Synthesis of Heteroatom-Containing Pyrrolidine Derivatives Based on Ti(O-*i*Pr)$_4$ and EtMgBr-Catalyzed Carbocyclization of Allylpropargyl Amines with Et_2Zn

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Supporting information

Reagents and methods

The reagents were obtained from Sigma-Aldrich or Acros. Hexane and dichloromethane were distilled over P_2O_5. Diethyl ether, tetrahydrofuran, 1,4-dioxane, toluene, benzene and anisole were dried over sodium. Dried 1,2-dimethoxyethane was obtained from Sigma-Aldrich. 2-Alkynylamines **1a-i** and **6,8** were prepared by aminomethylation of terminal alkynes with aqueous formaldehyde and secondary *N*-aryl-substituted allyl amines under CuBr catalysis [1]. Nitrogen-containing 1,6-enynes with terminal propargyl and allyl groups were prepared by alkylation of *N*-aryl-substituted allyl amines with propargyl bromide under NaH [2]. Allyl substituted but-2-yne-1,4-diamines **10** were prepared by aminomethylation of nitrogen-containing 1,6-enynes (with terminal propargyl and allyl groups) by bisamine [3]. Acetylenic ethers **13** were prepared by aminomethylation of ethers of acetylenic alcohols with aqueous formaldehyde and secondary *N*-aryl- substituted allyl amines under CuBr catalysis [1]. Nuclear magnetic resonance spectroscopy was performed on a Brucker Avance 500. The ^{1}H NMR spectra were recorded at 500 MHz and ^{13}C-{^{1}H} NMR spectra at 100 MHz in $CDCl_3$. The chemical shifts are reported in ppm relative to tetramethylsilane (TMS) as the internal

standard. The numbering of atoms in the ^{13}C-{^{1}H} and ^{1}H NMR spectra of the compounds **3a-g**, **3i**, **4h**,**f 5a**, **5h**, **7**, **9**, **11a-c**, **12a**, **14** is shown in Figures 1,2,3. Elemental analysis was performed using a Carlo-Erba CHN 1106 elemental analyser. Mass spectra were obtained on a Finnigan 4021 instrument. The yields were calculated from the isolated amount of pyrrolidine and pyrrolidone derivatives obtained from starting nitrogen-containing 1,6-enynes.

Preparation of 3-methyl-4-methylenepyrrolidines 3a-g, 3i, 4h,f and 5a,h via Ti-Mg-catalyzed carbozincation of *N*-allyl substituted propargylamines with Et_2Zn in CH_2Cl_2.

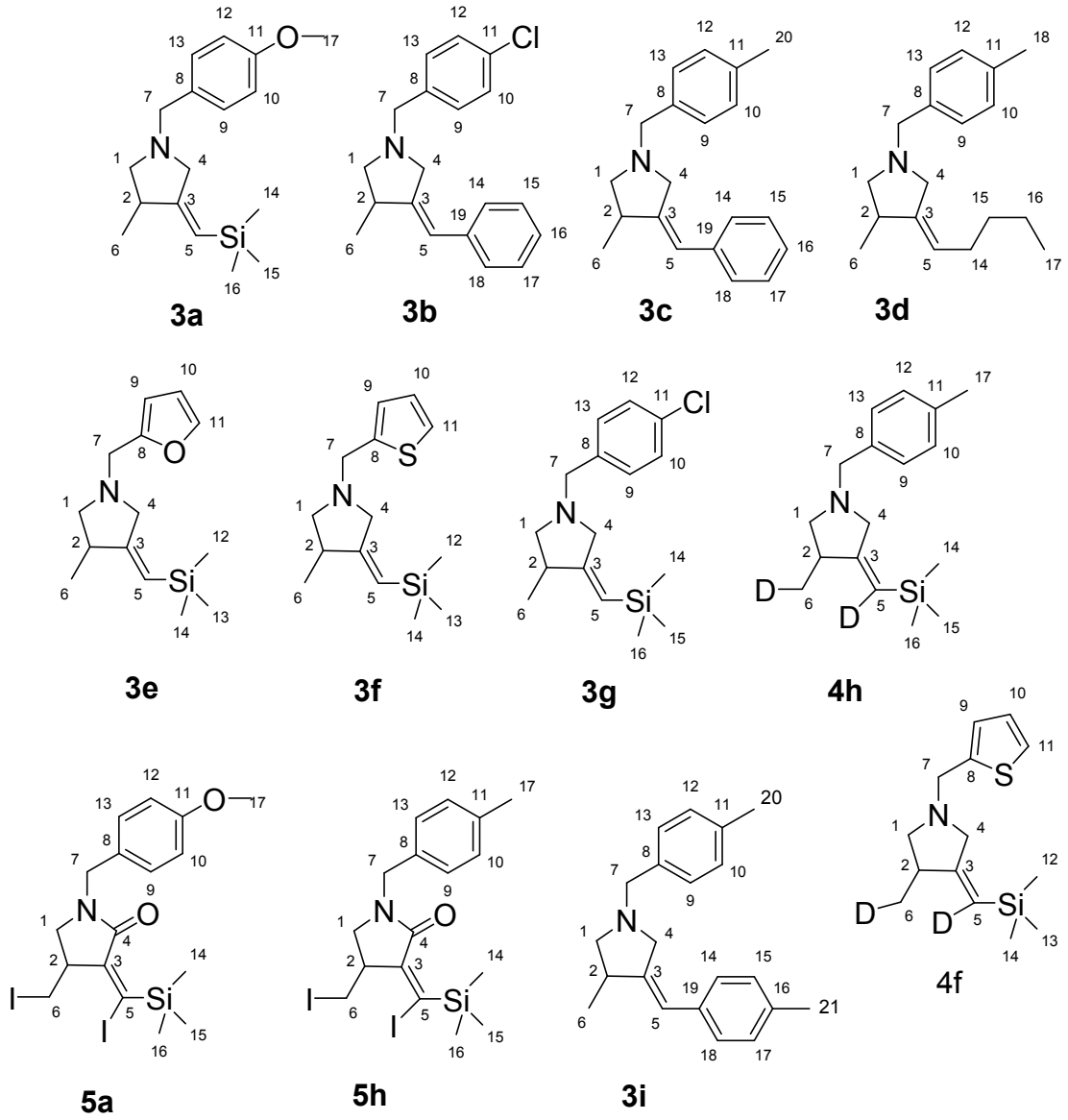


Figure 1 The numbering of atoms in the ^{13}C- and ^{1}H-NMR spectra of the compounds **3a-g**, **3i**, **4h,f and 5a**,**h.**

(*Z*)-1-(4-methoxybenzyl)-3-methyl-4-((trimethylsilyl)methylene)pyrrolidine; Typical Procedure.

To a solution of *N*-(4-methoxybenzyl)-*N*-(3-(trimethylsilyl)prop-2-yn-1-yl)prop-2-en-1-amine (574 mg, 2 mmol) and Et_2Zn (1 M in hexanes, 5 mL, 5 mmol) in CH_2Cl_2 (6 mL) was added Ti(O-*i*Pr)$_4$ (0.5 M in hexanes, 0.6 mL, 0.3 mmol). Ethylmagnesiurn bromide (2.5 M in Et_2O, 0.16 mL, 0.4 mmol) was then added and the reaction mixture rapidly turned black. After 18 h at 23 ^oC, the reaction mixture was diluted with Et_2O (5 mL), and 25 wt% KOH solution (3 mL) was added dropwise while the reaction flask was cooled in an ice bath. The aqueous layer was extracted with diethyl ether (3×5 mL). The combined organic layers were washed with brine (10 mL), dried over anhydrous $CaCl_2$. The reaction mixture was filtered through a filter paper and concentrated in vacuo to give crude product as a yellow oil. Evaporation of solvent and purification of the residue by column chromatography (diethyl ether : isopropyl alcohol : hexane = 1 : 1 :8) gave **3a** (509 mg, 88 %) as colorless oil. R_f 0.70.

^{1}H NMR (500MHz, $CDCl_3$): δ = 0.09 (s, 9H, C(14, 15,16)H$_3$), 1.09 (d, *J* = 7 Hz, 3H, C(6)H$_3$), 1.99 (t, *J* = 8 Hz, 1H(A), C(1)H$_2$), 2.68 (q, *J* = 7 Hz, 1H, C(2)H), 2.98 (t, *J* = 8 Hz, 1H(B), C(1)H$_2$), 3.03 (dt, *J* = 14 Hz, *J* = 2 Hz, 2H, C(4)H$_2$), 3.56 (d, *J* = 12Hz, 1H(A), C(7)H$_2$), 3.63 (d, *J* = 12Hz, 1H(B), C(7)H$_2$), 3.82 (s, 3H, C(17)H$_3$), 5.31 (q, *J* = 2 Hz, 1H, C(5)H), 6.89 (d, *J* = 8 Hz, 2H, C(10, 12)H), 7.28 (d, *J* = 8 Hz, 2H, C(9, 13)H).

^{13}C-{^{1}H} NMR (500MHz, $CDCl_3$): δ = -0.40 (C(14, 15, 16)), 17.34 (C(6)), 40.28 (C(2)), 55.22 (C(17)), 59.32 (C(4)), 60.12 (C(7)), 61.15 (C(1)), 113.63 (C(10, 12)), 116,74 (C(5)), 130.04 (C(9, 13)), 131.66 (C(8)), 158.68 (C(11)), 162.68 (C(3)).

MS (EI): m/z, % = 289 (1) [M^+], 287 (11), 214 (11), 166 (8), 121 (100).

Anal. calcd for $C_{17}H_{27}NOSi$, (%): C, 70.53; H, 9.40; N, 4.84. Found, %: C, 70.76; H, 9.57; N, 5.07.

***(Z)*-3-benzylidene-1-(4-chlorobenzyl)-4-methylpyrrolidine (3b)**

Using the procedure described above *N*-(4-chlorobenzyl)-*N*-(3-phenylprop-2-yn-1-yl)prop-2-en-1-amine (592 mg, 2 mmol) gave crude product that was purified by column chromatography (diethyl ether : isopropyl alcohol : hexane = 1 : 1 :8) to afford **3b** (471 mg, 79%) as colorless oil. R_f 0.59.

^{1}H NMR (500MHz, $CDCl_3$): δ = 1.30 (t, *J* = 6 Hz, 3H, C(6)H$_3$), 2.19 (m, 1H(A), C(1)H$_2$), 2.97 (s, 1H, C(2)H), 3.05 (m, 1H(B), C(1)H$_2$), 3.40 (d, *J* = 14 Hz, 1H(A), C(4)H$_2$), 3.70 (s, 2H, C(7)H$_2$), 3.82 (d, *J* = 14 Hz, 1H(B), C(4)H$_2$), 6.32 (s, 1H, C(5)H), 7.25 (m, 1H, C(16)H), 7.26 (m, 2H, C(14, 18)H), 7.36 (m, 2H, C(9, 13)H), 7.38 (m, 2H, C(10, 12)H), 7.40 (m, 2H, C(15, 17)H).

^{13}C-{^{1}H} NMR (500MHz, $CDCl_3$): δ = 18.10 (C(6)), 39.20 (C(2)), 58.43 (C(4)), 59.93 (C(7)), 61.23 (C(1)), 120.69 (C(5)), 126.27 (C(16)), 127.97 (C(14, 18)),

128.45 (C(15, 17)), 128.54 (C(10, 12)), 130.12 (C(9, 13)), 132.79 (C(11)), 137.40 (C(8)), 138.05 (C(19)), 146.98 (C(3)).

Anal. calcd for $C_{19}H_{20}ClN$, (%): C, 76.62; H, 6.77; N, 4.70. Found, %: C, 76.45; H, 6.91; N, 4.75.

(*Z*)-3-benzylidene-4-methyl-1-(4-methylbenzyl)pyrrolidine (3c)

Using the procedure described above *N*-(4-methylbenzyl)-*N*-(3-phenylprop-2-yn-1-yl)prop-2-en-1-amine (380 mg, 2 mmol) gave crude product that was purified by column chromatography (diethyl ether : isopropyl alcohol : hexane = 1 : 1 :8) to afford **3c** (382 mg, 69%) as colorless oil. R_f 0.61.

^{1}H NMR (500MHz, $CDCl_3$): δ = 1.33 (d, *J* = 7 Hz, 3H, C(6)H_3), 2.23 (t, *J* = 8 Hz, 1H(A), C(1)H_2), 2.45 (s, 3H, C(20)H_3), 3.02 (q, *J* = 7 Hz, 1HC(2)H), 3.11 (t, *J* = 8 Hz, 1H(B), C(1)H_2), 3.46 (d, *J* = 15 Hz, 1H(A), C(4)H_2), 3.77 (s, 2H, C(7)H), 3.92 (d, *J* = 15 Hz, 1H(B), C(4)H_2), 6.34 (s, 1H, C(5)H), 7.25 (d, J = 8 Hz, 2H, C(10, 12)H), 7.27 (m, 1H, C(16)H), 7.30 (d, *J* = 8 Hz, 2H, C(14, 18)H), 7.37 (d, *J* = 8 Hz, 2H, C(9, 13)H), 7.42 (d, *J* = 8 Hz, 2H, C(15, 17)H).

^{13}C-{^{1}H} NMR (500MHz, $CDCl_3$): δ = 18.13 (C(6)), 21.23 (C(20)), 39.31 (C(2)), 58.59 (C(4)), 60.46 (C(7)), 61.32 (C(1)), 120.45 (C(5)), 126.14 (C(16)), 128.00 (C(14, 18)), 128.41 (C(15, 17)), 128.75 (C(9, 13)), 129.09 (C(10, 11)), 136.00 (C(8)), 136.58 (C(11)), 138.23 (C(19)), 147.59 (C(3)).

MS (*m/z*, %): 277 (41) $[M]^+$, 262 (19), 172 (10), 129 (13), 105 (100).

Anal. calcd for $C_{20}H_{23}N$, (%): C, 86.59; H, 8.36; N, 5.05. Found, %: C, 86.62; H, 8.43; N, 4.85.

(*Z*)-3-methyl-1-(4-methylbenzyl)-4-pentylidenepyrrolidine (3d)

Using the procedure described above *N*-allyl-*N*-(4-methylbenzyl)hept-2-yn-1-amine (510 mg, 2 mmol) gave crude product that was purified by column chromatography (diethyl ether : isopropyl alcohol : hexane = 1 : 1 :8) to afford **3d** (494 mg, 73 %). R_f 0.68.

^{1}H NMR (500MHz, $CDCl_3$): δ = 0.91 (m, 3H, C(17)H_3), 1.08 (d, *J* = 7 Hz, 3H, C(6)H_3), 1.31 (m, 2H, C(16)H_2), 1.33 (m, 2H, C(14)H_2), 1.92 (q, *J* = 7 Hz, 2H, C(15)H_2), 2.05 (m, 1H(A),C(1)H_2), 2.37 (s, 3H, C(18)H_3), 2.69 (q, *J* = 7 Hz, 1H, C(2)H), 2.98 (d, *J* = 14 Hz, 1H(A), C(4)H_2), 3.01 (t, *J* = 8 Hz, 1H(B), C(1)H_2), 3.50 (d, *J* = 14 H, 1H(B), C(4)H_2), 3.62 (d, *J* = 13 Hz, 1H(A), C(7)H_2), 3.66 (d, *J* = 13 Hz, 1H(B), C(7)H_2), 5.15 (m, 1H, C(5)H), 7.26 (d, *J* = 8 Hz, 2H, C(9, 13)H), 7.16 (d, *J* = 8 Hz, 2H, C(10, 12)H).

^{13}C-{^{1}H} NMR (500MHz, $CDCl_3$): δ = 14.03 (C(17)), 17.59 (C(6)), 21.12 (C(18)), 22.35 (C(16)), 29.14 (C(15)), 31.75 (C(14)), 37.17 (C(2)), 56.59 (C(4)), 60.43 (C(7)), 62.07 (C(1)), 120.05 (C(5)), 136.61 (C(8)), 128.87 (C(9, 13)), 128.96 (C(10, 12)), 143.76 (C(3)).

MS (*m/z*, %): 257 (14) $[M]^+$, 200 (25), 152 (10), 105 (100).

Anal.calcd for $C_{18}H_{27}N$, (%): C, 83.99; H, 10.57; N, 5.44. Found, %: C, 84.28; H, 10.73; N, 5.30.

(*Z*)-1-(furan-2-ylmethyl)-3-methyl-4-((trimethylsilyl)methylene)pyrrolidine (3e)

Using the procedure described above *N*-(furan-2-ylmethyl)-*N*-(3-(trimethylsilyl)prop-2-yn-1-yl)prop-2-en-1-amine (494 mg, 2 mmol) gave crude product that was purified by column chromatography (diethyl ether : isopropyl alcohol : hexane = 1 : 1 :8) to afford **3e** (403 mg, 81 %). R_f 0.74.

^{1}H NMR (500MHz, $CDCl_3$): δ = 0.09 (s, 9H, C(12, 13, 14)H_3), 1.09 (d, *J* = 7 Hz, 3H, C(6)H_3), 2.05 (t, *J* = 9 Hz, 1H(A), C(1)H_2), 2.70 (q, *J* = 7 Hz, C(2)H), 3.04 (m, 1H(B), C(1)H_2), 3.06 (m, 1H(A), C(4)H_2), 3.59 (dd, *J* = 14 Hz, *J* = 2Hz, 1H(B), C(4)H_2), 3.65 (d, *J* = 14 Hz, 1H(A), C(7)H_2), 3.68 (d, *J* = 14 Hz, 1H(B), C(7)H_2), 5.30 (m, 1H, C(5)H), 6.22 (d, *J* = 3 Hz, 1H, C(9)H), 6.34 (m, 1H, C(10)H), 7.39 (dd, *J* = 2 Hz, *J* = 1 Hz, 1H, C(11)H).

^{13}C-{^{1}H} NMR (500MHz, $CDCl_3$): δ = -0.45 (C(12, 13, 14)), 17.17 (C(6)), 40.25 (C(2)), 52.19 (C(7)), 58.96 (C(4)), 107.86 (C(9)), 110.06 (C(10)), 116.84 (C(5)), 141.97 (C(11)), 152.45 (C(8)), 162.29 (C(3)).

MS (*m/z*, %): 249 (16) $[M]^+$, 176 (76), 152 (9), 81 (100).

Anal.calcd for $C_{14}H_{23}NOSi$, (%): C, 67.42; H, 9.29; N, 5.62. Found, %: C, 67.07; H, 9.14; N, 5.39.

(*Z*)-3-methyl-1-(thiophen-2-ylmethyl)-4-((trimethylsilyl)methylene)pyrrolidine (3f)

Using the procedure described above *N*-(thiophen-2-ylmethyl)-N-(3-(trimethylsilyl)prop-2-yn-1-yl)prop-2-en-1-amine (526 mg, 2 mmol) gave crude product that was purified by column chromatography (diethyl ether : isopropyl alcohol : hexane = 1 : 1 :8) to afford **3f** (403 mg, 76 %). R_f 0.80.

^{1}H NMR (500MHz, $CDCl_3$): δ = 0.09 (s, 9H, C(12, 13, 14)H_3), 1.10 (d, *J* = 7 Hz, 3H, C(6)H_3), 2.07 (t, *J* = 8 Hz, 1H(A), C(1)H_2), 2.70 (m, 1H, C(2)H), 3.04 (t, *J* = 8 Hz, 1H(B), C(1)H_2), 3.09 (dt, *J* = 14 Hz, *J* = 2 Hz, 1H(A), C(4)H_2), 3.61 (dd, *J* = 14 Hz, *J* = 2 Hz, 1H(B), C(4)H_2), 3.84 (d, *J* = 14 Hz, 1H(A), C(7)H_2), 3.88 (d, *J* = 14 Hz, 1H(B), C(7)H_2), 5.32 (m, 1H, C(5)H), 6.96 (m, 1H, C(11)H), 6.98 (t, *J* = 3 Hz, 1H, C(10)H), 7.25 (dd, *J* = 5 Hz, *J* = 1 Hz, 1H, C(9)H).

^{13}C-{^{1}H} NMR (500MHz, $CDCl_3$): δ = -0.42 (C(12, 13, 14)), 17.34 (C(6)), 40.35 (C(2)), 54.69 (C(7)), 59.06 (C(4)), 61.04 (C(1)), 116.89 (C(5)), 124.79 (C(9)), 125.50 (C(11)), 126.41 (C(10)), 142.10 (C(8)), 162.44 (C(3)).

MS (*m/z*, %): 265 (4) $[M]^+$, 192 (31), 97 (100), 73 (20).

Anal.calcd for $C_{14}H_{23}NSSi$, (%): C, 63.34; H, 8.73; N, 5.28. Found, %: C, 63.39; H, 8.64; N, 5.11.

(*Z*)-1-(4-chlorobenzyl)-3-methyl-4-((trimethylsilyl)methylene)pyrrolidine (3g)

Using the procedure described above *N*-(4-chlorobenzyl)-*N*-(3-(trimethylsilyl)prop-2-yn-1-yl)prop-2-en-1-amine (584 mg, 2 mmol) gave crude product that was purified by column chromatography (diethyl ether : isopropyl alcohol : hexane = 1 : 1 :8) to afford **3g** (500 mg, 85 %). R_f 0.68.

^{1}H NMR (500MHz, $CDCl_3$): δ = 0.08 (s, 9H, C(14, 15, 16)H_3), 1.09 (d, *J* = 7 Hz, 3H, C(6)H_3), 2.01 (t, *J* = 8 Hz, 1H(A), C(1)H_2), 2.67 (p, *J* = 7 Hz, 1H, C(2)H), 2.95 (t, *J* = 8 Hz, 1H(B), C(1)H_2), 3.03 (dt, *J* = 14 Hz, *J* = 2 Hz, 1H(A), C(4)H_2), 3.52 (dd, *J* = 14 Hz, *J* = 2 Hz, 1H(B), C(4)H_2), 3.58 (d, *J* = 13 Hz, 1H(A), C(7)H_2), 3.63 (d, *J* = 13 Hz, 1H(B), C(7)H_2), 5.32 (m, 1H, C(5)H), 7.30 (d, *J* = 3 Hz, 4H, C(9, 10, 12, 13)H).

^{13}C-{^{1}H} NMR (500MHz, $CDCl_3$): δ = -0.3 (C(14, 15, 16)), 17.45 (C(6)), 40.36 (C(2)), 59.32 (C(4)), 60.01 (C(7)), 61.26 (C(1)), 116.96 (C(5)), 128.39 (C(10, 12)), 130.06 (C(9, 13)), 132.63 (C(11)), 137.46 (C(8)), 162.45 (C(3)).

MS (*m/z*, %): 294 (4) $[M]^+$, 293 (9), 220 (73), 168 (13), 125 (100), 89 (13), 73 (29).

Anal.calcd for $C_{16}H_{24}ClNSi$, (%): C, 65.39; H, 8.23; N, 4.77. Found, %: C, 65.43; H, 8.27; N, 5.01.

(*Z*)-3-(methyl-*d*)-1-(4-methylbenzyl)-4-((trimethylsilyl)methylene-*d*)pyrrolidine (4h)

Using the procedure described above *N*-(4-methylbenzyl)-*N*-(3-(trimethylsilyl)prop-2-yn-1-yl)prop-2-en-1-amine (542 mg, 2 mmol) and D_2O (instead of H_2O)gave crude product that was purified by column chromatography (diethyl ether : isopropyl alcohol : hexane = 1 : 1 :8) to afford **4h** (226 mg, 82 %). R_f 0.63.

^{1}H NMR (500MHz, $CDCl_3$): δ = 0.10 (s, 1H, C(14, 15, 16)H_3), 1.09 (t, *J* = 8 Hz, 2H, C(6)DH_2), 2.01 (t, *J* = 8 Hz, 1H(A), C(1)H_2), 2.38 (s, 3H, C(17)H_3), 2.68 (p, *J* = 7 Hz, 1H, C(2)H), 2.99 (t, *J* = 8 Hz, 1H(B), C(1)H_2), 3.06 (d, *J* = 14 Hz, 2H, C(4)H_2), 3.58 (d, *J* = 13 Hz, 1H(A), C(7)H_2), 3.67 (d, *J* = 13 Hz, 1H(B), C(7)H_2), 7.17 (d, *J* = 8 Hz, 2H, C(10, 12)H), 7.26 (d, *J* = 8 Hz, 2H, C(9,13)H).

^{13}C-{^{1}H} NMR (500MHz, $CDCl_3$): δ = -0.41 (C(14, 15, 16)), 17.07 (t, *J* = 20 Hz, C(6)), 21.14 (C(17)), 40.22 (C(2)), 59.39 (C(4)), 60.49 (C(7)), 61.17 (C(1)), 116.70 (C(5)), 128.82 (C(9, 13)), 128.96 (C(10, 12)), 135.67 (C(8)), 136.53 (C(11)), 162.69 (C(3)).

MS (*m/z*, %): 276 (<1) $[M]^+$, 275 (<1), 258 (6), 200 (41), 105 (100), 73 (15).

Anal.calcd for $C_{17}H_{25}D_2NSi$, (%): C, 74.11; N, 5.08. Found, %: C, 74.53; N, 5.30.

(*Z*)-3-(methyl-*d*)-1-(thiophen-2-ylmethyl)-4-((trimethylsilyl)methylene-*d*)pyrrolidine (4f)

Using the procedure described above *N*-(thiophen-2-ylmethyl)-*N*-(3-(trimethylsilyl)prop-2-yn-1-yl)prop-2-en-1-amine (526 mg, 2 mmol) and D_2O gave crude product that was purified by column chromatography (diethyl ether : isopropyl alcohol : hexane = 1 : 1 :8) to afford **4f** (400 mg, 71 %). R_f 0.80.

^{1}H NMR (500MHz, $CDCl_3$): δ = 0.09 (s, 9H, C(12, 13, 14)H_3), 1.08 (d, *J* = 7 Hz, 3H, C(6)DH_2), 2.06 (t, *J* = 8 Hz, 1H(A), C(1)H_2), 2.69 (m, 1H, C(2)H), 3.04 (t, *J* = 8 Hz, 1H(B), C(1)H_2), 3.09 (dt, *J* = 14 Hz, *J* = 2 Hz, 1H(A), C(4)H_2), 3.61 (d, *J* = 14 Hz, 1H(B), C(4)H_2), 3.84 (d, *J* = 14 Hz, 1H(A), C(7)H_2), 3.88 (d, *J* = 14 Hz, 1H(B), C(7)H_2), 6.95 (m, 1H, C(11)H), 6.97 (t, *J* = 3 Hz, 1H, C(10)H), 7.25 (d, *J* = 5 Hz, 1H, C(9)H).

^{13}C-{^{1}H} NMR (500MHz, $CDCl_3$): δ = -0.44 (C(12, 13, 14)), 17.03 (t, *J* = 19 Hz, C(6)), 40.23 (C(2)), 54.68 (C(7)), 59.01 (C(4)), 61.00 (C(1)), 116.51 (t, C(5)), 124.79 (C(9)), 125.53 (C(11)), 126.41 (C(10)), 142.07 (C(8)), 162.37 (C(3)).

MS (*m/z*, %): 268 (2) $[M]^+$, 267 (7), 252 (6), 194 (62), 97 (100), 73 (40).

Anal.calcd for $C_{14}H_{21}D_2NSSi$, (%): C, 62.86; N, 5.24. Found, %: C, 62.54; N, 5.20.

(*Z*)-3-methyl-1-(4-methylbenzyl)-4-(4-methylbenzylidene)pyrrolidine (3i)

Using the procedure described above *N*-(4-methylbenzyl)-*N*-(3-(*p*-tolyl)prop-2-yn-1-yl)prop-2-en-1-amine (578 mg, 2 mmol) and H_2O (instead of D_2O)gave crude product that was purified by column chromatography (diethyl ether : isopropyl alcohol : hexane = 1 : 1 :8) to afford **3i** (265 mg, 91 %). R_f 0.54.

^{1}H NMR (500MHz, $CDCl_3$): δ = 1.27 (d, *J* = 7 Hz, 3H, C(6)H_3), 2.17 (t, *J* = 8 Hz, 1H(A), C(1)H_2), 2.39 (s, 3H, C(21)H_3), 2.41 (s, 3H, C(20)H_3), 2.96 (q, *J* = 7 Hz, 1H, C(2)H), 3.07 (t, *J* = 8 Hz, 1H(B), C(1)H_2), 3.39 (d, *J* = 15 Hz, 1H(A), C(4)H_2), 3.73 (s, 2H, C(7)H_2), 3.86 (d, *J* = 15 Hz, 1H(B), C(4)H_2), 6.26 (s, 1H, C(5)H), 7.17 (d, *J* = 5Hz, 2H, C(14, 18)H), 7.18 (m, 2H, C(15, 17)H), 7.20 (d, *J* = 8 Hz, 2H, C(10, 12)H), 7.32 (d, *J* = 8 Hz, 2H, C(9, 13)H).

^{13}C-{^{1}H} NMR (500MHz, $CDCl_3$): δ = 18.04 (C(6)), 21.17 (C(20, 21)), 39.17 (C(2)), 58.54 (C(4)), 60.45 (C(7)), 61.33 (C(1)), 120.19 (C(5)), 127.86 (C(14, 18)), 128,72 (C(9, 13)), 129.03 (C(15, 17)), 129.07 (C(10, 12)), 135.38 (C(19)), 135.71 (C(16)), 136.54 (C(11)), 137.97 (C(8)).

MS (*m/z*, %): 291 (77) $[M]^+$, 276 (30), 186 (11), 143 (15), 105 (100).

Anal.calcd for $C_{21}H_{25}N$, (%): C, 86.55; H, 8.65; N, 4.81. Found, %: C, 86.37; H, 8.60; N, 4.79.

***(E)*-3-(iodo(trimethylsilyl)methylene)-4-(iodomethyl)-1-(4-methoxybenzyl)pyrrolidin-2-one (5a); Typical Procedure.**

To a solution of *N*-(4-methoxybenzyl)-*N*-(3-(trimethylsilyl)prop-2-yn-1-yl)prop-2-en-1-amine (754 mg, 2 mmol) and Et_2Zn (1 M in hexanes, 5 mL, 5 mmol) in CH_2Cl_2 (6 mL) was added Ti(O-*i*Pr)$_4$ (0.5 M in hexanes, 0.6 mL, 0.3 mmol). Ethylmagnesiurn bromide (2.5 M in Et_2O, 0.16 mL, 0.4 mmol) was then added and the reaction mixture rapidly turned black. After 18 h at 23 °C, the reaction mixture was cooled to -78 °C, and a solution of I_2 (1575 mg, 12,5 mmol) in THF (12,5 mL) was added via cannula. The reaction mixture was warmed to 23 °C, and stirred overnight. The mixture was then

partitioned between 25% aqueous KOH and ether. The organic layer was washed with water and aqueous $Na_2S_2O_3$, drying over $MgSO_4$. Evaporation of solvent and purification of the residue by column chromatography (diethyl ether : isopropyl alcohol : hexane = 1 : 1 :8) to afford **5a** (617 mg, 57 %). R_f 0.85.

^{1}H NMR (500MHz, $CDCl_3$): δ = 0.40 (s, 9H, C(14, 15, 16)H_3), 3.17 (m, 1H(A), C(6)IH_2), 3.18 (m, 1H(A), C(1)H_2), 3.27 (m, 1H, C(2)H), 3.45 (m, 1H(B), C(1)H_2), 3.55 (dd, *J* = 10 Hz, *J* = 3 Hz, 1H(B), C(6)IH_2), 3.83 (s, 3H, C(17)H_3), 4.27 (d, *J* = 14 Hz, 1H(A), C(7)H_2), 4.62 (d, *J* = 14 Hz, 1H(B), C(7)H_2), 6.89 (d, *J* = 9 Hz, 2H, C(10, 12)H, 7.20 (d, *J* = 9 Hz, 2H, C(9, 13)H).

^{13}C-{^{1}H} NMR (500MHz, $CDCl_3$): δ = 2.21 (C(14, 15, 16)), 7.77 (C(6)), 47.03 (C(7)), 48.98 (C(2)), 49.22 (C(1)), 55.31(C(17)), 114.20 (C(10, 12)), 127.77 (C(8)), 129.72 (C(9, 13)), 153.11 (C(3)), 159.31 (C(11)), 162.60 (C(4)).

Anal.calcd for $C_{17}H_{23}I_2NO_2Si$, (%): C, 36.77; H, 4.18; N, 2.52. Found, %: C, 36.21; H, 4.42; N, 2.39.

(*E*)-3-(iodo(trimethylsilyl)methylene)-4-(iodomethyl)-1-(4-methylbenzyl)pyrrolidin-2-one (5h)

Using the procedure described above *N*-(4-methylbenzyl)-*N*-(3-(trimethylsilyl)prop-2-yn-1-yl)prop-2-en-1-amine (542 mg, 2 mmol) gave crude product that was purified by flash chromatography (diethyl ether : isopropyl alcohol : hexane = 1 : 1 :8) to afford **5h** (641 mg, 61 %). R_f 0.87.

^{1}H NMR (500MHz, $CDCl_3$): δ = 0.41 (s, 9H, C(14, 15, 16)H_3), 2.36 (s, 3H, C(17)H_3), 3.17 (m, 1H(A), C(6)IH_2), 3.19 (m, 1H(A), C(1)H_2), 3.27 (m, 1H, C(2)H), 3.46 (m, 1H(B), C(1)H_2), 3.56 (dd, *J* = 10 Hz, *J* = 3 Hz, 1H(B), C(6)IH_2), 4.28 (d, *J* = 14 Hz, 1H(A), C(7)H_2), 4.66 (d, *J* = 14 Hz, 1H(B), C(7)H_2), 7.17 (s, 4H, C(9, 10, 12, 13)H).

^{13}C-{^{1}H} NMR (500MHz, $CDCl_3$): δ = 2.22 (C(14, 15, 16)), 7.78 (C(6)), 21.17 (C(17)), 47.37 (C(7)), 49.09 (C(2)), 49.29 (C(1)), 125.63 (C(5)), 128.36 (C(9,13)), 129.52 (C(10,12)), 132.63 (C(8)), 137.64 (C(11)), 153.08 (C(3)), 162.66 (C(4)).

MS (*m/z*, %): 539 (4) $[M]^+$, 420 (8), 396 (8), 292 (8), 105 (100), 79 (15).

Anal.calcd for $C_{17}H_{23}I_2NOSi$, (%): C, 37.86; H, 4.30; N, 2.60. Found, %: C, 38.08; H, 4.27; N, 2.44.

Preparation of bis-3-methyl-4-methylenepyrrolidines 7 and 9 via Ti-Mg-catalyzed carbozincation of bis-*N*-allyl substituted propargylamines with Et_2Zn in CH_2Cl_2.

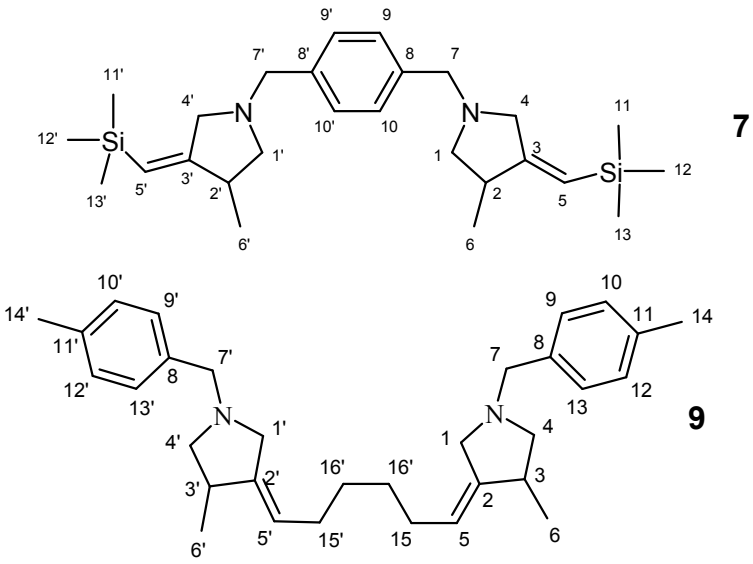


Figure 2 The numbering of atoms in the ^{13}C- and ^{1}H-NMR spectra of the compounds **7** and **9.**

1,4-bis(((*Z*)-3-methyl-4-((trimethylsilyl)methylene)pyrrolidin-1-yl)methyl)benzene (7); Typical Procedure.

To a solution of *N,N′*-(1,4-phenylenebis(methylene))bis(N-(3-(trimethylsilyl)prop-2-yn-1-yl)prop-2-en-1-amine) (874 mg, 2 mmol) and Et_2Zn (1 M in hexanes, 5 mL, 10 mmol) in CH_2Cl_2 (6 mL) was added Ti(O-*i*Pr)$_4$ (0.5 M in hexanes, 1.2 mL, 0.6 mmol). Ethylmagnesiurn bromide (2.5 M in Et_2O, 0.32 mL, 0.8 mmol) was then added and the reaction mixture rapidly turned black. After 18 h at 23 ^{o}C, the reaction mixture was diluted with Et_2O (5 mL), and 25 wt% KOH solution (3 mL) was added dropwise while the reaction flask was cooled in an ice bath. The aqueous layer was extracted with diethyl ether (3×5 mL). The combined organic layers were washed with brine (10 mL), dried over anhydrous $CaCl_2$. The reaction mixture was filtered through a filter paper and concentrated in vacuo to give crude product as a yellow oil. Evaporation of solvent and purification of the residue by column chromatography (diethyl ether : isopropyl alcohol : hexane = 1 : 1 :8) gave **7** (776 mg, 88 %) as colorless oil. R_f 0.52.

^{1}H NMR (500MHz, $CDCl_3$): δ = 0.08 (s, 18H, C(11, 12, 13, 11’, 12’, 13’)H_3), 1.09 (d, *J* = 7 Hz, 6H, C(6, 6’)H_3), 2.01 (t, *J* = 9 Hz, 2H(A), C(1, 1’)H_2), 2.67 (q, *J* = 7 Hz, 2H, C(2, 2’)H), 2.98 (t, *J* = 8 Hz, 2H(B), C(1, 1’)H_2), 3.03 (d, *J* = 14 Hz, 2H(A), C(4, 4’)H_2), 3.55 (d, *J* = 14 Hz, 2H(B), C(4, 4’)H_2), 3.60 (d, *J* = 13 Hz, 2H(A), C(7, 7’)H_2), 3.66 (d, *J* = 13 Hz, 2H(B), C(7, 7’)H_2), 5.30 (s, 2H, C(5, 5’)H), 7.31 (s, 4H, C(9, 10, 9’, 10’)H).

^{13}C-{^{1}H} NMR (500MHz, $CDCl_3$): δ = -0.43 (C(11, 12, 13, 11’, 12’, 13’)), 17.36 (C(6, 6’)), 40.32 (2, 2’), 59.42 (C(4, 4’)), 60.55 (C(7, 7’)), 61.31 (C(1, 1’)), 116.69 (C(5, 5’)), 128.78 (C(9, 10, 9’, 10’)), 137.65 (C(8, 8’)), 162.77 (C(3, 3’)).

MS (EI): m/z, % = 441 (16) [M^+], 440 (39), 367 (100), 272 (66), 207 (44), 168 (34), 104 (85), 73 (67), 44 (47).

Anal. calcd for $C_{26}H_{44}N_2Si_2$, (%): C, 70.84; H, 10.06; N, 6.35. Found, %: C, 71.07; H, 9.95; N, 6.39.

(4*Z*,4'*Z*)-4,4'-(octane-2,7-diylidene)bis(3-ethyl-1-(4-methylbenzyl)pyrrolidine) (9)

Using the procedure described above *N*^{1},*N*^{10}-diallyl-*N*^{1},*N*^{10}-bis(4-methylbenzyl)deca-*2,8*-diyne-1,10-diamine (906 mg, 2 mmol) gave crude product that was purified by flash chromatography (diethyl ether : isopropyl alcohol : hexane = 1 : 1 :8) to afford **9** (872 mg, 85 %). R_f 0.80.

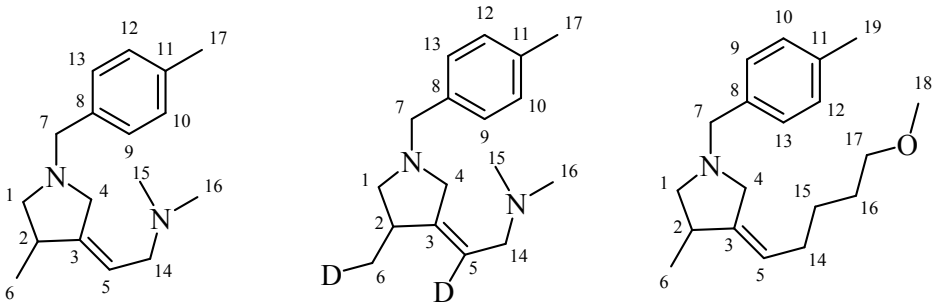
^{1}H NMR (500MHz, $CDCl_3$): δ = 1.10 (d, *J* = 7 Hz, 6H, C(6, 6')H_3), 1.36 (s, 4H, C(16, 16')H_2), 1.92 (d, *J* = 5Hz, 4H, C(15, 15')H_2), 2.04 (t, *J* = 9 Hz, 2H(A), C(4, 4')H_2), 2.38 (s, 6H, C(14, 14'), 2.70 (q, *J* = 7 Hz, 2H, C(3, 3')H), 2.97 (d, *J* = 14 Hz, 2H(A), C(1, 1')H_2), 3.00 (t, *J* = 8 Hz, 2H(B), C(4, 4')H_2), 3.48 (d, *J* = 14 Hz, 2H(B), C(1, 1')H_2), 3.61 (d, *J* = 13 Hz, 2H(A), C(7, 7')H_2), 3.65 (d, *J* = 13 Hz, 2H(B), C(7, 7')H_2), 5.15 (m, 2H, C(5,5')H), 7.17 (d, *J* = 8 Hz, 4H, C(10, 12, 10',12')H), 7.28 (d, *J* = 8 Hz, 4H, C(9, 13, 9', 13')H).

^{13}C-{^{1}H} NMR (500MHz, $CDCl_3$): δ = 17.75 (C(6, 6')), 21.15 (C(14, 14')), 29.24 (C(16, 16')), 29.37 (C(15, 15')), 37.33 (C(3, 3')), 56.82 (C(1, 1')), 60.61 (C(7, 7')), 62.28 (C(4, 4')), 119.69 (C(5, 5')), 128,77 (C(9, 13, 9', 13')), 128.94 (C(10, 12, 10', 12')), 136.07 (C(8, 8')), 136.46 (C(11, 11')), 144.09 (C(2, 2')).

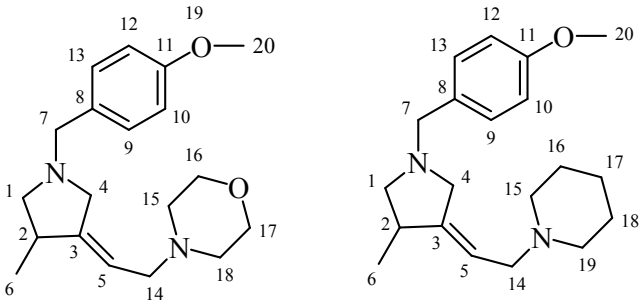
MS (*m/z*, %): 457 (3) $[M]^+$, 456 (3), 351 (1), 200 (10), 105 (100), 79 (6).

Anal.calcd for $C_{32}H_{44}N_2$, (%): C, 84.16; H, 9.71; N, 6.13. Found, %: C, 83.89; H, 9.50; N, 6.17.

Preparation of 3-methyl-4-methylenepyrrolidines 11a-c, 12a and 14 via Ti-Mg-catalyzed carbozincation of allyl substituted but-2-yne-1,4-diamines with Et_2Zn in CH_2Cl_2.



11a **12a** **14**



11b **11c**

Figure 3 The numbering of atoms in the ^{13}C- and ^{1}H-NMR spectra of the compounds **11a-c**, **12a** and **14**.

(*Z*)-*N*,*N*-dimethyl-2-(4-methyl-1-(4-methylbenzyl)pyrrolidin-3-ylidene)ethan-1-amine (11a)

To a solution of *N*^{1}-allyl-*N*^{4},*N*^{4}-dimethyl-*N*^{1}-(4-methylbenzyl)but-2-yne-1,4-diamine (512 mg, 2 mmol) and Et_2Zn (1 M in hexanes, 5 mL, 5 mmol) in CH_2Cl_2 (6 mL) was added Ti(O-*i*Pr)$_4$ (0.5 M in hexanes, 0.6 mL, 0.3 mmol). Ethylmagnesiurn bromide (2.5 M in Et_2O, 0.16 mL, 0.4 mmol) was then added and the reaction mixture rapidly turned black. After 18 h at 23 ^{o}C, the reaction mixture was diluted with Et_2O (5 mL), and 25 wt% KOH solution (3 mL) was added dropwise while the reaction flask was cooled in an ice bath. The aqueous layer was extracted with diethyl ether (3×5 mL). The combined organic layers were washed with brine (10 mL), dried over anhydrous $CaCl_2$. The reaction mixture was filtered through a filter paper and concentrated in vacuo to give crude product as a yellow oil. Evaporation of solvent and purification of the residue by column chromatography (diethyl ether : isopropyl alcohol : hexane = 1 : 1 :8) gave **11a** (464 mg, 90 %) as colorless oil. R_f 0.47.

^{1}H NMR (500MHz, $CDCl_3$): δ = 1.12 (d, *J* = 7 Hz, 3H, C(6)H_3), 2.07 (t, *J* = 9 Hz, 1H(A), C(1)H_2), 2.35 (s, 6H, C(15, 16)H_3), 2.36 (s, 3H, C(17)H_3), 2.75 (q, *J* = 7 Hz, 1H, C(2)H), 2.99 (m, 1H(A), C(4)H_2), 3.00 (m, 2H, C(14)H_2), 3.02 (m, 1H(B), C(1)H_2), 3.50 (d, *J* = 14 Hz, 1H(B), C(4)H_2), 3.60 (d, *J* = 13 Hz, 1H(A), C(7)H_2),

3.65 (d, J = 12 Hz, 1H(B), C(7)H_2), 5.31 (m, 1H, C(5)H), 7.15 (d, J = 8 Hz, 2H, C(10, 12)H), 7.24 (d, J = 8Hz, 2H, C(9, 13)H).

^{13}C-{^{1}H} NMR (500MHz, $CDCl_3$): δ = 17.49 (C(6)), 21.21 (C(17)), 37.69 (C(2)), 44.87 (C(15, 16)), 56.55 (C(4)), 57.66 (C(14)), 60.25 (C(7)), 61.64 (C(1)), 114.34 (C(5)), 128.77 (C(9, 13)), 129.02 (C(10, 12)), 135.36 (C(8)), 136.73 (C(11)), 149.76 (C(3)).

MS (EI): m/z, % = 258 (<1) [M^+], 257 (<1), 213 (80), 198 (57), 105 (100).

Anal. calcd for $C_{17}H_{26}N_2$, (%): C, 79.02; H, 10.14; N, 10.84. Found, %: C, 78.86; H, 10.09; N, 11.0.

(*Z*)-4-(2-(1-(4-methoxybenzyl)-4-methylpyrrolidin-3-ylidene)ethyl)morpholine (11b)

Using the procedure described above *N*-allyl-*N*-(4-methylbenzyl)-4-morpholinobut-2-yn-1-amine (596 mg, 2 mmol) gave crude product that was purified by column chromatography (diethyl ether : isopropyl alcohol : hexane = 1 : 1 :8) to afford **11b** (534 mg, 89 %). R_f 0.48.

^{1}H NMR (500MHz, $CDCl_3$): δ = 1.09 (d, J = 7 Hz, 3H, C(6)H_3), 2.01 (t, J = 8 Hz, 1H(A), C(1)H_2), 2.42 (s, 4H, C(15, 18)H_2), 2.71 (q, J = 8 Hz, 1H, C(2)H), 2.88 (d, J = 6 Hz, 2H, C(14)H_2), 2.93 (d, J = 14 Hz, 1H(A), C(4)H_2), 2.97 (t, J = 8 Hz, 1H(B), C(1)H_2), 3.47 (d, J = 14 Hz, 1H(B), C(4)H_2), 3.55 (d, J = 13 Hz, 1H(A), C(7)H_2), 3.59 (d, J = 13 Hz, 1H(B), C(7)H_2), 3.71 (s, 4H, C(16, 17)H_2), 3.80 (s, 3H, C(19)H_3), 5.25 (s, 1H, C(5)H), 6.87 (d, J = 8 Hz, 2H, C(10, 12)H), 7.25 (d, J = 8 Hz, 2H, C(9, 13)H).

^{13}C-{^{1}H} NMR (500MHz, CDl_3): δ = 17.53 (C(6)), 37.66 (C(2)), 53.61 (C(15, 18)), 55.21 (C(19)), 56.74 (C(4)), 57.82 (C(14), 60.04 (C(7)), 61.78 (C(1)), 66.99 (C(16, 17)), 113.63 (C(10, 12)), 115.49 (C(5)), 129.89 (C(9, 13)), 130.93 (C(8)), 148.32 (C(3)), 158.66 (C(11)).

MS (EI): m/z, % = 316 (<1) [M^+], 229 (39), 121 (100), 77 (4).

Anal.calcd for $C_{19}H_{28}N_2O_2$, (%): C, 72.12; H, 8.92; N, 8.85. Found, %: C, 72.15; H, 8.79; N, 8.49.

(*Z*)-1-(2-(1-(4-methoxybenzyl)-4-methylpyrrolidin-3-ylidene)ethyl)piperidine (11c)

Using the procedure described above *N*-allyl-*N*-(4-methoxybenzyl)-4-(piperidin-1-yl)but-2-yn-1-amine (624 mg, 2 mmol) gave crude product that was purified by column chromatography (diethyl ether : isopropyl alcohol : hexane = 1 : 1 :8) to afford **11c** (515 mg, 82 %). R_f 0.79.

^{1}H NMR (500MHz, $CDCl_3$): δ = 1.04 (d, J = 7 Hz, 3H, C(6)H_3), 1.44 (s, 2H, C(17)H_2), 1.59 (p, J = 6 Hz, 4H, (C(16, 18)), 1.99 (t, J = 9 Hz, 1H(A), C(1)H_2), 2.36 (s, 4H, C(15, 19)H_2), 2.71 (q, J = 8 Hz, 1H, C(2)H), 2.84 (d, J = 7 Hz, 2H, C(14)H_2), 2.93 (d, J = 14 Hz, 1H(A), C(4)H_2), 2.97 (t, J = 8 Hz, 1H(B), C(1)H_2), 3.47 (d, J = 14Hz, 1H(B), C(4)H_2), 3.55 (d, J = 13 Hz, 1H(A), C(7)H_2), 3.59 (d, J

= 13Hz, 1H(B), C(7)H_2), 3.81 (s, 3H, C(20)H_3), 5.29 (m, 1H, C(5)H), 6.87 (d, *J* = 8 Hz, 2H, C(10, 12)H), 7.26 (d, *J* = 8 Hz, 2H, C(9, 13)H).

^{13}C-{^{1}H} NMR (500MHz, $CDCl_3$): δ = 17.49 (C(6)), 24.39 (C(17)), 25.95 (C(16, 18)), 37.62 (C(2)), 54.52 (C(15, 19)), 55.23 (C(20)), 56.77 (C(4)), 58.24 (C(14)), 60.10 (C(7)), 61.86 (C(1)), 113.61 (C(10, 12)), 116.53 (C(5)), 129.91 (C(9, 13)), 131.05 (C(8)), 147.19 (C(3)), 158.63 (C(11)).

MS (EI): m/z, % = 314 (<1) [M^+], 121 (100), 77 (5).

Anal.calcd for $C_{20}H_{30}N_2O$, (%): C, 76.39; H, 9.62; N, 8.91. Found, %: C, 76.44; H, 9.86; N, 8.59.

(*Z*)-*N*,*N*-dimethyl-2-(4-(methyl-*d*)-1-(4-methylbenzyl)pyrrolidin-3-ylidene)ethan-1-amine-2-*d* (12a)

Using the procedure described above *N*^{1}-allyl-*N*^{4},*N*^{4}-dimethyl-*N*^{1}-(4-methylbenzyl)but-2-yne-1,4-diamine (512 mg, 2 mmol) and D_2O (instead of H_2O)gave crude product that was purified by column chromatography (diethyl ether : isopropyl alcohol : hexane = 1 : 1 :8) to afford **12a** (480 mg, 88 %). R_f 0.85.

^{1}H NMR (500MHz, $CDCl_3$): δ = 1.10 (m, 2H, C(6)DH_2), 2.04 (t, *J* = 8 Hz, 1H(A), C(1)H_2), 2.23 (s, 6H, C(15,16)H_3), 2.37 (s, 3H, C(17)H_3), 2.73 (p, *J* = 7 Hz, 1H, C(2)H), 2.83 (s, 2H, C(14)H_2), 2.96 (d, *J* = 14 Hz, 1H(A), C(4)H_2), 2.99 (t, *J* = 8 Hz, 1H(B), C(1)H_2), 3.49 (d, *J* = 14 Hz, 1H(B), C(4)H_2), 3.59 (d, *J* = 13 Hz, 1H(A), C(7)H_2), 3.64 (d, *J* = 13Hz,, 1H(B), C(7)H_2), 7.15 (d, *J* = 8 Hz, 2H, C(10, 12)H), 7.25 (d, *J* = 8 Hz, 2H, C(9, 13)H).

^{13}C-{^{1}H} NMR (500MHz, $CDCl_3$): δ = 17.39 (t, *J* = 19 Hz, C(6)), 21.12 (C(17)), 37.50 (C(2)), 45.11 (C(15, 16)), 56.69 (C(4)), 58.29 (C(14)), 60.45 (C(7)), 61.88(C(1)), 128.72 (C(9, 13)), 128.96 (C(10, 12)), 135.84 (C(8)), 136.55 (C(11)), 147.53 (C(3)).

MS (EI): m/z, % = 260 (<1) [M^+], 215 (36), 199 (30), 105 (100), 79 (7).

Anal.calcd for $C_{17}H_{24}D_2N_2$, (%): C, 78.41; N, 10.76. Found, %: C, 78.48; N, 11.08.

(*Z*)-3-(5-methoxypentylidene)-4-methyl-1-(4-methylbenzyl)pyrrolidine (14)

Using the procedure described above *N*-allyl-7-methoxy-*N*-(4-methylbenzyl)hept-2-yn-1-amine (570 mg, 2 mmol) and H_2O (instead of D_2O)gave crude product that was purified by column chromatography (diethyl ether : isopropyl alcohol : hexane = 1 : 1 :8) to afford **14** (517 mg, 90 %). R_f 0.63.

^{1}H NMR (500MHz, $CDCl_3$): δ = 1.08 (d, *J* = 7 Hz, 3H, C(6)H_3), 1.42 (p, *J* = 8 Hz, 2H, C(15)H_2), 1.58 (p, *J* = 8 Hz, 2H, C(16)H_2), 1.95 (qv, *J* = 7 Hz, 2H, C(14)H_2), 2.03 (t, *J* = 8 Hz, 1H(A), C(1)H_2), 2.37 (s, 3H, C(19)H_3), 2.96 (d, *J* = 13 Hz, 1H(A), C(4)H_2), 2.99 (t, *J* = 8 Hz, C(1)H_2), 3.34 (s, 3H, C(18)H_3), 3.37 (t, *J* = 7 Hz, 2H, C(17)H_2), 3.47 (d, *J* = 13 Hz, 1H(B), C(4)H_2), 3.59 (d, *J* = 13 Hz, 1H(A),

$C(7)H_2$), 3.64 (d, J = 13 Hz, 1H(B), $C(7)H_2$), 5.14 (m, 1H, C(5)H), 7.15 (d, *J* = 8 Hz, 2H, C(10, 12)H), 7.26 (d, *J* = 8 Hz, 2H, C(9, 13)H).

^{13}C-{^1H} NMR (500MHz, $CDCl_3$): δ = 17.68 (C(6)), 21.12 (C(19)), 26.08 (C(15)), 29.20 (C(14)), 29.25 (C(16)), 37.30 (C(2)), 56.73 (C(4)), 58.55 (C(18)), 60.54 (C(7)), 62.22 (C(1)), 119.43 (C(5)), 128.77 (C(9, 13)), 128.93 (C(10, 12)), 135.95 (C(8)), 136.47 (C(11)), 144.32 (C(3)).

MS (EI): m/z, % = 287 (18) [M^+], 200 (38), 105 (100), 79 (9).

Anal.calcd for $C_{19}H_{29}NO$, (%): C, 79.39; H, 10.17; N, 4.87. Found, %: C, 79.11; H, 10.00; N, 4.53.

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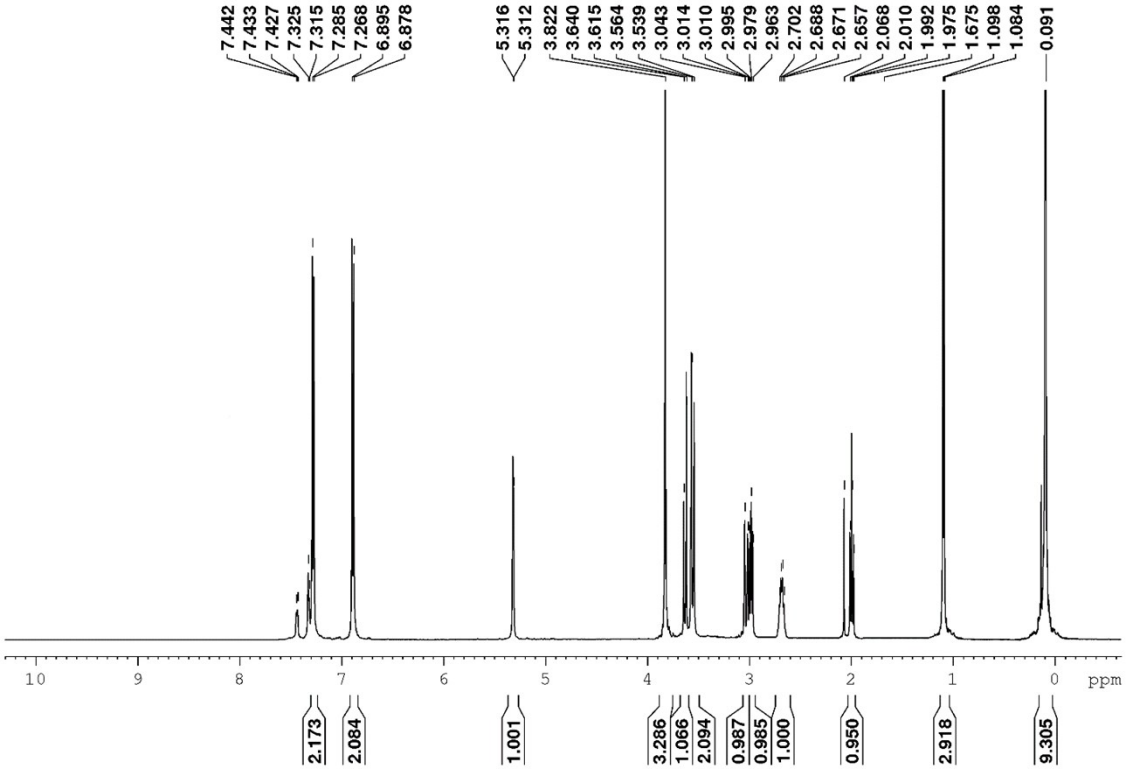
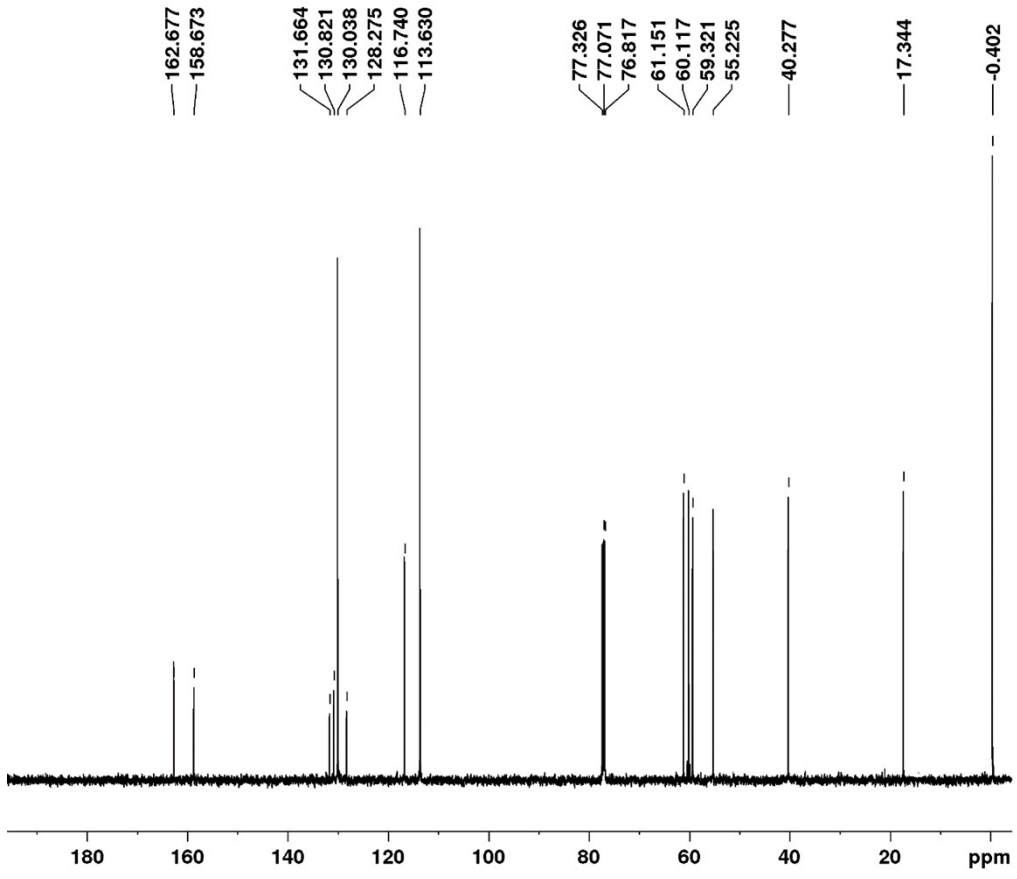
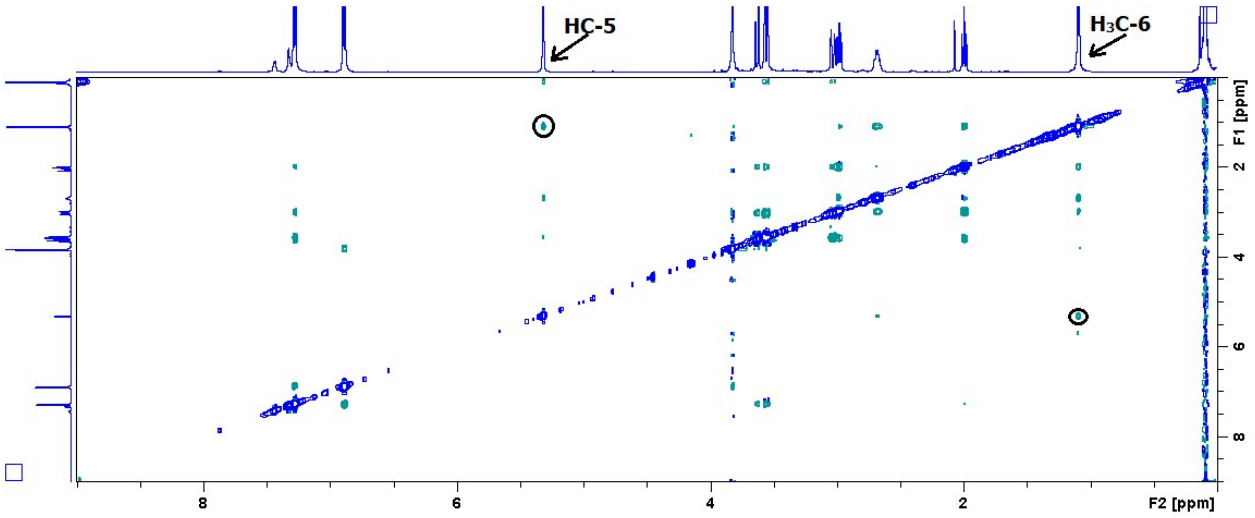
^{1}H-NMR spectrum of (*Z*)-1-(4-methoxybenzyl)-3-methyl-4-((trimethylsilyl)methylene)pyrrolidine (**3a**)



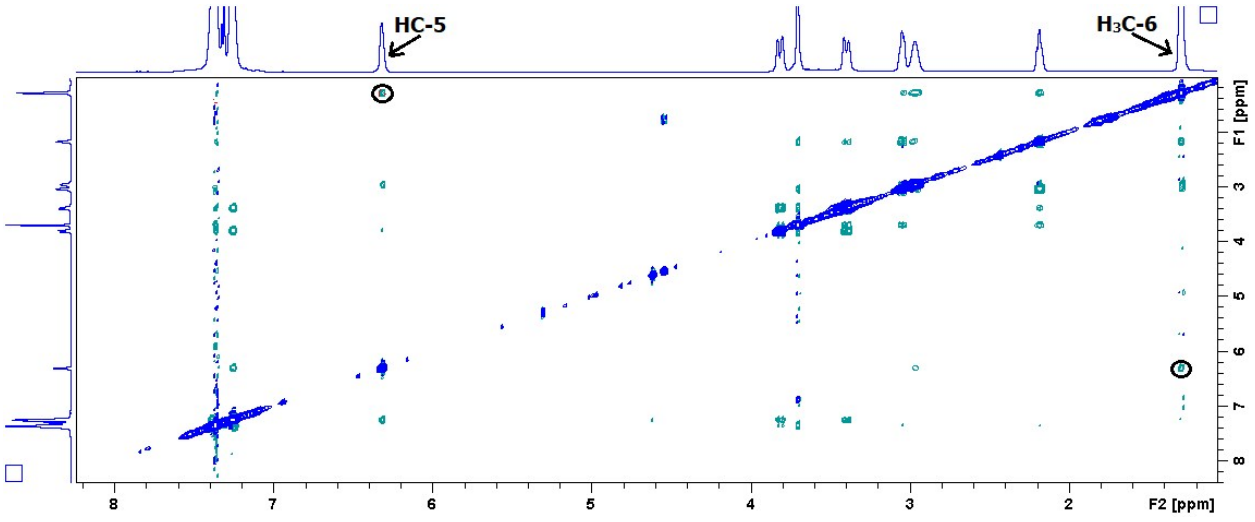
^{13}C-NMR spectrum of (*Z*)-1-(4-methoxybenzyl)-3-methyl-4-((trimethylsilyl)methylene)pyrrolidine (**3a**)

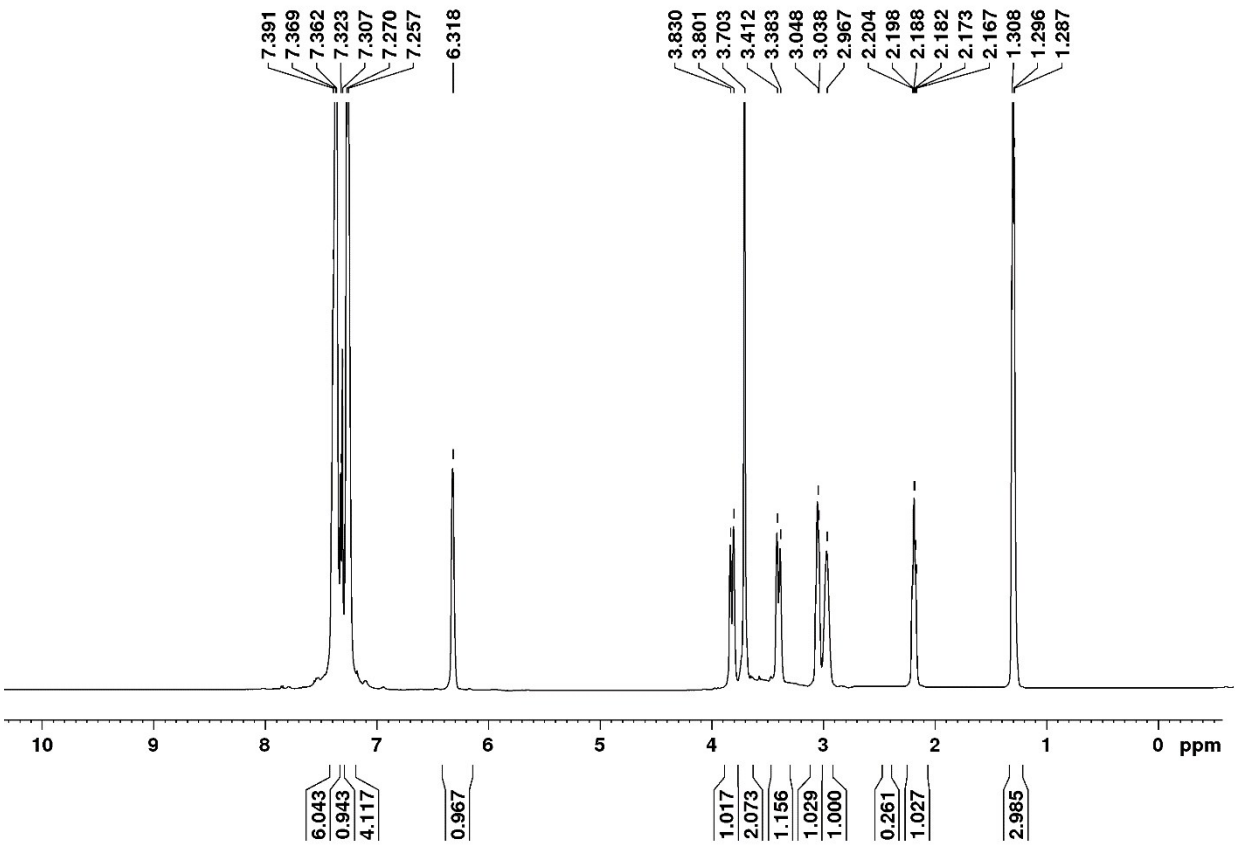


NOESY spectrum of (*Z*)-1-(4-methoxybenzyl)-3-methyl-4-((trimethylsilyl)methylene)pyrrolidine (**3a**)

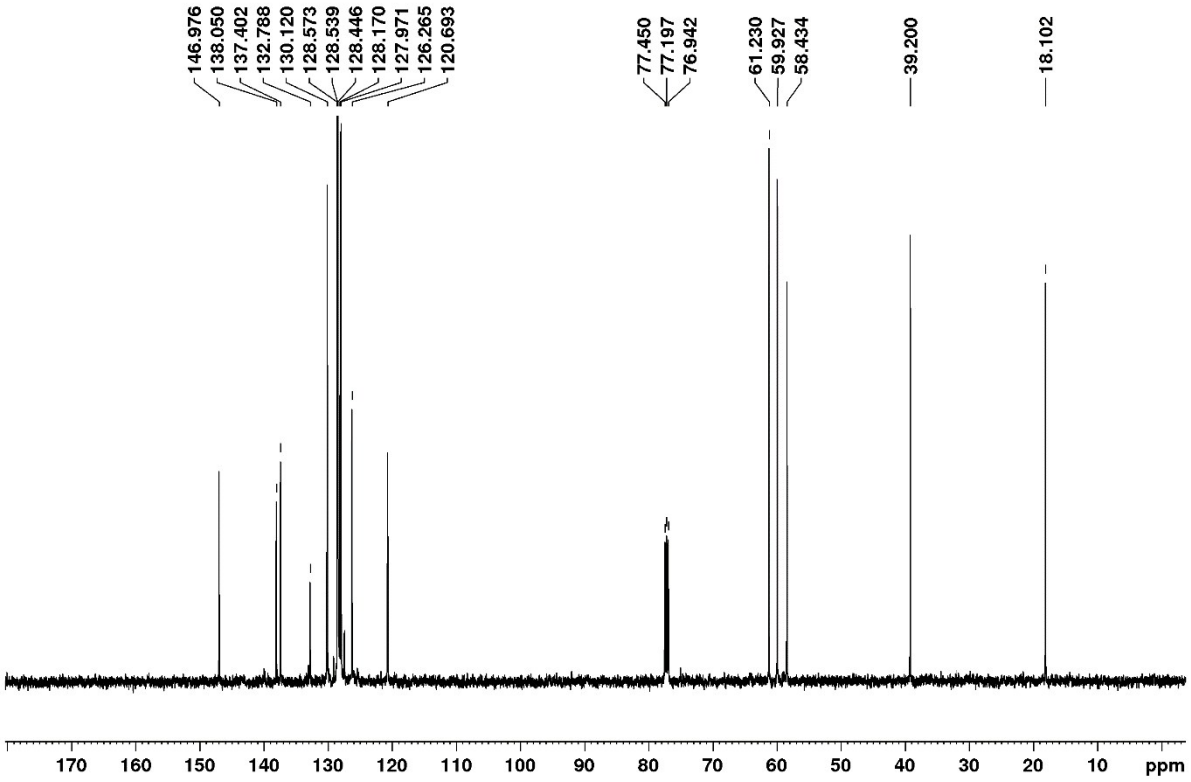


NOESY spectrum of (*Z*)-3-benzylidene-1-(4-chlorobenzyl)-4-methylpyrrolidine (**3b**)

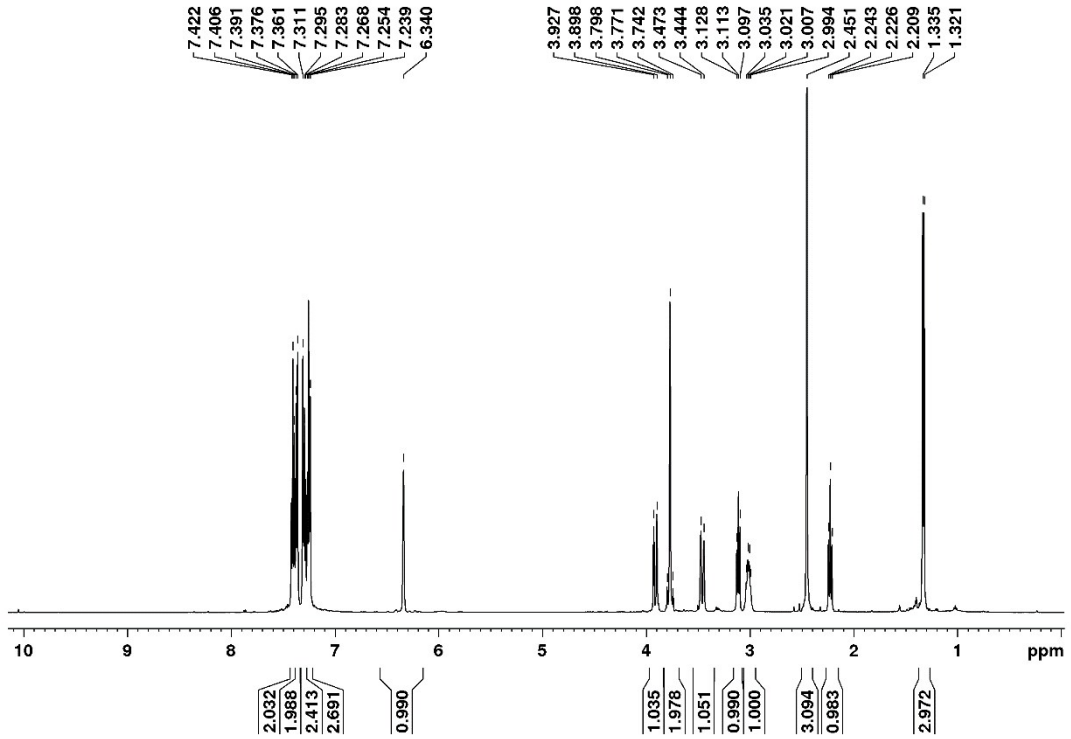




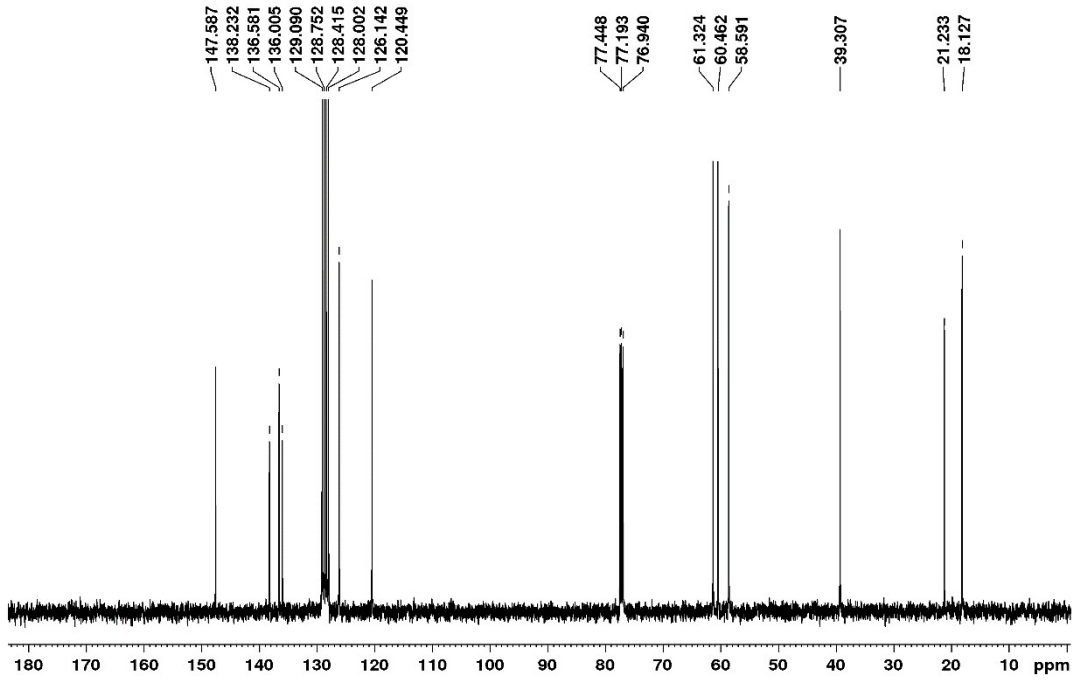
^{13}C-NMR spectrum of (*Z*)-3-benzylidene-1-(4-chlorobenzyl)-4-methylpyrrolidine (**3b**)



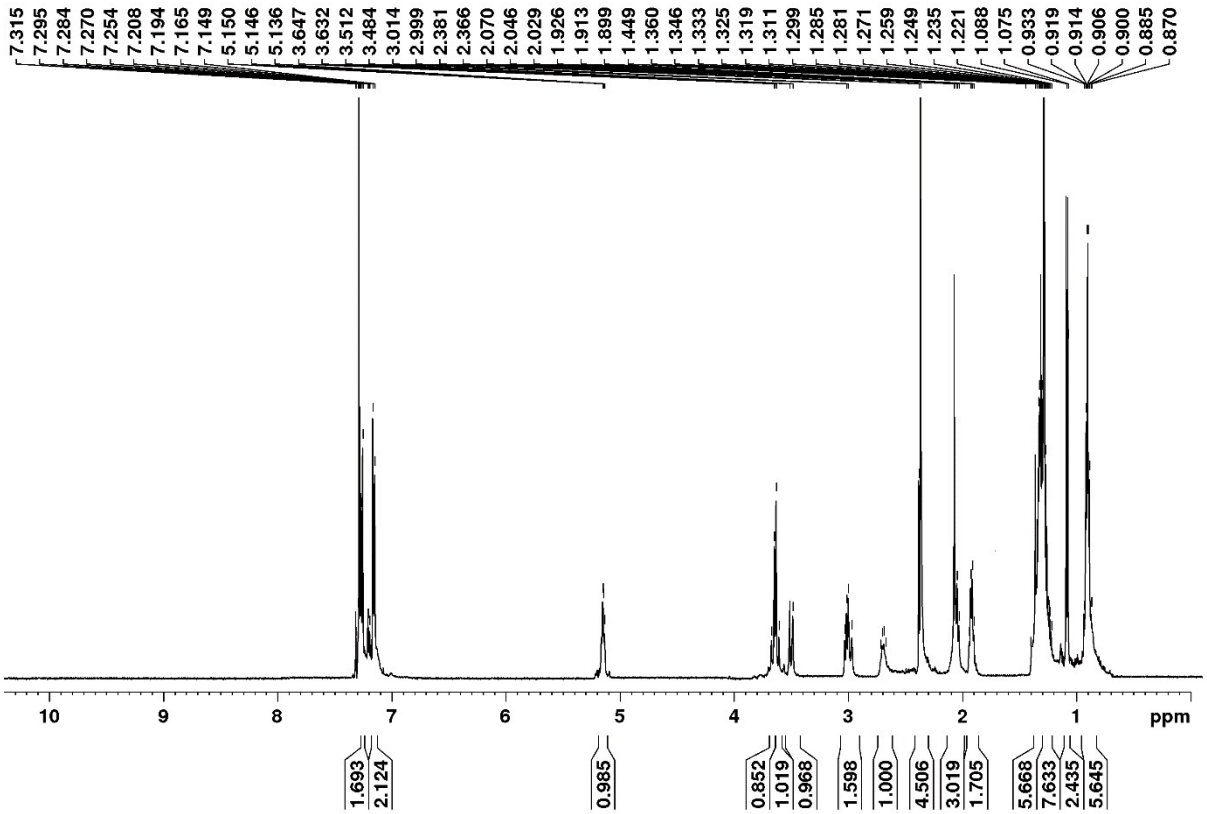
^{1}H-NMR spectrum of (*Z*)-3-benzylidene-4-methyl-1-(4-methylbenzyl)pyrrolidine (**3c**)



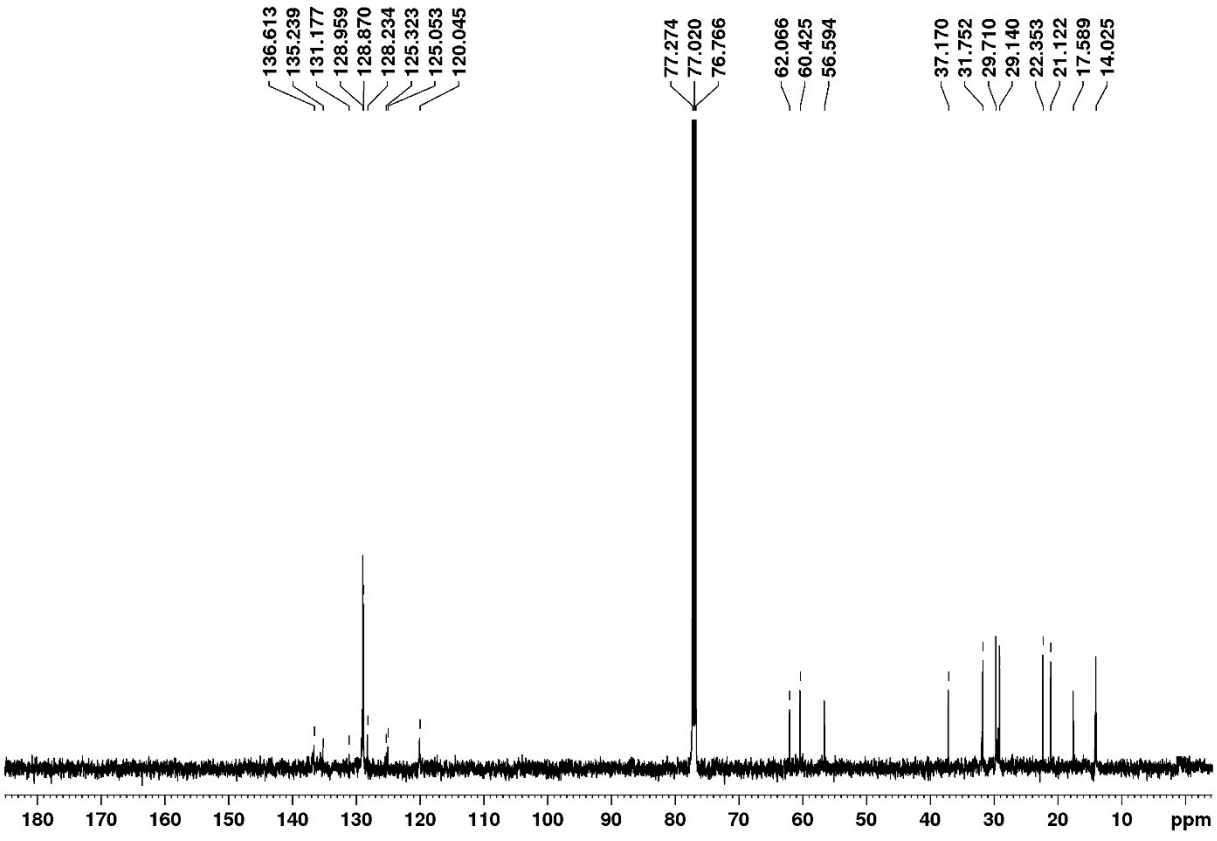
^{13}C-NMR spectrum of (*Z*)-3-benzylidene-4-methyl-1-(4-methylbenzyl)pyrrolidine (**3c**)



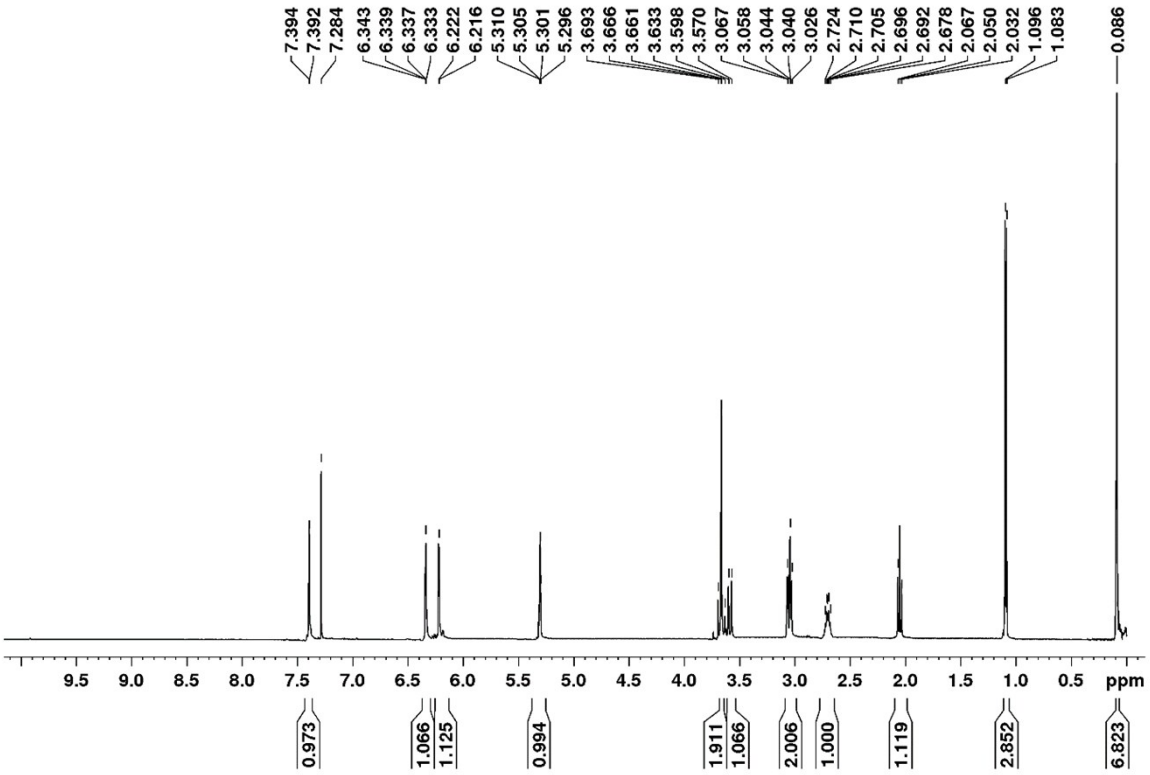
^{1}H-NMR spectrum of (*Z*)-3-methyl-1-(4-methylbenzyl)-4-pentylidenepyrrolidine (**3d**)



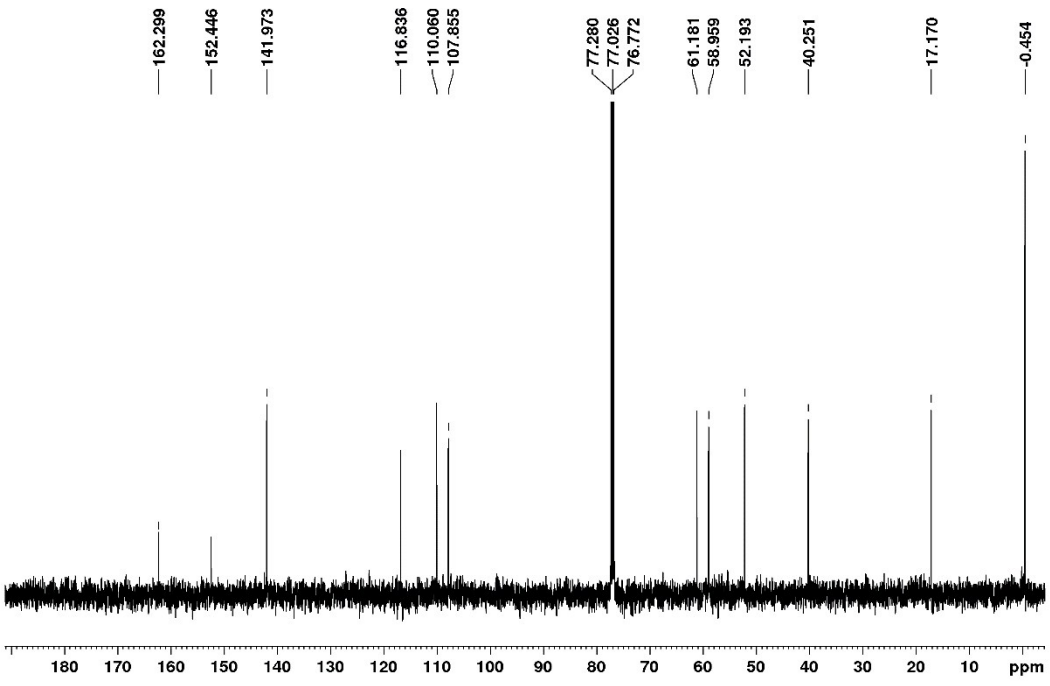
^{13}C-NMR spectrum of (*Z*)-3-methyl-1-(4-methylbenzyl)-4-pentylidenepyrrolidine (**3d**)



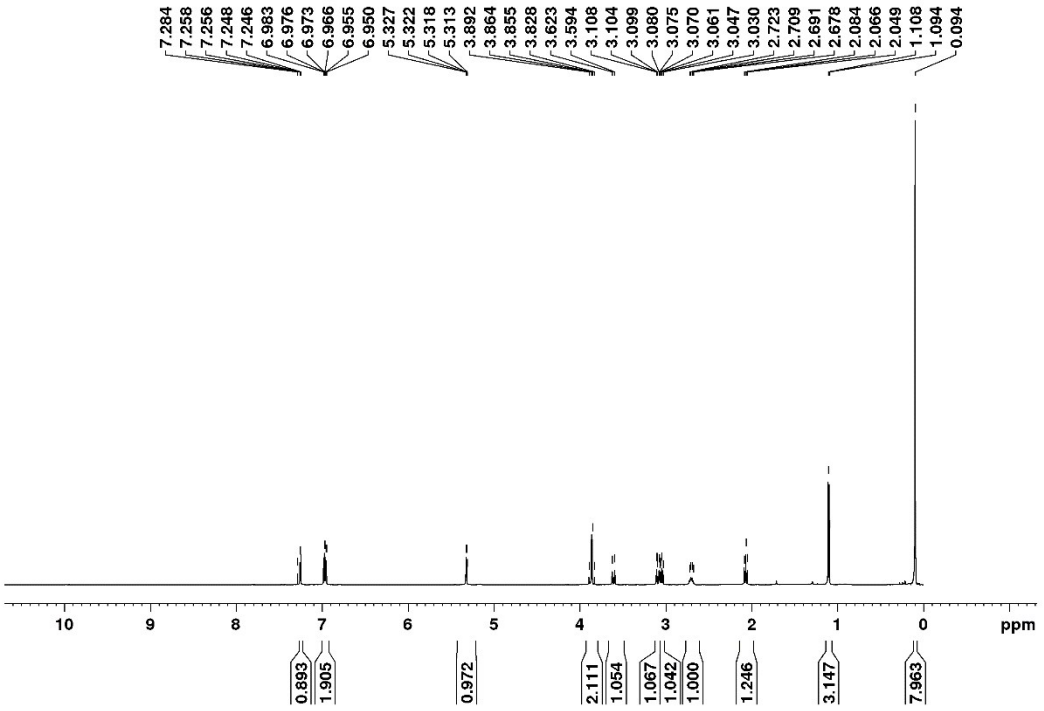
^{1}H-NMR spectrum of (*Z*)-1-(furan-2-ylmethyl)-3-methyl-4-((trimethylsilyl)methylene)pyrrolidine (**3e**)



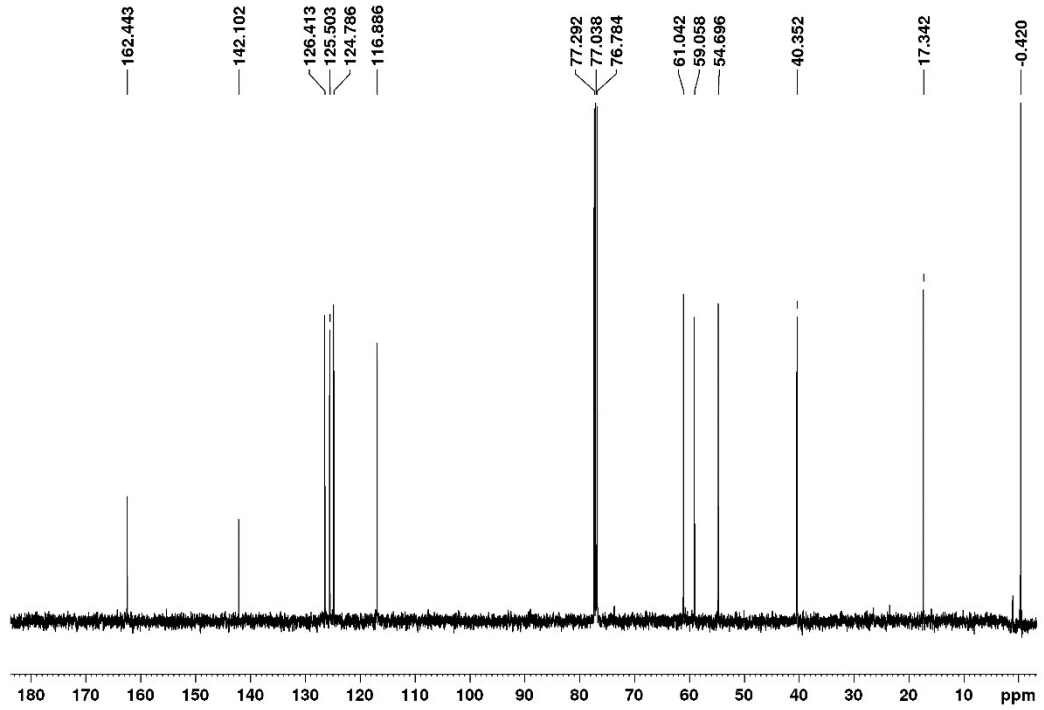
^{13}C-NMR spectrum of (Z)-1-(furan-2-ylmethyl)-3-methyl-4-((trimethylsilyl)methylene)pyrrolidine (**3e**)



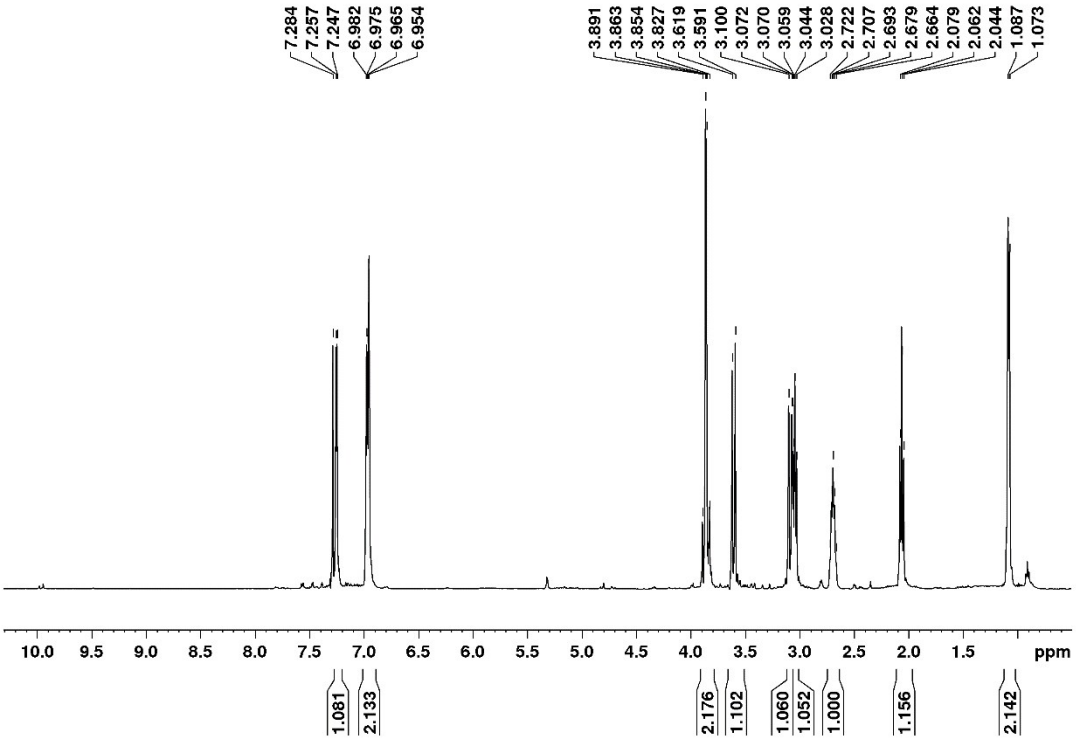
^{1}H-NMR spectrum of (*Z*)-3-methyl-1-(thiophen-2-ylmethyl)-4-((trimethylsilyl)methylene)pyrrolidine (**3f**)



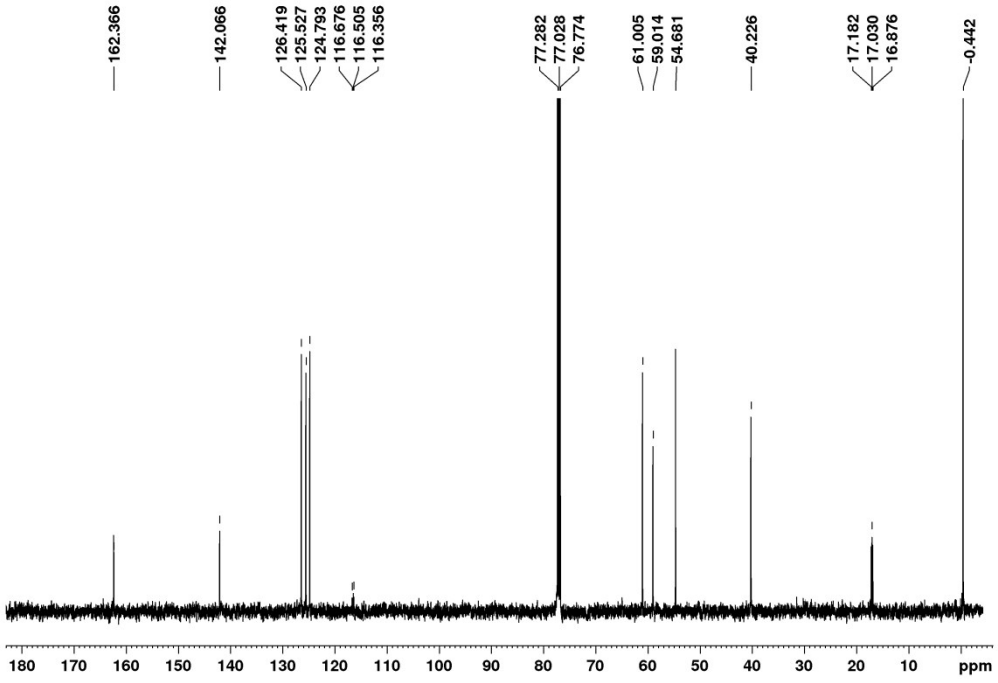
^{13}C-NMR spectrum of (*Z*)-3-methyl-1-(thiophen-2-ylmethyl)-4-((trimethylsilyl)methylene)pyrrolidine (**3f**)



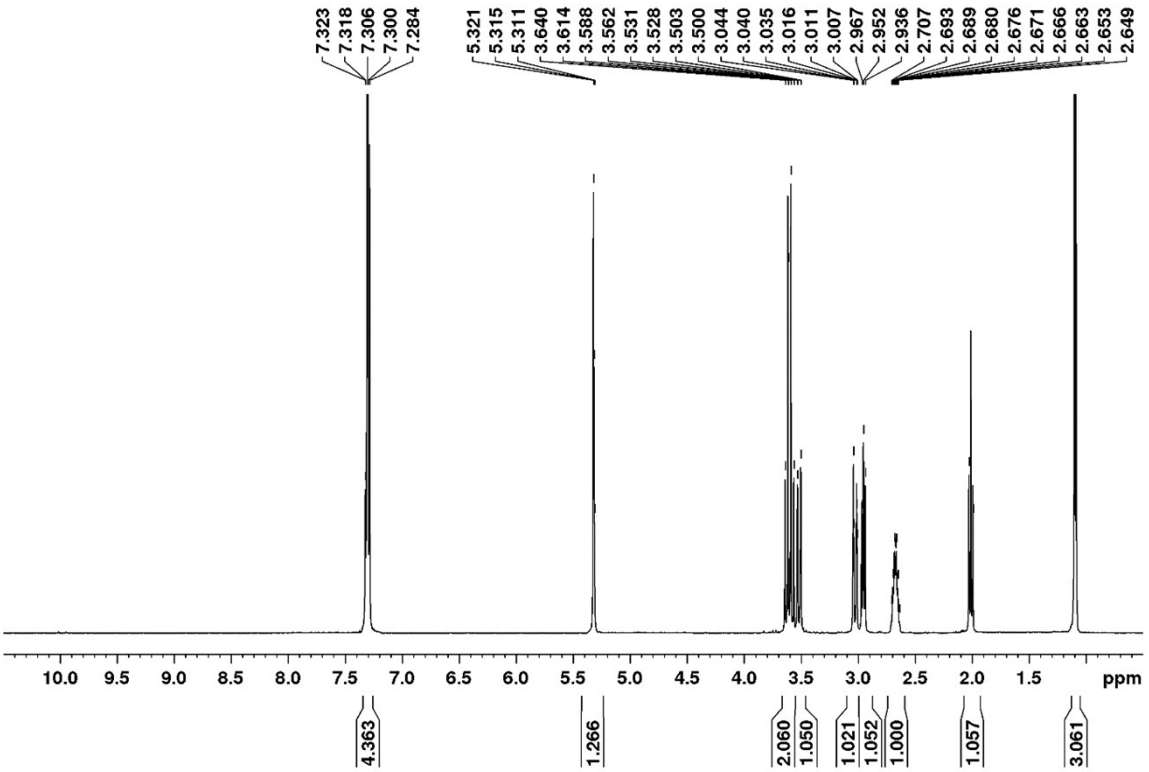
^{1}H-NMR spectrum of **(*Z*)-3-(methyl-*d*)-1-(thiophen-2-ylmethyl)-4-((trimethylsilyl)methylene-*d*)pyrrolidine (4f)**



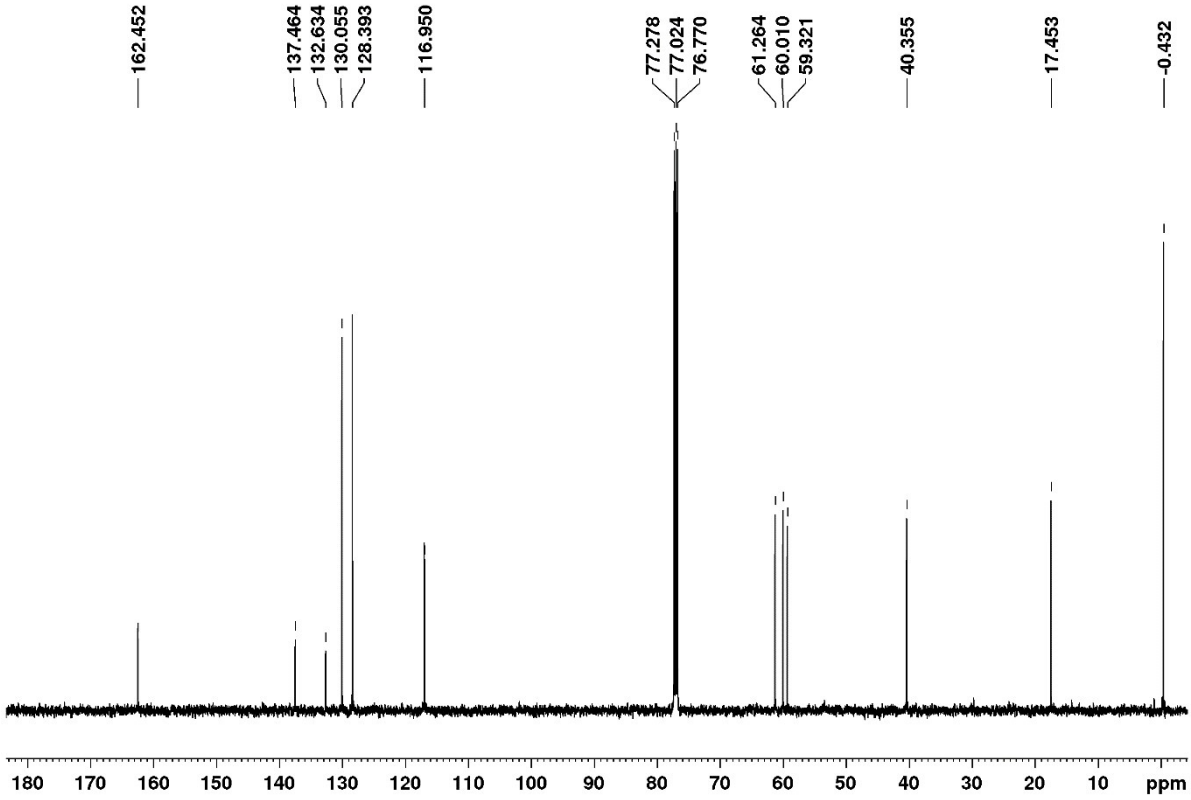
^{13}C-NMR spectrum of **(*Z*)-3-(methyl-*d*)-1-(thiophen-2-ylmethyl)-4-((trimethylsilyl)methylene-*d*)pyrrolidine (4f)**



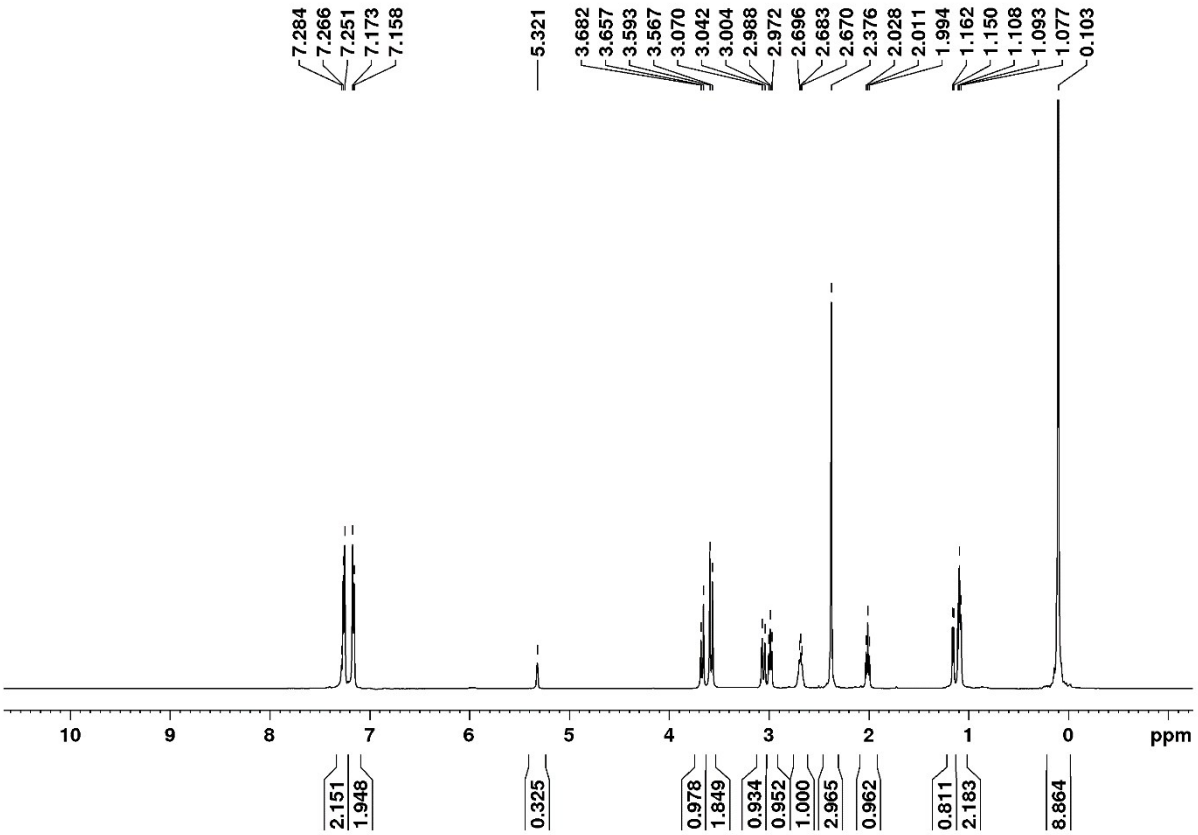
^{1}H-NMR spectrum of (*Z*)-1-(4-chlorobenzyl)-3-methyl-4-((trimethylsilyl)methylene)pyrrolidine (**3g**)



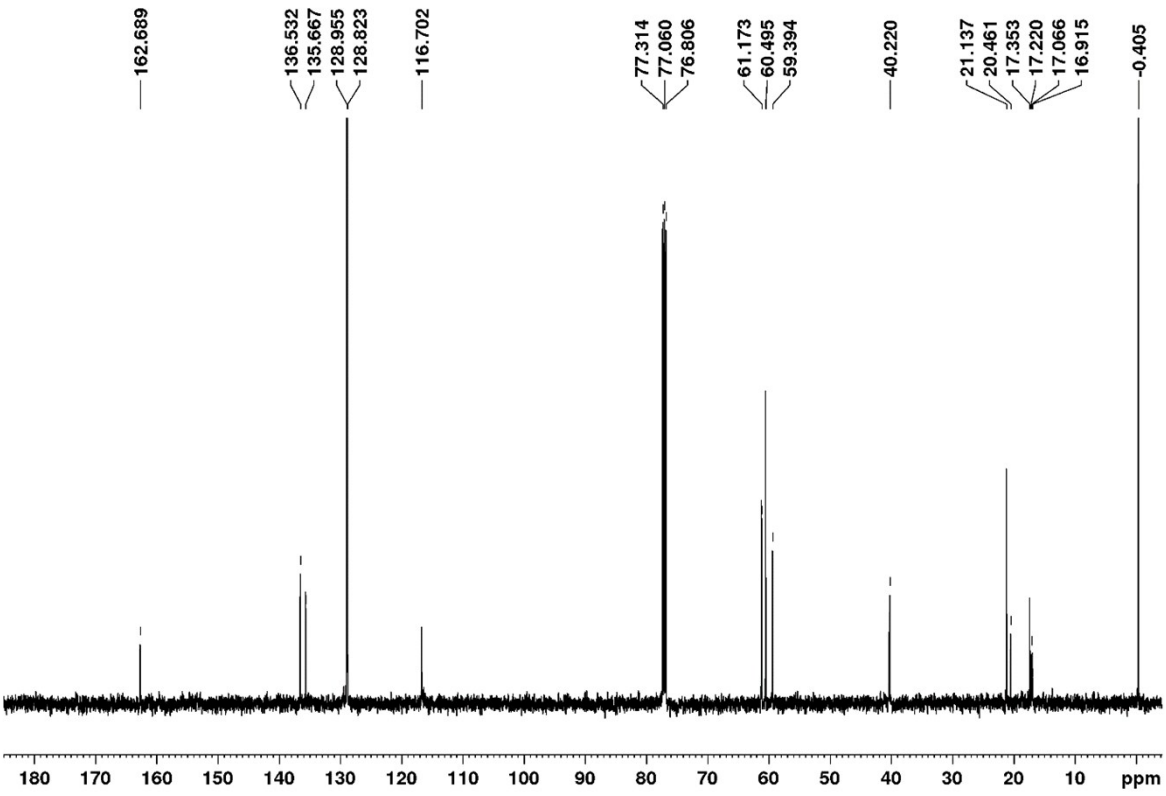
^{13}C-NMR spectrum of (*Z*)-1-(4-chlorobenzyl)-3-methyl-4-((trimethylsilyl)methylene)pyrrolidine (**3g**)



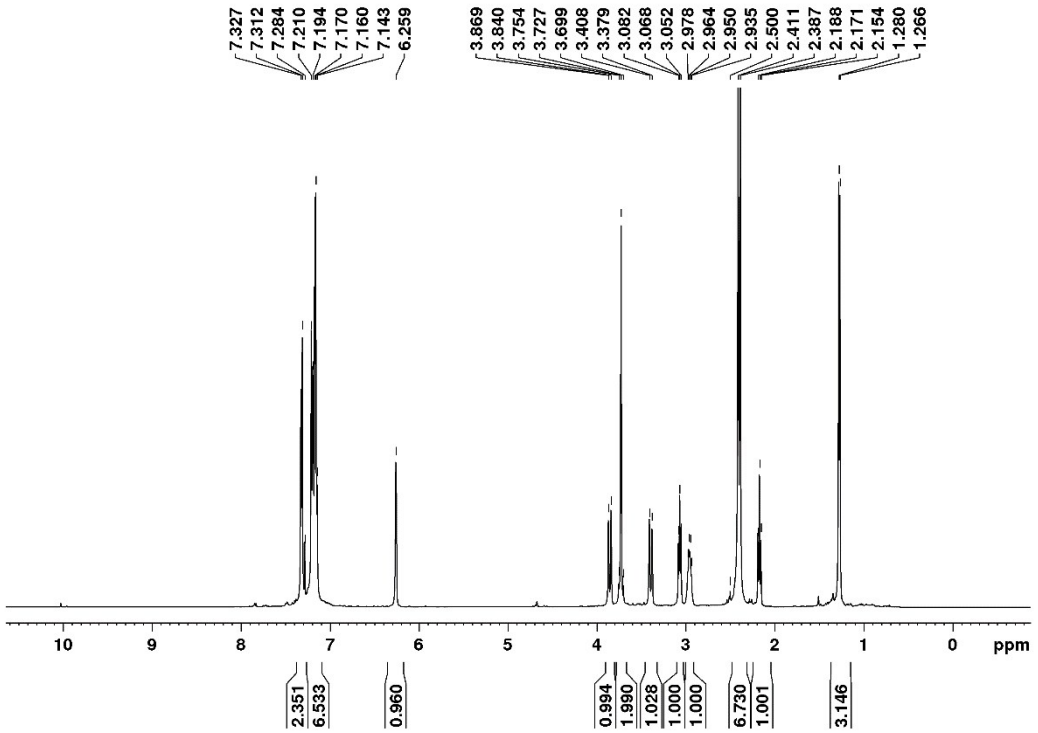
^{1}H-NMR spectrum of (*Z*)-3-(methyl-d)-1-(4-methylbenzyl)-4-((trimethylsilyl)methylene-d)pyrrolidine (**4h**)



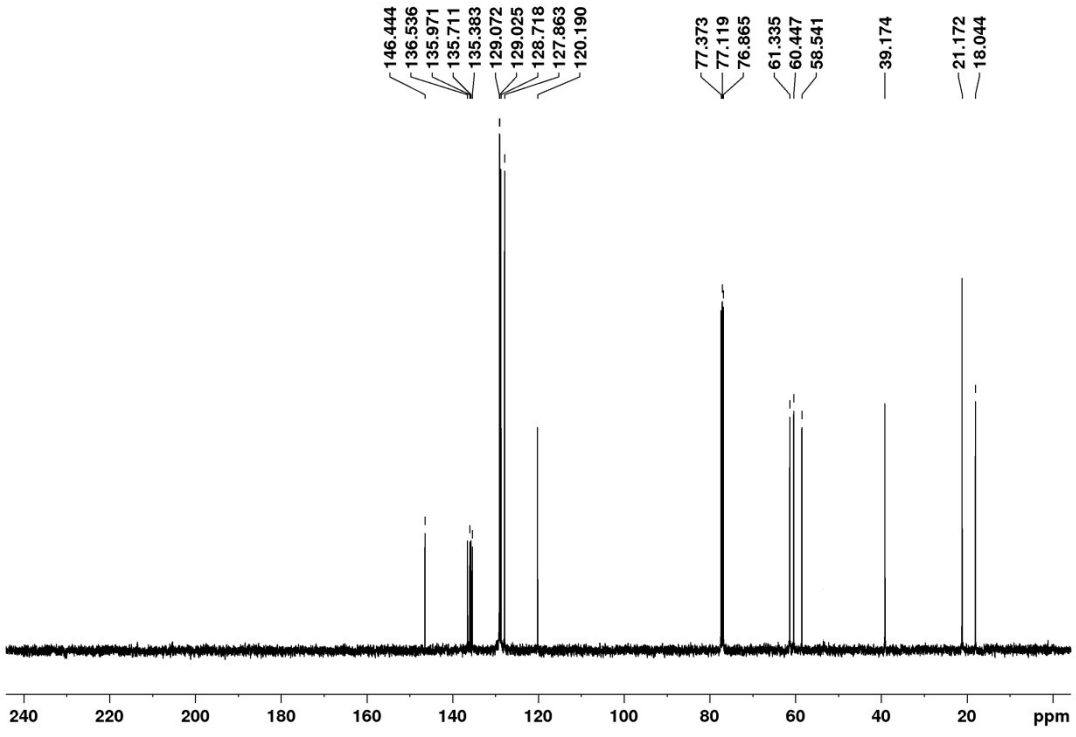
^{13}C-NMR spectrum of (*Z*)-3-(methyl-*d*)-1-(4-methylbenzyl)-4-((trimethylsilyl)methylene-d)pyrrolidine (**4h**)



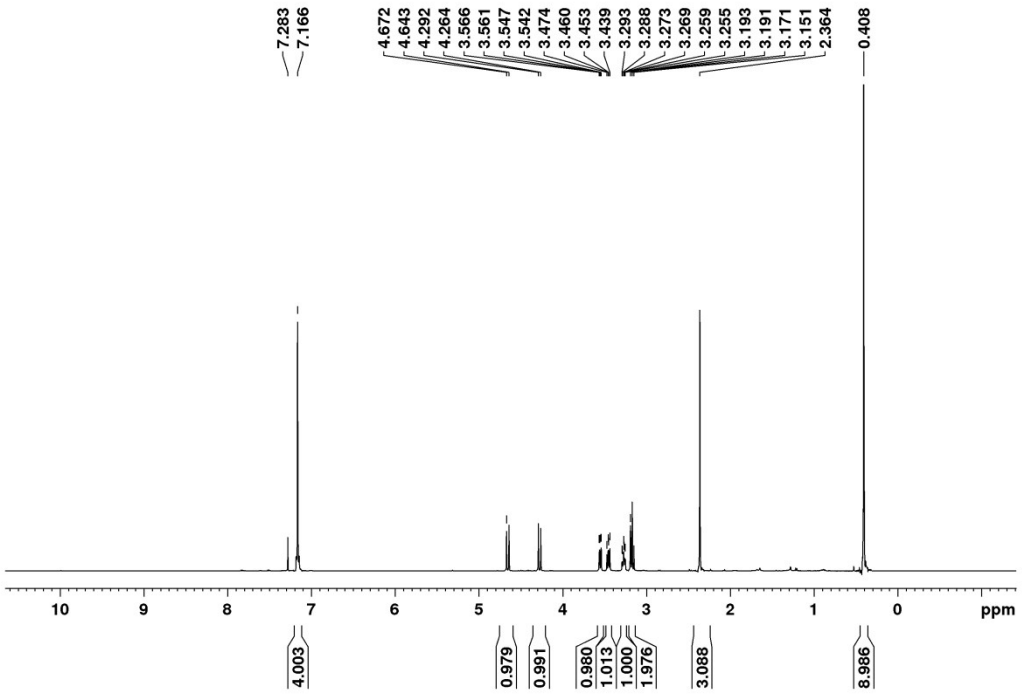
^{1}H-NMR spectrum of (*Z*)-3-methyl-1-(4-methylbenzyl)-4-(4-methylbenzylidene)pyrrolidine (**3i**)



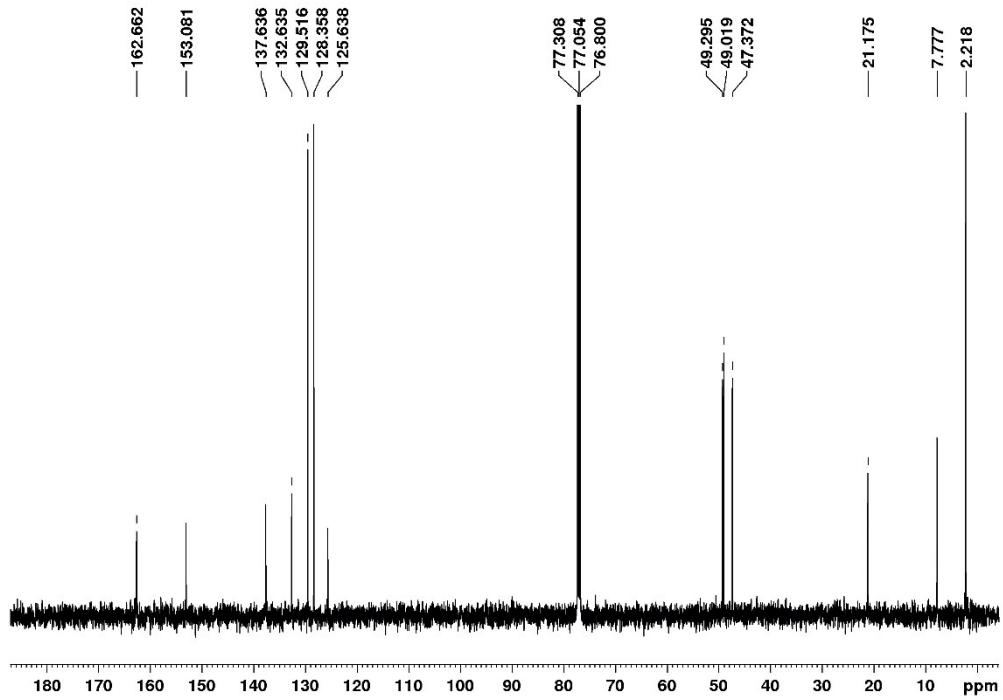
^{13}C-NMR spectrum of (*Z*)-3-methyl-1-(4-methylbenzyl)-4-(4-methylbenzylidene)pyrrolidine (**3i**)



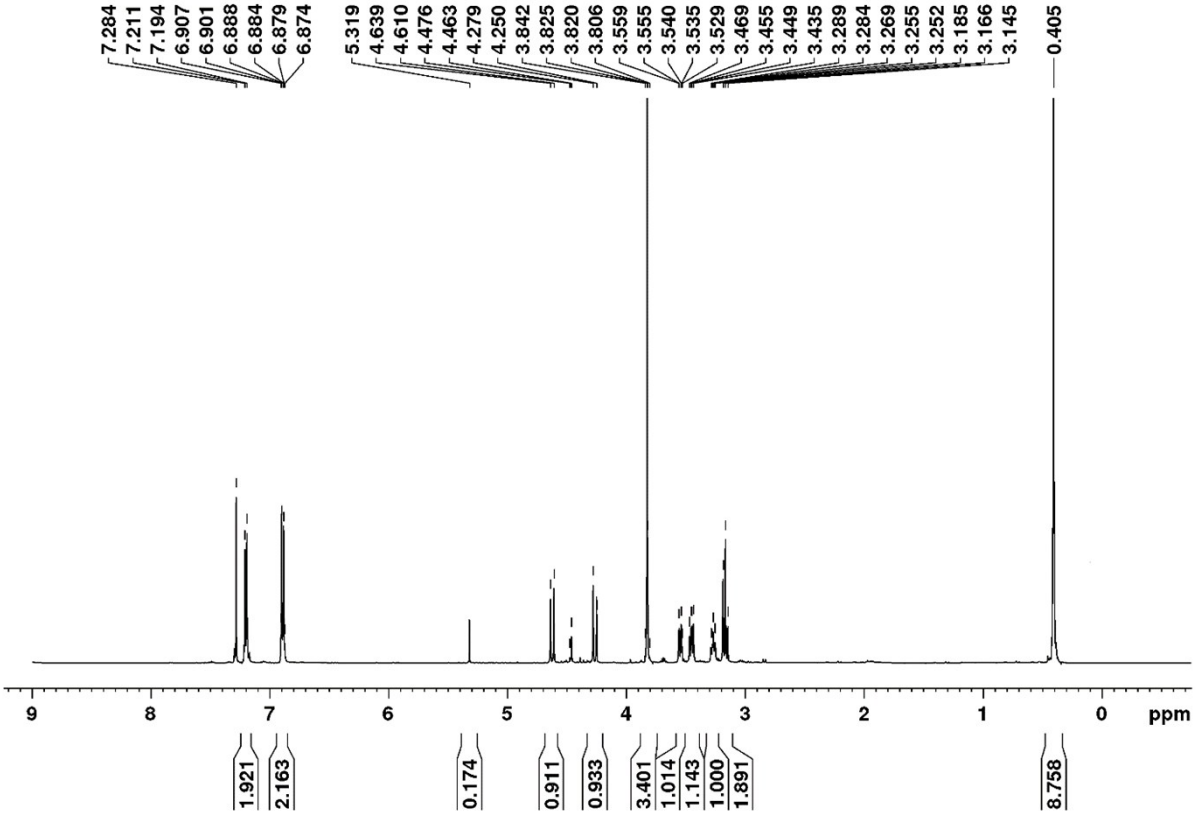
^{1}H-NMR spectrum of (*E*)-3-(iodo(trimethylsilyl)methylene)-4-(iodomethyl)-1-(4-methylbenzyl)pyrrolidin-2-one (**5h**)



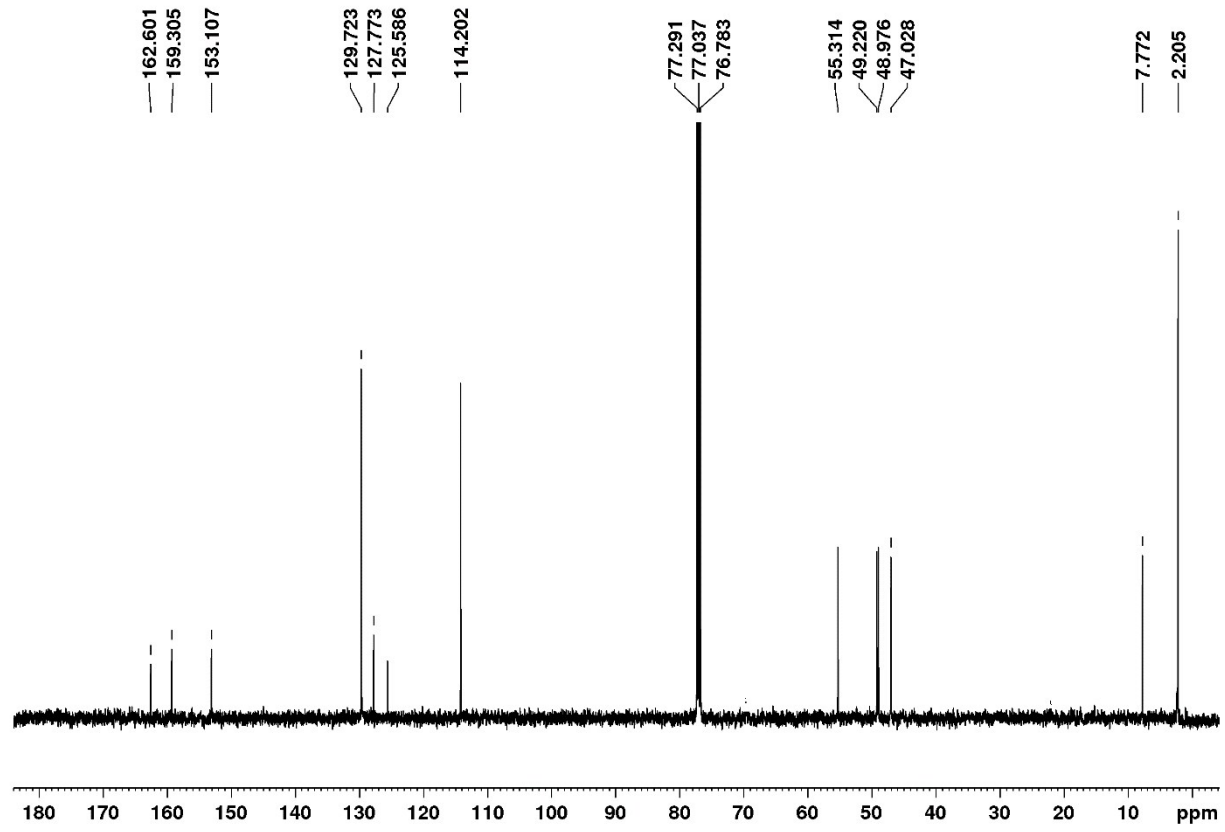
^{13}C-NMR spectrum of (*E*)-3-(iodo(trimethylsilyl)methylene)-4-(iodomethyl)-1-(4-methylbenzyl)pyrrolidin-2-one (**5h**)



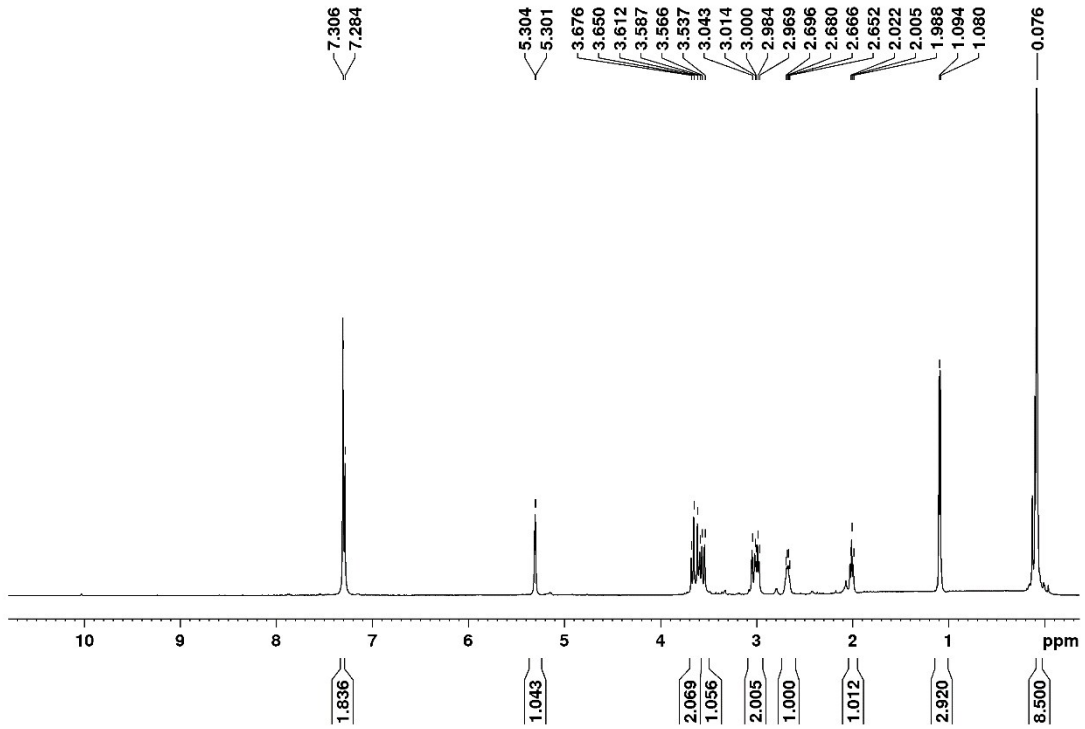
^{1}H-NMR spectrum of (*E*)-3-(iodo(trimethylsilyl)methylene)-4-(iodomethyl)-1-(4-methoxybenzyl)pyrrolidin-2-one (**5a**)



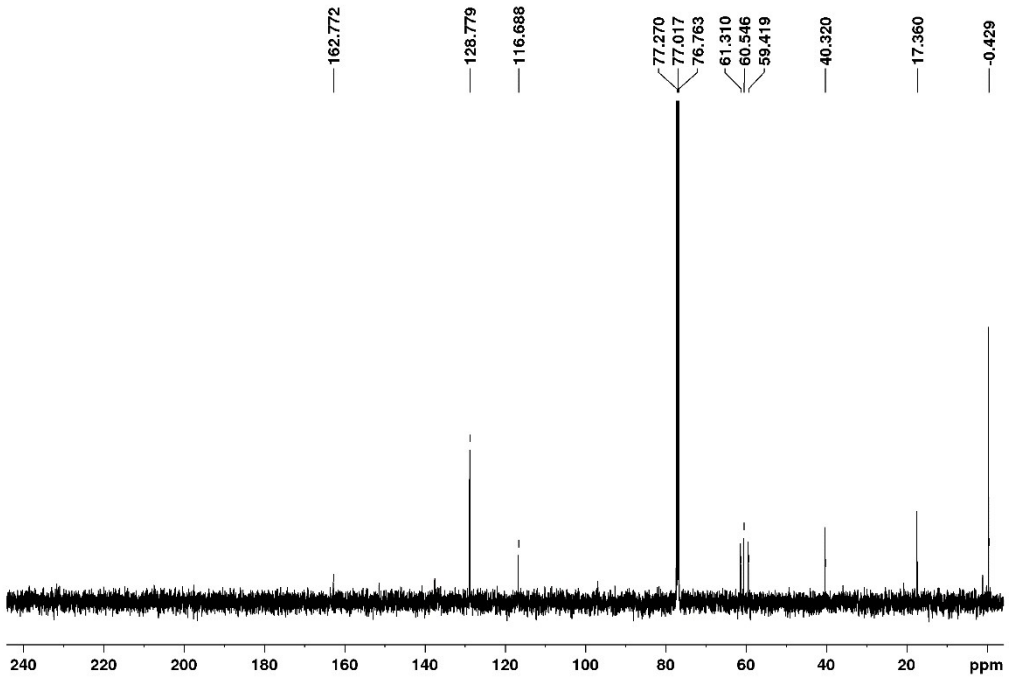
^{13}C-NMR spectrum of (*E*)-3-(iodo(trimethylsilyl)methylene)-4-(iodomethyl)-1-(4-methoxybenzyl)pyrrolidin-2-one (**5a**)



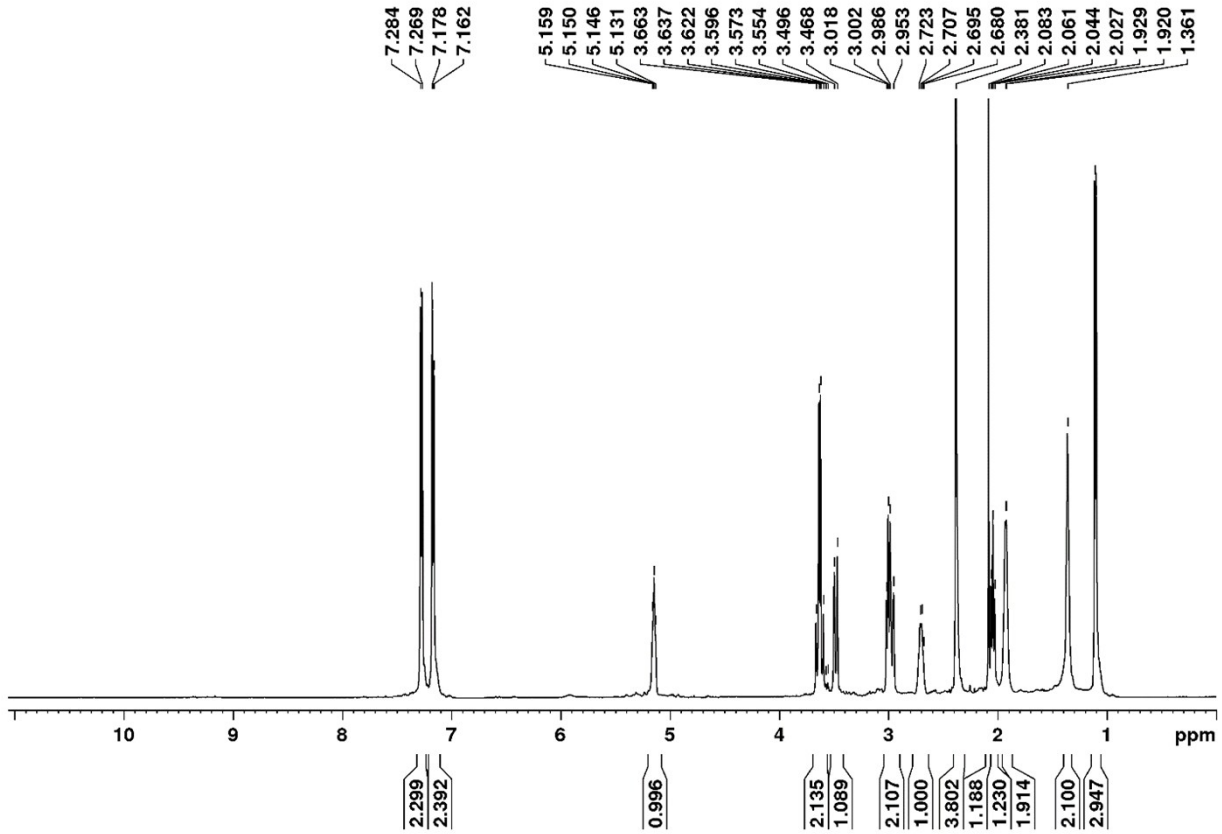
^{1}H-NMR spectrum of 1,4-bis(((*Z*)-3-methyl-4-((trimethylsilyl)methylene)pyrrolidin-1-yl)methyl)benzene (**7**)



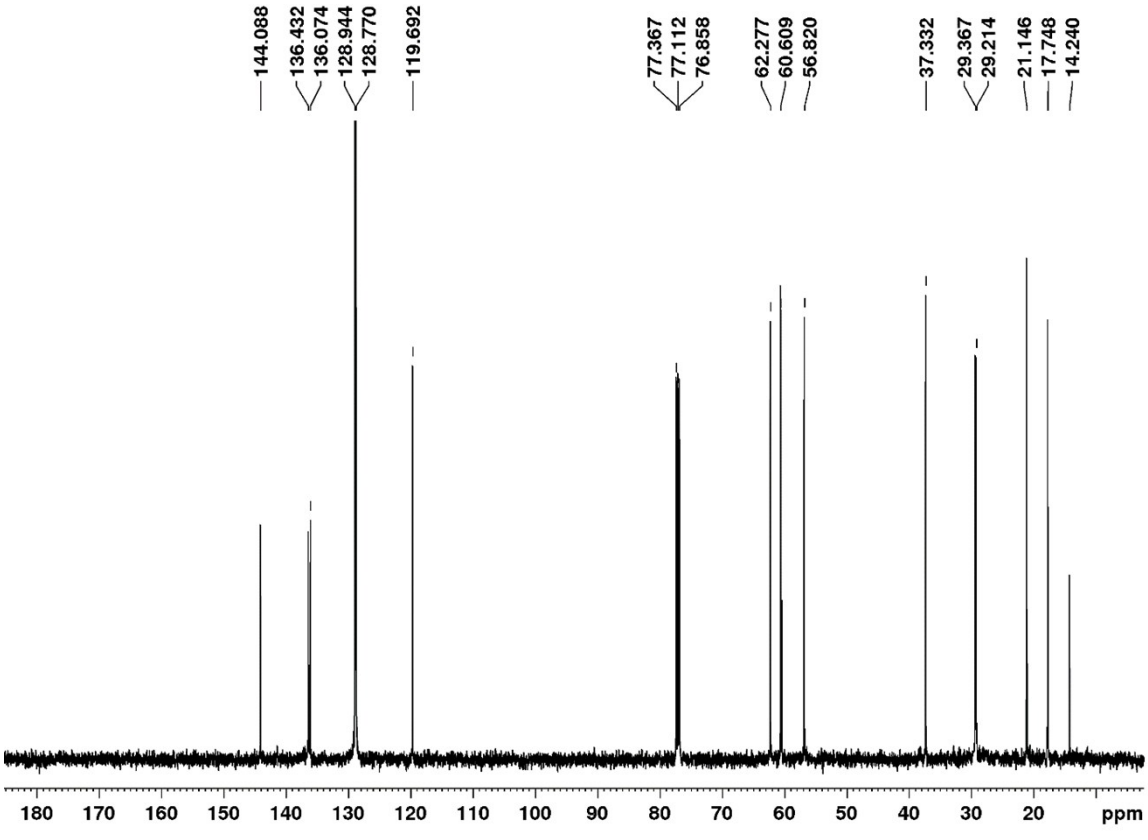
^{13}C-NMR spectrum of 1,4-bis(((*Z*)-3-methyl-4-((trimethylsilyl)methylene)pyrrolidin-1-yl)methyl)benzene (**7**)



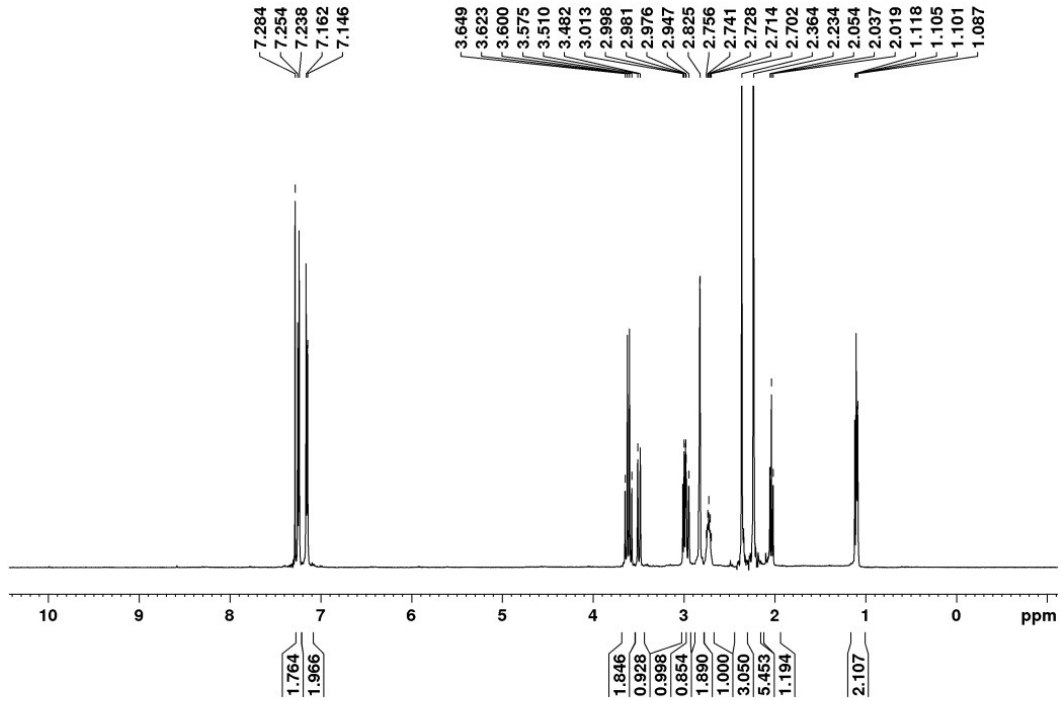
^{1}H-NMR spectrum of (4*Z*,4'*Z*)-4,4'-(octane-2,7-diylidene)bis(3-ethyl-1-(4-methylbenzyl)pyrrolidine) (**9**)



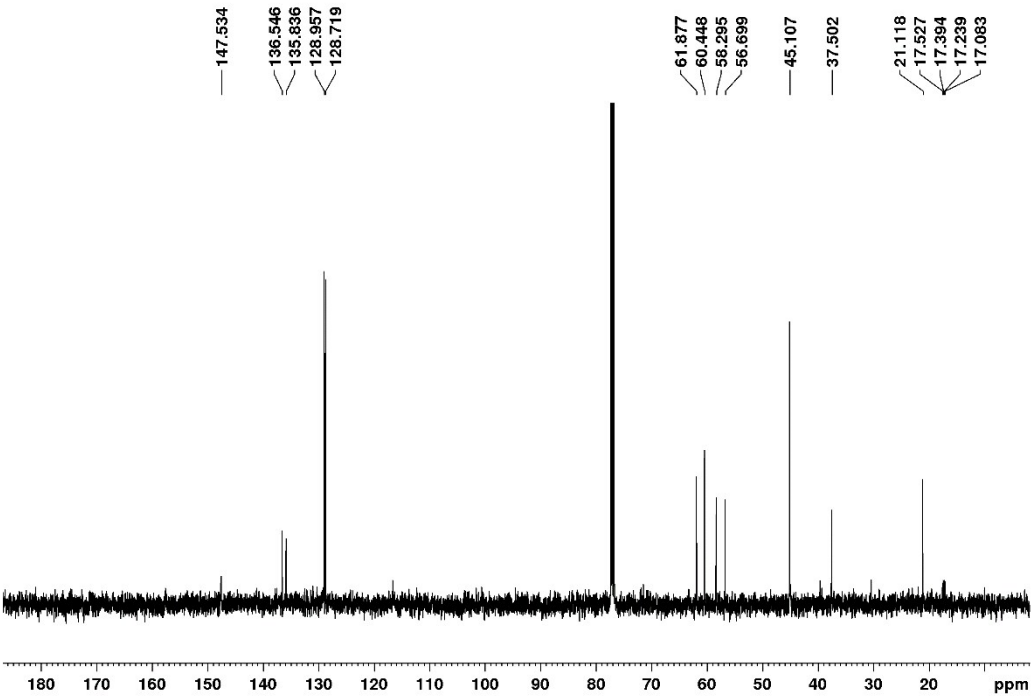
^{13}C-NMR spectrum of (4*Z*,4'*Z*)-4,4'-(octane-2,7-diylidene)bis(3-ethyl-1-(4-methylbenzyl)pyrrolidine) (**9**)



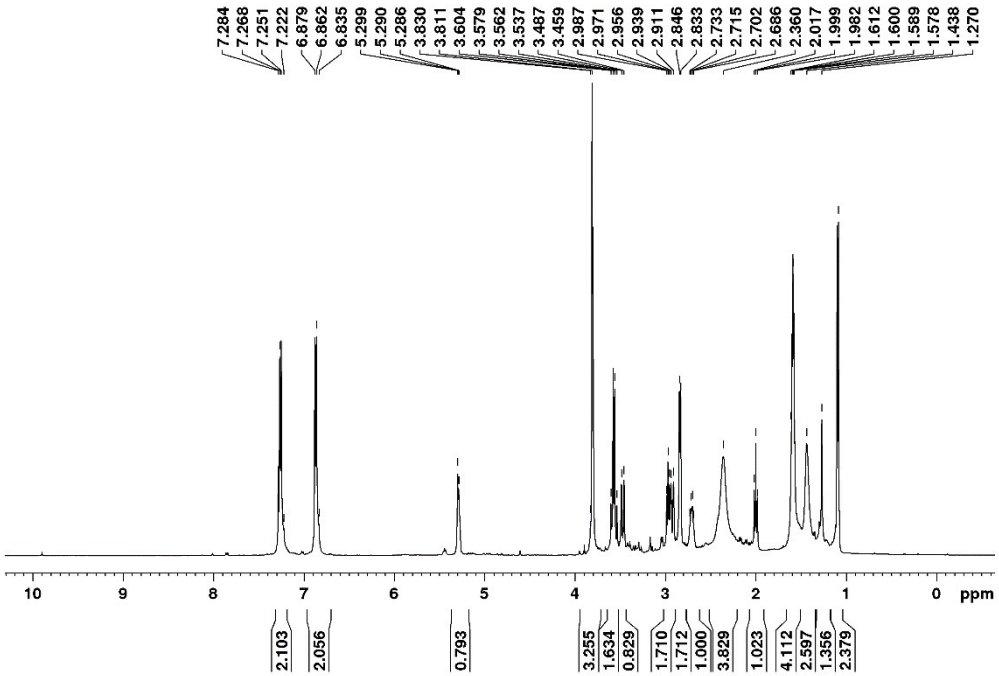
^{1}H-NMR spectrum of (*Z*)-*N*,*N*-dimethyl-2-(4-methyl-1-(4-methylbenzyl)pyrrolidin-3-ylidene)ethan-1-amine (**12a**)



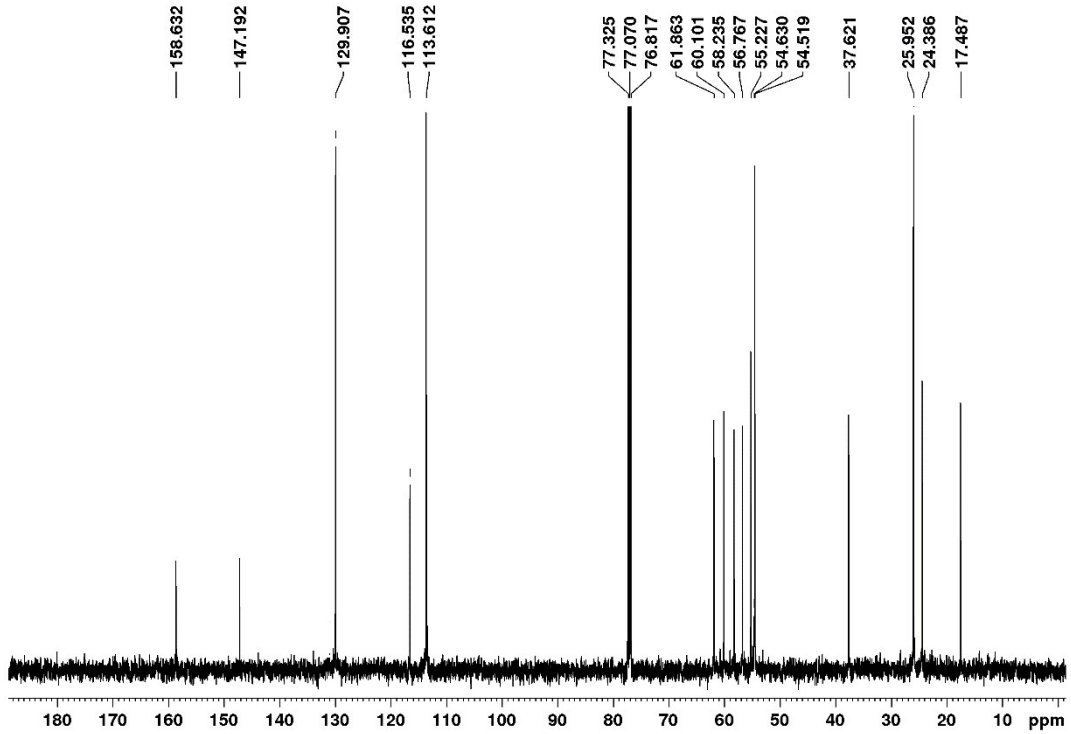
^{13}C-NMR spectrum of (*Z*)-*N*,*N*-dimethyl-2-(4-methyl-1-(4-methylbenzyl)pyrrolidin-3-ylidene)ethan-1-amine (**12a**)



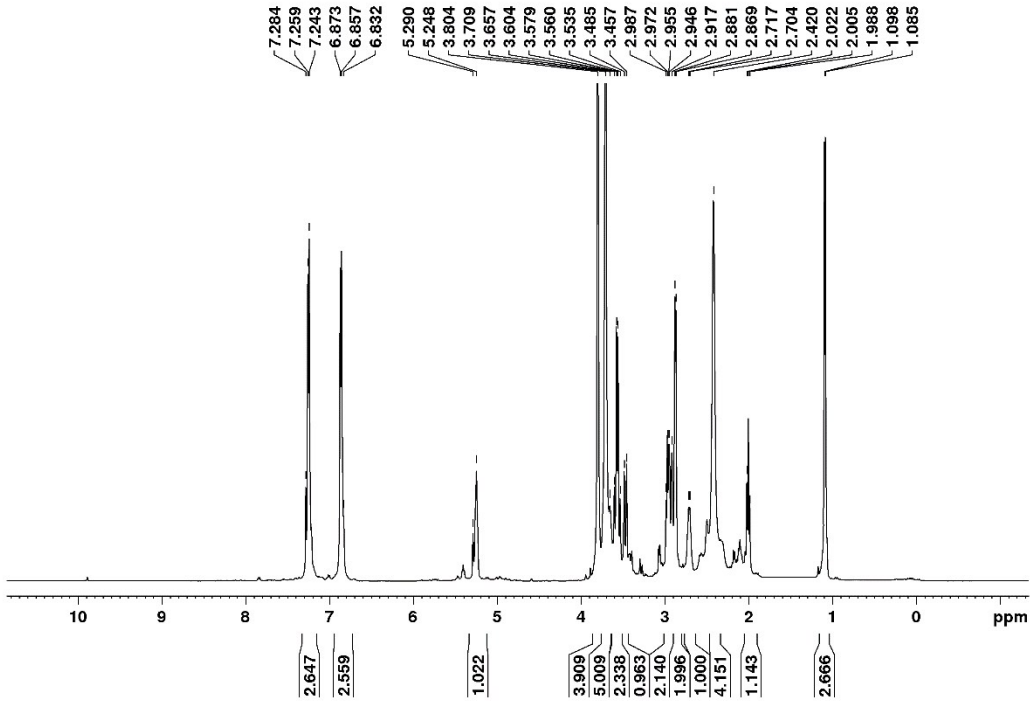
^{1}H-NMR spectrum of (*Z*)-1-(2-(1-(4-methoxybenzyl)-4-methylpyrrolidin-3-ylidene)ethyl)piperidine (**11c**)



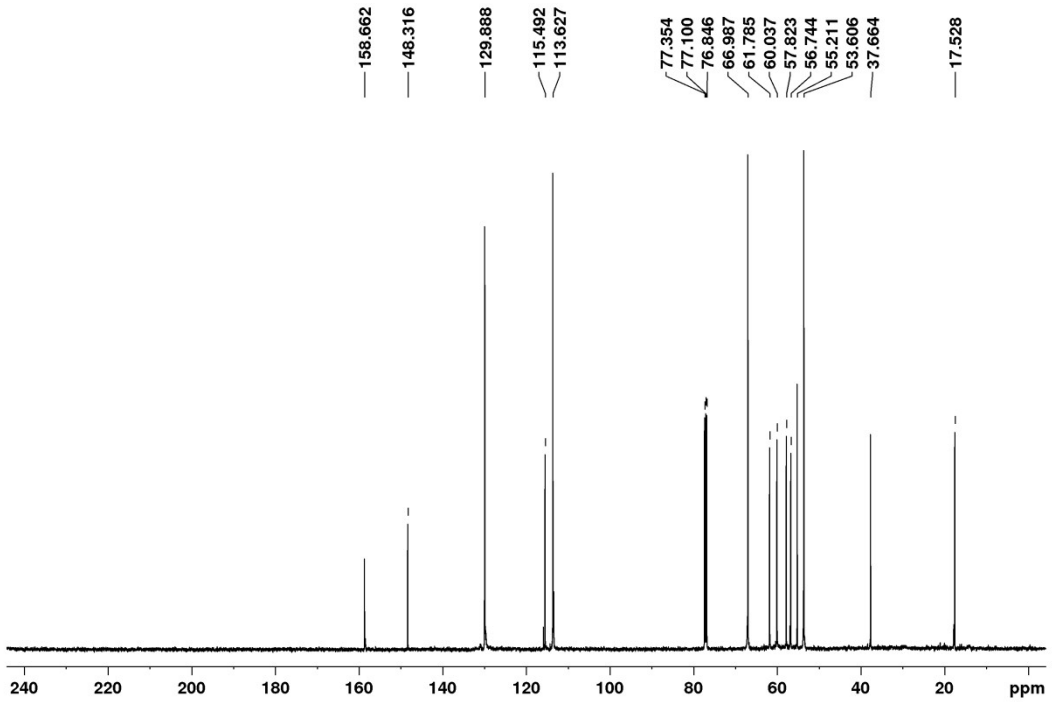
^{13}C-NMR spectrum of (*Z*)-1-(2-(1-(4-methoxybenzyl)-4-methylpyrrolidin-3-ylidene)ethyl)piperidine (**11c**)



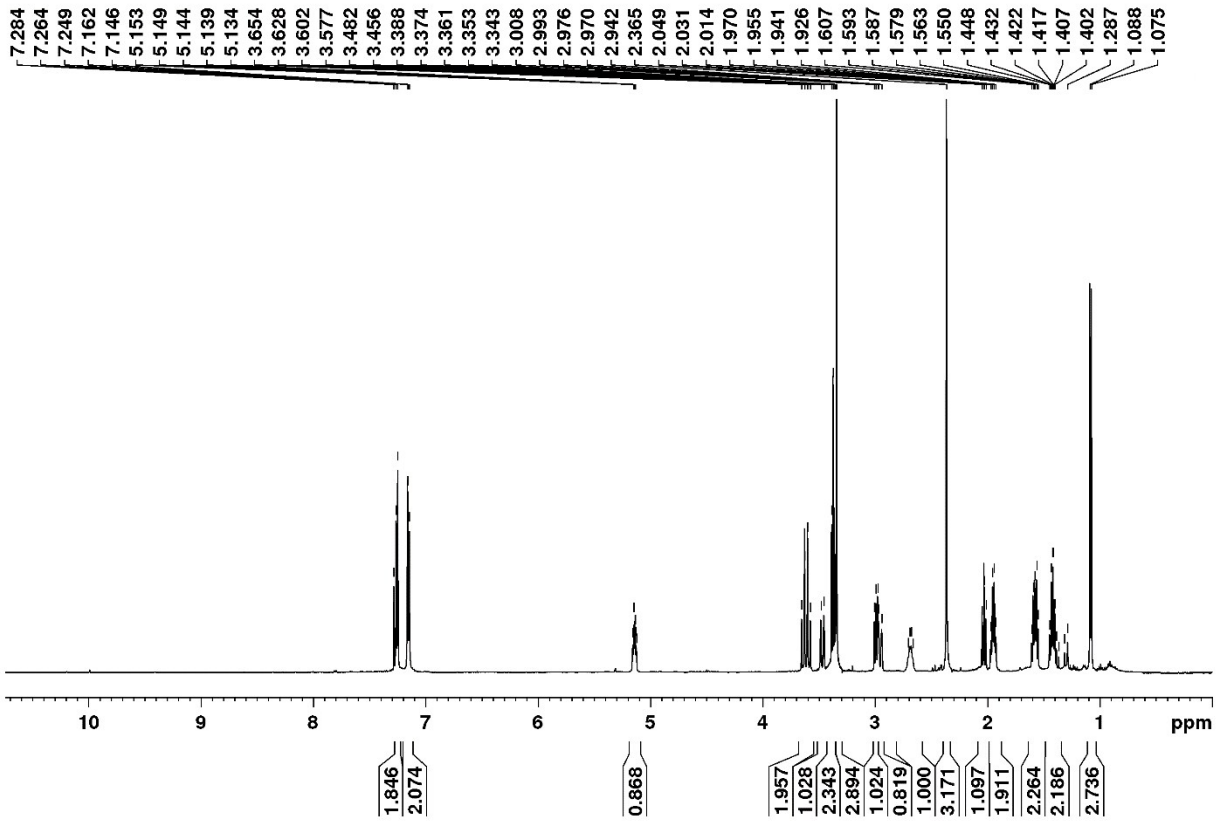
^{1}H-NMR spectrum of **(*Z*)-4-(2-(1-(4-methoxybenzyl)-4-methylpyrrolidin-3-ylidene)ethyl)morpholine (11b)**



^{13}C-NMR spectrum of **(*Z*)-4-(2-(1-(4-methoxybenzyl)-4-methylpyrrolidin-3-ylidene)ethyl)morpholine (11b)**



^{1}H-NMR spectrum of (*Z*)-3-(5-methoxypentylidene)-4-methyl-1-(4-methylbenzyl)pyrrolidine (**14a**)



^{13}C-NMR spectrum of (*Z*)-3-(5-methoxypentylidene)-4-methyl-1-(4-methylbenzyl)pyrrolidine (**14a**)