Supplementary Information

"Low viscosity alkanolguanidine and alkanolamidine liquids for CO_2 capture"

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General Experimental. All reactions were run under an atmosphere of argon, unless otherwise indicated. Solvents were transferred via plastic syringe or a dropping funnel. Flasks were oven-dried and cooled under vacuum. 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) **1**, 2-methyl-2-imidazoline **4**, 2-n-propyl-2-imidazoline **5**, 3-bromo-1-propanol, 6-bromo-1-hexanol, 2-chloro-1,3-dimethylimidazolinium chloride **9**, 1,1,3,3-tetraethylurea, 6-amino-1-hexanol, 5-amino-1-pentanol, 3-amino-2-propanol, 3-amino-2,2-dimethyl-1-propanol anhydrous Tetrahydrofuran (THF), triethylamine, oxalyl chloride, chlorotrimethylsilane (TMSCl) and dichloromethane (DCM) were purchased from commercially sources and used without purification. Selective silyl protection of the alcohol group was achieved following literature procedures.[1,2] High-resolution mass spectra (HRMS) and low-resolution mass spectra (MS) ESI accurate masses are reported for the molecular ion (M+1) or a suitable fragment ion. Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded with 300 MHz and 500MHz spectrometers. Chemical Shifts are reported in delta (δ) units, parts per million (ppm) downfield from tetramethylsilane. Coupling constants are reported in Hertz (Hz). Carbon-13 nuclear magnetic resonance (^{13}C NMR) spectra were recorded with 300 (75.5 MHz) and 500 (125.7 MHz) spectrometers. Chemical shifts are reported in delta (δ) units, parts per million (ppm) relative to the center of the triplet at 77.00 ppm for deuterochloroform. ^{13}C NMR spectra were routinely run with broadbrand. FTIR measurements were performed on NaCl disks using a Nicolet Magna-750 spectrometer running on OMNIC software. Vapor pressure and density measurements were performed by Wiltec Research Company, Inc, Provo, UT, U.S.A. Thermal conductivity, diffusivity and specific heat capacity were performed by ThermTest, Inc, Fredericton, NB, Canada.

10-(6-((trimethylsilyl)oxy)hexyl)-2,3,4,6,7,8,9,10-octahydropyrimido[1,2-a]azepine 2 A solution of *n*-BuLi (14 mL, 34.5 mmol, 2.5 M in hexanes) was added dropwise to a solution containing DBU (5.0g, 32.8 mmol) and THF (60 mL) at 0 °C. The reaction mixture was stirred at room temperature for 1h, and then 6-bromohexoxy)trimethylsilane (8.7g, 34.5 mmol) was added dropwise. The resulting solution was allowed to stir at room temperature overnight. At this point methanol (10 mL) was added and the solvent was evaporated in vacuo and the resulting residue was distilled under vacuum to afford (6.4g, 60%) of **2.** ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.58-3.35 (m, 7H) 3.08 (br s, 1H), 1.90 (br s, 2H), 1.8-1.53 (m, 8H) 1.43-1.38 (m, 2H), 1.33-1.32 (m, 7H), 0.03 (s, 9H). ^{13}C NMR (125.7 MHz, neat)□δ167.2, 61.7, 53.6, 49.9, 42.9, 38.3, 32.3, 28.7, 28.4, 26.9, 26.8, 25.2, 24.3 19.6, 0.5. FTIR (NaCl, film): 2926, 2852, 1608, 1484, 1424, 1364, 1312, 1207, 1105, 1062, 992, 714 cm^{-1} HRMS calculated [M+H$^+$] for $C_{18}H_{37}N_2OSi$ 325.2675 found 325.2673.

6-(2,3,4,6,7,8,9,10-octahydropyrimido[1,2-a]azepin-10-yl)hexan-1-ol (DBU-$(CH_2)_6$-OH **3a)** compound **2** (4.40 g, 13.5 mmol) was dissolved in methanol (50 mL) and the potassium carbonate (3.75g, 27.1 mmol) was added, the mixture was stirred at room temperature for 1h. The reaction mixture was diluted with an equal volume of chloroform followed by filtration and then evaporation in vacuo. The residue was distilled under vacuum to afford compound **3a** (3.25g, 95%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.51 (t, *J* = 6.0 Hz, 2H), 3.30 (m, 2H) 3.23 (t, *J* = 6.0 Hz, 2H), 3.14 (m, 2H), 2.37 (s, 1H), 1.77 (t, *J* = 6.0, 4H) 1.63-1.55 (m, 10H), 1.33-1.31 (m, 6H). ^{13}C NMR (125.7 MHz, neat)□δ163.2, 62.5, 51.9, 49.1, 44.2, 32.9, 32.1, 31.6, 29.7, 28.0, 27.6, 25.9, 22.7. FTIR (NaCl, film): 3178, 2926, 2853, 1616, 1486, 1443, 1365, 1313, 1235, 1200, 115, 1063, 992 cm^{-1} HRMS calculated [M+H$^+$] for $C_{15}H_{29}N_2O$ 253.2280 found 253.2281.

3-(2-methyl-4,5-dihydro-1H-imidazol-1-yl)propan-1-ol 6a 2-methyl-2-imidazoline (5.0g, 59.50 mmol), 3-bromo-1-propanol (9.93g, 71.42 mmol), DBU (10.7 mL, 71.42 mmol) and THF (12 mL) were charged into a clean dry flask. The mixture was heated at 60 °C for 12h. The resulting white solid was filtered off and the filtrate was isolated, THF was removed in *vacuo*. Fractional distillation of the residue furnished compound **6a** (3.5g, 41%). Improved yields can be obtained by running this reaction for a longer time. ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.67 (2t, *J* = 9.0 Hz, 4H), 3.03 (t, *J* = 9.0 Hz, 2H), 3.23 (t, *J* = 6.0 Hz, 2H), 1.94 (s, 3H), 1.74 (quin, *J* = 6.0Hz, 2H). ^{13}C NMR (125.7 MHz), $CDCl_3$) δ 170.6, 63.5, 48.9, 48.7, 39.0, 30.8, 23.2. FTIR (NaCl, film): 3277, 2932, 2863, 1653, 1607, 1495, 1429, 1374, 1275, 1061, 937 cm^{-1} HRMS calculated [M+H$^+$] for $C_7H_{15}N_2O$ 143.1184 found 143.1180.

6-(2-methyl-4,5-dihydro-1H-imidazol-1-yl)hexan-1-ol (7a) Following the same procedure as for **6a** using 2-methyl-2-imidazoline (1.0g, 11.90 mmol), 6-bromo-1-hexanol (2.6g, 14.3 mmol), DBU (2.2 mL, 14.3 mmol) and THF 12 mL provided compound **7a** (1.3 g, 60%). ^{1}H NMR (500 MHz, $CDCl_3$) δ3.65 (2t, *J* = 6.5Hz, 4H), 3.26 (t, *J* = 8.0 Hz, 2H), 3.05 (t, *J* = 9.0 Hz, 2H), 1.91 (s, 3H), 1.63-1.55 (quin, *J* = 8.0 Hz, 2H), 1.54-1.49 (quin, *J* = 8.0 Hz, 2H), 1.40-1.37 (m, 4H). ^{13}C NMR (125.7 MHz, $CDCl_3$) δ 170.6, 62.2, 49.2, 48.6, 38.9, 32.5, 29.6, 26.8, 25.5, 23.

FTIR (NaCl, film): 3281, 2930, 2857, 1657, 1610, 1562, 1431, 1372, 1275, 1058 cm^{-1} HRMS calculated [M+H^+] for $C_{10}H_{21}N_2O$ 185.1654 found 185.1652

6-(2-propyl-4,5-dihydro-1H-imidazol-1-yl)hexan-1-ol (8a) Following the same procedure as for **6a** using 2-propyl-2-imidazoline (5.0g, 44.6 mmol), 6-bromo-1-hexanol (9.63g, 53.53 mmol), DBU (8.0 mL, 53.54 mmol) and THF 45 mL provided compound **8a** (4.0 g, 42%) ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.65 (t, *J* = 9.0 Hz, 4H), 3.24 (t, *J* = 9.0 Hz, 2H), 3.03 (t, *J* = 8.0 Hz, 2H), 2.14 (t, *J* = 8.0 Hz, 2H), 1.85 (s, 1H), 1.69-1.62 (quin, *J* = 8.0Hz, 2H), 1.60-1.57 (quin, *J* = 8.0Hz, 2H), 1.56- 1.49 (quin *J* = 8.0 Hz, 2H), 1.41- 1.31 (m, 4H), 0.98 (t, *J* = 8.0Hz, 3H). ^{13}C NMR (75.5 MHz, neat) δ167.6, 62.2, 51.8, 49.9, 46.7, 32.7, 29.8, 28.6, 26.6, 25.6, 19.8, 14.0. FTIR (NaCl, film): 3283, 2931, 2859, 1651, 1606, 1457, 1378, 1216, 1058, 996, 731 cm^{-1} HRMS calculated [M+1] for $C_{12}H_{25}N_2O$ 213.1967 found 213.1965.

N-(1,3-dimethylimidazolidin-2-ylidene)-5-((trimethylsilyl)oxy)pentan-1-amine (10) A solution of 2-Chloro-1,3-dimethylimidazolinium chloride **9** (100g, 0.59 mol) in dichloromethane (200 mL) was added dropwise to a cooled (0 °C) solution of 5-((trimethylsilyl)oxy)pentan-1-amine (104g, 0.59 mol) and triethylamine (165 mL, 1.18 mol) in dichloromethane (200 mL). The resulting mixture was stirred at 25 °C for 72 hours. The solvent volume was reduced by rotary evaporation and the resulting solution was extracted with 30% aqueous KOH (3X100mL). The organic extracts were dried over anhydrous $MgSO_4$, filtered, and the solvent was removed under reduced pressure. The product was purified by vacuum distillation to afford compound **10a** (123.5 g, 77% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.58 (t, *J* = 6.0 Hz, 2H), 3.34 (t, *J* = 6.0 Hz, 2H), 3.14 (s, 4H), 2.84 (br s, 3H), 2.72 (br s, 3H) 1.54 (quin, *J* = 6.0 4H), 1.40 (quin, *J* = 60 Hz, 2H), 011 (s, 9H). ^{13}C NMR (125.7 MHz, $CDCl_3$) δ157.0, 62.6, 49.3, 47.3, 33.0, 32.5, 23.3, 0.6. FTIR (NaCl, film): 2932, 2859, 1664, 1480, 1435, 1381, 1250, 1093, 841, 747 cm^{-1} and MS calculated [M+H^+] for $C_{10}H_{29}N_3OSi$ 272.2 found 272.2.

5-((1,3-dimethylimidazolidin-2-ylidene)amino)pentan-1-ol (11a) Compound **10** (122.1g, 0.45 mol) was dissolved in methanol (500 mL) and potassium carbonate (68.2g, 0.49 mol) was added, the resulting mixture was allowed to stir at room temperature for 1h. At this point the product was filtered and methanol was removed by rotary evaporation, followed by vacuum distillation of the resultant solution to provide the desired compound **11a**, (46g, 51% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.67 (t, *J* = 5.0 Hz, 2H), 3.35 (t, *J* = 5.0 Hz, 2H), 3.14 (s, 4H), 2.88 (s, 3H), 2.69 (s, 3H) 1.65-1.57 (m, 4H), 1.48 (quin, *J* = 10Hz, 2H). ^{13}C NMR (125.7 MHz, $CDCl_3$) δ157.6, 61.6, 48.6, 47.2, 32.3, 32.1, 23.2. FTIR (NaCl, film): 3338, 2930, 2856, 1652, 1480, 1441, 1381, 1265, 1061, 1025, 955, 724, 641 cm^{-1}. MS calculated [M+H^+] for $C_{10}H_{22}N_3O$ 199.2 found 199.2.

N-(1,3-dimethylimidazolidin-2-ylidene)-6-((trimethylsilyl)oxy)hexan-1-amine (**12**) Following the same procedure as for **10** using 2-Chloro-1,3-dimethylimidazolinium chloride **9** (55.9g, 0.33 mol), 6-((trimethylsilyl)oxy)hexan-1-amine (62.6g, 0.33 mol) and triethylamine (101.3 mL, 0.73 mol) affords compound **12** (56.8 g, 60%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.57 (t, *J* = 6.0 Hz, 2H), 3.34 (t, *J* = 6.0 Hz, 2H), 3.14 (s, 4H), 2.89 (br s, 3H), 2.69 (br s, 3H) 1.55 (quin, *J* = 6.0 4H), 1.36 (quin, *J* = 60 Hz, 4H), 011 (s, 9H). ^{13}C NMR (125.7 MHz, $CDCl_3$) δ156.9, 62.5, 49.3, 47.4, 33.3, 32.6, 27.0, 25.6, 0.6. FTIR (NaCl, film): 2930, 2856, 1667, 1480, 1435, 1381, 1250, 1092, 1022,873, 840, 752, 722 $cm^{-1}$and MS calculated [M+H^+] for $C_{14}H_{31}N_3OSi$ 286.2 found 286.3.

6-((1,3-dimethylimidazolidin-2-ylidene)amino)hexan-1-ol (13a) Following the same procedure as for **11a** using compound **12** (56.0g, 0.20 mol), methanol (100 mL) and potassium carbonate (27.1g, 0.20 mol) provides compound **13a**, (30.7g, 73% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.63 (t, *J* = 6.0 Hz, 2H), 3.34 (t, *J* = 6.0 Hz, 2H), 3.14 (s, 4H), 2.87 (br s, 3H), 2.69 (br s, 3H) 1.55 (quin, *J* = 6.0 Hz 4H), 1.39 (quin, *J* = 60 Hz, 4H). ^{13}C NMR (75.4 MHz, $CDCl_3$) δ157.6, 62.0, 49.3, 47.4, 36.5, 33.1, 32.7, 27.0, 25.6, 0.6. FTIR (NaCl, film): 3225, 2928, 2853, 1645, 1482, 1439, 1383, 1065, 957, 724, 640 cm^{-1} and MS calculated [M+H^+] for $C_{11}H_{24}N_3O$ 214.2 found 214.2.

N-(1-butyl-3-methylimidazolidin-2-ylidene)-5-((trimethylsilyl)oxy)pentan-1-amine 15. 1-butyl-3-methylimidazolidin-2-one (9.5g, 60.8 mmol) was dissolved in anhydrous benzene (10 mL) and the solution was cooled to 0 °C. To this solution oxalyl chloride (5.7 mL, 66.9 mmol) was added dropwise via a dropping funnel, the resulting solution was refluxed for 5 hours, and then allowed to sit at room temperature overnight. The resulting suspension was decanted under a nitrogen atmosphere leaving a solid, which was then washed with benzene 2X 100 mL to give 1-butyl-2-chloro-3-methyl-4,5-dihydro-1H-imidazol-3-ium chloride **14** (12.9, 93%). Following the same procedure as for **10** using 1-butyl-2-chloro-3-methyl-4,5-dihydro-1H-imidazol-3-ium chloride **14** (12.9g, 60.8 mmol), 5-((trimethylsilyl)oxy)pentan-1-amine (10.6g, 60.8 mmol) and triethylamine (17 mL, 12.9 mol) affords

compound **15** (56.8 g, 26%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.58 (t, *J* = 6.0 Hz, 2H), 3.29 (t, *J* = 6.0 Hz, 2H), 3.14 (s, 4H), 2.85 (br s, 3H), 2.68 (br s, 3H) 1.61-1.55 (m, 6H), 1.43-1.27 (m, 4H) 0.93 (t, *J* = 6.0 Hz, 3H), 0.10 (s, 9H). ^{13}C NMR (125.7 MHz, $CDCl_3$) δ156.4, 62.6, 49.3, 47.3, 46.6, 32.9, 32.5, 30.1, 29.4, 23.3, 19.9, 13.8, -0.6. FTIR (NaCl, film): 2955, 2931, 2860, 1664, 1479, 1367, 1250, 1093, 840, 747 cm^{-1} and MS calculated [M+H$^+$] for $C_{16}H_{35}N_3OSi$ 314.2 found 314.3.

5-((1-butyl-3-methylimidazolidin-2-ylidene)amino)pentan-1-ol (16a). Following the same procedure as for **11a** using compound **15** (4.90g, 15.0 mmol), methanol (100 mL) and potassium carbonate (0.2g, 1.5 mmol) provides compound **16a**, (3.0g, 80% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.58 (t, *J* = 6.0 Hz, 2H), 3.29 (t, *J* = 6.0 Hz, 2H), 3.14 (s, 4H), 2.85 (br s, 3H), 2.68 (br s, 3H) 1.61-1.55 (m, 6H), 1.43-1.27 (m, 4H) 0.93 (t, *J* = 6.0 Hz, 3H), 0.10 (s, 9H). ^{13}C NMR (75.4 MHz, $CDCl_3$) δ157.0, 62.1, 49.1, 47.5, 46.9, 32.3, 29.4, 23.4, 20.0, 13.9. FTIR (NaCl, film): 3365, 2929, 2859, 1641, 1481, 1457, 1368, 1264, 1059, 723 cm^{-1} and MS calculated [M+H$^+$] for $C_{13}H_{28}N_3O$ 242.2 found 242.3.

1,1,3,3-tetraethyl-2-(5-((trimethylsilyl)oxy)pentyl)guanidine 18. 1,1,3,3-tetraethylurea (10g, 58.0 mmol) was dissolved in anhydrous benzene (10 mL) and the solution was cooled to 0 °C. To this solution oxalyl chloride (5.5 mL, 63.8 mmol) was added dropwise via a dropping funnel, the resulting solution was refluxed for 5 hours, and then allowed to sit at room temperature overnight. The resulting suspension was evaporated to dryness and further dried under high vacuum to afford crude N-(chloro(diethylamino)methylene)-N-ethylethanaminium **17** (10.54g). Following the same procedure as for **10** using crude N-(chloro(diethylamino)methylene)-N-ethylethanaminium **17** (10.54g), 5-((trimethylsilyl)oxy)pentan-1-amine (8.13g, 46.4 mmol) and triethylamine (13 mL, 92.8 mol) affords compound **18** (10.1 g, 66%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.57 (t, *J* = 6.0 Hz, 2H), 3.11 (t, *J* = 6.0 Hz, 4H), 3.00 (q, *J* = 6.0 Hz, 4H), 1.53 (quin, *J* = 6.0 Hz, 4H), 1.35 (quin, *J* = 60 Hz, 2H), 1.03 (t, *J* = 6.0 Hz, 12H), 010 (s, 9H). ^{13}C NMR (75.4 MHz, $CDCl_3$) δ158.2, 62.6, 49.5, 44.4, 41.3, 32.5, 32.2, 23.7, 13.5, 12.8, 0.7. ^{13}C NMR (125.7 MHz, $CDCl_3$) δ158.0, 62.7, 49.7, 42.4, 41.3, 32.6, 32.4, 23.7, 13.5, 12.8, -0.6. FTIR (NaCl, film): 2965, 2932, 2863, 1613, 1457, 1402, 1375, 1250, 1096, 840, 752, 683 cm^{-1} and MS calculated [M+H$^+$] for $C_{17}H_{40}N_3OSi$ 330.3 found 330.3.

1,1,3,3-tetraethyl-2-(5-hydroxypentyl)guanidine (19a) Following the same procedure as for **11a** using compound **18** (10.0 g, 30.3 mmol), methanol (100 mL) and potassium carbonate (0.42g, 3.0 mmol) provides compound **19a**, (5.5g, 71% yield).) δ 3.62 (t, *J* = 6.0 Hz, 2H), 3.11 (t, *J* = 6.0 Hz, 4H), 3.02 (q, *J* = 6.0 Hz, 4H), 1.58 (quin, *J* = 6.0 Hz, 4H), 1.43 (quin, *J* = 60 Hz, 2H), 1.02 (t, *J* = 6.0 Hz, 12H). ^{13}C NMR (75.4 MHz, $CDCl_3$) δ158.6, 62.0, 49.3, 42.5, 41.4, 32.4, 31.7, 23.6, 13.5, 12.8. FTIR (NaCl, film): 3193, 2967, 2930, 2866, 1593, 1458, 1410, 1376, 1265, 1070, 839, 781 cm^{-1} and MS calculated [M+H$^+$] for $C_{14}H_{32}N_3O$ 258.2 found 258.2.

N-(1,3-dimethylimidazolidin-2-ylidene)-2-((trimethylsilyl)oxy)propan-1-amine (20) Using the same procedure as for compound **10** reaction of 2-Chloro-1,3-dimethylimidazolinium chloride **9** (1101.1g, 6.5 mol) in dichloromethane (1000ML) and 2-((trimethylsilyl)oxy)propan-1-amine (1055g, 7.16 mol) and triethylamine (1997 mL, 14.3 mol) in dichloromethane (500 mL) affords compound **20** (700g, 2.88 mol, 44% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.84 (sex, *J* = 6.0 Hz, 1H), 3.50 (dd, *J* = 6.0 Hz, 3.0 Hz 2H), 3.17 (s, 4H), 2.89 (br s, 3H), 2.68 (br s, 3H) 1.18 (d, *J* = 3.0Hz, 3H), 013 (s, 9H). ^{13}C NMR (75.4 MHz, $CDCl_3$) δ157.8, 66.7, 53.8 , 48.9, 35.6, 20.0,1.9. FTIR (NaCl, film): 3305, 2961, 2869, 1668, 1484, 1445, 1380, 1249, 1093, 1024, 1003, 891, 840, 749 cm^{-1} and MS calculated [M+H$^+$] for $C_{11}H_{25}N_3OSi$ 244.2 found 244.2.

1-((1,3-dimethylimidazolidin-2-ylidene)amino)propan-2-ol (21a) Following the same procedure as for **11a** compound **20** (700g, 2.88 mol) in methanol (1000 mL) reacts with potassium carbonate (436.9g, 3.16 mol) to provide the compound **21a**, (369g, 2.16 mol, 75% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.84-3.70 (m, 1H), 3.50 (dd, *J* = 6.0 Hz, 3.0 Hz 1H), 3.18 (s, 4H), 3.09 (dd, *J* = 6.0 Hz, 3.0 Hz 1H), 2.89 (br s, 3H), 2.74 (br s, 3H) 1.18 (d, *J* = 3.0Hz, 3H). ^{13}C NMR (75.4 MHz, $CDCl_3$) δ157.4, 66.9, 54.0, 48.4 (d), 35.4 (d), 19.4. FTIR (NaCl, film): 3432, 2963, 2927, 2837, 1667, 1483, 1439, 1385, 1269, 1065, 1020, 958, 723, 643 cm^{-1} and MS calculated [M+H$^+$] for $C_8H_{17}N_3O$ 172.1 found 172.2.

3-((1,3-dimethylimidazolidin-2-ylidene)amino)-2,2-dimethylpropan-1-ol 22. Using the same procedure as for compound **10** reaction of 2-Chloro-1,3-dimethylimidazolinium chloride **9** (12.5g, 74.1 mmol) in dichloromethane (100ML) and 2,2-dimethyl-3-((trimethylsilyl)oxy)propan-1-amine (13.0g, 74.1 mmol) and triethylamine (21 mL, 148.2 mmol) in dichloromethane (200 mL) affords compound **22** (13.6g, 68% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.38 (s, 2H), 3.12 (s, 6H), 2.86 (br s, 3H), 2.69 (br s, 3H), 0.87 (s, 6H), 0.08 (s, 9H). ^{13}C NMR (75.4 MHz, $CDCl_3$)

δ157.3, 74.4, 60.2, 49.2, 34.7, 34.5, 23.3, 1.8. FTIR (NaCl, film): 2987, 2932, 2860, 1640, 1457, 1402, 1250, 1093, 840, 755, 667 cm^{-1} and MS calculated [$M+H^+$] for $C_{13}H_{29}N_3OSi$ 272.2 found 272.2.

3-((1,3-dimethylimidazolidin-2-ylidene)amino)-2,2-dimethylpropan-1-ol 23a. Following the same procedure as for **11a** compound **22** (13.0g, 47.9 mmol) in methanol (100 mL) reacts with potassium carbonate (7.3g, 52.7 mol) to provide the compound **23a**, (5.0g, 52% yield). ^1H NMR (500 MHz, $CDCl_3$) δ 3.56 (s, 2H), 3.46 (s, 4H), 3.36 (s, 2H), 3.17 (s, 4H), 2.80 (br s, 6H), 0.95 (s, 6H). ^{13}C NMR (75.4 MHz, $CDCl_3$) δ157.1, 74.2, 60.0, 49.0, 35.8, 34.5, 23.1. FTIR (NaCl, film): 3247, 2950, 2866, 1663, 1484, 1417, 1384, 1277, 1054, 957, 725, 643 cm^{-1}, MS calculated [M+H+] for C10H22N3O 200.2 found 200.2.

Vapor Pressure

Table S1. Vapor Pressure Measurements for alkanolguanidine **21a**

Temperature °C	Measured	Correlated	Deviation %
102.00	1.21	1.29	-2.80%
108.58	2.07	2.05	0.37%
113.97	3.06	2.93	1.87%
118.41	4.10	3.88	2.41%
125.15	5.75	5.81	-0.48%
128.51	7.32	7.05	1.65%
139.96	12.67	13.00	-1.13%
140.01	13.17	13.03	0.46%
150.00	20.82	21.19	-0.78%
150.00	20.61	21.19	-1.22%
160.00	32.12	33.18	-1.40%
169.99	50.12	50.16	-0.04%
170.00	50.28	50.18	0.09%
179.89	73.43	73.29	0.08%
180.05	73.21	73.75	-0.32%
189.97	103.99	104.96	-0.40%
190.07	104.95	105.32	-0.15%
200.03	152.67	146.50	1.79%

Single crystal X-ray diffraction

Crystals for structure determination were held on Mitegen mounts with Paratone oil. Diffraction data were collected on a Bruker Apex II diffractometer using Mo radiation, integrated using the Bruker SAINT software, and corrected for absorption using the multi-scan method. Stuctures were solved and refined using the SHELX software suite.[3]

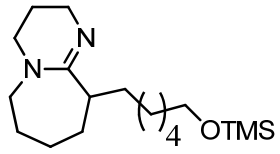
Viscosity measurements

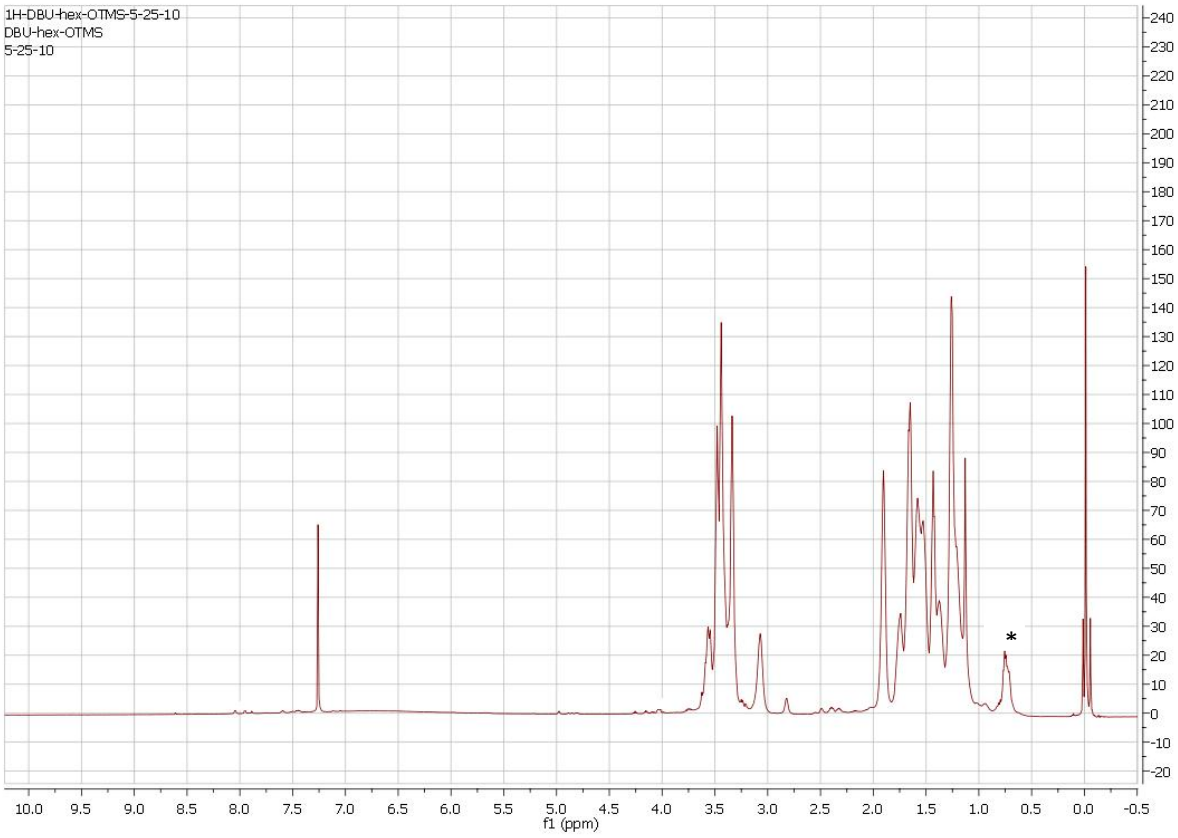
Viscosity was measured using viscometer VISCOPRO 2000 System (Cambridge Viscosity, Inc.) with the SPC-372 Sensor, and Density Software D2.11. This is a piston–style viscometer. The technology uses two magnetic coils within a stainless steel sensor. With the sensor inserted into pipe line, the magnetic piston is surrounded by the fluid sample deflected into measurement chamber. Two coils inside the sensor body are used to magnetically force the

piston back and forth a predetermined distance. By alternatively powering the coils with a constant force, the piston's roundtrip travel time is measured. An increase in viscosity is sensed as a slow piston travel time. The time required for the piston to complete a two way cycle is an accurate measure of viscosity. The deflecting fence acts continuously deflect fresh sample into the measurement chamber. The digital gear pump (Cole-Palmer brand) with flow rate about 100-110 ml/minute was uses to provide continuous flow of the testing liquid through the entire system. The system also includes the Parr 160 ml stainless steel cell, which was immersed into water bath to keep the temperature of the testing compound on the needed level. The same water bath was used to pump water through a thermal jacket surrounding the sensor to control the temperature and increase thermal stabilization inside the sensor. Submersible stirrer provides constant mixing of testing liquid (or liquid/injected gas) in the test cell. Special manifold system, including high capacity vacuum pump, was designed to inject known amount of gas into test cell. Required amount of (Ultra) High Purity CO_2 was accumulated initially in the 150ml syringe connected to the manifold and then injected into the cell under vacuum. The CO_2 injections were repeated as needed. The manifold also includes the pressure transducer and thermocouple. Another transducer was incorporated into test cell. A platinum resistance temperature detector (RTD) mounted at the base of the measurement chamber of the sensor. Final, correct amount of gas injected was calculated based on predetermined volume of the manifold and test cell as well as temperature and pressure data collected during the test. Viscosity was taken at the equilibrium pressure after each CO_2 injection.

^{1}H NMR ($CDCl_3$)

10-(6-((trimethylsilyl)oxy)hexyl)-2,3,4,6,7,8,9,10-octahydropyrimido[1,2-a]azepine (2.)

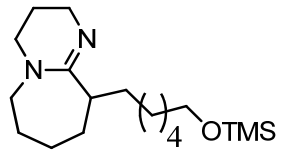


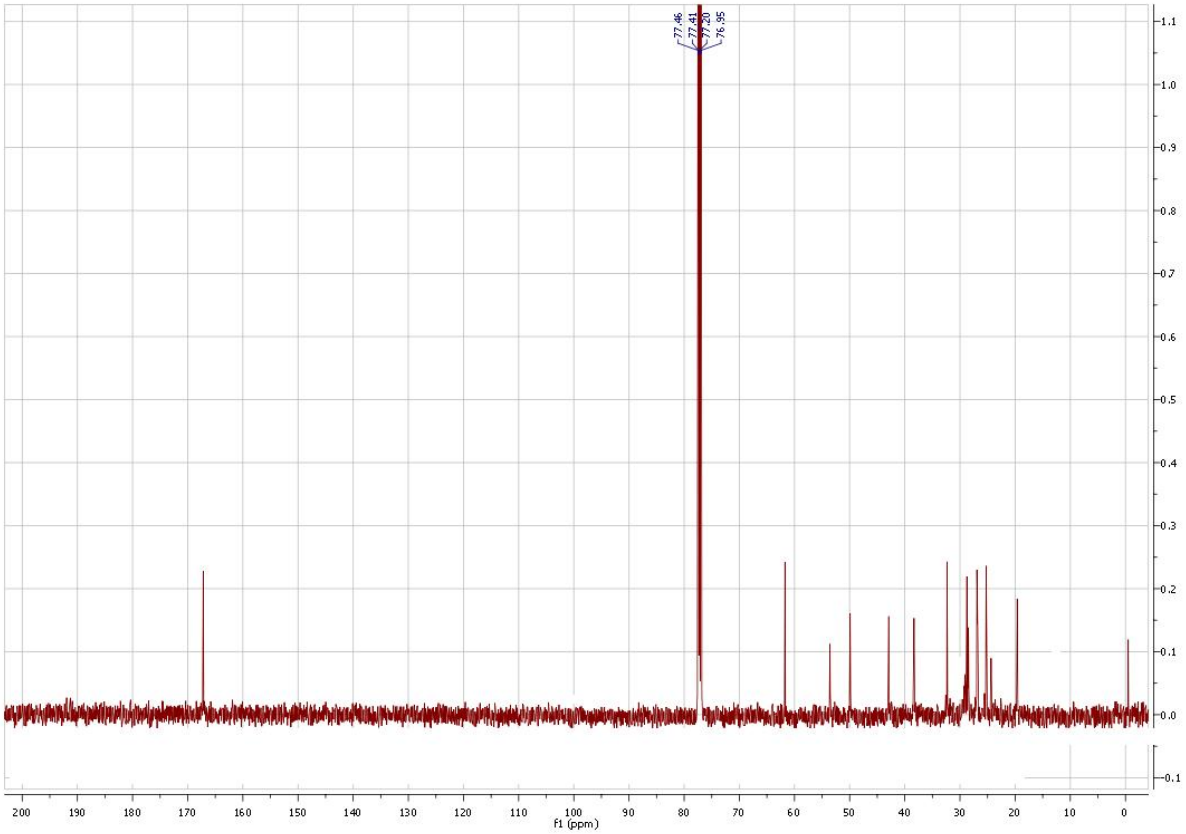


*This peak is attributed to grease contamination during vacuum distillation

^{13}C NMR ($CDCl_3$)

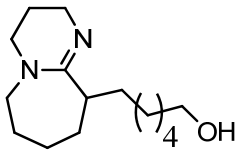
10-(6-((trimethylsilyl)oxy)hexyl)-2,3,4,6,7,8,9,10-octahydropyrimido[1,2-a]azepine (2.)

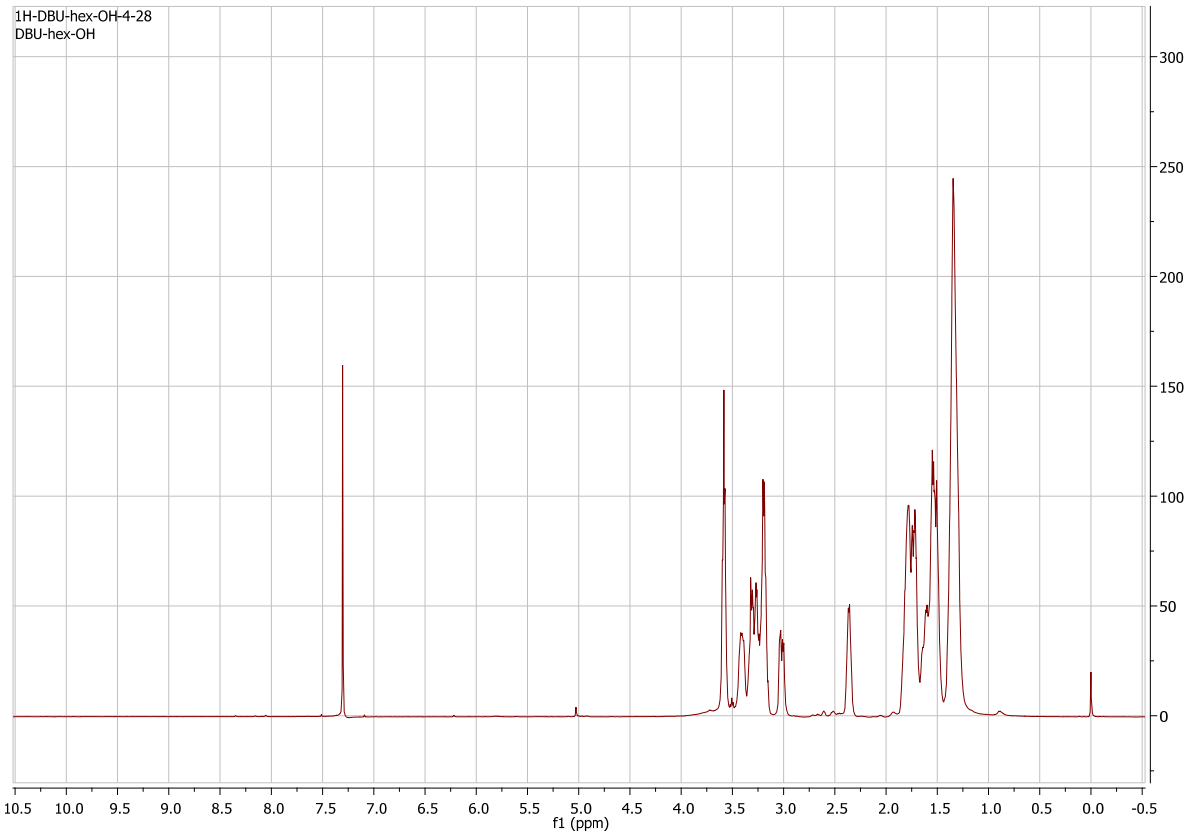




^{1}H NMR ($CDCl_3$)

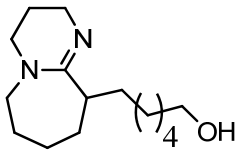
6-(2,3,4,6,7,8,9,10-octahydropyrimido[1,2-a]azepin-10-yl)hexan-1-ol (DBU-$(CH_2)_6$-OH **4a**)

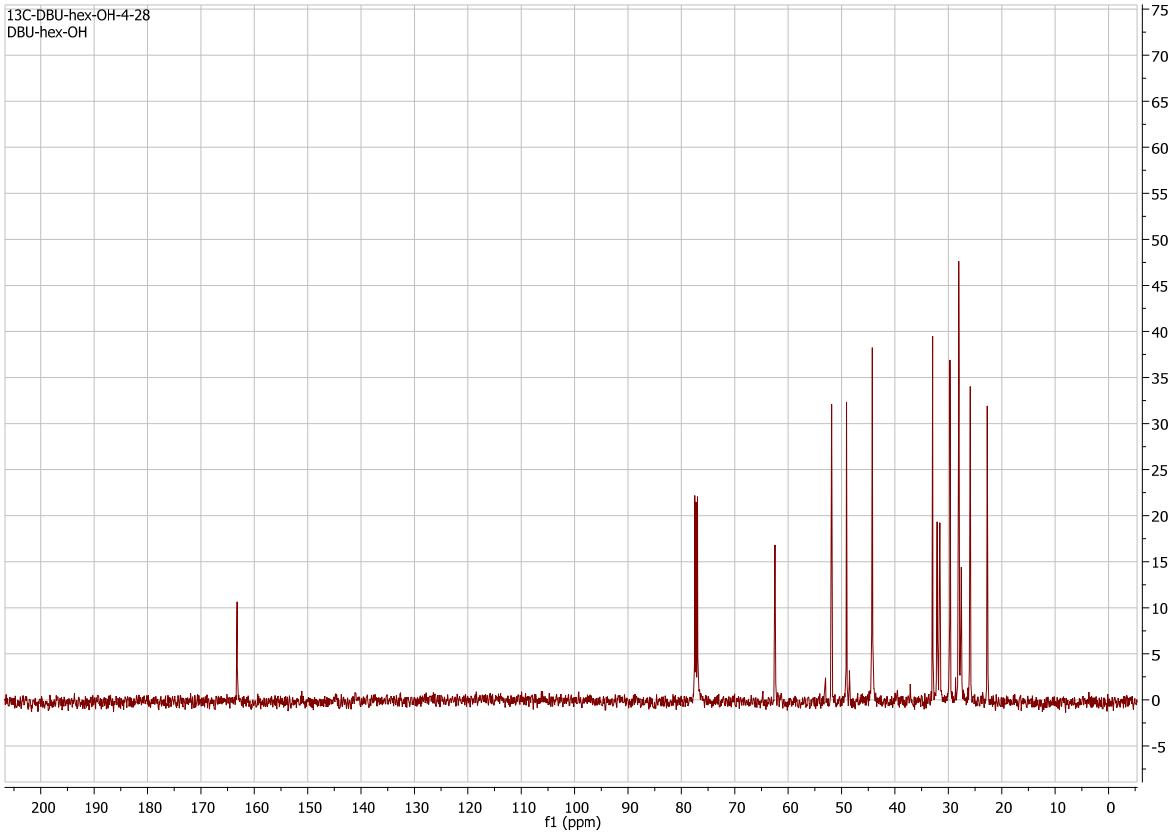




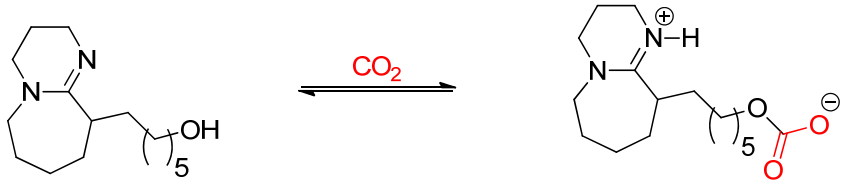
^{13}C NMR ($CDCl_3$)

6-(2,3,4,6,7,8,9,10-octahydropyrimido[1,2-a]azepin-10-yl)hexan-1-ol (DBU-$(CH_2)_6$-OH **4a**)



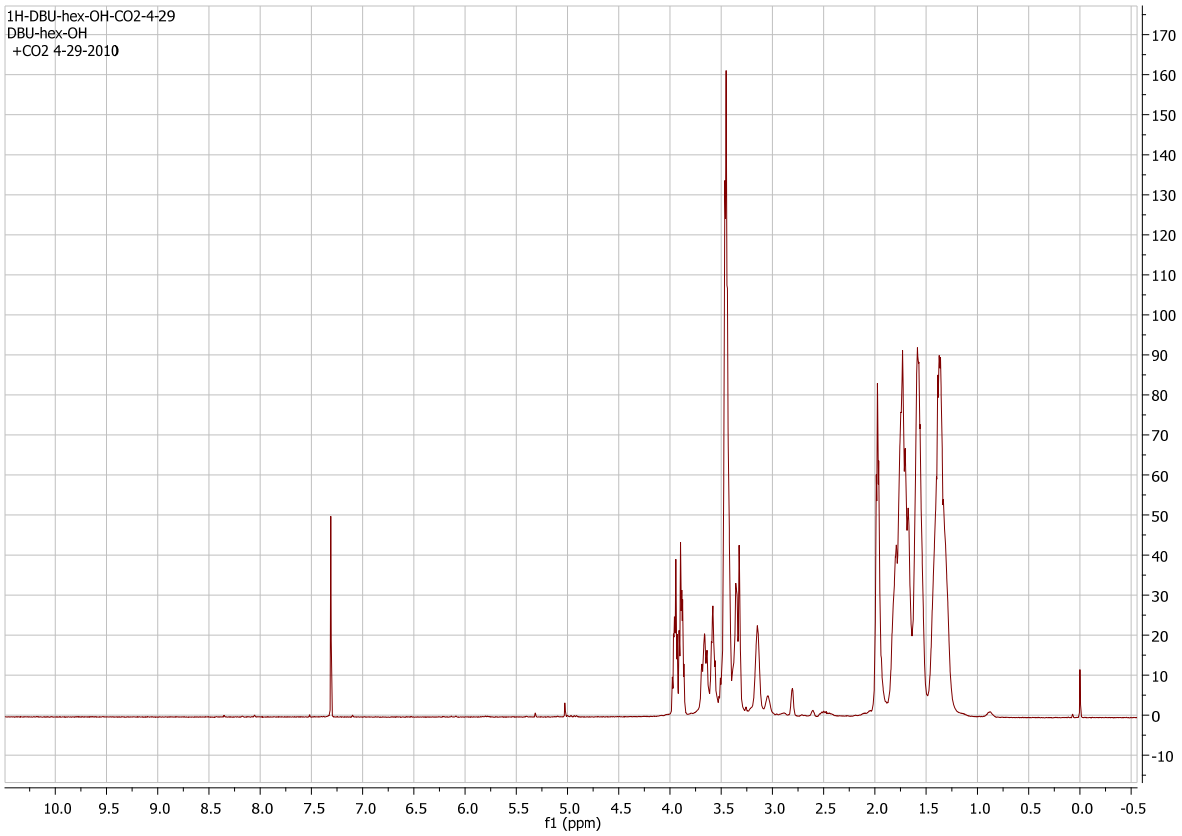


^{1}H NMR ($CDCl_3$)

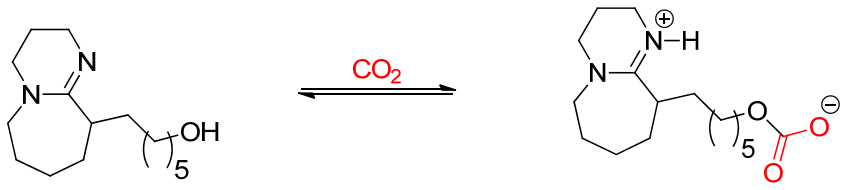


4a **4b**

Mixture of **4a** and **4b**

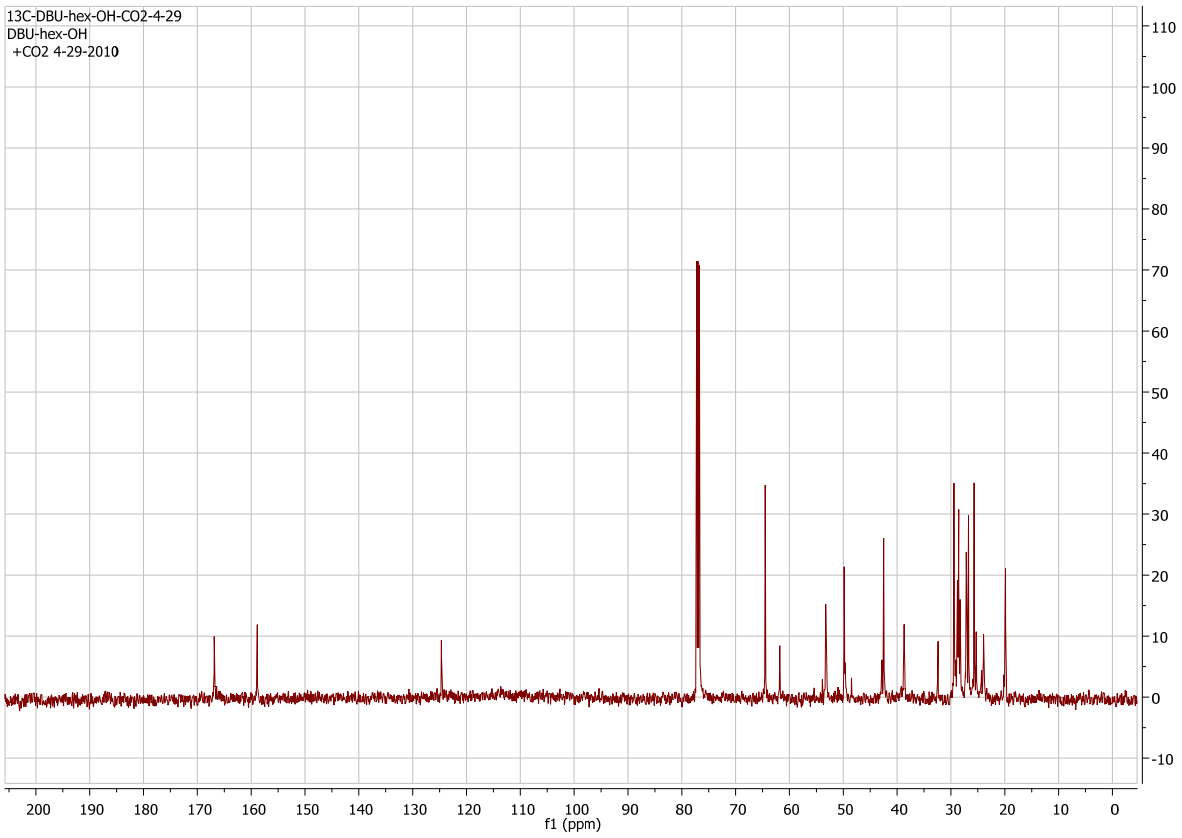


^{13}C NMR ($CDCl_3$)

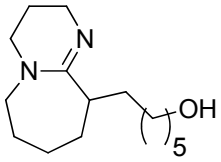


4a **4b**

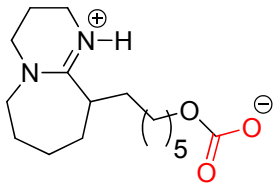
Mixture of **4a** and **4b** (1:4)



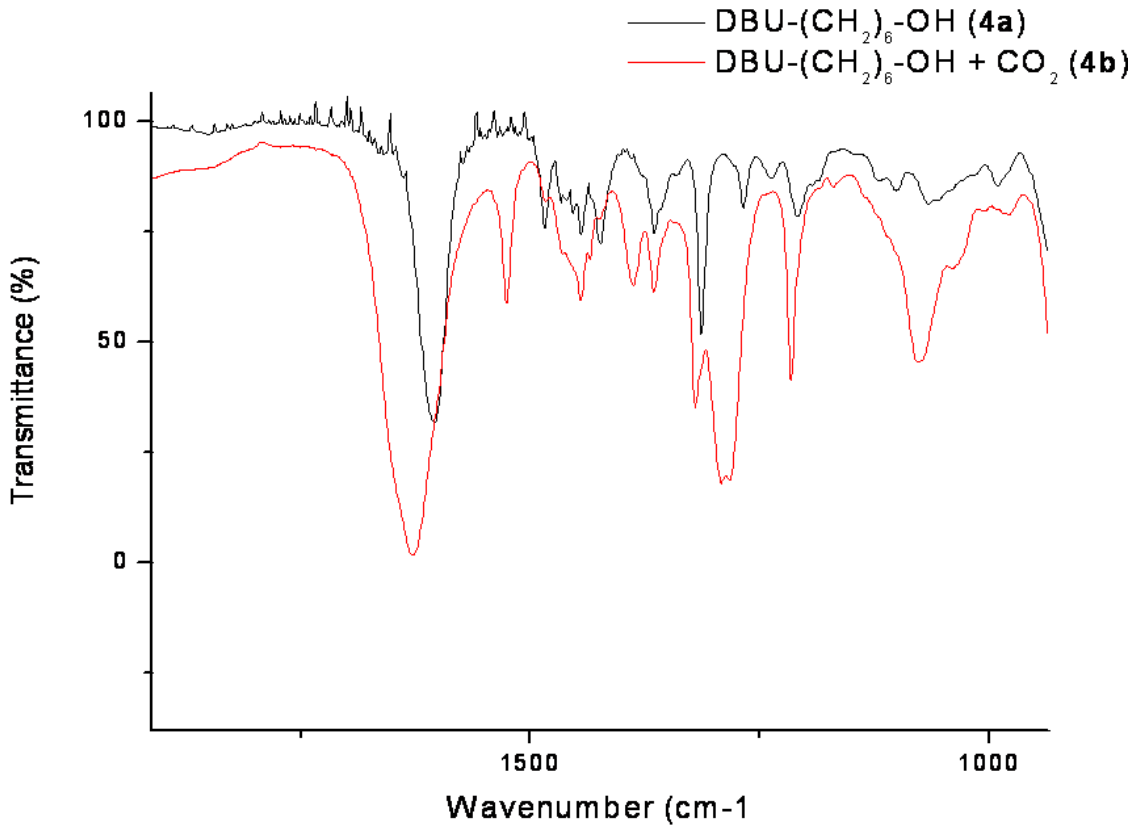
FTIR



DBU- $(CH_2)_6$-OH **4a**

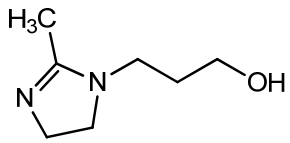


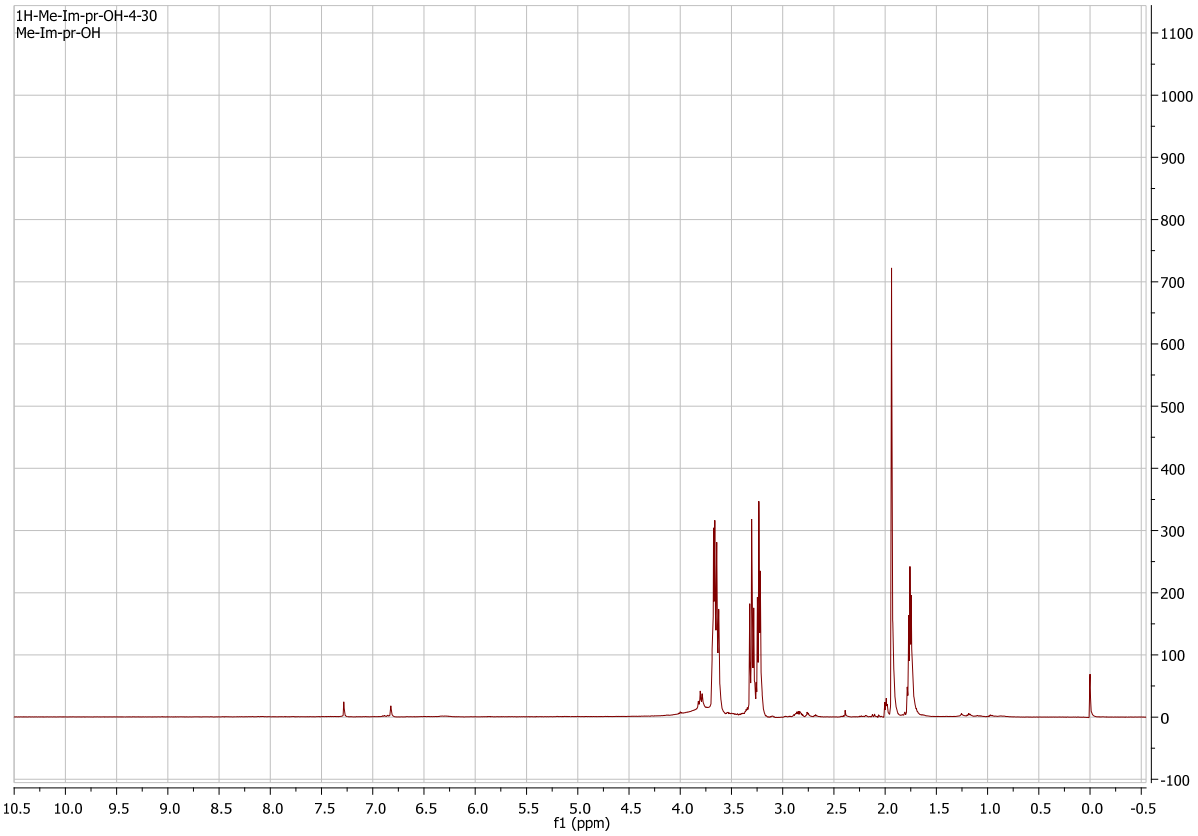
$^{+}$DBU-$(CH_2)_6$-OCO_2^{-} **4b**



^{1}H NMR ($CDCl_3$)

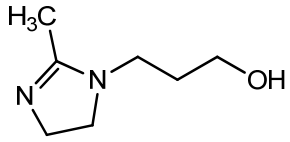
3-(2-methyl-4,5-dihydro-1H-imidazol-1-yl)propan-1-ol (6a)

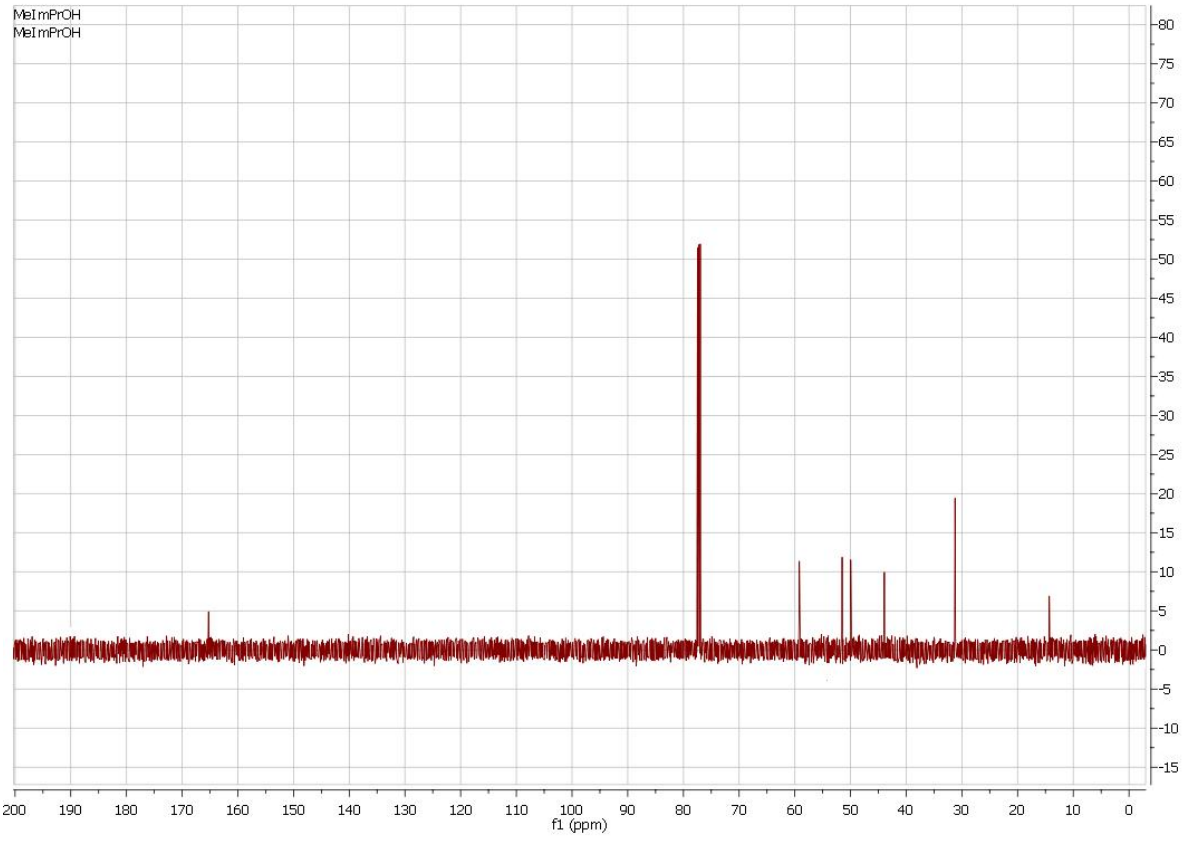




^{13}C NMR ($CDCl_3$)

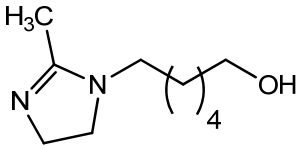
3-(2-methyl-4,5-dihydro-1H-imidazol-1-yl)propan-1-ol (6a)

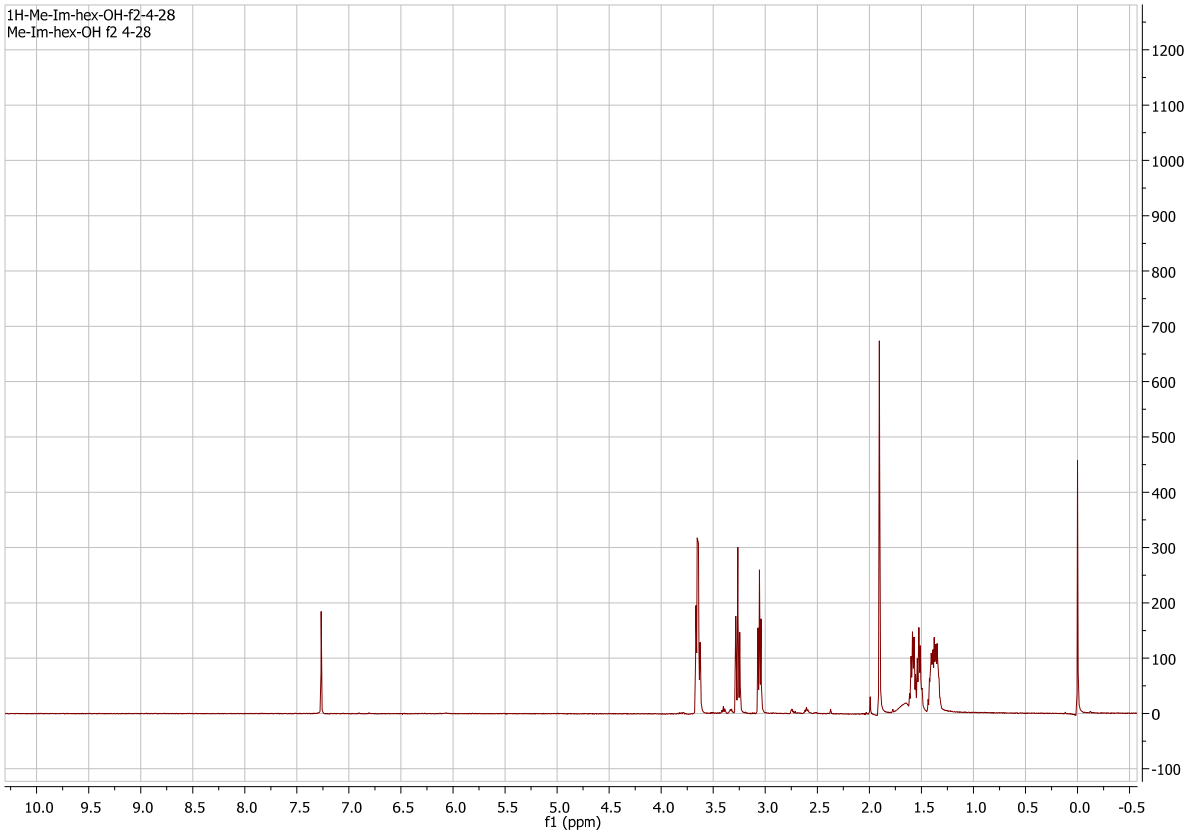




^{1}H NMR ($CDCl_3$)

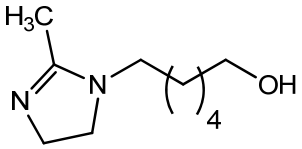
6-(2-methyl-4,5-dihydro-1H-imidazol-1-yl)hexan-1-ol (7a)

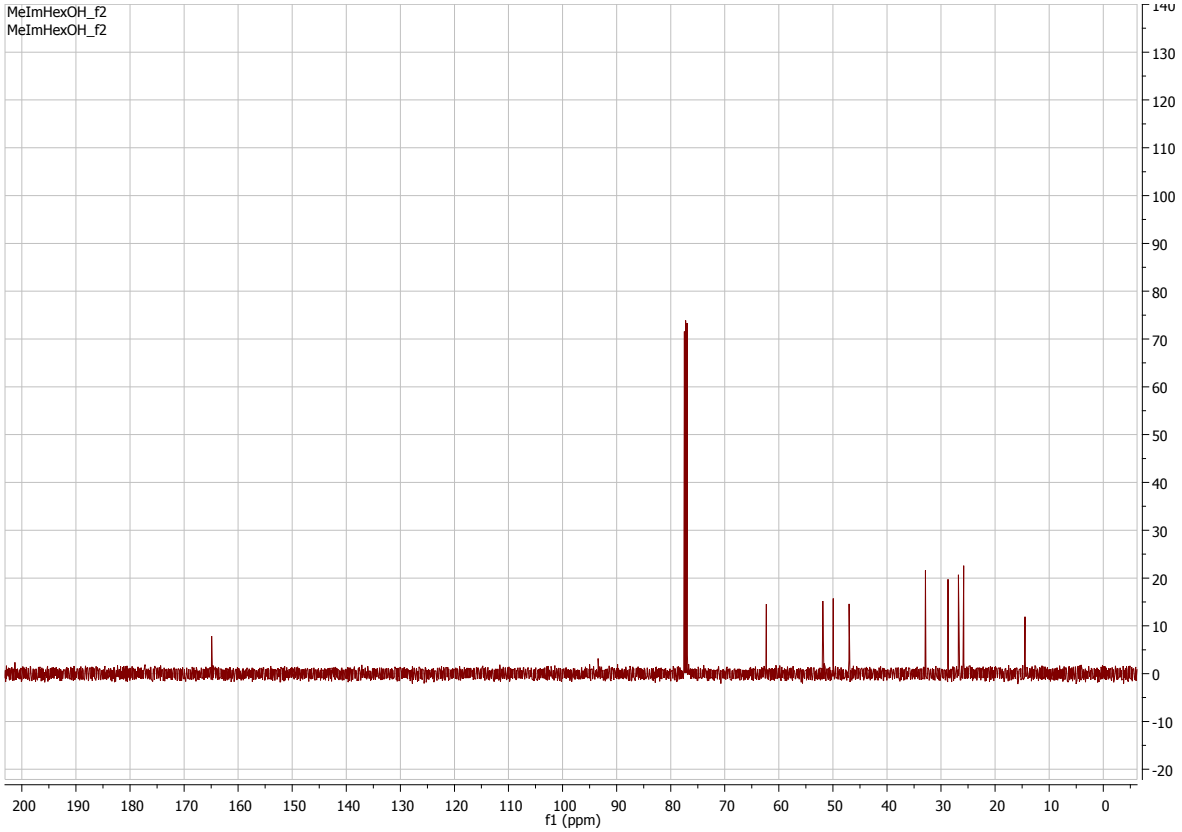




^{13}C NMR ($CDCl_3$)

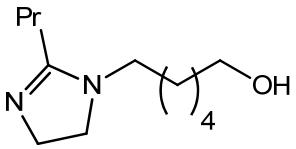
6-(2-methyl-4,5-dihydro-1H-imidazol-1-yl)hexan-1-ol (7a)

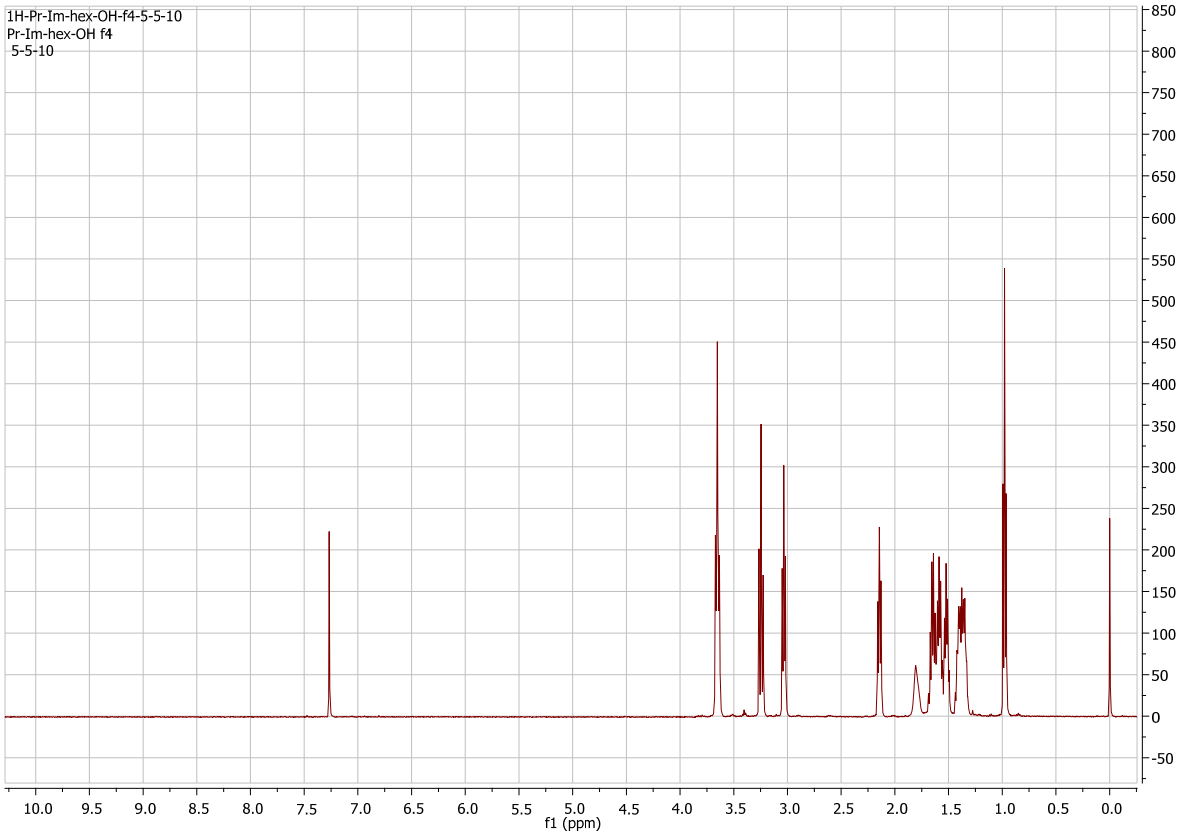




^{1}H NMR ($CDCl_3$)

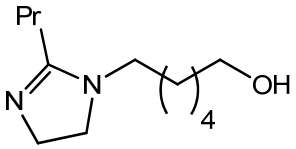
6-(2-propyl-4,5-dihydro-1H-imidazol-1-yl)hexan-1-ol (8a)

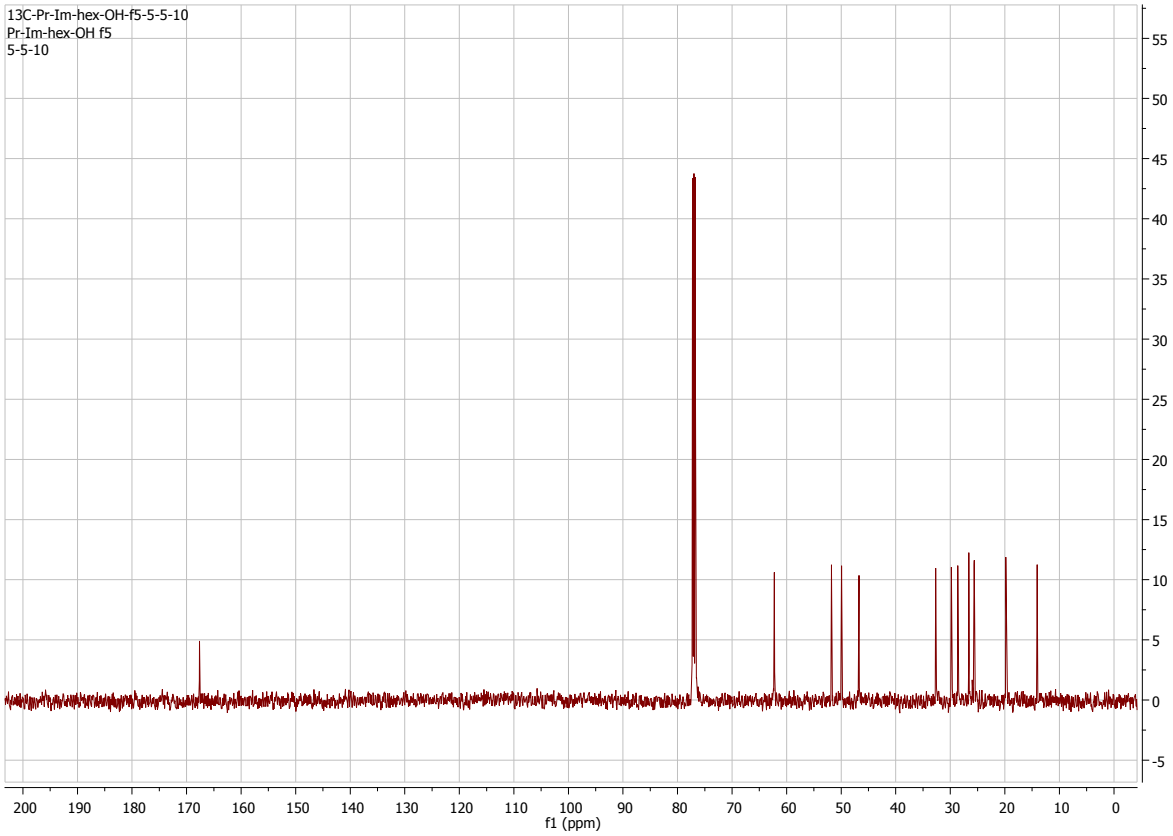




^{13}C NMR ($CDCl_3$)

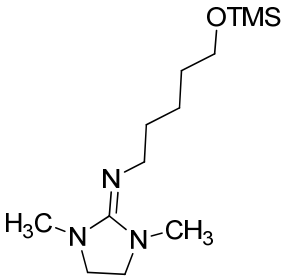
6-(2-propyl-4,5-dihydro-1H-imidazol-1-yl)hexan-1-ol (8a)

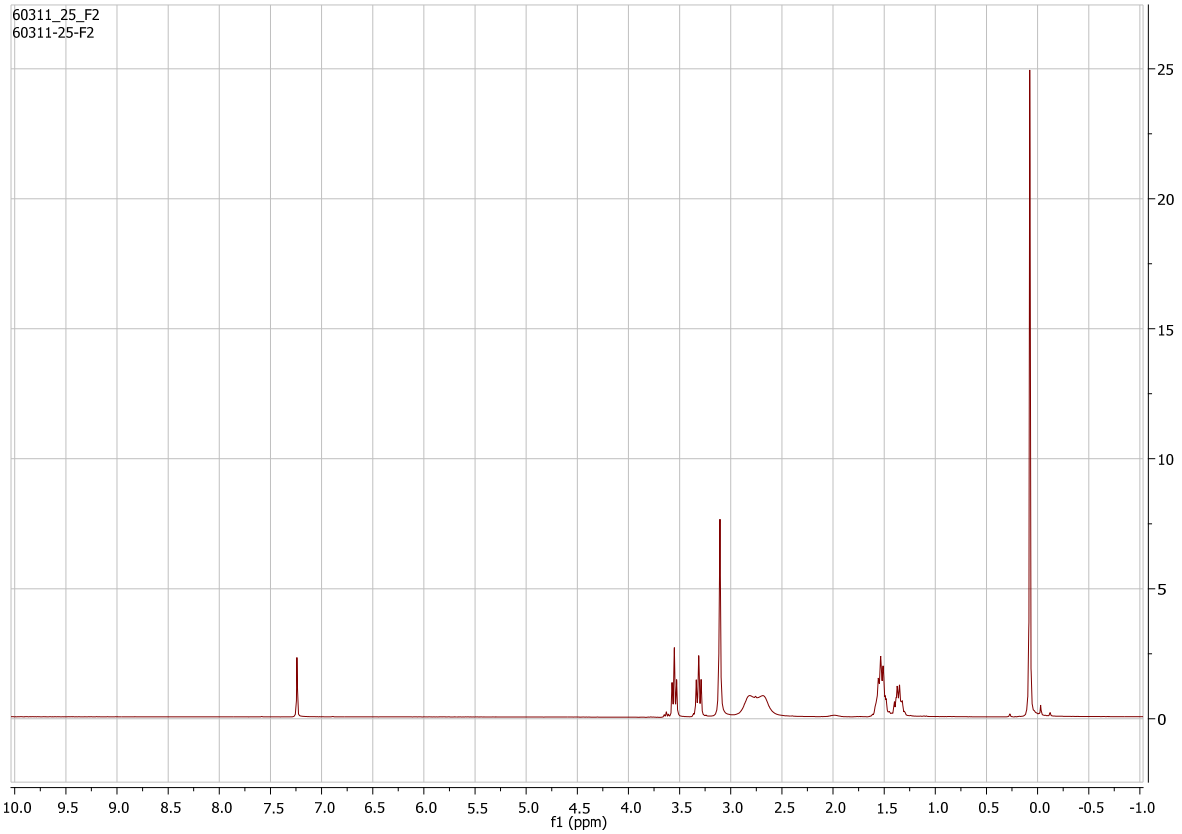




^{1}H NMR ($CDCl_3$)

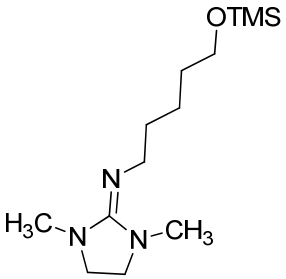
N-(1,3-dimethylimidazolidin-2-ylidene)-5-((trimethylsilyl)oxy)pentan-1-amine (10)

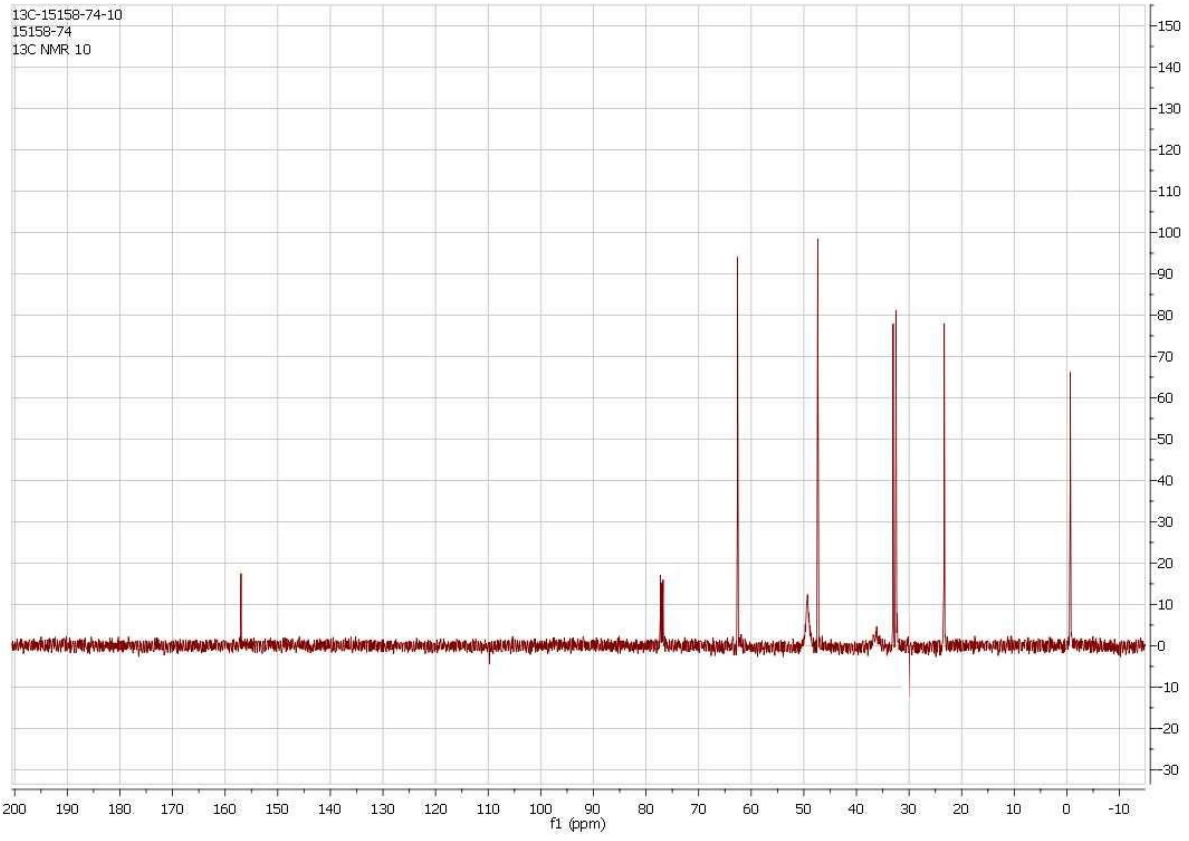




^{13}C NMR ($CDCl_3$)

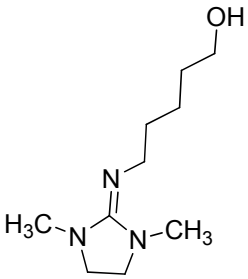
N-(1,3-dimethylimidazolidin-2-ylidene)-5-((trimethylsilyl)oxy)pentan-1-amine (10)

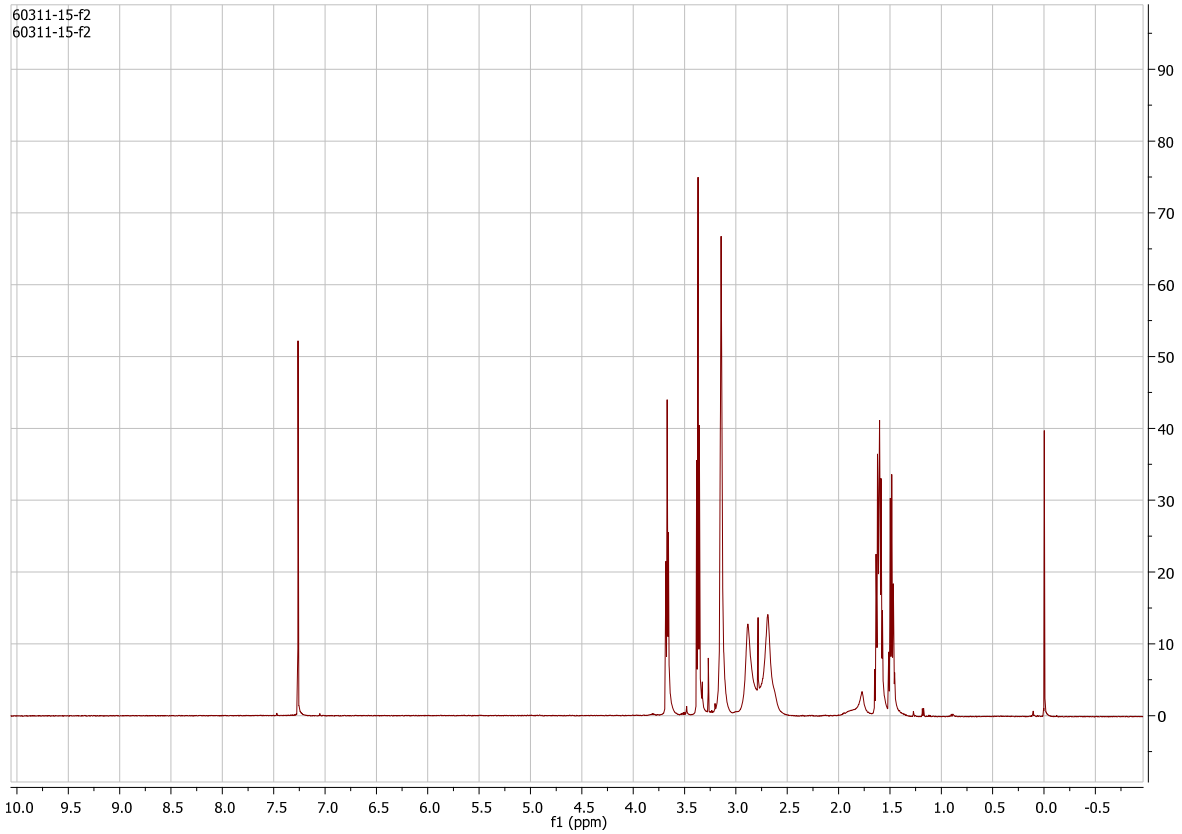




^{1}H NMR ($CDCl_3$)

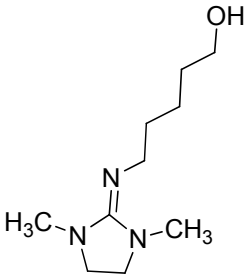
5-((1,3-dimethylimidazolidin-2-ylidene)amino)pentan-1-ol (11a)

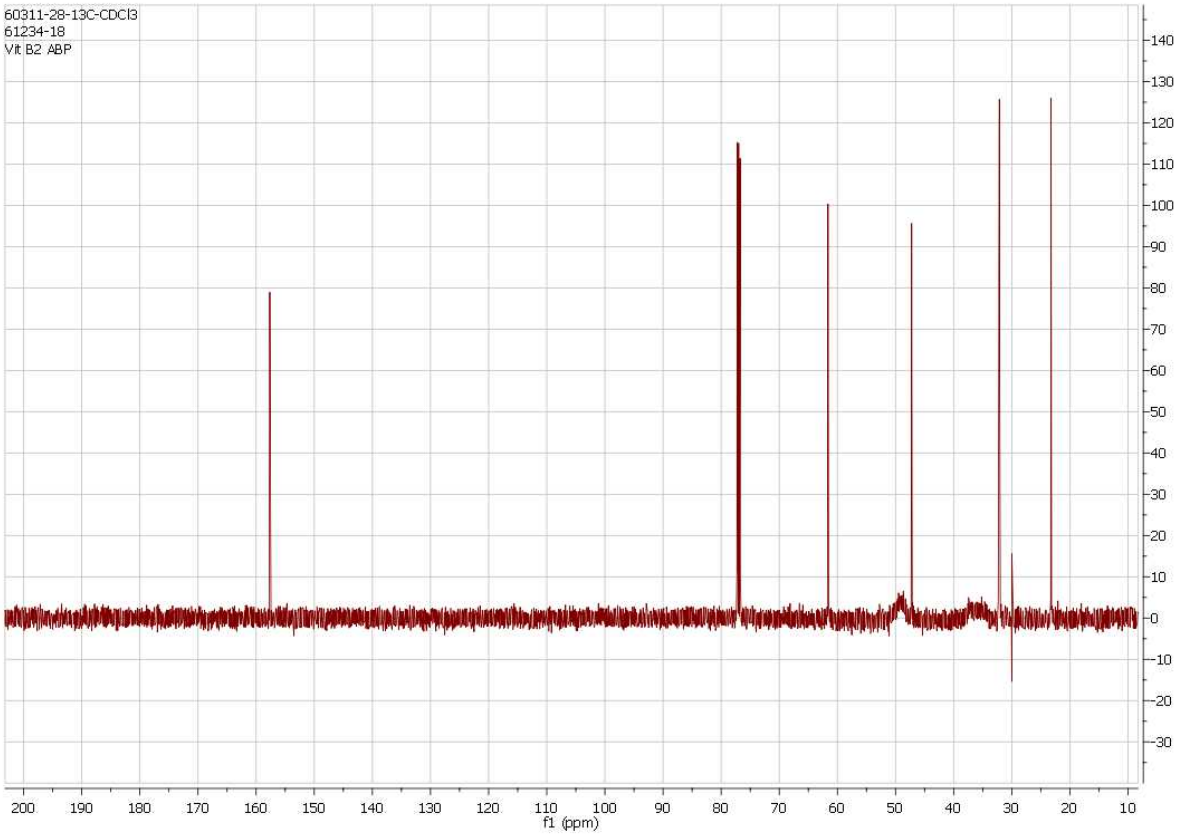




^{13}C NMR ($CDCl_3$)

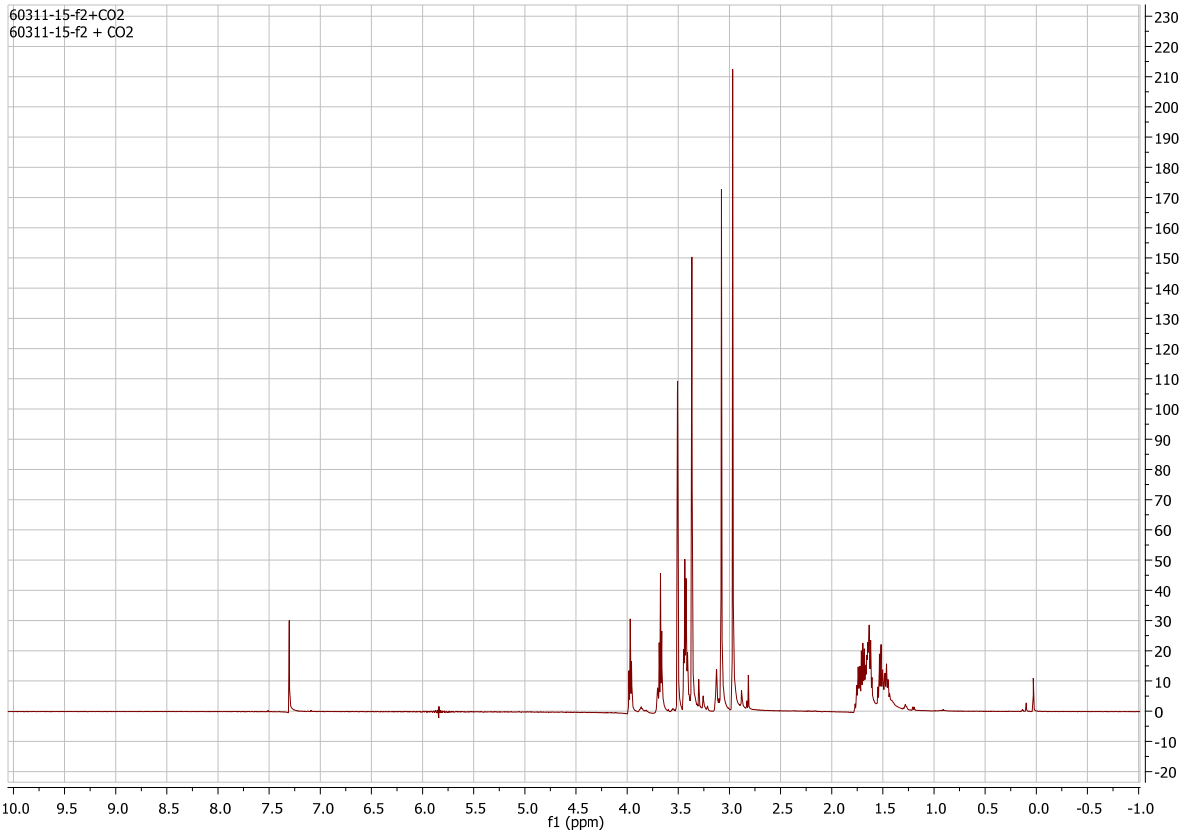
5-((1,3-dimethylimidazolidin-2-ylidene)amino)pentan-1-ol (11a)





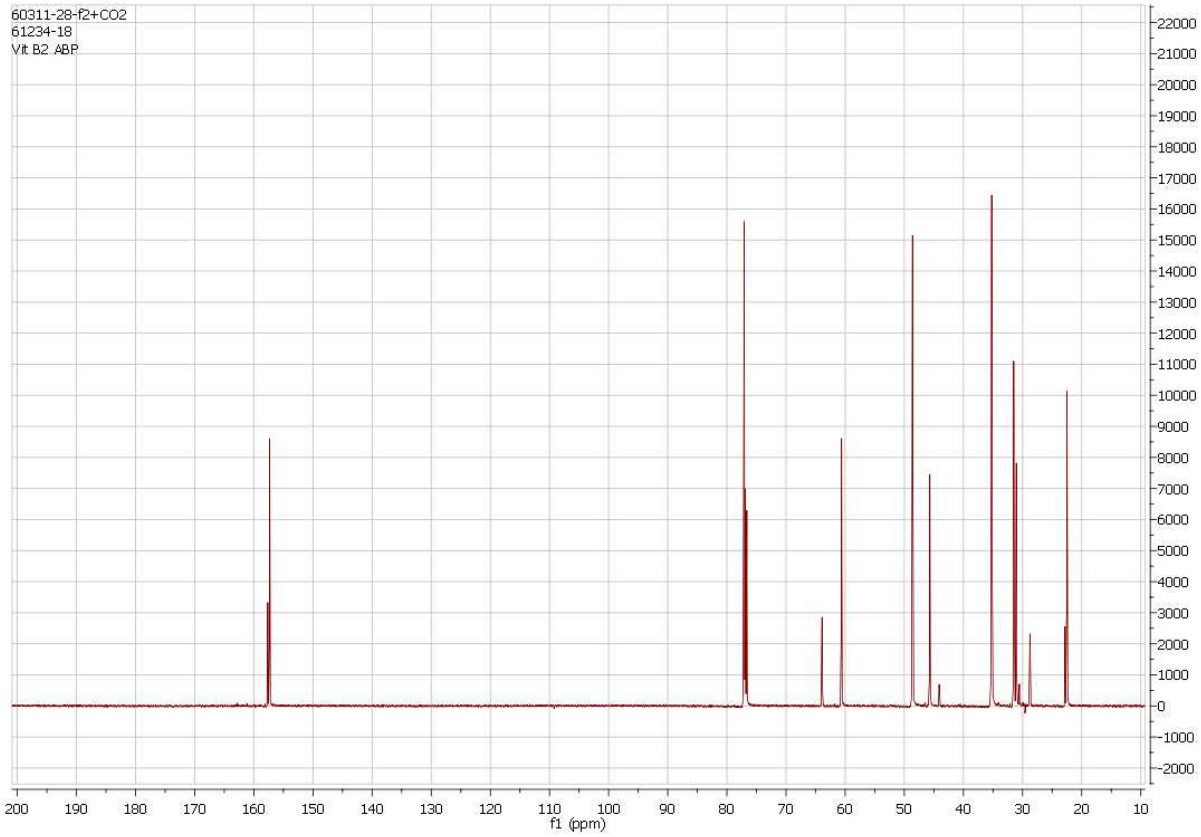
^{1}H NMR ($CDCl_3$)

5-((1,3-dimethylimidazolidin-2-ylidene)amino)pentan-1-ol (11b)



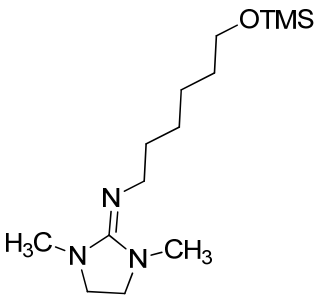
^{13}C NMR ($CDCl_3$)

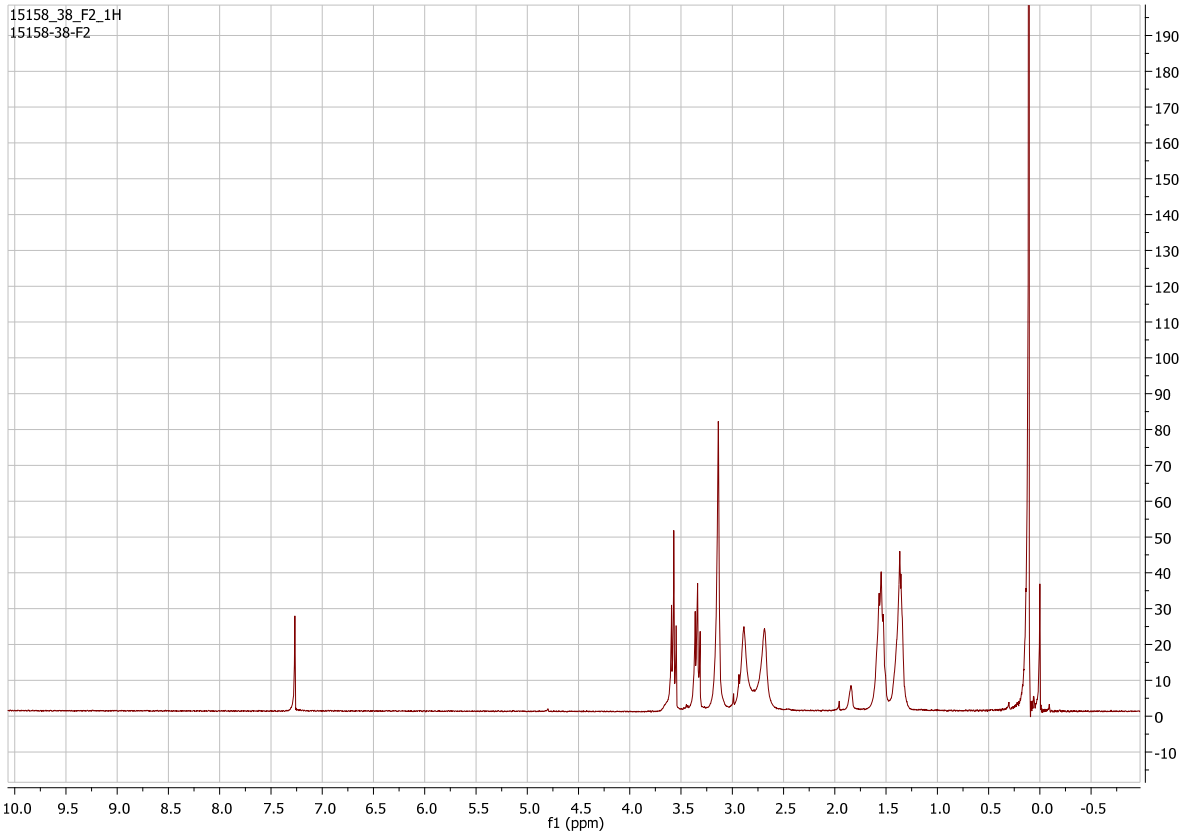
5-((1,3-dimethylimidazolidin-2-ylidene)amino)pentan-1-ol (11b)



^{1}H NMR $CDCl_3$

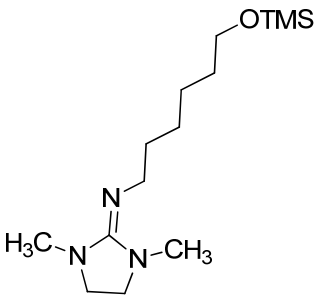
N-(1,3-dimethylimidazolidin-2-ylidene)-6-((trimethylsilyl)oxy)hexan-1-amine (12)

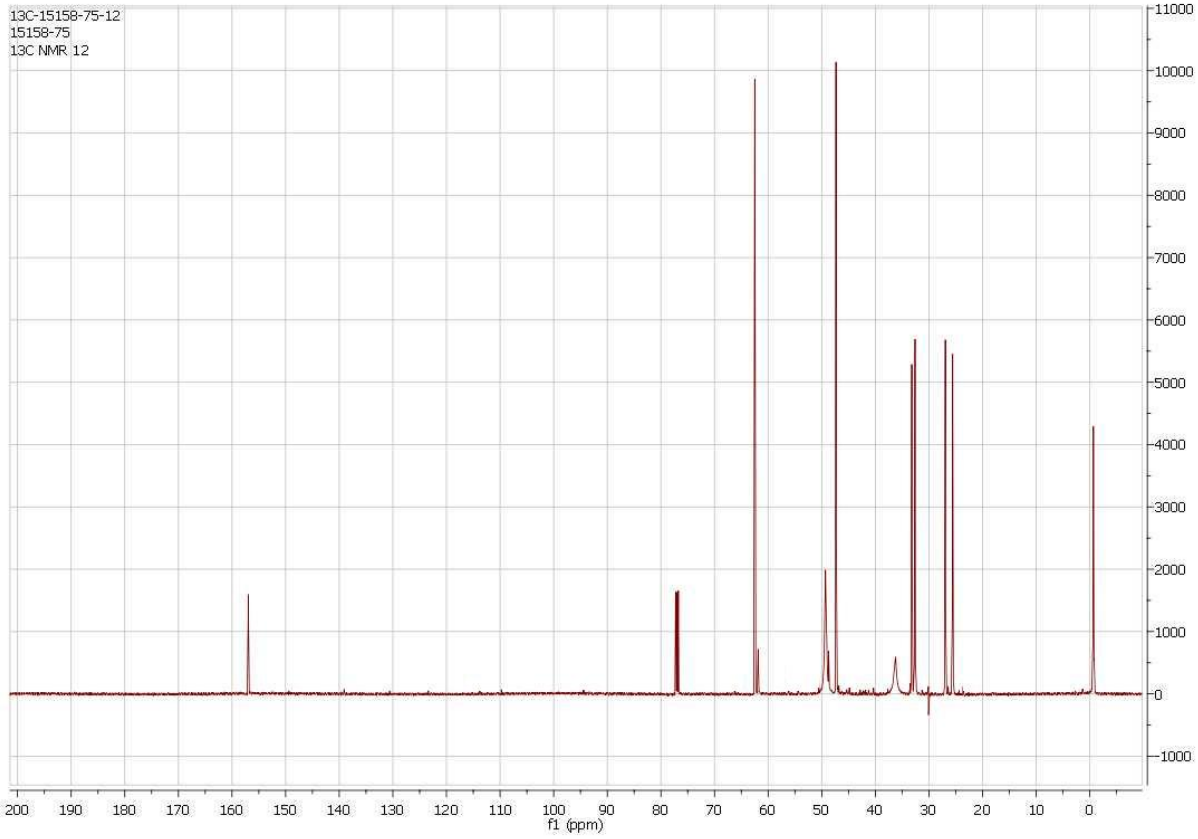




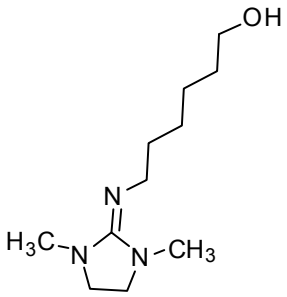
^{13}C NMR ($CDCl_3$)

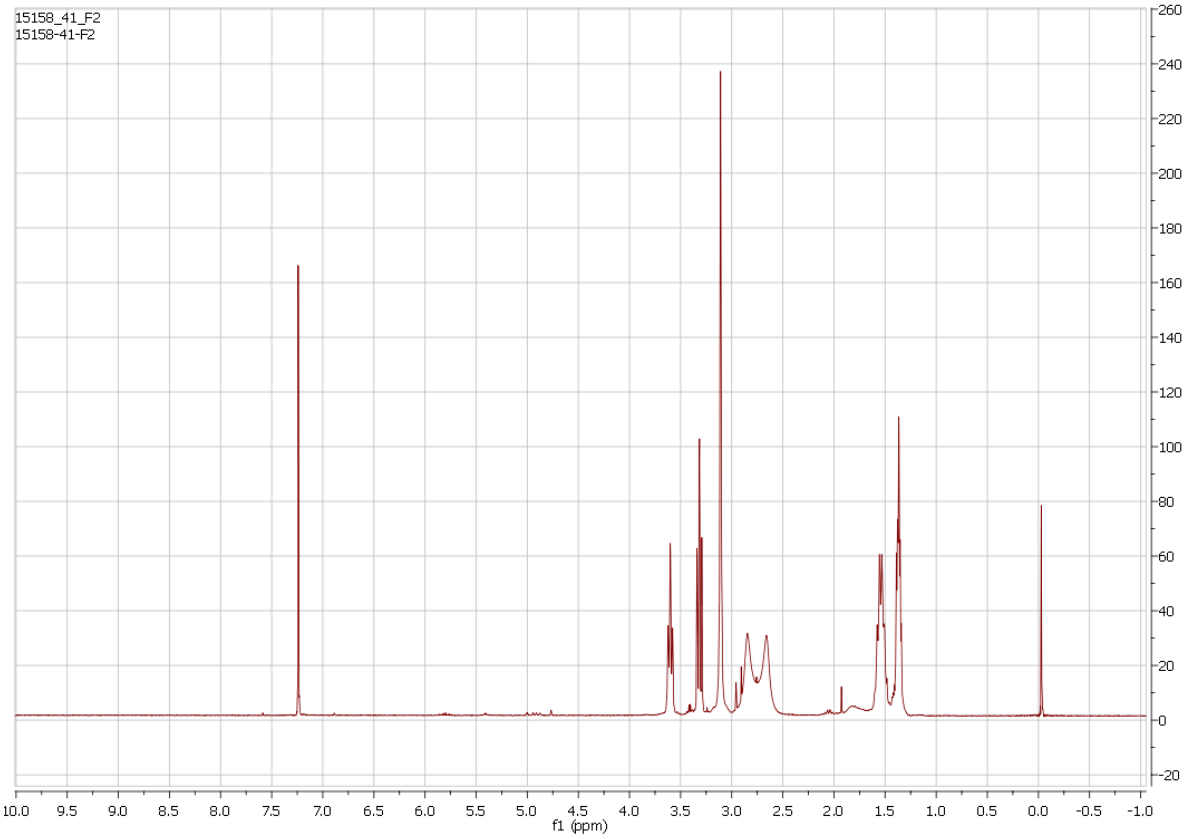
N-(1,3-dimethylimidazolidin-2-ylidene)-6-((trimethylsilyl)oxy)hexan-1-amine (12)



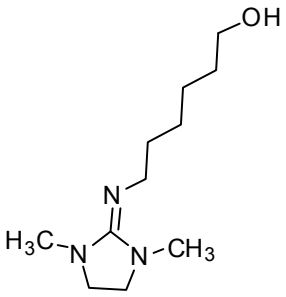


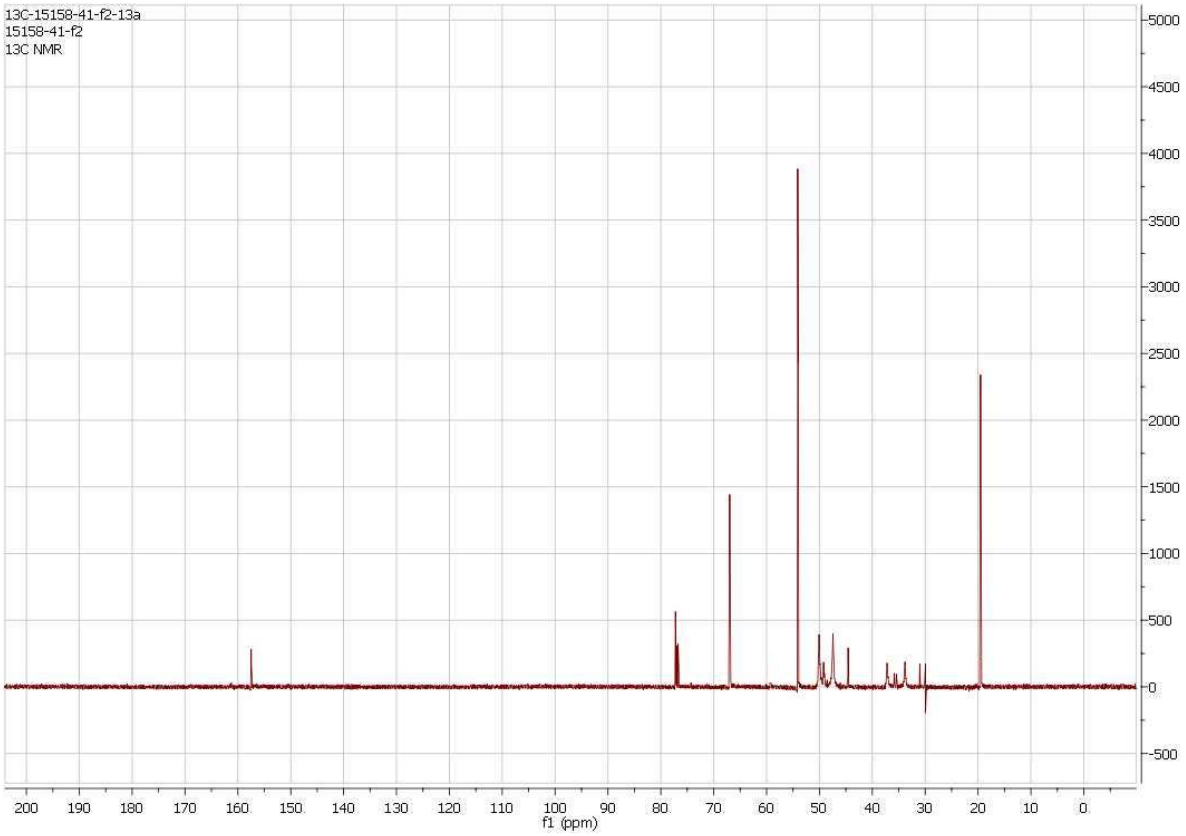
^{1}H NMR $CDCl_3$
6-((1,3-dimethylimidazolidin-2-ylidene)amino)hexan-1-ol (13a)





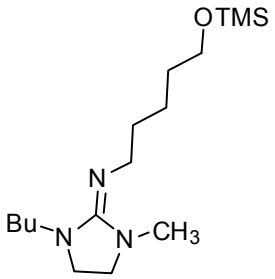
^{13}C NMR ($CDCl_3$)
6-((1,3-dimethylimidazolidin-2-ylidene)amino)hexan-1-ol (13a)

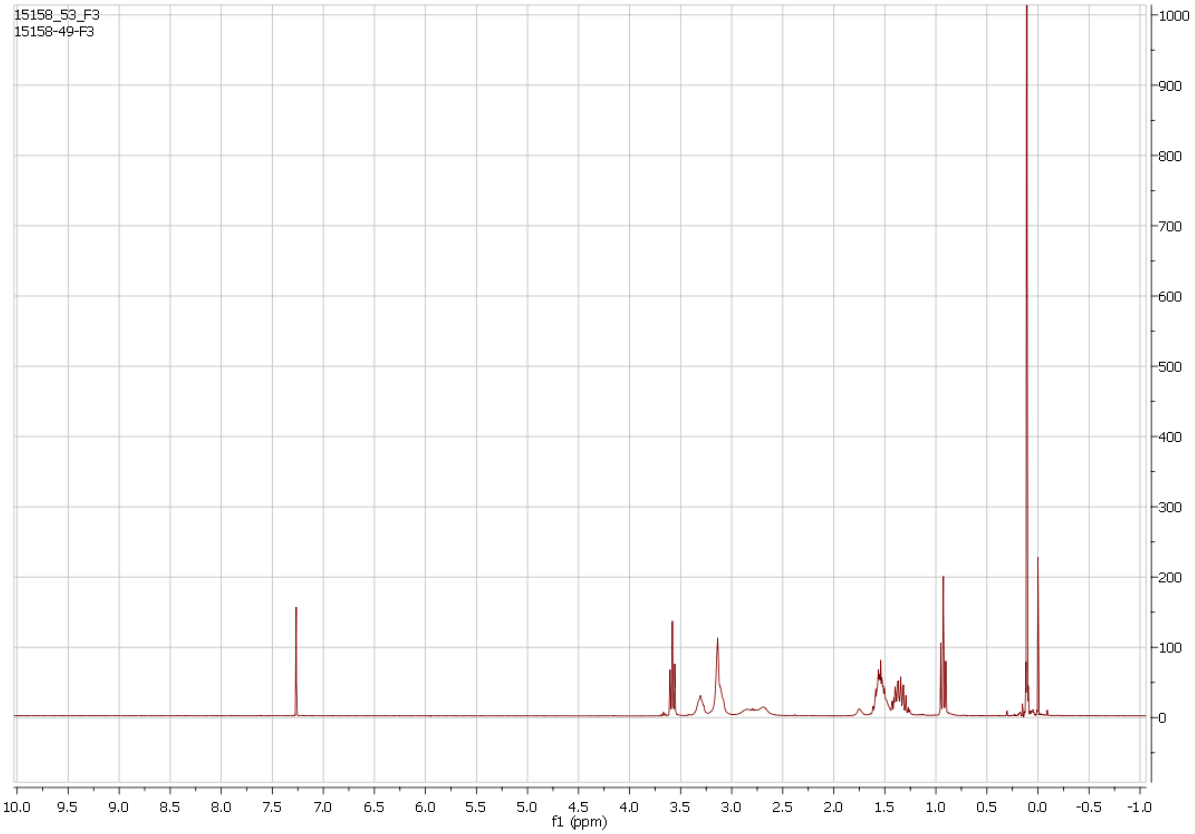




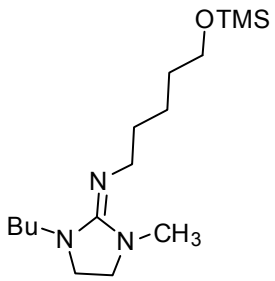
^{1}H NMR ($CDCl_3$)

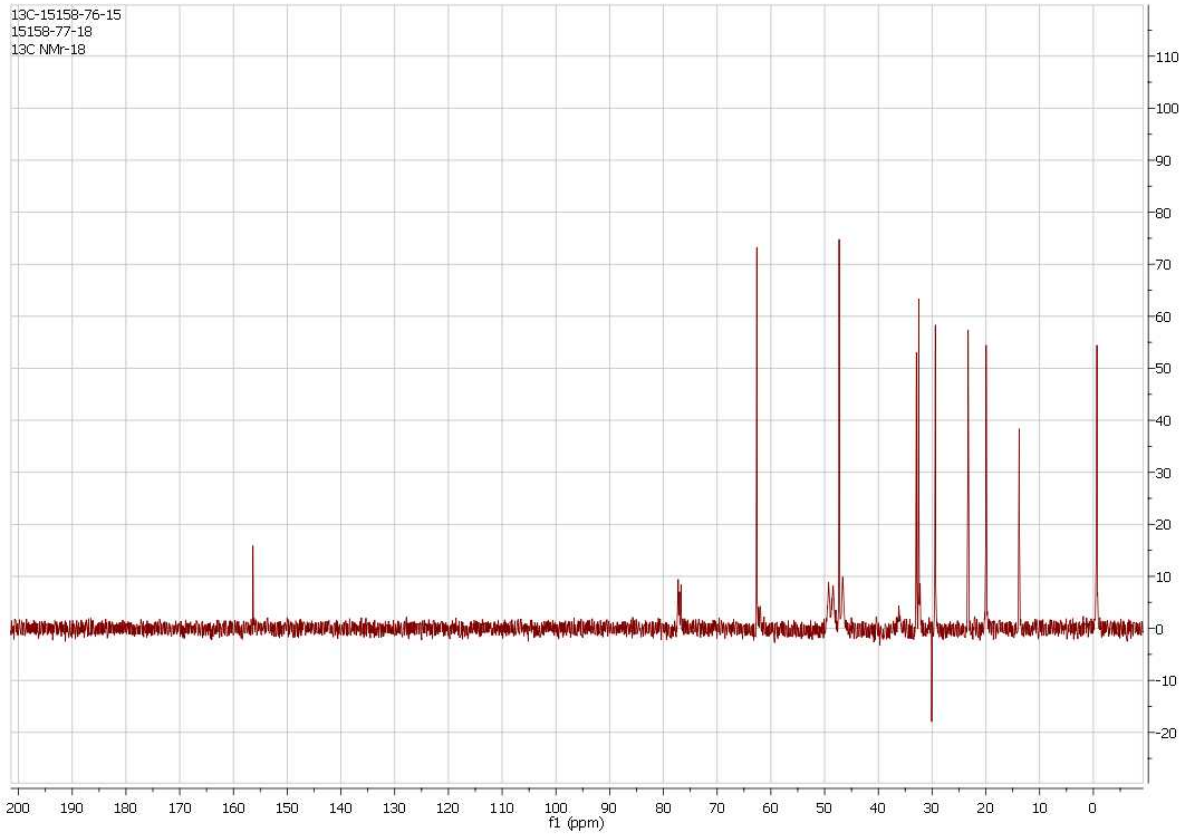
N-(1-butyl-3-methylimidazolidin-2-ylidene)-5-((trimethylsilyl)oxy)pentan-1-amine (15)



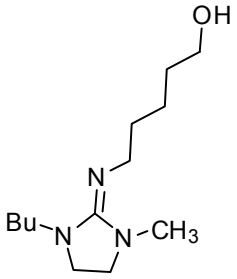


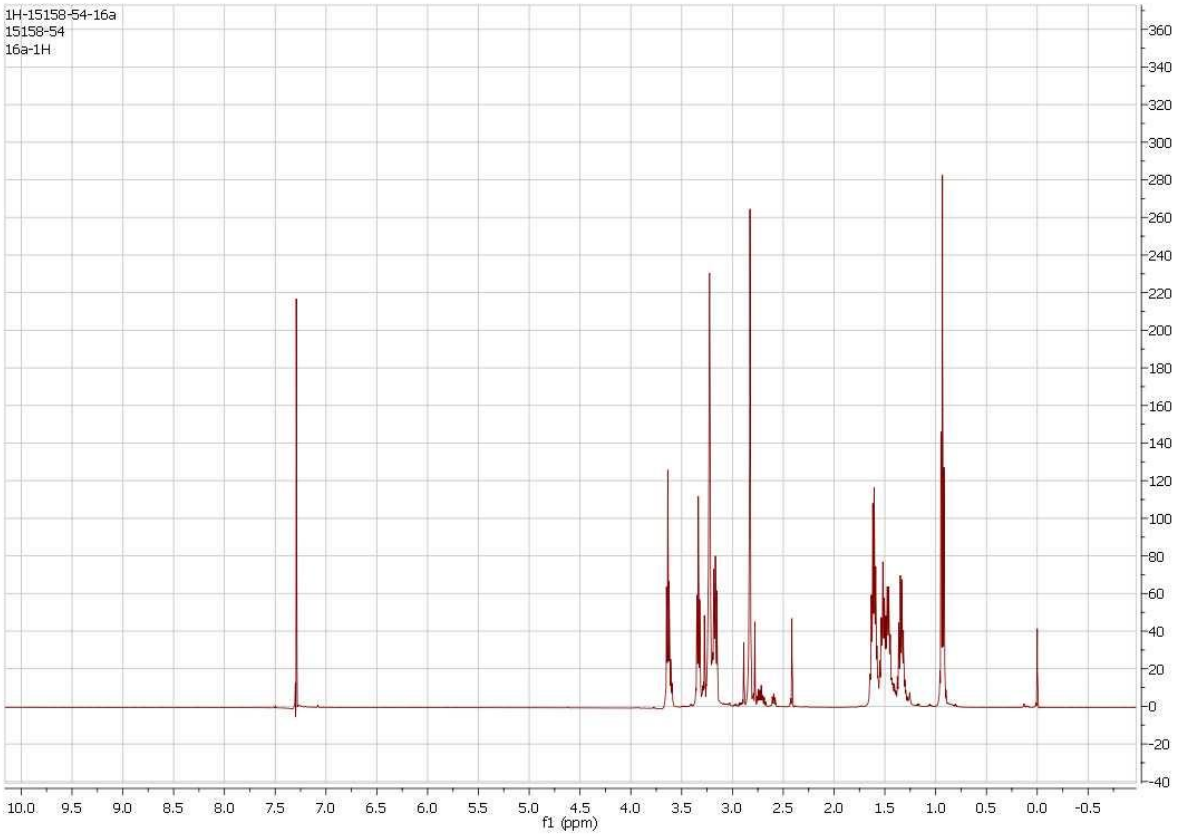
^{13}C NMR ($CDCl_3$)
N-(1-butyl-3-methylimidazolidin-2-ylidene)-5-((trimethylsilyl)oxy)pentan-1-amine 15



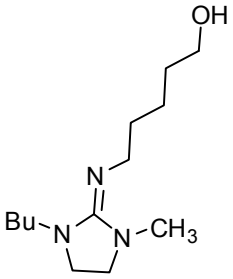


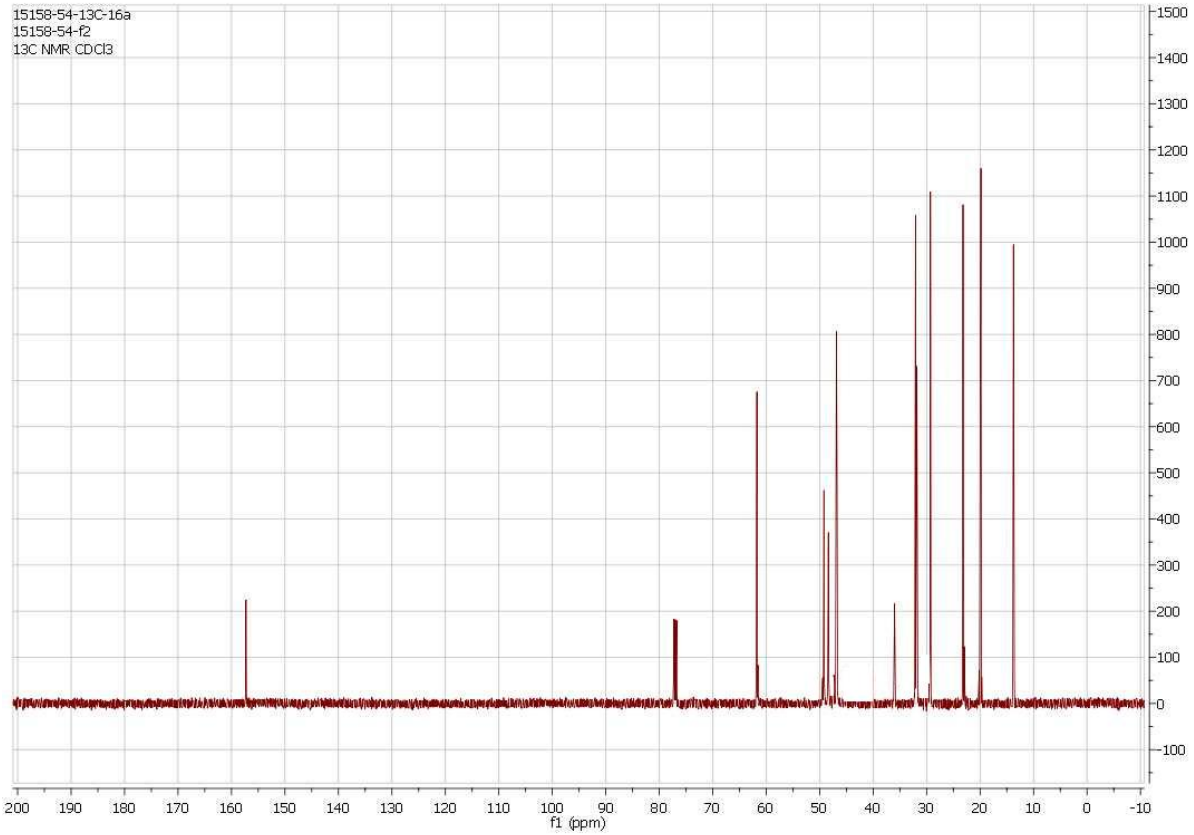
^{1}H NMR ($CDCl_3$)
5-((1-butyl-3-methylimidazolidin-2-ylidene)amino)pentan-1-ol (16a).



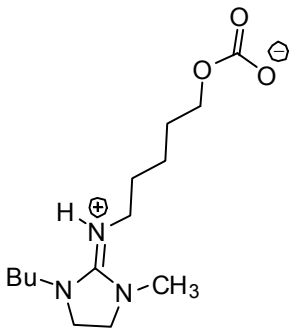


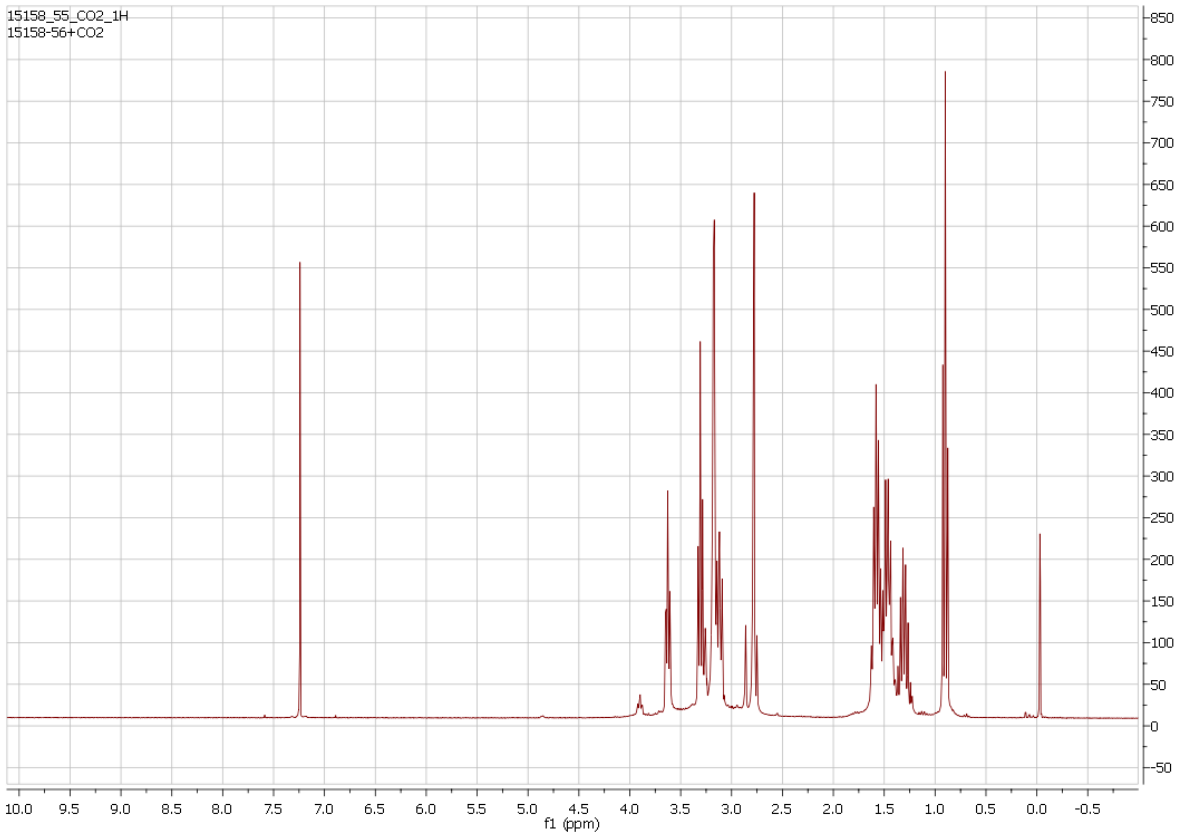
^{13}C NMR $CDCl_3$
5-((1-butyl-3-methylimidazolidin-2-ylidene)amino)pentan-1-ol (16a).



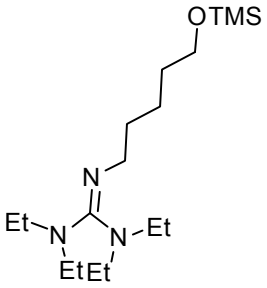


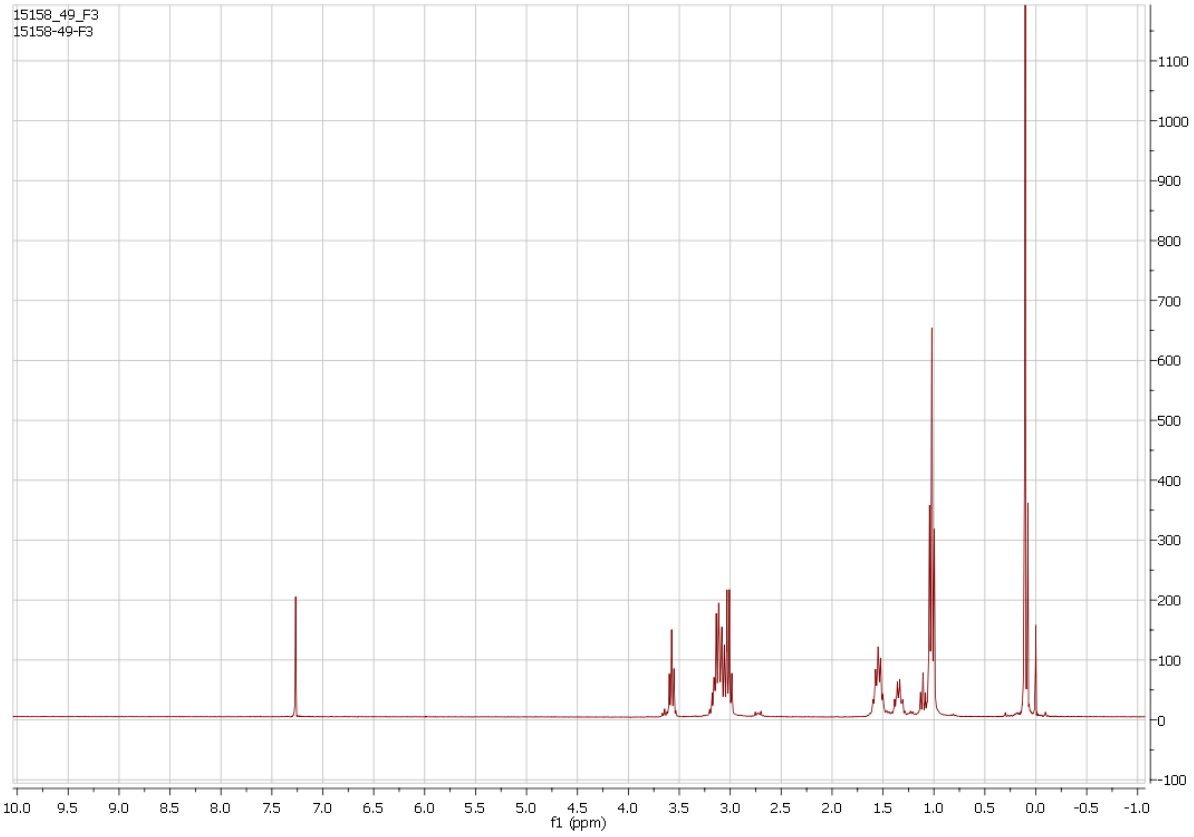
^{1}H NMR $CDCl_3$ (16b)





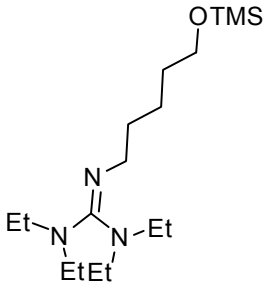
^{1}H NMR $CDCl_3$
1,1,3,3-tetraethyl-2-(5-((trimethylsilyl)oxy)pentyl)guanidine 18.

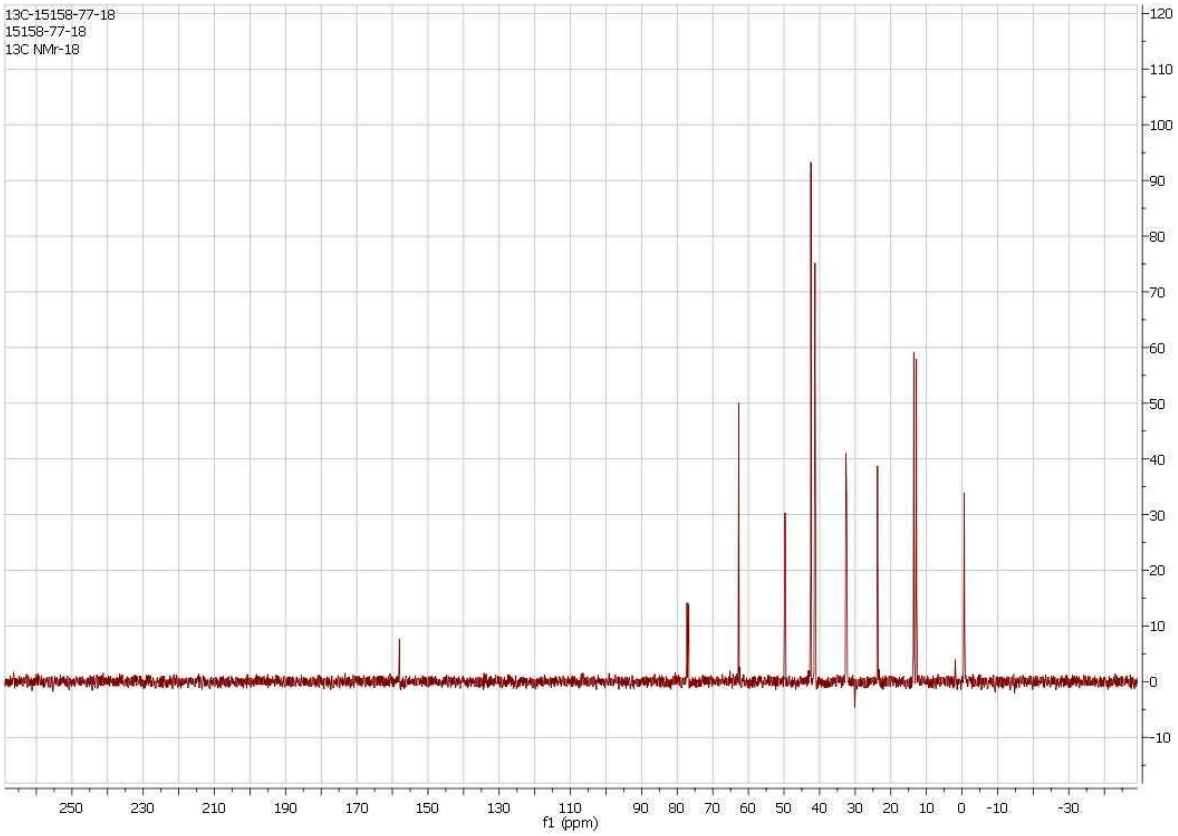




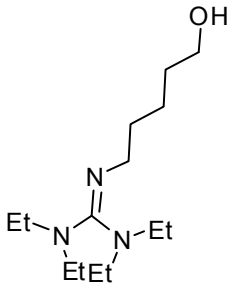
^{13}C NMR $CDCl_3$

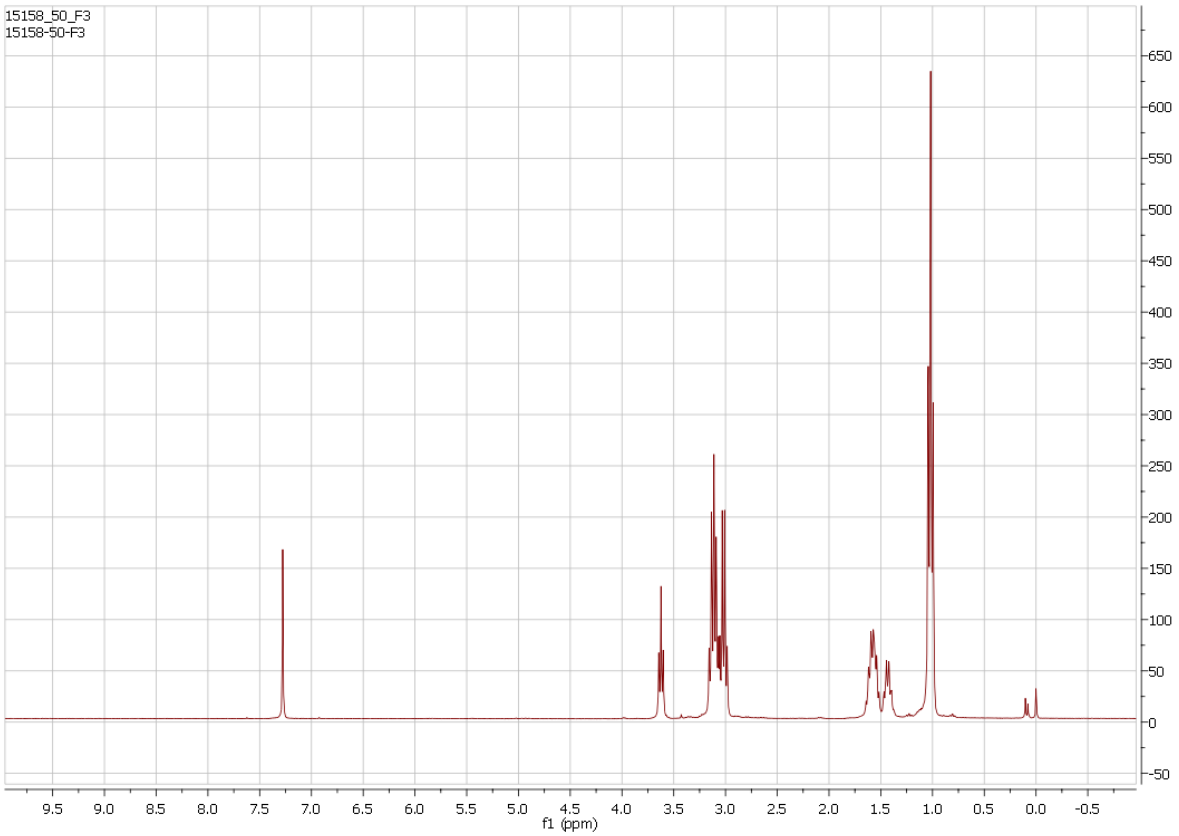
1,1,3,3-tetraethyl-2-(5-((trimethylsilyl)oxy)pentyl)guanidine 18.





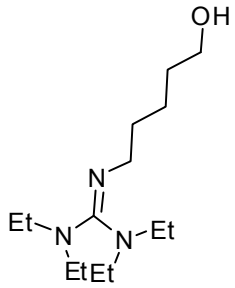
^{1}H NMR ($CDCl_3$)
1,1,3,3-tetraethyl-2-(5-hydroxypentyl)guanidine (19a)

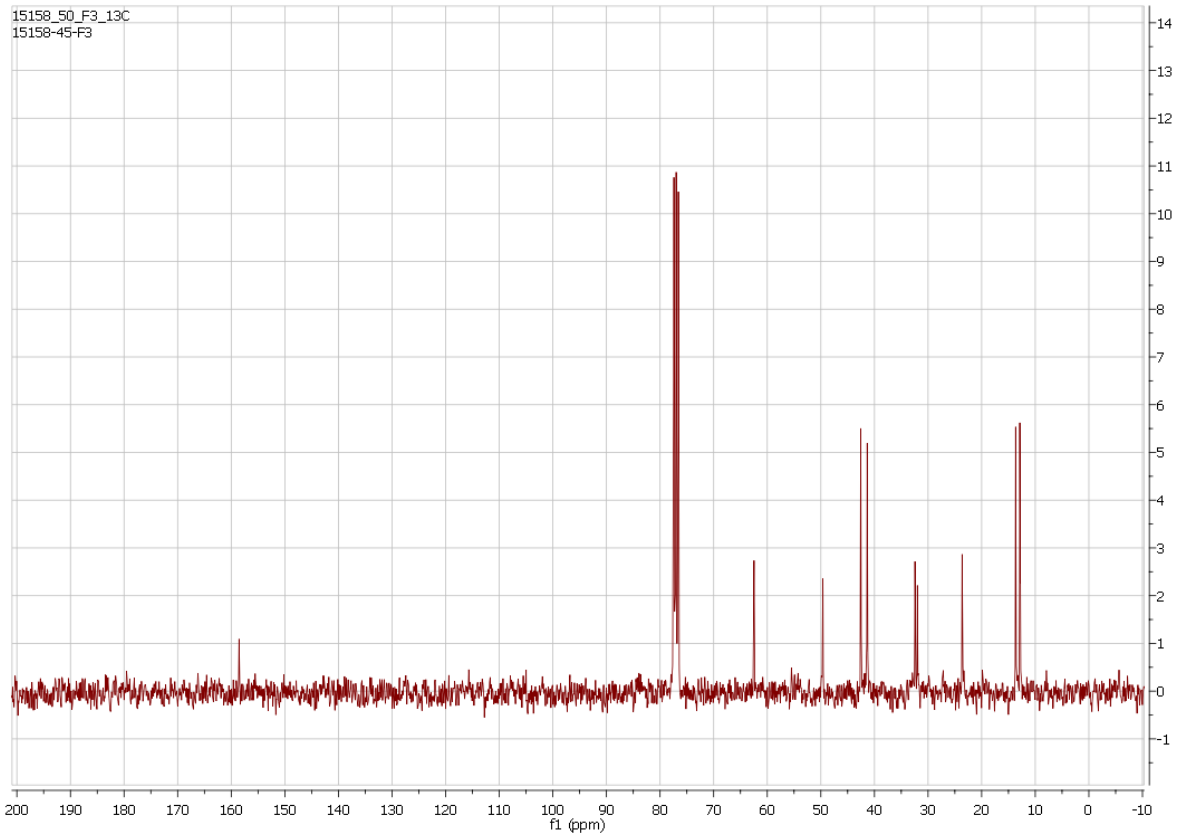




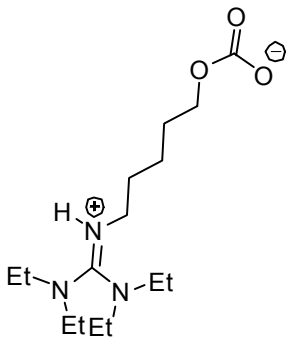
^{13}C NMR ($CDCl_3$)

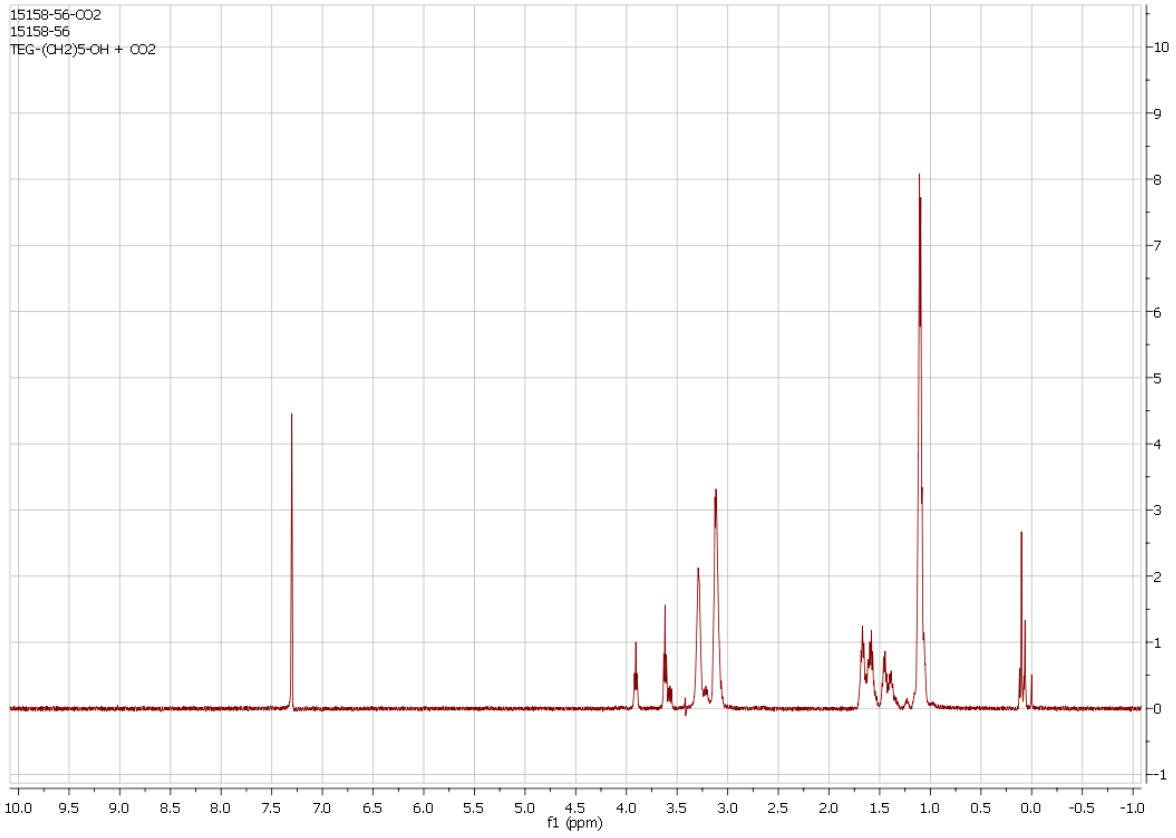
1,1,3,3-tetraethyl-2-(5-hydroxypentyl)guanidine (19a)



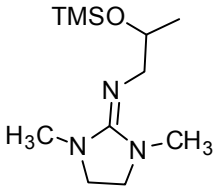


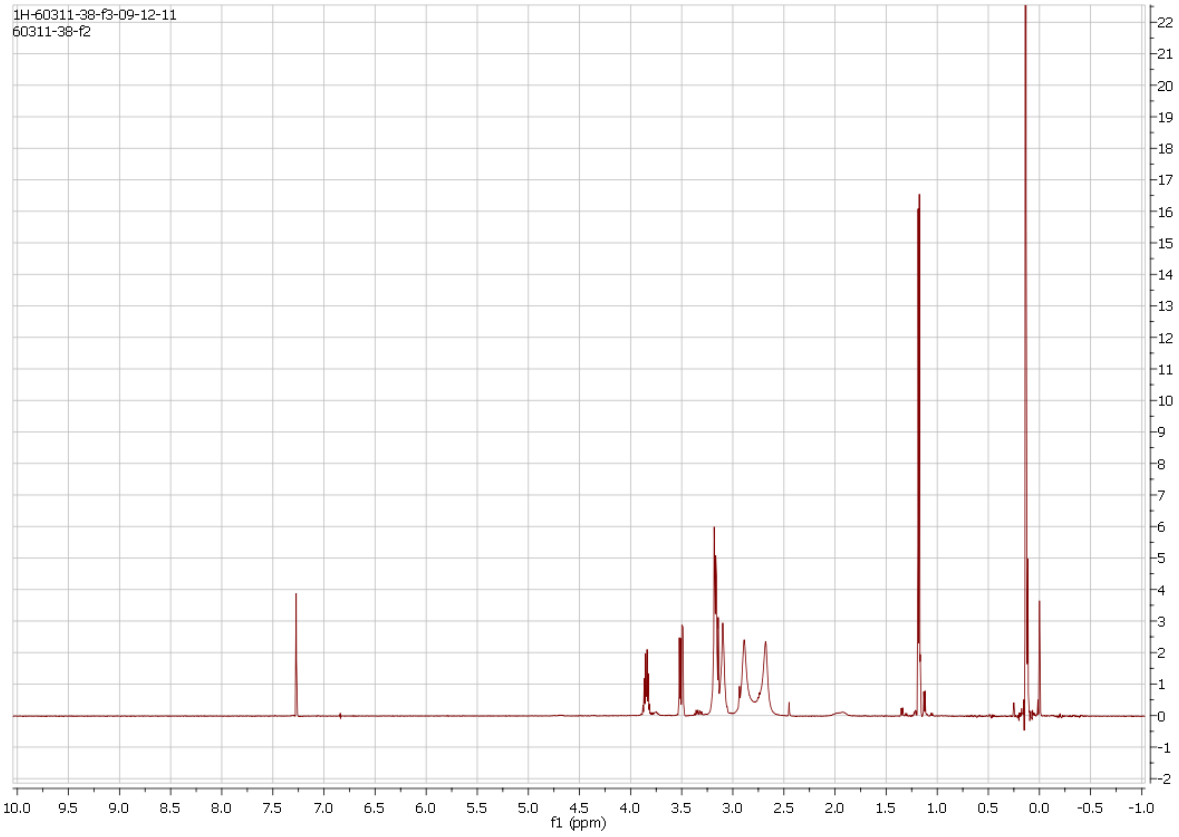
^{1}H NMR ($CDCl_3$) (19b)





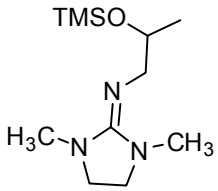
^{1}H NMR $CDCl_3$
N-(1,3-dimethylimidazolidin-2-ylidene)-2-((trimethylsilyl)oxy)propan-1-amine (20)

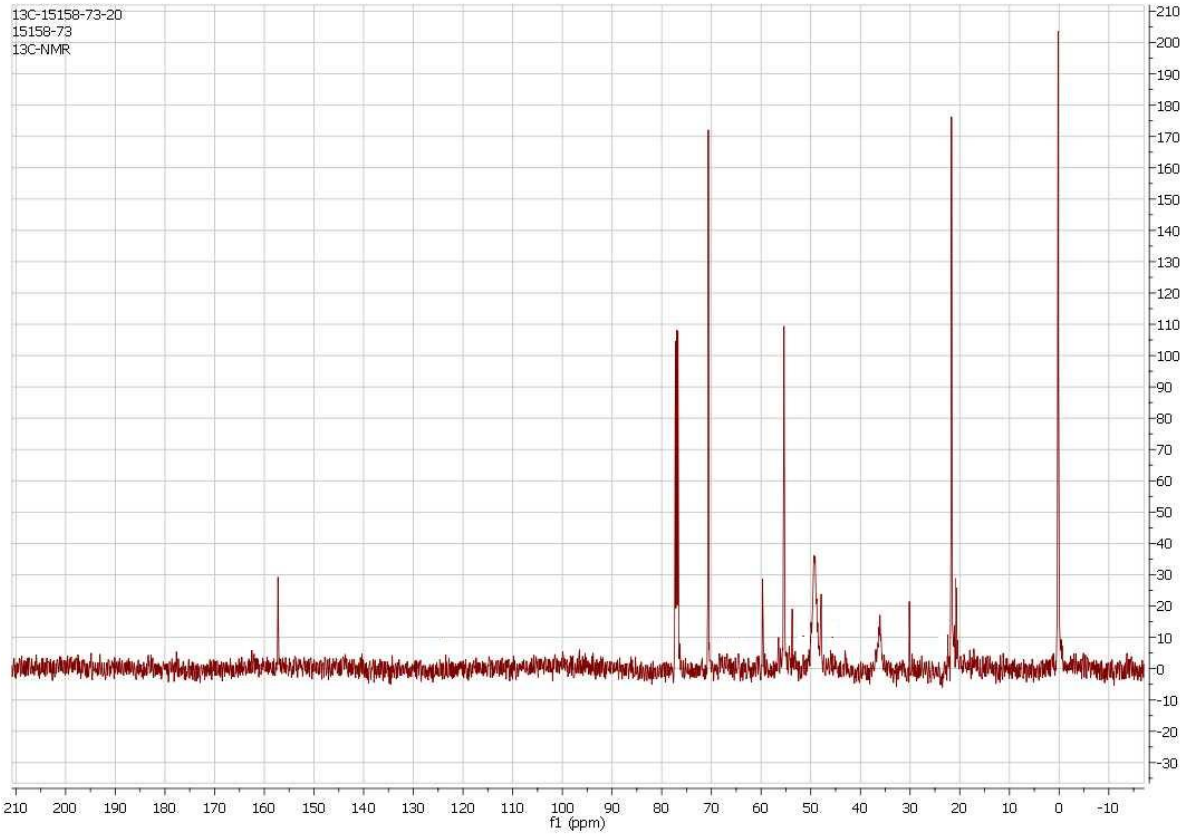




^{13}C NMR $CDCl_3$

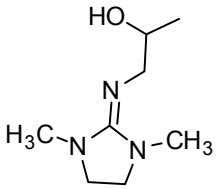
N-(1,3-dimethylimidazolidin-2-ylidene)-2-((trimethylsilyl)oxy)propan-1-amine (20)

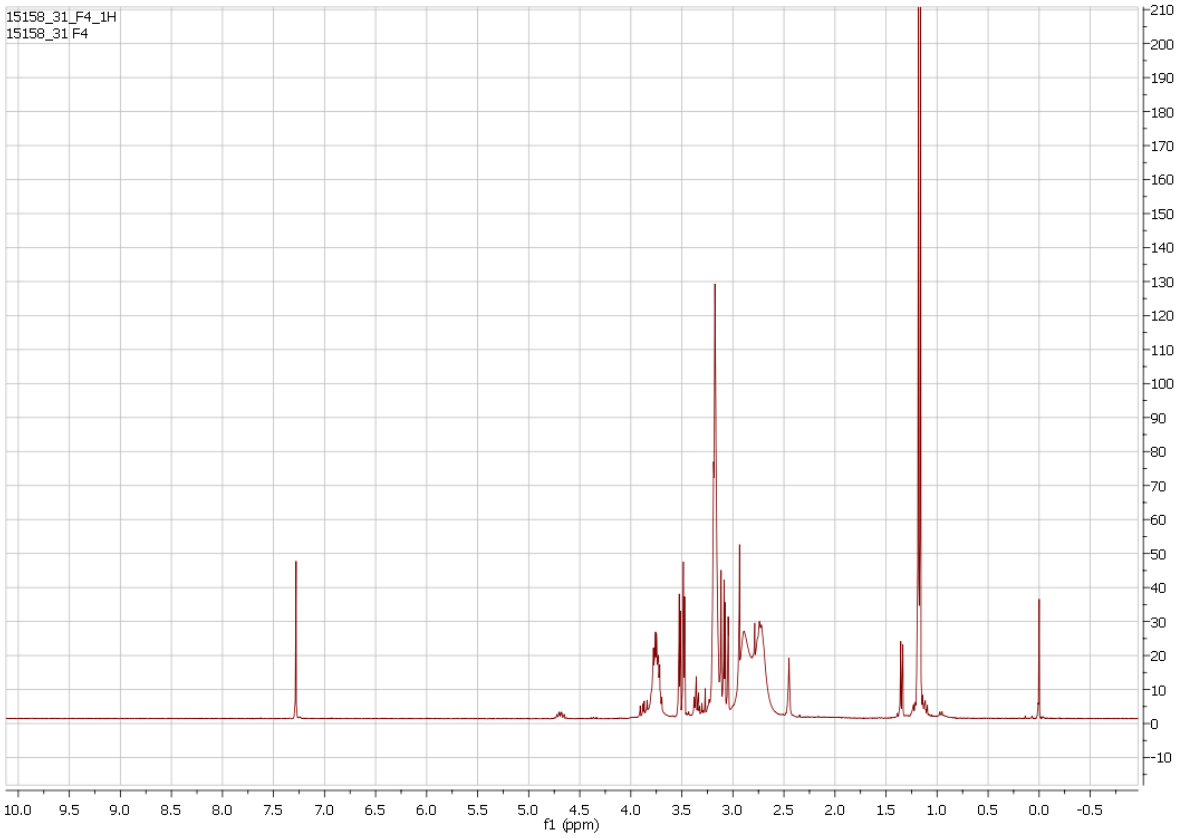




^{1}H NMR ($CDCl_3$)

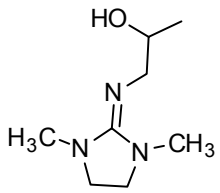
1-((1,3-dimethylimidazolidin-2-ylidene)amino)propan-2-ol (21a

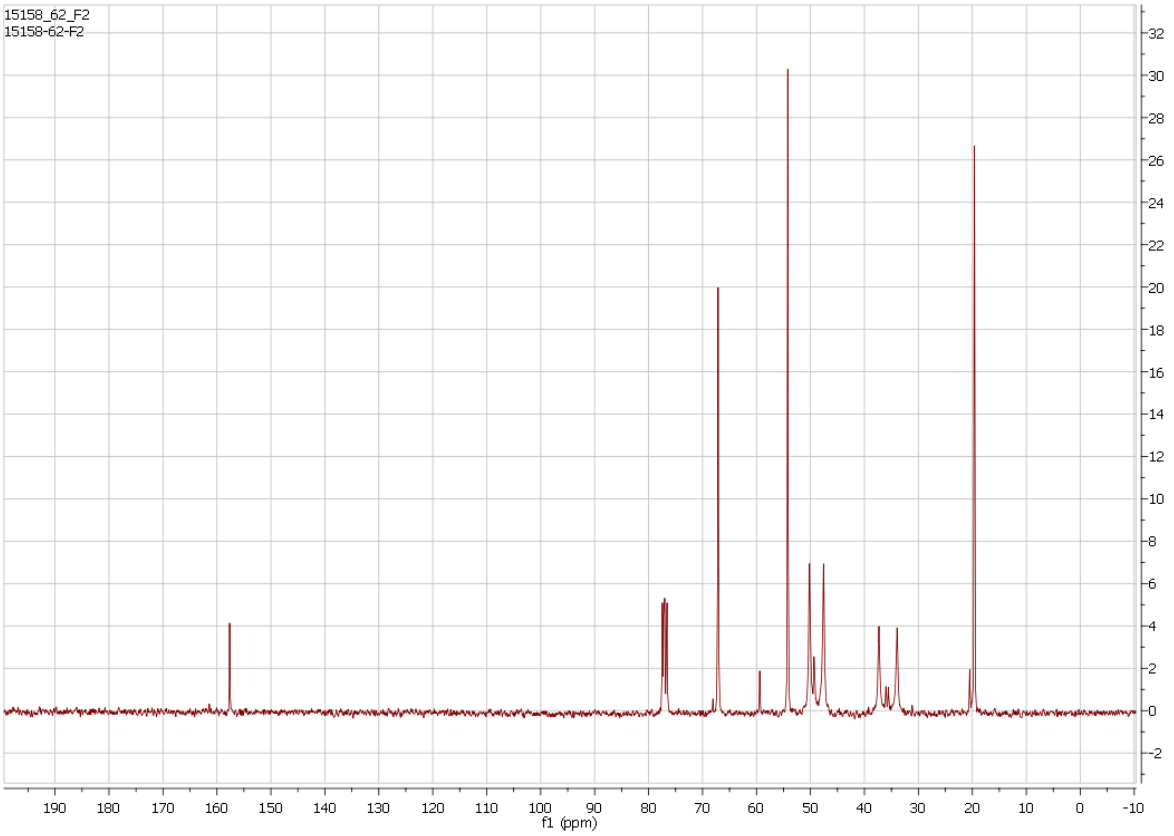




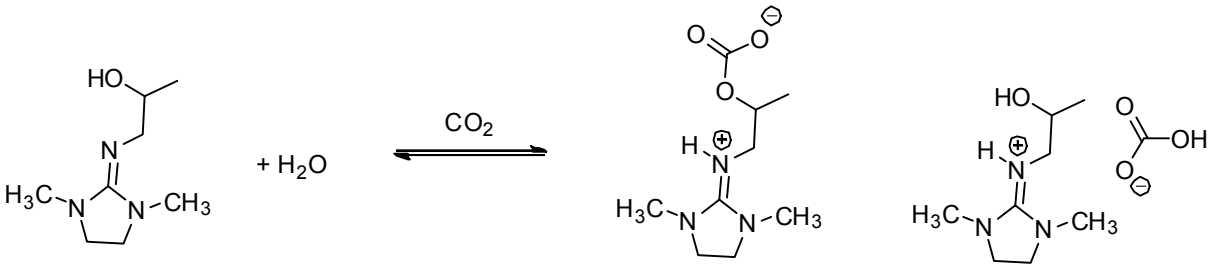
^{13}C NMR ($CDCl_3$)

1-((1,3-dimethylimidazolidin-2-ylidene)amino)propan-2-ol (21a

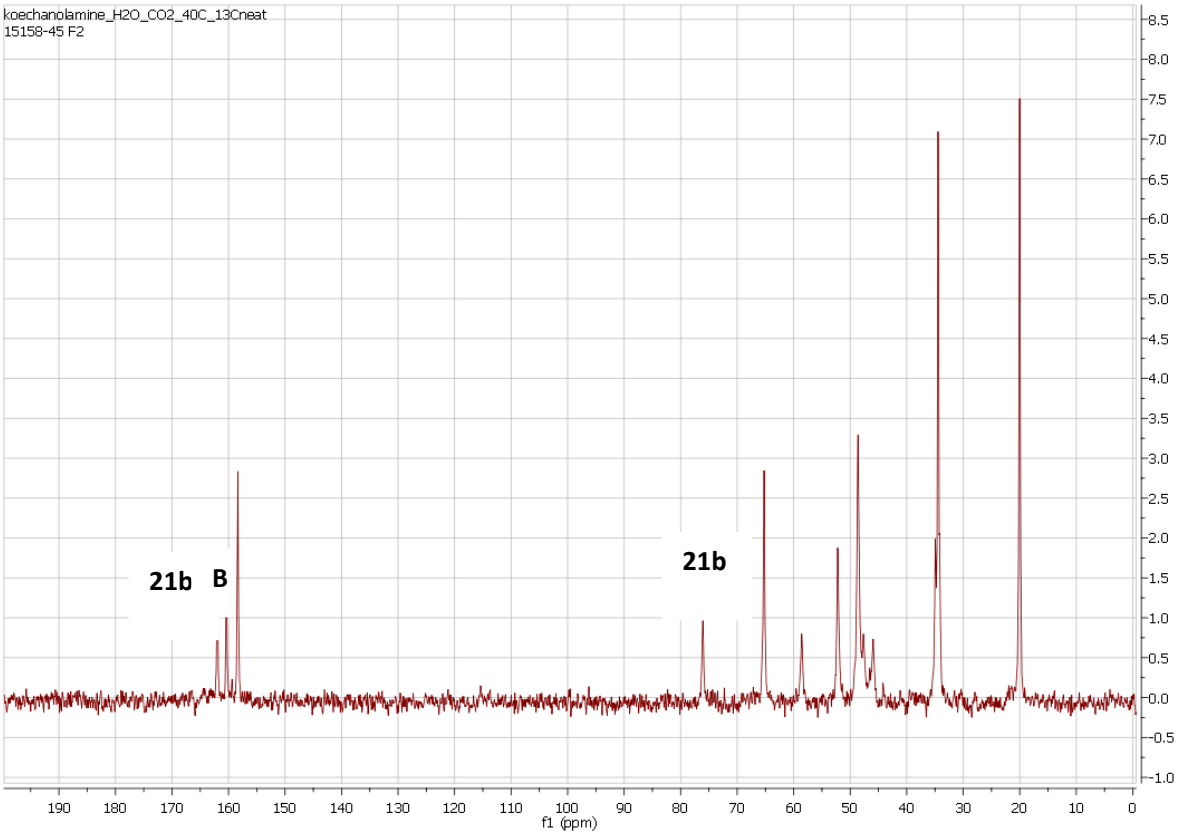




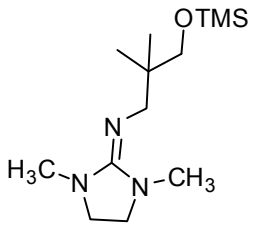
^{13}C NMR (Neat) of (1:1) H_2O:21a + CO_2

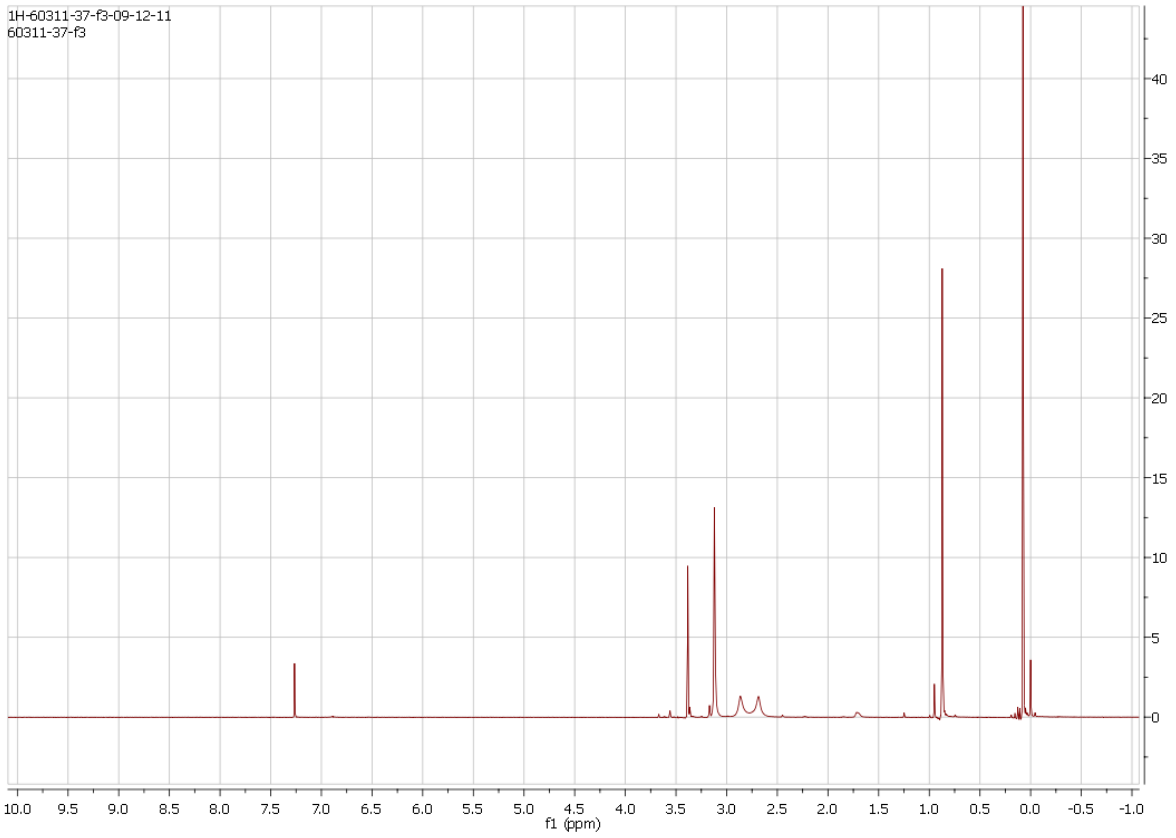


21a **Alkyl carbonate (21b)** **Bicarbonate (B)**



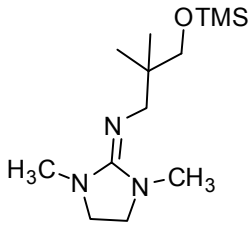
^{1}H NMR $CDCl_3$
3-((1,3-dimethylimidazolidin-2-ylidene)amino)-2,2-dimethylpropan-1-ol 22

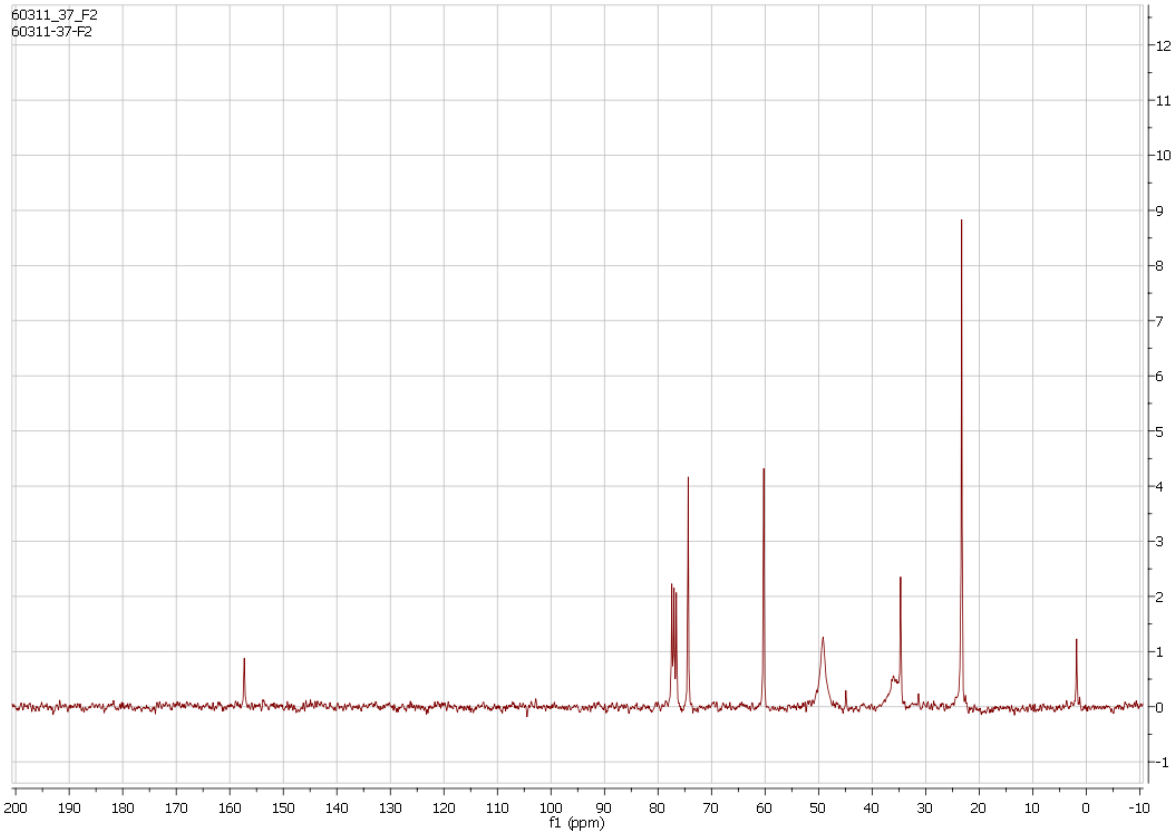




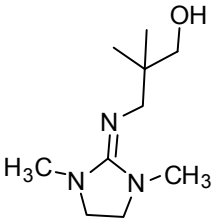
^{13}C NMR $CDCl_3$

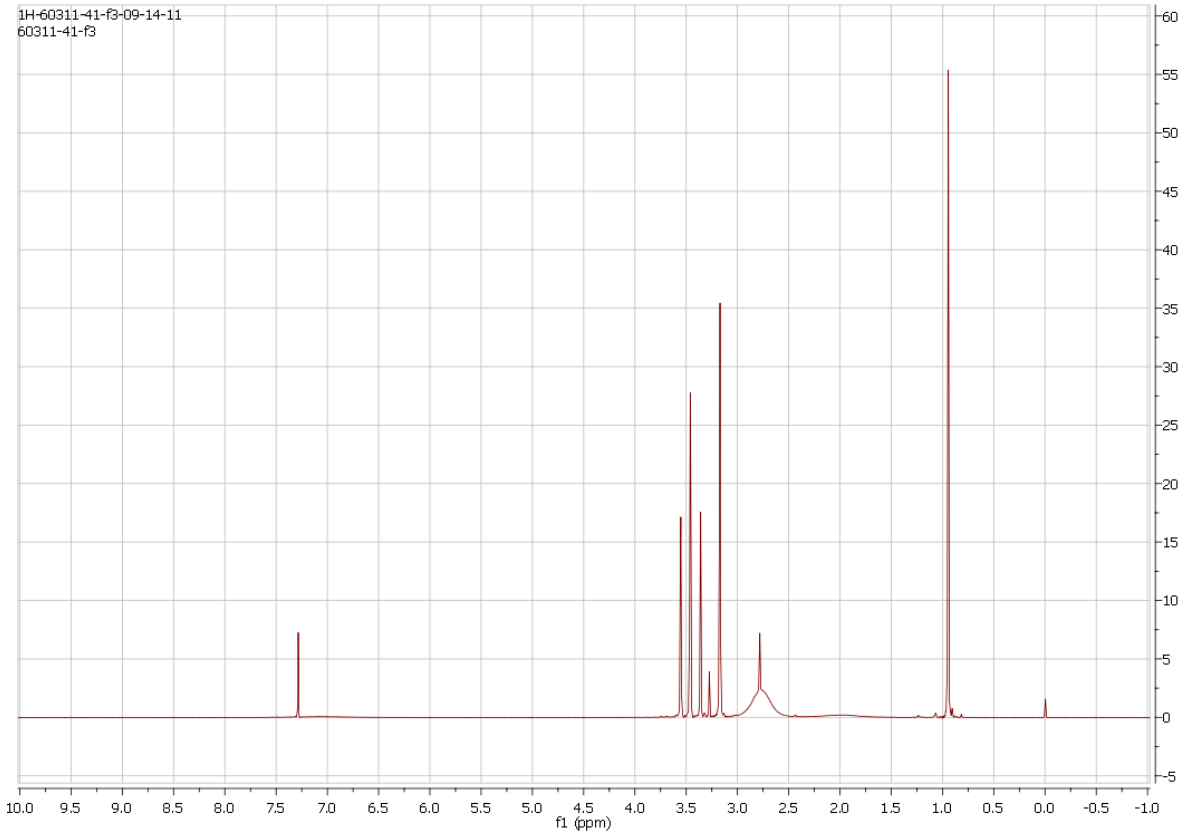
3-((1,3-dimethylimidazolidin-2-ylidene)amino)-2,2-dimethylpropan-1-ol 22



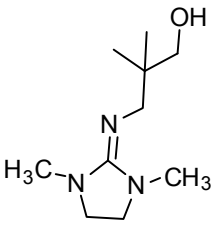


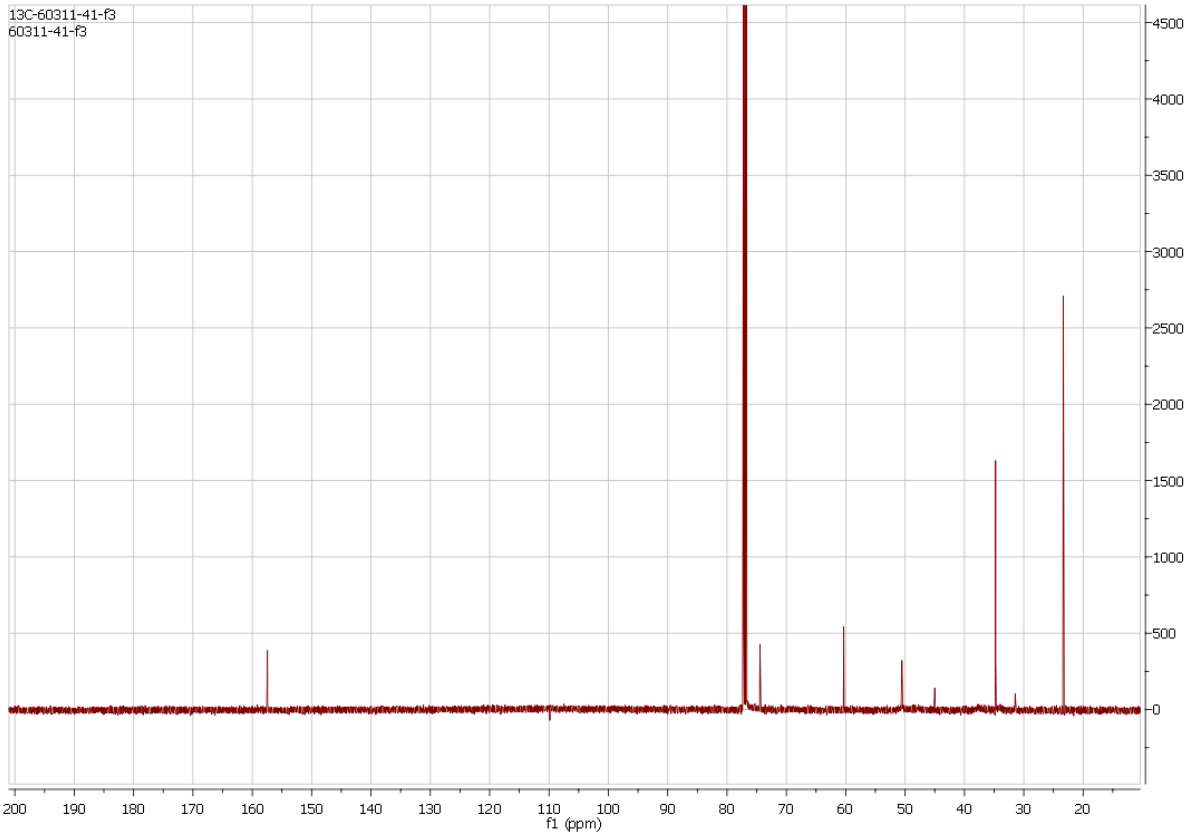
^{1}H NMR $CDCl_3$
3-((1,3-dimethylimidazolidin-2-ylidene)amino)-2,2-dimethylpropan-1-ol 23a.





^{13}C NMR $CDCl_3$
3-((1,3-dimethylimidazolidin-2-ylidene)amino)-2,2-dimethylpropan-1-ol 23a.





[1] Tanabe, Y.; Murakami, M.; Kitaichi, K.; Yoshida, Y. *Tetrahedron Lett.* **1994**, *35*, 8409.

[2] Anderson, J. C.; Chapman, H. A. *Org. Biomol. Chem.* **2007**, *5*, 2413.

[3] Sheldrick, G.M. *Acta Cryst*. **2008**, *A64*, 112.