

Transition metal halide promoted hydride transfer in *N,N*-diisoalkyl-*N*-propargylamines

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The reagents were obtained from Sigma-Aldrich or Acros. Dichloromethane was distilled over P₂O₅. Propargylic amines were prepared by the reaction of 1-alkynes with formaldehyde and diisopropyl amine in dioxane [S1]. NMR spectra were recorded on a Bruker Avance 400 instrument (400 MHz for ¹H and 100 MHz for ¹³C) in CDCl₃. The chemical shifts are reported in ppm relative to TMS as the internal standard. The numbering of atoms in the ¹³C and ¹H NMR spectra of the compounds **2a-d,3-5** is shown in Figure S1. Mass spectra were obtained on a Finnigan 4021 instrument.

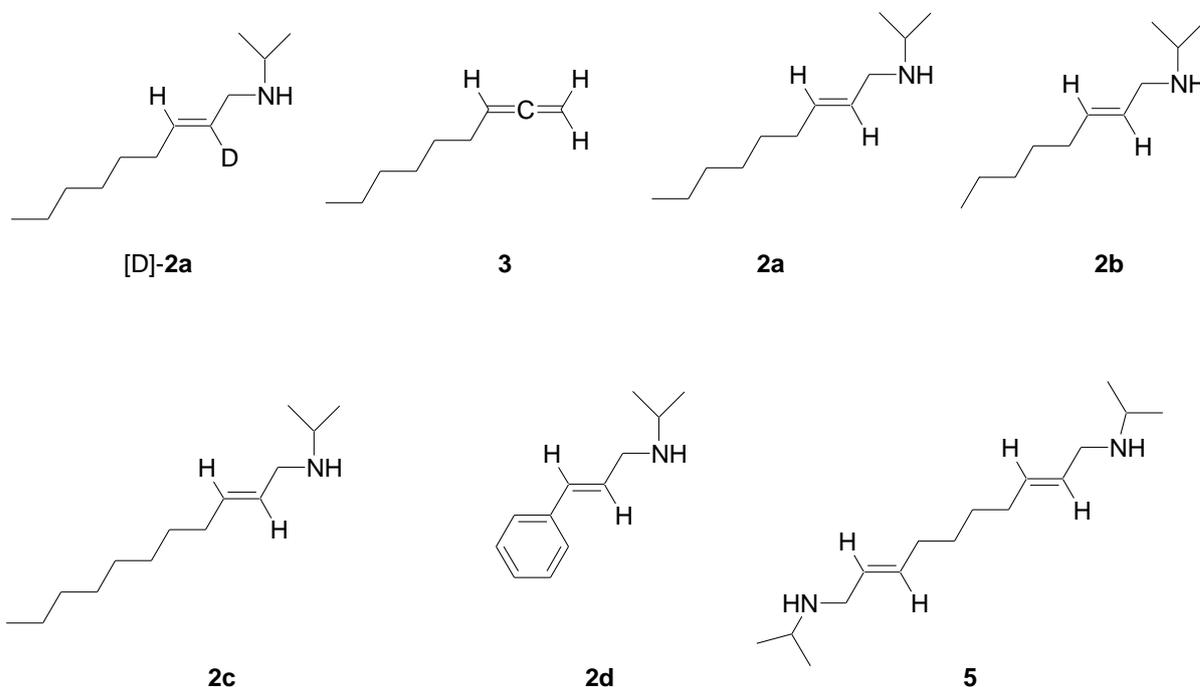


Figure S1. Atom numbering in ¹³C and ¹H NMR spectra of compounds [D]-**2a**, **2a-d**, **3**, **5**.

The reaction of *N,N*-diisopropylnon-2-yn-1-amine **1a with organometallic compounds under the action of transition-metal salts.** A 25-ml argon-flushed flask in an ice bath equipped with a magnetic stirrer and rubber septum was loaded with transition-metal salt (2 mmol) suspended in a solvent (10 ml) and organometallic compound (4 mmol). To this solution, *N,N*-diisopropylnon-2-yn-1-amine **1a** (447 mg, 2 mmol) was added dropwise, and this was stirred at room temperature. The reaction mixture was then diluted with hexane (5 ml), and treated with D₂O (3 ml) by dropwise addition on cooling in an ice bath. The precipitate was filtered on a filter paper. The aqueous layer was extracted with diethyl ether (3×5 ml). The combined organic layers were washed with brine (10 ml), dried over anhydrous CaCl₂. Evaporation of solvent and purification of the residue by column chromatography (hexane/ethyl acetate, 5:1) gave (*E*)-2-deuterio-*N*-isopropylnon-2-en-1-amine [D]-**2a** as a colourless oil. The yield was calculated from the isolated amount of the compound **1**. The yield of nona-1,2-diene **3** was obtained from GC analysis using undecane as an internal standard.

(*E*)-2-Deuterio-*N*-isopropylnon-2-en-1-amine ([D]-2a**).** ¹H NMR (400MHz, CDCl₃): δ = 0.85 (t, *J*= 7.2 Hz, 3 H, C(12)H₃), 1.03 (d, *J*= 6.5 Hz, 6 H, C(5,6)H₃), 1.30-1.45 (m, 8 H, C(8,9,10,11)H₂), 1.98 (q, *J*= 7.1 Hz, 2 H, C(7)H₂), 2.75-2.70 (m, 1 H, C(4)H), 3.14 (s, 2 H, C(1)H₂), 5.45-5.65 (m, 1 H, C(3)H). ¹³C NMR (100MHz, CDCl₃): δ = 14.1 (C(12)), 22.6 (C(11)), 23.0 (2 C, C(5,6)), 28.5 and 29.0 (C(8) and C(9)), 31.5 and 32.4 (C(7) and C(10)), 48.1 (C(4)), 49.4 (C(1)), 128.2 (t, ¹*J*_{CD}=19 Hz, C(2)), 132.4 (C(3)). MS (EI): *m/z* (%) = 184 (56) [M]⁺, 169 (20), 155 (3). Anal. calcd for C₁₂H₂₄DN, (%): C, 78.19; N, 7.60. Found, %: C, 78.3; N, 8.0.

Nona-1,2-diene (3**) [S2].** ¹H NMR (400MHz, CDCl₃): δ = 0.91 (t, *J*= 7.2 Hz, 3 H, C(12)H₃), 1.05 (d, *J*= 6.8 Hz, 3 H, C(9)H₃), 1.25-1.40 (m, 6 H, C(6-8)H₂), 1.40-1.50 (m, 2 H, C(5)H₂), 1.95-2.05 (m, 2 H, C(4)H₂), 4.66 (dt, *J*=6.4, 3.1 Hz, 2H), 5.11 (p, *J*=6.7 Hz, 1H). ¹³C NMR (100MHz, CDCl₃): δ = 14.2 (C(9)), 22.8 (C(8)), 28.4 and 28.9 and 29.3 and 31.8 (C(4) and C(5) and C(6) and C(7)), 74.6 (C(1)), 90.2 (C(3)), 208.7 (C(2)).

Preparation of *E*-alkenylamines **1a-d or **4** via the reaction of *N,N*-diisopropyl-substituted propargylic amines with ZnI₂-MAO reagent (general procedure).** A 25-ml argon-flushed flask in an ice bath, equipped with a magnetic stirrer and rubber septum, was charged with ZnI₂ (2 mmol) suspended in CH₂Cl₂ (10 ml) and MAO-12 (0.8 ml of 7 wt% Al in toluene, 2 mmol). To this solution, was added dropwise *N,N*-diisopropyl-substituted propargylic amine **1a-d** (2 mmol) or **4** (1 mmol), and this was stirred for 5 h at room temperature. Then, the mixture was diluted with hexane (5 ml), and H₂O (3 ml) was added dropwise while cooling the reactor flask in an ice bath. The precipitate was filtered on a filter paper. The aqueous layer was extracted with diethyl ether (3×5 ml). The combined organic layers were washed with brine (10 ml), dried

over anhydrous CaCl₂. Evaporation of solvent and purification of the residue by column chromatography (hexane/ethyl acetate, 5:1) gave the target products **2a-d** or **4**.

(E)-N-Isopropylnon-2-en-1-amine (2a) was obtained from **1a** (447 mg), colourless oil; yield: 308 mg (84%); *R_f* = 0.7 (hexane/ethyl acetate, 5:1). ¹H NMR (400MHz, CDCl₃): δ = 0.89 (t, *J* = 7.5 Hz, 3 H, C(12)H₃), 1.06 (d, *J* = 6.5 Hz, 6 H, C(5,6)H₃), 1.30-1.45 (m, 8 H, C(8,9,10,11)H₂), 2.02 (q, *J* = 7.1 Hz, 2 H, C(7)H₂), 2.75-2.70 (m, 1 H, C(4)H), 3.18 (d, *J* = 6.5 Hz, 2 H, C(1)H₂), 5.30-5.65 (m, 2 H, C(2,3)H). ¹³C NMR (100MHz, CDCl₃): δ = 14.1 (C(12)), 22.6 (C(11)), 23.0 (2 C, C(5,6)), 28.5 and 29.0 (C(8) and C(9)), 31.5 and 32.4 (C(7) and C(10)), 48.1 (C(4)), 49.4 (C(1)), 128.4 (C(2)), 132.4 (C(3)).

(E)-N-Isopropyloct-2-en-1-amine (2b) [S3] was obtained from **1b** (418 mg), colourless oil; yield: 260 mg (77%); *R_f* = 0.8 (hexane/ethyl acetate, 5:1). ¹H NMR (400MHz, CDCl₃): δ = 0.89 (t, *J* = 6.9 Hz, 3 H, C(11)H₃), 1.06 (d, *J* = 6.5 Hz, 6 H, C(5,6)H₃), 1.25-1.40 (m, 6 H, C(8,9,10)H₂), 2.01 (q, *J* = 7.1 Hz, 2 H, C(7)H₂), 2.50-2.80 (m, 1 H, C(4)H), 3.18 (d, *J* = 6.5 Hz, 2 H, C(1)H₂), 5.40-5.70 (m, 2 H, C(2,3)H). ¹³C NMR (100MHz, CDCl₃): δ = 14.0 (C(11)), 22.5 (C(10)), 22.9 (2 C, C(5,6)), 29.0 and 31.4 and 32.3 (C(7) and C(8) and C(9)), 48.0 (C(4)), 49.4 (C(1)), 128.4 (C(2)), 132.6 (C(3)). MS (EI): *m/z* (%) = 169 (10) [M]⁺, 154 (23), 69 (60), 44 (100), 41 (28).

(E)-N-Isopropylundec-2-en-1-amine (2c) was obtained from **1c** (502 mg), colourless oil; yield: 295 mg, (71%); *R_f* = 0.5 (hexane/ethyl acetate, 5:1). ¹H NMR (400MHz, CDCl₃): δ = 0.87 (t, *J* = 6.6 Hz, 3 H, C(14)H₃), 1.04 (d, *J* = 6.3 Hz, 6 H, C(5,6)H₃), 1.15-1.35 (m, 12 H, C(8-13)H₂), 1.99 (q, *J* = 6.9 Hz, 2 H, C(7)H₂), 2.60-2.80 (m, 1 H, C(4)H), 3.21 (d, *J* = 6.5 Hz, 2 H, C(1)H₂), 5.45-5.60 (m, 2 H, C(2,3)H). ¹³C NMR (100MHz, CDCl₃): δ = 14.3 (C(14)), 22.9 (C(13)), 23.2 (2 C, C(5,6)), 29.4 and 29.6 and 29.7 and 32.1 and 32.6 (C(7) and C(8) and C(9) and C(10) and C(11) and C(12)), 48.3 (C(4)), 49.6 (C(1)), 128.7 (C(2)), 132.7 (C(3)). MS (EI): *m/z* (%) = 211 (1) [M]⁺, 195 (23), 112 (18), 98 (22). Anal.calcd for C₁₄H₂₉N, (%): C, 79.55; H, 13.83; N, 6.63. Found, %: C, 79.3; H, 14.0; N, 6.6.

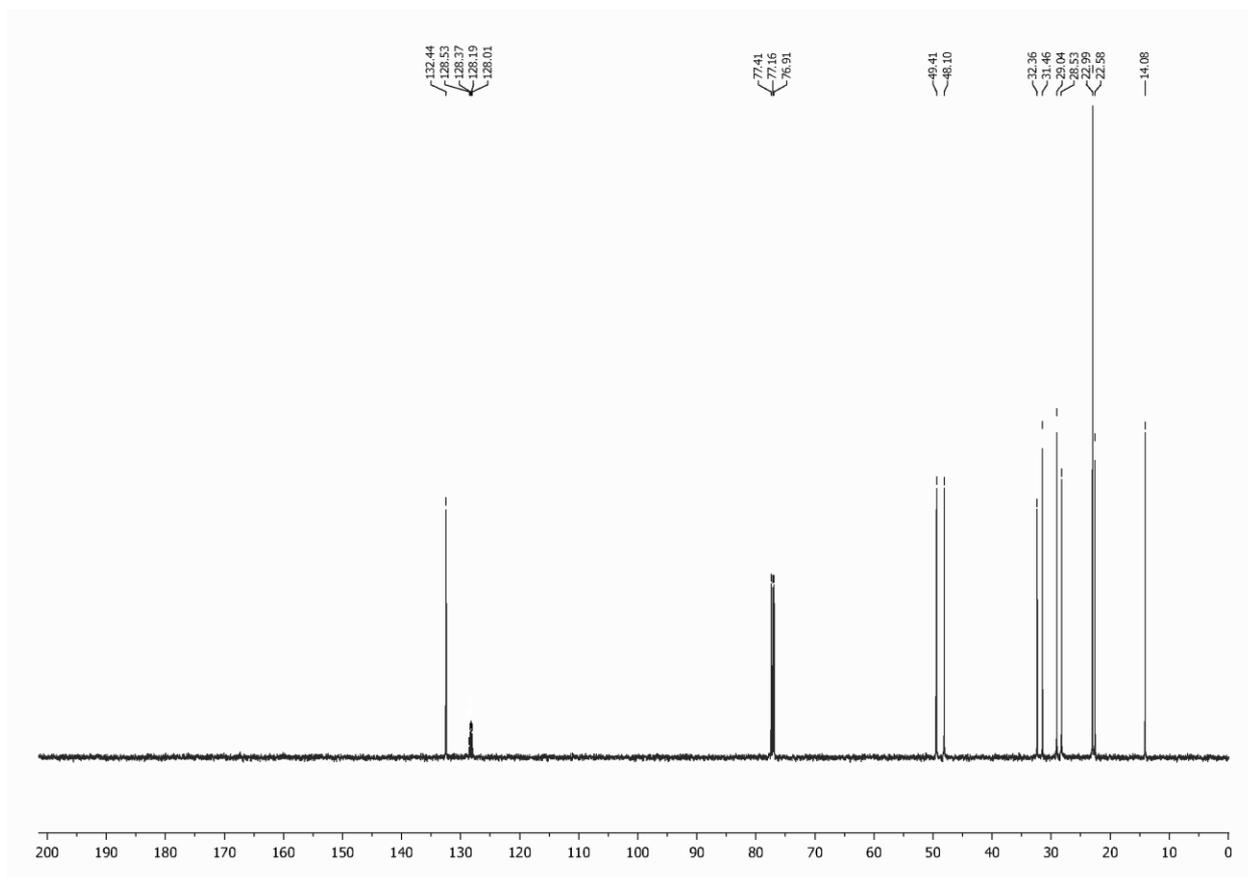
(E)-N-Isopropyl-3-phenylprop-2-en-1-amine (2d) [S3] was obtained from **1d** (430 mg), colorless oil; yield: 312 mg, (89%); *R_f* = 0.5 (hexane/ethyl acetate, 5:1). ¹H NMR (400MHz, CDCl₃): δ = 1.13 (d, *J* = 6.2 Hz, 6 H, C(5,6)H₃), 2.86-3.00 (m, 1 H, C(4)H), 3.44 (d, *J* = 6.3 Hz, 2 H, C(1)H₂), 6.30-6.37 (m, 1 H, C(2)H), 6.55 (d, *J* = 16 Hz, 1 H, C(3)H), 7.20-7.50 (m, 5 H, Ph). ¹³C NMR (100MHz, CDCl₃): δ = 23.0 (2 C, C(5,6)), 48.2 (C(4)), 49.5 (C(1)), 126.3 (2 C, C(8,12)), 127.3 C(10)), 128.5 (2 C, C(9,11)), 128.8 (C(2)), 131.0 (C(3)), 137.2 (C(7)).

(2*E*,8*E*)-*N*¹,*N*¹⁰-Diisopropyldeca-2,8-diene-1,10-diamine (**5**) was obtained from *N*¹,*N*¹,*N*¹⁰,*N*¹⁰-tetraisopropyldeca-2,8-diyne-1,10-diamine (333 mg, 1 mmol), colourless oil, yield: 174 mg, (69%); *R*_f = 0.6 (hexane/ethyl acetate, 5:1). ¹H NMR (400MHz, CDCl₃): δ = 1.03 (d, *J*= 6.2 Hz, 12 H, C(5,6)H₃), 1.30-1.40 (m, 4 H, C(8)H₂), 1.90-2.10 (m, 4 H, C(7)H₂), 2.70-2.90 (m, 2 H, C(4)H), 3.20 (d, *J*= 6.5 Hz, 4 H, C(1)H₂), 5.40-5.70 (m, 4 H, C(2,3)H). ¹³C NMR (100MHz, CDCl₃): δ = 23.1 (4 C, C(5,6)), 28.9 (2 C, C(8)), 32.3 (2 C, C(7)), 48.2 (2 C, C(4)), 49.4 (2 C, C(1)), 128.8 (2 C, C(2)), 132.2 (2 C, C(3)). Anal.calcd for C₁₆H₃₂N₂, (%): C, 76.13; H, 12.78; N, 11.10. Found, %: C, 76.1; H, 12.5; N, 11.1.

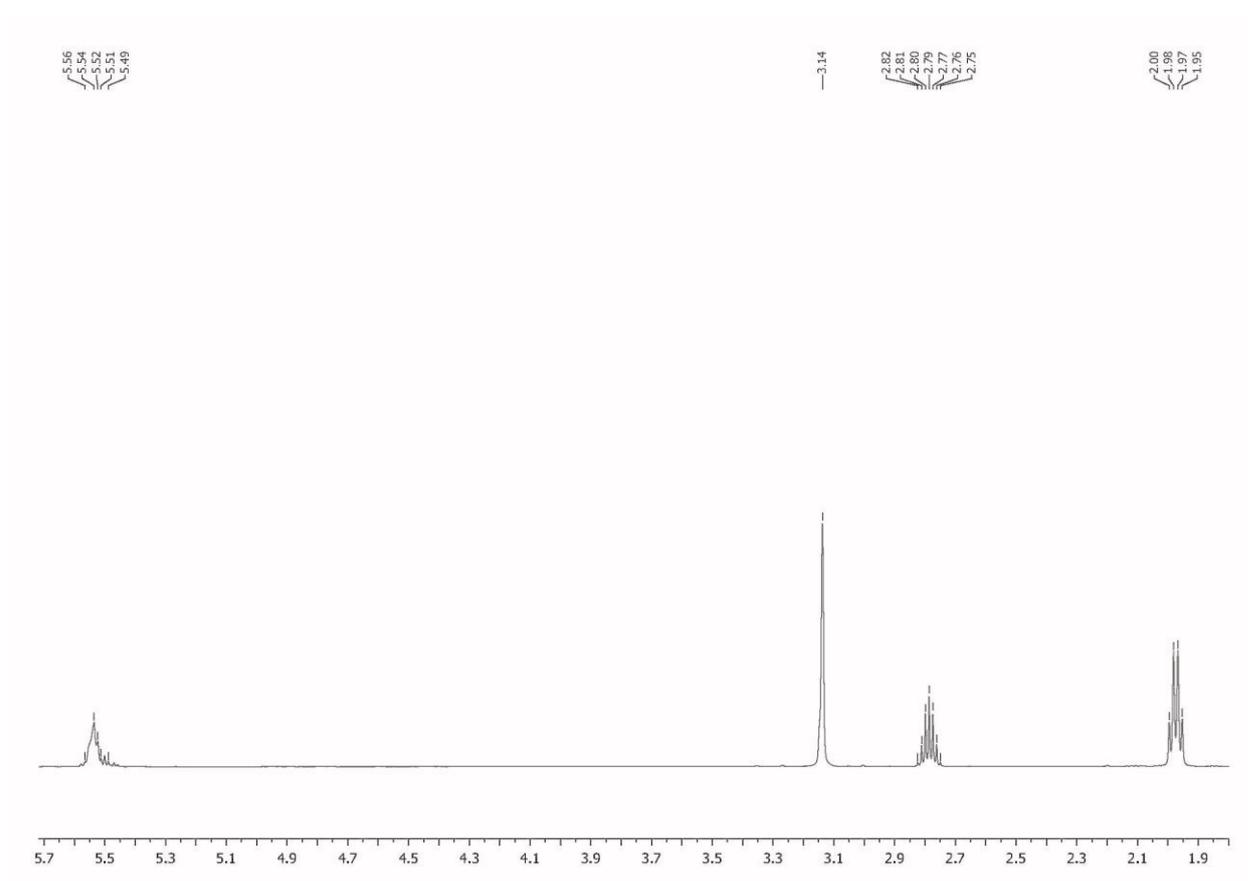
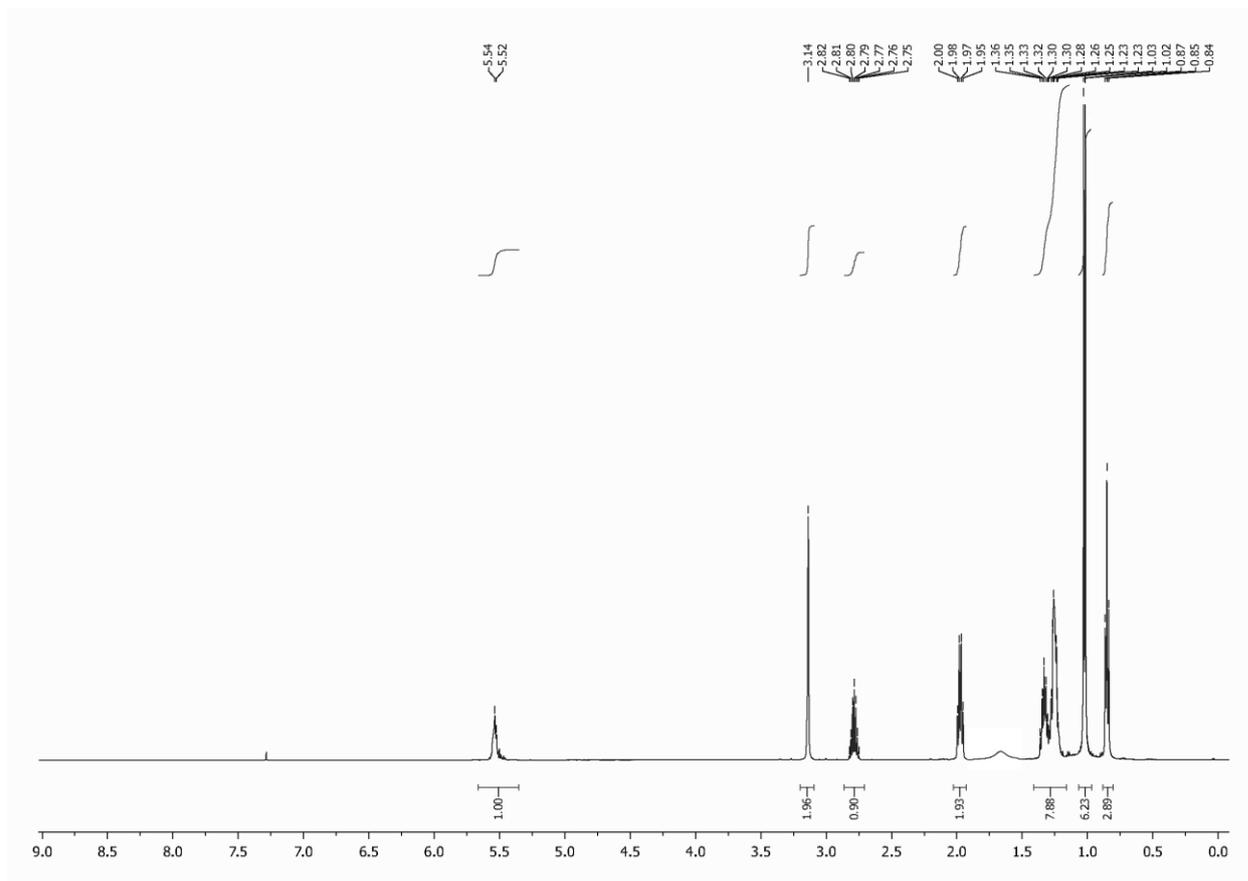
References

- S1 *Synthesis of Acetylenes, Allenes and Cumulenes: Methods and Techniques*, ed. L. Brandsma, Elsevier, Amsterdam, 2004.
- S2 K. M. Buchner, T. B. Clark, J. M. Loy, T. X. Nguyen and K. A. Woerpel, *Org. Lett.*, 2009, **11**, 2173.
- S3 I. R. Ramazanov, R. N. Kadikova, Z. R. Saitova and U. M. Dzhemilev, *Synlett*, 2018, **29**, 1191.

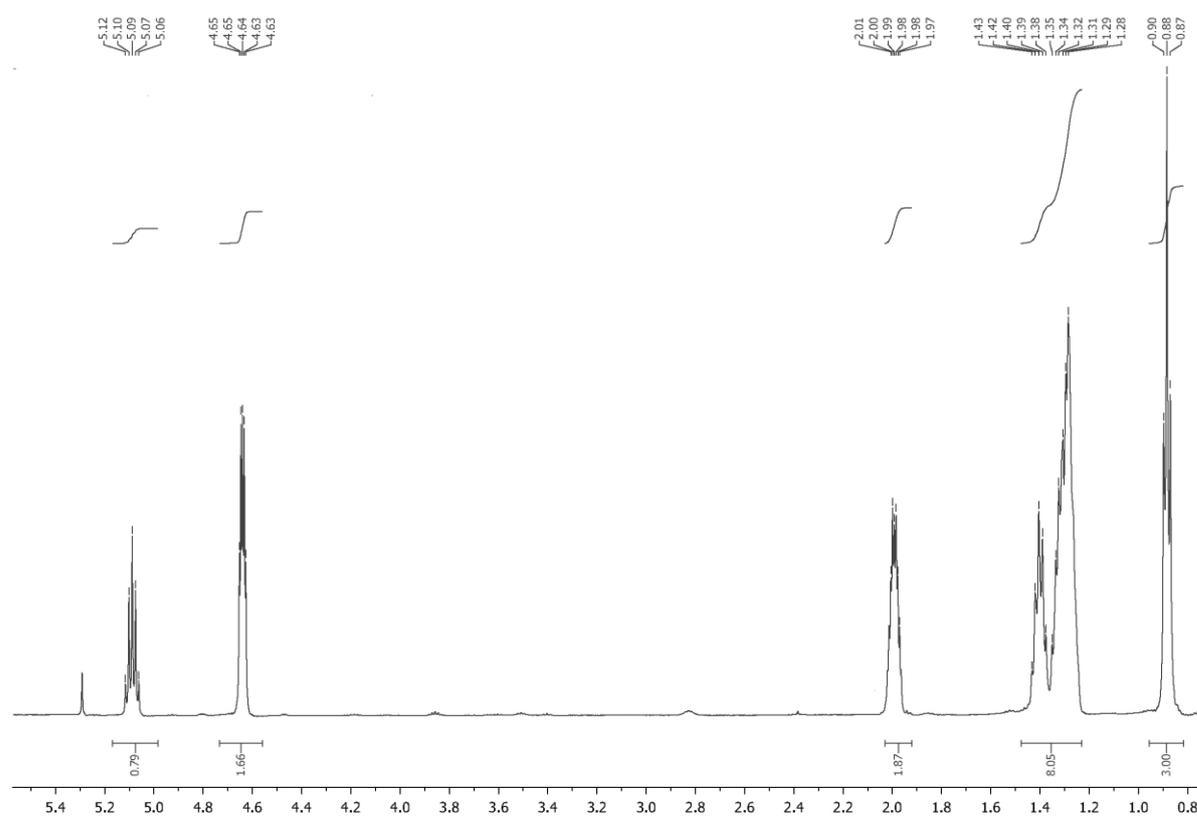
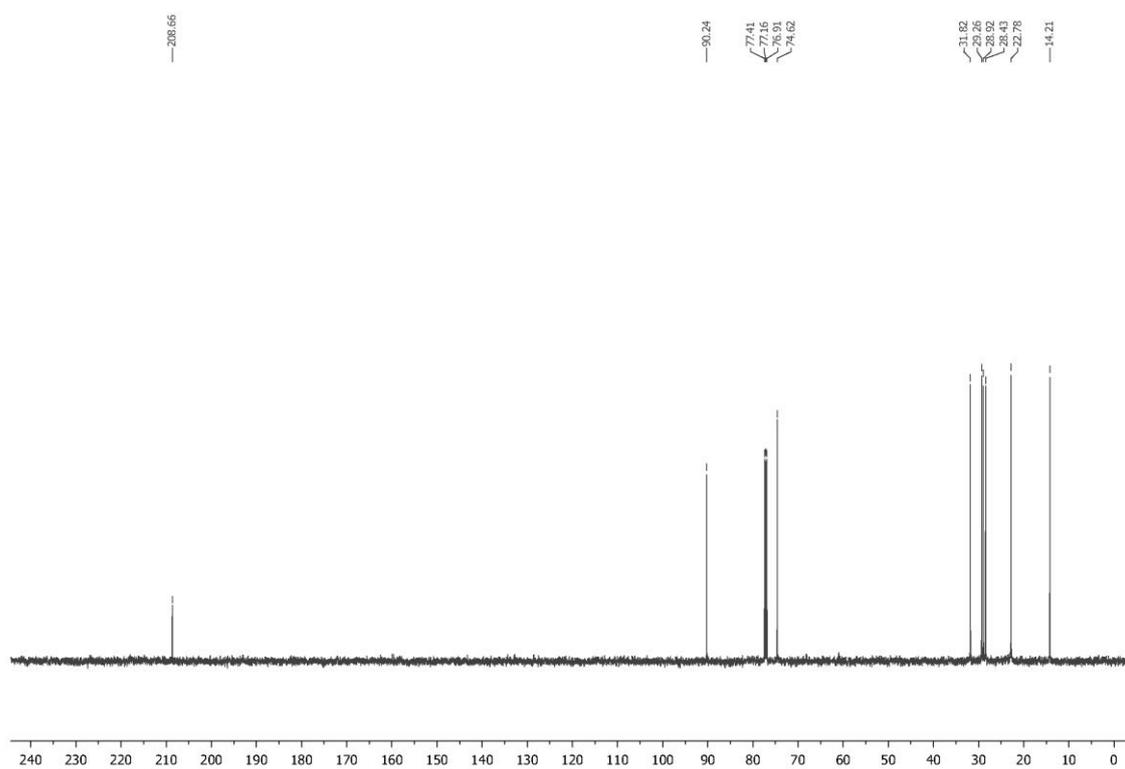
(*E*)-2-Deuterio-*N*-isopropylnon-2-en-1-amine ([D]-2a)



(E)-2-Deuterio-N-isopropylnon-2-en-1-amine ([D]-2a)

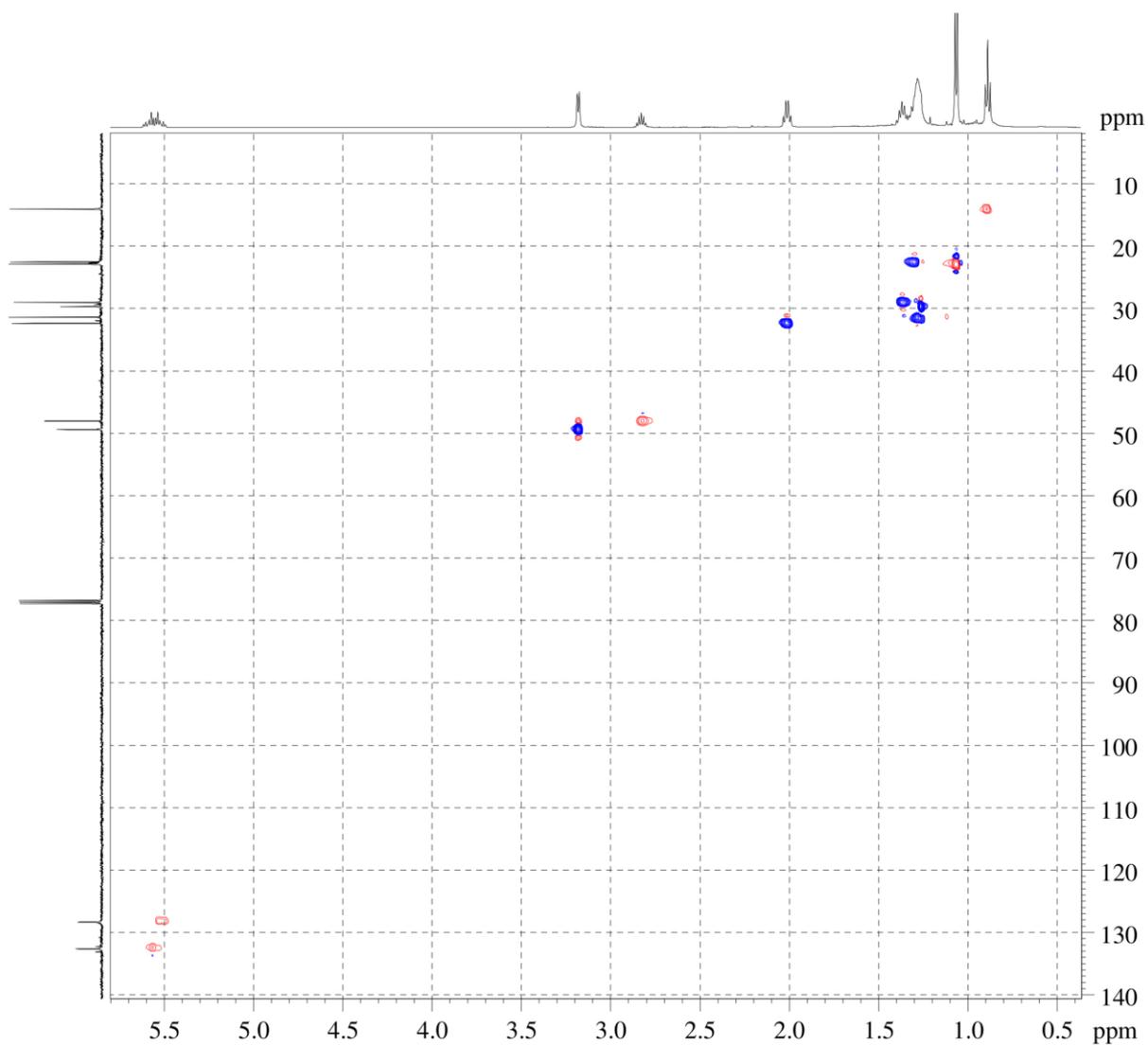


Nona-1,2-diene (3)

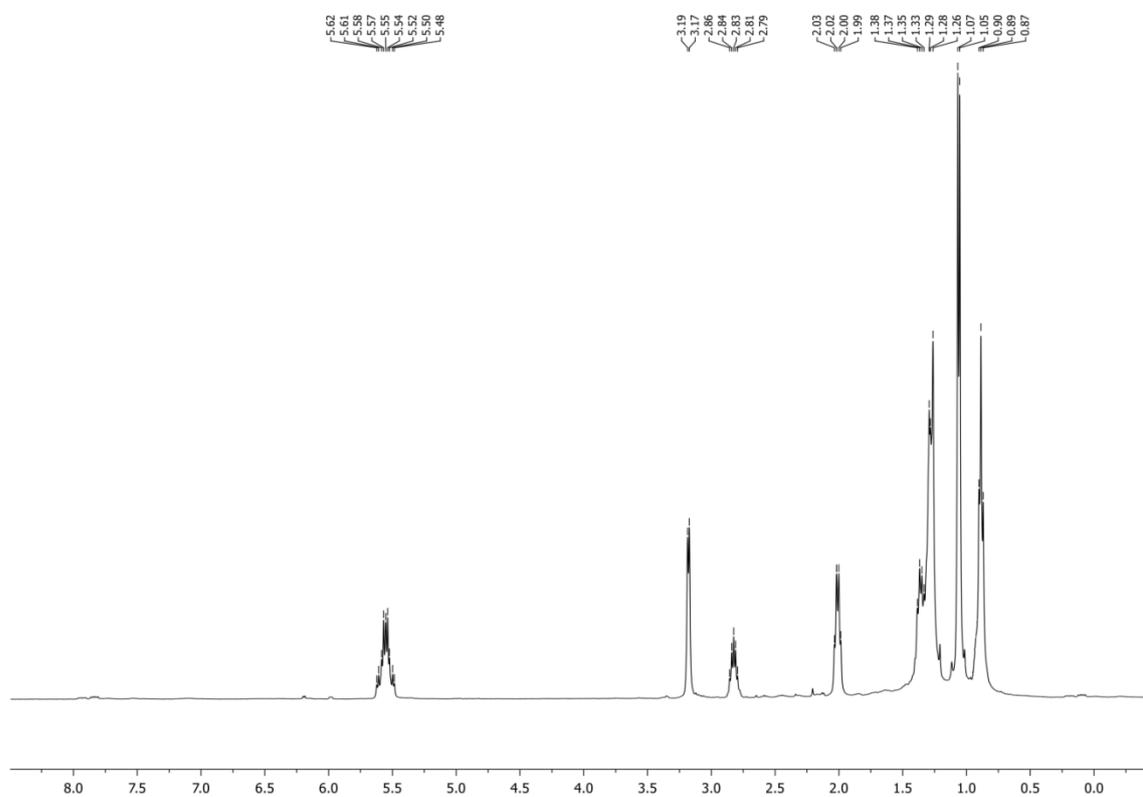
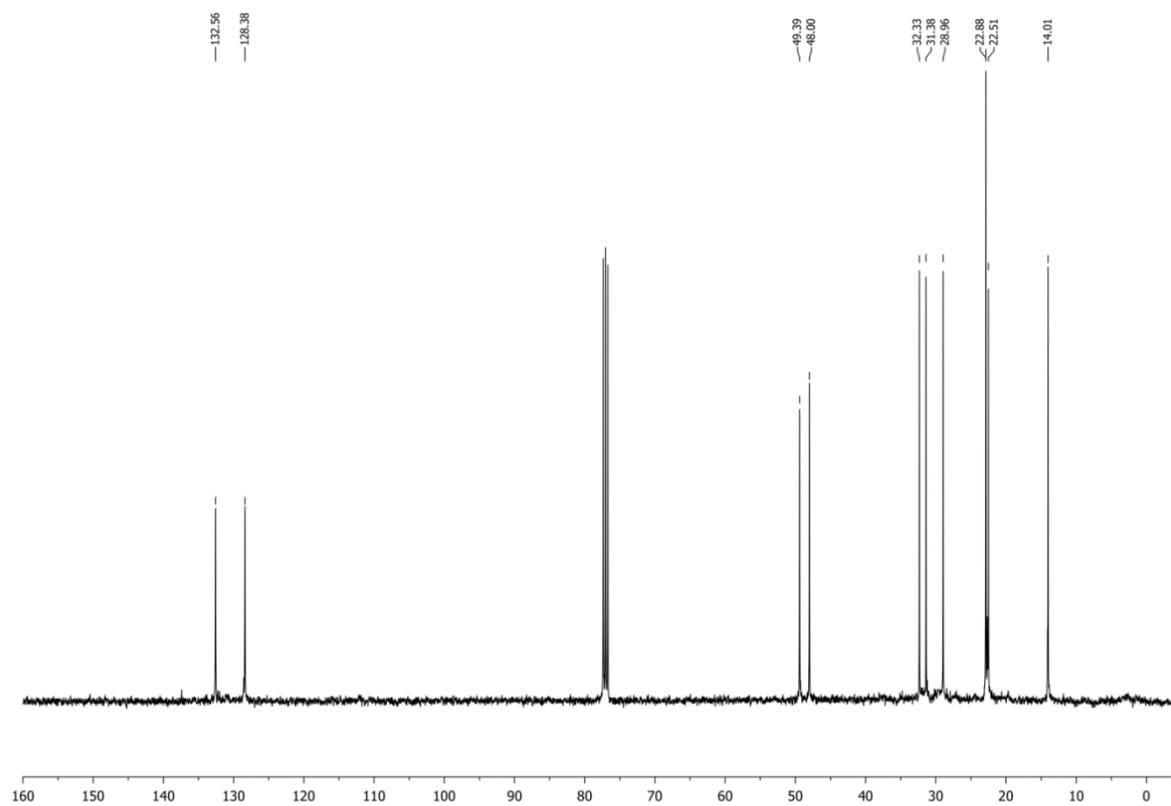


(E)-N-Isopropylnon-2-en-1-amine (2a)

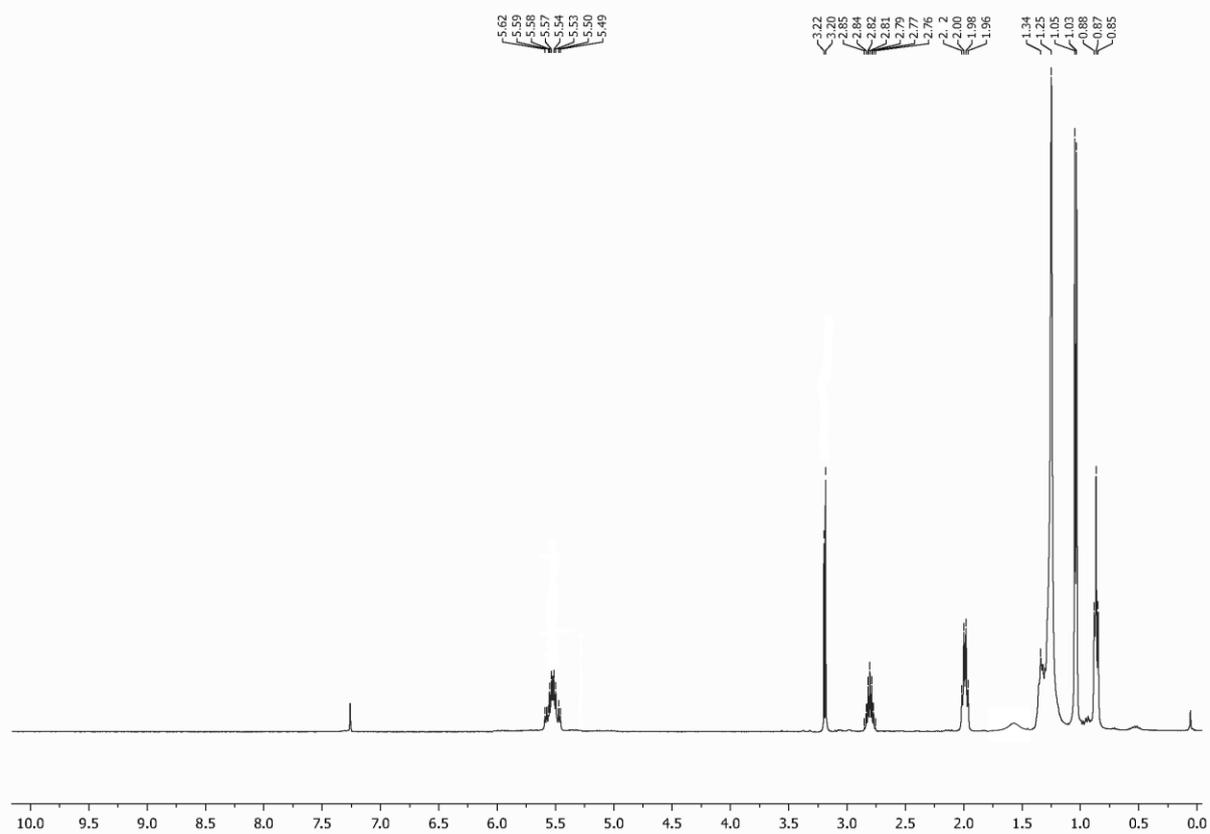
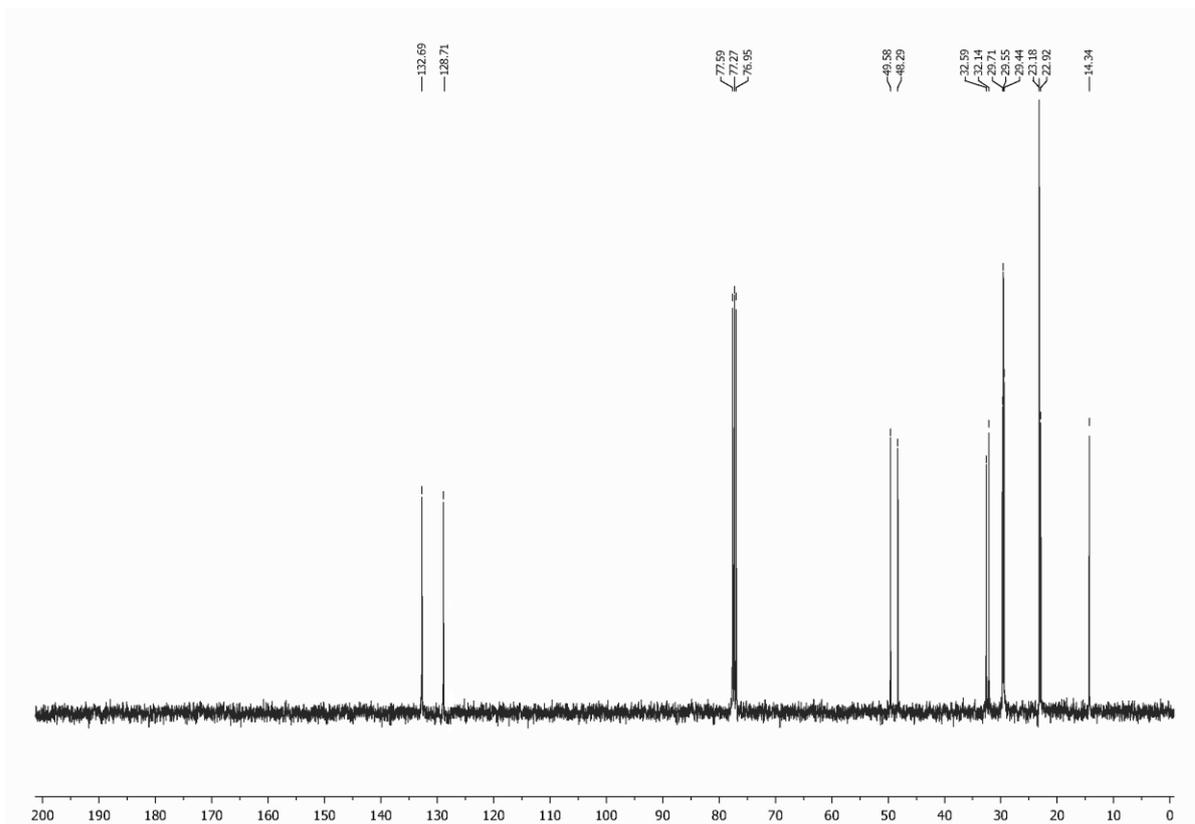
HSQC



(E)-N-Isopropyloct-2-en-1-amine (2b):

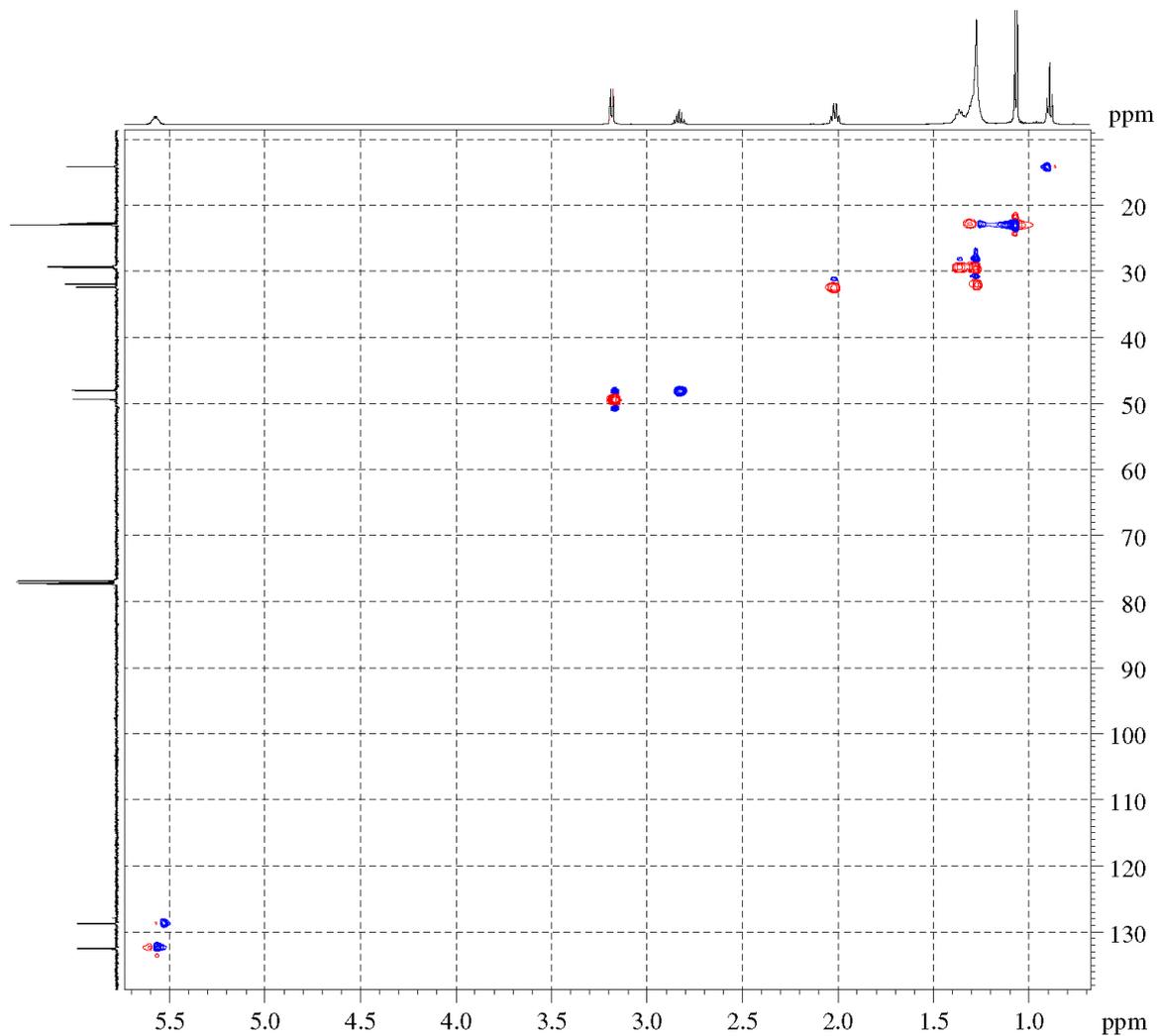


(E)-N-Isopropylundec-2-en-1-amine (2c):

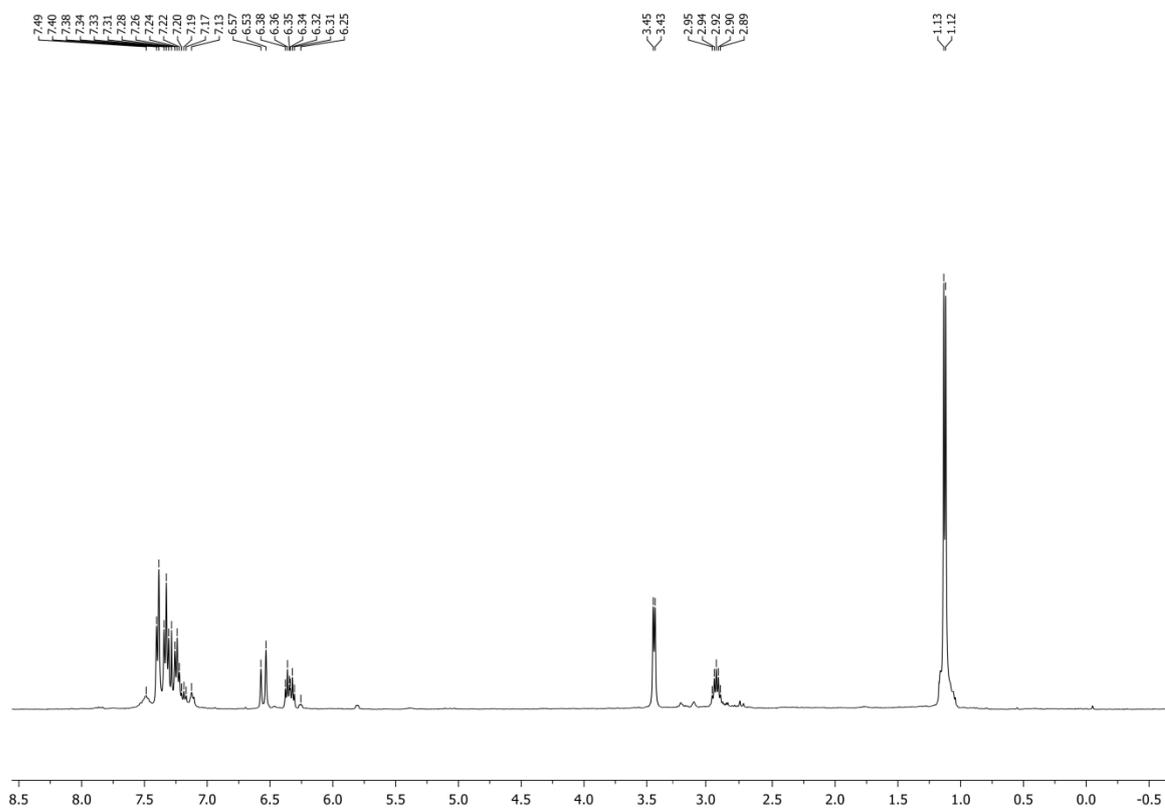
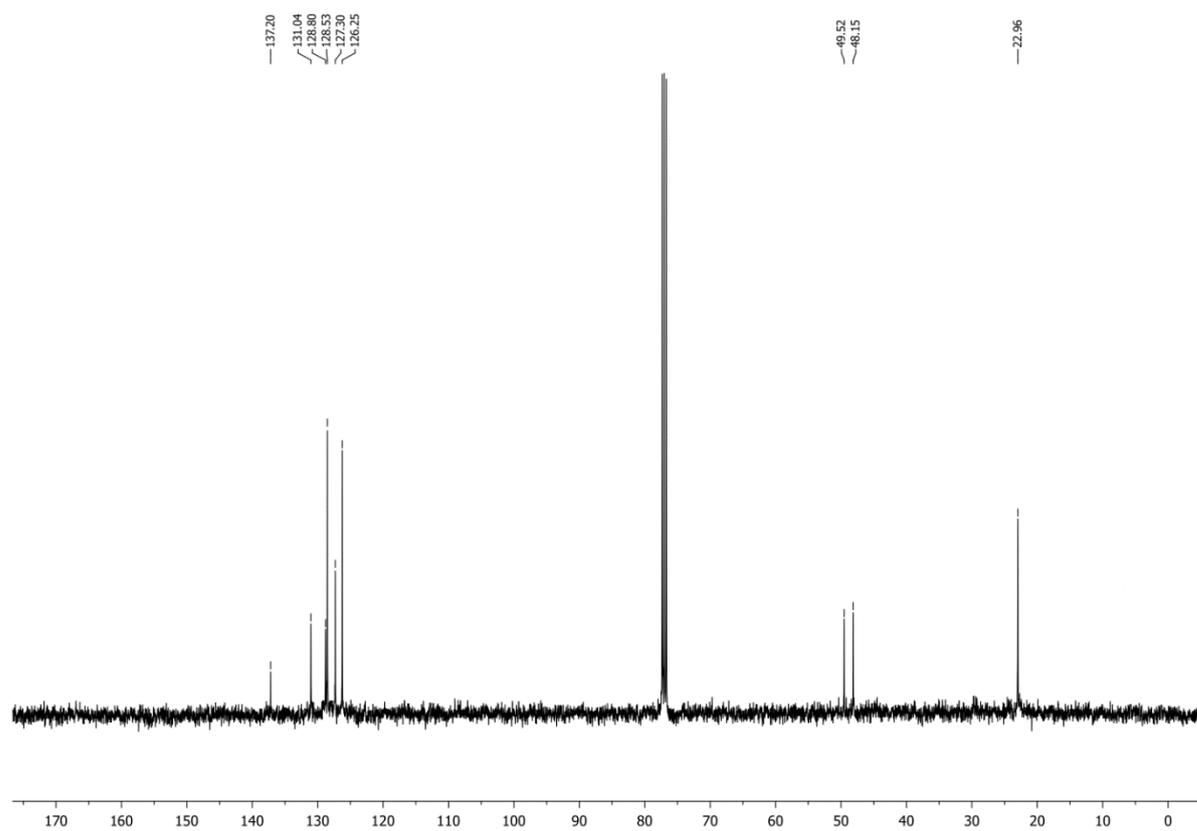


(E)-N-Isopropylundec-2-en-1-amine (2c)

HSQC

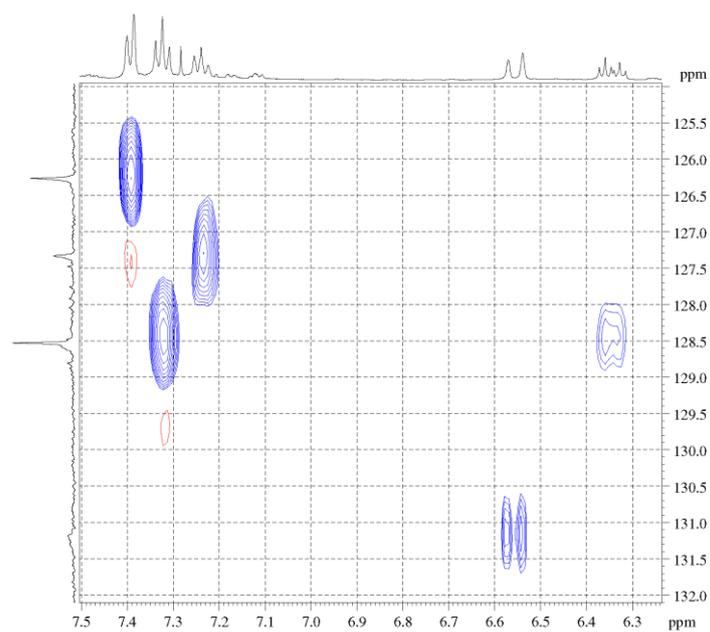
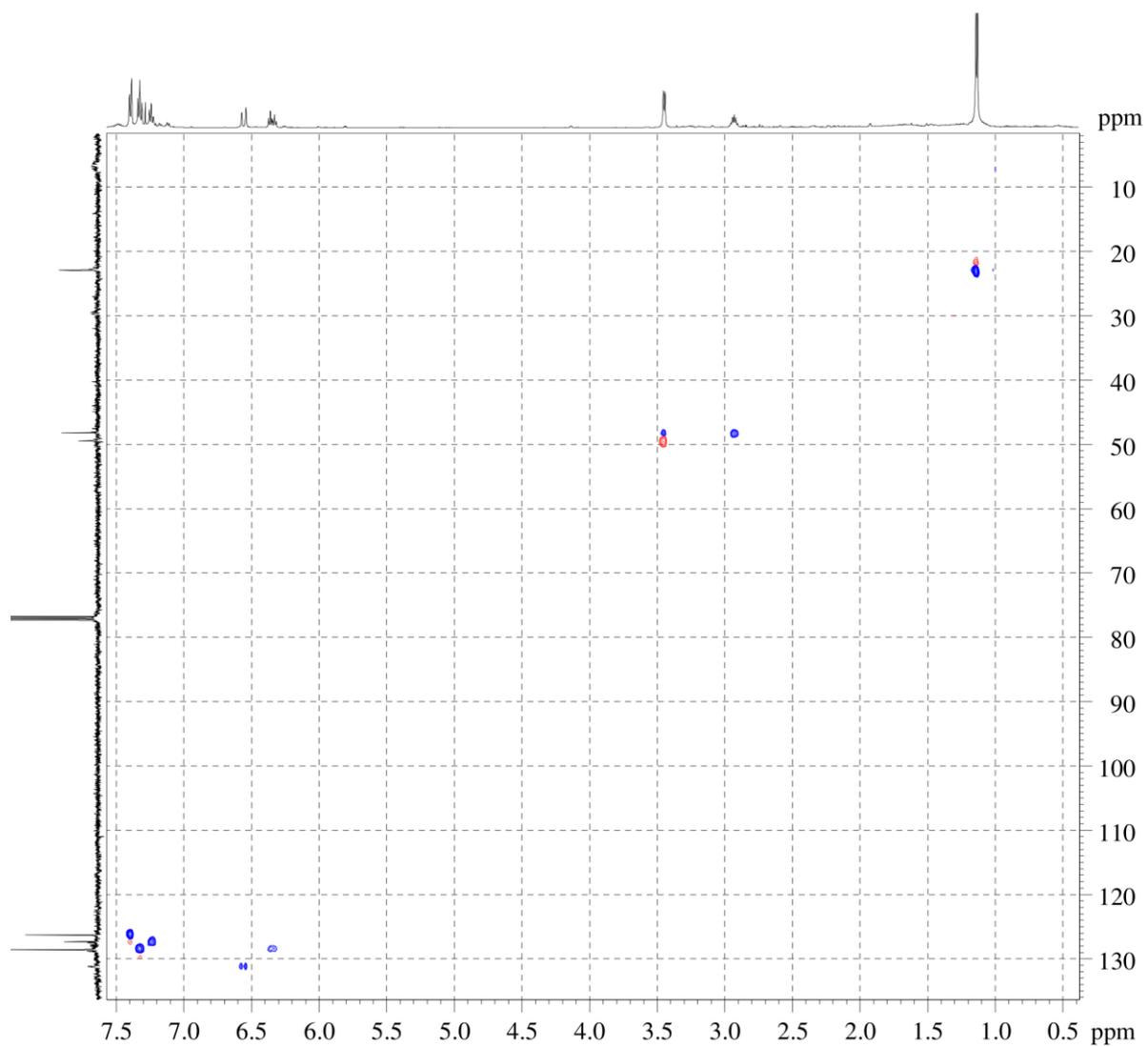


(E)-N-Isopropyl-3-phenylprop-2-en-1-amine (2d):



(E)-N-Isopropyl-3-phenylprop-2-en-1-amine (2d)

HSQC



(2E,8E)-N¹,N¹⁰-Diisopropyldeca-2,8-diene-1,10-diamine (5):

