CHEMISTRY
A European Journal

Supporting Information

Fluoromethylene Transfer from Diarylfluoromethylsulfonium Salts: Synthesis of Fluorinated Epoxides

Janis Veliks* and Armands Kazia[a]

chem_201900349_sm_miscellaneous_information.pdf

Table of Contents

General Remarks

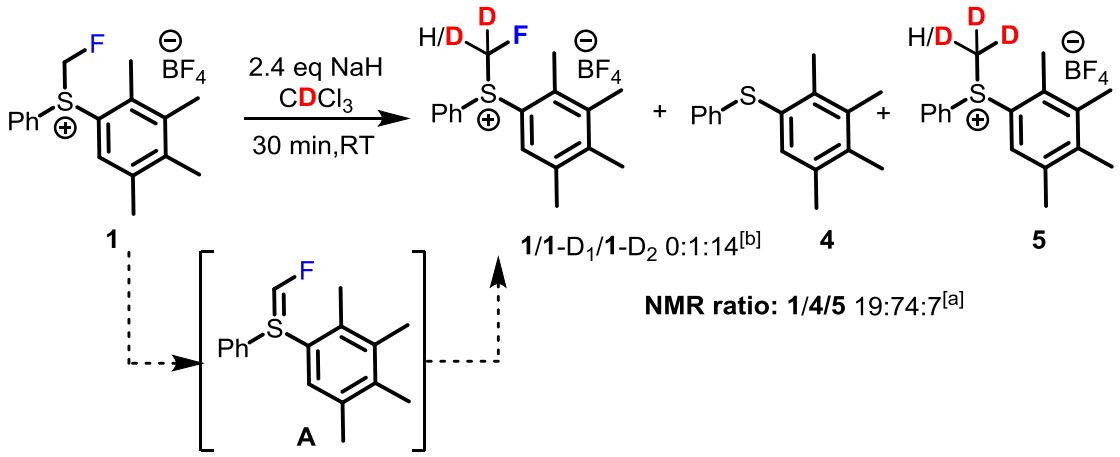
All procedures were performed under argon atmosphere unless noted otherwise. Reagents and starting materials were obtained from commercial sources and used as received. Ketones or aldehydes **2** were purchased form Fluorochem, Sigma Aldrich, Acros or Alfa Aeser and used as received. The solvents were purified and dried by standard procedures prior to use. Flash column chromatography was carried out using silica gel (230 − 400 mesh) or neutral aluminium oxide Brockmann III. Thin layer chromatography (TLC) was performed on silica gel using Merck TLC Silca gel 60 F_{254} Aluminium sheets pretreated with 2% Et_3N in petroleum ether (PE) and was visualized by UV lamp or staining with anisaldehyde stain. NMR spectra were recorded on 300, 400 and 600 MHz spectrometers with chemical shift values (δ) in parts per million using the residual chloroform signal as an internal standard. HRMS analyses were performed on a hybrid quadrupole time - of - flight mass spectrometer equipped with an electrospray ion source. Elemental analyses were performed by analytical service of LIOS.

A feasibility investigation of diaryl sulfur fluoromethylylide

Synthesis of S-fluoromethyl-S-phenyl-2,3,4,5-tetramethylphenylsulfonium tetrafluoroborate (1)

S-Fluoromethyl-S-phenyl-2,3,4,5-tetramethylphenylsulfonium tetrafluoroborate (**1**) was prepared following the literature procedure.[1]

Deuteration experiment of S-fluoromethyl-S-phenyl-2,3,4,5-tetramethylphenylsulfonium tetrafluoroborate (1)



To a solution of sulfonium salt **1** (20 mg, 0.055 mmol, 1 equiv) in dry $CDCl_3$ (0.7 mL) under Ar atmosphere was added 60% NaH (5.3 mg, 0.13 mmol, 2.4 equiv) at room temperature. The reaction mixture was stirred for 30 min at room temperature and then analyzed by NMR. ^{1}H NMR showed disappearance of the characteristic CFH_2 signal of **1** at ~6.5 ppm (Fig. S1 **A** vs. **B**). ^{1}H NMR ratio[a] of **1**-$D_{1,2}$/**4**/**5**[2] 19/74/7. ^{19}F NMR ratio[b] of **1**/**1**-D_1/**1**-D_2 0/1/14.

[1] G. K. S. Prakash, I. Ledneczki, S. Chacko, G. A. Olah, *Org. Lett.* **2008**, *10*, 557–560.
[2] Pat. WO2012/131286 A1

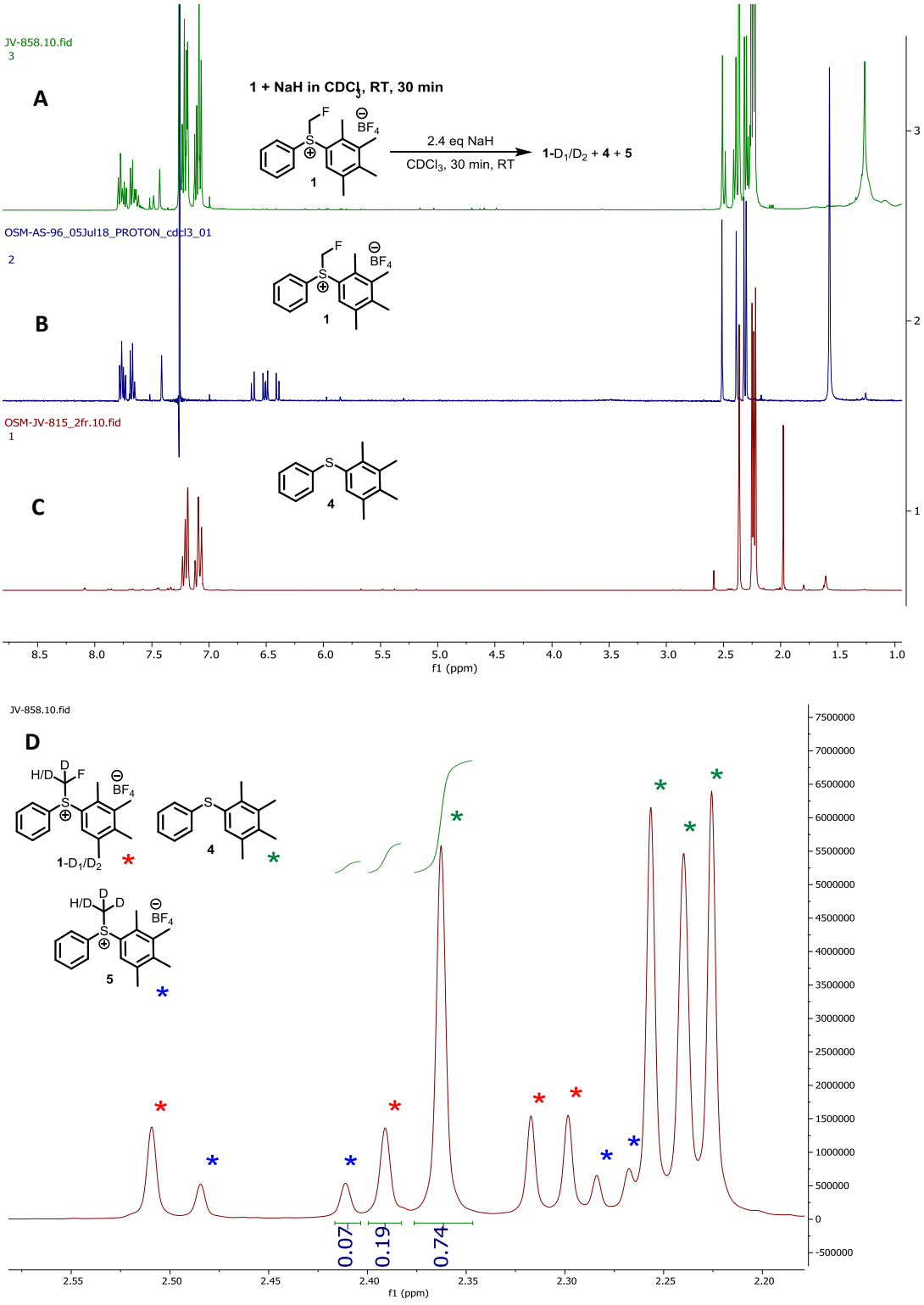


Figure S1. **A** ^{1}H NMR of the deuteration experiment of **1** with NaH in $CDCl_3$. **B** ^{1}H NMR of **1**. **C** ^{1}H NMR of **4**. **D** Selected region of ^{1}H NMR representing methyl groups of 1,2,3,4-tetramethylphenyl moiety in **1**, **4** and **5**.

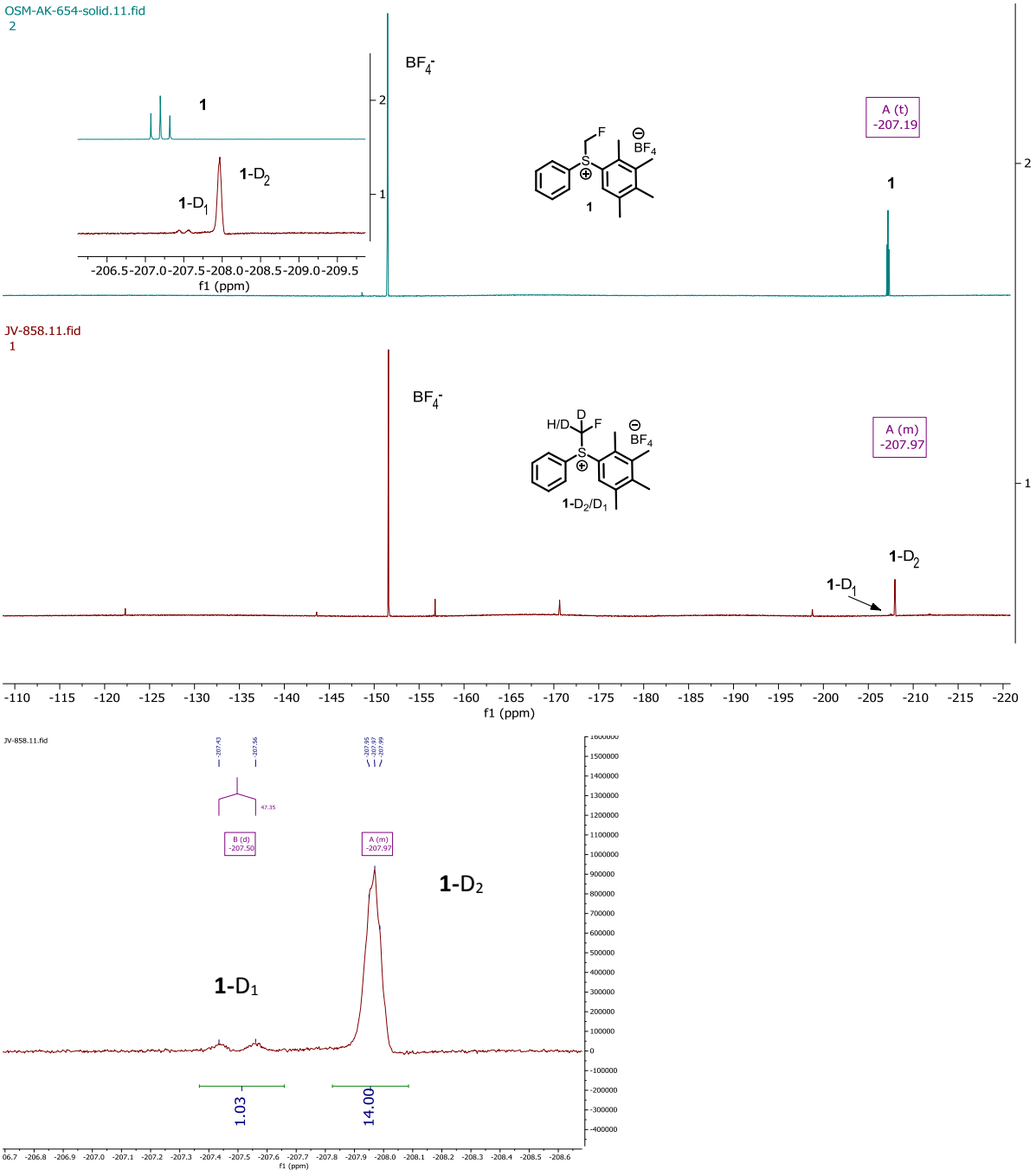
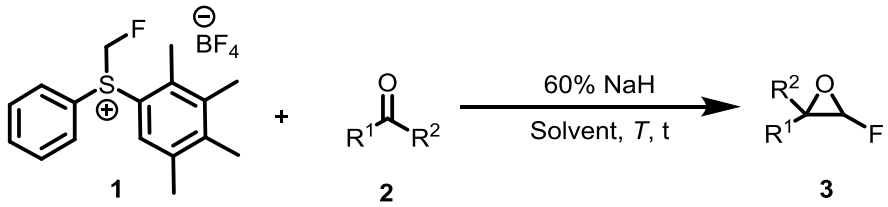


Figure S2. ^{19}F NMR of the deuteration experiment of sulfonium salt **1** with NaH in $CDCl_3$.

General procedure for the synthesis of fluoroepoxides 3 from ketones and aldehydes 2



Method A

To a solution of sulfonium salt **1** (75.0 mg, 0.207 mmol, 1.5 equiv) and ketone or aldehyde **2** (0.138 mmol, 1 equiv) in dry MeCN (2.8 mL) under Ar atmosphere was added 60% NaH (in mineral oil, 8.84 mg, 0.221 mmol, 1.6 equiv) at 0 °C. The reaction mixture was stirred at this temperature for 3-6 h. After completion (TLC control) the reaction mixture was worked up following the isolation methods **A**, **B** or **C**.

Method B

To a solution of sulfonium salt **1** (75.0 mg, 0.207 mmol, 1.5 equiv) and ketone or aldehyde **2** (0.138 mmol, 1 equiv) in dry $CHCl_3$ (1.4 mL) under Ar atmosphere was added 60% NaH (in mineral oil, 22.1 mg, 0.553 mmol, 4.0 equiv) at 0 °C. The reaction mixture was stirred at this temperature. If after 1 h (TLC control) starting material **2** is still present then additional portion of **1** (25 mg, 0.069 mmol, 0.5 equiv) can be added to reach full conversion. After completion (TLC control) (typically 2 to 5 h) the reaction mixture was worked up following the isolation methods **A**, **B** or **C**.

Isolation A

After completion (TLC control) the reaction was quenched with pentane (7 mL) then water (7 mL) at 0 °C. The organic phase was separated and the aqueous phase was extracted with pentane (7 mL x 2). The combined organic phases were directly poured on a neutral Al_2O_3 (Brockmann III) column and eluted with pentane till all phenyl(2,3,4,5-tetramethylphenyl)sulfane (**4**) was eluted. Then the eluent was switched to pentane:Et_2O. The solvent from the combined product fractions was evaporated under reduced pressure to give the desired product **3**.

Isolation B

After completion (TLC control) the reaction mixture was evaporated under reduced pressure ((*) The flask was kept above heating bath of the rotavap. Immersed only for a short time to remove formed ice on the flask). The residue was treated with pentane:Et_2O 40:7 (2.5 mL x 3) and filtered through a cotton plug. The filtrate was evaporated under reduced pressure (see above (*)). The crude product was dissolved in small amount of petroleum ether (PE) or Et_2O and applied on the analytical silica gel TLC plate (20 x 20 cm,

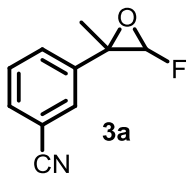
pretreated with 2% TEA in PE[3]). The crude mixture was separated using PE:EtOAc. The product containing bands were scraped off. The obtained silica gel was suspended in EtOAc, filtered and washed with EtOAc till no product detected in filtrate by TLC. The solvent was evaporated under reduced pressure (see above (*)) to give the desired product **3**.

Isolation C

The residue containing a mixture of fluoroepoxide **3** and sulfide **4** was dissolved in $CHCl_3$ (3 mL) and O_3/O_2 was passed through a solution (~1 to 2 min) till TLC showed complete consumption of sulfide **4**. Solvent was evaporated under reduced pressure. The residue was purified by silica gel column chromatography (pretreated with 2% Et_3N in PE) to give the desired product **3**.

Characterization data of fluoroepoxides 3

3-(3-Fluoro-2-methyloxiran-2-yl)benzonitrile (3a)



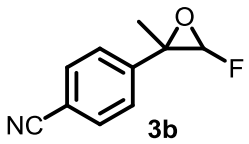
The general procedure **A** was followed using **2a** (20.0 mg, 0.138 mmol) at 0 °C for 4 h. Purification (Isolation **B**) by silicagel prep TLC (pretreated wtih 2% Et_3N in petroleum ether) PE:EtOAc 10:1 yielded *trans*-**3a** (12 mg, 49%) and *cis*-**3a** (12 mg, 49%) as a colorless oils. Total yield of **3a** (24 mg, 98%) d.r 1:1.

trans-**3a:** ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.60 – 7.39 (m, 4H), 5.28 (dd, *J* = 87.5, 0.4 Hz, 1H), 1.76 (dd, *J* = 1.2, 0.4 Hz, 3H). ^{13}C NMR (75 MHz, Chloroform-*d*) δ 139.5 (d, *J* = 3.9 Hz), 132.1, 129.9, 129.7, 129.3, 118.4, 113.2, 93.3 (d, *J* = 278.1 Hz), 60.8 (d, *J* = 17.2 Hz), 16.2. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -150.79 (d, *J* = 87.6 Hz). Unstable under HRMS conditions.

cis-**3a:** ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.72 (t, *J* = 1.8 Hz, 1H), 7.65 (ddt, *J* = 9.2, 8.0, 1.4 Hz, 2H), 7.50 (t, *J* = 7.8 Hz, 1H), 5.57 (d, *J* = 87.6 Hz, 1H), 1.66 (d, *J* = 2.7 Hz, 3H). ^{13}C NMR (75 MHz, Chloroform-*d*) δ 137.6 (d, *J* = 4.1 Hz), 132.0, 131.3, 130.7 (d, *J* = 4.5 Hz), 129.3, 118.6, 112.8, 93.2 (dd, *J* = 271.1, 5.1 Hz), 61.9 (d, *J* = 17.2 Hz), 20.36 – 20.00 (m). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -155.05 (dd, *J* = 87.5, 2.3 Hz). Unstable under HRMS conditions.

[3] T. Luo, R. Zhang, X. Shen, W. Zhang, C. Ni, J. Hu, *Dalton Trans.* **2015**, *44*, 19636–19641.

4-(3-Fluoro-2-methyloxiran-2-yl)benzonitrile (3b)

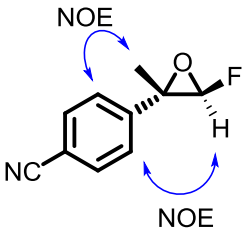


3b

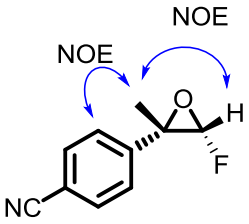
The general procedure **A** was followed using **2b** (20.0 mg, 0.138 mmol) at 0 °C for 1 h. Purification (Isolation **A**) by neutral Al_2O_3 (Brockmann III) (pentane then pentane:Et_2O 97:3) yielded **3b** (18.7 mg, 77%) trans/cis d.r. 1.2:1 as a colorless oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.67 – 7.62 (m, 4H)^{cis,trans}, 7.56 – 7.49 (m, 2H)^{cis}, 7.42 – 7.36 (m, 2H)^{trans}, 5.56 (d, *J* = 87.6 Hz, 1H)^{cis}, 5.32 (d, *J* = 87.8 Hz, 1H)^{trans}, 1.81 – 1.80 (d, *J* = 1.1 Hz, 3H)^{trans}, 1.64 (d, *J* = 2.8 Hz, 3H)^{cis}. ^{13}C NMR (101 MHz, Chloroform-*d*) δ 142.9 (d, *J* = 3.9 Hz), 141.1 (d, *J* = 4.3 Hz), 132.5, 132.2, 127.7, 126.40, 118.6, 118.4, 112.5, 112.3, 93.3 (d, *J* = 276.4 Hz), 93.3 (d, *J* = 271.3 Hz) , 62.2 (d, *J* = 17.2 Hz), 61.1 (d, *J* = 17.0 Hz), 20.1 (d, *J* = 4.3 Hz), 16.1 (d, *J* = 3.1 Hz).^{19}F NMR (376 MHz, Chloroform-*d*) δ -150.6 (d, *J* = 87.5 Hz)^{trans}, -154.9 (dq, *J* = 87.7, 2.7 Hz)^{cis}. Elemental analysis calculated for $C_{10}H_8FNO$: C, 67.79; H, 4.55; N, 7.91. Found: C, 68.00; H, 4.72; N, 7.50. Unstable under HRMS conditions.

Diastereomers could be separated using isolation method **B** by silicagel prep TLC (pretreated wtih 2% Et_3N in petroleum ether) PE:EtOAc 10:1.

Relative configuration of diastereomers was determined by 2D NOESY experiments.

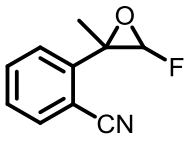


trans-**3b**: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.70 – 7.62 (m, 2H), 7.45 – 7.39 (m, 2H), 5.34 (d, *J* = 87.7 Hz, 1H), 1.83 (d, *J* = 1.1 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 143.0 (d, *J* = 3.9 Hz), 132.6, 126.4, 118.4, 112.5, 93.3 (d, *J* = 276.9 Hz), 61.1 (d, *J* = 17.0 Hz), 16.1 (d, *J* = 3.2 Hz). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -150.58 (d, *J* = 87.8 Hz).



cis-**3b**: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.70 – 7.65 (m, 2H), 7.56 – 7.52 (m, 2H), 5.58 (d, *J* = 87.6 Hz, 1H), 1.66 (d, *J* = 2.8 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 141.1 (d, *J* = 4.4 Hz), 132.2, 127.8, 118.6, 112.3, 93.3 (d, *J* = 271.3 Hz), 62.2 (d, *J* = 17.2 Hz), 20.1 (d, *J* = 4.3 Hz). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -154.82 (dq, *J* = 87.4, 2.9 Hz).

2-(3-Fluoro-2-methyloxiran-2-yl)benzonitrile (3c)

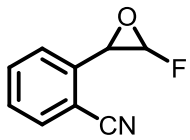


3c

The general procedure **A** was followed using **2c** (20.0 mg, 0.138 mmol) at 0 °C for 3 h. Purification (Isolation **B**) by silicagel prep TLC (pretreated wtih 2% Et_3N in petroleum ether) PE:EtOAc 10:1 yielded **3c** (19.3 mg, 79%) trans/cis d.r. 1.2:1 as a colorless oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.72 – 7.66 (m, 2H)$^{trans, cis}$, 7.65 – 7.58 (m, 3H)$^{trans, cis}$, 7.51 – 7.41 (m, 3H)^{trans,cis}, 5.67 (d, *J* = 86.4 Hz, 1H)^{cis}, 5.53 (dd, *J* = 86.7, 0.7 Hz, 1H)^{trans}, 1.84 (s, 3H)^{trans}, 1.68 (d, *J* = 2.7 Hz, 3H)^{cis}. ^{13}C NMR (101 MHz,) δ 142.2 (d, *J* = 4.2 Hz), 140.7 (d, *J* = 4.3 Hz), 133.4, 133.3, 133.2, 132.9, 129.0, 128.9, 128.5, 127.6, 127.6, 117.3, 117.1, 110.8, 110.3, 92.8 (d, *J* = 265.4 Hz), 92.7 (d, *J* = 280.4 Hz), 62.1 (d, *J* = 17.4 Hz), 61.7 (d, *J* = 17.4 Hz), 21.0 (d, *J* = 4.4 Hz), 17.9 (d, *J* = 2.9 Hz). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -151.08 (dq, *J* = 86.4, 2.7 Hz)^{cis}, -154.93 (d, *J* = 87.1 Hz)^{trans}. Elemental analysis calculated for $C_{10}H_8FNO$: C, 67.79; H, 4.55; N, 7.91. Found: C, 67.83; H, 4.92; N, 7.54. Unstable under HRMS conditions.

2-(3-Fluorooxiran-2-yl)benzonitrile (3d)

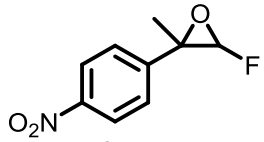


3d

The general procedure **A** was followed using **2d** (18.7 mg, 0.138 mmol) at 0 °C for 2.5 h. Purification (Isolation **A**) by neutral Al_2O_3 (Brockmann III) (pentane then pentane:Et_2O 97:3) yielded **3d** (7.2 mg, 32%) cis/trans d.r. 1.2:1 as a colorless oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.74 – 7.68 (m, 2H)$^{cis, trans}$, 7.67 – 7.59 (m, 2H)$^{cis, trans}$, 7.57 – 7.51 (m, 1H)^{cis}, 7.51 – 7.45 (m, 2H)$^{cis, trans}$, 7.24 – 7.20 (m, 1H), 5.85 (dd, *J* = 87.9, 2.2 Hz, 1H)^{cis}, 5.47 (d, *J* = 84.7 Hz, 1H)^{trans}, 4.49 (d, *J* = 2.4 Hz, 1H)^{trans}, 4.27 (t, *J* = 2.2 Hz, 1H)^{cis}. ^{13}C NMR (101 MHz, Chloroform-*d*) δ 136.8 (d, *J* = 3.8 Hz), 135.5 (d, *J* = 4.7 Hz), 133.3, 133.2, 132.9, 132.8, 129.5, 129.2, 127.9 (d, *J* = 2.3 Hz), 125.7 (d, *J* = 1.7 Hz), 116.9, 116.7, 111.9, 111.7, 90.0 (d, *J* = 277.7 Hz), 89.2 (d, *J* = 270.8 Hz), 55.3 (d, *J* = 17.8 Hz), 55.0 (d, *J* = 19.4 Hz). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -145.74 (dd, *J* = 84.8, 2.2 Hz)^{trans}, -163.12 (dt, *J* = 88.2, 2.1, 1.5 Hz)^{cis}. Unstable under HRMS conditions.

3-Fluoro-2-methyl-2-(4-nitrophenyl)oxirane (3e)



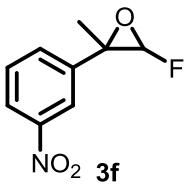
3e

The general procedure **A** was followed using **2e** (22.8 mg, 0.138 mmol) at 0 °C for 2.5 h. Purification (Isolation **A**) by neutral Al_2O_3 (Brockmann III) (pentane then pentane:Et_2O 97:3) yielded **3e** (26.3 mg, 97%) trans/cis d.r. 1.1:1 as a colorless oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.26 – 8.24 (m, 2H)^{cis}, 8.23 (m, 2H)^{trans}, 7.64 – 7.56 (m, 2H)^{cis}, 7.53 – 7.42 (m, 2H)^{trans}, 5.60 (d, *J* = 87.5 Hz, 1H)^{cis}, 5.36 (dq, *J* = 87.6, 0.6 Hz, 1H)^{trans}, 1.86 (dd, *J* = 1.2, 0.6 Hz, 3H)^{trans}, 1.69 (d, *J* = 2.8 Hz, 3H)^{cis}. ^{13}C NMR (101 MHz, Chloroform-*d*) δ 148.0, 147.9, 144.8 (d, *J* = 3.8 Hz), 143.0 (d, *J* = 4.2 Hz), 128.0, 126.7, 124.0, 123.6, 93.3 (d, *J* = 277.2 Hz), 93.3 (d, *J* = 271.6 Hz), 62.2 (d, *J* = 16.9 Hz), 61.1 (d, *J* = 17.1 Hz), 20.2 (d, *J* = 4.3 Hz), 16.3 (d, *J* = 3.2 Hz). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -150.65 (d, *J* = 87.6 Hz)^{trans}, -154.78 (dq, *J* = 87.3, 2.8 Hz)^{cis}. Elemental

analysis calculated for $C_9H_8FNO_3$: C, 54.83; H, 4.09; N, 7.10. Found: C, 55.27; H, 4.19; N, 6.87. Unstable under HRMS conditions.

3-Fluoro-2-methyl-2-(3-nitrophenyl)oxirane (3f)

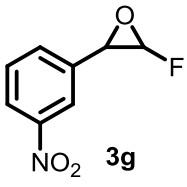


3f

The general procedure **A** was followed using **2f** (22.8 mg, 0.138 mmol) at 0 °C for 2.5 h. Purification (Isolation **A**) by neutral Al_2O_3 (Brockmann III) (pentane then pentane:Et_2O 97:3) yielded **3f** (23.2 mg, 85%) trans/cis d.r. 1.2:1 as a colorless oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.30 (ddt, *J* = 2.2, 1.7, 0.5 Hz, 1H), 8.22 – 8.16 (m, 3H)^{trans,cis}, 7.79 – 7.74 (m, 1H), 7.66 – 7.61 (m, 1H), 7.60 – 7.53 (m, 2H)$^{trans,\ cis}$, 5.60 (d, *J* = 87.5 Hz, 1H)^{cis}, 5.38 (dq, *J* = 87.4, 0.5 Hz, 1H)^{trans}, 1.87 (dd, *J* = 1.2, 0.5 Hz, 3H)^{trans}, 1.70 (d, *J* = 2.8 Hz, 3H)^{cis}. ^{13}C NMR (101 MHz, Chloroform-*d*) δ 148.6, 148.4, 140.1 (d, *J* = 4.1 Hz), 138.2 (d, *J* = 4.2 Hz), 133.0 (d, *J* = 0.7 Hz), 131.6 (d, *J* = 0.8 Hz), 129.9, 129.5, 123.5, 123.4, 122.2, 120.9 (d, *J* = 0.8 Hz), 93.3 (d, *J* = 276.5 Hz), 93.2 (d, *J* = 271.5 Hz), 61.9 (d, *J* = 17.1 Hz), 60.8 (d, *J* = 17.1 Hz), 20.2 (d, *J* = 4.5 Hz), 16.2 (d, *J* = 3.1 Hz). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -150.79 (d, *J* = 87.4 Hz)^{trans}, -155.00 (dq, *J* = 87.8, 2.7 Hz)^{cis}. Elemental analysis calculated for $C_9H_8FNO_3$: C, 54.83; H, 4.09; N, 7.10. Found: C, 55.06; H, 4.19; N, 6.87. Unstable under HRMS conditions.

2-Fluoro-3-(3-nitrophenyl)oxirane (3g)

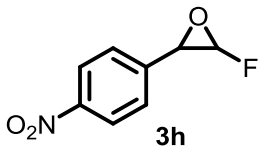


3g

The general procedure **A** was followed using **2g** (18.7 mg, 0.138 mmol) at 0 °C for 2.5 h. Purification (Isolation **A**) by neutral Al_2O_3 (Brockmann III) (pentane then pentane:Et_2O 97:3) yielded **3g** (13.9 mg, 55%) cis/trans d.r. 1.2:1 as a colorless oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.29 – 8.26 (m, 1H)^{cis}, 8.25 – 8.21 (m, 2H)^{cis,trans}, 8.14 – 8.09 (m, 1H)^{trans}, 7.76 – 7.71 (m, 1H)^{cis}, 7.62 – 7.55 (m, 3H)^{cis,trans}, 5.81 (dd, *J* = 88.1, 1.7 Hz, 1H)^{cis}, 5.50 (d, *J* = 84.9 Hz, 1H)^{trans}, 4.23 (dd, *J* = 2.4, 0.5 Hz, 1H)^{trans}, 4.01 (t, *J* = 2.1 Hz, 1H)^{cis}. ^{13}C NMR (101 MHz, Chloroform-*d*) δ 135.5 (d, *J* = 3.5 Hz), 134.1 (d, *J* = 5.0 Hz), 133.3, 133.3, 131.9, 131.9, 130.0, 129.5, 124.2, 123.9, 122.7 (d, *J* = 1.5 Hz), 121.1 (d, *J* = 0.8 Hz), 90.1 (d, *J* = 276.2 Hz), 89.3 (d, *J* = 270.1 Hz), 56.4 (d, *J* = 17.0 Hz), 56.2 (d, *J* = 18.4 Hz). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -146.02 (dd, *J* = 84.9, 2.2 Hz)^{trans}, -163.33 (dd, *J* = 88.1, 2.7 Hz)^{cis}. Unstable under HRMS conditions.

2-Fluoro-3-(4-nitrophenyl)oxirane (3h)



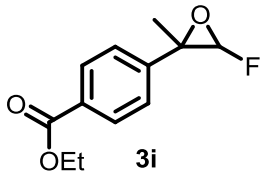
The general procedure **A** was followed using **2h** (20.9 mg, 0.138 mmol) at 0 °C for 3 h. Purification (Isolation **B**) by silicagel prep TLC (pretreated wtih 2% Et_3N in petroleum ether) PE:EtOAc 10:1 yielded *trans*-**3h** (7.4 mg, 29%) and *cis*-**3h** (7.4 mg, 29%) as a colorless oils. Total yield of **3h** (14.8 mg, 58%) d.r 1:1.

trans-**3h**: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.29 – 8.16 (m, 2H), 7.48 – 7.38 (m, 2H), 5.46 (d, *J* = 85.0 Hz, 1H), 4.22 (d, *J* = 2.3 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 148.6, 140.3 (d, *J* = 3.6 Hz), 126.9, 124.1, 90.2 (d, *J* = 276.8 Hz), 56.3 (d, *J* = 19.0 Hz). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -145.52 (dd, *J* = 85.3, 2.8 Hz).

cis-**3h**: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.28 – 8.18 (m, 2H), 7.61 – 7.50 (m, 2H), 5.81 (dd, *J* = 88.0, 1.8 Hz, 1H), 4.00 (t, *J* = 2.2 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 148.4, 139.0 (d, *J* = 4.8 Hz), 128.4 (d, *J* = 1.4 Hz), 123.6, 89.3 (d, *J* = 270.7 Hz), 56.5 (d, *J* = 17.5 Hz). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -163.05 (dd, *J* = 88.4, 2.8 Hz).

cis/trans-**3h**: Elemental analysis calculated for $C_8H_6FNO_3$: C, 52.47; H, 3.30; N, 7.65. Found: C, 52.67; H, 3.48; N, 7.29. Unstable under HRMS conditions.

Ethyl 4-(3-fluoro-2-methyloxiran-2-yl)benzoate (3i)

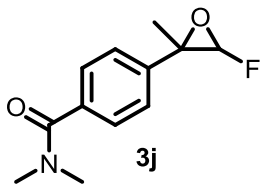


The general procedure **A** was followed using **2i** (26.5 mg, 0.138 mmol) at 0 °C for 4 h. Purification (Isolation **B**) by silicagel prep TLC (pretreated wtih 2% Et_3N in petroleum ether) PE:EtOAc (40:2) yielded *trans*-**3i** (14.3 mg, 46%) and *cis*-**3i** (8.0 mg, 26%) as a colorless oils. Total yield of **3i** (22.3 mg, 72%) d.r 1.8:1.

trans-**3i**: ^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.07 – 8.00 (m, 2H), 7.41 – 7.33 (m, 2H), 5.36 (d, *J* = 88.3 Hz, 1H), 4.38 (q, *J* = 7.1 Hz, 2H), 1.84 (d, *J* = 0.7 Hz, 3H), 1.39 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, Chloroform-*d*) δ 166.1, 142.4 (d, *J* = 4.0 Hz), 130.5, 129.8, 125.4, 93.6 (d, *J* = 274.5 Hz), 61.4 (d, *J* = 17.0 Hz), 61.2, 16.2, 14.3. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -150.79 (d, *J* = 88.3 Hz). Elemental analysis calculated for $C_{12}H_{13}FO_3$: C, 64.28; H, 5.84. Found: C, 61.64; H, 6.31. Unstable under HRMS conditions.

cis-**3i**: ^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.14 – 7.98 (m, 2H), 7.54 – 7.42 (m, 2H), 5.56 (d, *J* = 87.8 Hz, 1H), 4.38 (q, *J* = 7.1 Hz, 2H), 1.66 (d, *J* = 2.8 Hz, 3H), 1.39 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, Chloroform-*d*) δ 166.4, 140.7 (d, *J* = 4.0 Hz), 130.5, 129.6, 126.9, 93.5 (d, *J* = 269.9 Hz), 62.6 (d, *J* = 17.1 Hz), 61.2, 20.5, 14.5. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -154.76 (dq, *J* = 87.8, 2.7 Hz). Elemental analysis calculated for $C_{12}H_{13}FO_3$: C, 64.28; H, 5.84. Found: C, 62.75; H, 5.99. Unstable under HRMS conditions.

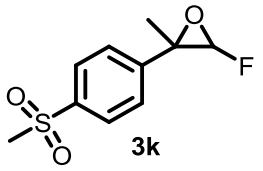
4-(3-Fluoro-2-methyloxiran-2-yl)-N,N-dimethylbenzamide (3j)



The general procedure **A** was followed using **2j** (26.4 mg, 0.138 mmol) at 0 °C for 4 h. Purification (Isolation **B**) by silicagel prep TLC (pretreated wtih 2% Et_3N in petroleum ether) PE:EtOAc (4:1) yielded **3j** (30.2 mg, 98%) d.r. 1:1 as a white amorphous solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.48 – 7.37 (m, 6H)$^{trans, cis}$, 7.35 – 7.29 (m, 2H), 5.55 (d, *J* = 88.0 Hz, 1H)^{cis}, 5.35 (d, *J* = 88.4 Hz, 1H)^{trans}, 3.10 (s, 6H), 2.97 (s, 3H), 2.95 (s, 3H), 1.81 (d, *J* = 1.1 Hz, 3H)^{trans}, 1.63 (d, *J* = 2.7 Hz, 3H)^{cis}. ^{13}C NMR (101 MHz, Chloroform-*d*) δ 171.2, 171.0, 139.07 (d, *J* = 3.9 Hz), 137.2 (d, *J* = 4.1 Hz), 136.4, 136.2, 127.4, 127.0, 126.8, 125.5, 93.7 (d, *J* = 275.7 Hz), 93.5 (d, *J* = 270.0 Hz), 62.5 (d, *J* = 17.3 Hz), 61.3 (d, *J* = 17.0 Hz), 39.6, 35.4, 20.5 (d, *J* = 4.4 Hz), 16.2 (d, *J* = 3.2 Hz). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -150.84 (d, *J* = 88.4 Hz)^{trans}, -154.64 (dq, *J* = 88.4, 2.7 Hz)^{cis}. Unstable under HRMS conditions.

3-Fluoro-2-methyl-2-(4-(methylsulfonyl)phenyl)oxirane (3k)

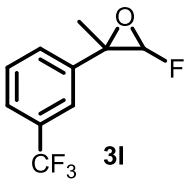


The general procedure **A** was followed using **2k** (27.4 mg, 0.138 mmol) at 0 °C for 4 h. Purification (Isolation **B**) by silicagel prep TLC (pretreated wtih 2% Et_3N in petroleum ether) PE:EtOAc (10:1) yielded *trans*-**3k** (10.9 mg, 34%) and *cis*-**3k** (11.0 mg, 35%) as a colorless oils. Total yield of **3k** (21.9 mg, 69%) d.r 1:1.

trans-**3k**: ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.99 – 7.90 (m, 2H), 7.54 – 7.48 (m, 2H), 5.35 (d, *J* = 87.7 Hz, 1H), 3.05 (s, 3H), 1.85 (dd, *J* = 1.2, 0.5 Hz, 3H). ^{13}C NMR (75 MHz, Chloroform-*d*) δ 143.9 (d, *J* = 3.9 Hz), 140.7, 127.9, 126.7, 93.3 (d, *J* = 277.9 Hz), 61.1 (d, *J* = 16.8 Hz), 44.6, 16.3. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -150.73 (d, *J* = 87.9 Hz). Elemental analysis calculated for $C_{10}H_{11}FO_3S$: C, 52.16; H, 4.82, S, 13.92. Found: C, 50.79; H, 4.93, S, 13.45. Unstable under HRMS conditions.

cis-**3k**: ^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.01 – 7.90 (m, 2H), 7.69 – 7.58 (m, 2H), 5.59 (d, *J* = 87.6 Hz, 1H), 3.06 (s, 3H), 1.68 (d, *J* = 2.8 Hz, 3H). ^{13}C NMR (75 MHz, Chloroform-*d*) δ 142.1 (d, *J* = 3.9 Hz), 140.5, 128.0, 127.5, 93.3 (d, *J* = 271.5 Hz), 62.3 (d, *J* = 17.5 Hz), 44.6, 20.3. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -154.70 (dq, *J* = 87.6, 2.7 Hz). Elemental analysis calculated for $C_{10}H_{11}FO_3S$: C, 52.16; H, 4.82, S, 13.92. Found: C, 46.81; H, 4.77, S, 12.47. Unstable under HRMS conditions.

3-Fluoro-2-methyl-2-(3-(trifluoromethyl)phenyl)oxirane (3l)

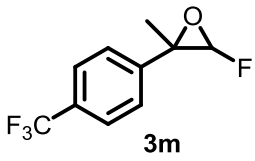


The general procedure **A** was followed using **2l** (26.0 mg, 0.138 mmol) at 0 °C for 4 h. Purification (Isolation **B**) by silicagel prep TLC (pretreated wtih 2% Et_3N in petroleum ether) PE (100%) yielded *trans*-**3l** (7.5 mg, 25%) (low stability) and *cis*-**3l** (15.8 mg, 52%) as a colorless oils. Total yield of **3l** (23.3 mg, 77%) d.r 1:2.

trans-**3l**: (Sample decompose during NMR measurement) ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.78 – 7.43 (m, 4H), 5.37 (d, *J* = 87.9 Hz, 1H), 1.85 (s, 3H). ^{13}C NMR (75 MHz, Chloroform-*d*) δ (chemical shifts from HSQC and HMBC spectrum. (CF_3 signal cannot be seen due to the low intensity of signal) 138.7, 130.6, 129.2, 128.7, 125.3, 122.3, 93.1 (d, *J* = 277 Hz), 61.0, 15.5. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -62.74 (s, 3F), -150.89 (d, *J* = 87.7 Hz, 1F). Unstable under HRMS conditions.

cis-**3l**: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.69 (d, *J* = 2.0 Hz, 1H), 7.65 – 7.57 (m, 2H), 7.54 – 7.46 (m, 1H), 5.57 (d, *J* = 87.7 Hz, 1H), 1.67 (d, *J* = 2.8 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 137.0 (d, *J* = 4.1 Hz), 130.9 (q, *J* = 32.6, 31.5 Hz), 130.3, 128.9, 125.5 (q, *J* = 273.4 Hz), 125.2 (q, *J* = 3.6 Hz), 123.9 (q, *J* = 3.5 Hz), 93.4 (d, *J* = 270.5 Hz), 62.3 (d, *J* = 17.0 Hz), 20.5 (d, *J* = 4.3 Hz). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -62.67, -154.92 (dq, *J* = 87.5, 2.8 Hz). Unstable under HRMS conditions.

3-Fluoro-2-methyl-2-(4-(trifluoromethyl)phenyl)oxirane (3m)

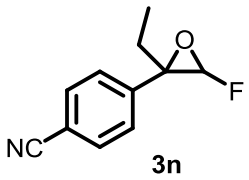


The general procedure **A** was followed using **2m** (26.0 mg, 0.138 mmol) at 0 °C for 4 h. Purification (Isolation **B**) by silicagel prep TLC (pretreated wtih 2% Et_3N in petroleum ether) PE (100%) yielded *trans*-**3m** (10.3 mg, 34%) (low stability) and *cis*-**3m** (10.3 mg, 34%) as a colorless oils. Total yield of **3m** (20.6 mg, 68%) d.r 1:1.

trans-**3m**: (Sample decompose during NMR measurement) ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.69 – 7.59 (m, 2H), 7.46 – 7.37 (m, 2H), 5.35 (d, *J* = 88.0 Hz, 1H), 1.84 (d, *J* = 1.1 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) (CF_3 signal cannot be seen due to the low intensity of signal) δ 141.8, 128.8, 126.0, 125.7 (q, *J* = 3.7 Hz), 93.6 (d, *J* = 276.1 Hz), 61.3 (d, *J* = 17.0 Hz), 16.3 (d, *J* = 3.2 Hz). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -62.73, -150.89 (d, *J* = 88.1 Hz). Unstable under HRMS conditions.

cis-**3m**: ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.74 – 7.59 (m, 2H), 7.55 (d, *J* = 8.5 Hz, 2H), 5.57 (d, *J* = 87.8 Hz, 1H), 1.67 (d, *J* = 2.8 Hz, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 139.9, 130.6 (q, *J* = 32.6 Hz), 127.3, 125.4 (q, *J* = 3.8 Hz), 124.1 (q, *J* = 272.1 Hz), 93.4 (d, *J* = 270.7 Hz), 62.4 (d, *J* = 17.1 Hz), 20.4 (d, *J* = 4.4 Hz). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -62.71, -154.86 (dq, *J* = 87.7, 2.5 Hz). Elemental analysis calculated for $C_{10}H_8F_4O$: C, 54.55; H, 3.66. Found: C, 52.16; H, 4.82. Unstable under HRMS conditions.

4-(2-Ethyl-3-fluorooxiran-2-yl)benzonitrile (3n)

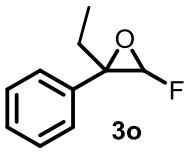


3n

The general procedure **A** was followed using **2n** (22.0 mg, 0.138 mmol) at 0 °C for 4 h. Purification (Isolation **B**) by silicagel prep TLC (pretreated wtih 2% Et_3N in petroleum ether) PE:EtOAc (10:1) yielded **3n** (20.4 mg, 77%) d.r. 1.1:1.

^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.73 – 7.62 (m, 4H), 7.57 – 7.47 (m, 2H), 7.47 – 7.37 (m, 2H), 5.58 (d, *J* = 87.5 Hz, 1H)^{cis}, 5.34 (d, *J* = 87.9 Hz, 1H)^{trans}, 2.34 – 2.12 (m, 2H), 2.09 – 1.95 (m, 1H), 1.80 – 1.61 (m, 1H), 0.99 (t, *J* = 7.5 Hz, 3H), 0.90 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (75 MHz, Chloroform-*d*) δ 141.6 (d, *J* = 3.9 Hz), 140.1 (d, *J* = 4.1 Hz), 132.5, 132.2, 128.1, 127.0, 118.6, 118.5, 112.4, 112.3, 93.9 (dd, *J* = 277.1, 4.9 Hz), 92.8 (dd, *J* = 270.5, 5.3 Hz), 66.2 (d, *J* = 16.9 Hz), 65.4 (d, *J* = 16.5 Hz), 26.6, 22.7, 8.8, 7.9. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -152.02 (d, *J* = 87.7 Hz)^{trans}, -154.62 (d, *J* = 86.9 Hz)^{cis}. Elemental analysis calculated for $C_{11}H_{10}FNO$: C, 69.10; H, 5.27, N, 7.33. Found: C, 68.61; H, 5.25, N, 7.29. Unstable under HRMS conditions.

2-Ethyl-3-fluoro-2-phenyloxirane (3o)



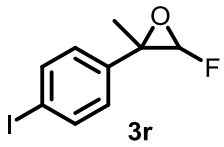
3o

The general procedure **A** was followed using **2o** (18.6 mg, 0.138 mmol) at 0 °C for 4 h. Purification (Isolation **B**) by silicagel prep TLC (pretreated wtih 2% Et_3N in petroleum ether) PE (100%) yielded *trans*-**3o** mixture with sulfide **4** (55 mg) and *cis*-**3o** (6.9 mg, 30%) d.r. >20:1 as a colorless oil. *trans*-**3o**/**4** mixture was subjected to O_3/O_2 following Isolation **C** to give *trans/cis*-**3o** (7.0 mg, 30 %) d.r. 1:10. Total yield of **3o** (13.9 mg, 60%) d.r 1.1:1.

trans-**3o**: ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.34 – 7.20 (m, 5H), 5.31 (d, *J* = 89.0 Hz, 1H), 2.27 – 2.06 (m, 1H), 1.95 (dqd, *J* = 14.7, 7.5, 1.5 Hz, 1H), 0.94 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 136.3 (d, *J* = 3.8 Hz), 128.7, 128.3, 126.2, 94.6 (d, *J* = 273.9 Hz), 66.1 (d, *J* = 16.6 Hz), 23.0 (d, *J* = 3.3 Hz), 9.0. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -157.81 (dd, *J* = 89.2, 5.7 Hz). Unstable under HRMS conditions.

cis-**3o**: ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.46 – 7.29 (m, 5H), 5.56 (d, *J* = 88.2 Hz, 1H), 2.16 (dqd, *J* = 14.9, 7.5, 1.4 Hz, 1H), 1.70 (dqd, *J* = 14.7, 7.4, 1.2 Hz, 1H), 0.91 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 134.7 (d, *J* = 3.9 Hz), 128.4, 128.2, 127.2, 93.3 (d, *J* = 268.5 Hz), 66.8 (d, *J* = 17.1 Hz), 27.3 (d, *J* = 4.4 Hz), 8.0. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -159.73 (d, *J* = 88.2 Hz). Unstable under HRMS conditions.

3-Fluoro-2-(4-iodophenyl)-2-methyloxirane (3r)



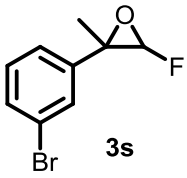
3r

The general procedure **B** was followed using **2r** (34.0 mg, 0.138 mmol) at 0 °C for 4 h. Purification (Isolation **B**) by silicagel prep TLC (pretreated wtih 2% Et_3N in petroleum ether) PE (100%) yielded *trans*-**3r** (6.3 mg, 16%) and *cis*-**3r** (9.9 mg, 26%) as a light yellow oils. Total yield of **3r** (16.2 mg, 42%) d.r 1:1.6.

trans-**3r**: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.80 – 7.58 (m, 2H), 7.11 – 6.97 (m, 2H), 5.33 (d, *J* = 88.2 Hz, 1H), 1.79 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 137.8, 137.6 (d, *J* = 3.7 Hz), 127.5, 94.3, 93.7 (d, *J* = 275.8 Hz), 61.4 (d, *J* = 17.0 Hz), 16.2 (d, *J* = 3.3 Hz). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -150.76 (d, *J* = 88.3 Hz). Unstable under HRMS conditions.

cis-**3r**: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.77 – 7.64 (m, 2H), 7.19 – 7.10 (m, 2H), 5.53 (d, *J* = 88.0 Hz, 1H), 1.62 (d, *J* = 2.8 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 137.2, 135.4 (d, *J* = 4.1 Hz), 128.5, 93.9, 93.2 (d, *J* = 270.0 Hz), 62.2 (d, *J* = 17.2 Hz), 20.1 (d, *J* = 4.4 Hz). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -154.81 (dq, *J* = 88.1, 2.7 Hz). Unstable under HRMS conditions.

2-(3-Bromophenyl)-3-fluoro-2-methyloxirane (3s)



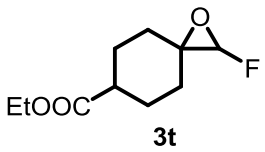
3s

The general procedure **B** was followed using **2s** (34.0 mg, 0.138 mmol) at 0 °C for 4 h. Purification (Isolation **B**) by silicagel prep TLC (pretreated wtih 2% Et_3N in petroleum ether) PE (100%) yielded *trans*-**3s** (14.2 mg, 45%) and *cis*-**3s** (6.5 mg, 20%) as a light yellow oils. Total yield of **3s** (20.7 mg, 65%) d.r 2.2:1.

trans-**3s**: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.53 – 7.34 (m, 2H), 7.26 – 7.21 (m, 2H), 5.34 (d, *J* = 88.2 Hz, 1H), 1.80 (d, *J* = 1.2 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 140.2 (d, *J* = 3.9 Hz), 131.6, 130.3, 128.8, 124.3, 123.0, 93.6 (d, *J* = 275.8 Hz), 61.0 (d, *J* = 17.0 Hz), 16.3 (d, *J* = 3.2 Hz). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -150.91 (d, *J* = 88.1 Hz). Elemental analysis calculated for C_9H_8BrFO: C, 46.78; H, 3.49. Found: C, 48.56; H, 4.04. Unstable under HRMS conditions.

cis-**3s**: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.58 (t, *J* = 1.9 Hz, 1H), 7.47 (ddd, *J* = 7.9, 2.0, 1.1 Hz, 1H), 7.35 (dt, *J* = 7.8, 1.4 Hz, 1H), 7.25 (t, *J* = 7.9 Hz, 1H), 5.54 (d, *J* = 87.9 Hz, 1H), 1.63 (d, *J* = 2.8 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 138.2 (d, *J* = 4.2 Hz), 131.5, 130.1, 130.0, 125.5, 122.5, 93.5 (d, *J* = 270.4 Hz), 62.2 (d, *J* = 17.4 Hz), 20.5 (d, *J* = 4.4 Hz). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -154.74 (dd, *J* = 87.8, 3.0 Hz). Unstable under HRMS conditions.

Ethyl 2-fluoro-1-oxaspiro[2.5]octane-6-carboxylate (3t)

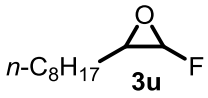


3t

The general procedure **B** was followed using **2t** (23.5 mg, 0.138 mmol) at 0 °C for 4 h. Purification (Isolation **B**) by silicagel prep TLC (pretreated wtih 2% Et_3N in petroleum ether) PE:EtOAc (20:1) yielded **3t** (26.9 mg, 96%) d.r 1.7:1.

^{1}H NMR (300 MHz, Chloroform-*d*) δ 5.36 (d, *J* = 87.3 Hz, 1H), 5.34 (d, *J* = 87.5 Hz, 1H), 4.14 (q, *J* = 7.1 Hz, 2H), 4.14 (q, *J* = 7.1 Hz, 2H), 2.51 – 2.35 (m, 1H), 2.14 – 1.31 (m, 8H), 1.25 (t, *J* = 7.1 Hz, 3H), 1.25 (t, *J* = 7.1 Hz, 3H). (75 MHz, Chloroform-*d*) δ 174.8, 174.7, 94.5 (dd, *J* = 266.2, 4.0 Hz), 94.2 (dd, *J* = 266.6, 5.2 Hz), 63.2 (d, *J* = 16.7 Hz), 63.1 (d, *J* = 17.5 Hz), 60.7, 60.6, 42.1, 41.4, 30.0 (d, *J* = 3.9 Hz), 29.9 – 29.6 (m), 27.2, 27.1, 26.6 – 26.2 (m), 26.1, 25.4, 14.3. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -157.92 (dd, *J* = 87.8, 5.5 Hz), -159.28 (d, *J* = 87.4 Hz). Elemental analysis calculated for $C_{10}H_{15}FO_3$: C, 59.39; H, 7.48. Found: C, 57.43; H, 7.38. Unstable under HRMS conditions.

2-Fluoro-3-octyloxirane (3u)



3u

The general procedure **B** was followed using **2u** (19.7 mg, 0.138 mmol) at 0 °C for 4 h. Product was not isolated due to volatility and instability on silica gel. The crude product was dissolved in $CDCl_3$ (0.7 mL), to the solution internal reference EtOAc (13.5 μL, 0.138 mmol, 1.0 eq) was added, and the sample was analyzed by ^{1}H NMR. NMR yield of **3u** (82%) d.r. 1.7:1.

^{1}H NMR (300 MHz, Chloroform-*d*) δ 5.44 (dd, *J* = 88.6, 1.7 Hz, 1H)^{cis}, 5.20 (d, *J* = 86.3 Hz, 1H)^{trans}, 3.13 – 3.03 (m, 1H)^{trans}, 2.82 – 2.70 (m, 1H)^{cis}, 1.67 – 0.93 (m, 28H)^{trans,cis}, 0.85 – 0.74 (m, 6H)^{trans,cis}. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -151.45 (d, *J* = 86.9 Hz)^{trans}, -163.89 (d, *J* = 88.6 Hz)^{cis}. Unstable under HRMS conditions.

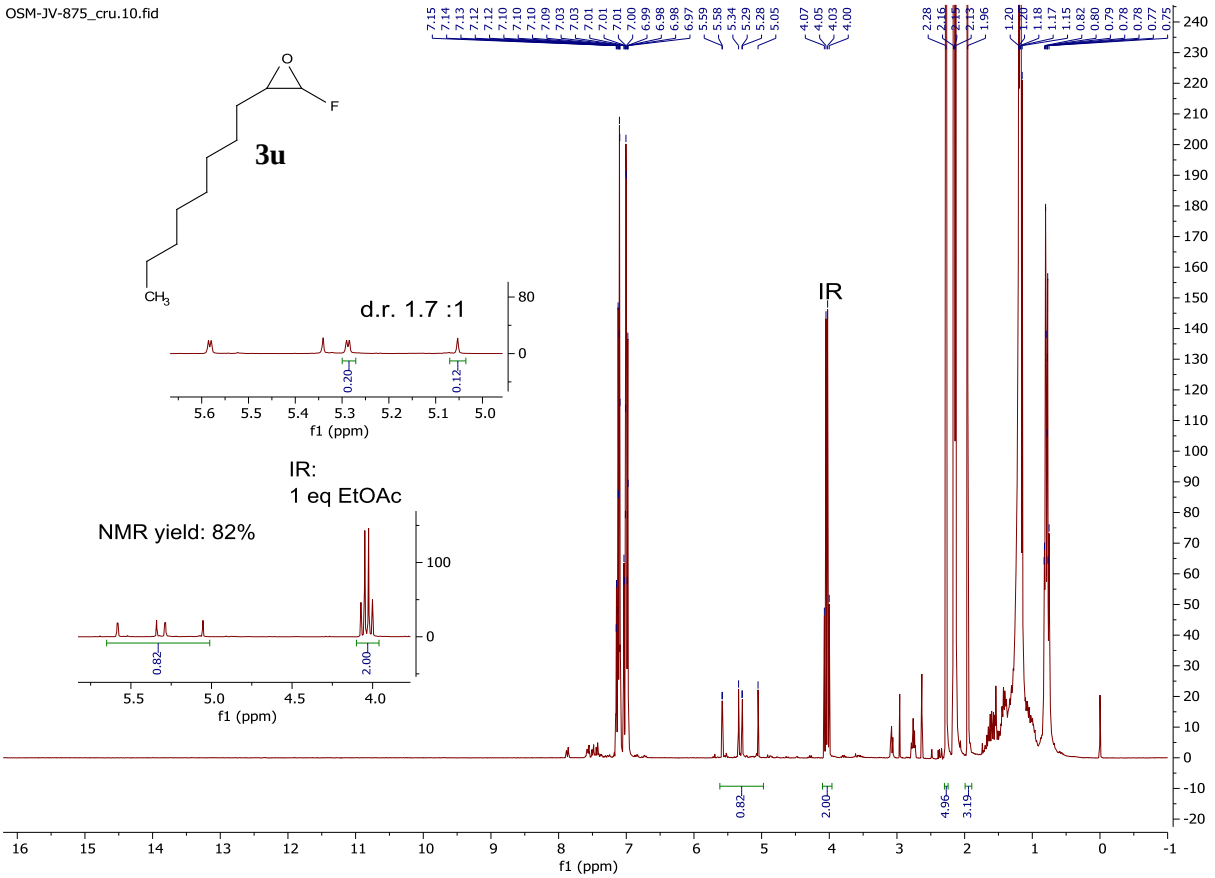


Figure S3.[1]H NMR spectrum of crude **3u**.

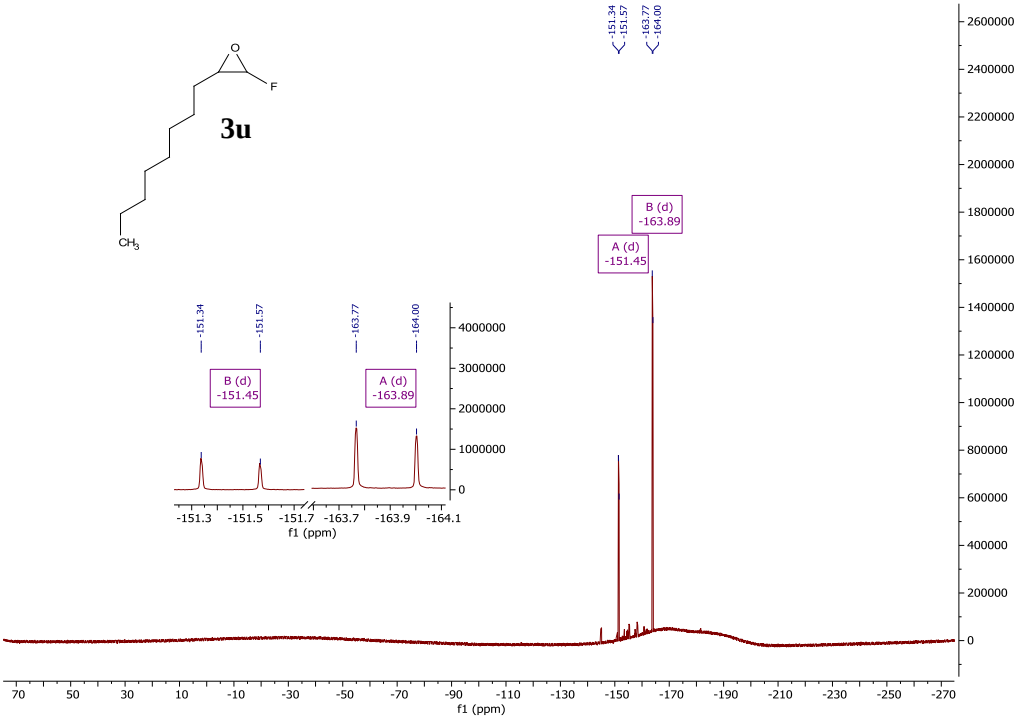
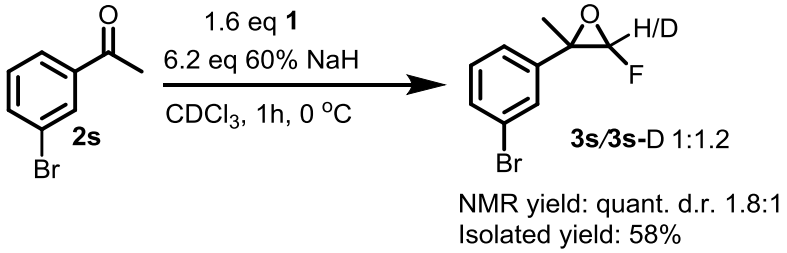


Figure S4.[19]F NMR spectrum of crude **3u**.

Reactivity and properties of sulfonium salt 1

Deuterium incorporation into fluoroepoxide 3s



The general procedure **B** was followed using **2s** (27.5 mg, 0.138 mmol), 60% NaH (in mineral oil, 34.3 mg, 0.856 mmol, 6.2 equiv) and $CDCl_3$ (1.4 mL) as a solvent at 0 °C for 1 h. Solvent was evaporated, the residue was treated with Et_2O and filtered through a cotton plug. After evaporation of solvent the crude product was dissolved in $CDCl_3$ (0.7 mL), to the solution internal reference EtOAc (13.5 μL, 0.138 mmol, 1.0 eq) was added, and the sample was analyzed by ^1H and ^{19}F NMR. NMR yield of **3s/3s**-D (~100%) d.r. 1.8:1. H/D ratio 1:1.2 (determined by ^{19}F NMR).

Purification (Isolation **B**) by silicagel prep TLC (pretreated wtih 2% Et_3N in petroleum ether) PE (100%) yielded *trans*-**3s/3s**-D (7.4 mg, 23%, H/D) and *cis*-**3s/3s**-D (11.2 mg, 35%) as a light yellow oils. Total yield of **3s** (18.6 mg, 58%) d.r 1:1.5.

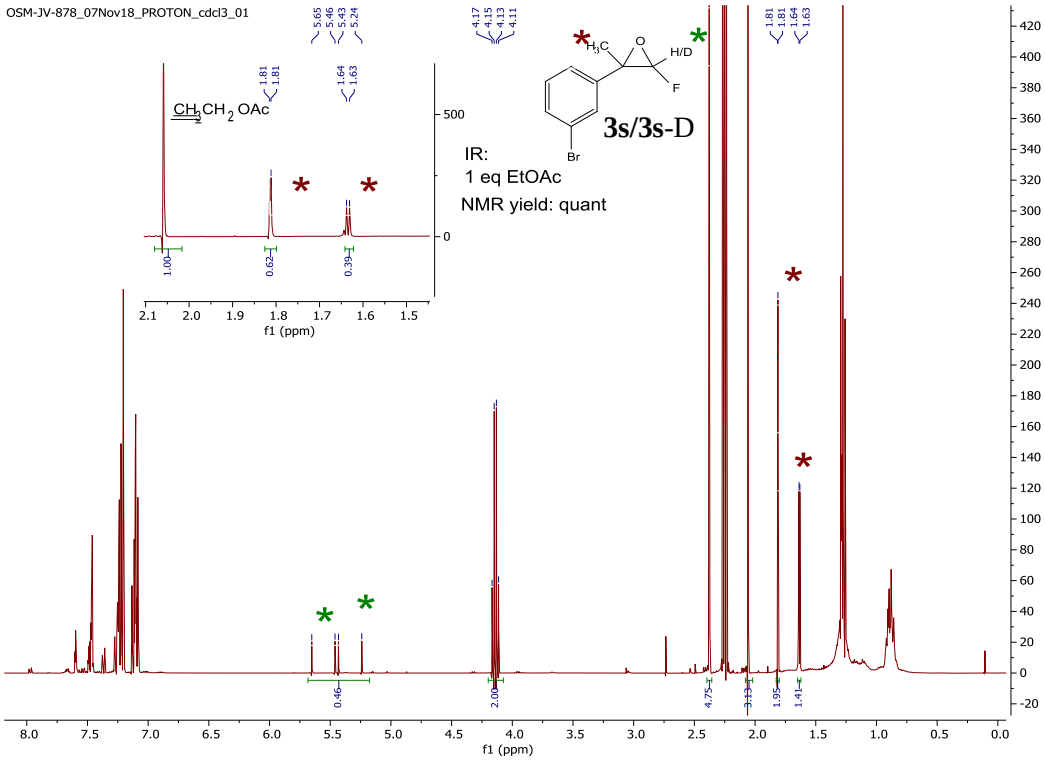


Figure S5.^1H NMR spectrum of crude **3s/3s**-D.

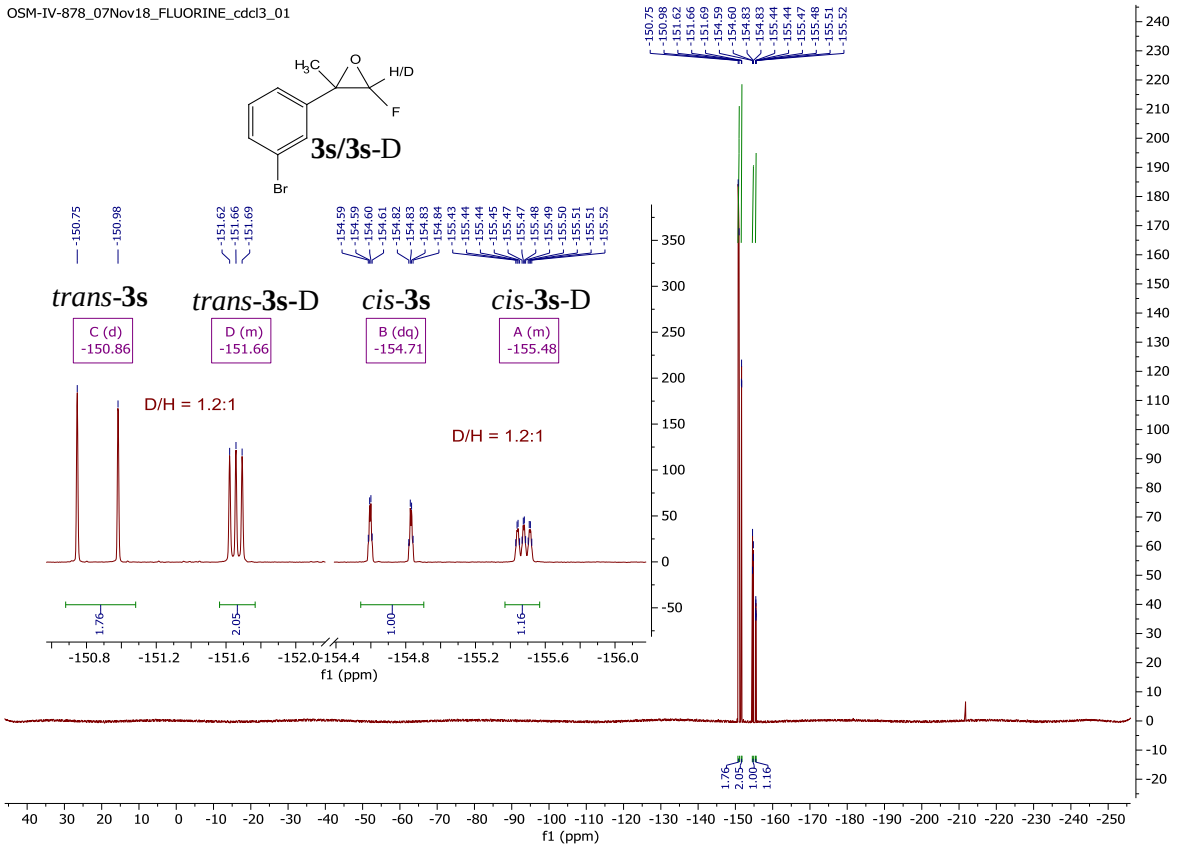
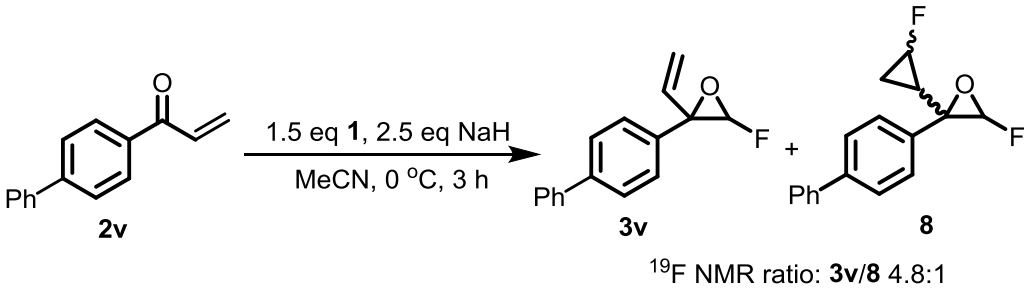


Figure S6.[19]F NMR spectrum of crude **3s/3s**-D.

Probing of 1,2- vs. 1,4- addition



The general procedure **A** was followed using **2v**[4] (30 mg, 0.144 mmol), 60% NaH (in mineral oil, 14.4 mg, 0.360 mmol, 2.5 equiv) and dry MeCN (1.5 mL) as a solvent at 0 °C for 3 h. Solvent was evaporated, the residue was treated with petroleum ether:Et_2O (40:7) and filtered through a cotton plug. After evaporation of solvent the crude product was dissolved in $CDCl_3$ (1 mL), to the solution internal reference EtOAc (14.1 µL, 0.144 mmol, 1.0 eq) was added, and the sample was analyzed by ^{1}H and ^{19}F NMR. ^{1}H NMR yield of **3v** (54%) d.r. 1.1:1. ^{19}F NMR ratio **3v**/**8** 4.8:1.

[4] S. Cheng, S. Yu, *Org. Biomol. Chem.* **2014**, *12*, 8607–8610.

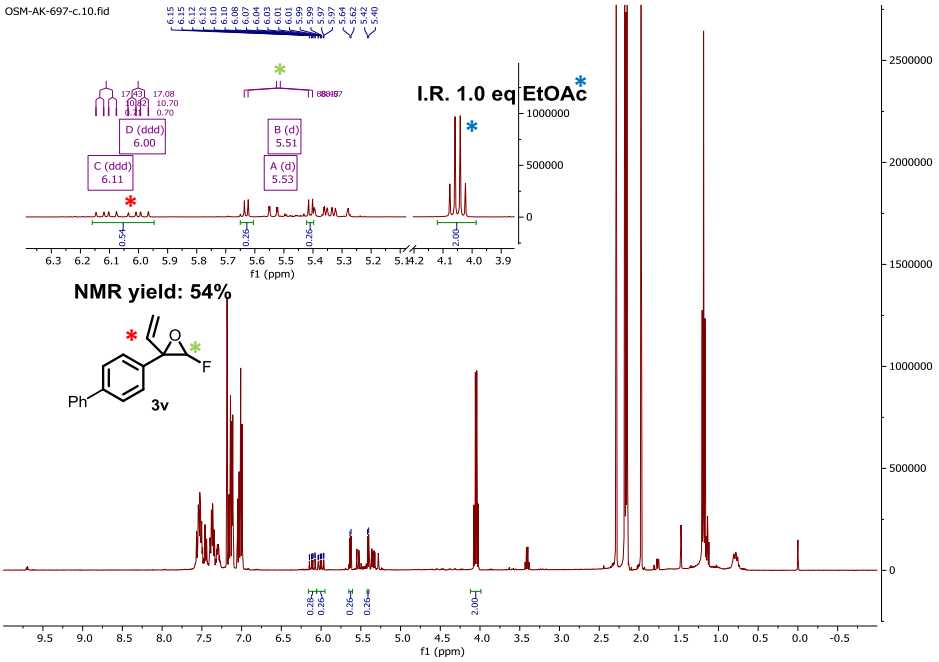


Figure S7. ^{1}H NMR spectrum of crude product mixture **3v**/**8**.

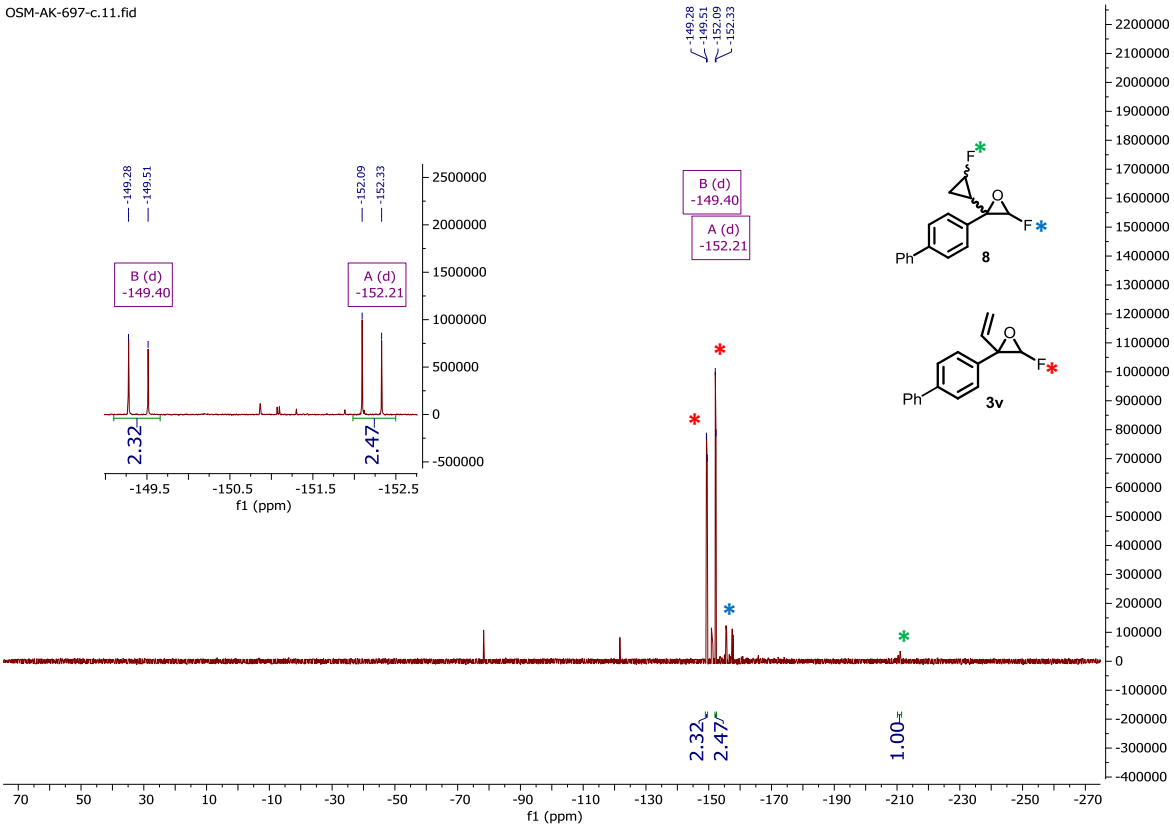
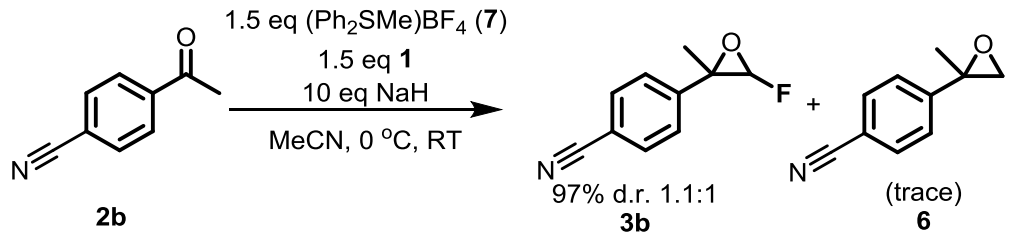


Figure S8. ^{19}F NMR spectrum of crude product mixture **3v**/**8**.

Competition experiment of 1 and methyldiphenylsulfonium tetrafluoroborate with 2e.



To a solution of sulfonium salt **1** (75.0 mg, 0.207 mmol, 1.5 equiv) and diphenyl methylsulfonium tetrafluoroborate (**7**) (59.6 mg, 0.207 mmol, 1.50 equiv) and ketone **2b** (20.0 mg, 0.138 mmol, 1 equiv) in dry MeCN (2.8 mL) under Ar atmosphere was added 60% NaH (in mineral oil, 55.2 mg, 1.38 mmol, 10 equiv) at 0 °C. The reaction mixture was stirred at this temperature for 3 h. After completion (TLC control) the solvent was evaporated under reduced pressure. The residue was treated with Et_2O, filtered through a cotton plug, and solvent was evaporate under the reduced pressure. The crude product was dissolved in $CDCl_3$ (0.7 mL), the internal reference was added EtOAc (13.5 μL, 0.138 mmol 1 equiv.) and the mixture was analyzed by ^1H NMR which showed the quantitative formation of **3b** (d.r. 1.1:1) and only traces of **6**[5]. Further the crude product was purified by isolation methods **B** to give *trans*-**3b** (11.3 mg, 46.2%) and *cis*-**3b** (12.3 mg, 50.3%) as a colorless oils. Overall yield of **3b** (23.6 mg, 97%).

[5] S. Pedragosa-Moreau, C. Morisseau, J. Zylber, A. Archelas, J. Baratti, R. Furstoss, *J. Org. Chem.* **1996**, *61*, 7402–7407.

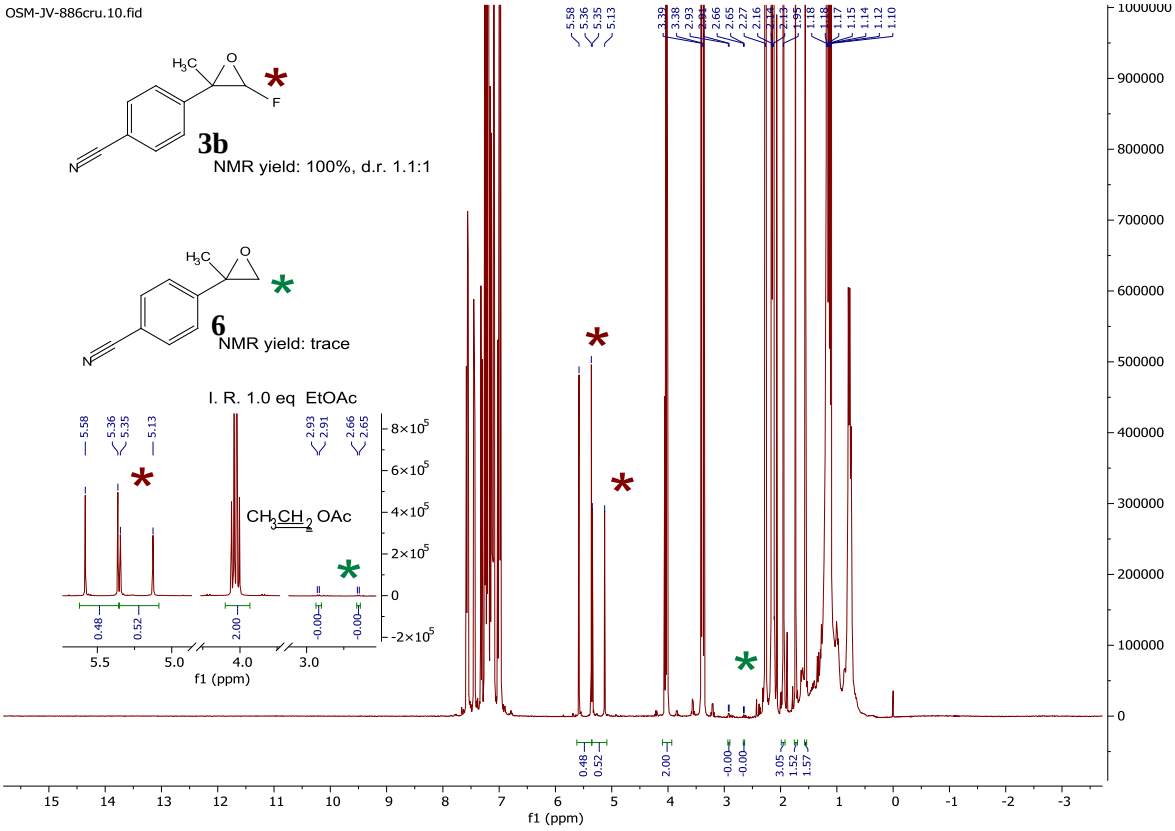
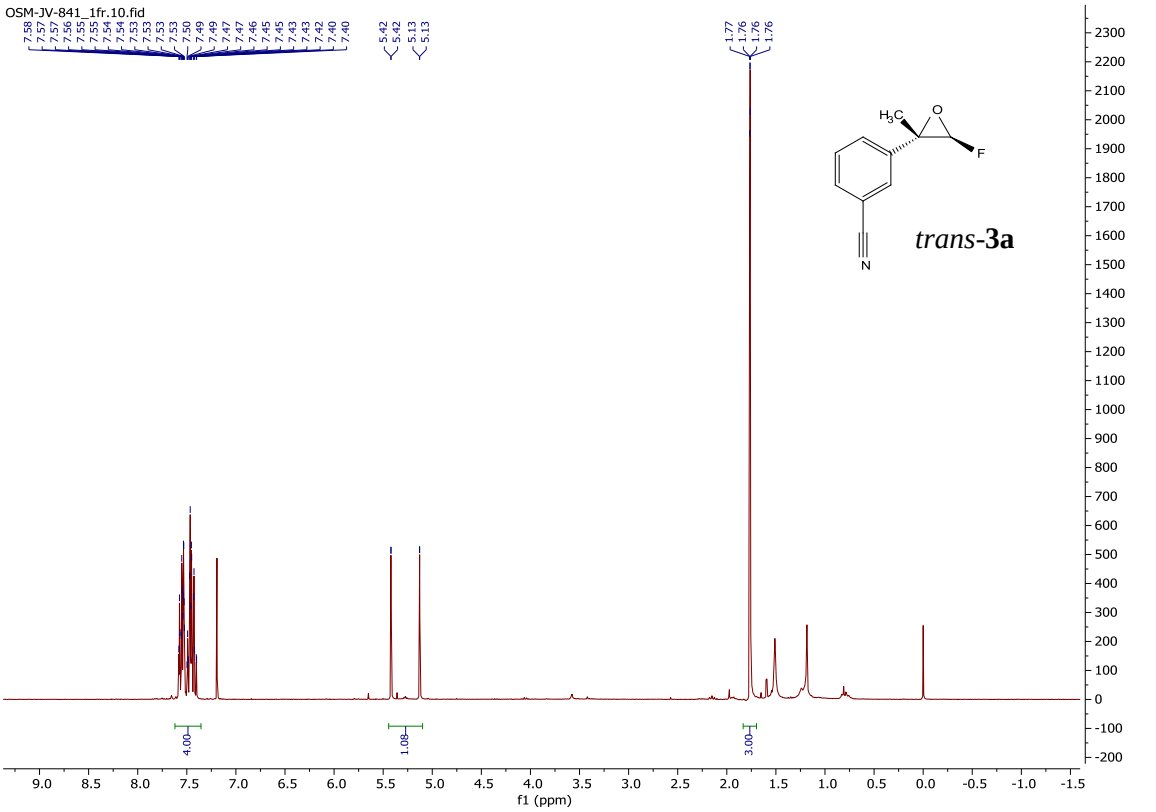
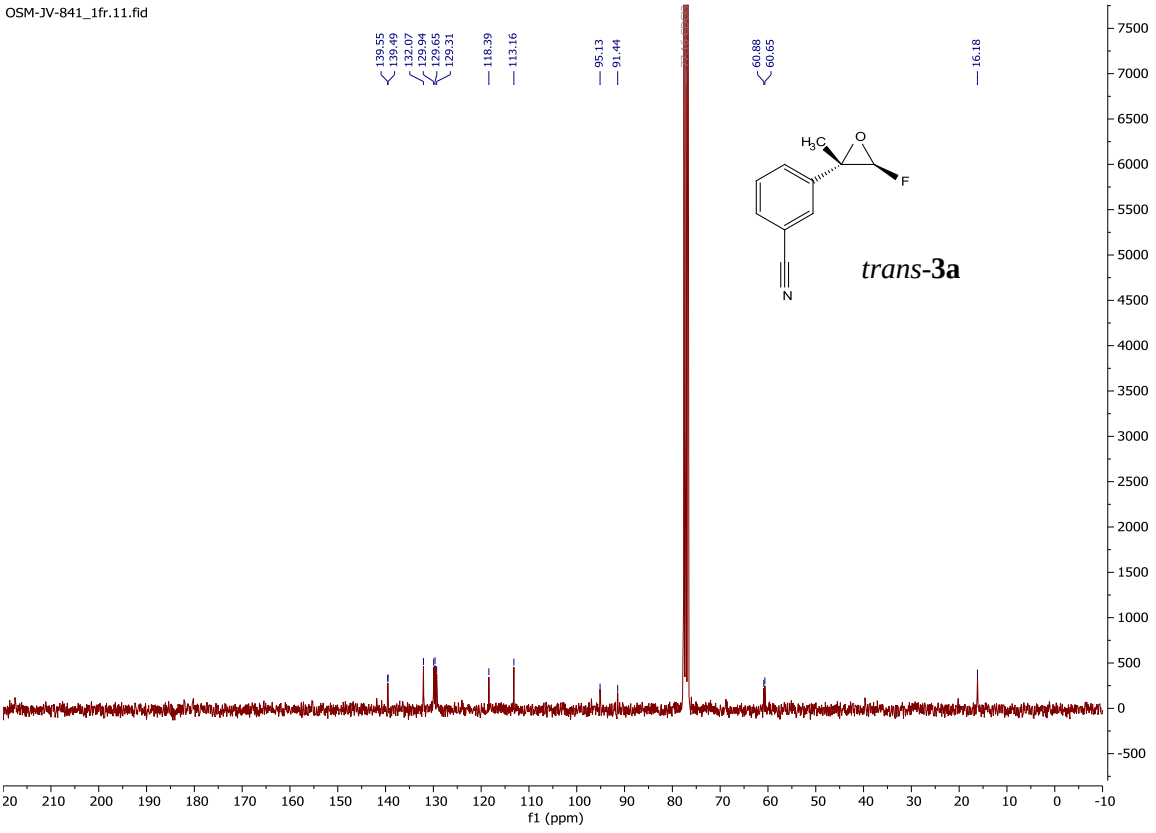
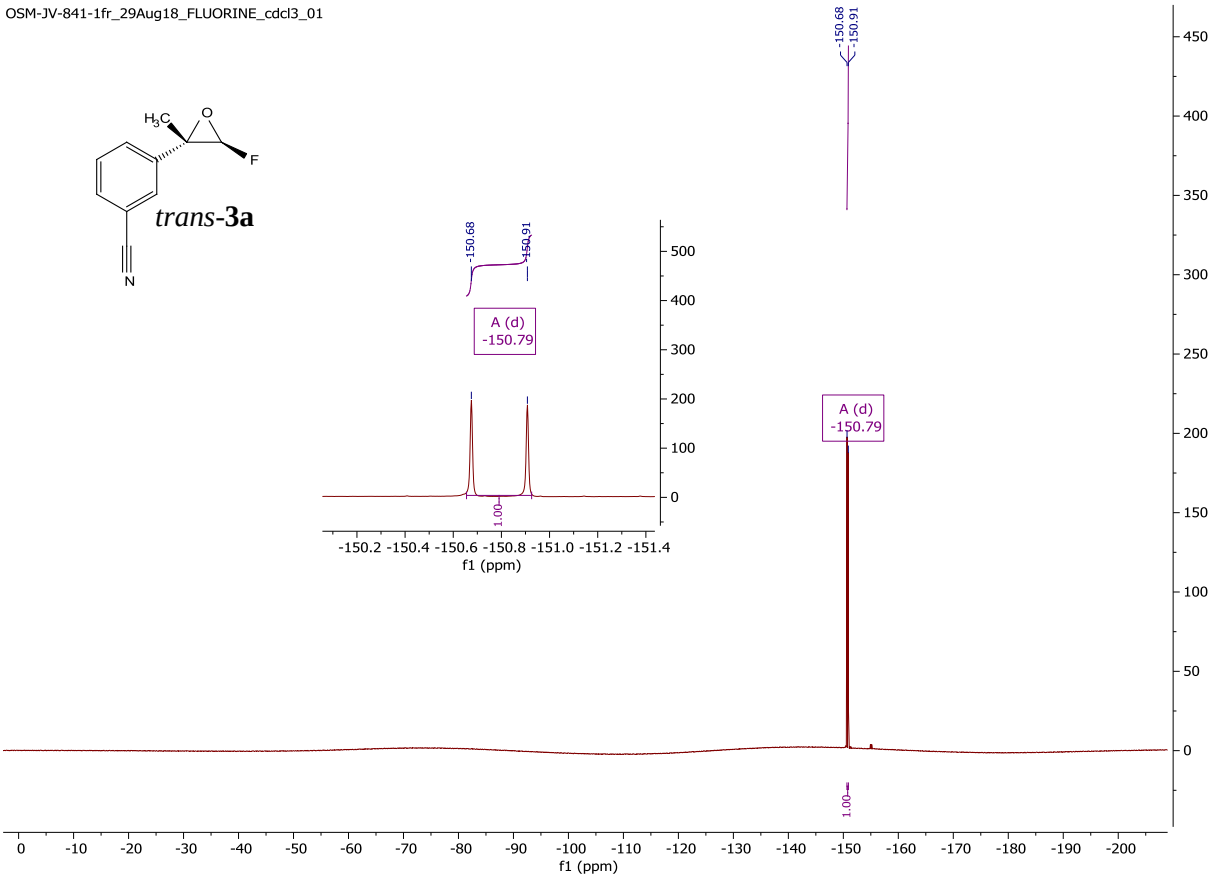


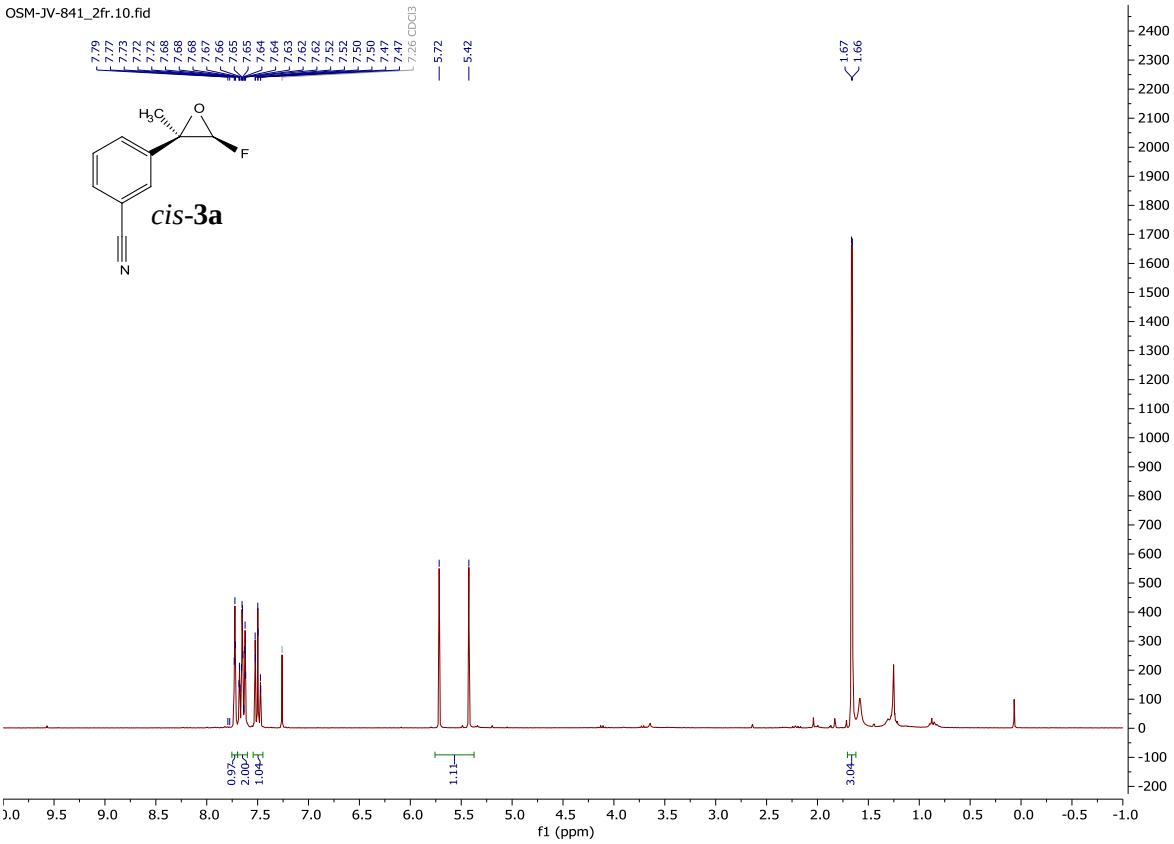
Figure S8. ^{1}H NMR spectrum of the crude **3b**/**6** mixture from the competition experiment between **1** and **7**.

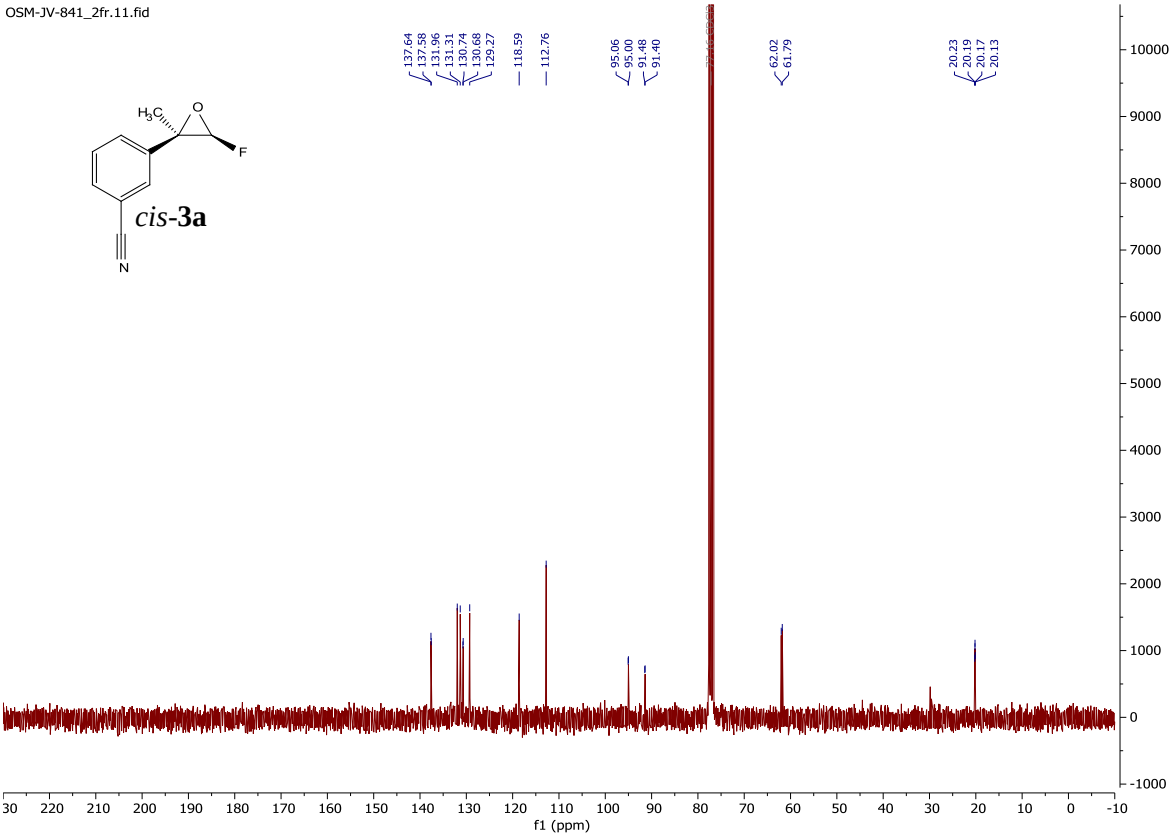
NMR spectra of fluoroepoxides 3

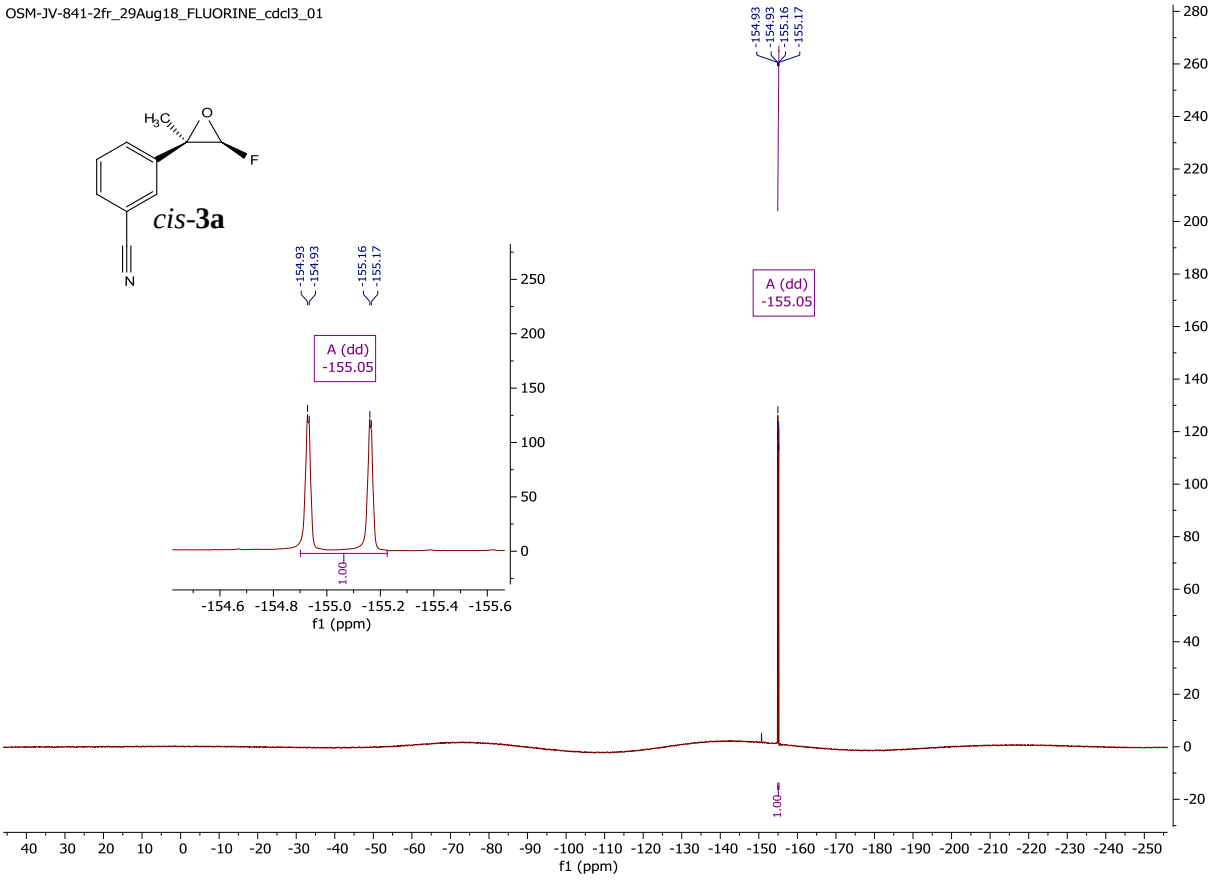


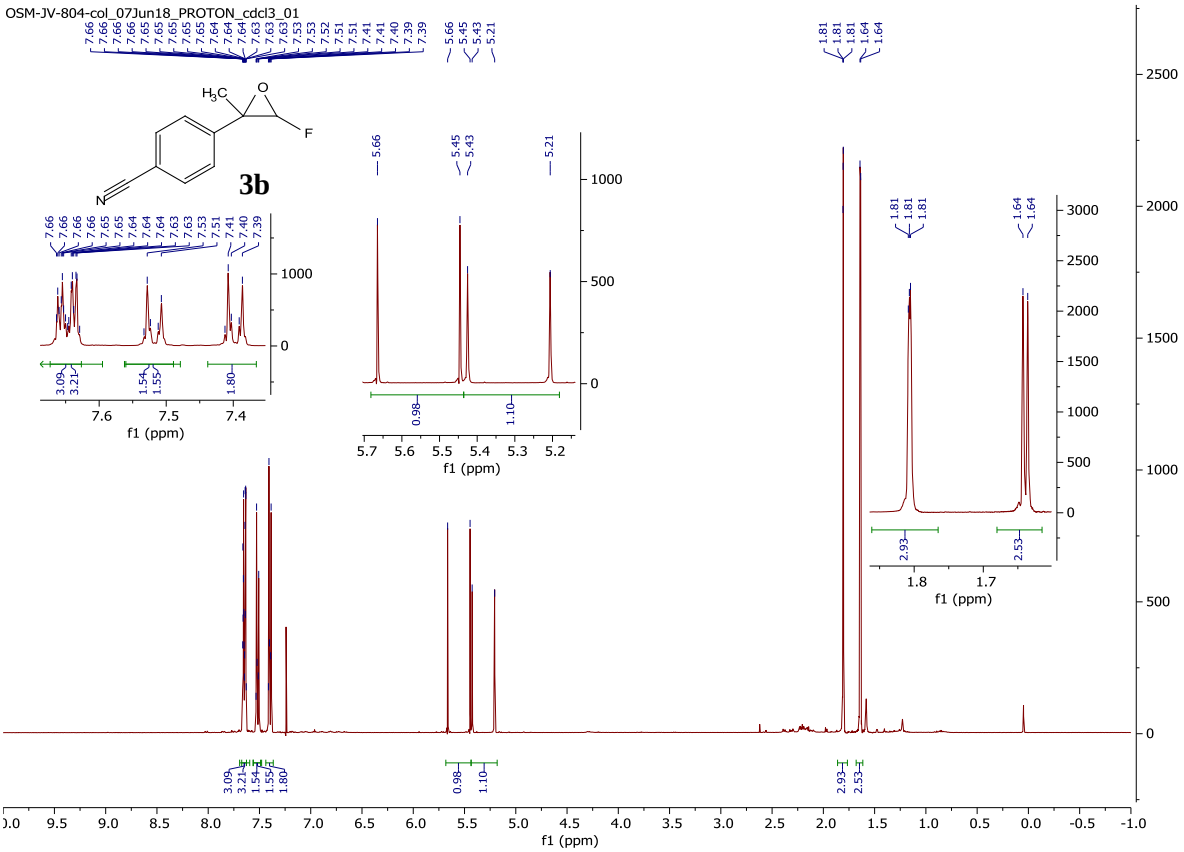


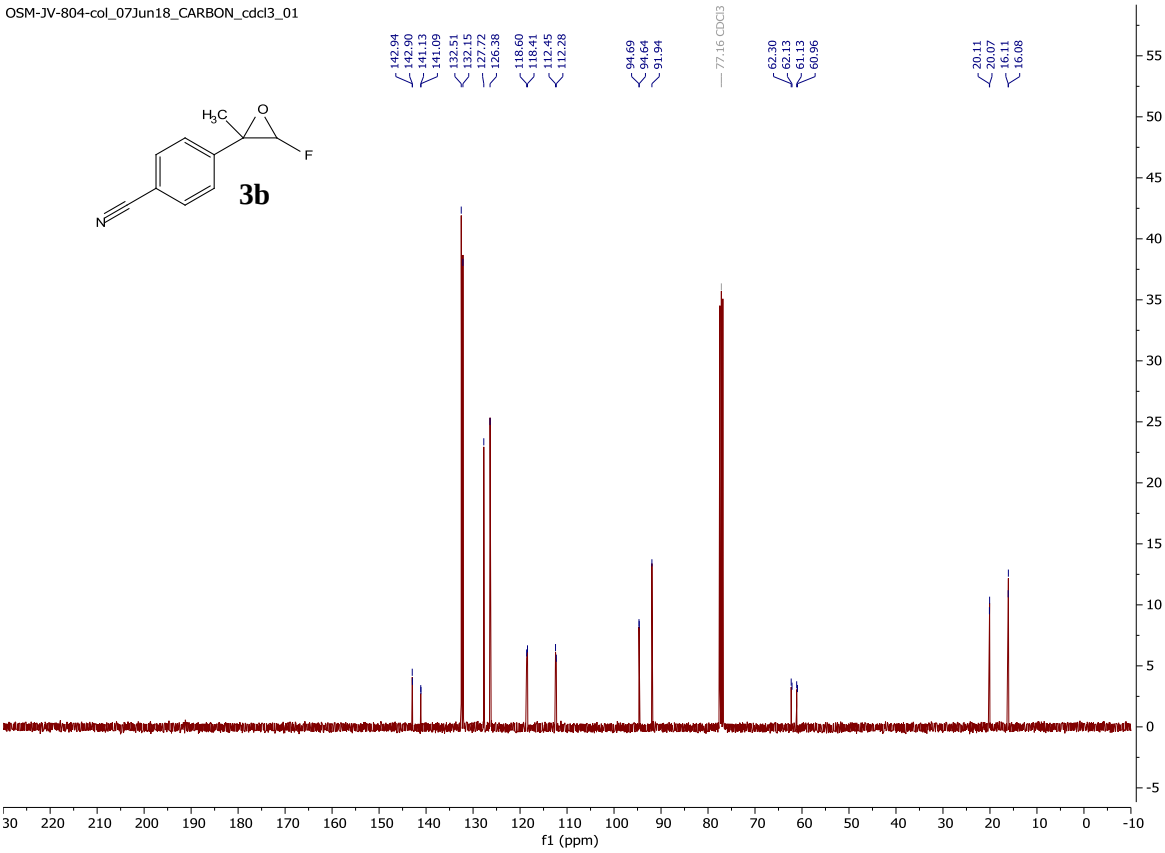

OSM-JV-841-1fr_29Aug18_FLUORINE_cdcl3_01
trans-3a
-150.68
-150.91
A (d)
-150.79
1.00
f1 (ppm)

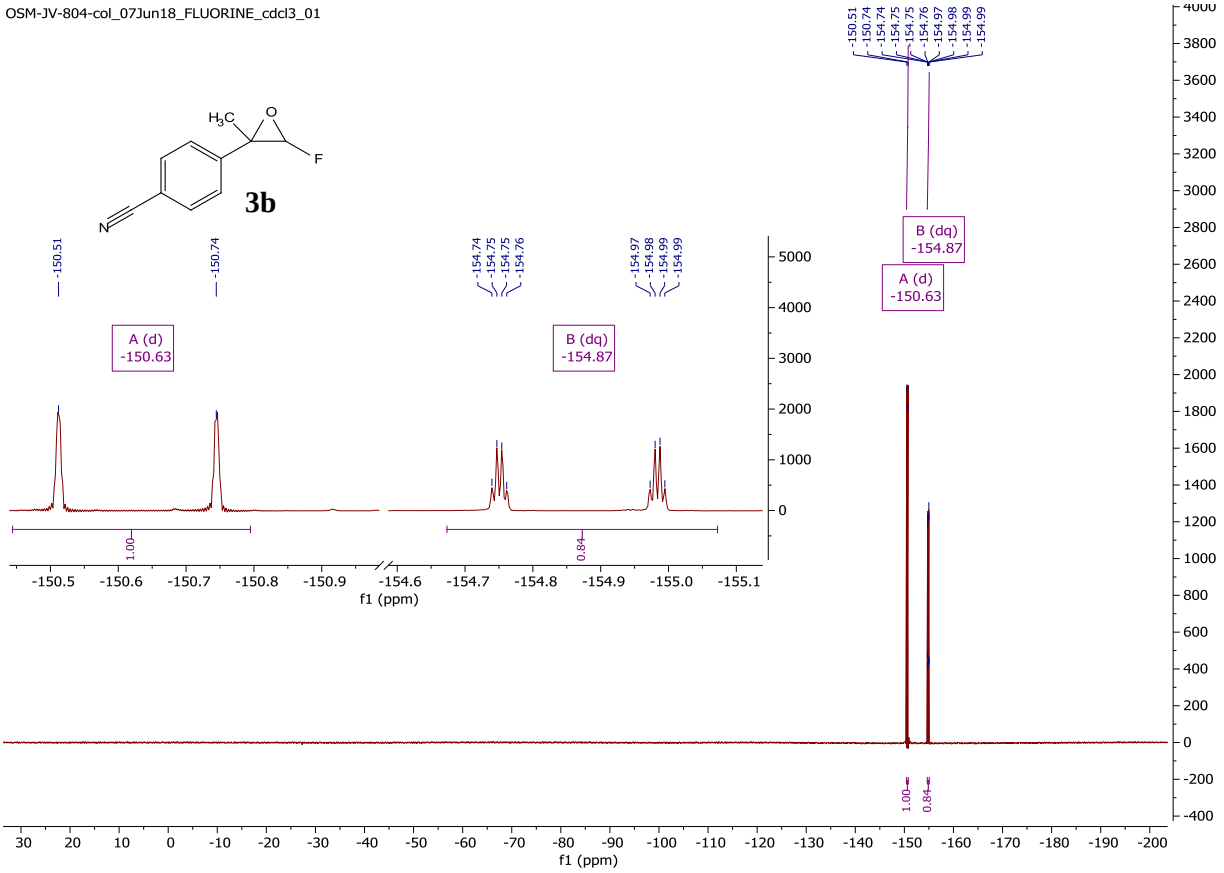

OSM-JV-841_2fr.10.fid
cis-3a
f1 (ppm)

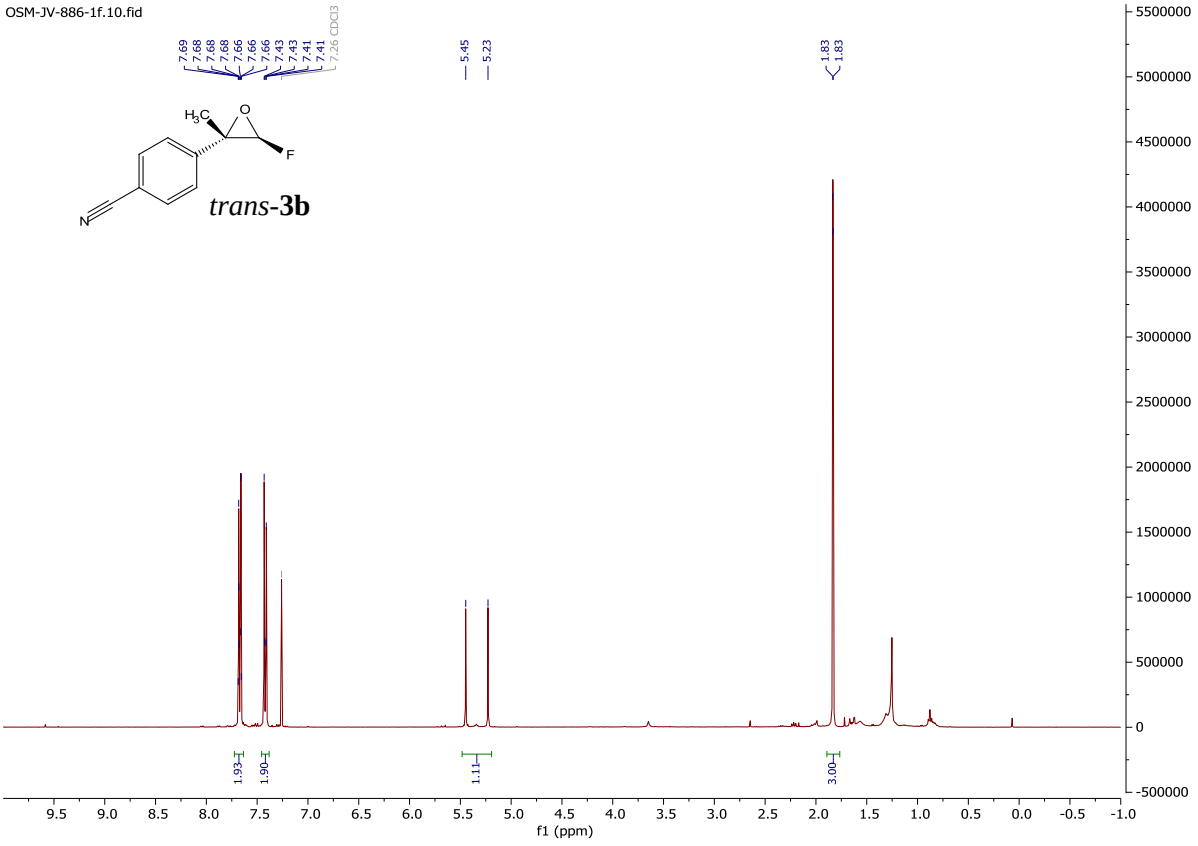

OSM-JV-841_2fr.11.fid
cis-3a
f1 (ppm)

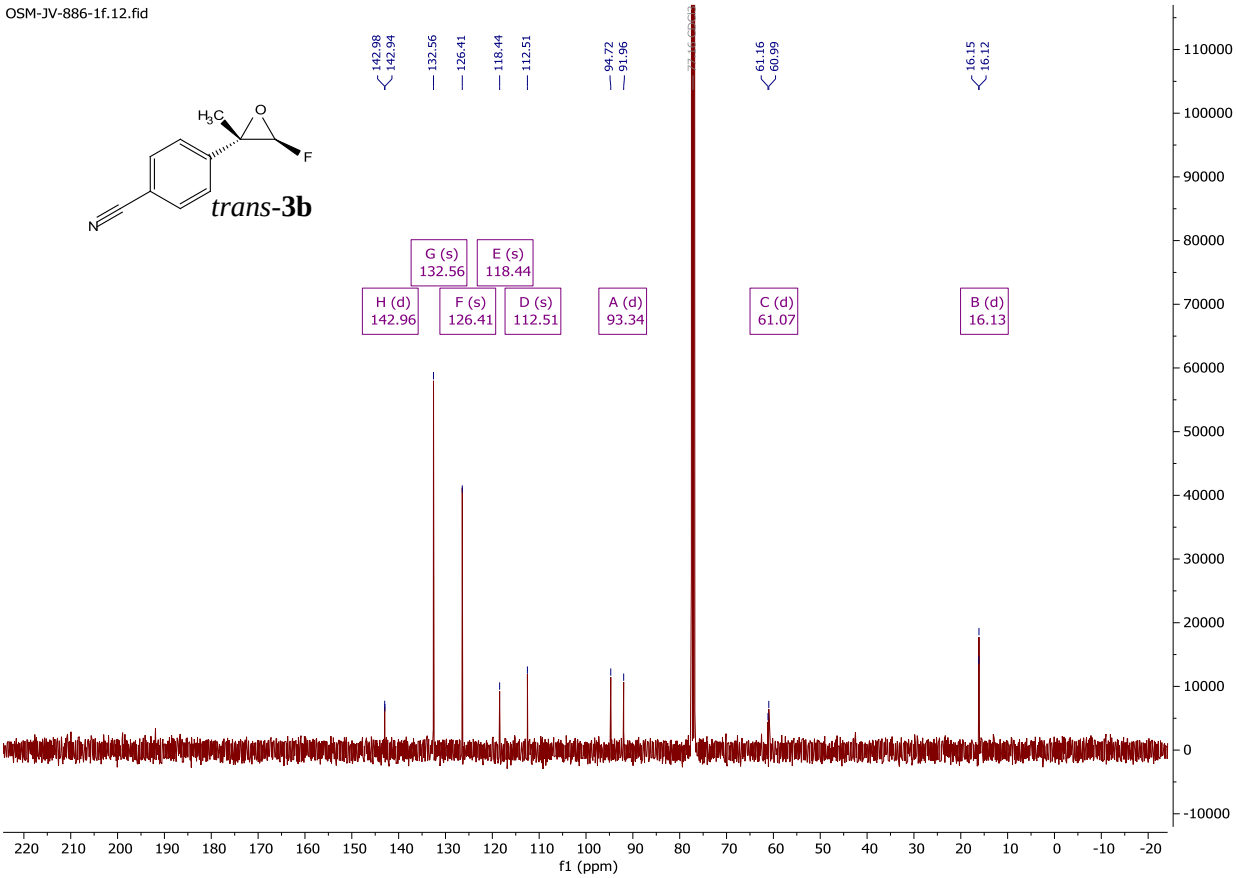

OSM-JV-841-2fr_29Aug18_FLUORINE_cdcl3_01
cis-3a
-154.93
-154.93
-155.16
-155.17
A (dd)
-155.05
1.00
f1 (ppm)

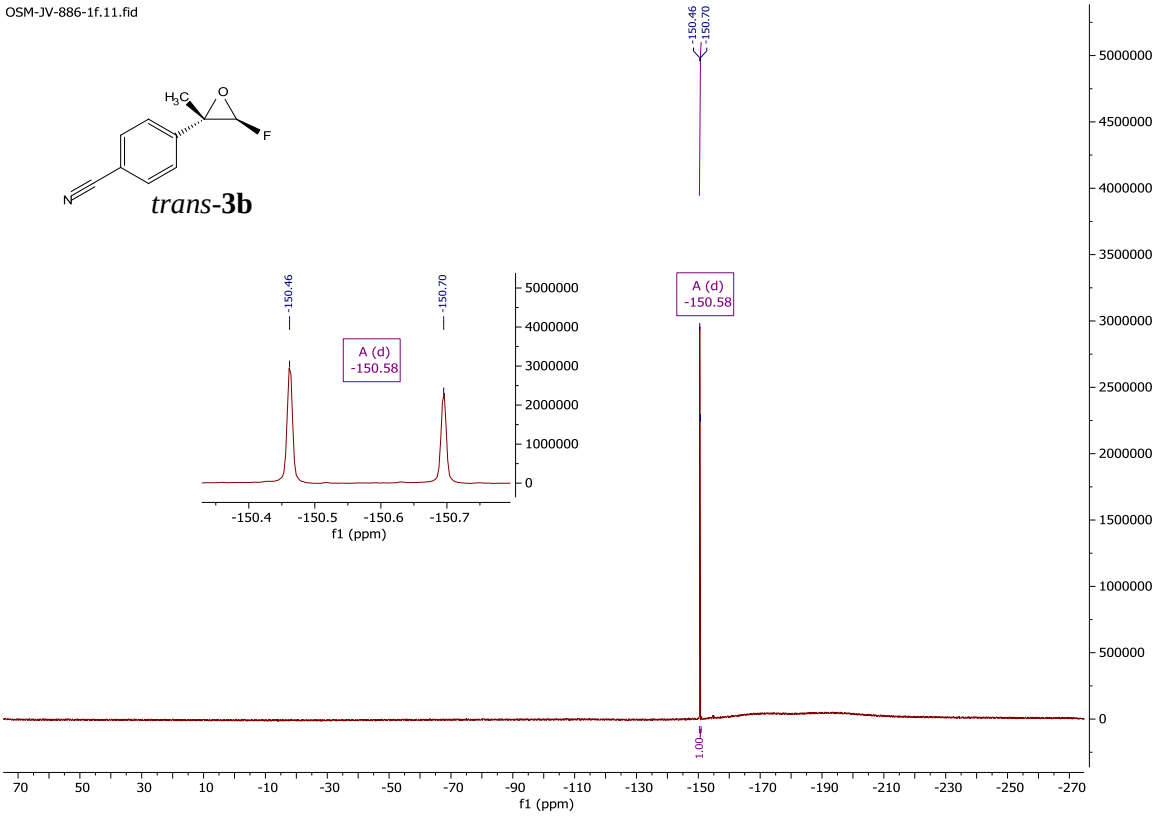

OSM-JV-804-col_07Jun18_PROTON_cdcl3_01
3b
f1 (ppm)

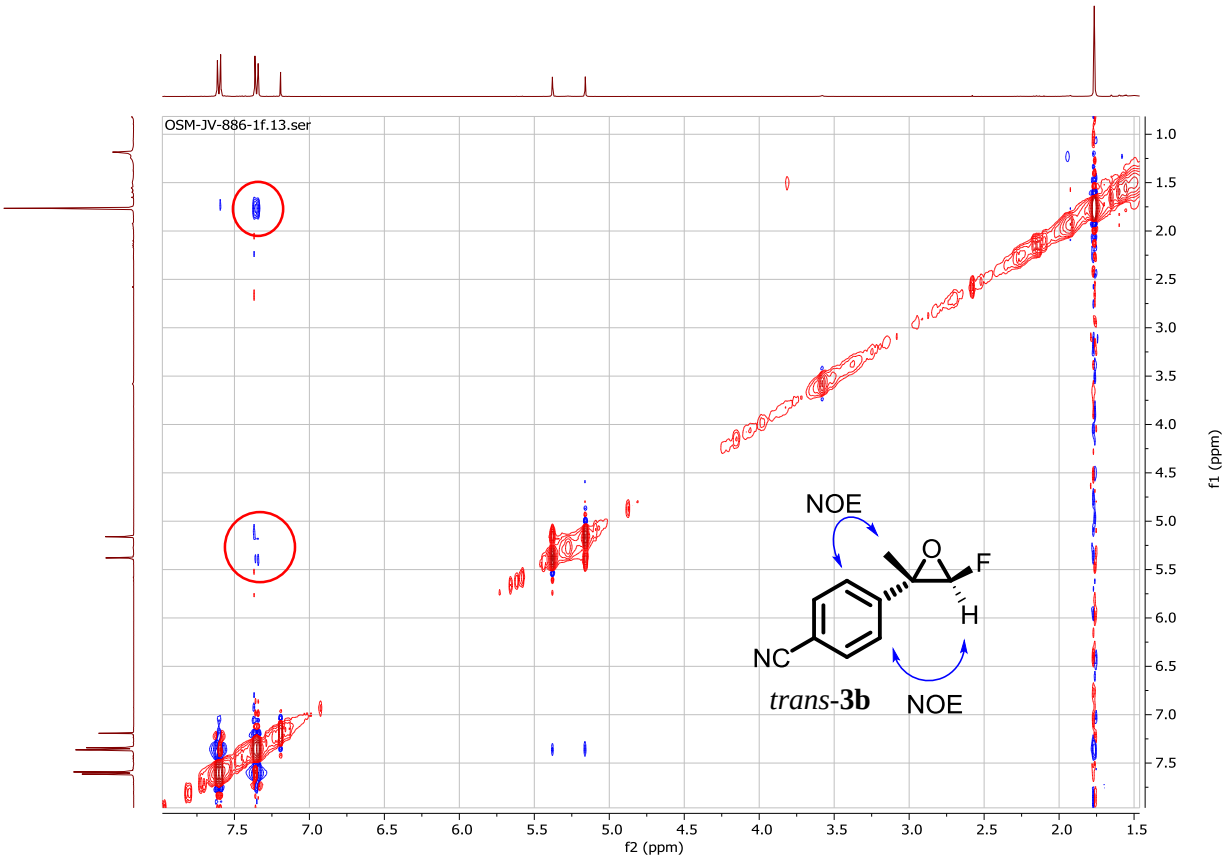

OSM-JV-804-col_07Jun18_CARBON_cdcl3_01
3b
77.16 CDCl3
f1 (ppm)

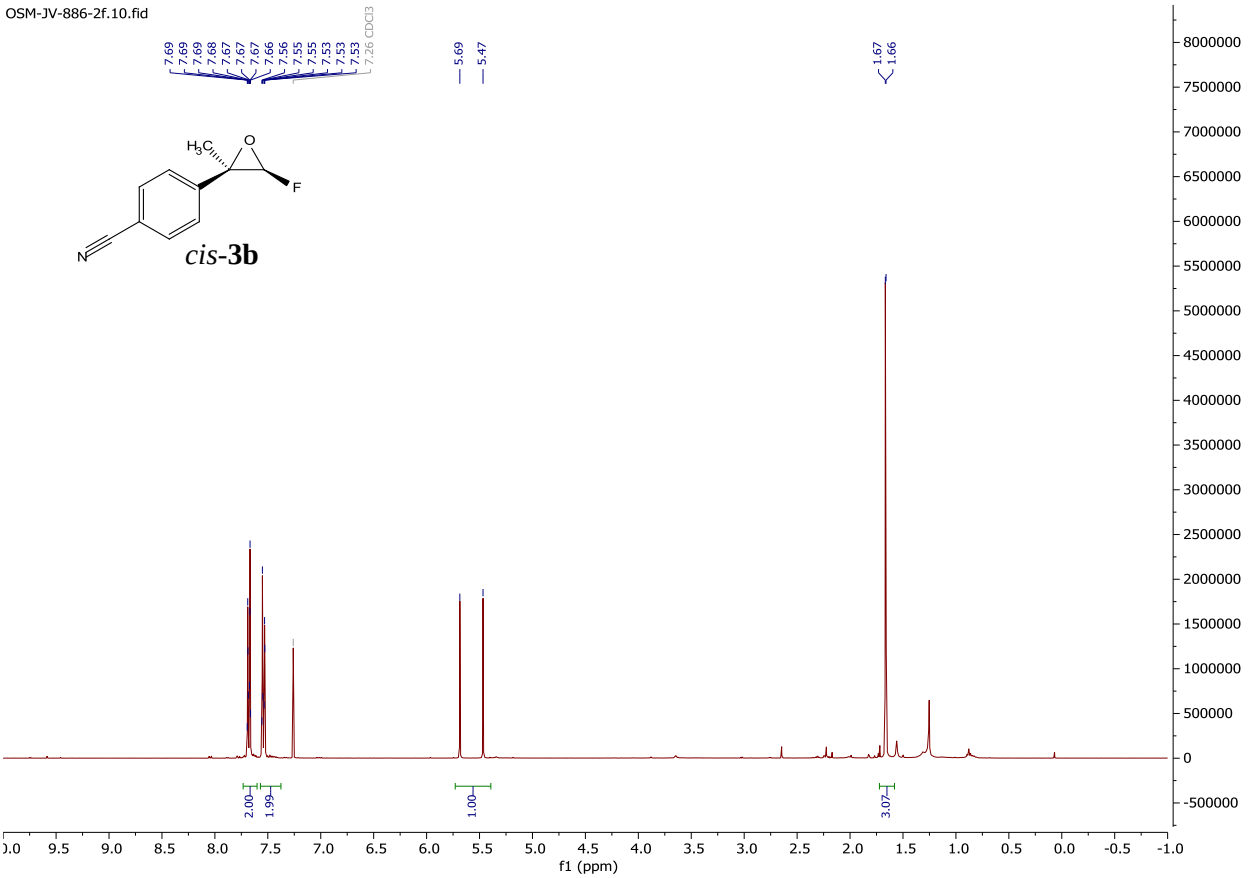

OSM-JV-804-col_07Jun18_FLUORINE_cdcl3_01
3b
A (d)
-150.63
B (dq)
-154.87
f1 (ppm)

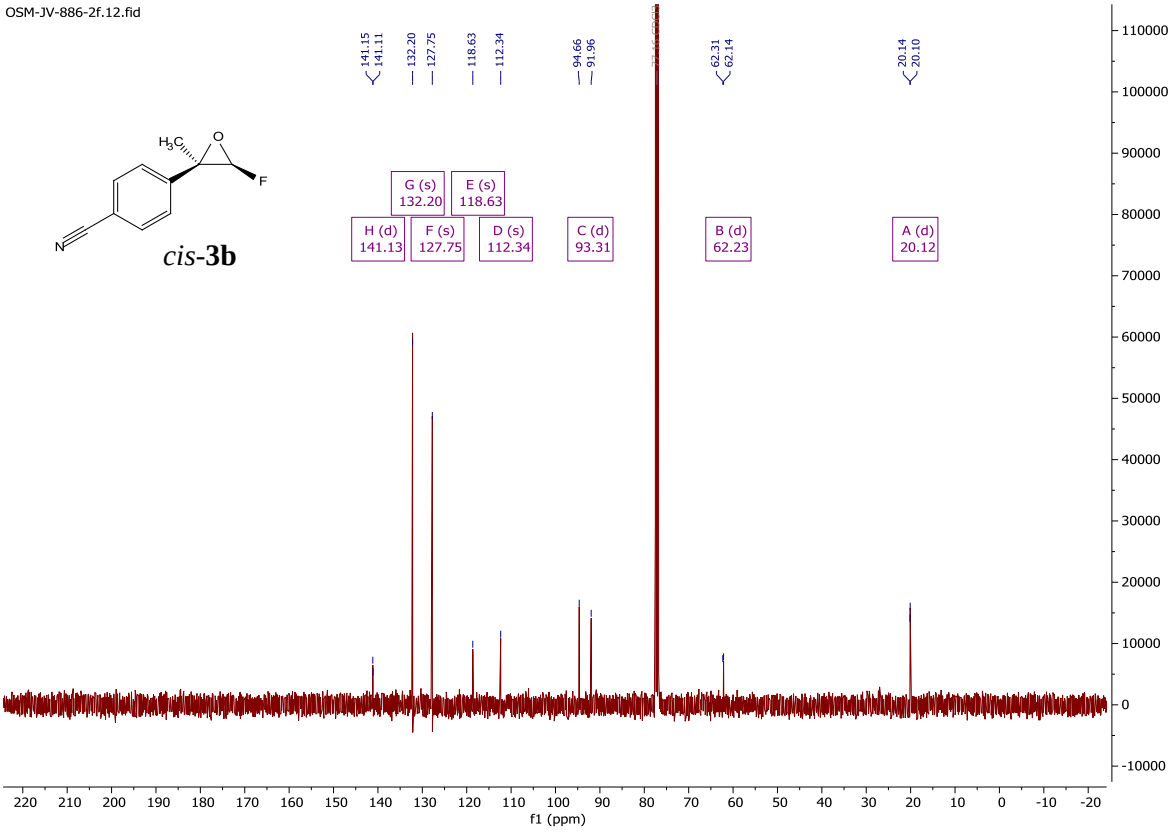

OSM-JV-886-1f.10.fid
trans-3b
f1 (ppm)

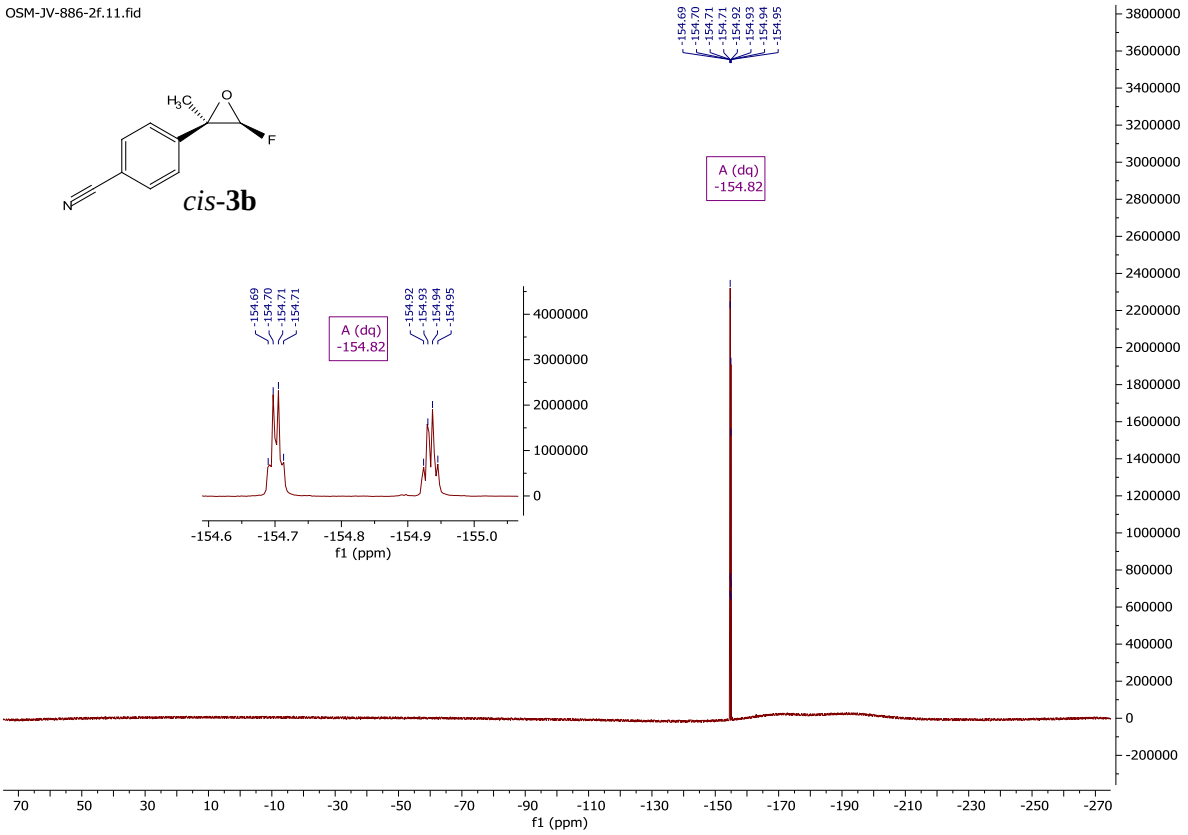

OSM-JV-886-1f.12.fid
142.98
142.94
132.56
126.41
118.44
112.51
94.72
91.96
77.46
77.04
76.62
61.16
60.99
16.15
16.12
trans-3b
G (s)
132.56
E (s)
118.44
H (d)
142.96
F (s)
126.41
D (s)
112.51
A (d)
93.34
C (d)
61.07
B (d)
16.13
f1 (ppm)

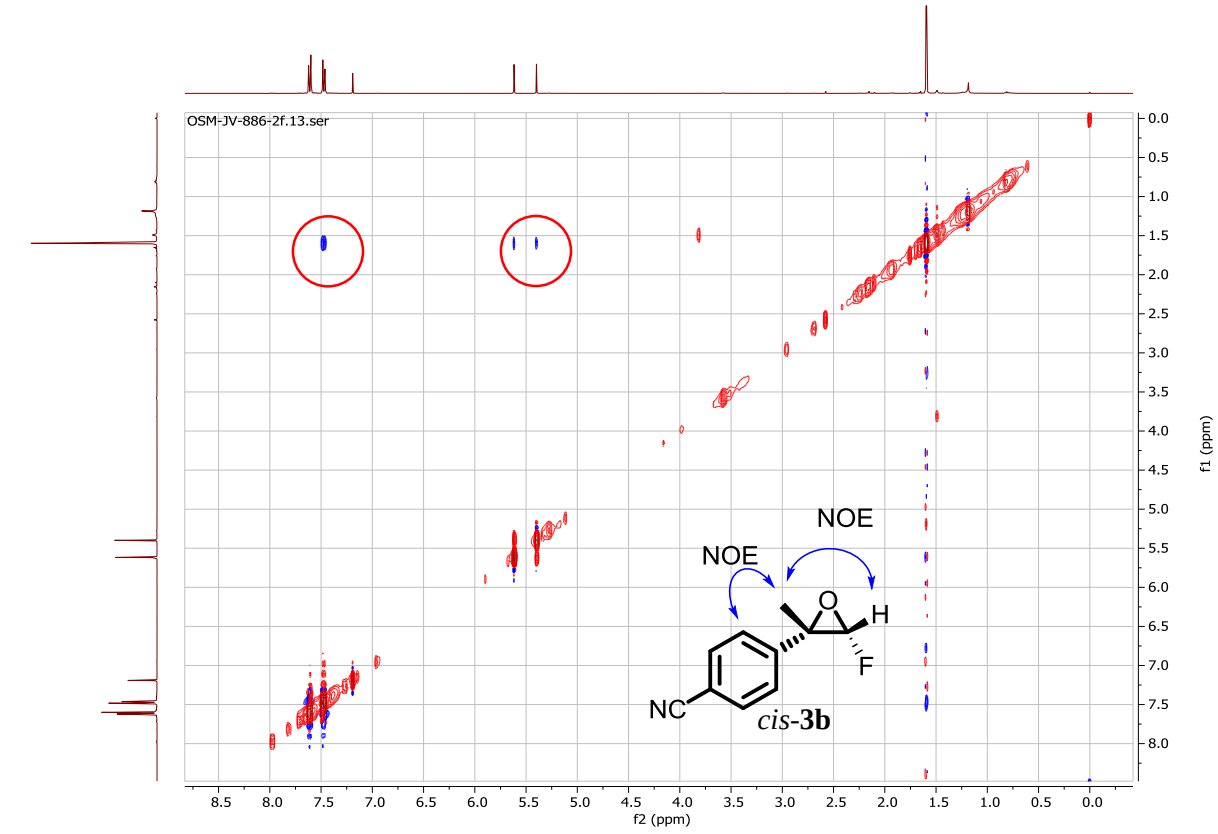

OSM-JV-886-1f.11.fid
-150.46
-150.70
trans-3b
-150.46
-150.70
A (d)
-150.58
A (d)
-150.58
1.00
f1 (ppm)

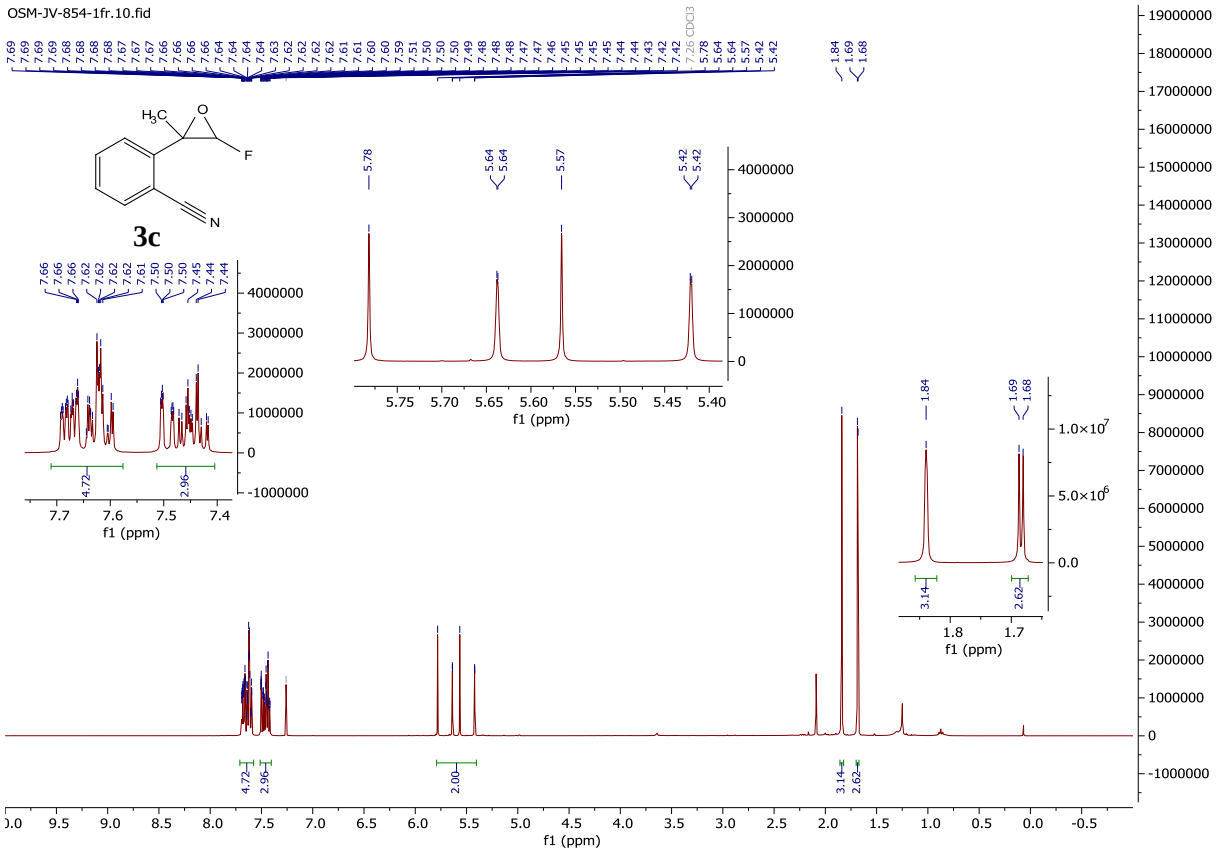

OSM-JV-886-1f.13.ser
NOE
O
F
H
NC
NOE
trans-3b
f2 (ppm)
f1 (ppm)

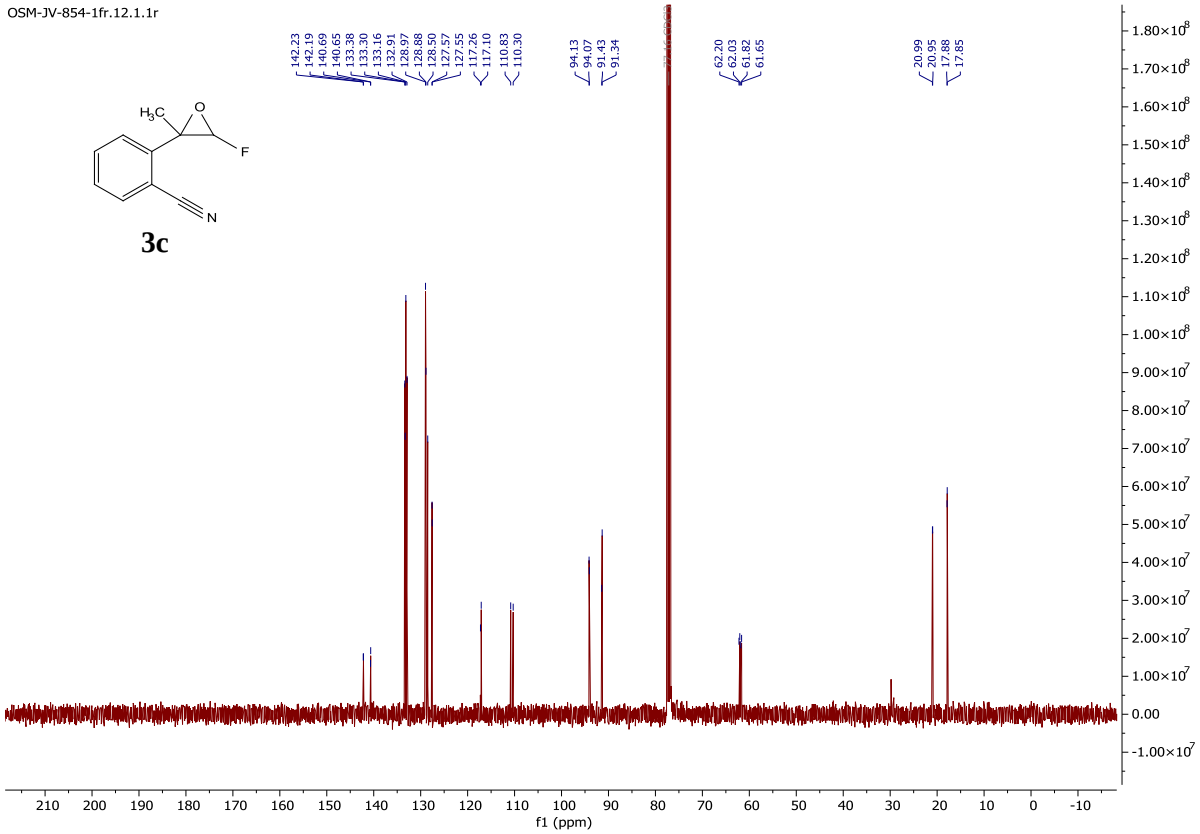

OSM-JV-886-2f.10.fid
7.69
7.69
7.69
7.68
7.67
7.67
7.67
7.66
7.56
7.55
7.55
7.53
7.53
7.53
7.26 CDCl3
5.69
5.47
1.67
1.66
cis-3b
2.00
1.99
1.00
3.07
f1 (ppm)

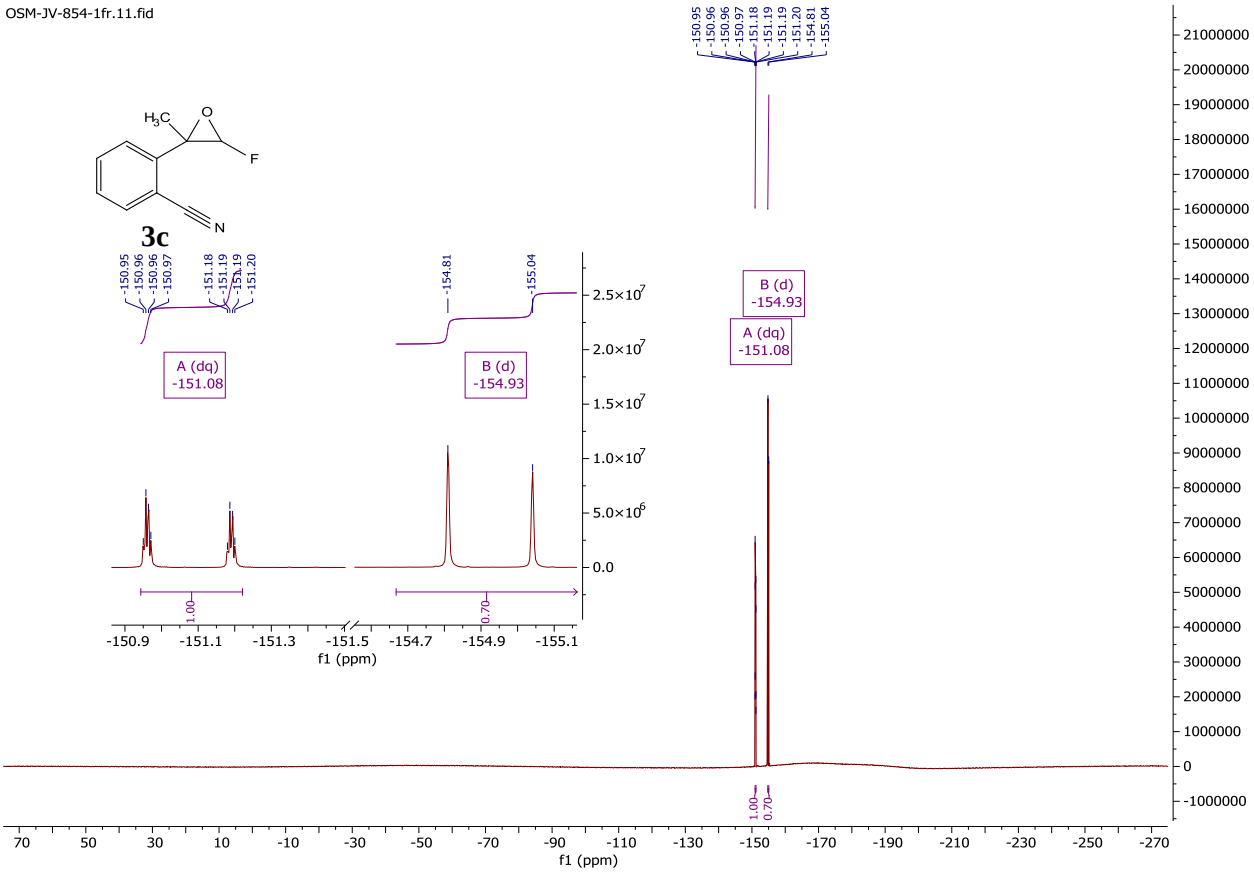

OSM-JV-886-2f.12.fid
141.15
141.11
132.20
127.75
118.63
112.34
94.66
91.96
77.41
77.00
76.59
62.31
62.14
20.14
20.10
G (s)
132.20
E (s)
118.63
H (d)
141.13
F (s)
127.75
D (s)
112.34
C (d)
93.31
B (d)
62.23
A (d)
20.12
cis-3b
f1 (ppm)

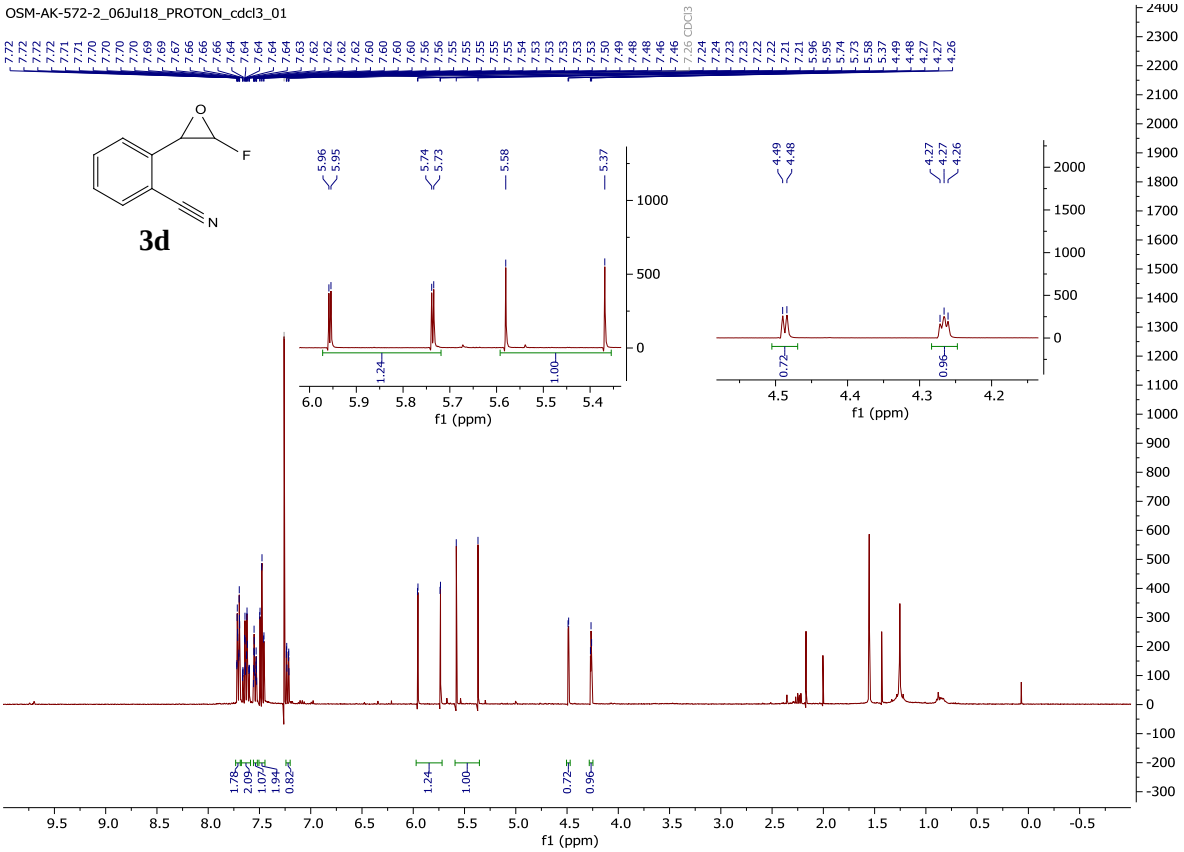

OSM-JV-886-2f.11.fid
-154.69
-154.70
-154.71
-154.71
-154.92
-154.93
-154.94
-154.95
A (dq)
-154.82
cis-3b
f1 (ppm)

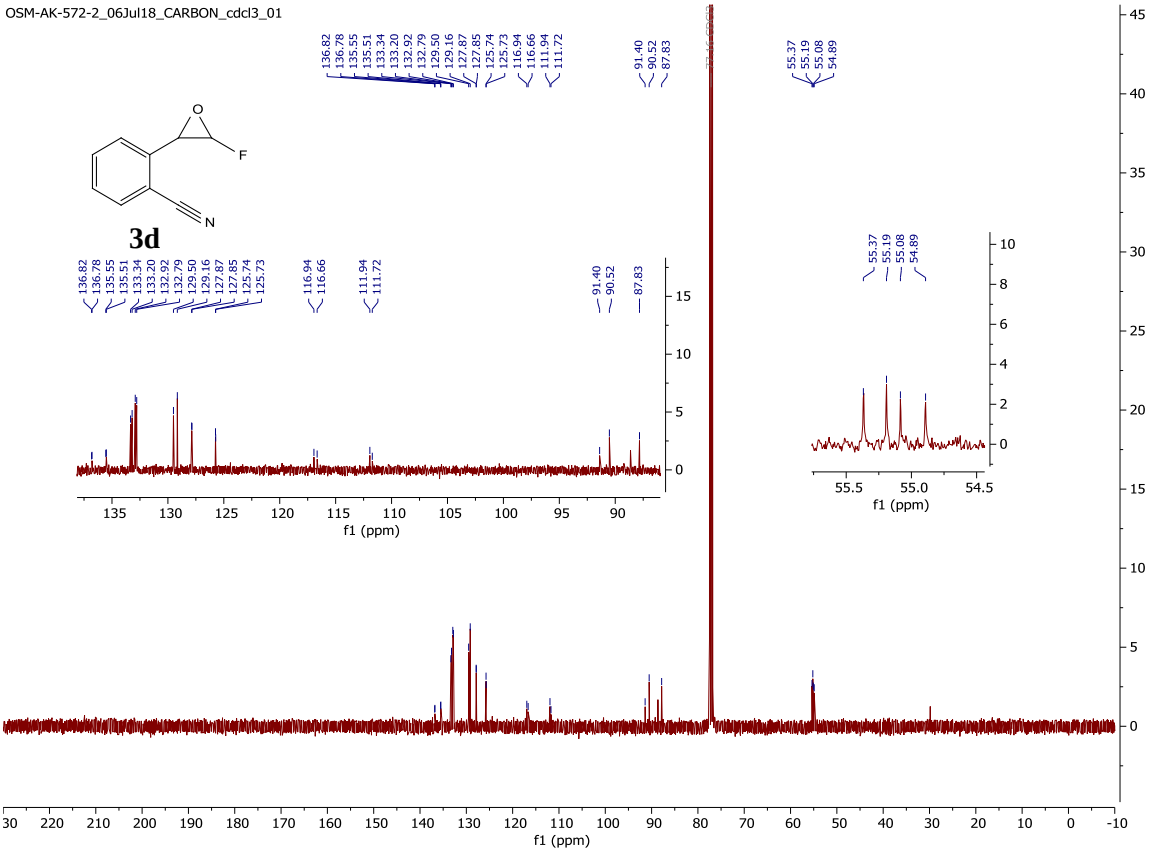

OSM-JV-886-2f.13.ser
NOE
NOE
cis-3b
f2 (ppm)
f1 (ppm)

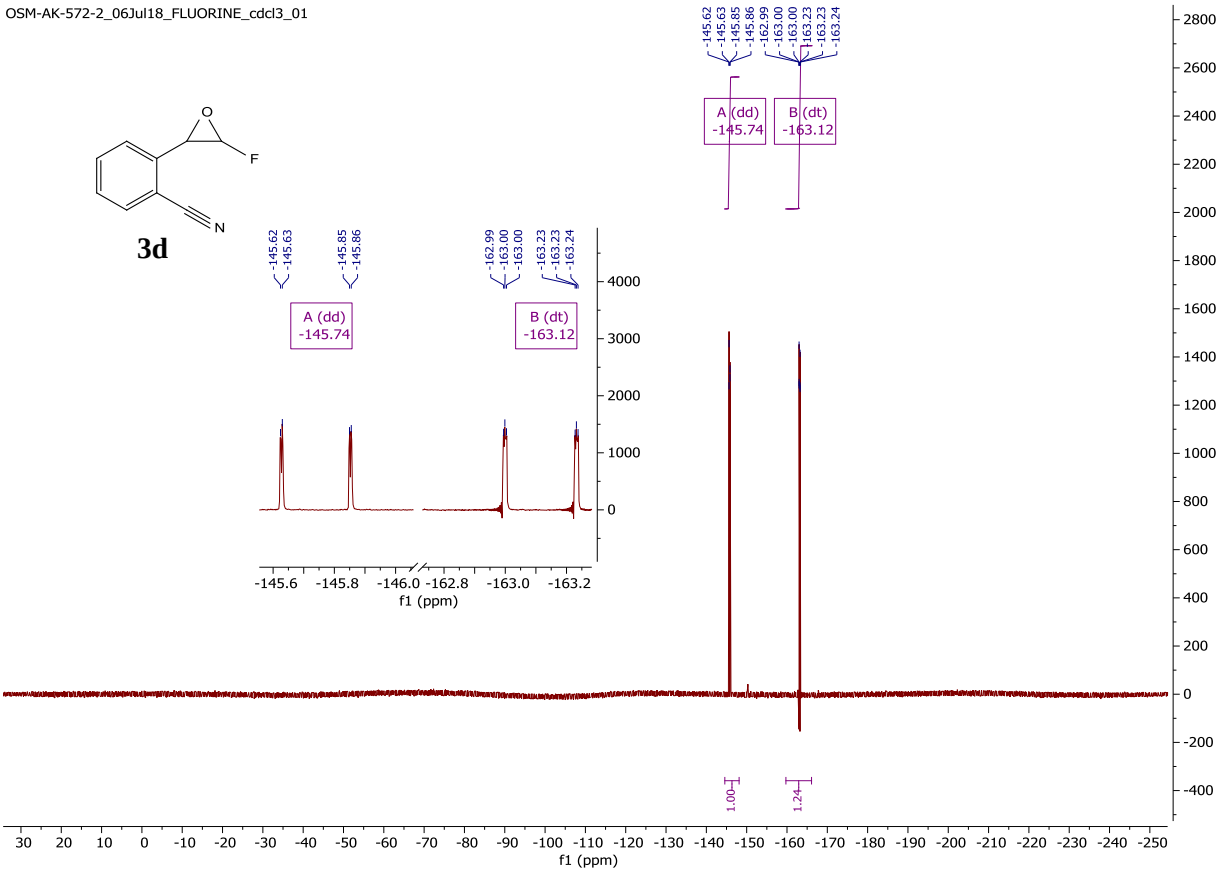

OSM-JV-854-1fr.10.fid
3c
f1 (ppm)

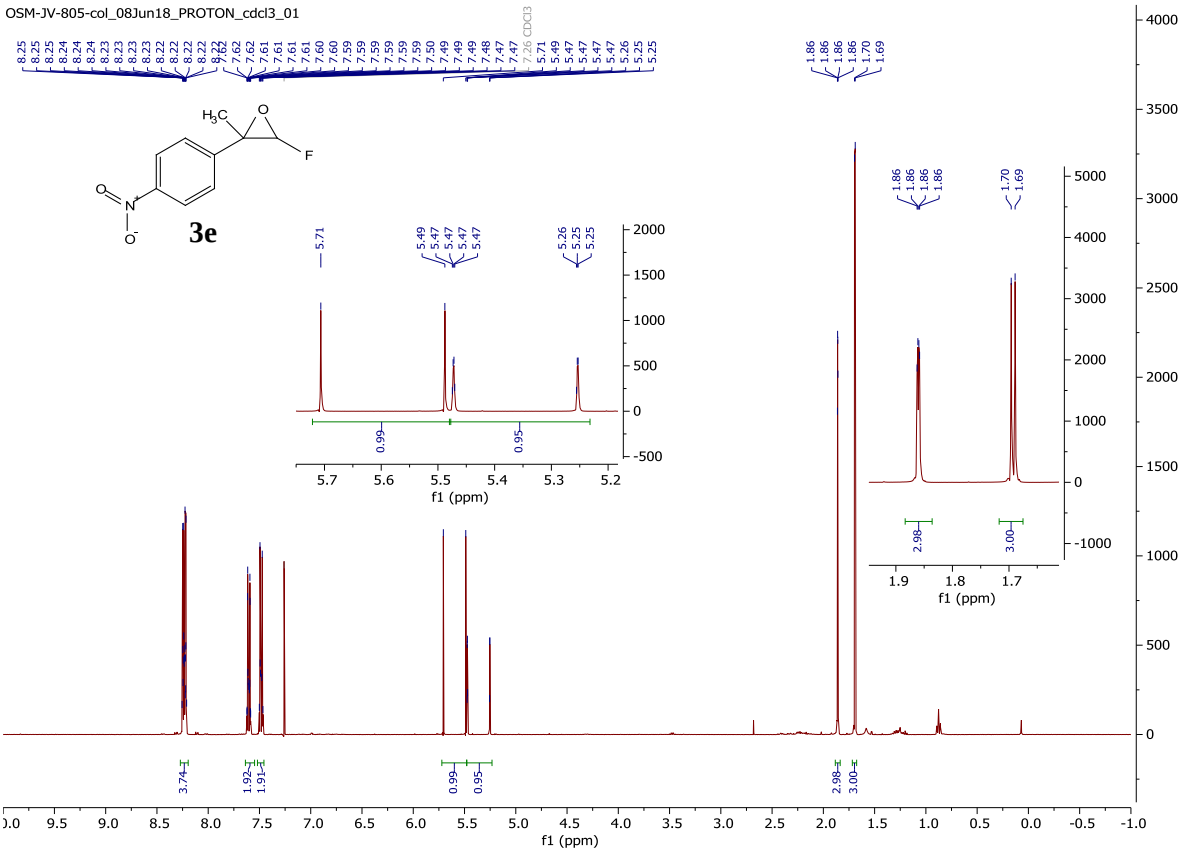

OSM-JV-854-1fr.12.1.1r
3c
f1 (ppm)

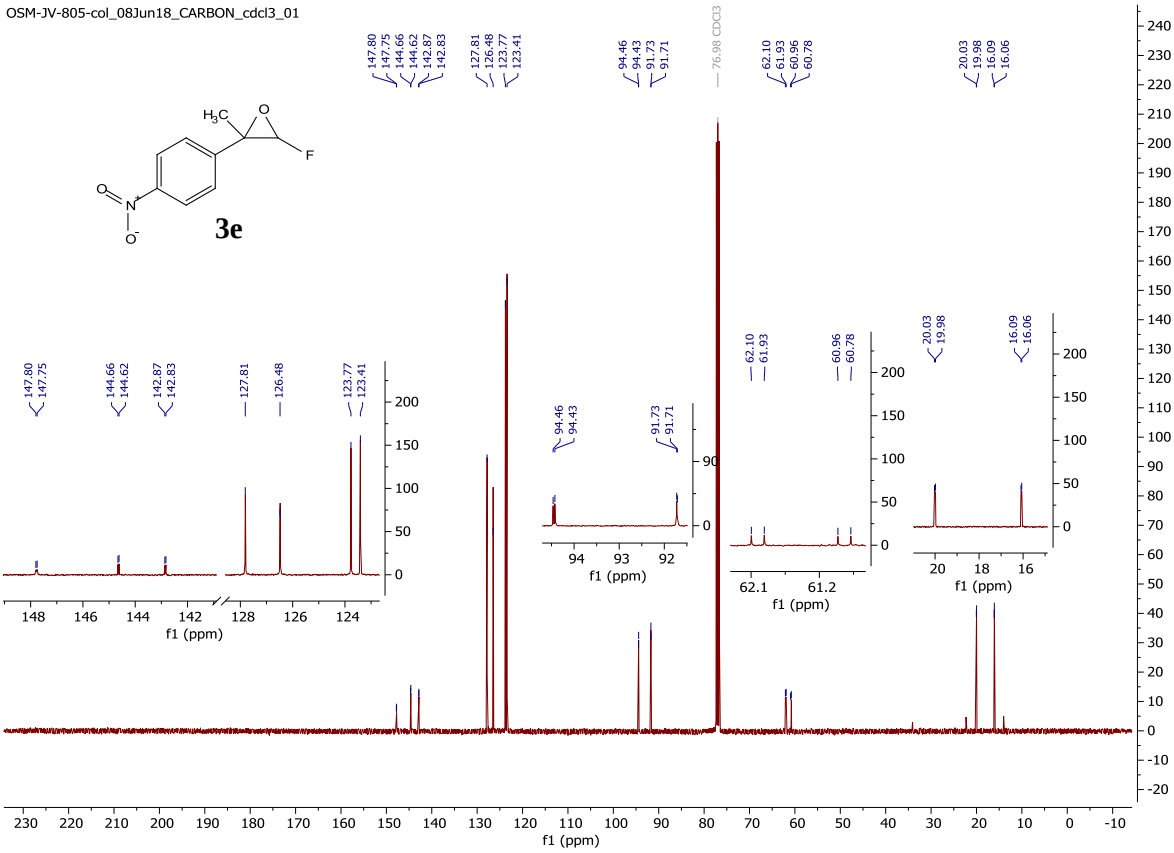

OSM-JV-854-1fr.11.fid
3c
A (dq)
-151.08
B (d)
-154.93
f1 (ppm)

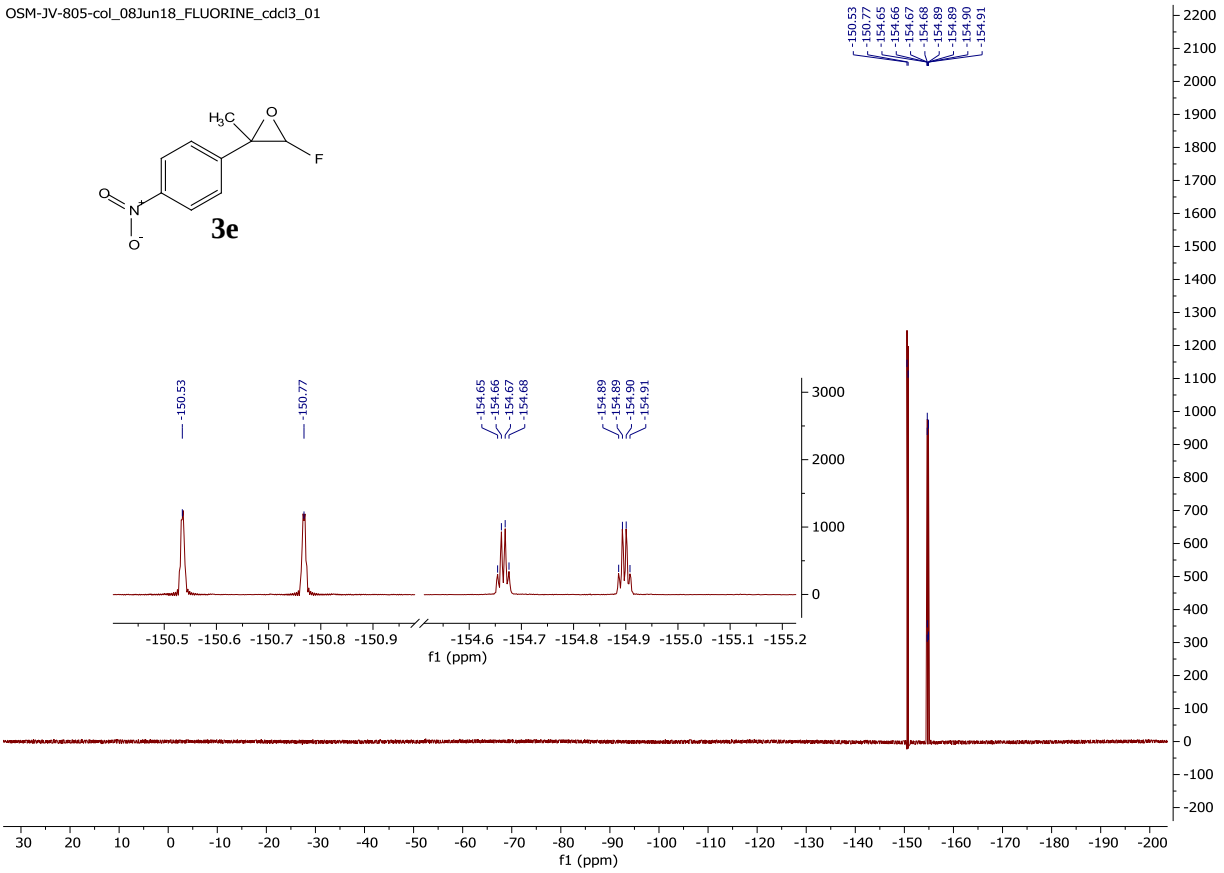

OSM-AK-572-2_06Jul18_PROTON_cdcl3_01
3d
f1 (ppm)

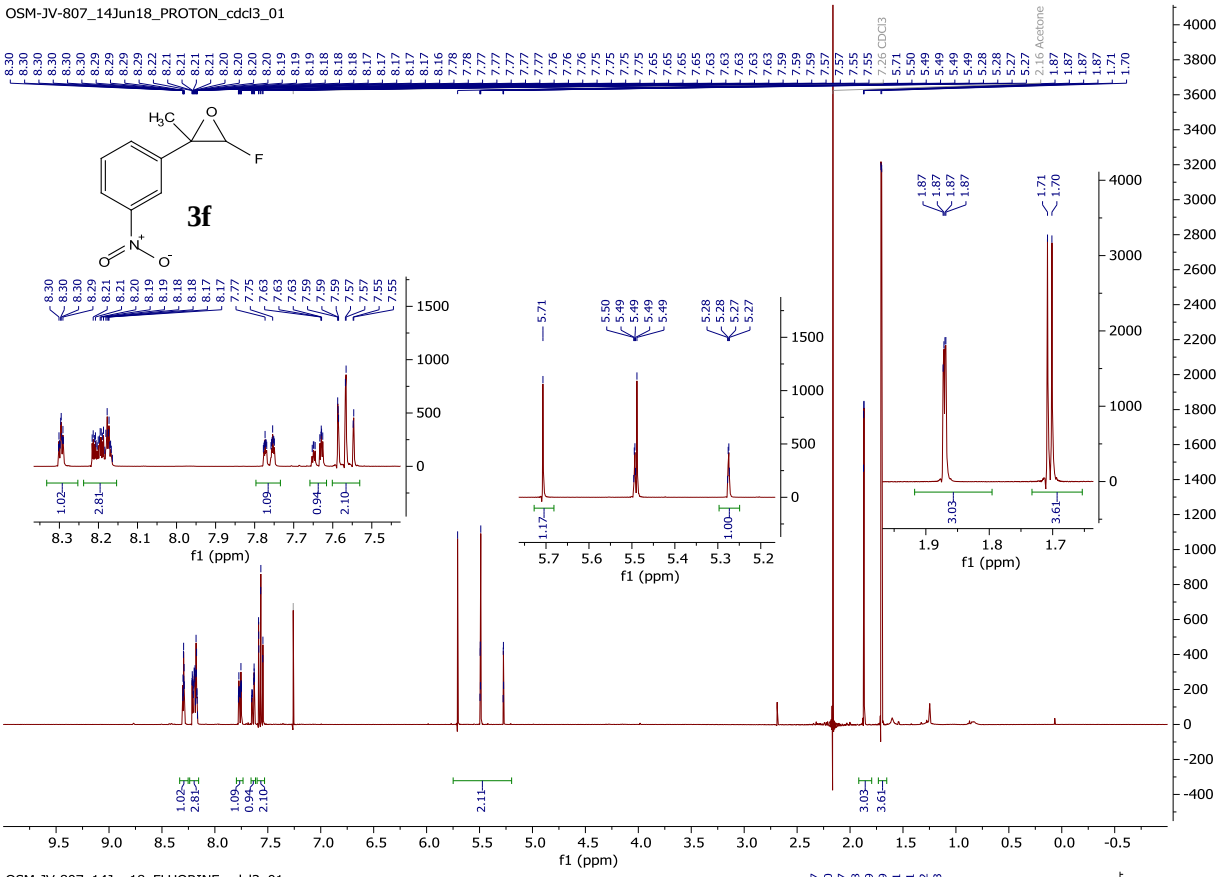

OSM-AK-572-2_06Jul18_CARBON_cdcl3_01
3d
f1 (ppm)

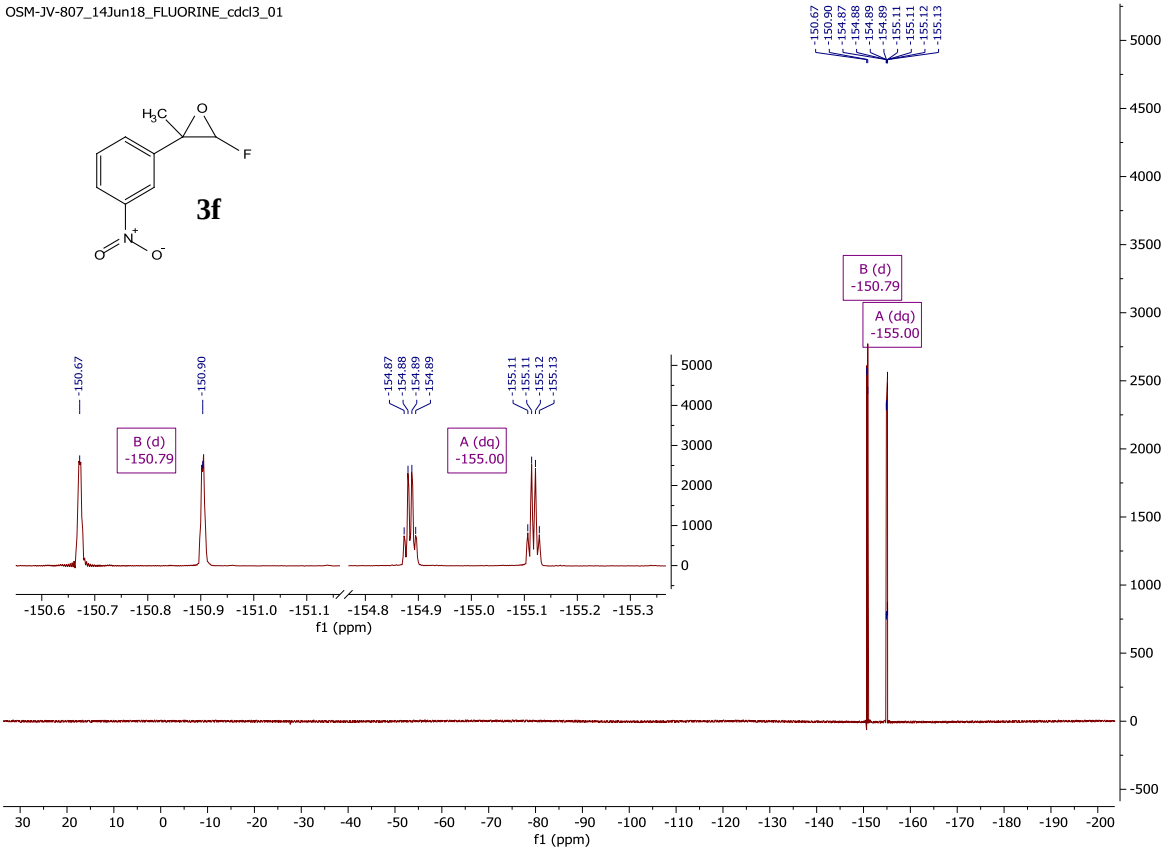

OSM-AK-572-2_06Jul18_FLUORINE_cdcl3_01
3d
A (dd)
-145.74
B (dt)
-163.12
f1 (ppm)
1.00
1.24

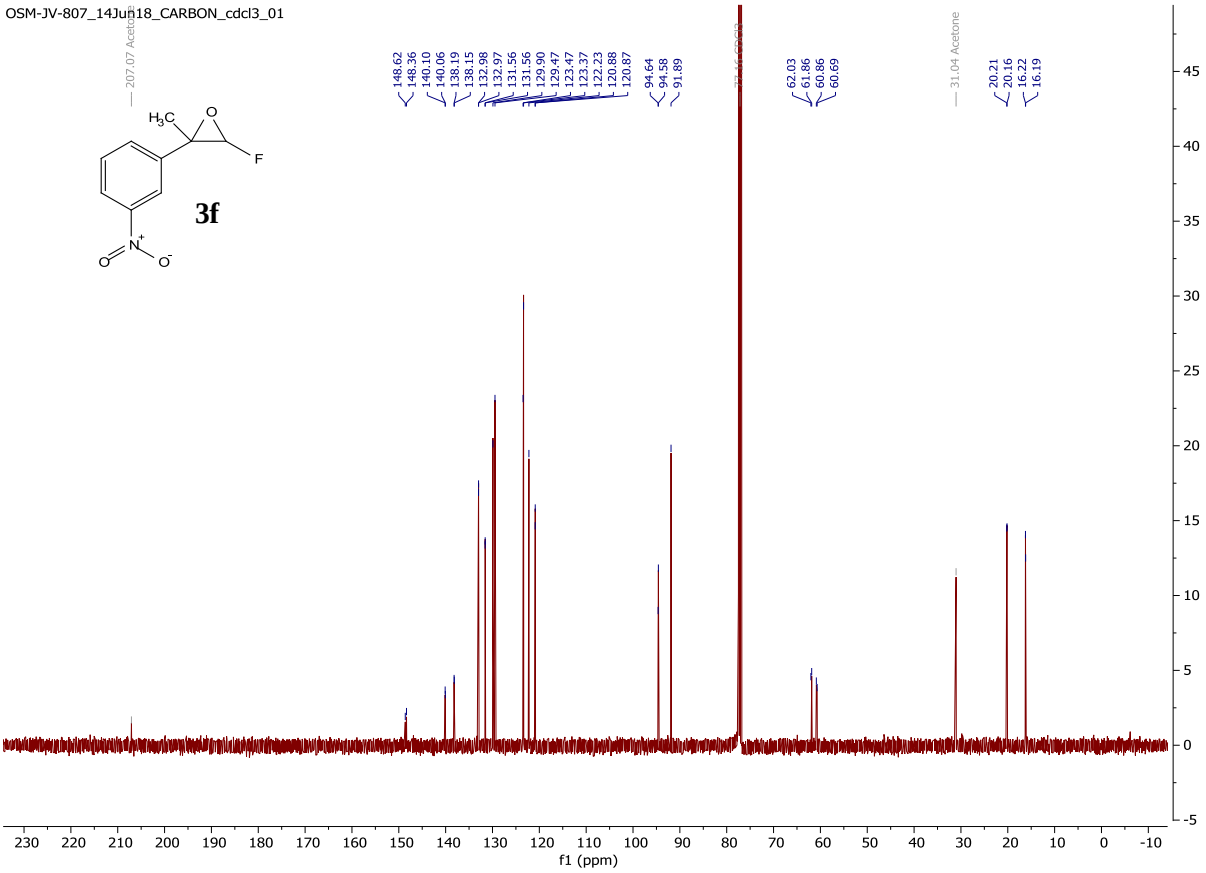

OSM-JV-805-col_08Jun18_PROTON_cdcl3_01
3e
f1 (ppm)

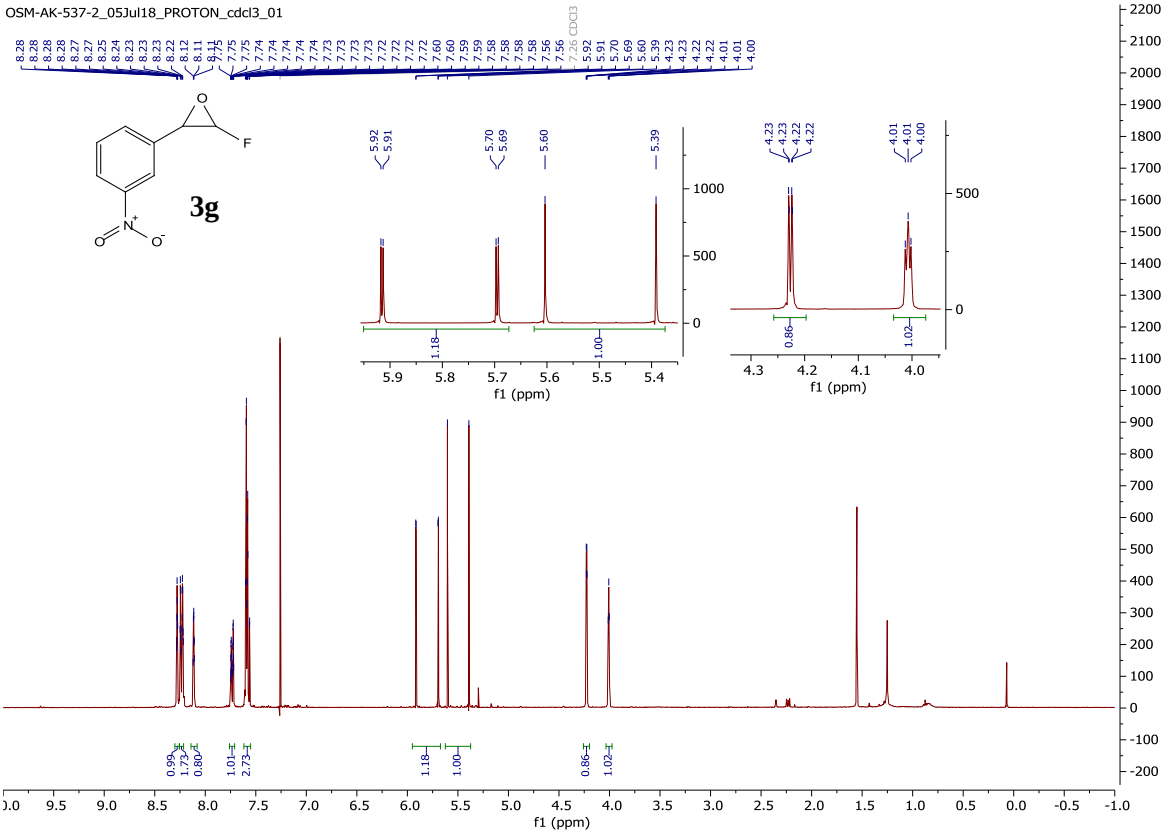

OSM-JV-805-col_08Jun18_CARBON_cdcl3_01
3e
f1 (ppm)

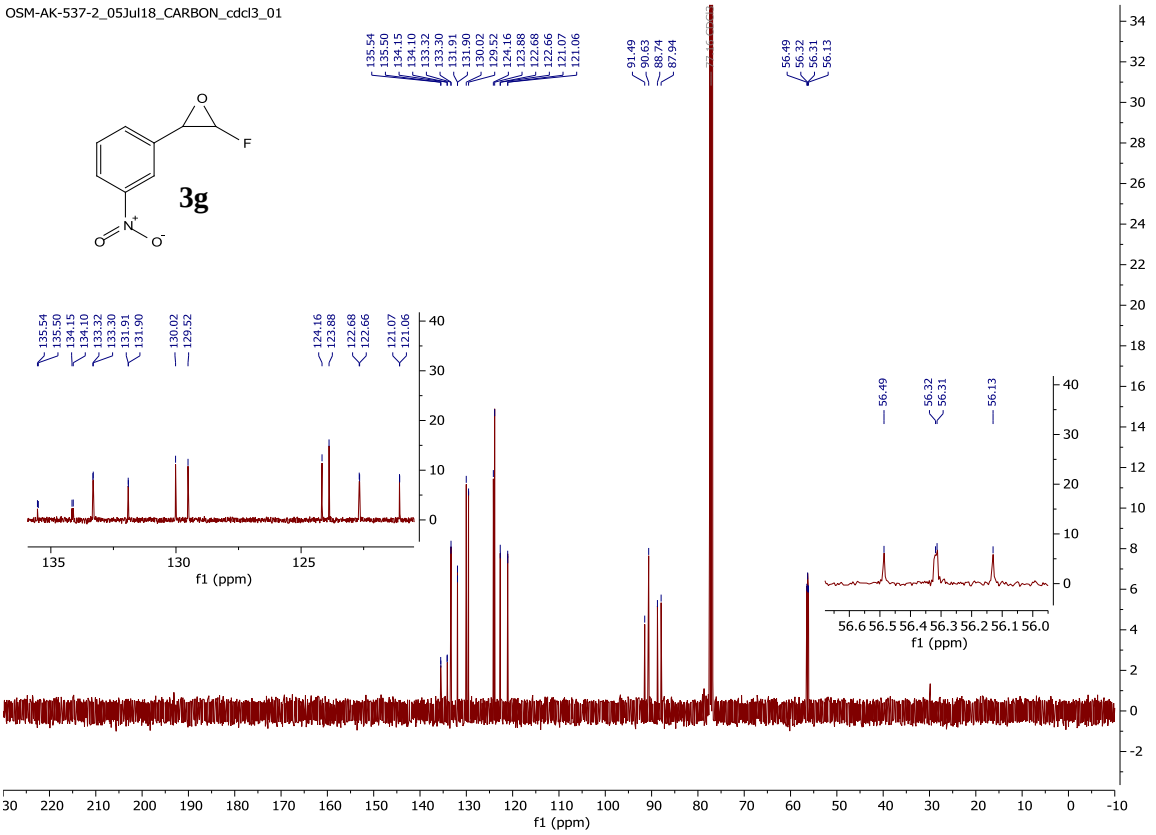

OSM-JV-805-col_08Jun18_FLUORINE_cdcl3_01
-150.53
-150.77
-154.65
-154.66
-154.67
-154.68
-154.89
-154.89
-154.90
-154.91
H3C
O
F
O
N+
O-
3e
f1 (ppm)
f1 (ppm)

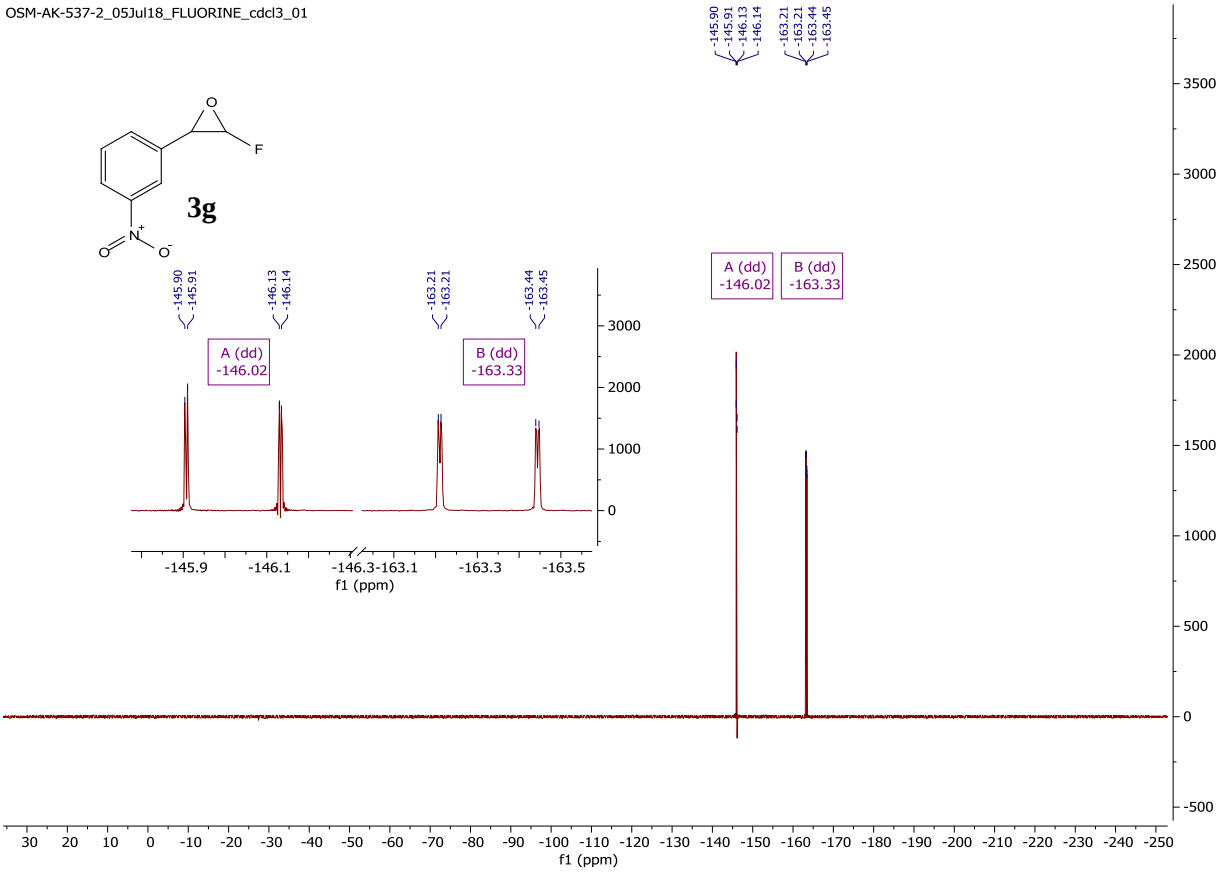

OSM-JV-807_14Jun18_PROTON_cdcl3_01
3f
f1 (ppm)

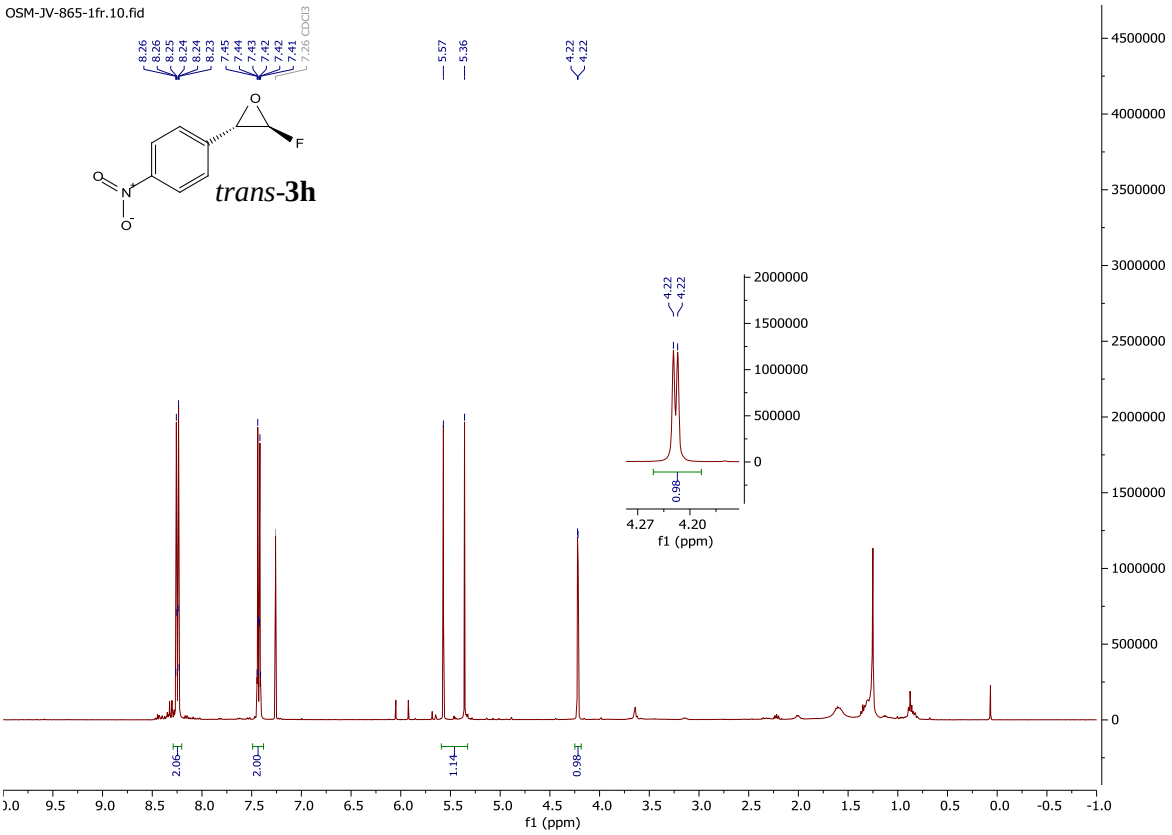

OSM-JV-807_14Jun18_FLUORINE_cdcl3_01
3f
B (d)
-150.79
A (dq)
-155.00
f1 (ppm)

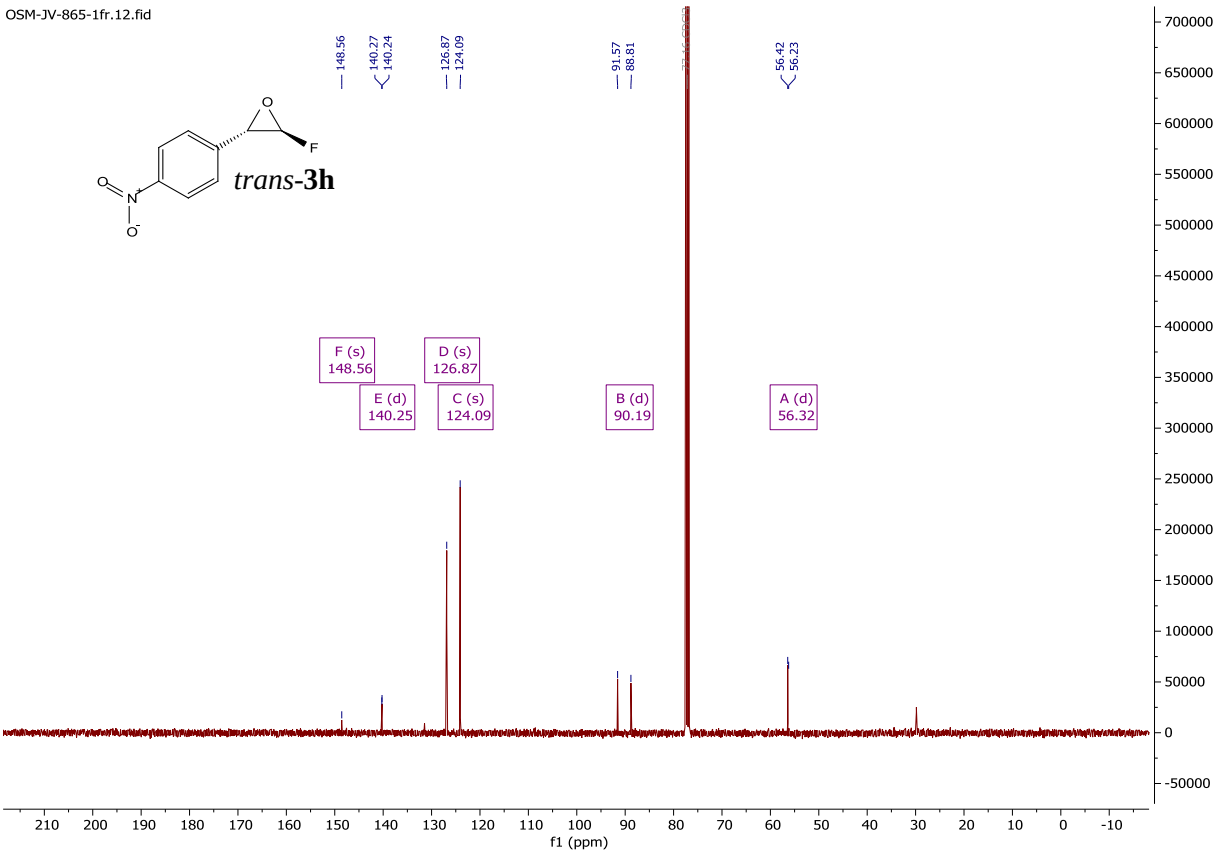

OSM-JV-807_14Jun18_CARBON_cdcl3_01
207.07 Acetone
148.62
148.36
140.10
140.06
138.19
138.15
132.98
132.97
131.56
131.56
129.90
129.47
123.47
123.37
122.23
120.88
120.87
94.64
94.58
91.89
77.46 CDCl3
62.03
61.86
60.86
60.69
31.04 Acetone
20.21
20.16
16.22
16.19
3f
f1 (ppm)

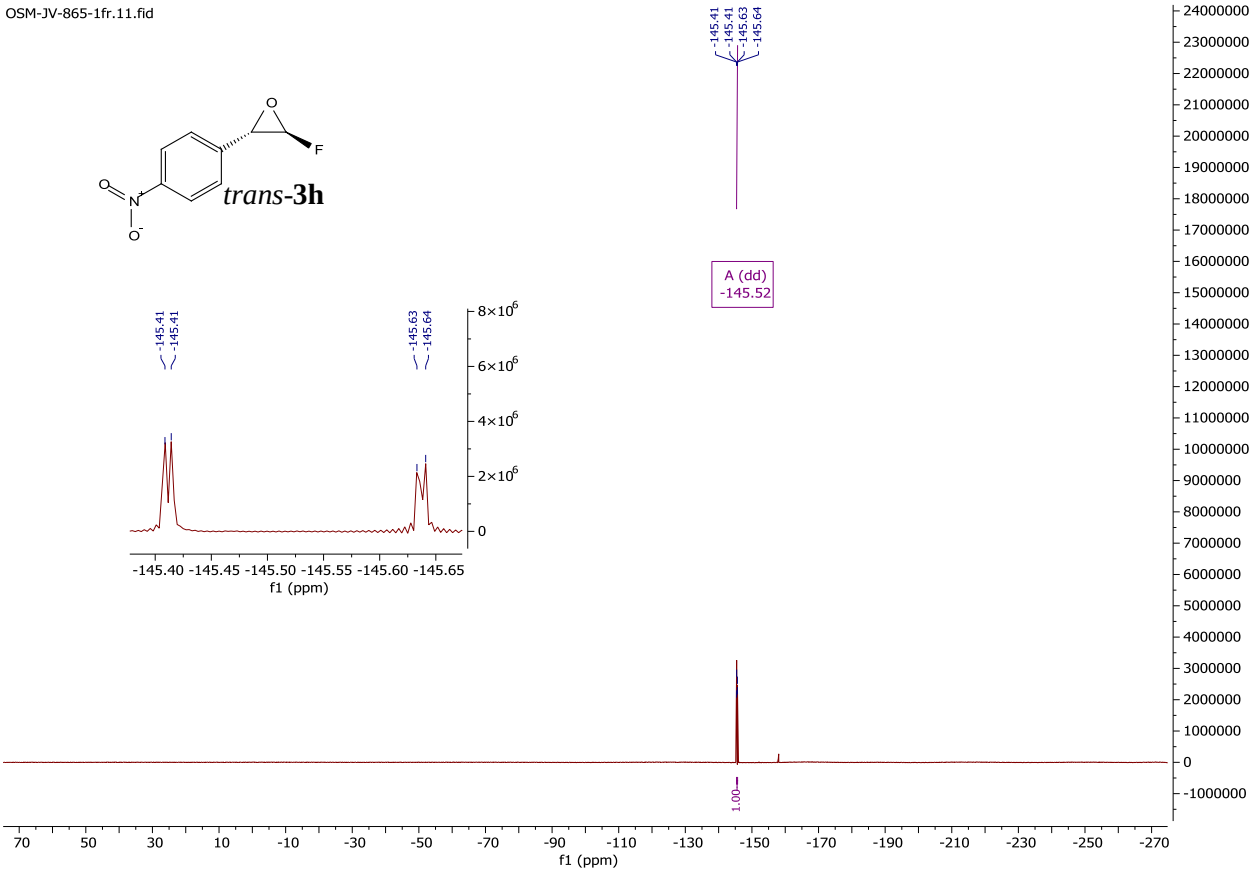

OSM-AK-537-2_05Jul18_PROTON_cdcl3_01
3g
f1 (ppm)

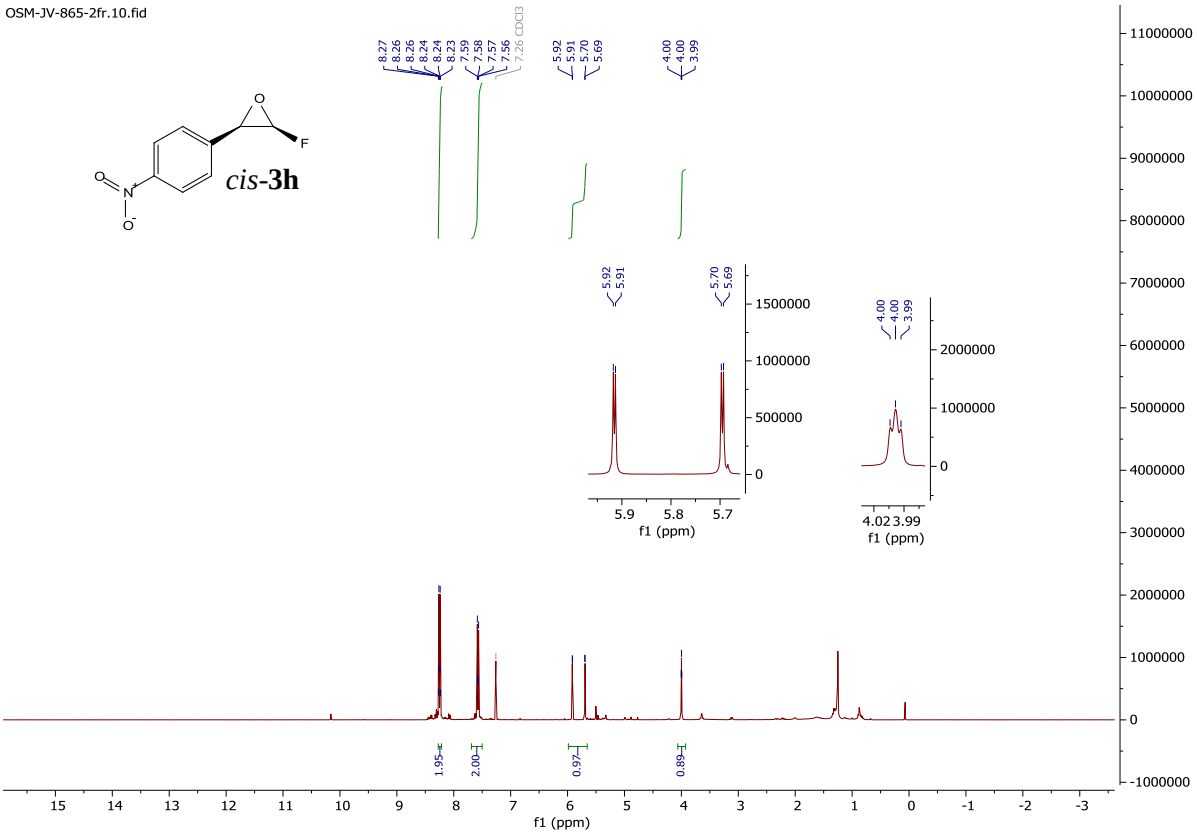

OSM-AK-537-2_05Jul18_CARBON_cdcl3_01
3g
f1 (ppm)

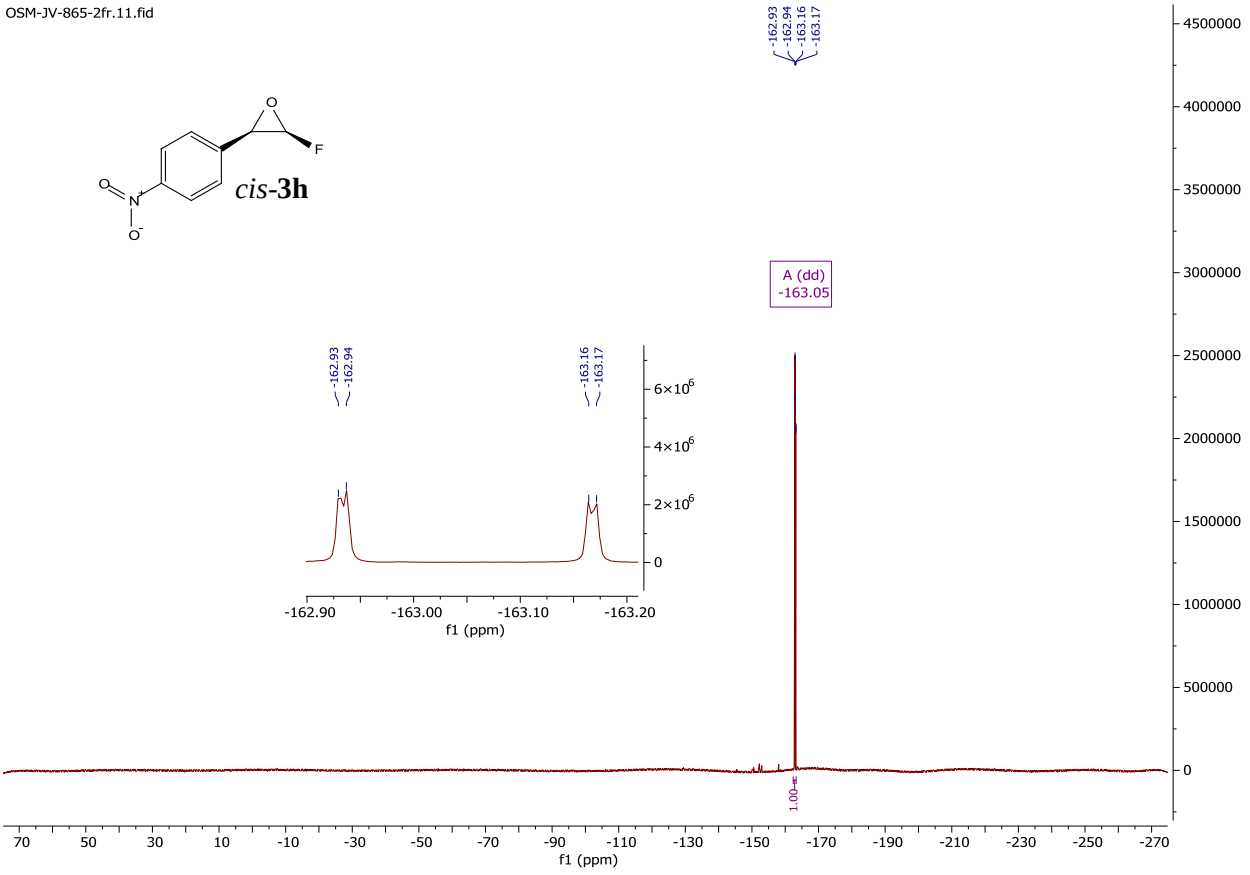

OSM-AK-537-2_05Jul18_FLUORINE_cdcl3_01
3g
A (dd)
-146.02
B (dd)
-163.33
f1 (ppm)

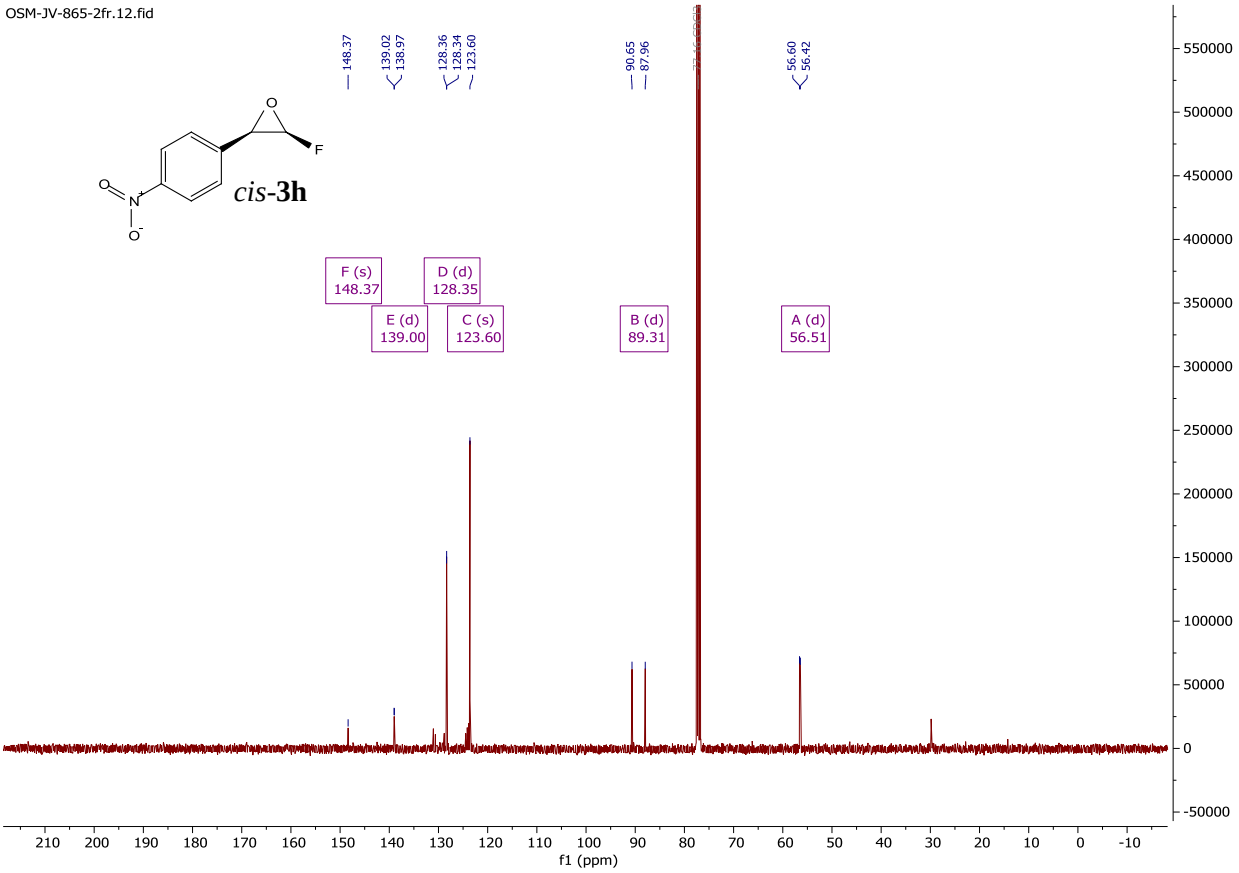

OSM-JV-865-1fr.10.fid
8.26
8.26
8.25
8.24
8.24
8.23
7.45
7.44
7.43
7.42
7.42
7.41
7.26 CDCl3
5.57
5.36
4.22
4.22
trans-3h
2.06
2.00
1.14
0.98
f1 (ppm)

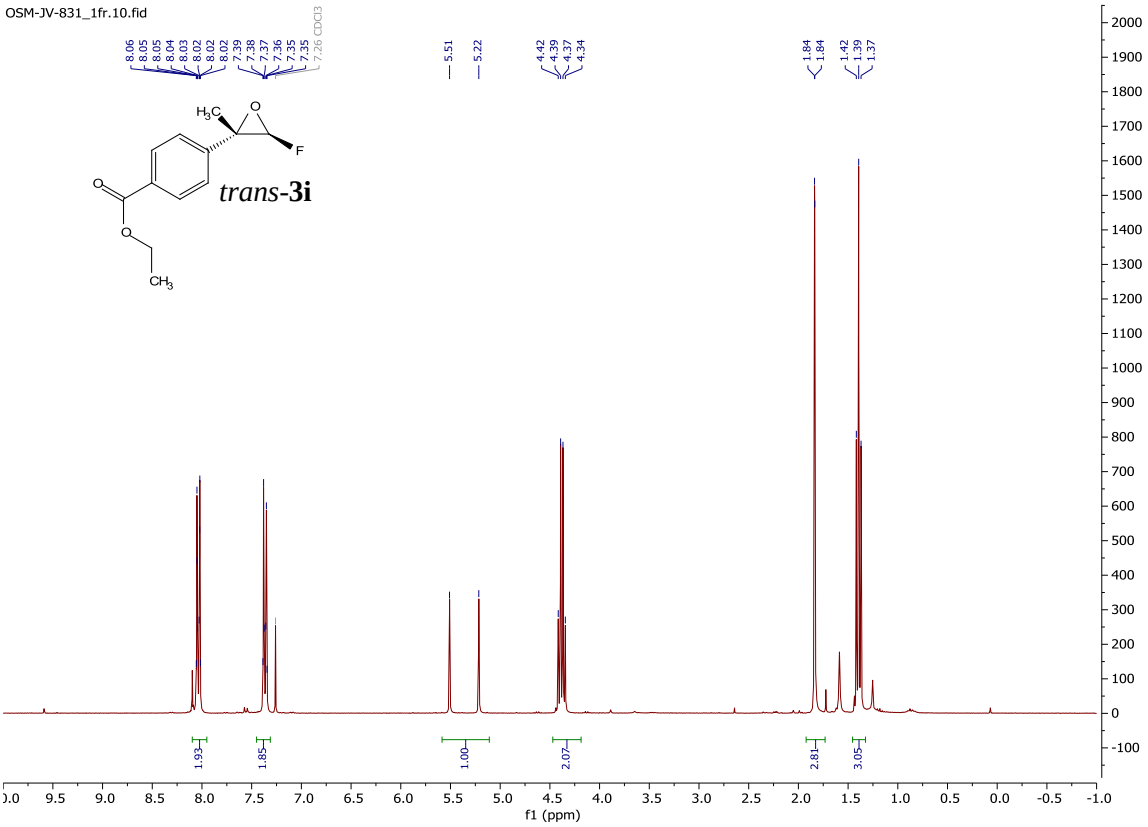

OSM-JV-865-1fr.12.fid
148.56
140.27
140.24
126.87
124.09
91.57
88.81
77.16 CDCl3
56.42
56.23
trans-3h
F (s)
148.56
D (s)
126.87
E (d)
140.25
C (s)
124.09
B (d)
90.19
A (d)
56.32
f1 (ppm)

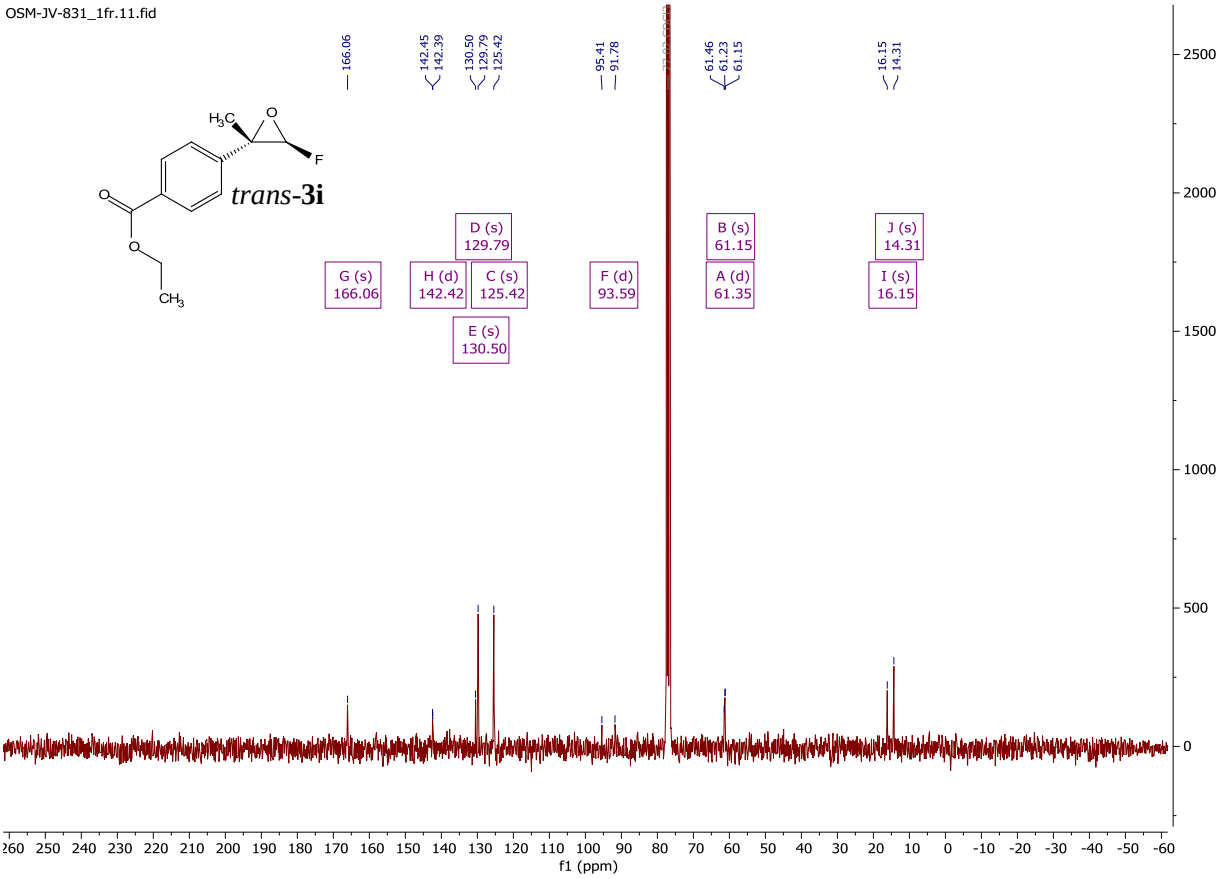

OSM-JV-865-1fr.11.fid
trans-3h
-145.41
-145.41
-145.63
-145.64
A (dd)
-145.52
1.00
f1 (ppm)

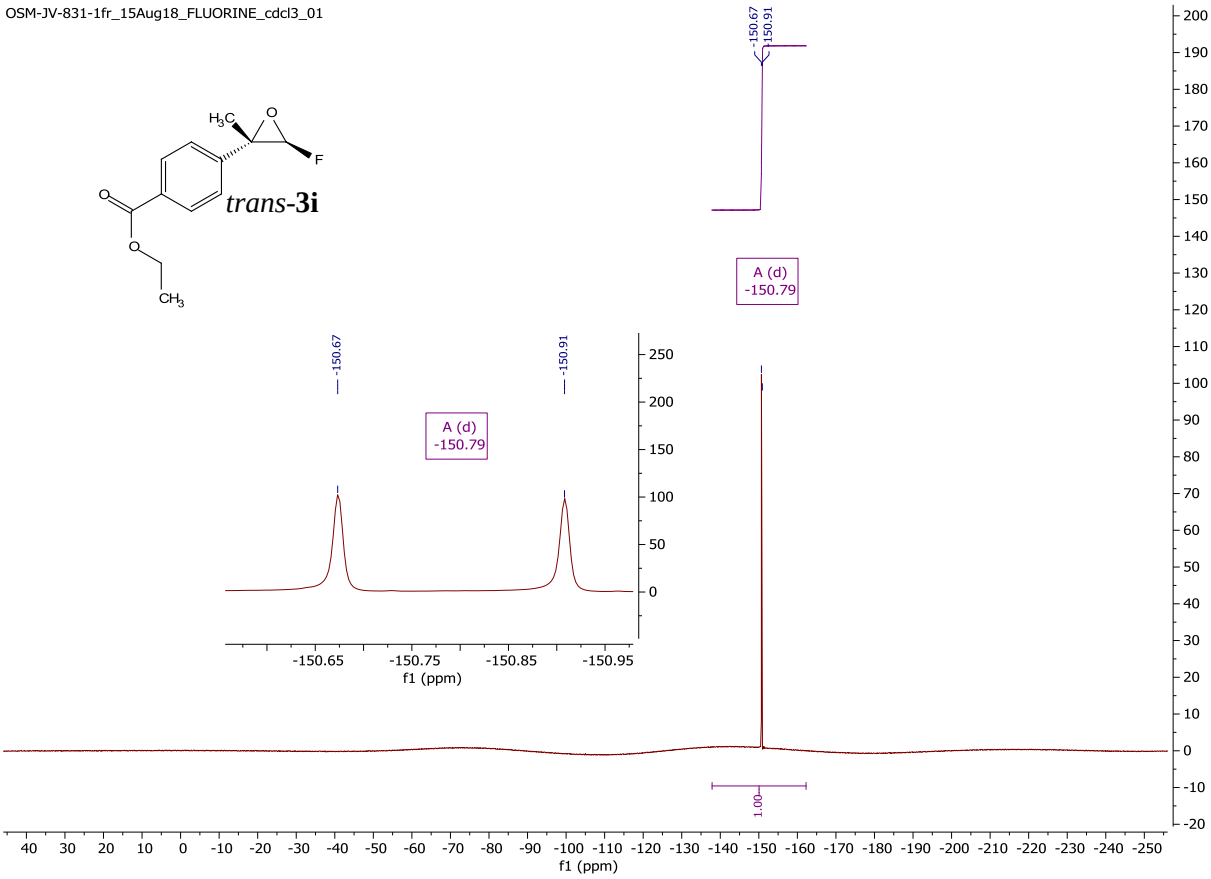

OSM-JV-865-2fr.10.fid
cis-3h
f1 (ppm)

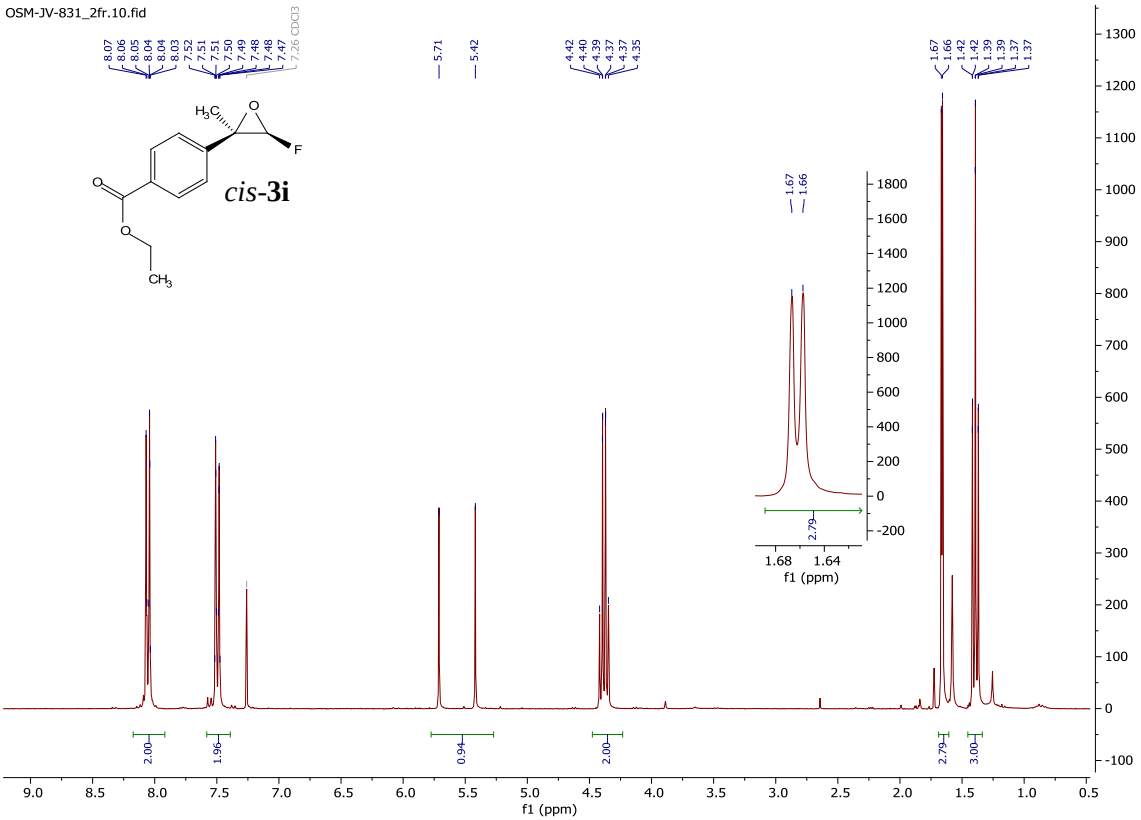

OSM-JV-865-2fr.11.fid
cis-3h
A (dd)
-163.05
f1 (ppm)

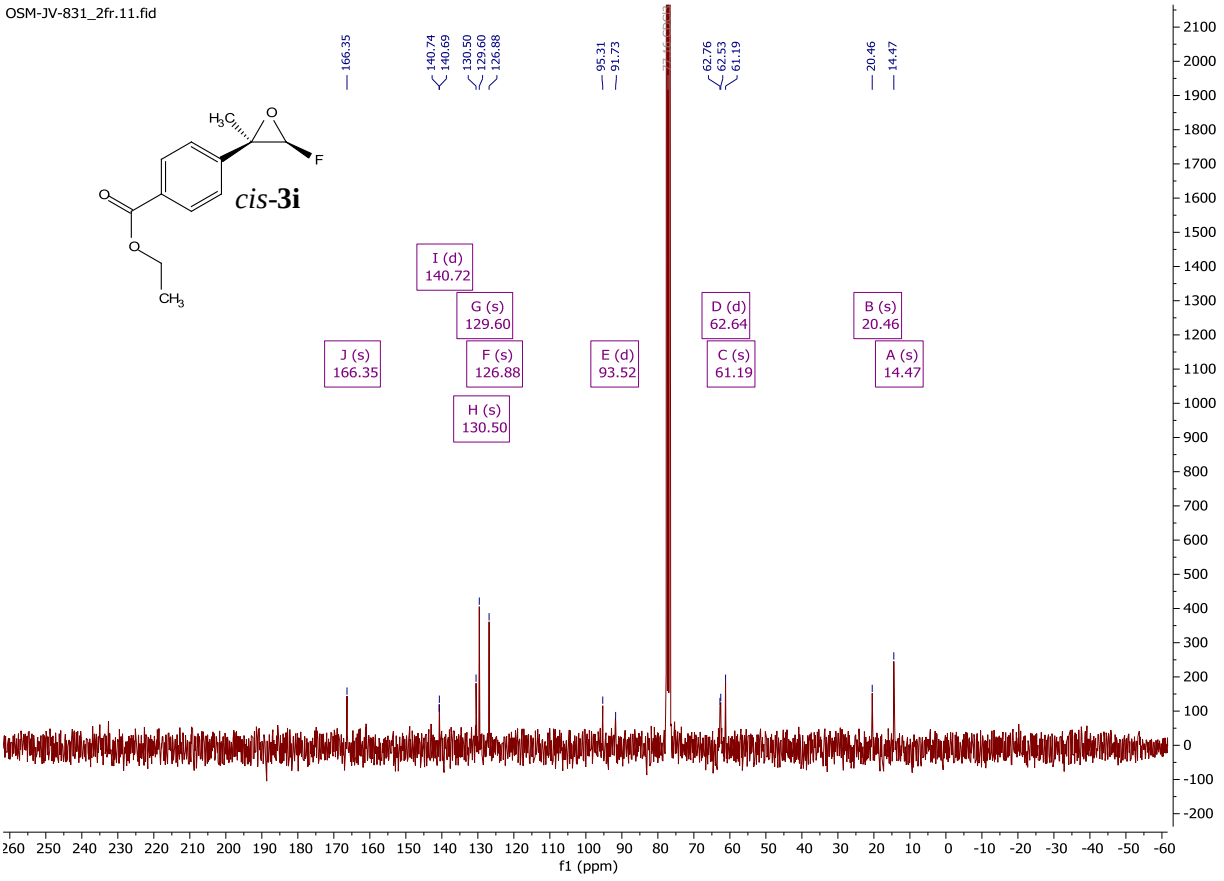

OSM-JV-865-2fr.12.fid
148.37
139.02
138.97
128.36
128.34
123.60
90.65
87.96
56.60
56.42
cis-3h
F (s)
148.37
D (d)
128.35
E (d)
139.00
C (s)
123.60
B (d)
89.31
A (d)
56.51
f1 (ppm)

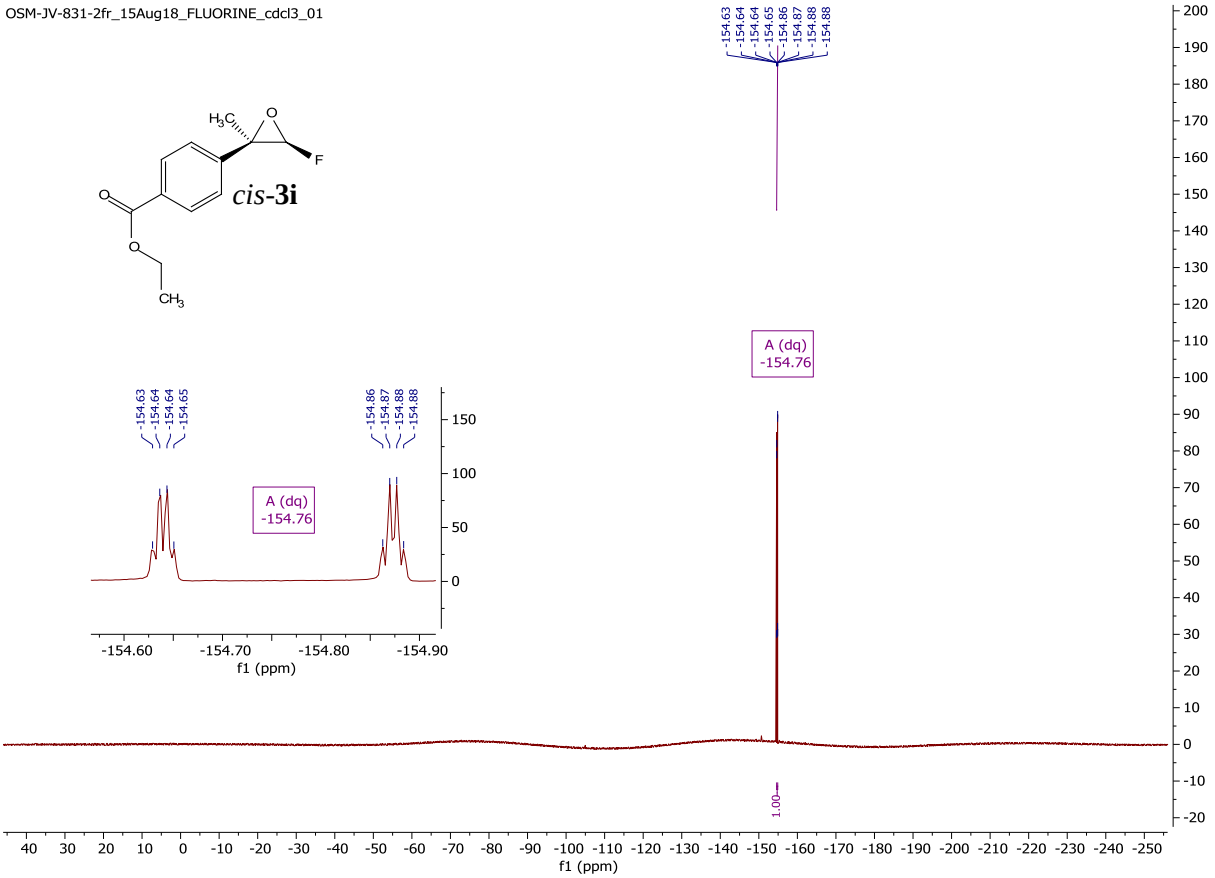

OSM-JV-831_1fr.10.fid
trans-3i
f1 (ppm)

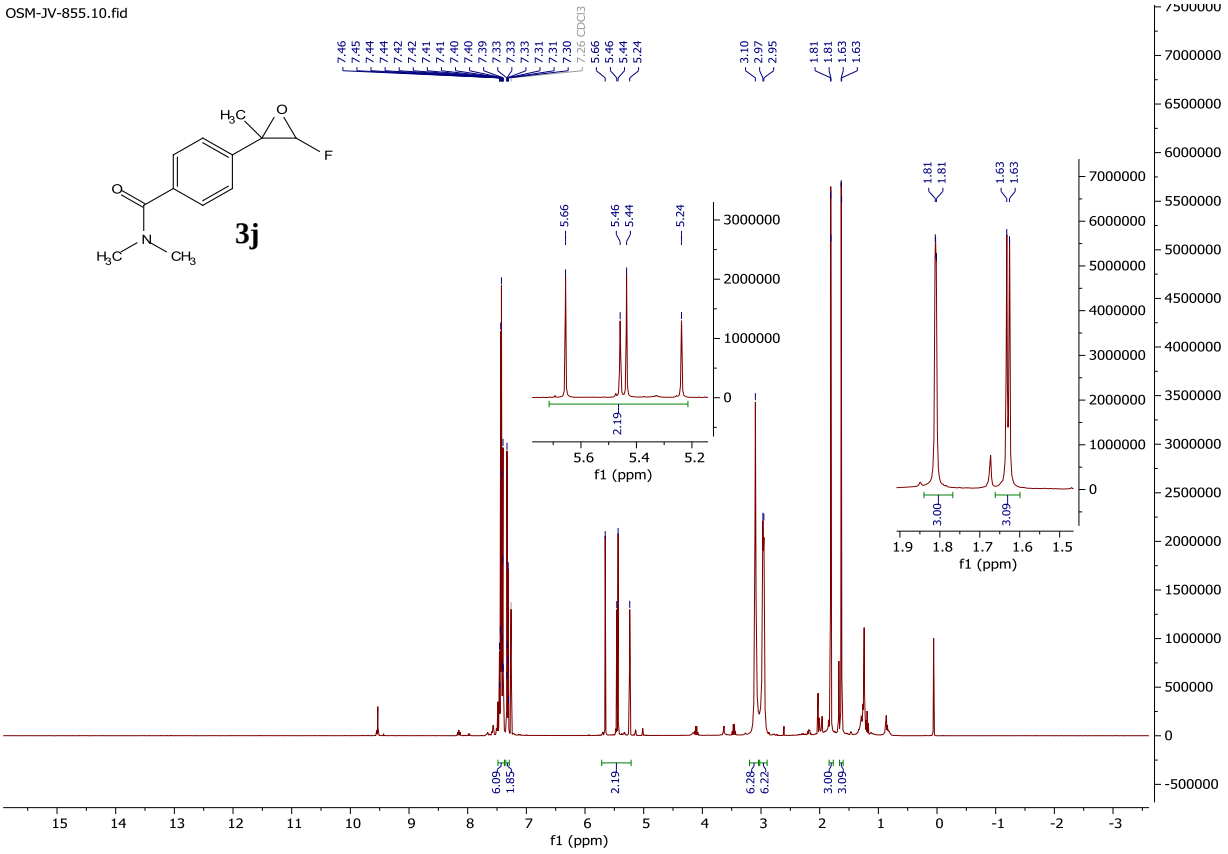

OSM-JV-831_1fr.11.fid
trans-3i
D (s) 129.79
B (s) 61.15
J (s) 14.31
G (s) 166.06
H (d) 142.42
C (s) 125.42
F (d) 93.59
A (d) 61.35
I (s) 16.15
E (s) 130.50
f1 (ppm)

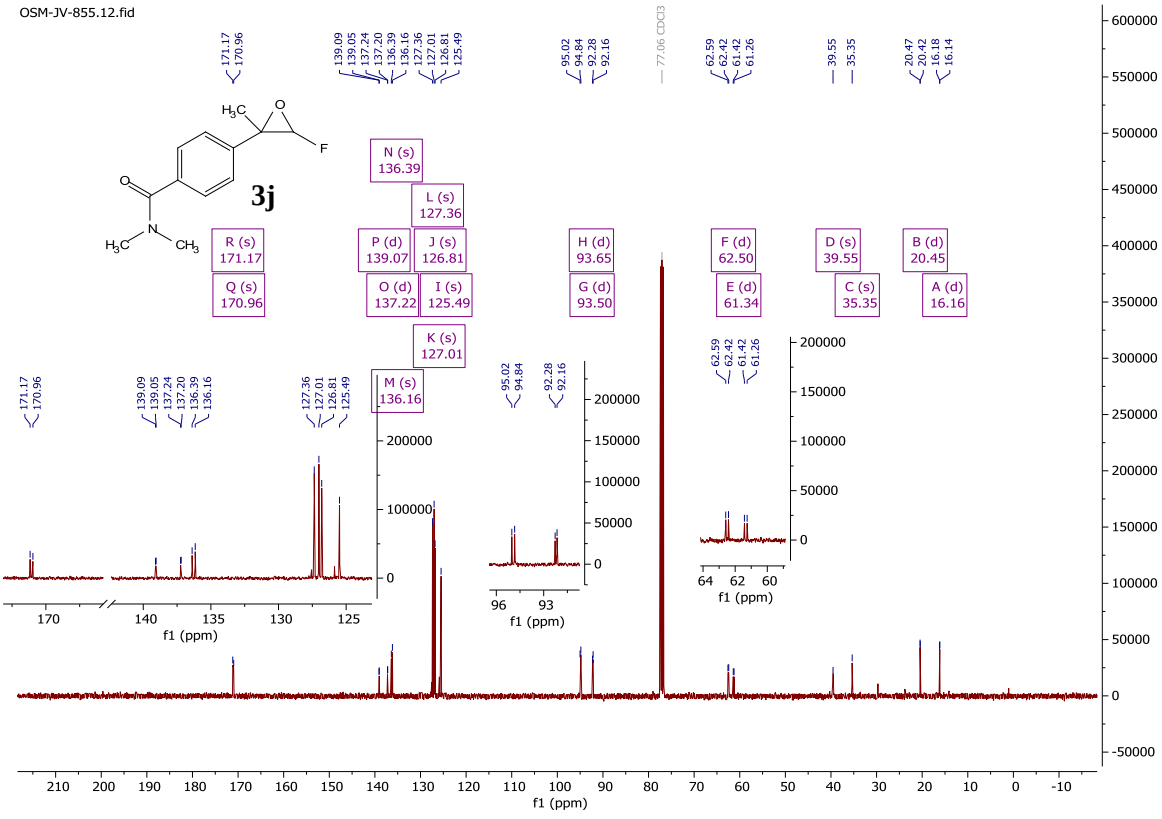

OSM-JV-831-1fr_15Aug18_FLUORINE_cdcl3_01
trans-3i
-150.67
-150.91
A (d)
-150.79
1.00
f1 (ppm)

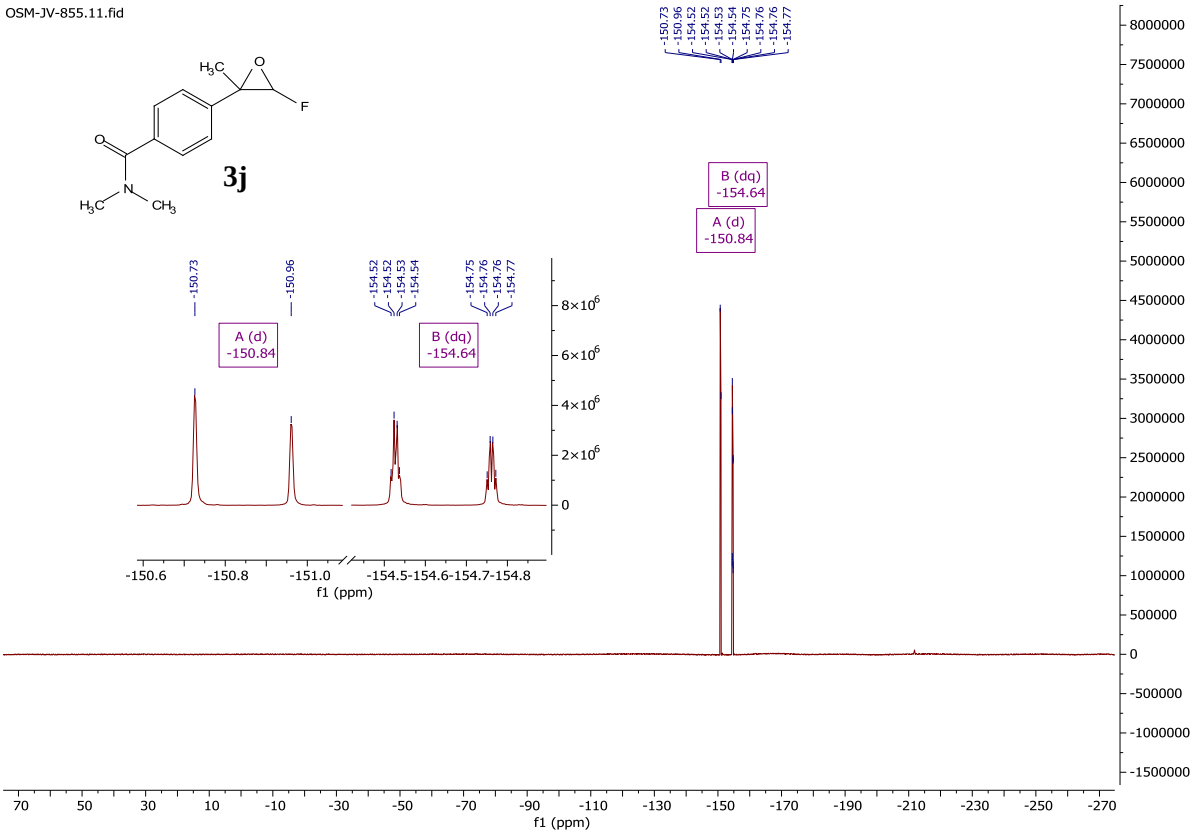

OSM-JV-831_2fr.10.fid
cis-3i
f1 (ppm)

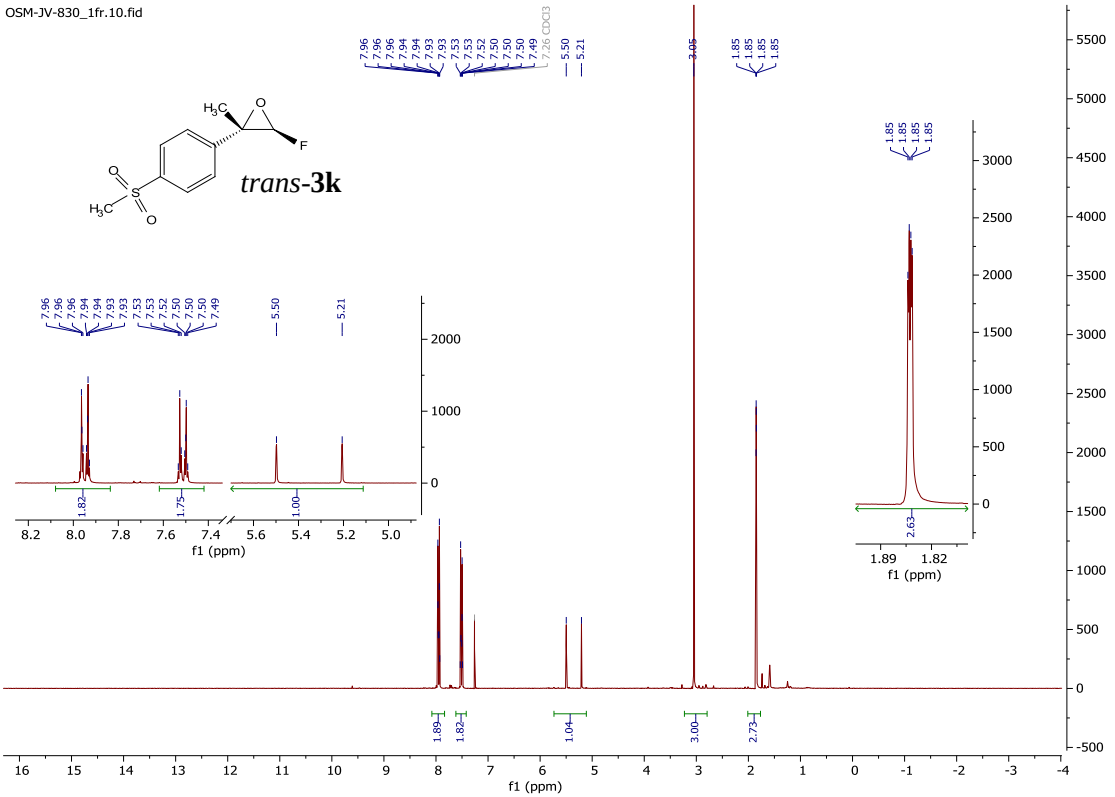

OSM-JV-831_2fr.11.fid
cis-3i
I (d) 140.72
G (s) 129.60
F (s) 126.88
H (s) 130.50
J (s) 166.35
E (d) 93.52
D (d) 62.64
C (s) 61.19
B (s) 20.46
A (s) 14.47
f1 (ppm)

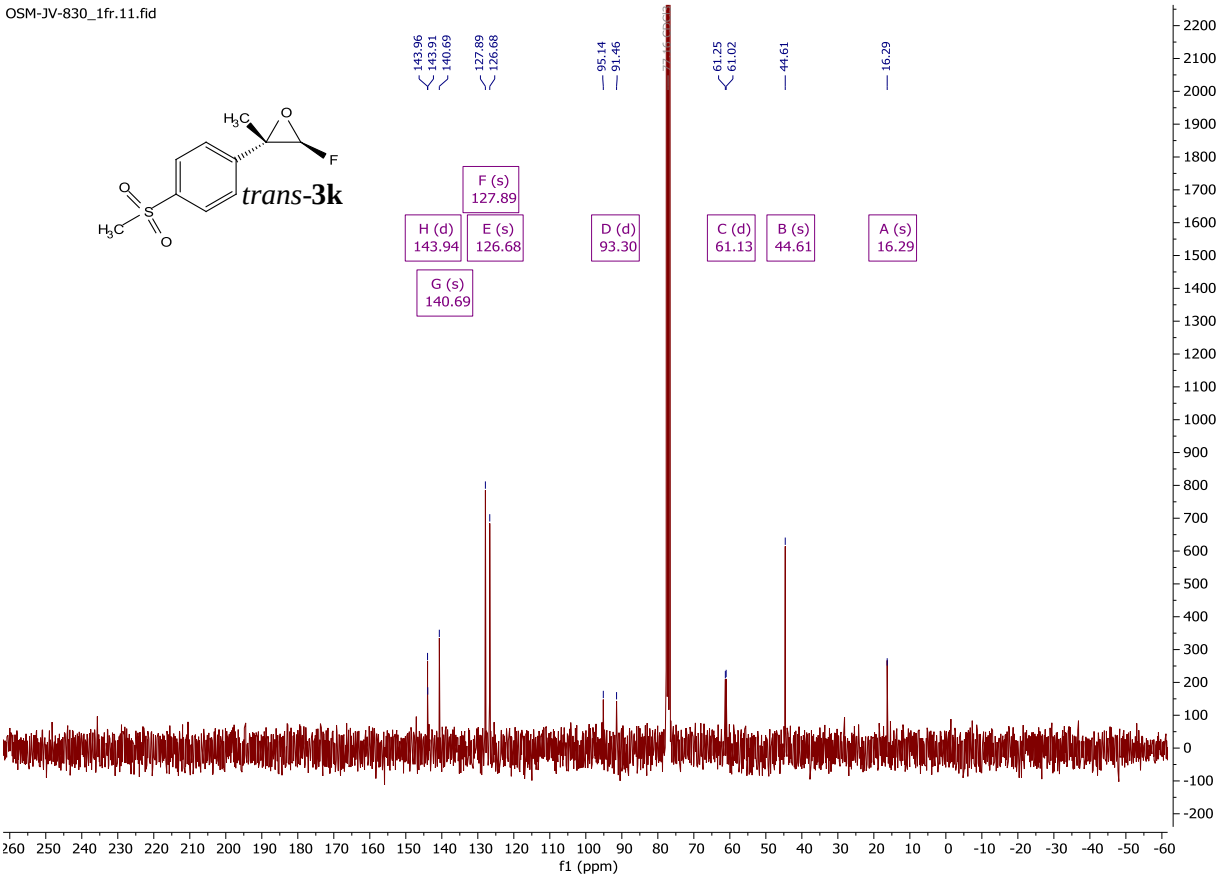

OSM-JV-831-2fr_15Aug18_FLUORINE_cdcl3_01
cis-3i
A (dq)
-154.76
f1 (ppm)

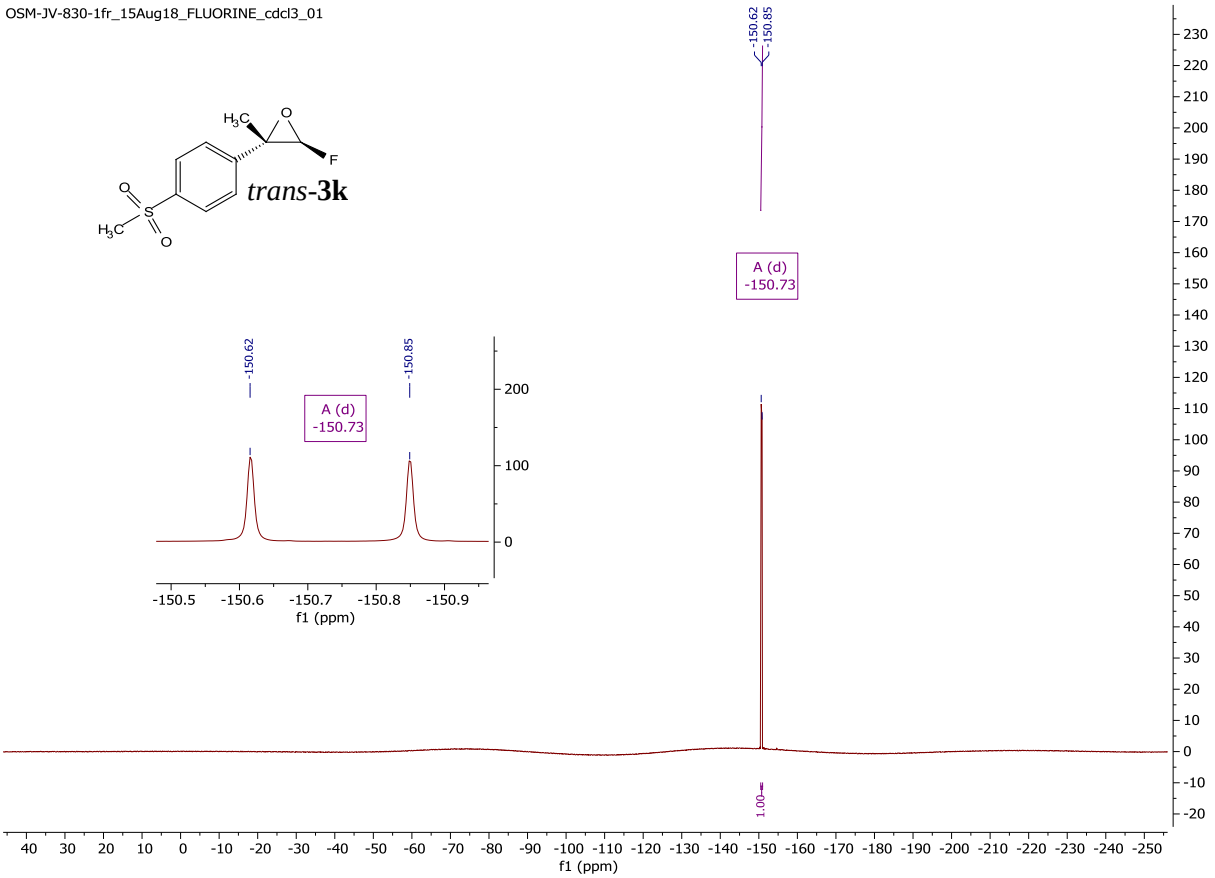

OSM-JV-855.10.fid
3j
f1 (ppm)

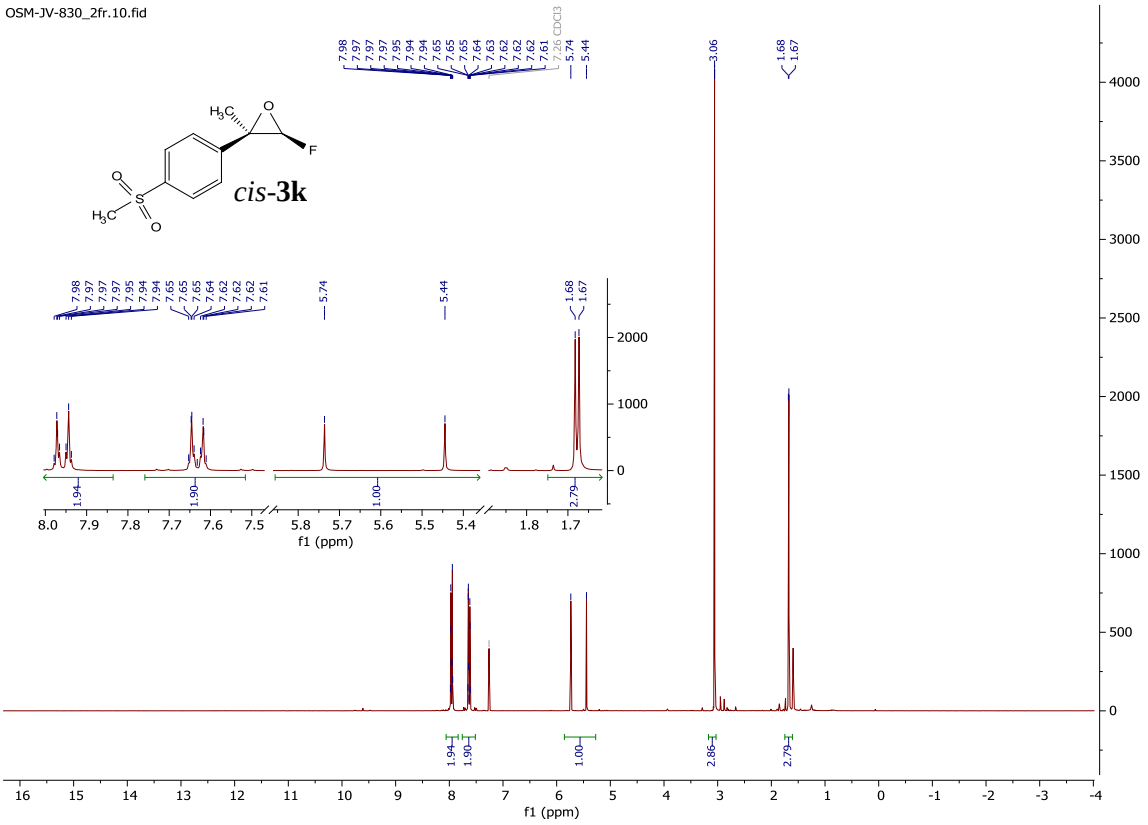

OSM-JV-855.12.fid
3j
N (s) 136.39
L (s) 127.36
R (s) 171.17
P (d) 139.07
J (s) 126.81
H (d) 93.65
F (d) 62.50
D (s) 39.55
B (d) 20.45
Q (s) 170.96
O (d) 137.22
I (s) 125.49
G (d) 93.50
E (d) 61.34
C (s) 35.35
A (d) 16.16
K (s) 127.01
M (s) 136.16
f1 (ppm)

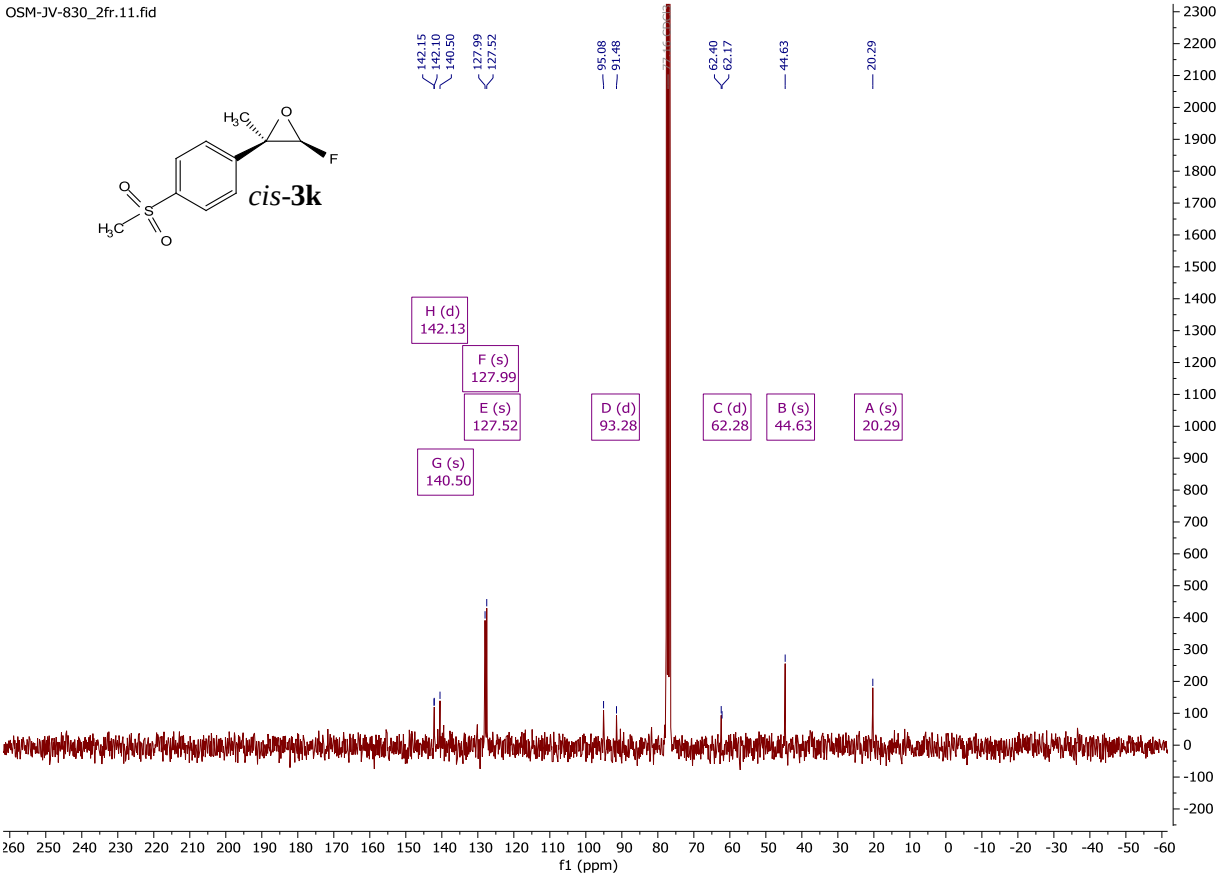

OSM-JV-855.11.fid
3j
-150.73
-150.96
-154.52
-154.52
-154.53
-154.54
-154.75
-154.76
-154.76
-154.77
B (dq)
-154.64
A (d)
-150.84
f1 (ppm)

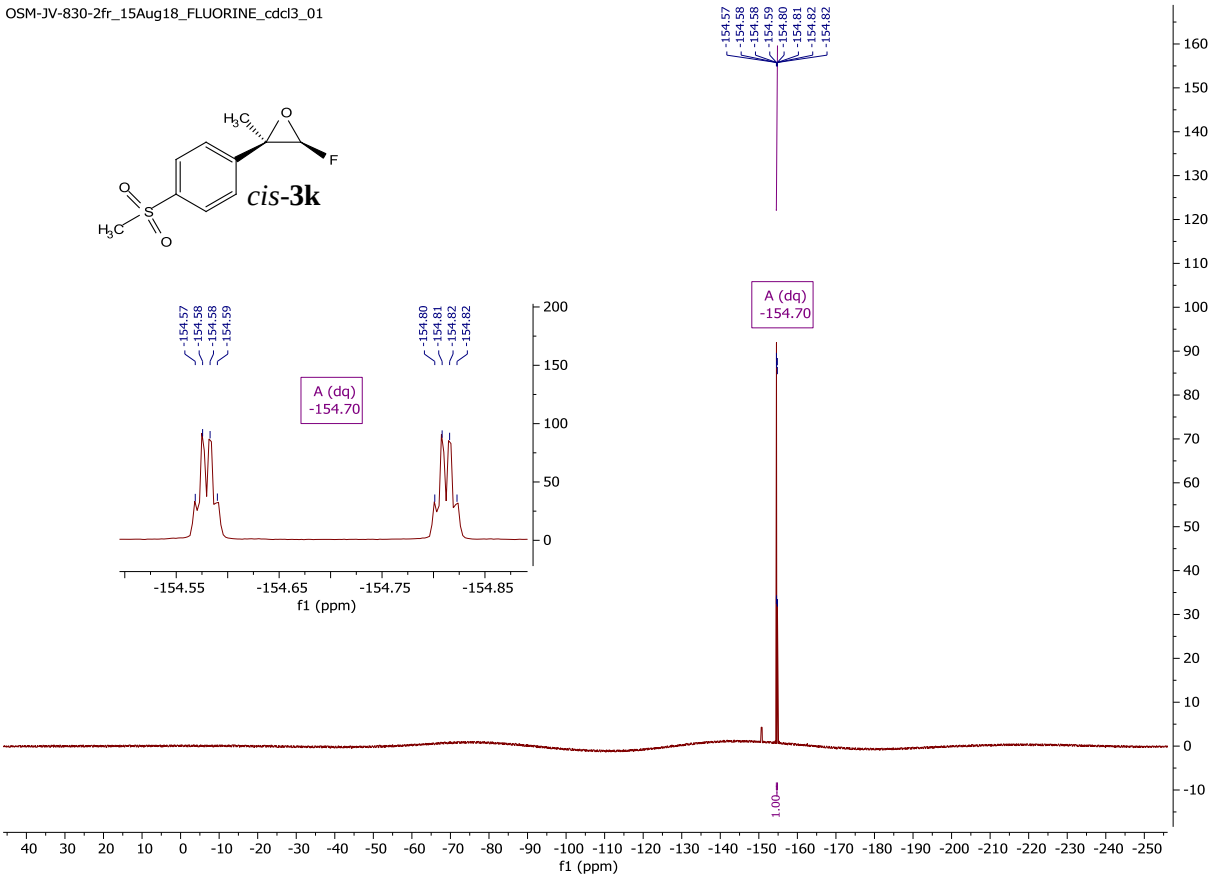

OSM-JV-830_1fr.10.fid
trans-3k
f1 (ppm)

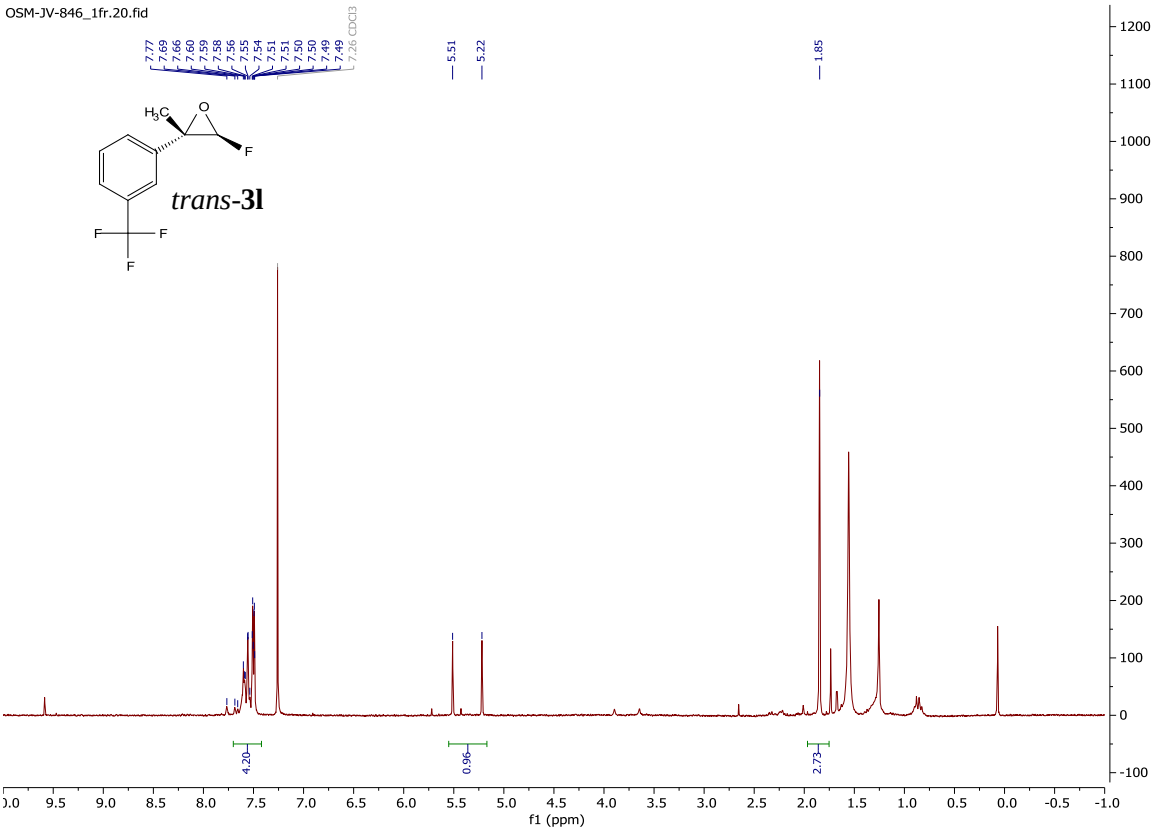

OSM-JV-830_1fr.11.fid
trans-3k
F (s) 127.89
H (d) 143.94
E (s) 126.68
D (d) 93.30
C (d) 61.13
B (s) 44.61
A (s) 16.29
G (s) 140.69
f1 (ppm)

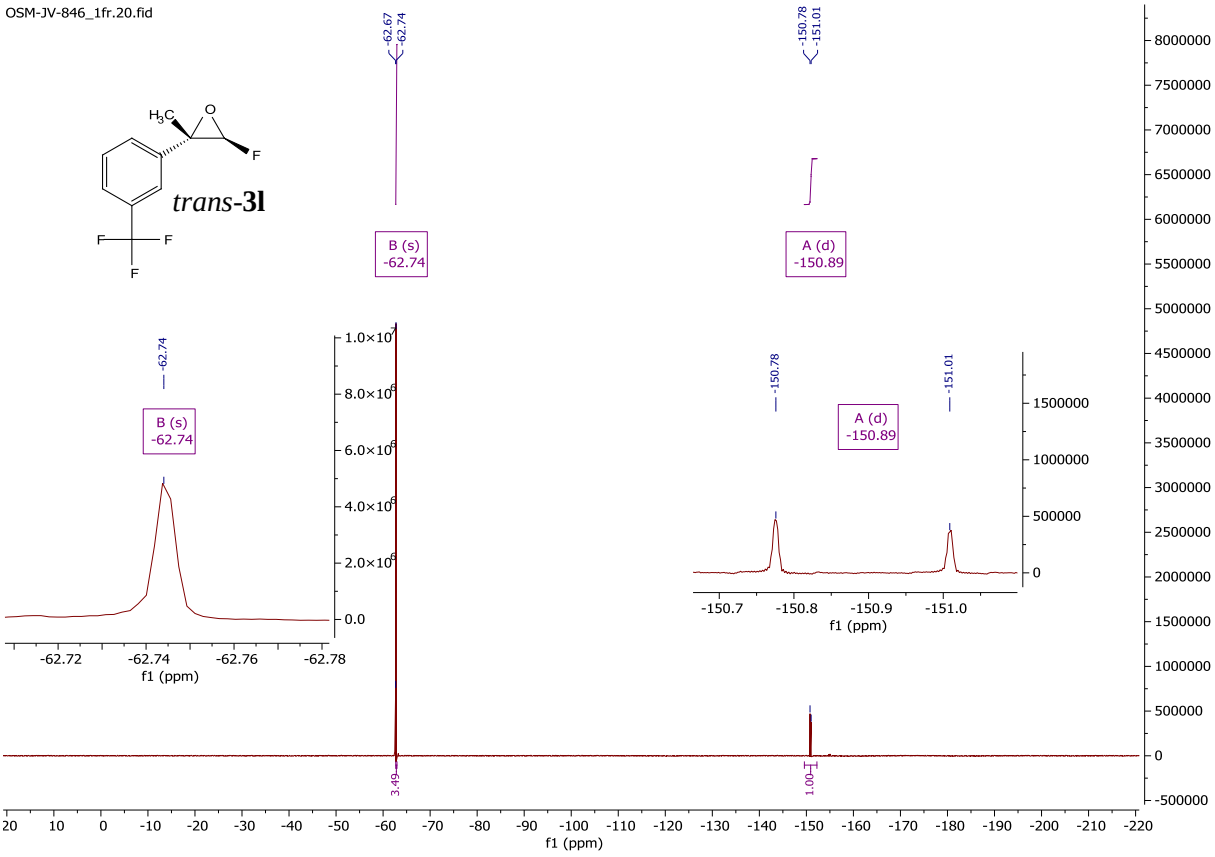

OSM-JV-830-1fr_15Aug18_FLUORINE_cdcl3_01
trans-3k
-150.62
-150.85
A (d)
-150.73
1.00
f1 (ppm)

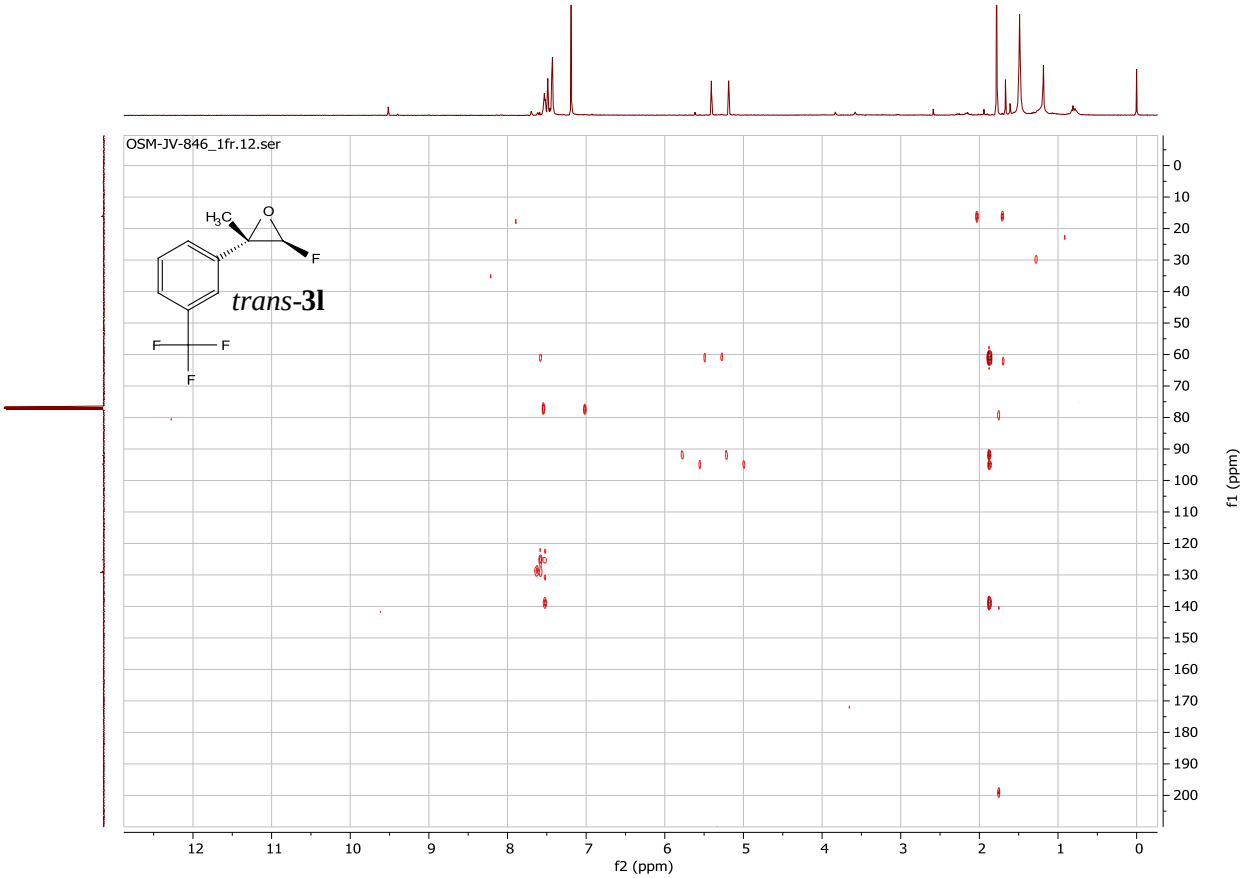

OSM-JV-830_2fr.10.fid
cis-3k
f1 (ppm)

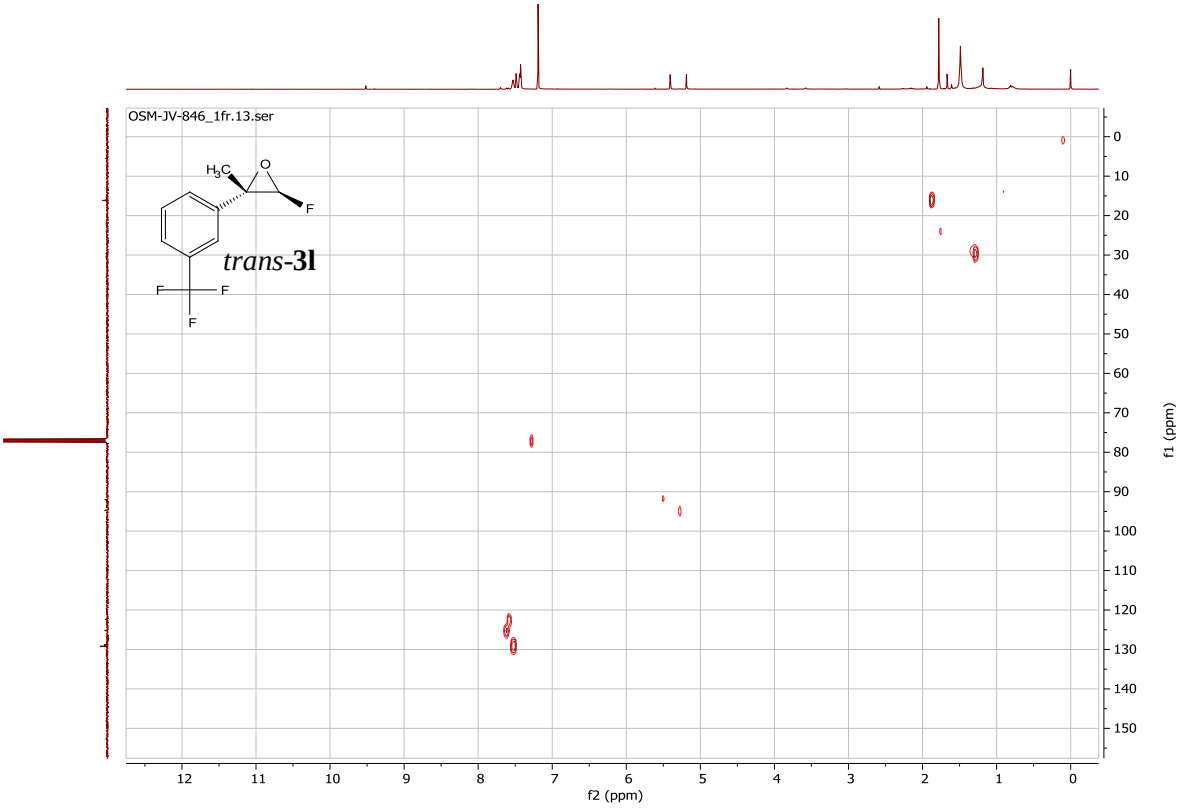

OSM-JV-830_2fr.11.fid
cis-3k
H (d) 142.13
F (s) 127.99
E (s) 127.52
G (s) 140.50
D (d) 93.28
C (d) 62.28
B (s) 44.63
A (s) 20.29
f1 (ppm)

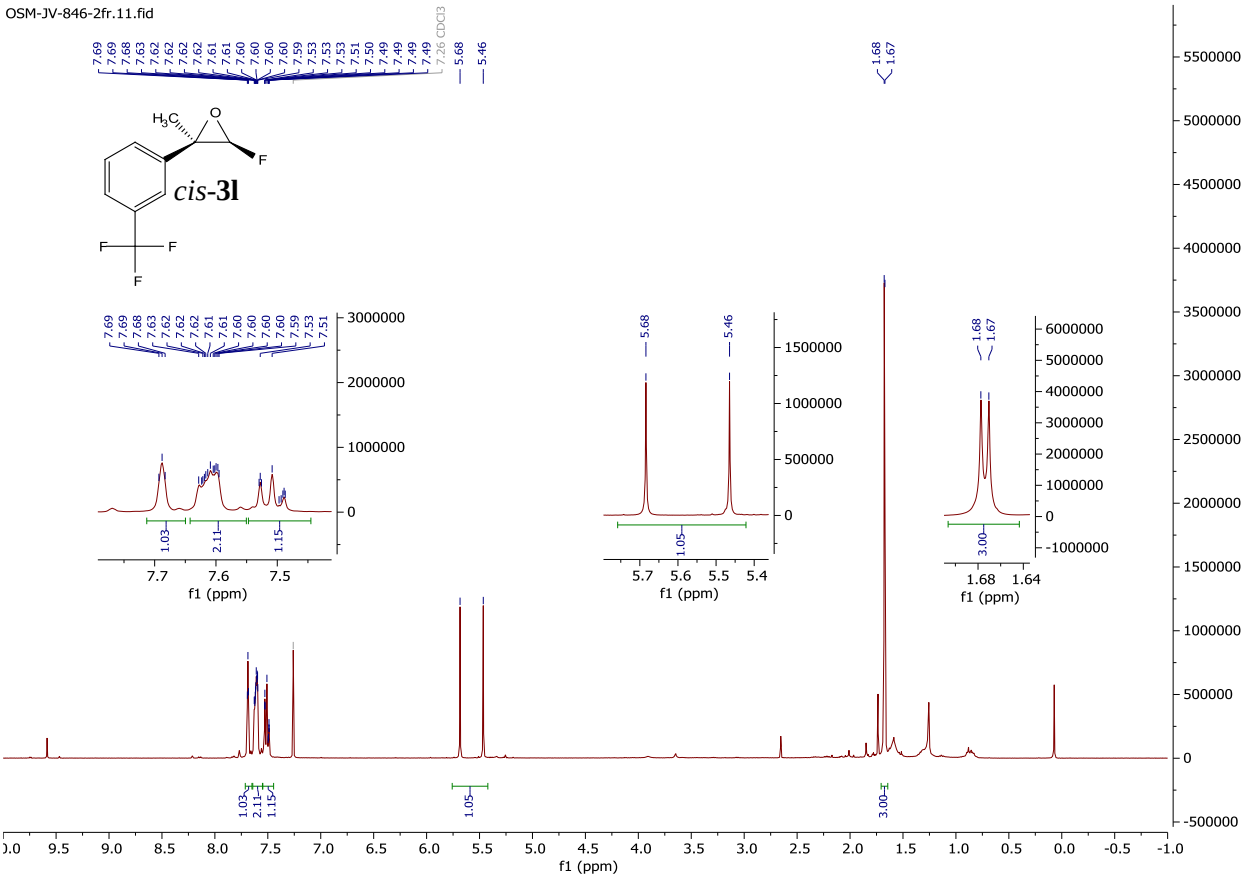

OSM-JV-830-2fr_15Aug18_FLUORINE_cdcl3_01
cis-3k
A (dq)
-154.70
f1 (ppm)
1.00

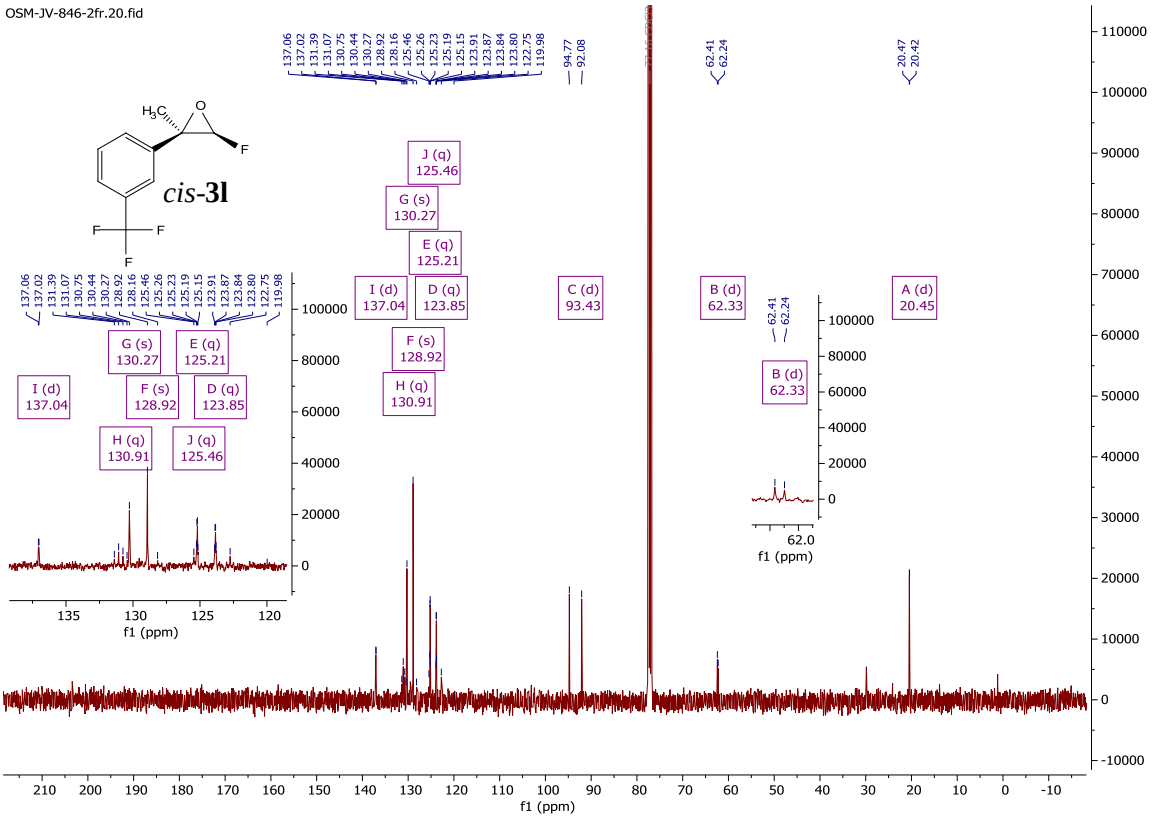

OSM-JV-846_1fr.20.fid
trans-3l
f1 (ppm)

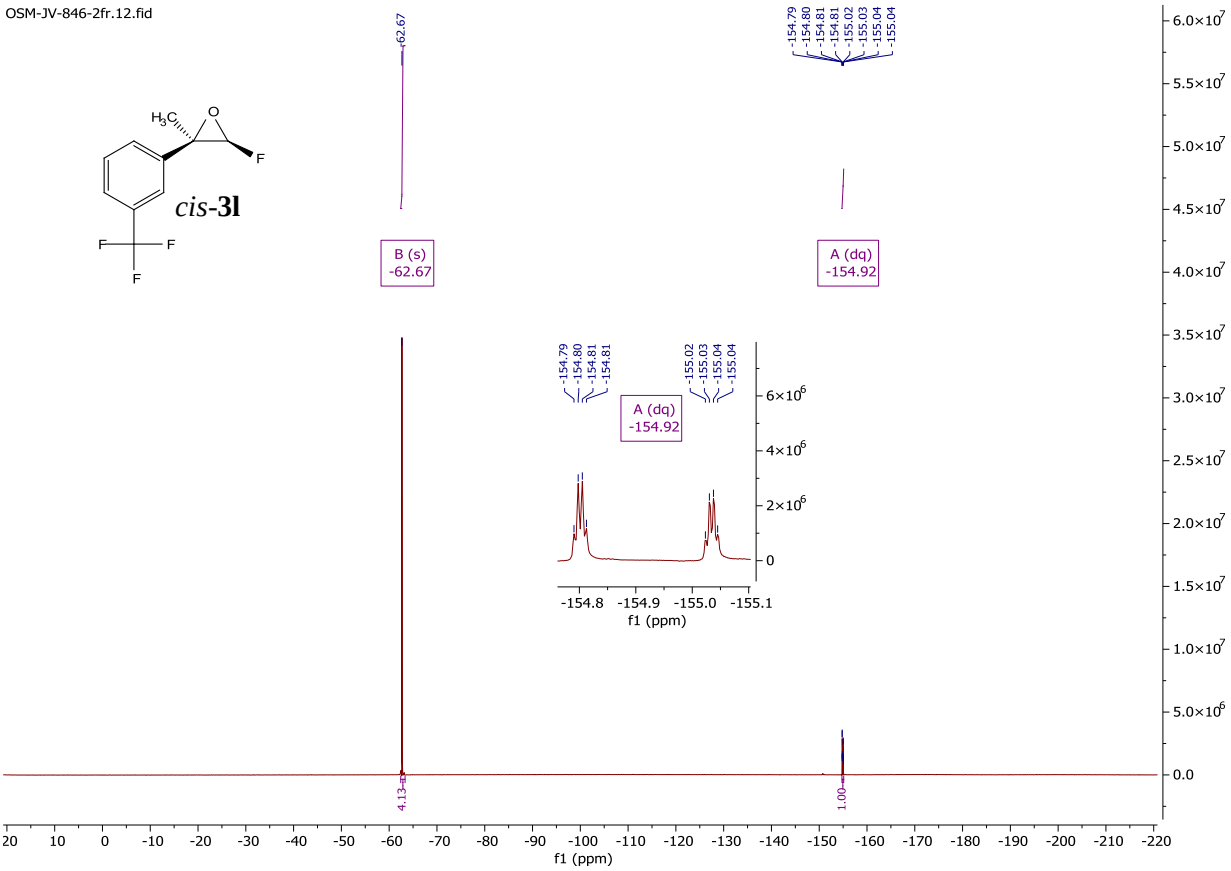

OSM-JV-846_1fr.20.fid
trans-3l
B (s)
-62.74
A (d)
-150.89
f1 (ppm)

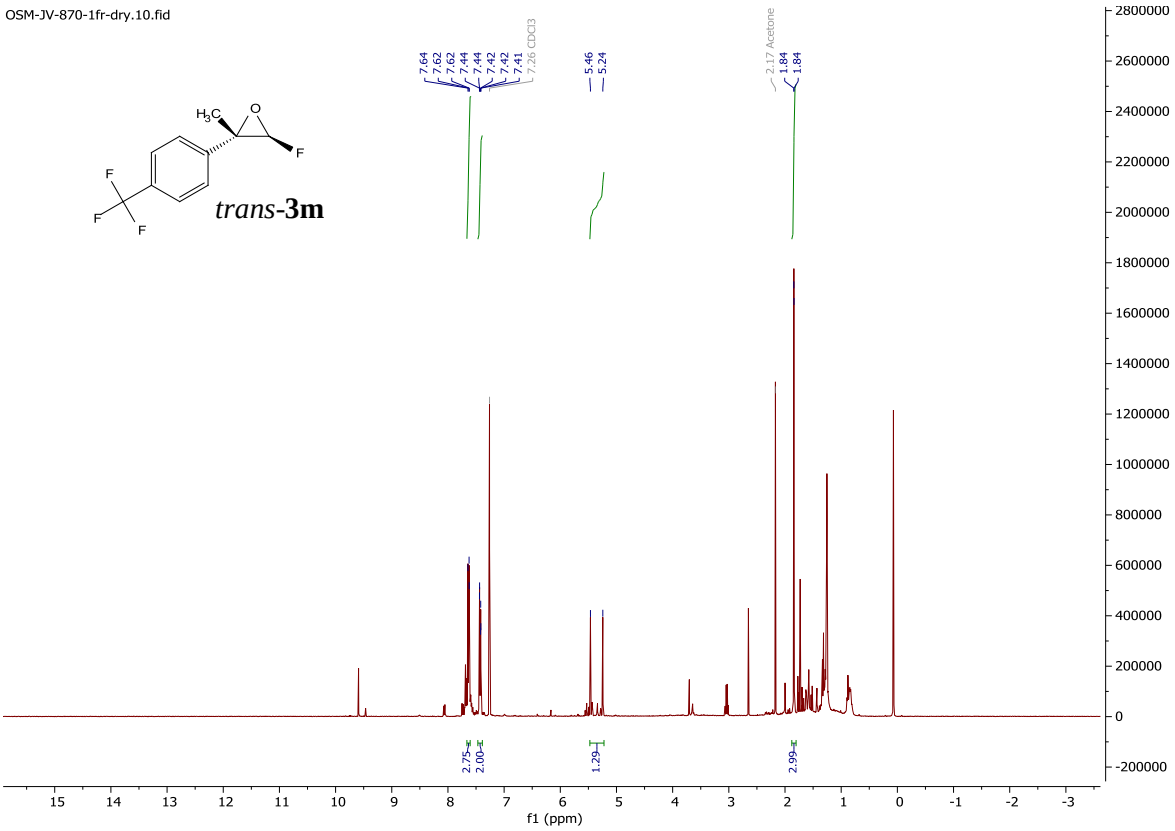

OSM-JV-846_1fr.12.ser
trans-3l
f2 (ppm)
f1 (ppm)

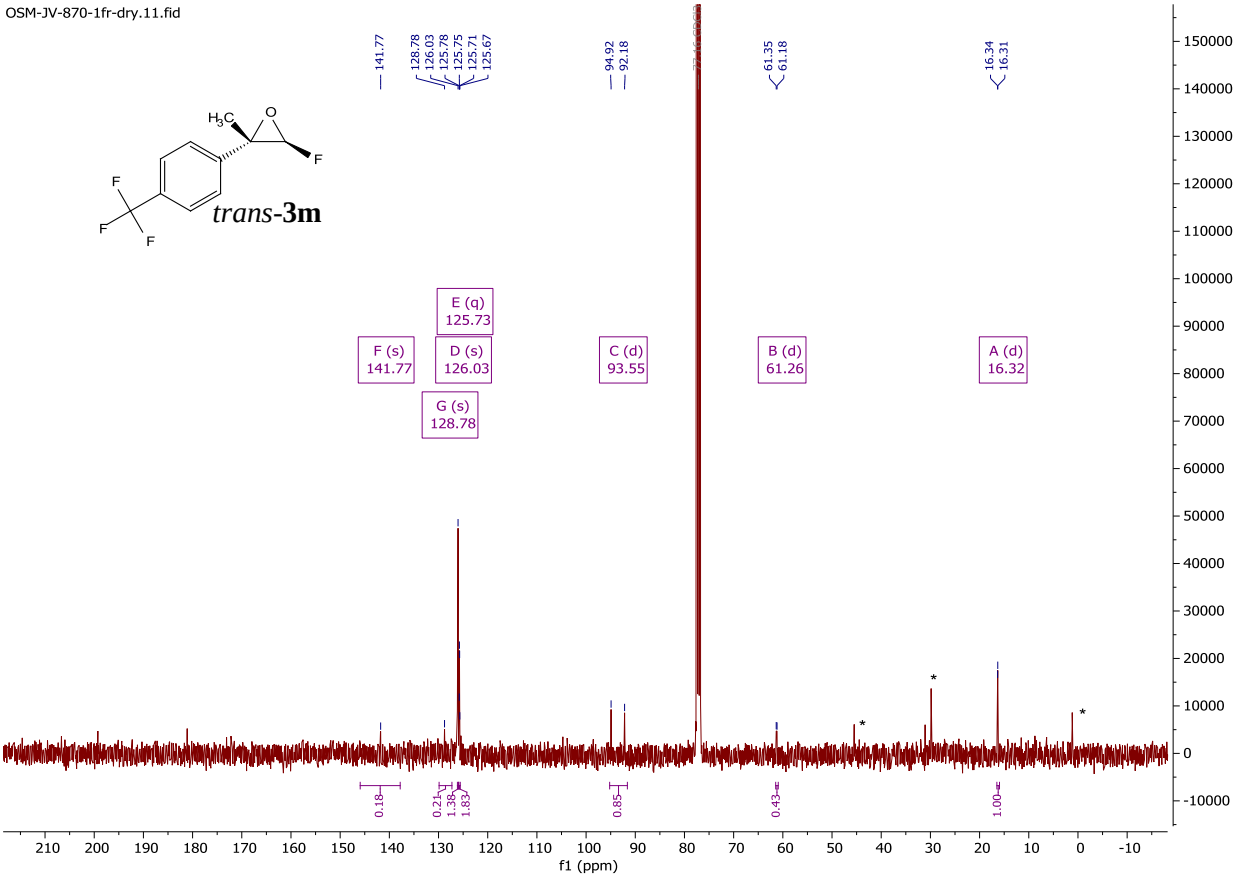

OSM-JV-846_1fr.13.ser
trans-3l
f2 (ppm)
f1 (ppm)

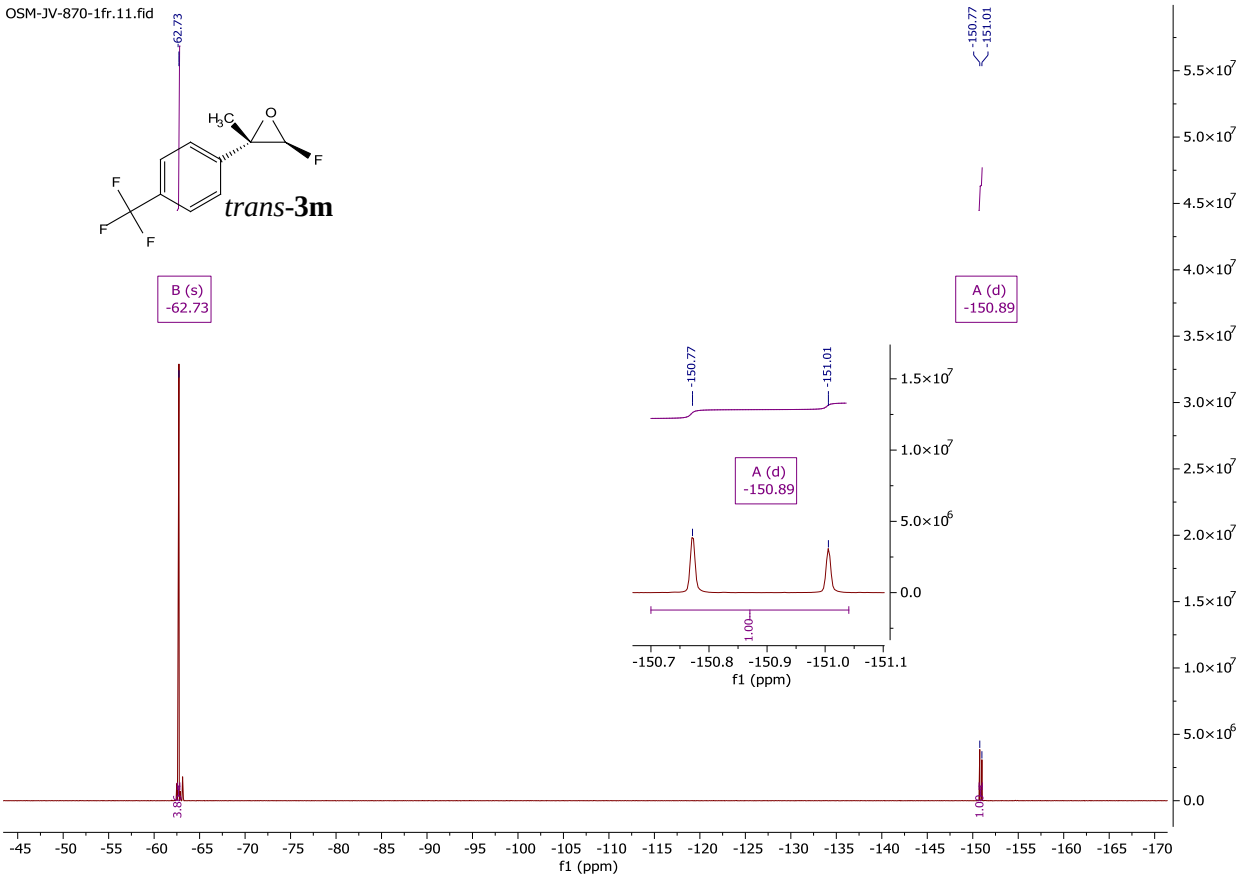

OSM-JV-846-2fr.11.fid
cis-3l
f1 (ppm)

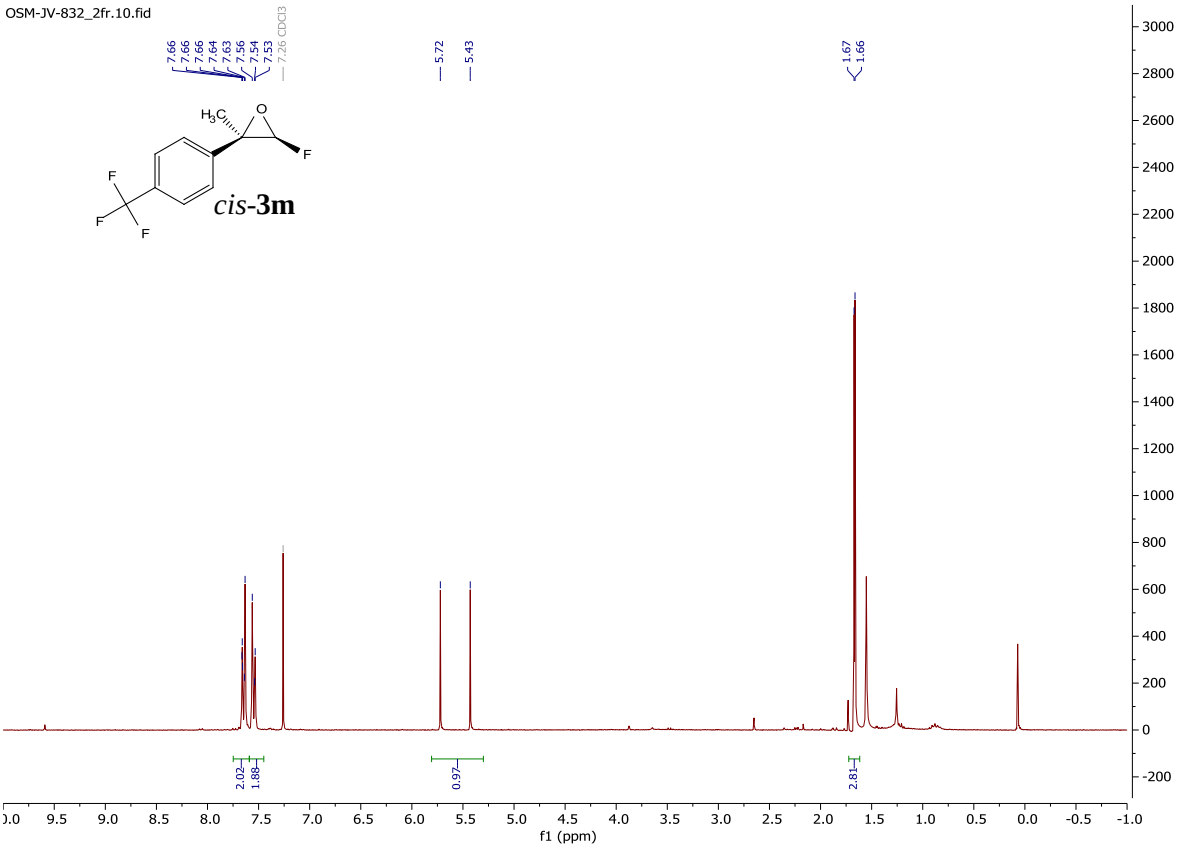

OSM-JV-846-2fr.20.fid
cis-3l
J (q) 125.46
G (s) 130.27
E (q) 125.21
I (d) 137.04
D (q) 123.85
F (s) 128.92
H (q) 130.91
C (d) 93.43
B (d) 62.33
A (d) 20.45
f1 (ppm)

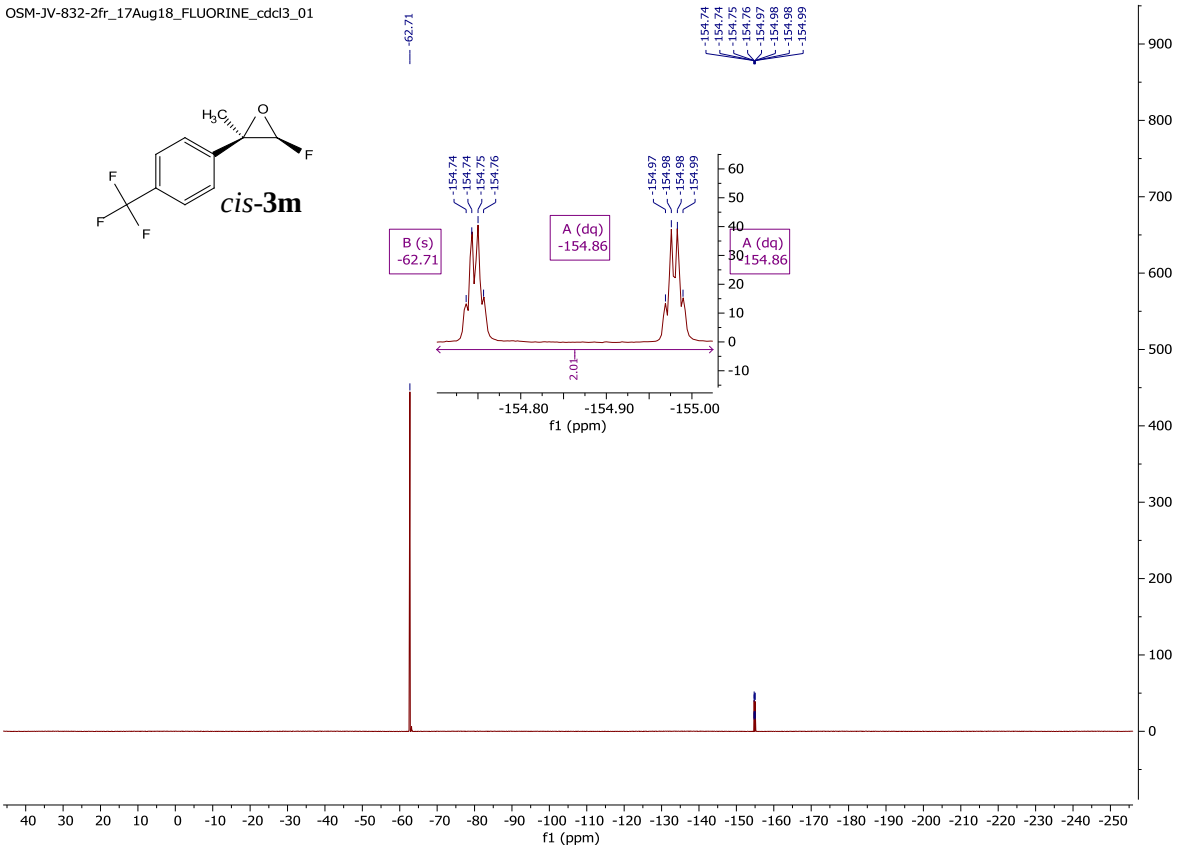

OSM-JV-846-2fr.12.fid
cis-3l
B (s)
-62.67
A (dq)
-154.92
f1 (ppm)

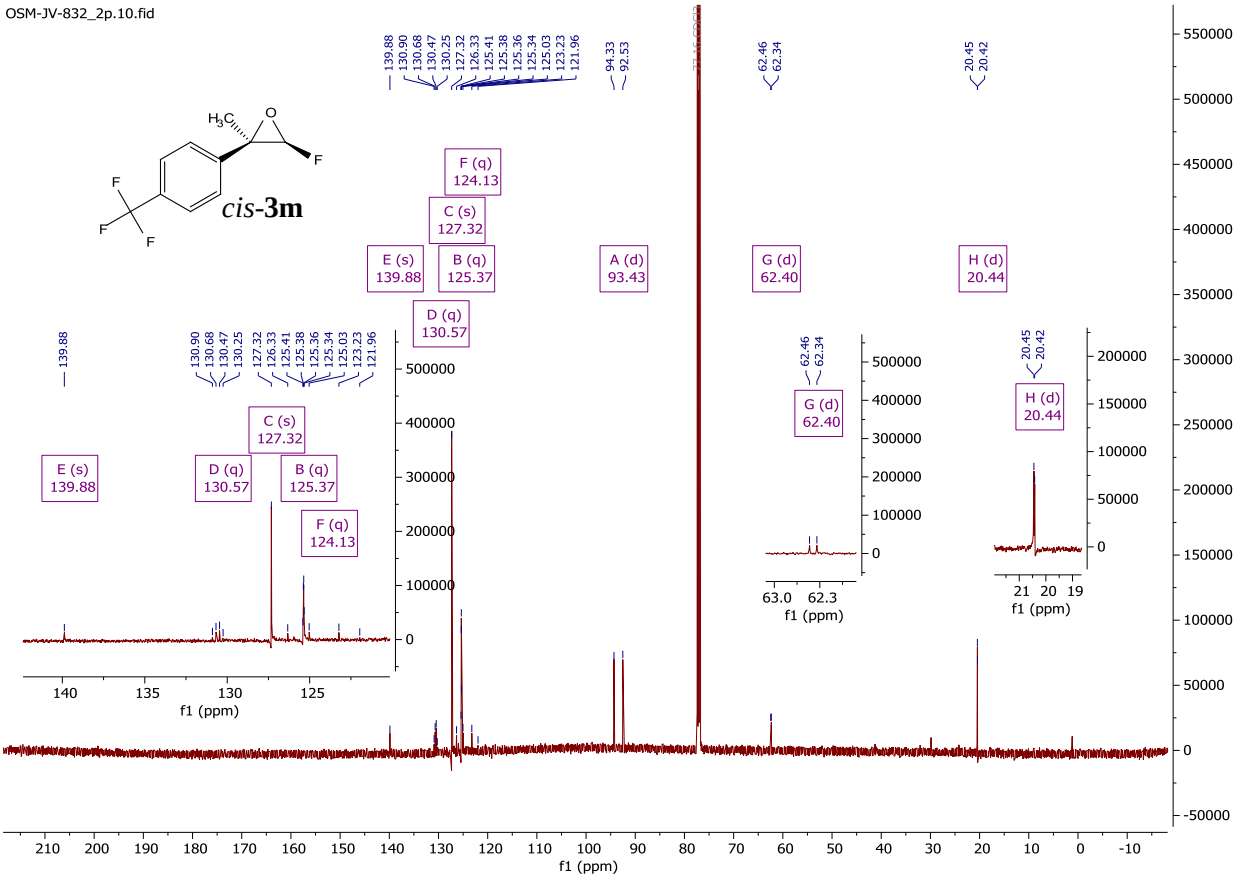

OSM-JV-870-1fr-dry.10.fid
trans-3m
7.64
7.62
7.62
7.44
7.44
7.42
7.42
7.41
7.26 CDCl3
5.46
5.24
2.17 Acetone
1.84
1.84
2.75
2.00
1.29
2.99
f1 (ppm)

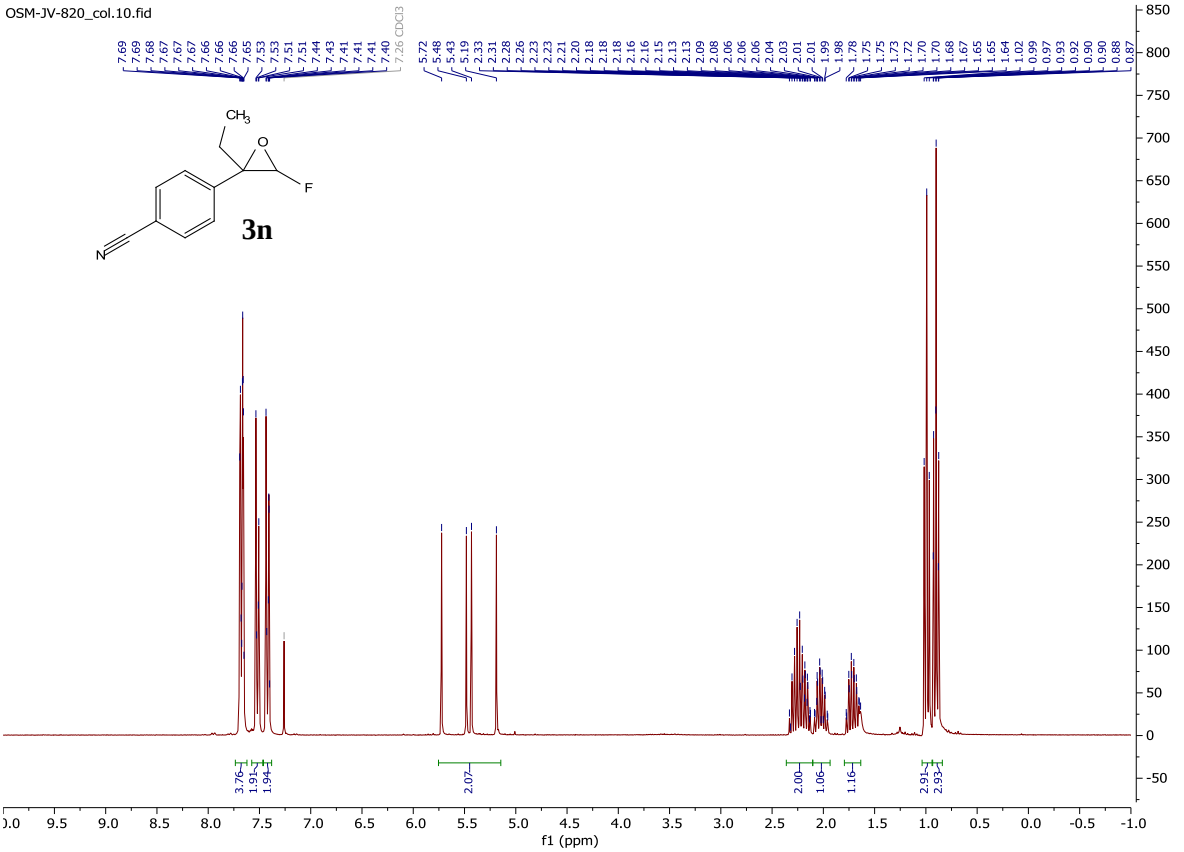

OSM-JV-870-1fr-dry.11.fid
trans-3m
141.77
128.78
126.03
125.78
125.75
125.71
125.67
94.92
92.18
61.35
61.18
16.34
16.31
E (q)
125.73
F (s)
141.77
D (s)
126.03
C (d)
93.55
B (d)
61.26
A (d)
16.32
G (s)
128.78
0.18
0.21
1.38
1.83
0.85
0.43
1.00
f1 (ppm)

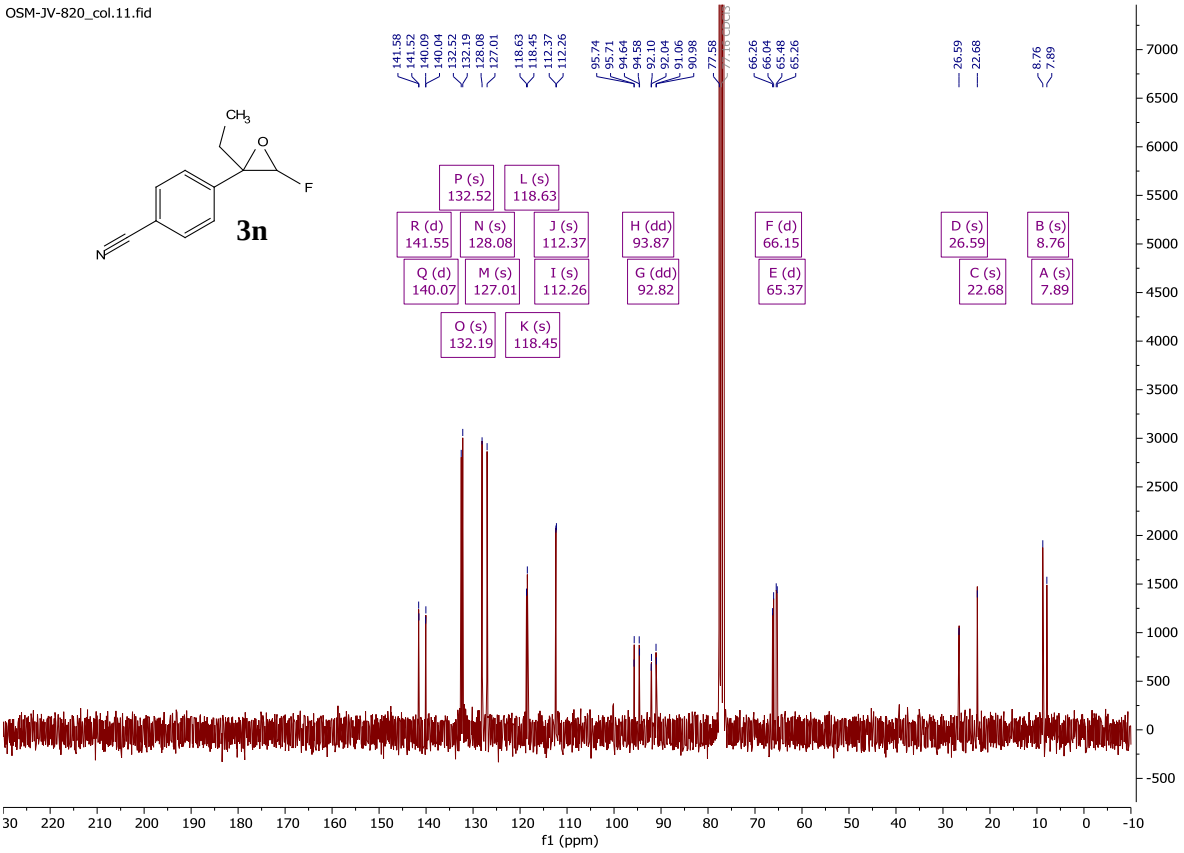

OSM-JV-870-1fr.11.fid
-62.73
-150.77
-151.01
trans-3m
B (s)
-62.73
A (d)
-150.89
A (d)
-150.89
1.00
3.05
1.00
f1 (ppm)
f1 (ppm)

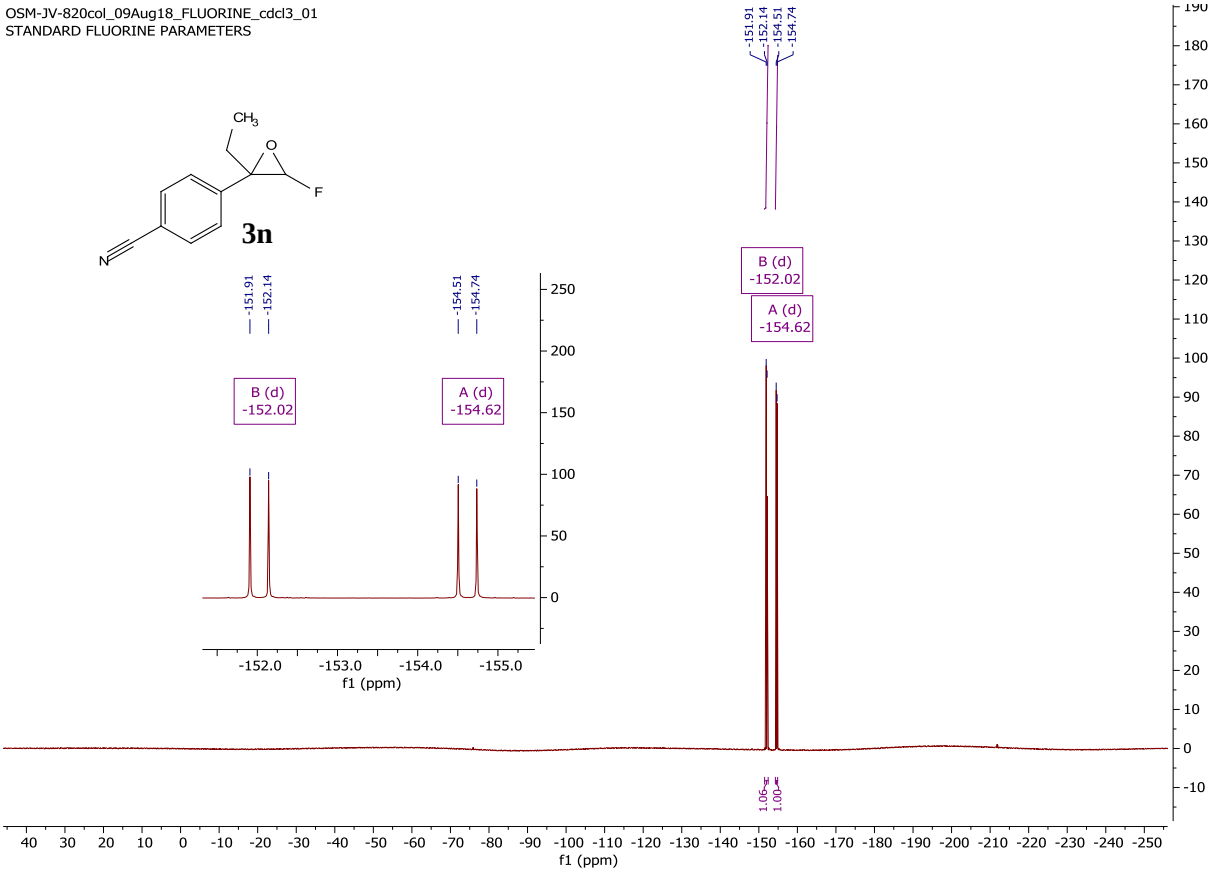

OSM-JV-832_2fr.10.fid
7.66
7.66
7.66
7.64
7.63
7.56
7.54
7.53
7.26 CDCl3
5.72
5.43
1.67
1.66
cis-3m
2.02
1.88
0.97
2.81
f1 (ppm)

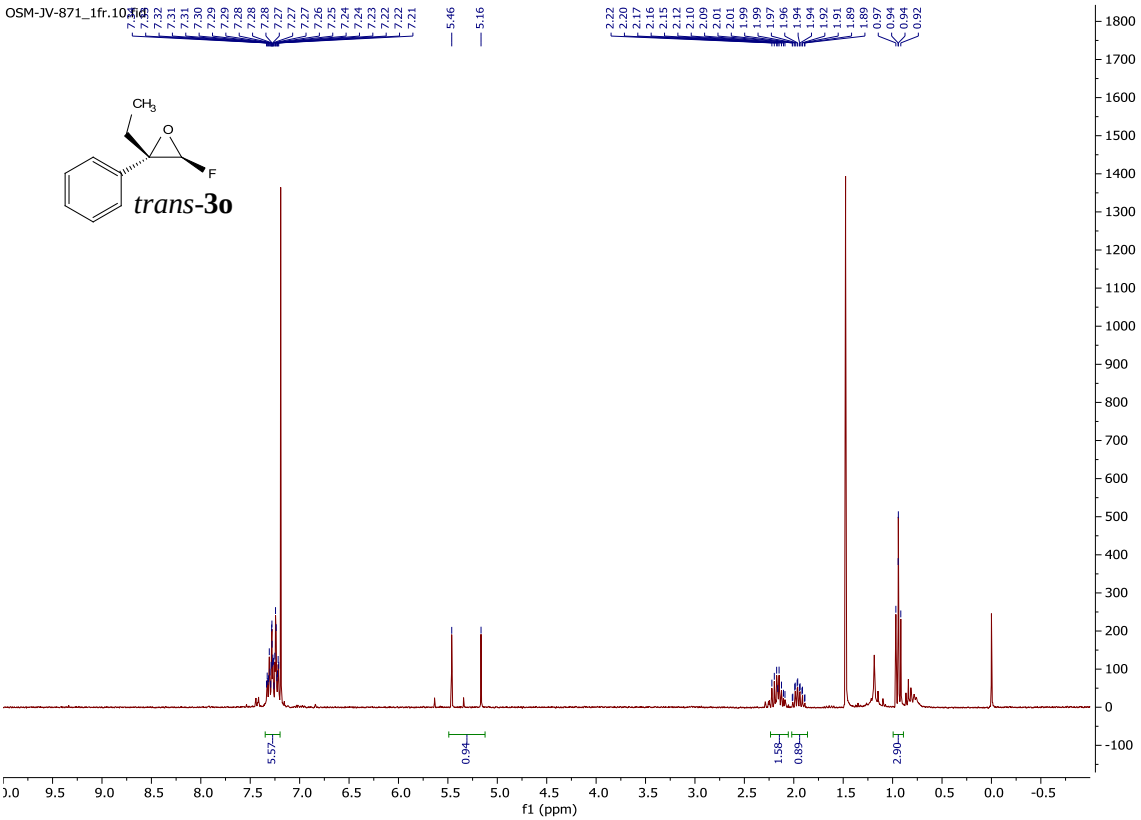

OSM-JV-832-2fr_17Aug18_FLUORINE_cdcl3_01
-62.71
-154.74
-154.74
-154.75
-154.76
-154.97
-154.98
-154.98
-154.99
cis-3m
B (s)
-62.71
A (dq)
-154.86
A (dq)
154.86
2.01
f1 (ppm)

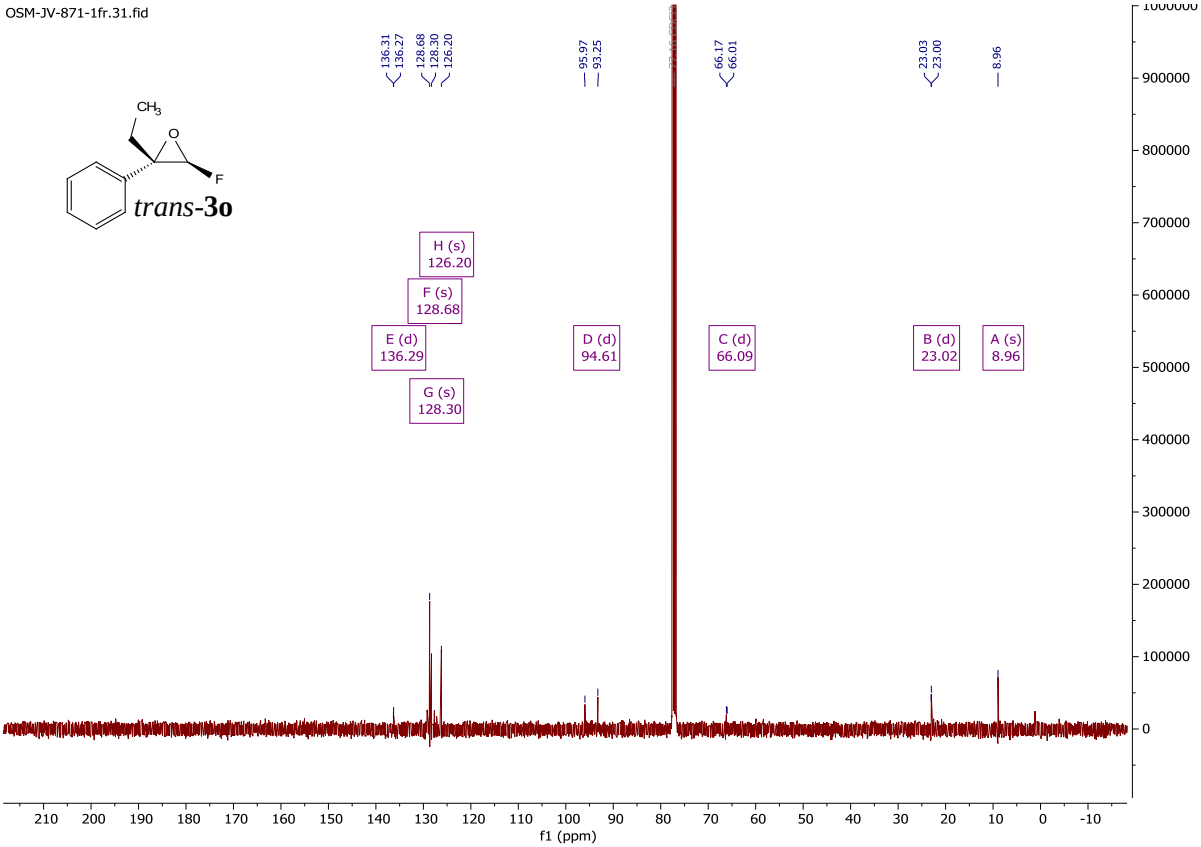

OSM-JV-832_2p.10.fid
cis-3m
F (q) 124.13
C (s) 127.32
E (s) 139.88
B (q) 125.37
D (q) 130.57
A (d) 93.43
G (d) 62.40
H (d) 20.44
f1 (ppm)

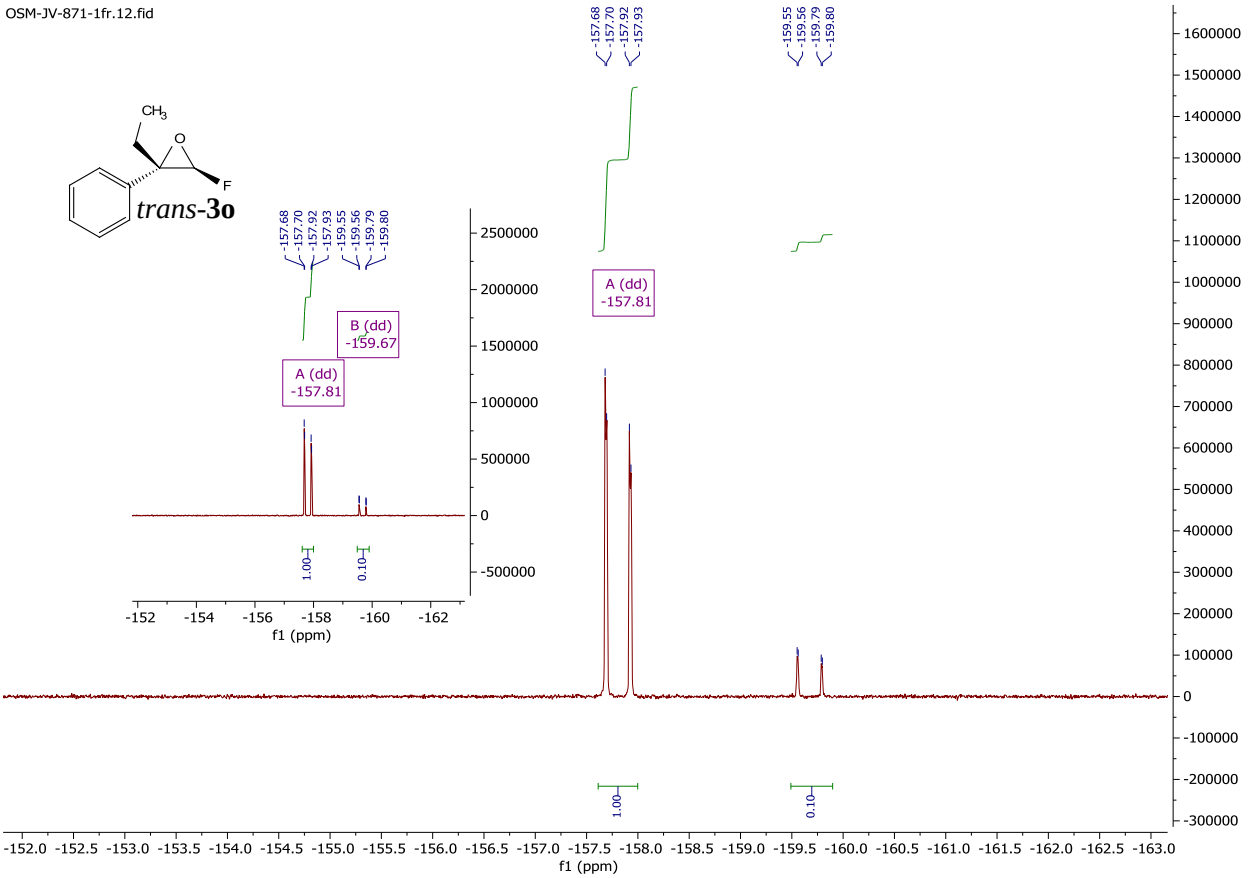

OSM-JV-820_col.10.fid
3n
f1 (ppm)

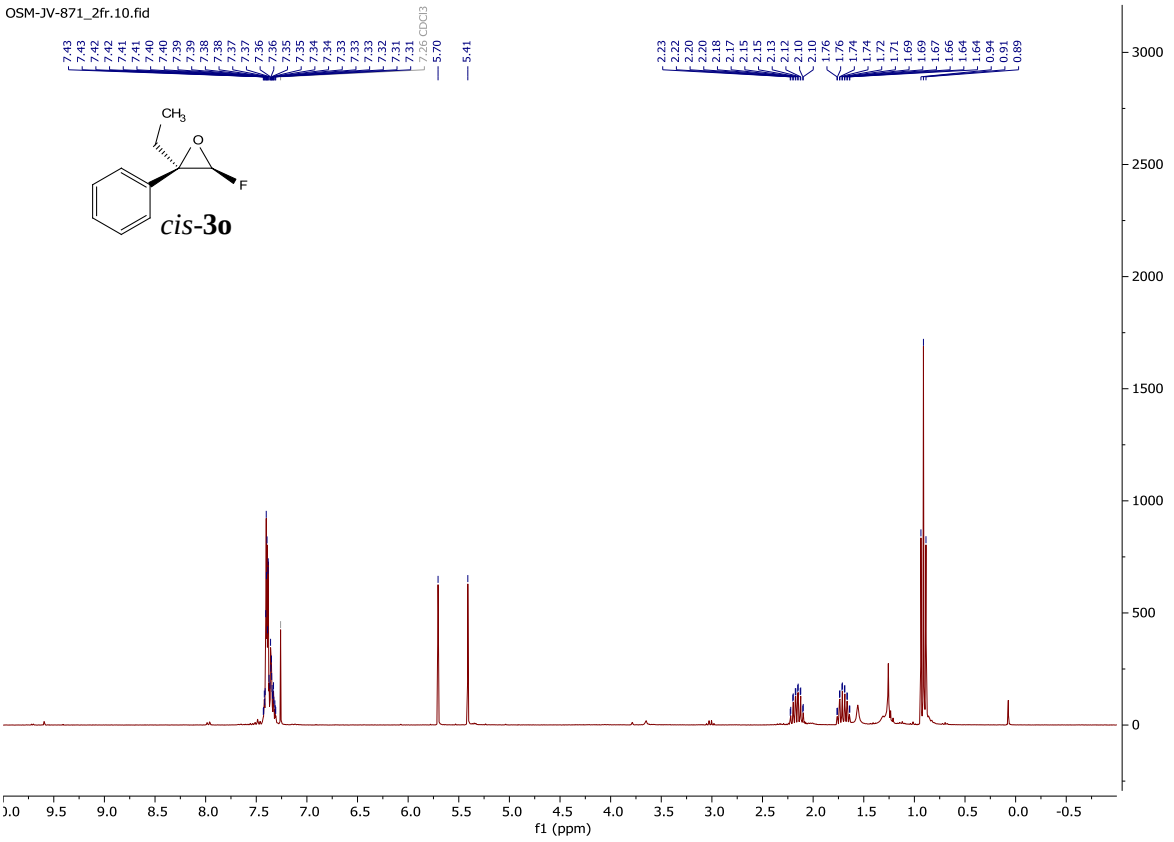

OSM-JV-820_col.11.fid
3n
P (s) 132.52
L (s) 118.63
R (d) 141.55
N (s) 128.08
J (s) 112.37
H (dd) 93.87
F (d) 66.15
D (s) 26.59
B (s) 8.76
Q (d) 140.07
M (s) 127.01
I (s) 112.26
G (dd) 92.82
E (d) 65.37
C (s) 22.68
A (s) 7.89
O (s) 132.19
K (s) 118.45
f1 (ppm)

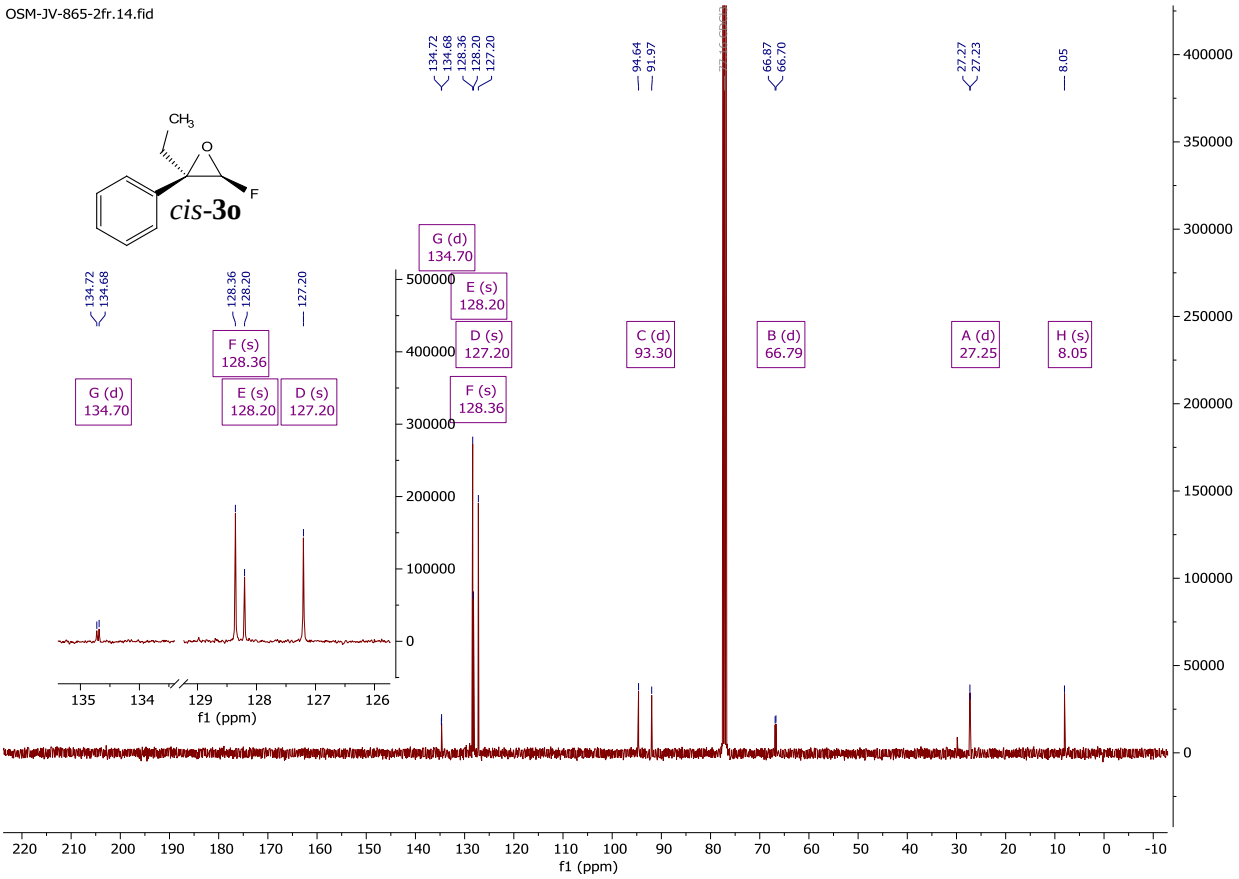

OSM-JV-820col_09Aug18_FLUORINE_cdcl3_01
STANDARD FLUORINE PARAMETERS
CH3
O
F
N
3n
-151.91
-152.14
-154.51
-154.74
B (d)
-152.02
A (d)
-154.62
1.06
1.00
f1 (ppm)

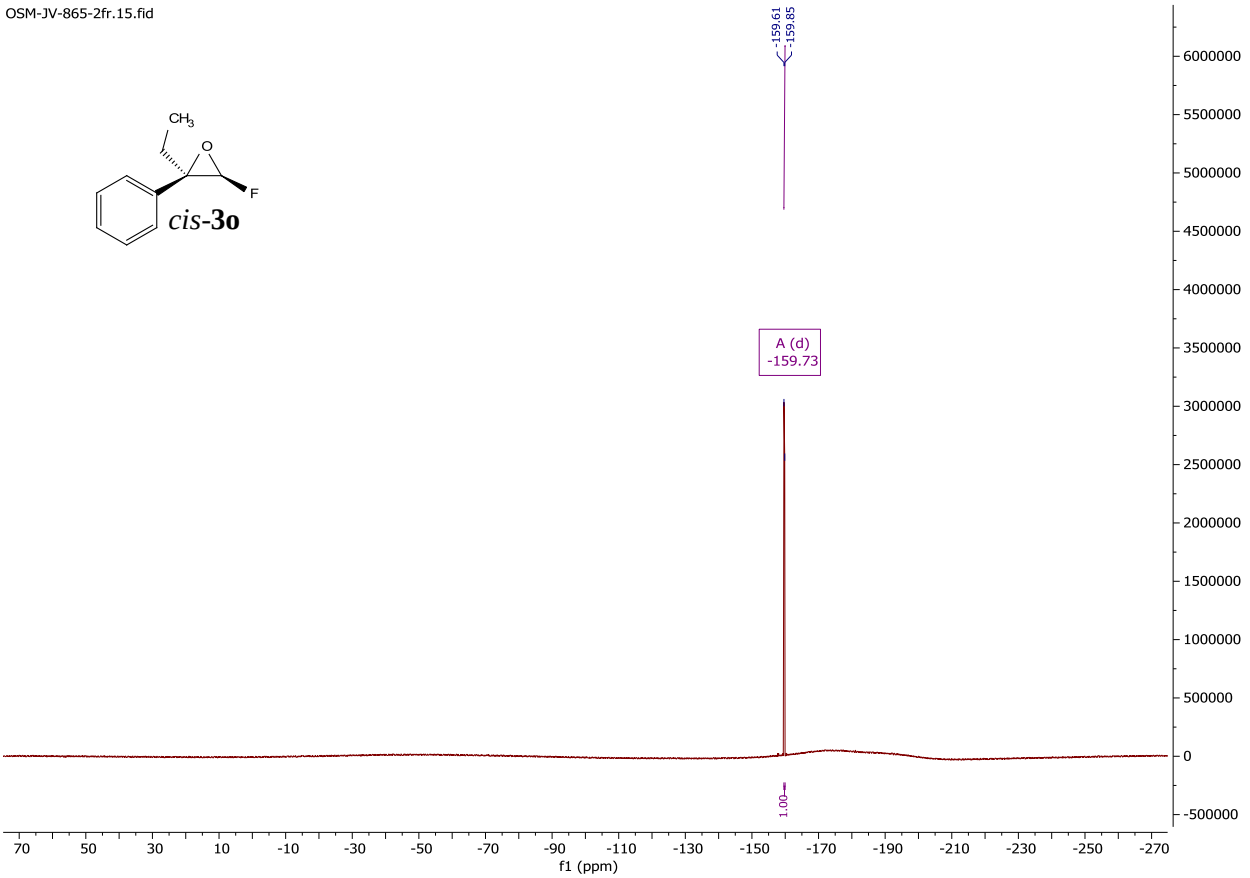

OSM-JV-871_1fr.10.fid
CH3
O
F
trans-3o
5.46
5.16
5.57
0.94
1.58
0.89
2.90
f1 (ppm)

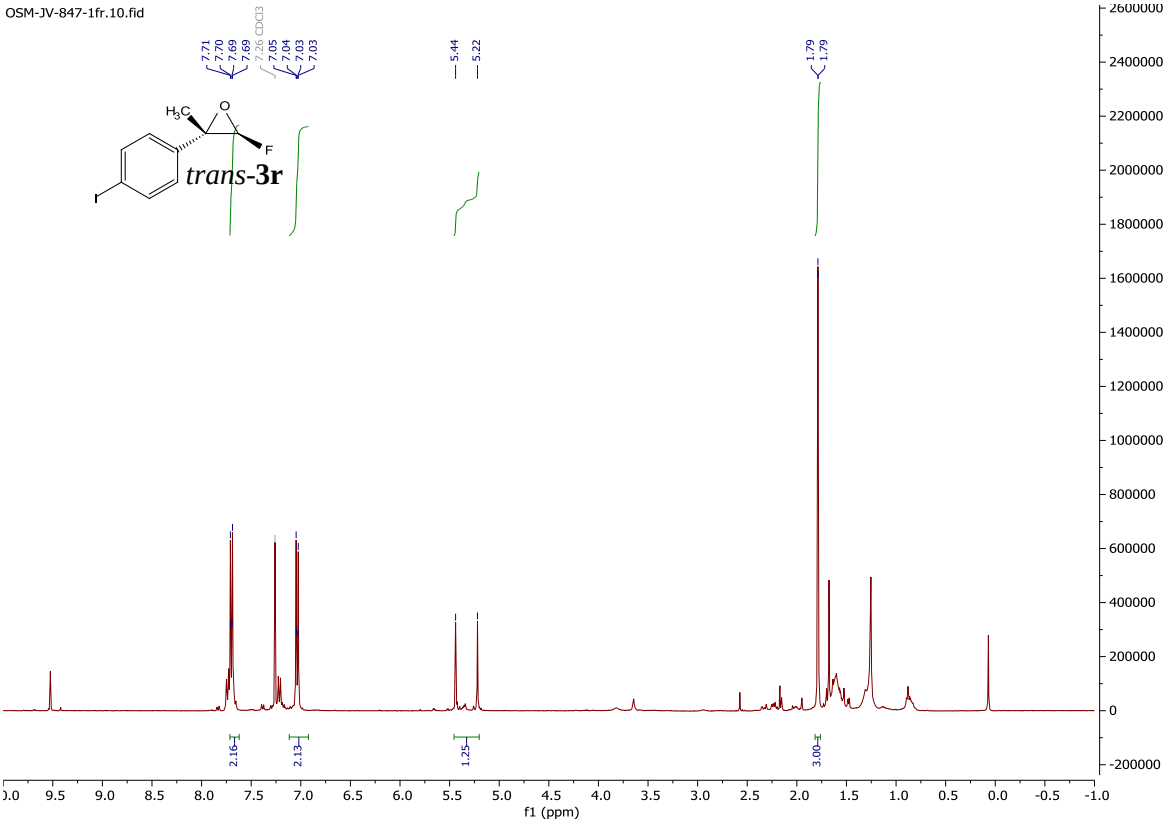

OSM-JV-871-1fr.31.fid
CH3
O
F
trans-3o
136.31
136.27
128.68
128.30
126.20
95.97
93.25
66.17
66.01
23.03
23.00
8.96
H (s)
126.20
F (s)
128.68
E (d)
136.29
G (s)
128.30
D (d)
94.61
C (d)
66.09
B (d)
23.02
A (s)
8.96
f1 (ppm)

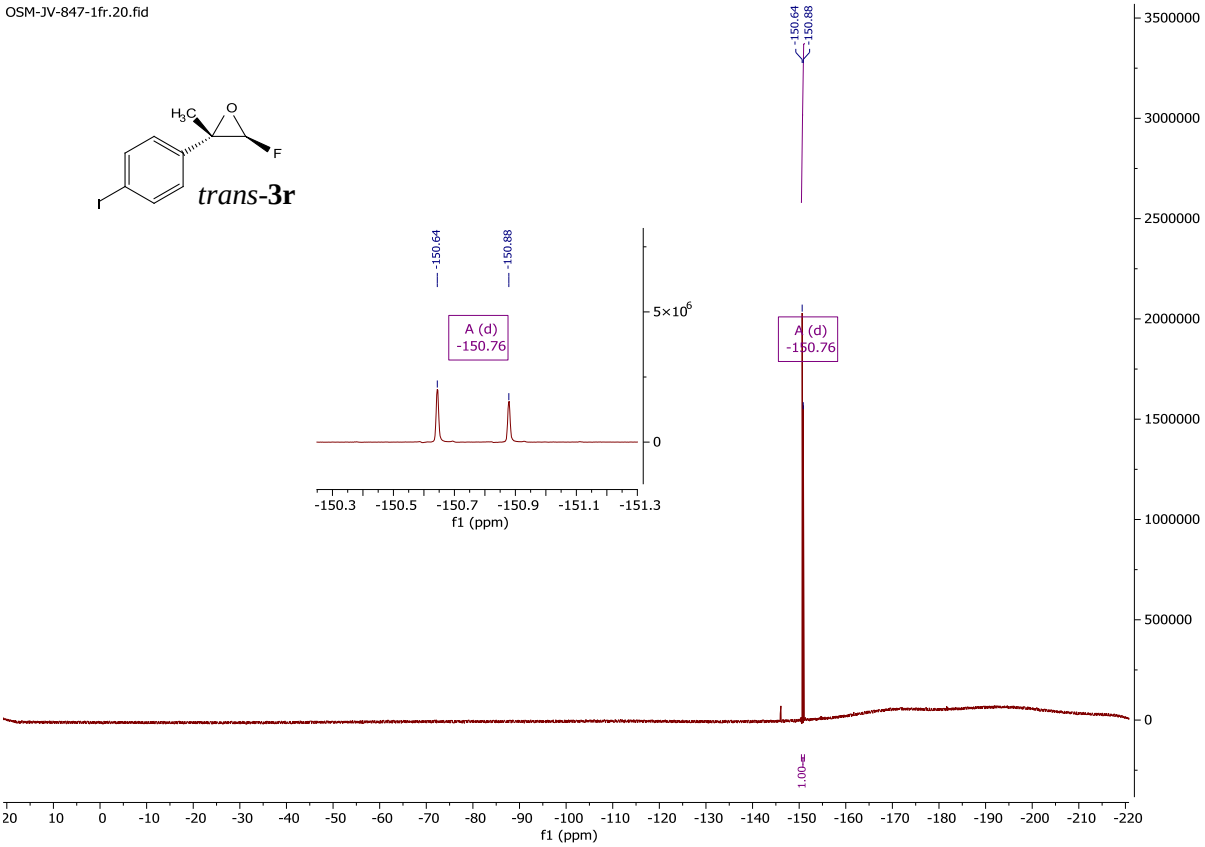

OSM-JV-871-1fr.12.fid
CH3
O
F
trans-3o
-157.68
-157.70
-157.92
-157.93
-159.55
-159.56
-159.79
-159.80
A (dd)
-157.81
B (dd)
-159.67
1.00
0.10
f1 (ppm)

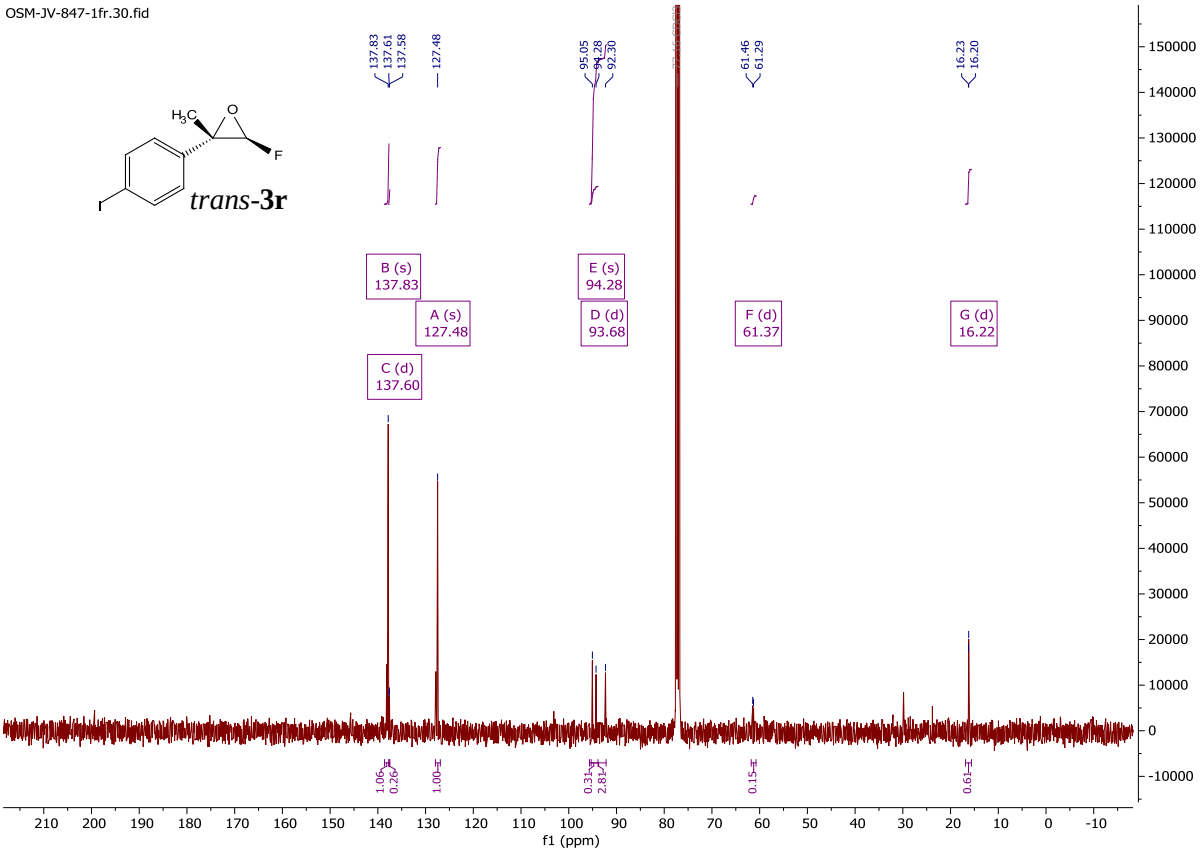

OSM-JV-871_2fr.10.fid
CH3
O
F
cis-3o
f1 (ppm)

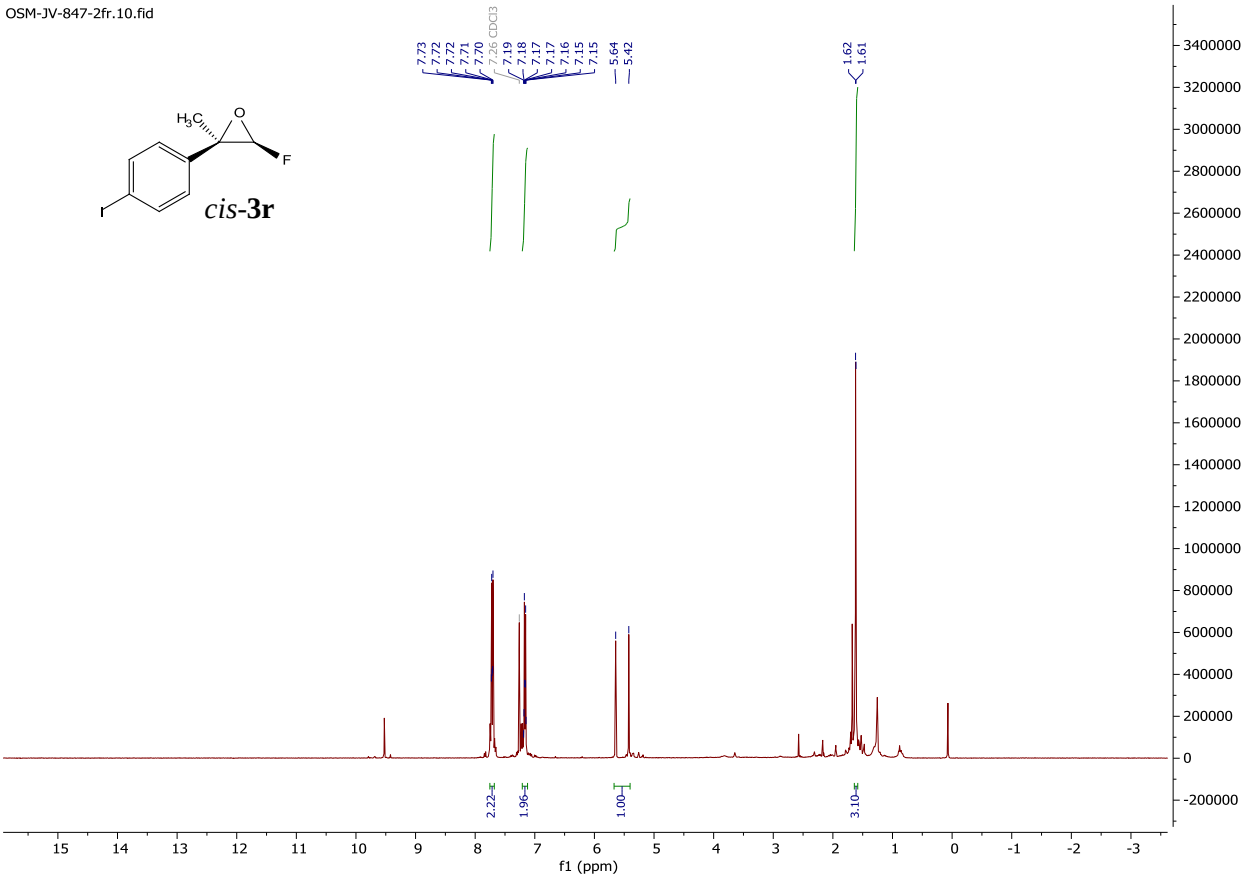

OSM-JV-865-2fr.14.fid
CH3
O
F
cis-3o
G (d) 134.70
E (s) 128.20
D (s) 127.20
F (s) 128.36
C (d) 93.30
B (d) 66.79
A (d) 27.25
H (s) 8.05
f1 (ppm)

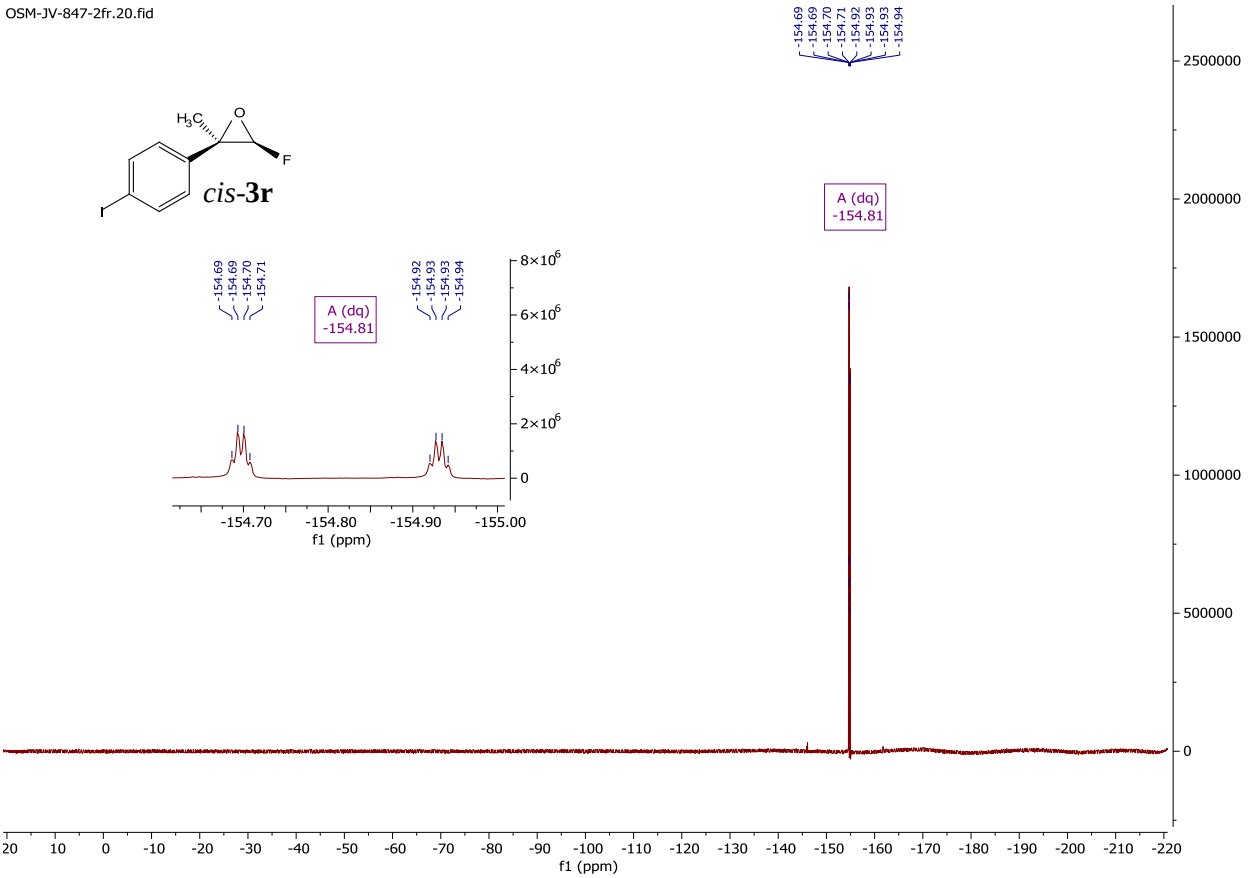

OSM-JV-865-2fr.15.fid
CH3
O
F
cis-3o
-159.61
-159.85
A (d)
-159.73
1.00
6000000
5500000
5000000
4500000
4000000
3500000
3000000
2500000
2000000
1500000
1000000
500000
0
-500000
70
50
30
10
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
-230
-250
-270
f1 (ppm)

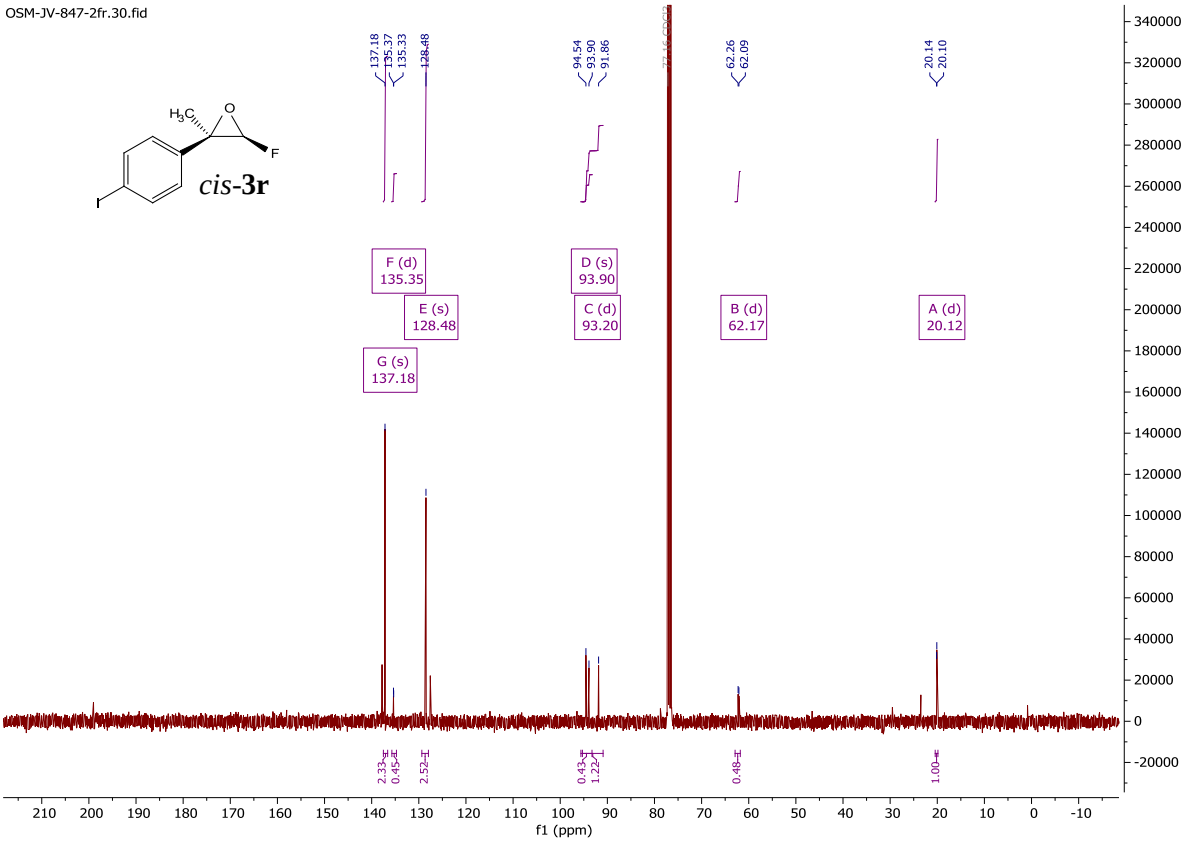

OSM-JV-847-1fr.10.fid
7.71
7.70
7.69
7.69
7.26 CDCl3
7.05
7.04
7.03
7.03
5.44
5.22
1.79
1.79
trans-3r
2.16
2.13
1.25
3.00
f1 (ppm)

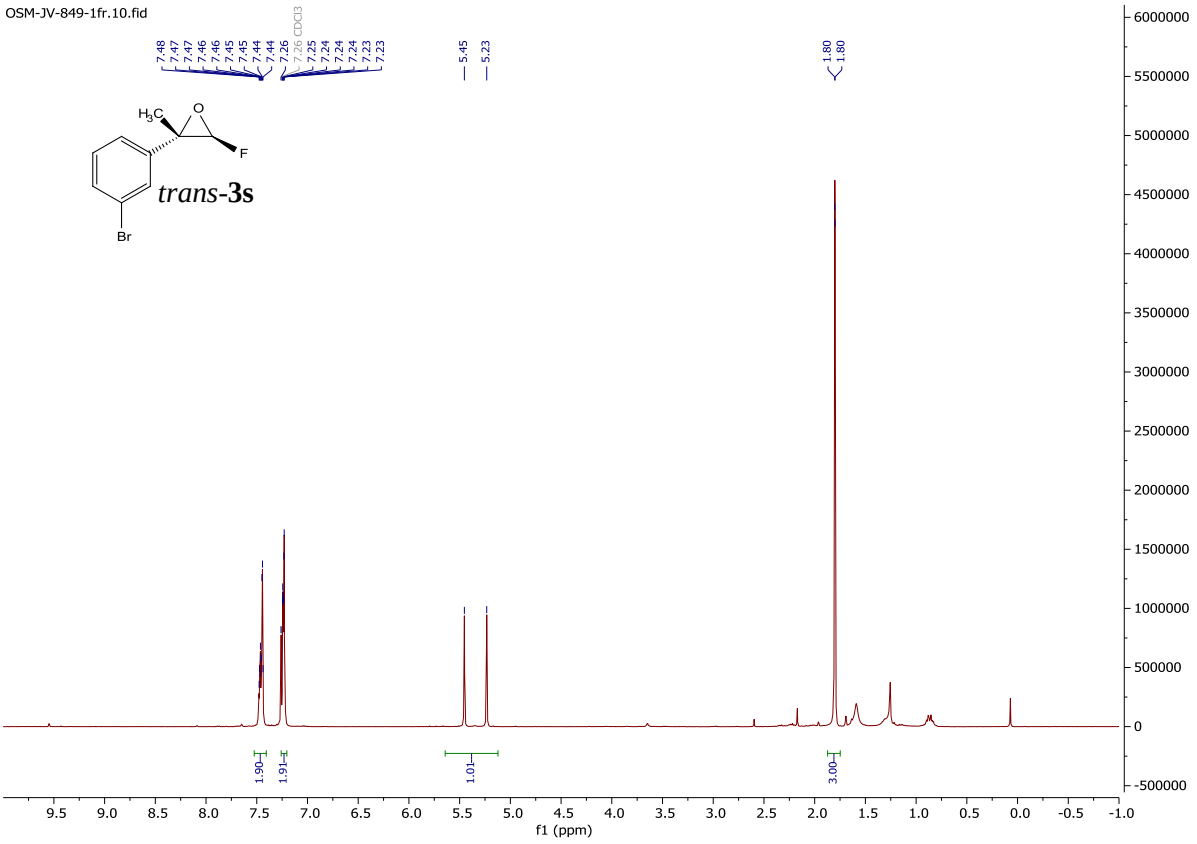

OSM-JV-847-1fr.20.fid
-150.64
-150.88
trans-3r
A (d)
-150.76
A (d)
-150.76
5×10^6
1.00
f1 (ppm)

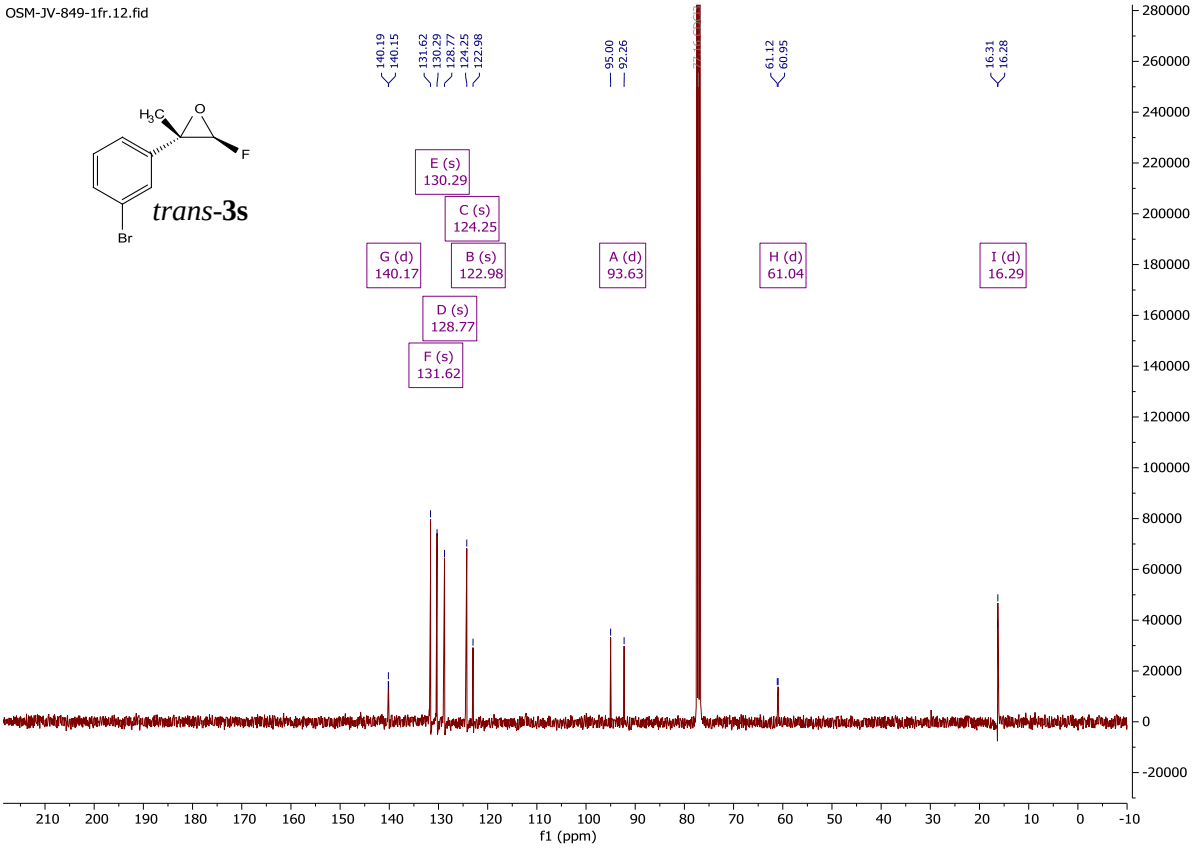

OSM-JV-847-1fr.30.fid
trans-3r
B (s)
137.83
A (s)
127.48
C (d)
137.60
E (s)
94.28
D (d)
93.68
F (d)
61.37
G (d)
16.22
f1 (ppm)

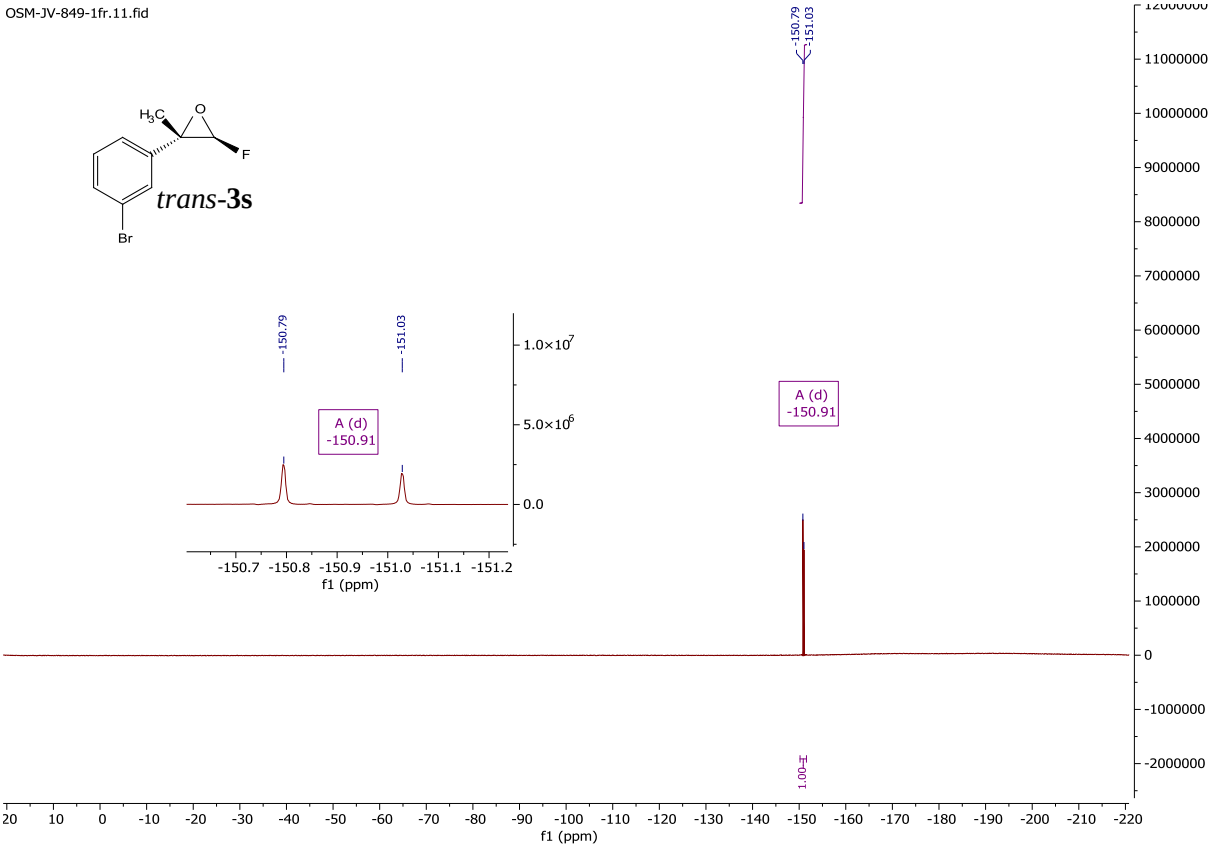

OSM-JV-847-2fr.10.fid
7.73
7.72
7.72
7.71
7.70
7.26 CDCl3
7.19
7.18
7.17
7.17
7.16
7.15
7.15
5.64
5.42
1.62
1.61
H3C
O
F
I
cis-3r
2.22
1.96
1.00
3.10
f1 (ppm)

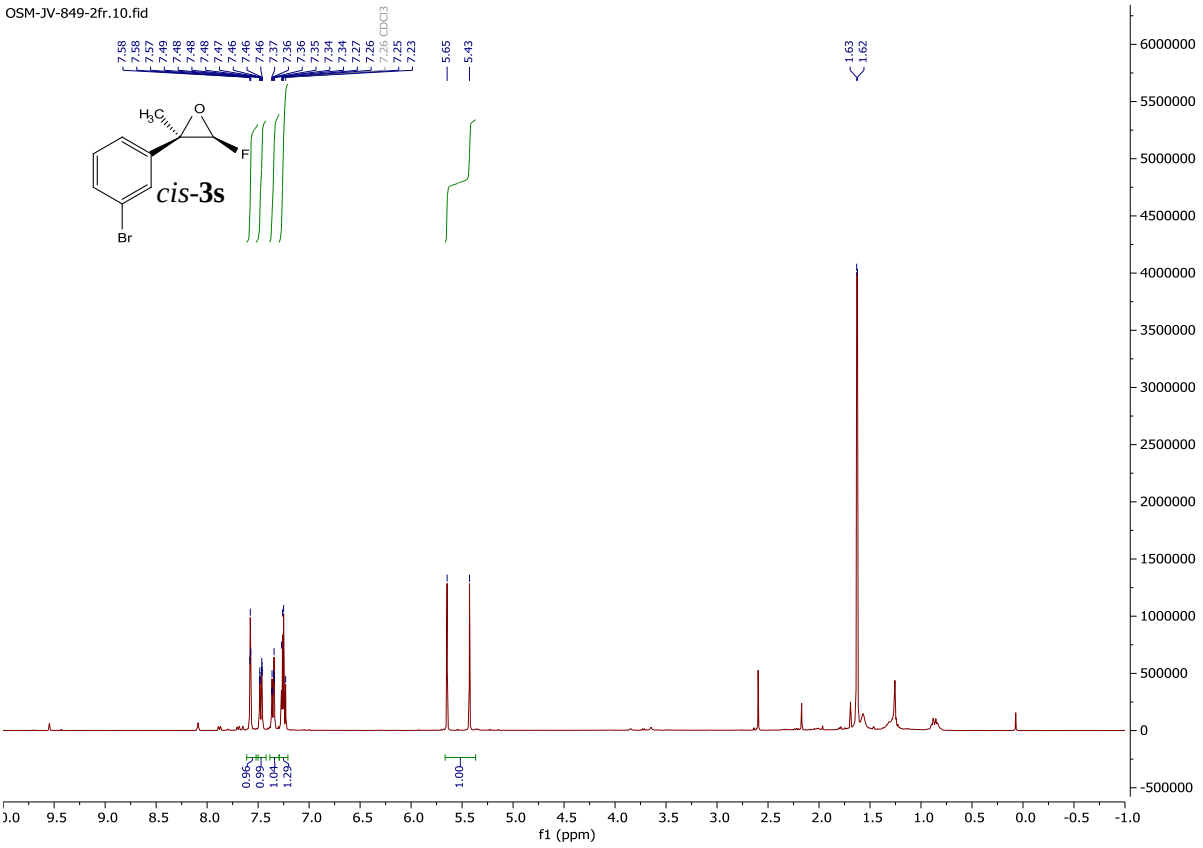

OSM-JV-847-2fr.20.fid
cis-3r
A (dq)
-154.81
f1 (ppm)

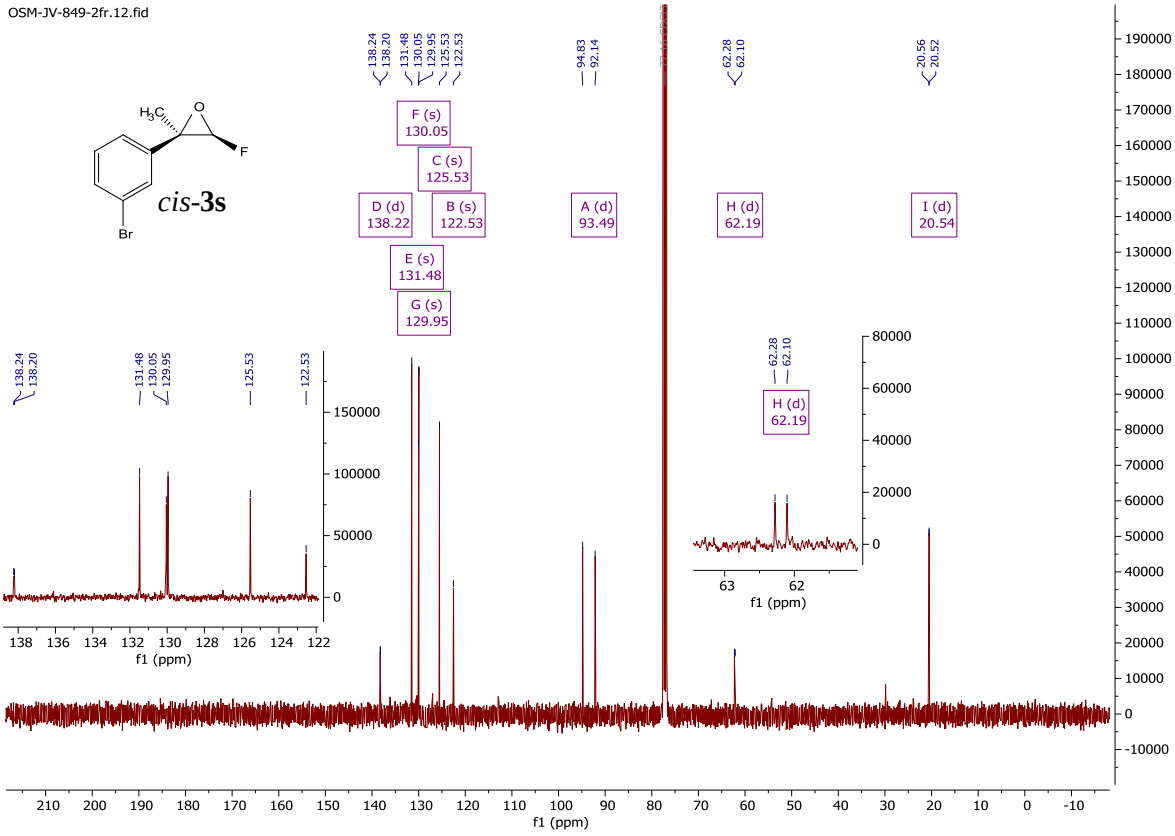

OSM-JV-847-2fr.30.fid
cis-3r
F (d)
135.35
E (s)
128.48
G (s)
137.18
D (s)
93.90
C (d)
93.20
B (d)
62.17
A (d)
20.12
f1 (ppm)

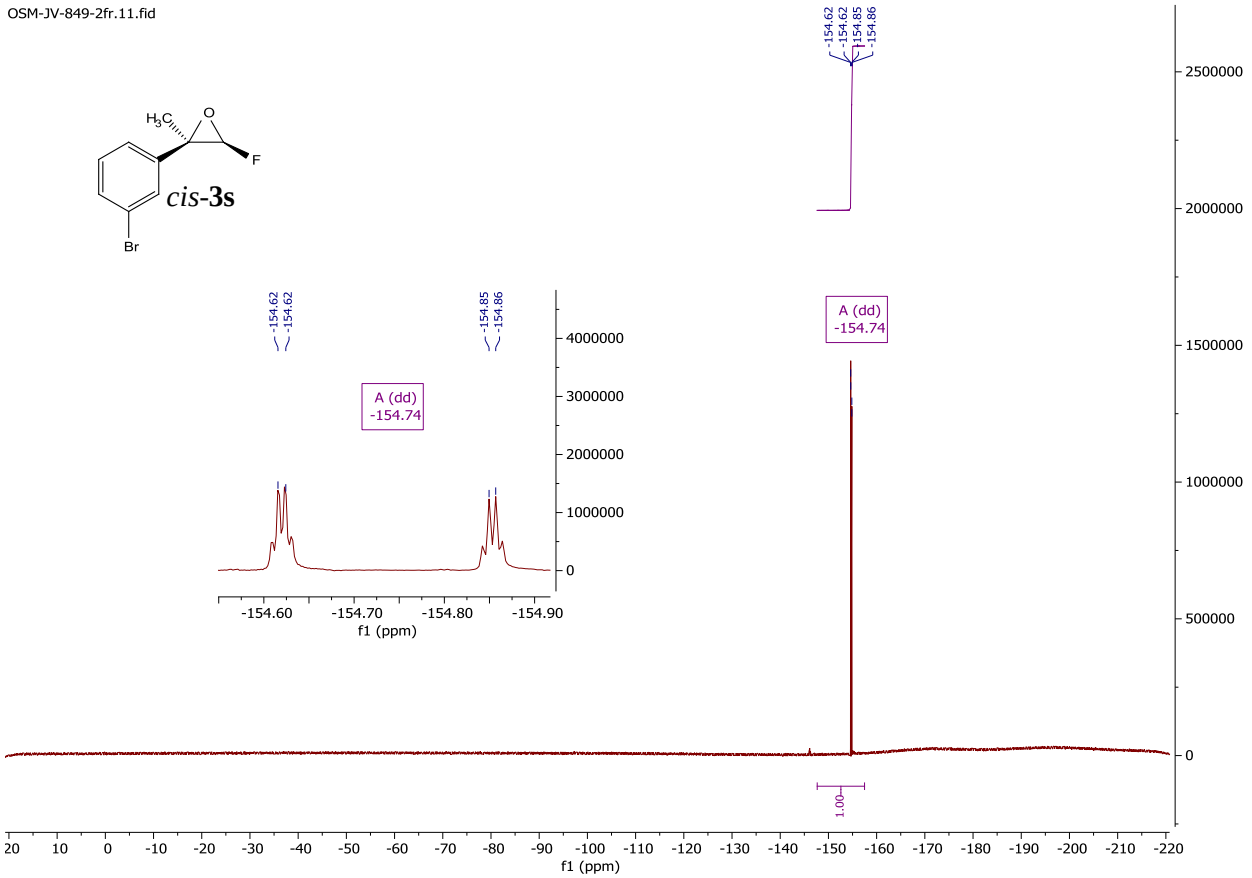

OSM-JV-849-1fr.10.fid
trans-3s
f1 (ppm)

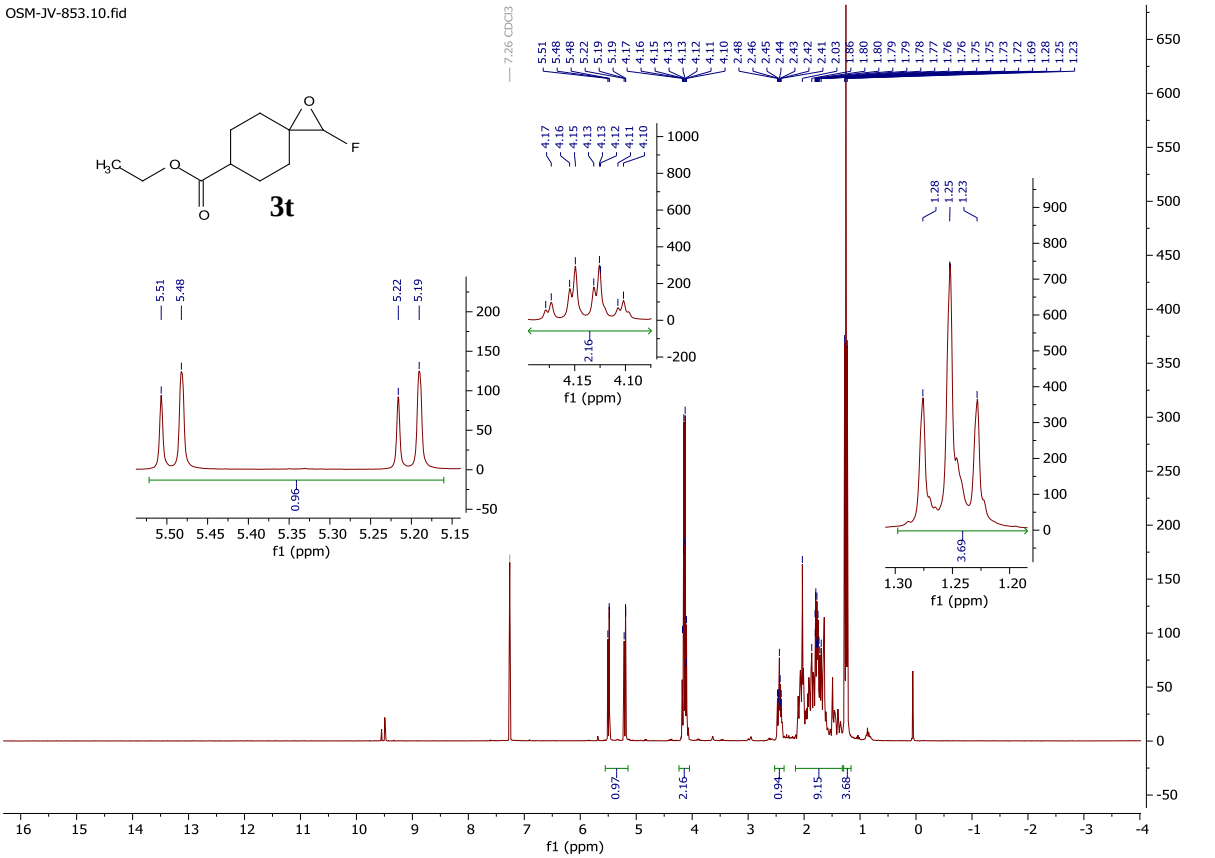

OSM-JV-849-1fr.12.fid
trans-3s
E (s) 130.29
C (s) 124.25
G (d) 140.17
B (s) 122.98
A (d) 93.63
H (d) 61.04
I (d) 16.29
D (s) 128.77
F (s) 131.62
f1 (ppm)

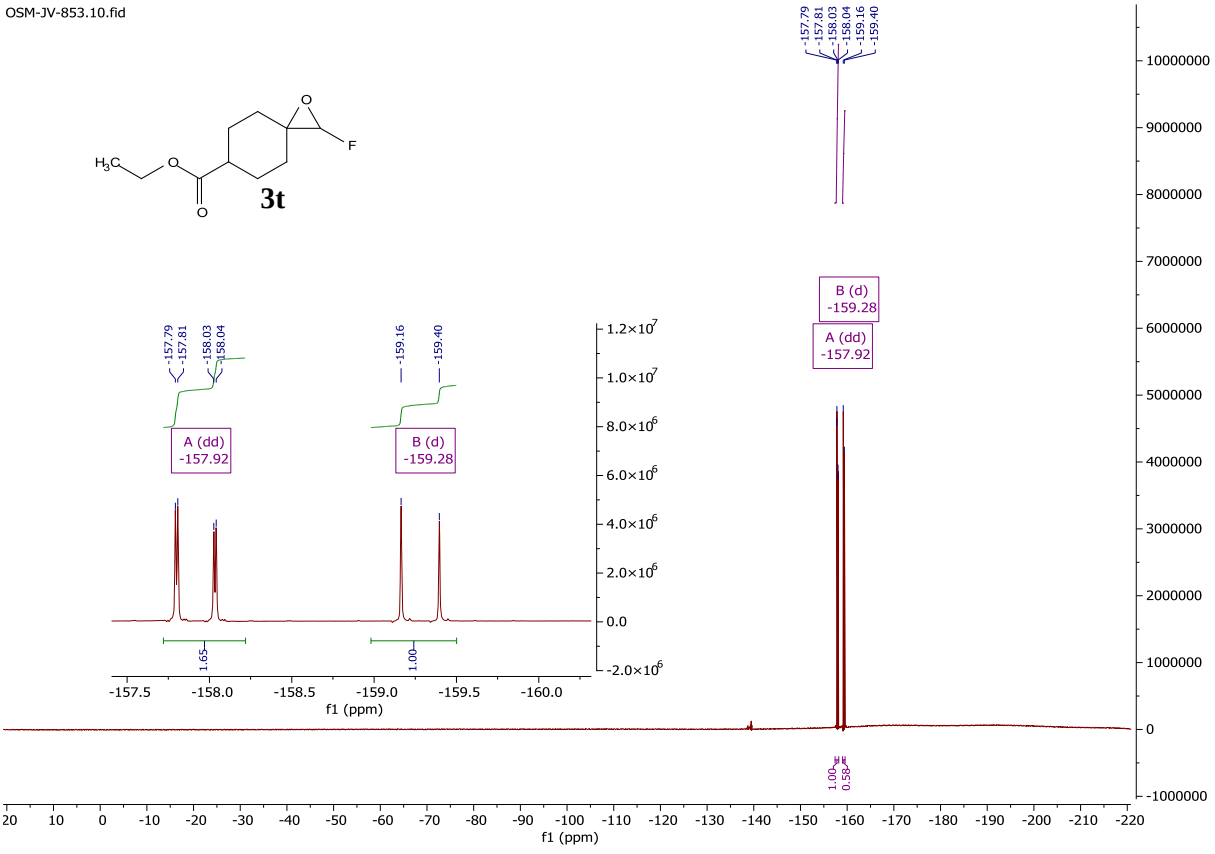

OSM-JV-849-1fr.11.fid
trans-3s
-150.79
-151.03
A (d)
-150.91
1.00
f1 (ppm)

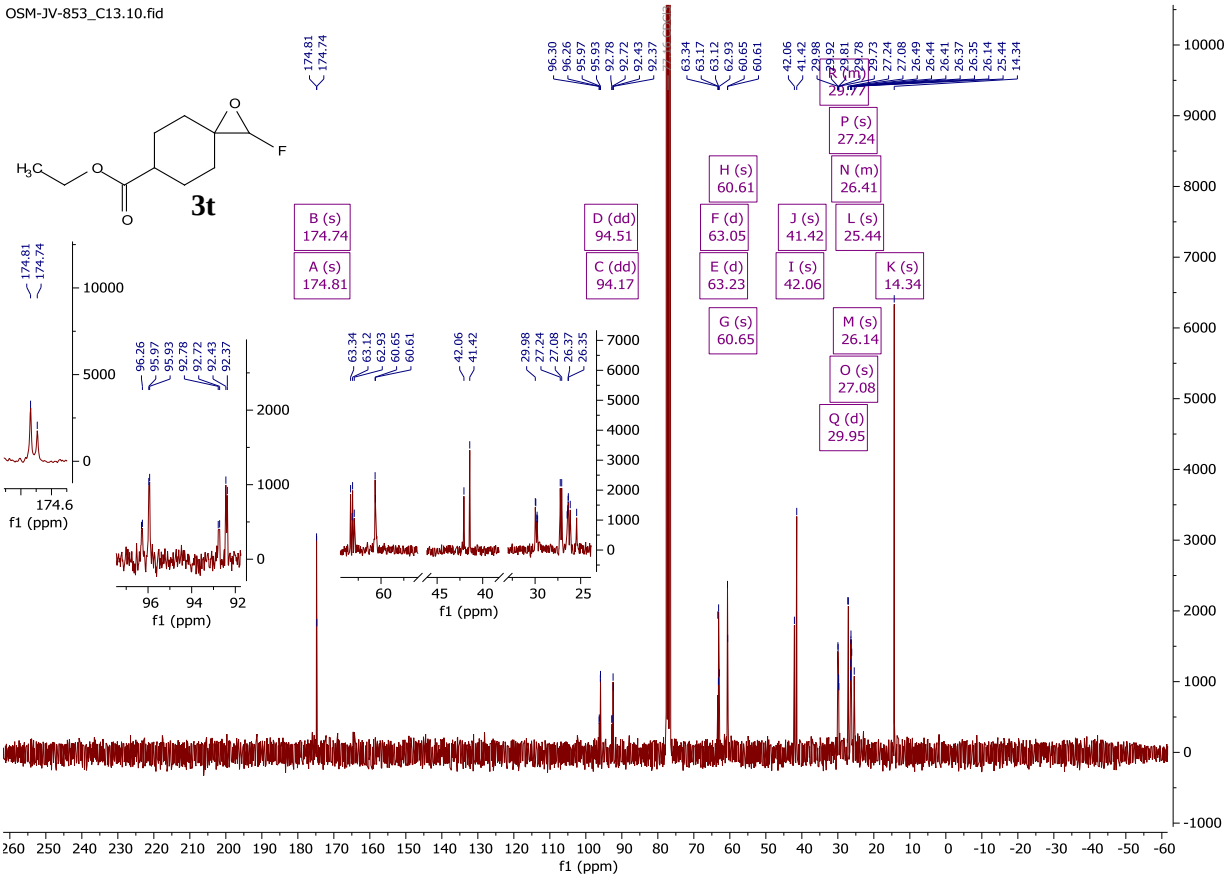

OSM-JV-849-2fr.10.fid
cis-3s
f1 (ppm)


OSM-JV-849-2fr.12.fid
cis-3s
F (s) 130.05
C (s) 125.53
D (d) 138.22
B (s) 122.53
A (d) 93.49
H (d) 62.19
I (d) 20.54
E (s) 131.48
G (s) 129.95
f1 (ppm)


OSM-JV-849-2fr.11.fid
cis-3s
Br
F
O
H3C
-154.62
-154.62
-154.85
-154.86
A (dd)
-154.74
1.00
f1 (ppm)


OSM-JV-853.10.fid
3t
f1 (ppm)


OSM-JV-853.10.fid
3t
A (dd)
-157.92
B (d)
-159.28
f1 (ppm)


OSM-JV-853_C13.10.fid
3t
B (s) 174.74
A (s) 174.81
D (dd) 94.51
C (dd) 94.17
H (s) 60.61
F (d) 63.05
E (d) 63.23
G (s) 60.65
J (s) 41.42
I (s) 42.06
L (s) 25.44
N (m) 26.41
K (s) 14.34
M (s) 26.14
P (s) 27.24
O (s) 27.08
Q (d) 29.95
f1 (ppm)