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Supporting Information

Titanium-Catalyzed Intermolecular Hydroaminoalkylation of Alkenes with Tertiary Amines

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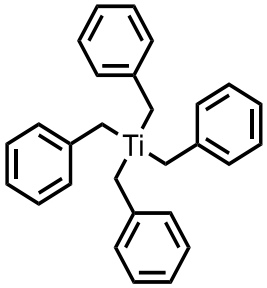
1. General Information

Unless otherwise noted, all reactions were performed under an inert atmosphere of nitrogen in oven-dried vials (25 mL) equipped with magnetic stirring bars (15 × 4.0 mm) or in oven-dried Schlenk tubes (Duran glassware, 100 mL, ø = 30 mm) equipped with Teflon® stopcocks and magnetic stirring bars (12 × 2.5 mm). Toluene was purified by distillation from sodium wire and degassed. Prior to use, all substrates were distilled or recrystallized and degassed. Tetrabenzyltitanium ($TiBn_4$), all amines, all alkenes, and toluene were stored in a nitrogen-filled glove box (Vigor, Sci-Lab). Methylenecyclohexane[1] (**2h**) and $TiBn_4$[2] were synthesized according to literature procedures. All other chemicals were purchased from commercial sources and were used without further purification. For flash chromatography, silica gel from GRACE Davison (particle size 0.037-0.063 mm) was used. Light petroleum ether (b.p. 40-60 °C, PE), diethylamine ($HNEt_2$), *n*-hexane (Hex), *n*-pentane, Et_2O, and EtOAc used for flash chromatography were distilled prior to use. For thin layer chromatography, silica on TLC aluminum foils with fluorescent indicator 254 nm from Fluka were used. The substances were detected with UV light or a H_2PtCl_6 / KI solution used as a spray reagent.[3] All products that have already been reported in the literature were identified by comparison of the obtained ^1H NMR and ^{13}C NMR spectra with those reported in the literature. New compounds were additionally characterized by infrared (IR) spectroscopy, GC-MS, high resolution mass spectrometry (HRMS), and ^{29}Si NMR spectroscopy (if applicable). NMR spectra were recorded on the following spectrometers: Bruker Avance DRX 500 or Bruker Avance III, 500 MHz. All ^1H NMR spectra are reported in δ units (ppm) relative to the signal of $CDCl_3$ at 7.26 or C_6D_6 at 7.16 ppm. *J* values are given in Hz. All ^{13}C NMR spectra are reported in δ units (ppm) relative to the central line of the triplet for $CDCl_3$ at 77.16 or C_6D_6 at 128.06 ppm. ^{29}Si NMR spectra are reported in δ units (ppm) relative to the external standard Me_2SiHCl (δ = 11.1 ppm) in relation to $SiMe_4$ (δ = 0.0 ppm). Infrared spectra were recorded on a Bruker Tensor 27 spectrometer (ATR) or a Shimadzu IRSpirit QATR-S spectrometer (ATR). GC analyses were performed on a Shimadzu GC-2010 gas chromatograph equipped with a flame ionization detector. High resolution mass spectra (HRMS) and mass spectra (MS) were recorded on a Waters Q-TOF Premier spectrometer in EI or ESI (ESI^+, TOF) mode.

2. Synthesis of Tetrabenzyltitanium ($TiBn_4$)[2]



Under an air atmosphere, in a 500 mL-flask with a magnetic stirring bar, reflux condenser, $CaCl_2$-tube and dropping funnel, magnesium turnings (25.6 g, 1.05 mol) were suspended in Et_2O (200 mL). Benzyl chloride (65.8 g, 520 mmol) was added dropwise. A second 500 mL-flask with a magnetic stirring bar, septum, dropping funnel and $CaCl_2$-tube was charged with Et_2O (200 mL) and cooled to −15 °C. $TiCl_4$ (22.8 g, 120 mmol) was slowly added via syringe at −15 °C. The Grignard solution was decanted from excess magnesium into the dropping funnel of the second setup. The solid residue of magnesium was extracted with Et_2O (50 mL) and the extract was added to the dropping funnel. The Grignard solution was added to the suspension at −15 °C and then stirred for 30 min at room temperature. The solvent was removed under reduced pressure at 0 °C and the remaining Et_2O was then removed under high vacuum at room temperature for 30 min, while shaking the flask to break up the solid. *n*-Hexane (200 mL) was added to the residue and the solid residue was filtered over a Schlenk frit with a Na_2SO_4 pad and the remaining residue was extracted with *n*-hexane (1 × 100 mL, 1 × 50 mL). The solvent of the combined extracts was removed under reduced pressure at 0 °C and then under high vacuum. Under inert atmosphere (Ar) and in oven-dried glassware the crude product was dissolved in *n*-hexane (50 mL) and filtrated through a new Schlenk frit with a pad of dry Na_2SO_4 into a 250 mL-Schlenk flask. The frit and Na_2SO_4 were washed with *n*-hexane (40 mL). The combined solution was stored at −30 °C for three days to crystallize the product. The solid was separated at −30 °C by filtration, washed with *n*-hexane (2 × 5 mL) and dried under vacuum. Finally, $TiBn_4$ was obtained as dry, very dark violet, almost black crystals (7.94 g, 19.2 mmol, 16 %).

^{1}H NMR (500 MHz, C_6D_6): δ = 7.12-7.04 (m, 8 H, Ar-C*H*), 6.98-6.90 (m, 4 H, Ar-C*H*), 6.65-6.59 (m, 8 H, Ar-C*H*), 2.84 (s, 8 H, CH_2) ppm.

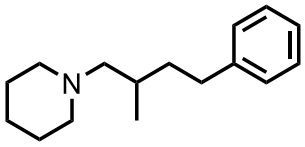
^{13}C {^{1}H} NMR (125 MHz, DEPT, C_6D_6): δ = 142.5 (C), 129.7 (CH), 129.3 (CH), 124.7 (CH), 98.6 (CH_2) ppm.

3. Hydroaminoalkylation Reactions

General Procedure for the Hydroaminoalkylation of Alkenes with Aliphatic Tertiary Amines

An oven-dried vial (25 mL) equipped with magnetic stirring bar was transferred into a nitrogen-filled glovebox and charged with $TiBn_4$ (0.10 mmol, 10 mol%) and toluene (1 mL). To this solution, the respective amine (1.00 mmol), the alkene (1.50 mmol), toluene (1 mL), $Ph_3C[B(C_6F_5)_4]$ (73.8 mg, 8 mol%), and additional toluene (3 mL) were added in this order. The vial was sealed with a lid and the reaction mixture was stirred at 28 °C for 18-96 h. Afterwards, the reaction mixture was removed from the glovebox and diluted with EtOAc (25 mL). The solvents were removed under reduced pressure and the residue was purified by column chromatography (SiO_2) or bulb-to-bulb distillation to give the pure hydroaminoalkylation product. Prior to flash chromatography, the regioselectivity of the reaction was determined by GC-analysis.

N-(2-Methyl-4-phenylbutyl)piperidine (3a)



The general procedure was used to synthesize compound **3a** from *N*-methylpiperidine (**1a**) and but-3-en-1-ylbenzene (**2a**). After stirring for 96 h, the mixture was purified by flash chromatography ($PE/Et_2O/HNEt_2$, 100:1:1) to give **3a** (230 mg, 0.99 mmol, 99 %) as a slightly yellow oil.

R_f (SiO_2, $PE/Et_2O/HNEt_2$, 100:1:1) = 0.05.

IR (neat): λ^{-1} = 3026, 2932, 2854, 2799, 2770, 1603, 1584, 1496, 1453, 1376, 1300, 1269, 1257, 1154, 1094, 1040, 1031, 1000, 859, 846, 697 cm^{-1}.

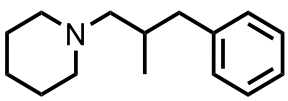
^{1}H NMR (500 MHz, C_6D_6): δ = 7.19-7.11 (m, 4 H, Ar-C*H*), 7.09-7.04 (m, 1 H, Ar-C*H*), 2.65 (ddd, *J* = 13.7, 10.2, 5.5 Hz, 1 H, CH_2), 2.52 (ddd, *J* = 13.6, 9.9, 6.5 Hz, 1 H, CH_2), 2.30-2.14 (m, 4 H, CH_2), 2.09 (dd, *J* = 12.1, 7.1 Hz, 1 H, CH_2), 1.98 (dd, *J* = 12.1, 7.5 Hz, 1 H, CH_2), 1.86-1.76 (m, 1 H, C*H*), 1.67-1.57 (m, 1 H, CH_2), 1.51-1.48 (m, 4 H, CH_2), 1.38-1.28 (m, 3 H, CH_2), 0.95 (d, *J* = 6.6 Hz, 3 H, CH_3) ppm.

^{13}C{^{1}H} NMR (125 MHz, DEPT, C_6D_6): δ = 143.3 (C), 128.8 (CH), 128.6 (CH), 126.0 (CH) 66.7 (CH_2), 55.5 (CH_2), 37.4 (CH_2), 33.7 (CH_2), 30.3 (CH), 26.6 (CH_2), 25.1 (CH_2), 18.6 (CH_3) ppm.

MS (ESI^+, TOF): *m*/*z* (%) = 232 (100) $[M+H]^+$.

HRMS (ESI^+, TOF): calculated $C_{16}H_{26}N$: 232.2065, found: 232.2064.

N-(2-Methyl-3-phenylpropyl)piperidine (3b)



The general procedure was used to synthesize compound **3b** from *N*-methylpiperidine (**1a**) and allylbenzene (**2b**). After stirring for 18 h, the mixture was purified by flash chromatography ($PE/Et_2O/HNEt_2$, 200:2:1) to give **3b** (168 mg, 0.77 mmol, 77 %) as a slightly yellow oil.

R_f (SiO_2, $PE/Et_2O/HNEt_2$, 200:2:1) = 0.05.

IR (neat): λ^{-1} = 3026, 2932, 2869, 2852, 2799, 2770, 2736, 1602, 1496, 1453, 1442, 1376, 1350, 1300, 1273, 1154, 1100, 1092, 1060, 1039, 1030, 1000, 859, 783, 739, 697 cm^{-1}.

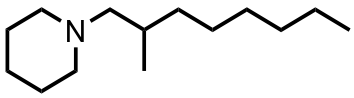
^{1}H NMR (500 MHz, C_6D_6): δ = 7.21-7.17 (m, 2 H, Ar-C*H*), 7.14-7.08 (m, 3 H, Ar-C*H*), 2.84 (dd, *J* = 13.3, 4.8 Hz, 1 H, CH_2), 2.32 – 2.20 (m, 5 H, CH_2), 2.09 (dd, *J* = 12.0, 7.5 Hz, 1 H, CH_2), 1.99 (dd, *J* = 12.0, 7.1 Hz, 1 H, CH_2), 1.96-1.88 (m, 1 H, C*H*), 1.55-1.49 (m, 4 H, CH_2), 1.36 1.29 (m, 3 H, CH_2), 0.87 (d, *J* = 6.5 Hz, 3 H, CH_3) ppm.

^{13}C{^{1}H} NMR (125 MHz, DEPT, C_6D_6): δ = 141.62 (C), 129.70 (CH), 128.44 (CH), 126.00 (CH), 66.01 (CH_2), 55.32 (CH_2), 41.66 (CH_2), 32.99 (CH), 26.62 (CH_2), 25.10 (CH_2), 18.23 (CH_3) ppm.

MS (EI, 70 eV): *m*/*z* (%) = 98 (100) $[C_6H_{12}N]^+$.

HRMS (EI, 70 eV): calculated $C_{15}H_{23}N$: 217.1825, found: 217.1820.

***N*-(2-Methyloctyl)piperidine (3c)**



The general procedure was used to synthesize compound **3c** from *N*-methylpiperidine (**1a**) and 1-octene (**2c**). After stirring for 96 h, the mixture was purified by flash chromatography (Hex/EtOAc, 3:1 + 0.02 vol% $HNEt_2$) to give **3c** (195 mg, 0.92 mmol, 92 %) as a slightly yellow oil.

R_f (SiO_2, Hex/EtOAc, 3:1 + 0.02 vol% $HNEt_2$) = 0.17.

IR (neat): λ^{-1} = 2953, 2924, 2853, 2799, 2770, 2736, 1467, 1457, 1442, 1156, 1113, 1102, 1040, 1000, 783 cm^{-1}.

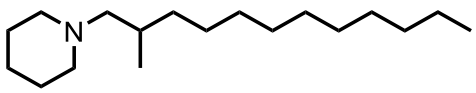
^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.40-2.24 (m, 4 H, CH_2), 2.12 (dd, *J* = 12.2, 6.4 Hz, 1 H, CH_2), 2.03 (dd, *J* = 12.2, 7.9 Hz, 1 H, CH_2), 1.67-1.59 (m, 1 H, C*H*), 1.58-1.52 (m, 4 H, CH_2), 1.44-1.19 (m, 11 H, CH_2), 1.09-0.96 (m, 1 H, CH_2), 0.90-0.83 (m, 6 H, CH_3) ppm.

^{13}C{^{1}H} NMR (125 MHz, DEPT, $CDCl_3$): δ = 66.7 (CH_2), 56.2 (CH_2), 35.6 (CH_2), 32.1 (CH_2), 30.5 (CH), 29.8 (CH_2), 27.2 (CH_2), 26.0 (CH_2), 24.7 (CH_2), 22.8 (CH_2), 18.7 (CH_3), 14.3 (CH_3) ppm.

MS (ESI^+, TOF): *m*/*z* (%) = 212 (100) $[M+H]^+$.

HRMS (ESI^+, TOF): calculated $C_{16h30}N$: 212.2378, found: 212.2380.

***N*-(2-Methyldodecyl)piperidine (3d)**



The general procedure was used to synthesize compound **3d** from *N*-methylpiperidine (**1a**) and 1-dodecene (**2c**). After stirring for 18 h, the mixture was purified by flash chromatography (Hex/EtOAc, 1:1 + 0.03 vol% $HNEt_2$) to give **3d** (177 mg, 0.66 mmol, 66 %) as a slightly yellow oil.

R_f (SiO_2, Hex/EtOAc, 1:1 + 0.03 vol% $HNEt_2$) = 0.23.

IR (neat): λ^{-1} =, 2954, 2924, 2872, 2855, 2799, 2770, 2736, 1467, 1457, 1442, 1376, 1156, 1113, 1102, 1040, 1000, 783 cm^{-1}.

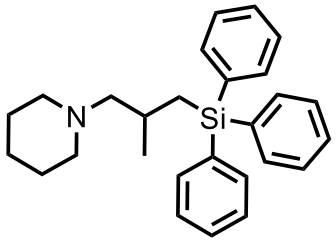
^{1}H NMR (500 MHz, C_6D_6): δ = 2.37-2.23 (m, 4 H, CH_2), 2.13 (dd, *J* = 12.1, 6.6 Hz, 1 H, CH_2), 2.02 (dd, *J* = 12.2, 7.8 Hz, 1 H, CH_2), 1.73.1.61 (m, 1 H, CH_2), 1.57-1.50 (m, 5 H, CH_2), 1.46-1.38 (m, 1 H, CH_2), 1.36-1.26 (m, 17 H, C*H*, CH_2), 1.15-1.09 (m, 1 H, CH_2), 0.99 (d, *J* = 6.4 Hz, 3 H, CH_3), 0.91 (t, *J* = 6.9 Hz, 3 H, CH_3) ppm.

^{13}C{^{1}H} NMR (125 MHz, DEPT, C_6D_6): δ = 67.1 (CH_2), 55.6 (CH_2), 35.8 (CH_2), 32.4 (CH_2), 31.0 (CH), 30.6 (CH_2), 30.2 (CH_2), 30.2 (CH_2), 29.9 (CH_2), 27.6 (CH_2), 27.5 (CH_2), 26.7 (CH_2), 25.2 (CH_2), 23.2 (CH_2), 18.8 (CH_3),14.4 (CH_3) ppm.

MS (EI, 70 eV): *m*/*z* (%) = 266 (1) $[M]^+$, 98 (100) $[C_6H_{12}N]^+$.

HRMS (EI, 70 eV): calculated $C_{18}H_{37}N$: 267.2921, found: 267.2914.

***N*-(2-Methyl-3-(triphenylsilyl)propyl)piperidine (3e)**



The general procedure was used to synthesize compound **3e** from *N*-methylpiperidine (**1a**) and allyltriphenylsilane (**2e**). After stirring for 96 h, the mixture was purified by flash chromatography (PE/Et_2O/$HNEt_2$, 100:1:1) to give **3e** (256 mg, 0.64 mmol, 64 %) as a colorless oil.

R_f (SiO_2, PE/Et_2O/$HNEt_2$, 100:1:1) = 0.11.

IR (neat): λ^{-1} = 3069, 3047, 3012, 2997, 2933, 2872, 1724, 1669, 1587, 1427, 1447, 1377, 1350, 1259, 1187, 1107, 1029, 997, 923, 909, 850, 723, 697 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.65-7.53 (m, 5 H, Ar-C*H*), 7.44-7.31 (m, 10 H, Ar-C*H*), 2.31-2.22 (m, 4 H, CH_2), 2.14-2.09 (m, 2 H, C*H*, CH_2), 2.03-1.93 (m, 1 H, CH_2), 1.82 (dd, *J* = 15.1, 3.7 Hz, 1 H, CH_2), 1.61-1.53 (m, 4 H, CH_2), 1.45-1.37 (m, 3 H, C*H*, CH_2), 0.81 (d, *J* = 6.4 Hz, 3 H, CH_3) ppm.

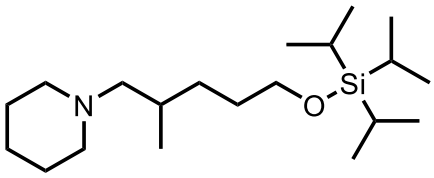
^{13}C{^{1}H} NMR (125 MHz, DEPT, $CDCl_3$): δ = 135.9 (CH), 135.7 (C), 129.4 (CH), 127.9 (CH), 69.3 (CH_2), 55.1 (CH_2), 26.7 (CH), 26.0 (CH_2), 24.6 (CH_2), 21.7 (CH_3), 19.0 (CH_2) ppm.

^{29}Si{^{1}H} NMR (99 MHz, $CDCl_3$): δ = -12.1 ppm.

MS (EI, 70 eV): *m*/*z* (%) = 398 (5) $[M]^+$, 259 (100) $[C_{18}H_{15}Si]^+$, 180 (19), 98 (85) $[C_6H_{12}N]^+$.

HRMS (EI, 70 eV): calculated $C_{27}H_{33}NSi$: 399.2377, found: 399.2381.

***N*-(2-Methyl-5-((triisopropylsilyl)oxy)pentyl)piperidine (3f)**



The general procedure was used to synthesize compound **3f** from *N*-methylpiperidine (**1a**) and triisopropyl(pent-4-en-1-yloxy)silane (**2f**). After stirring for 96 h, the mixture was purified by flash chromatography (Hex/EtOAc, 3:1 + 0.03 vol% $HNEt_2$) to give **3f** (327 mg, 0.96 mmol, 96 %) as a colorless oil.

R_f (SiO_2, Hex/EtOAc, 3:1 + 0.03 vol% $HNEt_2$) = 0.19.

IR (neat): λ^{-1} = 2934, 2893, 2866,2800,2770, 2757, 2736, 1463, 1443, 1380, 1257, 1156, 1099, 1070, 1040, 997, 939, 881, 859, 783, 721, 679, 657, 506 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.66 (t, *J* = 6.5 Hz, 2 H, CH_2), 2.47-2.31 (m, 4 H, CH_2), 2.24-2.06 (m, 2 H, CH_2), 1.76-1.67 (m, 1 H, C*H*), 1.64-1.54 (m, 5 H, CH_2), 1.49-1.37 (m, 4 H, CH_2), 1.27-1.23 (m, 1 H, CH_2), 1.09-1.00 (m, 21 H, C*H*, CH_2), 0.93 (d, *J* = 6.8 Hz, 3 H, CH_3) ppm.

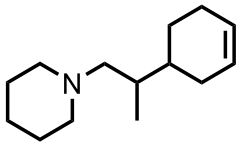
$^{13}C\{^1H\}$ NMR (125 MHz, DEPT, $CDCl_3$): δ = 66.2 (CH_2), 63.8 (CH_2), 55.0 (CH_2), 31.6 (CH_2), 30.6 (CH_2), 30.1 (CH), 25.6 (CH_2), 24.4 (CH_2), 18.7 (CH_3), 18.2 (CH_3), 12.2 (CH) ppm.

$^{29}Si\{^1H\}$ NMR (99 MHz, $CDCl_3$): δ = 12.1 ppm.

MS (EI, 70 eV): *m*/*z* (%) = 341 (43) $[M]^+$, 298 (15) $[C_{17}H_{36}NOSi]^+$, 98 (100) $[C_6H_{12}N]^+$, 84 (21), 55 (40).

HRMS (EI, 70 eV): calculated $C_{20}H_{43}NOSi$: 341.3108, found: 341.3117.

***N*-(2-(Cyclohex-3-en-1-yl)propyl)piperidine (3g)**



The general procedure was used to synthesize compound **3g** from *N*-methylpiperidine (**1a**) and 4-vinylcyclohex-1-ene (**2g**). After stirring for 96 h, the mixture was purified by flash chromatography (Hex/EtOAc, 3:1 + 0.03 vol% $HNEt_2$) to give **3g** (111 mg, 0.54 mmol, 54 %) as a colorless oil (mixture of two diastereomers).

R_f (SiO_2, Hex/EtOAc, 3:1 + 0.03 vol% $HNEt_2$) = 0.26.

IR (neat): λ^{-1} = 3022, 2930, 2920, 2853, 2838, 2799, 2770, 1744, 1653, 1467, 1442, 1376, 1350, 1302, 1269, 1257, 1237, 1154, 1120, 1098, 1057, 1040, 999, 859, 783, 656 cm^{-1}.

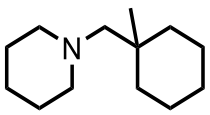
^1H NMR (500 MHz, $CDCl_3$, mixture of two diastereomers): δ = 5.70-5.61 (m, 2 H, C*H*), 2.42-2.21 (m, 5 H, CH_2), 2.11-2.00 (m, 3 H, CH_2), 1.97-1.80 (m, 2 H, CH_2), 1.70-1.61 (m, 2 H, CH_2), 1.60-1.53 (m, 5 H, CH_2), 1.41 (dd, *J* = 10.5, 4.5 Hz, 2 H, CH_2), 1.36-1.26 (m, 1 H, CH_2), 0.88-0.85 (m, 3 H, CH_3) ppm.

$^{13}C\{^1H\}$ NMR (125 MHz, DEPT, $CDCl_3$, mixture of two diastereomers): δ = 127.3 (CH), 127.2 (CH), 64.2 (CH_2), 55.3 (CH_2), 37.3 (CH), 34.8 (CH), 29.8 (CH_2), 27.1 (CH_2), 26.3 (CH_2), 26.2 (CH_2), 24.8 (CH_2), 15.1 (CH_3) ppm.

MS (ESI^+, TOF): *m*/*z* (%) = 208(100) $[M+H]^+$.

HRMS (ESI^+, TOF): calculated $C_{16h26}N$: 208.2065, found: 208.2066.

***N*-((Methylcyclohexyl)methyl)piperidine (3h)**



The general procedure was used to synthesize compound **3h** from *N*-methylpiperidine (**1a**) and methylenecyclohexane (**2h**). After stirring for 96 h, the mixture was purified by flash chromatography (Hex/EtOAc, 3:1 + 0.05 vol% $HNEt_2$) to give **3h** (108 mg, 0.55 mmol, 55 %) as a slightly yellow oil.

R_f (SiO_2, Hex/EtOAc, 3:1 + 0.05 vol% $HNEt_2$) = 0.43.

IR (neat): λ^{-1} = 2923, 2849, 2783, 2764, 2746, 1466, 1447, 1373, 1350, 1297, 1280, 1260, 1157, 1112, 1061, 1040, 1000, 859, 789, 697 cm^{-1}.

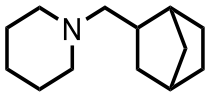
^1H NMR (500 MHz, $CDCl_3$): δ = 2.51-2.36 (m, 4 H, CH_2), 2.03 (br s, 2 H, CH_2), 1.58-1.35 (m, 11 H, CH_2), 1.33-1.19 (m, 5 H, CH_2), 0.87 (s, 3 H, CH_3) ppm.

$^{13}C\{^1H\}$ NMR (125 MHz, DEPT, $CDCl_3$): δ = 70.2 (CH_2), 57.7 (CH_2), 37.9 (CH_2), 36.0 (CH_2), 35.8 (CH_2), 26.8 (CH_2), 24.3 (C), 23.5 (CH_3), 22.3 (CH_2) ppm.

MS (EI, 70 eV): *m*/*z* (%) = 98 (100) $[C_6H_{12}N]^+$, 86 (50) $[C_5H_{12}N]^+$, 84 (85), 49 (29).

HRMS (EI, 70 eV): calculated $C_{13}H_{25}N$: 195.1982, found: 195.1976.

***N*-(Bicyclo[2.2.1]heptan-2-ylmethyl)piperidine (3i)**



The general procedure was used to synthesize compound **3i** from *N*-methylpiperidine (**1a**) and norbornene (**2i**). After stirring for 96 h, the mixture was purified by flash chromatography (Hex/EtOAc, 2:1 + 0.04 vol% $HNEt_2$) to give **3i** (162 mg, 0.84 mmol, 84 %) as a slightly yellow oil.

R_f (SiO_2, Hex/EtOAc, 2:1 + 0.04 vol% HNET2) = 0.12.

IR (neat): λ^{-1} = 2932, 2867, 2854, 2793, 2757, 2737, 1739, 1466, 1456, 1442, 1379, 1337, 1313, 1297, 1267, 1154, 1123, 1114, 1097, 1059, 1040, 991, 963, 859, 783 cm^{-1}.

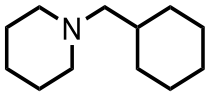
^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.45-2.34 (m, 4 H, CH_2), 2.26 (dd, *J* = 12.3, 7.7 Hz, 1 H, CH_2), 2.21-2.14 (m, 1 H, C*H*), 2.11-2.07 (m, 1 H, C*H*), 2.03 (t, *J* = 6.0 Hz, 1 H, CH_2), 1.70-1.62 (m, 1 H, C*H*), 1.63-1.57 (m, 4 H, CH_2), 1.49-1.46 (m, 2 H, CH_2), 1.44-1.39 (m, 4 H, CH_2), 1.19-1.05 (m, 4 H, CH_2) ppm.

^{13}C{^{1}H} NMR (125 MHz, DEPT, $CDCl_3$): δ = 65.9 (CH_2) 55.0 (CH_2), 40.5 (CH), 39.5 (CH), 37.4 (CH_2), 36.6 (CH), 35.6 (CH_2), 30.1 (CH_2), 29.0 (CH_2), 25.8 (CH_2), 24.5 (CH_2) ppm.

MS (EI, 70 eV): *m*/*z* (%) = 193 (8) $[M]^+$, 98 (64) $[C_6H_{12}N]^+$, 86 (61) $[C_5H_{12}N]^+$, 84 (100).

HRMS (EI, 70 eV): calculated $C_{13}H_{23}N$: 193.1825, found: 193.1829.

***N*-(Cyclohexylmethyl)piperidine (3j)**



The general procedure was used to synthesize compound **3j** from *N*-methylpiperidine (**1a**) and cyclohexene (**2j**). After stirring for 72 h, the mixture was purified by flash chromatography (Hex/EtOAc, 1:1 + 0.06 vol% $HNEt_2$) to give **3j** (44 mg, 0.24 mmol, 24 %) as a colorless oil.

R_f (SiO_2, Hex/EtOAc, 1:1 + 0.06 vol% $HNEt_2$) = 0.13.

IR (neat): λ^{-1} = 2920, 2850, 2796, 2757, 1447, 1376, 1361, 1350,1299, 1272, 1250, 1183, 1156, 1124, 1112, 1053, 1039, 999, 960, 893, 861, 776, 734 cm^{-1}.

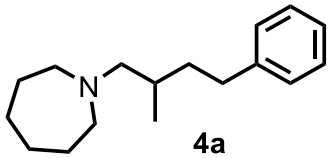
^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.41-2.32 (m, 4 H, CH_2), 2.11 (d, *J* = 6.9 Hz, 2 H, CH_2), 1.76 (ddd, *J* = 13.2, 5.4, 2.8 Hz, 2 H, CH_2), 1.72-1.62 (m, 3 H, CH_2), 1.59 (p, *J* = 5.7 Hz, 4 H, CH_2), 1.54-1.46 (m, 1 H, CH_2), 1.45-1.39 (m, 2 H, C*H*, CH_2), 1.31-1.11 (m, 5 H, CH_2) ppm.

^{13}C{^{1}H} NMR (125 MHz, DEPT, $CDCl_3$): δ = 66.5 (CH_2), 55.1 (CH_2), 35.1 (CH), 32.3 (CH_2), 26.9 (CH_2), 26.3 (CH_2), 26.0 (CH_2), 24.5 (CH_2) ppm.

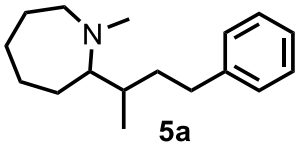
MS (ESI^+, TOF): *m*/*z* (%) = 182 (100) $[M+H]^+$.

HRMS (ESI^+, TOF): calculated $C_{12}H_{24}N$: 182.1909, found: 182.1905.

***N*-(2-Methyl-4-phenylbutyl)azepane (4a) and *N*-Methyl-2-(4-phenylbutan-2-yl)azepane (5a)**



4a



5a

The general procedure was used to synthesize **4a** and **5a** from *N*-methylazepane (**1b**) and 4-phenylbutene (**2a**). After stirring for 72 h, the mixture was purified by flash chromatography (PE/Et_2O/$HNEt_2$, 150:50:1) to give **4a** (90 mg, 0.22 mmol, 22 %) as a colorless resin and **5a** (153 mg, 0.37 mmol, 37 %) as a colorless oil.

GC: **4a**/**5a** = 38:62.

***N*-(2-Methyl-4-phenylbutyl)azepane (4a)**

R_f (SiO_2, PE/Et_2O/$HNEt_2$, 150:50:1) = 0.44.

IR (neat): λ^{-1} = 3084, 3060, 3026, 2926, 2857, 2807, 1739, 1603, 1560, 1496, 1453, 1229, 1202, 1182, 1079, 1030, 962, 907, 804, 744, 697 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.31-7.26 (m, 2 H, Ar-C*H*), 7.24-7.16 (m, 3 H, Ar-C*H*), 2.71 (ddd, *J* = 13.7, 10.4, 5.4 Hz, 1 H, CH_2), 2.66-2.57 (m, 5 H, CH_2), 2.39 (dd, *J* = 12.4, 6.9 Hz, 1 H, CH_2), 2.27 (dd, *J* = 12.3, 7.3 Hz, 1 H, CH_2), 1.81 (dddd, *J* = 13.4, 10.7, 6.4, 4.5 Hz, 1 H, CH_2), 1.67-158 (m, 9 H, C*H*, CH_2), 1.40 (dddd, *J* = 13.5, 10.4, 8.5, 5.8 Hz, 1 H, CH_2), 0.97 (d, *J* = 6.6 Hz, 3 H, CH_3) ppm.

^{13}C{^{1}H} NMR (125 MHz, DEPT, $CDCl_3$): δ = 143.2 (C), 128.5 (CH), 128.4 (CH), 125.7 (CH), 65.0 (CH_2), 55.9 (CH_2), 37.0 (CH_2), 33.5 (CH_2), 31.3 (CH), 28.1 (CH_2), 27.4 (CH_2), 18.5 (CH_3) ppm.

MS (EI, 70 eV): *m*/*z* (%) = 245 (28) $[M]^+$, 112 (100) $[C_7H_{14}N]^+$, 91 (78) $[C_7H_7]^+$, 55 (44).

HRMS (EI, 70 eV): calculated $C_{17}H_{27}N$: 245.2138, found: 245.2138.

***N*-(2-Methyl-4-phenylbutyl)azepane (5a)**

R_f (SiO_2, PE/Et_2O/$HNEt_2$, 150:50:1) = 0.34.

IR (neat): λ^{-1} = 3062, 3026, 2920, 2852, 2793, 2789, 1679, 1603, 1496, 1453, 1363, 1260, 1232, 1076, 1030, 1021, 980, 960, 801, 744, 697 cm^{-1}.

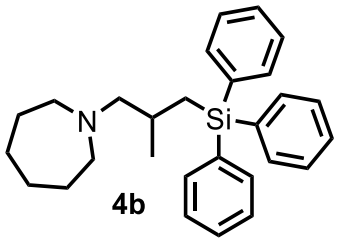
^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.31-7.15 (m, 5 H, Ar-C*H*), 3.08-2.96 (m, 1 H, CH_2), 2.94-2.84 (m, 1 H, CH_2), 2.77-2.65 (m, 1 H, CH_2), 2.64-2.51 (m, 1 H, CH_2), 2.46 (s, 3 H, CH_3), 2.41-2.32 (m, 1 H, C*H*), 1.94-1.79 (m, 2 H, CH_2), 1.75-1.62 (m, 5 H, C*H*, CH_2), 1.56-1.41 (m, 2 H, CH_2), 1.38-1.29 (m, 2 H, CH_2), 0.98 (d, *J* = 6.9 Hz, 3 H, CH_3) ppm.

^{13}C{^{1}H} NMR (125 MHz, DEPT, $CDCl_3$): δ = 143.3 (C), 128.6 (CH), 128.4 (CH), 125.7 (CH), 70.6 (CH), 54.9 (CH_2), 47.8 (CH), 42.1 (CH_3), 37.4 (CH_2), 34.6 (CH_2), 34.3 (CH_2), 29.0 (CH_2), 28.3 (CH_2), 24.7 (CH_2), 17.1 (CH_3) ppm.

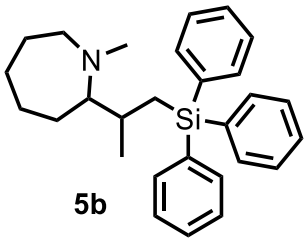
MS (EI, 70 eV): *m*/*z* (%) = 245 (14) $[M]^+$, 154 (13) $[C_{10}H_{20}N]^+$, 112 (100) $[C_7H_{14}N]^+$, 98 (42) $[C_6H_{12}N]^+$, 91 (61) $[C_7H_7]^+$, 84 (60).

HRMS (EI, 70 eV): calculated $C_{17}H_{27}N$: 245.2138, found: 245.2142.

***N*-(2-Methyl-3-(triphenylsilyl)propyl)azepane (4b) and *N*-Methyl-2-(1-(tri-phenylsilyl)propan-2-yl)azepane (5b)**



4b



5b

The general procedure was used to synthesize **4b** and **5b** from *N*-methylazepane (**1b**) and allyltriphenylsilane (**2e**). After stirring for 72 h, the mixture was purified by flash chromatography (PE/Et_2O/$HNEt_2$, 150:50:1) to give **4b** (143 mg, 0.35 mmol, 35 %) as a slightly yellow resin and **5b** (121 mg, 0.29 mmol, 29 %) as a colorless oil.

GC: **4b**/**5b** = 54:46.

***N*-(2-Methyl-3-(triphenylsilyl)propyl)azepane (4b)**

***R*$_f$** (SiO_2, PE/Et_2O/$HNEt_2$, 150:50:1) = 0.43.

IR (neat): λ^{-1} = 3067, 3047, 3023, 3012, 2997, 2923, 2862, 2809, 1589, 1567, 1486, 1456, 1427, 1357, 1332, 1304, 1259, 1187, 1157, 1107, 1029, 997, 964, 910, 856, 754, 723, 697 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.60-7.50 (m, 6 H, Ar-C*H*), 7.42-7.27 (m, 9 H, Ar-C*H*), 2.62-2.39 (m, 4 H, CH_2), 2.33-2.15 (m, 2 H, CH_2), 1.92-1.81 (m, 1 H, CH_2), 1.78-1.68 (m, 1 H, CH_2), 1.60-1.45 (m, 8 H, C*H*, CH_2), 1.20-1.09 (m, 1 H, CH_2), 0.91-0.74 (m, 3 H, CH_3) ppm.

^{13}C{^{1}H} NMR (125 MHz, DEPT, $CDCl_3$): δ = 135.9 (CH), 135.8 (C), 129.4 (CH), 127.9 (CH), 67.8 (CH_2), 55.9 (CH_2), 28.0 (CH), 27.4 (CH_2), 21.7 (CH_3), 18.9 (CH_2) ppm.

^{29}Si {^{1}H} NMR (99 MHz, $CDCl_3$): δ = -11.5 ppm.

MS (EI, 70 eV): *m*/*z* (%) = 413 (7) $[M]^+$, 259 (65) $[C_{18}H_{15}Si]^+$, 199 (23), 181 (24), 112 (100) $[C_7H_{14}N]^+$, 105 (11).

HRMS (EI, 70 eV): calculated $C_{28}H_{35}NSi$: 413.2533, found: 413.2538.

***N*-Methyl-2-(1-(triphenylsilyl)propan-2-yl)azepane (5b)**

***R*$_f$** (SiO_2, PE/Et_2O/$HNEt_2$, 150:50:1) = 0.34.

IR (neat): λ^{-1} = 3067, 3047, 3023, 3012, 2997, 2920, 2850, 2794, 2770, 2360, 2332, 1486, 1453, 1427, 1400, 1379, 1329, 1263, 1222, 1187, 1157, 1107, 1073, 1021, 997, 983, 957, 756, 727, 697, 669, 606 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.62-7.55 (m, 6 H, Ar-C*H*), 7.43-7.31 (m, 9 H, Ar-C*H*), 2.99 (dd, *J* = 14.8, 9.3 Hz, 1 H, CH_2), 2.80 (dd, *J* = 14.6, 7.0 Hz, 1 H, CH_2), 2.28 (s, 3 H, CH_3), 2.23-2.16 (m, 1 H, C*H*), 2.01-1.92 (m, 1 H, CH_2), 1.83-1.75 (m, 2 H, CH_2), 1.70-1.60 (m, 2 H, CH_2), 1.46-1.34 (m, 2 H, CH_2), 1.31-1.17 (m, 4 H, CH_2), 0.76 (d, *J* = 6.4 Hz, 3 H, CH_3) ppm.

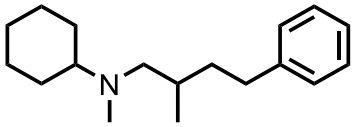
^{13}C{^{1}H} NMR (125 MHz, DEPT, $CDCl_3$): δ = 135.9 (CH), 135.8 (C), 129.4 (CH), 128.0 (CH), 72.5 (CH), 54.9 (CH_2), 42.0 (CH_3), 33.2 (CH), 29.0 (CH_2), 28.3 (CH_2), 27.2 (CH_2), 24.6 (CH_2), 18.8 (CH_2), 18.4 (CH_3) ppm.

^{29}Si {^{1}H} NMR (99 MHz, INEPT, $CDCl_3$): δ = -11.4 ppm.

MS (EI, 70 eV): *m*/*z* (%) = 413 (4) $[M]^+$, 259 (53) $[C_{18}H_{15}Si]^+$, 181 (21), 112 (100) $[C_7H_{14}N]^+$, 105 (18).

HRMS (EI, 70 eV): calculated $C_{28}H_{35}NSi$: 413.2533, found: 413.2531.

***N*-Methyl-*N*-(2-methyl-4-phenylbutyl)cyclohexylamine (6a)**



The general procedure was used to synthesize compound **6a** from *N*,*N*-dimethylcyclohexylamine (**1d**) and but-3-en-1-ylbenzene (**2a**). After stirring for 72 h, the mixture was purified by flash chromatography (Hex/EtOAc/$HNEt_2$, 200:1:1) to give **6a** (204 mg, 0.79 mmol, 79 %) as a colorless oil.

R_f (SiO_2, Hex/EtOAc/$HNEt_2$, 200:1:1) = 0.03.

IR (neat): λ^{-1} = 3026, 2926, 2853, 1739, 1603, 1496, 1452, 1374, 1346, 1260, 1217, 1117, 1043, 986, 890, 860, 836, 743, 697 cm^{-1}.

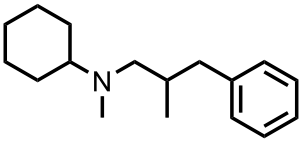
^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.29-7.25 (m, 2 H, Ar-C*H*), 7.22-7.16 (m, 3 H, Ar-C*H*), 2.71 (ddd, *J* = 13.6, 10.4, 5.4 Hz, 1 H, CH_2), 2.58 (ddd, *J* = 13.7, 10.2, 6.3 Hz, 1 H, CH_2), 2.39-2.29 (m, 2 H, C*H*, CH_2), 2.24 (s, 3 H, CH_3), 2.22-2.17 (m, 1 H, CH_2), 1.84-1.74 (m, 5 H, C*H*, CH_2), 1.69-1.58 (m, 2 H, CH_2), 1.38 (dddd, *J* = 13.5, 10.2, 8.2, 5.4 Hz, 1 H, CH_2), 1.26-1.16 (m, 4 H, CH_2), 1.12-1.04 (m, 1 H, CH_2), 0.97 (d, *J* = 6.6 Hz, 3 H, CH_3) ppm.

^{13}C{^{1}H} NMR (125 MHz, DEPT, $CDCl_3$): δ = 143.1 (C), 128.5 (CH), 128.4 (CH), 125.7 (CH), 63.4 (CH), 60.5 (CH_2), 38.7 (CH_3), 37.1 (CH_2), 33.5 (CH_2), 31.1 (CH), 28.4 (CH_2), 26.6 (CH_2), 26.2 (CH_2), 18.6 (CH_3) ppm.

MS (EI, 70 eV): *m*/*z* (%) = 259 (11) $[M]^+$, 126 (100) $[C_8H_{16}N]^+$, 91 (35) $[C_7H_7]^+$, 83 (13) $[C_6H_{11}]^+$, 55 (18), 44 (59).

HRMS (EI, 70 eV): calculated $C_{18}H_{29}N$: 259.2295, found: 259.2302.

***N*-Methyl-*N*-(2-methyl-3-phenylpropyl)cyclohexylamine (6b)**



The general procedure was used to synthesize compound **6b** from *N*,*N*-dimethylcyclohexylamine (**1d**) and allylbenzene (**2b**). After stirring for 72 h, the mixture was purified by flash chromatography (PE/Et_2O/$HNEt_2$, 200:1:1) to give **6b** (145 mg, 0.59 mmol, 59 %) as a colorless oil.

R_f (SiO_2, PE/Et_2O/$HNEt_2$, 200:1:1) = 0.03.

IR (neat): λ^{-1} = 3084, 3062, 3026, 2926, 2853, 2789, 1739, 1603, 1496, 1452, 1374, 1364, 1259, 1226, 1200, 1180, 1123, 1082, 1043, 987, 966, 890, 739, 699 cm^{-1}.

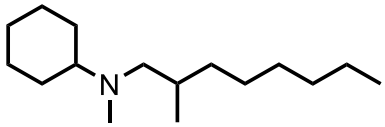
^{1}H NMR (500 MHz, C_6D_6): δ = 7.22-7.18 (m, 2 H, Ar-C*H*), 7.16-7.13 (m, 2 H, Ar-C*H*), 7.11-7.08 (m, 1 H, Ar-C*H*), 2.94 (dd, *J* = 13.3, 4.7 Hz, 1 H, CH_2), 2.31-2.26 (m, 1 H, C*H*), 2.26-2.14 (m, 2 H, CH_2), 2.17 (s, 3 H, CH_3), 1.88 (dqd, *J* = 9.0, 6.8, 4.6 Hz, 1 H, C*H*), 1.78-1.68 (m, 4 H, CH_2), 1.58-1.52 (m, 1 H, CH_2), 1.22-1.08 (m, 4 H, CH_2), 1.05-0.98 (m, 1 H, CH_2), 0.90 (d, *J* = 6.6 Hz, 3 H, CH_3) ppm.

^{13}C{^{1}H} NMR (125 MHz, DEPT, C_6D_6): δ = 142.1 (C), 129.6 (CH), 128.5 (CH), 126.0 (CH), 63.8 (CH), 60.8 (CH_2), 41.8 (CH_2), 38.0 (CH_3), 34.4 (CH), 29.1 (CH_2), 26.9 (CH_2), 26.5 (CH_2), 18.1 (CH_3) ppm.

MS (EI, 70 eV): *m*/*z* (%) = 245 (31) $[M]^+$, 126 (50) $[C_8H_{16}N]^+$, 91 (23) $[C_7H_7]^+$, 83 (8) $[C_6H_{11}]^+$, 55 (21), 44 (100).

HRMS (EI, 70 eV): calculated $C_{17}H_{27}N$: 245.2138, found: 245.2130.

***N*-Methyl-*N*-(2-methyloctyl)cyclohexylamine (6c)**



The general procedure was used to synthesize compound **6c** from *N*,*N*-dimethylcyclohexylamine (**1d**) and 1-octene (**2c**). After stirring for 72 h, the mixture was purified by distillation (0.1 mbar / 205 °C) to give **6c** (195 mg, 0.81 mmol, 81 %) as a colorless oil.

IR (neat): λ^{-1} =, 2953, 2924, 2853, 2790, 1746, 1690, 1450, 1376, 1260, 1116, 1059, 1043, 1026, 987, 890 cm^{-1}.

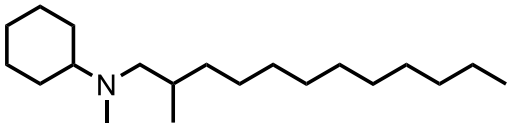
^{1}H NMR (500 MHz, C_6D_6): δ = 2.33-2.29 (m, 1 H, C*H*), 2.27 (dd, *J* = 12.3, 6.6 Hz, 1 H, CH_2), 2.20 (s, 3 H, CH_3), 2.14 (dd, *J* = 12.3, 7.7 Hz, 1 H, CH_2), 1.83-1.76 (m, 2 H, CH_2), 1.74-1.69 (m, 2 H, CH_2), 1.66-1.58 (m, 1 H, CH_2), 1.56-1.48 (m, 2 H, CH_2), 1.47-1.37 (m, 1 H, CH_2), 1.35-1.28 (m, 6 H, C*H*, CH_2), 1.21-1.09 (m, 5 H, CH_2), 1.00 (d, *J* = 6.6 Hz, 3 H, CH_3) 0.95-0.88 (m, 3 H, CH_3) ppm.

^{13}C{^{1}H} NMR (125 MHz, DEPT, C_6D_6): δ = 63.8 (CH), 61.3 (CH_2), 38.2 (CH_3), 35.6 (CH_2), 32.4 (CH_2), 32.0 (CH), 30.3 (CH_2), 29.1 (CH_2), 28.9 (CH_2), 27.6 (CH_2), 26.9 (CH_2), 26.6 (CH_2), 23.2 (CH_2), 18.6 (CH_3), 14.4 (CH_3) ppm.

MS (ESI^+, TOF): *m*/*z* (%) = 240 (100) $[M+H]^+$.

HRMS (ESI^+, TOF): calculated $C_{16}H_{34}N$: 240.2691, found: 240.2690.

***N*-Methyl-*N*-(2-methyldodecyl)cyclohexylamine (6d)**



The general procedure C was used to synthesize compound **6d** from *N*,*N*-dimethylcyclohexylamine (**1d**) and 1-dodecene (**2d**). After stirring for 18 h, the mixture was purified by flash chromatography (Hex/EtOAc, 3:1 + 0.01 vol% $HNEt_2$) to give **6d** (204 mg, 0.69 mmol, 69 %) as a slightly yellow oil.

R_f (SiO_2, Hex/EtOAc, 3:1 + 0.01 vol% $HNEt_2$) = 0.16.

IR (neat): λ^{-1} = 2923, 2853, 2790, 1452, 1376, 1346, 1260, 1116, 1059, 1044, 1024, 986, 890, 721, 699 cm^{-1}.

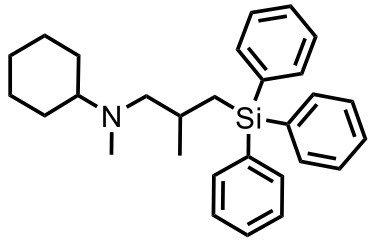
^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.48-2.35 (m, 1 H, C*H*), 2.28 (s, 3 H, CH_3), 2.22-2.10 (m, 1 H, CH_2), 1.88-1.74 (m, 4 H, CH_2), 1.66-1.54 (m, 2 H, CH_2), 1.43-1.33 (m, 2 H, CH_2), 1.28-1.24 (m, 20 H, CH_2), 1.13-1.01 (m, 2 H, CH_2), 0.87 (m, 6 H, CH_3) ppm.

^{13}C{^{1}H} NMR (125 MHz, DEPT, $CDCl_3$): δ = 63.5 (CH), 60.6 (CH_2), 38.9 (CH_3), 35.5 (CH_2), 32.1 (CH_2), 30.1 (CH_2), 29.9 (CH_2), 29.8 (CH_2), 29.8 (CH_2), 29.5 (CH_2), 28.6 (CH_2), 28.1 (CH_2), 27.2 (CH_2), 26.5 (CH_2), 26.2 (CH_2), 22.8 (CH_2), 18.7 (CH_3), 14.3 (CH_3) ppm.

MS (ESI^+, TOF): *m*/*z* (%) = 296 (100) $[M+H]^+$.

HRMS (ESI^+, TOF): calculated $C_{20}H_{42}N$: 296.3305, found: 296.3317.

***N*-Methyl-*N*-(2-methyl-3-(triphenylsilyl)propyl)cyclohexylamine (6e)**



The general procedure was used to synthesize compound **6e** from *N*,*N*-dimethylcyclohexylamine (**1d**) and allyltriphenylsilane (**2e**). After stirring for 24 h, the mixture was purified by flash chromatography (Hex/EtOAc, 3:1 + 0.01 vol% $HNEt_2$) to give **6e** (252 mg, 0.59 mmol, 59 %) as a slightly yellow oil.

R_f (SiO_2, Hex/EtOAc, 3:1 + 0.01 vol% $HNEt_2$) = 0.21.

IR (neat): λ^{-1} = 3069, 3049, 3023, 3011, 2997, 2926, 2853, 2784, 1486, 1450, 1427, 1374, 1343, 1259, 1156, 1107, 1043, 997, 986, 890, 851, 723, 697 cm^{-1}.

^{1}H NMR (500 MHz, C_6D_6): δ = 7.74-7.68 (m, 6 H, Ar-C*H*), 7.22-7.17 (m, 9 H, Ar-C*H*), 2.27-2.23 (m, 1 H, C*H*), 2.21 (dd, *J* = 12.2, 7.6 Hz, 1 H, CH_2), 2.15 (dd, *J* = 12.2, 6.6 Hz, 1 H, CH_2), 2.08 (s, 3 H, CH_3), 2.05-1.99 (m, 1 H, C*H*), 1.96 (dd, *J* = 14.9, 3.6 Hz, 1 H, CH_2), 1.74-1.65 (m, 4 H, CH_2), 1.57-1.51 (m, 1 H, CH_2), 1.17-1.08 (m, 5 H, C*H*, CH_2), 1.00 (tdd, *J* = 12.5, 6.0, 2.8 Hz, 1 H, C*H*), 0.92 (d, *J* = 6.5 Hz, 3 H, CH_3) ppm.

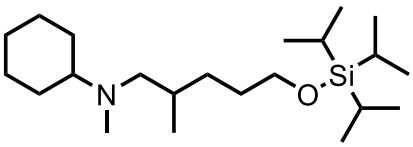
^{13}C{^{1}H} NMR (125 MHz, DEPT, C_6D_6): δ = 136.5 (CH), 136.3 (C), 129.6 (CH), 128.2 (CH), 64.2 (CH_2), 63.7 (CH), 38.1 (CH_3), 29.1 (CH_2), 28.2 (CH), 26.9 (CH_2), 26.6 (CH_2), 21.8 (CH_3), 19.1 (CH_2) ppm.

^{29}Si{^{1}H} NMR (99 MHz, $CDCl_3$): δ = -11.2 ppm.

MS (EI, 70 eV): *m*/*z* (%) = 427 (3) $[M]^+$, 259 (63) $[C_{18}H_{15}Si]^+$, 180 (25), 126 (100) $[C_8H_{16}N]^+$, 83 (21) $[C_6H_{11}]^+$, 55 (35), 44 (86).

HRMS (EI, 70 eV): calculated $C_{29}H_{37}NSi$: 427.2690, found: 427.2694.

***N*-Methyl-(2-methyl-5-((triisopropylsilyl)oxy)pentyl)cyclohexylamine (6f)**



The general procedure was used to synthesize compound **6f** from *N*,*N*-dimethylcyclohexylamine (**1d**) and triisopropyl(pent-4-en-1-yloxy)silane (**2e**). After stirring for 18 h, the mixture was purified by flash chromatography (Hex/EtOAc, 3:1 + 0.02 vol% $HNEt_2$) to give **6f** (237 mg, 0.64 mmol, 64 %) as a colorless oil.

R_f (SiO_2, Hex/EtOAc, 3:1 + 0.02 vol% $HNEt_2$) = 0.15.

IR (neat): λ^{-1} = 2926, 2864, 2854, 1740, 1463, 1452, 1382, 1346, 1259, 1247, 1102, 1070, 1044, 1013, 994, 987, 937, 918, 881, 836, 787, 721, 679, 657 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.66 (td, *J* = 6.7, 2.0 Hz, 2 H, CH_2), 2.41-2.32 (m, 1 H, C*H*), 2.25 (s, 3 H, CH_3), 2.20-2.13 (m, 1 H, CH_2), 1.83-1.75 (m, 4 H, CH_2), 1.64-1.58 (m, 3 H, C*H*, CH_2), 1.55-1.44 (m, 2 H, CH_2), 1.27-1.17 (m, 6 H, CH_2), 1.08-1.04 (m, 21 H, C*H*, CH_3), 0.90 (d, *J* = 6.8 Hz, 3 H, CH_3) ppm.

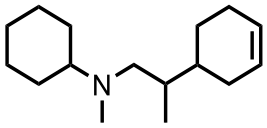
^{13}C{^{1}H} NMR (125 MHz, DEPT, $CDCl_3$): δ = 64.0 (CH_2), 63.5 (CH), 60.6 (CH_2), 38.8 (CH_3), 31.4 (CH_2), 30.7 (CH_2), 30.5 (CH), 29.8 (CH_2), 26.6 (CH_2), 26.2 (CH_2) 18.6 (CH_3), 18.2 (CH_3), 12.2 (CH) ppm.

^{29}Si{^{1}H} NMR (99 MHz, $CDCl_3$): δ = 12.1 ppm.

MS (EI, 70 eV): *m*/*z* (%) = 369 (1) $[M]^+$, 326 (7) $[C_{19}H_{40}NOSi]^+$, 126 (100) $[C_8H_{16}N]^+$, 84 (31), 83 (8) $[C_6H_{11}]^+$, 55 (18), 44 (37).

HRMS (EI, 70 eV): calculated $C_{22}H_{47}NOSi$: 369.3421, found: 369.3422.

***N*-(2-(Cyclohex-3-en-1-yl)propyl)-*N*-methylcyclohexylamine (6g)**



The general procedure was used to synthesize compound **6g** from *N*,*N*-dimethylcyclohexylamine (**1d**) and 4-vinylcyclohex-1-ene (**2g**). After stirring for 72 h, the mixture was purified by flash chromatography (Hex/EtOAc, 3:1 + 0.03 vol% $HNEt_2$) to give **6g** (129 mg, 0.55 mmol, 55 %) as a colorless oil (mixture of two diastereomers).

R_f (SiO_2, Hex/EtOAc, 3:1 + 0.03 vol% $HNEt_2$) = 0.12.

IR (neat): λ^{-1} = 3020, 2924, 2853, 2777, 1450, 1436, 1376, 1259, 1217, 1146, 1117, 1083, 1057, 1043, 1026, 986, 910, 890, 866, 836, 731, 713, 699, 656 cm^{-1}.

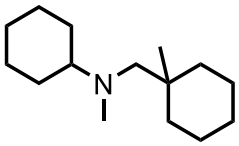
^{1}H NMR (500 MHz, $CDCl_3$, mixture of two diastereomers): δ = 5.70-5.61 (m, 2 H, C*H*), 2.44-2.31 (m, 2 H, C*H*, CH_2), 2.24 (s, 3 H, CH_3), 2.16 (ddd, *J* = 12.4, 7.7, 4.1 Hz, 1 H, CH_2), 2.10-2.00 (m, 2 H, CH_2), 1.95-1.87 (m, 1 H, CH_2), 1.85-1.73 (m, 5 H, CH_2), 1.68-1.52 (m, 4 H, C*H*, CH_2), 1.27-1.17 (m, 5 H, CH_2), 1.12-1.03 (m, 1 H, CH_2), 0.86 (d, *J* = 6.6 Hz, 3 H, CH_3) ppm.

^{13}C{^{1}H} NMR (125 MHz, DEPT, $CDCl_3$, mixture of two diastereomers): δ = 127.3 (CH), 127.2 (CH), 63.7 (CH), 58.2 (CH_2), 38.9 (CH_3), 36.8 (CH), 36.0 (CH), 30.1 (CH_2), 29.8 (CH_2), 29.0 (CH_2), 28.4 (CH_2), 27.3 (CH_2), 26.6 (CH_2), 26.3 (CH_2), 24.5 (CH_2), 14.8 (CH_3) ppm.

MS (ESI^+, TOF): *m*/*z* (%) = 236 (100) $[M+H]^+$.

HRMS (ESI^+, TOF): calculated $C_{26}H_{30}N$: 236.2378, found: 236.2371.

***N*-Methyl-*N*-((1-methylcyclohexyl)methyl)cyclohexylamine (6h)**



The general procedure was used to synthesize compound **4h** from *N*,*N*-dimethylcyclohexylamine (**1d**) and methylenecyclohexane (**2h**). After stirring for 48 h, the mixture was purified by flash chromatography (PE/Et_2O/$HNEt_2$, 200:50:1) to give **4h** (173 mg, 0.77 mmol, 77 %) as a slightly yellow oil.

R_f (SiO_2, PE/Et_2O/$HNEt_2$, 200:50:1) = 0.51.

IR (neat): λ^{-1} = 2923, 2852, 2783, 1494, 1466, 1449, 1374, 1343, 1277, 1260, 1203, 1120, 1047, 987, 890, 751, 729, 699, 606 cm^{-1}.

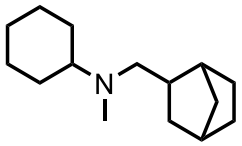
^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.27 (s, 3 H, CH_3), 2.24-2.19 (m, 1 H, C*H*), 2.15 (s, 2 H, CH_2), 1.81-1.70 (m, 4 H, CH_2), 1.64-1.56 (m, 1 H, CH_2), 1.53-1.37 (m, 5 H, CH_2), 1.31-1.13 (m, 9 H, CH_2), 1.09-0.99 (m, 1 H, CH_2), 0.85 (s, 3 H, CH_3) ppm.

^{13}C{^{1}H} NMR (125 MHz, DEPT, $CDCl_3$): δ = 66.9 (CH), 66.7 (CH_2), 40.9 (CH_3), 36.2 (CH_2), 35.8 (CH_2), 29.0 (CH_2), 26.8 (CH_2), 26.6 (C), 26.6 (CH_2), 23.3 (CH_3), 22.3 (CH_2) ppm.

MS (EI, 70 eV): *m*/*z* (%) = 83 (19) $[C_6H_{11}]^+$, 55 (36), 44 (100).

HRMS (EI, 70 eV): calculated $C_{15}H_{29}N$: 223.2295, found: 223.2295.

***N*-(Bicyclo[2.2.1]heptan-2-ylmethyl)-*N*-methylcyclohexylamine (6i)**



The general procedure was used to synthesize compound **6i** from *N*,*N*-dimethylcyclohexylamine (**1d**) and norbornene (**2i**). After stirring for 18 h, the mixture was purified by flash chromatography (Hex/EtOAc, 1:1 + 0.02 vol% $HNEt_2$) to give **6i** (122 mg, 0.55 mmol, 55 %) as a slightly yellow oil.

R_f (SiO_2, Hex/EtOAc, 1:1 + 0.02 vol% $HNEt_2$) = 0.08.

IR (neat): λ^{-1} = 2926, 2867, 2853, 2779, 1740, 1450, 1364, 1340, 1260, 1204, 1170, 1120, 1059, 1044, 1025, 984, 967, 890, 851, 835 cm^{-1}.

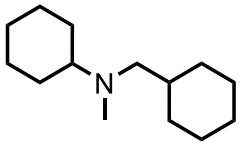
^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.33-2.30 (m, 1 H, CH_2), 2.29 (s, 3 H, CH_3), 2.21-2.16 (m, 1 H, C*H*), 2.11-2.07 (m, 2 H, C*H*, CH_2), 1.82-1.76 (m, 4 H, CH_2), 1.63-1.57 (m, 2 H, CH_2), 1.51-1.45 (m, 2 H, C*H*, CH_2), 1.38 (ddd, *J* = 11.3, 8.5, 2.3 Hz, 1 H, CH_2), 1.25-1.02 (m, 11 H, C*H*, CH_2) ppm.

^{13}C{^{1}H} NMR (125 MHz, DEPT, $CDCl_3$): δ = 63.5 (CH) 59.3 (CH_2), 40.4 (CH), 40.1 (CH), 38.8 (CH_3), 36.7 (CH_2), 36.6 (CH), 35.5 (CH_2), 30.2 (CH_2), 29.1 (CH_2), 28,4 (CH_2), 26,5 (CH_2), 26.2 (CH_2) ppm.

MS (EI, 70 eV): *m*/*z* (%) = 221 (5) $[M]^+$, 126 (100) $[C_8H_{16}N]^+$, 112 (21) $[C_7H_{14}N]^+$, 86 (35), 84 (56), 49 (19).

HRMS (EI, 70 eV): calculated $C_{15}H_{27}N$: 221.2138, found: 221.2135.

***N*-(Cyclohexylmethyl)-*N*-methylcyclohexylamine (6j)**



The general procedure was used to synthesize compound **6j** from *N*,*N*-dimethylcyclohexylamine (**1d**) and cyclohexene (**2j**). After stirring for 72 h, the mixture was purified by flash chromatography (Hex/EtOAc, 1:1 + 0.04 vol% $HNEt_2$) to give **6j** (92 mg, 0.44 mmol, 44 %) as a slightly yellow oil.

R_f (SiO_2, Hex/EtOAc, 1:1 + 0.04 vol% $HNEt_2$) = 0.10.

IR (neat): λ^{-1} = 2923, 2849, 2783, 2764, 2746, 1466, 1447, 1373, 1350, 1297, 1280, 1260, 1157, 1112, 1061, 1040, 1000, 859, 789, 697 cm^{-1}.

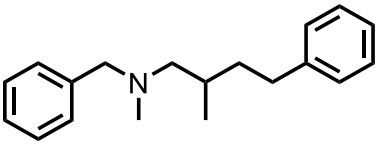
^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.39-2.30 (m, 1 H, C*H*), 2.25 (s, 3 H, CH_3), 2.20 (d, *J* = 6.8 Hz, 2 H, CH_2), 1.81-1.74 (m, 6 H, CH_2), 1.73-1.58 (m, 4 H, CH_2), 1.40 (ttt, *J* = 10.6, 6.9, 3.4 Hz, 1 H, C*H*), 1.28-1.12 (m, 7 H, CH_2), 1.12-1.04 (m, 1 H, CH_2), 0.88-0.78 (m, 2 H, CH_2) ppm.

^{13}C{^{1}H} NMR (125 MHz, DEPT, $CDCl_3$): δ = 63.4 (CH), 60.6 (CH_2), 39.1 (CH_3), 36.4 (CH), 32.2 (CH_2), 28.5 (CH_2), 27.0 (CH_2), 26.6 (CH_2), 26.4 (CH_2), 26.2 (CH_2) ppm.

MS (EI, 70 eV): *m*/*z* (%) = 209 (5) $[M]^+$, 166 (28), 126 (100) $[C_8H_{16}N]^+$.

HRMS (EI, 70 eV): calculated $C_{14}H_{27}N$: 209.2138, found: 209.2142.

***N*-Benzyl-*N*,2-dimethyl-4-phenylbutan-1-amine (7a)**



An oven-dried Schlenk tube (100 mL) equipped with a Teflon stopcock and a magnetic stirring bar was transferred into a nitrogen-filled glovebox and charged with $TiBn_4$ (0.10 mmol, 10 mol%) and toluene (1 mL). To this solution, *N*,*N*-Dimethylbenzylamine (**1e**, 1.00 mmol) and but-3-en-1-ylbenzene (**2a**, 1.50 mmol) were added in this order. Toluene (1 mL) was used to wash down the reagents. Finally, the remaining toluene (3 mL) was used to transfer $Ph_3C[B(C_6F_5)_4]$ (73.8 mg, 8 mol%) into the Schlenk tube as a suspension. The tube was sealed, removed from the glovebox, and placed in an aluminum heating block. The reaction mixture was heated to 35 °C for 18 h. After the reaction mixture had been cooled to room temperature, it was diluted with EtOAc (25 mL). The solvents were removed under reduced pressure and the residue was purified by flash chromatography (Hex/EtOAc, 3:1 + 0.02 vol% $HNEt_2$) to give **7a** (95 mg, 0.36 mmol, 36 %) as a slightly yellow oil.

R_f (SiO_2, Hex/EtOAc, 3:1 + 0.02 vol% $HNEt_2$) = 0.45.

IR (neat): λ^{-1} = 3084, 3062, 3026, 2927, 2872, 2840, 2784, 1739, 1603, 1584, 1494, 1453, 1367, 1250, 1154, 1127, 1074, 1026, 977, 906, 856, 737, 696 cm^{-1}.

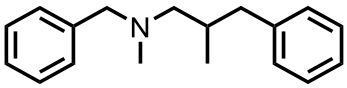
^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.35-7.26 (m, 7 H, Ar-C*H*), 7.22-7.16 (m, 3 H, Ar-C*H*), 3.49 (q, *J* = 13.2 Hz, 2 H, CH_2), 2.71 (ddd, *J* = 13.8, 10.2, 5.4 Hz, 1 H, CH_2), 2.59 (ddd, *J* = 13.7, 10.2, 6.3 Hz, 1 H, CH_2), 2.29 (dd, *J* = 12.1, 6.8 Hz, 1 H, CH_2), 2.21-2.15 (m, 4 H, CH_2, CH_3), 1.83 (dddd, *J* = 13.1, 10.4, 6.4, 4.5 Hz, 1 H, CH_2), 1.78-1.72 (m, 1 H, C*H*), 1.45-1.38 (m, 1 H, CH_2), 1.00 (d, *J* = 6.5 Hz, 3 H, CH_3) ppm.

^{13}C{^{1}H} NMR (125 MHz, DEPT, $CDCl_3$): δ = 143.1 (C) 139.4 (C), 129.2 (CH), 128.5 (CH), 128.4 (CH), 128.3 (CH), 127.0 (CH), 125.7 (CH), 64.6 (CH_2) 62.8 (CH_2), 42.8 (CH_3), 36.9 (CH_2), 33.4 (CH_2), 30.8 (CH), 18.4 (CH_3) ppm.

MS (EI, 70 eV): *m*/*z* (%) = 267 (15) $[M]^+$, 134 (16) $[C_9H_{12}N]^+$, 91 (100) $[C_7H_7]^+$, 65 (12).

HRMS (EI, 70 eV): calculated $C_{19}H_{25}N$: 267.1982, found: 267.1983.

***N*-Benzyl-*N*,2-dimethyl-3-phenylpropan-1-amine (7b)**



An oven-dried Schlenk tube (100 mL) equipped with a Teflon stopcock and a magnetic stirring bar was transferred into a nitrogen-filled glovebox and charged with $TiBn_4$ (0.10 mmol, 10 mol%) and toluene (1 mL). To this solution, *N*,*N*-Dimethylbenzylamine (**1e**, 1.00 mmol) and allylbenzene (**2b**, 1.50 mmol) were added in this order. Toluene (1 mL) was used to wash down the reagents. Finally, the remaining toluene (3 mL) was used to transfer $Ph_3C[B(C_6F_5)_4]$ (73.8 mg, 8 mol%) into the Schlenk tube as a suspension. The tube was sealed, removed from the glovebox, and placed in an aluminum heating block. The reaction mixture was heated to 35 °C for 18 h. After the reaction mixture had been cooled to room temperature, it was diluted with EtOAc (25 mL). The solvents were removed under reduced pressure and the residue was purified by flash chromatography (Hex/EtOAc, 3:1 + 0.02 vol% $HNEt_2$) to give **7b** (49 mg, 0.19 mmol, 19 %) as a slightly yellow oil.

R_f (SiO_2, Hex/EtOAc, 3:1 + 0.02 vol% $HNEt_2$) = 0.45.

IR (neat): λ^{-1} = 3084, 3062, 3026, 2952, 2926, 2872, 2840, 2784, 1600, 1584, 1494, 1452, 1419, 1366, 1226, 1074, 1026, 973, 909, 857, 737, 696 cm^{-1}.

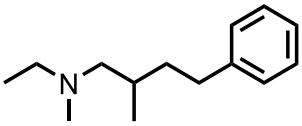
^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.36-7.33 (m, 2 H, Ar-C*H*), 7.23-7.17 (m, 4 H, Ar-C*H*), 7.15-7.07 (m, 4 H, Ar-C*H*), 3.34 (s, 2 H, CH_2), 2.86 (dd, *J* = 13.3, 4.9 Hz, 1 H, CH_2), 2.23-2.14 (m, 2 H, CH_2), 2.06 (s, 3 H, CH_3), 2.05 (dd, *J* = 12.0, 7.2 Hz, 1 H, CH_2), 1.90 (dqd, *J* = 8.6, 6.9, 4.8 Hz, 1 H, C*H*), 0.85 (d, *J* = 6.6 Hz, 3 H, CH_3) ppm.

^{13}C{^{1}H} NMR (125 MHz, DEPT, $CDCl_3$): δ = 141.6 (C), 140.3 (C), 129.6 (CH), 129.2 (CH), 128.5 (CH), 128.5 (CH), 127.2 (CH), 126.0 (CH), 64.5 (CH_2), 63.2 (CH_2), 42.6 (CH_3), 41.6 (CH_2), 33.8 (CH), 18.1 (CH_3) ppm.

MS (EI, 70 eV): *m*/*z* (%) = 253 (3) $[M]^+$, 134 (69) $[C_9H_{12}N]^+$, 91 (100) $[C_7H_7]^+$, 65 (12), 43 (54).

HRMS (EI, 70 eV): calculated $C_{18}H_{23}N$: 253.1825, found: 253.1838.

***N*-Ethyl-*N*,2-dimethyl-4-phenylbutan-1-amine (8a)**



The general procedure was used to synthesize compound **8a** from *N*,*N*-dimethylethylamine (**1f**) and 4-phenylbutene (**2a**). After stirring for 18 h, the mixture was purified by flash chromatography (Hex/EtOAc, 1:1 + 0.08 vol% $HNEt_2$) to give **8a** (72 mg, 0.35 mmol, 35 %) as a slightly yellow oil.

R_f (SiO_2, Hex/EtOAc, 1:1 + 0.08 vol% $HNEt_2$) = 0.08.

IR (neat): λ^{-1} = 3086, 3063, 3027, 2967, 2924, 2872, 2854, 2786, 1739, 1604, 1584, 1496, 1453, 1379, 1302, 1226, 1082, 1044, 1031, 970, 906, 804, 744, 697 cm^{-1}.

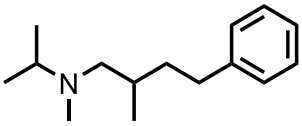
^{1}H NMR (500 MHz, C_6D_6): δ = 7.20-7.17 (m, 2 H, Ar-C*H*), 7.15-7.12 (m, 2 H, Ar-C*H*), 7.10-7.06 (m, 1 H, Ar-C*H*), 2.64 (ddd, *J* = 13.5, 10.3, 5.4 Hz, 1 H, CH_2), 2.51 (ddd, *J* = 13.6, 10.1, 6.5 Hz, 1 H, CH_2), 2.30-2.20 (m, 2 H, CH_2), 2.09 (dd, *J* = 12.1, 7.1 Hz, 1 H, CH_2), 2.05 (s, 3 H, CH_3), 1.98 (dd, *J* = 12.1, 7.5 Hz, 1 H, CH_2), 1.86-1.78 (m, 1 H, CH_2), 1.63-1.54 (m, 1 H, C*H*), 1.38-1.29 (m, 1 H, CH_2), 0.96 (t, *J* = 7.2 Hz, 3 H, CH_3), 0.95 (d, *J* = 6.6 Hz, 3 H, CH_3) ppm.

^{13}C{^{1}H} NMR (125 MHz, DEPT, C_6D_6): δ = 143.3 (C), 128.8 (CH), 128.6 (CH), 126.0 (CH), 64.9 (CH_2), 52.3 (CH_2), 42.1 (CH_3), 37.3 (CH_2), 33.7 (CH_2), 31.1 (CH), 18.5 (CH_3), 12.8 (CH_3) ppm.

MS (ESI^+, TOF): *m*/*z* (%) = 206 (100) $[M+H]^+$.

HRMS (ESI^+, TOF): calculated $C_{14}H_{24}N$: 206.1909, found: 206.1902.

***N*-Isopropyl-*N*,2-dimethyl-4-phenylbutan-1-amine (9a)**



The general procedure was used to synthesize compound **9a** from *N*,*N*-dimethyl-isopropylamine (**1g**) and but-3-en-1-ylbenzene (**2a**). After stirring for 18 h, the mixture was purified by flash chromatography (Hex/EtOAc, 1:1 + 0.05 vol% $HNEt_2$) to give **9a** (77 mg, 0.35 mmol, 35 %) as a slightly yellow oil.

R_f (SiO_2, Hex/EtOAc, 1:1 + 0.05 vol% $HNEt_2$) = 0.06.

IR (neat): λ^{-1} = 3086, 3063, 3027, 2962, 2924, 2870, 2854, 2794, 1739, 1604, 1584, 1496, 1454, 1376, 1360, 1319, 1293, 1229, 1160, 1031, 993, 906, 871, 743, 697 cm^{-1}.

^{1}H NMR (500 MHz, C_6D_6): δ = 7.21-7.17 (m, 2 H, Ar-C*H*), 7.16-7.11 (m, 2 H, Ar-C*H*), 7.10-7.06 (m, 1 H, Ar-C*H*), 2.70-2.62 (m, 2 H, C*H*, CH_2), 2.53 (ddd, *J* = 13.6, 10.2, 6.5 Hz, 1 H, CH_2), 2.15 (dd, *J* = 12.3, 7.1 Hz, 1 H, CH_2),

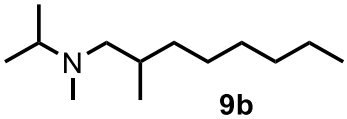
2.05 (s, 3 H, CH_3), 2.05-2.01 (m, 1 H, CH_2), 1.87-1.79 (m, 1 H, CH_2), 1.64-1.51 (m, 1 H, C*H*), 1.40-1.29 (m, 1 H, CH_2), 0.95 (d, *J* = 6.6 Hz, 3 H, CH_3), 0.91 (dd, *J* = 6.1, 1.7 Hz, 6 H, CH_3) ppm.

^{13}C {^{1}H} NMR (125 MHz, DEPT, C_6D_6): δ = 143.4 (C), 128.8 (CH), 128.6 (CH), 125.9 (CH), 60.6 (CH_2), 54.2 (CH), 37.2 (CH_2), 37.2 (CH_3), 33.8 (CH_2), 31.3 (CH), 18.4 (CH_3), 18.0 (CH_3), 17.8 (CH_3) ppm.

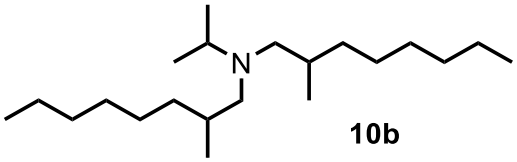
MS (ESI$^+$, TOF): *m*/*z* (%) = 220 (100) $[M+H]^+$.

HRMS (ESI$^+$, TOF): calculated $C_{15}H_{26}N$: 220.2065, found: 220.2066.

N-Isopropyl-*N*,2-dimethyloctan-1-amine (9b) and *N*-Isopropyl-2-methyl-*N*-(2-methyloctyl)octan-1-amine (10b)



9b



10b

The general procedure was used to synthesize compounds **9b** and **10b** from *N*,*N*-dimethyl-isopropylamine (**1g**) and 1-octene (**2c**). After stirring for 18 h, the mixture was purified by flash chromatography (Hex/EtOAc, 3:1 + 0.02 vol% $HNEt_2$) to give **9b** (72 mg, 0.36 mmol, 36 %) as a slightly yellow oil and **10b** (20 mg, 0.06 mmol, 6 %) as a slightly yellow oil.

GC: **9b**/**10b** = 83:17.

N-Isopropyl-*N*,2-dimethyloctan-1-amine (9b)

R_f (SiO_2, Hex/EtOAc, 3:1 + 0.02 vol% $HNEt_2$) = 0.07.

IR (neat): λ^{-1} = 2960, 2924, 2873, 2855, 2794, 1742, 1460, 1376, 1360, 1320, 1232, 1220, 1184, 1159, 1112, 1084, 1067, 994, 870, 771, 722 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.91-2.82 (m, 1 H, CH_2), 2.23 (s, 3 H, CH_3), 2.22-2.19 (m, 1 H, CH_2), 2.15-2.07 (m, 1 H, CH_2), 1.62-1.53 (m, 1 H, CH_2), 1.40-1.34 (m, 1 H, C*H*), 1.30-1.20 (m, 9 H, CH_2), 1.04-0.98 (m, 6 H, CH_3), 0.89 (q, 6 H, CH_3) ppm.

^{13}C{^{1}H} NMR (125 MHz, DEPT, $CDCl_3$): δ = 60.0 (CH_2), 54.2 (CH), 38.1 (CH_3), 35.5 (CH_2), 32.1 (CH_2), 31.3 (CH), 29.8 (CH_2), 27.2 (CH_2), 22.8 (CH_2), 18.7 (CH_3), 18.0 (CH_3), 17.4 (CH_3), 14.2 (CH_3) ppm.

MS (ESI$^+$, TOF): *m*/*z* (%) = 200 (100) $[M+H]^+$.

HRMS (ESI$^+$, TOF): calculated $C_{13}H_{30}N$: 200.2378, found: 200.2373.

N-Isopropyl-2-methyl-*N*-(2-methyloctyl)octan-1-amine (10b)

R_f (SiO_2, Hex/EtOAc, 3:1 + 0.02 vol% $HNEt_2$) = 0.19.

IR (neat): λ^{-1} = 2956, 2923, 2872, 2854, 1647, 1464, 1377, 1124, 723, 699, 669 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.54 (ddd, *J* = 11.7, 7.3, 5.8 Hz, 2 H, CH_2), 2.39 (dt, *J* = 11.7, 8.0 Hz, 2 H, CH_2), 2.21-2.17 (m, 1 H, C*H*), 1.68-1.60 (m, 2 H, C*H*), 1.30-1.23 (m, 20 H, CH_2), 0.93-0.85 (m, 18 H, CH_3) ppm.

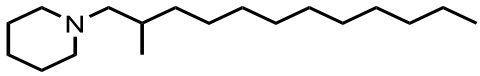
^{13}C{^{1}H} NMR (125 MHz, DEPT, $CDCl_3$): δ = 56.5 (CH_2), 38.0 (CH), 35.2 (CH_2), 32.9 (CH), 32.1 (CH), 29.7 (CH_2), 27.1 (CH_2), 22.8 (CH_2), 18.3 (CH_3), 14.2 (CH_3) ppm.

MS (EI, 70 eV): *m*/*z* (%) = 311 (31) $[M]^+$, 184 (28) $[C_{12}H_{26}N]^+$, 156 (100) $[C_{10}H_{22}N]^+$, 86 (44).

HRMS (ESI$^+$, TOF): calculated $C_{21}H_{46}N$: 312.3630, found: 312.3634.

4. Multigram Scale Hydroaminoalkylation

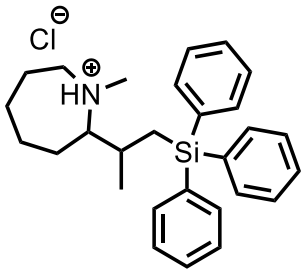
_N_-(2-Methyldodecyl)piperidine (3d)



An oven-dried Schlenk tube (100 mL) equipped with a Teflon stopcock and a magnetic stirring bar was transferred into a nitrogen-filled glovebox and charged with $TiBn_4$ (1.00 mmol, 5 mol%) and toluene (5 mL). To this solution, *N*-methylpiperidine (**1a**, 20.0 mmol) and 1-dodecene (**2d**, 30.0 mmol) were added in this order. Toluene (5 mL) was used to wash down the reagents from the wall of the Schlenk tube. Finally, the remaining toluene (15 mL) was used to transfer $Ph_3C[B(C_6F_5)_4]$ (0.80 mmol, 4 mol%) into the tube as a suspension. The tube was sealed, removed from the glovebox, and placed in an aluminum heating block. The reaction mixture was heated to 35 °C for 18 h. After the reaction mixture had been cooled to room temperature, it was diluted with EtOAc (100 mL). The solvents were removed under reduced pressure and the residue was purified by column chromatography to give **3d** (3.23 g, 12.1 mmol, 60 %) as a colorless oil. The analytical data for **3d** are described on page 6.

5. Crystallization of Compound 5b·HCl

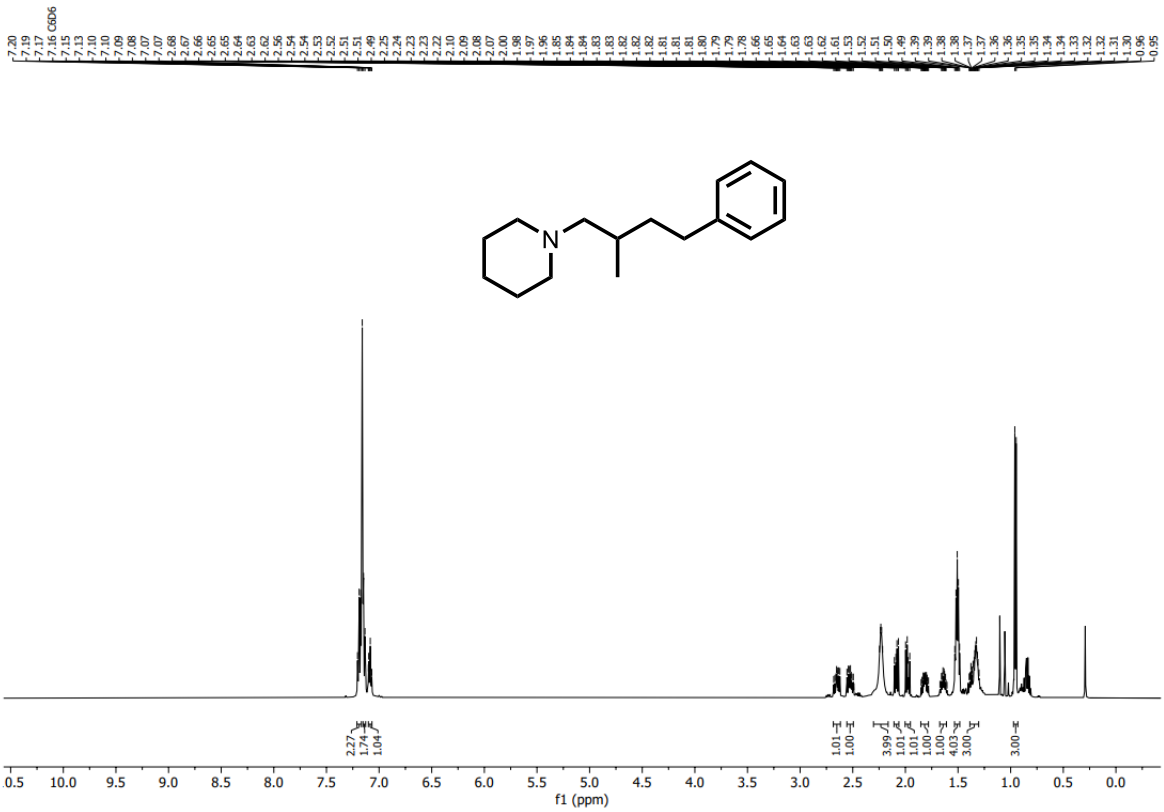
_N_-Methyl-2-(1-(triphenylsilyl)propan-2-yl)azepane hydrochloride (5b • HCl)



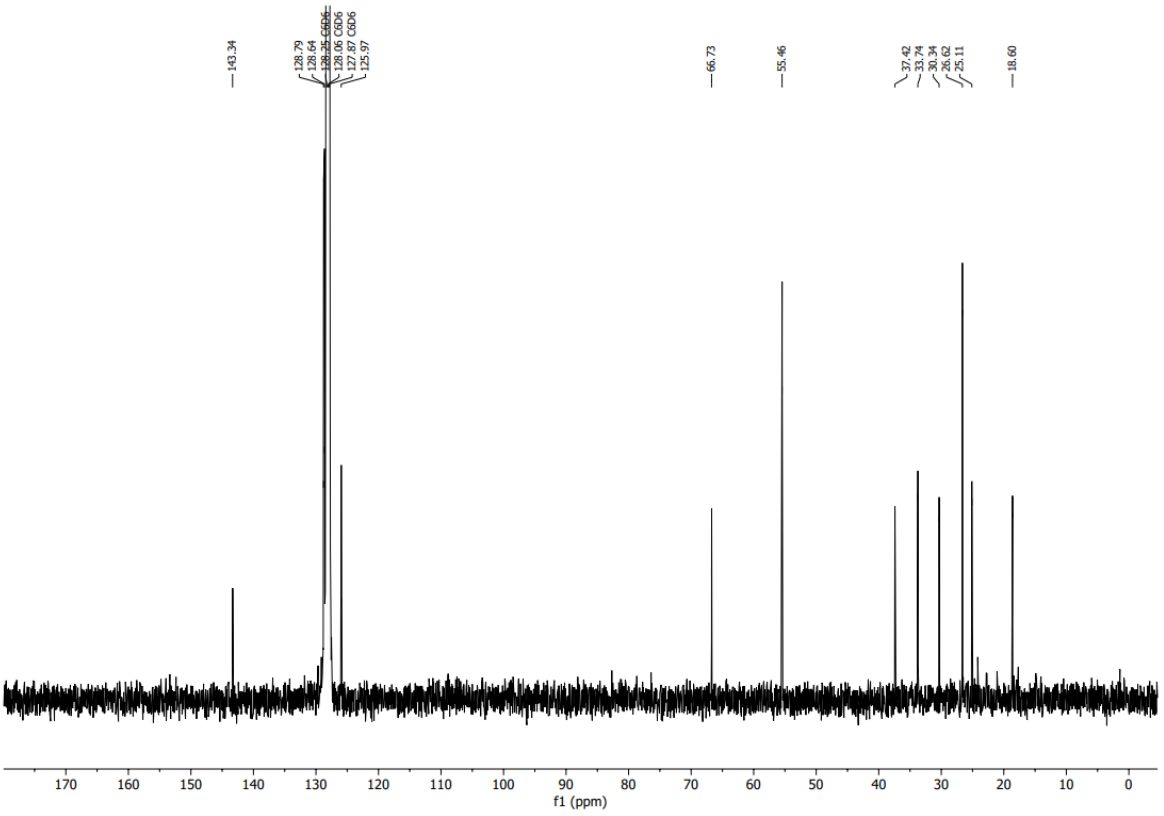
In a 10 mL vial, *N*-methyl-2-(1-(triphenylsilyl)propan-2-yl)azepane (**5b**, 40 mg, 0.09 mmol) was dissolved in Et_2O (1 mL). A second vial was charged with a solution of HCl in Et_2O (c = 2 $molL^{-1}$, 2 mL). At room temperature, both vials were stored under an upturned large beaker until crystals suitable for X-ray analysis were formed (3 days). Using this procedure, fine slightly yellow needles of **5b**·HCl were obtained.

6. NMR Spectra

N-(2-Methyl-4-phenylbutyl)piperidine (3a)

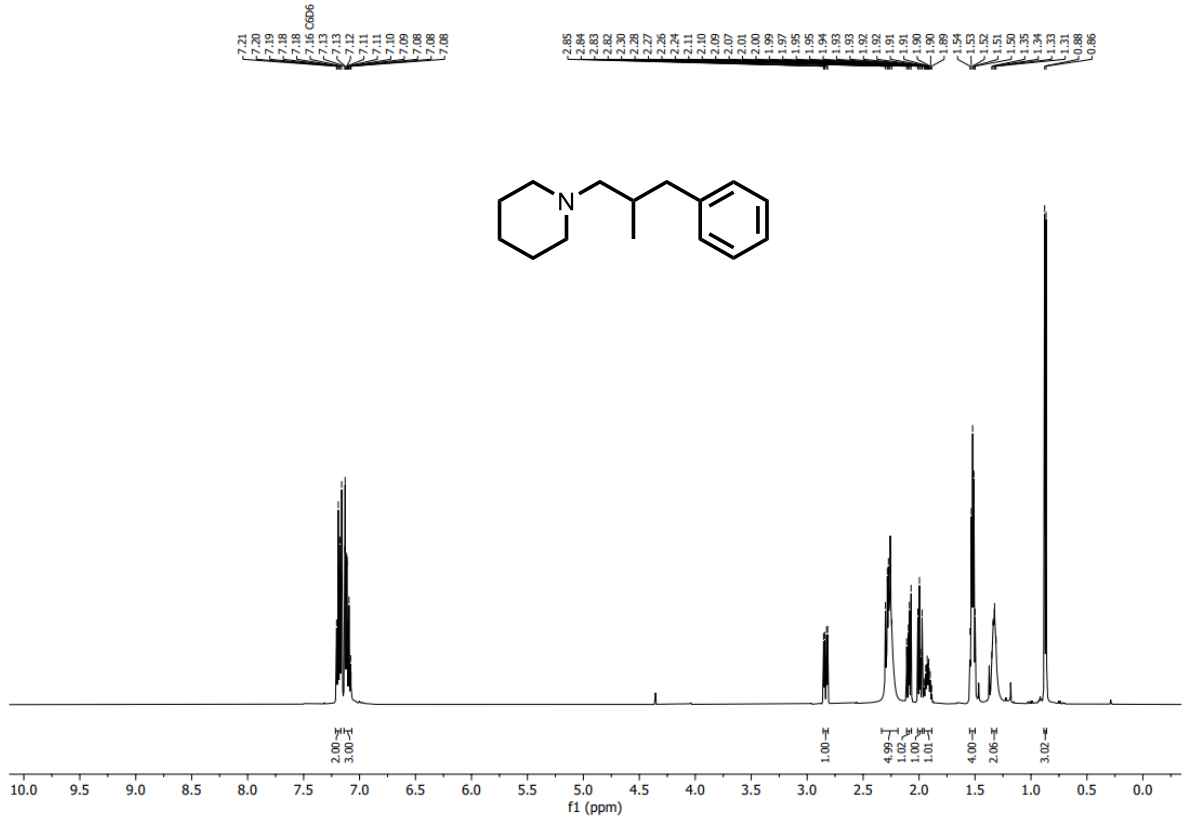


^{1}H NMR (500 MHz, C_6D_6)

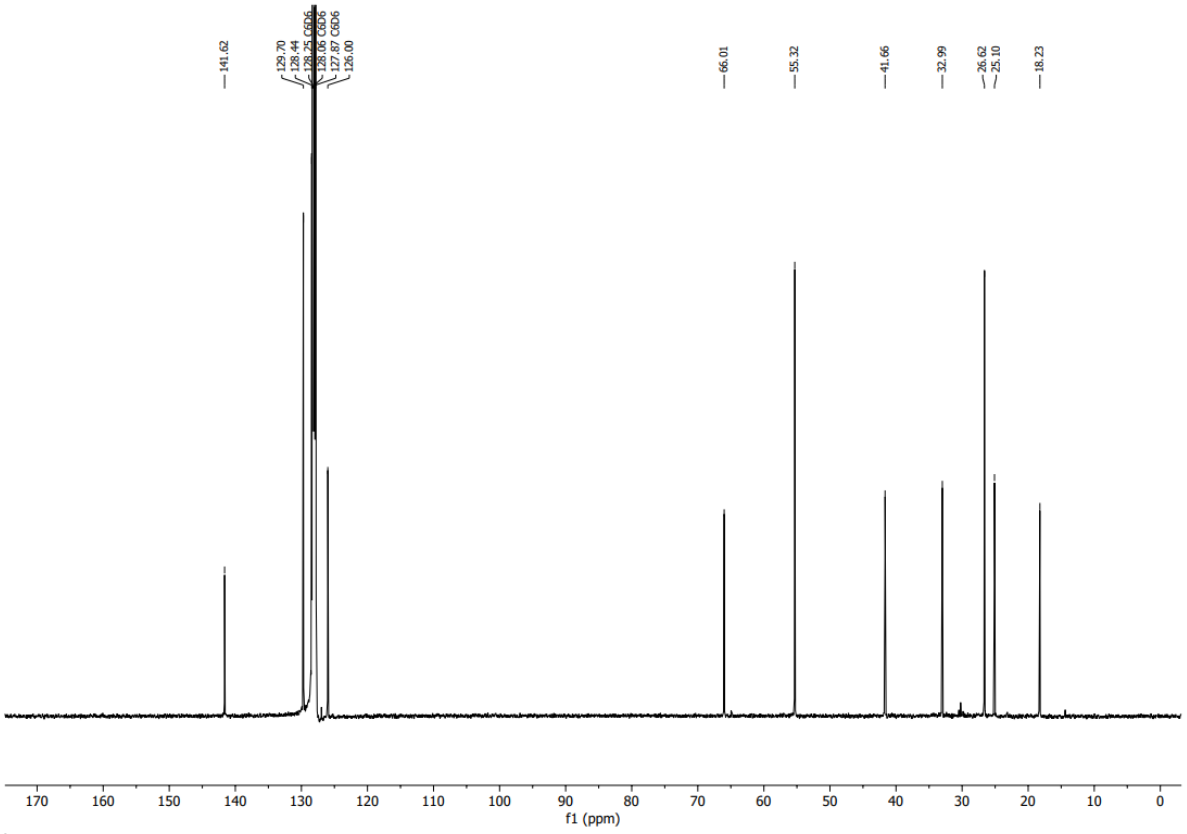


^{13}C{^{1}H} NMR (125 MHz, C_6D_6)

***N*-(2-Methyl-3-phenylpropyl)piperidine (3b)**

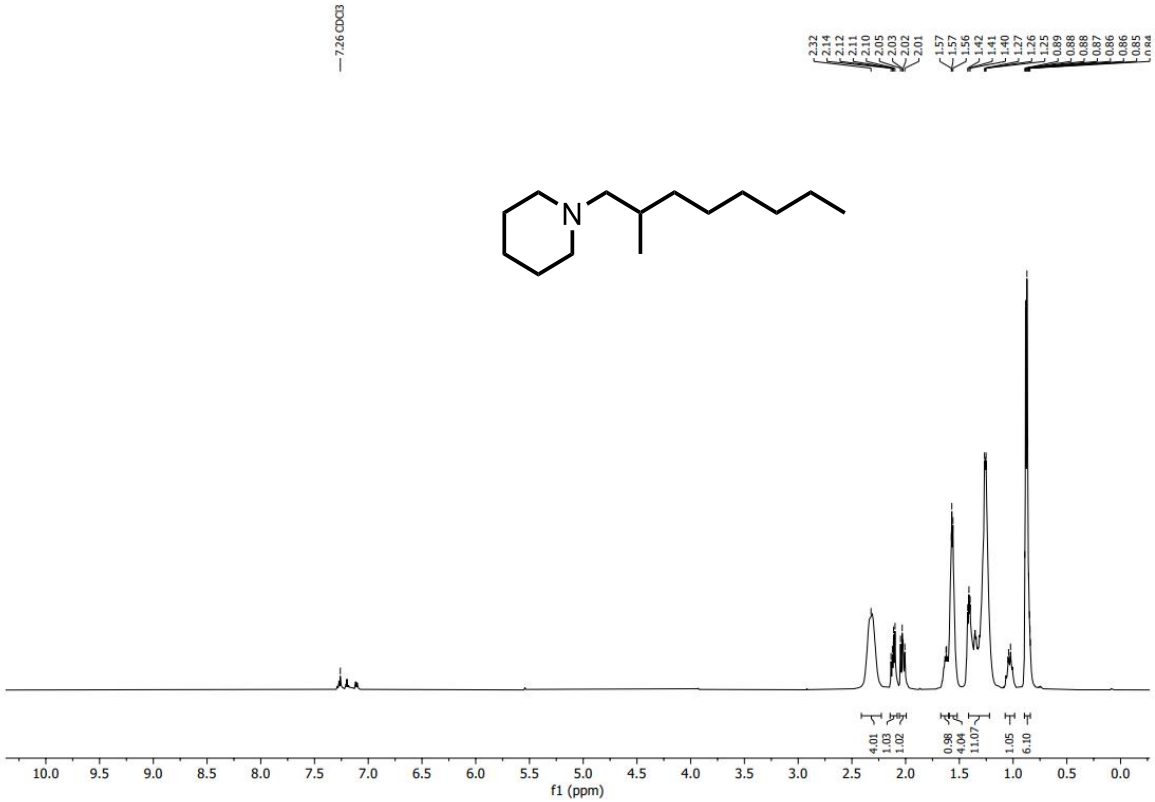


^{1}H NMR (500 MHz, C_6D_6)

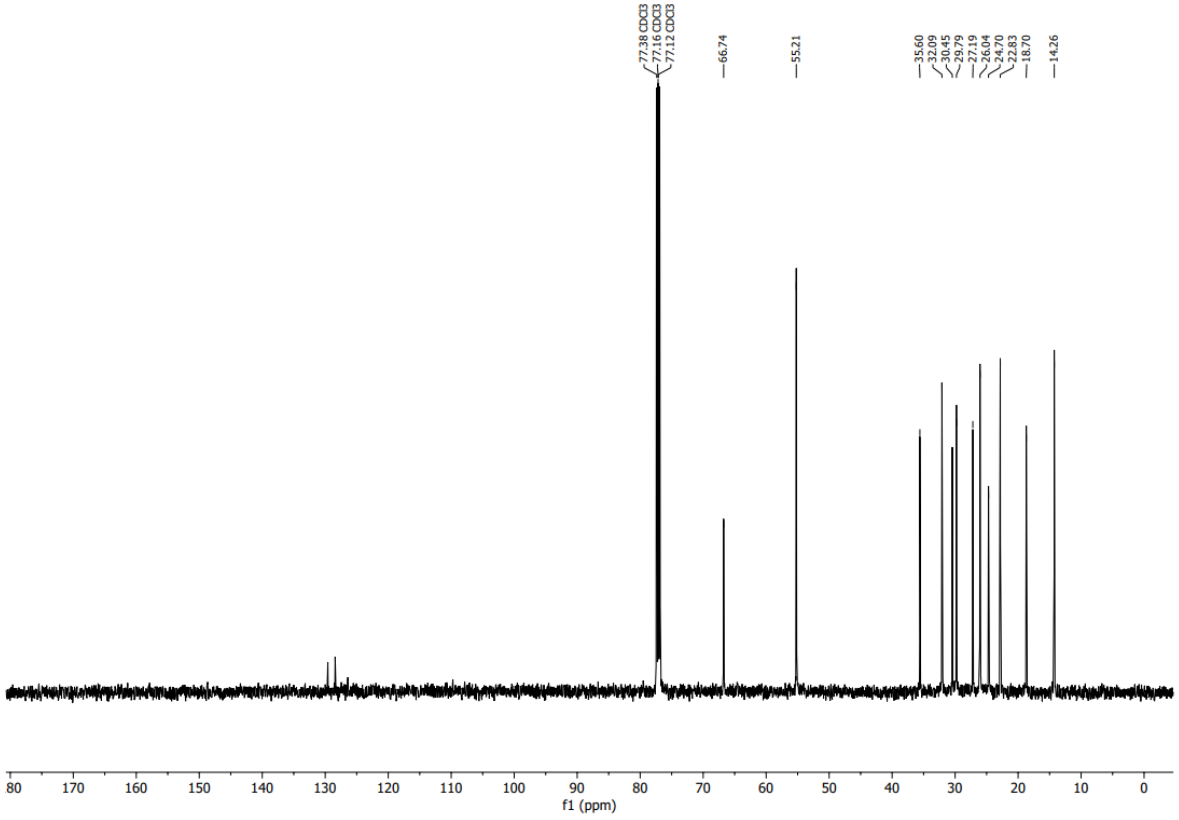


^{13}C{^{1}H} NMR (125 MHz, C_6D_6)

***N*-(2-Methyloctyl)piperidine (3c)**

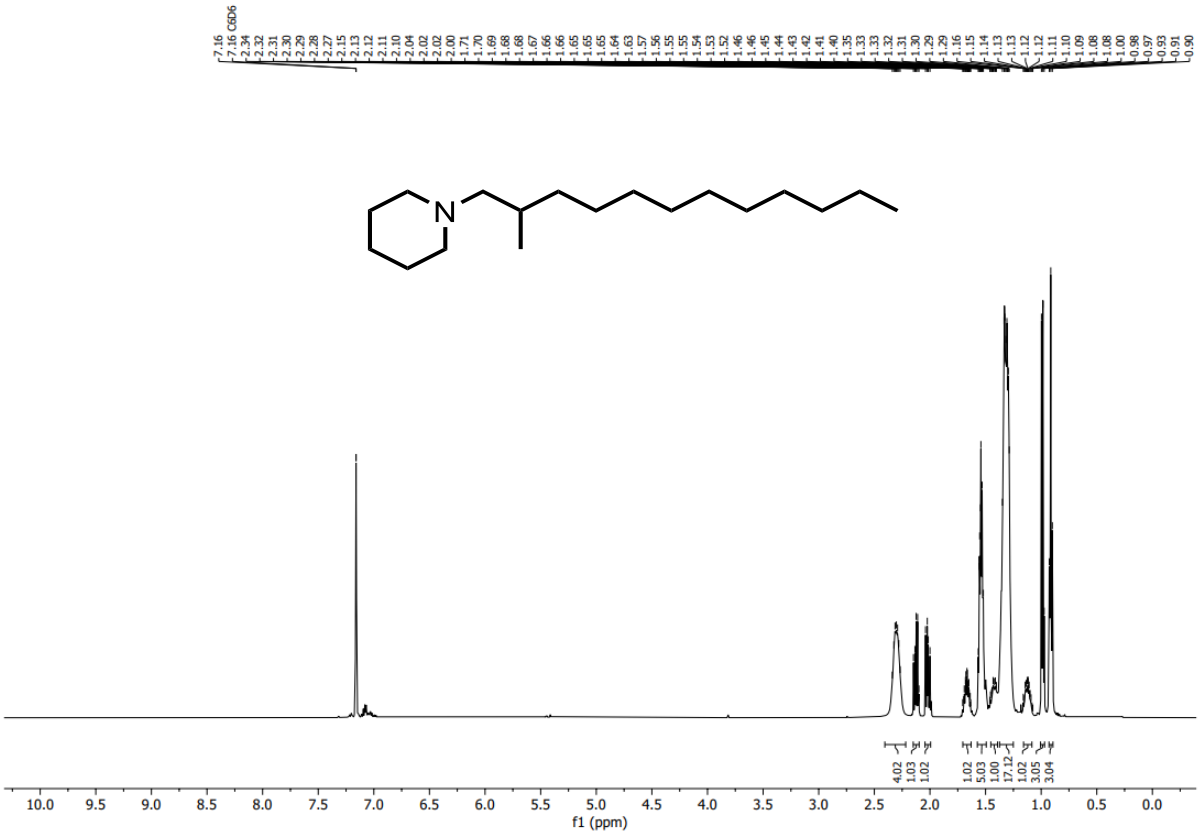


^{1}H NMR (500 MHz, $CDCl_3$)

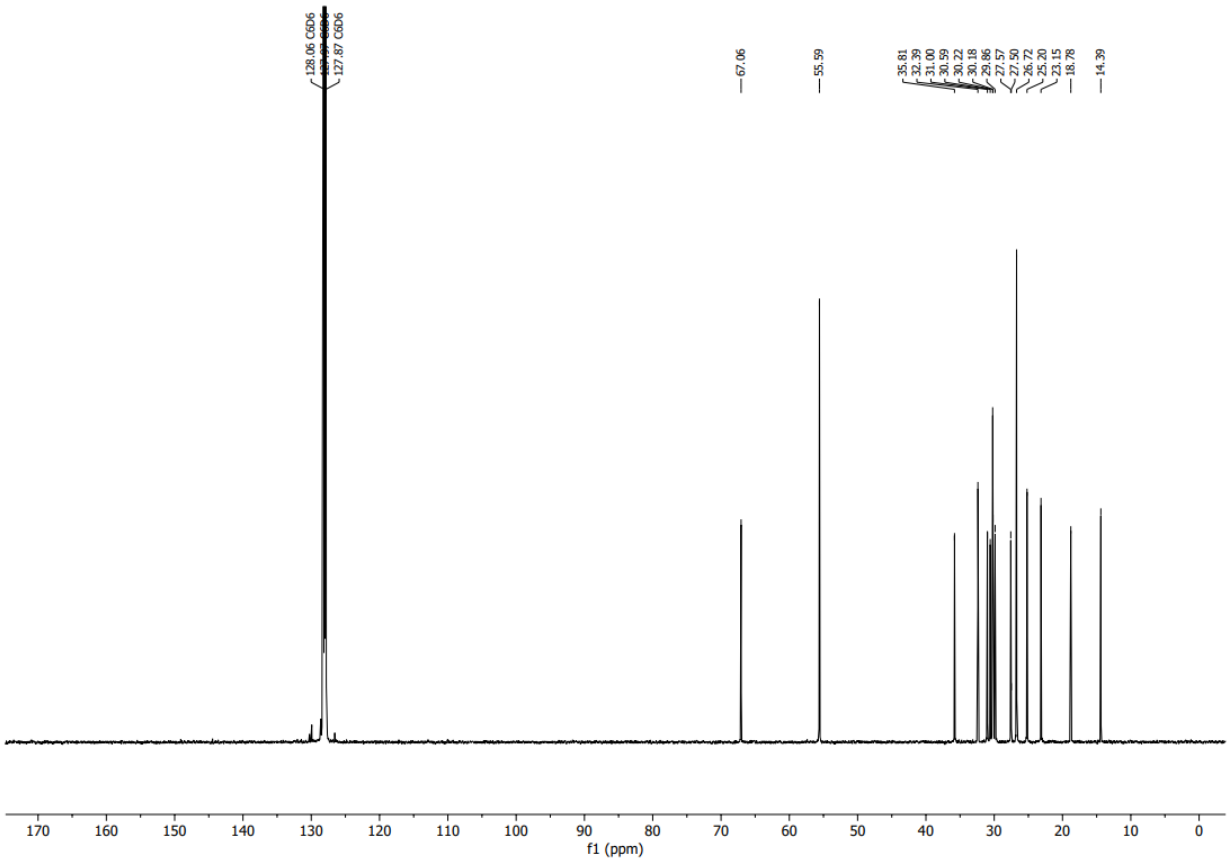


^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)

***N*-(2-Methyldodecyl)piperidine (3d)**

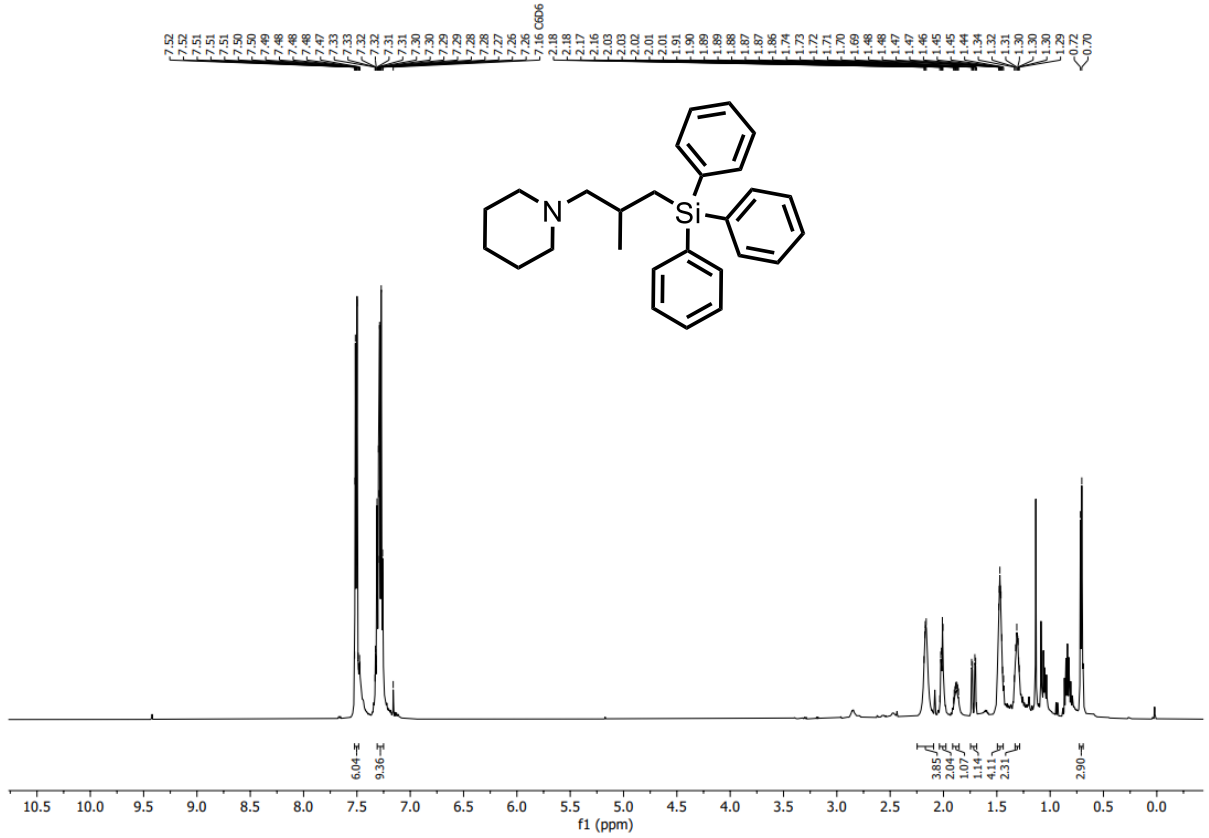


^{1}H NMR (500 MHz, C_6D_6)

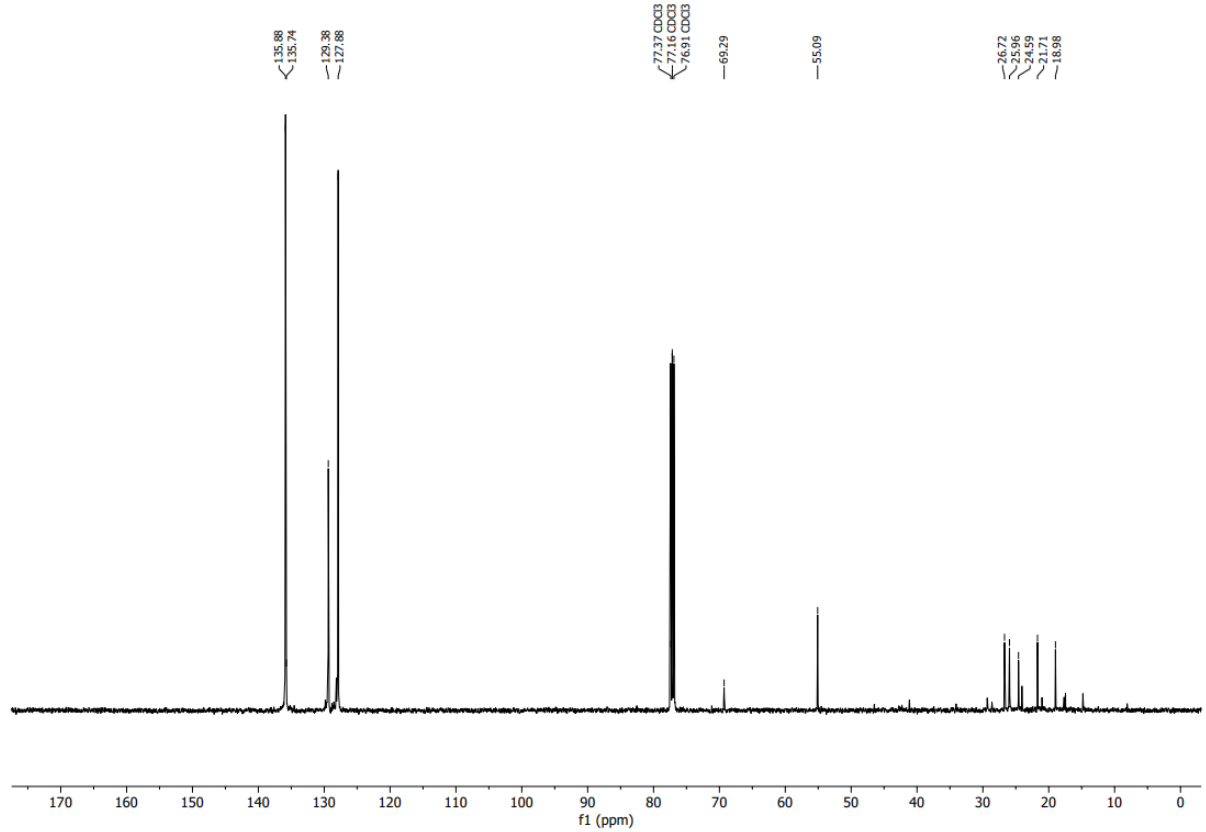


^{13}C{^{1}H} NMR (125 MHz, C_6D_6)

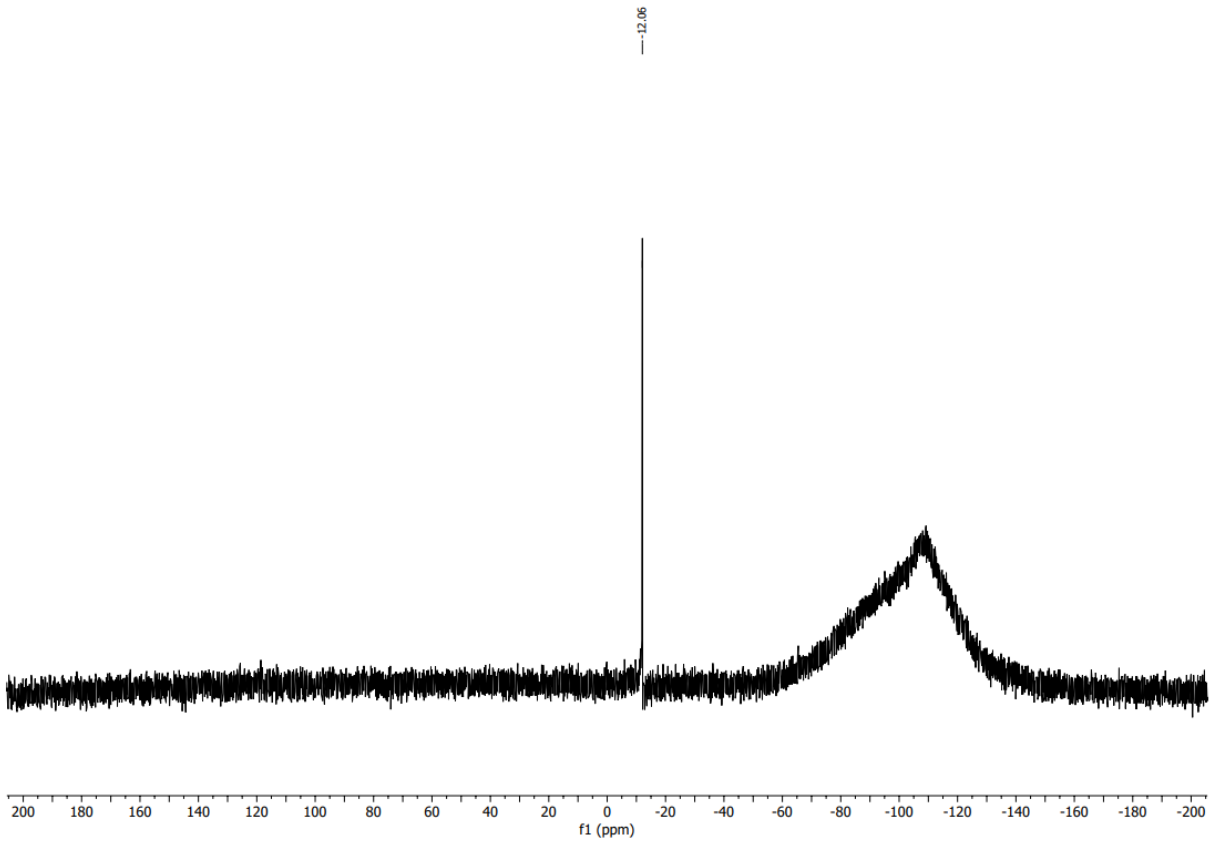
***N*-(2-Methyl-3-(triphenylsilyl)propyl)piperidine (3e)**



^{1}H NMR (500 MHz, $CDCl_3$)

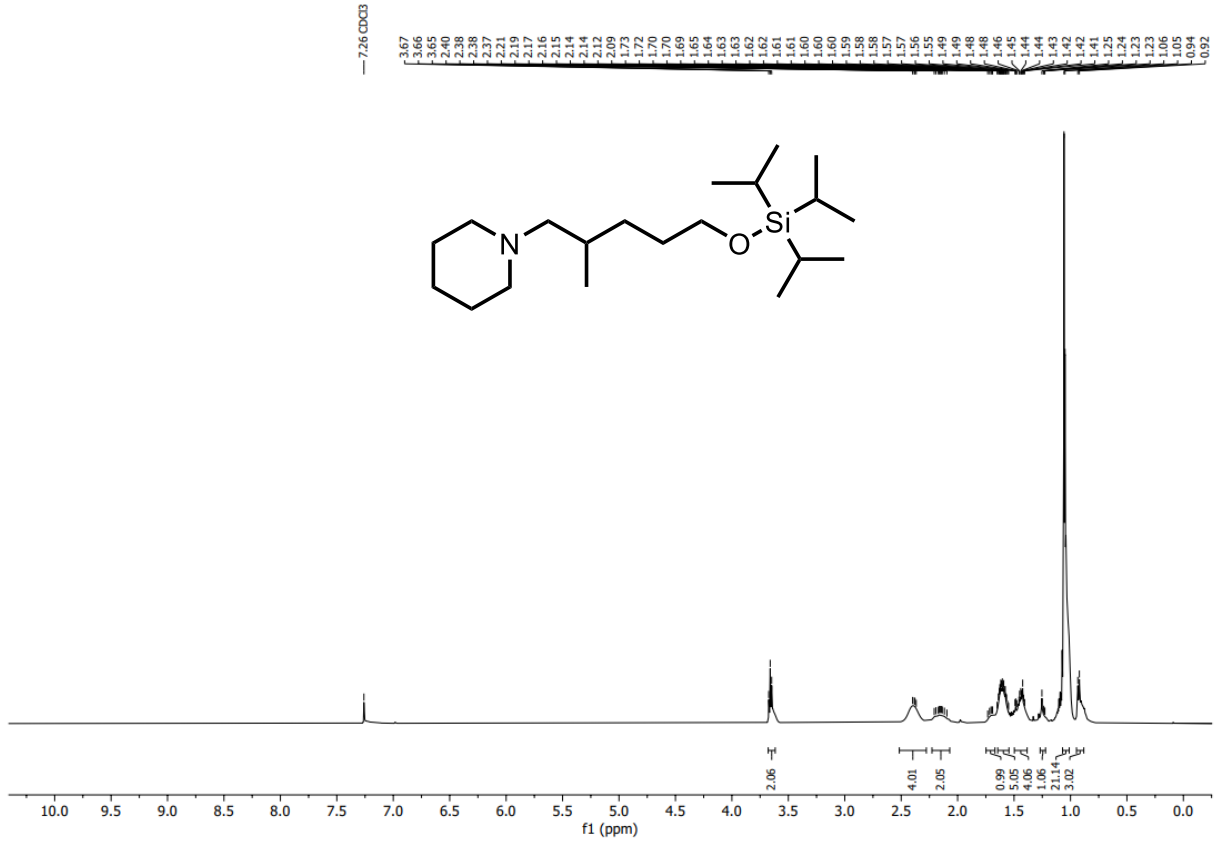


^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)

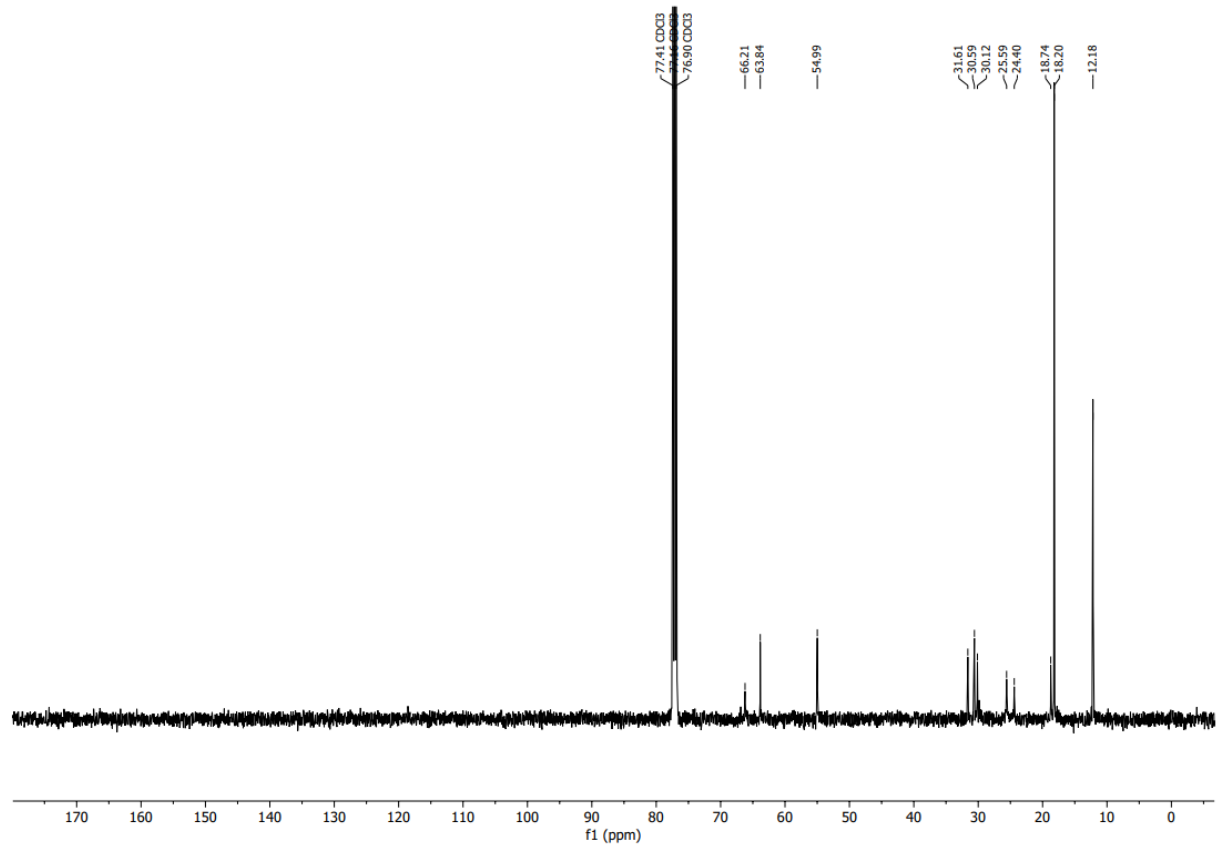


^{29}Si{^{1}H} NMR (99 MHz, $CDCl_3$)

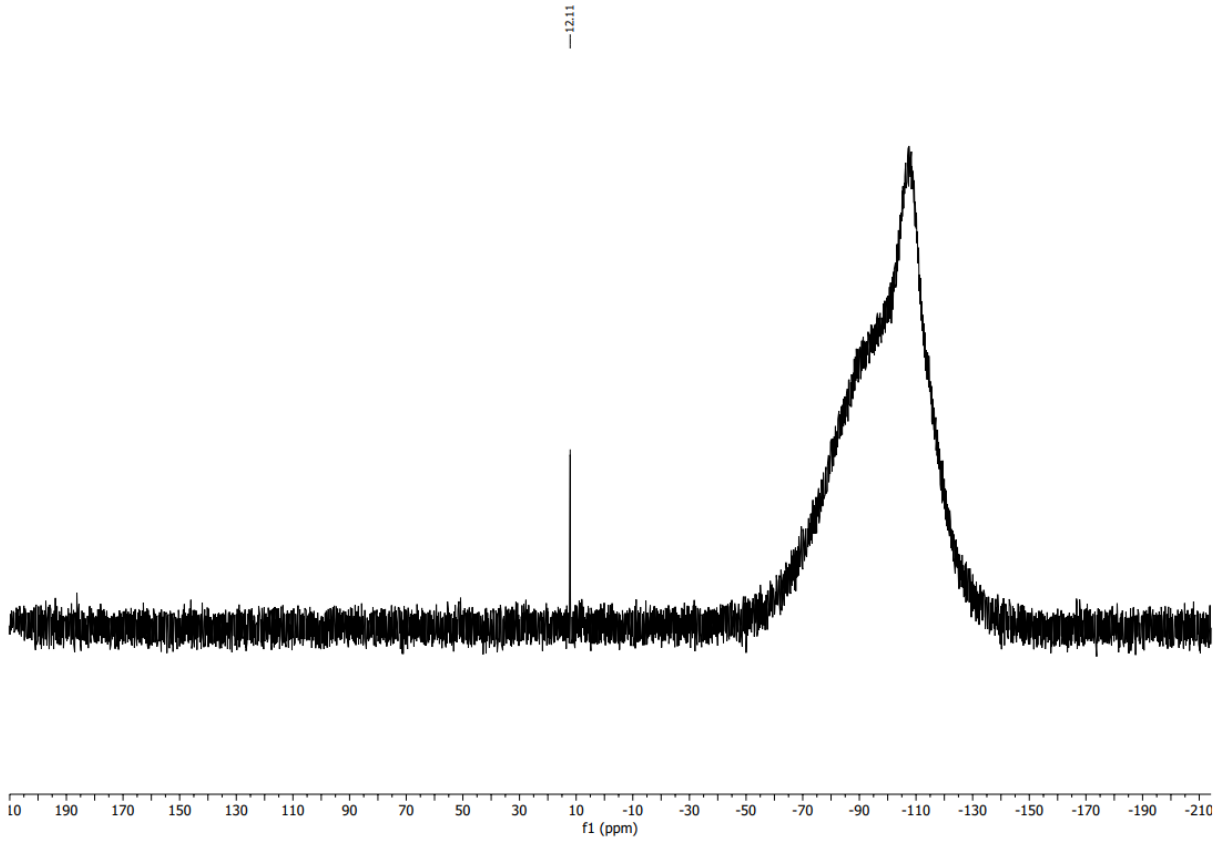
***N*-(2-Methyl-5-((triisopropylsilyl)oxy)pentyl)piperidine (3f)**



^{1}H NMR (500 MHz, $CDCl_3$)

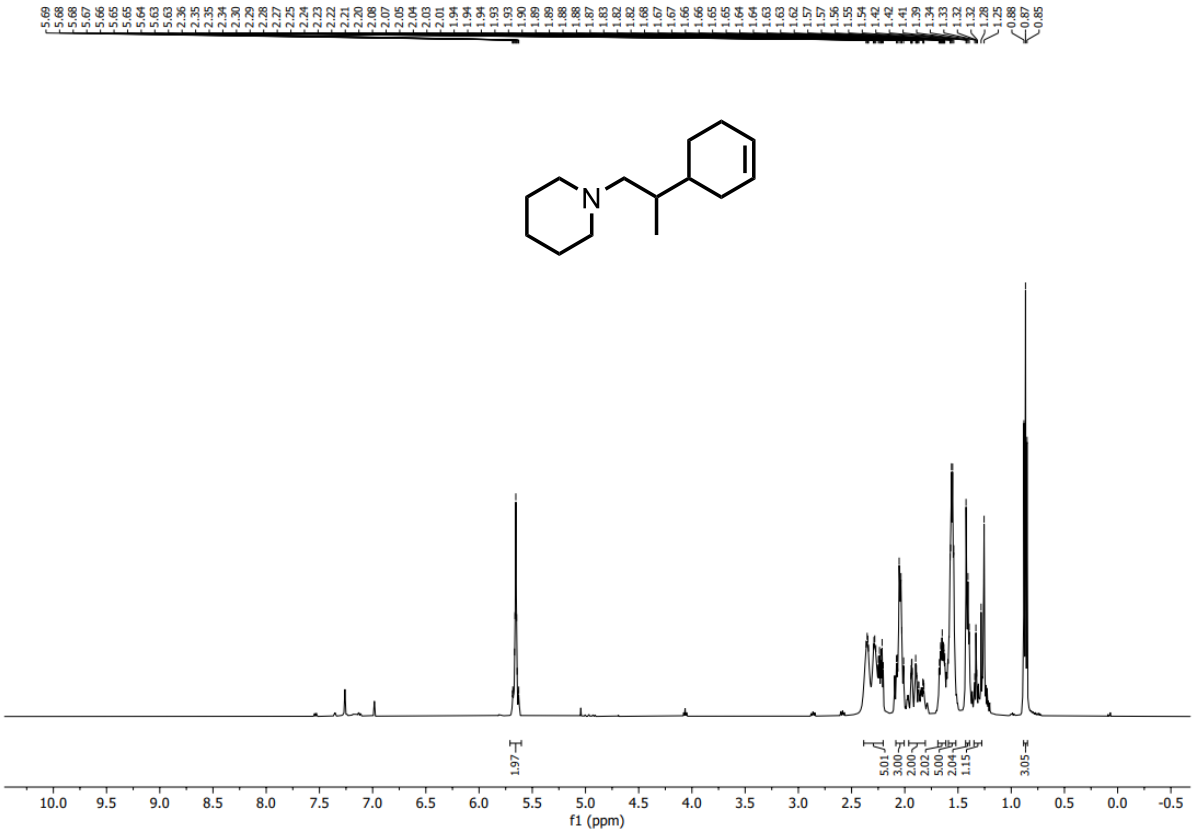


^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)

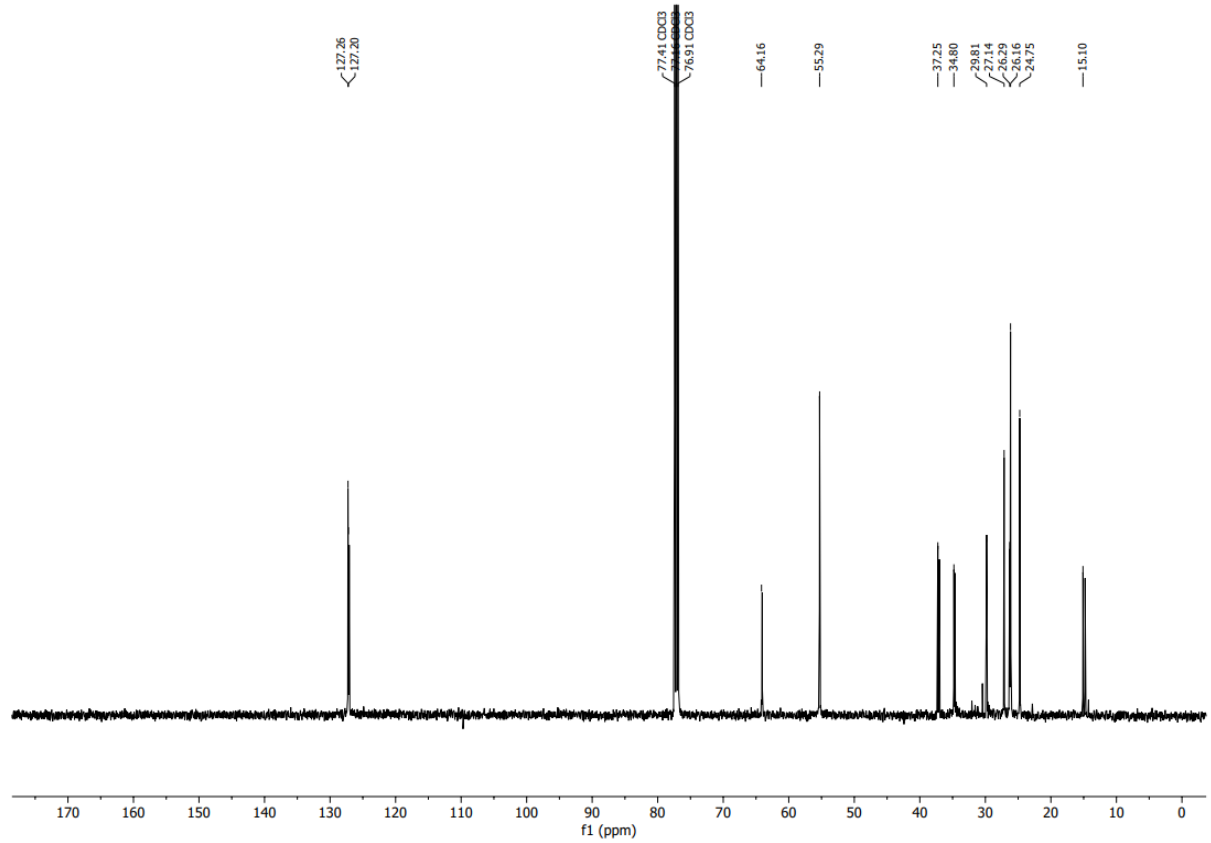


^{29}Si{^{1}H} NMR (99 MHz, $CDCl_3$)

***N*-(2-(Cyclohex-3-en-1-yl)propyl)piperidine (3g)**

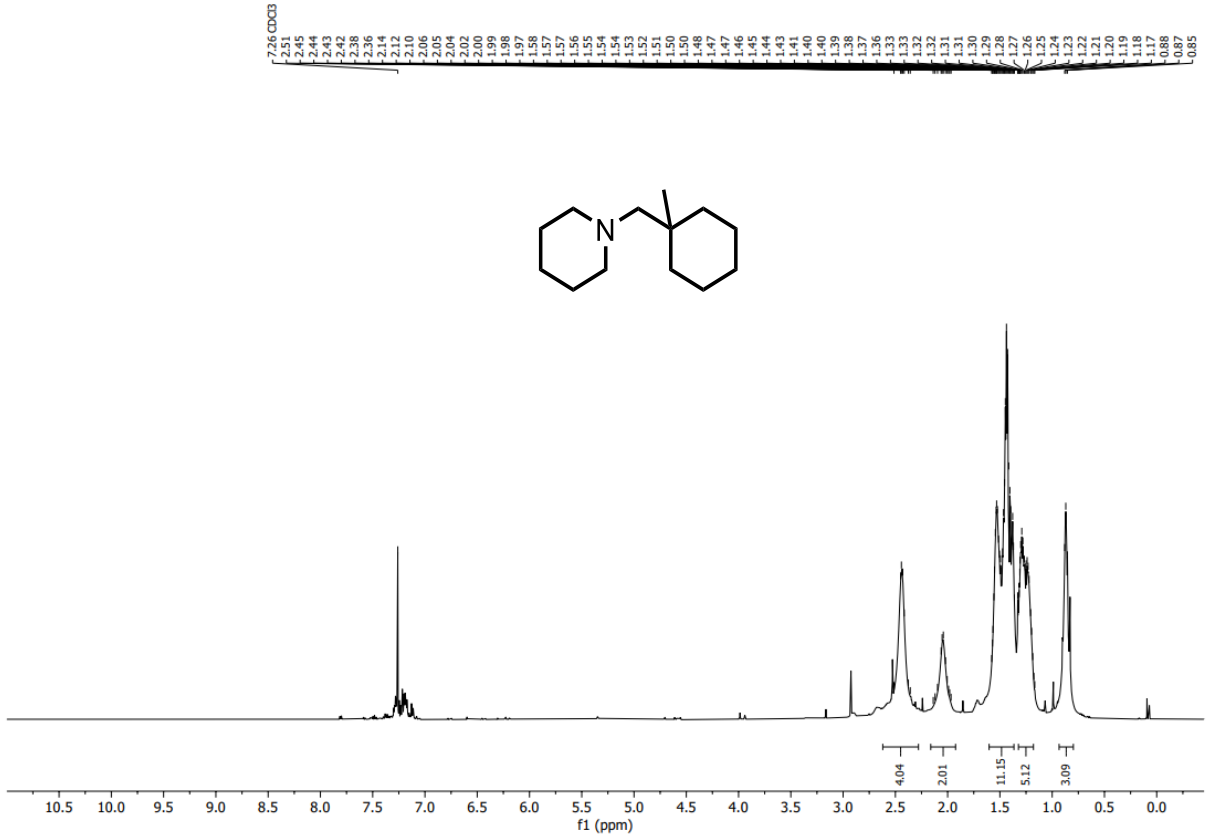


^{1}H NMR (500 MHz, $CDCl_3$)

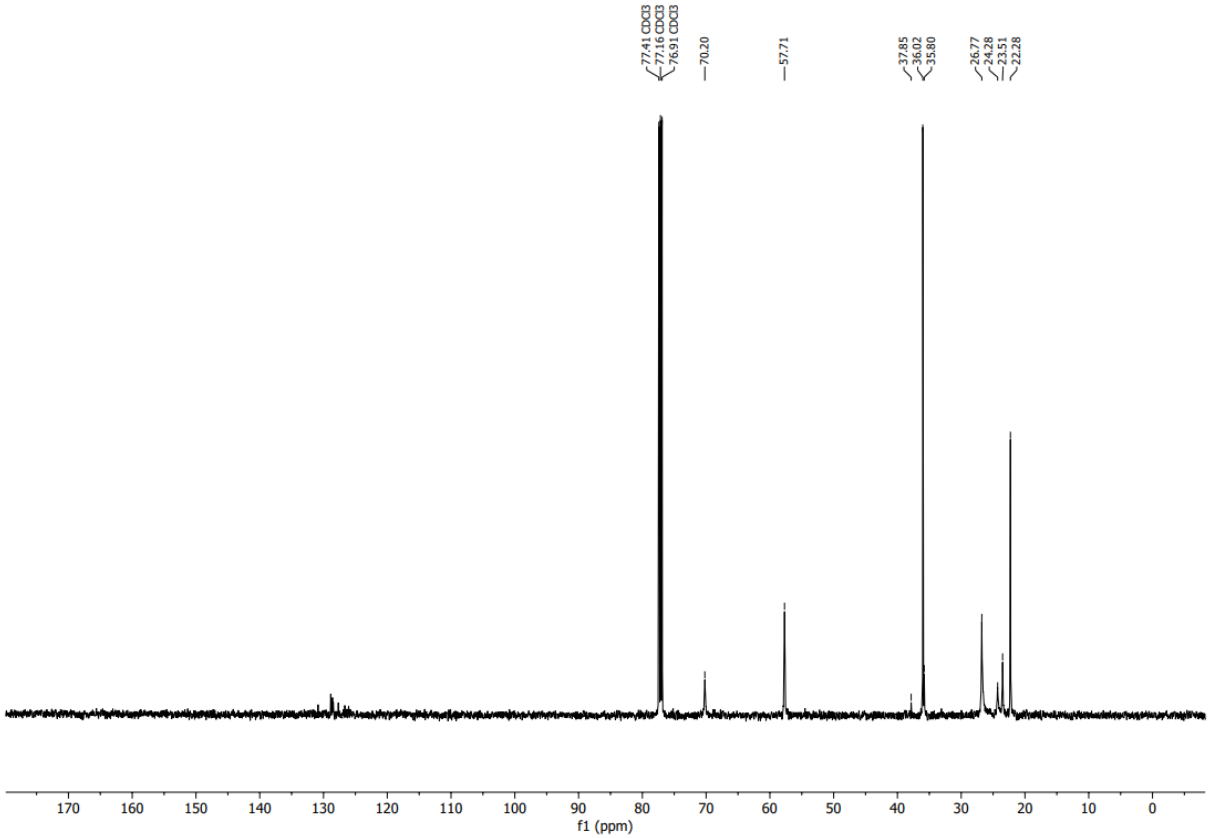


^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)

***N*-((Methylcyclohexyl)methyl)piperidine (3h)**

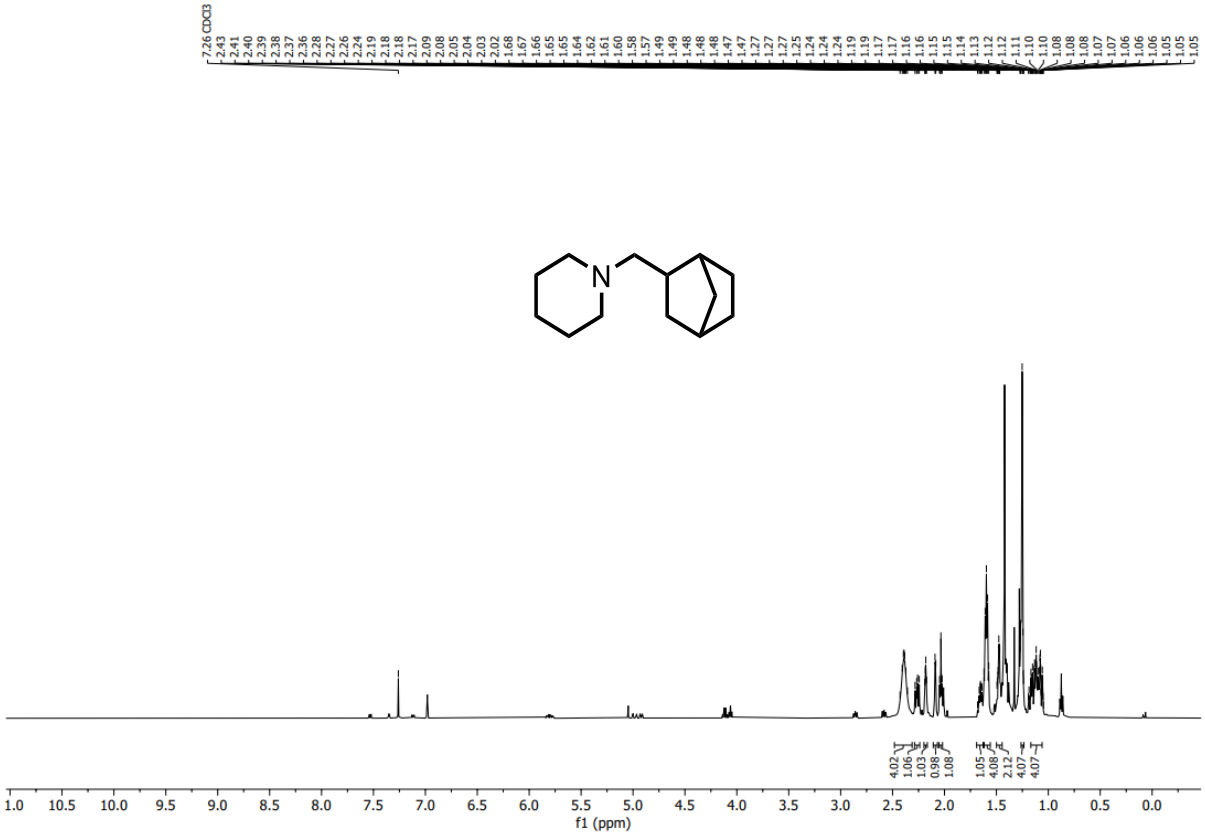


^{1}H NMR (500 MHz, $CDCl_3$)

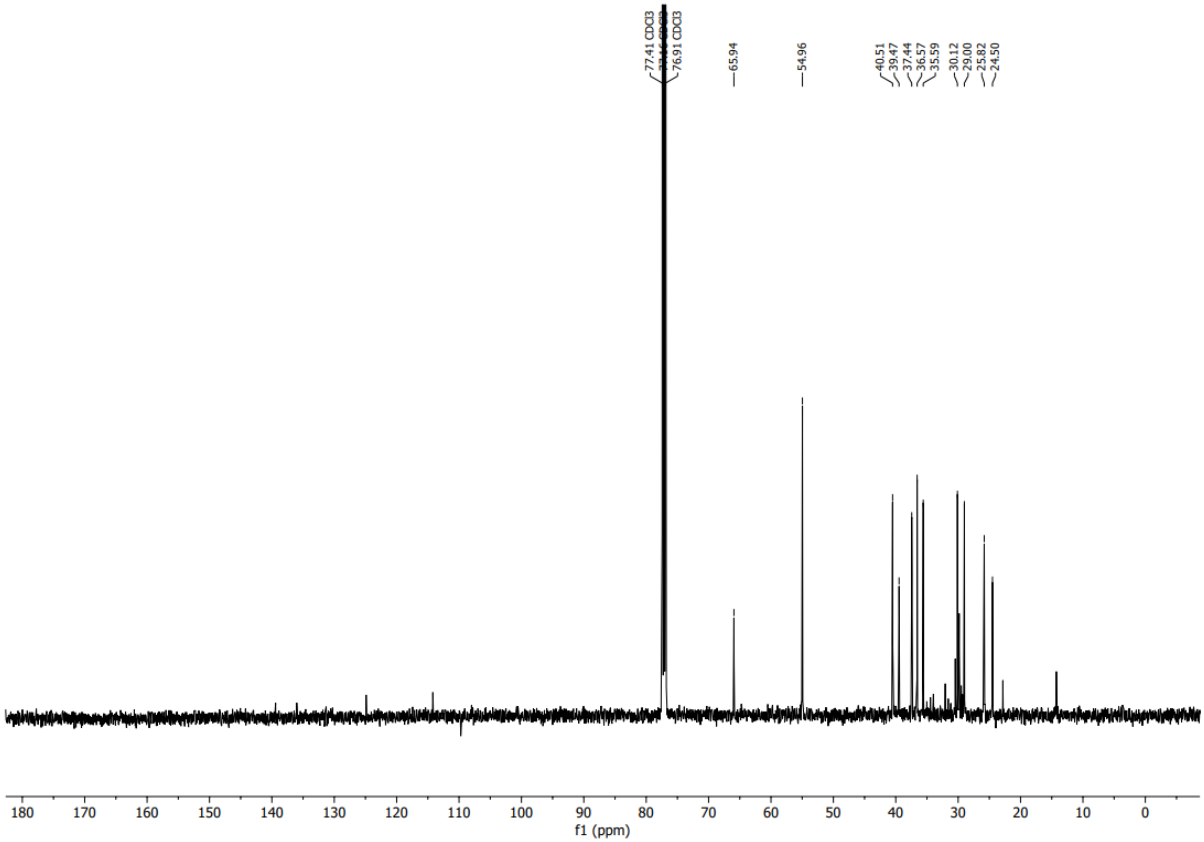


^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)

***N*-(Bicyclo[2.2.1]heptan-2-ylmethyl)piperidine (3i)**

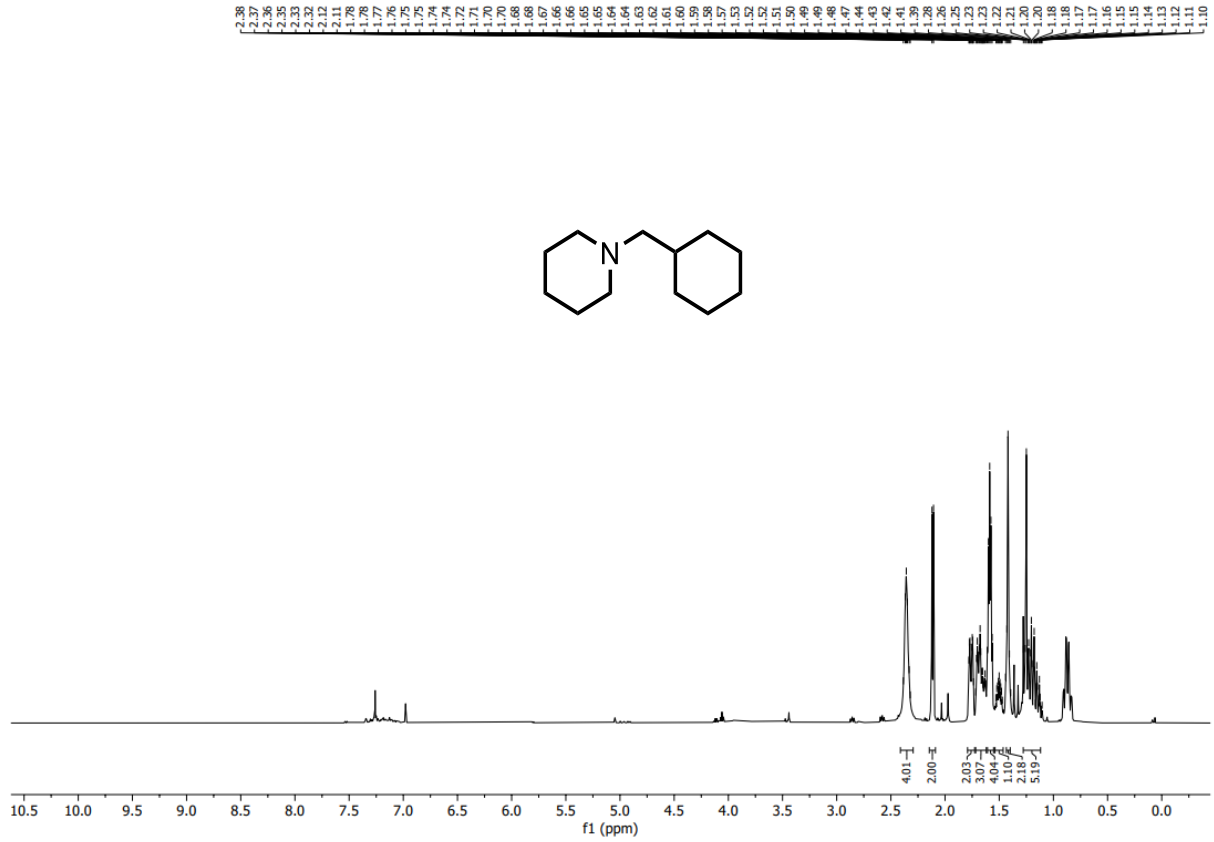


^{1}H NMR (500 MHz, $CDCl_3$)

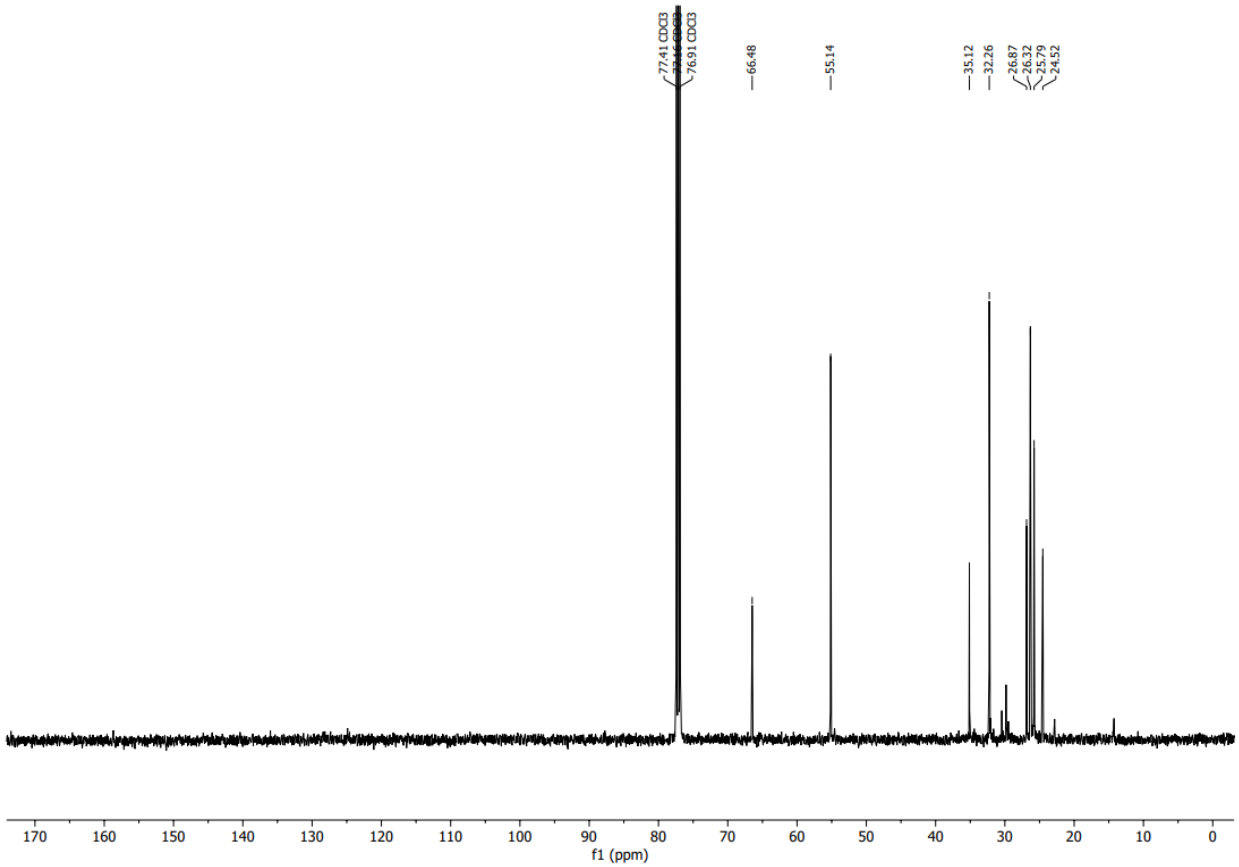


^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)

***N*-(Cyclohexylmethyl)piperidine (3j)**

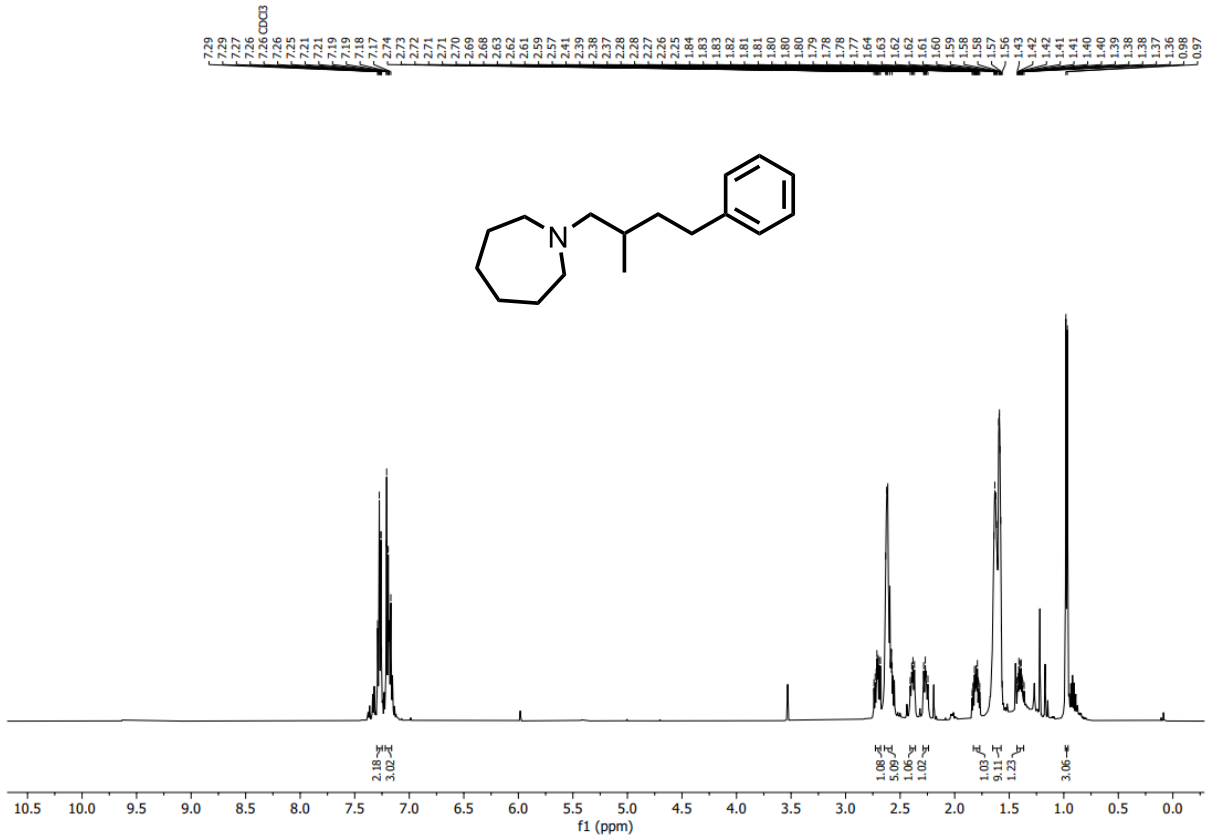


^{1}H NMR (500 MHz, $CDCl_3$)

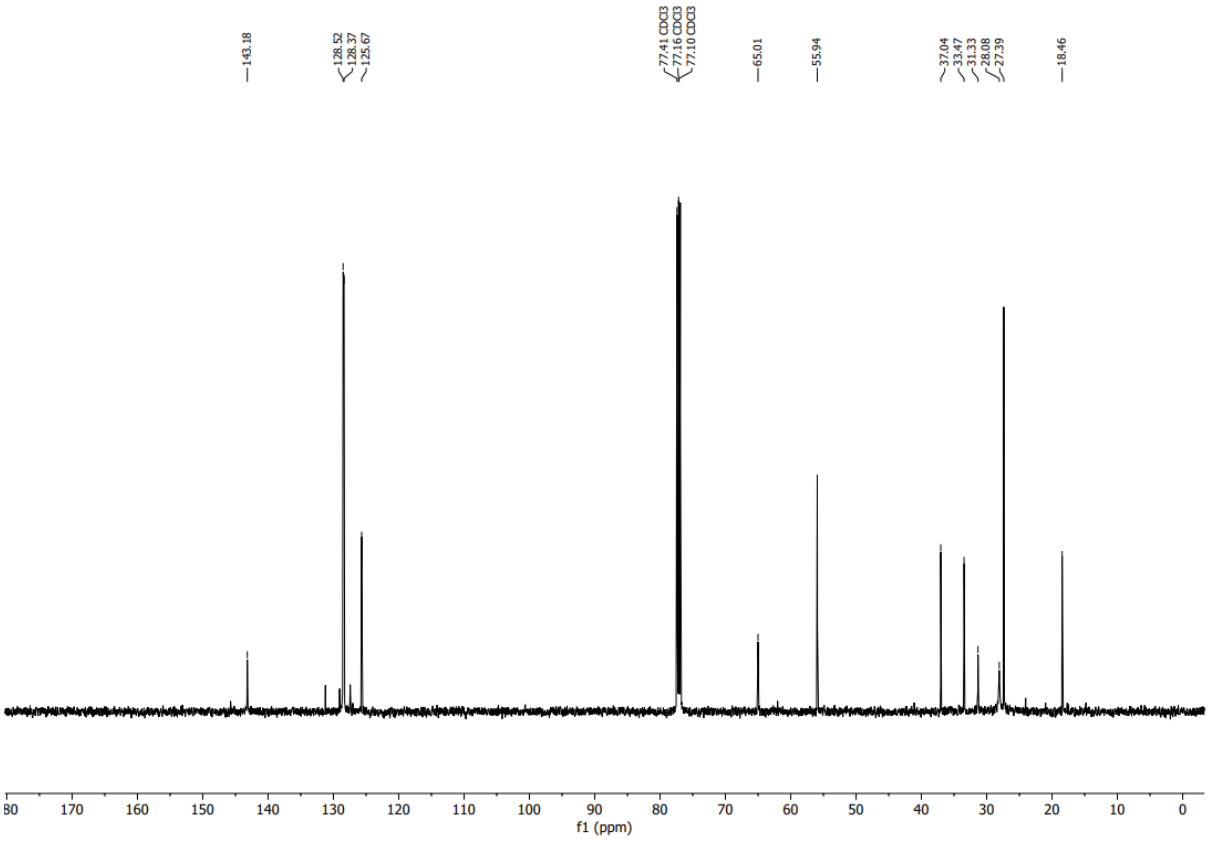


^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)

***N*-(2-Methyl-4-phenylbutyl)azepane (4a)**

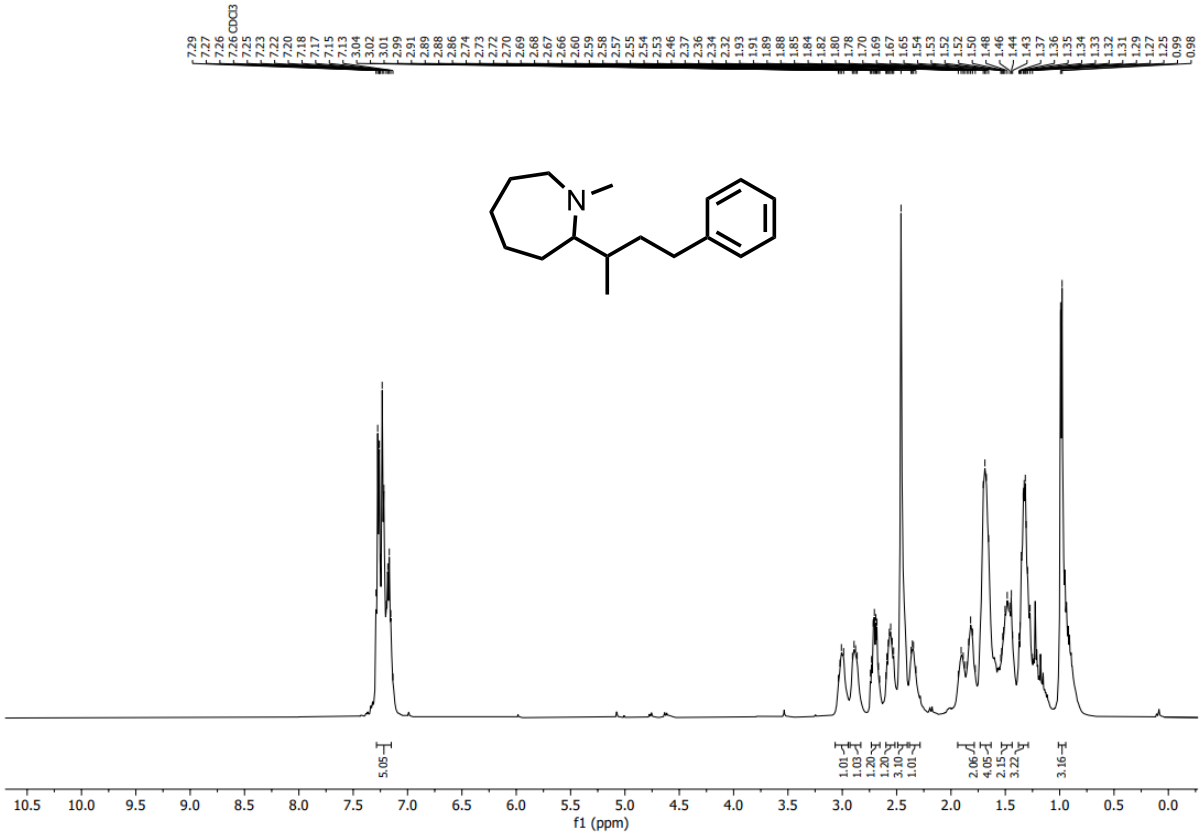


^{1}H NMR (500 MHz, $CDCl_3$)

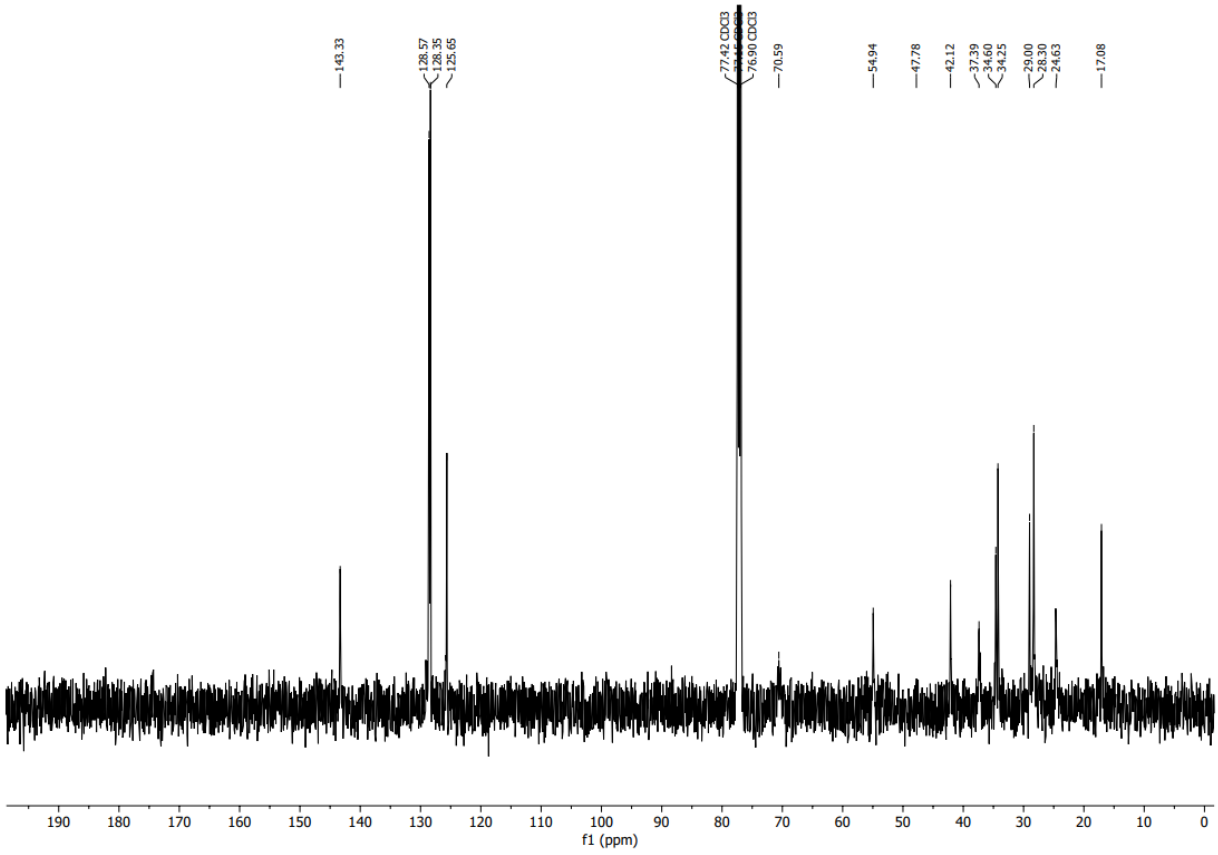


^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)

***N*-Methyl-2-(4-phenylbutan-2-yl)azepane (5a)**

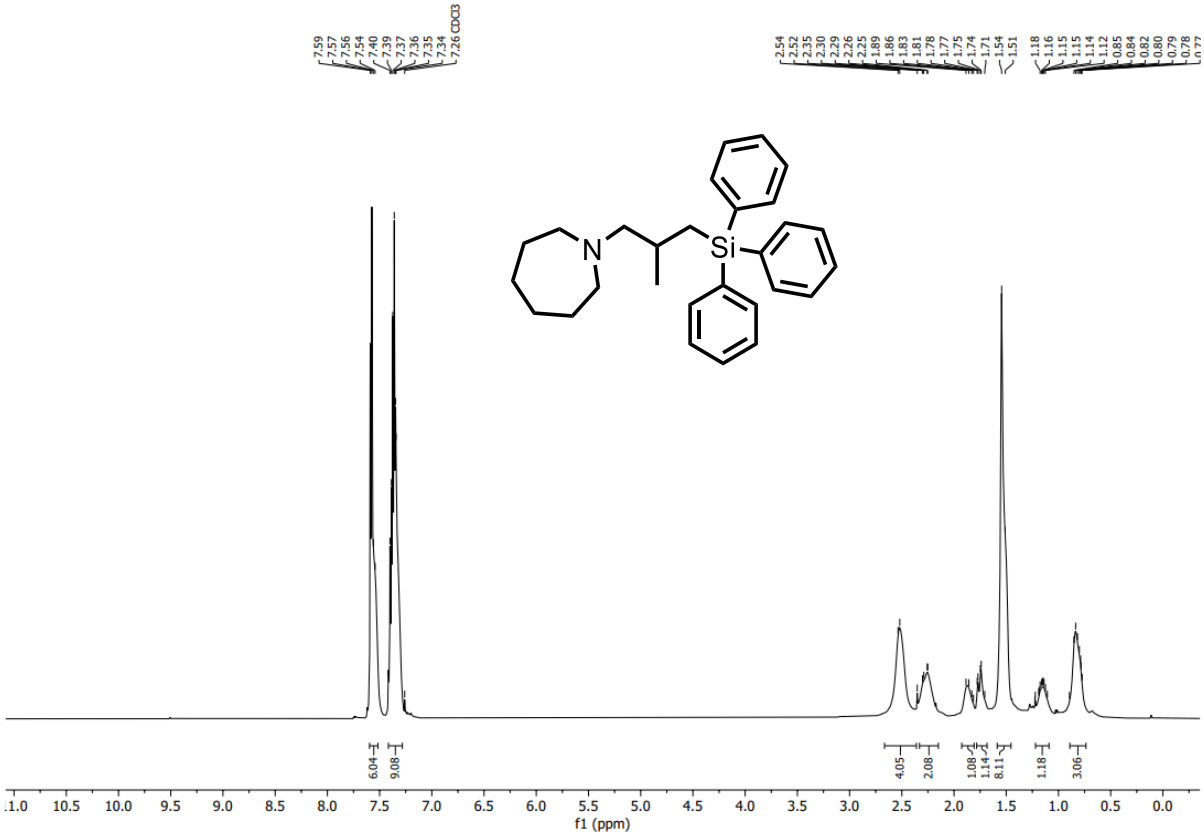


^{1}H NMR (500 MHz, $CDCl_3$)

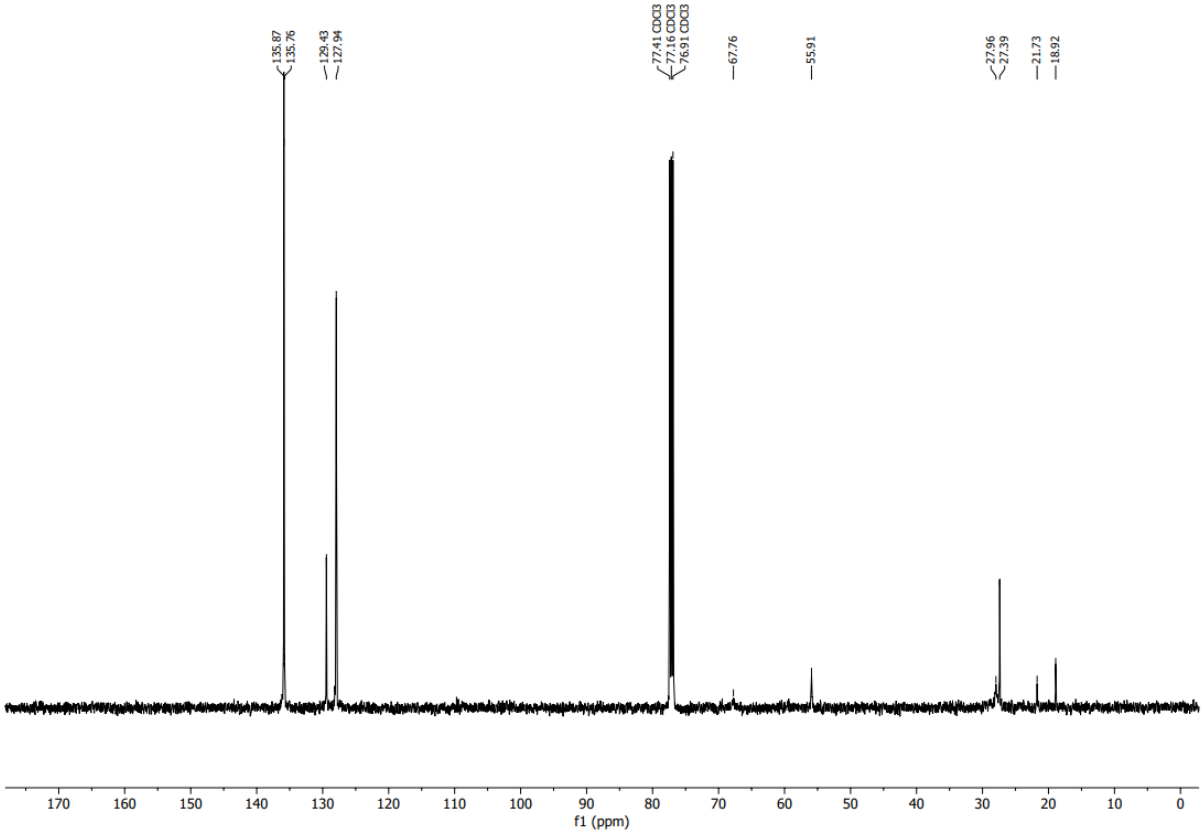


^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)

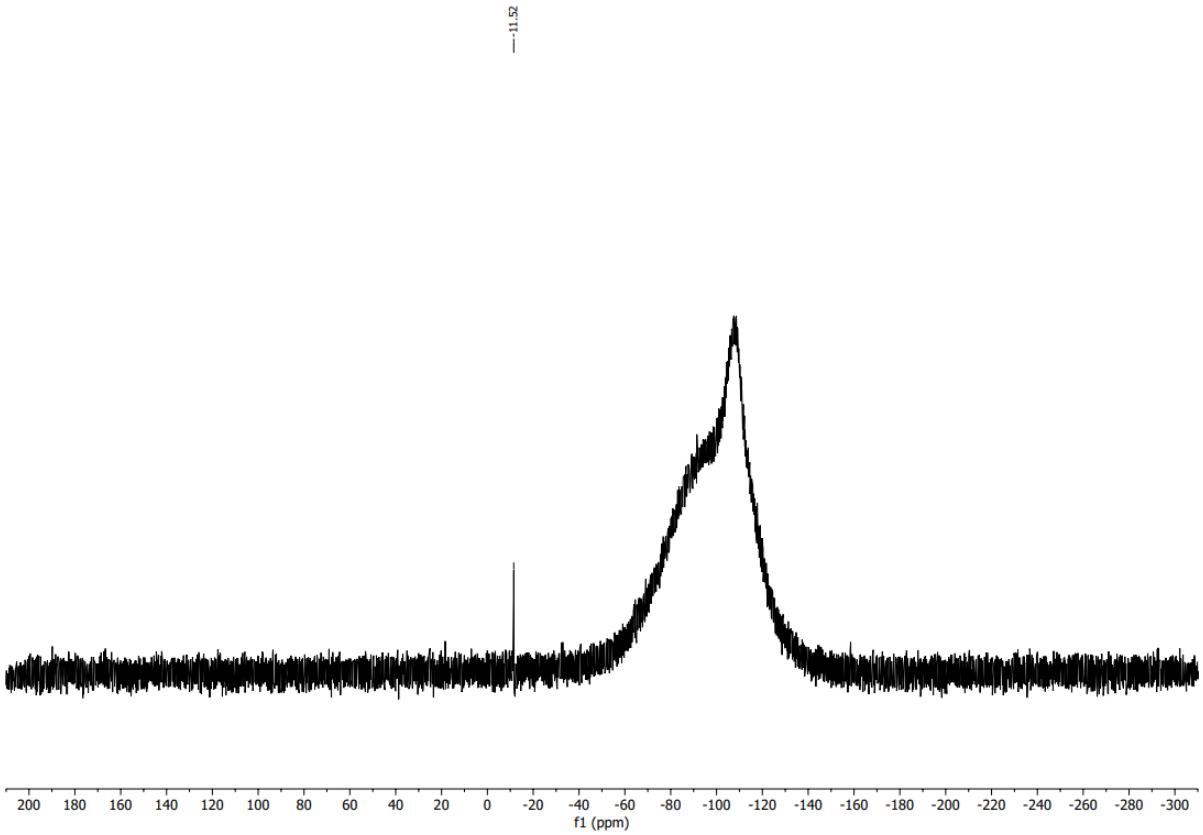
***N*-(2-Methyl-3-(triphenylsilyl)propyl)azepane (4b)**



^{1}H NMR (500 MHz, $CDCl_3$)

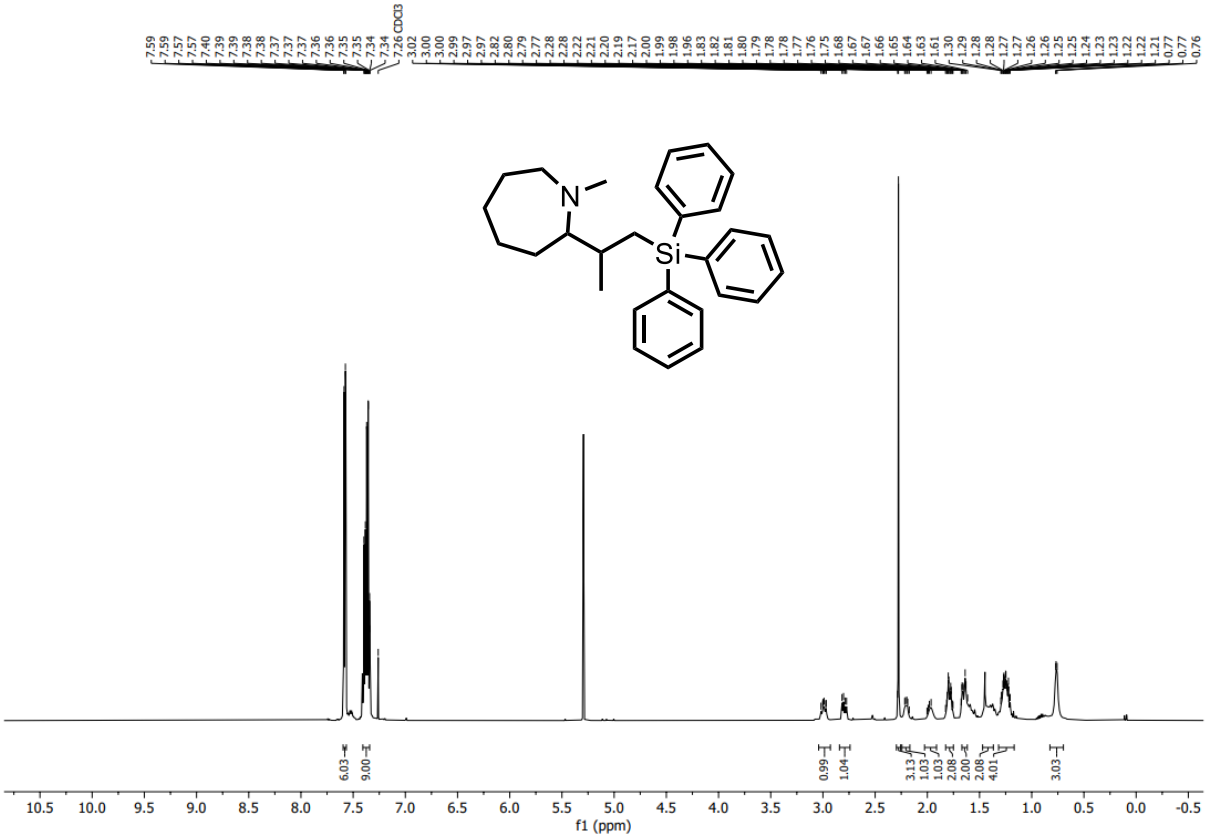


^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)

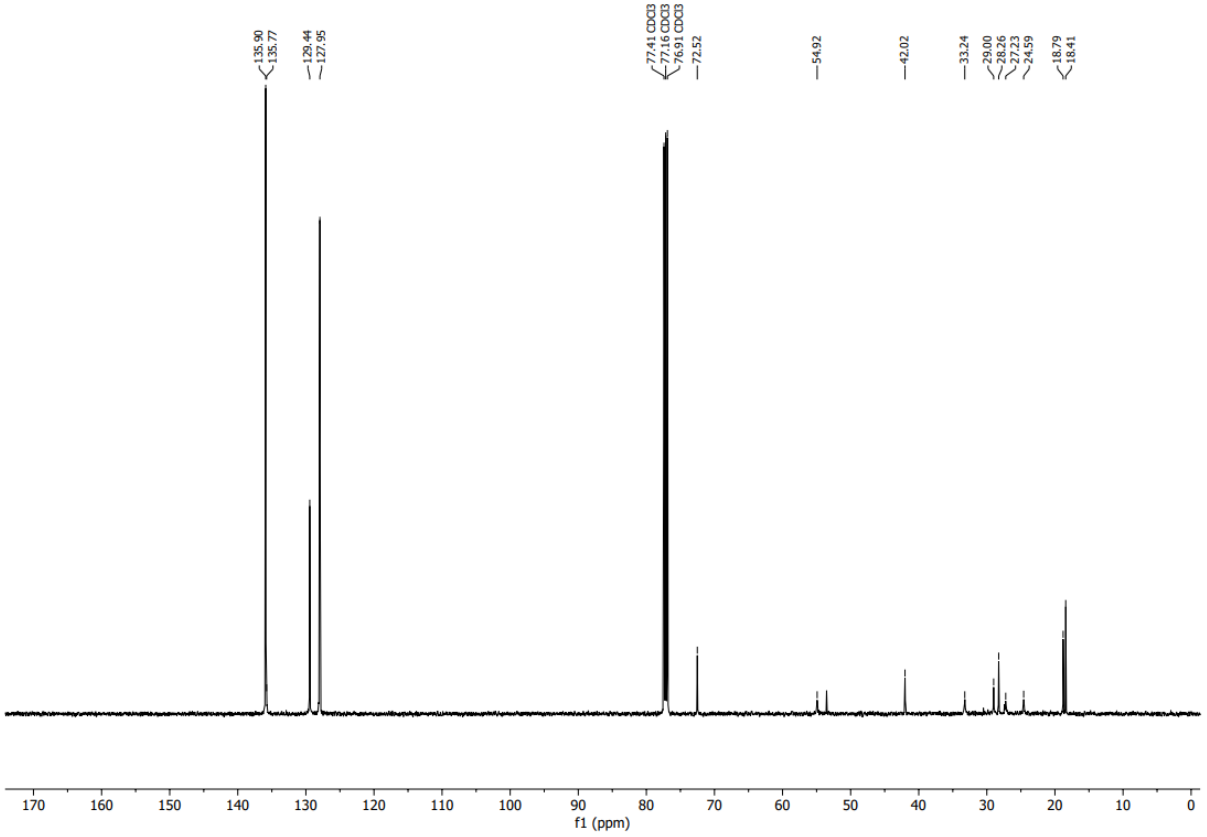


^{29}Si{^{1}H} NMR (99 MHz, $CDCl_3$)

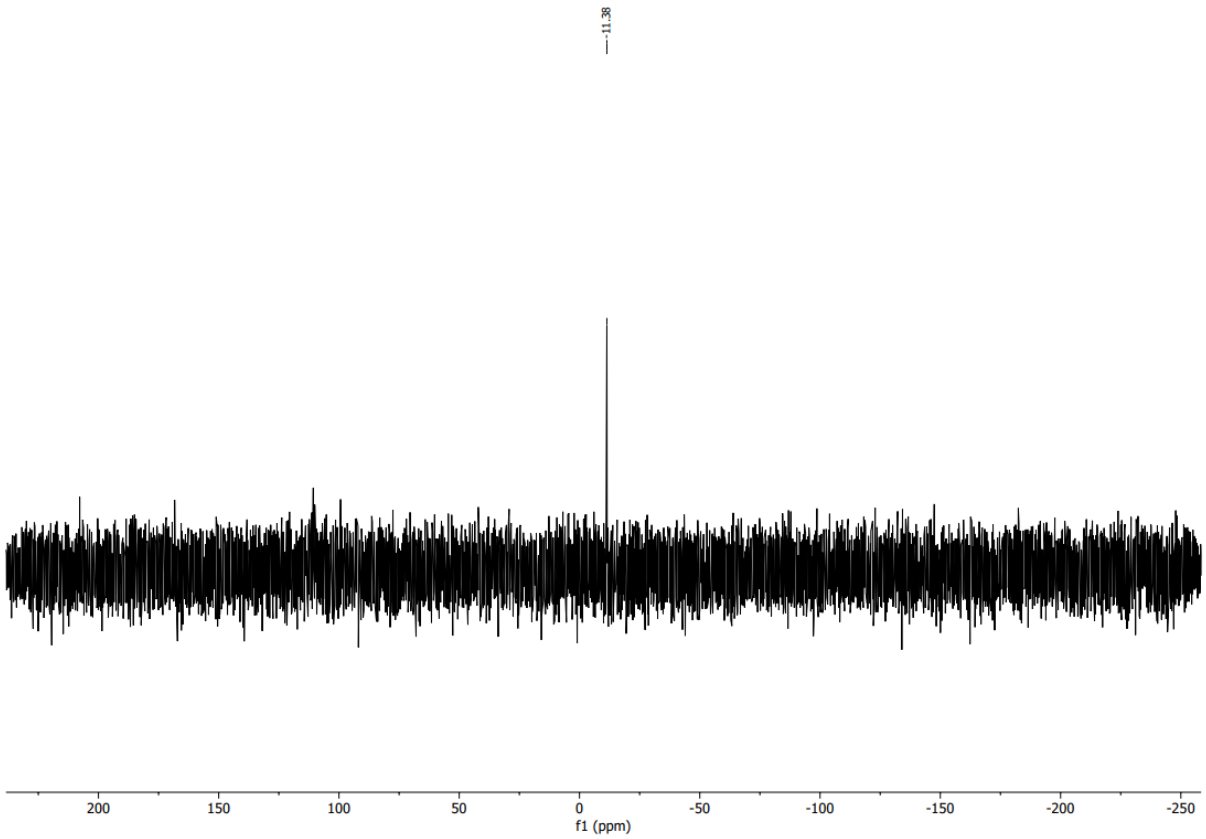
***N*-Methyl-2-(1-(tri-phenylsilyl)propan-2-yl)azepane (5b)**



^{1}H NMR (500 MHz, $CDCl_3$)

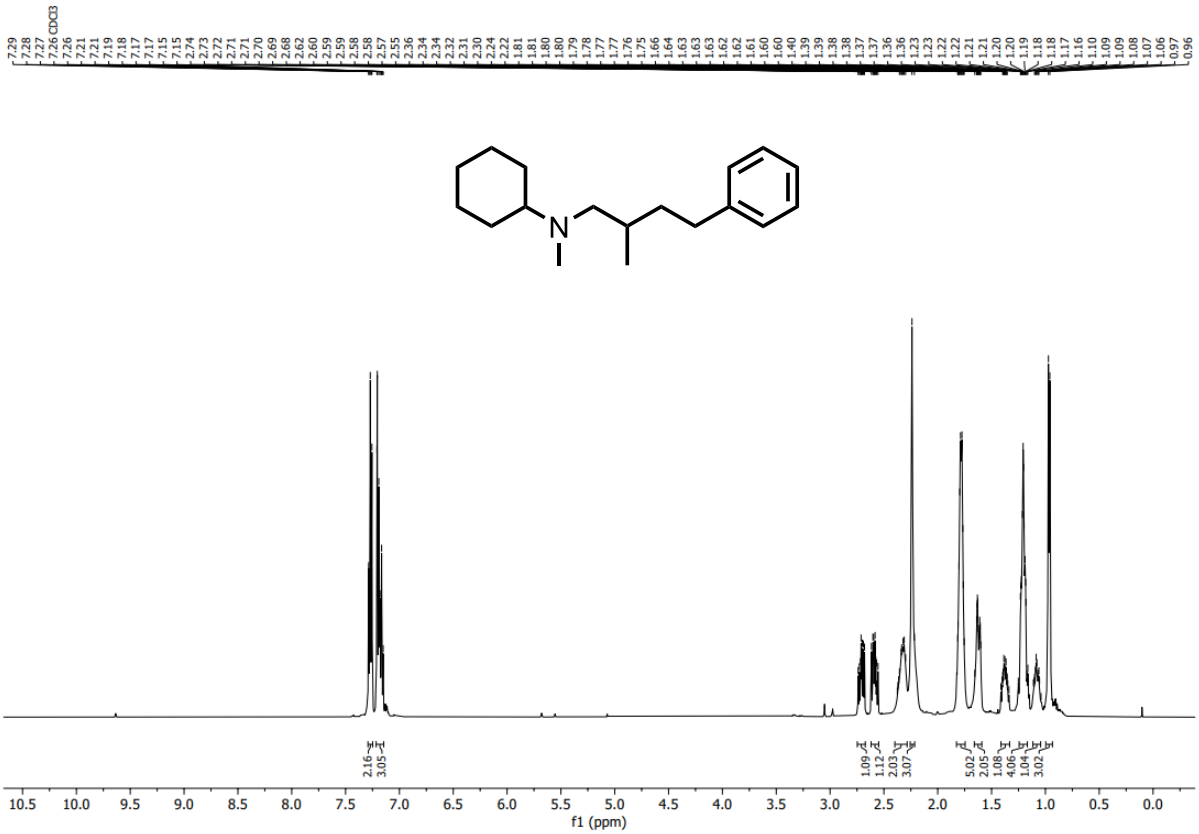


^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)

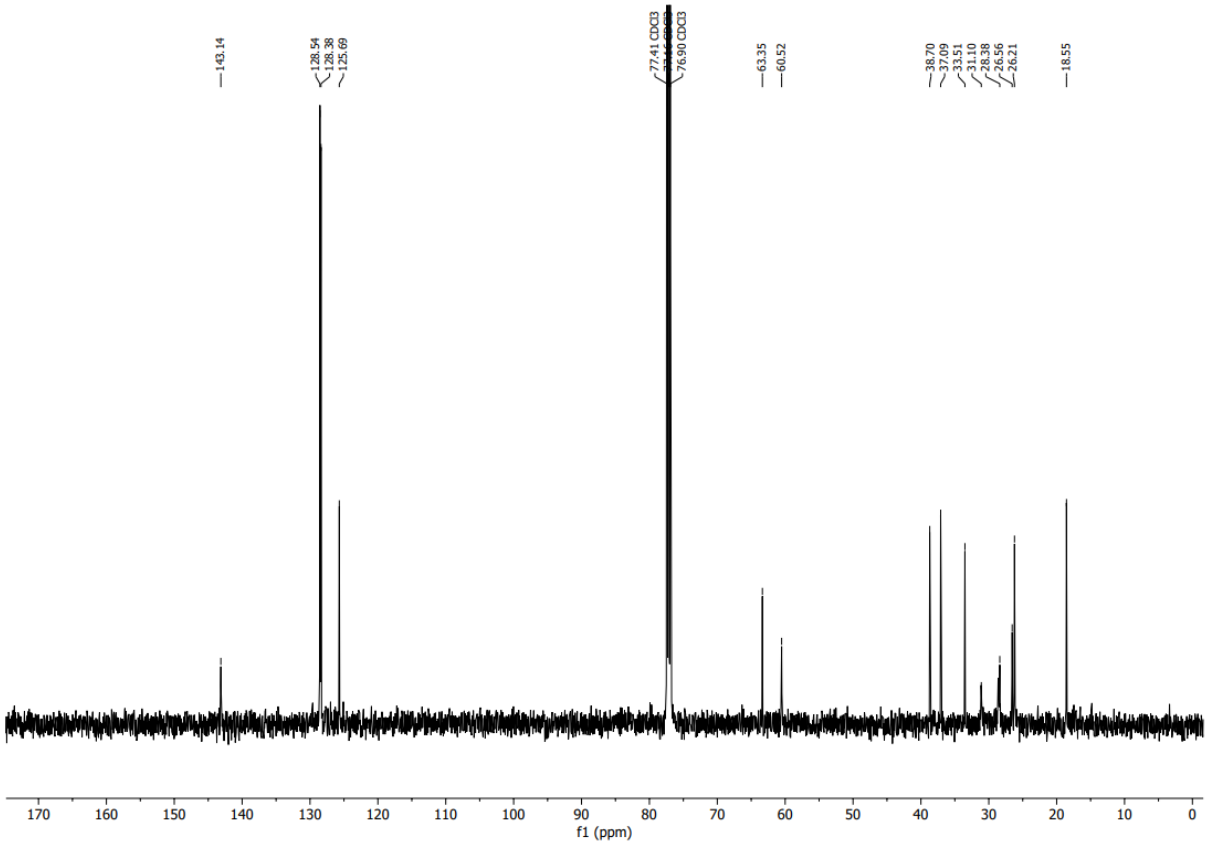


^{29}Si{^{1}H} NMR (99 MHz, $CDCl_3$)

***N*-Methyl-*N*-(2-methyl-4-phenylbutyl)cyclohexylamine (6a)**

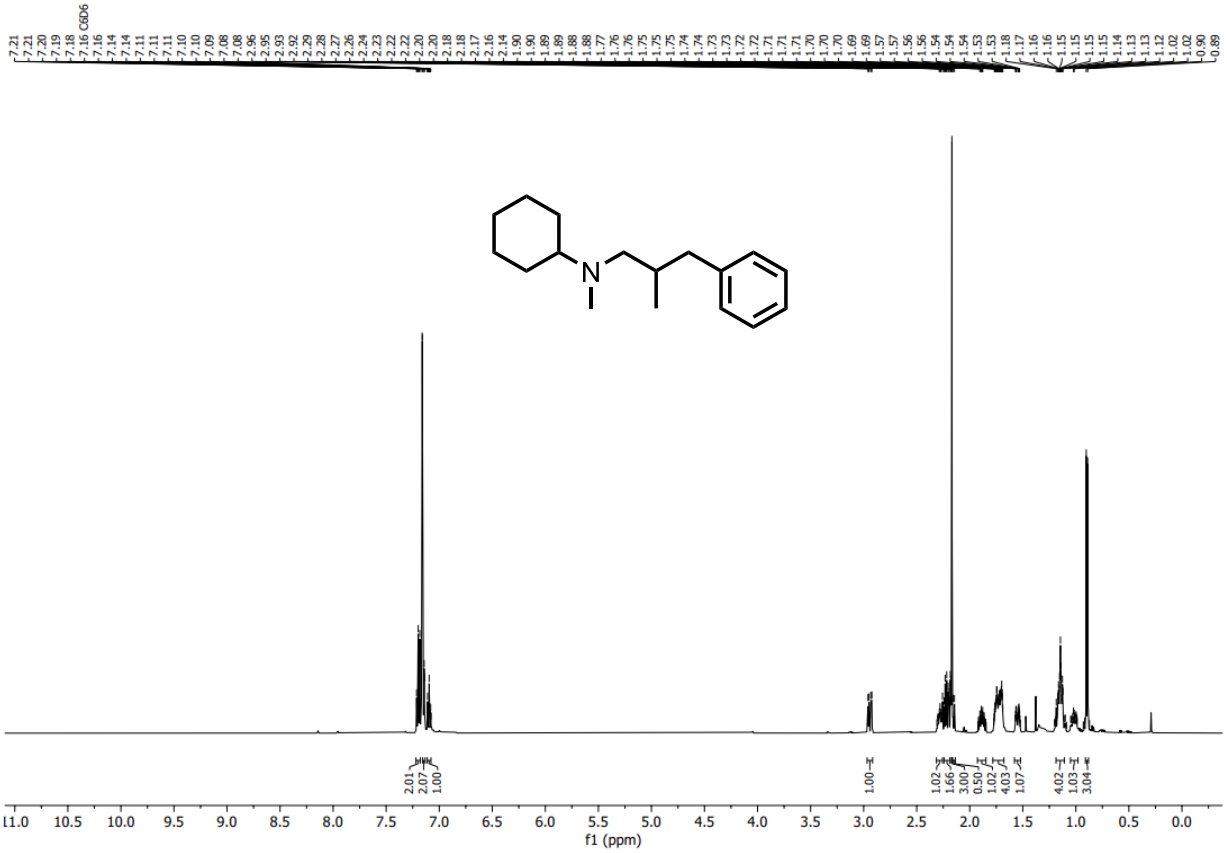


^{1}H NMR (500 MHz, $CDCl_3$)

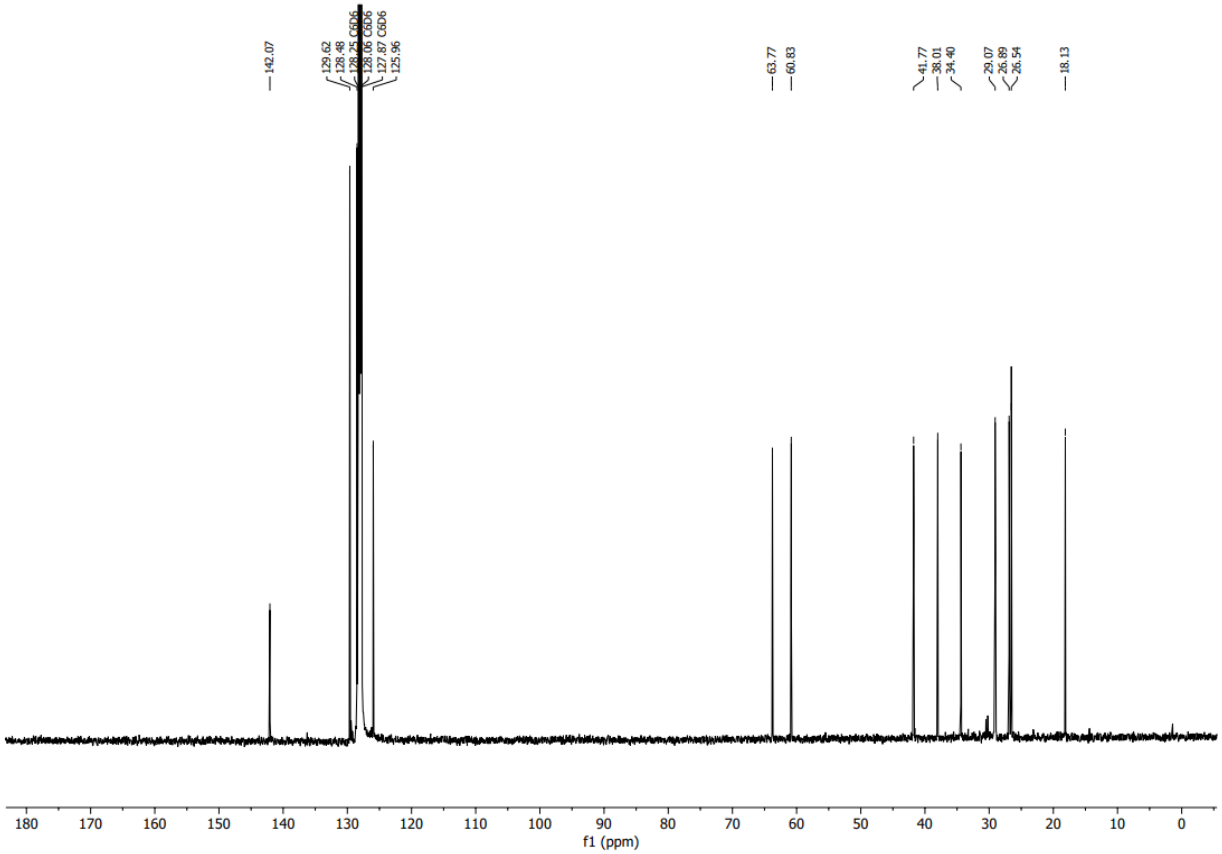


^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)

***N*-Methyl-*N*-(2-methyl-3-phenylpropyl)cyclohexylamine (6b)**

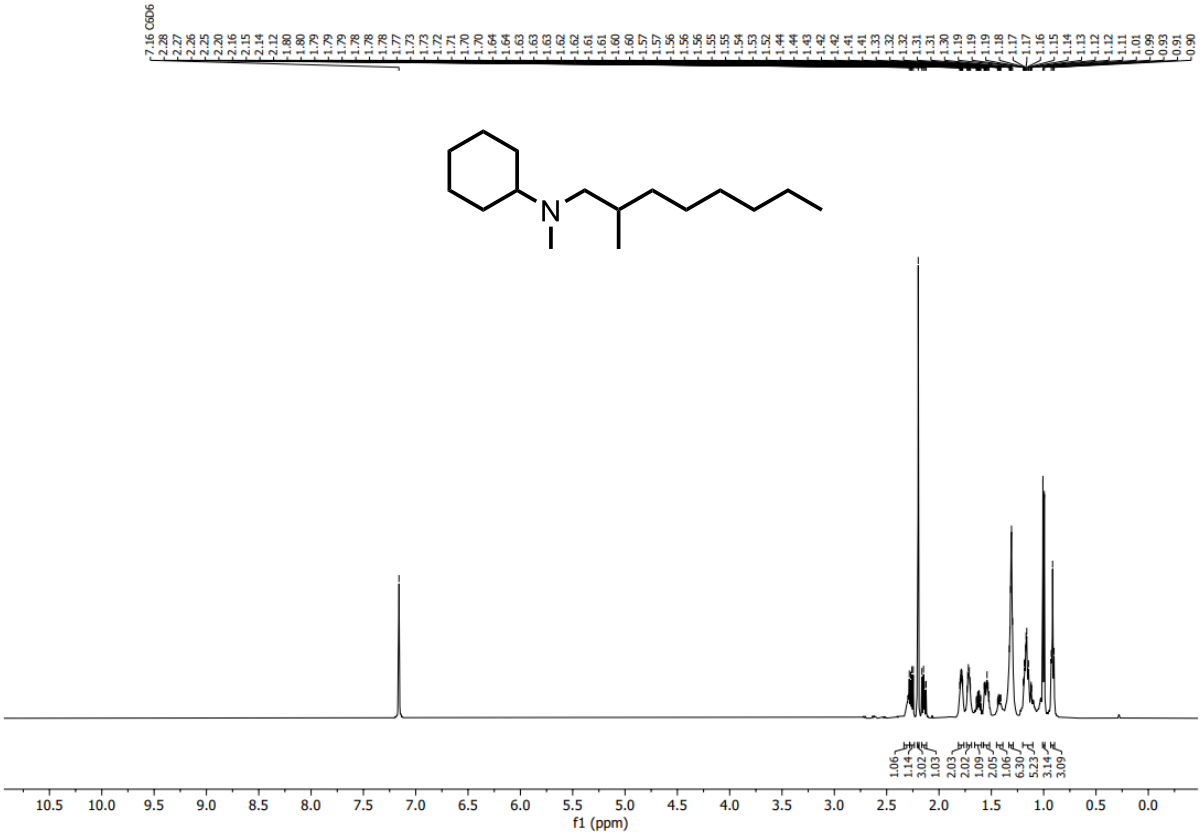


^{1}H NMR (500 MHz, C_6D_6)

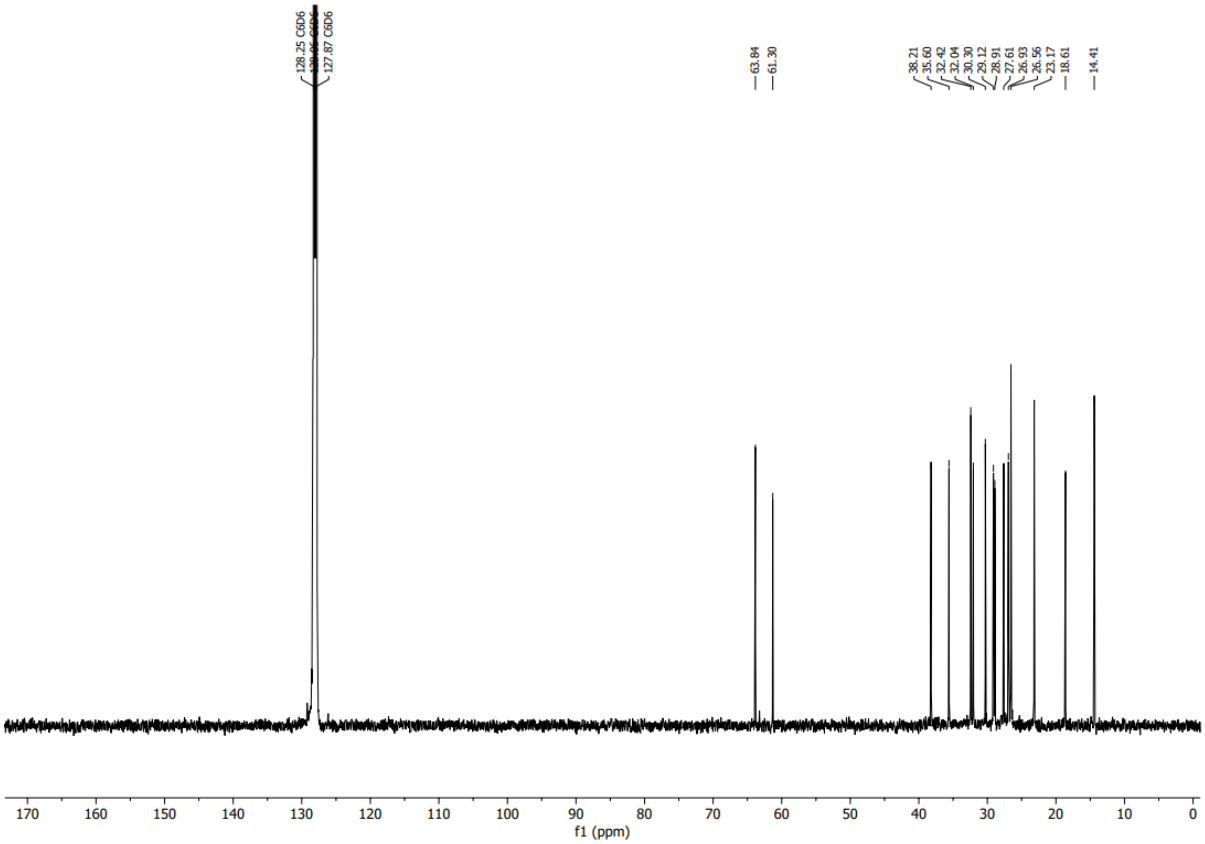


^{13}C{^{1}H} NMR (125 MHz, C_6D_6)

***N*-Methyl-*N*-(2-methyloctyl)cyclohexylamine (6c)**

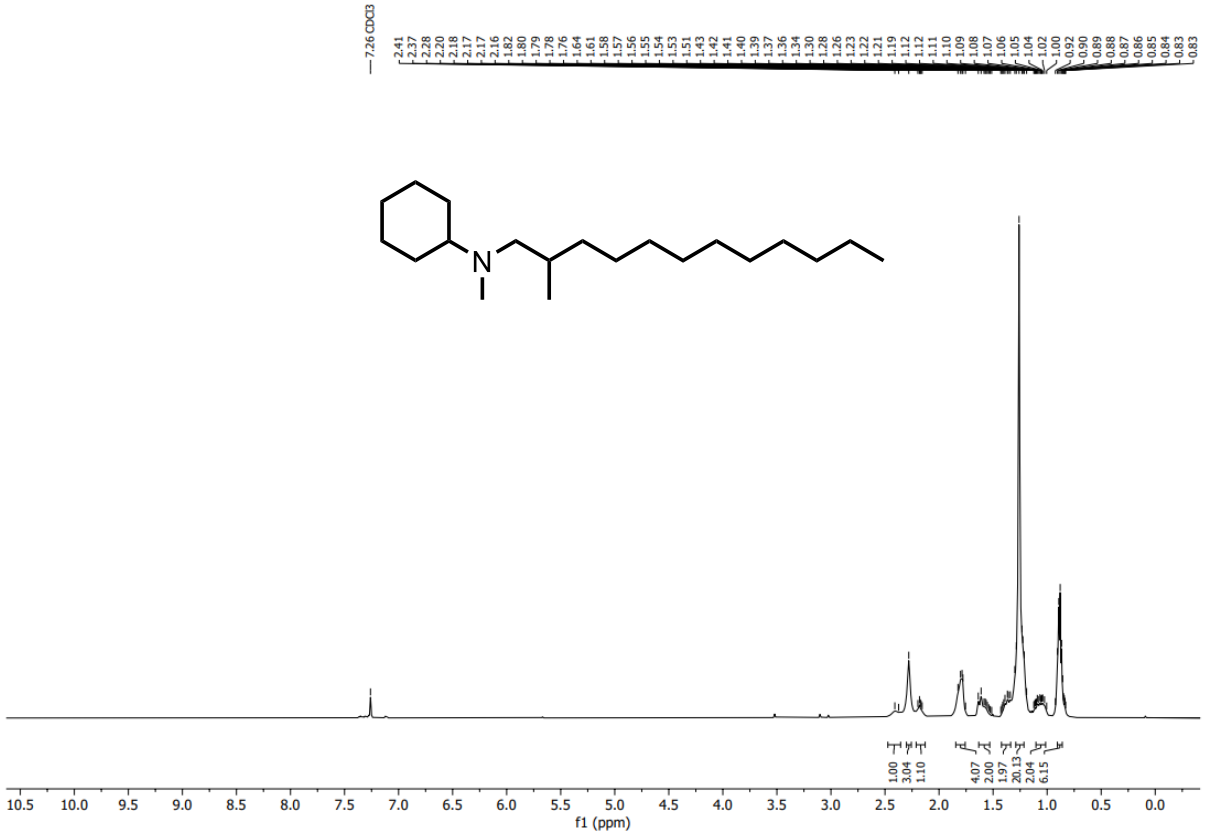


^{1}H NMR (500 MHz, C_6D_6)

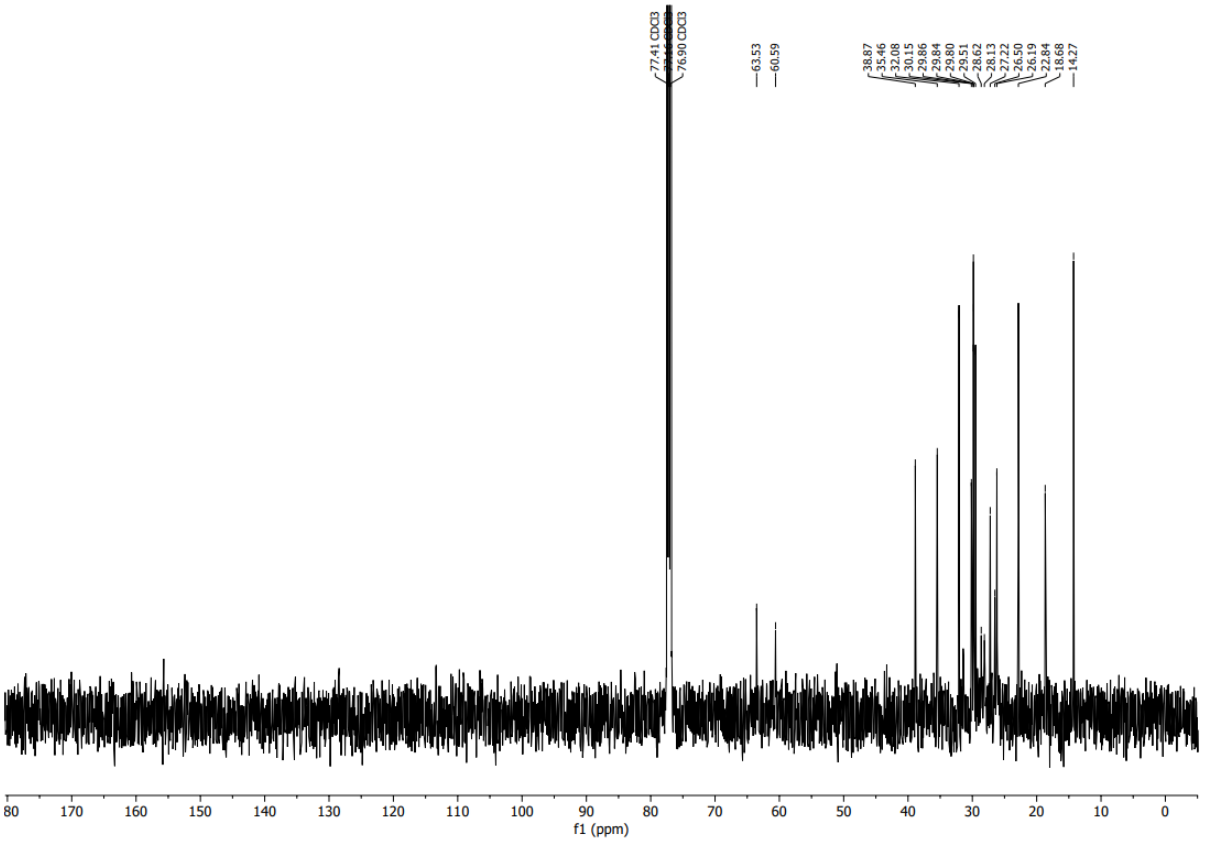


^{13}C{^{1}H} NMR (125 MHz, C_6D_6)

***N*-Methyl-*N*-(2-methyldodecyl)cyclohexylamine (6d)**

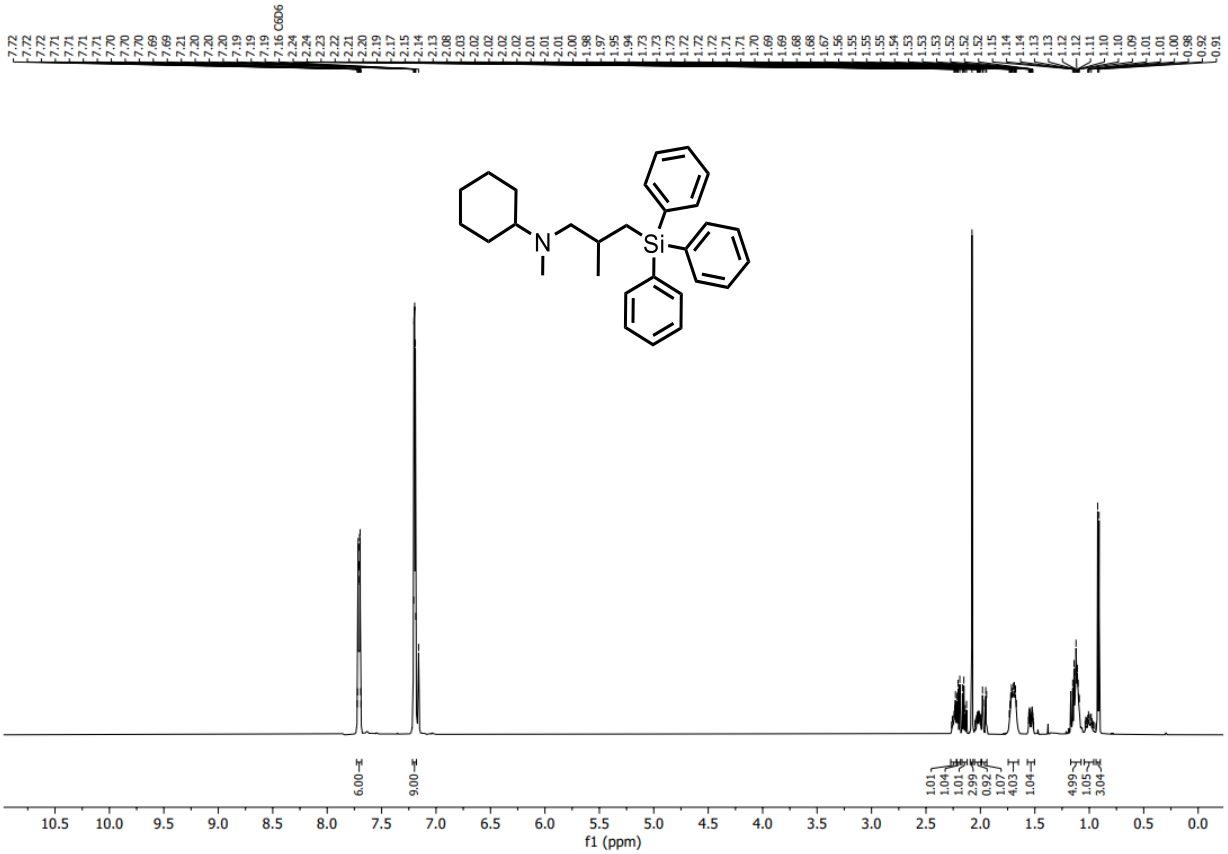


^{1}H NMR (500 MHz, $CDCl_3$)

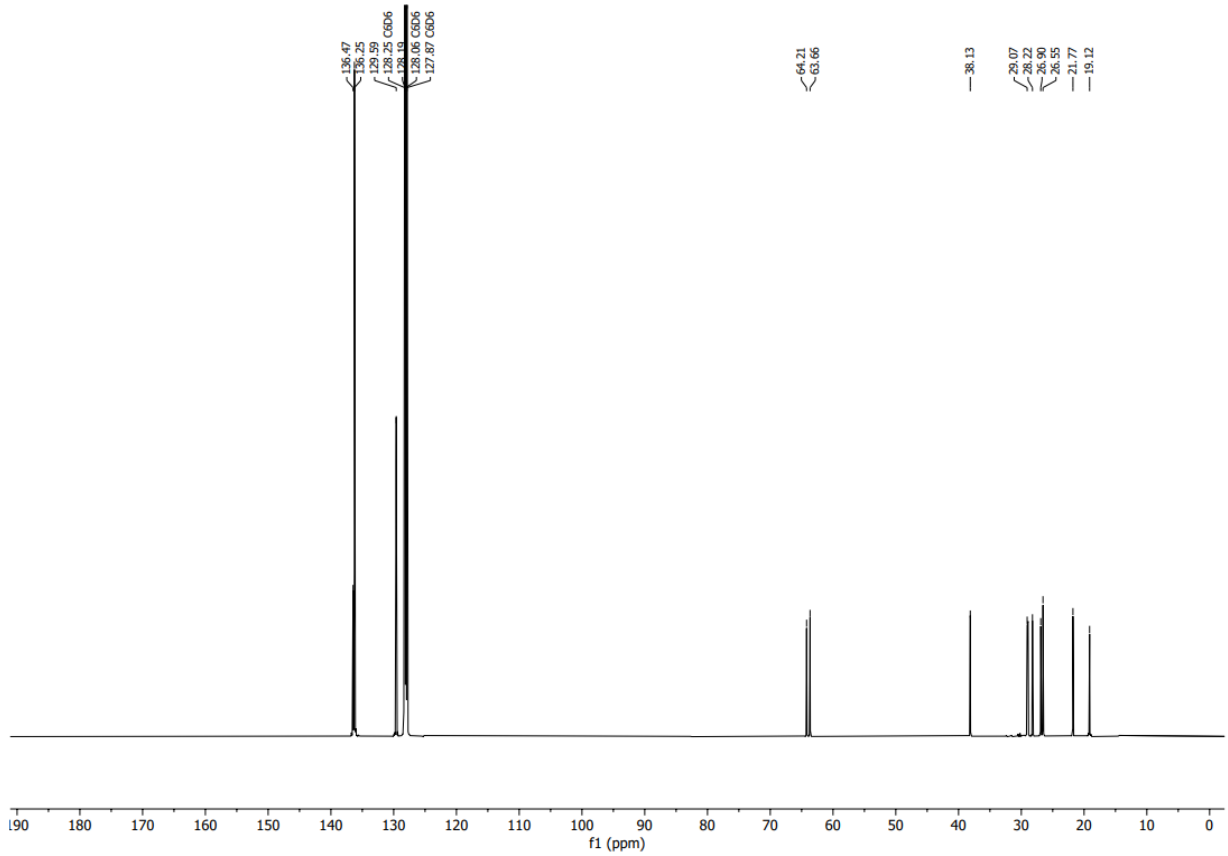


^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)

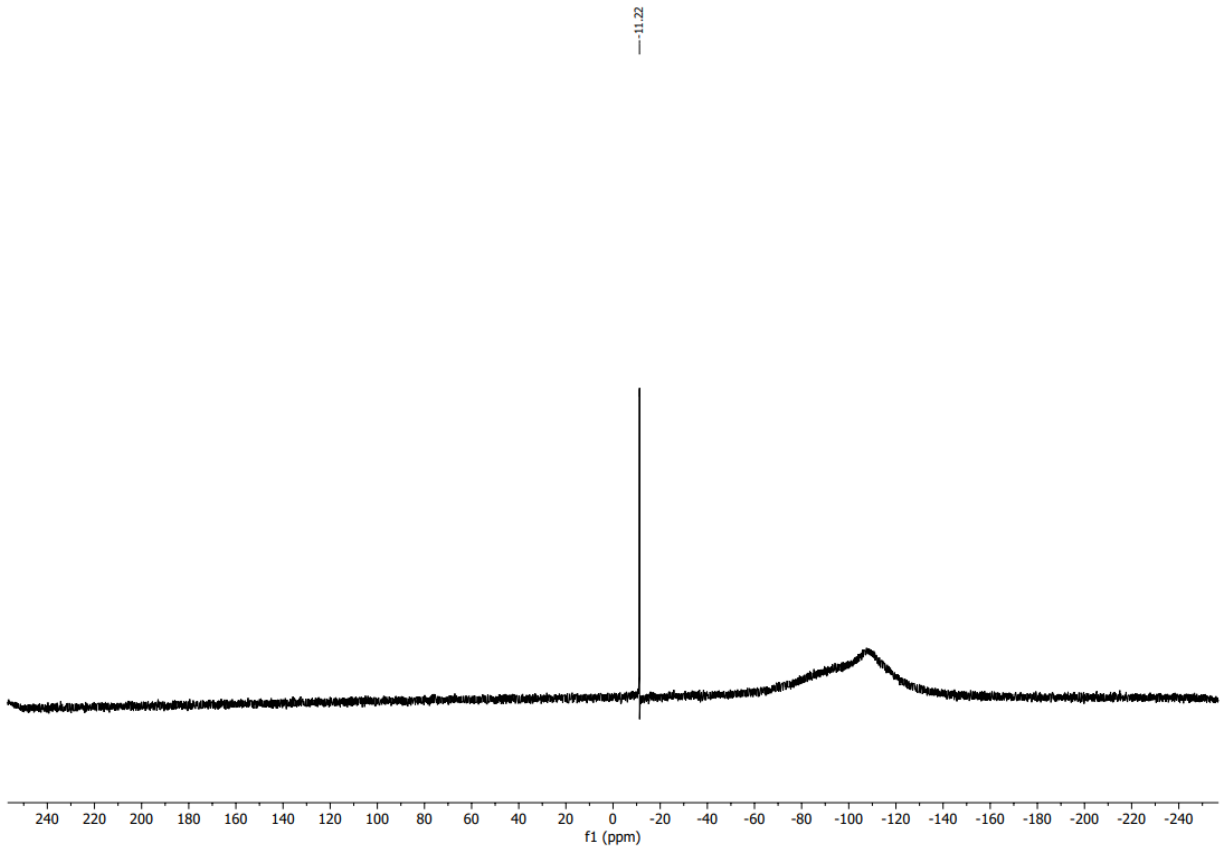
***N*-Methyl-*N*-(2-methyl-3-(triphenylsilyl)propyl)cyclohexylamine (6e)**



^{1}H NMR (500 MHz, C_6D_6)

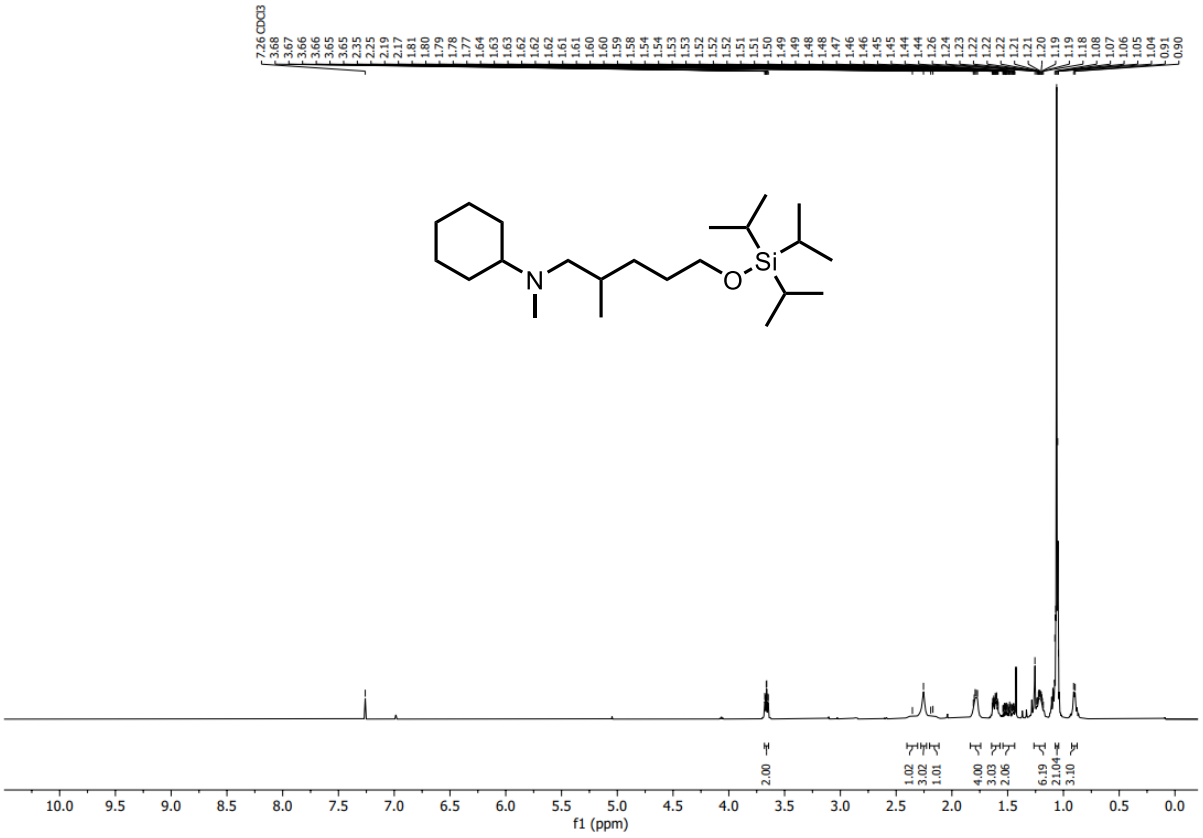


^{13}C{^{1}H} NMR (125 MHz, C_6D_6)

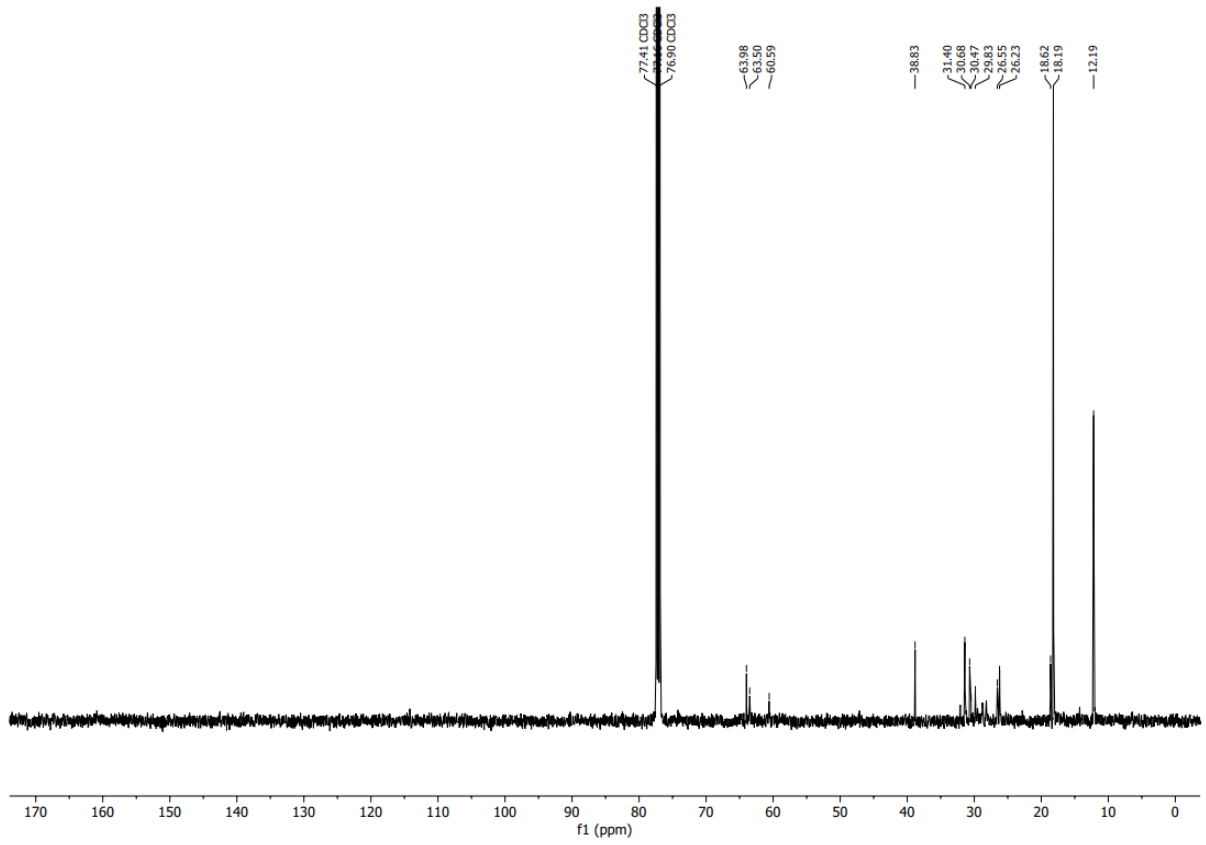


^{29}Si{^{1}H} NMR (99 MHz, C_6D_6)

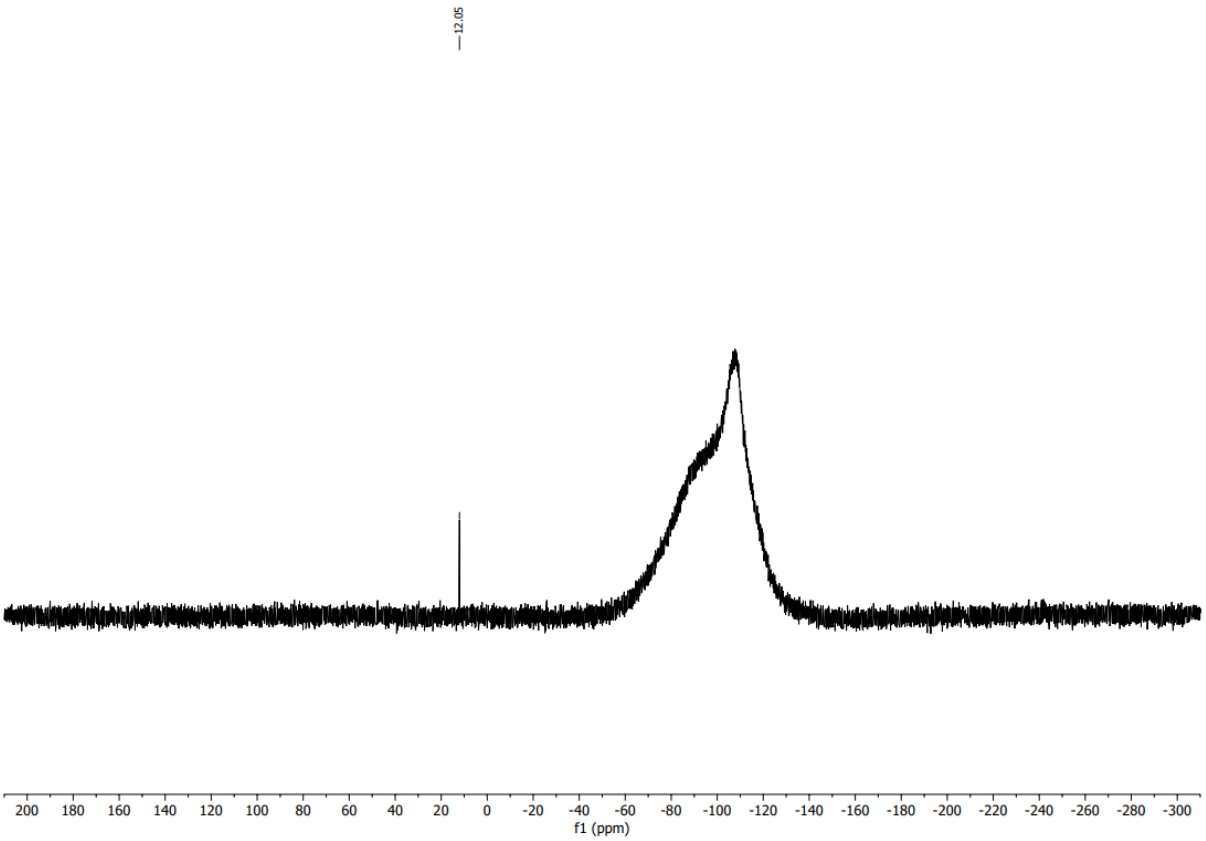
***N*-Methyl-(2-methyl-5-((triisopropylsilyl)oxy)pentyl)cyclohexylamine (6f)**



^{1}H NMR (500 MHz, $CDCl_3$)

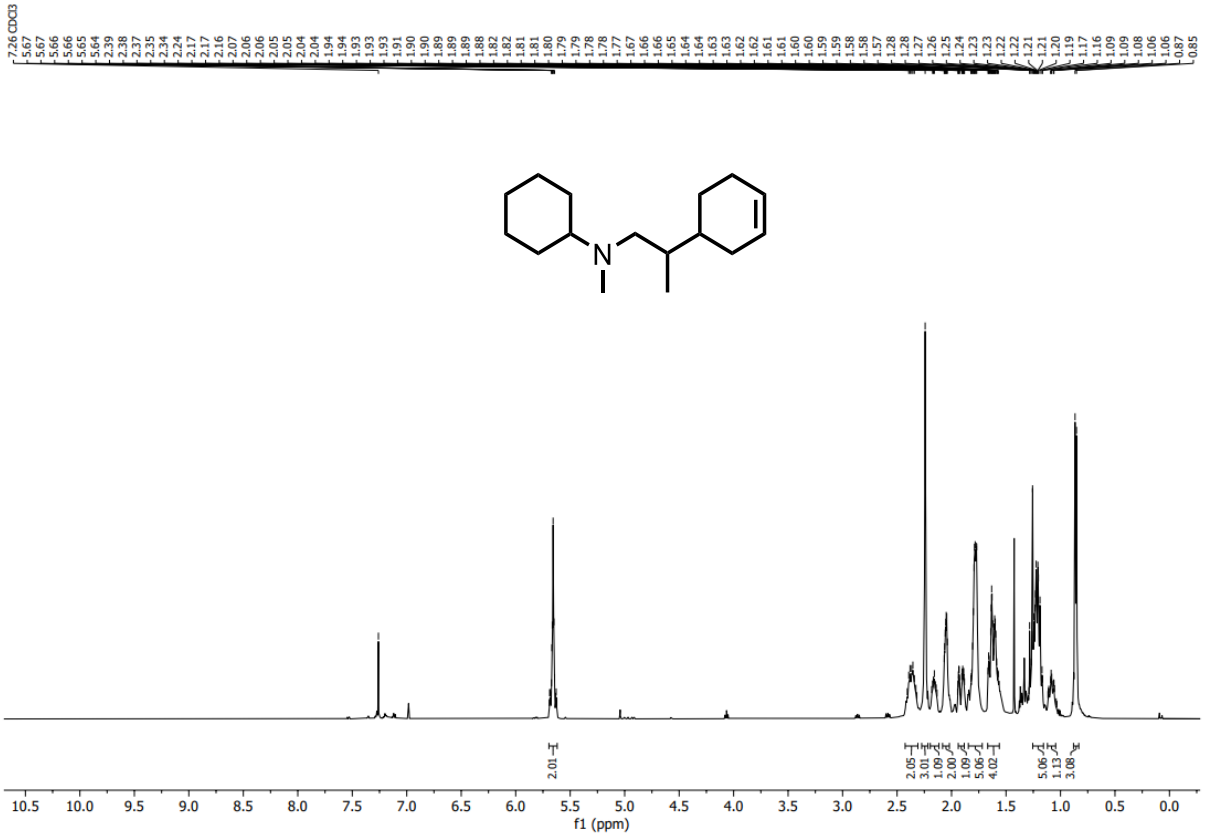


^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)

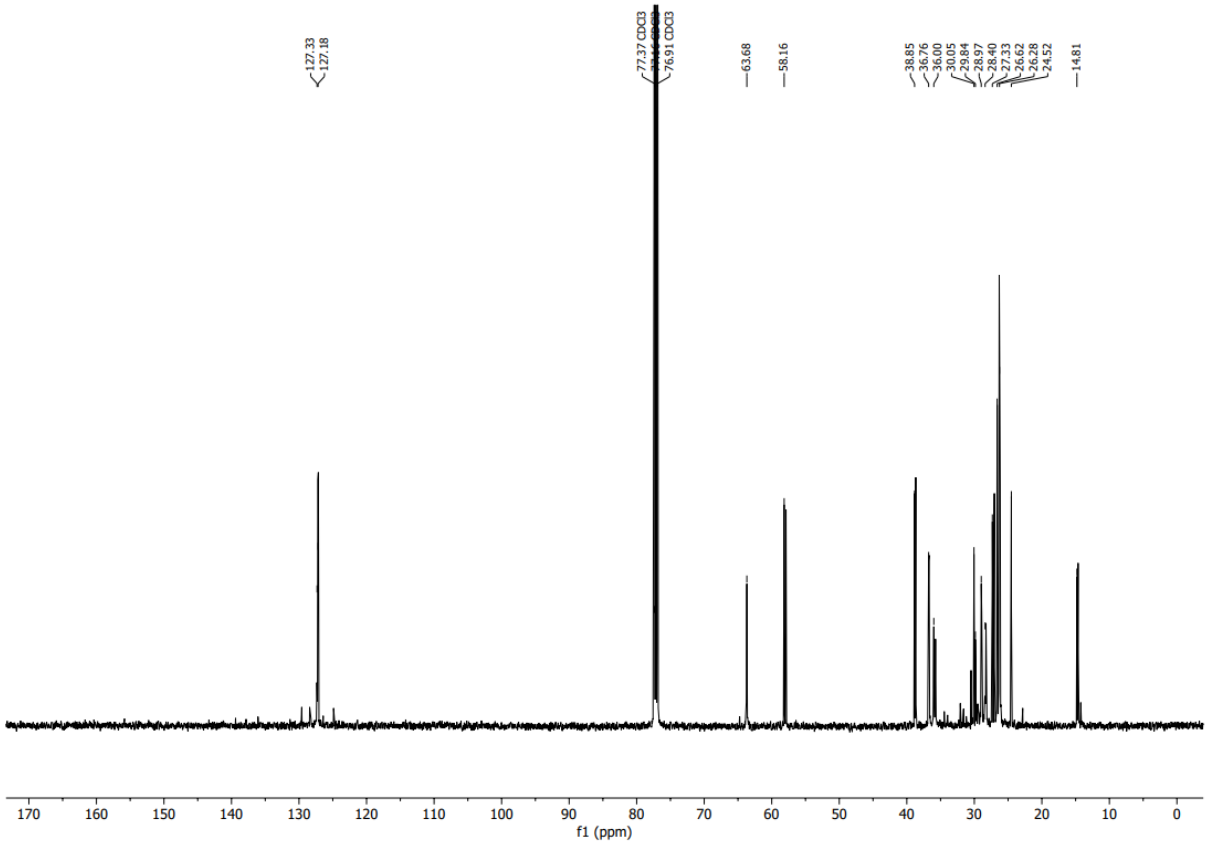


^{29}Si{^{1}H} NMR (99 MHz, $CDCl_3$)

***N*-(2-(Cyclohex-3-en-1-yl)propyl)-*N*-methylcyclohexylamine (6g)**

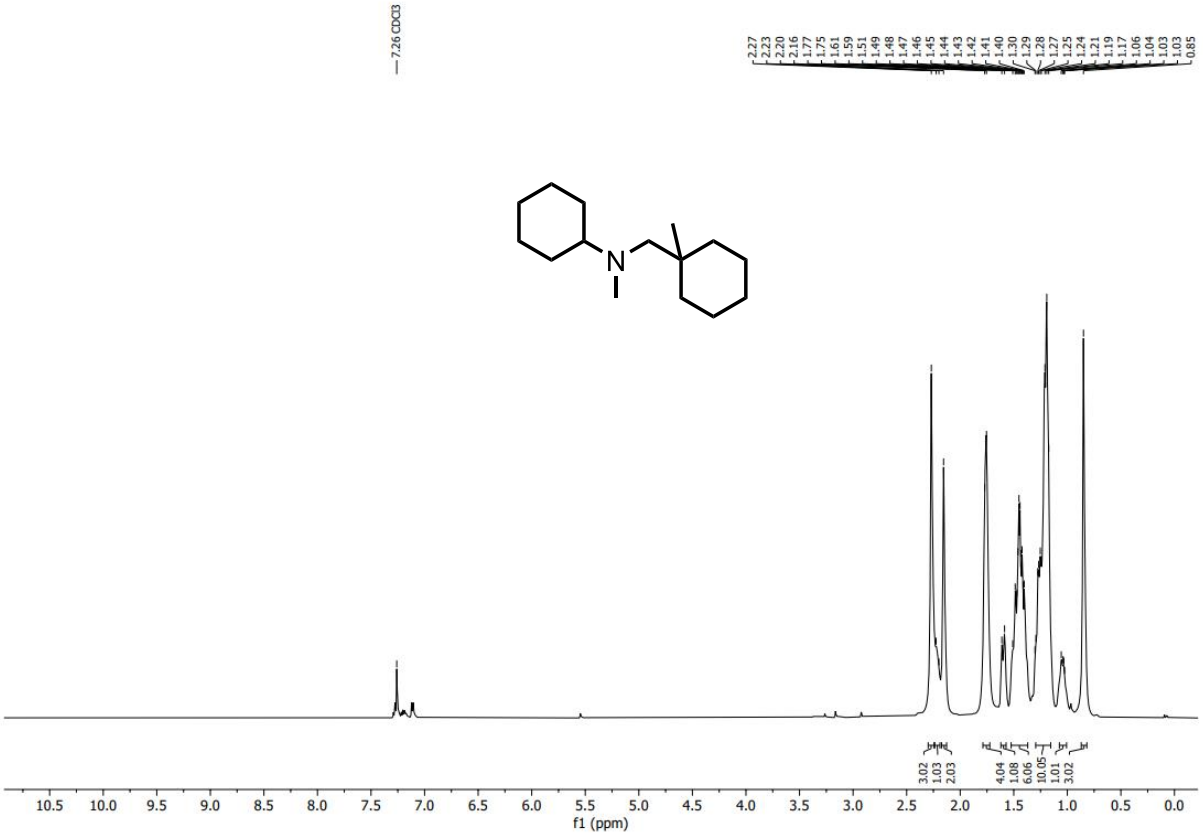


^{1}H NMR (500 MHz, $CDCl_3$)

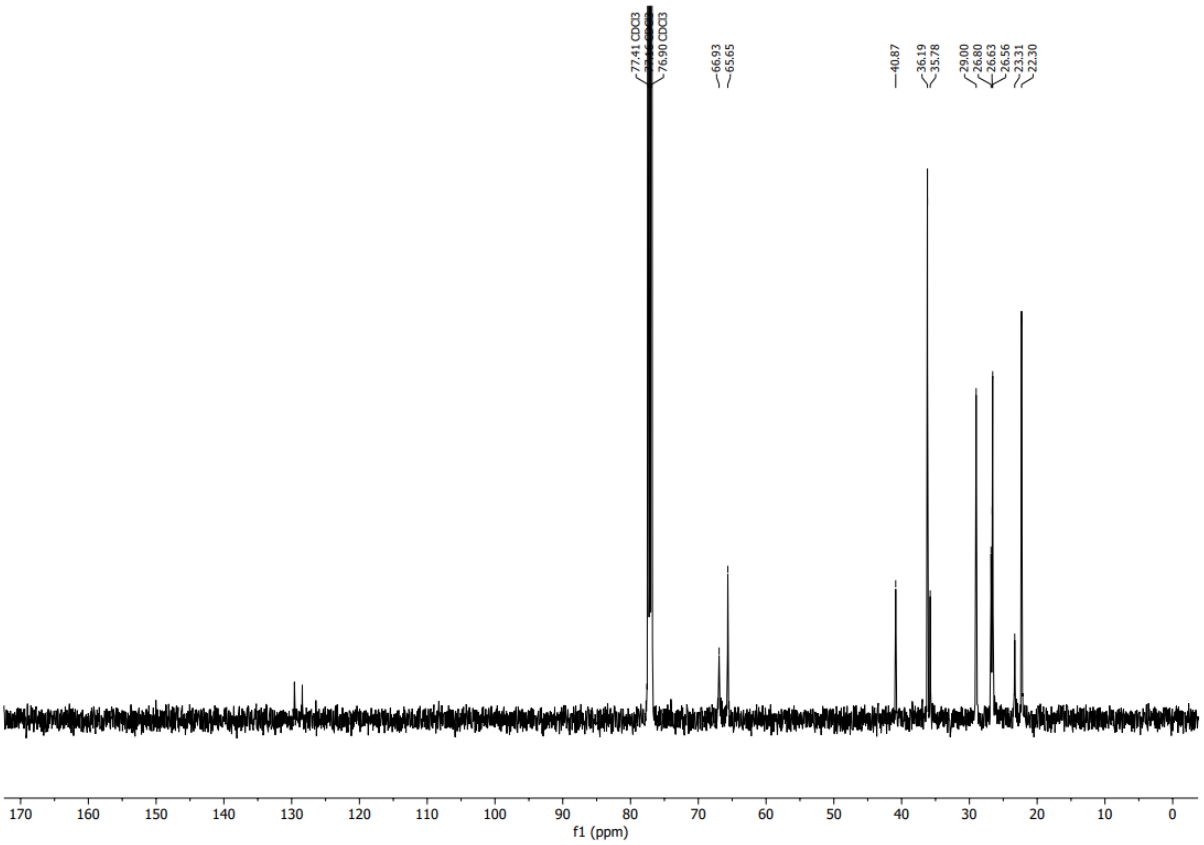


^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)

***N*-Methyl-*N*-((1-methylcyclohexyl)methyl)cyclohexylamine (6h)**

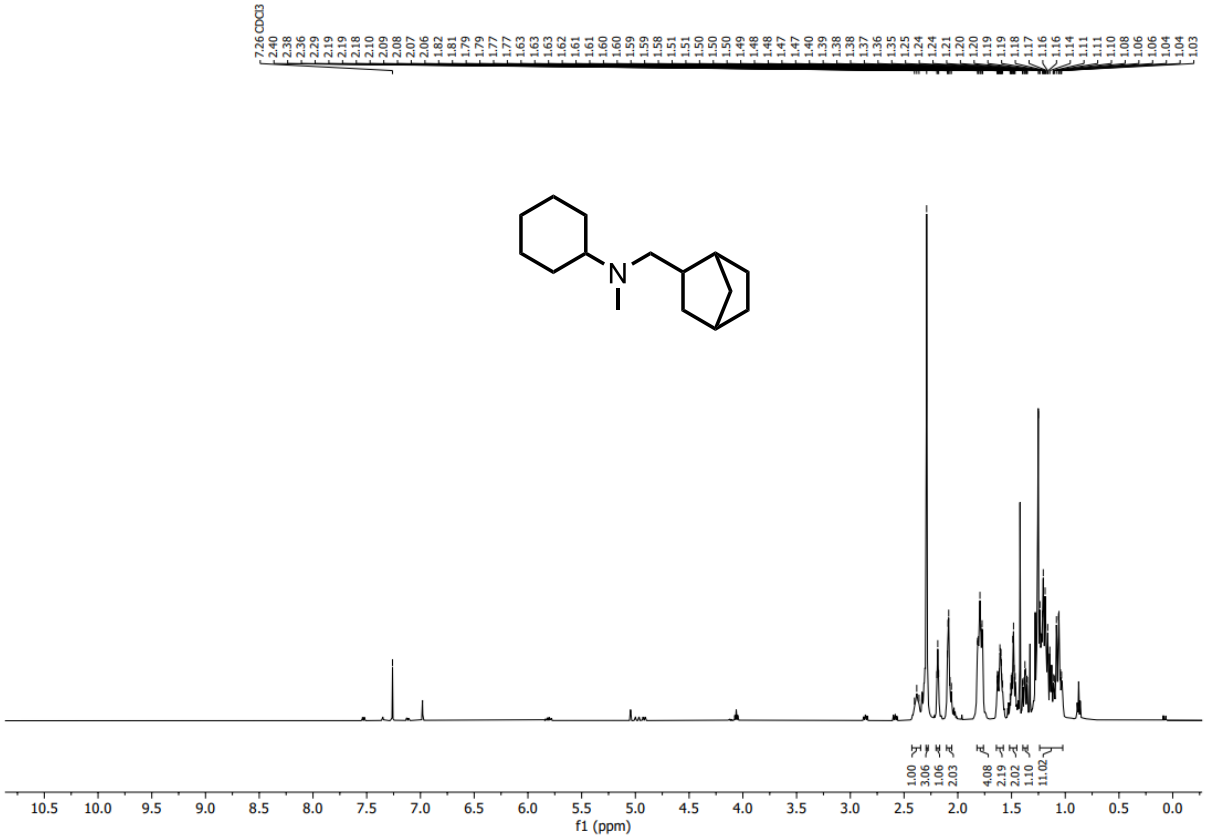


^{1}H NMR (500 MHz, $CDCl_3$)

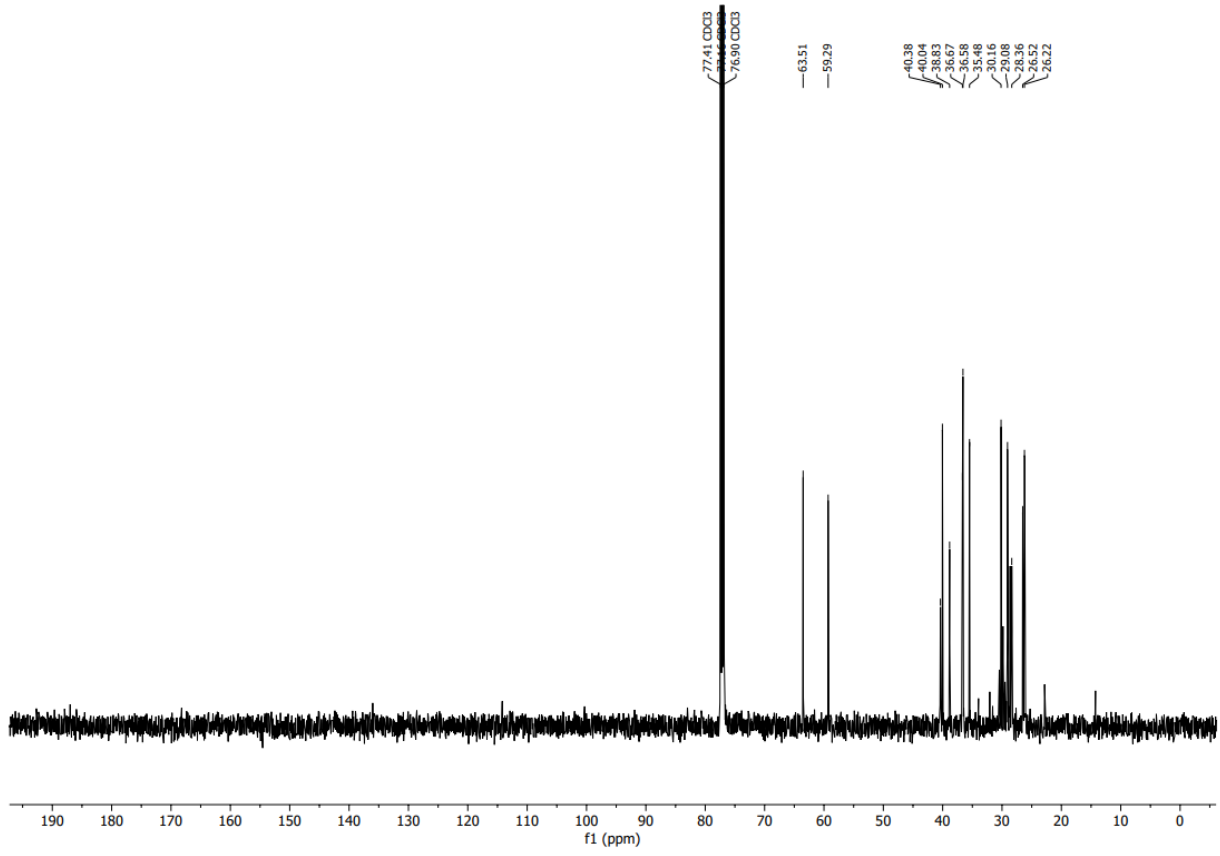


^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)

***N*-(Bicyclo[2.2.1]heptan-2-ylmethyl)-*N*-methylcyclohexylamine (6i)**

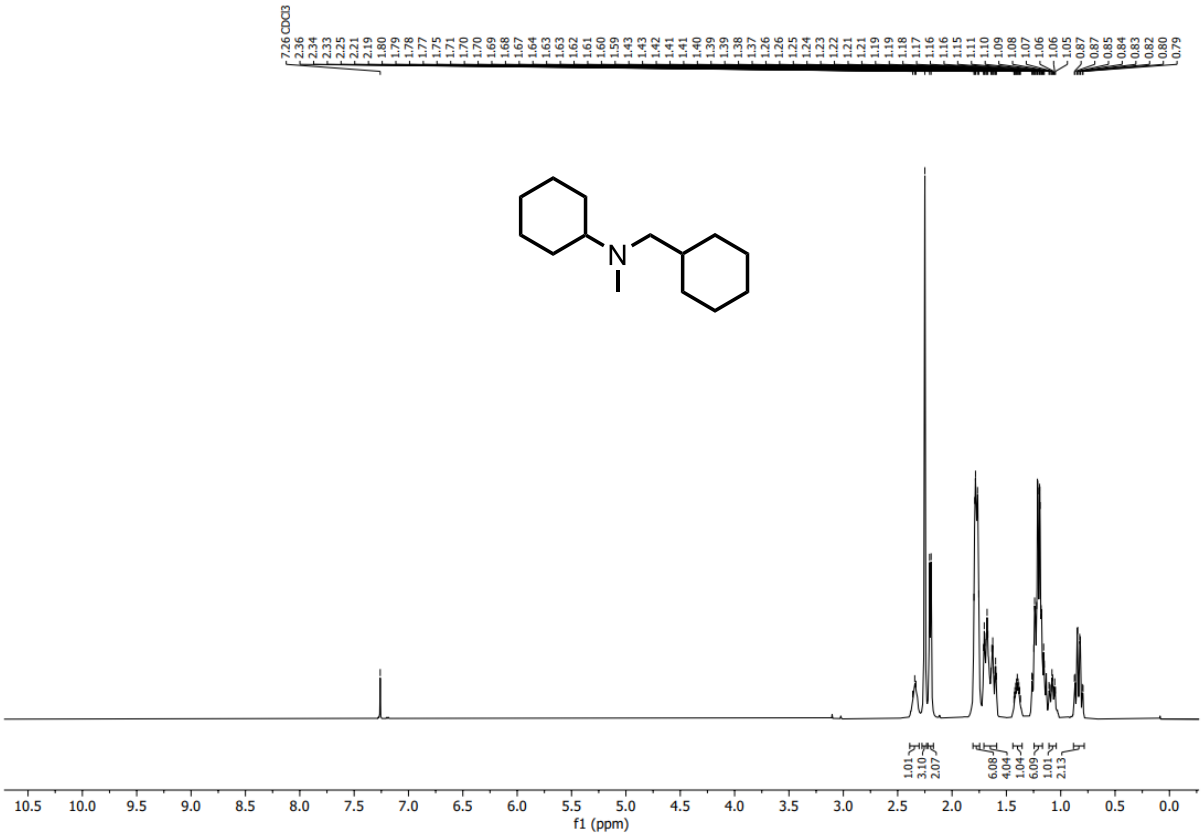


^{1}H NMR (500 MHz, $CDCl_3$)

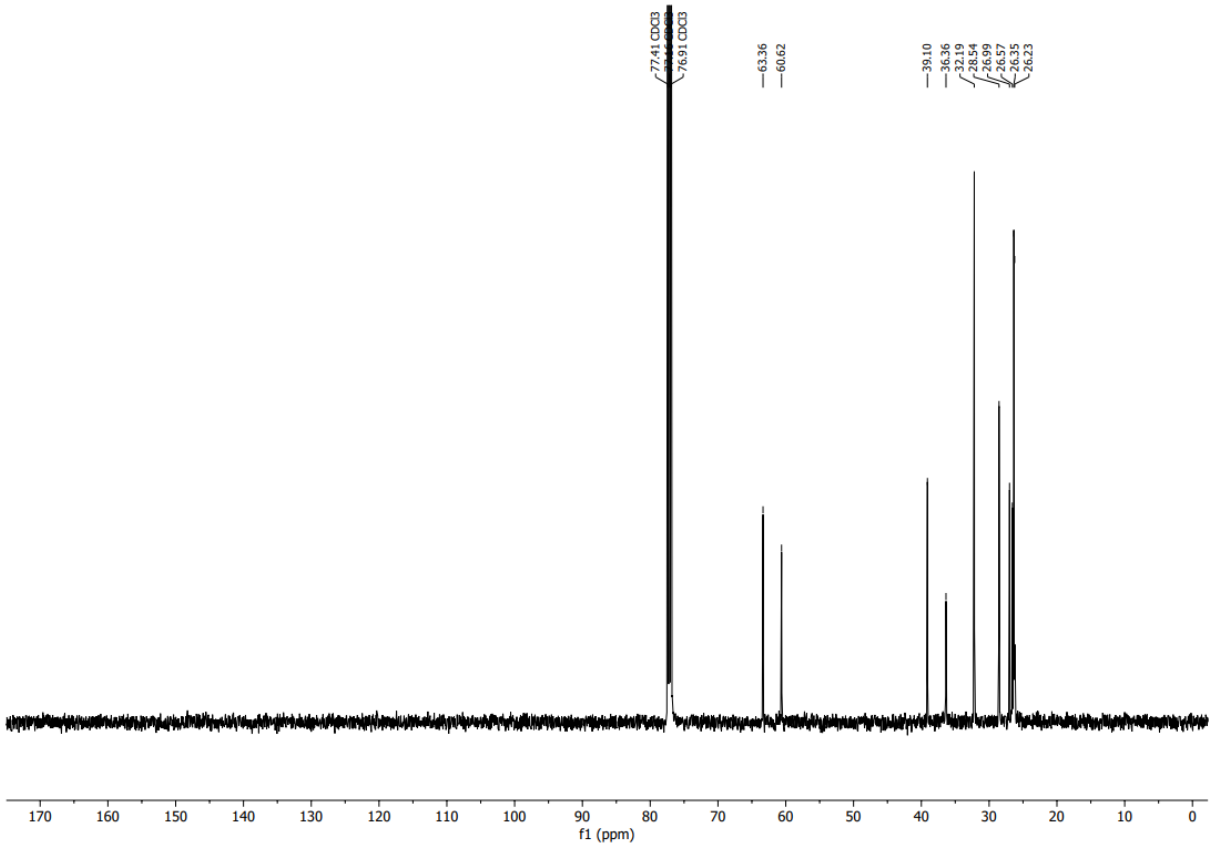


^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)

***N*-(Cyclohexylmethyl)-*N*-methylcyclohexylamine (6j)**

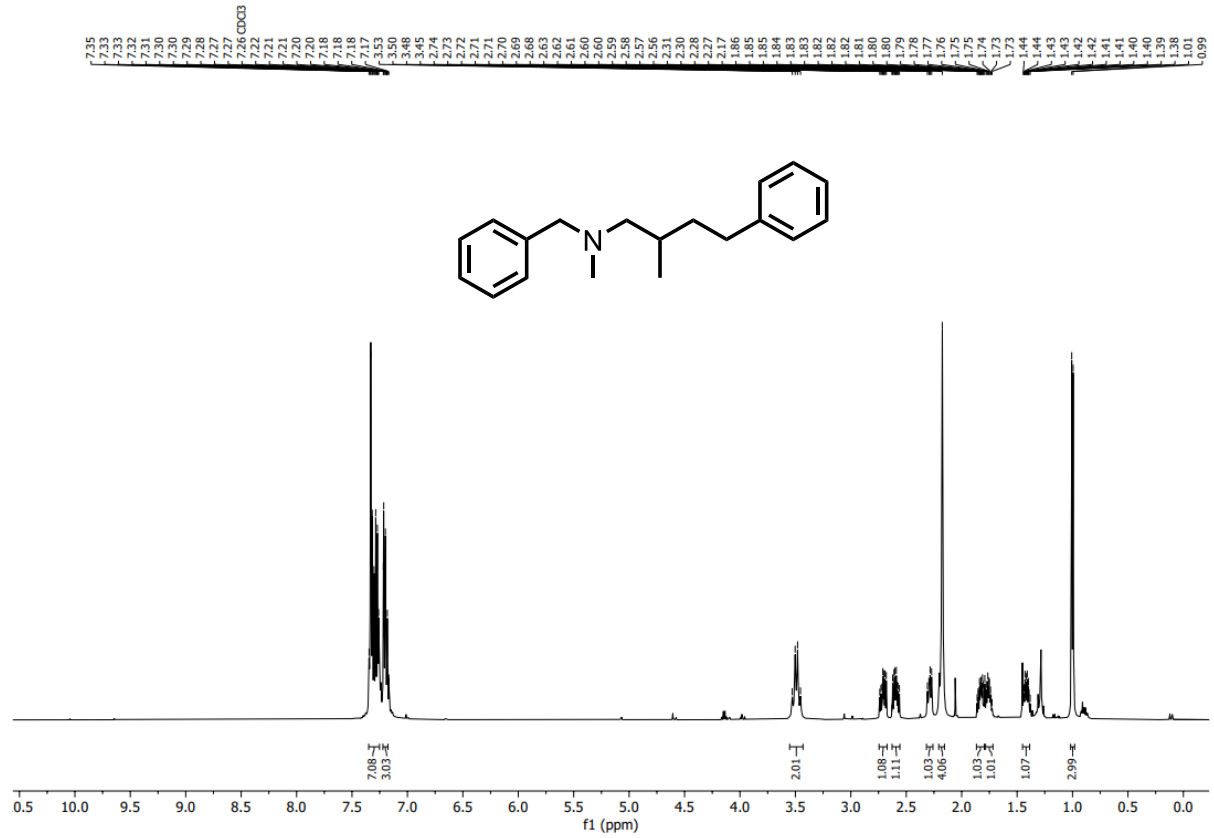


^{1}H NMR (500 MHz, $CDCl_3$)

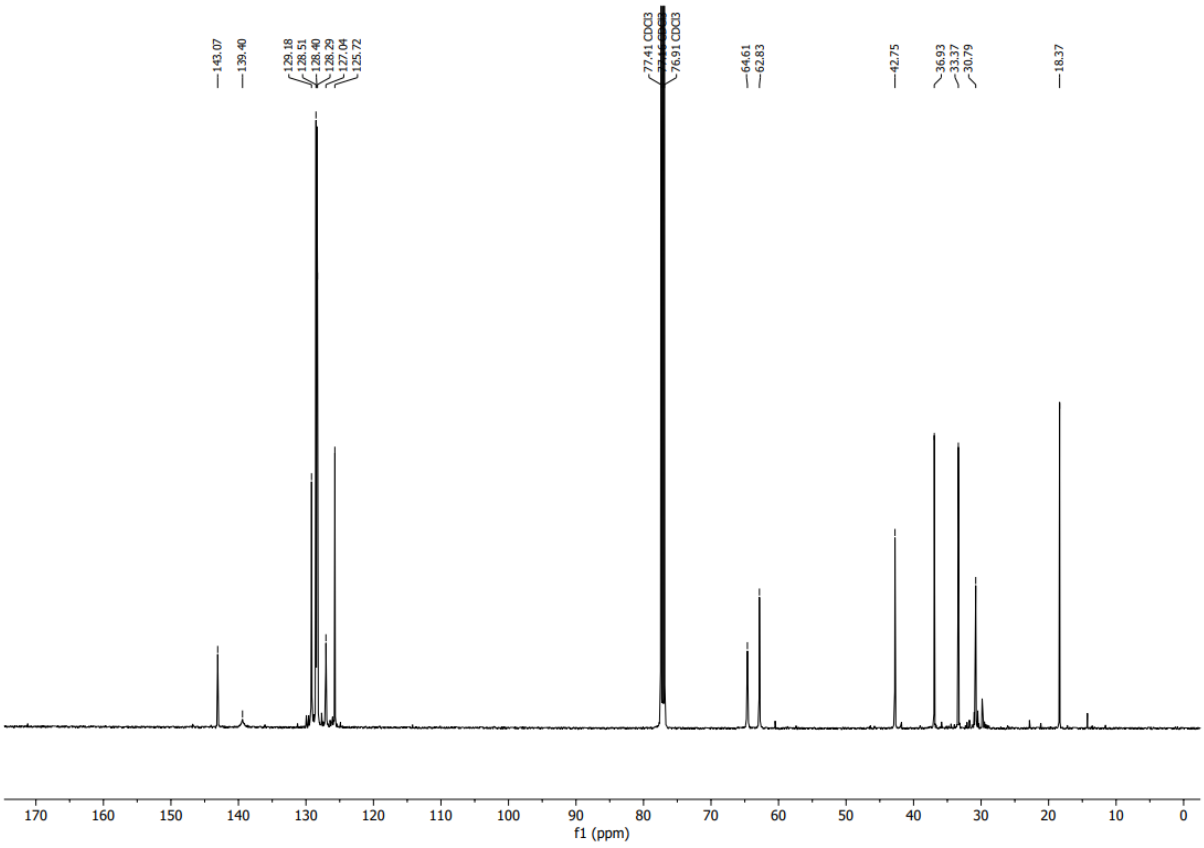


^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)

***N*-Benzyl-*N*,2-dimethyl-4-phenylbutan-1-amine (7a)**

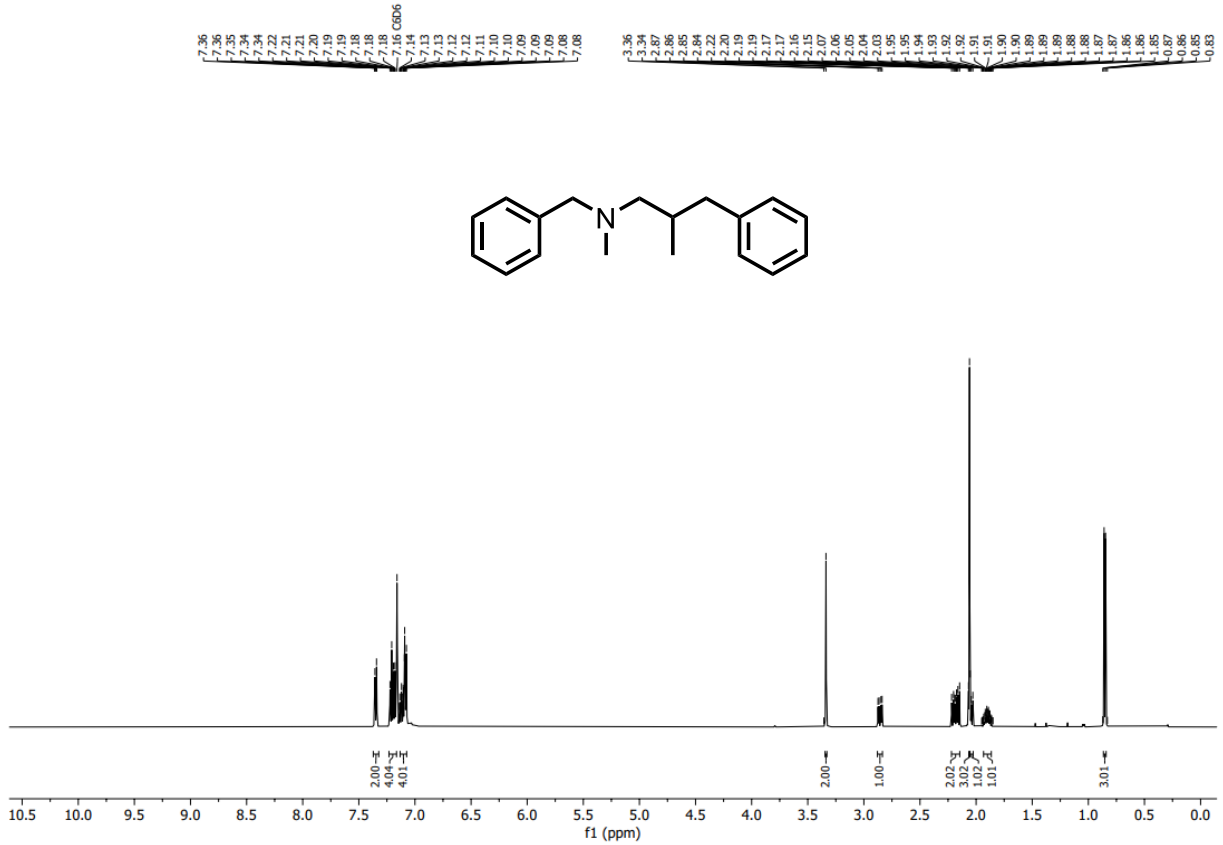


^{1}H NMR (500 MHz, $CDCl_3$)

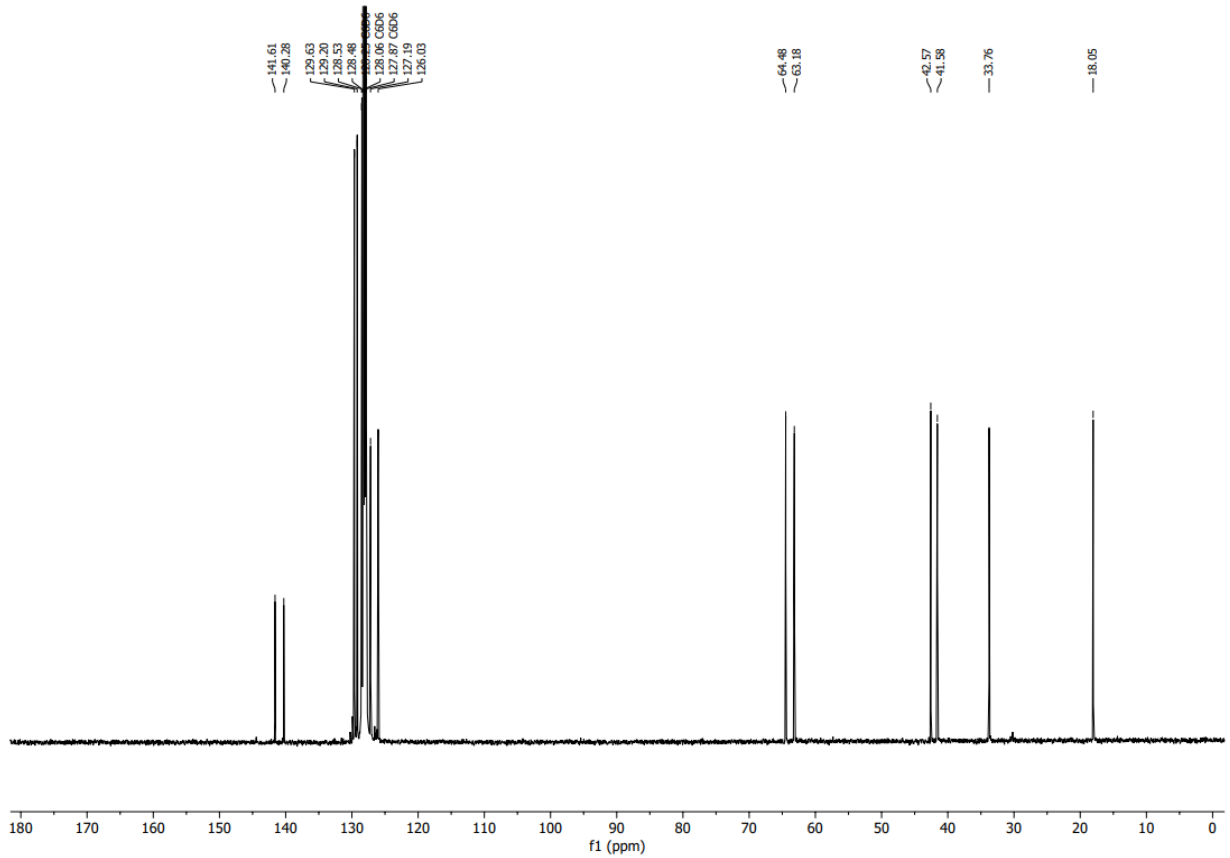


^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)

***N*-Benzyl-*N*,2-dimethyl-3-phenylpropan-1-amine (7b)**

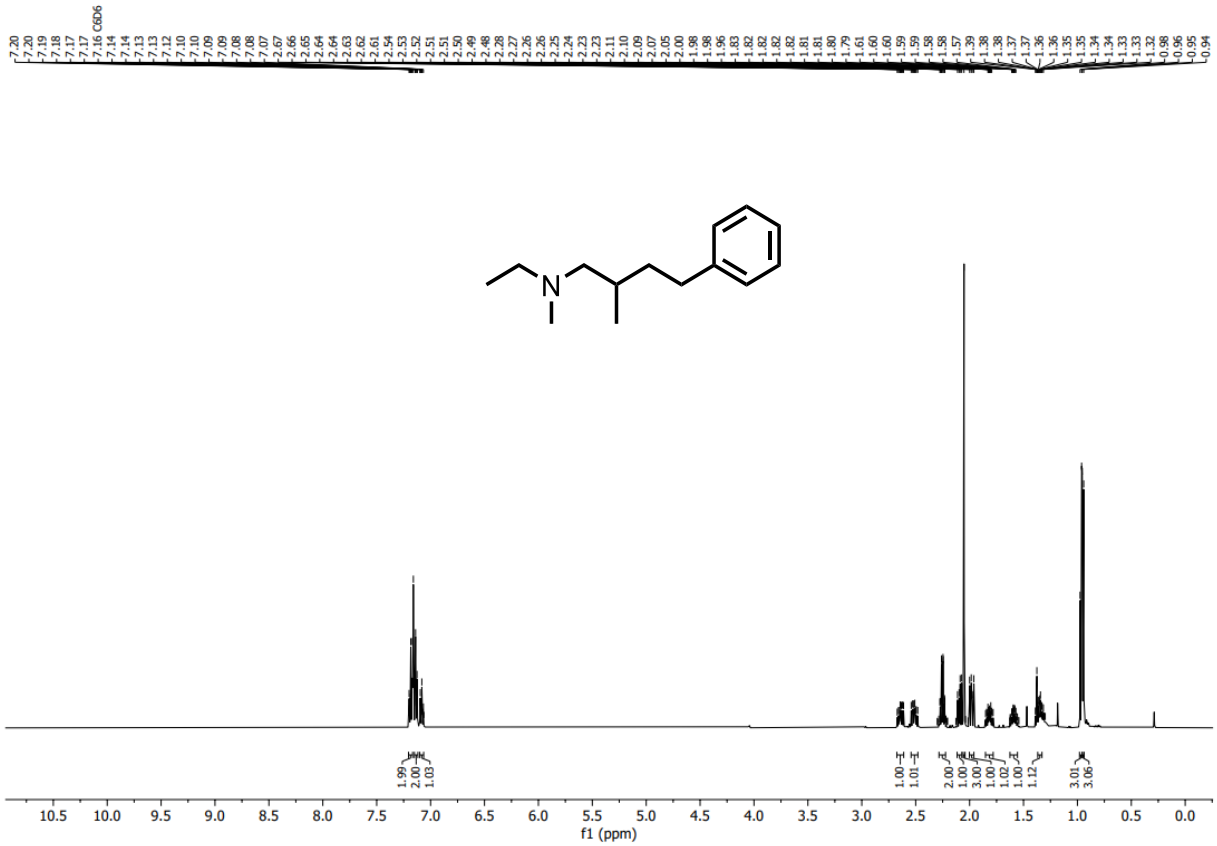


^{1}H NMR (500 MHz, C_6D_6)

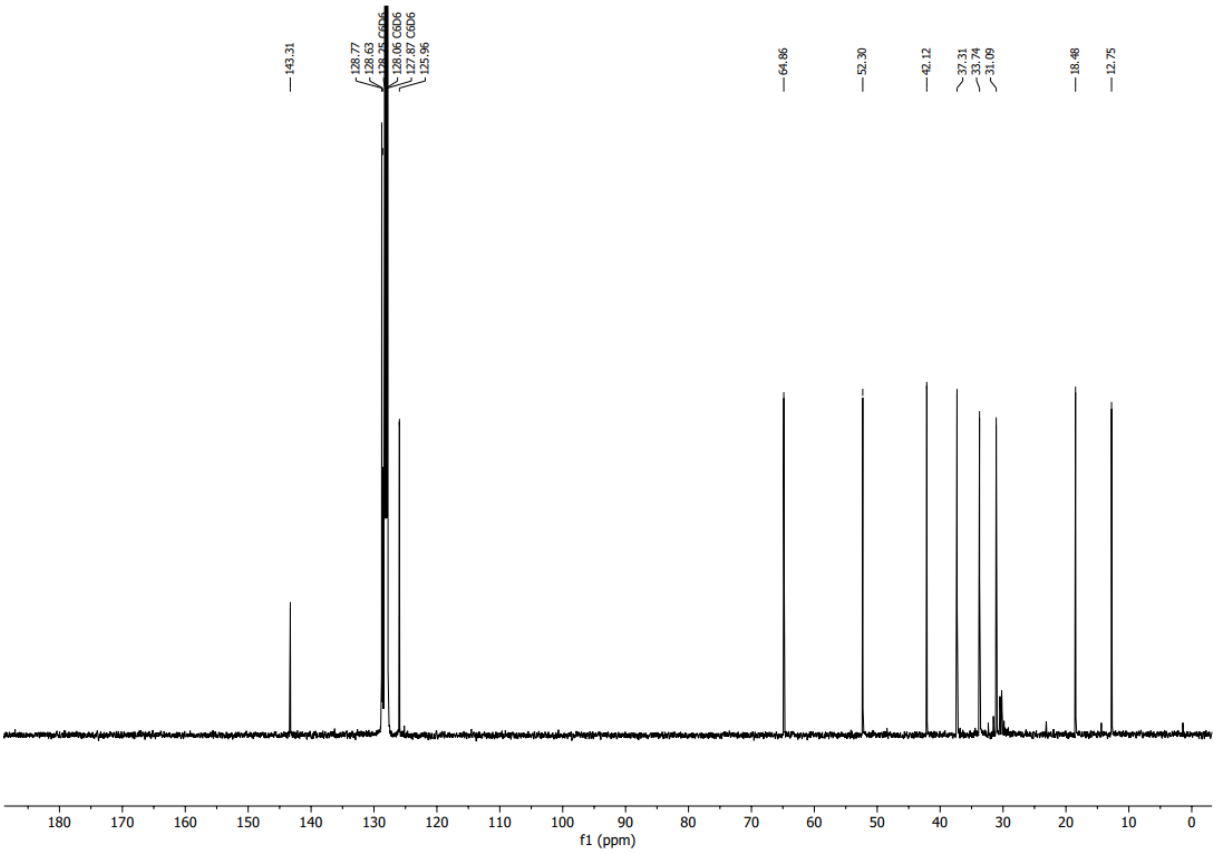


^{13}C{^{1}H} NMR (125 MHz, C_6D_6)

***N*-Ethyl-*N*,2-dimethyl-4-phenylbutan-1-amine (8a)**

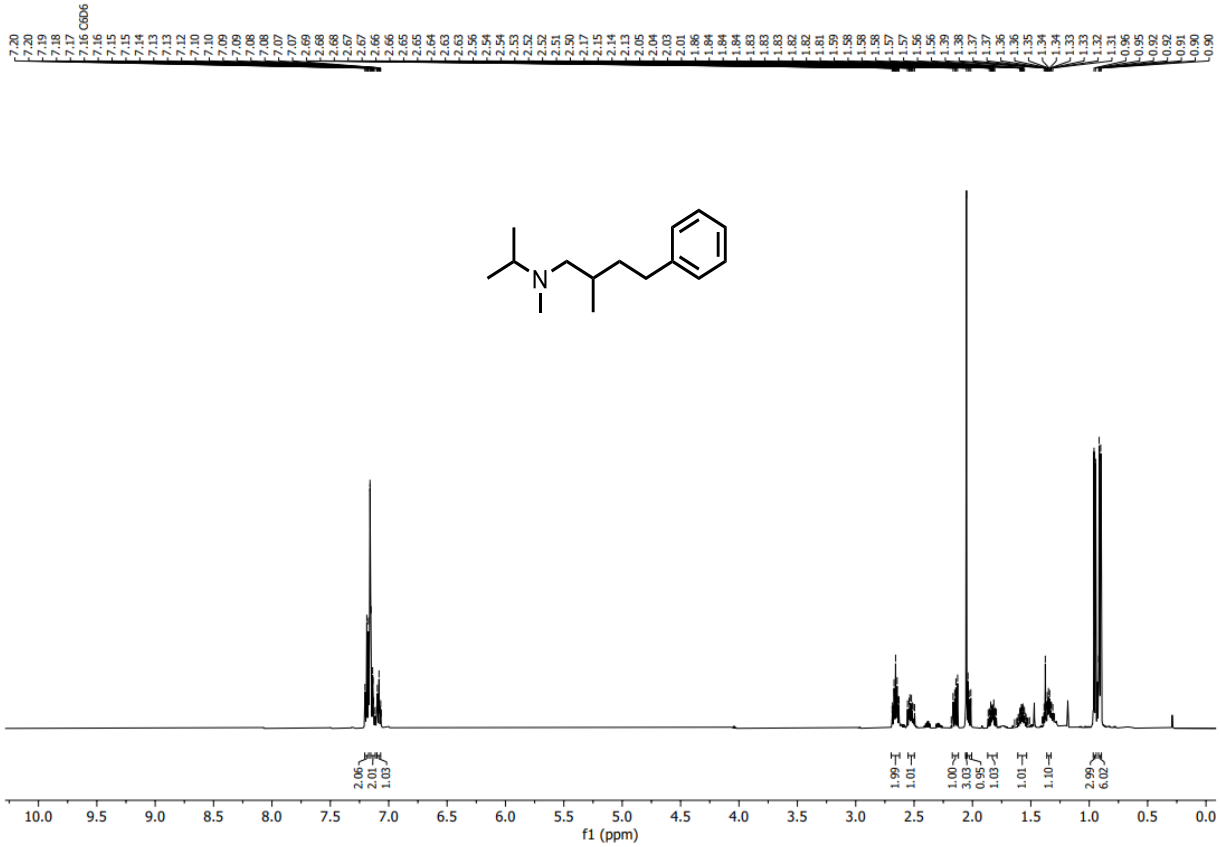


^{1}H NMR (500 MHz, C_6D_6)

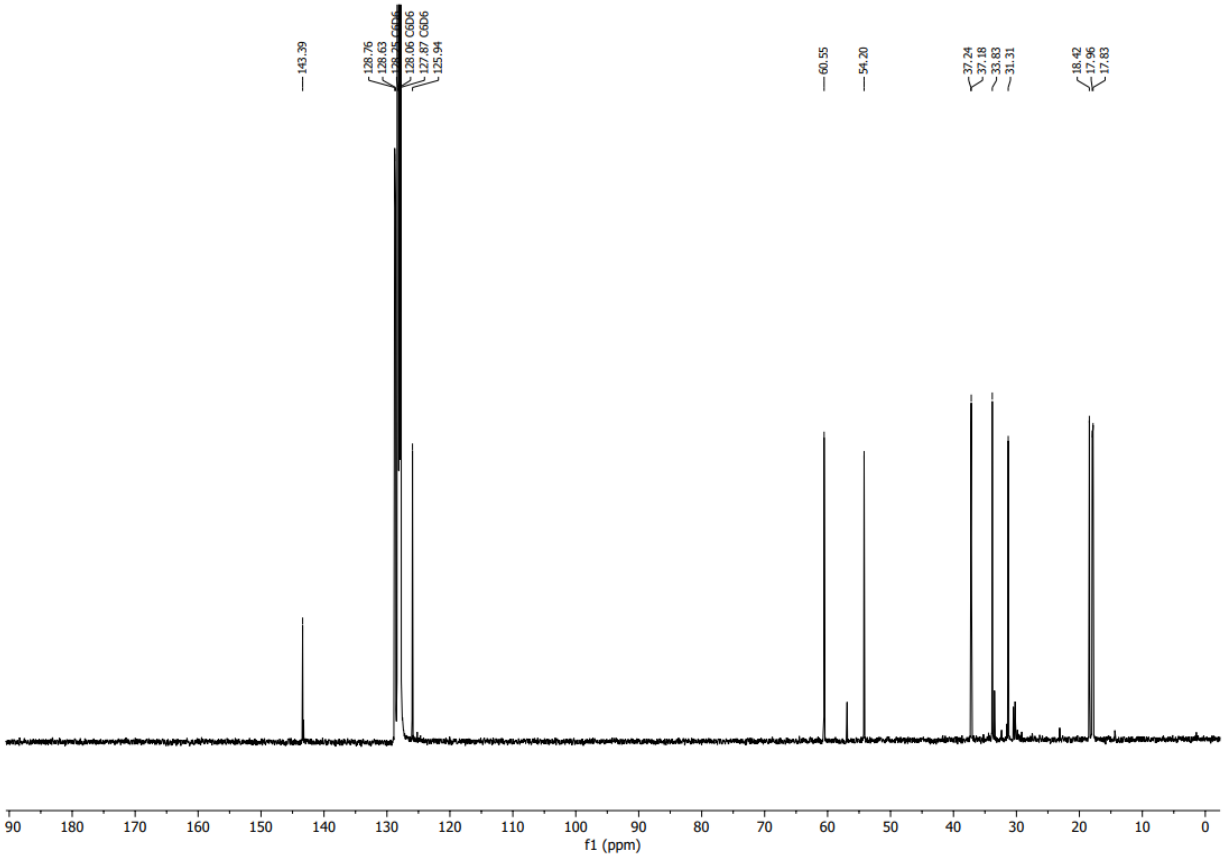


^{13}C{^{1}H} NMR (125 MHz, C_6D_6)

***N*-Isopropyl-*N*,2-dimethyl-4-phenylbutan-1-amine (9a)**

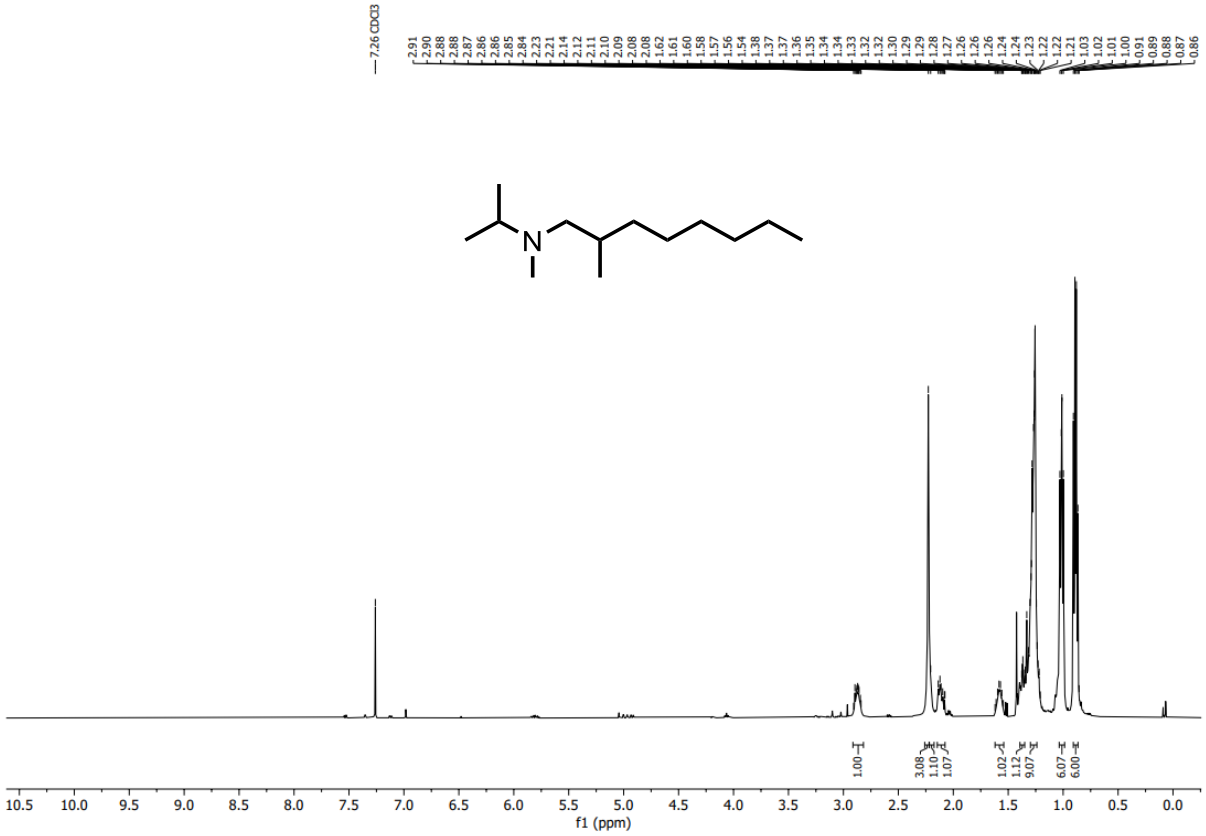


^{1}H NMR (500 MHz, C_6D_6)

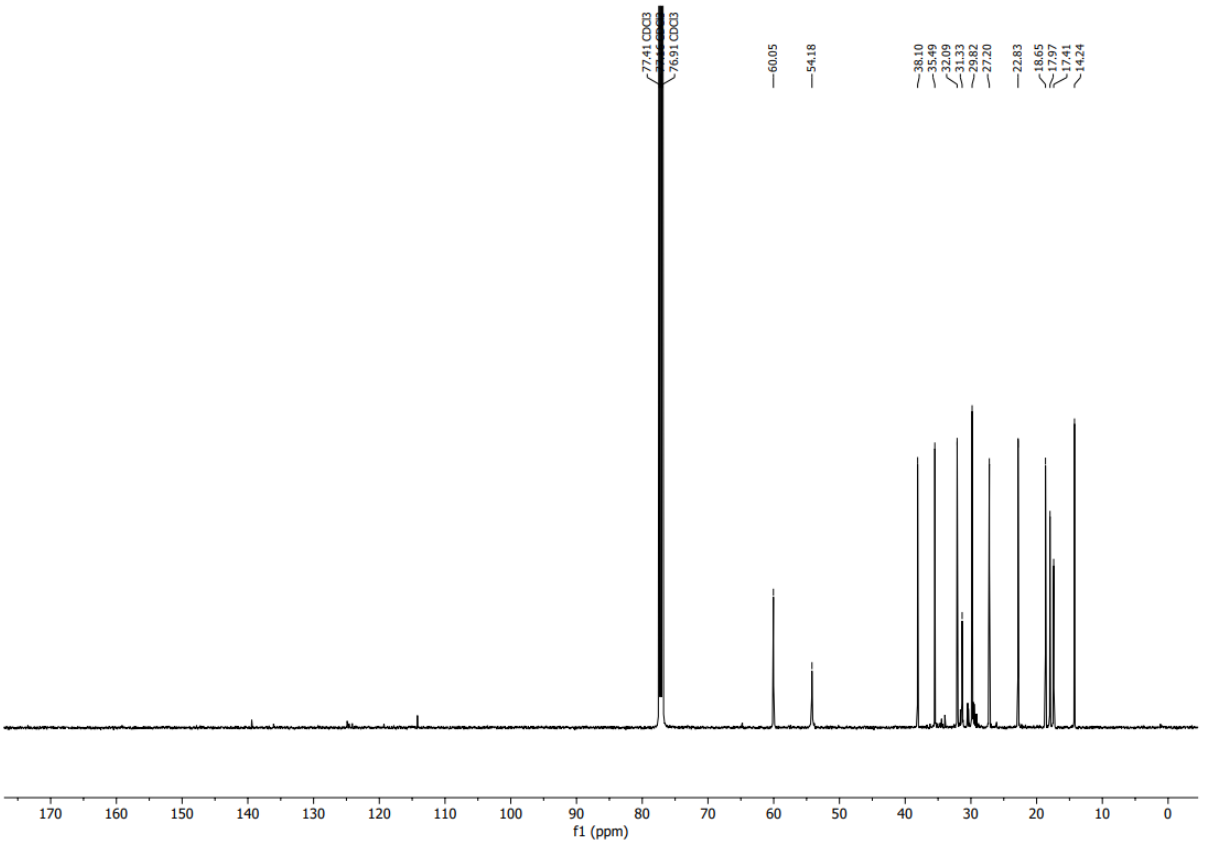


^{13}C{^{1}H} NMR (125 MHz, C_6D_6)

***N*-Isopropyl-*N*,2-dimethyloctan-1-amine (9b)**

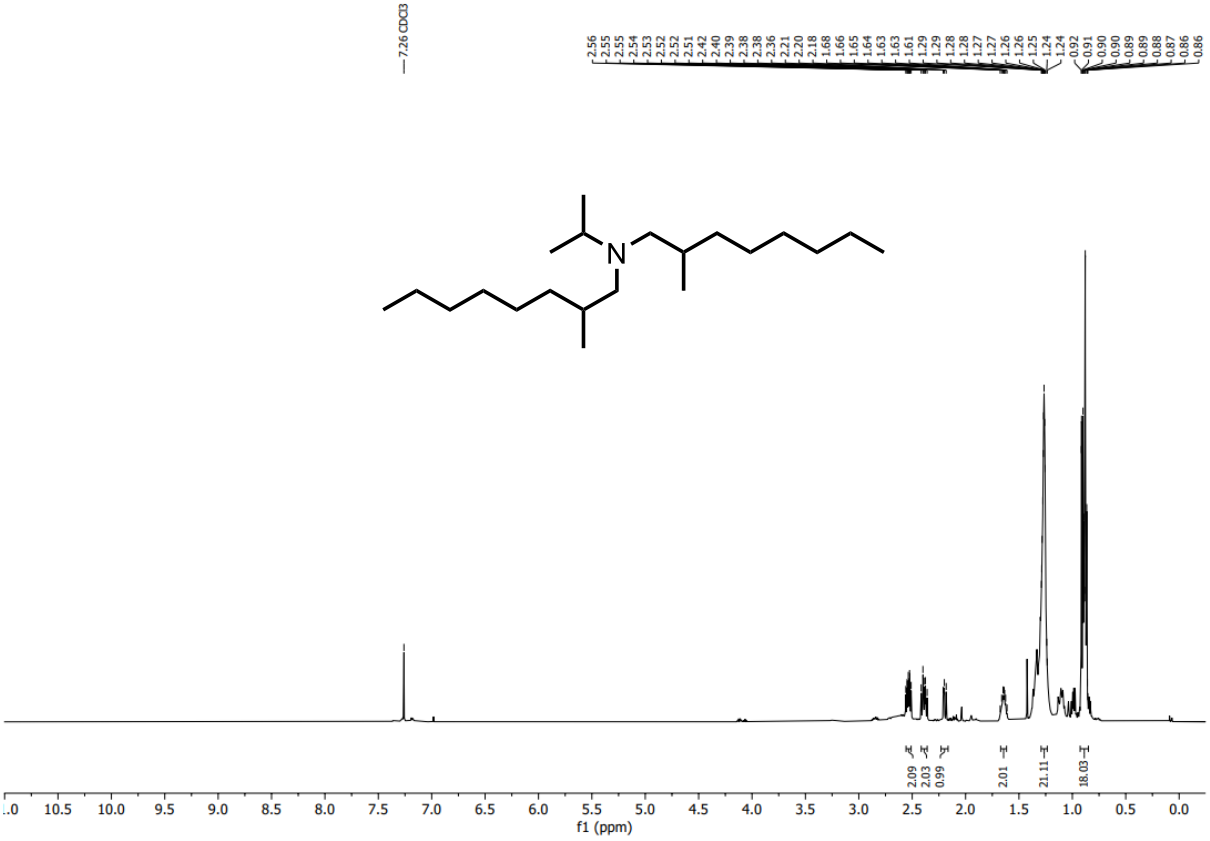


^{1}H NMR (500 MHz, $CDCl_3$)

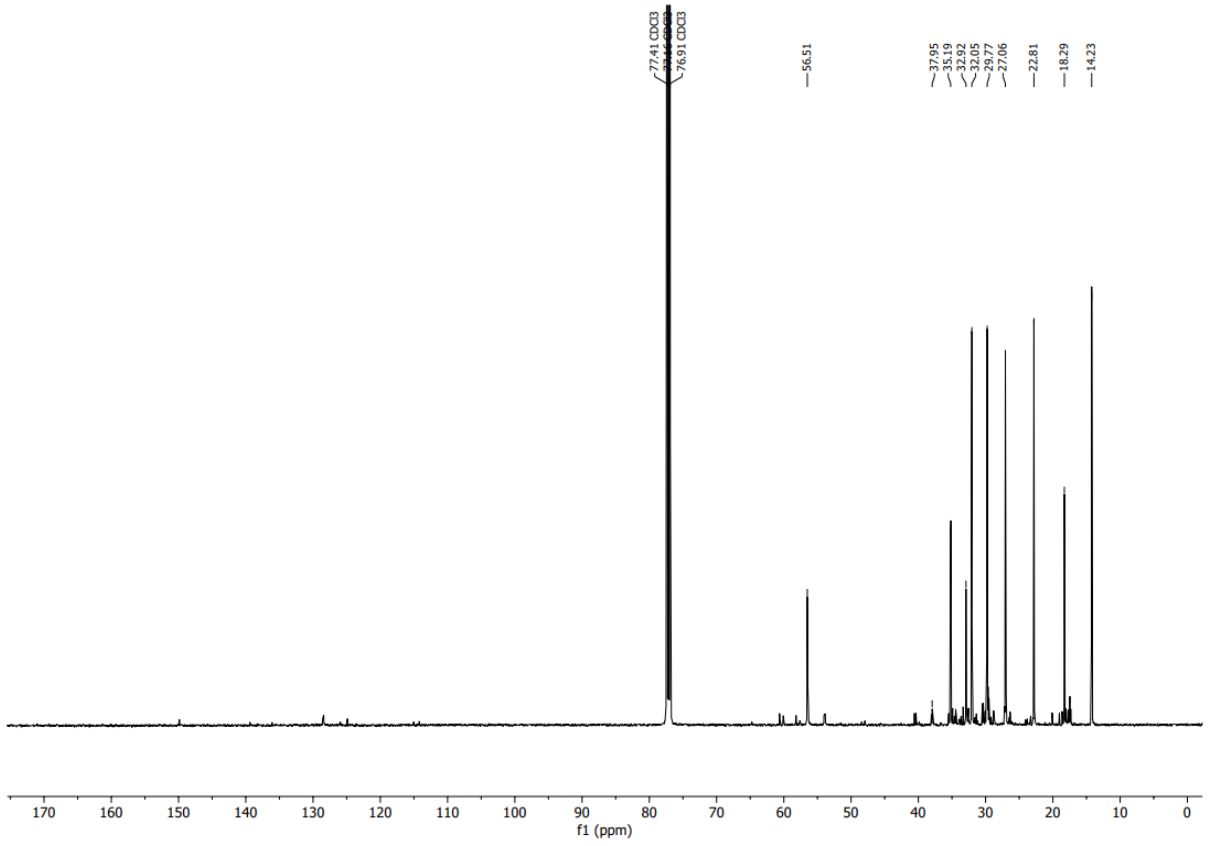


^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)

***N*-Isopropyl-2-methyl-*N*-(2-methyloctyl)octan-1-amine (10b)**

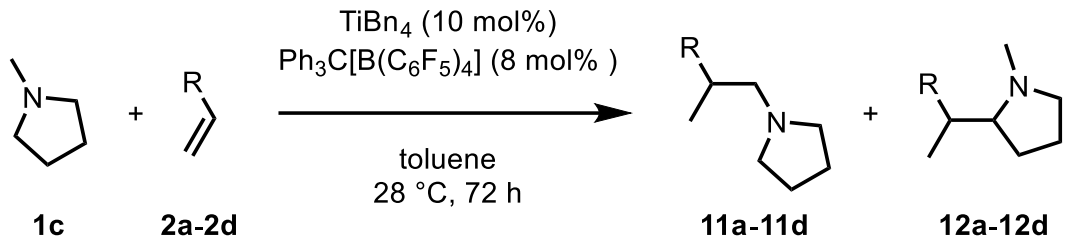


^{1}H NMR (500 MHz, $CDCl_3$)

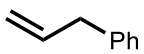
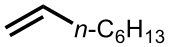
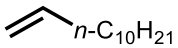


^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)

7. Investigations with *N*-Methylpyrrolidine (1c)

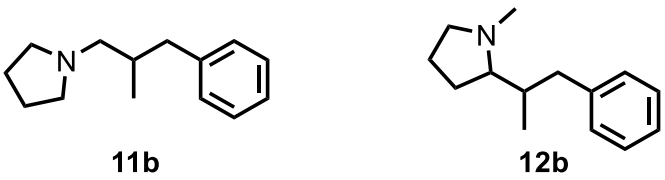


1c **2a-2d** **11a-11d** **12a-12d**

Entry[a]	Alken	Combined Yield [%][b] (**11**+**12**)	Yield **11** [%][b]	Sel. **11**/**12**[c]
1	 **2a**	– (**11a**+**12a**)	– (**11a**)	44:56
2	 **2b**	18 (**11b**+**12b**)	– (**11b**)	–[d]
3	 **2c**	29 (**11c**+**12c**)	8 (**11c**)	41:59
4	 **2d**	28 (**11d**+**12d**)	5 (**11d**)	42:58

[a] Reaction conditions: *N*-methylpyrrolidine (**1c**, 1.00 mmol), alkene (1.50 mmol), $TiBn_4$ (41 mg, 0.10 mmol, 10 mol%), $Ph_3C[B(C_6F_5)_4]$ (74 mg, 0.08 mmol, 8 mol%), toluene (5 mL), 28 °C, 72 °C, 25 mL vial. [b] Isolated yields. [c] Selectivity was determined by GC analysis prior to flash chromatography. [d] The products could not be separated by GC analysis.

***N*-(2-Methyl-3-phenylpropyl)pyrrolidine (11b) and 1-Methyl-2-(2-methyl-3-phenylpropyl)pyrrolidine (12b)**



11b **12b**

The general procedure was used to synthesize compounds **11b** and **12b** from *N*-methylpyrrolidine (**1c**) and allylbenzene (**2b**). After stirring for 72 h, the mixture was purified by flash chromatography (Hex/EtOAc/$HNEt_2$, 100:100:1) to give a mixture of **11b** and **12b** (36 mg, 0.18 mmol, 18 %) as a yellow oil.

R_f (SiO_2, Hex/EtOAc/$HNEt_2$, 100:100:1) = 0.31.

IR (neat): λ^{-1} = 3060, 3027, 2962, 2927, 1669, 1603, 1496, 1453, 1264, 1030, 911, 804, 731, 699 cm^{-1}.

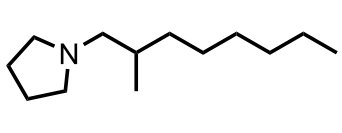
^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.30-7.26 (m, 4 H, Ar-C*H*), 7.22-7.15 (m, 6 H, Ar-C*H*), 3.28 (t, *J* = 8.2 Hz, 1 H, CH_2), 3.06 (dd, *J* = 13.2, 3.0 Hz, 1 H, CH_2), 2.87-2.77 (m, 4 H, CH_2), 2.63-2.53 (m, 2 H, CH_2), 2.49-2.44 (m, 1 H, CH_2), 2.47 (s, 3 H, CH_3), 2.40-2.27 (m, 2 H, C*H*, CH_2), 2.21-2.14 (m, 1 H, CH_2), 2.13-2.05 (m, 1 H, C*H*), 2.01 (ddt, *J* = 10.7, 7.2, 3.8 Hz, 1 H, C*H*), 1.97-1.90 (m, 4 H, CH_2), 1.89-1.70 (m, 5 H, CH_2), 129-13.4 (m 1 H, CH_2), 1.05 (d, *J* = 6.6 Hz, 3 H, CH_3), 0.88 (d, *J* = 6.8 Hz, 3 H, CH_3) ppm.

^{13}C {^{1}H} NMR (125 MHz, DEPT, $CDCl_3$): δ = 141.8 (C), 140.2 (C), 129.4 (CH), 129.3 (CH), 128.5 (CH), 128.3 (CH), 126.2 (CH), 125.8 (CH), 71.9 (CH), 62.6 (CH_2), 57.8 (CH_2), 54.6 (CH_2), 41.7 (CH_2), 41.2 (CH_3), 36.8 (CH_2), 36.4 (CH), 34.0 (CH), 26.0 (CH_2), 23.6 (CH_2), 22.4 (CH_2), 18.8 (CH_3), 17.2 (CH_3) ppm.

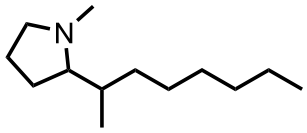
MS (EI, 70 eV): *m*/*z* (%) = 203 (2) $[M]^+$, 91 (21) $[C_7H_7]^+$, 84 (100) $[C_5H_{10}N]^+$.

HRMS (EI, 70 eV): calculated $C_{14}H_{21}N$: 203.1669, found: 203.1654.

***N*-(2-Methyloctyl)pyrrolidine (11c) and 2-(Octan-2-yl)-*N*-methylpyrrolidine (12c)**



11c



12c

The general procedure was used to synthesize compounds **11c** and **12c** from *N*-methyl-pyrrolidine (**1c**) and 1-octene (**2c**). After stirring for 72 h, the mixture was purified by flash chromatography (PE/Et_2O/$HNEt_2$, 150:50:1), to give **11c** (15 mg, 0.05 mmol, 8 %) as a colorless oil and a mixture of **11c** and **12c** (41 mg, 0.21 mmol, 21 %) as a slightly yellow oil.

***N*-(2-Methyloctyl)pyrrolidine (11c)**

GC: **11c**/**12c** = 41:59.

$\boldsymbol{R_f}$ (SiO_2, PE/Et_2O/DEA, 150:50:1) = 0.15.

IR (neat): λ^{-1} = 2956, 2925, 2856, 1674, 1457, 1379, 1262, 1020, 800, 724, 701 cm^{-1}.

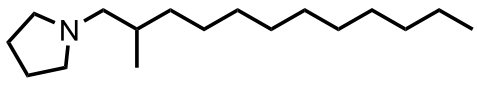
^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.72-2.58 (m, 4 H, CH_2), 2.44-2.35 (m, 2 H, CH_2), 1.89-1.82 (m, 4 H, CH_2), 1.72-1.63 (m, 1 H, C*H*), 1.47-1.39 (m, 1 H, CH_2), 1.30-1.24 (m, 9 H, CH_2), 0.97 (d, *J* = 6.6 Hz, 3 H, CH_3), 0.88 (t, *J* = 6.9 Hz, 3 H, CH_3) ppm.

^{13}C {^{1}H} NMR (125 MHz, DEPT, $CDCl_3$): δ = 63.9 (CH_2), 54.7 (CH_2), 35.5 (CH_2), 32.3 (CH), 32.1 (CH_2), 29.7 (CH_2), 27.0 (CH_2), 23.6 (CH_2), 22.8 (CH_2), 18.7 (CH_3), 14.3 (CH_3) ppm.

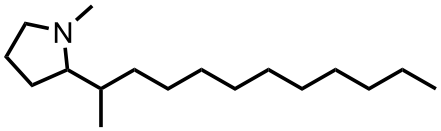
MS (EI, 70 eV): *m*/*z* (%) = 197 (10) $[M]^+$, 84 (100) $[C_5H_{10}N]^+$.

HRMS (EI, 70 eV): calculated $C_{13}H_{27}N$: 197.2138, found: 197.2140.

1-(2-Methyldodecyl)pyrrolidine (11d) and 2-(Dodecan-2-yl)-1-methyl-pyrrolidine (12d)



11d



12d

The general procedure was used to synthesize compounds **11d** and **12d** from *N*-methylpyrrolidine (**1c**) and 1-dodecene (**2d**). After stirring for 72 h, the mixture was purified by flash chromatography (PE/Et_2O/$HNEt_2$, 150:50:1) to give **11d** (12 mg, 0.05 mmol, 5 %) as a colorless oil and a mixture of **11d** and **12d** (55 mg, 0.23 mmol, 23 %) as a slightly yellow oil.

***N*-(2-methyldecyl)pyrrolidine (11d)**

GC: **11d**/**12d** = 42:58.

$\boldsymbol{R_f}$ (SiO_2, PE/Et_2O/DEA, 150:50:1) = 0.23.

IR (neat): λ^{-1} = 2956, 2923, 2853, 2784, 1457, 1379, 1264, 1232, 1159, 1082, 965, 736, 703 cm^{-1}.

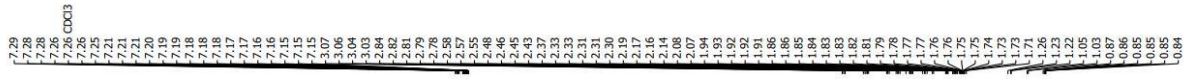
^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.65-2.53 (m, 4 H, CH_2), 2.39-2.28 (m, 2 H, CH_2), 1.87-1.79 (m, 4 H, CH_2), 1.70-1.59 (m, 1 H, C*H*), 1.32-1.21 (m, 17 H, CH_2), 1.12-1.04 (m, 1 H, CH_2), 0.95 (d, *J* = 6.6 Hz, 3 H, CH_3), 0.88 (t, *J* = 6.9 Hz, 3 H, CH_3) ppm.

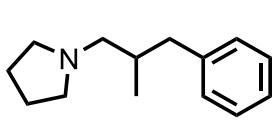
$^{13}C\ \{^{1}H\}$ NMR (125 MHz, DEPT, $CDCl_3$): δ = 64.0 (CH_2), 54.7 (CH_2), 35.5 (CH_2), 32.3 (CH), 32.1 (CH_2), 30.1 (CH_2), 29.9 (CH_2), 29.8 (CH_2), 29.8 (CH_2), 29.5 (CH_2), 27.2 (CH_2), 23.6 (CH_2), 22.8 (CH_2), 18.7 (CH_3), 14.2 (CH_3) ppm.

MS (ESI^+, TOF): *m*/*z* (%) = 254 (100) $[M+H]^+$.

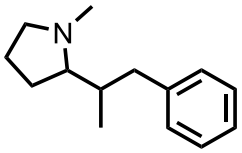
HRMS (ESI^+, TOF): calculated $C_{17}H_{36}N$: 254.2848, found: 254.2838.

***N*-(2-Methyl-3-phenylpropyl)pyrrolidine (11b) and 1-Methyl-2-(2-methyl-3-phenylpropyl)pyrrolidine (12b)**

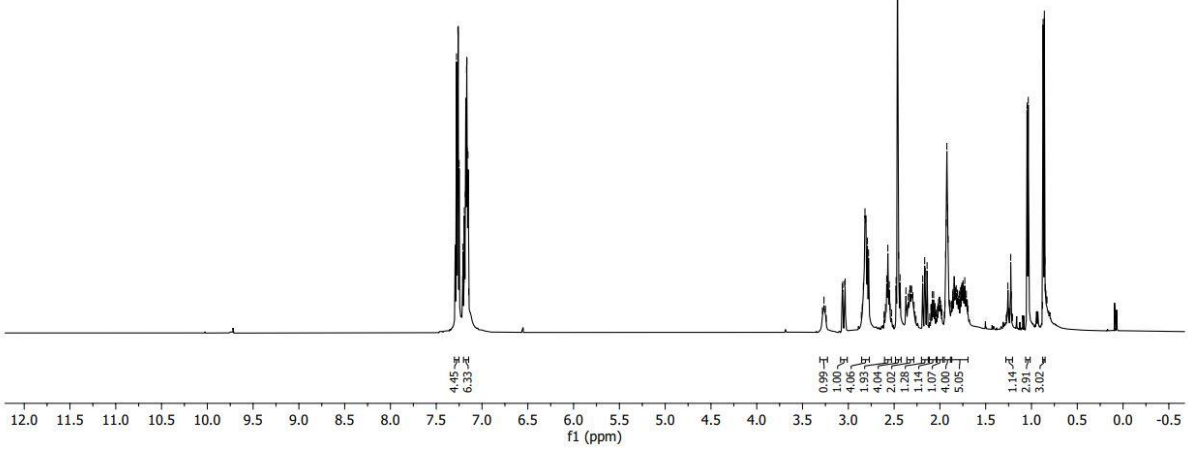




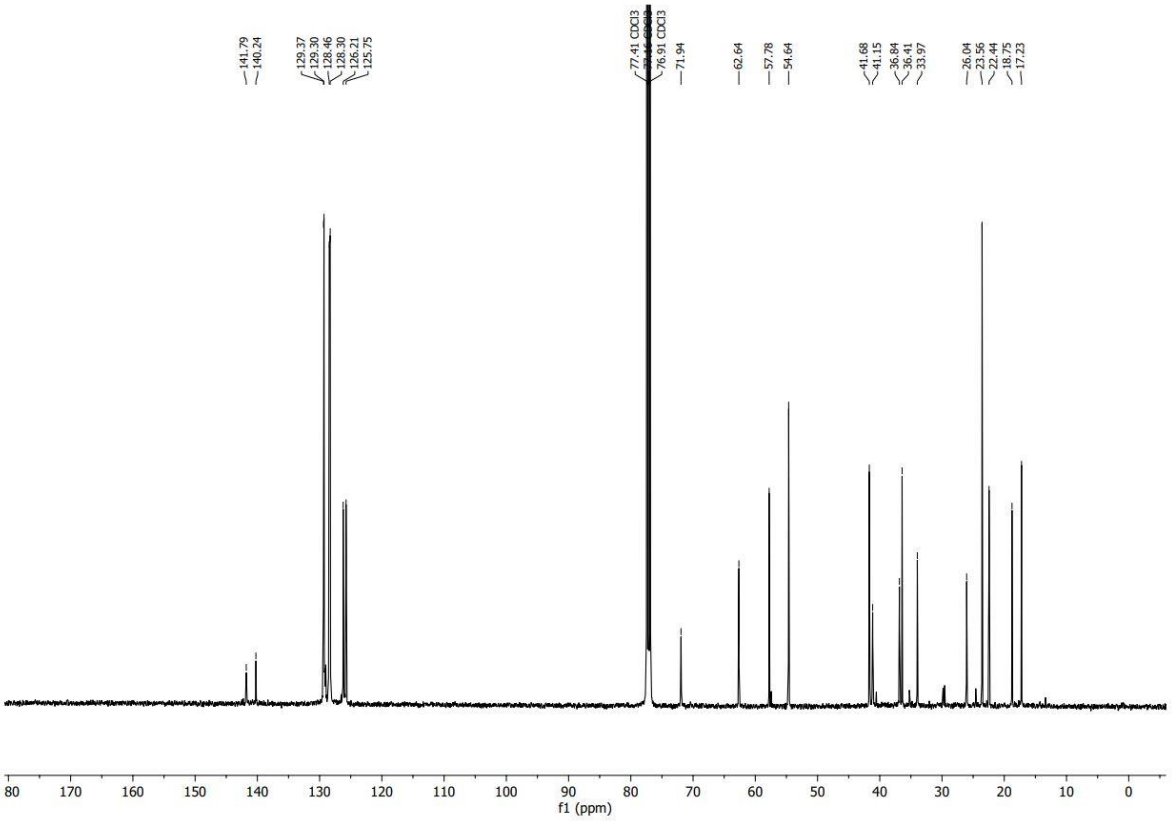
11b



12b

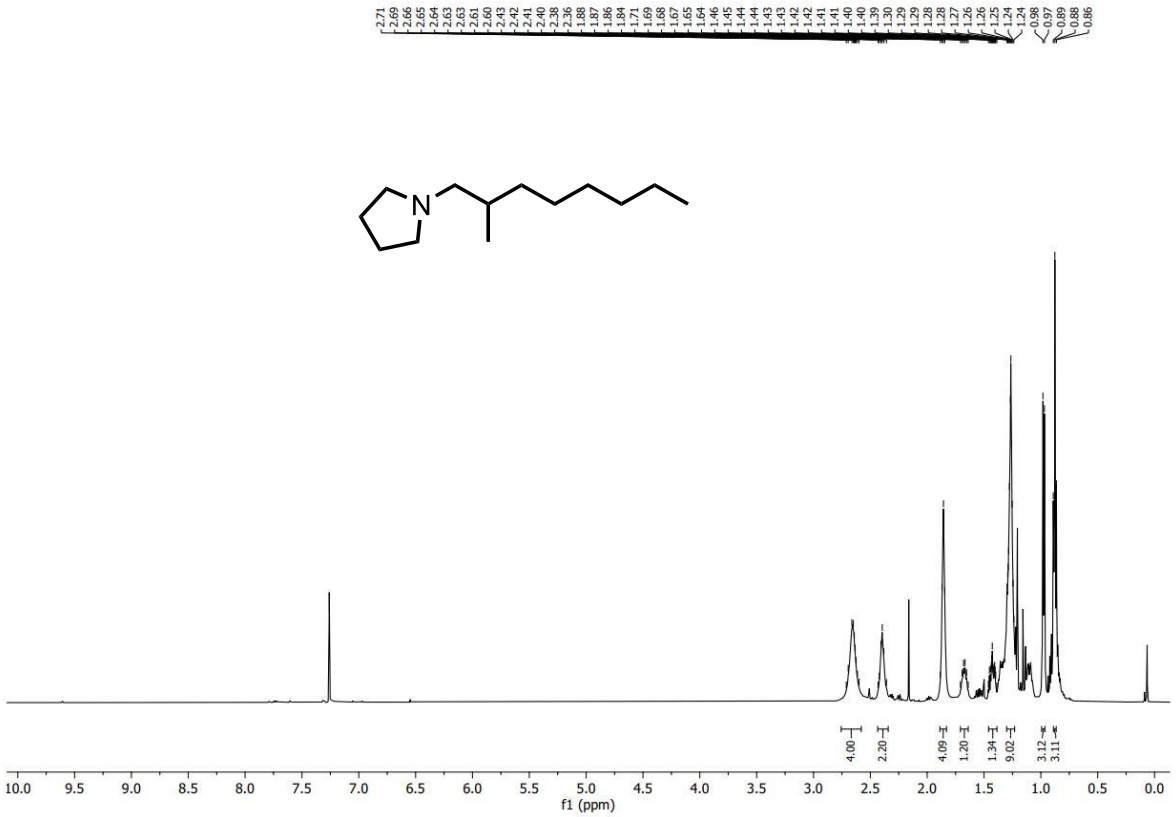


^{1}H NMR (500 MHz, $CDCl_3$)

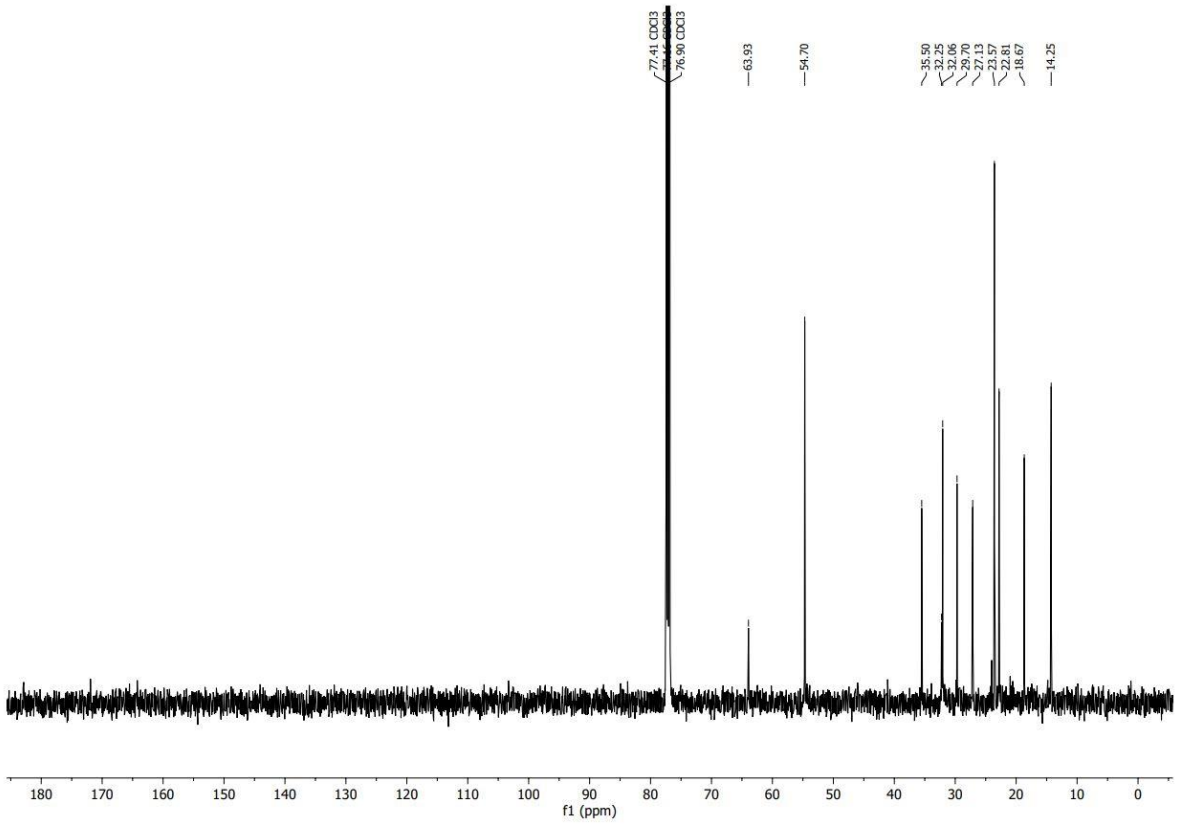


^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)

***N*-(2-Methyloctyl)pyrrolidine (11c)**

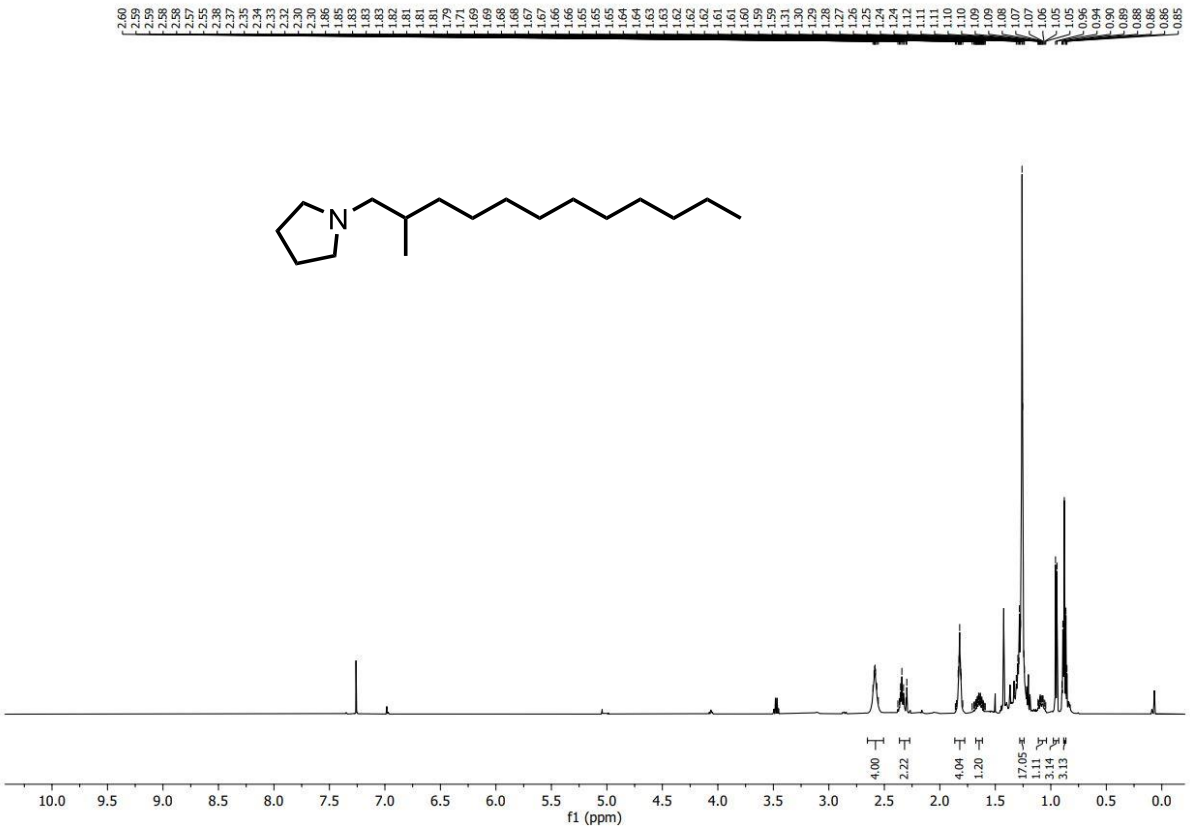


^{1}H NMR (500 MHz, $CDCl_3$)

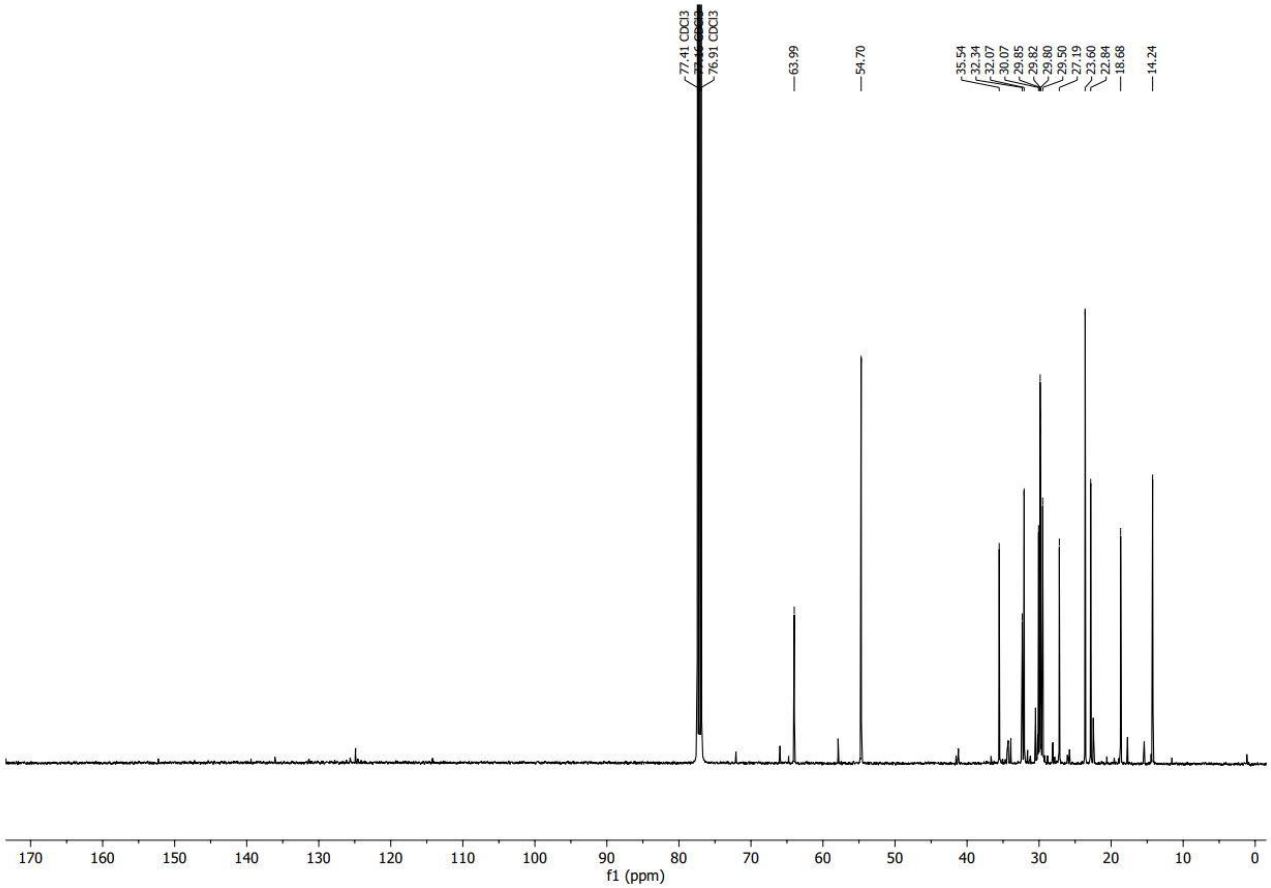


^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)

1-(2-Methyldodecyl)pyrrolidine (11d)



^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)

8. Crystallographic Data

Single crystal X-ray data for **5b·HCl** were measured on a Bruker AXS D8 Venture diffractometer (multilayer optics, Cu-Kα radiation with λ = 1.54178 Å, Kappa 4-circle goniometer, Photon III C14 CPAD detector). An empirical absorption corrections using equivalent reflections was performed with the program SADABS.[4] The structure was solved with the program SHELXS[5] and refined with SHELXL[6] using the OLEX2[7] GUI. All non H atoms were refined using anisotropic atomic displacement parameters, H atoms bonded to C were located in the difference Fourier map and placed on idealized geometric positions with idealized atomic displacement parameters using the riding model, the H atom bonded to N was refined freely.

The crystallographic data can be obtained free of charge from https://www.ccdc.cam.ac.uk/structures/ quoting the CCDC number 2049498.

Crystal structure data for compound **5b • HCl**

Empirical formula	$C_{28}H_{36}ClNSi$	
Formula weight	450.12	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystall system	Monoclinic	
Space group	P 2_1/c	
Unit cell dimensions	a = 20.8665(16) Å	α = 90 °
	b = 10.2195(8) Å	β = 91.799(6) °
	c = 11.9429(9) Å	γ = 90 °
Volume	2545.5(3) $Å^3$	
Z	4	
Density (calculated)	1.175 mg/m^3	
Absorption coefficient	1.874 mm^{-1}	
F(000)	968	
Crystal size	0.100 x 0.020 x 0.010 mm^3	
Theta range for data collection	4.239 bis 66.589 °	
Index ranges	-24<=h<=24, -12<=k<=9, -14<=l<=14	
Index ranges	26086	
Reflections collected	4494 (R(int) = 0.1199)	
Independent reflections	3051	
„Completeness to theta“ = 66.589 °	99.8 %	
Absorptions corrections	Semi-empirical from equivalents	
Max. and min. Transmission	1.0000 and 0.8350	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4494 / 0 / 286	

„Goodness-of-fit“ on F^2	1.005
Final R indices (I>2sigma(I))	R_1 = 0.0477, ωR_2 = 0.1053
R indices (sämtliche Daten)	R_1 = 0.0828, ωR_2 = 0.1205
Extinction coefficient	n/a
Largest Diff. „peak and hole“	0.254 and -0.317 e.$Å^{-3}$

9. References

[1] L. Fitjer, U. Quabeck, *Synth*. *Commun*. **1985**, *10*, 855-864:

[2] J. Bielefeld, S. Doye, *Angew*. *Chem*. **2020**, *132*, 6194-6199; *Angew*. *Chem*. *Int*. *Ed*. **2020**, *59*, 6138-6143.

[3] M. Večeřa J. Gasparič, *Detection and Identification of Organic Compounds*, Springer, Boston, MA, **1971**, pp 317-353.

[4] L. Krause, R. Herbst-Irmer, G.M. Sheldrick, D. Stalke, *J. Appl. Cryst.* **2015**, *48*, 3-10.

[5] G.M. Sheldrick, *Acta Cryst.* **2008**, *A64*, 112-122.

[6] G.M. Sheldrick, *Acta Cryst.* **2015**, *C71*, 3-8.

[7] O.V. Dolomanov, L.J. Bourhis, R.J. Gildea, J.A.K. Howard, H. Puschmann, *J. Appl. Cryst.* **2009**, *42*, 339-341.