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Carbozincation of substituted 2-alkynylamines, 1-alkynylphosphines, 1-alkynylphosphine sulfides with Et_2Zn in the presence of catalytic amounts of $Ti(O\text{-}iPr)_4$ and EtMgBr

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Supporting information

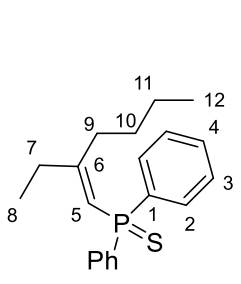
1. Reagents and methods.
2. Preparation of 1-alkenyl phosphine sulfides **3a-c, 4a** and **5,6** via titanium(IV) isopropoxide and ethylmagnesium bromide-catalyzed reaction of 1-alkynyl phosphine sulfides with Et_2Zn.
3. Crystal structure determination of (*Z*)-(1-cyclopropylbut-1-en-2-yl)diphenylphosphine sulfide (**6**).
4. Preparation of 1-alkenyl phosphine oxides **12a, 13b, 13c, 14c, 16** and **17** via titanium(IV) isopropoxide and ethylmagnesium bromide-catalyzed reaction of 1-alkynyl phosphines with Et_2Zn.
5. Preparation of allylic amines **8a, 9a-d** via titanium(IV) isopropoxide and ethylmagnesium bromide-catalyzed reaction of 2-alkynylamines with Et_2Zn.
6. The iodination of intermediate organozinc compounds.
7. References

1. Reagents and methods.

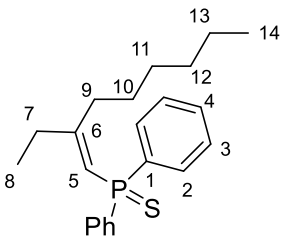
The reagents were obtained from Sigma-Aldrich or Acros. Hexane and dichloromethane were distilled over P_2O_5. Diethyl ether, tetrahydrofuran, 1,4-dioxane, toluene, benzene

and anisole were dried over sodium. Dried 1,2-dimethoxyethane was obtained from Sigma-Aldrich. 1-Alkynyl phosphine oxides and 1-alkynyl phosphine sulfides **1** were prepared by the oxidation of 1-alkynyl phosphines with 30% aq. H_2O_2[1] and by the reaction of 1-alkynyl phosphines with sulfur[2] respectively. 1-Alkynylamines **7a**, **7b** and **7d** were prepared by aminomethylation of terminal alkynes by bisamine.[3] Alkynylamines **7c** and **7e** were prepared by aminomethylation of terminal alkynes with aqueous formaldehyde and secondary amines under CuI catalysis.[4] Nuclear magnetic resonance spectroscopy was performed on a Brucker Avance 400. The ^{1}H NMR spectra were recorded at 400 MHz and ^{13}C 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 and ^{1}H NMR spectra of the compounds **3a-c, 4a, 5, 6, 8a, 9a-d, 10d, 10e, 12a, 13b,c, 14c, 16, 17**, is shown in Figures 1,2,3,4. 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 allylic amines obtained from starting alkynes.

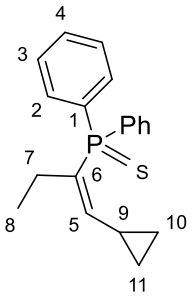
2. Preparation of 1-alkenyl phosphine sulfides 3a-c, 4a and 5,6 via titanium(IV) isopropoxide and ethylmagnesium bromide-catalyzed reaction of 1-alkynyl phosphine sulfides with Et_2Zn.



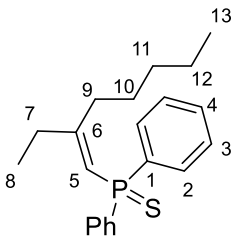
3a



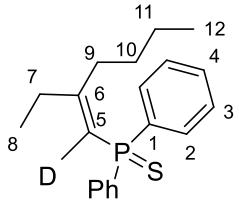
3b



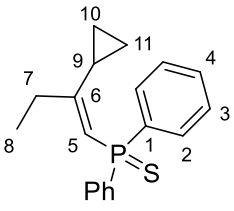
5



3c



4a



6

Figure 1 The numbering of atoms in the ^{13}C- and ^{1}H-NMR spectra of the compounds **3a-c and 4a, 5**, **6.**

(*Z*)-(2-ethylhex-1-en-1-yl)diphenylphosphine sulfide (3a); Typical Procedure.

To a solution of hex-1-yn-1-yldiphenylphosphine sulfide (596 mg, 2 mmol) and Et_2Zn (1 M in hexanes, 5 mL, 5 mmol) in ether (6 mL) was added $Ti(OPr\text{-}i)_4$ (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 (hexane : ethyl acetate : methanol = 5 : 2 :1)) gave **3a** (538 mg, 82 %) as colorless oil. R_f 0.42.

^{1}H NMR (δ, ppm, *J*/Hz): 0.73 (t, *J* = 7.3, 3H, $C(12)H_3$), 1.00-1.10 (m, 2H, $C(11)H_2$), 1.13 (t, *J* = 7.4, 2H, $C(8)H_3$), 1.20-1.30 (m, 2H, $C(10)H_2$), 2.29 (q, *J* = 7.5, 2H, $C(7)H_2$), 2.37 (t, *J* = 7.4, 2H, $C(9)H_2$), 6.03 (d, *J* = 23.5, 2H, $C(7)H_2$), 7.25-8.00 (m, 10H, Ph).

^{13}C NMR (δ, ppm, *J*/Hz): 12.17 (C(8)), 13.79 (C(12)), 22.80 (C(11)), 29.48 (C(10)), 31.21 (d, *J* = 16.4, C(7)), 33.92 (d, *J* = 9.3, C(9)), 115.99 (d, *J* = 89.4, C(5)), 128.43 (d, *J* = 12.3, 4C, C(3)), 131.01 (d, *J* = 2.5, 2C, C(4)), 131.20 (d, *J* = 10.5, 4C, C(2)), 135.21 (d, *J* = 84.2, 2C, C(1)), 168.22 (C(6)).

^{31}P NMR (δ, ppm): 28.68.

MS (EI): m/z, % = 328 (45) [M^+], 299 (18), 254 (4), 218 (100), 183 (48), 139 (30), 108 (18), 41 (17).

Anal. calcd for $C_{20}H_{25}PS$, (%): C, 73.14; H, 7.67. Found, %: C, 73.20; H, 7.71.

(*Z*)-(2-ethyloct-1-en-1-yl)diphenylphosphine sulfide (3b)

Using the procedure described above oct-1-yn-1-yldiphenylphosphine sulfide (652 mg, 2 mmol) gave crude product that was purified by column chromatography (hexane : ethyl acetate : methanol = 5 : 2 :1) to afford **3b** (547 mg, 79%) as colorless oil. R_f 0.45.

^{1}H NMR (δ, ppm, *J*/Hz): 0.83 (t, *J* = 7.3, 3H, $C(14)H_3$), 0.95-1.10 (m, 4H, $C(11,12)H_2$), 1.13 (t, *J* = 7.4, 3H, $C(8)H_3$), 1.15-1.20 (m, 2H, $C(13)H_2$), 1.20-1.35 (m, 2H, $C(10)H_2$), 2.28 (q, *J* = 7.5, 2H, $C(7)H_2$), 2.37 (t, *J* = 7.4, 2H, $C(9)H_2$), 6.03 (d, *J* = 23.4, 1H, $C(5)H_1$), 7.25-8.00 (m, 10H, Ph).

^{13}C NMR (δ, ppm, *J*/Hz): 12.16 (C(8)), 14.04 (C(14)), 22.47 (C(13)), 27.36 (C(10)), 29.35 and 31.52 (C(11) and C(12)), 31.19 (d, *J* = 16.8, C(7)), 34.19 (d, *J* = 9.3, C(9)), 115.97 (d, *J* = 89.4, C(5)), 128.43 (d, *J* = 12.3, 4C, C(3)), 131.00 (d, *J* = 2.4, 2C, C(4)), 131.20 (d, *J* = 10.5, 4C, C(2)), 135.23 (d, *J* = 84.2, 2C, C(1)), 168.23 (C(6)).

^{31}P NMR (δ, ppm): 28.69.

Anal. calcd for $C_{22}H_{29}PS$, (%): C, 74.12; H, 8.20. Found, %: C, 74.05; H, 8.31.

(*Z*)-(2-ethylhept-1-en-1-yl)diphenylphosphine sulfide (3c)

Using the procedure described above oct-1-yn-1-yldiphenylphosphine sulfide (624 mg, 2 mmol) gave crude product that was purified by column chromatography (hexane : ethyl acetate : methanol = 5 : 2 :1) to afford **3c** (447 mg, 69%) as colorless oil. R_f 0.47.

^{1}H NMR (δ, ppm, *J*/Hz): 0.79 (t, *J* = 7.3, 3H, C(13)H_3), 0.95-1.20 (m, 4H, C(11,12)H_2), 1.13 (t, *J* = 7.2, 3H, C(8)H_3), 1.20-1.35 (m, 2H, C(10)H_2), 2.30 (q, *J* = 7.3, 2H, C(7)H_2), 2.39 (t, *J* = 7.6, 2H, C(9)H_2), 6.04 (d, *J* = 23.4, 1H, C(5)H_1), 7.25-8.00 (m, 10H, Ph).

^{13}C NMR (δ, ppm, *J*/Hz): 12.19 (C(8)), 13.96 (C(13)), 22.37 (C(12)), 27.08 (C(10)), 31.22 (d, *J* = 16.4, C(7)), 34.15 (C(11), 34.15 (d, *J* = 9.2, C(9)), 116.01 (d, *J* = 89.3, C(5)), 128.45 (d, *J* = 12.2, 4C, C(3)), 131.02 (d, *J* = 2.5, 2C, C(4)), 131.20 (d, *J* = 10.5, 4C, C(2)), 135.25 (d, *J* = 84.2, 2C, C(1)), 168.25 (C(6)).

^{31}P NMR (δ, ppm): 28.65.

MS (*m/z*, %): 342 (67) $[M]^+$, 283 (100), 255 (2), 180 (10), 153 (14), 123 (17), 75 (20), 45 (<1).

Anal. calcd for $C_{21}H_{27}PS$, (%): C, 73.65; H, 7.95. Found, %: C, 73.68; H, 8.05.

(*Z*)-(2-ethylhex-1-en-1-yl-1-*d*)diphenylphosphine sulfide (4a)

Using the procedure described above hex-1-yn-1-yldiphenylphosphine sulfide (597 mg, 2 mmol) and D_2O instead of H_2O gave crude product that was purified by column chromatography (hexane : ethyl acetate : methanol = 5 : 2 :1) to afford **4a** (494 mg, 75 %). R_f 0.49.

^{1}H NMR (δ, ppm, *J*/Hz): 0.73 (t, *J* = 7.2, 3H, C(12)H_3), 1.00-1.10 (m, 2H, C(11)H_2), 1.13 (t, *J* = 7.4, 2H, C(8)H_3), 1.15-1.35 (m, 2H, C(10)H_2), 2.22 (q, *J* = 7.3, 2H, C(7)H_2), 2.37 (t, *J* = 7.7, 2H, C(9)H_2), 7.25-8.00 (m, 10H, Ph).

^{13}C NMR (δ, ppm, *J*/Hz): 12.14 (C(8)), 13.78 (C(12)), 21.74 (C(11)), 29.48 (C(10)), 31.14 (d, *J* = 16.7, C(7)), 33.88 (d, *J* = 9.0, C(9)), 128.43 (d, *J* = 12.3, 4C, C(3)), 131.00 (d, *J* = 2.6, 2C, C(4)), 131.20 (d, *J* = 10.4, 4C, C(2)), 135.20 (d, *J* = 84.7, 2C, C(1)), 168.14 (C(6)).

^{31}P NMR(δ, ppm): 28.58.

MS (*m/z*, %): 329 (38) $[M]^+$, 300 (9), 218 (100), 183 (46), 139 (21), 108 (30), 44 (32).

Anal.calcd for $C_{20}H_{24}DPS$, (%): C, 72.91. Found, %: C, 72.99.

(*Z*)-(2-cyclopropylbut-1-en-1-yl)diphenylphosphine sulfide (5)

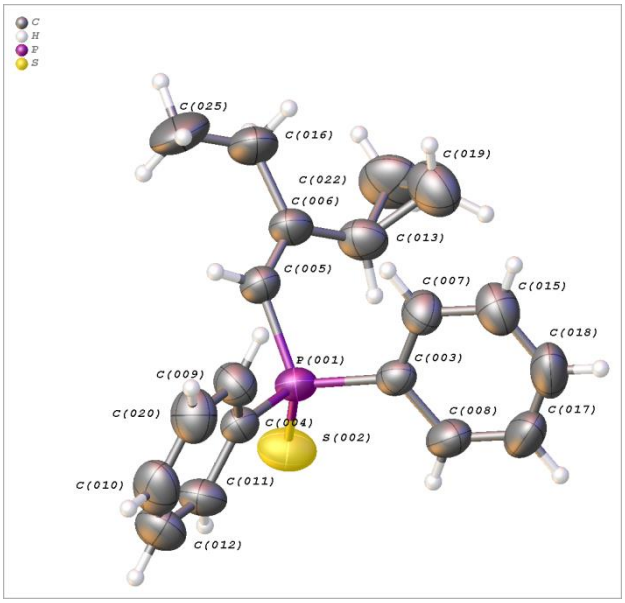
Using the procedure described above (cyclopropylethynyl)diphenylphosphine sulfide (564 mg, 2 mmol) and H_2O instead of D_2O gave crude product that was purified by column chromatography (hexane : ethyl acetate : methanol = 5 : 2 :1) to afford **5** and **6** (406 mg, overal yield 65 %). R_f 0.49.

MS (*m/z*, %): 312 (100) $[M]^+$, 297 (45), 284 (56), 279 (26), 217 (49), 183 (100), 127 (89), 108 (48).

***(Z*)-(1-cyclopropylbut-1-en-2-yl)diphenylphosphine sulfide (6)**

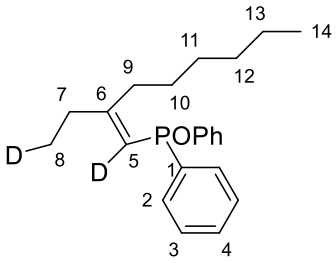
MS (*m/z*, %): 312 (95) $[M]^+$, 297 (34), 284 (78), 279 (30), 183 (100), 127 (96), 77 (50), 63 (40), 41 (37).

3. Crystal structure determination of (*Z*)-(1-cyclopropylbut-1-en-2-yl)diphenylphosphine sulfide (6)

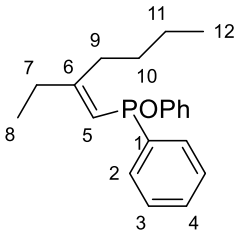


A suitable crystal of (*Z*)-(1-cyclopropylbut-1-en-2-yl)diphenylphosphine sulfide was selected and mounted on a Xcalibur, Eos diffractometer. The crystal was kept at 293(2) K during data collection. Using Olex2 [5], the structure was solved with the ShelXS [6] structure solution program using Direct Methods and refined with the ShelXL [7] refinement package using Least Squares minimization. **Crystal Data** for $C_{19}H_{21}PS$ (M =312.39 g/mol): monoclinic, space group $P2_1/n$ (no. 14), a = 11.5804(6) Å, b = 9.7366(5) Å, c = 15.1221(6) Å, β = 94.350(4)°, V = 1700.16(14) $Å^3$, Z = 4, T = 293(2) K, μ(MoKα) = 0.276 mm^{-1}, *Dcalc* = 1.220 g/cm^3, 18995 reflections measured (4.278° ≤ 2Θ ≤ 58.058°), 4149 unique (R_{int} = 0.0385, R_{sigma} = 0.0353) which were used in all calculations. The final R_1 was 0.0662 (I > 2σ(I)) and wR_2 was 0.1958 (all data).

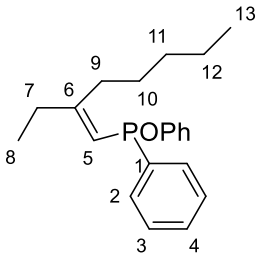
4. Preparation of 1-alkenyl phosphine oxides 12a, 13b, 13c, 14c, 16 and 17 via titanium(IV) isopropoxide and ethylmagnesium bromide-catalyzed reaction of 1-alkynyl phosphines with Et_2Zn.



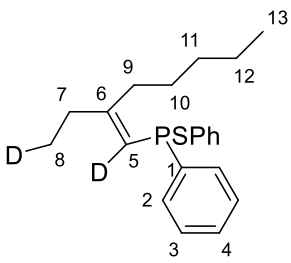
12a



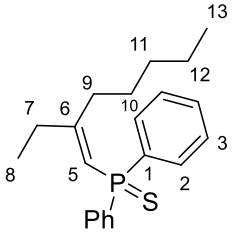
13b



13c



14c



16 (*Z*)

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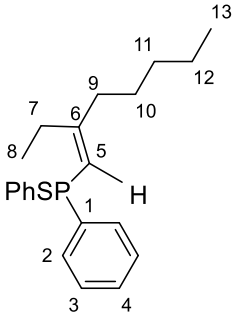

17 (*E*)

Figure 2 The numbering of atoms in the ^{13}C- and ^{1}H-NMR spectra of the compounds **12a**, **13b**, **13c**, **14c, 16 and 17.**

(*Z*)-(2-(Ethyl-2-*d*)oct-1-en-1-yl-1-*d*)diphenylphosphine oxide (12a); Typical Procedure.

To a solution of oct-1-yn-1-yldiphenylphosphane (588 mg, 2 mmol) and Et_2Zn (1 M in hexanes, 5 mL, 5 mmol) in dichloromethane (5 mL) was added $Ti(OPr\text{-}i)_4$ (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 48 h at 23 ^{o}C, the reaction mixture was diluted with CH_2Cl_2 (5 mL), and D_2O (3 mL) was added dropwise while the reaction flask was cooled in an ice bath. The aqueous layer was extracted with dichloromethane (3×5 mL). The combined organic layers were washed with brine (10 mL), dried over anhydrous $CaCl_2$. The solvent was evaporated. A 30% hydrogen peroxide solution (0.35 mL, 3 mmol) was slowly added dropwise with vigorous stirring to a solution of the crude residue (2-(Ethyl-2-d)oct-1-en-1-yl-1-d)diphenylphosphine oxide, in chloroform (5 mL). The reaction mixture was stirred for 1 h and washed with water (3×5 mL), the organic layer was dried over $MgSO_4$. The reaction mixture was filtered through a filter paper and concentrated in vacuo to give crude product as a yellow oil that was purified by column chromatography (silica gel, hexane : ethyl acetate : methanol = 5 : 2 :1) to afford **12a** (445 mg, 65%). R_f 0.59. The spectral properties (^{1}H NMR, ^{13}C NMR, MS) were in good agreement with those that were reported in the literature.[8]

(*Z*)-(2-ethylhex-1-en-1-yl)diphenylphosphine oxide (13b)

Using the procedure described above hex-1-yn-1-yldiphenylphosphane (532 mg, 2 mmol) and toluene (instead of CH_2Cl_2) and (H_2O (instead of D_2O) gave crude product that was purified by flash chromatography (silica gel, hexane : ethyl acetate : methanol = 5 : 2 :1) to afford a colorless oil; yield: 356 mg, (57%); *Rf* = 0.57. The spectral properties (^{1}H NMR, ^{13}C NMR, MS) were in good agreement with those that were reported in the literature.[8]

(*Z*)-(2-ethylhept-1-en-1-yl)diphenylphosphine oxide (13c)

Using the procedure described above hept-1-yn-1-yldiphenylphosphine oxide (592 mg, 2 mmol) and hexane (instead of toluene) gave crude product that was purified by flash chromatography (silica gel, hexane : ethyl acetate : methanol = 5 : 2 :1) to afford a colorless oil; yield: 456 mg, (70%); *Rf* = 0.57. The spectral properties (^{1}H NMR, ^{13}C NMR, MS) were in good agreement with those that were reported in the literature.[9]

(Z)-(2-(ethyl-2-d)hept-1-en-1-yl-1-d)diphenylphosphine sulfide (14c)

Using the procedure described above hept-1-yn-1-yldiphenylphosphine sulfide (624 mg, 2 mmol) and toluene (instead of hexane) gave crude product that was purified by flash chromatography (silica gel, hexane : ethyl acetate : methanol = 5 : 2 :1) to afford a

colorless oil; yield: 433 mg, (63%); *Rf* = 0.60. The spectral properties (^{1}H NMR, ^{13}C NMR, MS) were in good agreement with those that were reported in the literature.[9]

(*Z*)-(2-ethylhept-1-en-1-yl)diphenylphosphine sulfide (16) and (*E*)-(2-ethylhept-1-en-1-yl)diphenylphosphine sulfide (17)

Using the procedure described above hept-1-yn-1-yldiphenylphosphine sulfide (624 mg, 2 mmol) and dichloromethane (instead of toluene) gave crude product that was purified by flash chromatography (silica gel, hexane : ethyl acetate : methanol = 5 : 2 :1) to afford to afford **16** and **17** (over yield 486 mg, 71%); *Rf* = 0.61.

(*Z*)-(2-ethylhept-1-en-1-yl)diphenylphosphine sulfide (16)

^{1}H NMR (δ, ppm, *J*/Hz): 0.78 (t, *J* = 7, 3H, C(13)H_3), 1.13 (m, 2H, C(12)H_2), 1.02 (m, 2H, C(11)H_2), 1.28 (m, 2H, C(10)H_2), 2.39 (m, 2H, C(9)H_2), 1.12 (t, *J* = 7, 3H, C(8)H_3), 2.28 (m, 2H, C(7)H_2), 6.03 (d, *J* = 23, 1H, C(5)H_1), 7.25-8.00 (m, 10H, Ph).

^{13}C NMR (δ, ppm, *J*/Hz): 12.17 (C(8)), 13.94 (C(13)), 22.37 (C(12)), 27.07 (C(10)), 31.21 (d, *J* = 16, C(7)), 31.87 (C(11), 34.15 (d, *J* = 9, C(9)), 116.00 (d, *J* = 89, C(5)), 128.45 (d, *J* = 12, 4C, C(3)), 131.21 (d, *J* = 10, 2C, C(4)), 131.02 (d, *J* = 2, 4C, C(2)), 135.25 (d, *J* = 84, 2C, C(1)), 168.26 (C(6)).

^{31}P NMR (δ, ppm): 28.66.

MS (EI): m/z, % = 342 (69) [M^+], 313 (6), 299 (22), 218 (100), 183 (52), 139 (33), 108 (25), 63 (12), 41 (26).

Anal. calcd for $C_{21}H_{27}PS$, (%):C, 73.65; H, 7.95. Found, %: C, 73.77; H, 8.01.

(*E*)-(2-ethylhept-1-en-1-yl)diphenylphosphine sulfide (17)

^{1}H NMR (δ, ppm, *J*/Hz): 0.91 (m, 3H, C(13)H_3), 1.34 (m, 2H, C(12)H_2), 1.35 (m, 2H, C(11)H_2), 1.53 (m, 2H, C(10)H_2), 2.27 (m, 2H, C(9)H_2), 1.12 (t, *J* = 7, 3H, C(8)H_3), 2.41 (m, 2H, C(7)H_2), 6.03 (d, *J* = 23, 1H, C(5)H_1), 7.25-8.00 (m, 10H, Ph).

^{13}C NMR (δ, ppm, *J*/Hz): 11.51 (C(8)), 14.07 (C(13)), 22.49 (C(12)), 27.47 (C(10)), 27.07 (C(7)), 31.63 (C(11), 37.86 (d, *J* = 16, C(9)), 117.00 (d, *J* = 89, C(5)), 128.44 (d, *J* = 12, 4C, C(3)), 131.14 (d, *J* = 10, 2C, C(4)), 131.00 (d, *J* = 2, 4C, C(2)), 135.23 (d, *J* = 84, 2C, C(1)), 168.08 (C(6)).

^{31}P NMR (δ, ppm): 28.57.

MS (EI): m/z, % = 342 (60) [M^+], 313 (4), 299 (9), 233 (7), 218 (100), 183 (46), 139 (28), 108 (26), 63 (10), 41 (24).

5. Preparation of allylic amines 8a, 9a-d via titanium(IV) isopropoxide and ethylmagnesium bromide-catalyzed reaction of 2-alkynylamines with Et_2Zn.

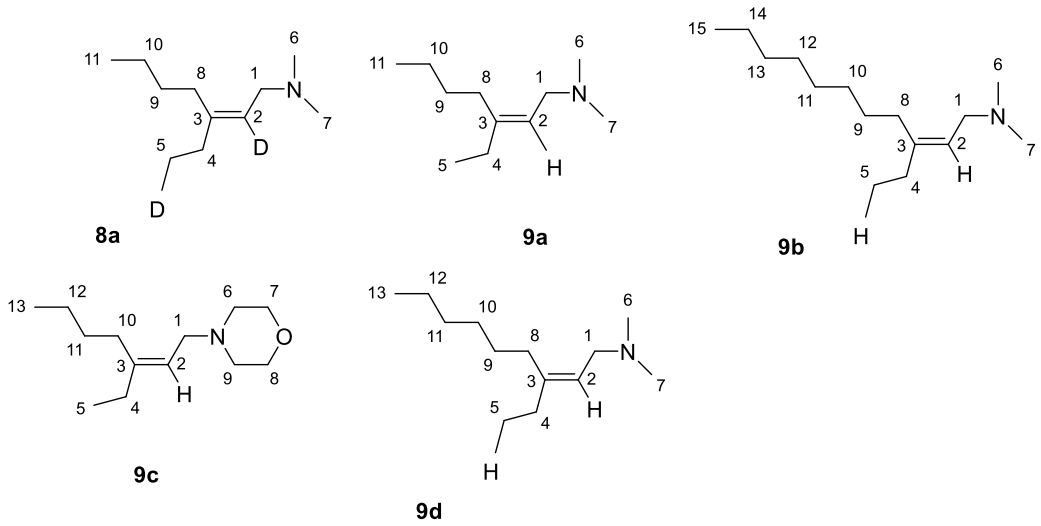

Figure 3 The numbering of atoms in the ^{13}C- and ^{1}H-NMR spectra of the compounds **8a** and **9a-d.**

(*Z*)-3-(Ethyl-2-*d*)-*N*,*N*-dimethylhept-2-en-1-amine-2-*d* (8a); Typical Procedure.

To a solution of *N*,*N*-dimethylhept-2-yn-1-amine (278 mg, 2 mmol) and Et_2Zn (1 M in hexanes, 5 mL, 5 mmol) in hexane (6 mL) was added Ti(OPr-*i*)$_4$ (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 D_2O (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. The residue was distilled through a micro column at 10 mmHg to give **8a** (287 mg, 84%) as a colourless oil. b.p. 87 – 89 ^{o}C (10 mmHg) (lit. [10] b.p. 91-93 ^{o}C (15 mmHg)).

^{1}H NMR (400MHz, $CDCl_3$): δ = 0.92 (t, *J* = 6.3 Hz, 3H, C(11)H_3), 1.00 (t, *J* = 7.7 Hz, 3H, C(5)H_3), 1.25-1.40 (m, 4H, C(9,10)H_2), 2.03 (t, *J* = 7.8 Hz, 2H, C(4)H_2), 2.10-2.35 (m, 2H, C(8)H_2), 2.23 (s, 6H, C(6,7)H_3), 2.90 (s, 2H, C(1)H_2).

^{13}C NMR (100MHz, $CDCl_3$): δ = 12.41 (t, C(5), $^{1}J_{CD}$=19.3 Hz), 14.02 (C(11)), 22.84 (C(10)), 29.41 and 30.30 and 30.71 (C(4,8,9)), 45.26 (2C(6,7)), 56.77 (C(1)), 144.27 (C(3)).

MS (EI): m/z, % = 171 (14) [M^+], 142 (10), 126 (18), 112 (21), 95 (100), 82 (32), 58 (49), 46 (48).

Anal. calcd for $C_{11}H_{21}D_2N$, (%): C, 77.12. Found, %: C, 77.21.

(*Z*)-3-ethyl-*N*,*N*-dimethylhept-2-en-1-amine (9a)

Using the procedure described above, reaction of 278 mg of *N*,*N*-dimethylhept-2-yn-1-amine (2 mmol) and 25 wt% NaOH solution (instead of D_2O) gave a crude product that was distilled through a micro column at 10 mmHg to afford **9a** (267 mg, 79%) as a

colourless oil. b.p. 88 – 90 ^{o}C (10 mmHg). The spectral properties (^{1}H NMR, ^{13}C NMR, MS) were in good agreement with those that were reported in the literature.[11]

(*Z*)-3-ethyl-*N*,*N*-dimethylundec-2-en-1-amine (9b)

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 **9b** (643 mg, 70%) as a colourless oil. b.p. 102 – 105 ^{o}C (1 mmHg). The spectral properties (^{1}H NMR, ^{13}C NMR, MS) were in good agreement with those that were reported in the literature.[11]

(*Z*)-4-(3-Ethylhept-2-en-1-yl)morpholine (9c)

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 1 mmHg to afford **9c** (371 mg, 88%) as a colourless oil. b.p. 103 – 105 ^{o}C (1 mmHg).

^{1}H NMR (400MHz, $CDCl_3$): δ = 0.91 (t, *J* = 6.9 Hz, 3H, C(13)H_3), 1.01 (t, *J* = 7.4 Hz, 3H, C(5)H_3), 1.20-1.40 (m, 4H, C(11,12)H_2), 1.95-2.15 (m, 4H, C(4,10)H_2), 2.45 (br.s., 4H, C(7,8)H_2)), 2.99 (d, *J* = 6.8 Hz, 2H, C(1)H_2), 3.72 (t, *J* = 4.6 Hz, 4H, C(6,9)H_2), 5.21 (t, *J* = 6.8 Hz, 1H, C(2)H_1).

^{13}C NMR (100MHz, $CDCl_3$): δ = 12.70 (C(5)), 14.01 (C(13)), 22.82 (C(12)), 29.60 and 30.39 and 30.70 (C(4.10,11)), 53.69 (2C(7,8)), 56.24 (C(1)), 67.04 (2C(6,9)), 119.04 (C(2)), 145.34 (C(3)).

MS (EI): m/z, % = 211 (15) [M^+], 182 (8), 154 (9), 124 (23), 95 (77), 87 (100), 57 (44), 41 (29).

Anal. calcd for $C_{13}H_{25}NO$, (%):C, 73.88; H, 11.92; N, 6.63. Found, %: C, 73.91; H, 12.00; N, 6.57.

(*Z*)-3-Ethyl-*N*,*N*-dimethylnon-2-en-1-amine (9d)

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 **9d** (303 mg, 77%) as a colourless oil. b.p. 104 – 106 ^{o}C (5 mmHg)**.**

^{1}H NMR (400MHz, $CDCl_3$): δ = 0.89 (t, *J* = 6.7 Hz, 3H, C(13)H_3), 1.02 (t, *J* = 7.4, Hz, 3H, C(5)H_3), 1.20-1.40 (m, 8H, C(9-12)H_2), 2.04 (q, *J* = 6.7, Hz, 2H, C(4)H_2), 2.10-2.30 (m, 2H, C(8)H_2), 2.27 (s, 6H, C(6,7)H_3), 2.97 (d, *J* = 6.9 Hz, 2H, C(1)H_2), 5.24 (t, *J* = 6.4 Hz, 1H, C(2)H_1).

^{13}C NMR (100MHz, $CDCl_3$): δ = 12.72 (C(5)), 14.07 (C(11)), 22.63 (C(12)), 28.45 and 29.44 and 29.59 and 30.59 and 31.76 (C(4, 8-11)), 44.89 (2C(6,7)), 56.61 (C(1)), 119.54 (C(2)), 145.29 (C(3)).

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, 79.14; H, 13.81; N, 7.03.

6. The iodination of intermediate organozinc compounds.

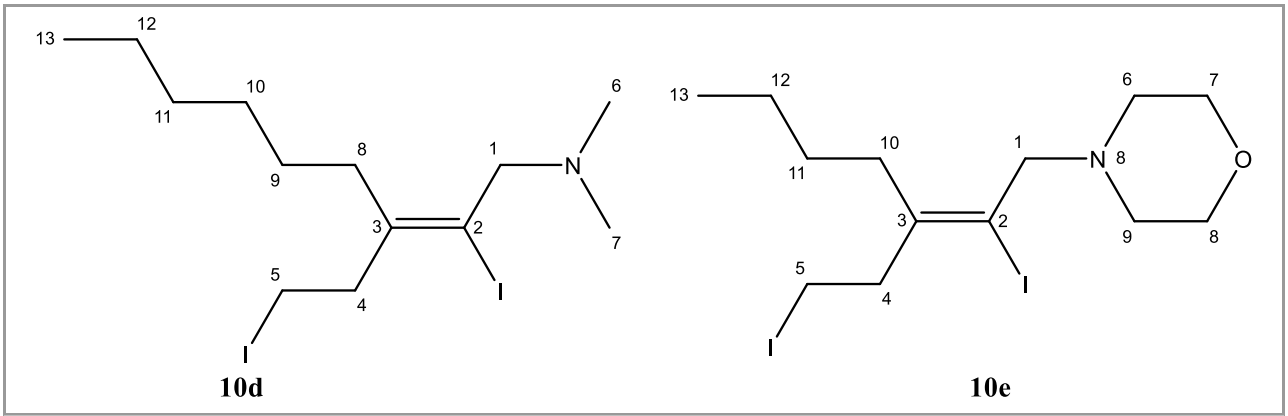

Figure 4 The numbering of atoms in the ^{13}C- and ^{1}H-NMR spectra of the compounds **10d,e**

(*Z*)-2-iodo-3-(2-iodoethyl)-*N*,*N*-dimethylnon-2-en-1-amine (10d); Typical Procedure.

To a solution of *N*,*N*-dimethylnon-2-yn-1-amine (334 g, 2 mmol) and Et_2Zn (1 M in hexanes, 5 mL, 5 mmol) in toluene (6 mL) was added $Ti(OPr\text{-}i)_4$ (0.5 M in hexanes, 0.3 mL, 0.2 mmol) followed by ethylmagnesium bromide (2,5 M in Et_2O, 0.16 mL, 0.4 mmol). 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: 503 mg, (56%); R_f = 0.73 (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.[11]

(*Z*)-4-(2-Iodo-3-(2-iodoethyl)hept-2-en-1-yl)morpholine (10e)

Using the procedure described above 4-(hept-2-yn-1-yl)morpholine (362 mg, 2 mmol) gave crude product that was purified by flash chromatography (silica gel, hexane/ethyl acetate, 5:1) to afford a colorless oil; yield: 565 mg, (61%); R_f = 0.58 (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.[11]

7. References

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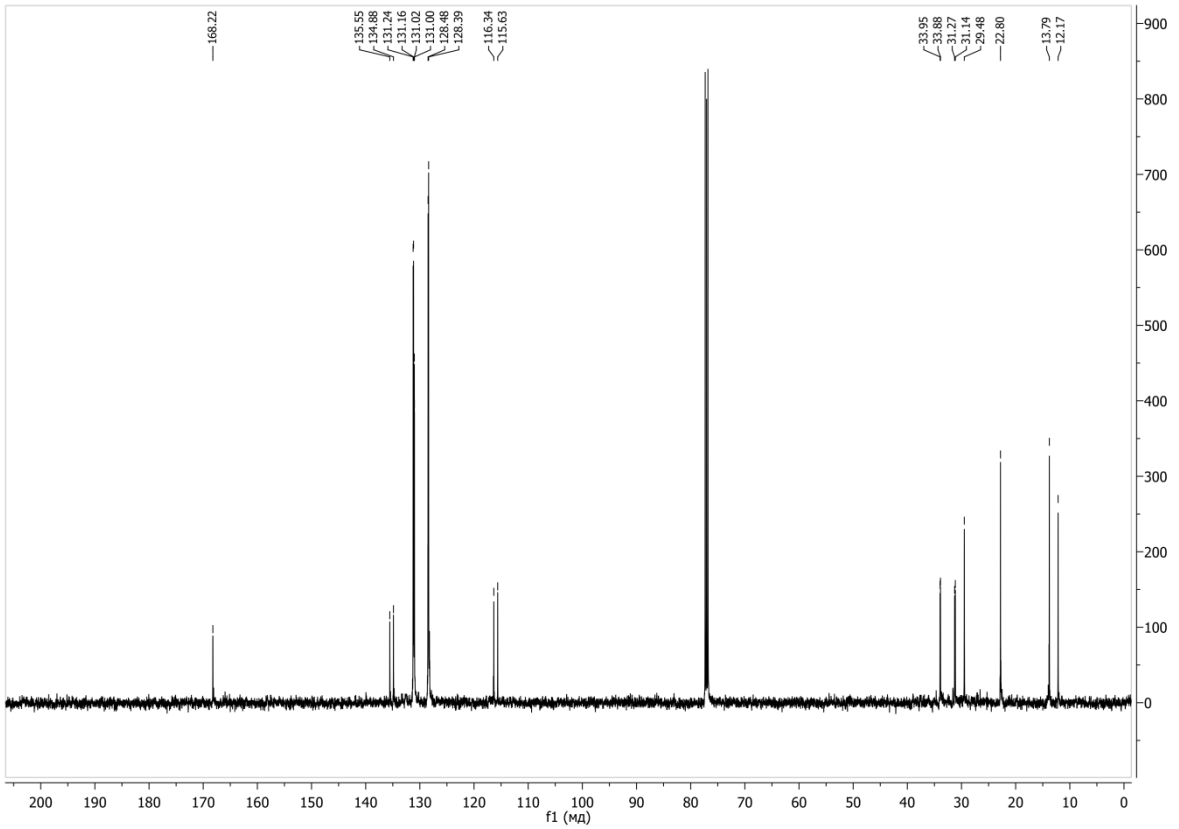
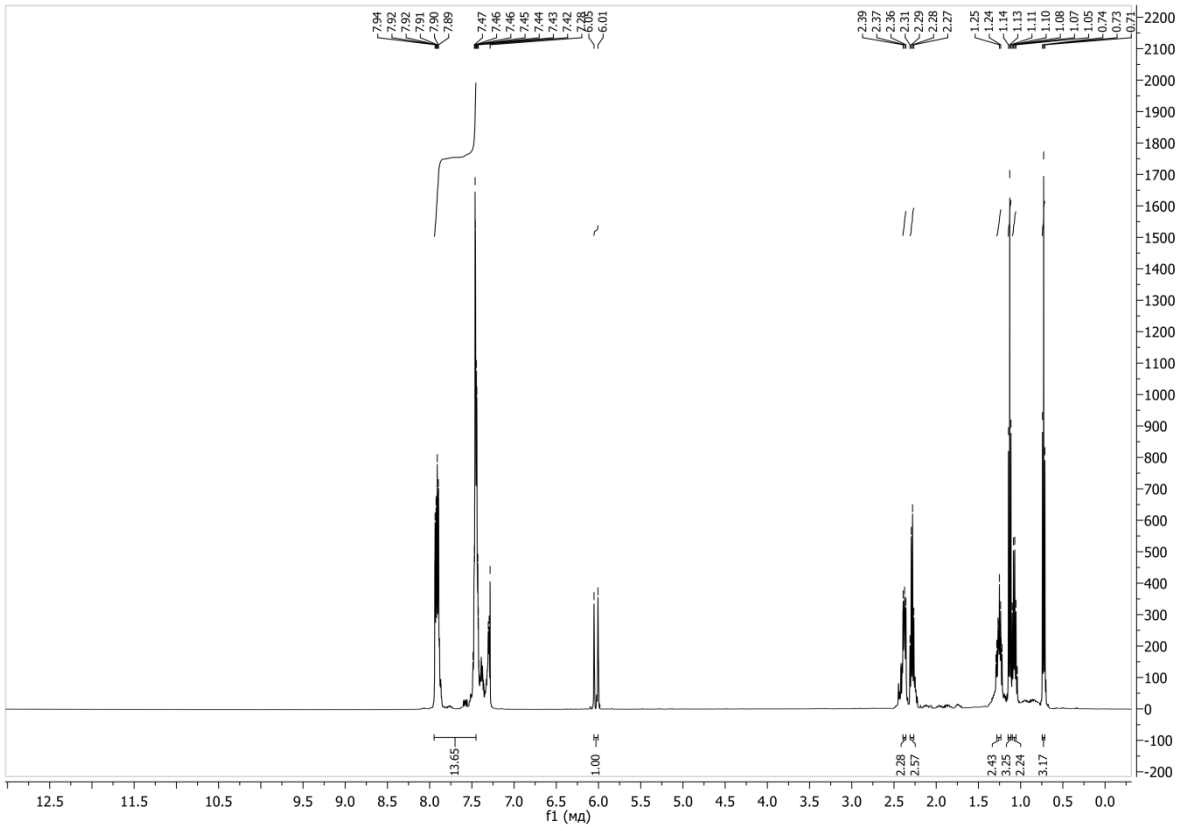
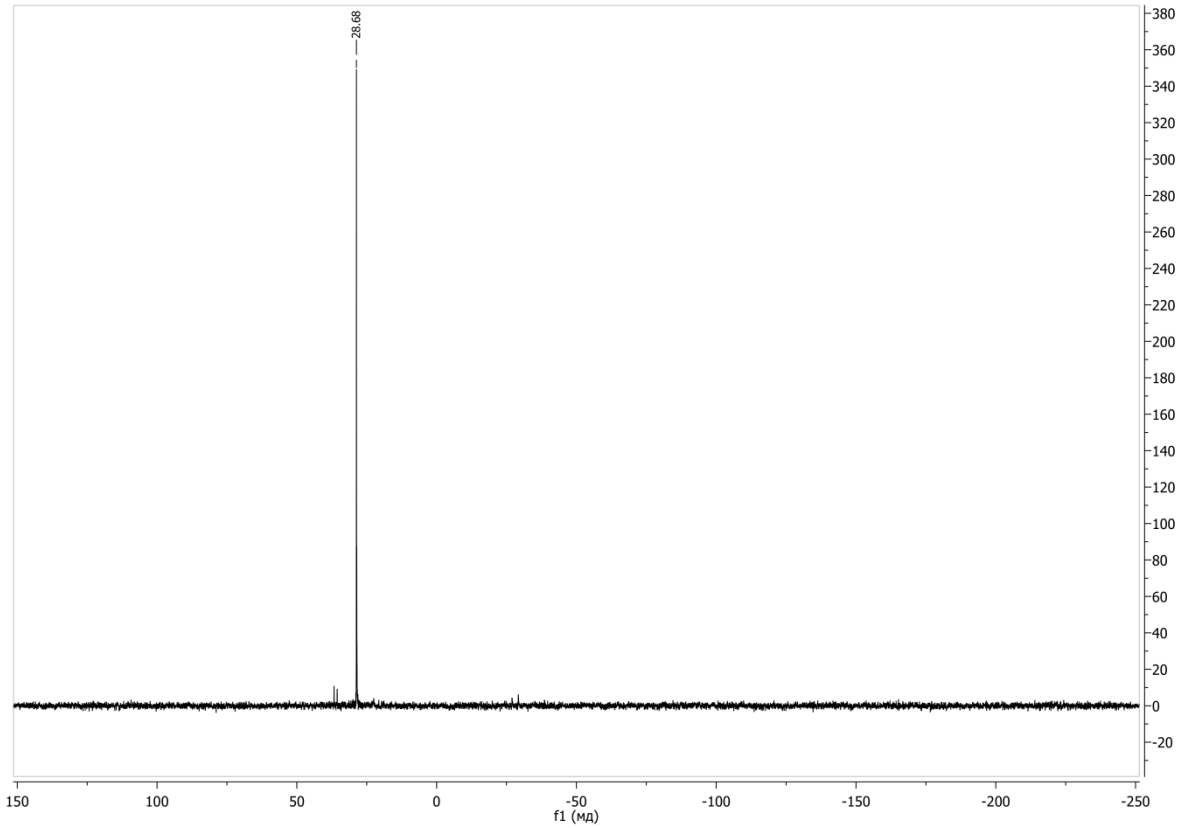
(*Z*)-(2-ethylhex-1-en-1-yl)diphenylphosphine sulfide (3a)







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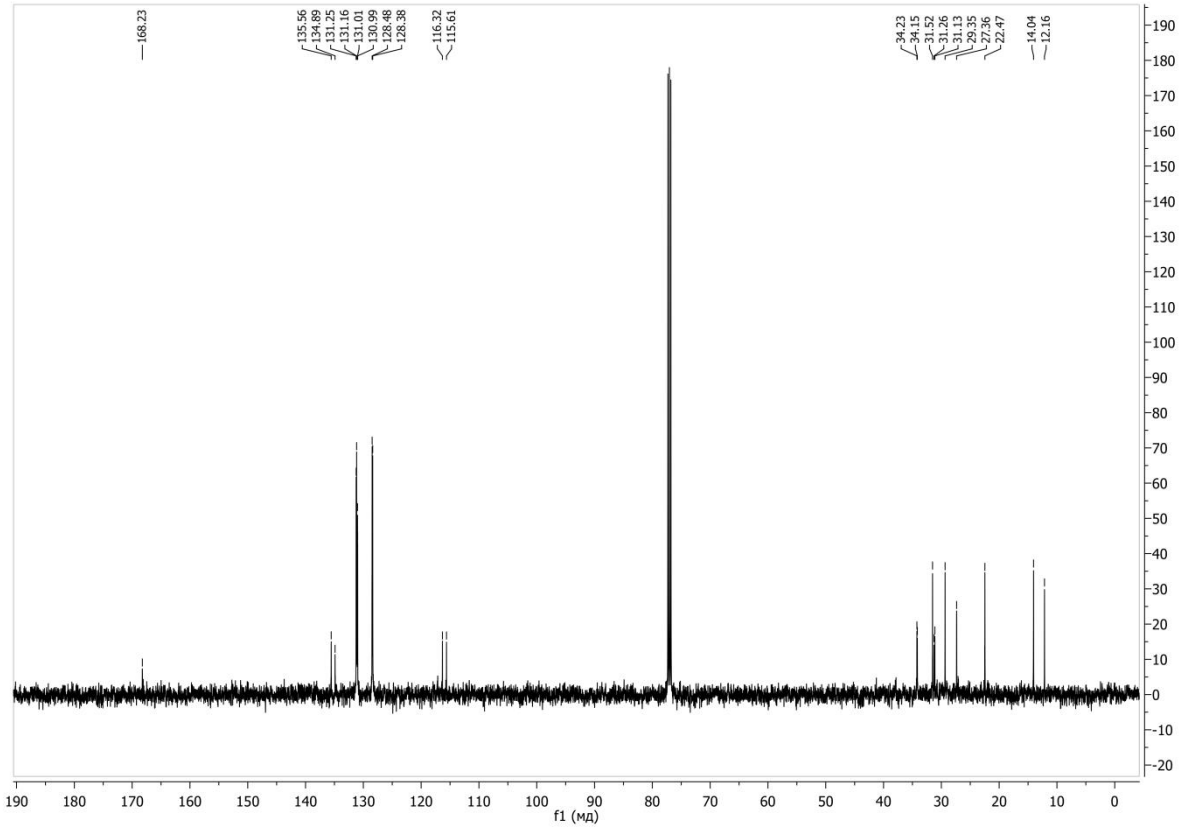

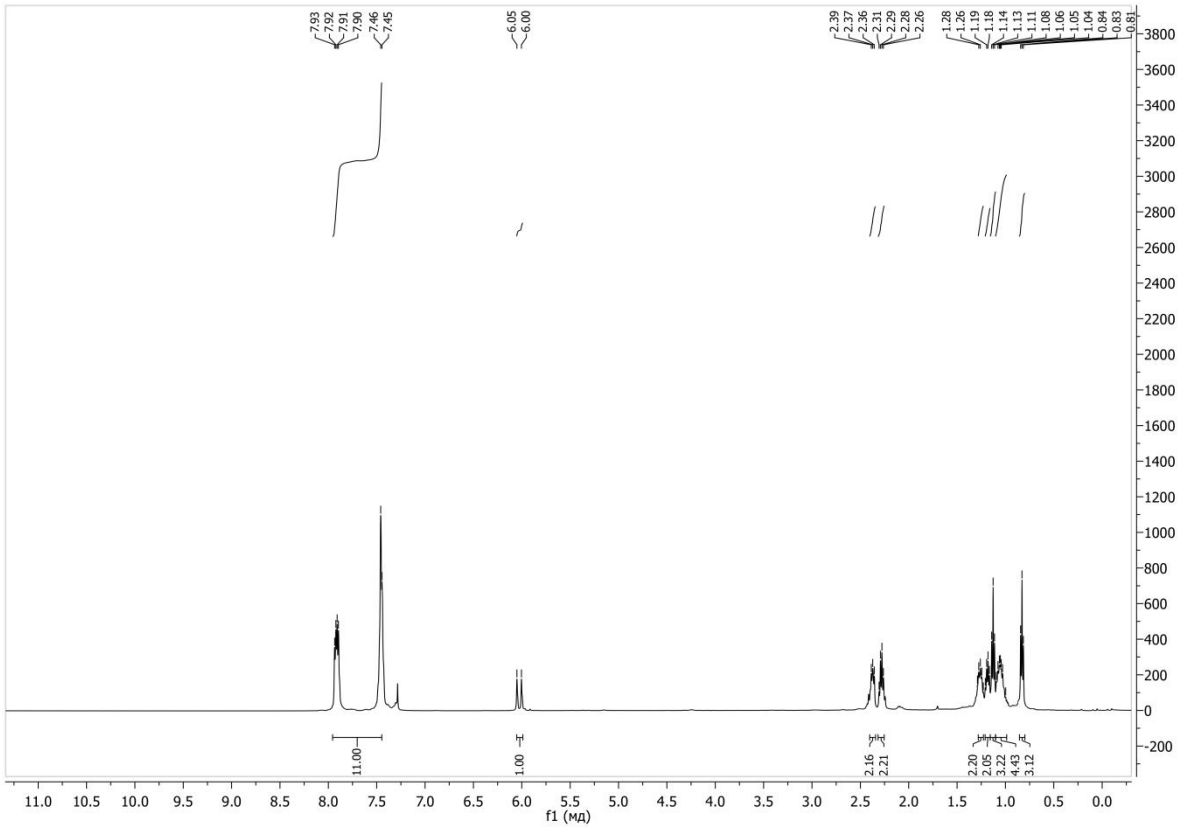
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1.13
1.11
1.08
1.06
1.05
1.04
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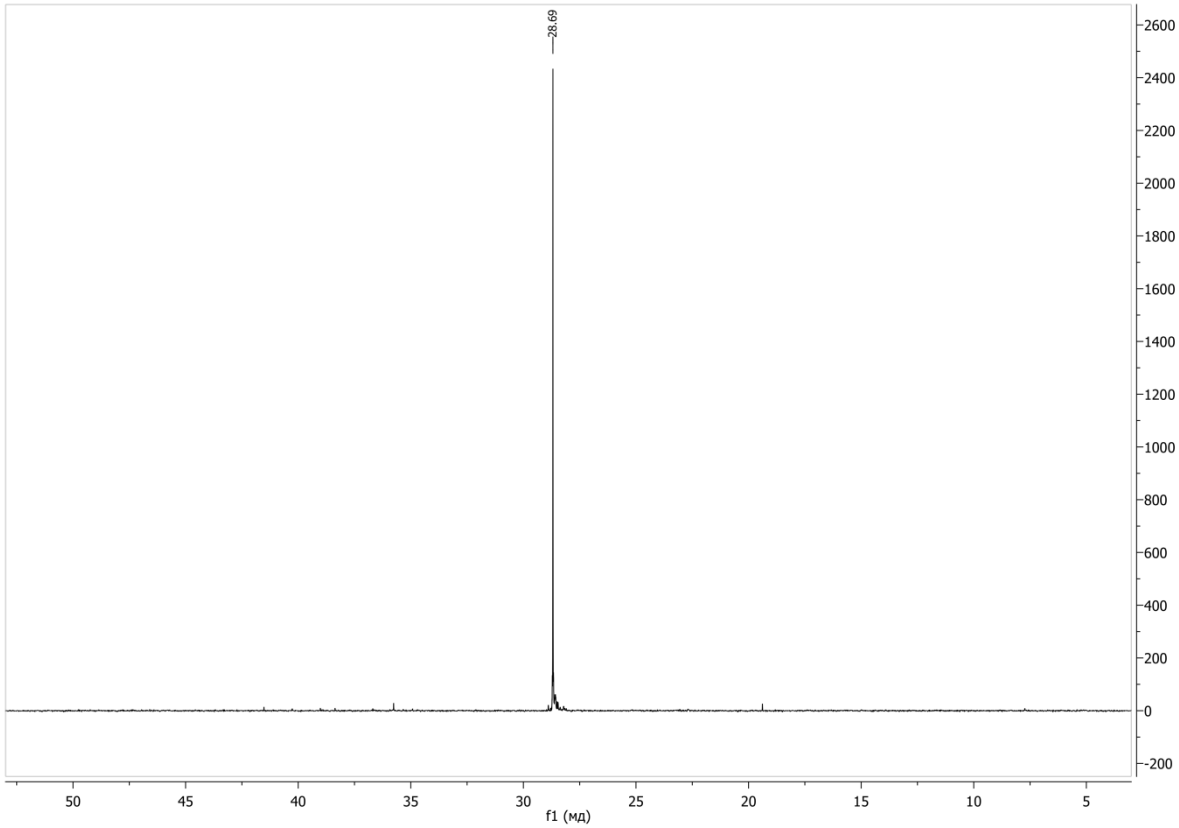
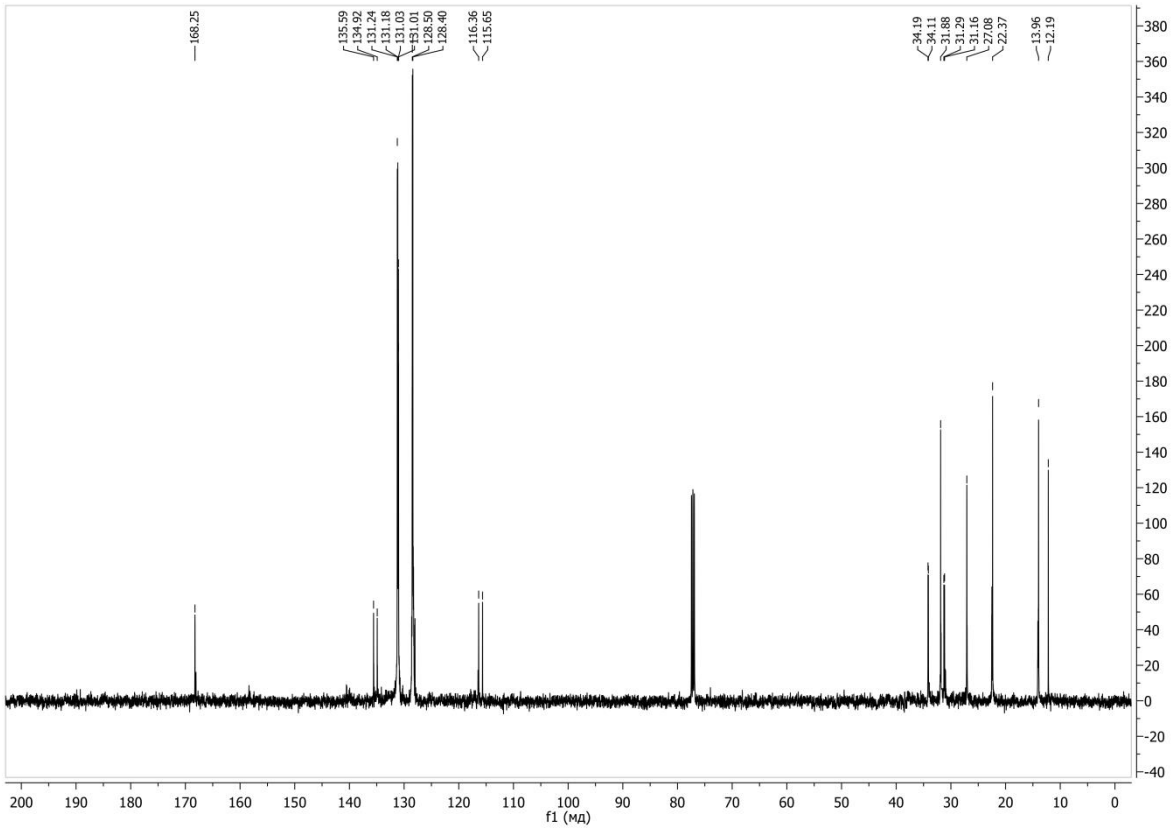
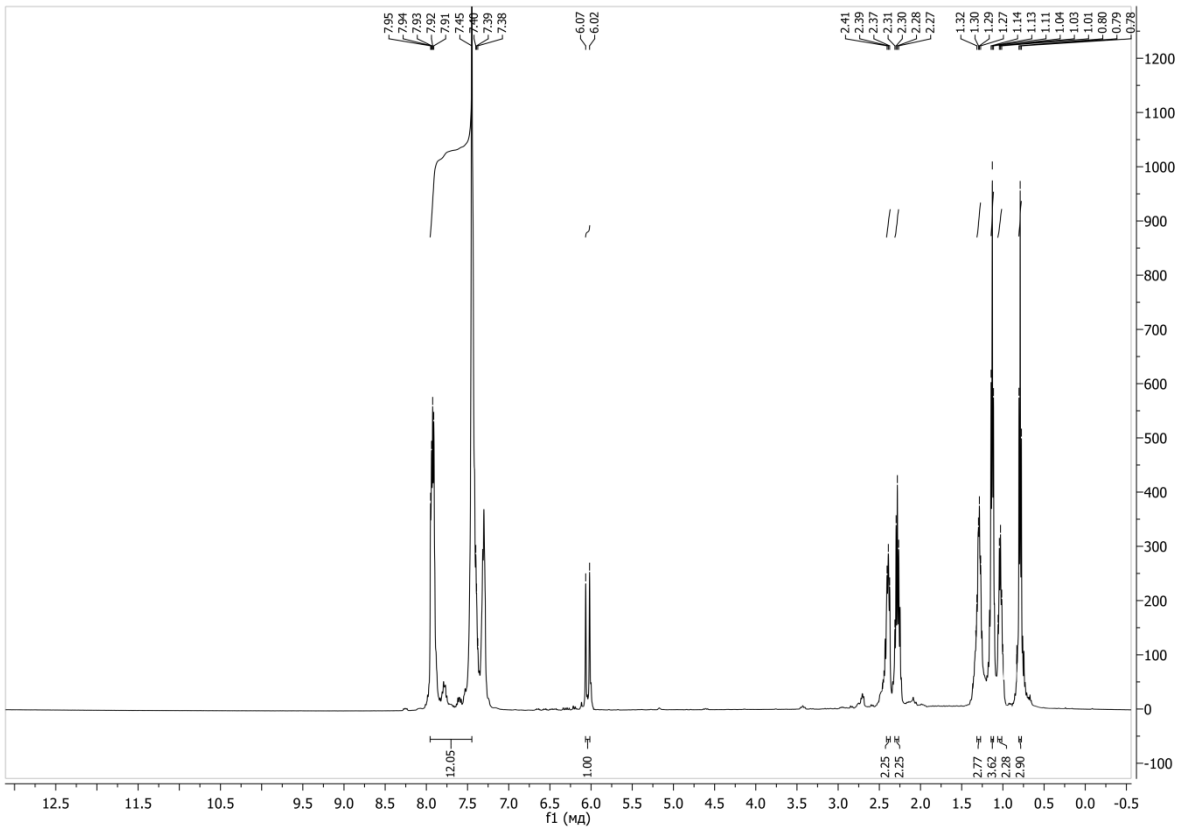
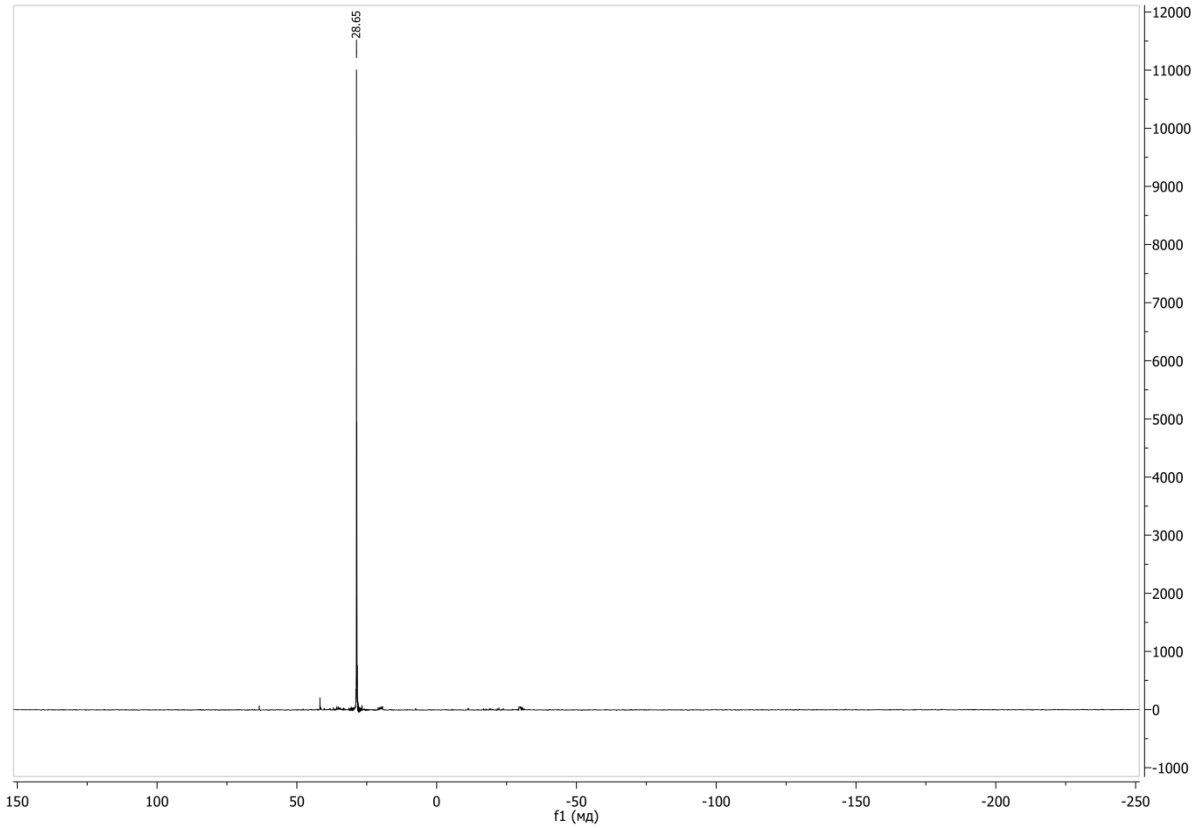
3.12
f1 (мд)


28.69
f1 (мд)

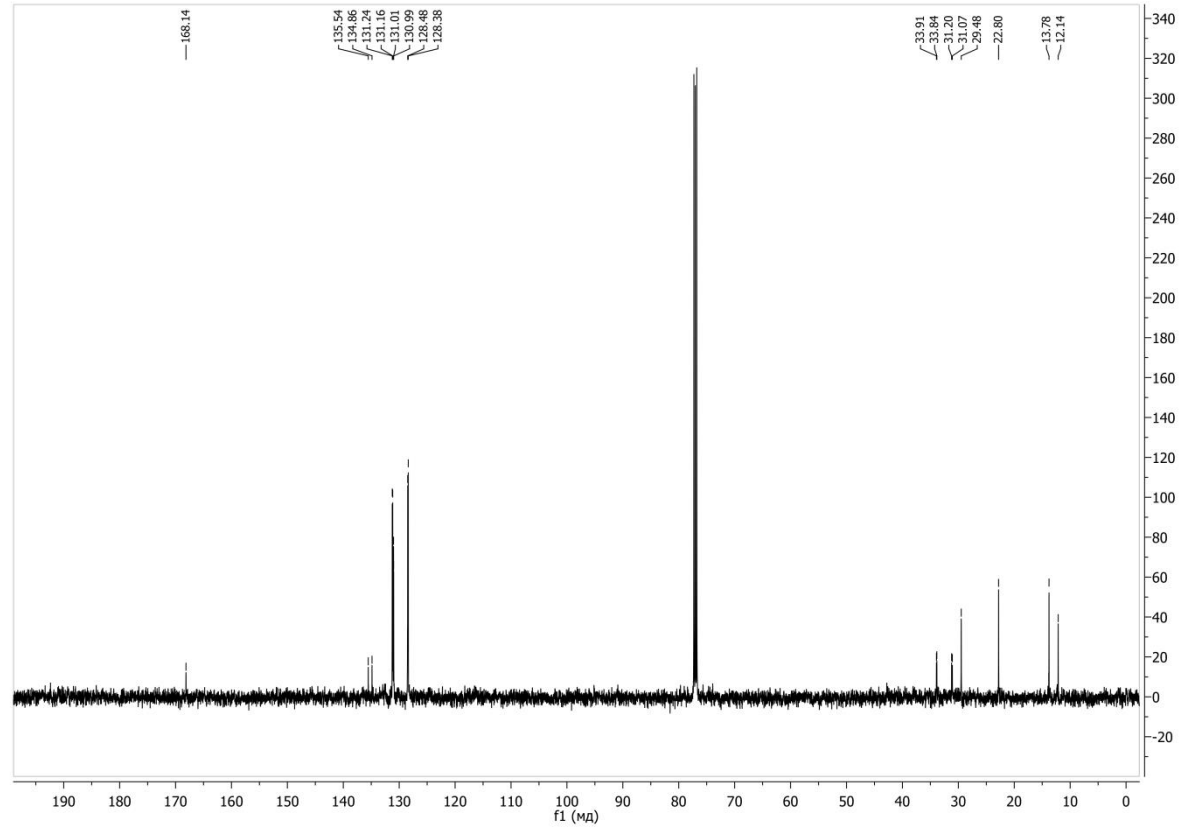
(*Z*)-(2-ethylhept-1-en-1-yl)diphenylphosphine sulfide (3c)

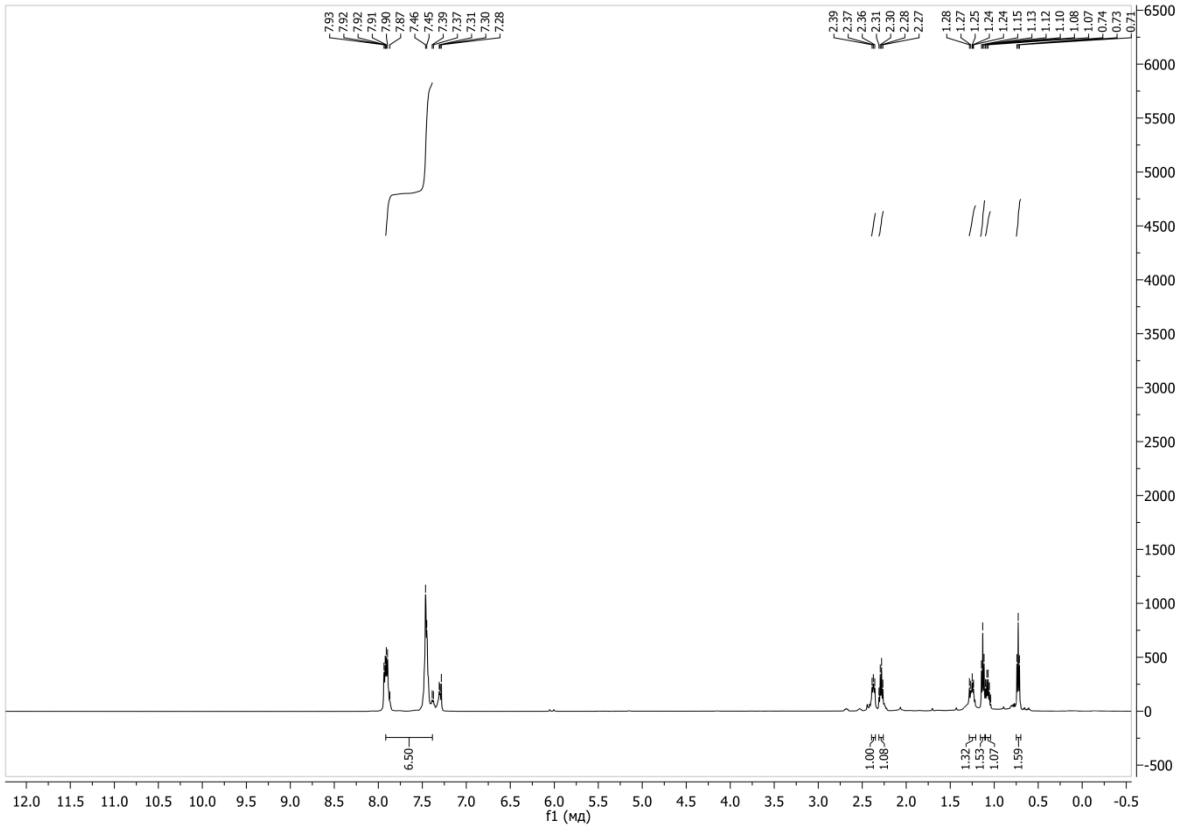






(*Z*)-(2-ethylhex-1-en-1-yl-1-*d*)diphenylphosphine sulfide (4a)

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1.27
1.25
1.24
1.24
1.15
1.13
1.12
1.10
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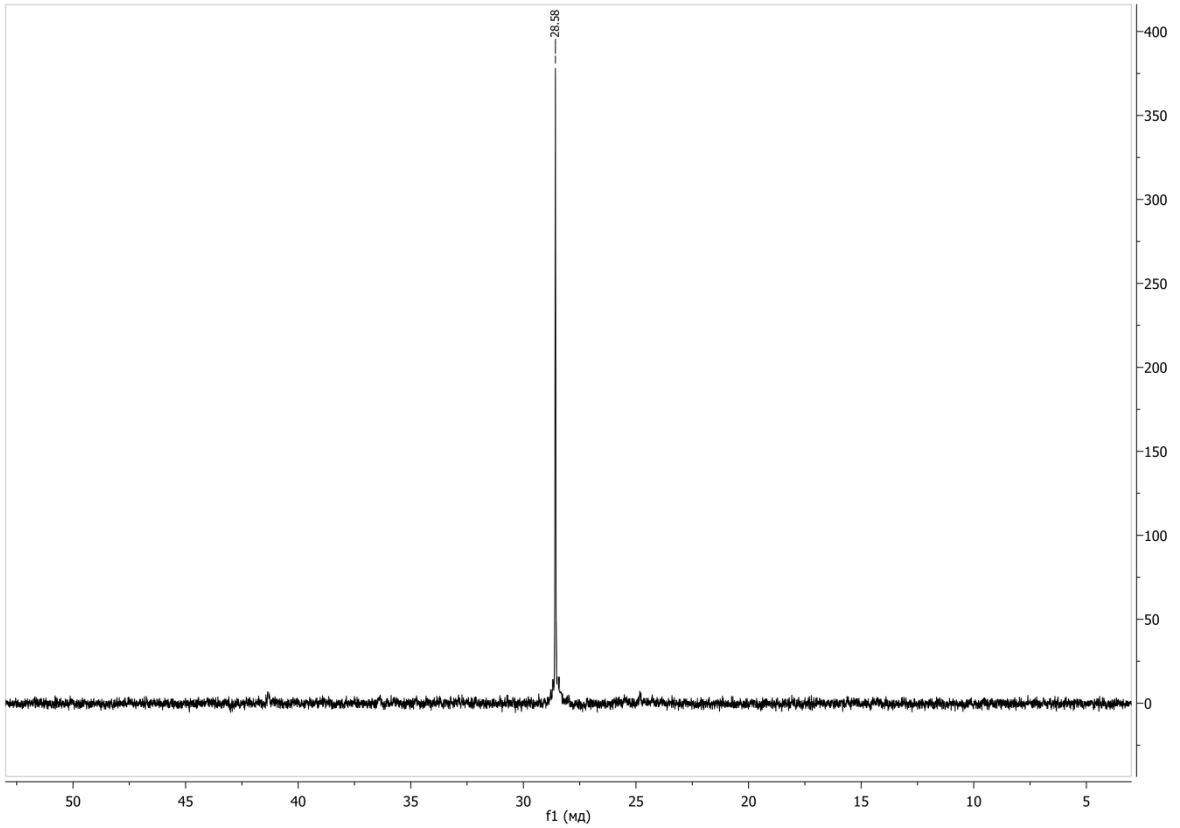
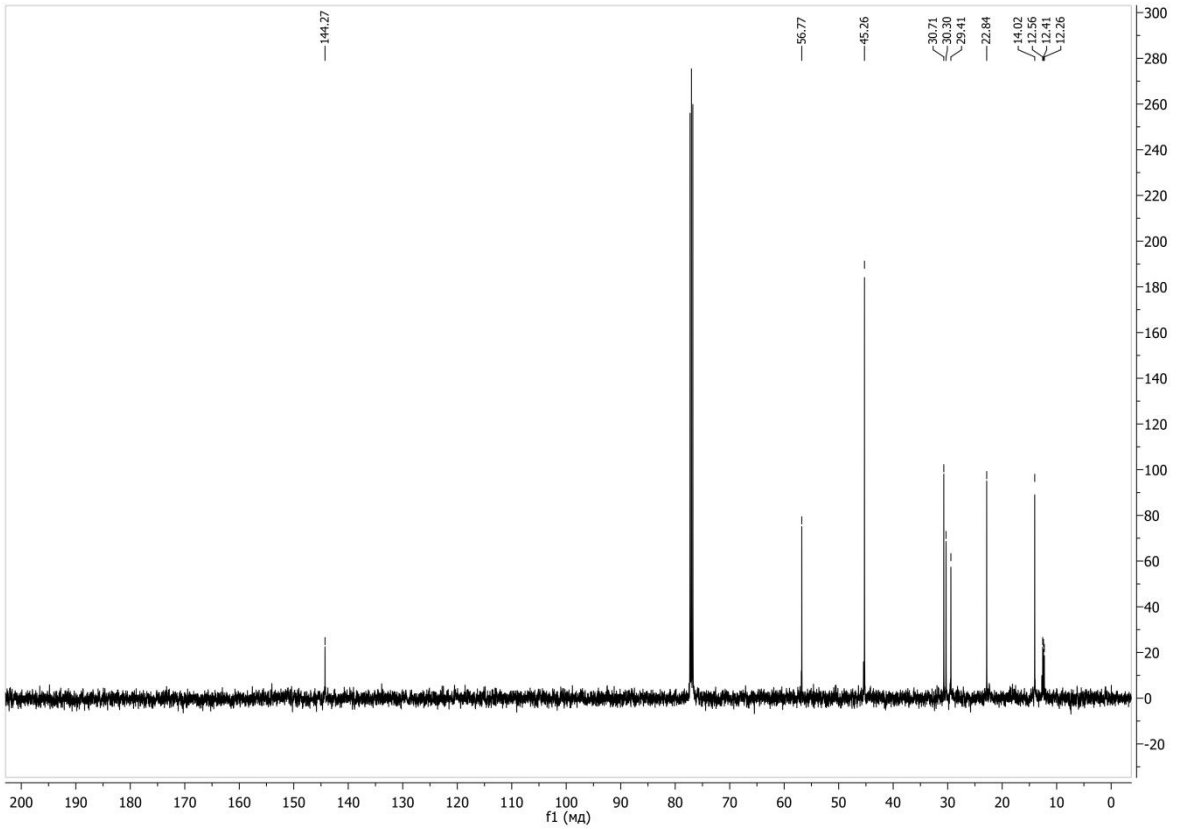
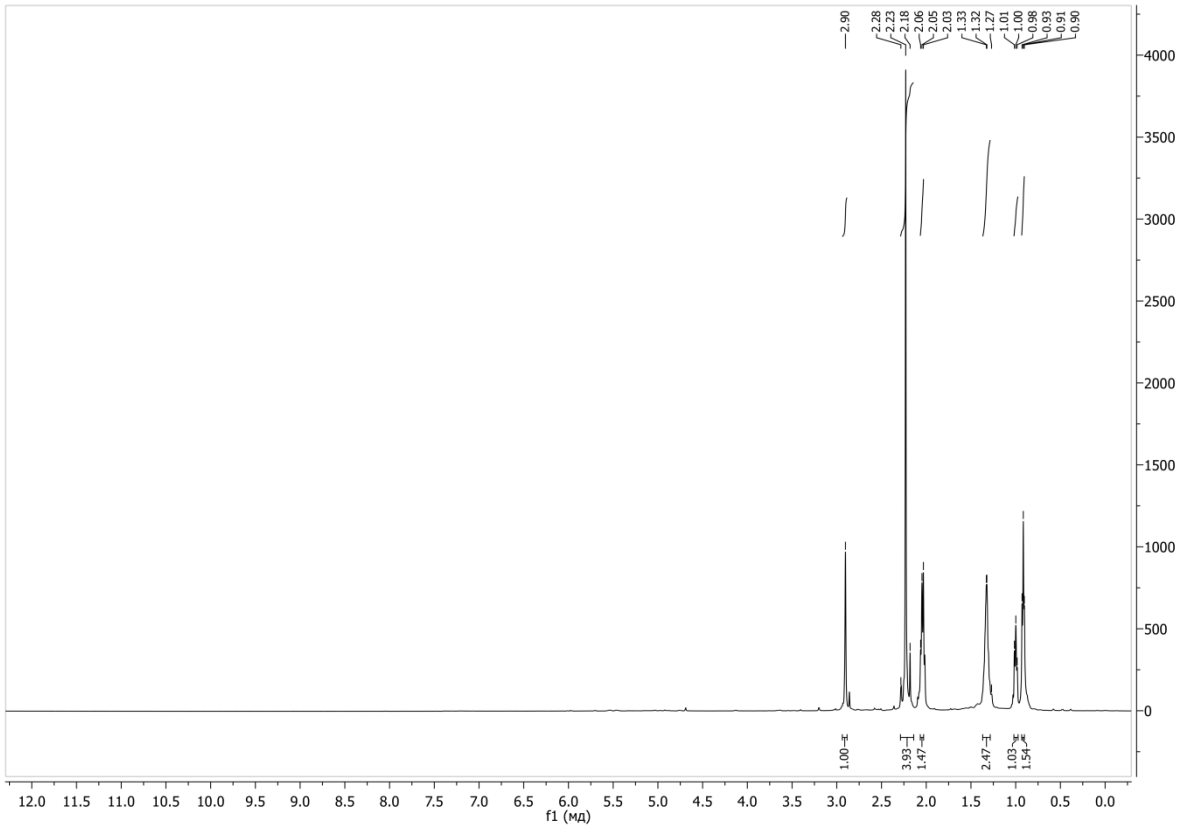
1.07
1.59
f1 (мд)

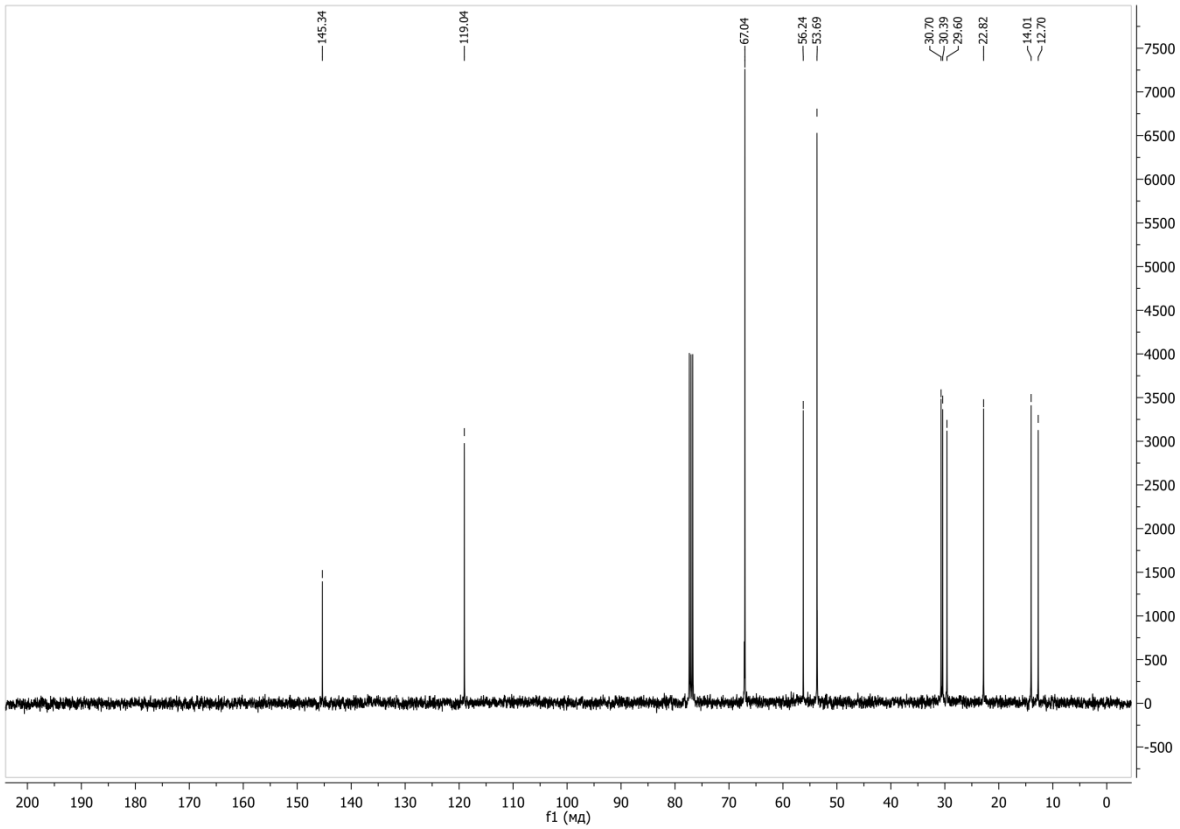

28.58
f1 (мд)

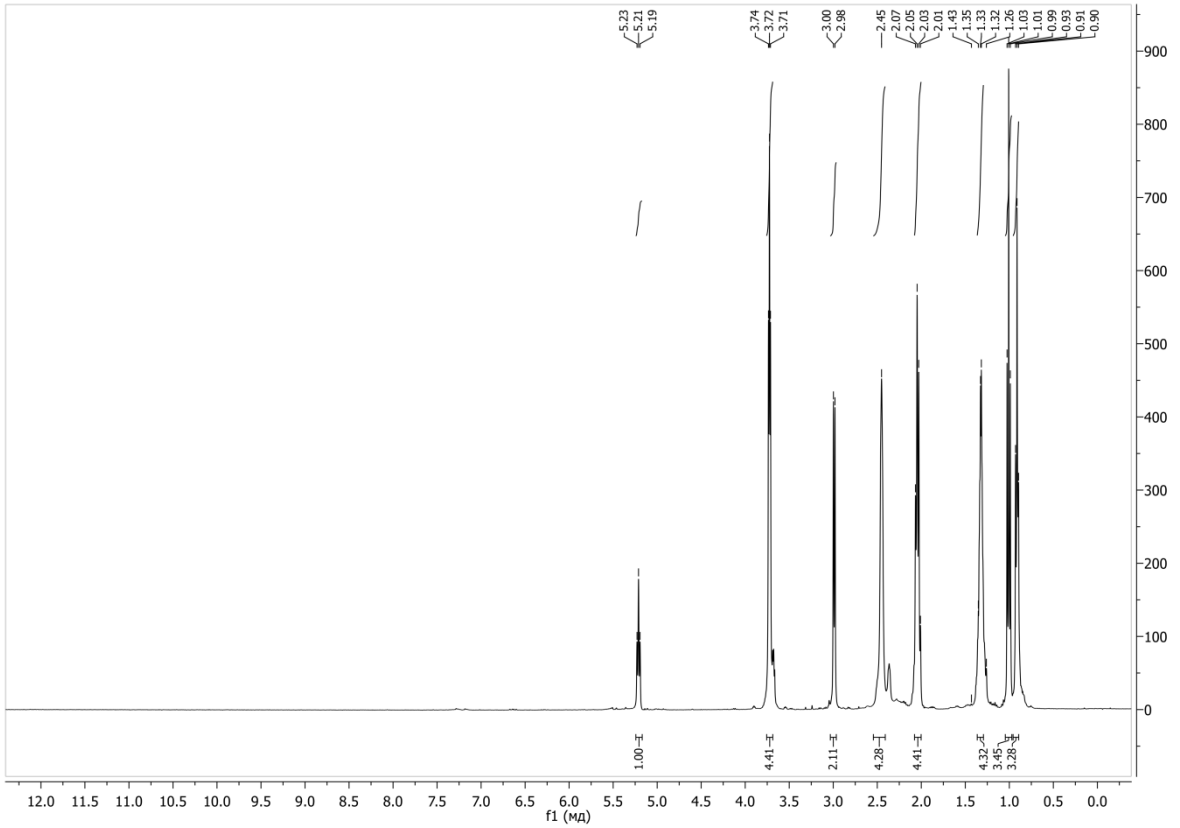
(*Z*)-3-(Ethyl-2-*d*)-*N*,*N*-dimethylhept-2-en-1-amine-2-*d* (8a)



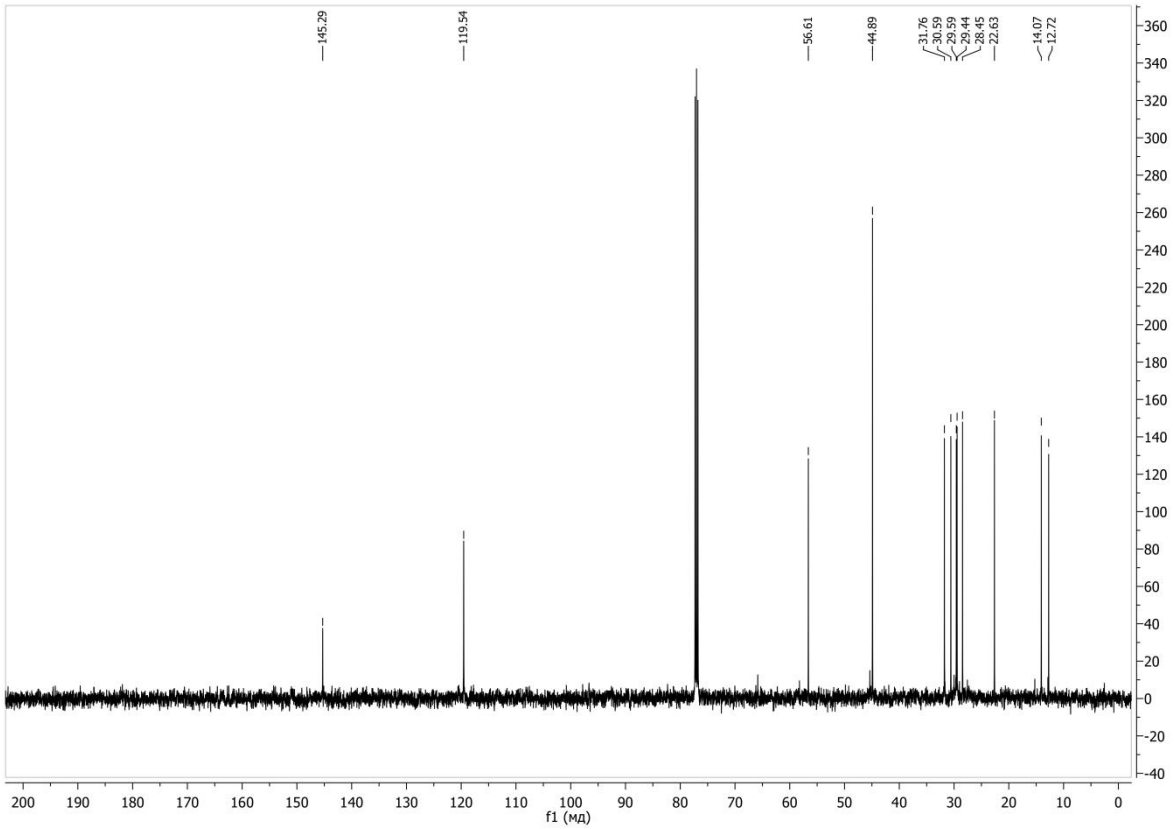


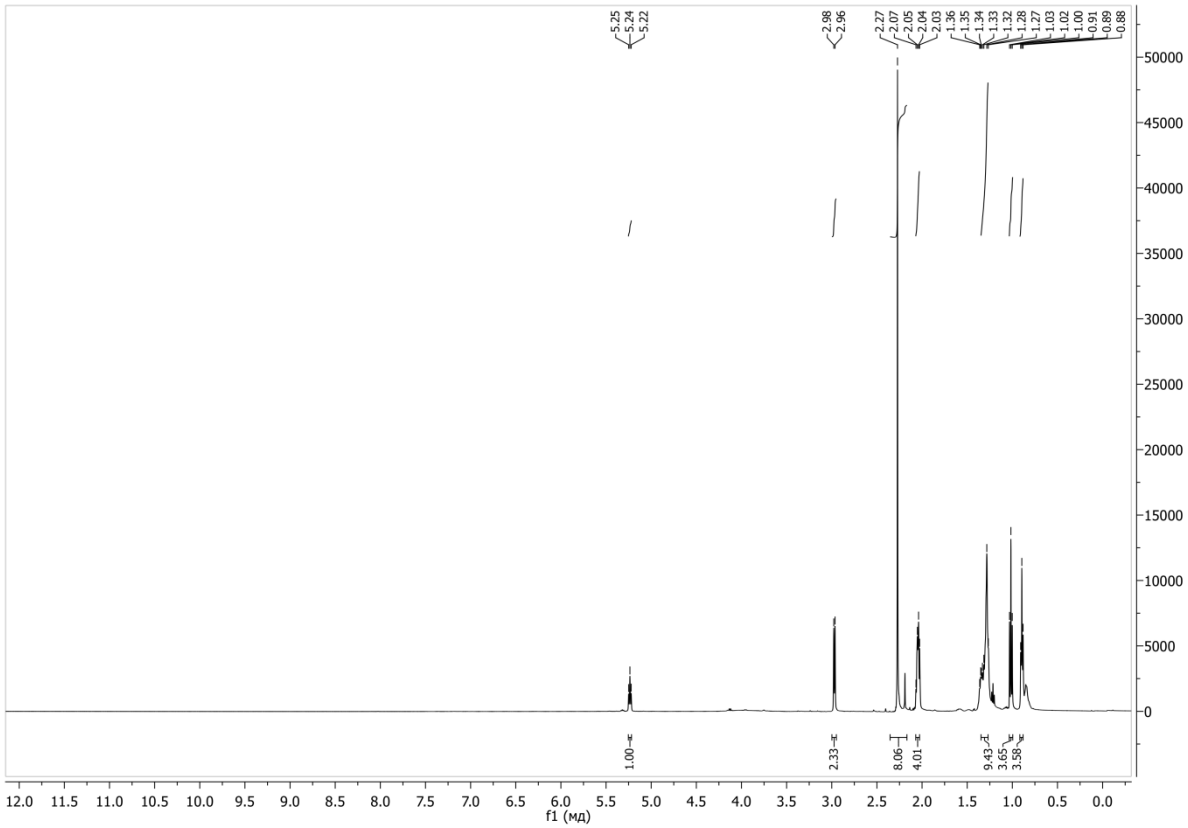
(Z)-4-(3-Ethylhept-2-en-1-yl)morpholine (9c)



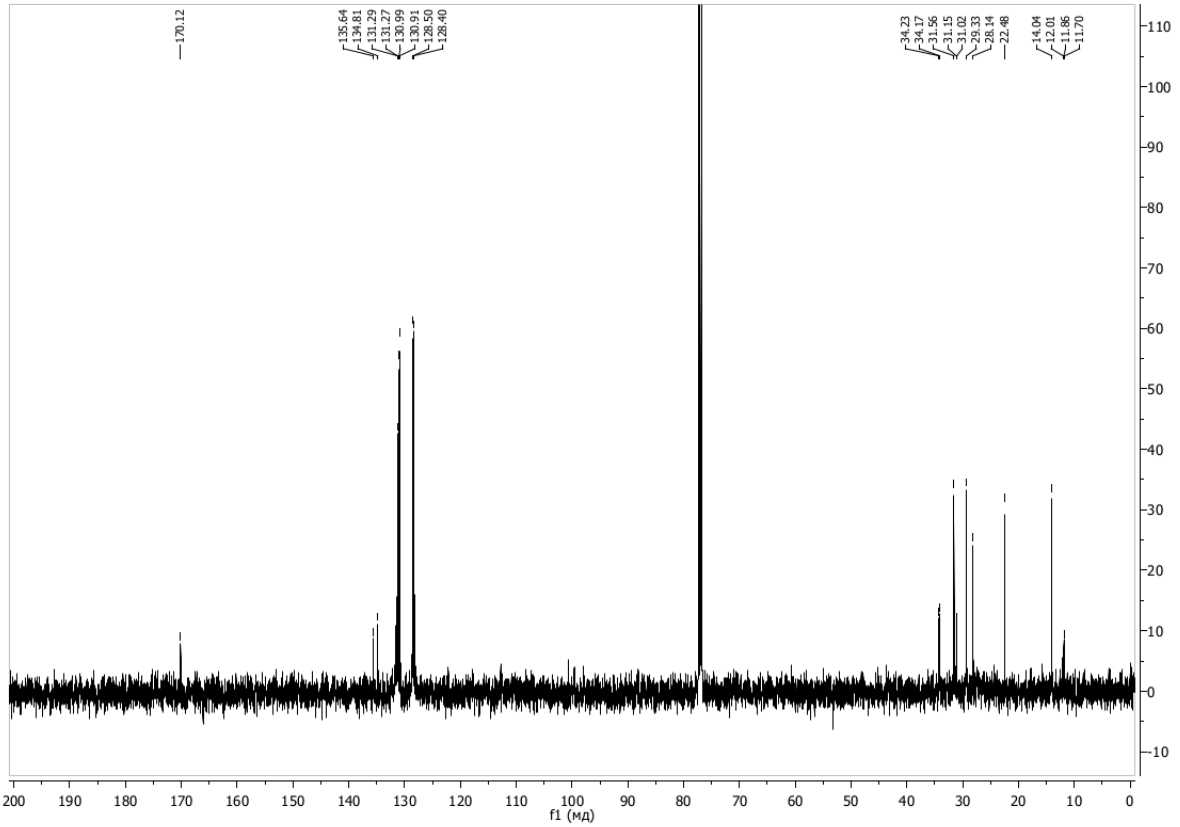


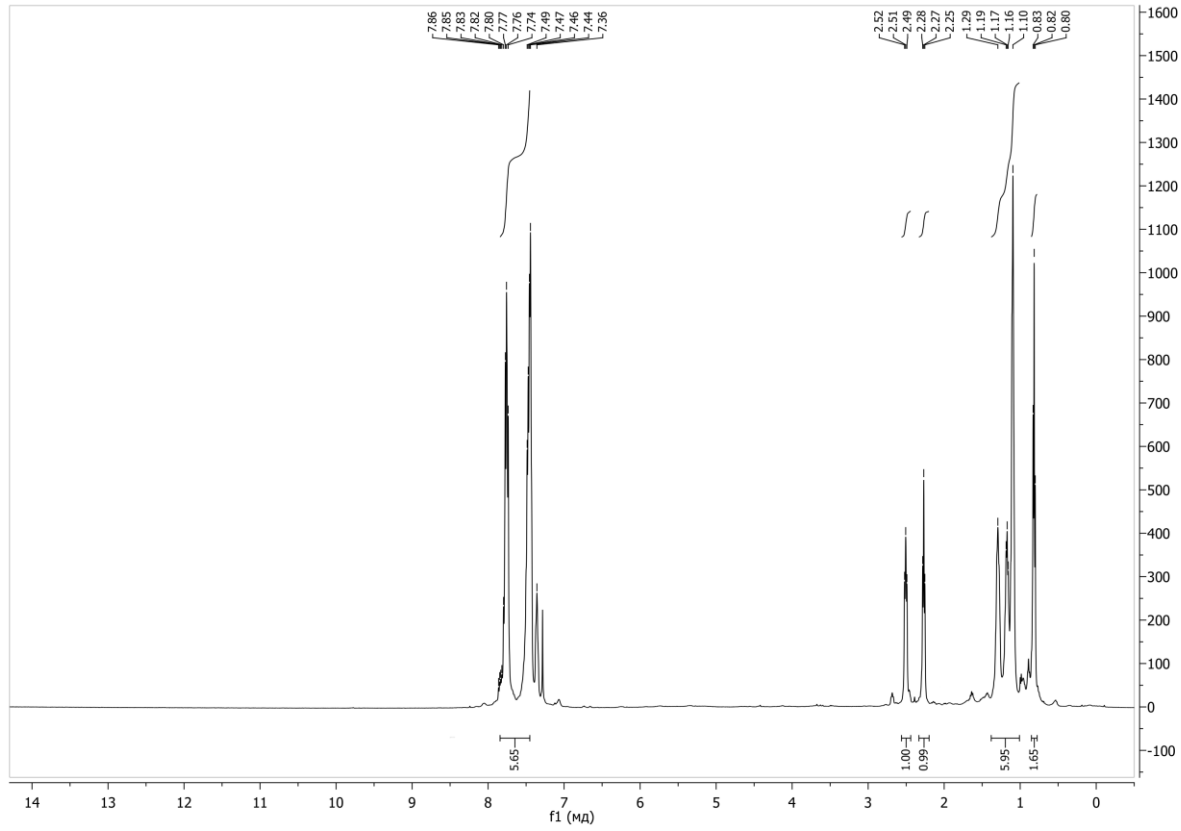
(*Z*)-3-Ethyl-*N*,*N*-dimethylnon-2-en-1-amine (9d)

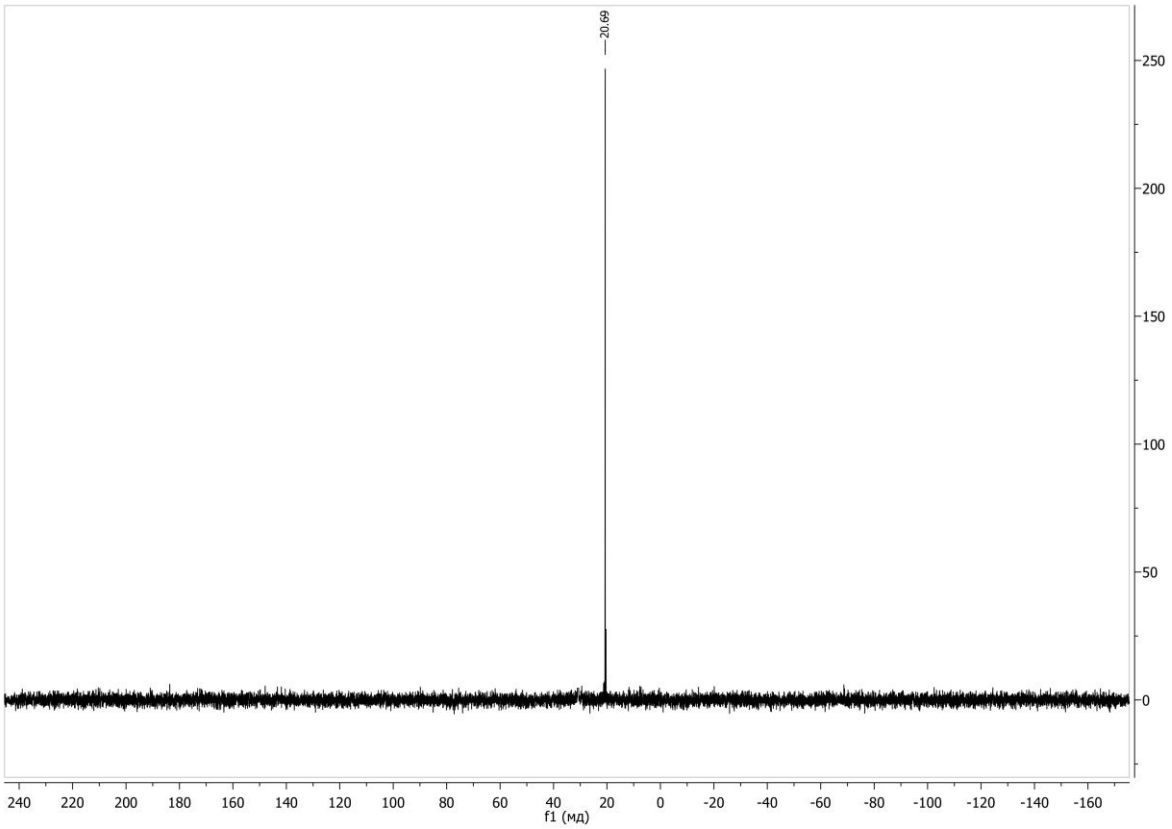




(*Z*)-(2-(Ethyl-2-*d*)oct-1-en-1-yl-1-*d*)diphenylphosphine oxide (12a)







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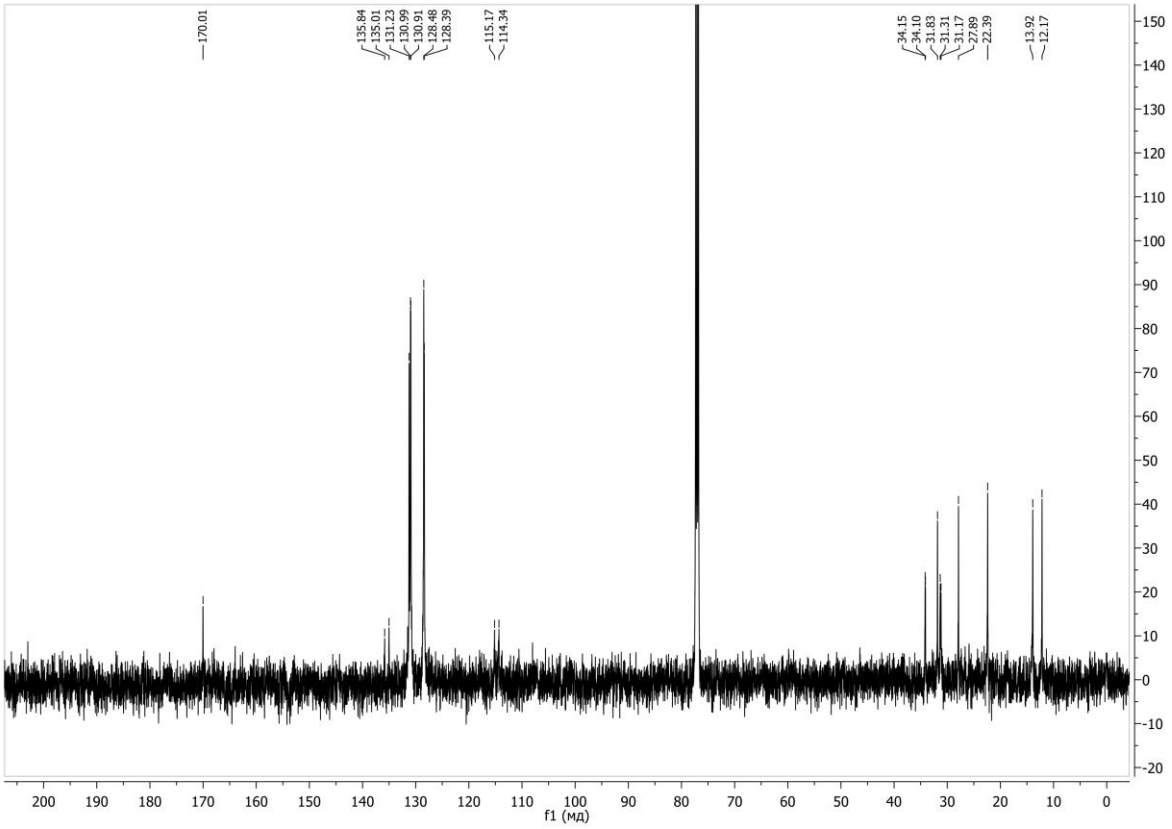
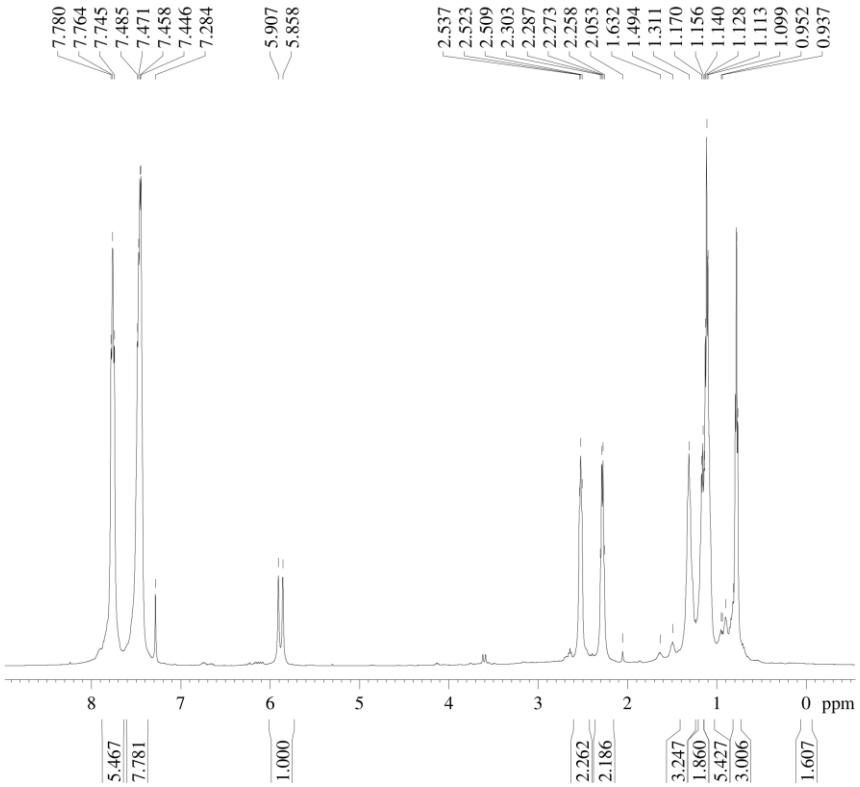
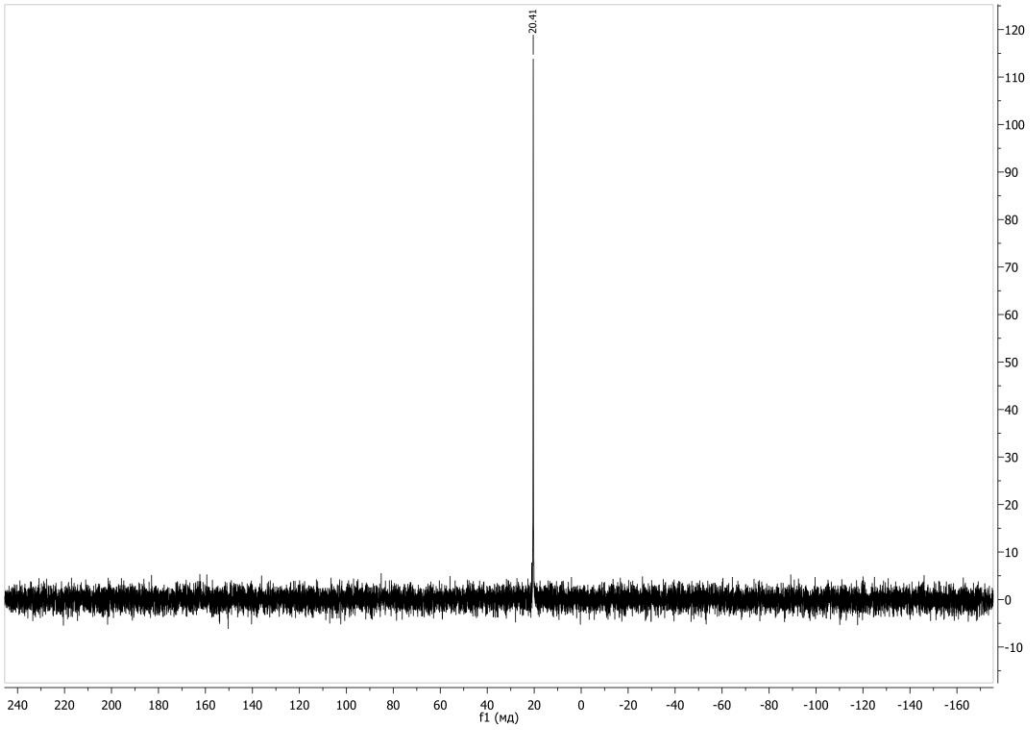
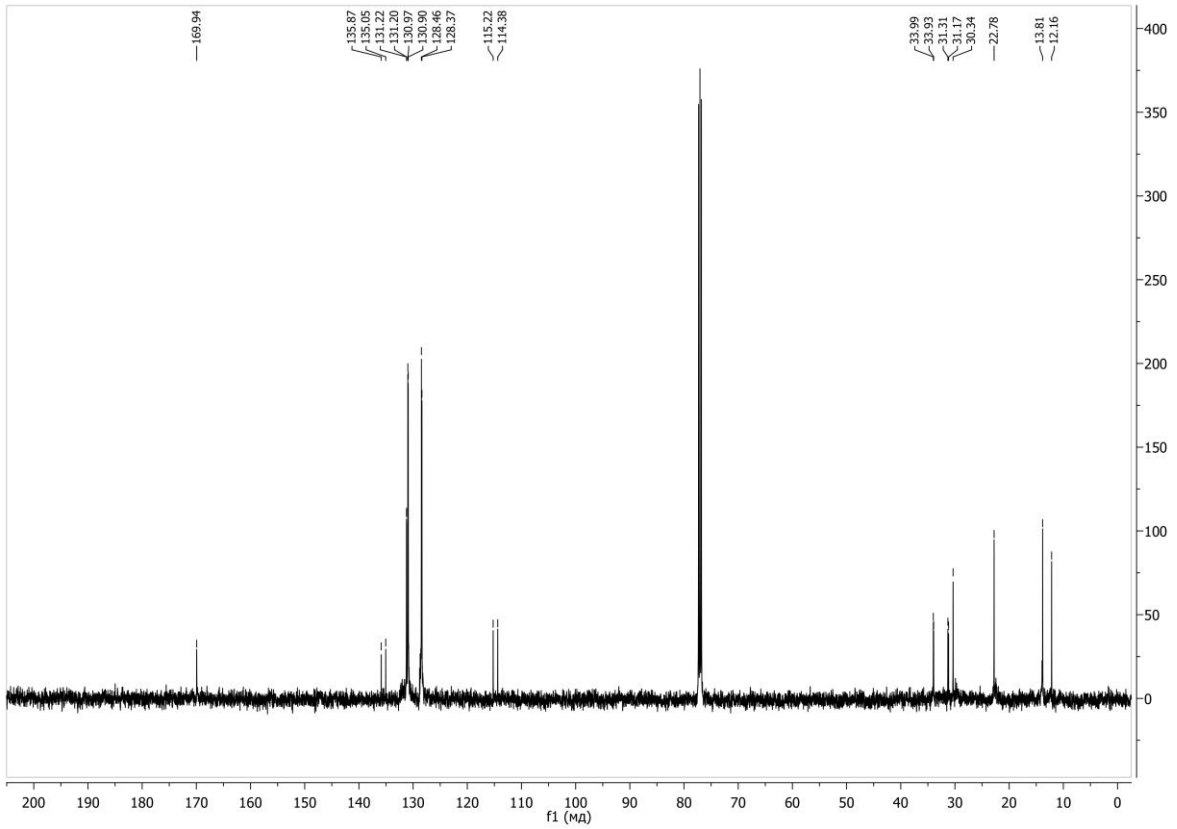






(Z)-(2-ethylhex-1-en-1-yl)diphenylphosphine oxide (13b)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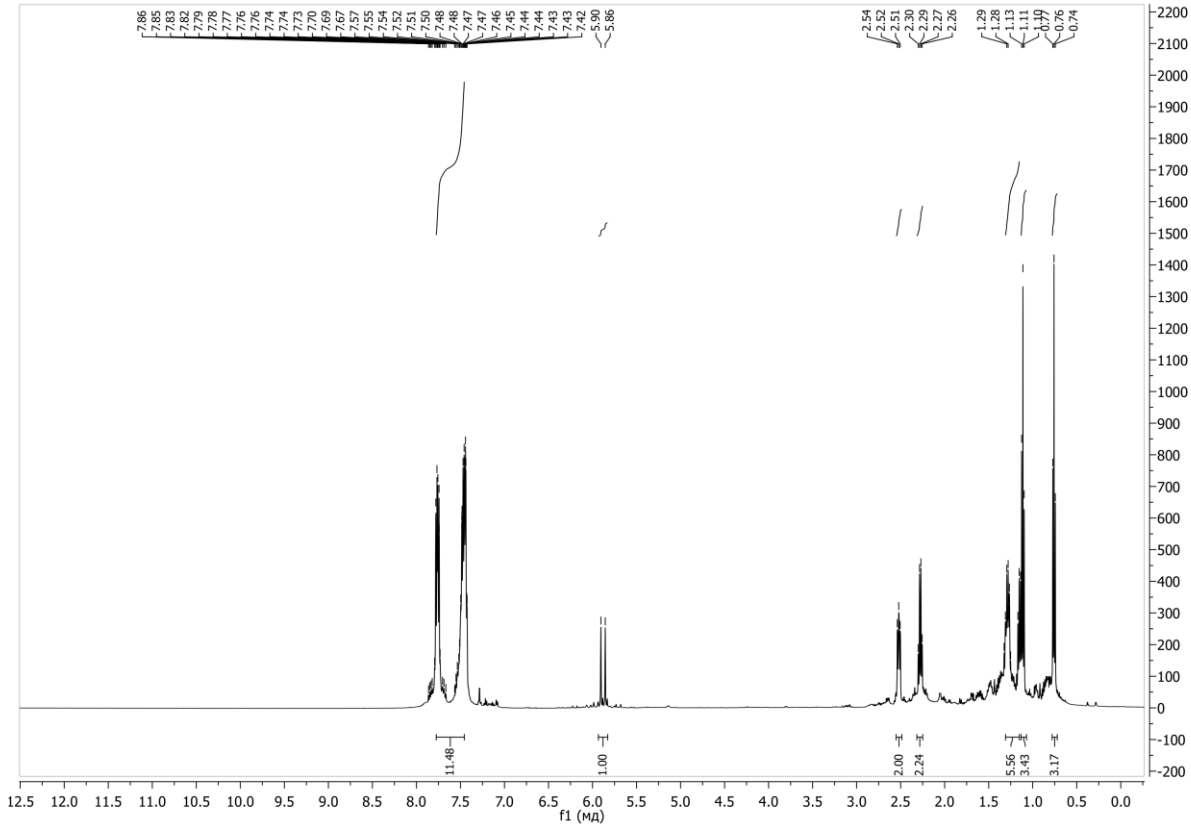
f1 (мд)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1.00
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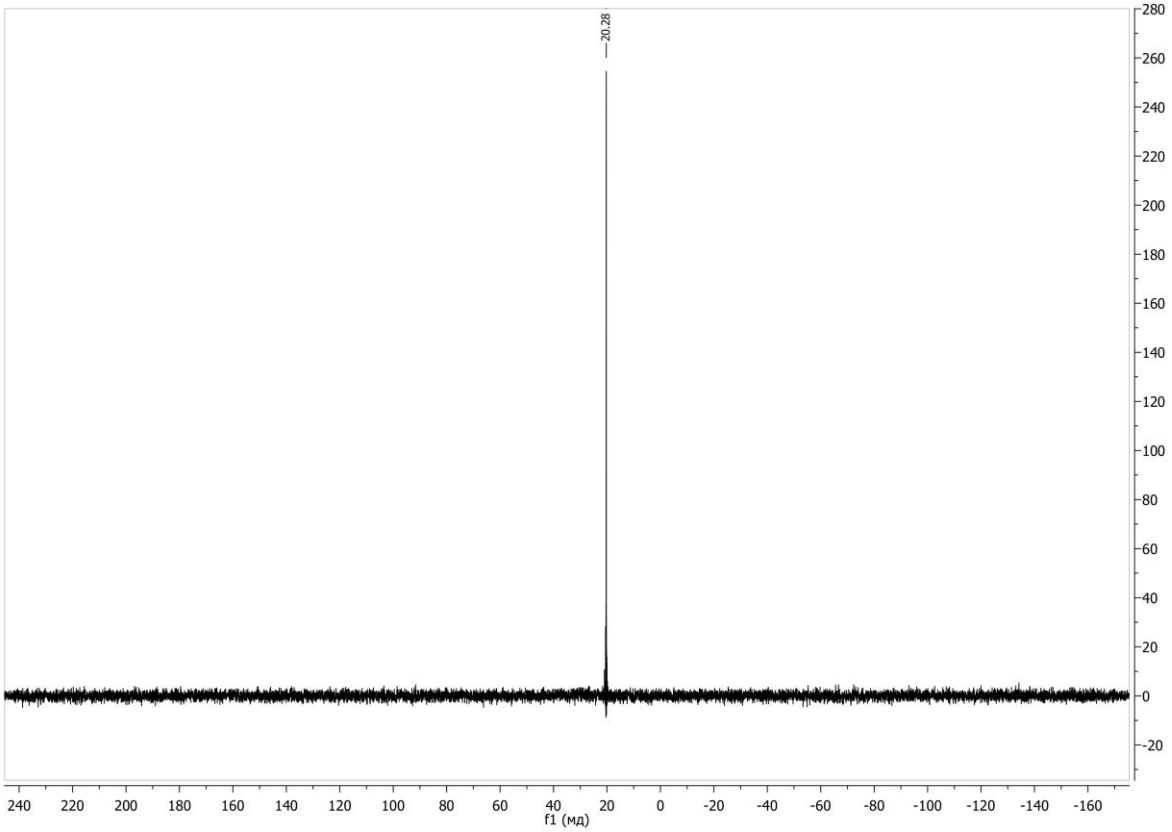
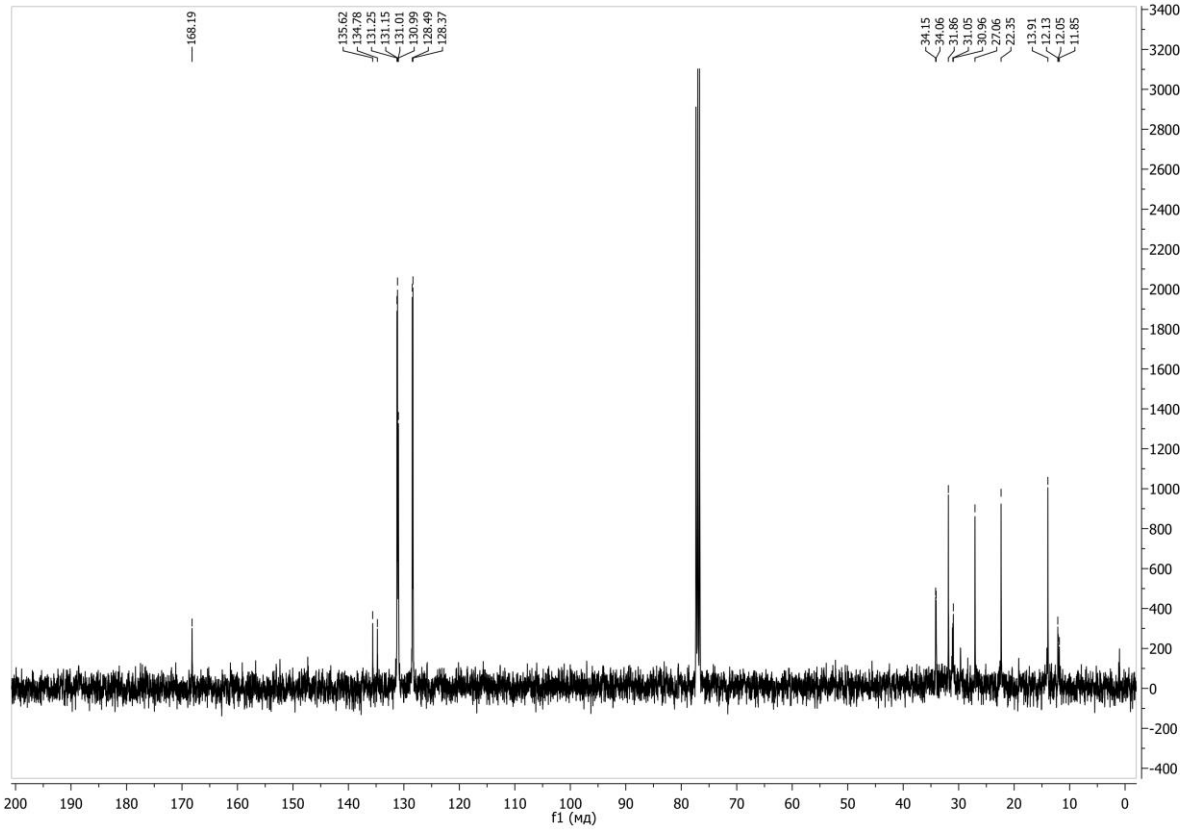
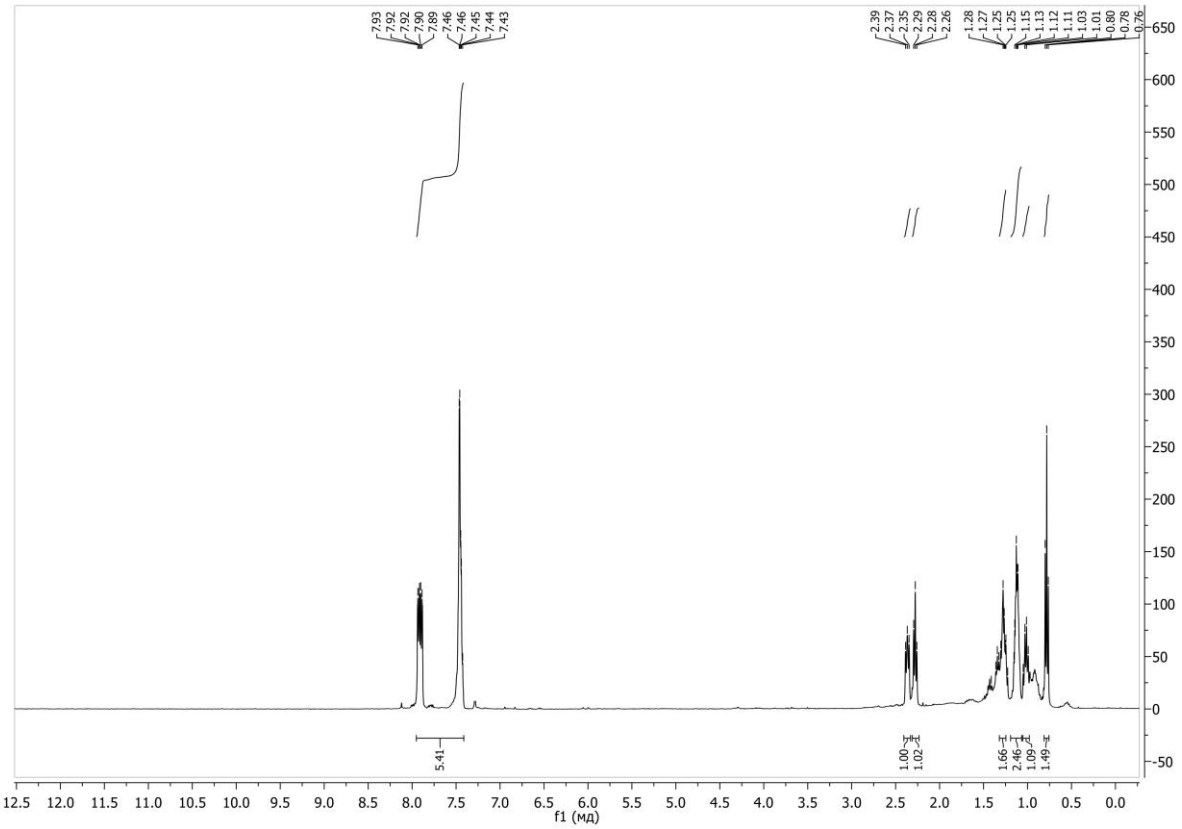
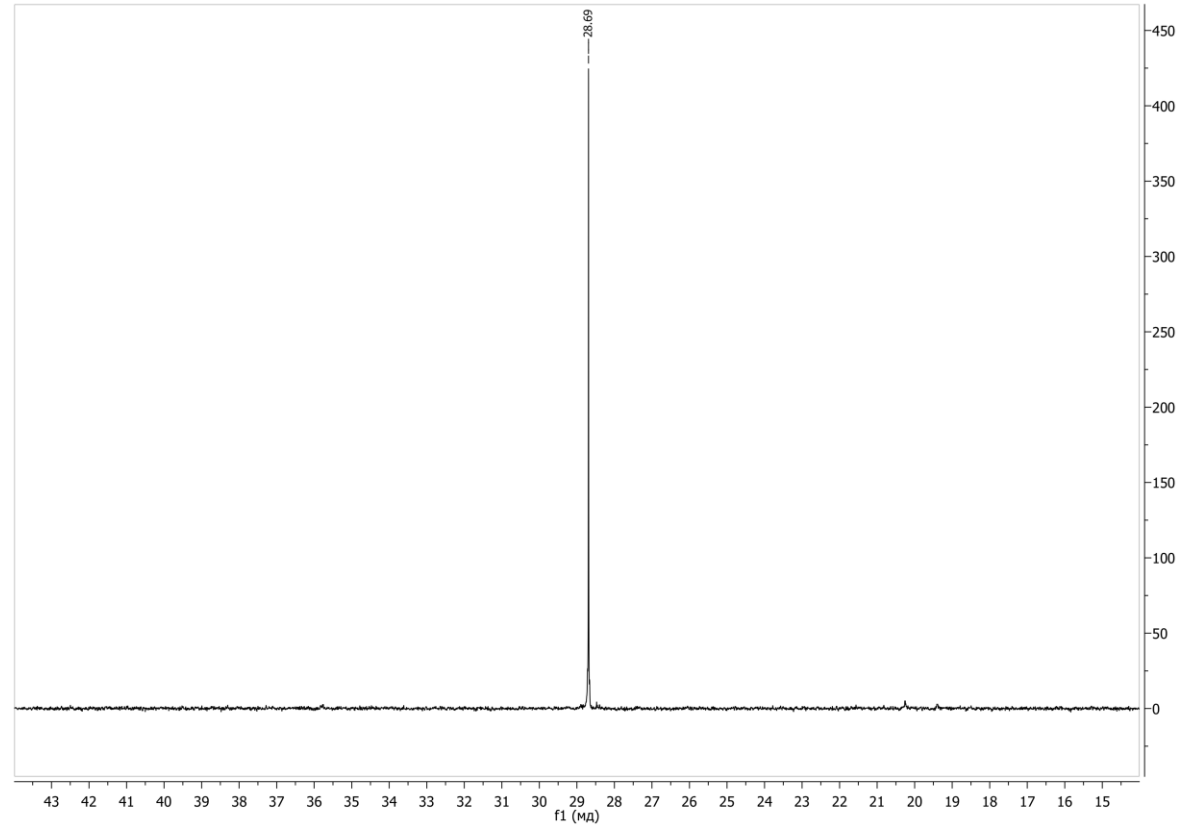
2.24
5.56
3.43
3.17
f1 (мд)



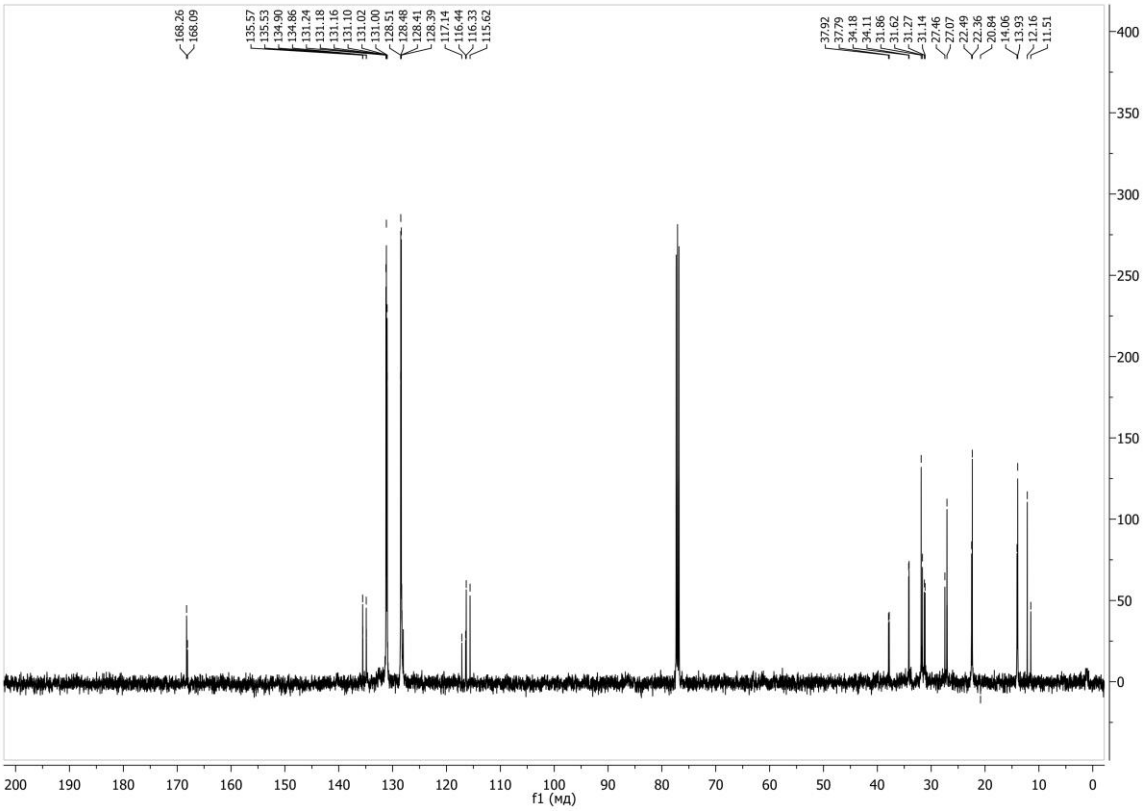
(*Z*)-(2-(ethyl-2-d)hept-1-en-1-yl-1-d)diphenylphosphine sulfide (14c)

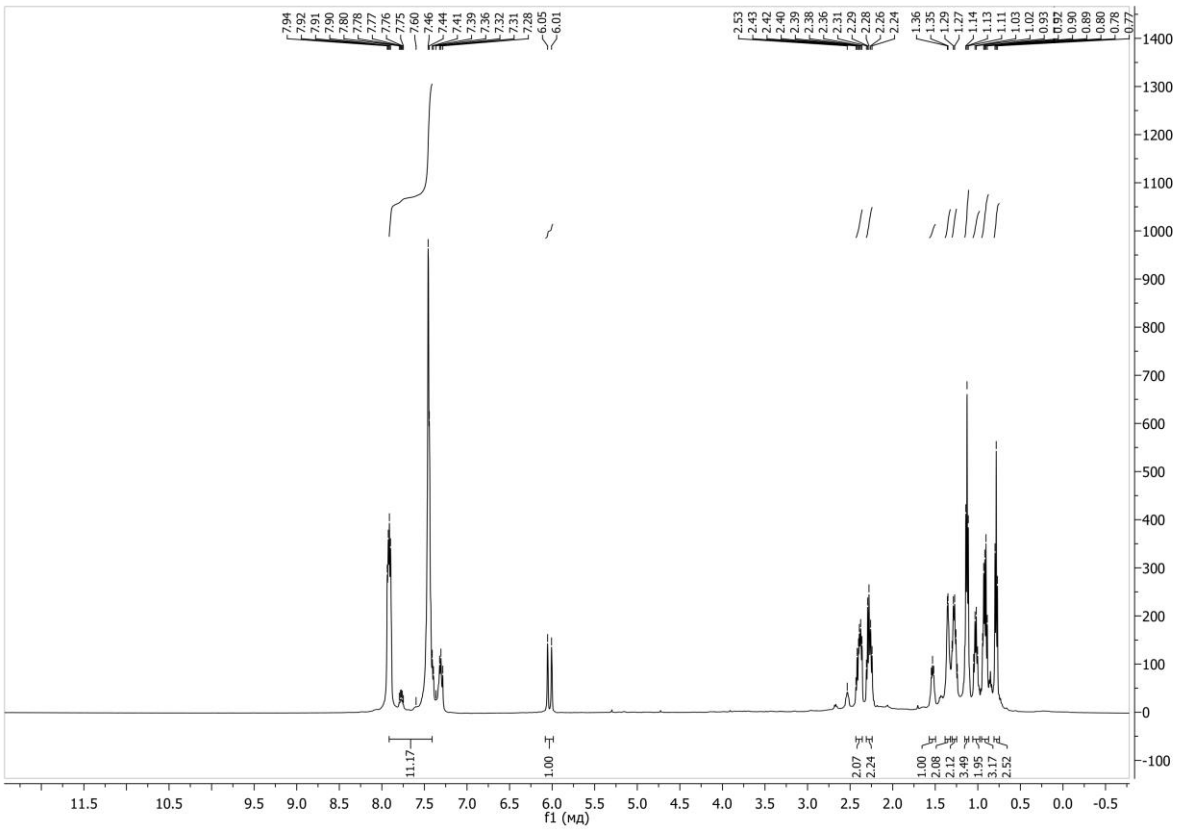


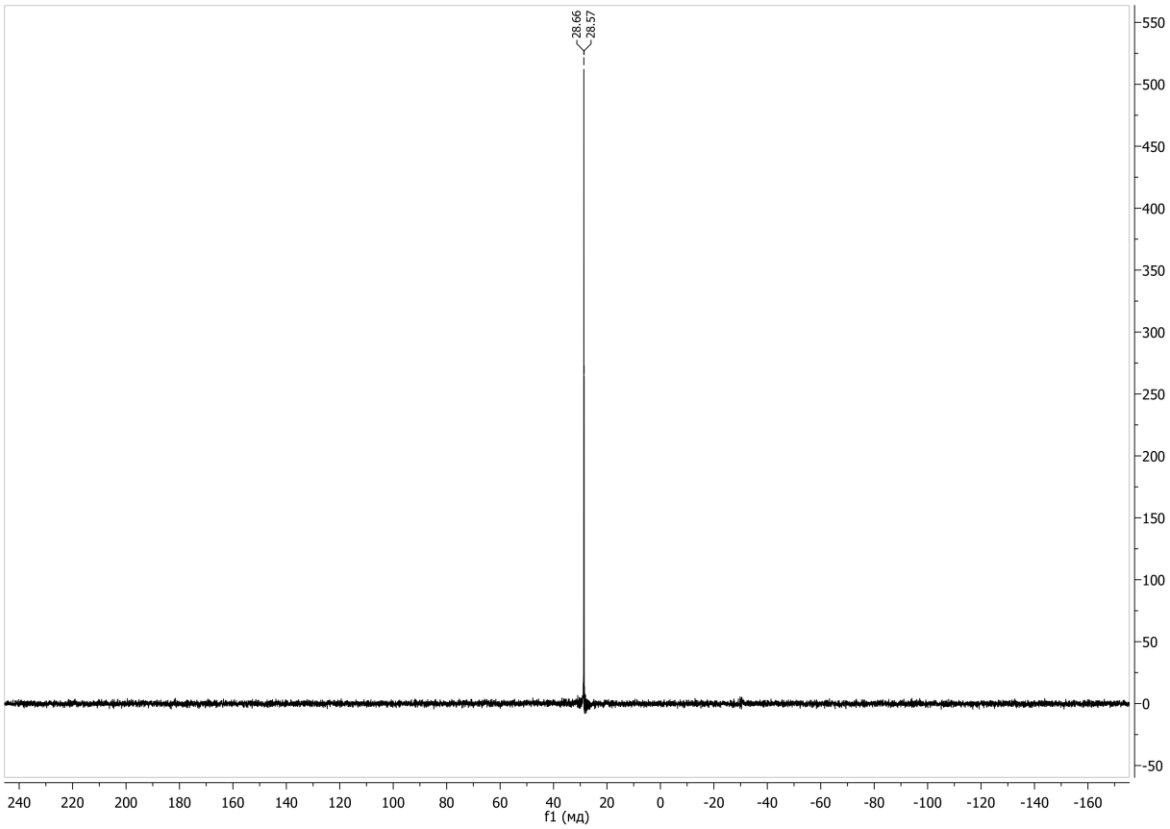

7.93
7.92
7.92
7.90
7.89
7.46
7.46
7.45
7.44
7.43
2.39
2.37
2.35
2.29
2.28
2.26
1.28
1.27
1.25
1.25
1.15
1.13
1.12
1.11
1.03
1.01
0.80
0.78
0.76
5.41
1.00
1.02
1.66
2.46
1.09
1.49
f1 (мд)


28.69
f1 (мд)

(*Z*)-(2-ethylhept-1-en-1-yl)diphenylphosphine sulfide (16) and (*E*)-(2-ethylhept-1-en-1-yl)diphenylphosphine sulfide (17)






28.66
28.57
550
500
450
400
350
300
250
200
150
100
50
0
-50
240
220
200
180
160
140
120
100
80
60
40
20
0
-20
-40
-60
-80
-100
-120
-140
-160
f1 (мд)