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Niobium- and zirconium-catalyzed reactions of substituted 2 alkynylamines with Et_2Zn

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Supporting information

Reagents and methods

General information

The reagents were obtained from Sigma-Aldrich or Acros. Hexane were distilled over P_2O_5. Diethyl ether, benzene and 1,2-dimethoxyethane were dried over sodium. 2-Alkynylamines **1b**,**d**,**f** were prepared by aminomethylation of terminal alkynes by bisamine [1]. Alkynylamines **1a**,**e**,**c**,**g** were prepared by aminomethylation of terminal alkynes with aqueous formaldehyde and secondary amines under CuI catalysis [2]. Nuclear magnetic resonance spectroscopy was performed on a Brucker Avance 500. The ^{1}H NMR spectra were recorded at 500 MHz and ^{13}C-{1H} 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-{1H} and ^{1}H NMR spectra of the compounds **2a-g**, **3b**,**e**, **5a-d**, **6d**, **7b** is shown in Figures 1,2. 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 allylamines obtained from starting 2-alkynylamines.

Preparation of allylamines **2a-g**, **3e**,**b** via Nb-Mg-catalyzed reaction of substituted propargylamines with Et_2Zn.

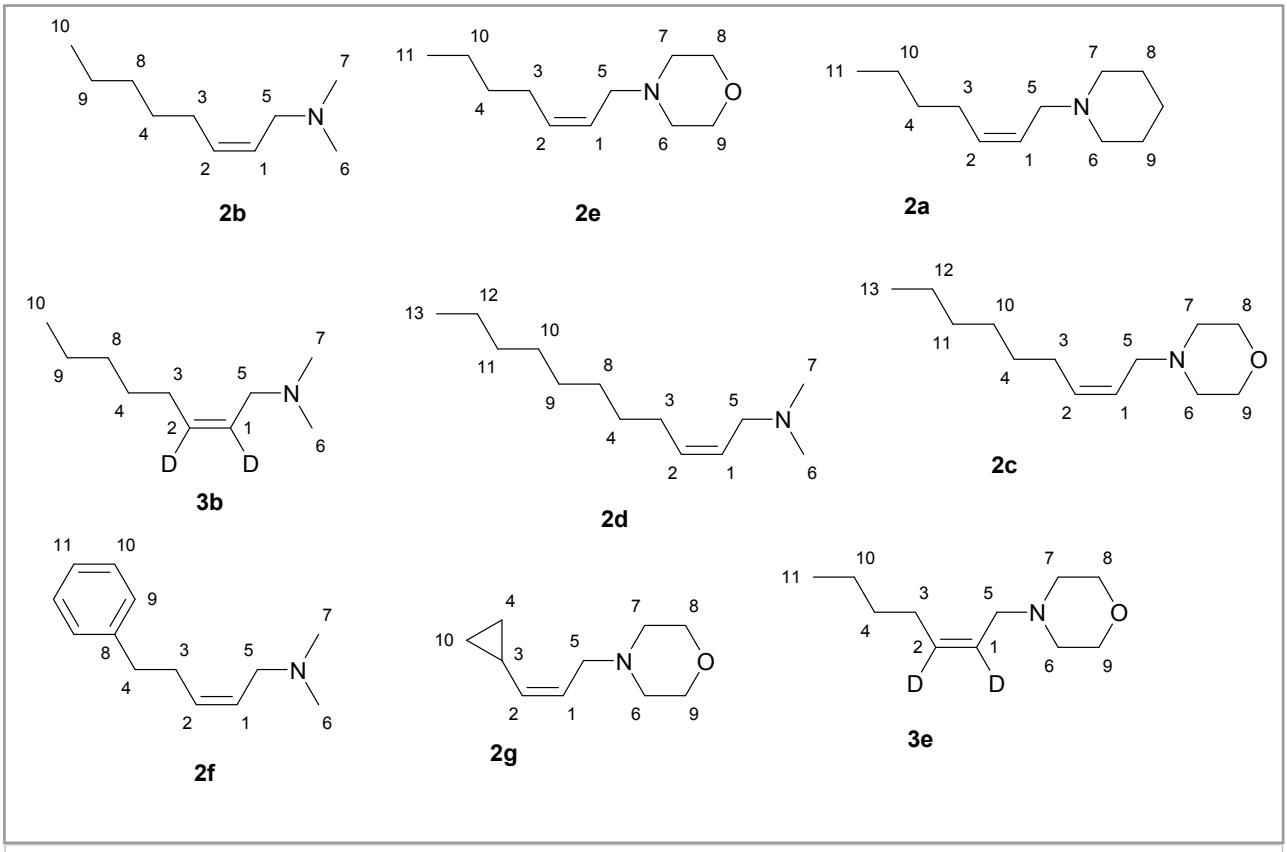

Figure 1. The numbering of atoms in the ^{13}C- and ^{1}H-NMR spectra of the compounds **2a-g**, **3b,e.**

(*Z*)-*N*,*N*-dimethyloct-2-en-1-amine; Typical Procedure.

To a solution of *N,N-dimethyloct-2-yn-1-amine* (306 mg, 2 mmol) and Et_2Zn (1 M in hexanes, 8 mL, 8 mmol) in Et_2O (6 mL) was added $NbCl_5$ (0.081g, 0.30 mmol). Ethylmagnesiurn bromide (1.4 M in Et_2O, 0.428 mL, 0.6 mmol) was then added and the reaction mixture rapidly turned black. After 18 h at 40 ^{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 (3×10 mL). The combined organic layers were washed with brine (20 mL), dried over anhydrous $MgSO_4$. The reaction mixture was filtered through a filter paper and concentrated in vacuo to give crude product as a yellow oil. The residue was distilled through a micro column at 20 mmHg to give **2b** (248 mg, 80%) as a colourless oil. b.p. 77 – 79 ^{o}C (20 mmHg).

^{1}H NMR (500MHz, $CDCl_3$): δ = 0.91 (s, 3H, C(10)H_3), 1.31 (s, 4H, C(9,8)H_2), 1.36 – 1.41 (m, 2H, C(4)H_2), 2.05 – 2.09 (m, 2H, C(3)H_2), 2.25 (s, 6H, C(6,7)H_3), 2.95 (d, *J* = 6 Hz, 2H, C(5)H_2), 5.44 – 5.49 (m, 1H, C(1)H), 5.53 – 5.61 (m, 1H, C(2)H).

^{13}C NMR (500MHz, $CDCl_3$): δ = 14.04 (C(10)), 22.54 (C(9)), 27.43 (C(3)), 29.24 (C(4)), 31.48 (C(8)), 45.22 (C(6,7)), 56.13 (C(5)), 126.59 ((C(1)), 132.97 (C(2).
MS (EI): m/z, % = 155 (18) [M^+], 98 (29), 84 (53), 58 (89), 45 (100).

Anal. calcd for $C_{10}H_{21}N$, (%): C, 77.35; H, 13.63; N, 9.02. Found, %: C, 77.58; H, 13.58; N, 8.71.

(*Z*)-1-(hept-2-en-1-yl)piperidine (2a)

Using the procedure described above 358 mg of *1-(hept-2-yn-1-yl)piperidine* (2 mmol) gave crude product that was distilled through a micro column at 3,4 mmHg to afford **2a** (239 mg, 66%) as a colourless oil. b.p. 107 – 110 ^{o}C (3,4 mmHg).

^{1}H NMR (500MHz, $CDCl_3$): δ = 0.88 (t, *J* = 7 Hz, 3H, C(11)H_3), 1.31 (s, 4H, C(4,10)H_2), 1.41 (m, 2H, C(12)H_2), 1.55 – 1.59 (m, 4H, C(8,9)H_2), 2.03 (q, *J* = 6 Hz, 2H, C(3)H_2), 2.36 (s, 4H, C(6,7)H_2), 2.95 (d, *J* = 6 Hz, 2H, C(5)H_2), 5.43 – 5.53 (m, 1H, C(1,2)H).

^{13}C NMR (500MHz, $CDCl_3$): δ = 13.93 (C(11)), 22.68 (C(10)), 24.37 (C(12)), 25.99 (C(8,9)), 27.16 (C(3)), 31.73 (C(4)), 54.51 (C(6,7)), 55.88 (C(5)), 126.43 ((C(1)), 132.71 (C(2)).

MS (EI): m/z, % = 181 (7) [M^+], 138 (4), 124 (10), 98 (29), 84 (100), 55 (30), 41 (15).

Anal. calcd for $C_{12}H_{23}N$, (%): C, 79.49; H, 12.79; N, 7.72; Found, %: C, 79.45; H, 12.92; N, 7.52.

(*Z*)-4-(non-2-en-1-yl)morpholine (2c)

Using the procedure described above 418 mg of *4-(non-2-yn-1-yl)morpholine* (2 mmol) gave crude product that was distilled through a micro column at 2,4 mmHg to afford **2c** (308 mg, 73%) as a colourless oil. b.p. 127 – 129 ^{o}C (2,4 mmHg).

^{1}H NMR (500MHz, $CDCl_3$): δ = 0.83 (t, *J* = 6 Hz, 3H, C(13)H_3), 1.22 – 1.25 (m, 6H, C(10 - 12)H_2), 1.26 – 1.30 (m, 2H, C(4)H_2), 1.98 – 2.02 (q, *J* = 7 Hz, 2H, C(3)H_2), 2.39 (s, 4H, C(6,7)H_2), 2.94 (d, *J* = 7 Hz, 2H, C(5)H_2), 3.64 – 3.66 (m, 4H, C(8,9)H_2), 5.36 – 5.40 (m, 1H, C(1)H), 5.49 – 5.53 (m, 1H, C(2)H).

^{13}C NMR (500MHz, $CDCl_3$): δ = 13.99 (C(13)), 22.55 (C(12)), 27.45 (C(3)), 28.87 (C(10)), 29.43 (C(4)), 31.65 (C(11)), 55.43 (C(5)), 53.59 (C(6,7)), 66.94 (C(8,9)), 125.33 (C(1)), 133.67 (C(2)).

MS (EI): m/z, % = 211 (3) [M^+], 126 (5), 87 (100), 86 (40), 57 (30), 40 (15).

Anal. calcd for $C_{13}H_{25}NO$, (%): C, 73.88; H, 11.92; N, 6.63; Found, %: C, 74.03; H, 12.08; N, 6.77.

(*Z*)-*N*,*N*-dimethylundec-2-en-1-amine (2d)

Using the procedure described above 390 mg of *N,N-dimethylundec-2-yn-1-amine* (2 mmol) gave crude product that was distilled through a micro column at 5 mmHg to afford **2d** (351 mg, 89%) as a colourless oil. b.p. 107 – 109 ^{o}C (5 mmHg).

^{1}H NMR (500MHz, $CDCl_3$): δ = 0.90 (t, *J* = 7 Hz, 3H, C(13)H_3), 1.29 (s, 8H, C(9 - 12)H_2), 1.35 – 1.38 (m, 4H, C(4,8)H_2), 2.04 – 2.09 (m, 2H, C(3)H_2), 2.25 (s, 6H,

C(6,7)H_3), 2.95 (d, *J* = 6 Hz, 2H, C(5)H_2), 5.44 – 5.49 (m, 1H, C(1)H), 5.52 – 5.57 (m, 1H, C(2)H).

^{13}C NMR (500MHz, $CDCl_3$): δ = 14.11 (C(13)), 22.68 (C(12)), 27.47 (C(3)), 29.29 (C(9, 10)), 29.49 (C(8)), 29.57 (C(4)), 31.89 (C(11)), 45.26 (C(6,7)), 56.16 (C(5)), 126.66 ((C(1)), 132.93 (C(2)).

MS (EI): m/z, % = 197 (9) [M^+], 110 (4), 98 (24), 84 (52), 58 (89), 45 (100).

Anal. calcd for $C_{13}H_{27}N$, (%): C, 79.11; H, 13.79; N, 7.10; Found, %: C, 79.16; H, 13.65; N, 6.95.

(*Z*)-4-(hept-2-en-1-yl)morpholine (2e)

Using the procedure described above 362 mg of *4-(hept-2-yn-1-yl)morpholine* (2 mmol) gave crude product that was distilled through a micro column at 5 mmHg to afford **2e** (275 mg, 75%) as a colourless oil. b.p. 110 – 112 °C (5 mmHg).

^{1}H NMR (500MHz, $CDCl_3$): δ = 0.89 (s, 3H, C(11)H_3), 1.21 – 1.25 (m, 4H, C(4, 10)H_2), 2.04– 2.07 (m, 2H, C(3)H_2), 2.45 (s, 4H, C(6,7)H_2), 3.01 (d, *J* = 6 Hz, 2H, C(5)H_2), 3.72 (s, 4H, C(8,9)H_2), 5.42 – 5.46 (m, 1H, C(1)H), 5.55 – 5.59 (m, 1H, C(2)H).

^{13}C NMR (500MHz, $CDCl_3$): δ = 13.94 (C(11)), 22.29 (C(10)), 27.20 (C(3)), 31.68 (C(4)), 53.46 (C(5)), 53.59 (C(6,7)), 66.98 (C(8,9)), 125.26 ((C(1)), 133.79 (C(2)).

MS (EI): m/z, % = 183 (10) [M^+], 140 (4), 110 (28), 87 (100), 57 (70), 41 (21).

Anal. calcd for $C_{11}H_{21}NO$, (%): C, 72.08; H, 11.55; N, 7.64; Found, %: C, 72.22; H, 11.56; N, 7.37.

(*Z*)-*N*,*N*-dimethyl-5-phenylpent-2-en-1-amine (2f)

Using the procedure described above 374 mg of *N,N-dimethyl-5-phenylpent-2-yn-1-amine* (2 mmol) gave crude product that was distilled through a micro column at 2,2 mmHg to afford **2f** (242 mg, 64%) as a colourless oil. b.p. 118 – 120 °C (2,2 mmHg).

^{1}H NMR (500MHz, $CDCl_3$): δ = 2.24 (s, 6H, C(6,7)H_3), 2.43 (q, *J* = 7 Hz, 2H, C(3)H_2), 2.71 (t, *J* = 7 Hz, 2H, C(4)), 2.94 (s, 2H, C(5)H_2), 5.51 – 5.55 (m, 1H, C(1)H), 5.59 – 5.64 (m, 1H, C(2)H), 7.30 (t, *J* = 7 Hz, 2H, C(9)H), 7.21 (d, *J* = 7 Hz, 3H, C(10,11)H).

^{13}C NMR (500MHz, $CDCl_3$): δ = 29.46 (C(3)), 35.80 (C(4)), 45.01 (C(6,7)), 55.93 (C(5)), 125.89 (C(11)), 127.38 (C(1)), 128.33 (C(9)), 128.49 (C(10), 131.73 (C(2)), 141.74 (C(8)).

MS (EI): m/z, % = 189 (16) [M^+], 144 (11), 143 (11), 129 (59), 98 (45), 91 (64), 58 (100), 45 (90).

Anal. calcd for $C_{13}H_{19}N$, (%): C, 82.48; H, 10.12; N, 7.40; Found, %: C, 82.44; H, 9.97; N, 7.27.

(*Z*)-4-(3-cyclopropylallyl)morpholine (2g)

Using the procedure described above 330 mg of *4-(3-cyclopropylprop-2-yn-1-yl)morpholine* (2 mmol) gave crude product that was distilled through a micro column at 4 mmHg to afford **2g** (230 mg, 69%) as a colourless oil. b.p. 90 – 92 °C (4 mmHg).

^{1}H NMR (500MHz, $CDCl_3$): δ = 0.26 – 0.28 (m, 2H (A), C(4,10)H_2), 0.68 – 0.71 (m, 2H (B), C(4,10)H_2), 1.26 – 1.30 (m, 2H, C(4)H_2), 1.49 – 1.57 (m, 1H, C(3)H), 2.44 (s, 4H, C(6,7)H_2), 3.08 (d, *J* = 7 Hz, 2H, C(5)H_2), 3.66 – 3.67 (m, 4H, C(8,9)H_2), 5.29 – 5.34 (m, 1H, C(1)H), 4.87 (t, *J* = 10 Hz, 1H, C(2)H).

^{13}C NMR (500MHz, $CDCl_3$): δ = 6.46 (C(4,10)), 9.76 (C(3)), 53.61 (C(6,7)), 55.84 (C(5)), 66.98 (C(8,9)), 123.39 (C(1)), 137.76 (C(2)).

MS (EI): m/z, % = 167 (10) [M^+], 138 (33), 87 (70), 79 (87), 56 (69), 40 (100).

Anal. calcd for $C_{10}H_{17}NO$, (%): C, 71.81; H, 10.25; N, 8.37; Found, %: C, 71.98; H, 10.35; N, 8.35.

(*Z*)-*N*,*N*-dimethyloct-2-en-1-amine-2,3-d_2 (3b)

Using the procedure described above 306 mg of *N,N-dimethyloct-2-yn-1-amine* (2 mmol) and D_2O gave crude product that was distilled through a micro column at 5 mmHg to afford **3b** (267 mg, 85%) as a colourless oil. b.p. 107 – 109 °C (5 mmHg).

^{1}H NMR (500MHz, $CDCl_3$): δ = 0.90 (s, 3H, C(10)H_3), 1.27 – 1.30 (m, 4H, C(8,9)H_2), 1.35 – 1.39 (m, 2H, C(4)H_2), 2.03 – 2.07 (m, 2H, C(3)H_2), 2.24 (s, 6H, C(6,7)H_3), 2.94 (d, *J* = 6 Hz, 2H, C(5)H_2).

^{13}C NMR (500MHz, $CDCl_3$): δ = 14.04 (C(10)), 22.54 (C(9)), 27.28 – 27.42 (C(3)), 29.23 (C(4)), 31.48 (C(8)), 45.25 (C(6,7)), 56.09 (d, *J* = 11 Hz, C(5)), 126.57 (d, *J* = 17 Hz, C(1)), 132.85 (d, *J* = 15 Hz, C(2)).

MS (EI): m/z, % = 157 (26) [M^+], 100 (21), 86 (36).

Anal. calcd for $C_{10}H_{19}D_2N$, (%): C, 76.36; N, 8.90; Found, %: C, 76.39; N, 9.02.

(*Z*)-4-(hept-2-en-1-yl-2,3-d_2)morpholine (3e)

Using the procedure described above 362 mg of *4-(hept-2-yn-1-yl)morpholine* (2 mmol) and D_2O gave crude product that was distilled through a micro column at 2,4 mmHg to afford **3e** (259 mg, 70%) as a colourless oil. b.p. 119 – 121 °C (2,4 mmHg).

^{1}H NMR (500MHz, $CDCl_3$): δ = 0.91 (t, *J* = 6 Hz, 3H, C(11)H_3), 1.23 – 1.28 (m, 4H, C(4,10)H_2), 2.07 (t, *J* = 6 Hz, 2H, C(3)H_2), 2.47 (s, 4H, C(6,7)H_2), 3.03 (s, 2H, C(5)H_2), 3.73 (s, 4H, C(8,9)H_2).

^{13}C NMR (500MHz, $CDCl_3$): δ = 13.96 (C(11)), 22.32 (C(10)), 27.07 (C(3)), 31.68 (C(4)), 53.59 (C(6,7)), 55.34 (C(5)), 66.99 (C(8,9)).

MS (EI): m/z, % = 185 (7) [M^+], 156 (1), 128 (6), 112 (19), 87 (100), 57 (70), 57 (70), 42 (13).

Anal. calcd for $C_{11}H_{19}D_2NO$, (%): C, 71.30; N, 7.56; Found, %: C, 71.46; N, 7.42.

Preparation of allylamines **5a-d**, **6d, 7b** via Zr-Mg-catalyzed reaction of substituted propargylamines with Et_2Zn.

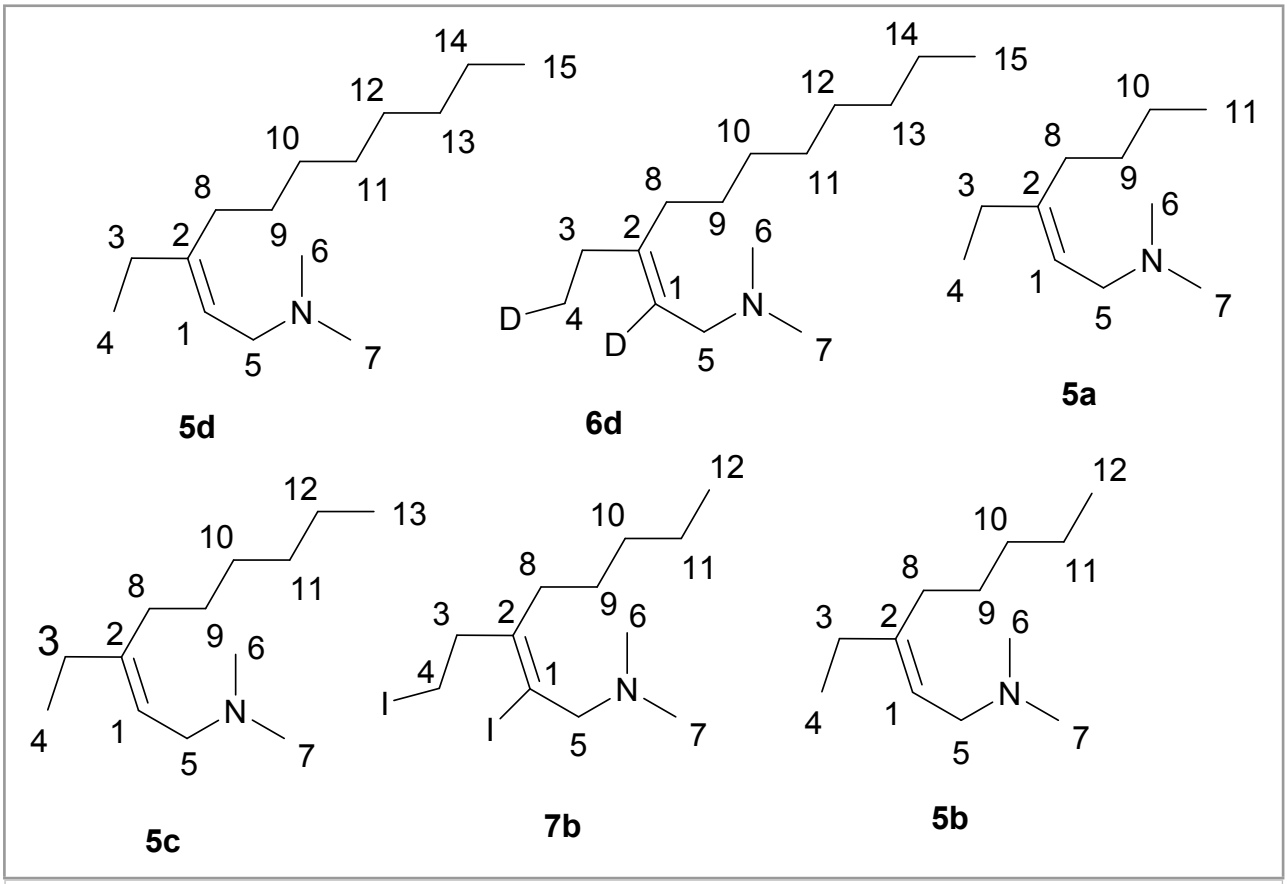

Figure 2. The numbering of atoms in the ^{13}C- and ^{1}H-NMR spectra of the compounds **5a-d**, **6d**, **7b.**

(*Z*)-3-ethyl-*N*,*N*-dimethylundec-2-en-1-amine; Typical Procedure.

To a solution of *N,N-dimethylundec-2-yn-1-amine* (390 mg, 2 mmol) and Et_2Zn (1 M in hexanes, 5 mL, 5 mmol) in Et_2O (6 mL) was added Cp_2ZrCl_2 (0.058g, 0.20 mmol). Ethylmagnesiurn bromide (1.6 M in Et_2O, 0.25 mL, 0.4 mmol) was then added and the reaction mixture rapidly turned black. After 18h at r.t. ^{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 (3×10 mL). The combined organic layers were washed with brine (20 mL), dried over anhydrous $MgSO_4$. The reaction mixture was filtered through a filter paper and concentrated in vacuo to give crude product as a yellow oil. The residue was distilled through a micro column at 1 mmHg to give **5d** (401 mg, 89%) as a colourless oil. b.p. 104 – 107 ^oC (1 mmHg).

^1H NMR (500MHz, $CDCl_3$): δ = 0.89 (t, *J* = 6 Hz, 3H, C(15)H_3), 1.01 (t, *J* = 7 Hz, 3H, C(4)H_3), 1.29 (s, 8H, C(10 - 13)H_2), 1.32 – 1.38 (m, 4H, C(9,14)H_2), 2.03 – 2.06 (m, 4H, C(3,8)H_2), 2.23 (s, 6H, C(6,7)H_3), 2.91 (d, *J* = 6 Hz, 2H, C(5)H_2), 5.22 (t, *J* = 6 Hz, 1H, C(1)H).

^{13}C NMR (500MHz, $CDCl_3$): δ = 12.74 (C(4)), 14.10 (C(15)), 22.07 (C(14)), 28.49 (C(9)), 29.29 (C(10)), 29.52 (C(12)), 29.57 (C(11)), 29.79 ((C(3)), 30.58 (C(8)), 31.89 (C(13)), 45.26 (C(6,7)), 56.86 (C(5)), 120.48 (C(1)), 144.41 (C(2)).

MS (EI): m/z, % = 225 (32) [M^+], 210 (15), 196 (17), 180 (14), 151 (19), 112 (47), 95 (100), 82 (81), 67 (74), 58 (79), 46 (96).

Anal. calcd for $C_{15}H_{31}N$, (%): C, 79.92; H, 13.86; N, 6.21. Found, %: C, 79.80; H, 13.82; N, 6.01.

(*Z*)-3-ethyl-*N*,*N*-dimethylhept-2-en-1-amine (5a)

Using the procedure described above 390 mg of *N*,*N*-dimethylhept-2-yn-1-amine (278 mg, 2 mmol) gave crude product that was distilled through a micro column at 10 mmHg to afford **5c** (294 mg, 87%) as a colourless oil. b.p. 88 – 91 ^oC (10 mmHg). The spectral properties (^1H NMR, ^{13}C NMR, MS) were in good agreement with those that were reported in the literature [54].

(*Z*)-3-ethyl-*N*,*N*-dimethylnon-2-en-1-amine (5c)

Using the procedure described above 334 mg of *N*,*N*-dimethylnon-2-yn-1-amine (2 mmol) gave crude product that was distilled through a micro column at 5 mmHg to afford **5c** (311 mg, 79%) as a colourless oil. b.p. 103 – 106 ^oC (5 mmHg)**.**

^1H NMR (500MHz, $CDCl_3$): δ = 0.91 (t, *J* = 6 Hz, 3H, C(13)H_3), 1.03 (t, *J* = 8 Hz, 3H, C(4)H_3), 1.28 – 1.31 (m, 6H, C(10 - 12)H_2), 1.33 – 1.39 (m, 2H, C(9)H_2), 2.03 – 2.07 (m, 4H, C(3,8)H_2), 2.25 (s, 6H, C(6,7)H_3), 2.93 (d, *J* = 6 Hz, 2H, C(5)H_2), 5.23 (t, *J* = 7 Hz, 1H, C(1)H).

^{13}C NMR (500MHz, $CDCl_3$): δ = 12.75 (C(4)), 14.09 (C(13)), 22.65 (C(12)), 28.47 (C(9)), 29.59 (C(10)), 29.70 (C(3)), 31.79 (C(11)), 45.24 (C(6,7)), 56.84 (C(5)), 120.41 (C(1)), 144.51 (C(2)).

MS (EI): m/z, % = 197 (32) [M^+], 182 (17), 168 (20), 152 (22), 123 (55), 112 (49), 95 (82), 82 (93), 67 (74), 58 (88), 46 (100).

Anal. calcd for $C_{13}H_{27}N$, (%): C, 79.11; H, 13.79; N, 7.10. Found, %: C, 79.10; H, 13.74; N, 6.89.

(*Z*)-3-ethyl-*N*,*N*-dimethyloct-2-en-1-amine (5b)

Using the procedure described above 306 mg of *N,N-dimethyloct-2-yn-1-amine* (2 mmol) gave crude product that was distilled through a micro column at 5 mmHg to afford **5b** (307 mg, 84%) as a colourless oil. b.p. 91 – 93 ^{o}C (5 mmHg). The spectral properties (^{1}H NMR, ^{13}C NMR, MS) were in good agreement with those that were reported in the literature [54].

(*Z*)-3-(ethyl-2-*d*)-*N*,*N*-dimethylundec-2-en-1-amine-2-*d* (6d)

Using the procedure described above 390 mg of *N,N-dimethylundec-2-yn-1-amine* (2 mmol) gave crude product that was distilled through a micro column at 1 mmHg to afford **6d** (409 mg, 90%) as a colourless oil. b.p. 103 – 106 ^{o}C (1 mmHg)**.**

^{1}H NMR (500MHz, $CDCl_3$): δ = 0.90 (t, *J* = 6 Hz, 3H, C(15)H_3), 1.02 (qv, *J* = 7 Hz, 2H, C(4)H_2D), 1.29 (s, 8H, C(10 - 13)H_2), 1.31 – 1.35 (M, 4H, C(9,14)H_2), 2.06 – 2.11 (M, 4H, C(3, 8)H_2), 2.19 (s, 6H, C(6,7)H_3), 2.87 (s, 2H, C(5)H_2).

^{13}C NMR (500MHz, $CDCl_3$): δ = 12.57 (t, *J* = 19 Hz, C(4)), 14.12 (C(15)), 22.69 (C(14)), 27.45 (C(8)), 28.28 (C(3)), 29.30 (C(10)), 29.37 (C(12)), 29.54 (C(11)), 30.03 (C(9)), 31.91 (C(13)), 45.47 (C(6,7)), 58.31 (C(5)).

MS (EI): m/z, % = 227 (12) [M^+], 212 (20), 210 (11), 198 (23).

Anal. calcd for $C_{15}H_{29}D_2N$, (%): C, 79.22; N, 6.16. Found, %: C, 79.36; N, 6.12.

(*Z*)-2-iodo-3-(2-iodoethyl)-*N*,*N*-dimethylnon-2-en-1-amine (7b)

To a solution of *N,N-dimethyloct-2-yn-1-amine* (306 mg, 2 mmol) and Et_2Zn (1 M in hexanes, 5 mL, 5 mmol) in ether (6 mL) was added Cp_2ZrCl_2 (0.058g, 0.20 mmol). Ethylmagnesiurn bromide (1.6 M in Et_2O, 0.25 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 ^{o}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 ^{o}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 (hexane/ethyl acetate, 5:1) gave a yellow oil; yield: 487 mg, (56%); *Rf* = 0.68 (hexane/ethyl acetate, 5:1). The spectral properties (^{1}H NMR, ^{13}C NMR, MS) were in good agreement with those that were reported in the literature [54]. Anal. calcd for $C_{13}H_{25}I_2N$, (%): C, 33.12; H, 5.33; N, 3.22. Found, %: C, 32.91; H, 5.30; N, 3.21.

Acknowledgements

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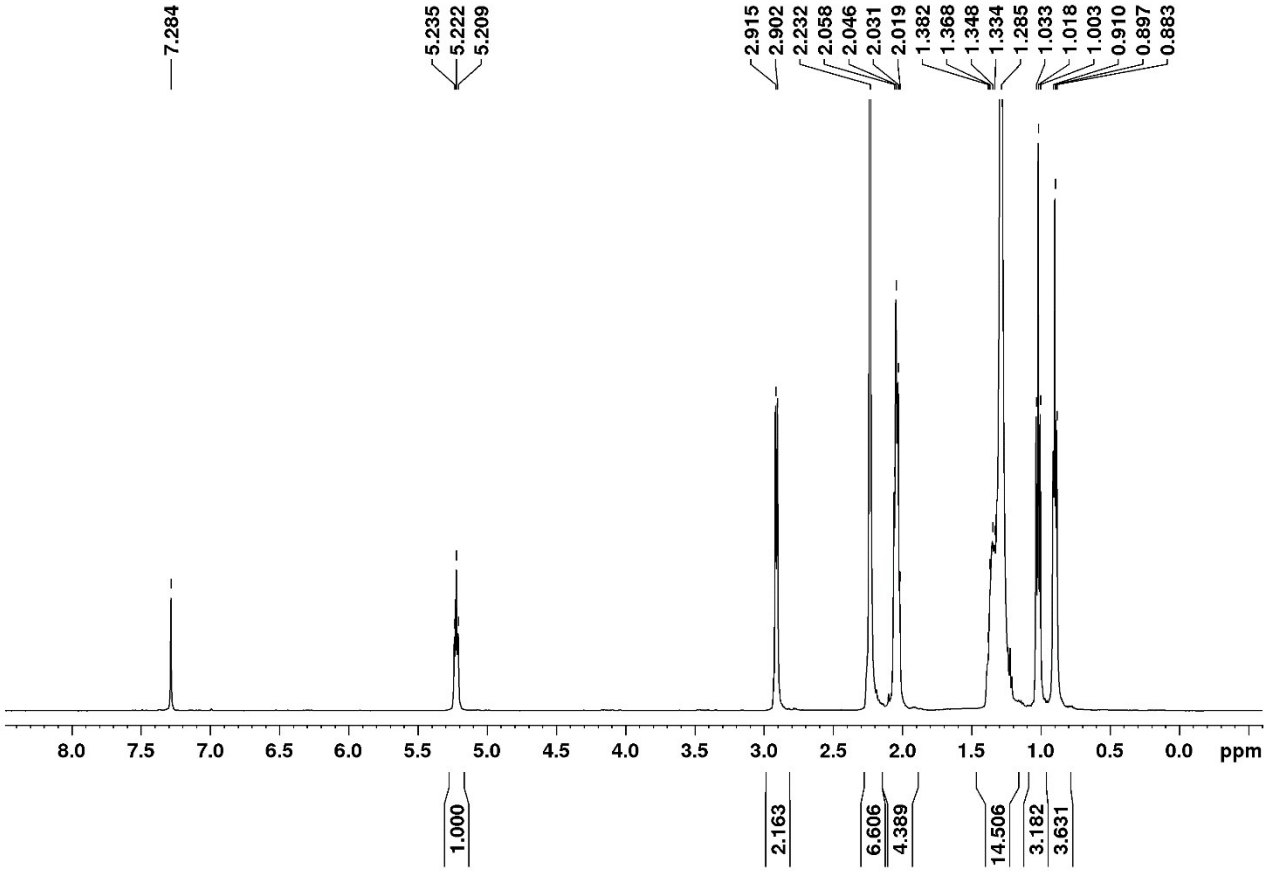
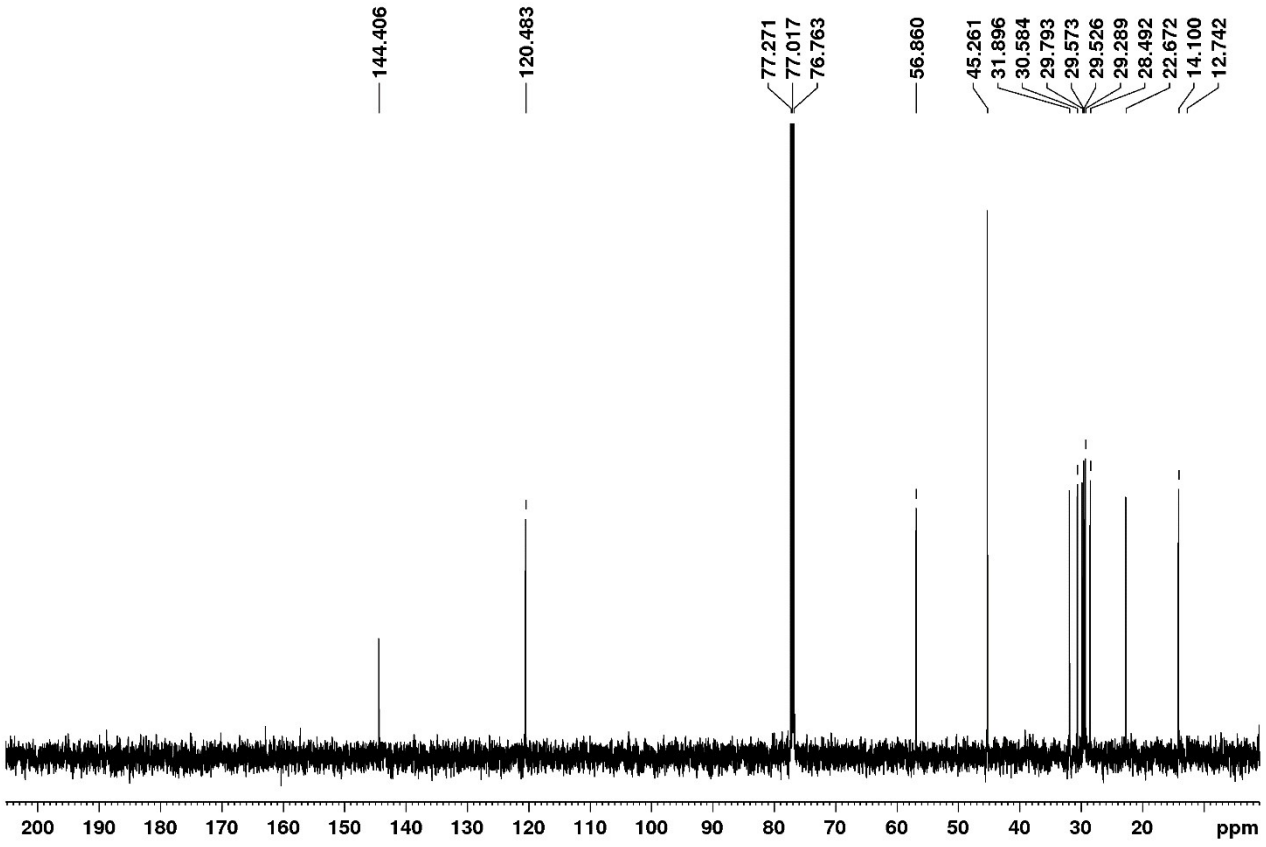
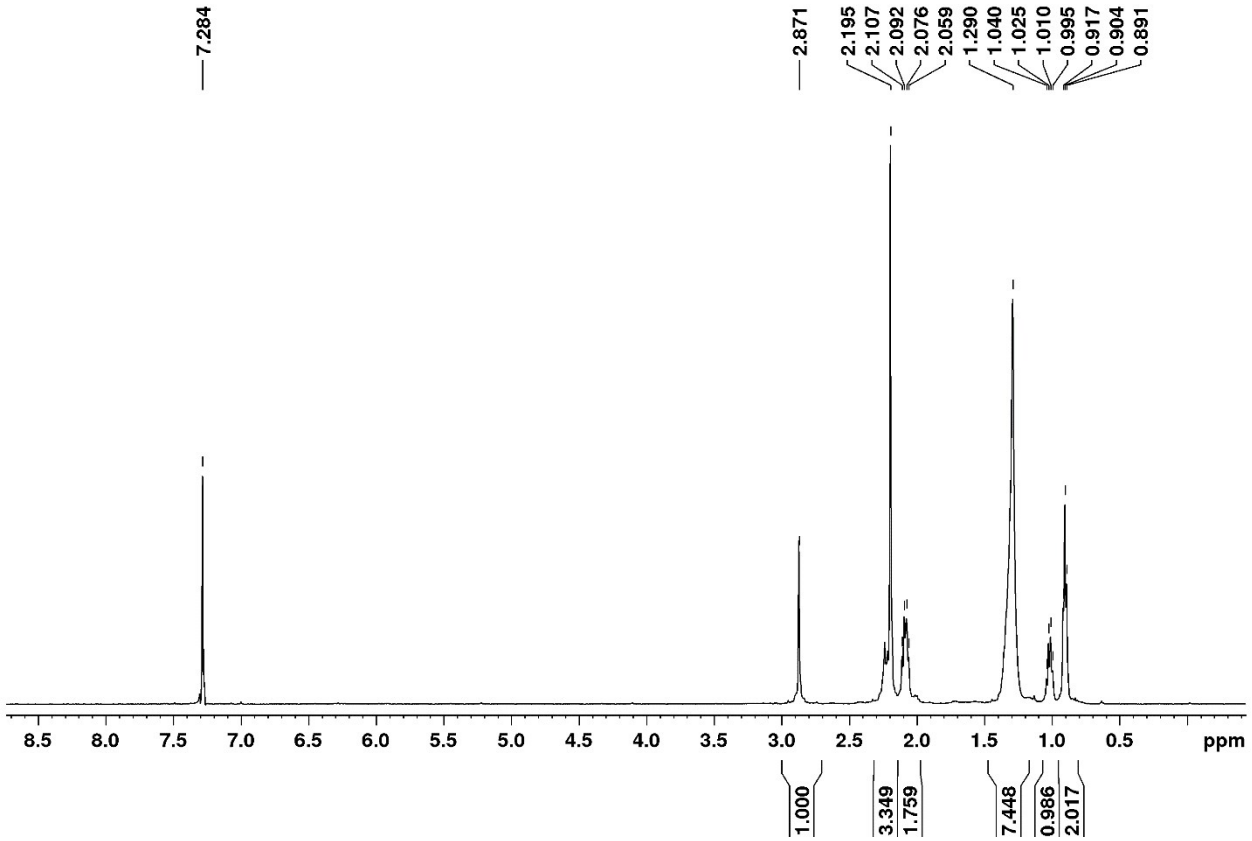
^{1}H-NMR spectrum of (*Z*)-3-ethyl-*N*,*N*-dimethylundec-2-en-1-amine (5d)



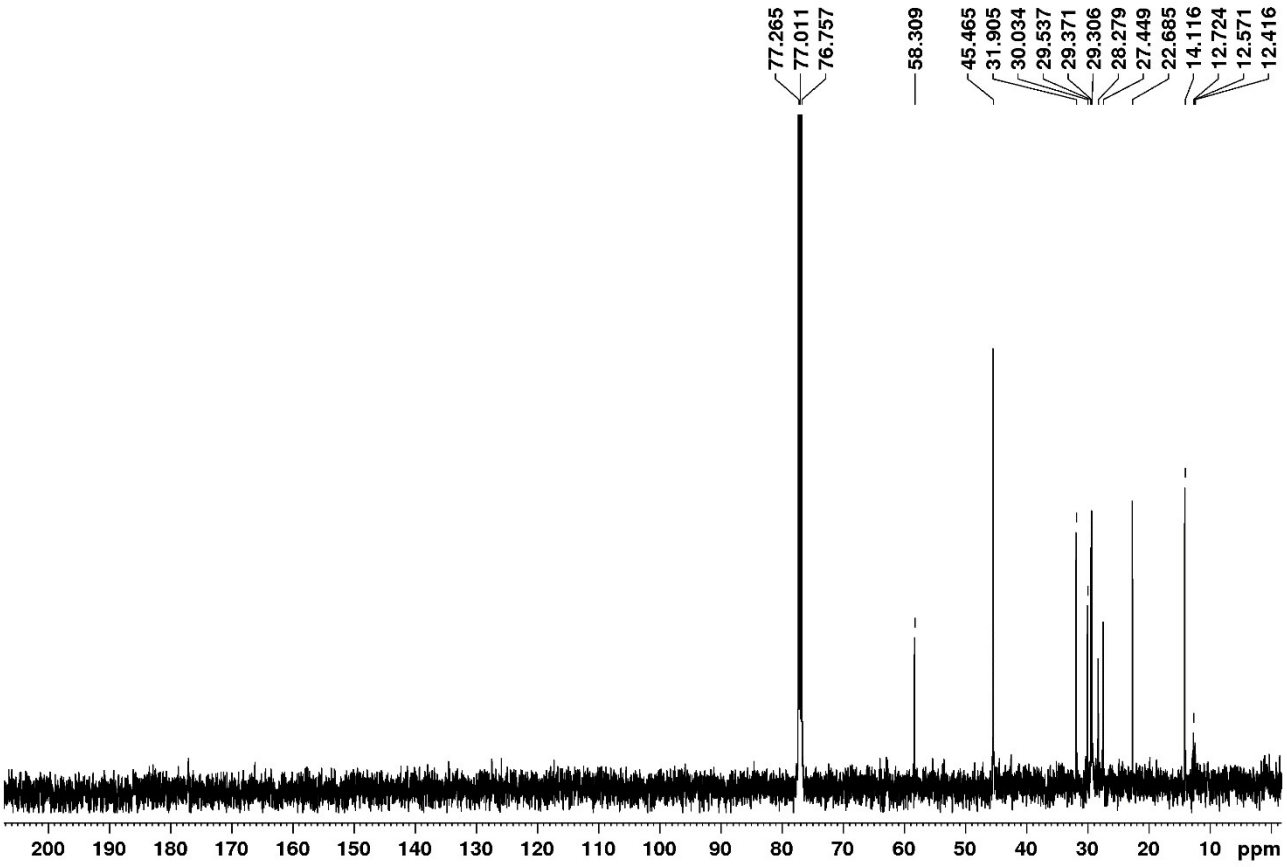
^{13}C-NMR spectrum of (*Z*)-3-ethyl-*N*,*N*-dimethylundec-2-en-1-amine (5d)



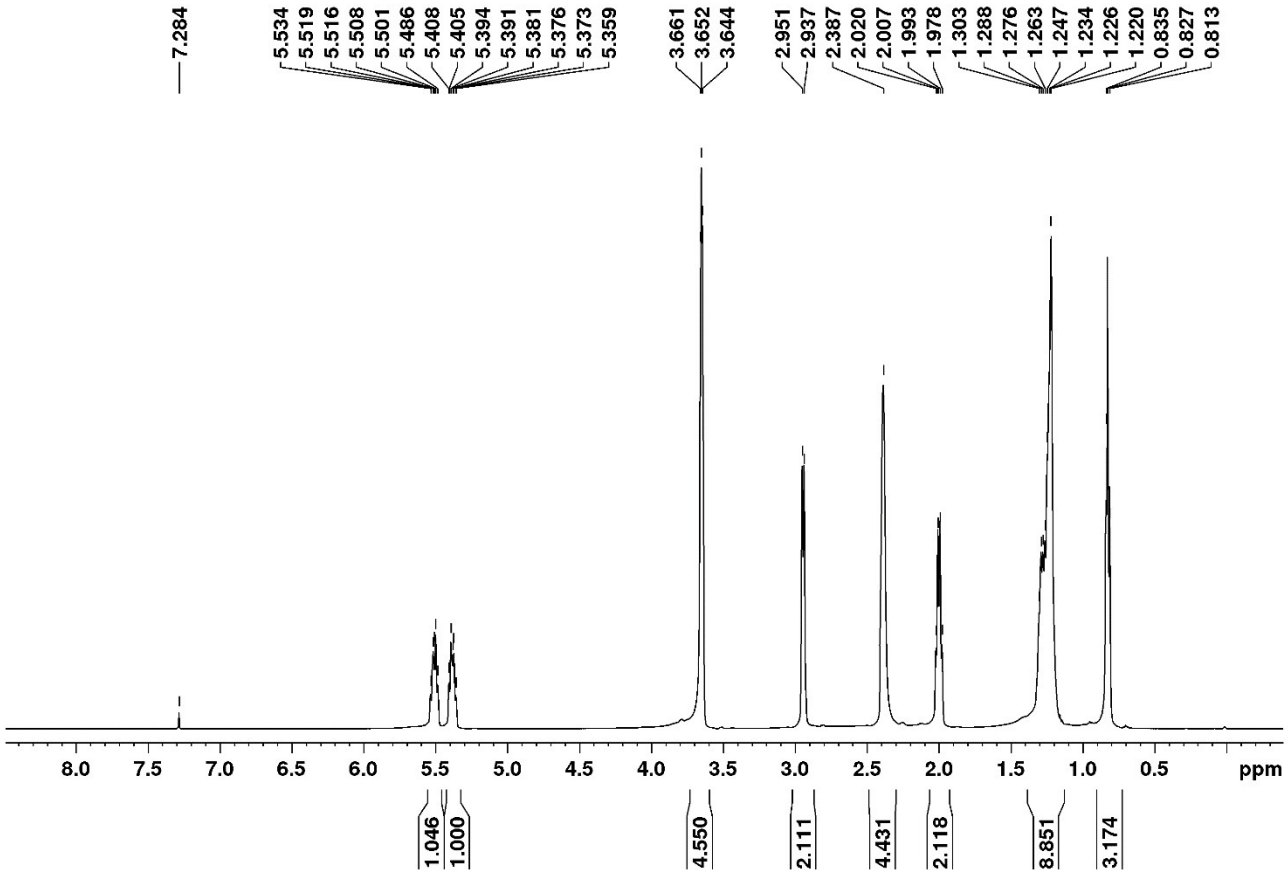
^{1}H-NMR spectrum of (*Z*)-3-(ethyl-2-*d*)-*N*,*N*-dimethylundec-2-en-1-amine-2-*d* (6d)



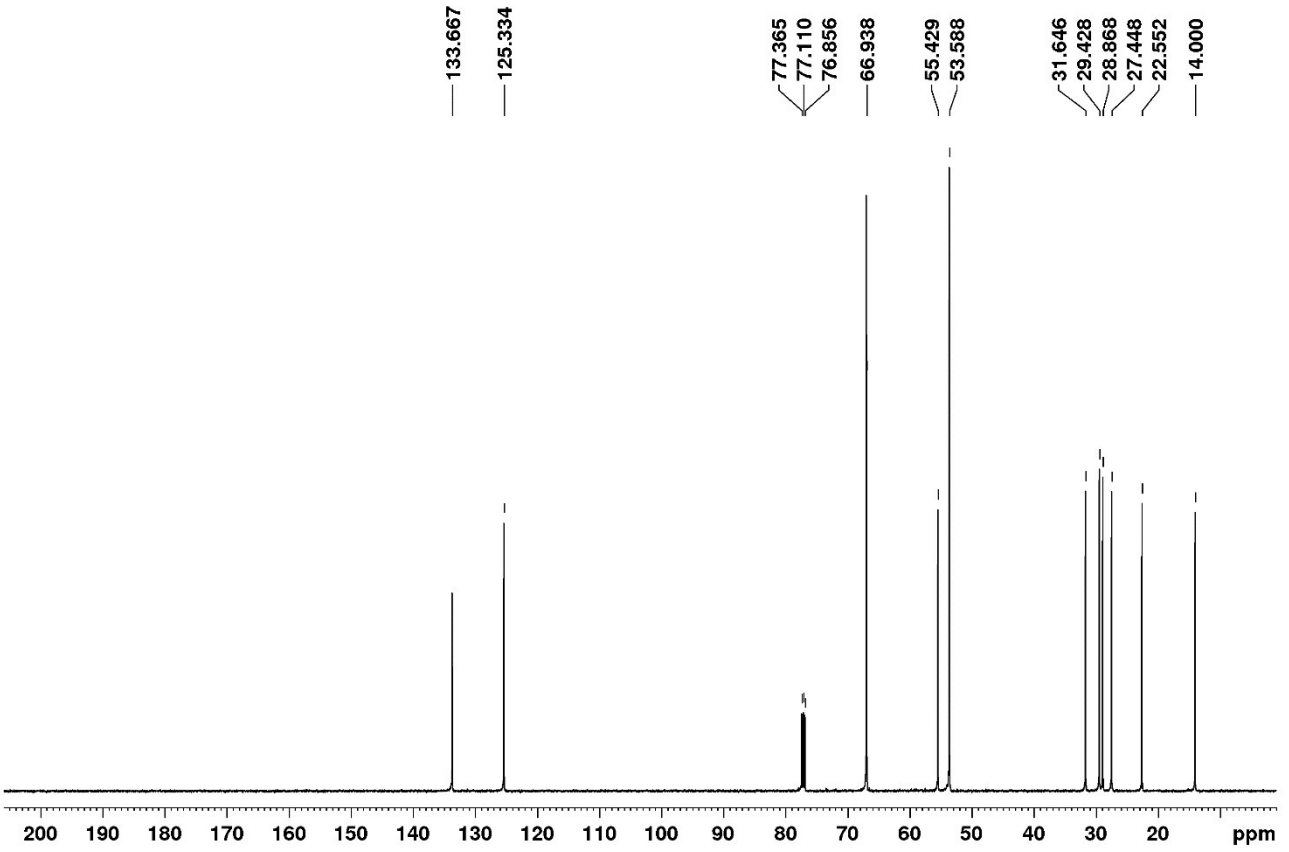
^{13}C-NMR spectrum of (*Z*)-3-(ethyl-2-*d*)-*N*,*N*-dimethylundec-2-en-1-amine-2-*d* (6d)



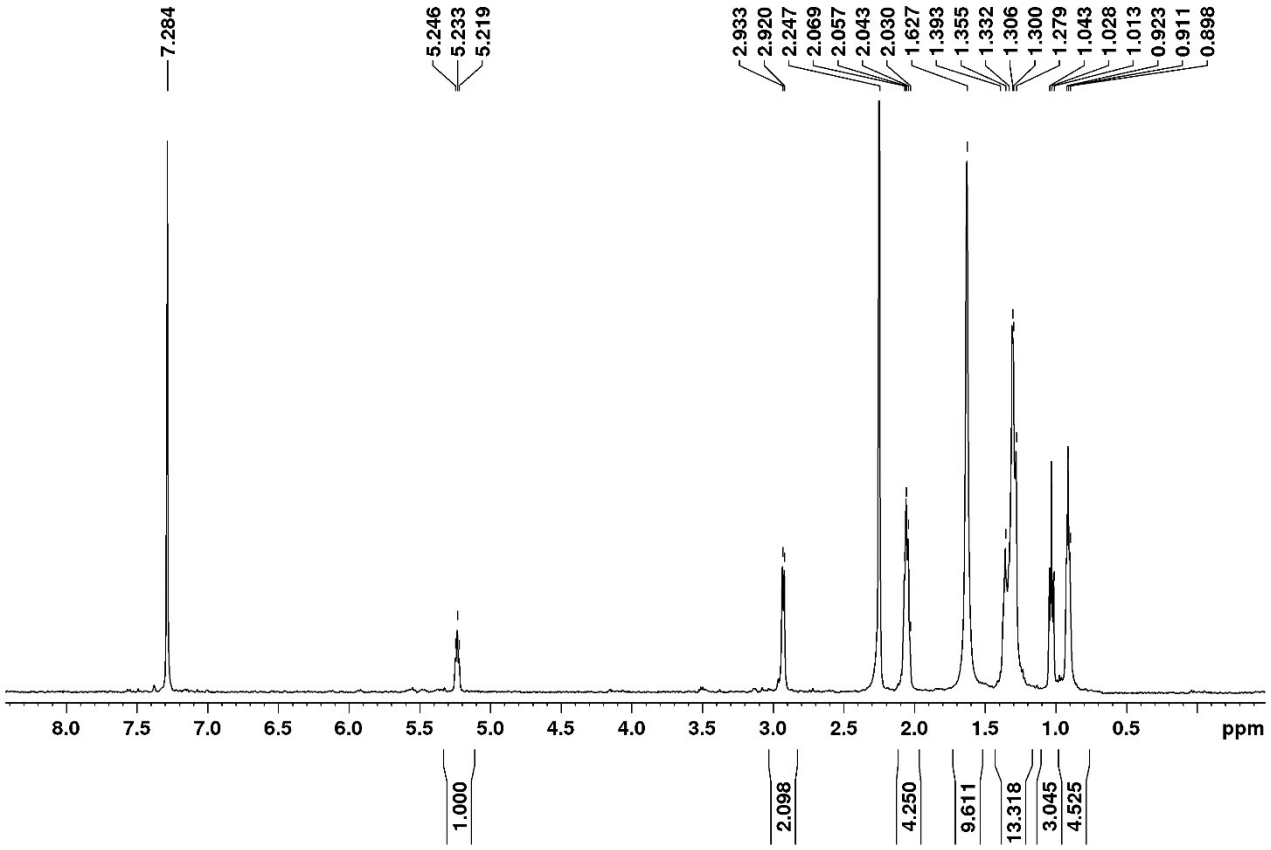
^{1}H-NMR spectrum of (*Z*)-4-(non-2-en-1-yl)morpholine (2c)



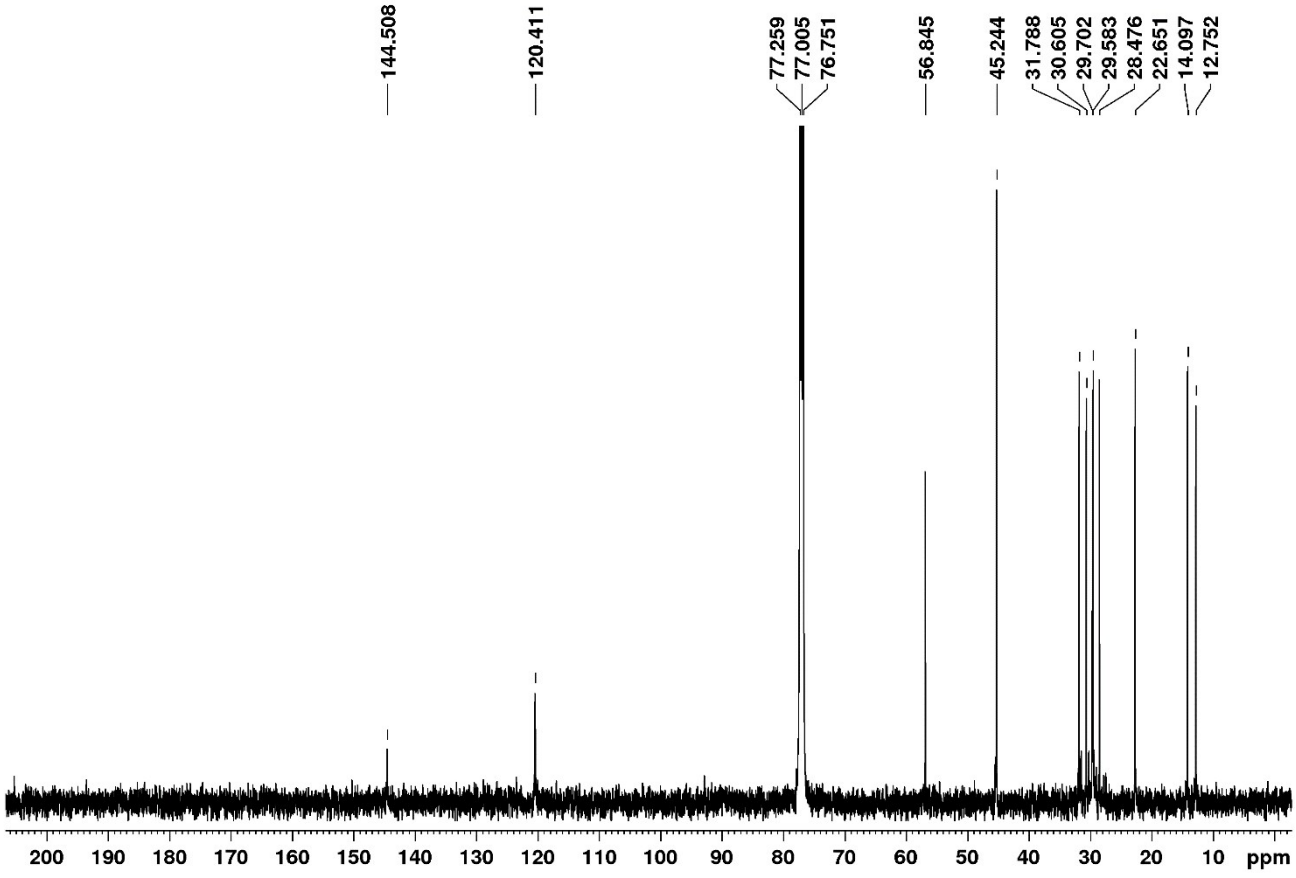
^{13}C-NMR spectrum of (*Z*)-4-(non-2-en-1-yl)morpholine (2c)



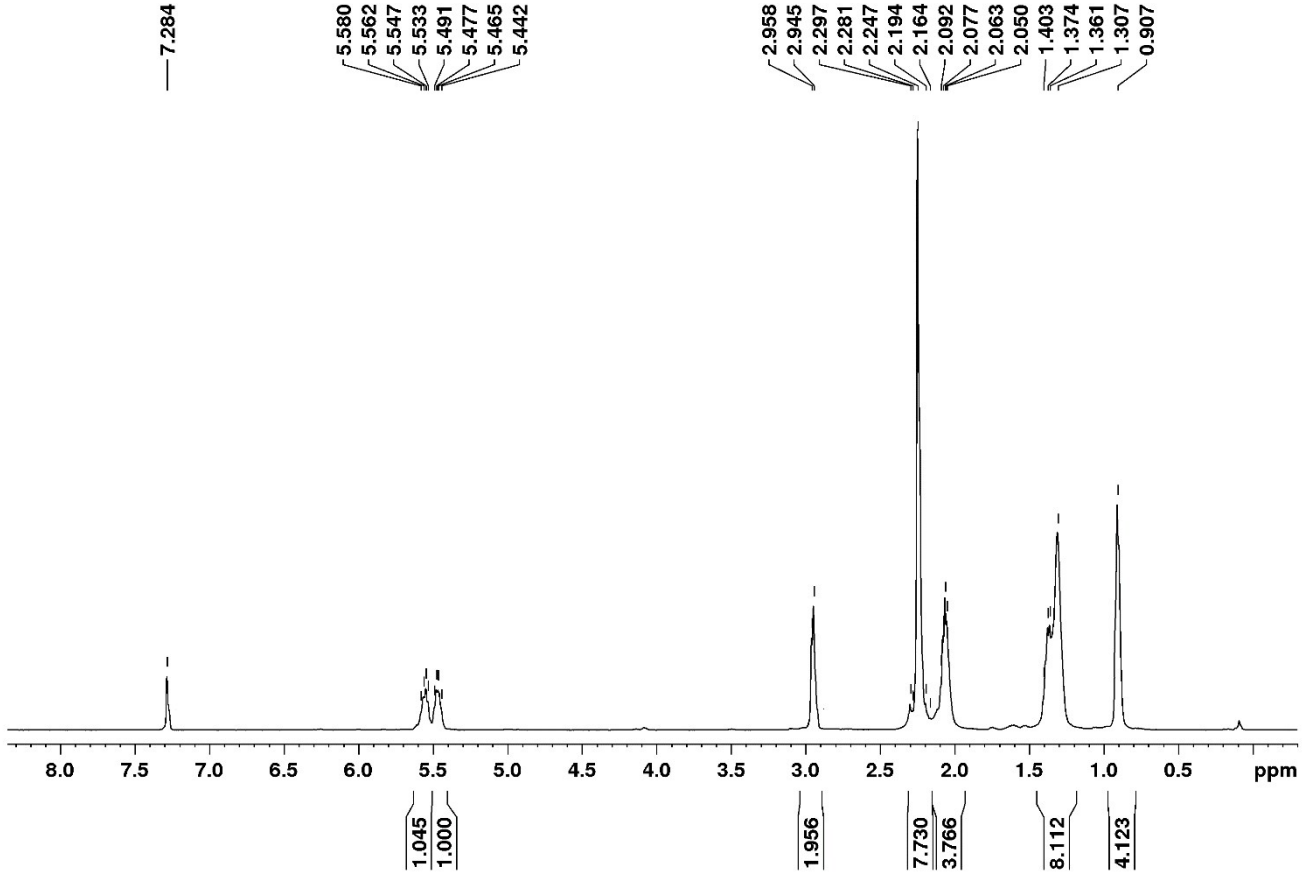
^{1}H-NMR spectrum of (*Z*)-3-ethyl-*N*,*N*-dimethylnon-2-en-1-amine (5c)



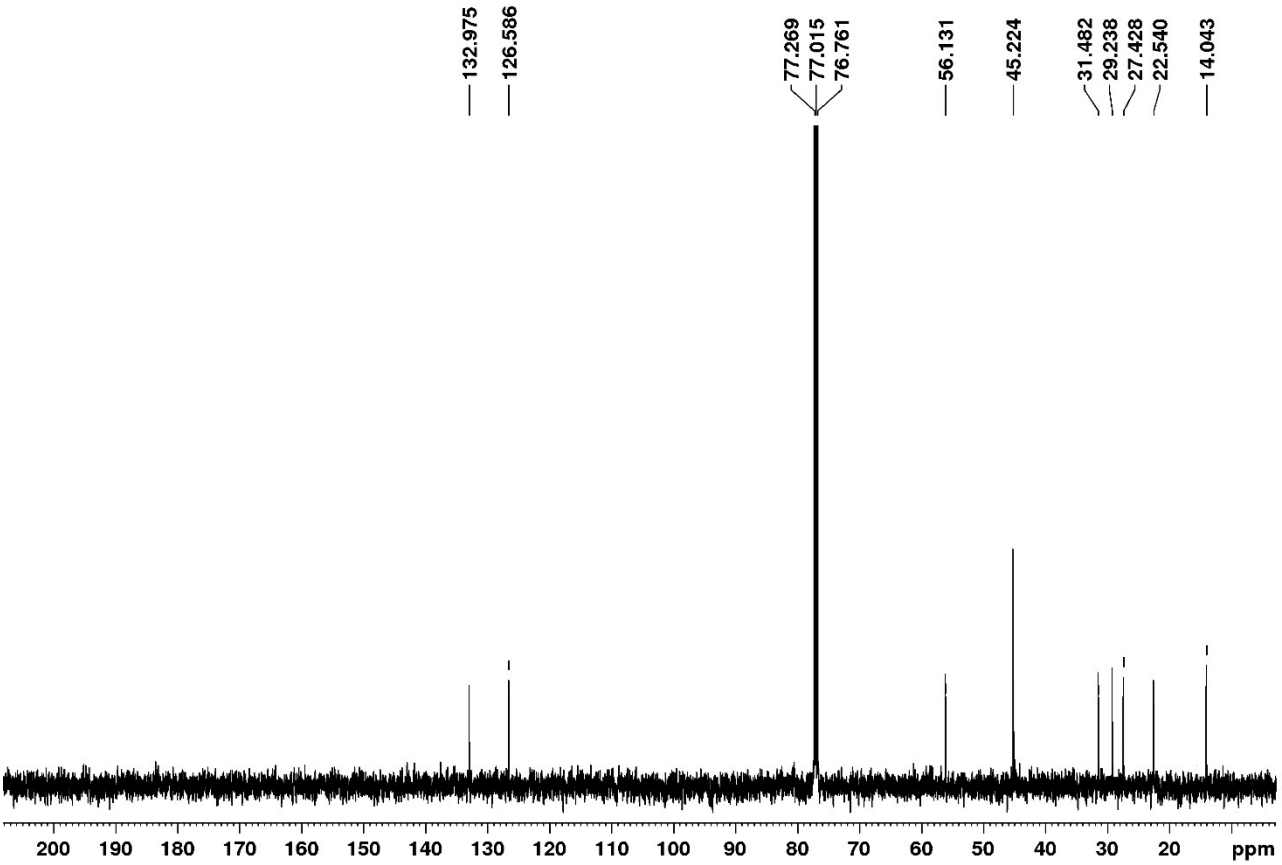
^{13}C-NMR spectrum of (*Z*)-3-ethyl-*N*,*N*-dimethylnon-2-en-1-amine (5c)



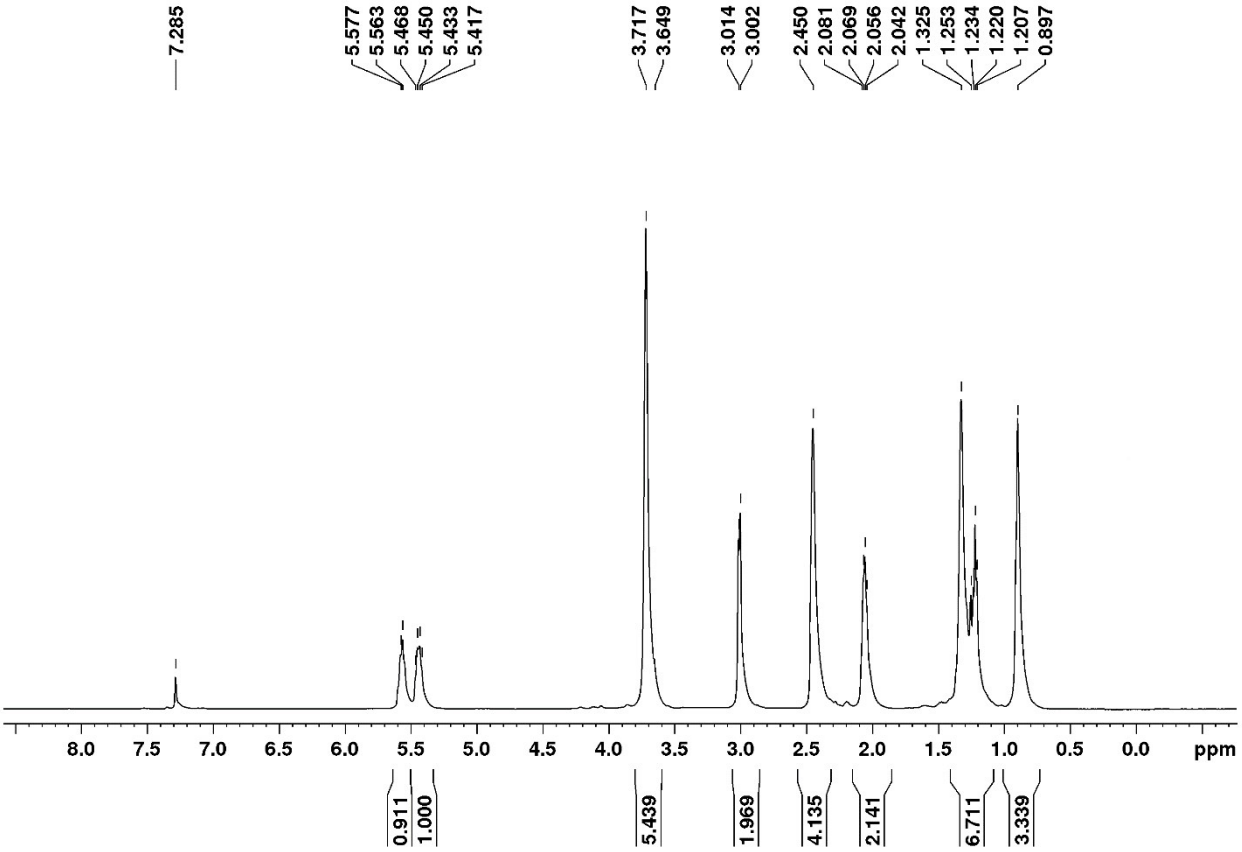
^{1}H-NMR spectrum of (*Z*)-*N*,*N*-dimethyloct-2-en-1-amine (2b)



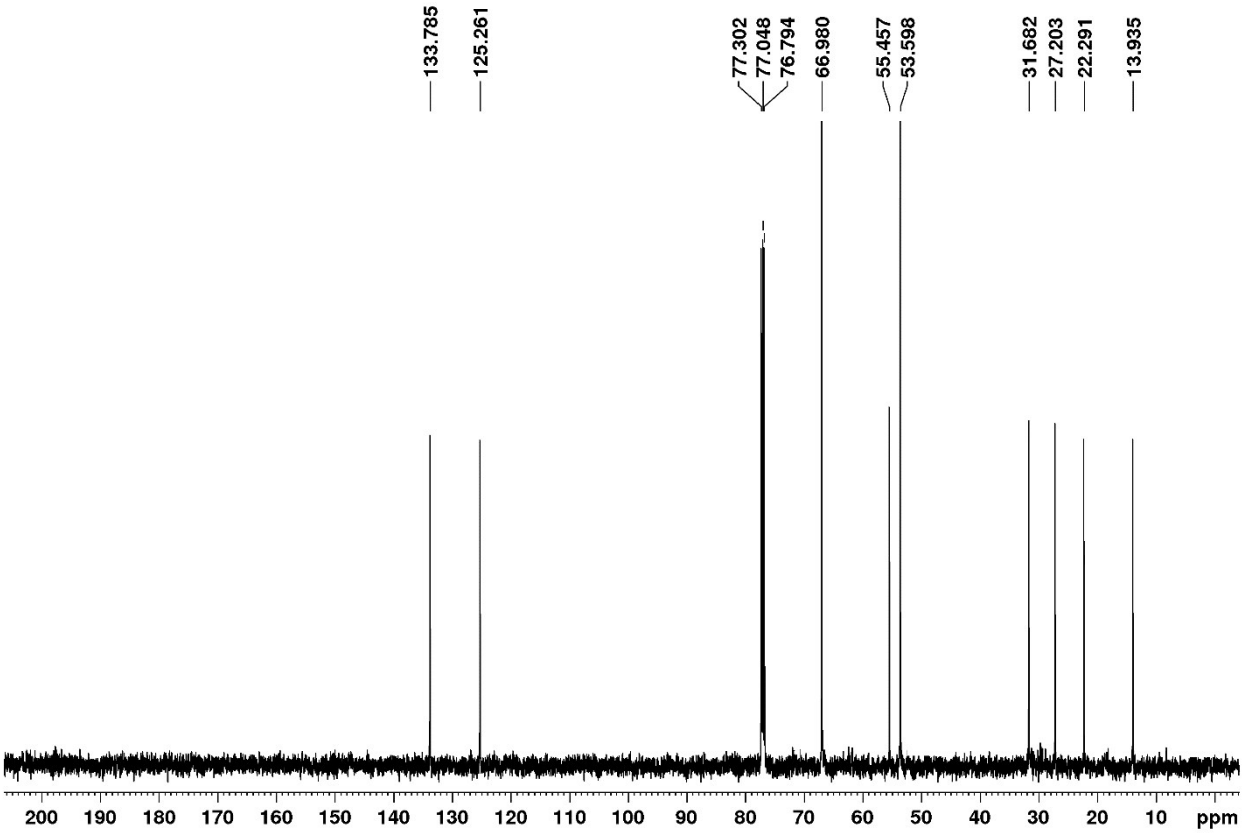
^{13}C-NMR spectrum of (*Z*)-*N*,*N*-dimethyloct-2-en-1-amine (2b)



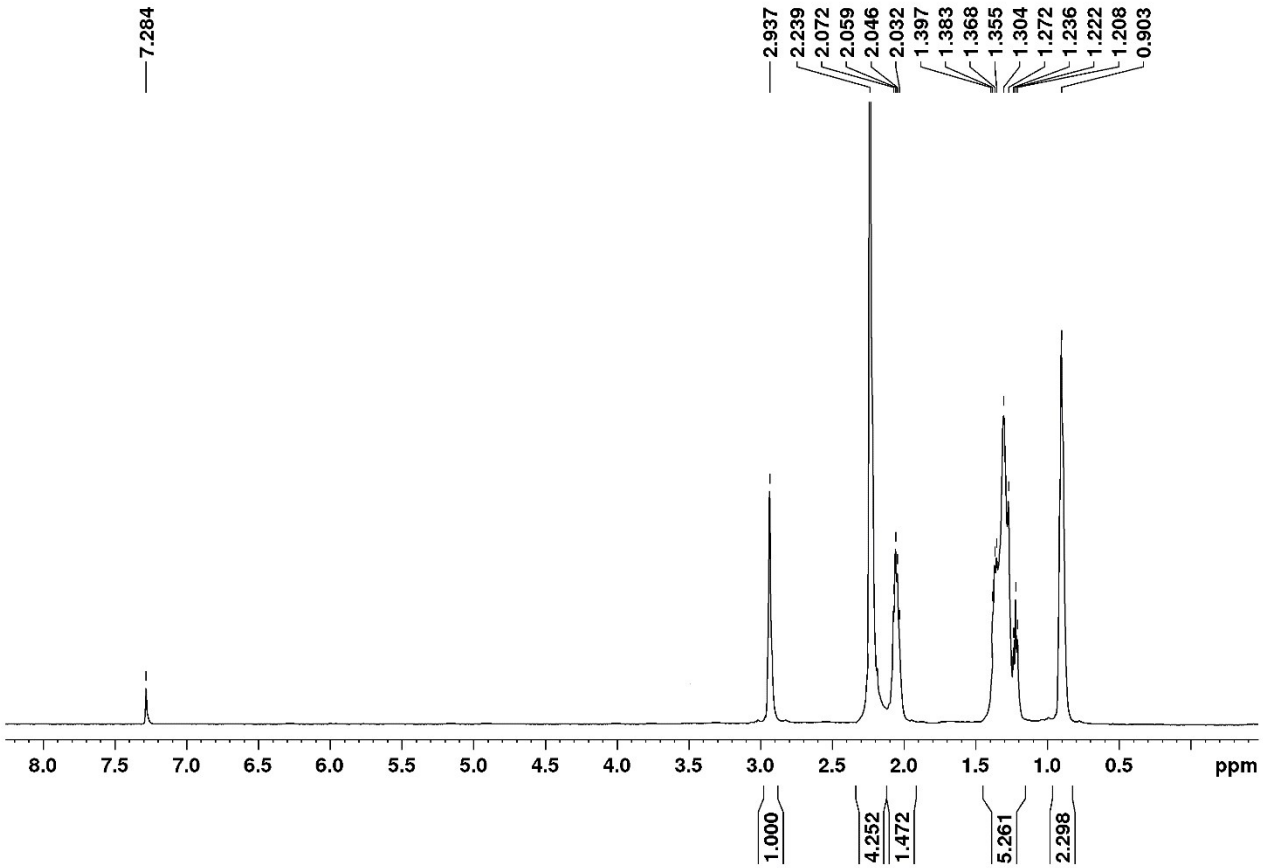
^{1}H-NMR spectrum of (*Z*)-4-(hept-2-en-1-yl)morpholine (2e)



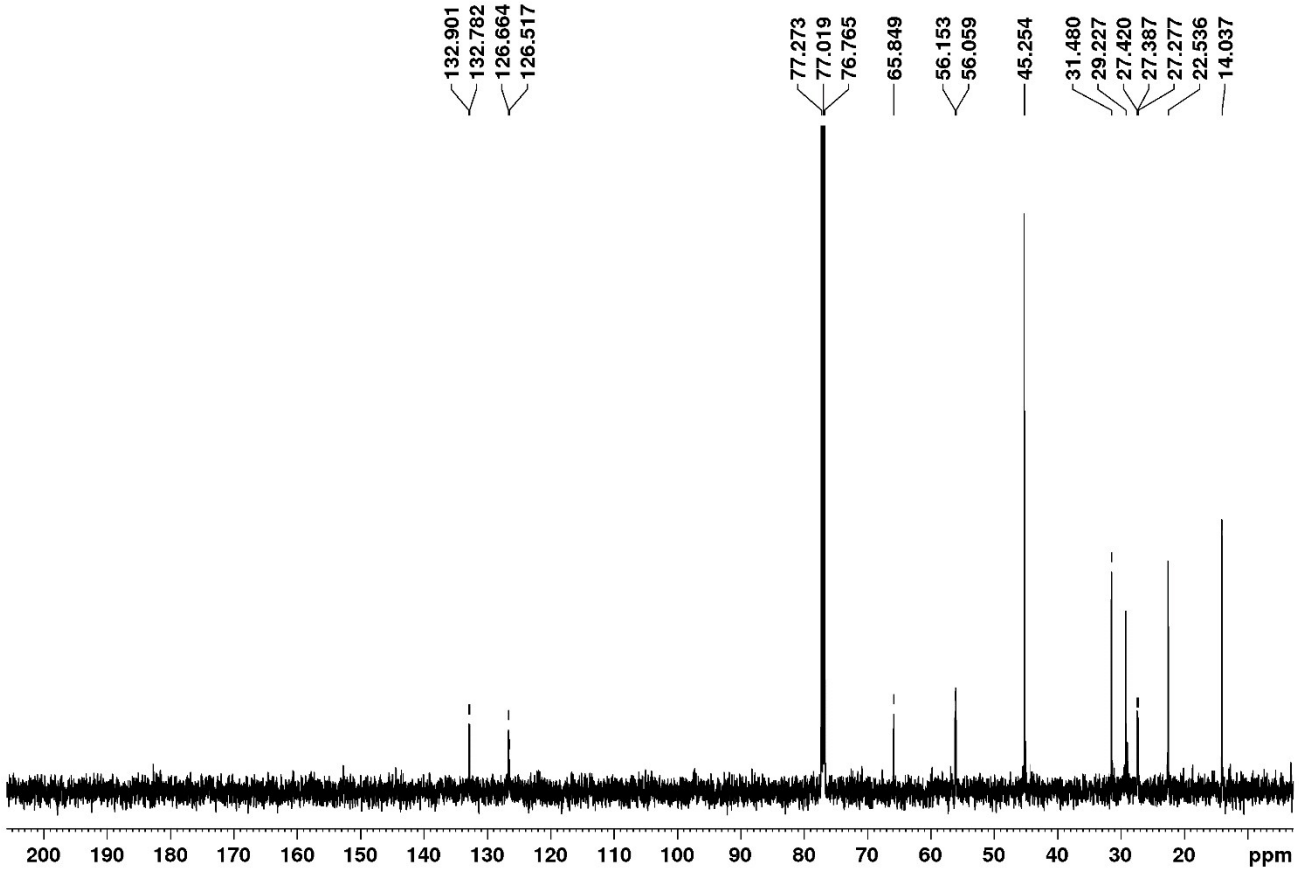
^{13}C-NMR spectrum of (*Z*)-4-(hept-2-en-1-yl)morpholine (2e)



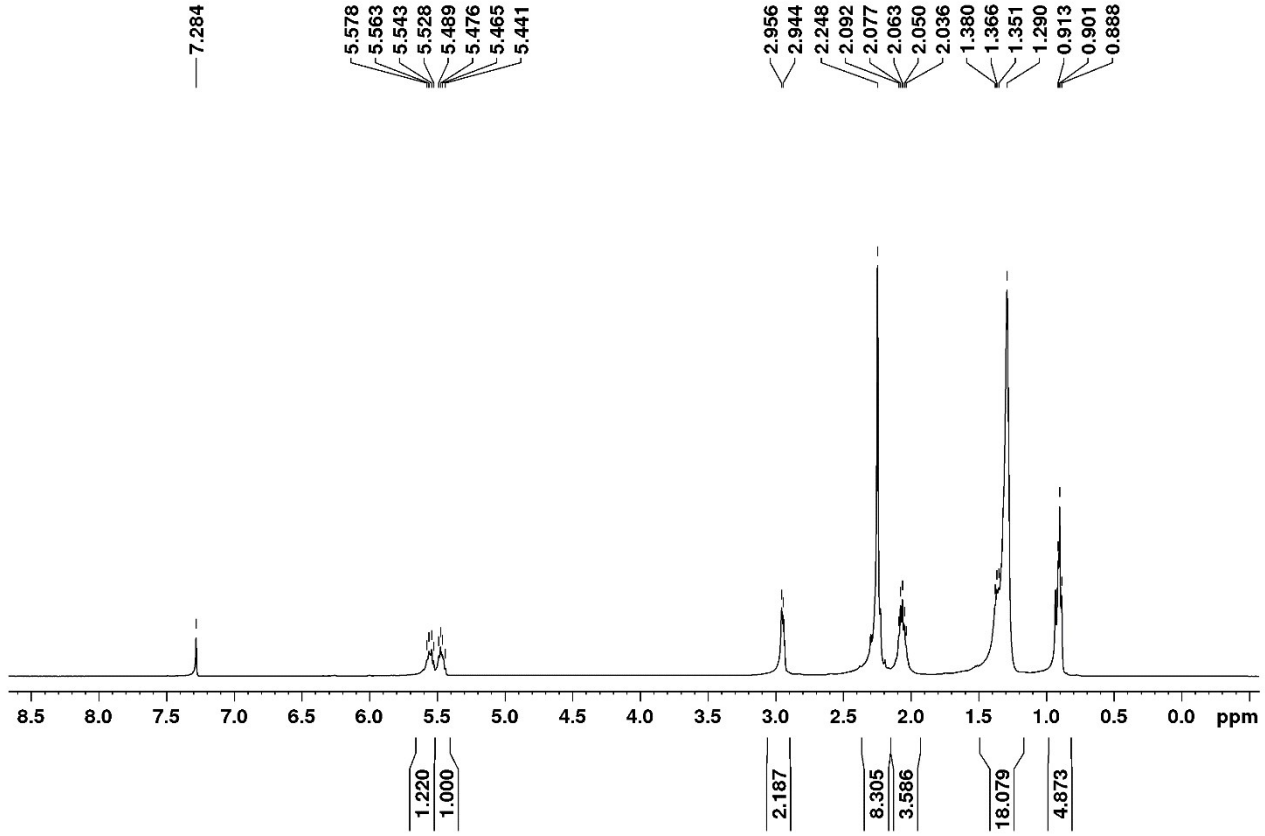
^{1}H-NMR spectrum of (*Z*)-*N*,*N*-dimethyloct-2-en-1-amine-2,3-d_2 (3b)



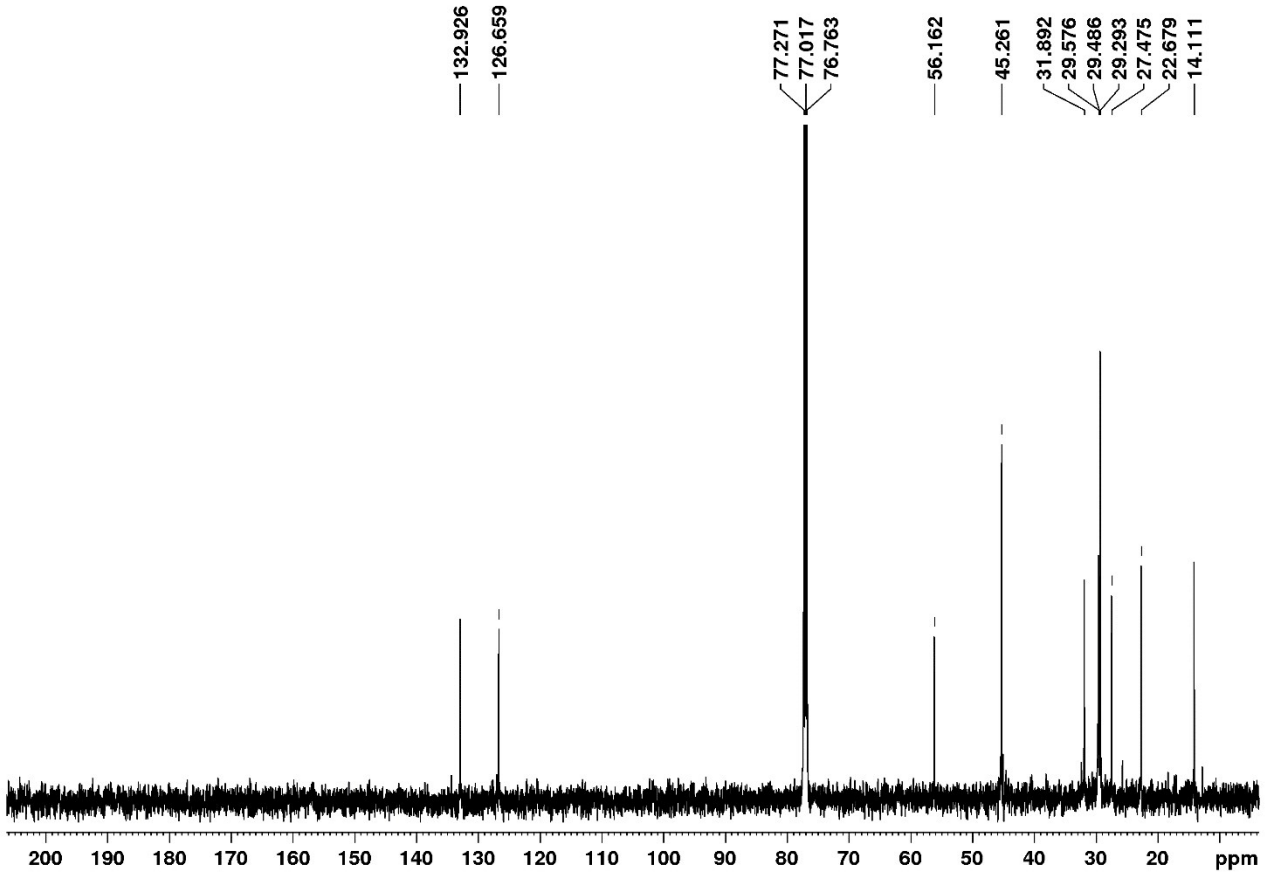
^{13}C-NMR spectrum of (*Z*)-*N*,*N*-dimethyloct-2-en-1-amine-2,3-d_2 (3b)



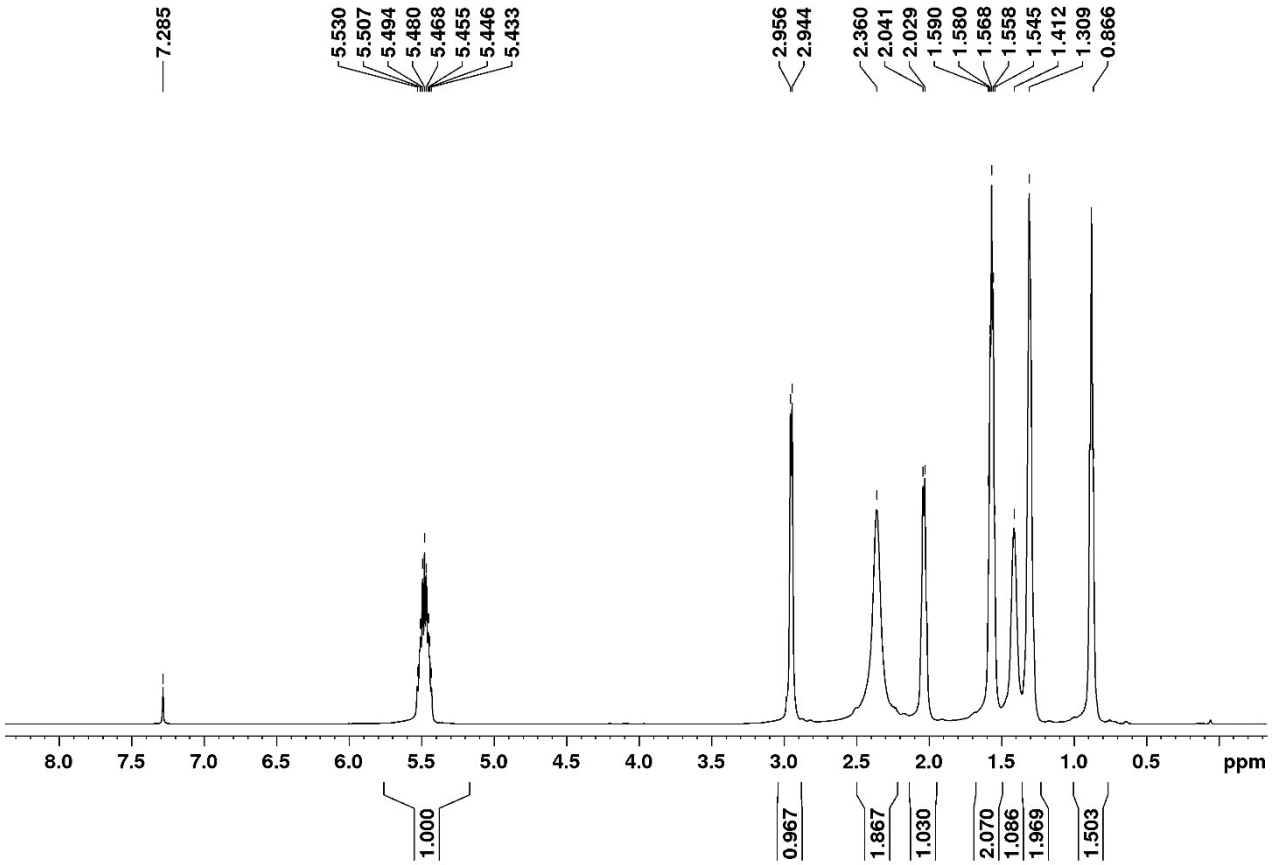
^{1}H-NMR spectrum of (*Z*)-*N*,*N*-dimethylundec-2-en-1-amine (2d)



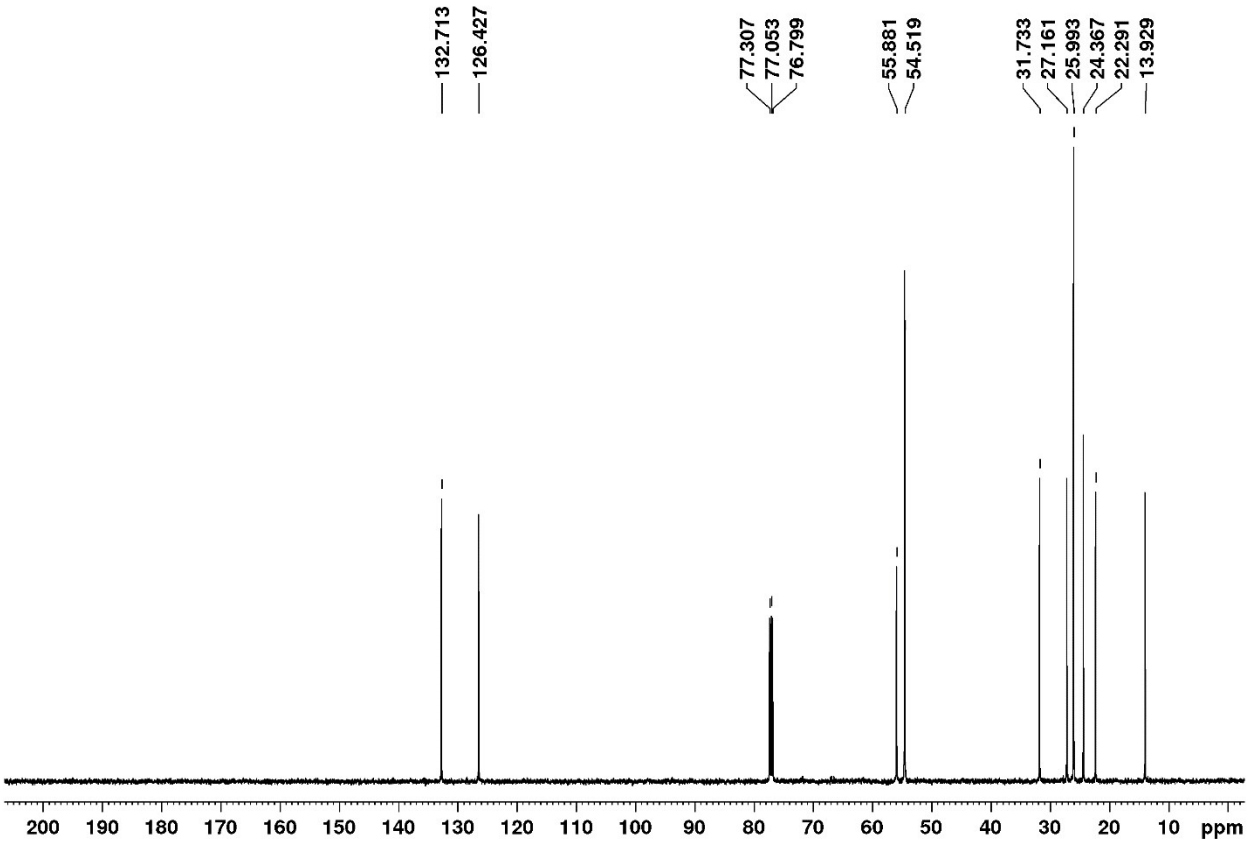
^{13}C-NMR spectrum of (*Z*)-*N*,*N*-dimethylundec-2-en-1-amine (2d)



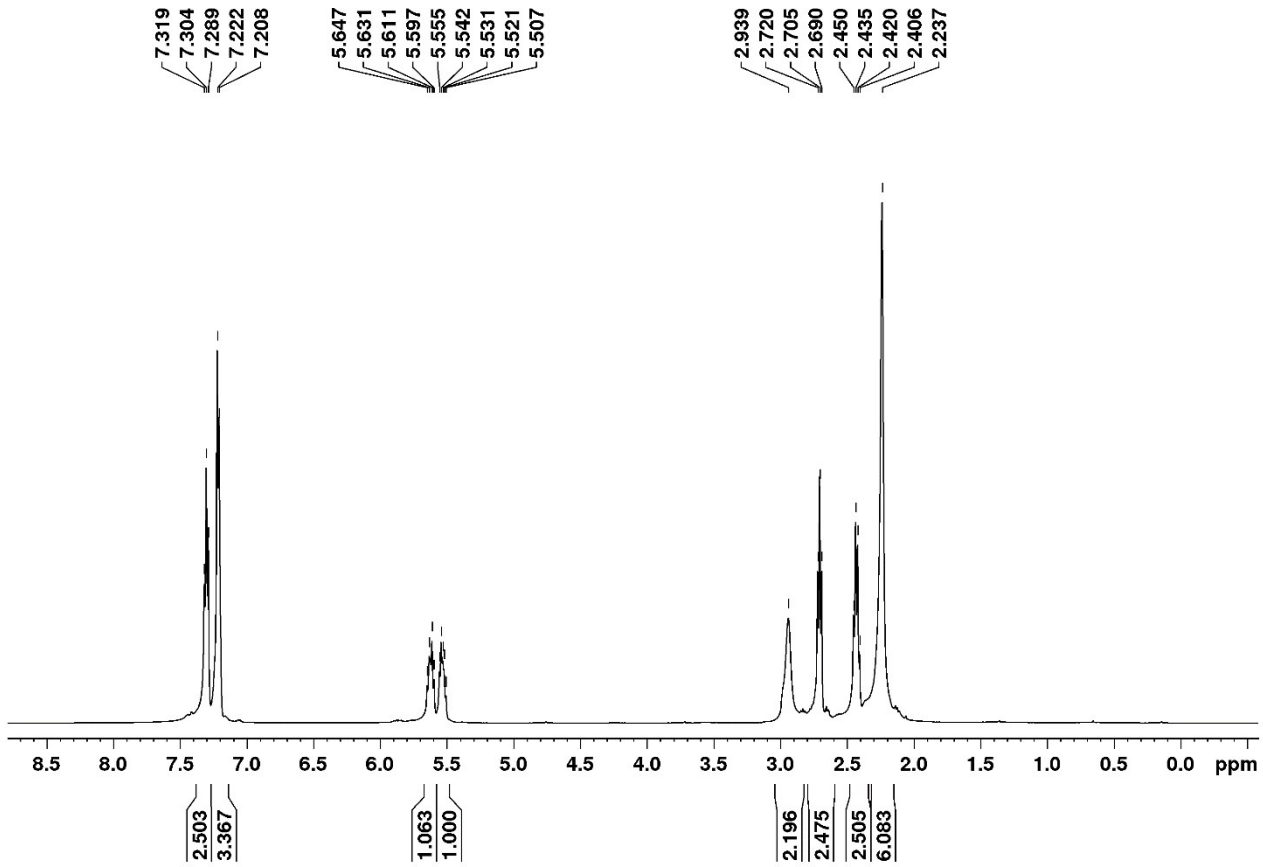
^{1}H-NMR spectrum of (*Z*)-1-(hept-2-en-1-yl)piperidine (2a)



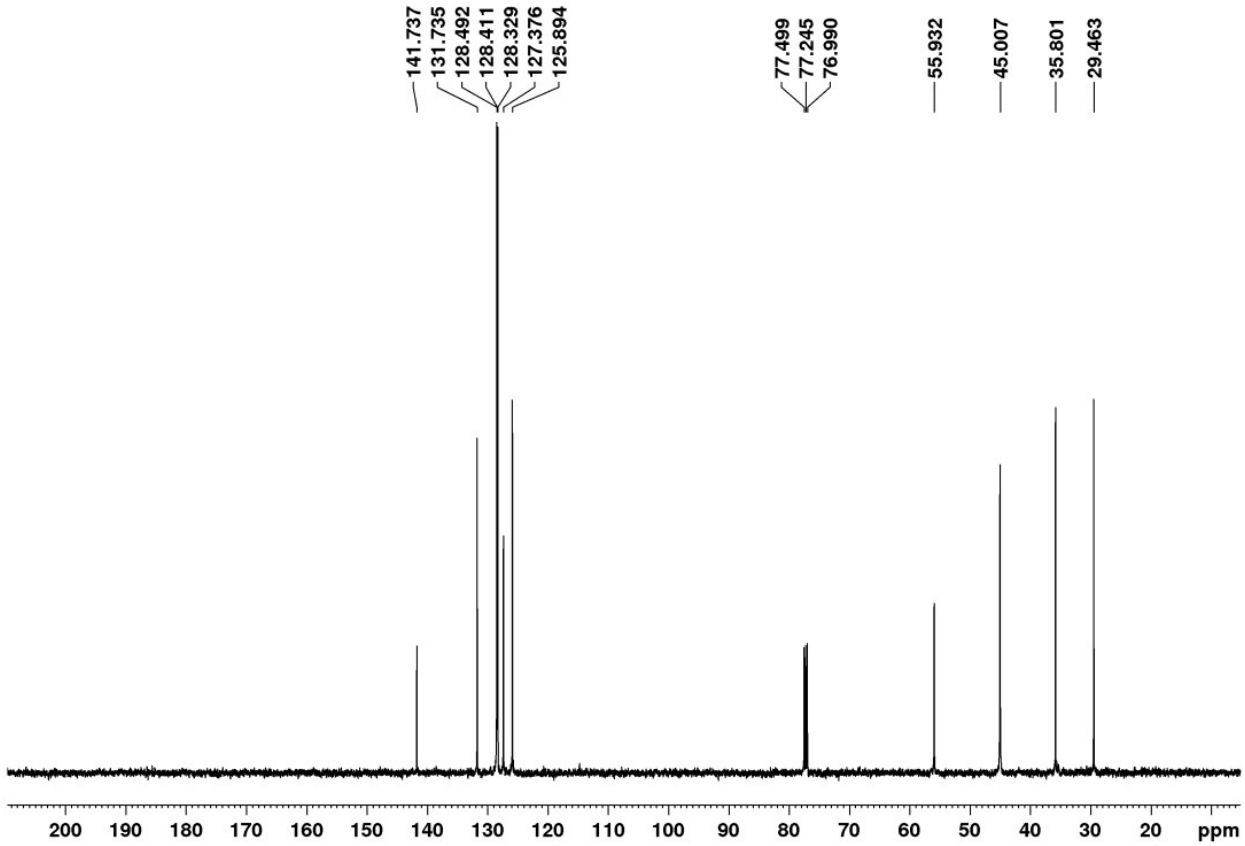
^{13}C-NMR spectrum of (*Z*)-1-(hept-2-en-1-yl)piperidine (2a)



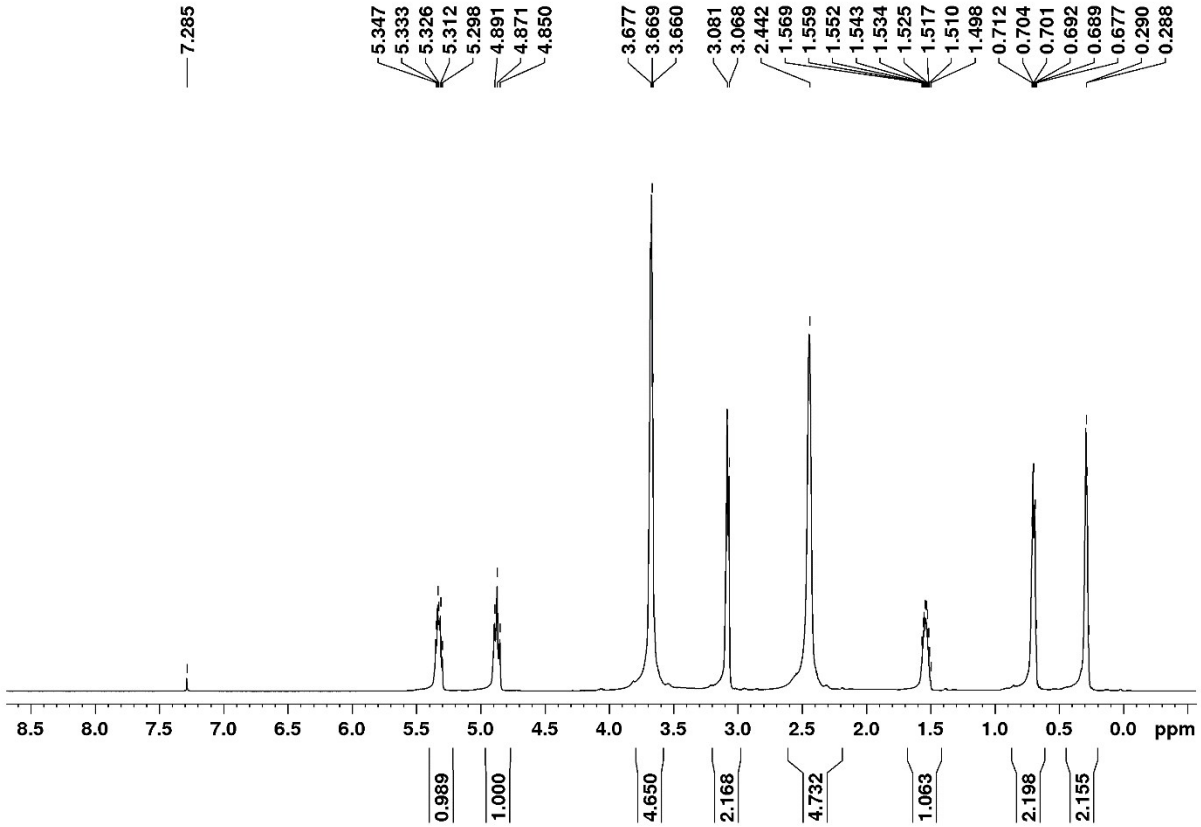
^{1}H-NMR spectrum of (*Z*)-*N*,*N*-dimethyl-5-phenylpent-2-en-1-amine (2f)



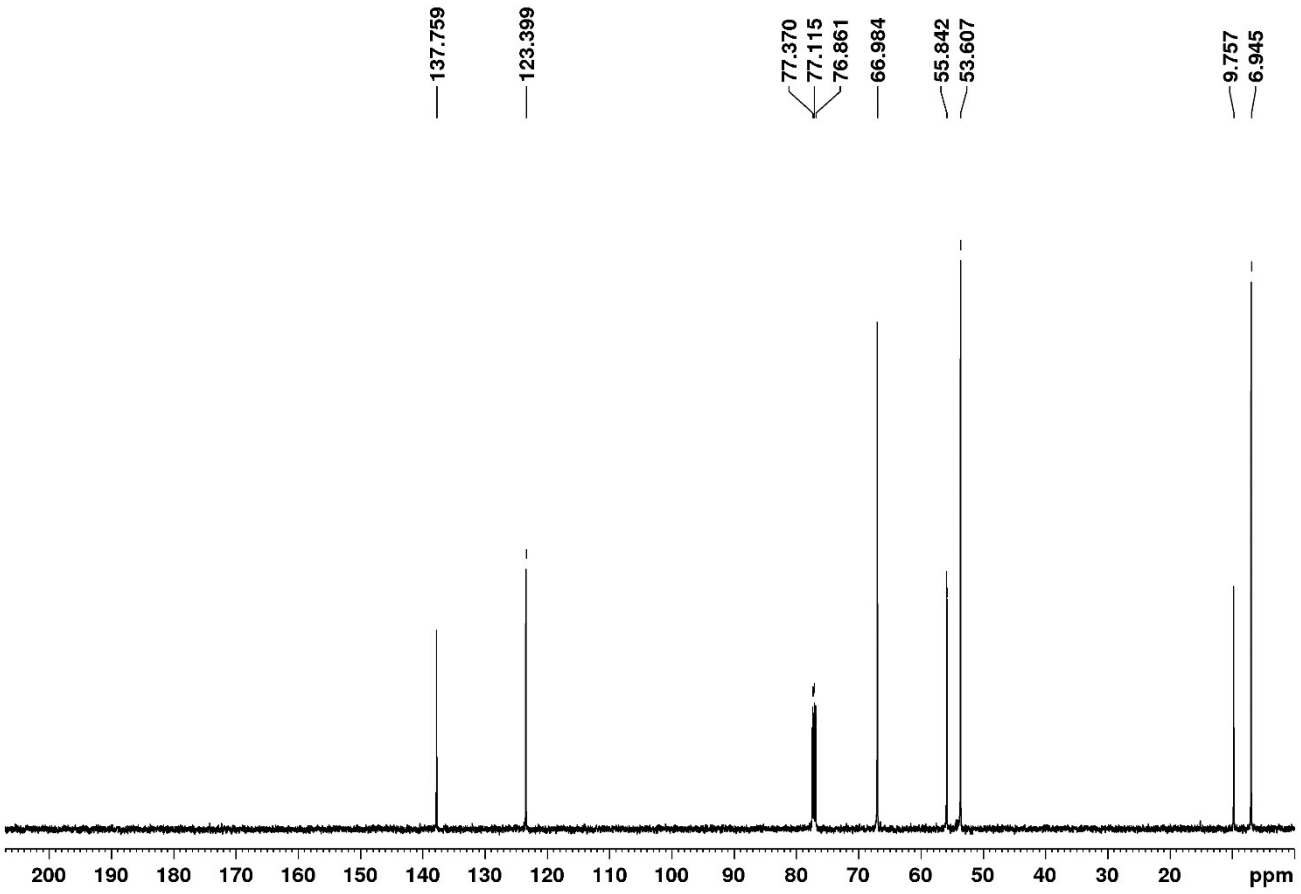
^{13}C-NMR spectrum of (*Z*)-*N*,*N*-dimethyl-5-phenylpent-2-en-1-amine (2f)



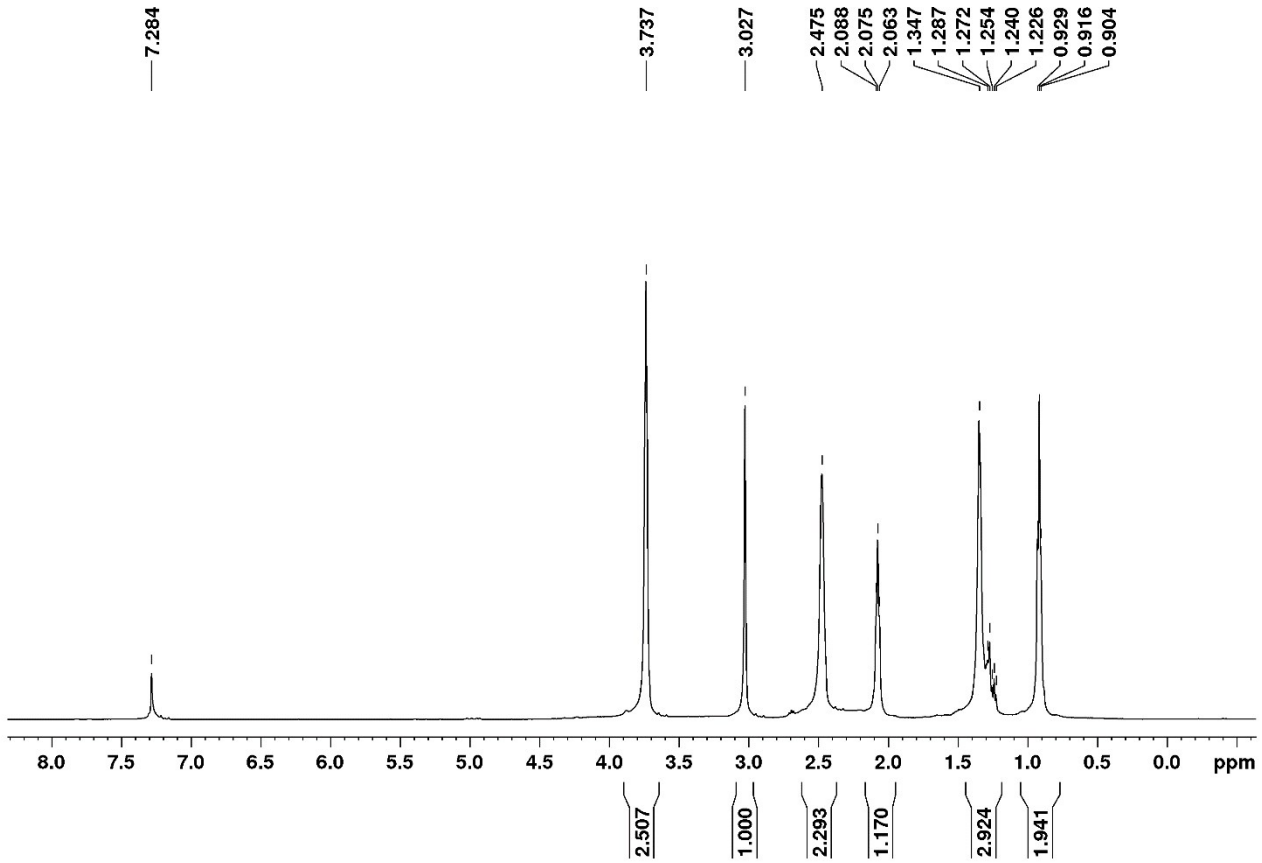
^{1}H-NMR spectrum of (*Z*)-4-(3-cyclopropylallyl)morpholine (2g)



^{13}C-NMR spectrum of (*Z*)-4-(3-cyclopropylallyl)morpholine (2g)



^{1}H-NMR spectrum of (*Z*)-4-(hept-2-en-1-yl-2,3-d_2)morpholine (3e)



^{13}C-NMR spectrum of (*Z*)-4-(hept-2-en-1-yl-2,3-d_2)morpholine (3e)