Trifluoroacetaldehyde N-tosylhydrazone as a Reagent for Trifluoroethylation of Terminal Alkynes

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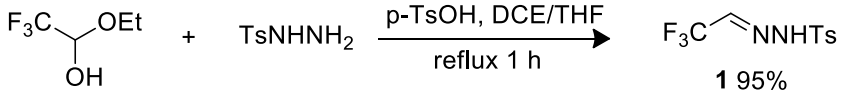
Experimental Procedures

General

All solvents were distilled prior to use. Acetonitrile and 1,2-dichloroethane were dried by distillation over P_2O_5. Chromatography was carried out using 230-400 mesh silica gel (Merck 40/60). ^{1}H NMR spectra were recorded on commercial instrument Agilent 400-MR (400 MHz). Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard ($CDCl_3$, δ = 7.26). ^{13}C{1H} NMR spectra were collected on commercial instrument Agilent 400-MR (100 MHz) with complete proton decoupling. HRMS (ESI) were recorded on a commercial apparatus. Thin layer chromatographies (TLC) were performed using Merck aluminium-foil baked plates precoated with Kieselgel 60 F254. The products were visualized using UV fluorescence (254 nm) or potassium permanganate stain. 1-ethoxy-2,2,2-trifluoroethanol, 1-methoxy-3,3,3,2,2-pentafluoropropanol, tosyl hydrazide and alkynes **2a-2w** were purchased from commercial sources, and used without further purification.

Synthesis of 2,2,2-trifluoroacetaldehyde N-tosylhydrazone (1)



To a round bottom flask surmounted with a reflux condenser was added tosyl hydrazide (4.17 g, 22.4 mmol), 1-ethoxy-2,2,2-trifluoroethanol (3.69 g, 25.6 mmol) and p-toluenesulfonic acid monohydrate (0.213 g, 1.10 mmol) in DCE (25 ml) and THF (25 ml). The reaction mixture was then stirred at reflux for 1 h. The solution was cooled down to rt and the volatiles were removed under reduced pressure. The residue was dissolved in EtOAc, washed with sodium hydrogen carbonate solution and dried with $MgSO_4$. The solvent was removed under reduced pressure to obtain white solid which was sufficiently pure and used in the next step without further purification. Yield 5.66 g (95 %). In some cases the product was recrystallized from minimal amount of EtOAc/hexane (1:1). M.p. 115-117 °C.

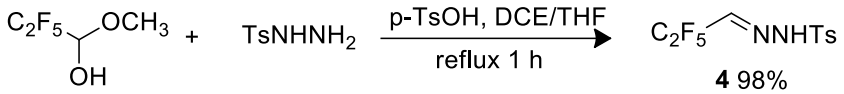
^{1}H NMR (400 MHz, $CDCl_3$) δ 11.80 (br s, 1H), 7.57 (d, J = 8.4 Hz, 2H), 7.13 (d, J = 8.5 Hz, 2H), 7.06 (q, J = 4.0 Hz, 1H), 2.24 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 143.8, 135.1, 131.9 (q, J_{CF} = 38.9 Hz), 129.2, 127.0, 119.3 (q, J_{CF} = 270.9 Hz), 21.1.

^{19}F NMR (376 MHz, $CDCl_3$) δ -67.8 (d, J = 4.1 Hz).

NMR spectral data for this compound were consistent with those in literature.[S1]

Synthesis of 3,3,3,2,2-pentafluoropropanal N-tosylhydrazone (4)



To a round bottom flask surmounted with a reflux condenser was added tosyl hydrazide (7.01 g, 38.0 mmol), 1-methoxy-3,3,3,2,2-pentafluoropropanol (7.76 g, 43.0 mmol) and p-toluenesulfonic acid monohydrate (0.352 g, 1.90 mmol) in DCE (40 ml) and THF (40 ml). The reaction mixture was then stirred at reflux for 1 h. The solution was cooled down to rt and volatiles were removed under reduced pressure. The residue was dissolved in EtOAc, washed with sodium hydrogen carbonate solution and dried with $MgSO_4$. The solvent was removed under reduced pressure to obtain white solid which was sufficiently pure and used in the next step without further purification. Yield 11.77 g (98 %). M.p. 109-111 °C.

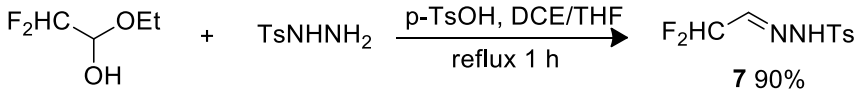
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.50 (br s, 1H), 7.78 (d, J = 8.3 Hz, 2H), 7.33 (d, J = 8.2 Hz, 2H), 7.18 (t, J = 5.9 Hz, 1H), 2.43 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 145.4, 133.9, 133.0 (t, J_{CF} = 29.6 Hz), 129.9, 127.9, 118.1 (qt, J_1 = 286.3 Hz, J_2 = 36.0 Hz), 109.3 (tq, J_1 = 252.6 Hz, J_2 = 38.8 Hz), 21.5.

^{19}F NMR (376 MHz, $CDCl_3$) δ -83.4 (dt, J_1 = 1.1 Hz, J_2 = 2.0 Hz, 3F), -116.8 (dq, J_1 = 6.0 Hz, J_2 = 2.0 Hz, 2F).

HRMS (ESI) m/z: $[M - H]^-$ Calcd for $C_{10}H_8F_5N_2O_2S$ 315.0232; Found 315.0233.

Synthesis of 2,2-difluoroacetaldehyde N-tosylhydrazone (7)



To a round bottom flask surmounted with a reflux condenser was added tosyl hydrazide (4.84 g, 26.0 mmol), 1-ethoxy-2,2-difluoroethanol (3.20 g, 28.6 mmol) and p-toluenesulfonic acid monohydrate (0.213 g, 1.10 mmol) in DCE (25 ml) and THF (25 ml). The reaction mixture was then stirred at reflux for 1 h. The solution was cooled down to rt and the volatiles were removed under reduced pressure. The residue was dissolved in EtOAc, washed with sodium hydrogen carbonate solution and dried with $MgSO_4$. The solvent was removed under reduced pressure to obtain white solid which was sufficiently pure and used in the next step without further purification. Yield 5.80 g (90 %). M.p. 118-119 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.84 (br s, 1H), 7.80 (d, J = 8.2 Hz, 2H), 7.35 (d, J = 8.1 Hz, 2H), 7.13 (m, 1H), 6.02 (td, J_{HF} = 54.5 Hz, J_{HH} = 5.9 Hz, 1H), 2.45 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 145.1, 139.1 (t, J_{CF} = 36.5 Hz), 134.4, 129.9, 127.8, 112.4 (t, J_{CF} = 235.1 Hz), 21.6.

^{19}F NMR (376 MHz, $CDCl_3$) δ -116.2 (dd, J_1 = 54.5 Hz, J_2 = 2.9 Hz).

NMR spectral data for this compound were consistent with those in literature.[S9]

Typical Procedure for Trifluoroethylation of Aromatic Terminal Alkynes 2a-n

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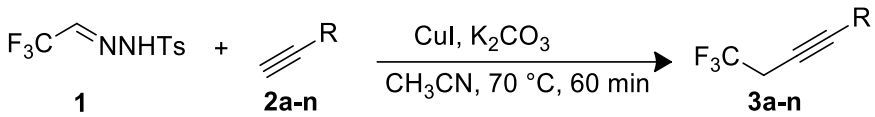
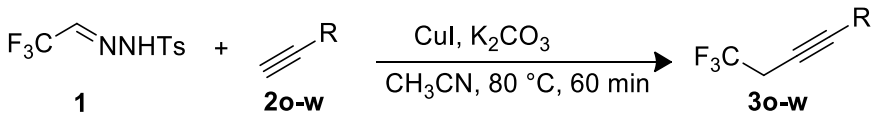


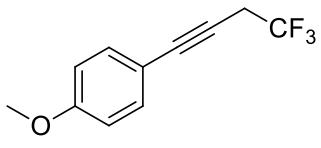
The Schlenk flask was loaded with hydrazone **1** (160 mg, 0.6 mmol), CuI (96 mg, 0.5 mmol), K_2CO_3 (207 mg, 1.5 mmol) and filled with argon. The solution of alkyne (0.5 mmol) in acetonitrile (10 ml) was added via syringe and the reaction mixture was then stirred at 70 °C for 60 min. A mixture was filtered and the solvent was removed under reduced pressure. The desired product was isolated by column chromatography (hexanes or EtOAc/hexanes).

Typical Procedure for Trifluoroethylation of Non-aromatic Terminal Alkynes 2o-w



The Schlenk flask was loaded with hydrazone **1** (160 mg, 0.6 mmol), CuI (96 mg, 0.5 mmol), K_2CO_3 (207 mg, 1.5 mmol) and filled with argon. The solution of alkyne (0.5 mmol) in acetonitrile (10 ml) was added via syringe and the reaction mixture was then stirred at 80 °C for 60 min. A mixture was filtered and the solvent was removed under reduced pressure. The desired product was isolated by column chromatography (hexanes or EtOAc/hexanes).

Characterization of Products



3a

1-methoxy-4-(4,4,4-trifluorobut-1-yn-1-yl)benzene (3a)

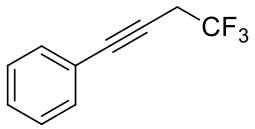
Prepared according to general procedure from (4-methoxyphenyl)acetylene, purified by silica gel chromatography (petroleum ether) and obtained as a colorless oil in 85 % yield (91 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, J = 8.7 Hz, 2H), 6.84 (d, J = 8.7 Hz, 2H), 3.82 (s, 3H), 3.26 (q, J = 9.6 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 159.8, 133.3, 128.7, 124.2 (q, J_{CF} = 277.2 Hz), 113.9, 84.2, 76.0, 55.2, 26.8 (q, J_{CF} = 34.6 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -66.6 (t, J_{FH} = 9.5 Hz).

NMR spectral data for this compound are consistent with those in literature.[S2]



3b

(4,4,4-trifluorobut-1-yn-1-yl)benzene (3b)

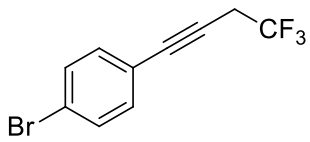
Prepared according to general procedure from phenylacetylene, purified by silica gel chromatography (petroleum ether) and obtained as a colorless oil in 70 % yield (64 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53-7.47 (m, 2H), 7.40-7.33 (m, 3H), 3.30 (q, J = 9.6 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 132.5, 131.8, 128.7, 128.3, 124.2 (q, J_{CF} = 276.8 Hz), 122.2, 84.3, 77.5, 26.7 (q, J_{CF} = 34.6 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -66.6 (t, J_{FH} = 9.5 Hz).

NMR spectral data for this compound are consistent with those in literature.[S2]



3c

1-bromo-4-(4,4,4-trifluorobut-1-yn-1-yl)benzene (3c)

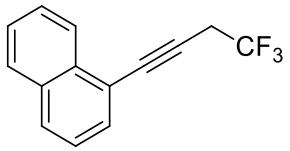
Prepared according to general procedure from (4-bromophenyl)acetylene, purified by silica gel chromatography (petroleum ether) and obtained as a colorless oil in 66 % yield (87 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, J = 8.4 Hz, 2H), 7.31 (d, J = 8.4 Hz, 2H), 3.27 (q, J = 9.5 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 133.3, 131.6, 124.0 (q, J_{CF} = 276.2 Hz), 123.0, 121.1, 83.3, 77.2, 26.8 (q, J_{CF} = 36.4 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -66.4 (t, J_{FH} = 9.5 Hz).

NMR spectral data for this compound are consistent with those in literature.[S3]



3d

1-(4,4,4-trifluorobut-1-yn-1-yl)naphtalene (3d)

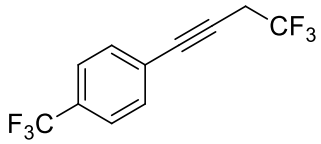
Prepared according to general procedure from 1-ethynylnaphthalene, purified by silica gel chromatography (petroleum ether) and obtained as yellow oil in 88 % yield (103 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (d, J = 8.4 Hz, 1H), 7.87 (m, 2H), 7.71 (dd, J_1 = 7.1 Hz, J_2 = 1.0 Hz, 1H), 7.61 (m, 1H), 7.55 (m, 1H), 7.44 (m, 1H), 3.46 (q, J = 9.5 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 133.3, 133.1, 130.8, 129.2, 128.3, 127.0, 126.5, 125.9, 125.1, 124.3 (q, J_{CF} = 277.9 Hz), 119.7, 82.4, 82.2, 27.1 (q, J_{CF} = 34.5 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -66.3 (t, J_{FH} = 9.5 Hz).

NMR spectral data for this compound are consistent with those in literature.[S2]



3e

1-trifluoromethyl-4-(4,4,4-trifluorobut-1-yn-1-yl)benzene (3e)

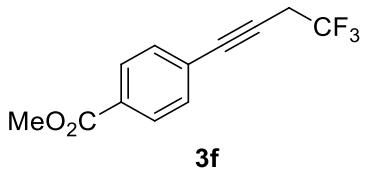
Prepared according to general procedure from (4-(trifluoromethyl)phenyl)acetylene, purified by silica gel chromatography (petroleum ether) and obtained as a colorless oil in 60 % yield (75 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63-7.55 (m, 4H), 3.31 (q, J = 9.5 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 132.8, 132.1, 130.4 (q, J_{CF} = 32.5 Hz), 125.2 (q, J_{CF} = 3.9 Hz), 124.0 (q, J_{CF} = 277.9 Hz), 123.8 (q, J_{CF} = 282.8 Hz), 83.0, 80.1, 26.8 (q, J_{CF} = 35.0 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -66.9 (s), -70.2 (t, J_{FH} = 9.5 Hz).

NMR spectral data for this compound are consistent with those in literature.[S4]



3f

methyl 4-(4,4,4-trifluorobut-1-yn-1-yl)benzoate (3f)

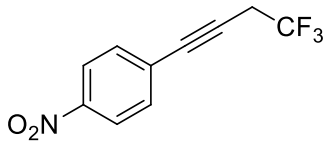
Prepared according to general procedure from methyl 4-ethynylbenzoate, purified by silica gel chromatography (petroleum ether) and obtained as a colorless oil in 89 % yield (107 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, J = 8.2 Hz, 2H), 7.51 (d, J = 8.1 Hz, 2H), 3.92 (s, 3H), 3.30 (q, J = 9.5 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 166.4, 131.8, 130.0, 129.4, 126.7, 124.0 (q, J_{CF} = 277.0 Hz), 83.6, 80.5, 52.2, 26.8 (q, J_{CF} = 35.0 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -66.3 (t, J_{FH} = 9.5 Hz).

NMR spectral data for this compound are consistent with those in literature.[S2]



3g

1-nitro-4-(4,4,4-trifluorobut-1-yn-1-yl)benzene (3g)

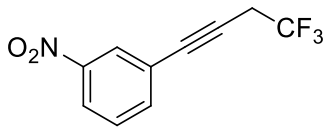
Prepared according to general procedure from (4-nitrophenyl)acetylene, purified by silica gel chromatography (petroleum ether/EtOAc 10:1) and obtained as a colorless oil in 61 % yield (69 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, J = 8.8 Hz, 2H), 7.60 (d, J = 8.8 Hz, 2H), 3.33 (q, J = 9.5 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 147.4, 132.7, 128.9, 123.9 (q, J_{CF} = 277.0 Hz), 123.5, 82.9, 82.5, 26.8 (q, J_{CF} = 34.8 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -66.1(t, J_{FH} = 9.5 Hz).

NMR spectral data for this compound are consistent with those in literature.[S5]



3h

1-nitro-3-(4,4,4-trifluorobut-1-yn-1-yl)benzene (3h)

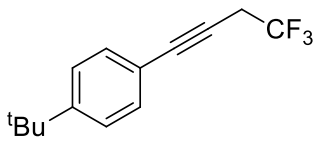
Prepared according to general procedure from (3-nitrophenyl)acetylene, purified by silica gel chromatography (petroleum ether/EtOAc 10:1) and obtained as a colorless oil in 69 % yield (78 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (s, 1H), 8.21 (m, 1H), 7.76 (d, J = 7.7 Hz, 1H), 7.53 (t, J = 8.0 Hz, 1H), 3.32 (q, J = 9.4 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 148.0, 137.5, 129.4, 126.7, 123.9 (q, J_{CF} = 277.0 Hz), 123.8, 123.5, 82.0, 80.4, 26.7 (q, J_{CF} = 34.9 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ –66.2 (t, J_{FH} = 9.5 Hz).

HRMS (ESI) m/z: $[M - H]^-$ Calcd for $C_{10}H_5F_3NO_2$ 228.0278; Found 228.0279.



3i

1-tert-butyl-4-(4,4,4-trifluorobut-1-yn-1-yl)benzene (3i)

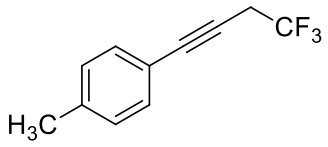
Prepared according to general procedure from (4-tert-butylphenyl)acetylene, purified by silica gel chromatography (petroleum ether) and obtained as a colorless oil in 77 % yield (92 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, J = 8.5 Hz, 2H), 7.36 (d, J = 8.5 Hz, 2H), 3.28 (q, J = 9.6 Hz, 2H), 1.33 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 152.0, 131.6, 125.3, 124.2 (q, J_{CF} = 276.4 Hz), 119.1, 84.4, 76.8, 34.8, 31.1, 26.6 (q, J_{CF} = 34.6 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -66.5 (t, J_{FH} = 9.7 Hz).

NMR spectral data for this compound are consistent with those in literature.[S6]



3j

1-methyl-4-(4,4,4-trifluorobut-1-yn-1-yl)benzene (3j)

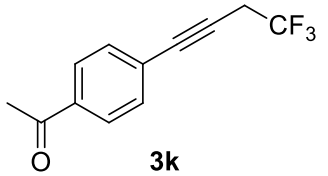
Prepared according to general procedure from (4-methylphenyl)acetylene, purified by silica gel chromatography (petroleum ether) and obtained as a colorless oil in 64 % yield (63 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, J = 8.0 Hz, 2H), 7.13 (d, J = 8.0 Hz, 2H), 3.27 (q, J = 9.6 Hz, 2H), 2.36 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 138.9, 131.7, 129.1, 124.3 (q, J_{CF} = 276.0 Hz), 119.1, 84.4, 76.8, 26.8 (q, J_{CF} = 35 Hz), 21.5.

^{19}F NMR (376 MHz, $CDCl_3$) δ -66.5 (t, J_{FH} = 9.5 Hz).

NMR spectral data for this compound are consistent with those in literature.[S2]



3k

1-acetyl-4-(4,4,4-trifluorobut-1-yn-1-yl)benzene (3k)

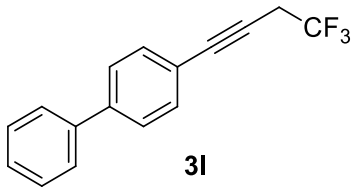
Prepared according to general procedure from (4-acetylphenyl)acetylene, purified by silica gel chromatography (petroleum ether/EtOAc 20:1) and obtained as a colorless oil in 79 % yield (63 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, J = 8.5 Hz, 2H), 7.13 (d, J = 8.4 Hz, 2H), 3.31 (q, J = 9.5 Hz, 2H), 2.60 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 197.2, 136.6, 131.9, 128.1, 126.9, 124.0 (q, J_{CF} = 277.0 Hz), 83.5, 80.8, 80.3, 26.8 (q, J_{CF} = 35 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -66.2 (t, J_{FH} = 9.5 Hz).

NMR spectral data for this compound are consistent with those in literature.[S5]



3l

4-(4,4,4-trifluorobut-1-yn-1-yl)biphenyl (3l)

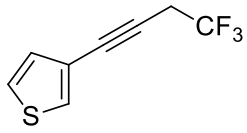
Prepared according to general procedure from 4-ethynylbiphenyl, purified by silica gel chromatography (petroleum ether/EtOAc 20:1) and obtained as a colorless oil in 67 % yield (87 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (m, 6H), 7.48 (m, 2H), 7.40 (m, 1H), 3.33 (q, J = 9.5 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 141.4, 140.2, 132.2, 128.8, 127.7, 127.0 (2C), 124.2 (q, J_{CF} = 276.8 Hz), 121.0, 84.2, 78.1, 26.8 (q, J_{CF} = 34.6 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -66.5 (t, J_{FH} = 9.5 Hz).

NMR spectral data for this compound are consistent with those in literature.[S5]



3m

3-(4,4,4-trifluorobut-1-yn-1-yl)thiophene (3m)

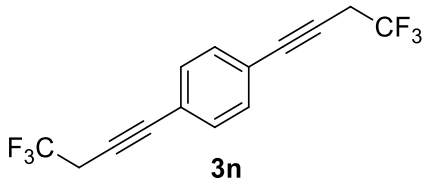
Prepared according to general procedure from 3-ethynylthiophene, purified by silica gel chromatography (petroleum ether/EtOAc 20:1) and obtained as a colorless oil in 62 % yield (59 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (dd, 1H, J_1 = 3.0 Hz, J_2 = 1.0 Hz), 7.27 (dd, 1H, J_1 = 3.0 Hz, J_2 = 5.0 Hz), 7.12 (dd, 1H, J_1 = 1.1 Hz, J_2 = 5.0 Hz), 3.26 (q, J = 9.6 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 129.8, 129.5, 125.4, 124.1 (q, J_{CF} = 276.8 Hz), 121.0, 89.1, 79.5, 26.8 (q, J_{CF} = 34.6 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -66.4 (t, J_{FH} = 9.5 Hz).

HRMS (ESI) m/z: $[M + K]^+$ Calcd for $C_8H_5F_3SK$ 228.9696; Found 228.9678.



3n

1,4-bis(4,4,4-trifluorobut-1-yn-1-yl)benzene (3n)

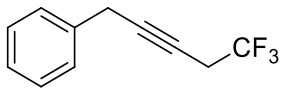
Prepared according to general procedure from 1,4-diethynylbenzene (63 mg, 0.5 mmol) and hydrazone **1** (399 mg, 1.5 mmol), purified by silica gel chromatography (petroleum ether/EtOAc 10:1) and obtained as a colorless oil in 63 % yield (91 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (s, 4H), 3.29 (q, J = 9.5 Hz, 4H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 131.7, 124.1 (q, J_{CF} = 276.8 Hz), 122.5, 83.8, 79.4 (q, J_{CF} = 5.2 Hz), 26.8 (q, J_{CF} = 34.8 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -66.3 (t, J_{FH} = 9.5 Hz).

HRMS (ESI) m/z: [M - H]$^-$ Calcd for $C_{14}H_7F_6$ 289.0457; Found 289.0456.



3o

(5,5,5-trifluoropent-2-yn-1-yl)benzene (3o)

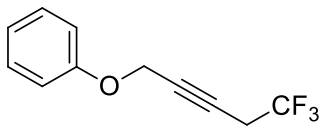
Prepared according to general procedure from propargylbenzene, purified by silica gel chromatography (petroleum ether) and obtained as a colorless oil in 70 % yield (69 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36-7.27 (m, 5H), 3.64 (s, 2H), 3.10 (q, J = 9.5 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 136.1, 128.5, 127.8, 126.7, 124.4 (q, J_{CF} = 276.6 Hz), 82.4, 70.5, 26.2 (q, J_{CF} = 34.2 Hz), 24.9.

^{19}F NMR (376 MHz, $CDCl_3$) δ -66.3 (t, J_{FH} = 9.5 Hz).

NMR spectral data for this compound are consistent with those in literature.[S4]



3p

(5,5,5-trifluoropent-2-yn-1-yloxy)benzene (3p)

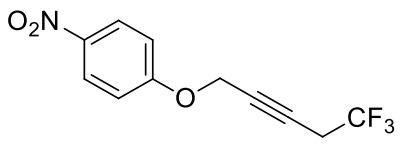
Prepared according to general procedure from propargyloxybenzene, purified by silica gel chromatography (petroleum ether/EtOAc 20:1) and obtained as a colorless oil in 75 % yield (80 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (m, 2H), 7.00 (m, 2H), 4.72 (s, 2H), 3.11 (q, J = 9.5 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 157.5, 129.5, 124.0 (q, J_{CF} = 276.8 Hz), 121.5, 114.8, 79.5, 75.9, 55.8, 26.2 (q, J_{CF} = 34.8 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -66.5 (t, J_{FH} = 9.5 Hz).

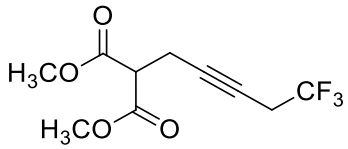
HRMS (ESI) m/z: [M - H]$^-$ Calcd for $C_{11}H_8F_3O$ 213.0533; Found 213.0558.



3q

4-nitro-1-(5,5,5-trifluoropent-2-yn-1-yloxy)benzene (3q)

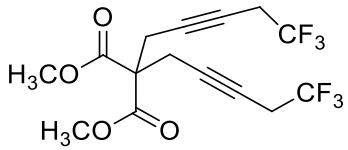
Prepared according to general procedure from 4-nitro-1-propargyloxybenzene, purified by silica gel chromatography (petroleum ether/EtOAc 10:1) and obtained as a colorless oil in 87 % yield (113 mg).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, J = 9.2 Hz, 2H), 7.03 (d, J = 9.3 Hz, 2H), 4.81 (t, J = 2.1 Hz, 2H), 3.11 (qt, J_1 = 9.5 Hz, J_2 = 2.0 Hz, 2H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 162.3, 142.0, 125.8, 123.8 (q, J_{CF} = 277.0 Hz), 114.9, 78.0, 77.3, 58.3, 26.1 (q, J_{CF} = 35.0 Hz).
^{19}F NMR (376 MHz, $CDCl_3$) δ -66.3 (t, J_{FH} = 9.5 Hz).
HRMS (ESI) m/z: $[M - H]^-$ Calcd for $C_{11}H_7F_3NO_3$ 258.0384; Found 258.0384.



3r

dimethyl 2-(5,5,5-trifluoropent-2-yn-1-yl)malonate (3r)

Prepared according to general procedure from dimethyl 2-propargylmalonate, purified by silica gel chromatography (petroleum ether/EtOAc 10:1) and obtained as a colorless oil in 63 % yield (74 mg).
^{1}H NMR (400 MHz, $CDCl_3$) δ 3.75 (s, 6H), 3.58 (t, J = 7.7 Hz, 1H), 2.98 (qt, J_1 = 9.6 Hz, J_2 = 2.3 Hz, 2H), 2.78 (dt, J_1 = 7.7 Hz, J_2 = 2.3 Hz, 2H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 168.2, 124.2 (q, J_{CF} = 276.8 Hz), 80.3, 70.7 (q, J_{CF} = 5.0 Hz), 52.7, 50.7, 26.1 (q, J_{CF} = 34.6 Hz), 18.6.
^{19}F NMR (376 MHz, $CDCl_3$) δ -66.9 (t, J_{FH} = 9.6 Hz).
NMR spectral data for this compound are consistent with those in literature.[S7]



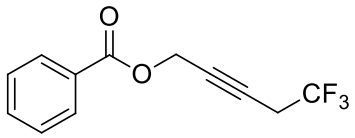
3s

dimethyl 2,2-bis(5,5,5-trifluoropent-2-yn-1-yl)malonate (3s)

Prepared according to general procedure from dimethyl 2,2-dipropargylmalonate (52 mg, 0.25 mmol) and hydrazone **1** (200 mg, 0.75 mmol), purified by silica gel chromatography (petroleum ether/EtOAc 10:1) and obtained as a colorless oil in 57 % yield (53 mg).
^{1}H NMR (400 MHz, $CDCl_3$) δ 3.75 (s, 6H), 2.98 (q, J = 9.5 Hz, 4H), 2.93 (s, 4H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 169.0, 124.2 (q, J_{CF} = 276.6 Hz), 78.9, 71.9, 56.6, 53.1, 26.0 (q, J_{CF} = 34.6 Hz), 22.9.

^{19}F NMR (376 MHz, $CDCl_3$) δ -66.5 (t, J_{FH} = 9.5 Hz).

HRMS (ESI) m/z: $[M - H]^-$ Calcd for $C_{15}H_{13}F_6O_4$ 323.0876; Found 323.0888.



3t

5,5,5-trifluoropent-2-yn-1-yl benzoate (3t)

Prepared according to general procedure from propargyl benzoate, purified by silica gel chromatography (petroleum ether/EtOAc 10:1) and obtained as a colorless oil in 54 % yield (65 mg). The product is contaminated with 17 mol % allene isomer.

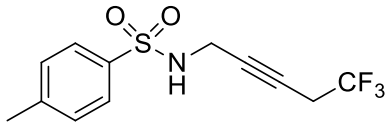
Analitical data taken from the mixture of isomers.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (m, 2H), 7.58 (m, 1H), 7.46 (m, 2H), 4.95 (t, J = 2.1 Hz, 2H), 3.12 (qt, J_1 = 9.5 Hz, J_2 = 2.1 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 165.8, 133.3, 129.8, 129.3, 128.4, 123.9 (q, J_{CF} = 277.0 Hz), 78.6, 75.4, 52.5, 26.4 (q, J_{CF} = 35.0 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -66.5 (t, J_{FH} = 9.5 Hz).

HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{12}H_9F_3O_2Na$ 265.0447; Found 265.0450.



3u

4-methyl-*N*-(5,5,5-trifluoropent-2-yn-1-yl)benzenesulfonamide (3u)

Prepared according to general procedure from N-tosylpropargylamine, purified by silica gel chromatography (petroleum ether/EtOAc 3:1) and obtained as a white solid in 30 % yield (44 mg). The product is contaminated with 10 mol % allene isomer.

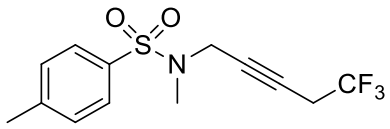
Analitical data taken from the mixture of isomers.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, J = 8.2 Hz, 2H), 7.31 (d, J = 8.1 Hz, 2H), 4.98 (bs, 1H), 3.84 (dt, J_1 = 6.1 Hz, J_2 = 2.2 Hz, 2H), 2.82 (qt, J_1 = 9.6 Hz, J_2 = 2.2 Hz, 2H), 2.42 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 143.8, 136.5, 129.8, 127.3, 123.7 (q, J_{CF} = 277.4 Hz), 78.7, 73.2, 32.9, 25.3 (q, J_{CF} = 35.0 Hz), 21.4.

^{19}F NMR (376 MHz, $CDCl_3$) δ -66.3 (t, J_{FH} = 9.5 Hz).

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{12}H_{13}F_3N_2OS$ 292.0614; Found 292.0615.



3v

N,4-dimethyl-*N*-(5,5,5-trifluoropent-2-yn-1-yl)benzenesulfonamide (3v)

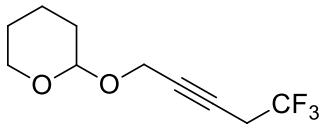
Prepared according to general procedure from N-methyl-N-tosylpropargylamine, purified by silica gel chromatography (petroleum ether/EtOAc 10:1) and obtained as a colorless oil in 72 % yield (111 mg)..

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, J = 8.1 Hz, 2H), 7.32 (d, J = 8.1 Hz, 2H), 4.04 (t, J = 1.8 Hz, 2H), 2.83 (qt, J_1 = 9.6 Hz, J_2 = 1.9 Hz, 2H), 2.81 (s, 3H), 2.43 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 143.7, 134.1, 129.5, 127.8, 123.8 (q, J_{CF} = 277.5 Hz), 77.2, 74.3, 39.8, 34.4, 25.9 (q, J_{CF} = 34.3 Hz), 21.5.

^{19}F NMR (376 MHz, $CDCl_3$) δ -66.6 (t, J_{FH} = 9.6 Hz).

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{13}H_{15}F_3N_2OS$ 306.0770; Found 306.0773.



3w

2-[(5,5,5-trifluoropent-2-yn-1-yl)oxy]tetrahydro-2*H*-pyran (3w)

Prepared according to general procedure from 2-(prop-2-yn-1-yloxy)tetrahydro-2*H*-pyran, purified by silica gel chromatography (petroleum ether/EtOAc 20:1) and obtained as a colorless oil in 63 % yield (70 mg).

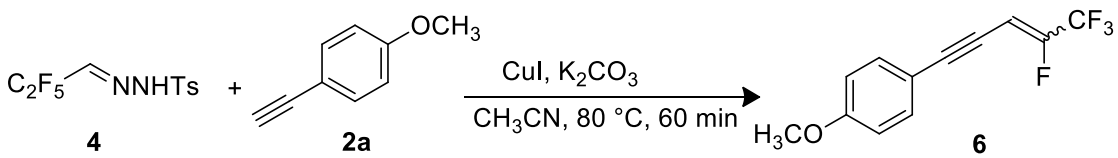
^{1}H NMR (400 MHz, $CDCl_3$) δ 4.80 (t, J = 3.3 Hz, 1H), 4.35-4.20 (m, 2H), 3.87-3.80 (m, 1H), 3.57-3.50 (m, 1H), 3.11 (qt, J_1 = 9.6 Hz, J_2 = 2.1 Hz, 2H), 1.87-1.70 (m, 2H), 1.68-1.50 (m, 4H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 124.1 (q, J_{CF} = 276.4 Hz), 96.9, 80.6, 74.3, 62.0, 54.1, 30.2, 26.4 (q, J_{CF} = 34.8 Hz), 25.3, 19.0.

^{19}F NMR (376 MHz, $CDCl_3$) δ -66.3 (t, J_{FH} = 9.6 Hz).

HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{10}H_{13}F_3NaO_2$ 245.0760; Found 245.0767.

Reaction of N-tosylhydrazone 4 with alkyne 2a.



4 **2a** **6**

The Schlenk flask was loaded with hydrazone **4** (190 mg, 0.6 mmol), CuI (96 mg, 0.5 mmol), K_2CO_3 (207 mg, 1.5 mmol) and filled with argon. The solution of 4-methoxyacetylene (66 mg, 0.5 mmol) in acetonitrile (10 ml) was added via syringe and the reaction mixture was then stirred at 80 °C for 60 min. A mixture was filtered and the solvent was removed under reduced pressure. The product **6** (Z/E 7:1) was isolated by column chromatography (EtOAc/hexanes 1:20) and obtained as a colorless oil in 78 % yield (95 mg).

(Z)-1-methoxy-4-(4,5,5,5-tetrafluoropent-3-en-1-yn-1-yl)benzene (6-Z**)**

Spectral data taken from a mixture of Z/E isomers.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, J = 8.8 Hz, 2H), 6.89 (d, J = 8.9 Hz, 2H), 5.92 (dd, J_{FH} = 29.1 Hz, 2H), 3.83 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 160.5, 151.4 (dq, $J_{CF(1)}$ = 271.8 Hz, $J_{CF(2)}$ = 39.1 Hz), 133.5, 118.4 (qd, J_{CF1} = 271.8 Hz, $J_{CF(2)}$ = 39.2 Hz), 114.1, 113.8, 100.4, 95.3, 76.5, 55.3.

^{19}F NMR (376 MHz, $CDCl_3$) δ -72.5 (d, J_{FF} = 11.5 Hz, 3F), -121.8 (qdd, J_{FF} = 11.5 Hz, $J_{FH(1)}$ = 29.2 Hz, $J_{FH(2)}$ = 1.7 Hz, 1F).

NMR spectral data for this compound are consistent with those in literature.[S8]

(E)-1-methoxy-4-(4,5,5,5-tetrafluoropent-3-en-1-yn-1-yl)benzene (6-E**)**

Spectral data taken from a mixture of Z/E isomers.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, J = 8.8 Hz, 2H), 6.89 (d, J = 8.9 Hz, 2H), 6.10 (dd, J_{FH} = 14.2 Hz, 2H), 3.83 (s, 3H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -69.1 (d, J_{FF} = 9.5 Hz, 3F), -121.8 (qdd, J_{FF} = 9.5 Hz, $J_{FH(1)}$ = 14.3 Hz, $J_{FH(2)}$ = 1.4 Hz, 1F).

NMR spectral data for this compound are consistent with those in literature.[S8]

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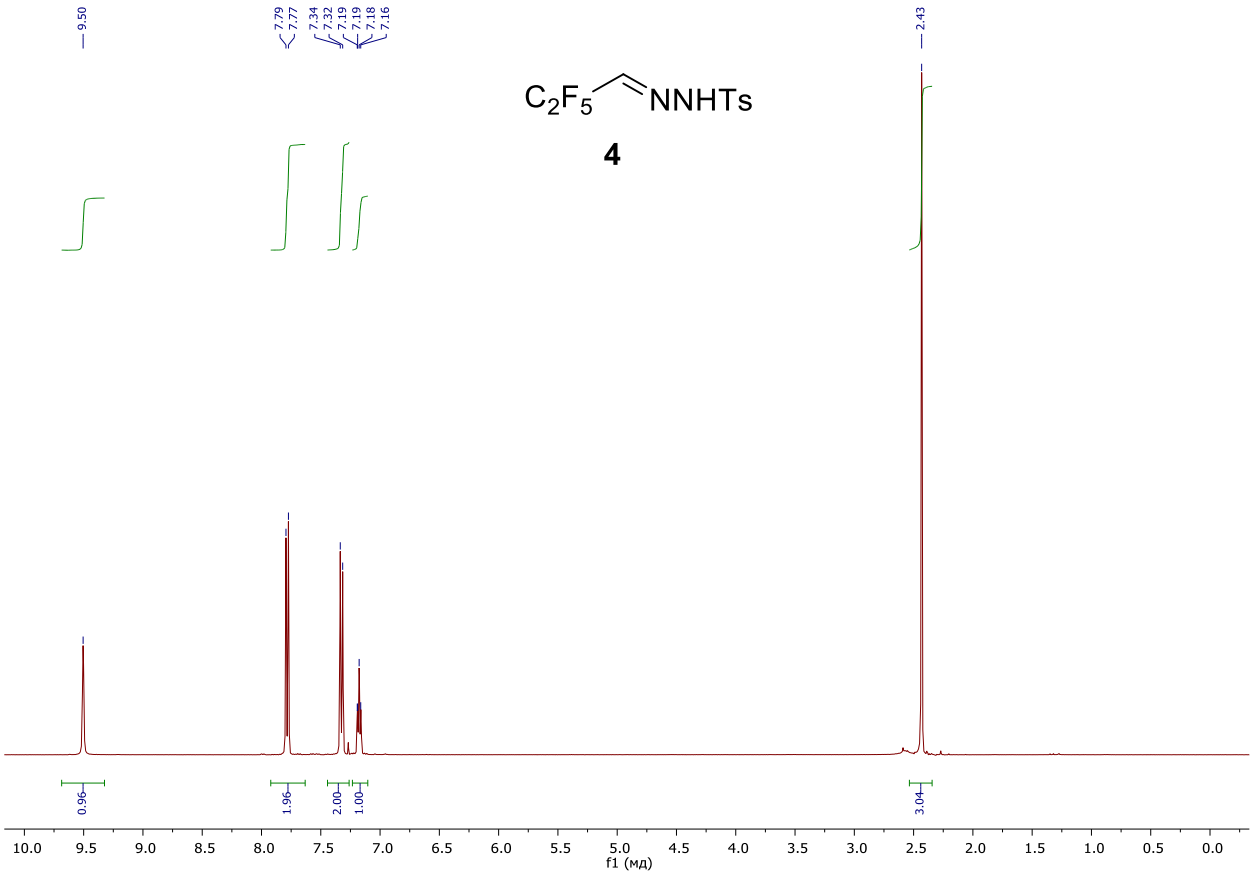
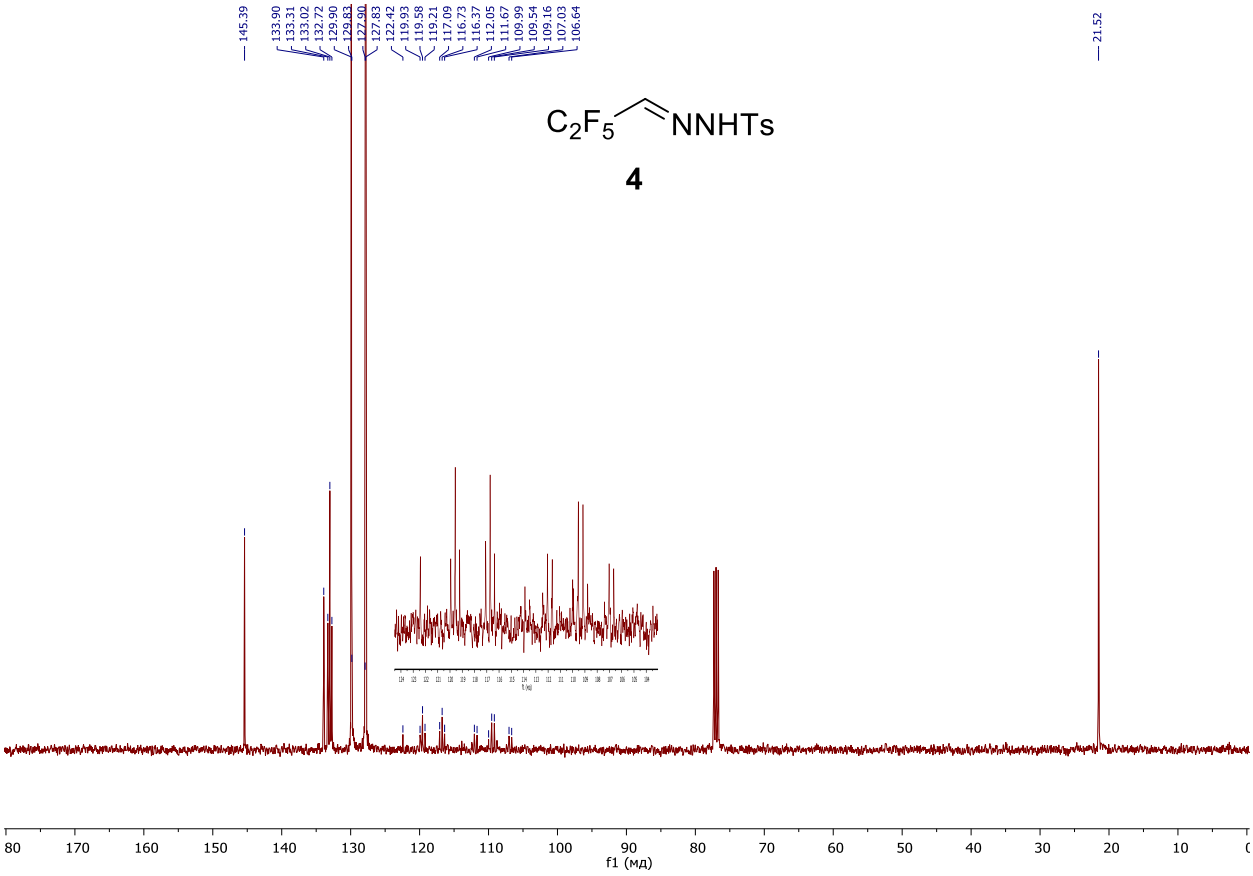
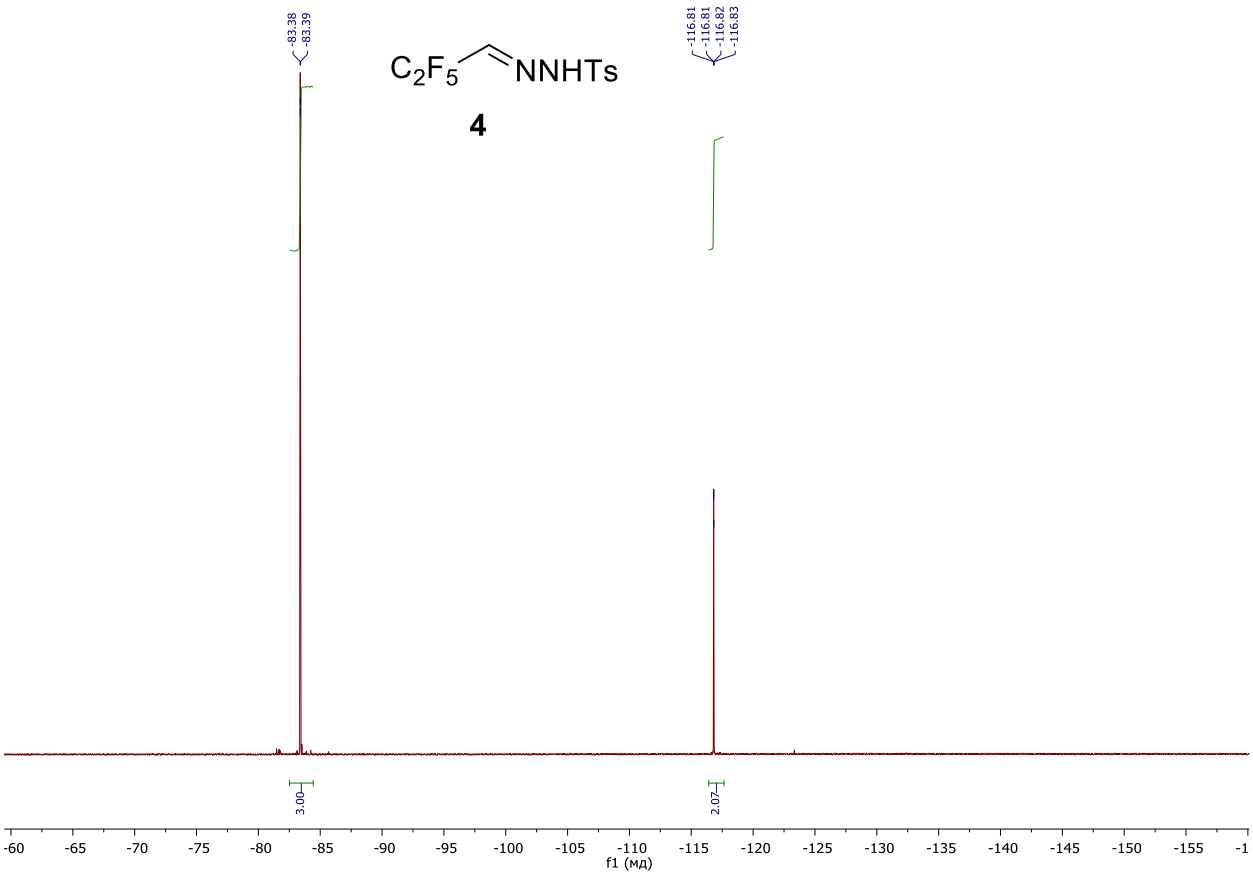
3,3,3,2,2-pentafluoropropanal N-tosylhydrazone (4) **^{1}H NMR (400 MHz, $CDCl_3$)**



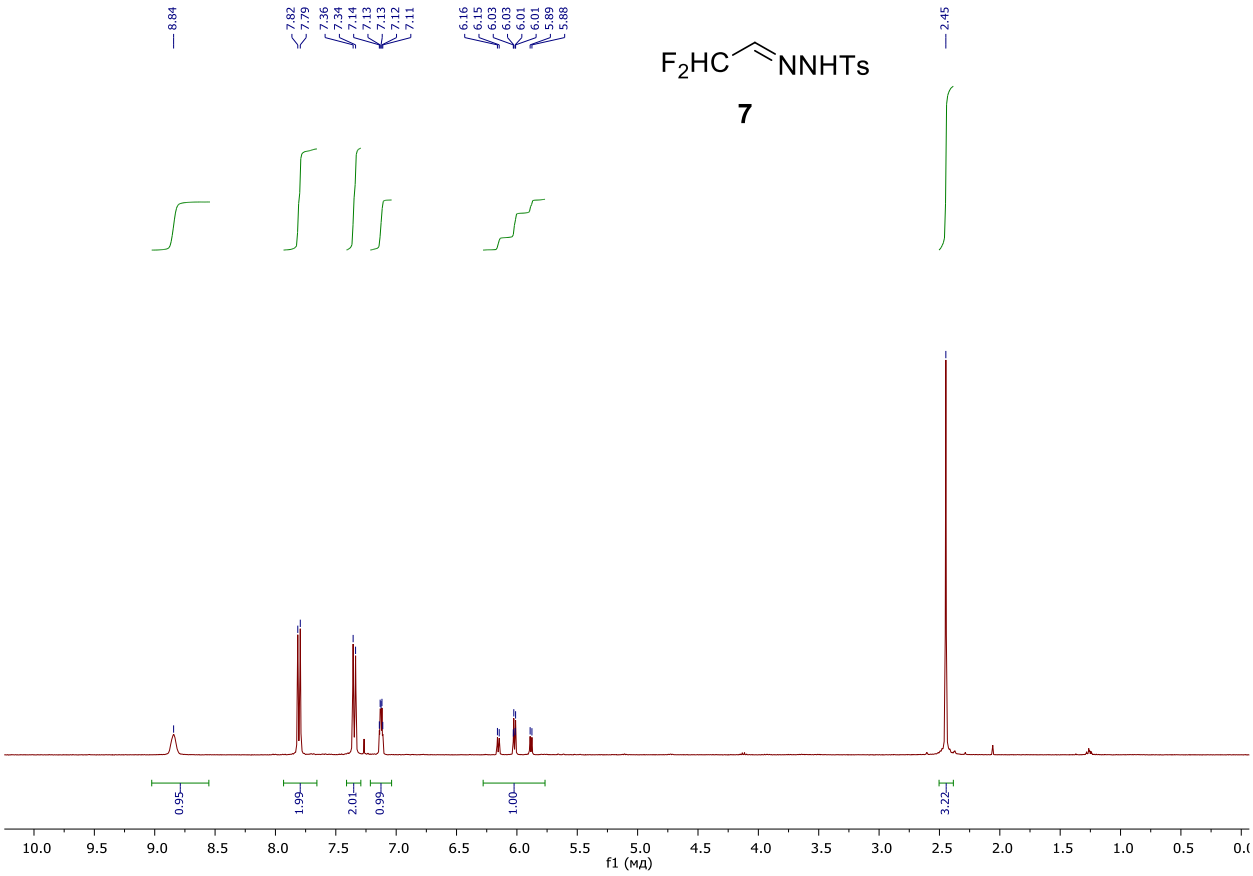
3,3,3,2,2-pentafluoropropanal N-tosylhydrazone (4) **^{13}C NMR (100 MHz, $CDCl_3$)**



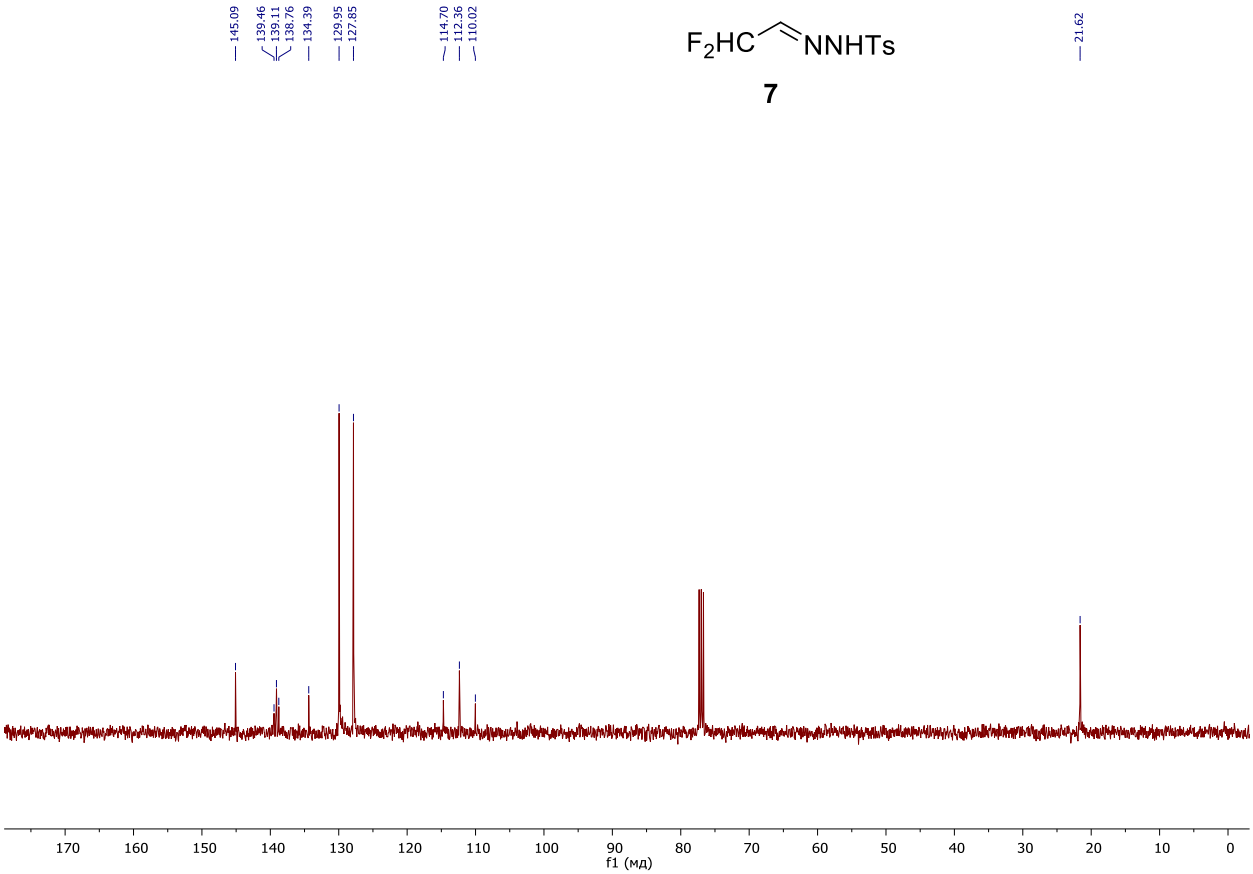
3,3,3,2,2-pentafluoropropanal N-tosylhydrazone (4) **^{19}F NMR (376 MHz, $CDCl_3$)**



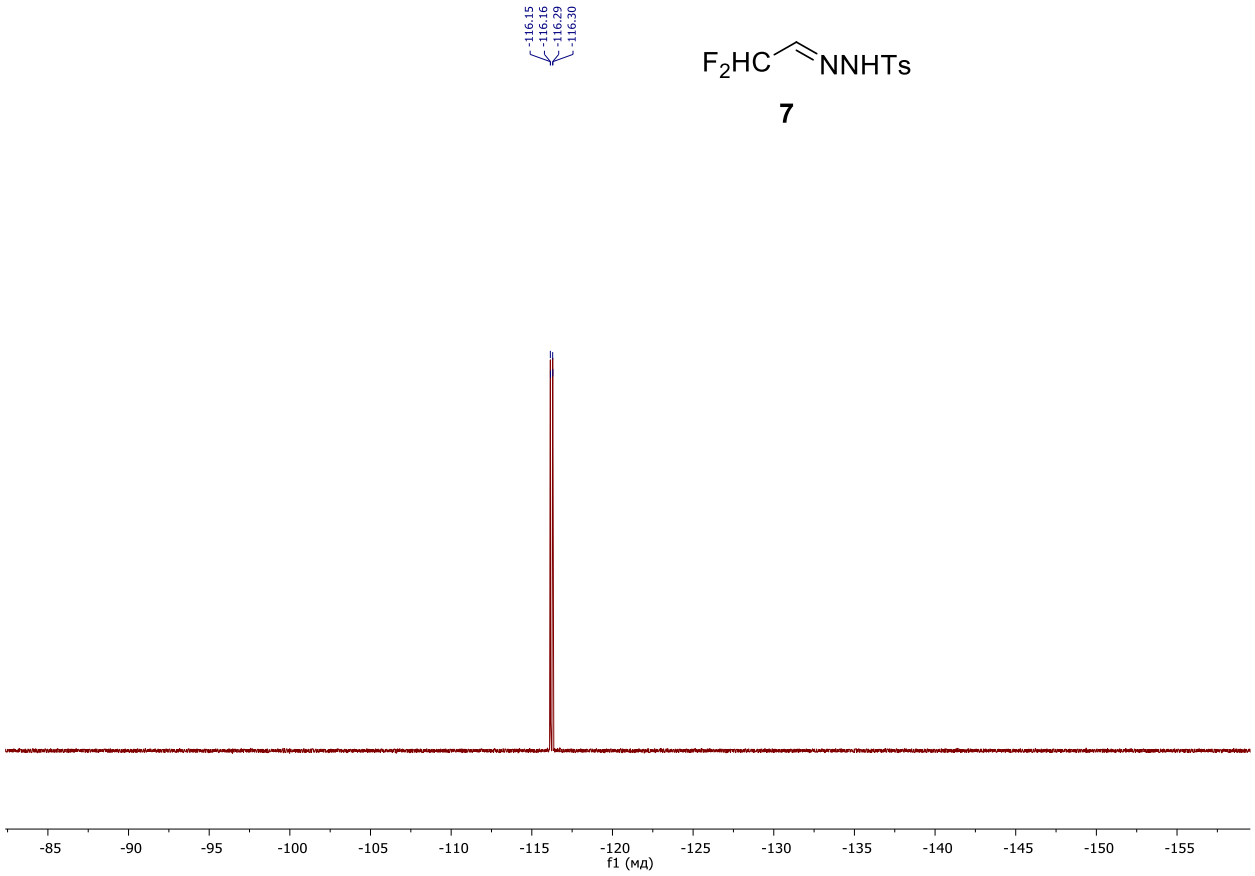
2,2-difluoroacetaldehyde N-tosylhydrazone (7) **^{1}H NMR (400 MHz, $CDCl_3$)**



2,2-difluoroacetaldehyde N-tosylhydrazone (7) **^{13}C NMR (100 MHz, $CDCl_3$)**

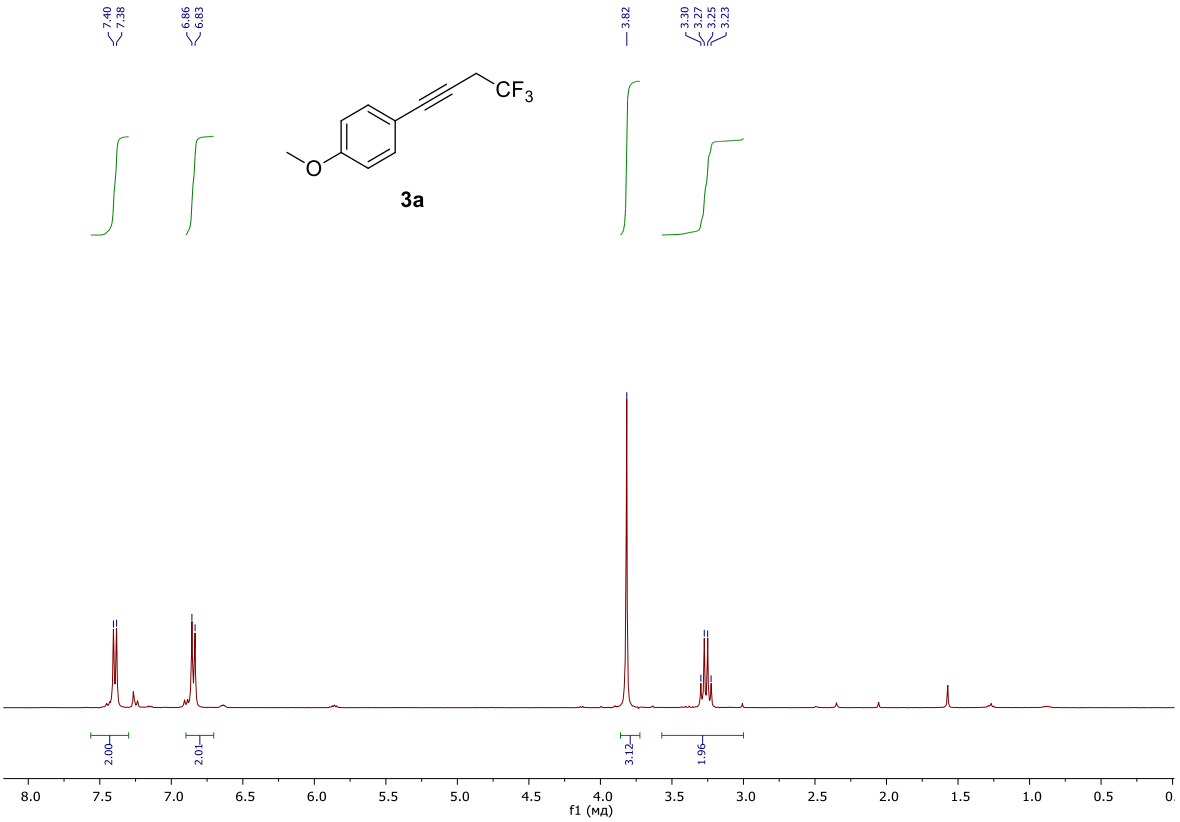


2,2-difluoroacetaldehyde N-tosylhydrazone (7) **^{19}F NMR (376 MHz, $CDCl_3$)**

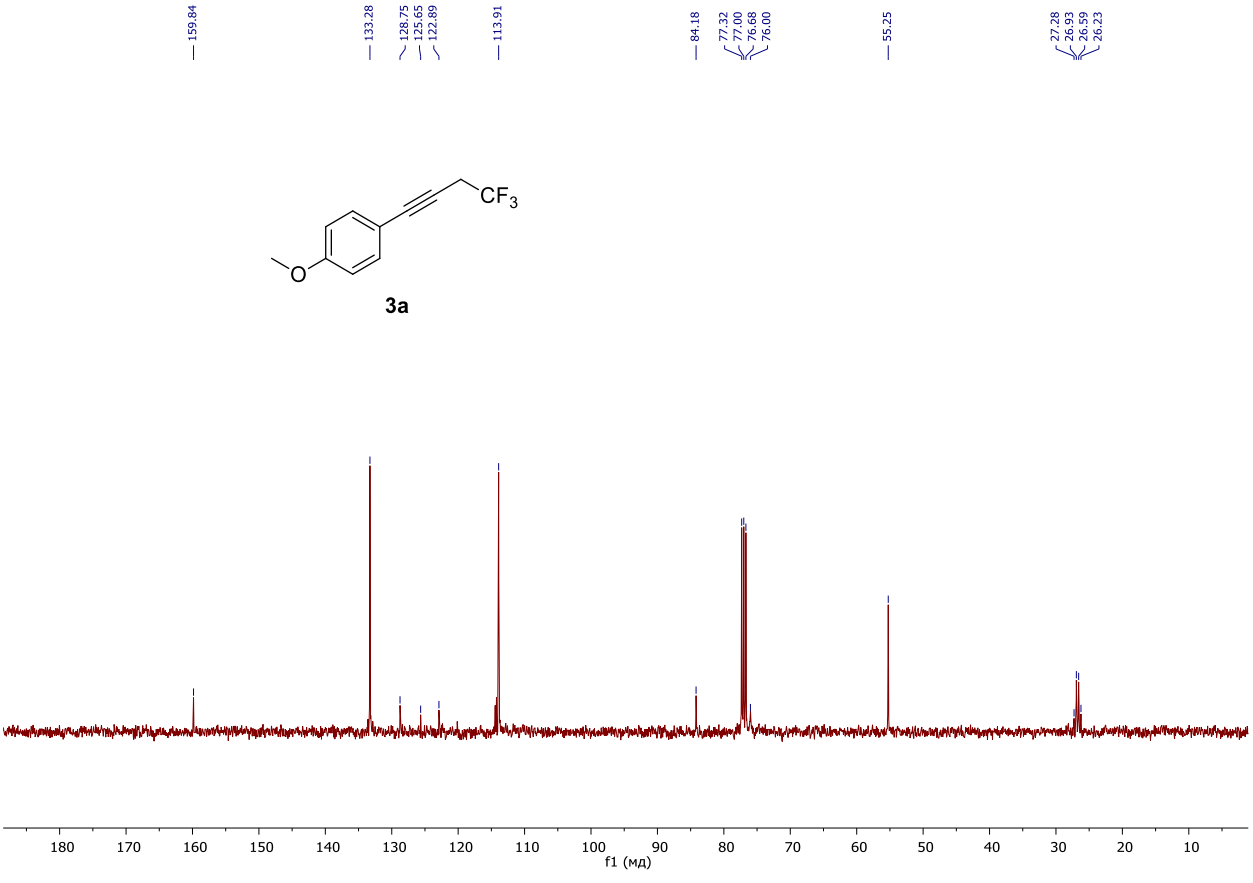


7

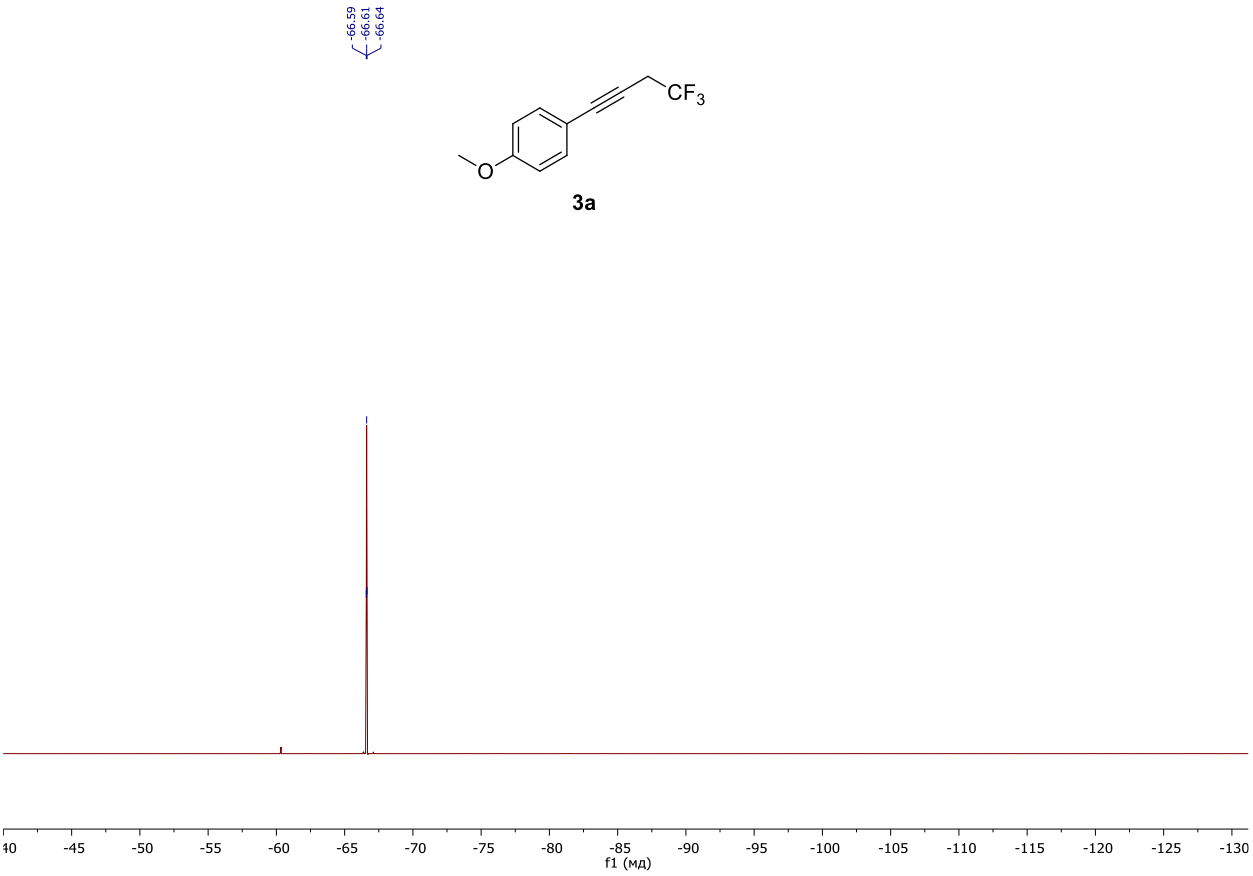
1-methoxy-4-(4,4,4-trifluorobut-1-yn-1-yl)benzene (3a) **^{1}H NMR (400 MHz, $CDCl_3$)**



1-methoxy-4-(4,4,4-trifluorobut-1-yn-1-yl)benzene (3a) **^{13}C NMR (100 MHz, $CDCl_3$)**

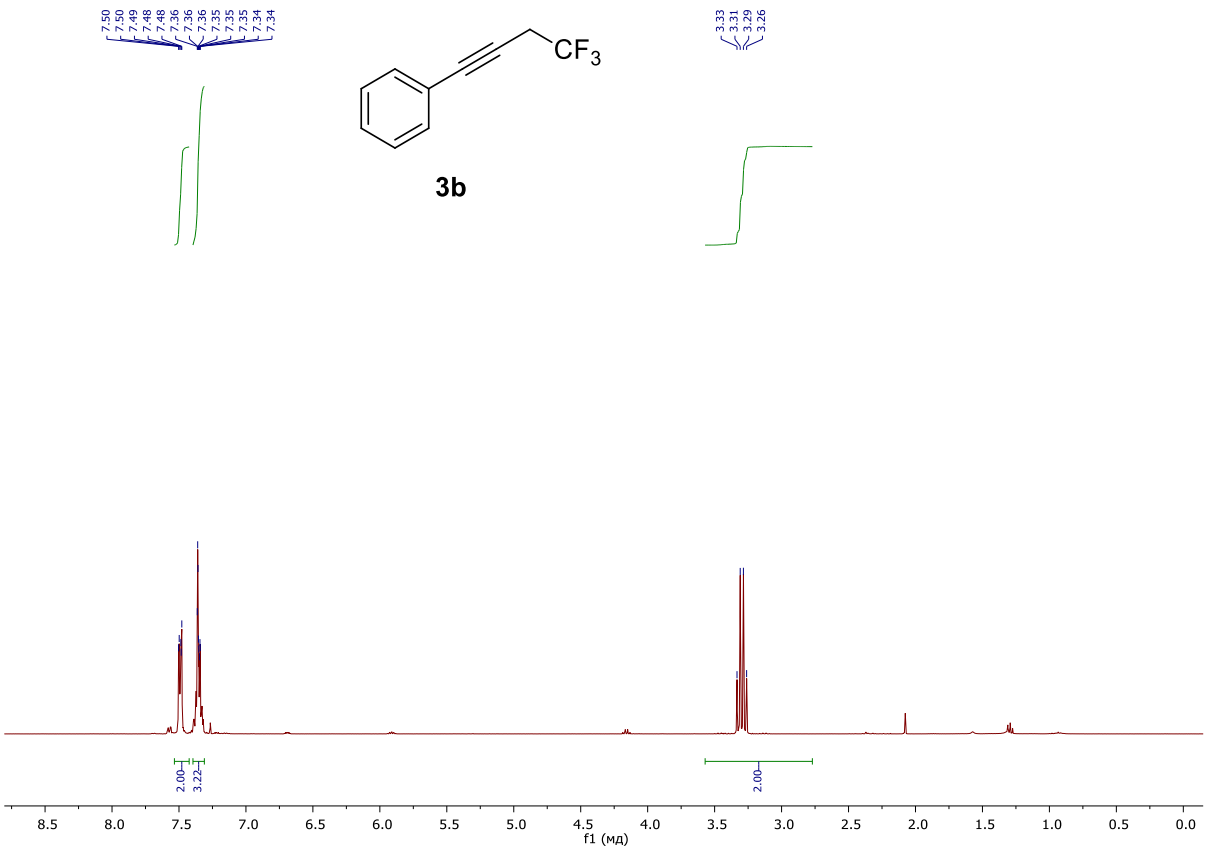


1-methoxy-4-(4,4,4-trifluorobut-1-yn-1-yl)benzene (3a) **^{19}F NMR (376 MHz, $CDCl_3$)**



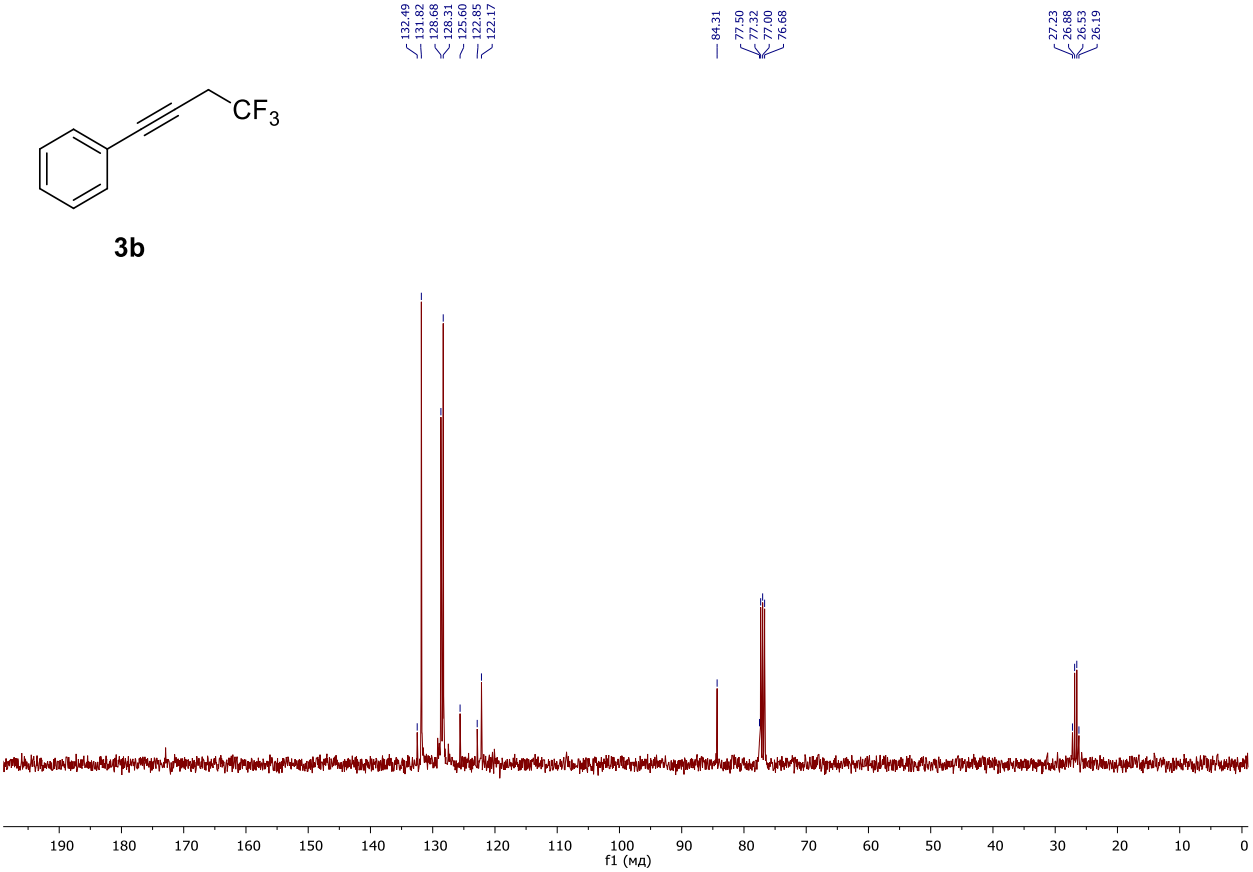
3a

(4,4,4-trifluorobut-1-yn-1-yl)benzene (3b) **^{1}H NMR (400 MHz, $CDCl_3$)**



3b

(4,4,4-trifluorobut-1-yn-1-yl)benzene (3b) **^{13}C NMR (100 MHz, $CDCl_3$)**

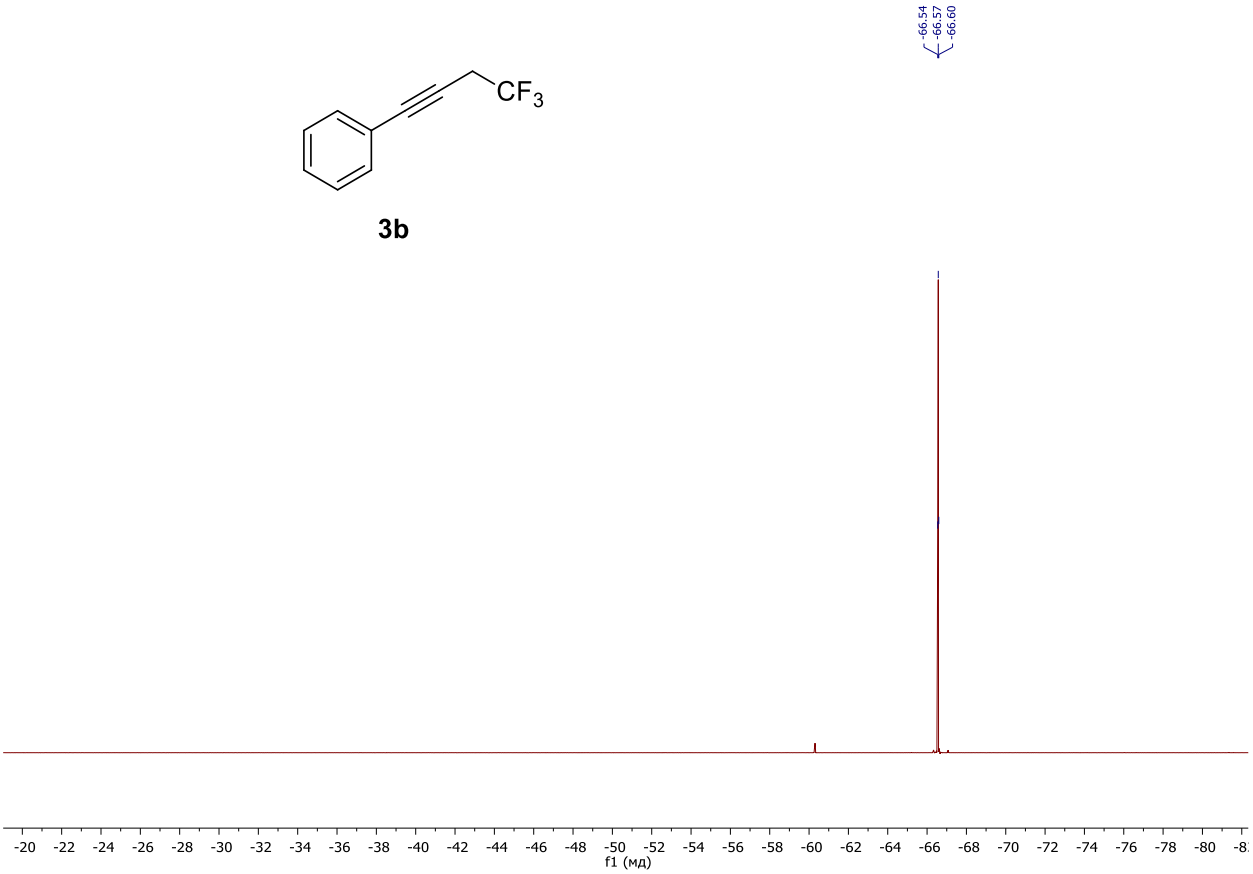


3b

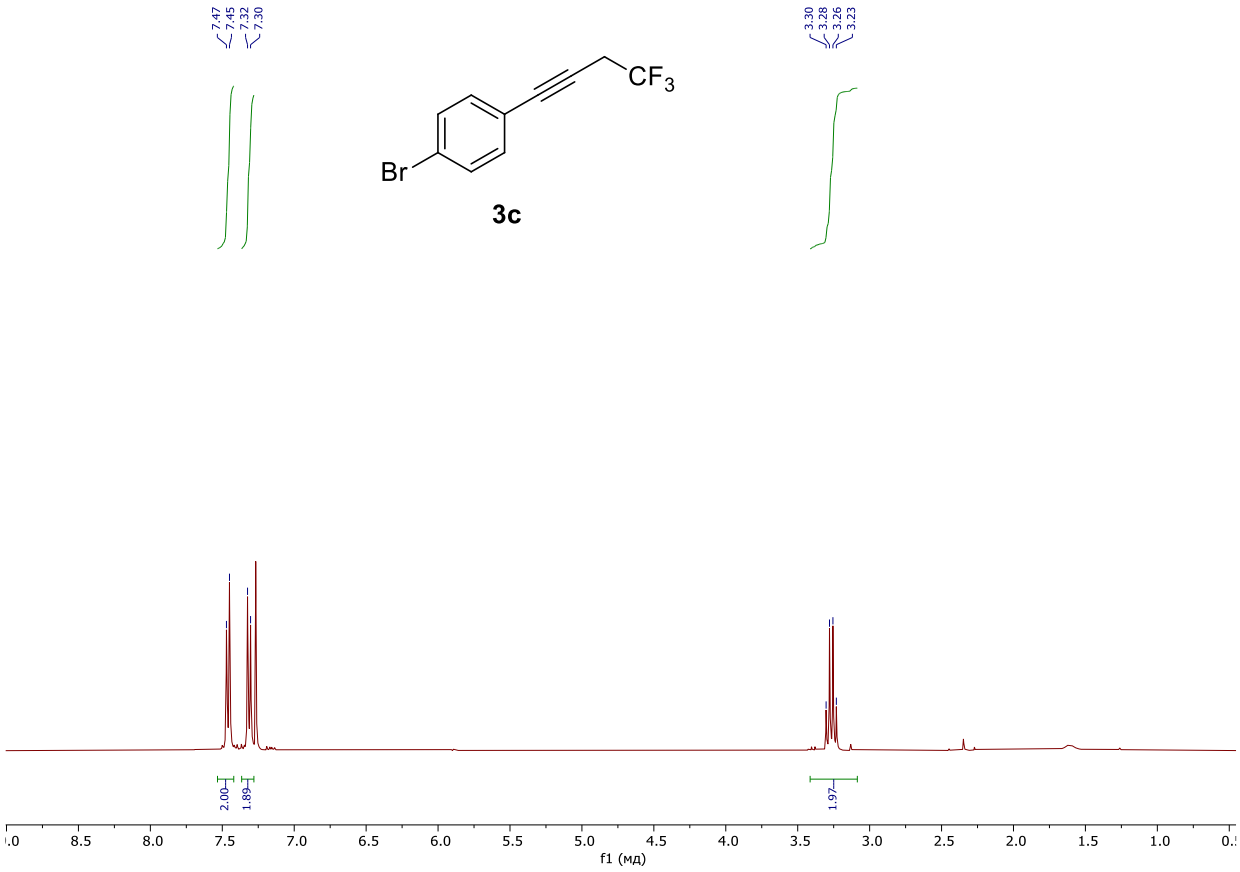
(4,4,4-trifluorobut-1-yn-1-yl)benzene (3b)

^{19}F NMR (376 MHz, $CDCl_3$)

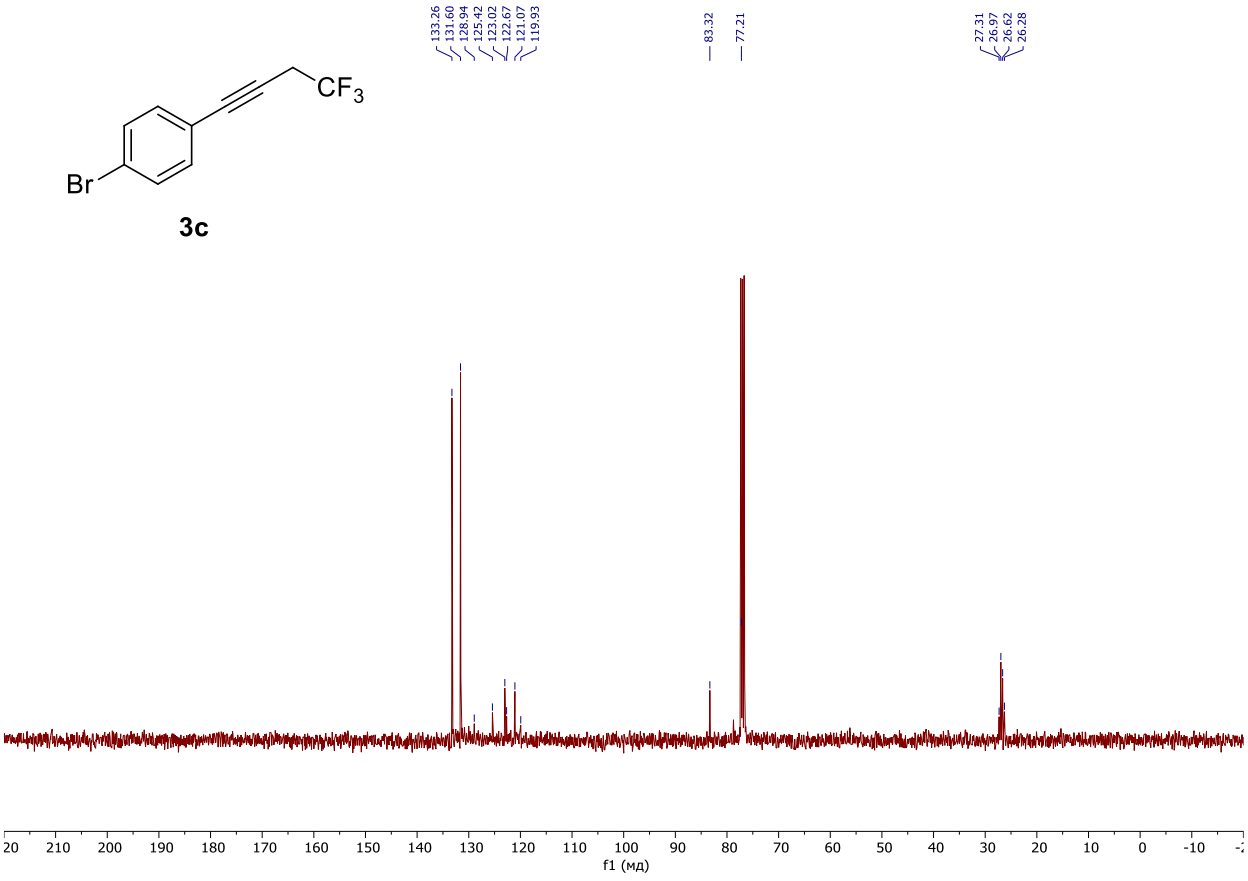
3b



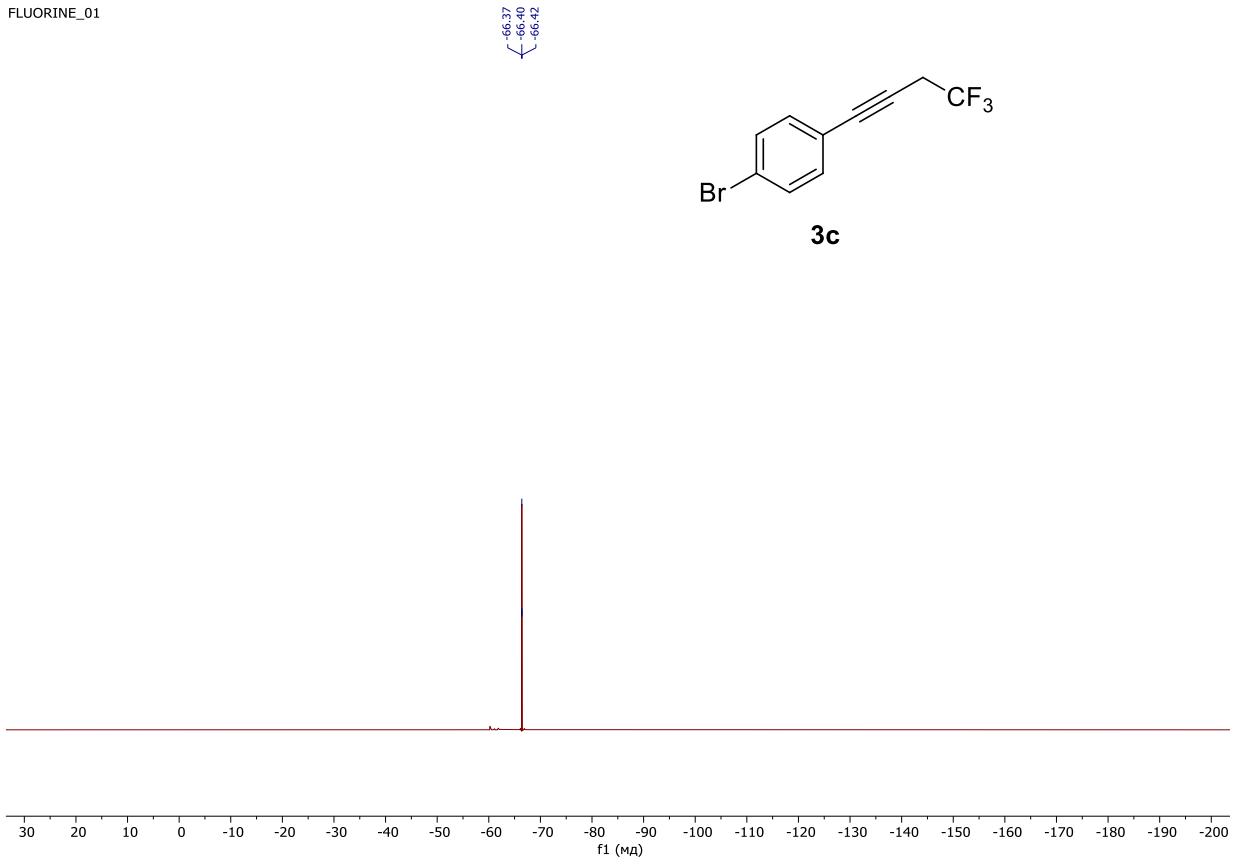
1-bromo-4-(4,4,4-trifluorobut-1-yn-1-yl)benzene (3c) **^{1}H NMR (400 MHz, $CDCl_3$)**



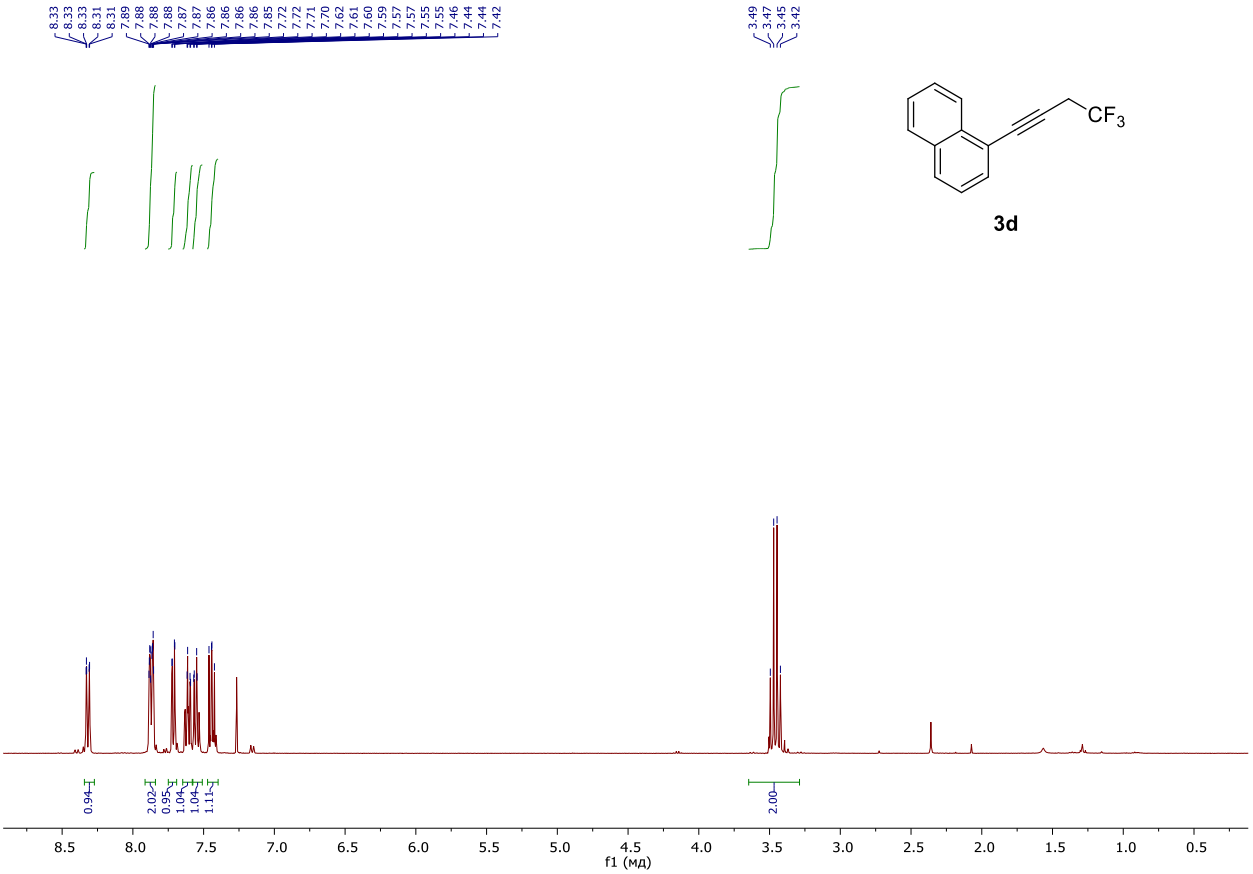
1-bromo-4-(4,4,4-trifluorobut-1-yn-1-yl)benzene (3c) **^{13}C NMR (100 MHz, $CDCl_3$)**



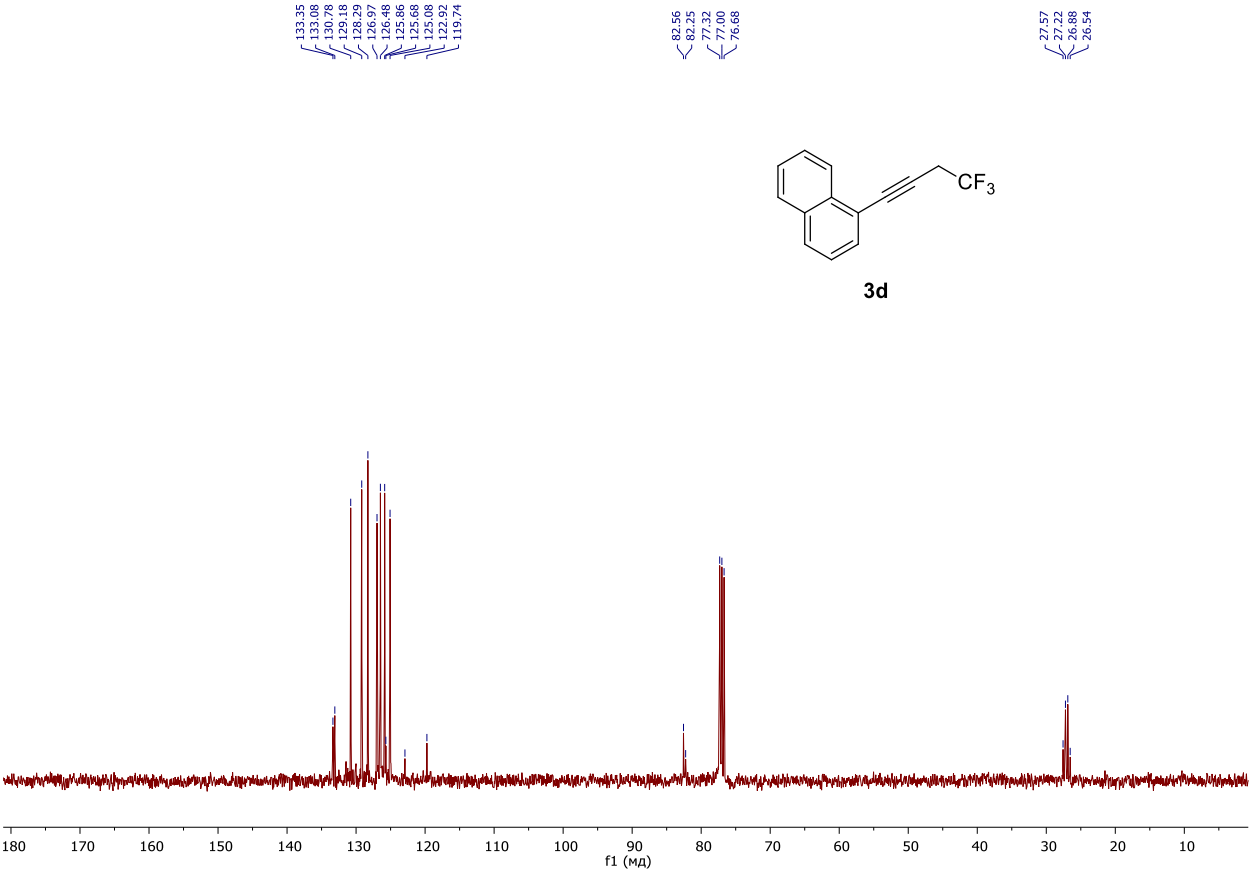
1-bromo-4-(4,4,4-trifluorobut-1-yn-1-yl)benzene (3c) **^{19}F NMR (376 MHz, $CDCl_3$)**



1-(4,4,4-trifluorobut-1-yn-1-yl)naphtalene (3d) **^{1}H NMR (400 MHz, $CDCl_3$)**

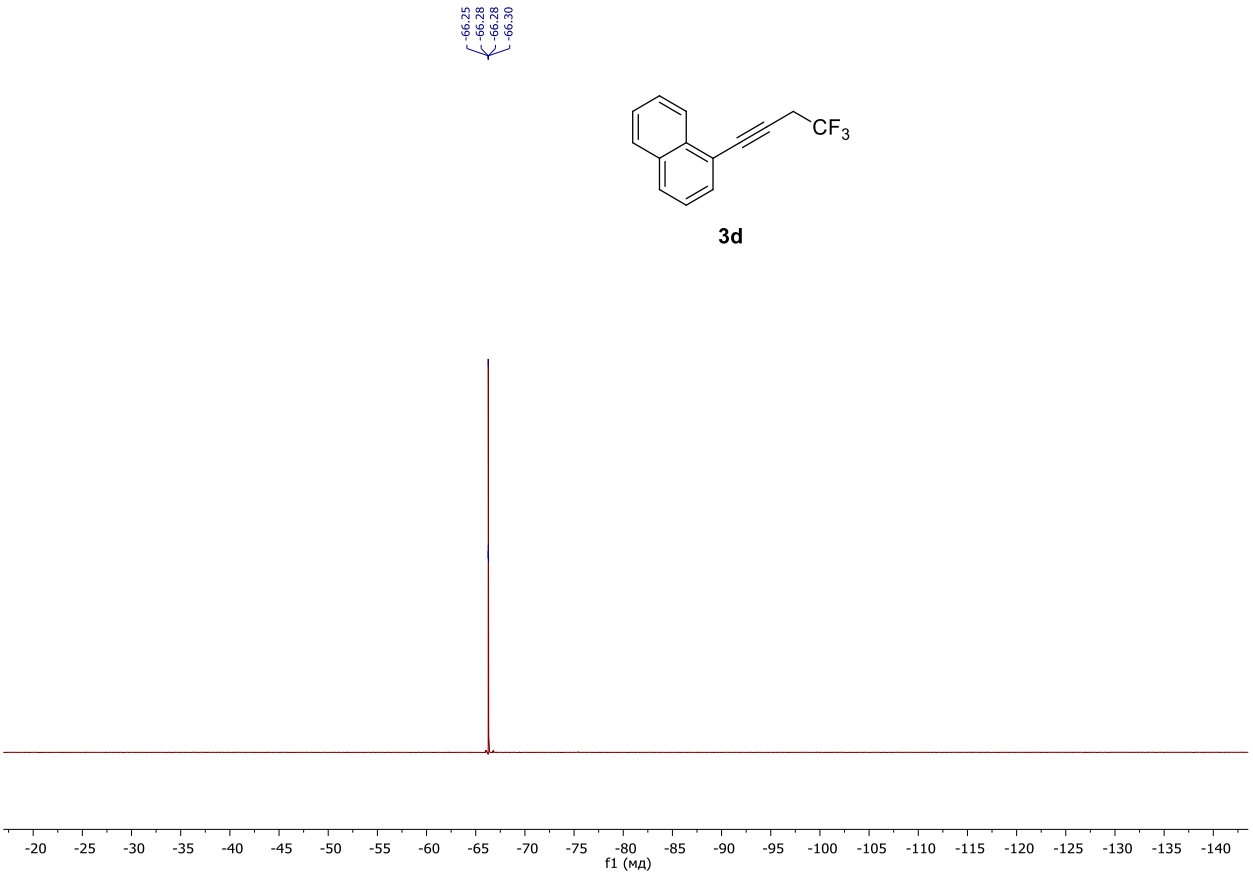


1-(4,4,4-trifluorobut-1-yn-1-yl)naphtalene (3d) **^{13}C NMR (100 MHz, $CDCl_3$)**



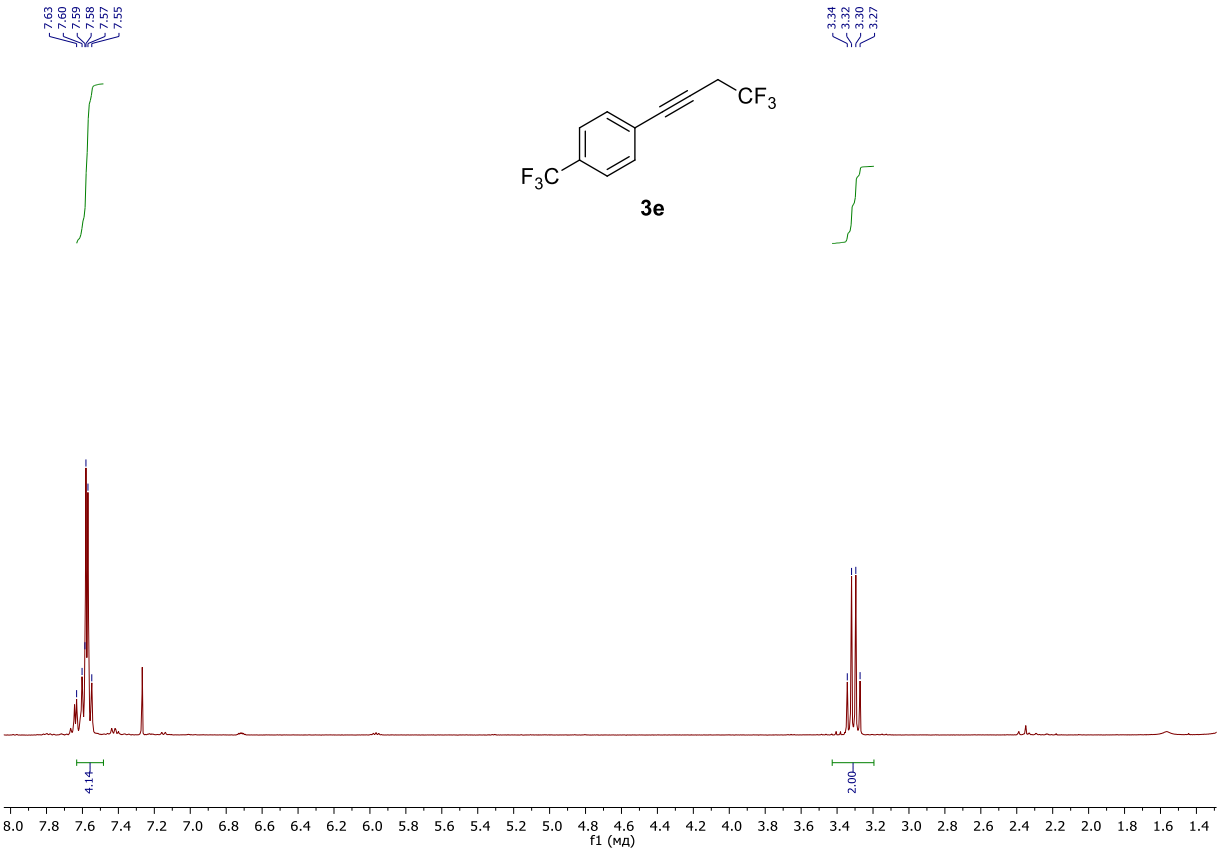
1-(4,4,4-trifluorobut-1-yn-1-yl)naphtalene (3d)

^{19}F NMR (376 MHz, $CDCl_3$)

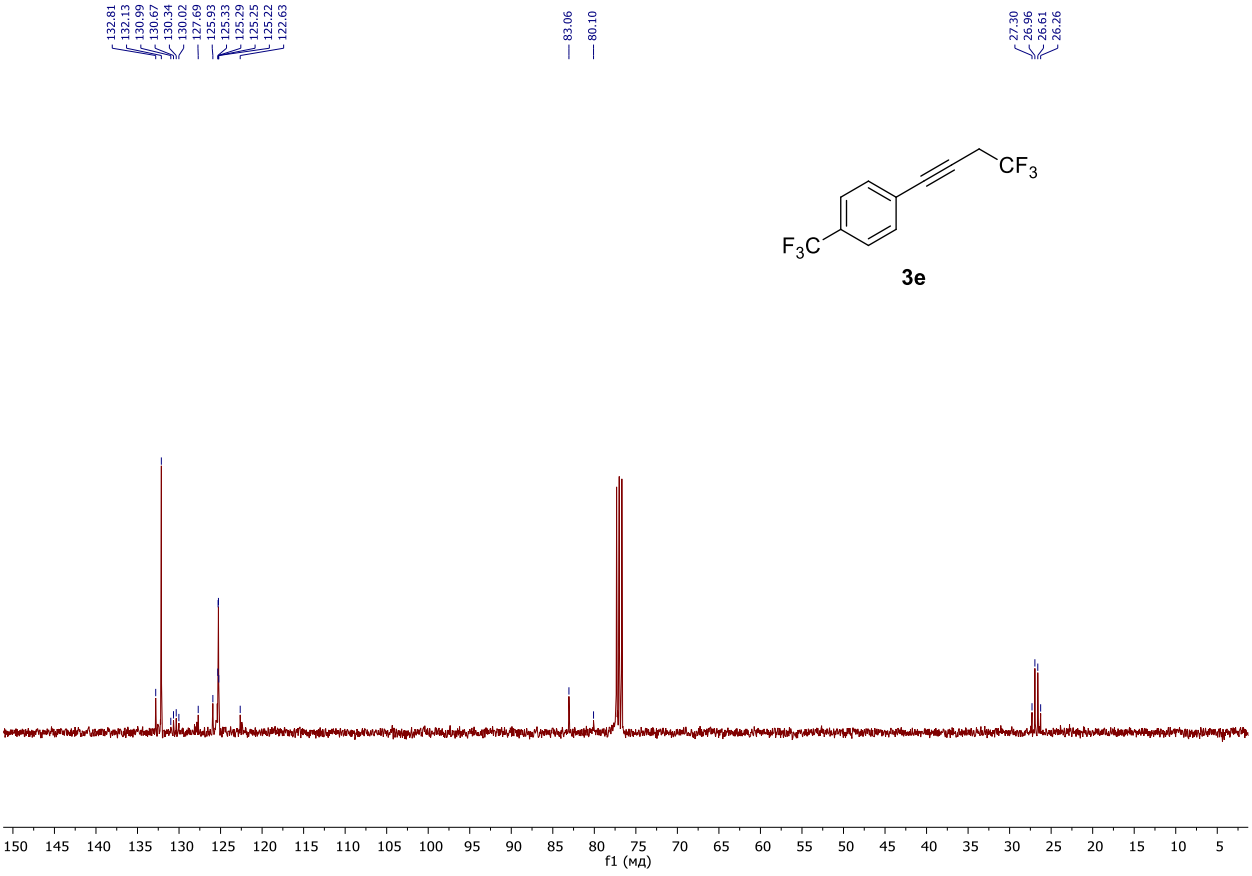


3d

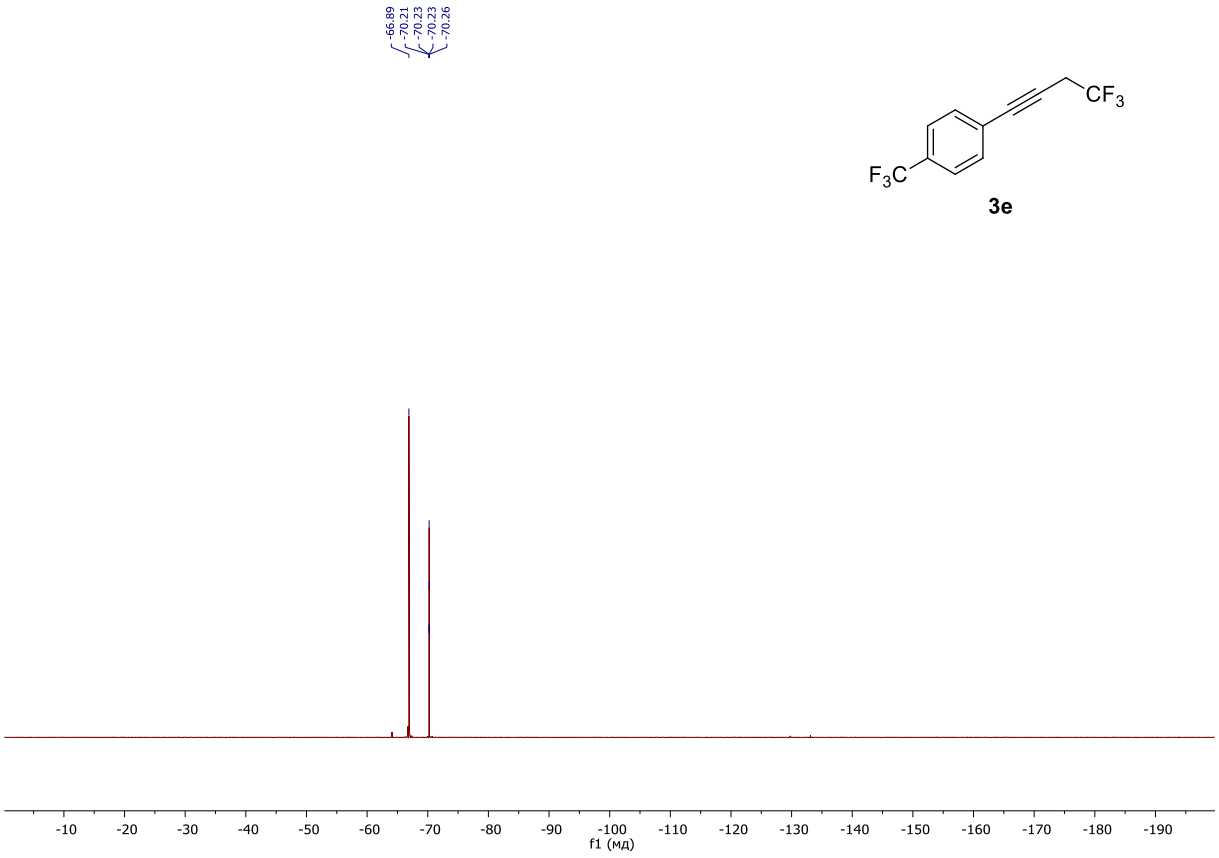
1-trifluoromethyl-4-(4,4,4-trifluorobut-1-yn-1-yl)benzene (3e) **^{1}H NMR (400 MHz, $CDCl_3$)**



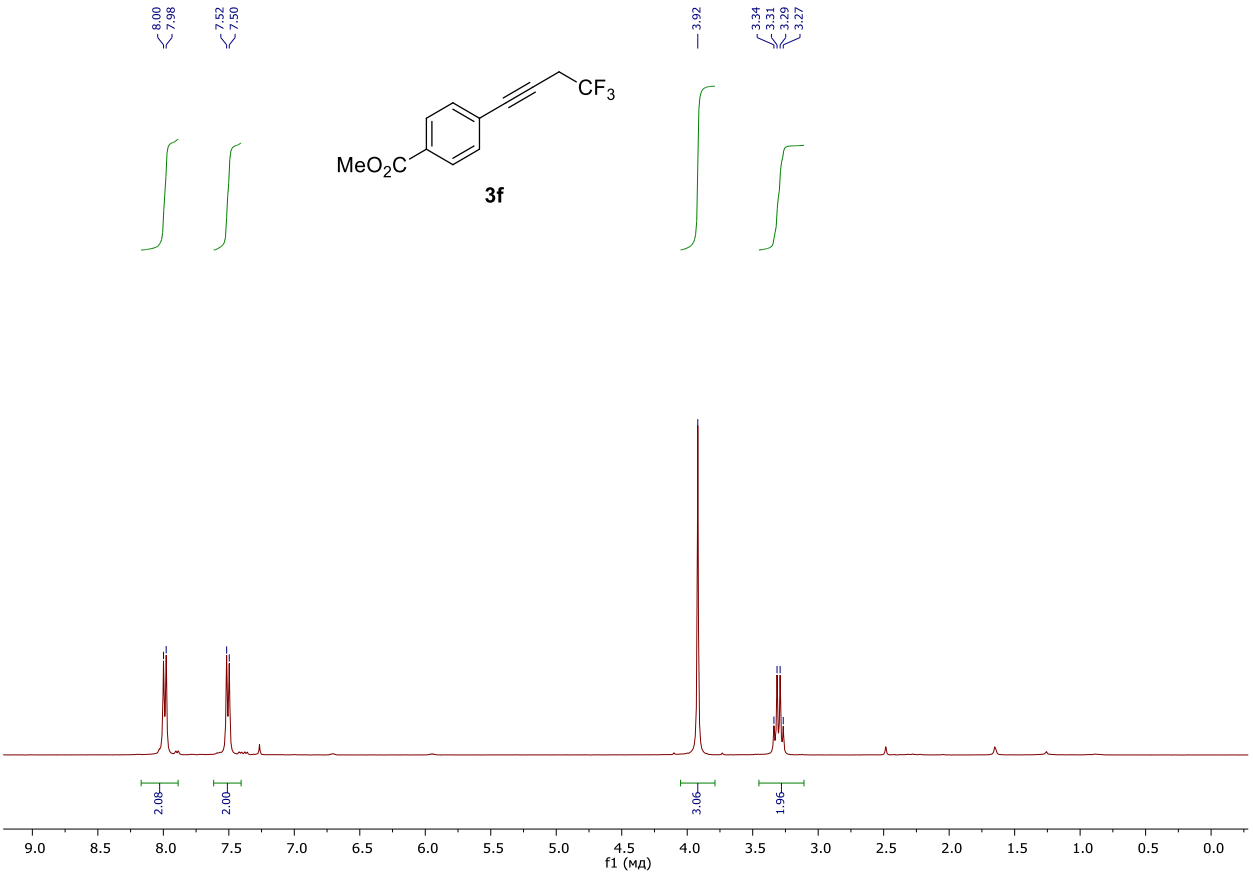
1-trifluoromethyl-4-(4,4,4-trifluorobut-1-yn-1-yl)benzene (3e) **^{13}C NMR (100 MHz, $CDCl_3$)**



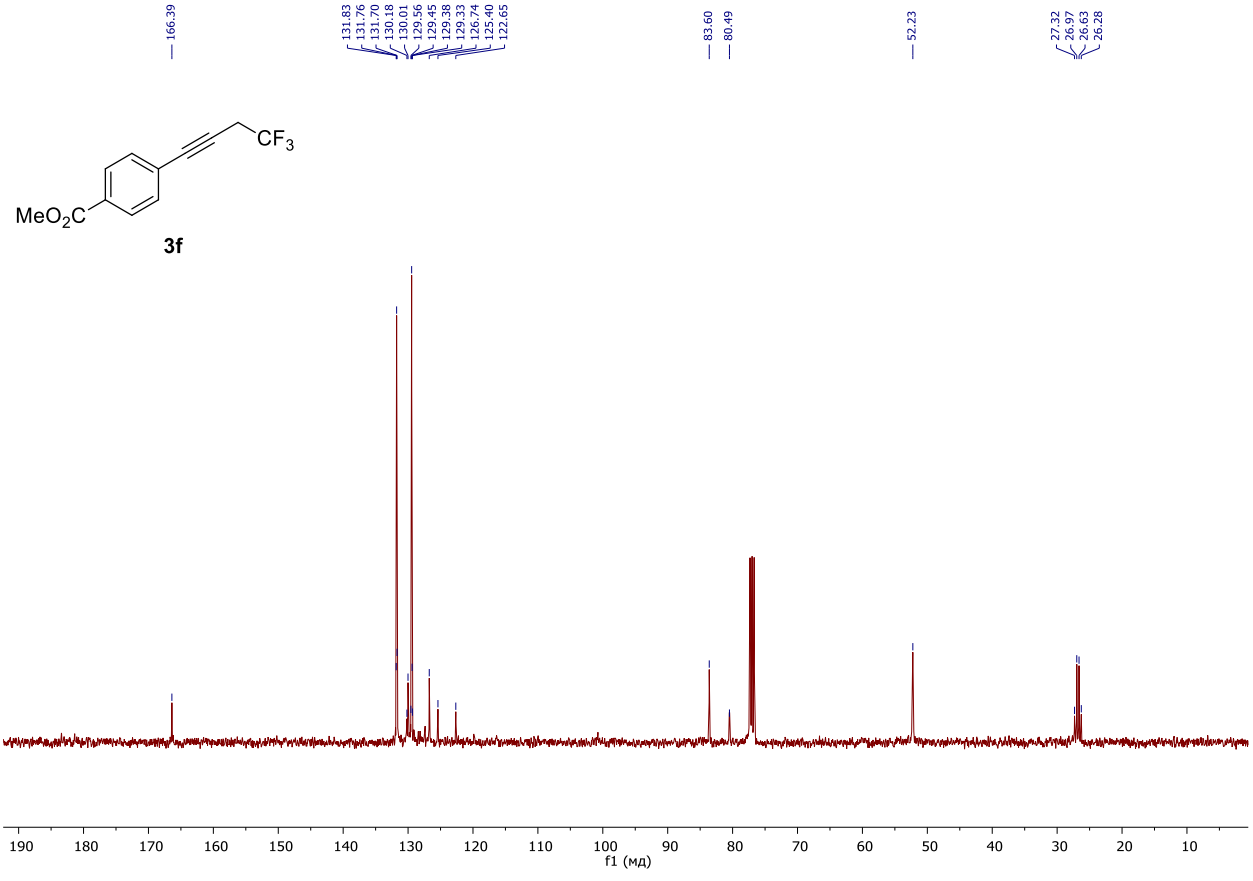
1-trifluoromethyl-4-(4,4,4-trifluorobut-1-yn-1-yl)benzene (3e) **^{19}F NMR (376 MHz, $CDCl_3$)**



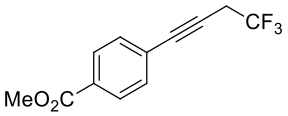
methyl 4-(4,4,4-trifluorobut-1-yn-1-yl)benzoate (3f) ^{1}H NMR (400 MHz, $CDCl_3$)



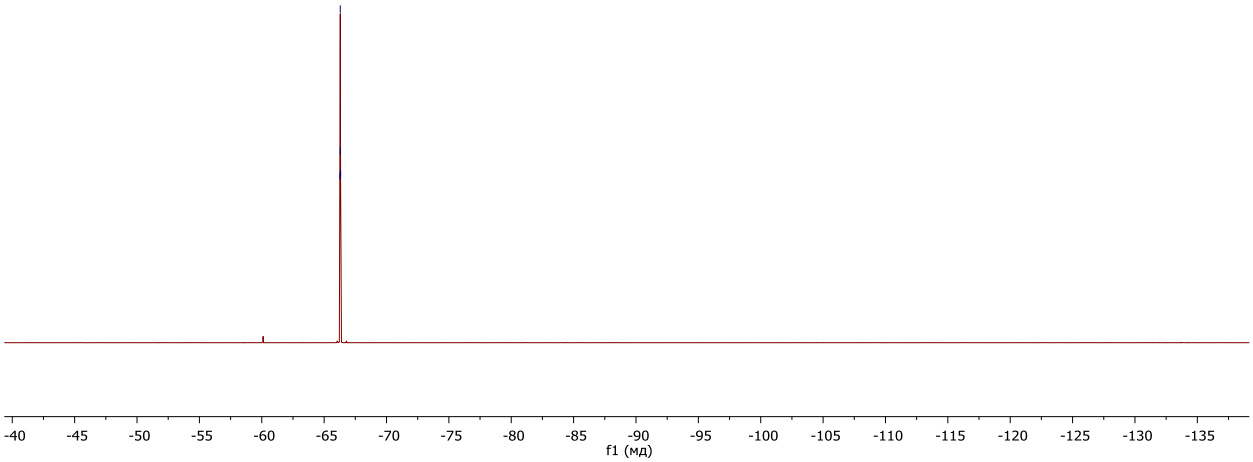
methyl 4-(4,4,4-trifluorobut-1-yn-1-yl)benzoate (3f) ^{13}C NMR (100 MHz, $CDCl_3$)



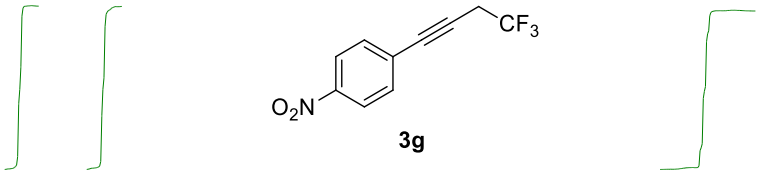
methyl 4-(4,4,4-trifluorobut-1-yn-1-yl)benzoate (3f) ^{19}F NMR (376 MHz, $CDCl_3$)



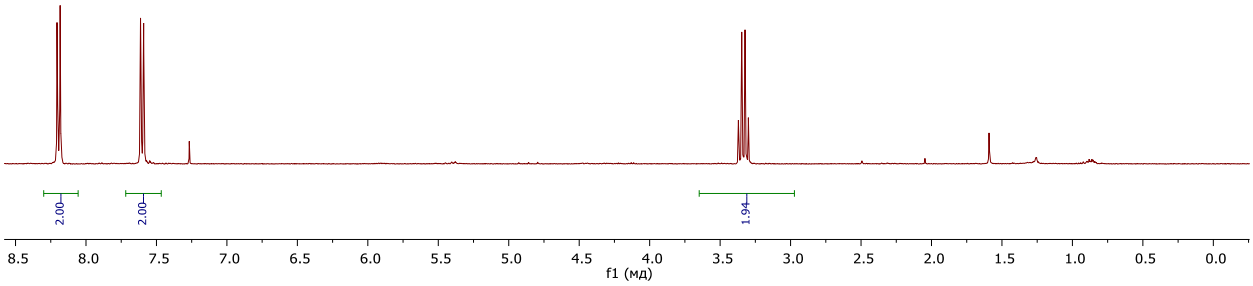
3f



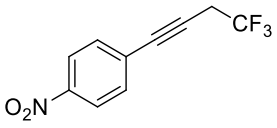
1-nitro-4-(4,4,4-trifluorobut-1-yn-1-yl)benzene (3g) **^{1}H NMR (400 MHz, $CDCl_3$)**



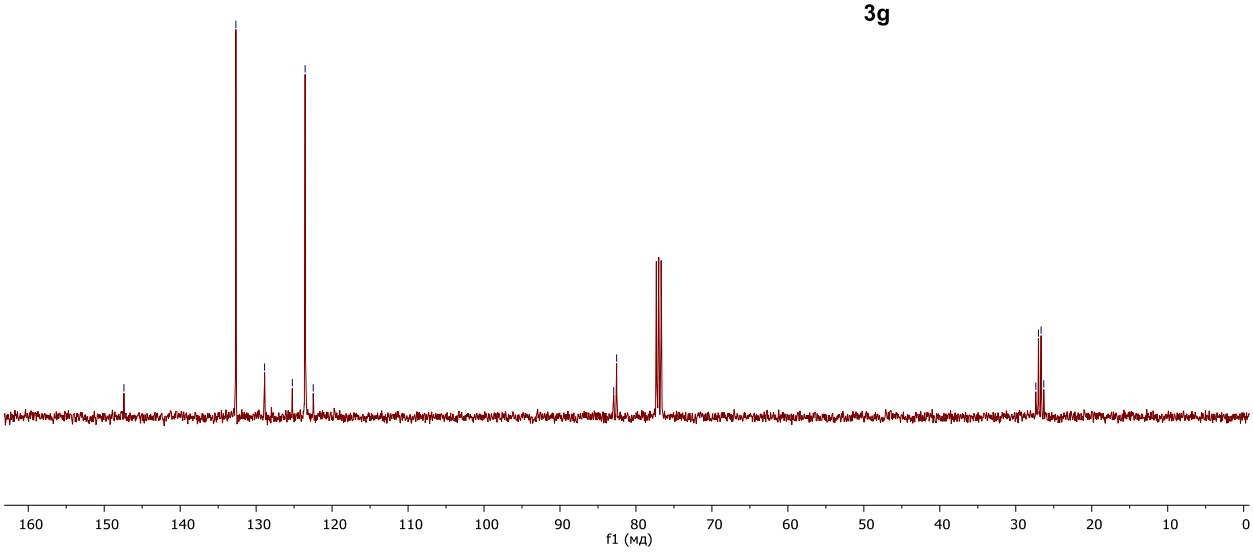
3g



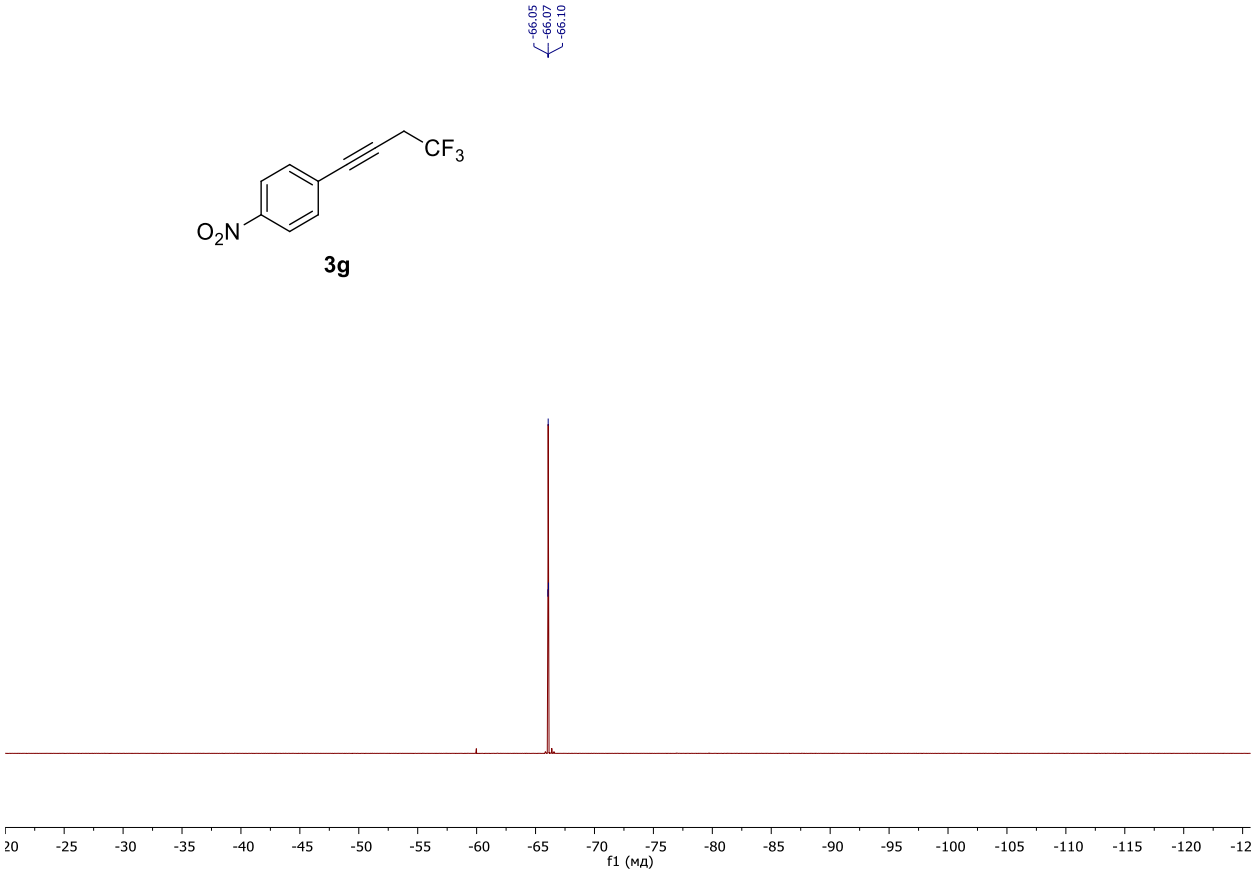
1-nitro-4-(4,4,4-trifluorobut-1-yn-1-yl)benzene (3g) **^{13}C NMR (100 MHz, $CDCl_3$)**



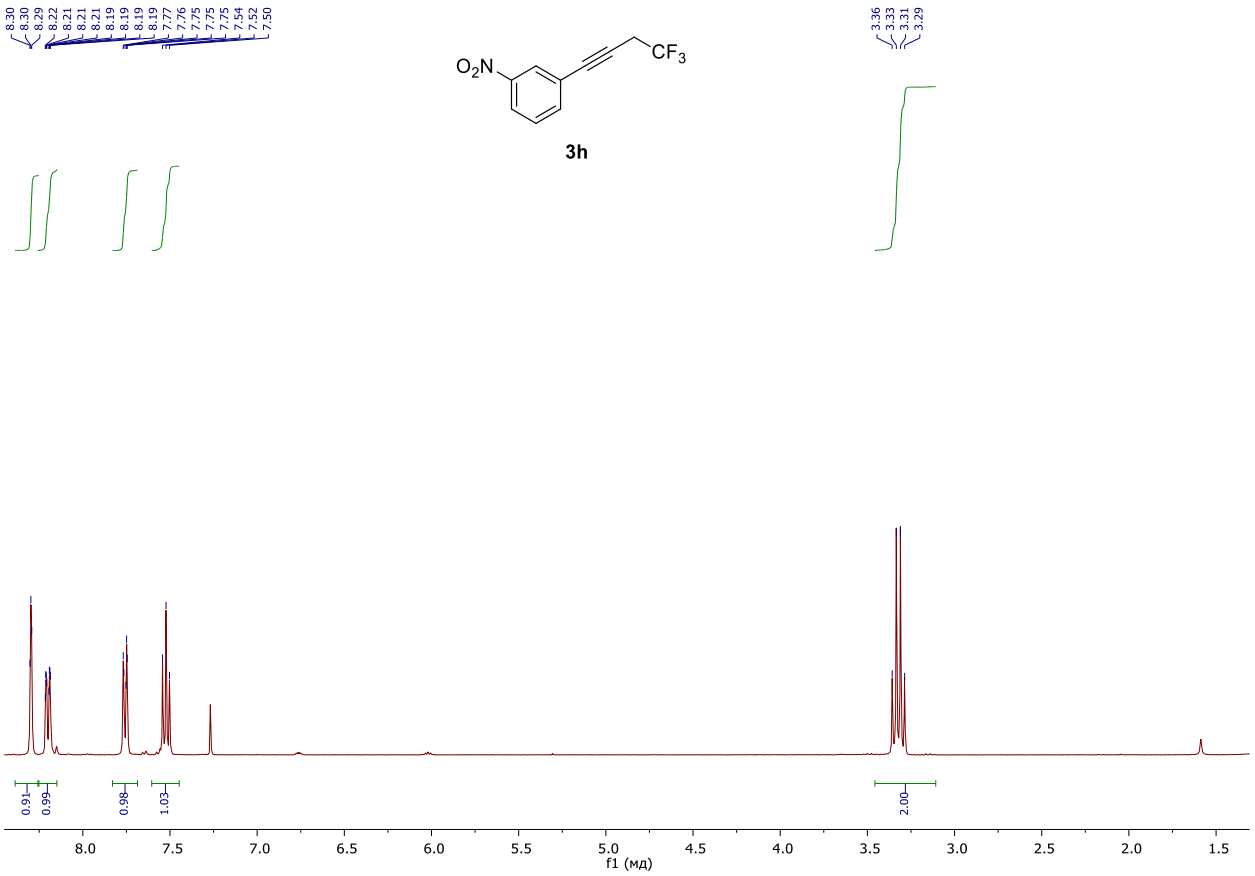
3g



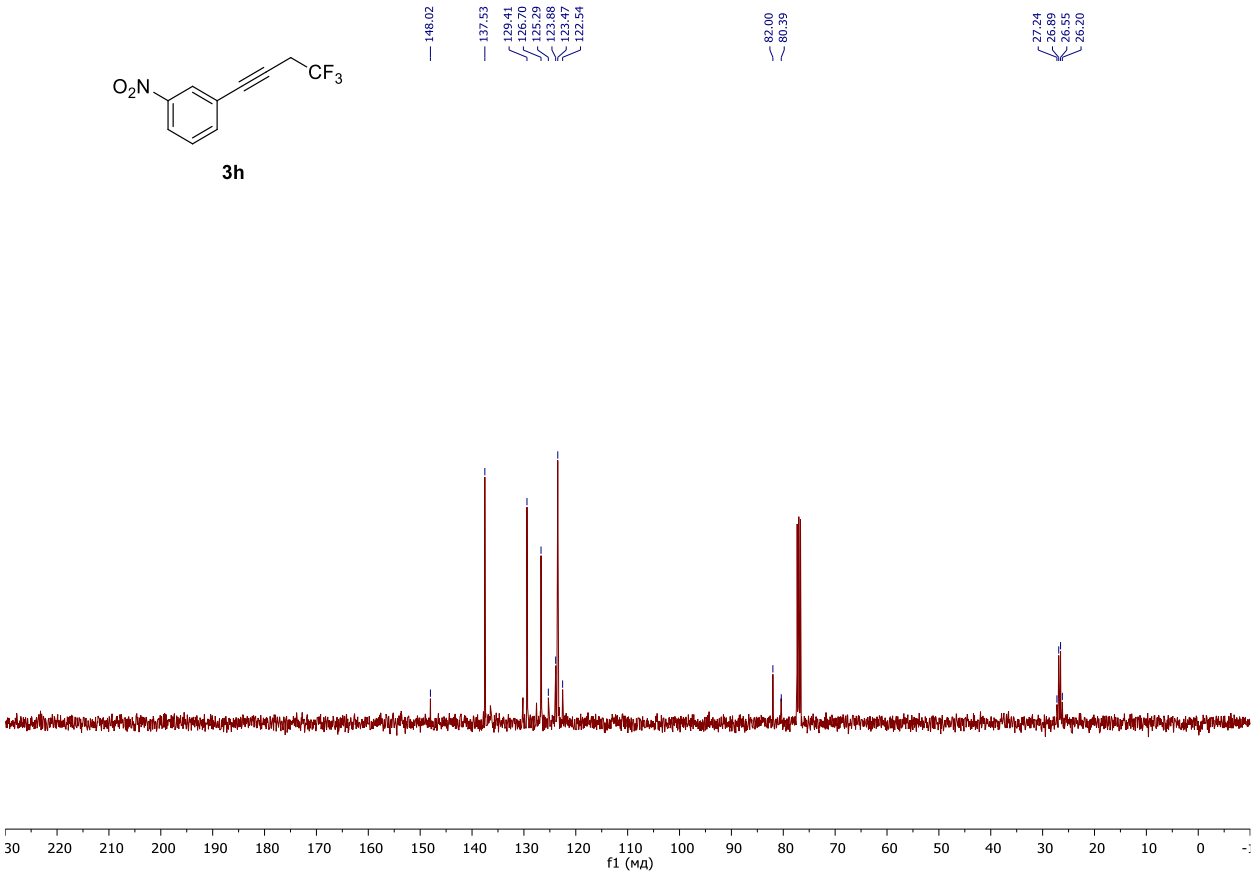
1-nitro-4-(4,4,4-trifluorobut-1-yn-1-yl)benzene (3g) **^{19}F NMR (376 MHz, $CDCl_3$)**



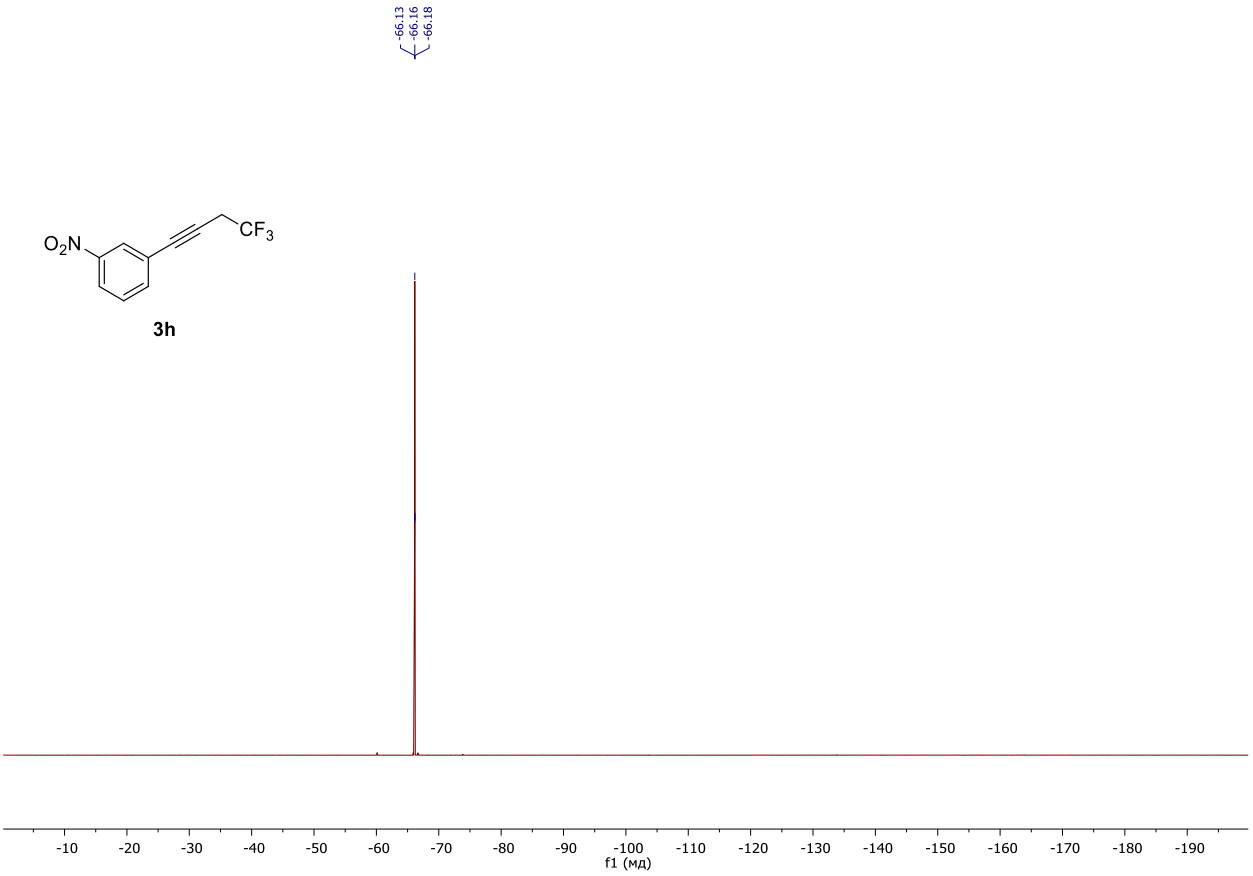
1-nitro-3-(4,4,4-trifluorobut-1-yn-1-yl)benzene (3h) **^{1}H NMR (400 MHz, $CDCl_3$)**



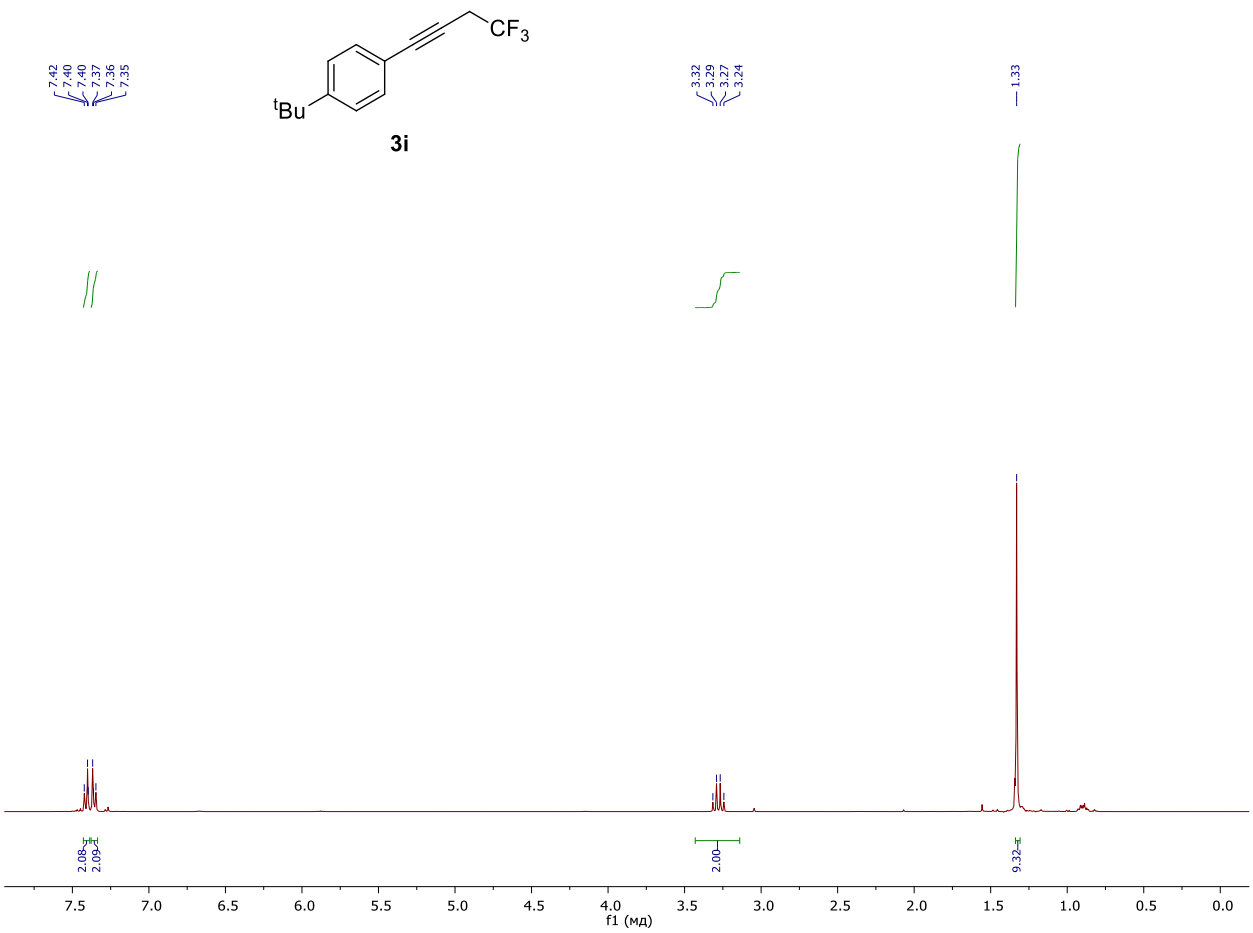
1-nitro-3-(4,4,4-trifluorobut-1-yn-1-yl)benzene (3h) **^{13}C NMR (100 MHz, $CDCl_3$)**



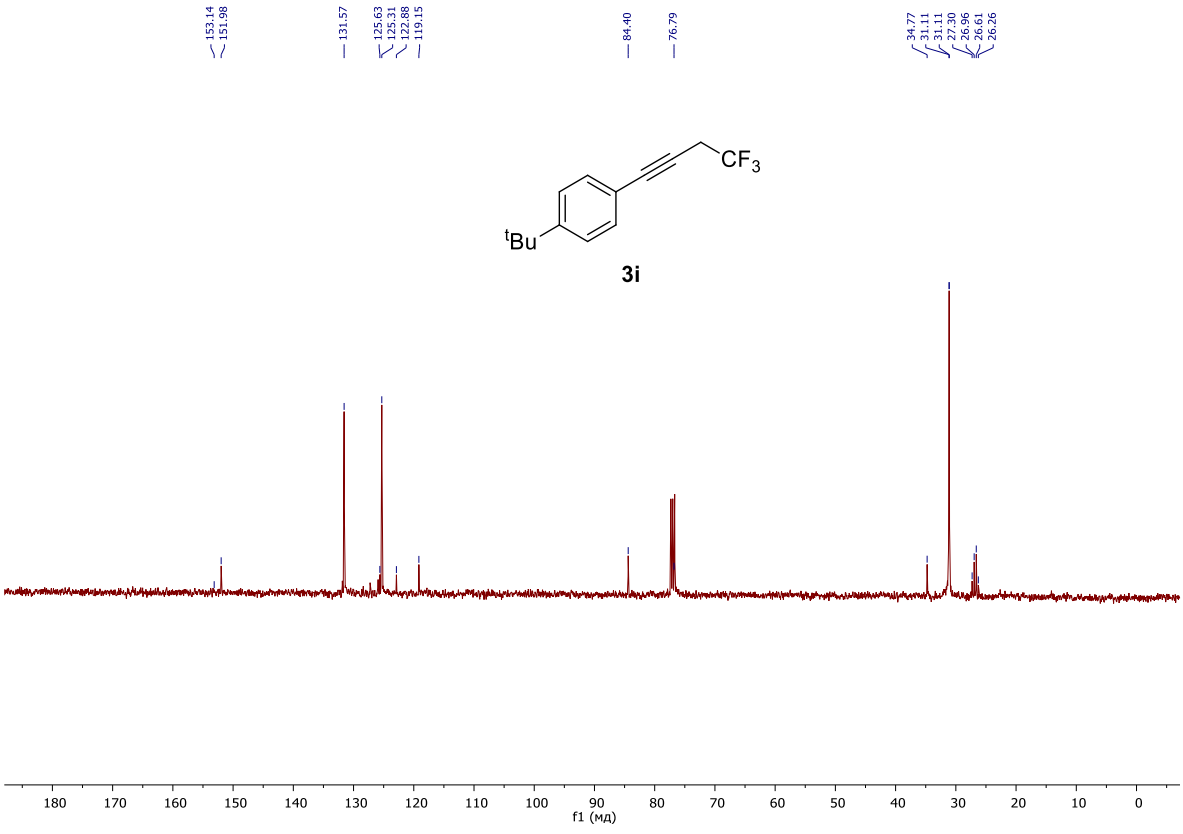
1-nitro-3-(4,4,4-trifluorobut-1-yn-1-yl)benzene (3h) **^{19}F NMR (376 MHz, $CDCl_3$)**



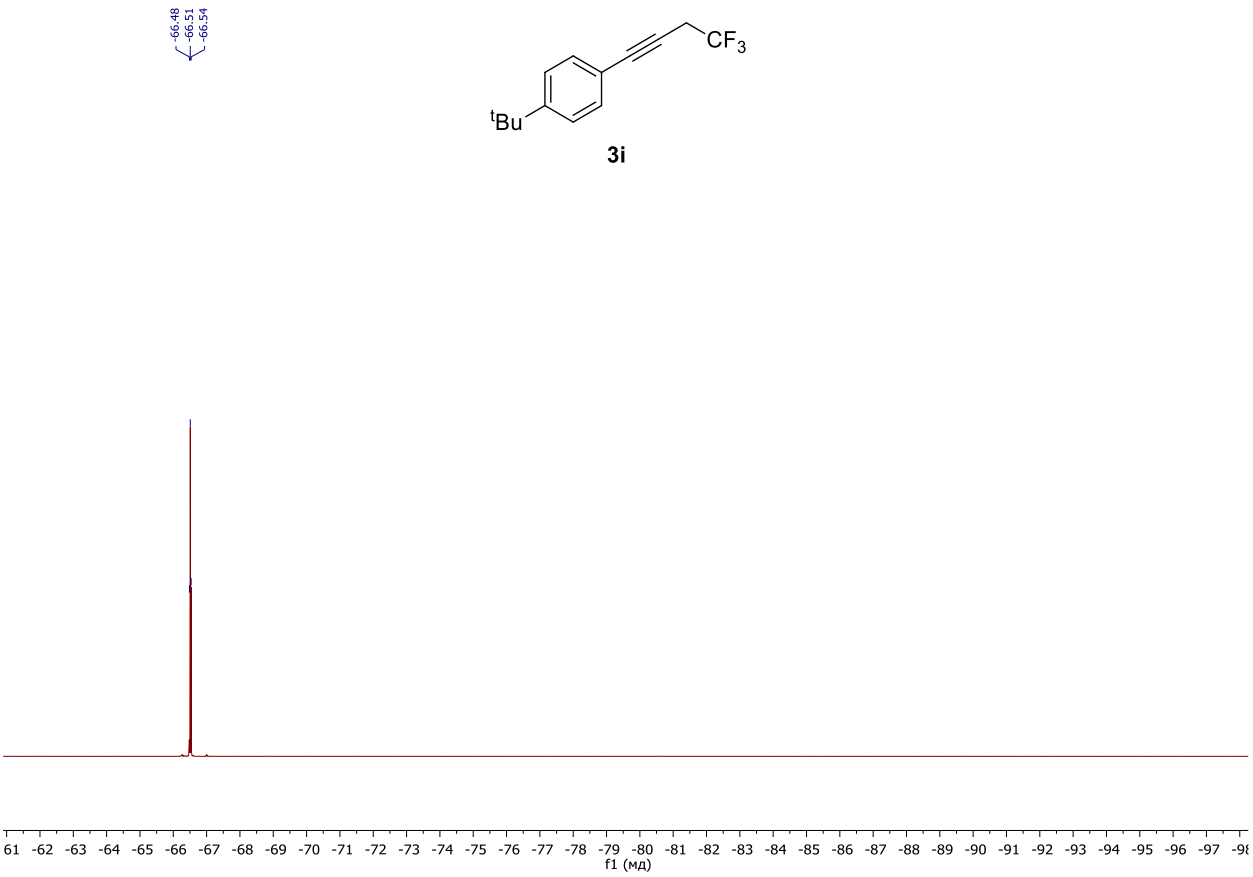
1-tert-butyl-4-(4,4,4-trifluorobut-1-yn-1-yl)benzene (3i) **^{1}H NMR (400 MHz, $CDCl_3$)**



1-tert-butyl-4-(4,4,4-trifluorobut-1-yn-1-yl)benzene (3i) **^{13}C NMR (100 MHz, $CDCl_3$)**

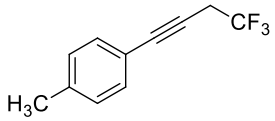


1-tert-butyl-4-(4,4,4-trifluorobut-1-yn-1-yl)benzene (3i) **^{19}F NMR (376 MHz, $CDCl_3$)**

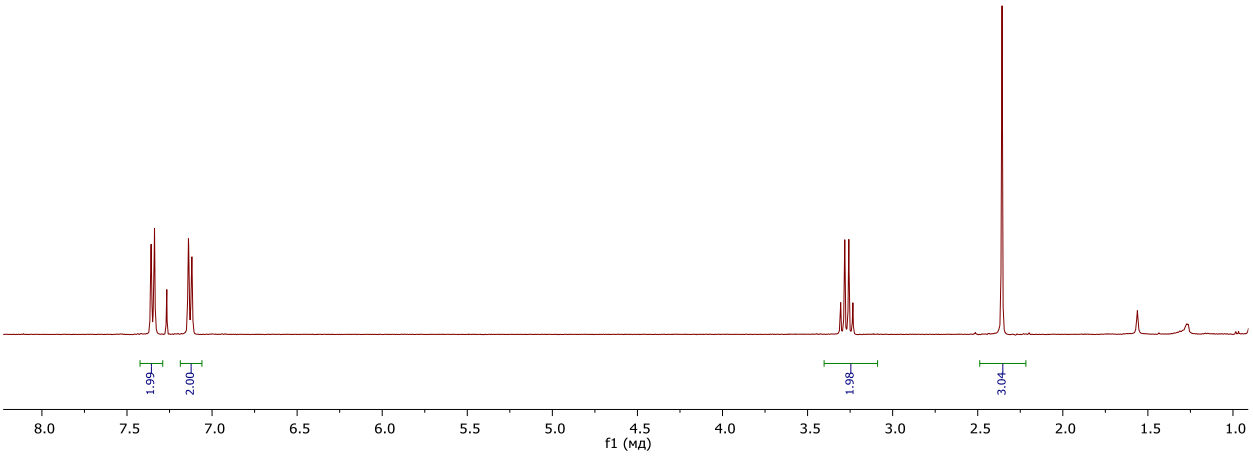


3i

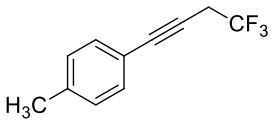
1-methyl-4-(4,4,4-trifluorobut-1-yn-1-yl)benzene (3j) **^{1}H NMR (400 MHz, $CDCl_3$)**



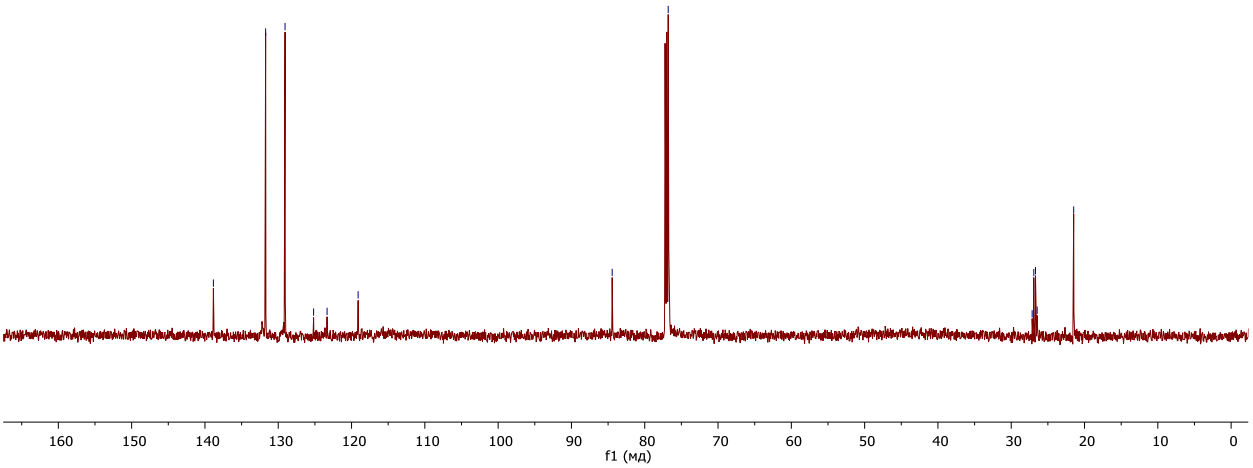
3j



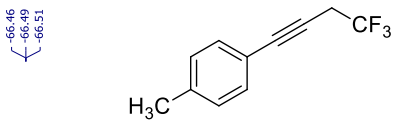
1-methyl-4-(4,4,4-trifluorobut-1-yn-1-yl)benzene (3j) **^{13}C NMR (100 MHz, $CDCl_3$)**



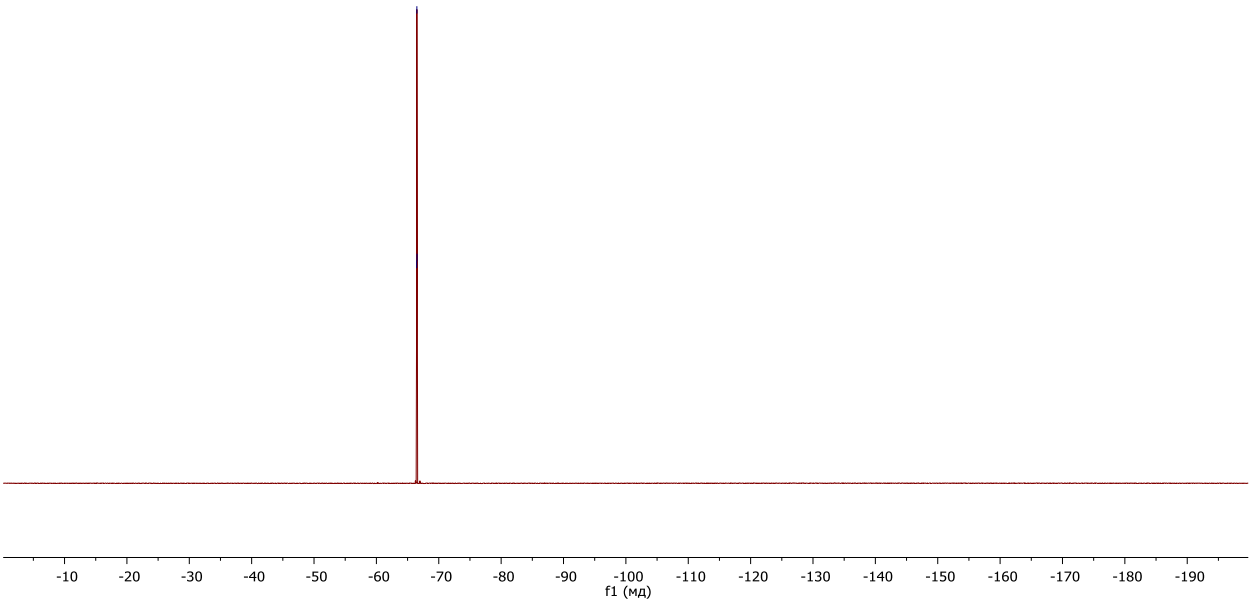
3j



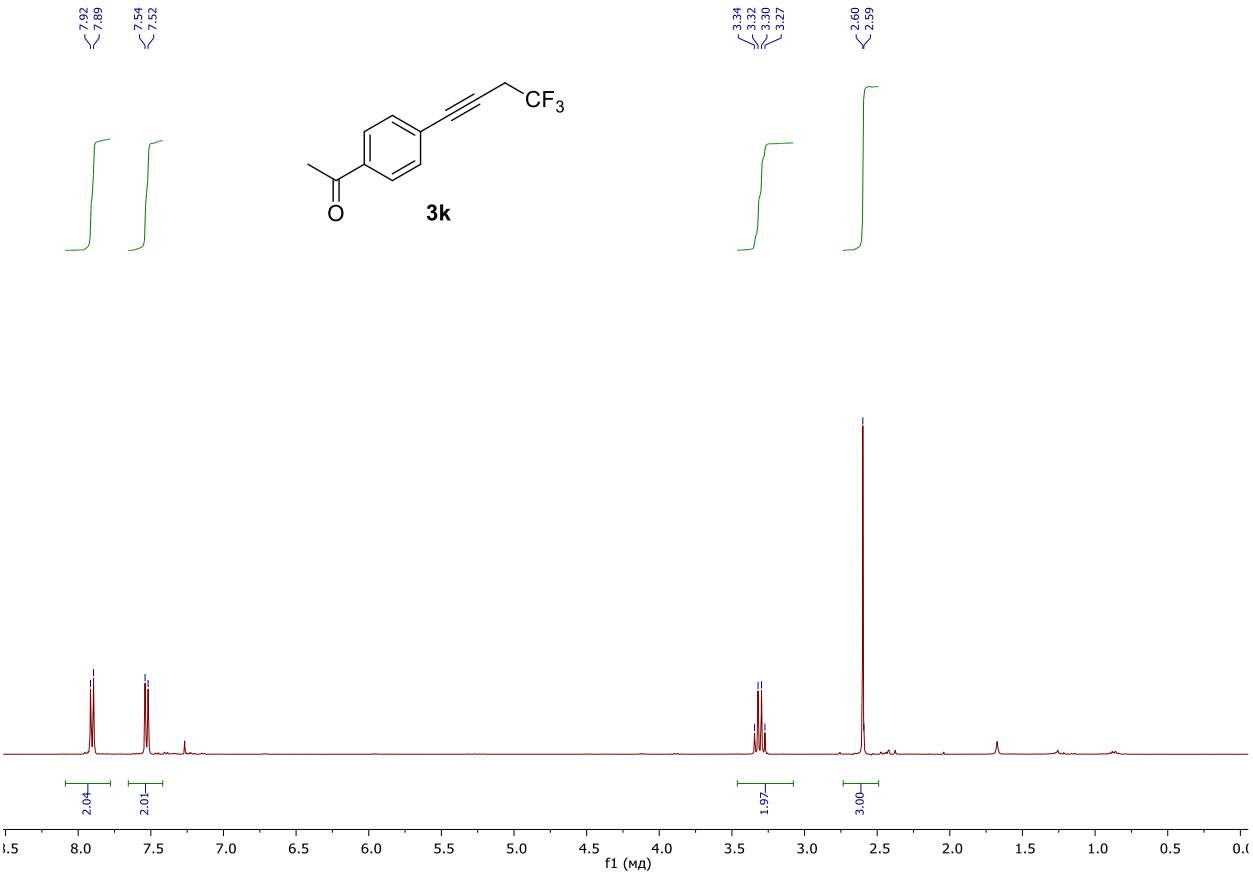
1-methyl-4-(4,4,4-trifluorobut-1-yn-1-yl)benzene (3j) **^{19}F NMR (376 MHz, $CDCl_3$)**



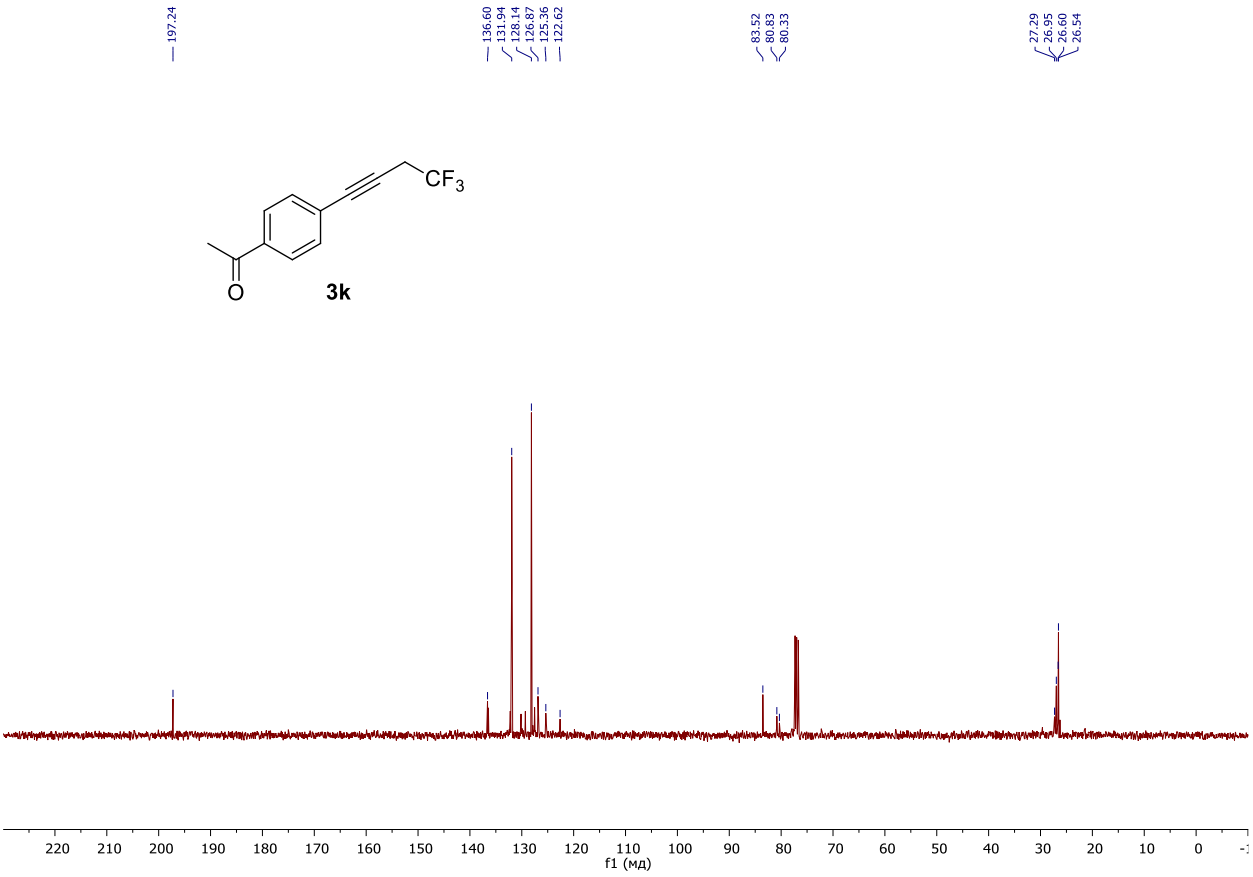
3j



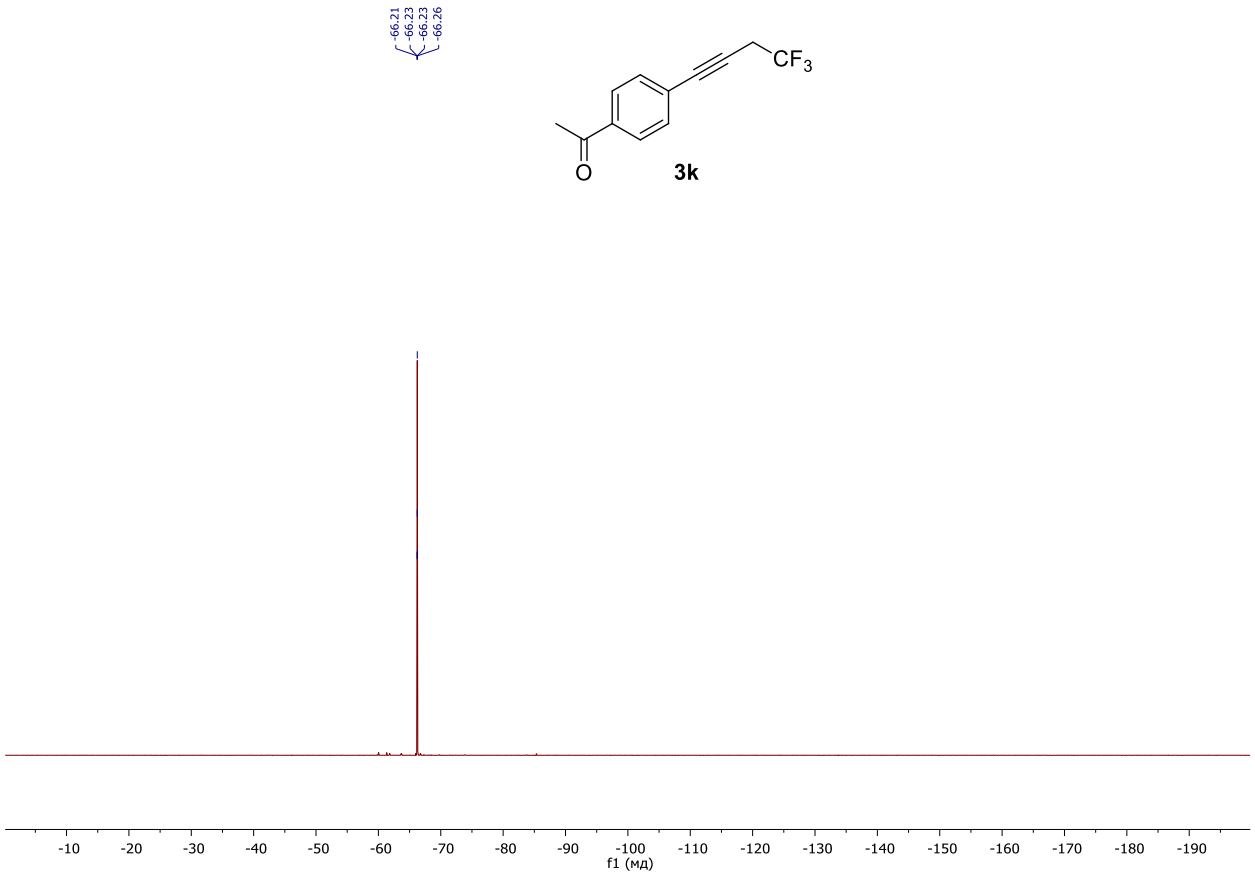
1-acetyl-4-(4,4,4-trifluorobut-1-yn-1-yl)benzene (3k) **^{1}H NMR (400 MHz, $CDCl_3$)**



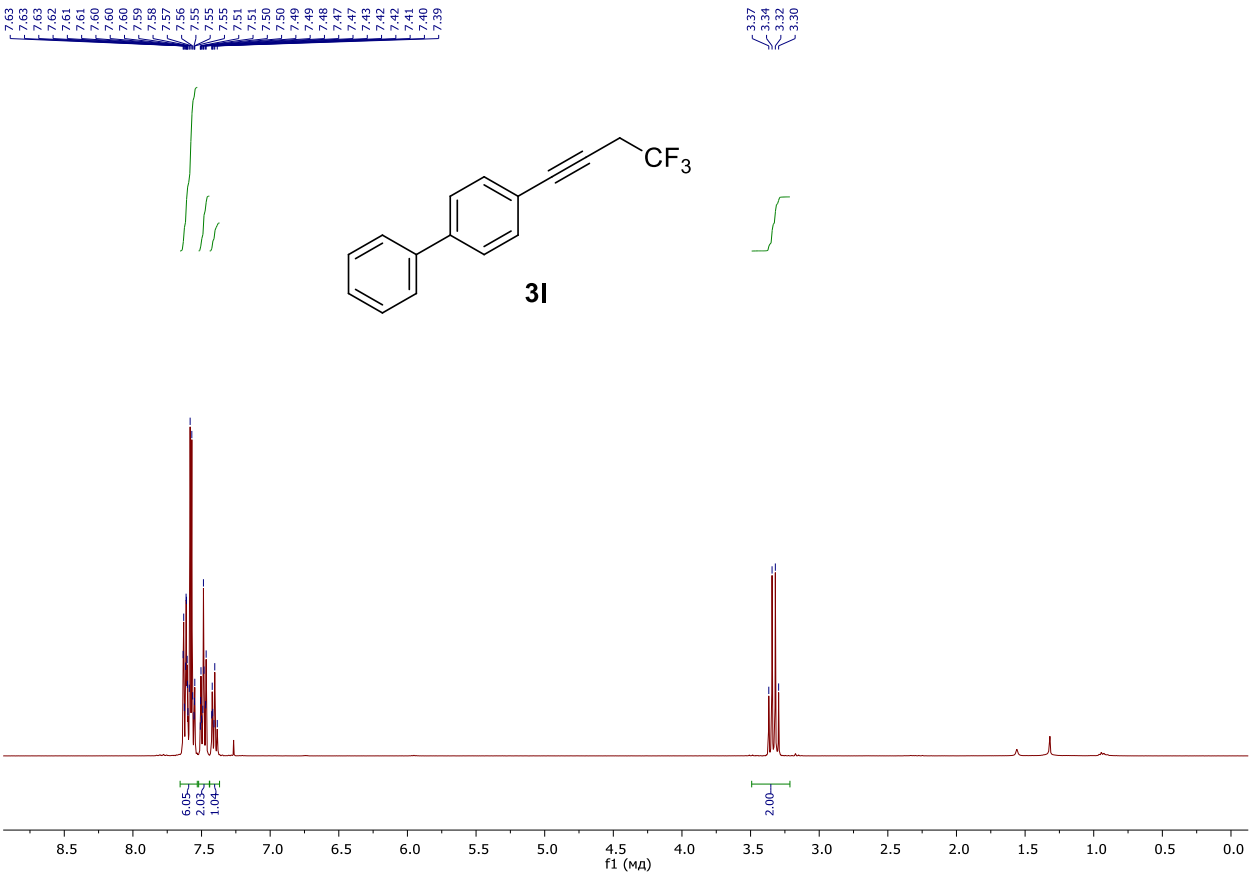
1-acetyl-4-(4,4,4-trifluorobut-1-yn-1-yl)benzene (3k) **^{13}C NMR (100 MHz, $CDCl_3$)**



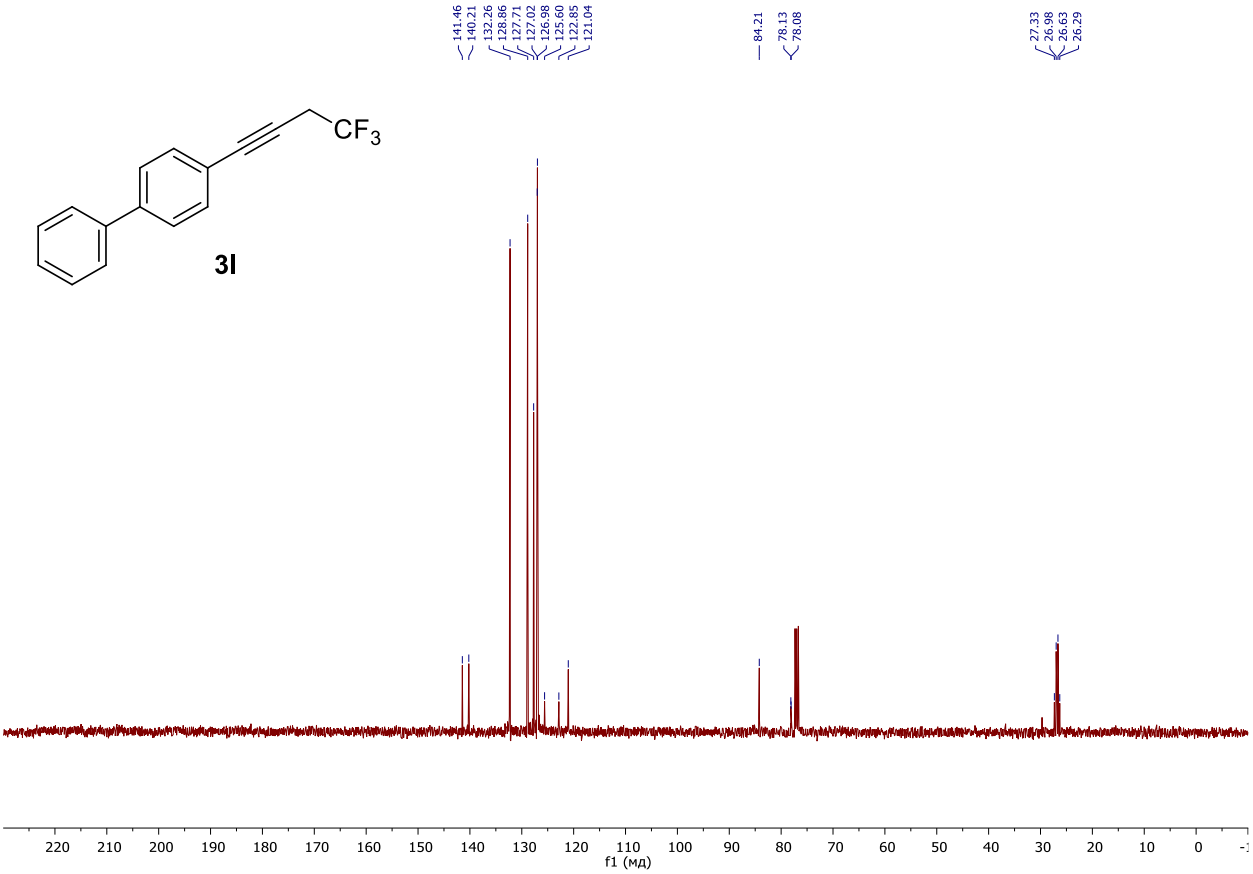
1-acetyl-4-(4,4,4-trifluorobut-1-yn-1-yl)benzene (3k) **^{19}F NMR (376 MHz, $CDCl_3$)**



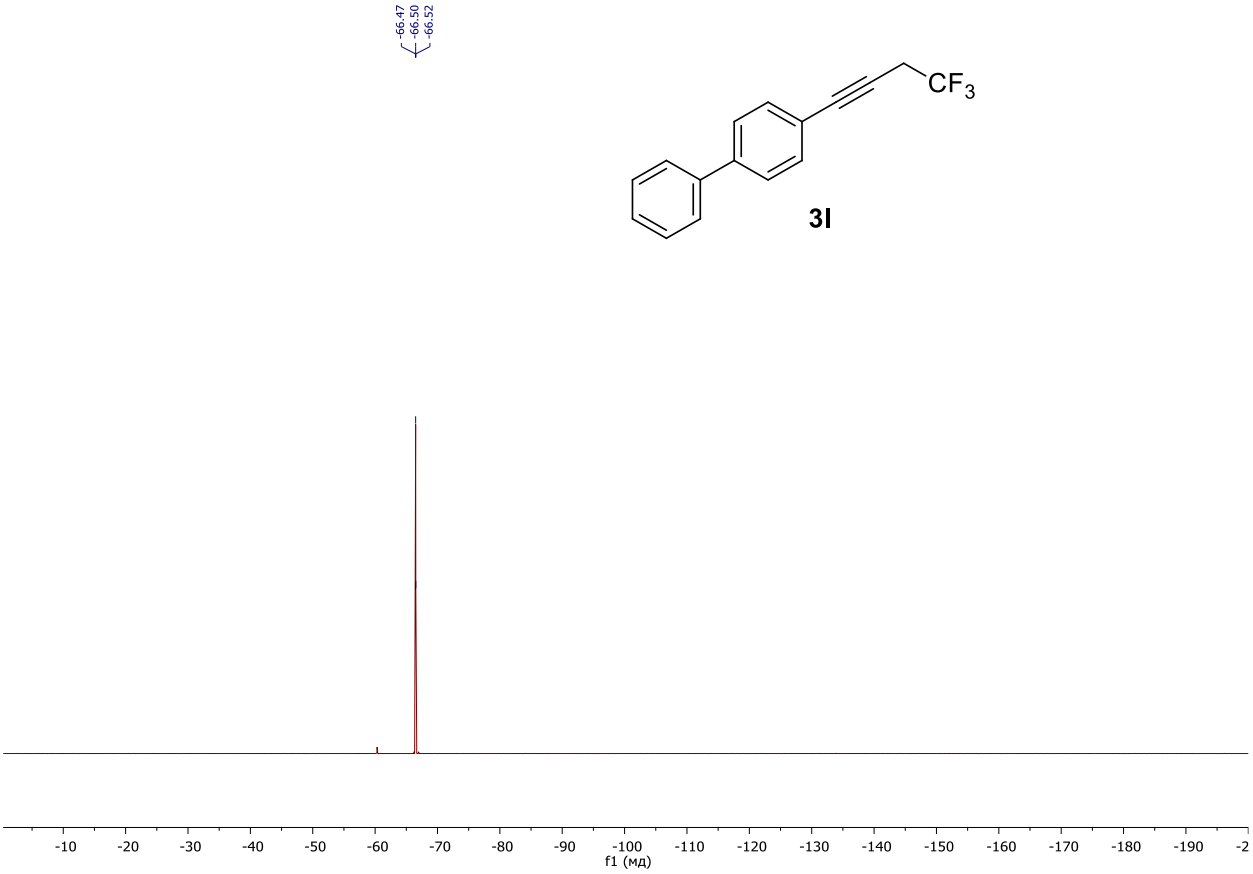
4-(4,4,4-trifluorobut-1-yn-1-yl)biphenyl (3l) **^{1}H NMR (400 MHz, $CDCl_3$)**



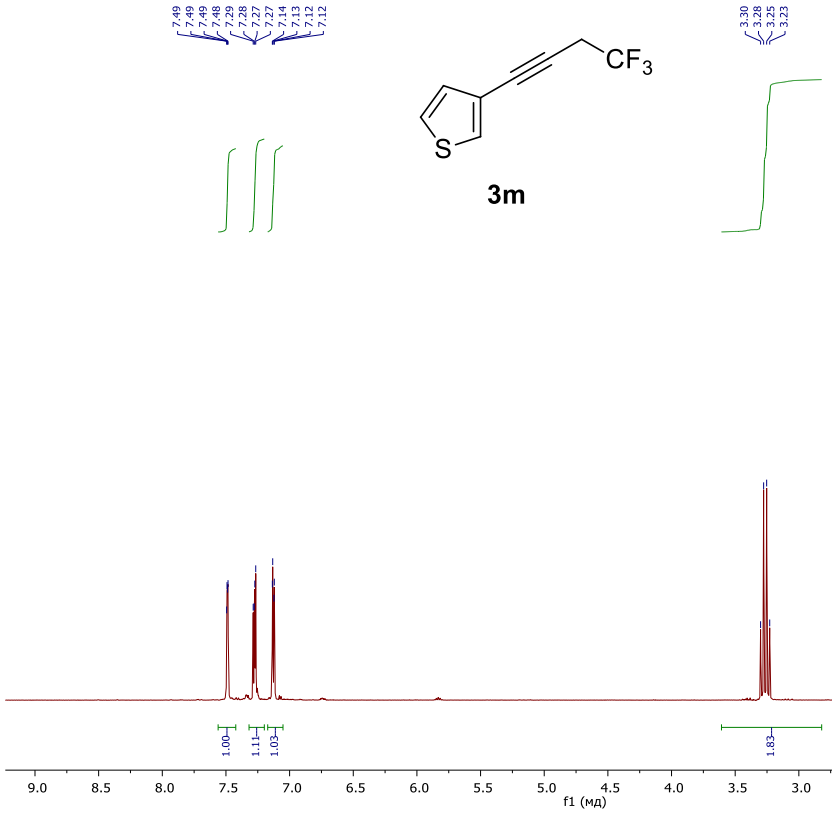
4-(4,4,4-trifluorobut-1-yn-1-yl)biphenyl (3l) **^{13}C NMR (100 MHz, $CDCl_3$)**



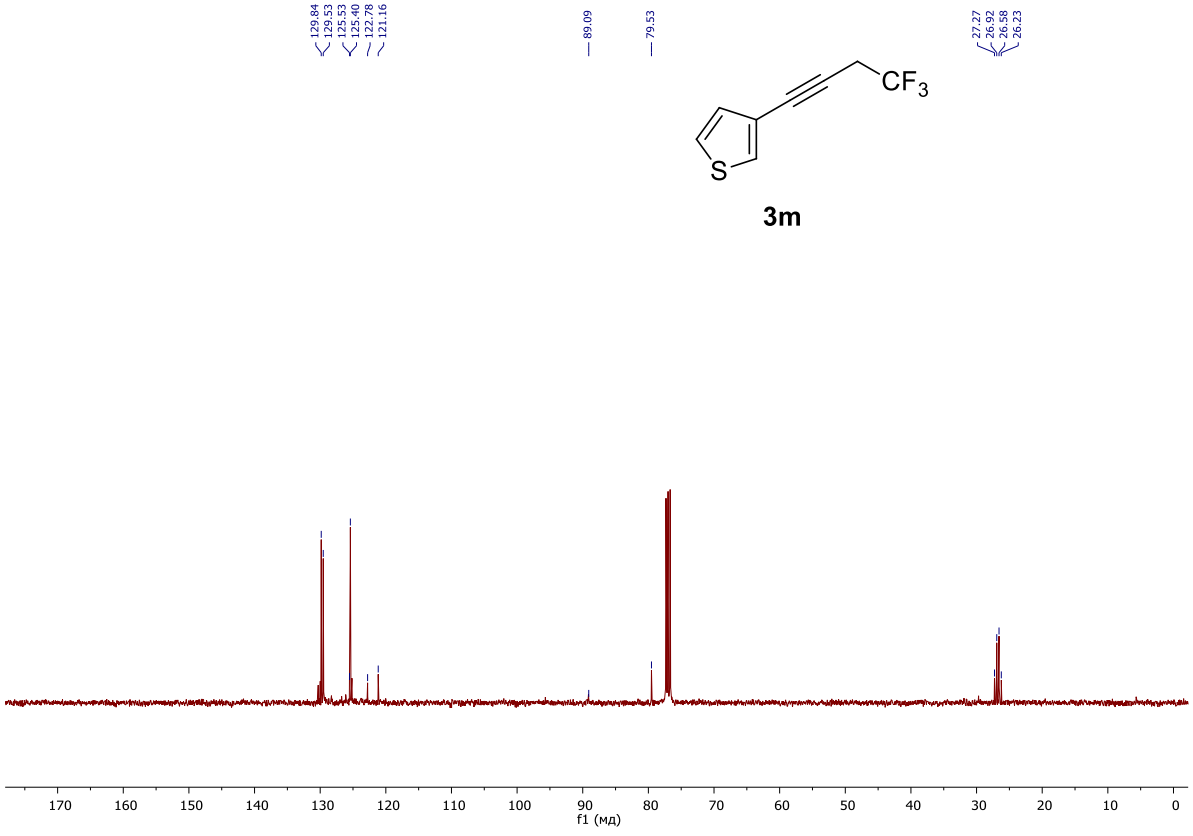
4-(4,4,4-trifluorobut-1-yn-1-yl)biphenyl (3l) **^{19}F NMR (376 MHz, $CDCl_3$)**



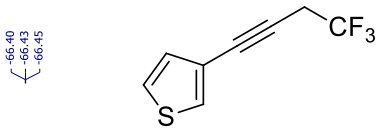
3-(4,4,4-trifluorobut-1-yn-1-yl)thiophene (3m) **^{1}H NMR (400 MHz, $CDCl_3$)**



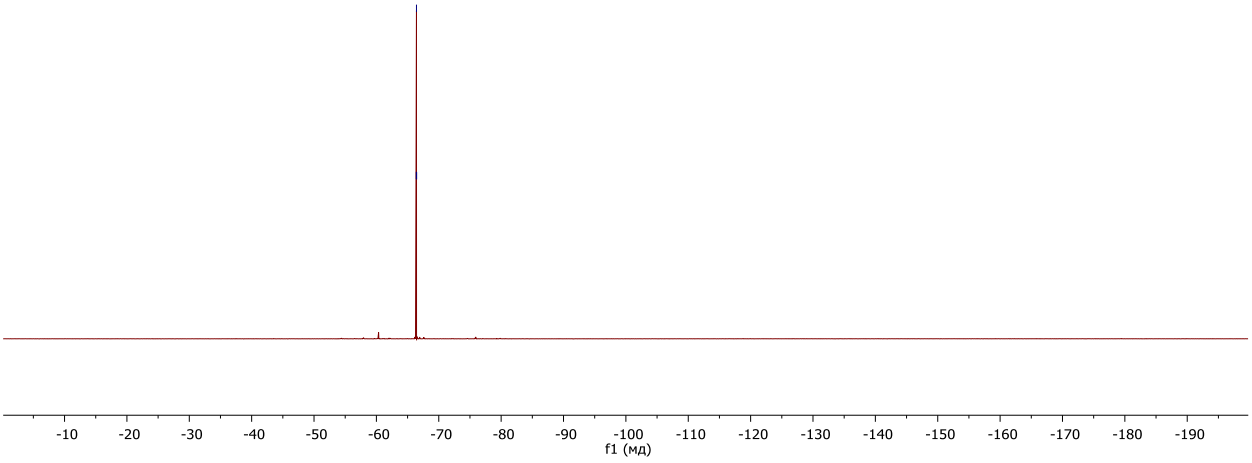
3-(4,4,4-trifluorobut-1-yn-1-yl)thiophene (3m) **^{13}C NMR (100 MHz, $CDCl_3$)**



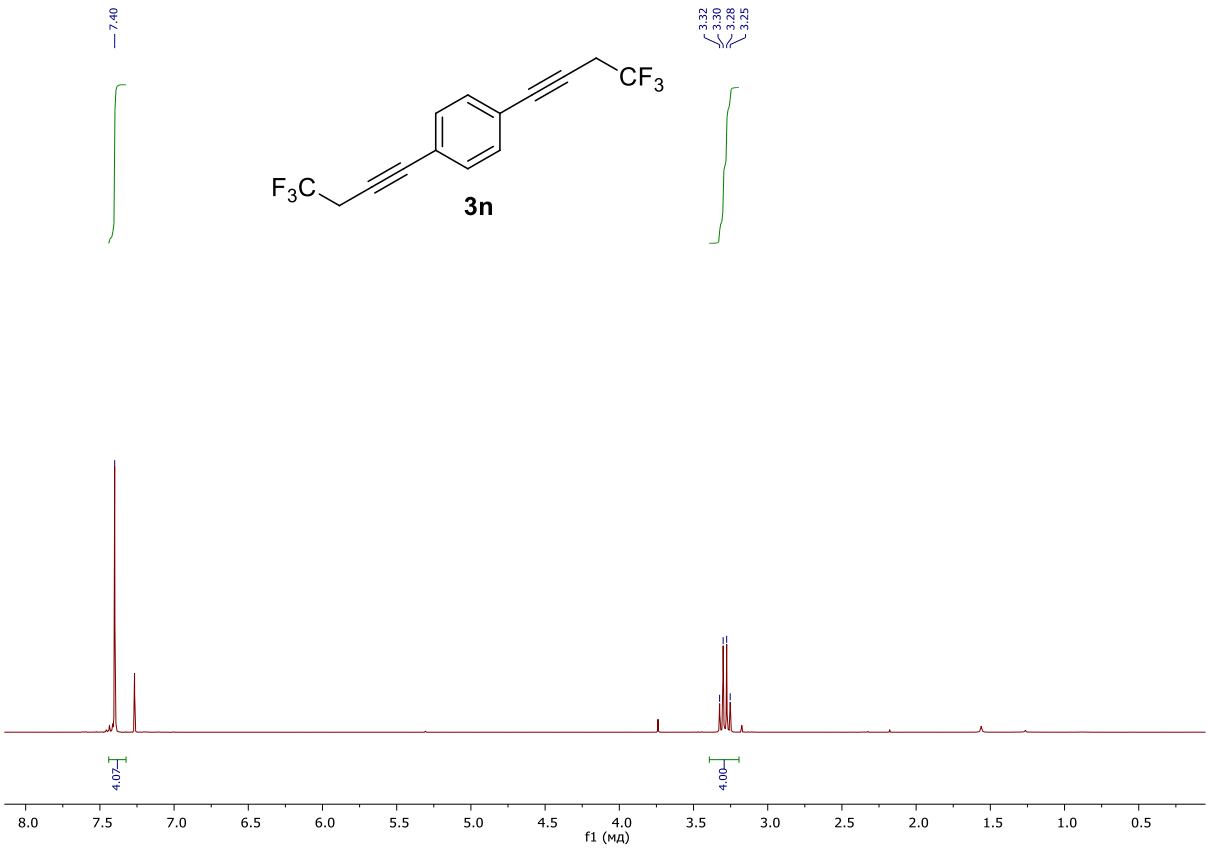
3-(4,4,4-trifluorobut-1-yn-1-yl)thiophene (3m) **^{19}F NMR (376 MHz, $CDCl_3$)**



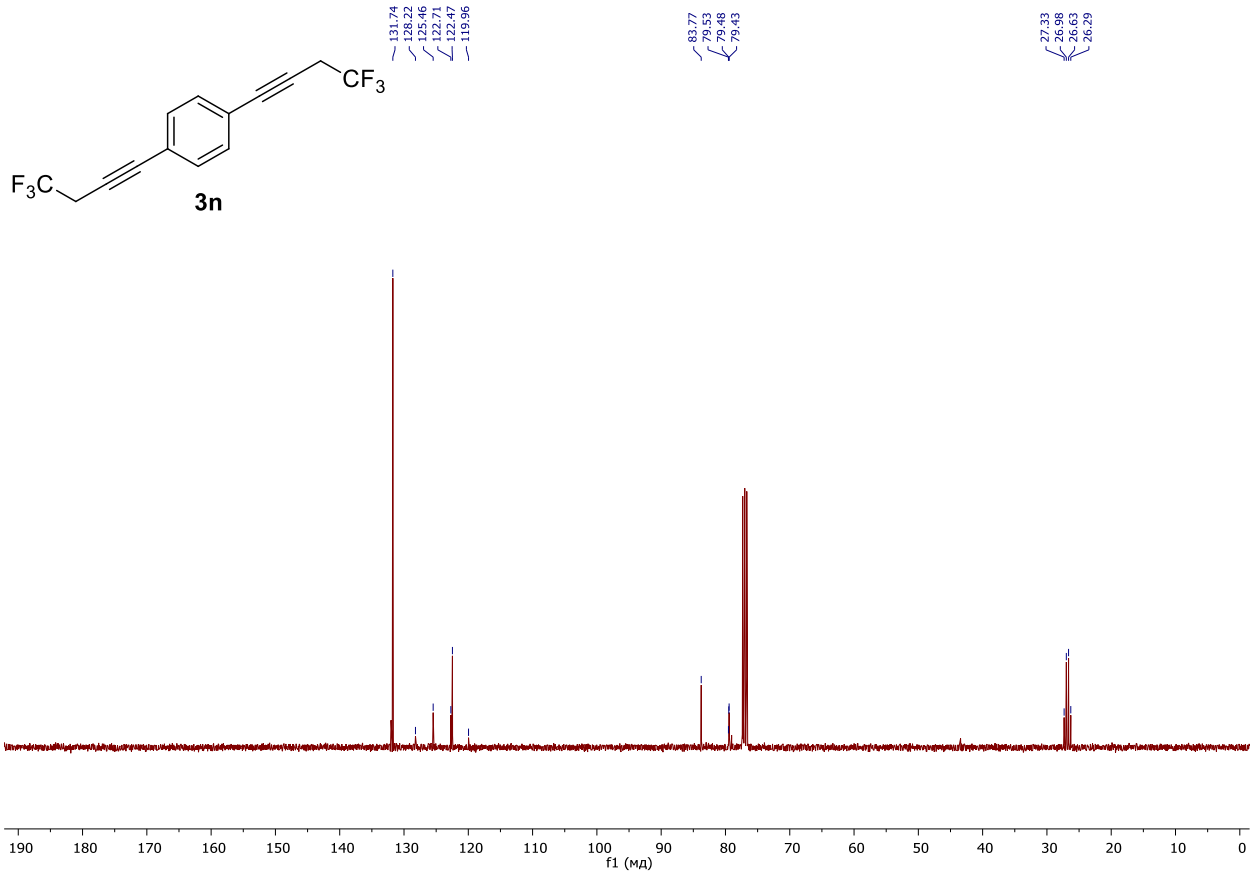
3m



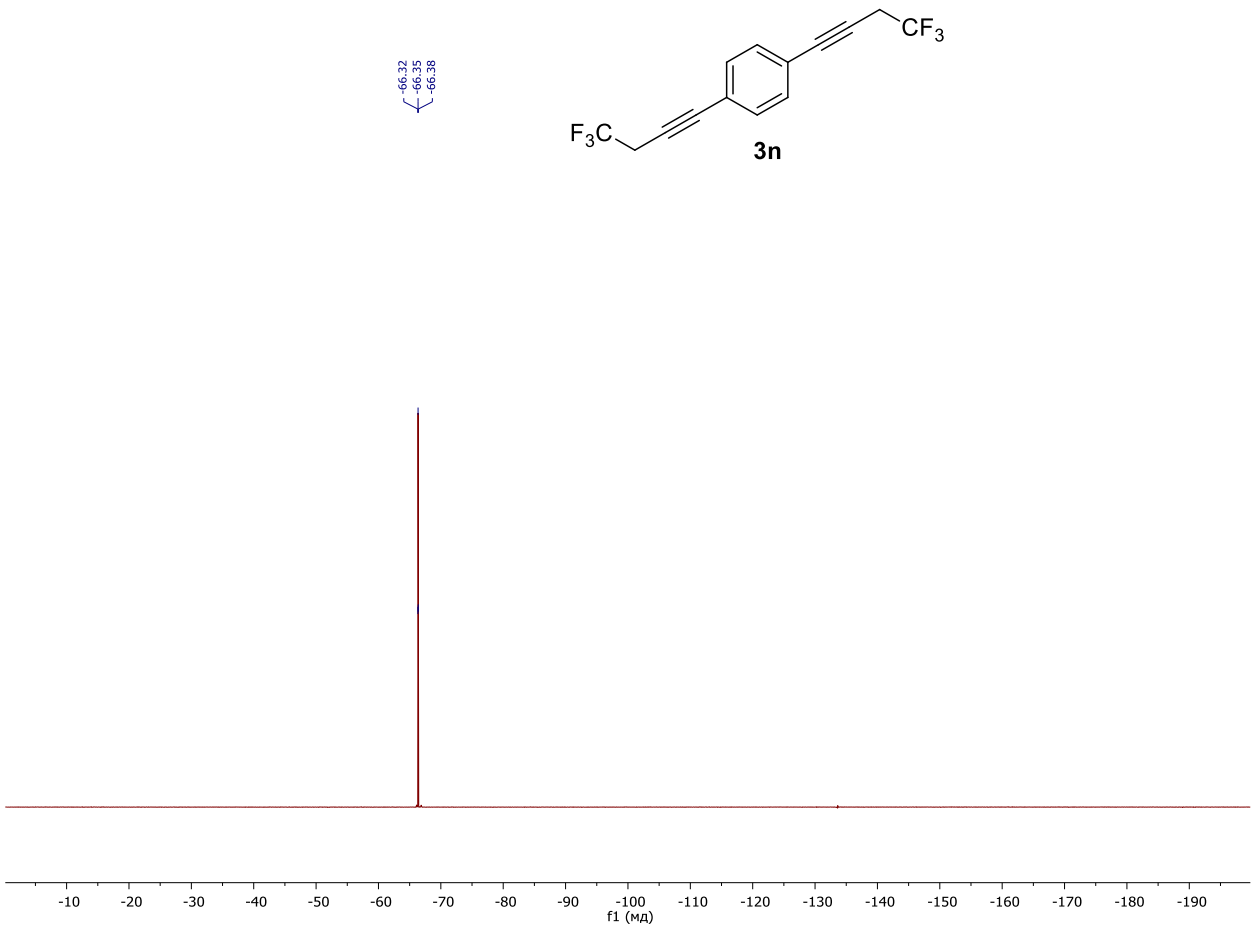
1,4-bis(4,4,4-trifluorobut-1-yn-1-yl)benzene (3n) **^{1}H NMR (400 MHz, $CDCl_3$)**



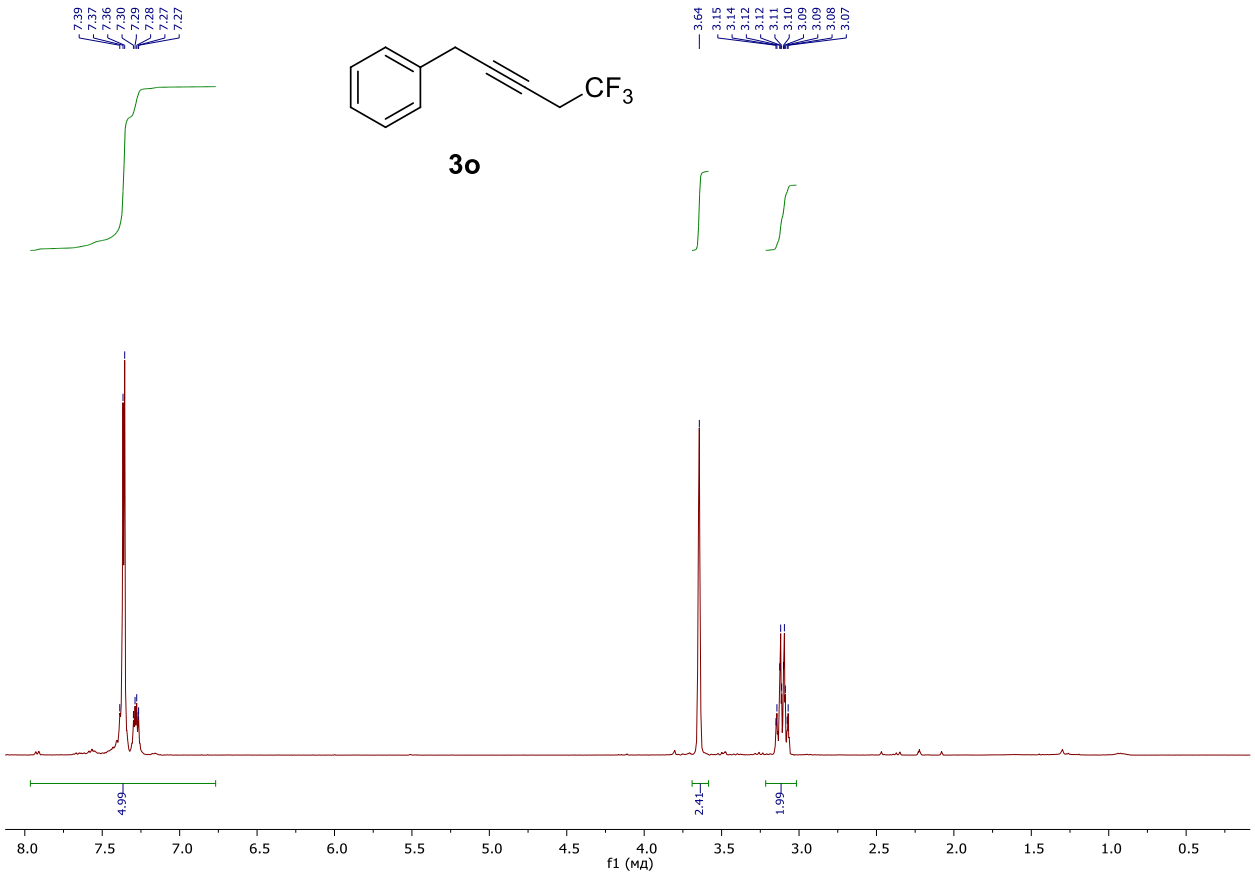
1,4-bis(4,4,4-trifluorobut-1-yn-1-yl)benzene (3n) **^{13}C NMR (100 MHz, $CDCl_3$)**



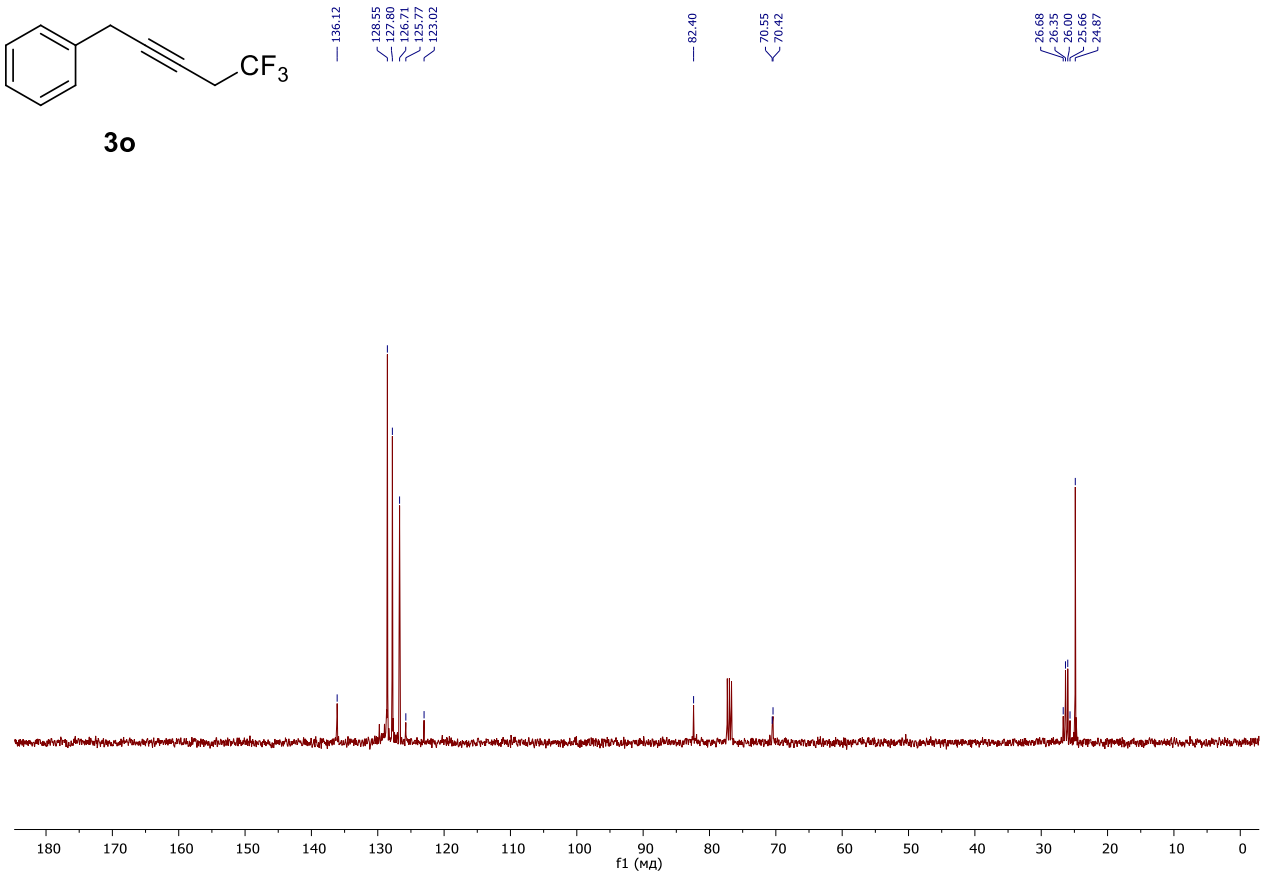
1,4-bis(4,4,4-trifluorobut-1-yn-1-yl)benzene (3n) **^{19}F NMR (376 MHz, $CDCl_3$)**


-66.32
-66.35
-66.38
F3C
CF3
3n
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
f1 (мд)

(5,5,5-trifluoropent-2-yn-1-yl)benzene (3o) **^{1}H NMR (400 MHz, $CDCl_3$)**

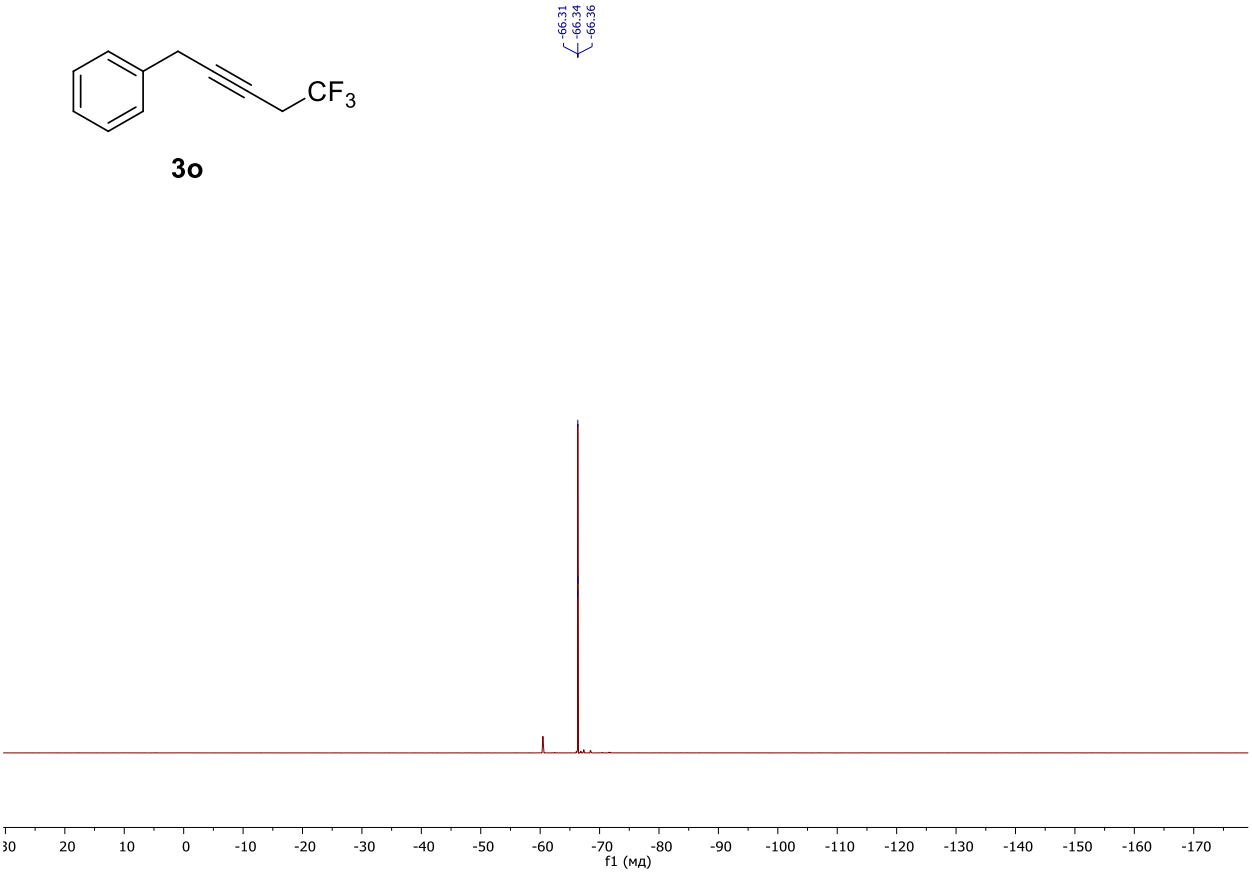


(5,5,5-trifluoropent-2-yn-1-yl)benzene (3o) **^{13}C NMR (100 MHz, $CDCl_3$)**

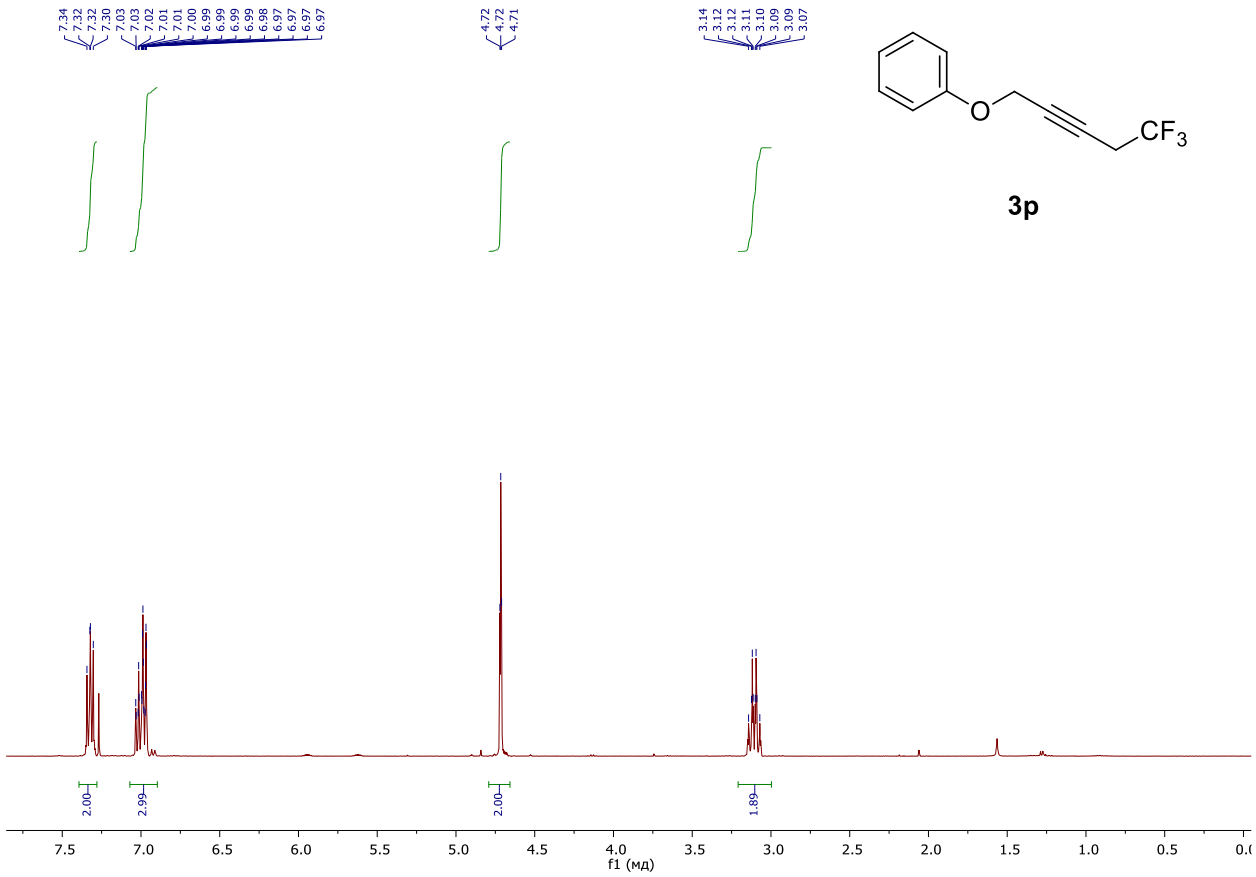


(5,5,5-trifluoropent-2-yn-1-yl)benzene (3o) **^{19}F NMR (376 MHz, $CDCl_3$)**

3o

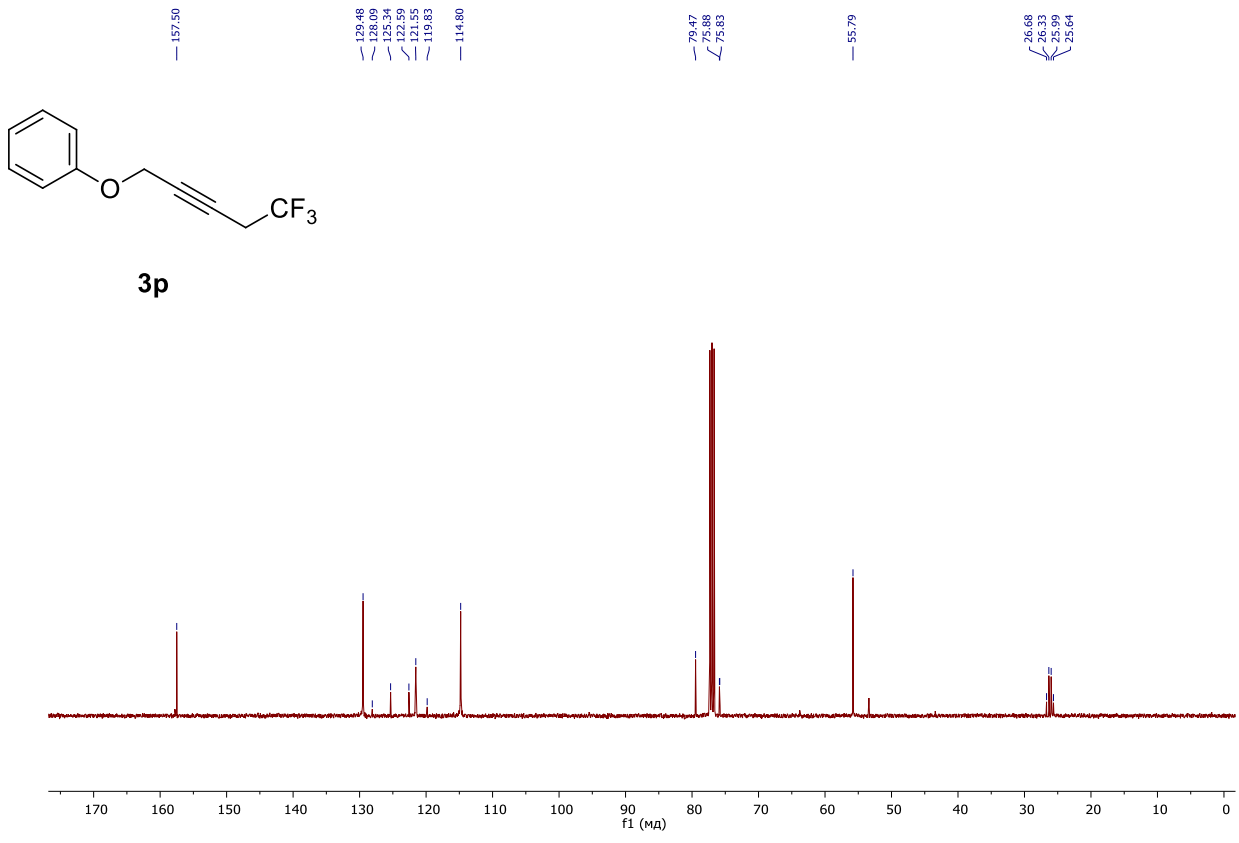


(5,5,5-trifluoropent-2-yn-1-yloxy)benzene (3p) **^{1}H NMR (400 MHz, $CDCl_3$)**



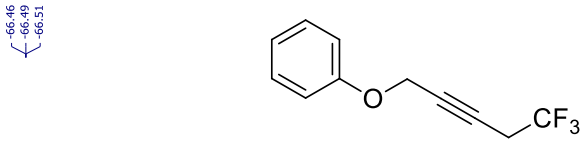
3p

(5,5,5-trifluoropent-2-yn-1-yloxy)benzene (3p) **^{13}C NMR (100 MHz, $CDCl_3$)**

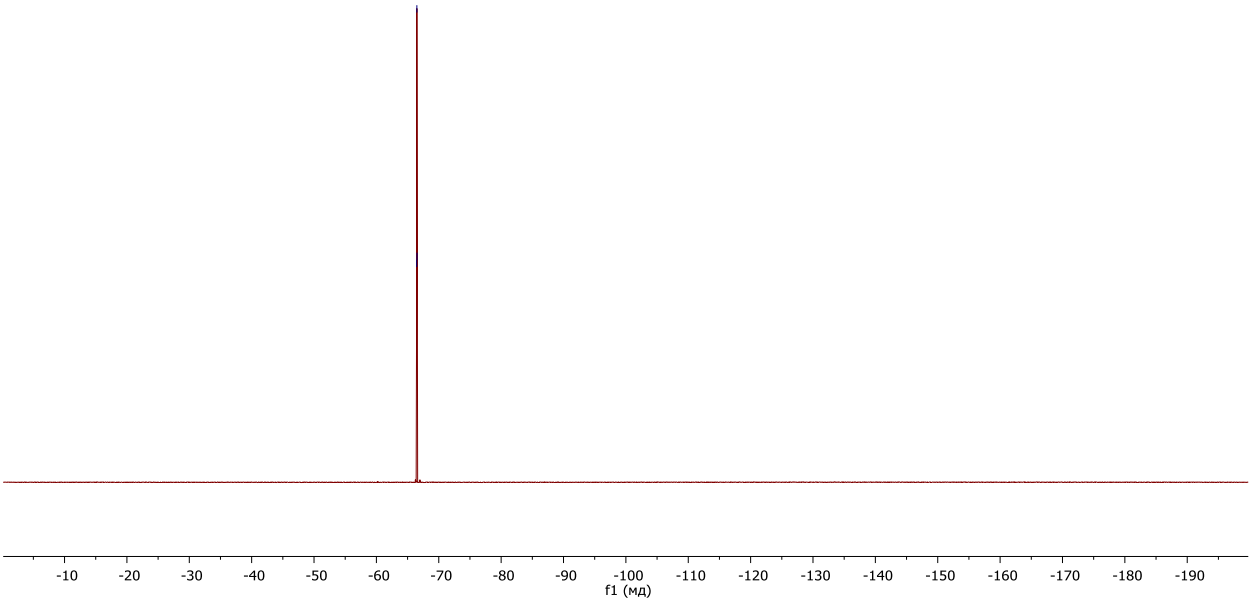


3p

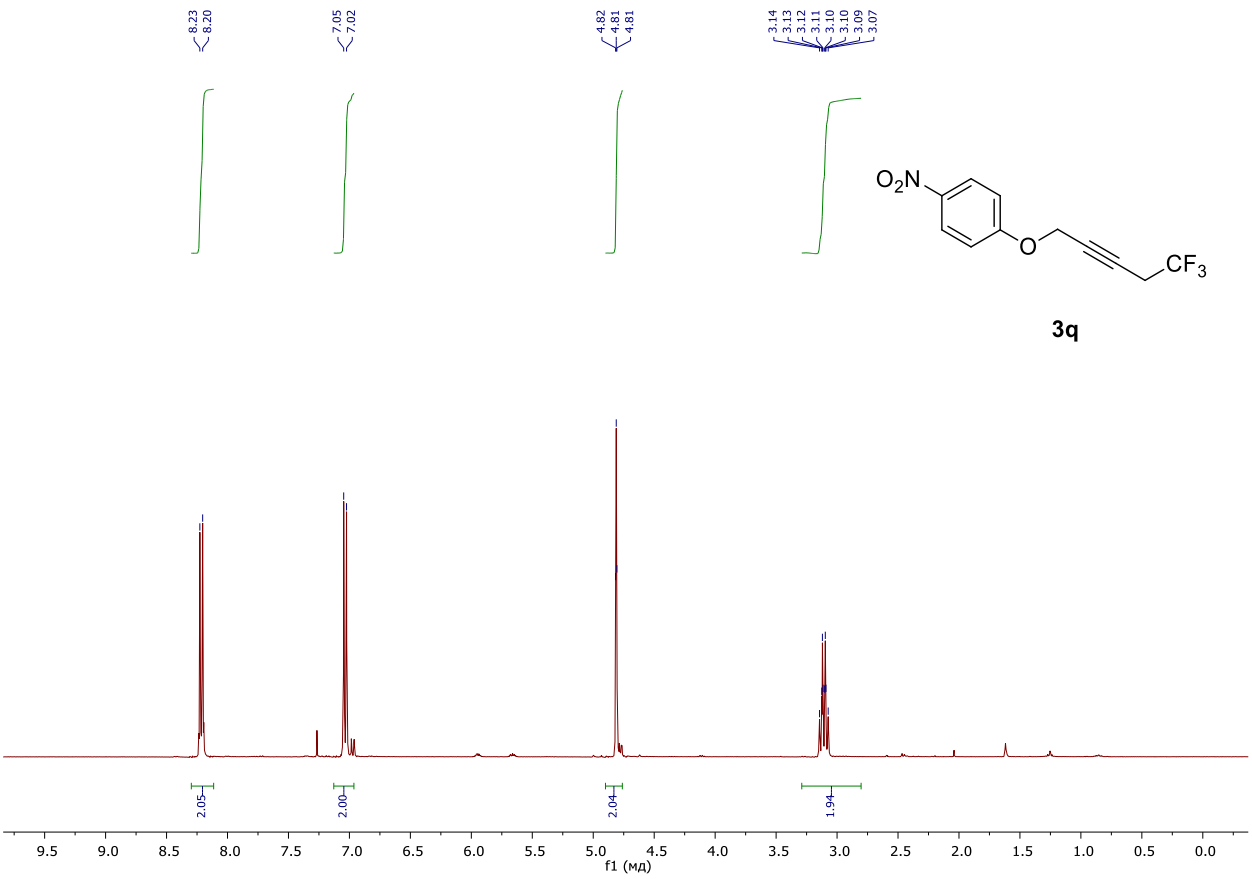
(5,5,5-trifluoropent-2-yn-1-yloxy)benzene (3p) **^{19}F NMR (376 MHz, $CDCl_3$)**



3p

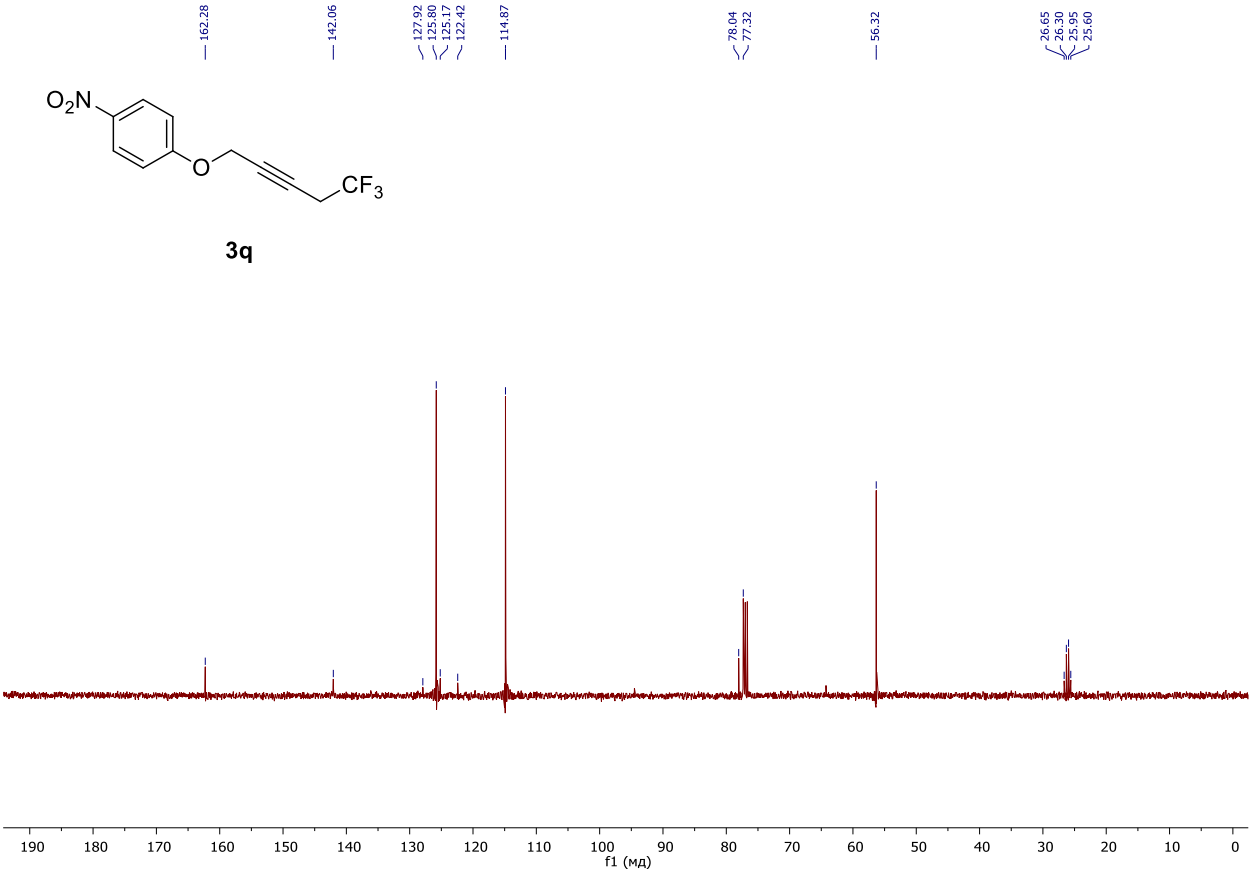


4-nitro-1-(5,5,5-trifluoropent-2-yn-1-yloxy)benzene (3q) **^{1}H NMR (400 MHz, $CDCl_3$)**



3q

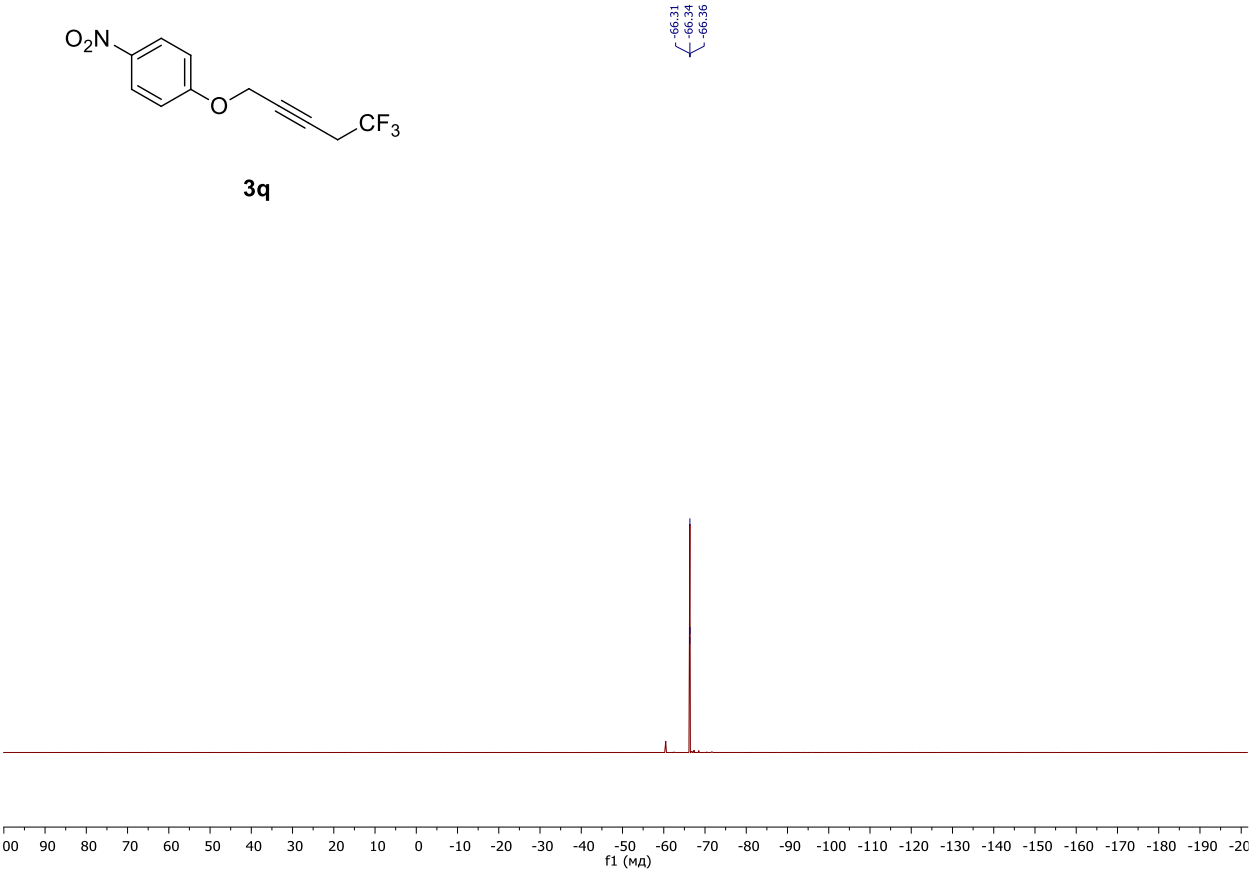
4-nitro-1-(5,5,5-trifluoropent-2-yn-1-yloxy)benzene (3q) **^{13}C NMR (100 MHz, $CDCl_3$)**



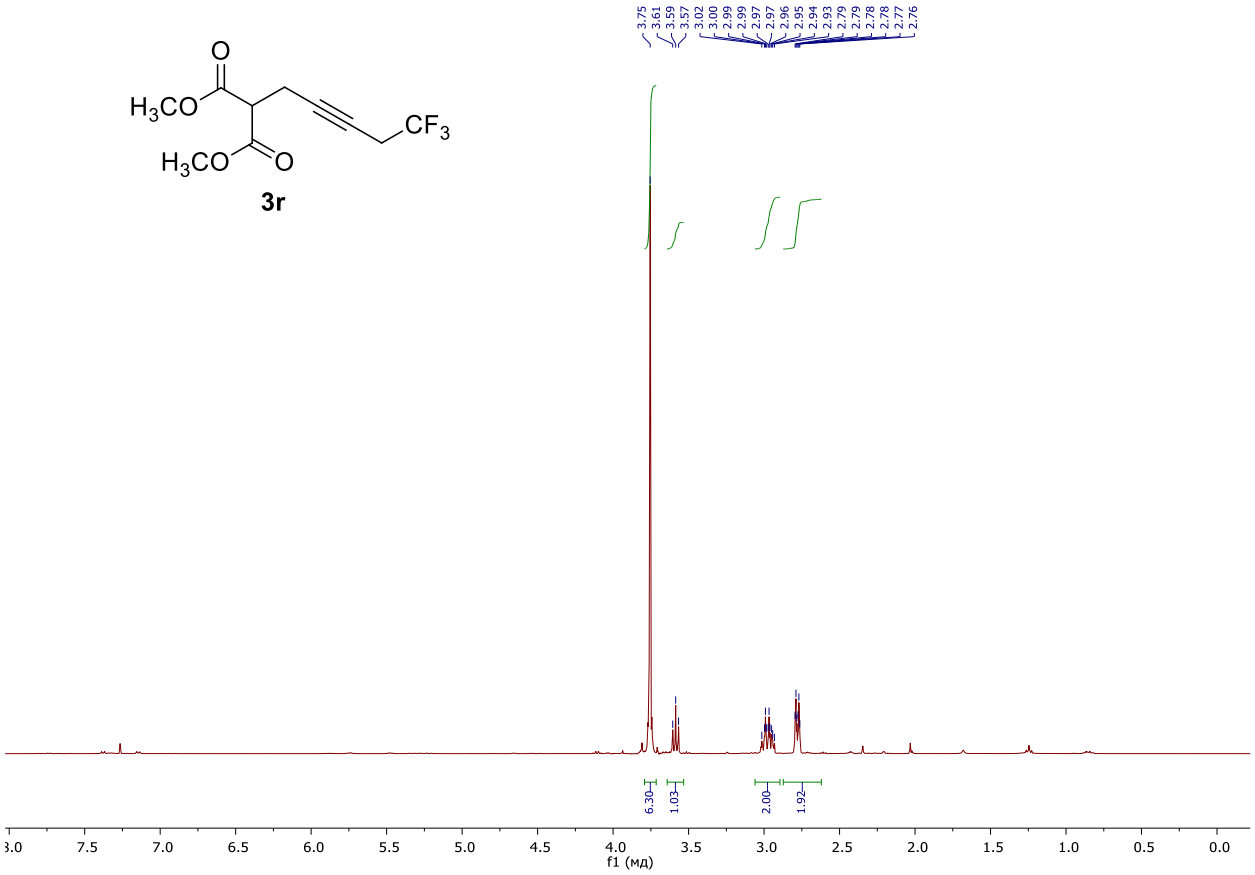
3q

4-nitro-1-(5,5,5-trifluoropent-2-yn-1-yloxy)benzene (3q) **^{19}F NMR (376 MHz, $CDCl_3$)**

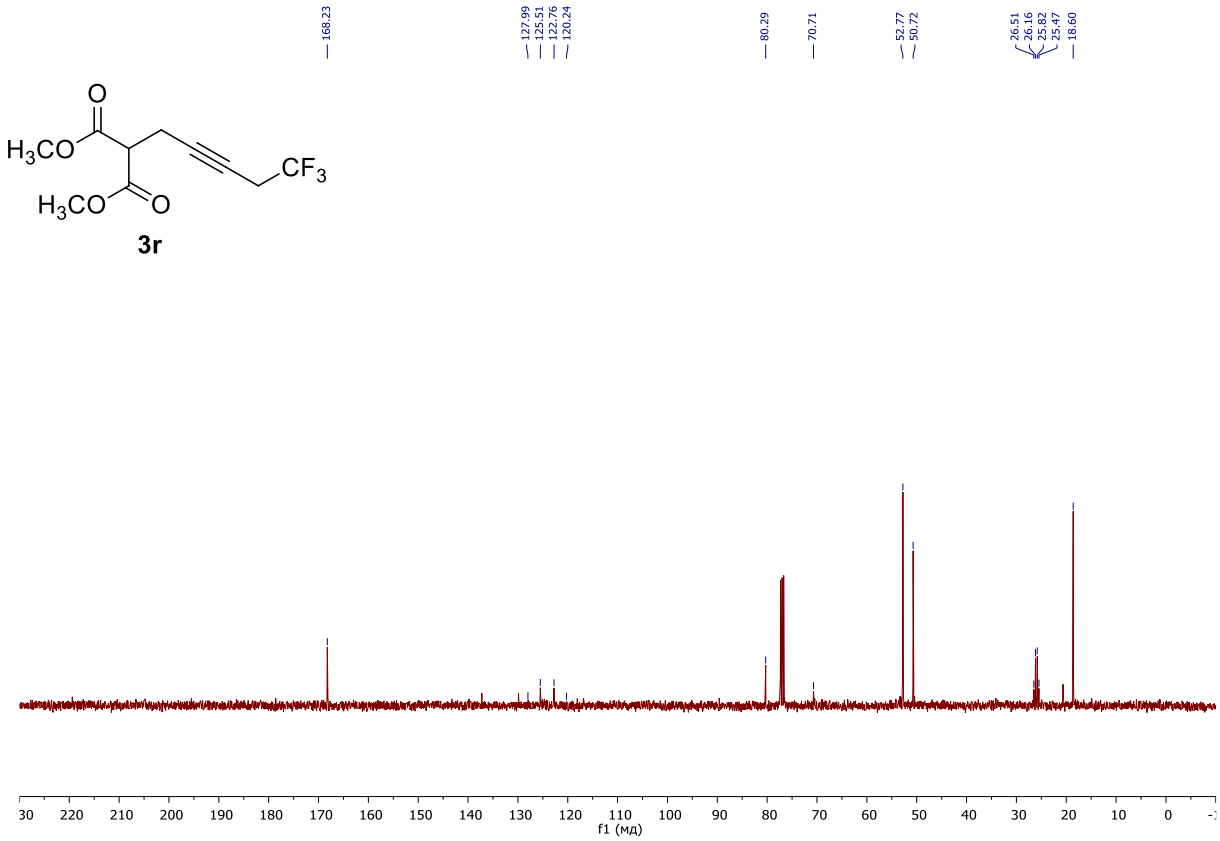
3q



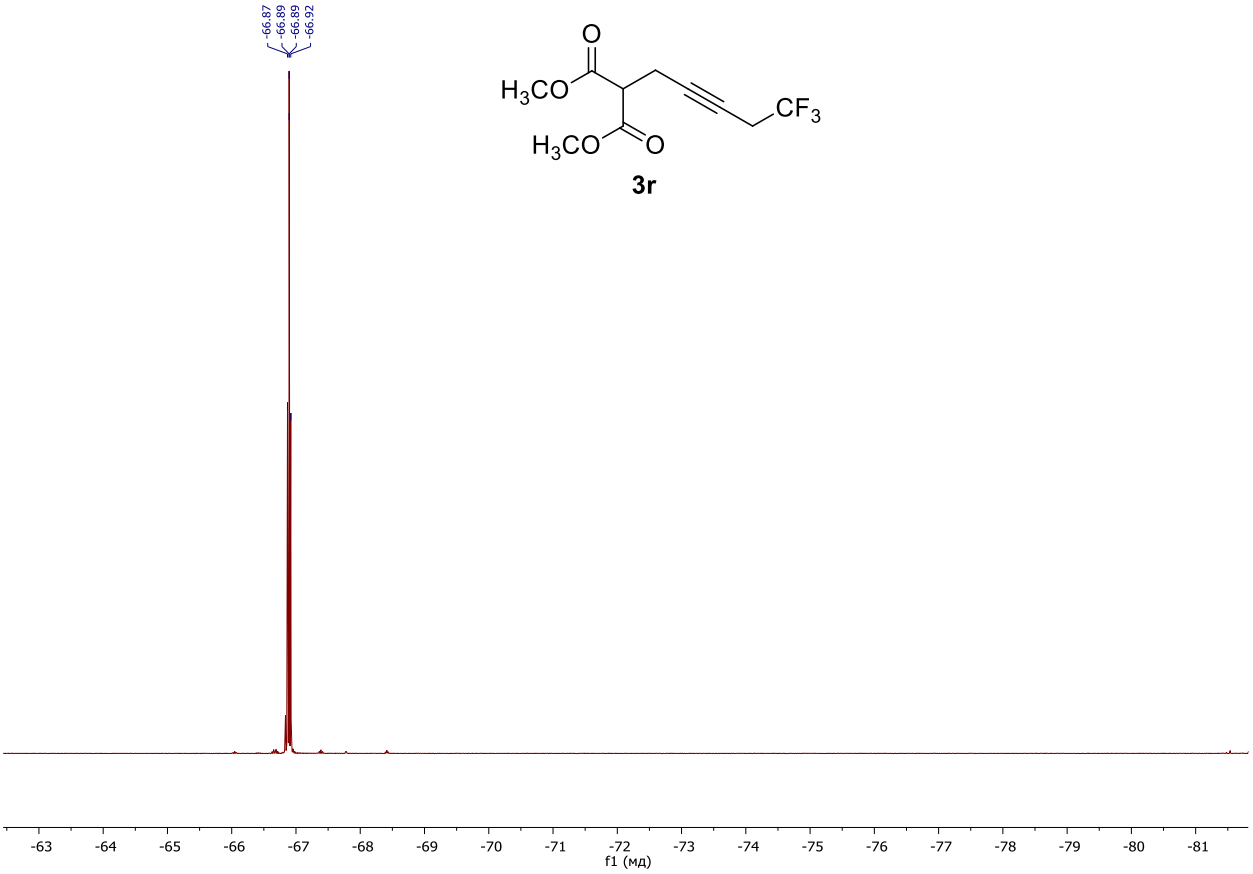
dimethyl 2-(5,5,5-trifluoropent-2-yn-1-yl)malonate (3r) **^{1}H NMR (400 MHz, $CDCl_3$)**



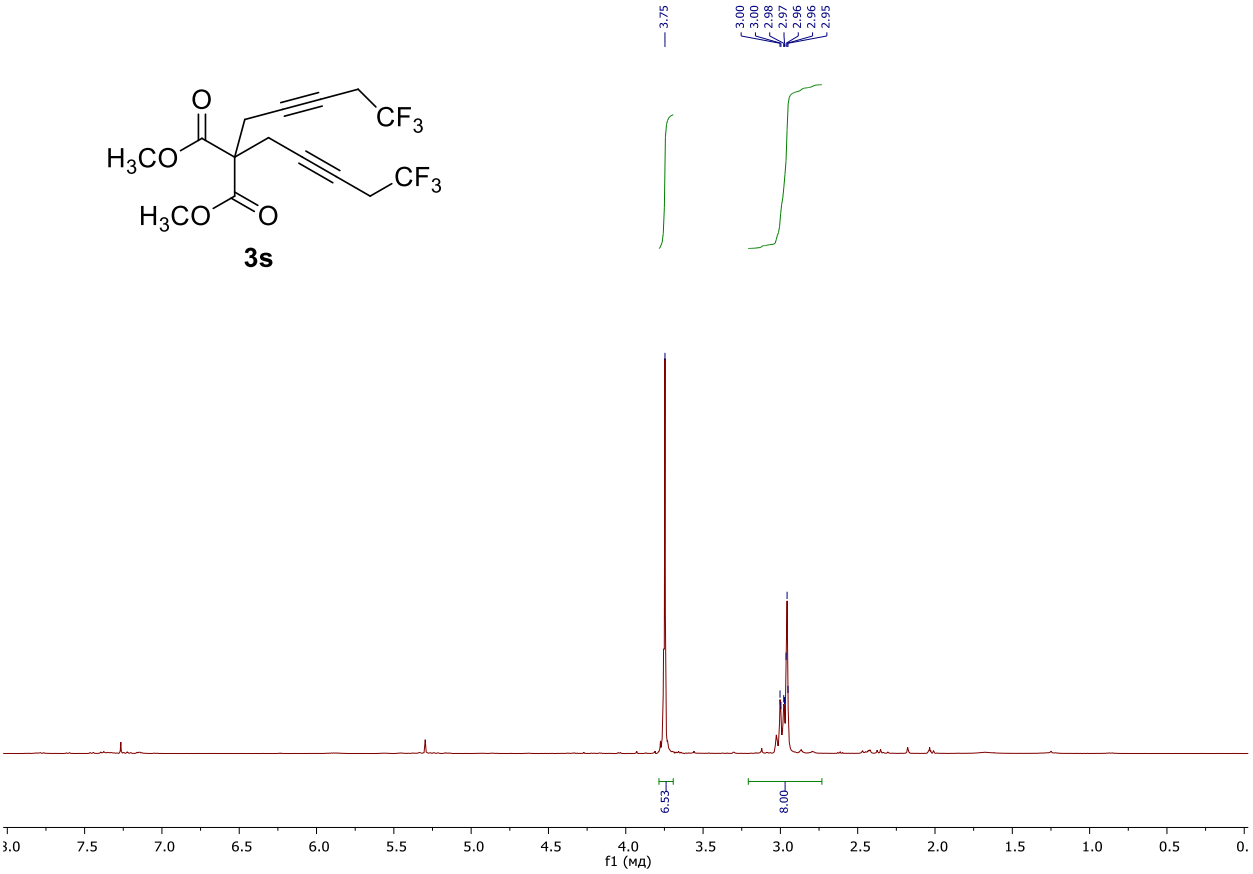
dimethyl 2-(5,5,5-trifluoropent-2-yn-1-yl)malonate (3r) **^{13}C NMR (100 MHz, $CDCl_3$)**



dimethyl 2-(5,5,5-trifluoropent-2-yn-1-yl)malonate (3r) **^{19}F NMR (376 MHz, $CDCl_3$)**

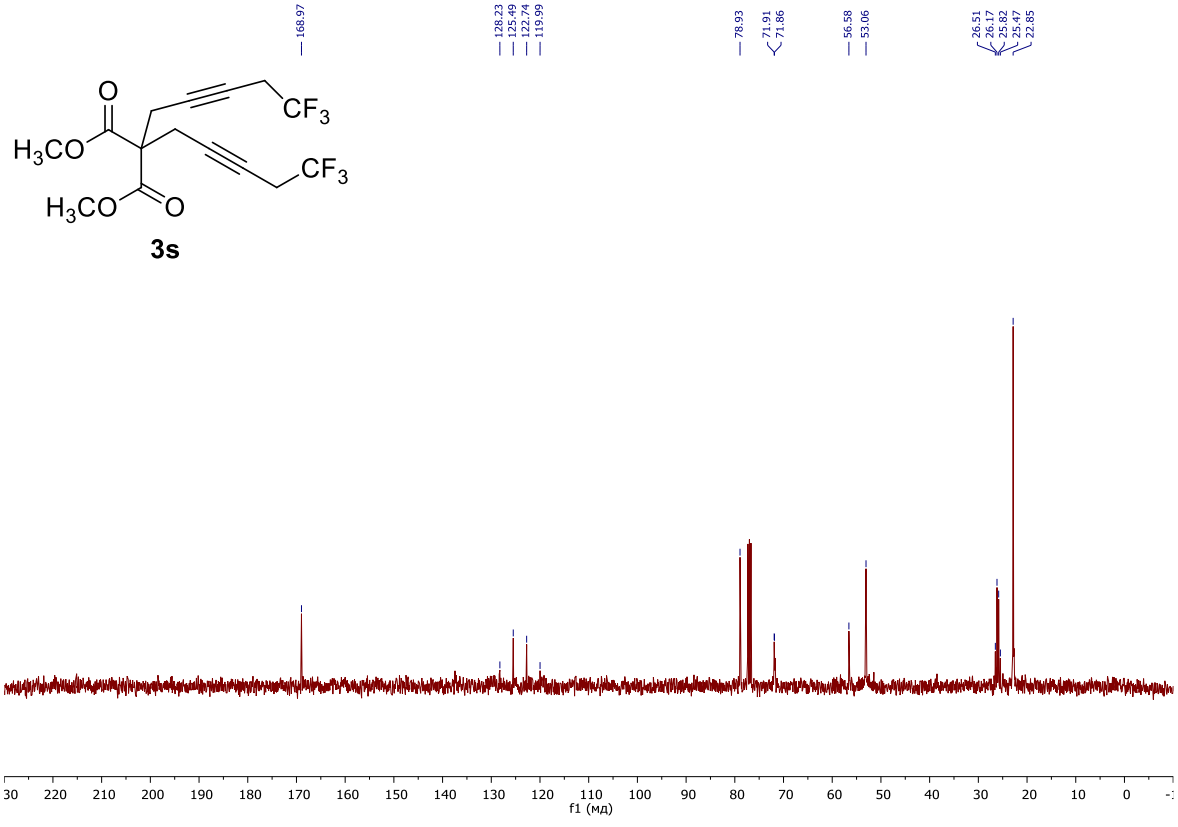


dimethyl 2,2-bis(5,5,5-trifluoropent-2-yn-1-yl)malonate (3s) **^{1}H NMR (400 MHz, $CDCl_3$)**



3s

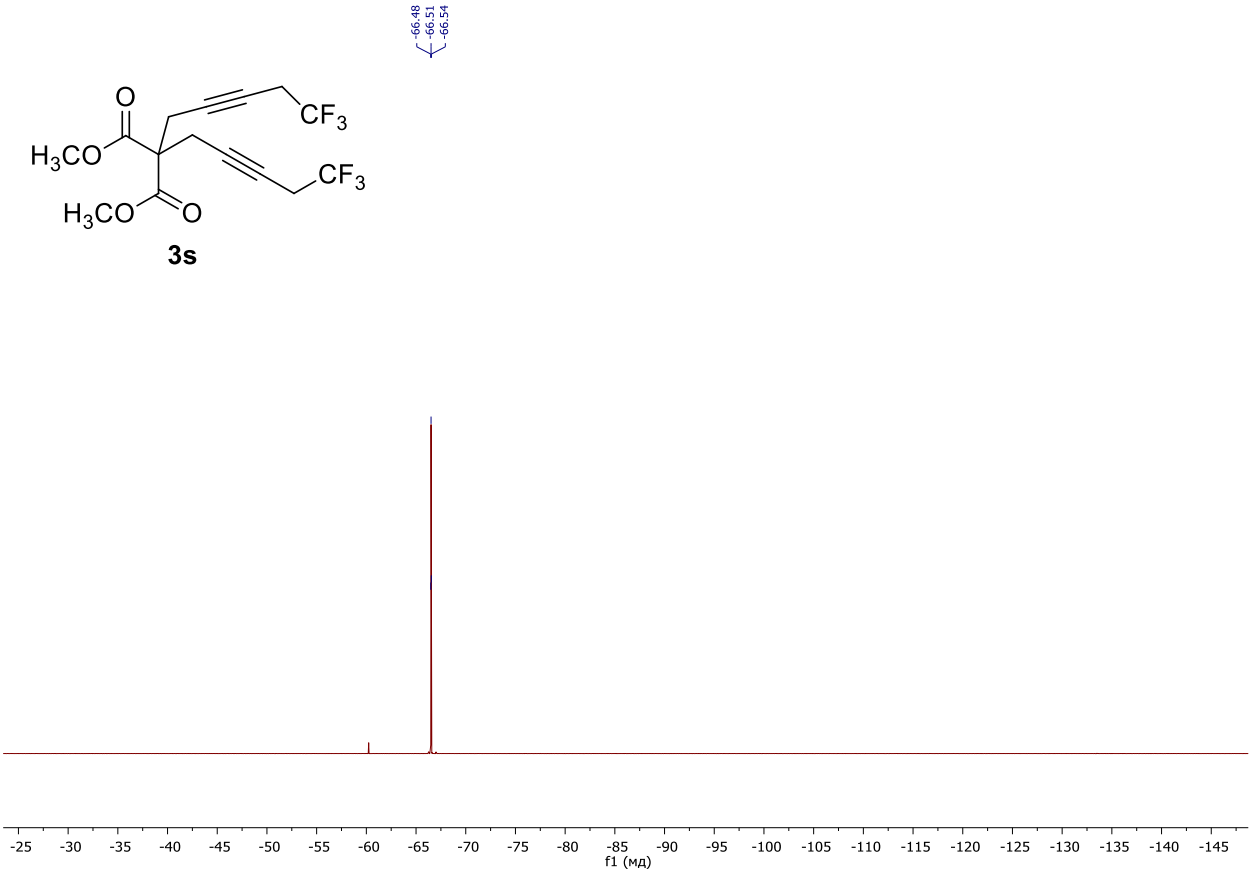
dimethyl 2,2-bis(5,5,5-trifluoropent-2-yn-1-yl)malonate (3s) **^{13}C NMR (100 MHz, $CDCl_3$)**



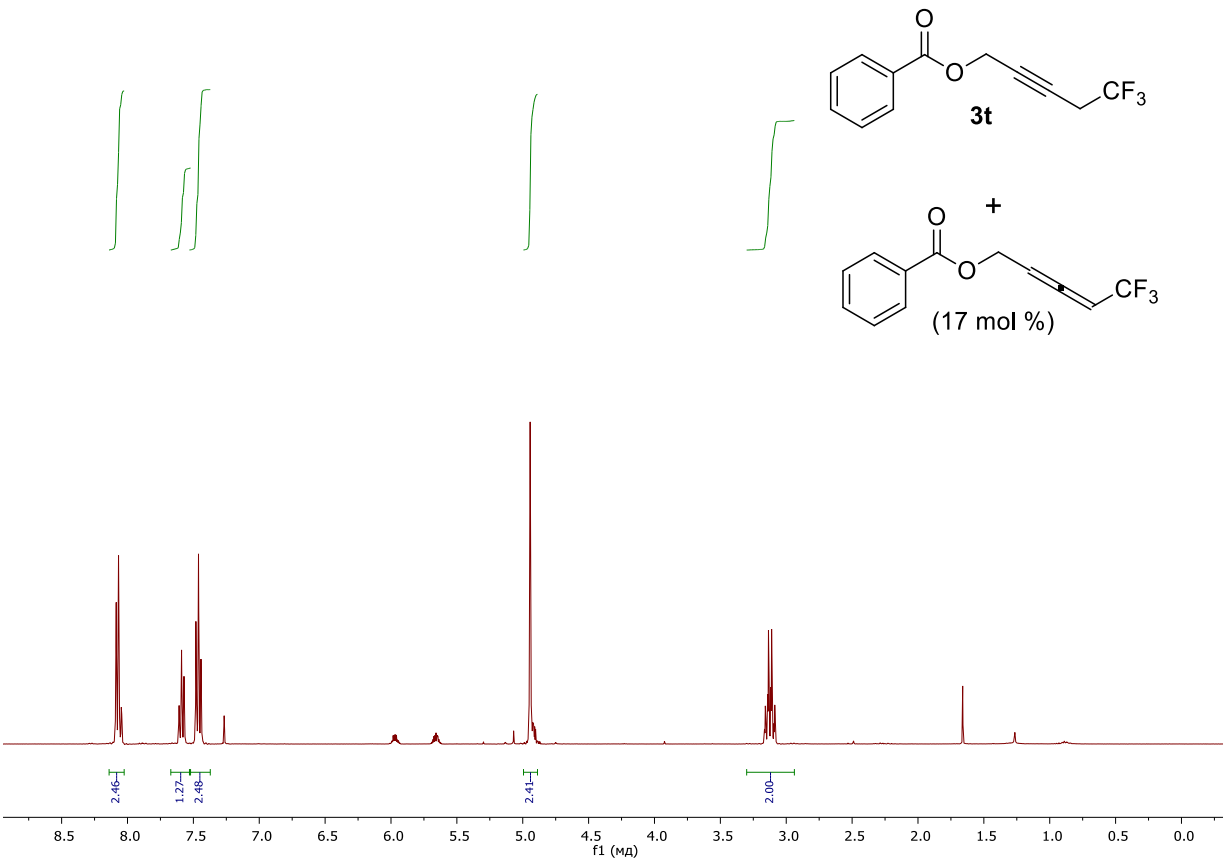
3s

dimethyl 2,2-bis(5,5,5-trifluoropent-2-yn-1-yl)malonate (3s) **^{19}F NMR (376 MHz, $CDCl_3$)**

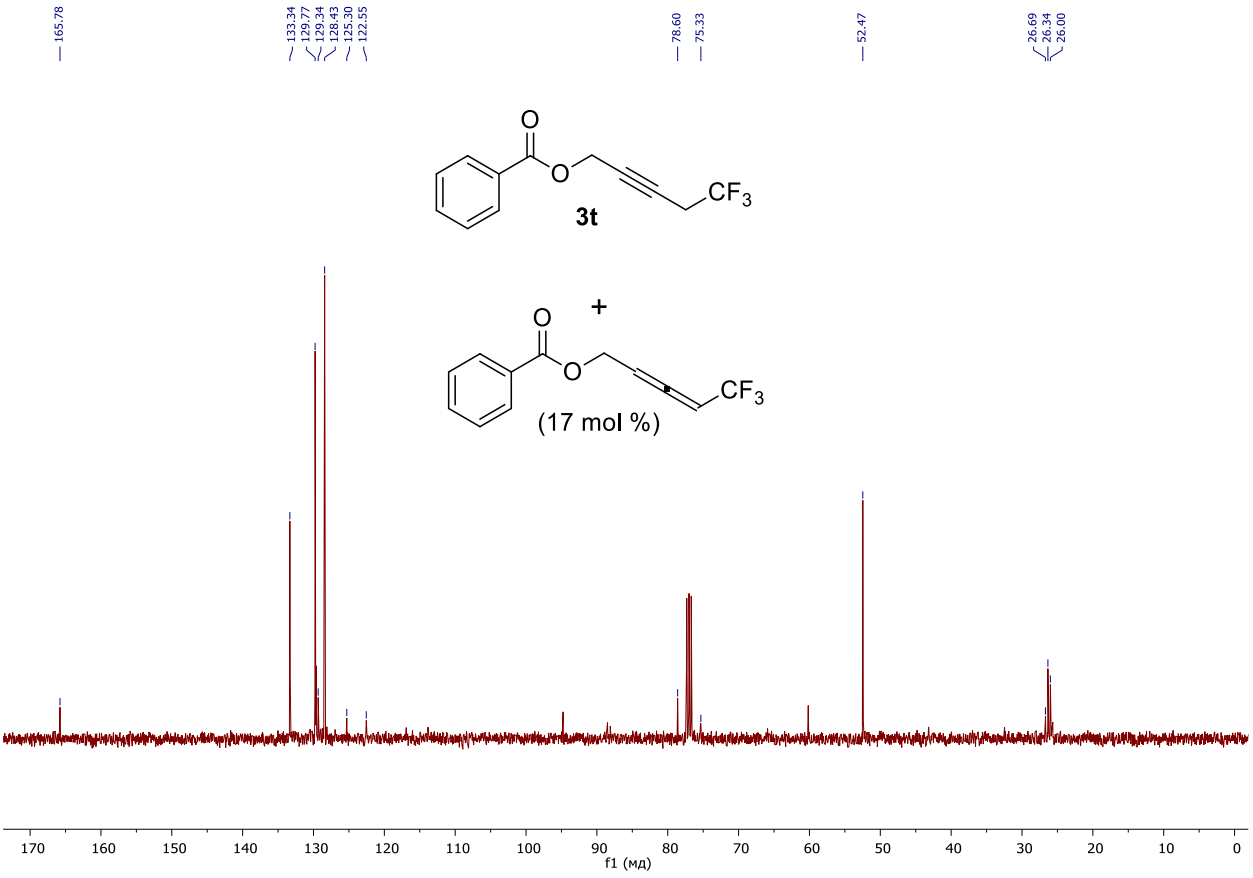
3s



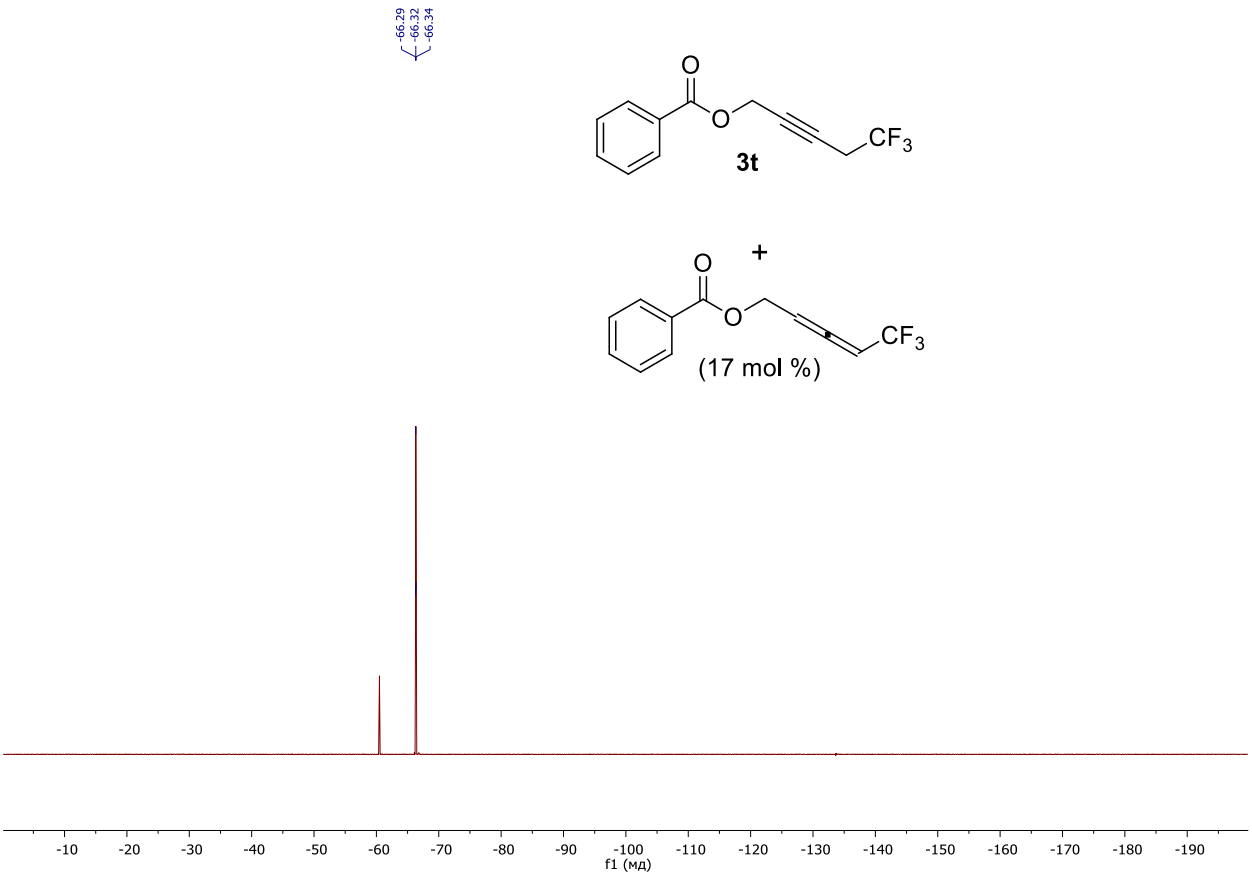
5,5,5-trifluoropent-2-yn-1-yl benzoate (3t) **^{1}H NMR (400 MHz, $CDCl_3$)**



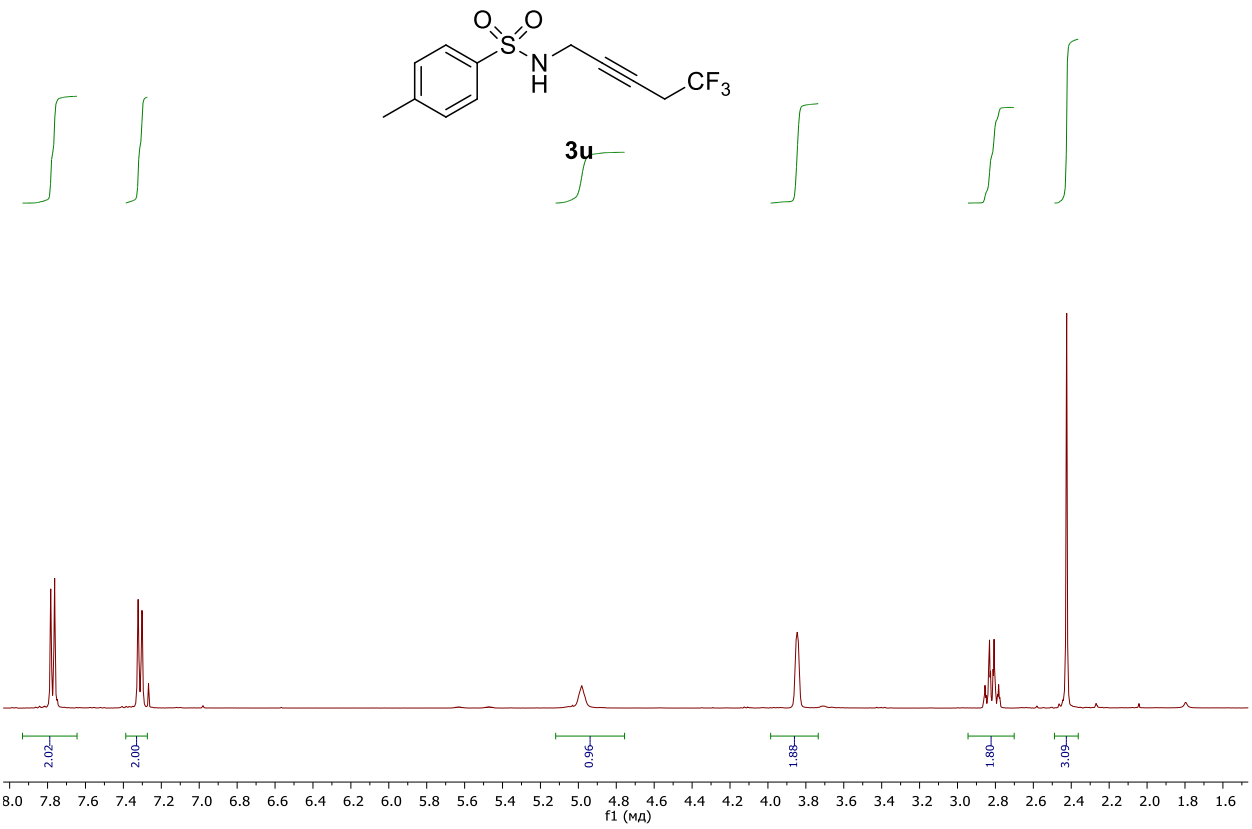
5,5,5-trifluoropent-2-yn-1-yl benzoate (3t) **^{13}C NMR (100 MHz, $CDCl_3$)**



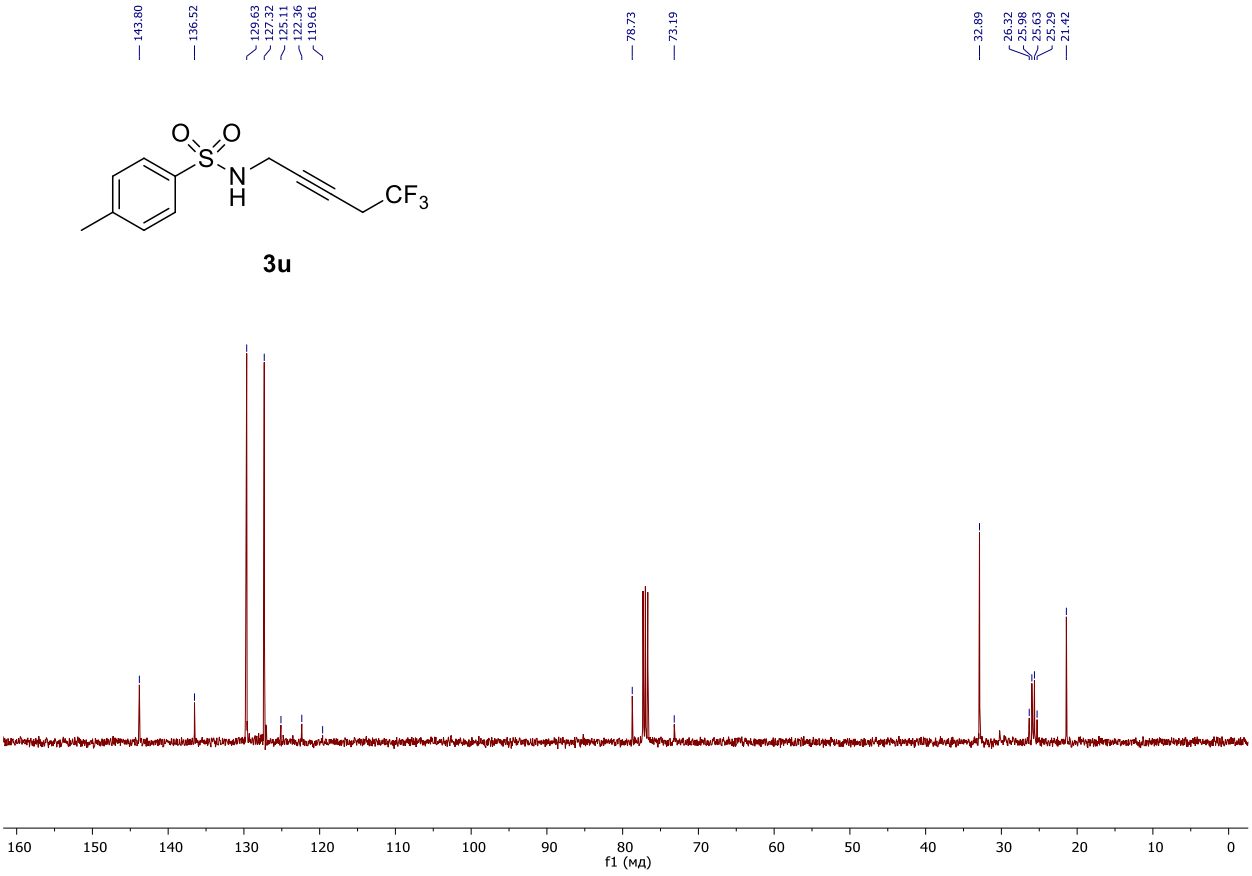
5,5,5-trifluoropent-2-yn-1-yl benzoate (3t) **^{19}F NMR (376 MHz, $CDCl_3$)**



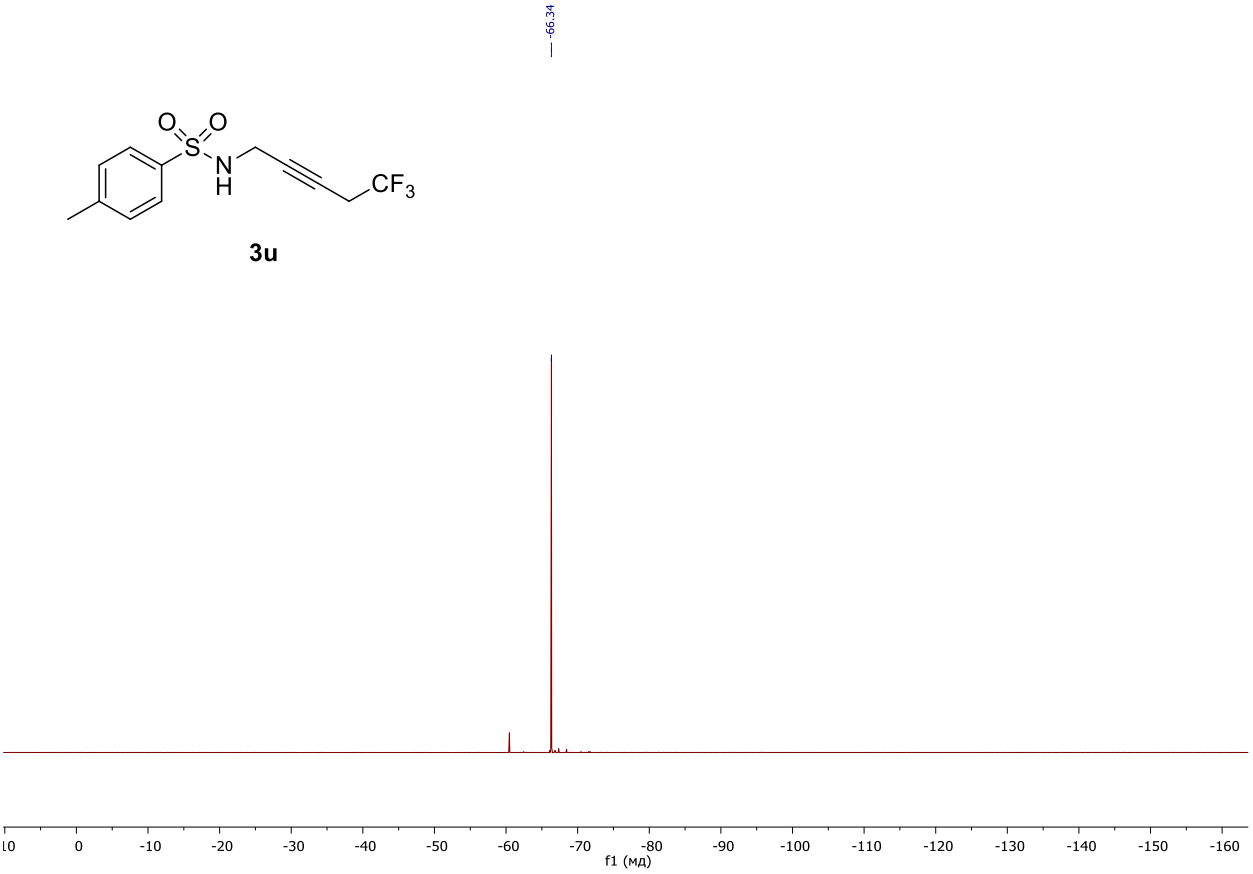
4-methyl-*N*-(5,5,5-trifluoropent-2-yn-1-yl)benzenesulfonamide (3u) ^{1}H NMR (400 MHz, $CDCl_3$)



4-methyl-*N*-(5,5,5-trifluoropent-2-yn-1-yl)benzenesulfonamide (3u) ^{13}C NMR (100 MHz, $CDCl_3$)

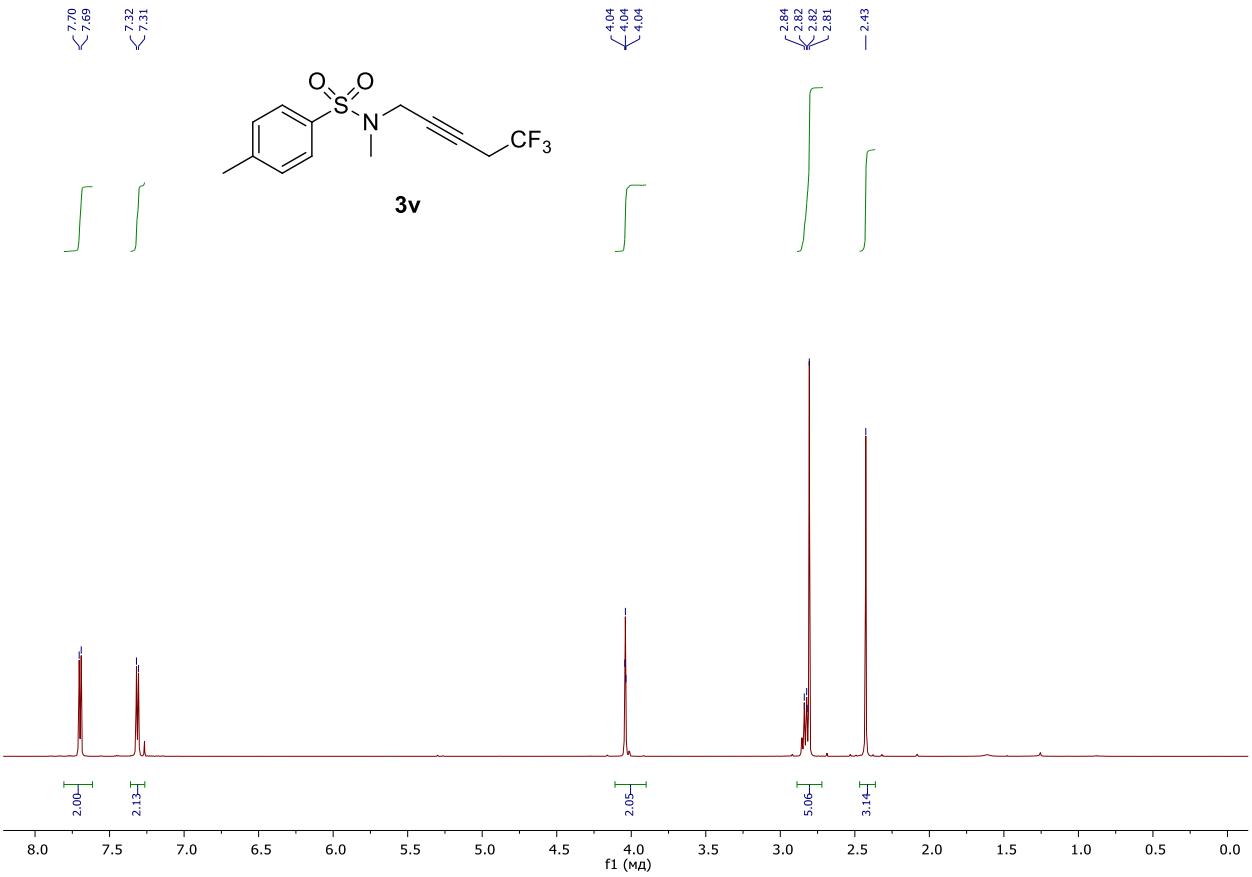


4-methyl-*N*-(5,5,5-trifluoropent-2-yn-1-yl)benzenesulfonamide (3u) ^{19}F NMR (376 MHz, $CDCl_3$)

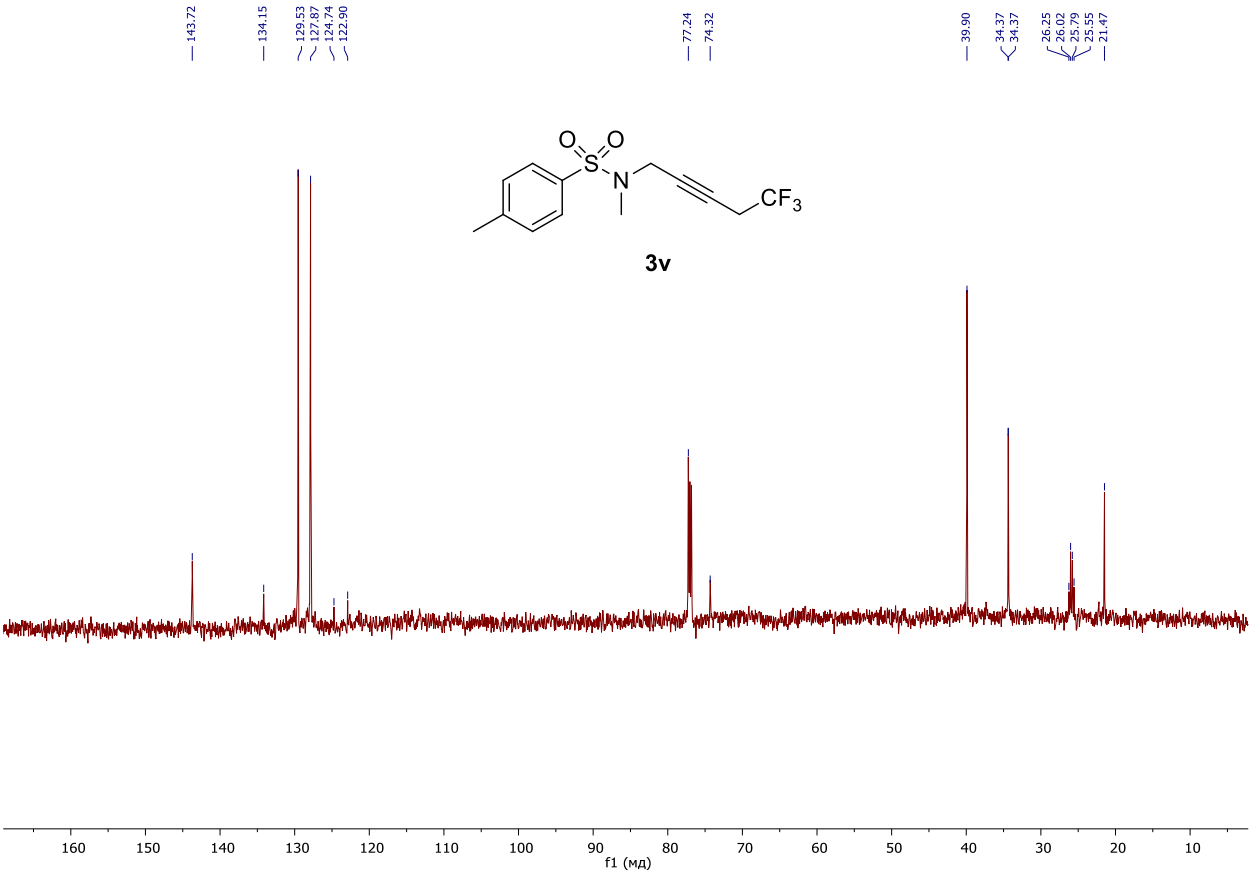


3u

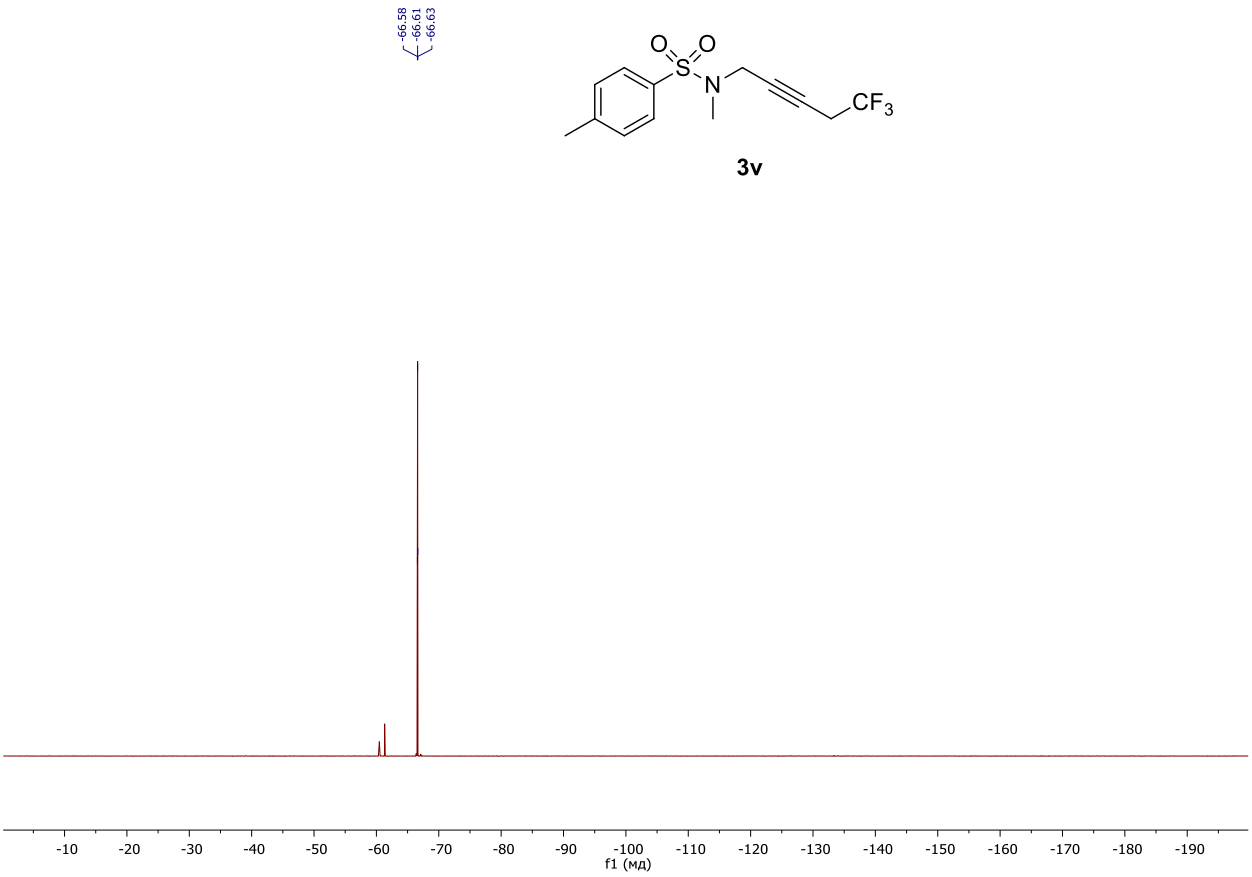
N,4-dimethyl-*N*-(5,5,5-trifluoropent-2-yn-1-yl)benzenesulfonamide (3v) ^{1}H NMR (400 MHz, $CDCl_3$)



N,4-dimethyl-*N*-(5,5,5-trifluoropent-2-yn-1-yl)benzenesulfonamide (3v) ^{13}C NMR (100 MHz, $CDCl_3$)

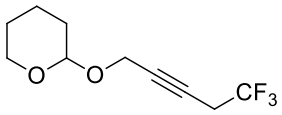


N,4-dimethyl-*N*-(5,5,5-trifluoropent-2-yn-1-yl)benzenesulfonamide (3v) ^{19}F NMR (376 MHz, $CDCl_3$)

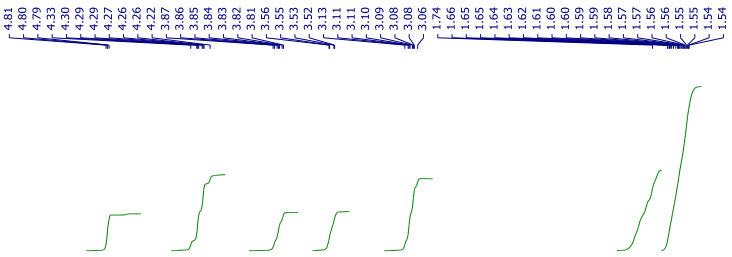


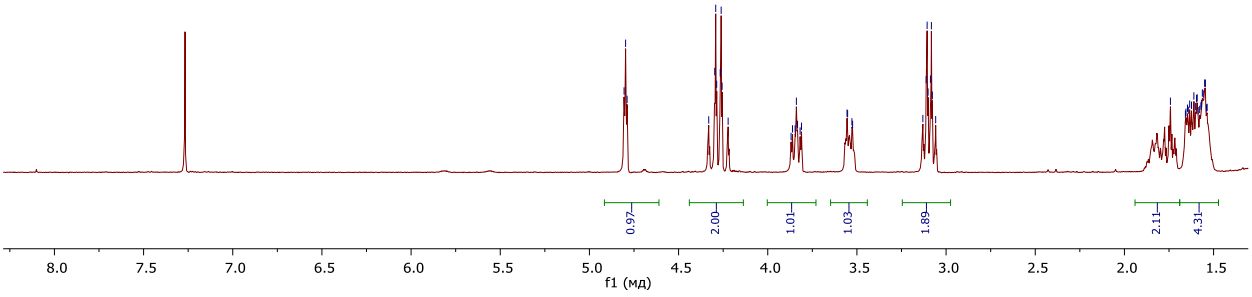
3v

2-[(5,5,5-trifluoropent-2-yn-1-yl)oxy]tetrahydro-2*H*-pyran (3w) **^{1}H NMR (400 MHz, $CDCl_3$)**

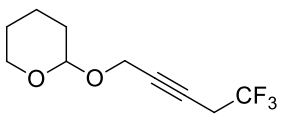


3w

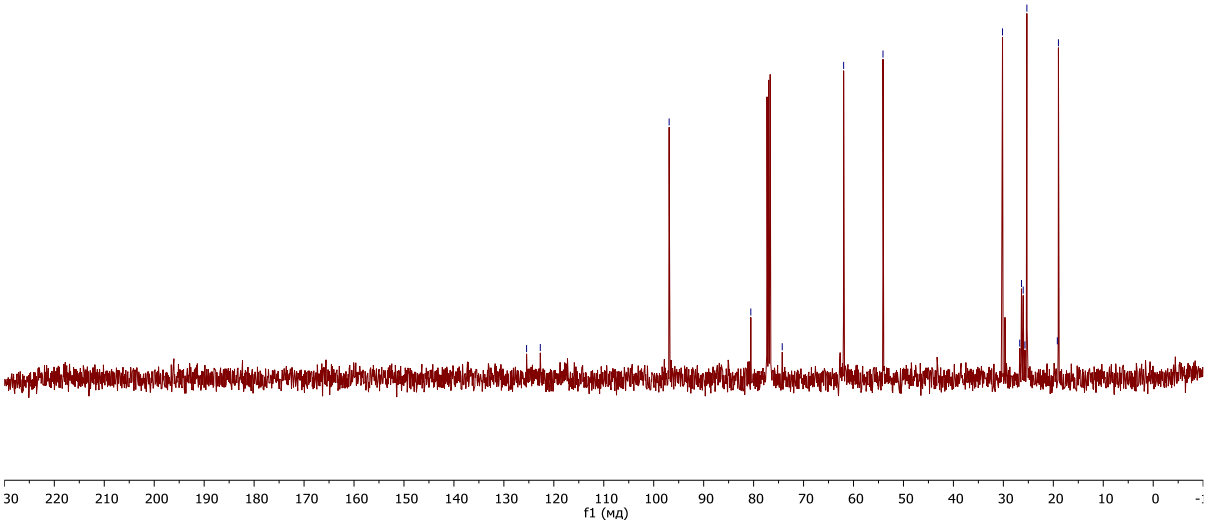




2-[(5,5,5-trifluoropent-2-yn-1-yl)oxy]tetrahydro-2*H*-pyran (3w) **^{13}C NMR (100 MHz, $CDCl_3$)**

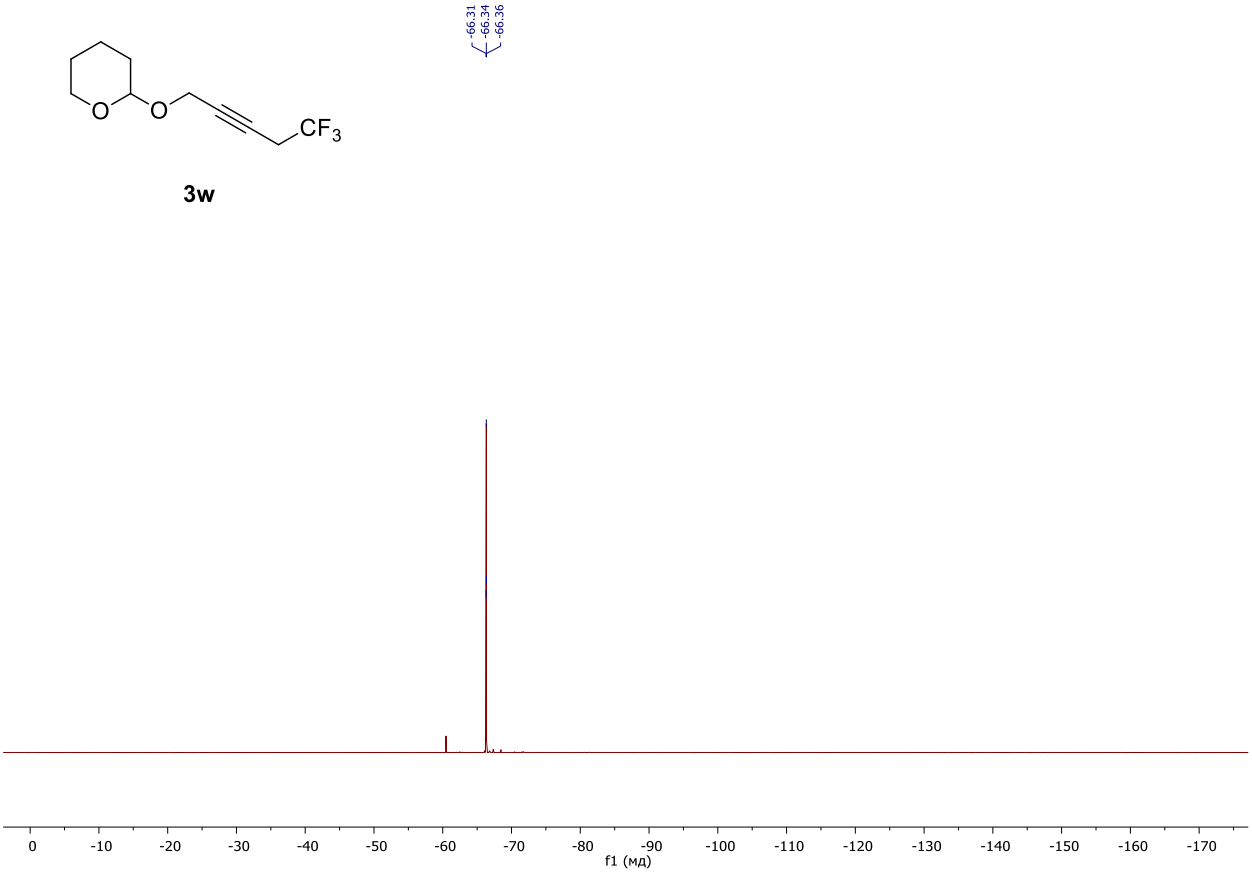


3w

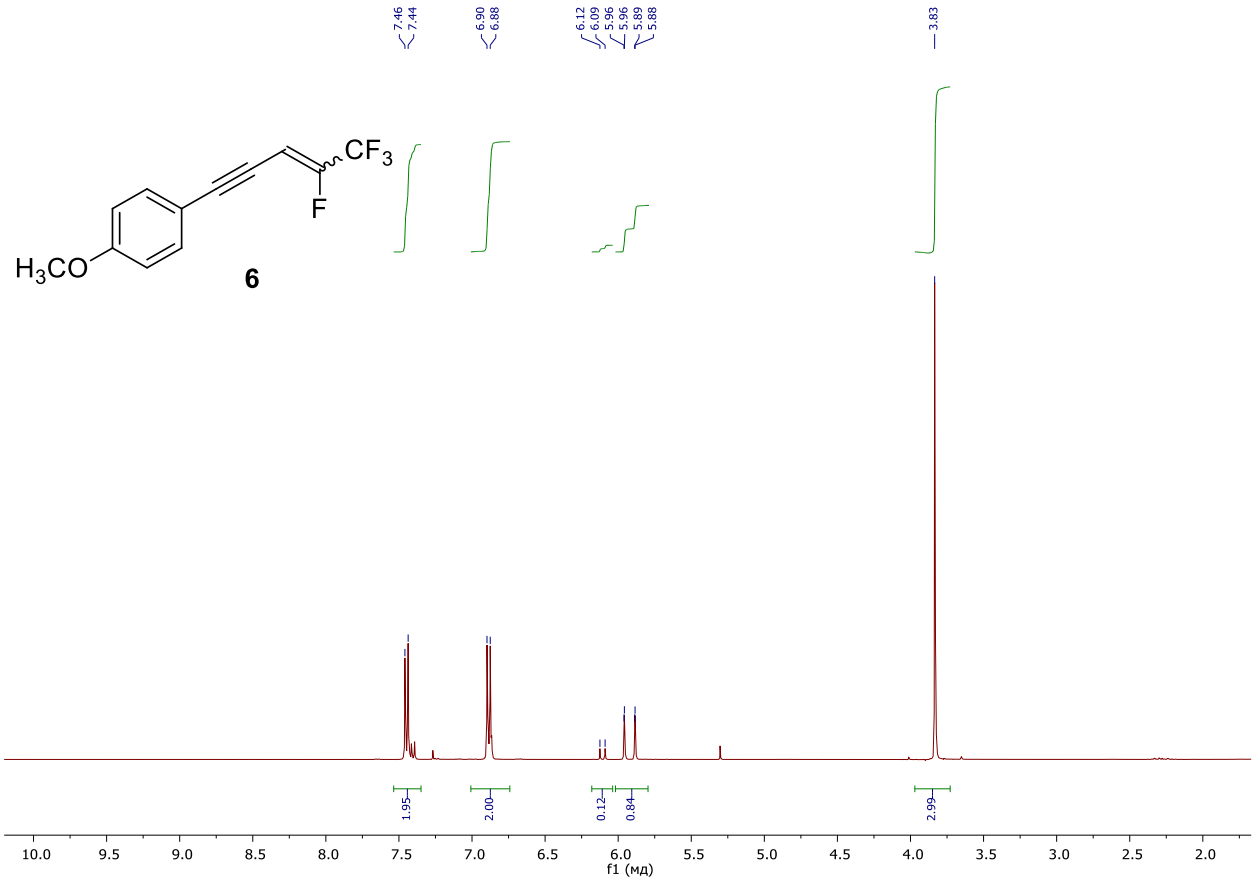


2-[(5,5,5-trifluoropent-2-yn-1-yl)oxy]tetrahydro-2*H*-pyran (3w) **^{19}F NMR (376 MHz, $CDCl_3$)**

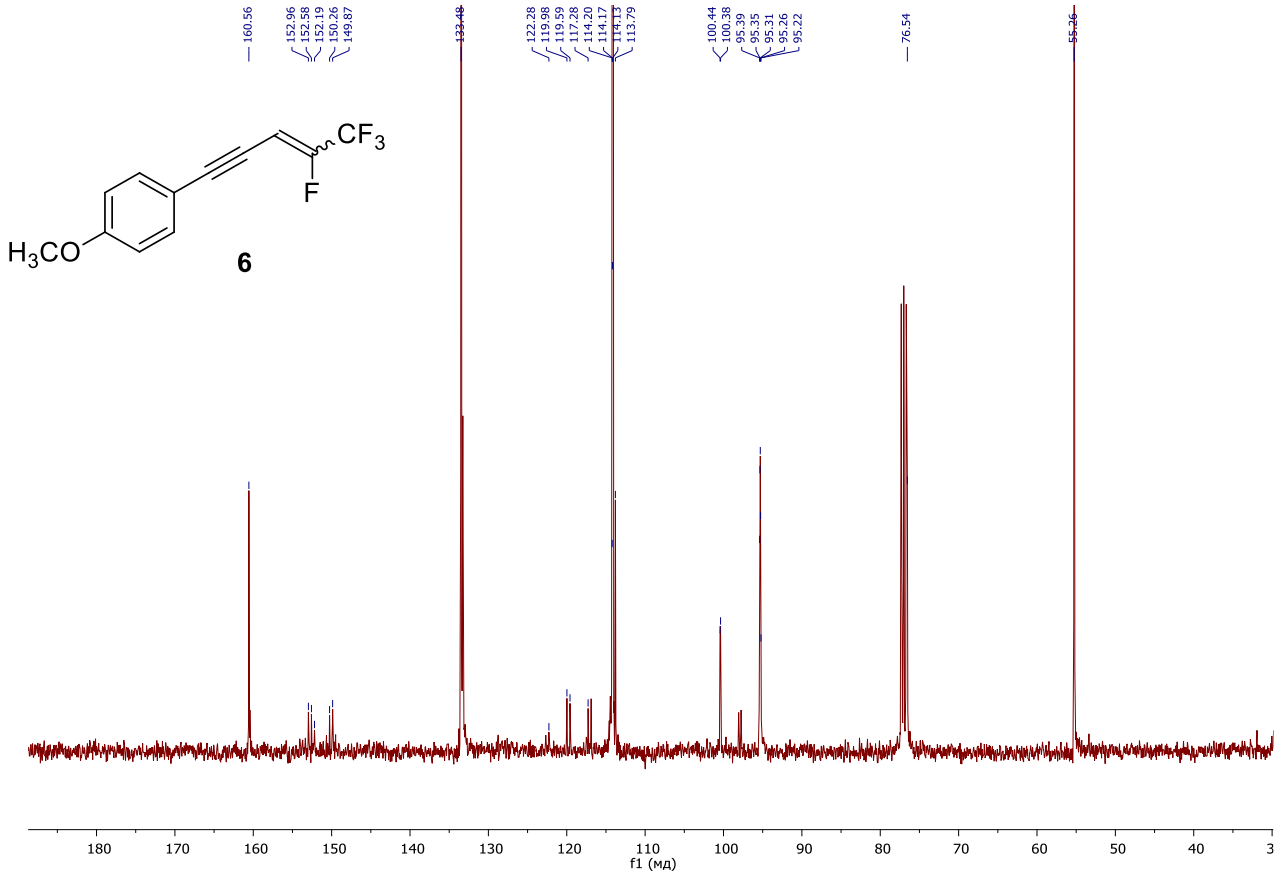
3w



1-methoxy-4-(4,5,5,5-tetrafluoropent-3-en-1-yn-1-yl)benzene (6) (Z/E 7:1) ^{1}H NMR (400 MHz, $CDCl_3$)



1-methoxy-4-(4,5,5,5-tetrafluoropent-3-en-1-yn-1-yl)benzene (6) (Z/E 7:1) ^{13}C NMR (100 MHz, $CDCl_3$)



1-methoxy-4-(4,5,5,5-tetrafluoropent-3-en-1-yn-1-yl)benzene (6) (Z/E 7:1) ^{19}F NMR (376 MHz, $CDCl_3$)