Supporting Information

Palladium-catalyzed Aerobic Oxidative Allylic C–H Direct Arylation of Alkenes with Polyfluorobenezenes

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Experimental Procedure and Spectral data

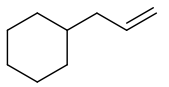
A. General Methods

^1H NMR spectra were recorded in $CDCl_3$ at 400 MHz and ^{13}C NMR spectra were recorded in $CDCl_3$ at 100 MHz respectively, and the chemical shifts (d) were referenced to TMS. GC–MS was

obtained using electron ionization. HRMS was carried out on a MAT 95XP (Thermo). IR spectra were obtained as potassium bromide pellets or as liquid films between two potassium bromide pellets with a Brucker Vector 22 spectrometer. TLC was performed using commercially prepared 100-400 mesh silica gel plates (GF_{254}), and visualization was effected at 254 nm.

1. Substrates

Unactivated Alkenes



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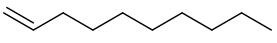

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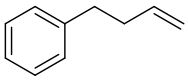

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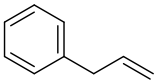
Activated Alkenes



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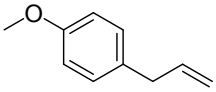

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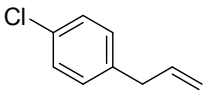

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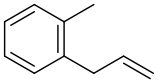

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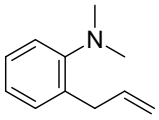

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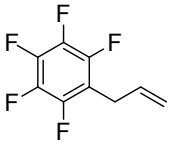

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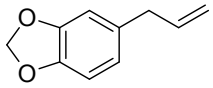

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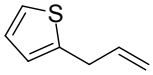

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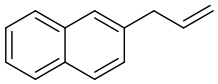

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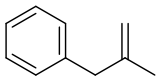

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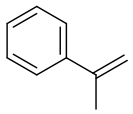

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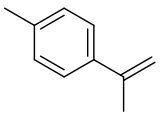

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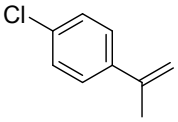

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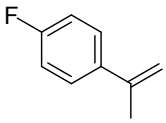

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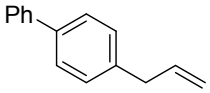

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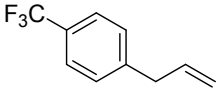
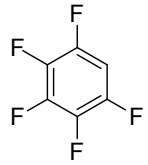


1s

Fluoroarenes



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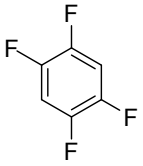

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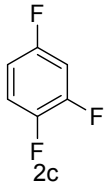

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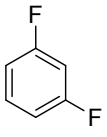

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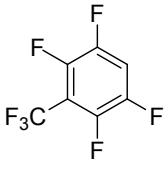

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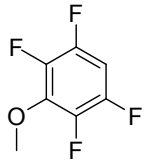
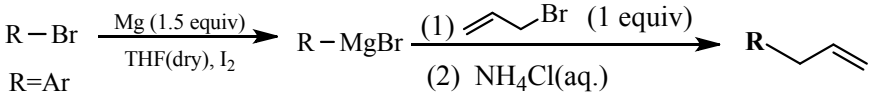


2f

Alkenes substrates **1a,1b,1c,1d,1e,1i,1m,1n,1o,1p,1q** and fluoroarenes were commercial reagents purchased from Sigma-Aldrich, Acros, Alfa Aesar, Strem, and TCI. Other alkenes substrates were synthesized through Grignard reaction

2. Typical reaction procedure for the synthesis of alkenes 1.



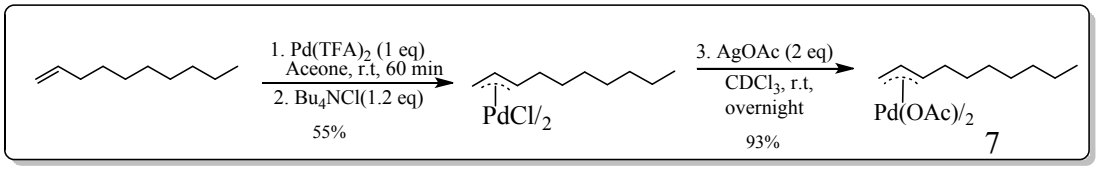
The aryl bromide was reacted with magnesium in THF using I_2 as initiator. After finished the reaction, the combined organics added to the THF solution of allyl bromide with magnetic stirring. After 1 hour, NH_4Cl $_{(aq.)}$ was added to the reaction mixture, washing with water and then concentrated for further purification.

B. General Procedure for the synthesis of 3.

To a septum-capped 25 mL sealed tube were added $Pd(OAc)_2$ (10 mol%) and Ag_2O (11.6 mg, 0.05 mmol, 0.1 equiv). After the sealed tube was refilled with O_2 three times, DMSO (1 mL), DMF (1 mL),and PivOH (25μL, 0.25 mmol, 0.5 equiv) were added with stirring **1** (0.5 mmol 1.0 equiv) and **2** (1.5 mmol, 3.0 equiv) were then added. The sealed tube was screw capped and heated to 120 ^oC (oil bath). After stirring for 24 h, the reaction mixture was cooled to room temperature, diluted with ethyl acetate, washed with H_2O and brine, dried over Na_2SO_4, filtered and concentrated. The crudes mixture were purified by column chromatography to afford allylic arylation product.

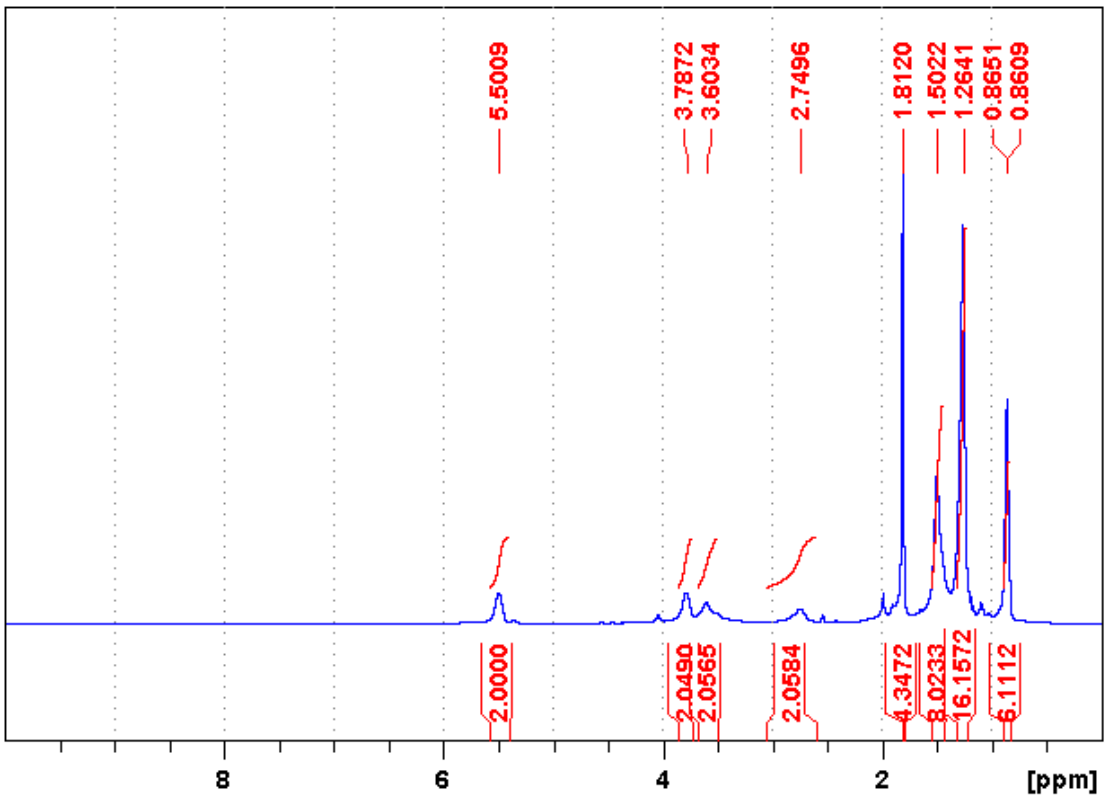
Because the mixture products contain confused C1 arylation and C2 arylation product and the mixtures can not be separated. In order to characterize the compound, some of the mixtures were hydrogenated by Pd/C (10%) under hydrogen (1 atm) in MeOH (10 mL) at room temperature overnight to afford hydrogenated compound with quantity yield. Then the reaction was diluted with solvent and filtered through a pad of cellite. The filtrate was concentrated. The residue was purified with silica gel chromatography to give hydrogenated product.

3. Synthesis of complex 7



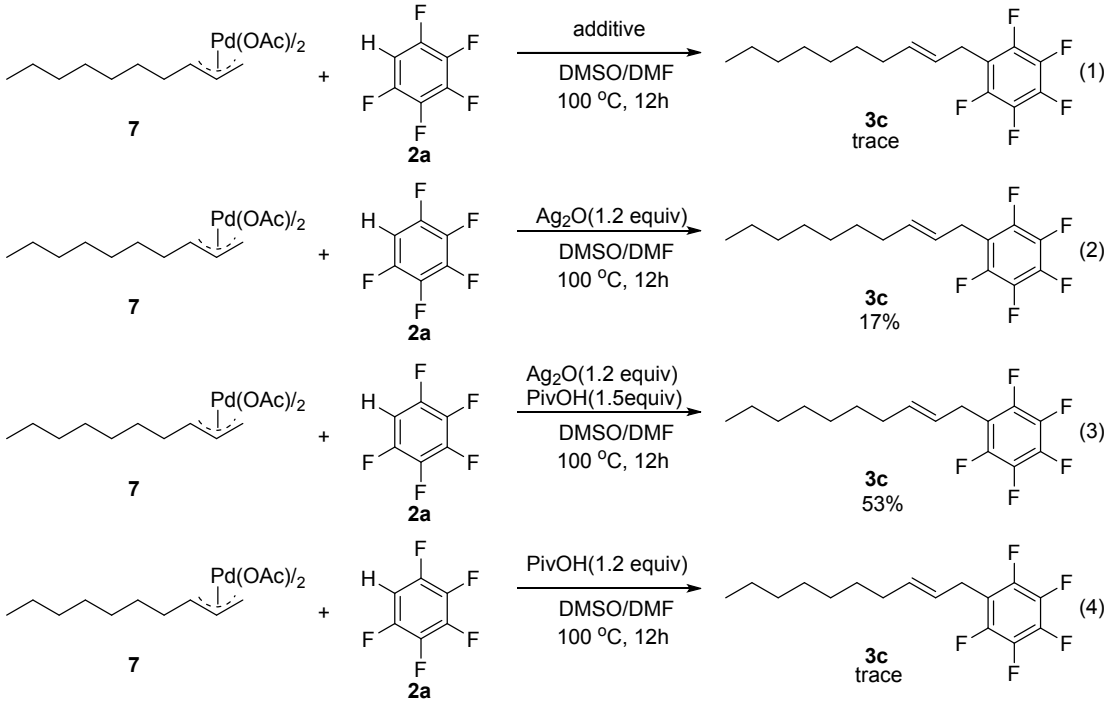
bis[acetate(1,2,3-trihapto-1-undecene)palladium(II)] 7, was synthesized using a literature procedure[1] with 51% yield (two step).

^1H NMR (400 MHz, DMSO-d_6) δ 5.49 (bs, 2H), 3.79 (bs, 2H), 3.60 (bs, 2H), 2.75 (bs, 2H), 1.81 (s, 4H), 1.50 (bs, 8H), 1.26 (bs, 16H), 0.86 (d, J = 1.7 Hz, 6H). This compound spectroscopy is consistent with the literature.[2] [^1H NMR (300 MHz, DMF-d7) δ 5.52 (bs, 2H), 3.74 (bs, 2H), 3.57 (bd, J = 5.7Hz, 2H), 2.69 (bs, 2H), 1.86 (bs, 4H), 1.42 (bs, 8H), 1.28 (bs, 16H), 0.86 (bs, 6H).]



4. Control Experiment

Reation of complexe 7 with pentafluorobenzene (2a).

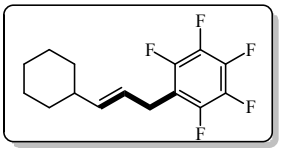


Typical procedure for reactions of complexe 7 with pentafluorobenzene. To a septum capped 25 mL of sealed tube were added **7** (0.3 mmol, 1 equiv), **2a** (3 equiv.), additive under N_2, followed by DMSO (1 mL), DMF (1 mL) with stirring. The sealed tube was screw capped and heated to 100

°C (oil bath). After stirring for 12h, the reaction mixture was cooled to room temperature and then detected by ^{19}F NMR.

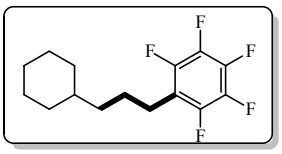
C. Characterization data for all prepared compounds:

The datas of unhydrogenated product are based on NMR analysis of the unpurified reaction mixture and not corrected for small response variations.



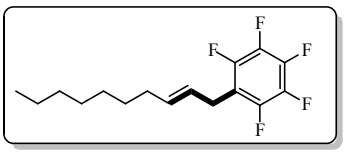
(E)-1-(3-cyclohexylallyl)-2,3,4,5,6-pentafluorobenzene(3a).[3]

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.44 (dtd, J = 21.7, 15.4, 6.3 Hz, 2H), 3.36 (d, J = 6.1 Hz, 2H), 1.91 (dt, J = 13.9, 7.5 Hz, 1H), 1.72 - 1.63 (m, 4H), 1.27 - 1.12 (m, 4H), 1.08 - 0.97 (m, 2H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -144.4 (dd, J = 22.2, 8.3 Hz, 2F), -158.2 (t, J = 20.7 Hz, 1F), -163.1 (dt, J = 22.2, 8.5 Hz, 2F).



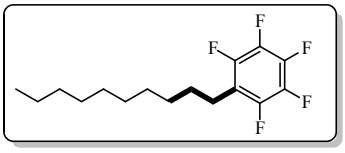
1-(3-cyclohexylpropyl)-2,3,4,5,6-pentafluorobenzene(5a).[4]

^{1}H NMR (400 MHz, $CDCl_3$) δ 2.70 (t, J = 7.6 Hz, 2H), 1.77 - 1.59 (m, 8H), 1.22 (ddd, J = 34.5, 17.2, 8.6 Hz, 5H), 0.90 (dd, J = 20.5, 10.6 Hz, 2H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -144.7 (dd, J = 22.3, 8.4 Hz, 2F), -158.7 (t, J = 20.7 Hz, 1F), -163.4 (td, J = 22.2, 8.3 Hz, 2F); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.0 (dm, J = 244.6 Hz), 139.4 (dm, J = 249.0 Hz), 137.4 (dm, J = 250.2 Hz), 115.6 (t, J = 20.9 Hz), 37.4, 36.9, 33.3, 26.7, 26.6, 26.3, 22.6; IR (KBr, cm^{-1}) ν 2926, 1745, 1508, 1454.



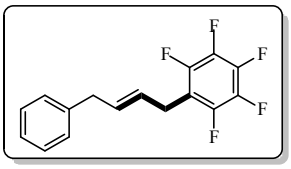
(E)-1-(dec-2-en-1-yl)-2,3,4,5,6-pentafluorobenzene(3b).[4]

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.59 - 5.41 (m, 2H), 3.38 (d, J = 6.1 Hz, 2H), 1.98 (dt, J = 11.3, 5.7 Hz, 2H), 1.26 (s, 10H), 0.88 (t, J = 6.1 Hz, 3H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -144.5 (dd, J = 22.2, 8.3 Hz, 2F), -158.3 (t, J = 20.4 Hz, 1F), -163.2 (ddd, J = 20.9, 8.3, 7.4 Hz, 2F).



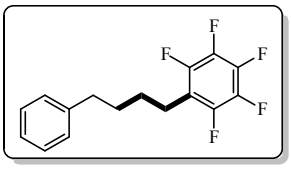
1-decyl-2,3,4,5,6-pentafluorobenzene(5b).[4]

^{1}H NMR (400 MHz, $CDCl_3$) δ 2.68 (d, J = 5.8 Hz, 1H), 1.56 (s, 1H), 1.28 (d, J = 17.8 Hz, 9H), 0.92 - 0.84 (m, 2H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -144.64 (d, J = 21.8 Hz, 2F), -158.65 (t, J = 20.7 Hz, 1F), -163.27 - -163.47 (m, 2F); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.0 (dm, J = 244.7 Hz), 139.3 (dm, J = 252.0 Hz), 137.4 (dm, J = 248.0 Hz), 115.6 (m), 31.9, 29.7, 29.6, 29.5, 29.3, 29.2, 29.1, 22.7, 22.3, 14.0; IR (KBr, cm^{-1}) ν 2928, 1653, 1508, 1461.



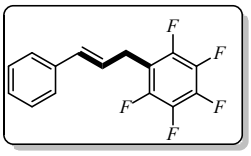
(E)-1,2,3,4,5-pentafluoro-6-(4-phenylbut-2-en-1-yl)benzene(3c)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (t, J = 7.5 Hz, 2H), 7.20 - 7.12 (m, 3H), 5.73 - 5.65 (m, 1H), 5.58 - 5.50 (m, 1H), 3.40 (d, J = 6.1 Hz, 2H), 3.33 (d, J = 6.6 Hz, 2H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -144.2 (dd, J = 22.3, 8.5 Hz, 2F), -157.8 (t, J = 20.8 Hz, 1F), -162.8 (dt, J = 22.4, 8.6 Hz, 2F).



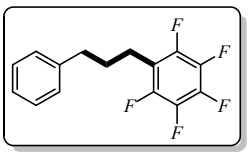
1,2,3,4,5-pentafluoro-6-(4-phenylbutyl)benzene(5c)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (t, J= 7.4 Hz, 2H), 7.16 (t, J= 8.6 Hz, 3H), 2.71 (t, J= 6.8 Hz, 2H), 2.63 (t, J= 7.1 Hz, 2H), 1.65 (dt, J= 9.2, 5.4 Hz, 4H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -144.4 (dd, J = 22.4, 8.3 Hz, 2F), -158.3 (t, J = 20.8 Hz, 1F), -163.1 (td, J = 22.0, 8.2 Hz, 2F); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.1 (dm, J = 243.4 Hz), 142.0, 139.7 (dm, 249.7 Hz), 137.4 (dm, J = 250.0Hz), 128.4, 125.9, 115.3 (t, J = 19.0 Hz), 35.5, 30.8, 28.8, 22.2; IR (KBr, cm^{-1}) ν 2934, 1663, 1506, 1457; HRMS (EI) m/z (M^+) calcd for $C_{16}H_{13}F_5$: 300.0937, found: 300.0933.



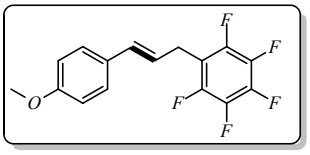
1-cinnamyl-2,3,4,5,6-pentafluorobenzene(3d).[4]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (qd, J = 8.2, 4.0 Hz, 5H), 6.44 (d, J = 15.8 Hz, 1H), 6.23 - 6.14 (m, 1H), 3.55 (dd, J = 6.7, 1.2 Hz, 2H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -144.1 (dd, J = 22.2, 8.4 Hz, 2F), -157.5 (t, J = 20.7 Hz, 1F), -162.7 (dt, J = 22.2, 8,6 Hz, 2F).



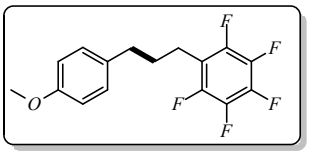
1,2,3,4,5-pentafluoro-6-(3-phenylpropyl)benzene(5d).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (dd, J = 9.9, 5.2 Hz, 2H), 7.28 (dd, J = 10.1, 4.4 Hz, 3H), 2.83 (t, J = 7.7 Hz, 2H), 2.78 (t, J = 7.8 Hz, 2H), 2.10 - 1.97 (m, 2H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -144.3 (dd, J = 22.3, 8.3 Hz, 2F), -158.2 (t, J = 20.7 Hz, 1F), -163.2 (dt, J = 14.4, 11.4 Hz, 2F); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.1(dm, J = 243.5 Hz), 141.2, 139.6(dm, J = 249.7 Hz), 137.5(dm, J = 250.3 Hz), 128.4, 128.3, 126.1, 115.2 (m), 35.4, 30.7, 22.1; IR (KBr, cm^{-1}) ν 2934, 1741, 1507, 1454; HRMS (EI) m/z (M^+) calcd for $C_{15}H_{11}F_5$: 286.0781, found: 286.0774.



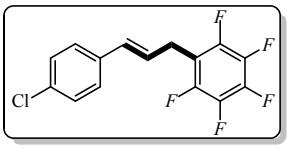
(E)-1,2,3,4,5-pentafluoro-6-(3-(4-methoxyphenyl)allyl)benzene(3e).[4]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 - 7.23 (m, 2H), 6.82 (d, J = 8.7 Hz, 2H), 6.41 (d, J = 15.7 Hz, 1H), 6.10 - 6.02 (m, 1H), 3.78 (s, 3H), 3.55 (d, J = 6.7 Hz, 2H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -144.0 (dd, J = 22.3, 8.3 Hz, 2F), -157.5 (t, J = 20.8 Hz, 1F), -162.7 (td, J = 22.2, 8.5 Hz, 2F).



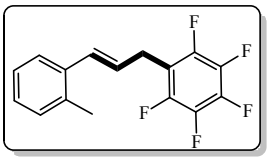
1,2,3,4,5-pentafluoro-6-(3-(4-methoxyphenyl)propyl)benzene(5e).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.08 (d, J = 8.4 Hz, 2H), 6.82 (d, J = 8.5 Hz, 2H), 3.78 (s,3H), 2.71 (t, J = 7.6 Hz, 2H), 2.61 (t, J = 7.7 Hz, 2H), 1.92 - 1.83 (m, 2H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -144.2 (dd, J = 22.4, 8.3 Hz, 2F), -158.1 (t, J = 20.8 Hz, 1F), -163.02(td, J = 22.1, 8.3 Hz, 2F); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.0, 145.0 (dm, J = 245.1 Hz), 139.5 (dm, J = 249.6 Hz), 137.4 (dm, J = 248.4 Hz), 133.2, 129.2, 115.2 (t, J = 18.8 Hz), 55.3, 34.5, 30.9, 22.0; IR (KBr, cm^{-1}) ν 2939, 1664, 1509, 1458; HRMS (EI) m/z (M^+) calcd for $C_{16}H_{13}F_5O$: 316.0887, found: 316.0882.



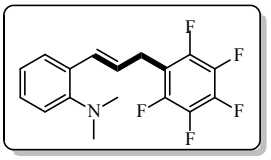
(E)-1-(3-(4-chlorophenyl)allyl)-2,3,4,5,6-pentafluorobenzene(3f).[4]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (s, 4H), 6.45 (d, J = 15.8 Hz, 1H), 6.27 - 6.18 (m, 1H), 3.62 (d, J = 6.7 Hz, 2H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -143.9 (dd, J = 22.2, 8.3 Hz, 2F), -157.0 (t, J = 20.8 Hz, 1F), -162.4 (td, J = 22.0, 8.5 Hz, 2F).



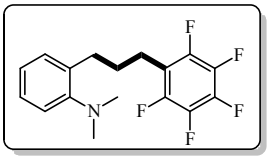
(E)-1,2,3,4,5-pentafluoro-6-(3-(o-tolyl)allyl)benzene(3g).[5]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (br, 1H), 7.13 (d, J = 3.4 Hz, 3H), 6.71 (d, J = 15.6 Hz, 1H), 6.06 (m, 1H), 3.61 (d, J = 6.8 Hz, 2H), 2.31 (s, 3H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -144.0 (dd, J = 22.2, 8.4 Hz, 2F), -157.3 (t, J = 20.7 Hz, 1F), -162.6 (dt, J = 22.2, 8.5 Hz, 2F); IR (KBr, cm^{-1}) ν 2925, 1650, 1506, 1459.



(E)-N,N-dimethyl-2-(3-(perfluorophenyl)prop-1-en-1-yl)aniline(3h).

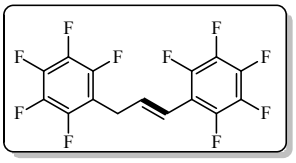
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, J = 7.6 Hz, 1H), 7.18 (t, J = 6.4 Hz, 1H), 7.01 - 6.92 (m, 2H), 6.78 (d, J = 15.9 Hz, 1H), 6.17 - 6.08 (m, 1H), 3.62 (d, J = 6.4 Hz, 2H), 2.68 (s, 6H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -144.0 (dd, J = 22.3, 8.4 Hz, 2F), -157.5 (t, J = 20.8 Hz, 1F), -162.7 (td, J = 21.7, 8.3 Hz, 2F).



N,N-dimethyl-4-(3-(perfluorophenyl)propyl)aniline(5h).

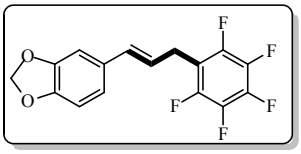
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 (t, J = 7.1 Hz, 2H), 7.11 (d, J = 7.8 Hz, 1H), 7.01 (t, J = 7.1 Hz, 1H), 2.76 (t, J = 6.8 Hz, 4H), 2.65 (s, 6H), 2.02 - 1.90 (m, 2H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -144.3

(dd, J = 21.9, 7.3 Hz, 2F), -158.4 (t, J = 20.8 Hz, 1F), -163.2 (td, J = 21.9, 8.1 Hz, 2F); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.9, 145.1 (dm, J = 245.1 Hz), 139.4 (dm, J = 249.6 Hz), 137.4 (dm, J = 250.1 Hz), 135.9, 129.4, 126.9, 123.4, 119.6, 115.4 (t, J = 19.0 Hz), 45.1, 30.4, 29.7, 22.4. IR (KBr, cm^{-1}) v 2931, 1740, 1506, 1458; HRMS (EI) m/z (M^+) calcd for $C_{15}H_{11}F_5$: 329.1203, found: 329.1198.



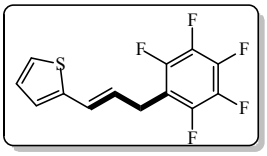
(E)-6,6'-(prop-1-ene-1,3-diyl)bis(1,2,3,4,5-pentafluorobenzene)(3i):

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.62 - 6.53 (m, 1H), 6.40 (d, J = 16.3 Hz, 1H), 3.66 (d, J = 6.4 Hz, 2H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -143.0 (dd, J = 21.4, 7.7 Hz, 2F), -143.6 (dd, J = 22.1, 8.4 Hz, 2F), -156.0 (t, J = 20.8 Hz, 1F), -156.2 (t, J = 20.8 Hz, 1F), -162.0 (dt, J = 21.8, 8.5 Hz, 2F), -162.9 (dt, J = 21.3, 8.0 Hz, 2F); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.1 (dm, J = 245.0 Hz), 144.7 (dm, 249.0), 141.4 (m), 138.9 (m), 136.4 (m), 133.9 (t, J = 9.0 Hz), 116.9, 115.3, 112.0 (t, J = 18.6 Hz), 111.4 (dd, J = 18.3, 14.1 Hz), 26.7; IR (KBr, cm^{-1}) v 2988, 1747, 1651, 1508 cm^{-1}; HRMS (EI) m/z (M^+) calcd for $C_{15}H_4F_{10}$: 374.0153, found: 374.0149.



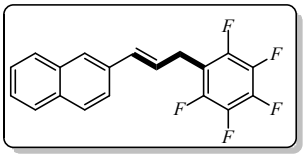
(E)-5-(3-(perfluorophenyl)prop-1-en-1-yl)benzo[d][1,3]dioxole(3j).[4]

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.85 (d, J = 1.3 Hz, 1H), 6.76 - 6.71 (m, 2H), 6.38 (d, J = 15.7 Hz, 1H), 6.03 (dt, J = 15.6, 6.8 Hz, 1H), 5.93 (s, 2H), 3.55 (dd, J = 6.8, 1.2 Hz, 2H).^{19}F NMR (376 MHz, $CDCl_3$) δ -143.99 (dd, J= 22.3, 8.4 Hz, 2F), -157.36 (t, J= 20.8 Hz, 1F), -162.56 (m, 2F).



(E)-2-(3-(perfluorophenyl)prop-1-en-1-yl)thiophene(3k).

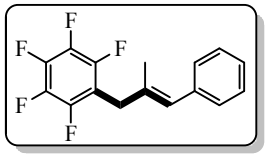
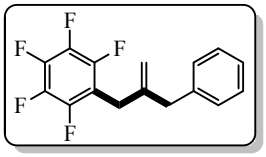
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, J = 3.7 Hz, 1H), 6.87 (d, J = 3.7 Hz, 1H), 6.01 (ddt, J = 16.7, 10.0, 6.7 Hz, 1H), 5.24 - 5.13 (m, 2H), 3.61 (d, J = 6.6 Hz,2H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -140.4 (dd, J = 21.8, 6.8 Hz, 2F), -156.8 (t, J = 21.1 Hz, 1F), -162.4 - -162.5 (m, 2F); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.4, 143.9 (dm, J = 252.0 Hz), 139.6 (dm, J = 253.0 Hz), 138.0 (dm, J = 251.0 Hz), 135.6, 130.3, 125.1, 124.4, 117.0, 110.2 (m), 34.1; IR (KBr, cm^{-1}) v 2979, 1644, 1495, 1407; HRMS (EI) m/z (M^+) calcd for $C_{13}H_7F_5S$: 290.0189, found: 290.0184.



(E)-2-(3-(perfluorophenyl)prop-1-en-1-yl)naphthalene(3l).

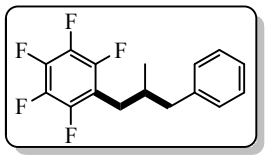
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (t, J = 8.3 Hz, 3H), 7.67 (s, 1H), 7.52 (d, J = 8.6 Hz, 1H), 7.43 (br, 2H), 6.62 (d, J = 15.7 Hz, 1H), 6.37 -6.29 (m, 1H), 3.63 (d, J = 6.6 Hz, 2H); ^{19}F NMR (376 MHz,

$CDCl_3$) δ -143.84 (dd, J= 22.2, 8.4 Hz, 2F), -157.18 (t, J= 20.8 Hz, 1F), -162.43 (dt, J= 22.2, 8.4 Hz, 2F); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.1(dm, J = 244.6 Hz), 139.9(dm, J = 250.4 Hz), 137.6(dm, J = 255.1 Hz), 134.1, 133.6, 133.0, 132.6, 128.3, 128.0, 127.7, 126.3, 126.2, 125.9, 124.7, 123.3, 113.3(t, J= 18.8 Hz), 25.7; IR (KBr, cm^{-1}) ν 2923, 1747, 1650, 1499; HRMS (EI) m/z (M^+) calcd for $C_{19}H_{11}F_5$: 334.0781, found: 334.0774.

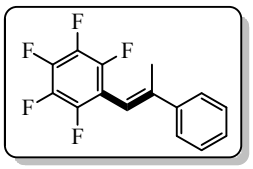
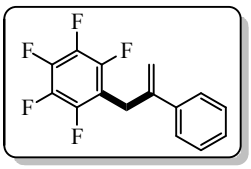

($3m_1$)(E:Z=3.3:1) mixed with 
($3m_2$)

(E)-1,2,3,4,5-pentafluoro-6-(2-methyl-3-phenylallyl)benzene($3m_1$).[5]

^1H NMR (400 MHz, $CDCl_3$) δ 7.34 - 7.30 (m, 2H), 7.24 (d, J = 7.9 Hz, 3H), 5.91 (s, 1H), 3.54 (s, 2H), 1.61 (d, J = 1.3 Hz, 3H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -139.8 - -140.0 (m, 2F), -157.1 (t, J = 20.8 Hz, 1F), -163.2 - -163.3 (m, 2F).

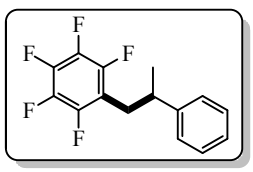

1,2,3,4,5-pentafluoro-6-(2-methyl-3-phenylpropyl)benzene(5m).

^1H NMR (400 MHz, $CDCl_3$) δ 7.26 (t, J = 7.3 Hz, 2H), 7.22 - 7.11 (m, 3H), 2.69 (ddd, J = 20.4, 13.6, 6.1 Hz, 2H), 2.53 (dt, J = 13.5, 9.1 Hz, 2H), 2.10 (dq, J = 14.5, 7.3 Hz, 1H), 0.86 (d, J = 6.7 Hz, 3H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -142.9 (dd, J = 22.5, 8.3 Hz, 2F), -157.9 (t, J = 20.8 Hz, 1F), -163.1 (dt, J = 22.5, 8.5 Hz, 2F); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.2 (dm, J = 243.4 Hz), 140.2, 139.5 (dm, J = 249.8 Hz), 137.4 (dm, J = 250.2 Hz), 129.0, 128.3, 126.1, 114.4 (m), 43.4, 35.3, 29.5, 19.0; IR (KBr, cm^{-1}) ν 2925, 1744, 1505, 1457; HRMS (EI) m/z (M^+) calcd for $C_{16}H_{13}F_5$: 300.0937, found: 300.0934.


(4n) (E:Z=3.3:1) and 
(3n)

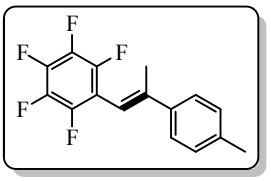
(E)-1,2,3,4,5-pentafluoro-6-(2-phenylprop-1-en-1-yl)benzene (4n indicated by*) and 1,2,3,4,5-pentafluoro-6-(2-phenylallyl)benzene(3ka).[6]

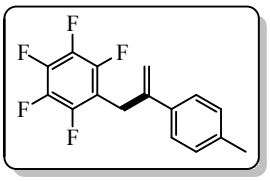
^1H NMR (400 MHz, $CDCl_3$) δ 7.53 (dd, J = 8.2, 1.3 Hz, 2H*), 7.45 - 7.29 (m, 3H*, 5H), 6.39 - 6.38 (m, 1H*), 5.37 (s, 1H), 4.87 (s, 1H), 3.86 (s, 2H), 2.08 (dd, J = 3.3, 2.0 Hz, 3H*); ^{19}F NMR (376 MHz, $CDCl_3$) δ -139.2 (dd, J = 23.0, 8.1 Hz, 2F*), -142.8 (dd, J = 22.2, 8.3 Hz, 2F*), -156.4 (t, J = 20.8 Hz, 1F*), -156.7 (t, J = 20.8 Hz, 1F), -162.5 - -162.7 (m, 2F), -162.8 - -162.9 (m, 2F*).



1,2,3,4,5-pentafluoro-6-(2-phenylpropyl)benzene(5n)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 - 7.35 (m, 2H), 7.29 (t, J= 6.6 Hz, 3H), 3.17 (dq, J= 14.1, 7.0 Hz, 1H), 3.11 - 2.99 (m, 2H), 1.41 (t, J= 7.3 Hz, 3H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -143.2 (dd, J = 22.3, 8.1 Hz, 2F), -157.7 (t, J = 20.7 Hz, 1F), -163.2 (dt, J = 22.4, 8.4 Hz, 2F); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.2 (dm, J = 244.0 Hz), 145.2, 139.6 (dm, J = 249.3), 137.4 (dm, J = 252.0 Hz), 128.5, 126.7, 126.7, 114.1 (m), 39.8, 31.4, 20.8; IR (KBr, cm^{-1}) v 2970, 1654, 1504, 1456; HRMS (EI) m/z (M^+) calcd for $C_{15}H_{11}F_5$: 286.0781, found: 286.0785.

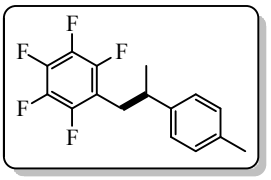


(4o) (E:Z=3.3:1) and 

(3o)

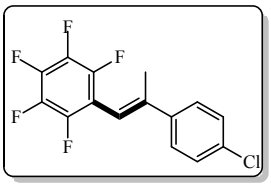
(E)-1,2,3,4,5-pentafluoro-6-(2-(p-tolyl)prop-1-en-1-yl)benzene(4la indicated by*) and 1,2,3,4,5-pentafluoro-6-(2-(p-tolyl)allyl)benzene(3la)

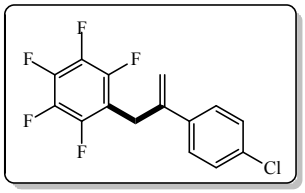
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, J = 8.2 Hz, 2H*), 7.32 (d, J = 8.1 Hz, 2H), 7.19 (d, J = 8.0 Hz, 2H*), 7.14 (d, J = 8.0 Hz, 2H), 6.36 (s, 1H*), 5.34 (s, 1H), 4.82 (s, 1H), 3.84 (s, 2H), 2.37 (s, 3H*), 2.34 (s, 2H), 2.05 (d, J = 1.2 Hz, 3H*); ^{19}F NMR (376 MHz, $CDCl_3$) δ -139.2 (dd, J = 23.0, 8.0 Hz, 2F*), -142.8 (dd, J = 22.1, 8.2 Hz, 2F), -156.6 (t, J = 20.8 Hz, 1F*), -156.8 (t, J = 20.8 Hz, 1F), -162.7 (dt, J = 22.4, 8.5 Hz, 2F), -163.0 (dt, J = 22.9, 8.1 Hz, 2F*).



1,2,3,4,5-pentafluoro-6-(2-(p-tolyl)propyl)benzene(5o)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12 - 7.04 (m, 4H), 3.02 (dq, J = 14.0, 7.0 Hz, 1H), 2.97 - 2.84 (m, 2H), 2.31 (s, 3H), 1.27 (d, J = 6.8 Hz, 3H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -143.1 (dd, J = 22.5, 8.2 Hz, 2F), -157.6 (t, J = 20.9 Hz, 1F), -163.1 (dd, J = 20.8, 14.2 Hz, 2F); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.1 (dm, J = 242.0 Hz), 142.1, 139.5 (dm, J = 254.0 Hz), 137.3 (dm, J = 256.0 Hz), 136.2, 129.2, 126.6, 114.0 (t, J = 16.9 Hz), 39.3, 31.4, 29.7, 21.0; IR (KBr, cm^{-1}) v 2990, 1743, 1541, 1463; HRMS (EI) m/z (M^+) calcd for $C_{16}H_{13}F_5$: 300.0937, found: 300.0931.

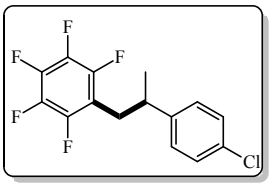


(4p indicated by*) and 

(3p)

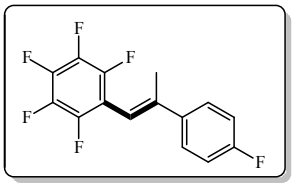
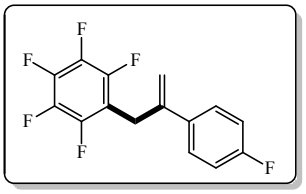
(E)-1-(2-(4-chlorophenyl)prop-1-en-1-yl)-2,3,4,5,6-pentafluorobenzene(4ma indicated by*) and 1-(2-(4-chlorophenyl)allyl)-2,3,4,5,6-pentafluorobenzene(3na)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, J = 8.6 Hz, 2H*), 7.38 - 7.29 (m, 2H*, 2H), 6.37 (s, 1H*),5.36 (s, 1H), 4.92 (s, 1H), 3.83 (s, 2H), 2.05 (d, J = 1.1 Hz, 3H*); ^{19}F NMR (376 MHz, $CDCl_3$) δ -139.1 (dd, J = 22.9, 7.8 Hz, 2F*), -142.8 (dd, J = 22.1, 8.3 Hz, 2F), -155.9 (t, J = 20.8 Hz, 1F*), -156.3 (t, J = 20.8 Hz, 1F), -162.4 (dt, J = 22.2, 8.4 Hz, 2F), -162.6 (dt, J = 22.4, 8.0 Hz, 2F*).



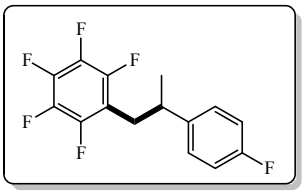
1-(2-(4-chlorophenyl)propyl)-2,3,4,5,6-pentafluorobenzene(5p)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 - 7.09 (m, 4H), 2.98 (dq, J = 13.6, 6.7 Hz, 1H), 2.92 - 2.79 (m, 2H), 1.23 (d, J = 6.8 Hz, 3H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -143.1 (dd, J = 22.6, 8.6 Hz, 2F), -157.5 (t, J = 20.8 Hz, 1F), -163.0 (dt, J = 22.6, 8.5 Hz, 2F); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.2 (dm, J = 244.0 Hz), 145.1, 139.6 (dm, J = 250.0 Hz), 137.3 (dm, J = 251.0 Hz), 128.5, 126.7, 126.7, 113.9 (t, J = 20.6 Hz), 39.8, 31.3, 20.8; IR (KBr, cm^{-1}) v 2935, 1742, 1651, 1496; HRMS (EI) m/z (M^+) calcd for $C_{15}H_{10}ClF_5$: 329.1203, found: 329.1196.


(4q) and

(3q) (2.9:1)

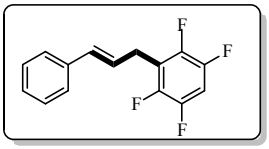
(E)-1,2,3,4,5-pentafluoro-6-(2-(4-fluorophenyl)prop-1-en-1-yl)benzene(4ma indicated by*) and 1,2,3,4,5-pentafluoro-6-(2-(4-fluorophenyl)allyl)benzene(3ma)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 - 7.47 (m, 2H*), 7.41 - 7.37 (m, 2H), 7.10 - 7.05 (m, 2H*), 7.04 - 6.99 (m, 2H), 6.33 (s, 1H*), 5.32 (s, 1H), 4.88 (s, 1H), 3.83 (s, 2H), 2.06 (dd, J = 3.2, 1.9 Hz, 3H*); ^{19}F NMR (376 MHz, $CDCl_3$) δ -113.7 (tt, J = 8.8, 5.4 Hz, 1F*), -114.2 (tt, J = 8.5, 5.3 Hz, 1F), -139.2 (dd, J = 22.9, 7.9 Hz, 2F*), -142.9 (dd, J = 22.1, 8.3 Hz, 2F), -156.2 (t, J = 20.8 Hz, 2F*), -156.5 (t, J = 20.8 Hz, 1F), -162.4 - -162.6 (m, 2F), -162.7 - -162.8 (m, 2F*).



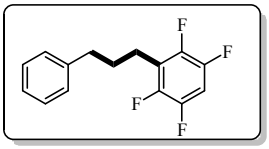
1,2,3,4,5-pentafluoro-6-(2-(4-fluorophenyl)propyl)benzene(5q)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.08 - 7.00 (m, 2H), 6.90 - 6.83 (m, 2H), 3.03 - 2.90 (m, 1H), 2.90 - 2.72 (m, 2H), 1.21 (d, J = 6.9 Hz, 3H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -116.4 (dq, J = 8.7, 5.3 Hz), -143.2 (dd, J = 22.4, 8.2 Hz), -157.3 (t, J = 20.8 Hz), -162.8 - -163.0 (m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.6 (d, J = 244.5 Hz, 0H), 145.1 (dm, J = 239.0 Hz), 140.7 (d, J = 3.2 Hz), 139,6 (dm, J = 232.0 Hz), 137.3 (dm, J = 248.0 Hz), 128.1 (d, J = 7.9 Hz), 115.2 (d, J = 21.2 Hz), 113.7 (t, J = 16.7 Hz), 39.1, 31.4, 21.0; IR (KBr, cm^{-1}) v 2927, 1743, 1509, 1459; HRMS (EI) m/z (M^+) calcd for $C_{15}H_{10}F_6$: 304.0687, found: 304.0680.



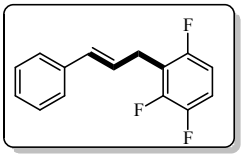
3-cinnamyl-1,2,4,5-tetrafluorobenzene(3r).[5]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 - 7.20 (m, 5H), 6.94 - 6.83 (m, 1H), 6.47 (d, J = 15.8 Hz, 1H), 6.22 (dt, J = 15.6, 6.7 Hz, 1H), 3.60 (dd, J = 6.7, 1.4 Hz, 2H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -139.5 - -139.7 (m, 2F), -144.4 - -144.5 (m, 2F).



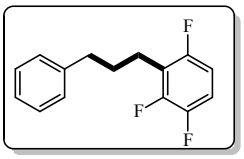
1,2,4,5-tetrafluoro-3-(3-phenylpropyl)benzene(5r).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 - 7.24 (m, 2H), 7.17 (dd, J = 7.6, 3.4 Hz, 3H), 6.86 (tt, J = 9.8, 7.4 Hz, 1H), 2.76 (t, J = 7.7 Hz, 2H), 2.69 - 2.65 (m, 2H), 1.98 - 1.88 (m, 2H);^{19}F NMR (376 MHz, $CDCl_3$) δ -140.0 - -140.1 (m, 2F), -144.7 - -144.9 (m, 2F); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.8 (dm, J = 245.2 Hz), 144.8 (dm, J = 232.5 Hz), 141.4, 128.4, 128.3, 126.1, 121.3 (t, J = 18.4 Hz), 103.5 (t, J = 22.7 Hz), 35.5, 30.7, 22.8. IR (KBr, cm^{-1}) ν 2935, 1743, 1504, 1456; HRMS (EI) m/z (M^+) calcd for $C_{15}H_{12}F_4$: 268.0875; Found: 268.0871.



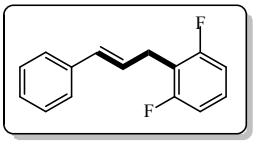
2-cinnamyl-1,3,4-trifluorobenzene(3s).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 - 7.23 (m, 5H), 6.97 (ddd, J = 18.3, 9.2, 5.0 Hz, 1H), 6.81 - 6.75 (m, 1H), 6.45 (d, J = 15.8 Hz, 1H), 6.25 (dt, J = 15.7, 6.7 Hz, 1H), 3.57 (dd, J = 6.7, 1.2 Hz, 2H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -120.7 - -120.8 (m, 1F), -138.6 (dd, J = 20.9, 8.3 Hz, 1F), -142.6 (dddd, J = 20.9, 15.2, 9.5, 3.7 Hz, 1F).



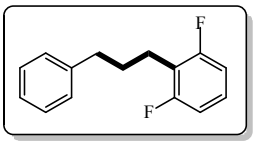
1,2,4-trifluoro-3-(3-phenylpropyl)benzene(5s).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 - 7.24 (m, 2H), 7.18 (t, J = 6.9 Hz, 3H), 6.97 - 6.89 (m, 1H), 6.74 (tdd, J = 9.0, 3.7, 2.2 Hz, 3H), 2.73 (t, J = 7.7 Hz, 2H), 2.69 - 2.64 (m, 2H), 1.96 - 1.88 (m, 2H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -121.0 (ddd, J = 13.8, 8.6, 4.4 Hz, 1F), -138.8 - -139.0 (m, 1F), -143.0 (dddd, J = 20.9, 15.3, 9.6, 3.8 Hz, 1F); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.7 (dm, J = 241.6 Hz),149.0 (dm, J = 246.3 Hz), 147.2 (dm, J = 242.0 Hz), 141.7, 128.4, 125.9, 119.9 (dd, J = 22.5, 16.8 Hz,), 114.2 (dd, J = 19.4, 11.3 Hz,), 110.2 (ddd, J = 25.3, 6.6, 4.1 Hz), 35.5 , 30.9 , 22.5 (d, J = 1.8 Hz); IR (KBr, cm^{-1}) ν 2932, 1742, 1495, 1457; HRMS (EI) m/z (M^+) calcd for $C_{15}H_{13}F_3$: 250.0969; Found: 250.0965.



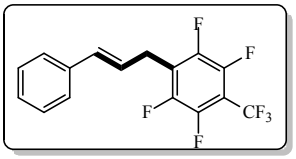
2-cinnamyl-1,3-difluorobenzene(3t).[5]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 - 7.12(m, 6H), 6.89 - 6.85 (m, 2H), 6.44 (d, J = 15.6 Hz, 1H), 6.29 (dt, J = 15.7, 6.6 Hz, 1H), 3.57 (dd, J = 6.6, 0.9 Hz, 2H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -115.7 (t, J = 6.6 Hz, 2F).



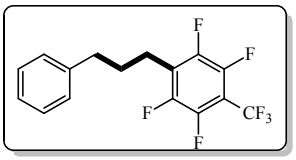
1,3-difluoro-2-(3-phenylpropyl)benzene(5t).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 - 7.23 (m, 2H), 7.22 - 7.15(dd, J = 7.5, 2.9 Hz, 3H), 7.11 (ddd, J = 8.3, 6.5, 1.9 Hz, 1H), 6.88 - 6.72 (m, 2H), 2.75 - 2.61(m, 4H), 1.96 - 1.87 (m, 2H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -115.97 (dd, J = 13.0, 6.5 Hz, 2F); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.6 (dd, J = 246.3, 9.1 Hz), 142.0, 128.4, 128.3, 127.2 (t, J = 10.3 Hz), 125.8, 117.7 (t, J = 20.4 Hz), 111.0 (m), 35.6, 31.1, 22.1 (t, J= 2.3 Hz); IR (KBr, cm^{-1}) ν 2925, 1743, 1505, 1465; HRMS (EI) m/z (M^+) calcd for $C_{15}H_{14}F_2$: 232.1064; Found: 232.1059.



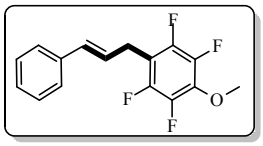
1-cinnamyl-2,3,5,6-tetrafluoro-4-(trifluoromethyl)benzene(3u).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (ddd, J = 15.5, 11.7, 4.9 Hz, 5H), 6.52 (d, J = 15.8 Hz, 1H), 6.20 (dt, J = 15.7, 6.9 Hz, 1H), 3.66 (dd, J = 6.9, 1.2 Hz, 2H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -56.3 (t, J = 21.6 Hz), -140.9 - -141.2 (m), -142.0 (td, J = 16.5, 6.6 Hz).



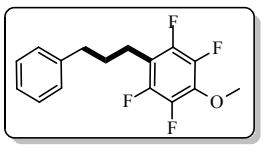
1,2,4,5-tetrafluoro-3-(3-phenylpropyl)-6-(trifluoromethyl)benzene(5u).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (t, J = 7.4 Hz, 2H), 7.18 (t, J = 8.1 Hz, 3H), 2.80 (t, J = 7.7 Hz, 2H), 2.70 (t, J = 7.7 Hz, 2H), 2.01 - 1.92 (m, 2H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -56.3 (t, J = 21.5 Hz), -141.5 - -141.8 (m), -142.3 (td, J = 15.9, 6.1 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.2 (dm, J = 243.8 Hz), 143.9 (dm, J = 256.5 Hz), 140.8, 128.5, 128.3, 126.2, 125.3 (t, J = 18.3 Hz), 121.0 (q, J = 274.2 Hz), 107.5 (m), 35.4, 30.2, 22.8; IR (KBr, cm^{-1}) ν 2934, 1744, 1668, 1494. HRMS (EI) m/z (M^+) calcd for $C_{16}H_{11}F_7$: 336.0749; Found: 336.0742.



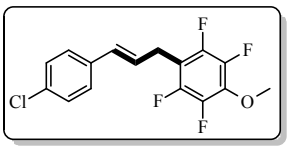
1-cinnamyl-2,3,5,6-tetrafluoro-4-methoxybenzene(3v).[5]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 - 7.22 (m, 5H), 6.44 (d, J = 15.8 Hz, 1H), 6.25 - 6.17 (m, 1H), 4.00 (s, 3H), 3.53 (d, J = 6.9 Hz, 2H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -145.7 (dd, J = 21.5, 9.0 Hz, 2F), -158.4 (dd, J = 21.6, 9.1 Hz, 2F).



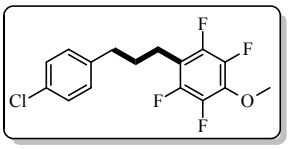
1,2,4,5-tetrafluoro-3-methoxy-6-(3-phenylpropyl)benzene(5v)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 - 7.23 (m, 2H), 7.16 (d, J = 6.2 Hz, 3H), 3.99 (s, 3H), 2.73 - 2.60 (m, 4H), 1.99 - 1.80 (m, 2H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -146.0 (dd, J = 21.7, 9.0 Hz,2F), -158.8 (dd, J = 21.6, 9.0 Hz, 2F); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.3 (dm, J = 243.2 Hz), 141.5, 141.0 (dm, J = 245.0), 136.5 (m), 128.4, 128.3, 126.0, 113.7 (t, J = 19.1 Hz), 62.1 (t, J = 3.6 Hz), 35.4, 30.9, 22.1; IR (KBr, cm^{-1}) v 2940, 1742, 1497, 1452; HRMS (EI) m/z (M^+) calcd for $C_{16}H_{14}F_4O$: 298.0981; Found: 298.0976.



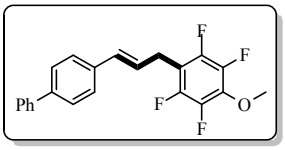
(E)-1-(3-(4-chlorophenyl)allyl)-2,3,5,6-tetrafluoro-4-methoxybenzene(3w).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (s, 4H), 6.40 (d, J = 15.8 Hz, 1H), 6.20 (dt, J = 15.7, 6.7 Hz, 1H), 4.04 (t, J = 1.1 Hz, 3H), 3.55 (dd, J = 6.7, 1.4 Hz, 2H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -145.7 (dd, J = 21.5, 9.0 Hz, 2F), -158.3 (dd, J = 21.4, 9.1 Hz, 2F).



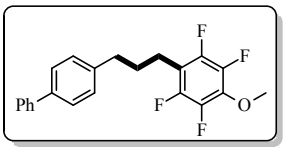
1-(3-(4-chlorophenyl)propyl)-2,3,5,6-tetrafluoro-4-methoxybenzene(5w).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27(m, 2H), 7.17 (m, 2H), 4.02 (s, 3H), 2.68 (m, 4H), 1.91 (m, 2H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -146.0 (dd, J = 21.7, 9.0 Hz, 2F), -158.8 (dd, J = 21.7, 9.1 Hz, 2F); ^{13}C NMR (100 MHz, $CDCl_3$) δ145.3 (dm, J = 241.2 Hz), 141.4, 140.9 (dm, J = 245.0 Hz), 136.4 (m), 128.4, 128.3, 126.0, 113.6 (t, J = 19.1 Hz), 62.1 (t, J = 3.5 Hz), 35.4, 30.8, 22.1; IR (KBr, cm^{-1}) v 2935, 1742, 1651, 1496; HRMS (EI) m/z (M^+) calcd for $C_{16}H_{13}ClF_4O$: 332.0591; Found: 332.0584.



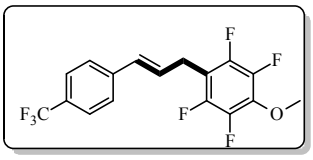
(E)-4-(3-(2,3,5,6-tetrafluoro-4-methoxyphenyl)prop-1-en-1-yl)-1,1'-biphen-yl(3x).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 - 7.59 (m, 5H), 7.50 (dt, J = 8.2, 5.3 Hz, 4H), 6.60 (d, J = 15.8 Hz, 1H), 6.37 (dt, J = 15.7, 6.7 Hz, 1H), 4.13 (s, 3H), 3.68 (dd, J = 6.7, 1.1 Hz, 2H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -145.6 (dd, J = 21.6, 9.0 Hz, 2F), -158.2 (dd, J = 21.6, 9.0 Hz, 2F).



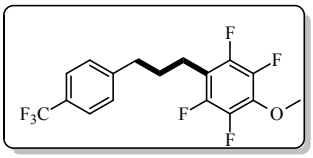
4-(3-(2,3,5,6-tetrafluoro-4-methoxyphenyl)propyl)-1,1'-biphenyl(5x).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, J = 8.0 Hz, 2H), 7.37 (d, J = 7.8 Hz, 2H), 7.27 (dd, J = 13.6, 6.2 Hz, 3H), 7.11 (d, J = 7.9 Hz, 2H), 3.86 (d, J = 0.8 Hz, 3H), 2.59 (dt, J = 15.3, 7.7 Hz, 4H), 1.89 - 1.75 (m, 2H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -145.8 (dd, J = 21.7, 9.0 Hz, 2F), -158.7 (dd, J = 21.8, 9.1 Hz, 2F); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.3 (dm, J = 247.6 Hz), 139.9 (dm, J = 245.0 Hz), 140.0, 139.5, 137.9, 137.9, 135.4 (m), 127.7, 126.0, 126.0, 125.9, 112.5 (t, J = 19.0 Hz), 61.0 (t, J = 3.5 Hz), 34.0, 29.7, 21.1; IR (KBr, cm^{-1}) v 3026, 2939, 1650, 1492; HRMS (EI) m/z (M^+) calcd for $C_{22}H_{18}F_4O$: 374.1294; Found: 374.1289.



(E)-1,2,4,5-tetrafluoro-3-methoxy-6-(3-(4-(trifluoromethyl)phenyl)allyl)benzene(3y).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, J = 8.2 Hz, 2H), 7.41 (d, J = 8.2 Hz, 2H), 6.48 (d, J = 15.8 Hz, 1H), 6.33 (dt, J = 15.7, 6.5 Hz, 1H), 4.05 (d, J = 1.2 Hz, 3H), 3.59 (dd, J = 6.6, 1.1 Hz, 2H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.6, -145.7 (dd, J = 21.4, 9.0 Hz), -158.2 (dd, J = 21.5, 9.0 Hz).



1,2,4,5-tetrafluoro-3-methoxy-6-(3-(4-(trifluoromethyl)phenyl)propyl)benzene(5y).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, J = 8.0 Hz, 2H), 7.29 (d, J = 8.0 Hz, 2H), 4.03 (s, 3H), 2.71(m, 4H), 1.94(m, 2H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.4 (s), -146.0 (dd, J = 21.6, 9.1 Hz), -158.7 (dd, J = 21.6, 9.1 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.5, 145.2 (dm, J = 247.0 Hz), 140.9 (dm, J = 245.0 Hz), 136.5, 129.0, 128.6, 125.3 (q, J = 3.8 Hz), 123.0, 113.2 (t, J = 19.0 Hz), 62.1, 35.1, 30.4, 22.0; IR (KBr, cm^{-1}) v 2942, 1742, 1618, 1497; HRMS (EI) m/z (M^+) calcd for $C_{17}H_{13}F_7O$: 366.0855; Found: 366.0850.

D. References

(1) B. M. Trost, P. J. Metzner, *J. Am. Chem. Soc*., 1980, **102**, 3572.

(2) G. Liu, G. Yin, L. Wu, *Angew. Chem., Int. Ed.*, 2008, **47**, 4733.

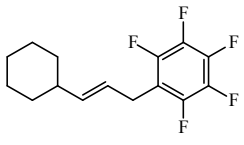
(3)Sumida, Y.; Hayashi, S.; Hirano, K.; Yorimitsu, H.; Oshima, K., *Org. Lett.*, 2008, **10**, 1629.

(4) S. Fan, F. Chen, X. Zhang, *Angew. Chem. Int. Ed.*, 2011, **50**, 5918.

(5) Y. Yu, S. Fan, and X. Zhang, *Chem.-Eur. J.*, 2012, **18**, 14643.

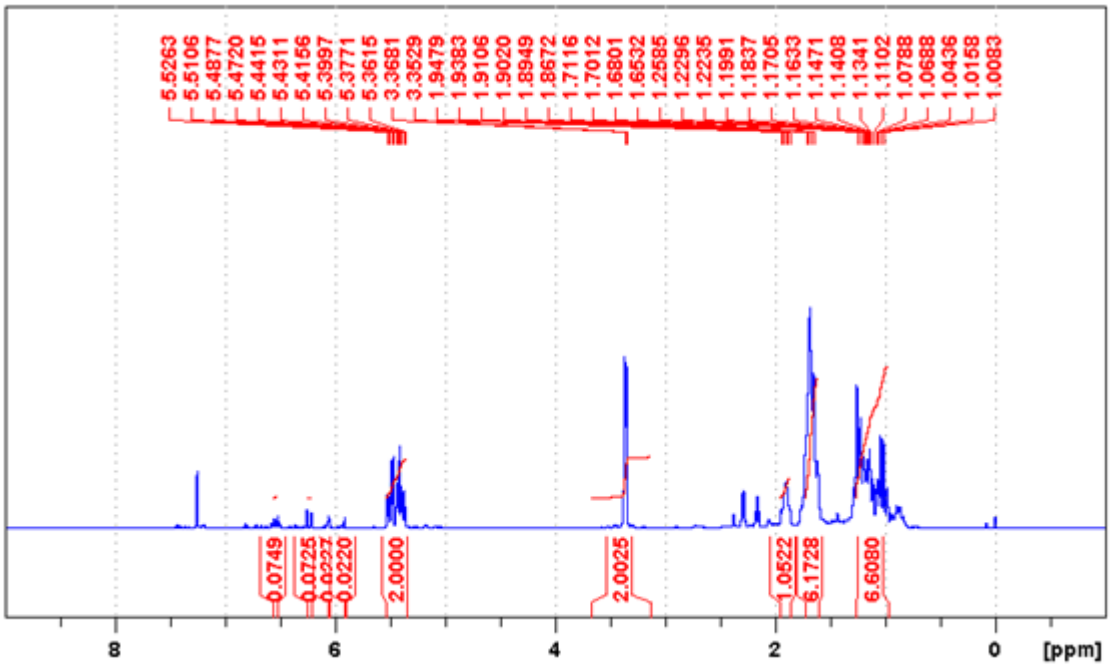
(6) X. Zhang, S. Fan, C. He, X. Wan, Q. Min, J. Yang, Z. Jiang, *J. Am. Chem. Soc.*, 2010, **132**, 4506.

E. NMR Spectra

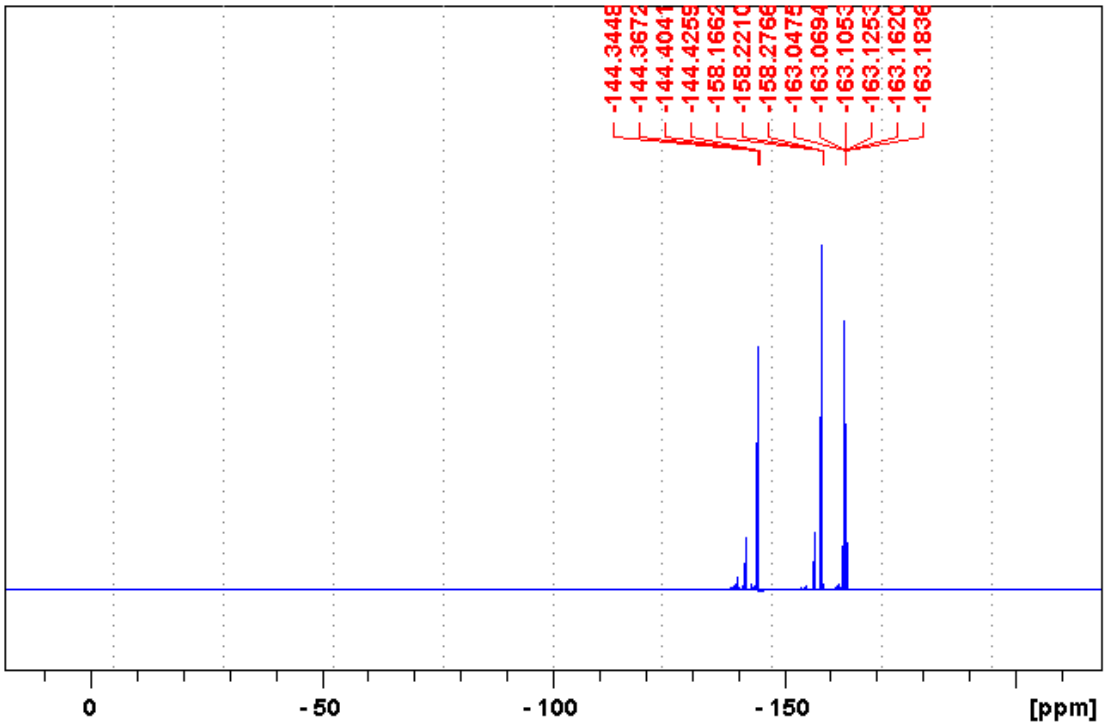


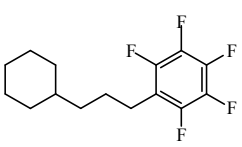
(3a) crude product

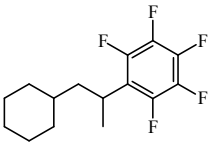
^{1}H NMR



^{19}F NMR

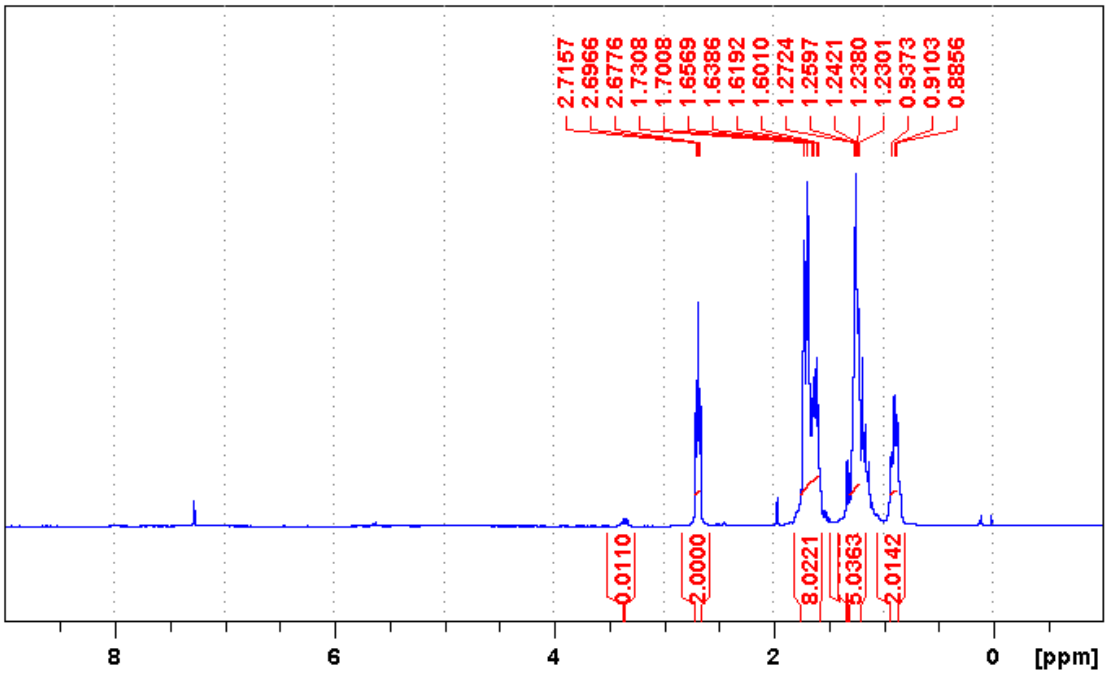




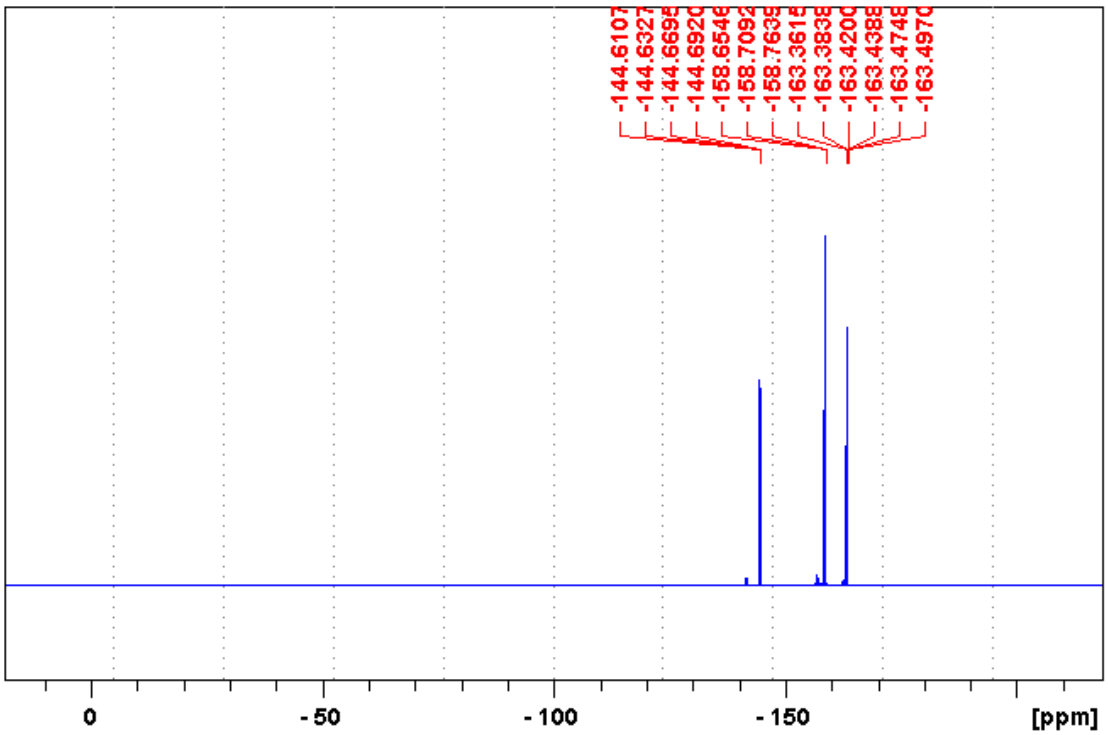
(5a) mixed with


99/1

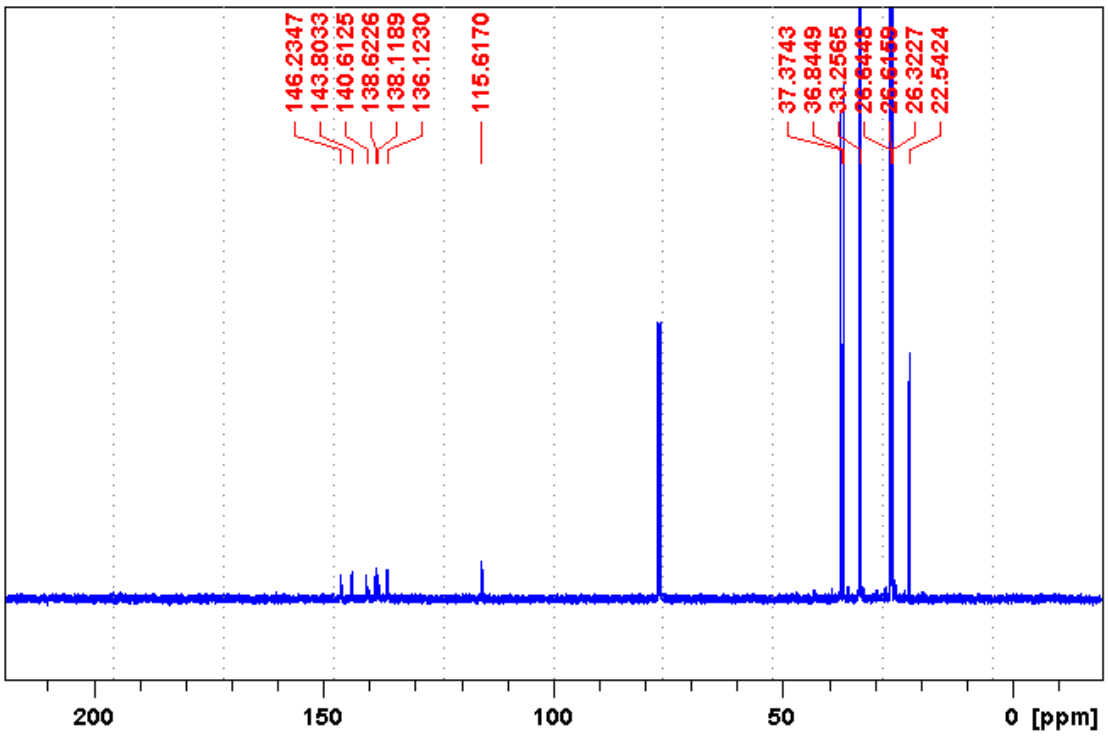
^{1}H NMR

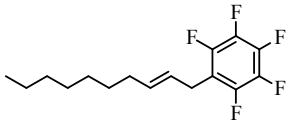


^{19}F NMR



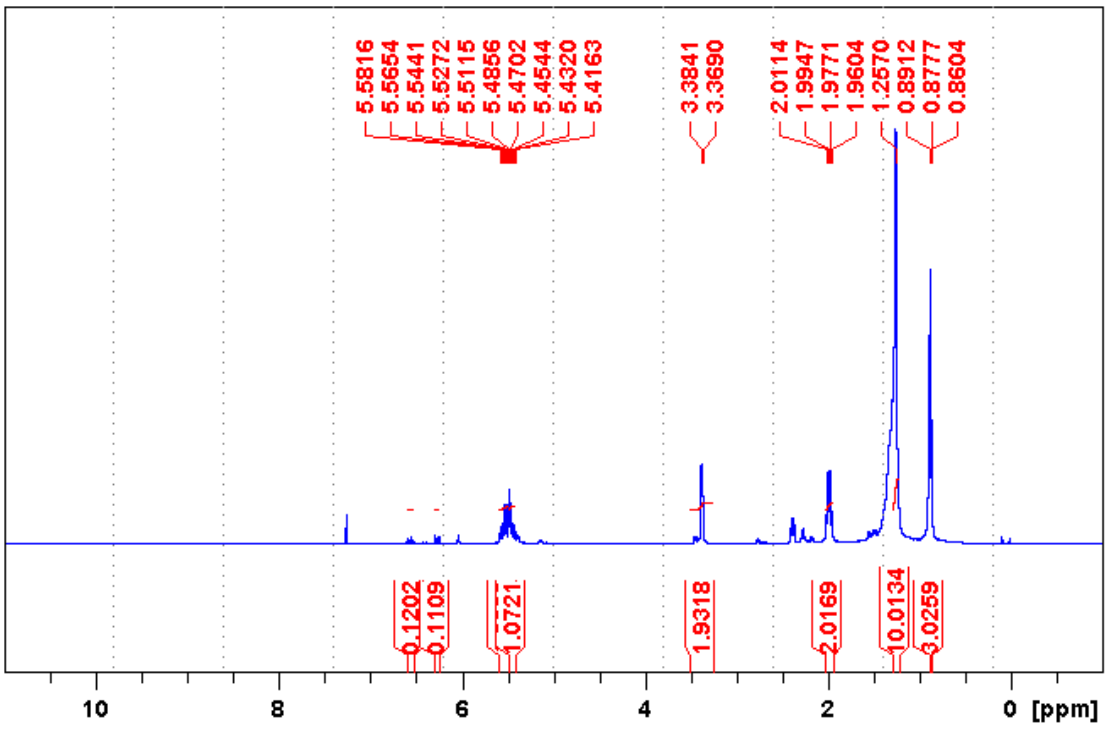
^{13}C NMR

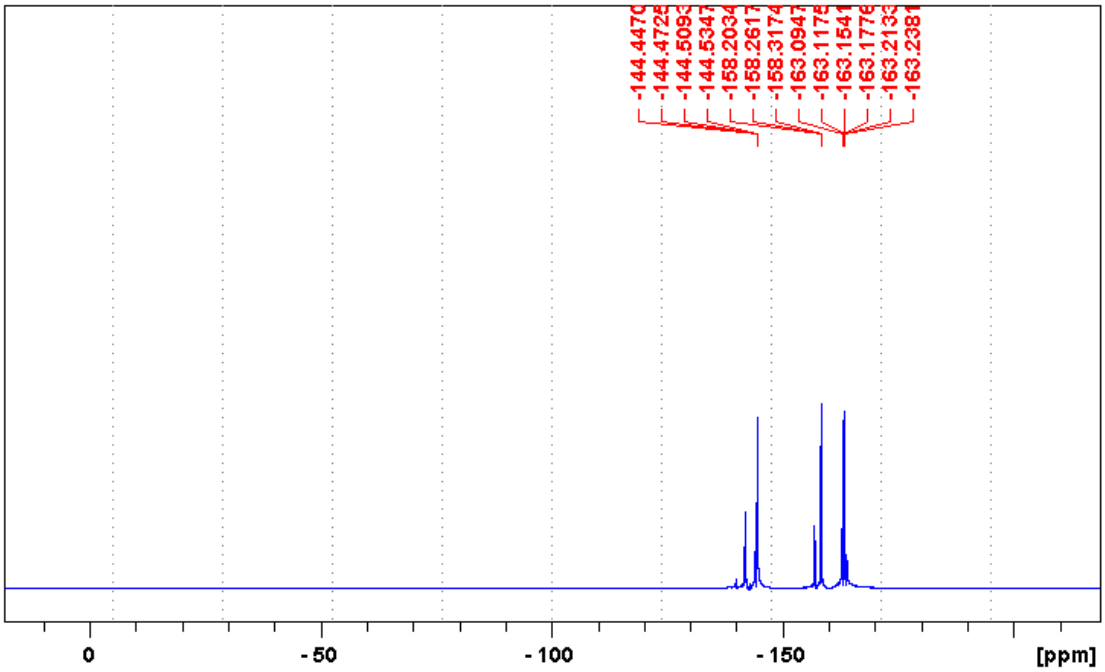


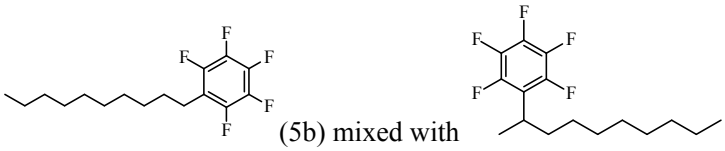


(3b) crude product

^{1}H NMR

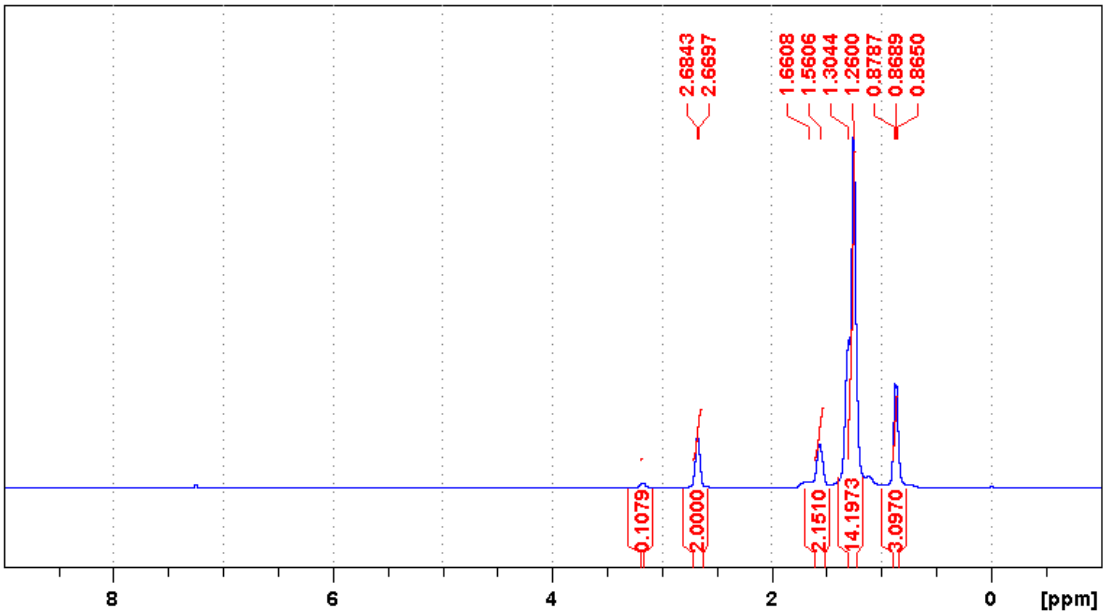




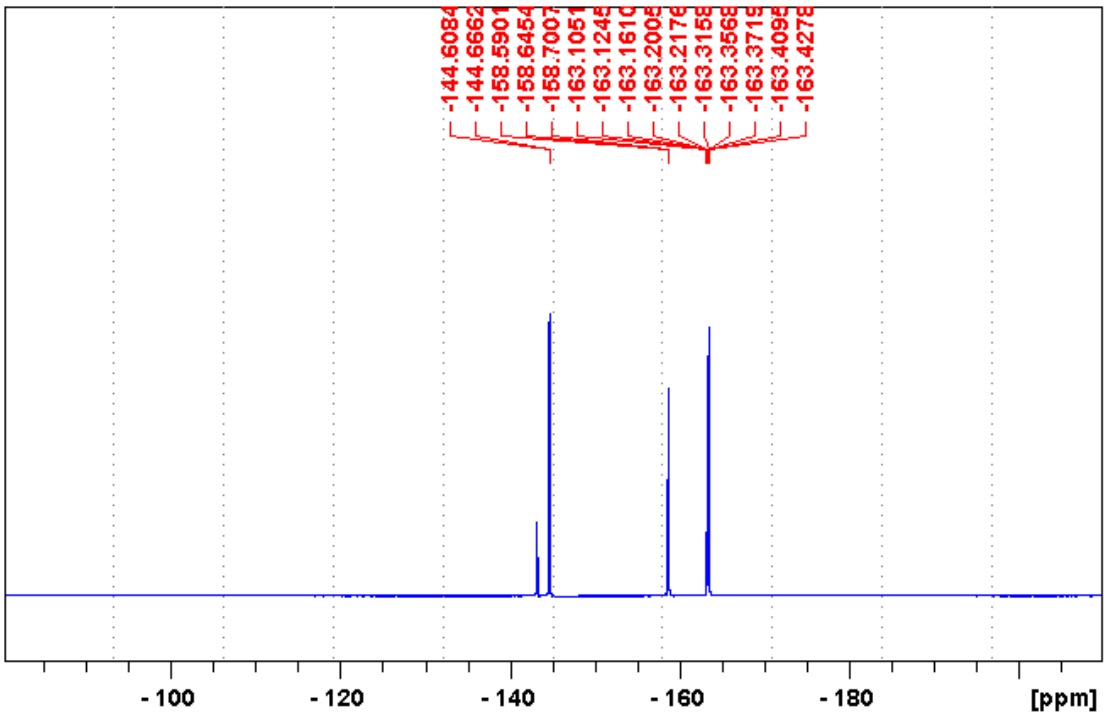


(5b) mixed with 90/10

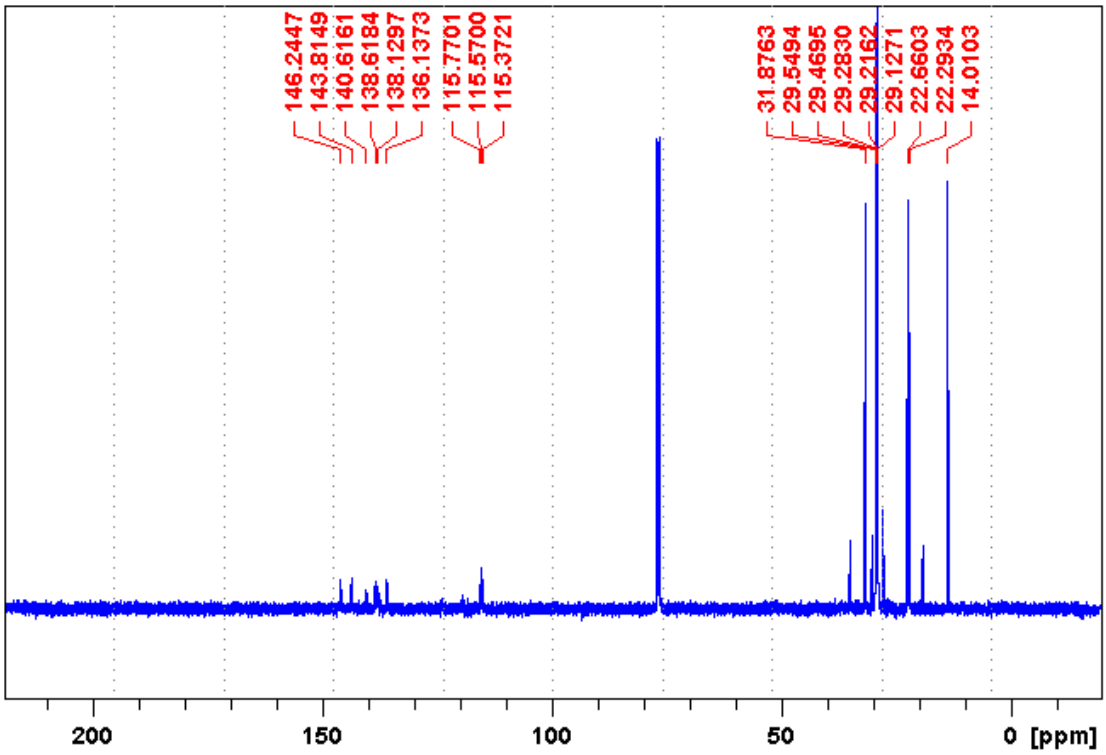
^{1}H NMR

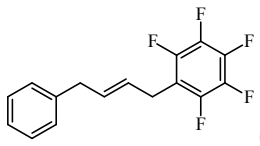


^{19}F NMR



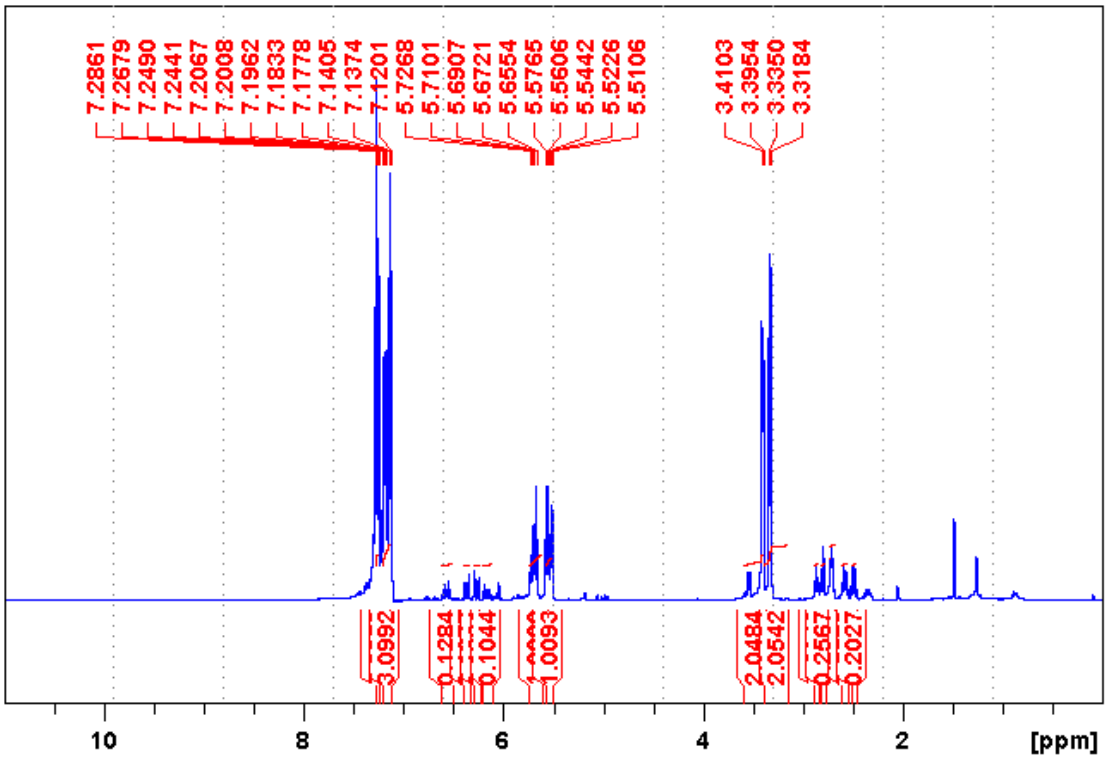
^{13}C NMR



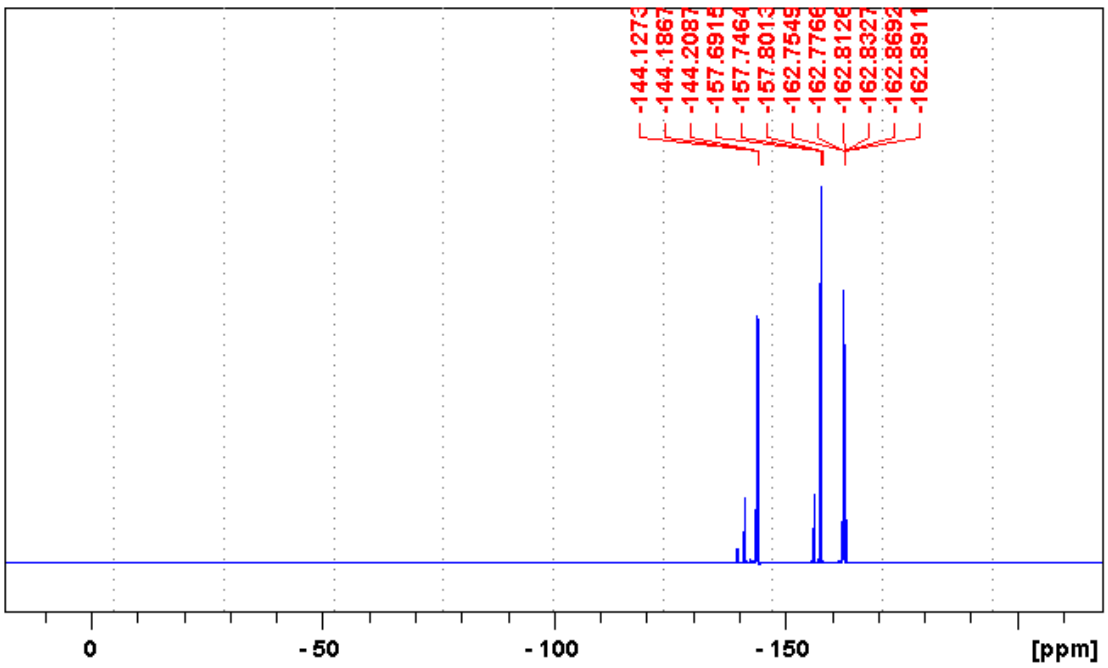


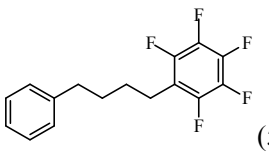
(3c) crude product

^{1}H NMR

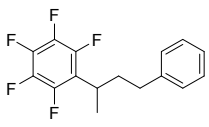


^{19}F NMR



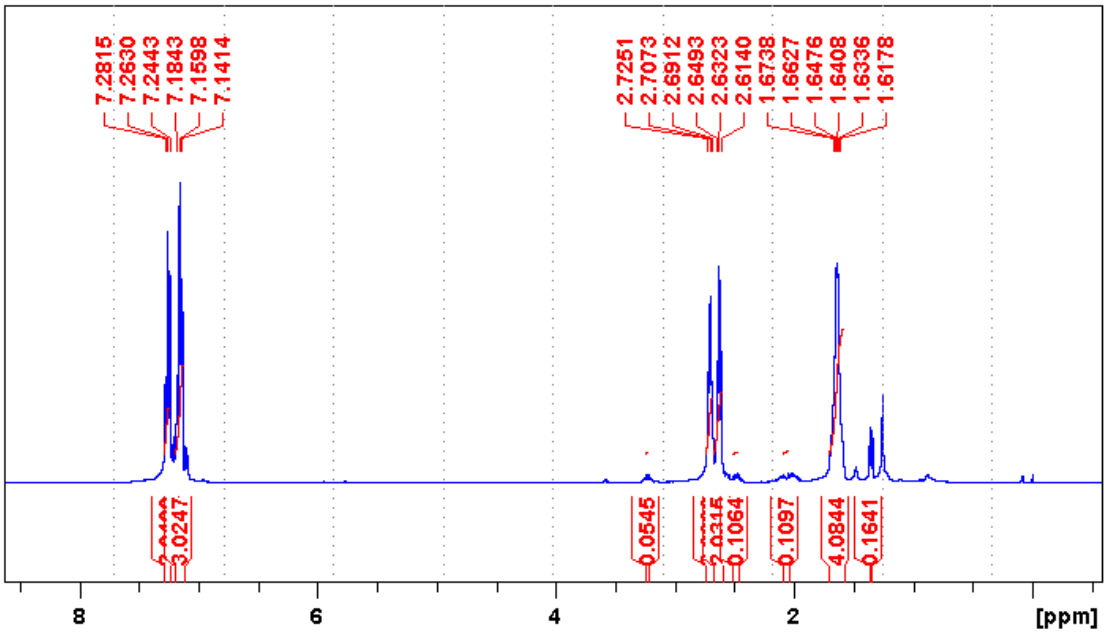


(5c) mixed with

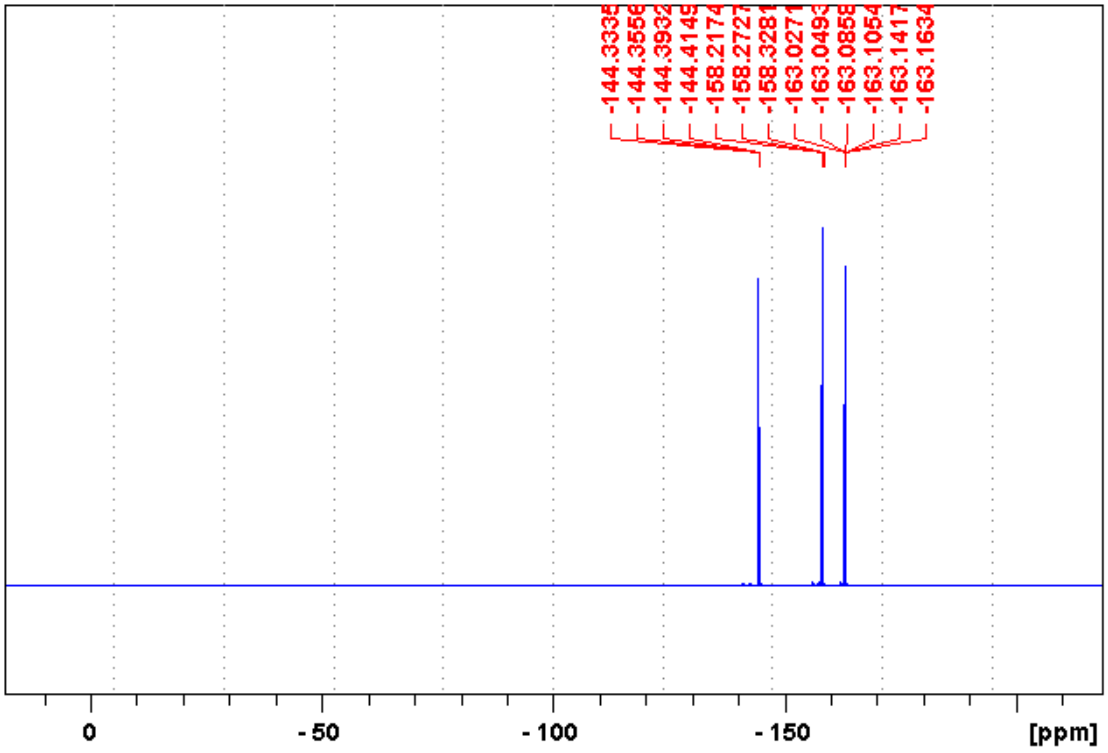


98/2

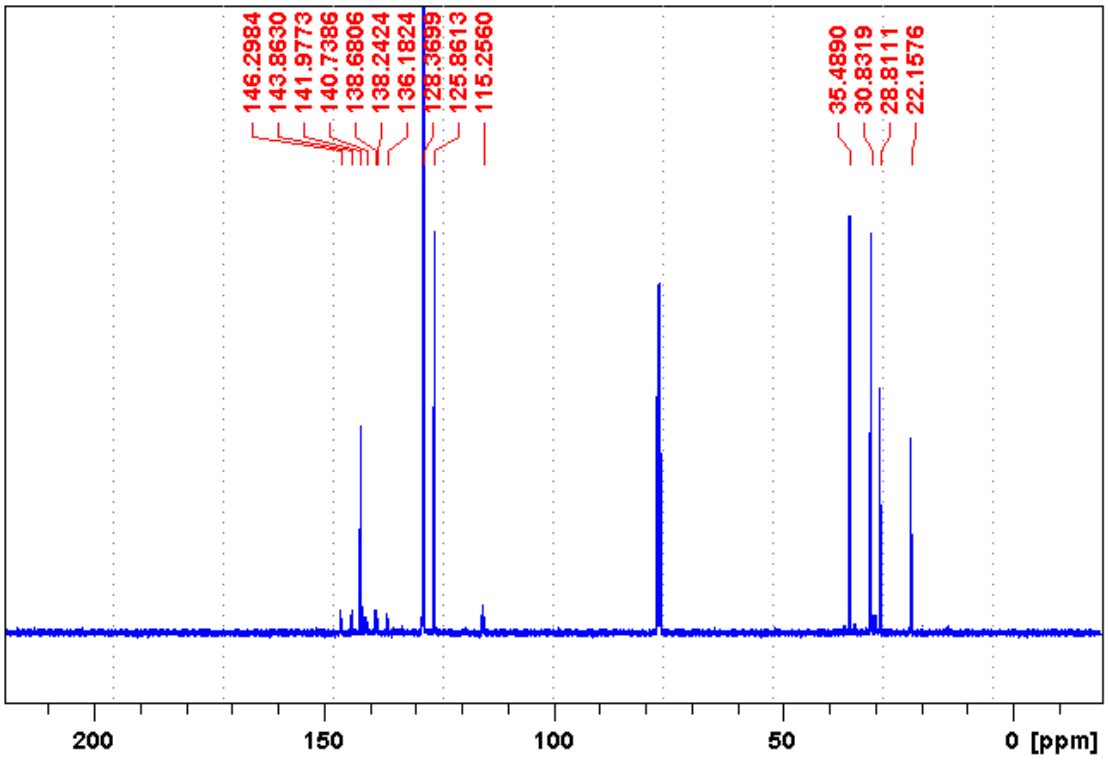
^{1}H NMR

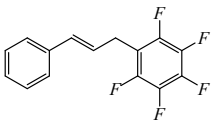


^{19}F NMR



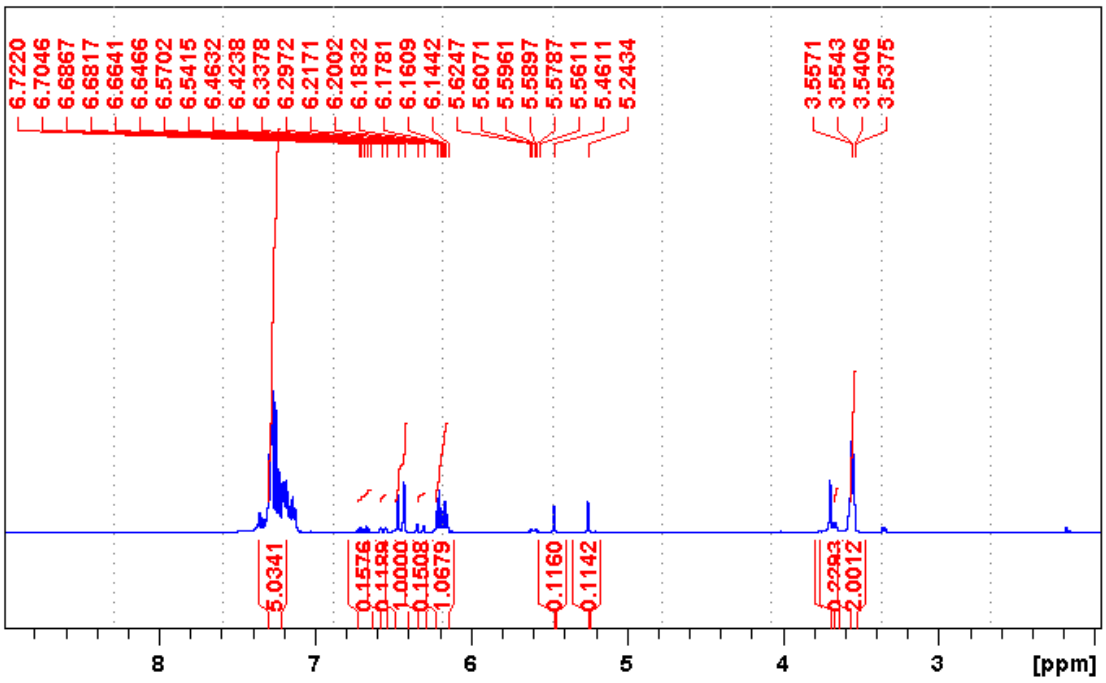
^{13}C NMR



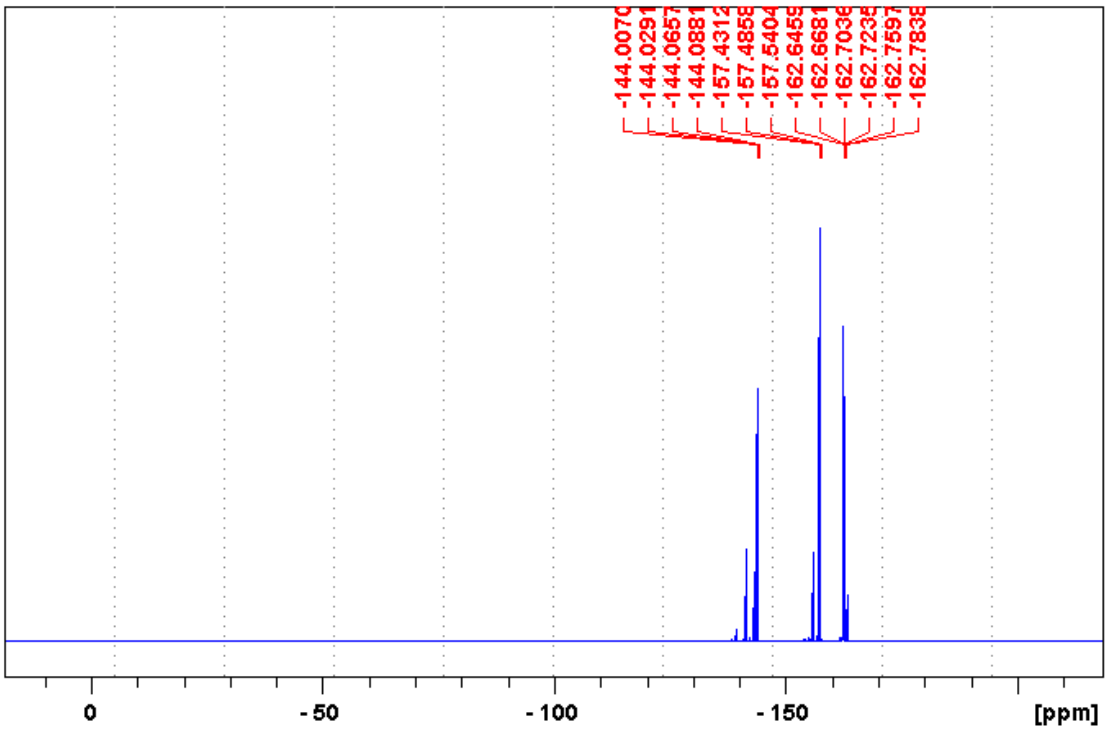


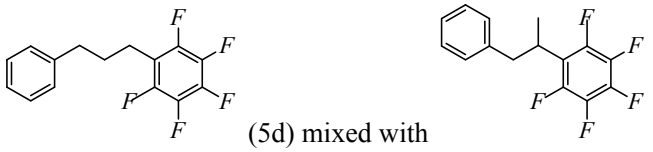
(3d) ccrude product

^{1}H NMR



^{19}F NMR

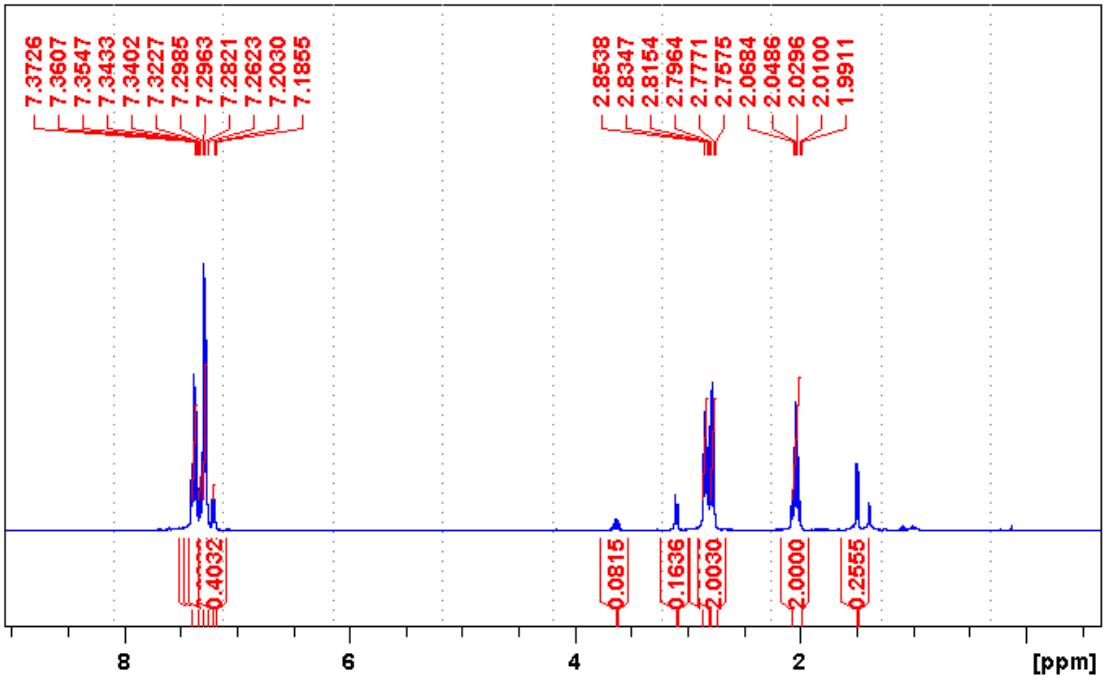




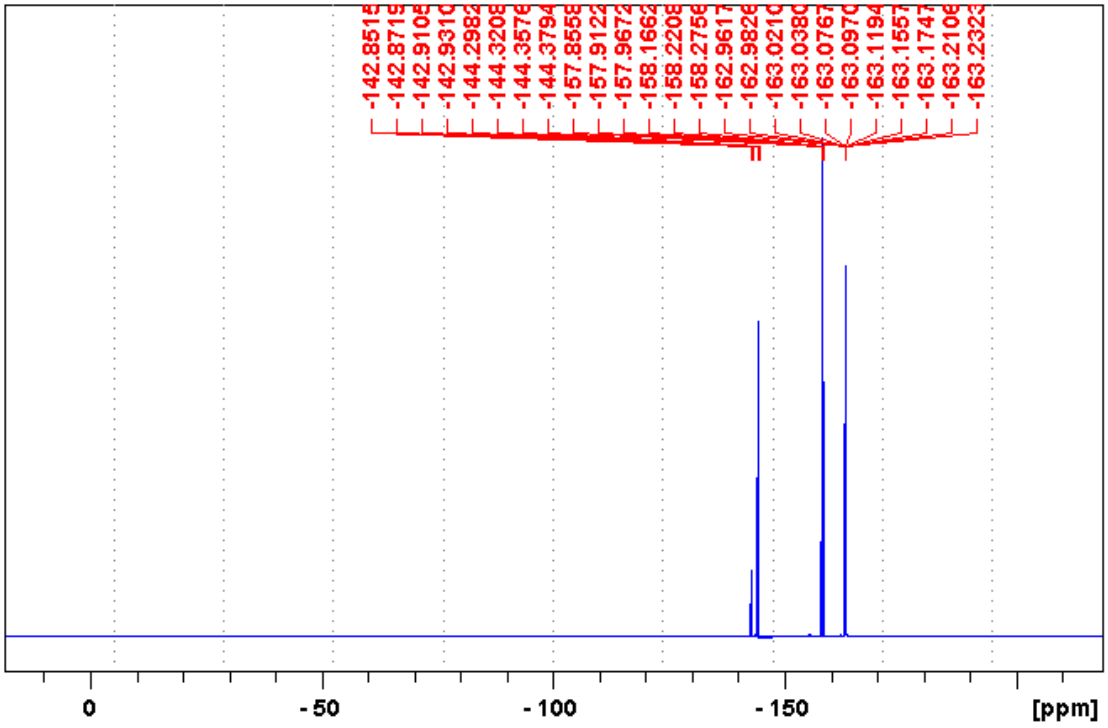
(5d) mixed with

92/8

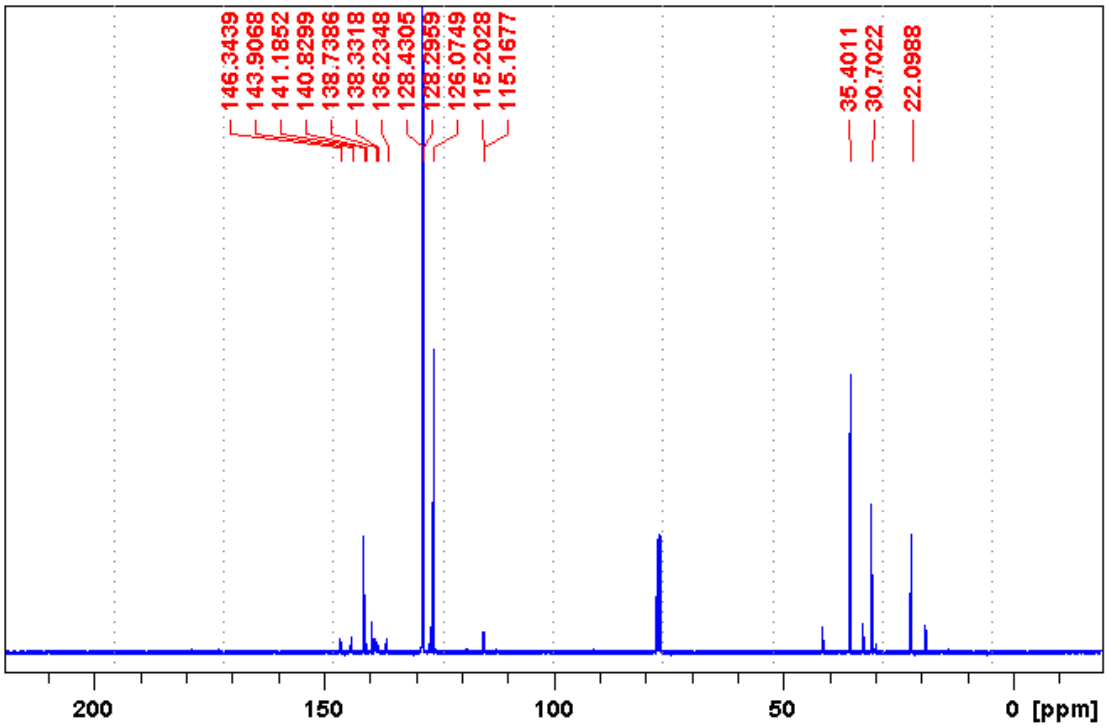
^{1}H NMR

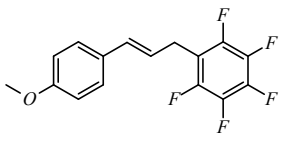


^{19}F NMR



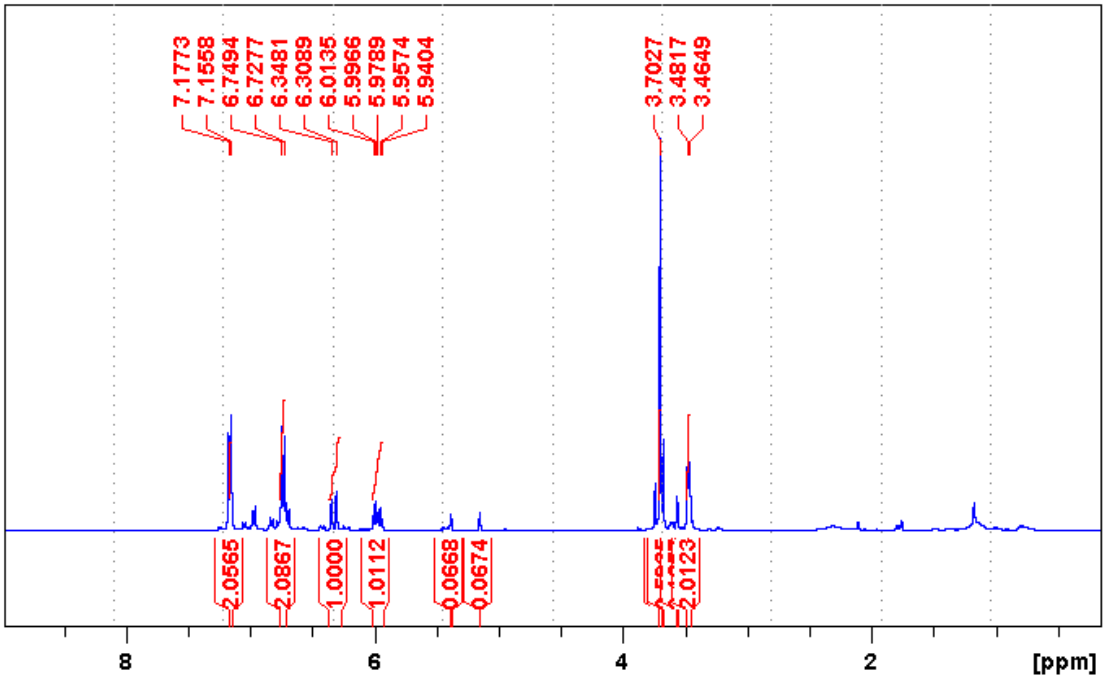
^{13}C NMR



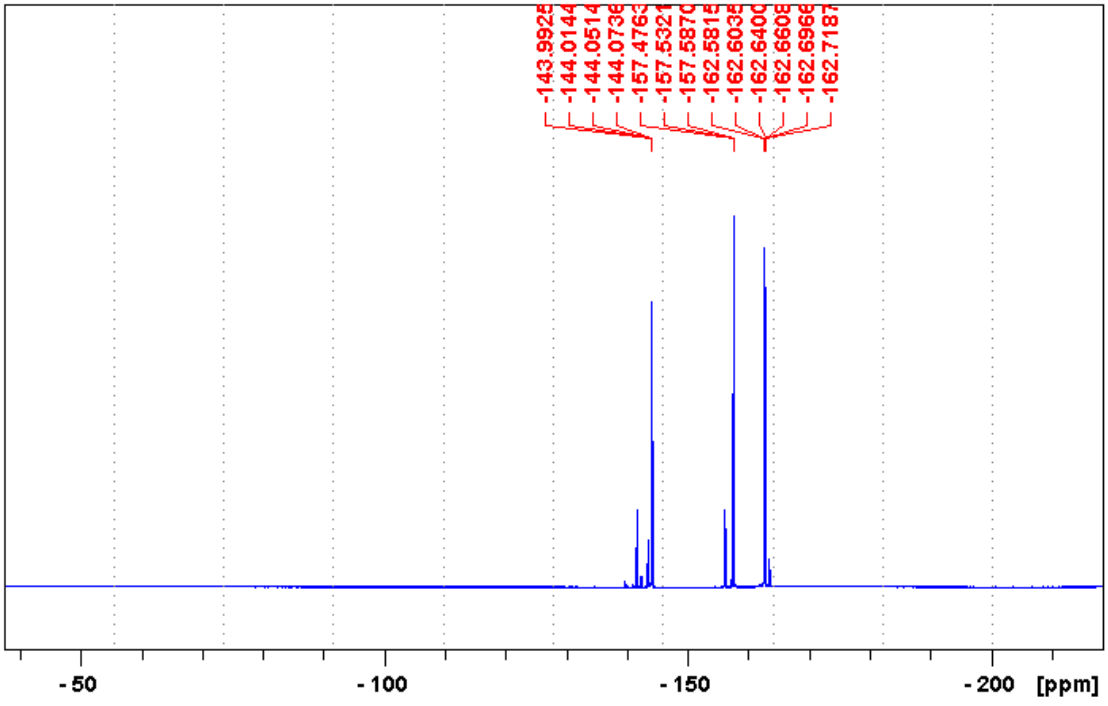


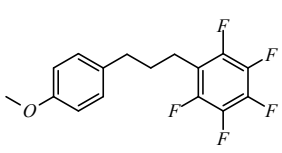
(3e) ccrude product

^{1}H NMR

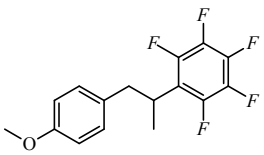


^{19}F NMR



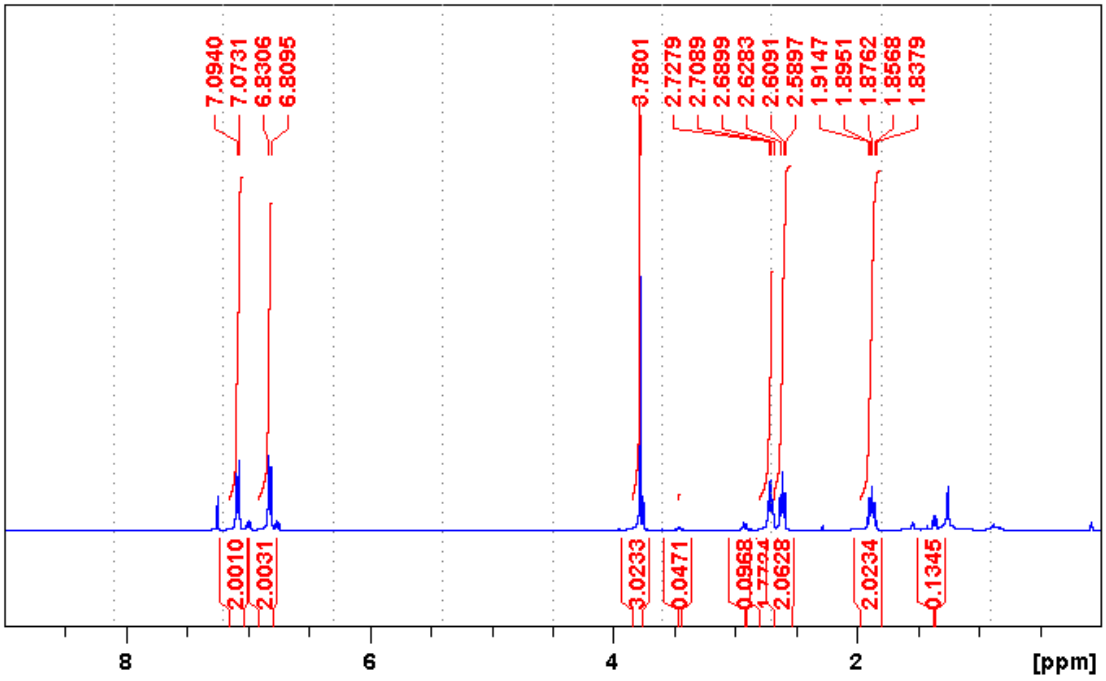


(5e) mixed with

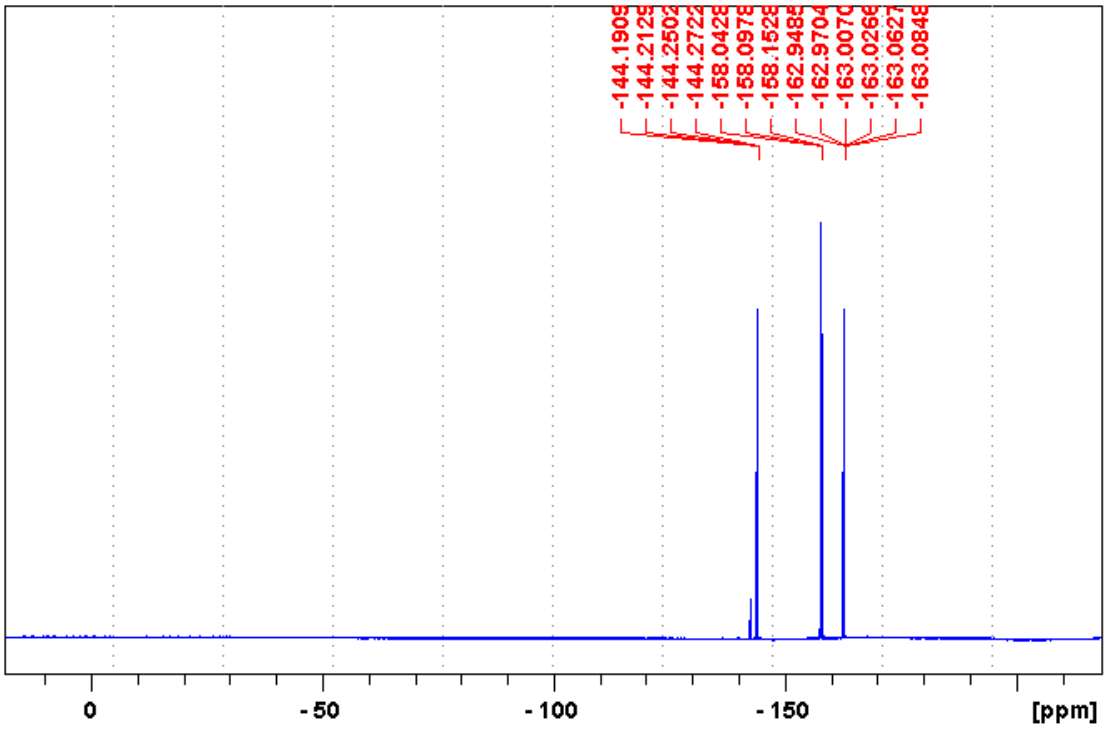


95/5

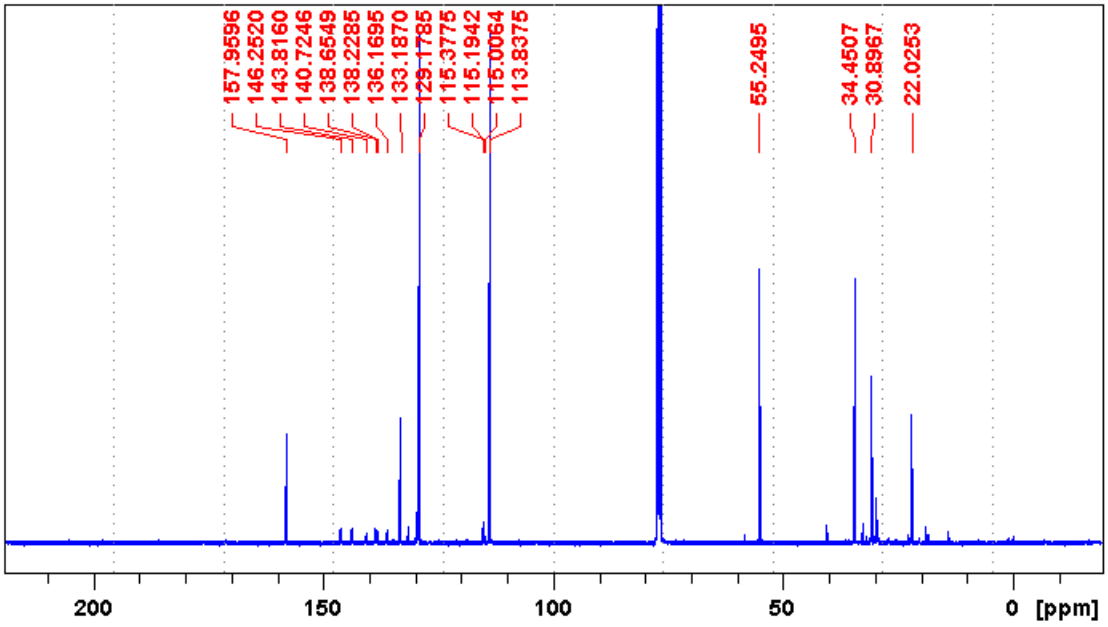
^{1}H NMR

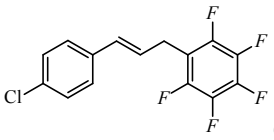


^{19}F NMR



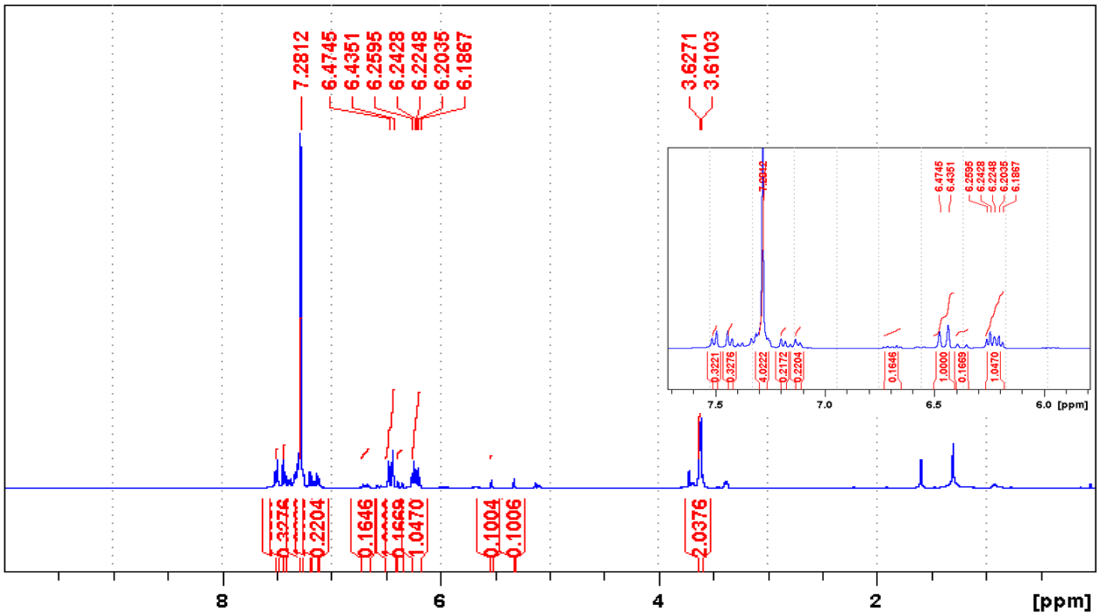
^{13}C NMR



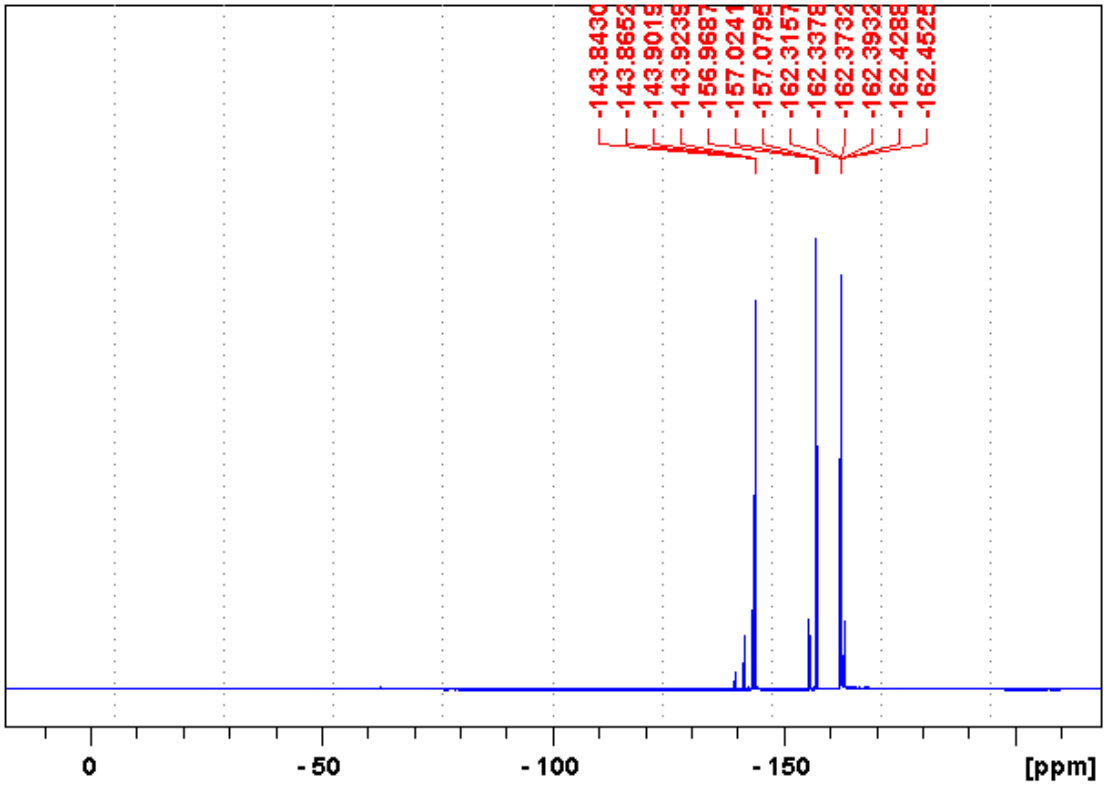


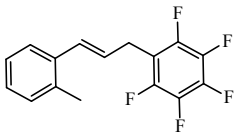
(3f) E:Z =6.3/1 3f/4f=93/7

^{1}H NMR



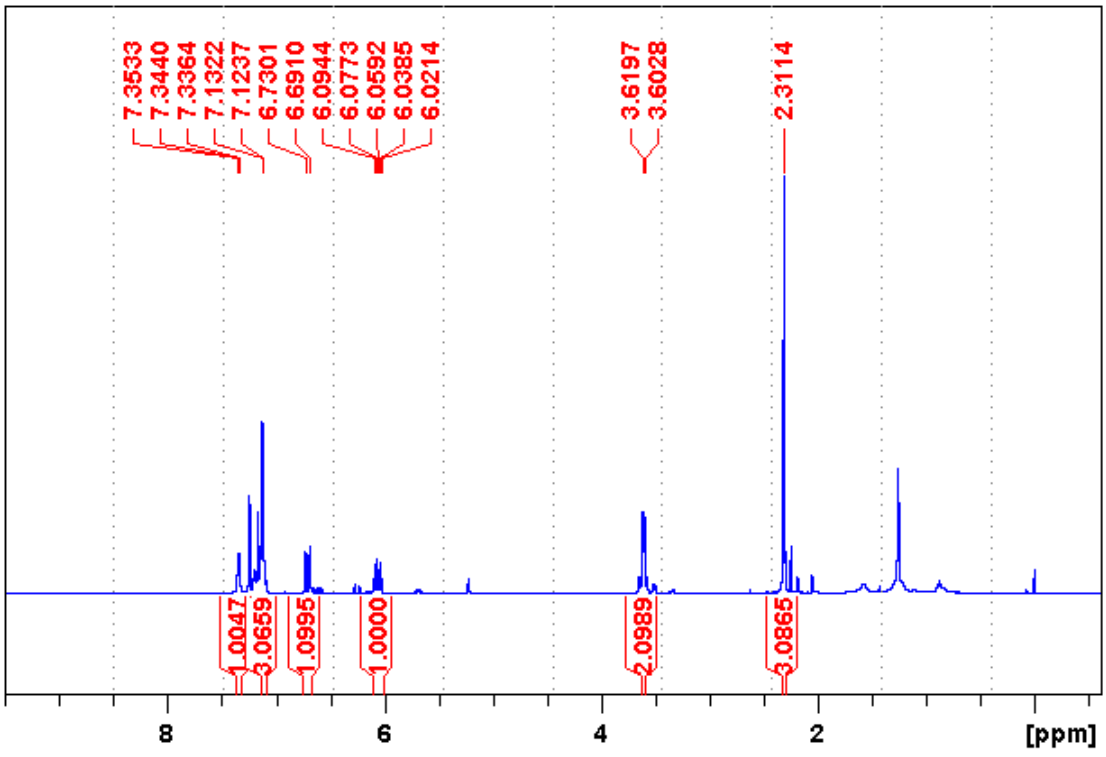
^{19}F NMR



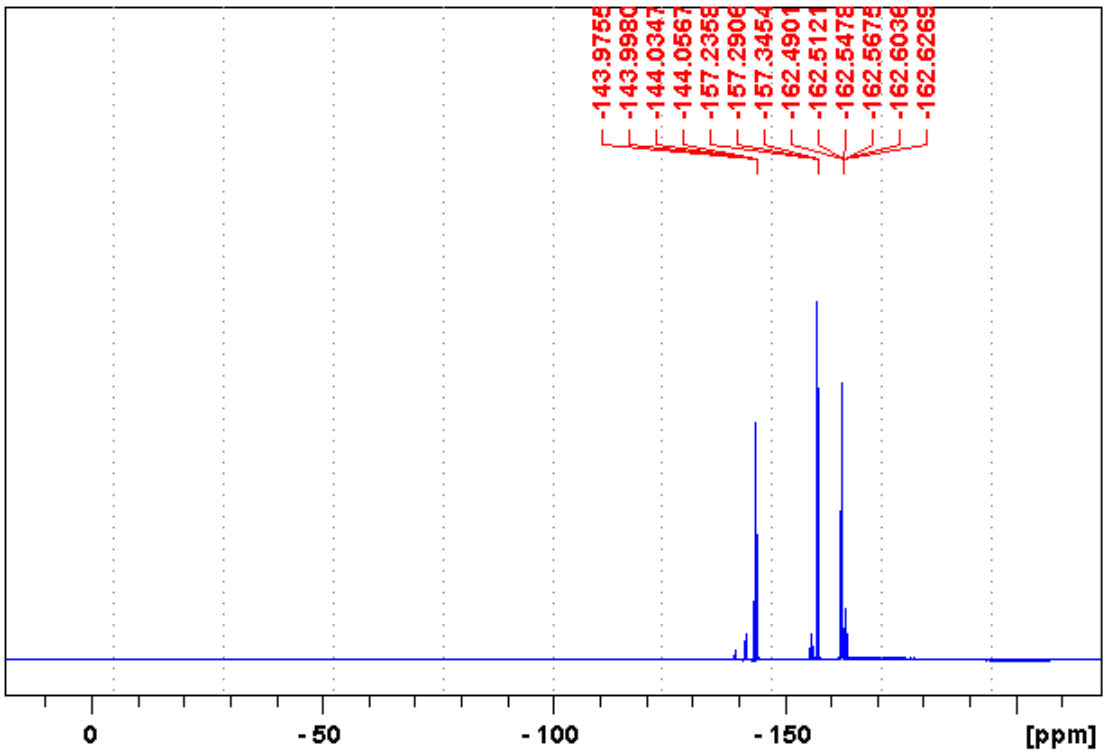


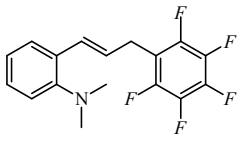
(3g) E:Z=10:1, 3g/4g=98:2

^{1}H NMR



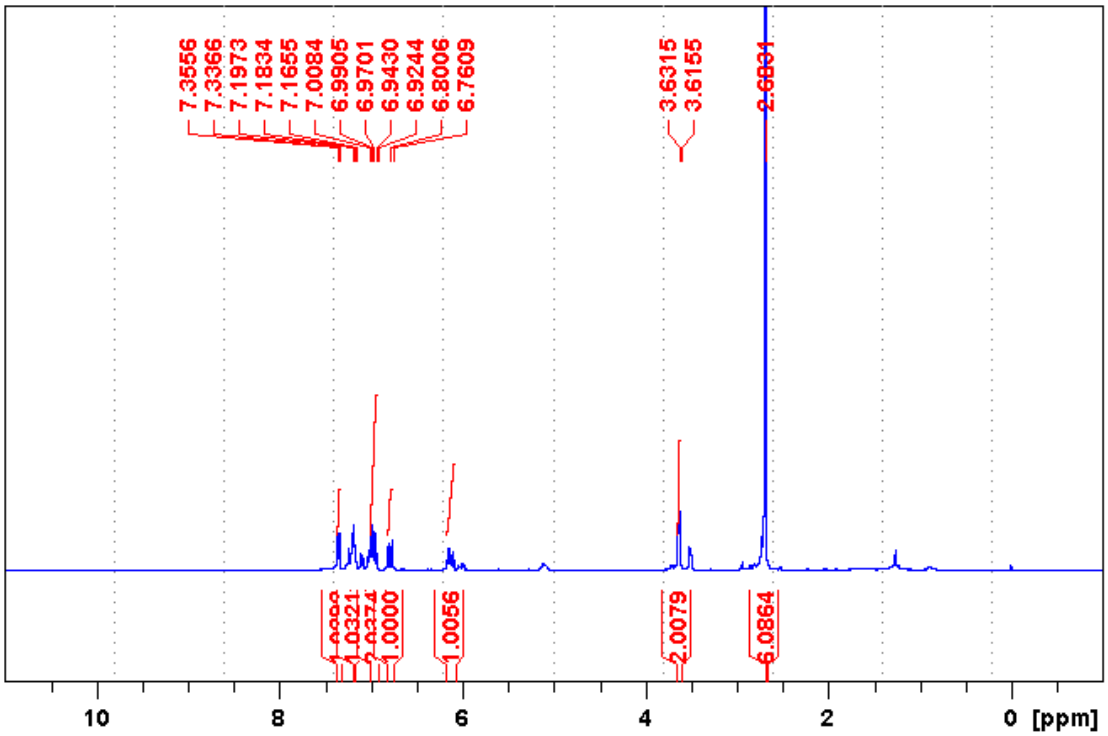
^{19}F NMR



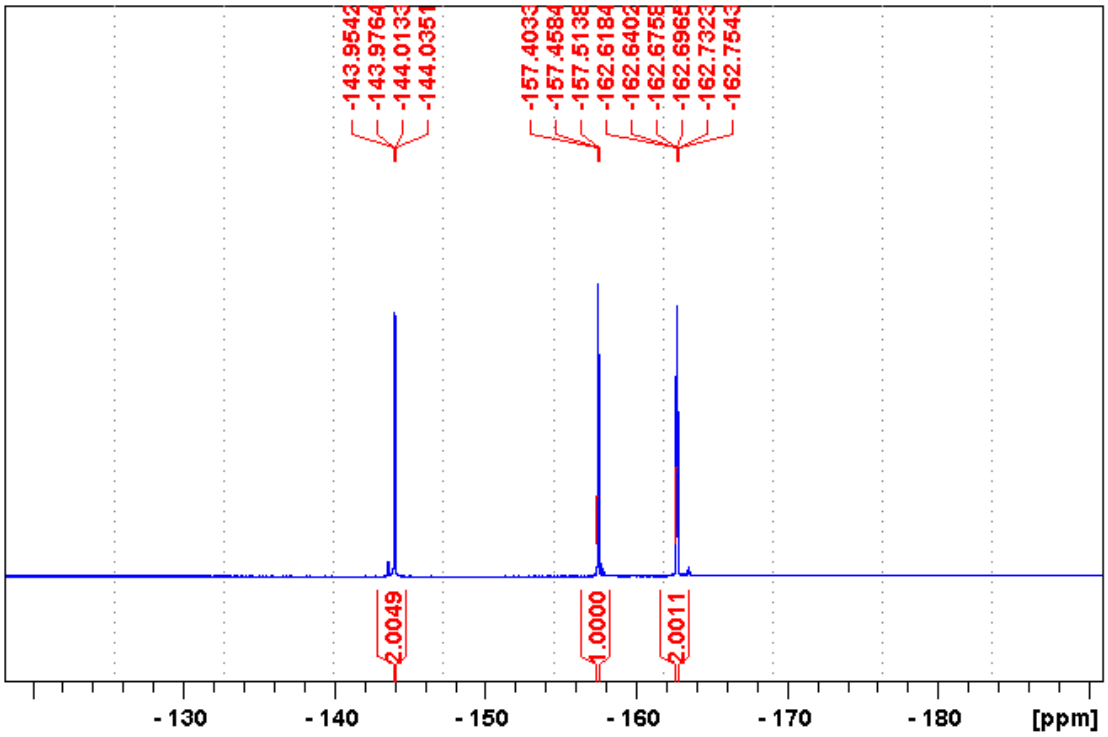


(3h) ccrude product

^{1}H NMR



^{19}F NMR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-162.6402
-162.6758
-162.6965
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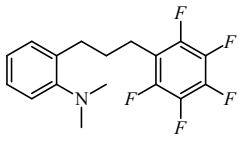
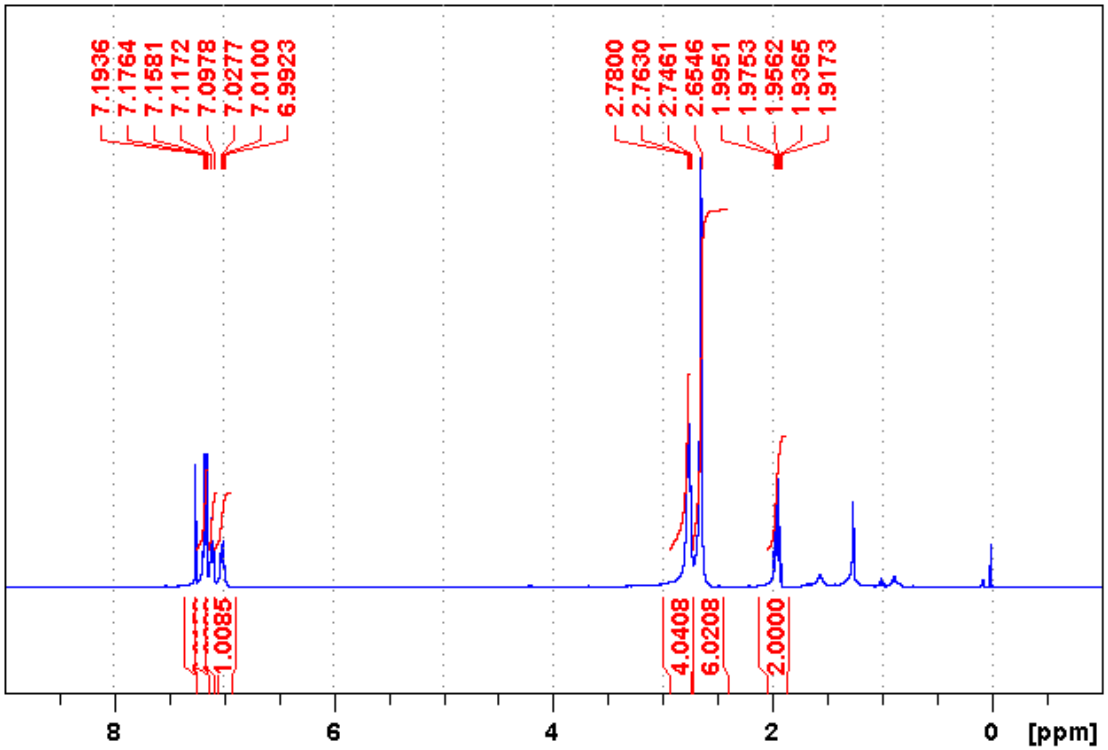
2.0049
1.0000
2.0011
- 130
- 140
- 150
- 160
- 170
- 180
[ppm]


F
F
F
F
F
N

(5h)

^{1}H NMR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7.1764
7.1581
7.1172
7.0978
7.0277
7.0100
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2.7461
2.6546
1.9951
1.9753
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2.0000
8
6
4
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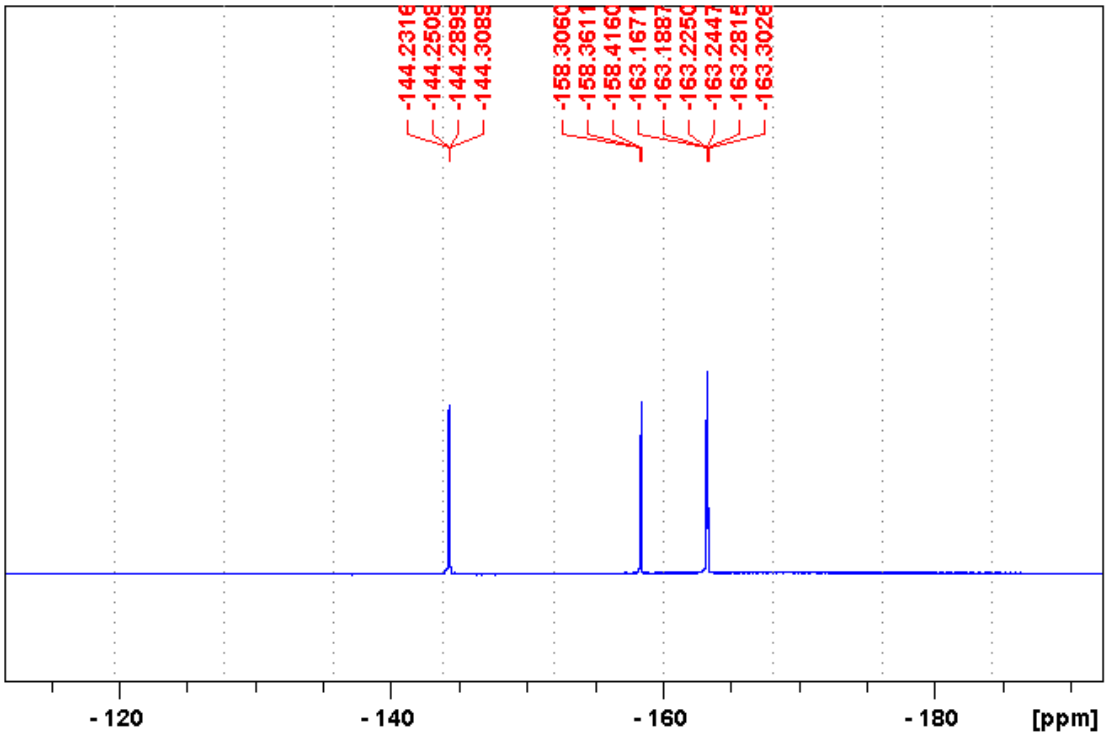
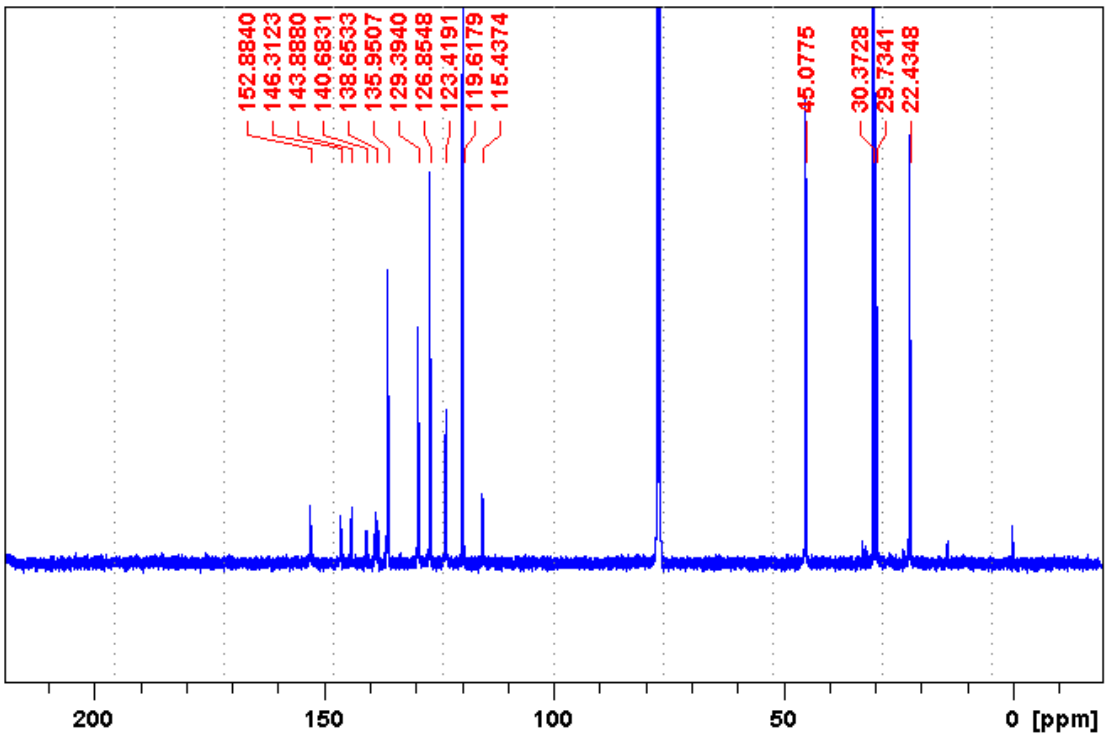
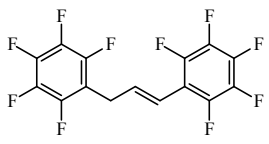
[ppm]

^{19}F NMR



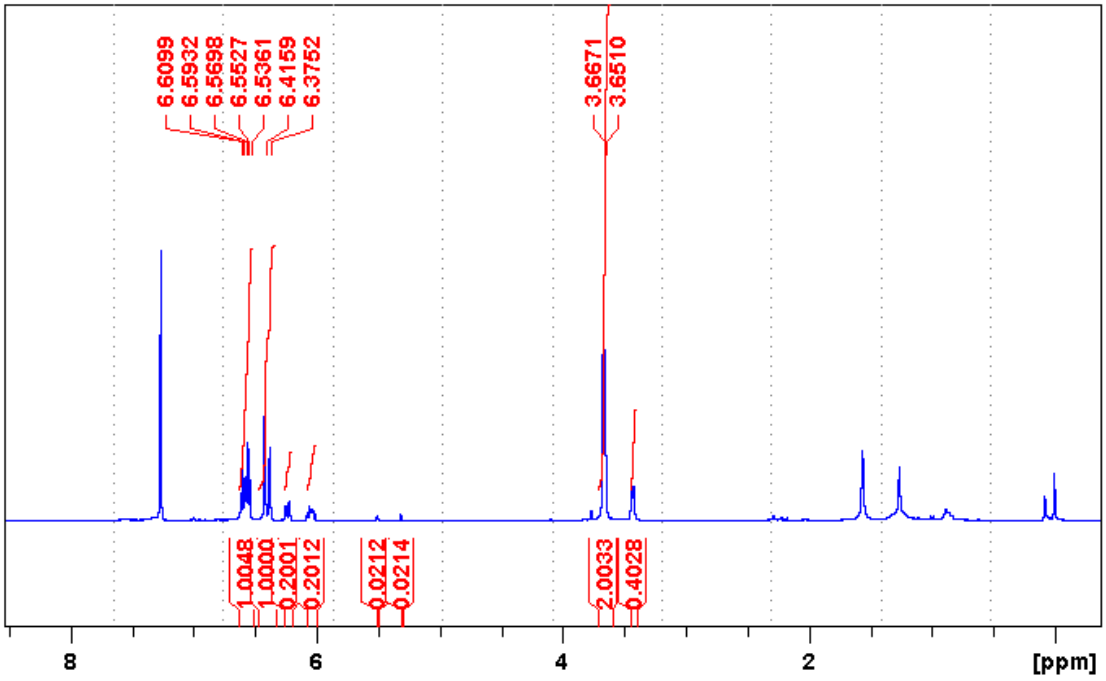
^{13}C NMR



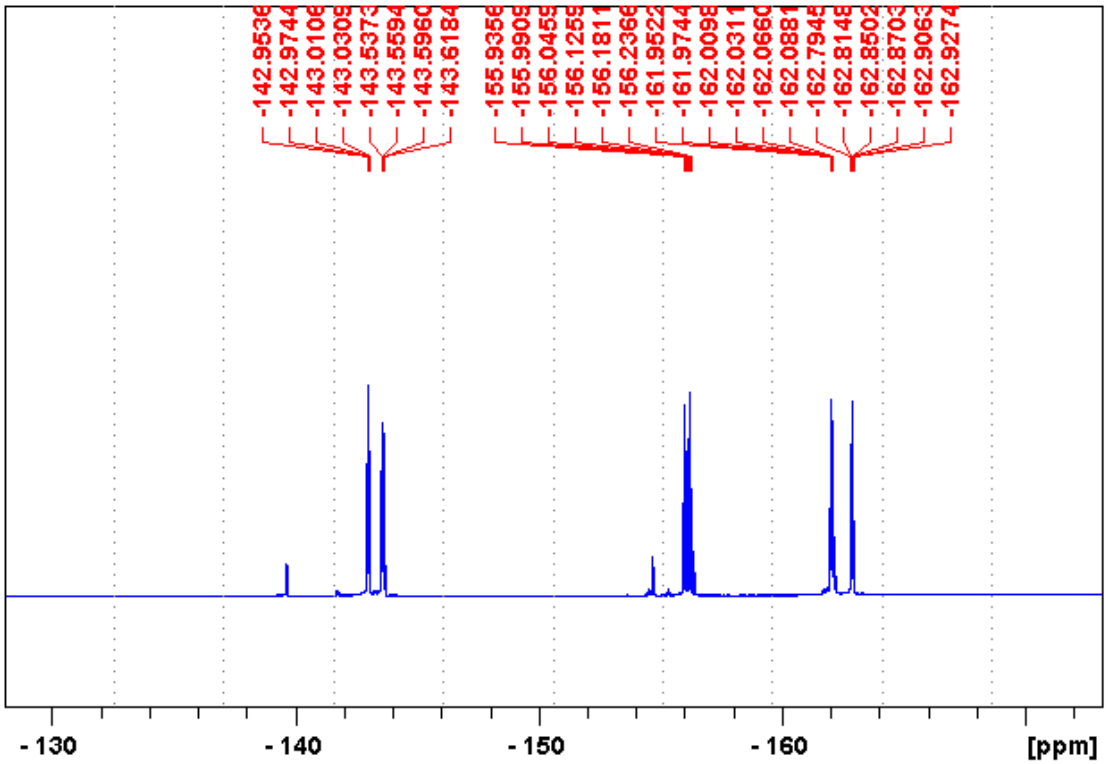


3i E/Z 5:1 3i/4i=98:2

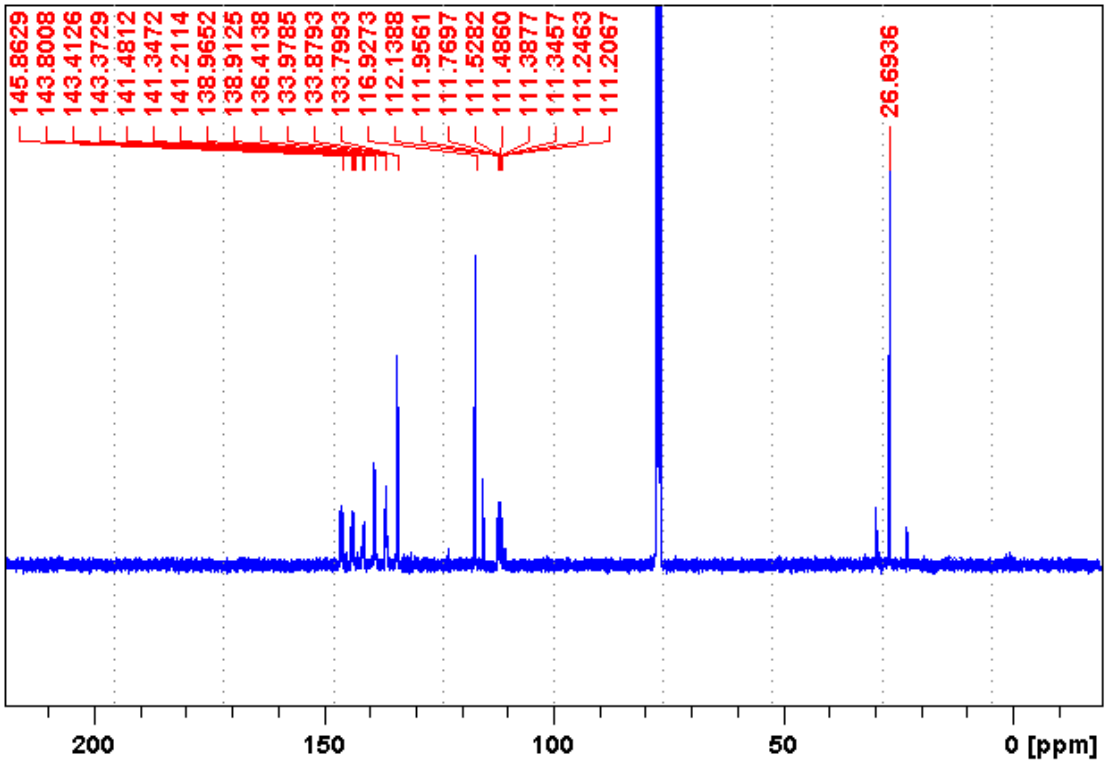
^{1}H NMR

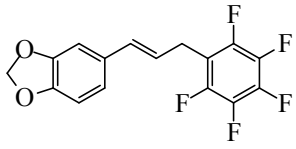


^{19}F NMR



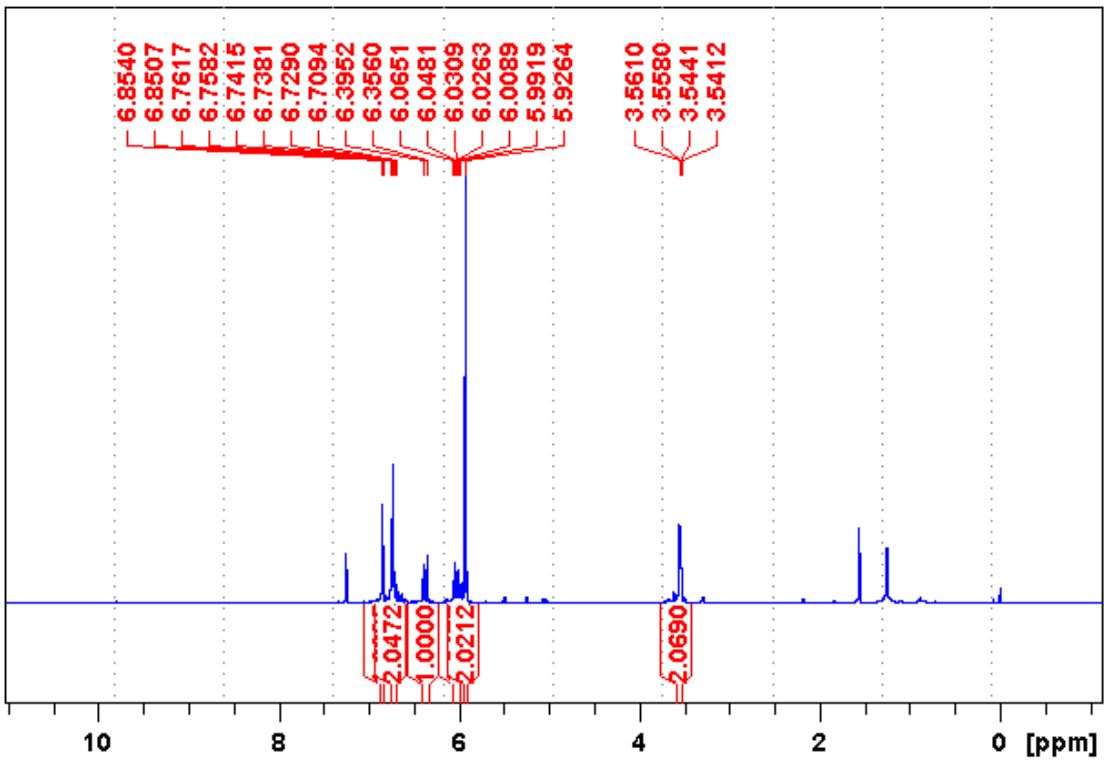
^{13}C NMR



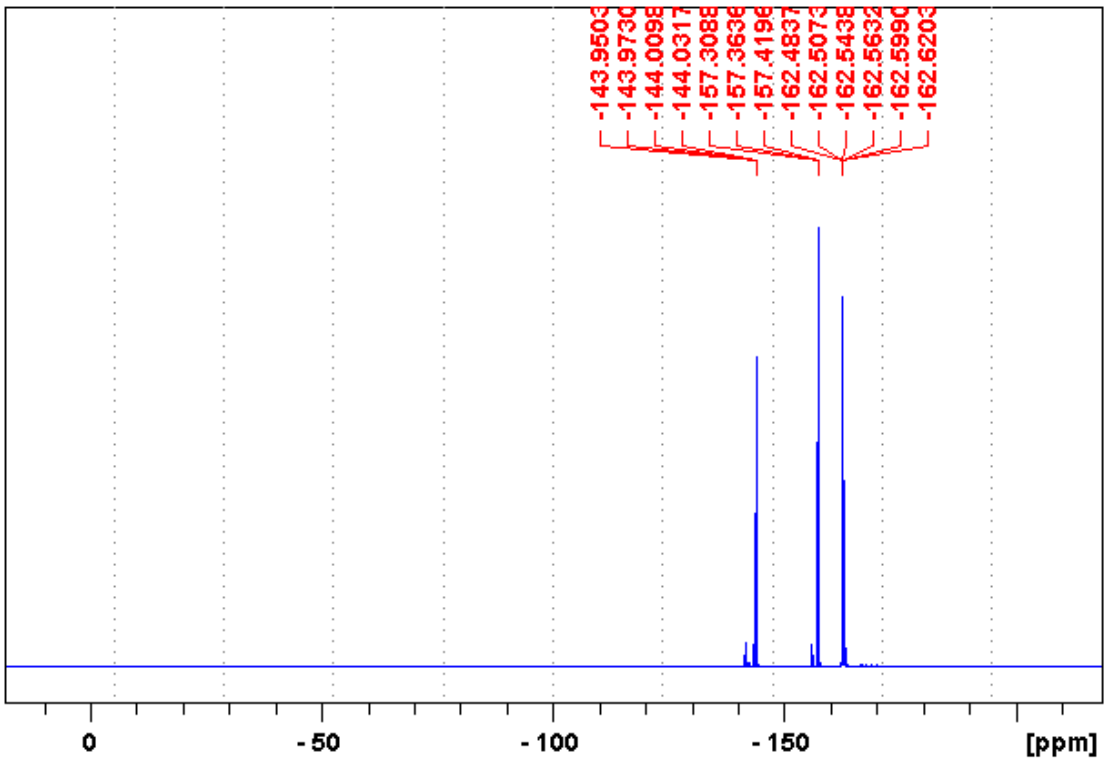


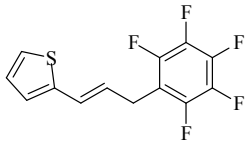
(3j) E/Z>20:1 3j/4j = 98:2

^{1}H NMR



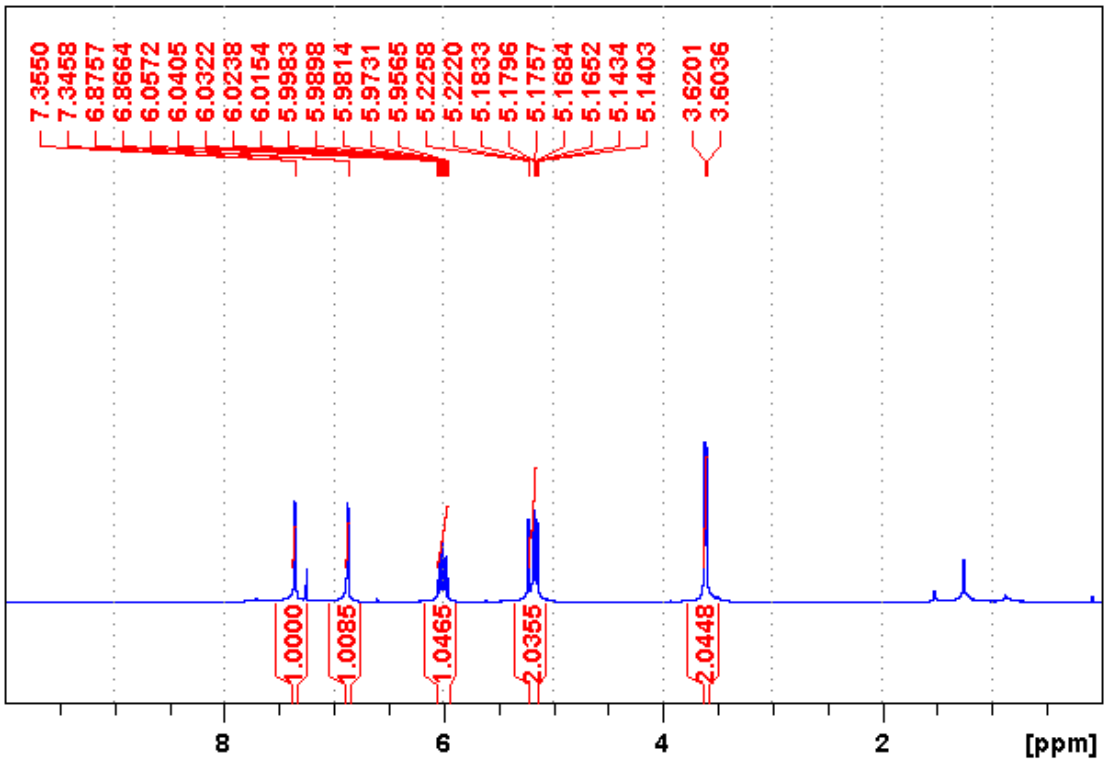
^{19}F NMR



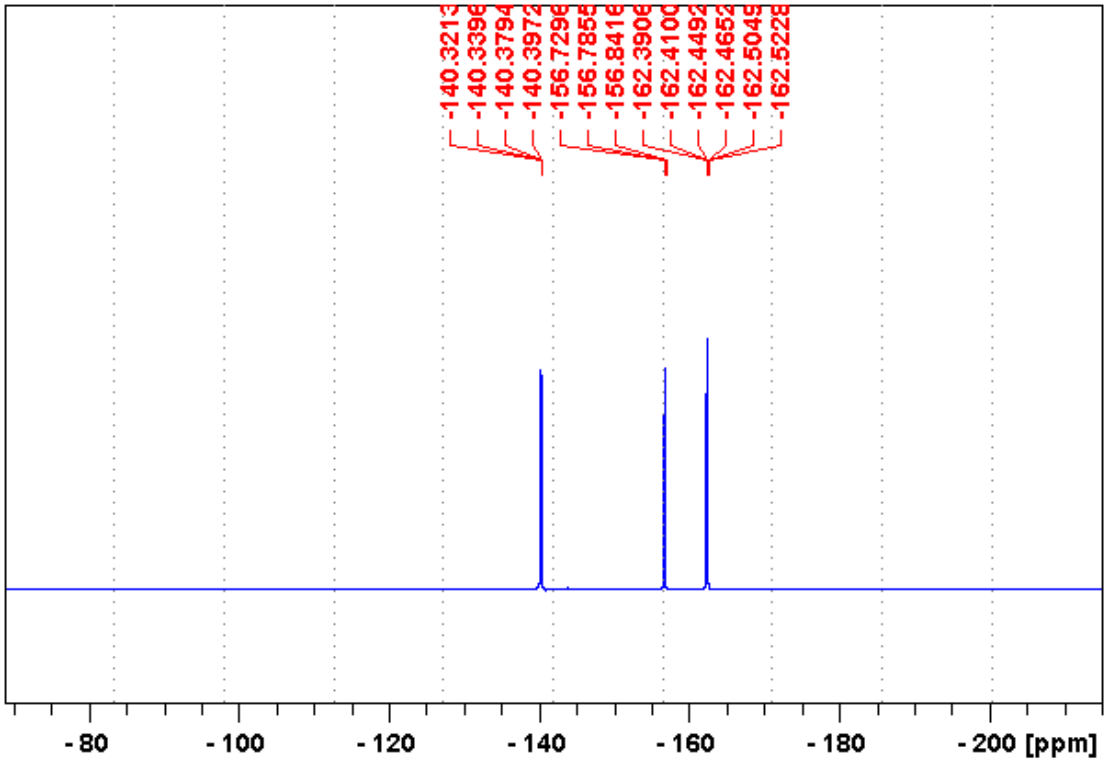


(3k)

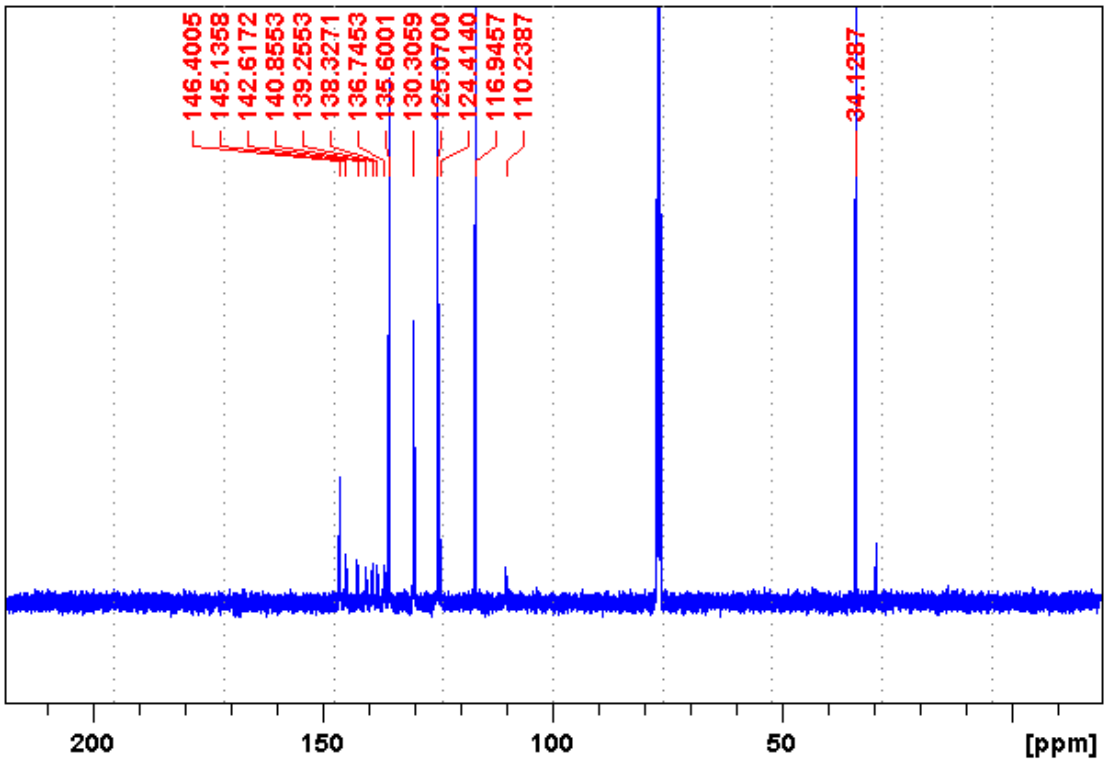
^{1}H NMR

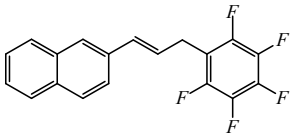


^{19}F NMR



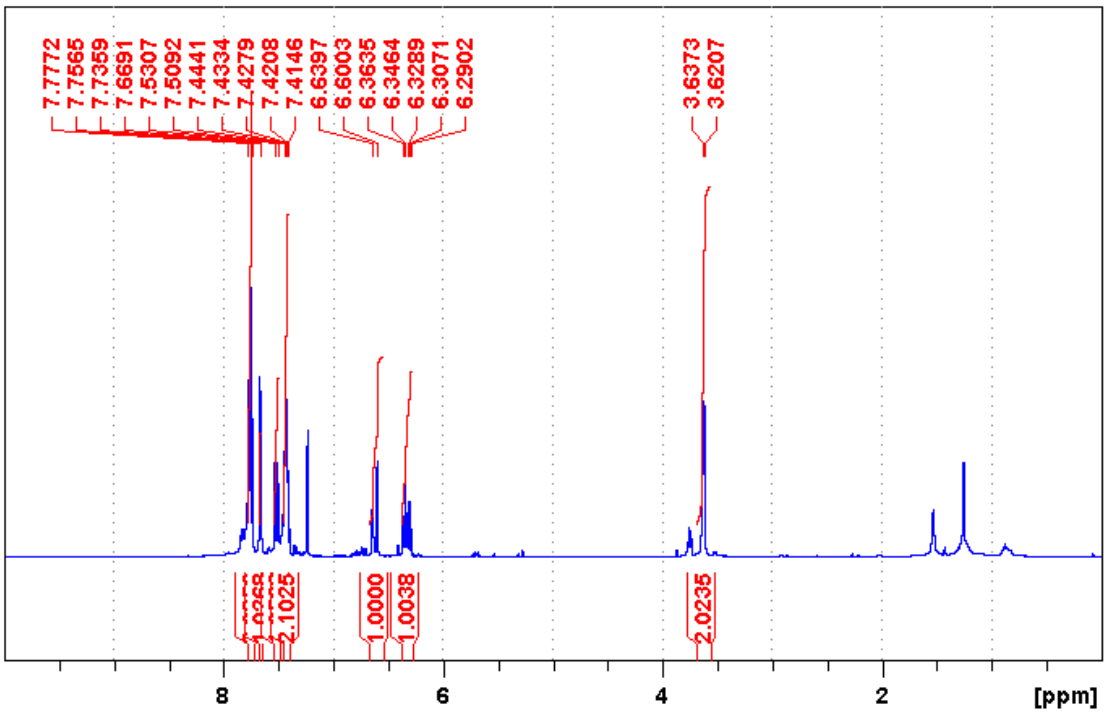
^{13}C NMR



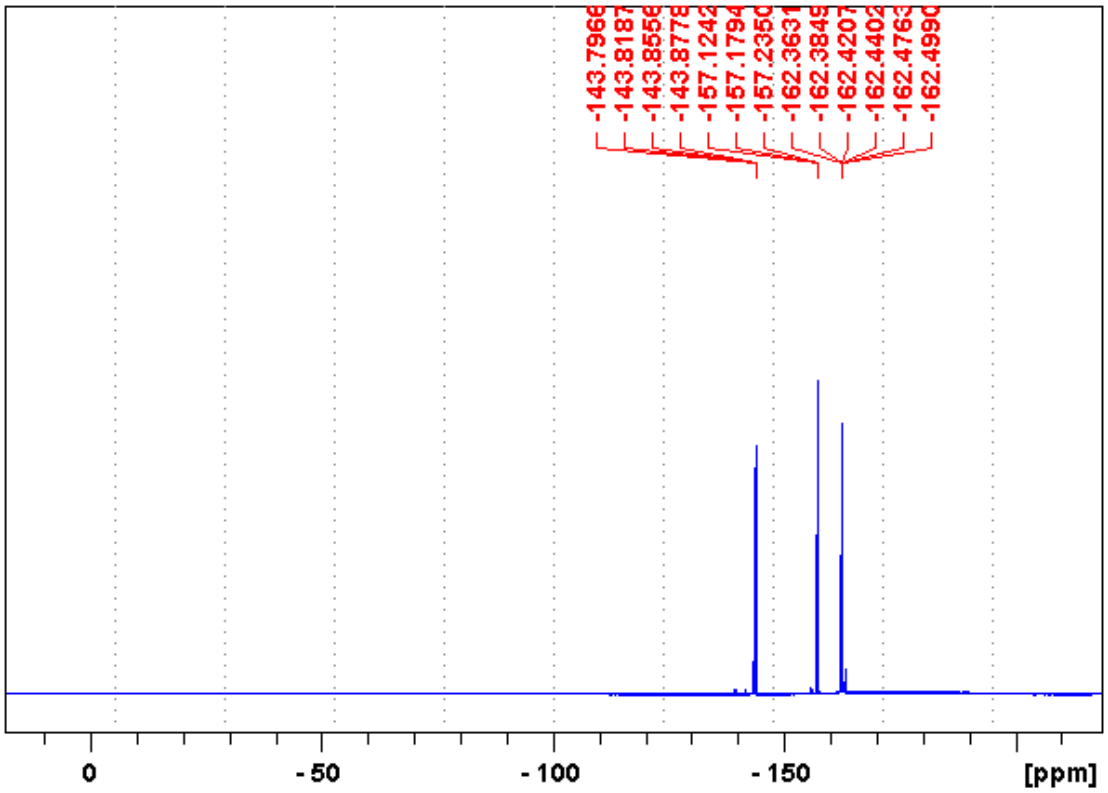


(3l) E:Z 33:1, 3ea/5ea =98:2

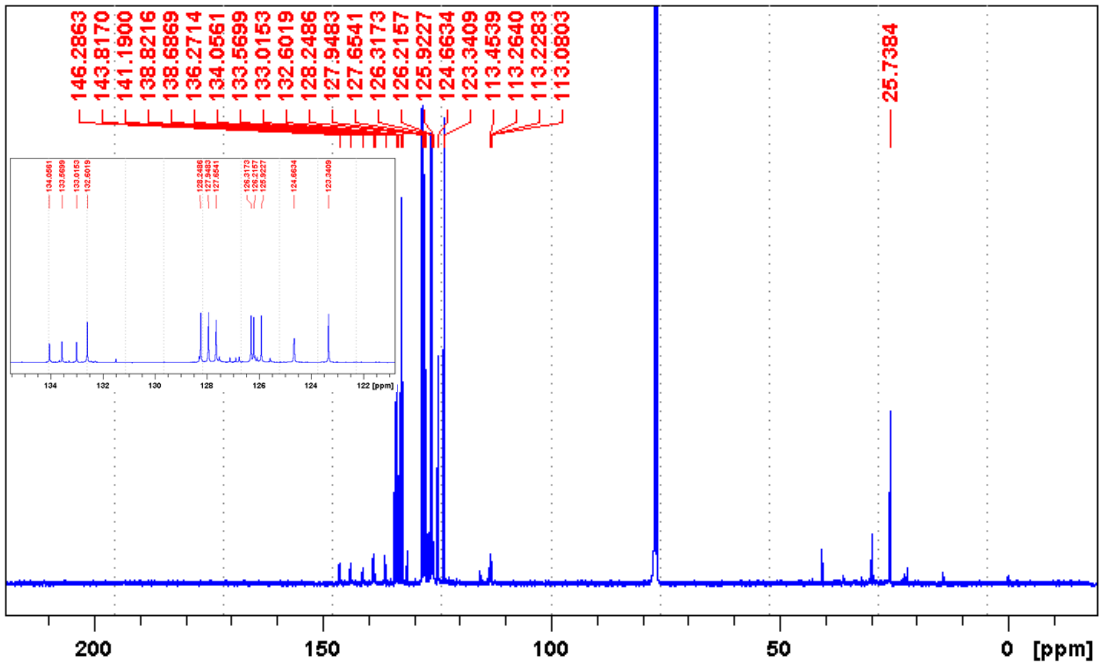
^{1}H NMR

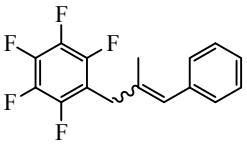


^{19}F NMR

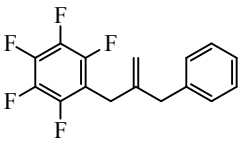


^{13}C NMR



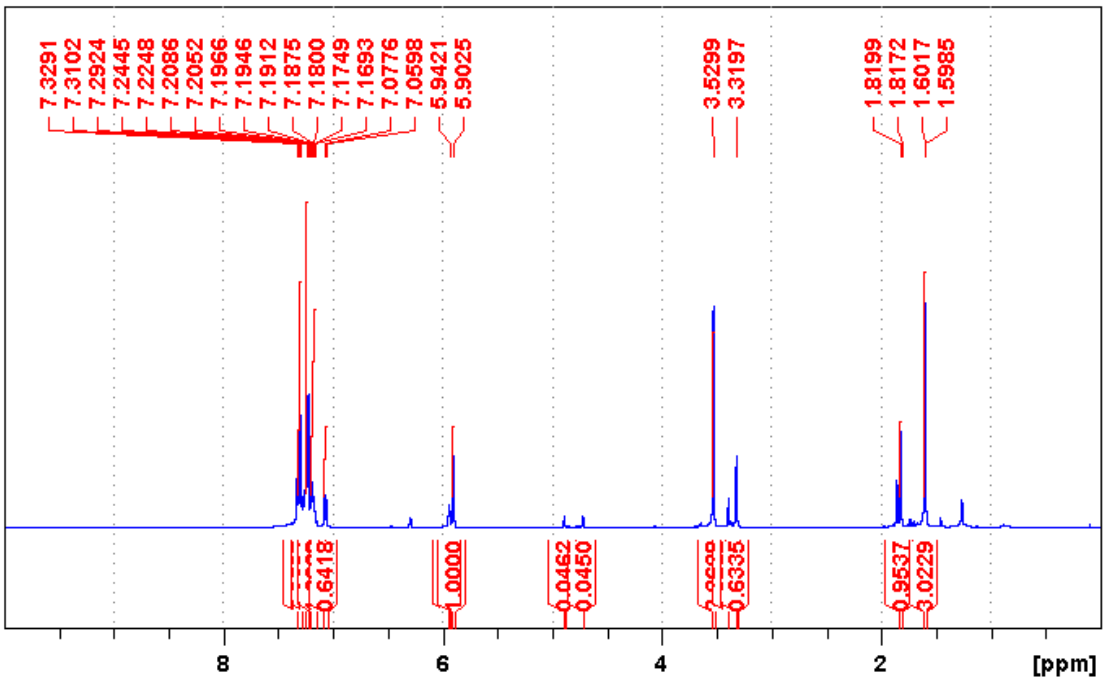


(3m$_1$, E/Z=3:1) mixed with

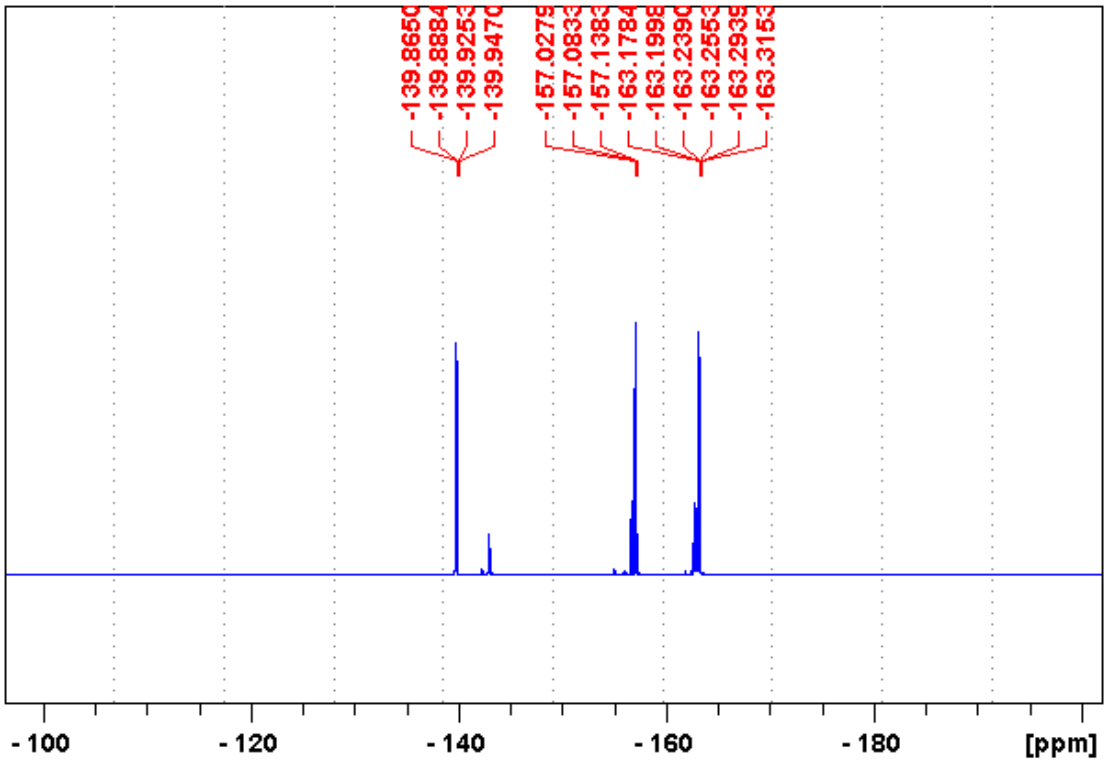


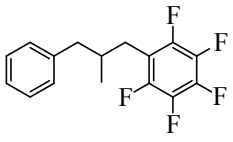
(3m$_2$) 3m$_1$:3m$_2$=26/1

^{1}H NMR



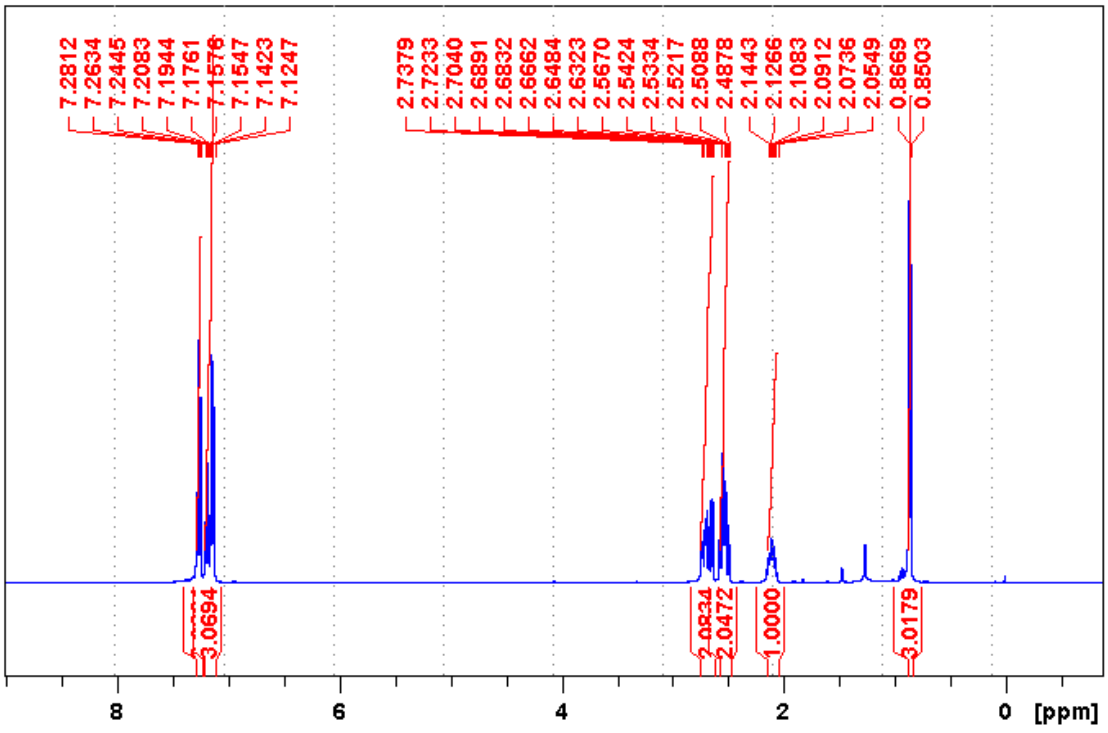
^{19}F NMR



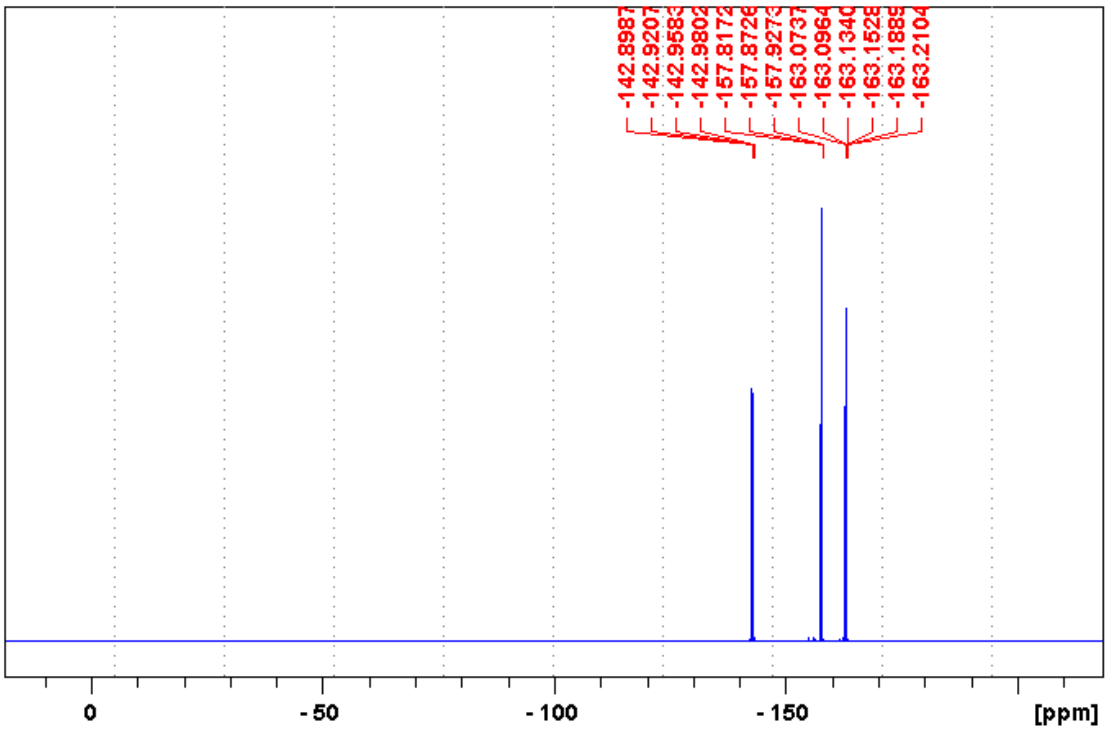


(5m)

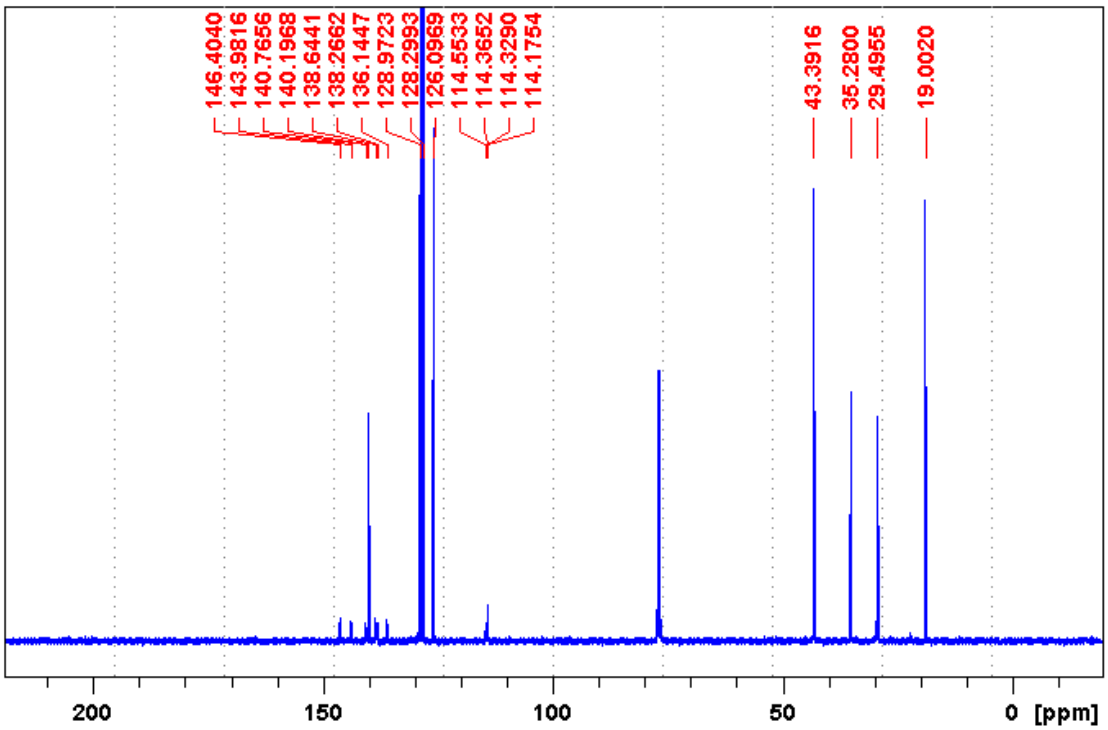
^{1}H NMR

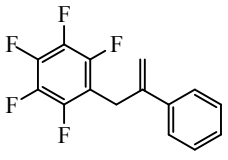


^{19}F NMR

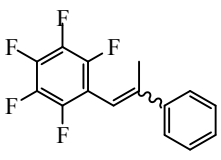


^{13}C NMR



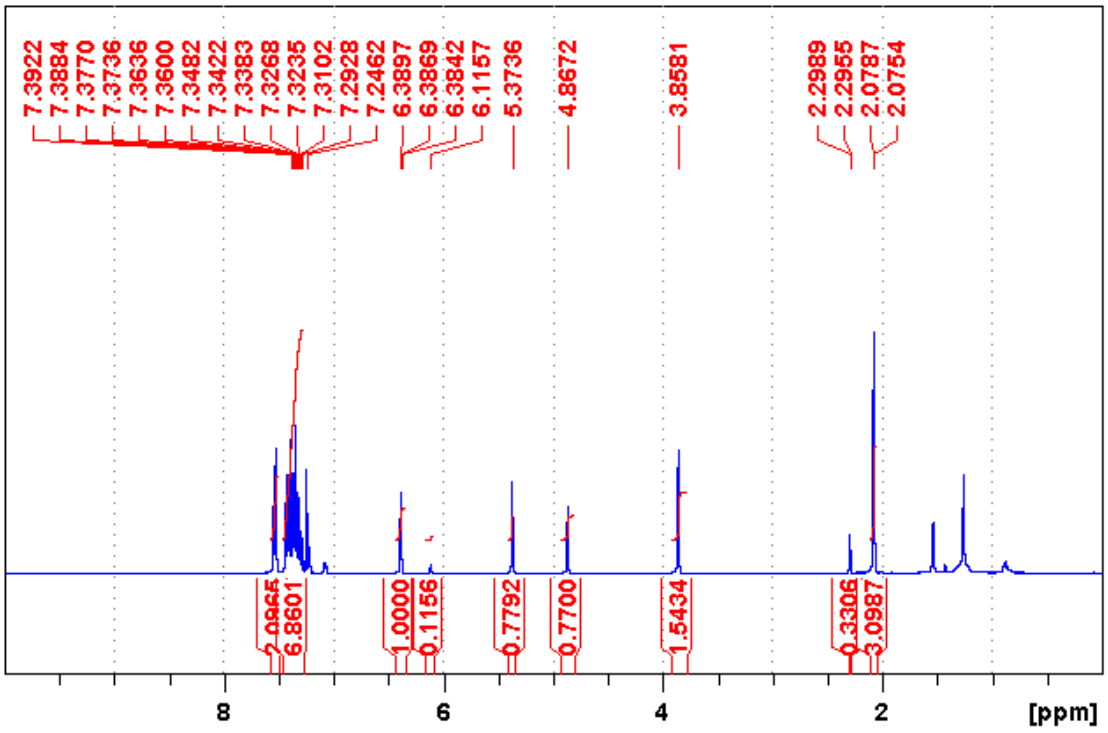


(3n) mixed with

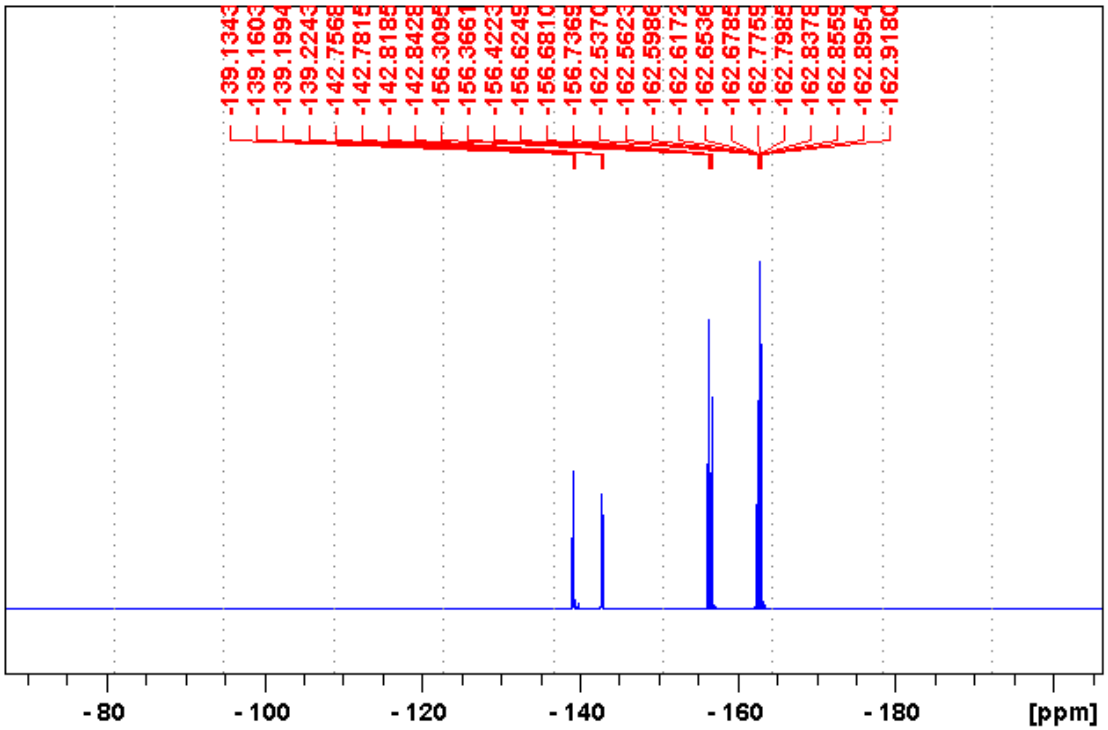


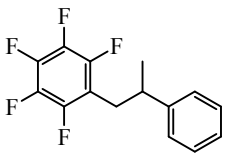
(4n, E:Z=9.1:1) 3n/4n=1:1.3

^{1}H NMR



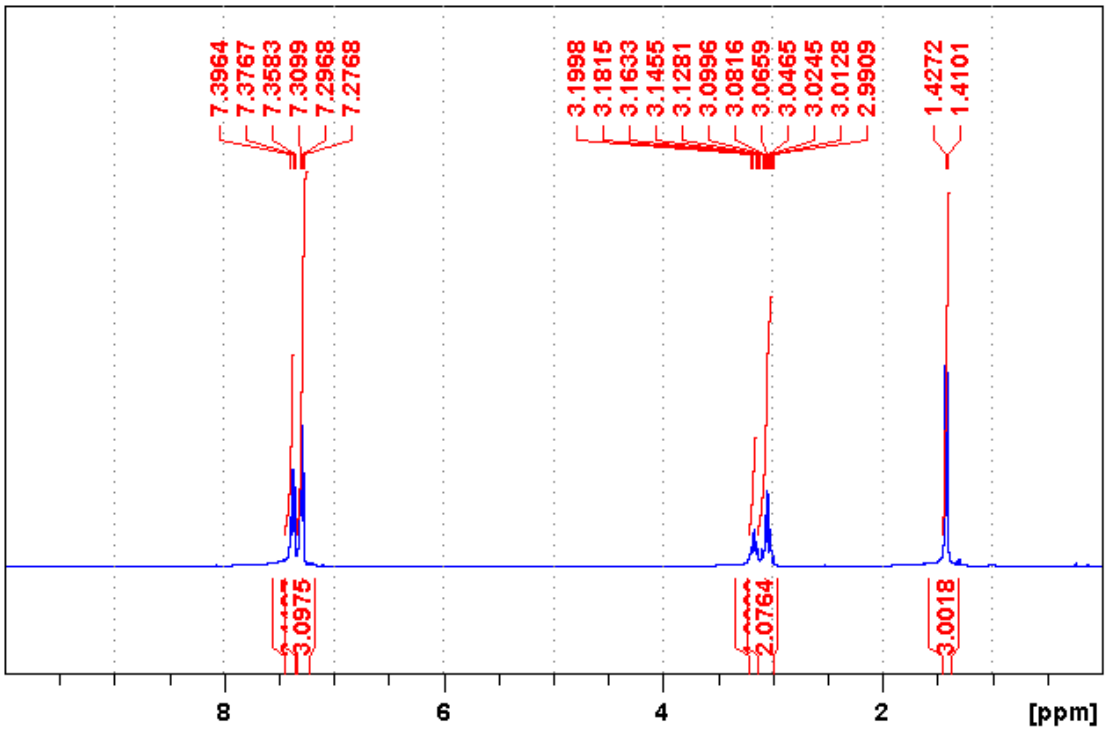
^{19}F NMR



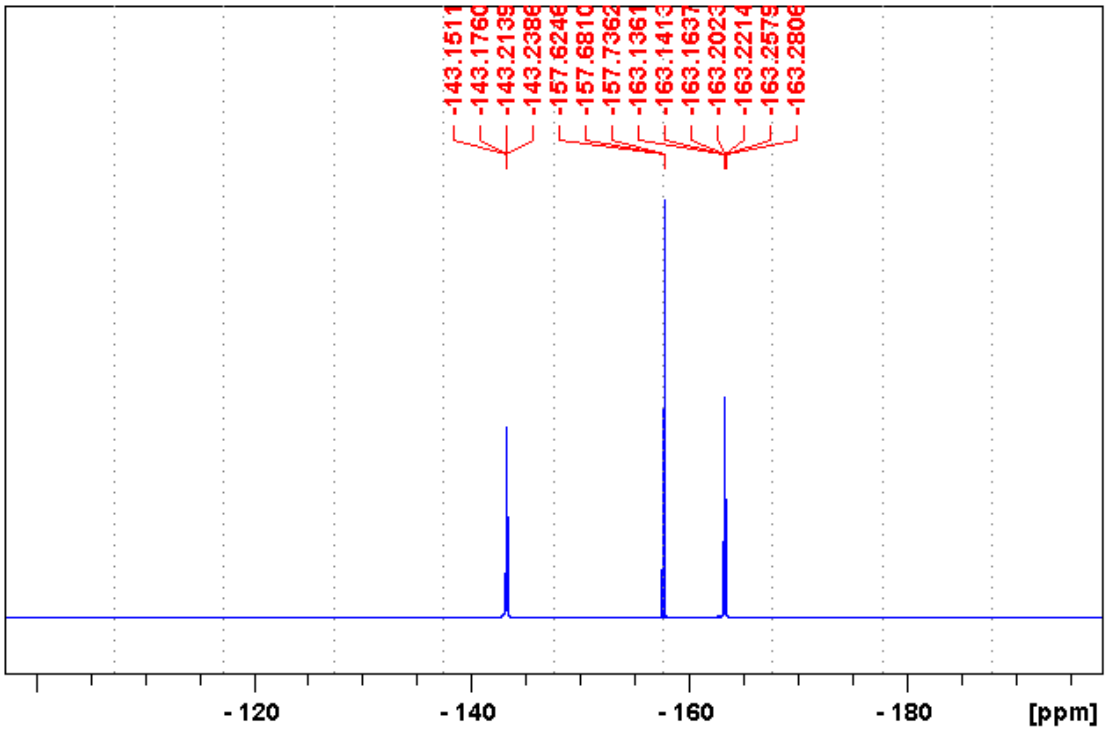


(5n)

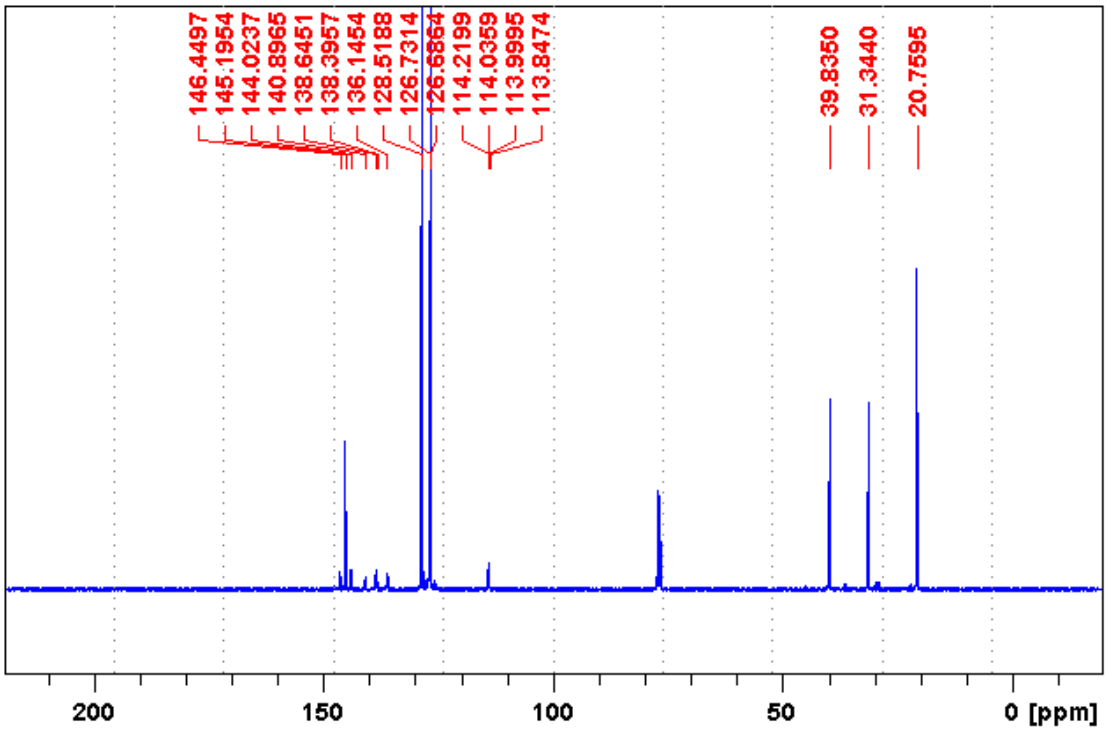
^{1}H NMR

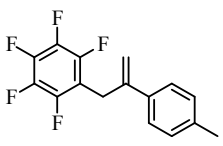


^{19}F NMR

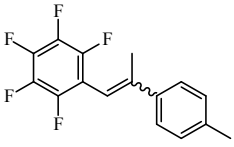


^{13}C NMR



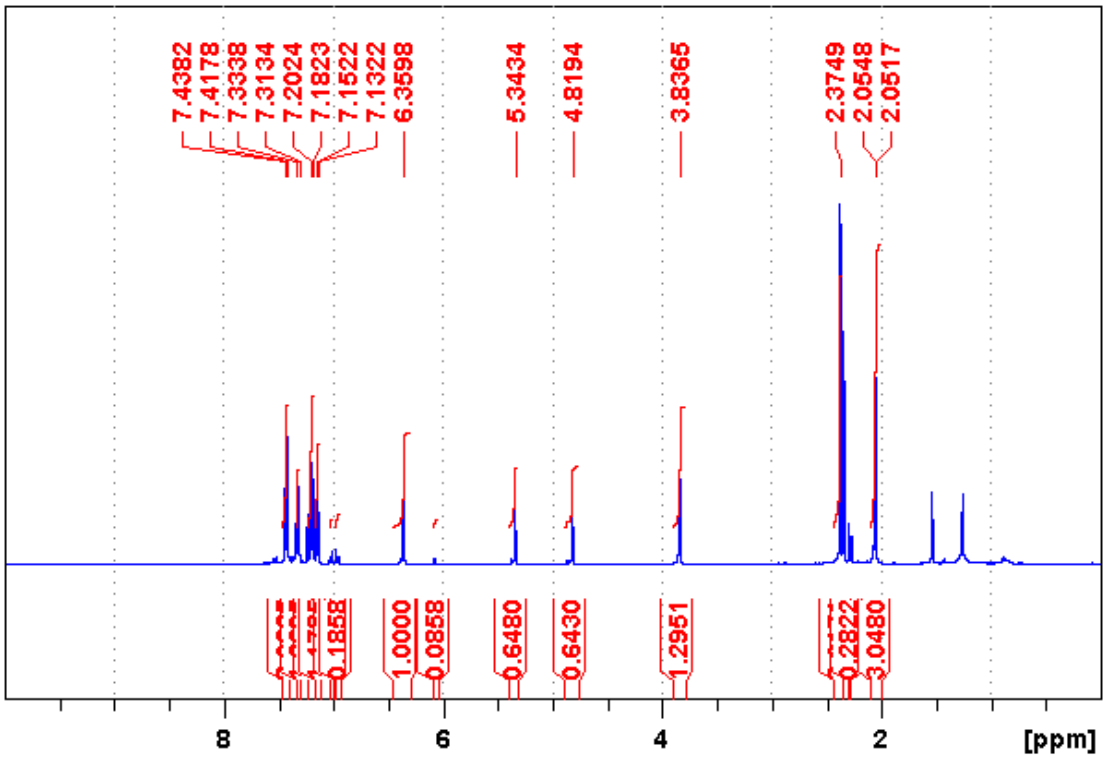


(3o) mixed with

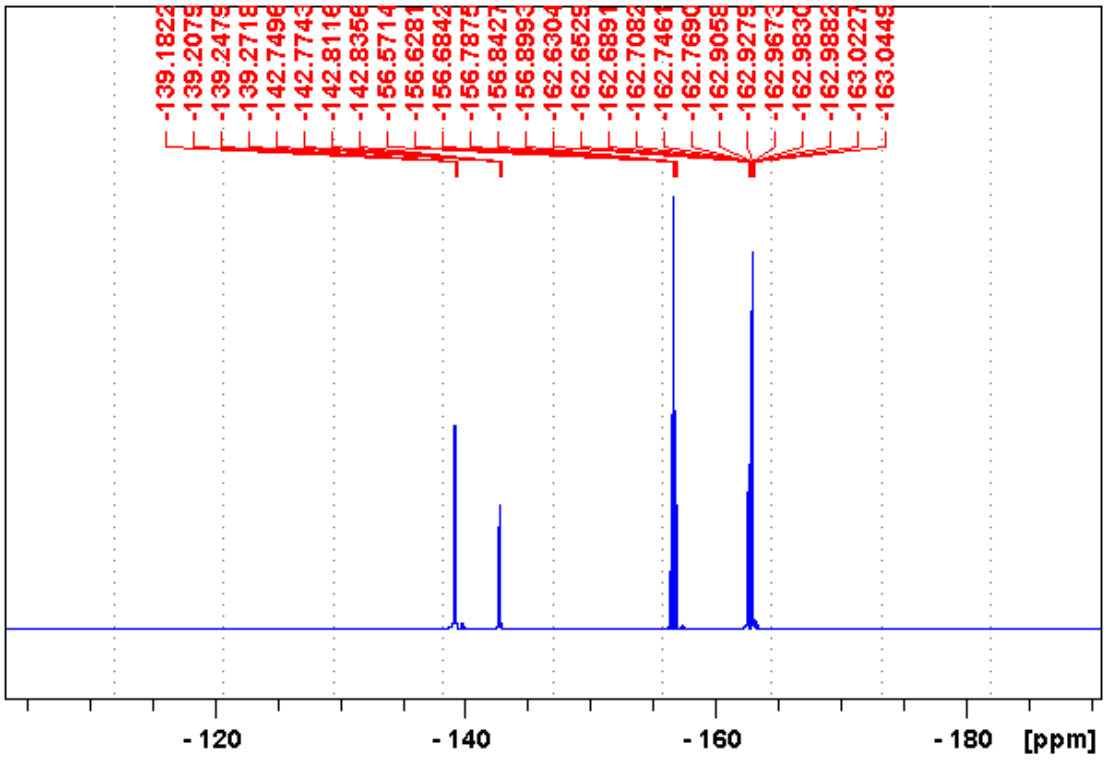


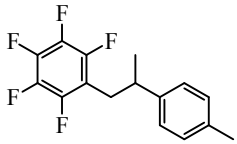
(4o, E/Z 12:1) 3o/4o=1/1.5

^{1}H NMR



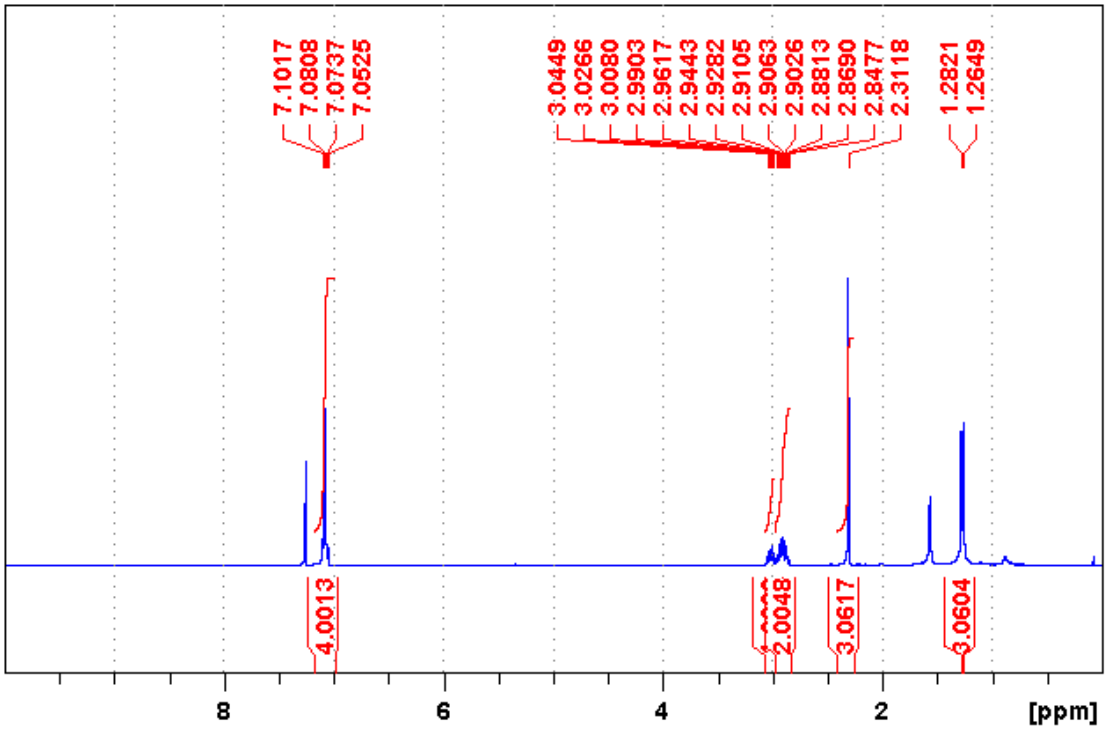
^{19}F NMR



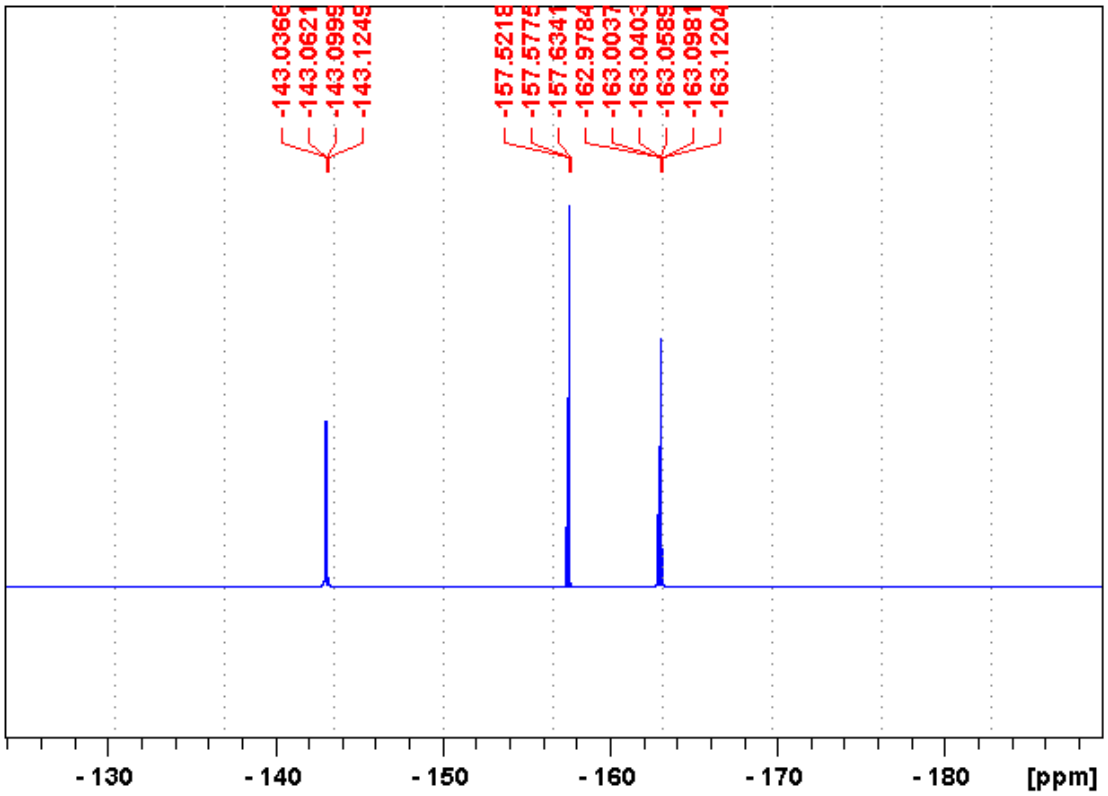


(5o)

^{1}H NMR



^{19}F NMR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-163.0037
-163.0403
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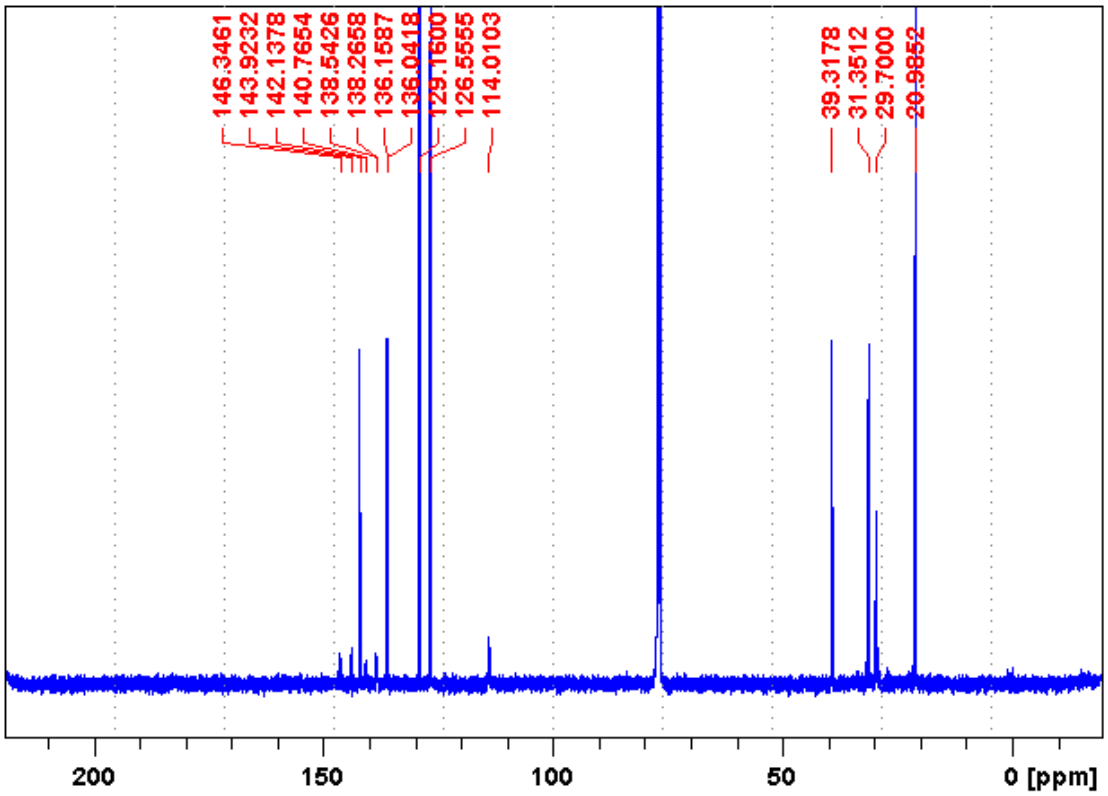
-163.0981
-163.1204
- 130
- 140
- 150
- 160
- 170
- 180
[ppm]

^{13}C NMR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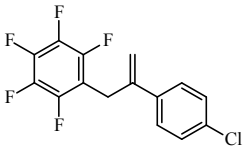
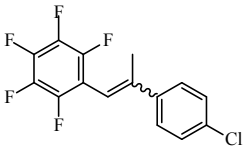
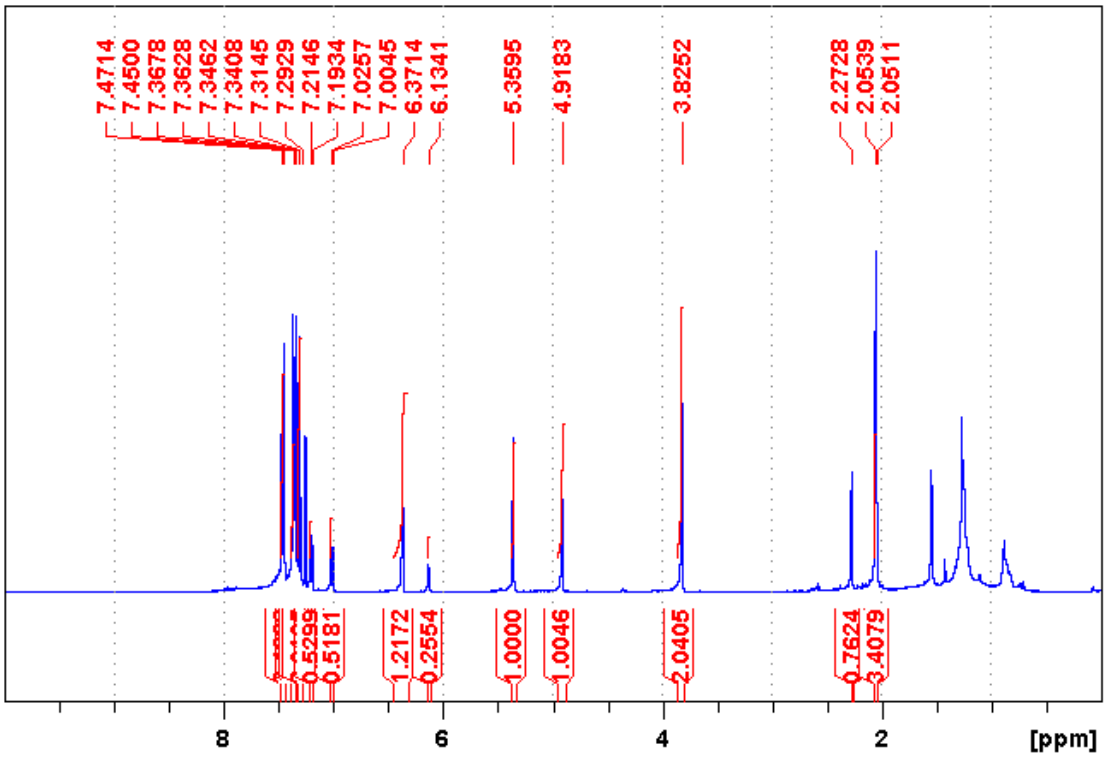
0 [ppm]



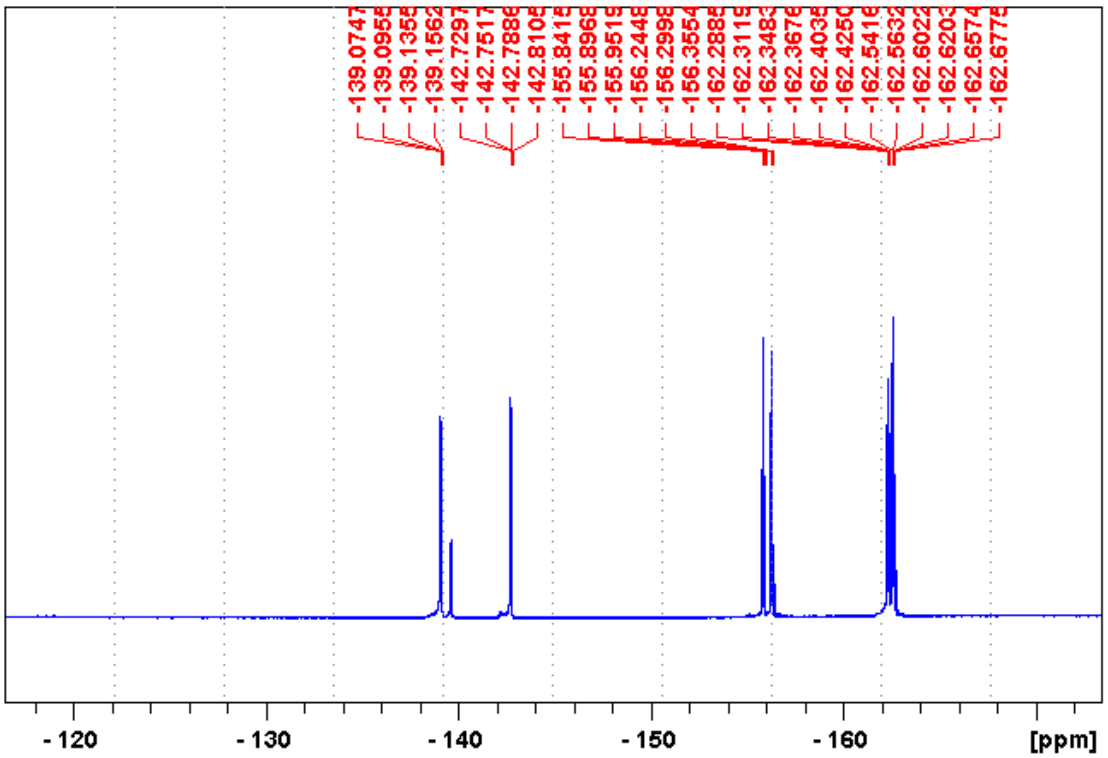
(3p) mixed with


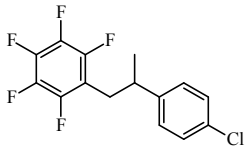
(4p, E/Z=4.8/1) 3p/4p=1/1.2

^{1}H NMR



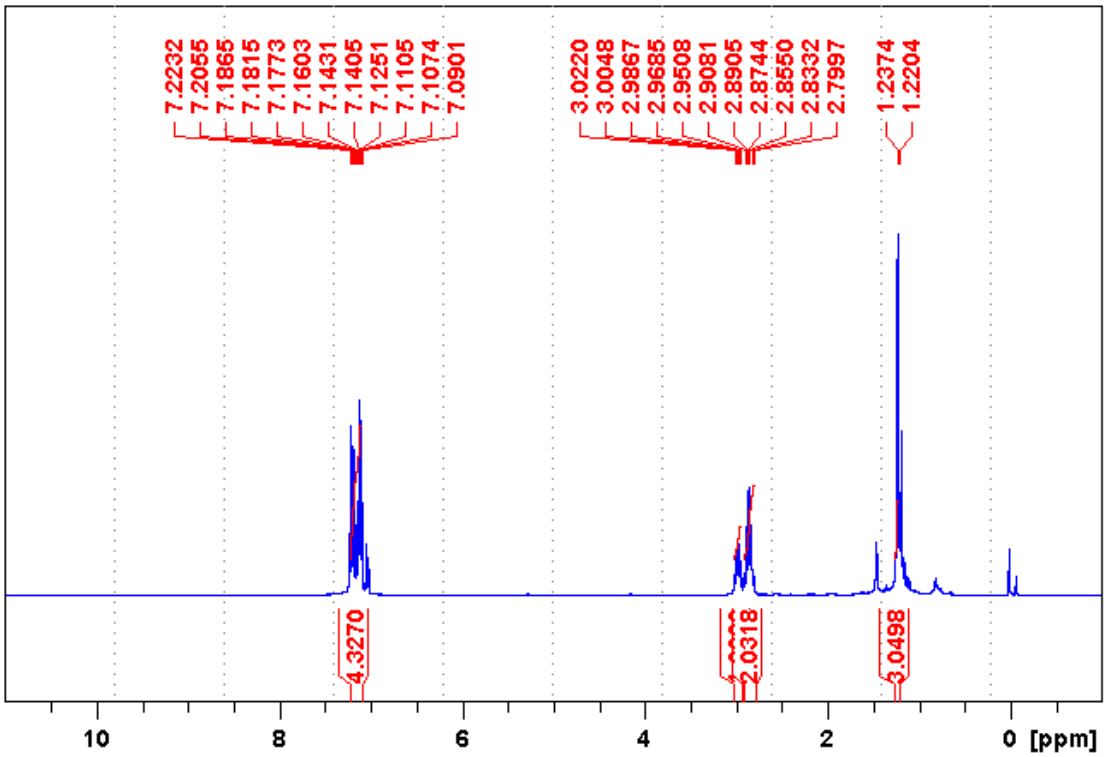
^{19}F NMR



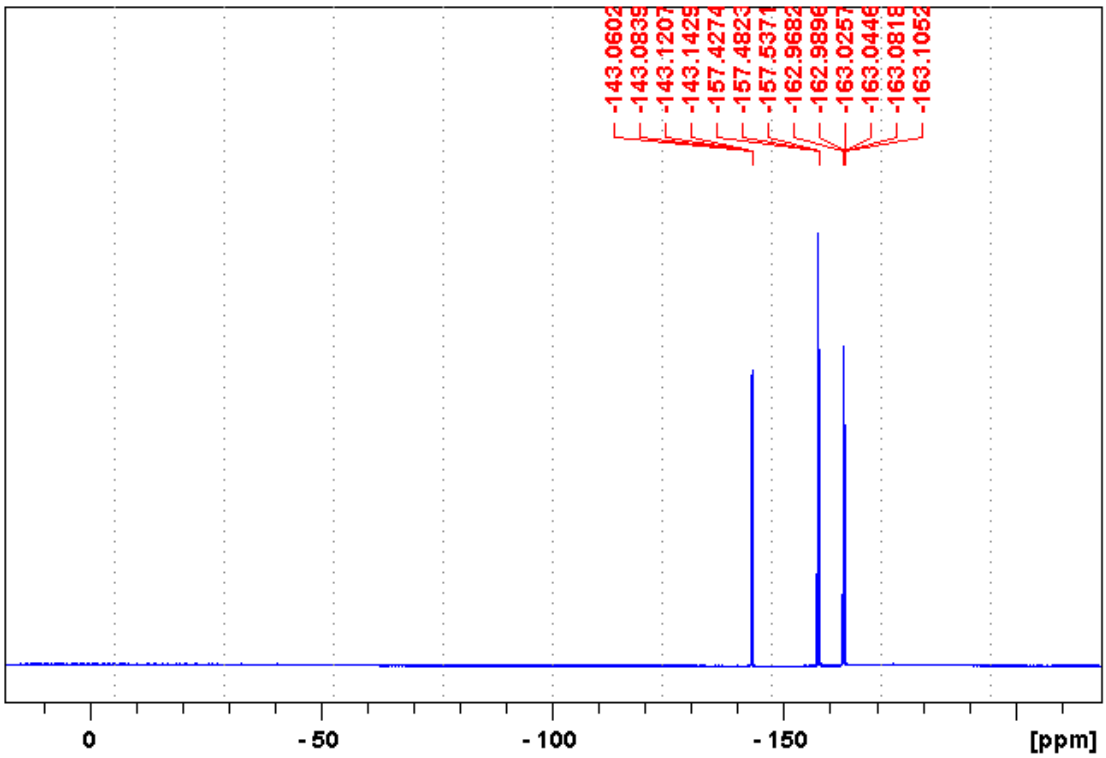


(5p)

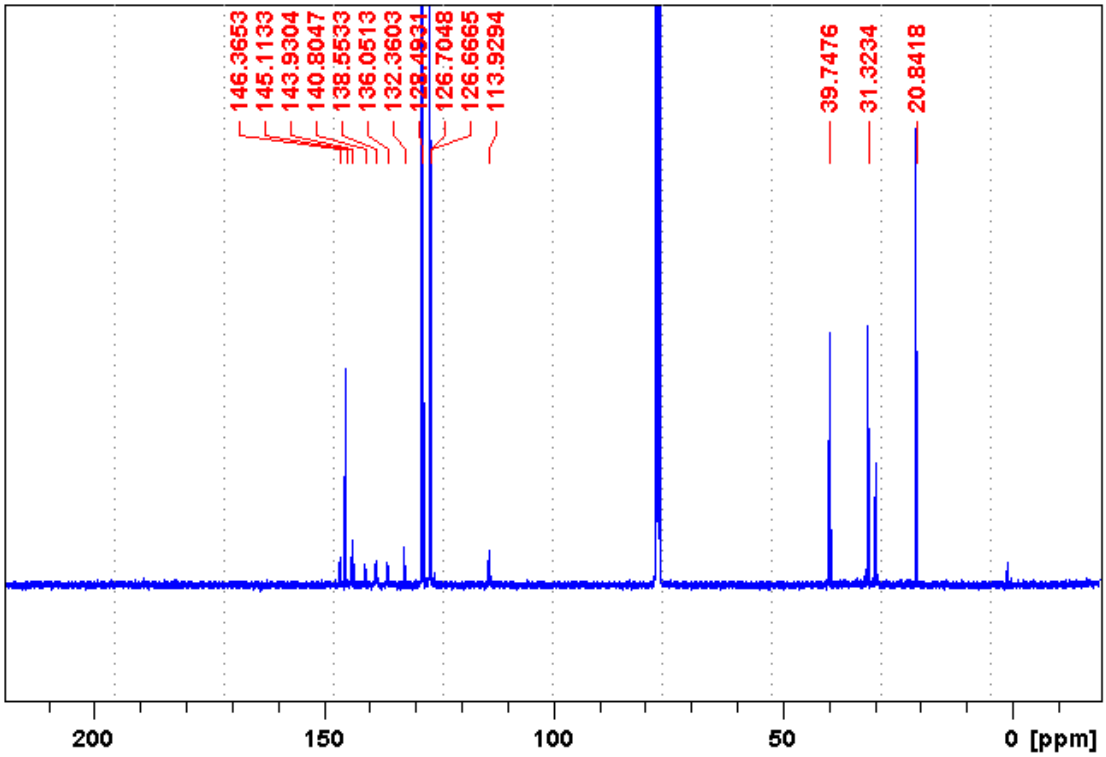
^{1}H NMR

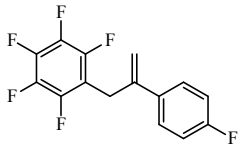
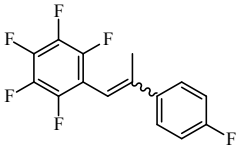


^{19}F NMR

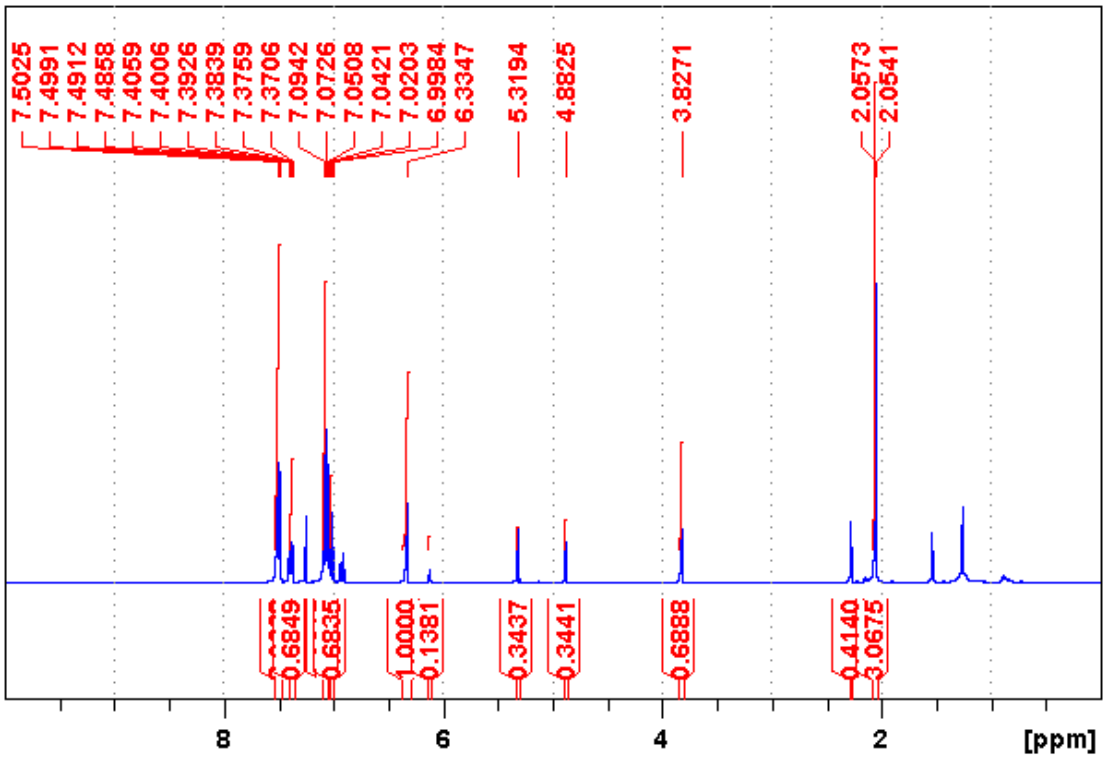


^{13}C NMR

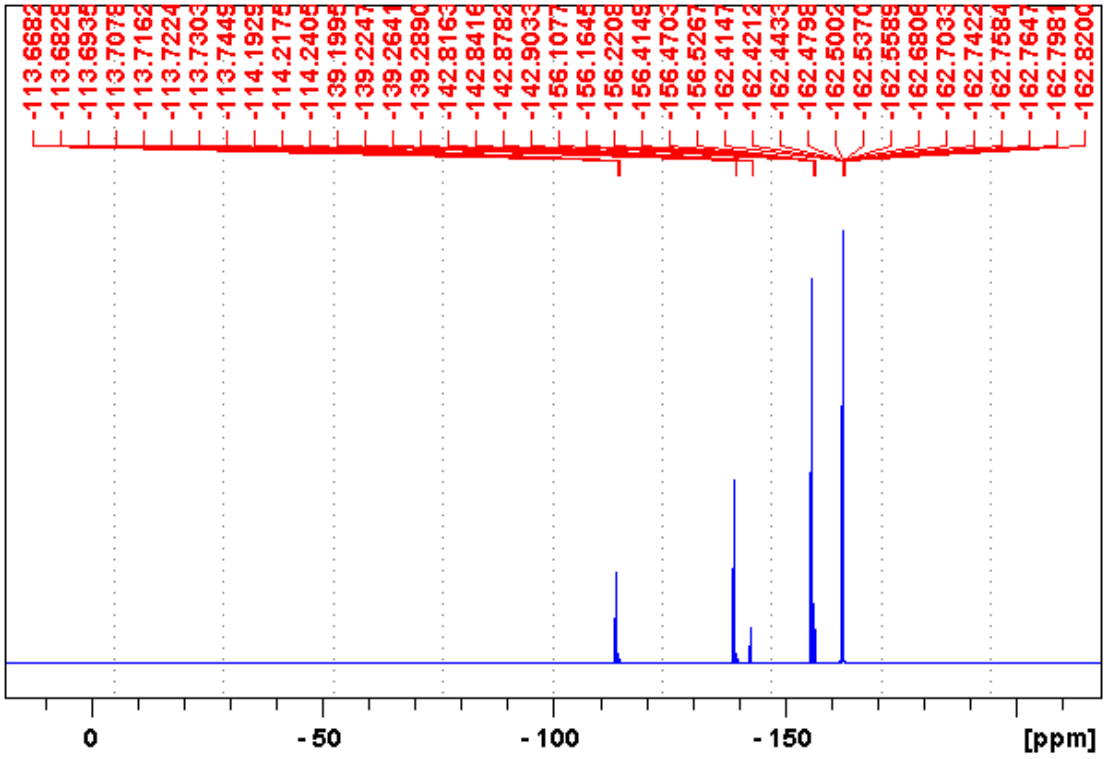


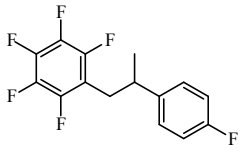

(3q) mixed with

(4q, E/Z=7.2:1) 3q/4q=1/2.9

^{1}H NMR



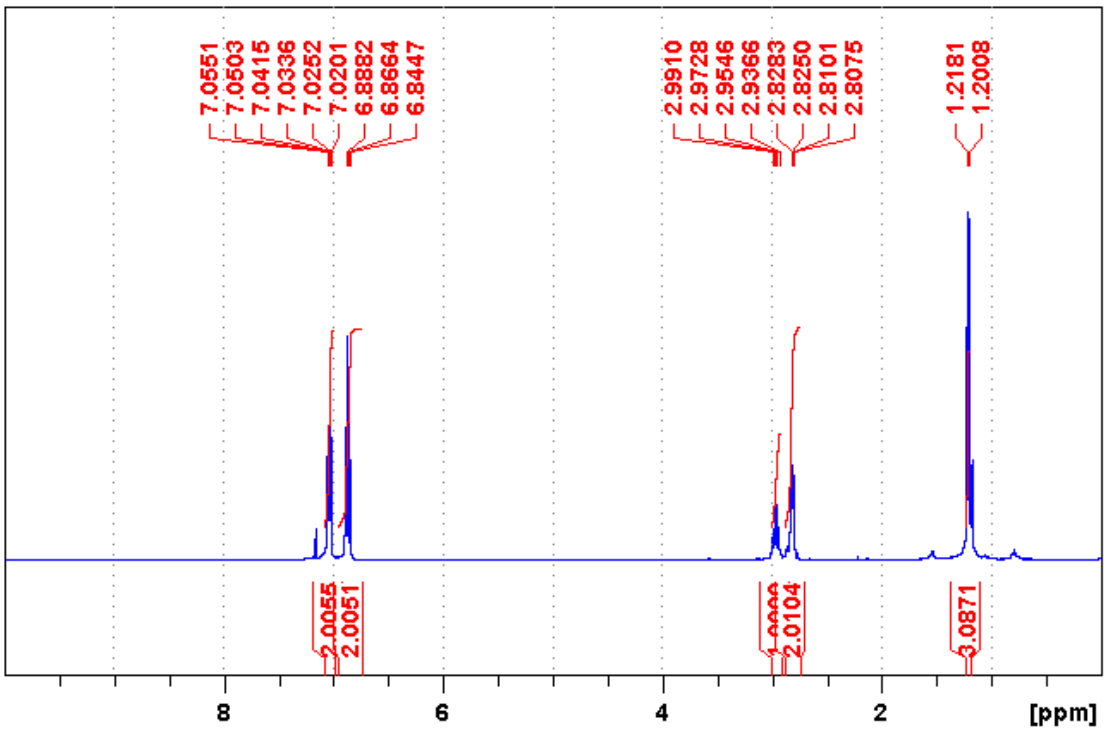
^{19}F NMR



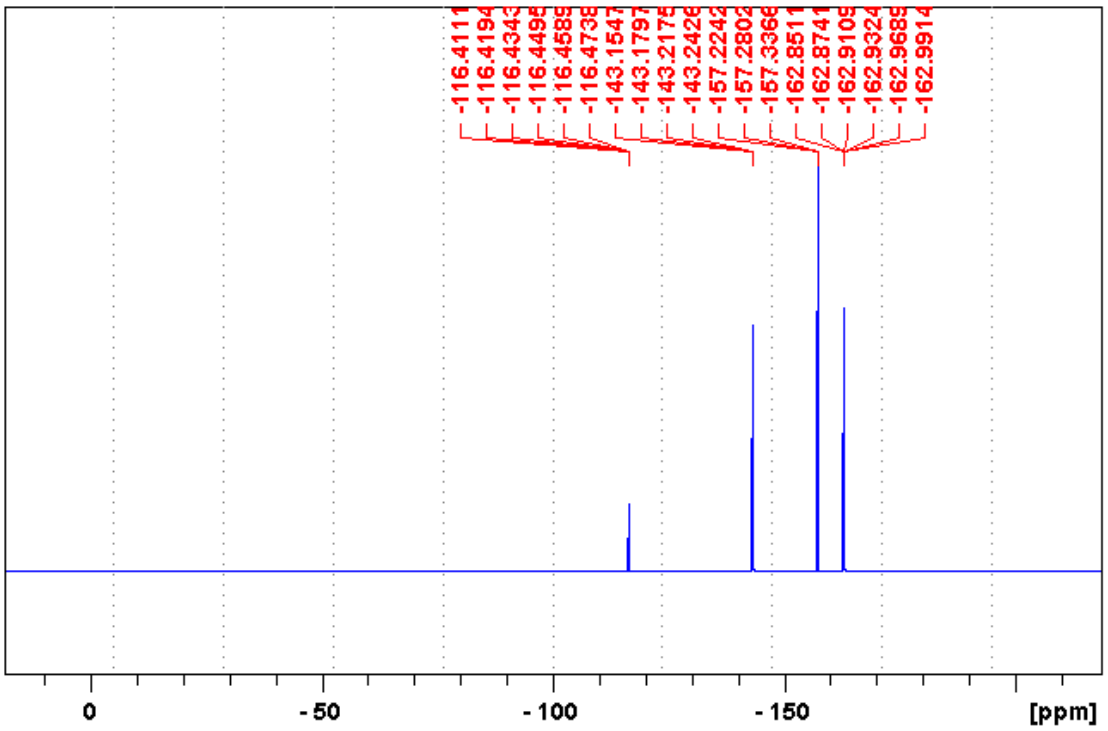


(5q)

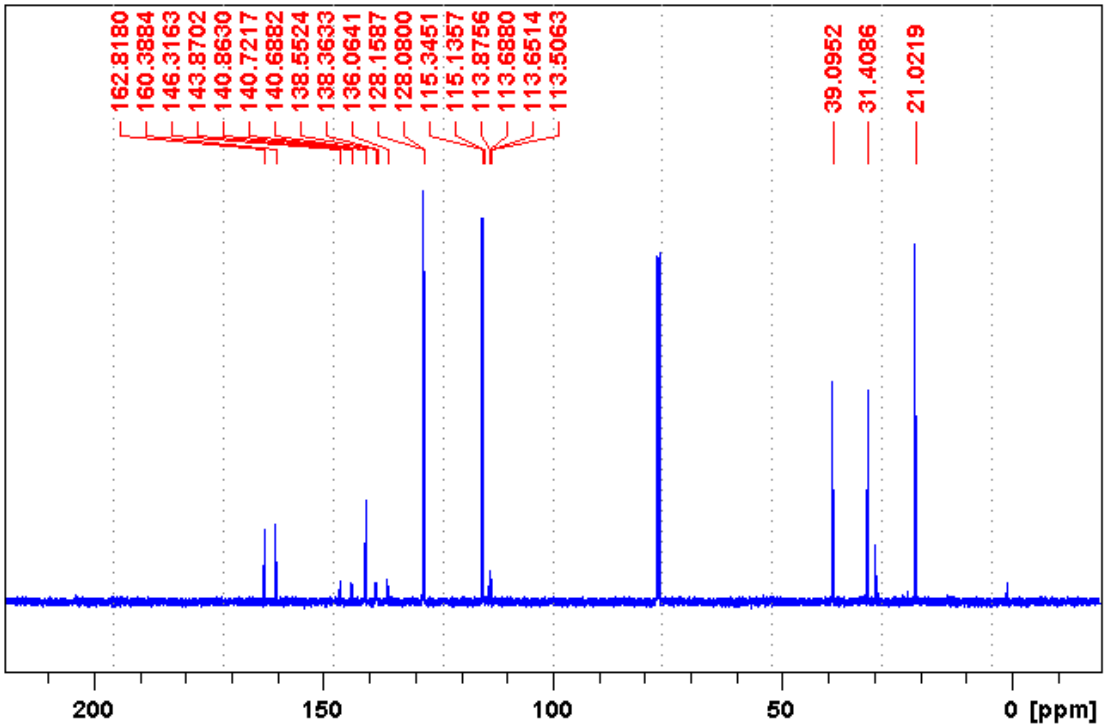
^{1}H NMR

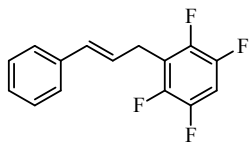


^{19}F NMR



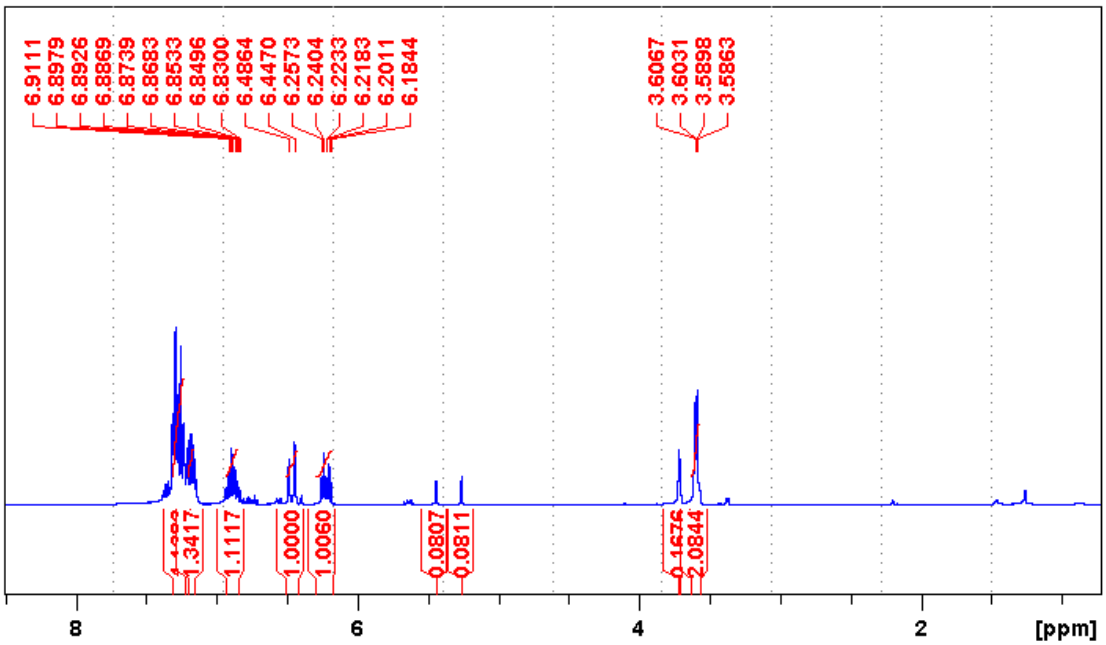
^{13}C NMR



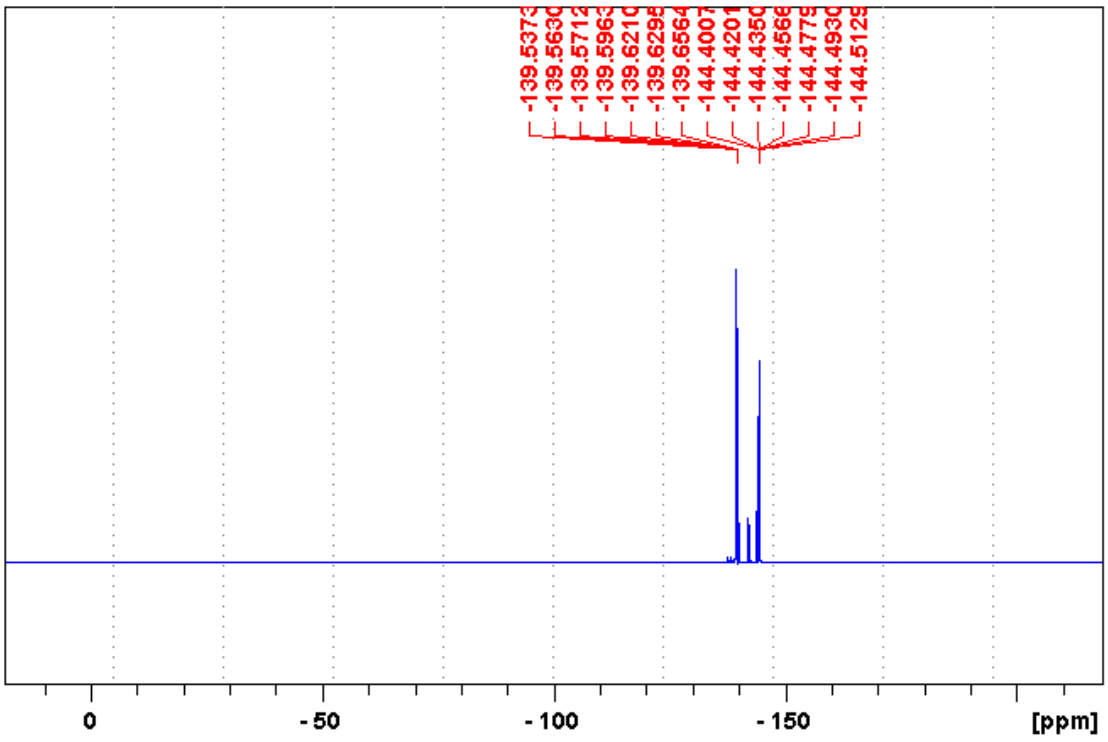


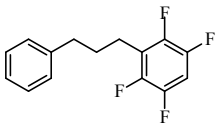
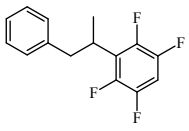
(3r) crude product

^{1}H NMR

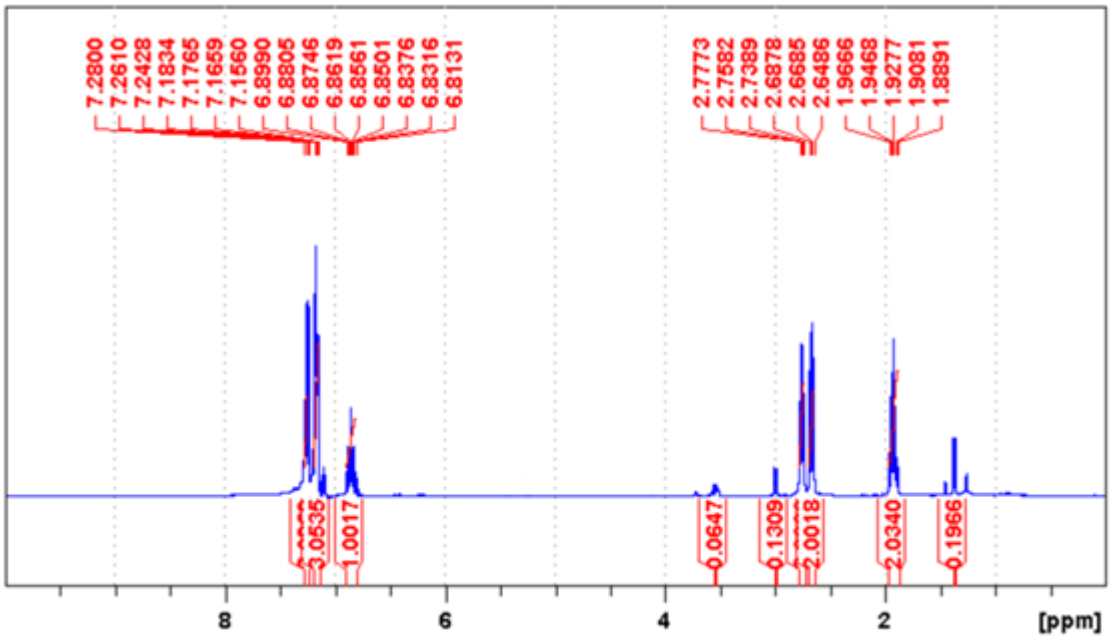


^{19}F NMR

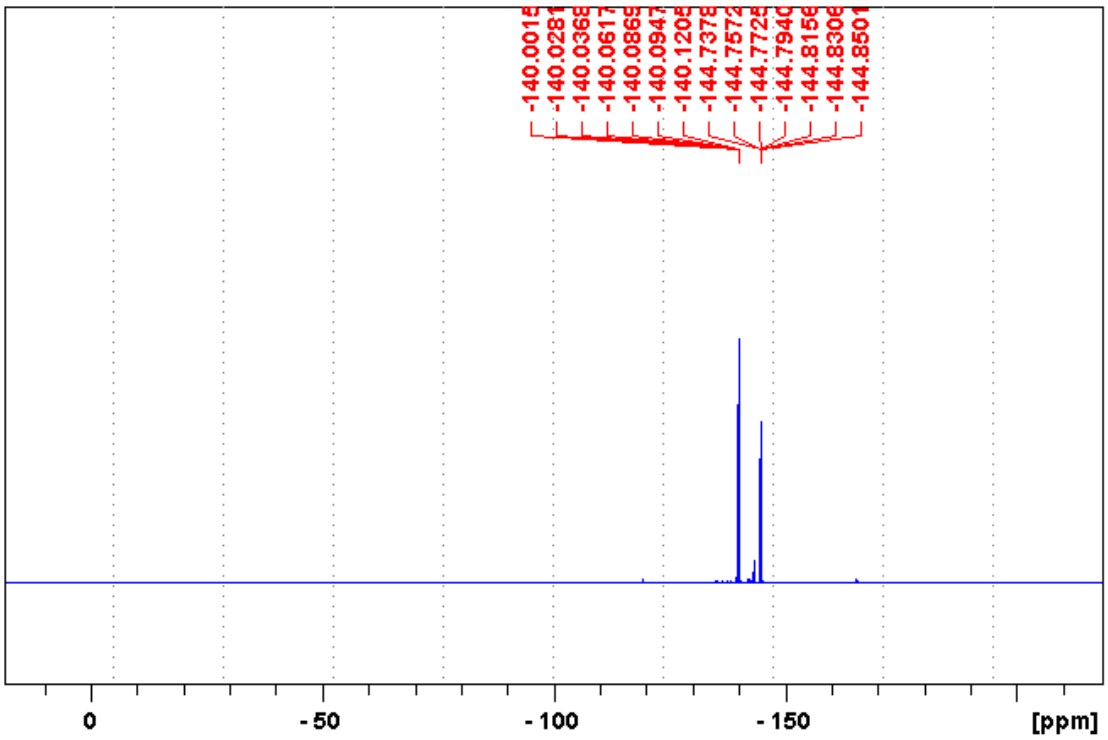



(5r) mixed with

94/6

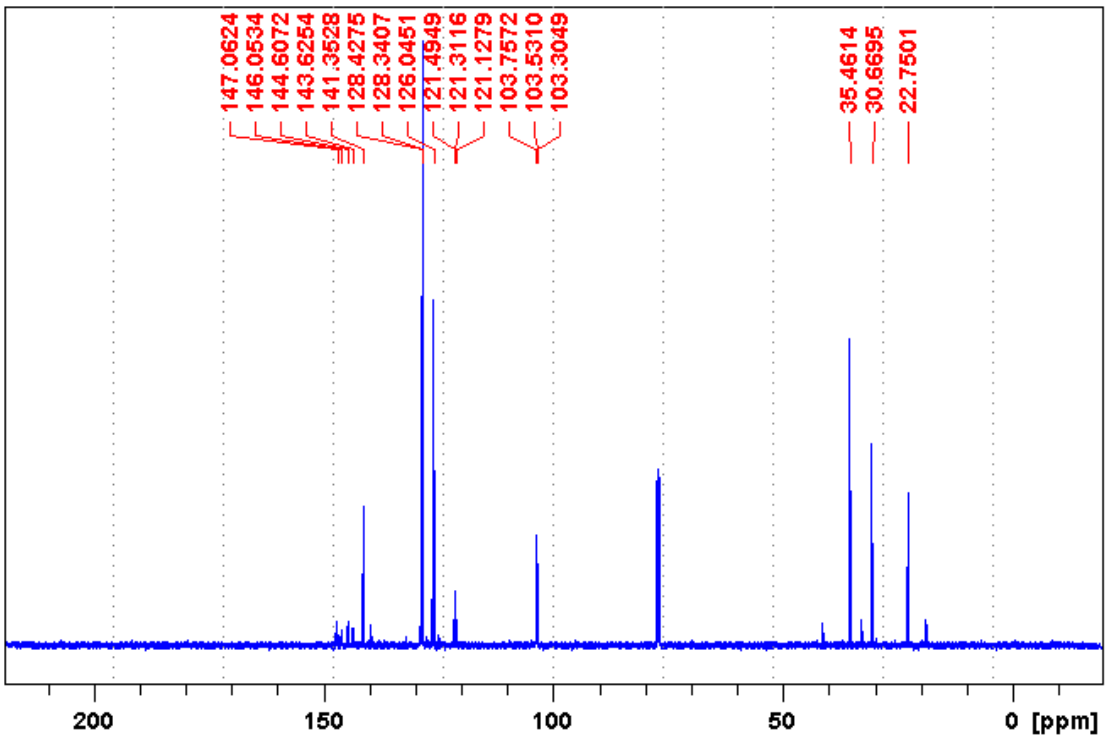
^{1}H NMR

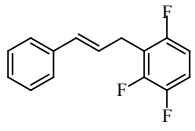


^{19}F NMR



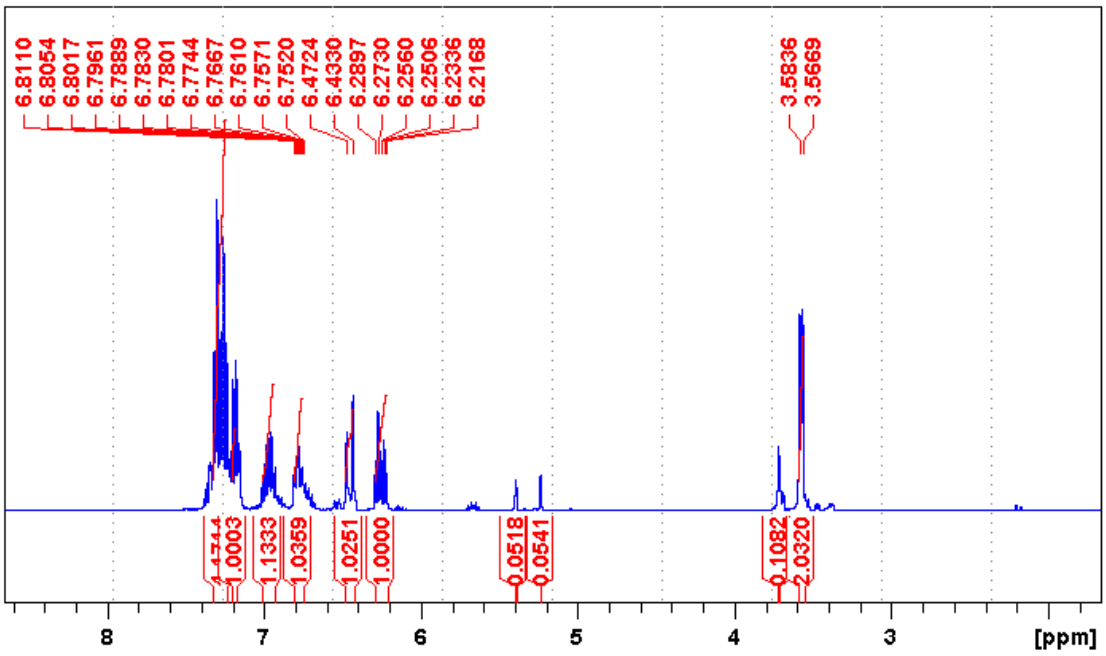
^{13}C NMR



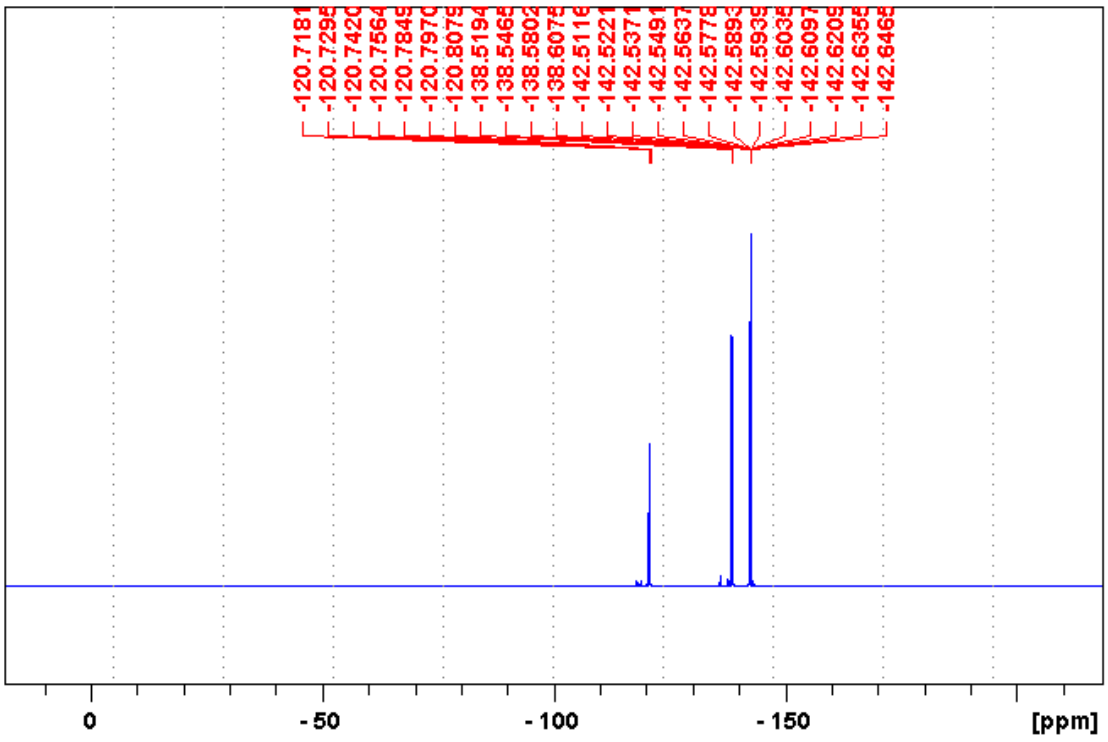


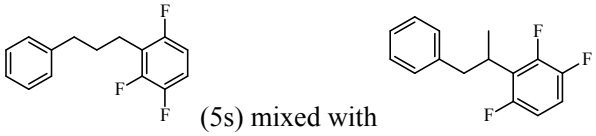
(3s) crude product

^{1}H NMR



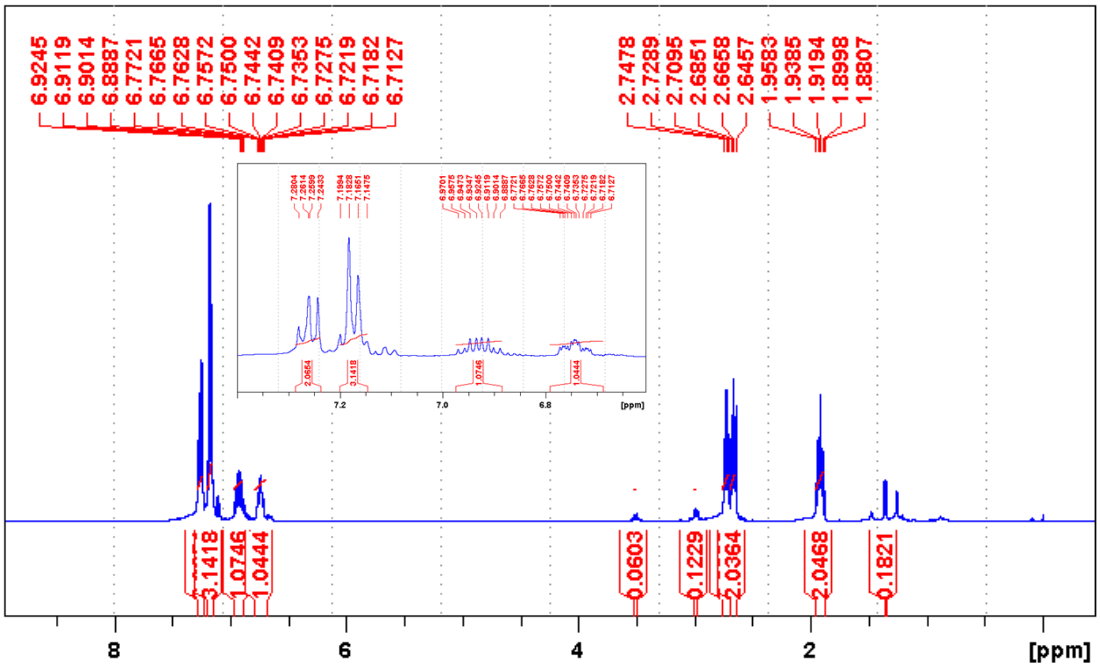
^{19}F NMR



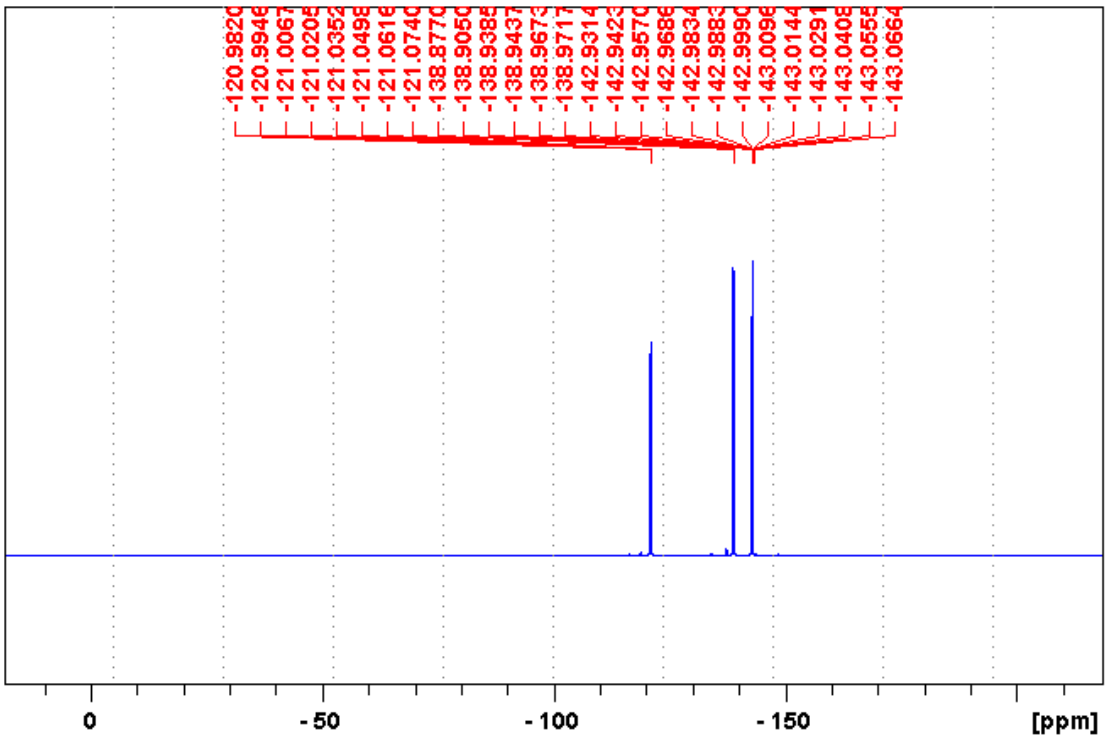


(5s) mixed with 94/6

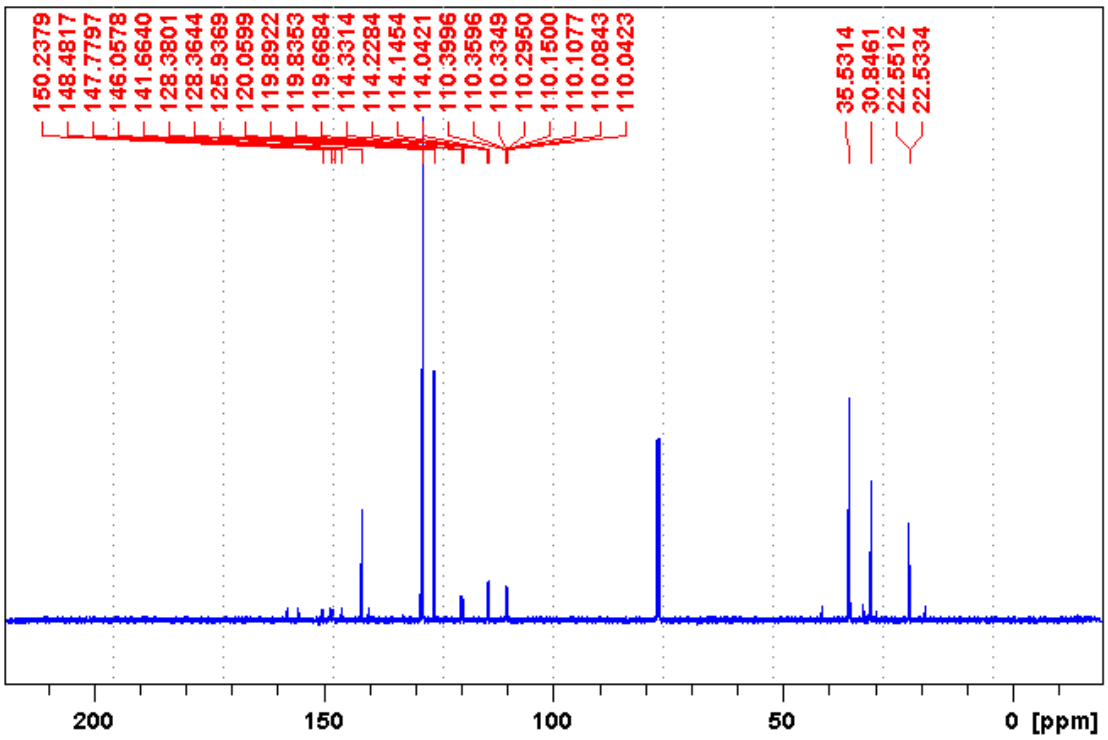
^{1}H NMR

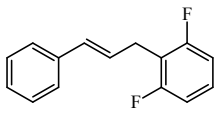


^{19}F NMR



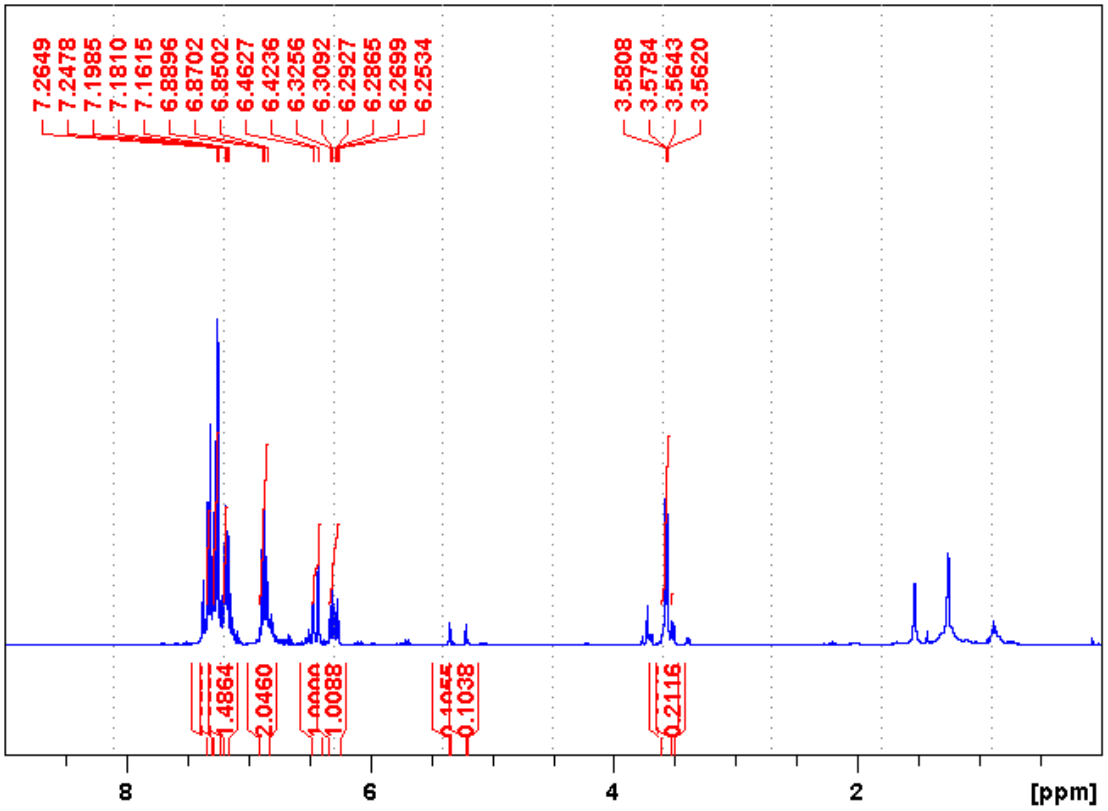
^{13}C NMR



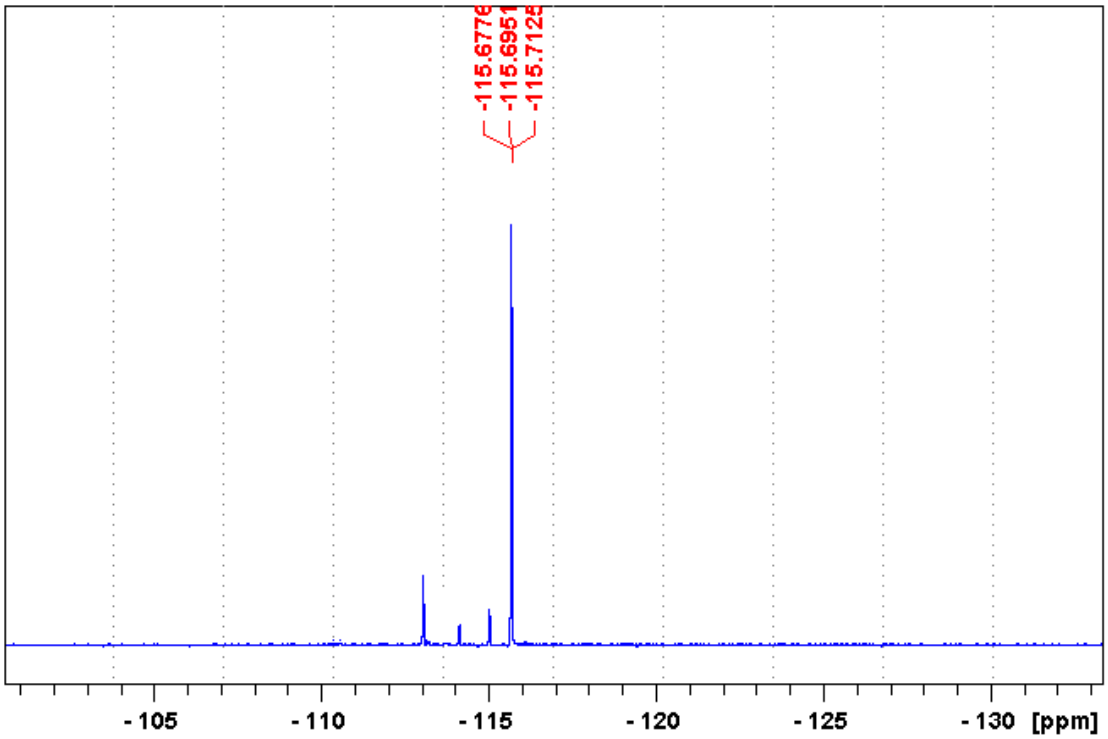


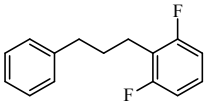
(3t) crude product

^{1}H NMR

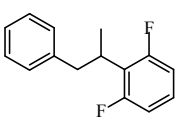


^{19}F NMR



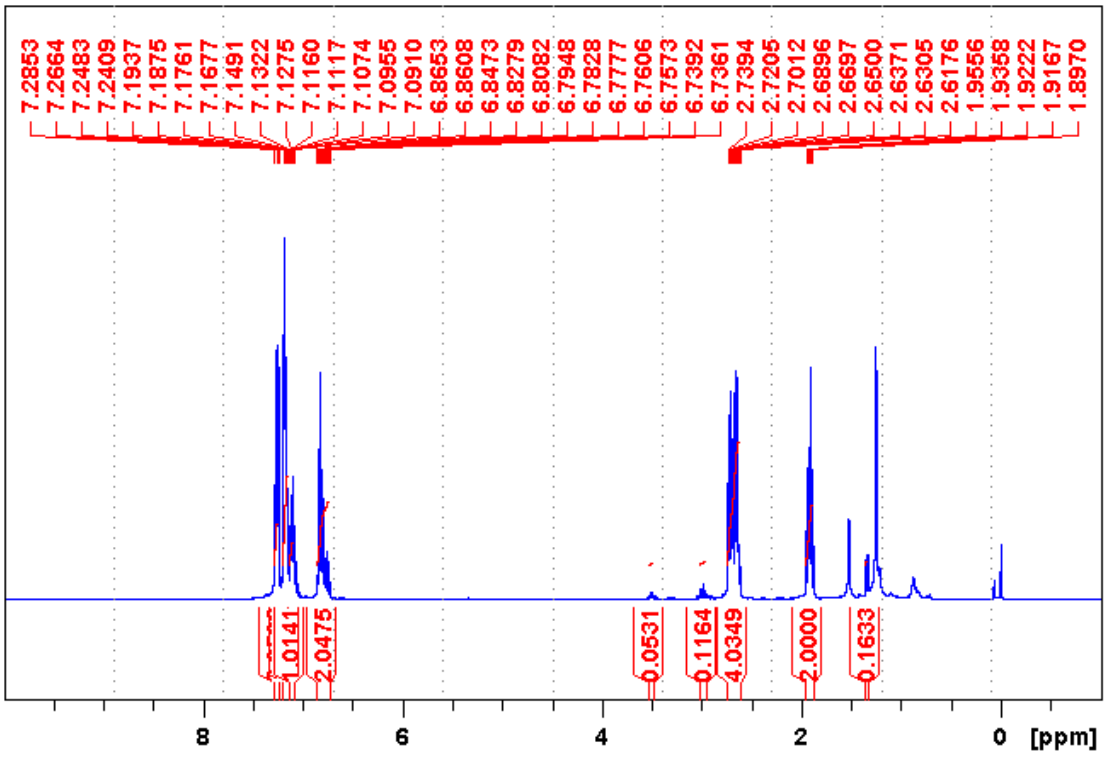


(5t) mixed with

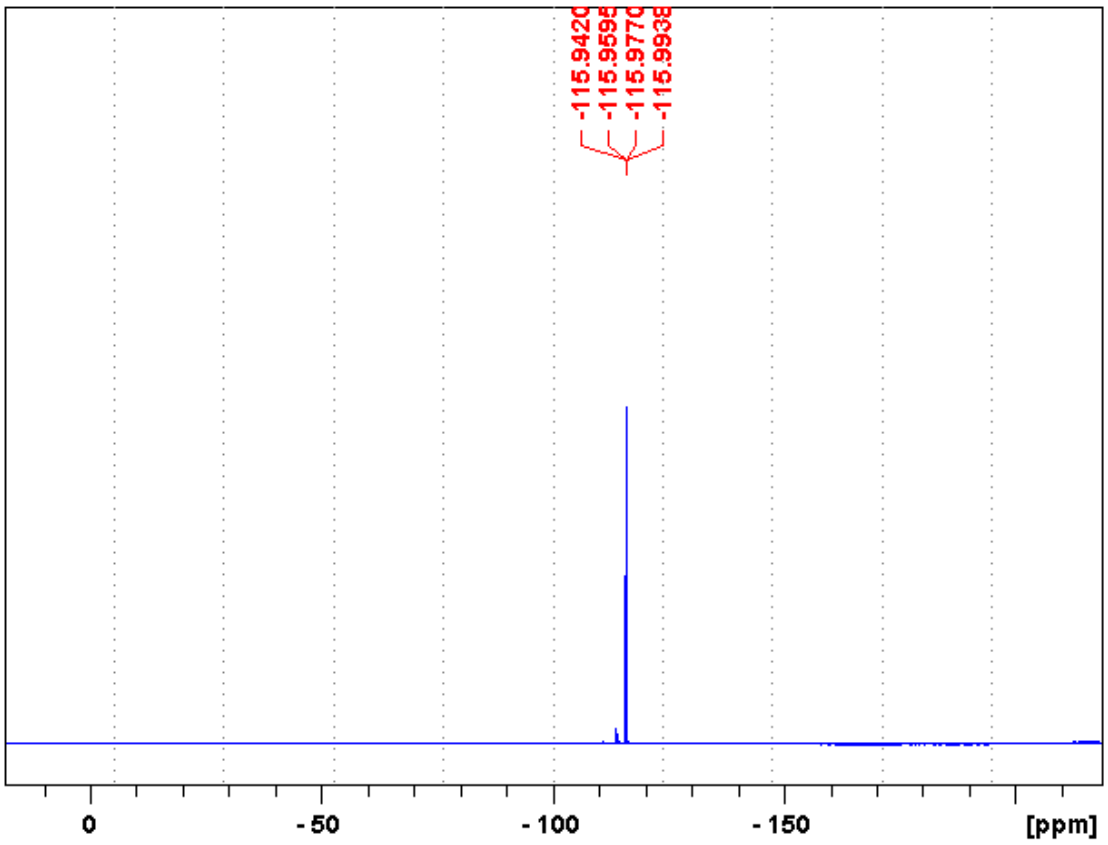


95:5

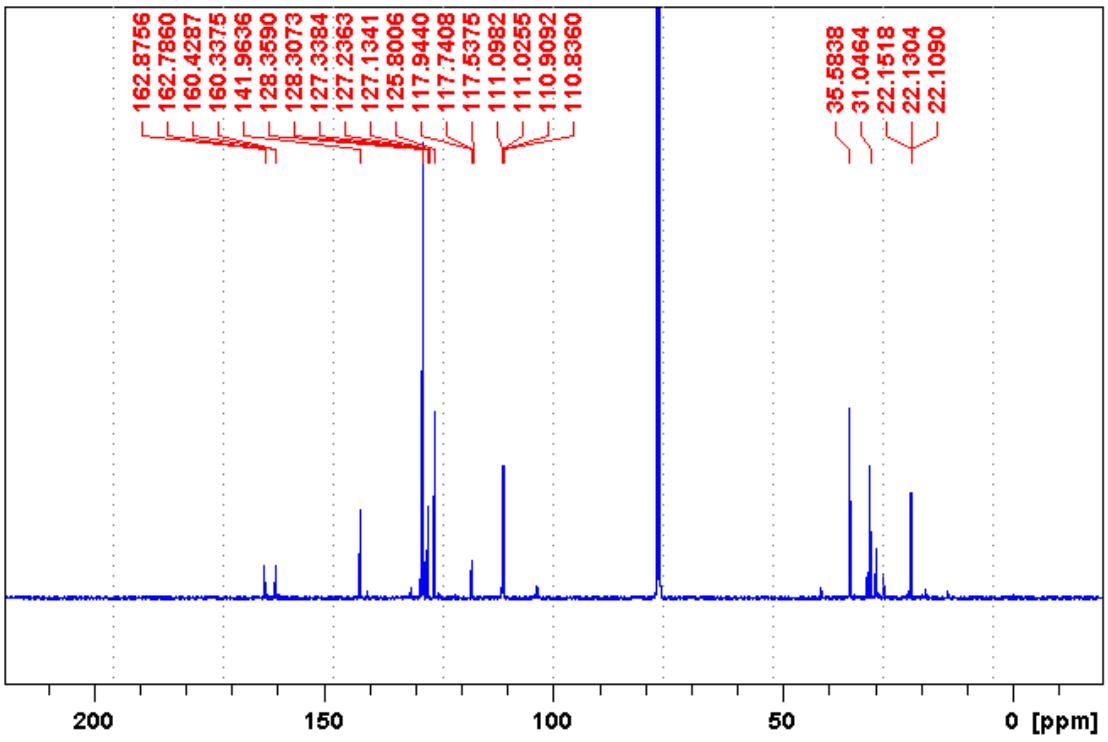
^{1}H NMR

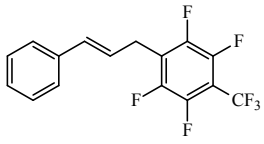


^{19}F NMR



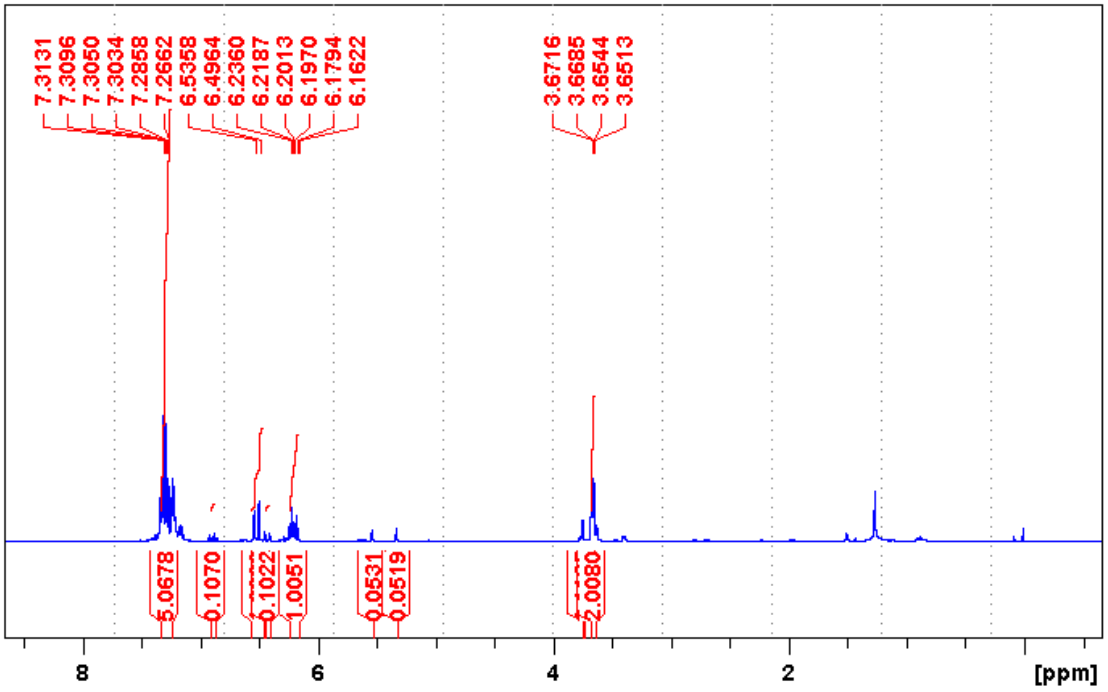
^{13}C NMR



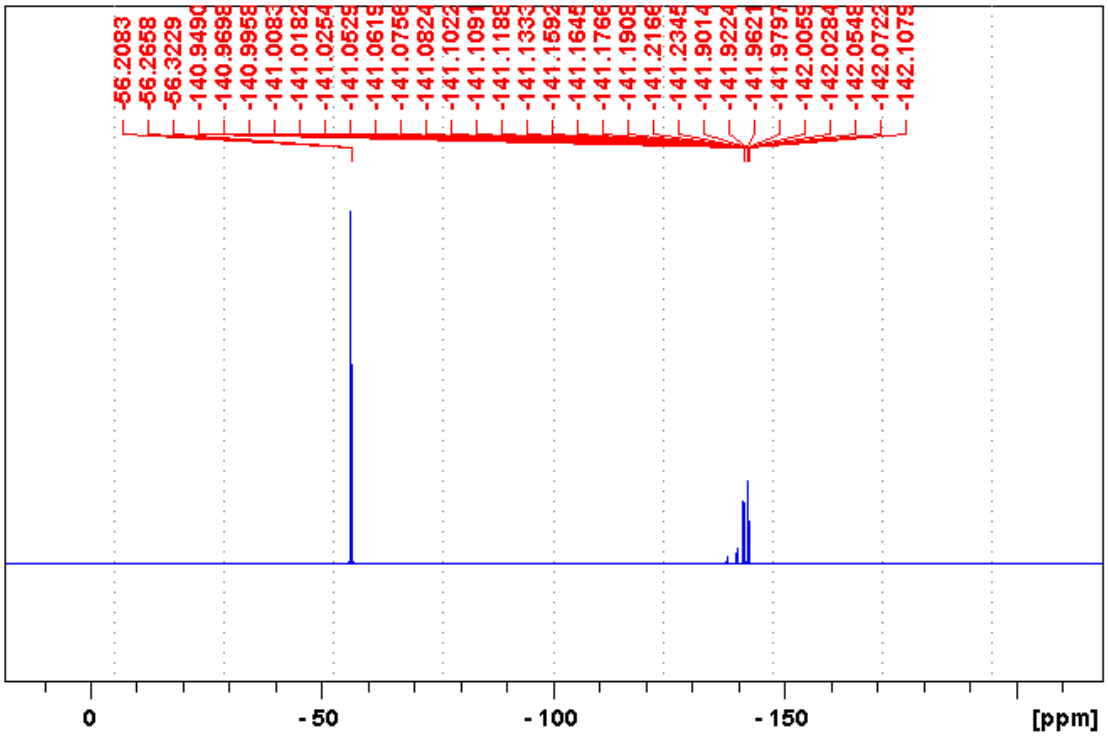


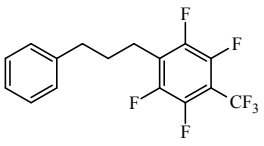
(3u) crude product

^{1}H NMR

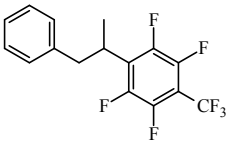


^{19}F NMR



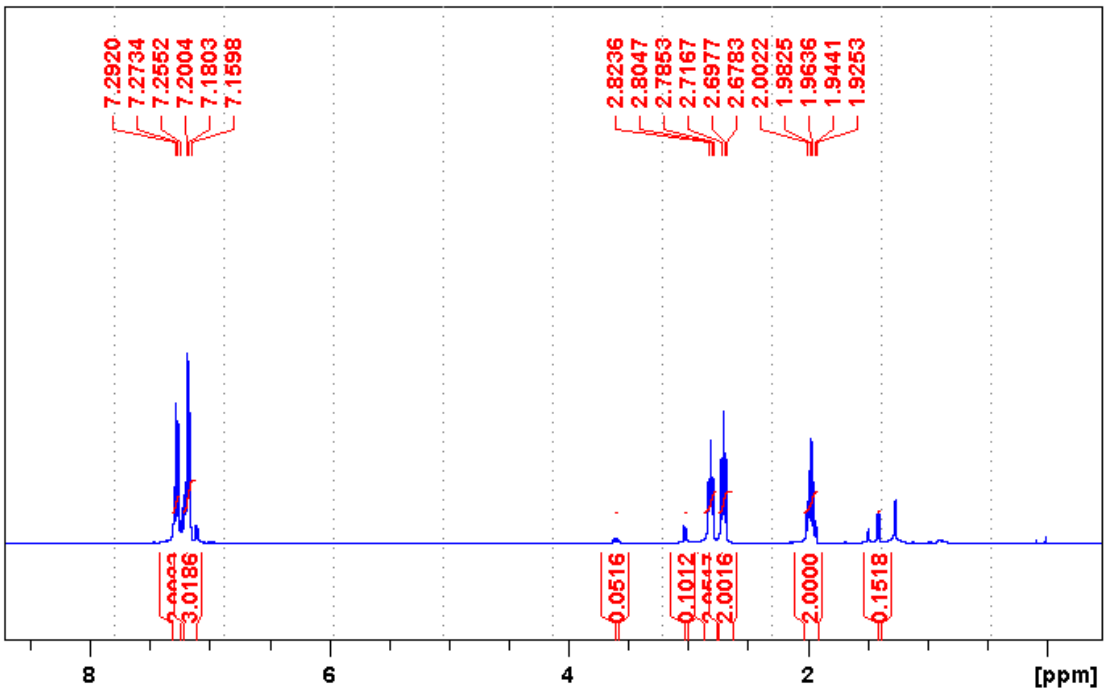


(5u) mixed with

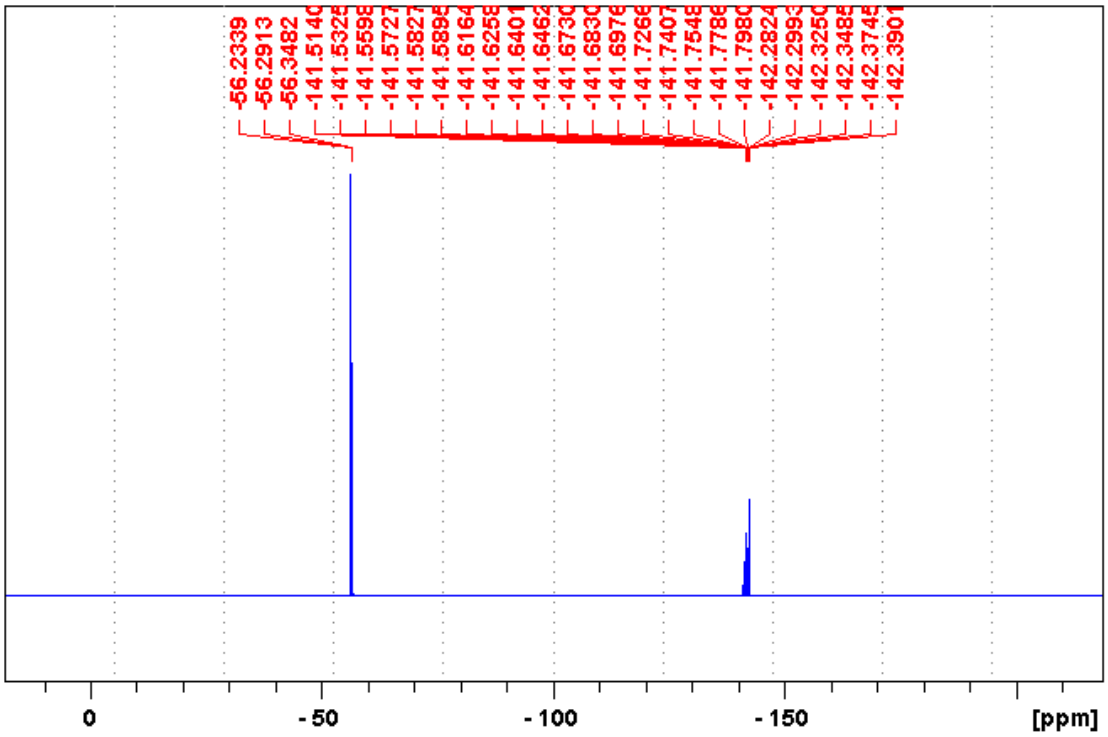


95/5

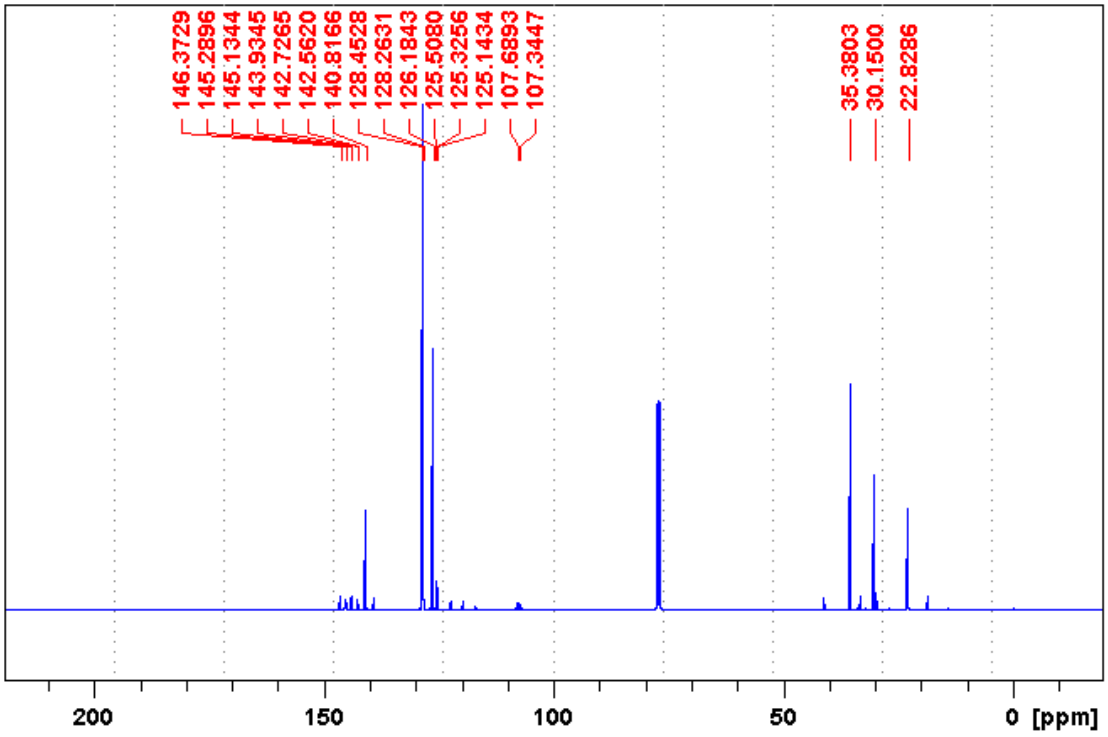
^{1}H NMR

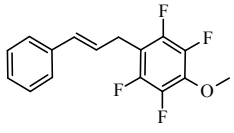


^{19}F NMR



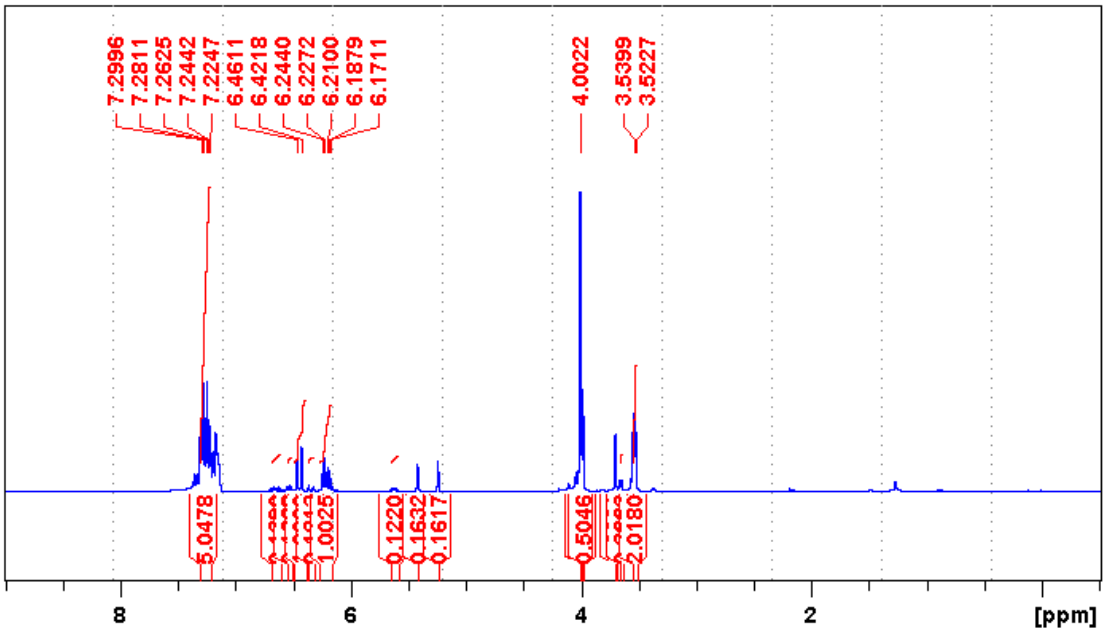
^{13}C NMR



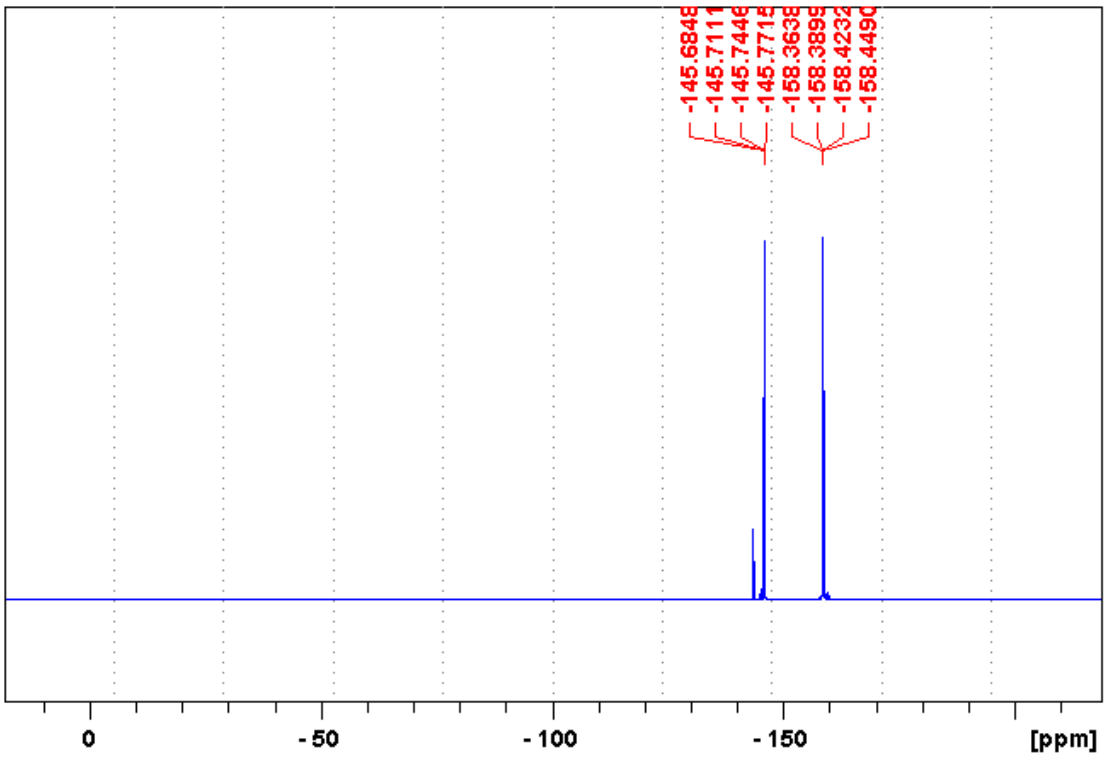


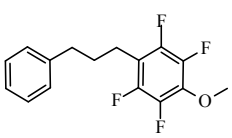
(3v) crude product

^{1}H NMR

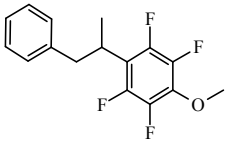


^{19}F NMR



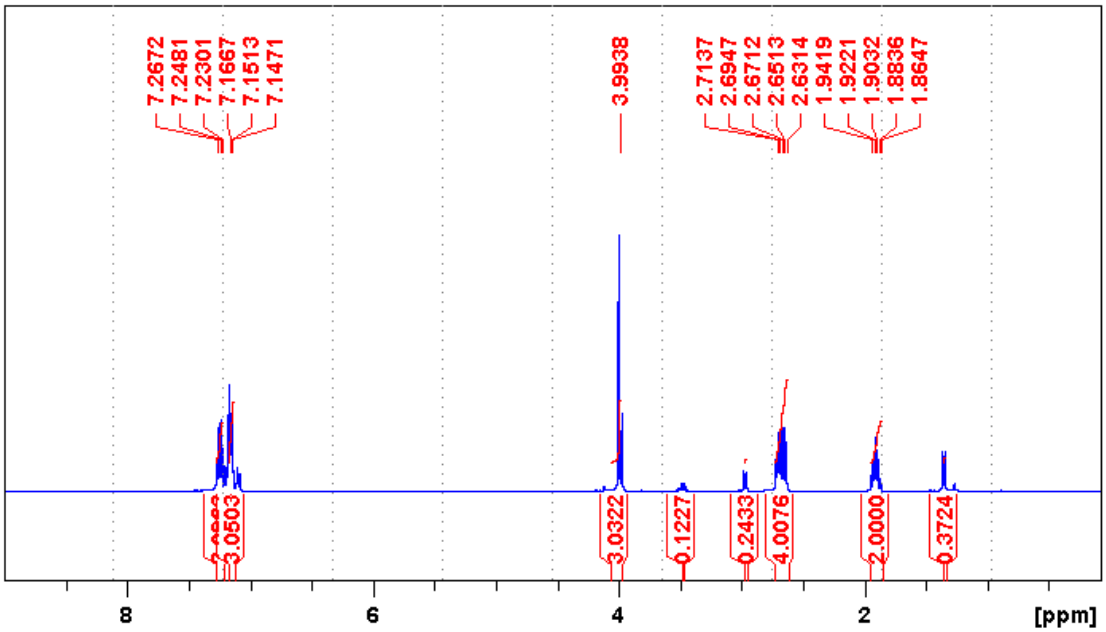


(5v) mixed with

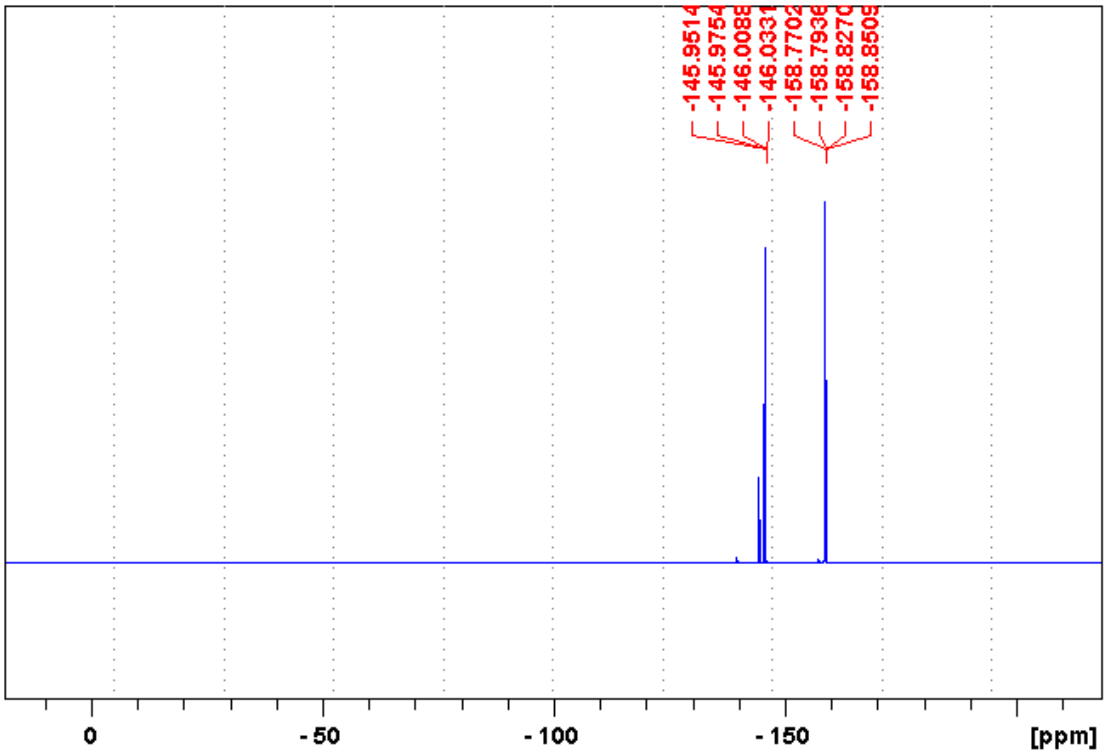


89/11

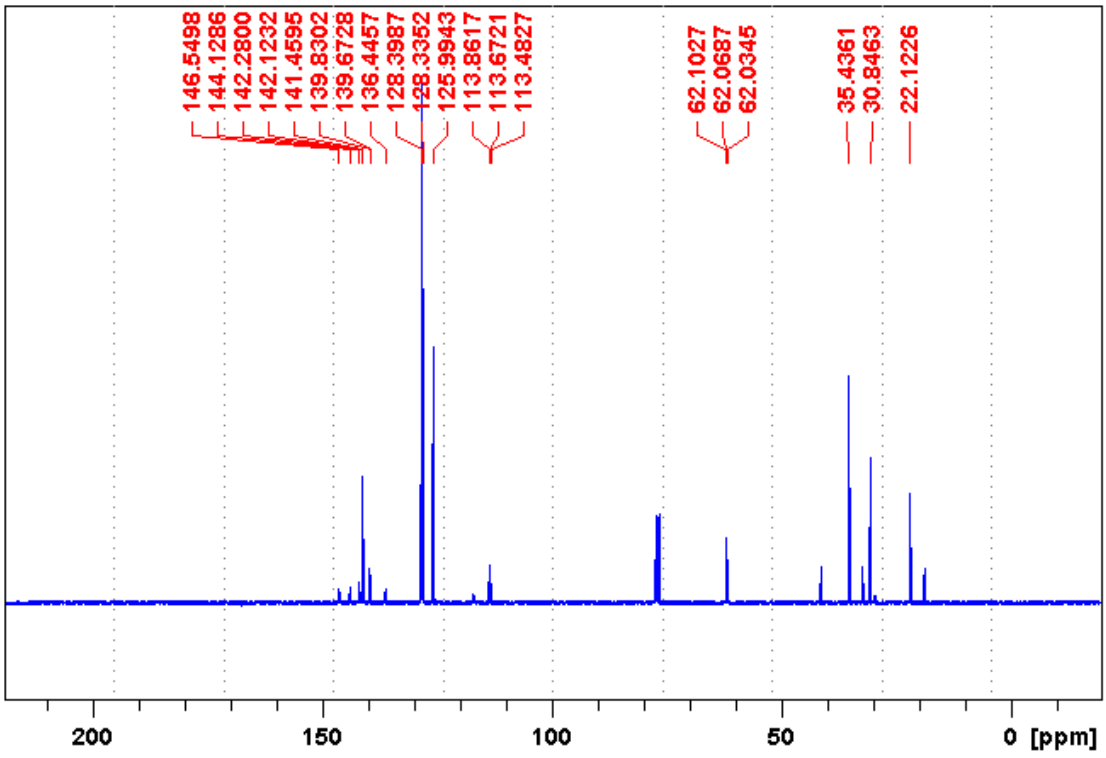
^{1}H NMR

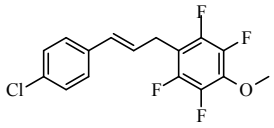


^{19}F NMR



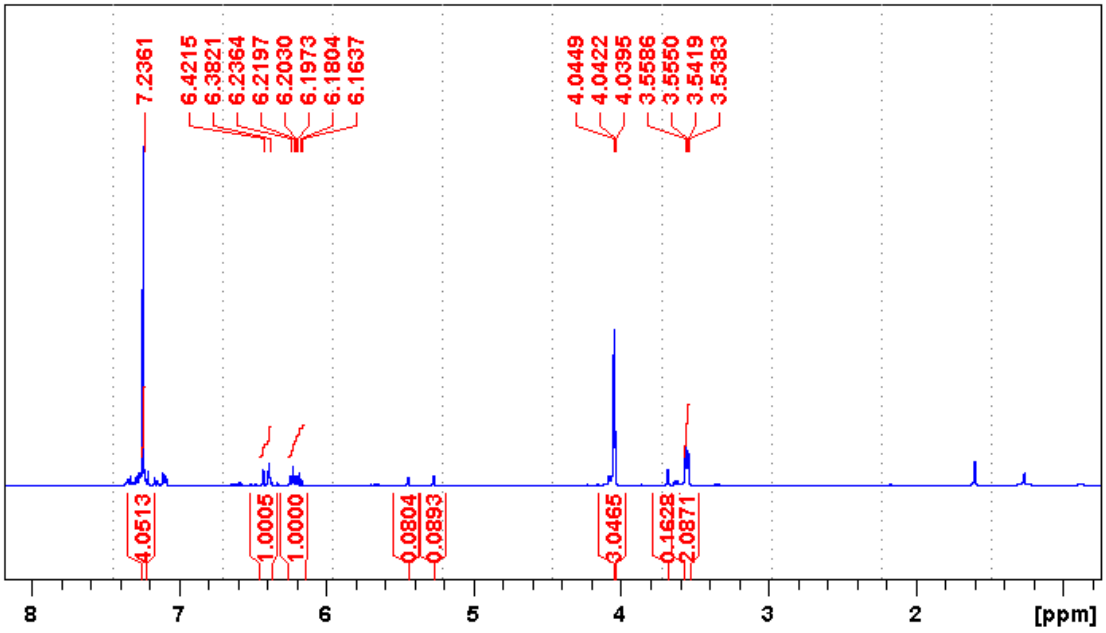
^{13}C NMR



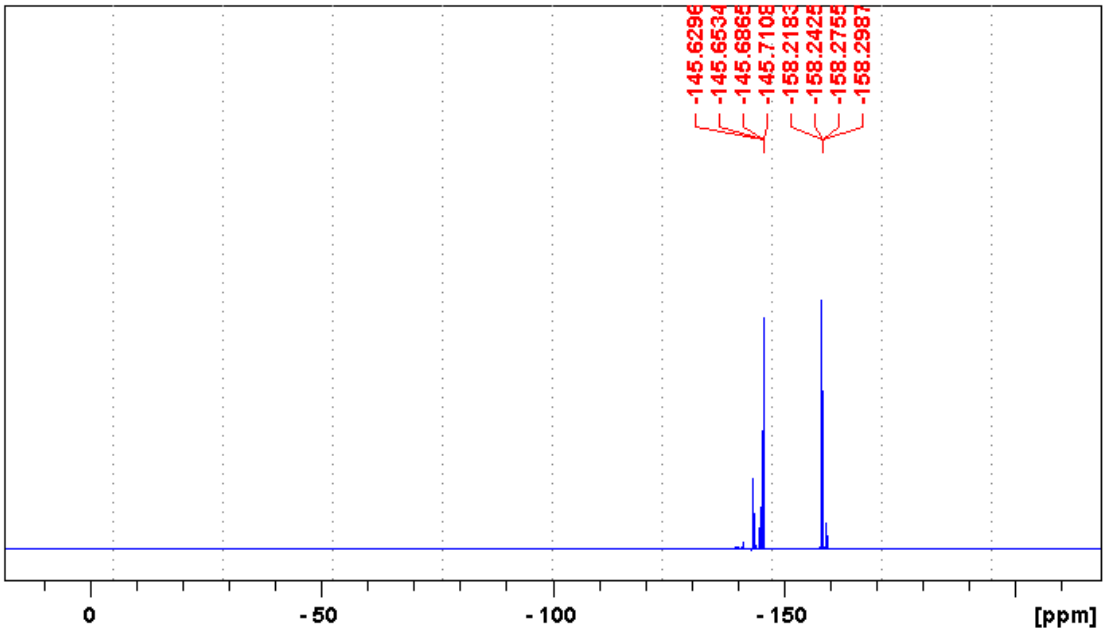


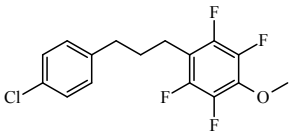
(3w) crude product

^{1}H NMR

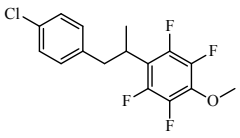


^{19}F NMR



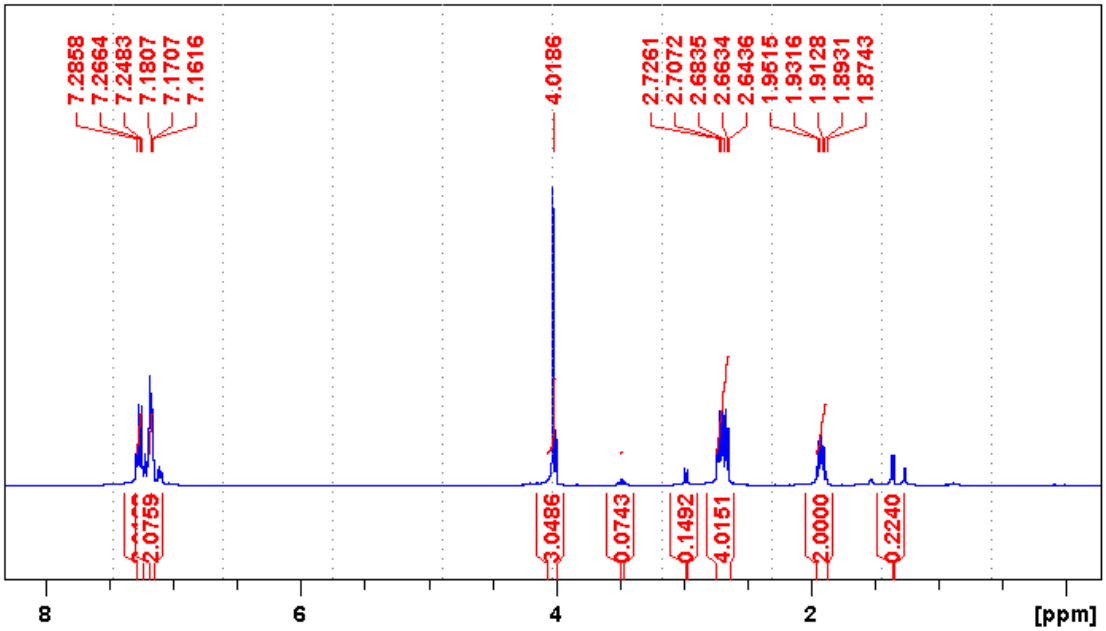


(5w) mixed with

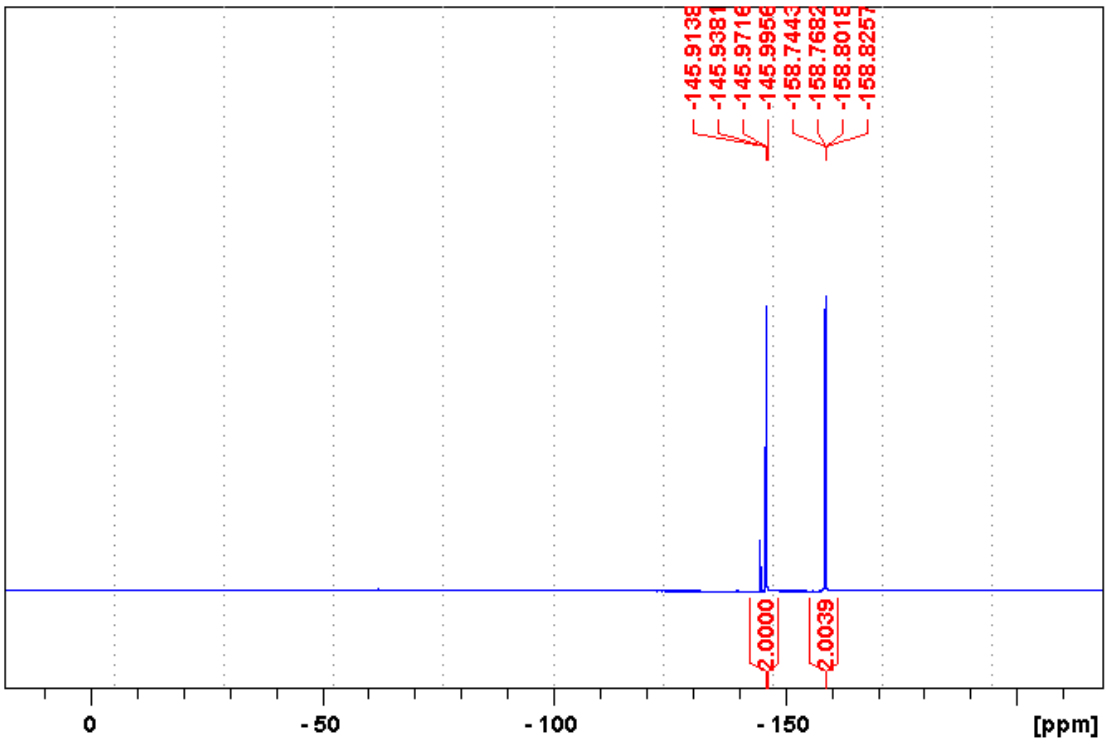


(93:7)

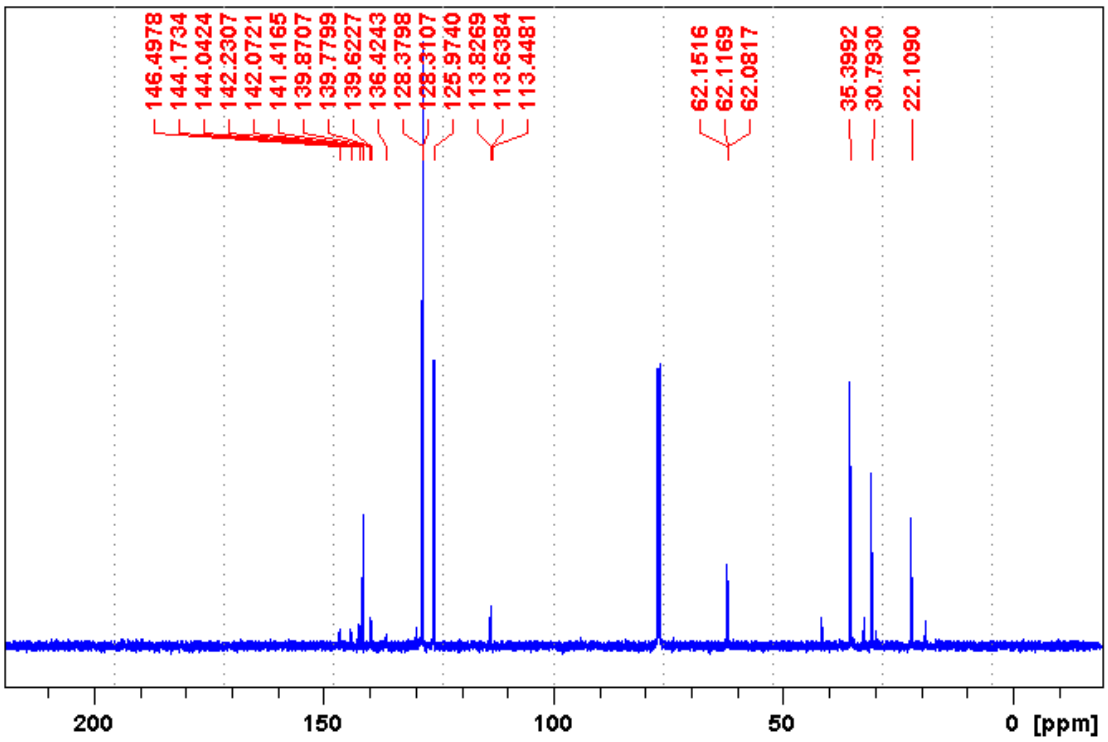
^{1}H NMR

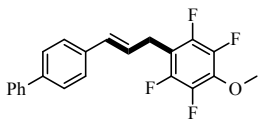


^{19}F NMR



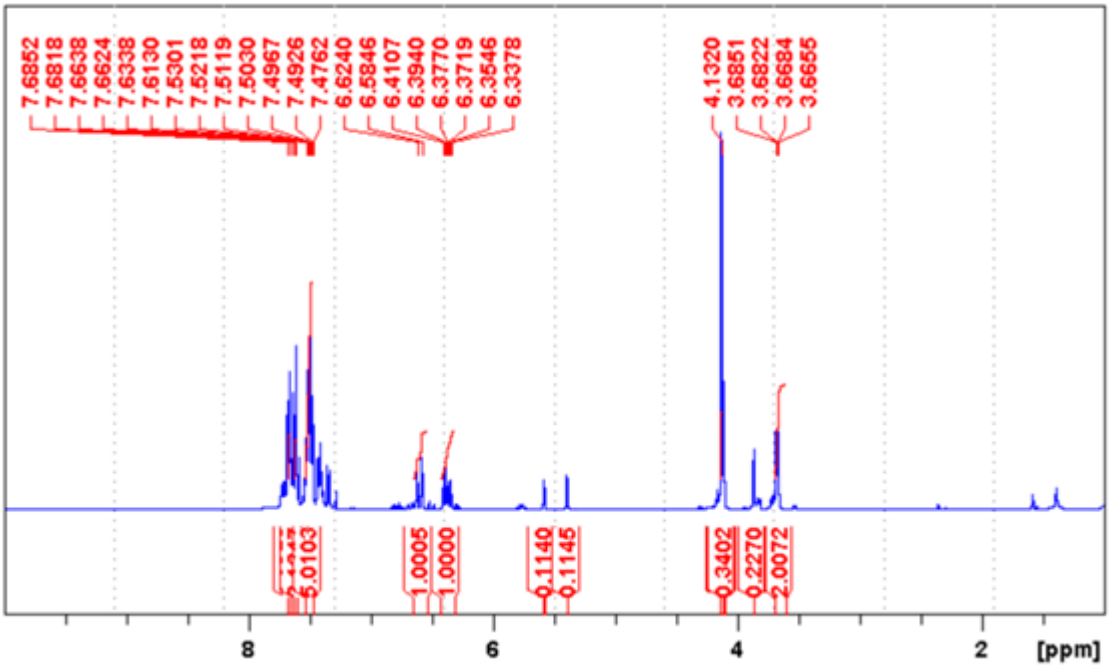
^{13}C NMR



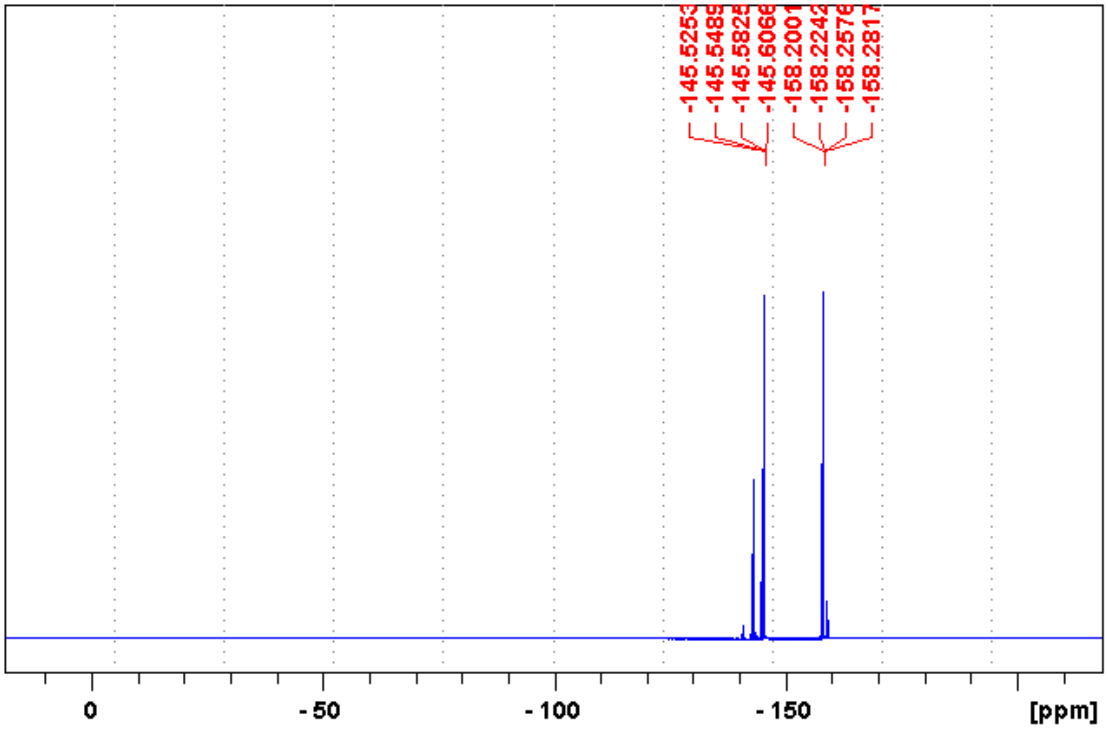


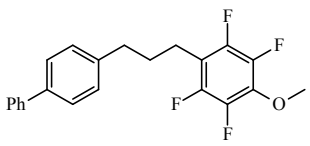
(3x) crude product

^{1}H NMR

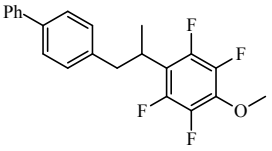


^{19}F NMR



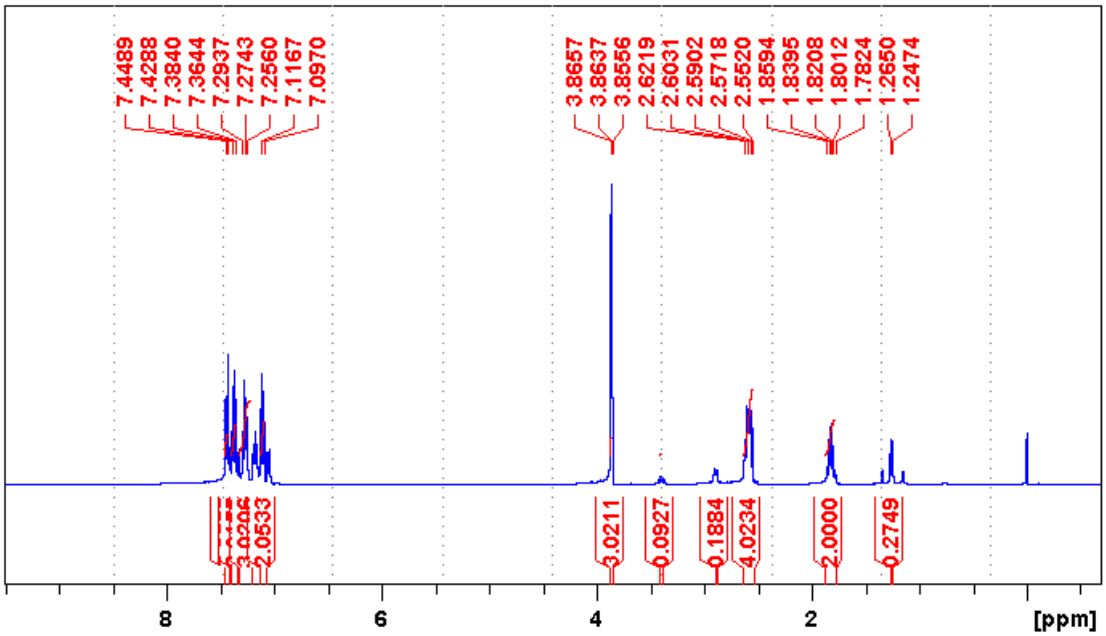


(5x) mixed with

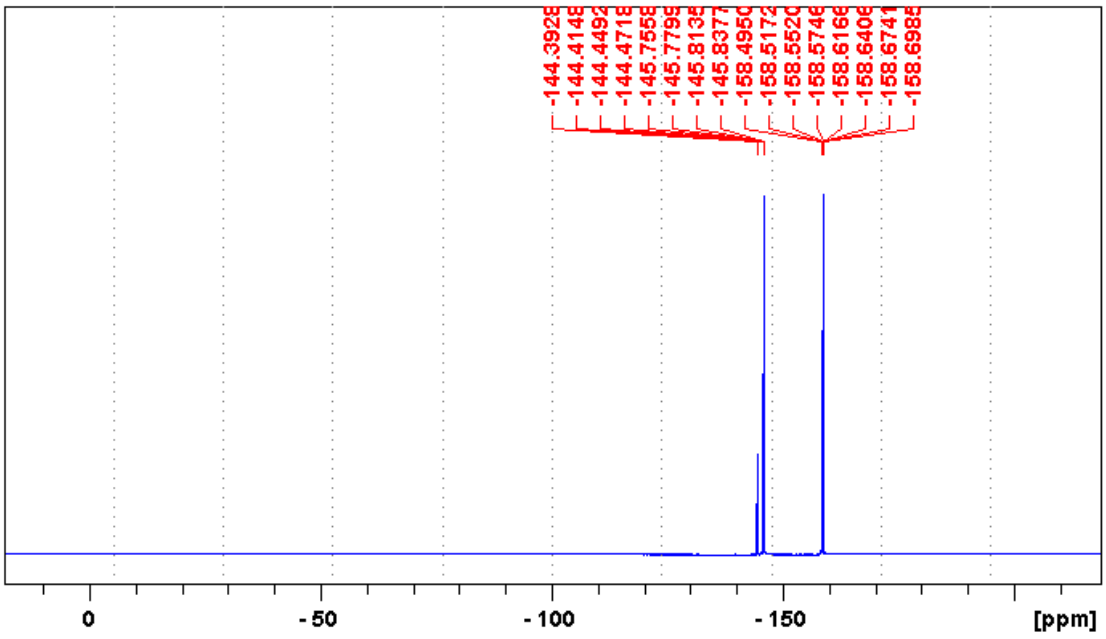


91:9

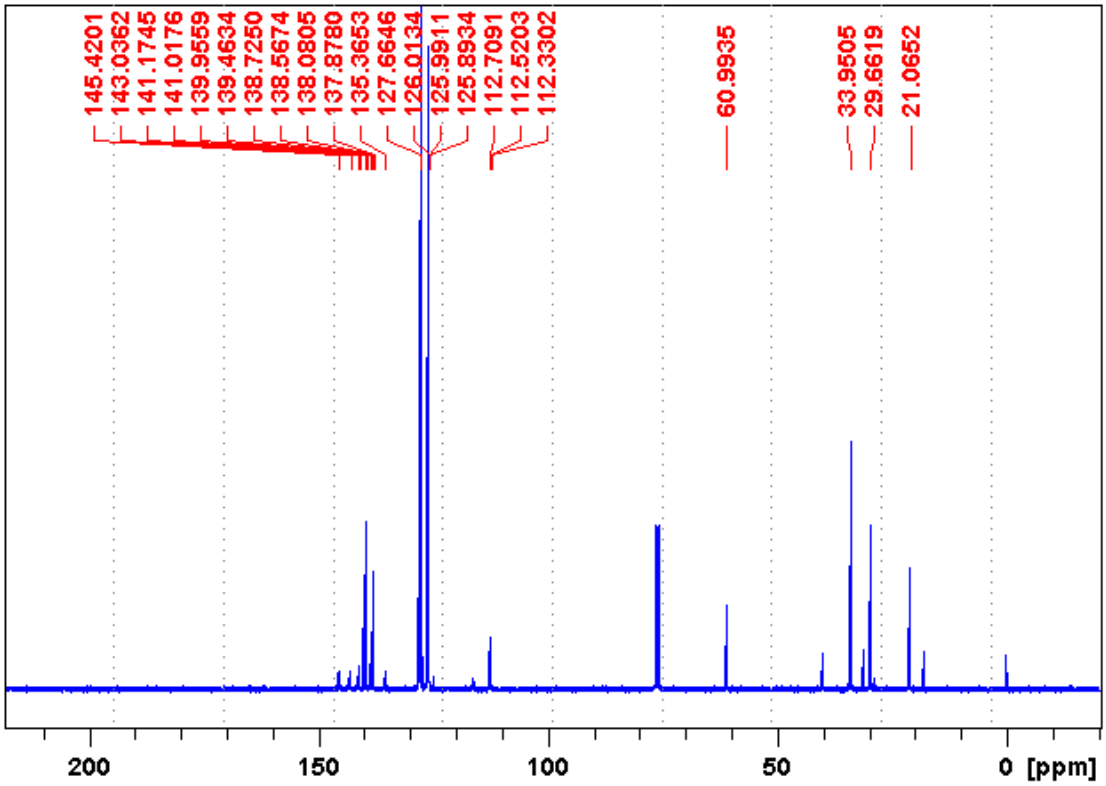
^{1}H NMR

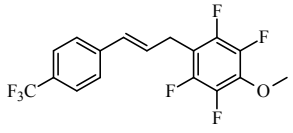


^{19}F NMR



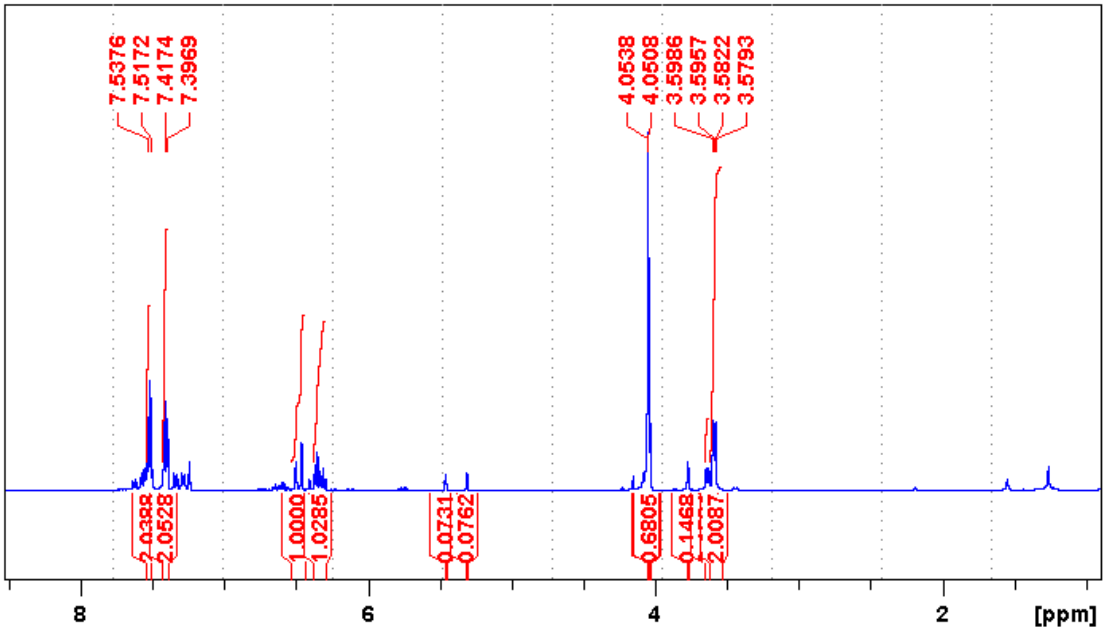
^{13}C NMR



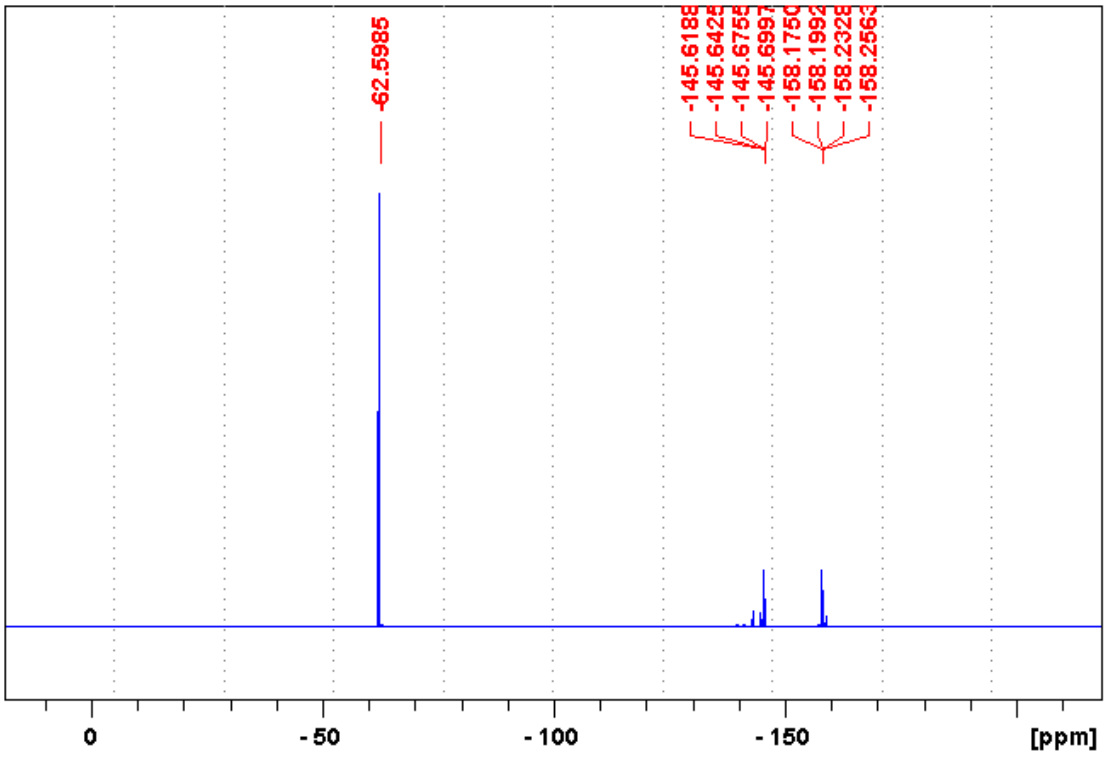


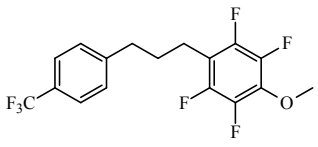
(3y) crude product

^{1}H NMR

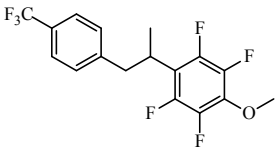


^{19}F NMR



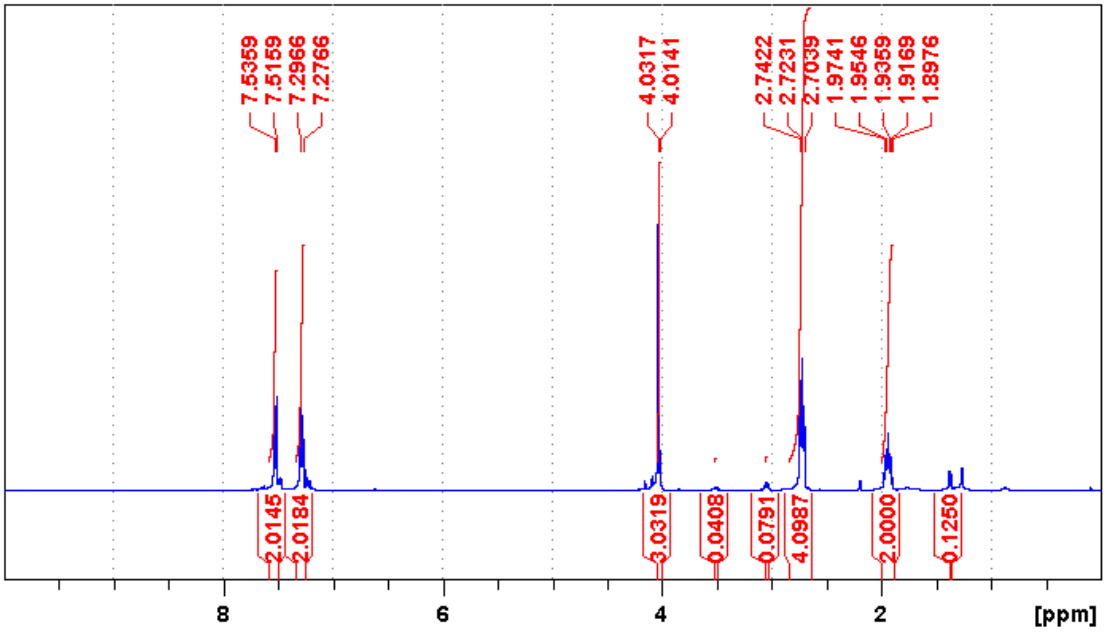


(5y) mixed with

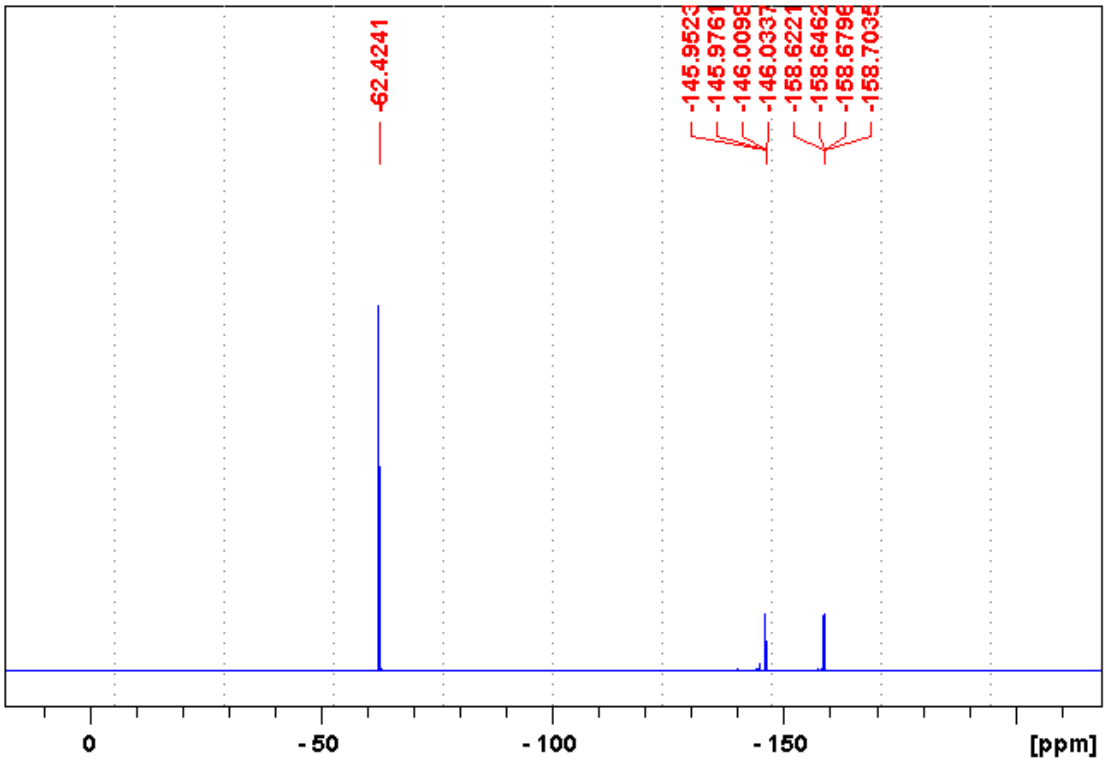


(97:3)

^{1}H NMR



^{19}F NMR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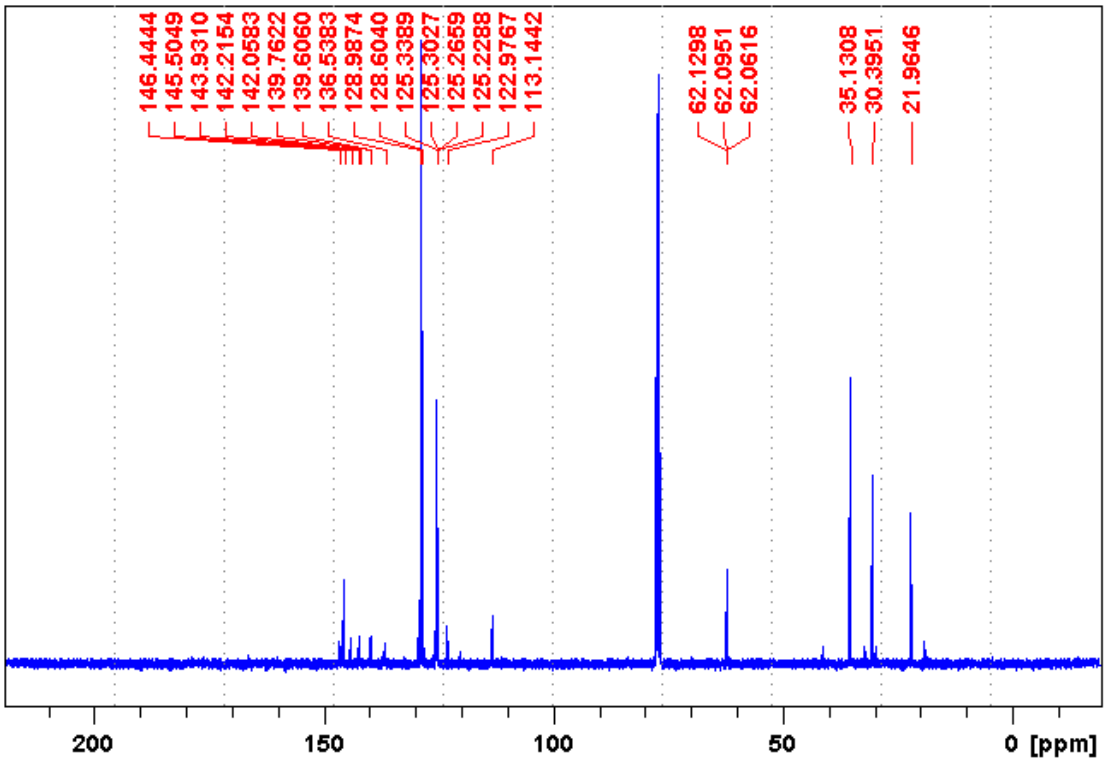
-145.9761
-146.0098
-146.0337
-158.6221
-158.6462
-158.6796
-158.7035
0
-50
-100
-150
[ppm]

^{13}C NMR


146.4444
145.5049
143.9310
142.2154
142.0583
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128.6040
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125.3027
125.2659
125.2288
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150
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50
0 [ppm]