Gate to Parallel Universe: Utilization of Biosurfactants in Micellar Catalysis

Electronic Supplementary Information

Réka Adamik,[a] Attila R. Herczegh,[a] Imre Varga,[b] Zoltán May,[c] Zoltán Novák*[a]

[a]Catalysis and Organic Synthesis Research Group, Institute of Chemistry, Eötvös Loránd University, Pázmány Péter stny. 1/A, H-1117 Budapest, Hungary

[b]Laboratory of Interfaces and Nanostructures, Institute of Chemistry, Eötvös Loránd University, Faculty of Science, Pázmány Péter stny. 1/A, H-1117 Budapest, Hungary

[c]Research Centre for Natural Sciences, Eötvös Loránd Research Network. Magyar Tudósok körútja 2, H-1117 Budapest, Hungary

Table of Contents

General information

Unless otherwise indicated, starting materials were obtained from commercial suppliers, and were used without further purification. Rhamnolipids 90% was purchased from Sigma-Aldrich. The surfactant solutions were prepared using degassed distilled water and were stored under nitrogen. Purification of the obtained products was carried out with a Teledyne ISCO Combiflash Nextgen 300+ Flash Chromatography system using Teledyne ISCO Redisep Gold or Bronze normal phase columns and *n*-hexane and ethyl acetate as eluents.

The photoaddition reaction was carried out in our own designed temperature-adjusted photoreactor using 10W 440-445 nm blue LEDs. Thermostat: Julabo CD-300F. For more information see the Supporting information of reference 5. Analytical thin-layer chromatography (TLC) was performed on Merck DC precoated TLC plates with 0.25 mm Kieselgel 60 F 254. Visualization was performed with a 254 nm UV lamp.

The ^{1}H, ^{19}F and ^{13}C NMR spectra were recorded on a Bruker Ascend 400 MHz spectrometer. Solvents' residual proton peaks were used as standards. Chemical shifts (δ) are reported in ppm, coupling constants (J) are reported in Hertz (Hz). Splitting patterns are designated as s (singlet), bs (broad singlet), d (doublet), t (triplet), q (quartet), h (hextet), hept (heptet) and m (multiplet).

IR spectra were obtained on a Bruker IFS55 spectrometer on a single-reflection diamond ATR unit.

All melting points were measured on a Büchi 501 or on a Bibby Scientific SMP10 apparatus and are uncorrected.

Conversions were determined on an Agilent 5890 Gas Chromatograph (30 m × 0.25 mm column with 0.25 μm HP-5MS coating, He carrier gas) with FID detector.

Low resolution mass spectrometry was obtained on an Agilent 6890N Gas Chromatograph (30 m x 0.25 mm column with 0.25 μm HP-5MS coating, He carrier gas) and Agilent 5973 Mass Spectrometer (Ion source: EI+, 70eV, 230 ° C interface 300 °C).

High-resolution mass spectra were acquired with two methods:

Method 1: an Agilent 7890 Gas Chromatograph coupled with a JEOL JMS-T200GCx time-of-flight mass spectrometer equipped with EI ion source. GC parameters: standard injection (1μl), split ratio: 50, carrier gas: helium; 60 °C initial temperature, 1.5 min hold time, 30 °C/min, final temperature: 320 °C, 3 min hold time; Column: RESTEK RTX-5, 15 m x 0.25 mm x 0.25 μm. MS parameters: Interface temperature: 250 °C, Source temperature: 250 °C, Ionizing voltage: 70eV. The obtained spectra were processed by msAXEL 1.1.6 software.

Method 2: an Agilent 6230 time-of-flight mass spectrometer equipped with a Jet Stream electrospray ion source in positive ion mode. Injections of 0.5µl were directed to the mass spectrometer at a flow rate 1.5 ml/min (5mM ammonium-formate in water and acetonitrile gradient program), using an Agilent 1290 Infinity HPLC system. Jet Stream parameters: drying gas (N_2) flow and temperature: 8.0 l/min and 325 °C, respectively; nebulizer gas (N_2) pressure: 30 psi; capillary voltage: 3000 V; sheath gas flow and temperature: 325 °C and 10.0 l/min; TOFMS parameters: fragmentor voltage: 100 V; skimmer potential: 60 V; OCT 1 RF Vpp:750 V. Full-scan mass spectra were acquired over the m/z range 105-1700 at an acquisition rate of 995.6 ms/spectrum and processed by Agilent MassHunter B.04.00 software.

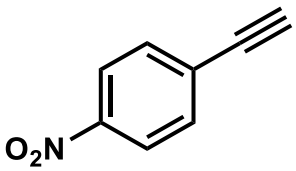
Elemental analytical measurements of reaction products were accomplished with Spectro Genesis ICP-OES (simultaneous spectrometer with axial plasma viewing) and Thermo Scientific iCAP Q (quadrupole) ICP-MS.

Synthesis of terminal acetylenes

The preparation of the terminal acetylene derivatives was carried out according to the literature procedure.[1]

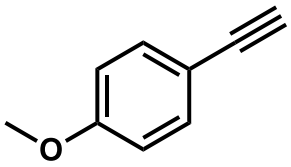
Into a screwcap vial CuI (1 mol%), $Pd(PPh_3)_2Cl_2$ (1 mol%) and aryl iodide if solid (2 mmol or 3 mmol, 1.0 equiv.) were measured. The vial was charged with stirring bar, sealed, evacuated and back-filled with nitrogen. DIPA (5 or 10 mL) and the aryl iodide if liquid (2 mmol or 3 mmol, 1.0 equiv.) was added. Lastly the trimethylsilylacetylene (1.2 equiv) was added via syringe and the reaction mixture was stirred at room temperature for 1 hour. The progress of the reaction was monitored by TLC or GC-MS. After completion of the reaction, the mixture was filtered through Celite and concentrated under vacuo. The TMS-derivative was purified with flash column chromatography. The isolated TMS-derivative was dissolved in 10 mL methanol, K_2CO_3 (1.2 equiv) was added, and the reaction mixture was stirred at room temperature for 2 hours or overnight. The inorganic salts were removed by filtration, the solution was concentrated and the final product was purified with flash column chromatography using hexane as eluent.

1-Ethynyl-4-nitro-benzene (4i)[2]



Prepared from 2 mmol starting material. Yield: 141 mg (0.96 mmol, 48% for two steps) yellow solid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.19 (d, *J* = 8.6 Hz, 2H), 7.63 (d, *J* = 8.6 Hz, 2H), 3.36 (s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 147.7, 133.1, 129.0, 123.7, 82.5, 81.7. **MS** (EI, 70 eV): *m/z* (%): 147(100[M^+]), 131(6), 117(54), 101(90), 89(46), 75(96), 63(18), 51(39).

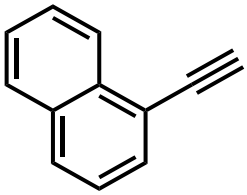
1-Ethynyl-4-methoxy-benzene (4g)[3]



Prepared from 2 mmol starting material. Yield: 101 mg (0.76 mmol, 38% for two steps) yellowish oil. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.30 (d, *J* = 8.8 Hz, 2H), 6.71 (d, *J* = 8.8 Hz, 2H), 3.68 (s, 3H), 2.87 (s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 160.1, 133.7, 114.3, 114.1,

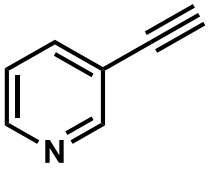
83.8, 75.9, 55.4. **MS** (EI, 70 eV): *m/z* (%): 132(100[M^+]), 117(36), 102(6), 89(62), 75(8), 63(29), 51(6).

1-Ethynyl-naphthalene (4e)[4]



Prepared from 3 mmol starting material. Yield: 438 mg (2.88 mmol, 96% for two steps) yellow oil. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.39 (d, *J* = 8.3 Hz, 1H), 7.87 (d, *J* = 8.3 Hz, 2H), 7.77 (d, *J* = 7.1 Hz, 1H), 7.61 (t, *J* = 7.9 Hz, 1H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.44 (t, *J* = 7.7 Hz, 1H), 3.50 (s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 133.6, 133.2, 131.4, 129.4, 128.4, 127.1, 126.6, 126.2, 125.2, 119.9, 82.1, 81.9. **MS** (EI, 70 eV): *m/z* (%): 152(100[M^+]), 126(7), 98(4), 87(4), 76(13), 63(10).

3-Ethynyl-pyridine (4j)[2]

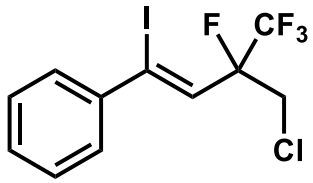


Prepared from 3 mmol 3-bromopyridine starting material using 50 °C reaction temperature and 24 h reaction time. Yield: 118 mg (1.15 mmol, 38% for two steps) orange oil. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.60 – 8.53 (m, 1H), 8.45 – 8.37 (m, 1H), 7.65 (ddt, *J* = 19.9, 7.8, 1.3 Hz, 1H), 7.14 – 7.03 (m, 1H), 3.08 (s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 152.9, 149.2, 139.2, 123.1, 119.4, 80.8. **MS** (EI, 70 eV): *m/z* (%): 103(100[M^+]), 76(49), 63(4), 50(46).

Synthesis of the vinyl iodide reagents

The preparation of the vinyl iodides was acquired according to the literature procedure.[5] In a 250 mL flask phenylacetylene (20 mmol, 2.04 g, 2.2 mL), TMEDA (2 equiv., 40 mmol, 4.65 g, 6 mL) and 3-chloro-1,1,1,2-tetrafluoro-2-iodopropane (3 equiv., 60 mmol, 16.5 g, 7 mL) was dissolved in 100 mL methanol. The resulting solution was irradiated with 440-445 nm LEDs while stirring for 30 minutes. After completion of the reaction excess Na_2SO_3 was added and the mixture was stirred at room temperature until the brown color disappeared. After that the mixture was concentrated onto silicagel and the product was isolated by flash column chromatography using hexane as eluent.

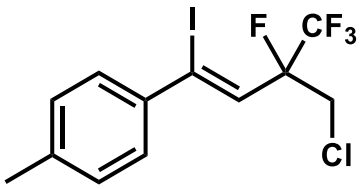
(*Z*)-(3-(Chloromethyl)-3,4,4,4-tetrafluoro-1-iodobut-1-en-1-yl)benzene (1a)[5]



Yield: 6.59 g (17.4 mmol, 87%) pale yellow oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.31 (d, *J* = 5.1 Hz, 5H), 6.38 (d, *J* = 22.2 Hz, 1H), 3.61 (dd, *J* = 24.0, 12.6 Hz, 2H). **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -78.50 (d, *J* = 7.7 Hz), -169.05 (q, *J* = 7.7 Hz). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 142.2 (d, *J* = 1.9 Hz), 129.9, 129.7, 128.8, 127.9, 127.1, 127.0, 121.7 (dd, *J* = 286.6, 28.7 Hz), 106.4 (d, *J* = 2.3 Hz), 94.7 (dd, *J* = 201.7, 30.9 Hz), 42.7 (d, *J* = 25.5 Hz). **MS** (EI, 70 eV): *m/z* (%): 378(1[M^+]), 329(1), 309(1), 251(100), 215(5), 195(71), 182(23), 165(9), 146(62), 133(24), 127(15), 102(50), 76(16), 69(6), 63(8).

(*Z*)-1-(3-(Chloromethyl)-3,4,4,4-tetrafluoro-1-iodobut-1-en-1-yl)-4-methylbenzene (1b)[5]

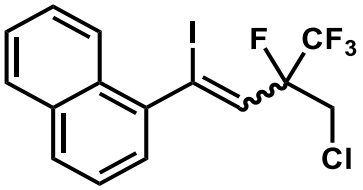


Prepared from 3 mmol 4-ethynyltoluene; Yield: 1061 mg (2.7 mmol, 90%) pale yellow oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.22 (d, *J* = 7.8 Hz, 2H), 7.12 (d, *J* = 7.9 Hz, 2H), 6.36 (d, *J* = 21.9 Hz, 1H), 3.60 (dd, *J* = 25.2, 12.7 Hz, 2H), 2.34 (s, 3H). **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -78.49 (d, *J* = 7.8 Hz), -168.32 (q, *J* = 7.7 Hz). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 139.3, 139.3, 138.9, 129.8, 129.6, 128.7, 127.1 (d, *J* = 2.7 Hz), 121.8 (dd, *J* =

286.6, 28.7 Hz), 106.9, 94.6 (dd, *J* = 201.5, 31.1 Hz), 42.6 (d, *J* = 25.5 Hz), 21.5. **MS** (EI, 70 eV): *m/z* (%): 392(1[M^+]), 342(2), 322(2), 265(100), 245(2), 209(41), 196(21), 160(42), 146(27), 127(11), 115(71), 89(11), 75(5), 63(8).

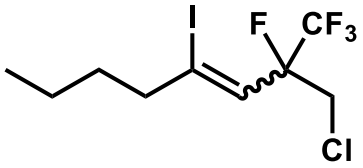
1-(3-(Chloromethyl)-3,4,4,4-tetrafluoro-1-iodobut-1-en-1-yl)naphthalene (1e)[5]



Prepared from 2.06 mmol 1-ethynyl-naphthalene. Mixture of *E*:*Z* isomers in 1:1 ratio. Yield: 585 mg (1.36 mmol, 67%) pale yellow solid. Mp= 68-71 °C.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.04 (dd, *J* = 28.6, 8.4 Hz, 1H), 7.86 (dd, *J* = 17.4, 8.1 Hz, 2H), 7.61 (t, *J* = 7.6 Hz, 1H), 7.57 – 7.44 (m, 2H), 7.44 – 7.37 (m, 1H), 6.68 (dd, *J* = 22.1, 7.2 Hz, 1H), 3.76 – 3.54 (m, 2H). **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -78.23 (dd, *J* = 19.7, 7.5 Hz), -171.85 (q, *J* = 7.8 Hz), -172.67 (q, *J* = 7.0 Hz). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 138.9 (dd, *J* = 9.5, 2.1 Hz), 133.6, 132.2 (d, *J* = 16.6 Hz), 131.9 (d, *J* = 16.9 Hz), 129.3, 128.4 (d, *J* = 4.3 Hz), 126.6, 126.3 (d, *J* = 4.7 Hz), 125.8 (d, *J* = 15.9 Hz), 125.1 (d, *J* = 11.9 Hz), 124.2 (dd, *J* = 8.0, 3.3 Hz), 123.6 – 119.6 (m), 104.5 (d, *J* = 31.1 Hz), 96.3 – 93.1 (m), 42.9 (dd, *J* = 25.7, 15.9 Hz). **MS** (EI, 70 eV): *m/z* (%): 426(5[M^+]), 301 (69), 265 (6), 245 (7), 225(3), 196(35), 183(21), 176(7), 152(100), 126(8), 98(6), 69(9).

2-(Chloromethyl)-1,1,1,2-tetrafluoro-4-iodooct-3-ene (1f)[5]

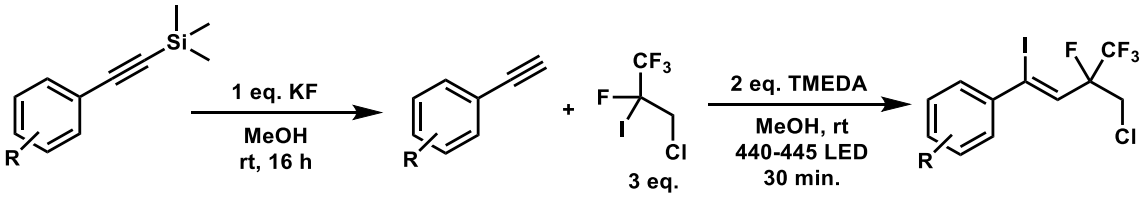


Prepared from 10 mmol 1-hexyne, pentane was used as eluent during chromatography. Mixture of *E*:*Z* isomers in 1:10 ratio. Only the NMR data of the major component is reported below. Yield: 1088 mg (3.0 mmol, 30%) colorless oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.06 (d, *J* = 24.3 Hz, 1H), 3.85 – 3.63 (m, 2H), 2.63 (q, *J* = 6.6 Hz, 2H), 1.55 (p, *J* = 7.5, 7.1 Hz, 2H), 1.35 (h, *J* = 7.3 Hz, 2H), 0.93 (t, *J* = 7.3 Hz, 3H). **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -78.79 (d, *J* = 7.7 Hz), -173.08 (q, *J* = 7.7 Hz). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 127.9 (d, *J* = 15.4 Hz), 121.9 (dd, *J* = 286.3, 29.3 Hz), 118.0, 95.3 (dd, *J* = 201.4, 30.8 Hz), 43.6 (d, *J* = 24.9 Hz), 40.9 (d, *J* = 9.1 Hz), 32.4, 21.8, 14.0. **MS** (EI,

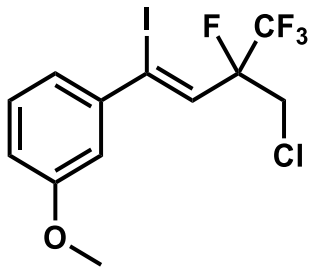
70 eV): *m/z* (%): 358(19[M^+]), 315(76), 231(9), 211(11), 189(32), 175(26), 167(29), 153(59), 147(21), 133(76), 127(100), 119(18), 101(19), 87(17), 77(45), 69(29), 61(45), 51(36).

Synthesis from TMS-protected acetylenes



The preparation of the vinyl iodides was acquired according to the literature procedure.[5] The TMS-protected acetylene derivative (1.0 equiv.) was dissolved in methanol (0.2 mmol / 1 mL), then KF (1.0 equiv.) was added and the mixture was stirred at room temperature for 16 hours. After the completion of the deprotection, TMEDA (2.0 equiv.) and 3-chloro-1,1,1,2-tetrafluoro-2-iodopropane (3.0 equiv.) was added and the reaction mixture was irradiated with 440-445 nm LEDs while stirring for 30 minutes. After completion of the reaction excess Na_2SO_3 was added and the mixture was stirred at room temperature until the brown color disappeared. After that the mixture was concentrated onto silicagel and the product was isolated by flash column chromatography using hexane and ethyl acetate as eluents.

(*Z*)-1-(3-(Chloromethyl)-3,4,4,4-tetrafluoro-1-iodobut-1-en-1-yl)-3-methoxybenzene (1c)

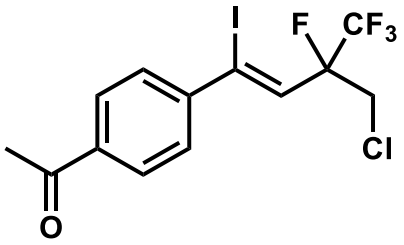


Prepared from 3.69 mmol TMS-protected acetylene derivative. Yield: 1260 mg (3.08 mmol, 84%) pale yellow oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.26 (dd, *J* = 14.5, 6.6 Hz, 1H), 6.96 – 6.80 (m, 3H), 6.39 (d, *J* = 22.0 Hz, 1H), 3.83 (s, 3H), 3.64 (dd, *J* = 25.3, 12.7 Hz, 2H). **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -78.46 (d, *J* = 7.7 Hz), -168.76 (q, *J* = 7.6 Hz). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 158.7, 143.1, 129.8, 129.6, 128.9, 121.6 (dd, *J* = 286.5, 28.6 Hz), 119.4 (d, *J* = 2.6 Hz), 114.6, 112.4 (d, *J* = 2.7 Hz), 105.8 (d, *J* = 2.6 Hz), 94.5 (dq, *J* = 201.7, 31.2 Hz), 55.3, 42.5 (d, *J* = 25.4 Hz). **MS** (EI, 70 eV): *m/z* (%): 408(16[M^+]), 319(1), 281(100), 245(11), 225(21), 212(41), 176(47), 162(17), 146(19), 132(68), 127(15), 102(46), 89(40), 75(14),

69(18), 63(27), 51(13). **IR** (ATR, cm^{-1}) 3006, 2962, 2837, 1639, 1594, 1578, 1483, 1465, 1429, 1316, 1285, 1253, 1241, 1180, 1123, 1099, 1042, 1021, 993, 920, 872, 839, 822, 777, 742, 691, 679, 632, 574, 532. **HRMS** *m/z* calcd for $C_{12}H_{10}ClF_4IO^+$: 407.9401, found: 407.93815.

(*Z*)-1-(4-(3-(Chloromethyl)-3,4,4,4-tetrafluoro-1-iodobut-1-en-1-yl)phenyl)ethan-1-one (1d)[5]

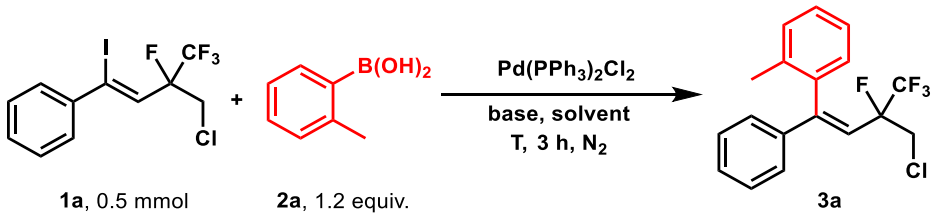


Prepared from 3.35 mmol TMS-protected acetylene derivative. Yield: 831 mg (1.98 mmol, 59%) yellow oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.91 (dt, *J* = 8.4, 2.0 Hz, 2H), 7.39 (d, *J* = 8.0 Hz, 2H), 6.39 (d, *J* = 23.2 Hz, 1H), 3.74 – 3.59 (m, 2H), 2.60 (s, 3H). **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -78.51 (d, *J* = 7.6 Hz), -171.15 (q, *J* = 7.5 Hz). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 197.2, 146.6, 136.8, 132.3, 130.3, 130.1, 127.9, 127.2 (d, *J* = 2.9 Hz), 121.5 (qd, *J* = 286.6, 28.5 Hz), 103.9, 95.0 (dq, *J* = 203.0, 31.2 Hz), 42.8 (d, *J* = 24.7 Hz), 26.6. **MS** (EI, 70 eV): *m/z* (%): 420(1[M^+]), 405(1), 356(3), 293(100), 278(4), 243(50), 229(3), 213(3), 195(13), 164(8), 151(25), 146(37), 129(79), 101(69), 75(38), 69(13), 63(10), 51(20).

Additional experiments

Full optimization table for the Suzuki-coupling of vinyl iodide 1a

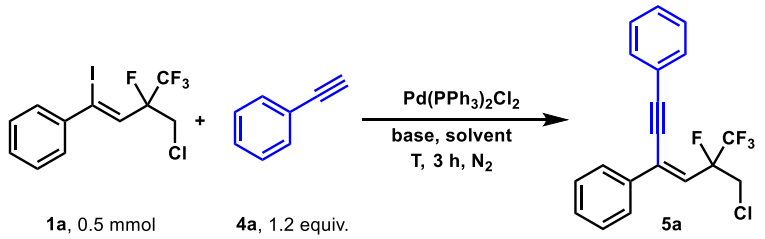


1a, 0.5 mmol **2a**, 1.2 equiv. **3a**

Entry	Catalyst amount	Base	Solvent	Temperature	Conversion
1	1000 ppm	2 eq. K_2CO_3	2% Rhamnolipids	35 °C	100%
2	1000 ppm	2 eq. K_2CO_3	1% Rhamnolipids	35 °C	83%
3	1000 ppm	2 eq. K_2CO_3	0.5% Rhamnolipids	35 °C	80%
4	1000 ppm	2 eq. K_2CO_3	0.2% Rhamnolipids	35 °C	71%
5	1000 ppm	2 eq. K_2CO_3	water	35 °C	54%
6	1000 ppm	2 eq. K_2CO_3	2% SDS	35 °C	76%
7	1000 ppm	2 eq. K_2CO_3	2% TPGS-750-M	35 °C	36%
8	1000 ppm	2 eq. K_2CO_3	2% Brij 30	35 °C	33%
9	1000 ppm	2 eq. K_2CO_3	2% Kolliphor EL	35 °C	33%
10	1000 ppm	2 eq. K_2CO_3	2% Tween 80	35 °C	26%
11	1000 ppm	2 eq. K_2CO_3	2% Triton X-100	35 °C	22%
12	1000 ppm	2 eq. K_2CO_3	2% Rhamnolipids	25 °C	82%
13	500 ppm	2 eq. K_2CO_3	2% Rhamnolipids	35 °C	82%
14	500 ppm	2 eq. K_2CO_3	2% Rhamnolipids	35 °C	88%[a]
15	1000 ppm	2 eq. K_2CO_3	2% Rhamnolipids	25 °C	82%
16	1000 ppm	2 eq. K_2CO_3	2% Rhamnolipids	50 °C	100%
17	1000 ppm	1.5 eq. K_2CO_3	2% Rhamnolipids	35 °C	83%
18	1000 ppm	1.2 eq. K_2CO_3	2% Rhamnolipids	35 °C	78%
19	1000 ppm	2 eq. Na_2CO_3	2% Rhamnolipids	35 °C	77%
20	1000 ppm	2 eq. KOAc	2% Rhamnolipids	35 °C	7%
21	1000 ppm	2 eq. KOH	2% Rhamnolipids	35 °C	6%
22	1000 ppm	2 eq. K_3PO_4	2% Rhamnolipids	35 °C	100%

[a]Reaction time: 5 hours

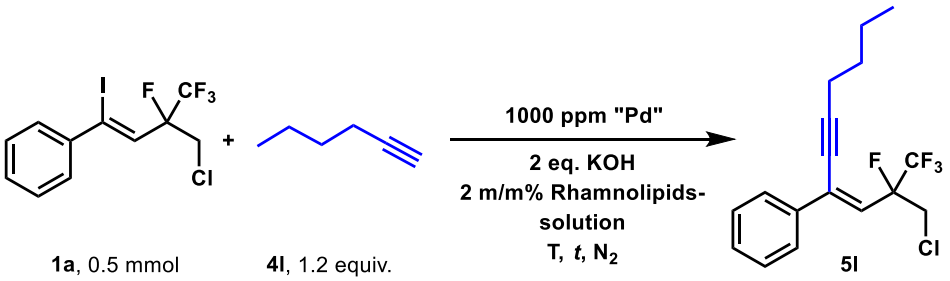
Full optimization table for the Sonogashira-coupling of vinyl iodide 1a with phenylacetylene



1a, 0.5 mmol **4a**, 1.2 equiv. **5a**

Entry	Catalyst amount	Base	Solvent	Temperature	Conversion
1	1000 ppm	2 eq. KOH	2% Rhamnolipids	90 °C	100%
2	1000 ppm	2 eq. KOH	2% Rhamnolipids	80 °C	100%
3	1000 ppm	2 eq. KOH	2% Rhamnolipids	70 °C	100%
4	1000 ppm	2 eq. KOH	2% Rhamnolipids	65 °C	100%
5	1000 ppm	2 eq. KOH	2% Rhamnolipids	60 °C	100%
6	1000 ppm	2 eq. KOH	2% Rhamnolipids	55 °C	96%
7	1000 ppm	2 eq. KOH	2% Rhamnolipids	45 °C	64%
8	1000 ppm	2 eq. KOH	2% Rhamnolipids	35 °C	20%
9	1000 ppm	2 eq. KOH	2% Rhamnolipids	25 °C	8%
10	1000 ppm	2 eq. KOH	water	60 °C	0%
11	1000 ppm	2 eq. KOH	1% Rhamnolipids	60 °C	47%
12	1000 ppm	2 eq. KOH	0.5% Rhamnolipids	60 °C	60%
13	1000 ppm	2 eq. KOH	0.2% Rhamnolipids	60 °C	43%
14	1000 ppm	2 eq. KOH	2% SDS	60 °C	14%
15	1000 ppm	2 eq. KOH	2% TPGS-750-M	60 °C	79%
16	1000 ppm	2 eq. KOH	2% Brij 30	60 °C	36%
17	1000 ppm	2 eq. KOH	2% Kolliphor EL	60 °C	100%
18	1000 ppm	2 eq. KOH	2% Tween 80	60 °C	10%
19	1000 ppm	2 eq. KOH	2% Triton X-100	60 °C	22%
20	500 ppm	2 eq. KOH	2% Rhamnolipids	60 °C	37%
21	1000 ppm + 1000 ppm CuI	2 eq. KOH	2% Rhamnolipids	45 °C	82%
22	1000 ppm + 1000 ppm CuI	2 eq. KOH	2% Rhamnolipids	25 °C	19%
23	1000 ppm	2 eq. K_2CO_3	2% Rhamnolipids	60 °C	85%
24	1000 ppm	2 eq. Na_2CO_3	2% Rhamnolipids	60 °C	96%
25	1000 ppm	2 eq. K_3PO_4	2% Rhamnolipids	60 °C	63%

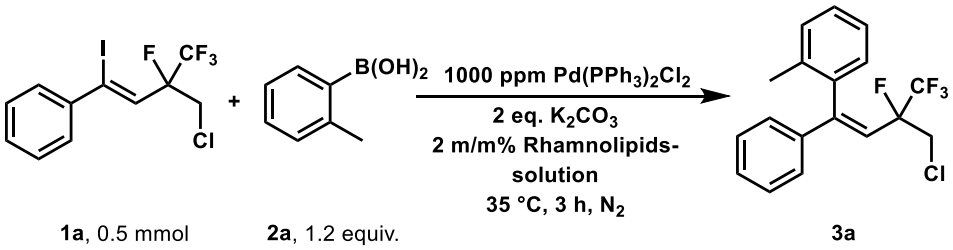
Optimization table for the Sonogashira-coupling of vinyl iodide 1a with 1-hexyne



1a, 0.5 mmol **4l**, 1.2 equiv. **5l**

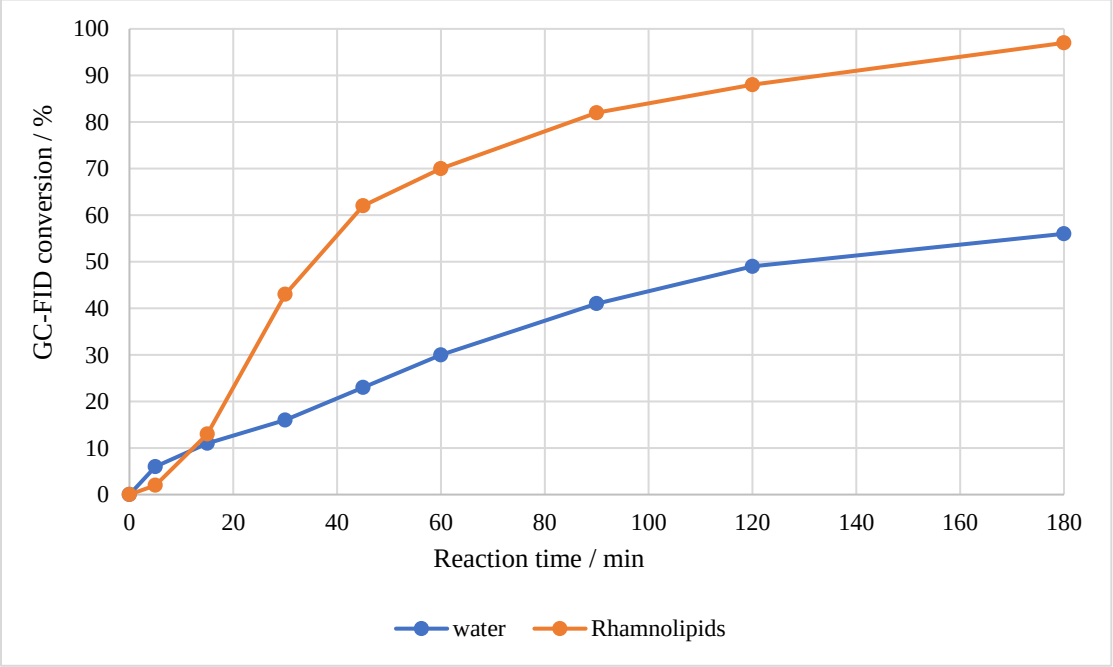
Entry	Catalyst	Reaction time	Temperature	Conversion
1	$Pd(PPh_3)_2Cl_2$	3 h	60 °C	18%
2	$Pd(PPh_3)_2Cl_2$	6 h	60 °C	22%
3	$Pd(PPh_3)_2Cl_2$	22 h	60 °C	29%
4	$Pd(PPh_3)_2Cl_2$	3 h	90 °C	76%
5	$Pd(PPh_3)_2Cl_2$	5 h	90 °C	100%
6	Pd(PCy3)2Cl2	3 h	90 °C	20%
7	Pd(XPhos)2Cl2	3 h	90 °C	8%
8	$[(cinnamyl)PdCl]_2$ + 4000 ppm ^{t}BuXPhos	3 h	90 °C	38%

Kinetic studies of the micellar Suzuki-coupling

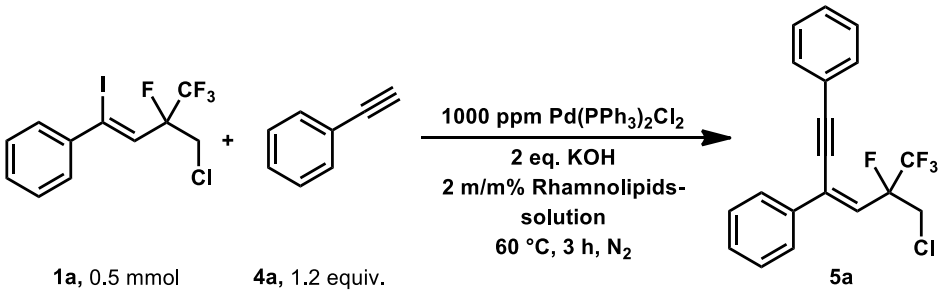


1a, 0.5 mmol **2a**, 1.2 equiv. **3a**

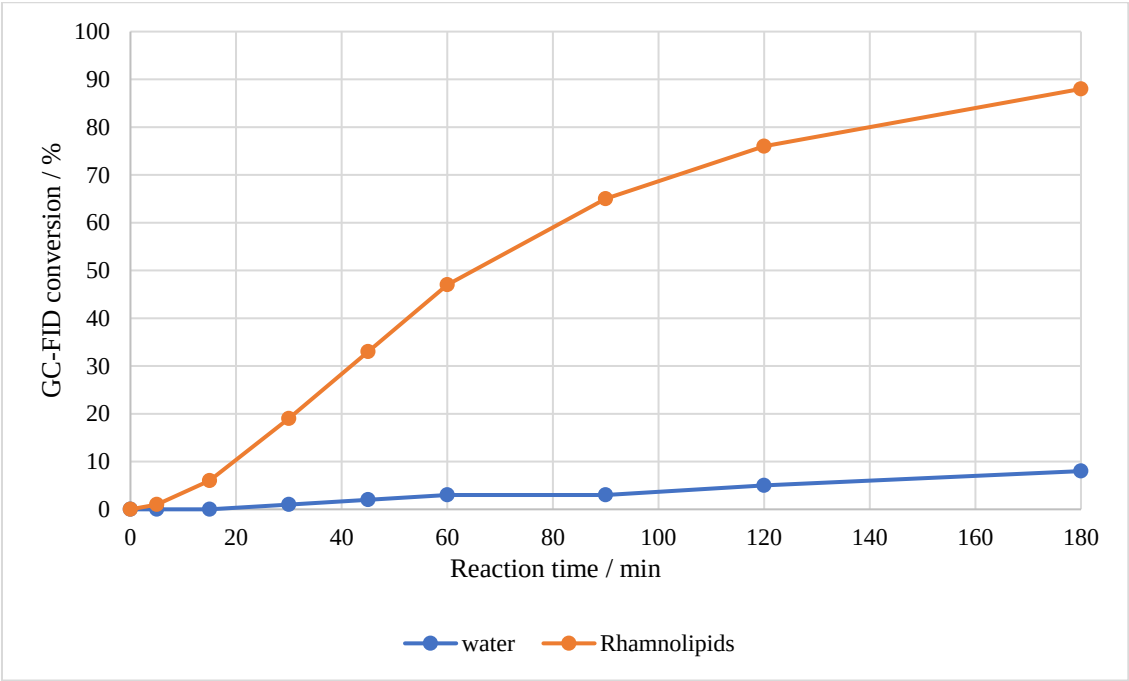
The experiment was carried out according to the general procedure. A 4 ml reaction vial was charged with $Pd(PPh_3)_2Cl_2$ (1000 ppm, 0.1 mol%, 0.0005 mmol, 0.4 mg), K_2CO_3 (2 equiv., 1 mmol, 138 mg) and *o*-tolylboronic acid (1.2 equiv., 0.6 mmol, 81 mg). A stirring bar was added, then the vial was sealed, evacuated and back-filled with nitrogen three times. Degassed rhamnolipids solution (1 mL) was added, then the vinyl iodide (1.0 equiv., 0.5 mmol, 189 mg, 117 µL) via syringe and the reaction mixture was vigorously stirred at 35 °C for 3 hours. The GC-FID samples were taken via syringe without opening the reaction vial. The measured conversions are presented on the figure below, all conversions are the average of two experiments.



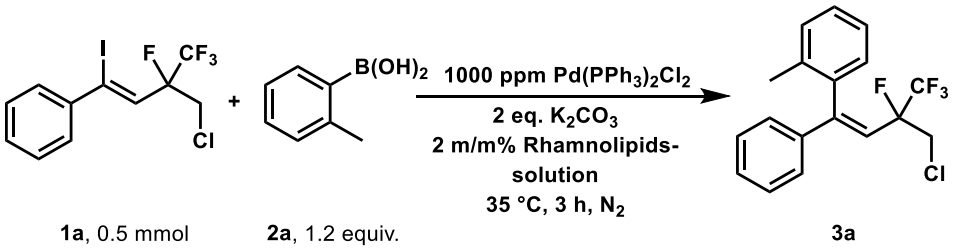
Kinetic studies of the micellar Sonogashira-coupling



The experiment was carried out according to the general procedure. A 4 ml reaction vial was charged with $Pd(PPh_3)_2Cl_2$ (1000 ppm, 0.1 mol%, 0.0005 mmol, 0.4 mg) and KOH (2 equiv., 1 mmol, 56 mg). A stirring bar was added, then the vial was sealed, evacuated and back-filled with nitrogen three times. Degassed rhamnolipids solution (1 mL) was added, then the vinyl iodide (1.0 equiv., 0.5 mmol, 189 mg, 117 µL) and phenylacetylene (1.2 equiv., 0.6 mmol, 61 mg, 66 µL) via syringe and the reaction mixture was vigorously stirred at 60 °C for 3 hours. The GC-FID samples were taken via syringe without opening the reaction vial. The measured conversions are presented on the figure below.



Recycling of the rhamnolipids-solution



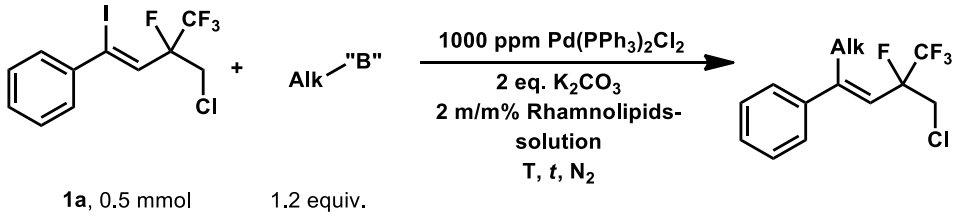
1a, 0.5 mmol **2a**, 1.2 equiv. **3a**

The experiments were carried out according to the general procedure. A 4 ml reaction vial was charged with $Pd(PPh_3)_2Cl_2$ (1000 ppm, 0.1 mol%, 0.0005 mmol, 0.4 mg), K_2CO_3 (2 equiv., 1 mmol, 138 mg) and *o*-tolylboronic acid (1.2 equiv., 0.6 mmol, 81 mg). A stirring bar was added, then the vial was sealed, evacuated and back-filled with nitrogen three times. Degassed rhamnolipids solution (1 mL) was added, then the vinyl iodide (1.0 equiv., 0.5 mmol, 189 mg, 117 μL) via syringe and the reaction mixture was vigorously stirred at 35 °C for 3 hours. The product was extracted with minimal amount of ethyl acetate and the remaining aqueous phase was used in the next reaction. The organic phase was dried on Na_2SO_4, and concentrated under vacuo.

Another 4 ml reaction vial was charged with $Pd(PPh_3)_2Cl_2$ (1000 ppm, 0.1 mol%, 0.0005 mmol, 0.4 mg), K_2CO_3 (2 equiv., 1 mmol, 138 mg) and *o*-tolylboronic acid (1.2 equiv., 0.6 mmol, 81 mg). A stirring bar was added, then the vial was sealed, evacuated and back-filled with nitrogen three times. The aqueous phase from the previous reaction was added then the vinyl iodide (1.0 equiv., 0.5 mmol, 189 mg, 117 μL) via syringe and the reaction mixture was vigorously stirred at 35 °C for 3 hours. After completion of the reaction the mixture was diluted with water and brine and ethyl acetate. The organic phase was separated, and the aqueous phase was extracted with 2x10 ml ethyl acetate. The combined organic phase was dried on Na_2SO_4, and concentrated under vacuo.

Both products were isolated by flash column chromatography using hexane as eluent.
Yield from the first reaction: 145 mg (0.42 mmol, 85%).
Yield from the second reaction: 136 mg (0.39 mmol, 80%).

Suzuki-coupling experiments with alkyl boronic acid derivatives



1a, 0.5 mmol 1.2 equiv.

I: Experiment with potassium cyclopropyltrifluoroborate

A 4 ml reaction vial was charged with $Pd(PPh_3)_2Cl_2$ (1000 ppm, 0.1 mol%, 0.0005 mmol, 0.4 mg), K_2CO_3 (2 equiv., 1 mmol, 138 mg) and potassium cyclopropyltrifluoroborate (1.2 equiv., 0.6 mmol, 89 mg). A stirring bar was added, then the vial was sealed, evacuated and back-filled with nitrogen three times. Degassed rhamnolipids solution (1 mL) was added, then the vinyl iodide (1.0 equiv., 0.5 mmol, 189 mg, 117 μL) via syringe and the reaction mixture was vigorously stirred at 50 °C for 3 hours. Analysis of the reaction mixture showed no formation of the desired product.

II: Experiment with cyclohexylboronic acid

A 4 ml reaction vial was charged with $Pd(PPh_3)_2Cl_2$ (1000 ppm, 0.1 mol%, 0.0005 mmol, 0.4 mg), K_2CO_3 (2 equiv., 1 mmol, 138 mg) and cyclohexylboronic acid (1.2 equiv., 0.6 mmol, 77 mg). A stirring bar was added, then the vial was sealed, evacuated and back-filled with nitrogen three times. Degassed rhamnolipids solution (1 mL) was added, then the vinyl iodide (1.0 equiv., 0.5 mmol, 189 mg, 117 μL) via syringe and the reaction mixture was vigorously stirred at 50 °C for 3 hours. Analysis of the reaction mixture showed no formation of the desired product. The experiment was repeated using 75 °C reaction temperature and 18 hours of reaction time but still no desired product could be detected.

Dynamic Light Scattering measurements

The hydrodynamic size of the Rhamnolipid micelles was determined by Dynamic Light Scattering (DLS) using a Brookhaven Instruments device containing a BI-200SM goniometer, a BI-9000AT digital autocorrelator, and a Coherent Genesis MX488-1000 STM laser. Vertically polarized light at a wavelength of 488.0 nm and 500 mW power was used for the measurements. The autocorrelation functions were measured at a scattering angle of 90° with a 100 μm pinhole size. The measured autocorrelation functions were analysed by the CONTIN method, and the obtained diffusion coefficient distribution was converted to hydrodynamic size distribution using the Stokes-Einstein equation.

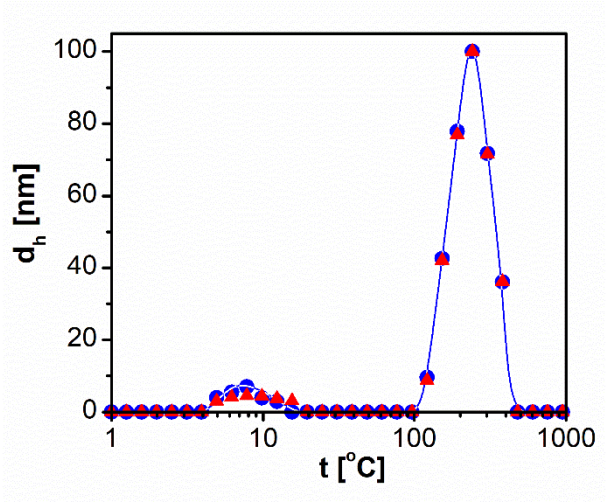


Figure S1. The hydrodynamic diameter (d_h) distribution of the Rhamnolipid micelles measured 2.0 w% (Blue circles) and 0.5 w% (red triangles) concentrations.

ICP analysis

The Pd content of product **3a** was measured by ICP-OES and ICP-MS measurements.

Sample preparation:

100 mg of the powder samples were weighed with analytical balance and transferred into PTFE tubes of Multiwave 3000 (Anton Paar) microwave assisted digestion system, then 6 mL of concentrated nitric acid (Suprapur, 65%) and 2 mL of concentrated hydrochloric acid (Suprapur, 30%) was added to the samples. After putting together these reaction vessels the following digestion program was run: heating up the samples to 200 °C degree in 30 minutes and keeping them in this temperature and pressure (20 bar) for 1 hour and then cooling down to ambient temperature in 60 minutes. After this the samples were washed into volumetric flasks (10 mL) with ultrapure (18.2 $M\Omega.cm^{-1}$) water (ELGA cleaning system) and measured directly with ICP-OES instrument to determine Pd content and other measurable elements. After 10-fold dilution of the samples ICP-MS measurements were also done to determine all precious metals beside palladium in the samples. All measurements were done with three parallels.

Determination method and technical parameters:

For quantitative determination of the elements multielement standard solutions were applied produced by Spectrascan for precious metals (Pd, Pt, Ru, Rh, Os, Ir, Au) and CPAChem for other 33 elements (Li, Be, Na, Mg, Al, P, S, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Rb, Sr, Nb, Mo, Ag, Cd, In, Sb, Ba, Tl, Pb, Bi, U) for making calibration curves.

1. Technical parameters of Spectro Genesis ICP-OES:

Optical alignment: Paschen-Runge

Wavelength range: 175-775 nm

Detector system: 15 linear CCD detector

Resolution: 0.029 nm

Generator frequency: 27.12 MHz

Plasma power (changeable) 750 – 1700 W

2. Technical parameters of Thermo Scientific iCAP Q ICP-MS:

Ion optics: RAPID Lens (Right Angle Positive Ion Deflection), QCell (quadrupole, collision cell), DA (differential aperture) Assembly

Mass analyser: Quadrupole

Detector: SEM (secondary electron multiplier)

Additional gas for KED (kinetic energy discrimination) mode: Helium

All ICP-MS measurements were done with KED mode.

ICP-OES results:

mg/kg (ppm)	**Pd 348.115**	**P 177.495**
	mg/l	mg/l
3a	< QL	< QL
3a	< QL	< QL

ICP-MS results:

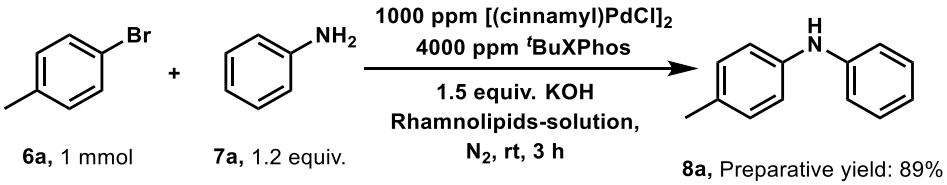
mg/kg (ppm)	**^{105}Pd**	**^{106}Pd**	**^{108}Pd**	**^{110}Pd**
3a	0.032	0.032	0.032	0.035
3a	0.045	0.042	0.043	0.043

Average: 0.038 mg/kg (ppm) = 38 μg/kg (ppb)

General procedures for the micellar Buchwald-Hartwig-couplings

Buchwald-Hartwig amination with aniline derivatives

4-Methyl-*N*-phenyl-benzenamine (8a)[6]

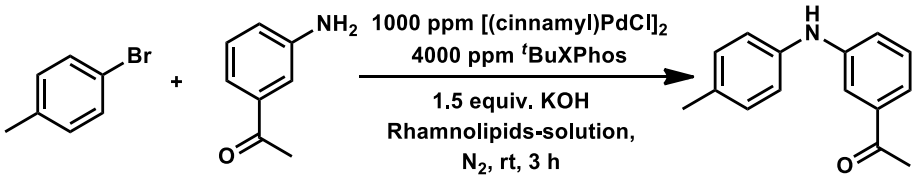


A 4 ml reaction vial was charged with [(cinnamyl)PdCl]$_2$ (1000 ppm, 0.1 mol%, 0.001 mmol, 0.6 mg), ^{t}BuXPhos (4000 ppm, 0.4 mol%, 0.004 mmol, 1.6 mg), KOH (1.5 equiv., 1.5 mmol, 84 mg) and the 4-bromotoluene (1.0 equiv., 1 mmol, 171 mg). A stirring bar was added, then the vial was sealed, evacuated and back-filled with nitrogen three times. Degassed rhamnolipids solution (2 mL) was added, then aniline (1.2 equiv., 1.2 mmol, 112 mg, 110 µL) via syringe and the reaction mixture was vigorously stirred at room temperature for 3 hours. After completion of the reaction (monitored by GC-MS) the mixture was diluted with water or brine and ethyl acetate. The organic phase was separated, and the aqueous phase was extracted with 2x10 ml ethyl acetate. The combined organic phase was dried on Na_2SO_4, and concentrated under vacuo. The product was isolated by flash column chromatography using hexane and ethyl acetate as eluents.

Yield: 164 mg (0.89 mmol, 89%) white solid. Mp= 94-104 °C.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.17 (t, *J* = 7.8 Hz, 2H), 7.00 (d, *J* = 8.1 Hz, 2H), 6.91 (dd, *J* = 8.3, 2.2 Hz, 4H), 6.79 (t, *J* = 7.3 Hz, 1H), 5.50 (s, 1H), 2.22 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 144.1, 140.4, 131.1, 129.9, 129.4, 120.4, 119.0, 117.0, 20.8. **MS** (EI, 70 eV): *m/z* (%): 183(100[M^+]), 167(21), 141(2), 115(3), 91(17), 77(14), 65(7), 51(8).

1-(3-(*p*-Tolylamino)phenyl)ethan-1-one (8b)[7]



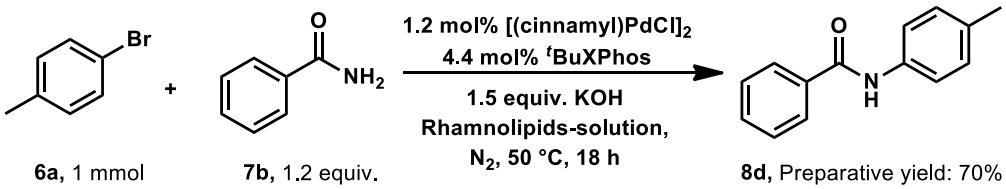
The preparation of the product was carried out similarly to product **8a** using 3-aminoacetophenone as the coupling reagent.

Yield: 206 mg (0.91 mmol, 92%) yellow solid. Mp= 87-91 °C.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.57 (s, 1H), 7.43 (d, *J* = 7.6 Hz, 1H), 7.31 (t, *J* = 7.8 Hz, 1H), 7.23 – 7.17 (m, 1H), 7.12 (d, *J* = 8.1 Hz, 2H), 7.02 (d, *J* = 8.3 Hz, 2H), 5.81 (s, 1H), 2.57 (s, 3H), 2.33 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 198.4, 144.8, 139.6, 138.4, 132.0, 130.1, 129.6, 120.8, 120.2, 119.7, 115.7, 26.8, 20.8. **MS** (EI, 70 eV): *m/z* (%): 225(100[M^+]), 210(16), 182(65), 167(74), 152(6), 139(5), 91(15), 77(11), 65(13).

Buchwald-Hartwig amidation with benzamide

N-*p*-Tolyl-benzamide (8d)[8]



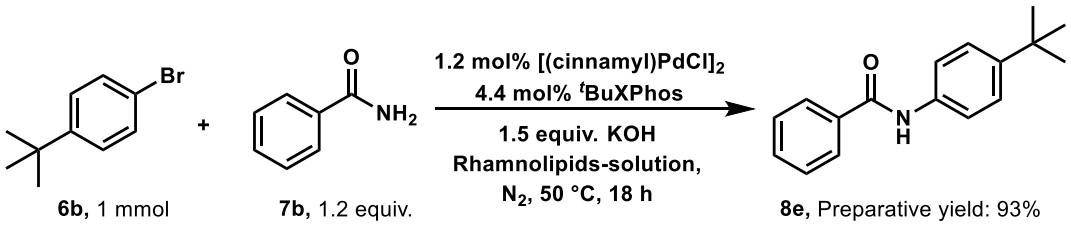
6a, 1 mmol **7b**, 1.2 equiv. **8d**, Preparative yield: 70%

A 4 ml reaction vial was charged with [(cinnamyl)PdCl]$_2$ (1.2 mol%, 0.012 mmol, 6.2 mg), ^{t}BuXPhos (4.4 mol%, 0.044 mmol, 18.7 mg), KOH (1.5 equiv., 1.5 mmol, 84 mg), benzamide (1.2 equiv., 1.2 mmol, 145 mg) and the 4-bromotoluene (1.0 equiv., 1 mmol, 171 mg). A stirring bar was added, then the vial was sealed, evacuated and back-filled with nitrogen three times. Degassed rhamnolipids solution (2 mL) was added via syringe and the reaction mixture was vigorously stirred at 50 °C for 18 hours. After completion of the reaction (monitored by GC-MS) the mixture was diluted with water or brine and ethyl acetate. The organic phase was separated, and the aqueous phase was extracted with 2x10 ml DCM. The combined organic phase was dried on Na_2SO_4, and concentrated under vacuo. The product was isolated by flash column chromatography using hexane and ethyl acetate as eluents.

Yield: 149 mg (0.70 mmol, 70%) white solid. Mp= 157-161 °C.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.01 – 7.76 (m, 3H), 7.59 – 7.40 (m, 5H), 7.16 (d, *J* = 8.2 Hz, 2H), 2.34 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.8, 135.5, 135.2, 134.3, 131.8, 129.7, 128.8, 127.1, 120.5, 21.0. **MS** (EI, 70 eV): *m/z* (%): 211(33[M^+]), 105(100), 77(62), 51(12).

***N*-(4-(*tert*-Butyl)phenyl)benzamide (8e)**[9]



6b, 1 mmol **7b,** 1.2 equiv. **8e,** Preparative yield: 93%

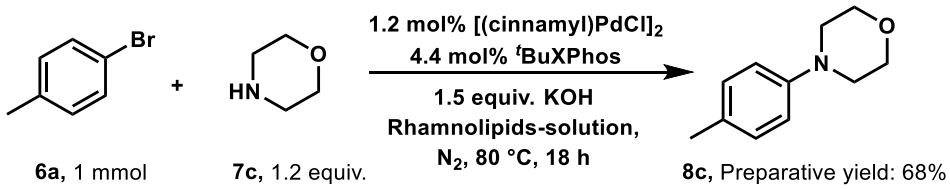
The preparation of the product was carried out similarly to product **8b**.

Yield: 236 mg (0.93 mmol, 93%) light brown solid. Mp= 140-143 °C.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.98 (s, 1H), 7.85 (d, *J* = 7.2 Hz, 2H), 7.54 (dd, *J* = 22.7, 7.9 Hz, 3H), 7.44 (t, *J* = 7.4 Hz, 2H), 7.37 (d, *J* = 8.6 Hz, 2H), 1.33 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.9, 147.7, 135.4, 135.2, 131.8, 128.8, 127.2, 126.0, 120.2, 34.5, 31.5. **MS** (EI, 70 eV): *m/z* (%): 253(25[M^+]), 238(61), 135(13), 105(100), 91(8), 77(61), 51(8).

Buchwald-Hartwig amination with morpholine

***N*-(4-Methylphenyl)morpholine (8c)**[10]



6a, 1 mmol **7c,** 1.2 equiv. **8c,** Preparative yield: 68%

A 4 ml reaction vial was charged with $[(cinnamyl)PdCl]_2$ (1.2 mol%, 0.012 mmol, 6.2 mg), ^{t}BuXPhos (4.4 mol%, 0.044 mmol, 18.7 mg), KOH (1.5 equiv., 1.5 mmol, 84 mg) and the 4-bromotoluene (1.0 equiv., 1.0 mmol, 171 mg). A stirring bar was added, then the vial was sealed, evacuated and back-filled with nitrogen three times. Degassed rhamnolipids solution (2 mL) was added, then morpholine (1.2 equiv., 1.2 mmol, 105 mg, 106 μL) via syringe and the reaction mixture was vigorously stirred at 80 °C for 18 hours. After completion of the reaction (monitored by GC-MS) the mixture was diluted with water or brine and ethyl acetate. The organic phase was separated, and the aqueous phase was extracted with 2x10 ml ethyl acetate. The combined organic phase was dried on Na_2SO_4, and concentrated under vacuo. The product was isolated by flash column chromatography using hexane and ethyl acetate as eluents.

Yield: 121 mg (0.68 mmol, 68%) brown solid. Mp= 43-44 °C.

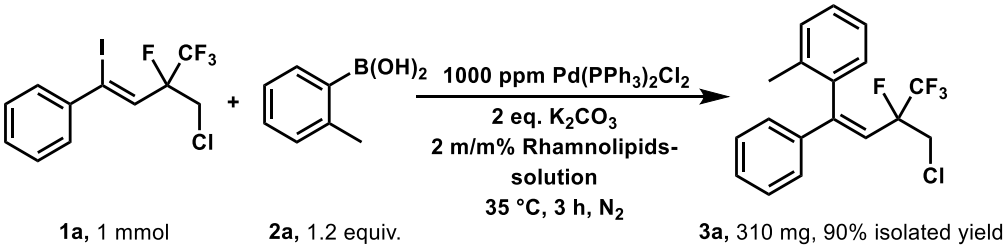
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.10 (d, *J* = 8.6 Hz, 2H), 6.85 (d, *J* = 8.6 Hz, 2H), 3.88 – 3.86 (m, 4H), 3.13 – 3.10 (m, 4H), 2.29 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 149.3, 129.84, 129.7, 116.2, 67.1, 50.1, 20.5. **MS** (EI, 70 eV): *m/z* (%): 177(37[M^+]), 119(100), 91(35), 77(4), 65(10), 51(3).

General procedure for the micellar Suzuki-couplings

Suzuki-coupling with vinyl iodides

A 4 ml reaction vial was charged with $Pd(PPh_3)_2Cl_2$ (1000 ppm, 0.1 mol%, 0.0005 mmol, 0.4 mg), K_2CO_3 (2 equiv., 1 mmol, 138 mg) and the phenylboronic acid derivative (1.2 equiv.). A stirring bar was added, then the vial was sealed, evacuated and back-filled with nitrogen three times. Degassed rhamnolipids solution (1 mL) was added, then the vinyl iodide derivative (1.0 equiv., 0.5 mmol) via syringe and the reaction mixture was vigorously stirred at the appropriate temperature. After completion of the reaction (monitored by GC-MS or GC-FID) the mixture was cooled back to room temperature, was diluted with water or brine and ethyl acetate. The organic phase was separated, and the aqueous phase was extracted with 2x10 ml ethyl acetate. The combined organic phase was dried on Na_2SO_4, and concentrated under vacuo. The product was isolated by flash column chromatography using hexane and ethyl acetate as eluents.

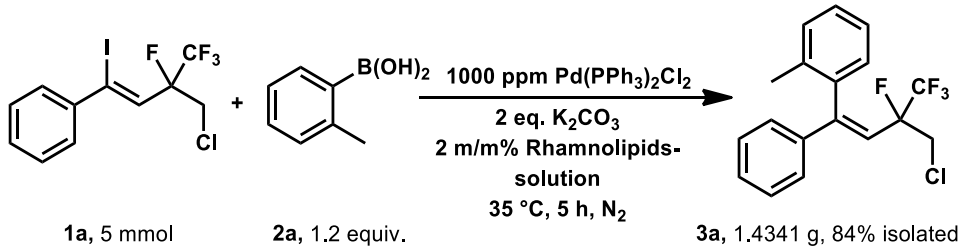
1 mmol scale reaction



1a, 1 mmol **2a,** 1.2 equiv. **3a,** 310 mg, 90% isolated yield

A 4 ml reaction vial was charged with $Pd(PPh_3)_2Cl_2$ (1000 ppm, 0.1 mol%, 0.001 mmol, 0.8 mg), K_2CO_3 (2 equiv., 2 mmol, 276 mg) and *o*-tolylboronic acid (1.2 equiv., 1.2 mmol, 204 mg). A stirring bar was added, then the vial was sealed, evacuated and back-filled with nitrogen three times. Degassed rhamnolipids solution (2 mL) was added, then the vinyl iodide (1.0 equiv., 1.0 mmol, 378 mg, 234 μL) via syringe and the reaction mixture was vigorously stirred at 35 °C for 3 hours. After completion of the reaction (monitored by GC-MS or GC-FID) the mixture was cooled back to room temperature, was diluted with brine and ethyl acetate. The organic phase was separated, and the aqueous phase was extracted with 2x10 ml ethyl acetate. The combined organic phase was dried on Na_2SO_4, and concentrated under vacuo. The product was isolated ((310 mg, 0.9 mmol; 90%)) by flash column chromatography using hexane as eluent.

Large scale (5 mmol) reaction

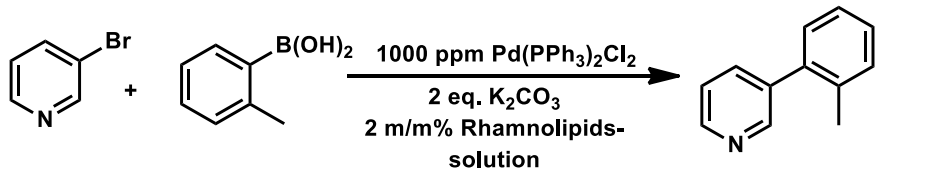


1a, 5 mmol **2a**, 1.2 equiv. **3a**, 1.4341 g, 84% isolated yield

A 20 ml reaction vial was charged with $Pd(PPh_3)_2Cl_2$ (1000 ppm, 0.1 mol%, 0.005 mmol, 3.5 mg), K_2CO_3 (2 equiv., 10 mmol, 1382 mg) and *o*-tolylboronic acid (1.2 equiv., 6 mmol, 816 mg). A stirring bar was added, then the vial was sealed, evacuated and back-filled with nitrogen three times. Degassed rhamnolipids solution (10 mL) was added, then the vinyl iodide (1.0 equiv., 5.0 mmol, 1893 mg, 1170 μL) via syringe and the reaction mixture was vigorously stirred at 35 °C for 5 hours. After completion of the reaction (monitored by GC-MS or GC-FID) the mixture was cooled back to room temperature, was diluted with brine and ethyl acetate. The organic phase was separated, and the aqueous phase was extracted with 2x30 ml ethyl acetate. The combined organic phase was dried on Na_2SO_4, and concentrated under vacuo. The product was isolated (1.43g, 4.2mmol; 84%) by flash column chromatography using hexane as eluent.

Suzuki-couplings with other substrates

3-(2-Methylphenyl)-pyridine (11a)[11]



9a, 1 mmol **2a**, 1.2 equiv. **11a**, Preparative yield: 72%

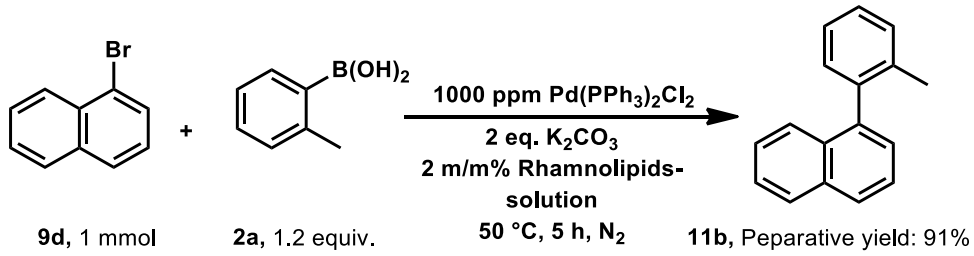
A 4 ml reaction vial was charged with $Pd(PPh_3)_2Cl_2$ (1000 ppm, 0.1 mol%, 0.001 mmol, 0.8 mg), K_2CO_3 (2 equiv., 2 mmol, 276 mg) and *o*-tolylboronic acid (1.2 equiv., 1.2 mmol, 204 mg). A stirring bar was added, then the vial was sealed, evacuated and back-filled with nitrogen three times. Degassed rhamnolipids solution (2 mL) was added, then the vinyl 3-bromopyridine (1.0 equiv., 1 mmol, 158 mg, 96 μL) via syringe and the reaction mixture was vigorously stirred at 50 °C for 5 hours. After completion of the reaction (monitored by GC-MS or GC-FID) the mixture was cooled back to room temperature, was diluted with brine and ethyl acetate. The organic phase was separated, and the aqueous phase was extracted with 2x10 ml ethyl acetate.

The combined organic phase was dried on Na_2SO_4, and concentrated under vacuo. The product was isolated by flash column chromatography using hexane as eluent.

Yield: 121 mg (0.72 mmol, 72%) yellow oil.

^{1}H NMR (400 MHz, Acetonitrile-d_3) δ 8.2 (d, *J* = 5.6 Hz, 2H), 7.4 (dt, *J* = 7.7, 1.8 Hz, 1H), 7.1 (dd, *J* = 7.4, 5.1 Hz, 1H), 7.0 – 6.9 (m, 4H), 1.9 (s, 3H). **^{13}C NMR** (101 MHz, CD_3CN) δ 150.57, 149.04, 139.13, 138.23, 137.35, 136.57, 131.45, 130.73, 129.07, 127.03, 124.06, 20.44. **MS** (EI, 70 eV): *m/z* (%): 169(100[M^+]), 141(22), 115(31), 89(9), 84(7), 63(10), 51(6).

1-(2-Methylphenyl)-naphthalene (11b)[12]

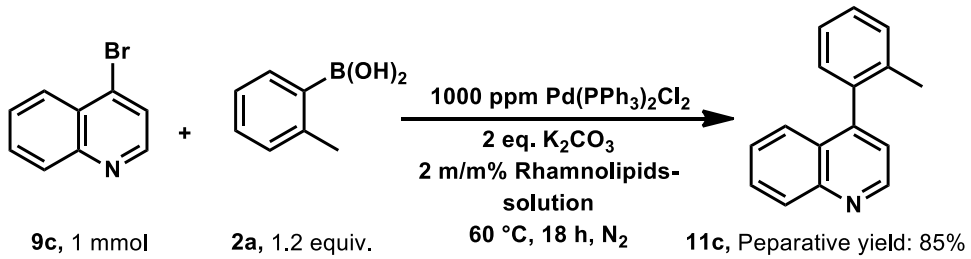


The preparation of the product was carried out similarly to product **10a**.

Yield: 199 mg (0.91 mmol, 91%) white solid. Mp= 65-68 °C.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.8 (dd, *J* = 15.5, 8.0 Hz, 2H), 7.5 – 7.4 (m, 3H), 7.3 – 7.2 (m, 6H), 1.9 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 140.4, 139.9, 136.9, 133.7, 132.1, 130.5, 130.0, 128.3, 127.7, 127.6, 126.8, 126.2, 126.1, 125.8, 125.7, 125.5, 20.2. **MS** (EI, 70 eV): *m/z* (%): 218(100[M^+]), 203(59), 189(14), 163(4), 108(11), 94(8), 63(5).

4-(2-Methylphenyl)-quinoline (11c)[13]



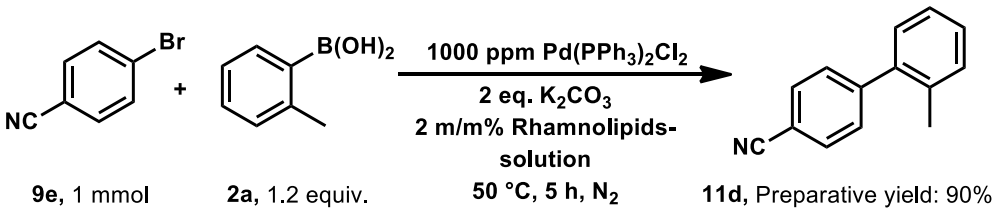
The preparation of the product was carried out similarly to product **10a** using 60 °C reaction temperature and 18 hours of reaction time.

Yield: 186 mg (0.85 mmol, 85%) light yellowish oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.9 (d, *J* = 4.3 Hz, 1H), 8.1 (d, *J* = 8.4 Hz, 1H), 7.7 – 7.6 (m, 1H), 7.4 – 7.1 (m, 7H), 1.9 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 149.9, 149.0, 148.1, 137.5, 136.1, 130.3, 129.6, 128.6, 127.4, 126.9, 126.1, 125.9, 121.6, 20.1. **MS** (EI, 70 eV): *m/z*

(%): 218(100[M^+]), 204(23), 192(32), 189(15), 176(7), 165(8), 115(6), 108(16), 101(5), 89(7), 75(10), 63(7).

4-Carbonitrile-2′-methyl-biphenyl (11d)[14]



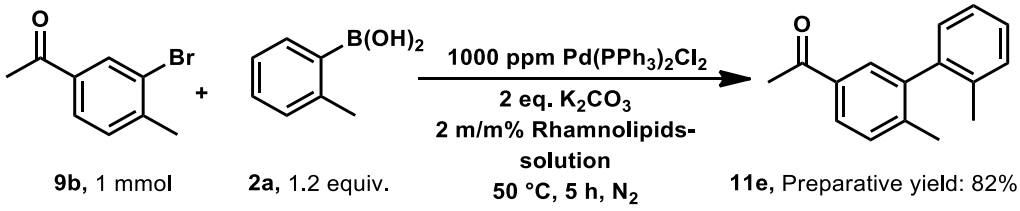
9e, 1 mmol **2a**, 1.2 equiv. **11d**, Preparative yield: 90%

The preparation of the product was carried out similarly to product **10a**.

Yield: 174 mg (0.90 mmol, 90%) white solid. Mp= 68-72 °C.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.63 (d, *J* = 8.3 Hz, 2H), 7.36 (d, *J* = 8.3 Hz, 2H), 7.20 (dd, *J* = 15.3, 4.0 Hz, 3H), 7.11 (d, *J* = 7.2 Hz, 1H), 2.18 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 146.9, 140.1, 135.2, 132.1, 130.8, 130.1, 129.5, 128.4, 126.2, 119.1, 110.9, 20.4. **MS** (EI, 70 eV): *m/z* (%): 193(100[M^+]), 178(15), 165(46), 152(8), 115(5), 89(6), 82(9), 75(5), 63(8).

1-(2’,6-Dimethyl[1,1’-biphenyl]-3-yl)ethenone (11e)[15]



9b, 1 mmol **2a**, 1.2 equiv. **11e**, Preparative yield: 82%

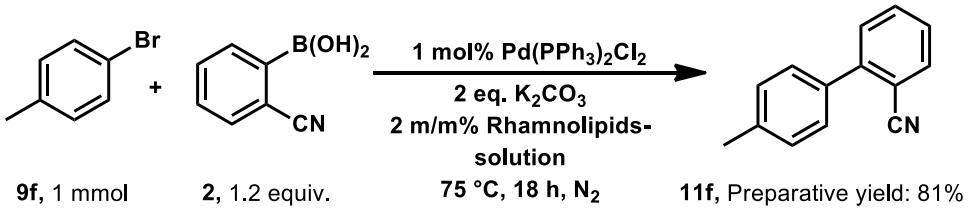
A 4 ml reaction vial was charged with $Pd(PPh_3)_2Cl_2$ (1000 ppm, 0.1 mol%, 0.001 mmol, 0.8 mg), K_2CO_3 (2 equiv., 2 mmol, 276 mg), 3-bromo-4-methylacetophenone (1.0 equiv., 1.0 mmol, 213 mg) and *o*-tolylboronic acid (1.2 equiv., 1.2 mmol, 204 mg). A stirring bar was added, then the vial was sealed, evacuated and back-filled with nitrogen three times. Degassed rhamnolipids solution (2 mL) was added via syringe and the reaction mixture was vigorously stirred at 50 °C for 5 hours. After completion of the reaction (monitored by GC-MS or GC-FID) the mixture was cooled back to room temperature, was diluted with brine and ethyl acetate. The organic phase was separated, and the aqueous phase was extracted with 2x10 ml ethyl

acetate. The combined organic phase was dried on Na_2SO_4, and concentrated under vacuo. The product was isolated by flash column chromatography using hexane as eluent.

Yield: 184 mg (0.82 mmol, 82%) clear oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.93 – 7.86 (m, 1H), 7.77 – 7.70 (m, 1H), 7.38 (d, *J* = 8.0 Hz, 1H), 7.35 – 7.23 (m, 3H), 7.12 (d, *J* = 7.2 Hz, 1H), 2.60 (s, 3H), 2.14 (s, 2H), 2.07 (s, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 198.0, 142.1, 142.0, 140.6, 135.8, 135.1, 130.3, 130.1, 129.6, 129.3, 127.8, 127.3, 125.9, 26.7, 20.2, 19.9. **MS** (EI, 70 eV): *m/z* (%): 224(41[M^+]), 209(100), 178(9), 165(61), 152(9), 139(6), 128(5), 115(9), 97(7), 89(7), 63(5).

4′-Methyl-(1,1′-biphenyl)-2-carbonitrile (11f)[16]



9f, 1 mmol **2**, 1.2 equiv. **11f**, Preparative yield: 81%

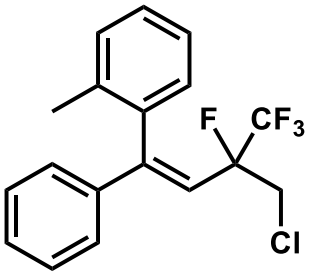
A 4 ml reaction vial was charged with $Pd(PPh_3)_2Cl_2$ (1 mol%, 0.01 mmol, 7 mg), K_2CO_3 (2 equiv., 2 mmol, 276 mg), 4-bromotoluene (1.0 equiv., 1.0 mmol, 171 mg) and 2-cyanophenylboronic acid (1.2 equiv., 1.2 mmol, 176 mg). A stirring bar was added, then the vial was sealed, evacuated and back-filled with nitrogen three times. Degassed rhamnolipids solution (2 mL) was added via syringe and the reaction mixture was vigorously stirred at 75 °C for 18 hours. After completion of the reaction (monitored by GC-MS or GC-FID) the mixture was cooled back to room temperature, was diluted with brine and ethyl acetate. The organic phase was separated, and the aqueous phase was extracted with 2x10 ml ethyl acetate. The combined organic phase was dried on Na_2SO_4, and concentrated under vacuo. The product was isolated by flash column chromatography using hexane and ethyl acetate as eluent.

Yield: 157 mg (0.81 mmol, 81%) white solid. Mp= 49-51 °C.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.78 – 7.73 (m, 1H), 7.67 – 7.60 (m, 1H), 7.53 – 7.39 (m, 4H), 7.31 (d, *J* = 7.8 Hz, 2H), 2.43 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 145.6, 138.8, 135.4, 133.8, 132.9, 130.1, 129.6, 128.7, 127.4, 119.0, 111.3, 21.4. **MS** (EI, 70 eV): *m/z* (%): 193(100[M^+]), 177(6), 165(35), 152(3), 139(4), 96(5), 82(6), 75(4).

Characterization of the Suzuki-products

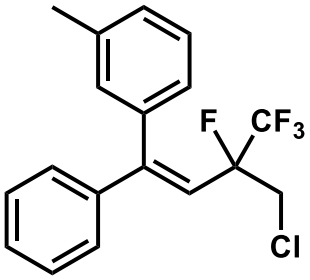
(*Z*)-1-(3-(Chloromethyl)-3,4,4,4-tetrafluoro-1-phenylbut-1-en-1-yl)-2-methylbenzene (3a)[5]



Yield: 127 mg (0.37 mmol, 74%) white solid. Mp = 72-75 °C.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.29 (dd, *J* = 7.5, 2.9 Hz, 5H), 7.25 – 7.13 (m, 4H), 5.60 (d, *J* = 24.3 Hz, 1H), 3.85 – 3.70 (m, 2H), 2.24 (s, 3H). **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -78.62 (d, *J* = 7.7 Hz), -166.41 (q, *J* = 7.7 Hz). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 151.9 (d, *J* = 2.2 Hz), 143.2, 138.5, 135.5, 130.8, 129.3, 128.9, 128.9, 128.2, 127.9, 127.7, 125.9, 122.7 (dd, *J* = 286.4, 29.1 Hz), 119.2, 119.1, 96.2 – 91.4 (m), 43.4 (d, *J* = 26.4 Hz), 20.4. **MS** (EI, 70 eV): *m/z* (%): 342(7[M^+]), 293(7), 273(5), 233(3), 220(4), 202(9), 179(100), 165(5), 146(4), 127(4), 115(8).

(*Z*)-1-(3-(Chloromethyl)-3,4,4,4-tetrafluoro-1-phenylbut-1-en-1-yl)-3-methylbenzene (3b)[5]

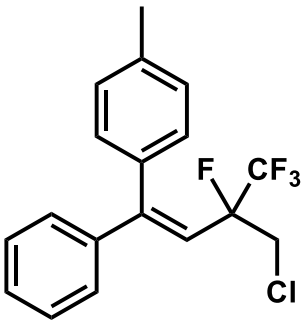


Yield: 165 mg (0.48 mmol, 96%) clear oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.41 – 7.34 (m, 3H), 7.31 – 7.27 (m, 2H), 7.22 (t, *J* = 7.6 Hz, 1H), 7.16 (d, *J* = 7.4 Hz, 1H), 7.12 – 7.03 (m, 2H), 5.96 (d, *J* = 23.2 Hz, 1H), 3.79 – 3.62 (m, 2H), 2.36 (s, 3H). **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -78.57 (d, *J* = 7.8 Hz), -166.13 (q, *J* = 7.7 Hz). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 150.9, 141.8, 138.3, 138.2, 129.6, 129.2, 129.2, 128.4, 128.2, 127.9, 127.8, 124.9, 122.7 (dd, *J* = 286.4, 29.2 Hz), 116.6, 116.4, 93.8 (dq, *J* = 197.8, 30.5 Hz), 43.4 (d, *J* = 26.9 Hz), 21.6. **MS** (EI, 70 eV): *m/z* (%): 342(40[M^+]),

293(100), 273(47), 237(14), 224(18), 209(24), 202(37), 191(15), 178(15), 165(13), 146(13), 127(12), 115(12), 101(13), 77(9).

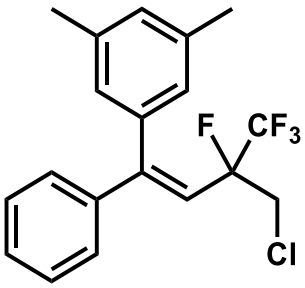
(*Z*)-1-(3-(Chloromethyl)-3,4,4,4-tetrafluoro-1-phenylbut-1-en-1-yl)-4-methylbenzene (3c)[5]



Yield: 160 mg (0.47 mmol, 93%) light yellow oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.28 – 7.22 (m, 3H), 7.19 – 7.14 (m, 2H), 7.08 – 6.99 (m, 4H), 5.85 (d, *J* = 23.1 Hz, 1H), 3.61 (dd, *J* = 17.0, 14.4 Hz, 2H), 2.25 (s, 3H). **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -78.58 (d, *J* = 7.8 Hz), -165.82 (q, *J* = 7.7 Hz). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 150.7, 150.6, 138.9, 138.9, 138.4, 129.2, 129.2, 127.8, 127.6, 122.7 (dd, *J* = 286.3, 29.1 Hz), 115.8, 115.6, 93.8 (dq, *J* = 197.6, 30.4 Hz), 43.4 (d, *J* = 26.8 Hz), 21.3. **MS** (EI, 70 eV): *m/z* (%): 342(44[M^+]), 293(100), 273(48), 253(5), 237(11), 223(17), 209(20), 202(32), 189(13), 165(9), 146(10), 127(9), 115(10), 91(8).

(*Z*)-1-(3-(Chloromethyl)-3,4,4,4-tetrafluoro-1-phenylbut-1-en-1-yl)-3,5-dimethylbenzene (3d)

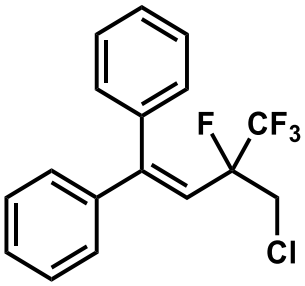


Yield: 168 mg (0.47 mmol, 94%) light yellow oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.31 – 7.24 (m, 3H), 7.19 – 7.14 (m, 2H), 6.88 (s, 1H), 6.76 (s, 2H), 5.83 (d, *J* = 23.2 Hz, 1H), 3.67 – 3.55 (m, 2H), 2.19 (s, 6H). **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -78.56 (d, *J* = 7.8 Hz), -165.94 (q, *J* = 7.7 Hz). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 151.1, 141.9, 138.4, 138.1, 129.2, 129.1, 127.8, 125.5, 122.7 (dd, *J* = 286.4, 29.0 Hz), 116.5, 116.3, 93.7 (dd, *J* = 197.7, 30.5 Hz), 43.4 (d, *J* = 26.9 Hz), 21.4. **MS** (EI, 70

eV): *m/z* (%): 356(49[M^+]), 307(100), 287(42), 272(5), 238(13), 223(23), 202(19), 165(9), 146(10), 127(9), 107(4), 91(6). **IR** (ATR, cm^{-1}) 3024, 2921, 1639, 1598, 1494, 1443, 1312, 1286, 1177, 1124, 1103, 1066, 1028, 991, 842, 777, 698, 676, 628, 605, 587, 502. **HRMS** *m/z* calcd for $C_{19}H_{17}ClF_4^+$: 356.0955, found: 356.09666.

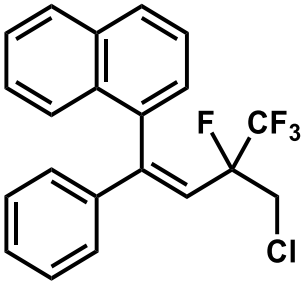
(3-(Chloromethyl)-3,4,4,4-tetrafluorobut-1-ene-1,1-diyl)dibenzene (3e)[5]



Yield: 151 mg (0.46 mmol, 92%) clear oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.31 – 7.25 (m, 3H), 7.24 – 7.15 (m, 7H), 5.87 (d, *J* = 23.2 Hz, 1H), 3.69 – 3.60 (m, 2H). **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -78.56 (d, *J* = 7.8 Hz), -166.26 (q, *J* = 7.7 Hz). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 150.8, 150.8, 141.8, 138.2, 138.2, 129.2, 129.2, 128.8, 128.5, 127.9, 127.9, 127.7, 122.7 (dd, *J* = 286.5, 29.0 Hz), 116.7, 116.5, 93.8 (dq, *J* = 198.2, 30.6 Hz), 43.4 (d, *J* = 26.8 Hz). **MS** (EI, 70 eV): *m/z* (%): 328(44[M^+]), 279(100), 259(47), 239(11), 210(23), 203(38), 189(11), 178(15), 165(11), 127(14), 101(8), 89(6), 77(8), 63(4).

(*Z*)-1-(3-(Chloromethyl)-3,4,4,4-tetrafluoro-1-phenylbut-1-en-1-yl)naphthalene (3f)

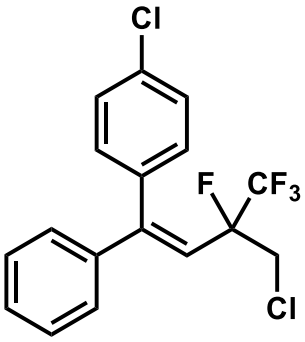


Yield: 179 mg (0.47 mmol, 94%) white solid. Mp = 85-88 °C.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.16 – 8.07 (m, 1H), 7.79 – 7.68 (m, 2H), 7.43 – 7.28 (m, 6H), 7.23 – 7.15 (m, 3H), 5.70 (d, *J* = 24.3 Hz, 1H), 3.83 – 3.64 (m, 2H). **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -78.49 (d, *J* = 7.9 Hz), -166.51 (q, *J* = 7.7 Hz). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 150.5, 141.0, 139.2, 134.1, 131.1, 128.6, 128.5, 128.0, 127.8, 126.7, 126.7, 126.1, 125.6, 125.3, 122.7 (dd, *J* = 286.6, 29.0 Hz), 120.6, 120.4, 93.9 (dd, *J* = 199.3, 30.4 Hz), 43.5 (d, *J* = 26.4 Hz). **MS** (EI, 70 eV): *m/z* (%): 378(13[M^+]), 259(9), 229(100), 202(3), 183(7),

151(5), 126(7), 113(4). **IR** (ATR, cm^{-1}) 3016, 2966, 3047, 1662, 1592, 1506, 1493, 1428, 1392, 1310, 1286, 1201, 1181, 1126, 1109, 1076, 994, 859, 803, 783, 770, 698, 638, 579, 519. **HRMS** *m/z* calcd for $C_{21}H_{15}ClF_4^+$: 378.0798, found: 378.08070.

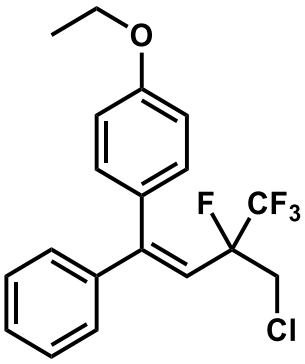
(*Z*)-1-Chloro-4-(3-(chloromethyl)-3,4,4,4-tetrafluoro-1-phenylbut-1-en-1-yl)benzene (3g)



Yield: 170 mg (0.47 mmol, 94%) light yellow solid. Mp = 47-50 °C.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.31 – 7.25 (m, 3H), 7.22 – 7.13 (m, 4H), 7.12 – 7.06 (m, 2H), 5.84 (d, *J* = 23.1 Hz, 1H), 3.73 – 3.57 (m, 2H). **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -78.56 (d, *J* = 7.8 Hz), -166.62 (q, *J* = 7.7 Hz). **^{13}C NMR** (101 MHz, Chloroform-d) δ 149.8, 149.7, 140.3, 137.8, 137.8, 134.9, 129.1, 129.1, 128.9, 128.7, 128.1, 128.0, 122.6 (dd, J = 286.3, 29.0 Hz), 117.0, 116.9, 93.7 (dq, J = 198.4, 30.5 Hz), 43.4 (d, J = 26.5 Hz). **MS** (EI, 70 eV): *m/z* (%): 362(38[M+]), 313(100), 293(50), 257(18), 245(7), 238(19), 222(51), 209(54), 202(52), 176(20), 163(12), 151(16), 127(24), 110(23), 88(10), 75(20), 63(10). **IR** (ATR, cm^{-1}) 3022, 2972, 1645, 1589, 1489, 1429, 1309, 1290, 1180, 1109, 1088, 1012, 990, 865, 828, 773, 710, 699, 682, 603, 527. **HRMS** *m/z* calcd for $C_{17}H_{12}Cl_2F_4^+$: 362.0252, found: 362.0256.

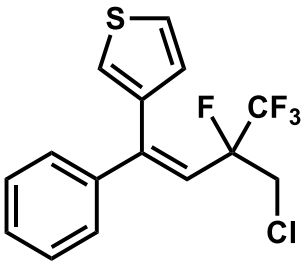
(*Z*)-1-(3-(Chloromethyl)-3,4,4,4-tetrafluoro-1-phenylbut-1-en-1-yl)-4-ethoxybenzene (3h)[5]



Yield: 174 mg (0.47 mmol, 93%) pale yellow oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.27 (dd, *J* = 4.9, 1.8 Hz, 3H), 7.19 – 7.14 (m, 2H), 7.10 – 7.04 (m, 2H), 6.73 (d, *J* = 8.8 Hz, 2H), 5.80 (d, *J* = 22.9 Hz, 1H), 3.93 (q, *J* = 7.0 Hz, 2H), 3.67 – 3.54 (m, 2H), 1.32 (t, *J* = 7.0 Hz, 3H). **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -78.61 (d, *J* = 8.0 Hz), -165.27 (q, *J* = 7.8 Hz). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 159.6, 150.3, 150.2, 138.5, 134.1, 129.3, 129.2, 128.9, 127.8, 122.7 (qd, *J* = 286.5, 29.3 Hz), 114.6, 114.4, 114.4, 93.7 (dq, *J* = 197.3, 30.4 Hz), 63.7, 43.4 (d, *J* = 27.1 Hz), 14.9. **MS** (EI, 70 eV): *m/z* (%): 372(100[M^+]), 323(96), 303(53), 295(40), 275(45), 247(25), 226(19), 220(32), 196(44), 178(23), 165(45), 152(17), 133(10), 127(16), 115(10), 101(5), 89(6), 77(9).

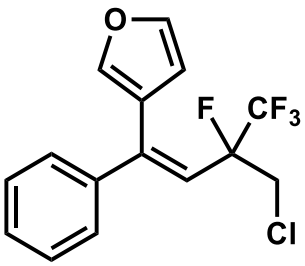
(*Z*)-3-(3-(Chloromethyl)-3,4,4,4-tetrafluoro-1-phenylbut-1-en-1-yl)thiophene (3i)



Yield: 147 mg (0.44 mmol, 88%) pale yellow oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.42 – 7.34 (m, 3H), 7.30 (q, *J* = 5.1 Hz, 3H), 7.23 – 7.19 (m, 1H), 6.85 – 6.78 (m, 1H), 6.02 (d, *J* = 22.7 Hz, 1H), 3.73 – 3.61 (m, 2H). **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -78.60 (d, *J* = 7.8 Hz), -165.79 (q, *J* = 7.8 Hz). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 144.9, 143.3, 137.9, 128.7, 128.7, 127.8, 127.8, 126.3, 125.5, 125.4, 122.5 (dd, *J* = 286.5, 29.1 Hz), 114.8, 114.7, 95.5 – 91.7 (m), 43.2 (d, *J* = 26.6 Hz). **MS** (EI, 70 eV): *m/z* (%): 334(60[M^+]), 285(100), 265(71), 245(7), 229(21), 215(45), 201(53), 196(31), 183(56), 165(22), 152(23), 127(22), 108(12), 92(10), 69(18). **IR** (ATR, cm^{-1}) 3108, 3026, 1638, 1493, 1443, 1309, 1289, 1175, 1122, 1099, 1022, 993, 848, 784, 715, 699, 668, 590, 518. **HRMS** *m/z* calcd for $C_{15}H_{11}ClF_4S^+$: 334.0206, found: 334.02119.

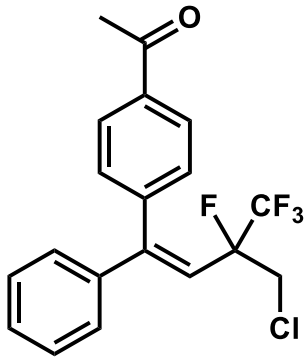
(*Z*)-3-(3-(Chloromethyl)-3,4,4,4-tetrafluoro-1-phenylbut-1-en-1-yl)furan (3j)[5]



Yield: 145 mg (0.45 mmol, 91%) yellow oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.43 – 7.39 (m, 1H), 7.39 – 7.33 (m, 3H), 7.32 – 7.27 (m, 2H), 6.85 (s, 1H), 6.61 – 6.56 (m, 1H), 5.82 (d, *J* = 22.6 Hz, 1H), 3.74 – 3.59 (m, 2H). **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -78.69 (d, *J* = 7.9 Hz), -165.65 (q, *J* = 7.9 Hz). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 144.1, 143.2, 141.9 (d, *J* = 3.7 Hz), 137.4, 129.0, 128.6, 128.6, 127.9, 127.9, 122.6 (dd, *J* = 286.4, 29.2 Hz), 113.8, 113.6, 107.7, 93.8 (dd, *J* = 196.6, 30.6 Hz), 43.3 (d, *J* = 26.3 Hz). **MS** (EI, 70 eV): *m/z* (%): 318(69[M+]), 269(100), 249(60), 221(16), 201(57), 183(31), 171(36), 165(63), 152(22), 139(19), 127(14), 115(14), 102(6), 89(5), 77(11), 63(12).

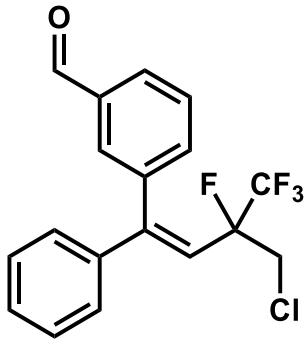
(*Z*)-1-(4-(3-(Chloromethyl)-3,4,4,4-tetrafluoro-1-phenylbut-1-en-1-yl)phenyl)ethan-1-one (3k)



Yield: 164 mg (0.44 mmol, 88%) yellow solid. Mp = 65-70 °C.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.91 (d, *J* = 8.5 Hz, 2H), 7.43 – 7.33 (m, 5H), 7.29 – 7.24 (m, 2H), 6.04 (d, *J* = 23.2 Hz, 1H), 3.85 – 3.71 (m, 2H), 2.61 (s, 3H). **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -78.48 (d, *J* = 7.7 Hz), -167.20 (q, *J* = 7.6 Hz). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 197., 149.90, 149.9, 146.1, 137.5, 137.5, 137.0, 129.1, 129.1, 128.6, 128.2, 128.1, 127.9, 122.5 (dd, *J* = 286.5, 28.9 Hz), 118.5, 118.4, 93.8 (dq, *J* = 199.0, 30.5 Hz), 43.4 (d, *J* = 26.3 Hz), 26.8. **MS** (EI, 70 eV): *m/z* (%): 370(45[M^+]), 355(100), 321(11), 301(4), 259(23), 239(13), 220(14), 209(40), 202(24), 178(31), 143(10), 125(11), 101(13), 77(7). **IR** (ATR, cm^{-1}) 3029, 2971, 1677, 1604, 1435, 1405, 1360, 1304, 1266, 1177, 1114, 1075, 990, 963, 868, 831, 774, 716, 699, 688, 605, 587, 523. **HRMS** *m/z* calcd for $C_{19}H_{15}ClF_4O^+$: 370.0748, found: 370.07526.

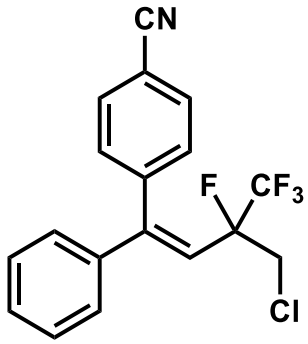
(*Z*)-3-(3-(Chloromethyl)-3,4,4,4-tetrafluoro-1-phenylbut-1-en-1-yl)benzaldehyde (3l)



Yield: 156 mg (0.44 mmol, 87%) pale yellow oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.01 (s, 1H), 7.89 – 7.82 (m, 1H), 7.83 – 7.77 (m, 1H), 7.55 – 7.47 (m, 2H), 7.44 – 7.36 (m, 3H), 7.29 (d, *J* = 4.0 Hz, 2H), 6.04 (d, *J* = 23.2 Hz, 1H), 3.86 – 3.71 (m, 2H). **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -78.49 (d, *J* = 7.7 Hz), -167.34 (q, *J* = 7.6 Hz). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 192.1, 149.7, 142.8, 137.5, 136.7, 133.6, 129.9, 129.3, 129.1, 129.1, 128.5, 128.3, 128.1, 122.5 (dd, *J* = 286.5, 28.8 Hz), 118.2, 118.0, 93.8 (dq, *J* = 198.9, 30.5 Hz), 43.5 (d, *J* = 26.2 Hz). **MS** (EI, 70 eV): *m/z* (%): 356(82[M^+]), 327(4), 307(27), 287(38), 279(100), 259(74), 239(32), 220(28), 209(73), 203(95), 189(33), 178(49), 165(28), 146(24), 127(34), 101(22), 77(25). **IR** (ATR, cm^{-1}) 3058, 2834, 2728, 1697, 1598, 1580, 1443, 1268, 1180, 1123, 1100, 994, 854, 797, 698, 649, 577. **HRMS** *m/z* calcd for $C_{18}H_{13}ClF_4O^+$: 356.0591, found: 356.0588.

(*Z*)-4-(3-(Chloromethyl)-3,4,4,4-tetrafluoro-1-phenylbut-1-en-1-yl)benzonitrile (3m)

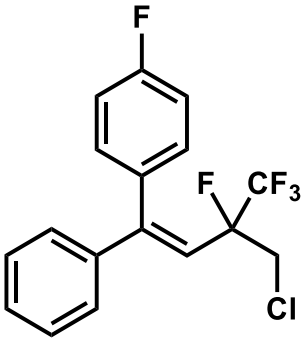


Yield: 132 mg (0.37 mmol, 75%) yellow oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.60 (d, *J* = 8.5 Hz, 2H), 7.41 – 7.32 (m, 5H), 7.25 – 7.19 (m, 2H), 6.00 (d, *J* = 23.2 Hz, 1H), 3.86 – 3.68 (m, 2H). **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -78.46 (d, *J* = 7.7 Hz), -167.77 (q, *J* = 7.6 Hz). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 149.3, 149.3, 146.0, 136.9, 136.9, 132.4, 129.0, 129.0, 128.4, 128.3, 128.2, 122.4 (dd, *J* = 286.5, 28.9 Hz), 119.4, 119.2, 118.6, 112.4, 93.8 (dq, *J* = 199.6, 30.5 Hz), 43.4 (d, *J* = 26.3 Hz). **MS** (EI,

70 eV): *m/z* (%): 353(47[M^+]), 304(100), 284(96), 264(13), 248(66), 234(50), 227(30), 214(15), 201(19), 177(16), 152(16), 127(26), 101(10), 77(18), 63(8). **IR** (ATR, cm^{-1}) AR1040C 3026, 2969, 2229, 1605, 1502, 1443, 1368, 1310, 1292, 1178, 1124, 1099, 1021, 993, 831, 776, 699, 596, 544, 513. **HRMS** *m/z* calcd for $C_{18}H_{12}ClF_4N^+$: 353.0594, found: 353.0582.

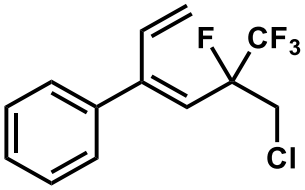
(*Z*)-1-(3-(Chloromethyl)-3,4,4,4-tetrafluoro-1-phenylbut-1-en-1-yl)-4-fluorobenzene (3n)[5]



Yield: 148 mg (0.43 mmol, 85%) pale yellow oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.28 (dd, *J* = 4.4, 2.1 Hz, 3H), 7.15 (tt, *J* = 8.9, 4.0 Hz, 4H), 6.95 – 6.86 (m, 2H), 5.81 (d, *J* = 23.1 Hz, 1H), 3.71 – 3.57 (m, 2H). **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -78.60 (d, *J* = 7.9 Hz), -113.04, -166.38 (q, *J* = 7.7 Hz). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 164.3, 161.8, 149.7 (d, *J* = 2.5 Hz), 137.9 (d, *J* = 1.4 Hz), 137.9 – 137.7 (m), 129.4, 129.3, 128.9 (d, *J* = 3.0 Hz), 127.9, 127.8, 122.5 (dd, *J* = 286.5, 29.0 Hz), 116.4, 116.2, 115.4, 115.2, 93.6 (dq, *J* = 198.4, 30.7, 30.3 Hz), 43.3 (d, *J* = 26.7 Hz). **MS** (EI, 70 eV): *m/z* (%): 346(44[M^+]), 297(100), 277(59), 257(13), 241(12), 227(35), 221(49), 202(5), 196(17), 183(14), 164(8), 145(13), 127(15), 110(8), 98(7), 75(6).

(*E*)-(5-(Chloromethyl)-5,6,6,6-tetrafluorohexa-1,3-dien-3-yl)benzene (3o)

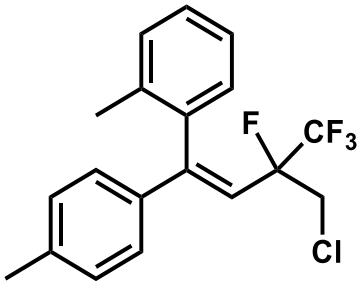


Yield: 94 mg (0.33 mmol, 67%) clear oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.39 – 7.32 (m, 3H), 7.22 – 7.14 (m, 2H), 6.62 (dd, *J* = 17.1, 10.4 Hz, 1H), 5.61 (d, *J* = 22.8 Hz, 1H), 5.29 (d, *J* = 10.4 Hz, 1H), 4.79 (d, *J* = 17.1 Hz, 1H), 3.70 – 3.54 (m, 2H). **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -78.66 (d, *J* = 7.8 Hz), -166.04 (q, *J* = 7.8 Hz).**^{13}C NMR** (101 MHz, Chloroform-*d*) δ 149.2, 149.1, 140.6, 135.4, 128.9, 128.9, 127.7, 122.5 (dd, *J* = 286.4, 29.0 Hz), 120.7, 119.8, 119.6, 93.5 (dq, *J* = 196.5, 30.7 Hz), 43.1

(d, *J* = 26.4 Hz). **MS** (EI, 70 eV): *m/z* (%): 278(20[M^+]), 229(38), 209(30), 189(10), 173(10), 159(36), 153(25), 146(9), 129(100), 115(23), 102(12), 91(25), 77(14), 63(9). **IR** (ATR, cm^{-1}) 3060, 2934, 1709, 1493, 1443, 1310, 1289, 1177, 1116, 1027, 994, 773, 699, 605, 519. **HRMS** *m/z* calcd for $C_{13}H_{11}ClF_4^+$: 278.0486, found: 278.0493.

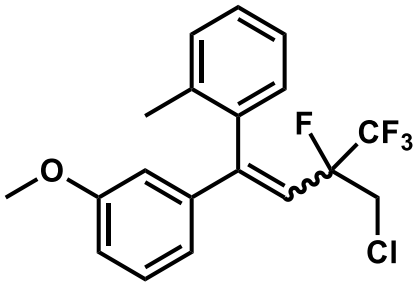
(*Z*)-1-(3-(Chloromethyl)-3,4,4,4-tetrafluoro-1-(p-tolyl)but-1-en-1-yl)-2-methylbenzene (3p)



Yield: 160 mg (0.45 mmol, 89%) white solid. Mp= 75-79 °C.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.23 – 7.08 (m, 8H), 5.58 (d, *J* = 24.0 Hz, 1H), 3.85 – 3.69 (m, 2H), 2.34 (s, 3H), 2.22 (s, 3H). **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -78.63 (d, *J* = 7.8 Hz), -165.43 (q, *J* = 7.8 Hz). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 152.0, 152.0, 143.4, 137.8, 135.6, 135.5, 130.8, 129.3, 128.9, 128.9, 128.4, 128.1, 125.9, 122.8 (dd, *J* = 286.6, 29.1 Hz), 118.8 (d, *J* = 17.0 Hz), 93.7 (dd, *J* = 198.5, 30.3 Hz), 43.3 (d, *J* = 26.8 Hz), 21.4, 20.4. **MS** (EI, 70 eV): *m/z* (%): 356(11[M^+]), 341(9), 307(14), 287(9), 272(2), 238(5), 222(3), 215(9), 203(7), 193(100), 178(44), 165(7), 141(8), 115(12), 91(5). **IR** (ATR, cm^{-1}) 3020, 2971, 2924, 1656, 1510, 1487, 1456, 1425, 1310, 1290, 1270, 1180, 1112, 991, 854, 828, 812, 776, 756, 698, 647, 594, 513. **HRMS** *m/z* calcd for $C_{19}H_{17}ClF_4^+$: 356.0955, found [M-CF_3]$^+$: 287.10082.

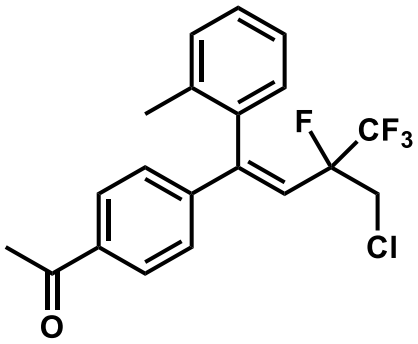
1-(3-(Chloromethyl)-3,4,4,4-tetrafluoro-1-(3-methoxyphenyl)but-1-en-1-yl)-2-methylbenzene (3q)



Yield: 151 mg (0.41 mmol, 81%) pale yellow oil. Mixture of stereoisomers in 8:1 ratio. Only the NMR data of the major component is reported below.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.20 (td, *J* = 12.5, 10.4, 6.8 Hz, 5H), 6.92 – 6.80 (m, 3H), 5.59 (d, *J* = 24.0 Hz, 1H), 3.80 (d, *J* = 11.6 Hz, 5H), 2.26 (s, 3H). **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -78.61 (d, *J* = 7.7 Hz), -165.93 (q, *J* = 7.7 Hz). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 158.9, 151.6, 142.9, 139.8, 135.4, 130.8, 129.3, 128.7, 128.2, 125.9, 124.2 (d, *J* = 29.1 Hz), 121.5 (d, *J* = 3.7 Hz), 119.3 (d, *J* = 17.1 Hz), 114.9 (d, *J* = 4.2 Hz), 113.2, 95.3 – 91.9 (m), 55.3, 43.3 (d, *J* = 26.5 Hz), 20.4. **MS** (EI, 70 eV): *m/z* (%): 372(35[M^+]), 323(10), 303(9), 252(4), 223(51), 209(100), 178(32), 165(22), 152(10), 133(6), 115(35), 91(7), 63(5). **IR** (ATR, cm^{-1}) 3063, 3017, 2942, 2837, 1598, 1578, 1486, 1458, 1431, 1286, 1259, 1232, 1178, 1048, 991, 849, 767, 729, 696, 611, 516. **HRMS** *m/z* calcd for $C_{19}H_{17}ClF_4O^+$: 372.0904, found: 372.08878.

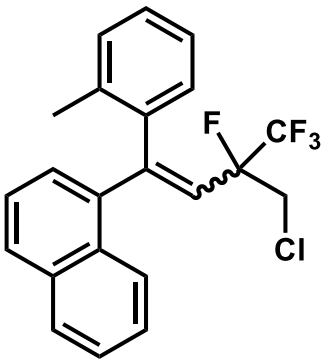
(*Z*)-1-(4-(3-(Chloromethyl)-3,4,4,4-tetrafluoro-1-(o-tolyl)but-1-en-1-yl)phenyl)ethan-1-one (3r)



Yield: 139 mg (0.36 mmol, 72%) pale yellow oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.89 (d, *J* = 8.3 Hz, 2H), 7.45 – 7.37 (m, 2H), 7.26 – 7.10 (m, 4H), 5.63 (d, *J* = 25.9 Hz, 1H), 3.90 – 3.72 (m, 2H), 2.59 (s, 3H), 2.23 (s, 3H). **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -78.58 (d, *J* = 7.5 Hz), -169.61 (q, *J* = 7.4 Hz). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 197.7, 150.6, 143.6, 143.5, 142.3, 135.4, 130.9, 129.3, 129.2, 129.1, 128.5, 127.7, 126.1, 122.5 (dd, *J* = 286.4, 29.0 Hz), 120.2, 120.0, 94.1 (dq, *J* = 201.2, 30.5 Hz), 43.8 (d, *J* = 25.5 Hz), 26.71, 20.4. **MS** (EI, 70 eV): *m/z* (%): 384(23[M^+]), 369(40), 341(34), 273(6), 235(27), 221(24), 202(23), 191(27), 178(100), 165(14), 152(7), 139(5), 125(6), 115(13), 101(7), 91(6), 77(4), 65(6). **IR** (ATR, cm^{-1}) 3019, 2969, 1682, 1604, 1487, 1431, 1404, 1357, 1265, 1180, 1124, 1017, 991, 957, 838, 771, 753, 699, 601, 583, 533. **HRMS** *m/z* calcd for $C_{20}H_{17}ClF_4O^+$: 384.0904, found $[M\text{-}CF_3]^+$: 315.09599.

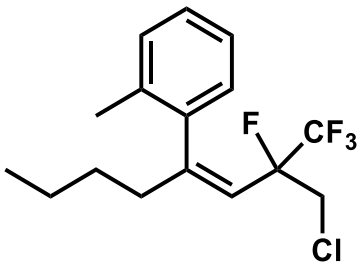
1-(3-(Chloromethyl)-3,4,4,4-tetrafluoro-1-(o-tolyl)but-1-en-1-yl)naphthalene (3s)



Yield: 153 mg (0.39 mmol, 83%) white solid from 0.47 mmol vinyl iodide starting material. Stereoisomeric mixture in 1:1.12 ratio. Mp= 131-136 °C.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.05 – 7.89 (m, 1H), 7.86 (d, *J* = 5.5 Hz, 2H), 7.58 – 7.42 (m, 4H), 7.32 – 7.15 (m, 3H), 7.08 (d, *J* = 6.8 Hz, 1H), 5.97 (dd, *J* = 23.6, 12.6 Hz, 1H), 3.85 – 3.68 (m, 2H), 2.63 (d, *J* = 9.1 Hz, 3H). **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -78.29 (dd, *J* = 26.0, 7.4 Hz), -168.10 (q, *J* = 7.6 Hz), -170.26 (q, *J* = 6.7 Hz). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 149.02, 148.49, 141.63 (d, *J* = 12.9 Hz), 136.61 (d, *J* = 6.3 Hz), 134.90 (d, *J* = 4.2 Hz), 133.62, 131.66, 129.18, 128.42, 128.37, 128.06, 127.21 (d, *J* = 3.3 Hz), 127.05 (d, *J* = 3.5 Hz), 126.27 (d, *J* = 4.7 Hz), 126.13, 125.88 (d, *J* = 2.9 Hz), 124.89, 124.71, 122.75 (dd, *J* = 287.9, 28.7 Hz), 122.44 (d, *J* = 3.4 Hz), 122.28 (d, *J* = 5.0 Hz), 93.64 (dt, *J* = 200.6, 31.6 Hz), 43.47 (t, *J* = 26.2 Hz), 21.27. **MS** (EI, 70 eV): *m/z* (%): 392(29[M^+]), 323(4), 247(5), 257(11), 243(100), 229(39), 215(12), 202(6), 183(8), 165(9), 135(7), 126(14), 115(17), 91(21). **IR** (ATR, cm^{-1}) 3066, 3017, 2928, 1655, 1592, 1506, 1426, 1309, 1289, 1194, 1180, 1131, 1102, 990, 864, 804, 783, 756, 726, 698, 628, 598, 587, 540. **HRMS** *m/z* calcd for $C_{22}H_{17}ClF_4^+$: 392.0955, found: 392.09429.

(*Z*)-1-(2-(Chloromethyl)-1,1,1,2-tetrafluorooct-3-en-4-yl)-2-methylbenzene (3t)



Yield: 138 mg (0.43 mmol, 86%) clear oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.23 – 7.13 (m, 3H), 7.07 (d, *J* = 7.2 Hz, 1H), 5.15 (d, *J* = 26.5 Hz, 1H), 3.99 – 3.70 (m, 2H), 2.65 – 2.49 (m, 2H), 2.30 (s, 3H), 1.35 – 1.25 (m, 4H), 0.85 (t, *J* = 6.8 Hz, 3H). **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -79.00 (d, *J* = 7.6 Hz), -175.04

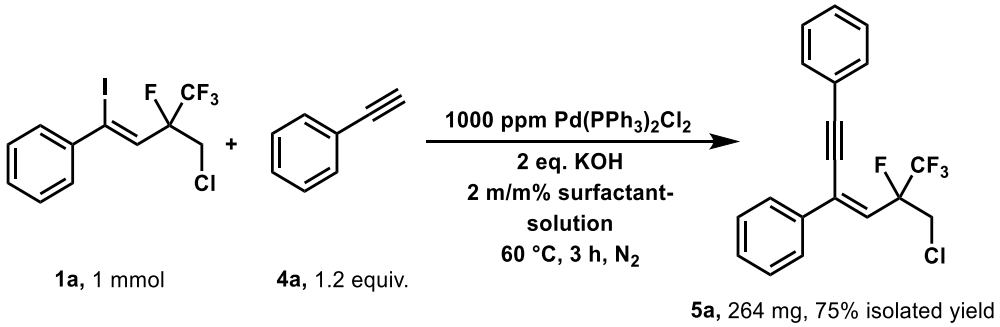
(q, *J* = 7.6 Hz). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 153.7, 143.1, 134.8, 130.4, 128.3, 127.4, 125.5, 122.9 (dd, *J* = 286.2, 29.7 Hz), 117.3 (d, *J* = 15.9 Hz), 94.4 (dq, *J* = 198.7, 30.6 Hz), 44.6 (d, *J* = 25.1 Hz), 33.2 (d, *J* = 8.3 Hz), 30.4, 23.1, 19.8, 13.9. **MS** (EI, 70 eV): *m/z* (%): 322(9[M^+]), 307(9), 293(14), 280(87), 265(17), 245(23), 231(33), 223(11), 217(22), 209(16), 197(19), 175(18), 159(100), 146(41), 129(53), 115(79), 105(56), 91(36), 77(14), 65(13). **IR** (ATR, cm^{-1}) 2959, 2932, 2864, 1656, 1487, 1458, 1381, 1313, 1283, 1178, 1105, 988, 844, 780, 753, 729, 693. **HRMS** *m/z* calcd for $C_{16}H_{19}ClF_4^+$: 322.1111, found [M-$C_4H_6F_3$]$^+$: 211.07140.

General procedure for the micellar Sonogashira-coupling

Sonogashira-coupling with vinyl iodides

A 4 ml reaction vial was charged with $Pd(PPh_3)_2Cl_2$ (1000 ppm, 0.1 mol%, 0.0005 mmol, 0.4 mg) and KOH (2 equiv., 1 mmol, 56 mg) and the acetylene derivative if solid (1.2 equiv.). A stirring bar was added, then the vial was sealed, evacuated and back-filled with nitrogen three times. Degassed rhamnolipids solution (1 mL) was added, then the vinyl iodide derivative (1.0 equiv., 0.5 mmol) and acetylene derivative if liquid (1.2 equiv.) via syringe and the reaction mixture was vigorously stirred at the appropriate temperature. After completion of the reaction (monitored by GC-MS or GC-FID) the mixture was cooled back to room temperature, was diluted with water or brine and ethyl acetate. The organic phase was separated, and the aqueous phase was extracted with 2x10 ml ethyl acetate. The combined organic phase was dried on Na_2SO_4, and concentrated under vacuo. The product was isolated by flash column chromatography using hexane and ethyl acetate as eluents.

1 mmol scale reaction

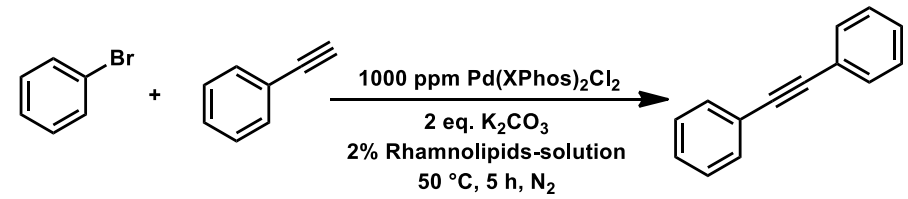


1a, 1 mmol **4a,** 1.2 equiv. **5a,** 264 mg, 75% isolated yield

A 4 ml reaction vial was charged with $Pd(PPh_3)_2Cl_2$ (1000 ppm, 0.1 mol%, 0.001 mmol, 0.8 mg) and KOH (2 equiv., 2 mmol, 112 mg). A stirring bar was added, then the vial was sealed, evacuated and back-filled with nitrogen three times. Degassed rhamnolipids solution (2 mL) was added, then the vinyl iodide (1.0 equiv., 1 mmol, 378 mg, 234 μL) and phenylacetylene (1.2 equiv., 1.2 mmol, 122 mg, 0.132 ml) via syringe and the reaction mixture was vigorously stirred at 60 °C for 3 hours. After completion of the reaction (monitored by GC-MS or GC-FID) the mixture was cooled back to room temperature, was diluted with water or brine and ethyl acetate. The organic phase was separated, and the aqueous phase was extracted with 2x10 ml ethyl acetate. The combined organic phase was dried on Na_2SO_4, and concentrated under vacuo. The product (264 mg, 0.75 mmol, 75 % yield) was isolated by flash column chromatography using hexane as eluent.

Sonogashira-couplings with other substrates

1,2-Diphenylacetylene (10a)[17]



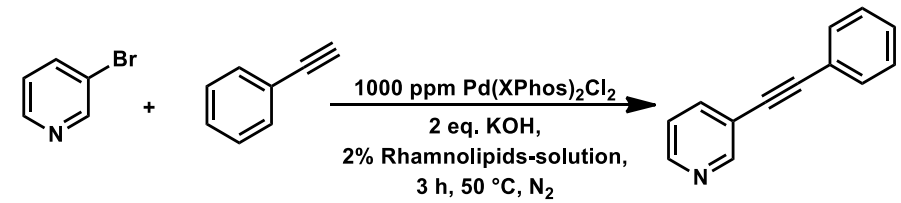
9g, 1 mmol **4a**, 1.2 equiv. **10a**, Preparative yield: 56%

A 4 ml reaction vial was charged with $Pd(XPhos)_2Cl_2$ (1000 ppm, 0.1 mol%, 0.001 mmol, 1.1 mg) and K_2CO_3 (2 equiv., 2 mmol, 276 mg). A stirring bar was added, then the vial was sealed, evacuated and back-filled with nitrogen three times. Degassed rhamnolipids solution (2 mL) was added, then the bromobenzene (1.0 equiv., 1 mmol, 157 mg, 105 μL) and phenylacetylene (1.2 equiv.) via syringe and the reaction mixture was vigorously stirred at 50 °C for 5 hours. After completion of the reaction (monitored by GC-MS or GC-FID) the mixture was cooled back to room temperature, was diluted with water or brine and ethyl acetate. The organic phase was separated, and the aqueous phase was extracted with 2x10 ml ethyl acetate. The combined organic phase was dried on Na_2SO_4, and concentrated under vacuo. The product was isolated by flash column chromatography using hexane as eluent.

Yield: 100 mg (0.56 mmol, 56%) light yellow solid. Mp= 58-62 °C.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.59 – 7.52 (m, 4H), 7.36 (dd, *J* = 4.6, 2.0 Hz, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 131.8, 128.5, 128.4, 123.4, 89.5. **MS** (EI, 70 eV): *m/z* (%): 178(100[M^+]), 152(17), 126(7), 98(7), 89(8), 76(12), 63(6), 50(5).

3-(2-Phenylethynyl)pyridine (10b)[16]



9a, 1 mmol **4a**, 1.2 equiv. **10b**, Preparative yield: 91%

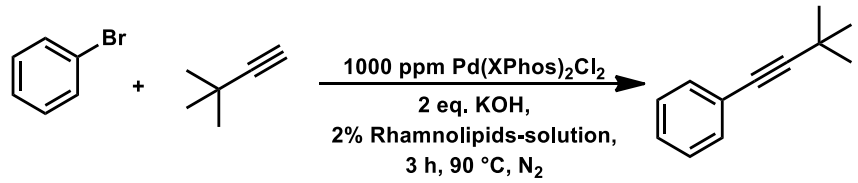
The preparation of the product was carried out similarly to product **10a** using KOH as the base and 3 hours reaction time.

Yield: 162 mg (0.91 mmol, 91%) yellow solid. Mp= 46-48 °C.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.7 – 8.7 (m, 1H), 8.5 – 8.4 (m, 1H), 7.7 (dt, *J* = 7.8, 1.8 Hz, 1H), 7.5 – 7.4 (m, 2H), 7.3 – 7.3 (m, 3H), 7.2 – 7.2 (m, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$)

δ 152.0, 148.3, 138.8, 131.8, 129.0, 128.6, 123.3, 122.6, 120.7, 93.0, 85.9. **MS** (EI, 70 eV): *m/z* (%): 179(100[M^+]), 151(13), 126(18), 98(10), 87(8), 76(14), 63(5).

1-Phenyl-2-*tert*-butylacetylene (10c)[18]



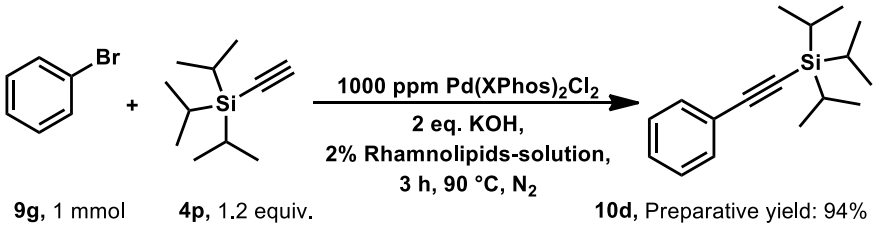
9g, 1 mmol **4m**, 1.2 equiv. **10c**, Preparative yield: 69%

The preparation of the product was carried out similarly to product **10a** using KOH as the base, 90 °C reaction temperature and 3 hours reaction time.

Yield: 109 mg (0.69 mmol, 69%) clear oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.3 (dd, *J* = 7.5, 1.9 Hz, 2H), 7.2 – 7.1 (m, 3H), 1.2 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 131.7, 128.2, 127.5, 124.2, 98.6, 79.2, 31.2, 28.1. **MS** (EI, 70 eV): *m/z* (%): 158(28[M^+]), 143(100), 128(58), 115(32), 103(14), 91(9), 77(20) 63(8), 51(5).

1-Phenyl-2-(triisopropylsilyl)acetylene (10d)[19]



9g, 1 mmol **4p**, 1.2 equiv. **10d**, Preparative yield: 94%

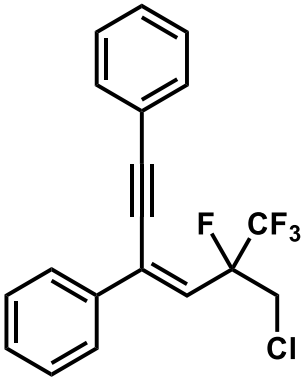
The preparation of the product was carried out similarly to product **10a** using KOH as the base, 90 °C reaction temperature and 3 hours reaction time.

Yield: 243 mg (0.94 mmol, 94%) yellowish oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.3 – 7.3 (m, 2H), 7.1 (dd, *J* = 4.1, 2.3 Hz, 3H), 1.0 (s, 21H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 132.2, 128.4, 128.3, 123.7, 107.3, 90.6, 18.8, 11.5. **MS** (EI, 70 eV): *m/z* (%): 258(7[M^+]), 215(100), 187(34), 173(48), 159(73), 145(90), 129(34), 105(35), 79(8), 59(7).

Characterization of the Sonogashira products

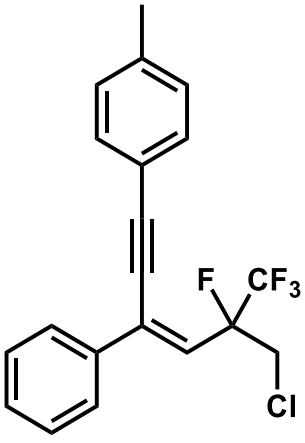
(*Z*)-(5-(Chloromethyl)-5,6,6,6-tetrafluorohex-3-en-1-yne-1,3-diyl)dibenzene (5a)[5]



Yield: 163 mg (0,46 mmol, 92%) pale yellow oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.48 – 7.41 (m, 4H), 7.41 – 7.29 (m, 6H), 6.09 (d, *J* = 23.9 Hz, 1H), 3.80 – 3.64 (m, 2H). **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -78.33 (d, *J* = 7.9 Hz), -167.51 (q, *J* = 7.8 Hz). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 136.5, 136.5, 133.8, 133.8, 131.9, 129.0, 128.5, 128.4, 128.3, 128.3, 128.0, 124.6, 124.4, 122.5, 122.3 (dd, *J* = 286.7, 28.8 Hz), 93.7 (dq, *J* = 199.9, 31.0 Hz), 92.7, 90.1 (d, *J* = 2.2 Hz), 43.2 (d, *J* = 26.1 Hz). **MS** (EI, 70 eV): *m/z* (%): 352(43[M^+]), 303(100), 283(41), 246(22), 233(46), 228(20), 201(13), 170(17), 127(13), 113(6), 77(8).

(*Z*)-1-(5-(Chloromethyl)-5,6,6,6-tetrafluoro-3-phenylhex-3-en-1-yn-1-yl)-4-methylbenzene (5b)[5]

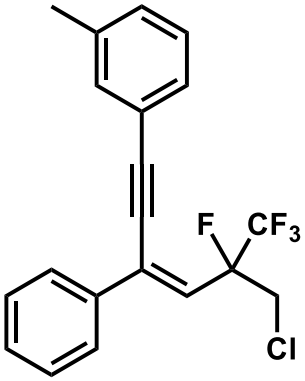


Yield: 155 mg (0,42 mmol, 85%) pale yellow solid. Mp = 55-58 °C.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.47 – 7.41 (m, 2H), 7.40 – 7.30 (m, 5H), 7.12 (d, *J* = 7.9 Hz, 2H), 6.07 (d, *J* = 23.9 Hz, 1H), 3.80 – 3.64 (m, 2H), 2.35 (s, 3H). **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -78.34 (d, *J* = 7.9 Hz), -167.30 (q, *J* = 7.8 Hz). **^{13}C NMR** (101 MHz,

Chloroform-*d*) δ 139.3, 136.7, 136.6, 133.9, 133.9, 131.8, 129.3, 128.4, 128.3, 128.3, 128.0, 124.2, 124.1, 122.4 (dd, *J* = 286.6, 29.0 Hz), 119.4, 93.7 (dq, *J* = 199.6, 30.8 Hz), 93.0, 89.5 (d, *J* = 2.1 Hz), 43.2 (d, *J* = 26.2 Hz), 21.7. **MS** (EI, 70 eV): *m/z* (%): 366(38[M^+]), 317(100), 297(33), 262(24), 246(35), 233(26), 226(12), 215(23), 202(10), 177(7), 165(18), 110(9), 91(7).

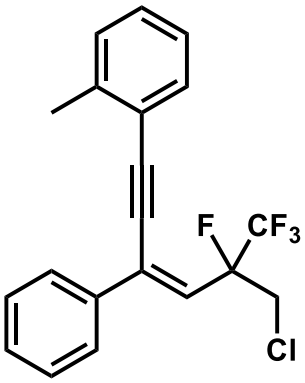
(*Z*)-1-(5-(Chloromethyl)-5,6,6,6-tetrafluoro-3-phenylhex-3-en-1-yn-1-yl)-3-methylbenzene (5c)[5]



Yield: 163 mg (0.44 mmol, 89%) light yellow oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.38 – 7.31 (m, 2H), 7.31 – 7.22 (m, 4H), 7.10 (dt, *J* = 13.3, 8.4 Hz, 2H), 7.01 (d, *J* = 7.2 Hz, 1H), 5.96 (d, *J* = 23.8 Hz, 1H), 3.70 – 3.54 (m, 2H), 2.25 (s, 3H). **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -78.33 (d, *J* = 7.9 Hz), -167.23 (q, *J* = 7.8 Hz). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 140.7, 136.7 (d, *J* = 1.4 Hz), 134.1, 132.1, 129.7, 129.7, 128.4, 128.3, 128.2, 128.0, 125.7, 124.0, 123.8, 122.4 (dd, *J* = 286.7, 28.8 Hz), 122.2, 94.0 (d, *J* = 2.2 Hz), 93.7 (dq, *J* = 199.3, 30.7 Hz), 91.9, 43.2 (d, *J* = 26.1 Hz), 20.7. **MS** (EI, 70 eV): *m/z* (%): 366(42[M^+]), 317(100), 297(30), 277(5), 262(16), 246(45), 233(27), 228(37), 215(49), 202(31), 183(19), 170(18), 151(10), 146(25), 127(25), 115(41), 91(25), 77(19), 63(13).

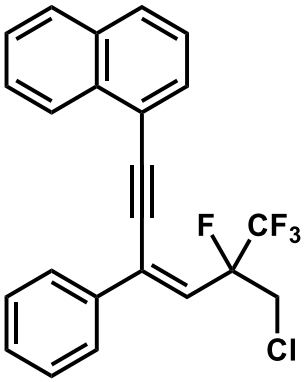
(*Z*)-1-(5-(Chloromethyl)-5,6,6,6-tetrafluoro-3-phenylhex-3-en-1-yn-1-yl)-2-methylbenzene (5d)[5]



Yield: 167 mg (0.45 mmol, 91%) light orange oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.38 – 7.32 (m, 2H), 7.28 (dd, *J* = 4.9, 1.9 Hz, 3H), 7.20 – 7.09 (m, 3H), 7.05 (d, *J* = 7.1 Hz, 1H), 5.99 (d, *J* = 23.9 Hz, 1H), 3.71 – 3.55 (m, 2H), 2.23 (s, 3H). **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -78.34 (d, *J* = 7.9 Hz), -167.47 (q, *J* = 7.8 Hz). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 138.1, 136.5, 133.8, 133.8, 132.3, 129.8, 128.8, 128.3, 128.2, 128.1, 127.9, 124.3, 124.2, 122.2 (dd, *J* = 286.6, 28.8 Hz), 122.1, 93.6 (dq, *J* = 199.8, 30.8 Hz), 92.8, 89.6 (d, *J* = 2.1 Hz), 43.0 (d, *J* = 26.0 Hz), 21.2. **MS** (EI, 70 eV): *m/z* (%): 366(37[M^+]), 317(100), 297(32), 282(9), 262(15), 246(35), 233(21), 207(21), 170(7), 165(19), 147(8), 127(21), 110(10), 91(10), 73(20).

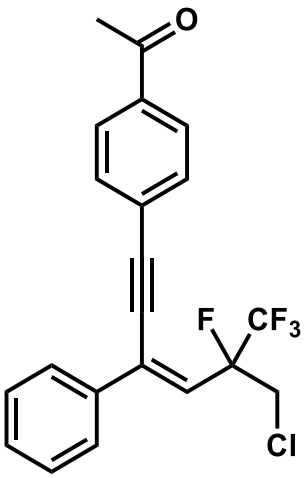
(*Z*)-1-(5-(Chloromethyl)-5,6,6,6-tetrafluoro-3-phenylhex-3-en-1-yn-1-yl)naphthalene (5e)



Yield: 153 mg (0.38 mmol, 76%) clear oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.19 – 8.12 (m, 1H), 7.84 (d, *J* = 8.3 Hz, 2H), 7.71 – 7.65 (m, 1H), 7.58 – 7.48 (m, 4H), 7.46 – 7.36 (m, 4H), 6.20 (d, *J* = 23.8 Hz, 1H), 3.75 (dd, *J* = 23.1, 12.5 Hz, 2H). **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -78.25 (d, *J* = 7.8 Hz), -167.36 (q, *J* = 7.8 Hz). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 136.6, 133.9, 133.3, 133.3, 131.0, 129.6, 128.5, 128.4, 128.3, 128.3, 128.1, 127.1, 126.7, 126.1, 125.3, 124.5, 124.3, 122.4 (dd, *J* = 287.0, 28.8 Hz), 120.1, 94.9, 94.9, 95.5 – 91.7 (m), 91.2, 43.2 (d, *J* = 26.0 Hz). **MS** (EI, 70 eV): *m/z* (%): 402(100[M^+]), 353(80), 333(55), 298(37), 283(87), 276(42), 265(11), 252(32), 237(10), 220(19), 201(48), 176(20), 147(26), 141(46), 138(31), 127(30), 113(10), 100(5), 77(9), 63(7), 51(14). **IR** (ATR, cm^{-1}) 3058, 2195, 1621, 1494, 1443, 1398, 1285, 1269, 1180, 1127, 1090, 997, 798, 769, 696, 605, 564, 525. **HRMS** *m/z* calcd for $C_{23}H_{15}ClF_4^+$: 402.0798, found: 402.07991.

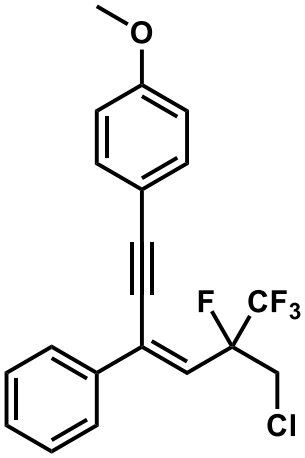
(*Z*)-1-(4-(5-(Chloromethyl)-5,6,6,6-tetrafluoro-3-phenylhex-3-en-1-yn-1-yl)phenyl)ethan-1-one (5f)



Yield: 179 mg (0.45 mmol, 91%) pale yellow solid. Mp = 70-75 °C.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.90 (d, *J* = 8.4 Hz, 2H), 7.51 (d, *J* = 8.4 Hz, 2H), 7.42 (s, 2H), 7.40 – 7.33 (m, 3H), 6.13 (d, *J* = 24.0 Hz, 1H), 3.81 – 3.65 (m, 2H), 2.59 (s, 3H). **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -78.29 (d, *J* = 7.8 Hz), -168.06 (q, *J* = 7.7 Hz). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 197.4, 136.8, 136.1, 136.1, 133.4, 133.4, 132.0, 128.6, 128.4, 128.3, 128.2, 128.1, 127.3, 125.7, 125.5, 122.3 (dd, *J* = 286.7, 28.7 Hz), 93.8 (dq, *J* = 199.8, 30.5 Hz), 92.8 (d, *J* = 2.0 Hz), 91.5, 43.2 (d, *J* = 25.9 Hz), 26.8. **MS** (EI, 70 eV): *m/z* (%): 394(55[M^+]), 379(27), 345(100), 325(29), 302(15), 275(8), 246(17), 226(13), 200(10), 177(7), 155(11), 127(9), 110(6). **IR** (ATR, cm^{-1}) 3063, 2961, 1680, 1598, 1493, 1445, 1401, 1356, 1265, 1177, 1123, 1106, 1075, 990, 858, 828, 763, 696, 661, 601, 588, 535. **HRMS** *m/z* calcd for $C_{21}H_{15}ClF_4O^+$: 394.0748, found: 394.07458.

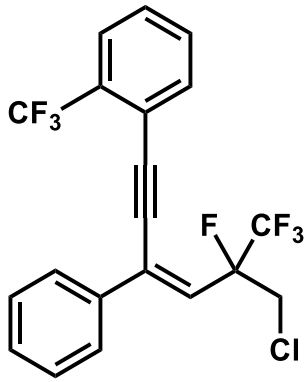
(*Z*)-1-(5-(Chloromethyl)-5,6,6,6-tetrafluoro-3-phenylhex-3-en-1-yn-1-yl)-4-methoxybenzene (5g)[5]



Yield: 155 mg (0.40 mmol, 81%) yellow solid. Mp = 78-82 °C.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.43 (d, *J* = 4.6 Hz, 2H), 7.40 – 7.33 (m, 5H), 6.84 (d, *J* = 8.7 Hz, 2H), 6.05 (d, *J* = 23.8 Hz, 1H), 3.81 (s, 3H), 3.78 – 3.64 (m, 2H). **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -78.37 (d, *J* = 7.9 Hz), -167.12 (q, *J* = 7.8 Hz). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 160.1, 136.6, 133.9, 133.3, 128.2, 128.2, 128.1, 127.9, 123.7, 123.5, 124.4 – 120.2 (m), 114.4, 114.0, 93.6 (dq, *J* = 199.2, 30.6 Hz), 92.6, 88.9 (d, *J* = 2.1 Hz), 55.3, 43.0 (d, *J* = 26.1 Hz). **MS** (EI, 70 eV): *m/z* (%): 382(56[M^+]), 333(100), 313(28), 278(68), 263(19), 246(17), 220(41), 215(17), 189(17), 170(9), 127(14), 110(11), 77(7).

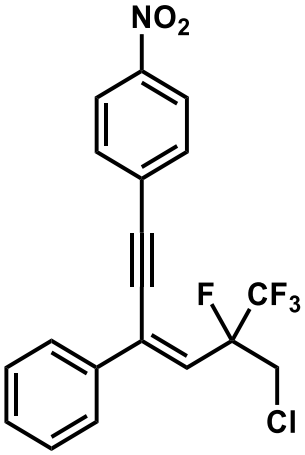
(*Z*)-1-(5-(Chloromethyl)-5,6,6,6-tetrafluoro-3-phenylhex-3-en-1-yn-1-yl)-2-(trifluoromethyl)benzene (5h)



Yield: 194 mg (0.46 mmol, 92%) pale yellow oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.66 (d, *J* = 7.7 Hz, 1H), 7.56 (d, *J* = 7.6 Hz, 1H), 7.52 – 7.41 (m, 4H), 7.40 – 7.33 (m, 3H), 6.10 (d, *J* = 24.0 Hz, 1H), 3.73 (dd, *J* = 24.0, 12.7 Hz, 2H). **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -62.37, -78.28 (d, *J* = 7.8 Hz), -167.88 (q, *J* = 7.7 Hz). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 135.8, 134.0, 133.5, 133.5, 131.8 (q, *J* = 30.5 Hz), 131.6, 128.8, 128.6, 128.4, 128.3, 128.0, 126.1 (q, *J* = 5.1 Hz), 125.5, 125.3, 123.5 (q, *J* = 273.6 Hz), 120.7, 95.0, 93.8 (dd, *J* = 199.9, 30.8 Hz), 88.2, 43.1 (d, *J* = 25.9 Hz). **MS** (EI, 70 eV): *m/z* (%): 420(35[M^+]), 371(100), 351(56), 315(6), 301(20), 282(44), 275(62), 251(30), 233(25), 219(21), 201(10), 177(12), 151(13), 141(31), 127(33), 77(10), 51(18). **IR** (ATR, cm^{-1}) 3060, 1621, 1574, 1492, 1452, 1317, 1262, 1170, 1126, 1106, 1062, 1032, 988, 851, 764, 696, 651, 596, 515. **HRMS** *m/z* calcd for $C_{20}H_{12}ClF_7^+$: 420.0516, found: 420.0515.

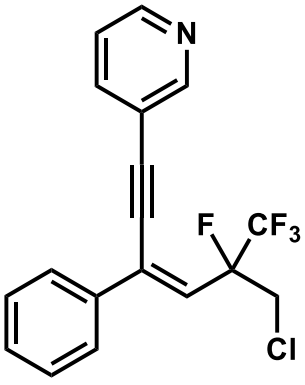
(*Z*)-1-(5-(Chloromethyl)-5,6,6,6-tetrafluoro-3-phenylhex-3-en-1-yn-1-yl)-4-nitrobenzene (5i)



Yield: 141 mg (0.35 mmol, 71%) yellow solid. Mp = 85-89 °C.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.18 (d, *J* = 8.8 Hz, 2H), 7.58 (d, *J* = 8.8 Hz, 2H), 7.45 – 7.36 (m, 5H), 6.16 (d, *J* = 24.0 Hz, 1H), 3.82 – 3.66 (m, 2H). **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -78.27 (d, *J* = 7.8 Hz), -168.46 (q, *J* = 7.7 Hz). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 147.5, 135.7, 135.7, 132.9, 132.9, 132.6, 129.3, 128.7, 128.2, 128.2 (d, *J* = 1.8 Hz), 126.6, 126.4, 123.7, 124.1 – 120.5 (m), 94.5 (d, *J* = 2.1 Hz), 93.8 (dd, *J* = 200.6, 30.9 Hz), 90.2, 43.2 (d, *J* = 25.5 Hz). **MS** (EI, 70 eV): *m/z* (%): 397(30[M^+]), 348(100), 328(32), 302(15), 282(12), 246(46), 233(37), 220(19), 213(11), 200(14), 189(8), 177(13), 170(8), 150(7), 127(13), 110(9). **IR** (ATR, cm^{-1}) 3060, 2961, 2847, 2205, 1624, 1591, 1516, 1492, 1445, 1343, 1285, 1191, 1123, 1103, 988, 851, 777, 747, 698, 608, 526. **HRMS** *m/z* calcd for $C_{19}H_{12}ClF_4NO_2^+$: 397.0493, found: 397.04929.

(*Z*)-3-(5-(Chloromethyl)-5,6,6,6-tetrafluoro-3-phenylhex-3-en-1-yn-1-yl)pyridine (5j)

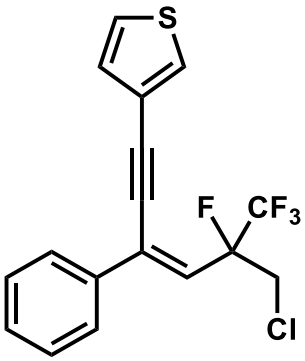


Yield: 140 mg (0.39 mmol, 79%) light orange solid. Mp = 86-90 °C

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.53 (s, 1H), 8.40 (d, *J* = 3.4 Hz, 1H), 7.57 (dt, *J* = 7.8, 1.7 Hz, 1H), 7.31 – 7.21 (m, 5H), 7.14 – 7.08 (m, 1H), 5.98 (d, *J* = 24.0 Hz, 1H), 3.67 – 3.51

(m, 2H). **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -78.30 (d, *J* = 7.8 Hz), -168.25 (q, *J* = 7.7 Hz). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 152.3, 149.2, 138.8, 135.9, 133.2, 128.6, 128.2, 128.2, 128.1, 125.7, 125.6, 123.2, 122.2 (dd, *J* = 286.5, 28.7 Hz), 119.8, 93.8 (dq, *J* = 199.9, 30.7 Hz), 93.0 (d, *J* = 2.0 Hz), 88.9, 43.2 (d, *J* = 25.8 Hz). **MS** (EI, 70 eV): *m/z* (%): 353(40[M^+]), 304(100), 284(47), 248(47), 234(25), 220(13), 207(11), 177(11), 152(12), 127(127), 110(7). **IR** (ATR, cm^{-1}) 3060, 2959, 2856, 2202, 1624, 1561, 1476, 1445, 1407, 1306, 1282, 1187, 1107, 1075, 990, 856, 807, 754, 696, 605, 520. **HRMS** *m/z* calcd for $C_{18}H_{12}ClF_4N^+$: 353.0594, found: 353.0595.

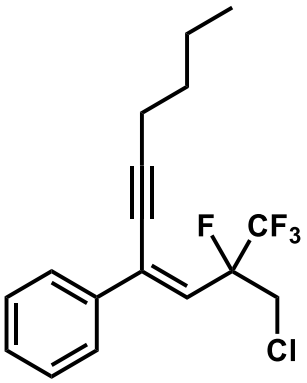
(*Z*)-3-(5-(Chloromethyl)-5,6,6,6-tetrafluoro-3-phenylhex-3-en-1-yn-1-yl)thiophene (5k)



Yield: 172 mg (0,48 mmol, 96%) pale yellow oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.45 – 7.41 (m, 1H), 7.38 (d, *J* = 4.9 Hz, 2H), 7.35 – 7.29 (m, 3H), 7.22 (dd, *J* = 4.8, 2.9 Hz, 1H), 7.09 – 7.04 (m, 1H), 6.02 (d, *J* = 23.9 Hz, 1H), 3.75 – 3.59 (m, 2H). **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -78.35 (d, *J* = 7.9 Hz), -167.53 (q, *J* = 7.8 Hz). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 136.4, 133.8, 129.9, 129.8, 128.4, 128.3, 128.3, 128.0, 125.7, 124.5, 124.3, 122.3 (dd, *J* = 286.7, 28.9 Hz), 121.6, 93.7 (dq, *J* = 199.2, 30.7 Hz), 89.6 (d, *J* = 1.8 Hz), 87.9, 43.2 (d, *J* = 25.9 Hz). **MS** (EI, 70 eV): *m/z* (%): 358(44), 309(100), 289(44), 254(31), 239(45), 220(31), 207(29), 189(9), 170(11), 157(22), 127(23), 110(6), 98(9), 69(11). **IR** (ATR, cm^{-1}) 3117, 3024, 2206, 1638, 1492, 1426, 1361, 1309, 1287, 1184, 1124, 1106, 1046, 983, 924, 852, 769, 696, 624, 601, 520. **HRMS** *m/z* calcd for $C_{17}H_{11}ClF_4S^+$: 358.0206, found: 358.02109.

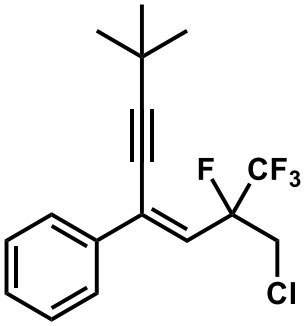
(*Z*)-(2-(Chloromethyl)-1,1,1,2-tetrafluorodec-3-en-5-yn-4-yl)benzene (5l)[5]



Yield: 141 mg (0.42 mmol, 85%) orange oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.33 (dd, *J* = 7.1, 2.9 Hz, 5H), 5.90 (d, *J* = 23.8 Hz, 1H), 3.74 – 3.59 (m, 2H), 2.32 (t, *J* = 7.1 Hz, 2H), 1.52 (p, *J* = 7.0 Hz, 2H), 1.39 (dq, *J* = 14.3, 7.1 Hz, 2H), 0.91 (t, *J* = 7.3 Hz, 3H). **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -78.49 (d, *J* = 7.9 Hz), -166.98 (q, *J* = 7.8 Hz). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 137.2, 134.3, 128.2, 128.1, 128.1, 127.9, 123.4, 123.2, 122.4 (dd, *J* = 286.6, 29.0 Hz), 94.7, 95.1 – 91.8 (m), 81.8 (d, *J* = 2.2 Hz), 43.1 (d, *J* = 26.3 Hz), 30.6, 22.2, 19.3, 13.7. **MS** (EI, 70 eV): *m/z* (%): 332(72[M^+]), 303(10), 283(100), 263(46), 241(29), 227(24), 207(14), 201(26), 183(94), 171(54), 165(74), 152(29), 141(46), 139(26), 127(21), 115(36), 105(13), 91(55), 77(19), 63(12).

(*Z*)-(2-(Chloromethyl)-1,1,1,2-tetrafluoro-7,7-dimethyloct-3-en-5-yn-4-yl)benzene (5m)

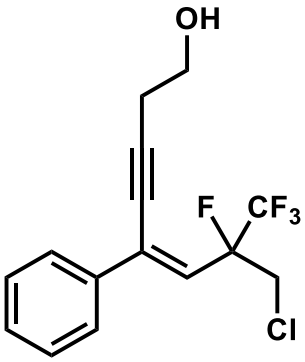


Yield: 147 mg (0.44 mmol, 88%) mauve oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.39 – 7.30 (m, 5H), 5.88 (d, *J* = 23.7 Hz, 1H), 3.74 – 3.59 (m, 2H), 1.23 (s, 9H). **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -78.41 (d, *J* = 8.0 Hz), -166.41 (q, *J* = 7.9 Hz). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 137.3, 134.5, 134.4, 128.3, 128.2, 128.2, 127.8, 123.1, 122.9, 122.4 (dd, *J* = 286.7, 29.0 Hz), 102.2, 93.5 (dq, *J* = 198.8, 30.6 Hz), 80.5, 80.5, 43.1 (d, *J* = 26.2 Hz), 30.8, 28.2. **MS** (EI, 70 eV): *m/z* (%): 332(18[M^+]), 317(21), 283(6), 268(8), 253(5), 233(5), 199(8), 183(100), 168(22), 153(15), 128(8), 115(11), 91(14),

77(8). **IR** (ATR, cm^{-1}) 2969, 2870, 2216, 1632, 1434, 1365, 1309, 1282, 1184, 1113, 1072, 993, 852, 808, 773, 698, 605, 522. **HRMS** *m/z* calcd for C17H17ClF4+: 332.0955, found: 332.0957.

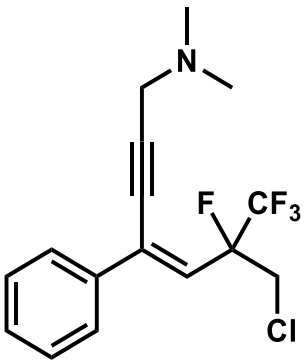
(*Z*)-7-(Chloromethyl)-7,8,8,8-tetrafluoro-5-phenyloct-5-en-3-yn-1-ol (5n)



Yield: 119 mg (0.37 mmol, 74%) orange oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.34 (s, 5H), 5.95 (d, *J* = 23.9 Hz, 1H), 3.77 – 3.59 (m, 4H), 2.60 (t, *J* = 6.2 Hz, 2H). **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -78.44 (d, *J* = 7.8 Hz), -167.79 (q, *J* = 7.7 Hz). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 136.7, 133.6, 128.2, 127.9, 127.9, 127.9, 124.3, 124.1, 122.2 (dd, *J* = 286.7, 28.7 Hz), 93.5 (dq, *J* = 199.5, 30.9 Hz), 90.4, 83.3 (d, *J* = 2.1 Hz), 60.8, 42.9 (d, *J* = 26.0 Hz), 23.9. **MS** (EI, 70 eV): *m/z* (%): 320(81[M^{+}]), 291(13), 271(33), 253(17), 241(77), 233(32), 221(36), 215(13), 201(52), 183(100), 170(67), 165(95), 152(31), 141(44), 127(24), 115(31), 102(11), 91(14), 77(23), 63(17). **IR** (ATR, cm^{-1}) 3368, 2939, 2891, 2219, 1625, 1493, 1445, 1310, 1289, 1178, 1122, 1042, 1018, 990, 848, 777, 696, 605, 520. **HRMS** *m/z* calcd for $C_{15}H_{13}ClF_4O^{+}$: 320.0591, found: 320.05986.

(*Z*)-6-(Chloromethyl)-6,7,7,7-tetrafluoro-*N*,*N*-dimethyl-4-phenylhept-4-en-2-yn-1-amine (5o)

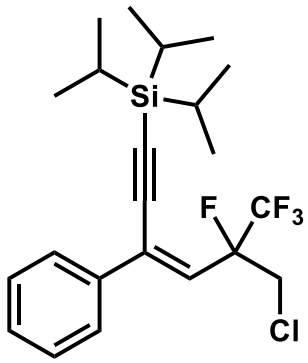


Yield: 121 mg (0.36 mmol, 73%) orange oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.33 (dt, *J* = 7.0, 2.9 Hz, 5H), 5.97 (d, *J* = 23.9 Hz, 1H), 3.75 – 3.60 (m, 2H), 3.38 (s, 2H), 2.29 (s, 6H). **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -78.45

(d, *J* = 7.8 Hz), -167.72 (q, *J* = 7.7 Hz). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 136.5, 133.4, 133.4, 128.2, 128.0, 127.9, 127.8, 124.4, 124.2, 122.2 (dd, *J* = 286.5, 28.8 Hz), 93.5 (dq, *J* = 199.4, 31.4, 30.6 Hz), 88.3, 86.2 (d, *J* = 2.1 Hz), 48.4, 44.1, 42.9 (d, *J* = 25.9 Hz). **MS** (EI, 70 eV): *m/z* (%): 332(16[M^+]), 298(21), 278(4), 233(7), 214(4), 201(6), 184(55), 170(28), 165(17), 152(7), 139(12), 115(13), 91(7), 82(100), 77(8), 58(18 **IR** (ATR, cm^{-1}) 2973, 2824, 2778, 1626, 1468, 1445, 1357, 1321, 1289, 1180, 1122, 1089, 1028, 988, 838, 766, 698, 605, 523.). **HRMS** *m/z* calcd for $C_{16}H_{16}ClF_4N^+$: 333.0907, found $[M+H]^+$: 334.0983.

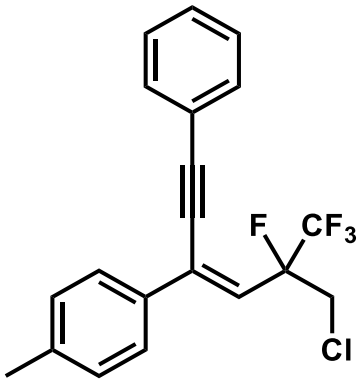
(*Z*)-(5-(Chloromethyl)-5,6,6,6-tetrafluoro-3-phenylhex-3-en-1-yn-1-yl)triisopropylsilane (5p)[5]



Yield: 195 mg (0.45 mmol, 90%) yellow oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.42 – 7.36 (m, 2H), 7.35 – 7.29 (m, 3H), 6.00 (d, *J* = 23.8 Hz, 1H), 3.77 – 3.61 (m, 2H), 1.06 (d, *J* = 2.5 Hz, 21H). **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -78.30 (d, *J* = 7.8 Hz), -167.03 (q, *J* = 7.8 Hz). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 136.4, 133.9, 133.9, 128.2 (d, *J* = 1.6 Hz), 128.1, 127.7, 124.5, 124.3, 122.2 (dd, *J* = 286.7, 29.0 Hz), 107.2 (d, *J* = 2.0 Hz), 95.1, 95.0 – 91.7 (m), 42.9 (d, *J* = 26.1 Hz), 18.6, 11.2. **MS** (EI, 70 eV): *m/z* (%): 389(31[M^+]), 361(10), 333(14), 248(11), 229(15), 201(79), 183(74), 170(20), 165(37), 152(42), 127(11), 115(14), 105(11), 97(22), 81(24), 77(100), 63(23).

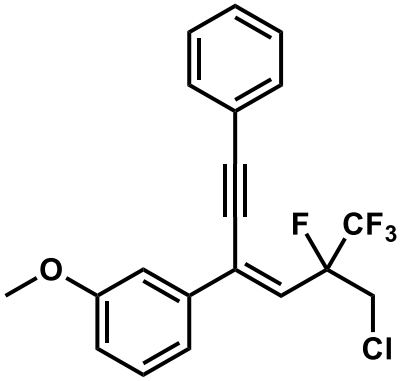
(*Z*)-1-(5-(Chloromethyl)-5,6,6,6-tetrafluoro-1-phenylhex-3-en-1-yn-3-yl)-4-methylbenzene (5q)



Yield: 158 mg (0.43 mmol, 86%) pale yellow oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.44 (dd, *J* = 7.2, 2.3 Hz, 2H), 7.37 – 7.28 (m, 5H), 7.18 (d, *J* = 7.9 Hz, 2H), 6.07 (d, *J* = 23.6 Hz, 1H), 3.80 – 3.63 (m, 2H), 2.39 (s, 3H). **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -78.33 (d, *J* = 8.0 Hz), -166.63 (q, *J* = 7.8 Hz). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 138.4, 133.9, 133.9, 133.6, 133.6, 131.9, 128.9, 128.8, 128.5, 128.3, 128.2, 124.4, 124.2, 122.6, 122.4 (dd, *J* = 286.6, 28.8 Hz), 93.7 (dd, *J* = 199.2, 30.7 Hz), 92.4, 90.3 (d, *J* = 2.2 Hz), 43.1 (d, *J* = 26.3 Hz), 21.5. **MS** (EI, 70 eV): *m/z* (%): 366(41[M^+]), 317(100), 297(38), 262(9), 246(32), 233(26), 215(12), 202(8), 183(7), 170(9), 151(13), 146(6), 123(9), 113(4), 91(6), 77(6), 63(5), 51(7). **IR** (ATR, cm^{-1}) 3031, 2924, 2203, 1611, 1510, 1490, 1312, 1285, 1177, 1126, 1106, 993, 837, 754, 689, 586, 526. **HRMS** *m/z* calcd for $C_{20}H_{15}ClF_4^+$: 366.0798, found: 366.07973.

(*Z*)-1-(5-(Chloromethyl)-5,6,6,6-tetrafluoro-1-phenylhex-3-en-1-yn-3-yl)-3-methoxybenzene (5r)

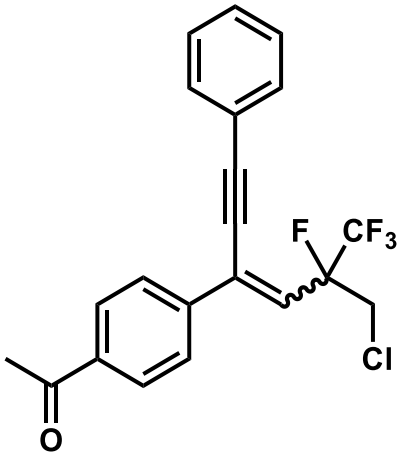


Yield: 175 mg (0.46 mmol, 91%) pale orange oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.34 – 7.26 (m, 2H), 7.20 – 7.11 (m, 4H), 6.92 – 6.83 (m, 2H), 6.80 – 6.73 (m, 1H), 5.94 (d, *J* = 23.6 Hz, 1H), 3.69 (s, 3H), 3.66 – 3.51 (m, 2H). **^{19}F**

NMR (376 MHz, Chloroform-*d*) δ -78.32 (d, *J* = 7.8 Hz), -167.06 (q, *J* = 7.8 Hz). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 159.2, 137.7, 133.6, 133.6, 131.9, 129.1, 129.1, 128.5, 124.7, 124.6, 122.5, 122.4 (dd, *J* = 286.7, 28.9 Hz), 120.7 (d, *J* = 3.2 Hz), 114.2, 113.9 (d, *J* = 3.7 Hz), 93.6 (dd, *J* = 199.5, 30.8 Hz), 92.7, 89.9 (d, *J* = 2.2 Hz), 55.4, 43.1 (d, *J* = 25.9 Hz). **MS** (EI, 70 eV): *m/z* (%): 382(59[M^+]), 333(100), 313(47), 298(4), 277(9), 263(10), 249(16), 233(37), 220(45), 207(21), 202(10), 189(15), 170(7), 151(12), 139(7), 126(7), 115(7), 103(4), 91(6), 77(7), 63(7), 51(7). **IR** (ATR, cm^{-1}) 3031, 2924, 2203, 1611, 1510, 1490, 1312, 1285, 1177, 1126, 1106, 993, 837, 754, 689, 586, 526. **HRMS** *m/z* calcd for $C_{20}H_{15}ClF_4O^+$: 382.0748, found: 382.07281.

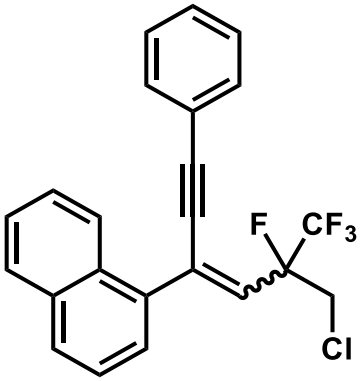
1-(4-(5-(Chloromethyl)-5,6,6,6-tetrafluoro-1-phenylhex-3-en-1-yn-3-yl)phenyl)ethan-1-one (5s)



Yield: 172 mg (0.44 mmol, 87%) orange oil. Mixture of isomers in 1:5 ratio. Only the NMR data of the major component is reported below.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.96 (d, *J* = 8.3 Hz, 2H), 7.52 (dt, *J* = 8.3, 1.8 Hz, 2H), 7.42 (dq, *J* = 4.6, 2.1 Hz, 2H), 7.32 (td, *J* = 5.4, 2.6 Hz, 3H), 6.10 (d, *J* = 25.2 Hz, 1H), 3.81 – 3.65 (m, 2H), 2.62 (s, 3H). **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -78.32 (d, *J* = 7.6 Hz), -170.15 (q, *J* = 7.5 Hz). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 197.7, 141.5, 141.5, 136.8, 132.7, 131.9, 129.3, 128.5, 128.1, 127.3, 125.2, 125.1, 122.2, 122.2 (dd, *J* = 286.9, 28.6 Hz), 94.0 (dd, *J* = 201.3, 30.9 Hz), 93.5, 89.2 (d, *J* = 1.9 Hz), 43.5 (d, *J* = 25.2 Hz), 26.8. **MS** (EI, 70 eV): *m/z* (%): 394(89[M^+]), 379(34), 345(72), 325(26), 283(51), 275(13), 263(28), 246(37), 233(100), 228(43), 220(15), 202(26), 189(11), 175(6), 165(21), 151(18), 137(19), 126(12), 113(15), 101(8), 88(6), 77(13), 51(9). **IR** (ATR, cm^{-1}) 3054, 2928, 2203, 1683, 1604, 1490, 1402, 1358, 1263, 1183, 1126, 1106, 1017, 991, 957, 845, 754, 689, 661, 601, 529. **HRMS** *m/z* calcd for $C_{21}H_{15}ClF_4O^+$: 394.0748, found: 394.07296.

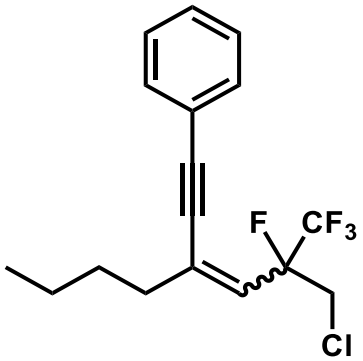
1-(5-(Chloromethyl)-5,6,6,6-tetrafluoro-1-phenylhex-3-en-1-yn-3-yl)naphthalene (5t)



Yield: 159 mg (0.39 mmol, 79%) white solid. Mixture of *E*:*Z* isomers in 1:1 ratio. Mp= 83-92 °C.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.13 (dd, *J* = 25.6, 7.7 Hz, 1H), 7.90 (t, *J* = 7.2 Hz, 2H), 7.60 – 7.46 (m, 4H), 7.42 – 7.35 (m, 2H), 7.34 – 7.26 (m, 3H), 6.41 (dd, *J* = 23.6, 7.3 Hz, 1H), 3.83 – 3.61 (m, 2H). **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -78.12 (d, *J* = 7.9 Hz), -78.18 (d, *J* = 7.1 Hz), -169.97 (q, *J* = 7.7 Hz), -171.49 (q, *J* = 6.9 Hz). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 133.9, 133.7, 133.5, 132.4, 131.9, 130.9, 128.9, 128.7, 128.4 (d, *J* = 2.9 Hz), 128.3, 127.2, 127.1 (d, *J* = 4.6 Hz), 126.9, 126.4 (d, *J* = 2.1 Hz), 126.2, 125.9 (d, *J* = 6.9 Hz), 125.7 (d, *J* = 3.9 Hz), 125.2, 125.0, 122.4, 122.3 (dd, *J* = 287.0, 30.2 Hz), 93.1 (d, *J* = 9.6 Hz), 89.5 (d, *J* = 2.3 Hz), 43.4 (dd, *J* = 26.3, 7.7 Hz). **MS** (EI, 70 eV): *m/z* (%): 402(35[M^+]), 367(8), 333(7), 295(6), 283(40), 276(13), 264(8), 253(100), 250(13), 220(18), 207(12), 177(6), 151(9), 140(7), 126(24), 113(6), 77(8), 51(6). **IR** (ATR, cm^{-1}) 3061, 2966, 2203, 1629, 1594, 1489, 1428, 1309, 1269, 1183, 1133, 1107, 1082, 995, 977, 801, 778, 756, 691, 617, 598. **HRMS** *m/z* calcd for $C_{23}H_{15}ClF_4^+$: 402.0798, found: 402.07594.

(*Z*)-(3-(2-(Chloromethyl)-2,3,3,3-tetrafluoropropylidene)hept-1-yn-1-yl)benzene (5u)[5]



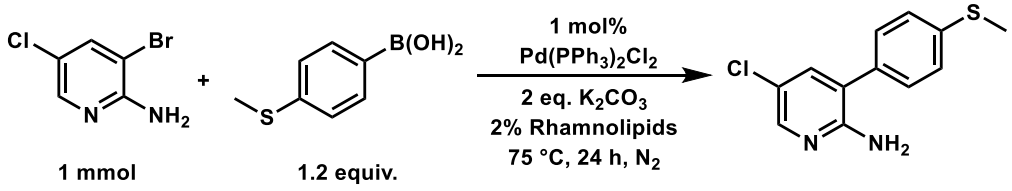
Yield: 99 mg (0.29 mmol, 60%) orange oil. Stereoisomeric mixture in 14:1 ratio. Only the NMR data of the major component is reported below.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.47 (dd, *J* = 6.4, 3.0 Hz, 2H), 7.36 – 7.32 (m, 3H), 5.75 (d, *J* = 25.5 Hz, 1H), 3.95 – 3.70 (m, 2H), 2.52 – 2.43 (m, 2H), 1.65 (p, *J* = 7.6 Hz, 2H), 1.41 (h, *J* = 7.3 Hz, 2H), 0.95 (t, *J* = 7.3 Hz, 3H). **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -78.59 (d, *J* = 7.8 Hz), -173.62 (q, *J* = 7.8 Hz). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 135.6, 132.7, 131.9, 128.8, 128.6, 128.5, 122.9, 122.8, 122.5 (dd, *J* = 286.5, 29.4 Hz), 94.2 (dq, *J* = 198.9, 30.8 Hz), 90.7, 89.9 (d, *J* = 1.7 Hz), 44.2 (d, *J* = 25.3 Hz), 32.1 (d, *J* = 8.4 Hz), 30.9, 22.6, 14.1. **MS** (EI, 70 eV): *m/z* (%): 332(19[M^+]), 302(6), 290(100), 255(44), 227(35), 219(10), 201(17), 183(47), 170(40), 165(55), 152(26), 142(70), 128(27), 115(45), 105(16), 91(46), 77(22), 69(7), 63(8), 51(12).

General procedures for the synthesis of APIs and intermediates

Etoricoxib intermediate[20]

5-Chloro-3-[4-(methylthio)phenyl]-2-pyridinamine (**11g**)



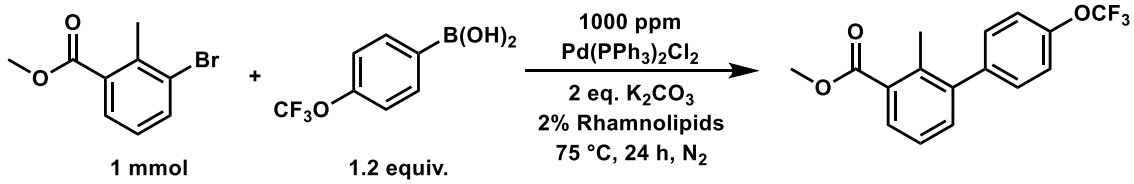
A 4 ml reaction vial was charged with $Pd(PPh_3)_2Cl_2$ (1 mol%, 0.01 mmol, 7 mg), K_2CO_3 (2 equiv., 2 mmol, 276 mg), 4-(methylthiophenyl)boronic acid (1.2 equiv., 1.2 mmol, 201 mg) and 2-amino-3-bromo-5-chloropyridine (1 equiv., 1 mmol, 207 mg). A stirring bar was added, then the vial was sealed, evacuated and back-filled with nitrogen three times. Degassed rhamnolipids solution (2 mL) was added via syringe and the reaction mixture was vigorously stirred at 75 °C for 24 h. After completion of the reaction (monitored by GC-MS or GC-FID) the mixture was cooled back to room temperature, was diluted with water or brine and ethyl acetate. The organic phase was separated, and the aqueous phase was extracted with 2x10 ml ethyl acetate. The combined organic phase was dried on Na_2SO_4, and concentrated under vacuo. The product was isolated by flash column chromatography using hexane and ethyl acetate as eluents.

Yield: 193 mg (0.77 mmol, 77%) mustard yellow solid. Mp= 93-100 °C.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.96 (d, *J* = 2.4 Hz, 1H), 7.34 (d, *J* = 4.7 Hz, 5H), 5.01 (s, 2H), 2.51 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 154.4, 144.2, 139.6, 137.8, 132.8, 129.0, 127.0, 123.0, 121.1, 15.6. **MS** (EI, 70 eV): *m/z* (%): 250(100[M^+]), 234(15), 214(11), 202(44), 168(30), 140(17), 114(12), 102(8), 89(10), 75(9), 63(7).

Sonidegib intermediate[21]

2-Methyl-4′-(trifluoromethoxy)-[1,1′-biphenyl]-3-carboxylic acid methyl ester (**11h**)



A 4 ml reaction vial was charged with $Pd(PPh_3)_2Cl_2$ (1000 ppm, 0.1 mol%, 0.001 mmol, 0.7 mg), K_2CO_3 (2 equiv., 2 mmol, 276 mg), 4-(trifluoromethoxy)phenylboronic acid (1.2 equiv., 1.2 mmol, 247 mg) and methyl 3-bromo-2-methylbenzoate (1.0 equiv., 1 mmol, 229 mg). A stirring bar was added, then the vial was sealed, evacuated and back-filled with nitrogen

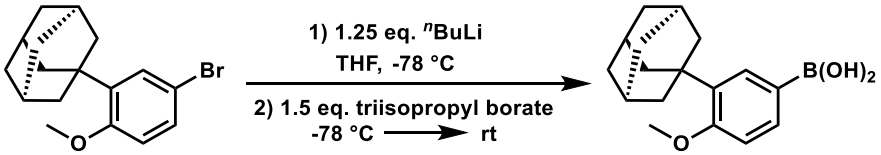
three times. Degassed rhamnolipids solution (2 mL) was added via syringe and the reaction mixture was vigorously stirred at 75 °C for 24 h. After completion of the reaction (monitored by GC-MS or GC-FID) the mixture was cooled back to room temperature, was diluted with water or brine and ethyl acetate. The organic phase was separated, and the aqueous phase was extracted with 2x10 ml ethyl acetate. The combined organic phase was dried on Na_2SO_4, and concentrated under vacuo. The product was isolated by flash column chromatography using hexane and ethyl acetate as eluents.

Yield: 276 mg (0.89 mmol, 89%) light yellow oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.77 – 7.72 (m, 1H), 7.27 – 7.18 (m, 6H), 3.84 (s, 3H), 2.32 (s, 3H). **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -57.79. **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 168.8, 148.6, 142.5, 140.3, 136.8, 133.3, 131.7, 130.9, 129.7, 125.5, 120.8, 120.7 (d, *J* = 257.3 Hz), 52.2, 18.6. **MS** (EI, 70 eV): *m/z* (%): 310(44[M^+]), 279(31), 250(34), 193(31), 181(16), 165(100), 152(37), 139(17), 115(7), 102(6), 89(6), 77(6), 63(8).

Protected adapalene

3-(1-Adamantyl)-4-methoxyphenylboronic acid[22]



2 mmol

A 20 ml reaction vial fitted with a magnetic stirring bar was charged with 2-(1-adamantyl)-4-bromanisole (1 equiv., 2 mmol, 642 mg), then the the vial was sealed, evacuated and back-filled with nitrogen three times. Dry THF (5 mL) was added via syringe and the solution was cooled to -78°C. To this solution was added *n*-butyllithium (1.25 equiv. 2.5 mmol, 2.5 mol/l in hexane, 1 mL) dropwise and the mixture was stirred for 2 h at -78 °C. Next triisopropyl borate (1.5 equiv., 3 mmol, 564 mg, 692 µl) was dissolved in 2 mL dry THF and this solution was also added to the reaction mixture dropwise. The solution was allowed to warm to room temperature overnight. After that the reaction was quenched with 6 M HCl (7 mL) and the mixture was stirred for 3 h at room temperature. The resulted biphasic solution was extracted with Et_2O (2x10 mL). The organic phase was washed water and brine, dried on Na_2SO_4 and concentrated by rotary evaporation. The resulted product was used without further purification.

Yield: 549 mg (1.9 mmol, 96%) white solid.

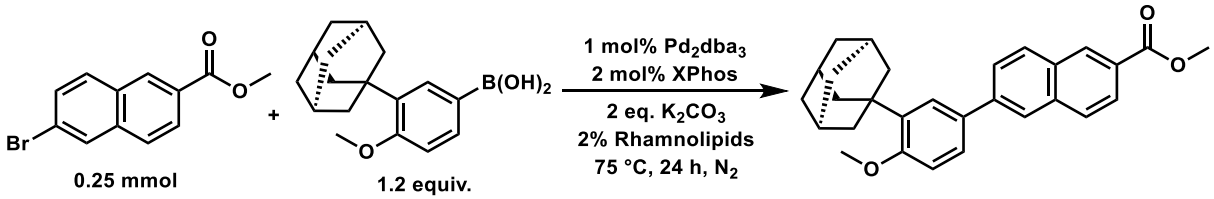
^{1}H NMR spectrum of the boronic acid corresponds to a mixture of the acid itself and its cyclic trimer (boroxine) in a random ratio (as described in ref 22) so the NMR spectra was obtained using the boronic acid pinacol ester after esterification.

Esterification with pinacol: the boronic acid (1.0 equiv., 0.48 mmol, 138 mg) was dissolved in triethyl amine (2 mL) and pinacol (1.5 equiv., 0.72 mmol, 85 mg) was added and the resulting solution was stirred at room temperature for 1 h. After the reaction completion the mixture was diluted with acetone and concentrated unto silicagel. The product was isolated by by flash column chromatography using hexane and ethyl acetate as eluents.

Yield: 130 mg (0.35 mmol, 74%) white solid. Mp= 170-173 °C.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.67 (d, *J* = 7.7 Hz, 2H), 6.87 (d, *J* = 8.0 Hz, 1H), 3.85 (s, 3H), 2.13 (s, 6H), 2.07 (s, 3H), 1.77 (s, 6H), 1.33 (s, 12H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 161.6, 137.7, 134.4, 133.2, 111.1, 83.5, 55.0, 40.6, 37.3, 37.1, 29.2, 25.0. **MS** (EI, 70 eV): *m/z* (%): 368(100[M^+]), 353 (5), 311(8), 274(6), 269(25), 247(4), 211(30), 196(16), 175(4), 153(8), 135(12), 115(6), 101(6), 83(15), 55(11).

Methyl 6-(3-(1-adamantyl)-4-methoxyphenyl)-2-naphthoate (**11i**)[23]



A 20 ml reaction vial was charged with Pd_2dba_3 (1 mol%, 0.01 mmol, 9.1 mg), XPhos (2 mol%, 0.02 mmol, 9.5 mg), K_2CO_3 (2.0 equiv, 2.0 mmol, 276 mg), 3-(1-adamantyl)-4-methoxyphenylboronic acid (1.2 equiv., 1.2 mmol, 343 mg) and 6-bromo-2-naphthalenecarboxylic acid methyl ester (1.0 equiv., 1.0 mmol, 265 mg). A stirring bar was added, then the vial was sealed, evacuated and back-filled with nitrogen three times. Degassed rhamnolipids solution (3 mL) was added via syringe and the reaction mixture was vigorously stirred at 75 °C for 24 h. After completion of the reaction (monitored by TLC) the mixture was cooled back to room temperature, was diluted with brine and was extracted with chloroform (3x20 mL). The combined organic phase was dried on $MgSO_4$, and concentrated under vacuo. The product was isolated by flash column chromatography using hexane and ethyl acetate as eluents.

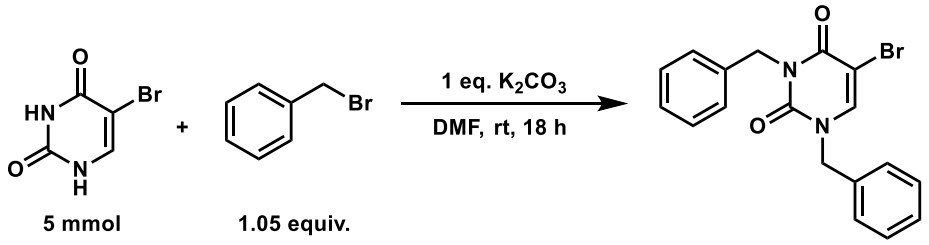
Yield: 189 mg (0.44 mmol, 44%) white solid. Mp= 228-230 °C.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.62 (s, 1H), 8.11 – 8.04 (m, 1H), 8.04 – 7.96 (m, 2H), 7.92 (d, *J* = 8.6 Hz, 1H), 7.83 – 7.76 (m, 1H), 7.63 – 7.51 (m, 2H), 7.00 (d, *J* = 8.4 Hz, 1H),

3.99 (s, 3H), 3.91 (s, 3H), 2.19 (s, 6H), 2.11 (s, 3H), 1.81 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.5, 159.1, 141.5, 139.1, 136.1, 132.7, 131.4, 131.0, 129.8, 128.4, 127.1, 126.6, 126.1, 125.9, 125.7, 124.9, 112.2, 55.3, 52.3, 40.7, 37.3, 37.3, 29.2.

Synthesis of protected eniluracil

5-Bromo-1,3-bis(phenylmethyl)-2,4(1*H*,3*H*)-pyrimidinedione[24]

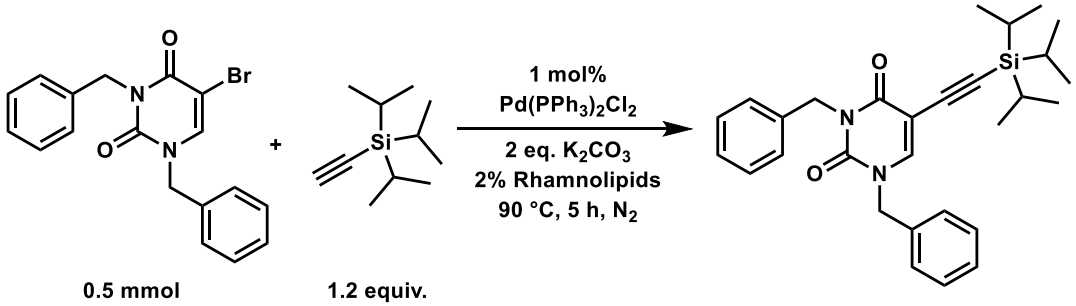


5-Bromouracil (1.0 equiv., 5.0 mmol, 955 mg) was dissolved in anhydrous DMF (20 mL) under sonication. Anhydrous K_2CO_3 was added (1.0 equiv., 5.0 mmol, 691 mg) and the heterogeneous solution was stirred at room temperature for 15 min. The obtained potassium salt was treated dropwise with benzyl bromide (1.05 equiv., 5.25 mmol, 898 mg, 624 μl) and the reaction mixture was stirred at room temperature for 18 h. The heterogeneous solution was acidified with acetic acid, evaporated in vacuo and coevaporated two times with acetonitrile. The residue was dissolved in water (20 mL) and extracted with ethyl acetate (3×25 mL). The combined organic phase was dried on Na_2SO_4, and concentrated under vacuo. The product was isolated by flash column chromatography using hexane and ethyl acetate as eluents.

Yield: 651 mg (1.75 mmol, 35%) white solid. Mp= 128-130 °C.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.51 (d, *J* = 6.4 Hz, 2H), 7.47 (s, 1H), 7.38 (q, *J* = 5.5 Hz, 3H), 7.34 – 7.26 (m, 5H), 5.19 (s, 2H), 4.92 (s, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.2, 151.1, 141.5, 136.3, 134.8, 129.5, 129.4, 128.9, 128.6, 128.3, 128.0, 96.8, 52.7, 46.1.

1,3-Bis(phenylmethyl)-5-[2-[tris(1-methylethyl)silyl]ethynyl]-2,4(1*H*,3*H*)-pyrimidinedione (**10e**)



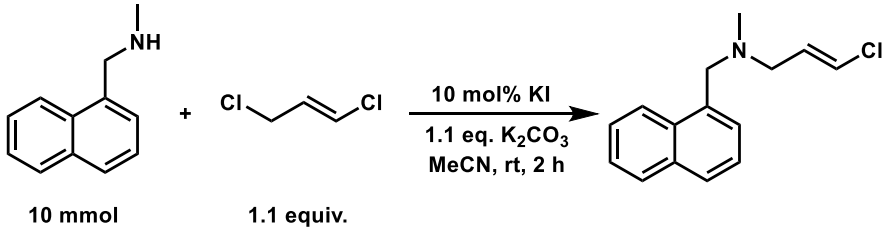
A 4 ml reaction vial was charged with $Pd(PPh_3)_2Cl_2$ (1 mol%, 0.005 mmol, 3.5 mg), K_2CO_3 (2 equiv., 1 mmol, 138 mg) and 5-bromo-1,3-bis(phenylmethyl)-2,4(1*H*,3*H*)-pyrimidinedione (1.0 equiv., 0.5 mmol, 186 mg). A stirring bar was added, then the vial was sealed, evacuated and back-filled with nitrogen three times. Degassed rhamnolipids solution (1 mL) and (triisopropylsilyl)acetylene (1.2 equiv. 0.6 mmol, 109 mg, 135 µl) was added via syringe and the reaction mixture was vigorously stirred at 90 °C for 5 h. After completion of the reaction (monitored by GC-MS or GC-FID) the mixture was cooled back to room temperature, was diluted with water or brine and ethyl acetate. The organic phase was separated, and the aqueous phase was extracted with 2x10 ml ethyl acetate. The combined organic phase was dried on Na_2SO_4, and concentrated under vacuo. The product was isolated by flash column chromatography using hexane and ethyl acetate as eluents.

Yield: 109 mg (0.23 mmol, 46%) light yellow solid. Mp= 129-133 °C.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.53 – 7.45 (m, 3H), 7.40 (t, *J* = 7.3 Hz, 3H), 7.35 – 7.27 (m, 5H), 5.18 (s, 2H), 4.95 (s, 2H), 1.13 (s, 21H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 161.3, 151.0, 145.0, 136.5, 135.0, 129.3, 129.2, 128.8, 128.5, 128.0, 127.8, 100.4, 97.7, 96.1, 52.9, 45.2, 18.8, 11.4. **MS** (EI, 70 eV): *m/z* (%): 472(1[M^+]), 429 (31), 401(2), 206(3), 181(1), 91(100), 65(8). **IR** (ATR, cm^{-1}) 3075, 3033, 2971, 2942, 2864, 2157, 1704, 1632, 1584, 1493, 1442, 1381, 1348, 1336, 1323, 1248, 1209, 1141, 1073, 1017, 1000, 976, 917, 881, 825, 791, 763, 750, 676, 605, 537, 522.

Synthesis of Terbinafine[25]

(*E*)-*N*-Methyl-*N*-naphtyl methylene-3-chloro-prop-2-en-1-amine

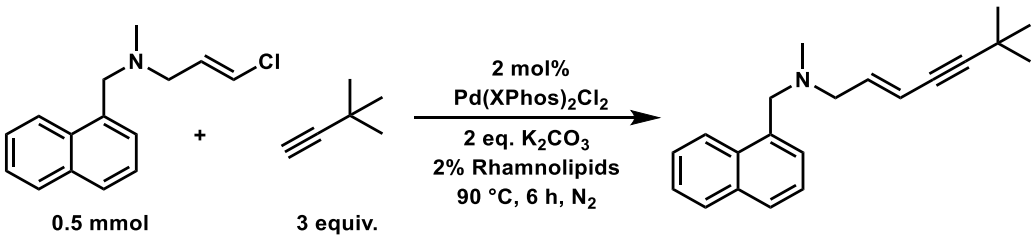


A round bottom flask was charged with KI (10 mol%, 1 mmol, 166 mg) and K_2CO_3 (1.1 eq., 11 mmol, 1520 mg) and the solids were suspended in 50 mL acetonitrile. *N*-Methyl-1-naphthylmethylamine (10 mmol, 1712 mg) and trans-1,3-dichloropropene (1.1 eq., 11 mmol, 1220 mg, 1020 µl) was added and the reaction mixture was stirred at room temperature for two hours. Then the mixture was filtered, the resulting solution concentrated and the crude product was purified by flash column chromatography using hexane and ethyl acetate as eluents.

Yield: 1.394 g (5.67 mmol, 57%) pale yellow oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.25 (d, *J* = 8.2 Hz, 1H), 7.86 (d, *J* = 7.5 Hz, 1H), 7.83 – 7.76 (m, 1H), 7.52 (dtd, *J* = 13.3, 6.8, 3.6 Hz, 2H), 7.42 (d, *J* = 7.2 Hz, 2H), 6.18 (d, *J* = 13.3 Hz, 1H), 6.09 (dt, *J* = 13.4, 6.7 Hz, 1H), 3.93 (s, 2H), 3.13 (d, *J* = 6.6 Hz, 2H), 2.27 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 134.3, 134.0, 132.5, 130.8, 128.6, 128.3, 127.6, 126.1, 125.8, 125.2, 124.6, 120.5, 59.8, 57.4, 42.2. **MS** (EI, 70 eV): *m/z* (%): 245(11[M^+]), 210 (10), 182(3), 168(6), 141(100), 115(44), 104(39), 89(6), 75(24), 63(4).

Terbinafine (**10f**)

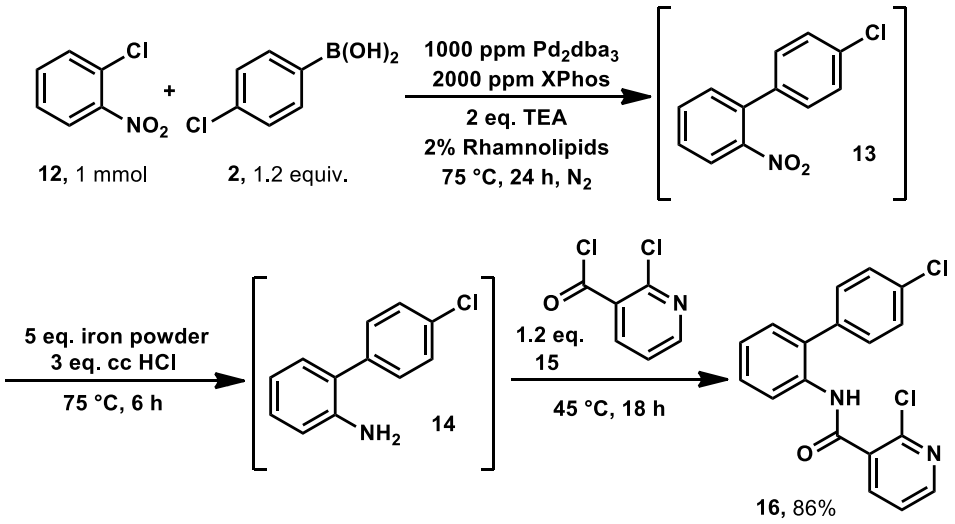


A 4 ml reaction vial was charged with $Pd(XPhos)_2Cl_2$ (2 mol%, 0.01 mmol, 11 mg), K_2CO_3 (2 eq., 1 mmol, 138 mg) and (*E*)-*N*-methyl-*N*-naphtyl methylene-3-chloro-prop-2-en-1-amine (0.5 mmol, 123 mg). A stirring bar was added, then the vial was sealed, evacuated and back-filled with nitrogen three times. Degassed rhamnolipids solution (2 mL) and the first half of 3,3-dimethyl-1-butyne (1.5 eq., 0.75 mmol, 62 mg, 92 µl) was added via syringe and the reaction mixture was vigorously stirred at 90 °C for 4 h. After 4 hours the second half of 3,3-dimethyl-1-butyne (1.5 eq., 0.75 mmol, 62 mg, 92 µl) was added and the mixture was stirred for an additional 2 hours. After completion of the reaction (monitored by GC-MS or GC-FID) the mixture was cooled back to room temperature, was diluted with water or brine and ethyl acetate. The organic phase was separated, and the aqueous phase was extracted with 2x10 ml ethyl acetate. The combined organic phase was dried on Na_2SO_4, and concentrated under vacuo. The product was isolated by flash column chromatography using hexane and ethyl acetate as eluents.

Yield: 91 mg (0.31 mmol, 62%) yellow oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.28 (d, *J* = 8.2 Hz, 1H), 7.89 – 7.82 (m, 1H), 7.78 (d, *J* = 7.6 Hz, 1H), 7.56 – 7.38 (m, 4H), 6.17 (dt, *J* = 15.8, 6.6 Hz, 1H), 5.70 (d, *J* = 15.8 Hz, 1H), 3.92 (s, 2H), 3.15 (d, *J* = 5.8 Hz, 2H), 2.24 (s, 3H), 1.26 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 139.3, 134.8, 134.0, 132.6, 128.6, 128.1, 127.5, 126.0, 125.7, 125.2, 124.7, 113.0, 98.6, 77.3, 60.1, 59.8, 42.4, 31.1, 28.0. **MS** (EI, 70 eV): *m/z* (%): 291(2[M^+]), 276(13), 248(3), 234(9), 196(6), 182(5), 150(6), 141(100), 115(32), 105(4), 91(12), 77(7), 65(3).

One-pot synthesis of Boscalid (16)[26]



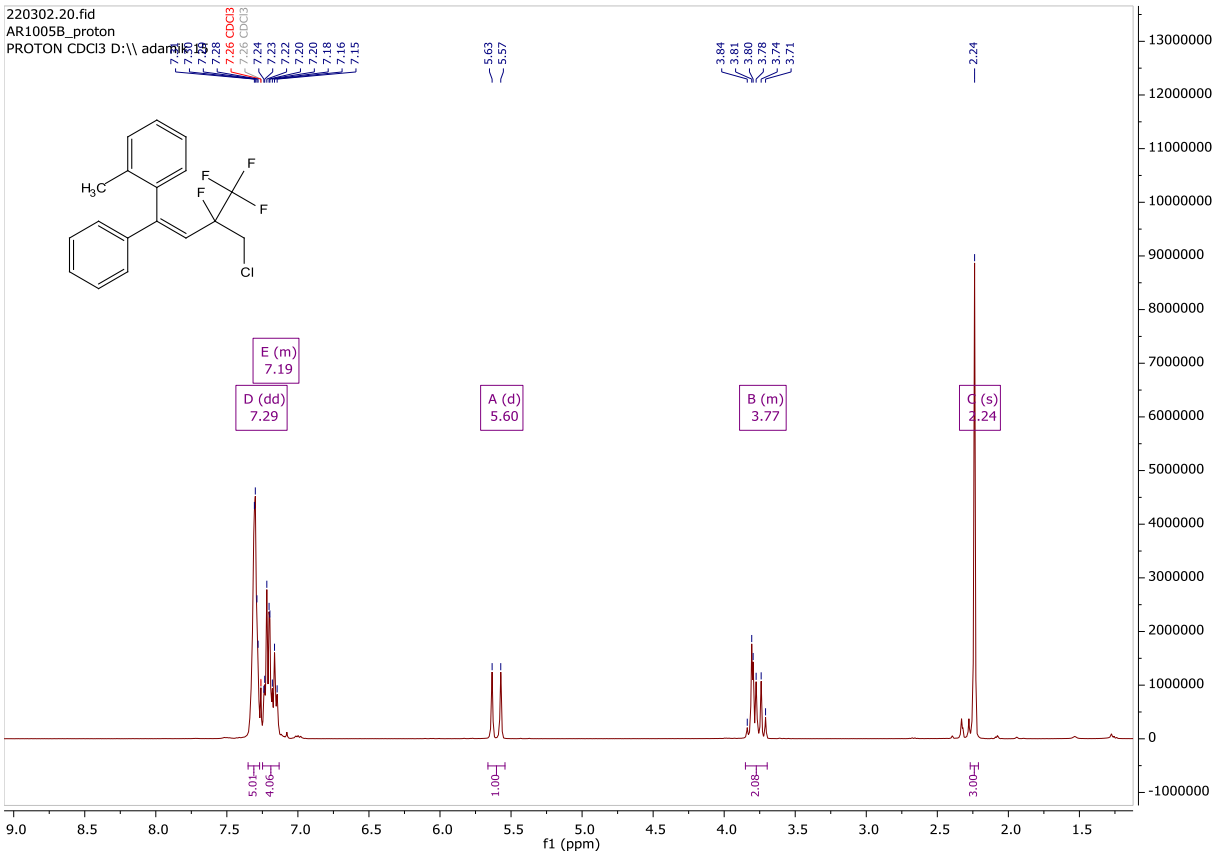
A 4 ml reaction vial was charged with Pd_2dba_3 (1000 ppm, 0.1 mol%, 0.001 mmol, 0.9 mg), XPhos (2000 ppm, 0.002 mmol, 1 mg), 4-chlorophenylboronic acid (1.2 equiv., 1.2 mmol, 187 mg) and 1-chloro-2-nitrobenzene (1 equiv., 1 mmol, 157 mg). A stirring bar was added, then the vial was sealed, evacuated and back-filled with nitrogen three times. Degassed rhamnolipids solution (2 mL) and TEA (2 equiv., 2 mmol, 204 mg, 283 μl) was added via syringe and the reaction mixture was vigorously stirred at 75 °C for 24 h. After the reaction completion iron powder (5 equiv., 5 mmol, 279 mg) and cc HCl (35%, 3 equiv., 3 mmol, 109 mg, 264 μl) was added to the mixture and the stirring at 75 °C was continued for another 6 hours. Lastly 2-chloronicotinoyl chloride (1.2 equiv., 1.2 mmol, 211 mg) was added in two portions and the reaction mixture was stirred at 45 °C for another 18 hours. After the reaction completion the mixture was diluted with acetone and concentrated unto silicagel. The product was isolated by by flash column chromatography using hexane and ethyl acetate as eluents.

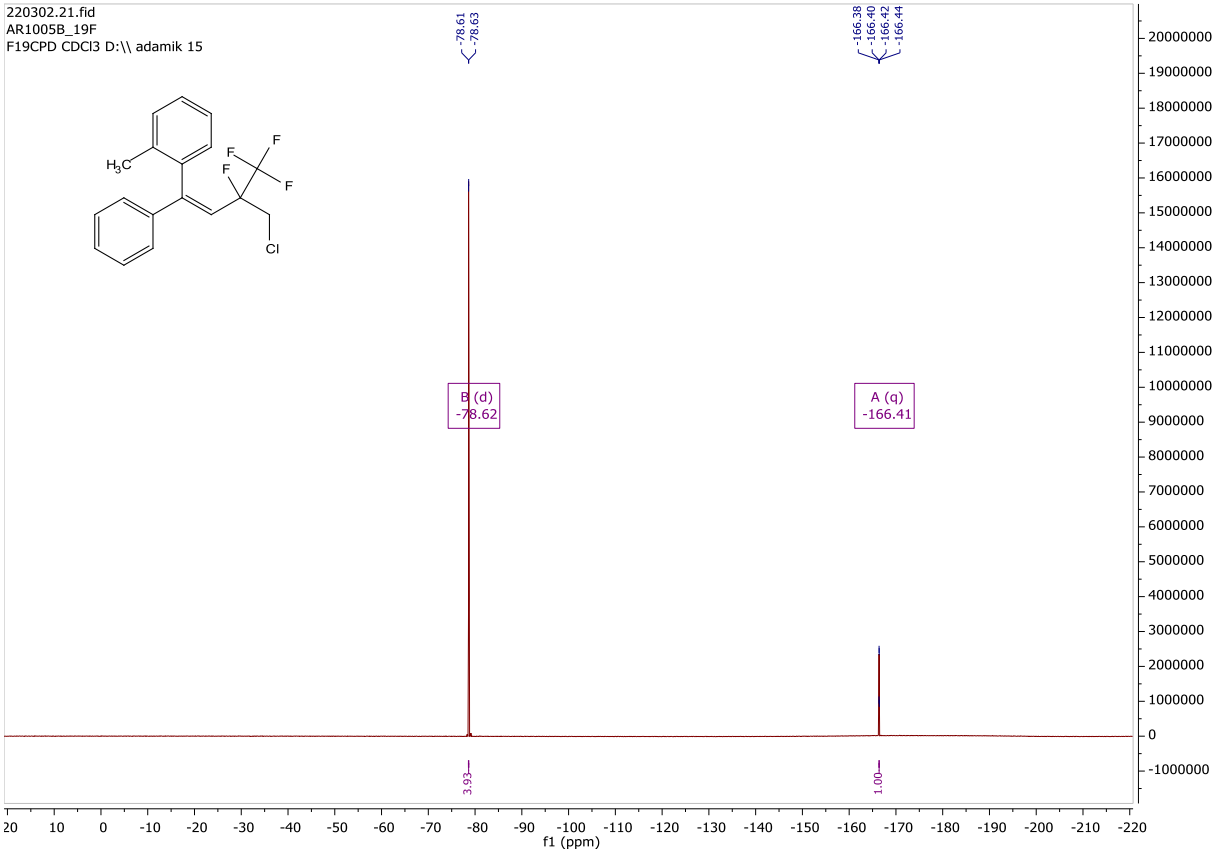
Yield: 294 mg (0.86 mmol, 86%) light mauve solid. Mp= 141-144 °C.

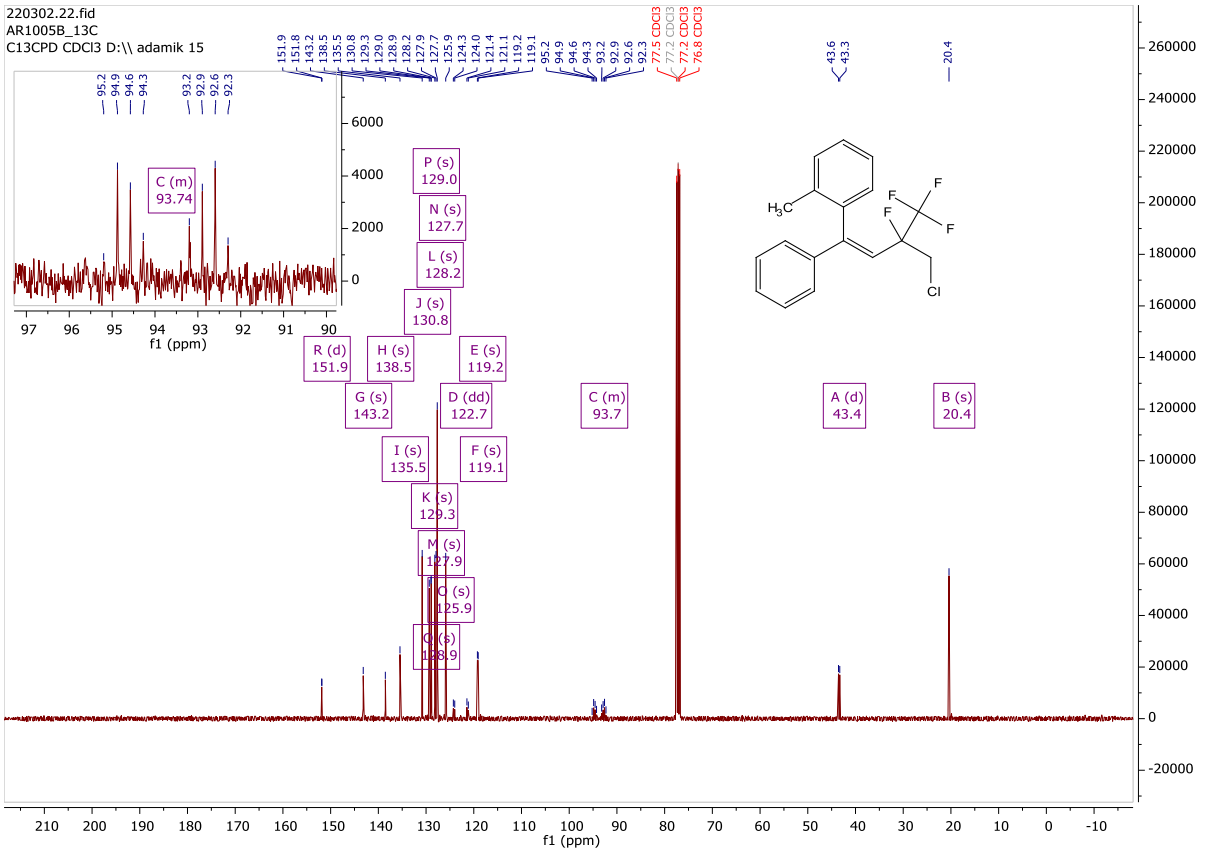
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.49 – 8.39 (m, 2H), 8.25 – 8.09 (m, 2H), 7.51 – 7.42 (m, 3H), 7.40 – 7.33 (m, 3H), 7.29 (d, *J* = 3.6 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.6, 151.4, 146.8, 140.3, 136.4, 134.6, 134.4, 132.4, 131.2, 130.9, 130.4, 129.4, 129.0, 125.5, 123.0, 122.3. **MS** (EI, 70 eV): *m/z* (%): 342(26[M^+]), 307(4), 207(7), 167(19), 139(100), 112(49), 105(7), 76(19).

NMR Spectra

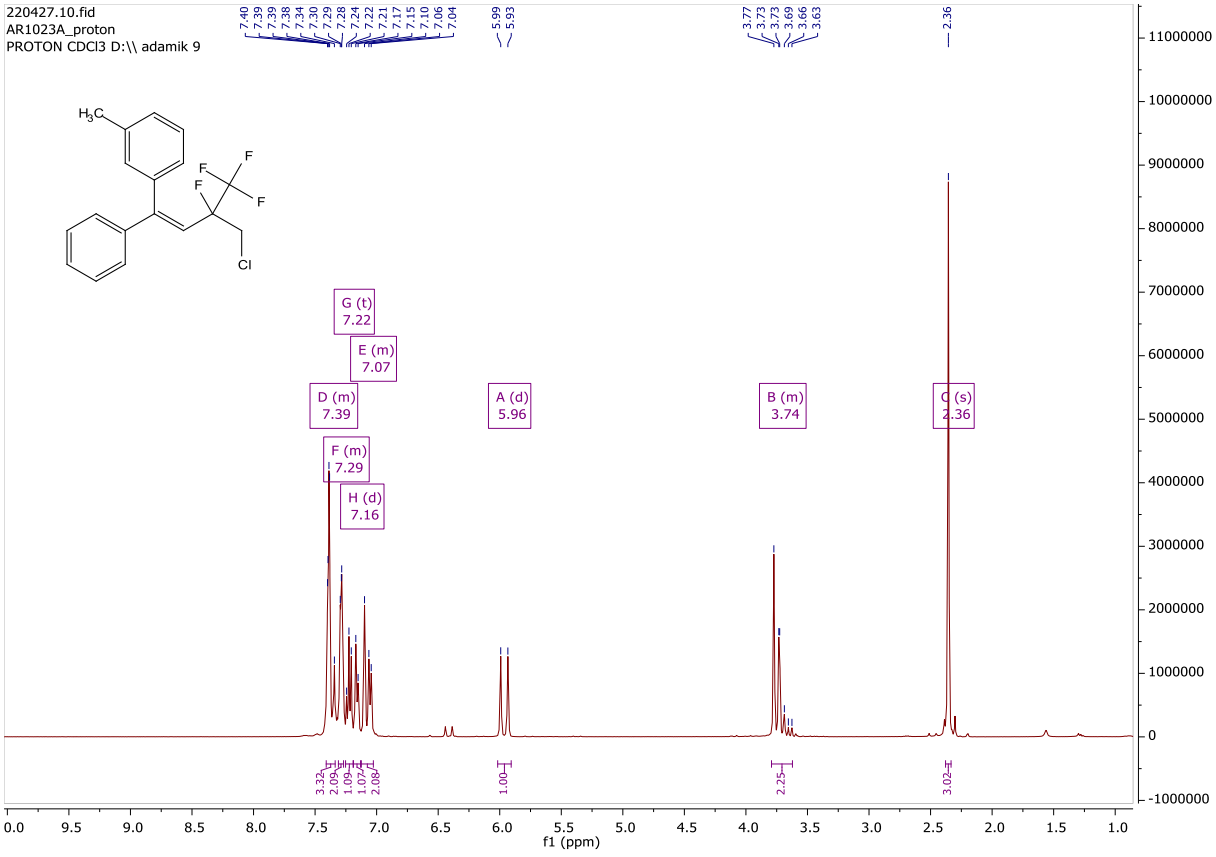
3a

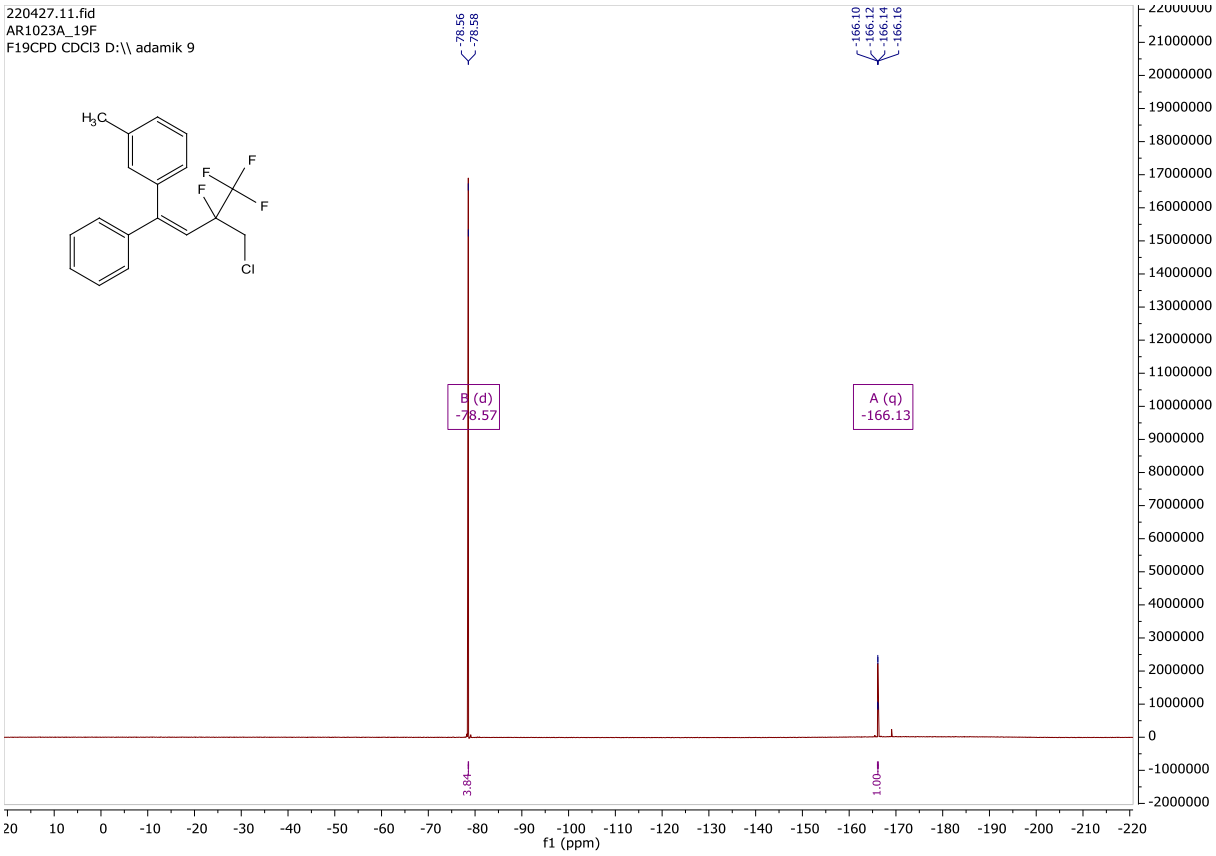


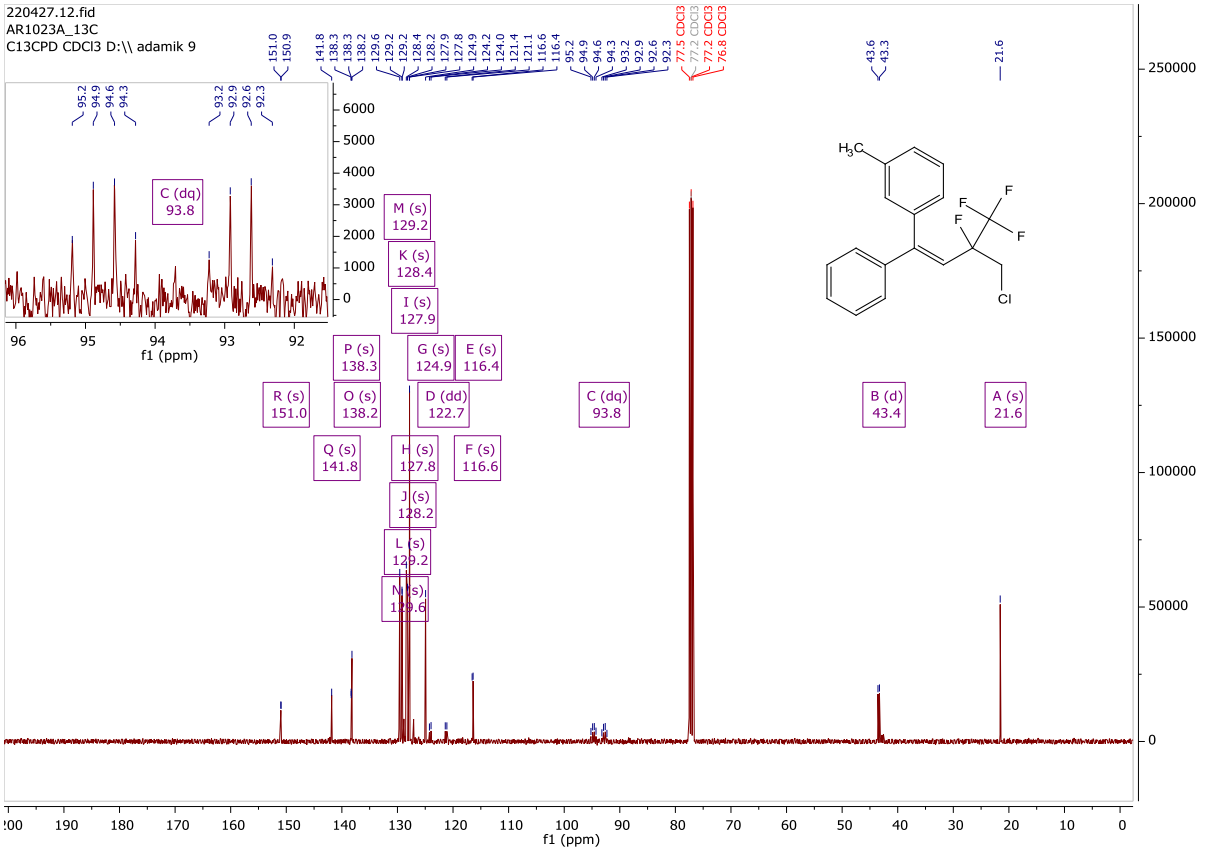



220302.22.fid
AR1005B_13C
C13CPD CDCl3 D:\\ adamik 15
C (m) 93.74
P (s) 129.0
N (s) 127.7
L (s) 128.2
J (s) 130.8
R (d) 151.9
H (s) 138.5
E (s) 119.2
G (s) 143.2
D (dd) 122.7
C (m) 93.7
A (d) 43.4
B (s) 20.4
I (s) 135.5
F (s) 119.1
K (s) 129.3
M (s) 127.9
O (s) 125.9
Q (s) 138.9
f1 (ppm)

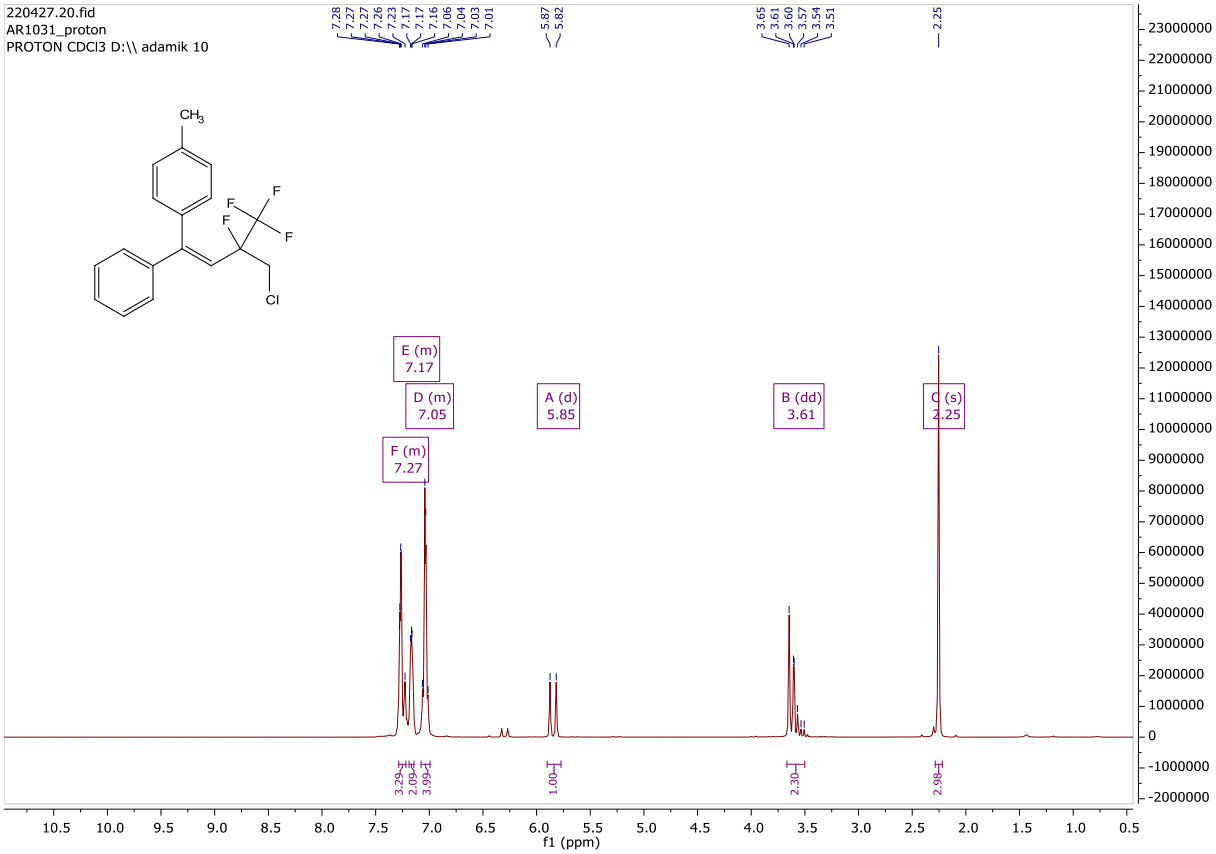
3b

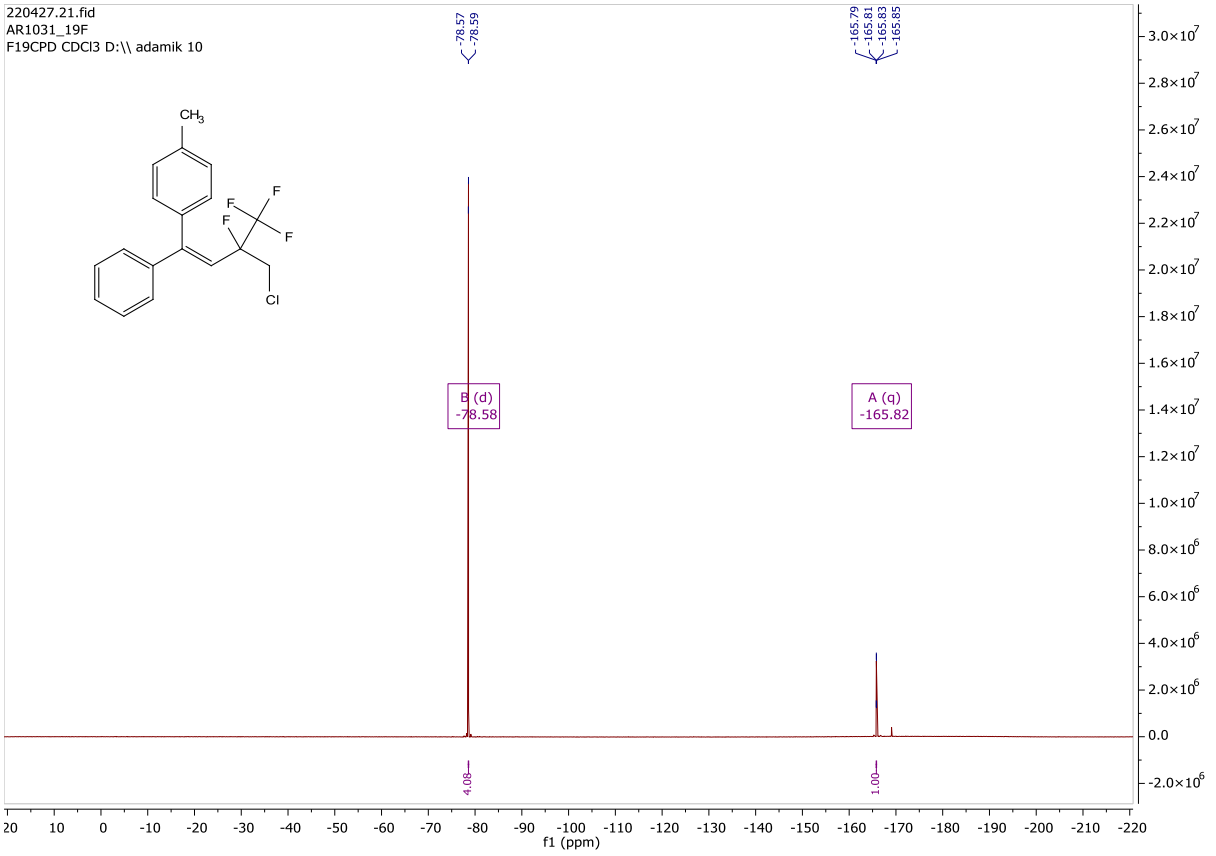

220427.10.fid
AR1023A_proton
PROTON CDCl3 D:\\ adamik 9
G (t) 7.22
E (m) 7.07
D (m) 7.39
A (d) 5.96
B (m) 3.74
C (s) 2.36
F (m) 7.29
H (d) 7.16
f1 (ppm)

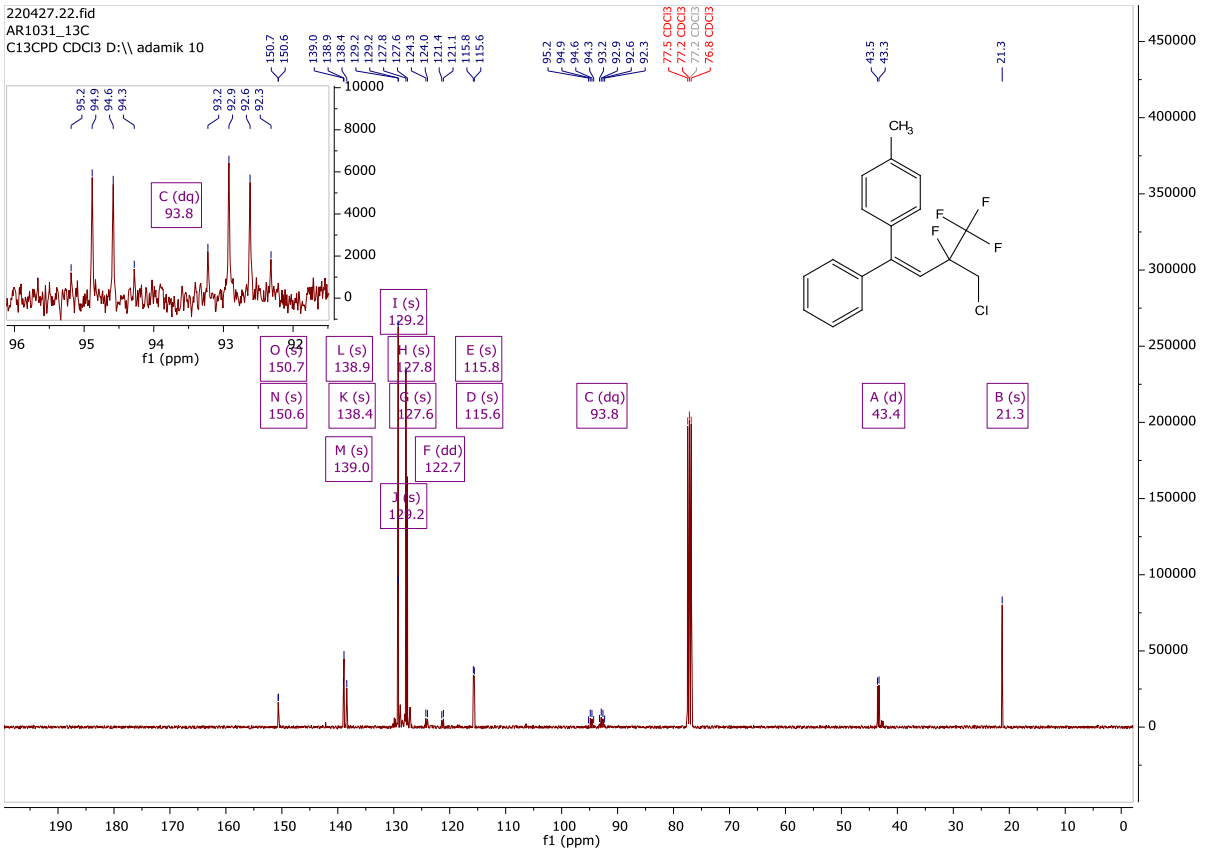

220427.11.fid
AR1023A_19F
F19CPD CDCl3 D:\\ adamik 9
-78.56
-78.58
-166.10
-166.12
-166.14
-166.16
B (d)
-78.57
A (q)
-166.13
3.84
1.00
f1 (ppm)


220427.12.fid
AR1023A_13C
C13CPD CDCl3 D:\\ adamik 9
C (dq)
93.8
M (s)
129.2
K (s)
128.4
I (s)
127.9
P (s)
138.3
G (s)
124.9
E (s)
116.4
R (s)
151.0
O (s)
138.2
D (dd)
122.7
Q (s)
141.8
H (s)
127.8
F (s)
116.6
J (s)
128.2
L (s)
129.2
N (s)
129.6
B (d)
43.4
A (s)
21.6
f1 (ppm)

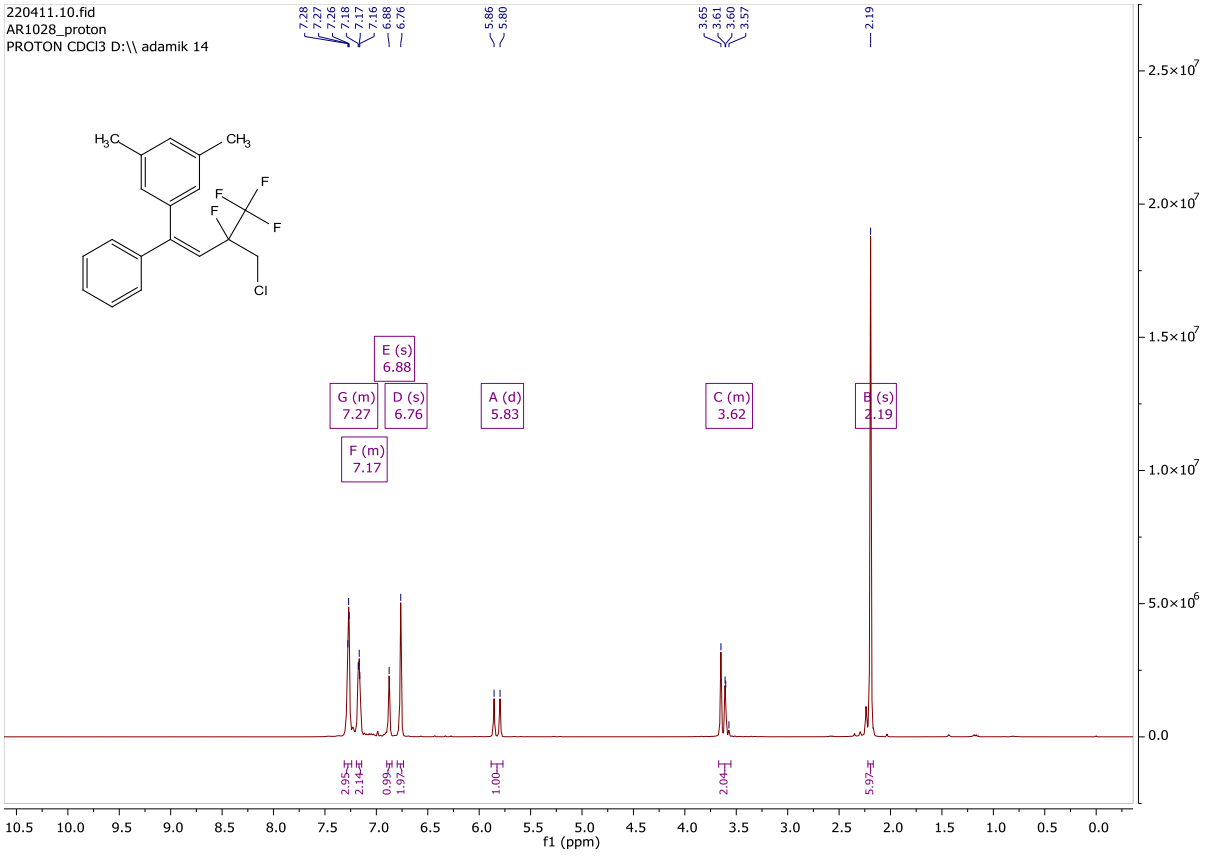
3c

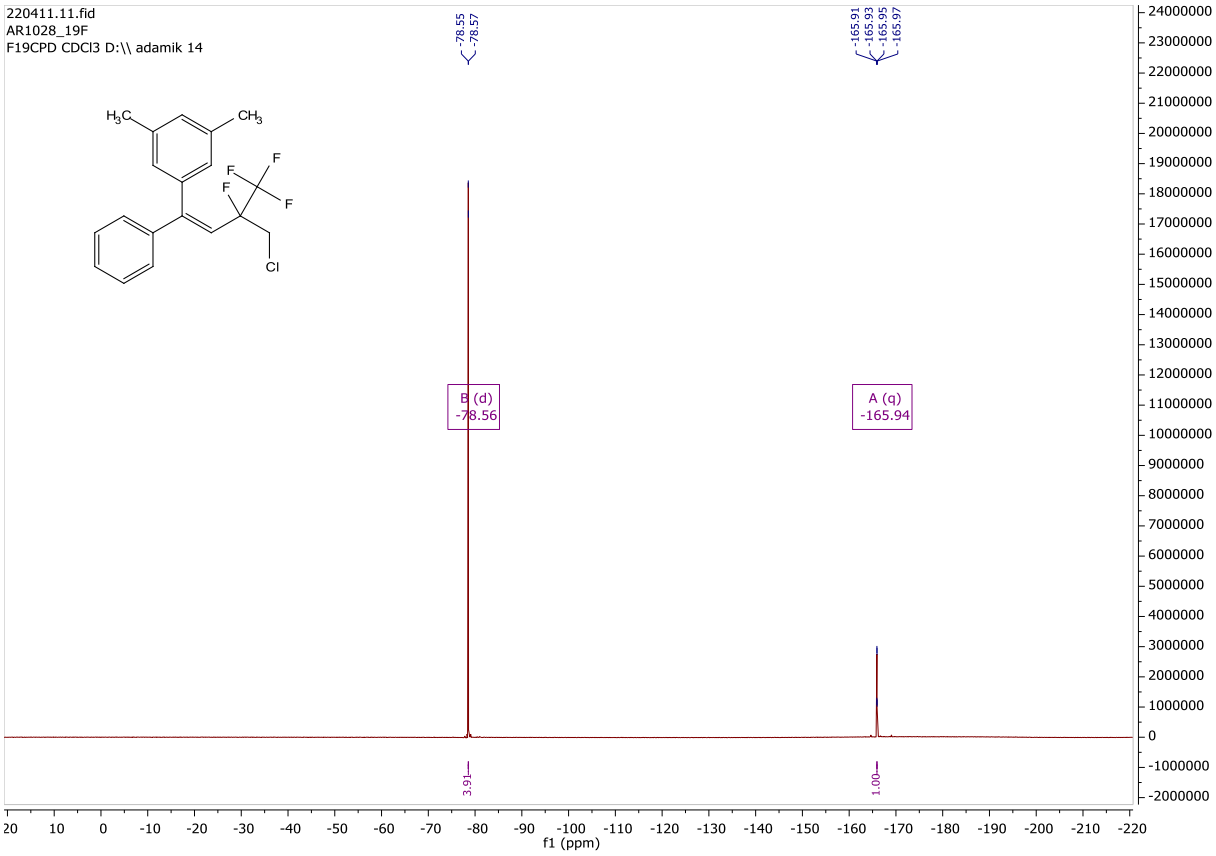

220427.20.fid
AR1031_proton
PROTON CDCl3 D:\\ adamik 10
E (m) 7.17
D (m) 7.05
A (d) 5.85
B (dd) 3.61
C (s) 2.25
F (m) 7.27
f1 (ppm)

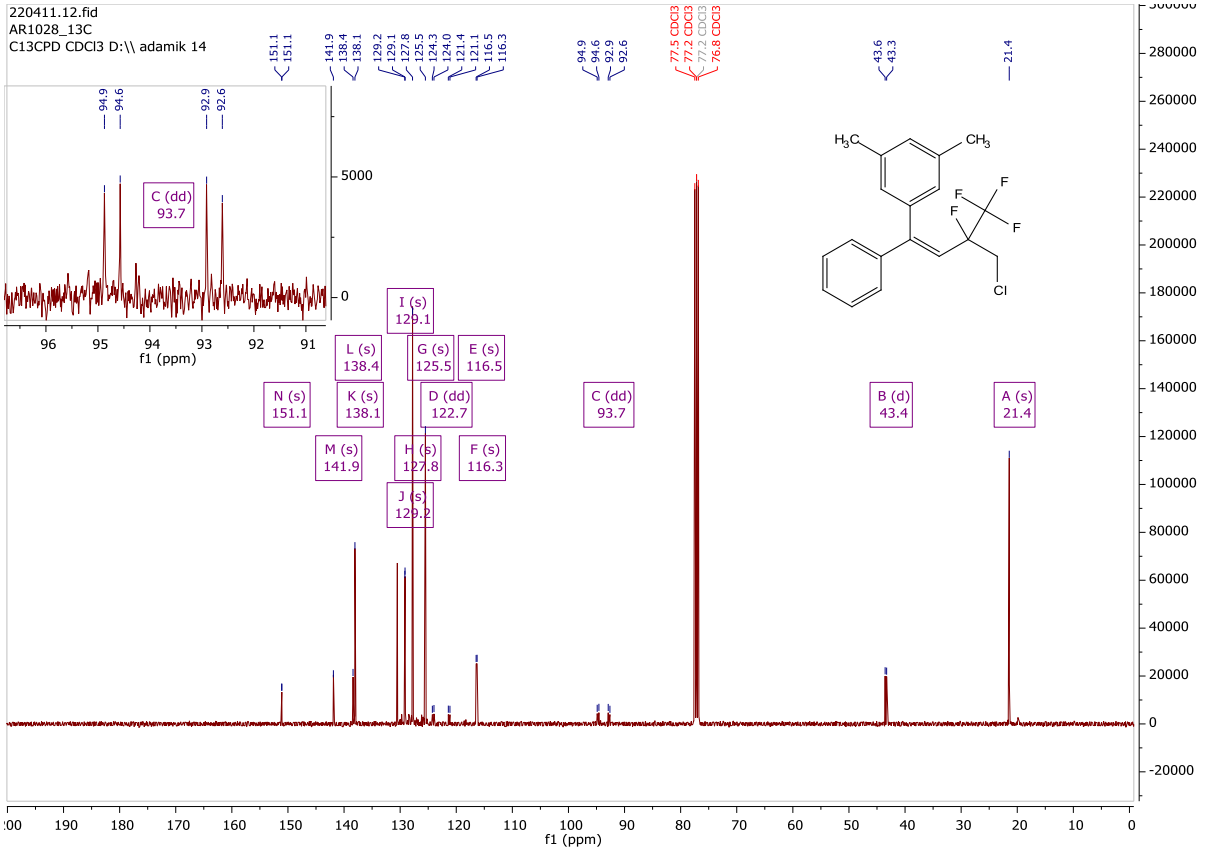

220427.21.fid
AR1031_19F
F19CPD CDCl3 D:\\ adamik 10
B (d) -78.58
A (q) -165.82
f1 (ppm)


220427.22.fid
AR1031_13C
C13CPD CDCl3 D:\\ adamik 10
C (dq) 93.8
I (s) 129.2
O (s) 150.7
N (s) 150.6
L (s) 138.9
K (s) 138.4
M (s) 139.0
H (s) 127.8
G (s) 127.6
F (dd) 122.7
J (s) 129.2
E (s) 115.8
D (s) 115.6
C (dq) 93.8
A (d) 43.4
B (s) 21.3
f1 (ppm)

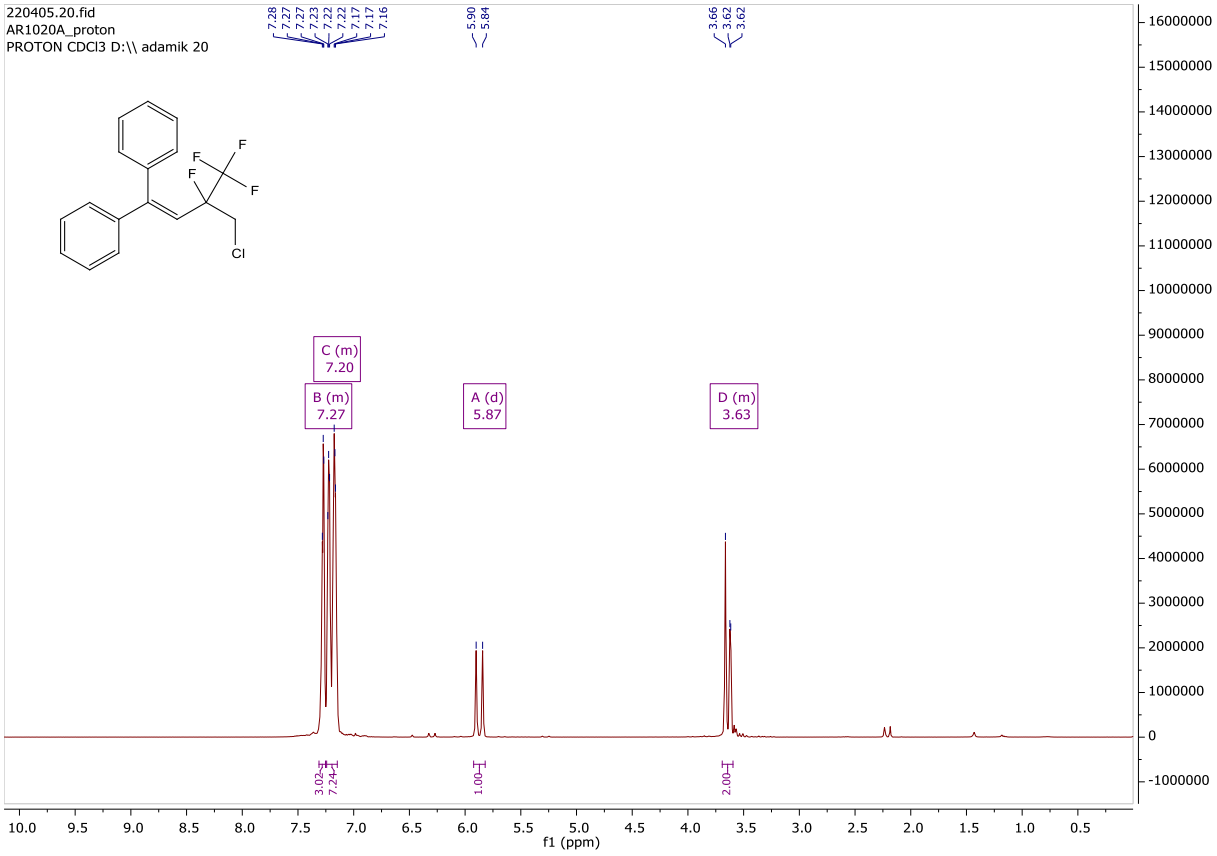
3d

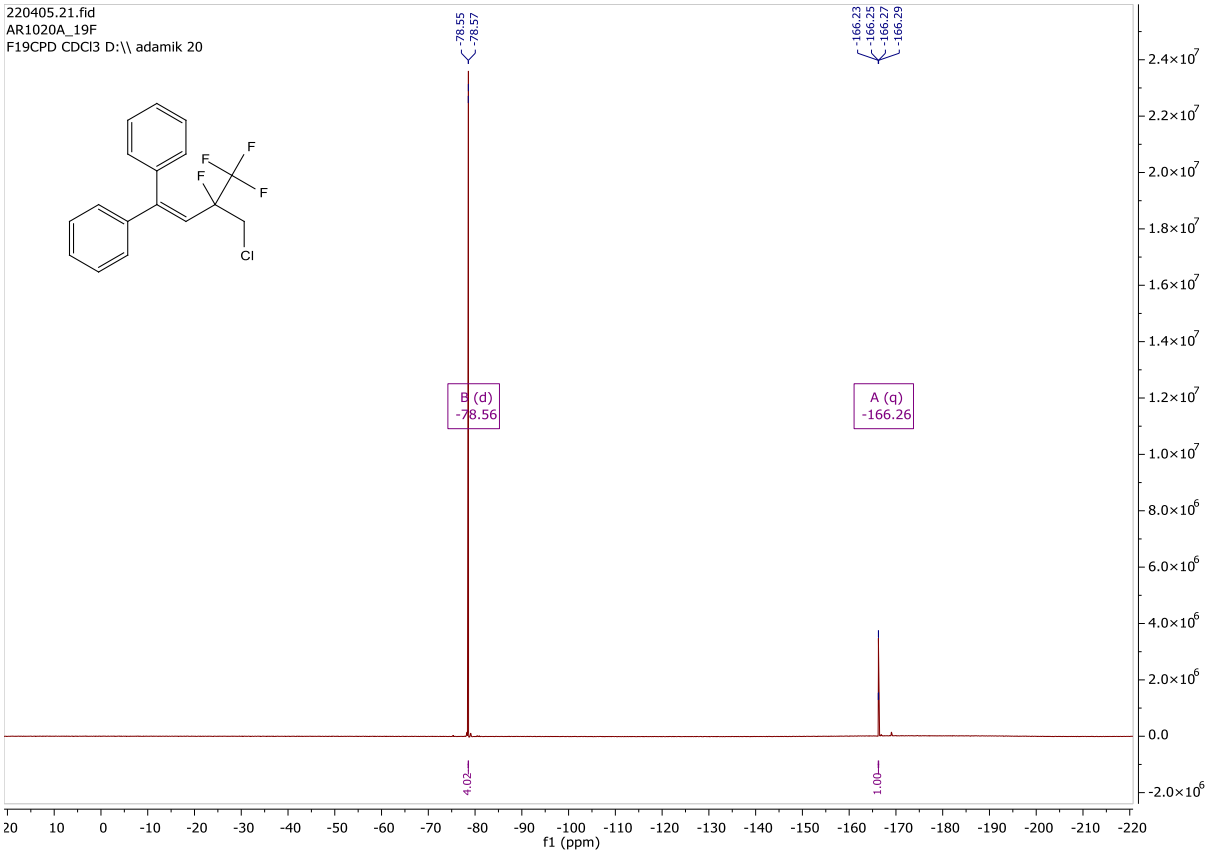

220411.10.fid
AR1028_proton
PROTON CDCl3 D:\\ adamik 14
E (s) 6.88
G (m) 7.27
D (s) 6.76
F (m) 7.17
A (d) 5.83
C (m) 3.62
B (s) 2.19
f1 (ppm)

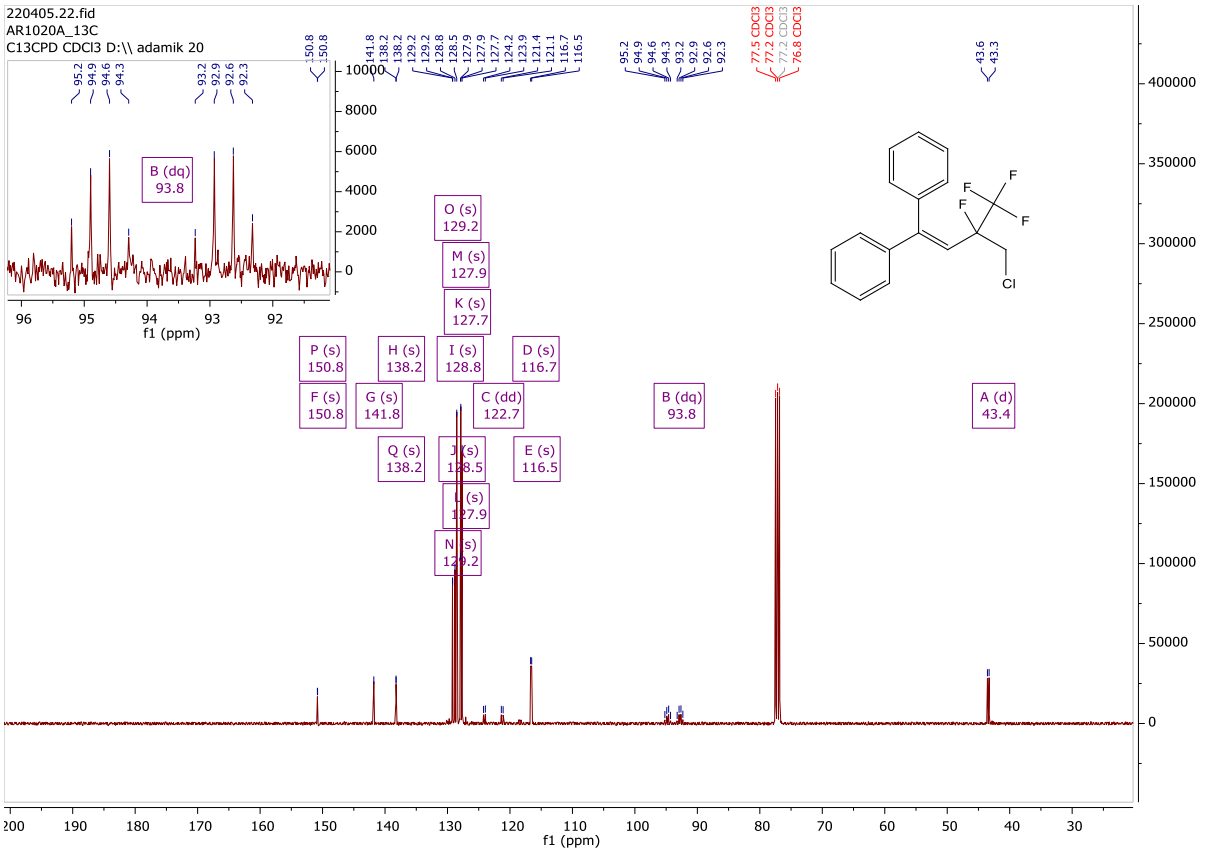

220411.11.fid
AR1028_19F
F19CPD CDCl3 D:\\ adamik 14
-78.55
-78.57
-165.91
-165.93
-165.95
-165.97
B (d)
-78.56
A (q)
-165.94
3.91
1.00
f1 (ppm)


220411.12.fid
AR1028_13C
C13CPD CDCl3 D:\\ adamik 14
C (dd)
93.7
I (s)
129.1
L (s)
138.4
G (s)
125.5
E (s)
116.5
N (s)
151.1
K (s)
138.1
D (dd)
122.7
C (dd)
93.7
B (d)
43.4
A (s)
21.4
M (s)
141.9
H (s)
127.8
F (s)
116.3
J (s)
129.2
f1 (ppm)

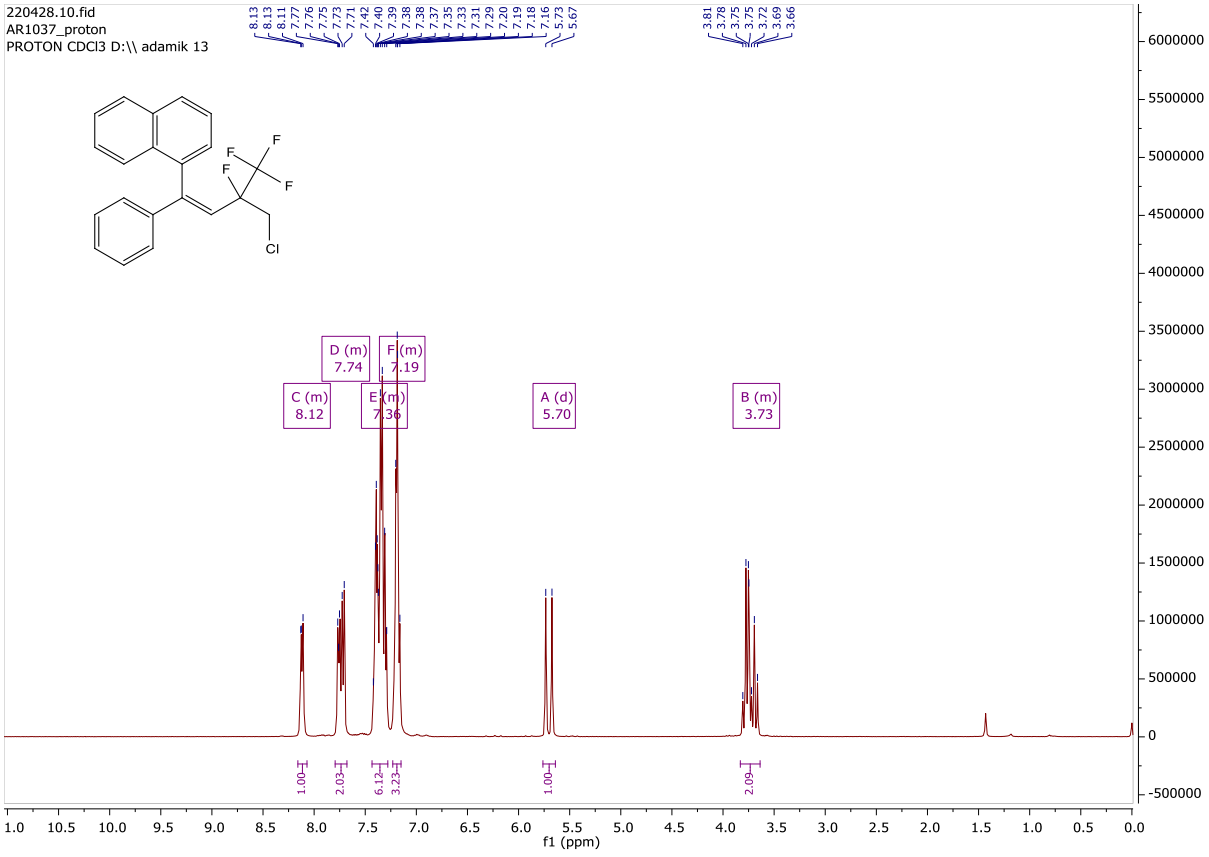
3e


220405.20.fid
AR1020A_proton
PROTON CDCl3 D:\\ adamik 20
7.28
7.27
7.27
7.23
7.22
7.22
7.17
7.17
7.16
5.90
5.84
3.66
3.62
3.62
F
F
F
F
Cl
C (m)
7.20
B (m)
7.27
A (d)
5.87
D (m)
3.63
3.02
7.24
1.00
2.00
f1 (ppm)

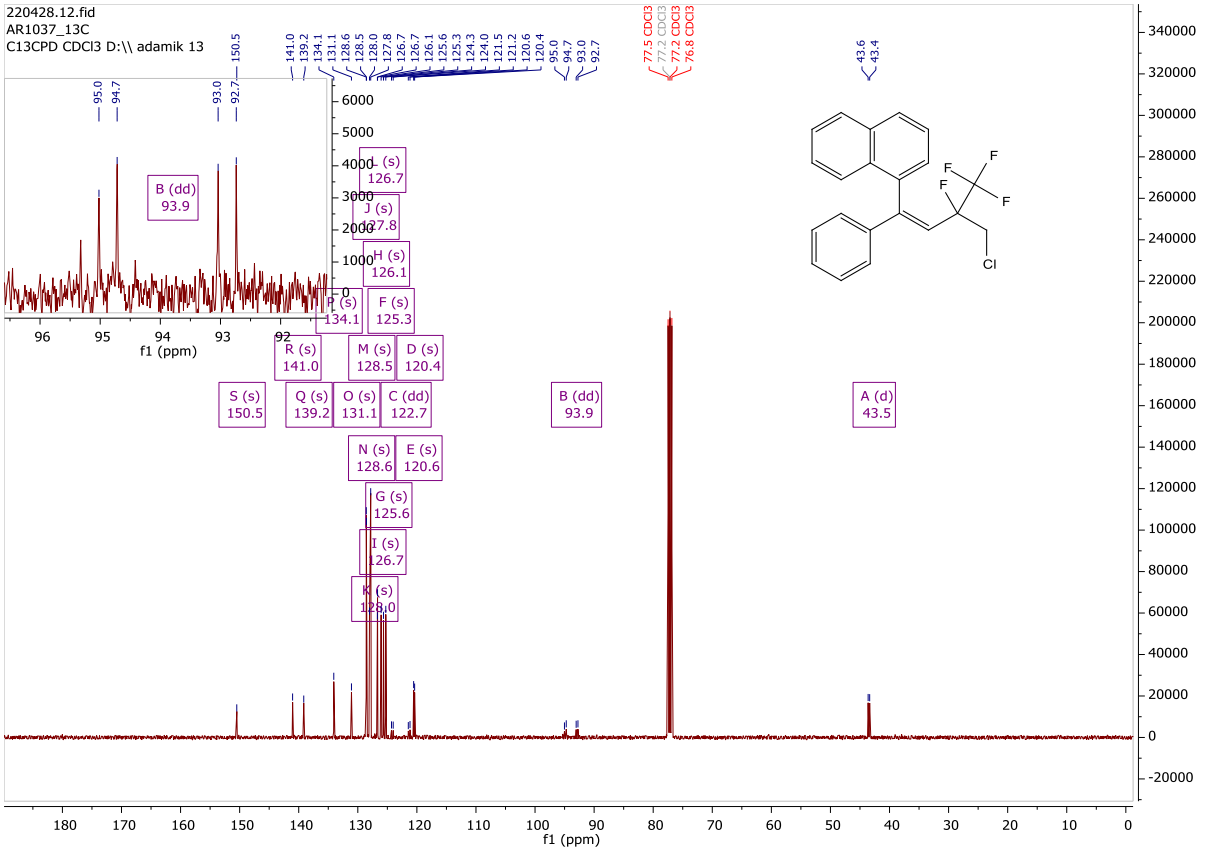

220405.21.fid
AR1020A_19F
F19CPD CDCl3 D:\\ adamik 20
-78.55
-78.57
-166.23
-166.25
-166.27
-166.29
F
F
F
F
Cl
B (d)
-78.56
A (q)
-166.26
4.02
1.00
f1 (ppm)


220405.22.fid
AR1020A_13C
C13CPD CDCl3 D:\\ adamik 20
B (dq)
93.8
O (s)
129.2
M (s)
127.9
K (s)
127.7
P (s)
150.8
H (s)
138.2
I (s)
128.8
D (s)
116.7
F (s)
150.8
G (s)
141.8
C (dd)
122.7
B (dq)
93.8
A (d)
43.4
Q (s)
138.2
J (s)
128.5
E (s)
116.5
L (s)
127.9
N (s)
129.2
f1 (ppm)

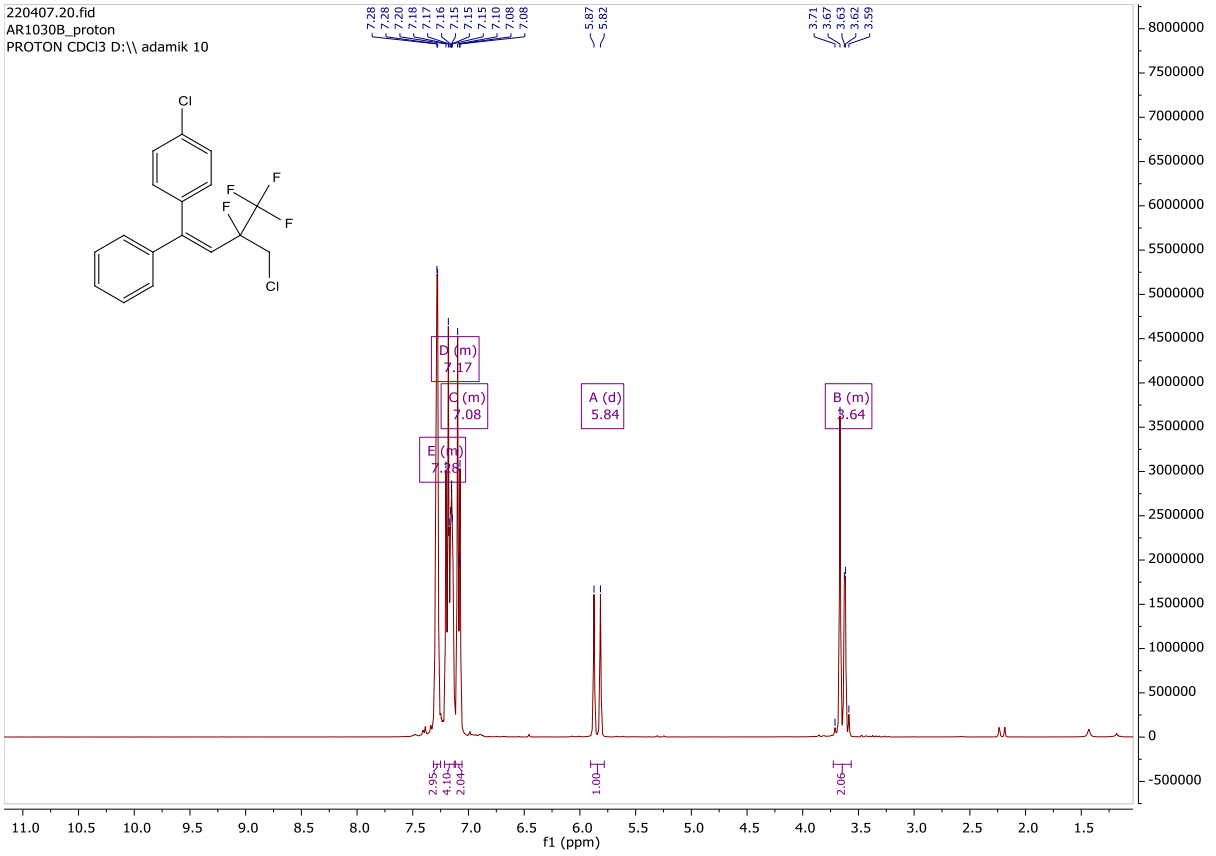
3f

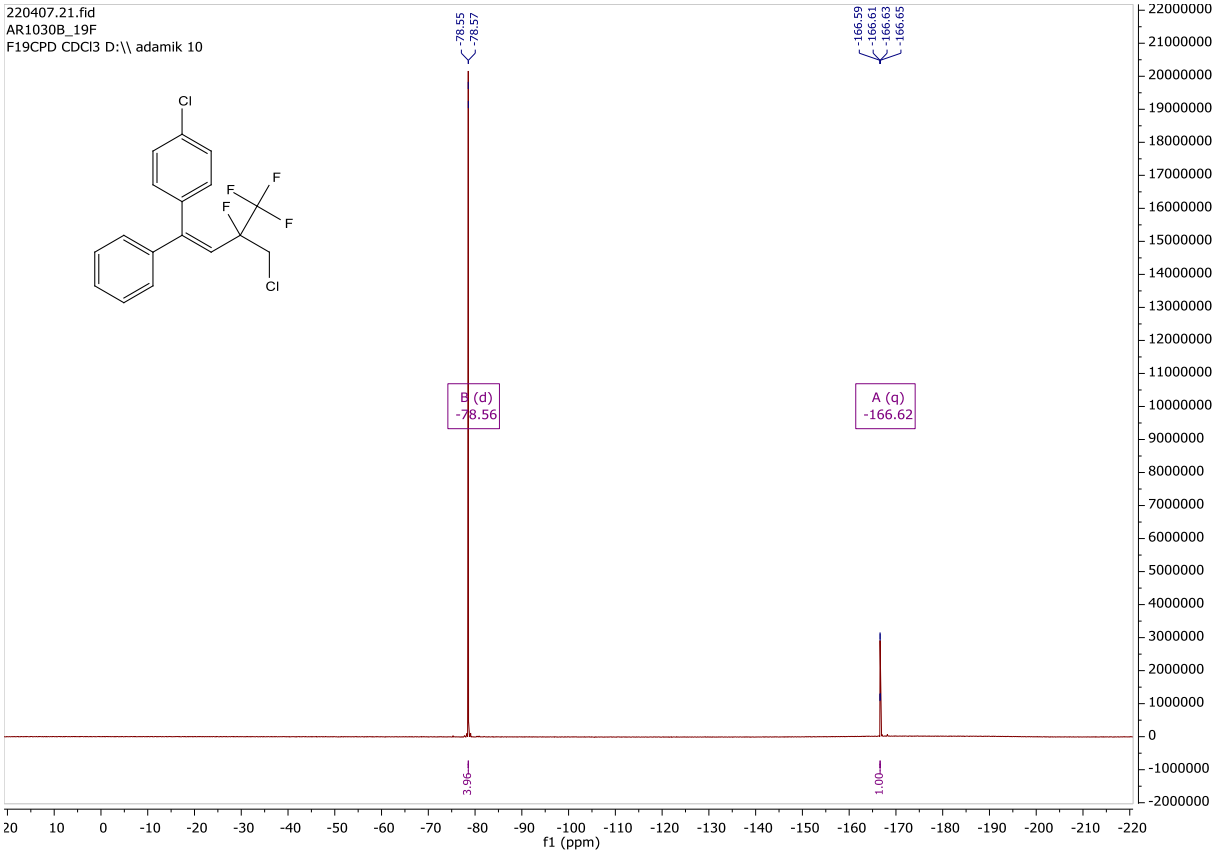

220428.10.fid
AR1037_proton
PROTON CDCl3 D:\\ adamik 13
D (m)
7.74
F (m)
7.19
C (m)
8.12
E (m)
7.36
A (d)
5.70
B (m)
3.73
f1 (ppm)

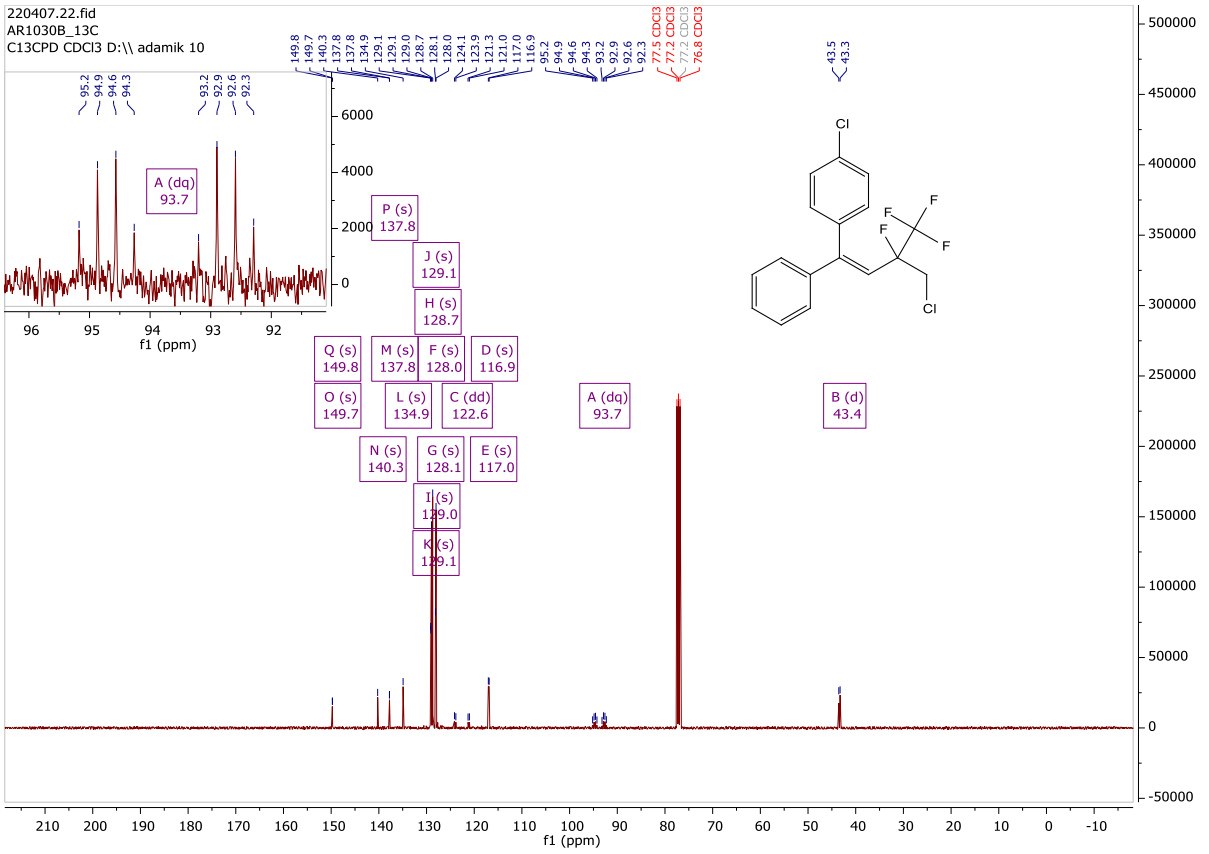

220428.11.fid
AR1037_19F
F19CPD CDCl3 D:\\ adamik 13
-78.48
-78.50
-166.48
-166.50
-166.52
-166.55
B (d)
-78.49
A (q)
-166.51
3.69
0.99
f1 (ppm)


220428.12.fid
AR1037_13C
C13CPD CDCl3 D:\\ adamik 13
77.5 CDCl3
77.2 CDCl3
76.8 CDCl3
43.6
43.4
B (dd)
93.9
A (d)
43.5
f1 (ppm)

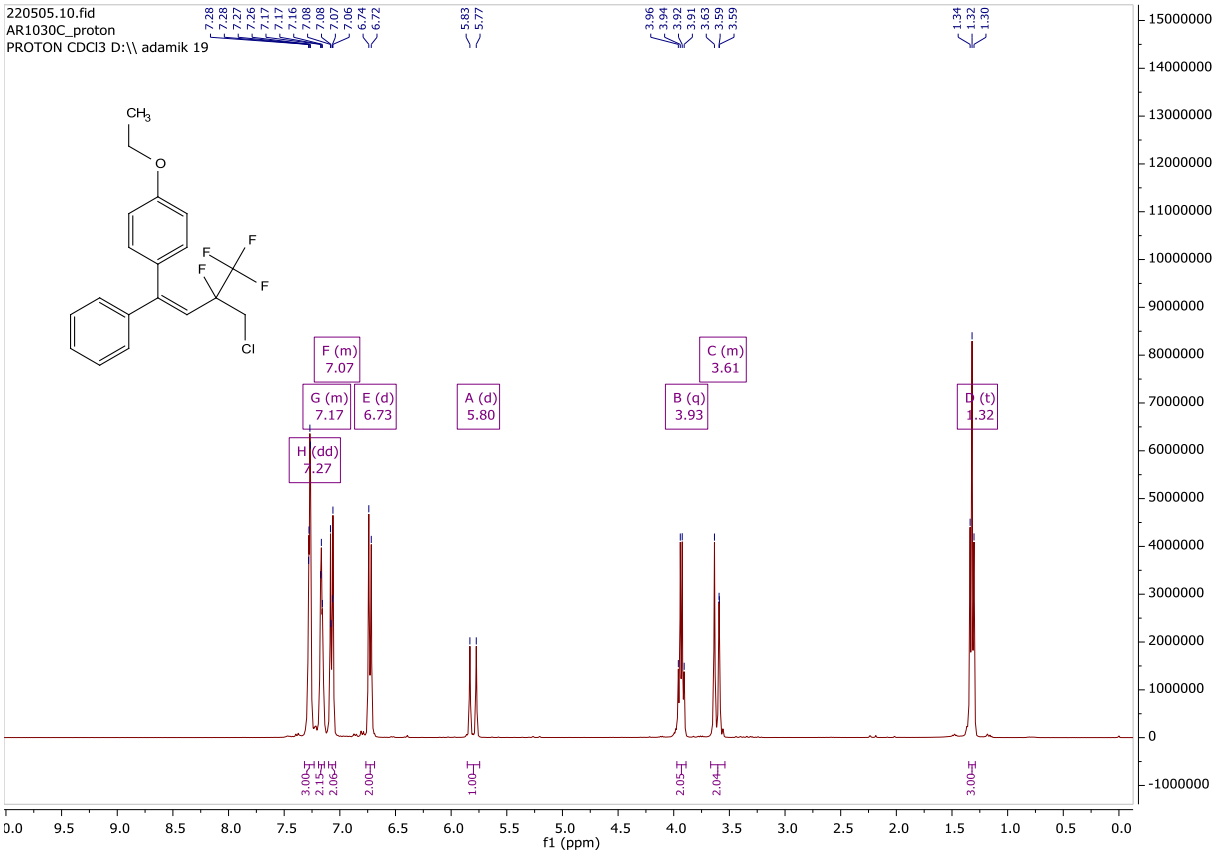
3g

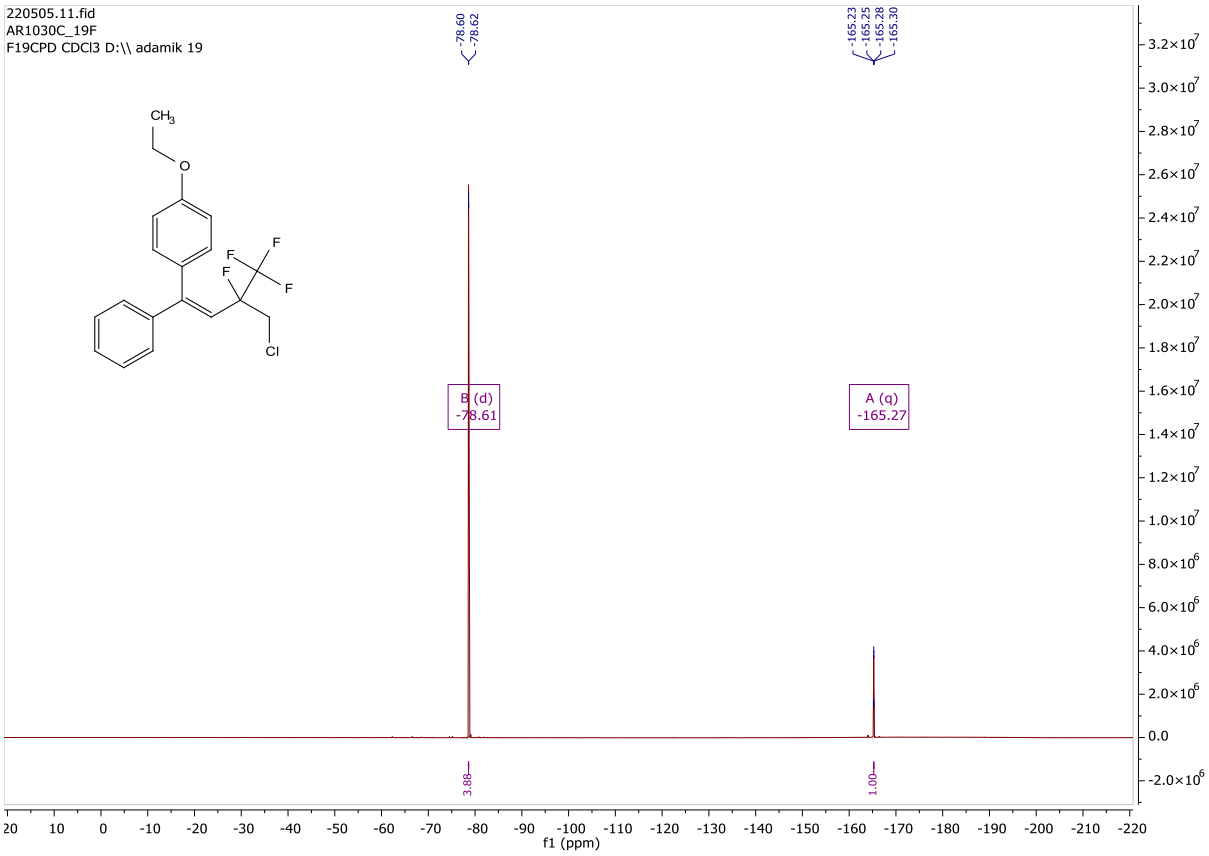

220407.20.fid
AR1030B_proton
PROTON CDCl3 D:\\ adamik 10
Cl
F
F
F
F
Cl
D (m)
7.17
C (m)
7.08
A (d)
5.84
B (m)
3.64
f1 (ppm)

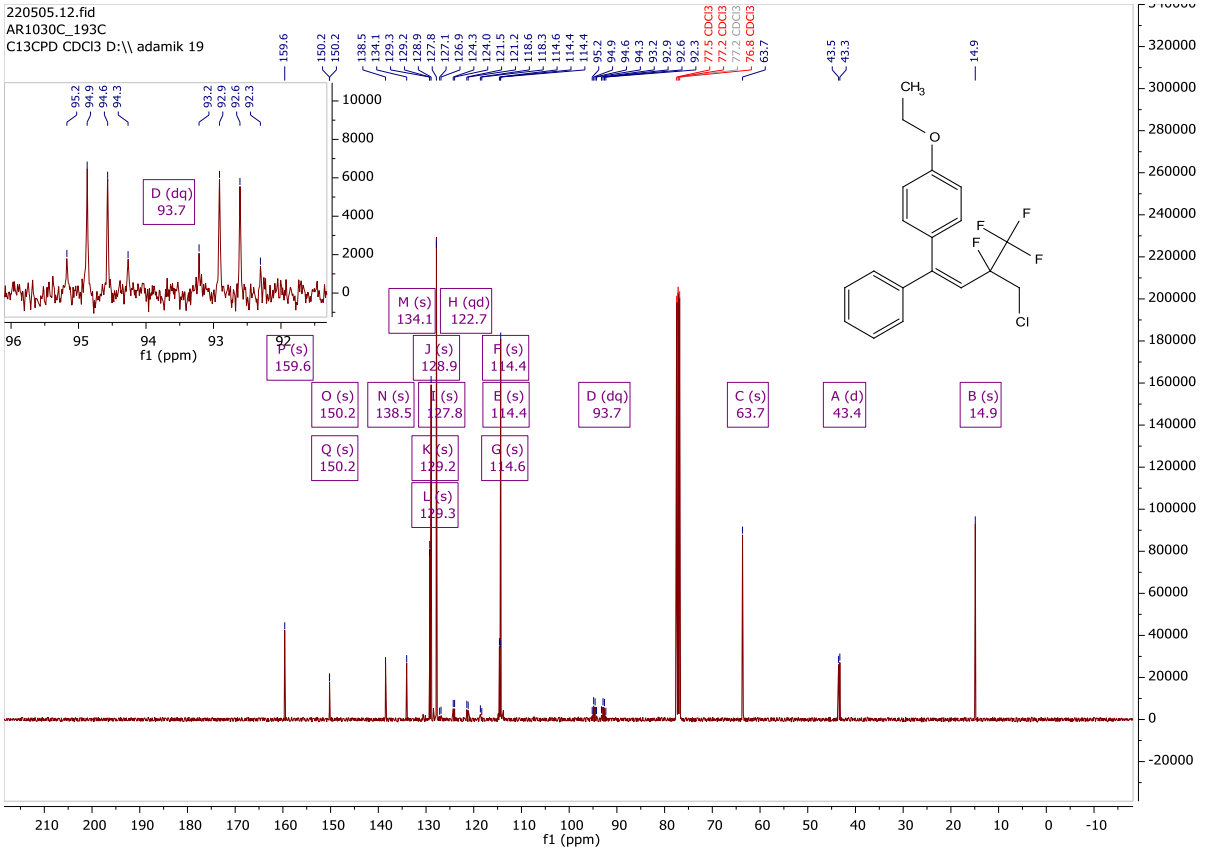

220407.21.fid
AR1030B_19F
F19CPD CDCl3 D:\\ adamik 10
Cl
F
F
F
F
Cl
B (d)
-78.56
A (q)
-166.62
f1 (ppm)


220407.22.fid
AR1030B_13C
C13CPD CDCl3 D:\\ adamik 10
A (dq) 93.7
P (s) 137.8
J (s) 129.1
H (s) 128.7
Q (s) 149.8
M (s) 137.8
F (s) 128.0
D (s) 116.9
O (s) 149.7
L (s) 134.9
C (dd) 122.6
A (dq) 93.7
B (d) 43.4
N (s) 140.3
G (s) 128.1
E (s) 117.0
I (s) 129.0
K (s) 129.1
f1 (ppm)

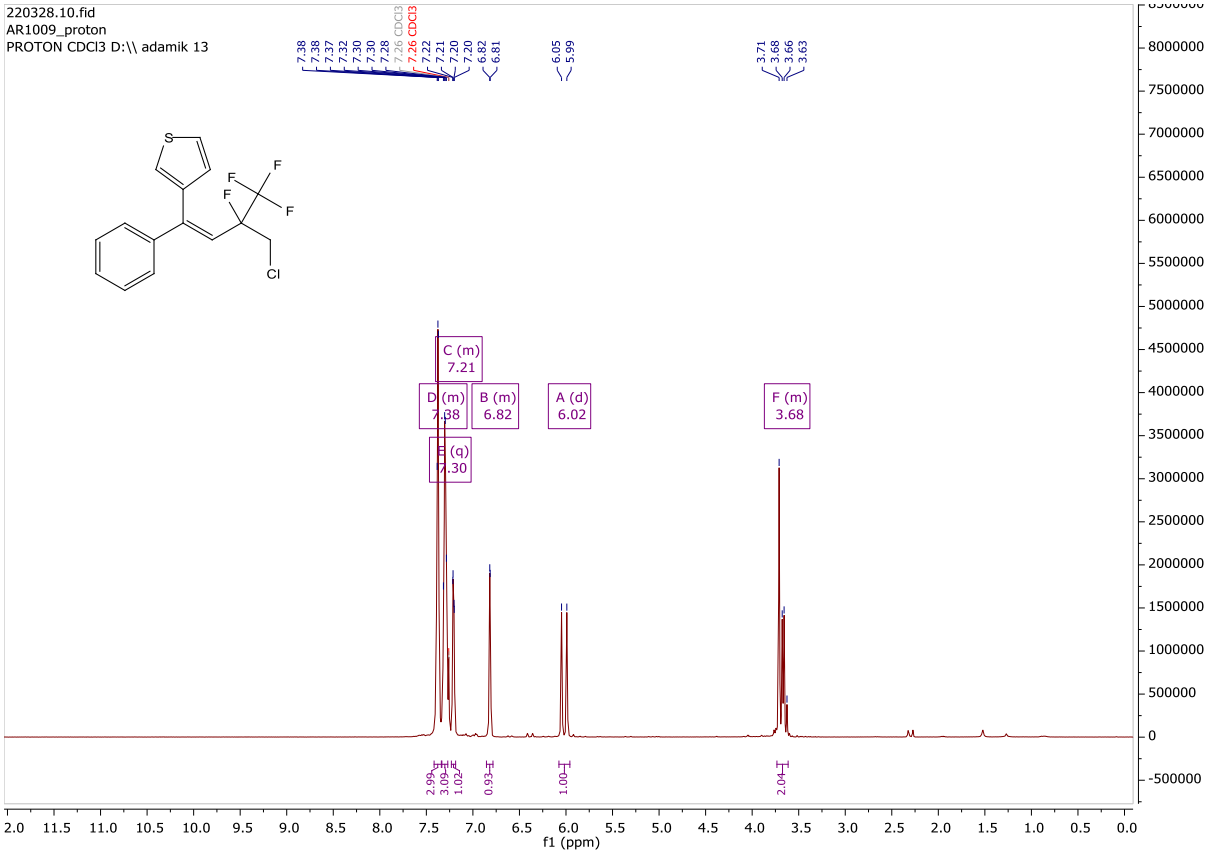
3h

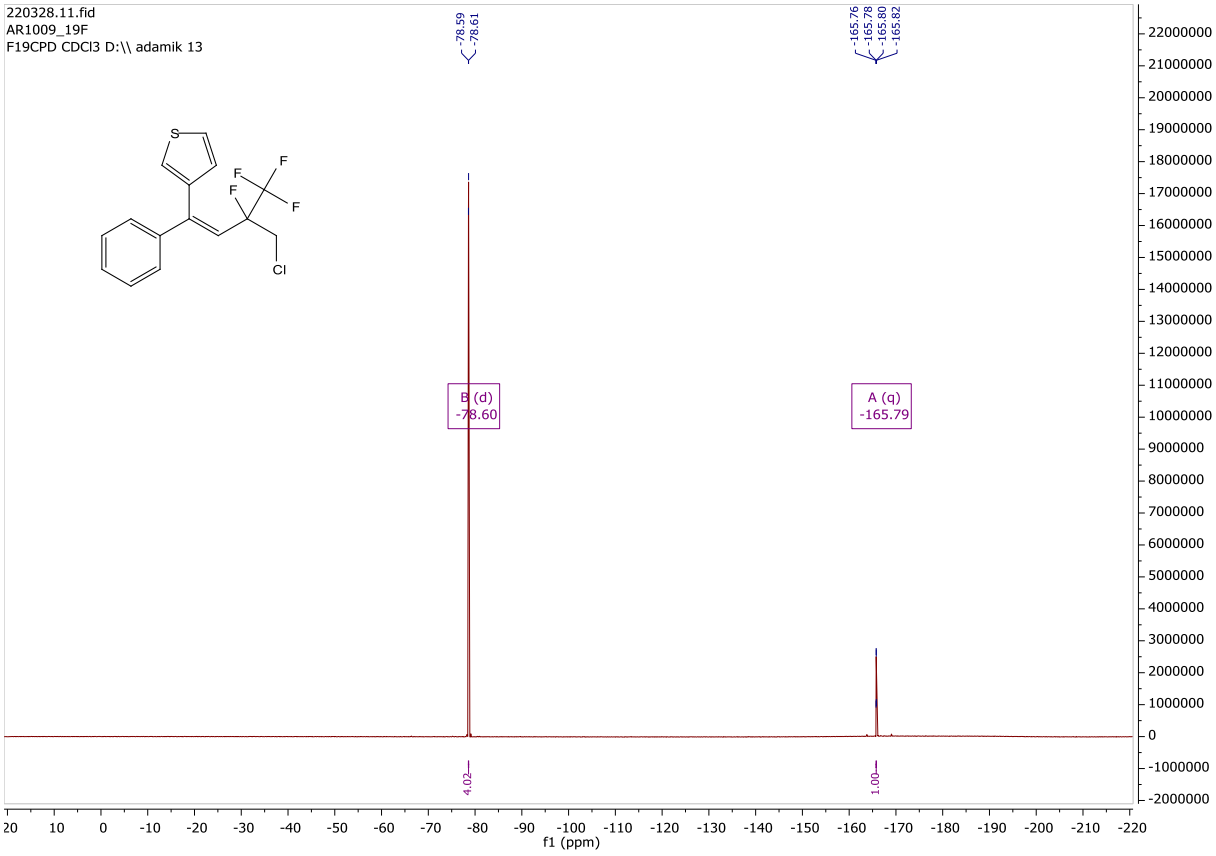

220505.10.fid
AR1030C_proton
PROTON CDCl3 D:\\ adamik 19
F (m) 7.07
G (m) 7.17
E (d) 6.73
A (d) 5.80
C (m) 3.61
B (q) 3.93
D (t) 1.32
H (dd) 7.27
f1 (ppm)

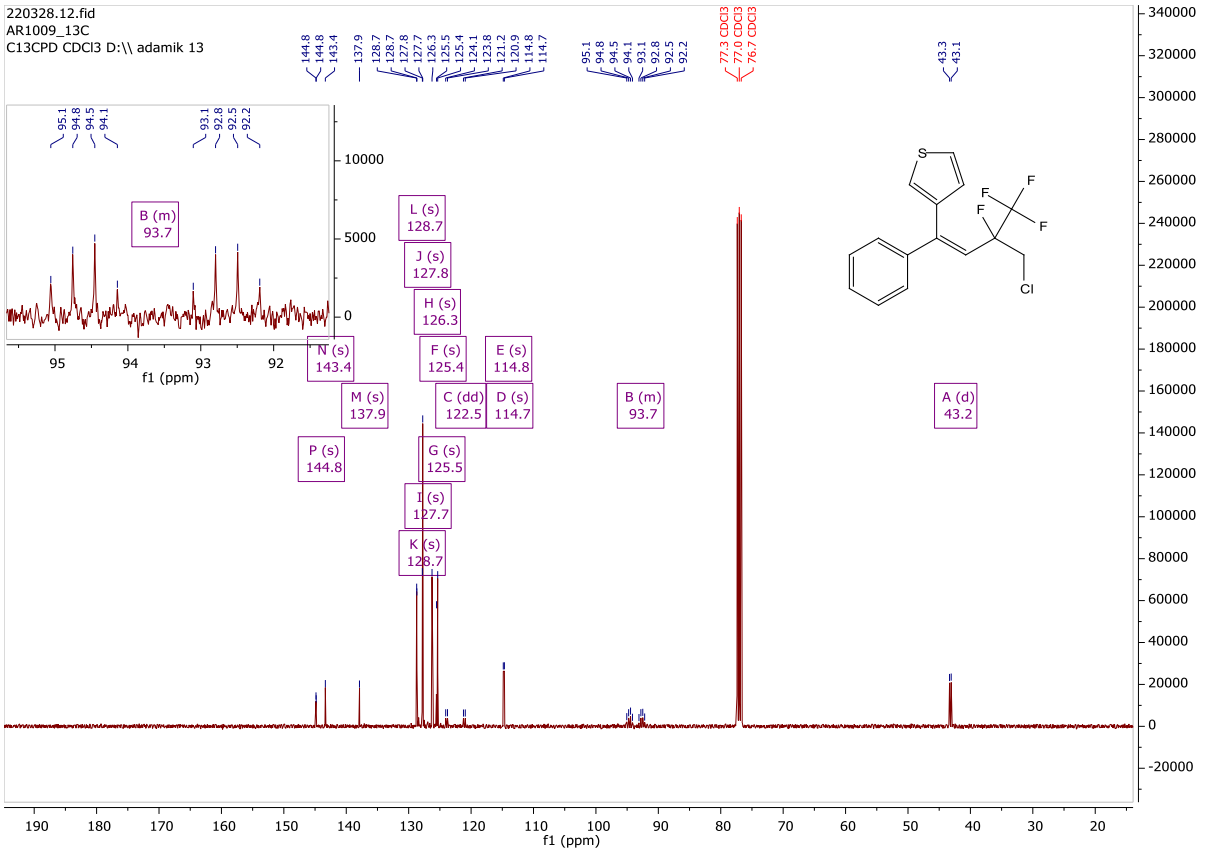

220505.11.fid
AR1030C_19F
F19CPD CDCl3 D:\\ adamik 19
-78.60
-78.62
-165.23
-165.25
-165.28
-165.30
B (d)
-78.61
A (q)
-165.27
3.88
1.00
f1 (ppm)


220505.12.fid
AR1030C_193C
C13CPD CDCl3 D:\\ adamik 19
D (dq)
93.7
P (s)
159.6
O (s)
150.2
Q (s)
150.2
N (s)
138.5
M (s)
134.1
K (s)
129.2
L (s)
129.3
J (s)
128.9
I (s)
127.8
H (qd)
122.7
F (s)
114.4
E (s)
114.4
G (s)
114.6
D (dq)
93.7
C (s)
63.7
A (d)
43.4
B (s)
14.9
f1 (ppm)

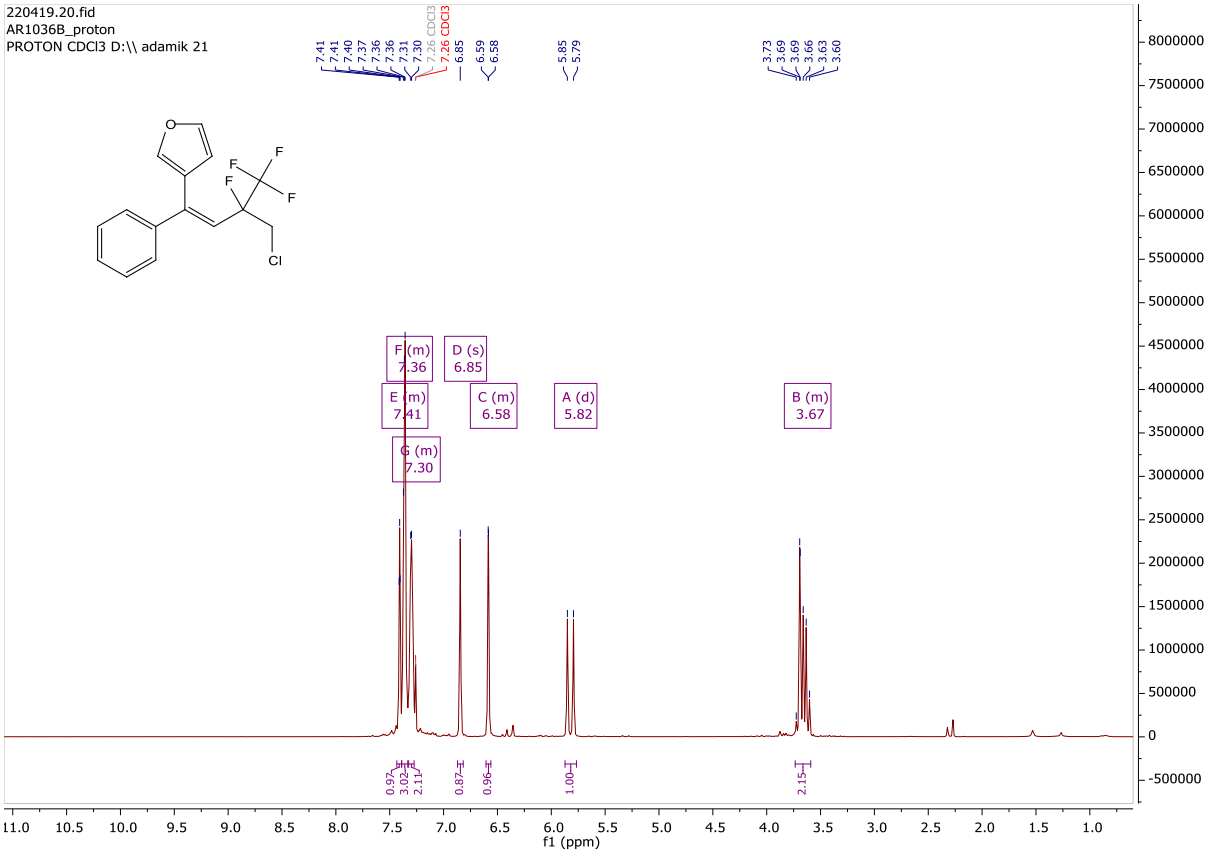
3i


220328.10.fid
AR1009_proton
PROTON CDCl3 D:\\ adamik 13
C (m)
7.21
D (m)
7.38
B (m)
6.82
A (d)
6.02
F (m)
3.68
E (q)
7.30
f1 (ppm)

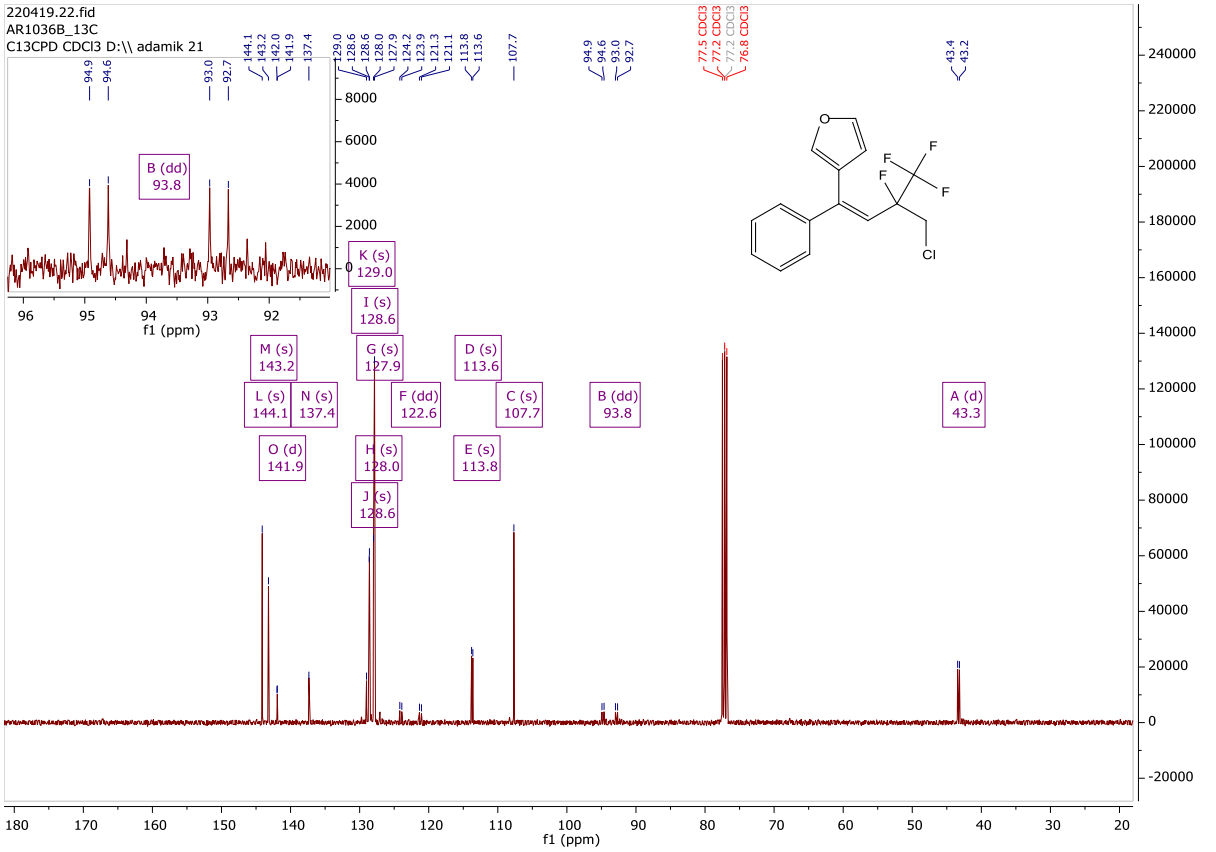

220328.11.fid
AR1009_19F
F19CPD CDCl3 D:\\ adamik 13
B (d)
-78.60
A (q)
-165.79
f1 (ppm)


220328.12.fid
AR1009_13C
C13CPD CDCl3 D:\\ adamik 13
B (m) 93.7
L (s) 128.7
J (s) 127.8
H (s) 126.3
N (s) 143.4
F (s) 125.4
E (s) 114.8
M (s) 137.9
C (dd) 122.5
D (s) 114.7
B (m) 93.7
A (d) 43.2
P (s) 144.8
G (s) 125.5
I (s) 127.7
K (s) 128.7
f1 (ppm)

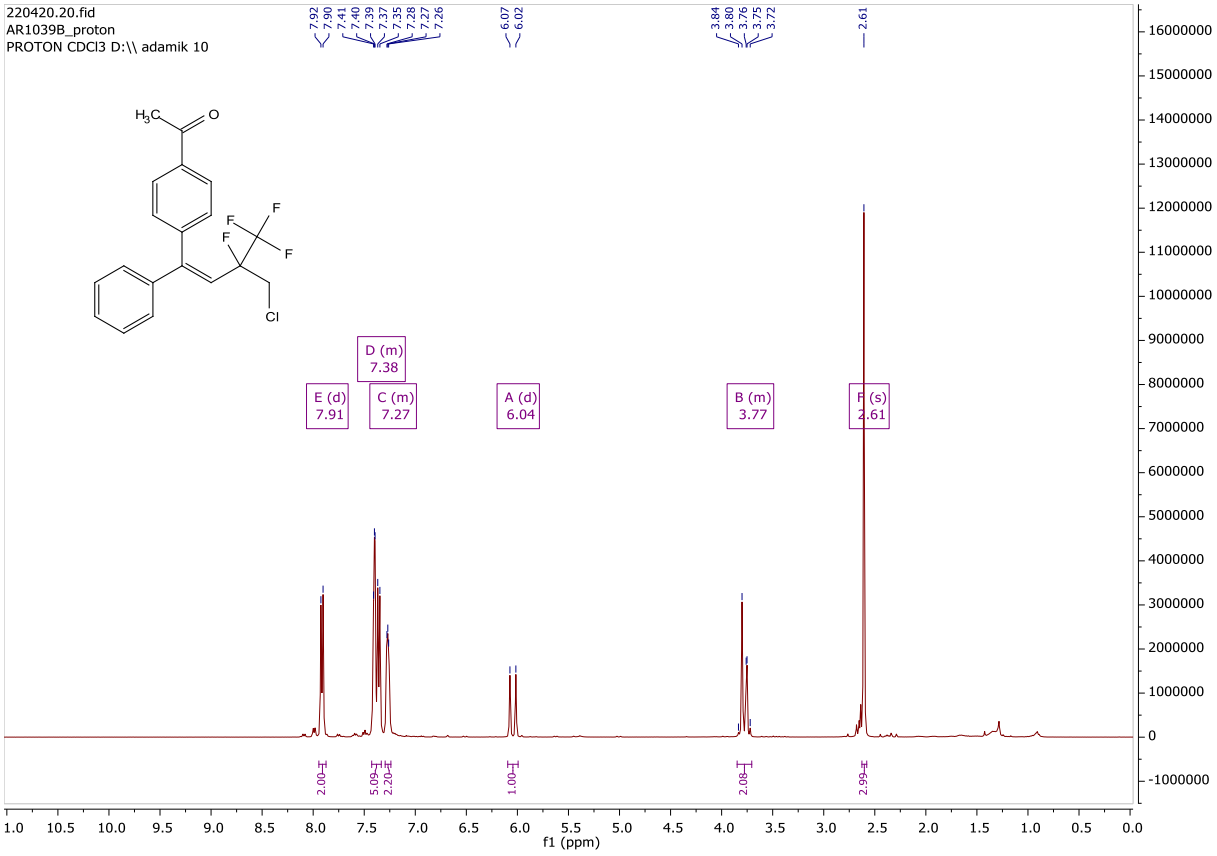
3j

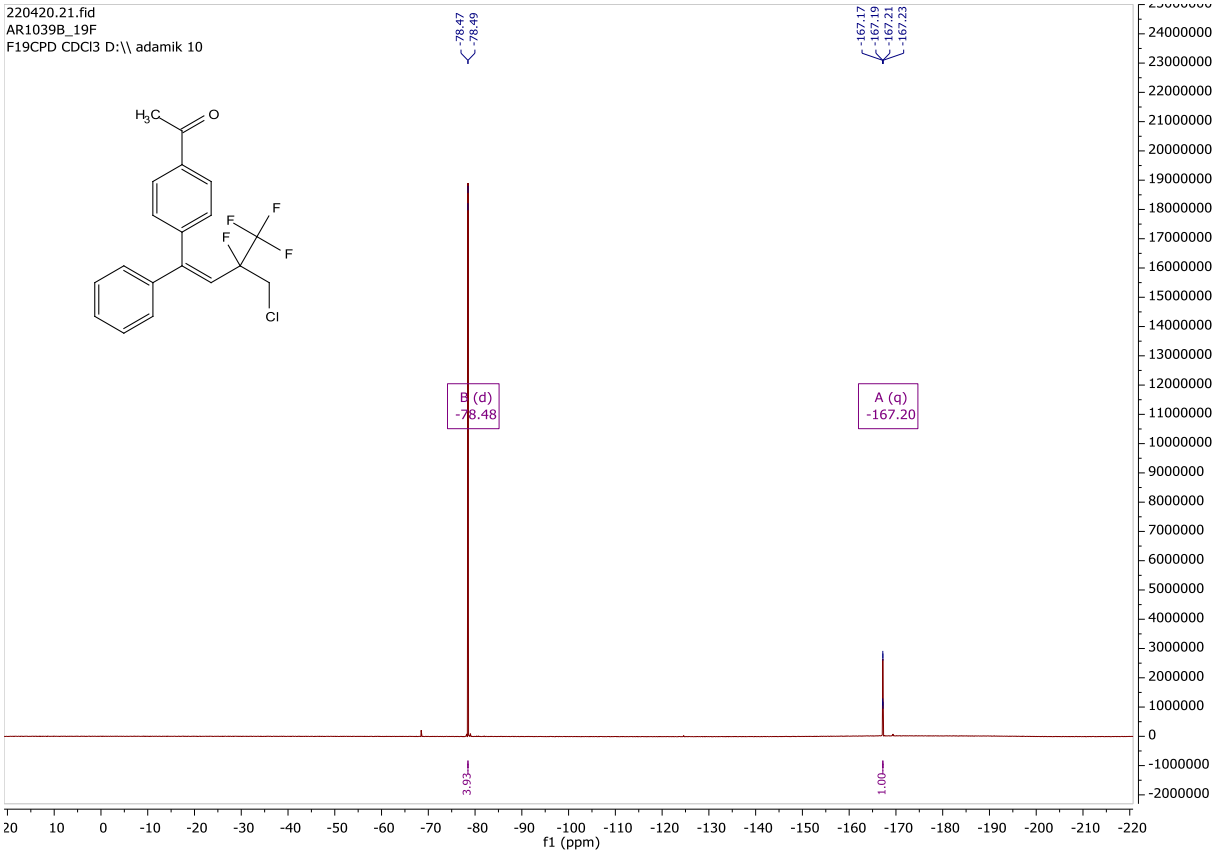

220419.20.fid
AR1036B_proton
PROTON CDCl3 D:\\ adamik 21
F (m) 7.36
D (s) 6.85
E (m) 7.41
C (m) 6.58
A (d) 5.82
B (m) 3.67
G (m) 7.30
f1 (ppm)

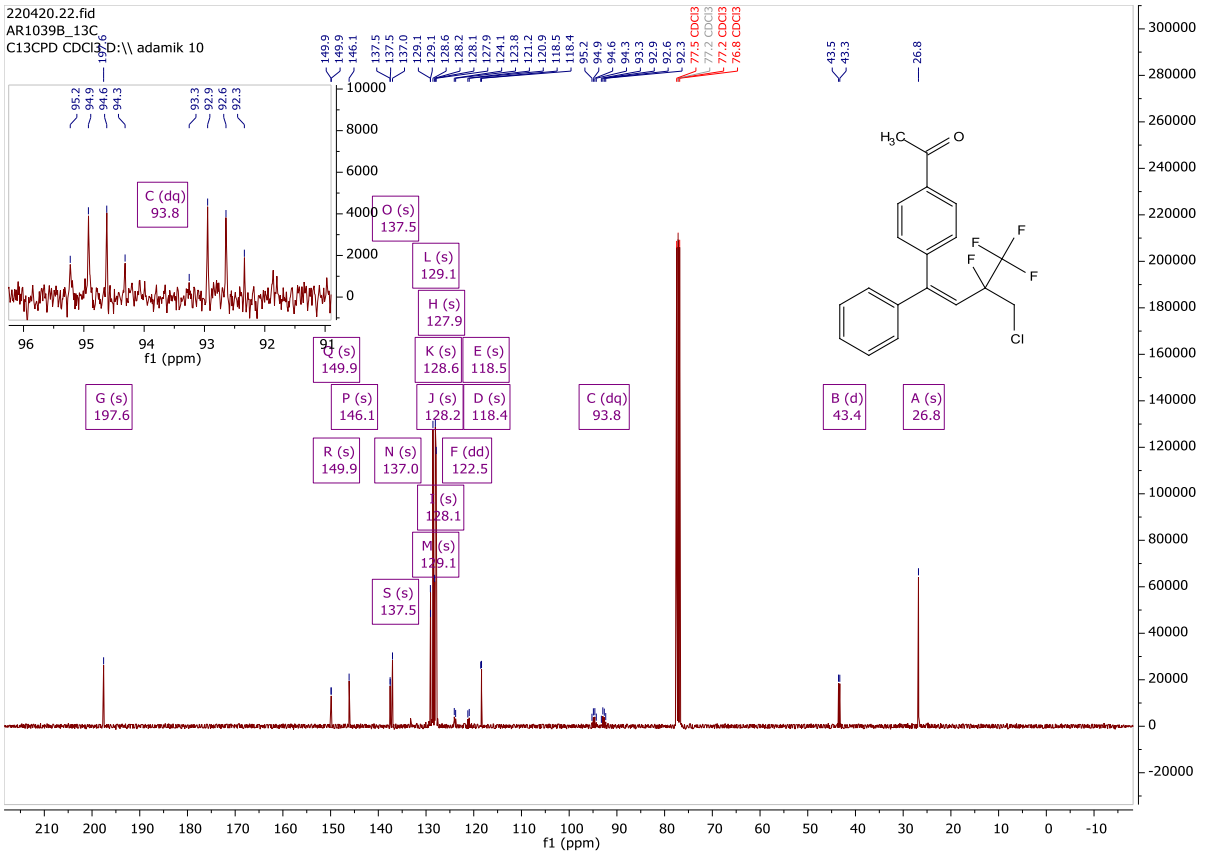

220419.21.fid
AR1036B_19F
F19CPD CDCl3 D:\\ adamik 21
-78.68
-78.70
-165.62
-165.64
-165.66
-165.68
B (d)
-78.69
A (q)
-165.65
4.17
1.00
f1 (ppm)


220419.22.fid
AR1036B_13C
C13CPD CDCl3 D:\\ adamik 21
B (dd)
93.8
K (s)
129.0
I (s)
128.6
M (s)
143.2
G (s)
127.9
D (s)
113.6
L (s)
144.1
N (s)
137.4
F (dd)
122.6
C (s)
107.7
B (dd)
93.8
A (d)
43.3
O (d)
141.9
H (s)
128.0
E (s)
113.8
J (s)
128.6
f1 (ppm)

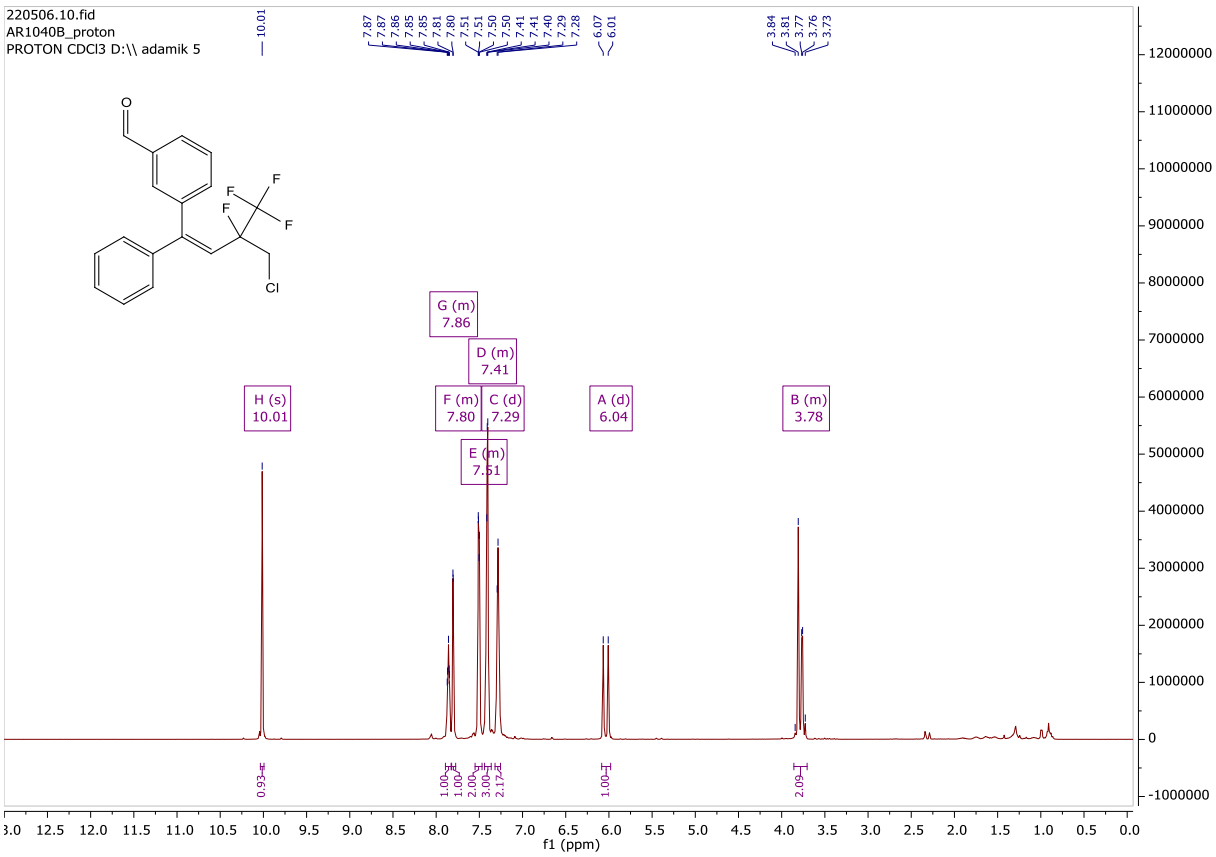
3k

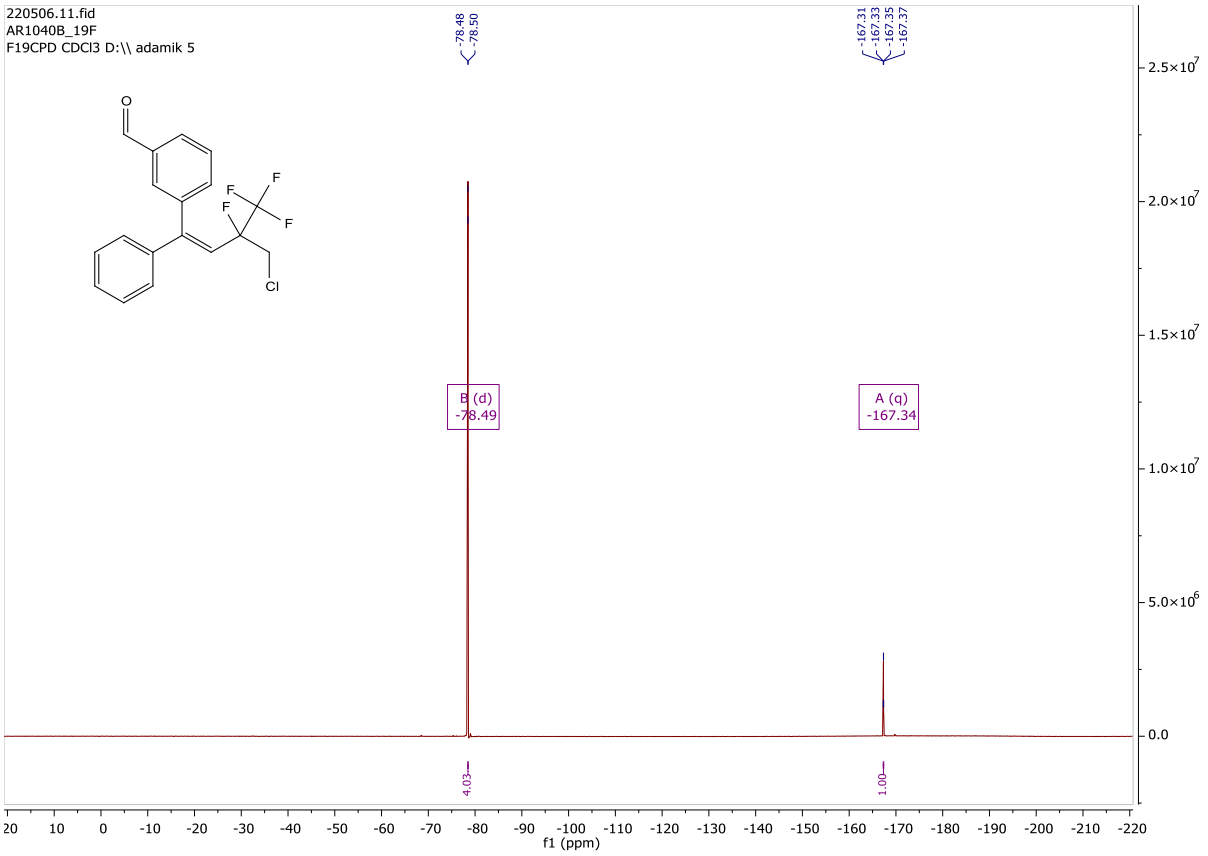

220420.20.fid
AR1039B_proton
PROTON CDCl3 D:\\ adamik 10
7.92
7.90
7.41
7.40
7.39
7.37
7.35
7.28
7.27
7.26
6.07
6.02
3.84
3.80
3.76
3.75
3.72
2.61
D (m)
7.38
E (d)
7.91
C (m)
7.27
A (d)
6.04
B (m)
3.77
F (s)
2.61
2.00
5.09
2.20
1.00
2.08
2.99
f1 (ppm)

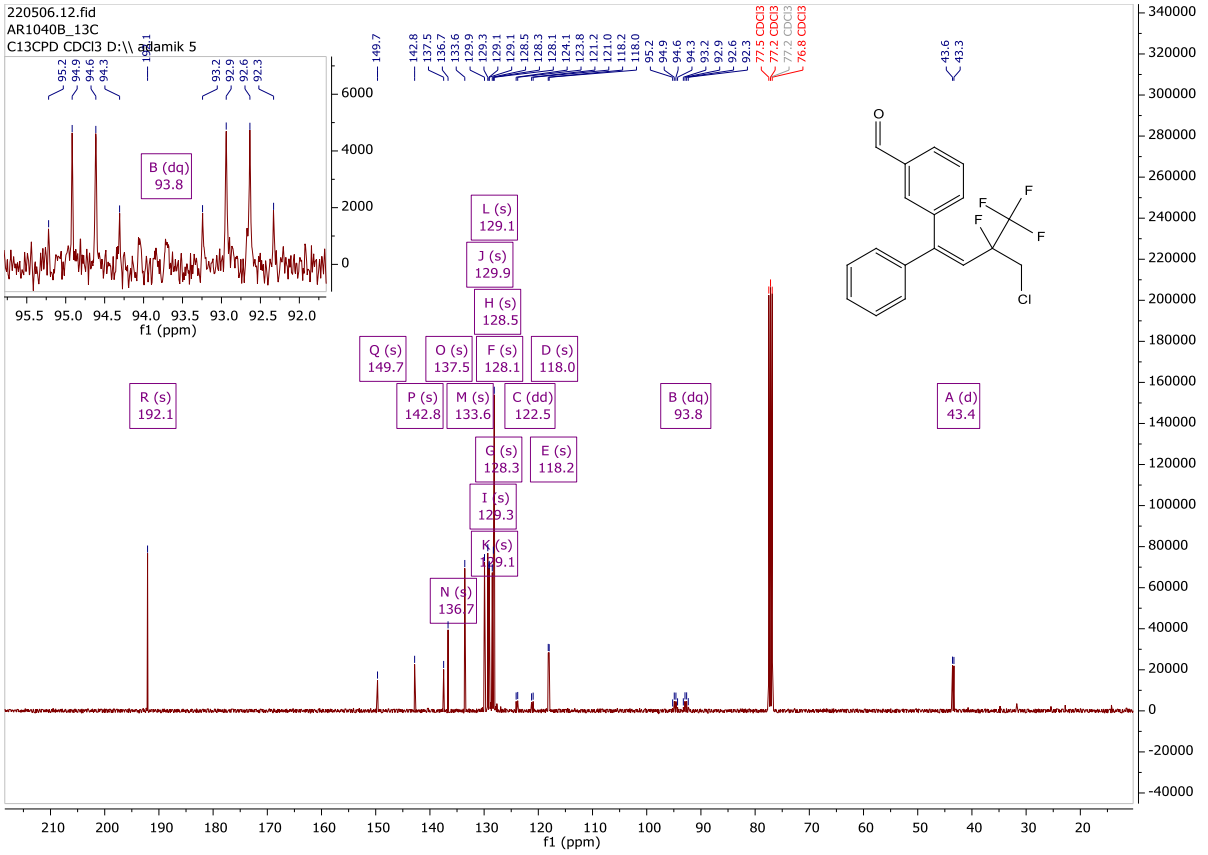

220420.21.fid
AR1039B_19F
F19CPD CDCl3 D:\\ adamik 10
-78.47
-78.49
-167.17
-167.19
-167.21
-167.23
B (d)
-78.48
A (q)
-167.20
3.93
1.00
f1 (ppm)


220420.22.fid
AR1039B_13C
C13CPD CDCl3 D:\\ adamik 10
C (dq) 93.8
O (s) 137.5
L (s) 129.1
H (s) 127.9
Q (s) 149.9
K (s) 128.6
E (s) 118.5
G (s) 197.6
P (s) 146.1
J (s) 128.2
D (s) 118.4
C (dq) 93.8
B (d) 43.4
A (s) 26.8
R (s) 149.9
N (s) 137.0
F (dd) 122.5
I (s) 128.1
M (s) 129.1
S (s) 137.5
f1 (ppm)

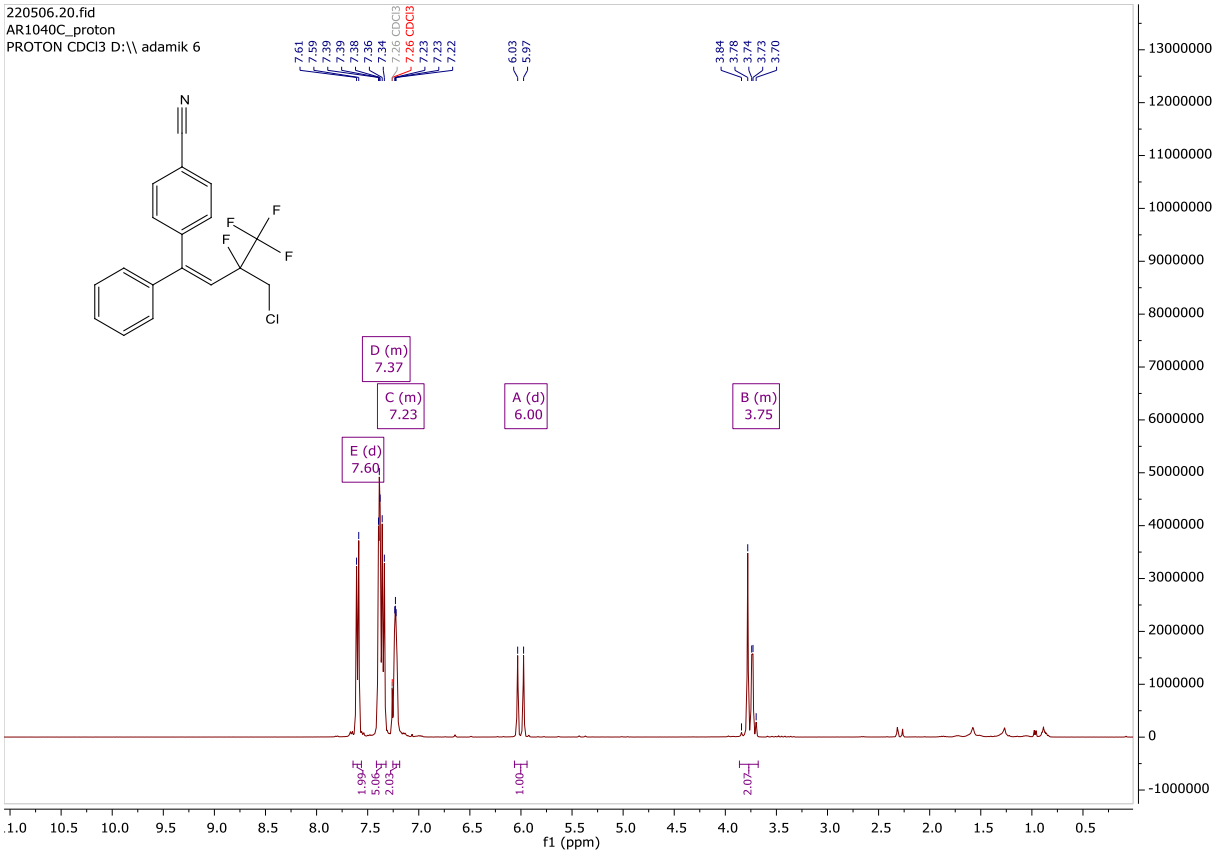
3l

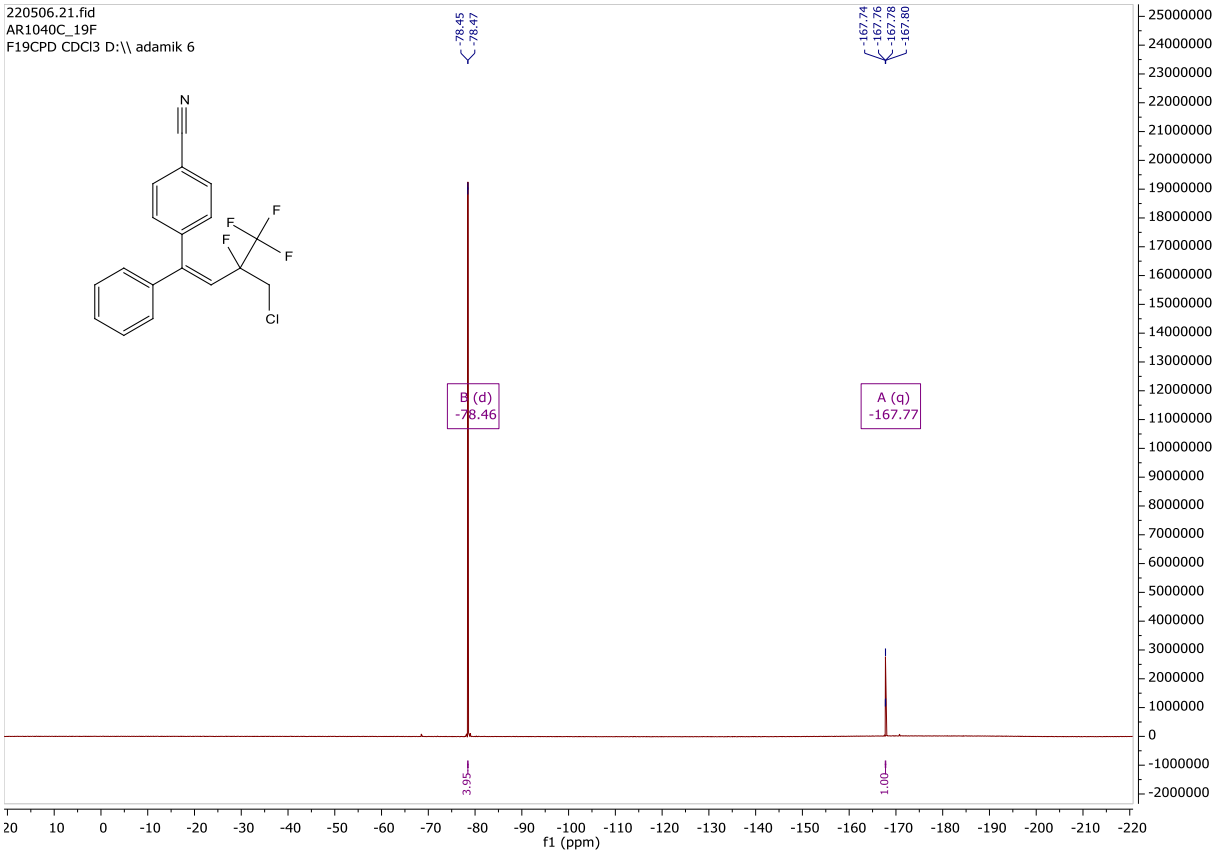

220506.10.fid
AR1040B_proton
PROTON CDCl3 D:\\ adamik 5
G (m) 7.86
D (m) 7.41
H (s) 10.01
F (m) 7.80
C (d) 7.29
A (d) 6.04
B (m) 3.78
E (m) 7.51
f1 (ppm)

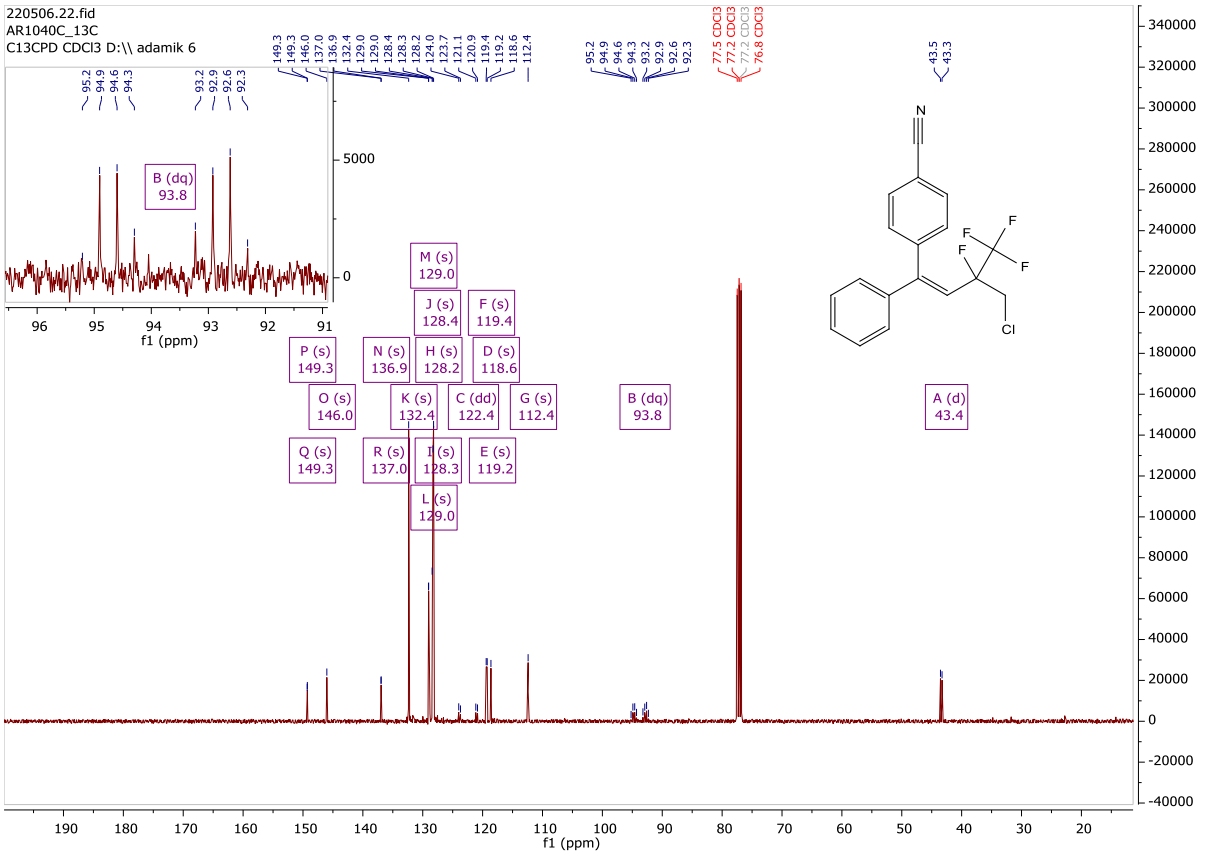

220506.11.fid
AR1040B_19F
F19CPD CDCl3 D:\\ adamik 5
-78.48
-78.50
-167.31
-167.33
-167.35
-167.37
B (d)
-78.49
A (q)
-167.34
4.03
1.00
f1 (ppm)


220506.12.fid
AR1040B_13C
C13CPD CDCl3 D:\\ adamik 5
B (dq)
93.8
L (s)
129.1
J (s)
129.9
H (s)
128.5
Q (s)
149.7
O (s)
137.5
F (s)
128.1
D (s)
118.0
P (s)
142.8
M (s)
133.6
C (dd)
122.5
G (s)
128.3
E (s)
118.2
I (s)
129.3
K (s)
129.1
N (s)
136.7
R (s)
192.1
B (dq)
93.8
A (d)
43.4
77.5 CDCl3
77.2 CDCl3
76.8 CDCl3
f1 (ppm)

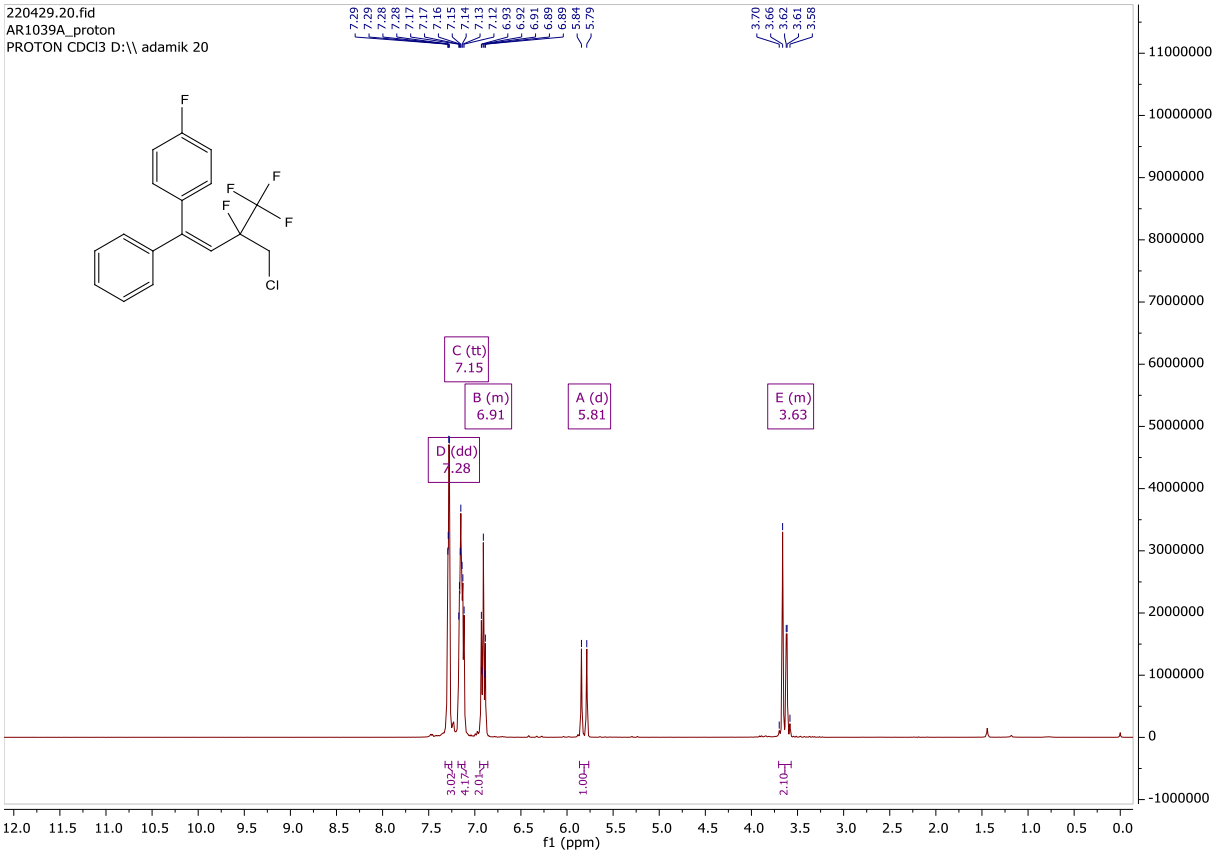
3m


220506.20.fid
AR1040C_proton
PROTON CDCl3 D:\\ adamik 6
7.61
7.59
7.39
7.39
7.38
7.36
7.34
7.26 CDCl3
7.26 CDCl3
7.23
7.23
7.22
6.03
5.97
3.84
3.78
3.74
3.73
3.70
N
F
F
F
Cl
D (m)
7.37
C (m)
7.23
A (d)
6.00
B (m)
3.75
E (d)
7.60
1.99
5.06
2.03
1.00
2.07
f1 (ppm)

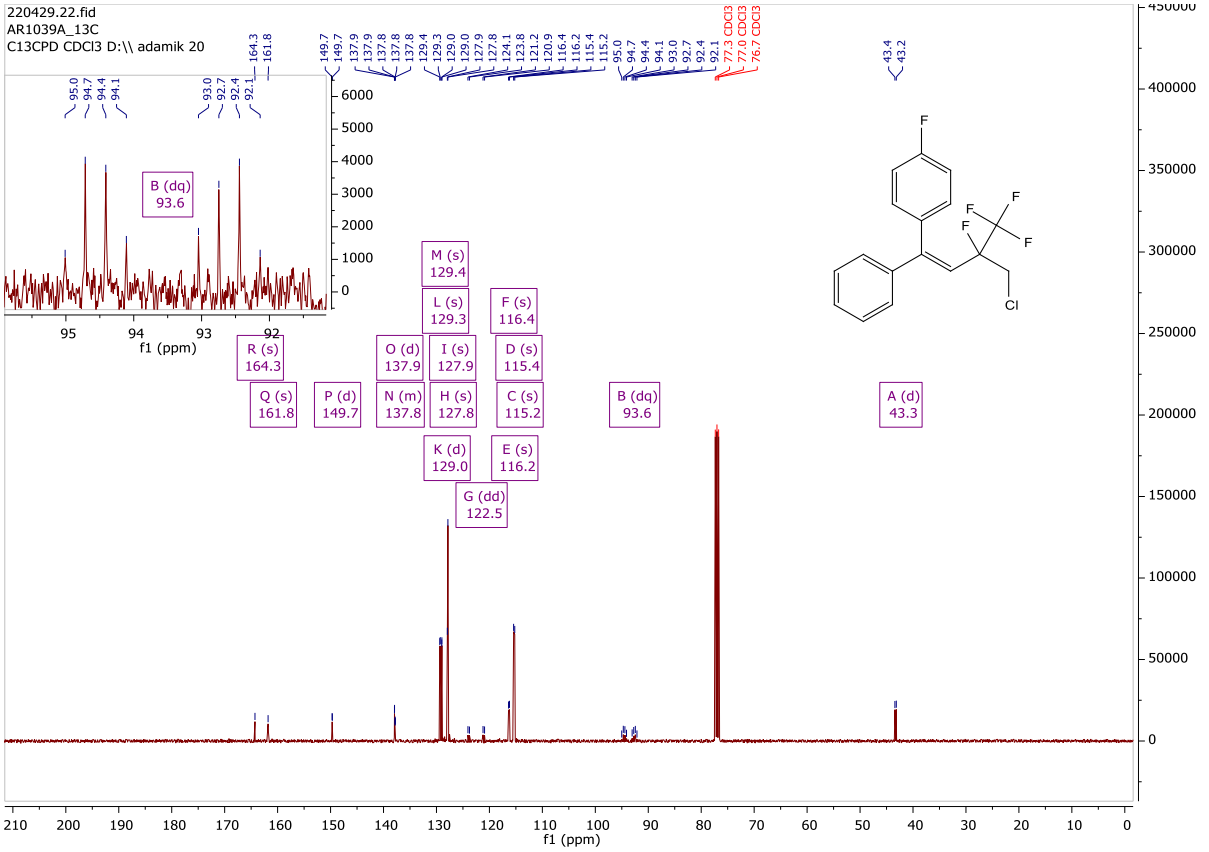

220506.21.fid
AR1040C_19F
F19CPD CDCl3 D:\\ adamik 6
-78.45
-78.47
-167.74
-167.76
-167.78
-167.80
N
F
F
F
Cl
B (d)
-78.46
A (q)
-167.77
3.95
1.00
f1 (ppm)


220506.22.fid
AR1040C_13C
C13CPD CDCl3 D:\\ adamik 6
B (dq)
93.8
M (s)
129.0
J (s)
128.4
F (s)
119.4
P (s)
149.3
N (s)
136.9
H (s)
128.2
D (s)
118.6
O (s)
146.0
K (s)
132.4
C (dd)
122.4
G (s)
112.4
B (dq)
93.8
A (d)
43.4
Q (s)
149.3
R (s)
137.0
I (s)
128.3
E (s)
119.2
L (s)
129.0
f1 (ppm)

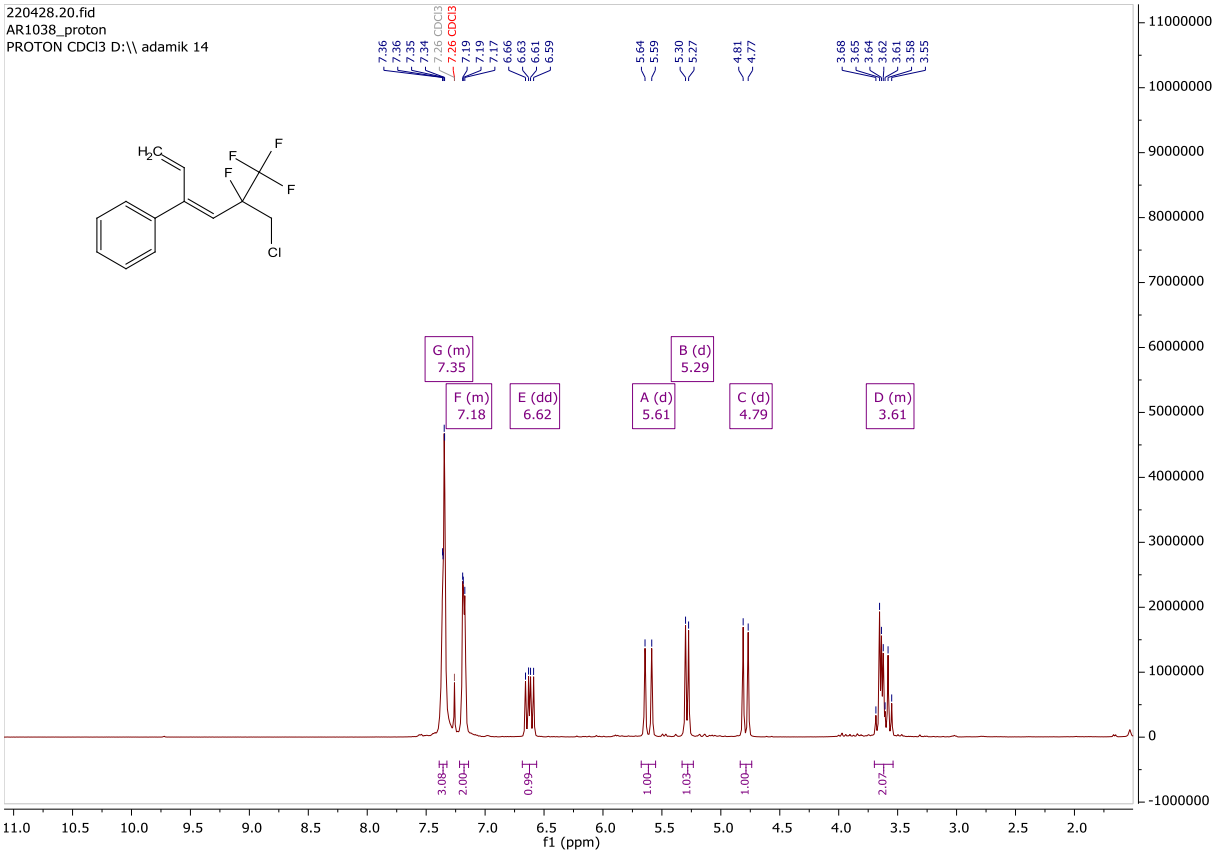
3n

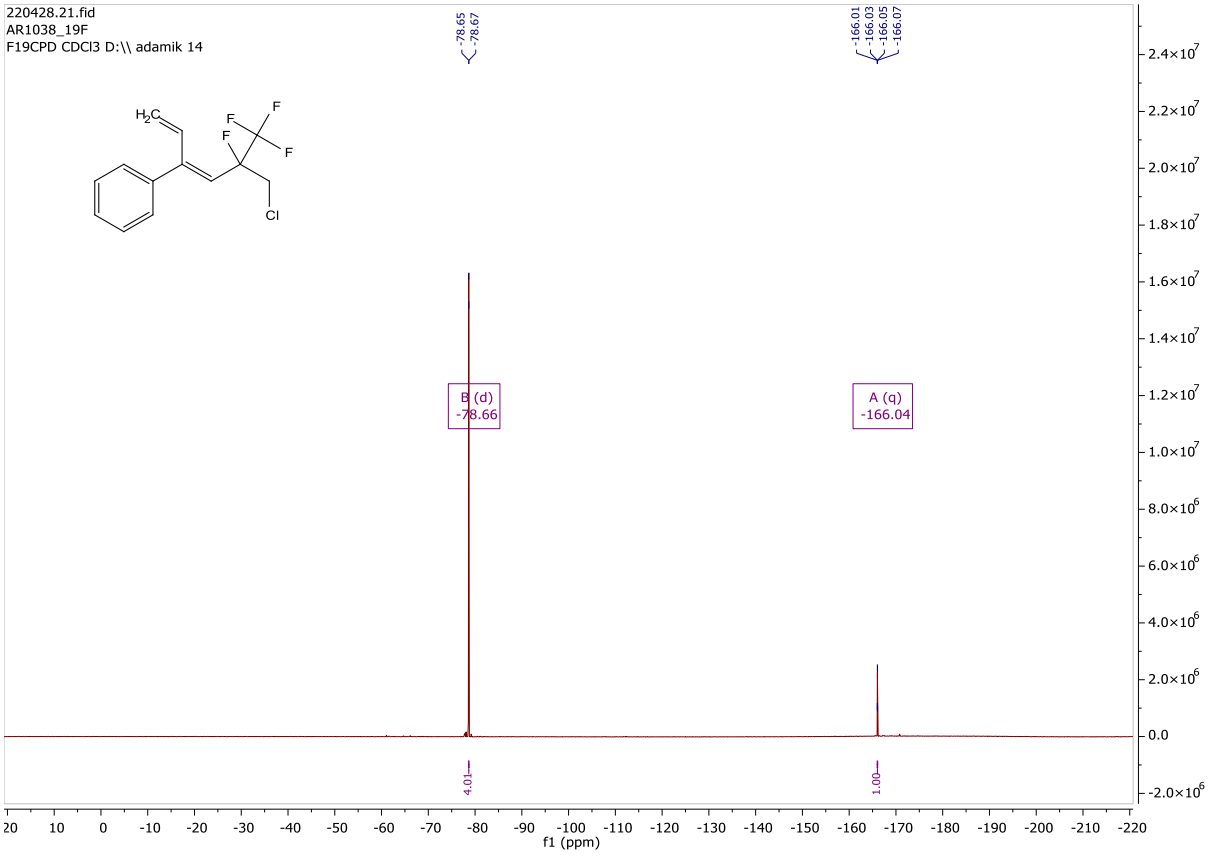

220429.20.fid
AR1039A_proton
PROTON CDCl3 D:\\ adamik 20
C (tt)
7.15
B (m)
6.91
A (d)
5.81
E (m)
3.63
D (dd)
7.28
f1 (ppm)

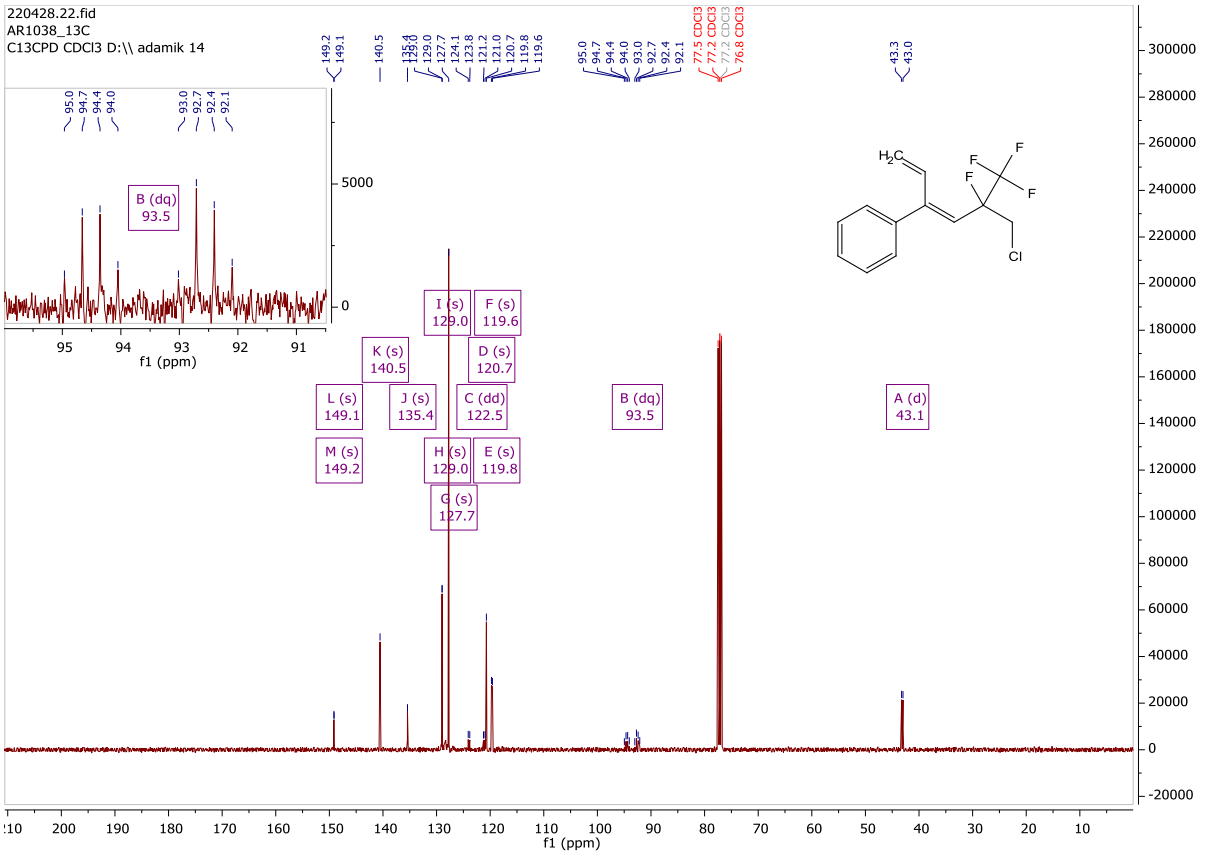

220429.21.fid
AR1039A_19F
F19CPD CDCl3 D:\\ adamik 20
-78.59
-78.61
-113.04
-166.35
-166.37
-166.39
-166.41
C (d)
-78.60
B (s)
-113.04
A (q)
-166.38
4.20
0.84
1.00
f1 (ppm)


220429.22.fid
AR1039A_13C
C13CPD CDCl3 D:\\ adamik 20
B (dq)
93.6
M (s)
129.4
L (s)
129.3
F (s)
116.4
R (s)
164.3
O (d)
137.9
I (s)
127.9
D (s)
115.4
Q (s)
161.8
P (d)
149.7
N (m)
137.8
H (s)
127.8
C (s)
115.2
B (dq)
93.6
A (d)
43.3
K (d)
129.0
E (s)
116.2
G (dd)
122.5
f1 (ppm)

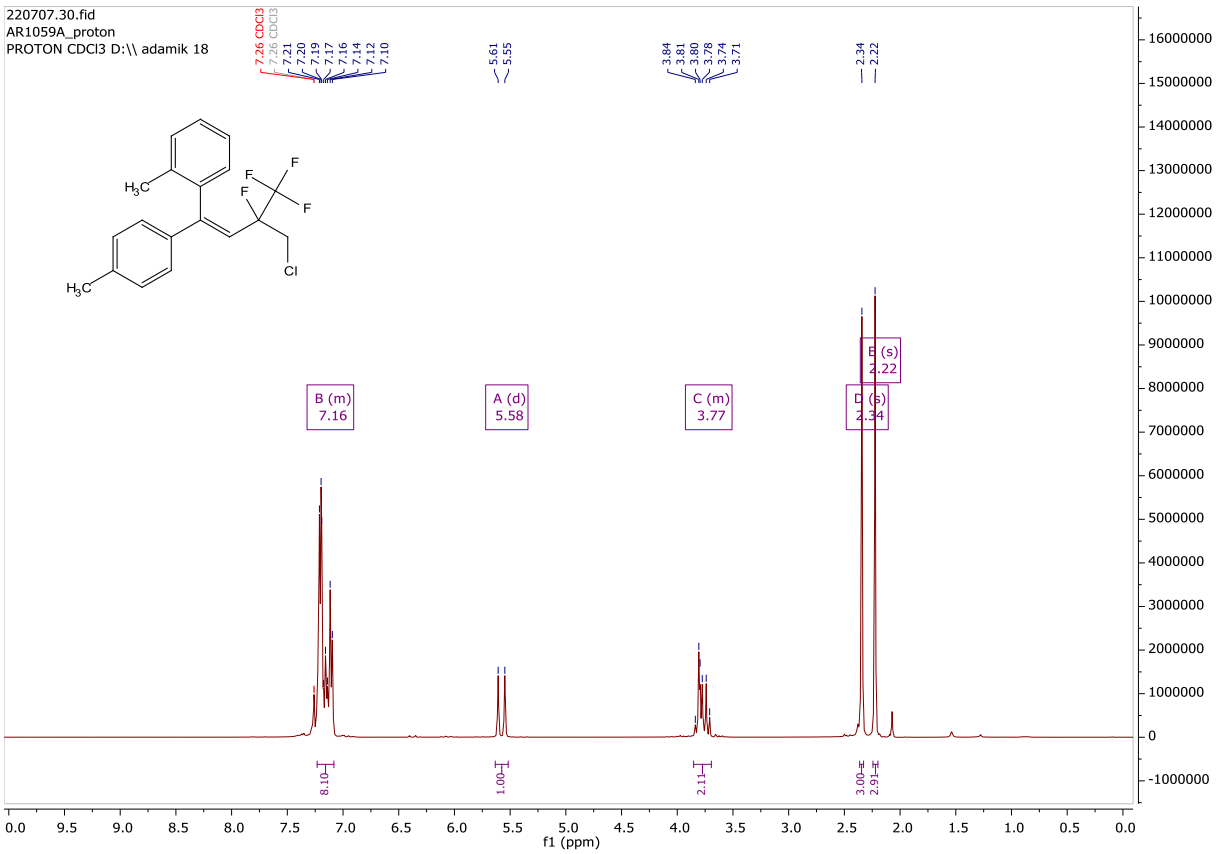
3o

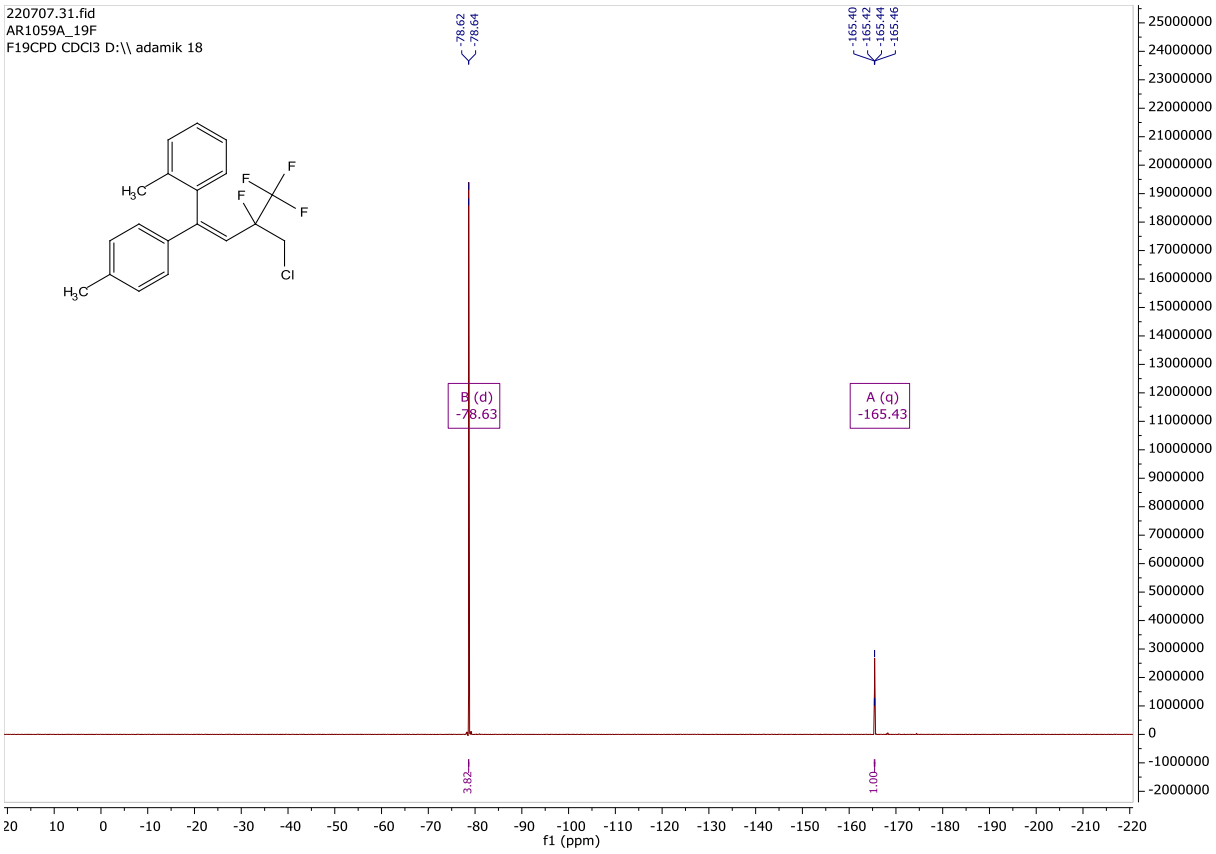

220428.20.fid
AR1038_proton
PROTON CDCl3 D:\\ adamik 14
7.36
7.36
7.35
7.34
7.26 CDCl3
7.26 CDCl3
7.19
7.19
7.17
6.66
6.63
6.61
6.59
5.64
5.59
5.30
5.27
4.81
4.77
3.68
3.65
3.64
3.62
3.61
3.58
3.55
H2C
F
F
F
Cl
G (m)
7.35
F (m)
7.18
E (dd)
6.62
B (d)
5.29
A (d)
5.61
C (d)
4.79
D (m)
3.61
3.08
2.00
0.99
1.00
1.03
1.00
2.07
f1 (ppm)

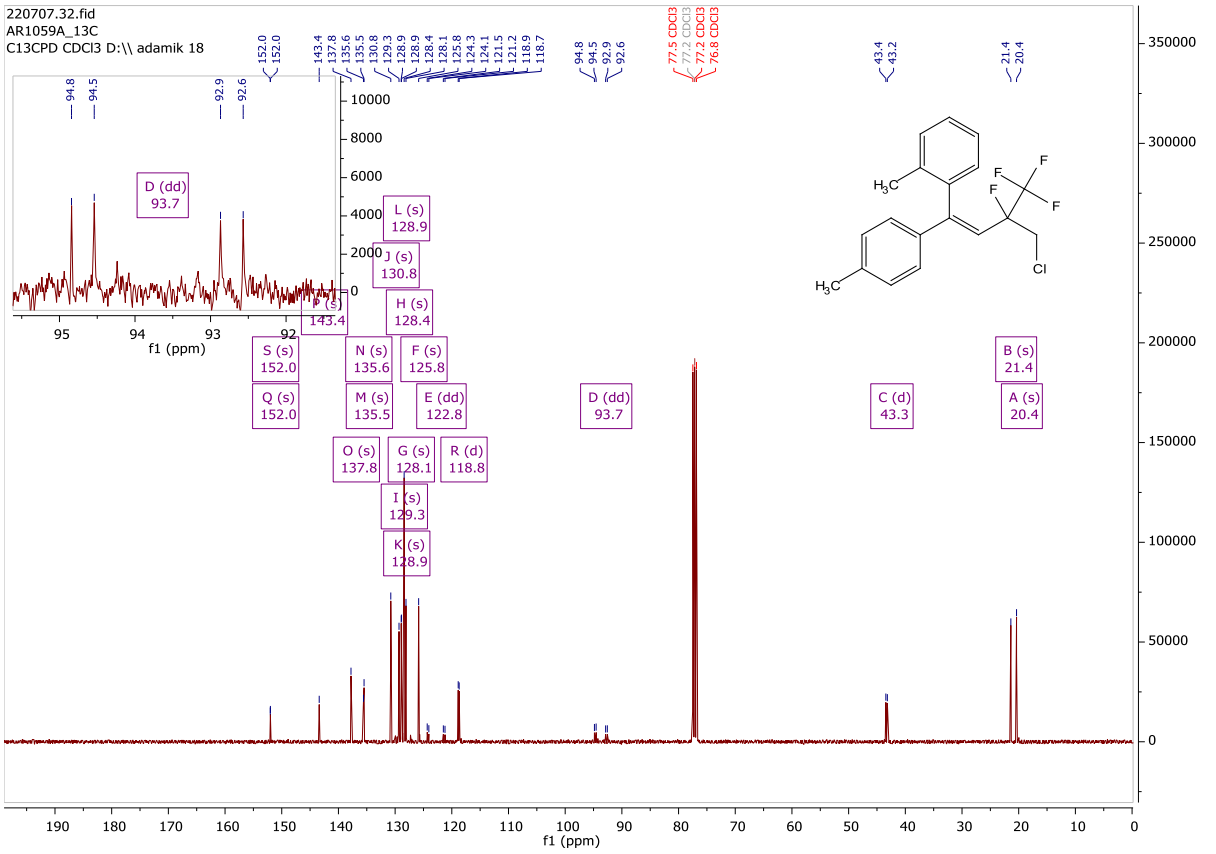

220428.21.fid
AR1038_19F
F19CPD CDCl3 D:\\ adamik 14
-78.65
-78.67
-166.01
-166.03
-166.05
-166.07
H2C
F
F
F
Cl
B (d)
-78.66
A (q)
-166.04
4.01
1.00
f1 (ppm)


220428.22.fid
AR1038_13C
C13CPD CDCl3 D:\\ adamik 14
B (dq)
93.5
I (s)
129.0
F (s)
119.6
K (s)
140.5
D (s)
120.7
L (s)
149.1
J (s)
135.4
C (dd)
122.5
B (dq)
93.5
A (d)
43.1
M (s)
149.2
H (s)
129.0
E (s)
119.8
G (s)
127.7
f1 (ppm)

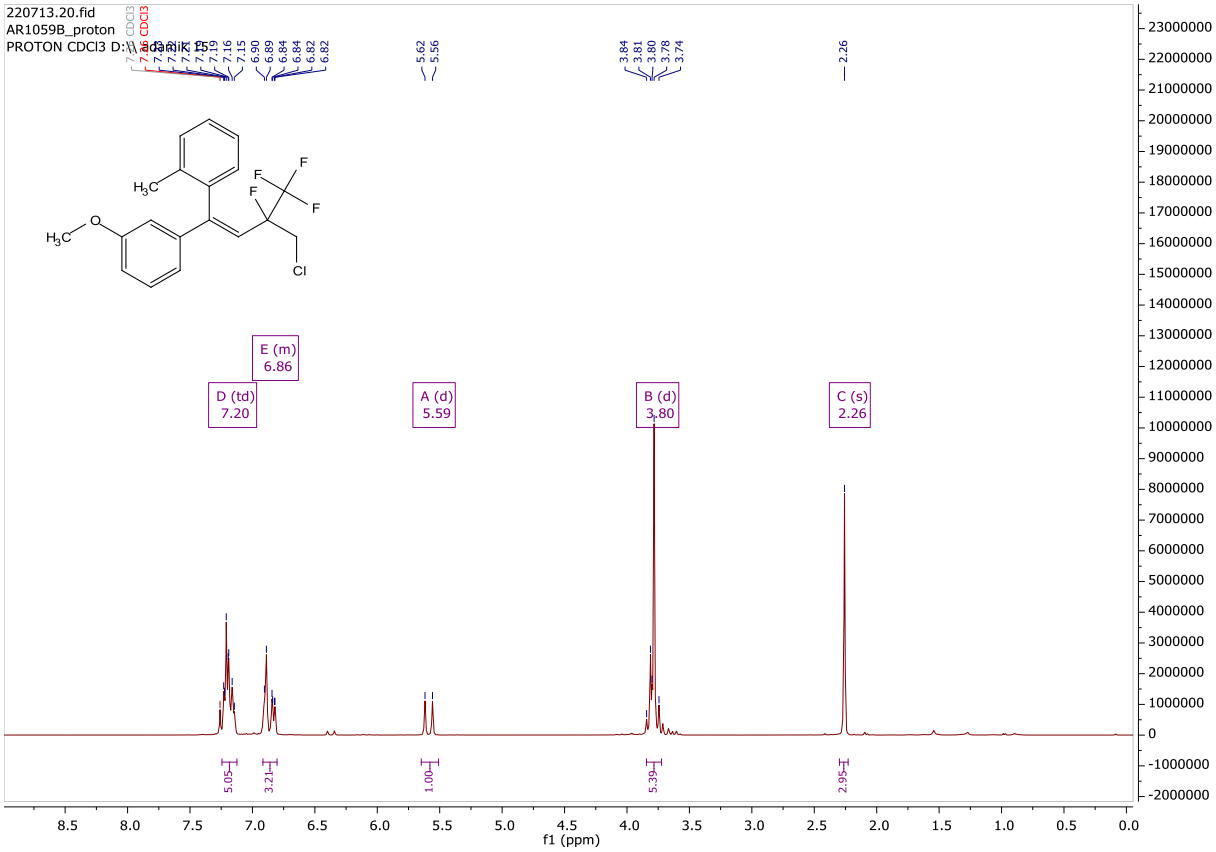
3p

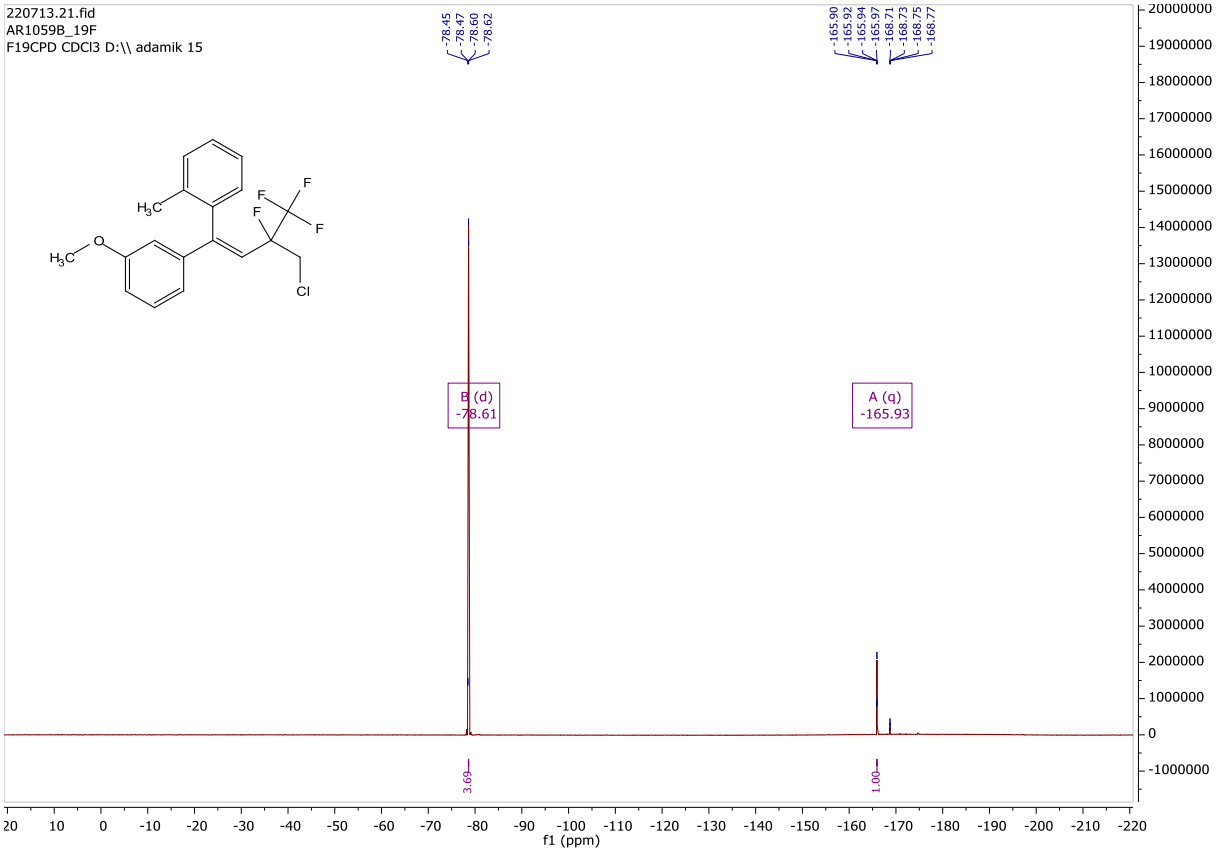

220707.30.fid
AR1059A_proton
PROTON CDCl3 D:\\ adamik 18
B (m)
7.16
A (d)
5.58
C (m)
3.77
D (s)
2.34
E (s)
2.22
f1 (ppm)

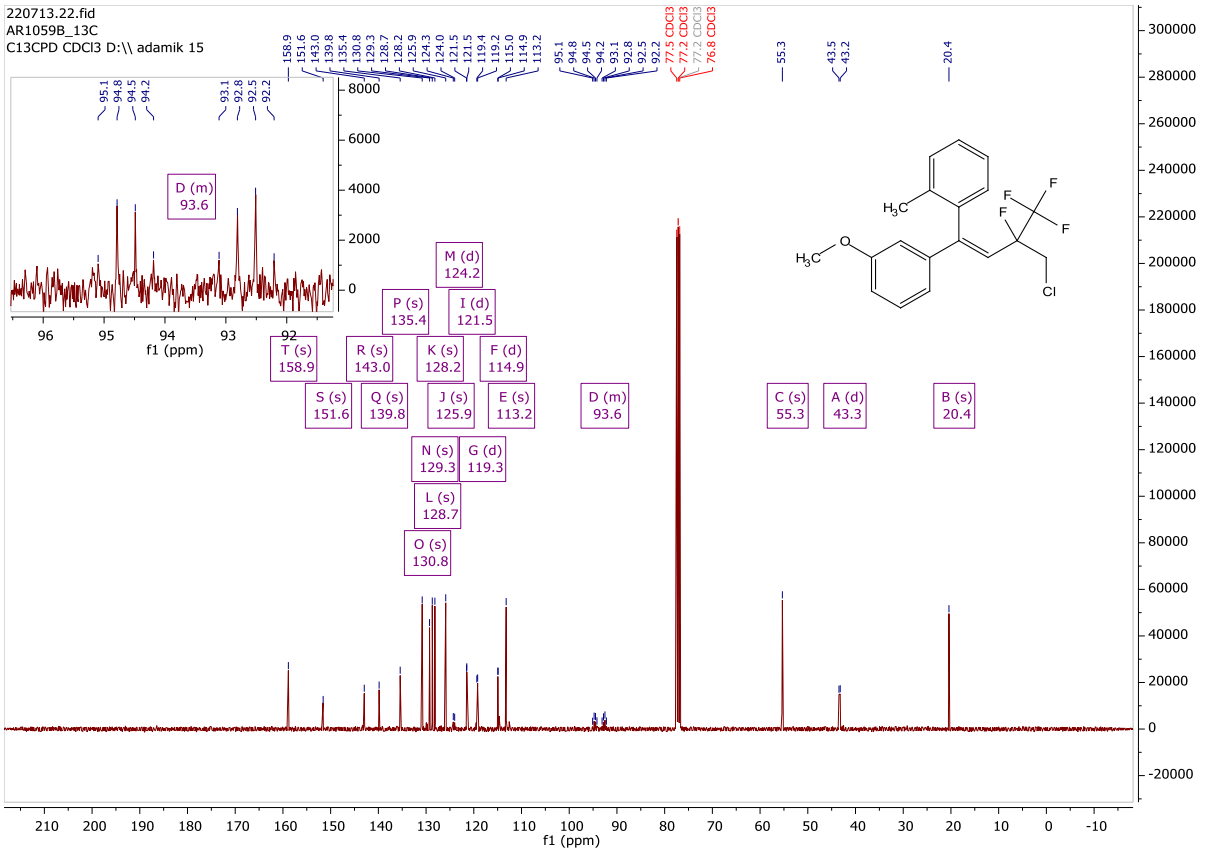

220707.31.fid
AR1059A_19F
F19CPD CDCl3 D:\\ adamik 18
-78.62
-78.64
-165.40
-165.42
-165.44
-165.46
B (d)
-78.63
A (q)
-165.43
3.82
1.00
f1 (ppm)


220707.32.fid
AR1059A_13C
C13CPD CDCl3 D:\\ adamik 18
152.0
152.0
143.4
137.8
135.6
135.5
130.8
129.3
128.9
128.9
128.4
128.1
125.8
124.3
124.1
121.5
121.2
118.9
118.7
94.8
94.5
92.9
92.6
77.5 CDCl3
77.2 CDCl3
77.2 CDCl3
76.8 CDCl3
43.4
43.2
21.4
20.4
D (dd)
93.7
L (s)
128.9
J (s)
130.8
H (s)
128.4
S (s)
152.0
N (s)
135.6
F (s)
125.8
Q (s)
152.0
M (s)
135.5
E (dd)
122.8
O (s)
137.8
G (s)
128.1
R (d)
118.8
I (s)
129.3
K (s)
128.9
D (dd)
93.7
C (d)
43.3
B (s)
21.4
A (s)
20.4
f1 (ppm)

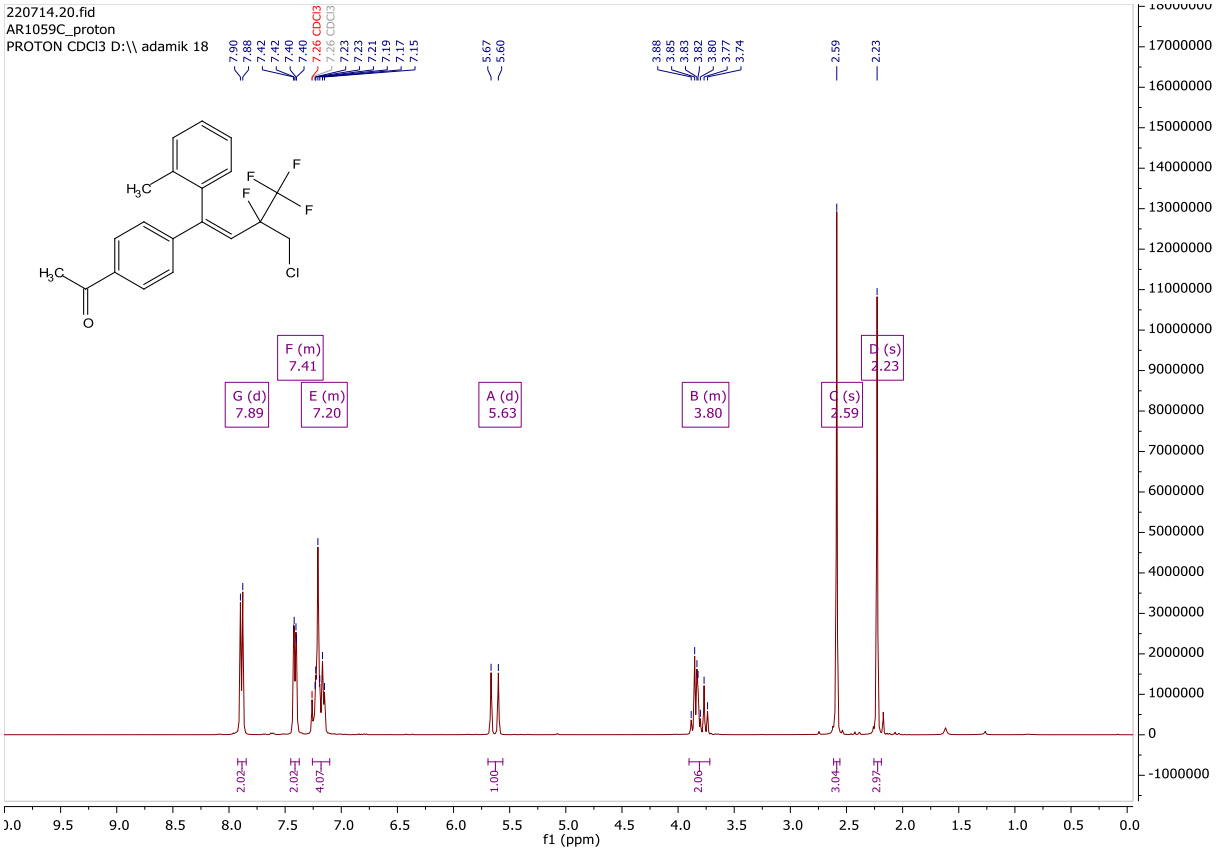
3q

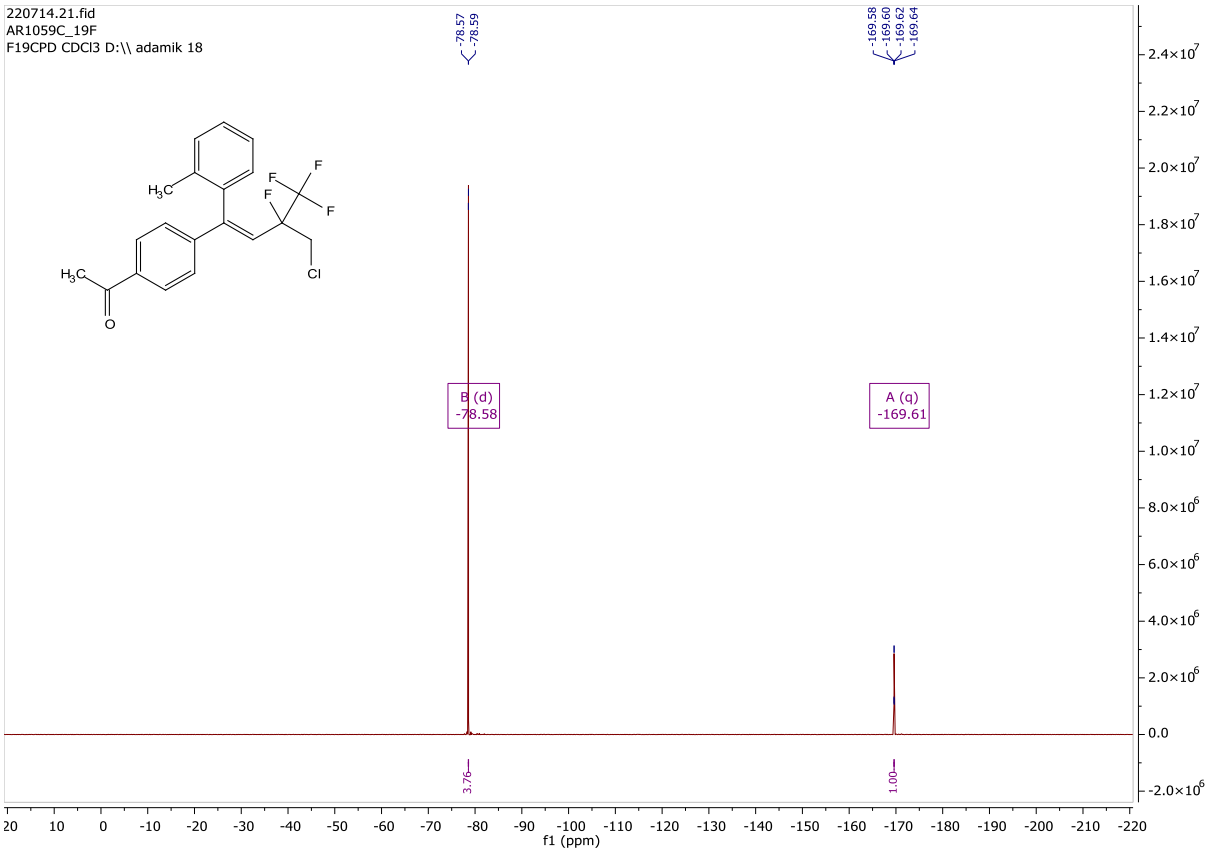

220713.20.fid
AR1059B_proton
PROTON CDCl3 D:\\ adamik 15
CDCl3
7.26
7.20
7.19
7.16
7.15
6.90
6.89
6.84
6.84
6.82
6.82
5.62
5.56
3.84
3.81
3.80
3.78
3.74
2.26
E (m)
6.86
D (td)
7.20
A (d)
5.59
B (d)
3.80
C (s)
2.26
5.05
3.21
1.00
5.39
2.95
f1 (ppm)

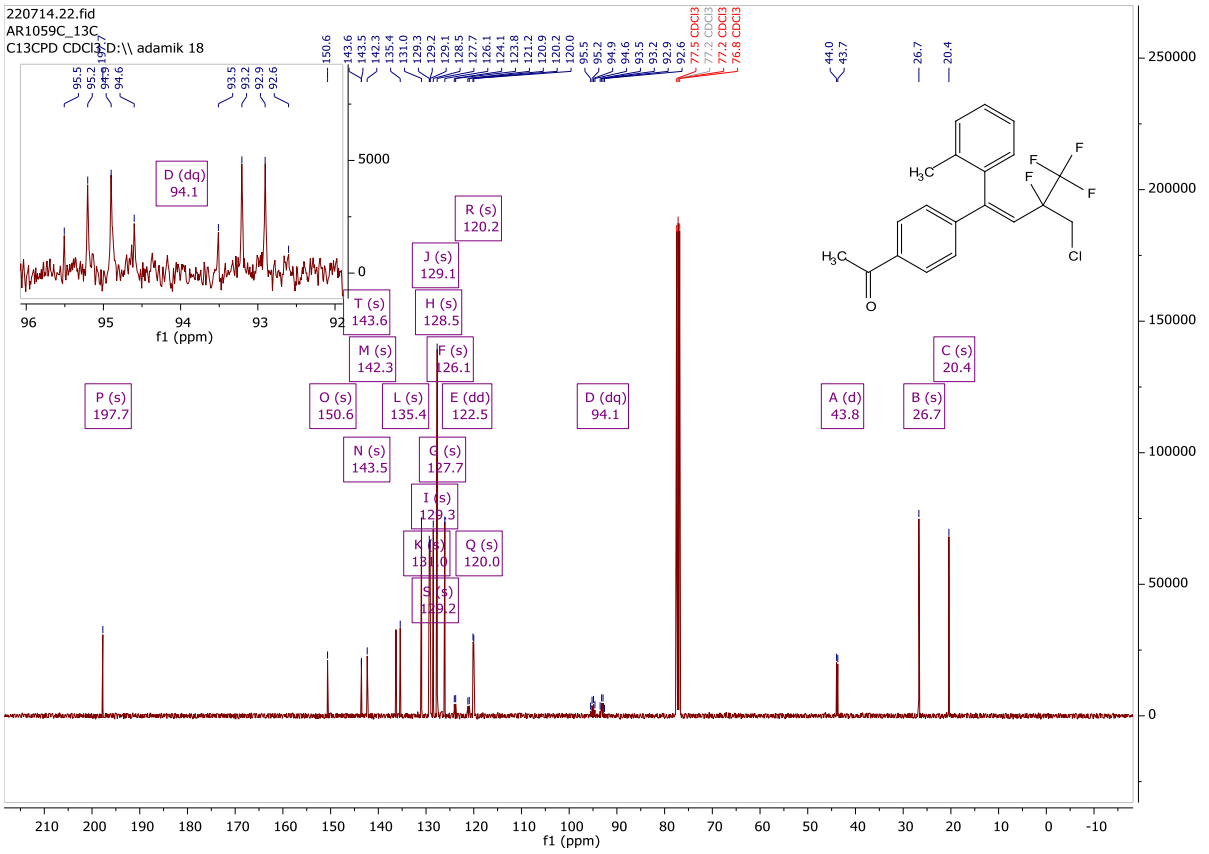

220713.21.fid
AR1059B_19F
F19CPD CDCl3 D:\\ adamik 15
-78.45
-78.47
-78.60
-78.62
-165.90
-165.92
-165.94
-165.97
-168.71
-168.73
-168.75
-168.77
B (d)
-78.61
A (q)
-165.93
3.69
1.00
f1 (ppm)


220713.22.fid
AR1059B_13C
C13CPD CDCl3 D:\\ adamik 15
D (m) 93.6
M (d) 124.2
P (s) 135.4
I (d) 121.5
T (s) 158.9
R (s) 143.0
K (s) 128.2
F (d) 114.9
S (s) 151.6
Q (s) 139.8
J (s) 125.9
E (s) 113.2
D (m) 93.6
C (s) 55.3
A (d) 43.3
B (s) 20.4
N (s) 129.3
G (d) 119.3
L (s) 128.7
O (s) 130.8
f1 (ppm)

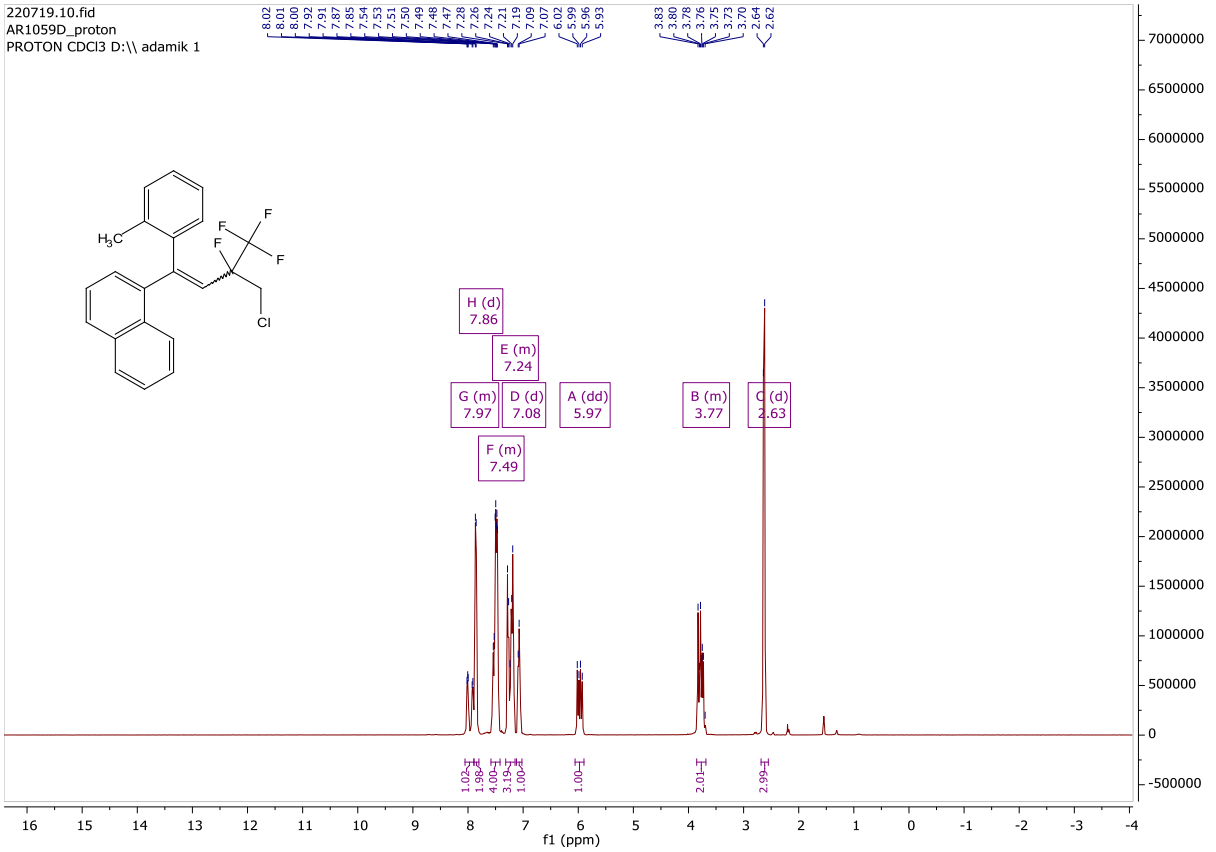
3r


220714.20.fid
AR1059C_proton
PROTON CDCl3 D:\\ adamik 18
F (m) 7.41
G (d) 7.89
E (m) 7.20
A (d) 5.63
B (m) 3.80
C (s) 2.59
D (s) 2.23
f1 (ppm)

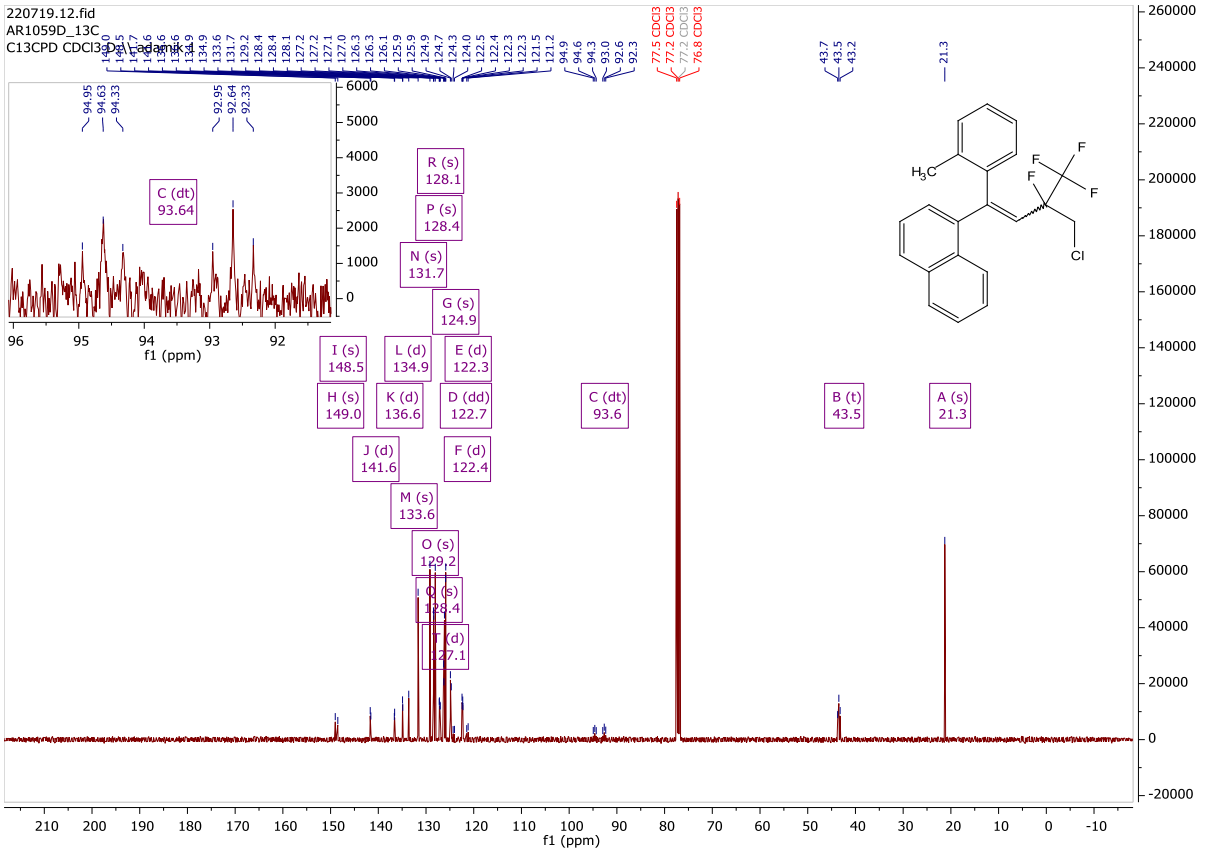

220714.21.fid
AR1059C_19F
F19CPD CDCl3 D:\\ adamik 18
-78.57
-78.59
-169.58
-169.60
-169.62
-169.64
B (d)
-78.58
A (q)
-169.61
3.76
1.00
f1 (ppm)


220714.22.fid
AR1059C_13C
C13CPD CDCl3 D:\\ adamik 18
D (dq)
94.1
R (s)
120.2
J (s)
129.1
T (s)
143.6
H (s)
128.5
M (s)
142.3
F (s)
126.1
P (s)
197.7
O (s)
150.6
L (s)
135.4
E (dd)
122.5
D (dq)
94.1
A (d)
43.8
B (s)
26.7
C (s)
20.4
N (s)
143.5
G (s)
127.7
I (s)
129.3
K (s)
131.0
Q (s)
120.0
S (s)
129.2
77.5 CDCl3
77.2 CDCl3
76.8 CDCl3
f1 (ppm)

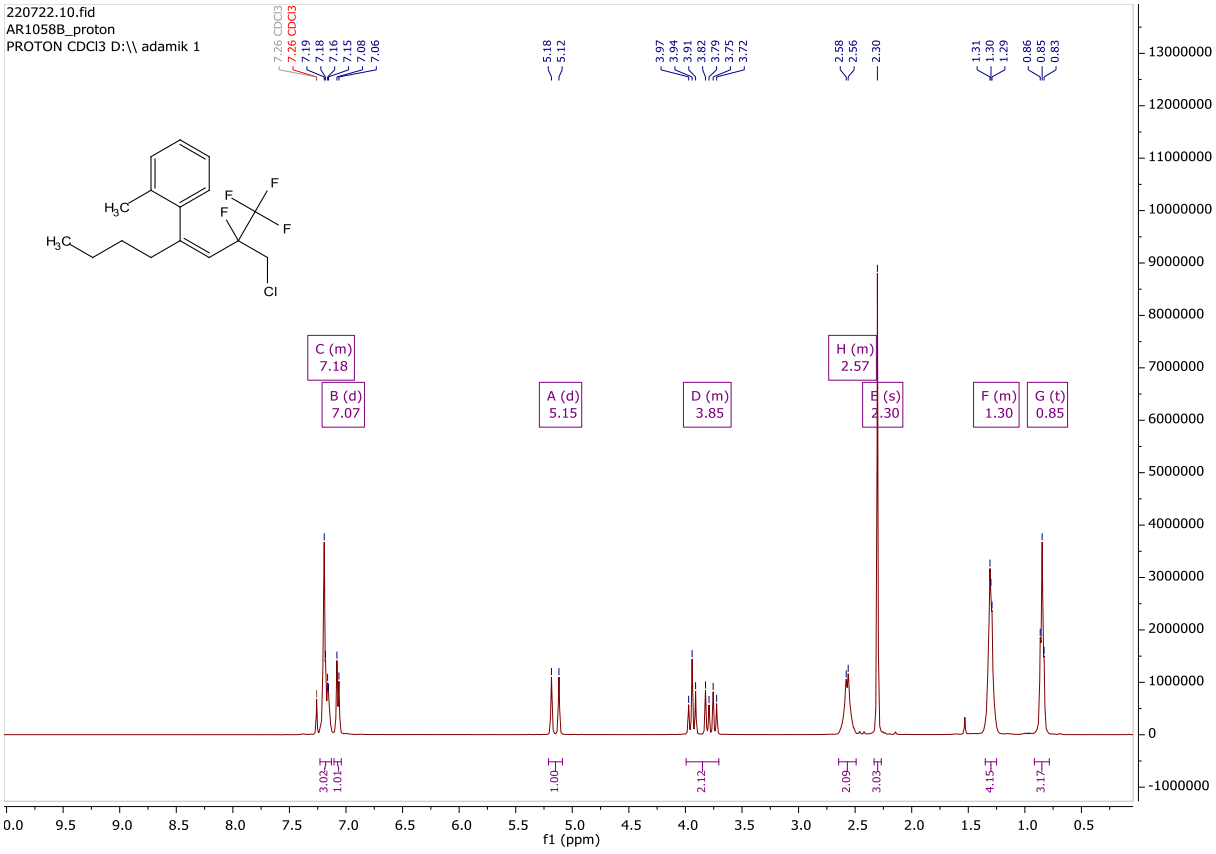
3s

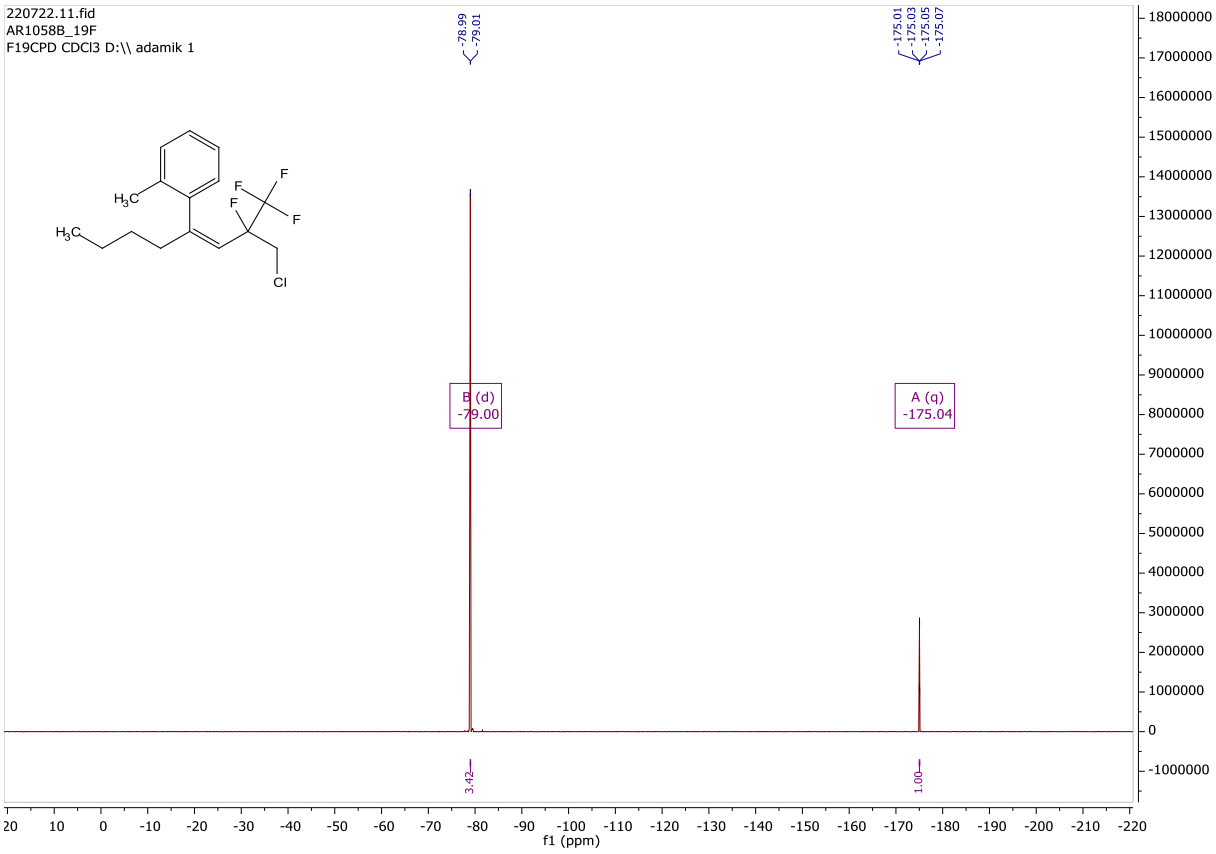

220719.10.fid
AR1059D_proton
PROTON CDCl3 D:\\ adamik 1
H (d) 7.86
E (m) 7.24
G (m) 7.97
D (d) 7.08
A (dd) 5.97
B (m) 3.77
C (d) 2.63
F (m) 7.49
f1 (ppm)

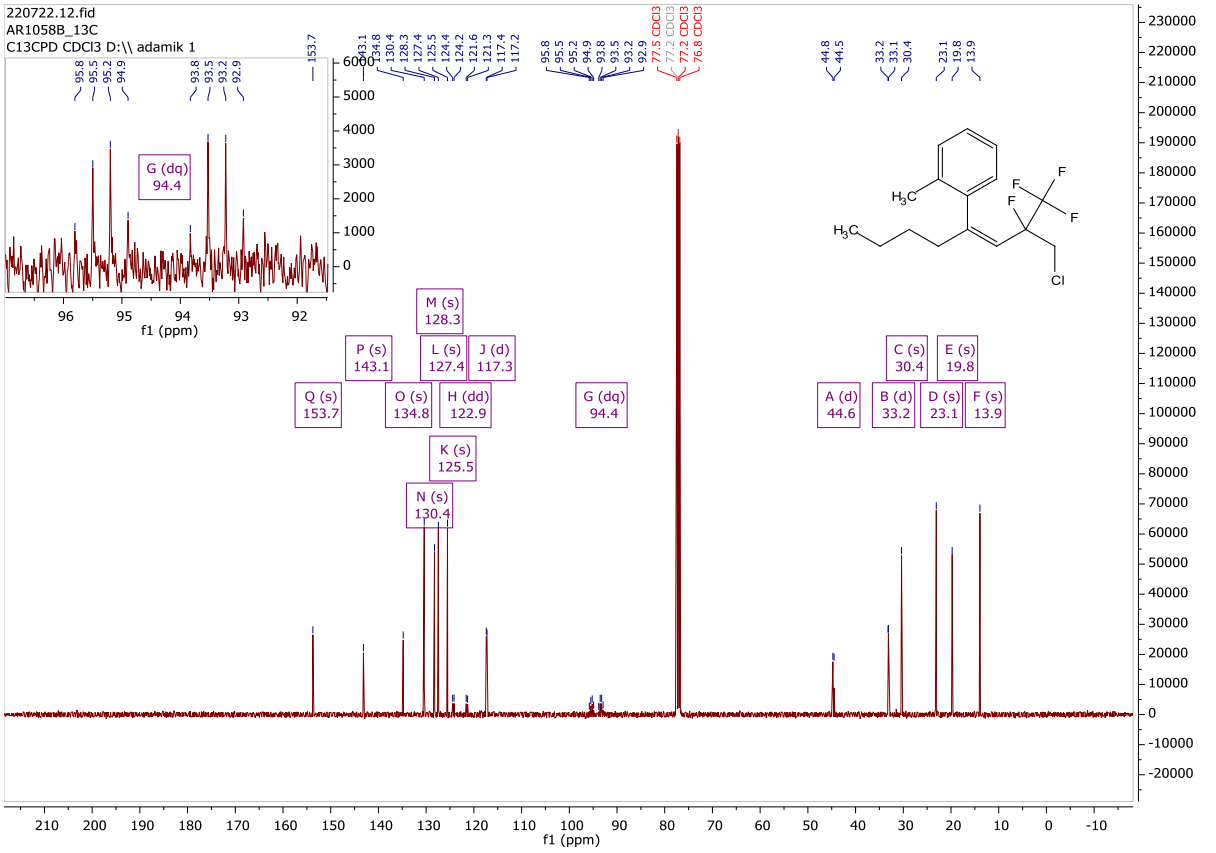

220719.11.fid
AR1059D_19F
F19CPD CDCl3 D:\\ adamik 1
C (dd) -78.29
B (q) -170.26
A (q) -168.10
f1 (ppm)


220719.12.fid
AR1059D_13C
C13CPD CDCl3 D:\\ adamik 1
C (dt) 93.64
R (s) 128.1
P (s) 128.4
N (s) 131.7
G (s) 124.9
I (s) 148.5
L (d) 134.9
E (d) 122.3
H (s) 149.0
K (d) 136.6
D (dd) 122.7
C (dt) 93.6
B (t) 43.5
A (s) 21.3
J (d) 141.6
F (d) 122.4
M (s) 133.6
O (s) 129,2
Q (s) 128.4
T (d) 127.1
f1 (ppm)

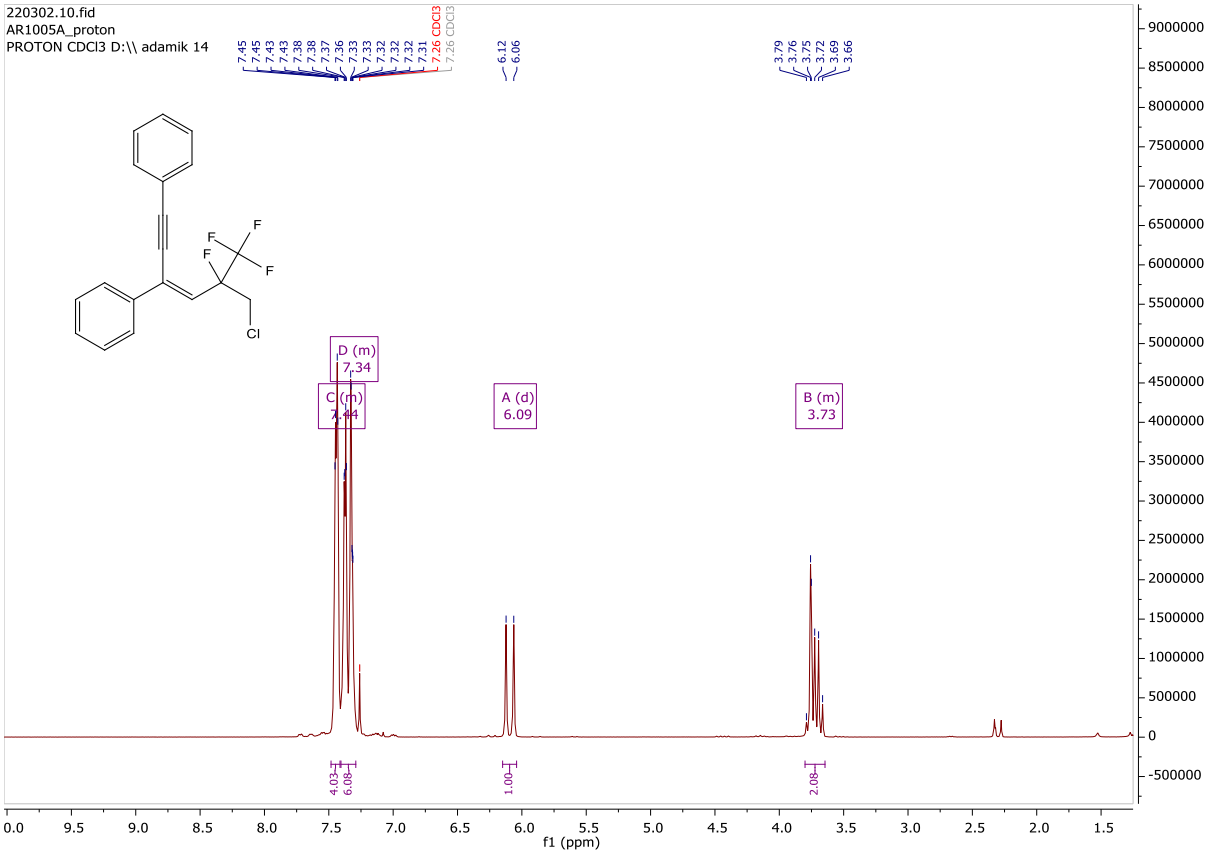
3t

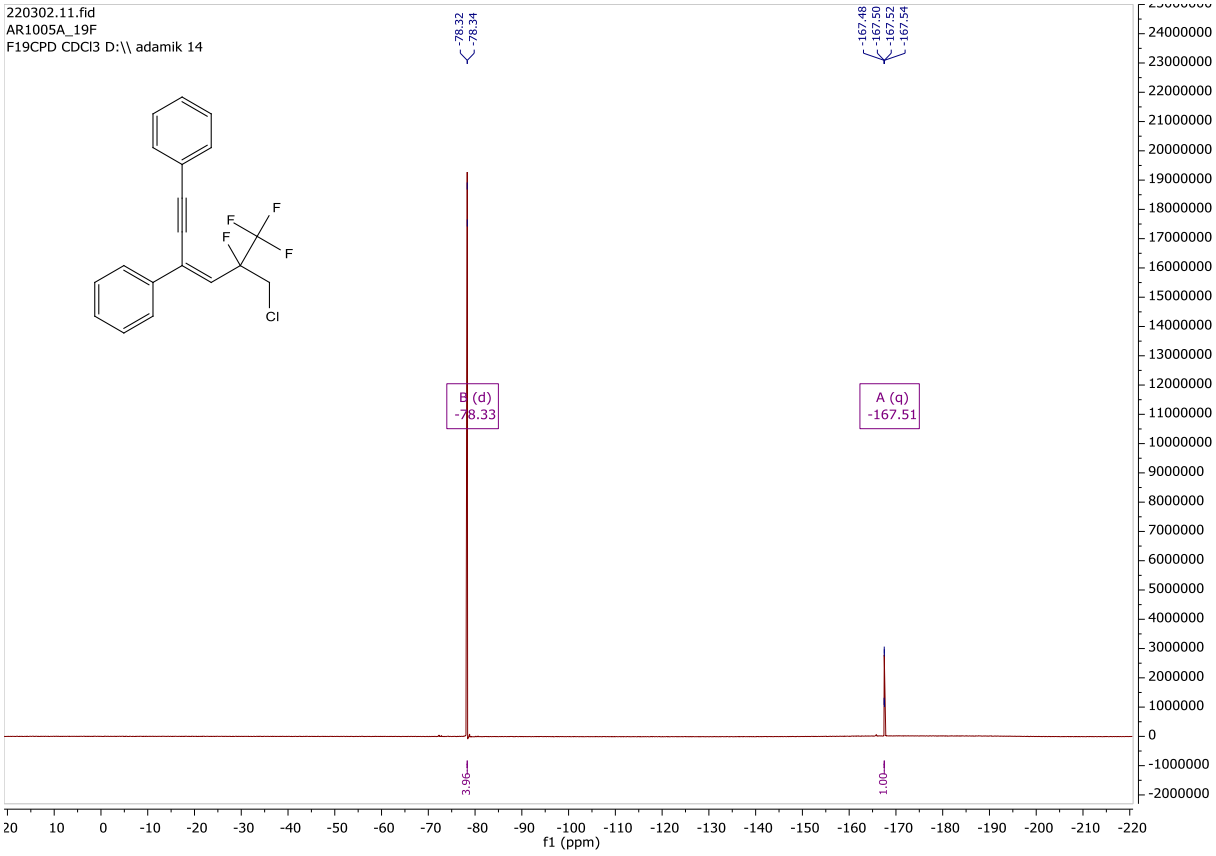

220722.10.fid
AR1058B_proton
PROTON CDCl3 D:\\ adamik 1
C (m) 7.18
B (d) 7.07
A (d) 5.15
D (m) 3.85
H (m) 2.57
E (s) 2.30
F (m) 1.30
G (t) 0.85
f1 (ppm)

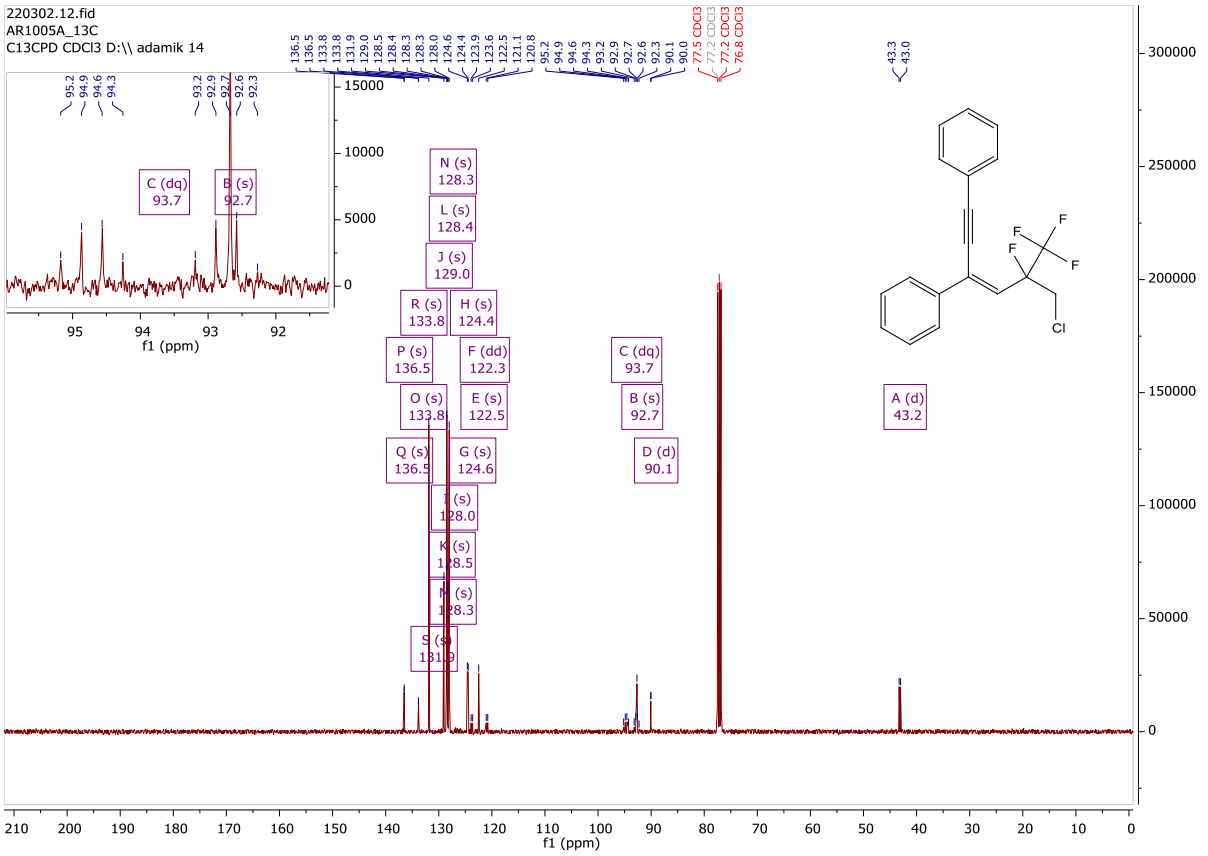

220722.11.fid
AR1058B_19F
F19CPD CDCl3 D:\\ adamik 1
-78.99
-79.01
-175.01
-175.03
-175.05
-175.07
B (d)
-79.00
A (q)
-175.04
3.42
1.00
f1 (ppm)


220722.12.fid
AR1058B_13C
C13CPD CDCl3 D:\\ adamik 1
G (dq)
94.4
M (s)
128.3
P (s)
143.1
L (s)
127.4
J (d)
117.3
Q (s)
153.7
O (s)
134.8
H (dd)
122.9
G (dq)
94.4
K (s)
125.5
N (s)
130.4
A (d)
44.6
B (d)
33.2
C (s)
30.4
D (s)
23.1
E (s)
19.8
F (s)
13.9
f1 (ppm)

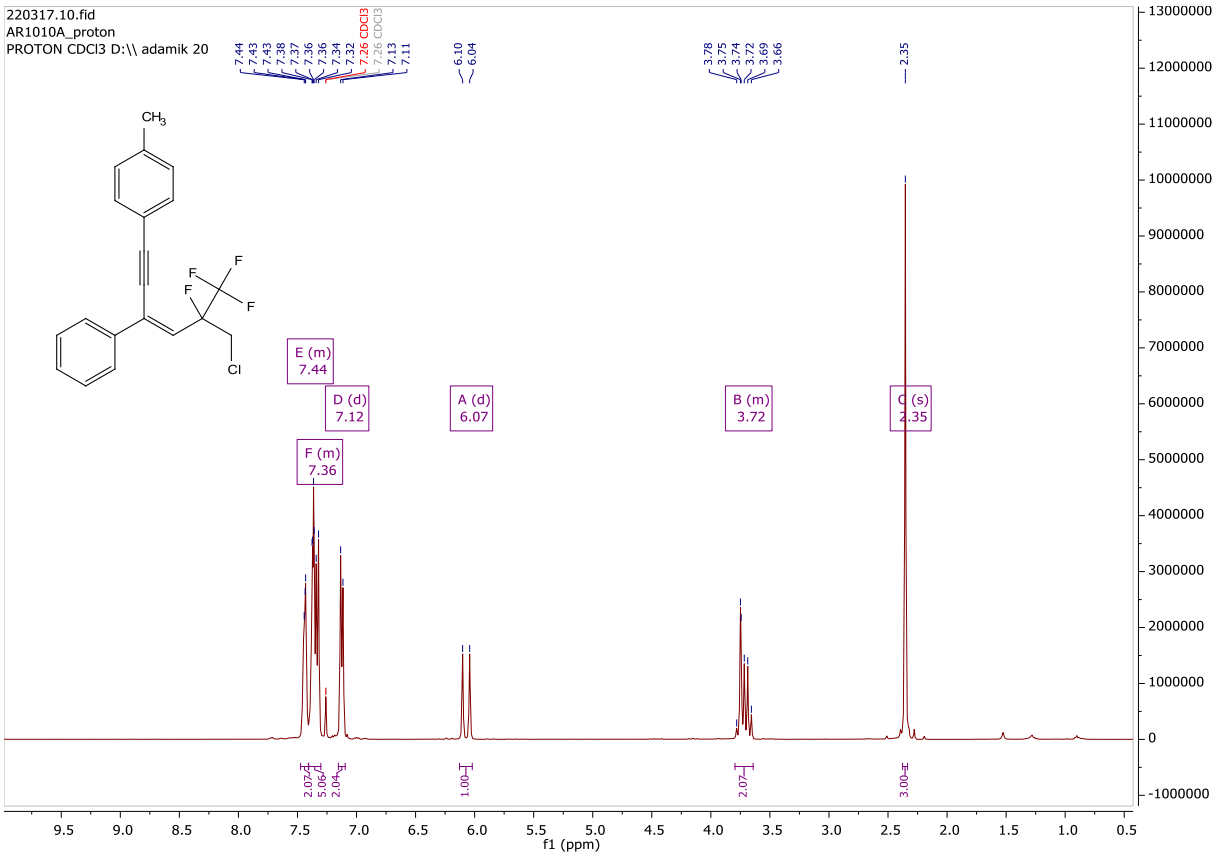
5a

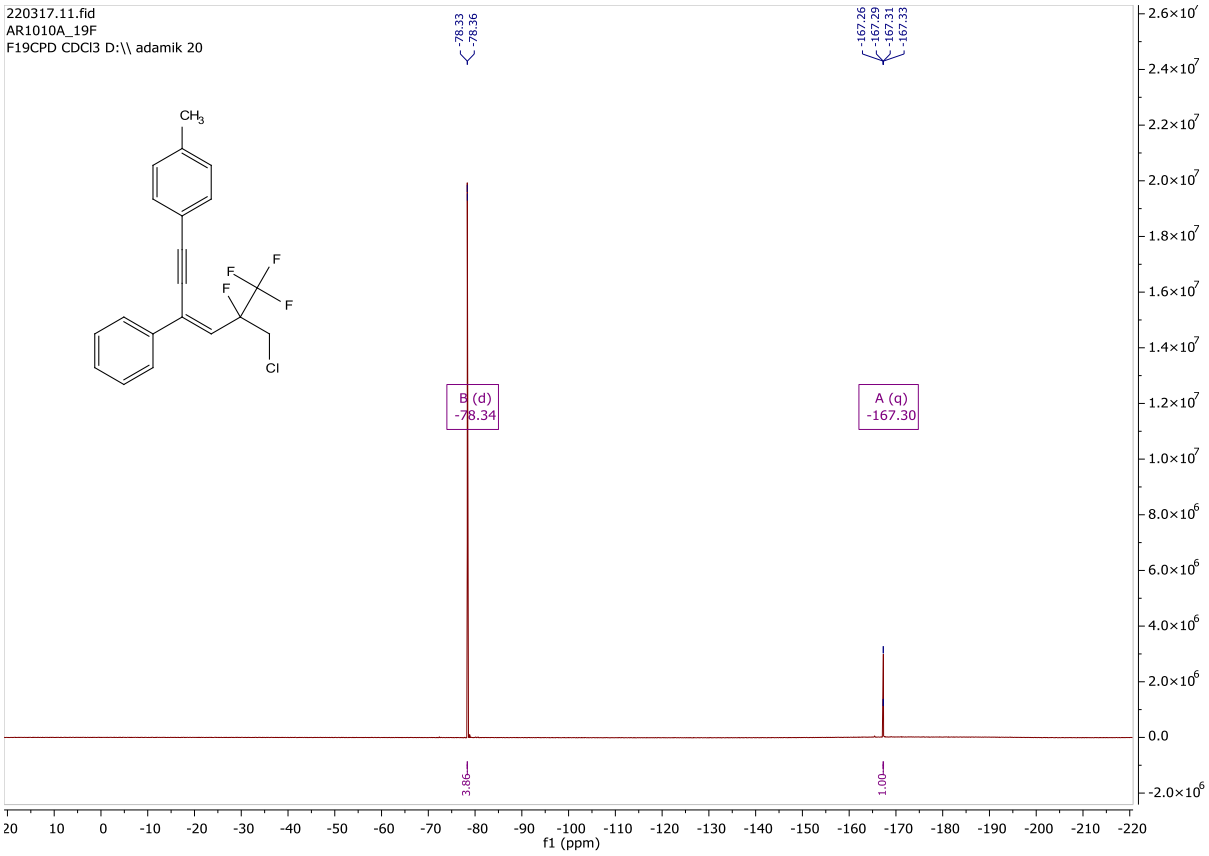

220302.10.fid
AR1005A_proton
PROTON CDCl3 D:\\ adamik 14
7.45
7.45
7.43
7.43
7.38
7.38
7.37
7.36
7.33
7.33
7.32
7.32
7.32
7.31
7.26 CDCl3
7.26 CDCl3
6.12
6.06
3.79
3.76
3.75
3.72
3.69
3.66
F
F
F
F
Cl
D (m)
7.34
C (m)
7.44
A (d)
6.09
B (m)
3.73
4.03
6.08
1.00
2.08
f1 (ppm)

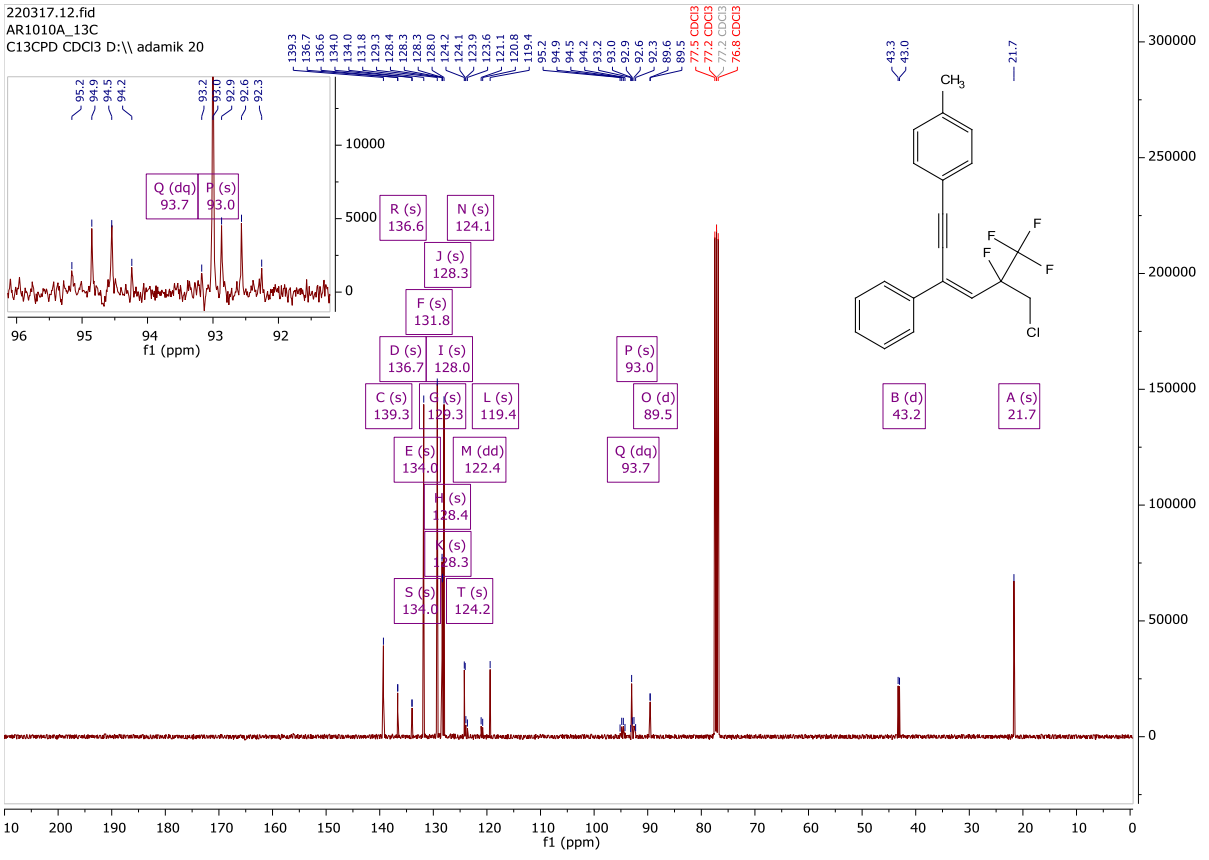

220302.11.fid
AR1005A_19F
F19CPD CDCl3 D:\\ adamik 14
-78.32
-78.34
-167.48
-167.50
-167.52
-167.54
F
F
F
F
Cl
B (d)
-78.33
A (q)
-167.51
3.96
1.00
f1 (ppm)


220302.12.fid
AR1005A_13C
C13CPD CDCl3 D:\\ adamik 14
C (dq) 93.7
B (s) 92.7
N (s) 128.3
L (s) 128.4
J (s) 129.0
R (s) 133.8
H (s) 124.4
P (s) 136.5
F (dd) 122.3
O (s) 133.8
E (s) 122.5
Q (s) 136.5
G (s) 124.6
I (s) 128.0
K (s) 128.5
M (s) 128.3
S (s) 131.9
C (dq) 93.7
B (s) 92.7
D (d) 90.1
A (d) 43.2
f1 (ppm)

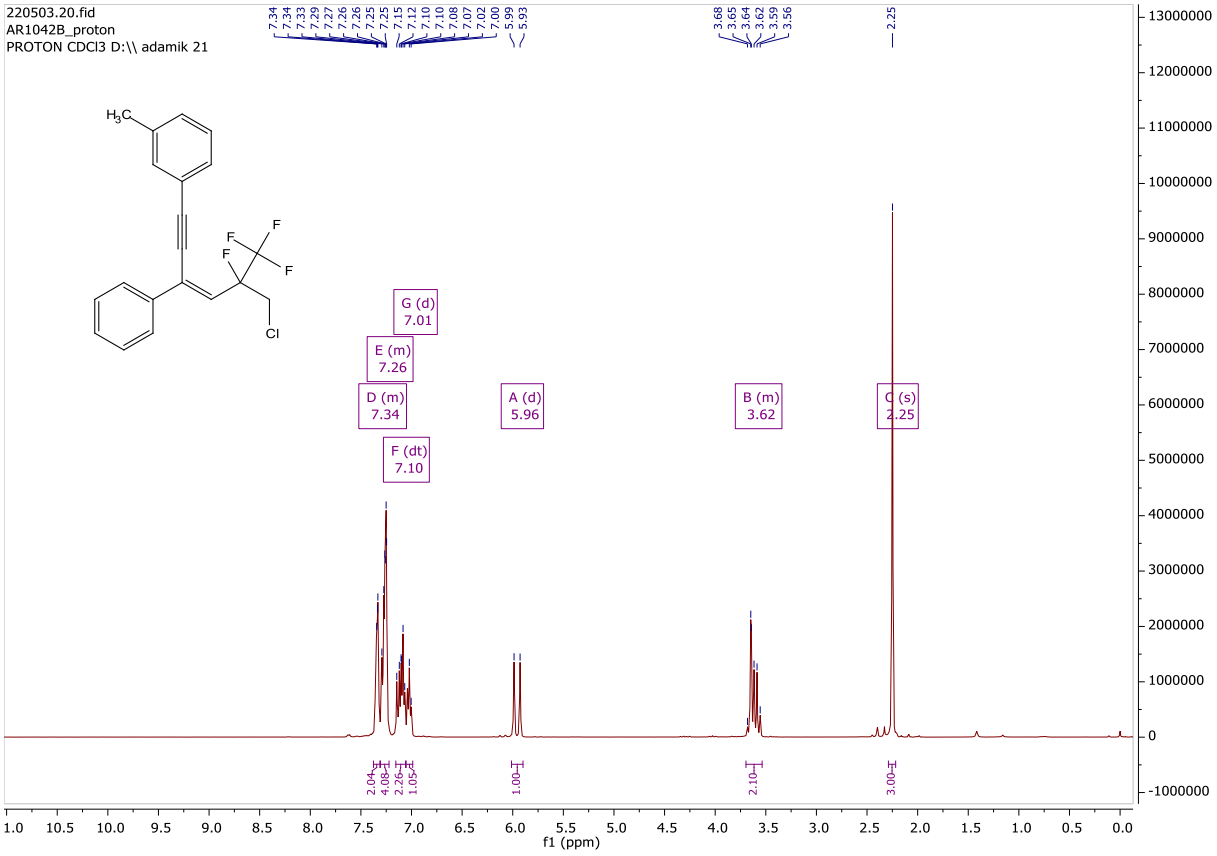
5b

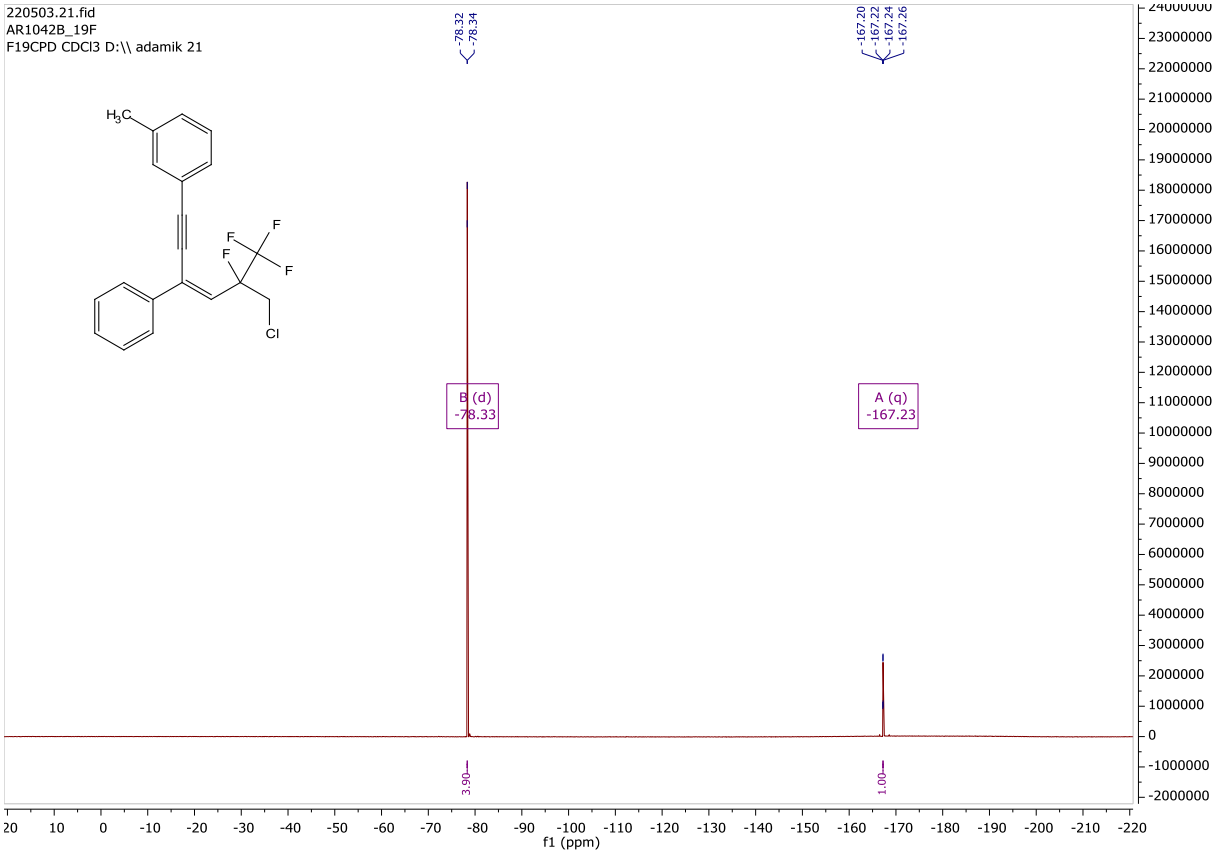

220317.10.fid
AR1010A_proton
PROTON CDCl3 D:\\ adamik 20
E (m) 7.44
D (d) 7.12
F (m) 7.36
A (d) 6.07
B (m) 3.72
C (s) 2.35
f1 (ppm)

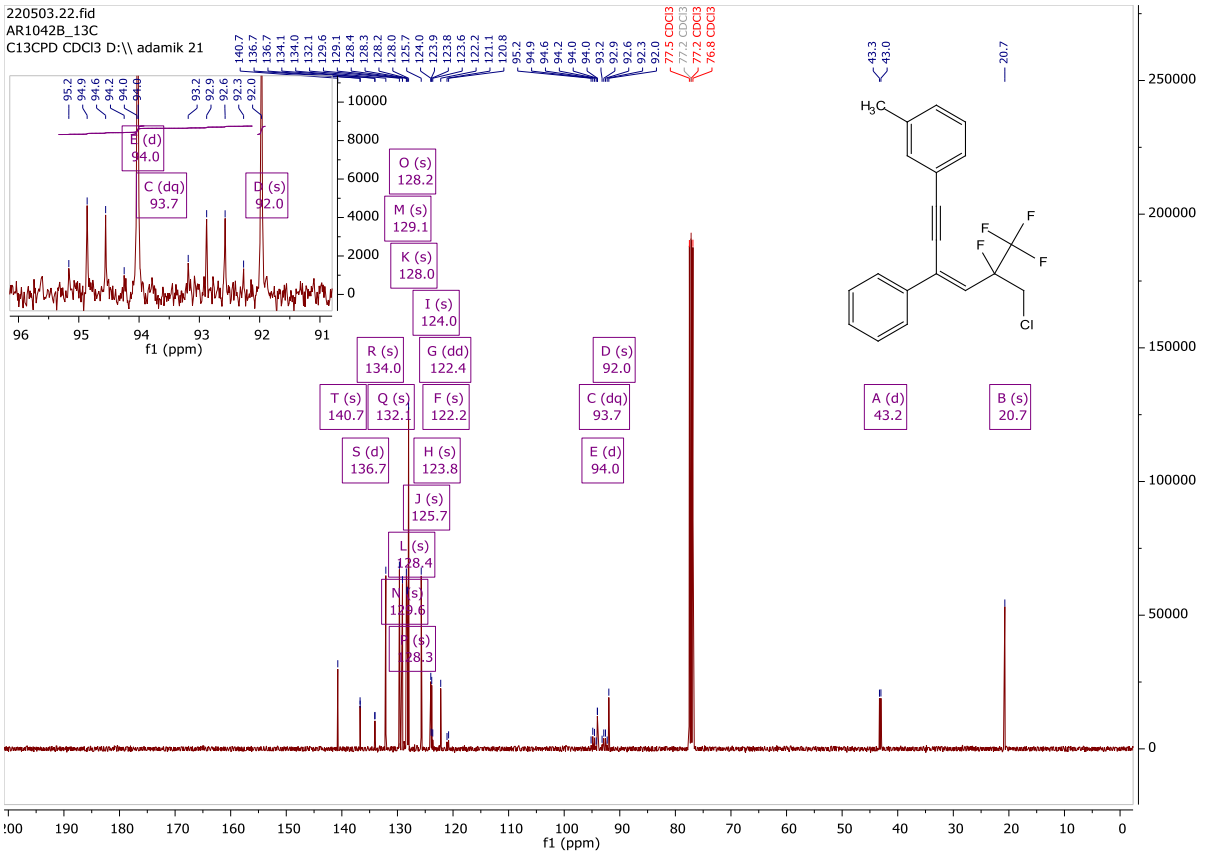

220317.11.fid
AR1010A_19F
F19CPD CDCl3 D:\\ adamik 20
-78.33
-78.36
-167.26
-167.29
-167.31
-167.33
B (d)
-78.34
A (q)
-167.30
3.86
1.00
f1 (ppm)


220317.12.fid
AR1010A_13C
C13CPD CDCl3 D:\\ adamik 20
Q (dq)
93.7
P (s)
93.0
R (s)
136.6
N (s)
124.1
J (s)
128.3
F (s)
131.8
D (s)
136.7
I (s)
128.0
C (s)
139.3
G (s)
129.3
L (s)
119.4
E (s)
134.0
M (dd)
122.4
H (s)
128.4
K (s)
128.3
S (s)
134.0
T (s)
124.2
P (s)
93.0
O (d)
89.5
Q (dq)
93.7
B (d)
43.2
A (s)
21.7
f1 (ppm)

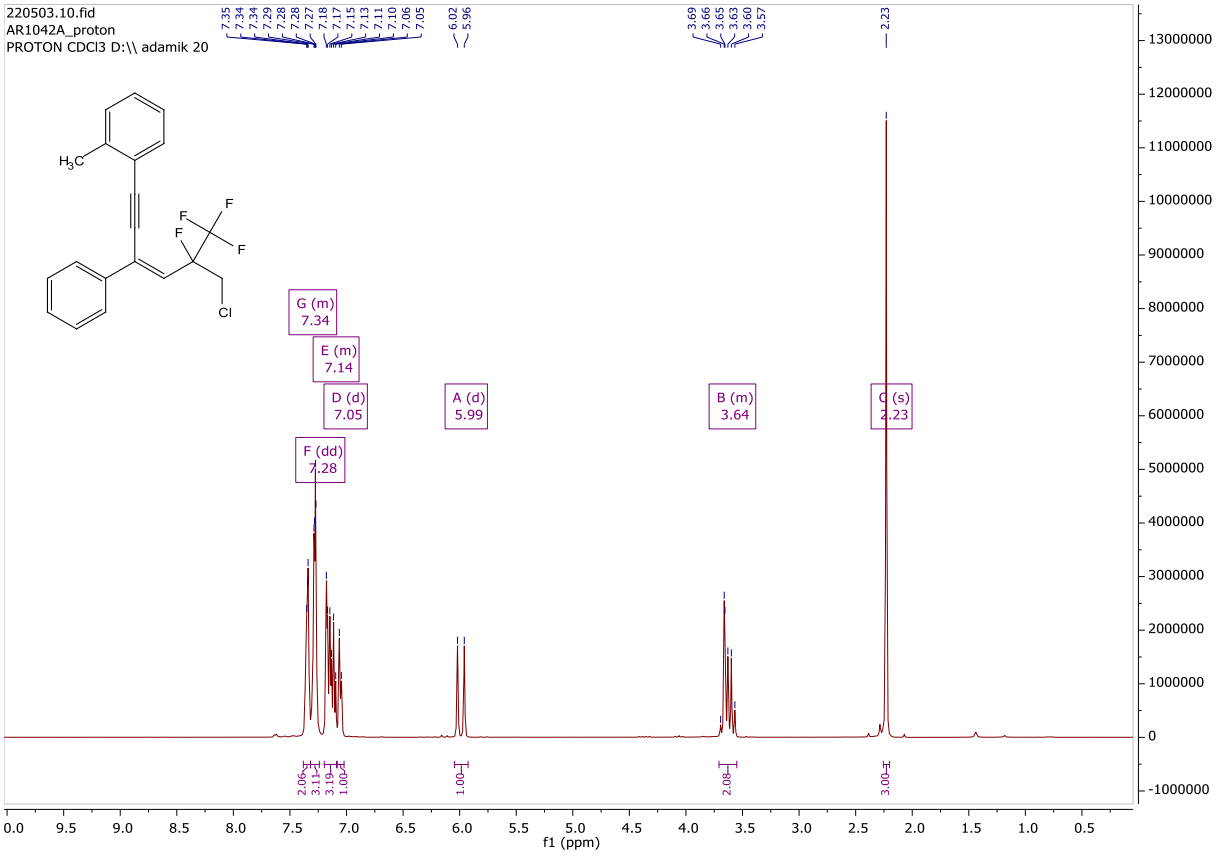
5c


220503.20.fid
AR1042B_proton
PROTON CDCl3 D:\\ adamik 21
G (d) 7.01
E (m) 7.26
D (m) 7.34
A (d) 5.96
F (dt) 7.10
B (m) 3.62
C (s) 2.25
f1 (ppm)

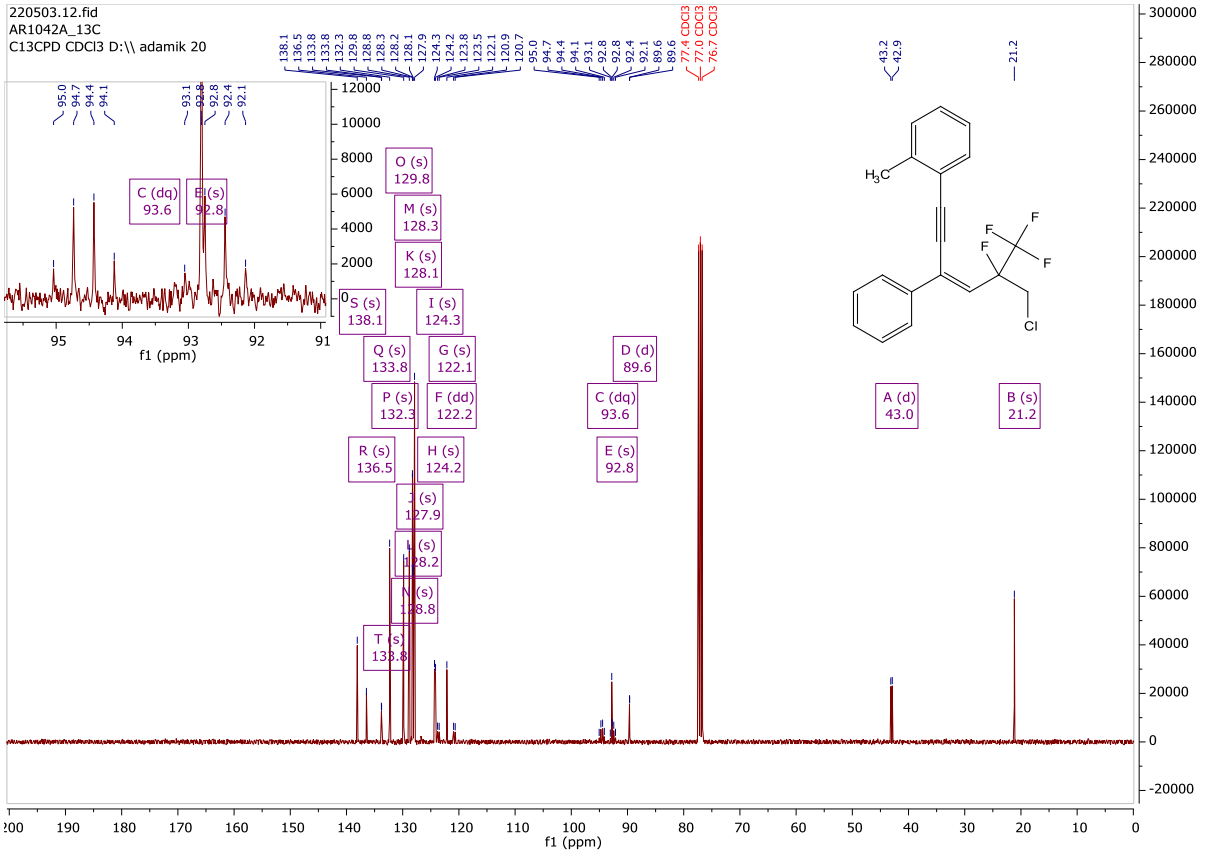

220503.21.fid
AR1042B_19F
F19CPD CDCl3 D:\\ adamik 21
B (d) -78.33
A (q) -167.23
f1 (ppm)


220503.22.fid
AR1042B_13C
C13CPD CDCl3 D:\\ adamik 21
f1 (ppm)

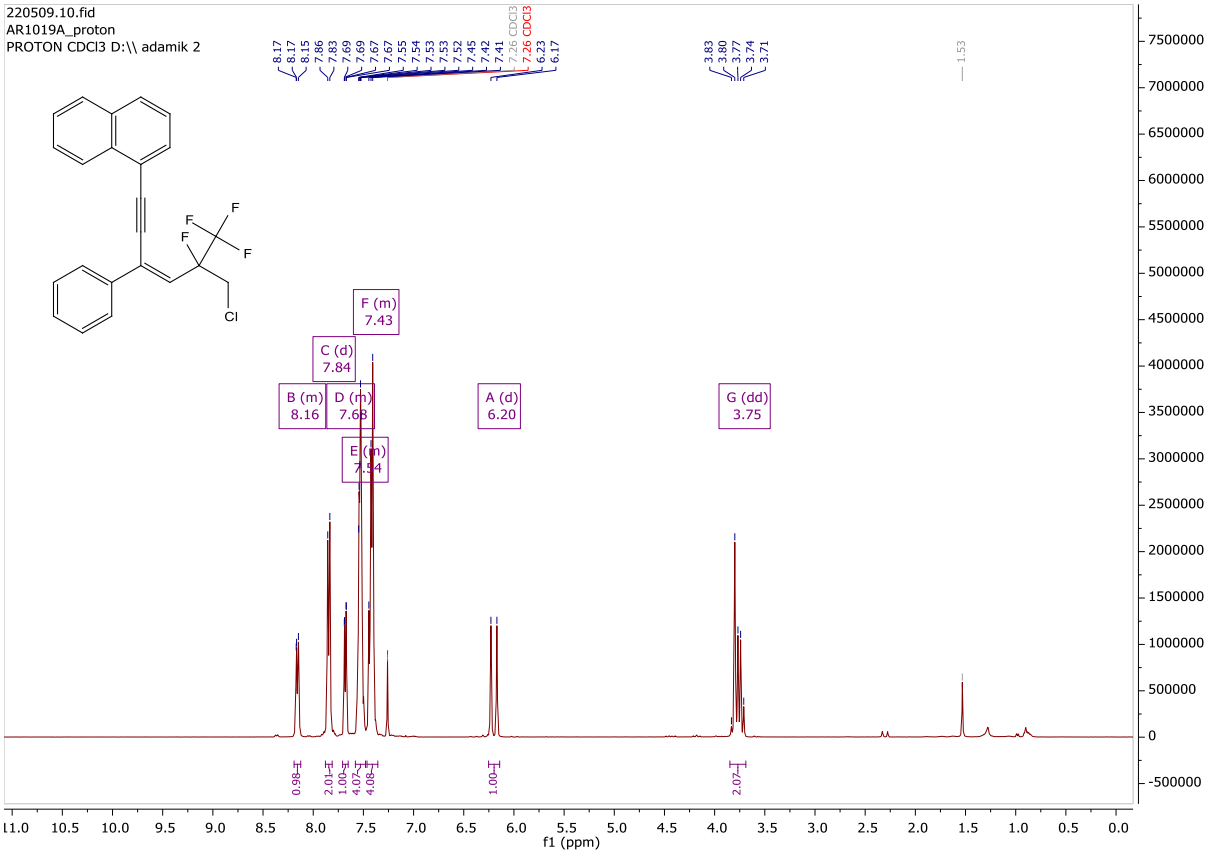
5d

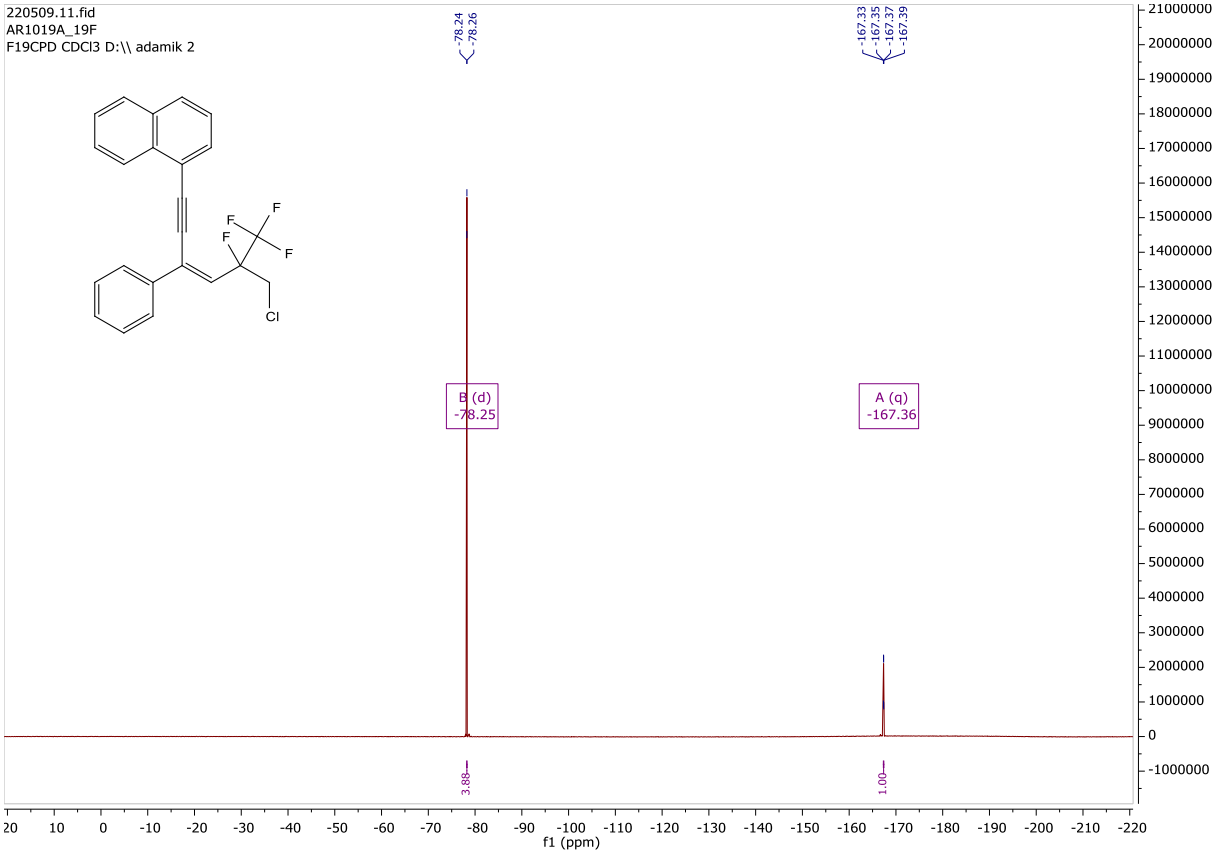

220503.10.fid
AR1042A_proton
PROTON CDCl3 D:\\ adamik 20
f1 (ppm)

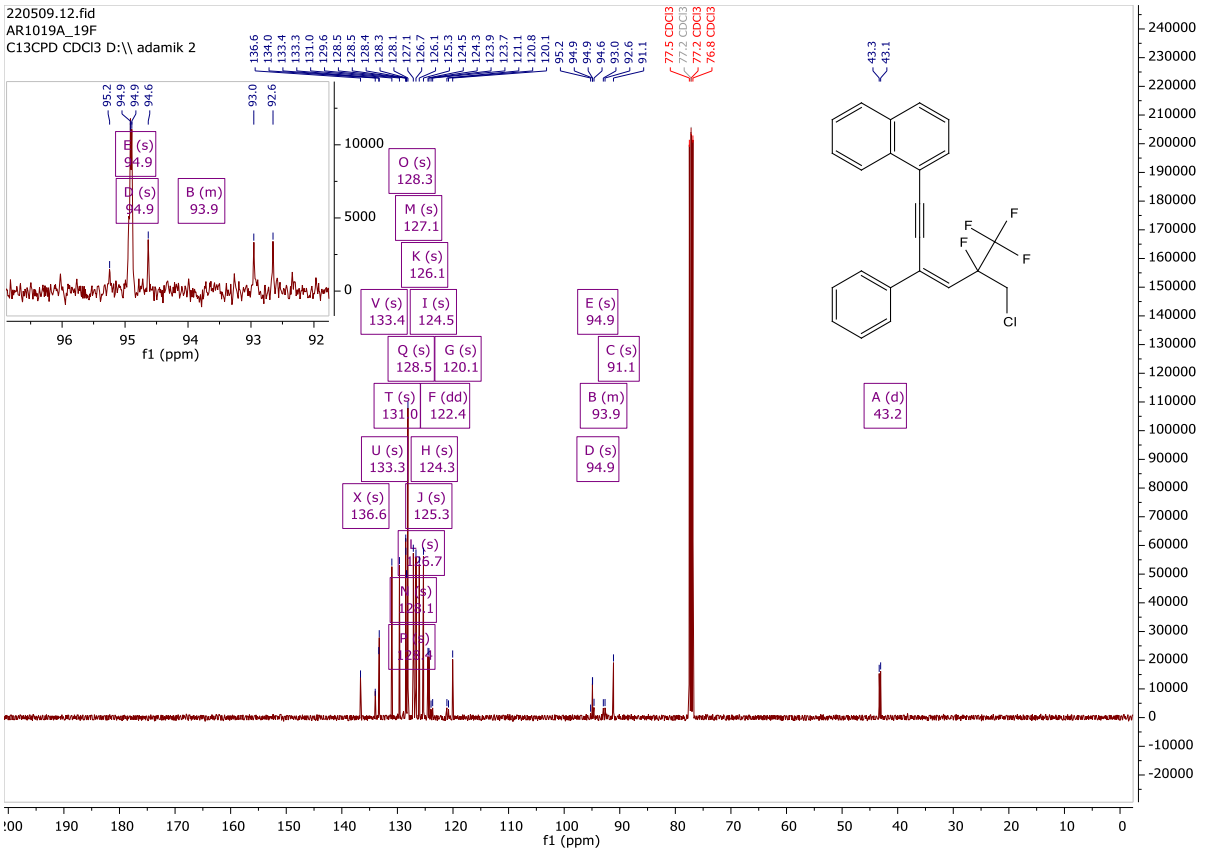

220503.11.fid
AR1042A_19F
F19CPD CDCl3 D:\\ adamik 20
-78.33
-78.35
-167.44
-167.46
-167.48
-167.51
B (d)
-78.34
A (q)
-167.47
4.01
1.00
f1 (ppm)


220503.12.fid
AR1042A_13C
C13CPD CDCl3 D:\\ adamik 20
C (dq)
93.6
E (s)
92.8
O (s)
129.8
M (s)
128.3
K (s)
128.1
S (s)
138.1
I (s)
124.3
Q (s)
133.8
G (s)
122.1
P (s)
132.3
F (dd)
122.2
R (s)
136.5
H (s)
124.2
D (d)
89.6
C (dq)
93.6
E (s)
92.8
A (d)
43.0
B (s)
21.2
f1 (ppm)

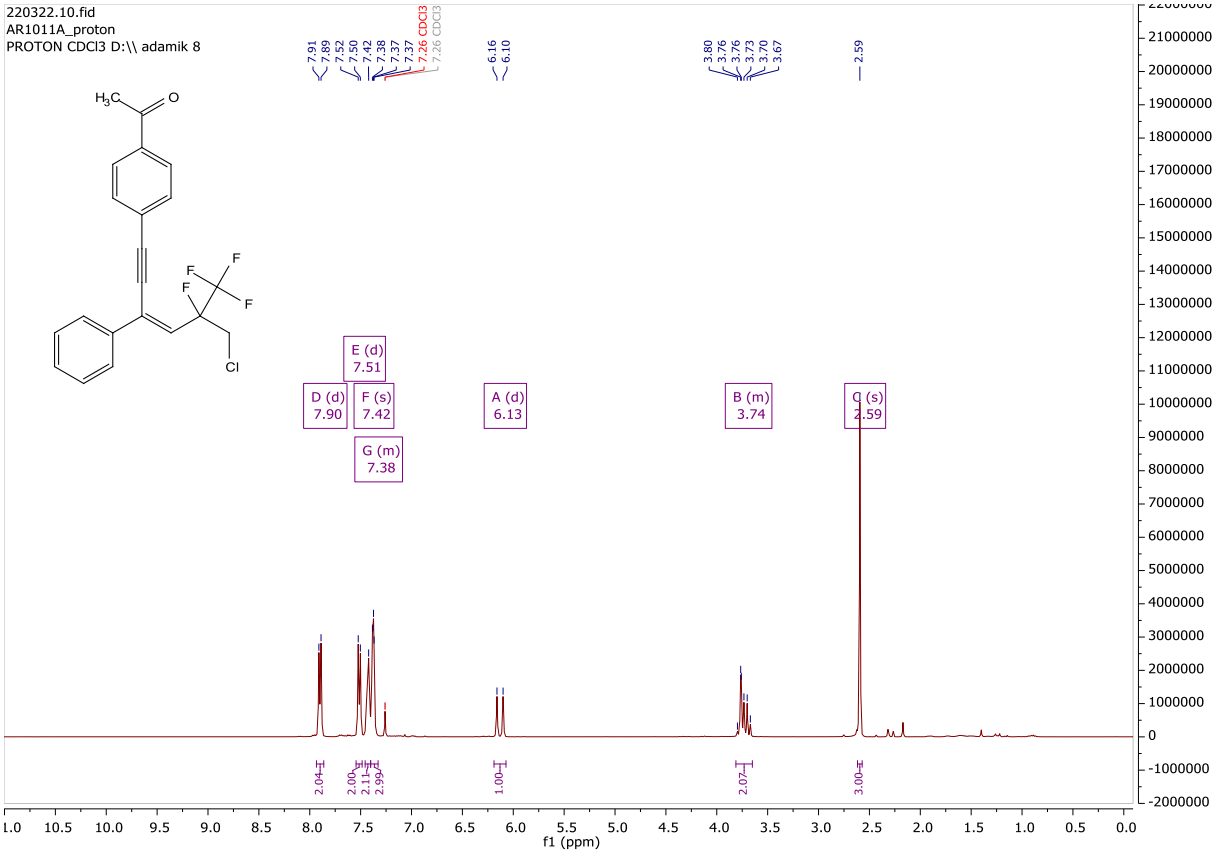
5e


220509.10.fid
AR1019A_proton
PROTON CDCl3 D:\\ adamik 2
F (m)
7.43
C (d)
7.84
B (m)
8.16
D (m)
7.68
E (m)
7.54
A (d)
6.20
G (dd)
3.75
f1 (ppm)

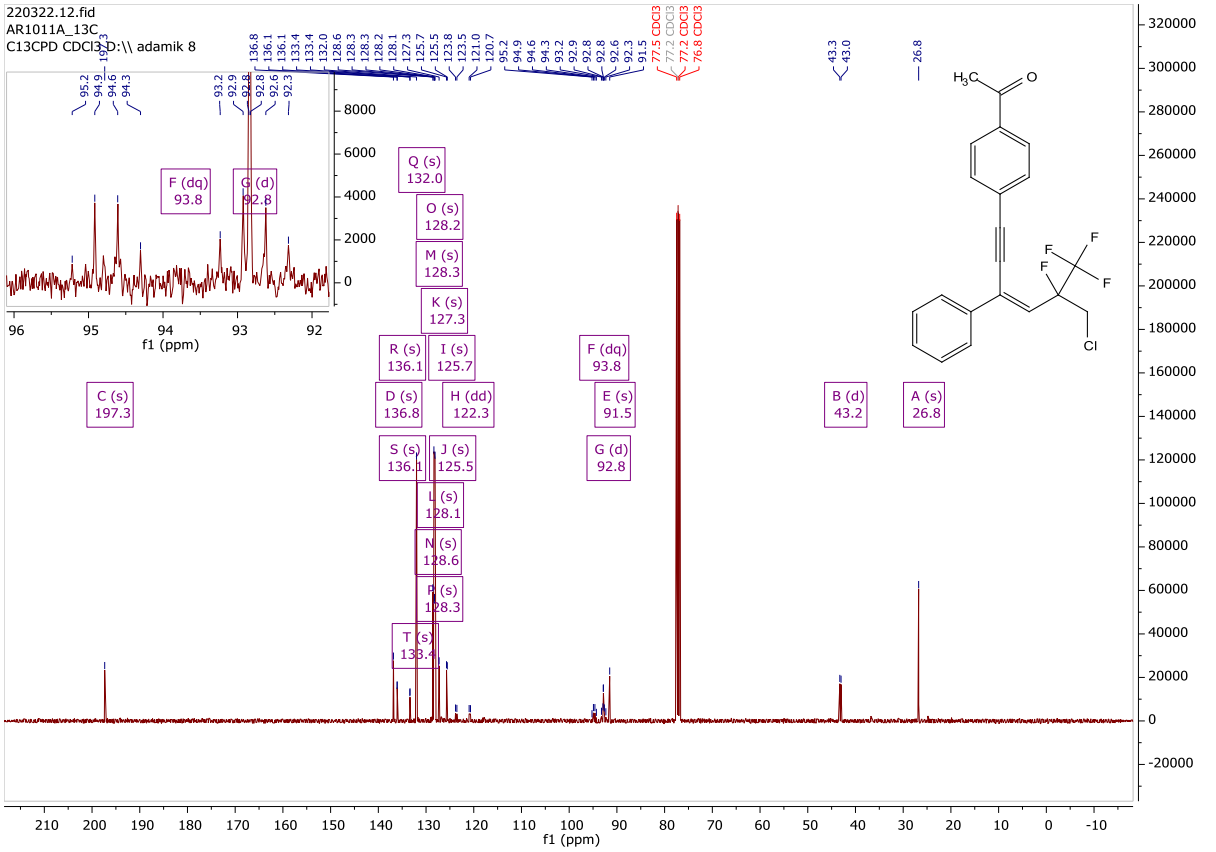

220509.11.fid
AR1019A_19F
F19CPD CDCl3 D:\\ adamik 2
B (d)
-78.25
A (q)
-167.36
f1 (ppm)


220509.12.fid
AR1019A_19F
C13CPD CDCl3 D:\\ adamik 2
f1 (ppm)

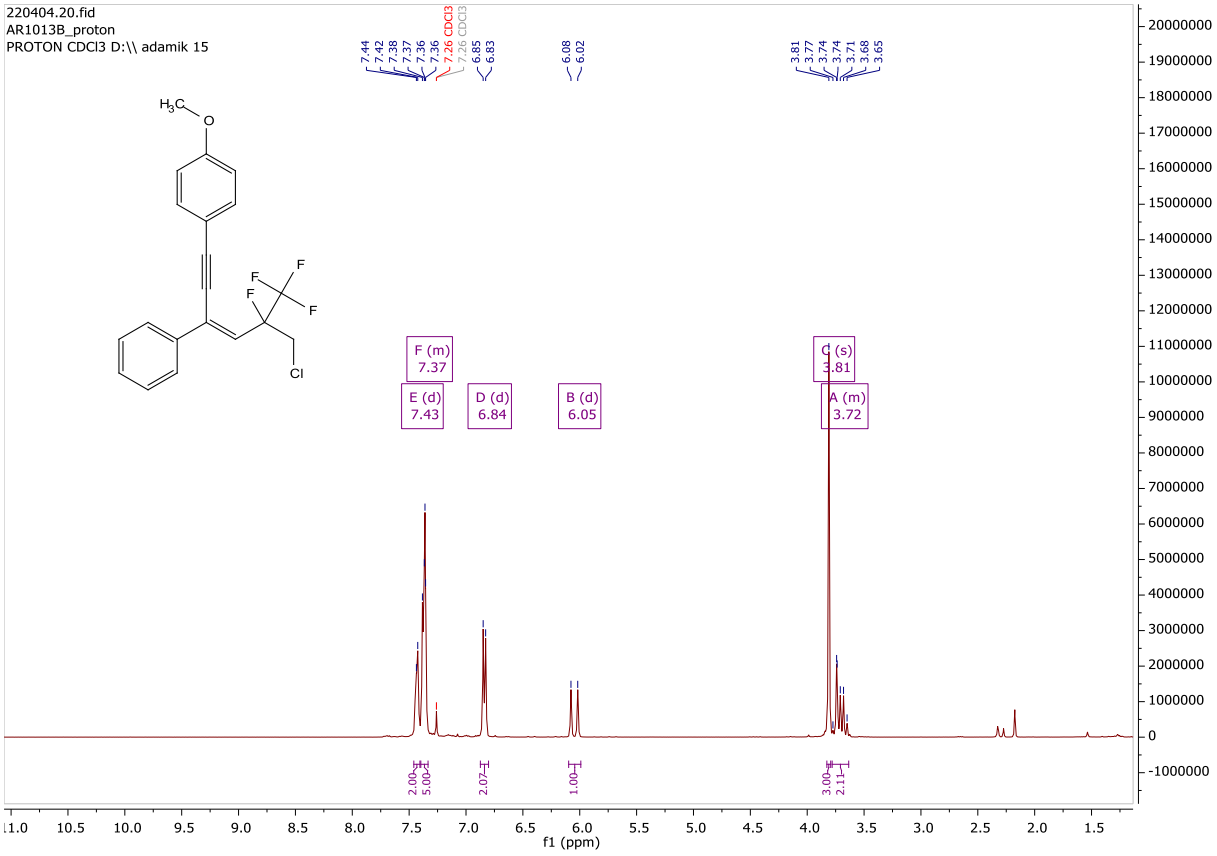
5f

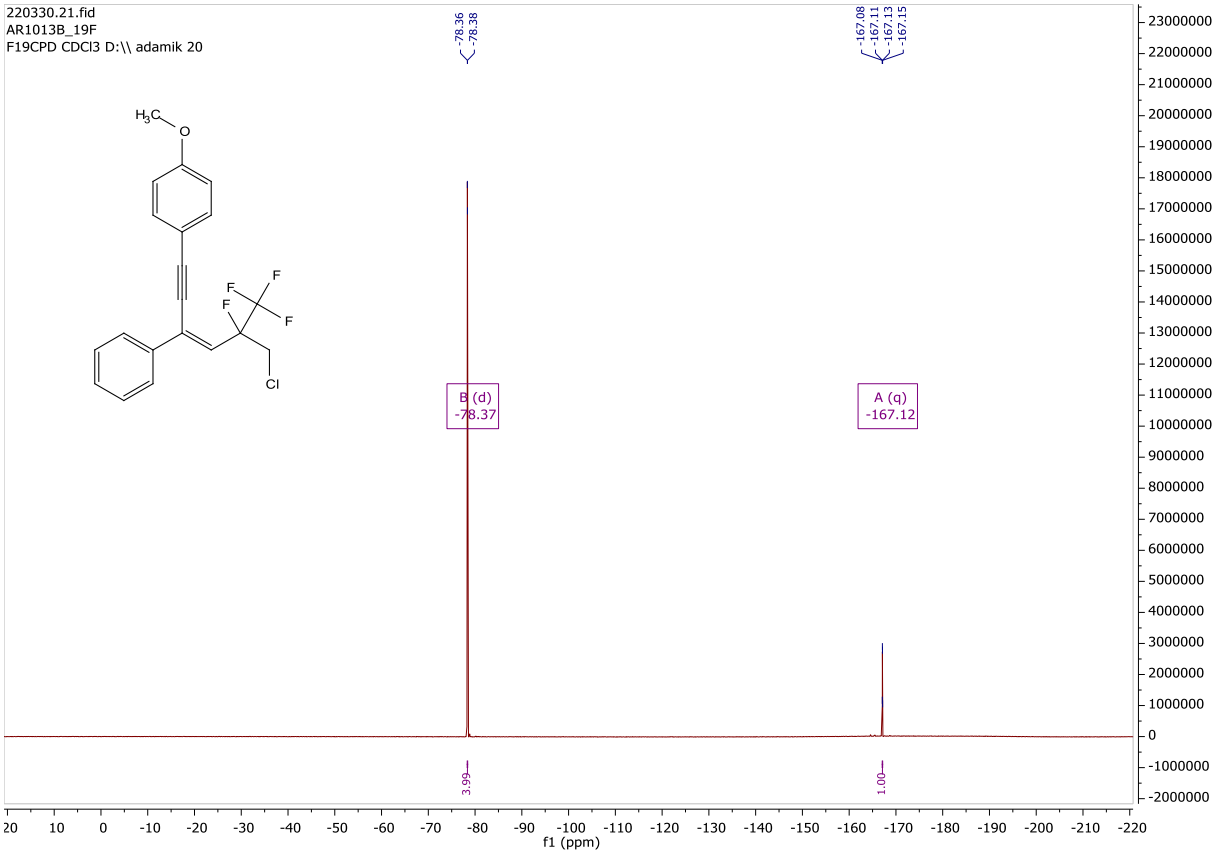

220322.10.fid
AR1011A_proton
PROTON CDCl3 D:\\ adamik 8
f1 (ppm)

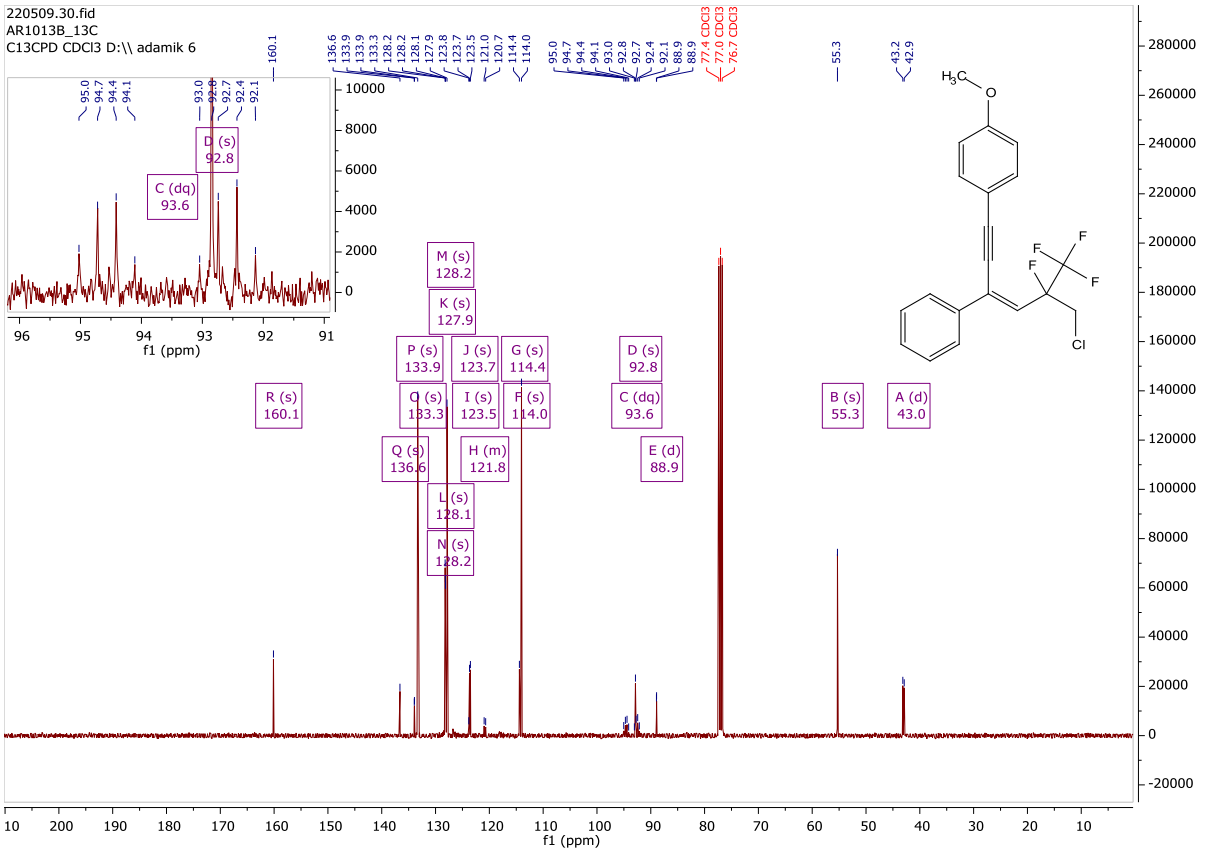

220322.11.fid
AR1011A_19F
F19CPD CDCl3 D:\\ adamik 8
B (d)
-78.29
A (q)
-168.06
f1 (ppm)


220322.12.fid
AR1011A_13C
C13CPD CDCl3 D:\\ adamik 8
F (dq)
93.8
G (d)
92.8
Q (s)
132.0
O (s)
128.2
M (s)
128.3
K (s)
127.3
R (s)
136.1
I (s)
125.7
D (s)
136.8
H (dd)
122.3
S (s)
136.1
J (s)
125.5
L (s)
128.1
N (s)
128.6
P (s)
128.3
T (s)
133.4
C (s)
197.3
F (dq)
93.8
E (s)
91.5
G (d)
92.8
B (d)
43.2
A (s)
26.8
f1 (ppm)

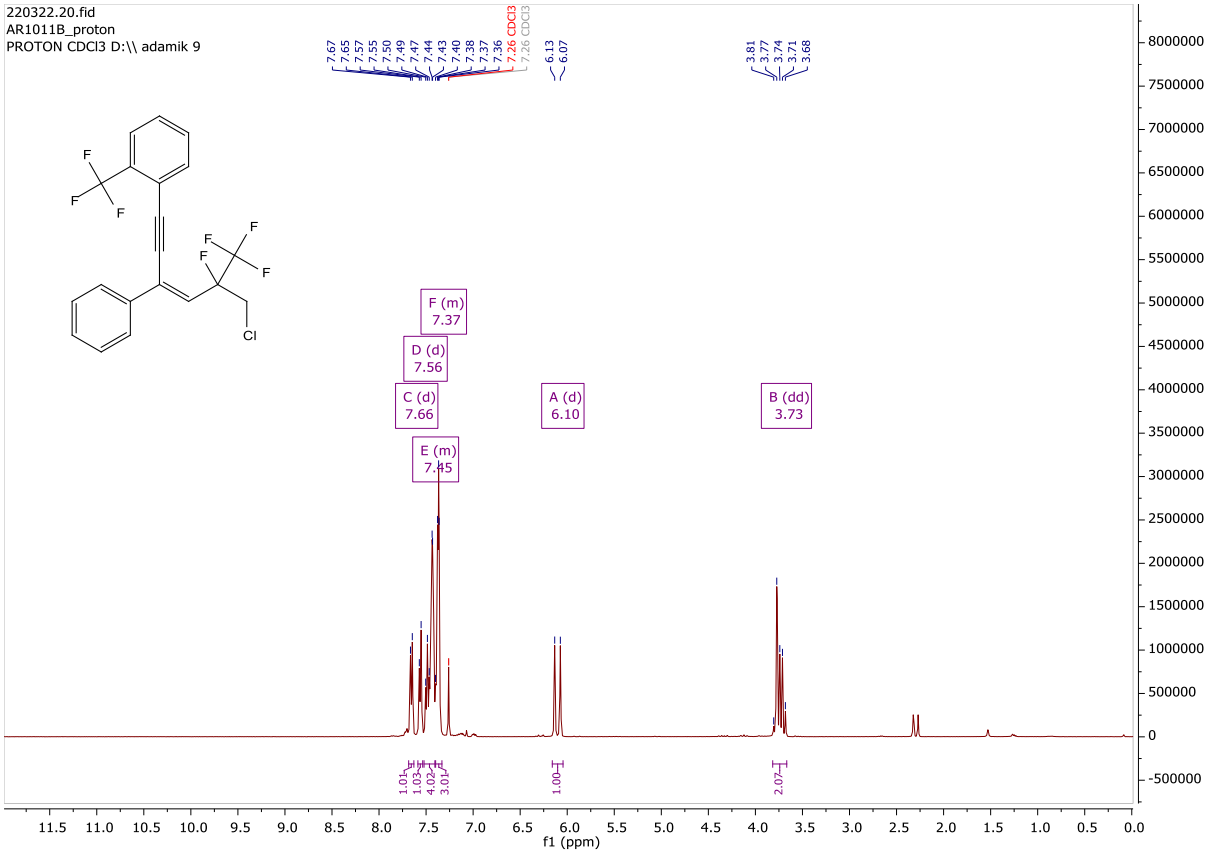
5g


220404.20.fid
AR1013B_proton
PROTON CDCl3 D:\\ adamik 15
F (m)
7.37
E (d)
7.43
D (d)
6.84
B (d)
6.05
C (s)
3.81
A (m)
3.72
f1 (ppm)

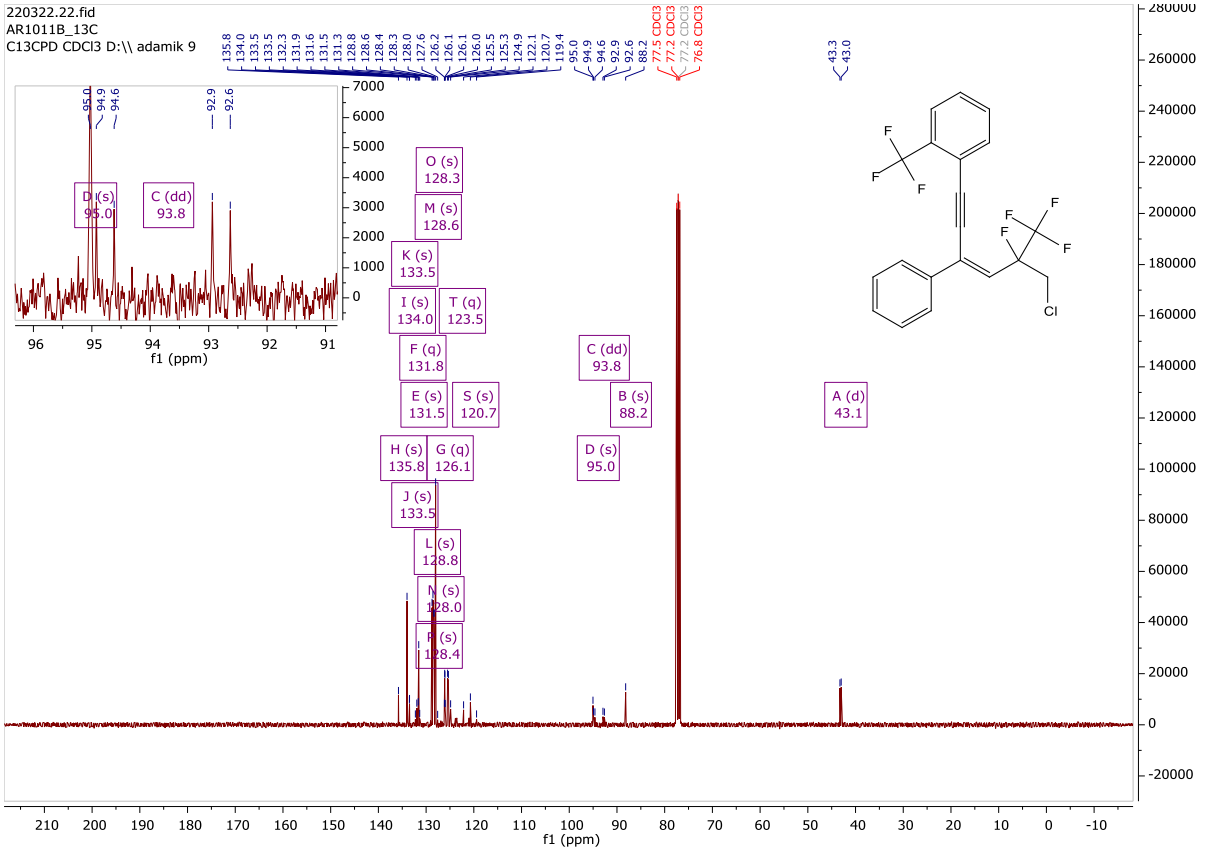

220330.21.fid
AR1013B_19F
F19CPD CDCl3 D:\\ adamik 20
B (d)
-78.37
A (q)
-167.12
f1 (ppm)


220509.30.fid
AR1013B_13C
C13CPD CDCl3 D:\\ adamik 6
f1 (ppm)
M (s) 128.2
K (s) 127.9
P (s) 133.9
J (s) 123.7
G (s) 114.4
D (s) 92.8
R (s) 160.1
Q (s) 133.3
I (s) 123.5
F (s) 114.0
C (dq) 93.6
B (s) 55.3
A (d) 43.0
Q (s) 136.6
H (m) 121.8
E (d) 88.9
L (s) 128.1
N (s) 128.2
D (s) 92.8
C (dq) 93.6

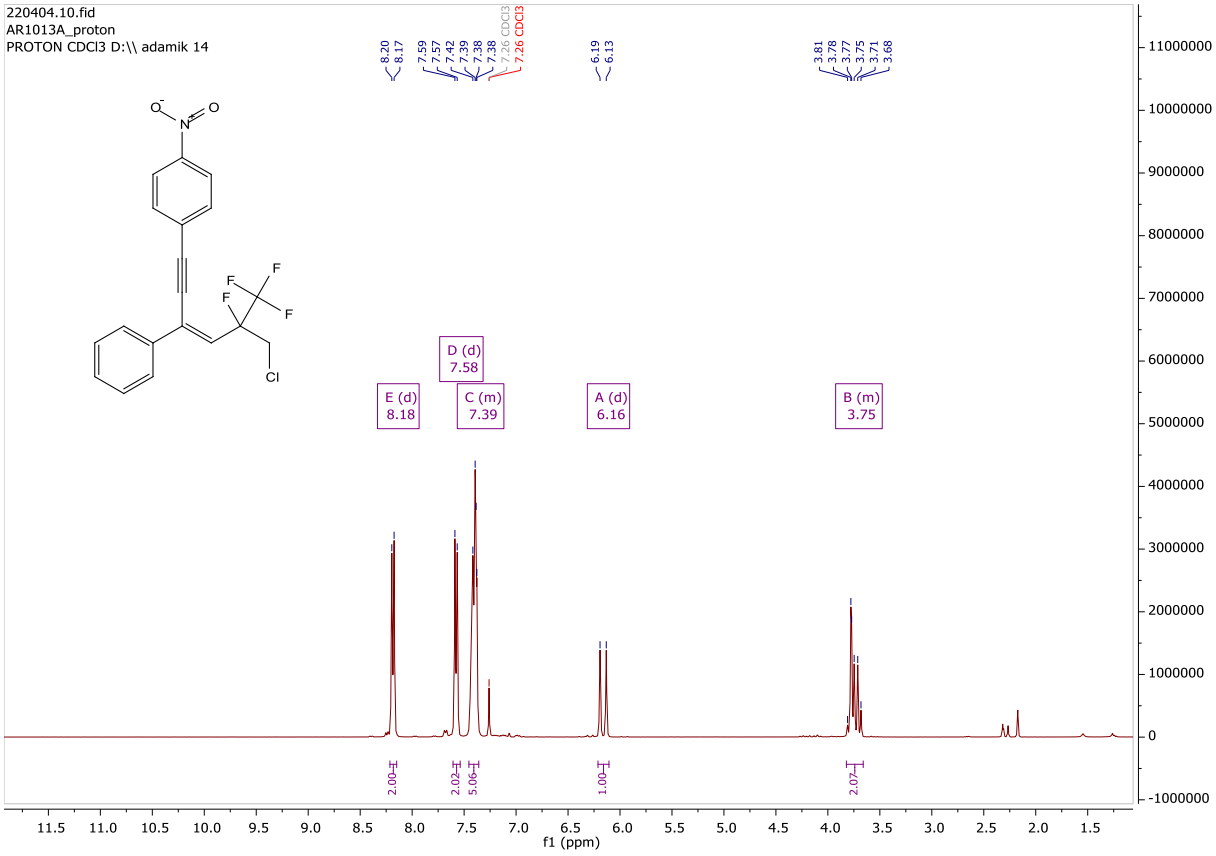
5h

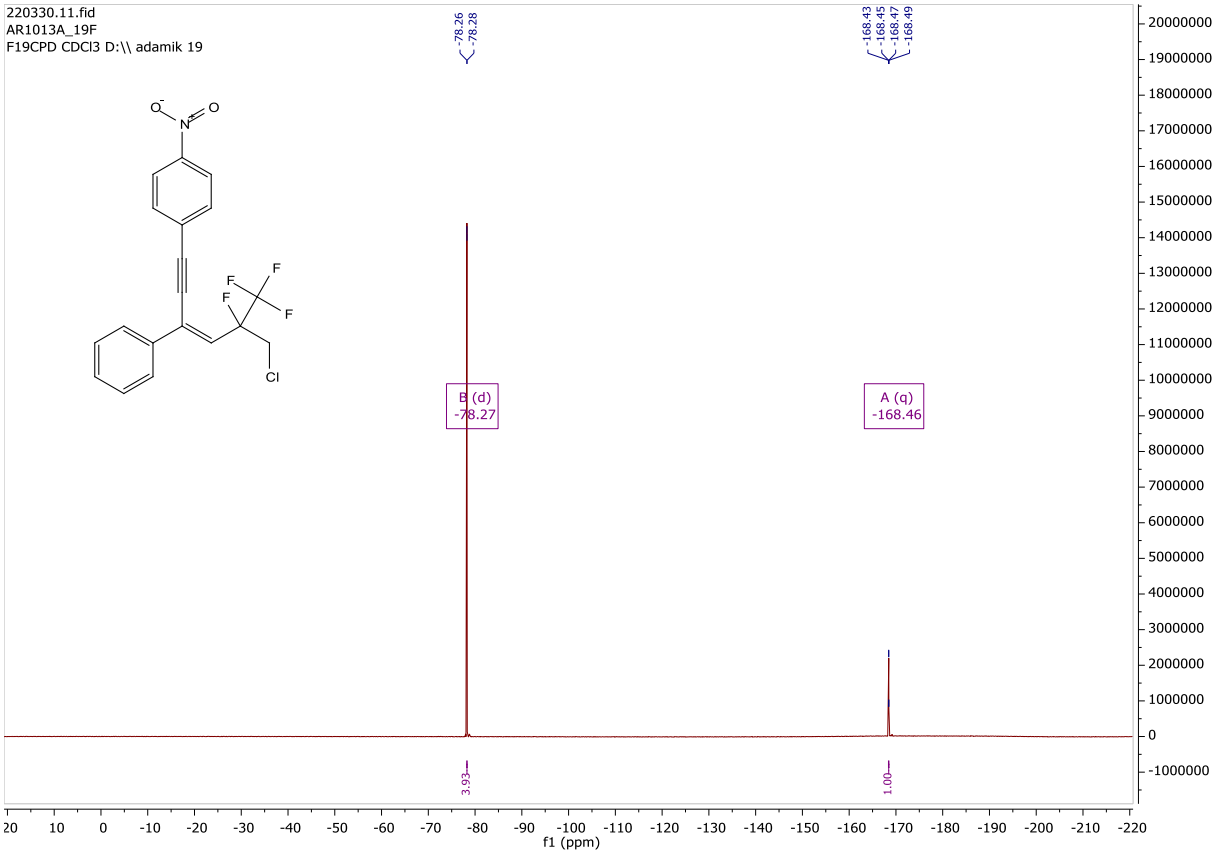

220322.20.fid
AR1011B_proton
PROTON CDCl3 D:\\ adamik 9
f1 (ppm)
F (m) 7.37
D (d) 7.56
C (d) 7.66
A (d) 6.10
B (dd) 3.73
E (m) 7.45

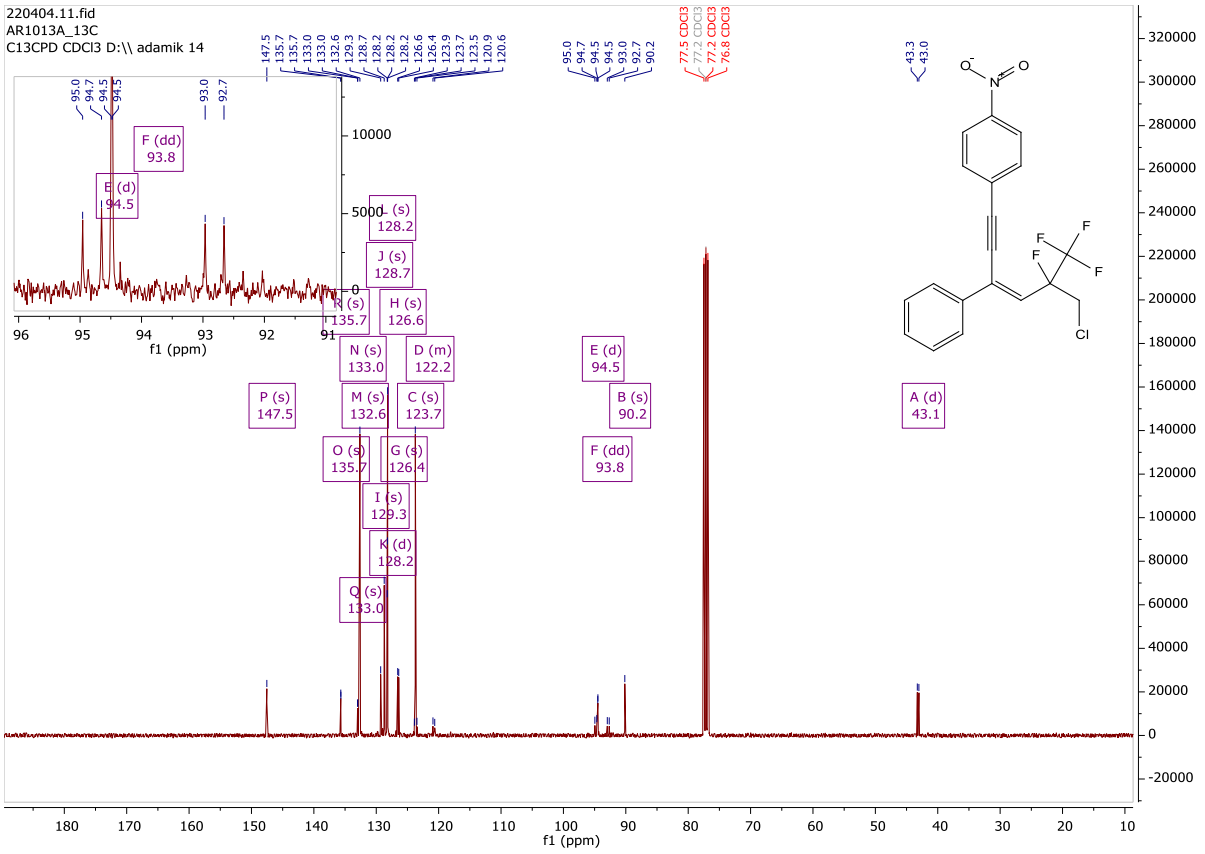

220322.21.fid
AR1011B_19F
F19CPD CDCl3 D:\\ adamik 9
-62.37
-78.27
-78.29
-167.85
-167.87
-167.89
-167.91
C (s)
-62.37
B (d)
-78.28
A (q)
-167.88
3.01
4.00
0.99
f1 (ppm)


220322.22.fid
AR1011B_13C
C13CPD CDCl3 D:\\ adamik 9
95.0
94.9
94.6
92.9
92.6
D (s)
95.0
C (dd)
93.8
O (s)
128.3
M (s)
128.6
K (s)
133.5
I (s)
134.0
T (q)
123.5
F (q)
131.8
E (s)
131.5
S (s)
120.7
H (s)
135.8
G (q)
126.1
J (s)
133.5
L (s)
128.8
N (s)
128.0
P (s)
128.4
C (dd)
93.8
B (s)
88.2
D (s)
95.0
A (d)
43.1
f1 (ppm)

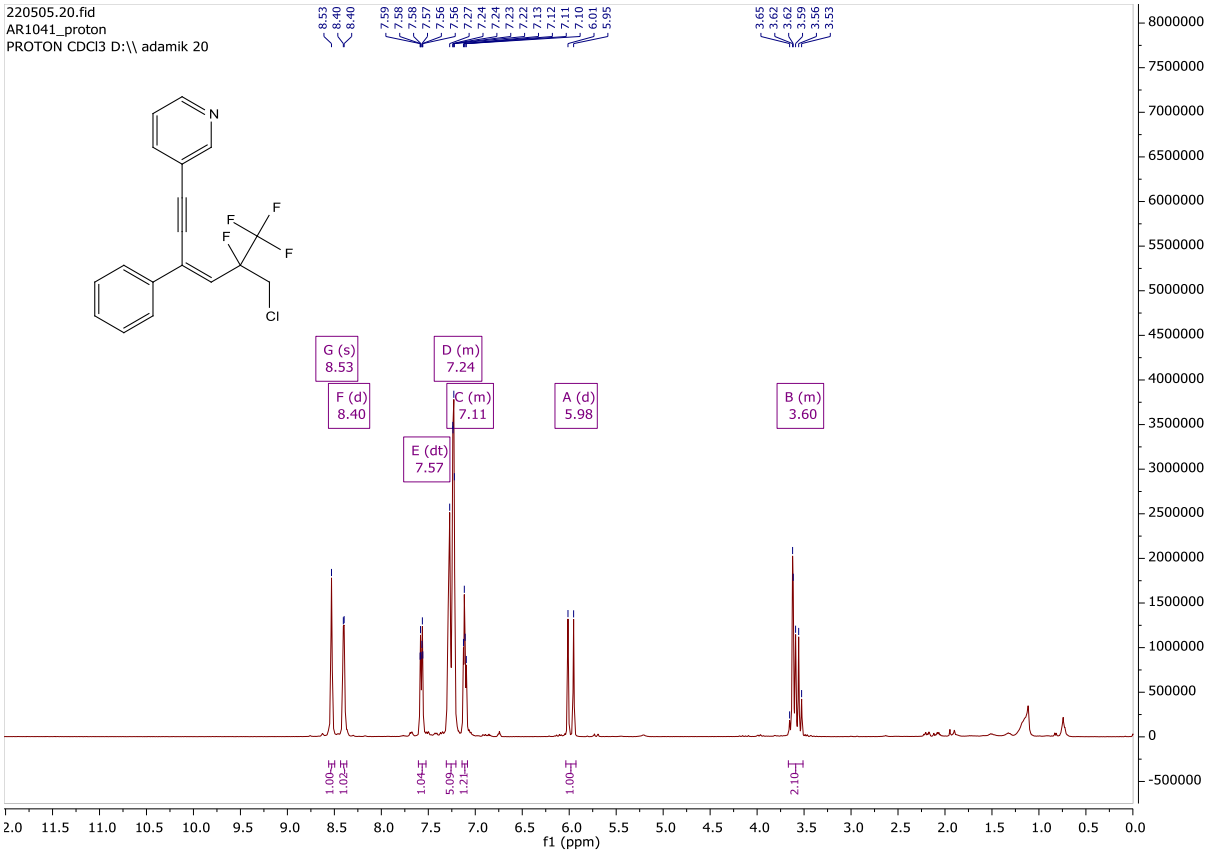
5i


220404.10.fid
AR1013A_proton
PROTON CDCl3 D:\\ adamik 14
8.20
8.17
7.59
7.57
7.42
7.39
7.38
7.38
7.26 CDCl3
7.26 CDCl3
6.19
6.13
3.81
3.78
3.77
3.75
3.71
3.68
D (d)
7.58
E (d)
8.18
C (m)
7.39
A (d)
6.16
B (m)
3.75
2.00
2.02
5.06
1.00
2.07
f1 (ppm)

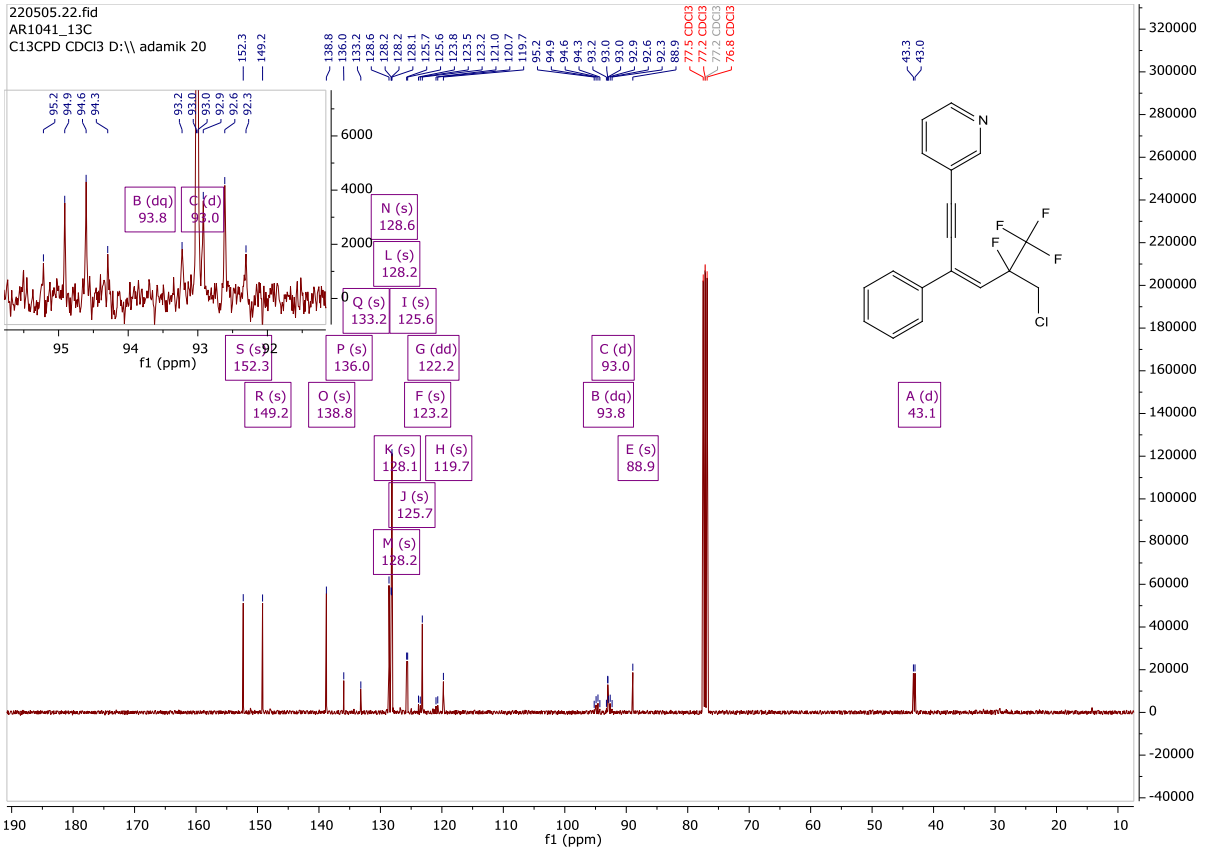

220330.11.fid
AR1013A_19F
F19CPD CDCl3 D:\\ adamik 19
-78.26
-78.28
-168.43
-168.45
-168.47
-168.49
B (d)
-78.27
A (q)
-168.46
3.93
1.00
f1 (ppm)


220404.11.fid
AR1013A_13C
C13CPD CDCl3 D:\\ adamik 14
F (dd) 93.8
E (d) 94.5
f1 (ppm)
P (s) 147.5
M (s) 132.6
C (s) 123.7
O (s) 135.7
G (s) 126.4
I (s) 129.3
K (d) 128.2
Q (s) 133.0
N (s) 133.0
D (m) 122.2
L (s) 128.2
J (s) 128.7
R (s) 135.7
H (s) 126.6
E (d) 94.5
B (s) 90.2
F (dd) 93.8
A (d) 43.1
Cl
f1 (ppm)

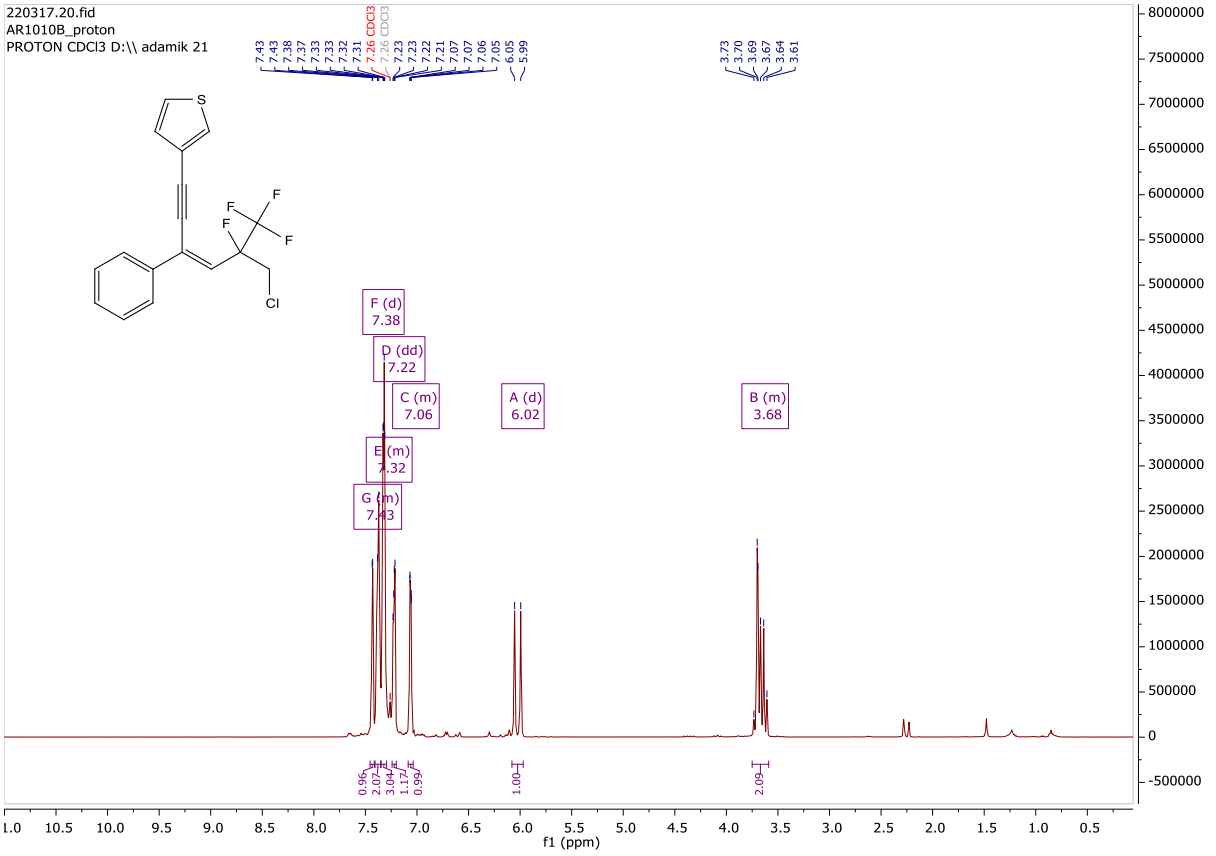
5j


220505.20.fid
AR1041_proton
PROTON CDCl3 D:\\ adamik 20
N
Cl
G (s) 8.53
F (d) 8.40
D (m) 7.24
C (m) 7.11
E (dt) 7.57
A (d) 5.98
B (m) 3.60
f1 (ppm)

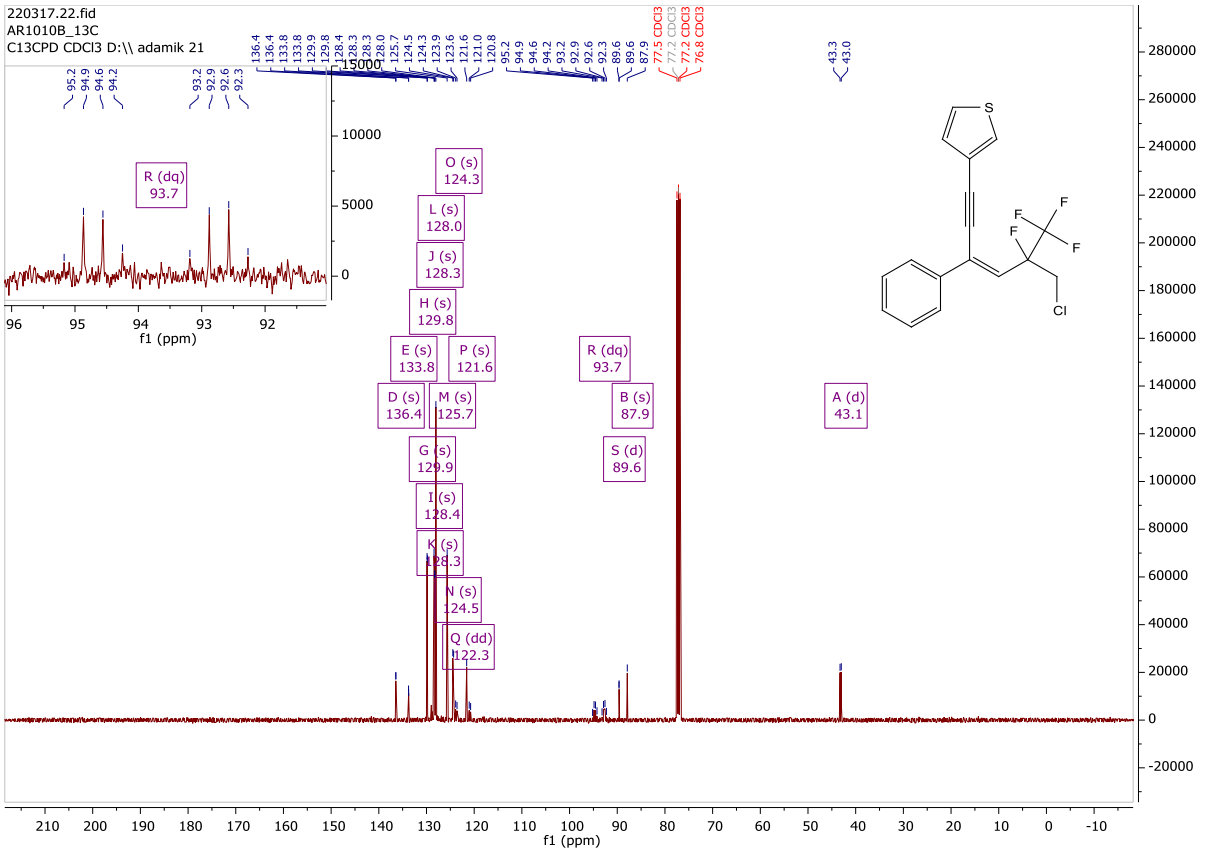

220505.21.fid
AR1041_19F
F19CPD CDCl3 D:\\ adamik 20
-78.29
-78.31
-168.22
-168.24
-168.26
-168.28
B (d)
-78.30
A (q)
-168.25
3.94
1.00
f1 (ppm)


220505.22.fid
AR1041_13C
C13CPD CDCl3 D:\\ adamik 20
B (dq)
93.8
C (d)
93.0
N (s)
128.6
L (s)
128.2
Q (s)
133.2
I (s)
125.6
S (s)
152.3
P (s)
136.0
G (dd)
122.2
R (s)
149.2
O (s)
138.8
F (s)
123.2
K (s)
128.1
H (s)
119.7
J (s)
125.7
M (s)
128.2
C (d)
93.0
B (dq)
93.8
E (s)
88.9
A (d)
43.1
f1 (ppm)

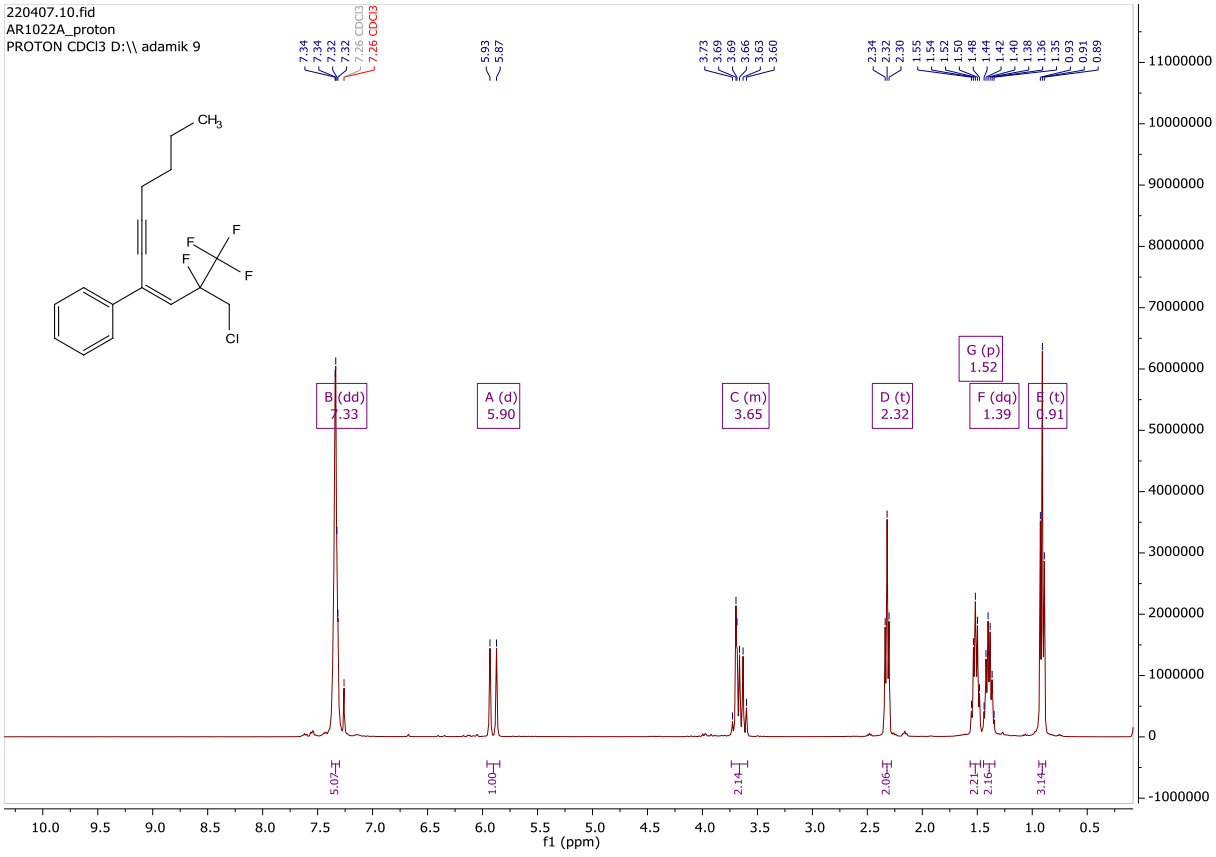
5k

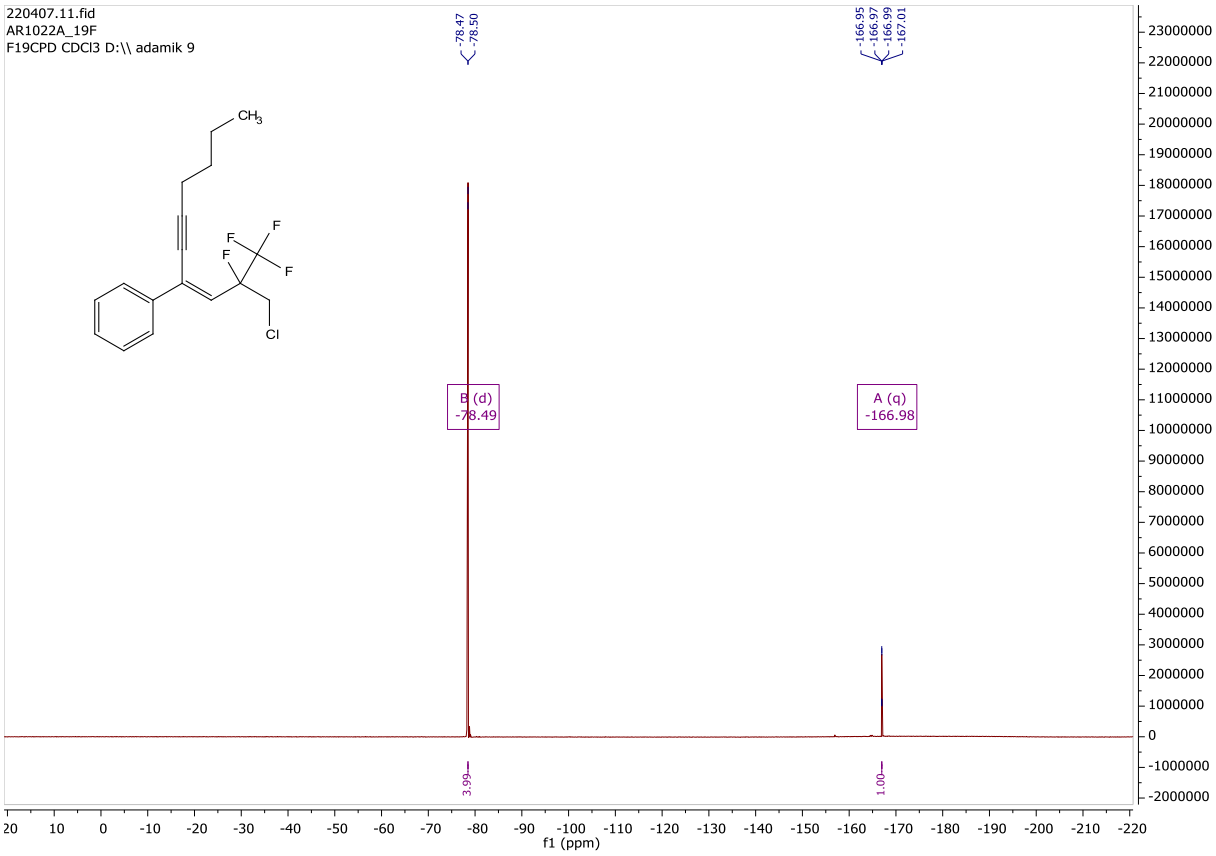

220317.20.fid
AR1010B_proton
PROTON CDCl3 D:\\ adamik 21
F (d)
7.38
D (dd)
7.22
C (m)
7.06
A (d)
6.02
B (m)
3.68
E (m)
7.32
G (m)
7.43
f1 (ppm)

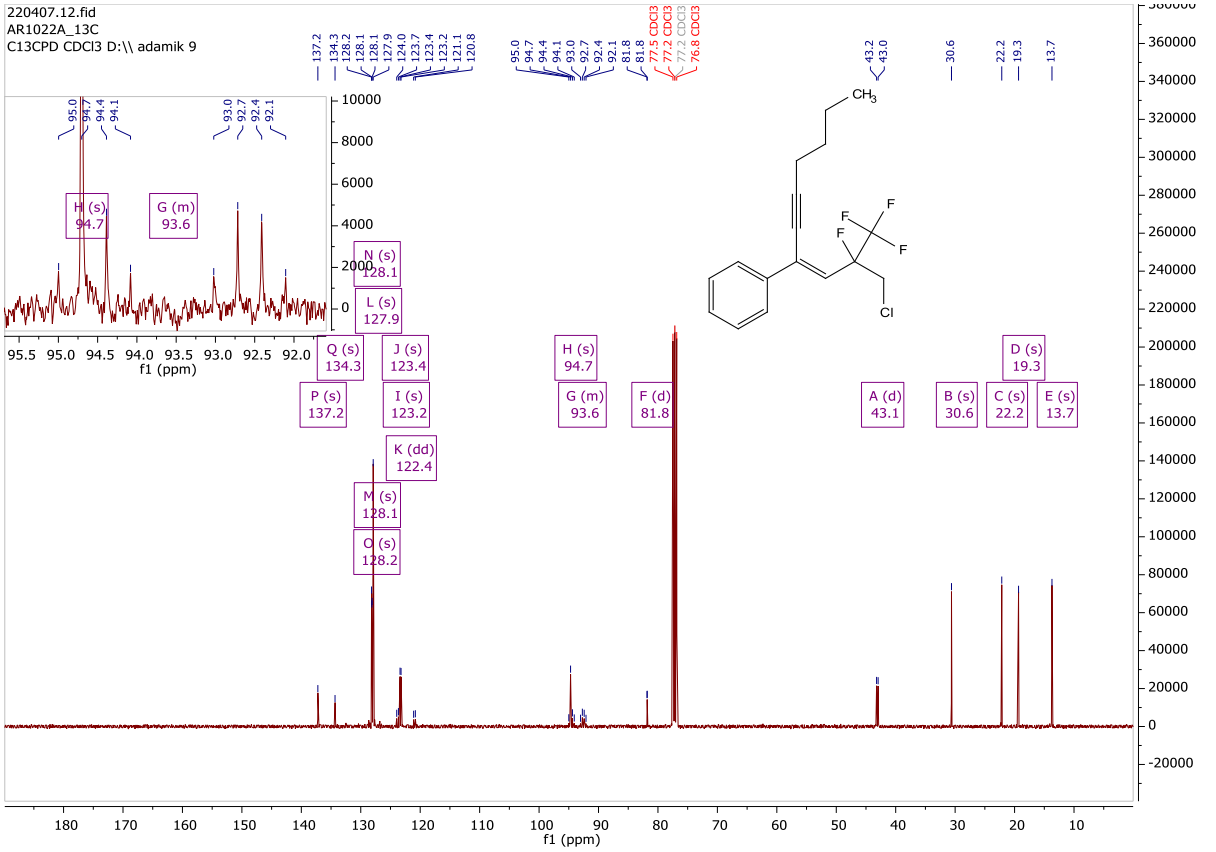

220317.21.fid
AR1010B_19F
F19CPD CDCl3 D:\\ adamik 21
B (d)
-78.35
A (q)
-167.53
f1 (ppm)


220317.22.fid
AR1010B_13C
C13CPD CDCl3 D:\\ adamik 21
R (dq) 93.7
O (s) 124.3
L (s) 128.0
J (s) 128.3
H (s) 129.8
E (s) 133.8
P (s) 121.6
D (s) 136.4
M (s) 125.7
G (s) 129.9
I (s) 128.4
K (s) 128.3
N (s) 124.5
Q (dd) 122.3
R (dq) 93.7
B (s) 87.9
S (d) 89.6
A (d) 43.1
f1 (ppm)

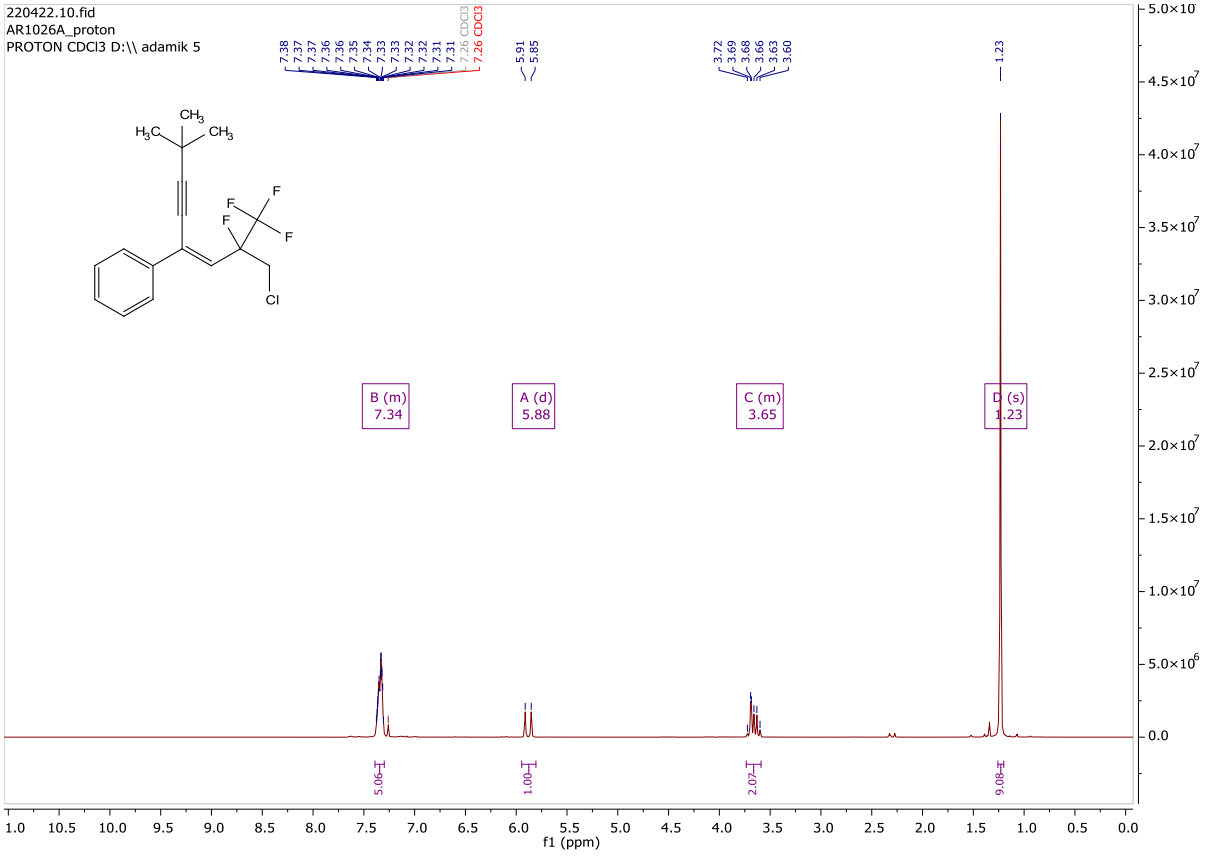
5l

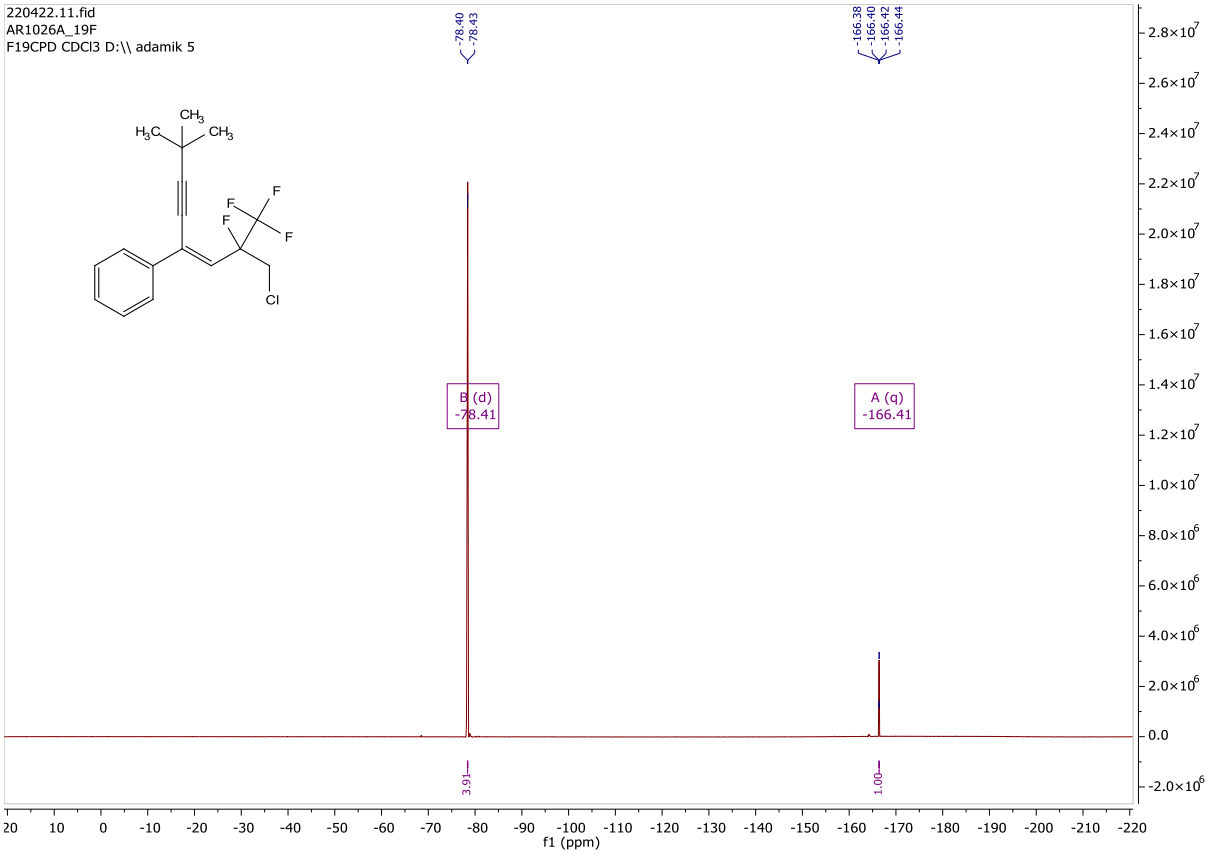

220407.10.fid
AR1022A_proton
PROTON CDCl3 D:\\ adamik 9
B (dd) 7.33
A (d) 5.90
C (m) 3.65
D (t) 2.32
G (p) 1.52
F (dq) 1.39
E (t) 0.91
f1 (ppm)

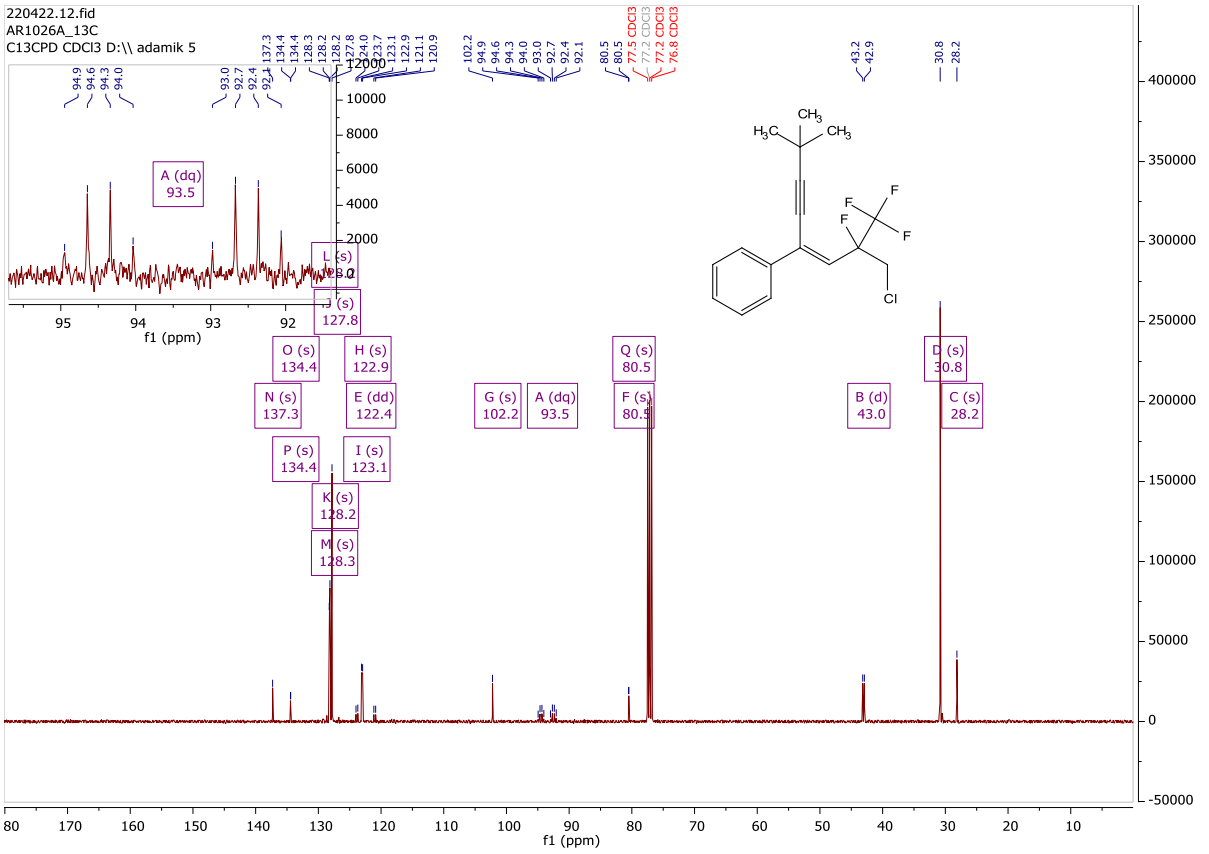

220407.11.fid
AR1022A_19F
F19CPD CDCl3 D:\\ adamik 9
-78.47
-78.50
-166.95
-166.97
-166.99
-167.01
B (d)
-78.49
A (q)
-166.98
3.99
1.00
f1 (ppm)


220407.12.fid
AR1022A_13C
C13CPD CDCl3 D:\\ adamik 9
H (s)
94.7
G (m)
93.6
N (s)
128.1
L (s)
127.9
Q (s)
134.3
J (s)
123.4
P (s)
137.2
I (s)
123.2
K (dd)
122.4
M (s)
128.1
O (s)
128.2
F (d)
81.8
A (d)
43.1
B (s)
30.6
C (s)
22.2
D (s)
19.3
E (s)
13.7
f1 (ppm)

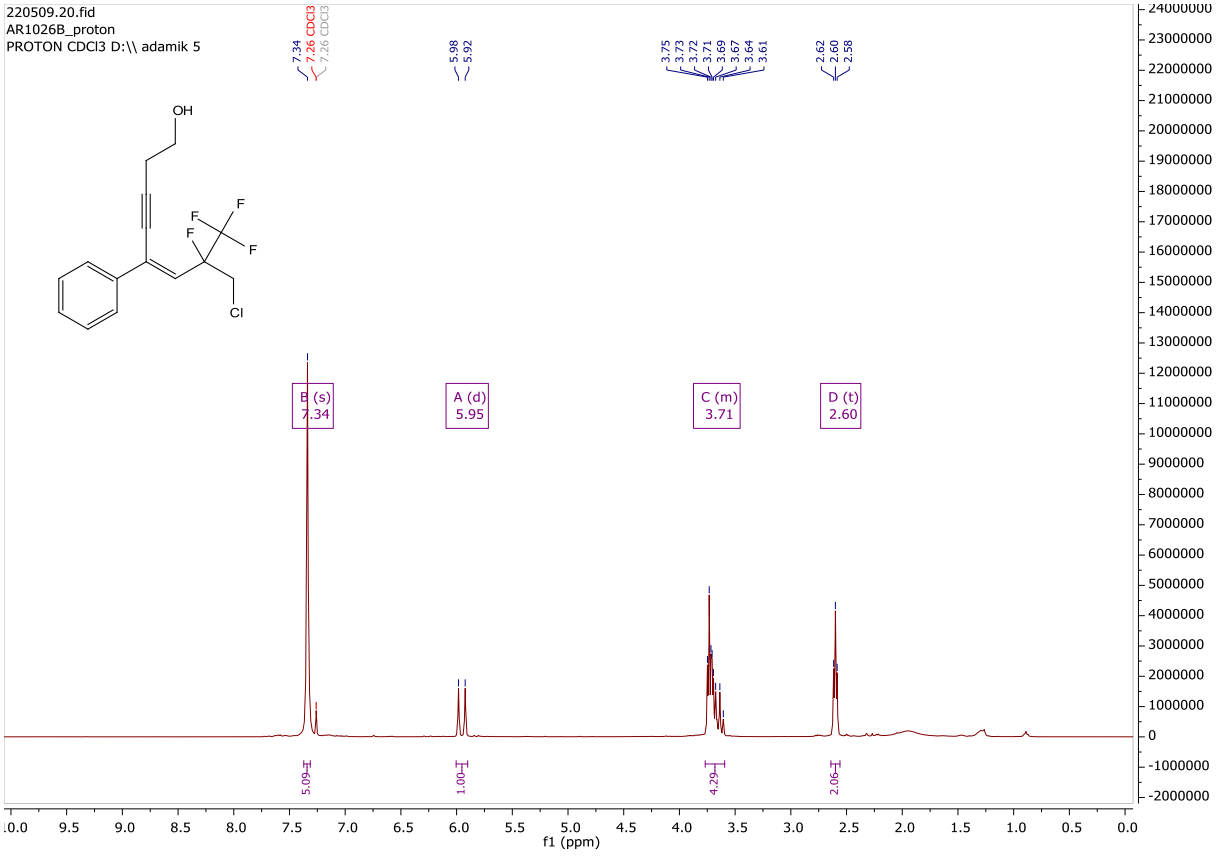
5m

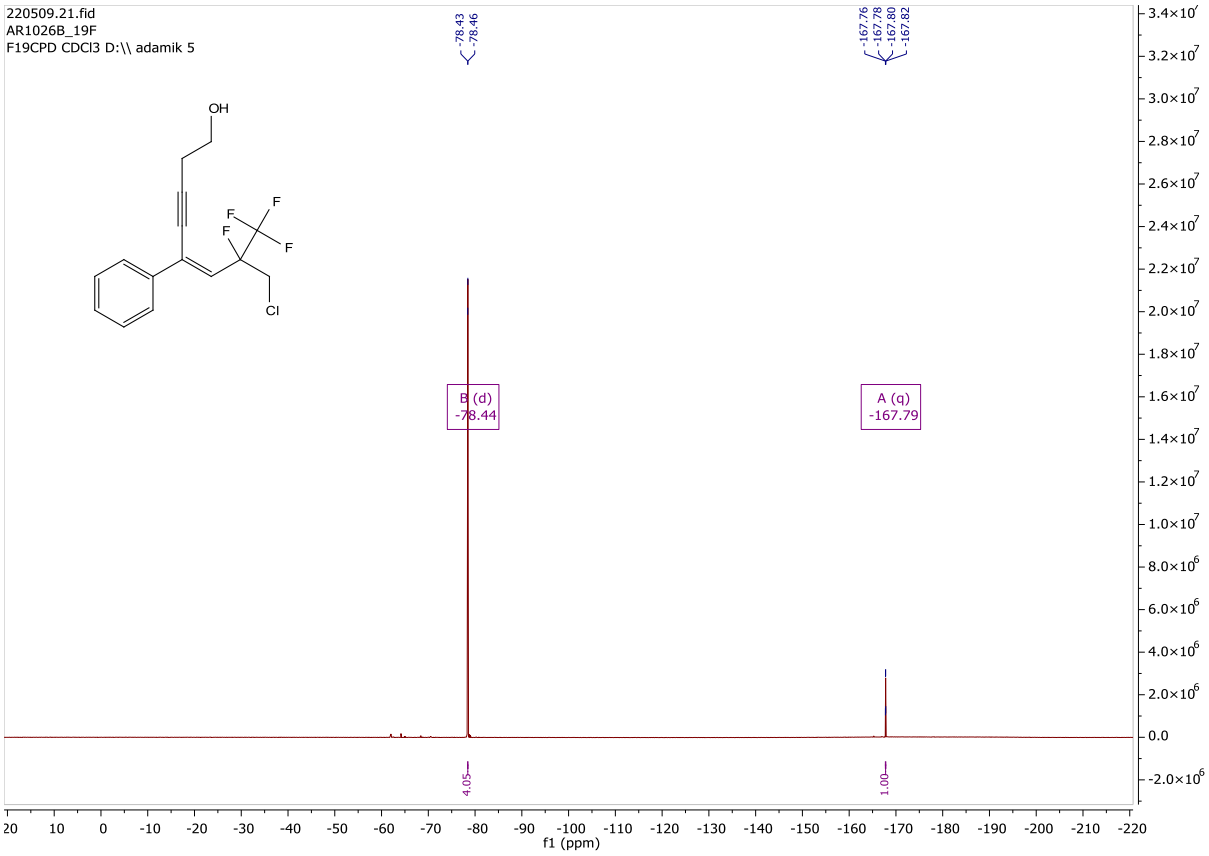

220422.10.fid
AR1026A_proton
PROTON CDCl3 D:\\ adamik 5
7.38 7.37 7.37 7.36 7.36 7.35 7.34 7.33 7.33 7.32 7.32 7.31 7.31 7.26 CDCl3 7.26 CDCl3
5.91 5.85
3.72 3.69 3.68 3.66 3.63 3.60
1.23
B (m) 7.34
A (d) 5.88
C (m) 3.65
D (s) 1.23
5.06
1.00
2.07
9.08
f1 (ppm)

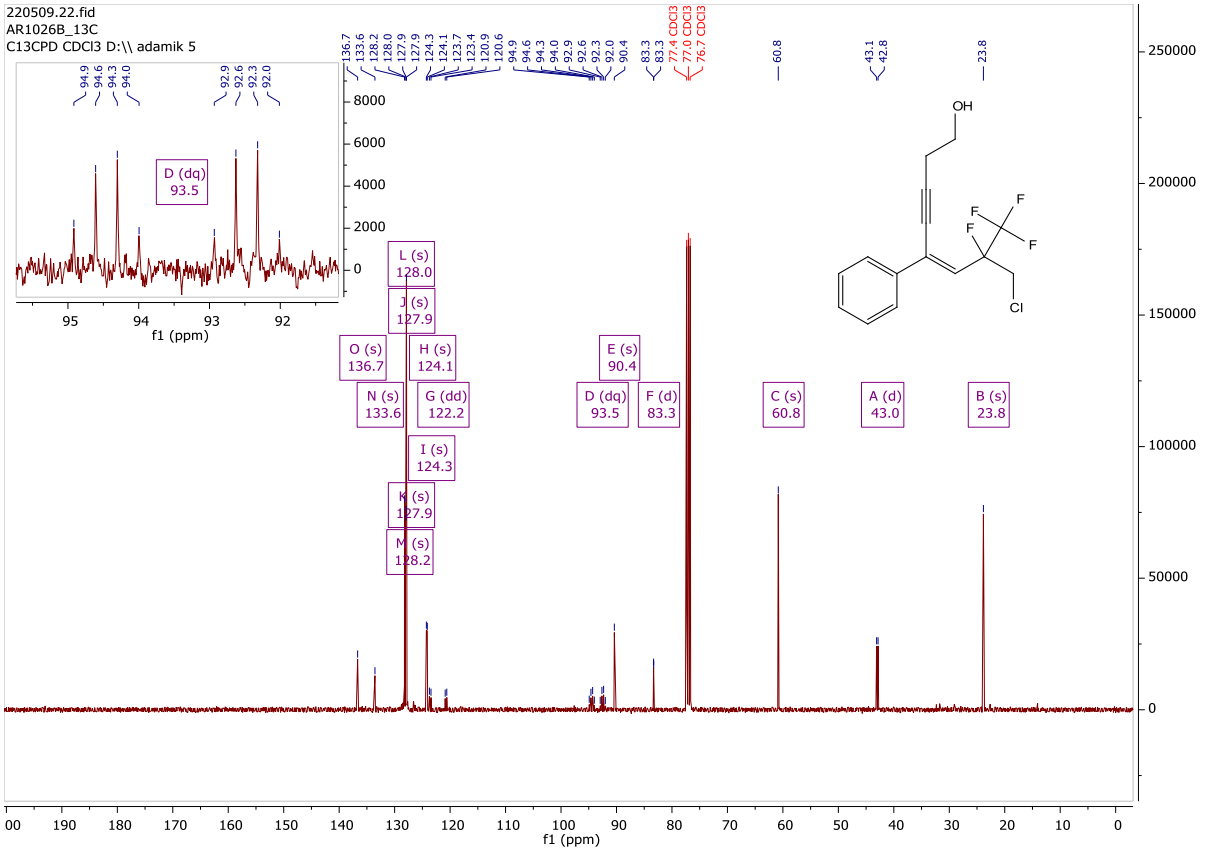

220422.11.fid
AR1026A_19F
F19CPD CDCl3 D:\\ adamik 5
-78.40 -78.43
-166.38 -166.40 -166.42 -166.44
B (d) -78.41
A (q) -166.41
3.91
1.00
f1 (ppm)


220422.12.fid
AR1026A_13C
C13CPD CDCl3 D:\\ adamik 5
A (dq)
93.5
L (s)
J (s)
127.8
O (s)
134.4
H (s)
122.9
N (s)
137.3
E (dd)
122.4
G (s)
102.2
A (dq)
93.5
Q (s)
80.5
F (s)
80.5
B (d)
43.0
D (s)
30.8
C (s)
28.2
P (s)
134.4
I (s)
123.1
K (s)
128.2
M (s)
128.3
f1 (ppm)

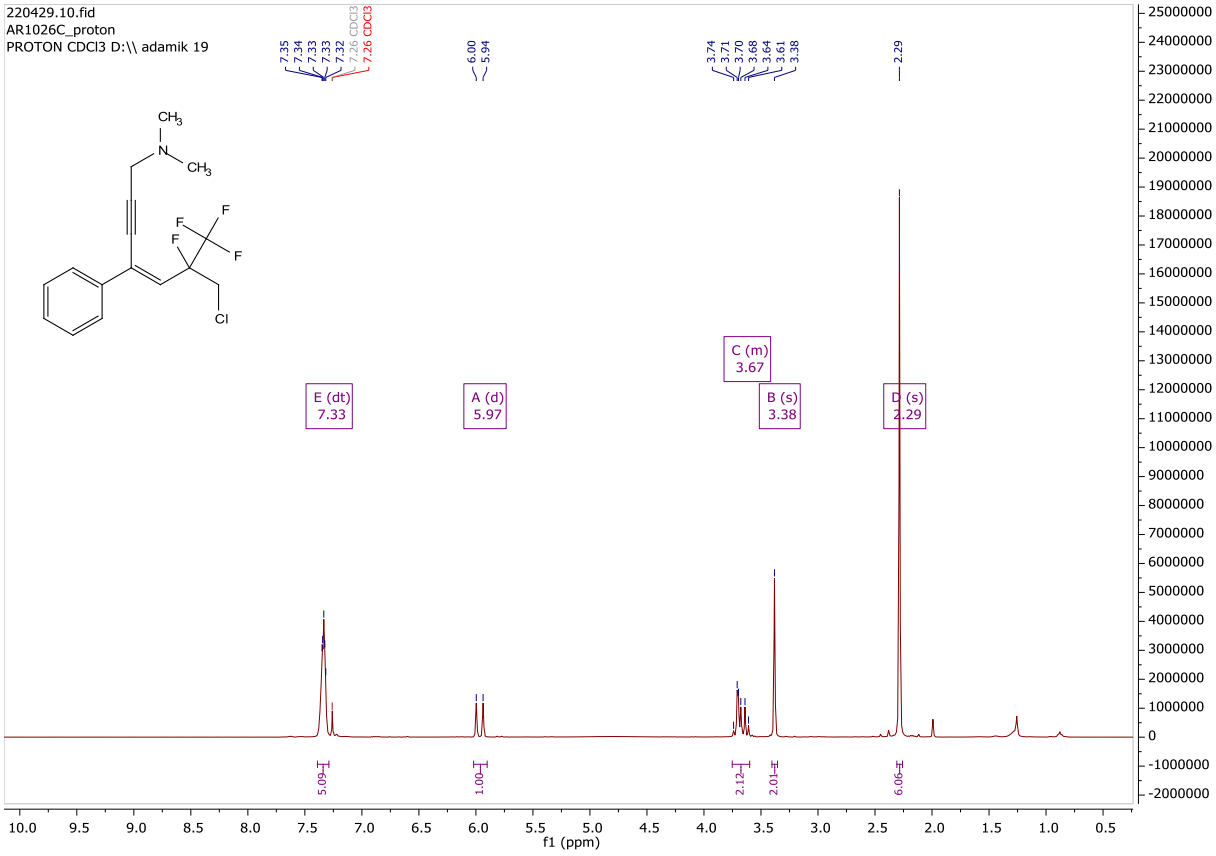
5n

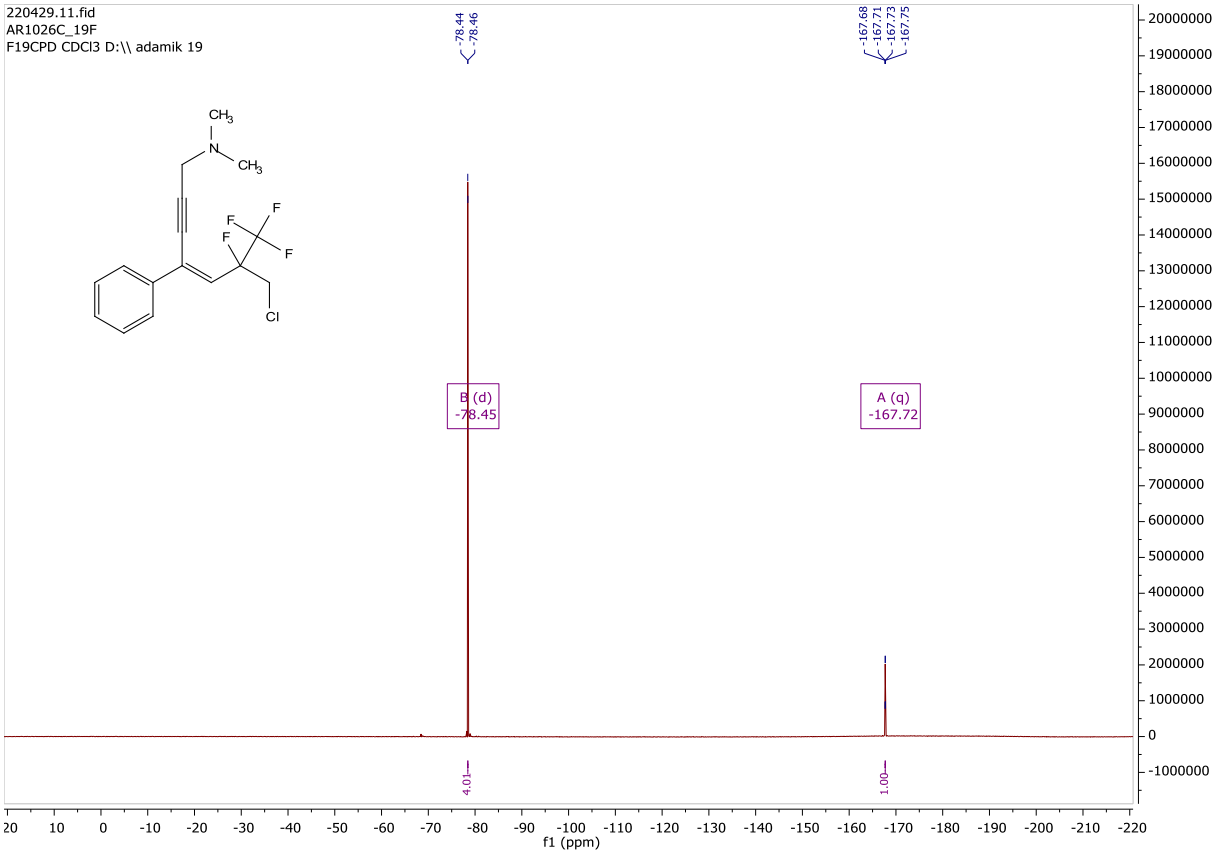

220509.20.fid
AR1026B_proton
PROTON CDCl3 D:\\ adamik 5
B (s)
7.34
A (d)
5.95
C (m)
3.71
D (t)
2.60
f1 (ppm)

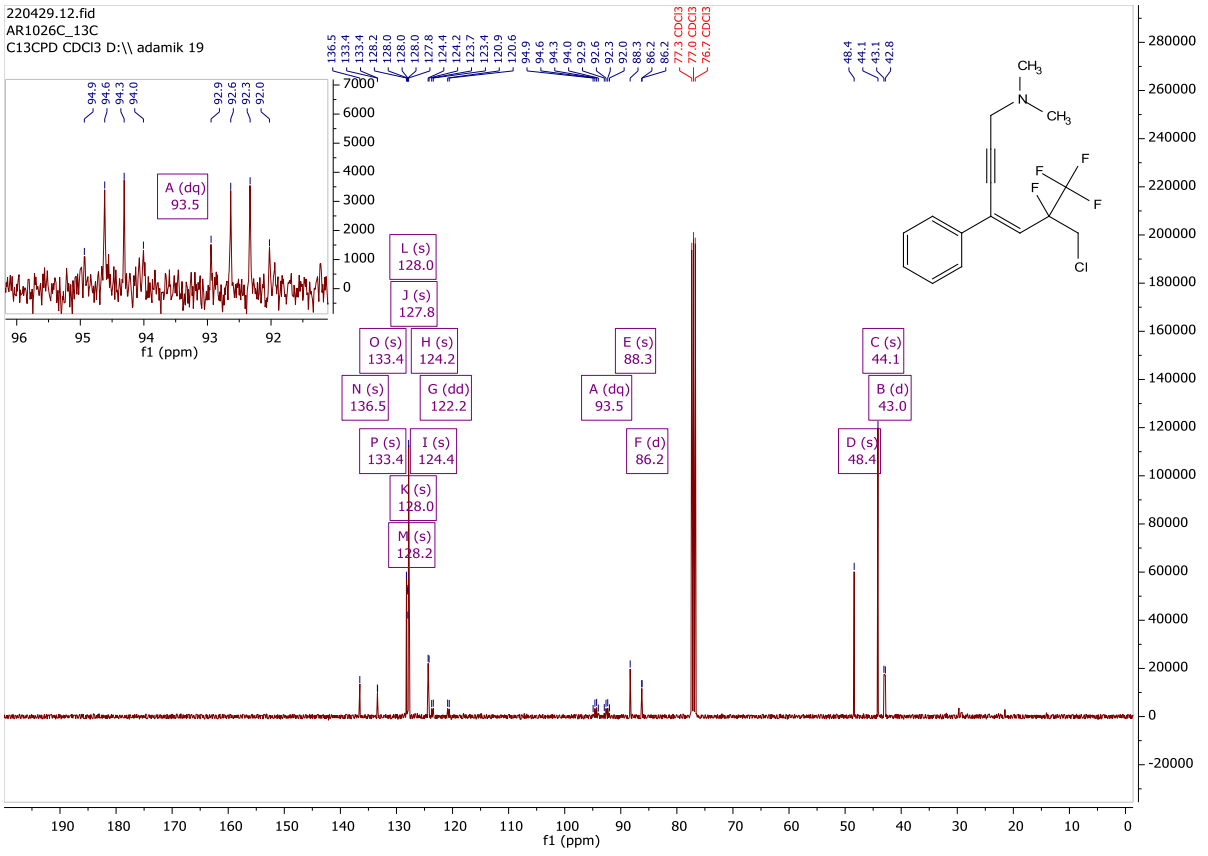

220509.21.fid
AR1026B_19F
F19CPD CDCl3 D:\\ adamik 5
-78.43
-78.46
-167.76
-167.78
-167.80
-167.82
OH
F
F
F
F
Cl
B (d)
-78.44
A (q)
-167.79
4.05
1.00
f1 (ppm)


220509.22.fid
AR1026B_13C
C13CPD CDCl3 D:\\ adamik 5
136.7
133.6
128.2
128.0
127.9
127.9
124.3
124.1
123.7
123.4
120.9
120.6
94.9
94.6
94.3
94.0
92.9
92.6
92.3
92.0
90.4
83.3
83.3
77.4 CDCl3
77.0 CDCl3
76.7 CDCl3
60.8
43.1
42.8
23.8
D (dq)
93.5
L (s)
128.0
J (s)
127.9
O (s)
136.7
H (s)
124.1
E (s)
90.4
N (s)
133.6
G (dd)
122.2
D (dq)
93.5
F (d)
83.3
C (s)
60.8
A (d)
43.0
B (s)
23.8
I (s)
124.3
K (s)
127.9
M (s)
128.2
OH
F
F
F
F
Cl
f1 (ppm)

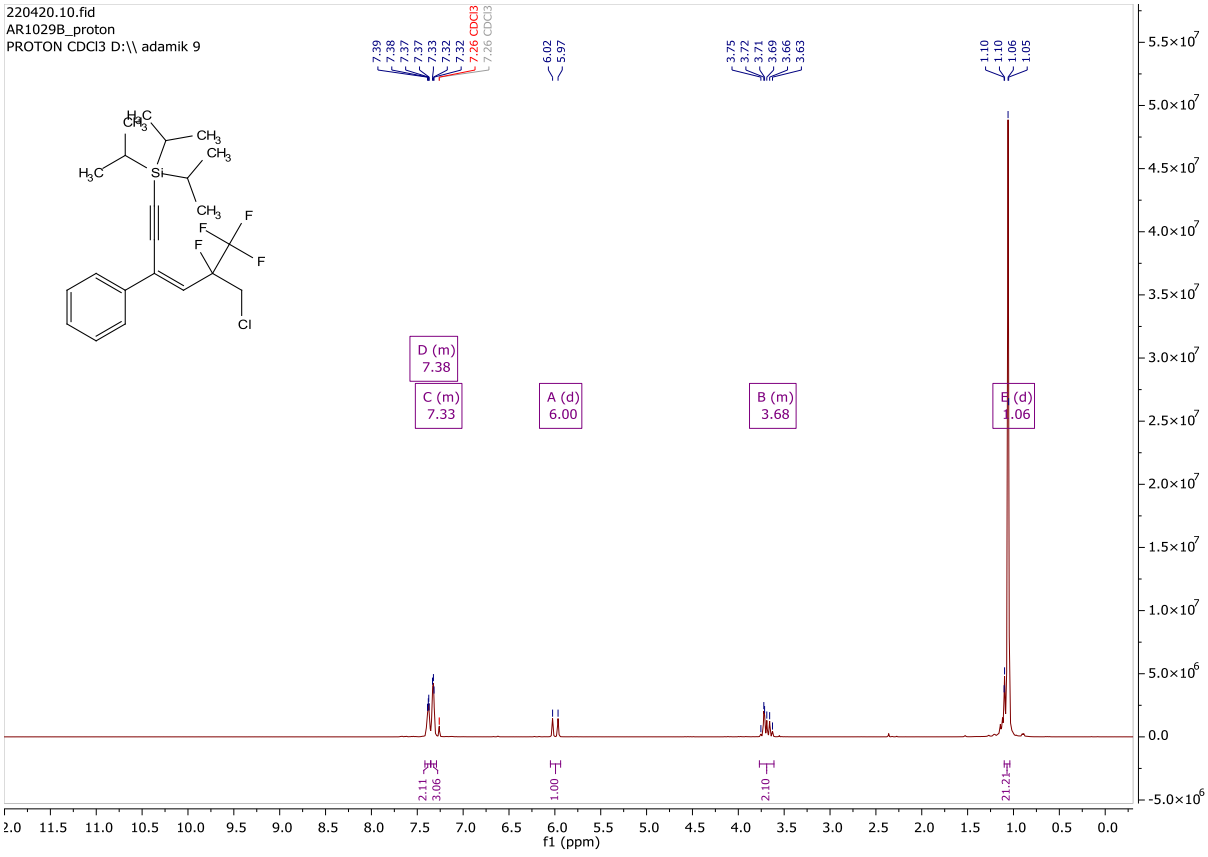
5o


220429.10.fid
AR1026C_proton
PROTON CDCl3 D:\\ adamik 19
7.35
7.34
7.33
7.33
7.32
7.26 CDCl3
7.26 CDCl3
6.00
5.94
3.74
3.71
3.70
3.68
3.64
3.61
3.38
2.29
CH3
N
CH3
F
F
F
F
Cl
E (dt)
7.33
A (d)
5.97
C (m)
3.67
B (s)
3.38
D (s)
2.29
5.09
1.00
2.12
2.01
6.06
f1 (ppm)

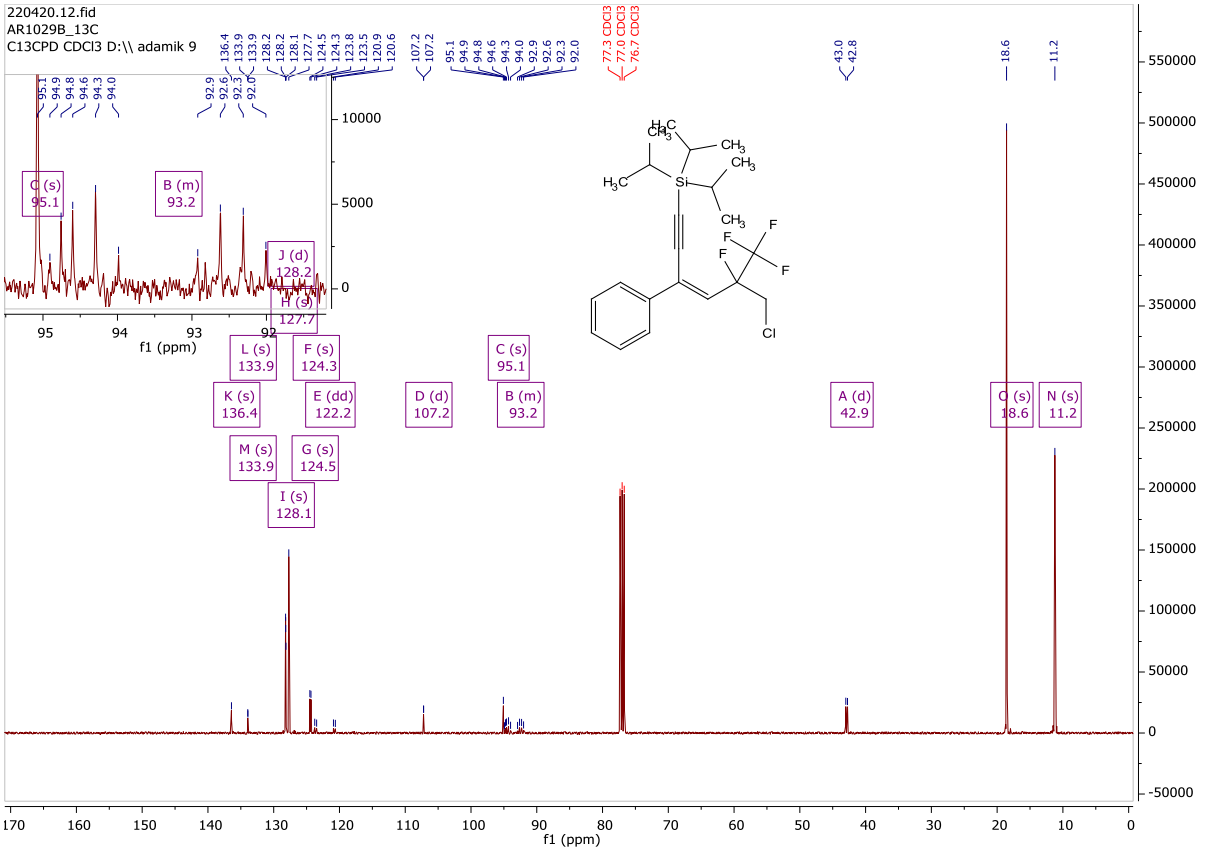

220429.11.fid
AR1026C_19F
F19CPD CDCl3 D:\\ adamik 19
-78.44
-78.46
-167.68
-167.71
-167.73
-167.75
CH3
N
CH3
F
F
F
F
Cl
B (d)
-78.45
A (q)
-167.72
4.01
1.00
f1 (ppm)


220429.12.fid
AR1026C_13C
C13CPD CDCl3 D:\\ adamik 19
A (dq)
93.5
L (s)
128.0
J (s)
127.8
O (s)
133.4
H (s)
124.2
N (s)
136.5
G (dd)
122.2
P (s)
133.4
I (s)
124.4
K (s)
128.0
M (s)
128.2
E (s)
88.3
A (dq)
93.5
F (d)
86.2
C (s)
44.1
B (d)
43.0
D (s)
48.4
f1 (ppm)

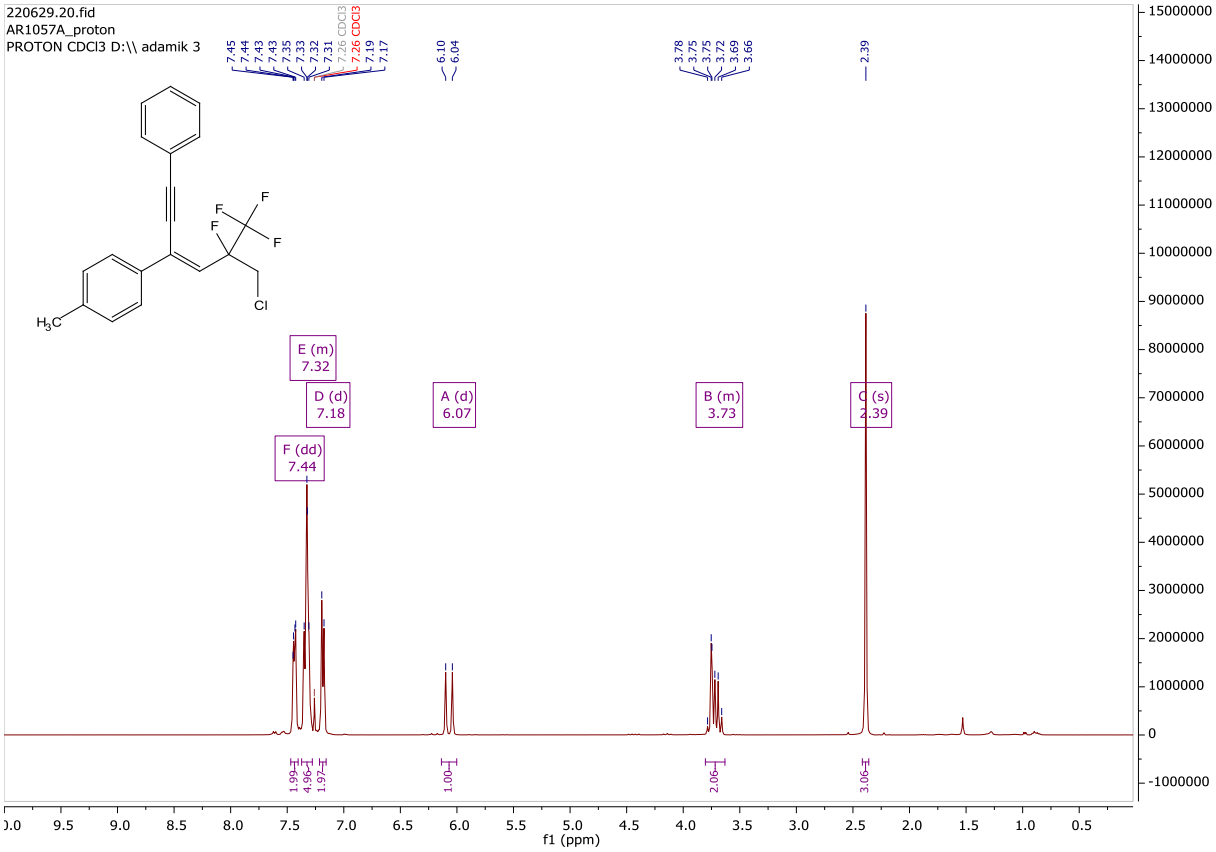
5p

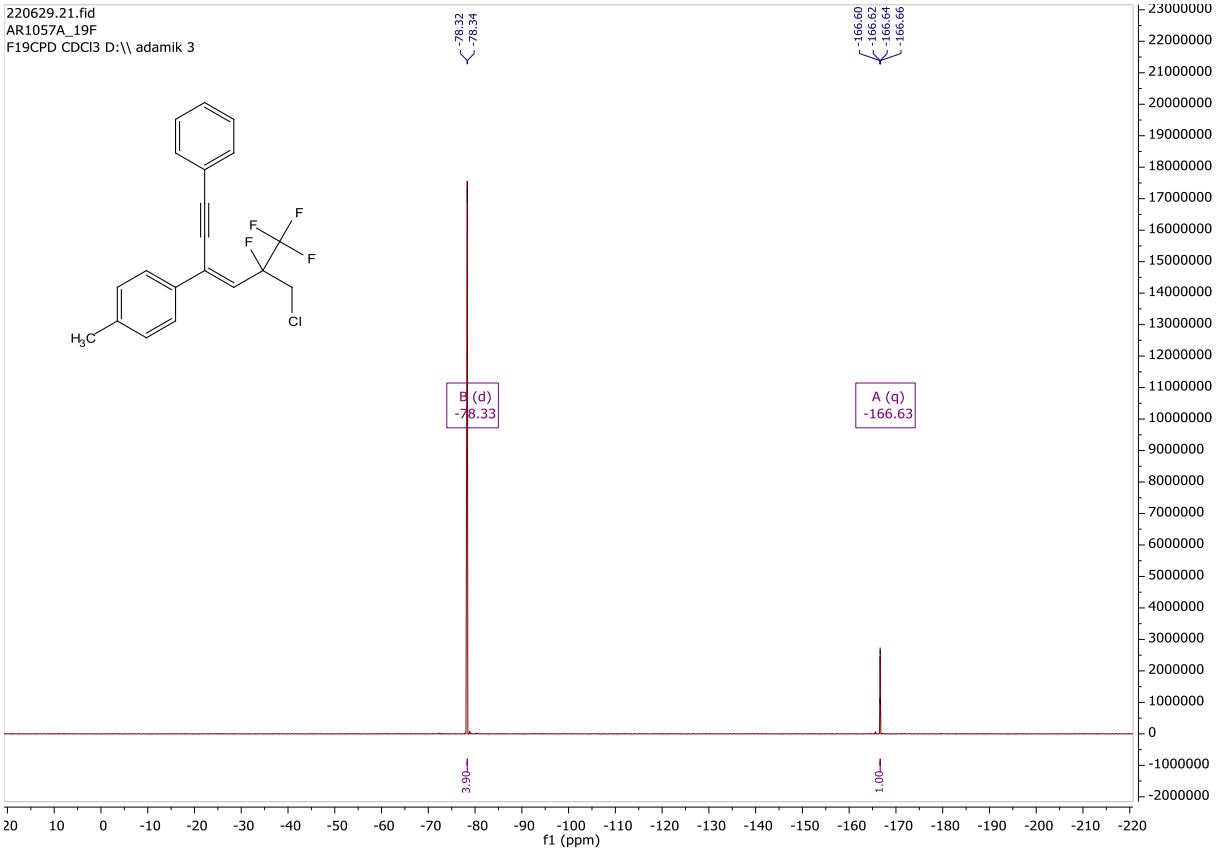

220420.10.fid
AR1029B_proton
PROTON CDCl3 D:\\ adamik 9
D (m)
7.38
C (m)
7.33
A (d)
6.00
B (m)
3.68
E (d)
1.06
f1 (ppm)

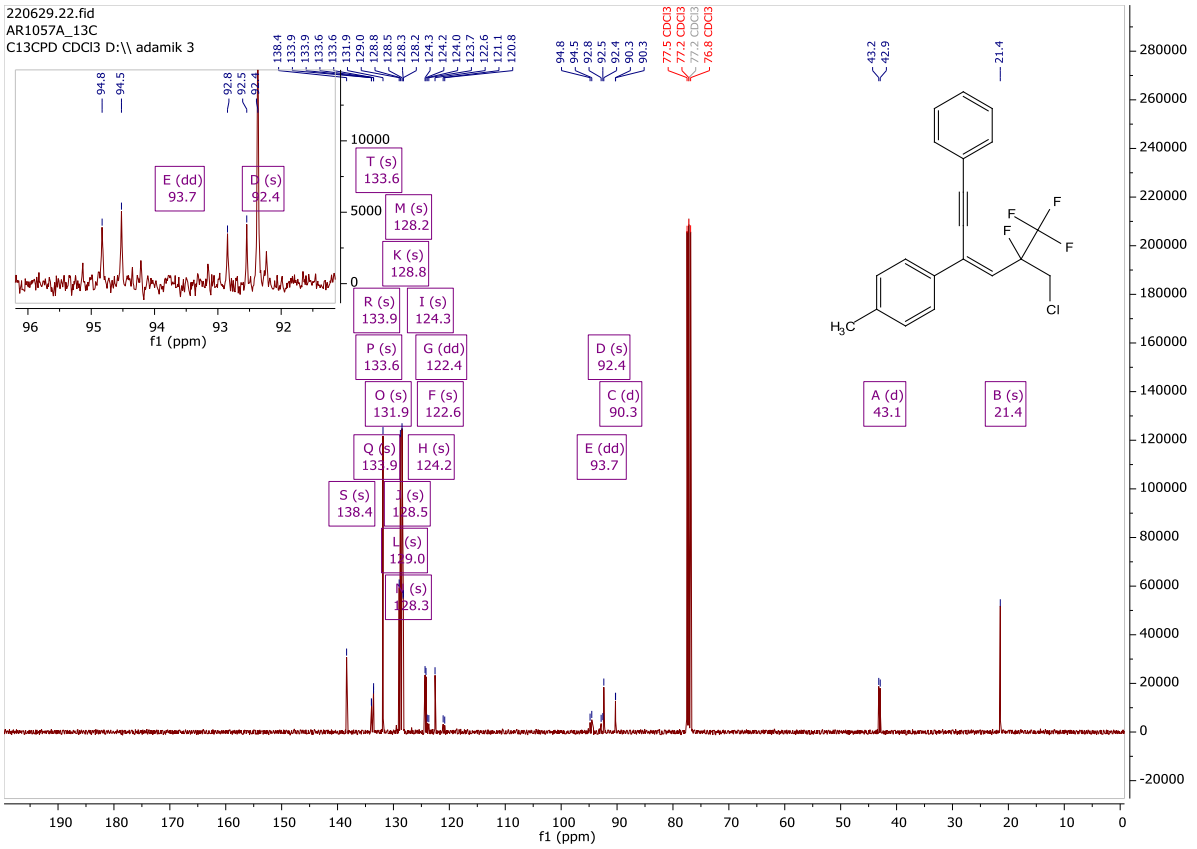

220420.11.fid
AR1029B_19F
F19CPD CDCl3 D:\\ adamik 9
-78.29
-78.31
-167.00
-167.02
-167.04
-167.06
B (d)
-78.30
A (q)
-167.03
3.97
1.00
f1 (ppm)


220420.12.fid
AR1029B_13C
C13CPD CDCl3 D:\\ adamik 9
77.3 CDCl3
77.0 CDCl3
76.7 CDCl3
C (s)
95.1
B (m)
93.2
J (d)
128.2
H (s)
127.7
L (s)
133.9
F (s)
124.3
K (s)
136.4
E (dd)
122.2
D (d)
107.2
C (s)
95.1
B (m)
93.2
M (s)
133.9
G (s)
124.5
I (s)
128.1
A (d)
42.9
O (s)
18.6
N (s)
11.2
f1 (ppm)

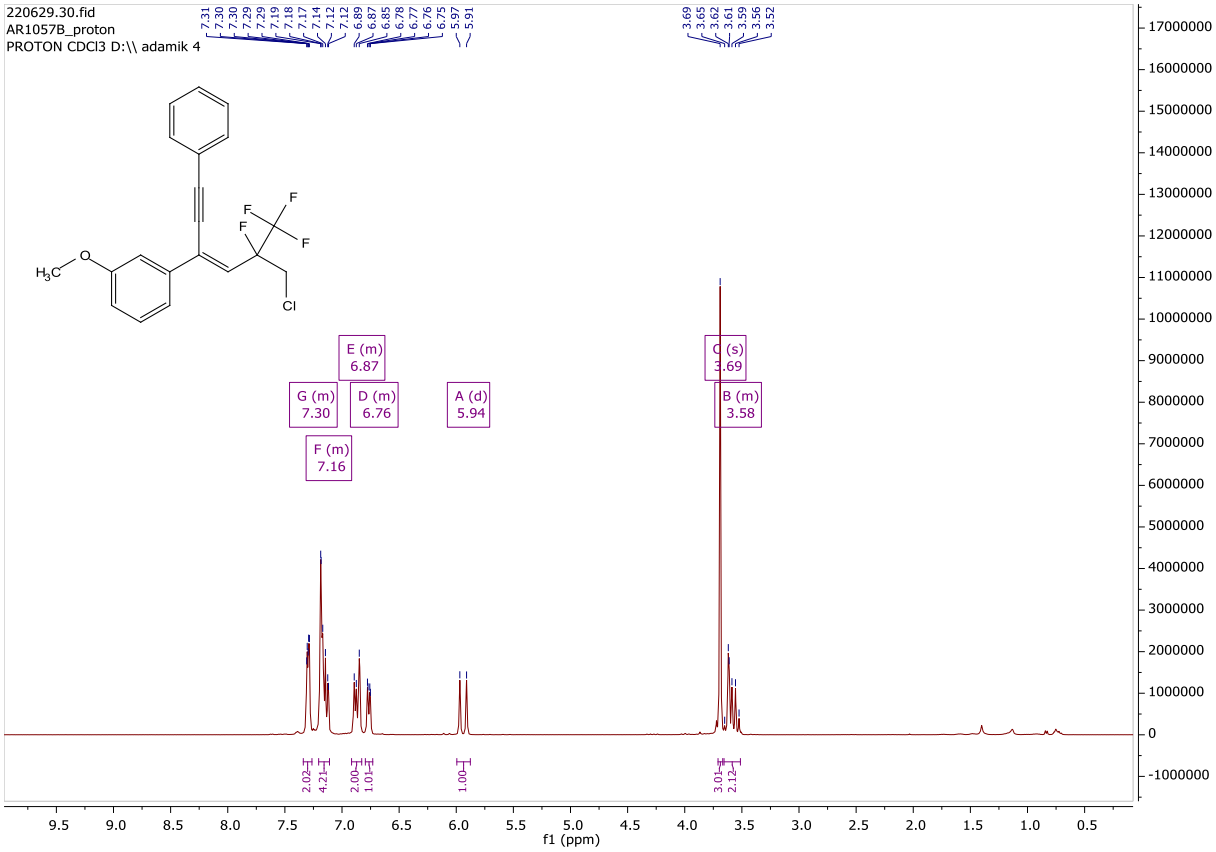
5q


220629.20.fid
AR1057A_proton
PROTON CDCl3 D:\\ adamik 3
E (m)
7.32
D (d)
7.18
A (d)
6.07
F (dd)
7.44
B (m)
3.73
C (s)
2.39
f1 (ppm)

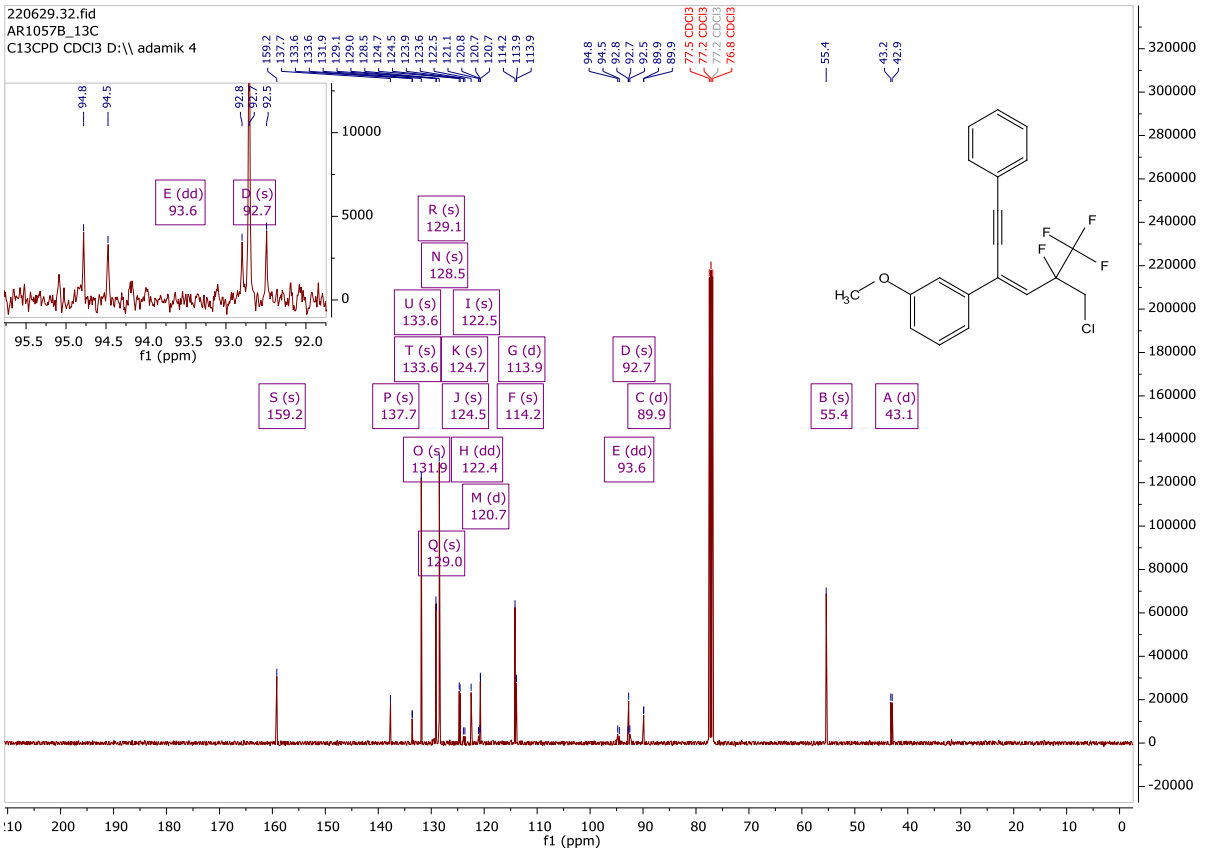

220629.21.fid
AR1057A_19F
F19CPD CDCl3 D:\\ adamik 3
B (d)
-78.33
A (q)
-166.63
f1 (ppm)


220629.22.fid
AR1057A_13C
C13CPD CDCl3 D:\\ adamik 3
f1 (ppm)

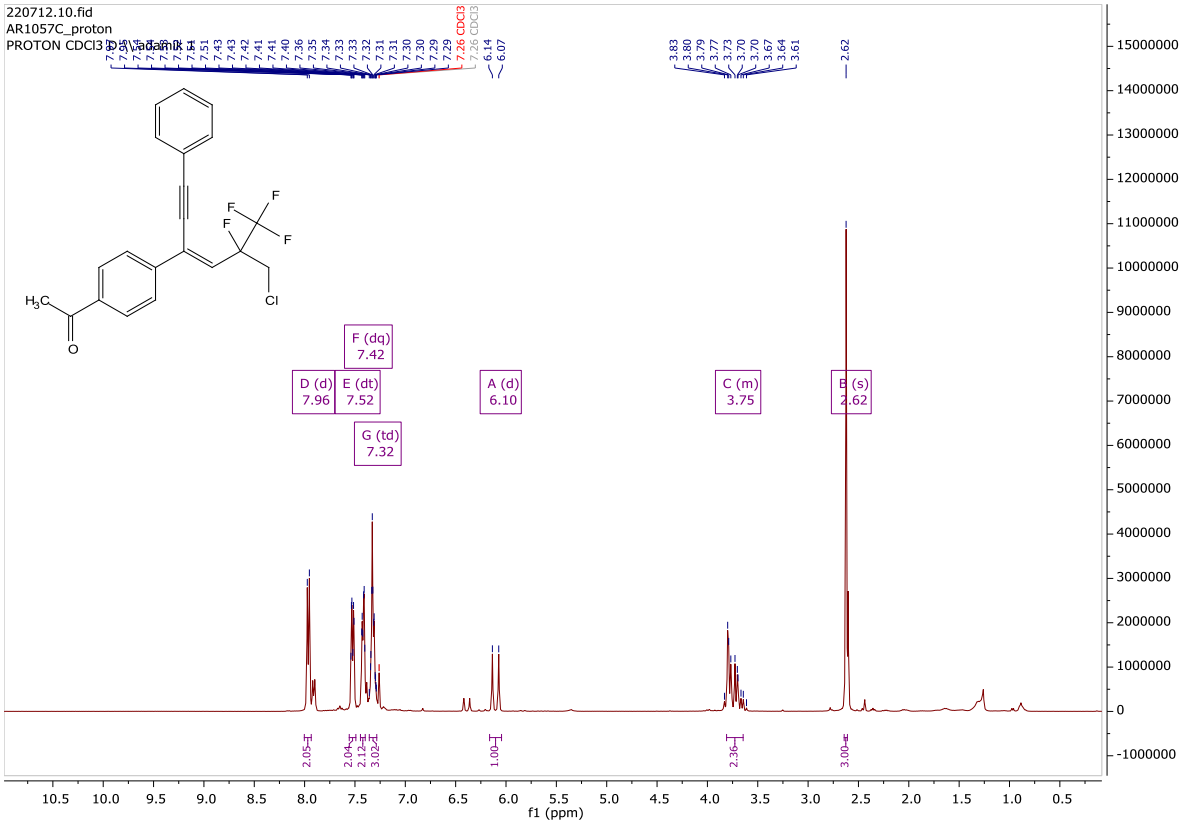
5r


220629.30.fid
AR1057B_proton
PROTON CDCl3 D:\\ adamik 4
f1 (ppm)

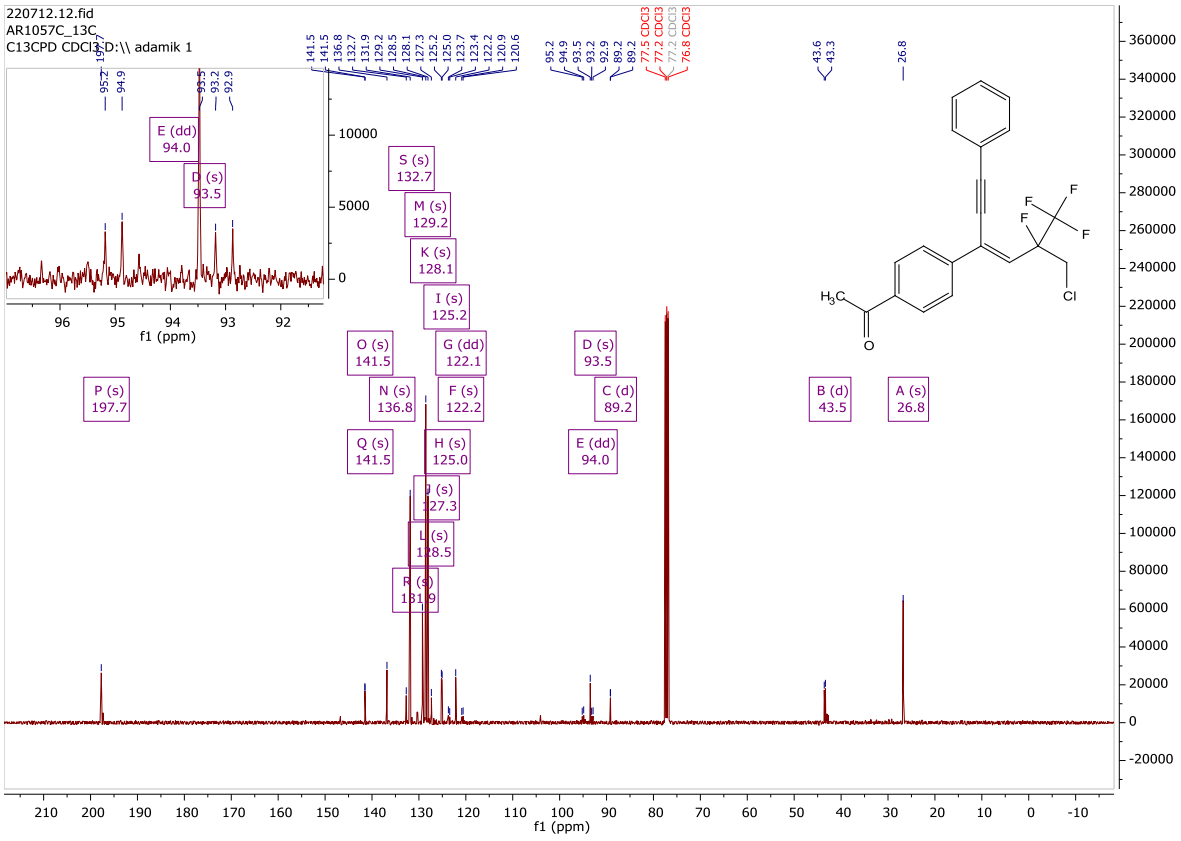

220629.31.fid
AR1057B_19F
F19CPD CDCl3 D:\\ adamik 4
-78.31
-78.33
-167.03
-167.05
-167.07
-167.09
B (d)
-78.32
A (q)
-167.06
3.87
1.00
f1 (ppm)


220629.32.fid
AR1057B_13C
C13CPD CDCl3 D:\\ adamik 4
159.2
137.7
133.6
133.6
131.9
129.1
129.0
128.5
124.7
124.5
123.9
123.6
122.5
121.1
120.8
120.7
120.7
114.2
113.9
113.9
94.8
94.5
92.8
92.7
92.5
89.9
89.9
77.5 CDCl3
77.2 CDCl3
77.2 CDCl3
76.8 CDCl3
55.4
43.2
42.9
E (dd)
93.6
D (s)
92.7
R (s)
129.1
N (s)
128.5
U (s)
133.6
I (s)
122.5
T (s)
133.6
K (s)
124.7
G (d)
113.9
S (s)
159.2
P (s)
137.7
J (s)
124.5
F (s)
114.2
O (s)
131.9
H (dd)
122.4
M (d)
120.7
Q (s)
129.0
D (s)
92.7
C (d)
89.9
E (dd)
93.6
B (s)
55.4
A (d)
43.1
f1 (ppm)

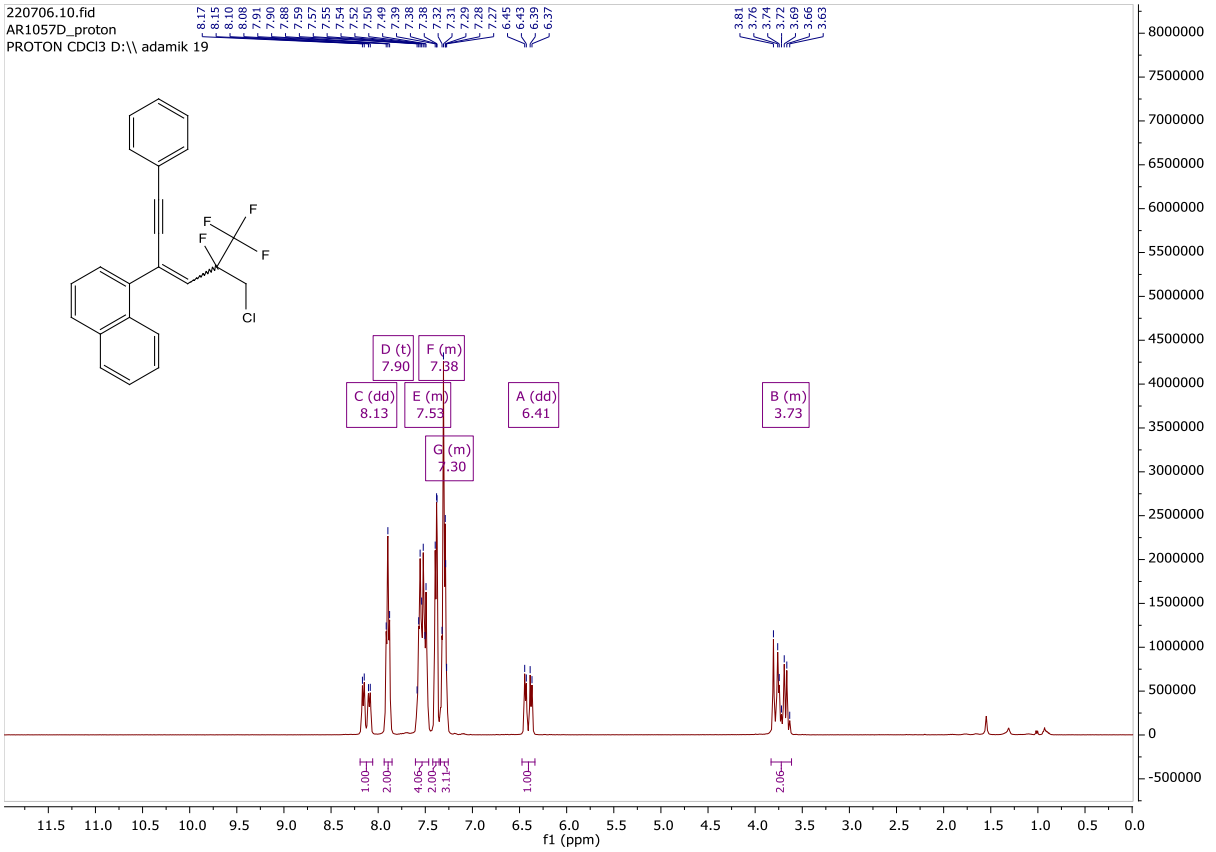
5s

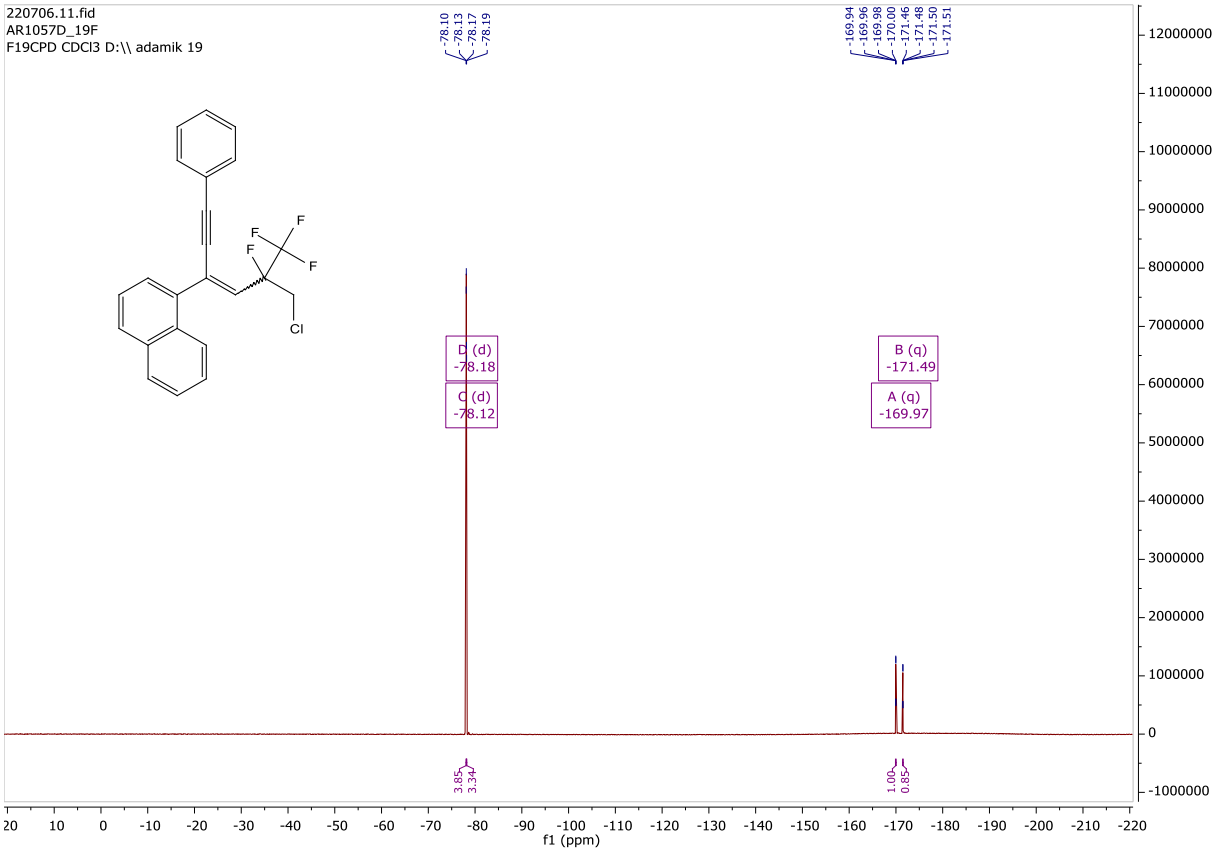

220712.10.fid
AR1057C_proton
PROTON CDCl3 D:\vadamk
F (dq)
7.42
D (d)
7.96
E (dt)
7.52
G (td)
7.32
A (d)
6.10
C (m)
3.75
B (s)
2.62
f1 (ppm)

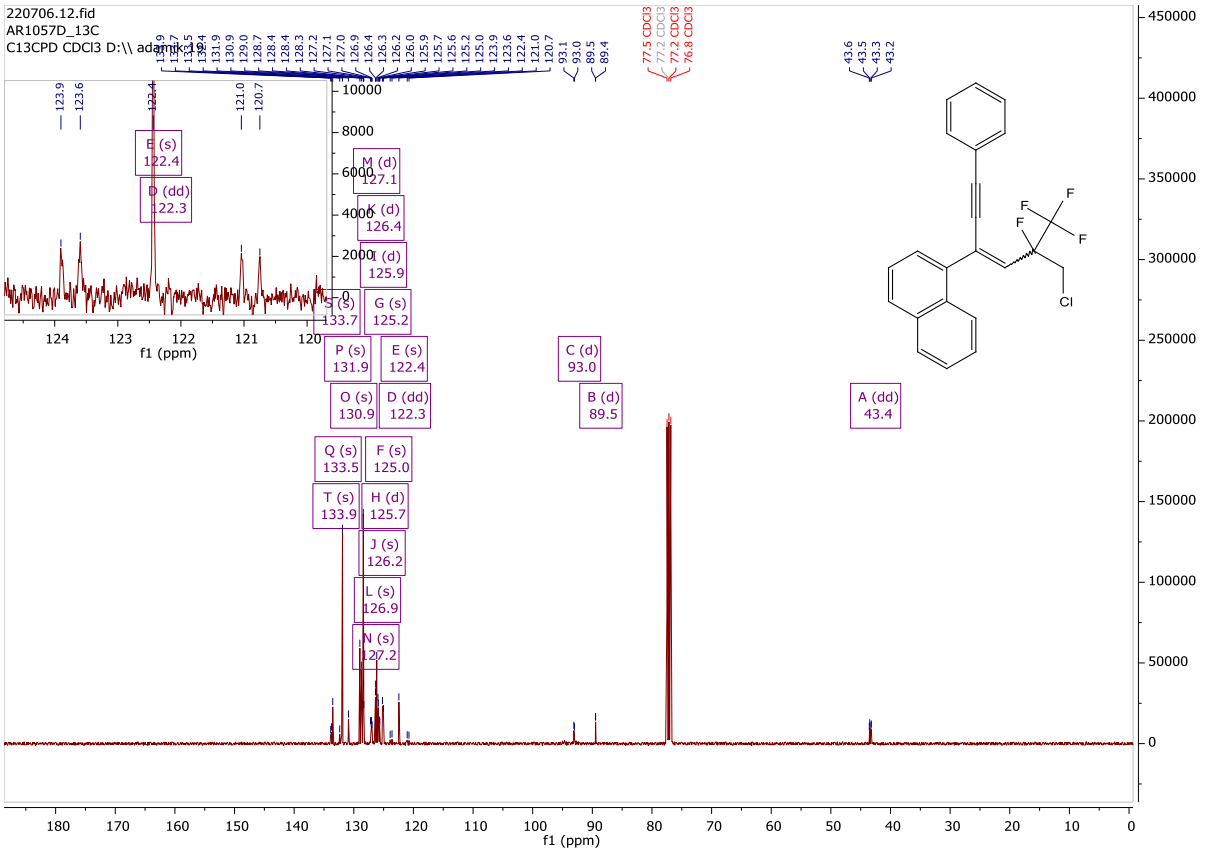

220712.11.fid
AR1057C_19F
F19CPD CDCl3 D:\\ adamik 1
-78.31
-78.33
-78.50
-78.52
-170.12
-170.14
-170.16
-170.18
-171.12
-171.14
-171.16
-171.18
B (d)
-78.32
A (q)
-170.15
4.02
1.00
f1 (ppm)


220712.12.fid
AR1057C_13C
C13CPD CDCl3 D:\\ adamik 1
E (dd)
94.0
D (s)
93.5
S (s)
132.7
M (s)
129.2
K (s)
128.1
I (s)
125.2
O (s)
141.5
G (dd)
122.1
N (s)
136.8
F (s)
122.2
P (s)
197.7
Q (s)
141.5
H (s)
125.0
J (s)
127.3
L (s)
128.5
R (s)
131.9
D (s)
93.5
C (d)
89.2
E (dd)
94.0
B (d)
43.5
A (s)
26.8
f1 (ppm)

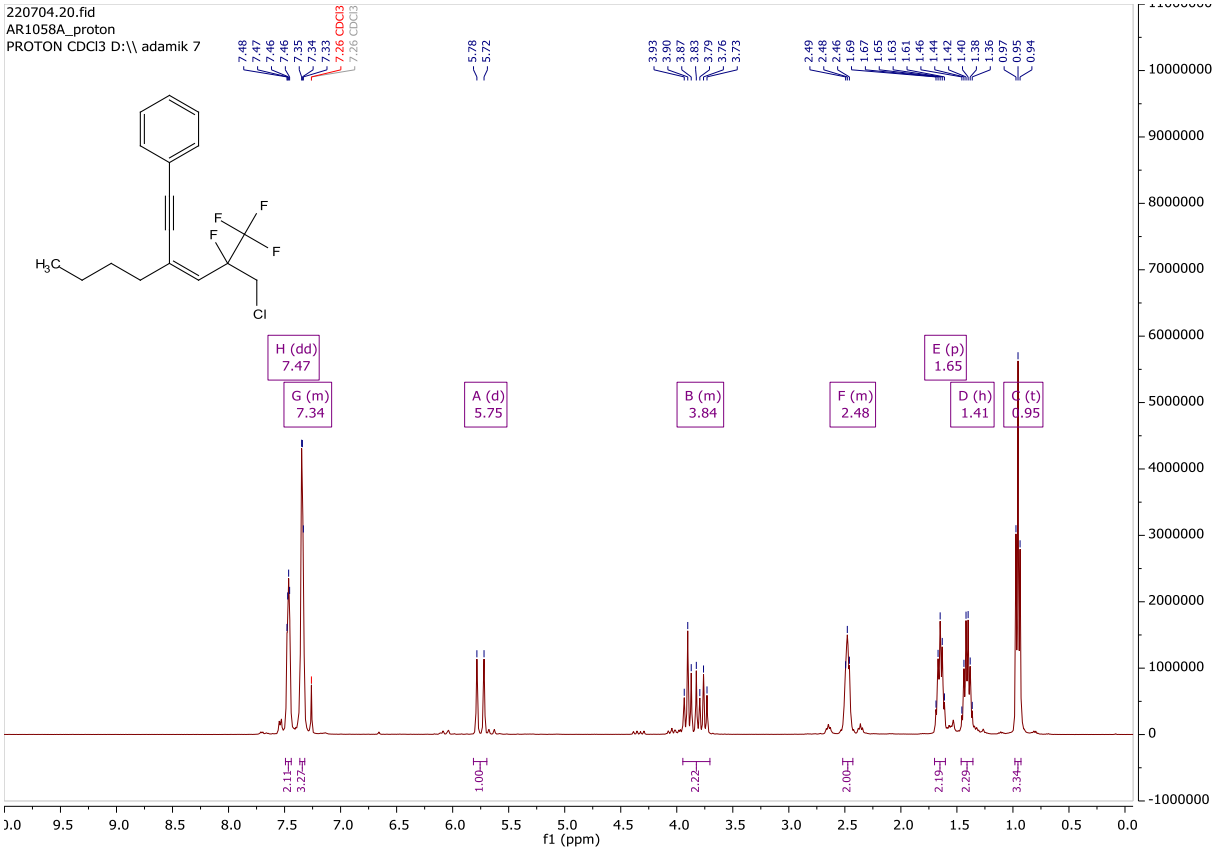
5t

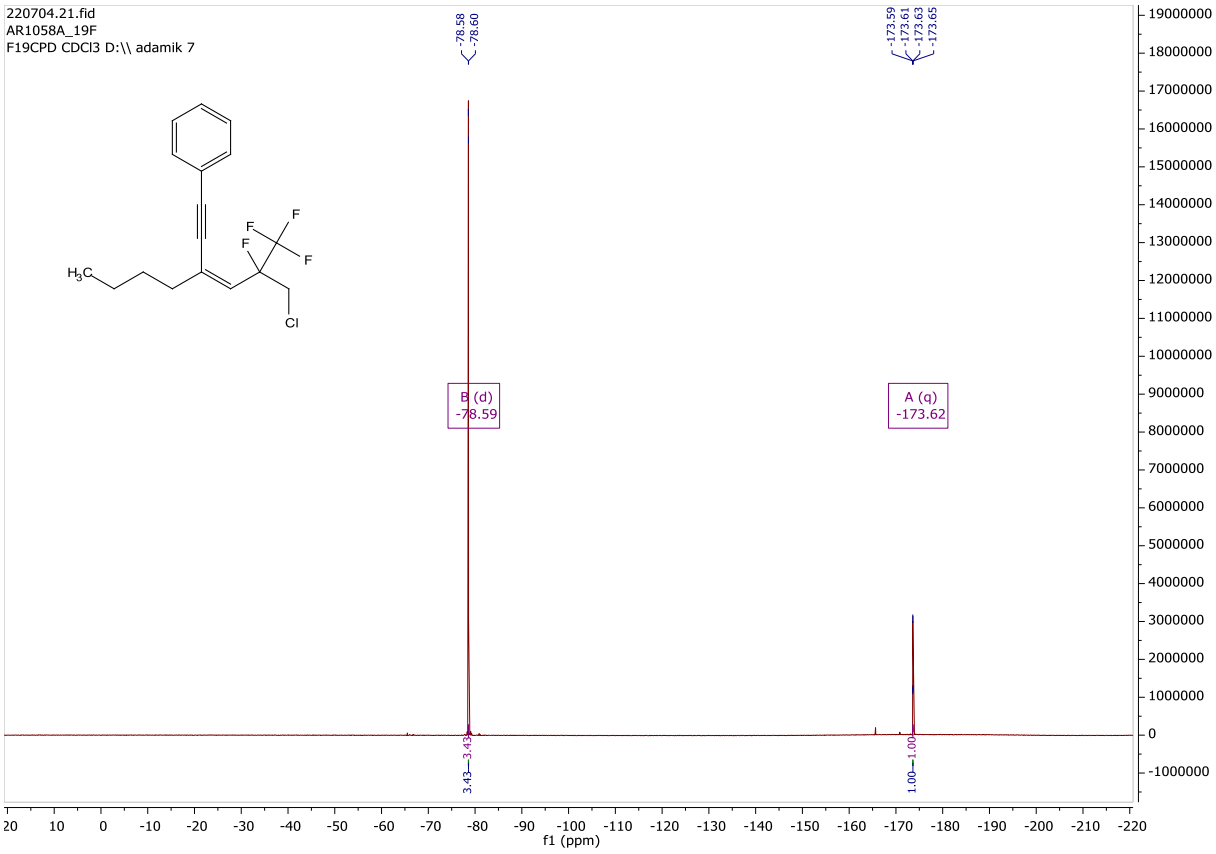

220706.10.fid
AR1057D_proton
PROTON CDCl3 D:\\ adamik 19
D (t) 7.90
F (m) 7.38
C (dd) 8.13
E (m) 7.53
A (dd) 6.41
B (m) 3.73
G (m) 7.30
Cl
f1 (ppm)

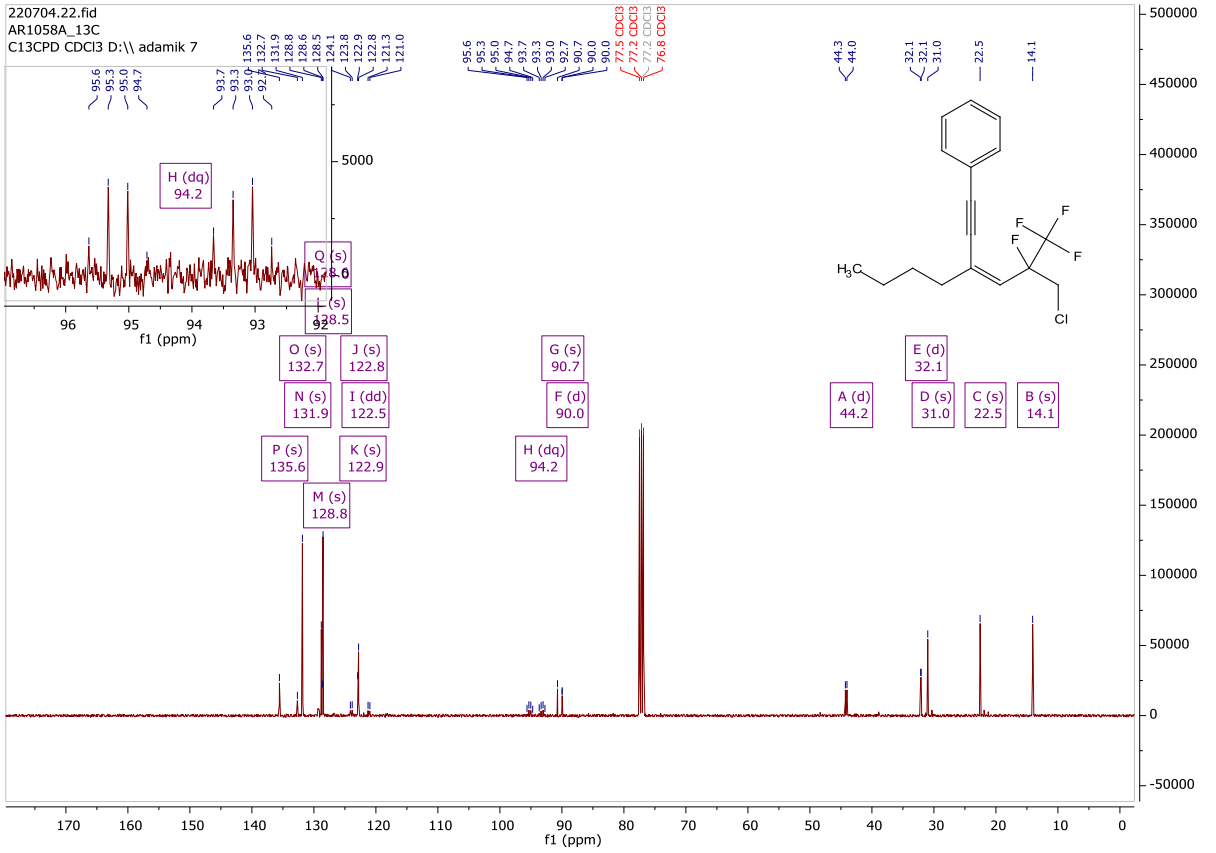

220706.11.fid
AR1057D_19F
F19CPD CDCl3 D:\\ adamik 19
D (d) -78.18
C (d) -78.12
B (q) -171.49
A (q) -169.97
Cl
f1 (ppm)


220706.12.fid
AR1057D_13C
C13CPD CDCl3 D:\\ adamik 19
E (s) 122.4
D (dd) 122.3
M (d) 127.1
K (d) 126.4
I (d) 125.9
S (s) 133.7
G (s) 125.2
P (s) 131.9
E (s) 122.4
O (s) 130.9
D (dd) 122.3
Q (s) 133.5
F (s) 125.0
T (s) 133.9
H (d) 125.7
J (s) 126.2
L (s) 126.9
N (s) 127.2
C (d) 93.0
B (d) 89.5
A (dd) 43.4
f1 (ppm)

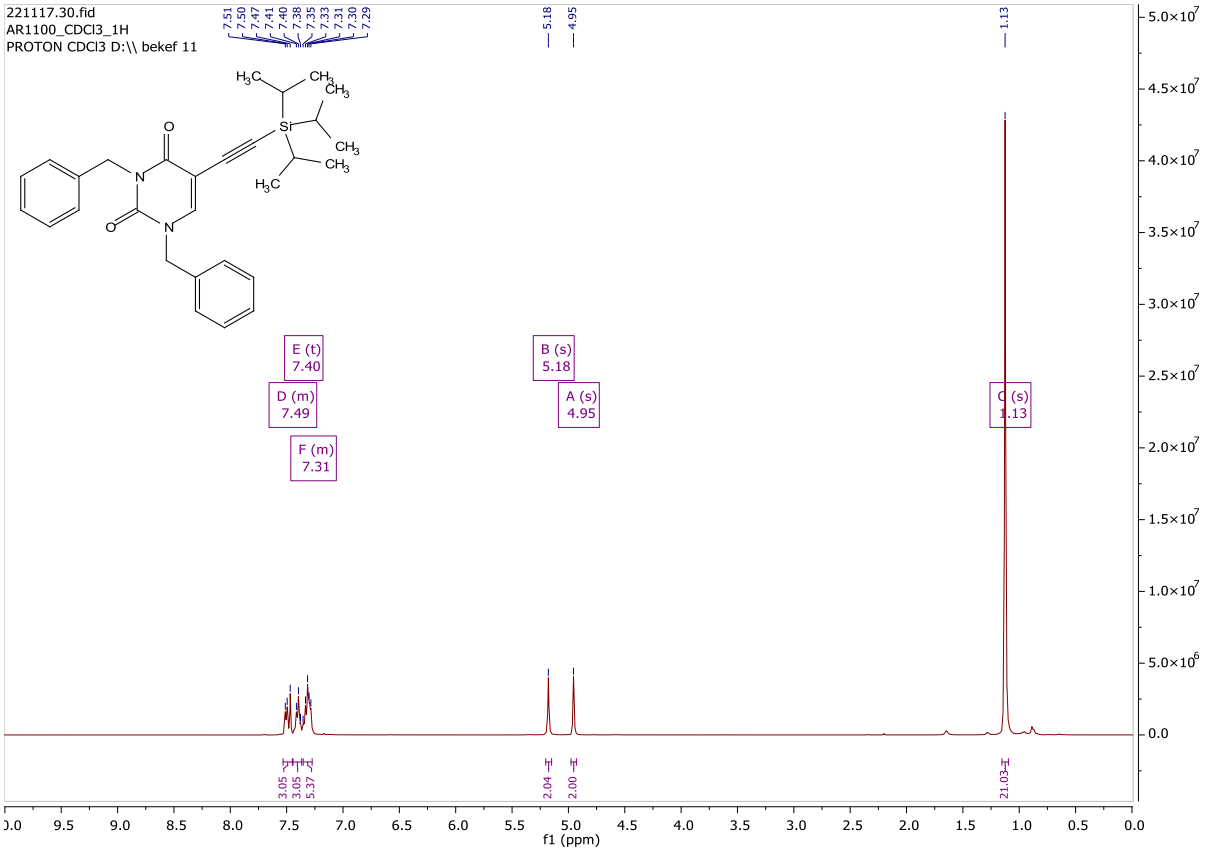
5u

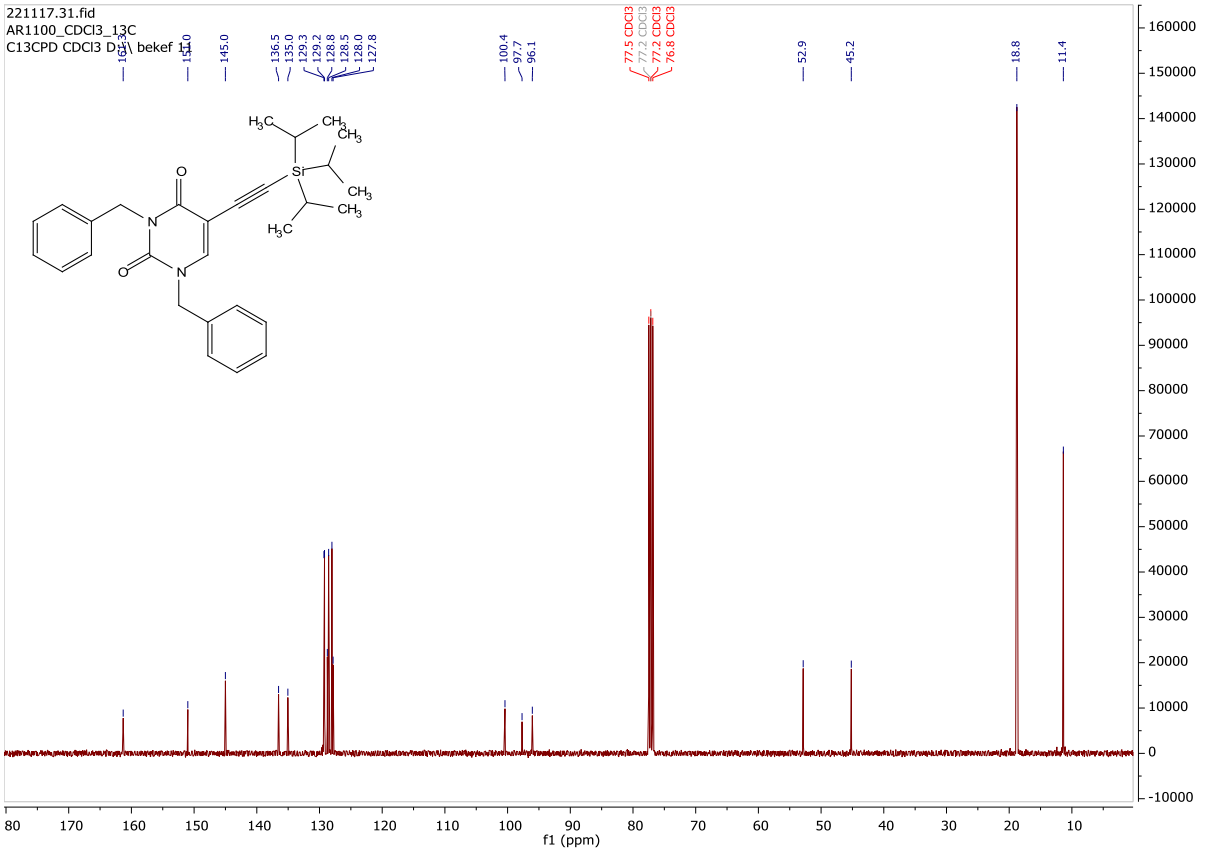

220704.20.fid
AR1058A_proton
PROTON CDCl3 D:\\ adamik 7
H (dd) 7.47
G (m) 7.34
A (d) 5.75
B (m) 3.84
F (m) 2.48
E (p) 1.65
D (h) 1.41
C (t) 0.95
f1 (ppm)


220704.21.fid
AR1058A_19F
F19CPD CDCl3 D:\\ adamik 7
-78.58
-78.60
-173.59
-173.61
-173.63
-173.65
B (d)
-78.59
A (q)
-173.62
3.43
1.00
f1 (ppm)


220704.22.fid
AR1058A_13C
C13CPD CDCl3 D:\\ adamik 7
H (dq)
94.2
Q (s)
78.0
(s)
128.5
O (s)
132.7
J (s)
122.8
N (s)
131.9
I (dd)
122.5
P (s)
135.6
K (s)
122.9
M (s)
128.8
G (s)
90.7
F (d)
90.0
H (dq)
94.2
E (d)
32.1
A (d)
44.2
D (s)
31.0
C (s)
22.5
B (s)
14.1
f1 (ppm)

10e


221117.30.fid
AR1100_CDCl3_1H
PROTON CDCl3 D:\\ bekef 11
7.51
7.50
7.47
7.41
7.40
7.38
7.35
7.33
7.31
7.30
7.29
5.18
4.95
1.13
E (t)
7.40
D (m)
7.49
F (m)
7.31
B (s)
5.18
A (s)
4.95
C (s)
1.13
3.05
3.05
5.37
2.04
2.00
21.03
f1 (ppm)


221117.31.fid
AR1100_CDCl3_13C
C13CPD CDCl3 D:\\ bekef 11
159.3
151.0
145.0
136.5
135.0
129.3
129.2
128.8
128.5
128.0
127.8
100.4
97.7
96.1
77.5 CDCl3
77.2 CDCl3
76.8 CDCl3
52.9
45.2
18.8
11.4
f1 (ppm)

References

[1] D. Lasányi, Á. Mészáros, Z. Novák and G. L. Tolnai, *J. Org. Chem.* 2018, **83**, 8281–8291.
[2] Y.-S. Feng, C.-Q. Xie, W.-L. Qiao and H.-J.Xu, *Org. Lett.* 2013, **15**, 936–939.
[3] A. Elangovan, Y.-H. Wang and T. -I. Ho, *Org. Lett.* 2003, **5**, 1841–1844.
[4] N. G. Kundu and M. W. Khan, *Tetrahedron* 2000, **56**, 4777–4792.
[5] B. Varga, B. L. Tóth, F. Béke, J. T. Csenki, A. Kotschy and Z Novák, *Org. Lett.* 2021, **23**, 4925–4929.
[6] X. Tian, J. Lin, S. Zou, J. Lv, Q. Huang, J. Zhu, S. Huang and Q. Wang, *J. Organomet. Chem.* 2018, **861**, 125–130.
[7] M. O. Akram, A. Das, I. Chakrabarty and N. T. Patil, *Org. Lett.* 2019, **21**, 8101–8105.
[8] S. Naik, G. Bhattacharjya, B. Talukdar and B. K. Patel, *Eur. J. Org. Chem.* 2004, 1254–1260.
[9] C. W. Cheung, M. L. Ploeger, and X. Hu, *ACS Catal.* 2017, **7**, 7092–7096.
[10] Q. Shen, T. Ogata andJ. F. Hartwig, *J. Am. Chem. Soc.* 2008, **130**, 6586–6596.
[11] X. L. Fu, L.-L. Wu, H.-Y Fu, H. Chen and R.-X. Li, *Eur. J. Org. Chem.* **2009**, 2051–2054.
[12] Z. Zhou, H. Liang, W. Xia, H. Chen, Y. Zhang, X. He, S. Yu, R. Cao and L. Qiu, *New J. Chem.* 2018, **42**, 5967–5971.
[13] H. Xu, K. Ekoue-Kovi and C. Wolf *J. Org. Chem.* 2008, **73**, 7638–7650.
[14] K. Inamoto, C. Hasegawa, K. Hiroya, Y. Kondo, T. Osako, Y. Uozumi and T. Doi, *Chem. Commun.* 2012, **48**, 2912.
[15] F. S. Kamounah, and S. J. Titinchi, *Spectroscopy* 1997, **13**, 125–129.
[16] C. Liu, Q. Ni,F. Bao and J. Qiu, *Green Chem.* 2011, **13**, 1260.
[17] B. Liang, M. Dai, J. Chen and Z. Yang, *J. Org. Chem.* 2004, **70**, 391–393.
[18] G. Cahiez, O. J. Gager, Buendia. *Angew. Chem. Int. Ed.* 2010, **49**, 1278–1281.
[19] W. Srimontree, A. Chatupheeraphat, H. H. Liao and M. Rueping, *Org. Lett.* 2017, **19**, 3091–3094.
[20] F. Filace, D. Sucunza, M. L. Izquierdo, C. Burgos, C. and J. Alvarez-Builla, *Tetrahedron* 2013, **69**, 6088–6094.
[21] B. S. Takale, R. R. Thakore, S. Handa, F. Gallou, J. Reilly and B. H Lipshutz, *Chem. Sci.* 2019, **10**, 8825–8831.
[22] V. G. Tribulovich, A. V. Garabadzhiu and I Kalvins, *Russ. J. Gen. Chem.* 2010, **80**, 868–869.
[23] Z. Liu and J. Xiang, *Org. Process Res. Dev.* 2006, **10**, 285–288.
[24] G. Paragi, Z. Kupihár, G. Endre, C. F. Guerra and L. Kovács, *Org. Biomol. Chem.* 2017, **15**, 2174–2184.
[25] M. Alami, B. Crousse and F. Ferri, *J. Organomet. Chem.* 2001, **624**, 114–123.
[26] T. N. Glasnov and C. O. Kappe, *Adv. Synth. Catal.* 2010, **352**, 3089–3097.