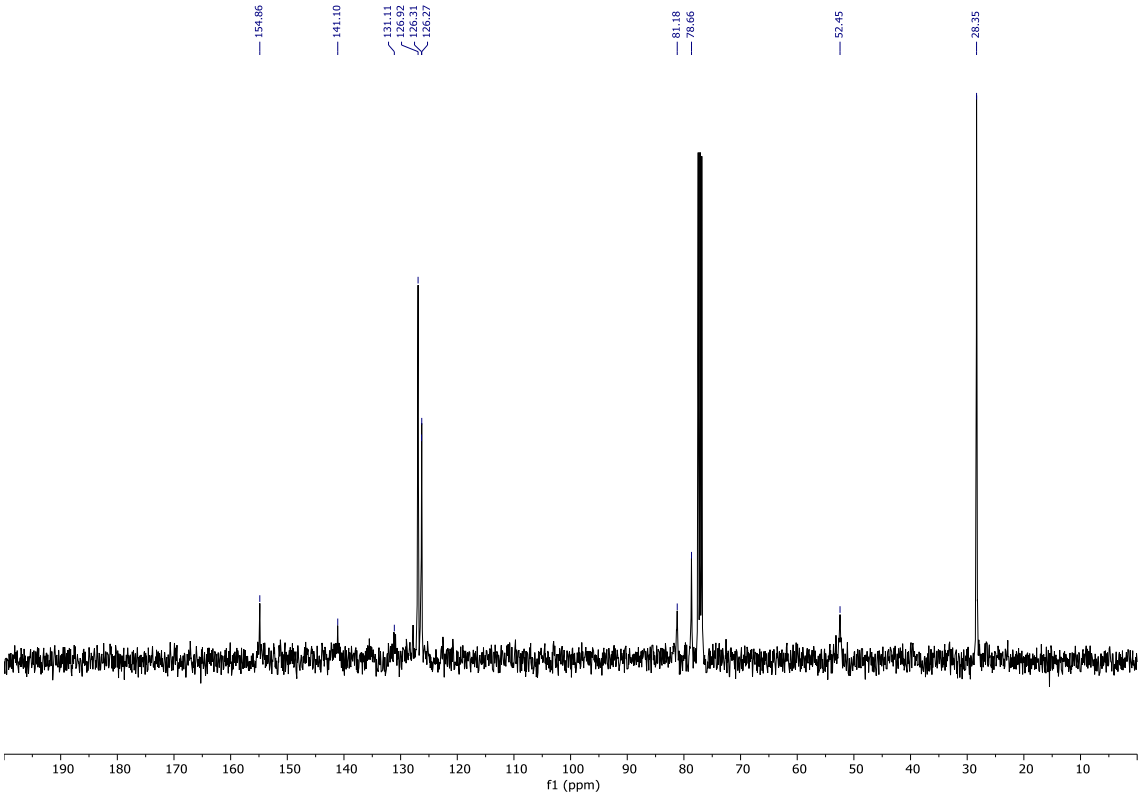
Tert-butyl (*R*)-(1-(2-bromophenyl)-2-nitroethyl)carbamate (4j) (Acetone-d6, ^{1}H 400 MHz, ^{13}C 101 MHz)

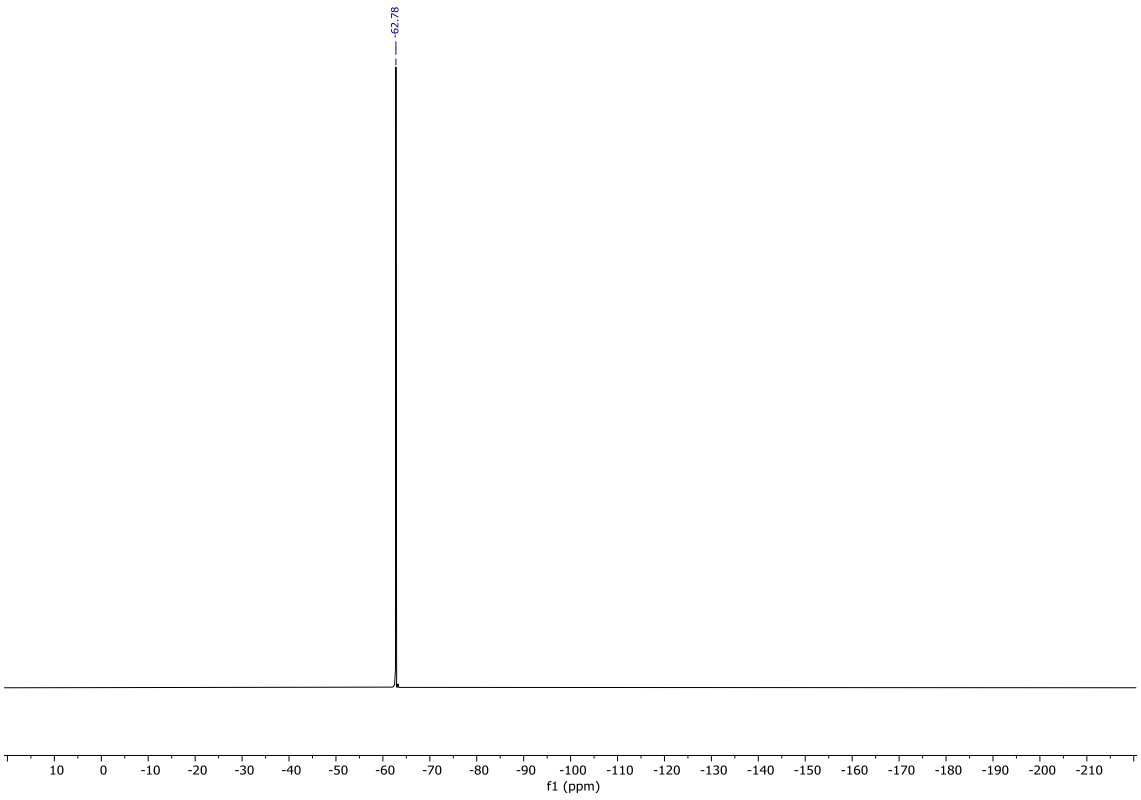




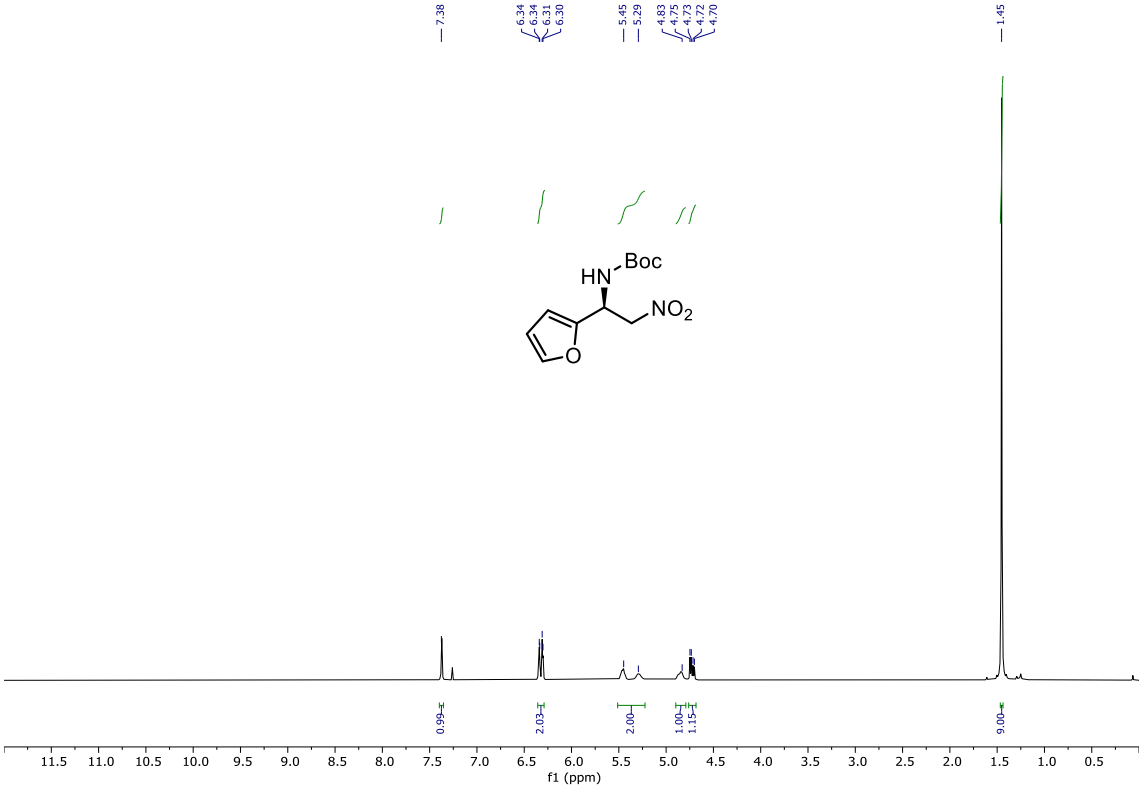
Tert-butyl (*R*)-(2-nitro-1-(4-(trifluoromethyl)phenyl)ethyl)carbamate (4k) ($CDCl_3$, ^{1}H 400 MHz, ^{13}C 101 MHz, ^{19}F 376 MHz)

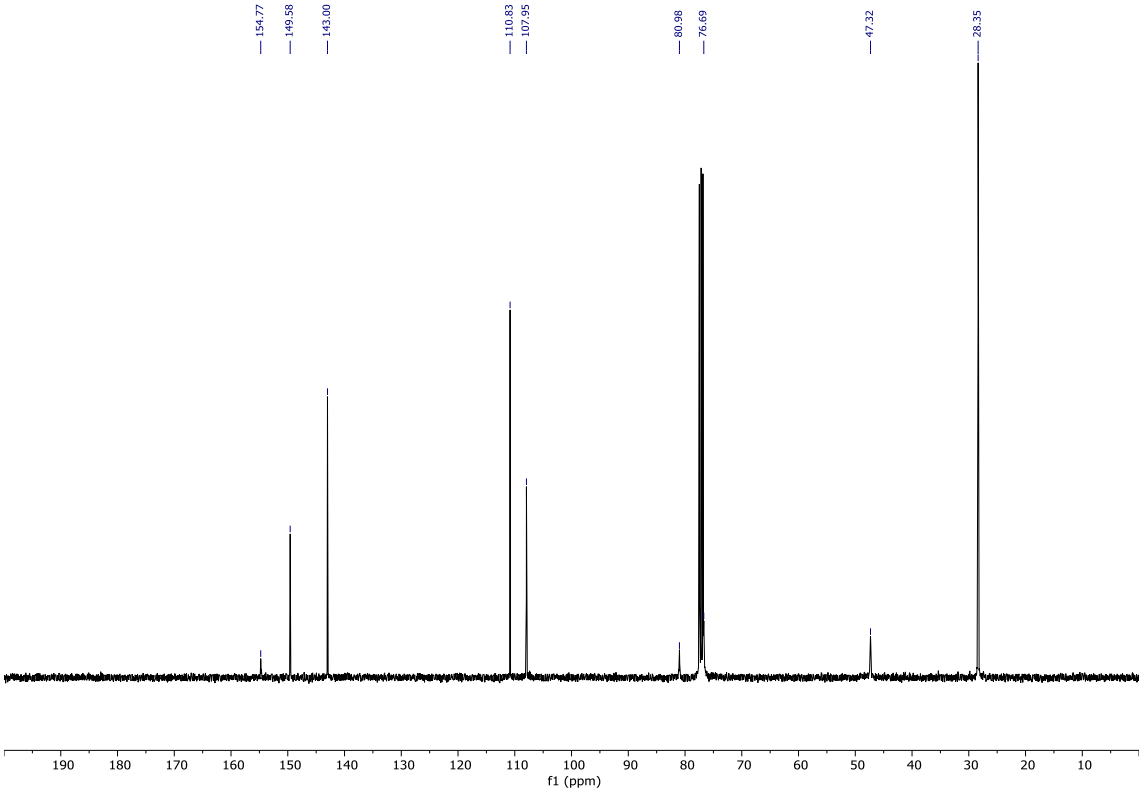





-62.78
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

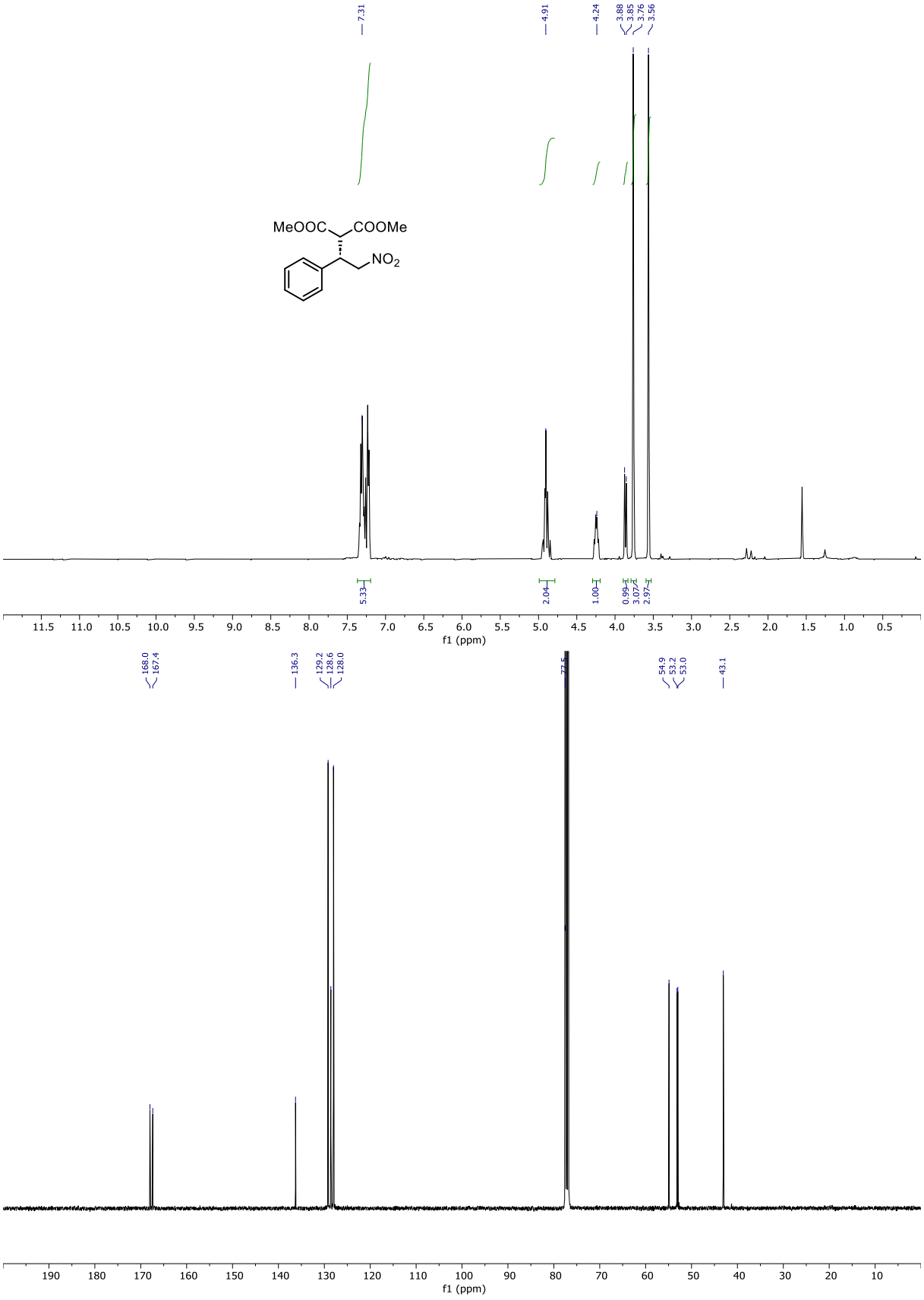
Tert-butyl (*R*)-(1-(furan-2-yl)-2-nitroethyl)carbamate (4l) ($CDCl_3$, ^1H 400 MHz, ^{13}C 101 MHz)



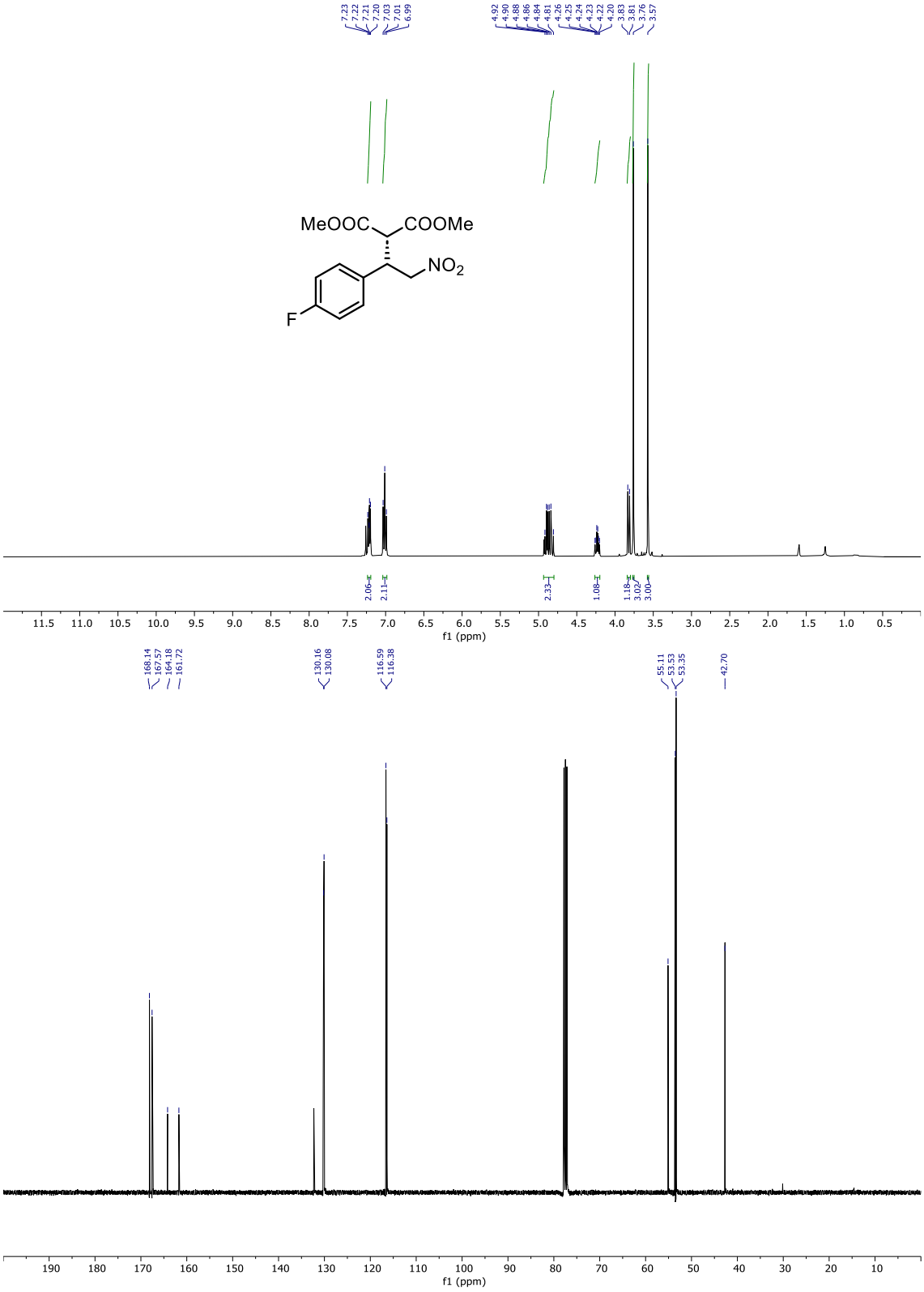


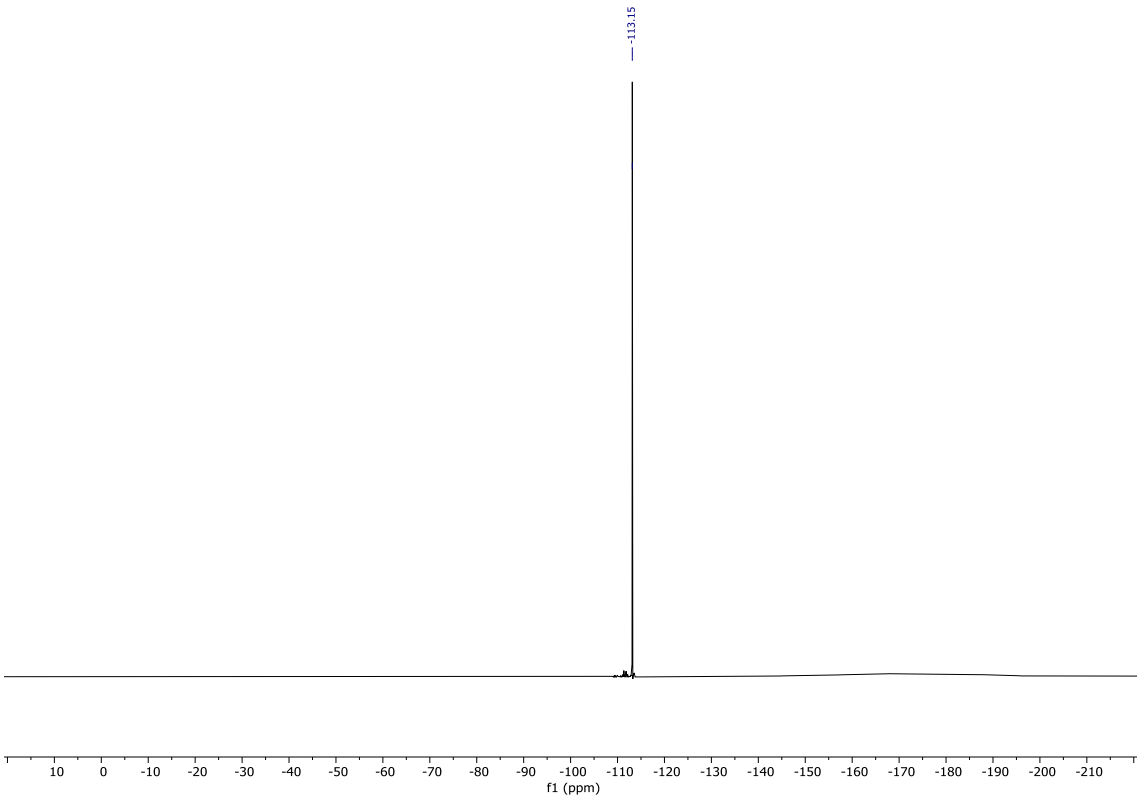
NMR spectra of 6

(*S*)-dimethyl 2-(2-nitro-1-phenylethyl)malonate (6a) ($CDCl_3$, ^1H 400 MHz, ^{13}C 101 MHz)

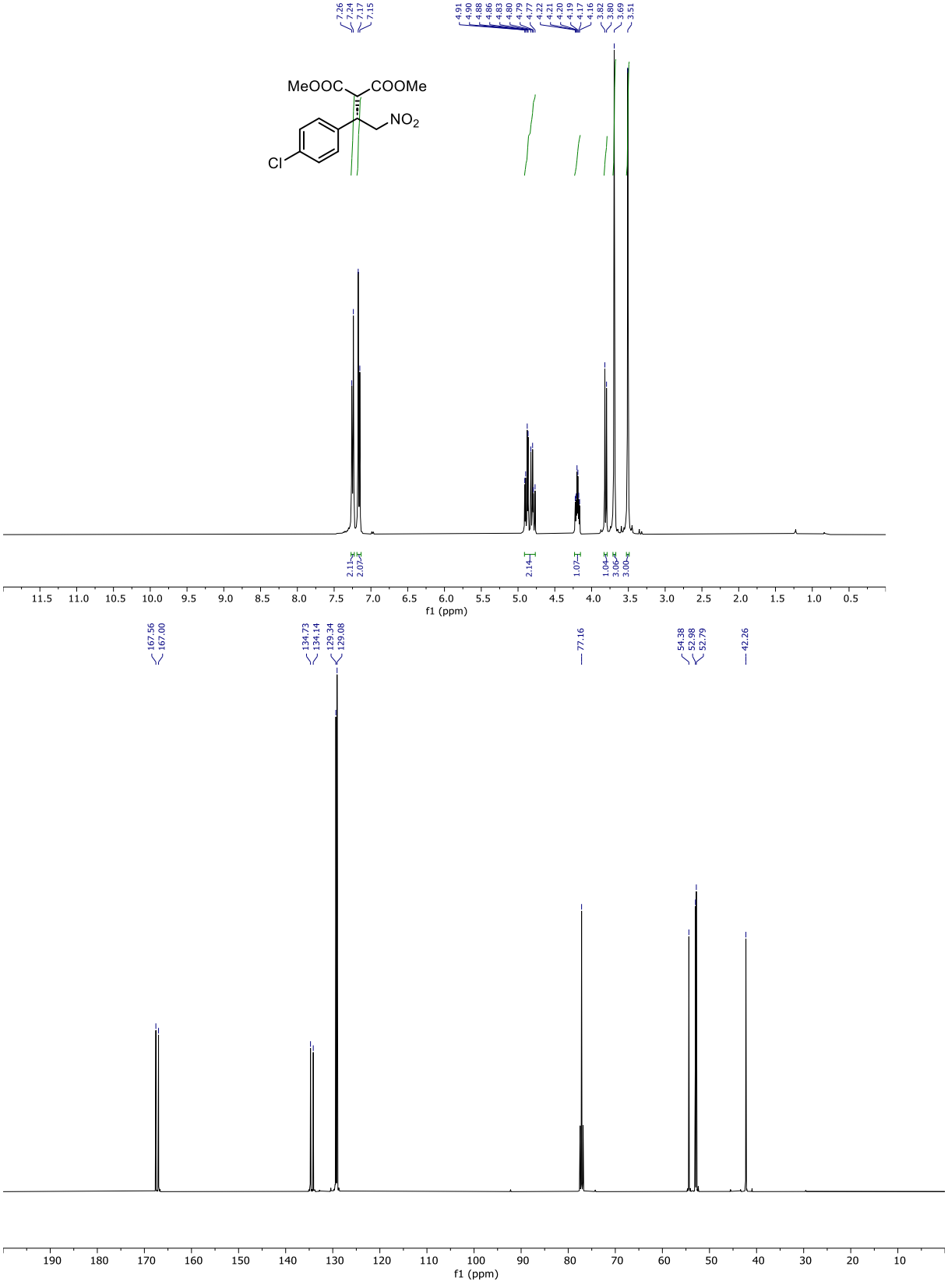


(*S*)-dimethyl 2-(1-(4-fluorophenyl)-2-nitroethyl)malonate (6b) ($CDCl_3$, ^1H 400 MHz, ^{13}C 101 MHz, ^{19}F 376 MHz)

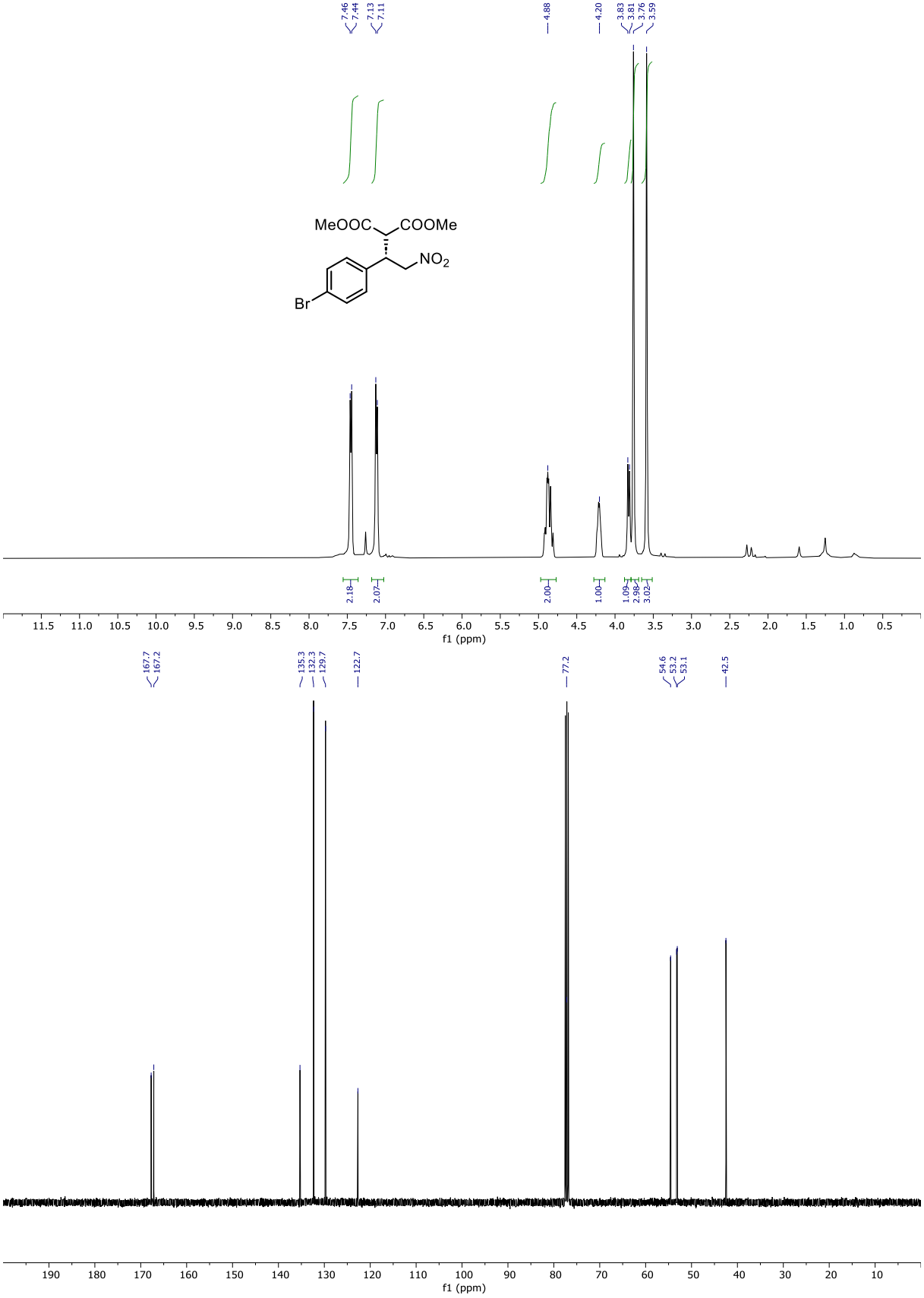



-113.15
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

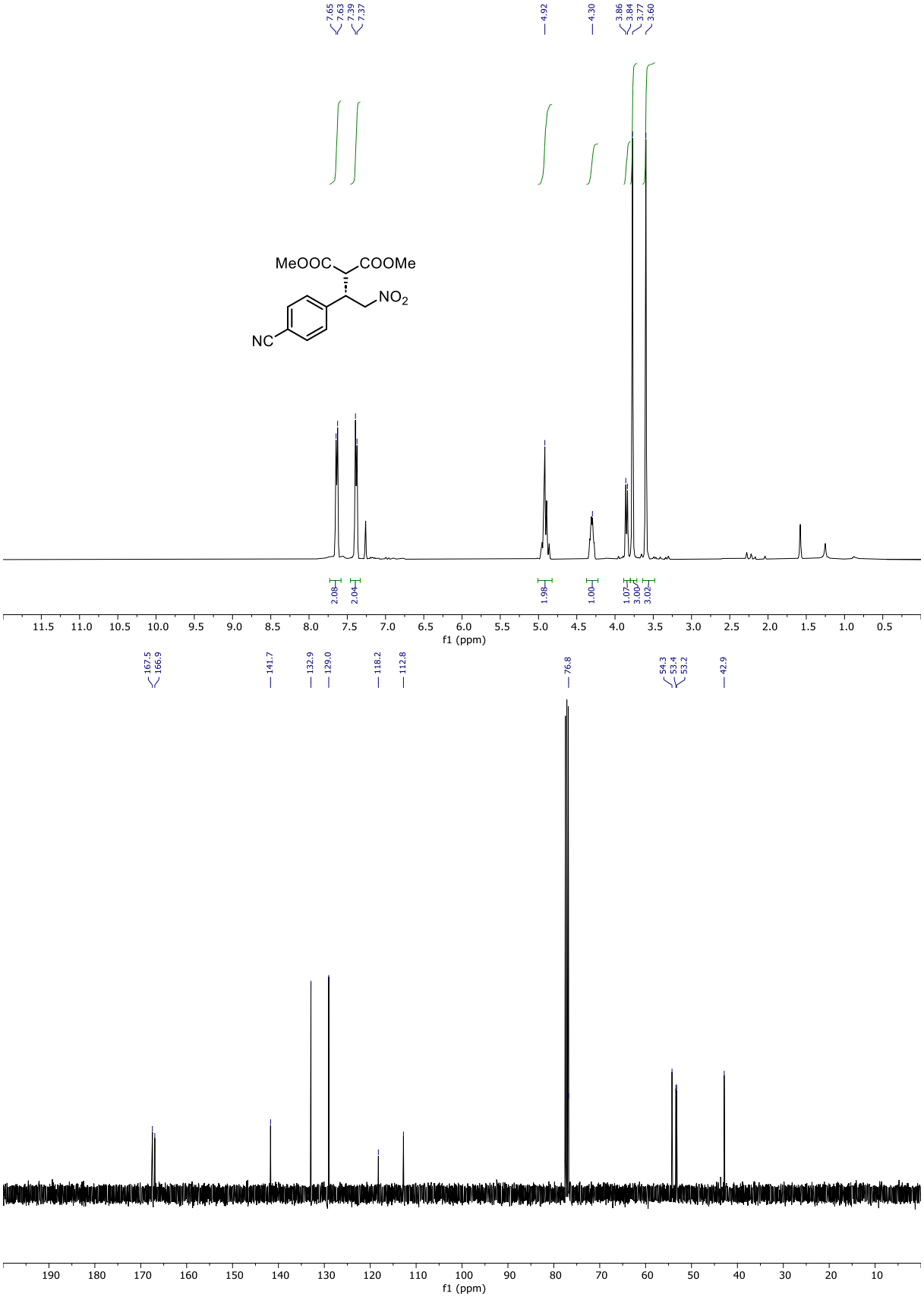
(*S*)-dimethyl 2-(1-(4-chlorophenyl)-2-nitroethyl)malonate (6c) ($CDCl_3$, ^1H 400 MHz, ^{13}C 101 MHz)



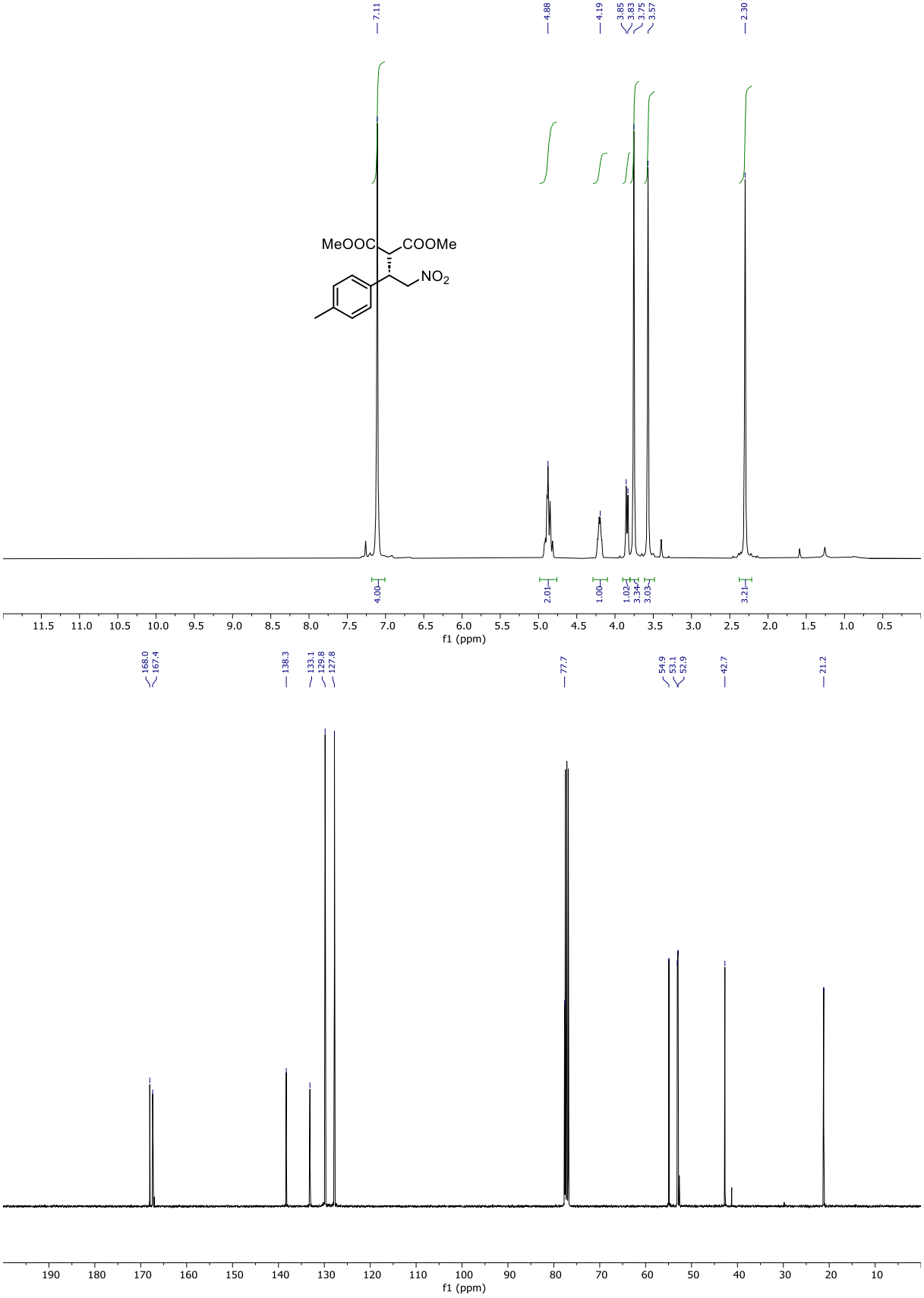
(*S*)-dimethyl 2-(1-(4-bromophenyl)-2-nitroethyl)malonate (6d) ($CDCl_3$, ^1H 400 MHz, ^{13}C 101 MHz)



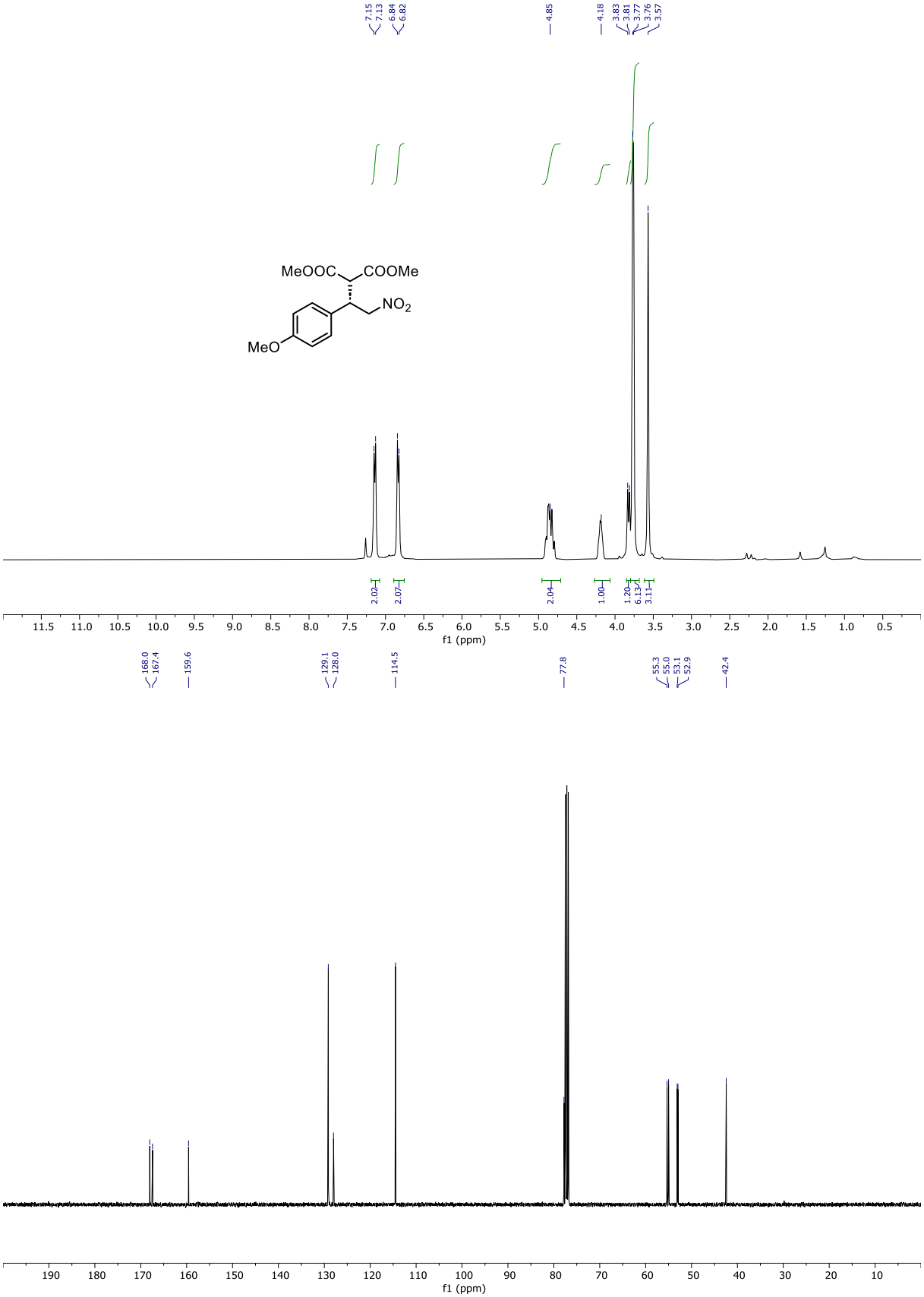
(*S*)-dimethyl 2-(1-(4-cyanophenyl)-2-nitroethyl)malonate (6e) ($CDCl_3$, ^1H 400 MHz, ^{13}C 101 MHz)



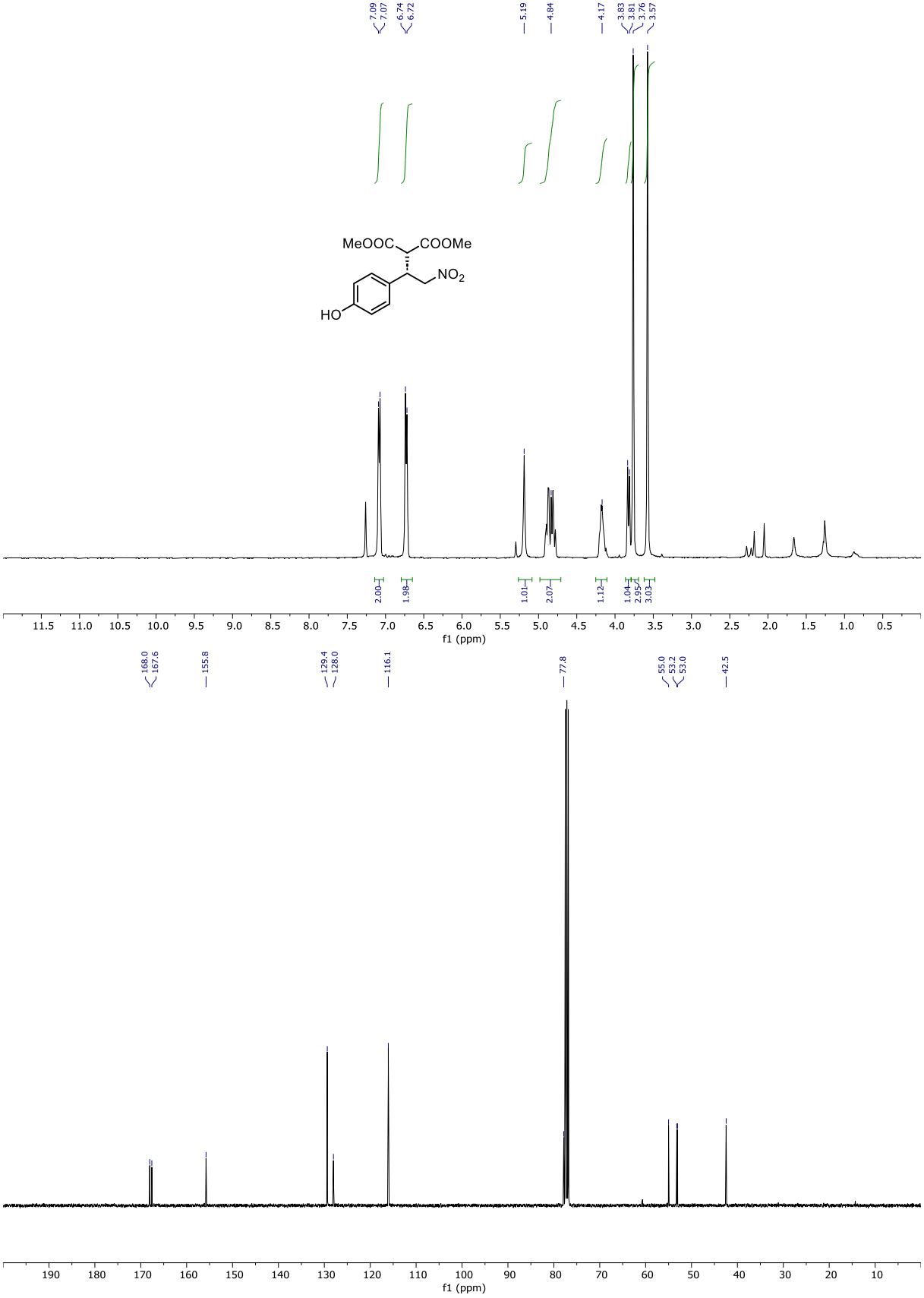
(*S*)-dimethyl 2-(2-nitro-1-(p-tolyl)ethyl)malonate (6f) ($CDCl_3$, ^1H 400 MHz, ^{13}C 101 MHz)



(*S*)-dimethyl 2-(1-(4-methoxyphenyl)-2-nitroethyl)malonate (6g) ($CDCl_3$, ^1H 400 MHz, ^{13}C 101 MHz)



(*S*)-dimethyl 2-(1-(4-hydroxyphenyl)-2-nitroethyl)malonate (6h) ($CDCl_3$, ^1H 400 MHz, ^{13}C 101 MHz)



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