

Convenient Synthesis of (Z)-7- and (E)-9-dodecene-1-yl Acetate, Components of Some Lepidoptera Insect Sex Pheromone

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Were developed new and practical synthesis of (Z)-7-dodecene-1-yl acetate and (E)-9-dodecene-1-yl acetate. The routes involve, as the key step, the use of the mercury derivative of the terminal-alkyne ω -functionalised as intermediate. The synthesis of (Z)-7-dodecene-1-yl acetate was based on a $C_6 + C_2 = C_8$ and $C_8 + C_4 = C_{12}$ coupling scheme, starting from 1,6-hexane-diol. The first coupling reaction took place between 1-tert-butoxy-6-bromo-hexane and lithium acetylide-ethylendiamine complex obtaining 1-tert-butoxy-oct-7-yne, which is transformed in di[tert-butoxy-oct-7-yne]mercury. The mercury derivative was directly lithiated and then alkylated with 1-bromobutane obtaining 1-tert-butoxy-dodec-7-yne. After acetylation and reduction with lithium aluminium hydride of 7-dodecyne-1-yl acetate gave (Z)-7-dodecene-1-yl acetate with 96 % purity. The synthesis of (E)-9-dodecene-1-yl acetate was based on a $C_8 + C_2 = C_{10}$ and $C_{10} + C_2 = C_{12}$ coupling scheme, starting from 1,8-octane-diol. The first coupling reaction took place between 1-tert-butoxy-8-bromo-octane and lithium acetylide-ethylendiamine complex obtaining 1-tert-butoxy-dec-9-yne, which is transformed in di[tert-butoxy-dec-9-yne]mercury. The mercury derivative was directly lithiated and then alkylated with 1-bromoethane obtaining 1-tert-butoxy-dodec-9-yne. After reduction with lithium aluminium hydride of 1-tert-butoxy-(E)-9-dodecene and acetylation was obtained (E)-9-dodecene-1-yl acetate with 97 % purity.

Keywords: (Z)-7-dodecene-1-yl acetate, (E)-9-dodecene-1-yl acetate, Lepidoptera, sex pheromone

(Z)-7-dodecene-1-yl acetate and (E)-9-dodecene-1-yl acetate are components of lots of *Lepidoptera* insect sex pheromones [1]. Some important economic pest insects are: *Trichoplusia ni* (cabbage looper) and *Sparganothis Pilleriana* (vine leafroller).

The synthesis of (Z)-7-dodecene-1-yl acetate [2-5], (E)-9-dodecene-1-yl acetate [6, 7] and (Z)- and (E)-8-dodecene-1-yl-acetate [8] are well known in the literature. Also, the synthesis of (11Z, 13Z)-hexadecadien-1-yl was studied in [9].

Experimental part

GS-MS analysis were performed on a GS-MS spectrometer Agilent 7890A GC& 5975 GS/MS Serie MSD. $^1\text{H-NMR}$ (300 MHz) and $^{13}\text{C-NMR}$ (75 MHz) spectra were recorded at *rt* in CDCl_3 on a Bruker 300 MHz spectrometer, using TMS line as reference. A Perkin Elmer Spectrometer Model 700 was used for IR spectra.

6-Bromo-hexane-1-ol (4)

To a solution 59 g (0.5 mole) of 1,6-hexane-diol solved in 300 mL benzene was added 86 mL hydrobromic acid 47%. The reaction mixture was refluxed for 2.5 h. The organic layer was separated and washed with brine, saturated NaHCO_3 solution and dried over anhydrous MgSO_4 . After distillation of the solvent, 44.1g of 6-bromo-hexane-1-ol (4) were obtained. Yield: 75%, GC purity: 99%.

Mass spectrum (m/z. %): 162(1.47), 135(12.74), 133(13.72), 108(3.92), 109(4.41), 96(1.96), 94(1.96), 84(3.92), 83(57.84), 82(16.17), 81(4.9), 80(<1), 79(1.96), 69(15.68), 68(2.45), 67(13.72), 57(6.86), 56(8.82), 55(100), 54(11.76), 53(8.82), 51(1.96), 50(<1), 45(2.94), 44(4.41), 43(19.6), 42(28.43), 41(80.39), 40(7.35), 39(41.17), 38(2.94), 31(50.98), 29(27.45), 28(9.8).

1-tert-Butoxy-6-bromo-hexane (5)

To a solution 33.1 g (182 mmoles) of 4-bromo-hexane-1-ol (4) and 154 mL *tert*-butyl-methyl-ether was added dropwise 9.3 mL concentrated sulfuric acid under cooling. The reaction mixture was maintained at 40°C. The reaction was checked by TLC on silica gel G (benzene:ether 2:1, detection with H_2SO_4 d=1.25). The reaction mixture was diluted with water. After removal of the *tert*-butyl-methyl-ether under reduced pressure, the mixture was extracted with ethyl ether (3x50 mL). The combined ethereal extracts were washed with saturated NaHCO_3 solution up to basic and dried over Na_2SO_4 . After the removal of the solvent, 28.5 g of 1-*tert*-butoxy-4-bromo-hexane (5) were obtained. Yield: 84%, GC purity: 97%. Mass spectrum (m/z. %): 221(13.72), 181(<1), 163(13.23), 135(<1), 121(<1), 107(<1), 83(44.12), 67(<1), 57(100), 41(51.47), 29(24.51).

1-tert-Butoxy-oct-7-yne (6)

All operations were performed in an inert gas atmosphere and under stirring.

To a stirred and cooled (0°) suspension of 5.35 g (58 mmoles) lithium acetylide-ethylendiamine complex in 29 mL anhydrous dimethyl sulfoxide was slowly added (60 min) 6.87 g (28 mmoles) compound 5. The reaction mixture was stirred at room temperature for 6h, then it was poured into ice water and extracted with hexane. The combined hexane extracts were washed with water, brine and dried over MgSO_4 . After removal of the solvent, 4.3 g of 1-*tert*-butoxy-oct-7-yne (6) were obtained. Yield: 76 %, GC purity: 94 %. Mass spectrum (m/z. %): 168(<1), 167(22.55), 149(<1), 137(<1), 126(<1), 110(<1), 109(13.72), 93(<1), 81(16.67), 67(52.94), 57(100), 43(20.59), 41(53.92), 29(19.61).

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Di[1-tert-Butoxy-oct-7-yne]mercury (7)

To 15.93 g of potassium iodide dissolved in 15.93 mL water was added 6.44 g mercury (II) chloride and the mixture was stirred till the mercury salt was dissolved. To the mixture were added 12.98 mL of 10% sodium hydroxide solution. After external cooling of reaction mixture with ice, were added dropwise 4 g (21.97 mmoles) of 1-*tert*-butoxy-oct-7-yne (**6**) dissolved in 68.36 mL cooling ethyl alcohol. The reaction mixture was completed in 1 hour under stirring. The obtained precipitate was filtrated and washed on the filter with cooling aqueous ethylic alcohol 50%. After drying were obtained, 3 g of di[*tert*-butoxy-oct-7-yne] mercury (**7**). Yield: 75%, m.p.= 99° C.

1-tert-Butoxy-dodec-7-yne (8)

All operations were performed in an inert gas atmosphere and under stirring.

1.65 g (2.93 mmoles) of compound **8** in 7.36 mL diglyme was treated with 0.04 g lithium (5.72 mmoles) at 100-115° C for 20 min. 2 g (14.59 mmoles) of butyl bromide dissolved in 3 mL diglyme was added dropwise at 90-93° C then the temperature was raised to 115-120° C under stirring for 6 hours. The mixture was poured out over the 100 g of break ice. The reaction mixture was extracted with petroleum ether. The ethereal solution was washed successively with 10% HCl, water and brine till neutral pH of the washings. After drying over MgSO₄, the solvent was removed and 1.3 g of 1-*tert*-butoxy-dodec-7-yne (**8**) was obtained. Yield: 65%, GC purity: 95%. Mass spectrum (m/z, %): 223(<1), 209(<1), 195(<1), 182(<1), 164(<1), 152(<1), 135(<1), 123(10.29), 109(38.23), 95(45.1), 81(44.12), 67(38.23), 57(100), 41(44.12), 29(13.72).

7-dodecyne-1-yl acetate (9)

3 g (12.60 mmol) of 1-*tert*-butoxy-dodec-7-yne (**8**) was dissolved in 12.60 mL of 1:10 mixture of acetyl chloride:acetic acid and was refluxed for 4-5 h. The reaction development was checked up by TLC on silica gel G (hexane:ether, 15:1, detection with H₂SO₄ d=1.25). The solution was poured on crushed ice, extracted with petroleum ether, washed with brine and with aqueous NaHCO₃ till neutral pH of the washings was obtained.

After drying over MgSO₄ and removal of the solvent was obtained 2 g of 7-dodecyne-1-yl acetate (**9**). Yield: 67%, GC purity: 95%. Mass spectrum (m/z, %): 181(<1), 164(<1), 149(<1), 135(<1), 122(9.8), 107(19.11), 93(46.08), 81(41.18), 79(59.8), 67(45.1), 54(27.45), 43(100), 41(40.2), 29(10.78).

(Z)-7-dodecene-1-yl acetate (1)

7-dodecyne-1-yl acetate (**9**) was hydrogenated at (*Z*)-7-dodecene-1-yl acetate (**1**) in the presence of the NiP-2/EDA catalyst, prepared in situ according to the standard procedure [11]. (*Z*)-7-dodecene-1-yl acetate (**1**) was obtained in yield of 85%, GC purity: 96 %. Mass spectrum (m/z, %): 183(<1), 168(<1), 166(12.14), 151(<1), 138(<1), 123(<1), 109(19.42), 96(38.83), 81(61.16), 68(32.04), 67(69.9), 55(62.14), 43(100), 29(14.56).

¹H-NMR (CDCl₃, 300 MHz): 0.80 (3H, t, J = 6 Hz, CH₃), 1.23 (10H, s, 5CH₂), 1.48-1.54 (2H, m, CH₂), 1.92-1.94 (7H, m, 2CH₂, CH₃), 3.95 (2H, t, J = 6 Hz, OCH₂), NMR 5.19-5.31 (2H, m, J = 11.4 Hz, HC=CH).

¹³C-NMR (CDCl₃, 75 Hz): 64.1 (OCH₂), 28.4 (CH₃), 25.6 (CH₂), 29.4 (CH₂), 28.7 (CH₂), 26.7 (CH₂), 129.4 (=CH), 129.8 (HC=), 26.9 (CH₂), 31.8 (CH₂), 22.2 (CH₂), 13.8 (CH₃), 170.9 (C=O), 20.7 (CH₃).

8-bromo-octane-1-ol (11)

To a solution 73 g (0.5 mole) of 1,8-octane-diol solved in 300 mL benzene was added 86 mL hydrobromic acid 47%. The reaction mixture was refluxed for 2.5 hours. The organic layer was separated and washed with brine, saturated NaHCO₃ solution and dried over anhydrous MgSO₄. After distillation of the solvent, 62.7g of 8-bromo-octane-1-ol (**11**) were obtained. n_D¹⁸=1,478, Yield: 60%, GC purity: 97%. Mass spectrum (m/z, %): 190(<1), 178(<1), 164(<1), 151(<1), 111(<1), 109(<1), 148(34.80), 97(26.47), 83(43.13), 69(87.25), 55(100), 41(74.01), 31(29.41).

1-tert-Butoxy-8-bromo-octane (12)

To a solution 66.85 g (319 mmoles) of 4-bromo-octane-1-ol (**11**) and 342.29 mL *tert*-butyl-methyl-ether was added dropwise 20.66 mL concentrated sulfuric acid under cooling. The reaction mixture was maintained at 40° C. The reaction was checked by TLC on silica gel G (benzene:ether 2:1, detection with H₂SO₄ d=1.25). The reaction mixture was diluted with water. After removal of the *tert*-butyl-methyl-ether under reduced pressure, the mixture was extracted with ethyl ether (3x50 mL). The combined ethereal extracts were washed with saturated NaHCO₃ solution up to basic and dried over Na₂SO₄. After the removal of the solvent, 62 g of 1-*tert*-butoxy-8-bromo-octane (**12**) were obtained. b.p. = 102°-104° C/3 mm Hg, n_D¹⁸ = 1,456, Yield: 90%, GC purity: 97%.

Mass spectrum (m/z, %): 277(<1), 236(<1), 219(<1), 177(<1), 163(<1), 137(<1), 121(<1), 97(<1), 83.29(<1), 59(100), 41(21.56).

1-tert-Butoxy-dec-9-yne (13)

All operations were performed in an inert gas atmosphere and under stirring.

To a stirred and cooled (0°) suspension of 3.8 g (41.30 mmoles) lithium acetylide-ethylendiamine complex in 21 mL anhydrous dimethyl sulfoxide was slowly added 5.47 g (20.64 mmoles) 1-*tert*-butoxy-8-bromo-octane (**12**). The reaction mixture was stirred at room temperature for 6h, and then it was poured into ice water and extracted with hexane. The combined hexane extracts were washed with water, brine and dried over Na₂SO₄. After removal of the solvent, 4.04 g of 1-*tert*-butoxy-dec-9-yne (**13**) were obtained. b.p.= 94°-100° C/4 mmHg, n_D¹⁸ = 1,441, Yield: 84.52 %, GC purity: 90.62 %. Mass spectrum (m/z, %): 195(24.50), 177(<1), 154(<1), 153(<1), 135(<1), 121(<1), 107(<1), 95(28.43), 81(35.78), 67(6.37), 59(100), 57(89.21), 55(26.96), 41(46.07), 29(17.64).

Di[1-tert-Butoxy-dec-9-yne]mercury (14)

To 6.53 g of potassium iodide dissolved in 6.53 mL water were added 2.64 g mercury (II) chloride and the mixture was stirred till the mercury salt was dissolved. To the mixture were added 5 mL of 10% sodium hydroxide solution. After external cooling of reaction mixture with ice, were added dropwise 1.89 g (9 mmoles) of 1-*tert*-butoxy-dec-9-yne (**13**) dissolved in 28 mL cooling ethyl alcohol. The obtained precipitate was filtrated and washed on the filter with cooling aqueous ethylic alcohol 50%. After drying were obtained, 3.15 g of di[*tert*-butoxy-dec-9-yne]mercury (**14**). Yield: 57%, m.p.= 102° C.

1-tert-Butoxy-dodec-9-yne (15)

All operations were performed in an inert gas atmosphere and under stirring.

4 g (6.4 mmoles) of compound **14** in 16.17 mL diglyme was treated with 0.088 g lithium (12.8 mmoles) at 105-122° C for 2 h. 3 g (27.52 mmoles) of ethyl bromide dissolved in 4 mL diglyme was added dropwise at 78-80° C then the temperature was raised to 120-122° C under stirring for 4 h.

The mixture was poured out over the 100 g of break ice. The reaction mixture was extracted with petroleum ether. The ethereal solution was washed successively with 10% HCl, water and brine till neutral pH of the washings. After drying over MgSO₄, the solvent was removed and 1 g of 1-*tert*-butoxy-dodec-9-yne (15) was obtained. Yield: 65%, GC purity: 91%.

Mass spectrum (m/z, %): 223(24.51), 209(<1), 182(<1), 164(<1), 153(<1), 135(<1), 123(11.76), 109(54.9), 95(50.98), 81(47.06), 67(54.9), 57(100), 41(87.25), 29(25.49).

1-*tert*-Butoxy-E-9-dodecene (16)

All operations were performed in an inert gas atmosphere and under stirring.

1.33 g (35 mmoles) of LiAlH₄ was placed in a solution of 3 mL of anhydrous THF and 22 mL of diglyme. The solvent was partially removed (3mL) and the temperature was raised at 140° C. After cooling at 10° C, the suspension was treated with 2.5 g (10.50 mmoles) of compounds 15 in 3 mL diglyme maintaining the temperature below 10° C. The mixture was heated at 145-150° C for 20 h. The reaction was checked by TLC on silica gel G (benzene ether 15:1, detection with H₂SO₄ d=1.28). After cooling, the solution was treated with 15 mL of H₂SO₄ dil. (d=1.28). The reaction mixture was extracted with diethyl ether, washed with brine and dried over MgSO₄. After removal of the solvent was obtained 1.6 g of 1-*tert*-butoxy-E-9-dodecene (16). GC purity: 80 %. Yield 90%.

Mass spectrum (m/z, %): 240(2.08), 225(4.16), 184(1.04), 166(4.16), 138(2.08), 111(10.41), 97(14.58), 83(14.45), 59(72.91), 57(100), 41(43.75).

(E)-9-Dodecene-1-yl acetate (2)

4.5 g (20 mmoles) of 1-*tert*-butoxy-dodec-9-ene (9) was dissolved in 21 mL of 1:10 mixture of acetyl chloride:acetic acid and was maintained for 8 h at 50-55° C. The reaction development was checked up by TLC on silica gel G (benzene:ether, 8:2, detection with H₂SO₄ d=1.25). The solution was poured on crushed ice, extracted with petroleum ether, washed with brine and with aqueous NaHCO₃ till neutral pH of the washings. After drying over MgSO₄ and removal of the solvent the product was purified by distillation (94°-96° C/1mmHg) obtaining 0.5 g of E-9-dodecene-1-yl acetate (2). Yield: 66%, GC purity: 97%. Mass spectrum (m/z, %): 183(<1), 166(12.66), 151(<1), 137(<1), 125(<1), 123(<1), 110(14.56), 96(29.11), 95(31.01), 82(68.35), 68(77.21), 61(10.81), 55(60.13), 43(100), 29(8.86).

¹H-NMR (CDCl₃, 300 MHz): 0.89 (3H, t, J = 6Hz, CH₃), 1.23 (10H, s, 5CH₂), 1.50-1.57 (2H, m, CH₂), 1.89-1.96 (7H, s+m, 2CH₂, CH₃), 3.98 (2H, t, J = 6 Hz, OCH₂), 5.26-5.43 (2H, m, J_{trans} = 15.52 Hz, HC=CH).

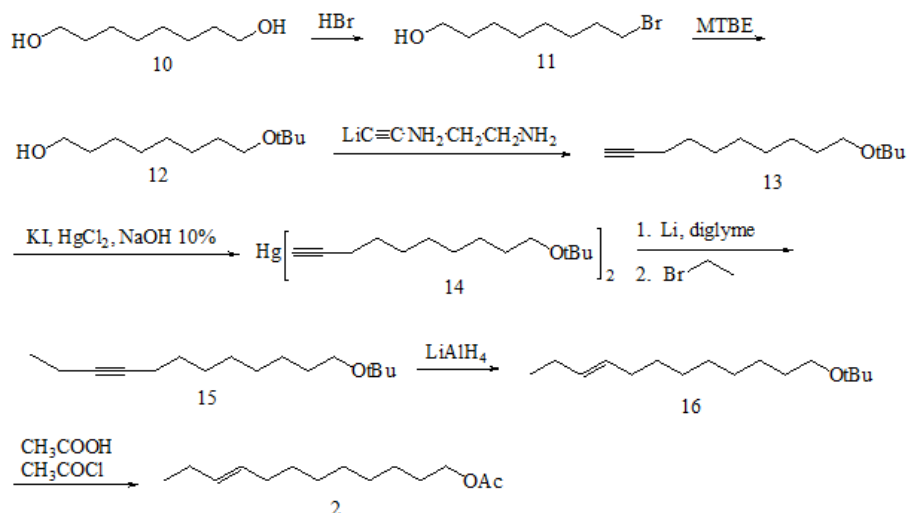
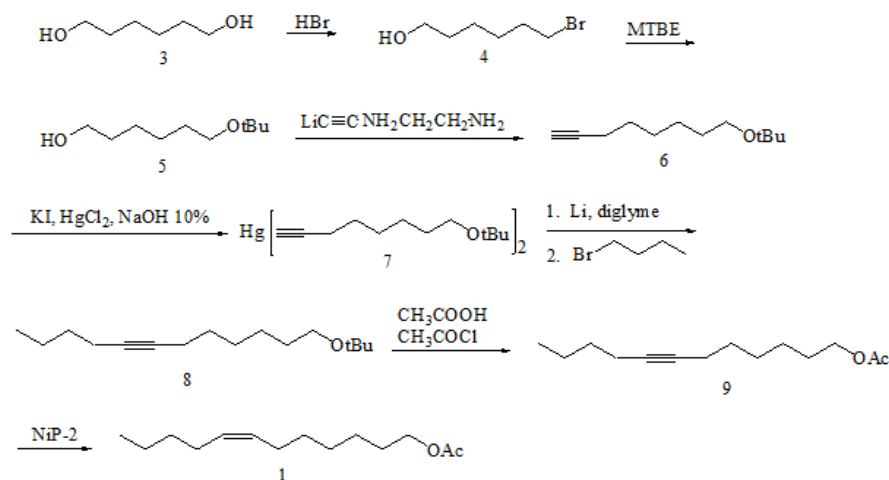
¹³C-NMR (CDCl₃, 75 Hz): 63.9 (OCH₂), 28.8 (CH₃), 25.3 (CH₂), 29.0 (CH₂), 28.0 (CH₂), 28.4 (CH₂), 28.6 (CH₂), 31.9 (CH₂), 128.6 (=CH), 131.2 (CH=), 25.0 (CH₂), 13.3 (CH₃), 170.4 (C=O), 20.3 (CH₃).

Results and discussions

The paper describes new and practical synthesis of (Z)-7-dodecene-1-yl acetate (1) and (E)-9-dodecene-1-yl acetate (2) based on the C-alkylation reaction, using mercury derivative of the terminal alkyne w-functionalized.

The synthesis of (Z)-7-dodecene-1-yl-acetate (1) was based on a C₆+C₂=C₈ and C₈+C₄=C₁₂ coupling scheme, starting from 1,6-hexane-diol.

Scheme 1



Scheme 2

The synthesis of (E)-9-dodecene-1-yl-acetate (**2**) was based on a $C_8 + C_2 = C_{10}$ and $C_{10} + C_2 = C_{12}$ coupling scheme, starting from 1,8-hexane-diol.

Use has been made of methyl-*t*-butyl-ether [10] in acid catalysis in order to protect the -OH function of the 6-bromo-hexane-1-ol (**4**) (scheme 1) respectively 8-bromo-octane-1-ol (**11**) (scheme 2).

The first coupling reaction took place between 1-*tert*-butoxy-6-bromo-hexane (**5**) scheme 1, respectively 1-*tert*-butoxy-8-bromo-octane (**12**), scheme 2, and lithium acetylide-ethylendiamine complex [11] obtaining 1-*tert*-butoxy-oct-7-yne (**6**), (scheme 1), respectively 1-*tert*-butoxy-dec-9-yne (**13**), (scheme 2).

1-*tert*-Butoxy-oct-7-yne (**6**) scheme 1, respectively 1-*tert*-butoxy-dec-9-yne (**13**) scheme 2, were checked by means of IR spectrum (film, cm^{-1} : 895 m, 1110 vs, 1220 vs, 2160 w -C \equiv C-, 3280 s \equiv CH), which presents the vibration of terminal triple bond and the mass spectrum characteristic to *tert*-butyl ethers.

1-*tert*-Butoxy-oct-7-yne (**6**) with mercuric chloride in an aqueous solution containing potassium iodide and sodium hydroxide (Nessler's reagent) [12] were precipitated as di[1-*tert*-butoxy-oct-7-yne]mercury (**7**) (scheme 1). The mercury derivative was directly lithiated and then alkylated with 1-bromobutane obtaining 1-*tert*-butoxy-dodec-7-yne (**8**). After acetylation and reduction in the presence of Ni-P2 catalyst [13] of 7-dodecyne-1-yl acetate (**9**) gave (Z)-7-dodecene-1-yl acetate (**1**) with 96 % purity.

1-*tert*-Butoxy-dec-9-yne (**13**) with Nessler' reagent was transformed in di[*tert*-butoxy-dec-9-yne]mercury (**14**). The mercury derivative was directly lithiated and then alkylated with 1-bromoethane obtaining 1-*tert*-butoxy-dodec-9-yne (**15**). After reduction with lithium aluminium hydride of 1-

tert-butoxy-(E)-9-dodecene (**15**) and acetylation was obtained (E)-9-dodecene-1-yl acetate with (**2**) with 97% purity.

The mass spectrum of (Z)-7-dodecene-1-yl acetate (**1**) and (E)-9-dodecene-1-yl acetate (**2**) are characteristic to alkenol acetates figure 1 and figure 2.

Are present: m/z 166 resulted from the cleavage of acetic acid from the molecular ion, m/z 61 as ion of double transposition ($CH_3COOH_2^+$) and m/z 43 (CH_3CO^+).

The position and configuration of the final compounds was confirmed by 1H -NMR and (fig. 3 and fig. 4) and ^{13}C -NMR spectroscopy (fig. 5 and fig. 6).

The 1H -NMR spectrum of the compound **1** (fig. 3) shows six type of signals: a triplet (3H) at 0.80 ppm corresponds to the methyl protons; a singlet (10H) at 1.23 ppm corresponds to the methylene protons; a multiplet (7H) corresponds to the protons H 6,9,13 (δ 1.48-1.54); a triplet (H2) at 3.95 ppm corresponds to a methylene bonded to oxygen and a multiplet (2H) indicates a disubstituted double bond (δ 5.19-5.31 ppm).

The ^{13}C -NMR spectrum of compound **1** (fig. 4) shows the signal of C_1 at 64.4 ppm, the signal of C_9 at 28.4 ppm, the signal of C_3 at 26.7 ppm. The signals at 22.2, 25.6, 26.9, 28.7, 29.4, 31.8 ppm corresponds to other methylene groups. The signal at 20.7 ppm corresponds to C_{13} and the signal at 170.9 ppm corresponds to the carbon in carbon-oxygen double bond. Sp^2 -hybridized carbon atoms from double bond are easily recognised because of the larger chemical shifts at 129.4 ppm and 129.5 ppm.

The 1H -NMR spectrum of the compound **2** (fig. 5) shows the presence of a triplet (3H) corresponds to the protons H 12 at 0.89 ppm, a singlet (10H) corresponds to the protons

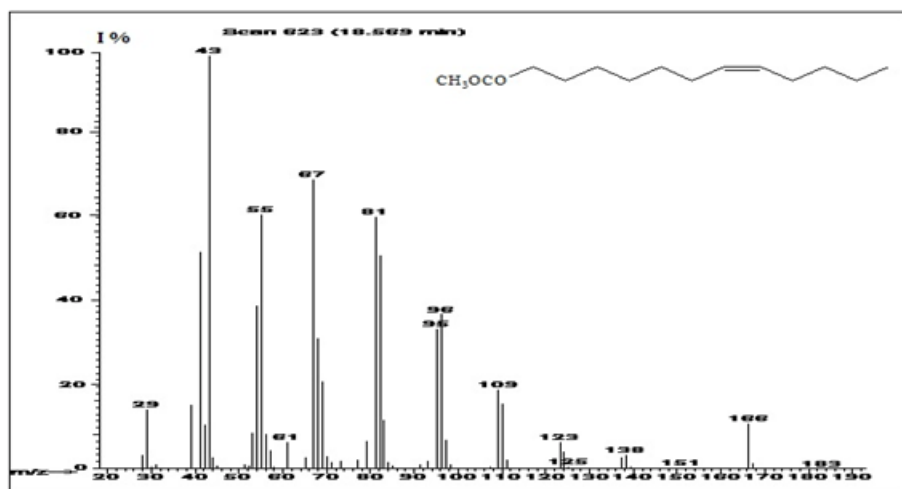


Fig. 1 Mass spectrum of (Z)-7-dodecene-1-yl acetate (**1**)

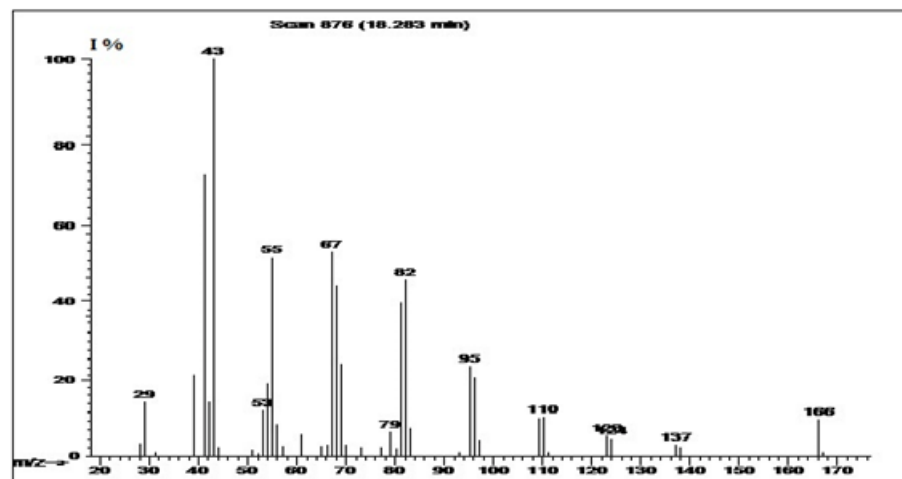


Fig. 2 Mass spectrum of (E)-9-dodecene-1-yl acetate (**2**)

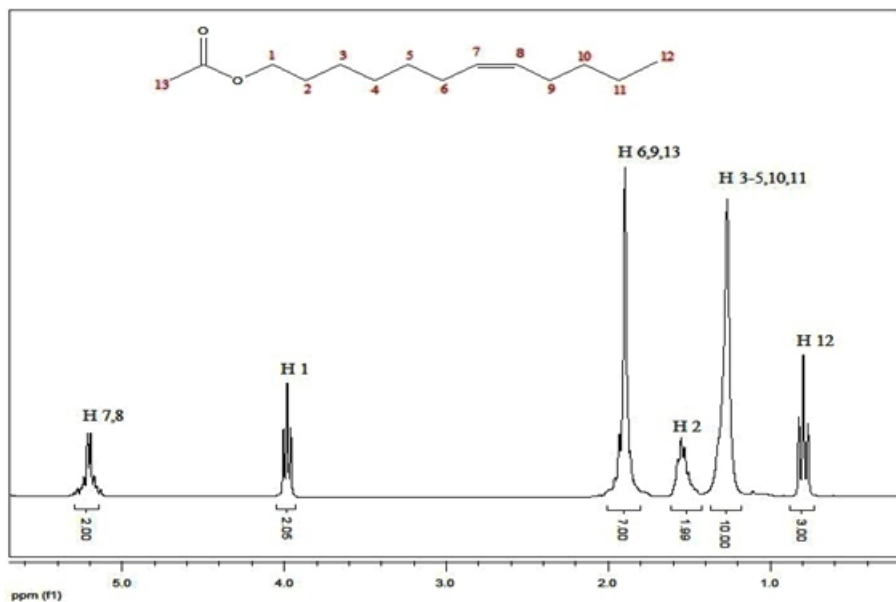


Fig. 3. $^1\text{H-NMR}$ spectrum of (Z)-7-dodecene-1-yl acetate (**1**)

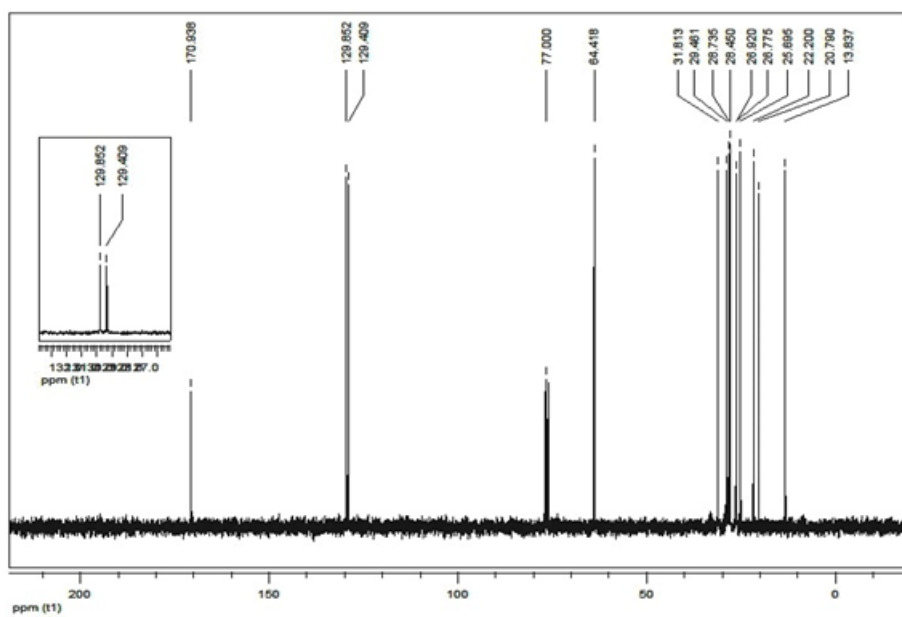


Fig. 4. $^{13}\text{C-NMR}$ spectrum of (Z)-7-dodecene-1-yl acetate (**1**)

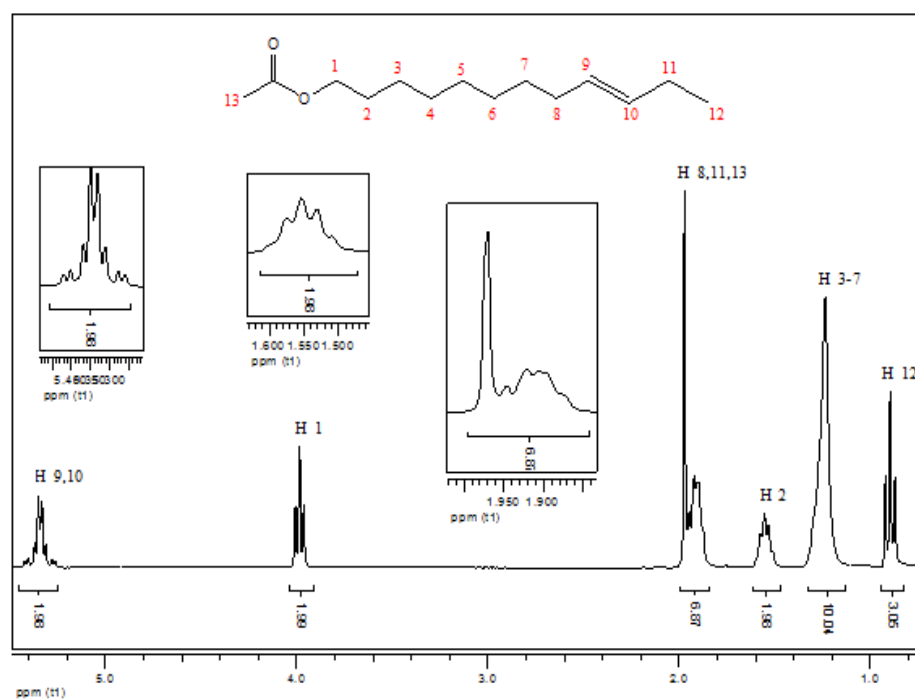


Fig. 5. $^1\text{H-NMR}$ spectrum of (E)-9-dodecene-1-yl acetate (**2**)

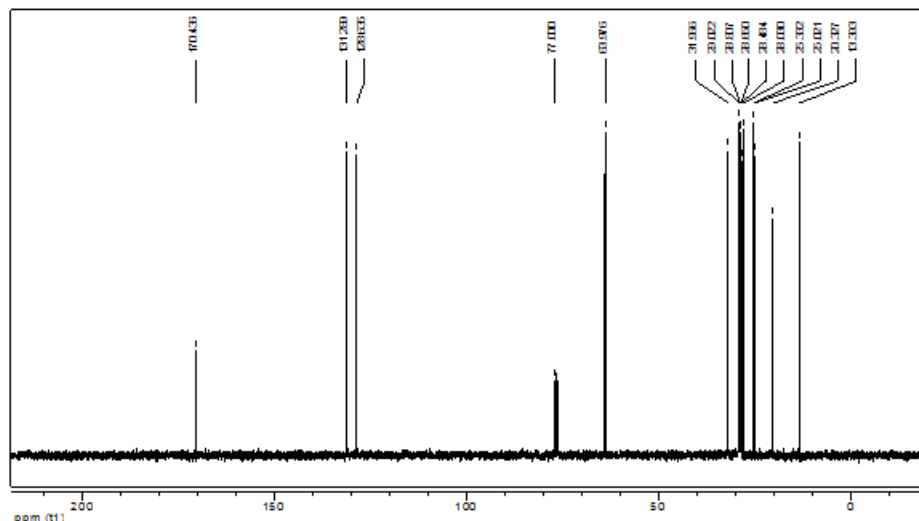


Fig. 6 ^{13}C -NMR spectrum of (*E*)-9-dodecene-1-yl acetate (**2**)

H 3-7 at 1.23 ppm, a multiplet (2H) corresponds to the protons H 2 (δ 1.50-1.57 ppm), a singlet + a multiplet (7H) corresponds to the protons H 8,11,13 (δ 1.89-1.96 ppm), a triplet (2H) corresponds to the protons H 1 at 3.98 ppm and a multiplet (H2) for the protons H 9,10 (δ 5.26-5.42 ppm).

In ^{13}C -NMR spectrum of compound **2** (fig. 6) the carbon atoms involved in double bond presents larger chemical shifts (128.6 ppm and 131.2 ppm). 25.0 ppm chemical shift corresponds to the allylic carbon.

Conclusions

It was presented a new synthesis of (*Z*)-7-dodecene-1-yl acetate and (*E*)-9-dodecene-1-yl acetate, components of Lepidoptera insects sex pheromones, using as intermediate the mercury derivative of the terminal-alkyne ω -functionalized. The mercury compounds were directly lithiated and then alkylated with 1-bromobutane, respectively 1-bromoethane, followed by acetylation and hydrogenation in the presence of Ni-P2 catalyst for (*Z*)-7-dodecene-1-yl acetate, respectively reduction with lithium aluminium hydride and acetylation for (*E*)-9-dodecene-1-yl acetate.

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