Supporting information

Inexpensive and Multifaceted Ion Exchange Resin-Supported Hydrogen Fluoride: A Path to Flow Hydrofluorination

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Contents

Section 1. General experimental details

^{1}H NMR and ^{13}C NMR spectra were recorded at 400 MHz and 100 MHz respectively, using $CDCl_3$ as a solvent. The chemical shifts are reported in δ (ppm) values relative to $CHCl_3$ (δ 7.26 ppm for ^{1}H NMR), multiplicities are indicated by s (singlet), d (doublet), t (triplet), q (quartet), p (pentet), h (hextet), m (multiplet) and br (broad). Coupling constants, *J*, are reported in Hertz.

Solvents like DCM, Et_2O, Toluene, DMF were chemically dried using a commercial solvent purification system. Other solvents like DCE, dioxane, EtOAc and DMSO were dried with activated 4 Å molecular sieves overnight. Anhydrous hydrogen fluoride (HF) gas cylinder was purchased from Synquest Laboratories Inc. The three anionic ion exchange resins --Amberlite IRN78 hydroxide form, Amberlyst A21 free base and Amberlyst A26 hydroxide form were from sigma Aldrich.

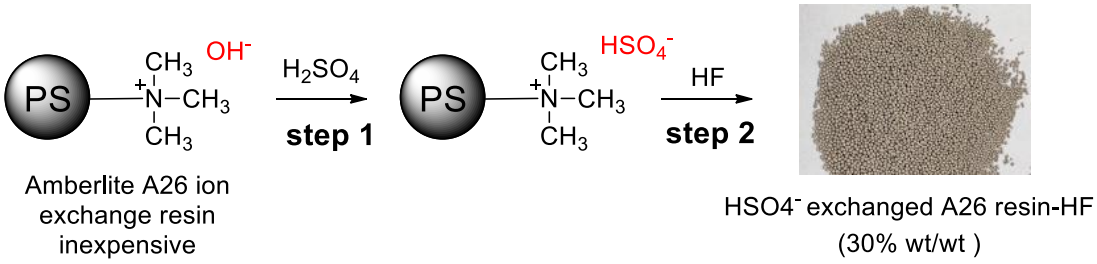
All other reagents and solvents were employed without further purification. The products were purified using a CombiFlash system. TLC was developed on Merck silica gel 60 F254 aluminum sheets and $KMnO_4$ stain was used for TLC developing. $KMnO_4$ stain was prepared by dissolving $KMnO_4$ (1.5 g), K_2CO_3 (10 g), and NaOH (10 wt%, 1.25 mL) in 200 mL water. All NMR solvents were purchased from Cambridge Isotope Laboratories, Inc.

Most of the substrates in the reactions were purchased or synthesized according to the literature. Therefore, we only used ^{1}H NMR spectra to confirm the identity of those known compounds.

Section 2. Preparation of Resin- HF complex

Properties of the anionic resins:

Amberlite IRN78 hydroxide form (capacity: 1.1 meq/mL by wetted bed volume), Amberlyst A21 free base (capacity: 1.3 meq/mL by wetted bed volume), and Amberlyst A26 hydroxide form (capacity: 0.8 meq/mL by wetted bed volume)



Scheme S 1. Preparation of polymer supported HF reagent.

Step 1: Modification of the resin with H_2SO_4 (taking Amberlyst A26 hydroxide form as example)

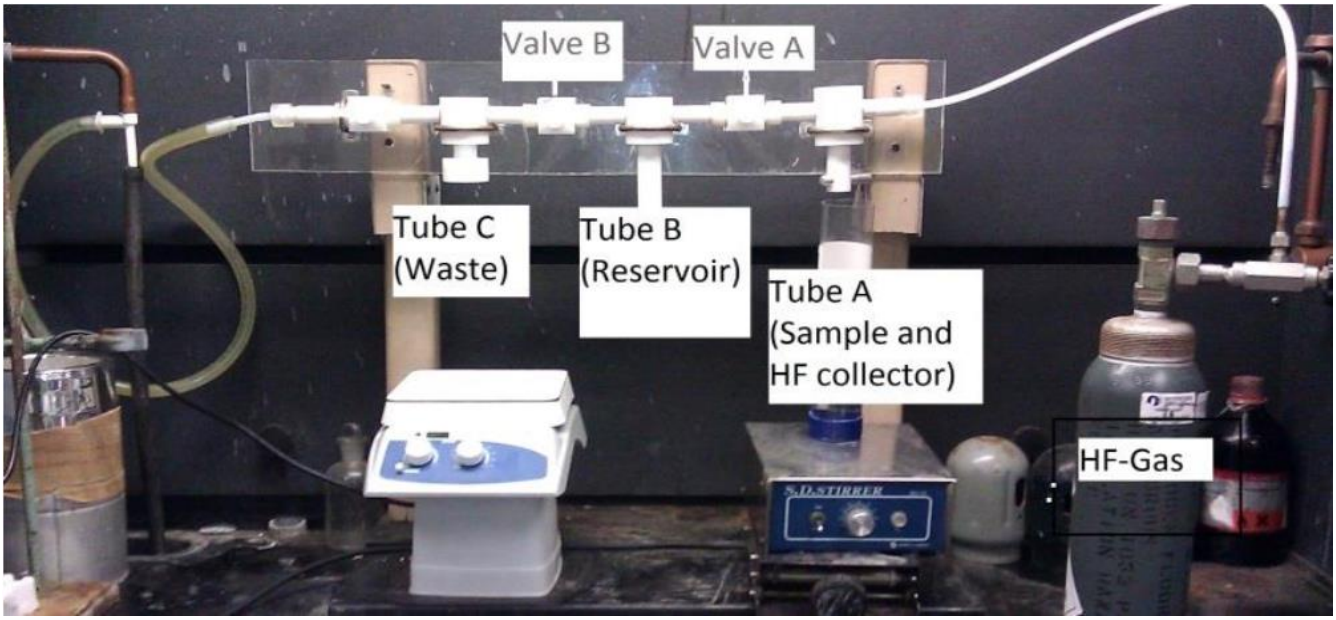
Concentrated sulfuric acid (98%, 5.2 mL) diluted with deionized water (150 mL) were prepared and divided into 3 aliquots. Wet A26 resin (40 mL) was soaked in the aliquot of diluted H_2SO_4 solution and sonicated for 0.5 hour. The aqueous solution was decanted and the sediment resin was retreated the H_2SO_4 aliquots twice. The modified resin with washed with water (50 mL x 3), ethanol (50 mL x 2) sequentially and then dried on rotavapor to afford modified resin (9.5 g).

To calculate the volume for 3 equivalents of concentrated H_2SO_4:

40 mL resin × 0.8 meq/mL × 3 equiv H_2SO_4 × 0.001mol/mmol × 98 g/mol ÷ 98% ÷ 1.84 g/mL = 5.2 mL H_2SO_4

Step 2: Complex modified resin with anhydrous hydrogen fluoride:

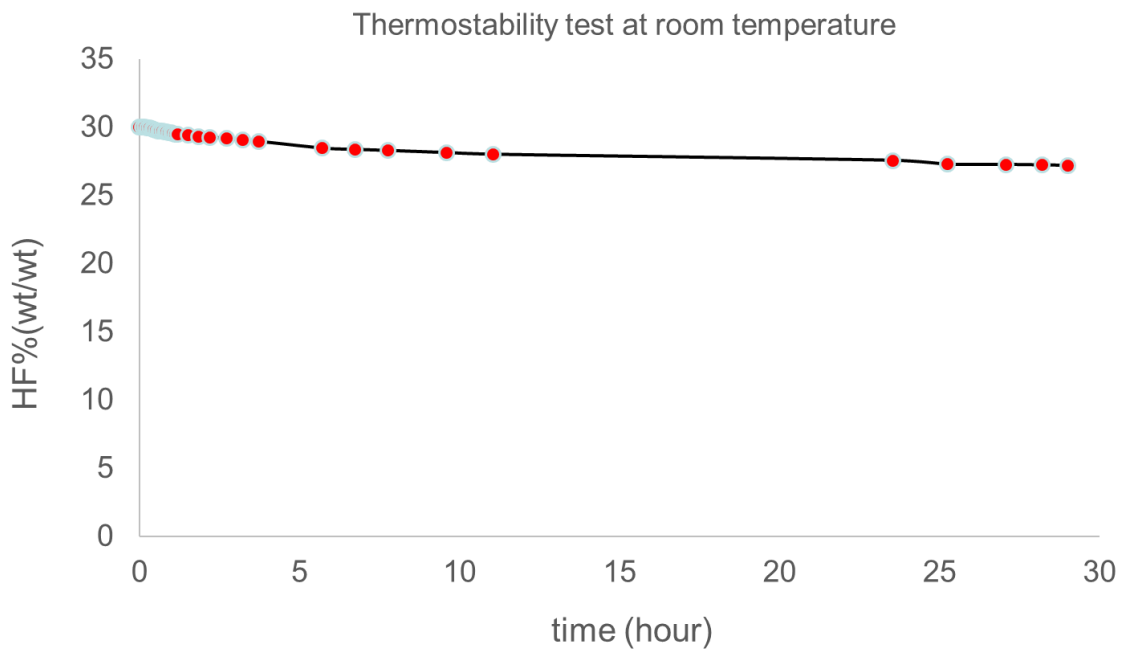
The modified resin (5g) was added into a long Teflon tube (Tube A) which was cooled to 0 ^oC. Anhydrous HF gas was then condensed into the Teflon tube A under stirring. The obtained complex was poured to a High-density polyethylene (HDPE) bottle (30 mL) with a screw cap. It is bench stable, but for long term storage, it was stored in a refrigerator (4 ^oC).



Scheme S 2. Flow reaction with polymer supported HF reagent.

Thermostability test for the resin HF complex:

At room temperature, we did not detect noticeable HF loss in a capped polypropylene container over 2 months. To investigate the stability and safety profile of the ion exchange-supported HF reagent, we conducted an HF loss experiment in open air at room temperature in a well-vented fume hood. HSO_4^- A26 resin-HF complex (HF 30% wt/wt)(1.45 g) was introduced into a 8 mL polypropylene vial, the vial was left at room temperature in open air.



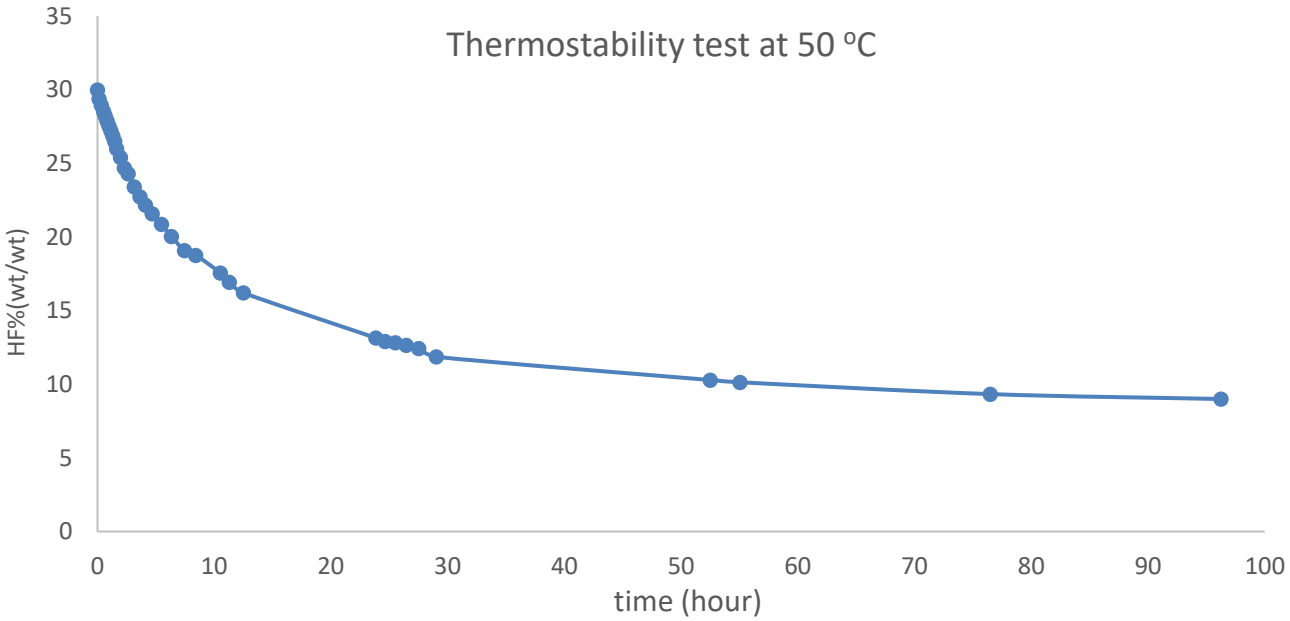
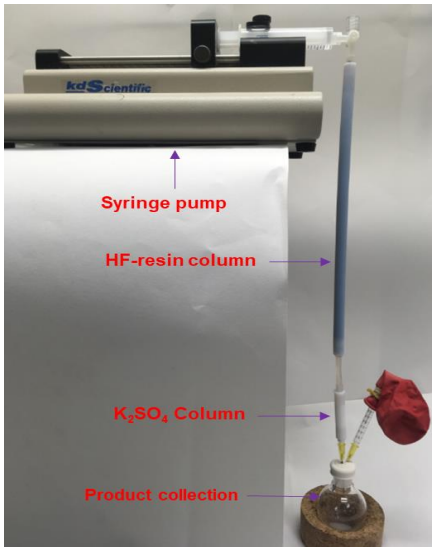


Figure S 1. Loss of HF in open air at room temperature and 50 °C.

Section 3. Flow reaction with resin-HF complex.

HSO_4^- A26 resin - HF (30%) (4.4 g) was loaded into an empty column (6 mm * 250 mm) made by PTFE tube. The starting material (0.57g) was injected into the column and flashed with dry DCE at 0.5 mL/h flow rate. A 6 mm x 50 mm column charged with K_2SO_4 was attached to remove excess HF in the eluent. A flask (50 mL) equipped with a balloon buffer was attached to the K_2SO_4 column to collect the final product solution (see Scheme S2).



Scheme S 3. Flow reaction with polymer supported HF reagent.

Section 4. Preparation of substrates

Synthesized alkene substrates 1 (these substrates were confirmed with ^1H and ^{13}C NMR spectra).

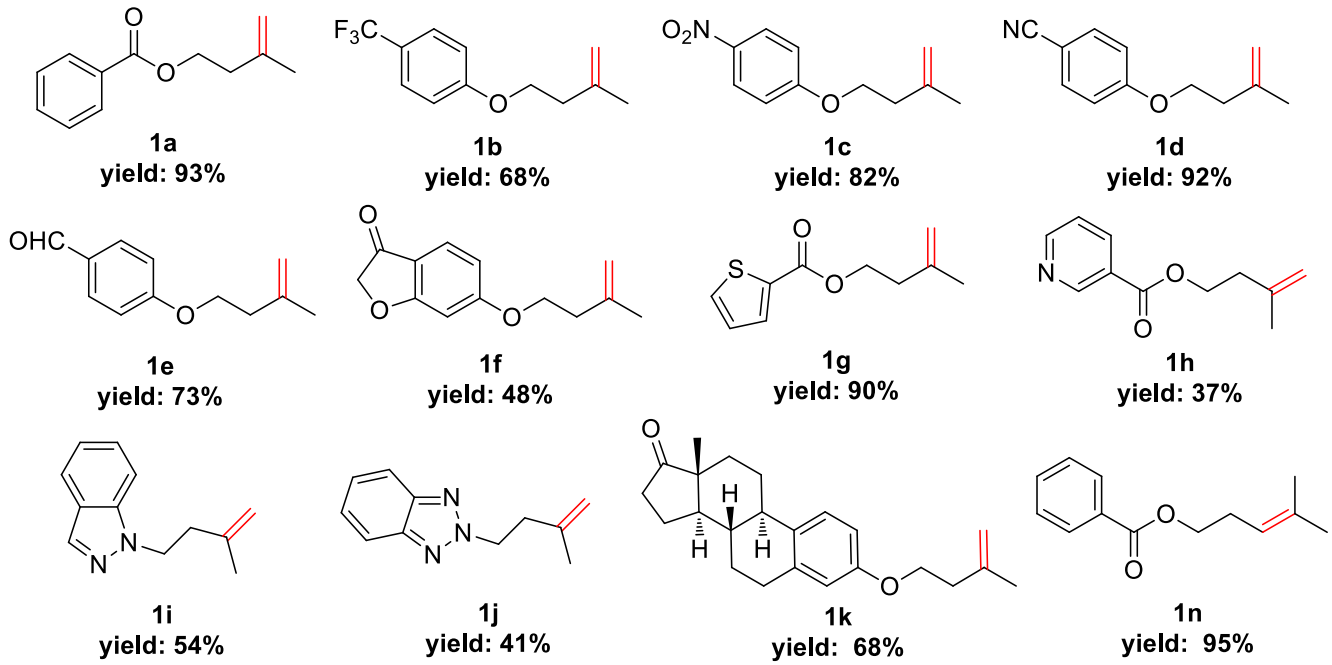


Figure S 2. Prepared alkene substrates.

Synthesized aziridine substrates 3 (these substrates were synthesized and confirmed with the literature data by their NMR spectra).[1]

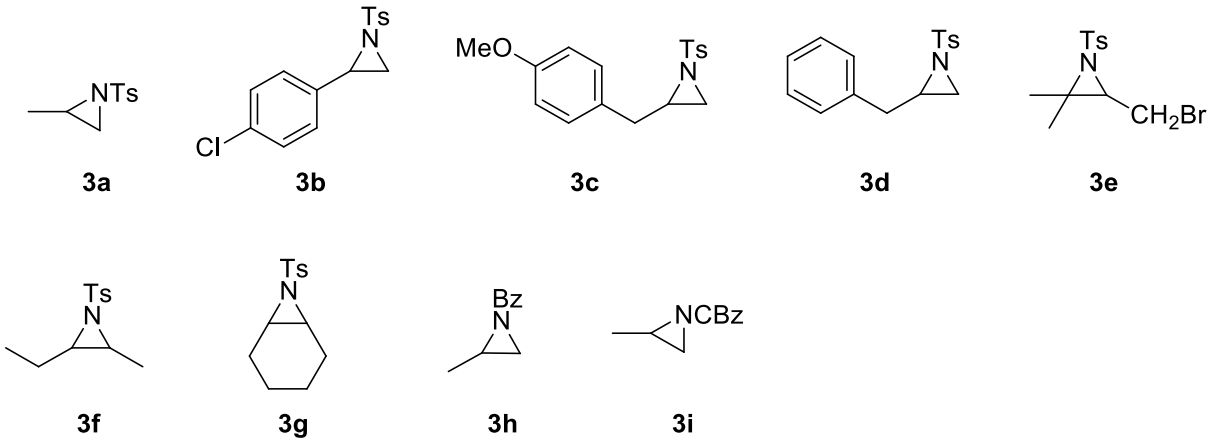


Figure S 3. Prepared aziridine substrates.

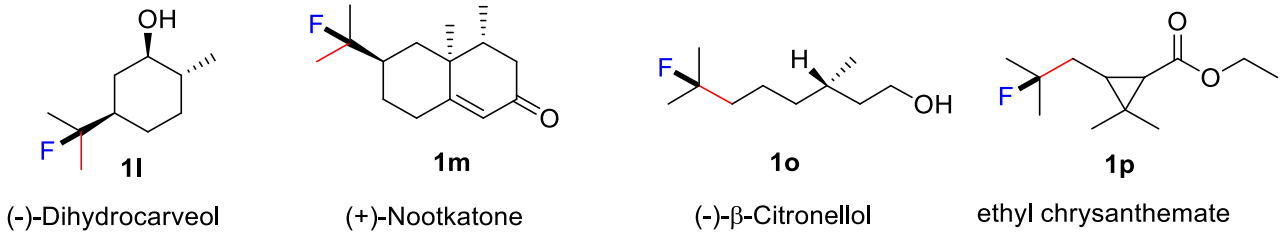
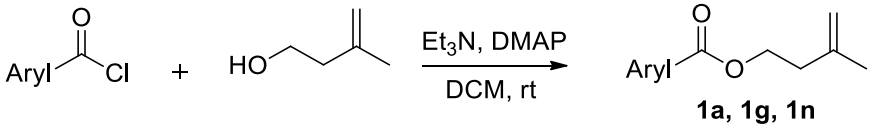


Figure S 4. Alkene substrates from commercial sources.

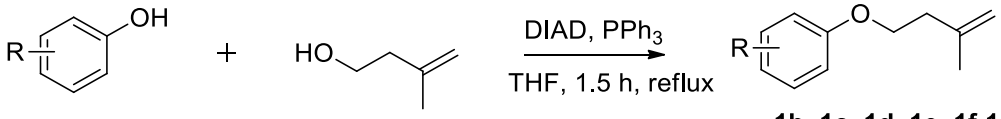
General synthetic procedure for the synthesis of esters 1a, 1g, 1n.



1a, 1g, 1n

A 20-mL vial fitted with a stirring bar was charged with alcohol (2 mmol), Et_3N (2 equiv) and dry DCM (10 mL). The mixture was cooled down to 0 ^oC and benzoyl chloride (1.2 equiv) and 5 mg DMAP were then added sequentially. The mixture was stirred overnight and then it was diluted with 50 mL DCM, washed with 1M aqueous HCl (2 x 20 mL), saturated $NaHCO_3$ (20 mL) and brine (20 mL), sequentially. The organic layer was then dried with Na_2SO_4 and concentrated. The residue was purified with column chromatography to afford the desired esters **1a** (yield: 93%), **1g** (yield: 90%), **1n** (yield: 95%).

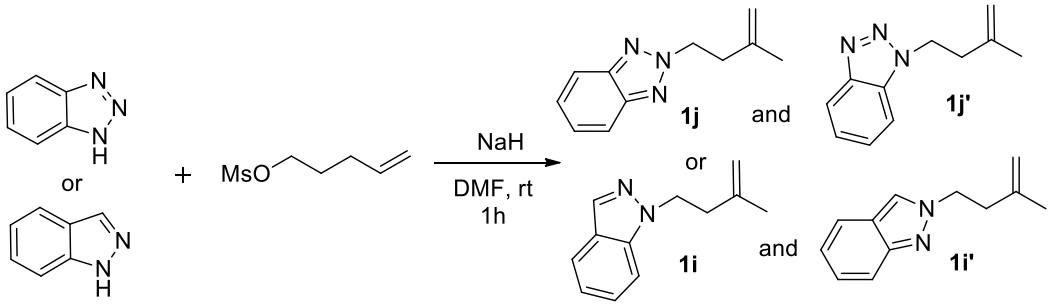
General synthetic procedure for the synthesis of ethers 1b, 1c, 1d, 1e, 1f, 1k.



1b, 1c, 1d, 1e, 1f,1k

A solution of phenol (3 mmol), 3-methyl-3-buten-1-ol (3.6 mmol), triphenylphosphine (3.6 mmol), diisopropyl azodicarboxylate (3.6 mmol) in THF (27 mL) was heated for 1.5 hours at reflux. After concentrated in vacuo, the residue was purified by flash column chromatography to give the desired ethers **1b** (yield: 68%), **1c** (yield: 82%), **1d** (yield: 92%), **1e** (yield: 73%), **1f** (yield: 48%), **1k** (yield: 68%).

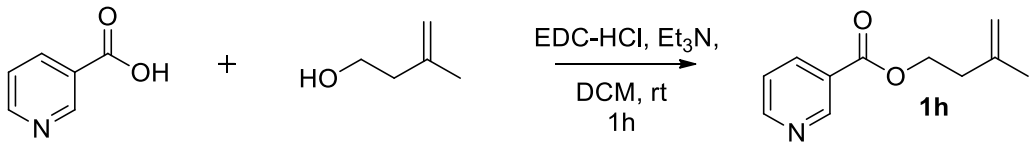
General synthetic procedure for the synthesis of 1i, 1j.



A 50-mL flask fitted with a stirring bar was charged with a solution of starting material (2 mmol) in DMF (10 mL). The mixture was cooled down to 0 ^oC and NaH (1.5 equiv) was then added. The mesylate was also added and the mixture was stirred at rt for 1h. The reaction was quenched by NH_4Cl (1 M) and diluted with CH_2Cl_2 (50 mL). After being washed with 5% LiCl aqueous solution (2 x 20 mL), the

aqueous layer was extracted with CH_2Cl_2 (20 mL). The combined organic extracts were washed with water (20 mL), dried and concentrated in vacuo. The resulting residues was purified by silica gel flash chromatography to afford **1i** (yield: 54%), **1i'** (yield: 30%), **1j** (yield: 41%), **1j'** (yield: 40%).

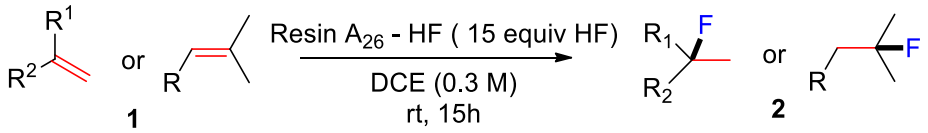
General synthetic procedure for the preparation of ester 1h.



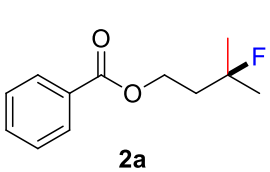
A 50-mL flask fitted with a stirring bar was charged with a solution of alcohol (2 mmol), EDCI (1.2 equiv), triethylamine (1.5 equiv), and DMAP (0.1 equiv) in dichloromethane (10 mL). Nicotinic acid (1 equiv) was then added at 0 °C and the reaction mixture was stirred overnight at room temperature. After the reaction was complete, the resulting mixture was diluted with DCM (50 mL), washed by 1 N HCl (2 x 20 mL), 1 N aqueous $NaHCO_3$ (2 x 20 mL), and brine (1 x 20 mL). The organic layer was dried (Na_2SO_4) and evaporated in vacuo. The resulting residue was purified by column chromatography to afford the desired ester **1h** (yield: 37%).

Section 5. General procedure for reactions with resin-HF complex

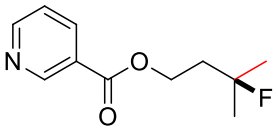
5.1 Hydrofluorination of alkenes.



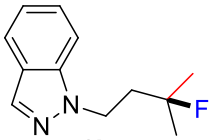
An 8-mL Polytetrafluoroethylene (PTFE) vial fitted with a stirring bar was charged with dry DCE (0.6 mL) and alkene starting material (0.2 mmol). HSO_4^- A26 Resin- HF (200 mg, 15.0 equiv based on HF) was then added in one portion at room temperature. The progress of reaction was monitored by TLC (visualized by $KMnO_4$ stain). The product usually shows a slightly more polar spot than the starting material on TLC (R_f difference < 0.1 in most cases). The reaction was then filtered, and the resin was washed with ethyl acetate (2 mL x 2). The filtrate was concentrated, and the residue was purified with flash chromatography.



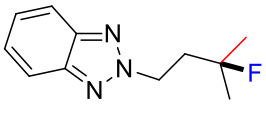
2a



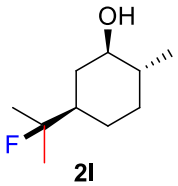
2h



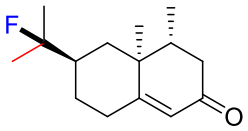
2i



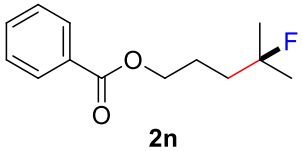
2j



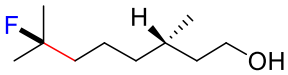
2l



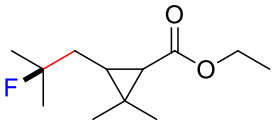
2m



2n

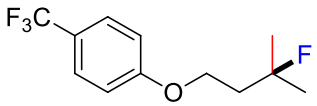


2o



2p

The NMR data for the above compound are in accord with the literature.[2] Therefore, chemical shift data were not reported here, and only the NMR spectra was attached in the spectral data section.



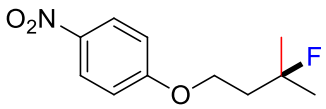
2b

^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.56 (d, *J* = 8.6 Hz, 2H), 6.97 (d, *J* = 8.6 Hz, 2H), 4.19 (t, *J* = 6.7 Hz, 2H), 2.17 (dt, *J* = 19.8, 6.7 Hz, 2H), 1.46 (d, *J* = 21.5 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 161.11, 126.92, 126.88, 125.78, 123.06, 122.73, 114.41, 95.26, 93.61, 63.88 (d, *J* = 5.9 Hz), 40.12 (d, *J* = 22.9 Hz), 27.16 (d, *J* = 24.6 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ = -61.49 (s, 3F), -136.11 – -141.04 (m, 1F).

HRMS: (EI^+) [M] cal. for $C_{12}H_{14}F_4O$: 250.0981; found:250.0976.



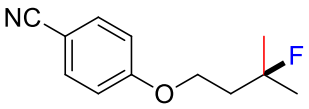
2c

^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.28 – 8.05 (m, 2H), 6.98 – 6.90 (m, 2H), 4.23 (t, *J* = 6.7 Hz, 2H), 2.18 (dt, *J* = 19.9, 6.7 Hz, 2H), 1.46 (d, *J* = 21.5 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 163.75, 141.54, 125.95, 114.45, 95.12, 93.47, 64.58 (d, *J* = 5.7 Hz), 40.01 (d, *J* = 22.9 Hz), 27.19 (d, *J* = 24.5 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ = -137.98 – -141.01 (m, 1F).

HRMS: ($APCI^+$) [M+H] cal. for $C_{11}H_{15}FNO_3$: 228.1036; found:228.1030.



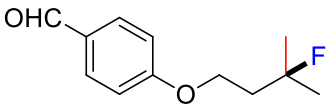
2d

^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.63 – 7.54 (m, 2H), 7.01 – 6.90 (m, 2H), 4.18 (t, *J* = 6.7 Hz, 2H), 2.16 (dt, *J* =19.9, 6.7 Hz, 2H), 1.45 (d, *J* = 21.5 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 162.04, 134.09, 119.29, 115.26, 104.08, 95.22, 93.57, 64.16 (d, *J* = 5.8 Hz), 40.08 (d, *J* = 22.9 Hz), 27.25 (d, *J* = 24.6 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ = -137.06 – -140.61 (m, 1F).

HRMS: (APCI$^+$) [M+H] cal. for $C_{12}H_{15}FNO$: 208.1138; found:208.1133.



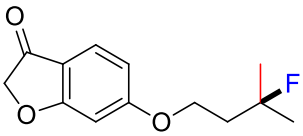
2e

^{1}H NMR (500 MHz, $CDCl_3$) δ = 9.89 (s, 1H), 7.84 (d, *J* = 8.6 Hz, 2H), 7.01 (d, *J* = 8.7 Hz, 2H), 4.22 (t, *J* = 6.7 Hz, 2H), 2.17 (dt, *J* = 19.8, 6.7 Hz, 2H), 1.46 (d, *J* = 21.5 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 190.76, 163.62, 131.91, 129.82, 117.64, 95.09, 93.44, 63.95 (d, *J* = 5.8 Hz), 39.95 (d, *J* = 22.9 Hz), 27.05 (d, *J* = 24.6 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ = -137.84 – -140.61 (m, 1F).

HRMS: (APCI$^+$) [M+H] cal. for $C_{12}H_{16}FO_2$: 211.1134; found:211.1129.



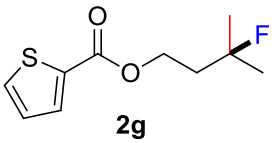
2f

^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.56 (d, *J* = 8.6 Hz, 1H), 6.64 (dd, *J* = 8.6, 2.0 Hz, 1H), 6.55 (d, *J* = 1.9 Hz, 1H), 4.62 (s, 2H), 4.20 (t, *J* = 6.7 Hz, 2H), 2.17 (dt, *J* =19.8, 6.7 Hz, 2H), 1.45 (d, *J* = 21.5 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 192.45, 171.39, 162.15, 120.02, 109.29, 106.84, 91.77, 90.01, 88.36, 70.44, 59.37 (d, *J* = 5.7 Hz), 34.84 (d, *J* = 22.9 Hz), 22.07 (d, *J* = 24.5 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ = -141.82 – -146.58 (m, 1F).

HRMS: ($APCI^+$) [M+H] cal. for $C_{13}H_{16}FO_3$: 239.1083; found:239.1077.



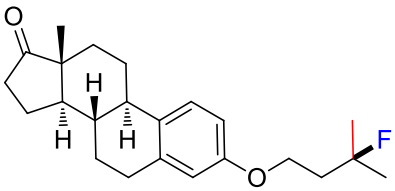
2g

^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.81 (dd, *J* = 3.7, 1.0 Hz, 1H), 7.56 (dd, *J* = 5.0, 1.1 Hz, 1H), 7.11 (dd, *J* = 4.8, 3.9 Hz, 1H), 4.46 (t, *J* = 6.8 Hz, 2H), 2.11 (dt, *J* = 19.3, 6.8 Hz, 2H), 1.45 (d, *J* = 21.5 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 162.38, 134.02, 133.74, 132.70, 128.06, 95.36, 93.71, 61.36 (d, *J* = 6.4 Hz), 40.10 (d, *J* = 23.2 Hz), 27.38 (d, *J* = 24.6 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ = -136.80 – -139.31 (m, 1F).

HRMS: (EI^+) [M] cal. for $C_{10}H_{13}FO_2S$: 216.0620; found:216.0613.



2k

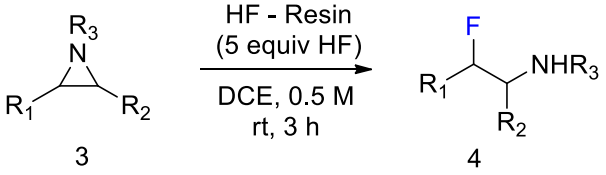
^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.21 (d, *J* = 8.6 Hz, 1H), 6.73 (dd, *J* = 8.6, 2.6 Hz, 1H), 6.66 (d, *J* = 2.5 Hz, 1H), 4.11 (t, *J* = 6.6 Hz, 2H), 2.96 – 2.86 (m, 2H), 2.52 (dd, *J* = 19.0, 8.7 Hz, 1H), 2.44 – 2.37 (m, 1H), 2.26 (dd, *J* = 13.6, 7.2 Hz, 1H), 2.20 – 1.94 (m, 6H), 1.69 – 1.40 (m, 13H), 0.92 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 220.56, 156.36, 137.44, 131.79, 126.00, 114.15, 111.79, 95.17, 93.54, 63.22, 50.08, 47.67, 43.65, 40.18, 39.96, 38.04, 35.54, 31.25, 29.32, 26.95, 26.70, 26.22, 25.58, 21.25, 13.52.

^{19}F NMR (376 MHz, $CDCl_3$) δ = -135.59 – -138.79 (m, 1F).

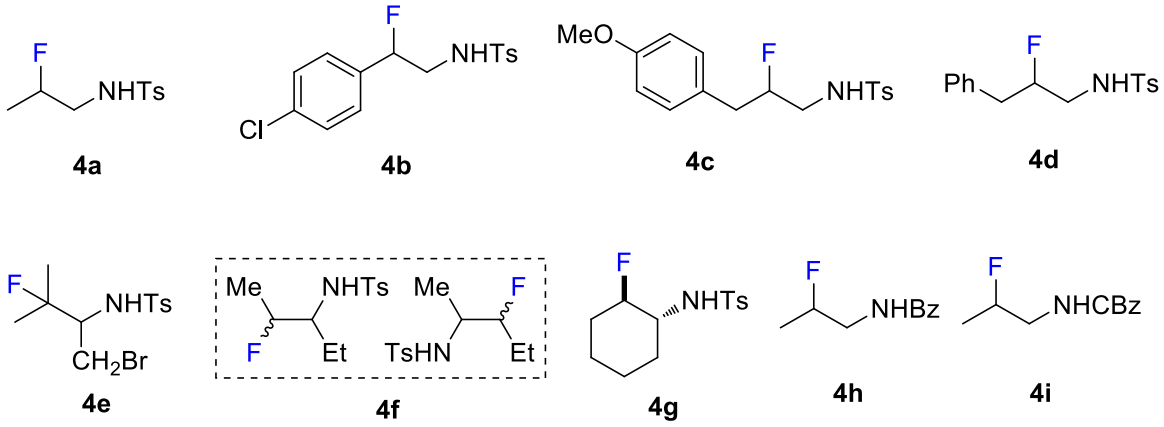
HRMS: ($APCI^+$) [M+H] cal. for $C_{23}H_{32}FO_2$: 359.2386; found:359.2383.

5.2 Ring opening of aziridines.

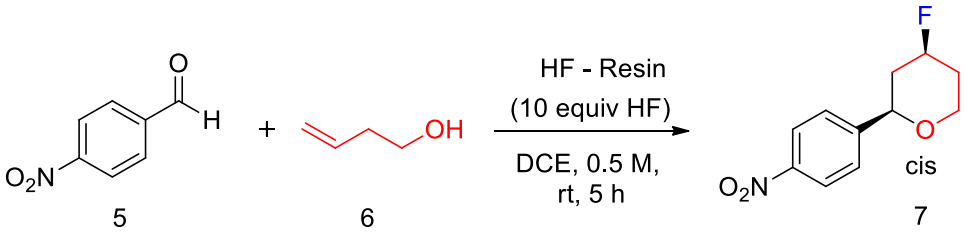


An 8-mL PTFE vial fitted with a stirring bar was charged with dry DCE (0.4 mL) and aziridine starting material (0.2 mmol). HSO_4^- A26 Resin- HF (66 mg, 5.0 equiv based on HF) was then added in one portion at room temperature. The progress of the reaction was monitored by TLC (visualized by $KMnO_4$ stain). The reaction was then filtered, and the resin was washed with ethyl acetate (2 mL x 2). The filtrate was concentrated, and the residue was purified with flash chromatography.

The NMR data for all of the β-fluoroamine products are in accord with the reference.[1] Therefore, chemical shift data was not reported here and only their NMR spectra was attached in the spectral data section.

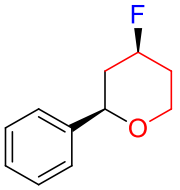


5.3 Fluoro-Prins reaction.

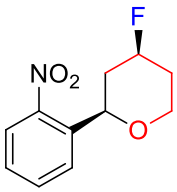


In an 8-mL PTFE vial charged with a magnetic stirring bar, homoallylic alcohol (0.2 mmol) and aldehyde (0.2 mmol) were dissolved in 0.4 mL dichloroethane, then HSO_4^- A26 Resin- HF (133 mg, 10.0 equiv based on HF) was added to the mixture and was stirred for 5 h at room temperature. The progress of the reaction was monitored by TLC (green or dark brown dots on anisaldehyde stain). After completion

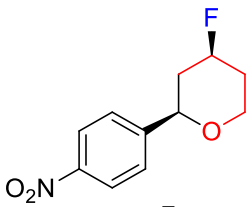
of the reaction the mixture was quenched with solid $NaHCO_3$, filtered and the filtrate was concentrated. The crude product was chromatographed to afford the corresponding fluoro-tetrahydropyrans.



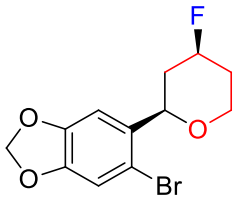
7a



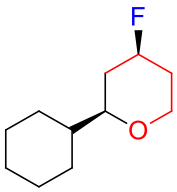
7b



7c

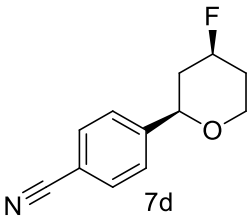


7f



7h

The NMR data for the above products are in accord with the reference.[3] Therefore, chemical shift data was not reported here and only their NMR spectra was attached in the spectral data section.



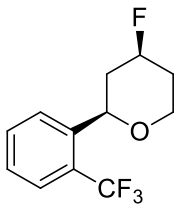
7d

^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.75 (d, *J* = 8.3 Hz, 2H), 7.56 (d, *J* = 8.1 Hz, 2H), 5.07 – 4.79 (dm, *J* = 60 Hz, 1H), 4.48 (d, *J* = 11.6 Hz, 1H), 4.39 – 4.26 (m, 1H), 3.67 (t, *J* = 12.3 Hz, 1H), 2.50 – 2.38 (m, 1H), 2.30 – 2.19 (m, 1H), 1.95 (tdd, *J* = 17.5, 12.4, 5.2 Hz, 1H), 1.76 (dt, *J* = 22.6, 11.4 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 146.67, 132.42, 126.46, 118.80, 111.63, 89.80, 88.03, 65.51 (d, *J* = 11.9 Hz), 40.54 (d, *J* = 17.8 Hz), 32.85 (d, *J* = 17.8 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ = -169.52 – -171.77 (m, 1F).

HRMS: (APCI$^+$) [M+H] cal. for $C_{12}H_{13}FNO$: 206.0981; found:206.0976.



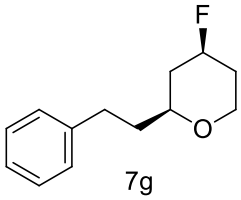
7e

^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.76 (d, *J* = 7.9 Hz, 1H), 7.61 (dd, *J* = 18.8, 7.9 Hz, 2H), 7.40 (t, *J* = 7.6 Hz, 1H), 4.96 – 4.72 (m, 1H), 4.68 (d, *J* = 11.2 Hz, 1H), 4.29 – 4.13 (m, 1H), 3.60 (t, *J* = 12.4 Hz, 1H), 2.43 – 2.28 (m, 1H), 2.16 (d, *J* = 12.3 Hz, 1H), 2.00 – 1.79 (m, 1H), 1.68 (dt, *J* = 22.6, 11.3 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 140.21, 132.34, 127.94, 127.77, 126.73, 126.42, 125.61, 125.48, 125.42, 124.77, 122.89, 89.82, 88.05, 73.89, 73.77, 65.57 (d, *J* = 12.1 Hz), 41.17 (d, *J* = 17.4 Hz), 32.94 (d, *J* = 17.8 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ = -58.50 (s, 3F), -169.88 (dd, *J* = 48.9, 4.6, 1F).

HRMS: (EI^+) [M] cal. for $C_{12}H_{12}F_4O$: 248.0824; found:248.0819.



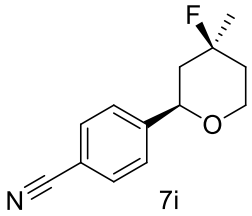
7g

^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.32 (dd, *J* = 13.8, 6.5 Hz, 1H), 7.24 (m, 3H), 4.67 (dm, *J* = 49.3 Hz, 1H), 4.12 (dt, *J* = 11.4, 5.6 Hz, 1H), 3.40 (t, *J* = 12.2 Hz, 1H), 3.28 (ddd, *J* = 12.4, 4.2, 2.0 Hz, 1H), 2.83 (m, 1H), 2.77 – 2.67 (m, 1H), 2.17 – 2.03 (m, 2H), 2.02 – 1.90 (m, 1H), 1.85 – 1.73 (m, 2H), 1.58 – 1.44 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 141.82, 128.49, 128.41, 125.88, 90.15, 88.40, 74.69, 74.58, 64.99 (d, *J* = 11.6 Hz), 38.80 (d, *J* = 16.7 Hz), 37.71, 33.15 (d, *J* = 17.4 Hz), 31.65.

^{19}F NMR (376 MHz, $CDCl_3$) δ = -169.45 (ddd, *J* = 49.3, 9.8, 4.8, 1F).

HRMS: (EI^+) [M] cal. for $C_{13}H_{17}FO$: 208.1263; found:208.1259.



7i

^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.52 (d, *J* = 8.2 Hz, 1H), 7.35 (d, *J* = 8.1 Hz, 1H), 4.61 (d, *J* = 11.7 Hz, 1H), 4.03 – 3.89 (m, 1H), 3.81 (td, *J* = 11.9, 4.7 Hz, 1H), 2.02 – 1.87 (m, 1H), 1.69 (m, 2H), 1.55 – 1.35 (m, 1H), 1.31 (d, *J* = 21.3 Hz, 2H).

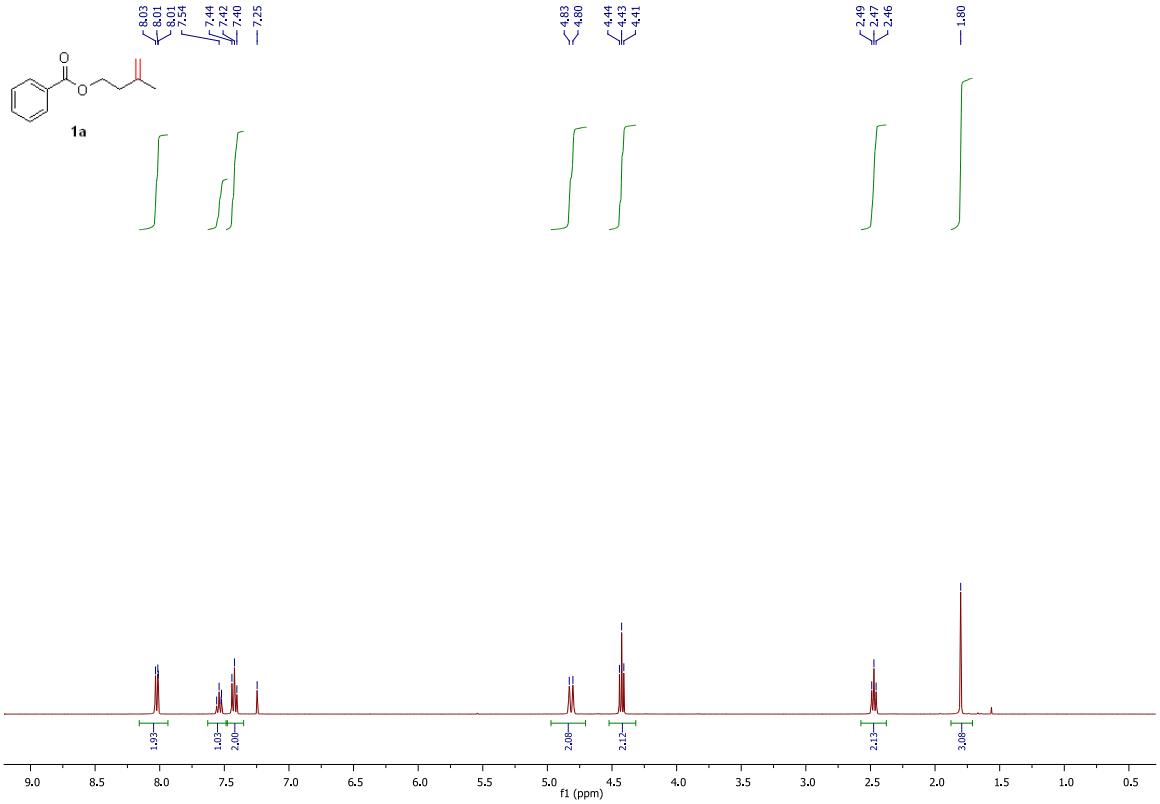
^{13}C NMR (100 MHz, $CDCl_3$) δ = 147.54, 132.13, 126.18, 118.71, 111.07, 92.70, 91.02, 74.17, 63.74, 44.21 (d, *J* = 21.5 Hz), 35.95 (d, *J* = 21.9 Hz), 27.45 (d, *J* = 24.1 Hz).

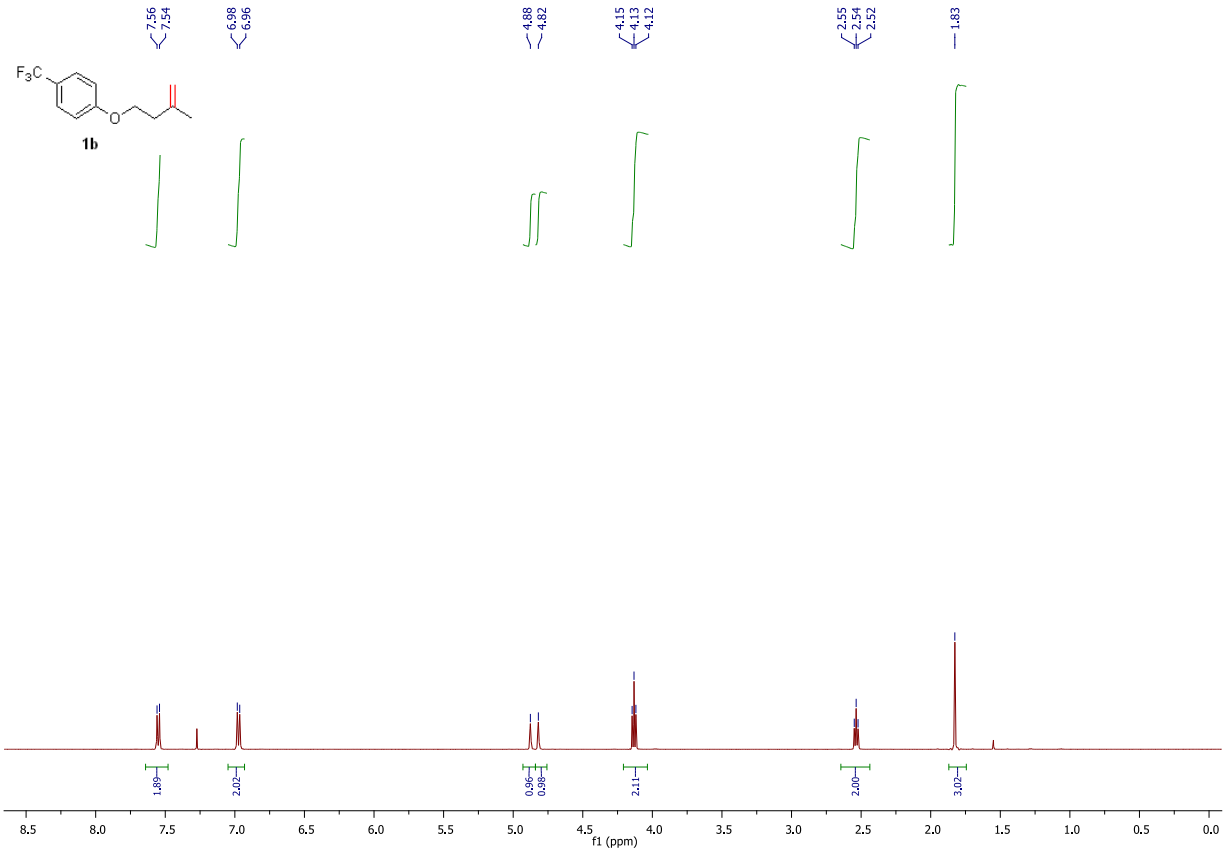
^{19}F NMR (376 MHz, $CDCl_3$) δ = -151.26 – -154.55 (m, 1F).

HRMS: ($APCI^+$) [M+H] cal. for $C_{13}H_{15}FNO$: 220.1138; found:220.1133.

Section 6. Spectral data of starting materials and products

6.1 Starting materials NMR spectra.

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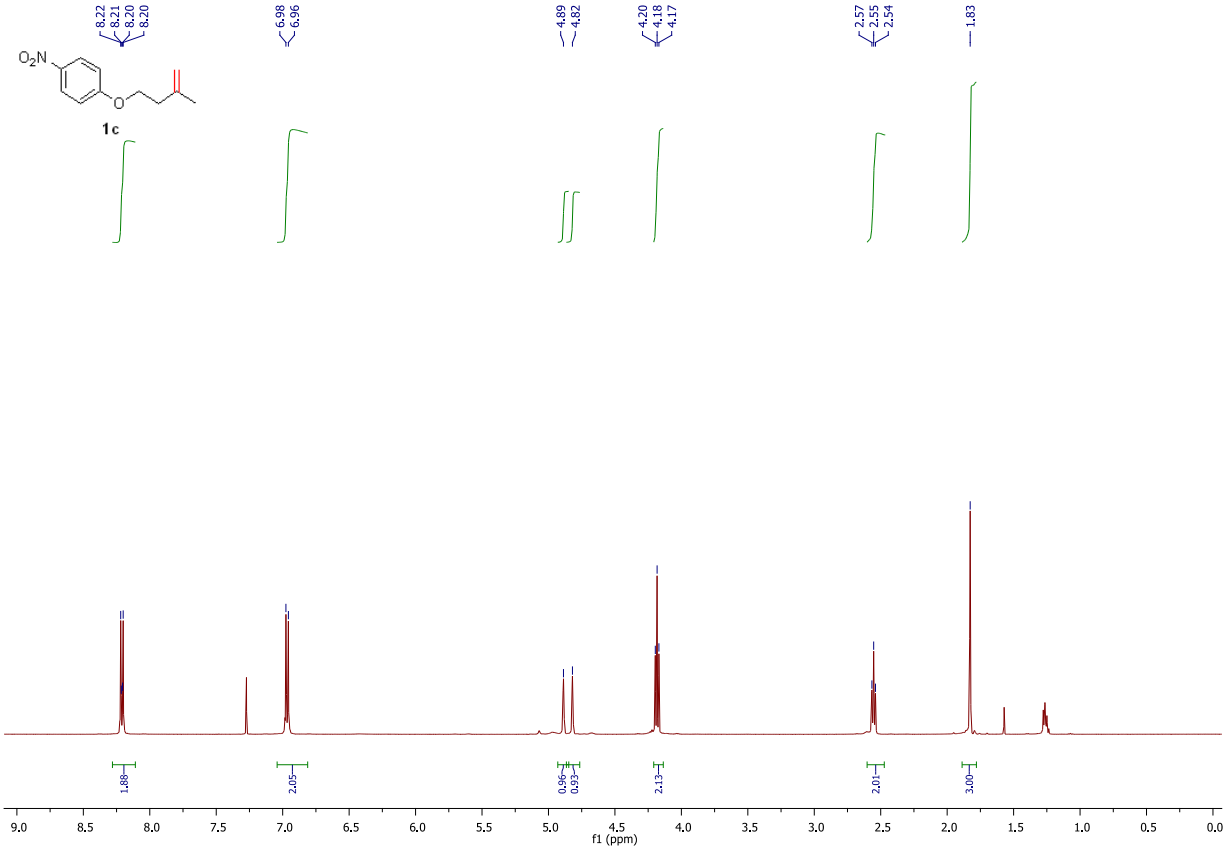
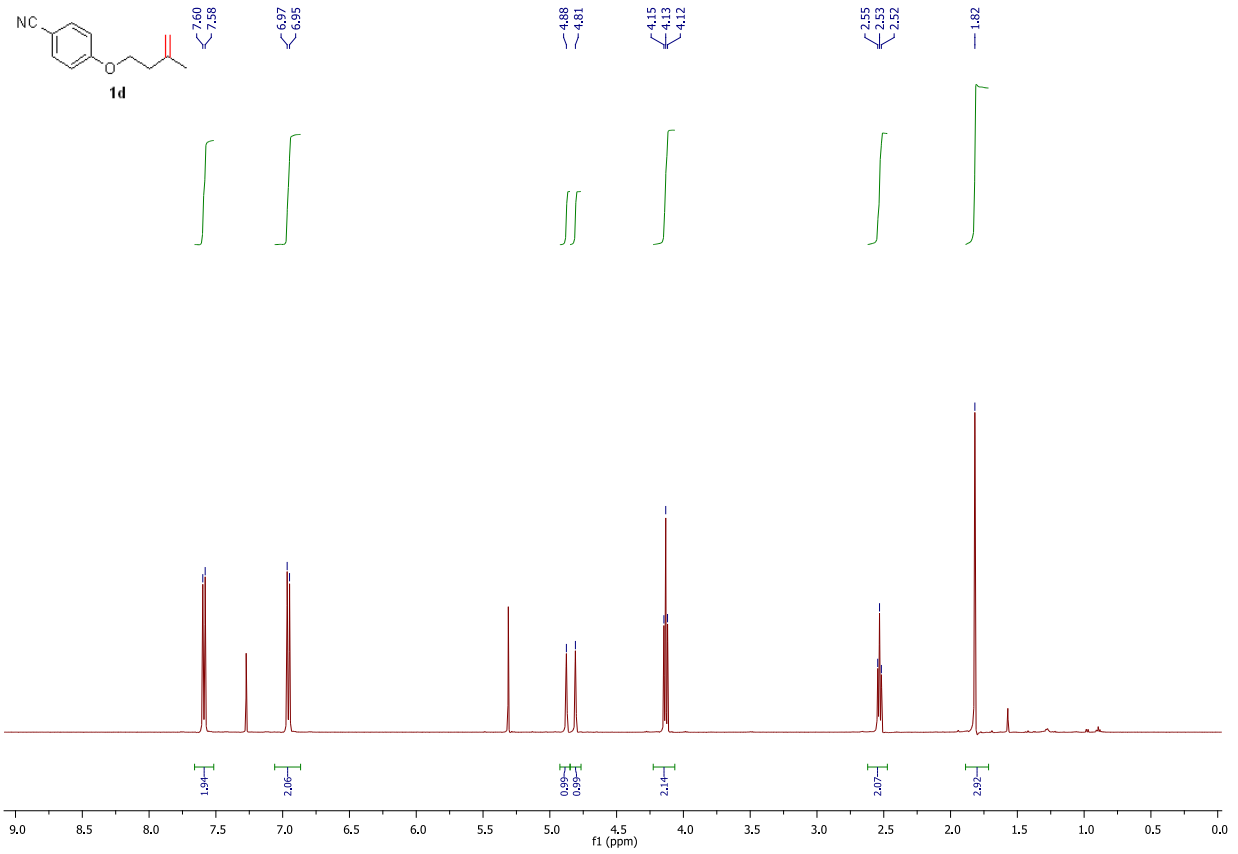
7.54
6.98
6.96
4.88
4.82
4.15
4.13
4.12
2.55
2.54
2.52
1.83
F3C
O
1b
1.89
2.02
0.96
0.98
2.11
2.00
3.02
f1 (ppm)


8.22
8.21
8.20
8.20
6.98
6.96
4.89
4.82
4.20
4.18
4.17
2.57
2.55
2.54
1.83
O2N
O
1c
1.88
2.05
0.96
0.93
2.13
2.01
3.00
f1 (ppm)


NC
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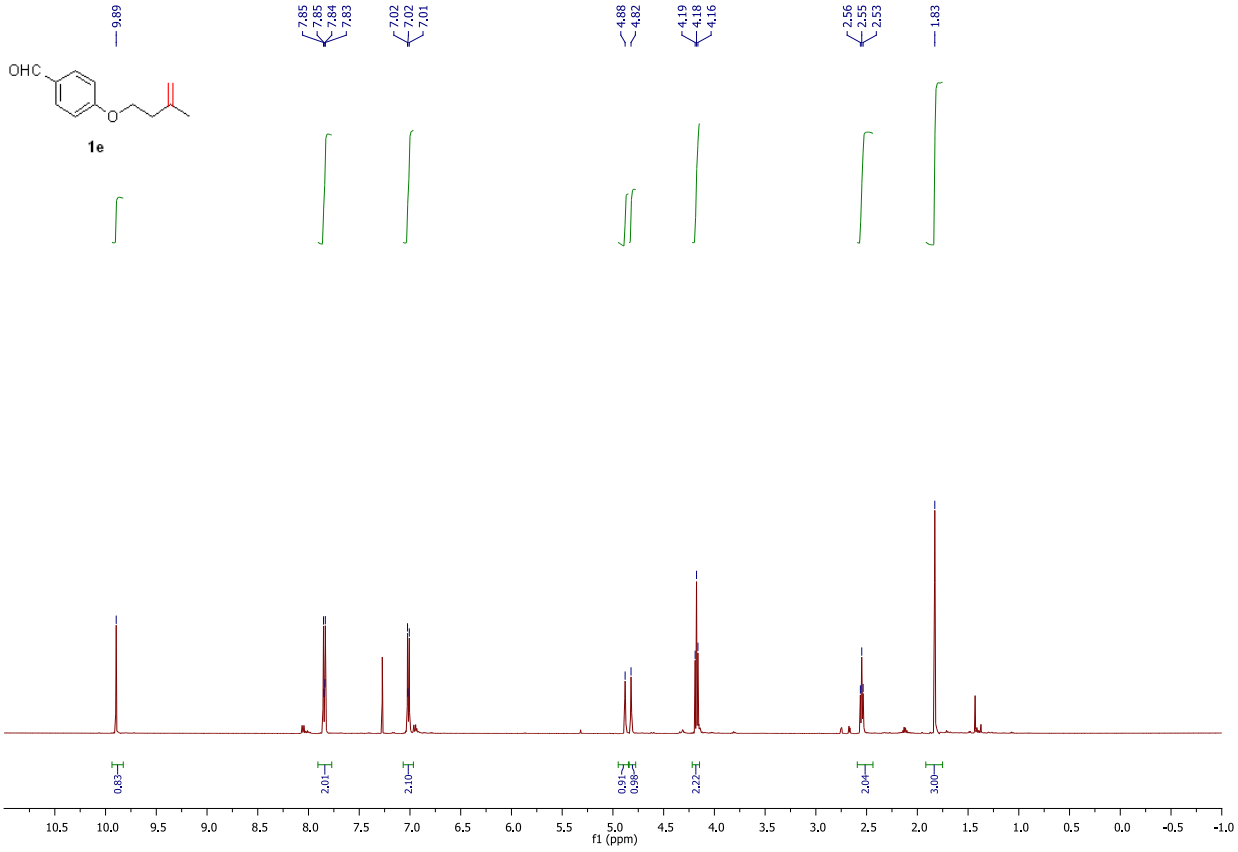
7.58
6.97
6.95
4.88
4.81
4.15
4.13
4.12
2.55
2.53
2.52
1.82
1.94
2.06
0.99
0.99
2.14
2.07
2.92
f1 (ppm)


OHC
1e
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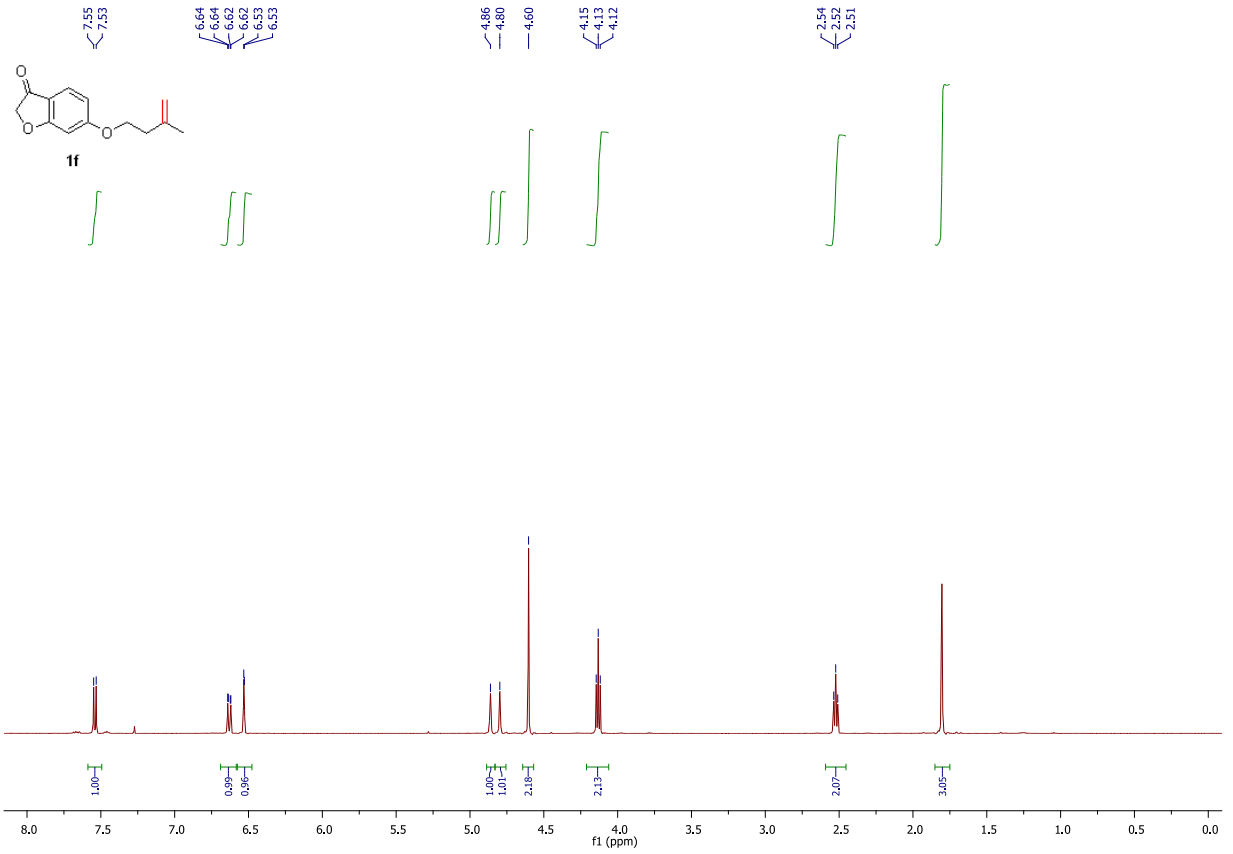
7.85
7.85
7.84
7.83
7.02
7.02
7.01
4.88
4.82
4.19
4.18
4.16
2.56
2.55
2.53
1.83
0.83
2.01
2.10
0.91
0.98
2.22
2.04
3.00
f1 (ppm)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6.62
6.53
6.53
4.86
4.80
4.60
4.15
4.13
4.12
2.54
2.52
2.51
1f
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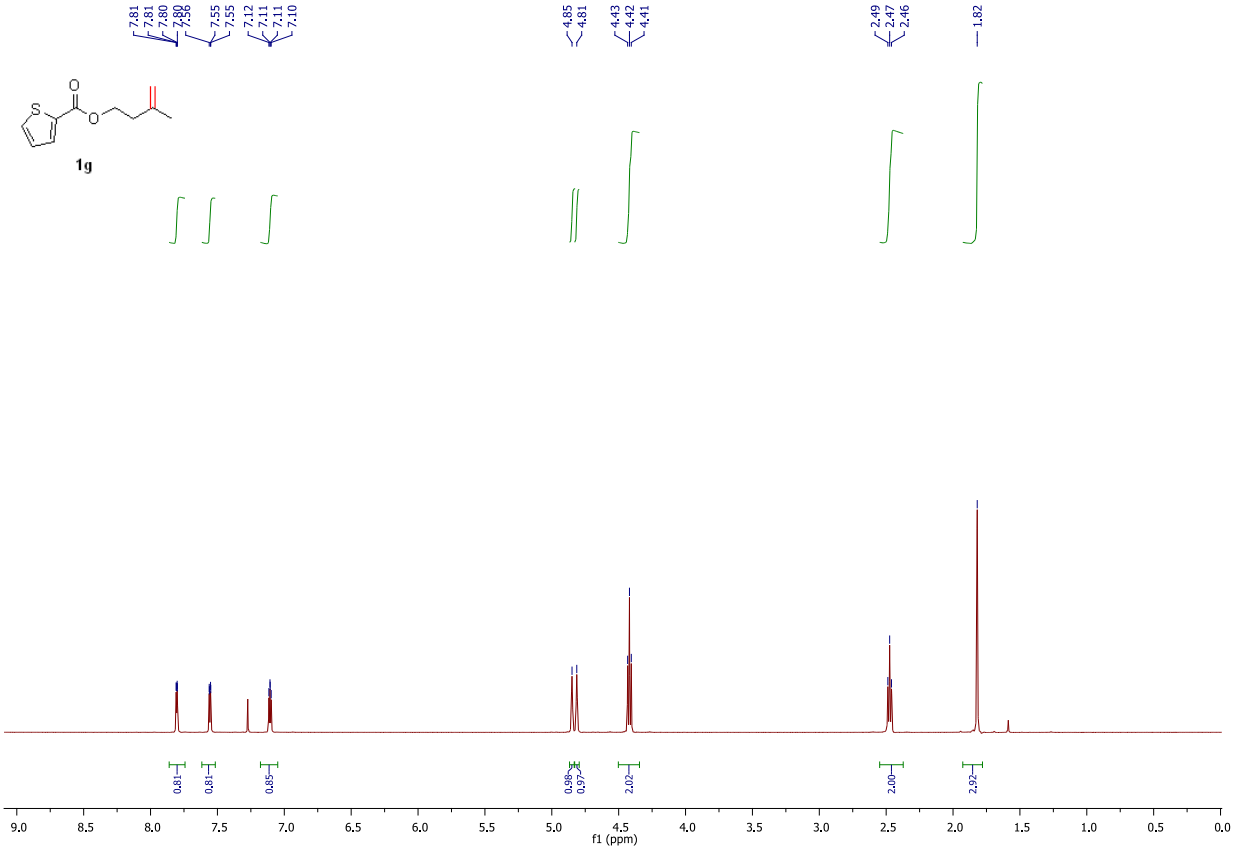
0.99
0.96
1.00
1.01
2.18
2.13
2.07
3.05
f1 (ppm)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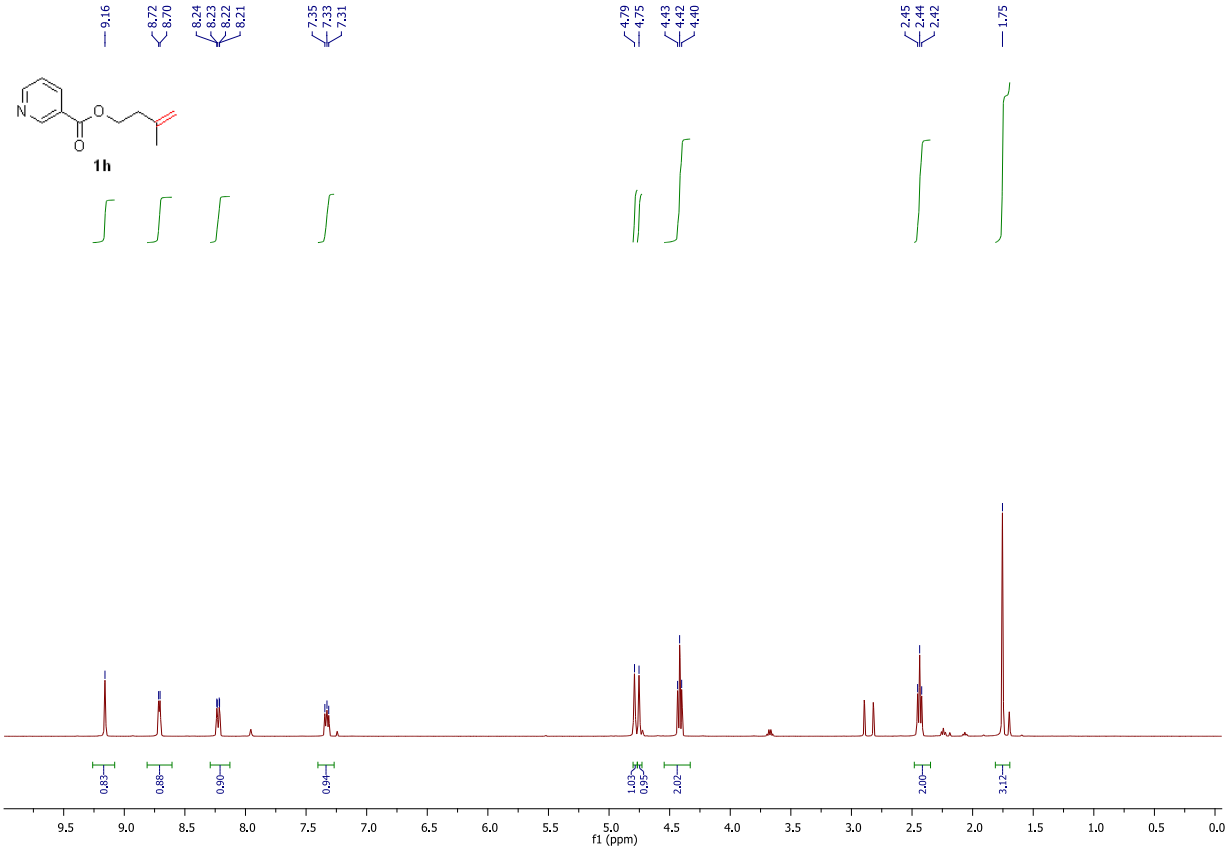
7.81
7.80
7.80
7.56
7.55
7.55
7.12
7.11
7.11
7.10
4.85
4.81
4.43
4.42
4.41
2.49
2.47
2.46
1.82
1g
0.81
0.81
0.85
0.98
0.97
2.02
2.00
2.92
f1 (ppm)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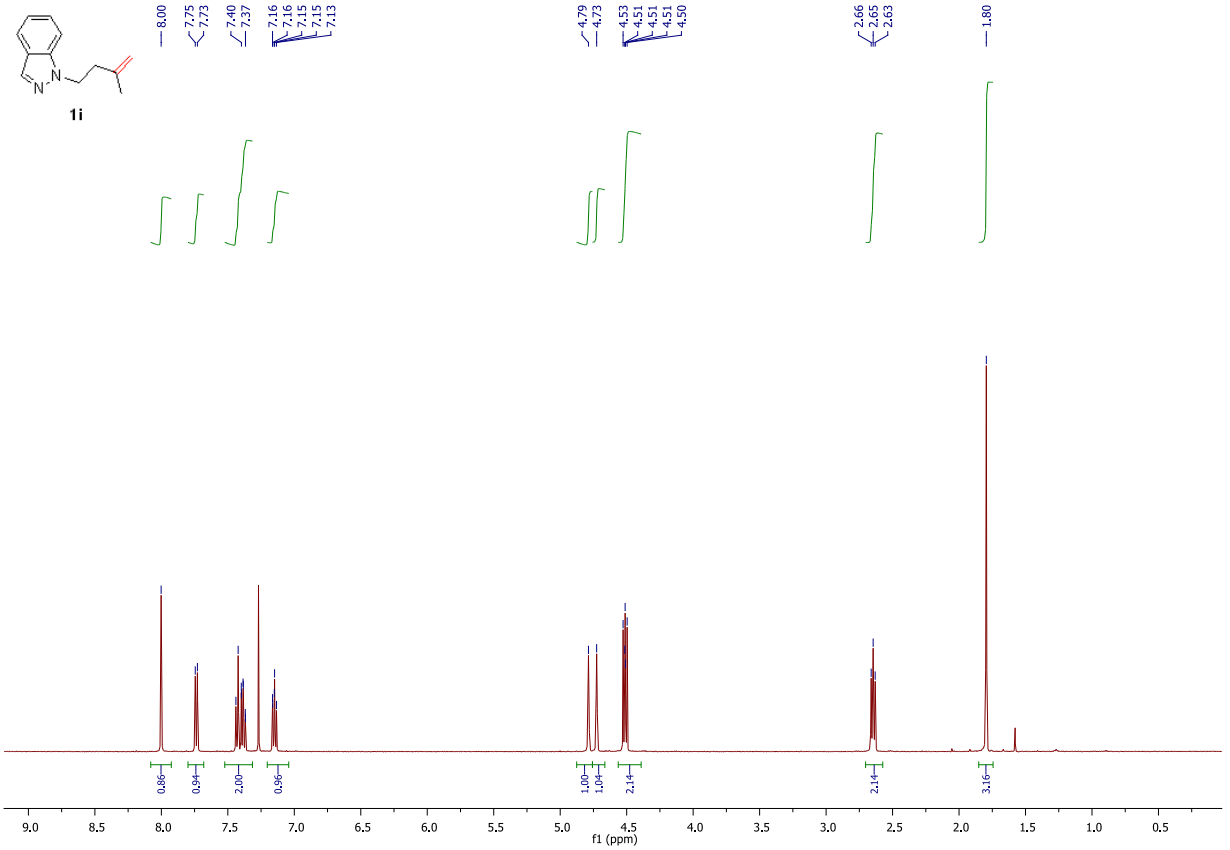
7.31
4.79
4.75
4.43
4.42
4.40
2.45
2.44
2.42
1.75
1h
0.83
0.88
0.90
0.94
1.03
0.95
2.02
2.00
3.12
f1 (ppm)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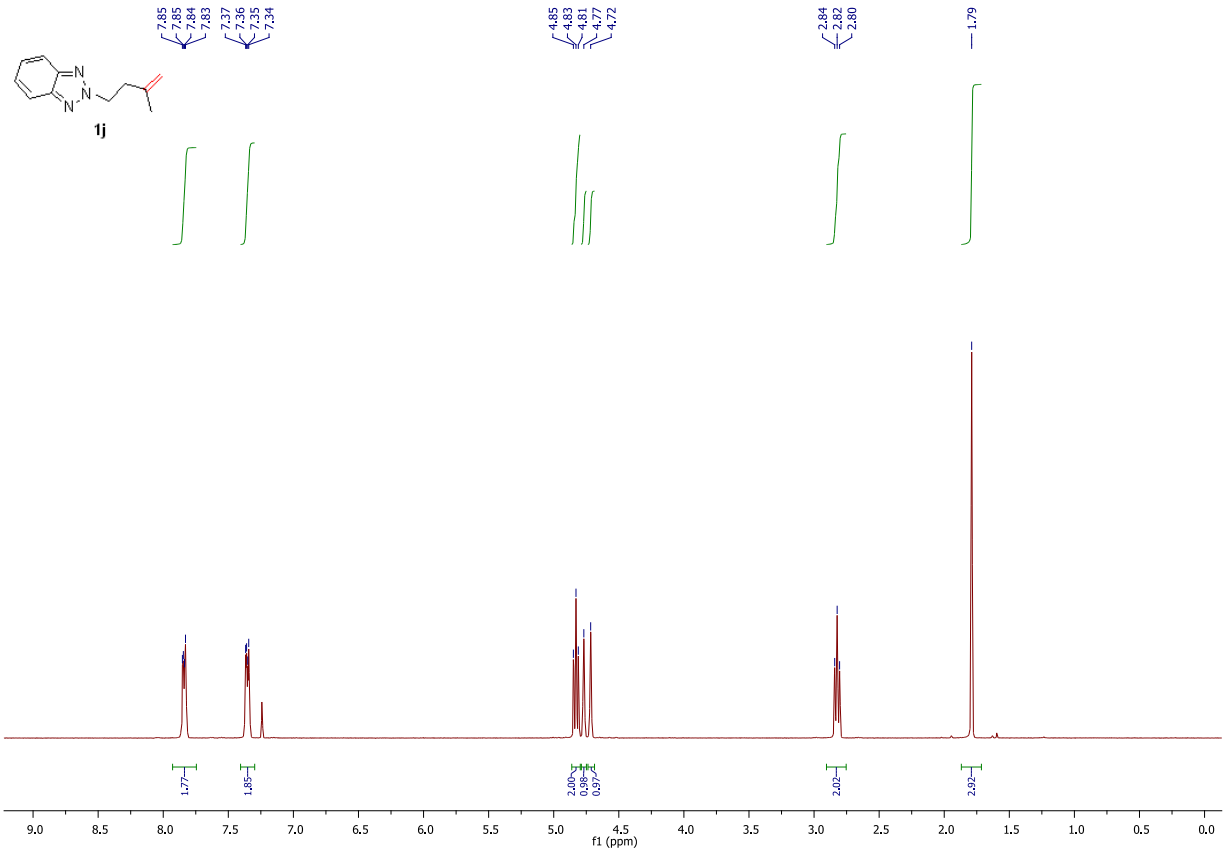
7.15
7.15
7.13
4.79
4.73
4.53
4.51
4.51
4.51
4.50
2.66
2.65
2.63
1.80
1i
0.86
0.94
2.00
0.96
1.00
1.04
2.14
2.14
3.16
f1 (ppm)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7.85
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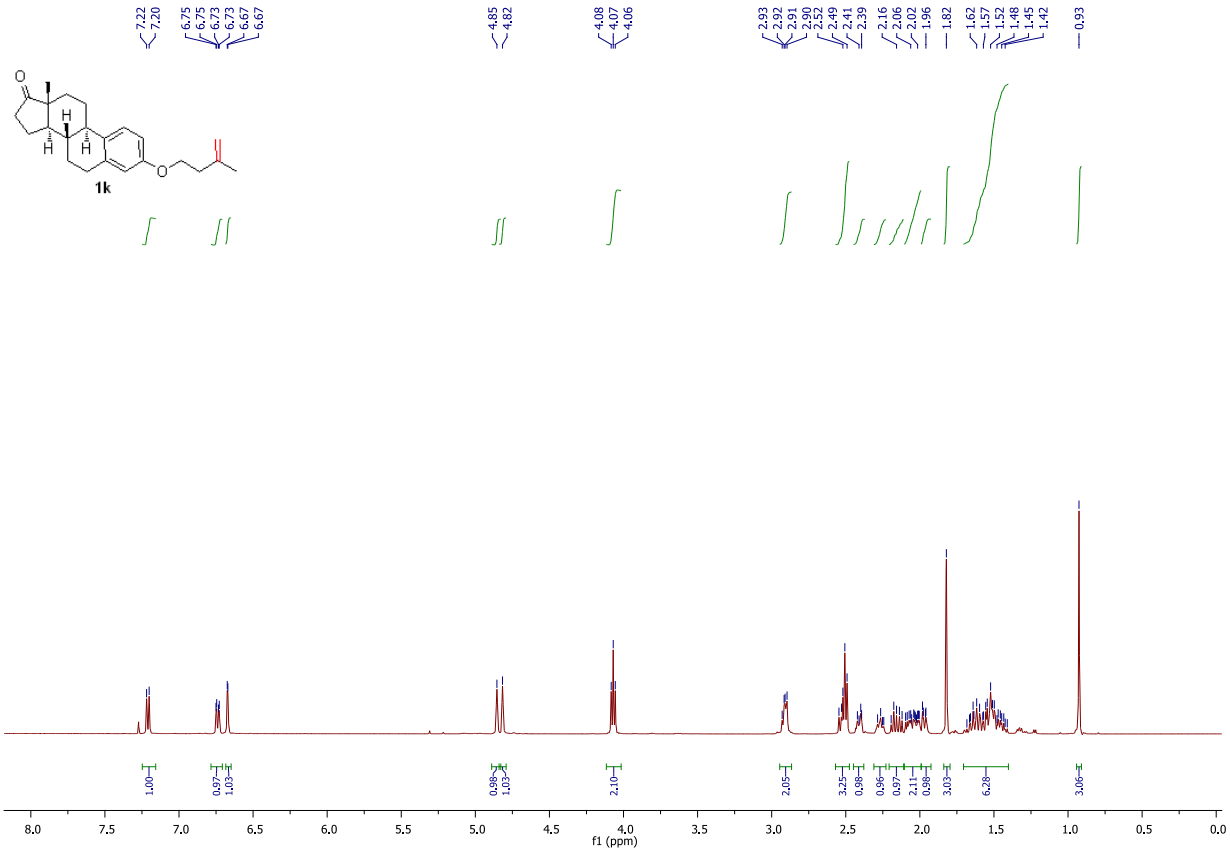
7.36
7.35
7.34
4.85
4.83
4.81
4.77
4.72
2.84
2.82
2.80
1.79
1j
1.77
1.85
2.00
0.98
0.97
2.02
2.92
f1 (ppm)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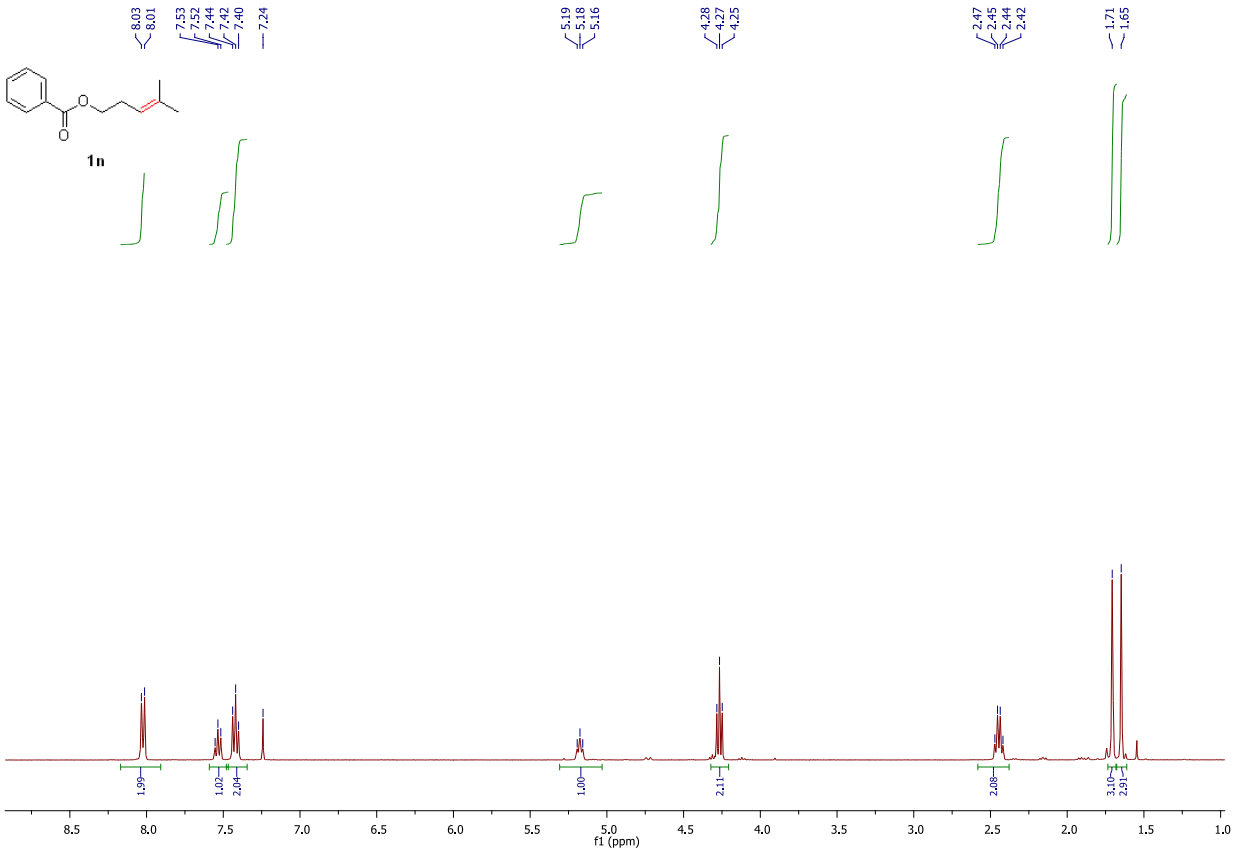
7.20
6.75
6.75
6.73
6.73
6.67
6.67
4.85
4.82
4.08
4.07
4.06
2.93
2.92
2.91
2.90
2.52
2.49
2.41
2.39
2.16
2.06
2.02
1.96
1.82
1.62
1.57
1.52
1.48
1.45
1.42
0.93
1k
1.00
0.97
1.03
0.98
1.03
2.10
2.05
3.25
0.98
0.96
0.97
2.11
0.98
3.03
6.28
3.06
f1 (ppm)


8.03
8.01
7.53
7.52
7.44
7.42
7.40
7.24
5.19
5.18
5.16
4.28
4.27
4.25
2.47
2.45
2.44
2.42
1.71
1.65
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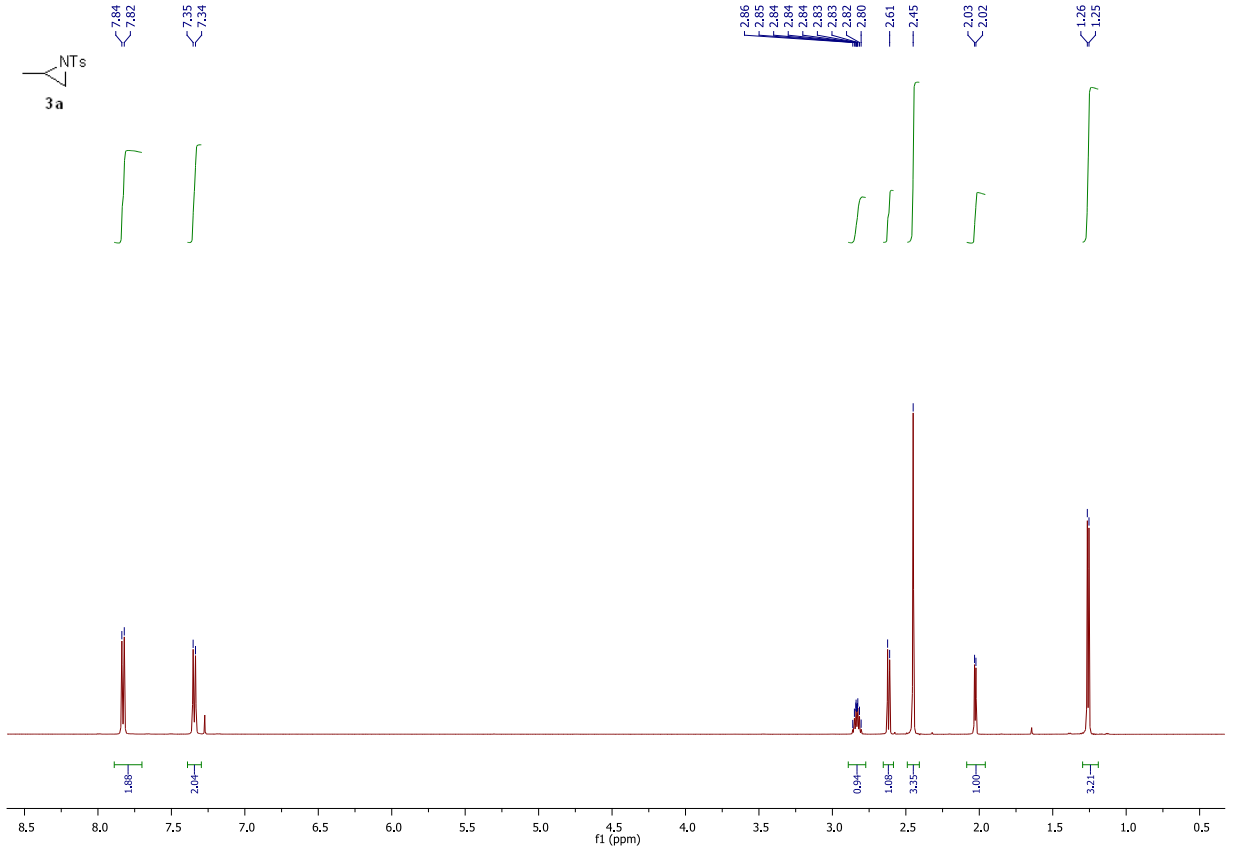
1.99
1.02
2.04
1.00
2.11
2.08
3.10
2.91
f1 (ppm)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7.34
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2.84
2.84
2.84
2.83
2.83
2.82
2.80
2.61
2.45
2.03
2.02
1.26
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NTs
3a
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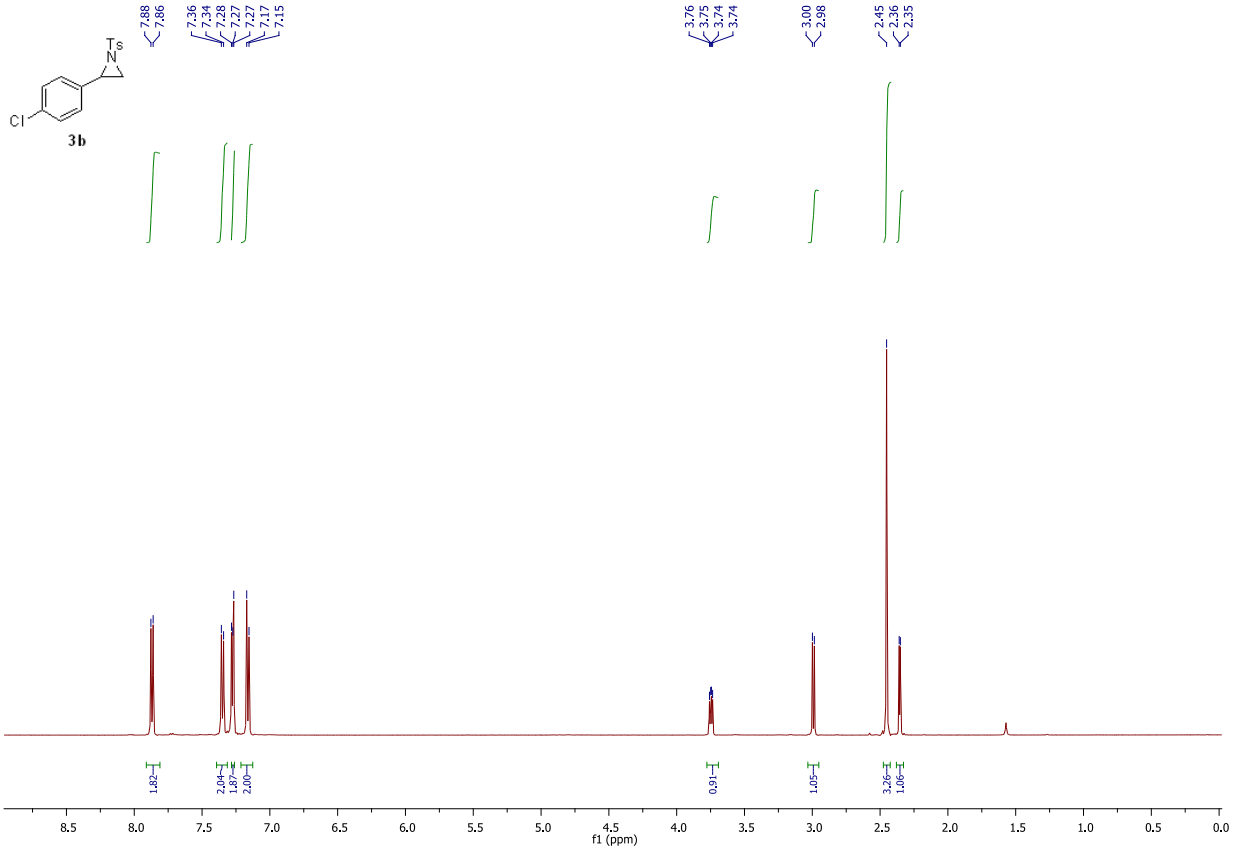
1.08
3.35
1.00
3.21
f1 (ppm)


Ts
N
Cl
3b
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7.86
7.36
7.34
7.28
7.27
7.27
7.17
7.15
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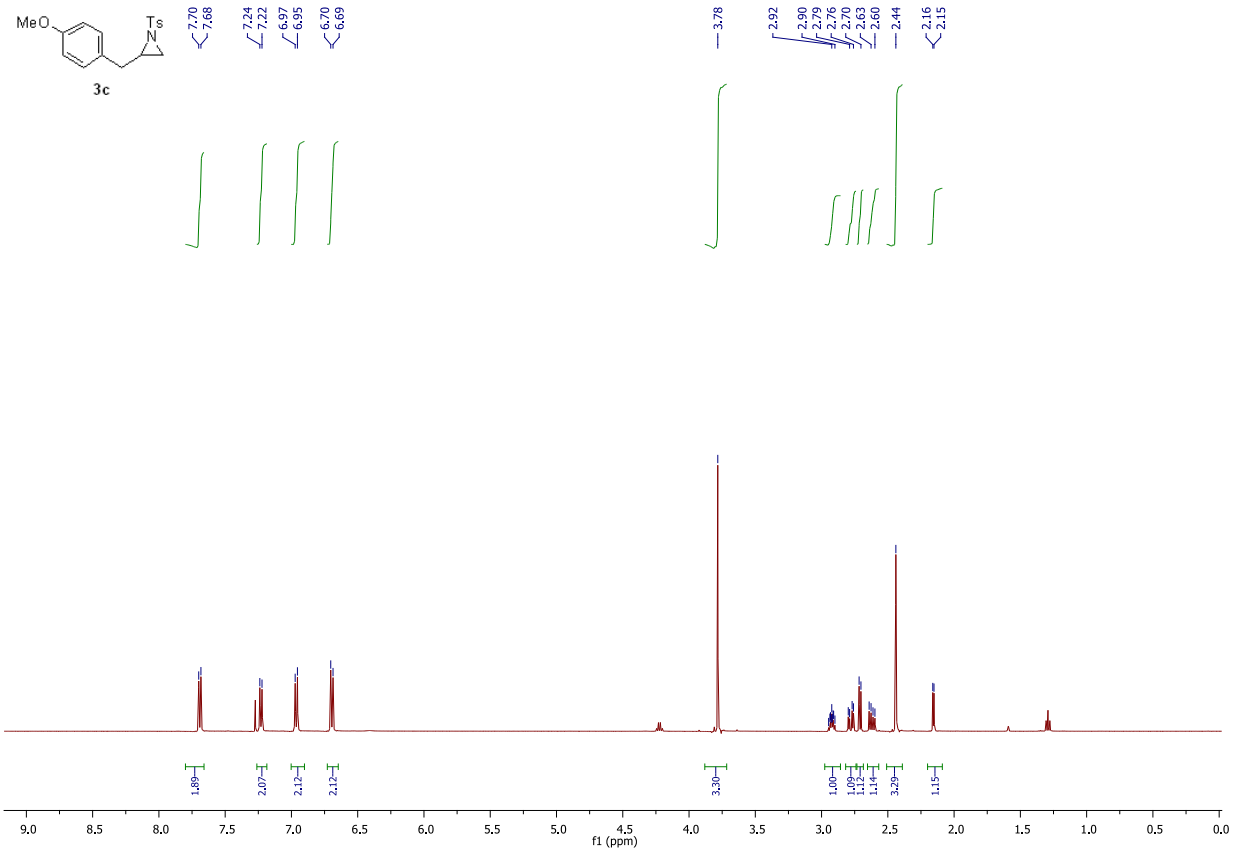
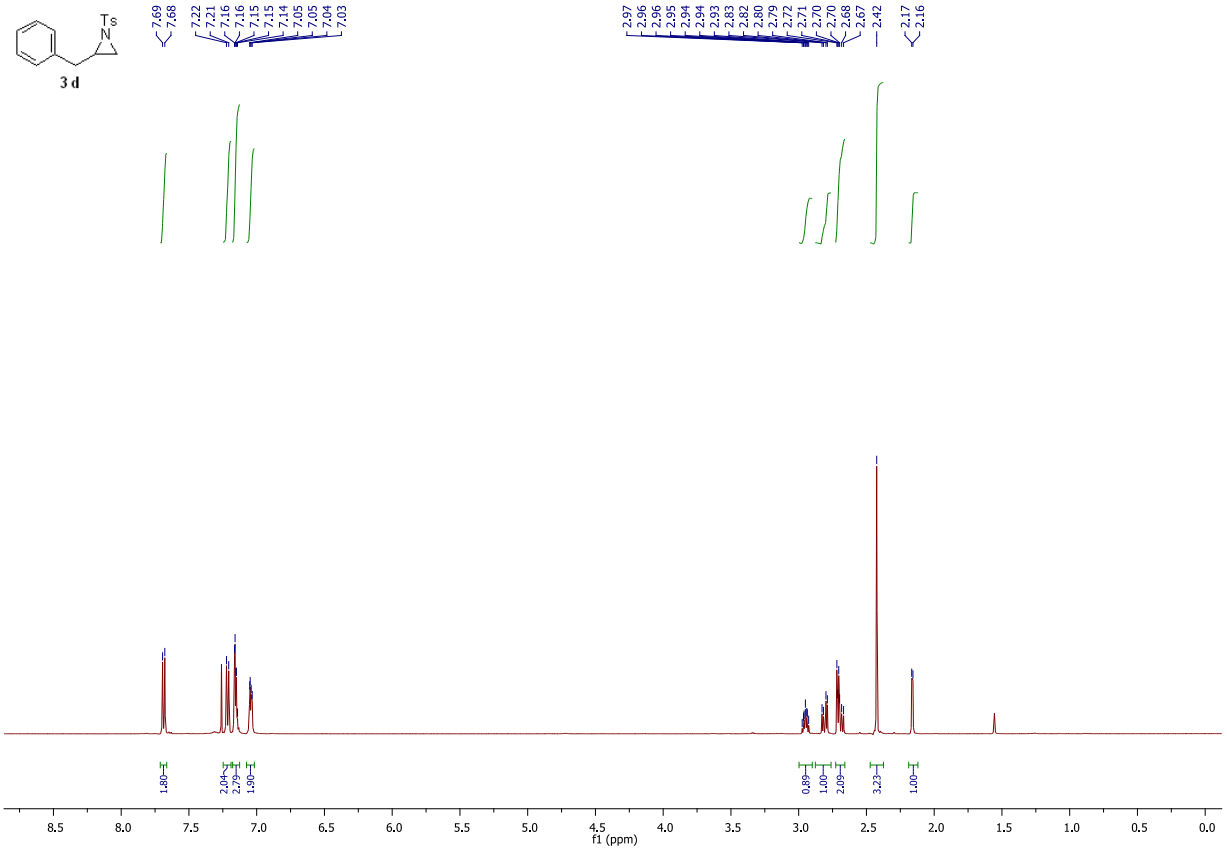
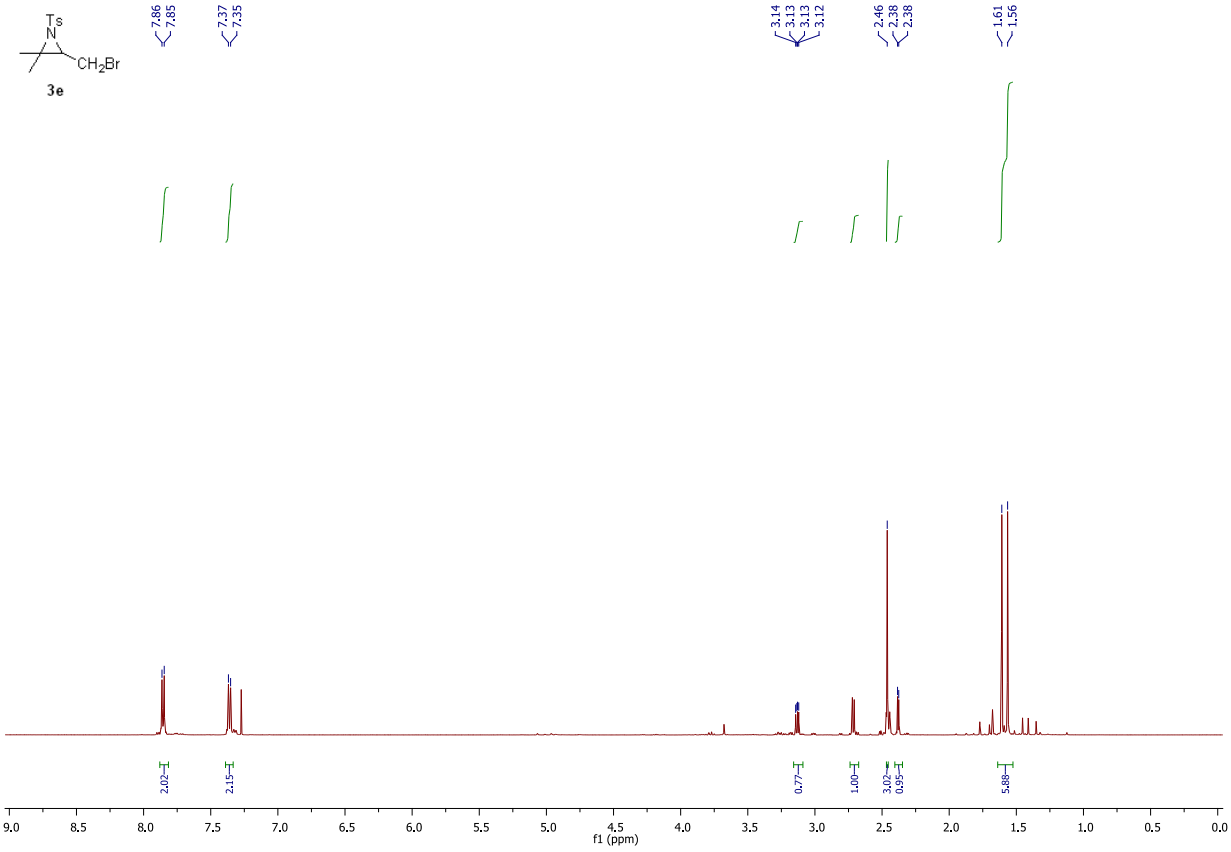
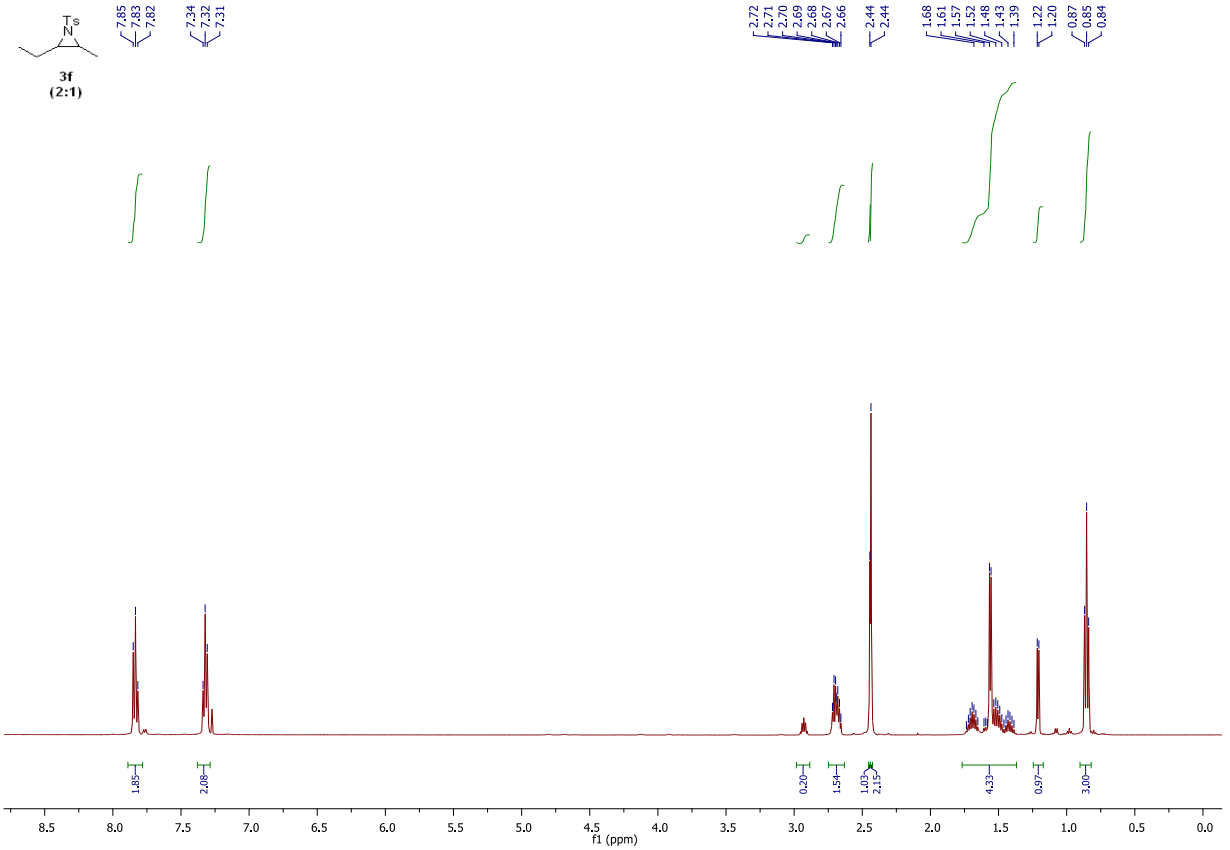
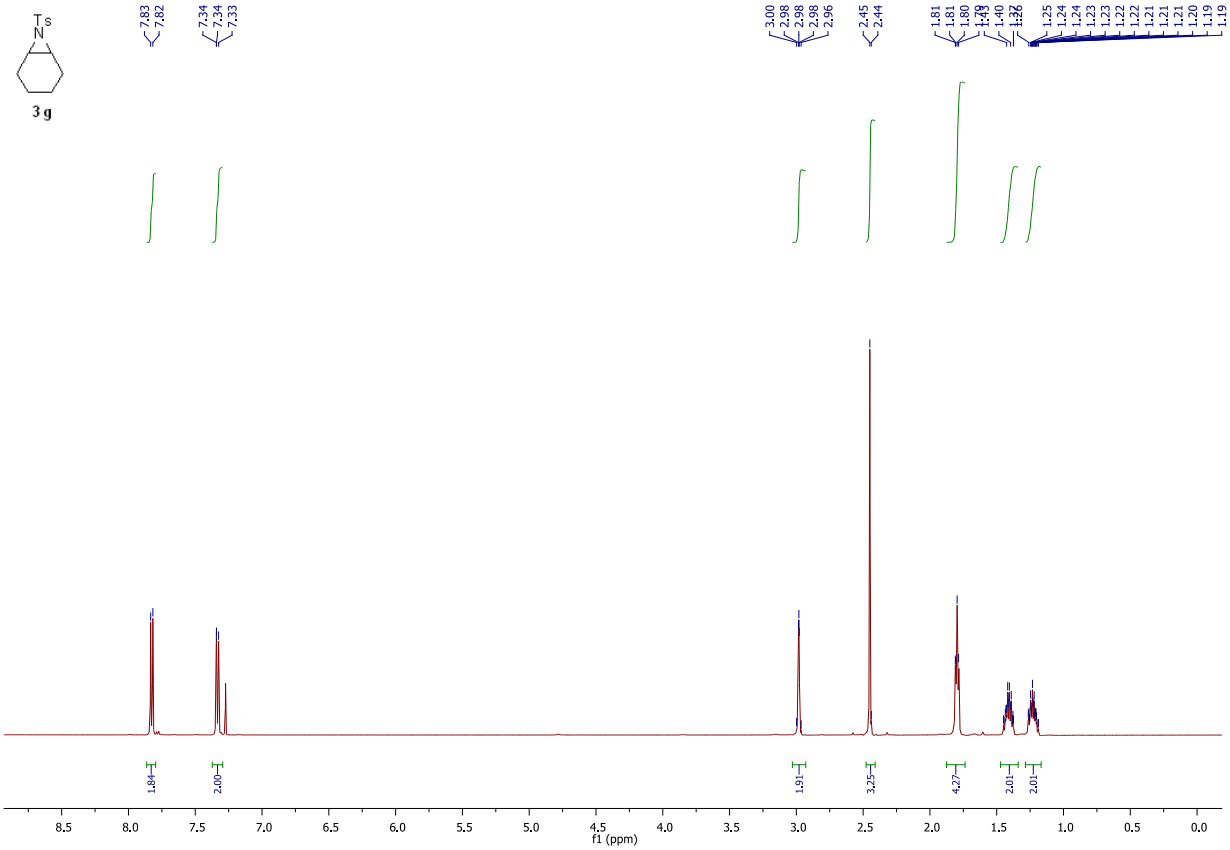
3.75
3.74
3.74
3.00
2.98
2.45
2.36
2.35
1.82
2.04
1.87
2.00
0.91
1.05
3.26
1.06
f1 (ppm)

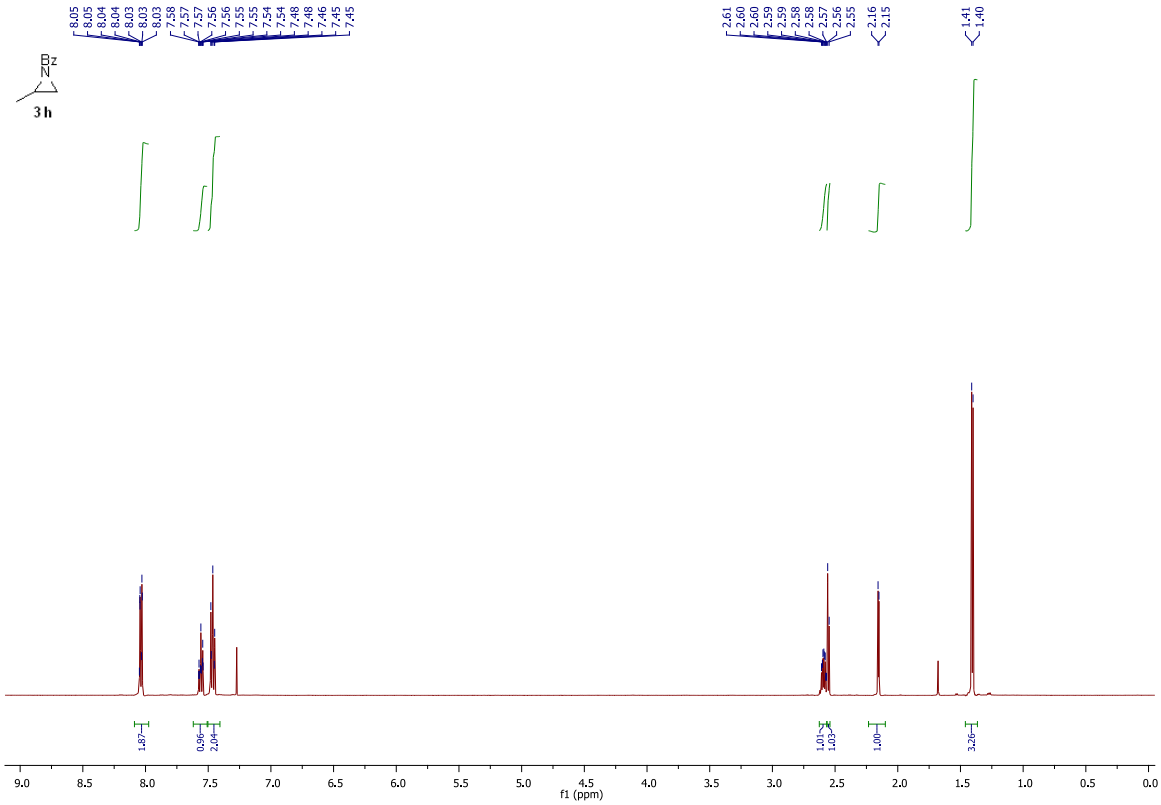

MeO
Ts
N
3c
7.70
7.68
7.24
7.22
6.97
6.95
6.70
6.69
3.78
2.92
2.90
2.79
2.76
2.70
2.63
2.60
2.44
2.16
2.15
1.89
2.07
2.12
2.12
3.30
1.00
1.09
1.12
1.14
3.29
1.15
f1 (ppm)

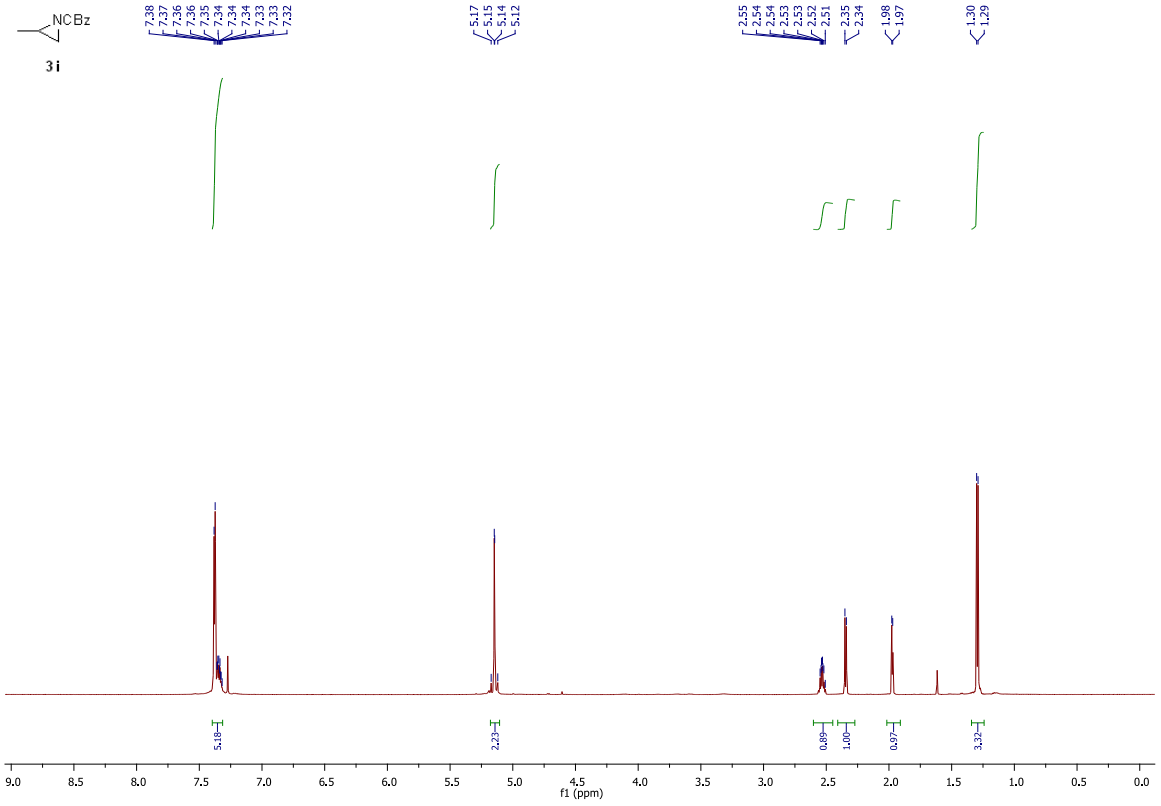

Ts
N
3 d
7.69
7.68
7.22
7.21
7.16
7.16
7.15
7.15
7.14
7.05
7.05
7.04
7.03
2.97
2.96
2.96
2.95
2.94
2.94
2.93
2.83
2.82
2.80
2.79
2.72
2.71
2.70
2.70
2.68
2.67
2.42
2.17
2.16
1.80
2.04
2.79
1.90
0.89
1.00
2.09
3.23
1.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


Ts
N
CH2Br
3e
7.86
7.85
7.37
7.35
3.14
3.13
3.13
3.12
2.46
2.38
2.38
1.61
1.56
2.02
2.15
0.77
1.00
3.02
0.95
5.88
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

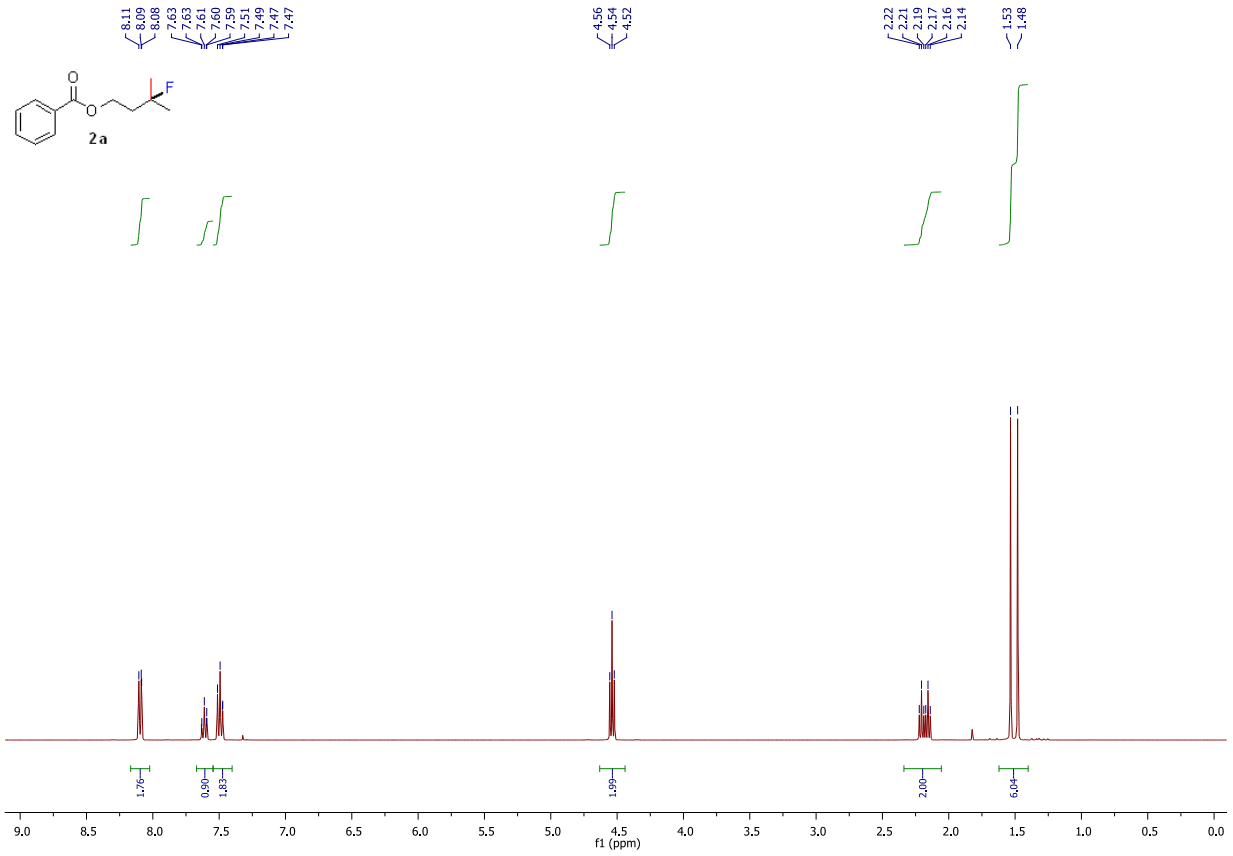

3f
(2:1)
f1 (ppm)

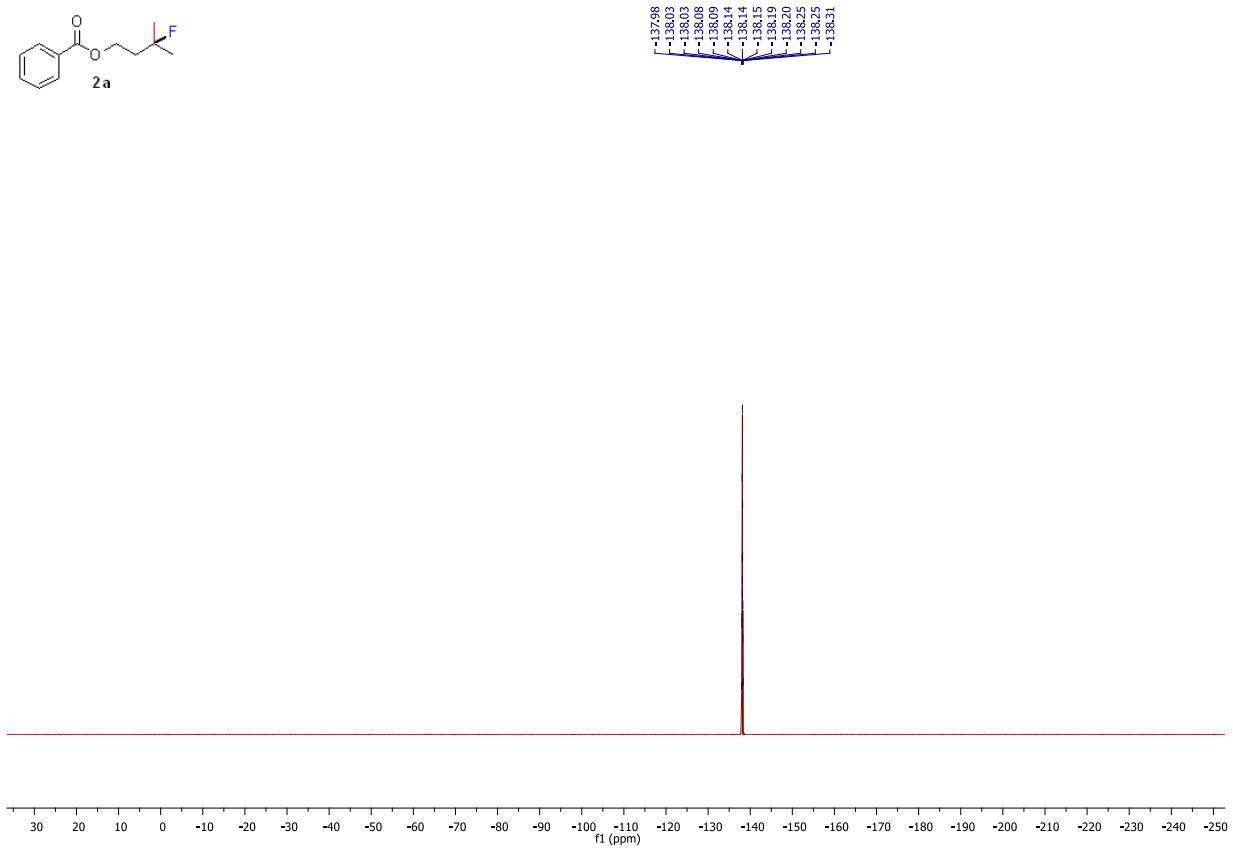

3 g
f1 (ppm)

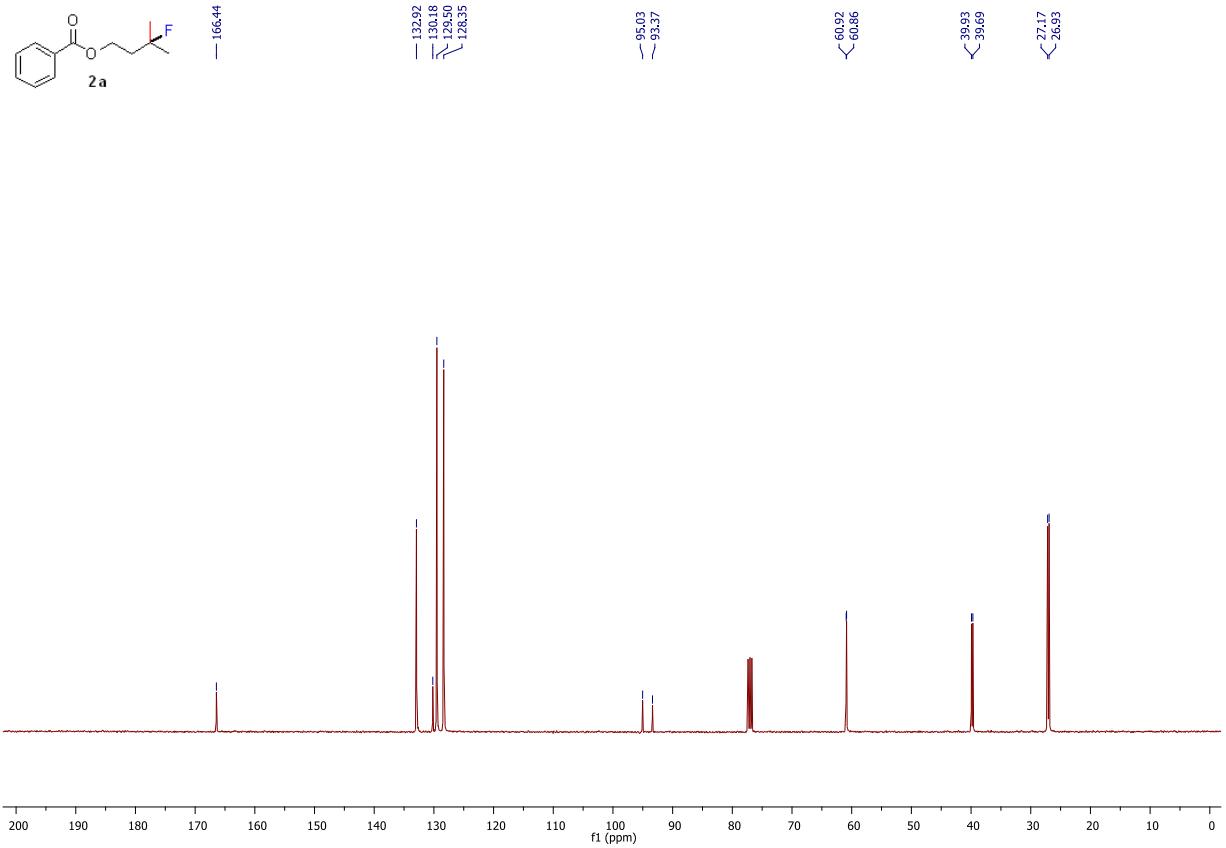


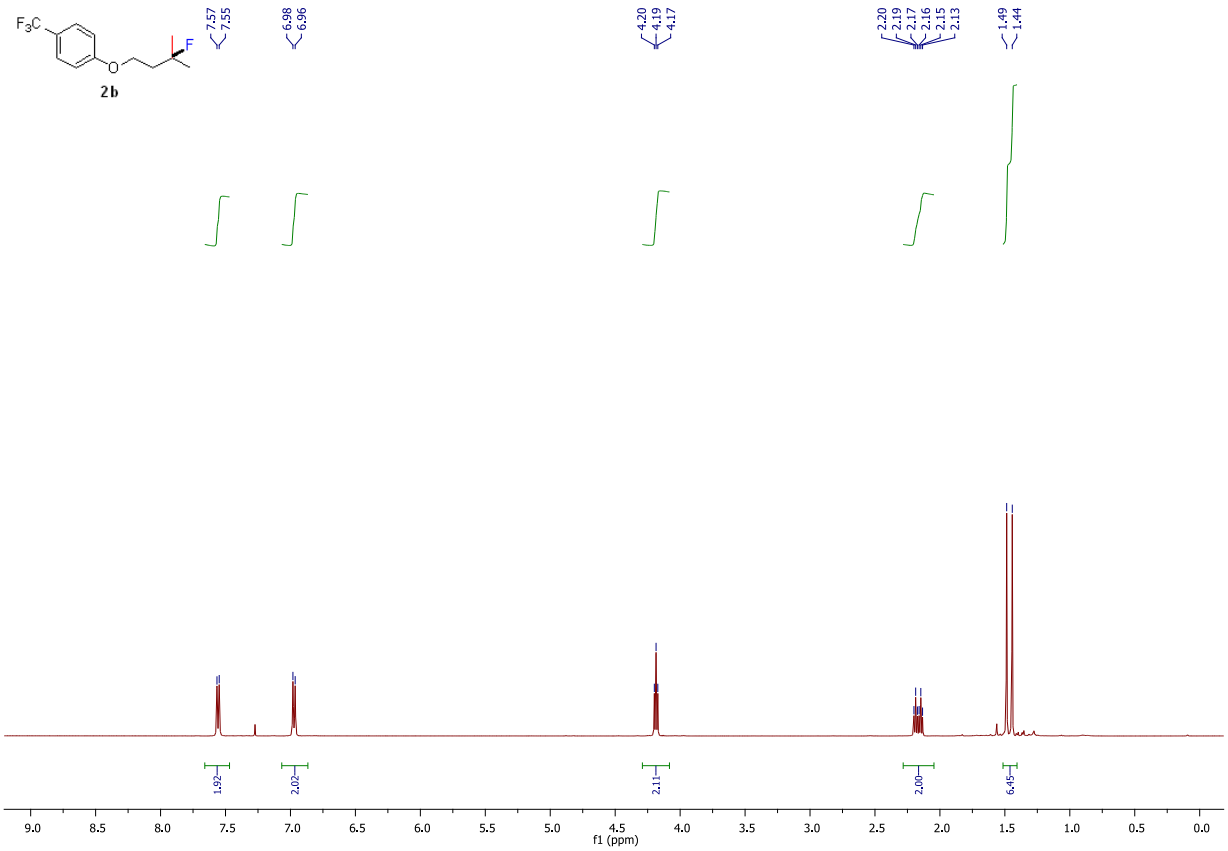


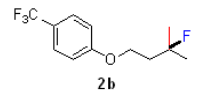
6.2 Products NMR spectra.


8.11
8.09
8.08
7.63
7.63
7.61
7.60
7.59
7.51
7.49
7.47
7.47
4.56
4.54
4.52
2.22
2.21
2.19
2.17
2.16
2.14
1.53
1.48
O
O
F
2a
1.76
0.90
1.83
1.99
2.00
6.04
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

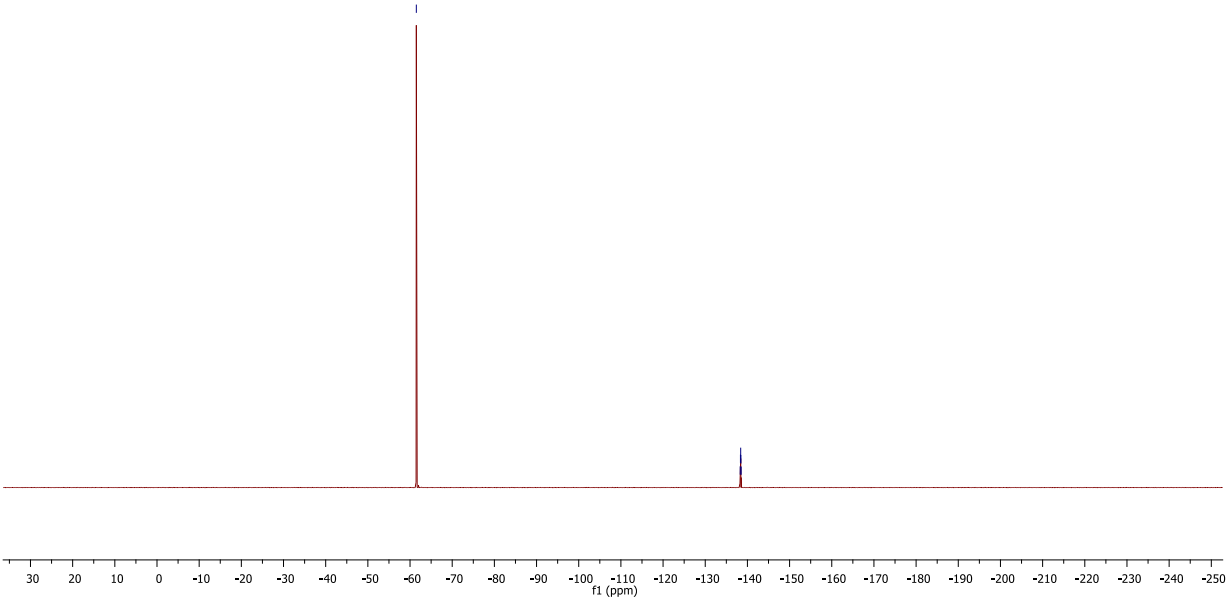

O
O
F
2a
-137.98
-138.03
-138.03
-138.08
-138.09
-138.14
-138.14
-138.15
-138.19
-138.20
-138.25
-138.25
-138.31
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
-220
-230
-240
-250
f1 (ppm)

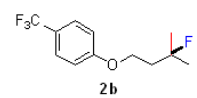

2a
166.44
132.92
130.18
129.50
128.35
95.03
93.37
60.92
60.86
39.93
39.69
27.17
26.93
f1 (ppm)


2b
7.57
7.55
6.98
6.96
4.20
4.19
4.17
2.20
2.19
2.17
2.16
2.15
2.13
1.49
1.44
1.92
2.02
2.11
2.00
6.45
f1 (ppm)


F3C
F
O

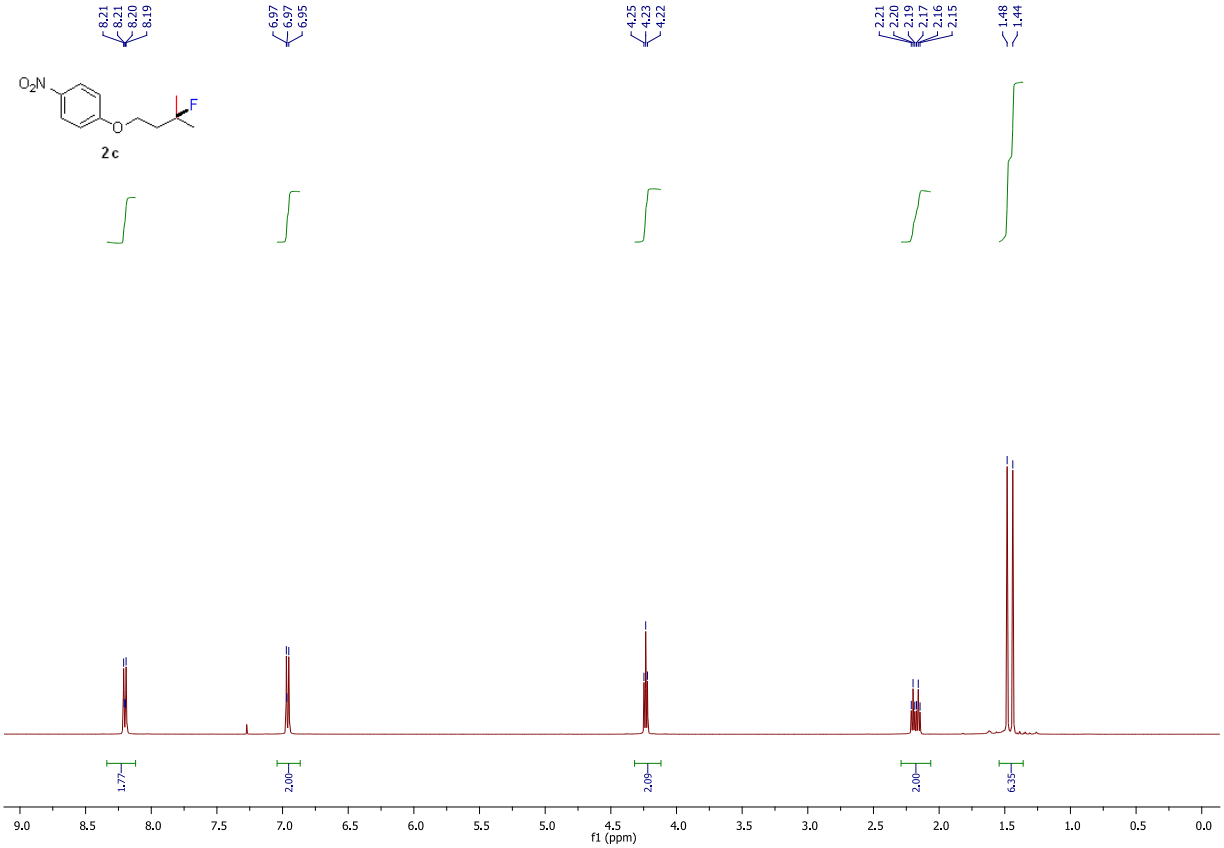
2b

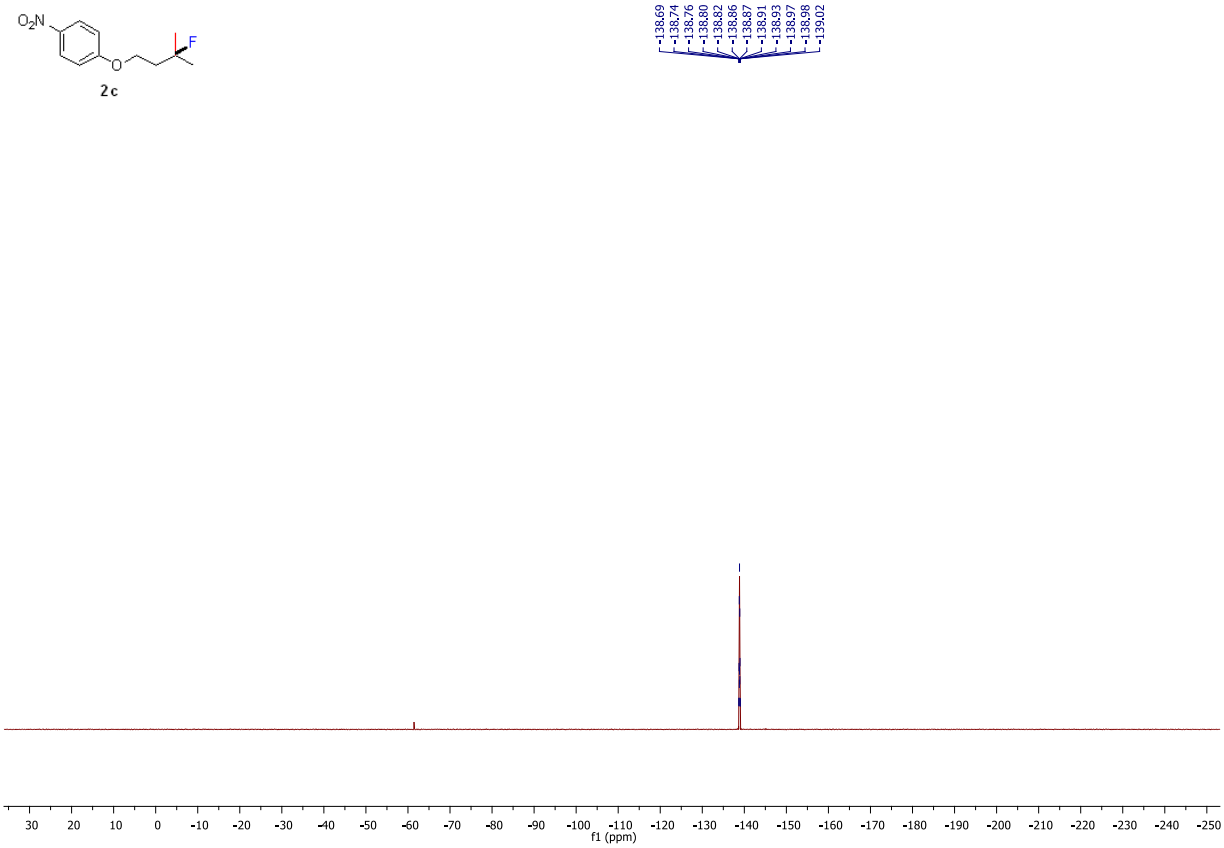

-61.49
-138.29
-138.35
-138.41
-138.46
-138.52
30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240 -250
f1 (ppm)

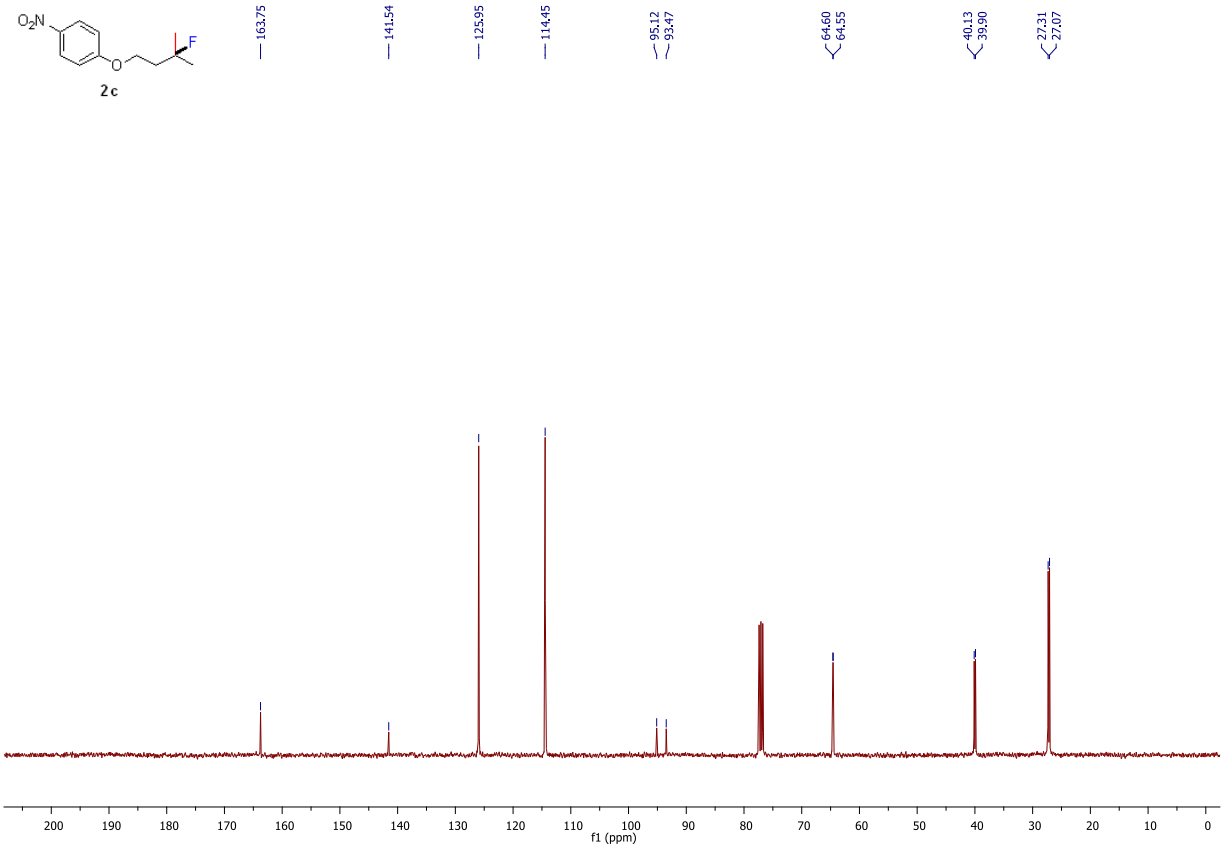

F3C
F
O

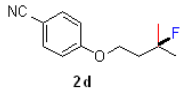
2b

161.11
126.92
126.68
125.78
123.06
122.73
114.41
95.26
93.61
63.91
63.85
40.23
40.01
27.28
27.04
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


8.21
8.21
8.20
8.19
6.97
6.97
6.95
4.25
4.23
4.22
2.21
2.20
2.19
2.17
2.16
2.15
1.48
1.44
O2N
F
O
2c
1.77
2.00
2.09
2.00
6.35
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

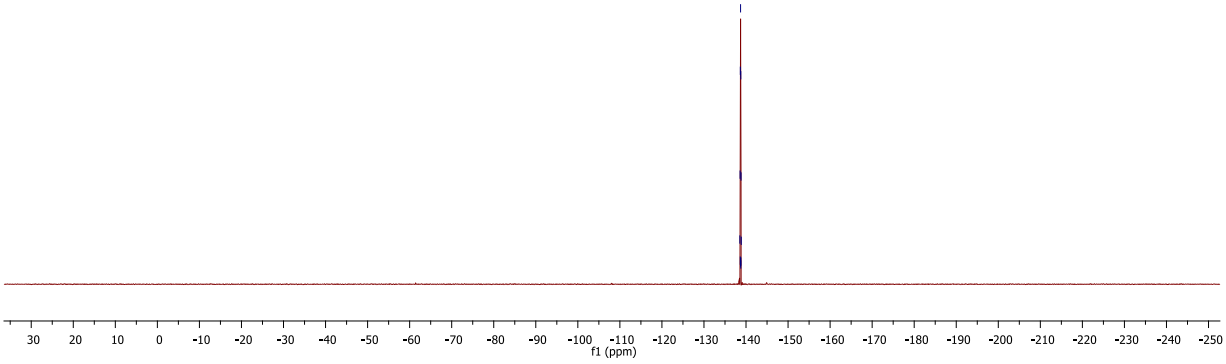

O2N
F
O
2c
-138.69
-138.74
-138.76
-138.80
-138.82
-138.86
-138.87
-138.91
-138.93
-138.97
-138.98
-139.02
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
-220
-230
-240
-250
f1 (ppm)

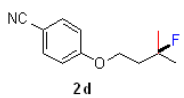

O2N
F
O
2c
163.75
141.54
125.95
114.45
95.12
93.47
64.60
64.55
40.13
39.90
27.31
27.07
f1 (ppm)
7.60
7.59
7.58
7.58
6.96
6.96
6.95
6.95
4.20
4.18
4.17
2.19
2.18
2.16
2.15
2.14
2.12
1.47
1.43
NC
F
O
2d
1.84
2.01
2.08
2.00
6.20
f1 (ppm)


NC
O
F

2d

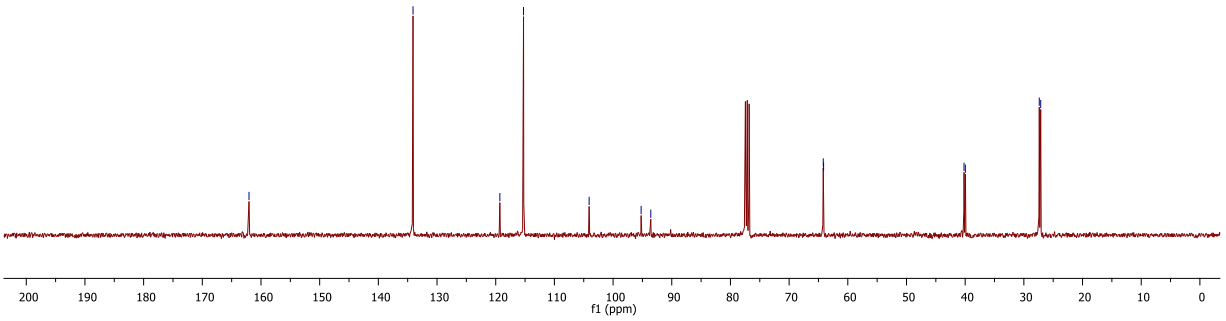

138.54
138.59
138.64
138.65
138.69
138.70
138.75
138.76
138.77
138.81
138.87

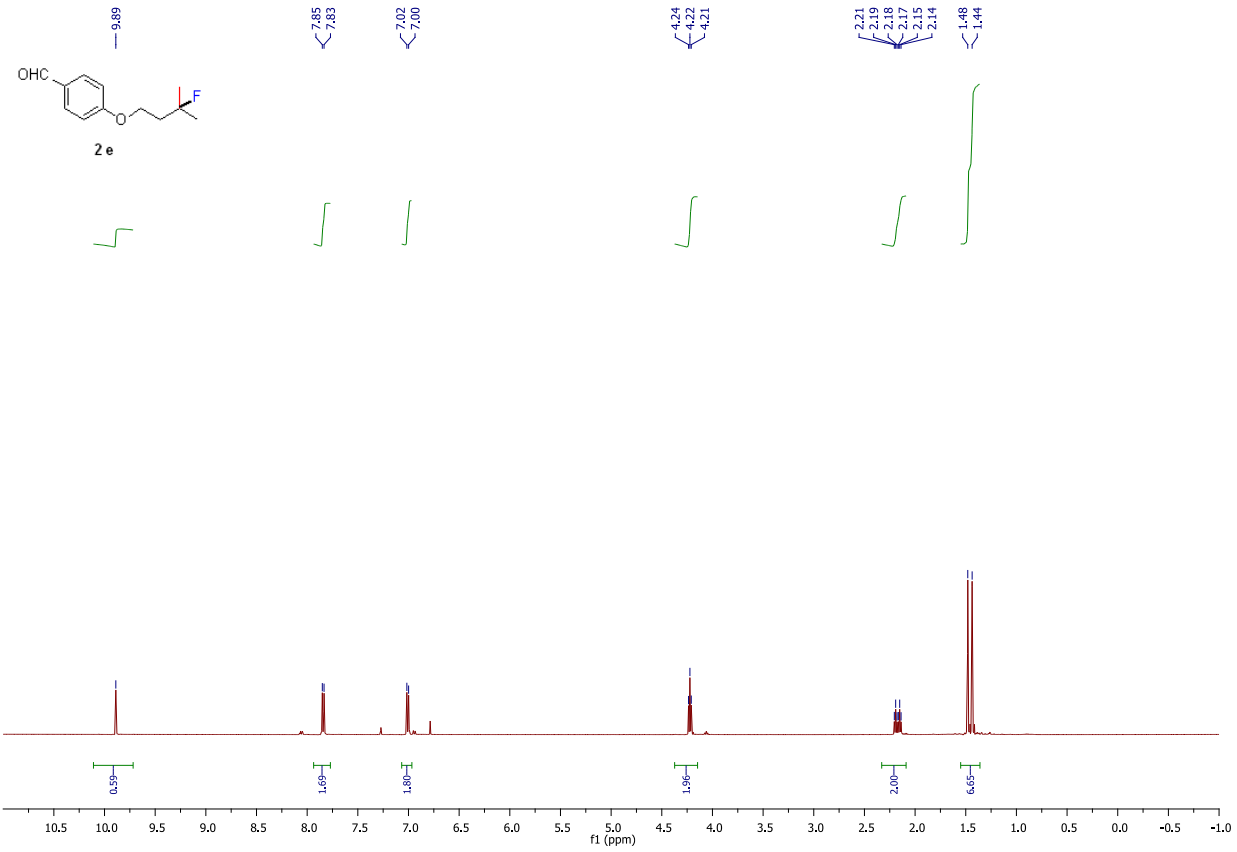

30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240 -250
f1 (ppm)

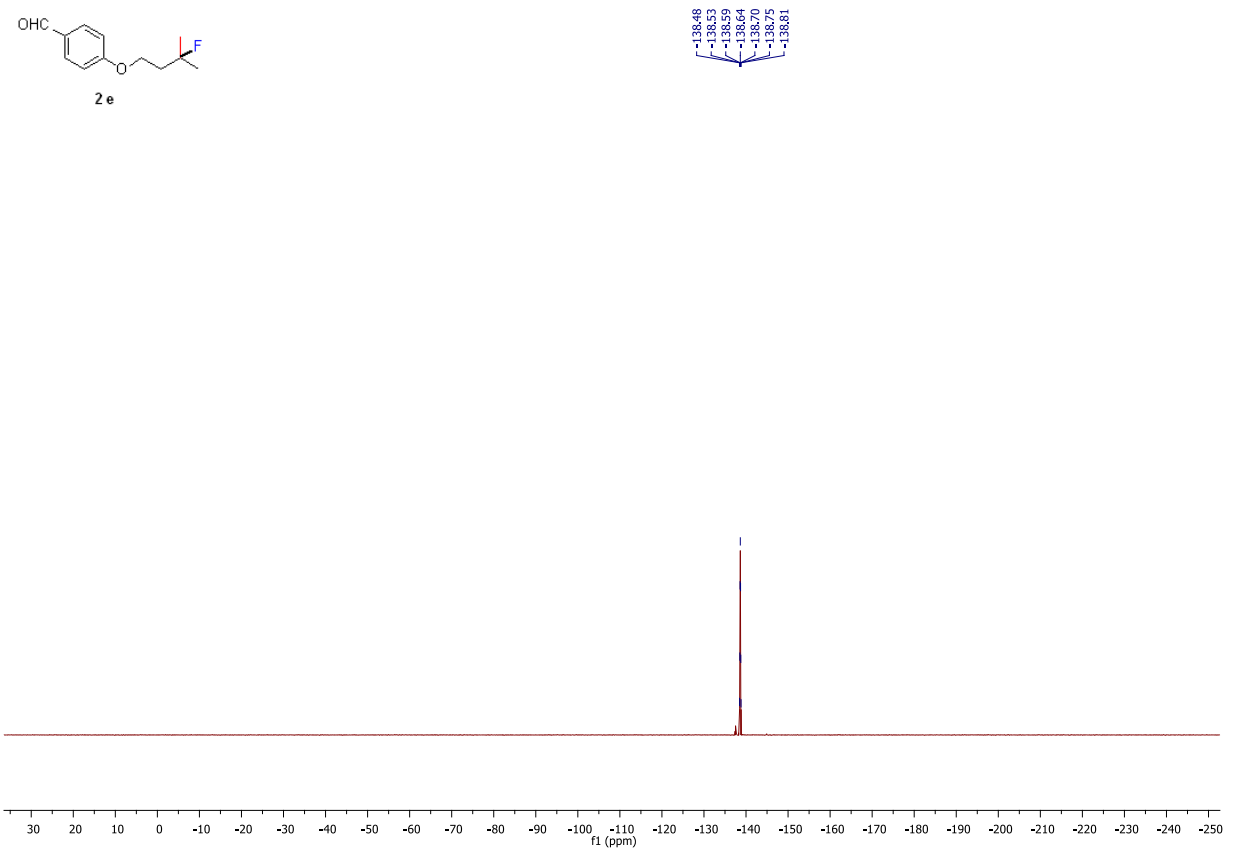

NC
O
F

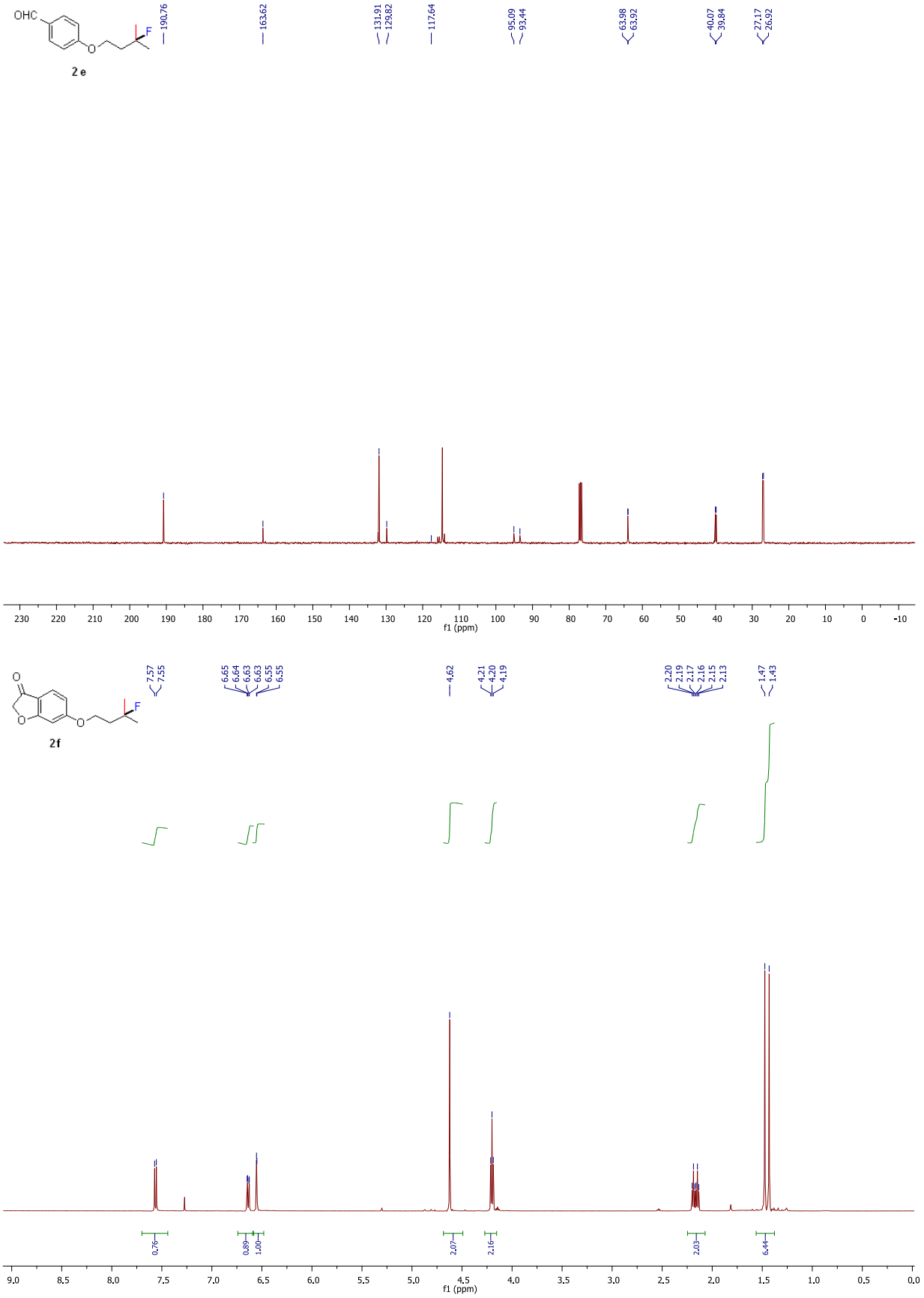
2d

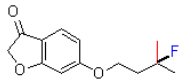

162.04
134.09
119.29
115.26
104.08
95.22
93.57
64.19
64.13
40.20
39.97
27.37
27.13


200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

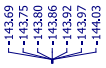

9.89
7.85
7.83
7.02
7.00
4.24
4.22
4.21
2.21
2.19
2.18
2.17
2.15
2.14
1.48
1.44
OHC
F
O
2 e
0.59
1.69
1.80
1.96
2.00
6.65
f1 (ppm)

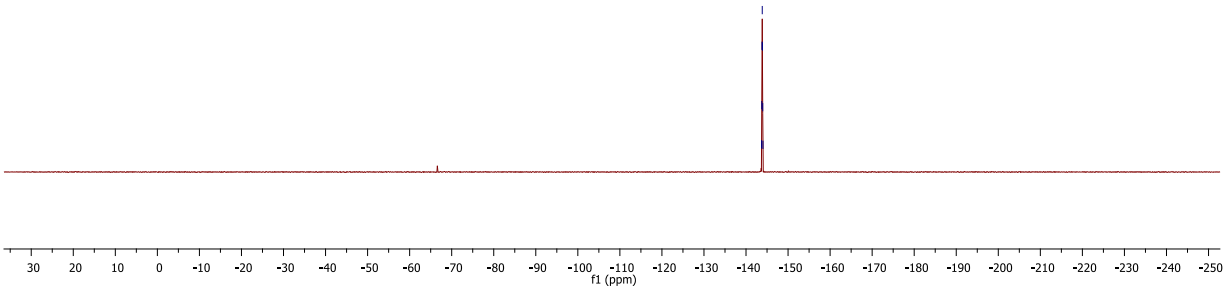

-138.48
-138.53
-138.59
-138.64
-138.70
-138.75
-138.81
OHC
F
O
2 e
f1 (ppm)

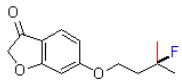

OHC
F
O
2e
190.76
163.62
131.91
129.82
117.64
95.09
93.44
63.98
63.92
40.07
39.84
27.17
26.92
f1 (ppm)
O
O
F
2f
7.57
7.55
6.65
6.64
6.63
6.63
6.55
6.55
4.62
4.21
4.20
4.19
2.20
2.19
2.17
2.16
2.15
2.13
1.47
1.43
0.76
0.89
1.00
2.07
2.16
2.03
6.44
f1 (ppm)



2f

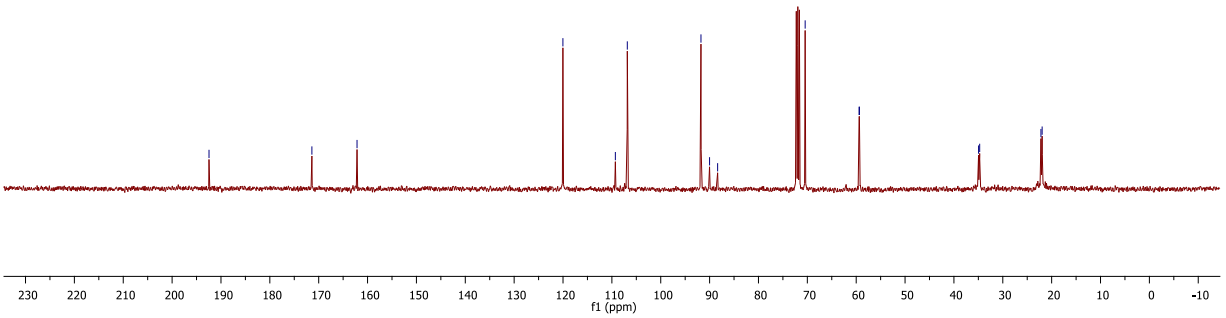

-143.69
-143.75
-143.80
-143.86
-143.92
-143.97
-144.03

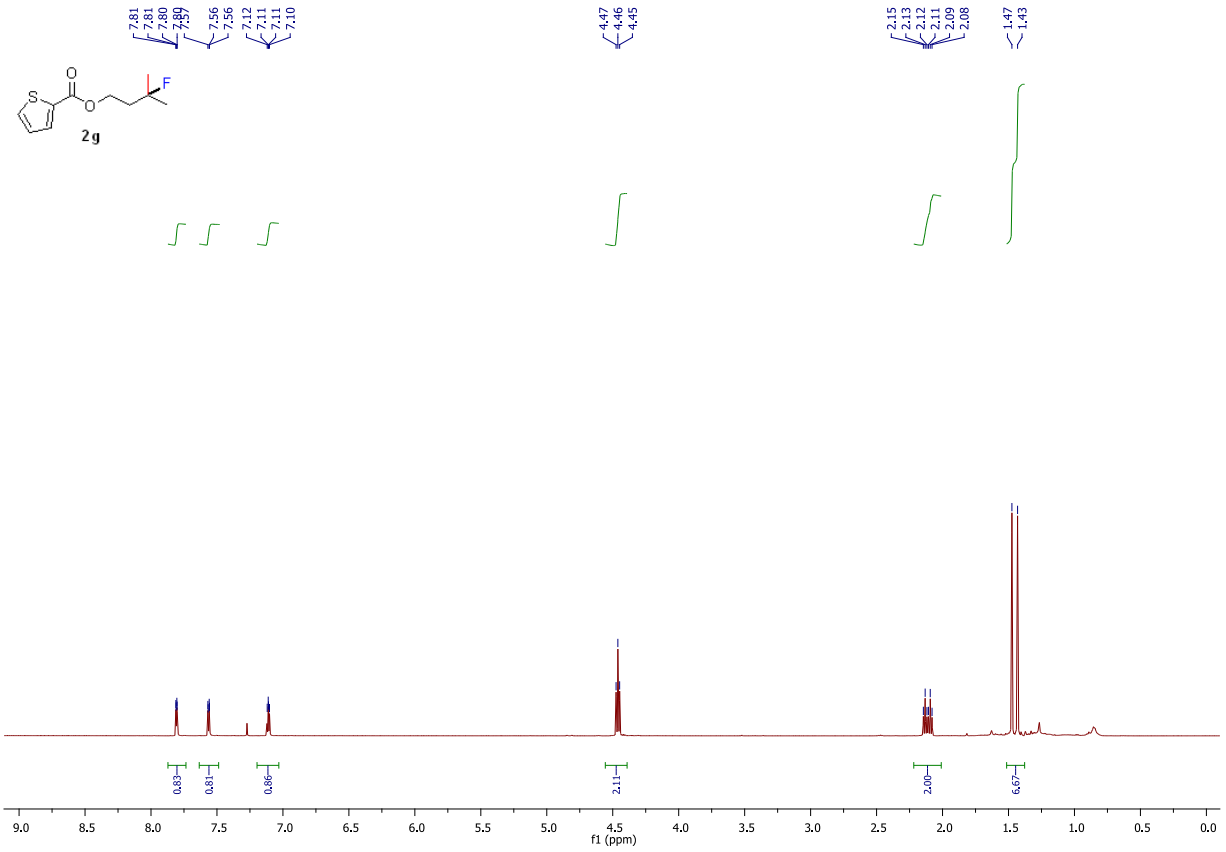

30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240 -250
f1 (ppm)

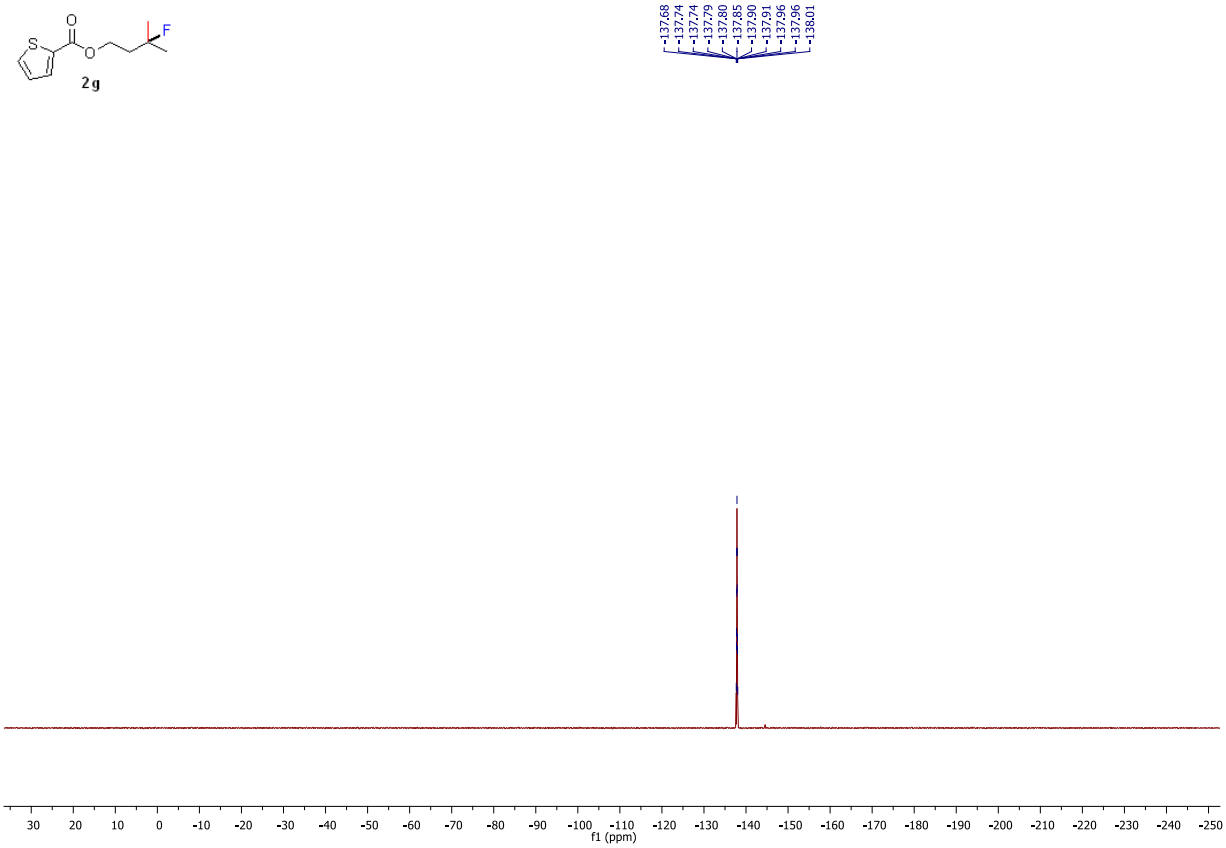


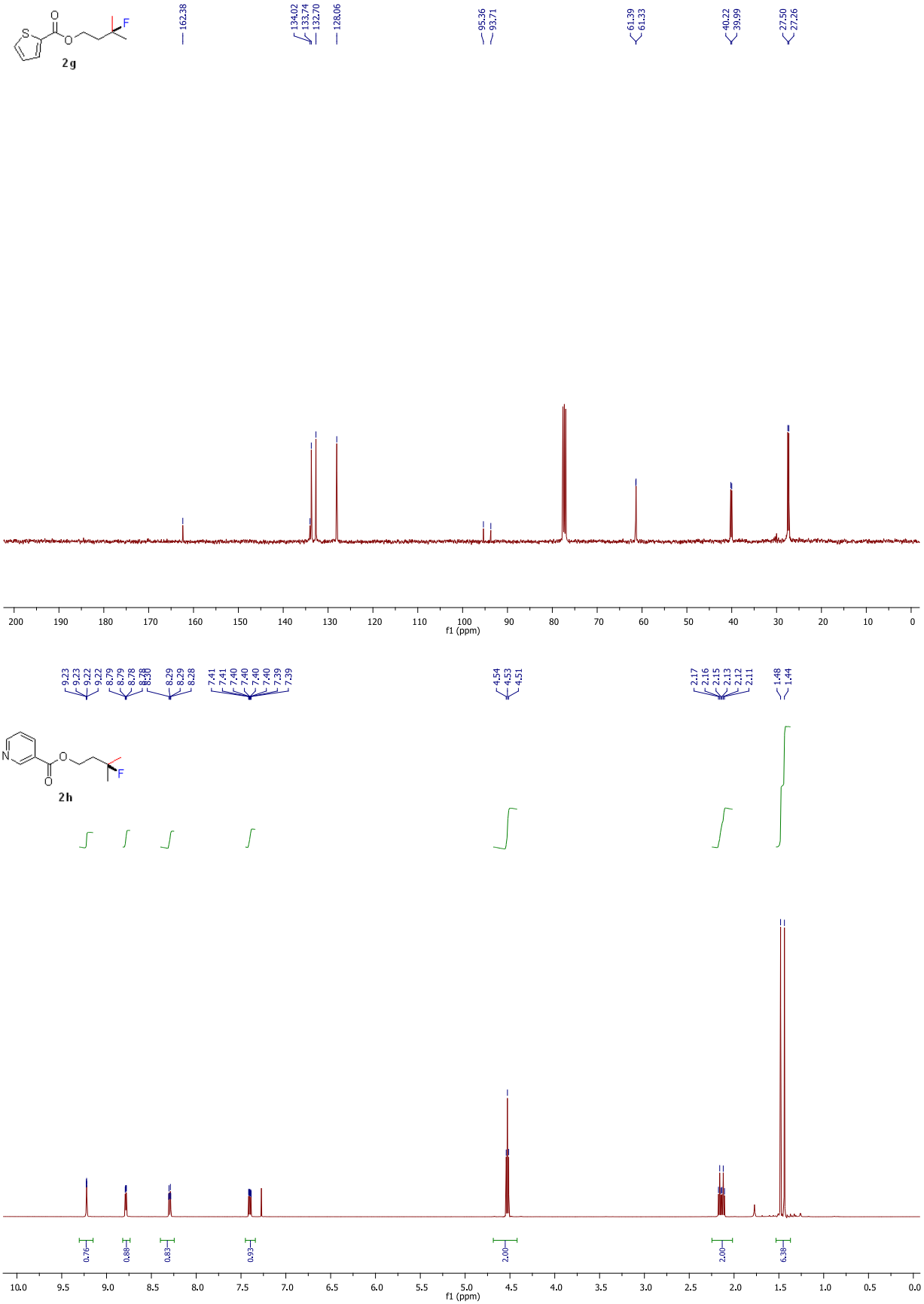
2f

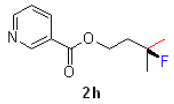

192.45
171.39
162.15
120.02
109.29
106.84
91.77
90.01
88.36
70.44
59.40
59.34
34.96
34.73
22.19
21.95


230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.81
7.81
7.80
7.80
7.57
7.56
7.56
7.12
7.11
7.11
7.10
4.47
4.46
4.45
2.15
2.13
2.12
2.11
2.09
2.08
1.47
1.43
O
S
O
F
2g
0.83
0.81
0.86
2.11
2.00
6.67
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

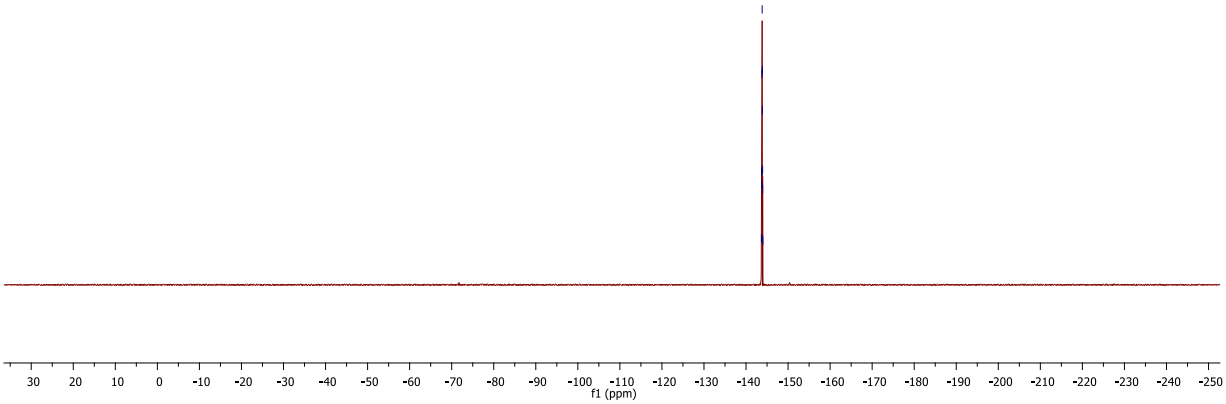

-137.68
-137.74
-137.74
-137.79
-137.80
-137.85
-137.90
-137.91
-137.96
-137.96
-138.01
O
S
O
F
2g
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
-220
-230
-240
-250
f1 (ppm)

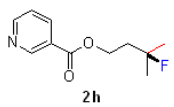

2g
162.38
134.02
133.74
132.70
128.06
95.36
93.71
61.39
61.33
40.22
39.99
27.50
27.26
f1 (ppm)
2h
9.23
9.22
8.79
8.78
8.29
8.28
7.41
7.40
7.39
4.54
4.53
4.51
2.17
2.16
2.15
2.13
2.12
2.11
1.48
1.44
0.76
0.88
0.83
0.93
2.00
2.00
6.38
f1 (ppm)


N
O
O
F

2h

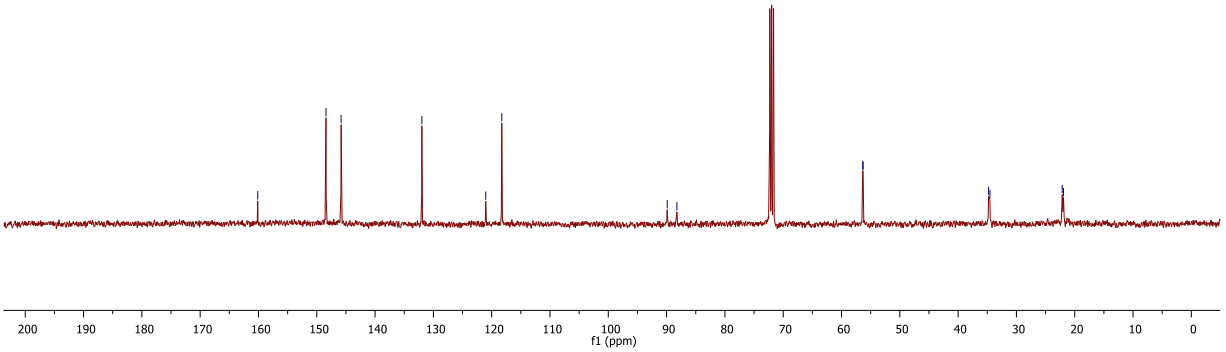

143.67
143.73
143.73
143.78
143.84
143.89
143.89
143.95
143.95
144.00

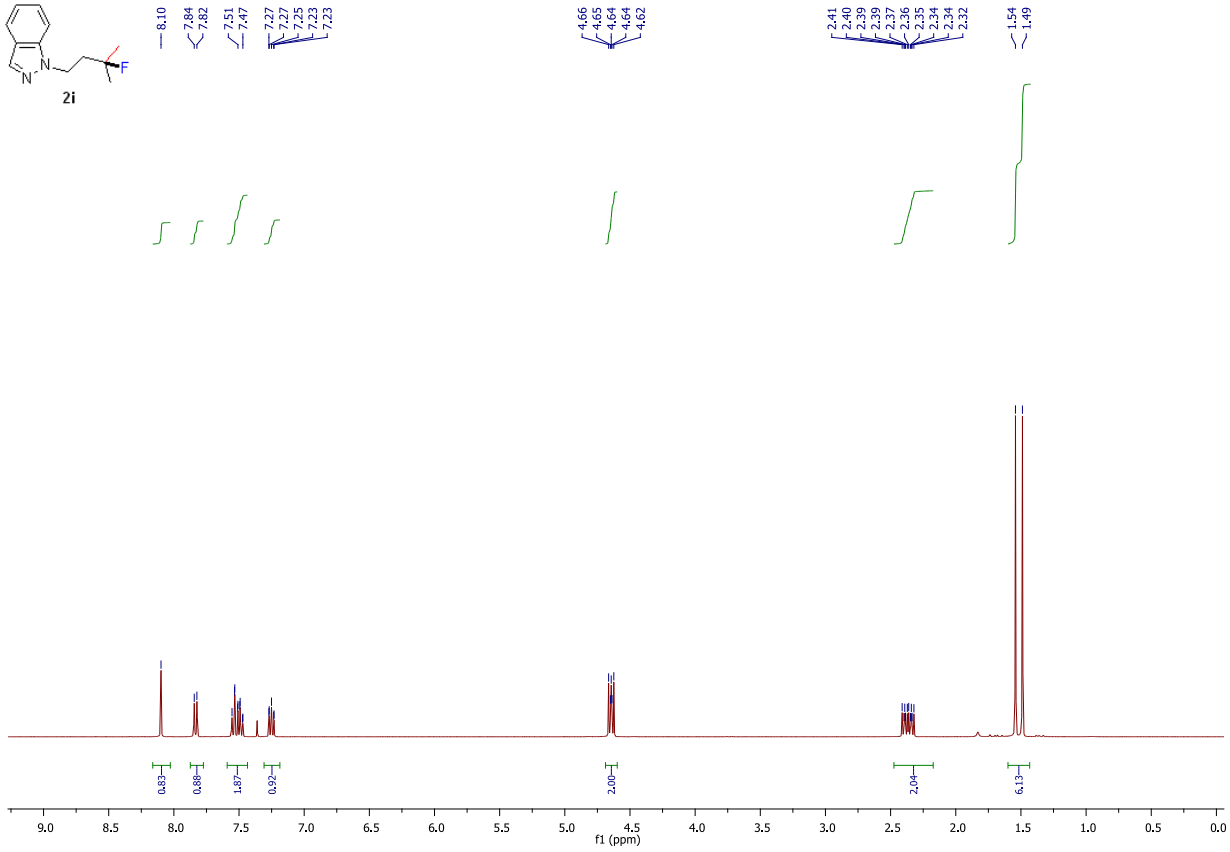

30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240 -250
f1 (ppm)

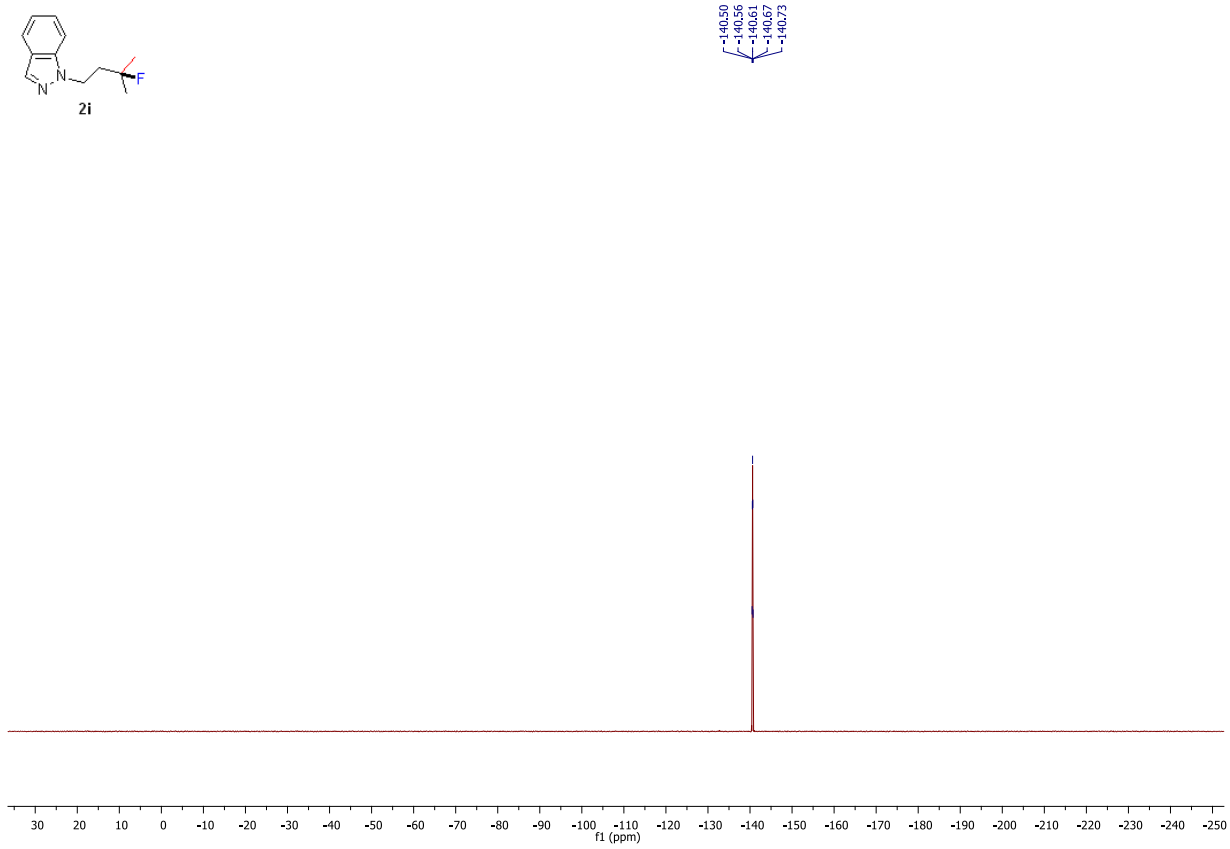

N
O
O
F

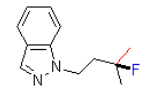
2h


160.13
148.42
145.82
131.97
121.02
118.27
89.89
88.24
56.36
56.30
34.78
34.55
22.14
21.93

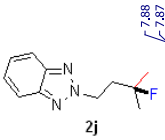

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


2i
8.10
7.84
7.82
7.51
7.47
7.27
7.27
7.25
7.23
7.23
4.66
4.65
4.64
4.64
4.62
2.41
2.40
2.39
2.39
2.37
2.36
2.35
2.34
2.34
2.32
1.54
1.49
0.83
0.88
1.87
0.92
2.00
2.04
6.13
f1 (ppm)

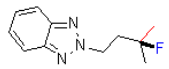

2i
-140.50
-140.56
-140.61
-140.67
-140.73
f1 (ppm)


2i

139.29
133.10
126.35
124.16
121.25
120.63
109.02
95.24
93.59
44.18
44.12
40.75
40.52
27.02
26.78
f1 (ppm)

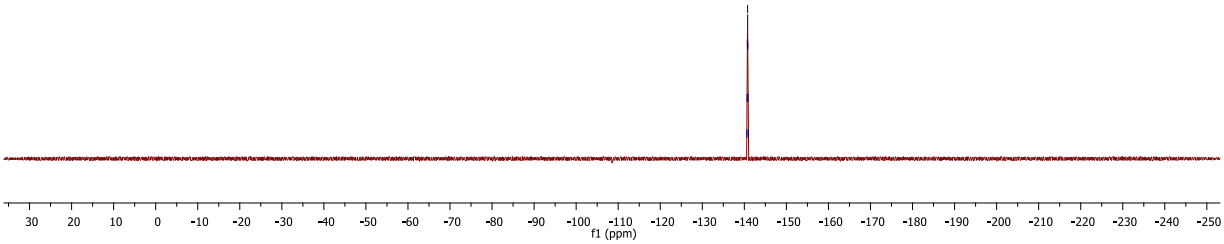

2j

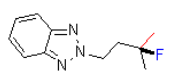
7.88
7.87
7.87
7.86
7.41
7.40
7.39
7.39
4.92
4.91
4.91
4.90
4.89
2.54
2.53
2.53
2.52
2.51
2.50
2.49
2.49
2.48
2.47
1.58
1.46
1.42
1.70
1.92
2.09
2.00
6.55
f1 (ppm)



2j

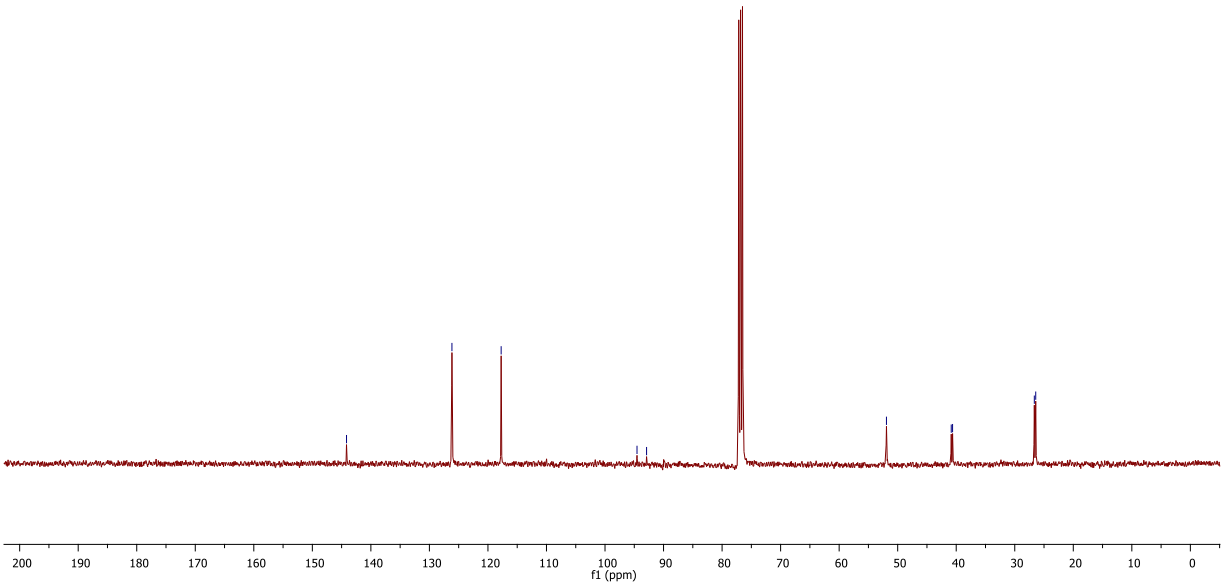

140.61
140.66
140.72
140.77
140.83
140.88
140.94

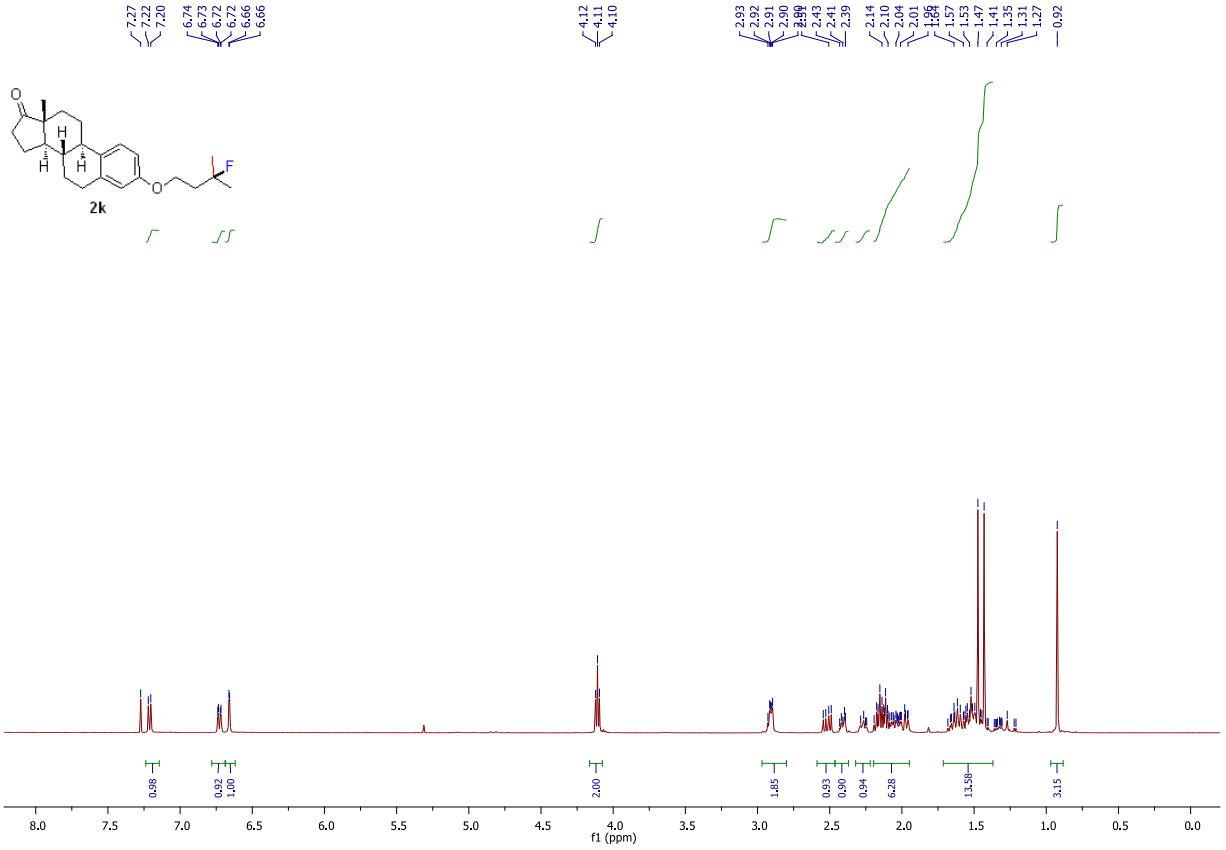

30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240 -250
f1 (ppm)

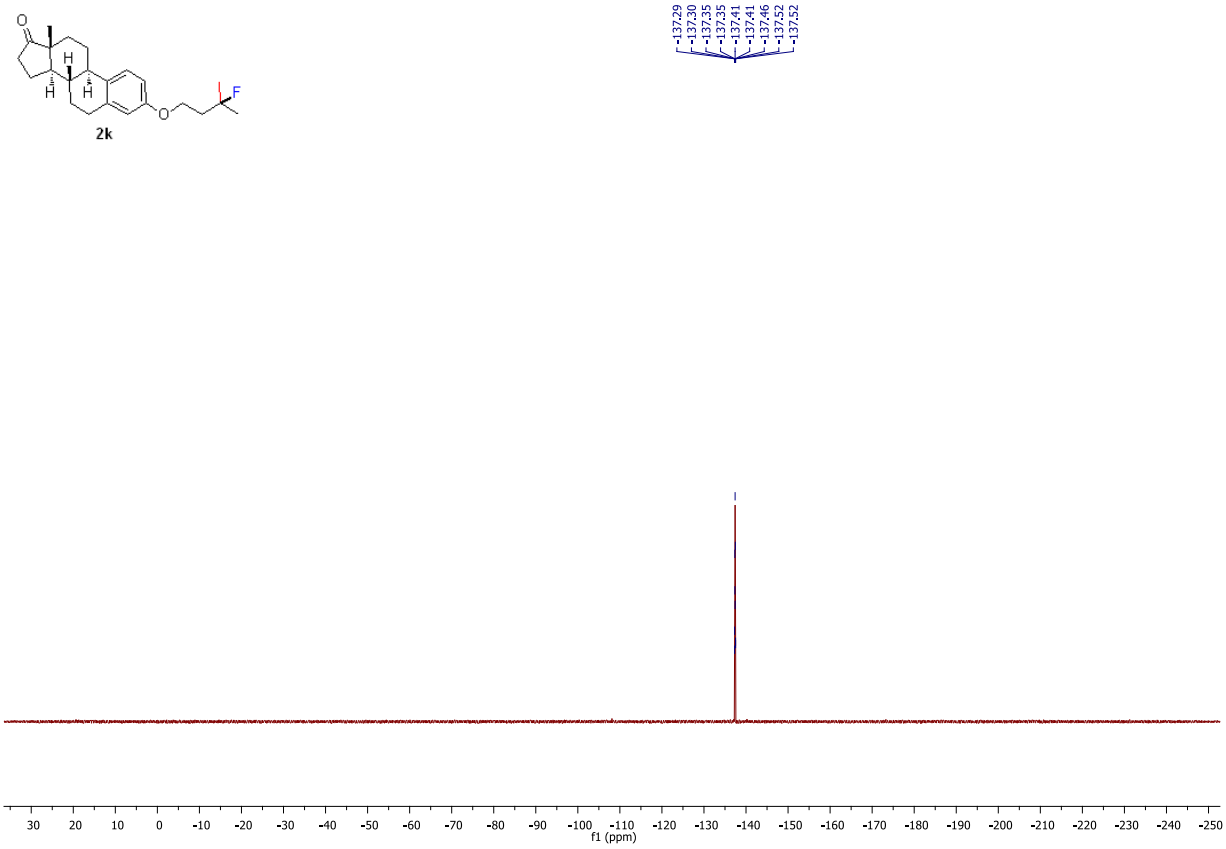


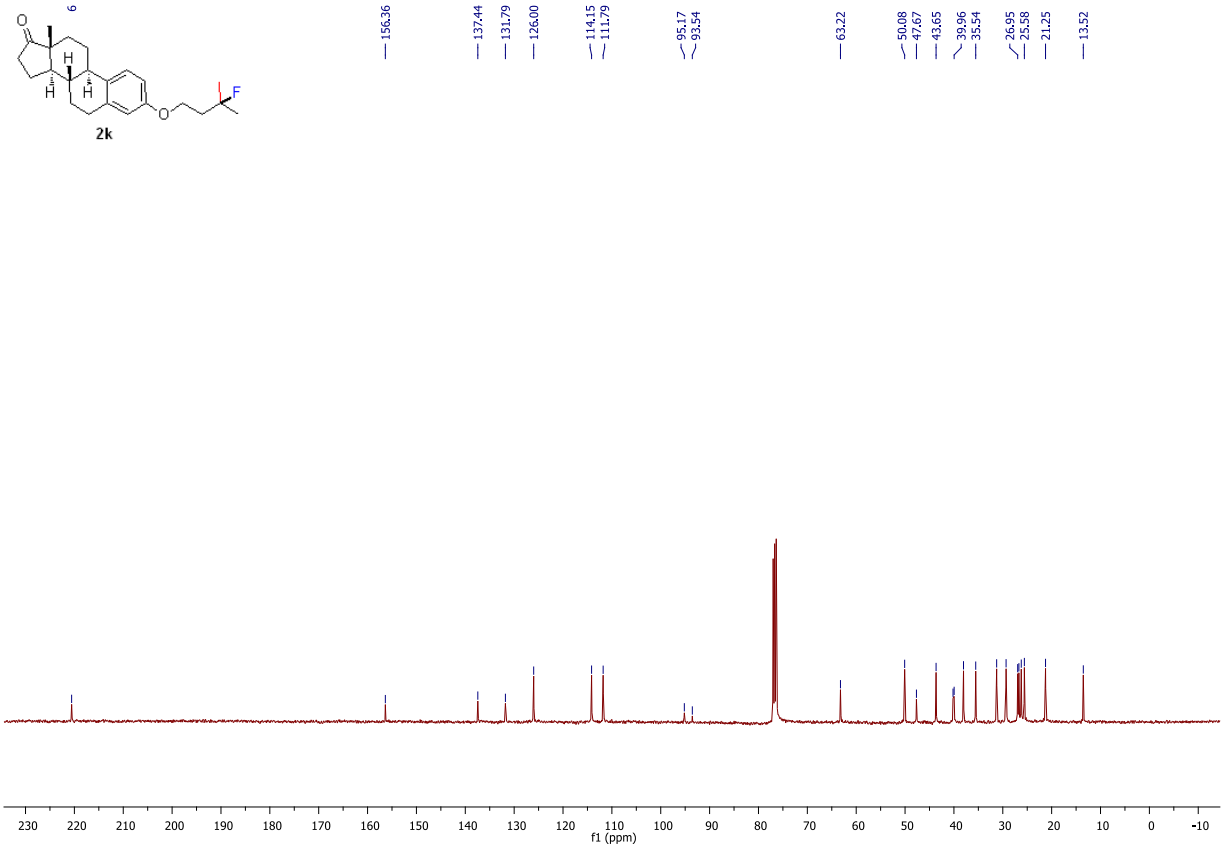
2j

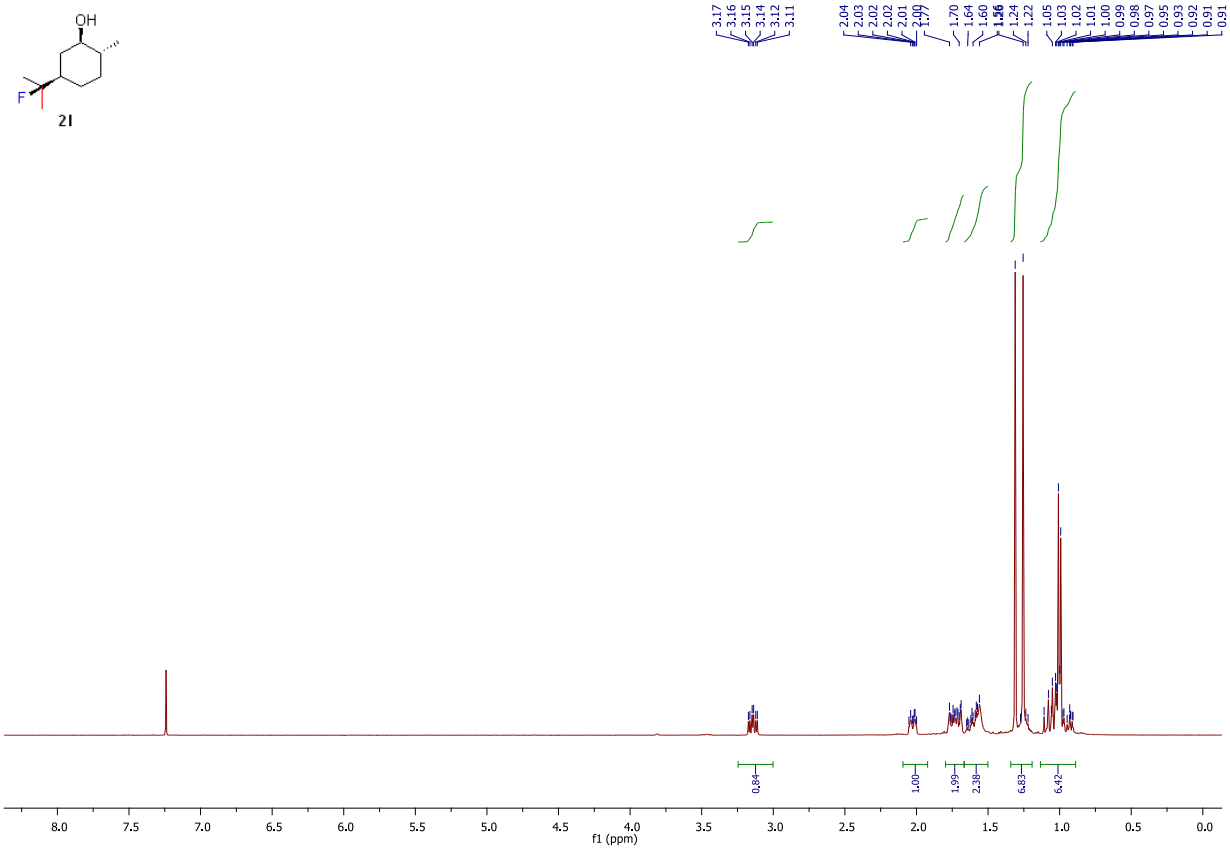

144.16
126.15
117.74
94.53
92.90
51.92
40.85
40.62
26.66
26.42

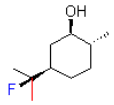

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.27
7.22
7.20
6.74
6.73
6.72
6.72
6.66
6.66
4.12
4.11
4.10
2.93
2.92
2.91
2.90
2.43
2.41
2.39
2.14
2.10
2.04
2.01
1.57
1.53
1.47
1.41
1.35
1.31
1.27
0.92
O
H
H
H
F
O
2k
0.98
0.92
1.00
2.00
1.85
0.93
0.90
0.94
6.28
13.58
3.15
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


-137.29
-137.30
-137.35
-137.35
-137.41
-137.41
-137.46
-137.52
-137.52
O
H
H
H
F
O
2k
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
-220
-230
-240
-250
f1 (ppm)

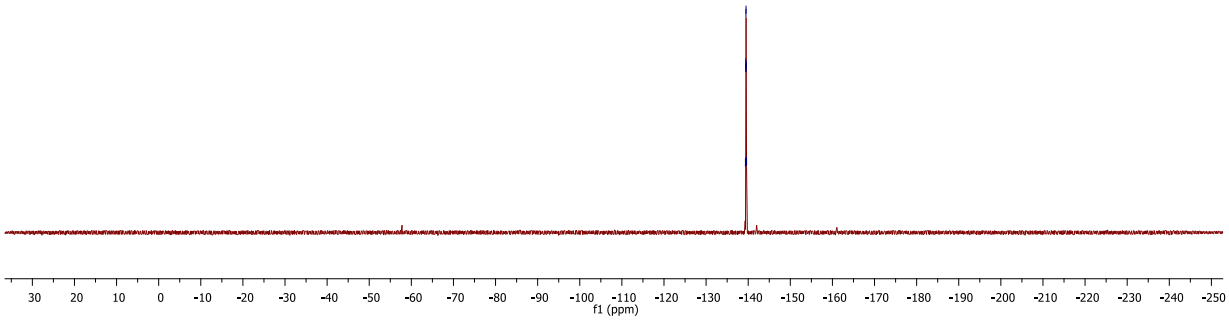

2k
156.36
137.44
131.79
126.00
114.15
111.79
95.17
93.54
63.22
50.08
47.67
43.65
39.96
35.54
26.95
25.58
21.25
13.52
f1 (ppm)

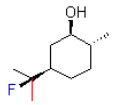

2l
3.17
3.16
3.15
3.14
3.12
3.11
2.04
2.03
2.02
2.02
2.01
2.00
1.77
1.70
1.64
1.60
1.24
1.22
1.05
1.03
1.02
1.01
1.00
0.99
0.98
0.97
0.95
0.93
0.92
0.91
0.91
0.84
1.00
1.99
2.38
6.83
6.42
f1 (ppm)


OH
F

2l

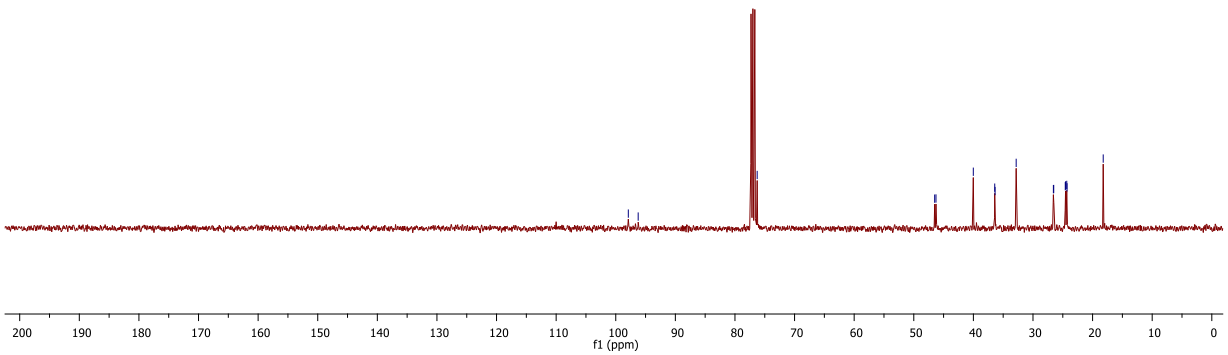

139.34
139.37
139.40
139.43
139.46
139.49
139.52
139.55
139.58
139.61

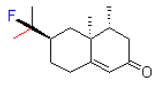

30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240 -250
f1 (ppm)


OH
F

2l

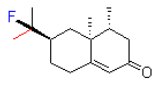

97.89
96.24
76.27
46.50
46.28
40.01
36.36
32.82
24.58
24.54
24.33
24.29
18.22


200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


F
O

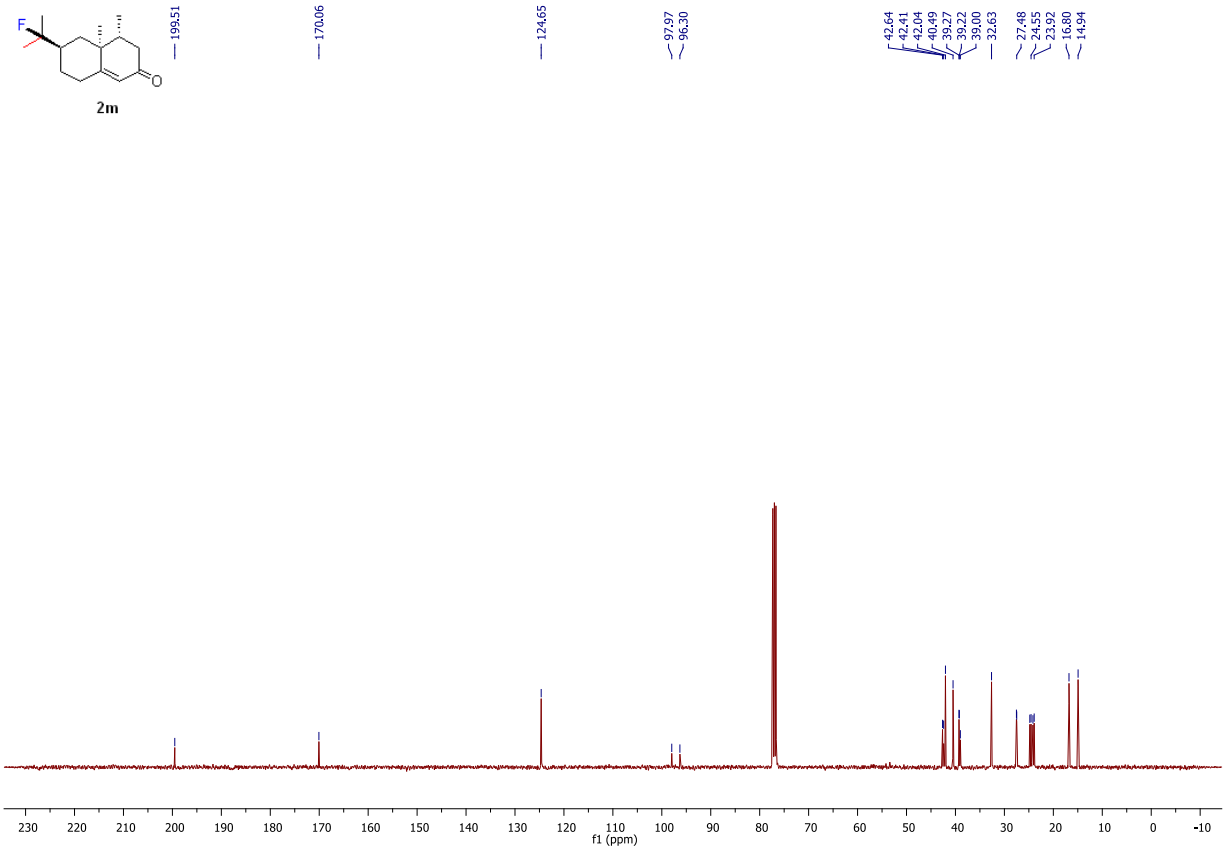
2m

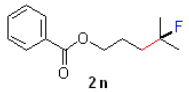
5.76
2.52
2.51
2.49
2.48
2.45
2.44
2.40
2.36
2.33
2.30
2.29
2.26
2.24
2.21
2.20
2.00
1.94
1.91
1.36
1.33
1.30
1.28
1.25
1.23
1.22
1.19
1.18
1.16
1.15
1.09
1.04
1.00
0.98
0.97
0.96
1.05
1.06
2.00
4.20
6.28
1.25
3.09
0.93
3.29
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


F
O

2m

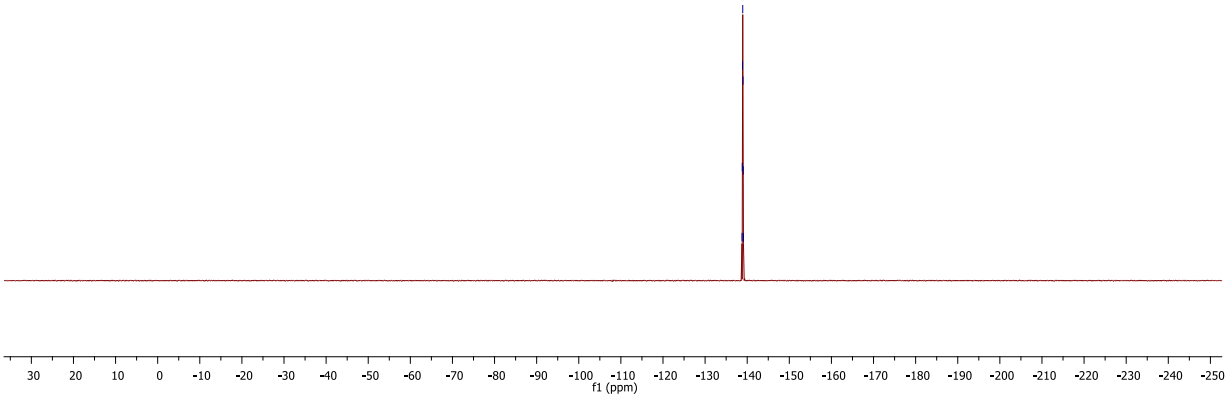
139.28
139.31
139.34
139.37
139.40
139.43
139.46
139.49
139.52
139.55
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
-220
-230
-240
-250
f1 (ppm)

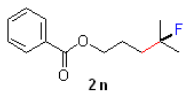

F
O
2m
199.51
170.06
124.65
97.97
96.30
42.64
42.41
42.04
40.49
39.27
39.22
39.00
32.63
27.48
24.55
23.92
16.80
14.94
f1 (ppm)
7.96
7.96
7.94
7.94
7.48
7.46
7.45
7.44
7.37
7.35
7.33
4.27
4.25
4.23
1.81
1.78
1.78
1.77
1.71
1.70
1.69
1.68
1.66
1.66
1.65
1.64
1.63
1.62
1.31
1.26
F
O
O
2n
1.79
0.92
1.85
2.00
2.02
2.11
6.02
f1 (ppm)


F
O
O

2n

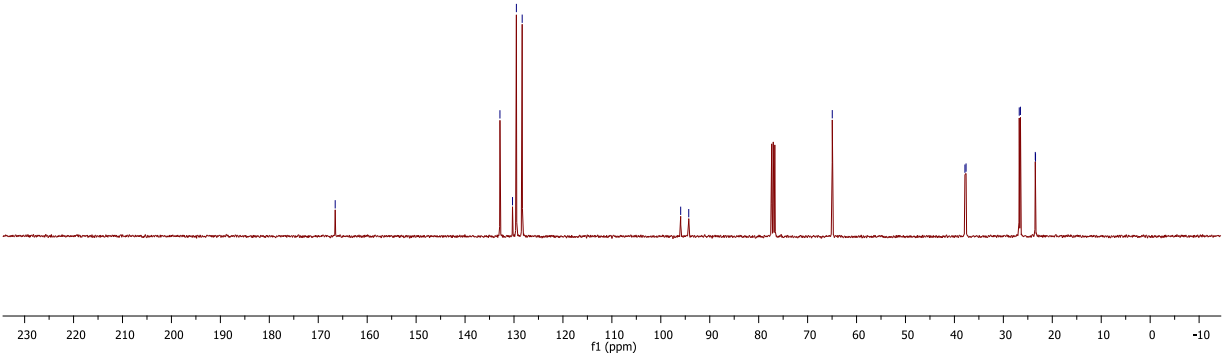

138.78
138.83
138.89
138.94
139.00
139.05
139.11

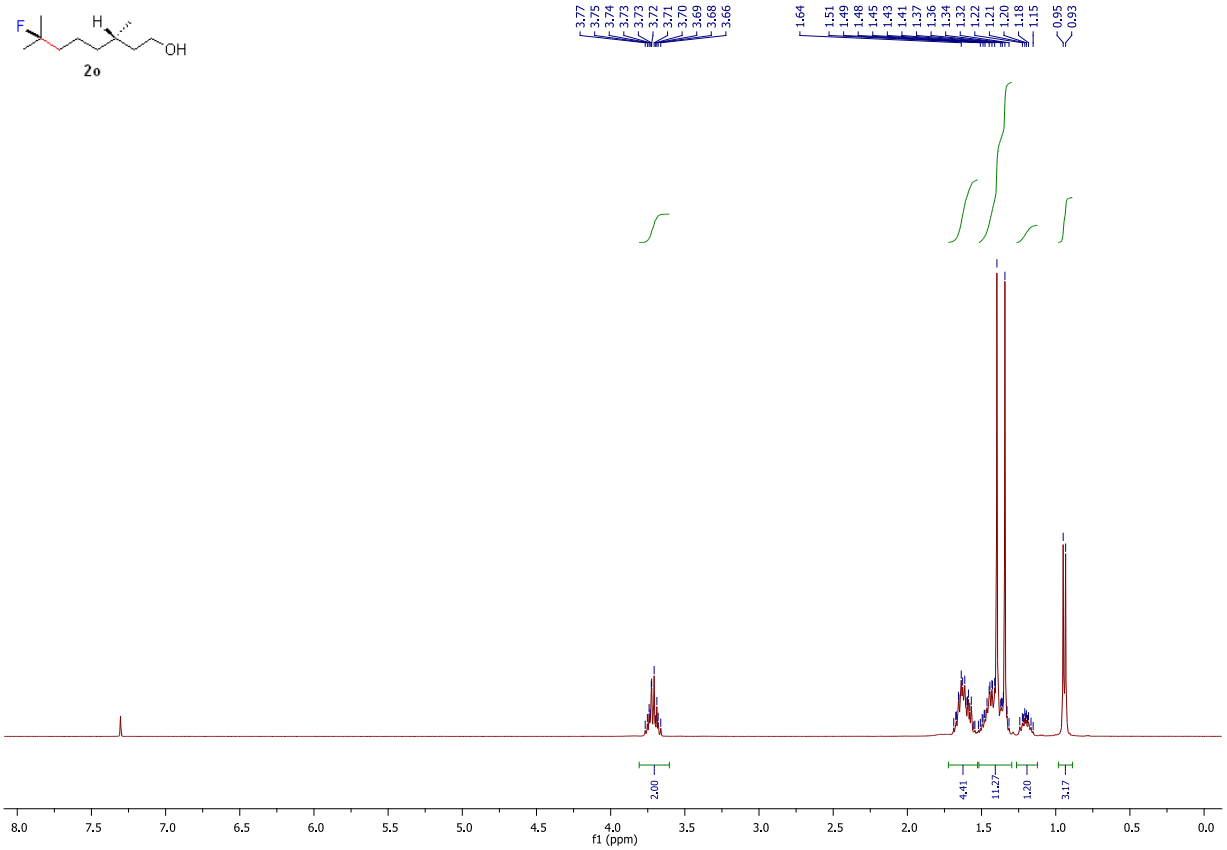

30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240 -250
f1 (ppm)

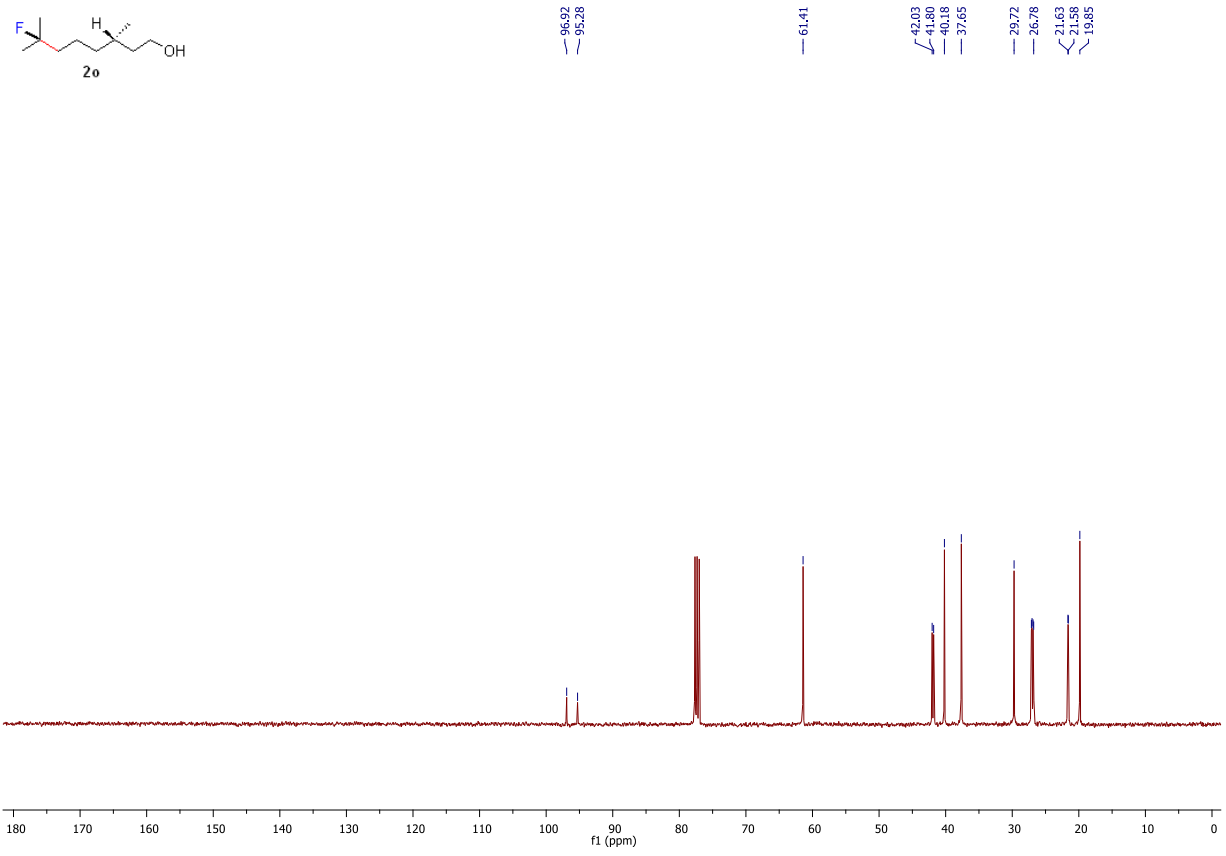

F
O
O

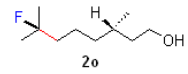
2n


166.54
132.87
130.30
129.51
128.33
95.94
94.29
64.96
37.85
37.62
26.75
26.51
23.47
23.43


230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

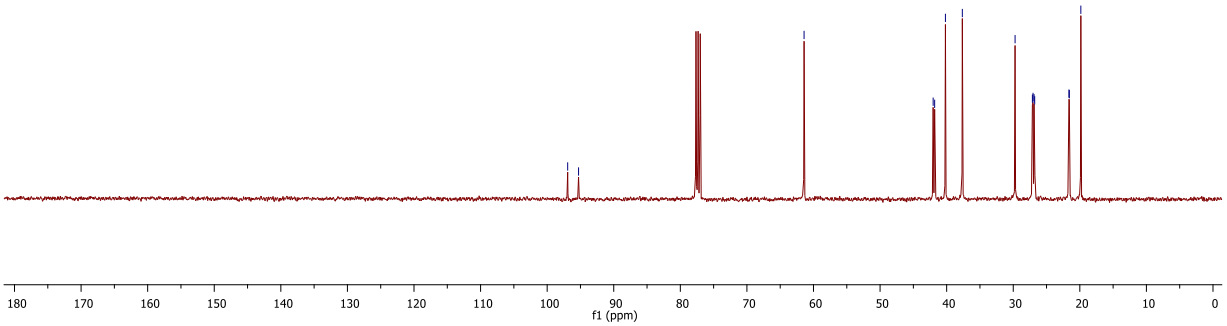

F
H
OH
2o
3.77
3.75
3.74
3.73
3.73
3.72
3.71
3.70
3.69
3.68
3.66
1.64
1.51
1.49
1.48
1.45
1.43
1.41
1.37
1.36
1.34
1.32
1.22
1.21
1.20
1.18
1.15
0.95
0.93
2.00
4.41
11.27
1.20
3.17
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

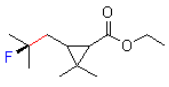

F
H
OH
2o
96.92
95.28
61.41
42.03
41.80
40.18
37.65
29.72
26.78
21.63
21.58
19.85
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


F
H
OH

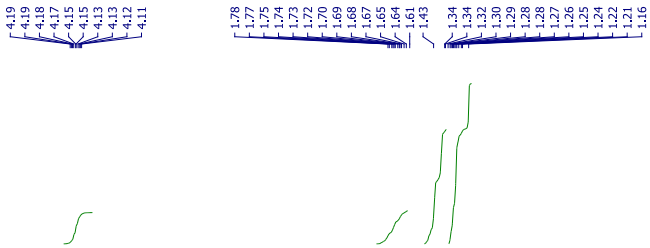
2o

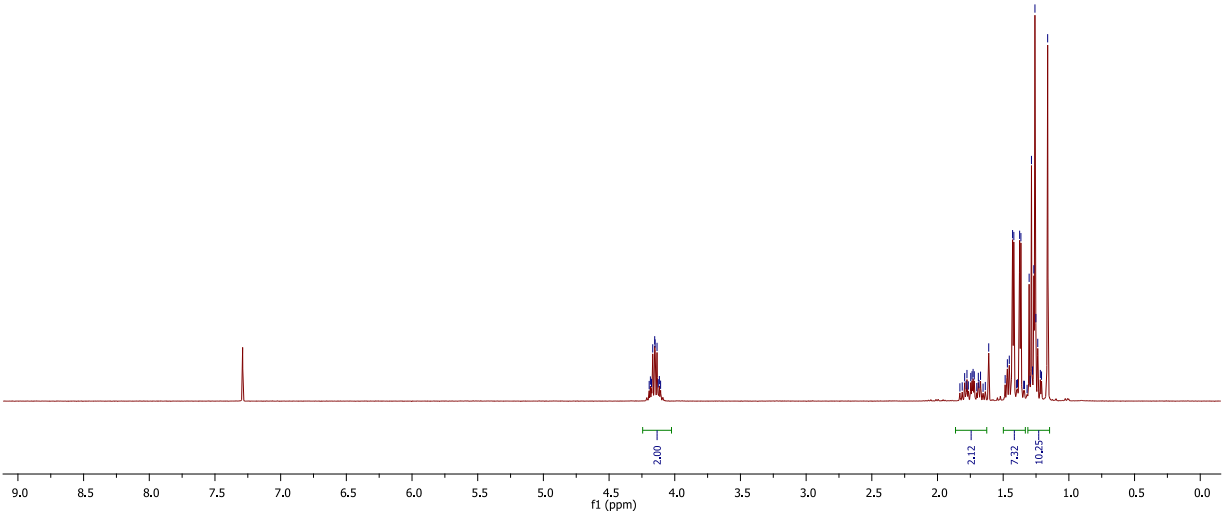

96.92
95.28
61.41
42.03
41.80
40.18
37.65
29.72
26.78
21.63
21.58
19.85

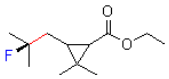

180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


O
O
F

2p

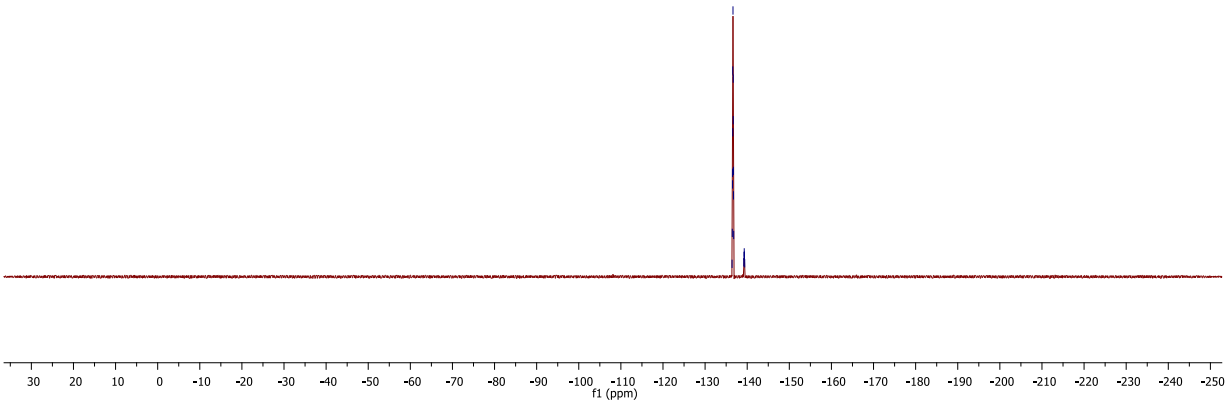

4.19
4.19
4.18
4.17
4.15
4.15
4.13
4.13
4.12
4.11
1.78
1.77
1.75
1.74
1.73
1.72
1.70
1.69
1.68
1.67
1.65
1.64
1.61
1.43
1.34
1.34
1.32
1.30
1.29
1.28
1.28
1.27
1.26
1.25
1.24
1.22
1.21
1.16

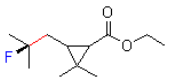

2.00
2.12
7.32
10.25
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)



2p

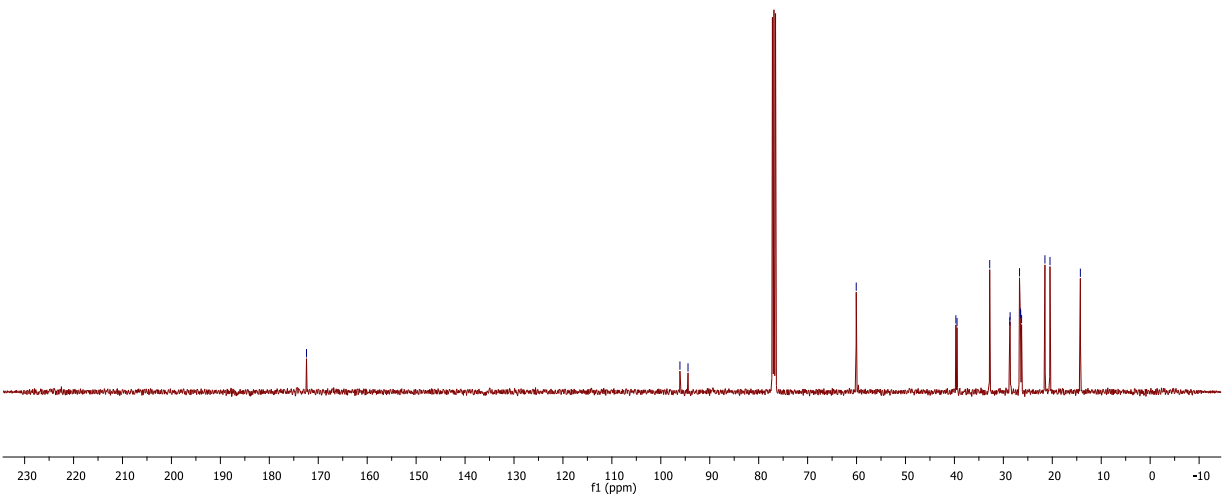

136.40
136.46
136.51
136.52
136.57
136.57
136.63
136.68
136.68
136.73
136.74
136.79
139.18
139.24
139.30
139.35
139.41

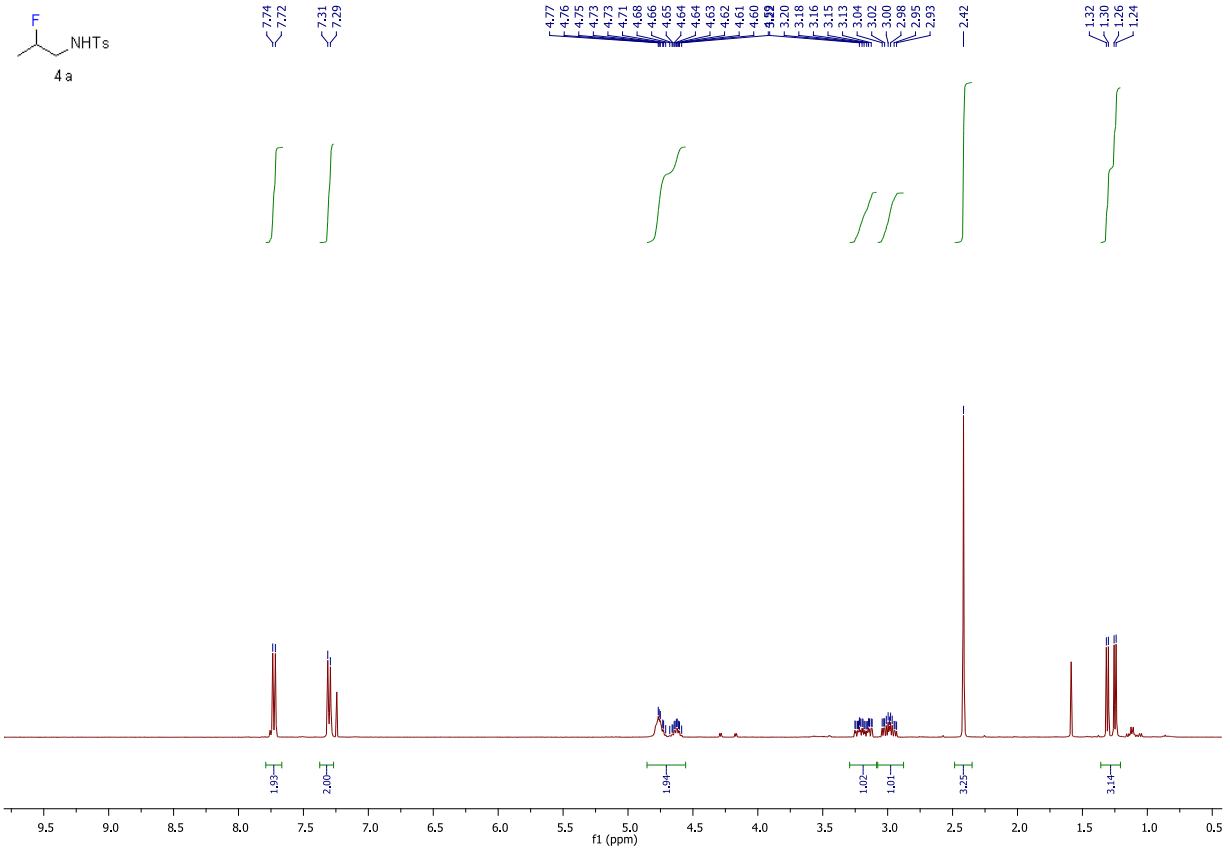

30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240 -250
f1 (ppm)



2p


172.40
96.09
94.44
60.06
39.70
39.47
32.79
26.52
21.50
20.47
14.26


230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


F
NHTs
4 a
7.74
7.72
7.31
7.29
4.77
4.76
4.75
4.73
4.73
4.71
4.68
4.66
4.65
4.64
4.64
4.63
4.62
4.61
4.60
3.20
3.18
3.16
3.15
3.13
3.04
3.02
3.00
2.98
2.95
2.93
2.42
1.32
1.30
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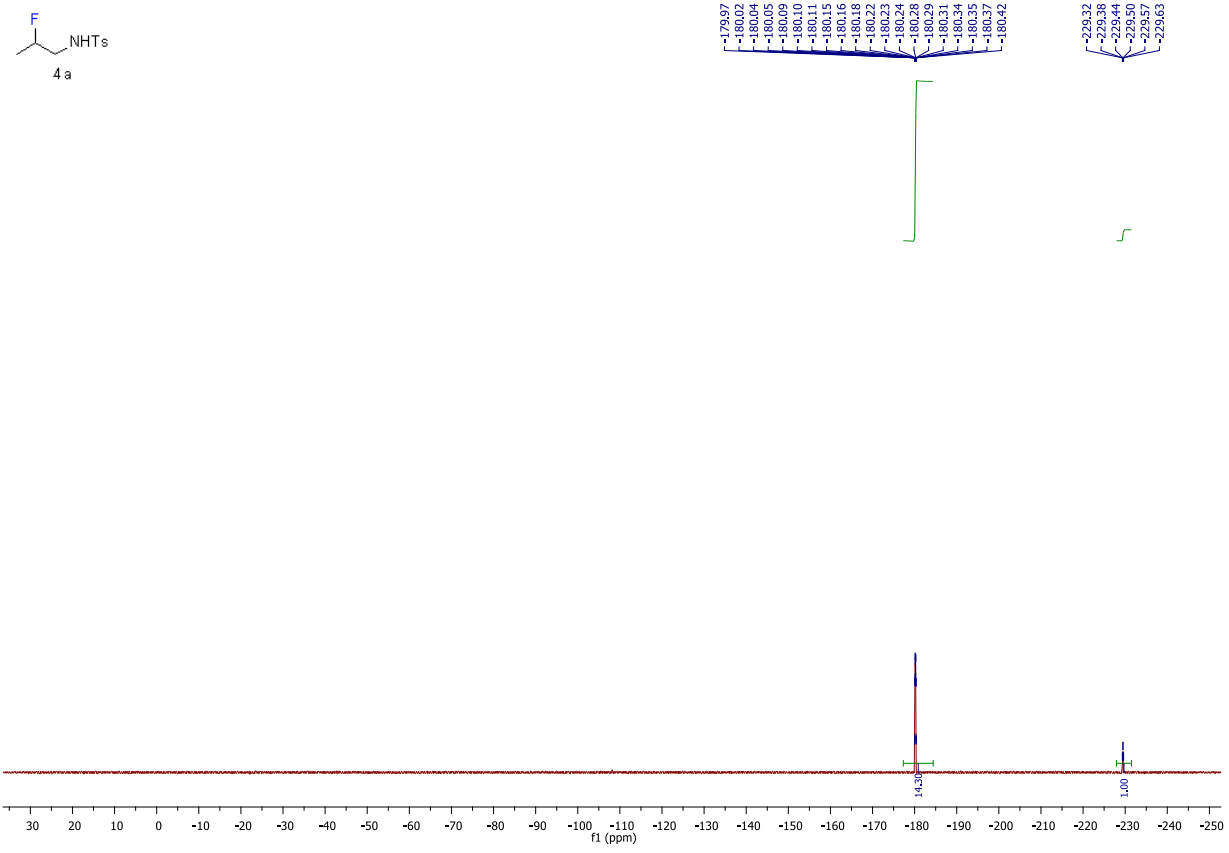
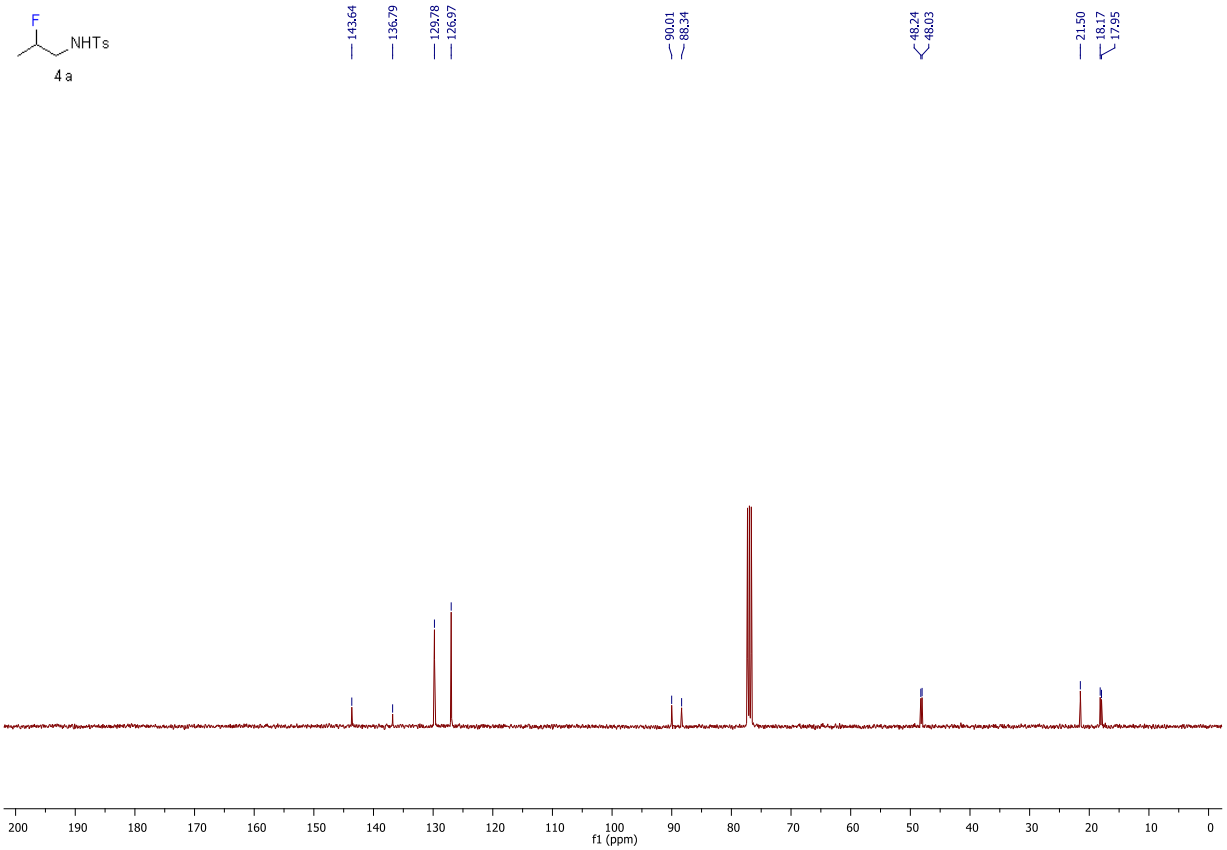
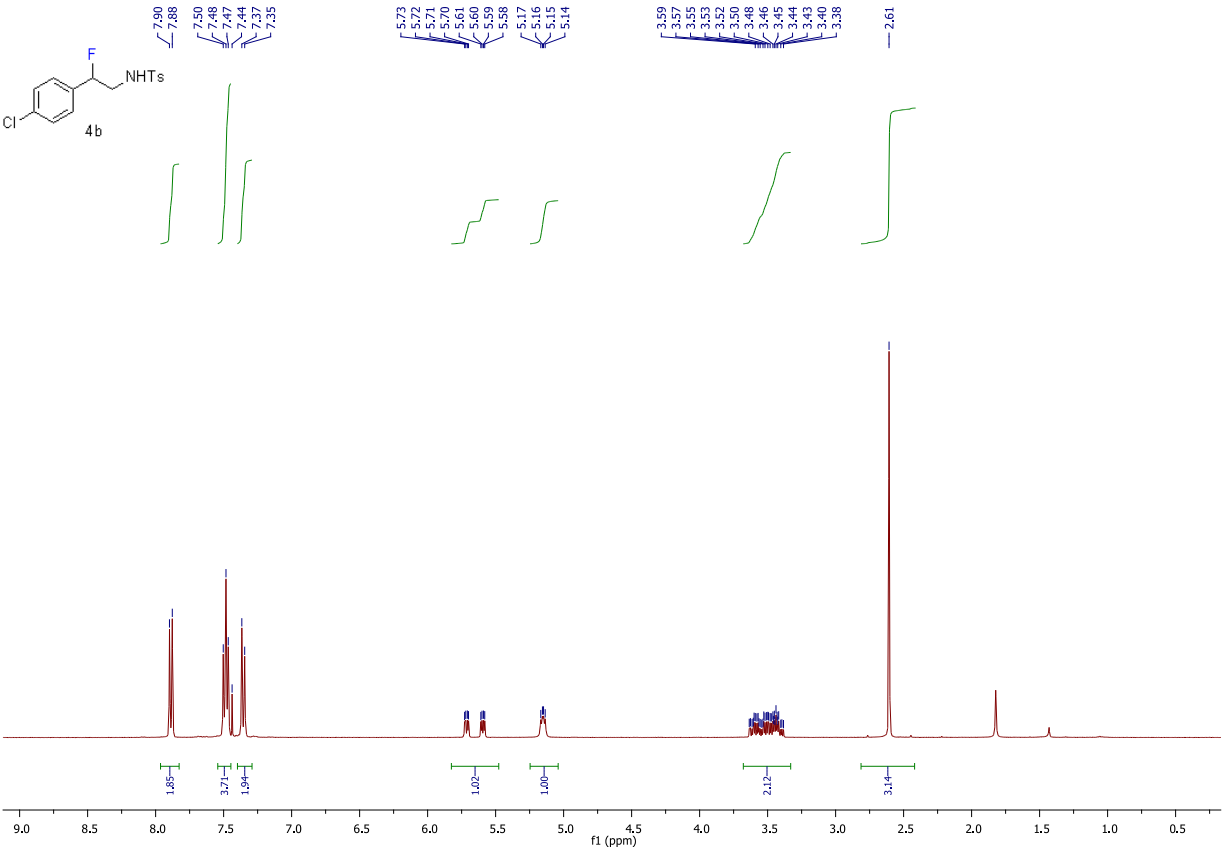
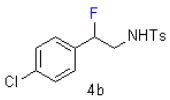
1.24
1.93
2.00
1.94
1.02
1.01
3.25
3.14
f1 (ppm)

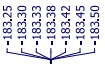

F
NHTs
4 a
179.97
180.02
180.04
180.05
180.09
180.10
180.11
180.15
180.16
180.18
180.22
180.23
180.24
180.28
180.29
180.31
180.34
180.35
180.37
180.42
229.32
229.38
229.44
229.50
229.57
229.63
14.30
1.00
f1 (ppm)

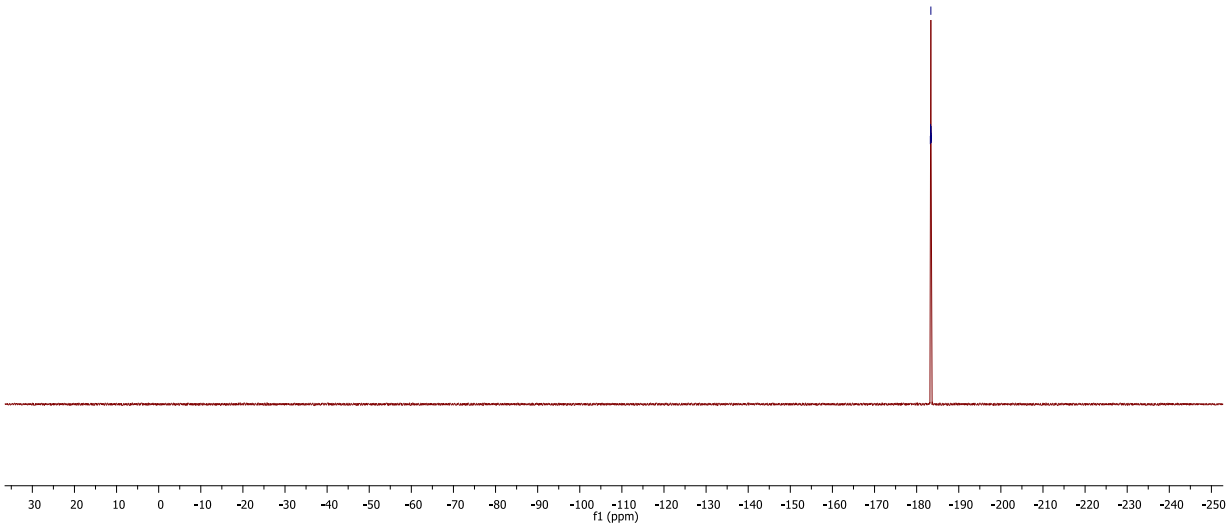

F
NHTs
4 a
143.64
136.79
129.78
126.97
90.01
88.34
48.24
48.03
21.50
18.17
17.95
f1 (ppm)

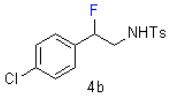

7.90
7.88
7.50
7.48
7.47
7.44
7.37
7.35
5.73
5.72
5.71
5.70
5.61
5.60
5.59
5.58
5.17
5.16
5.15
5.14
3.59
3.57
3.55
3.53
3.52
3.50
3.48
3.46
3.45
3.44
3.43
3.40
3.38
2.61
F
NHTs
Cl
4 b
1.85
3.71
1.94
1.02
1.00
2.12
3.14
f1 (ppm)


F
NHTs
Cl

4b

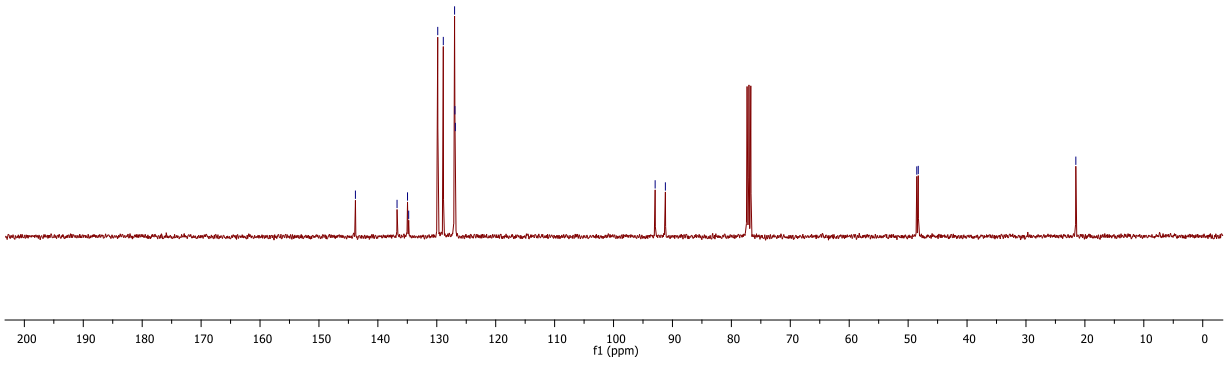

-183.25
-183.30
-183.33
-183.38
-183.42
-183.45
-183.50

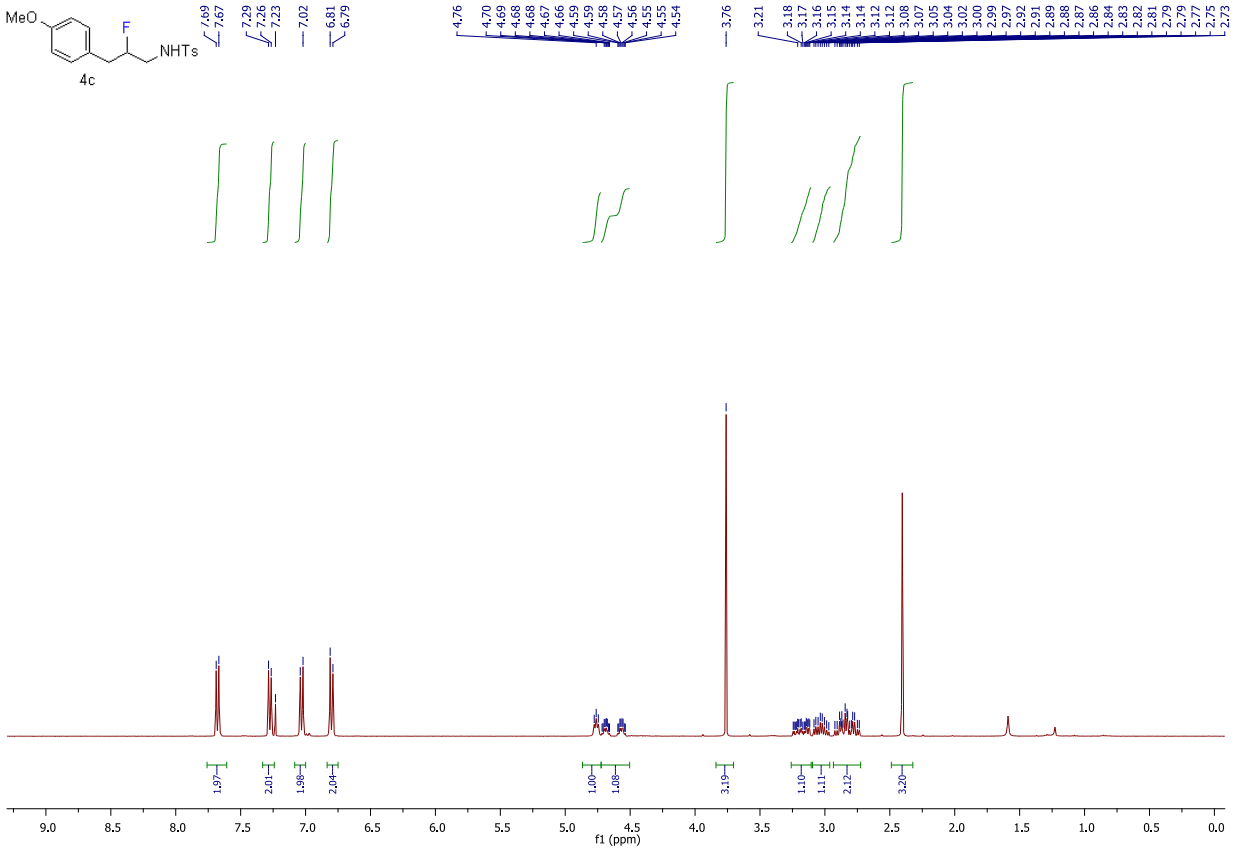

30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240 -250
f1 (ppm)

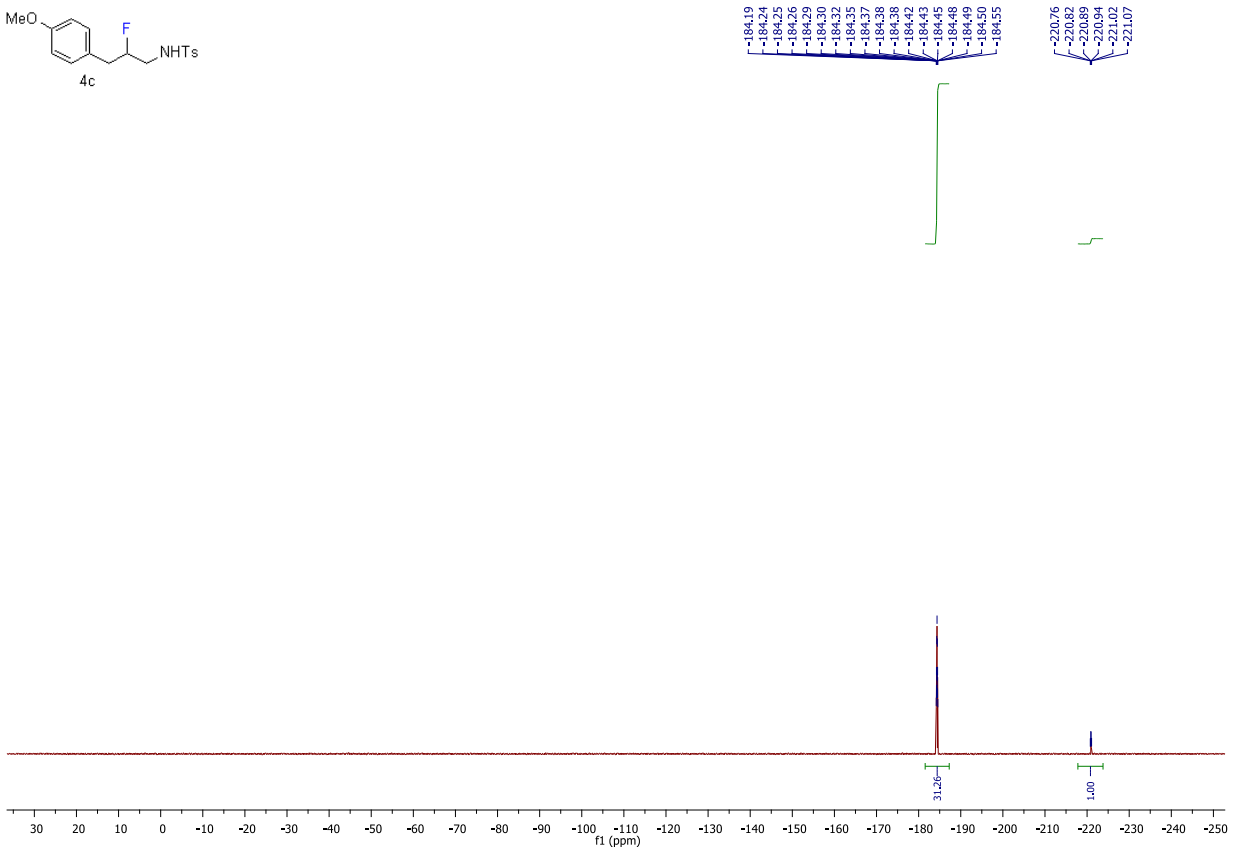

F
NHTs
Cl

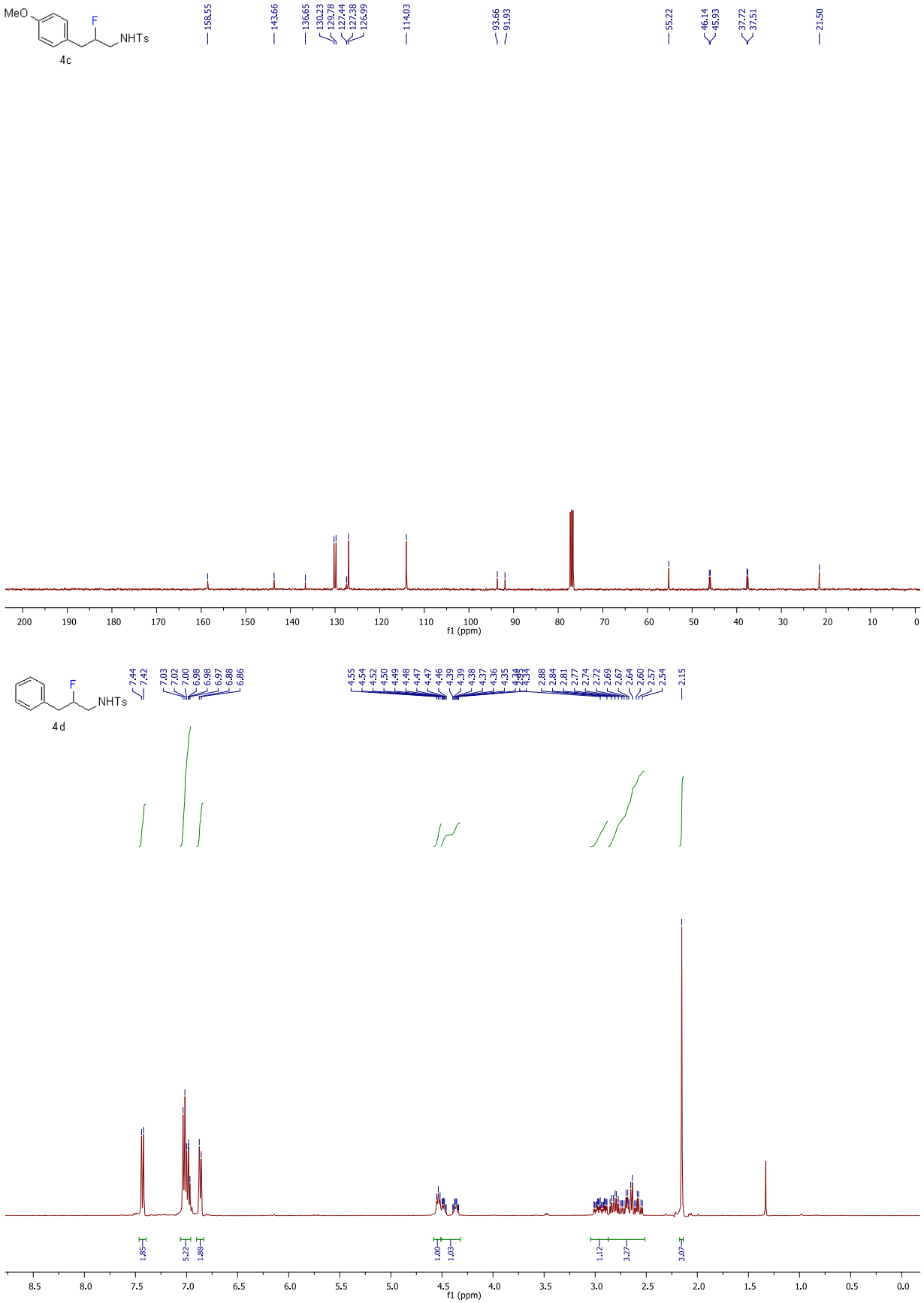
4b

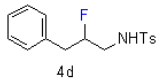

143.81
136.75
134.97
134.77
129.84
128.89
126.98
126.92
126.85
92.94
91.20
48.53
48.28
21.54


200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


MeO
F
NHTs
4c
f1 (ppm)

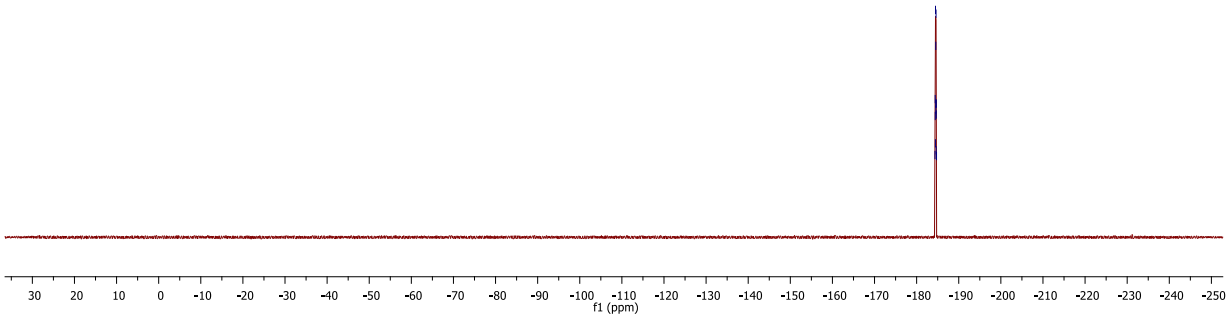

MeO
F
NHTs
4c
f1 (ppm)

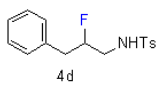

MeO
F
NHTs
4c
158.55
143.66
136.65
130.23
129.78
127.44
127.38
126.99
114.03
93.66
91.93
55.22
46.14
45.93
37.72
37.51
21.50
f1 (ppm)
F
NHTs
4d
7.44
7.42
7.03
7.02
7.00
6.98
6.98
6.97
6.88
6.86
4.55
4.54
4.52
4.50
4.49
4.48
4.47
4.47
4.46
4.39
4.39
4.38
4.37
4.36
4.35
2.88
2.84
2.81
2.77
2.74
2.72
2.69
2.67
2.64
2.60
2.57
2.54
2.15
1.85
5.22
1.88
1.00
1.03
1.12
3.27
3.07
f1 (ppm)


F
NHTs

4d

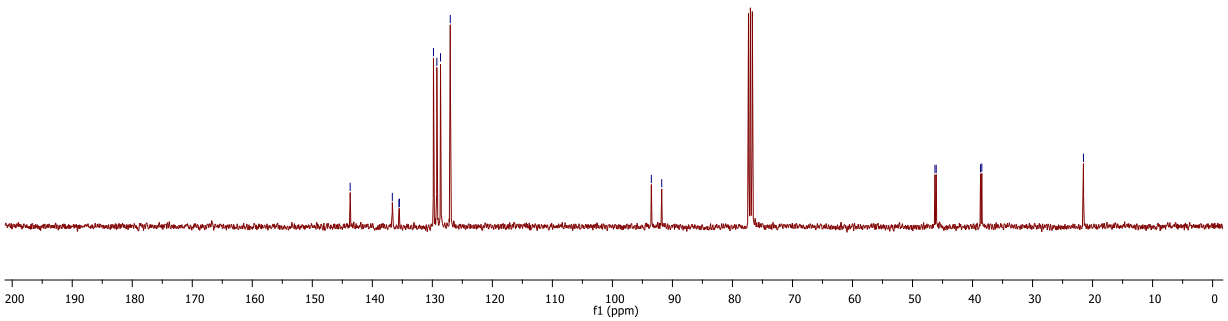

-184.36
-184.41
-184.43
-184.46
-184.48
-184.53
-184.54
-184.56
-184.61
-184.62
-184.66
-184.67
-184.72

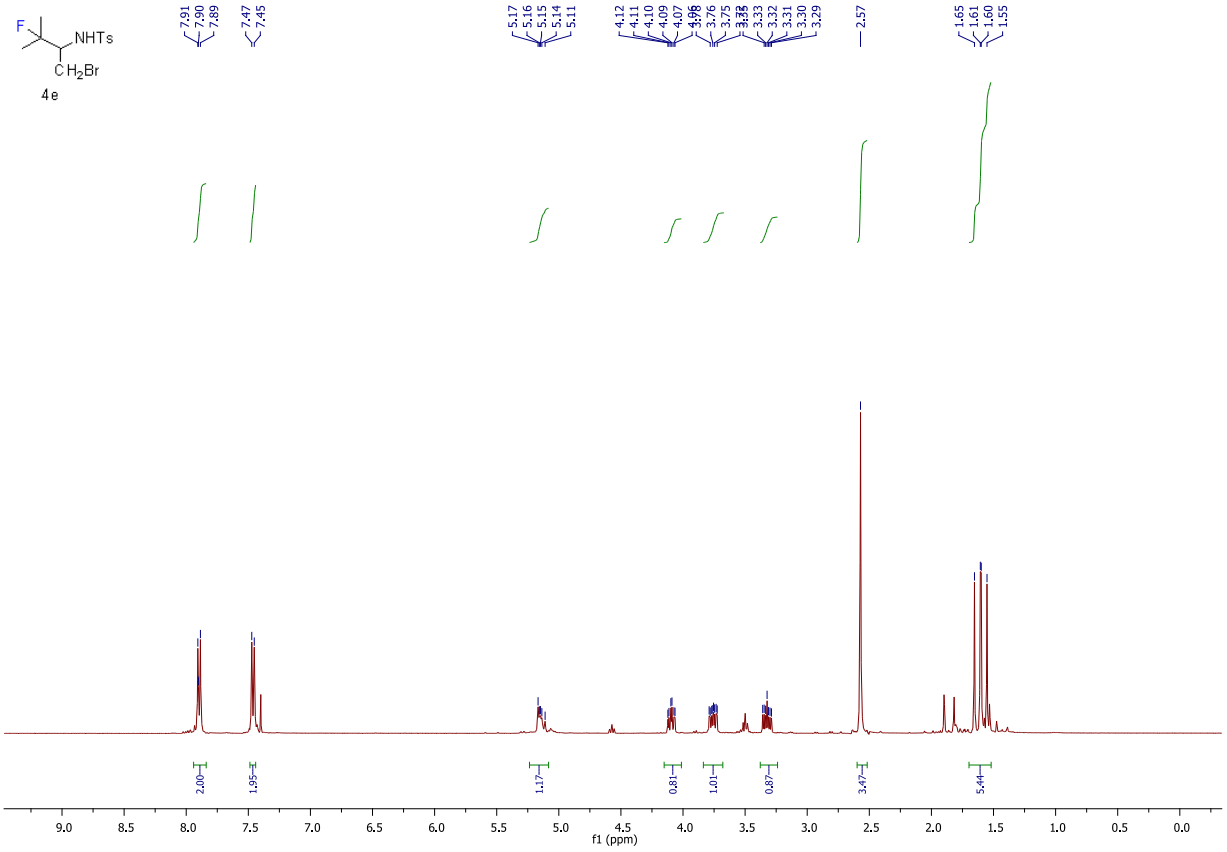

30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240 -250
f1 (ppm)

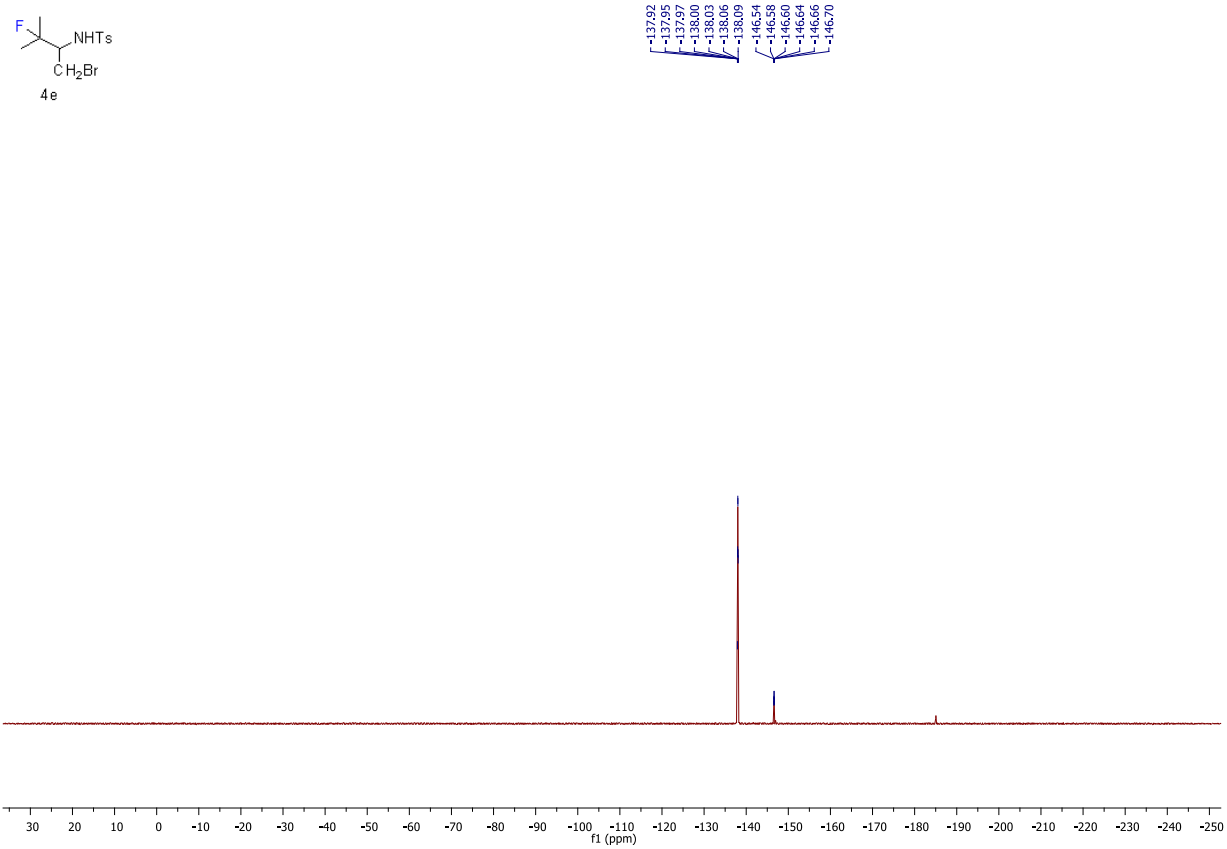

F
NHTs

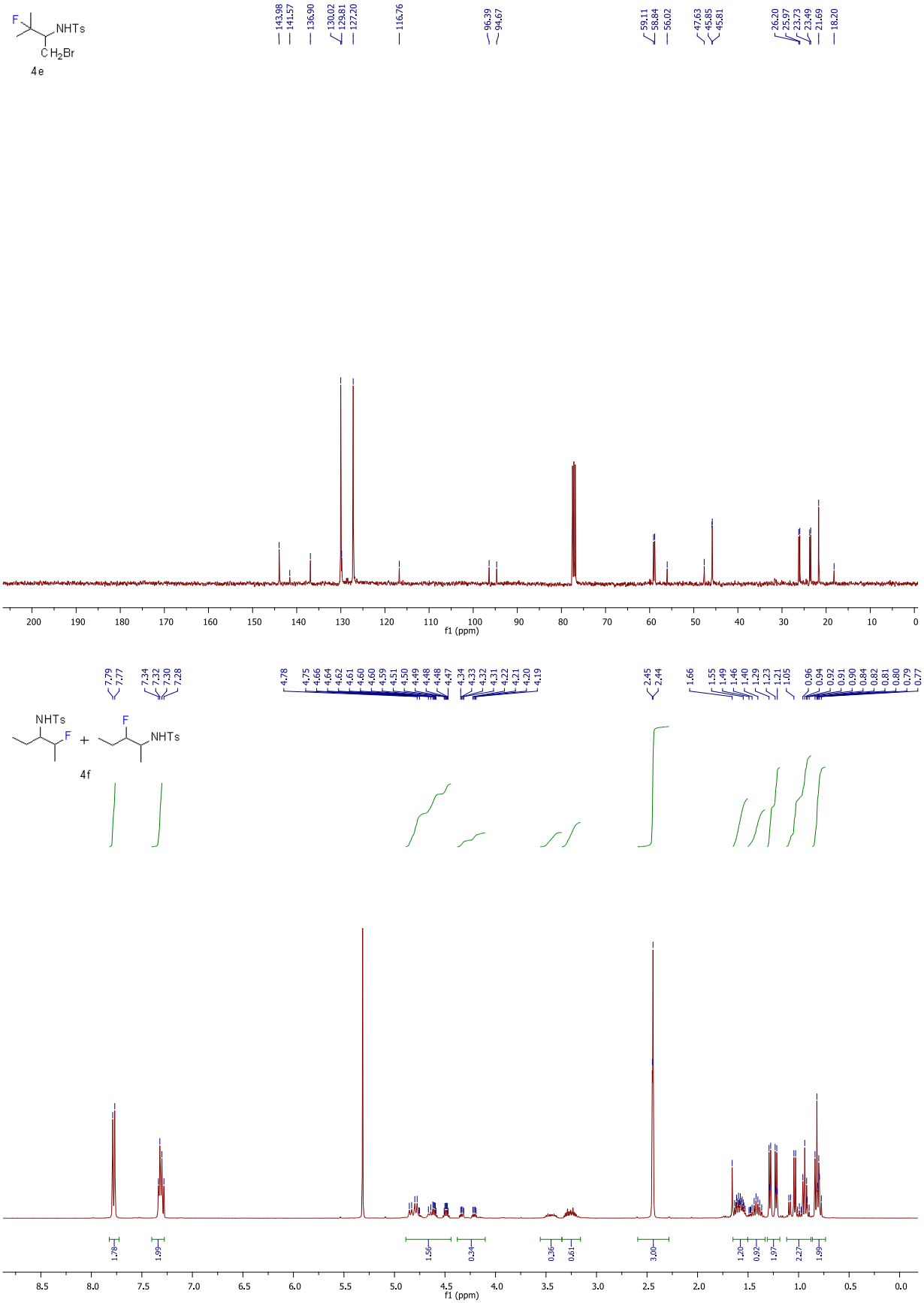
4d

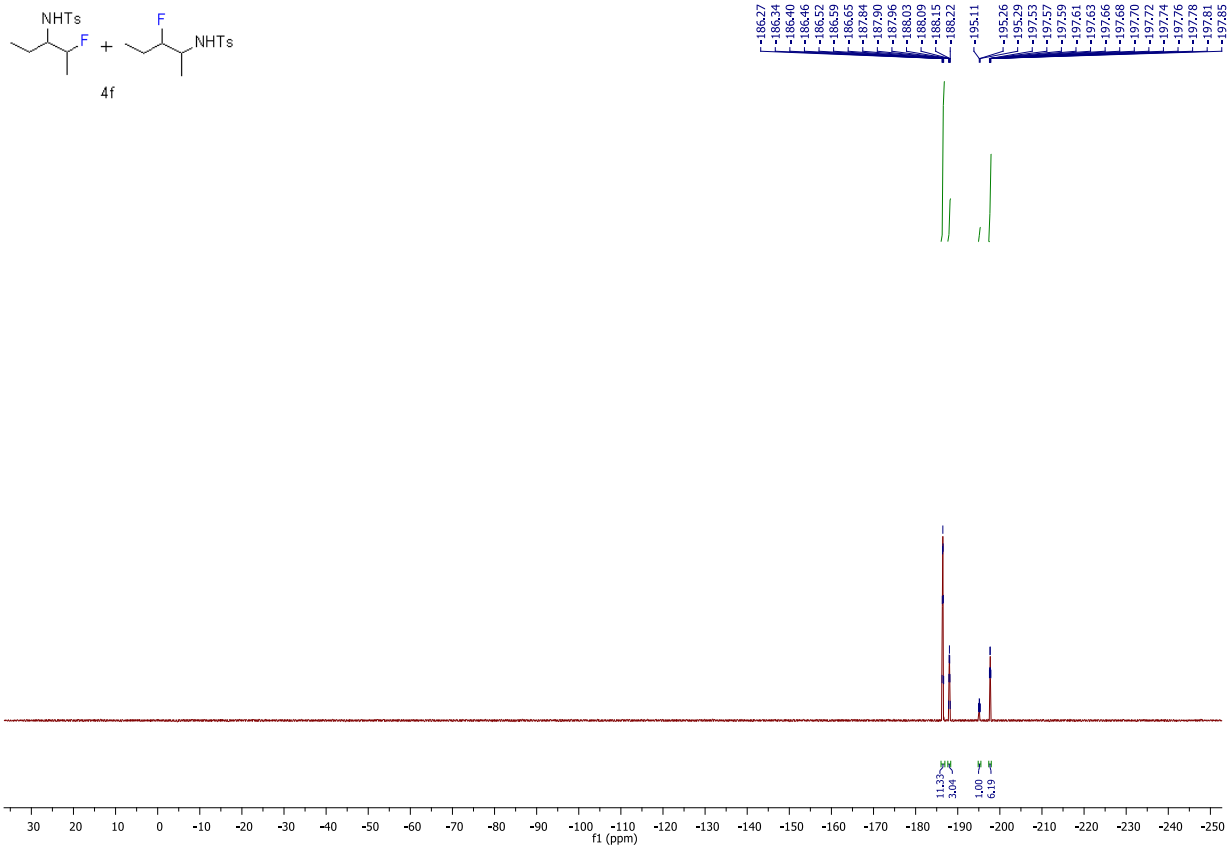

143.69
136.67
135.51
129.81
129.25
128.64
127.01
93.52
91.79
46.26
46.05
38.66
38.46
21.52

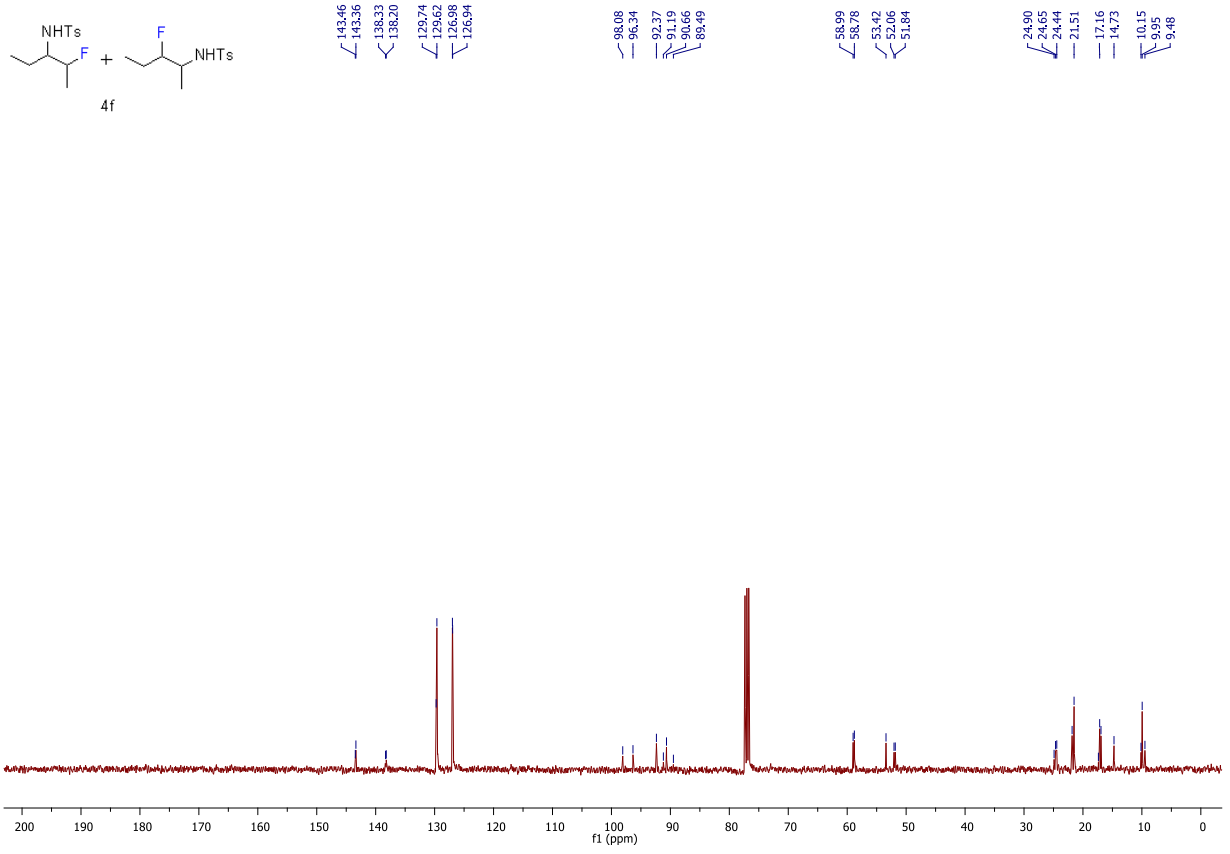

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

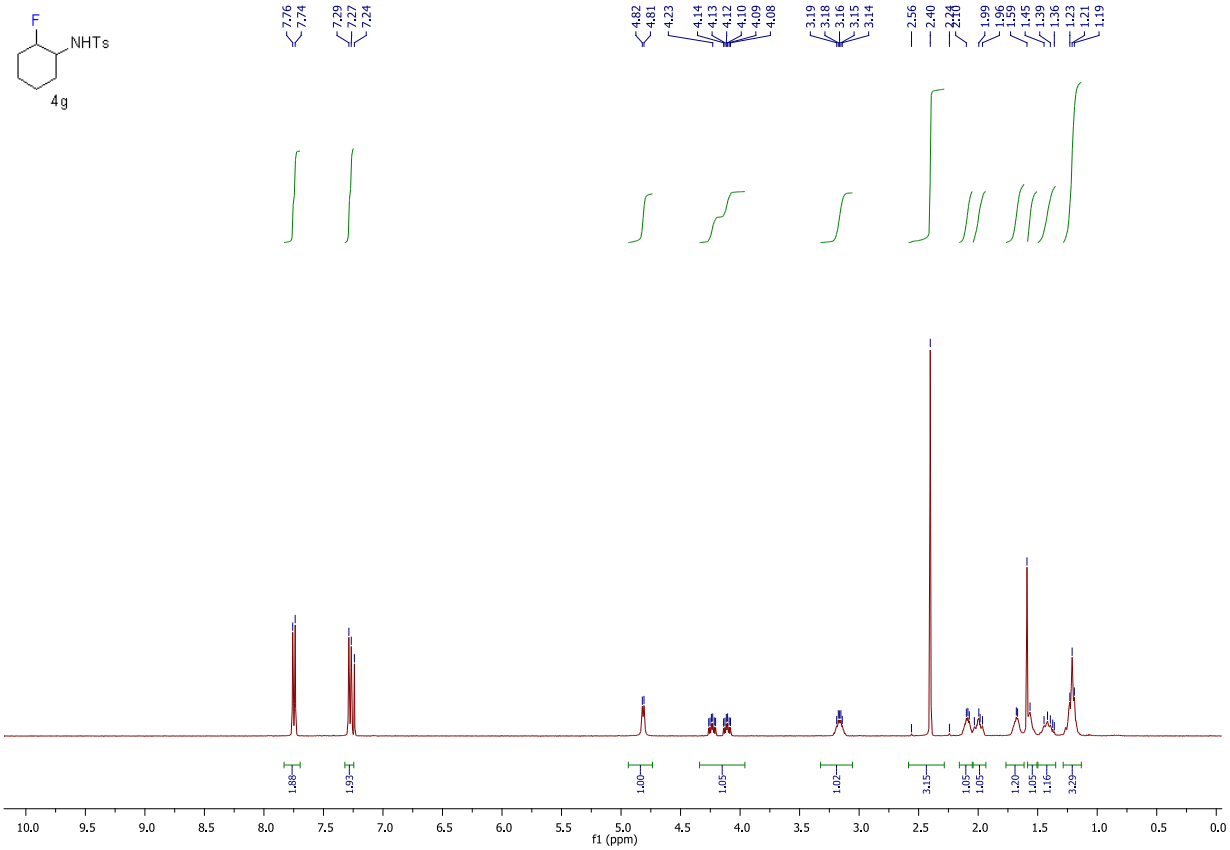

F
NHTs
CH2Br
4e
7.91
7.90
7.89
7.47
7.45
5.17
5.16
5.15
5.14
5.11
4.12
4.11
4.10
4.09
4.07
3.76
3.75
3.33
3.32
3.31
3.30
3.29
2.57
1.65
1.61
1.60
1.55
2.00
1.95
1.17
0.81
1.01
0.87
3.47
5.44
f1 (ppm)

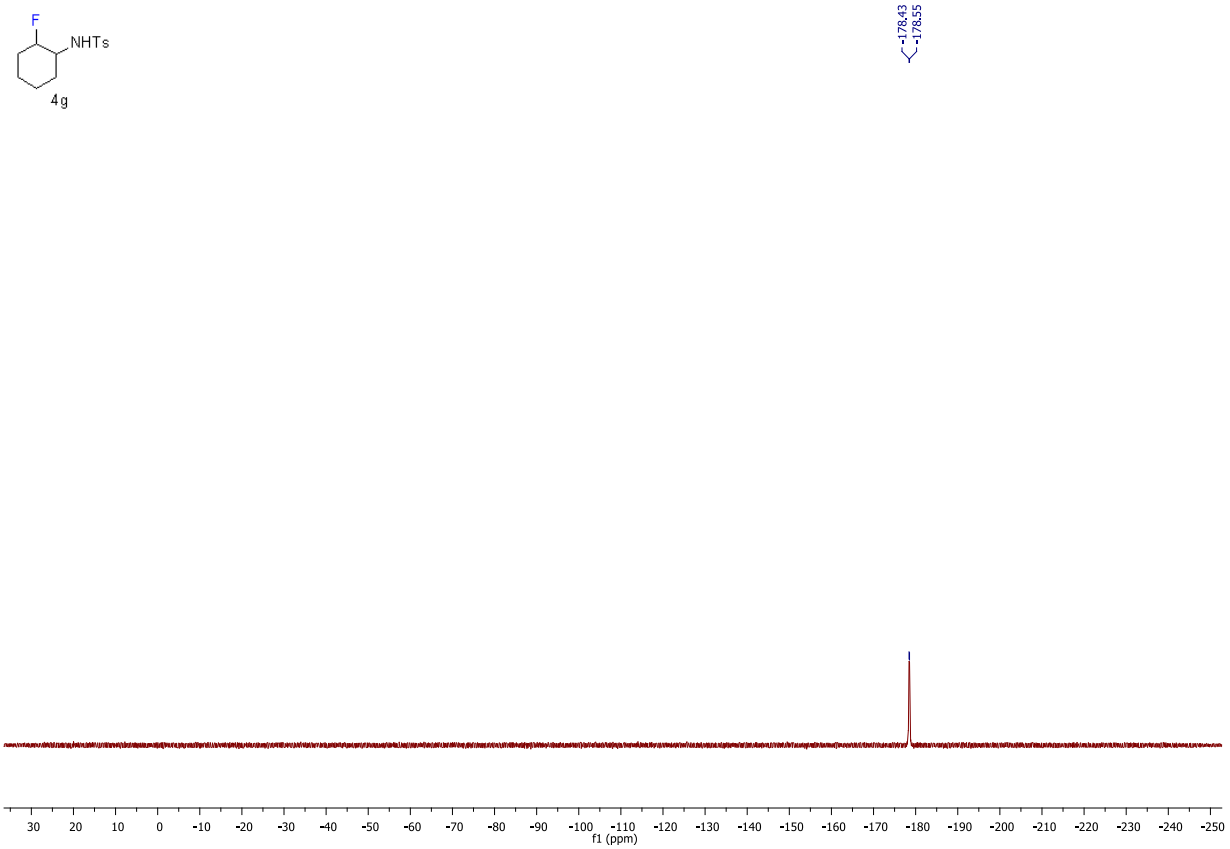

F
NHTs
CH2Br
4e
-137.92
-137.95
-137.97
-138.00
-138.03
-138.06
-138.09
-146.54
-146.58
-146.60
-146.64
-146.66
-146.70
f1 (ppm)

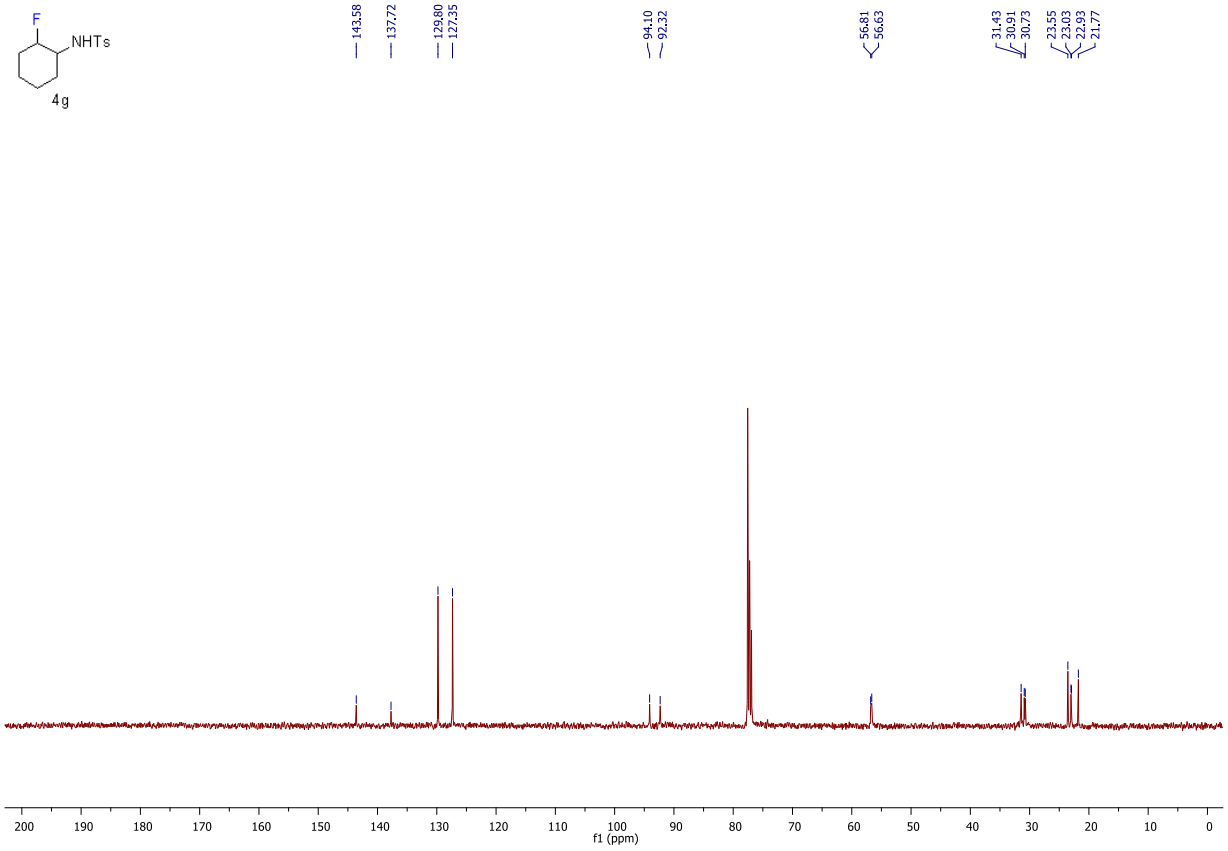

F
NHTs
CH2Br
4e
143.98
141.57
136.90
130.02
129.81
127.20
116.76
96.39
94.67
59.11
58.84
56.02
47.63
45.85
45.81
26.20
25.97
23.73
23.49
21.69
18.20
f1 (ppm)
7.79
7.77
7.34
7.32
7.30
7.28
4.78
4.75
4.66
4.64
4.62
4.61
4.60
4.60
4.59
4.51
4.50
4.49
4.48
4.48
4.47
4.34
4.33
4.32
4.31
4.22
4.21
4.20
4.19
2.45
2.44
1.66
1.55
1.49
1.46
1.40
1.29
1.23
1.21
1.05
0.96
0.94
0.92
0.91
0.90
0.84
0.82
0.81
0.80
0.79
0.77
NHTs
F
+
F
NHTs
4f
1.78
1.99
1.56
0.34
0.26
0.61
3.00
1.20
0.92
1.97
2.27
1.99
f1 (ppm)

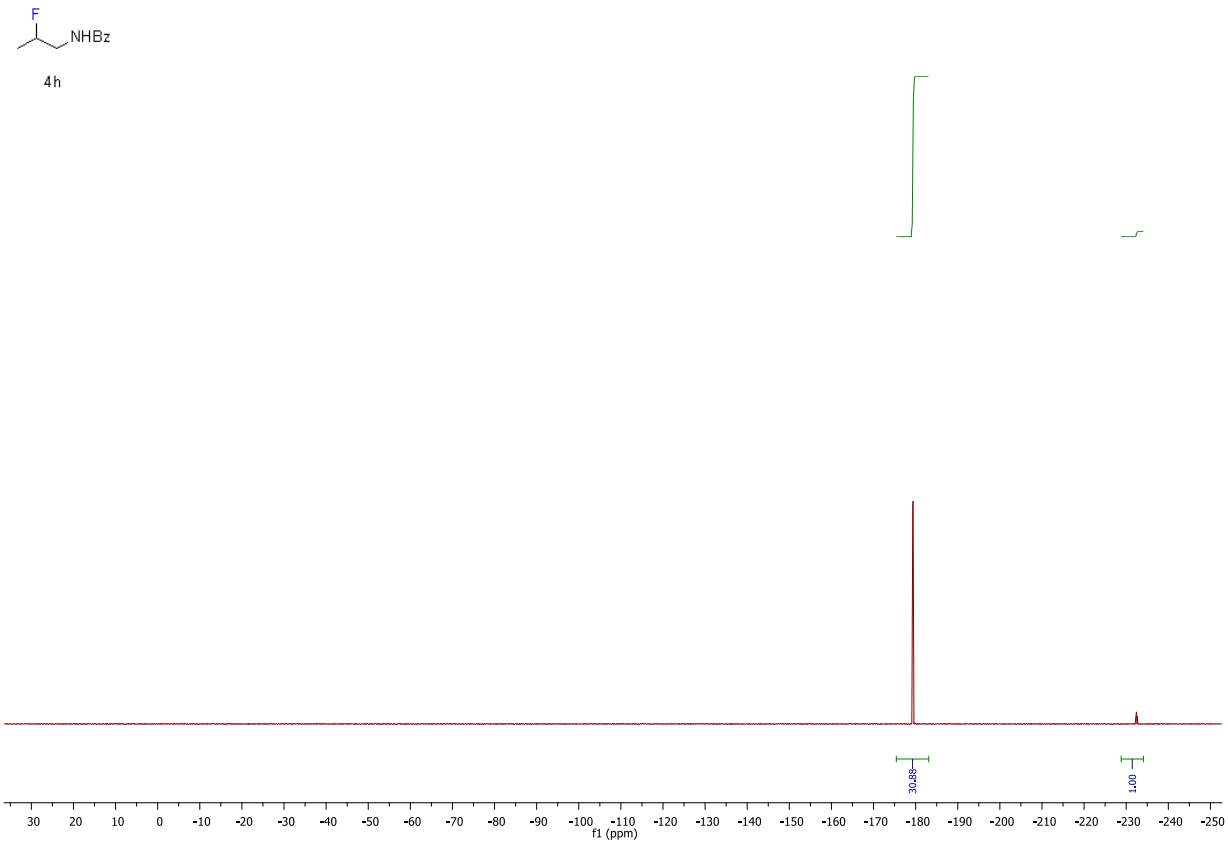

NHTs
F
+
F
NHTs
4f
-186.27
-186.34
-186.40
-186.46
-186.52
-186.59
-186.65
-187.84
-187.90
-187.96
-188.03
-188.09
-188.15
-188.22
-195.11
-195.26
-195.29
-197.53
-197.57
-197.59
-197.61
-197.63
-197.66
-197.68
-197.70
-197.72
-197.74
-197.76
-197.78
-197.81
-197.85
11.33
3.04
1.00
6.19
f1 (ppm)

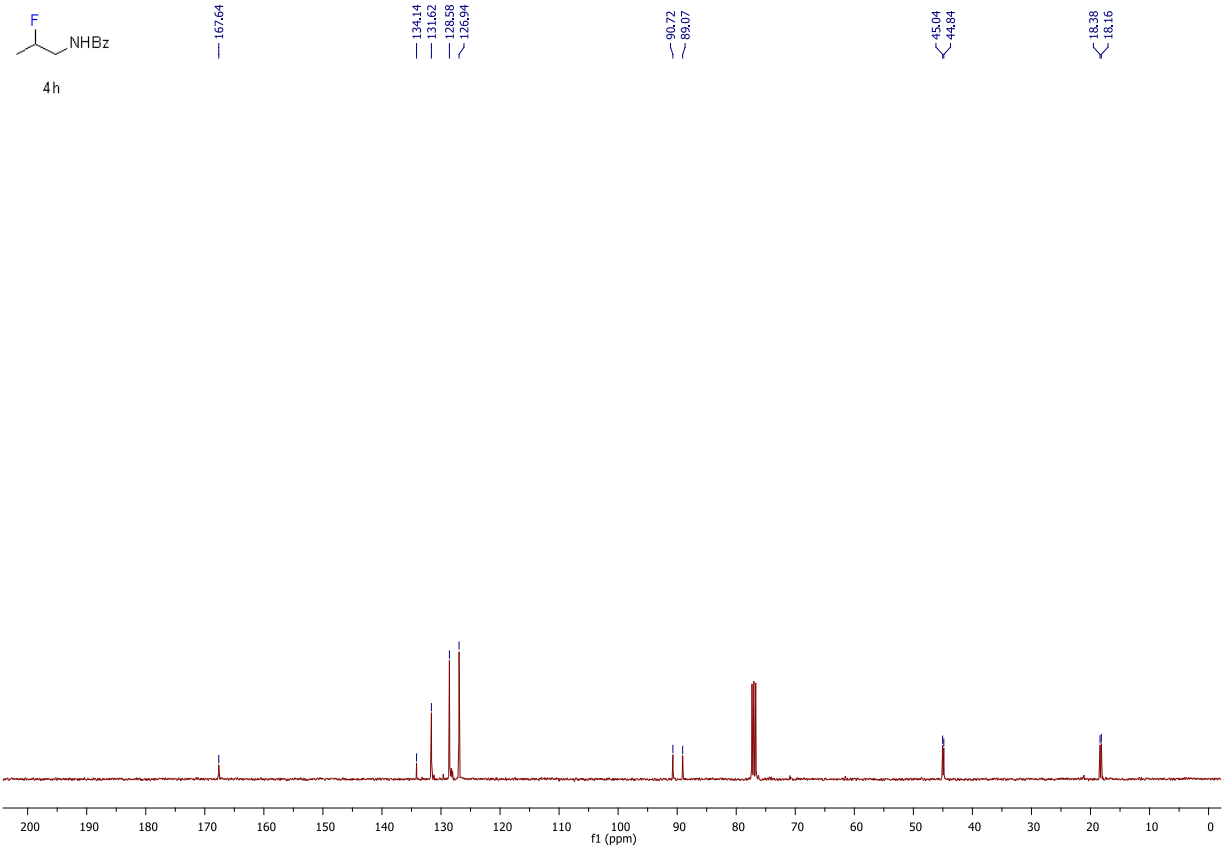

NHTs
F
+
F
NHTs
4f
143.46
143.36
138.33
138.20
129.74
129.62
126.98
126.94
98.08
96.34
92.37
91.19
90.66
89.49
58.99
58.78
53.42
52.06
51.84
24.90
24.65
24.44
21.51
17.16
14.73
10.15
9.95
9.48
f1 (ppm)

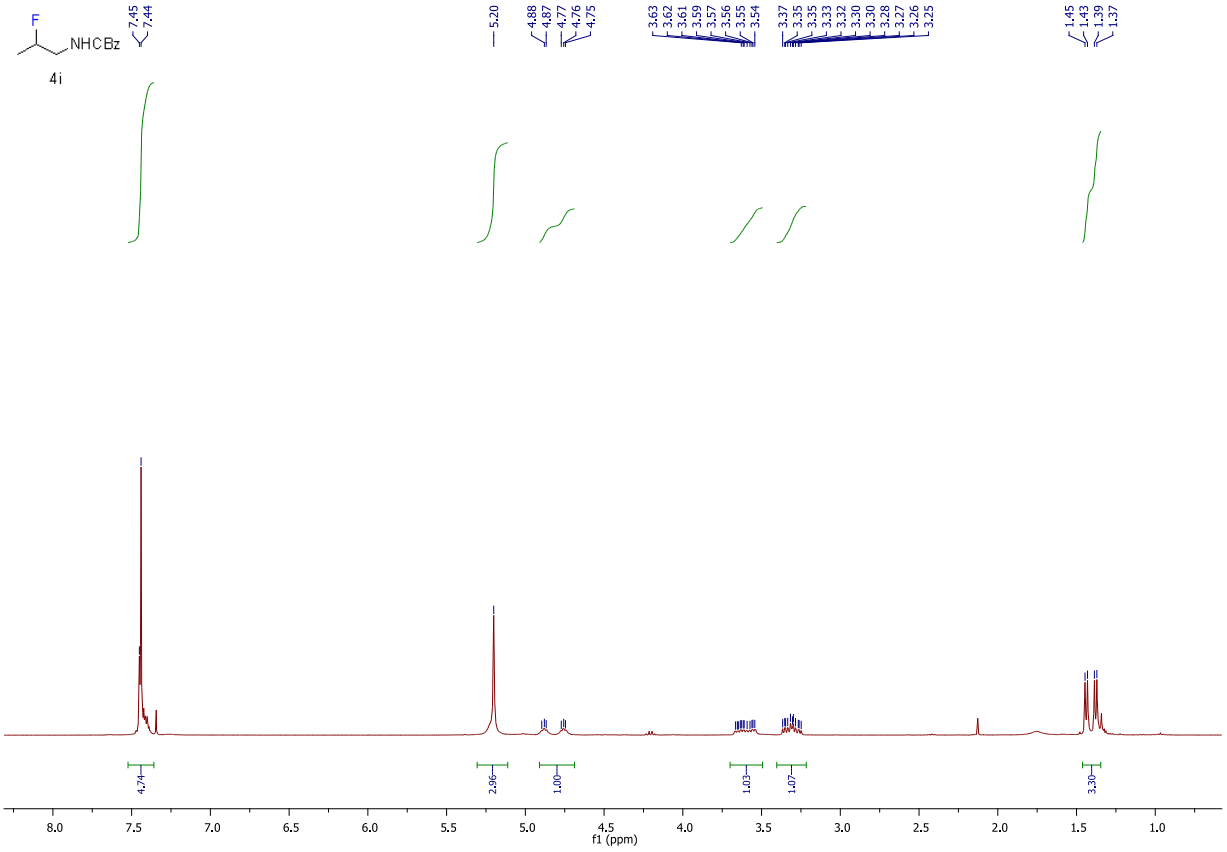

F
NHTs
4g
7.76
7.74
7.29
7.27
7.24
4.82
4.81
4.23
4.14
4.13
4.12
4.10
4.09
4.08
3.19
3.18
3.16
3.15
3.14
2.56
2.40
2.24
2.10
1.99
1.96
1.59
1.45
1.39
1.36
1.23
1.21
1.19
1.88
1.93
1.00
1.05
1.02
3.15
1.05
1.05
1.20
1.05
1.16
3.29
f1 (ppm)

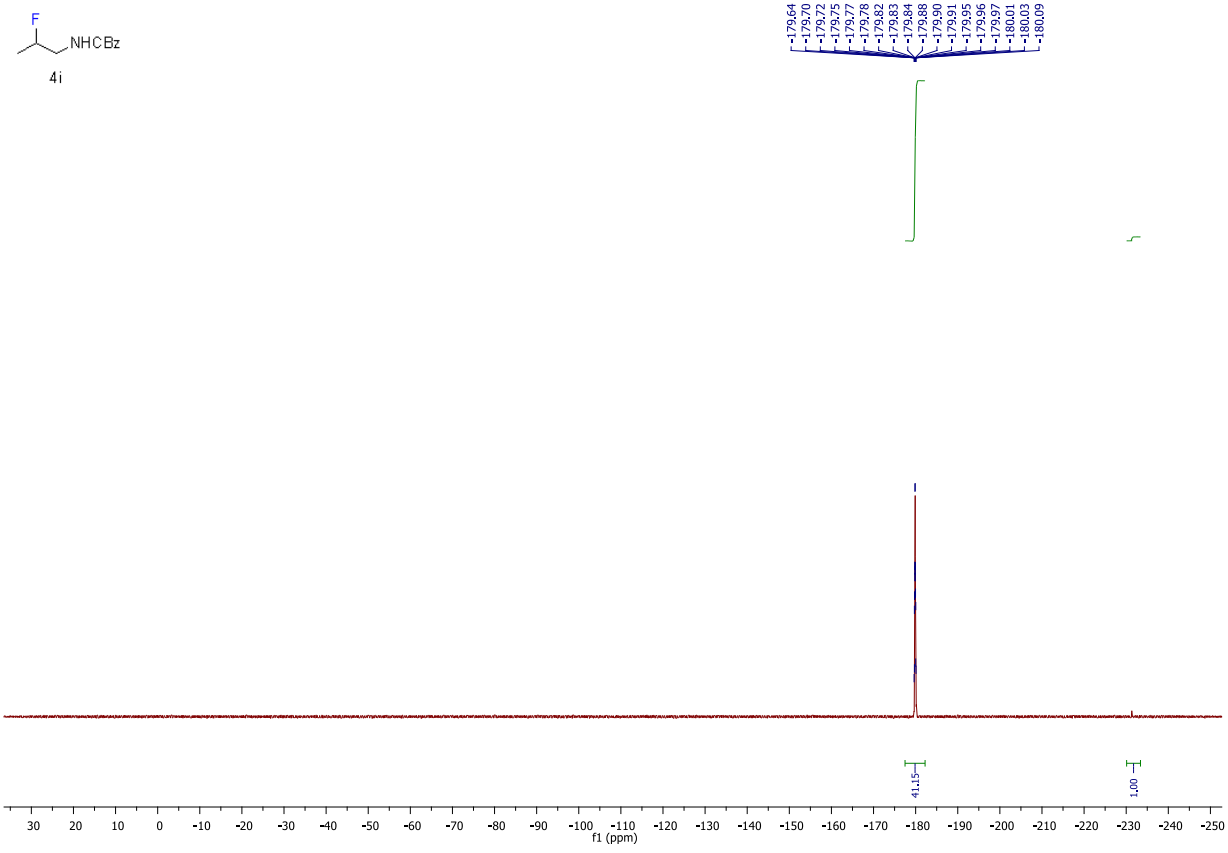

F
NHTs
4g
-178.43
-178.55
f1 (ppm)

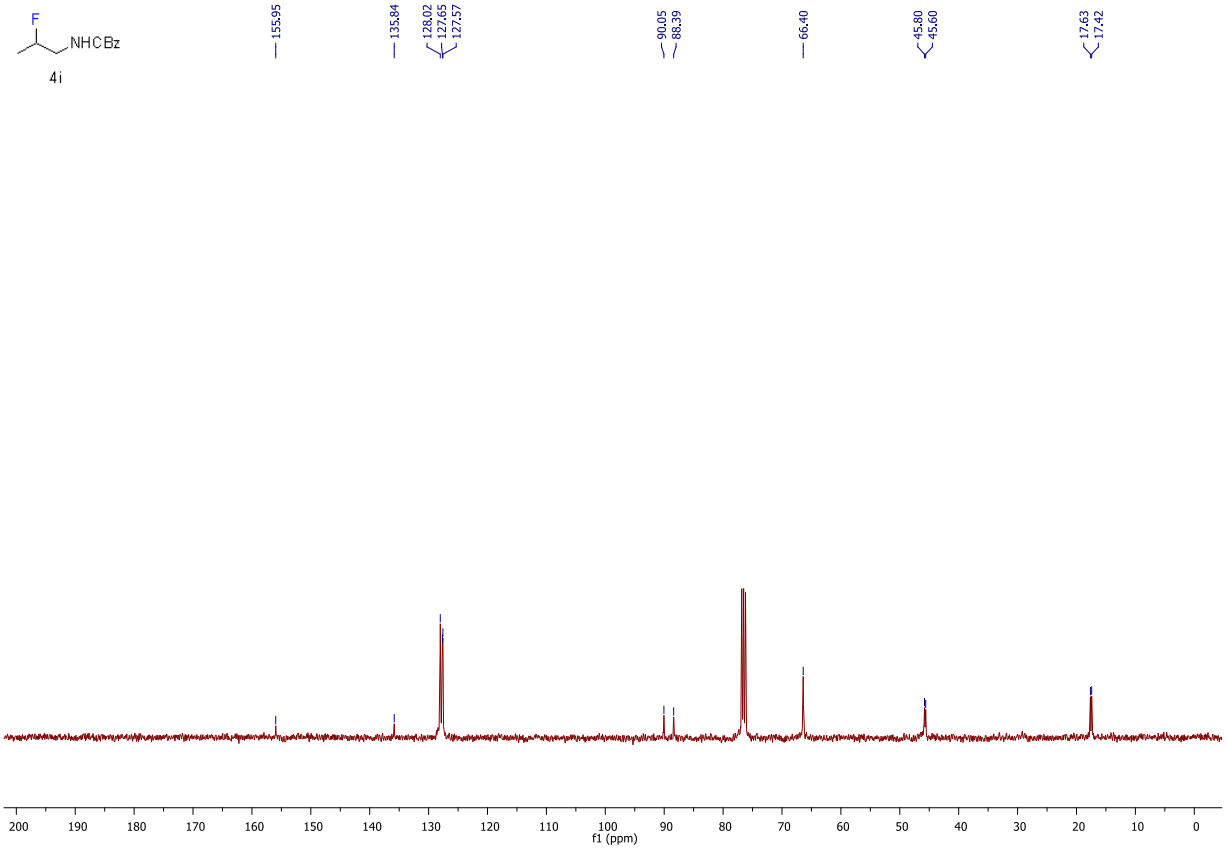

F
NHTs
4g
143.58
137.72
129.80
127.35
94.10
92.32
56.81
56.63
31.43
30.91
30.73
23.55
23.03
22.93
21.77
f1 (ppm)
F
NHBz
4h
7.79
7.77
7.50
7.48
7.44
7.42
7.40
7.40
6.61
4.90
4.84
4.83
4.83
4.81
4.81
4.80
4.79
4.78
4.76
4.76
4.74
3.88
3.87
3.84
3.83
3.81
3.43
3.41
3.41
3.40
3.39
3.38
3.36
3.36
3.34
1.41
1.39
1.35
1.33
1.87
1.01
2.21
0.90
1.00
1.05
0.99
f1 (ppm)

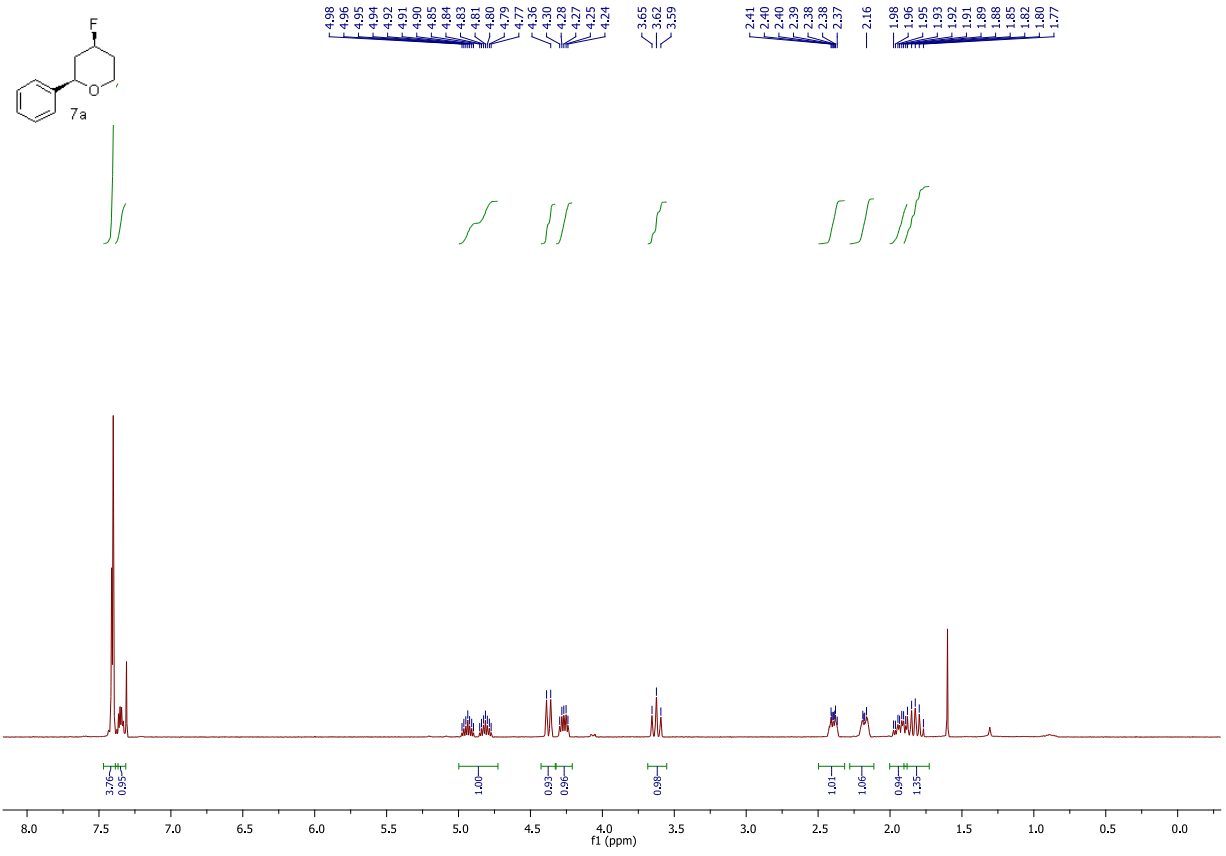

F
NHBz
4h
30.88
1.00
f1 (ppm)

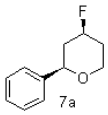

F
NHBz
4h
167.64
134.14
131.62
128.58
126.94
90.72
89.07
45.04
44.84
18.38
18.16
f1 (ppm)


F
NHCBz
4i
7.45
7.44
5.20
4.88
4.87
4.77
4.76
4.75
3.63
3.62
3.61
3.59
3.57
3.56
3.55
3.54
3.37
3.35
3.35
3.33
3.32
3.30
3.30
3.28
3.27
3.26
3.25
1.45
1.43
1.39
1.37
4.74
2.96
1.00
1.03
1.07
3.30
f1 (ppm)

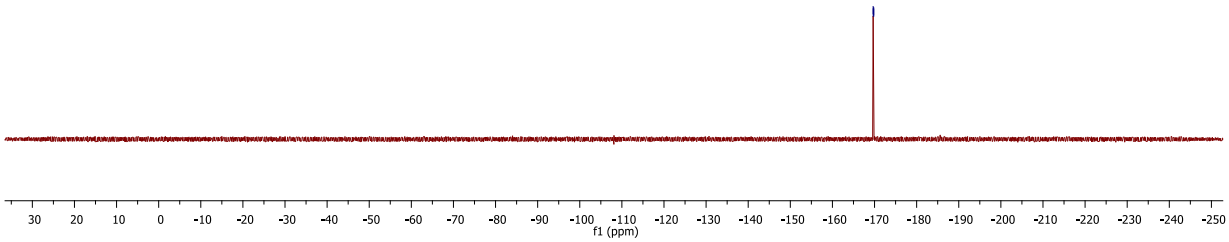

F
NHCBz
4i
179.64
179.70
179.72
179.75
179.77
179.78
179.82
179.83
179.84
179.88
179.90
179.91
179.95
179.96
179.97
180.01
180.03
180.09
41.15
1.00
f1 (ppm)

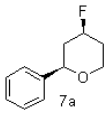

F
NHCBz
4i
155.95
135.84
128.02
127.65
127.57
90.05
88.39
66.40
45.80
45.60
17.63
17.42
f1 (ppm)


F
O
7a
4.98
4.96
4.95
4.94
4.92
4.91
4.90
4.85
4.84
4.83
4.81
4.80
4.79
4.77
4.36
4.30
4.28
4.27
4.25
4.24
3.65
3.62
3.59
2.41
2.40
2.40
2.39
2.38
2.38
2.37
2.16
1.98
1.96
1.95
1.93
1.92
1.91
1.89
1.88
1.85
1.82
1.80
1.77
3.76
0.95
1.00
0.93
0.96
0.98
1.01
1.06
0.94
1.35
f1 (ppm)

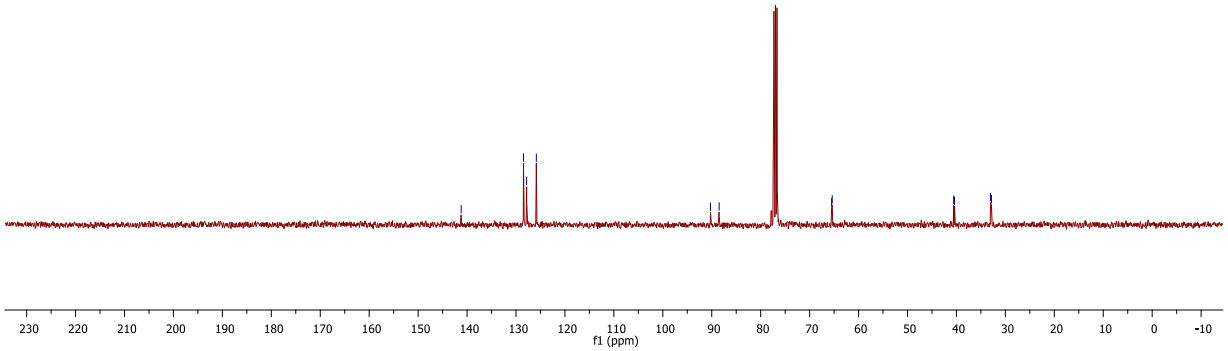

F
O
7a

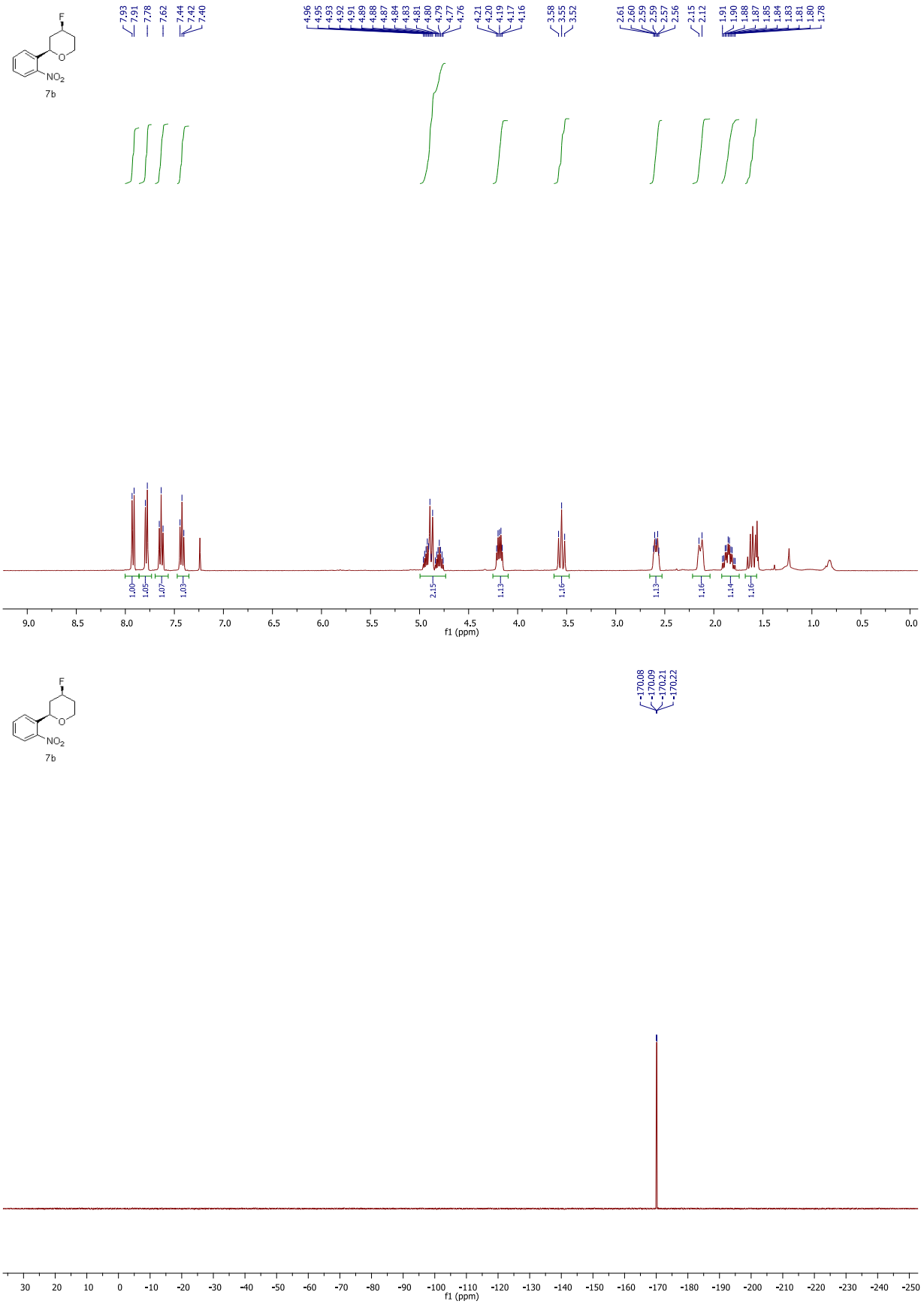

169.67
169.68
169.80
169.81

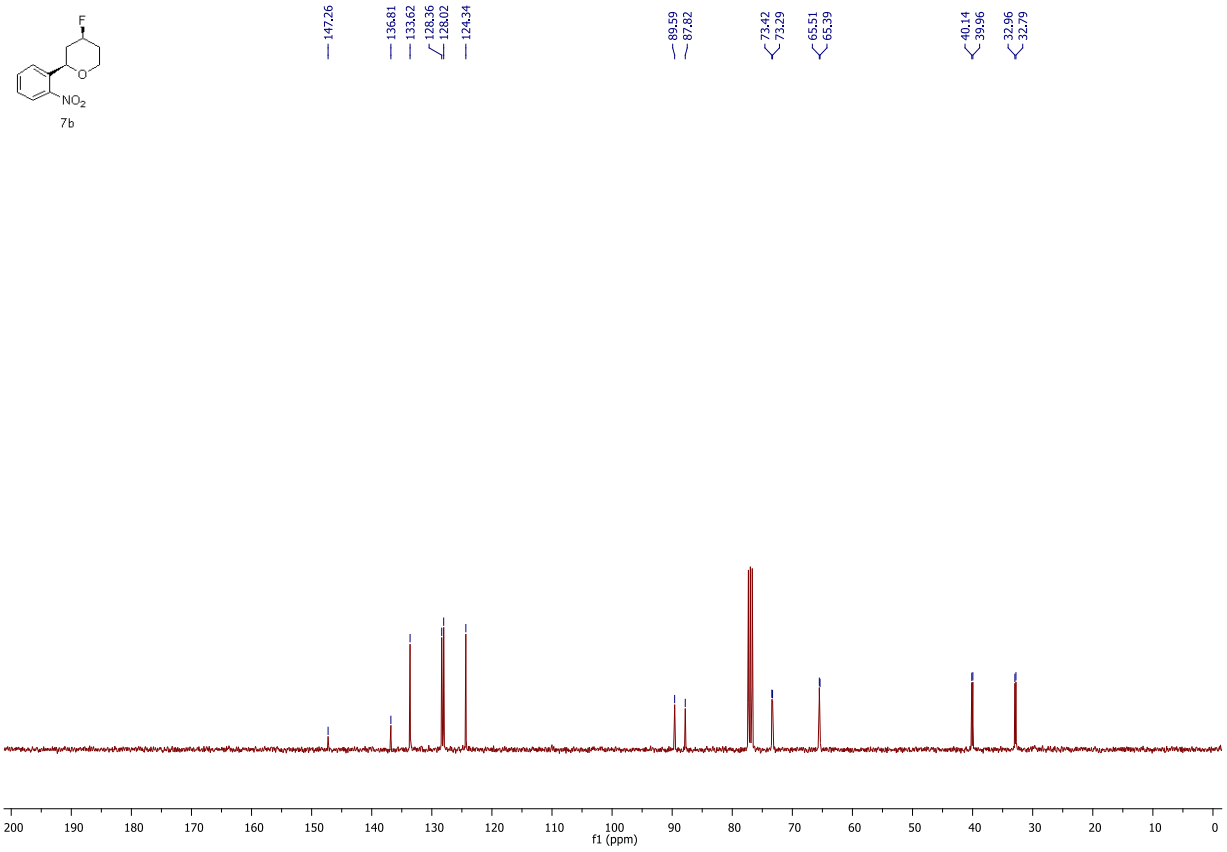

30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240 -250
f1 (ppm)

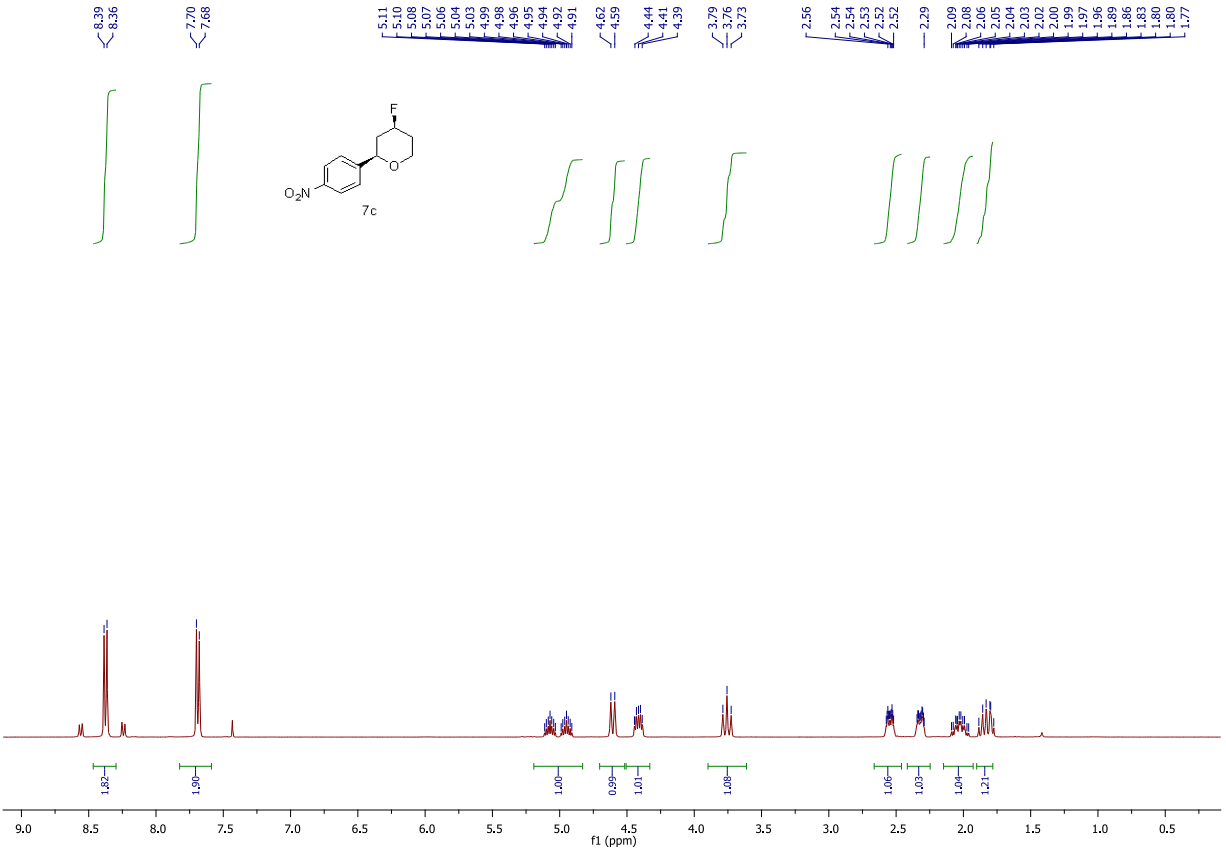

F
O
7a

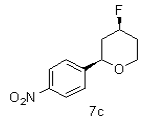

141.21
128.46
127.82
125.84
90.25
88.49
65.50
65.38
40.57
40.40
33.03
32.86


230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.93
7.91
7.78
7.62
7.44
7.42
7.40
4.96
4.95
4.93
4.92
4.91
4.89
4.88
4.87
4.84
4.83
4.81
4.80
4.79
4.77
4.76
4.21
4.20
4.19
4.17
4.16
3.58
3.55
3.52
2.61
2.60
2.59
2.59
2.57
2.56
2.15
2.12
1.91
1.90
1.88
1.87
1.85
1.84
1.83
1.81
1.80
1.78
F
O
NO2
7b
1.00
1.05
1.07
1.03
2.15
1.13
1.16
1.13
1.16
1.14
1.16
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
-170.08
-170.09
-170.21
-170.22
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
-220
-230
-240
-250
f1 (ppm)

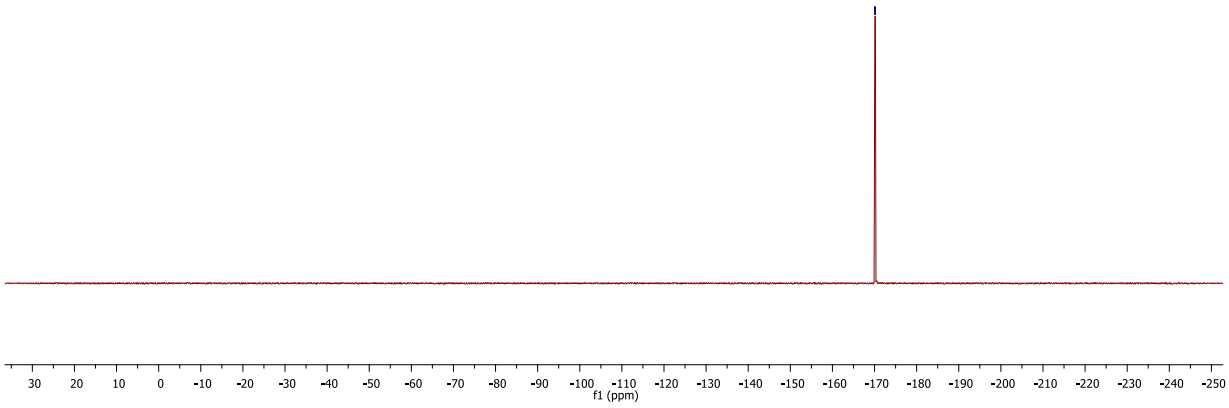

F
O
NO2
7b
147.26
136.81
133.62
128.36
128.02
124.34
89.59
87.82
73.42
73.29
65.51
65.39
40.14
39.96
32.96
32.79
f1 (ppm)

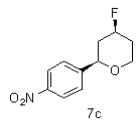

8.39
8.36
7.70
7.68
5.11
5.10
5.08
5.07
5.06
5.04
5.03
4.99
4.98
4.96
4.95
4.94
4.92
4.91
4.62
4.59
4.44
4.41
4.39
3.79
3.76
3.73
2.56
2.54
2.54
2.53
2.52
2.52
2.29
2.09
2.08
2.06
2.05
2.04
2.03
2.02
2.00
1.99
1.97
1.96
1.89
1.86
1.83
1.80
1.80
1.77
F
O
O2N
7c
1.82
1.90
1.00
0.99
1.01
1.08
1.06
1.03
1.04
1.21
f1 (ppm)


F
O
O_2N

7c

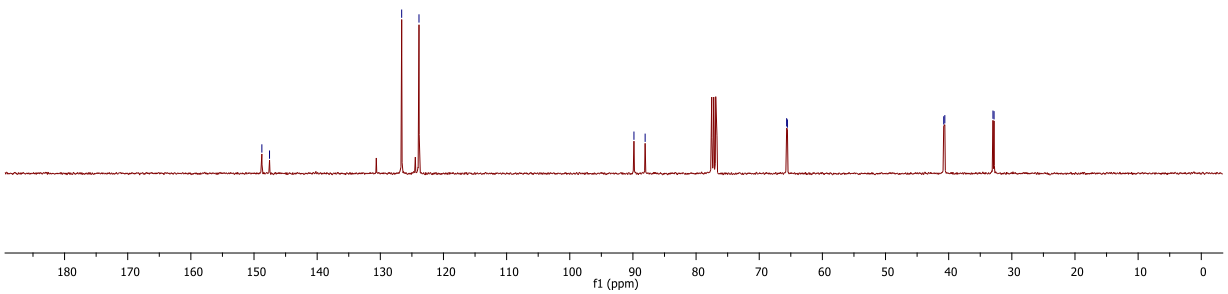

170.07
170.08
170.20
170.21

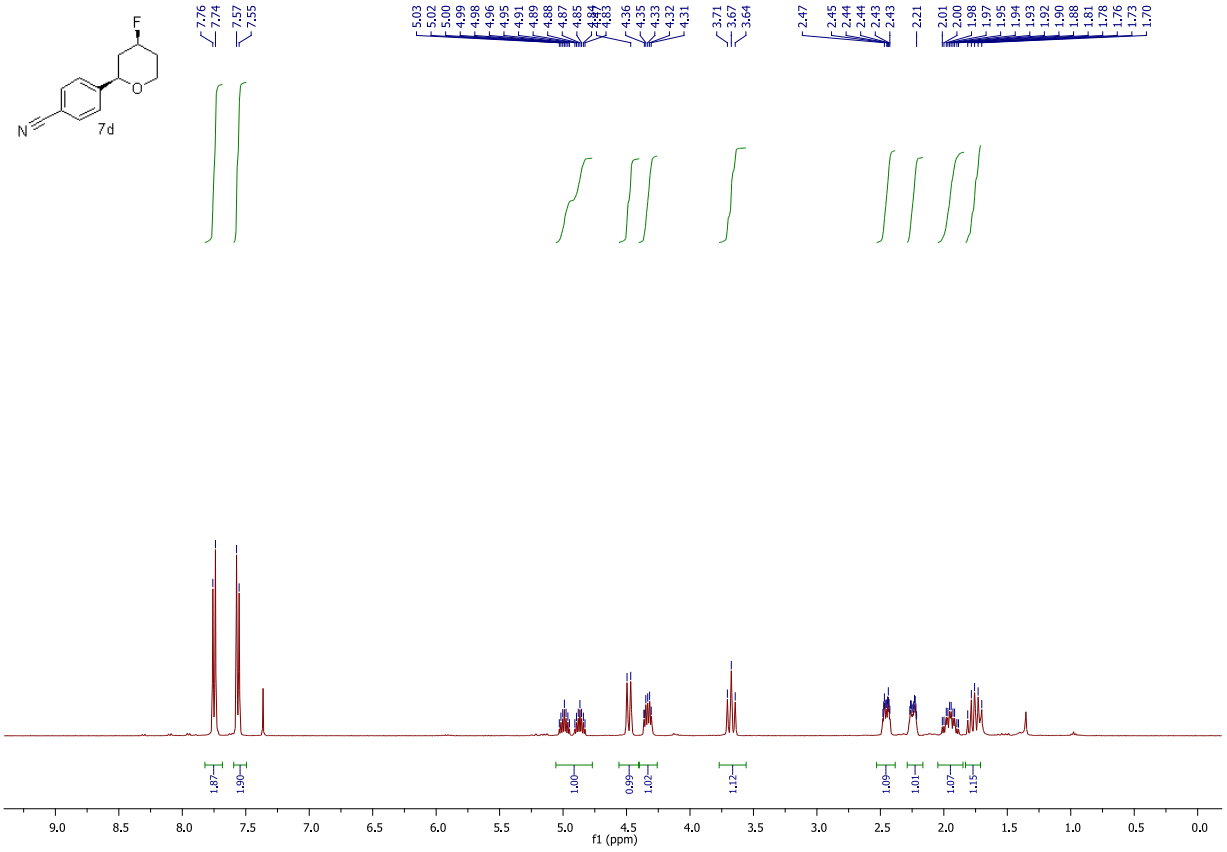

30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240 -250
f1 (ppm)

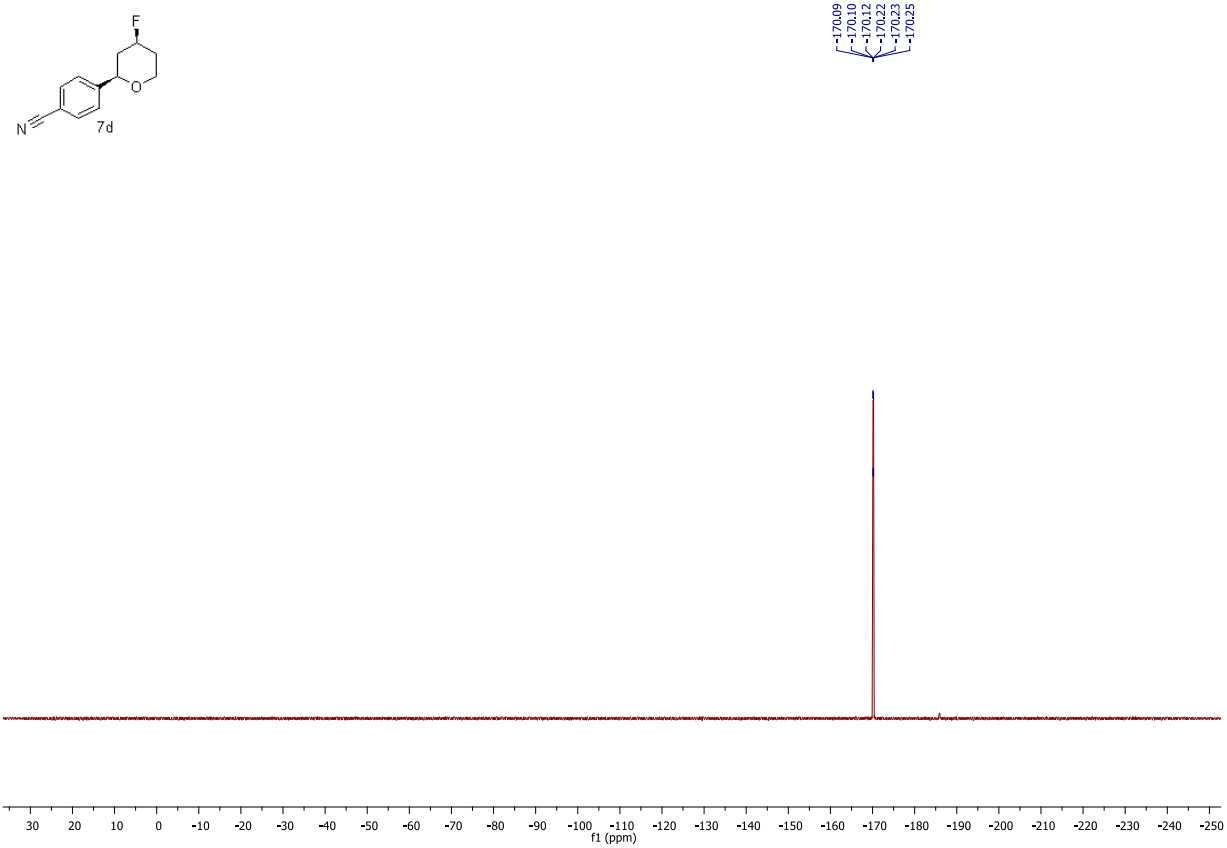

F
O
O_2N

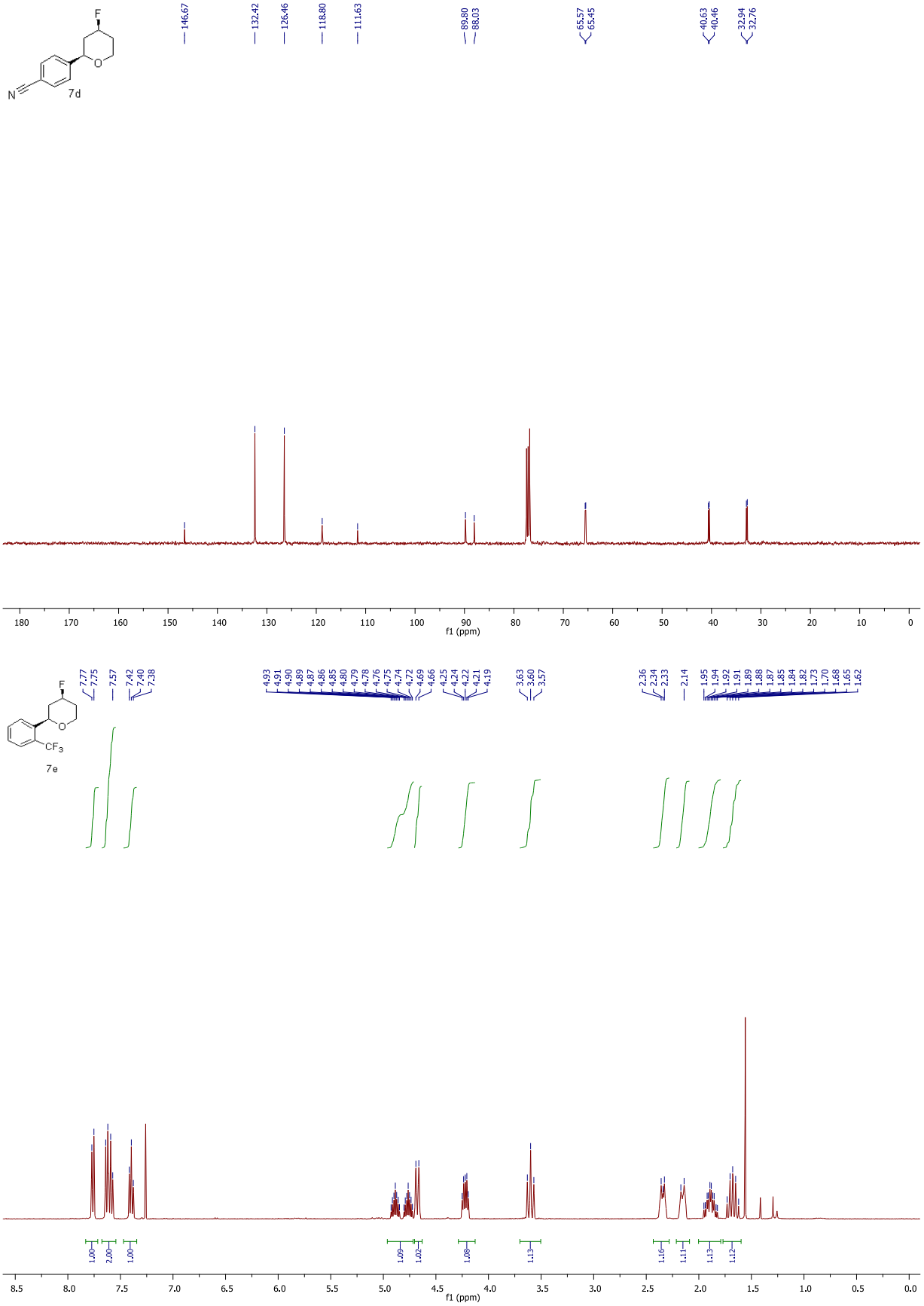
7c

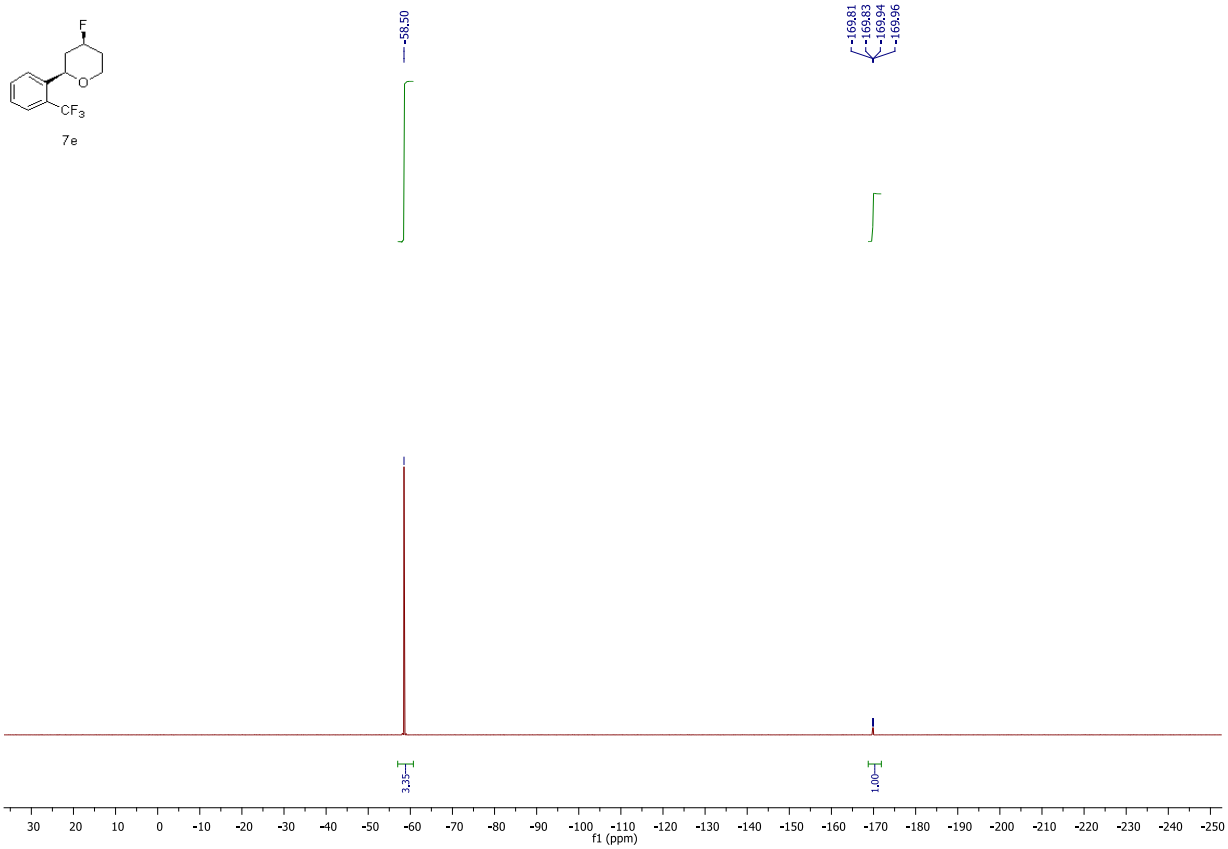

148.76
147.54
126.62
123.88
89.84
88.07
65.66
65.54
40.78
40.61
32.99
32.81

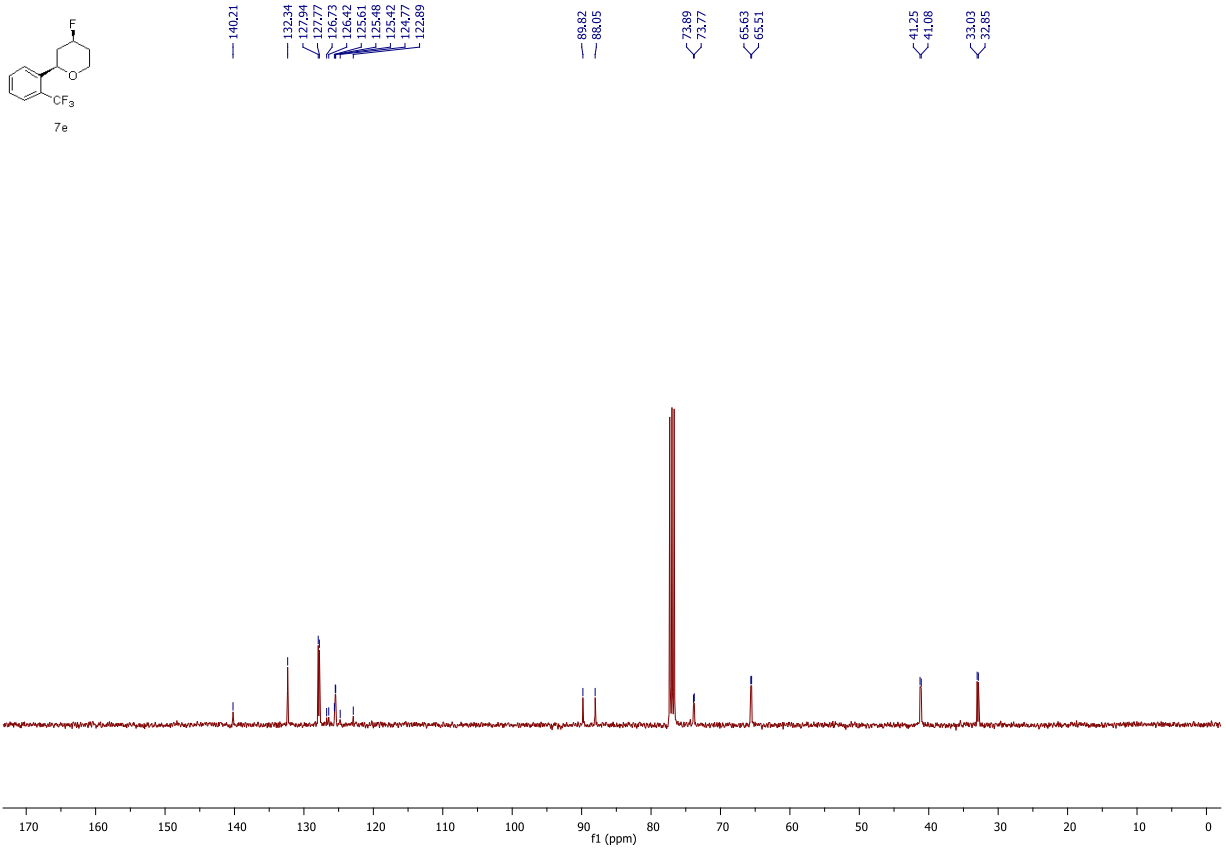

180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

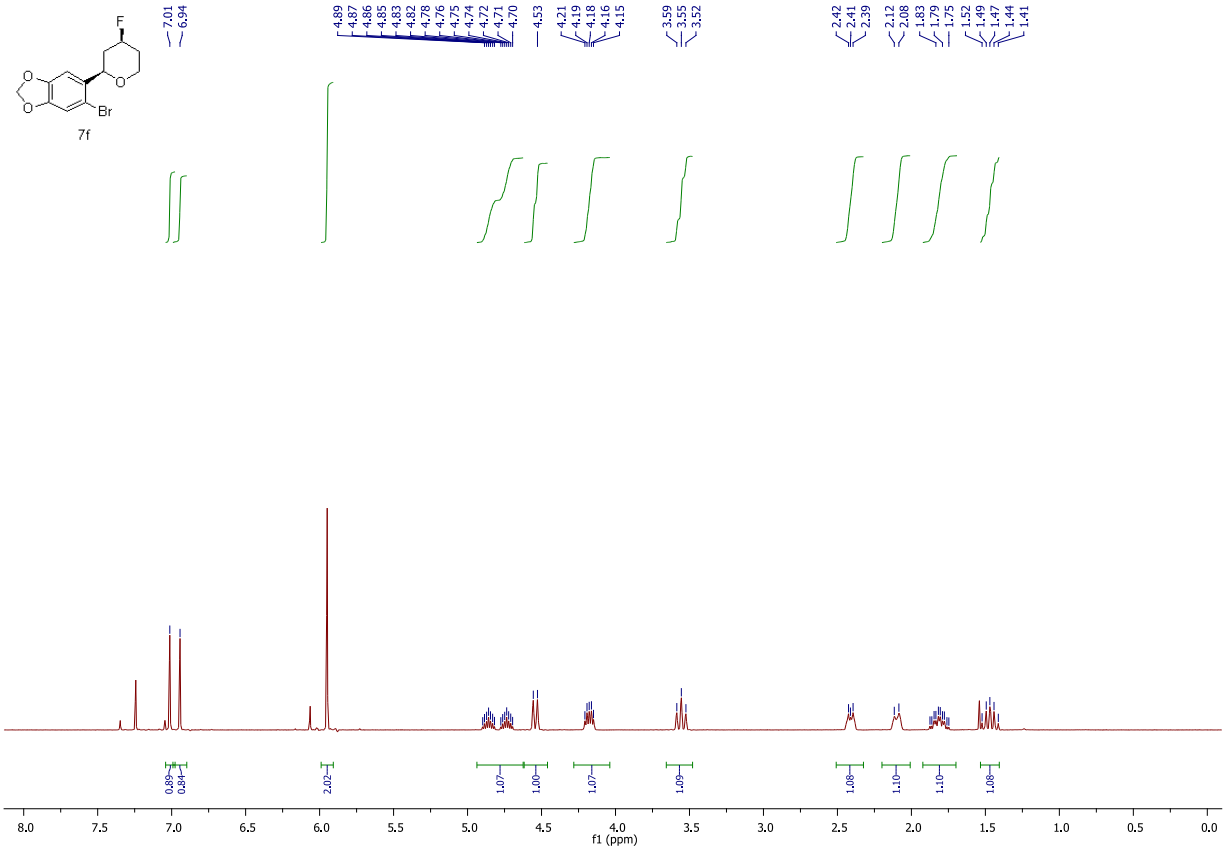

F
O
N
7d
7.76
7.74
7.57
7.55
5.03
5.02
5.00
4.99
4.98
4.96
4.95
4.91
4.89
4.88
4.87
4.85
4.84
4.83
4.36
4.35
4.33
4.32
4.31
3.71
3.67
3.64
2.47
2.45
2.44
2.44
2.43
2.43
2.21
2.01
2.00
1.98
1.97
1.95
1.94
1.93
1.92
1.90
1.88
1.81
1.78
1.76
1.73
1.70
1.87
1.90
1.00
0.99
1.02
1.12
1.09
1.01
1.07
1.15
f1 (ppm)

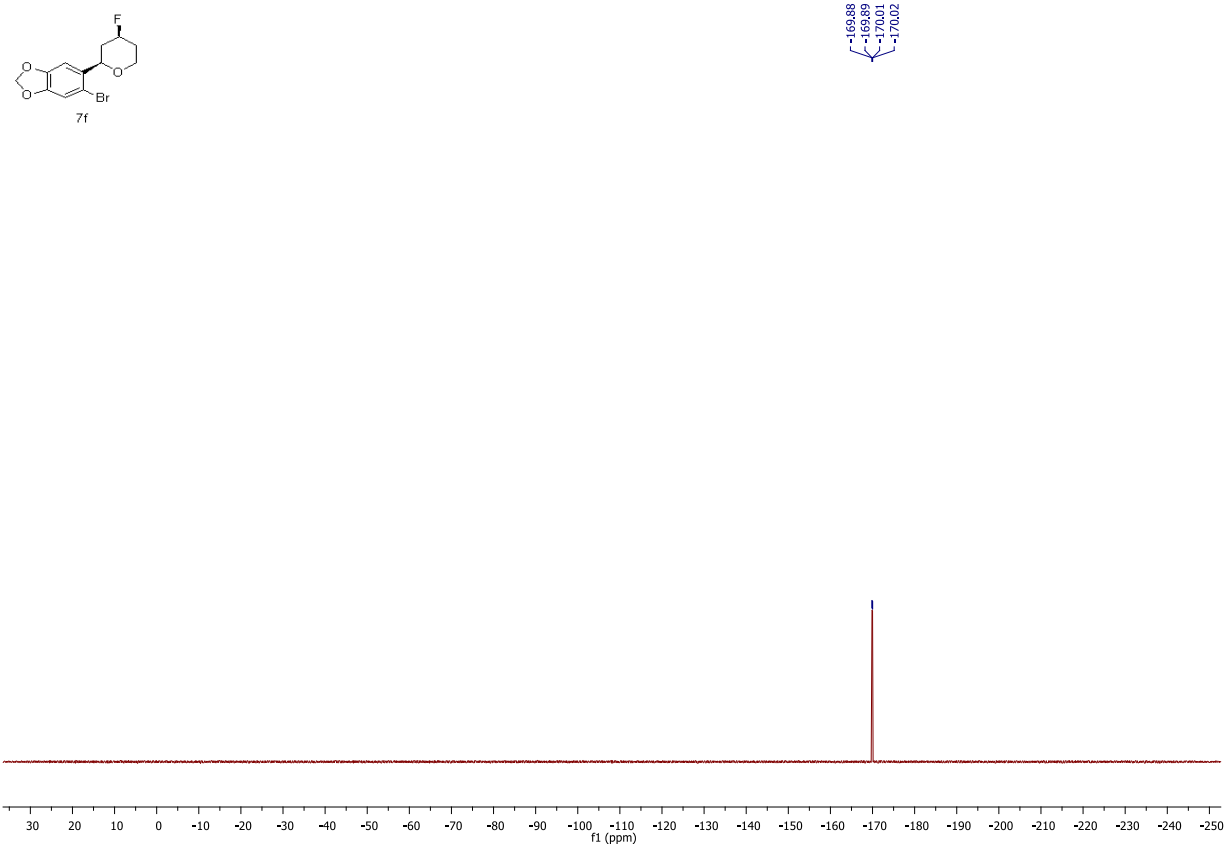

F
O
N
7d
-170.09
-170.10
-170.12
-170.22
-170.23
-170.25
f1 (ppm)

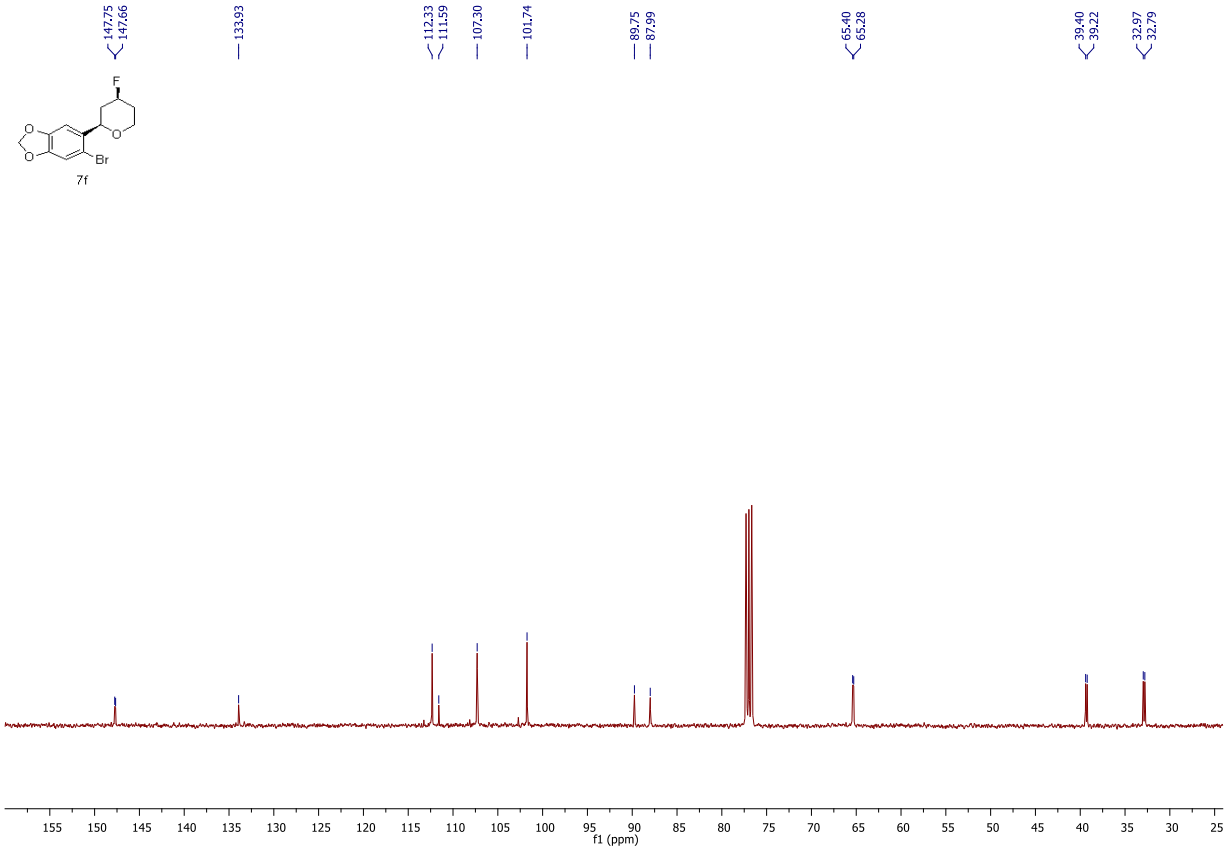

F
O
N
7d
146.67
132.42
126.46
118.80
111.63
89.80
88.03
65.57
65.45
40.63
40.46
32.94
32.76
f1 (ppm)
F
O
CF3
7e
7.77
7.75
7.57
7.42
7.40
7.38
4.93
4.91
4.90
4.89
4.87
4.86
4.85
4.80
4.79
4.78
4.76
4.75
4.74
4.72
4.69
4.66
4.25
4.24
4.22
4.21
4.19
3.63
3.60
3.57
2.36
2.34
2.33
2.14
1.95
1.94
1.92
1.91
1.89
1.88
1.87
1.85
1.84
1.82
1.73
1.70
1.68
1.65
1.62
1.00
2.00
1.00
1.09
1.02
1.08
1.13
1.16
1.11
1.13
1.12
f1 (ppm)

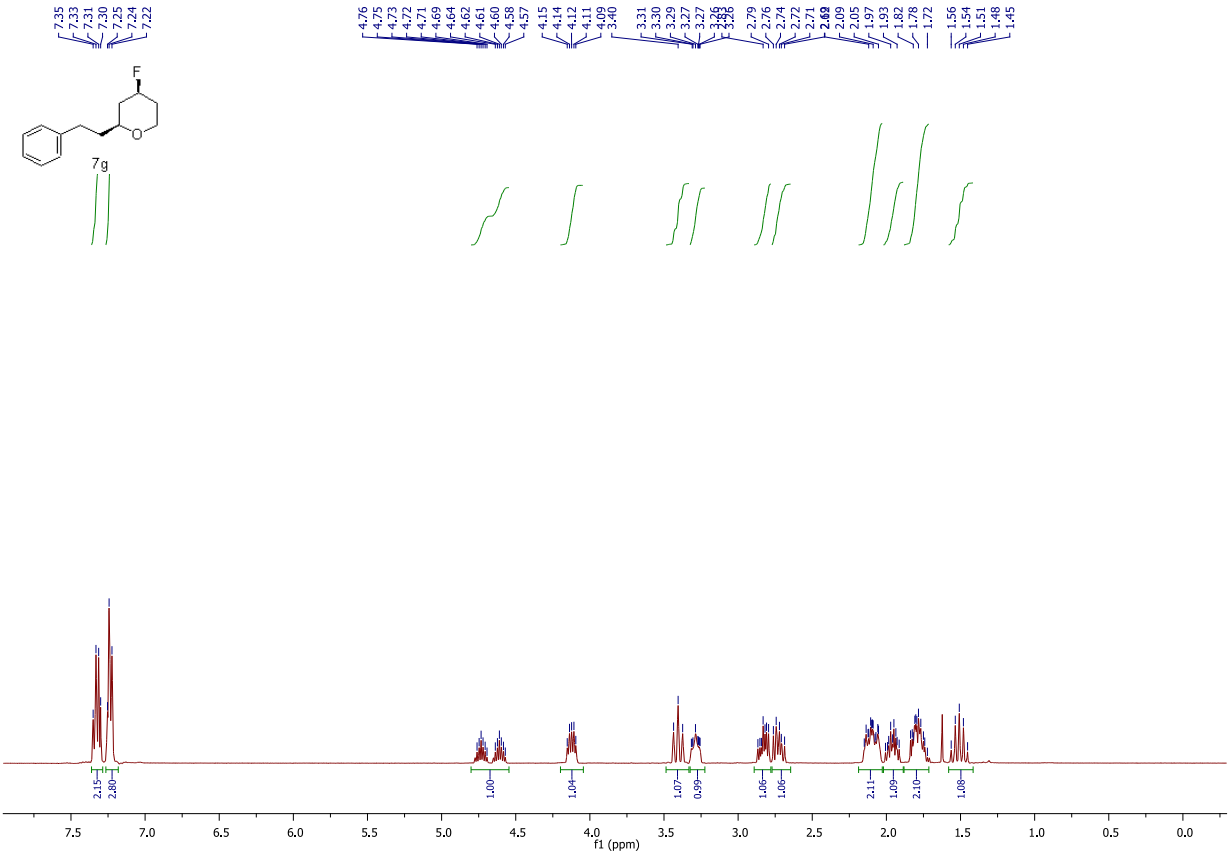

F
O
CF3
7e
-58.50
-169.81
-169.83
-169.94
-169.96
3.35
1.00
f1 (ppm)

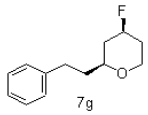

F
O
CF3
7e
140.21
132.34
127.94
127.77
126.73
126.42
125.61
125.48
125.42
124.77
122.89
89.82
88.05
73.89
73.77
65.63
65.51
41.25
41.08
33.03
32.85
f1 (ppm)


7.01
6.94
4.89
4.87
4.86
4.85
4.83
4.82
4.78
4.76
4.75
4.74
4.72
4.71
4.70
4.53
4.21
4.19
4.18
4.16
4.15
3.59
3.55
3.52
2.42
2.41
2.39
2.12
2.08
1.83
1.79
1.75
1.52
1.49
1.47
1.44
1.41
F
O
O
O
Br
7f
0.89
0.84
2.02
1.07
1.00
1.07
1.09
1.08
1.10
1.10
1.08
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

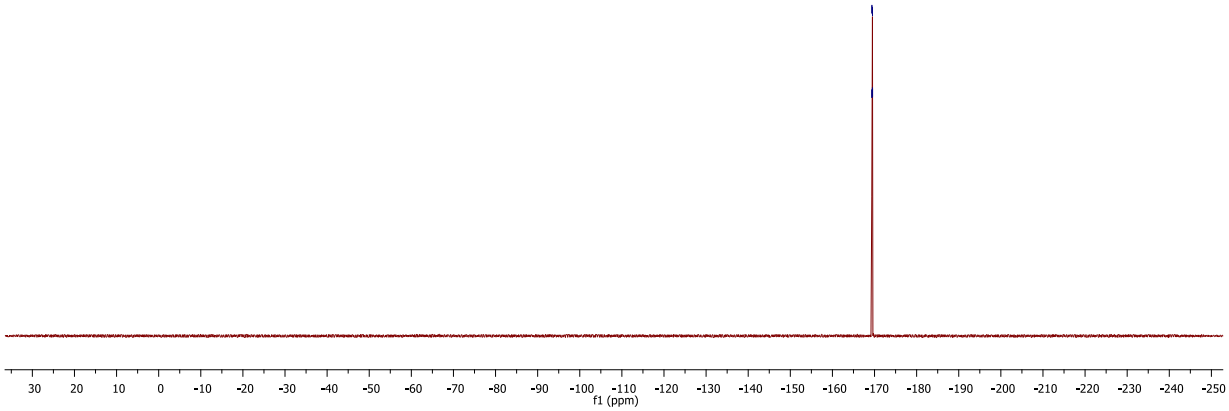

169.88
169.89
170.01
170.02
F
O
O
O
Br
7f
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
-220
-230
-240
-250
f1 (ppm)

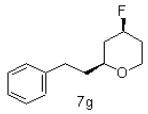

147.75
147.66
133.93
112.33
111.59
107.30
101.74
89.75
87.99
65.40
65.28
39.40
39.22
32.97
32.79
F
O
O
Br
7f
f1 (ppm)


7.35
7.33
7.31
7.30
7.25
7.24
7.22
4.76
4.75
4.73
4.72
4.71
4.69
4.64
4.62
4.61
4.60
4.58
4.57
4.15
4.14
4.12
4.11
4.09
3.40
3.31
3.30
3.29
3.27
3.27
2.79
2.76
2.74
2.72
2.71
2.09
2.05
1.97
1.93
1.82
1.78
1.72
1.56
1.54
1.51
1.48
1.45
F
O
7g
2.15
2.80
1.00
1.04
1.07
0.99
1.06
1.06
2.11
1.09
2.10
1.08
f1 (ppm)

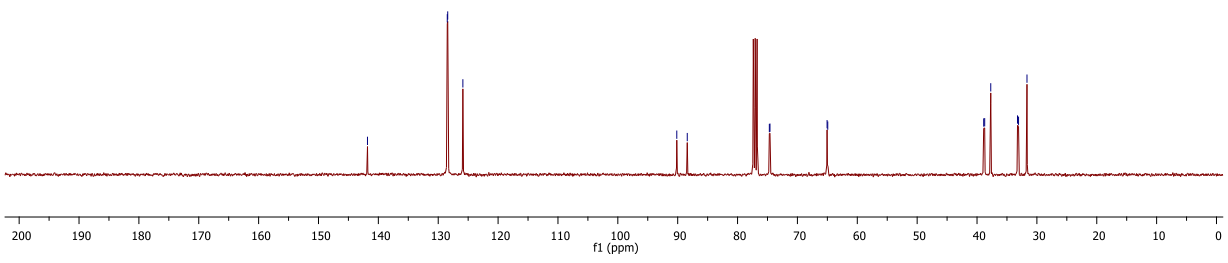

F
O
7g

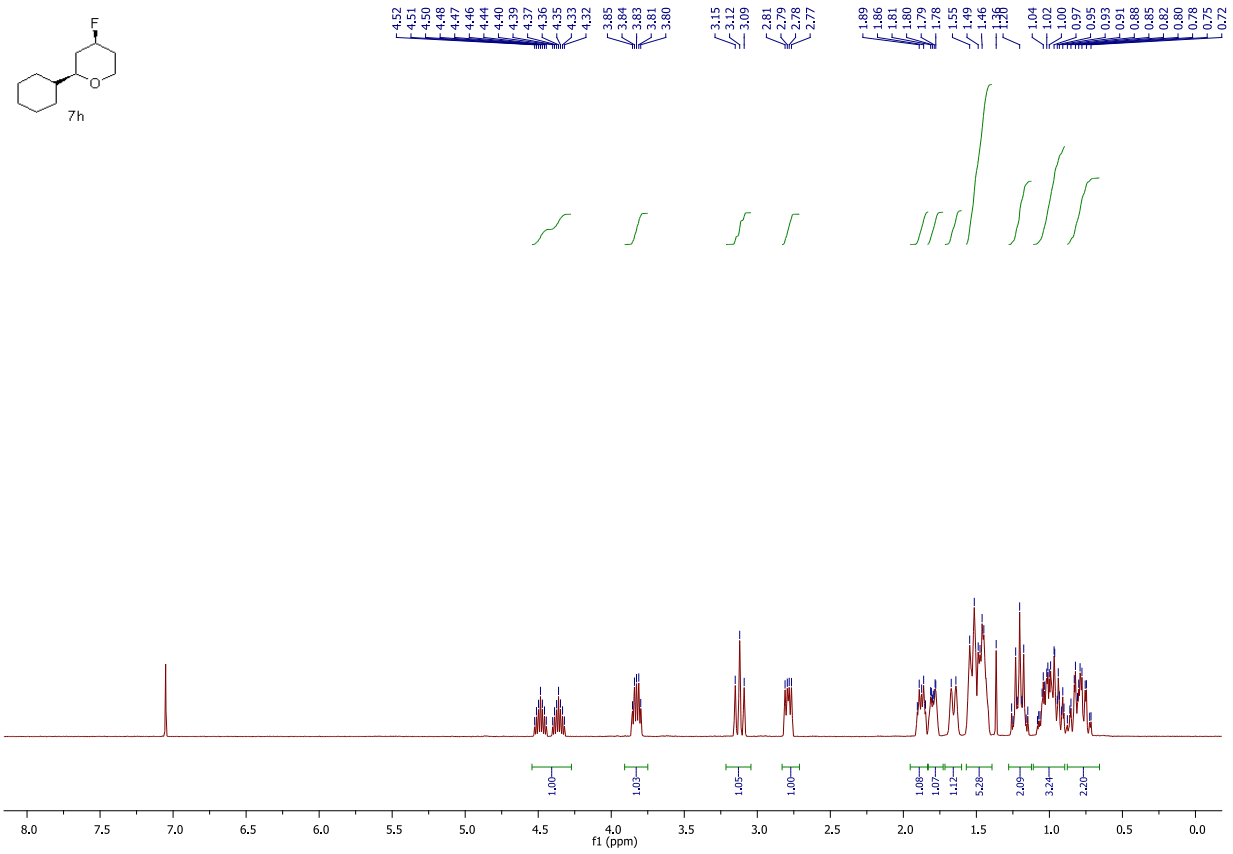

169.36
169.37
169.39
169.40
169.49
169.50
169.52
169.53

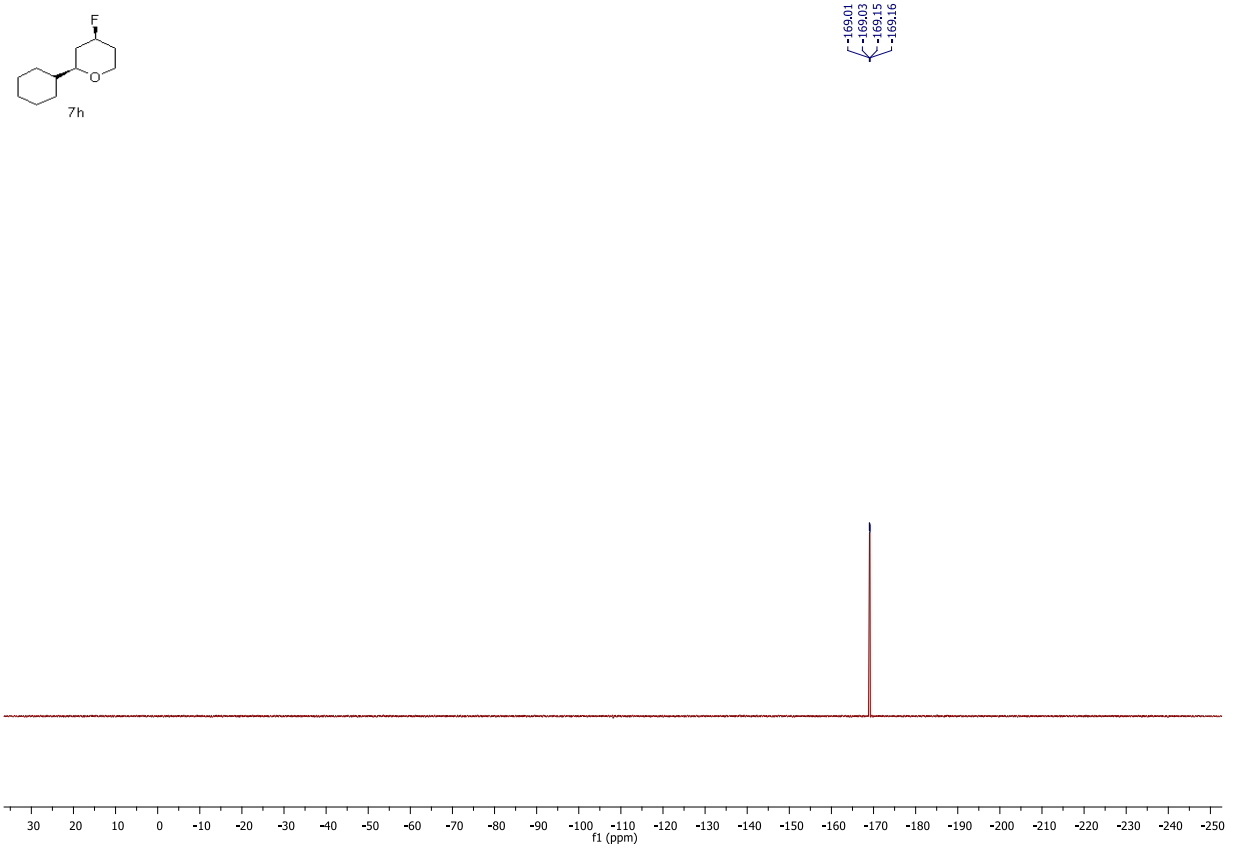

30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240 -250
f1 (ppm)

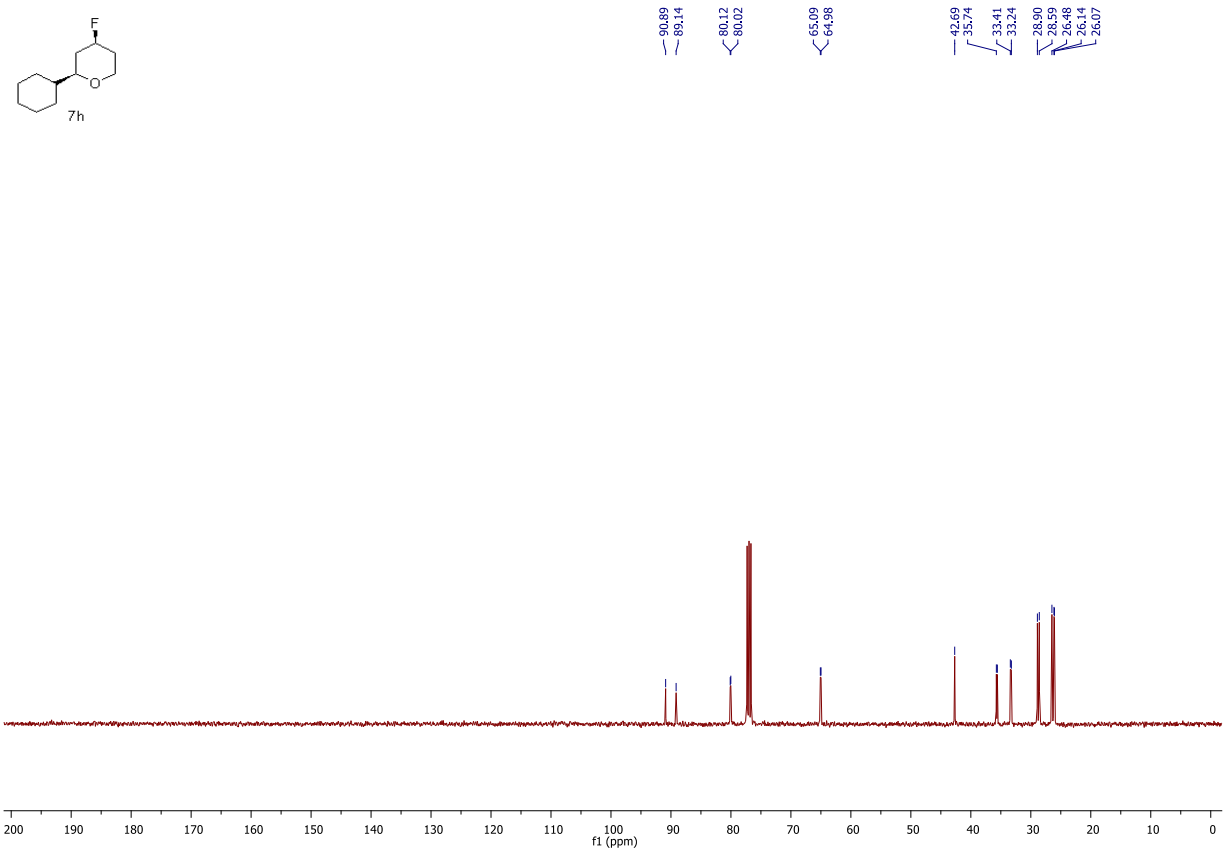

F
O
7g

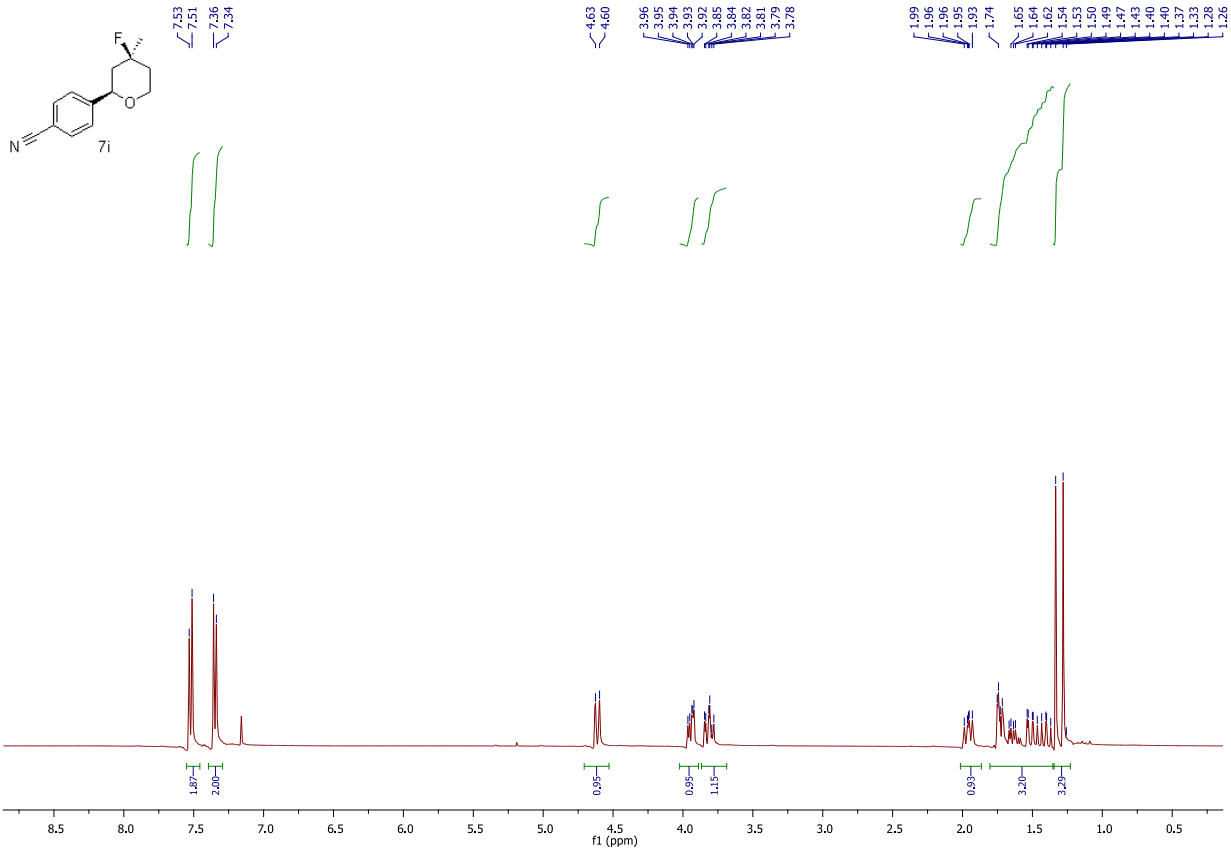

141.82
128.49
128.41
125.88
90.15
88.40
74.69
74.58
65.05
64.93
38.89
38.72
37.71
33.24
33.07
31.65

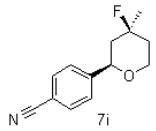

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


F
O
7h
4.52
4.51
4.50
4.48
4.47
4.46
4.44
4.40
4.39
4.37
4.36
4.35
4.33
4.32
3.85
3.84
3.83
3.81
3.80
3.15
3.12
3.09
2.81
2.79
2.78
2.77
1.89
1.86
1.81
1.80
1.79
1.78
1.55
1.49
1.46
1.36
1.04
1.02
1.00
0.97
0.95
0.93
0.91
0.88
0.85
0.82
0.80
0.78
0.75
0.72
1.00
1.03
1.05
1.00
1.08
1.07
1.12
5.28
2.09
3.24
2.20
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

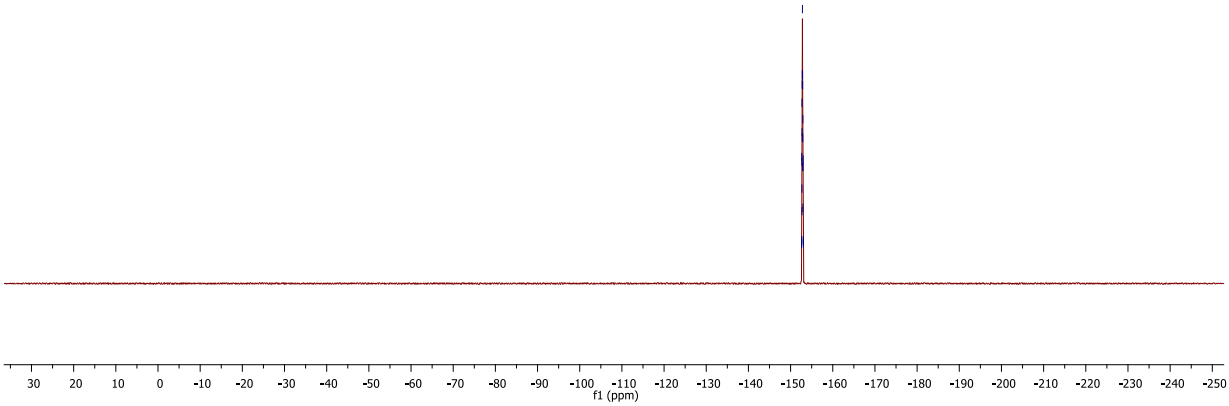

F
O
7h
-169.01
-169.03
-169.15
-169.16
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
-220
-230
-240
-250
f1 (ppm)

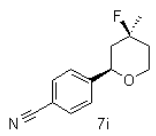

F
O
7h
90.89
89.14
80.12
80.02
65.09
64.98
42.69
35.74
33.41
33.24
28.90
28.59
26.48
26.14
26.07
f1 (ppm)


F
O
N
7i
7.53
7.51
7.36
7.34
4.63
4.60
3.96
3.95
3.94
3.93
3.92
3.85
3.84
3.82
3.81
3.79
3.78
1.99
1.96
1.96
1.95
1.93
1.74
1.65
1.64
1.62
1.54
1.53
1.50
1.49
1.47
1.43
1.40
1.40
1.37
1.33
1.28
1.26
1.87
2.00
0.95
0.95
1.15
0.93
3.20
3.29
f1 (ppm)

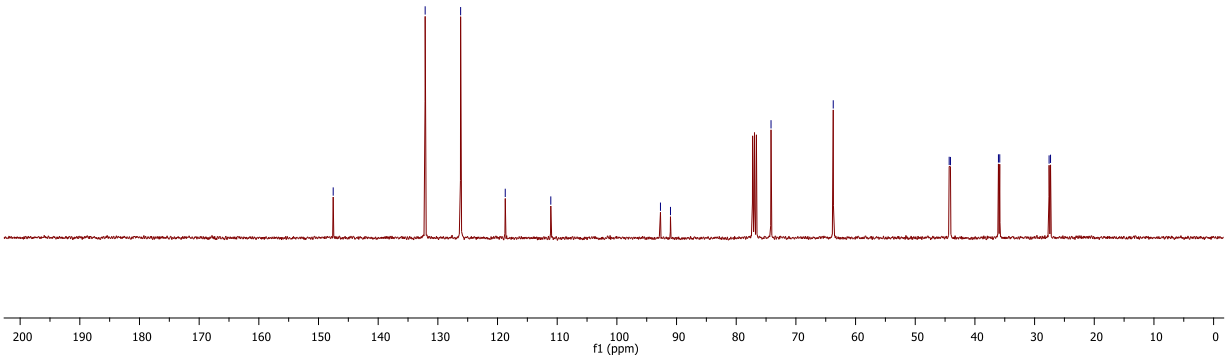

F
O
N
7i


152.59
152.62
152.65
152.67
152.68
152.70
152.71
152.73
152.75
152.76
152.78
152.81
152.83
152.85
152.86
152.88
152.91
152.92
152.94
152.96
153.00
153.02


30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240 -250
f1 (ppm)


F
O
N
7i


147.54
132.13
126.18
118.71
111.07
92.70
91.02
74.17
63.74
44.31
44.10
36.05
35.84
27.57
27.33


200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

Section 7. References

1. Okoromoba, O. E.; Li, Z.; Robertson, N.; Mashuta, M. S.; Couto, U. R.; Tormena, C. F.; Xu, B.; Hammond, G. B. *Chem. Commun.* **2016,** *52*, 13353-13356.
2. Lu, Z.; Zeng, X.; Hammond, G. B.; Xu, B. *J. Am. Chem. Soc.* **2017,** *139*, 18202-18205.
3. Okoromoba, O. E.; Hammond, G. B.; Xu, B. *Org. Lett.* **2015,** *17*, 3975-3977.