Supporting Information

for

Continuous flow heterogeneous catalytic reductive aminations under aqueous micellar conditions enabled by an oscillatory plug flow reactor

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1. Materials and Analytical Methods

Commercial reagents and solvents were purchased from commercial vendors (Sigma-Aldrich, Alfa Aesar, TCI or VWR) and used as received, without further purification, unless otherwise stated.

Chromatographic purification of reaction products was accomplished by means of a Biotage Isolera automated flash chromatography system equipped with cartridges packed with KP-SIL, 60 Å (32–63 µm particle size) and using mixtures of EtOAc/cyclohexane as eluent.

GC-FID analysis was performed on a Shimadzu GCFID 2030 with a flame ionization detector, using a RTX-5MS column (30 m ×0.25 mm ID ×0.25 µm) and helium as carrier gas (40 cm/s linear velocity). The injector temperature was set to 280 °C. After 1 min at 50 °C, the temperature was increased by 25 °C min^{-1} to 300 °C and kept constant at 300 °C for 3 min. The detector gases used for flame ionization were hydrogen and synthetic air (5.0 quality).

NMR spectra were recorded on Bruker Avance III 300 MHz spectrometer (^{1}H: 300 MHz, ^{13}C: 75 MHz). Chemical shifts (δ) are given in ppm relative to residual signals of the solvent ($CDCl_3$, 7.26 ppm in ^{1}H-NMR and 77.16 ppm in ^{13}C-NMR). Coupling constants are given in Hz units. The following abbreviations are used to indicate the multiplicity: s, singlet; d, doublet; t, triplet; q, quartet; dd, doublet of doublets; ddd, doublet of doublet of doublets; m, multiplet.

The amount of residual palladium was determined by ICP-MS analysis. 100 mg of the crude reaction product sample was dissolved in 5 mL nitric acid and placed in a vial for microwave-assisted digestion using an MLS UltraClave IV instrument. The temperature was ramped up in 30 min to 250 °C and was kept there for an additional 30 min. After appropriate dilution, palladium content was quantitatively determined at m/z 105 using an Agilent 7500ce inductively coupled plasma mass spectrometer. Calibration was performed with an external calibration curve established using 1.000 g of Pd/L standard sample (CPI International). Palladium content was also measured after silica gel filtration using a EtOAc/cyclohexane 1:3 as eluent.

2. General Information on the Flow Setup

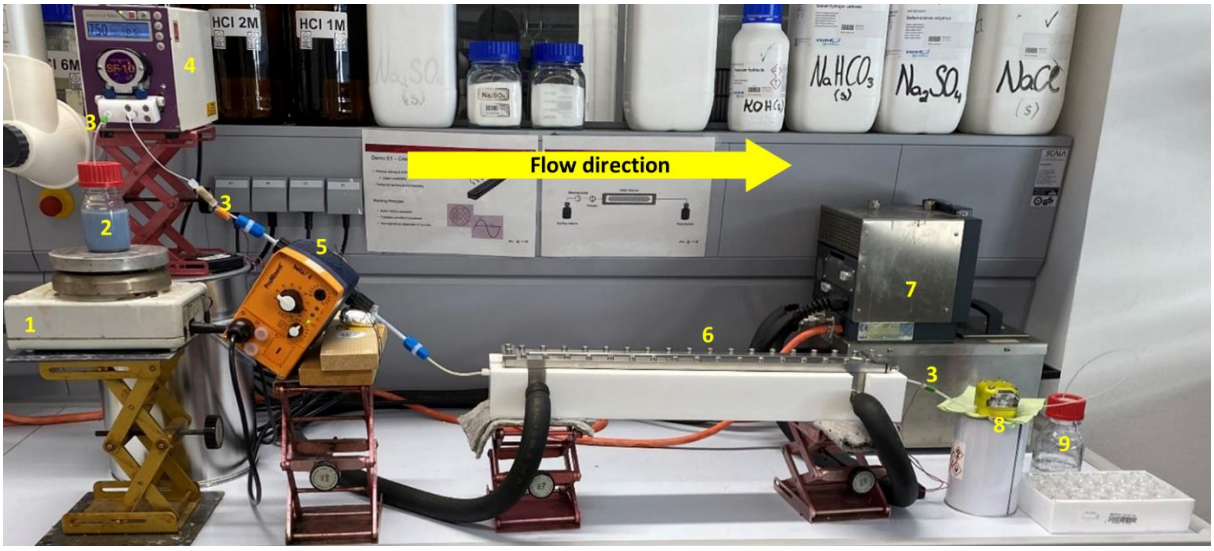


Figure S1 Photograph of the single-feed setup used for optimization and substrate scope investigation. 1) Magnetic stirrer, 2) starting material suspension, 3) electric vibrator motors, 4) metering peristaltic pump, 5) pulsator pump, 6) HANU reactor module, 7) thermostat, 8) backpressure regulator, 9) product collection.

Metering pump: Vapourtec SF-10 peristaltic pump equipped with 'blue' tubing (0.02–10.00 mL min^{-1}). Capable of handling solids including slurries and suspensions.

Reactor module: HANU™ HX 15 Flow Reactor, Creaflow. A microstructured plug flow reactor made of Hastelloy and held in a PTFE housing; contains a series of 2×2×2 mm cubic static mixers (see also Figure S6). Outer dimensions: 540×60×60 mm; channel dimensions: 480×20×2 mm, 15 mL internal volume.

Pulsator pump: Creaflow-customized ProMinent Beta/4 pump equipped with PTFE/carbon pump head. Capable of delivering tunable amplitude (in the range of <5–100%, approximately 0.04–0.44 mL per stroke) and adjustable frequency (in the range of 10–100%, corresponding to 0.3–3 Hz).

Temperature control: Huber CC304 thermostat filled with silicon oil, temperature range: –20–195 °C.

Back pressure regulator: An adjustable dome-type back pressure regulator (Zaiput Flow Technologies, BPR-10) with a set point of 3 bar. Capable of handling solids including slurries and suspensions.

General connections: Parts of the setup were connected using 1/8" OD (1.6 mm ID) or 1/16" OD (0.8 mm ID) PTFE or PFA tubes along with PEEK or stainless steel fittings. Fittings were lined with PTFE tape in order to ensure a tight sealing.

3. Residence Time Distribution Experiments

Residence time distribution (RTD) experiments were performed as shown in Figure S2. Rose Bengal was used as a tracer in H_2O solution (10^{-2} M concentration) and injected (1 mL) *via* a Y-piece mixer between the metering pump and the pulsator, in a carrier stream of pure H_2O. An in-line UV-Vis flow cell was installed after the back pressure regulator and connected to a spectrometer. UV-Vis spectra were recorded using a fiber-coupled Avantes Starline AvaSpec-2048 spectrometer, with an Avantes AvaLight-DHc lamp as the light source. The recorded spectra were processed using Avasoft 8.7 software. The RTD profiles for the screening experiments setup are shown in Figure S3.

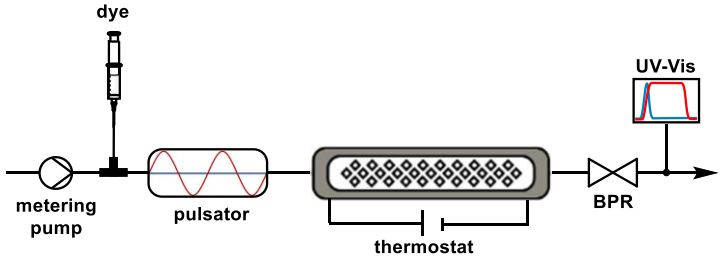


Figure S2 Schematic setup for the RTD experiments.

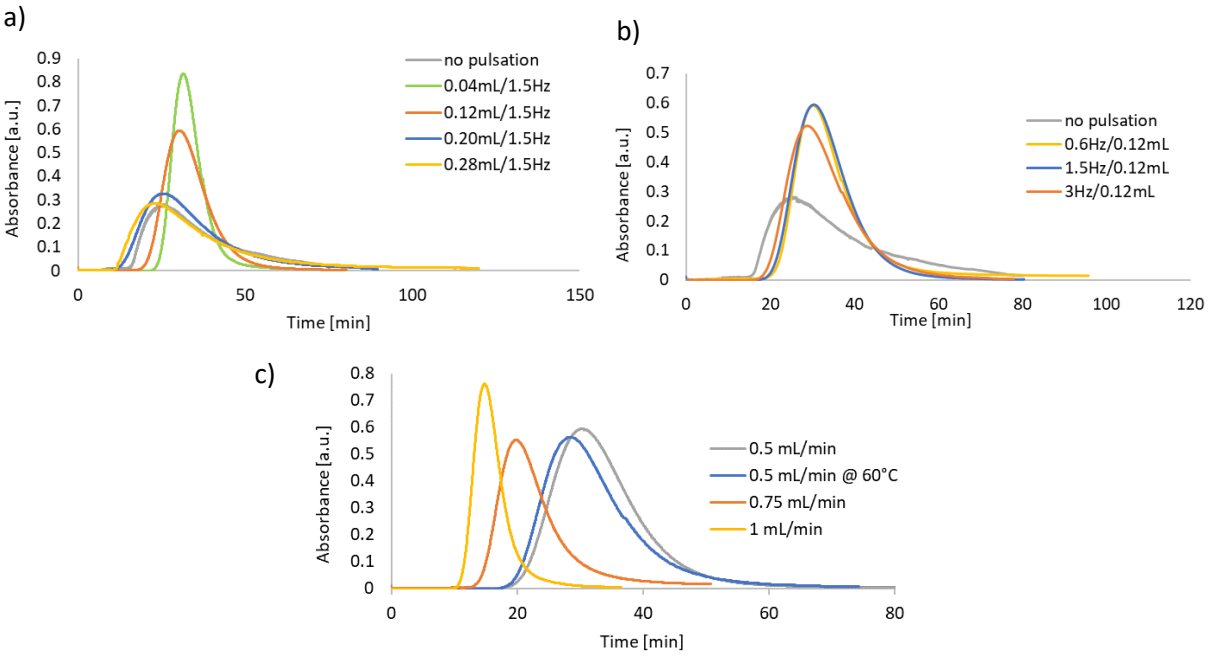
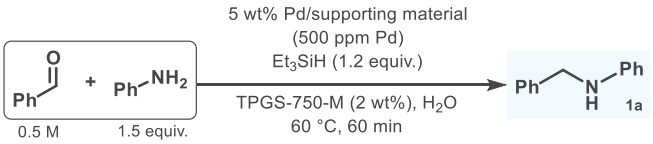


Figure S3 RTD profiles in water recorded at 563 nm. Conditions: flow rate = 500 µL min^{-1}, 3 bar pressure, 1 mL tracer injected, 1 cm optical path length, 25 °C temperature. a) Experiments performed at 1.5 Hz pulsation frequency and different pulsation amplitudes. b) Experiments performed at different pulsation frequencies and 0.12 mL pulsation amplitude. c) Experiments performed at different flow rates (0.12mL amplitude and 1.5Hz Frequency, at 25°C, unless differently stated).

4. The Effects of Different Catalyst Supports and Surfactants

Table S1 Batch screening of different catalyst supports in reductive amination of benzaldehyde with aniline under aqueous micellar conditions.

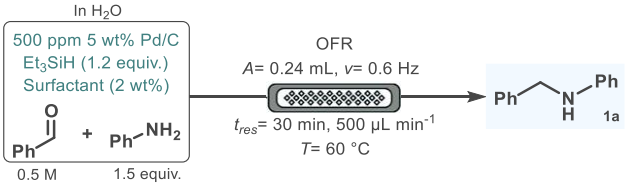


Entry[a]	5% Pd on support	Support density[1] [g mL^{-1}]	Conv.[b] [%]	Select.[c] [%]
1	C	2.01	>99	86
2	SiO_2	2.65	>99	96
3	Al_2O_3	4.00	>99	97
4	$BaSO_4$	4.29	>99	66
5	$BaCO_3$	4.49	>99	>99

[a]1 mL scale, stirring at 500 rpm. [b]Consumption of starting material, based on GC-FID area. [c]Selectivity, determined by GC-FID area. (The corresponding imine was detected as the only side product.)

Figure S4 Settling of Pd/Al_2O_3 particles in the connection tubing before the pulsator pump during screening of different catalyst supports under flow conditions.

Table S2 Flow screening of different surfactants in reductive amination of benzaldehyde with aniline under aqueous micellar conditions.



Entry[a]	Surfactant	Conv.[b] [%]	Select.[c] [%]	Notes
1	SDS	>99	28	Clogging
2	Kolliphore EL	>99	39	Clogging
3	Brij S 100	>99	56	Clogging
4	TPGS-750-M	>99	>99	None

[a]25 mL scale. [b]Consumption of starting material, based on GC-FID area. [c]Selectivity, determined by GC-FID area. (The corresponding imine was detected as the only side product.)

5. Long-Run and Recycling Experiments

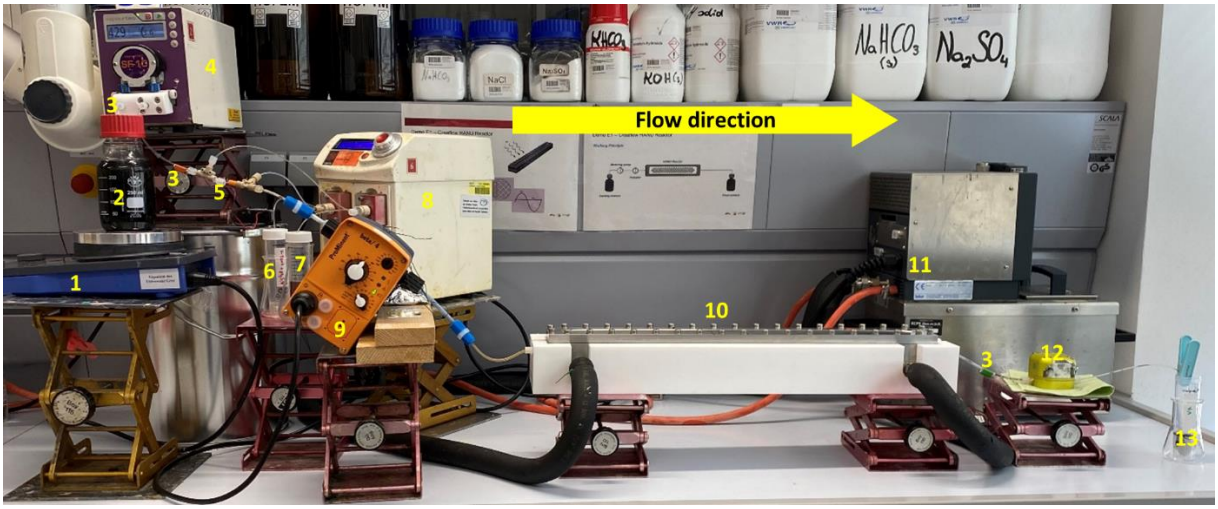


Figure S5 Photograph of the three-feed setup used for long-run as well as for the recycling experiments. 1) Magnetic stirrer, 2) feed 1 (aqueous surfactant solution plus Pd/C), 3) electric vibrator motors, 4) metering peristaltic pump (Vapourtec SF-10), 5) T-mixers, 6) feed 2 (neat mixture of 4-fluorobenzaldehyde and Et_3SiH), 7) feed 3 (neat aniline), 8) Syrris Asia syringe pump module, 9) pulsator pump, 10) HANU™ HX 15 Flow Reactor, 11) thermostat (Huber CC304), 12) backpressure regulator (Zaiput Flow Technologies, BPR-10), 13) product collection.

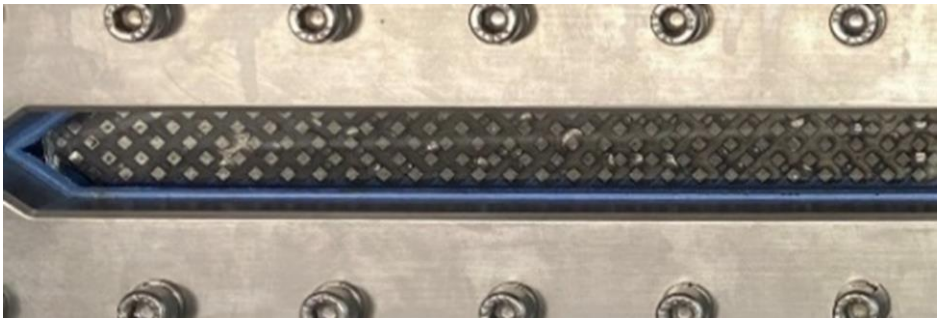


Figure S6 Photograph of the process channel taken during the long-run experiment. (The pale gray coloring at some points of the channel is caused by reflection.)

The recycling experiments were performed using the 3-feed flow system, which is described in the Experimental Section of the manuscript and shown in Figure S5. Between each run, the collected reaction mixture was extracted with EtOAc (2x10 mL), then Pd/C was filtered off from the aqueous phase, washed with EtOAc and water and carefully dried at room temperature. Subsequently the residual EtOAc was removed from the aqueous surfactant solution under reduced pressure.

Table S3 Comparison of used and recovered catalyst and surfactant amounts of the recycling experiment.

Cycle number	TPGS-750-M solution used [mL]	Recovered TPGS-750-M solution [mL|%]	Pd/C used [mg]	Recovered Pd/C [mg|%]
1	175	174|>99	91.9	83.7|91
2	75	75|>99	39.4	36.7|93
3	60	60|>99	31.5	29.7|94
4	55	55|>99	29.6	28.2|95
5	45	45|>99	27.3	25.4|93

6. Calculations

Space time yield (STY) of the long-run:

$$STY = \frac{productivity}{volumn\ reactor} = \frac{2.14\ g\ h^{-1}}{0.015\ L} = 143\ g\ h^{-1}L^{-1} \qquad \text{[Equation S1]}$$

E-factor for the long-run:

Table S2 Substance masses used for calculation of the E-factor.

Substance	Mass used or produced [g]
Aniline	9.75
4-fluorobenzaldehyde	10.88
Et_3SiH	12.17
1b	15.00

$$E-factor = \frac{total\ waste\ mass}{product\ mass} = \frac{total\ mass\ input - product\ mass}{product\ mass} = \frac{32.80\ g - 15.00\ g}{15.00\ g} = 1.2 \qquad \text{[Equation S2]}$$

The mass of the waste did not include water. Substances that can be reused (i.e., the heterogeneous catalyst, the aqueous surfactant solution and solvents used for work-up) are not considered as waste and are thus excluded from the E-factor calculation.

7. Liberation of Amino Acid Methyl Esters

40 mmol of the corresponding amino acid methyl ester hydrochloride salt was dissolved in 25 mL $CHCl_3$. Subsequently 40 mmol Et_3N in 25 mL $CHCl_3$ was slowly added to the reaction mixture and stirred for 4 h at RT and for 2 h at 70 °C. Subsequently, the solvent was removed under reduced pressure and the residual white solid was taken up in 50 mL Et_2O. The solid was filtered off and washed with 2×10 mL Et_2O. The filtrate was evaporated to dryness and the corresponding amino acid methyl ester was obtained as an oil.

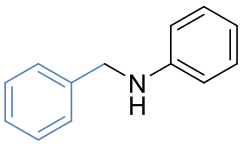
Methyl L-phenylalaninate was isolated as a light yellow oil (7.05 g, 99%). ^1H, and ^{13}C NMR data are in good agreement with the previously reported values.[2]

methyl L-Leucinate was isolated as a light yellow oil (5.67g, 97%). ^1H, and ^{13}C NMR data are in good agreement with the previously reported values.[2]

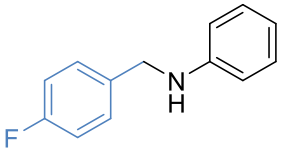
methyl L-prolinate was isolated as a clear oil (5.01 g, 97%). ^1H, and ^{13}C NMR data are in good agreement with the previously reported values.[2]

methyl L-methioninate was isolated as a light yellow oil (6.18 g, 95%). ^1H, and ^{13}C NMR data are in good agreement with the previously reported values.[2]

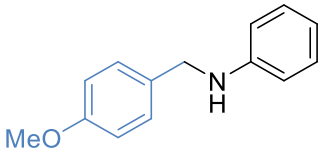
8. NMR Data of Reaction Products



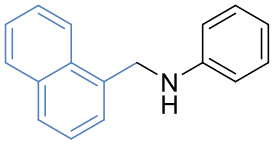
***N*-benzylaniline**, **1a** was prepared according to the single-feed procedure described in the manuscript and was obtained as a yellow oil, 620 mg (84 % yield).^{1}H NMR (300 MHz, $CDCl_3$) δ 7.58 – 7.17 (m, 7H), 6.89 – 6.64 (m, 3H), 4.40 (s, 2H), 4.08 (s, 1H).^{13}C NMR (75 MHz, $CDCl_3$) δ 148.2, 139.5, 129.4, 128.7, 127.6, 127.3, 117.6, 112.9, 48.4. NMR data is in accordance with literature.[3]



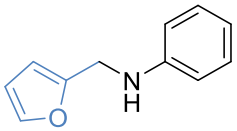
***N*-(4-fluorobenzyl) aniline**, **1b** was prepared by using the 3-feed system during the long run described in the manuscript and was obtained as a yellow oil, 15.0 g (85% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.59 – 6.96 (m, 6H), 6.96 – 6.58 (m, 3H), 4.36 (s, 2H), 4.07 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.7, 160.5, 148.0, 135.2, 135.2, 129.4, 129.1, 129.0, 117.8, 115.7, 115.4, 112.9, 47.6. NMR data is in accordance with literature.[4]



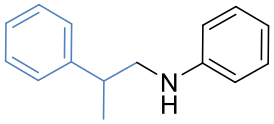
N-(4-methoxybenzyl) aniline, **1c** was prepared according to the single feed procedure described in the manuscript and was obtained as a pale yellow oil, 710 mg (81% yield)**.** ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38 – 7.12 (m, 4H), 6.98 – 6.59 (m, 5H), 4.29 (s, 2H), 3.98 (s, 1H), 3.84 (s, 3H)**,** ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.9, 148.2, 131.4, 129.3, 128.8, 117.5, 114.0, 112.8, 55.3, 47.8. NMR data is in accordance with literature.[3]



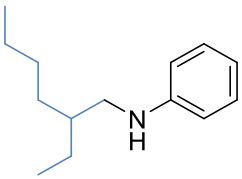
***N*-(naphthalen-1-ylmethyl)aniline**, **1d** was prepared according to the single feed procedure described in the main manuscript and was obtained as a pale yellow oil, 557 mg (58% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.24 – 8.07 (m, 1H), 8.03 – 7.75 (m, 2H), 7.71 – 7.42 (m, 4H), 7.40 – 7.18 (m, 2H), 6.93 – 6.60 (m, 3H), 4.79 (s, 2H), 4.04 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 148.3, 134.4, 134.0, 131.6, 129.4, 128.8, 128.2, 126.4, 126.1, 125.9, 125.6, 123.7, 117.6, 112.8, 46.5. NMR data is in accordance with literature.[8]



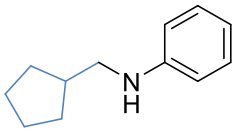
***N*-(furan-2-ylmethyl)aniline**, **1e** was prepared according to the single feed procedure described in the manuscript and was obtained as an orange oil, 557 mg (73% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.48 – 7.35 (m, 1H), 7.35 – 7.15 (m, 2H), 6.88 – 6.64 (m, 3H), 6.44 – 6.22 (m, 2H), 4.37 (s, 2H), 4.06 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 152.8, 147.7, 142.0, 129.3, 118.1, 113.2, 110.4, 107.0, 41.5. NMR data is in accordance with literature.[3]



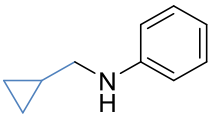
***N*-(2-phenylpropyl)aniline**, **1f** was prepared according to the single feed procedure described in the manuscript and was obtained as a pale yellow oil, 541 mg (71% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.48 – 7.16 (m, 7H), 6.84 – 6.54 (m, 3H), 3.62 (s, 1H), 3.48 – 3.25 (m, 2H), 3.25 – 3.02 (m, 1H), 1.41 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 148.2, 144.6, 129.3, 128.7, 127.3, 126.7, 117.4, 113.0, 51.0, 39.3, 19.8. NMR data is in accordance with literature.[5]



***N*-(2-ethylhexyl)aniline**, **1g** was prepared according to the single feed procedure described in the manuscript and was obtained as a yellow oil, 625 mg (75% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.27 – 7.14 (m, 2H), 6.81 – 6.55 (m, 3H), 3.65 (s, 1H), 3.06 (d, *J* = 6.1 Hz, 2H), 1.74 – 1.28 (m, 9H), 1.03 – 0.90 (m, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 148.8, 129.24, 116.9, 112.6, 47.0, 39.1, 31.4, 29.0, 24.5, 23.2, 14.2, 11.0. NMR data is in accordance with literature.[6]

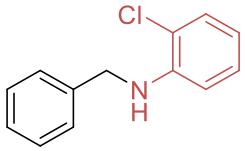


***N*-(cyclopentylmethyl)aniline**, **1h** was prepared according to the single feed procedure described in the main manuscript and was obtained as a yellow oil, 580 mg (72% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.34 – 7.14 (m, 2H), 6.82 – 6.55 (m, 3H), 3.70 (s, 1H), 3.07 (d, *J* = 7.2 Hz, 2H), 2.21 (p, *J* = 7.6 Hz, 1H), 1.98 – 1.80 (m, 2H), 1.80 – 1.51 (m, 4H), 1.42 – 1.21 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 148.6, 129.3, 117.3, 112.8, 49.1, 11.00, 3.5. NMR data is in accordance with literature.[7]

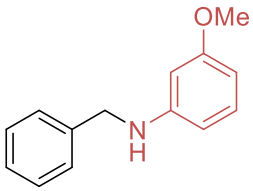


***N*-(cyclopropylmethyl)aniline**, **1i** was prepared according to the single feed procedure described in the manuscript and was obtained as a yellow oil, 430 mg (71% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38 –

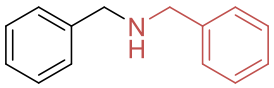
7.14 (m, 2H), 6.86 – 6.62 (m, 3H), 3.85 (s, 1H), 3.04 (d, *J* = 6.9 Hz, 2H), 1.33 – 1.10 (m, 1H), 0.72 – 0.52 (m, 2H), 0.45 – 0.25 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 148.6, 129.3, 117.3, 112.8, 49.1, 11.0, 3.5. NMR data is in accordance with literature.[8]



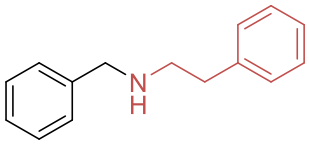
***N*-benzyl-2-chloroaniline**, **2a** was prepared according to the single feed procedure described in the main manuscript and was obtained as a pale yellow oil, 647 mg (72% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.56 – 7.24 (m, 6H), 7.22 – 7.06 (m, 1H), 6.78 – 6.59 (m, 2H), 4.80 (s, 1H), 4.45 (d, *J* = 5.5 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.9, 138.8, 129.1, 128.8, 127.8, 127.4, 127.3, 119.1, 117.5, 111.5, 47.9. NMR data is in accordance with literature.[9]



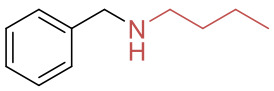
***N*-benzyl-3-methoxyaniline**, **2b** was prepared according to the single feed procedure described in the manuscript and was obtained as a pale yellow oil, 694mg (79% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.57 – 6.99 (m, 6H), 6.45 – 6.18 (m, 3H), 4.37 (s, 2H), 4.12 (s, 1H), 3.81 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.9, 149.6, 139.4, 130.1, 128.7, 127.6, 127.3, 127.1, 106.0, 102.7, 98.9, 55.1, 48.4. NMR data is in accordance with literature.[9]



Dibenzylamine, **2c** was prepared according to the single feed procedure described in the manuscript and was obtained as a colorless oil, 720 mg (89% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.54 – 7.23 (m, 10H), 3.88 (s, 4H), 1.68 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.4, 128.5, 128.2, 127.0, 53.2. NMR data is in accordance with literature.[3]

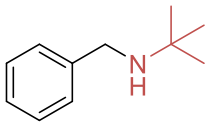


***N*-benzyl-2-phenylethan-1-amine**, **2d** was prepared according to the single feed procedure described in the manuscript and was obtained as a pale yellow oil, 604 mg (70% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.49 – 7.13 (m, 10H), 3.86 (s, 2H), 3.14 – 2.77 (m, 4H), 1.48 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.4, 140.11, 128.8, 128.5, 128.4, 128.1, 127.0, 126.2, 53.9, 50.6, 36.4. NMR data is in accordance with literature.[4]

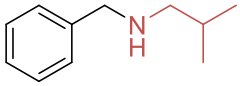


***N*-benzylbutan-1-amine**, **2e** was prepared according to the single feed procedure described in the manuscript and was obtained as a colorless oil, 522 mg (85% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.48 – 7.14 (m, 5H), 3.81 (s, 2H), 2.82 – 2.46 (m, 2H), 1.59 – 1.30 (m, 5H), 0.94 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (75

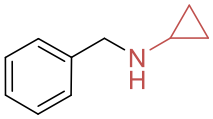
MHz, $CDCl_3$) δ 140.6, 128.4, 128.1, 126.9, 54.1, 49.2, 32.3, 20.5, 14.1. NMR data is in accordance with literature.[3]



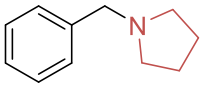
***N*-benzyl-2-methylpropan-2-amine**, **2f** was prepared according to the single feed procedure described in the manuscript and was obtained as a colorless oil, 510 mg (78% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42 – 7.16 (m, 5H), 3.75 (s, 2H), 1.21 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 141.5, 128.4, 128.3, 126.7, 50.7, 47.3, 29.2. NMR data is in accordance with literature.[11]



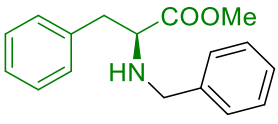
***N*-benzyl-2-methylpropan-1-amine**, **2g** was prepared according to the single feed procedure described in the manuscript and was obtained as a colorless oil, 520 mg (80% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.46 – 7.19 (m, 5H), 3.82 (s, 2H), 2.48 (d, *J* = 6.8 Hz, 2H), 1.90 – 1.69 (m, 1H), 1.38 (s, 1H), 0.95 (d, *J* = 6.6 Hz, 6H).^{13}C NMR (75 MHz, $CDCl_3$) δ 140.8, 128.4, 128.1, 126.8, 57.5, 54.1, 28.4, 20.7. NMR data is in accordance with literature.[11]



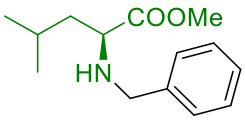
***N*-benzylcyclopropanamine**, **2h** was prepared according to the single feed procedure described in the manuscript and was obtained as a pale yellow oil, 435 mg (74% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.44 – 7.21 (m, 5H), 3.87 (s, 2H), 2.22-2.15 (m, 1H), 1.86 (s, 1H), 0.53 – 0.33 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.6, 128.4, 128.2, 126.9, 53.8, 30.1, 6.5. NMR data is in accordance with literature.[11]



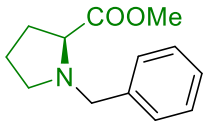
1-benzylpyrrolidine, **2i** was prepared according to the single feed procedure described in the manuscript and was obtained as a pale yellow oil, 523 mg (79% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42 – 7.21 (m, 5H), 3.65 (s, 2H), 2.63 – 2.40 (m, 4H), 1.84-1.70 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.4, 128.9, 128.2, 126.9, 60.8, 54.2, 23.5. NMR data is in accordance with literature.[11]



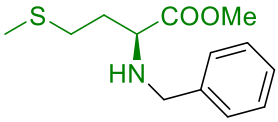
methyl benzyl-*L*-phenylalaninate, **3a** was prepared according to the single feed procedure described in the manuscript and was obtained as a colorless oil, 523 mg (79 % yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38 – 7.18 (m, 10H), 3.87 (d, *J* = 13.2 Hz, 1H), 3.73 – 3.65 (m, 4H), 3.60 (t, *J* = 6.9 Hz, 1H), 3.07 – 2.93 (m, 2H), 1.90 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 175.1, 139.6, 137.4, 129.3, 128.4, 128.4, 128.2, 127.1, 126.7, 62.1, 52.0, 51.7, 39.8. NMR data is in accordance with literature.[12]



methyl benzyl-*L*-leucinate, **3b** was prepared according to the single feed procedure described in the manuscript and was obtained as a colorless oil, 602 mg (62 % yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.43 – 7.15 (m, 5H), 3.89 – 3.56 (m, 5H), 3.33 (t, *J* = 7.2 Hz, 1H), 1.95 – 1.61 (m, 2H), 1.54 – 1.42 (m, 2H), 0.91 (dd, *J* = 19.7, 6.6 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 176.6, 139.9, 128.3, 128.3, 127.0, 59.3, 52.2, 51.6, 42.9, 24.9, 22.8, 22.2. NMR data is in accordance with literature.[13]



methyl benzyl-*L*-prolinate, **3c** was prepared according to the single feed procedure described in the manuscript and was obtained as a colorless oil, 431 mg (48 % yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.47 – 7.15 (m, 5H), 3.90 (d, *J* = 12.7 Hz, 1H), 3.68 – 3.52 (m, 4H), 3.34 – 3.20 (m, 1H), 3.12 – 2.99 (m, 1H), 2.51 – 2.31 (m, 1H), 2.23 – 1.69 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.6, 138.3, 129.3, 128.2, 127.1, 65.3, 58.8, 53.3, 51.7, 29.4, 23.0. NMR data is in accordance with literature.[14]



methyl benzyl-*L*-methioninate, **3d** was prepared according to the single feed procedure described in the manuscript and was obtained as a colorless oil, 781 mg (75 % yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.46 – 7.17 (m, 5H), 3.92 – 3.56 (m, 5H), 3.43 (dd, *J* = 8.0, 5.3 Hz, 1H), 2.73 – 2.52 (m, 2H), 2.09 (s, 3H), 2.03 – 1.74 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 175.6, 139.8, 128.4, 128.2, 127.1, 59.6, 52.2, 51.9, 32.9, 30.6, 15.4. NMR data is in accordance with literature.[15]

9. References

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10. Collection of NMR Spectra

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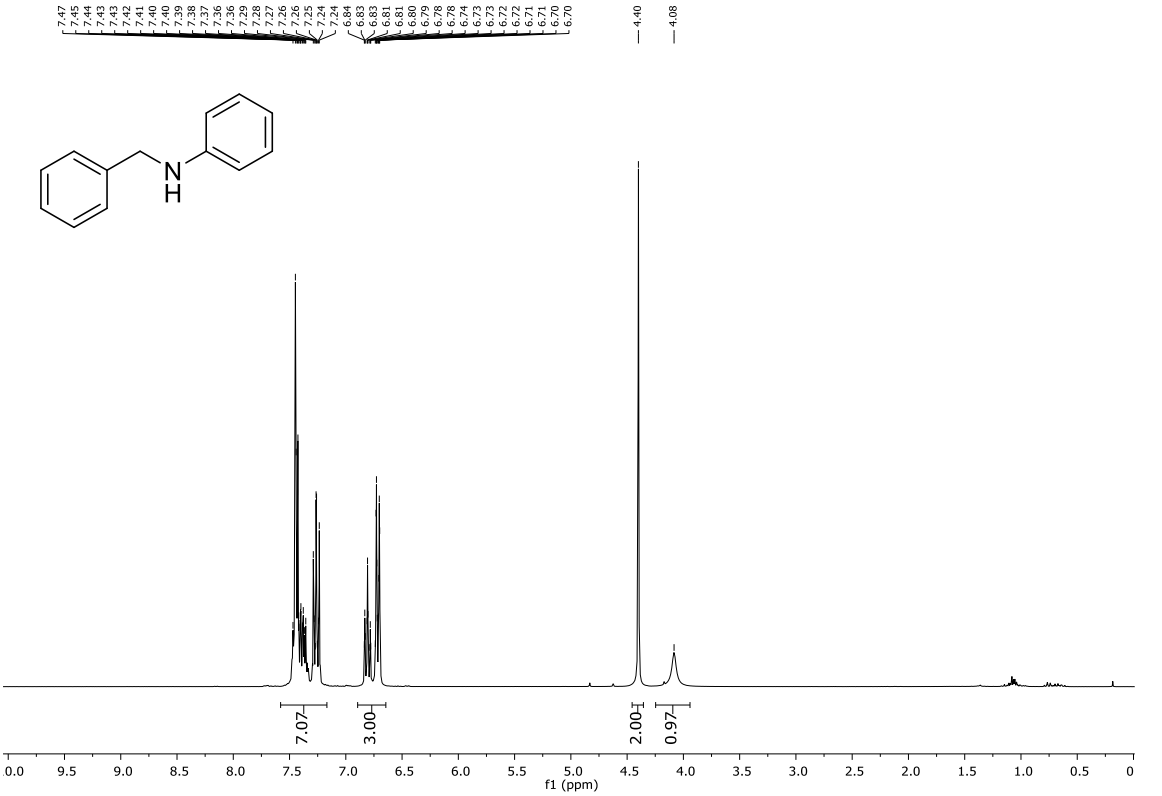
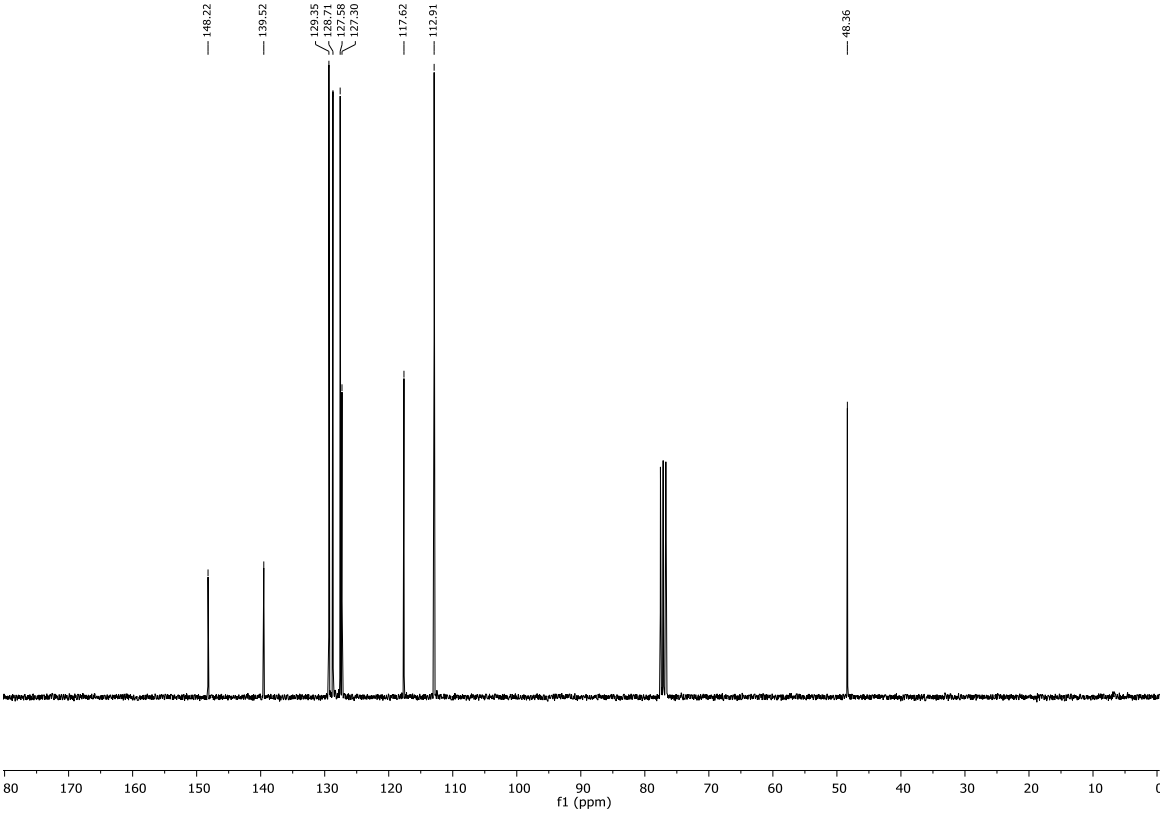
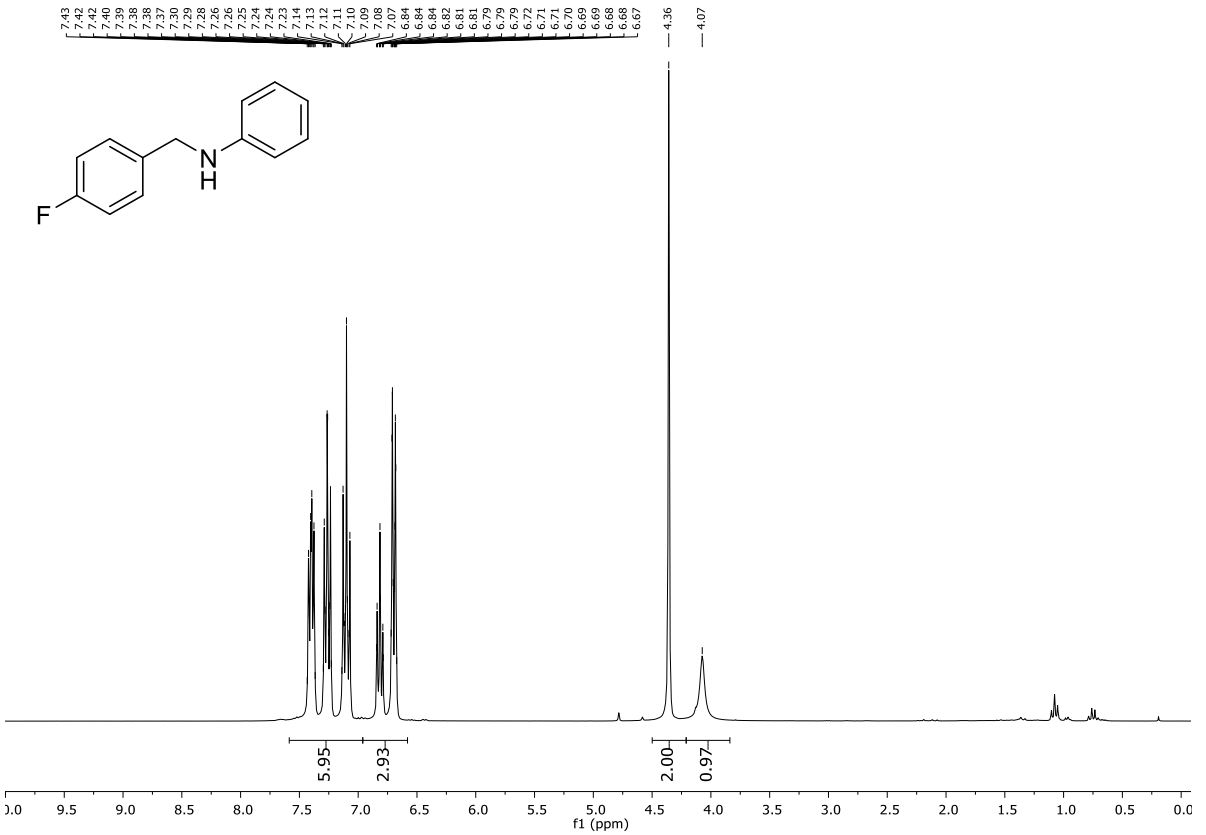
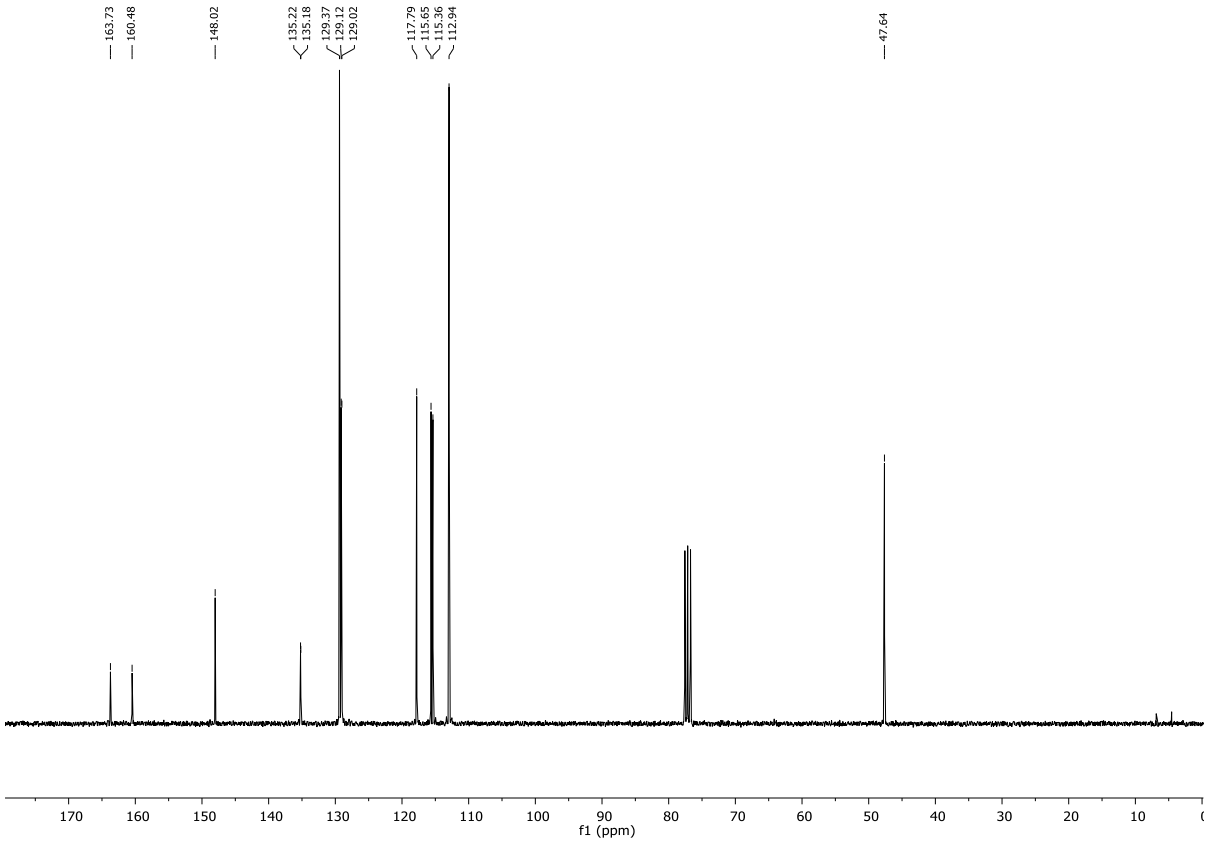




***N*-(4-fluorobenzyl)aniline, 1b**





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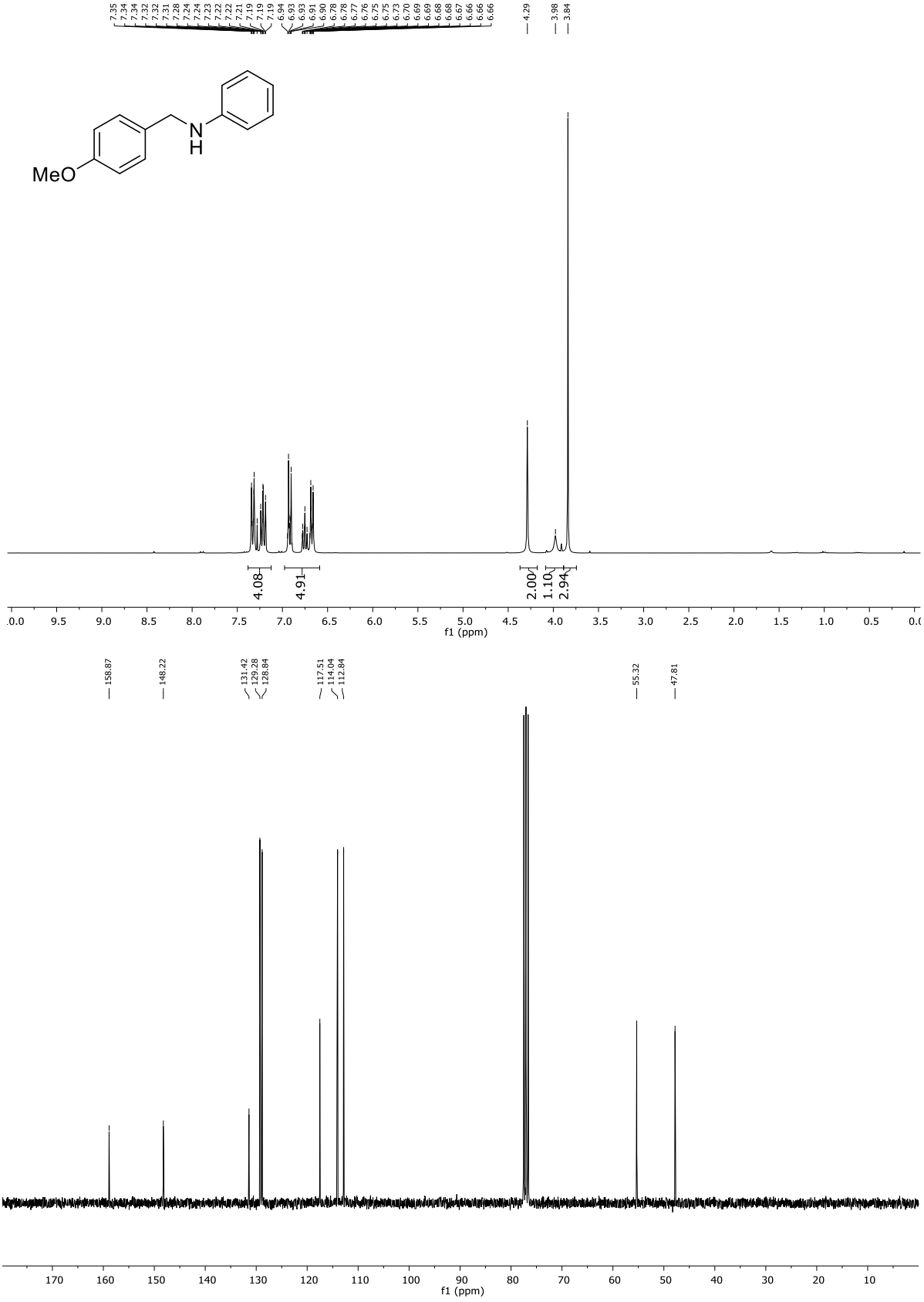
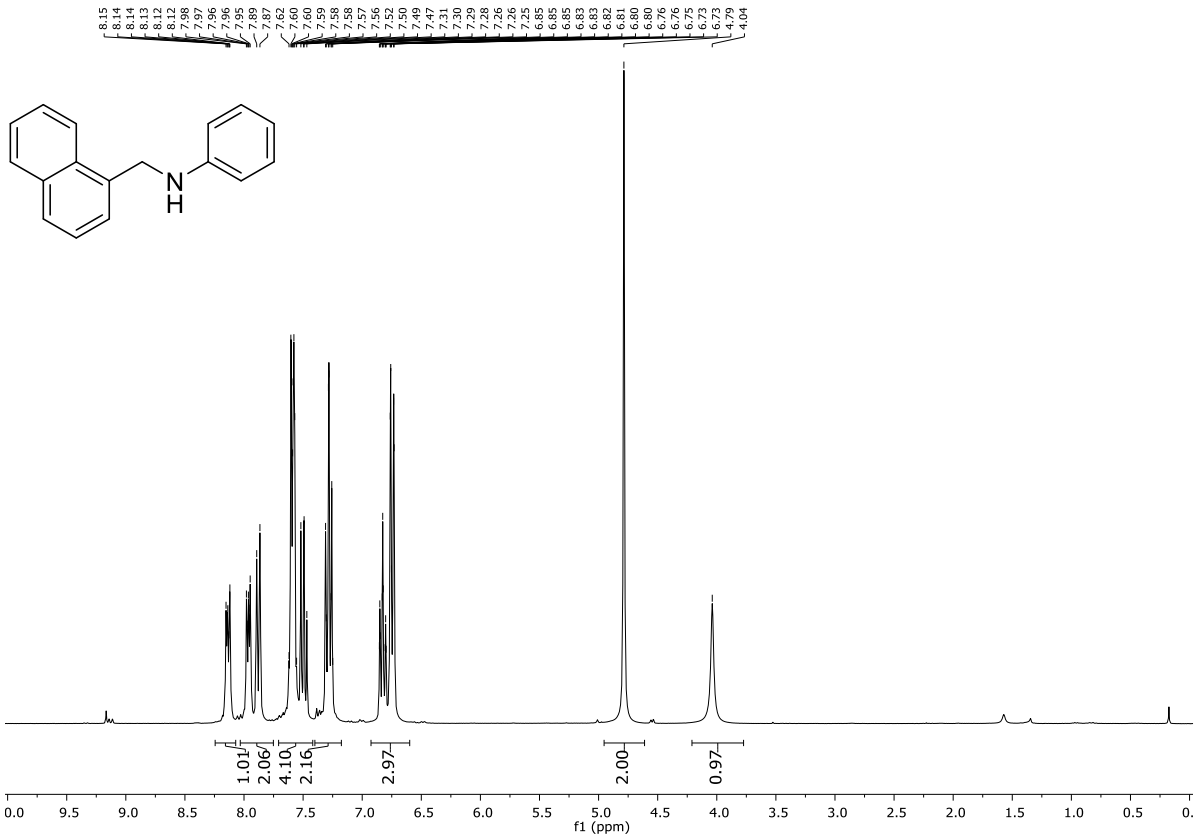
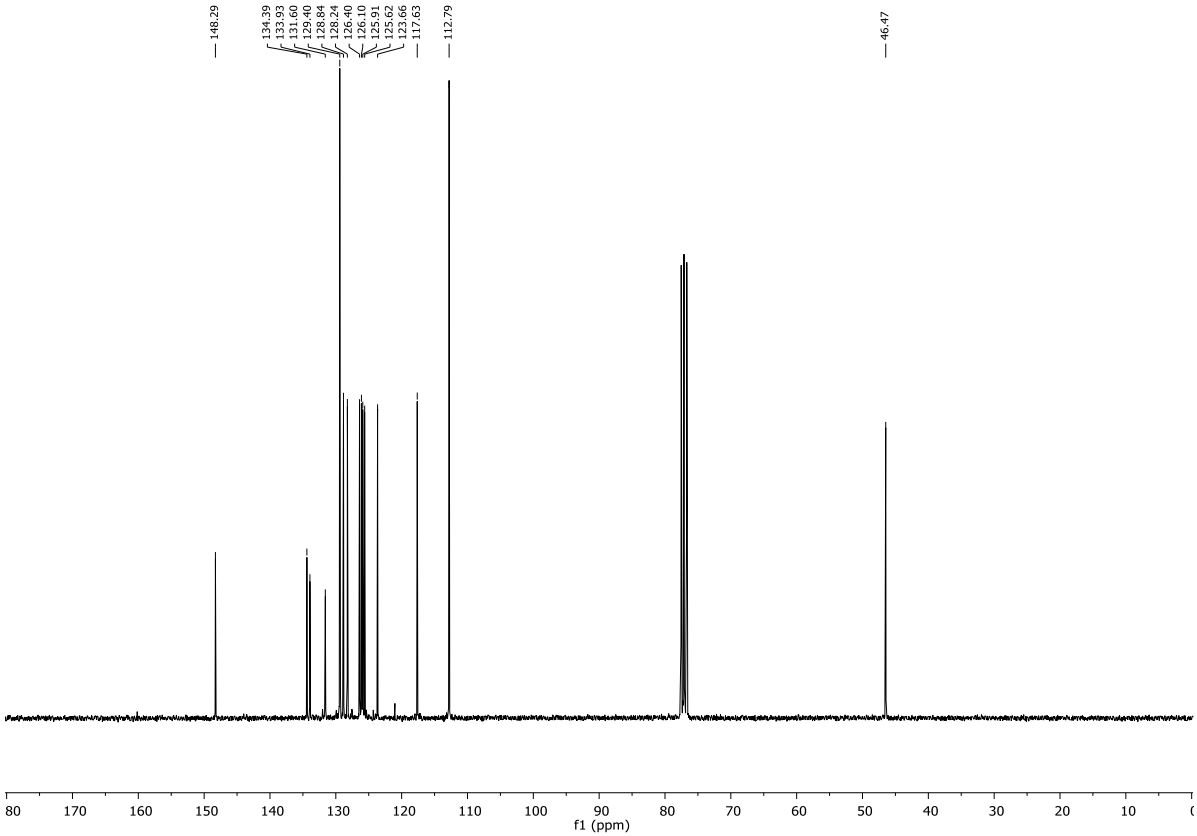


_N_-(naphthalen-1-ylmethyl)aniline, 1d





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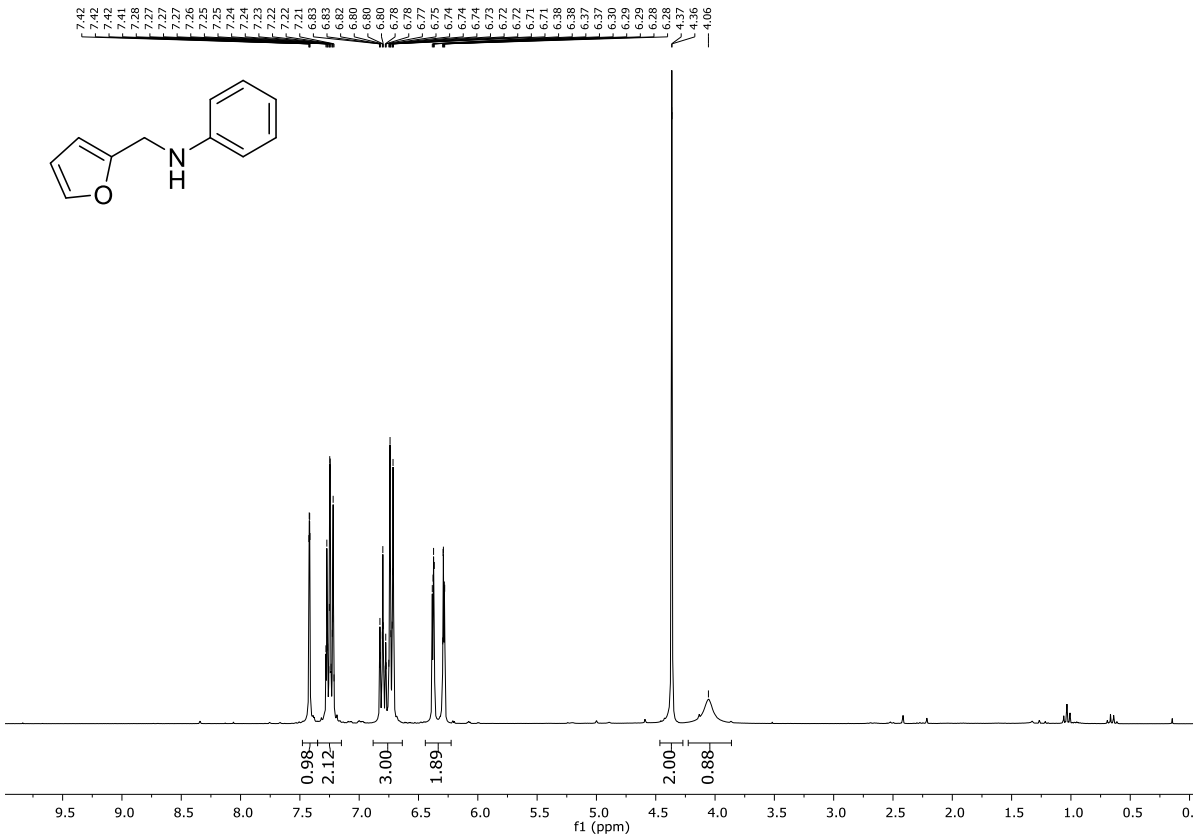

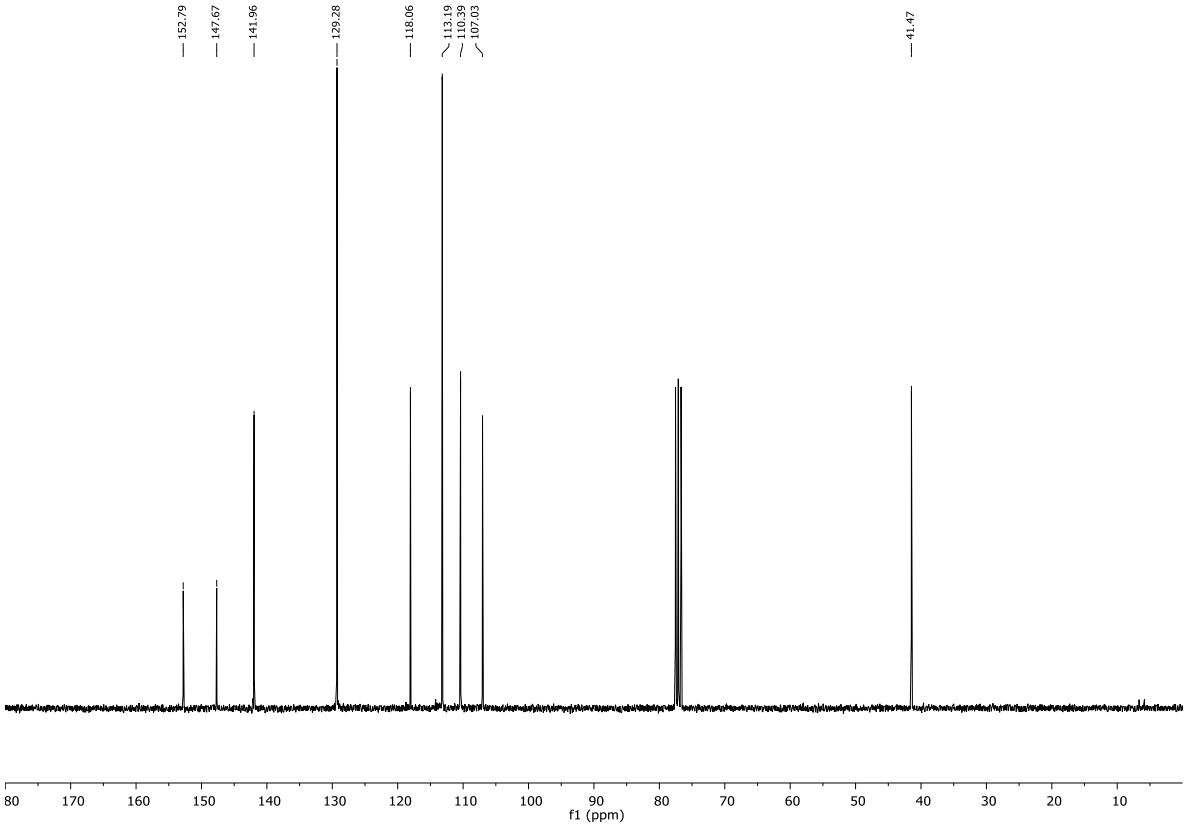

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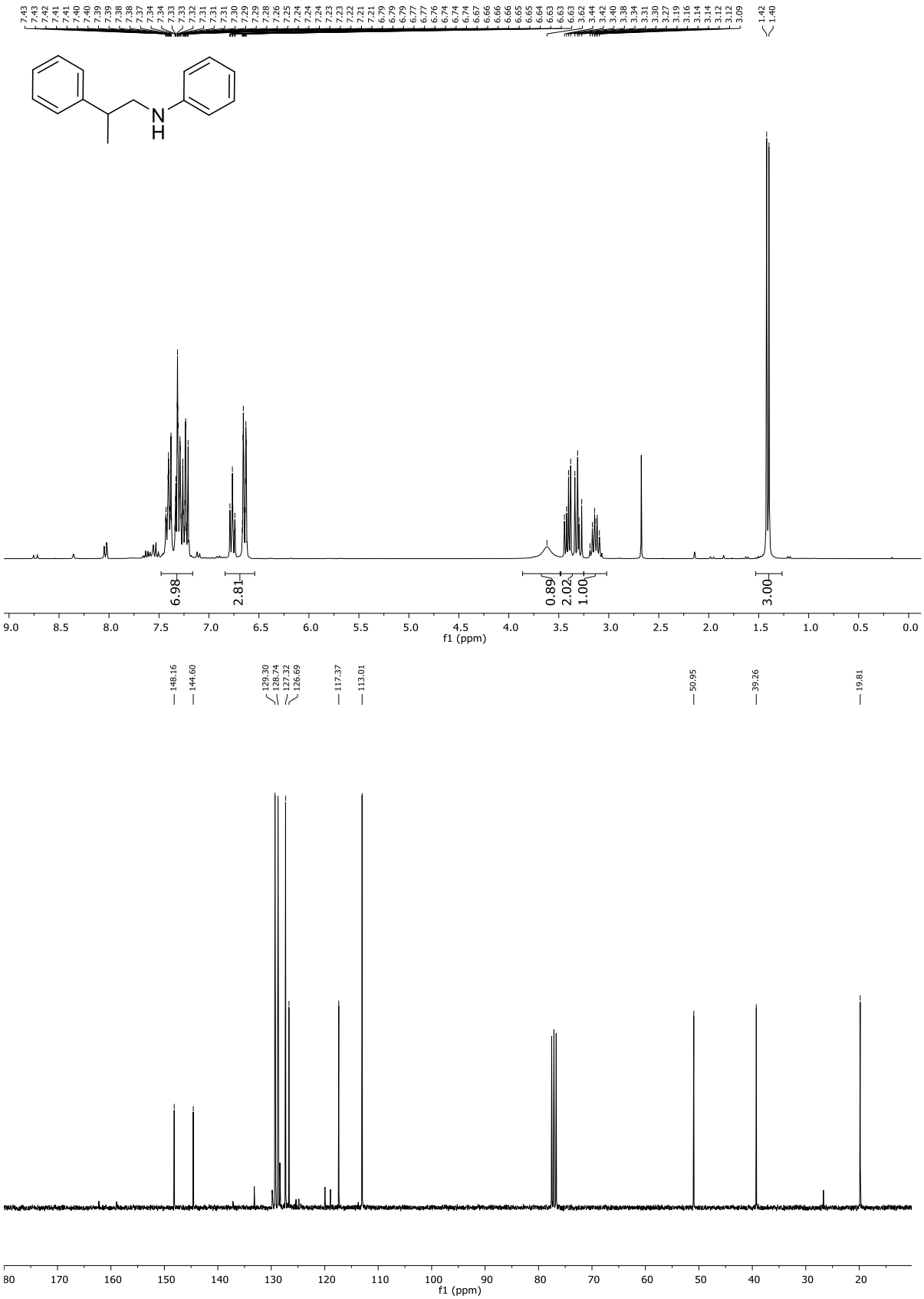

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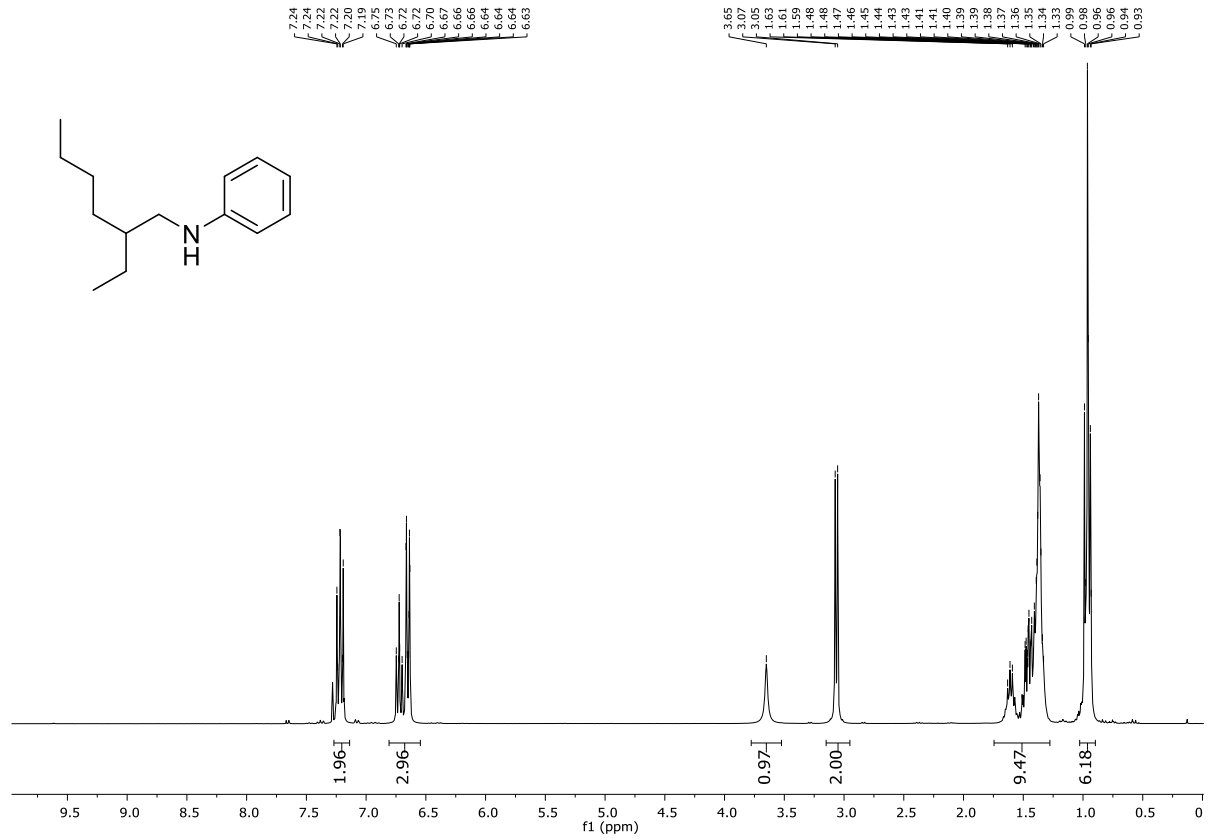
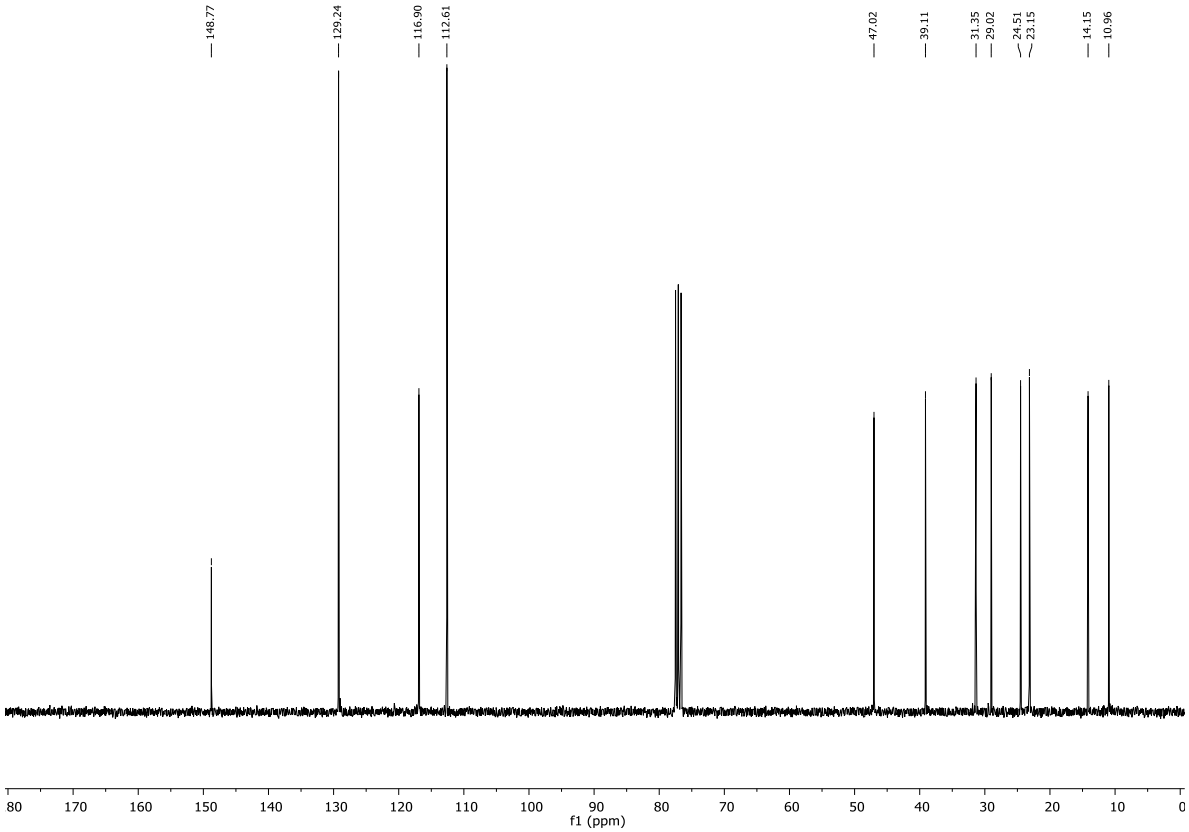
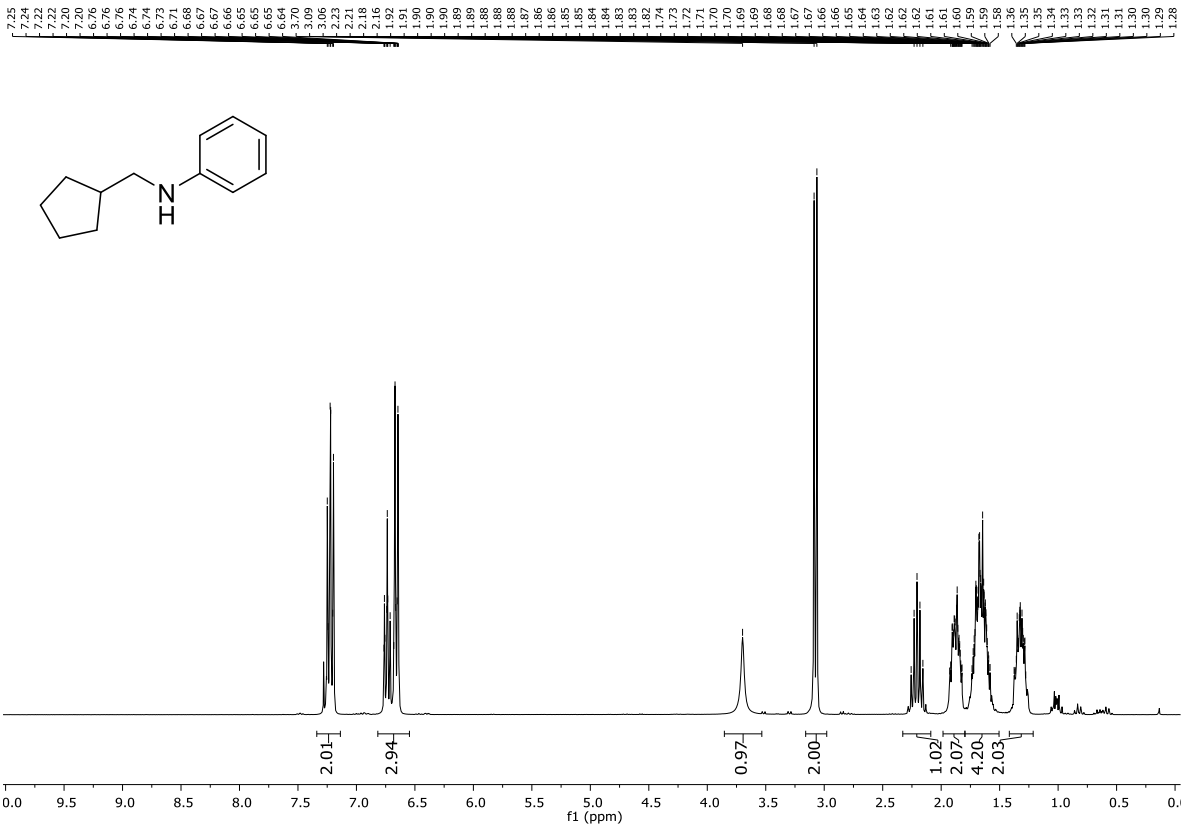
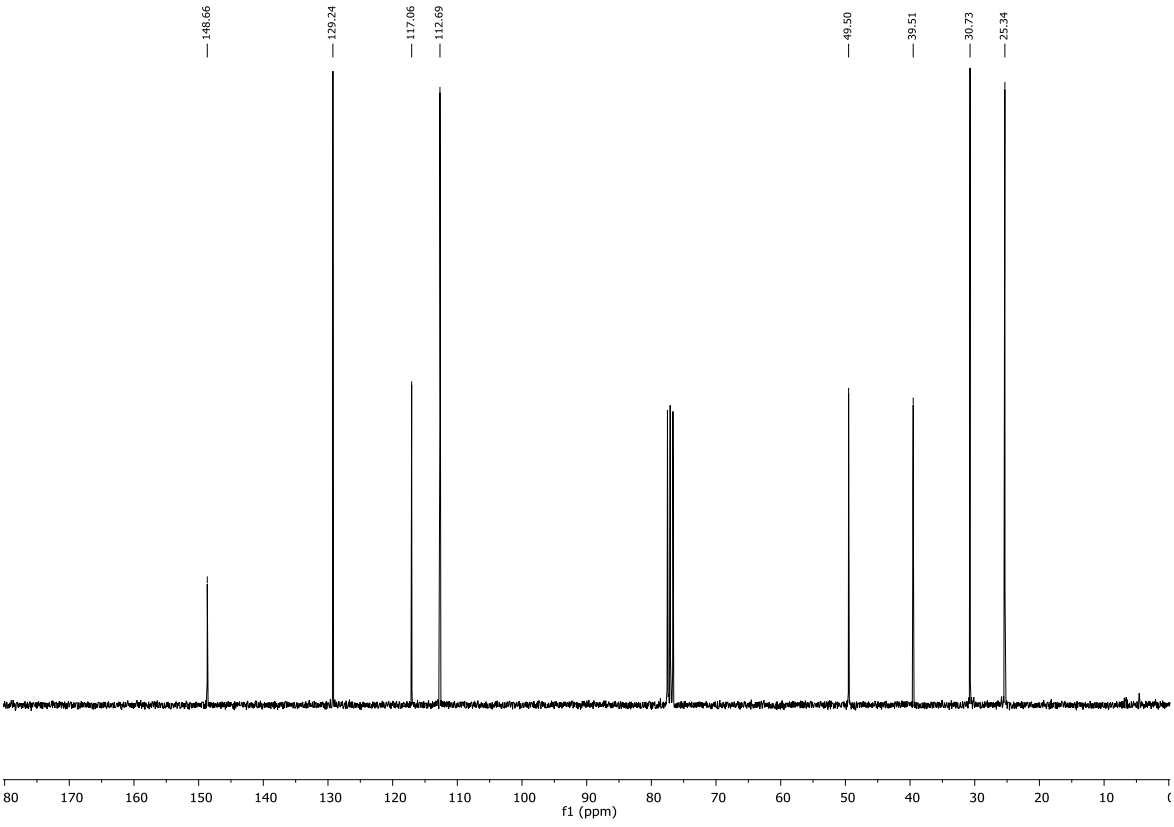




_N_-(cyclopentylmethyl)aniline, 1h





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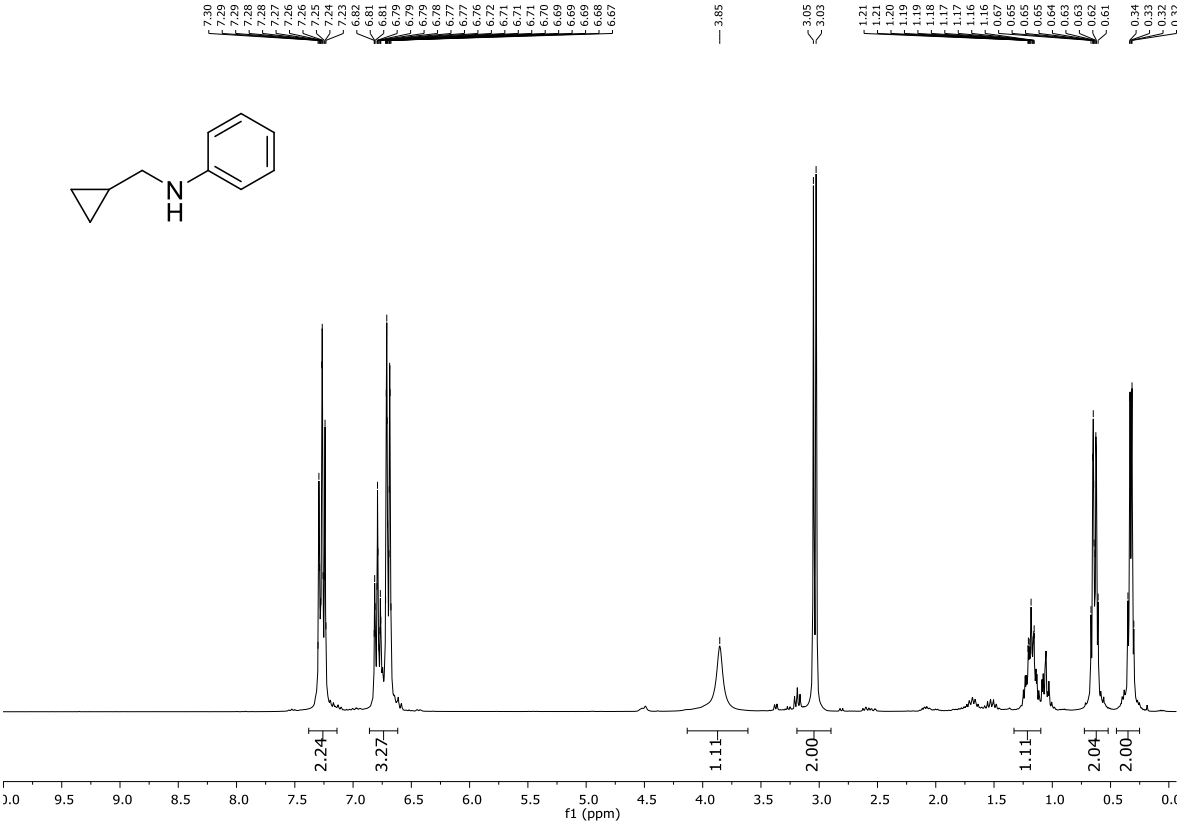

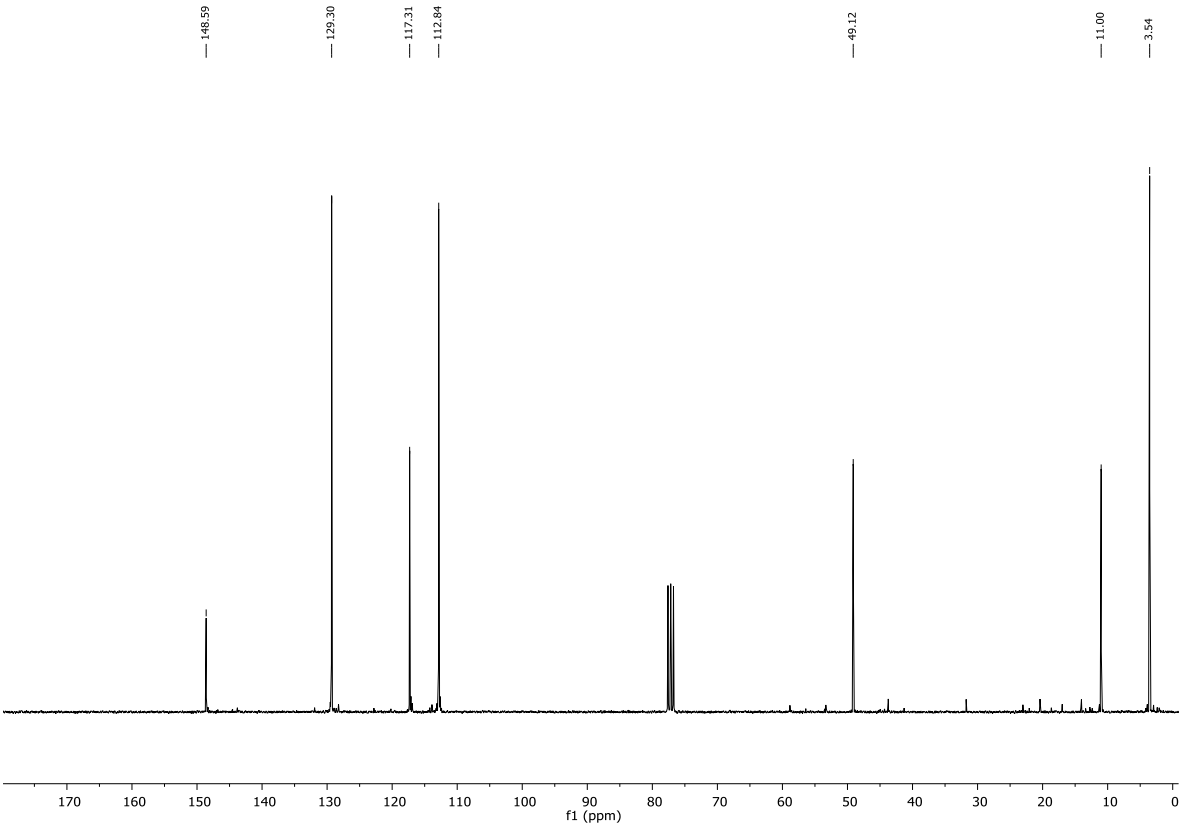

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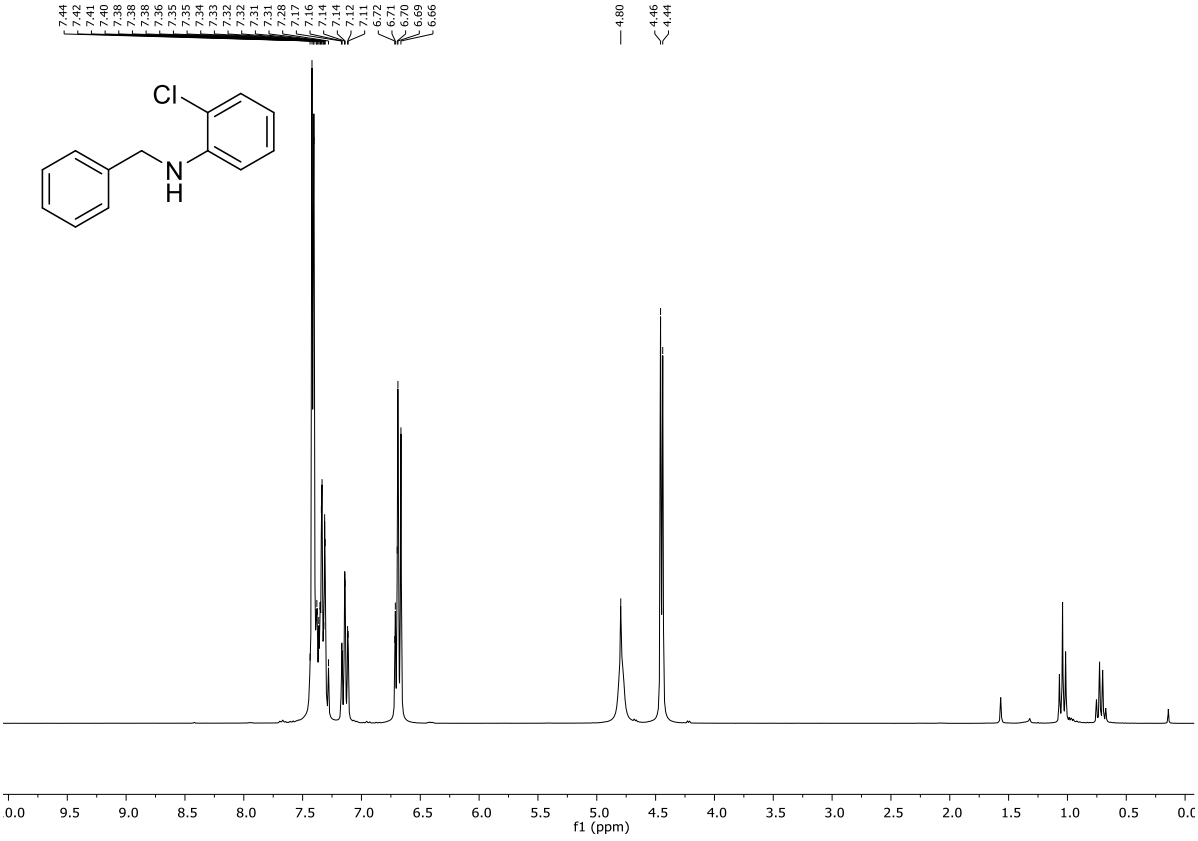

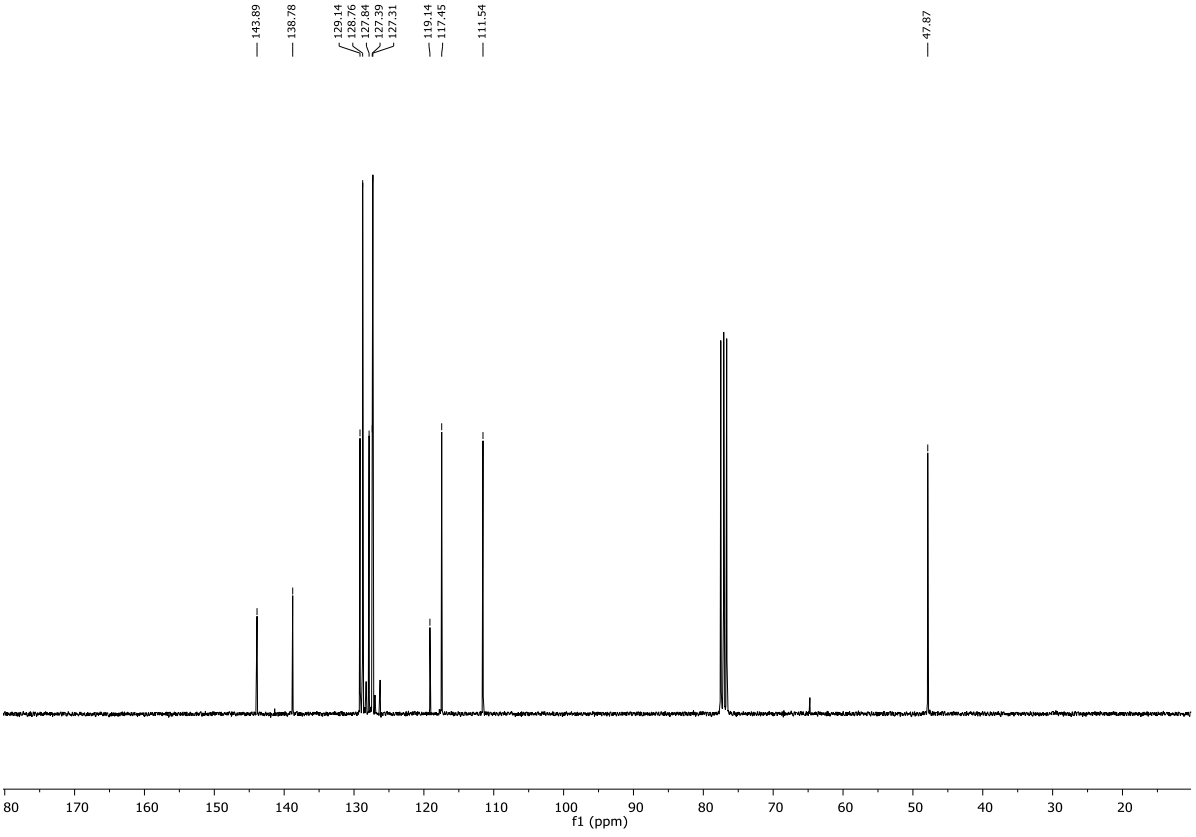

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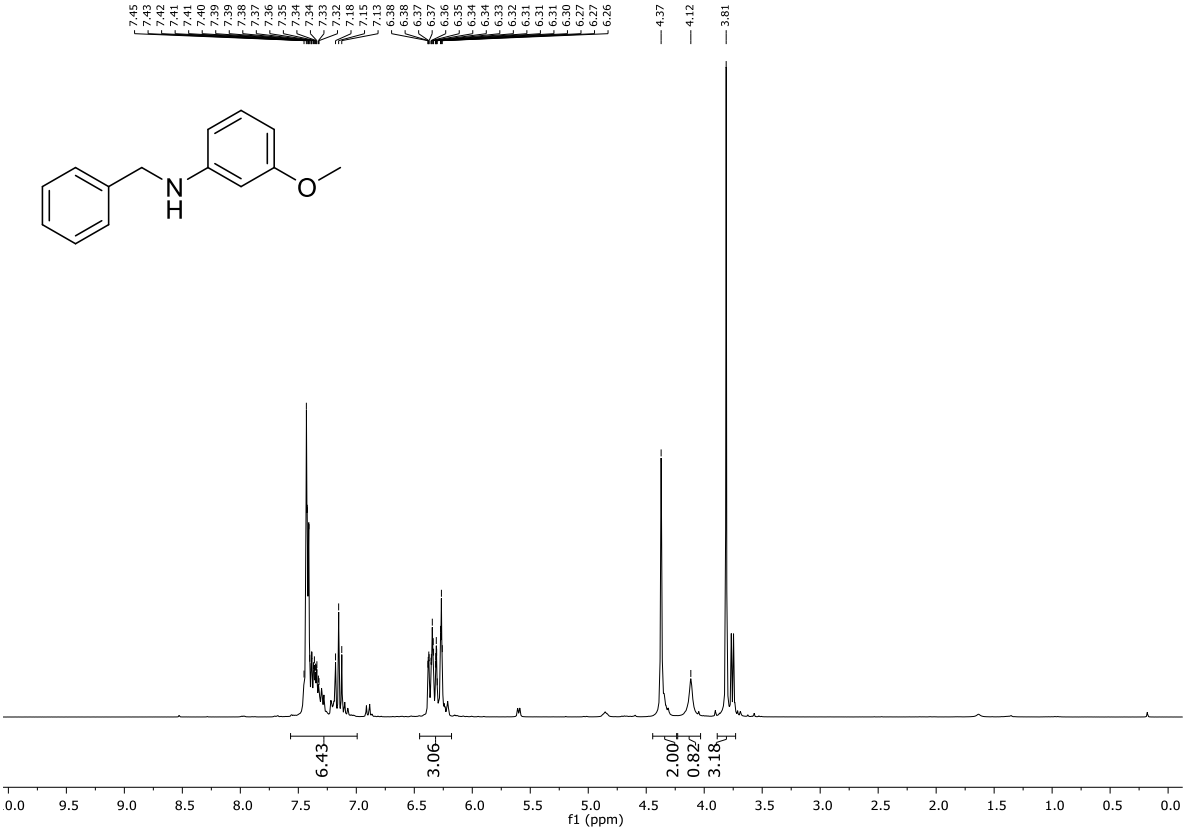
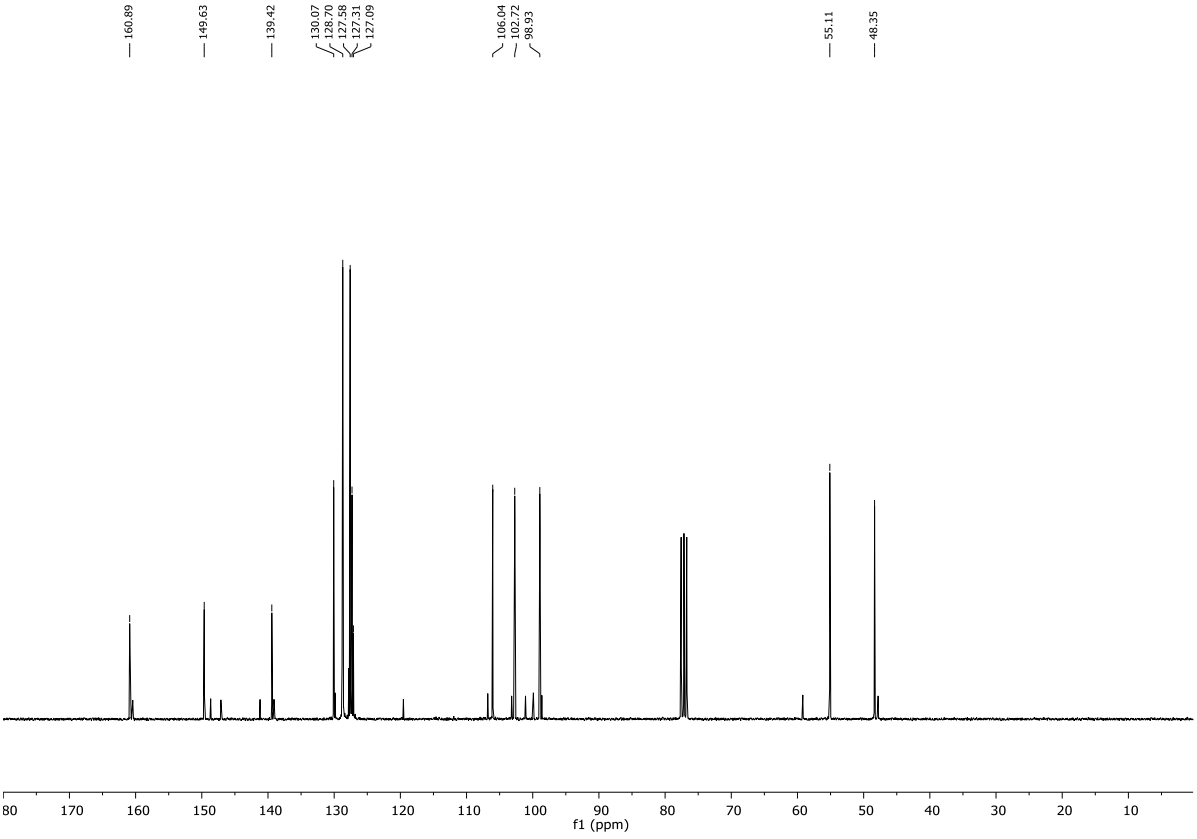
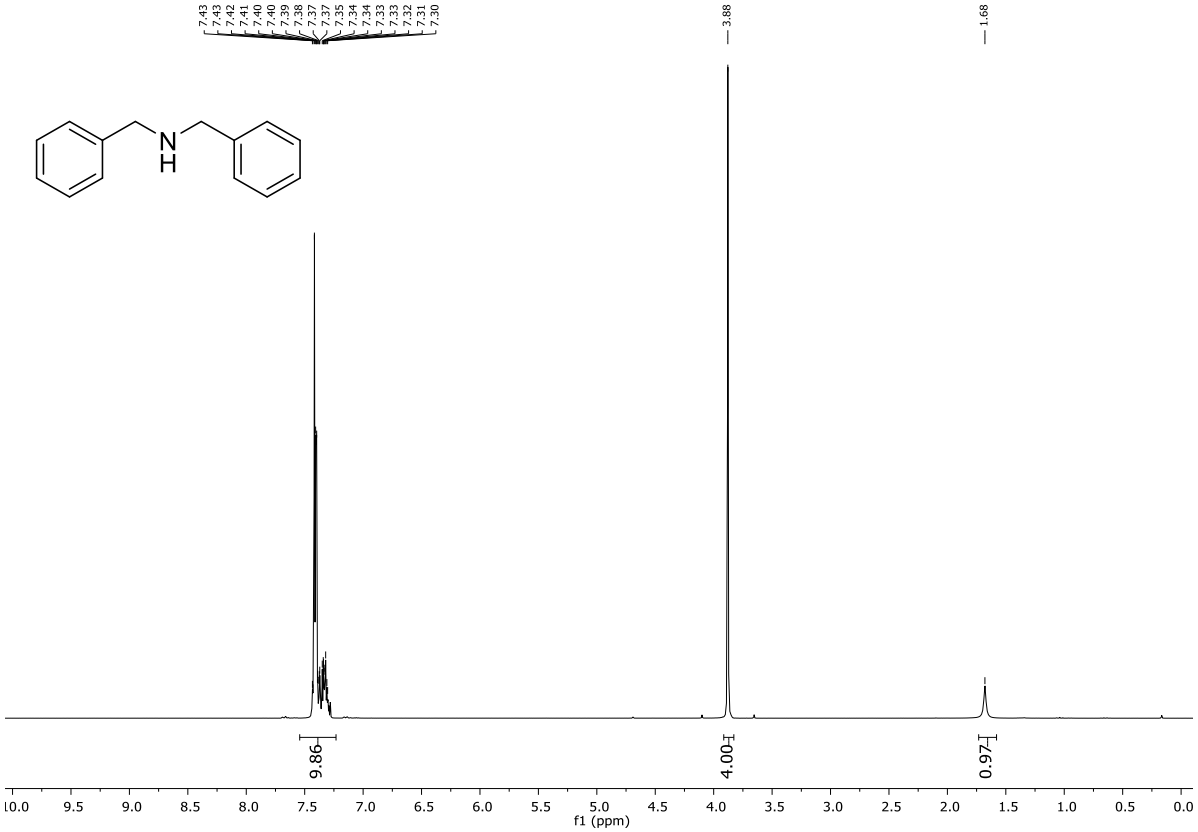
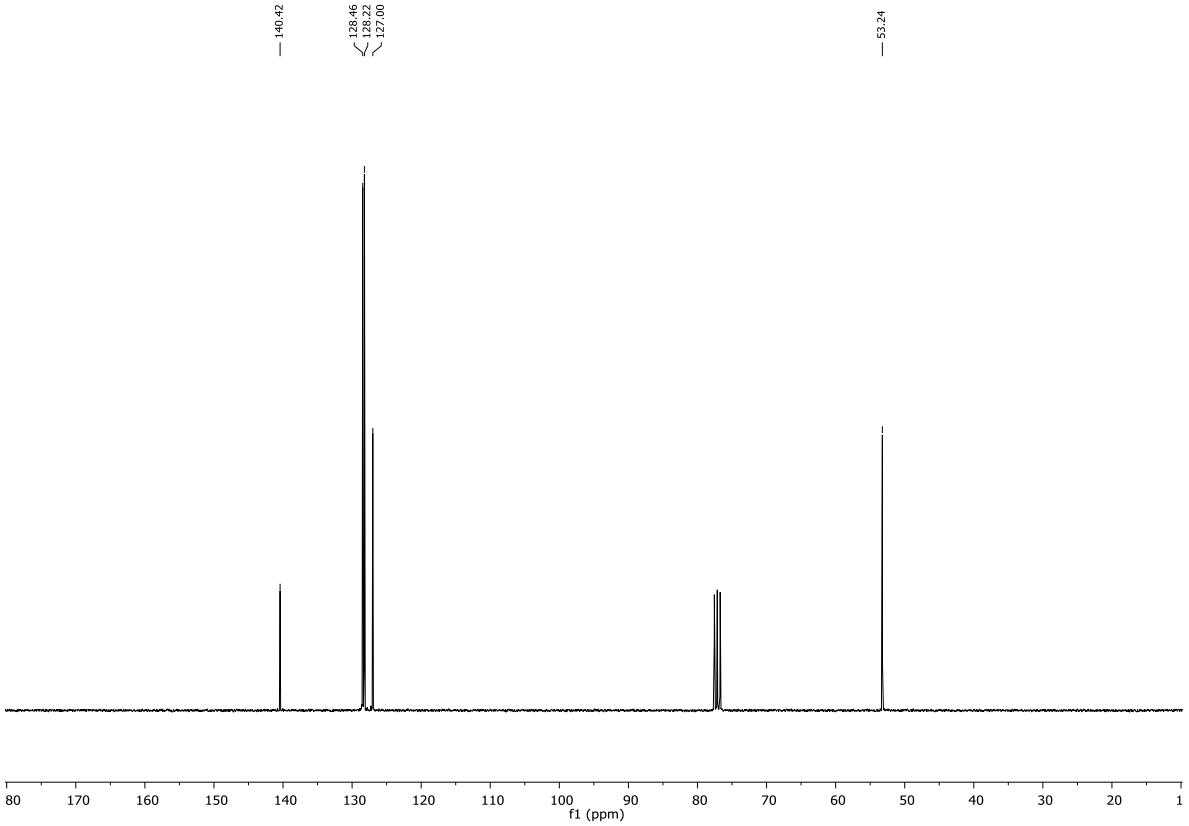




Dibenzylamine, 2c





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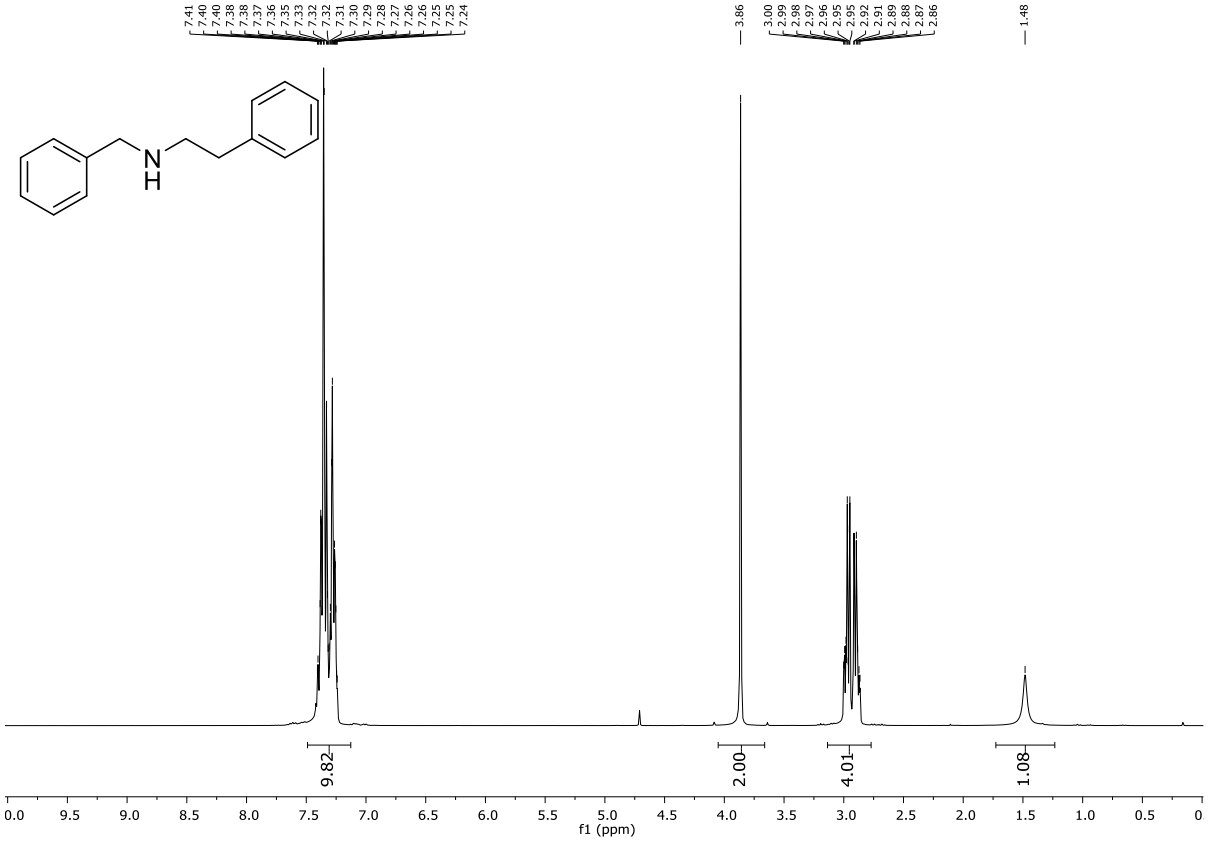

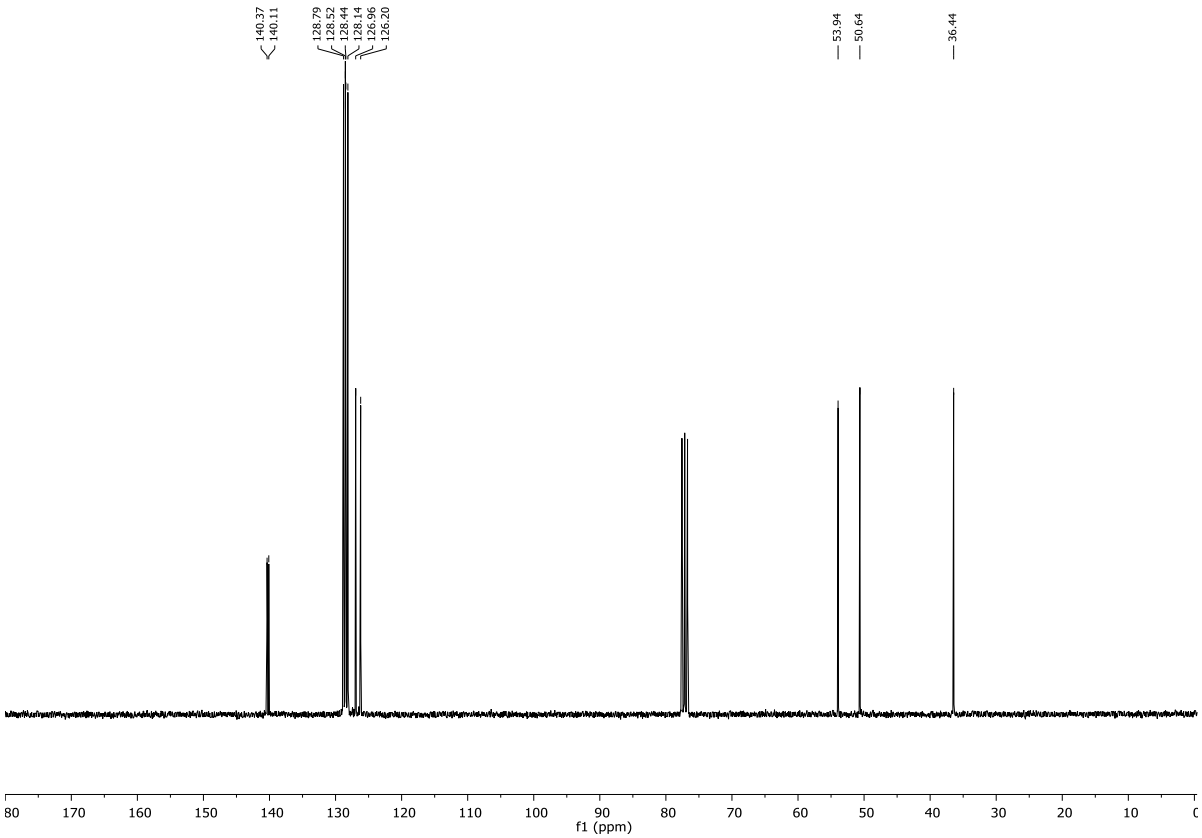

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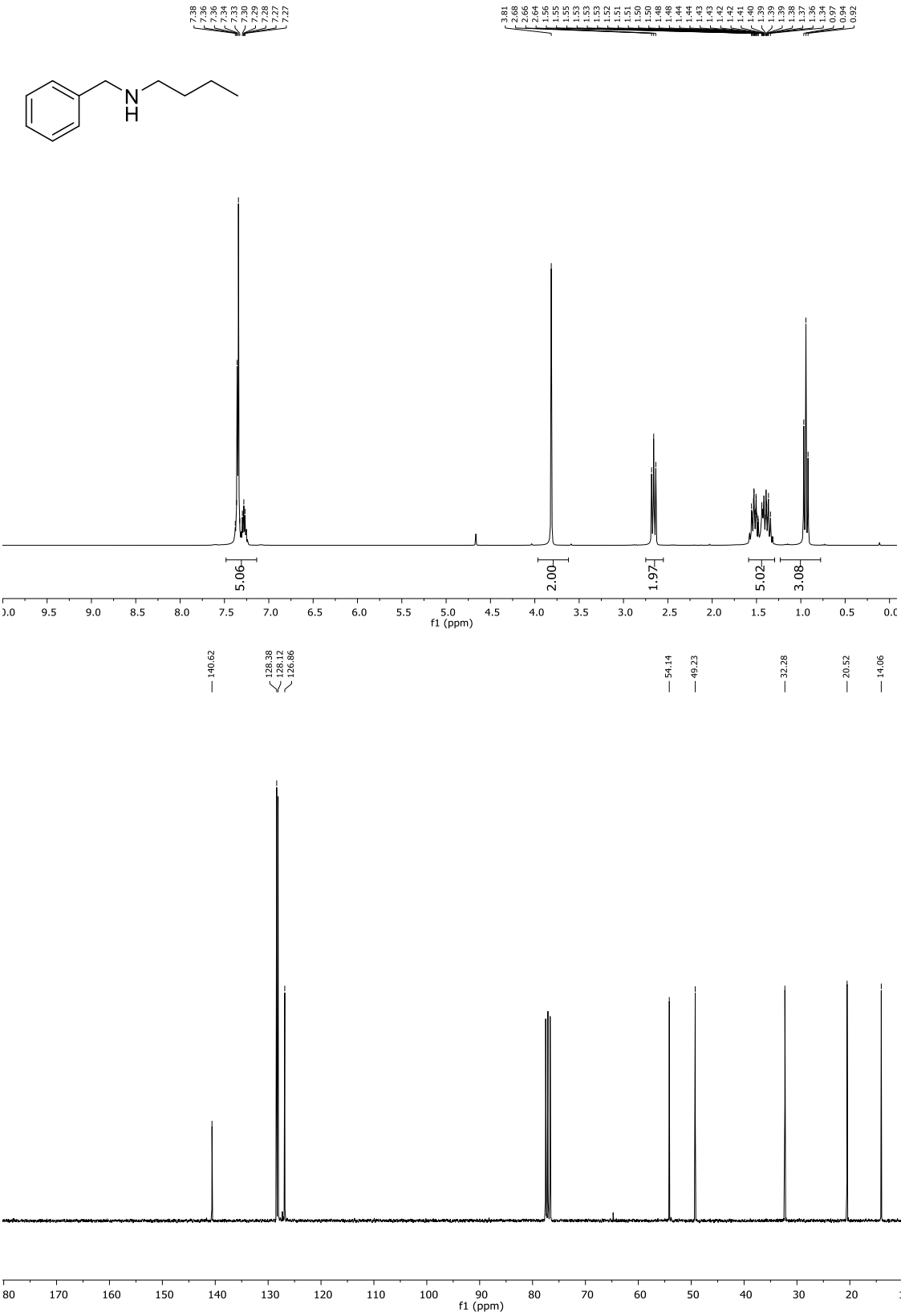
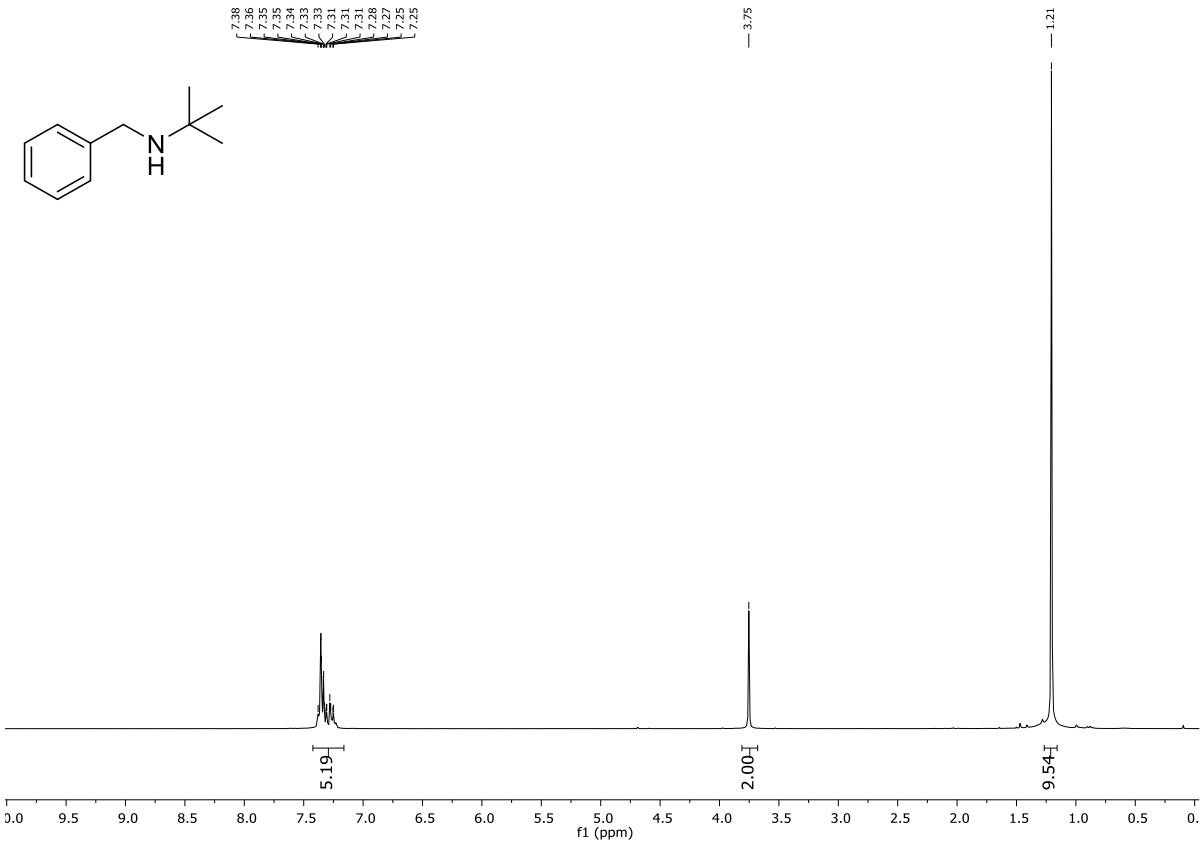
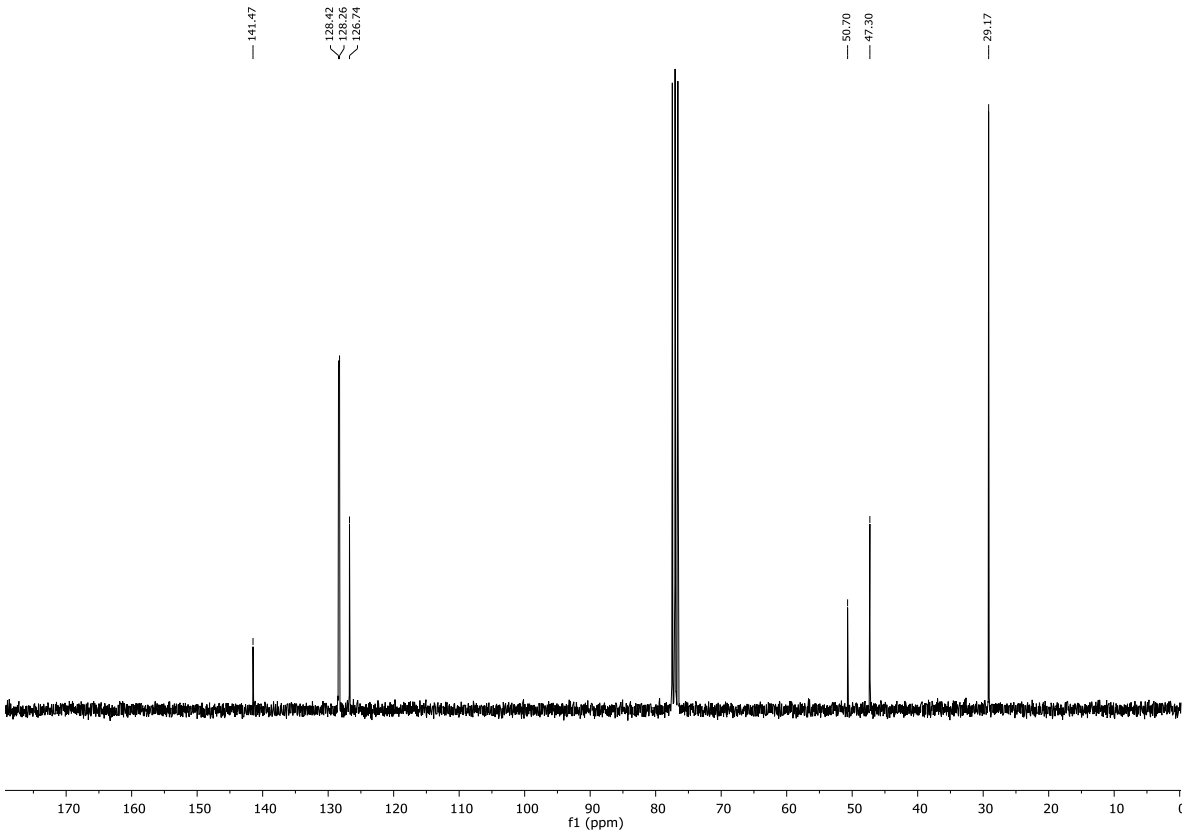


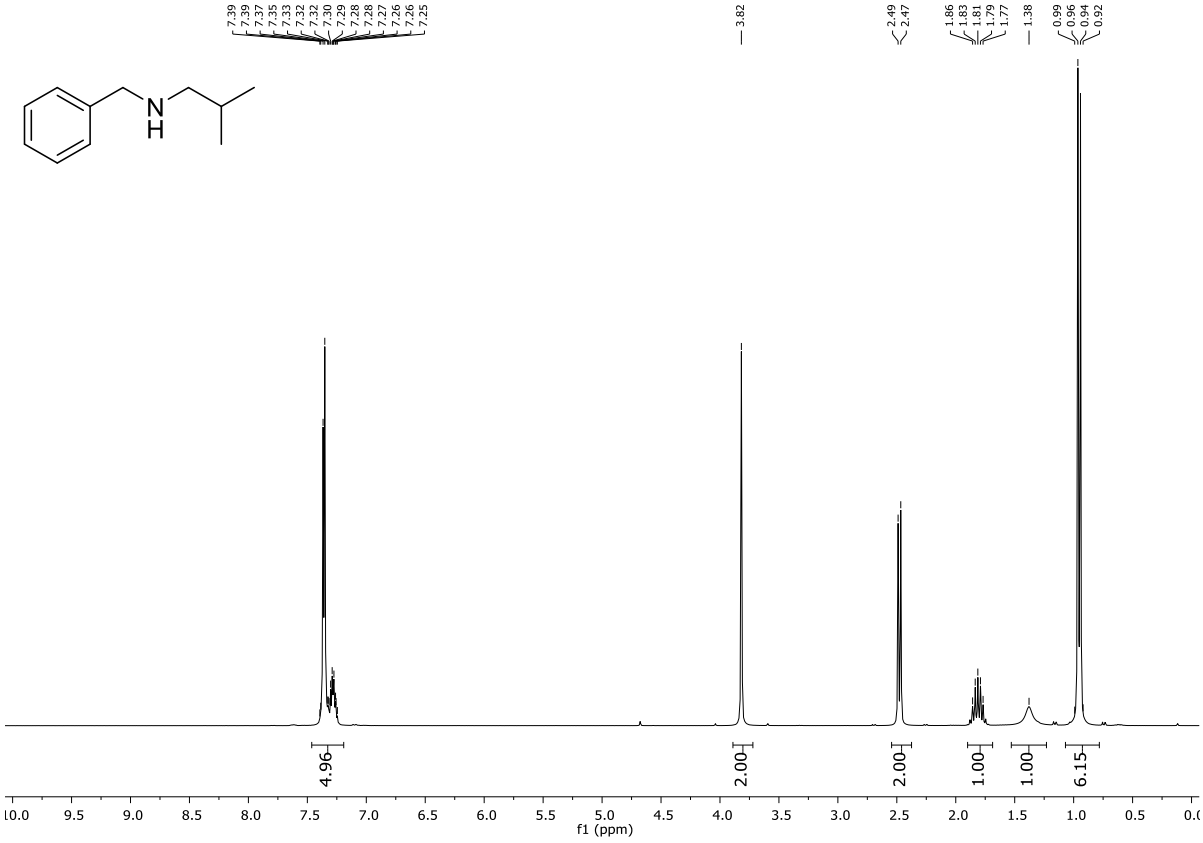
***N*-**

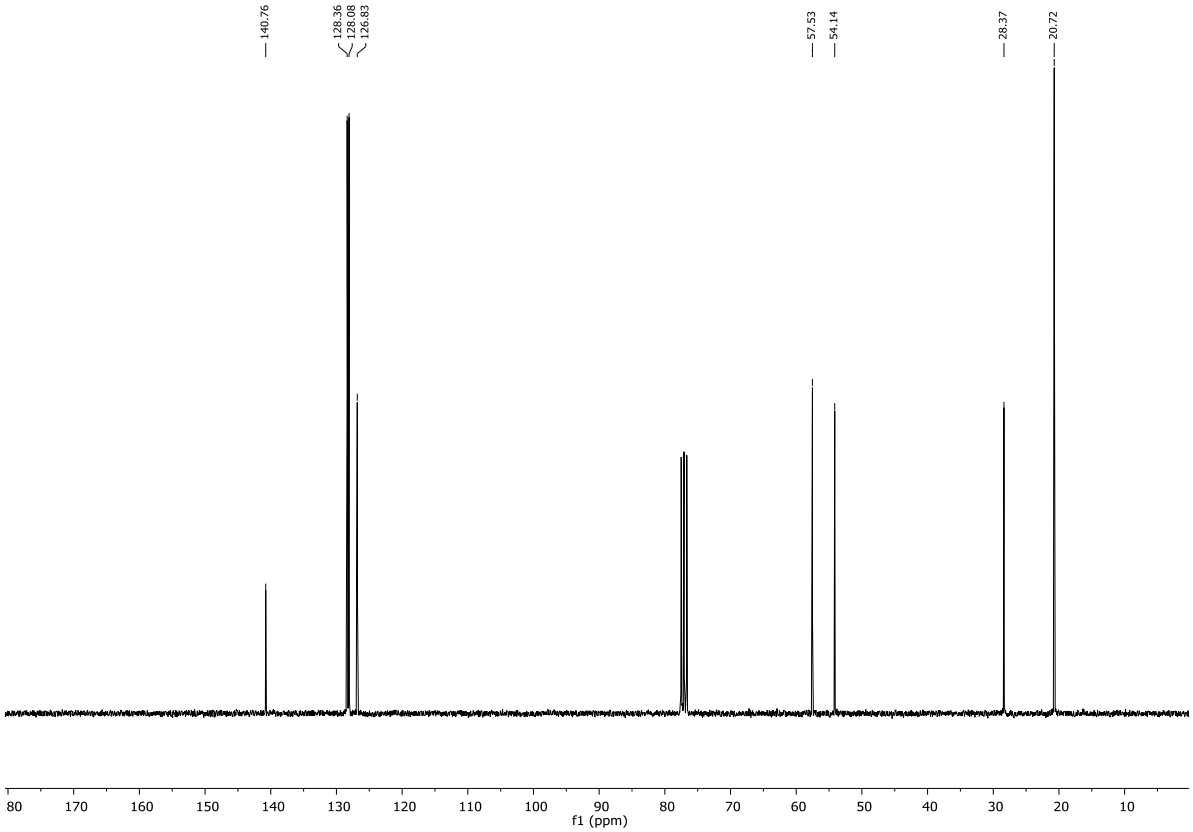
_N_-benzyl-2-methylpropan-2-amine, 2f



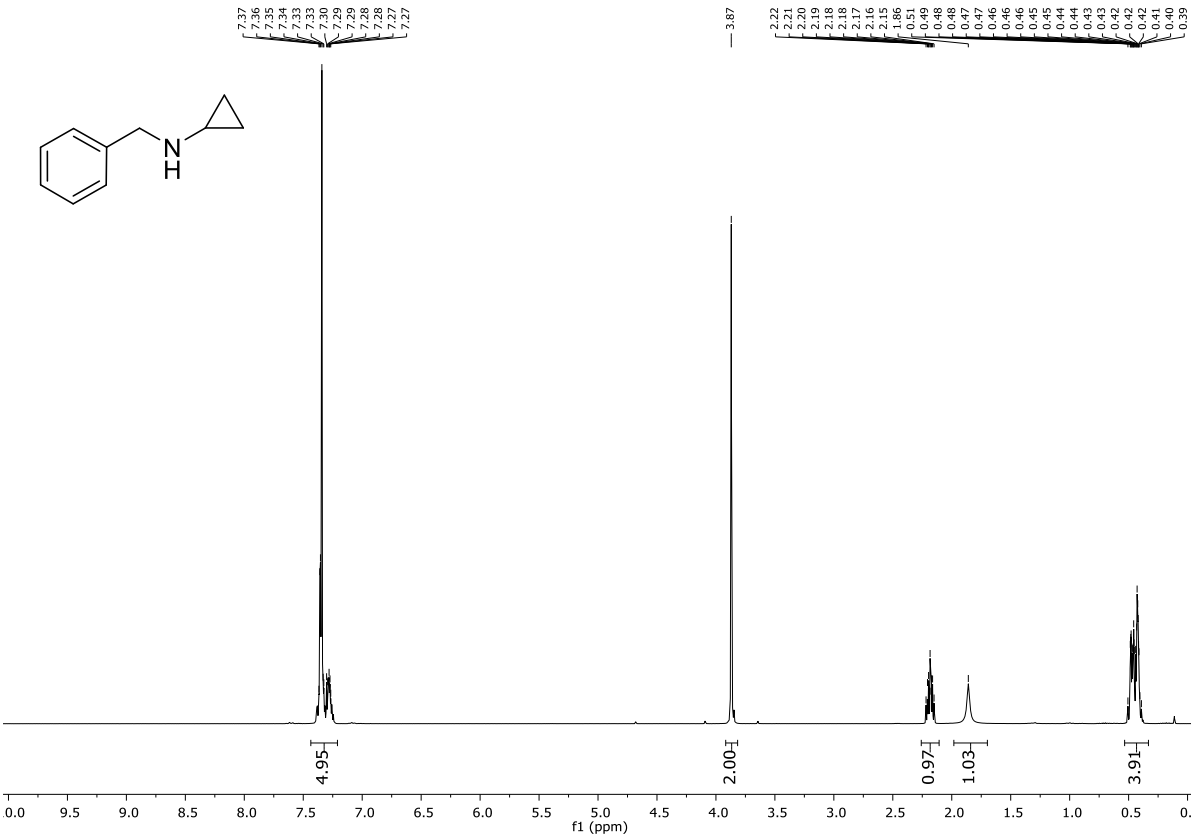


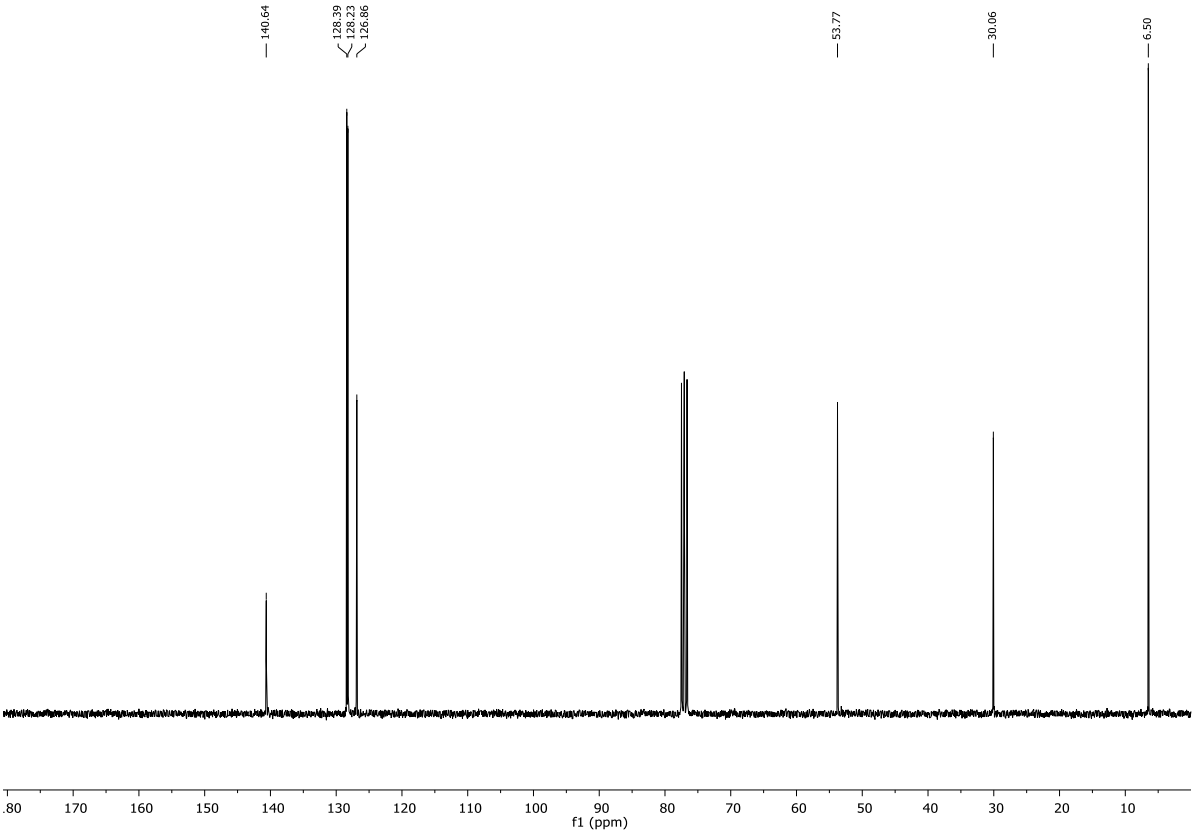
_N_-benzyl-2-methylpropan-1-amine, 2g



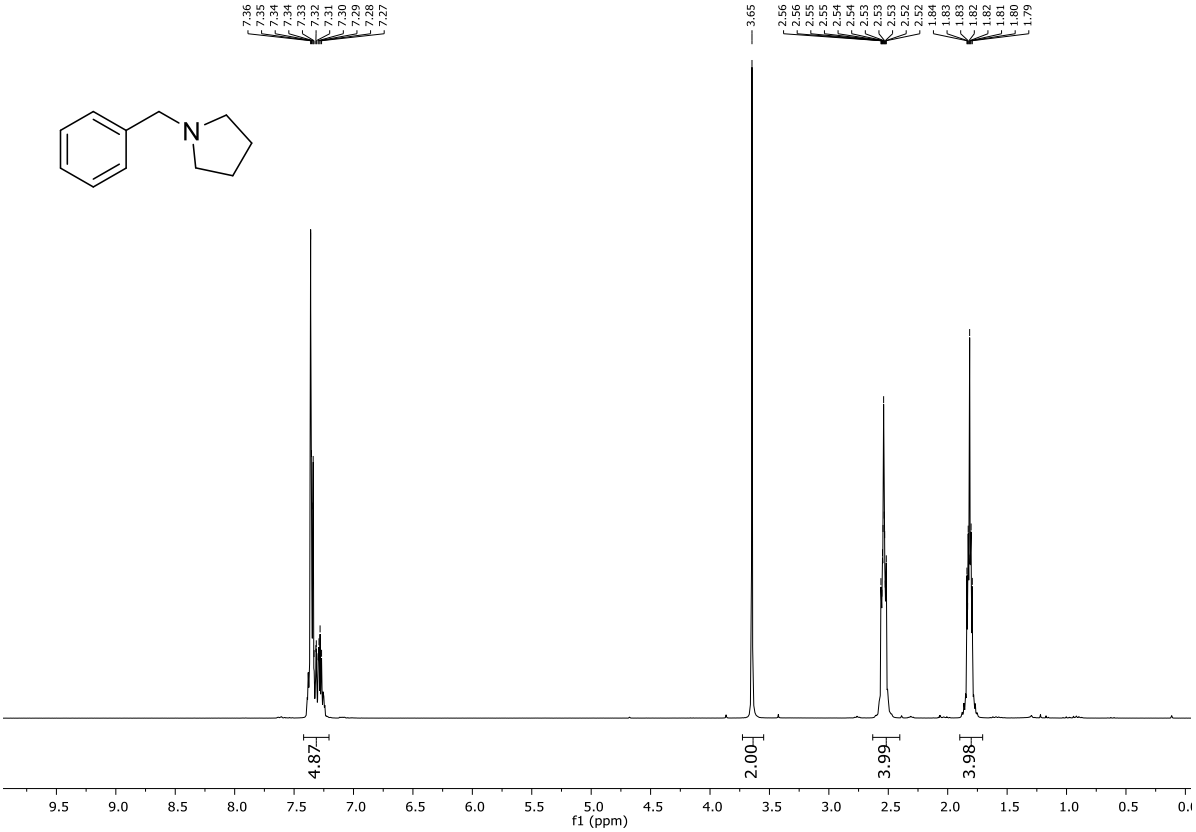


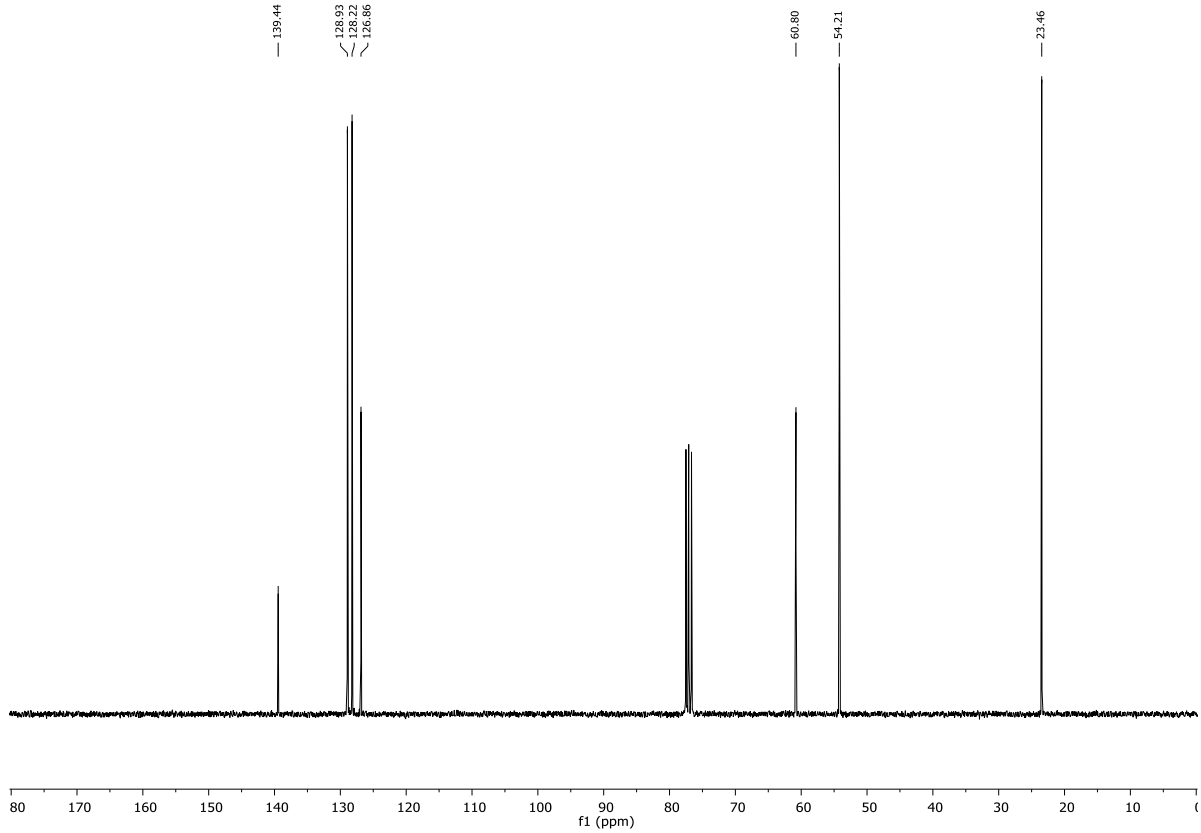
benzylcyclopropanamine, 2h



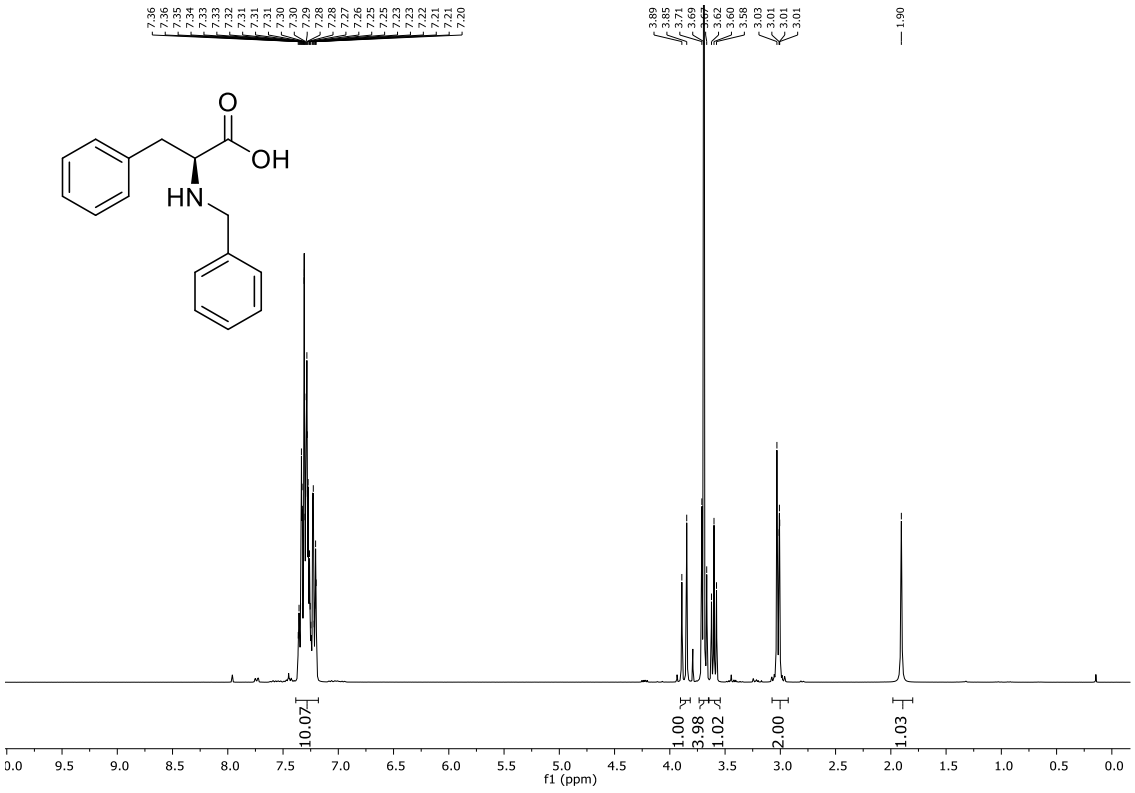


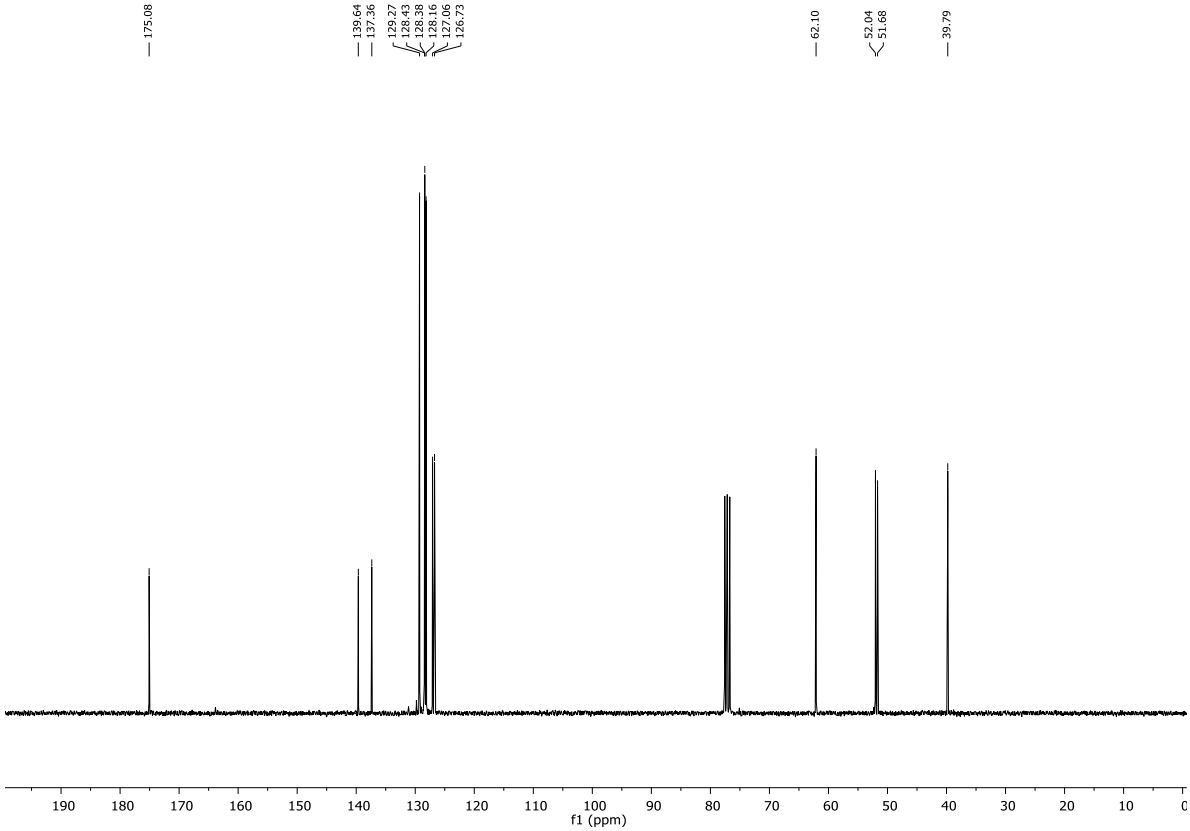
1-benzylpyrrolidine, 2i



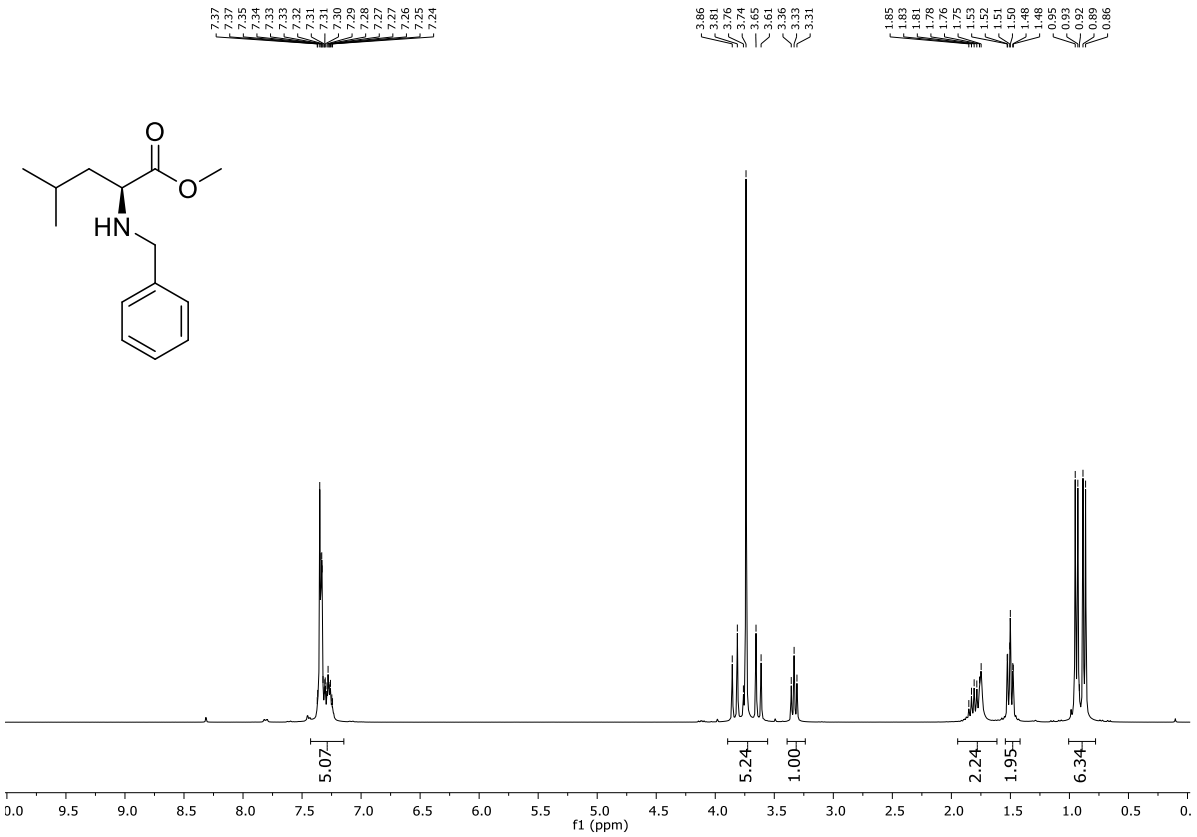


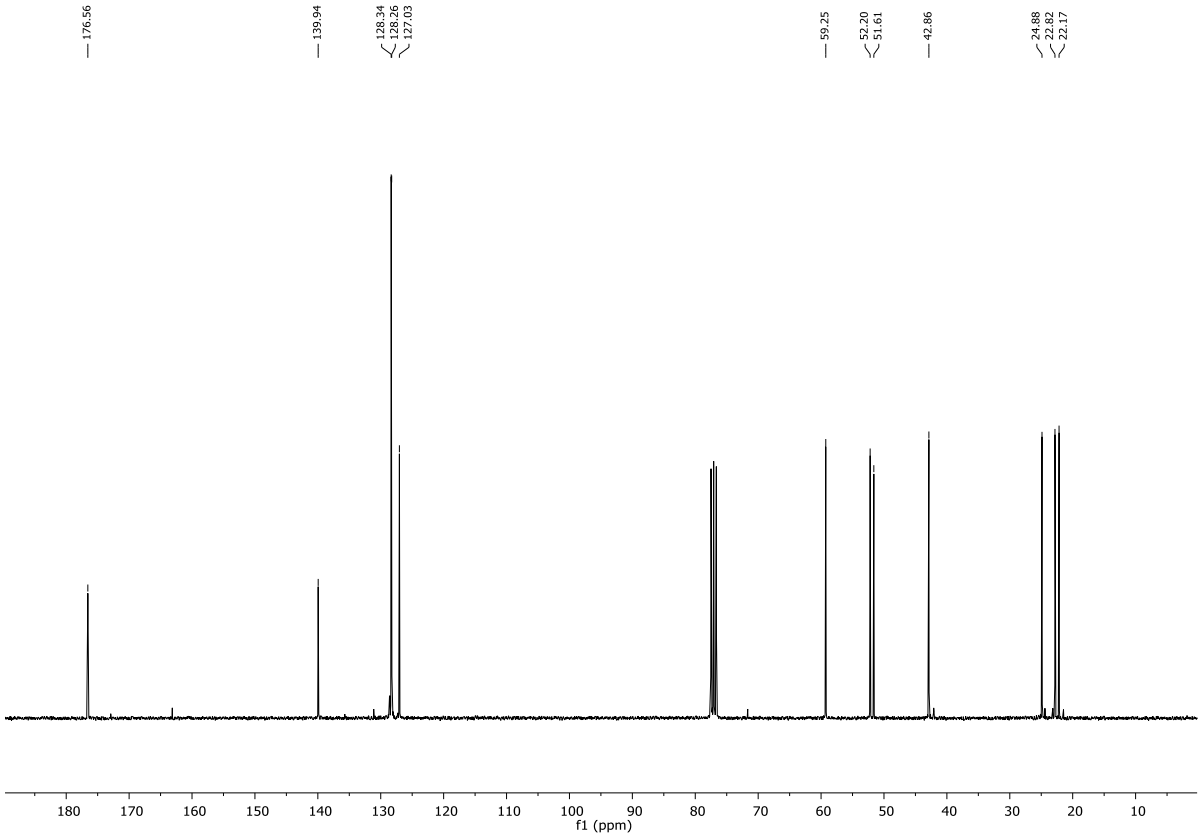
methyl benzyl-L-phenylalaninate, 3a



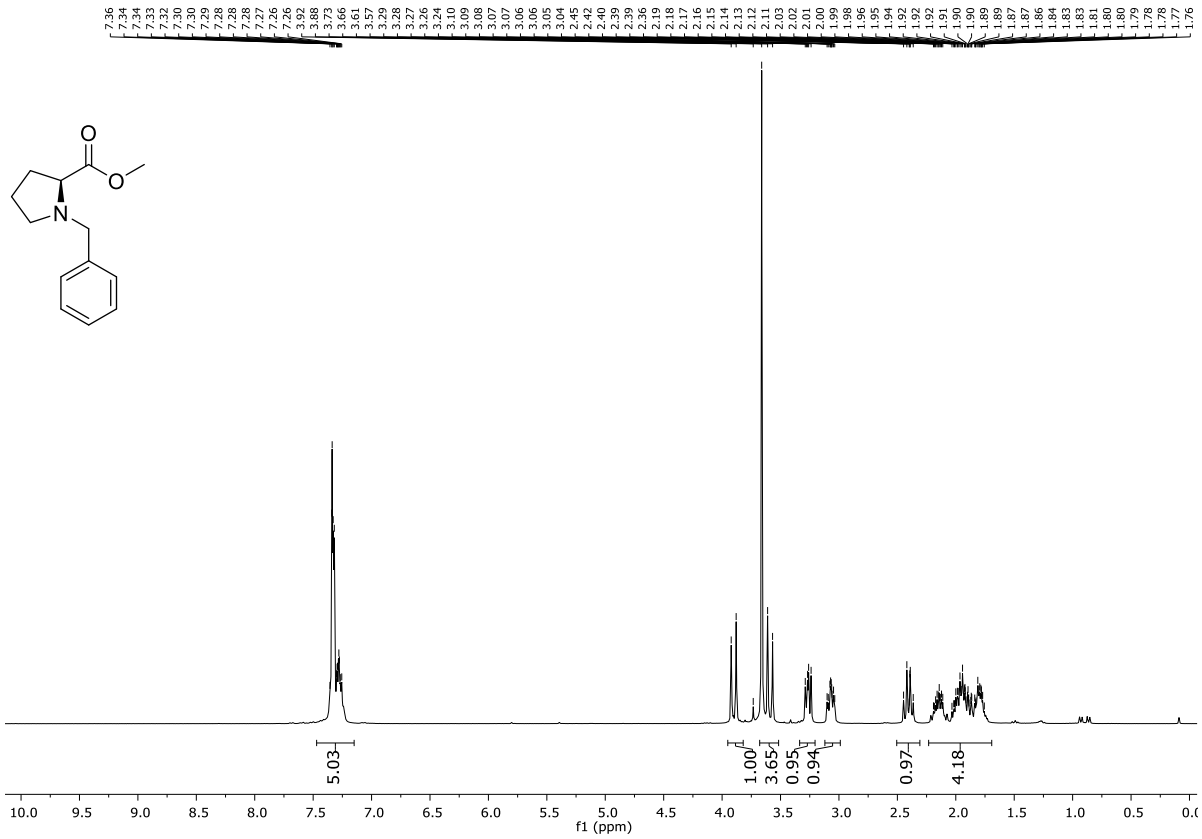


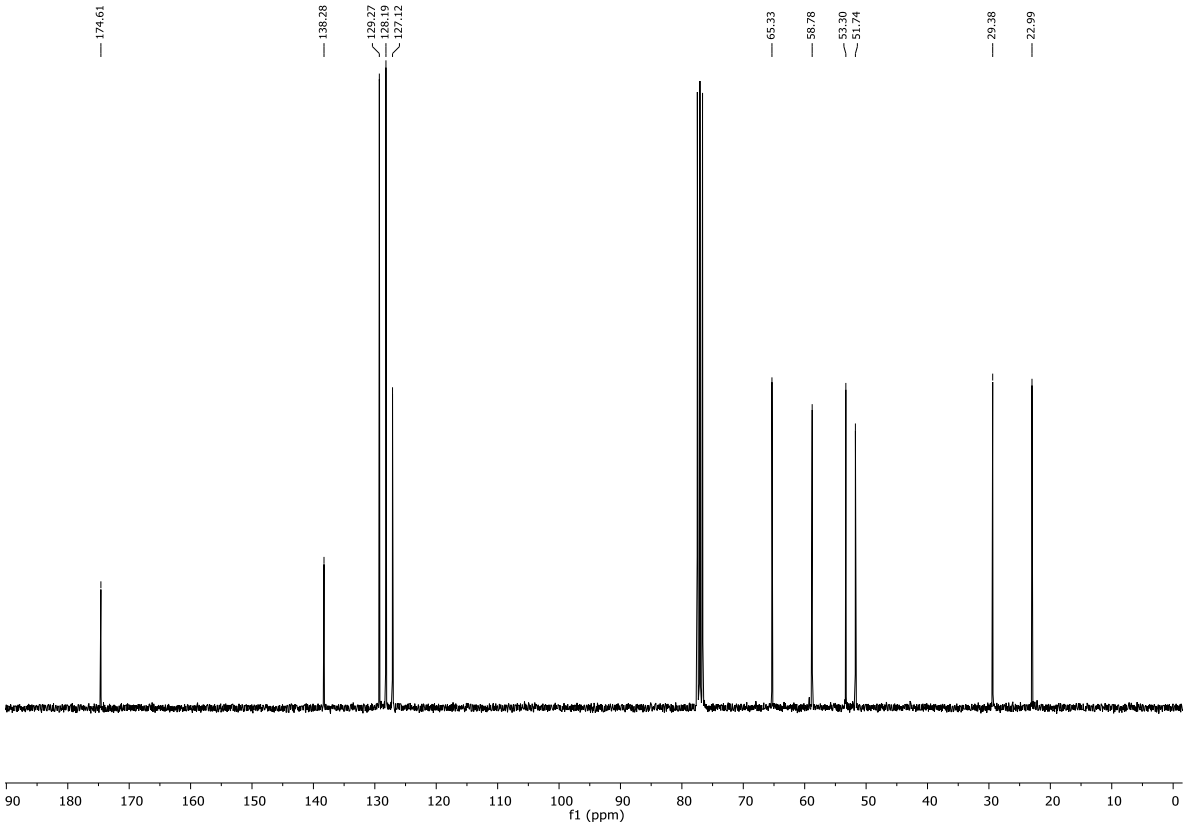
methyl benzyl-L-leucinate, 3b





methyl benzyl-L-prolinate, 3c





methyl benzyl-L-methioninate, 3d