Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Pyrrolizidines for Direct Air Capture and CO_2 Conversion

Jan M. Hanusch,[1] Isabel P. Kerschgens,[1] Florian Huber,[1] Markus Neuburger[2] and Karl Gademann*[1]

[1] J. M. Hanusch, Dr. I. P. Kerschgens, Dr. F. Huber and Prof. Dr. K. Gademann
Department of Chemistry, University of Zurich, Winterthurerstrasse 190, CH-8057 Zurich
E-mail: karl.gademann@uzh.ch

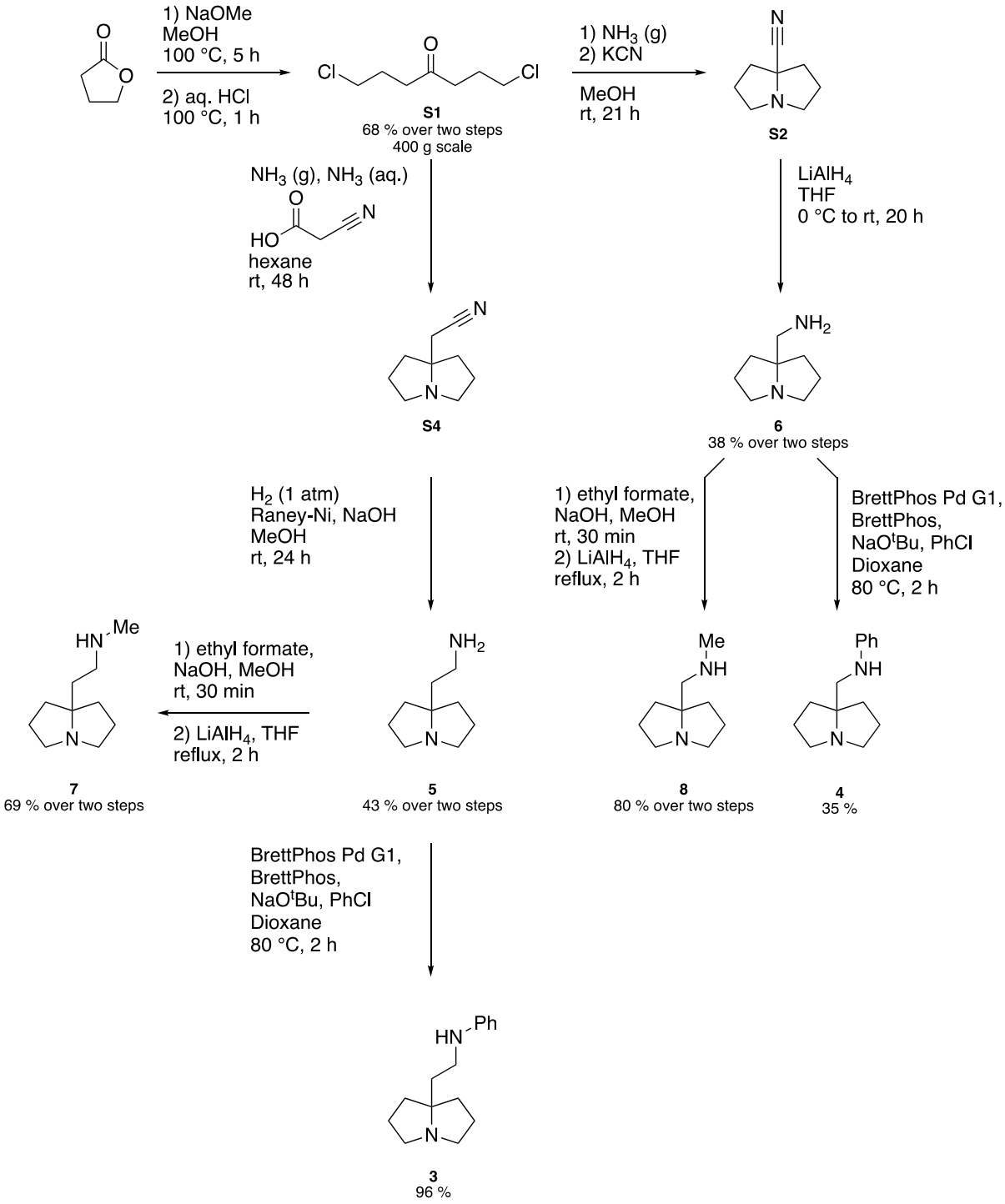
[2] Dr. M. Neuburger
Department of Chemistry, University of Basel, Mattenstrasse 24a, CH-4058 Basel

Table of Contents

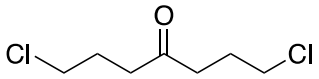
1. General Information, Materials and Equipment

All chemicals were purchased from Sigma-Aldrich, Acros, Alfa Aesar or Fluka and were used without further purification. Ru-MACHO®-BH was purchased from Strem. Reactions involving air sensitive compounds were performed under an inert gas atmosphere or in a glovebox (LABmaster) from MBraun. Solvents applied for chemical transformations were either puriss quality or HPLC grade solvents. For work-up and purification solvents were distilled from technical grade. All synthetic transformations have been monitored by either thin layer chromatography (TLC), ^{1}H-NMR spectroscopy or GC/EI-MS. TLC was performed on Merck silica gel 60 F_{254} plates (0.25 mm thickness) precoated with a fluorescent indicator. The developed plates were examined under UV light and stained with ceric ammonium molybdate, potassium permanganate or ninhydrin followed by heating. GC/EI-MS measurements were performed on a Finnigan Trace GC ultra from Thermo Electron Corporation with EI (electron ionization), Zebron ZB-5MS (30 m) column and Finnigan Trace DSQ. Concentration under reduced pressure was performed by rotary evaporation at 40 °C. Flash chromatography was performed using silica gel 60 (230-400 mesh) from Sigma-Aldrich with a forced flow eluent at 0.3-0.5 bar pressure. All ^{1}H and ^{13}C-NMR spectra were recorded using Bruker 300 MHz (^{1}H) or Bruker 400 MHz (^{1}H) & 101 MHz (^{13}C) or Bruker 500 MHz (^{1}H) & 126 MHz (^{13}C) spectrometers at room temperature. Chemical shifts (δ-values) are reported in ppm, spectra were calibrated related to solvents residual proton chemical shifts ($CHCl_3$, δ = 7.26; MeOH-d_3, δ = 3.31; DMSO-d_5, δ = 2.50) and solvents residual carbon chemical shifts ($CDCl_3$, δ = 77.16; MeOH-d_4, δ = 49.00; DMSO-d_6, δ = 39.52), multiplicity is reported as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet or unresolved and coupling constant *J* in Hz. IR spectra were recorded on a Varian 800 FT-IR ATR spectrophotometer. The absorptions are reported in cm^{-1}. All high-resolution mass spectra (HRMS-ESI) were recorded by Dr. Heinz Nadig at the University of Basel on a Bruker maXis 4G QTOF ESI mass spectrometer or by the mass spectrometry service at the University of Zürich on a Thermo QExactive mass spectrometer coupled to an Ultimate 3000 UHPLC system. Melting points (M.p.) were determined using a Büchi B-545 apparatus in open capillaries and are uncorrected. PH-values were recorded, using a Mettler Toledo InLab 409 electrode on a Mettler Toledo SevenEasy pH-meter. CO_2-uptake experiments were performed using Bronkhorst F-201CV-020-AGD-33-V (CO_2) or F-200CV-005-AGD-33-V (N_2) flow controller with a flow range from 0.18-9.0 mL/min. Nitrogen, Hydrogen and CO_2 were purchased from PanGas with a purity of 5.0 (N_2), 5.0 (H_2) and 5.3 (CO_2). For Direct Air Capture the in-house pressed air system was used, pre-dried with a 4Å molecular sieve column. To adjust the flow rate of air, the N_2 flow controller was used with a flow of 9 mL/min. For flue gas capture, a flow rate of 1 mL/min CO_2 was combined with 9 mL/min N_2 in a mixing chamber, affording a 10% CO_2 gas stream. Hydrogenations were conducted in a stainless steel autoclave from Premex Reactor AG. Aziridine **10** was synthesized following known literature procedures.[1-3] Solutions of HCl in organic solvents were prepared by addition of aq. HCl soln. (32 or 37 %) into conc. H_2SO_4. The resulting dry HCl gas was bubbled through the desired organic solvent. Concentrations were determined by titration with NaOH (1M) and a phenolphtalein indicator.[4]

2. Synthesis


1) NaOMe
MeOH
100 °C, 5 h
2) aq. HCl
100 °C, 1 h
S1
68 % over two steps
400 g scale
1) NH3 (g)
2) KCN
MeOH
rt, 21 h
S2
NH3 (g), NH3 (aq.)
hexane
rt, 48 h
LiAlH4
THF
0 °C to rt, 20 h
S4
6
38 % over two steps
H2 (1 atm)
Raney-Ni, NaOH
MeOH
rt, 24 h
1) ethyl formate,
NaOH, MeOH
rt, 30 min
2) LiAlH4, THF
reflux, 2 h
BrettPhos Pd G1,
BrettPhos,
NaOtBu, PhCl
Dioxane
80 °C, 2 h
1) ethyl formate,
NaOH, MeOH
rt, 30 min
2) LiAlH4, THF
reflux, 2 h
7
69 % over two steps
5
43 % over two steps
8
80 % over two steps
4
35 %
BrettPhos Pd G1,
BrettPhos,
NaOtBu, PhCl
Dioxane
80 °C, 2 h
3
96 %

1,7-Dichloroheptan-4-one (S1)



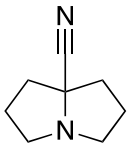
1,7-Dichloroheptan-4-one (**S1**) was synthesized by a modified literature procedure.[5] MeOH (180 mL) was cooled to 0 °C and Na (14.8 g, 0.64 mol, 1.1 eq.) was added in small portions. After Na was fully dissolved, γ-butyrolactone (90.0 mL, 1.17 mol, 2.0 eq.) was added, the reaction mixture was heated to 100 °C for 3 h, and then MeOH was removed from the reaction mixture with a Dean-Stark apparatus. Towards the end of the reaction, MeOH was removed under reduced pressure to yield the desired product as a highly viscous yellowish oil, which turned solid after cooling to rt.

The crude (*E*)-4,4',5,5'-tetrahydro-2'*H*,3*H*-[2,3'-bifuranylidene]-2'-one was heated to 100 °C. Hydrochloric acid (32 %, 270 mL) was slowly added *via* a dropping funnel, with concomitant formation of CO_2. After complete addition, the mixture was heated to reflux for 1 h at 100 °C and then cooled to rt. The reaction mixture was diluted with H_2O (250 mL) until all the salts were dissolved, and the mixture was extracted with Et_2O (3x 150 mL). The combined organic layers were washed with H_2O (200 mL) and sat. aq. $NaHCO_3$ soln. (3x 150 mL). The combined aq. layers were back-extracted with Et_2O (100 mL) and the combined organic layers were dried over $MgSO_4$. Filtration and evaporation of the solvent afforded the desired crude product (71.8 g, 392 mmol, 68 %) as a green liquid. In general, the quality of heptanone was sufficient to be used in the next steps without further purification, otherwise it was purified by column chromatography (Et_2O/Pentane, 1:4). Analytical data matched those reported in the literature.[6]

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 3.58 (t, *J* = 6.4 Hz, 4H), 2.64 (t, *J* = 7.2 Hz, 4H), 2.05 (m, 4H) ppm.

^{13}C-NMR (101 MHz, $CDCl_3$): δ = 208.6, 44.5, 39.6, 26.4 ppm.

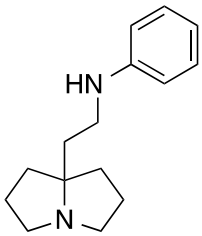
(1-Azabicyclo[3.3.0]octane-5-yl)carbonitrile (S2)



1,7-Dichloroheptan-4-one (**S1**, 10.5 g, 57.4 mmol, 1.0 eq.) was dissolved in MeOH (100 mL) and NH_3 gas was introduced for 1.5 h at rt and the mixture was stirred for additional 3 h. KCN (7.71 g, 118 mmol, 2.0 eq.) was added in one portion and the mixture was stirred for 17 h at rt. The solvent was evaporated and an aq. NaOH soln. (20 %, 150 mL) was added to the solid residue. The product was extracted with CH_2Cl_2 (3x, total 350 mL) and washed with brine (2x, total 300 mL). The combined organic layers were dried over Na_2SO_4. Filtration and removal of the solvent under reduced pressure afforded the crude product (8.08 g) as a slightly yellowish oil, which was used without further purification. Analytical data matched those reported in the literature.[7]

^{1}H-NMR (250 MHz, $CDCl_3$): δ = 3.25-3.17 (m, 2H), 2.62-2.53 (m, 2H), 2.39-2.30 (m, 2H), 2.12-1.86 (m, 6H) ppm.

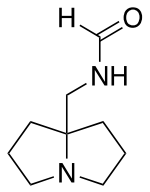
***N*-(2-(tetrahydro-1*H*-pyrrolizin-7a(5*H*)-yl)ethyl)aniline (3)**



According to the procedure of Buchwald *et al.*,[8-9] an oven dried Schlenk tube was charged with BrettPhos Pd G1 (35.0 mg, 43.8 µmol, 1 mol %), BrettPhos (24.0 mg, 44.7 µmol, 1 mol %), and NaO*t*Bu (838 mg, 8.72 mmol, 2.0 eq.), and was three times evacuated and backfilled with argon. Then [2-(1-azabicyclo[3.3.0]octane-5-yl)ethyl]amine (**5**, 803 mg, 5.21 mmol, 1.2 eq.) was added with dioxane (15 mL). Chlorobenzene (0.45 mL, 4.44 mmol, 1.0 eq.) was added and the mixture was heated to 80 °C for 1.5 h until GC/EI-MS showed full conversion. After cooling to rt, EtOAc (10 mL) was added and the mixture was transferred into a separation funnel and washed with H_2O (15 mL). The aq. layer was back extracted with EtOAc and the combined organic layers were dried over Na_2SO_4 resulting in the crude product. This was treated with HCl•Et_2O (18 %, 15 mL) and washed with Et_2O. The resulting solid was recrystallized from EtOH/*i*PrOH (3:1, 15 mL) and after cooling to rt treated with Et_2O. The resulting solid was washed with Et_2O, leading to the HCl-salt of the desired product. This was suspended in Et_2O and NH_3 gas was introduced for 1 h. After stirring for 4 h the solid was

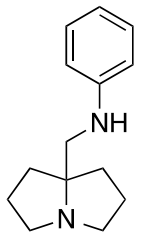
removed by filtration. Subsequent removing of the solvent afforded the desired product (951 mg, 4.13 mmol, 96 %) as yellow oil.
^{1}H-NMR (400 MHz, CD_3OD): δ = 7.12-7.08 (m, 2H), 6.64-6.59 (m, 3H), 3.12-3.08 (m, 2H), 3.00-2.94 (m, 2H), 2.65-2.60 (m, 2H), 1.88-1.63 (m, 10H) ppm.
^{13}C-NMR (101 MHz, CD_3OD): δ = 150.3, 130.0, 118.1, 114.2, 74.0, 56.0, 42.2, 41.7, 38.3, 25.6 ppm.
FTIR *v* = 3255, 3021, 2951, 2864, 1601, 1506, 1319, 1289, 1179, 1122, 864, 746, 690 cm^{-1}.
HR-MS (ESI): $C_{15}H_{23}N_2^+$ $[M+H]^+$: calculated: 231.1856 found: 231.1859.

***N*-((Tetrahydro-1*H*-pyrrolizin-7a(5*H*)-yl)methyl)formamide (S3)**



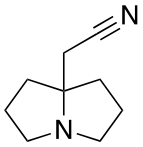
To a solution of 5-aminomethyl-1-azabicyclo[3.3.0]octane (**6**, 377 mg, 2.69 mmol, 1.0 eq.) and NaOH (244 mg, 6.10 mmol, 2.0 eq.) in MeOH (3.5 mL), ethyl formate (1.1 mL, 13.5 mmol, 10 eq.) was added and the mixture was stirred at rt for 30 min, until GC/EI-MS showed full conversion. The solvent was removed under reduced pressure, followed by addition of Et_2O (15 mL) to the residue and stirring for 10 min. Filtration and subsequent removal of the solvent afforded the desired product as a mixture of isomers (428 mg, 2.54 mmol, 95 %) and as a colorless oil. Two rotamers in a ratio of around 4:1 were detected by ^{1}H-NMR spectroscopy.
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.22 (m, 0.8H), 8.06 (d, *J* = 12.2 Hz, 0.2H), 6.15 (br. s, 0.8H), 5.95 (br. s, 0.2H), 3.20 (d, *J* = 6.6 Hz, 1.6H), 3.02 (d, *J* = 6.5 Hz, 0.4H), 2.99-2.93 (m, 2H), 2.65-2.58 (m, 2H), 1.84-1.58 (m, 8H) ppm.
^{13}C-NMR (101 MHz, $CDCl_3$): δ = 161.5, 72.8, 55.8, 45.8, 36.4, 25.2 ppm.
FTIR *v* = 3291, 3058, 2955, 2867, 2361, 1669, 1539, 1455, 1384, 1239, 1091, 758, 698 cm^{-1}.
HR-MS (ESI): $C_9H_{17}N_2O^+$ $[M+H]^+$: calculated: 169.1335 found: 169.1338.

***N*-((Tetrahydro-1*H*-pyrrolizin-7a(5*H*)-yl)-methyl)aniline (4)**



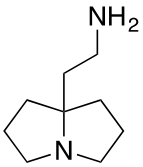
According to the procedure of Buchwald *et al.*,[8-9] an oven-dried flask was charged with NaO^{t}Bu (13.3 mg, 139 µmol, 2.0 eq.), BrettPhos Pd G1 (2.60 mg, 3.25 µmol, 5 mol %), BrettPhos ligand (1.99 mg, 3.71 µmol, 6 mol %) and three times evacuated and backfilled with Ar. 5-Aminomethyl-1-azabicyclo[3.3.0]octane (**6**, 10.8 mg, 76.0 µmol, 1.2 eq.), dioxane (0.7 mL) and chlorobenzene (0.6 µL, 63.0 µmol, 1.0 eq.) were added successively. The reaction mixture was heated to 80 °C for 2 h until GC/EI-MS showed full consumption of the chlorobenzene. After cooling to rt, the reaction mixture was diluted with EtOAc (1.5 mL), washed with H_2O (0.5 mL) and the aq. layer was back extracted with EtOAc (3x 1.5 mL). The combined organic layers were dried over Na_2SO_4, filtered and concentrated under reduced pressure. The crude residue was treated with HCl•*i*PrOH (21 %, 1.0 mL) and the resulting hydrochloride salt was recrystallized from EtOH/*i*PrOH (7:1, 0.1 mL) and treated with Et_2O (0.5 mL). The resulting crystals were filtered off and resuspended in Et_2O (5 mL). NH_3 gas was bubbled through the reaction mixture until saturation occurred and the suspension was stirred for 5 h at rt. Filtration and removal of the solvent afforded the desired product (4.3 mg, 0.02 mmol, 34 %) as colorless oil.
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.18-7.14 (m, 2H), 6.69-6.65 (m, 1H), 6.64-6.62 (m, 2H), 4.15 (br. s, 1H), 3.06-3.00 (m, 2H), 2.55 (d, *J* = 5.6 Hz, 2H), 2.68-2.62 (m, 2H), 1.90-1.71 (m, 8H), 1.65-1.60 (m, 2H) ppm.
^{13}C-NMR (101 MHz, $CDCl_3$): δ = 149.4, 129.3, 117.1, 113.1, 73.2, 55.8, 52.4, 36.9, 25.3 ppm.
FTIR *v* = 3360, 2953, 2865, 2357, 1604, 1504, 1315, 1260 cm^{-1}.
HR-MS (ESI): $C_{14}H_{21}N_2^+$ $[M+H]^+$: calculated: 217.1699 found: 217.1703.

(1-Azabicyclo[3.3.0]octane-5-yl)acetonitrile (S4)



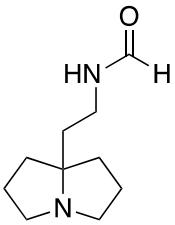
1,7-Dichloroheptan-4-one (**S1**, 30.0 g, 164 mmol, 1.0 eq.) was dissolved in aq. NH_3 soln. (25 %, 97 mL) and cyanoacetic acid (41.8 g, 492 mmol, 3.0 eq.) was added slowly. NH_3 gas was bubbled through the reaction mixture for 1 h before hexane (30 mL) was added and the mixture was stirred for 48 h at rt. After GC/EI-MS indicated full conversion, the aq. NH_3 soln. was removed under reduced pressure and aq. NaOH soln. (20 %, 200 mL) was added to the solid residue. The aq. layer was extracted with EtOAc (3x 200 mL) and the combined organic layers were dried over Na_2SO_4. Filtration and removal of the solvent afforded the crude product (21.5 g) as brown oil. After vacuum destillation (9-10 mbar, 95-100 °C) the product (11.2 g, 74.6 mmol, 45 %) was received as a colourless oil. Analytical data matched those reported in the literature.[9]
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 3.13-3.08 (m, 2H), 2.63-2.57 (m, 2H), 2.41 (s, 2H), 1.94-1.71 (m, 8H) ppm.

[2-(1-Azabicyclo[3.3.0]octane-5-yl)ethyl]amine (5)



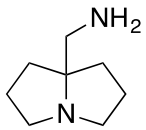
Lithium aluminium hydride (5.64 g, 149 mmol, 2.0 eq.) was dissolved in THF (300 mL) and cooled to 0 °C. (1-azabicyclo[3.3.0]octane-5-yl)acetonitrile (**S4**, 11.2 g, 74.6 mmol, 1.0 eq.) was dissolved in THF (60 mL) and added slowly to the reaction mixture. The reaction mixture was refluxed for 4 h. After the reaction has been cooled to 0 °C, water (12 mL) was added dropwise and the mixture was refluxed for 1 h. The reaction was filtered and washed with additional THF (300 mL). The combined organic layers were dried over Na_2SO_4 and the solvent was removed in vacuum. The product (10.9 g, 70.7 mmol, 95 %) was received as a colorless oil. Analytical data matched those reported in the literature.[9]
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 3.01-2.95 (m, 2H), 2.75-2.71 (m, 2H), 2.60-2.54 (m, 2H), 1.78-1.48 (m, 10H), 1.26 (br. s, 2H) ppm.
^{13}C-NMR (101 MHz, $CDCl_3$): δ = 72.3, 55.5, 46.5, 39.3, 37.9, 25.1 ppm.

***N*-(2-(Tetrahydro-1*H*-pyrrolizin-7a(5*H*)-yl)ethyl)formamide (S5)**



To a solution of [2-(1-azabicyclo[3.3.0]octane-5-yl)ethyl]amine (**5**, 741 mg, 4.80 mmol, 1.0 eq.) and NaOH (401 mg, 10.0 mmol, 2.0 eq.) in MeOH (5.0 mL) was added ethyl formate (1.90 mL, 23.5 mmol, 5.0 eq.) and the reaction mixture was stirred for 30 min until GC/EI-MS indicated full conversion. The solvent was removed under reduced pressure and the resulting residue was suspended in Et_2O and stirred for 1 h. Filtration and subsequent removal of the solvent afforded the product (764 mg, 93 %) as colorless oil.
^{1}H-NMR (400 MHz, $CDCl_3$): δ=8.43 (br. s, 1H), 8.11 (s, 1H), 3.42-3.38 (m, 2H), 3.00-2.94 (m, 2H), 2.62-2.56 (m, 2H), 1.82-1.58 (m, 10H) ppm.
^{13}C-NMR (101 MHz, $CDCl_3$): δ = 161.1, 73.4, 55.4, 38.3, 37.9, 35.6, 25.0 ppm.
FTIR *v* = 3463, 3276, 3058, 2953, 2867, 2357, 2137, 1667, 1540, 1457, 1384, 1244, 1088, 926, 833, 717 cm^{-1}.
HR-MS (ESI): $C_{10}H_{19}N_2O^+$ $[M+H]^+$: calculated: 183.1492 found: 183.1491.

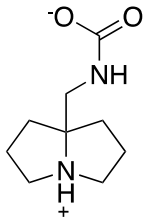
5-Aminomethyl-1-azabicyclo[3.3.0]octane (6)



An oven-dried flask was charged with $LiAlH_4$ (4.80 g, 126 mmol, 2.0 eq.) and was three times evacuated and backfilled with nitrogen. Anhydrous THF (100 mL) was added and the reaction mixture was cooled to 0 °C. The crude mixture of (1-azabicyclo[3.3.0]octane-5-yl)carbonitrile (**S2**, 8.08 g) was slowly added in dry THF (20 mL) to the reaction mixture. The suspension was allowed to warm to rt and stirred for 20 h. The reaction mixture was cooled to 0 °C, diluted with THF (100 mL) and quenched with slow addition of H_2O (10 mL). The suspension was heated to reflux for 1 h. After cooling to rt, the slurry was filtered and the organic layer was dried with Na_2SO_4. Filtration and evaporation of the solvent affords crude product (5.72 g) as colorless oil. The crude product was dissolved in Et_2O and HCl•Et_2O (2.5M, 20 mL) was added dropwise to precipitate the corresponding dihydrochloride salt. The salt was washed with Et_2O and subsequently triturated with EtOH/*i*PrOH (4:1, 15 mL) at 80°C. After cooling to rt, the salt was dried and suspended in Et_2O. NH_3 gas was introduced for 1 h and stirred for another 1 h to liberate the free base. Filtration and evaporation of the solvent afforded pure product (3.03 g, 57.3 mmol, 38 % over 2 steps) as a colorless oil. Analytical data matched those reported in the literature.[7]
^{1}H-NMR (400 MHz, CD_3OD): δ = 2.98-2.92 (m, 2H), 2.68-2.63 (m, 2H), 2.52 (s, 2H), 1.89-1.57 (m, 8H) ppm.
^{13}C-NMR (101 MHz, CD_3OD): δ = 76.1, 55.4, 51.3, 36.9, 25.6 ppm.

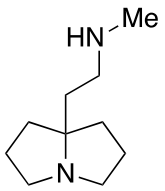
General procedure for carbamate generation
The pure amine was dissolved in MeOH or MeOH-d_4 and CO_2 was bubbled through the solution until dryness. This procedure was repeated 2-3 times. The semi solid residue can optionally be dried under reduced pressure (20 mbar, rt) to remove residual MeOH.

((Hexahydropyrrolizin-4-ium-7a(1*H*)-yl)methyl)carbamate (S6)



Pure 5-aminomethyl-1-azabicyclo[3.3.0]octane (**6**, 15 mg) was dissolved in CD_3OD (1 mL) and CO_2 was bubbled through the solution until dryness. The residue was then fully dried under reduced pressure. The resulting white solid was then analyzed by standard analytical methods.
^{1}H-NMR (400 MHz, CD_3OD): δ = 3.50-3.43 (m, 2H), 3.28 (s, 2H), 3.12-3.06 (m, 2H), 2.15-2.04 (m, 6H), 1.93-1.86 (m, 2H) ppm.
^{13}C-NMR (101 MHz, CD_3OD): δ = 166.8, 126.3, 84.2, 55.5, 35.5, 25.6 ppm.
FTIR *v* = 3373, 2974, 2361, 2172, 1589, 1462, 1411, 1325, 1165, 1010, 687, 631 cm^{-1}.
M.p. = 85-91°C.

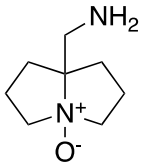
***N*-Methyl-2(tetrahydro-1*H*-pyrrolizin-7a(5*H*)-yl)ethyl-1-amine (7)**



An oven-dried two-neck flask was charged with $LiAlH_4$ (154 mg, 4.06 mmol, 2.0 eq.) and was evacuated and backfilled with argon for three times. After cooling to 0 °C, anhydrous THF (5 mL) was added followed by dropwise addition of a solution *N*-(2-(tetrahydro-1*H*-pyrrolizin-7a(5*H*)-yl)ethyl)formamide (**S5**, 370 mg, 2.03 mmol, 1.0 eq.) in anhydrous THF (14 mL). The reaction mixture was refluxed for 2 h. After cooling to 0 °C, remaining $LiAlH_4$ was quenched by the addition of H_2O (1 mL/g $LiAlH_4$), aq. NaOH soln. (15 %, 1 mL/g $LiAlH_4$) and H_2O (3 mL/g $LiAlH_4$). The resulting slurry was

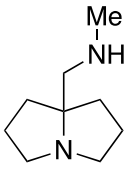
suspended in Et_2O (15 mL), Na_2SO_4 was added and the mixture was stirred for 15 min. Filtration over Celite® and removal of the solvent afforded the crude product (348 mg, quant.) as a yellowish oil. This was treated with HCl•Et_2O (18 %, 8 mL) and the dihydrochloric salt was recrystallized from EtOH/*i*PrOH (4:1, 11 mL) leading to the pure HCl-salt of the product (413 mg, 84 %). The HCl-salt was suspended in Et_2O and NH_3 gas was introduced for 1 h and the mixture was stirred at rt. Filtration and subsequent removal of the solvent afforded the pure product (254 mg, 1.51 mmol, 74 %) as colorless oil.
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 3.00-2.95 (m, 2H), 2.61-2.53 (m, 4H), 2.42 (s, 3H), 1.78-1.49 (m, 10H) ppm.
^{13}C-NMR (101 MHz, $CDCl_3$): δ = 77.4, 55.5, 49.3, 42.3, 37.8, 36.9, 25.1 ppm.
FTIR *v* = 3287, 2950, 2865, 2362, 1550, 1478, 1382, 1308, 1261, 1163, 1059, 929, 814, 706 cm^{-1}.
HR-MS (ESI): $C_{10}H_{21}N_2^+$ $[M+H]^+$: calculated: 169.1700 found: 169.1702.

7a-(Aminomethyl)hexahydropyrrolizidine 4(1*H*)-oxide (S7)



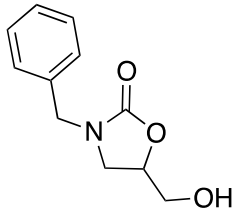
According to a procedure of Rosenau *et al*.,[11] amine **6** (500 mg, 3.57 mmol) was cooled to 0 °C and H_2O_2 (30 %, 675 μL) was added and the mixture stirred at rt for 22 h. Remaining peroxide was quenched by addition of MnO_2 (326 mg, 3.75 mmol). The solids were filtered off and washed with EtOH (20 mL). Solvent was evaporated and the oily residue was diluted with MeCN (5 mL) and Et_2O (10 mL). HCl•Et_2O (2.5M, 25 mL) was added dropwise and the resulting solid was washed with Et_2O. The hydrochloric salt was triturated with *i*PrOH/EtOH (1:4, 5 mL) and the salt was suspended in Et_2O and NH_3 gas was introduced. Filtration and evaporation afforded the desired product (367 mg, 66%) as brownish oil.
^{1}H-NMR (400 MHz, CD_3OD): δ = 3.88-3.82 (m, 2H), 3.60-3.54 (m, 2H), 3.41 (s, 2H), 2.33-2.20 (m, 4H), 2.16-2.05 (m, 4H) ppm.
^{13}C-NMR (101 MHz, CD_3OD): δ = 82.4, 69.8, 44.6, 34.6, 22.4 ppm.
FTIR *v* = 3395, 2969, 2328, 2239, 1457, 1062, 978, 551, 506 cm^{-1}.
HR-MS (ESI): $C_8H_{17}N_2O^+$ $[M+H]^+$: calculated: 157.1335 found: 157.1336.

***N*-Methyl-1-(tetrahydro-1*H*-pyrrolizin-7a(5*H*)-yl)methanamine (8)**



An oven-dried two-neck flask was charged with $LiAlH_4$ (195 mg, 5.14 mmol, 2.0 eq.) and was evacuated and backfilled with argon three times. After cooling to 0 °C, anhydrous THF (5.0 mL) was added and *N*-((tetrahydro-1*H*-pyrrolizin-7a(5*H*)-yl)methyl)formamide (**S3**, 428 mg, 2.54 mmol, 1.0 eq.) in anhydrous THF (10 mL) was added dropwise. The reaction mixture was heated to reflux for 2 h until ^{1}H-NMR analysis indicated full consumption of the formamide. After cooling to 0 °C, remaining $LiAlH_4$ was quenched by the addition of H_2O (1 mL/g $LiAlH_4$), aq. NaOH soln. (15 %, 1 mL/g $LiAlH_4$) and H_2O (3 mL/g $LiAlH_4$). The resulting slurry was suspended with Et_2O (10 mL) and stirred for 5 min, treated with Na_2SO_4 and the suspension was stirred for 15 min. Filtration over Celite® and removal of the solvent afforded the desired product (330 mg, 2.14 mmol, 84 %) as a colorless oil.
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 2.99-2.93 (m, 2H), 2.62 (m, 2H), 2.43 (s, 2H), 2.43 (s, 3H), 1.88-1.50 (m, 8H), 1.26 (br. s, 1H) ppm.
^{13}C-NMR (101 MHz, $CDCl_3$): δ = 73.1, 62.7, 55.9, 37.4, 37.2, 25.3 ppm.
FTIR *v* = 3320, 2949, 2865, 2785, 2687, 2361, 1685, 1457, 1319, 1262, 1136, 1095, 1024, 904, 794, 700, 633 cm^{-1}.
HR-MS (ESI): $C_9H_{19}N_2^+$ $[M+H]^+$: calculated: 155.1543 found: 155.1544.

3-Benzyl-5-(hydroxymethyl)oxazolidin-2-one (11)



An oven-dried Schlenk-tube was filled with aziridine **10** (30.0 mg, 184 µmol, 1.0 eq.), amine **7** (15.5 mg, 92.0 µmol, 0.5 eq.) and dimethylsulfoxide (0.92 mL). The tube was degassed and filled with a carbon dioxide atmosphere for three times. The reaction was heated to 160 °C for 15 h under a carbon dioxide atmosphere. After cooling to rt the mixture was treated with H_2O (15 mL) and extracted with CH_2Cl_2 (3 x 20 mL). The combined organic extracts were washed with brine (20 mL), dried over sodium sulfate and the solvent was removed in vacuum. After flash chromatography on silica (EtOAc/Pentane, 7:3) compound **11** was obtained (30.2 mg, 146 µmol, 79 %). Analytical data matched those reported in the literature.[10]

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.31-7.19 (m, 5H), 4.54-4.46 (m, 1H), 4.43-4.26 (m, 2H), 3.75 (dd, *J* = 12.5, 3.3, 1H), 3.53 (dd, *J* = 12.5, 4.4, 1H), 3.39-3.25 (m, 2H), 3.03 (s, 1H).

^{13}C-NMR (400 MHz, $CDCl_3$): δ = δ 158.3, 135.7, 128.9, 128.1, 128.1, 73.8, 63.0, 48.4, 45.3.

3. CO_2-Uptake Measurements

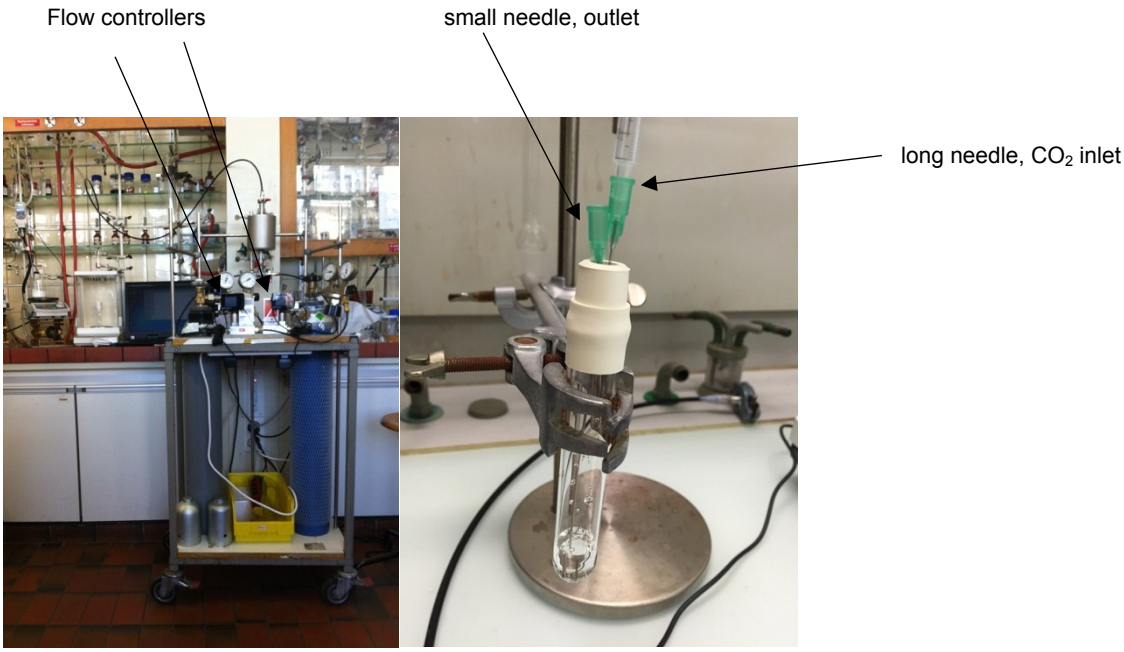
3.1 Procedure

Uptake:

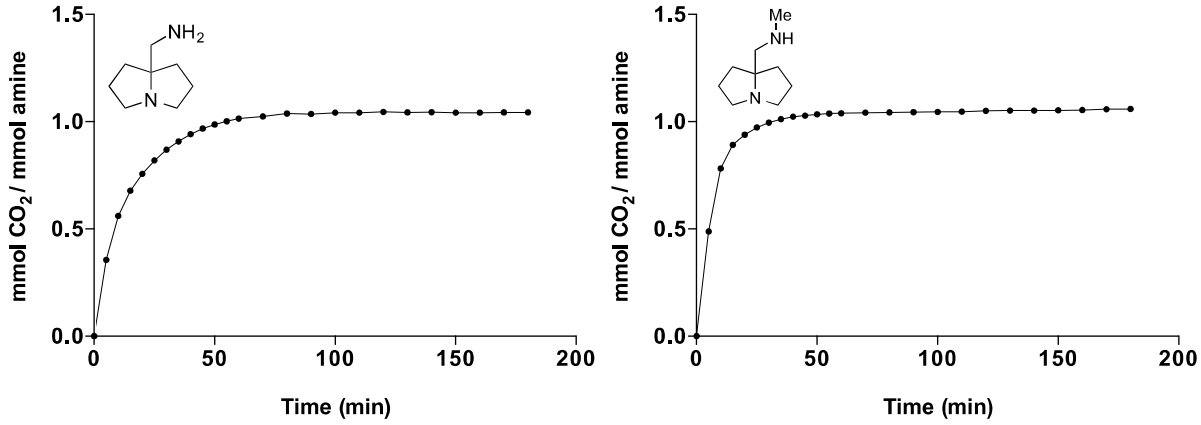
An oven dried vial was allowed to cool to rt and the weight of the empty vial was recorded. Then, amine (3 mmol) and PEG_{200} (12 mmol) were added to the vial and carefully mixed. The vial was equipped with a septum and two needles for CO_2 inlet and outlet (see picture below). Then, the atmosphere of the headspace in the vial was exchanged with CO_2 for 2-3 min. Afterwards the weight of the vial was recorded and the CO_2-capture experiment was started by bubbling CO_2 through the solution. A flow rate of 9.0 mL CO_2/min was applied and the weight was recorded every 5 min. After 1 h the weight was measured every 10 min.

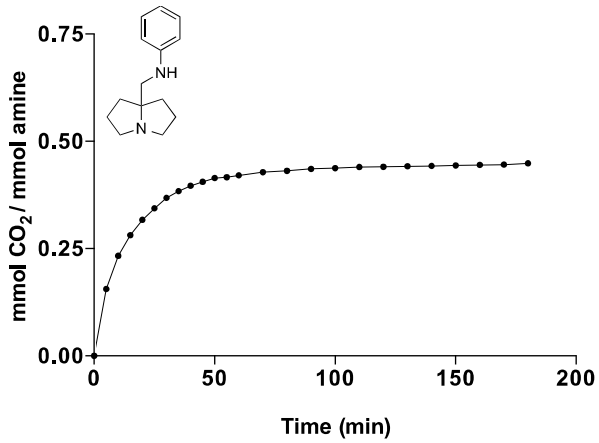
Release:

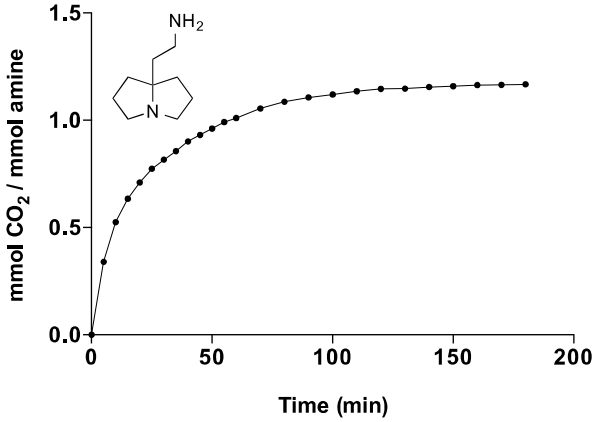
When the desired saturation level was reached, the headspace was exchanged with N_2 for 2-3 min and the weight was recorded. For the release measurements, the vial was placed in a 65 °C hot water bath and N_2 was bubbled through the solution with a flow of 9.0 mL N_2/min. The weight decrease was recorded every 10 min.

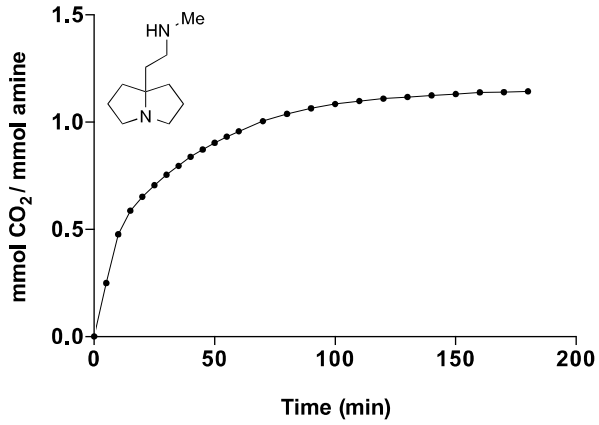


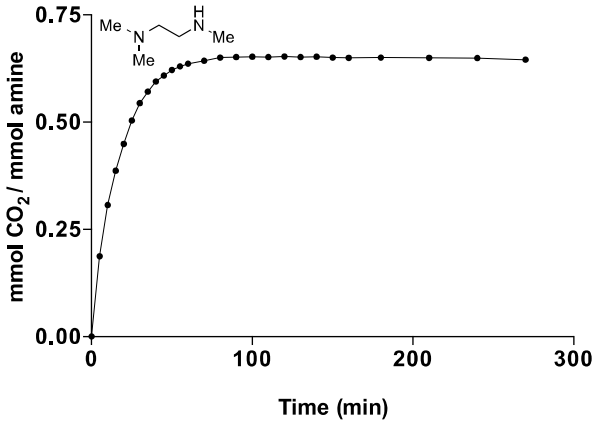
3.2 Saturation Curves

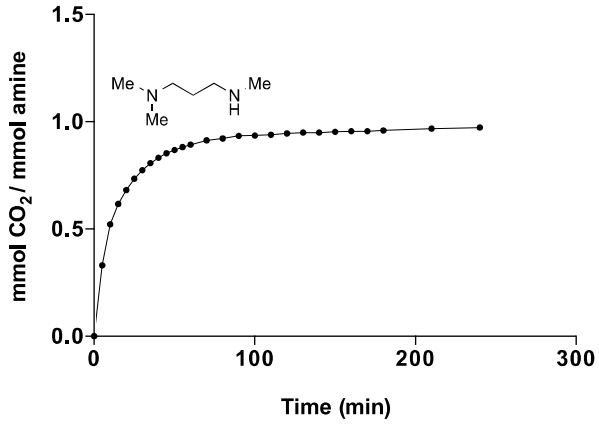


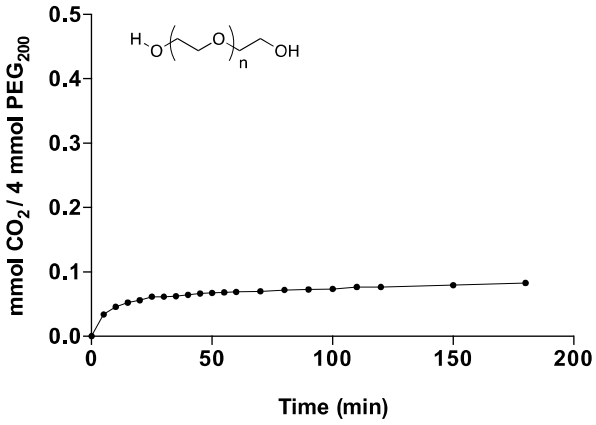












3.3 Non-linear Fit

For the calculation of the $t_{90\%}$ values, nonlinear regression (curve fit) with Prism6 software was used. Therefore, all the saturation curves were fitted with one site – specific binding to receive a function [Y=Bmax*X/(Kd+X)] describing the curve. This function was then used to calculate the time (X) until 90%, 70% and 50% of saturation for each absorbent.

Substrate	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**
One site -- Specific binding								
Best-fit values								
Bmax	0.8086	0.7268	0.6822	0.4807	1.282	1.135	1.278	1.105
Kd	17.25	11.4	50.94	9.772	15.82	9.471	19.58	4.362
Std. Error								
Bmax	0.008569	0.01062	0.02094	0.003042	0.007764	0.009704	0.009323	0.009794
Kd	0.7807	0.879	4.162	0.3621	0.4401	0.4817	0.5914	0.3493
95% Confidence Intervals								
Bmax	0.7908 to 0.8264	0.7047 to 0.7488	0.6389 to 0.7255	0.4744 to 0.487	1.266 to 1.298	1.115 to 1.155	1.259 to 1.297	1.085 to 1.125
Kd	15.62 to 18.87	9.580 to 13.23	42.33 to 59.55	9.023 to 10.52	14.91 to 16.73	8.474 to 10.47	18.35 to 20.8	3.639 to 5.085
Goodness of Fit								
Degrees of Freedom	21	22	23	23	23	23	23	23
R square	0.9938	0.9822	0.985	0.9955	0.9973	0.9917	0.997	0.9842
Absolute Sum of Squares	0.005256	0.01189	0.00937	0.001255	0.005523	0.01306	0.006483	0.02071
Sy.x	0.01582	0.02325	0.02018	0.007388	0.0155	0.02383	0.01679	0.03001
Number of points Analyzed	23	24	25	25	25	25	25	25

3.4 $T_{50\%}$ and $T_{70\%}$ values

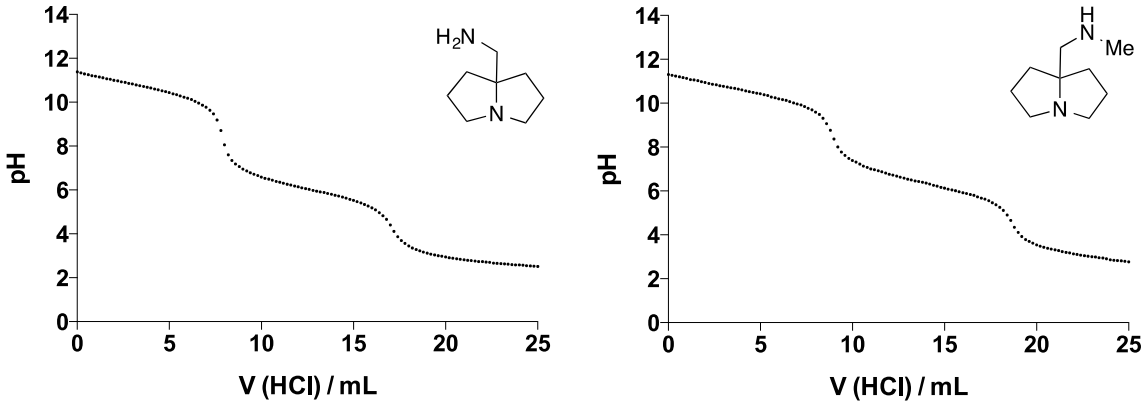
Absorbent	100% Uptake[a]	90% Uptake[a]	70% Uptake[a]	50% Uptake[a]	$T_{90\%}$ [min]	$T_{70\%}$ [min]	$T_{50\%}$ [min]
1	0.67	0.603	0.469	0.335	87	24	12
2	0.65	0.585	0.455	0.325	47	19	9
3	0.42	0.378	0.294	0.21	63	39	23
4	0.45	0.405	0.315	0.225	52	19	9
5	1.17	1.053	0.819	0.585	73	28	13
6	1.04	0.936	0.728	0.52	45	17	8
7	1.14	1.026	0.798	0.57	80	33	16
8	1.06	0.954	0.742	0.53	28	9	4

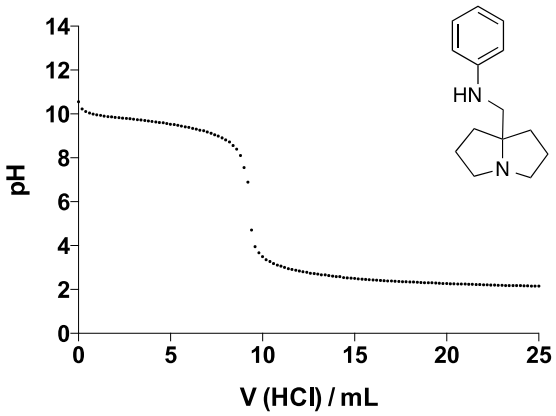
[a] Uptake values refer to mmol CO_2 / mmol amine ratios.

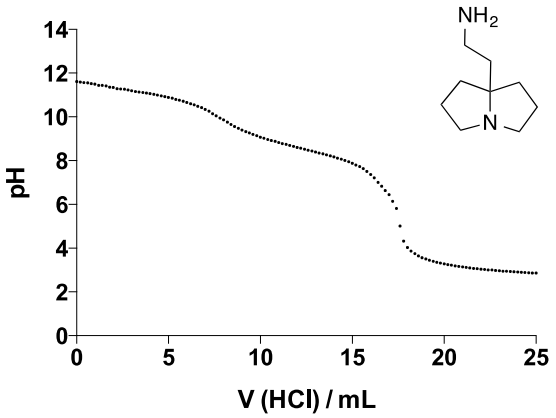
4. Analysis

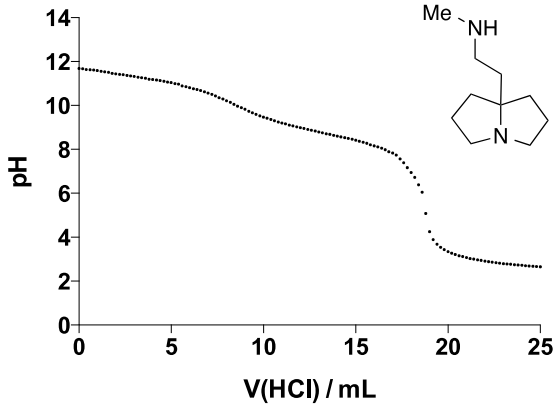
4.1 Titration Curves

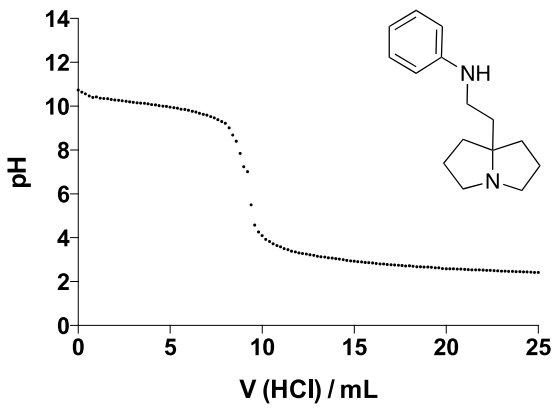
An aq. soln. of diamine (0.01M) was prepared by dissolving diamine (0.1 mmol) in H_2O (10 mL) and added to a flask equipped with a stirring bar. A pH-electrode (calibrated before each experiment) was placed in the flask. The amine solution was titrated using an aq. soln. HCl (0.01M, 0.2 mL portions) and the corresponding pH values were recorded.
In the case of phenyl substituted diamines (**3** and **4**), the compounds did not fully dissolve in pure H_2O. These samples was dissolved in MeOH (10 mL) and titrated with aq. soln. HCl (0.1M). The pKa values obtained with the solvent mixture were corrected to the corresponding pKa values to H_2O.







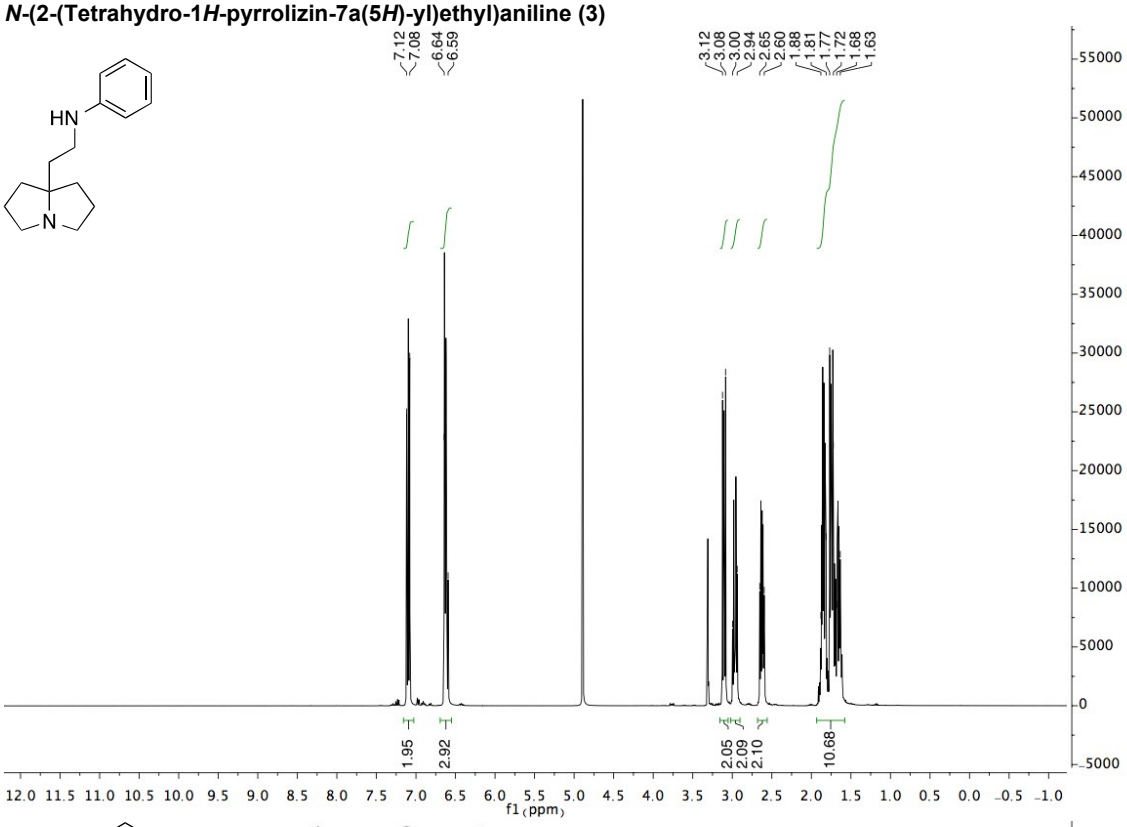


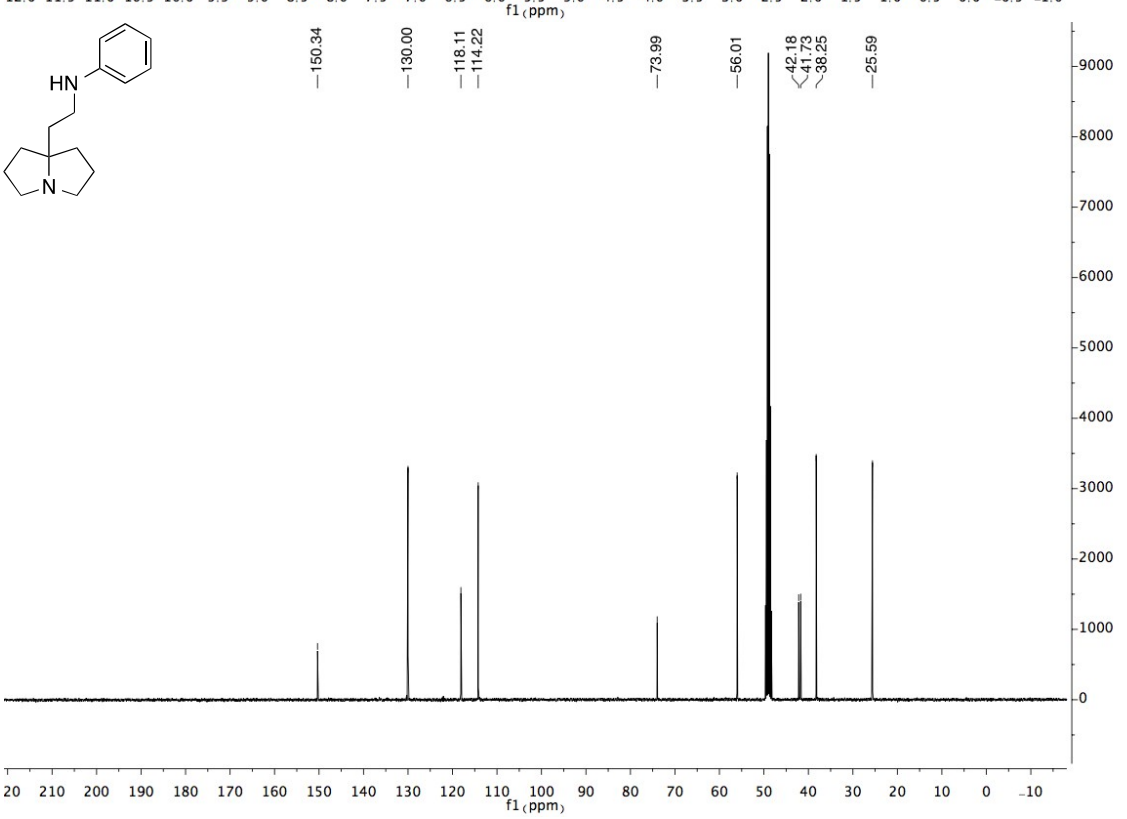


During the *p*Ka measurements, it was discovered that the titration curves of phenyl substituted pyrrolizidines **3** and **4** displayed the shape of a typical buffer with one equivalence point such as triethylamine instead of showing two distinct protonations for the secondary amines. By showing only one protonation at the tertiary amine, pyrrolizidine **4** reveals a drastically reduced nucleophilicity of the phenyl substituted amine caused by delocalization of the lone pair over the aromatic ring. If the aniline nitrogen of **4** stays unreactive towards a proton, it appeared to be unreactive towards CO_2. This suggested that compound **4** probably binds CO_2 as a bicarbonate salt instead of a carbamate. This hypothesis is further supported by the observation that these aniline derivatives never formed solids under neat CO_2 treatment. To further corroborate this hypothesis, ^{13}C-NMR investigations of the CO_2 captured amine **8**, ammonium bicarbonate and the CO_2 adducts of **1** were performed. For the CO_2 captured amine **8** a chemical shift of 166.40 ppm was observed for the carbamate carbon. The bicarbonate carbon of NH_4HCO_3 was at 161.48 ppm and the chemical shift of the carbamate of the CO_2 adduct of amine **4** was 161.56 ppm. The similarity of the carbon shift of NH_4HCO_3 and CO_2 adduct of **4** suggests that **4** forms a bicarbonate when treated with CO_2. This observation is consistent with the finding of only one equivalence point for **4** and implicates that **4** only acts as a tertiary amine and ease the formation of bicarbonate salts. However, due to the influence of chemical shifts to various parameters, other reasons for the observed data cannot fully excluded at present. For example, the ^{13}C-signals of the carbamate can shift due to different structures or aggregates of the absorbent or pH values, which could end up in carbamic acid formation or even a mixture of both. For a detailed discussion, the reader is referred to the following literature,[12,13] where a detailed NMR-investigation of different amine absorbents in CO_2 capture was performed.

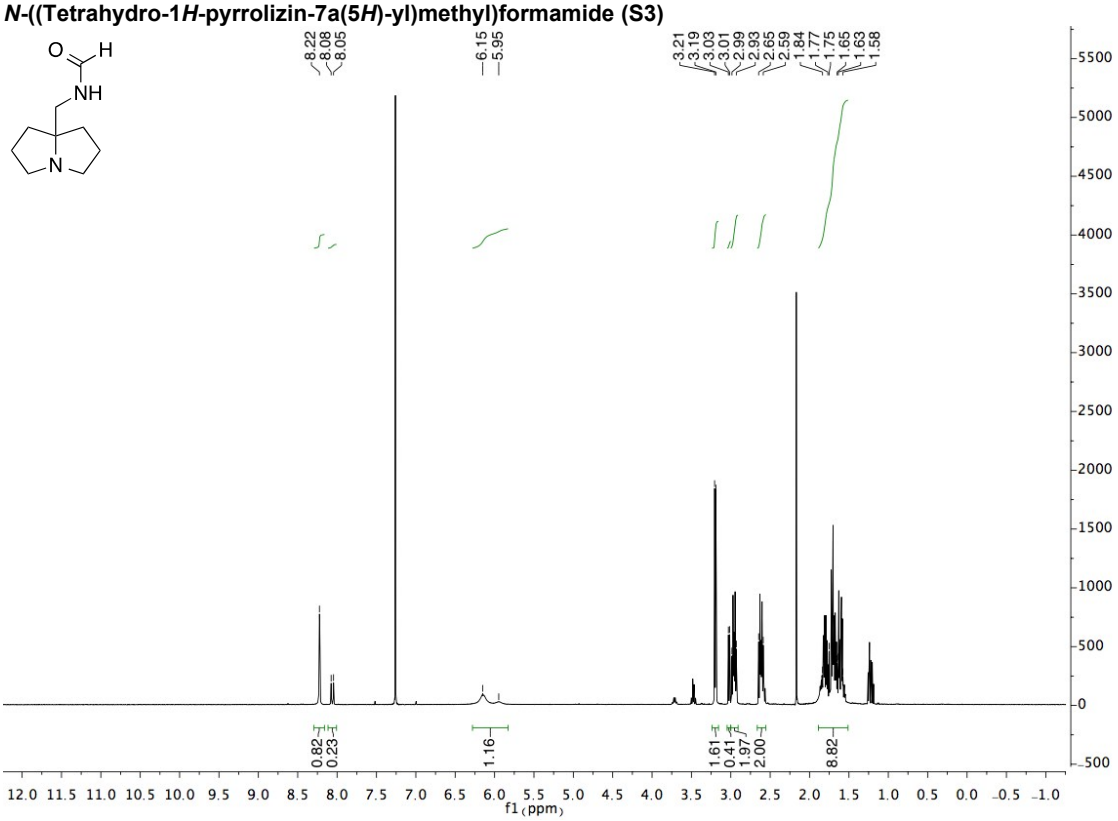
4.2 NMR-Spectra

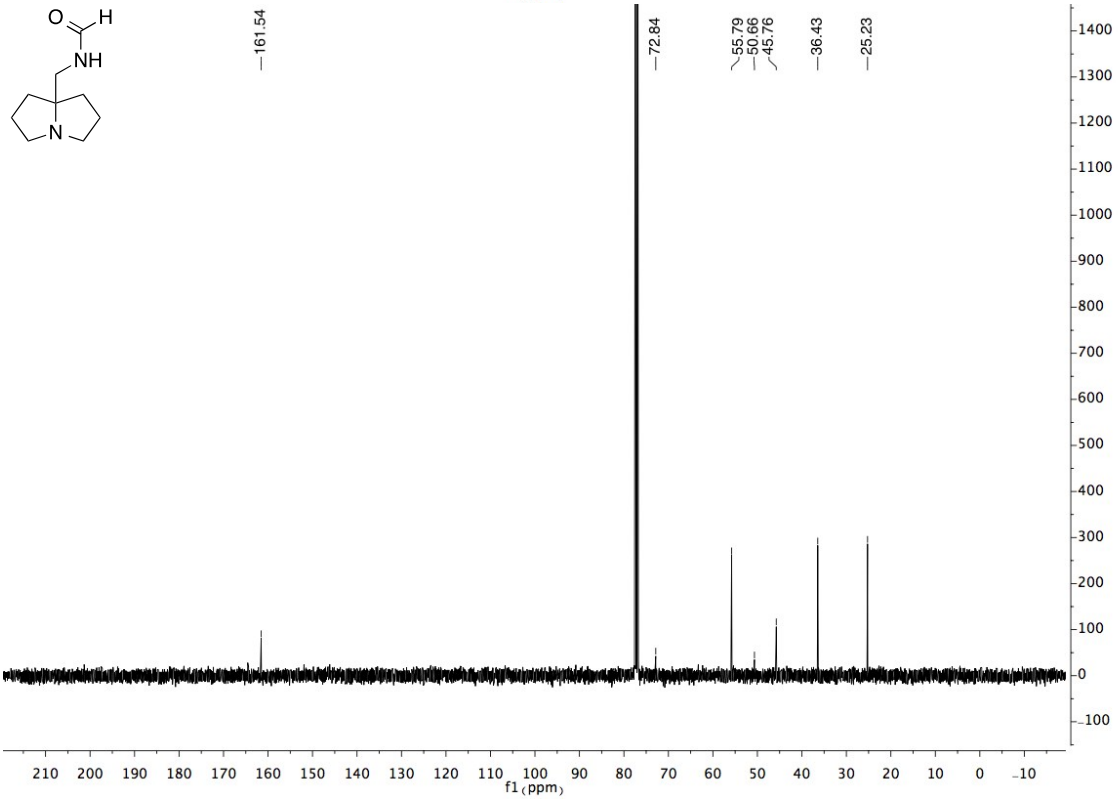
***N*-(2-(Tetrahydro-1*H*-pyrrolizin-7a(5*H*)-yl)ethyl)aniline (3)**



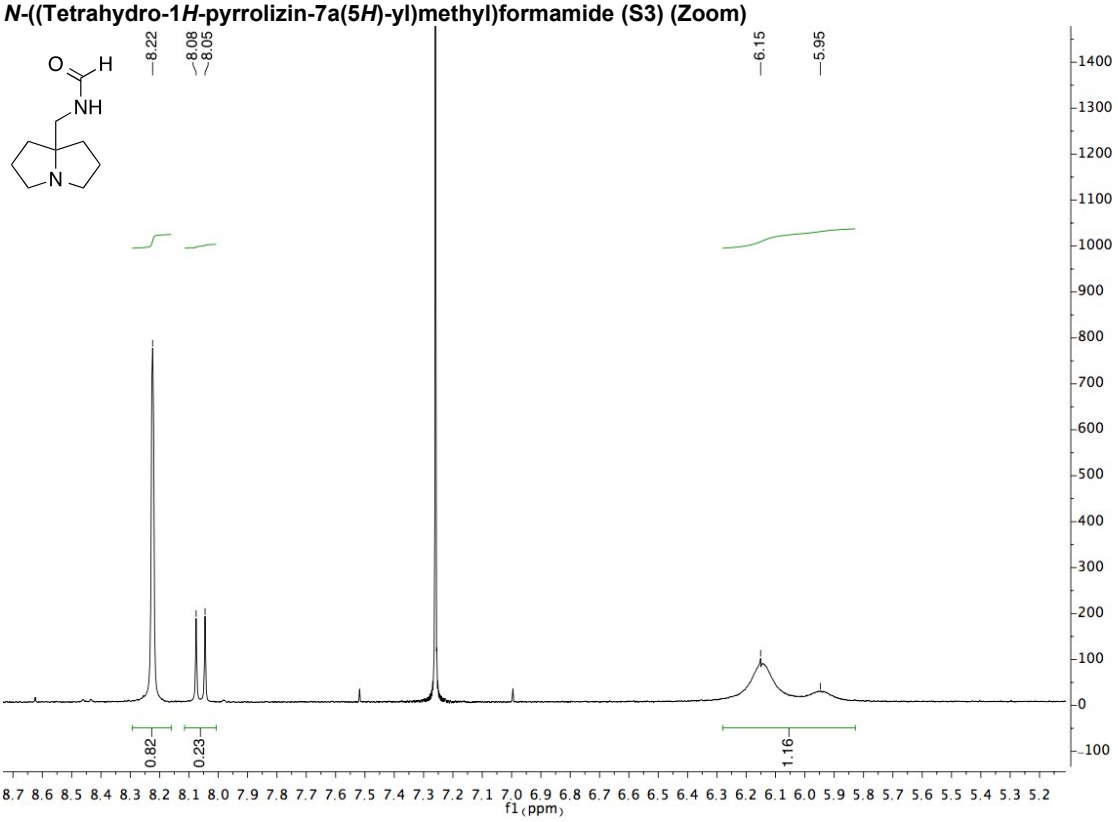


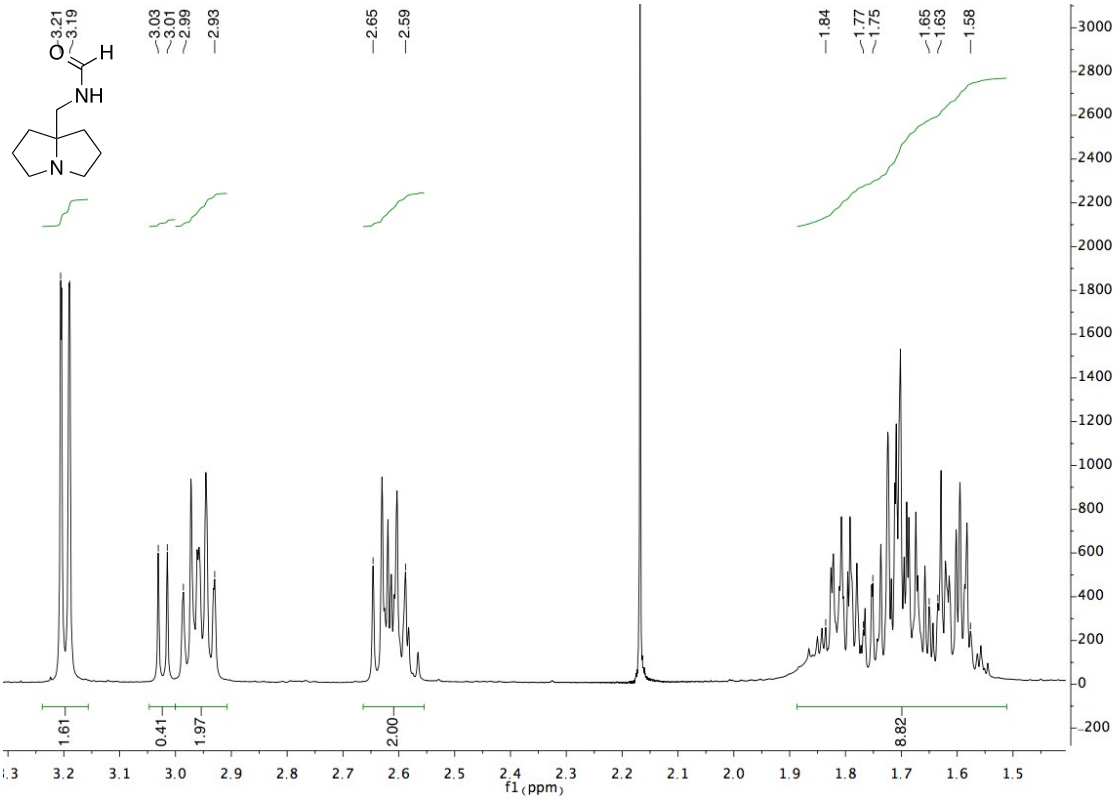
***N*-((Tetrahydro-1*H*-pyrrolizin-7a(5*H*)-yl)methyl)formamide (S3)**



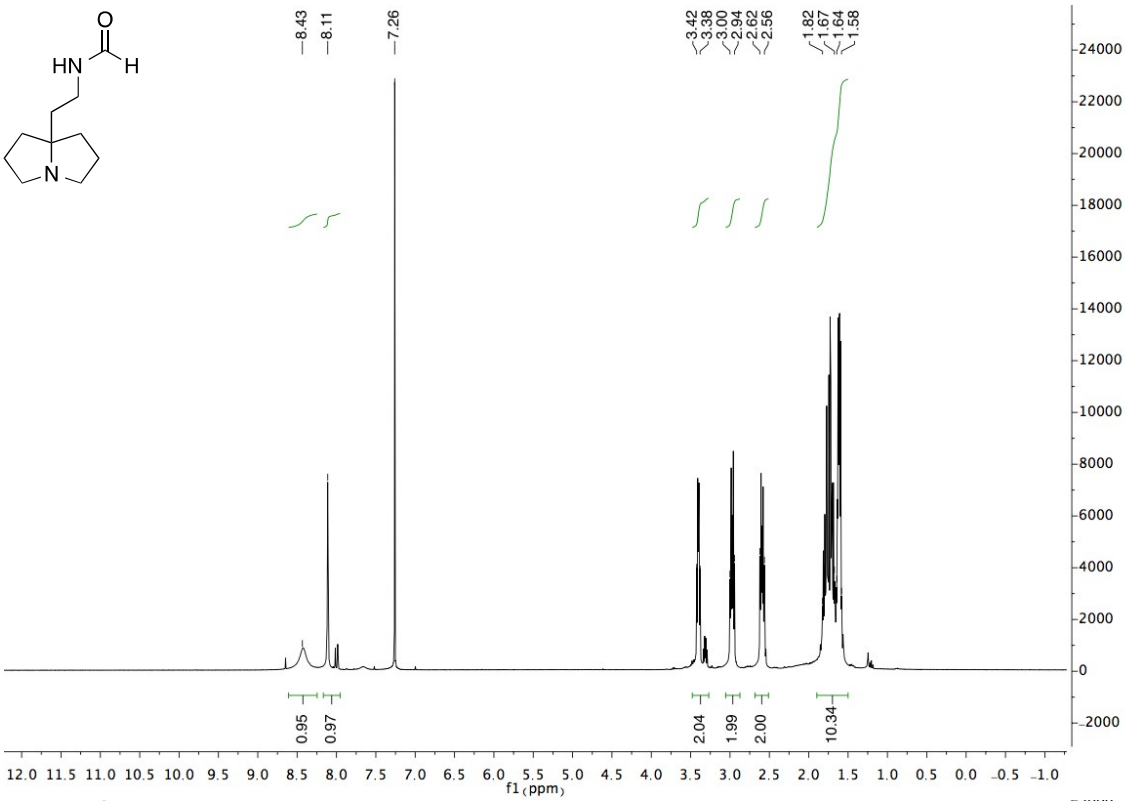


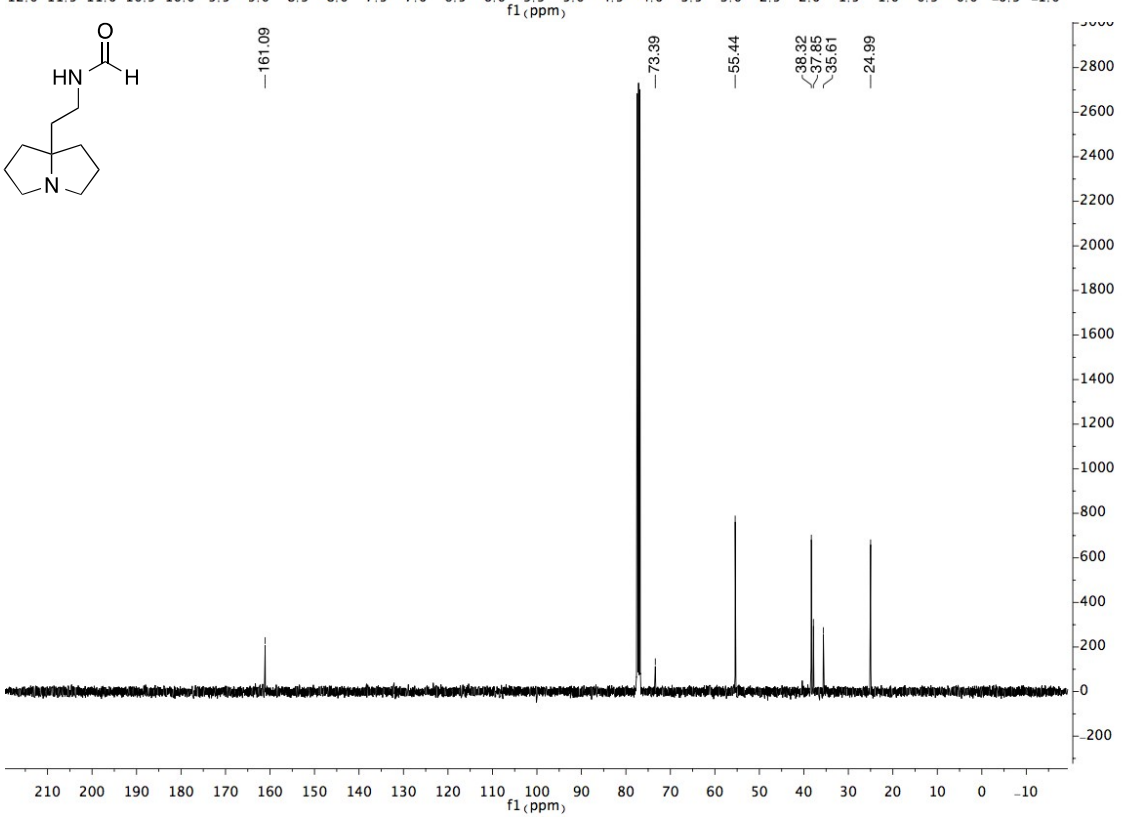
***N*-((Tetrahydro-1*H*-pyrrolizin-7a(5*H*)-yl)methyl)formamide (S3) (Zoom)**



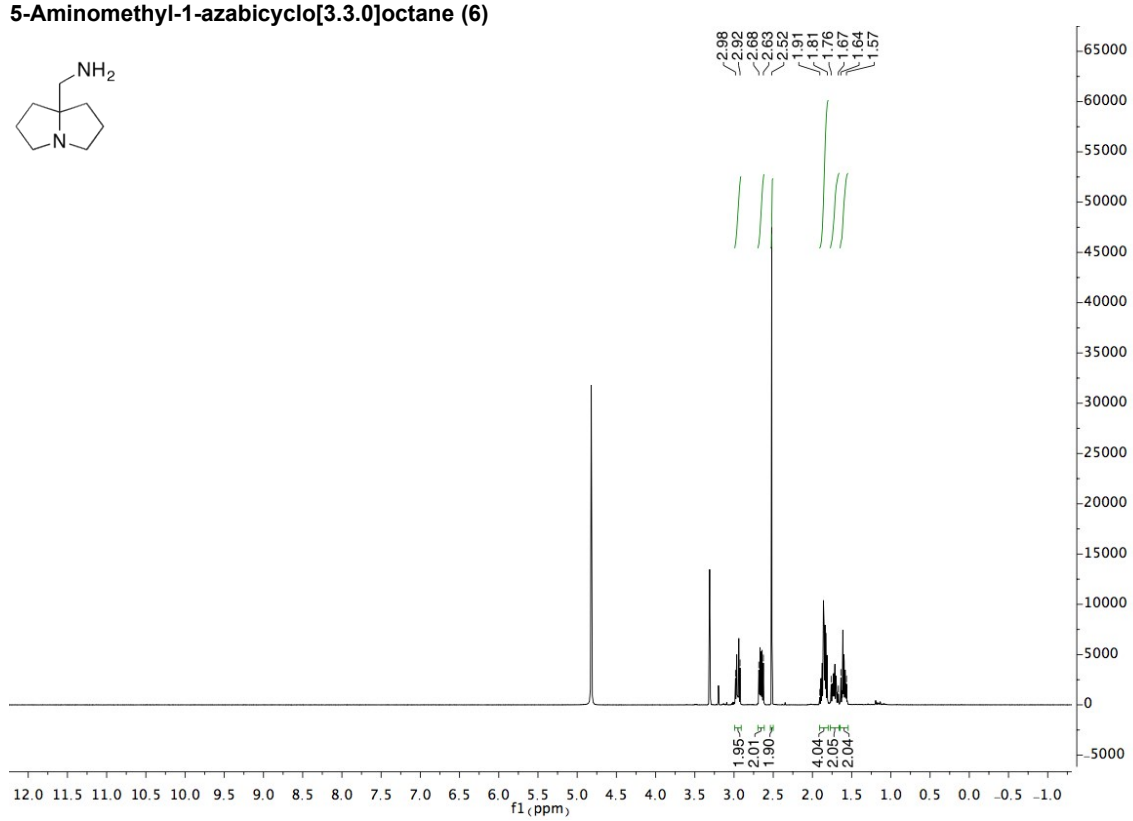


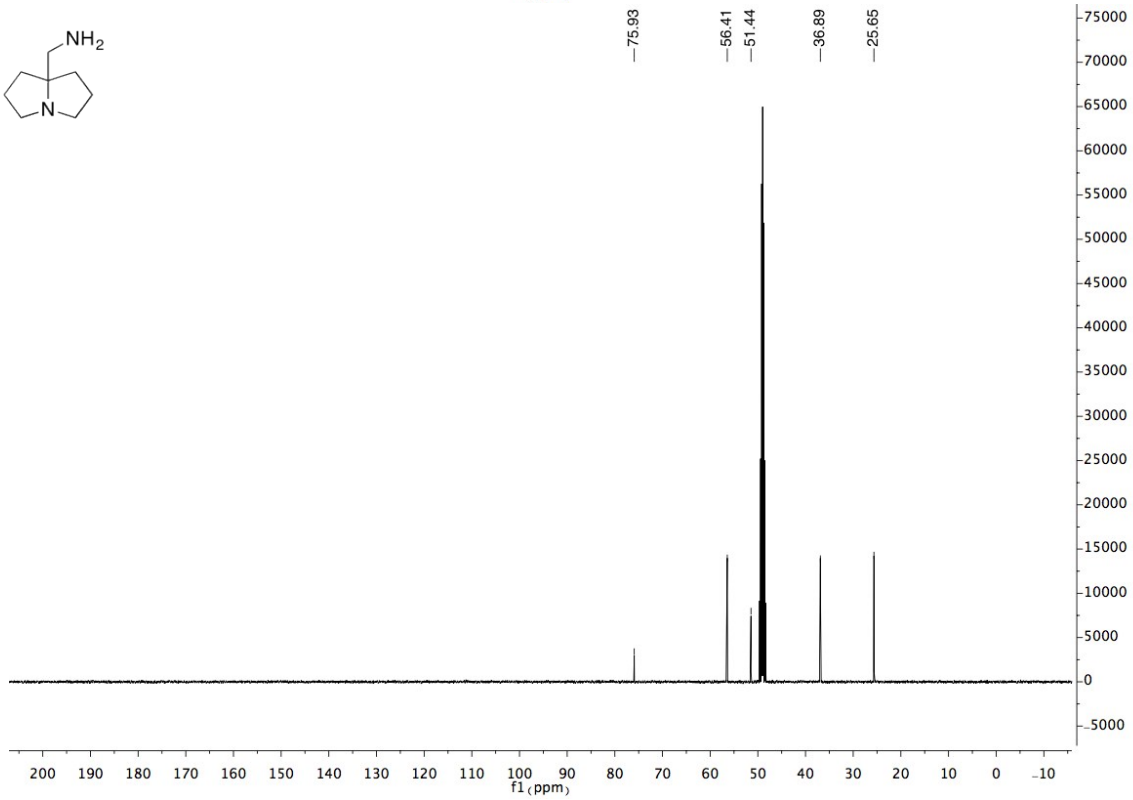
***N*-(2-(Tetrahydro-1*H*-pyrrolizin-7a(5*H*)-yl)ethyl)formamide (S5)**



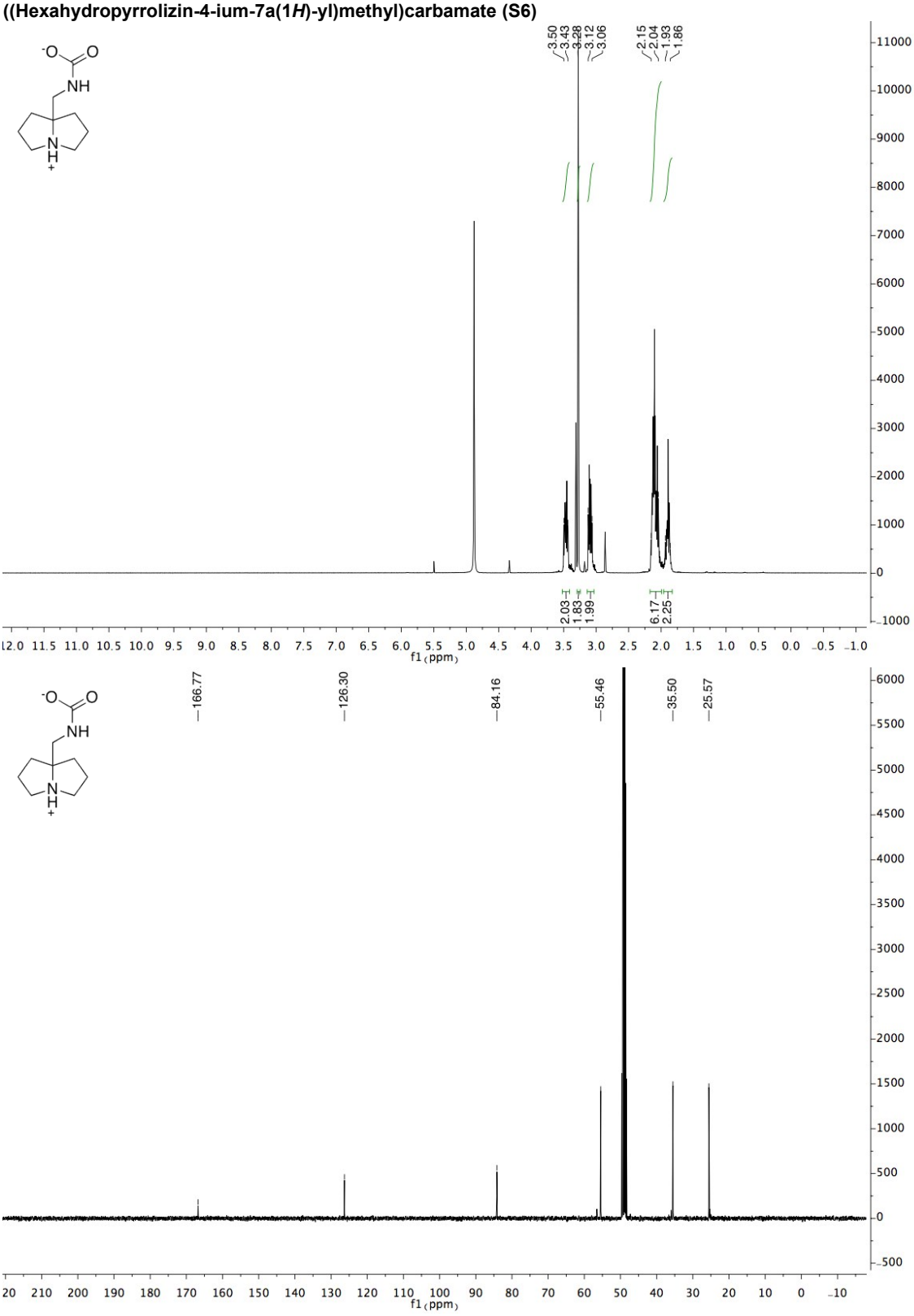


5-Aminomethyl-1-azabicyclo[3.3.0]octane (6)

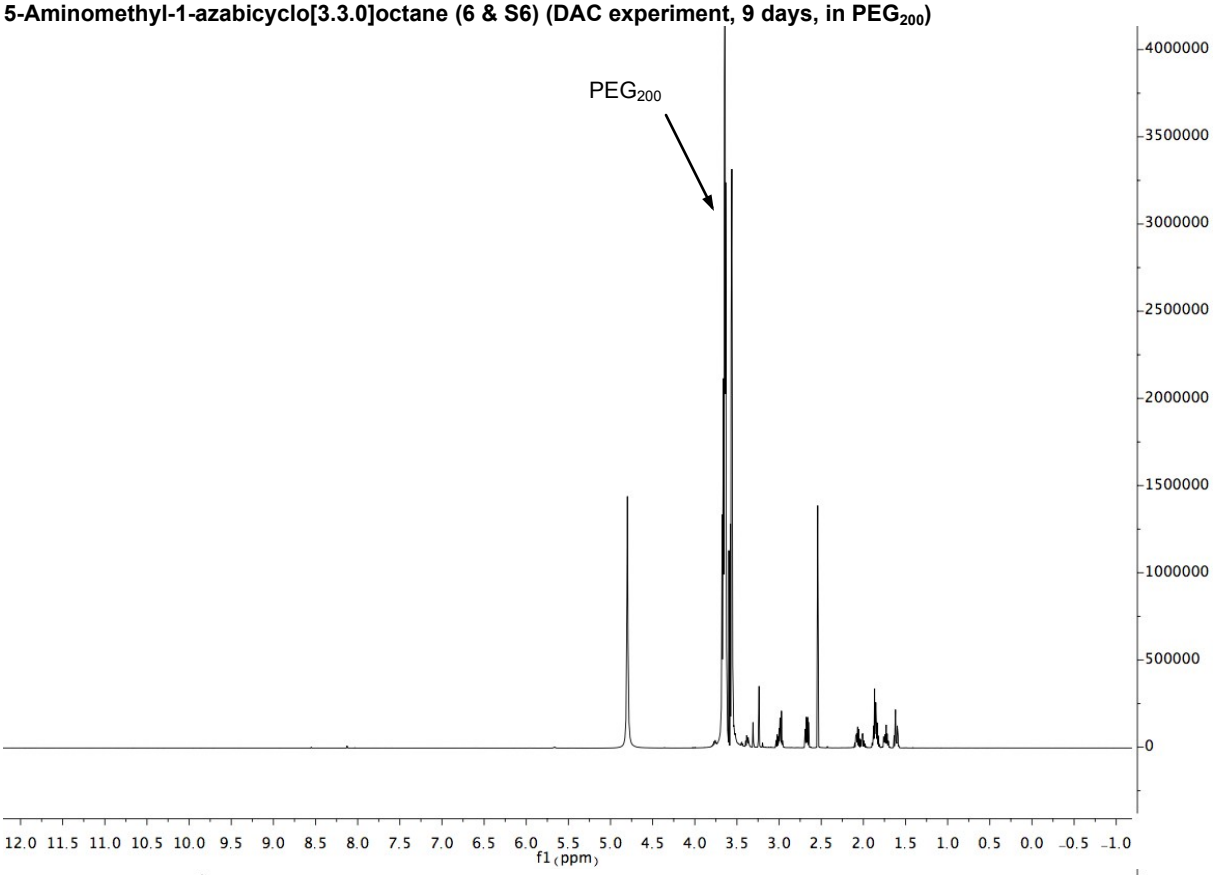


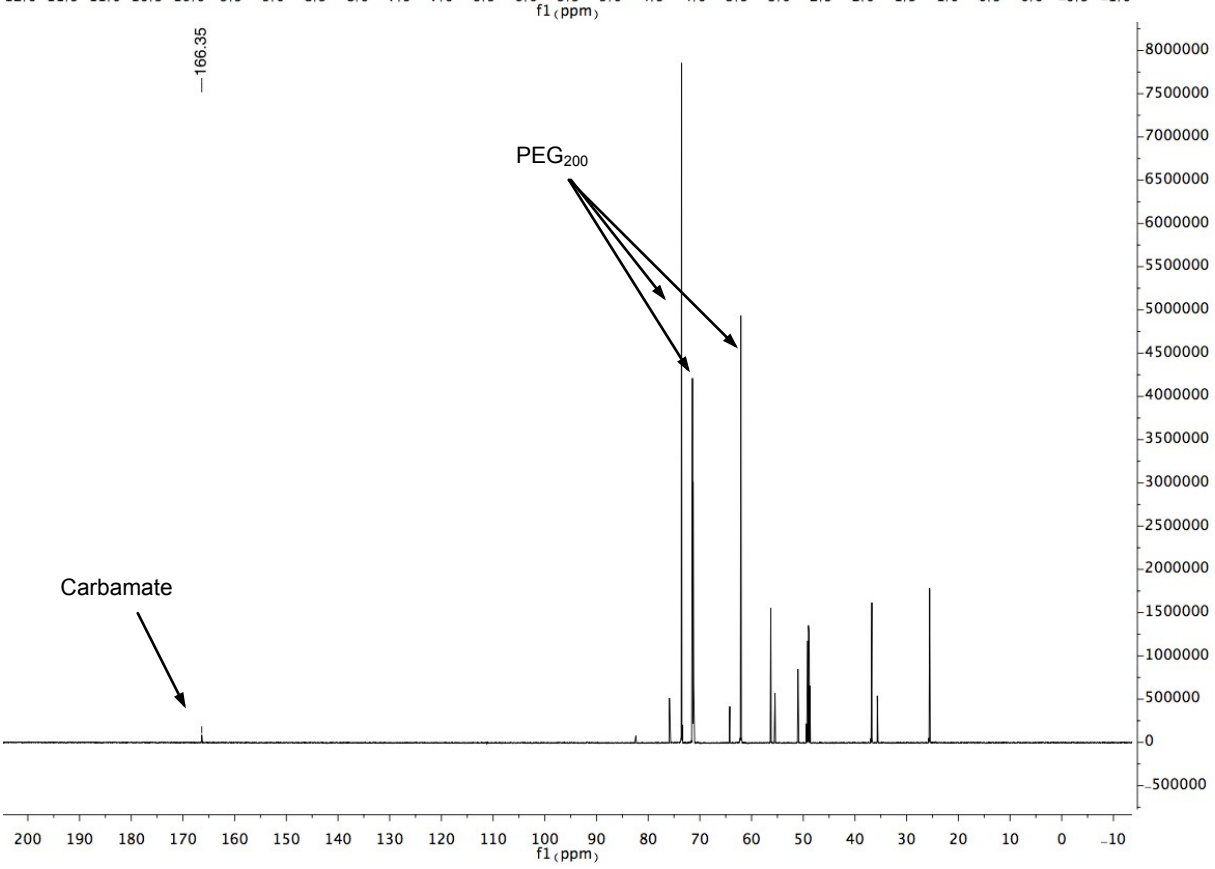


((Hexahydropyrrolizin-4-ium-7a(1*H*)-yl)methyl)carbamate (S6)

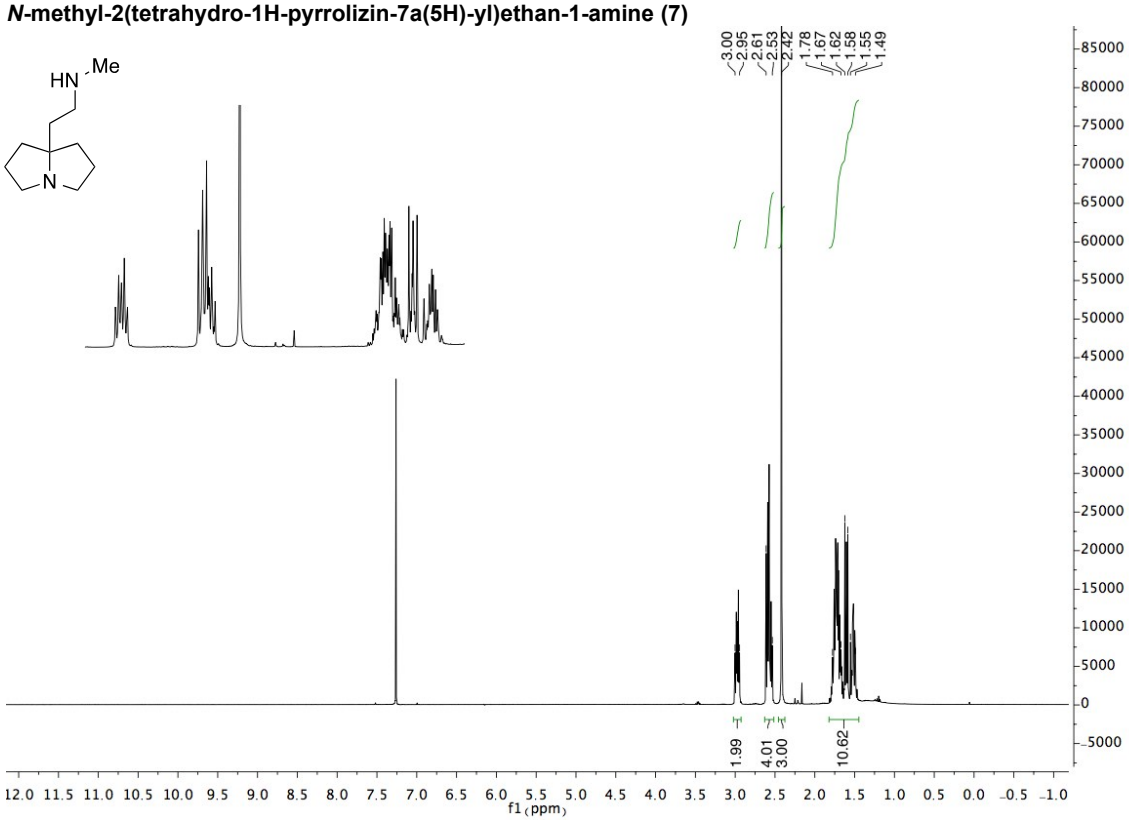


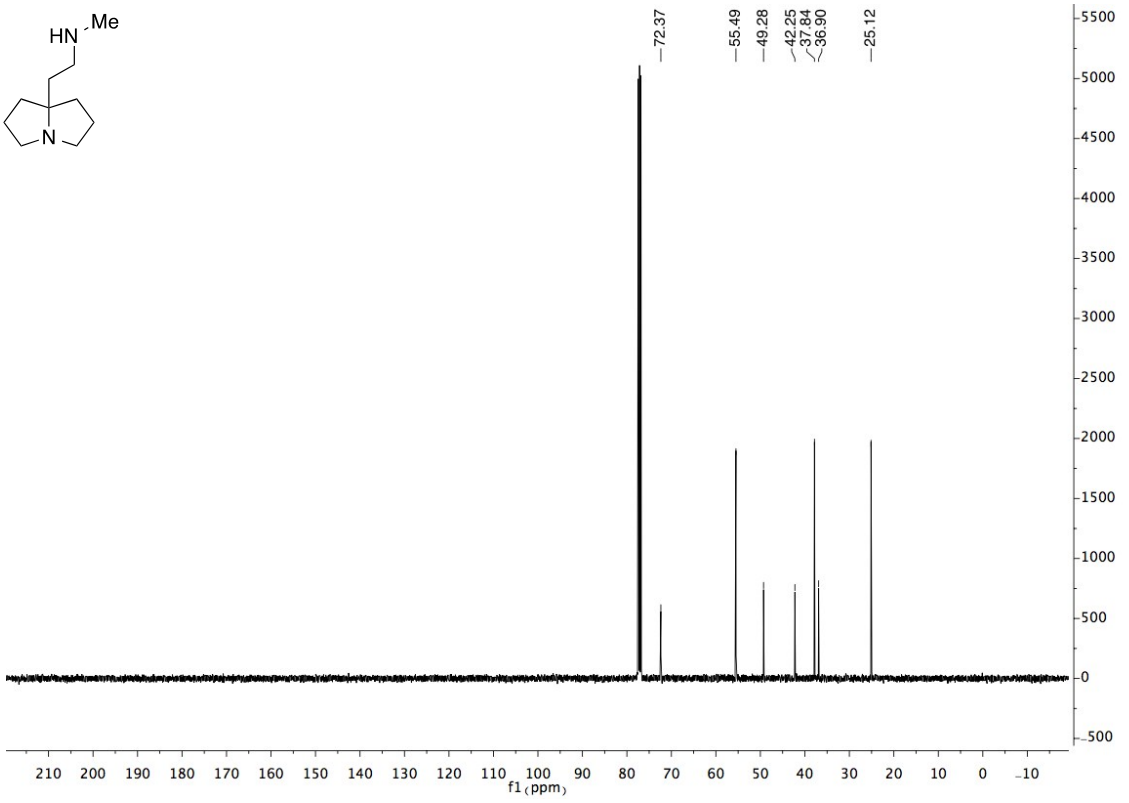
5-Aminomethyl-1-azabicyclo[3.3.0]octane (6 & S6) (DAC experiment, 9 days, in PEG_{200})



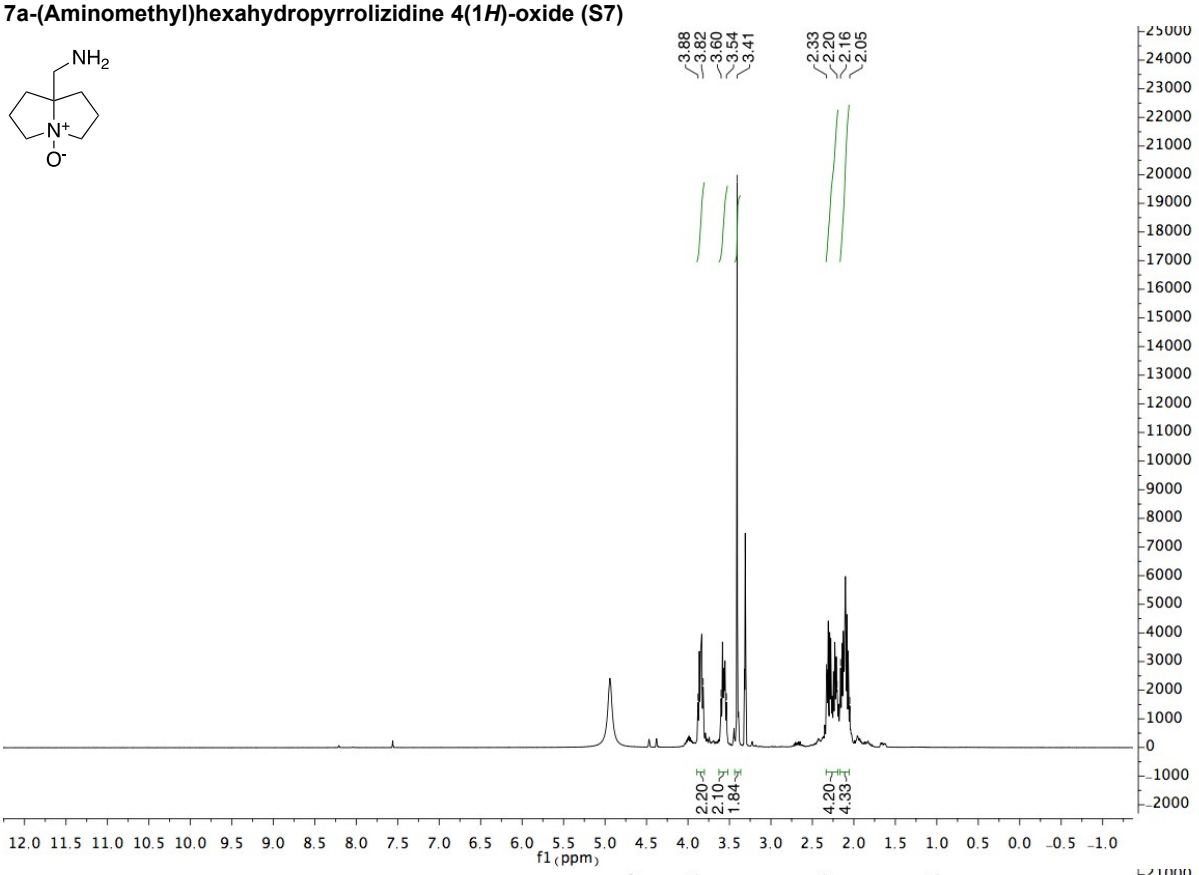


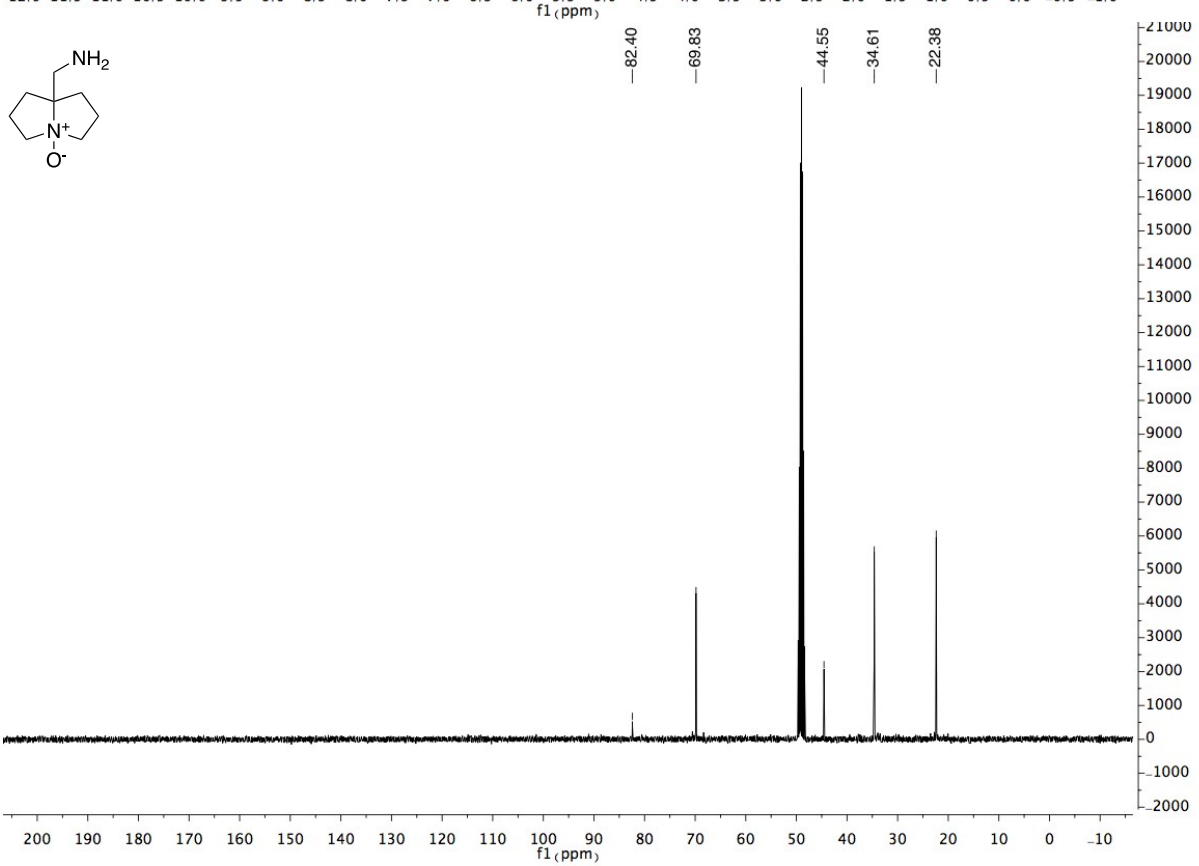
***N*-methyl-2(tetrahydro-1H-pyrrolizin-7a(5H)-yl)ethan-1-amine (7)**



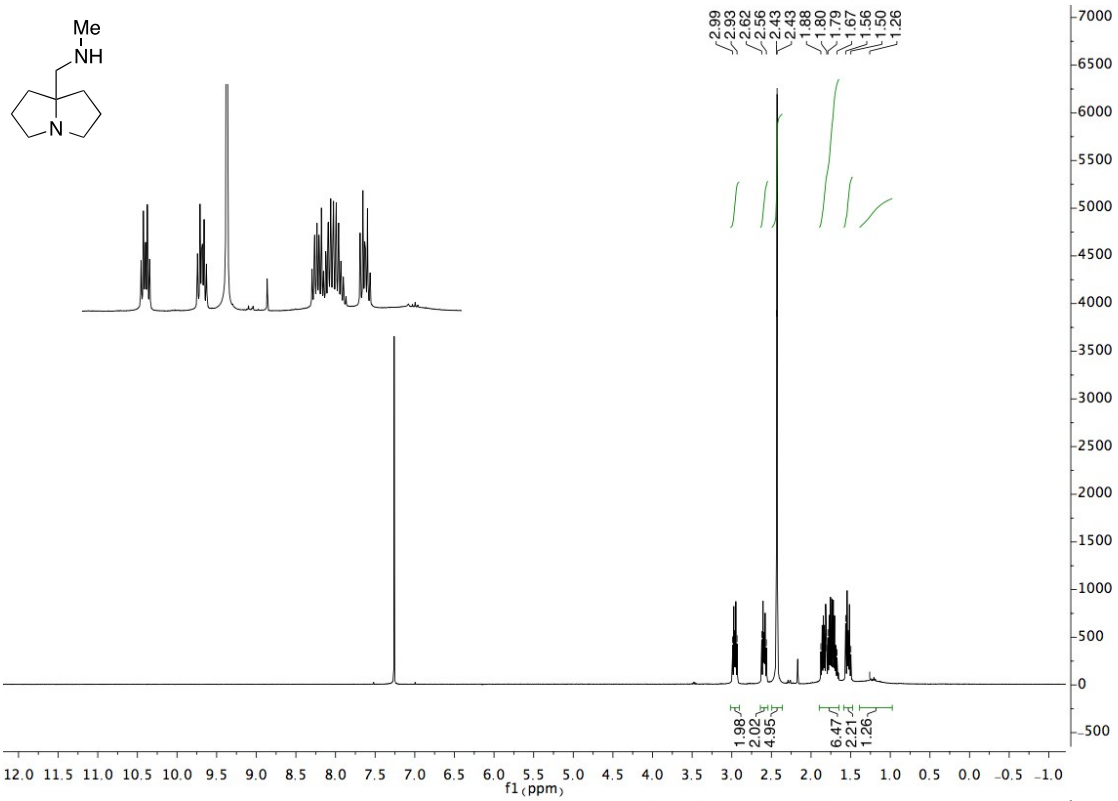


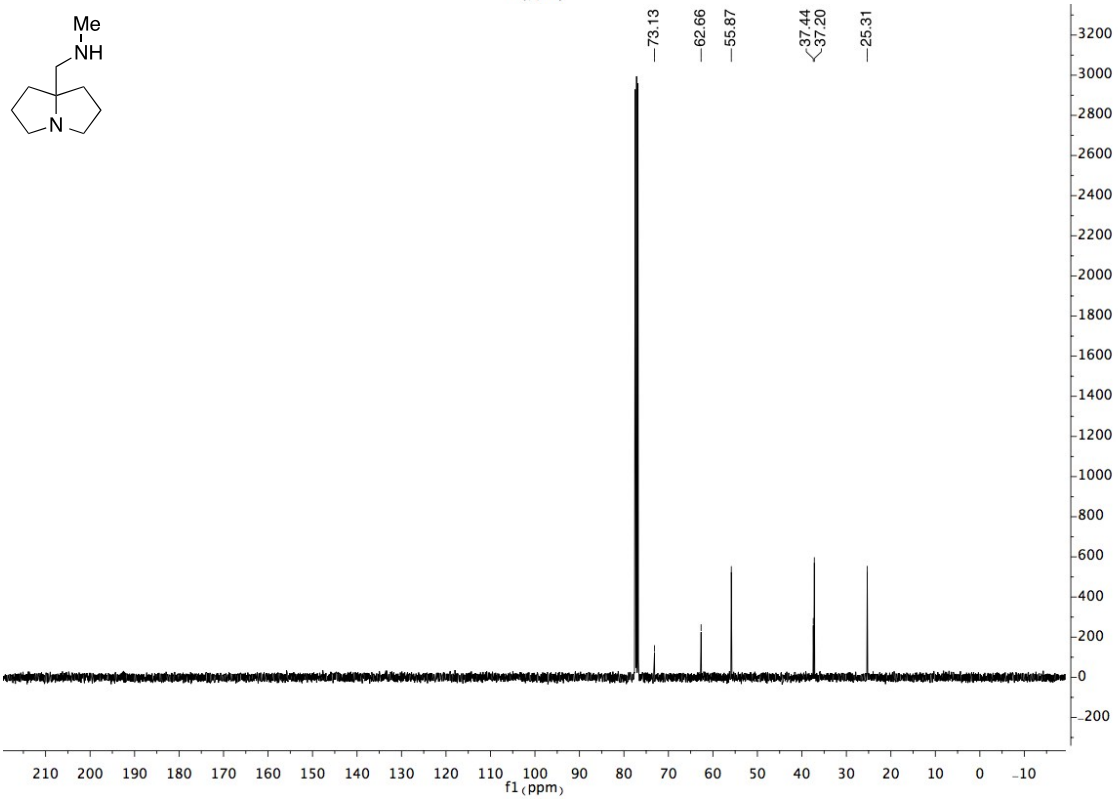
7a-(Aminomethyl)hexahydropyrrolizidine 4(1*H*)-oxide (S7)





***N*-Methyl-1-(tetrahydro-1*H*-pyrrolizin-7a(5*H*)-yl)methanamine (8)**



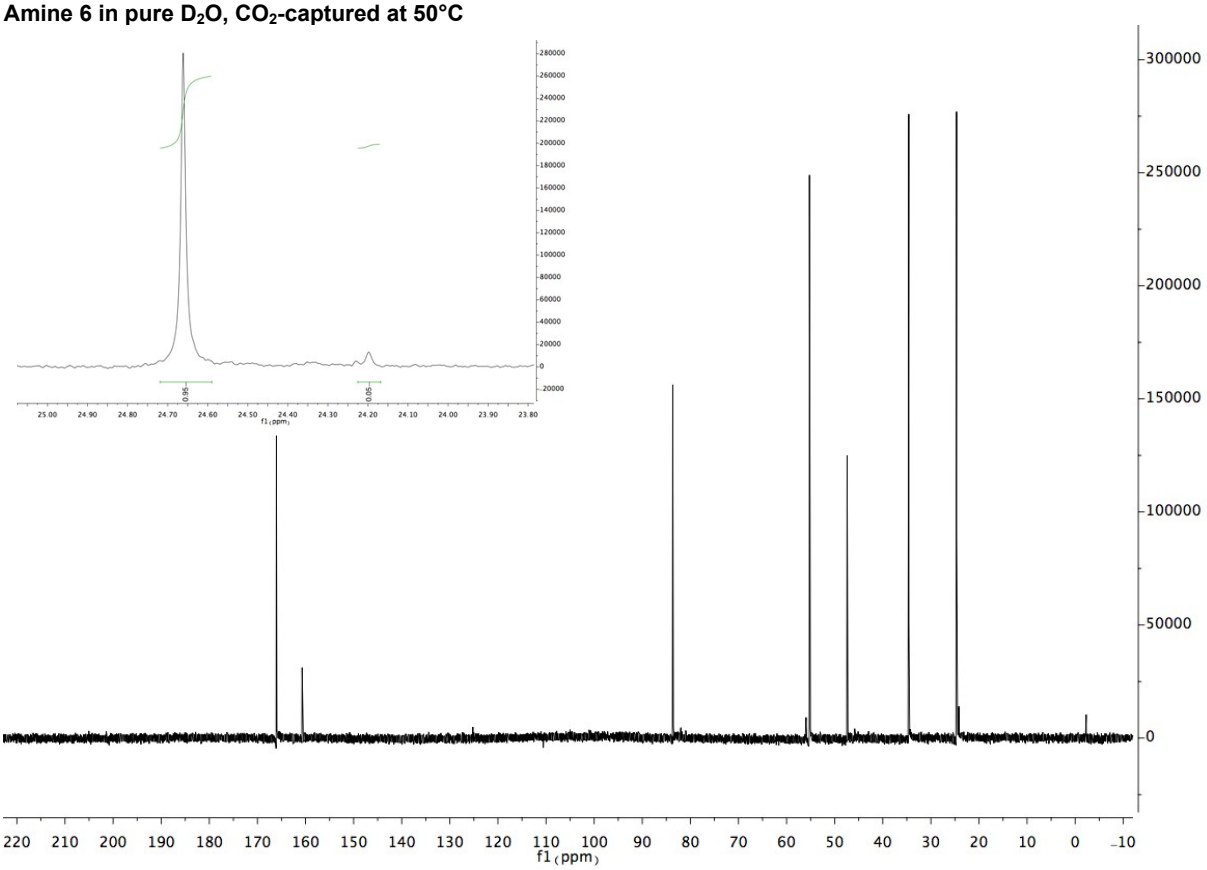


4.3 Quantitative ^{13}C-NMR Experiments

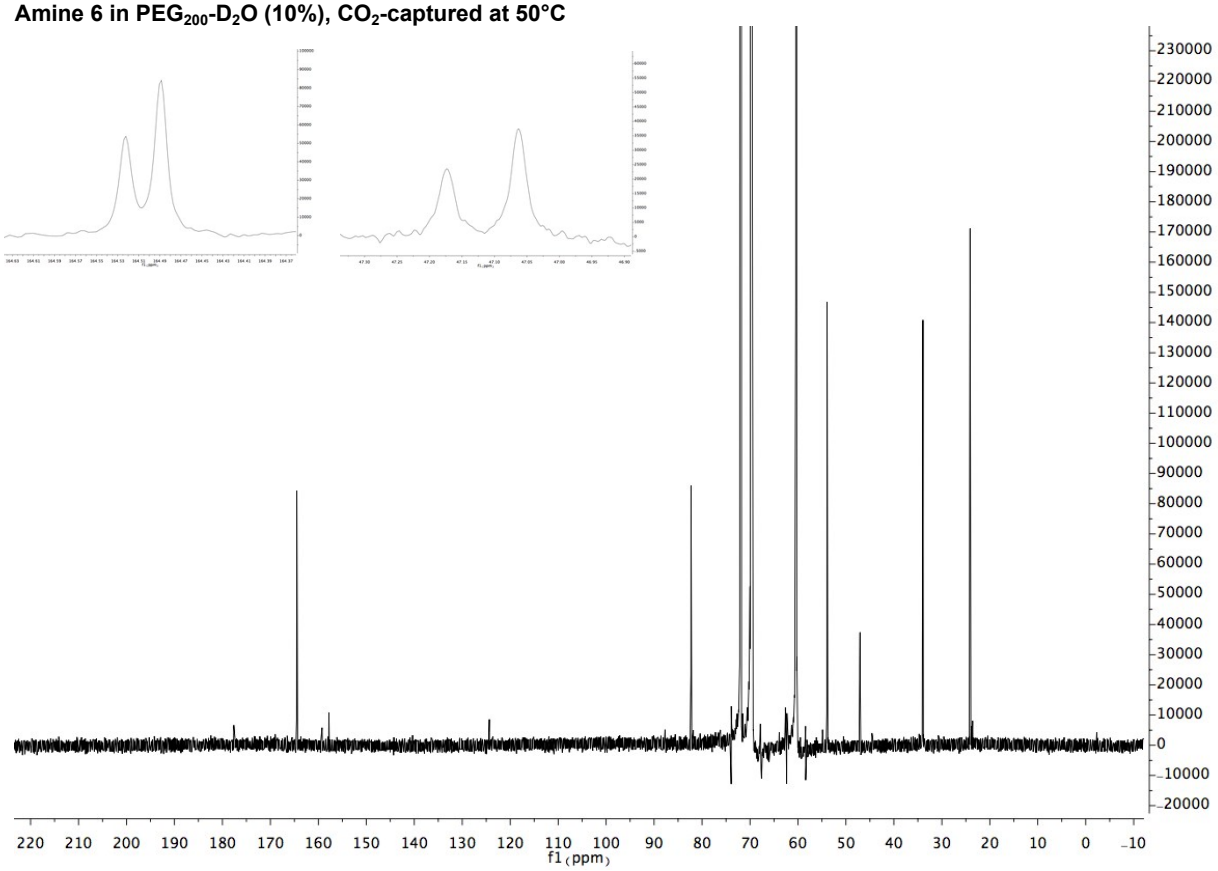
We wanted to demonstrate the ability of the amine **6** to capture CO_2 in water or in the presence of water to study the influence of water. Since flue gas CO_2 capture normally is carried out at elevated temperatures (>40°C), capturing experiments were also conducted in a 50°C oil bath and monitored by quantitative ^{13}C-NMR experiments. For comparison, we used pure D_2O as solvent at RT and 50°C, as well as PEG_{200} with D_2O (10%) at RT and 50°C and an experiment in pure PEG_{200} at 50°C was also performed. The results observed clearly established high CO_2 capture performance under all these conditions. For the NMR-experiments, a longer T1 time of up to 60s and the zgip pulse sequence was used, as well as TSP-d_4 as an internal reference.[14]

We observed high capture performance within a short time period in all tested solvents and solvent mixtures. This suggests good performance also in more applied and industrial conditions. Additionally, the bicarbonate signal is much larger in the presence of water, which will lead to a higher overall CO_2-uptake. An interesting observation is the splitting of the carbamate signal, as well as the carbon at 47 ppm in the PEG_{200}-D_2O (10%) solvent mixture. This splitting is only observed in the mixture, not in pure D_2O nor pure PEG_{200} and will be further investigated.

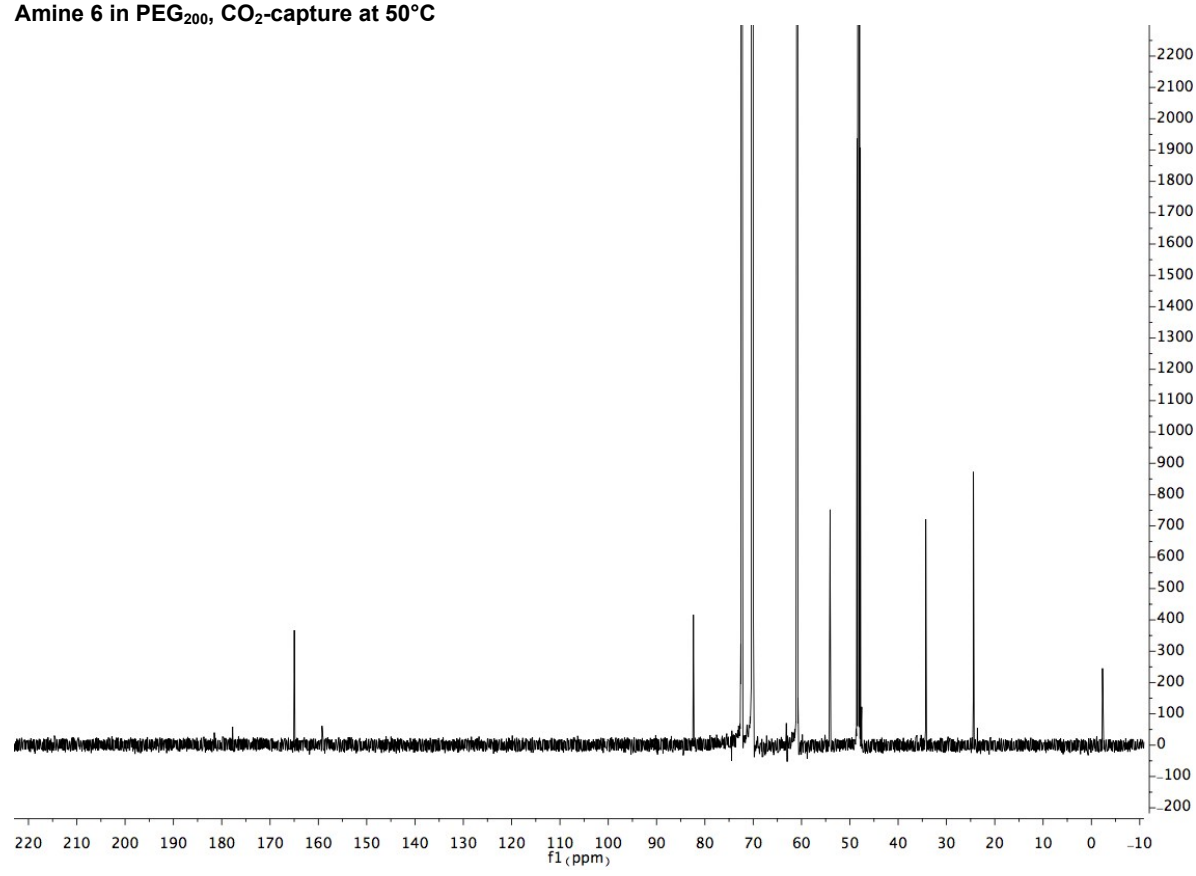
Amine 6 in pure D_2O, CO_2-captured at 50°C



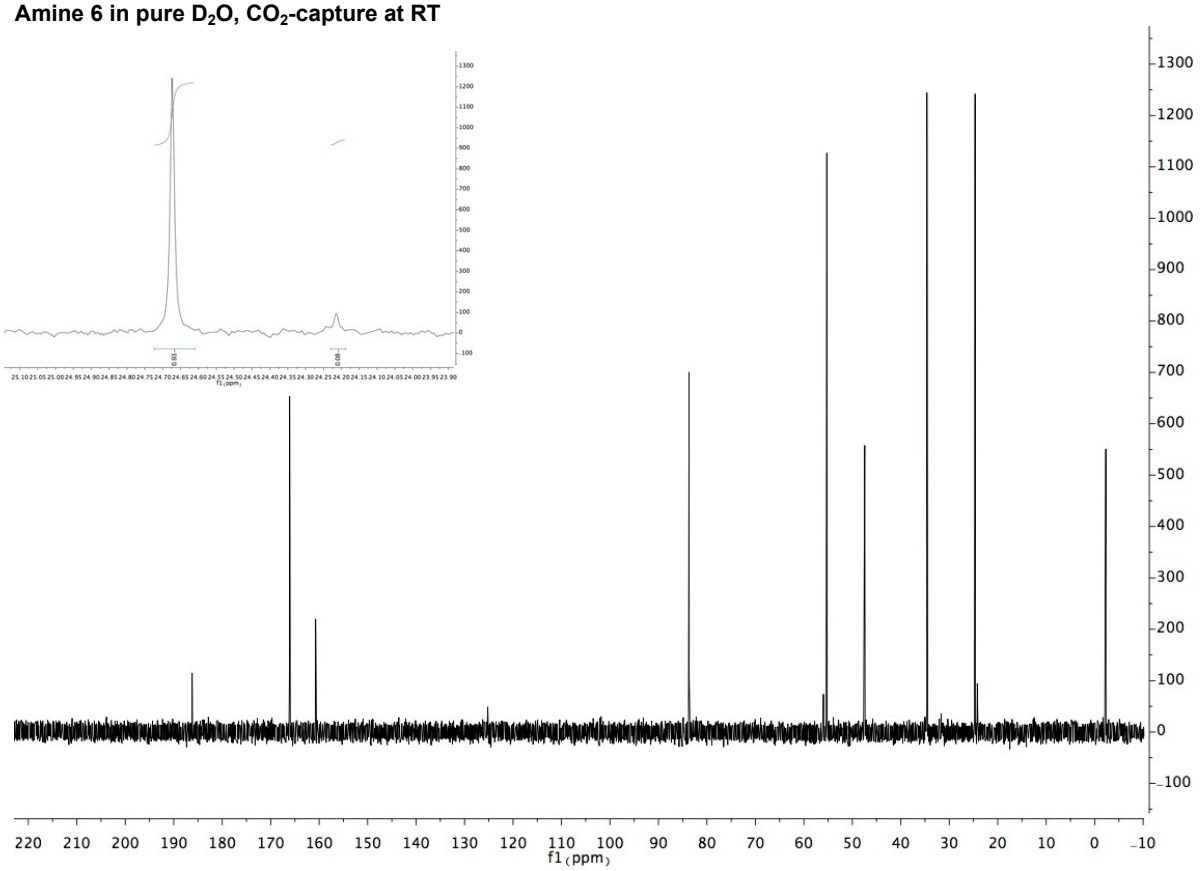
Amine 6 in PEG_{200}-D_2O (10%), CO_2-captured at 50°C



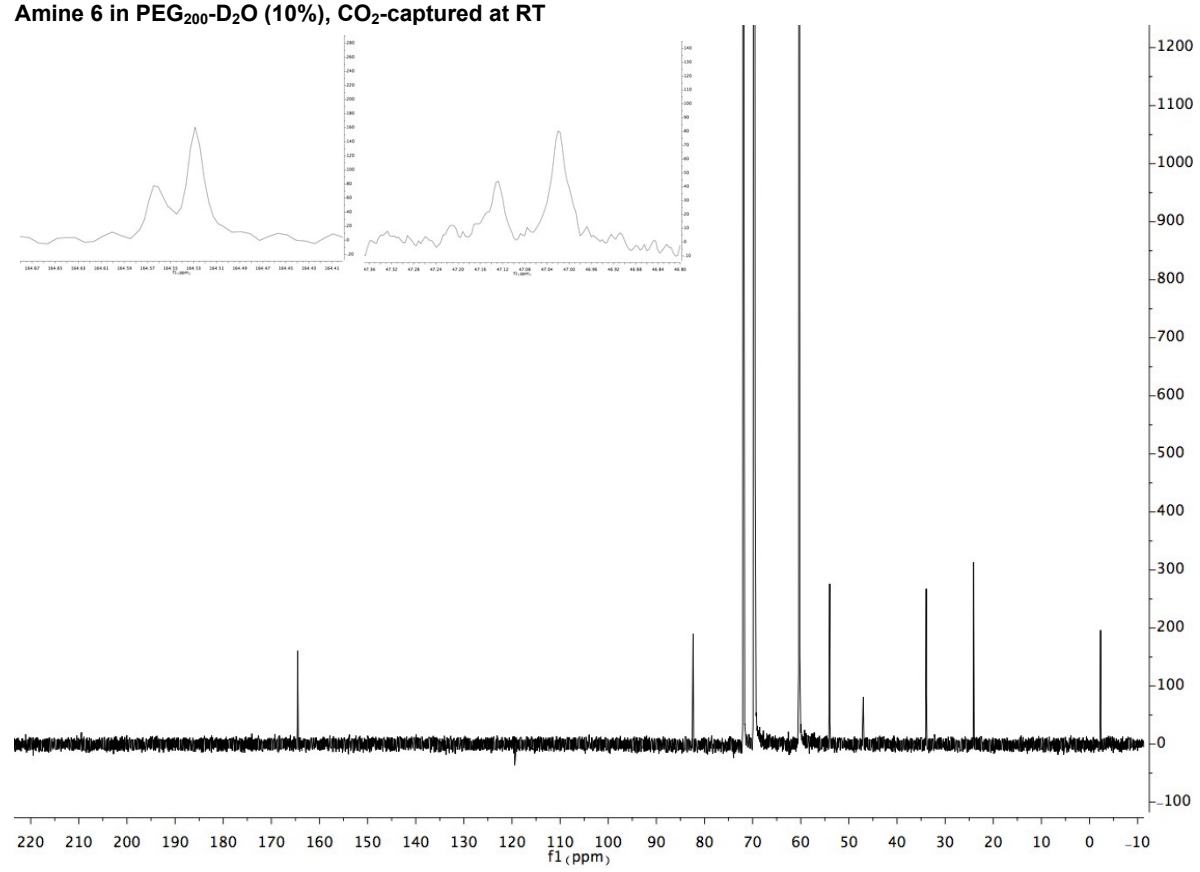
Amine 6 in PEG_{200}, CO_2-capture at 50°C



Amine 6 in pure D_2O, CO_2-capture at RT

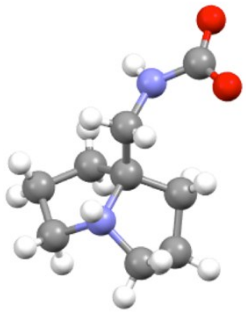


Amine 6 in PEG_{200}-D_2O (10%), CO_2-captured at RT



4.4 X-ray Crystallography

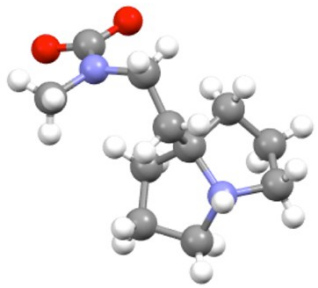
X-Ray of 5-aminomethyl-1-azabicyclo[3.3.0]octane (6) with CO_2



Crystal data for 5-aminomethyl-1-azabicyclo[3.3.0]octane (**6**) with CO_2

Formula	$C_{18}H_{38}N_4O_7$
formula weight	422.52
Z, calculated density	4, 1.343 Mg · m-3
F(000)	919.991
description and size of crystal	colourless plate, 0.020 · 0.110 · 0.180 mm3
absorption coefficient	0.854 mm-1
min/max transmission	0.91 / 0.98
temperature	123K
radiation(wavelength)	Cu Kα (λ = 1.54178 Å)
Crystal system, space group	monoclinic, P n
a	7.8954(8) Å
b	22.637(2) Å
c	11.6950(11) Å
α	90°
β	90.952(7)°
γ	90°
V	2089.9(2) Å3
min/max Θ	3.905° / 68.901°
number of collected reflections	15770
number of independent refections	6655 (merging r = 0.070)
number of observed reflections	5647 (I>2.0σ(I))
number of refined parameters	584
r	0.0453
rW	0.0773
goodness of fit	1.1157

X-Ray of *N*-methyl-2(tetrahydro-1H-pyrrolizin-7a(5H)-yl)ethan-1-amine (7) with CO_2



Crystal data for N-methyl-2(tetrahydro-1H-pyrrolizin-7a(5H)-yl)ethan-1-amine (**7**) with CO_2

Formula	$C_{11}H_{28}N_2O_6$
formula weight	284.35
Z, calculated density	4, 1.273 Mg · m-3
F(000)	624
description and size of crystal	colourless block, 0.040 · 0.110 · 0.230 mm3
absorption coefficient	0.856 mm-1
min/max transmission	0.91 / 0.97
temperature	123K
radiation(wavelength)	Cu Kα (λ = 1.54178 Å)
Crystal system, space group	monoclinic, P 21/n
a	7.0751(5) Å
b	16.6440(12) Å
c	13.0818(9) Å
α	90°
β	105.578(2)°
γ	90°
V	1483.89(10) Å3
min/max Θ	4.401° / 69.119°
number of collected reflections	9721
number of independent refections	2692 (merging r = 0.022)
number of observed reflections	2629 (I>2.0σ(I))
number of refined parameters	199
r	0.0319
rW	0.0360
goodness of fit	1.1204

5. Reduction of CO_2

The results of the reduction of CO_2 are reported as an average of two runs. In the glovebox, a high pressure autoclave was filled with amine **7** (518 mg, 3.08 mmol, 1290 eq.), Ru-MACHO®-BH (1.40 mg, 2.39 µmol, 1.0 eq.), K_3PO_4 (25.4 mg, 120 µmol, 50 eq.) and THF (1.7 mL). The autoclave was removed from the glovebox and pressured with 10 bar CO_2 and 65 bar H_2. The reaction was heated up to 155 °C for 134 h. After cooling to 0 °C the pressure was released and 1,3,5-trimethoxybenzene was added as an internal standard. A sample of the reaction was transferred into a NMR-tube, DMSO-d_6 and two drops of half concentrated aq. HCl soln. were added. The NMR was measured using solvent suppression for THF.

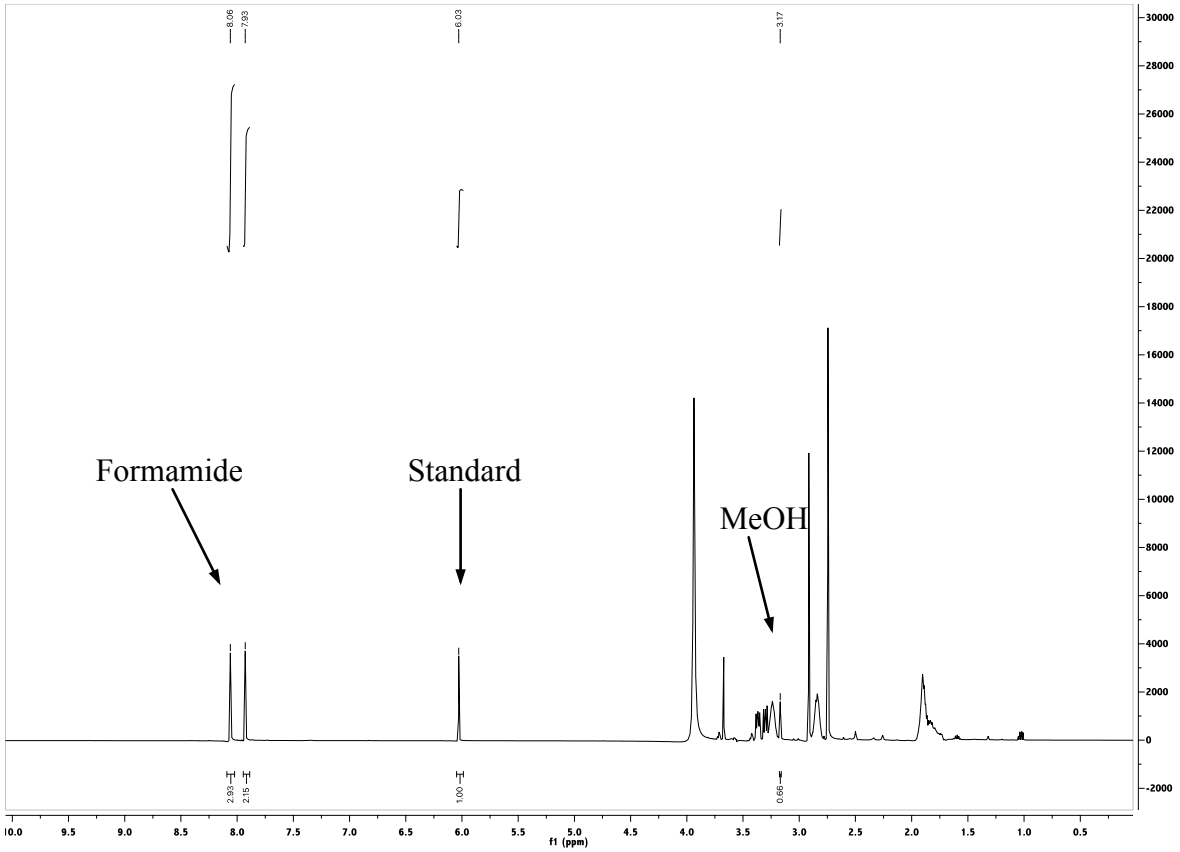
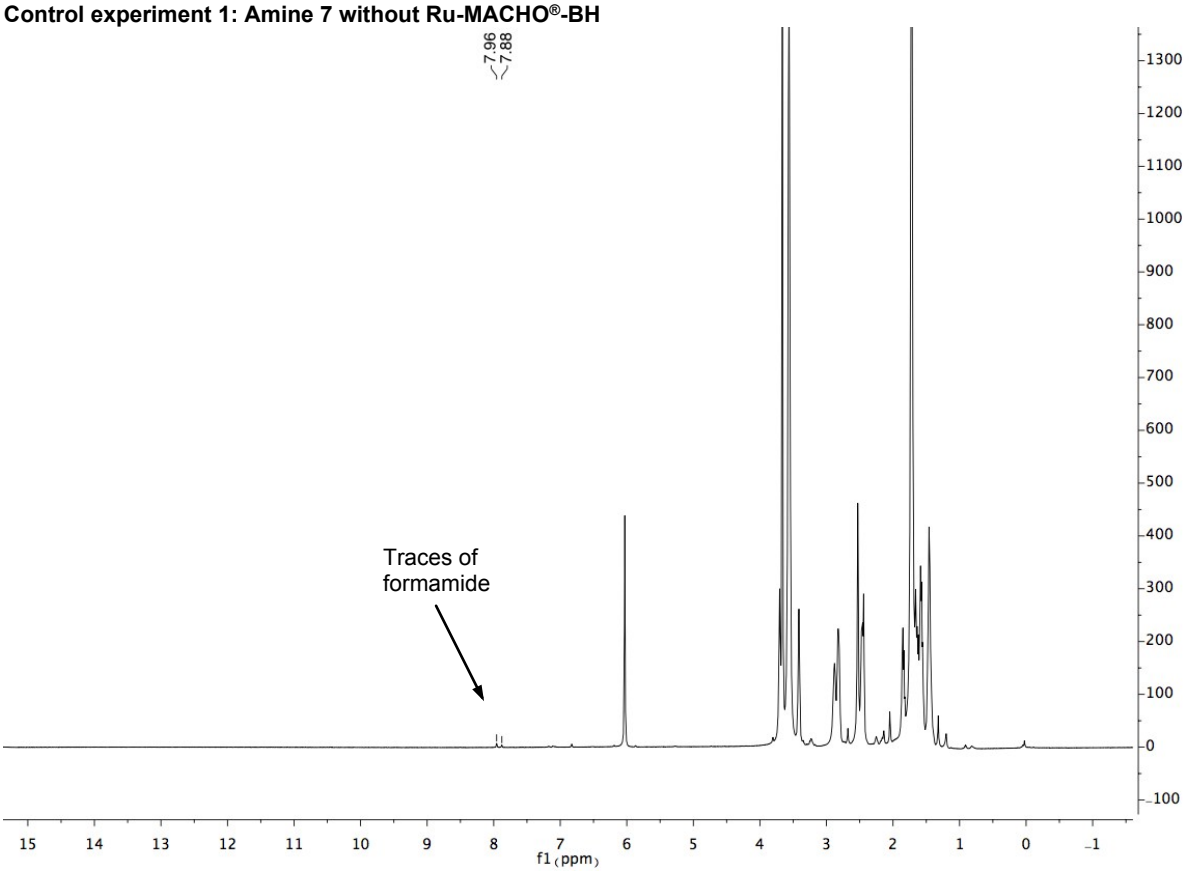


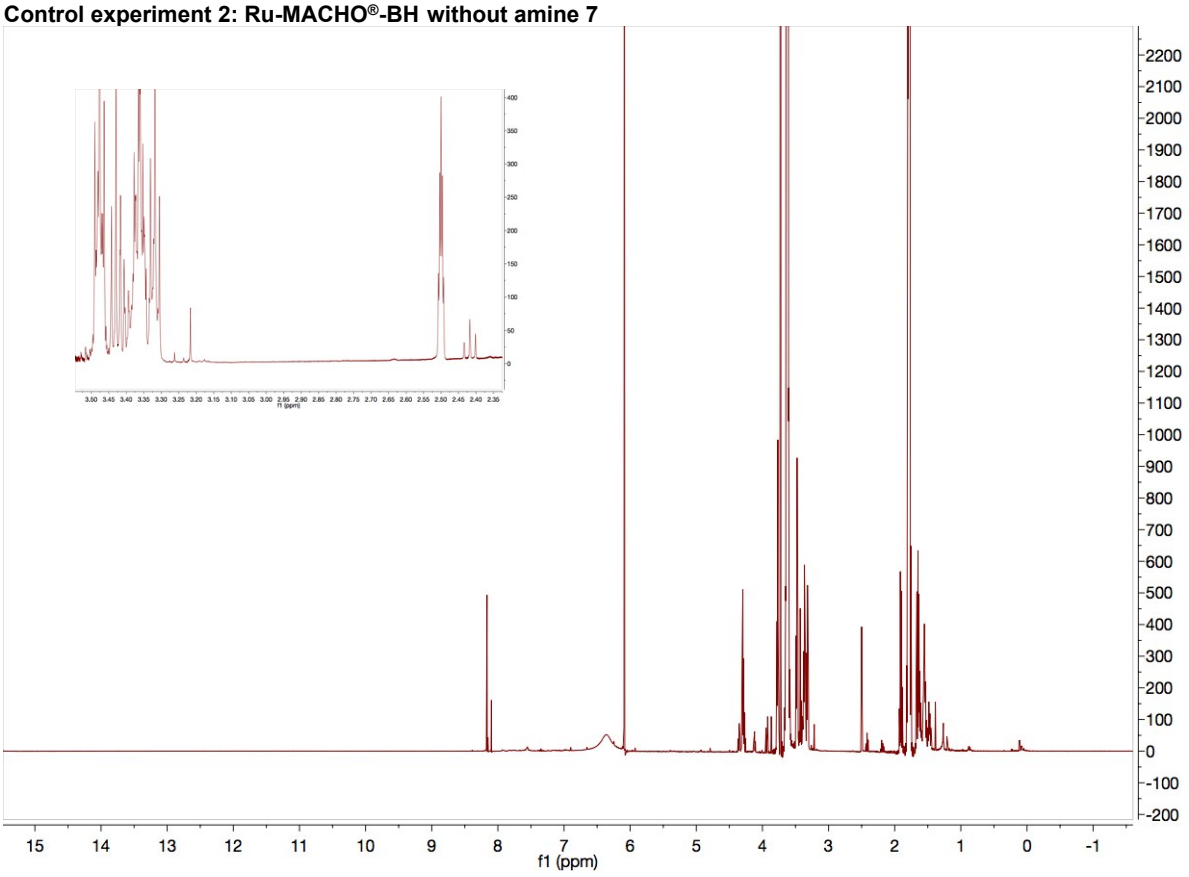
Figure 1: Representative ^{1}H-NMR Spectrum for the reduction of CO_2.

Two different control experiments were conducted. In the control experiment 1, amine **7** was used in the presence of K_3PO_4, THF, H_2 (60 bar) and CO_2 (10 bar), but without Ru-MACHO®-BH. The experiment was conducted at 155 °C for 48 h and showed only trace formation of the corresponding formamide, which clearly indicates the importance of the catalyst for the observed high turnover numbers. In the control experiment 2, Ru-MACHO®-BH was used together with K_3PO_4, THF, H_2 (60 bar) and CO_2 (10 bar), but without amine **7**. This experiment was also conducted at 155 °C over 48 h and no MeOH generation was observed. Both control experiments clearly showed the importance of both the amine and the catalyst for the generation of both formamide and MeOH.

Control experiment 1: Amine 7 without Ru-MACHO®-BH



Control experiment 2: Ru-MACHO®-BH without amine 7



References

[1] Davoli, P., Forni, A., Moretti, I., Prati, F. & Torre, G. On the effect of ring substituents in the carbonylation of aziridines. *Tetrahedron* **57**, 1801-1812 (2001).

[2] Shieh, W.-C., Chen, G.-P., Xue, S., McKenna, J., Jiang, X., Prasad, K. & Repič, O. A Facile preparation of octahydropyrrolo[2,3-c]pyridine enantiomer. *Organic Process Research & Development* **11**, 711-715 (2007).

[3] Andersson, P. G., Guijarro, D. & Tanner, D. Preparation and Use of Aziridino Alcohols as Promoters for the Enantioselective Addition of Dialkylzinc Reagents to N-(Diphenylphosphinoyl) Imines. *Org. Chem.* 62, 7364-7375 (1997).

[4] Arnáiz, F. J. A convenient way to generate hydrogen chloride in the freshman lab. *J. Chem. Educ.* **72**, 1139 (1995).

[5] Curtis, O. E., Sandri, J. M., Crocker, R. E. & Hart, H. Dicyclopropyl ketone. *Org. Synth.* **38**, 19-20 (1958).

[6] Kagermeier, N., Werner, K., Keller, M., Baumeister, P., Bernhardt, G., Seifert, R. & Buschauer, A. Dimeric carbamoylguanidine-type histamine H2 receptor ligands: A new class of potent and selective agonists. *Bioorg. Med. Chem.* **23**, 3957-3969 (2015).

[7] Suzuki, T., Usui, T., Oka, M., Suzuki, T. & Kataoka, T. Synthesis and muscarinic activitiy of series of quinolines and naphtalenes with 1-azabicyclo[3.3.0]octane moiety. *Chem. Pharm. Bull.* **46**, 1265-1273 (1998).

[8] Fors, B. P., Watson, D. A., Biscoe, M. R. & Buchwald, S. L. A Highly Active Catalyst for Pd-Catalyzed Amination Reactions: Cross-Coupling Reactions Using Aryl Mesylates and the Highly Selective Monoarylation of Primary Amines Using Aryl Chlorides. *J. Am. Chem. Soc.* **130**, 13552-13554 (2008).

[9] Maiti, D., Fors, B. P., Henderson, J. L., Nakamura, Y. & Buchwald, S. L. Palladium-Catalyzed Coupling of Functionalized Primary and Secondary Amines with Aryl and Heteroaryl Halides: Two Ligands Suffice in Most Cases. *Chem. Sci.* **2**, 57-68 (2011).

[10] Davies, S. G., Fletcher, A. M., Kurosawa, W., Lee, J. A., Poce, G., Roberts, P. M., Thomson, J. E. & Williamson, D. M. One-Pot Conversions of Olefins to Cyclic Carbonates and Secondary Allylic and Homoallylic Amines to Cyclic Carbamates. *J. Org. Chem.* **75**, 7745-7756 (2010).

[11] Adelwöhrer, C., Yoneda, Y., Nakatsubo, F. & Rosenau, T. Synthesis of the perdeuterated cellulose solvents N-methylmorpholine N-oxide (NMMO-d11) and N,N-dimethylacetamide (DMAc-d9). *J. Label Compd. Radiopharm* **51**, 28-32 (2008).

[12] Kortunov, P. V., Siskin, M., Saunders Baugh, L. & Calabro, D. C. *In Situ* Nuclear Magnetic Resonance Mechanistic Studies of Carbon Dioxide Reactions with Liquid Amines in Aqueous Systems: New Insights on Carbon Capture Reaction Pathways. *Energy Fuels*, **29**, 5919-5939 (2015).

[13] Kortunov, P. V., Saunders Baugh, L. & Siskin, M. Pathways of the Chemical Reaction of Carbon Dioxide with Ionic Liquids and Amines in Ionic Liquid Solution. *Energy Fuels*, **29**, 5990-6007 (2015).

[14] Huckerby, T. N. Accurate Referencing of ^{13}C NMR Spectra from Glycosaminoglycan and other Polysaccharides in Aqueous Medium. *Organic Magnetic Resonance*, **21**, *1*, 67-70 (1983).