Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supporting information

Johnson–Corey–Chaykovsky Fluorocyclopropanation of Double Activated Alkenes: Scope and Limitations

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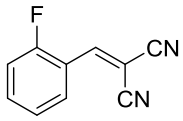
1. GENERAL REMARKS

All procedures were performed under argon atmosphere unless noted otherwise. Reagents and starting materials were obtained from commercial sources and used as received. Starting materials and dry solvents (1,4-dioxane, MeCN) were purchased from *Fluorochem*, *Sigma Aldrich*, *Acros* or *Alfa Aeser* and used as received. The solvents were purified and dried by standard procedures prior to use. Dry THF and DCM were obtained from dry solvent still. Flash column chromatography was carried out using *Kieselgel* silicagel (35 - 70 un 60 - 200 μm). Thin layer chromatography (TLC) was performed on silica gel using Merck TLC Silca gel 60 F_{254} Aluminium sheets and was visualized by UV lamp, staining with $KMnO_4$. Preparative TLC was carried out on 20x20 cm Merck TLC Silca gel 60 F_{254} Aluminium sheets. NMR spectra were recorded on 300 or 400 MHz *Bruker* 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.

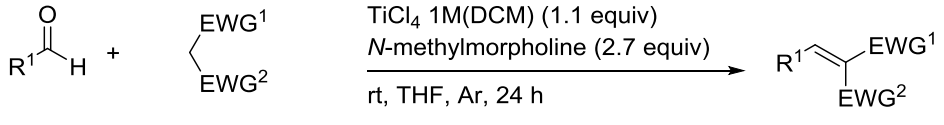
2. SUBSTRATE SYNTHESIS

(2-Fluorobenzylidene)malononitrile (**3a**) [1]**:** Product was obtained following the procedure described in literature [2]. A mixture of 2-fluorobenzaldehyde (481 mg, 3.9 mmol, 1 equiv), malononitrile (256 mg, 3.9 mmol, 1 equiv) and anh. $ZnCl_2$ (52.8 mg, 0.39 mmol, 10 mol%) was heated at 88 ºC for 20 min. Afterwards the mixture was allowed to cool to r.t. and 1% EtOH solution in water (10 mL) was added. The formed product was filtered off and washed with water (20 mL) and Et_2O (20 mL). Product was obtained as a white solid (540 mg, 68%).



^{1}H NMR (400 MHz, DMSO-d_6) δ 8.56 (s, 1H), 8.03 (tdd, *J* = 7.4, 1.8, 0.9 Hz, 1H), 7.80 – 7.62 (m, 1H), 7.52 – 7.32 (m, 2H).

General scheme for preperation of EWG activated alkenes [3]**:**



1 equiv 1 or 0.7 equiv **4a**

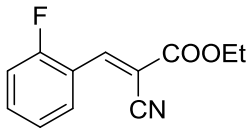
R^1 = Alkyl, Aryl
EWG^1 = CN, COOR, $COONR_2$
EWG^2 = COOR, $COONR_2$

General method for preperation of EWG activated alkenes

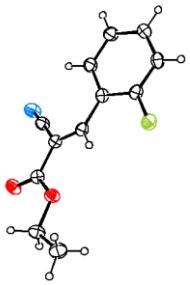
Ethyl (*E*)-2-cyano-3-phenylacrylate (**4a**) [4]: A solution of benzaldehyde (0.38 mL, 3.76 mmol, 1 equiv) and ethylcyanoacetate (0.28 mL, 2.64 mmol. 0.7 equiv) in dry THF (8.75 mL) was cooled in ice/water bath to 0 ºC. To the cooled solution was slowly added 1M $TiCl_4$ in DCM (4.1 mL, 4.1 mmol, 1.1 equiv). The mixture was left to stir at the same temperature for 30 min. Afterwards *N*-methylmorpholine (1.12 mL, 10.18 mmol, 2.7 equiv) was added and the mixture was left to stir at rt for 24 h. After completion the reaction was quenched by addition of H_2O (10 mL). The layers were seperated and the aqueous layer was extracted with DCM (3 x 10 mL). The combined organic phases were dried over anh. Na_2SO_4 and filtered. The filtrate was concentrated under reduced pressure. The crude product was purified via collumn chromatography (Eluent PE:EtOAc 20:1). Product was obtained as a white solid (358 mg, 67%).

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.41 (s, 1H), 8.13 – 7.98 (m, 2H), 7.72 – 7.52 (m, 3H), 4.33 (q, *J* = 7.1 Hz, 2H), 1.31 (t, *J* = 7.1 Hz, 3H). Stereochemistry similar to compound **4b**.

Ethyl (*E*)-2-nitro-3-(2-fluorophenyl)acrylate (**4b**) [5]: Compound was obtained following the general procedure using 2-fluorobenzaldehyde (0.34 mL, 1.61 mmol, 1 equiv) and ethylcyanoacrylate (0.23 mL, 2.16 mmol, 0.7 equiv). Product was obtained as a light yellow oil that crystallised over time (410 mg, 58%).

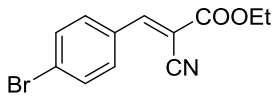


^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 (s, 1H), 8.38 (td, *J* = 7.6, 1.7 Hz, 1H), 7.66 – 7.46 (m, 1H), 7.33 – 7.27 (m, 1H), 7.19 (ddd, *J* = 10.3, 8.3, 1.2 Hz, 1H), 4.40 (q, *J* = 7.1 Hz, 2H), 1.41 (t, *J* = 7.1 Hz, 3H). Stereochemistry determined via X-Ray (see figure 1.)



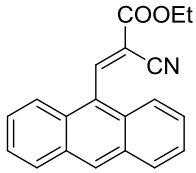
Firgure 1. Stereochemistry of alkene **4b**

Ethyl (*E*)-3-(4-bromophenyl)-2-cyanoacrylate (**4c**) [4]: Compound was obtained following the general procedure using *p*-bromobenzaldehyde (449 mL, 2.24 mmol, 1 equiv) and ethylcyanoacrylate (0.18 mL, 1.70 mmol, 0.7 equiv). Product was obtained as a white solid (257 mg, 54%).



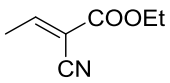
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (s, 1H), 7.92 – 7.76 (m, 2H), 7.70 – 7.56 (m, 2H), 4.38 (q, *J* = 7.1 Hz, 2H), 1.40 (t, *J* = 7.2 Hz, 3H). Stereochemistry similar to compound **4b**.

Ethyl (*E*)-3-(anthracene-9-yl)-2-cyanoacrylate (**4d**) [6]: Compound was obtained following the general procedure using 9-anthraldehyde (500 mg, 2.24 mmol, 1 equiv) and ethylcyanoacrylate (0.18 mL, 1.70 mmol, 0.7 equiv). Product was obtained as a yellow solid (382 mg, 75%).



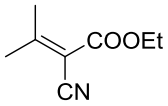
^{1}H NMR (300 MHz, DMSO-d_6) δ 9.34 (s, 1H), 8.83 (s, 1H), 8.25 – 8.17 (m, 2H), 8.08 – 7.99 (m, 2H), 7.71 – 7.56 (m, 4H), 4.43 (q, *J* = 7.1 Hz, 2H), 1.40 (t, *J* = 7.1 Hz, 3H). Stereochemistry similar to compound **4b**.

Ethyl (*E*)-2-cyanobut-2-enoate (**4e**) [7]: Compound was obtained following the general procedure using acetaldehyde (0.16 mL, 3 mmol, 1 equiv) and ethylcyanoacrylate (0.22 mL, 2.1 mmol, 0.7 equiv). Product was obtained as a light yellow oil (102 mg, 34 %).



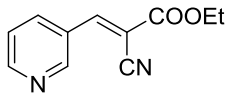
^{1}H NMR (400 MHz, DMSO-d_6) δ 7.81 (q, *J* = 7.1 Hz, 1H), 4.25 (q, *J* = 7.1 Hz, 2H), 2.17 (d, *J* = 7.1 Hz, 3H), 1.26 (q, *J* = 7.0 Hz, 3H). Stereochemistry similar to compound **4b**.

Ethyl 2-cyano-3-methylbut-2-enoate (**4f**) [8]: Compound was obtained following the general procedure using acetone (0.22 mL, 3 mmol, 1 equiv) and ethylcyanoacrylate (0.22 mL, 2.1 mmol, 0.7 equiv). Product was obtained as a colorless oil (68 mg, 21%).



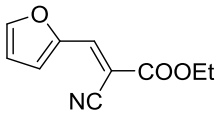
^{1}H NMR (400 MHz, $CDCl_3$) δ 4.27 (q, *J* = 7.1 Hz, 2H), 2.40 (s, 3H), 2.30 (s, 3H), 1.34 (t, *J* = 7.1 Hz, 3H).

Ethyl (*E*)-2-cyano-3-(pyridine-3-yl)acrylate (**4g**) [9]: Compound was obtained following the general procedure using 3-pyridinecarboxaldehyde (0.28 mL, 3 mmol, 1 equiv) and ethylcyanoacrylate (0.22 mL, 2.1 mmol, 0.7 equiv). Product was obtained as a light yellow solid (0.28 g, 66%).



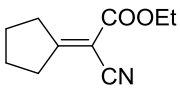
^{1}H NMR (300 MHz, DMSO-d_6) δ 9.14 – 9.05 (m, 1H), 8.77 (dd, *J* = 4.8, 1.6 Hz, 1H), 8.51 – 8.43 (m, 2H), 7.64 (dd, *J* = 8.0, 5.1 Hz, 1H), 4.34 (q, *J* = 7.1 Hz, 2H), 1.32 (t, *J* = 7.1 Hz, 3H). Stereochemistry similar to compound **4b**.

Ethyl (*E*)-2-cyano-3-(furan-2-yl)acrylate (**4h**) [10]: Compound was obtained following the general procedure using 2-furaldehyde (0.25 mL, 3 mmol, 1 equiv) and ethylcyanoacrylate (0.22 mL, 2.1 mmol, 0.7 equiv). Product was obtained as a white solid (203 mg, 50 %).



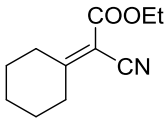
^{1}H NMR (400 MHz, DMSO-d_6) δ 8.23 – 8.21 (m, 1H), 8.14 (s, 1H), 7.53 (d, *J* = 4.1 Hz, 1H), 6.87 (dd, *J* = 3.6, 1.8 Hz, 1H), 4.28 (q, *J* = 7.1 Hz, 2H), 1.29 (t, *J* = 7.1 Hz, 3H). Stereochemistry similar to compound **4b**.

Ethyl 2-cyano-2-cyclopentylideneacetate (**4i**) [11]: Compound was obtained following the general procedure using cyclopentanone (0.27 mL, 3 mmol, 1 equiv) and ethylcyanoacrylate (0.22 mL, 2.1 mmol, 0.7 equiv). The crude product was purified via collumn chromatography (Eluent PE:EtOAc 1:1). Product was obtained as a white amorphous solid (118 mg, 31%).



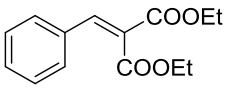
^{1}H NMR (400 MHz, $CDCl_3$) δ 4.27 (q, *J* = 7.1 Hz, 2H), 3.02 – 2.96 (m, 2H), 2.84 – 2.77 (m, 2H), 1.91 – 1.76 (m, 4H), 1.34 (t, *J* = 7.1 Hz, 3H).

Ethyl 2-cyano-2-cyclohexylideneacetate (**4j**) [12]: Compound was obtained following the general procedure using cyclohexanone (0.31 mL, 3 mmol, 1 equiv) and ethylcyanoacrylate (0.22 mL, 2.1 mmol, 0.7 equiv). Product was obtained as a colorless oil (232 mg, 57%).



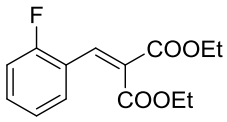
^{1}H NMR (400 MHz, $CDCl_3$) δ 4.27 (q, *J* = 7.1 Hz, 2H), 3.01 – 2.93 (m, 2H), 2.70 – 2.61 (m, 2H), 1.84 – 1.62 (m, 7H), 1.34 (t, *J* = 7.1 Hz, 3H).

Diethyl 2-benzylidenemalonate (**4k**) [13]: Compound was obtained following the general procedure using benzaldehyde (0.24 mL, 2.40 mmol, 1 equiv) and diethylmalonate (0.36 mL, 2.40 mmol, 1 equiv). The crude product was purified via collumn chromatography (Eluent Pe:EtOAc 10:1 to 4:1). Product was obtained as a colorless oil (500 mg, 84%).



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (s, 1H), 7.49 – 7.42 (m, 2H), 7.41 – 7.34 (m, 3H), 4.34 (q, *J* = 7.1 Hz, 2H), 4.31 (q, *J* = 7.1 Hz, 2H), 1.33 (t, *J* = 7.1 Hz, 3H), 1.29 (t, *J* = 7.1 Hz, 3H).

Diethyl 2-(2-fluorobenzylidene)malonate (**4l**) [14]: Compound was obtained following the general procedure using 2-fluorobenzaldehyde (0.32 mL, 3 mmol, 1 equiv) and diethylmalonate (0.46 mL, 3 mmol, 1 equiv). The crude product was purified via collumn chromatography (Eluent PE:EtOAc 4:1). Product was obtained as a colorless oil (644 mg, 81%).

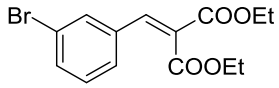


^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (s, 1H), 7.48 – 7.42 (m, 1H), 7.41 – 7.34 (m, 1H), 7.16 – 7.06 (m, 2H), 4.32 (q, *J* = 7.1 Hz, 2H), 4.30 (q, *J* = 7.1 Hz, 2H), 1.34 (t, *J* = 7.1 Hz, 3H), 1.26 (t, *J* = 7.1 Hz, 3H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -112.72 – -112.82 (m).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.1, 163.8, 162.1, 159.6, 134.8 (d, *J* = 5.1 Hz), 132.3 (d, *J* = 8.7 Hz), 129.4 (d, *J* = 2.2 Hz), 128.2 (d, *J* = 1.6 Hz), 121.3 (d, *J* = 12.4 Hz), 115.9 (d, *J* = 21.7 Hz), 61.8, 61.7, 14.1, 13.9.

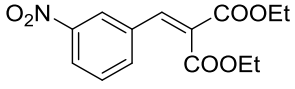
Diethyl 2-(3-bromobenzylidene)malonate (**4m**) [15]: Compound was obtained following the general procedure using 3-bromobenzaldehyde (0.35 mL, 3 mmol, 1 equiv) and diethylmalonate (0.46 mL, 3 mmol, 1 equiv). The crude product was purified via collumn chromatography (Eluent PE:EtOAc 4:1). Product was obtained as a colorless oil (330 mg, 34 %).



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (s, 1H), 7.61 – 7.58 (m, 1H), 7.54 – 7.50 (m, 1H), 7.40 – 7.35 (m, 1H), 7.28 – 7.21 (m, 1H), 4.34 (q, *J* = 7.2 Hz, 2H), 4.31 (q, *J* = 7.1 Hz, 2H), 1.33 (t, *J* = 7.1 Hz, 3H), 1.30 (t, *J* = 7.1 Hz, 3H).

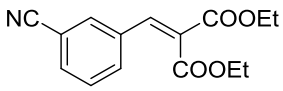
^{13}C NMR (101 MHz, $CDCl_3$) δ 166.1, 163.7, 140.3, 135.0, 133.3, 132.0, 130.3, 127.9, 127.8, 122.8, 61.9, 61.9, 14.1, 13.9.

Diethyl 2-(3-nitrobenzylidene)malonate (**4n**) [16]: Compound was obtained following the general procedure using 3-nitrobenzaldehyde (453 mg, 3 mmol, 1 equiv) and diethylmalonate (0.46 mL, 3 mmol, 1 equiv). The crude product was purified via collumn chromatography (Eluent 4:1). Product was obtained as a light yellow oil (485 mg, 55%).



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 – 8.32 (m, 1H), 8.28 – 8.22 (m, 1H), 7.80 – 7.69 (m, 2H), 7.58 (t, *J* = 8.0 Hz, 1H), 4.38 (q, *J* = 7.2 Hz, 2H), 4.33 (q, *J* = 7.2 Hz, 2H), 1.35 (t, *J* = 7.1 Hz, 3H), 1.32 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.7, 163.4, 148.5, 139.0, 135.1, 134.6, 129.9, 129.4, 124.8, 123.7, 62.2, 62.1, 14.1, 13.9.

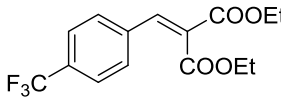
Diethyl 2-(3-cyanobenzylidene)malonate (**4o**): Compound was obtained following 

the general procedure using 3-cyanobenzaldehyde (393 mg, 3 mmol, 1 equiv) and diethylmalonate (0.46 mL, 3 mmol, 1 equiv). The crude product was purified via collumn chromatography (Eluent PE:EtOAc 4:1). Product was obtained as a colorless oil (670 mg, 82%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (s, 1H), 7.75 – 7.69 (m, 1H), 7.60 – 7.56 (m, 2H), 7.52 – 7.45 (m, 1H), 4.34 (q, *J* = 7.1 Hz, 2H), 4.26 (q, *J* = 7.1 Hz, 2H), 1.35 (t, *J* = 7.1 Hz, 3H), 1.21 (t, *J* = 7.1 Hz, 3H).

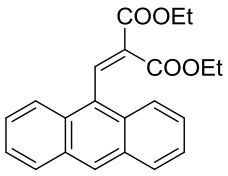
^{13}C NMR (101 MHz, $CDCl_3$) δ 165.4, 163.2, 137.4, 136.6, 133.3, 132.8, 130.9, 130.2, 128.5, 116.8, 113.2, 77.4, 62.1, 61.9, 14.1, 13.8.

Elemental analysis: Calc.: C, 65,92%; H, 5,53%; N, 5,13%. Found: C, 65,60%; H, 5,54%; N, 5,03%.

Diethyl 2-(4-(trifluoromethyl)benzylidene)malonate (**4p**) [17]: Compound was 

obtained following the general procedure using *p*-trifluoromethylbenzaldehyde (0.41 mL, 3 mmol, 1 equiv) and diethylmalonate (0.46 mL, 3 mmol, 1 equiv). The crude product was purified via collumn chromatography (Eluent PE:EtOAc 10:1 to 4:1). Product was obtained as a white solid (873 mg, 92%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (s, 1H), 7.64 (d, *J* = 8.2 Hz, 2H), 7.56 (d, *J* = 8.1 Hz, 2H), 4.33 (q, *J* = 8.0, 7.6 Hz, 2H), 4.32 (q, *J* = 6.7, 6.2 Hz, 2H), 1.34 (t, *J* = 7.1 Hz, 3H), 1.28 (t, *J* = 7.2 Hz, 3H).

Diethyl 2-(anthracene-9-yl)-methylenemalonate (**4r**): Compound was obtained 

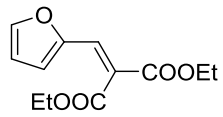
following the general procedure using 9-anthraldehyde (619 mg, 3 mmol, 1 equiv) and diethylmalonate (0.46 mL, 3 mmol, 1 equiv). The crude product was purified via collumn chromatography (Eluent PE:EtOAc 10:1 to 4:1). Product was obtained as a yellow oil that crystallized after time (958 mg, 92%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67 (d, *J* = 1.2 Hz, 1H), 8.46 (s, 1H), 8.04 – 7.95 (m, 4H), 7.53 – 7.45 (m, 4H), 4.45 (q, *J* = 7.2 Hz, 2H), 3.65 (q, *J* = 7.1 Hz, 2H), 1.43 (t, *J* = 7.1 Hz, 3H), 0.36 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 164.7, 163.7, 143.4, 133.1, 131.0, 128.7, 128.7, 128.0, 126.2, 125.5, 125.5, 62.0, 60.8, 14.3, 13.0.

Elemental analysis: Calc.: C, 75,84%; H, 5,79%. Found: C, 75,67%; H, 5,74%.

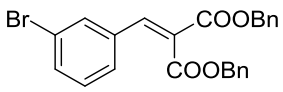
Diethyl 2-(furan-2-yl)-methylenemalonate (**4s**) [18]: Compound was obtained



following the general procedure using 2-furaldehyde (0.25 mL, 3 mmol, 1 equiv) and diethylmalonate (0.46 mL, 3 mmol, 1 equiv). The crude product was purified via collumn chromatography (Eluent PE:EtOAc 10:1 to 4:1). Product was obtained as a light yellow oil (605 mg, 85%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.48 (m, 1H), 7.44 (s, 1H), 6.76 (d, *J* = 3.6 Hz, 1H), 6.49 (dd, *J* = 3.5, 1.8 Hz, 1H), 4.40 (q, *J* = 7.1 Hz, 2H), 4.28 (q, *J* = 7.1 Hz, 2H), 1.36 (t, *J* = 7.2 Hz, 3H), 1.32 (t, *J* = 7.1 Hz, 3H).

Dibenzyl 2-(3-bromobenzylidene)malonate (**4t**) [19]: Compound was obtained

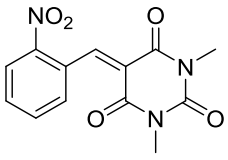


following the general procedure using 3-bromobenzaldehyde (0.28 mL, 2.40 mmol, 1 equiv) and dibenzylmalonate (0.60 mL, 2.40 mmol, 1 equiv). The crude product was purified via collumn chromatography (Eluent PE:EtOAc 10:1). Product was obtained as a white solid (516 mg, 48%).

^{1}H NMR (400 MHz, DMSO-d_6) δ 7.82 (s, 1H), 7.76 – 7.72 (m, 1H), 7.68 – 7.62 (m, 1H), 7.42 – 7.35 (m, 6H), 7.35 – 7.26 (m, 6H), 5.29 (s, 2H), 5.28 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.8, 163.5, 141.4, 135.3, 134.8, 134.7, 133.4, 132.3, 130.3, 128.8, 128.6, 128.6, 128.4, 128.1, 127.7, 127.2, 122.9, 67.8, 67.4.

1,3-dimethyl-5-(2-nitrobenzylidene)pyrimidine-2,4,6(1H,3H,5H)-trione (**4u**):

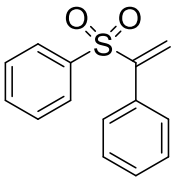


Prepared according to procedure described in literature [20]. A mixture of barbirutic acid (193.6 mg, 1.28 mmol, 1 equiv) and 2-nitrobenzaldehyde (200 mg, 1.28 mmol, 1 equiv) was refluxed in water for 2 hours. Afterwards the mixture was allowed to cool and

the product was filtered off, washed with water and ether. Product was obtained as a white solid (170 mg, 51 %).

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.71 (s, 1H), 8.26 (dd, *J* = 8.3, 1.2 Hz, 1H), 7.81 (td, *J* = 7.6, 1.3 Hz, 1H), 7.58 – 7.45 (m, 1H), 3.26 (s, 3H), 3.07 (s, 3H).

(1-(Phenylsulfonyl)vinyl)benzene (**4x**)**:**



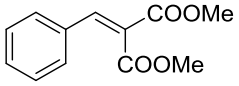
To a solution of sodium benzenesulfinate (1.00 g, 6.09 mmol, 1 equiv) in dry DMF (12 mL) under Ar atmosphere was added (1,2-dibromoethyl)benzene (3.22 g, 12.2 mmol, 2 equiv). The reaction mixture was heated to 80 ^{o}C for 18 h and allowed to cool to RT. To the mixture water (60 ml) was added. The mixture was extracted with EtOAc (3×20 ml). The combined organic phases were washed with sat. aq. NaCl (3 x 30 ml), dried over Na2SO4, filtered and evaporated under reduced pressure. The crude product was purified by silica gel column chromatography (eluents: PE, PE/EtOAc, 8/1 – 4/1). Vinyl sulfone **4x** 1.02 g (69 %) was obtained as a light yellow solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.64 (dt, *J* = 8.5, 1.6 Hz, 2H), 7.50 – 7.45 (m, 1H), 7.38 – 7.33 (m, 3H), 7.29 – 7.19 (m, 4H), 6.59 (s, 1H), 5.91 (s, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 151.10, 138.84, 133.51, 129.46, 129.27, 128.99, 128.83, 128.50, 128.41, 126.03.

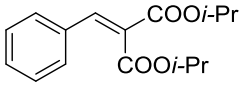
HRMS (ESI) [M+H]+: calculated $C_{14}H_{13}O_2S$, 245.0636, Found 245.0643.

Dimethyl 2-benzylidenemalonate (**4y**) [21]: Compound was obtained following the



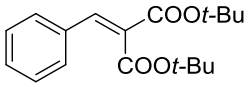
general procedure using benzaldehyde (0.24 mL, 2.40 mmol, 1 equiv) and dimethylmalonate (0.28 mL, 2.40 mmol, 1 equiv). The crude product was purified via collumn chromatography (Eluent PE:EtOAc 10:1 to 4:1). Product was obtained as a colorless oil (405 mg, 77%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (s, 1H), 7.45 – 7.36 (m, 5H), 3.85 (s, 3H), 3.85 (s, 3H).



Diisopropyl 2-benzylidenemalonate (**4z**) [22]: Compound was obtained following the general procedure using benzaldehyde (0.24 mL, 2.40 mmol, 1 equiv) and diisopropylmalonate (0.46 mmol, 2.40 mmol, 1 equiv). Product was purified via collumn chromatography (Eluent PE:EtOAc 10:1 to 4:1). Product was obtained as a colorless oil (482 mg, 73 %).

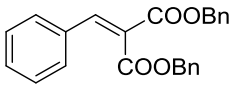
^{1}H NMR (400 MHz, DMSO-d_6) δ 7.66 (s, 1H), 7.55 – 7.50 (m, 2H), 7.48 – 7.43 (m, 3H), 5.15 (hept, *J* = 6.3 Hz, 1H), 5.04 (hept, *J* = 6.2 Hz, 1H), 1.27 – 1.21 (m, 12H).



Di-*tert*-butyl 2-benzylidenemalonate (**4aa**) [23]: Compound was obtained following the general procedure using benzaldehyde (0.24 mL, 2.40 mmol, 1 equiv) and di-*tert*-butylmalonate (0.54 mL, 2.40 mmol, 1 equiv). The crude product was purified via collumn chromatography (Eluent PE:EtOAc 10:1). Product was obtained as a colorless oil (433 mg, 59%).

^{1}H NMR (400 MHz, DMSO-d_6) δ 7.57 – 7.51 (m, 3H), 7.49 – 7.42 (m, 3H), 1.48 (s, 18H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.0, 163.5, 139.8, 133.4, 130.1, 129.4, 129.2, 128.6, 82.3, 82.0, 28.1, 27.9.

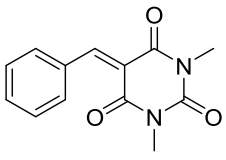


Dibenzyl 2-benzylidenemalonate (**4ab**): Compound was obtained following the general procedure using benzaldehyde (0.24 mL, 2.40 mmol, 1 equiv) and dibenzylmalonate (0.60 mL, 2.40 mmol, 1 equiv). The crude product was purified via collumn chromatography (Eluent PE:EtOAc 10:1). Product was obtained as a white solid (549 mg, 62 %).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (s, 1H), 7.30 – 7.25 (m, 8H), 7.24 – 7.15 (m, 7H), 5.20 (s, 2H), 5.20 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.4, 163.9, 143.2, 135.5, 134.8, 132.7, 130.7, 129.5, 128.9, 128.8, 128.6, 128.6, 128.5, 128.3, 128.1, 125.7, 67.6, 67.2.

Elemental analysis: Calc.: C, 77.40%; H, 5.41%. Found: C, 77.45%; H, 5.41%.

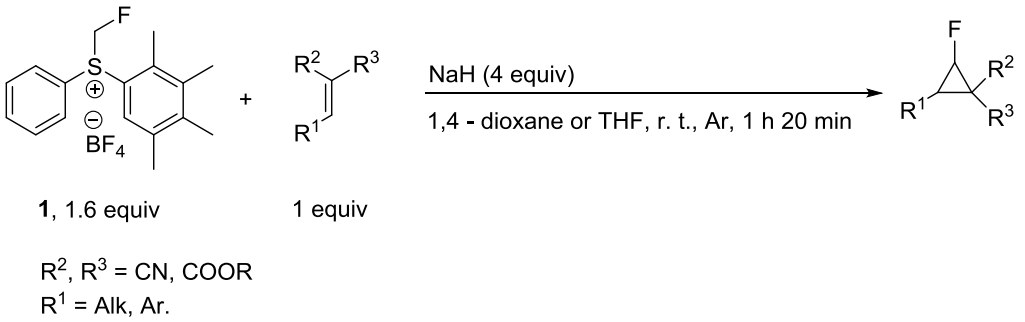


5-benzylidene-1,3-dimethylpyrimidene-2,4,6(1H,3H,5H)-trione (**4ab**): Prepared according to procedure described in literature [24]: To a solution of barbituric acid (469 mg, 3 mmol, 1 equiv) in EtOH (21 mL) was added benzaldehyde (0.4 mL, 3 mmol, 1 equiv) and 10% KOH in H_2O (15 drops). The reaction was left to stir at r.t. for 24 h. Afterwards the formed product was filtered off, washed with H_2O and dried under reduced pressure to give product as a white solid (515 mg, 70%).

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.36 (s, 1H), 8.03 (d, *J* = 6.6 Hz, 2H), 7.59 – 7.51 (m, 1H), 7.50 – 7.45 (m, 2H), 3.24 (s, 3H), 3.18 (s, 3H).

3. FLUOROCYCLOPROPANATION OF DOUBLE ACTIVATED ALKENES

General scheme for preperation of cyclopropanes

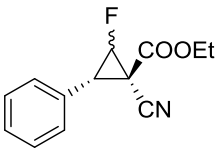


Scheme 1. General method for preperation of cyclopropanes

General procedure for cyclopropanation

Workup method A:

Ethyl-(1*S,3*S**)-1-cyano-2-fluoro-3-phenylcyclopropane-1-carboxylate (5a):**



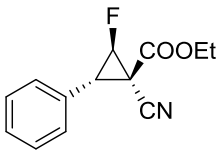
To a solution of alkene **4a** (42 mg, 0.21 mmol, 1 equiv) and sulfonium salt **1** (120 mg, 0.33 mmol, 1.6 equiv) in dry 1,4-dioxane (3 mL) under argon atmosphere was added 60% NaH (in mineral oil, 33 mg, 0.82 mmol, 4 equiv). The reaction mixture was left to stir at rt. After completion (TLC control) the solvent was evaporated under reduced pressure. The crude product was suspended in PE:Et_2O 40:7 (3 x 5 mL) and filtered through a cotton plug. The filtrate was evaporated to dryness. Afterwards an NMR sample was prepared: The crude product was dissolved in $CDCl_3$ (1 mL) and internal standart EtOAc (1 equiv) was added. From the stock solution 0.1 mL was used for the NMR experiment. The rest was evaporated to dryness. Product was dissolved in a minimal amount of Et_2O and purified via preperative TLC (Eluent PE:EtOAc 10:1). The strands containing product were scraped off, suspended in EtOAc (3 x 5 mL) and filtered through a cotton plug. The filtrate was evaporated to dryness. (NMR yield quant., *d.r.* 1:1.24 *cis*/*trans*) Product was obtained in 2 fractions (total yield 48 mg, 99%)

Fraction 1: a mixture of (1*S**,2*R**,3*S**)-**5a** and (1*S**,2*S**,3*S**)-**5a** (33 mg, 68%, *d.r.* 1:2.57) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.35 (m, 5H), 5.35 (dd, *J* = 61.2, 5.2 Hz, 1H)$^{(1S^*,2R^*,3S^*)}$, 5.30 (dd, *J* = 62.3, 6.3 Hz, 1H)$^{(1S^*,2S^*,3S^*)}$, 4.41 – 4.29 (m, 2H), 3.89 (dd, *J* = 21.4, 5.2 Hz, 1H)$^{(1S^*,2R^*,3S^*)}$,3.21 (dd, *J* = 12.0, 6.3 Hz, 1H)$^{(1S^*,2S^*,3S^*)}$, 1.39 (t, *J* = 7.2 Hz, 3H), 1.38 (t, *J* = 7.2 Hz, 3H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -207.73 (dd, *J* = 61.3, 21.3 Hz)$^{(1S^*,2R^*,3S^*)}$, -212.31 (dd, *J* = 62.5, 12.6 Hz)$^{(1S^*,2S^*,3S^*)}$.

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.6 (d, *J* = 1.0 Hz), 161.8 (d, *J* = 1.2 Hz), 130 (d, *J* = 2.3 Hz), 129.2, 129.1, 128.9, 128.3 (d, *J* = 1.7 Hz), 128.3, 113.8 (d, *J* = 2.3 Hz), 112.0 (d, *J* = 4.4 Hz), 77.6 (d, *J* = 247.3 Hz), 63.7, 63.6, 37.7 (d, *J* = 6.7 Hz), 37.3 (d, *J* = 9.4 Hz), 26.8 (d, *J* = 10.0 Hz), 14.1 (d, *J* = 1.8 Hz).



Fraction 2: isolated (1*S**2*R**3*S**)-**5a** (15 mg, 31%) as a colorless oil.

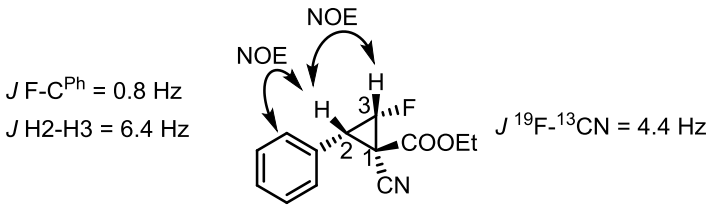
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.32 (m, 3H), 7.32 – 7.22 (m, 2H), 5.34 (dd, *J* = 61.2, 5.3 Hz, 1H), 4.38 (qd, *J* = 7.1, 0.8 Hz, 2H), 3.96 (dd, *J* = 21.4, 5.3 Hz, 1H), 1.39 (t, *J* = 7.1 Hz, 3H).

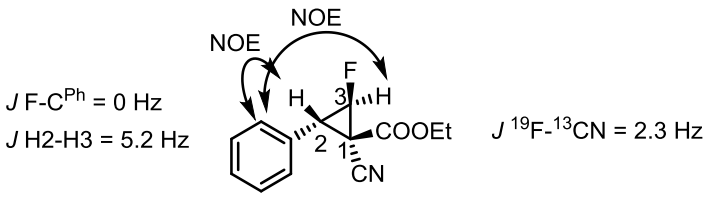
^{19}F NMR (376 MHz, $CDCl_3$) δ -207.7 (dd, *J* = 61.2, 21.5 Hz).

^{13}C NMR (101 MHz, $CDCl_3$) δ 161.8 (d, *J* = 1.1 Hz), 129.8, 129.2, 129.1, 128.3, 113.8 (d, *J* = 2.3 Hz), 78.8 (d, *J* = 254.8 Hz), 63.7, 37.3 (d, *J* = 9.4 Hz), 29.2 (d, *J* = 15.7 Hz), 14.1.

Corresponding fragments observed: **HRMS (ESI)** m/z calcd for $C_{11}H_8NO_2$ $[M\text{-}F\text{-}CH_3CH_2]^+$: 186.0550, found: 186.0549. $C_{15}H_{16}BrO_4$ $[M\text{-}F]^+$: 341.0206, found: 341.0220.

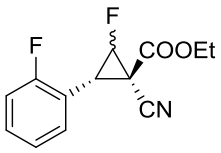
Determination of stereochemistry





Workup method B:

Ethyl-(1*S,3*R**)-1-cyano-2-fluoro-3-(2-fluorophenyl)cyclopropane-1-carboxylate**



(**5b**): Compound obtained following the general procedure using alkene **4b** (45 mg, 0.21 mmol, 1 equiv) and sulfonium salt **1** (120 mg, 0.33 mmol, 1.6 equiv). Product purified via silicagel collumn chromatography using an eluent gradient (PE to PE:EtOAc 4:1). (NMR yield quant, *d.r.* 1:1). Product was obtained as a mixture of (1*S**,2*S**,3*R**)-**5b** and (1*S**,2*R**,3*R**)-**5b** diastereomers (46.1 mg, 89%, *d.r.* 1:1).

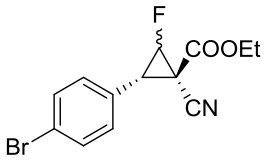
^{1}H NMR (400 MHz, CD_3CN) δ 7.53 – 7.36 (m, 2H), 7.28 – 7.19 (m, 2H), 5.68 (dd, *J* = 60.4, 5.3 Hz, 1H)$^{(1S^*,2R^*,3R^*)}$, 5.48 (dd, *J* = 61.5, 6.4 Hz, 1H)$^{(1S^*,2S^*,3R^*)}$, 4.34 (q, *J* = 7.1 Hz, 2H), 4.30 (q, *J* = 7.1 Hz, 2H), 3.97 (dd, *J* = 21.5, 5.2 Hz, 1H)$^{(1S^*,2R^*,3R^*)}$, 3.34 (dd, *J* = 11.3, 6.2 Hz, 1H)$^{(1S^*,2S^*,3R^*)}$, 1.32 (t, *J* = 7.1 Hz, 3H), 1.32 (t, *J* = 7.1 Hz, 3H).

^{19}F NMR (376 MHz, CD_3CN) δ -115.44 – -115.76 (m), -117.02 – -117.41 (m), -209.86 (dd, *J* = 60.4, 21.4 Hz), -212.47 (ddd, *J* = 62.0, 11.4, 4.0 Hz).

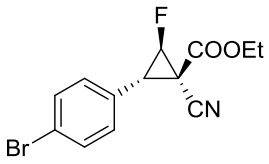
^{13}C NMR (101 MHz, CD_3CN) δ 165.3 (d, *J* = 1.0 Hz), 162.6 (d, *J* = 247.5 Hz), 162.4 (d, *J* = 0.7 Hz), 162.0 (dd, *J* = 247.0, 1.1 Hz), 131.9 (t, *J* = 2.8 Hz), 131.7 (d, *J* = 7.4 Hz), 131.6 (d, *J* = 7.3 Hz), 130.4 (d, *J* = 2.8 Hz), 125.3 (d, *J* = 3.7 Hz), 125.1 (d, *J* = 3.7 Hz), 118.7 (d, *J* = 13.8 Hz), 117.2 (dd, *J* = 14.6, 2.4 Hz), 116.3 (d, *J* = 12.0 Hz), 116.1 (d, *J* = 12.1 Hz), 114.6 (d, *J* = 1.8 Hz), 113.3 (d, *J* = 5.0 Hz), 78.9 (dd, *J* = 250.7, 2.3 Hz), 78.0 (d, *J* = 244.1 Hz), 64.1, 63.9, 32.4 (dd, *J* = 10.8, 3.5 Hz), 32.0 (dd, *J* = 6.7, 2.8 Hz), 28.9 (d, *J* = 16.4 Hz), 27.0 (d, *J* = 11.1 Hz), 13.9, 13.9.

Elemental analysis, %: Calc.: $C_{13}H_{11}F_2NO_2$ (251.08): C 62.15; H 4.41; N 5.58. Found: C 61.09; H 4.62; N 5.72.

Ethyl-(1*S,2*S**)-2-(4-bromophenyl)-1-cyano-3-fluorocyclopropane-1-carboxylate**



(5c): Compound obtained following the general procedure using alkene **4c** (41.7 mg, 0.21 mmol, 1 equiv) and sulfonium salt **1** (120 mg, 0.33 mmol, 1.6 equiv). (NMR yield quant., *d.r.* 1:1). Following workup method A product was obtained in 2 fractions (total yield 39.5 mg, 61%).

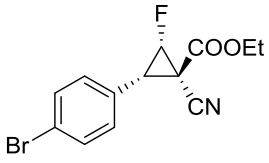


Fraction 1: isolated (1*S**,2*S**,3*R**)-**5c** (19.6 mg, 30%) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.51 (m, 2H), 7.20 – 7.12 (m, 2H), 5.30 (dd, *J* = 61.0, 5.2 Hz, 1H), 4.41 – 4.34 (m, 2H), 3.90 (dd, *J* = 21.0, 5.2 Hz, 1H), 1.39 (t, *J* = 7.2 Hz, 3H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -207.59 (dd, *J* = 60.7, 21.2 Hz).

^{13}C NMR (101 MHz, $CDCl_3$) δ 161.5 (d, *J* = 1.2 Hz), 132.4, 130.0, 128.9, 123.4, 113.6 (d, *J* = 2.2 Hz), 78.51 (d, *J* = 255.5 Hz), 63.8, 36.5 (d, *J* = 9.7 Hz), 29.2 (d, *J* = 15.9 Hz), 14.1. **Elemental analysis, %**: Calc.: $C_{13}H_{11}BrFNO_2$ (311.00): C 50.02; H 3.55; N 4.49. Found: C 50.34; H 3.61; N 4.15.



Fraction 2: isolated (1*S**,2*S**,3*S**)-**5c** (19.9 mg, 31%) as a colorless oil.

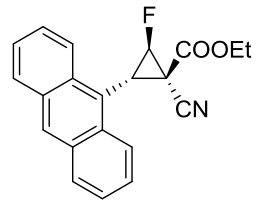
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 – 7.43 (m, 2H), 7.37 – 7.26 (m, 2H), 5.28 (dd, *J* = 62.2, 6.3 Hz, 1H), 4.40 – 4.28 (m, 1H), 3.22 (dd, *J* = 11.7, 6.3 Hz, 1H), 1.38 (t, *J* = 7.2 Hz, 3H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -212.51 (dd, *J* = 62.1, 11.6 Hz).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.3, 132.1, 131.6 (d, *J* = 2.3 Hz), 127.3 (d, *J* = 1.6 Hz), 123.3, 111.8 (d, *J* = 4.6 Hz), 77.4 (d, *J* = 247.7 Hz), 63.8, 36.8 (d, *J* = 6.7 Hz), 26.7 (d, *J* = 10.0 Hz), 14.1.

Following workup method B product was obtained as a mixture of diastereomers (60.7 mg, 94%, *d.r*. 1:1) as a colorless oil.

Ethyl-(1*S,2*S**,3*R**)-2-(anthracene-9-yl)-1-cyano-3-fluorocyclopropane-1-carboxylate (5d):** Compound obtained following the general procedure using alkene **4d** (62.4 mg, 0.21 mmol, 1 equiv) and sulfonium salt **1** (120 mg, 0.33 mmol, 1.6 equiv). (NMR yield 100 %, *d.r*. 1:2.7). Following workup procedure A product was obtained as an isolated (1*S**,2*S**,3*R**)-**5d** (10 mg, 15%) as an unstable yellow oil that decomposed in air.



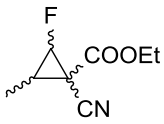
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52 (s, 1H), 8.06 (d, *J* = 8.5 Hz, 3H), 7.66 – 7.59 (m, 2H), 7.56 – 7.50 (m, 3H), 5.48 (dd, *J* = 61.3, 5.4 Hz, 1H), 4.58 – 4.48 (m, 3H), 1.49 (t, *J* = 7.1 Hz, 3H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -206.28 (dd, *J* = 61.2, 20.8 Hz).

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.4 (d, *J* = 1.5 Hz), 131.5, 130.9, 129.7, 127.3, 125.3, 123.2, 120.2, 113.9 (d, *J* = 2.1 Hz), 82.0 (d, *J* = 253.4 Hz), 64.0, 33.7 (d, *J* = 9.7 Hz), 30.0 (d, *J* = 15.6 Hz), 14.2.

Compound unstable under HRMS conditions.

Ethyl-1-cyano-2-fluoro-3-methylcyclopropane-1-carboxylate (**5e**): Compound



obtained following the general procedure using alkene **4e** (29 mg, 0.21 mmol, 1 equiv) and sulfonium salt **1** (120 mg, 0.33 mmol, 1.6 equiv). Following workup procedure A product was obtained as a mixture of 4 possible diastereomers ($6^{(1S^*,2R^*,3S^*)}$:$3^{(1S^*,2S^*,3S^*)}$:1:1) (10 mg, 28%) as a light yellow oil.

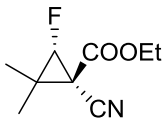
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.01 (dd, *J* = 62.9, 6.1 Hz, 1H)$^{(1S^*,2S^*,3S^*)}$, 4.73 (dd, *J* = 61.7, 4.9 Hz, 1H)$^{(1S^*,2R^*,3S^*)}$, 4.36 – 4.21 (m, 2H), 2.71 (dqd, *J* = 20.8, 6.7, 4.9 Hz, 1H) $^{(1S^*,2R^*,3S^*)}$, 2.25 – 2.09 (m, 1H)$^{(1S^*,2S^*,3S^*)}$, 1.38 – 1.31 (m, 6H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -201.22 (dd, *J* = 61.2, 21.9 Hz), -205.70 (dd, *J* = 61.6, 20.6 Hz), -213.93 (dd, *J* = 61.7, 11.2 Hz), -216.42 (dd, *J* = 62.9, 11.0 Hz).

Because of the difficult mixture **^{13}C NMR** (400 MHz, $CDCl_3$) signals are shown for major diastereomers. δ 162.9, 162.3, 114.7, 81.0 (d, *J* = 253.8 Hz), 77.7 (d, *J* = 269.5 Hz), 63.3, 63.2, 29.2 (d, *J* = 8.1 Hz), 27.9 (d, *J* = 8.0 Hz), 26.5 (d, *J* = 16.2 Hz), 14.1, 14.1, 11.7, 7.3, 7.3.

Elemental analysis, %: Calc.: $C_8H_{10}FNO_2$ (171.07): C 56.14; H 5.89; N 8.18. Found: C 55.59; H 6.02; N 6,60.

Ethyl-1-cyano-3-fluoro-2,2-dimethylcyclopropane-1-carboxylate (**5f**): Compound



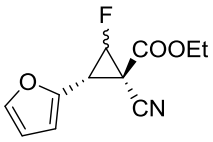
obtained following the general procedure using alkene **4f** (32 mg, 0.21 mmol, 1 equiv) and sulfonium salt **1** (120 mg, 0.33 mmol, 1.6 equiv). (NMR yield 83%, *d.r.* 1:2.5). Following workup method A product was obtained as a mixture of (1*S**,3*S**)-**5f** and (1*S**,3*R**)-**5f** (14.1 mg, 41%, *d.r.* 1:2.5) as a light yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.94 (d, *J* = 62.0 Hz, 1H)$^{(1S^*,3R^*)}$, 4.68 (d, *J* = 61.9 Hz, 1H)$^{(1S^*,3S^*)}$, 4.20 (q, *J* = 7.2 Hz, 2H), 4.19 (q, *J* = 7.1 Hz, 2H), 1.49 (d, *J* = 1.6 Hz, 3H)$^{(1S^*,3R^*)}$, 1.45 (d, *J* = 1.4 Hz, 3H)$^{(1S^*,3S^*)}$, 1.38 (d, *J* = 2.1 Hz, 3H)$^{(1S^*,3S^*)}$, 1.27 (t, *J* = 7.2 Hz, 3H), 1.24 (d, *J* = 2.3 Hz, 3H)$^{(1S^*,3R^*)}$.

^{19}F NMR (376 MHz, $CDCl_3$) δ -210.54 (d, *J* = 62.0 Hz), -212.97 (d, *J* = 61.8 Hz).

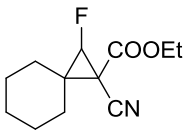
^{13}C NMR (101 MHz, $CDCl_3$) δ 164.3 (d, *J* = 1.7 Hz), 161.9, 115.9, 113.6 (d, *J* = 4.5 Hz), 82.2 (d, *J* = 253.6 Hz), 81.3 (d, *J* = 246.3 Hz), 63.0, 62.6, 37.5 (d, *J* = 8.3 Hz), 33.8 (d, *J* = 7.5 Hz), 29.7, 29.6, 22.5, 17.2, 17.0 (d, *J* = 7.8 Hz), 14.1, 14.1, 12.9 (d, *J* = 7.3 Hz). **Elemental analysis, %**: Calc.: $C_9H_{12}FNO_2$ (185.09): C 58.37; H 6.53; N 7.56. Found: C 55.48; H 5,79; N 6,44.

Ethyl-(1*S,3*R**)-1-cyano-2-fluoro-3-(furan-2-yl)cyclopropane-1-carboxylate** (**5h**):



Compound obtained following the general procedure using alkene **4h** (40 mg, 0.21 mmol, 1 equiv) and sulfonium salt **1** (120 mg, 0.33 mmol, 1.6 equiv). (NMR yield 92%, *d.r.* 1:1). Product decomposes under chromatographic conditions.

Ethyl-1-cyano-2-fluorospiro[2.5]octane-1-carboxylate (**5j**): Compound was



obtained following the general procedure using alkene **4j** (40 mg, 0.21 mmol, 1 equiv) and sulfonium salt **1** (120 mg, 0.33 mmol, 1.6 equiv). (NMR yield 74%, *d.r.* 1:1.5). Following workup procedure A product was obtained as a mixture of (1*S**,2*S**)-**5j**, (1*S**,2*R**)-**5j** and an unidentified -CH_2F group cointaining impurity (68%, *d.r.* 1:1.36). Product and -CH_2F group containing impurity NMR ratio 10:1 (determined from ^{19}F NMR).

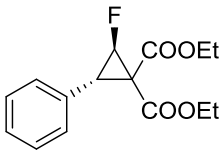
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.00 (d, *J* = 62.1 Hz, 1H), 4.74 (d, *J* = 61.9 Hz, 1H), 4.33 – 4.14 (m, 4H), 2.15 – 1.50 (m, 26H), 1.41 – 1.28 (m, 7H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -213.52 (d, *J* = 62.1 Hz), -215.81 (d, *J* = 61.9 Hz).

^{13}C NMR (101 MHz, $CDCl_3$) δ 164.3 (d, *J* = 2.0 Hz), 162.0, 115.9 (d, *J* = 1.9 Hz), 113.6 (d, *J* = 4.2 Hz), 82.1 (d, *J* = 253.3 Hz), 81.0 (d, *J* = 245.7 Hz), 62.9, 62.5, 44.2 (d, *J* = 7.9 Hz), 40.4 (d, *J* = 7.1 Hz), 32.2, 28.6, 28.3, 27.2 (d, *J* = 6.3 Hz), 26.6, 25.5, 25.4, 24.9, 24.6, 24.6 (d, *J* = 1.0 Hz), 24.2, 22.6 (d, *J* = 5.9 Hz), 14.1, 14.1.

Unstable under HRMS conditions

Diethyl-2-fluoro-3-phenylcyclopropane-1,1-dicarboxylate (**5k**):



Compound was obtained following the general procedure using alkene **4k** (63 mg, 0.21 mmol, 1 equiv) and sulfonium salt **1** (150 mg, 0.41 mmol, 2 equiv). (NMR yield 51%, *d.r.* 1:1.7). Reaction was done in dry MeCN (3 mL). Attempts to purify the product via preperative collumn chromatography (Eluent PE:EtOAc 100:0 to 90:10) yielded the (2*R**,3*S**)

diastereomer (13%, 7.6 mg) as a colorless oil. The obtained product is unstable on silica gel.

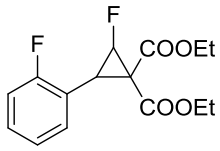
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.20 (m, 5H), 5.56 (dd, *J* = 62.8, 4.7 Hz, 1H), 4.37 (q, *J* = 7.1 Hz, 1H), 4.35 (q, *J* = 7.1 Hz, 1H), 4.30 (q, *J* = 7.1 Hz, 1H), 4.27 (q, *J* = 7.1 Hz, 1H), 3.98 – 3.82 (m, 3H), 1.32 (t, *J* = 7.1 Hz, 3H), 0.92 (t, *J* = 7.1 Hz, 3H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -213.74 (dd, *J* = 63.1, 22.0 Hz).

^{13}C NMR (101 MHz, $CDCl_3$) δ 164.6 (d *J* = 0.7 Hz), 164.5 (d, *J* = 3.4 Hz), 131.6 (d, *J* = 0.8 Hz), 128.6, 128.5, 127.9, 77.2 (d, *J* = 237.0 Hz), 62.4, 61.5, 43.6 (d, *J* = 12.6 Hz), 36.1 (d, *J* = 11.0 Hz), 14.1, 13.7.

Unstable under HRMS conditions

Diethyl-2-fluoro-3-(2-fluorophenyl)cyclopropane-1,1-dicarboxylate (**5l**):



Compound was obtained following the general procedure using alkene **4l** (166 mg, 0.62 mmol, 1 equiv) and sulfonium salt **1** (361 mg, 1.00 mmol, 1.6 equiv). Reaction was done in dry THF (9 mL). (NMR yield 100 %, *d.r*. 1.2:1). Following workup method B (Eluent PE to PE:EtOAc 10:1) product was obtained as a mixture of (2*S**,3*R**)-**5l** and (2*R**,3*R**)-**5l** (170 mg, 91 %, *d.r*. 1:1.27) as a colorless oil.

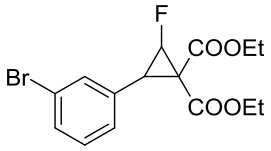
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.21 (m, 1H), 7.41 – 7.12 (m, 1H), 7.10 – 6.98 (m, 2H), 5.56 (dd, *J* = 62.5, 4.6 Hz, 1H), 5.25 (dd, *J* = 63.4, 6.4 Hz, 1H), 4.42 – 4.22 (m, 4H), 4.10 – 3.99 (m, 2H), 3.94 (q, *J* = 7.1 Hz, 2H), 3.85 (dd, *J* = 21.8, 4.9 Hz, 1H), 3.03 (dd, *J* = 11.2, 6.4 Hz, 1H), 1.33 (t, *J* = 7.1 Hz, 3H), 1.31 (t, *J* = 7.1 Hz, 3H), 1.02 (t, *J* = 7.1 Hz, 3H), 0.95 (t, *J* = 7.1 Hz, 3H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -113.43 – -114.00 (m), -115.43 – -115.70 (m), -213.13 (dd, *J* = 62.3, 22.1 Hz), -220.37 (dd, *J* = 63.4, 11.2 Hz).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.8, 164.7, 164.1 (d, *J* = 3.4 Hz), 162.8 (d, *J* = 2.4 Hz), 162.7 (d, *J* = 248.2 Hz), 161.9 (d, *J* = 248.7 Hz), 129.8 – 129.6 (m), 129.3 (d, *J* = 8.3 Hz), 124.0 (d, *J* = 3.8 Hz), 123.7 (d, *J* = 3.6 Hz), 119.3 – 118.9 (m), 115.6 (d, *J* = 21.2 Hz), 114.9 (d, *J* = 21.5 Hz), 76.9 (dd, *J* = 237.5, 2.6 Hz), 76.7 (d, *J* = 240.6 Hz), 62.4, 62.4, 61.6, 61.5, 42.8 (d, *J* = 12.7 Hz), 37.6 (d, *J* = 10.0 Hz), 30.7 (dd, *J* = 12.0, 3.1 Hz), 27.4 (dd, *J* = 6.7, 4.8 Hz), 14.1, 14.0, 13.7, 13.6.

Elemental analysis, %: Calc.: $C_{15}H_{17}FO_4$ (298.10): C 60.40; H 5.41. Found: C 60.51; H 5.50.

Diethyl-2-(3-bromophenyl)-3-fluorocyclopropane-1,1-dicarboxylate (**5m**):



Compound was obtained following the generel procedure using alkene **4m** (68 mg, 0.21 mmol, 1 equiv) and sulfonium salt **1** (120 mg, 0.33 mmol, 1.6 equiv). The reaction was done in dry THF (3 mL). (NMR yield 89%, *d.r*. 1.2:1). Following workup method B (Eluent PE to PE:EtOAc 10:1) product was obtained as a mixture of (2*S**,3*S**)-**5m** and (2*S**,3*R*)-**5m** (49.4 mg, 66%, *d.r*. 1:0.82) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.50 (m, 2H), 7.43 – 7.36 (m, 2H), 7.31 – 7.27 (m, 2H), 7.20 – 7.11 (m, 2H), 5.51 (dd, *J* = 62.5, 4.6 Hz, 1H)$^{(2S^*,3R)}$, 5.12 (dd, *J* = 63.5, 6.5 Hz, 1H)$^{(2S^*,3S^*)}$, 4.41 – 4.18 (m, 2H), 4.08 (q, *J* = 7.1 Hz, 2H), 4.08 (q, *J* = 7.1 Hz, 2H), 3.96 (q, *J* = 7.1 Hz, 2H), 3.82 (dd, *J* = 21.7, 4.7 Hz, 1H)$^{(2S^*,3R)}$, 2.98 (dd, *J* = 11.2, 6.5 Hz, 1H)$^{(2S^*,3S^*)}$, 1.32 (t, *J* = 7.1 Hz, 3H), 1.30 (t, *J* = 7.2 Hz, 3H), 1.08 (t, *J* = 7.1 Hz, 3H), 0.98 (t, *J* = 7.1 Hz, 3H).

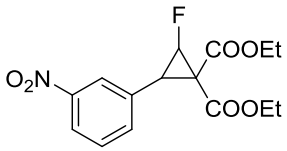
^{19}F NMR (376 MHz, $CDCl_3$) δ -213.52 (dd, *J* = 62.3, 22.0 Hz), -219.72 (dd, *J*= 63.30, 11.36 Hz).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.8, 164.4, 164.1 (d, *J* = 3.2 Hz), 162.8 (d, *J* = 1.6 Hz), 133.9, 133.3 (d, *J* = 1.6 Hz), 133.0 (d, *J* = 3.5 Hz), 131.9, 131.1, 130.7, 130.1, 129.6, 128.6 (d, *J* = 3.5 Hz), 127.2, 122.5, 122.1, 76.9 (d, *J* = 238.0 Hz), 76.5 (d, *J* = 242.1 Hz), 62.6, 62.5, 61.8, 61.7, 43.5 (d, *J* = 12.7 Hz), 38.2 (d, *J* = 9.3 Hz), 35.3 (d, *J* = 11.4 Hz), 32.7 (d, *J* = 6.8 Hz), 14.1, 14.0, 13.8, 13.8.

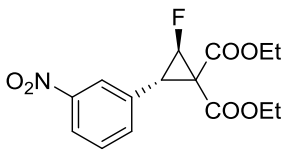
LCMS (ESI) m/z calcd for $C_{15}H_{16}BrO_4$ $[M-F]^+$: 341.0, found: 341.3. $C_{15}H_{17}BrFO_4$ $[M+H]^+$: 361.0, found: 361.4.

Corresponding fragments observed: **HRMS (ESI)** m/z calcd for $C_{13}H_{12}BrO_4$ $[M-F-CH_3CH_2]^+$: 312.9893, found: 312.9906. $C_{15}H_{16}BrO_4$ $[M-F]^+$: 341.0206, found: 341.0220.

Diethyl-2-fluoro-3-(3-nitrophenyl)cyclopropane-1,1-dicarboxylate (**5n**):



Compound was obtained following the general procedure using alkene (**4n**, 61 mg, 0.21 mmol, 1 equiv) and sulfonium salt **1** (120 mg, 0.33 mmol, 1.6 equiv). Reaction was done in dry THF (3 mL). (NMR yield 84%, *d.r*. 1:1.3). Following workup method B product was obtained in 2 fractions (total yield 49.8 mg, 74%).

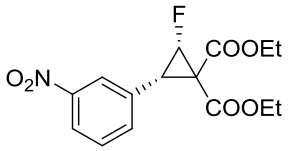


Fraction 1: isolated (2*R**,3*S**)-**5n** (25.9 mg, 38%) as a light yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 – 8.08 (m, 2H), 7.61 – 7.55 (m, 1H), 7.53 – 7.44 (m, 1H), 5.58 (dd, *J* = 62.2, 4.6 Hz, 1H), 4.38 (dq, *J* = 10.8, 7.2 Hz, 1H), 4.30 (dq, *J* = 10.8, 7.2 Hz, 1H), 4.03 – 3.86 (m, 3H), 1.34 (t, *J* = 7.1 Hz, 3H), 1.00 (t, *J* = 7.1 Hz, 3H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -213.21 (dd, *J* = 62.2, 21.6 Hz).

^{13}C NMR (101 MHz, $CDCl_3$) δ 164.4, 164.0 (d, *J* = 3.4 Hz), 148.4, 134.9, 134.0, 129.8, 123.8 (d, *J* = 0.8 Hz), 123.1, 76.9 (d, *J* = 238.9 Hz), 62.9, 62.1, 43.8 (d, *J* = 12.7 Hz), 35.2 (d, *J* = 11.6 Hz), 14.2, 14.0.



Fraction 2: isolated (2*S**,3*S**)-**5n** (23.9 mg, 36%) as a light yellow oil.

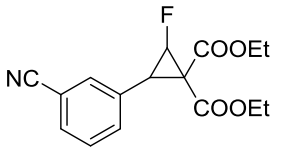
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 – 8.23 (m, 1H), 8.19 – 8.11 (m, 1H), 7.73 – 7.65 (m, 1H), 7.53 – 7.45 (m, 1H), 5.21 (dd, *J* = 63.4, 6.4 Hz, 1H), 4.41 – 4.22 (m, 2H), 4.10 (q, *J* = 7.1 Hz, 2H), 3.08 (dd, *J* = 10.7, 6.5 Hz, 1H), 1.32 (t, *J* = 7.1 Hz, 3H), 1.10 (t, *J* = 7.1 Hz, 3H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -219.41 (dd, *J* = 63.7, 10.5 Hz).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.5, 162.5, 148.0, 136.2 (d, *J* = 2.84 Hz), 133.1, 129.0, 125.3 (d, *J* = 3.4 Hz), 122.6, 76.1 (d, *J* = 225.8 Hz), 62.8, 61.9, 38.3 (d, *J* = 9.7 Hz), 32.3 (d, *J* = 6.6 Hz), 13.9 (d, *J* = 24.9 Hz).

For the mixture of diastereomers: **HRMS (ESI)** m/z calcd for $C_{15}H_{17}NO_6F$ $[M+H]^+$: 326.1040, found: 326.1044.

Diethyl-2-(3-cyanophenyl)-3-fluorocyclopropane-1,1-dicarboxylate (**5o**):



Compound was obtained following the general procedure using alkene **4o** (24 mg, 0.09 mmol, 1 equiv) and sulfonium salt **1** (51 mg, 0.14 mmol, 1.6 equiv). Reaction was done in dry THF (3 mL). (NMR yield 96%, *d.r.* 1:1.3). Following workup method B (Eluent PE to PE:EtOAc 4:1) product was obtained as a mixture of (2*S**,3*R**)-**5o** and (2*S**,3*S**)-**5o** (23.5 mg, 87%, *d.r.* 1:0.87) as a colorless oil.

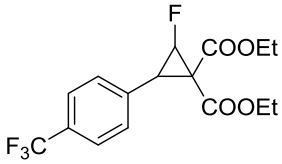
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 – 7.62 (m, 2H), 7.56 – 7.48 (m, 3H), 7.42 – 7.35 (m, 2H), 7.31 – 7.26 (m, 1H), 5.63 (dd, *J* = 62.1, 4.7 Hz, 1H), 5.34 (dd, *J* = 63.3, 6.3 Hz, 1H), 4.42 – 4.26 (m, 4H), 4.13 – 3.93 (m, 5H), 3.15 (dd, *J* = 10.8, 6.3 Hz, 1H), 1.37 – 1.29 (m, 6H), 1.03 (t, *J* = 7.1 Hz, 4H), 0.98 (t, *J* = 7.1 Hz, 3H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -212.75 (dd, *J* = 62.2, 21.1 Hz), -219.46 (dd, *J* = 63.3, 10.9 Hz).

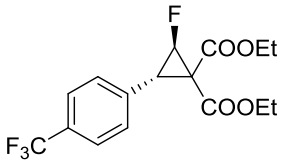
^{13}C NMR (101 MHz, $CDCl_3$) δ 167.4, 164.4, 163.5 (d, *J* = 3.3 Hz), 162.4 (d, *J* = 3.1 Hz), 135.5, 133.2, 132.7, 132.5, 132.4, 129.2, 129.1, 129.0, 128.5, 128.0, 117.7, 116.8, 116.2, 114.1 (d, *J* = 1.0 Hz), 76.7 (d, *J* = 239.4 Hz), 76.4 (d, *J* = 239.4 Hz), 62.7, 62.6, 61.9, 61.7, 43.4 (d, *J* = 12.6 Hz), 38.3 (d, *J* = 10.5 Hz), 34.5 (d, *J* = 12.0 Hz), 31.5 (d, *J* = 6.7 Hz), 14.1, 14.0, 13.8, 13.7.

HRMS (ESI) m/z calcd for $C_{16}H_{16}NO_4FNa$ $[M+H]^+$: 328.0961, found: 328.0976.

Diethyl-2-fluoro-3-(4-(trifluoromethyl)phenyl)cyclopropane-1,1-dicarboxylate



(**5p**): Compound was obtained following the general procedure using alkene **4p** (65.5 mg, 0.21 mmol, 1 equiv) and sulfonium salt **1** (120 mg, 0.33 mmol, 1 equiv). Reaction was done in dry THF (3 mL). (NMR yield quant., *d.r.* 1:1.3). Following workup method A (Eluent PE to PE:EtOAc 1:1) product was obtained in 2 fractions (total yield 41.76 mg, 58%):



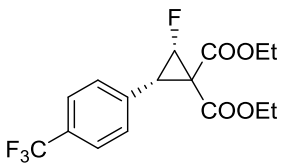
Fraction 1: isolated (2*R**,3*S**)-**5p** (23.5 mg, 32%) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.53 (m, 2H), 7.38 – 7.32 (m, 2H), 5.56 (dd, *J* = 62.4, 4.7 Hz, 1H), 4.33 (dq, *J* = 41.8, 7.1 Hz, 1H), 4.33 (dq, *J* = 20.2, 7.1 Hz, 1H), 4.01 – 3.84 (m, 3H), 1.33 (t, *J* = 7.1 Hz, 3H), 0.94 (t, *J* = 7.1 Hz, 3H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -62.75, -213.46 (dd, *J* = 62.7, 21.5 Hz).

^{13}C NMR (101 MHz, $CDCl_3$) δ 164.3, 164.0 (d, *J* = 3.4 Hz), 135.7, 130.2 (q, *J* = 32.6 Hz), 129.0, 125.5 (q, *J* = 3.8 Hz), 123.9 (q, *J* = 272.1 Hz), 76.8 (d, *J* = 238.2 Hz), 62.6, 61.8, 43.7 (d, *J* = 12.6 Hz), 35.5 (d, *J* = 11.5 Hz), 14.1, 13.7.

Compound unstable under HRMS conditions



Fraction 2: isolated (2*S**,3*S**)-**5p** (18.28 mg, 26%) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 – 7.52 (m, 2H), 7.50 – 7.43 (m, 2H), 5.17 (dd, *J* = 63.5, 6.4 Hz, 1H), 4.27 (q, *J* = 7.2 Hz, 1H), 4.26 (q, *J* = 7.1 Hz, 1H), 4.07 (q, *J* = 7.1 Hz, 2H), 3.05 (dd, *J* = 11.0, 6.4 Hz, 1H), 1.31 (t, *J* = 7.1 Hz, 3H), 1.05 (t, *J* = 7.1 Hz, 3H).

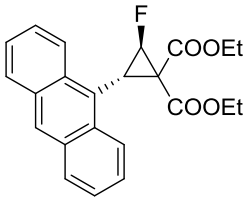
^{19}F NMR (376 MHz, $CDCl_3$) δ -62.71, -219.75 (dd, *J* = 63.6, 11.5 Hz).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.8, 162.7 (d, *J* = 1.9 Hz), 135.4, 130.3 (d, *J* = 3.6 Hz), 129.8 (q, *J* = 32.7 Hz), 125.0 (q, *J* = 3.7 Hz), 124.0 (q, *J* = 272.0 Hz), 76.6 (d, *J* = 241.9 Hz), 62.6, 61.7, 38.3 (d, *J* = 9.4 Hz), 32.8 (d, *J* = 6.8 Hz), 14.0, 13.7.

Following workup method B compound was obtained as a mixture of diastereomers (62.4 mg, 87%, d.r. 1:1.2) as a colorless oil.

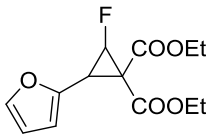
For the mixture of diastereomers: **HRMS (ESI)** m/z calcd for $C_{16}H_{17}O_4F_4$ $[M+H]^+$: 349.1063, found: 349.1054.

Diethyl-(2*S,3*R**)-2-(anthracene-9-yl)-3-fluorocyclopropane-1,1-dicarboxylate**



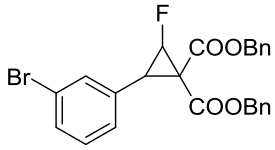
(**5r**): Compound was obtained following the general procedure using alkene **4r** (72 mg, 0.21 mmol, 1 equiv) and sulfonium salt **1** (120 mg, 0.33 mmol, 1.6 equiv) in dry THF (3 mL). (NMR yield 45 %, *d.r.* >1:20). Compound decomposes under chromatographic conditions.

Diethyl-2-fluoro-3-(furan-2-yl)cyclopropane-1,1-dicarboxylate (**5s**): Compound

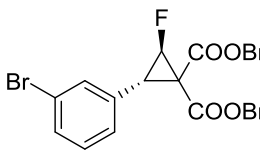


was obtained following the general procedure using alkene **4s** (49 mg, 0.21 mmol, 1 equiv) and sulfonium salt **1** (120 mg, 0.33 mmol, 1.6 equiv) in dry THF (3 mL). (NMR yield 51 %, *d.r.* 1:2.2). Compound decomposes under chromatographic conditions.

Dibenzyl-2-(3-bromophenyl)-3-fluorocyclopropane-1,1-dicarboxylate (**5t**):



Compound was obtained following the general procedure using alkene **4t** (93 mg, 0.21 mmol, 1 equiv) and sulfonium salt **1** (120 mg, 0.33 mmol, 1.6 equiv). Reaction was done in dry THF (3 mL). (NMR yield 37%, *d.r.* 1:3). Following workup method A product was obtained in 2 fractions (total yield 18 mg, 19%).



Fraction 1: isolated (2*S**,3*R**)-**5t** (14 mg, 14%) as a colorless oil.

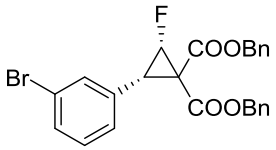
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.35 (m, 2H), 7.34 – 7.29 (m, 5H), 7.29 – 7.21 (m, 3H), 7.11 – 7.05 (m, 2H), 7.00 –

6.96 (m, 2H), 5.55 (dd, *J* = 62.4, 4.7 Hz, 1H), 5.32 (d, *J* = 12.3 Hz, 1H), 5.21 (d, *J* = 12.3 Hz, 1H), 4.90 (d, *J* = 12.1 Hz, 1H), 4.82 (d, *J* = 12.1 Hz, 1H), 3.88 (dd, *J* = 21.7, 4.7 Hz, 1H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -212.91 (dd, *J* = 62.3, 22.0 Hz).

^{13}C NMR (101 MHz, $CDCl_3$) δ 164.2, 164.0 (d, *J* = 3.2 Hz), 135.1, 134.6, 133.6, 131.8, 131.3, 130.2, 128.6, 128.6, 128.4, 128.4, 128.2, 127.1, 122.6, 77.1 (d, *J* = 238.9 Hz), 68.2, 67.7, 43.5 (d, *J* = 12.7 Hz), 35.8 (d, *J* = 11.3 Hz).

Compound unstable under HRMS conditions.



Fraction 2: enriched (2*S**,3*S**)-**5t** fraction (4 mg, 4%) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.25 (m, 5H), 7.24 – 7.14 (m, 7H), 7.06 – 6.95 (m, 3H), 5.15 – 5.07 (m, 1H), 5.08 (dd, *J* = 63.3, 6.5 Hz, 1H), 4.94 (d, *J* = 12.2 Hz, 1H), 4.89 (d, *J* = 12.2 Hz, 1H), 2.95 (dd, *J* = 11.0, 6.5 Hz, 2H).

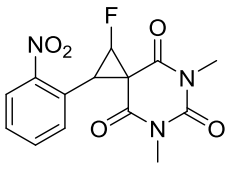
^{19}F NMR (376 MHz, $CDCl_3$) δ -219.34 (dd, *J* = 63.2, 11.1 Hz).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.5, 162.6 (d, *J* = 1.6 Hz), 134.8, 134.7, 133.0 (d, *J* = 1.5 Hz), 133.0, 133.0, 130.9, 129.7, 128.7, 128.6, 128.5, 128.4, 128.3, 128.1, 122.2, 76.7 (d, *J* = 243.1 Hz), 68.1, 67.6, 38.2 (d, *J* = 9.4 Hz), 33.1 (d, *J* = 6.8 Hz).

Compound unstable under HRMS conditions.

Following workup method B compound was obtained as a mixture of (2*S**,3*S**)-**5t** abd (2*S**,3*R**)-**5t** (31 mg, 31%, *d*.r. 1:2.6) as a colorless oil.

1-Fluoro-5,7-dimethyl-2-(2-nitrophenyl)-5,7-diazaspiro[2.5]-octane-4,6,8-trione



(**5u**): Compound was obtained following the general procedure using arylidene **4u** (60 mg, 0.207 mmol, 1 equiv) and sulfonium salt **1** (120 mg, 0.33 mmol, 1.6 equiv). NMR yield (49 %, *d.r.* 1:1.72). Product was purified via preperative TLC Eluent (PE:MTBE:Acetone 3:3:1). Product was obtained as a mixture of diastereomers (6.8 mg, 10 %, *d.r.* 1:1) as a light yellow solid.

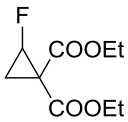
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 – 7.95 (m, 1H), 7.81 – 7.62 (m, 2H), 7.62 – 7.50 (m, 1H), 5.60 (dd, *J* = 62.3, 6.0 Hz, 1H), 5.56 (dd, *J* = 62.5, 6.1 Hz, 1H), 4.59 (dd, *J* = 20.1, 6.0 Hz, 1H), 3.88 (dd, *J* = 11.7, 6.1 Hz, 1H), 3.46 (s, 3H), 3.41 (s, 3H), 3.17 (s, 3H), 3.14 (s, 3H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -206.12 (dd, *J* = 62.4, 20.3), -214.86 (dd, *J* = 62.6, 11.6 Hz).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.3 (d, *J* = 0.72 Hz), 164.2 (d, *J* = 2.1 Hz), 163.0, 161.3, 151.3 (d, *J* = 5.1 Hz), 148.7 (d, *J* = 28.4 Hz), 134.0, 133.8, 132.4 (d, *J* = 3.8 Hz), 131.9, 129.8, 129.5, 126.8 (d, *J* = 1.4 Hz), 125.6, 125.4, 125.3, 84.1 (d, *J* = 256.8 Hz), 82.5 (d, *J* = 257.0 Hz), 42.6 (d, *J* = 8.7 Hz), 40.0 (d, *J* = 12.2 Hz), 38.6 (d, *J* = 3.6 Hz), 36.9 (d, *J* = 9.1 Hz), 29.2, 29.1, 28.6, 28.5.

Unstable under HRMS conditions.

Diethyl 2-fluorocyclopropane-1,1-dicarboxylate (**5v**) [25]:



To a cooled in an ice bath solution of diethyl methylydenemalonate **4v** (22.2 mg, 0.129 mmol, 1.0 equiv) in dry THF (12 mL) under Ar atmosphere was added sulfonium salt **1** (93 mg, 0.258 mmol, 2.0 equiv) followed by NaH (60% in paraffin oil, 20 mg, 0.52 mmol, 4.0 equiv). The reaction mixture was stirred for 15 min (TLC control) at 0 ^{o}C (Reaction is very sensitive to temperature). The reaction mixture was evaporated under reduced pressure (Do note immerse flask into the heating bath, volatile product!!!). The crude residue was suspended in Et_2O and the solution was filtered through a cotton plug. The filtrate was evaporated. The crude product was purified by silica gel column chromatography (Pasteur pipette used as a column), eluent PE, then 4:1 PE:Et_2O. Solvent evaporated under reduced pressure (Do note immerse flask into the heating bath, volatile product!!!) to give the desired product **5v** (9.3 mg, 35%) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.06 (ddd, *J* = 64.4, 6.1, 4.2 Hz, 1H), 4.37 – 4.09 (m, 4H), 2.21 – 2.09 (m, 1H), 1.63 – 1.53 (m, 1H), 1.30 (t, *J* = 7.1 Hz, 3H), 1.27 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.04, 164.73 (d, *J* = 3.3 Hz), 75.03 (d, *J* = 234.6 Hz), 62.23, 62.02, 34.57 (d, *J* = 12.3 Hz), 20.05 (d, *J* = 9.1 Hz), 14.21, 14.15.

^{19}F NMR (376 MHz, Chloroform-*d*) δ -212.50 (ddd, *J* = 64.3, 22.2, 14.2 Hz).

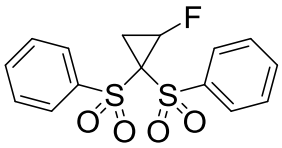
Synthesis of fluorocyclopropylsulfones 5w and 5x

General procedure:

To a solution of vinylsulfone **4** (0.20 mmol, 1 equiv) in dry THF (2 ml) under Ar atmosphere was added *S*-fluoromethylphenyl-2,3,4,5-tetramethylphenylsulfonium tetrafluoroborate (**1**) (146 mg, 0.40 mmol, 2 equiv). The obtained mixture was stirred

for 5 min, till sulfonium salt evenly suspended, then NaH (60% in silicon oil) (32.2 mg, 0.81 mmol, 4 equiv) was added. The reaction mixture was stirred at RT till completion (typically 2~3h) (TLC control). The reaction mixture was filtered through a cotton plug and the resulting precipitate on the plug was washed with THF (3×2 ml). The filtrate was evaporated under reduced pressure. The crude product was purified by prep. TLC (eluents: PE, PE/EtOAc, 8/1 – 3/1).

(2-Fluorocyclopropane-1,1-disulfonyl)dibenzene (**5w**):



Prepared following the general procedure from ethene-1,1-diyldisulfonyl)dibenzene (62.1 mg, 0.201 mmol, 1 equiv). The fluorocyclopropane **5w** 56.6 mg (83 %) was obtained as a colorless oil.

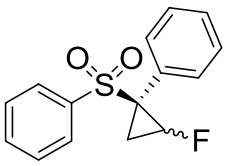
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.06 (dt, *J* = 8.7, 1.5 Hz, 2H), 8.00 – 7.95 (m, 2H), 7.74 – 7.65 (m, 2H), 7.61 – 7.52 (m, 4H), 5.50 (ddd, *J* = 64.2, 6.9, 4.8 Hz, 1H), 2.90 (ddd, *J* = 20.3, 8.8, 4.8 Hz, 1H), 2.07 (ddd, *J* = 12.6, 8.8, 6.9 Hz, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 138.8, 137.7, 134.9, 134.6, 130.1, 129.9, 129.8, 129.1, 128.8, 73.6 (d, *J* = 247.9 Hz), 61.2 (d, *J* = 10.9 Hz), 20.2 (d, *J* = 9.9 Hz).

^{19}F NMR (376 MHz, Chloroform-*d*) δ -213.25 (ddd, *J* = 64.2, 20.3, 12.6 Hz).

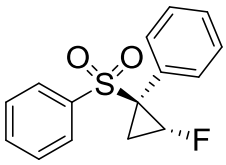
Elemental analysis, %: calculated $C_{15}H_{13}FO_4S_2$: C, 52.93; H, 3.85; S, 18.84. Found: C, 50.21; H, 3.85; S, 17.53.

2-Fluoro-1-(phenylsulfonyl)cyclopropyl)benzene (5x):



Prepared following the general procedure from (1-(phenylsulfonyl)vinyl)benzene (**4x**) (48.6 mg, 0.199 mmol, 1 equiv). (NMR yield 69%, *d.r.* 1:1.8) The product was obtained as mixture of two diastereomers (overall yield 55.4 mg, 68 %) as a colorless oils.

***trans*-2-Fluoro-1-(phenylsulfonyl)cyclopropyl)benzene (*trans*-5x):** (24.2 mg, 44%)



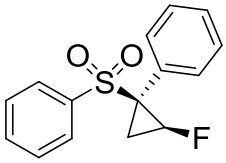
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.60 (tt, *J* = 7.4, 1.5 Hz, 1H), 7.48 – 7.38 (m, 4H), 7.35 – 7.30 (m, 1H), 7.23 (td, *J* = 6.9, 1.6 Hz, 2H), 7.12 – 7.07 (m, 2H), 5.45 (ddd, *J* = 64.2, 6.9, 3.6 Hz, 1H), 2.28 – 2.20 (m, 1H), 1.76 (ddd, *J* = 19.8, 7.7, 3.6 Hz, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 137.07, 133.99, 132.96, 129.44, 129.22, 128.86, 128.82, 128.37, 72.67 (d, *J* = 237.5 Hz), 50.44 (d, *J* = 10.3 Hz), 19.34 (d, *J* = 9.3 Hz).

^{19}F NMR (376 MHz, Chloroform-*d*) δ -209.98 (ddd, *J* = 64.2, 19.8, 11.8 Hz).

Elemental analysis, %: calculated $C_{15}H_{13}FO_2S$: C, 65.20; H, 4.74; S, 11.60. Found: C, 64.30; H, 4.94; S, 11.64.

***cis*-2-Fluoro-1-(phenylsulfonyl)cyclopropyl)benzene (*cis*-5x):** (13.2 mg, 24%)

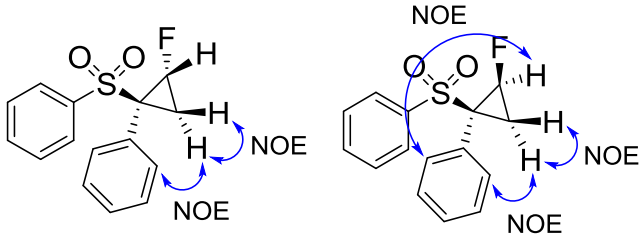


^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.62 – 7.56 (m, 3H), 7.45 – 7.39 (m, 2H), 7.31 – 7.26 (m, 1H), 7.24 – 7.18 (m, 2H), 7.08 (dt, *J* = 8.4, 1.8 Hz, 2H), 4.85 (ddd, *J* = 64.5, 6.3, 4.1 Hz, 1H), 2.86 – 2.76 (m, 1H), 1.69 (ddd, *J* = 10.3, 7.8, 6.3 Hz, 1H).

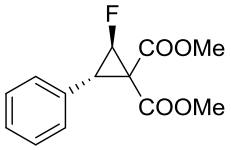
^{13}C NMR (101 MHz, Chloroform-*d*) δ 138.16, 133.75, 132.84 (d, *J* = 1.0 Hz), 131.73 (d, *J* = 1.8 Hz), 129.34, 129.22 (d, *J* = 2.0 Hz), 128.73, 128.64, 75.92 (d, *J* = 239.7 Hz), 51.32 (d, *J* = 11.0 Hz), 18.51 (d, *J* = 11.5 Hz).

^{19}F NMR (376 MHz, Chloroform-*d*) δ -214.77 (ddd, *J* = 64.5, 21.7, 10.3 Hz).

Elemental analysis, %: calculated $C_{15}H_{13}FO_2S$: C, 65.20; H, 4.74; S, 11.60. Found: C, 65.00; H, 5.15; S, 11.33.



Dimethyl-2-fluoro-3-phenylcyclopropane-1,1-dicarboxylate (**5y**): Compound was obtained following the general procedure using alkene **4y** (46 mg, 0.21 mmol, 1 equiv) and sulfonium salt **1** (120 mg, 0.33 mmol, 1.6 equiv). (NMR yield 19%, *d.r.* 1:1.8). Reaction was done in dry MeCN (3 mL). Attempts to purify the product via preperative collumn chromatography (Eluent PE:EtOAc 100:0 to 90:10) yielded the (2*R**,3*S**) diastereomer (12%, 6 mg) as a colorless oil. The obtained product is unstable on silica gel.



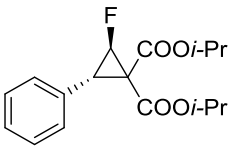
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.24 (m, 3H), 7.23 – 7.18 (m, 2H), 5.56 (dd, *J* = 62.6, 4.7 Hz, 1H), 3.89 (dd, *J* = 22.7, 4.9 Hz, 1H overlap with ester group) 3.86 (s, 3H), 3.44 (s, 3H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -213.13 (dd, *J* = 62.5, 22.3 Hz).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.1 (d, *J* = 0.9 Hz), 164.9 (d, *J* = 3.2 Hz), 131.5 (d, *J* = 0.8 Hz), 128.6, 128.4, 128.0, 77.3 (d, *J* = 237.8 Hz), 53.3, 52.5, 43.3 (d, *J* = 12.7 Hz), 36.4 (d, *J* = 11.0 Hz).

Unstable under HRMS conditions.

Diisopropyl-(2*R,3*S**)-2-fluoro-3-phenylcyclopropane-1,1-dicarboxylate** (**5z**):



Compound was obtained following the general procedure using alkene **4v** (57 mg, 0.21 mmol, 1 equiv) and sulfonium salt **1** (120 mg, 0.41 mmol, 1.6 equiv). Reaction was done in dry MeCN (3 mL). (NMR yield 91%, *d.r*. 1:2). Following workup method A product was obtained as colorless oil (15.5 mg, 24%).

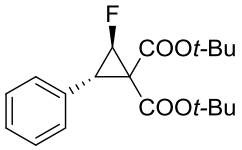
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 – 7.16 (m, 5H), 5.52 (dd, *J* = 62.8, 4.6 Hz, 1H), 5.16 (hept, *J* = 6.3 Hz, 1H), 4.75 (hept, *J* = 6.3 Hz, 1H), 3.82 (dd, *J* = 21.9, 4.9 Hz, 1H), 1.29 (d, *J* = 6.2 Hz, 3H), 1.27 (d, *J* = 1.28, 3H), 0.99 (d, *J* = 6.3 Hz, 3H), 0.84 (d, *J* = 6.2 Hz, 3H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -214.80 (dd, *J* = 60.9, 22,4 Hz).

^{13}C NMR (101 MHz, $CDCl_3$) δ 164.2 (d, *J* = 0.7 Hz), 164.0 (d, *J* = 3.4 Hz), 131.6 (d, *J* = 0.8 Hz), 128.6 (d, *J* = 0.7 Hz), 128.5, 127.8, 77.1 (d, *J* = 236.6 Hz), 70.1, 69.2, 43.9 (d, *J* = 12.6 Hz), 35.8 (d, *J* = 11.2 Hz), 21.8, 21.6, 21.3, 21.2.

Unstable under HRMS conditions.

Di-*tert*-butyl-(2*S,3*R**)-2-fluoro-3-phenylcyclopropane-1,1-dicarboxylate** (**5aa**):



Compound was obtained following the general procedure using alkene **4aa** (63 mg, 0.21 mmol, 1 equiv) and sulfonium salt **1** (150 mg, 0.41 mmol, 2 equiv). (NMR yield 23%, *d.r*. 1:5). Reaction was done in dry MeCN (3 mL). Attempts to purify the product via preperative collumn chromatography (Eluent PE:EtOAc 100:0 to 90:10) yielded the (2*S**,3*R**) diastereomer (12%, 8 mg) as a colorless oil. The obtained product is unstable on silica gel.

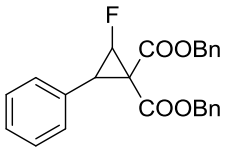
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.20 (m, 5H), 5.45 (dd, *J* = 63.0, 4.5 Hz, 1H), 3.72 (dd, *J* = 22.4, 4.5 Hz, 1H), 1.52 (s, 9H), 1.16 (s, 9H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -215.66 (dd, *J* = 63.2, 22.1 Hz).

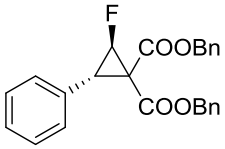
^{13}C NMR (101 MHz, $CDCl_3$) δ 163.8, 163.6 (d, *J* = 3.8 Hz), 131.9, 128.7, 128.3, 127.6, 82.7, 82.0, 77.0 (d, *J* = 235.4 Hz), 45.4 (d, *J* = 12.6 Hz), 35.3 (d, *J* = 11.3 Hz), 28.0, 27.6.

Unstable under HRMS conditions.

Dibenzyl-2-fluoro-3-phenylcyclopropane-1,1-dicarboxylate (**5ab**): Compound was



obtained following the general procedure using alkene **5ab** (77 mg, 0.21 mmol, 1 equiv) and sulfonium salt **2** (150 mg, 0.41 mmol, 2 equiv). Reaction was done in dry THF (3 mL). Product was purified using eluent (PE to PE:EtOAc 1:1). Following workup method A product was obtained in 2 fractions. (total yield 15.9 mg, 19%):



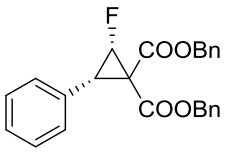
Fraction 1: isolated (2*R**,3*S**)-**5ab** (12.6 mg, 15%) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (s, 5H), 7.22 – 7.08 (m, 8H), 6.90 – 6.86 (m, 2H), 5.52 (dd, *J* = 62.6, 4.8 Hz, 1H), 5.26 (d, *J* = 12.3 Hz, 1H), 5.15 (d, *J* = 12.3 Hz, 1H), 4.80 (d, *J* = 12.1 Hz, 1H), 4.72 (d, *J* = 12.2 Hz, 1H), 3.87 (dd, *J* = 22.3, 4.8 Hz, 1H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -213.11 (dd, *J* = 62.4, 22.3 Hz).

^{13}C NMR (101 MHz, $CDCl_3$) δ 164.5 (d, *J* = 0.72 Hz), 164.3 (d, *J* = 3.1 Hz), 135.2, 134.8, 131.3 (d, *J* = 0.8 Hz), 128.6, 128.6, 128.5, 128.4, 128.4, 128.3, 128.3, 128.1, 128.0, 77.5 (d, *J* = 238.2 Hz), 68.1, 67.4, 43.5 (d, *J* = 12.8 Hz), 36.6 (d, *J* = 11.0 Hz).

Elemental analysis, %: Calc.: $C_{25}H_{21}FO_4$ (404.14): C 74.25; H 5.23. Found: C 73.84; H 5.62.



Fraction 2: isolated (2*S**,3*S**)-**5ab** (3.3 mg, 4%) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.11 (m, 13H), 6.99 – 6.92 (m, 2H), 5.18 – 5.06 (m, 2H), 5.10 (dd, *J* = 63.4, 6.6 Hz, 1H), 4.93 (d, *J* = 12.2 Hz, 1H), 4.87 (d, *J* = 12.2 Hz, 1H).

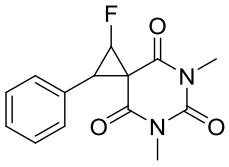
^{19}F NMR (376 MHz, $CDCl_3$) δ -219.65 (dd, *J* = 63.2, 11.8 Hz).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.8, 162.9 (d, *J* = 1.5 Hz), 134.9 (d, *J* = 5.4 Hz), 130.8 (d, *J* = 1.5 Hz), 129.9 (d, *J* = 3.3 Hz), 128.6, 128.5, 128.4, 128.3, 128.2, 128.0, 127.7, 77.0 (d, *J* = 243.0 Hz), 67.9, 67.4, 38.1 (d, *J* = 9.4 Hz), 34.0 (d, *J* = 6.7 Hz).

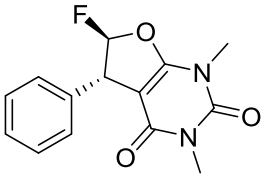
Elemental analysis, %: Calc.: $C_{25}H_{21}FO_4$ (404.14): C 74.25; H 5.23. Found: C 73.78; H 5.36.

Following workup method B product was obtained as a mixture of (2*R**,3*S**)-**5ab** and (2*S**,3*S**)-**5ab** (44,3 mg, 53%, *d.r.* 1:2.8) as a colorless oil.

1-Fluoro-5,7-dimethyl-2-phenyl-5,7-diazaspiro[2.5]octane-4,6,8-trione (**5ac**):



Product was obtained following the general procedure using arylidene barbiturate **4ac** (51 mg, 0.21 mmol, 1 equiv) and sulfonium salt **1** (120 mg, 0.33 mmol, 1 equiv). Reaction was done in dry THF (3 mL). (NMR yield 78%, *d.r.* 1:1). Product unstable under chromatographic conditions. As a rearrangement product was isolated **6-fluoro-1,3-dimethyl-5-phenyl-5,6-dihydrofuro[2,3-d]pyrimidine-2,4(1H,3H)-dione** (**6ac**):

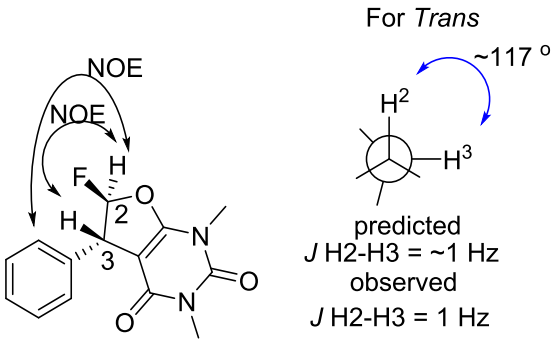


Prep. TLC (silicagel pretreated with 2% Et_3N in PE) (eluent PE:EtOAc). **6ac** (6.4 mg, 11%) as a colorless amorphous solid: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.39 – 7.29 (m, 3H), 7.21 – 7.15 (m, 2H), 6.16 (dd, *J* = 60.3, 1.0 Hz, 1H), 4.58 (d, *J* = 27.7 Hz, 1H), 3.48 (s, 3H), 3.32 (s, 3H).

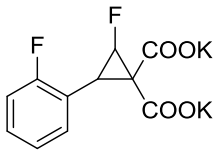
^{13}C NMR (101 MHz, $CDCl_3$) δ 160.6, 159.5, 151.6, 136.0 (d, *J* = 12.6 Hz), 129.4, 128.5, 127.3, 118.6 (d, *J* = 249.7 Hz), 89.1, 52.6 (d, *J* = 23.3 Hz), 30.1, 28.3.

^{19}F NMR (376 MHz, $CDCl_3$) δ -110.86 (dd, *J* = 60.2, 28.0 Hz).

HRMS (ESI) m/z calcd for $C_{14}H_{14}FN_2O_3$ $[M+H]^+$: 277.0988, found: 277.0996.



Potassium 2-fluoro-3-(2-fluorophenyl)cyclopropane-1,1-dicarboxylate (**7l**):



Product was obtained following the method described in literature [26]. Cyclopropane (**5l**) (40.1 mg, 0.13 mmol, 1 equiv, *d.r.* 1:1) was dissolved in MeOH (1 mL). To the solution was added KOH (18.5 mg, 0.34 mmol, 2.5 equiv) and the reaction mixture was left to stir at rt for 5

hours. Afterwards the reaction mixture was concentrated under reduced pressure. The crude was washed with MeCN (0.5 mL) 3 times and then with PE (0.5 mL) 3 times. Product was obtained as an off-white solid (37.3 mg, 87 %, *d.r*. 1:1.1).

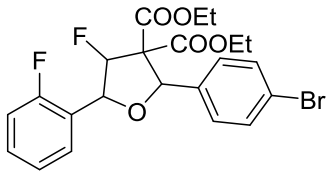
^{1}H NMR (400 MHz, D_2O) δ 7.36 – 7.03 (m, 4H), 5.39 (dd, *J* = 65.1, 3.9 Hz, 1H), 5.03 (dd, *J* = 66.8, 6.4 Hz, 1H), 3.39 (dd, *J* = 22.6, 4.0 Hz, 1H), 2.93 (dd, *J* = 10.8, 6.4 Hz, 1H).

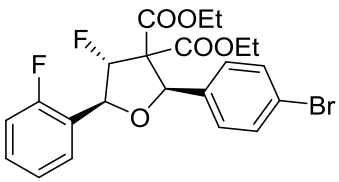
^{19}F NMR (376 MHz, D_2O) δ -116.15 – -118.46 (m), -211.55 (dd, *J* = 65.0, 22.6 Hz), -221.80 (dd, *J* = 66.7, 10.8 Hz).

^{13}C NMR (101 MHz, D_2O) δ 176.0, 172.1, 162.1 (d, *J* = 244.0 Hz), 161.7 (d, *J* = 243.7 Hz), 129.4 (dd, *J* = 7.6, 3.0 Hz), 129.1 (d, *J* = 3.6 Hz), 128.7 (d, *J* = 8.3 Hz), 128.1 (d, *J* = 8.4 Hz), 124.1 (d, *J* = 3.5 Hz), 123.6 (d, *J* = 3.2 Hz), 121.8 (d, *J* = 14.6 Hz), 121.7 (d, *J* = 13.4 Hz), 115.1 (d, *J* = 41.1 Hz), 115.0 (d, *J* = 41.9 Hz), 78.1 (d, *J* = 227.8 Hz), 79.3 – 75.6 (m), 49.1 (d, *J* = 11.5 Hz), 43.3 (d, *J* = 7.4 Hz), 28.7 (dd, *J* = 11.6, 3.4 Hz), 24.4 – 23.9 (m), 24.1 (t, 7.35 Hz).

HRMS (ESI) m/z calcd for $C_{11}H_7F_2O_4^-$ [M^-]: 241.0318, found: 241.0310.

Diethyl 2-(4-bromophenyl)-4-fluoro-5-(2-fluorophenyl)dihydrofuran-3,3(2H)-dicarboxylate (**8l**): Cyclopropane (**5l**) (27.7 mg, 0.093 mmol, 1 equiv, d.r. 1:1) was flushed with argon and dissolved in dry DCM (1.5 mL) under argon atmosphere. To the solution was added 4-bromobenzaldehyde (17.2 mg, 0.093 mmol, 1 equiv) and $Sc(OTf)_3$ (46 mg, 0.093 mmol, 1 equiv). The mixture was left to stir at rt until completion. After completion (TLC control, ~ 3 h) to the reaction mixture was added water (2 mL). The phases were seperated and the aqueous phase was extracted with DCM. The combined organic phase was washed with brine, dried over anh. Na_2SO_4, filtered and concentrated under reduced pressure. The crude material was dissolved in $CDCl_3$ (1 mL). Internal standart (EtOAc 1 equiv) was added and 0.1 mL of the bulk solution was used for NMR experiment. (NMR yield ~60 %, d.r. 1:1). The product was purified via collumn chromatography (Eluent PE:EtOAc 20:1 to 10:1). The 2 fractions obtained contained aldehyde and defluorinated side product. Additional purification by preperative TLC (Eluent PE:EtOAc 100:0 to 80:20) yielded 3 fractions:





Fraction 1: isolated (2*R**,4*R**,5*S**)-(**8l**) as a colorless oil (6.7 mg, 15 %).

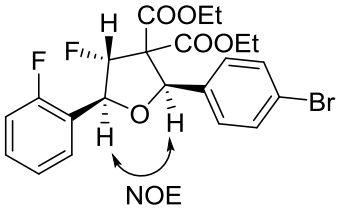
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 – 7.71 (m, 1H), 7.49 (s, 4H), 7.39 – 7.30 (m, 1H), 7.29 – 7.21 (m, 1H), 7.16 – 7.07 (m, 1H), 5.57 (ddd, *J* = 53.8, 3.5, 1.2 Hz, 1H), 5.45 (dd, *J* = 29.6, 3.6 Hz, 1H), 4.29 (q, *J* = 7.1 Hz, 2H), 3.84 (dq, *J* = 10.7, 7.1 Hz, 1H), 3.54 (dq, *J* = 10.7, 7.2 Hz, 1H), 1.26 (t, *J* = 7.1 Hz, 3H), 0.78 (t, *J* = 7.2 Hz, 3H).

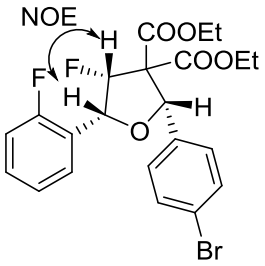
^{19}F NMR (376 MHz, $CDCl_3$) δ -117.95 – -118.06 (m), -179.73 (ddd, *J* = 53.4, 29.4, 4.0 Hz).

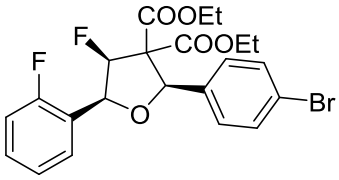
^{13}C NMR (101 MHz, $CDCl_3$) δ 166.3 (d, *J* = 9.0 Hz), 165.4 (d, *J* = 5.9 Hz), 159.9 (d, *J* = 246.8 Hz), 135.2, 131.2, 129.8 (d, *J* = 8.2 Hz), 128.5, 128.0 (d, *J* = 3.7 Hz), 124.7 (dd, *J* = 12.6, 6.9 Hz), 124.3 (d, *J* = 3.4 Hz), 122.5, 115.2 (d, *J* = 20.9 Hz), 99.3 (d, *J* = 189.2 Hz), 82.3, 79.8 (dd, *J* = 31.1, 3.1 Hz), 69.7, 69.5, 61.9 (d, *J* = 33.5 Hz), 14.0, 13.3.

GCMS (EI) m/z calcd for $C_{22}H_{21}BrF_2O_5$ $[M]^+$: 482.0, 484.0, found: 482.2, 484.2. Unstable under HRMS conditions

Determination of stereochemistry.





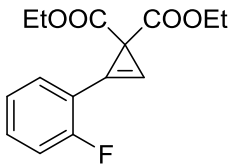


Fraction 2: 3.5:1 mixture of (2*R**,4*R**,5*R**)-**8l** and cyclopropene sideproduct **9l** (3.5 mg, 7.8 %).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (td, *J* = 7.5, 1.8 Hz, 1H), 7.46 – 7.35 (m, 4H), 7.35 – 7.22 (m, 1H), 7.16 (td, *J* = 7.6, 1.2 Hz, 1H), 7.07 – 6.98 (m, 1H), 5.71 (ddd, *J* = 52.0, 3.3, 1.5 Hz, 1H), 5.41 (s, 1H), 5.27 (dd, *J* = 26.3, 3.3 Hz, 1H), 4.33 (qd, *J* = 7.1, 0.8 Hz, 1H), 4.24 (qd, *J* = 7.1, 5.3 Hz, 1H), 3.87 – 3.74 (m, 2H), 1.31 (t, *J* = 7.1 Hz, 3H), 0.91 (t, *J* = 7.1 Hz, 3H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -117.95 – -119.87 (m), -195.04 (dd, *J* = 51.8, 26.5 Hz).

GCMS (EI) m/z calcd for $C_{22}H_{21}BrF_2O_5$ $[M]^+$: 482.0, 484.0, found: 482.2, 484.2. Unstable under HRMS conditions.



Fraction 3: **Diethyl 2-(2-fluorophenyl)cycloprop-2-ene-1,1-dicarboxylate** (**9l**)**:** Obtained as a byproduct from the cycle expansion reaction of cyclopropane (**5l**). Product was obtained as a colorless oil (2 mg, 8%). NMR yield 16 %.

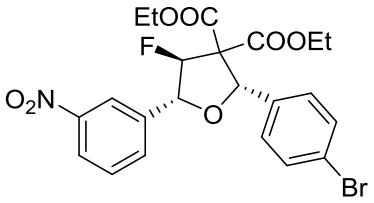
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (td, *J* = 7.7, 2.0 Hz, 1H), 7.15 – 7.00 (m, 3H), 6.96 (d, *J* = 3.4 Hz, 1H), 4.50 (q, *J* = 7.1 Hz, 2H), 4.22 (q, *J* = 7.1 Hz, 2H), 1.46 (t, *J* = 7.1 Hz, 3H), 1.28 (t, *J* = 7.1 Hz, 3H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -114.25 – -114.35 (m).

^{13}C NMR (101 MHz, $CDCl_3$) δ 163.0, 161.5, 158.4 (d, *J* = 250.7 Hz), 137.8 (d, *J* = 2.7 Hz), 127.9 (d, *J* = 8.2 Hz), 124.9 (d, *J* = 3.0 Hz), 124.2 (d, *J* = 3.7 Hz), 116.0 (d, *J* = 21.2 Hz), 111.6 (d, *J* = 11.9 Hz), 94.4, 68.2, 60.0, 29.7, 15.0, 14.5.

HRMS (ESI) m/z calcd for $C_{15}H_{16}FO_4$ $[M+H]^+$: 279.1033, found: 279.0993.

Diethyl (2S*,4S*,5R*)-2-(4-bromophenyl)-4-fluoro-5-(3-nitrophenyl)dihydrofuran-3,3(2H)-dicarboxylate (*trans,cis or* (*2S*,4S*,5R**)**-8n**):



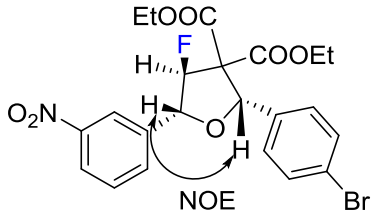
Starting material *cis*-**5n** (*cis* disatereomer, 29 mg, 0.089 mmol, 1 equiv) was flushed with argon 3 times. Afterwards it was dissolved in dry DCM (0.37 mL). *p*-Bromobenzaldehyde (16.5 mg, 0.089 mmol, 1 equiv) and $Sc(OTf)_3$ (44 mg, 0.089 mmol, 1 equiv) were subsequently added and the mixture was left to stir at rt. After completion (TLC control, ~1.5 h) the mixture was quenched with water (2 mL). The phases were seperated and the aqueous phase was extracted with DCM (3 x 5 mL). The combined organic phases were washed with brine, dried over anh. Na_2SO_4, filtered and concentrated under reduced pressure. NMR yield – 80 %, d.r. .>20:1 (Internal standart 1 equiv EtOAc). Product was purified via collumn chromatography (Eluent PE:EtOAc 10:1 to 4:1). Product was obtained as **2S*,4S*,5R*** diastereomer as a light yellow oil (27.5 mg, 60%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 (t, *J* = 2.0 Hz, 1H), 8.25 (ddd, *J* = 8.2, 2.3, 1.1 Hz, 1H), 7.92 (ddt, *J* = 7.8, 1.8, 0.9 Hz, 1H), 7.63 (t, *J* = 8.0 Hz, 1H), 7.55 – 7.49 (m, 2H), 7.49 – 7.42 (m, 2H), 5.86 (s, 1H), 5.53 (dd, *J* = 54.2, 3.8 Hz, 1H), 5.23 (dd, *J* = 29.5, 3.7 Hz, 1H), 4.30 (qd, *J* = 7.1, 1.3 Hz, 2H), 3.86 (dq, *J* = 10.7, 7.1 Hz, 1H), 3.55 (dq, *J* = 10.7, 7.2 Hz, 1H), 1.27 (t, *J* = 7.1 Hz, 3H), 0.79 (t, *J* = 7.2 Hz, 3H).

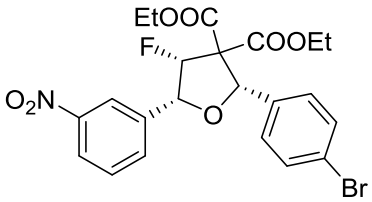
^{13}C NMR (101 MHz, $CDCl_3$) δ 166.54 (d, *J* = 8.5 Hz), 165.29 (d, *J* = 5.7 Hz), 148.55, 139.63 (d, *J* = 6.5 Hz), 134.80, 132.46, 131.45, 129.77, 128.52, 123.54, 122.87, 121.60, 99.75 (d, *J* = 189.3 Hz), 84.51 (d, *J* = 30.0 Hz), 82.94, 69.57 (d, *J* = 20.6 Hz), 62.36, 62.12, 14.11, 13.42.

^{19}F NMR (376 MHz, $CDCl_3$) δ -179.76 (dd, *J* = 54.2, 29.3 Hz).

GCMS (EI) m/z calcd for $C_{22}H_{21}BrFNO_7$ $[M]^+$: 509.0, 511.0, found: 509.1, 511.1. Unstable under HRMS conditions.



Diethyl (2S*,4R*,5R*)-2-(4-bromophenyl)-4-fluoro-5-(3-nitrophenyl)dihydrofuran-3,3(2H)-dicarboxylate (*cis,cis* or (*2S*,4R*,5R**)-**8n**):



Starting material *trans*-**5n** (*trans* diastereomer, 34 mg, 0.104 mmol, 1 equiv) was flushed with argon 3 times. Afterwards it was dissolved in dry DCM (0.43 mL). *p*-Bromobenzaldehyde (19.3 mg, 0.104 mmol, 1 equiv) and $Sc(OTf)_3$ (51 mg, 0.104 mmol, 1 equiv) were subsequently added and the mixture was left to stir at rt. After completion (TLC control, ~1.5 h) the mixture was quenched with water (2 mL). The phases were seperated and the aqueous phase was extracted with DCM (3 x 5 mL). The combined organic phases were washed with brine, dried over anh. Na_2SO_4, filtered and concentrated under reduced pressure. NMR yield – 62 % (Internal standart 1 equiv EtOAc). Product was purified via collumn chromatography (Eluent PE:EtOAc 10:1 to 4:1). Product was obtained as **2S*,4R*,5R*** diastereomer as a colorless oil (23.6 mg, 44%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (t, *J* = 2.0 Hz, 1H), 8.24 (ddd, *J* = 8.2, 2.3, 1.1 Hz, 1H), 7.89 (ddd, *J* = 7.6, 1.7, 0.8 Hz, 1H), 7.61 (t, *J* = 8.0 Hz, 1H), 7.54 – 7.46 (m, 4H), 5.71 (dd, *J* = 52.0, 3.3 Hz, 1H), 5.46 (s, 1H), 5.18 (dd, *J* = 25.8, 3.3 Hz, 1H), 4.48 – 4.34 (m, 2H), 3.91 (qd, *J* = 7.1, 2.1 Hz, 2H), 1.39 (t, *J* = 7.1 Hz, 3H), 1.00 (t, *J* = 7.1 Hz, 3H).

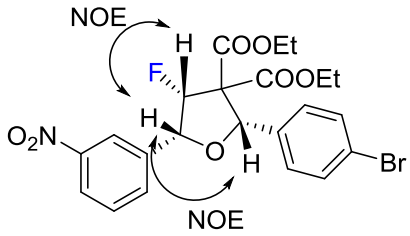
^{13}C NMR (101 MHz, $CDCl_3$) δ 168.3 (d, *J* = 9.2 Hz), 163.5 (d, *J* = 4.6 Hz), 148.4, 136.2 (d, *J* = 4.5 Hz), 135.9, 133.7, 131.2, 129.5, 129.5 (d, *J* = 1.8 Hz), 123.7, 122.7,

122.6, 95.8 (d, *J* = 199.6 Hz), 83.5, 81.9 (d, *J* = 20.2 Hz), 69.2 (d, *J* = 19.6 Hz), 63.2, 62.1, 14.2, 13.8.

^{19}F NMR (376 MHz, $CDCl_3$) δ -195.46 (dd, *J* = 51.9, 25.8 Hz).

GCMS (EI) m/z calcd for $C_{22}H_{21}BrFNO_7$ $[M]^+$: 509.0, 511.0, found: 509.1, 511.1.

Unstable under HRMS conditions.



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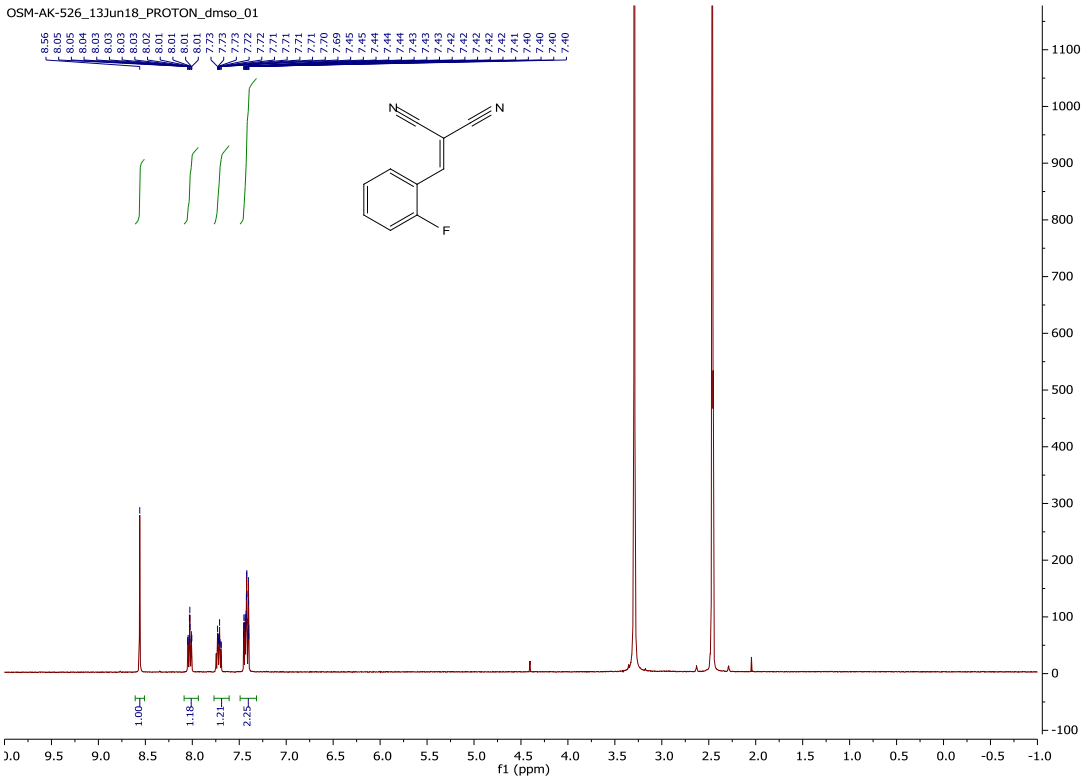
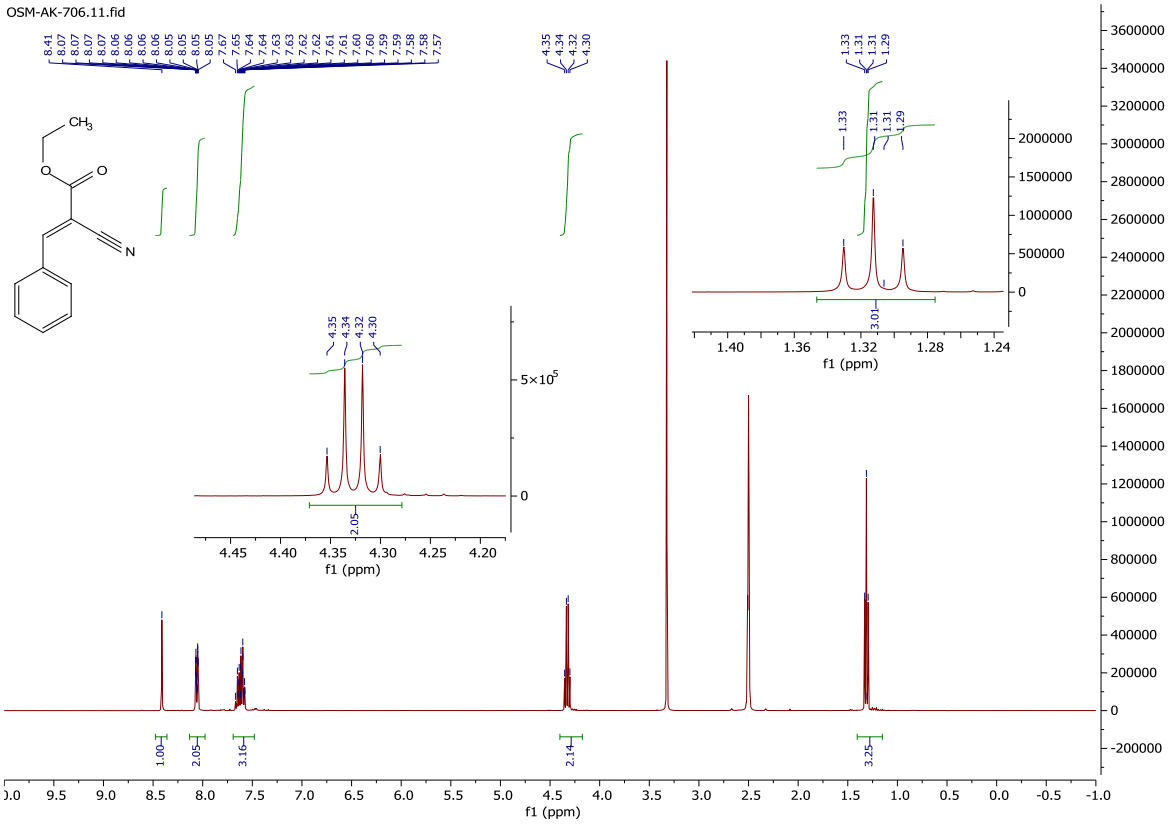
NMR SPECTRA

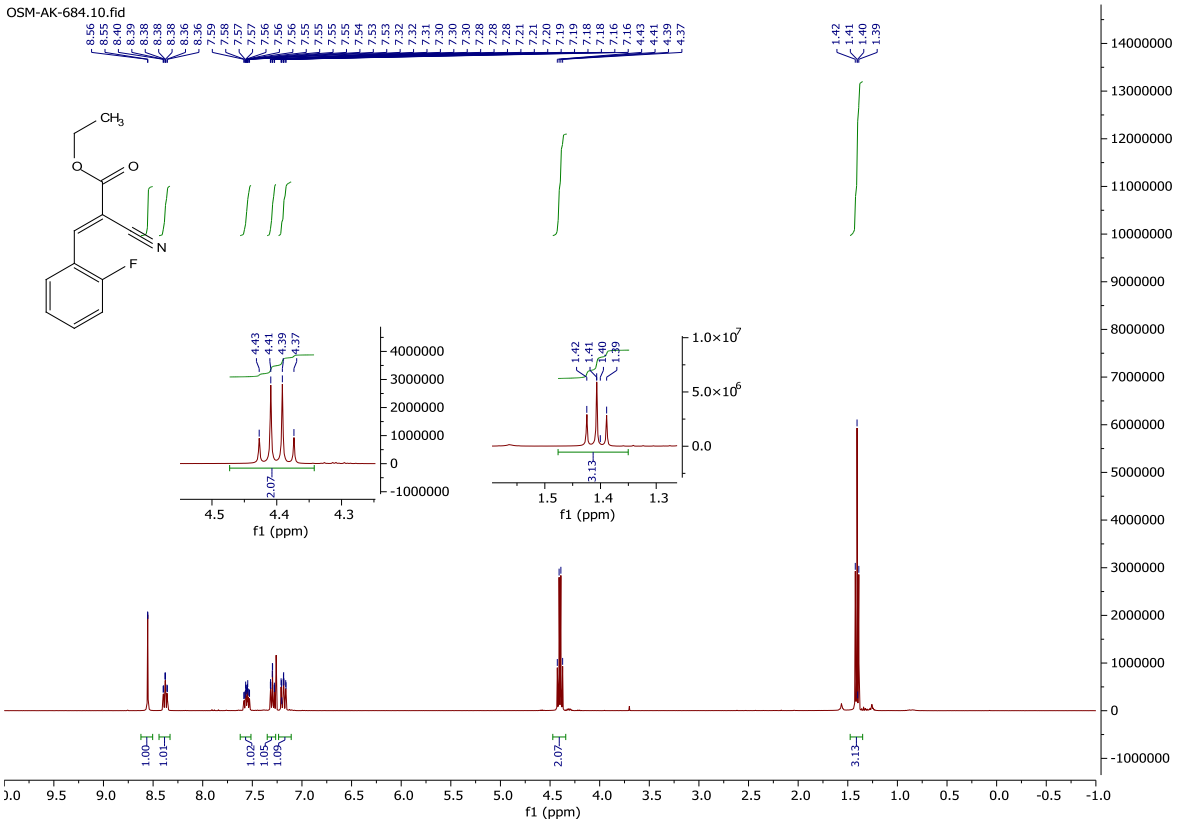
Compound **2a** ^{1}H NMR (400 MHz, DMSO-*d6*)



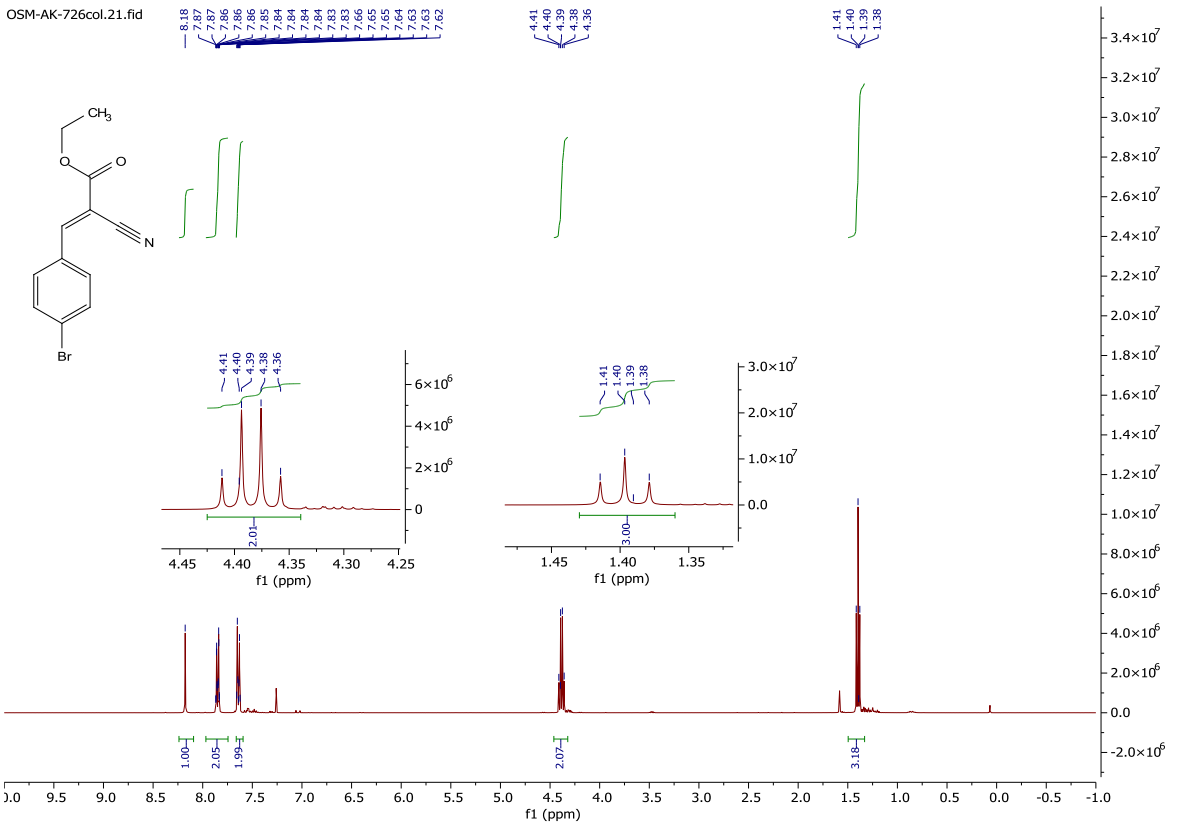
Compound **4a** ^{1}H NMR (400 MHz, DMSO-*d6*)



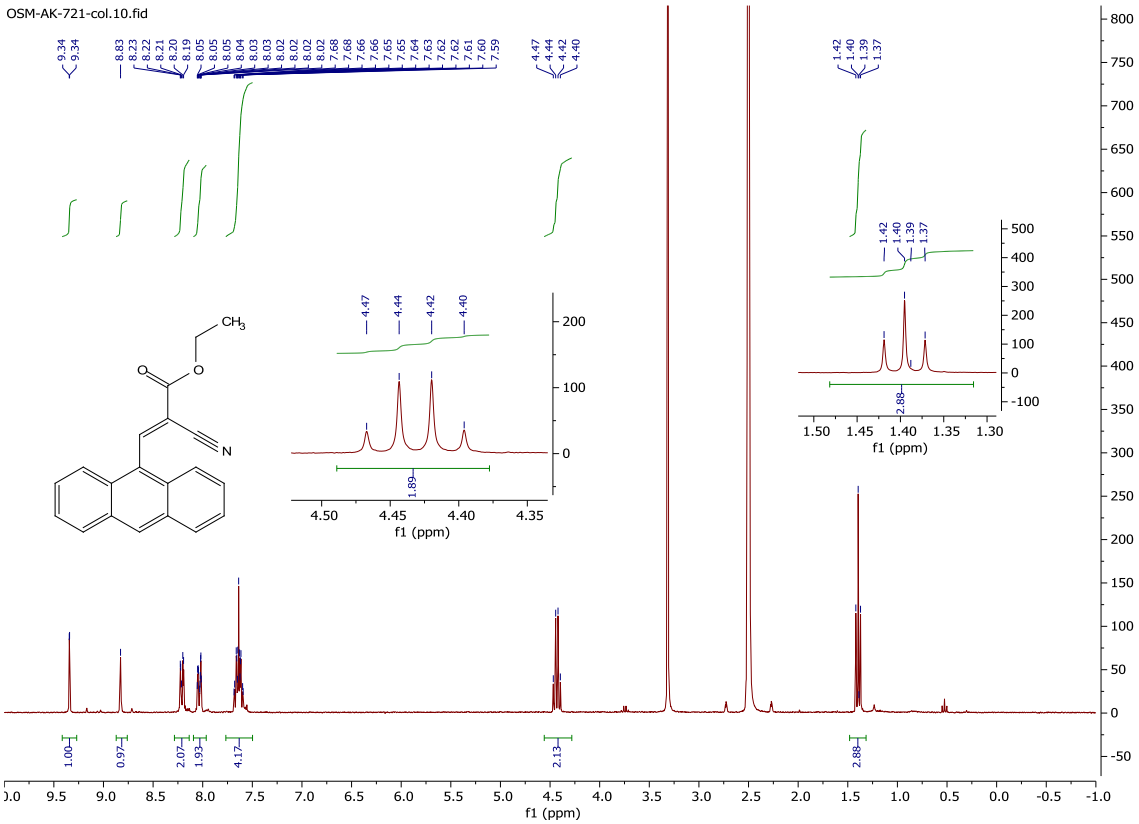
Compound **4b** ^{1}H NMR (400 MHz, $CDCl_3$)



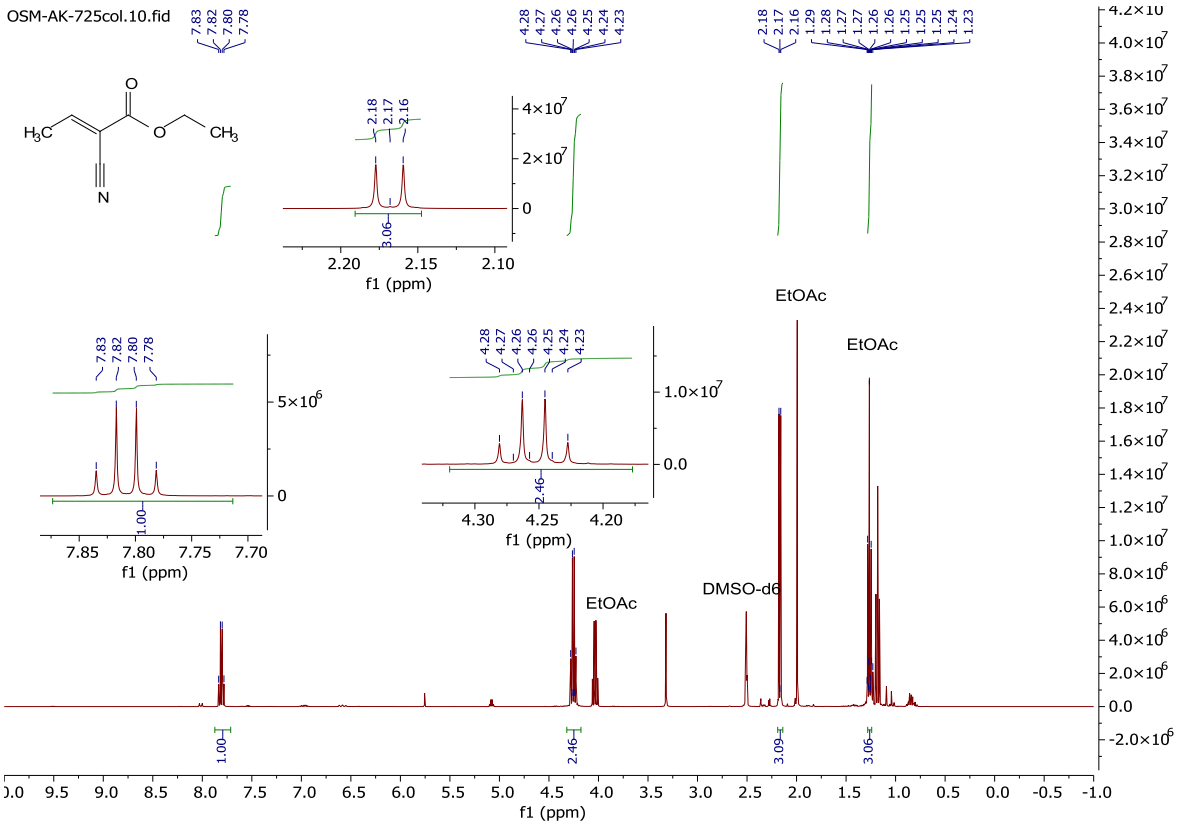
Compound **4c** ^{1}H NMR (400 MHz, $CDCl_3$)



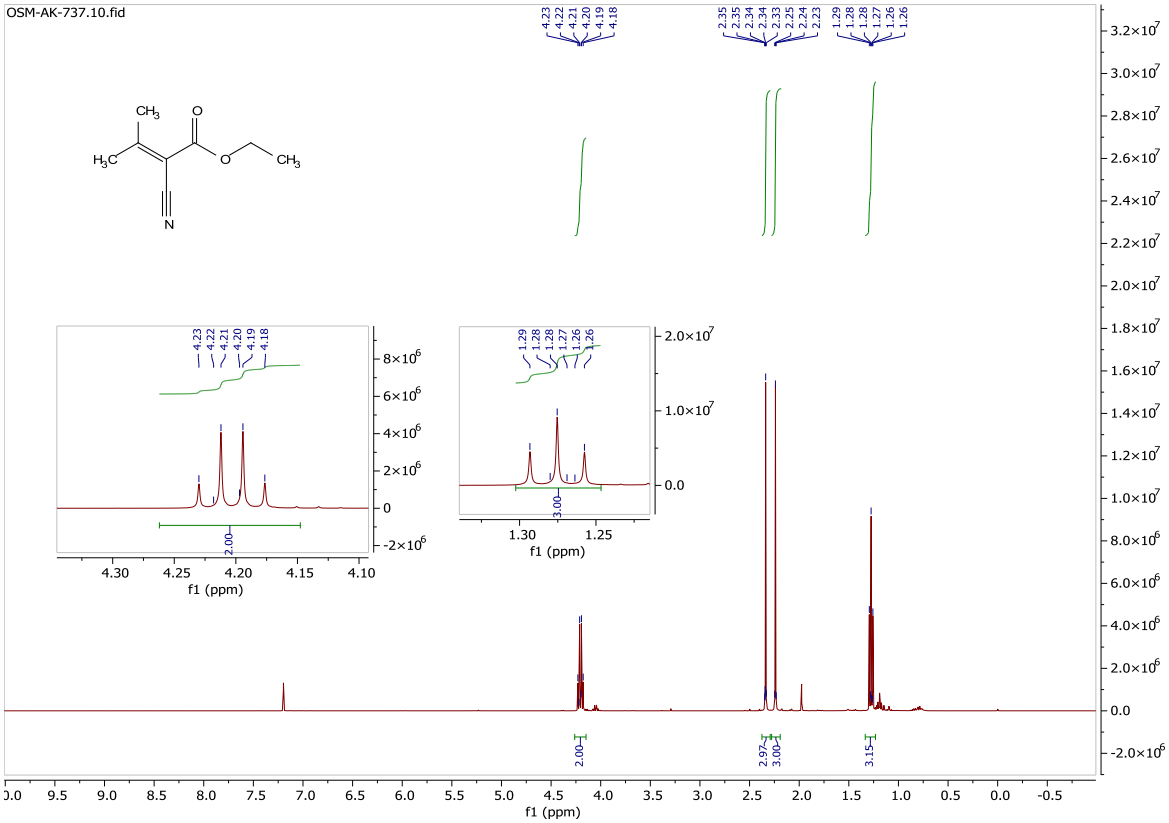
Compound **4d** ^{1}H NMR (400 MHz, DMSO-*d6*)



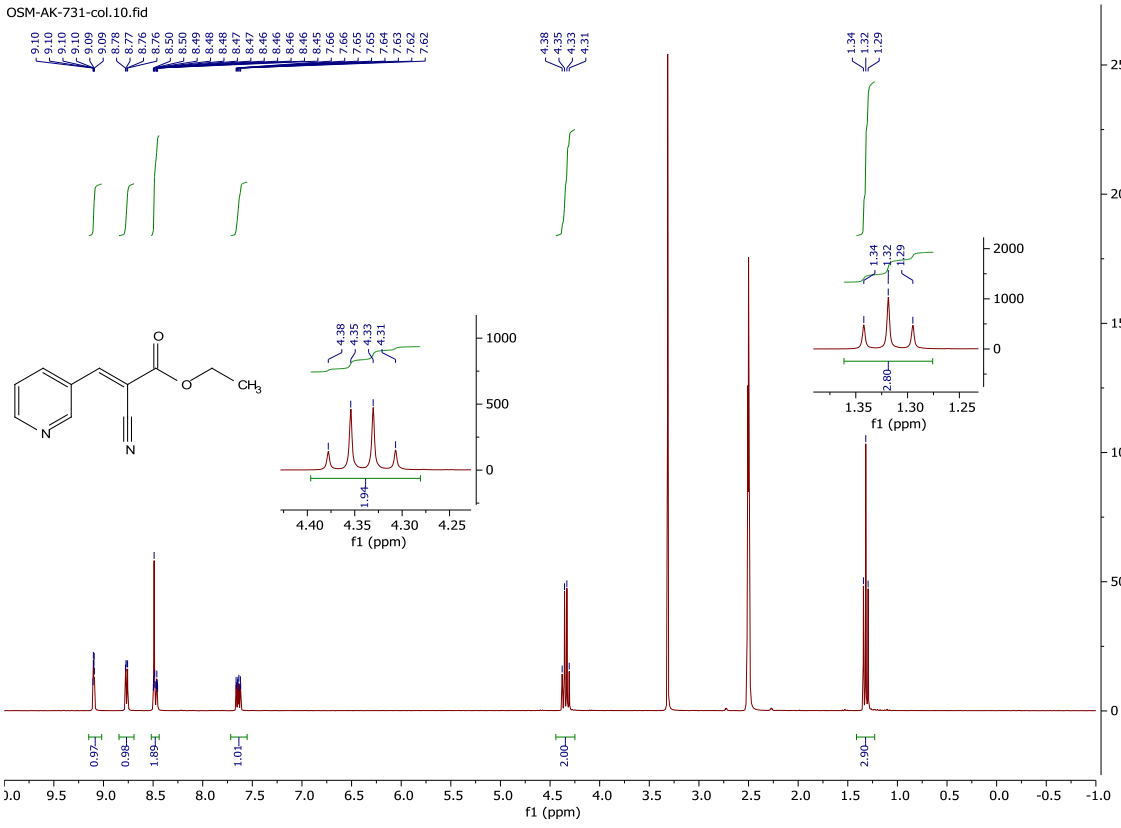
Compound **4e** ^{1}H NMR (400 MHz, DMSO-*d6*)



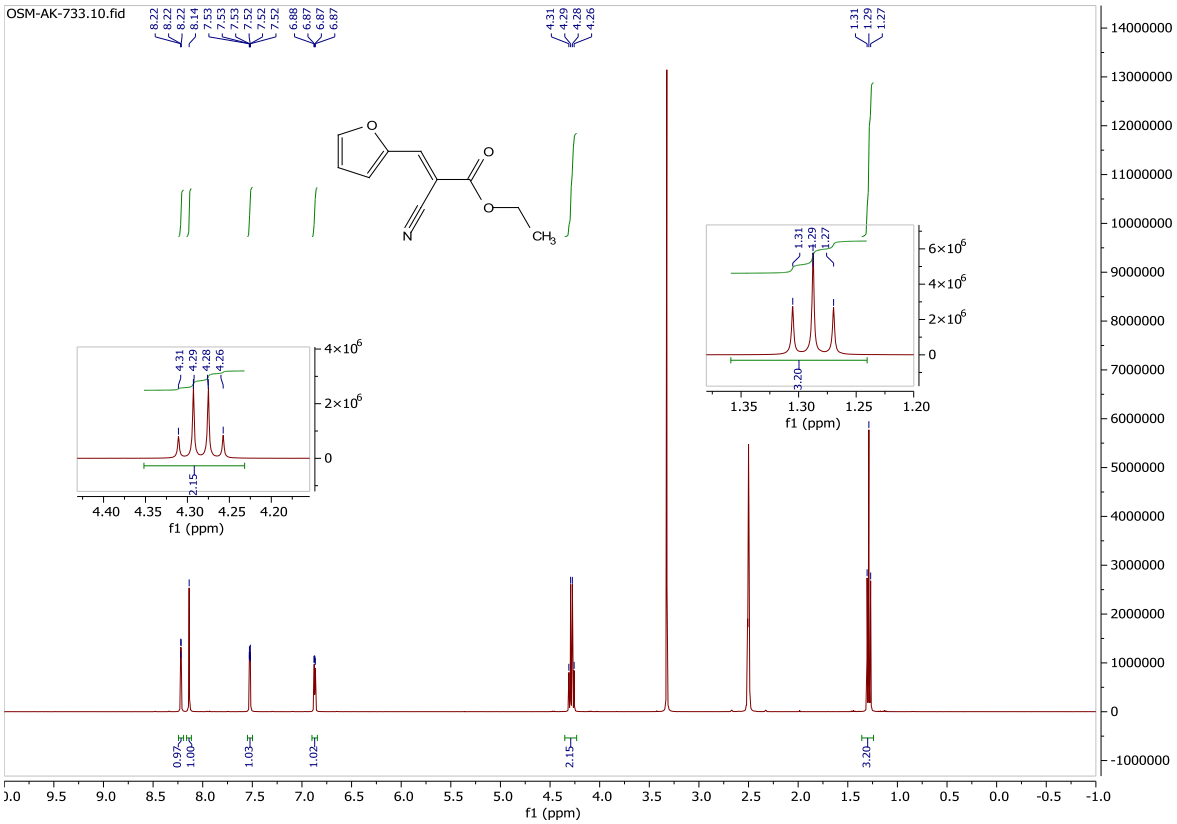
Compound **4f** ^{1}H NMR (400 MHz, $CDCl_3$)



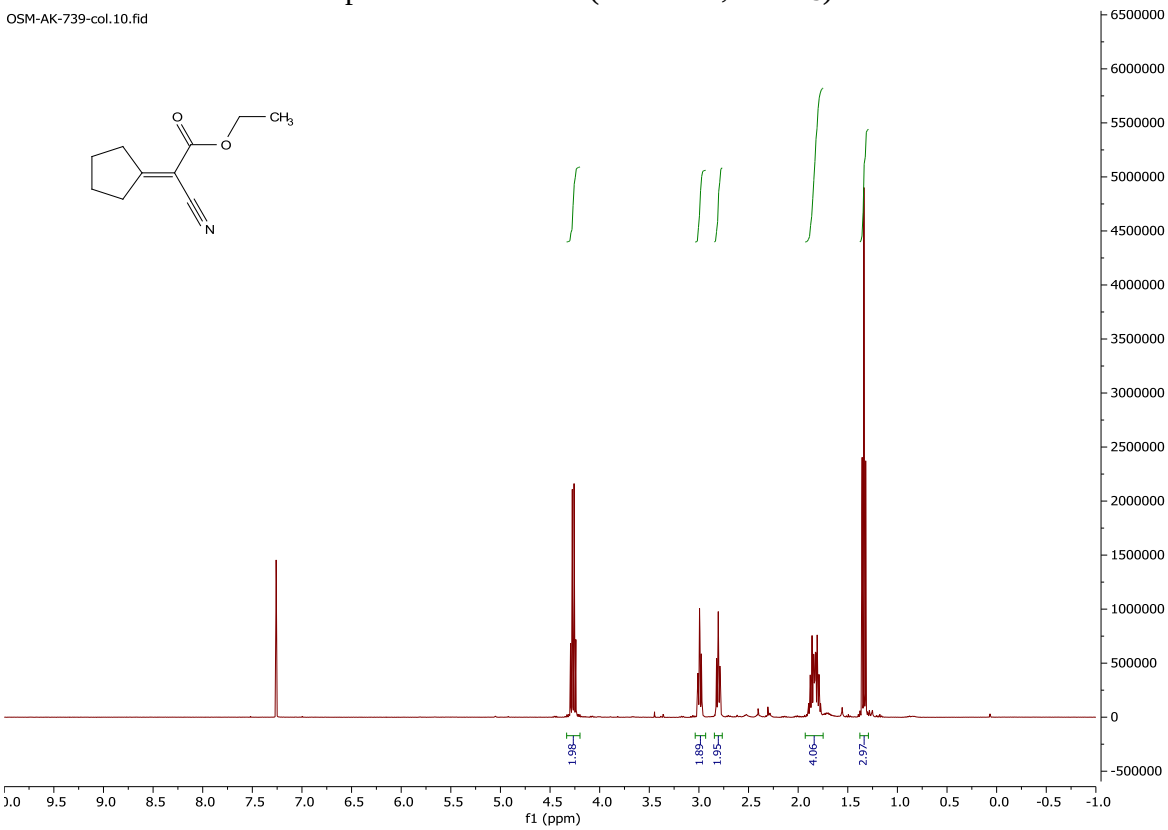
Compound **4g** ^{1}H NMR (400 MHz, DMSO-*d6*)



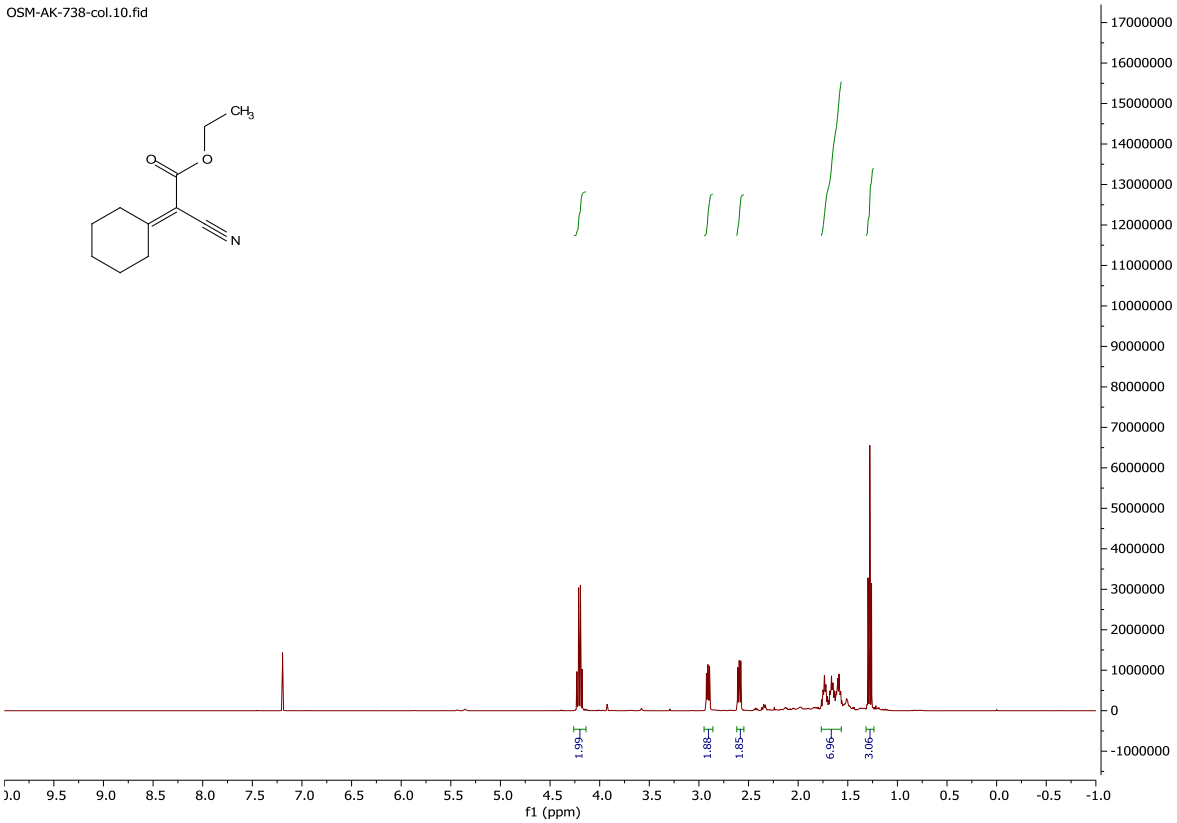
Compound **4h** ^{1}H NMR (400 MHz, DMSO-*d6*)



Compound **4i** ^{1}H NMR (400 MHz, $CDCl_3$)



Compound **4j** ^{1}H NMR (400 MHz, $CDCl_3$)



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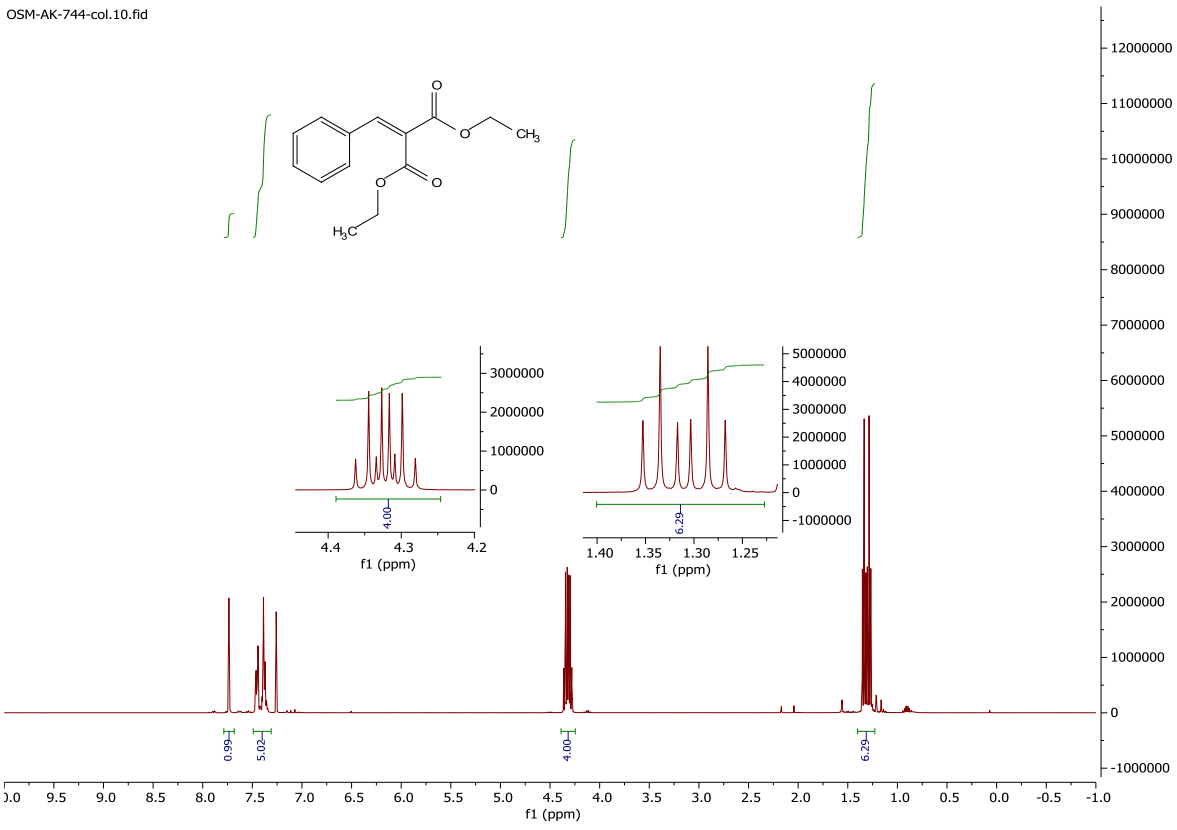
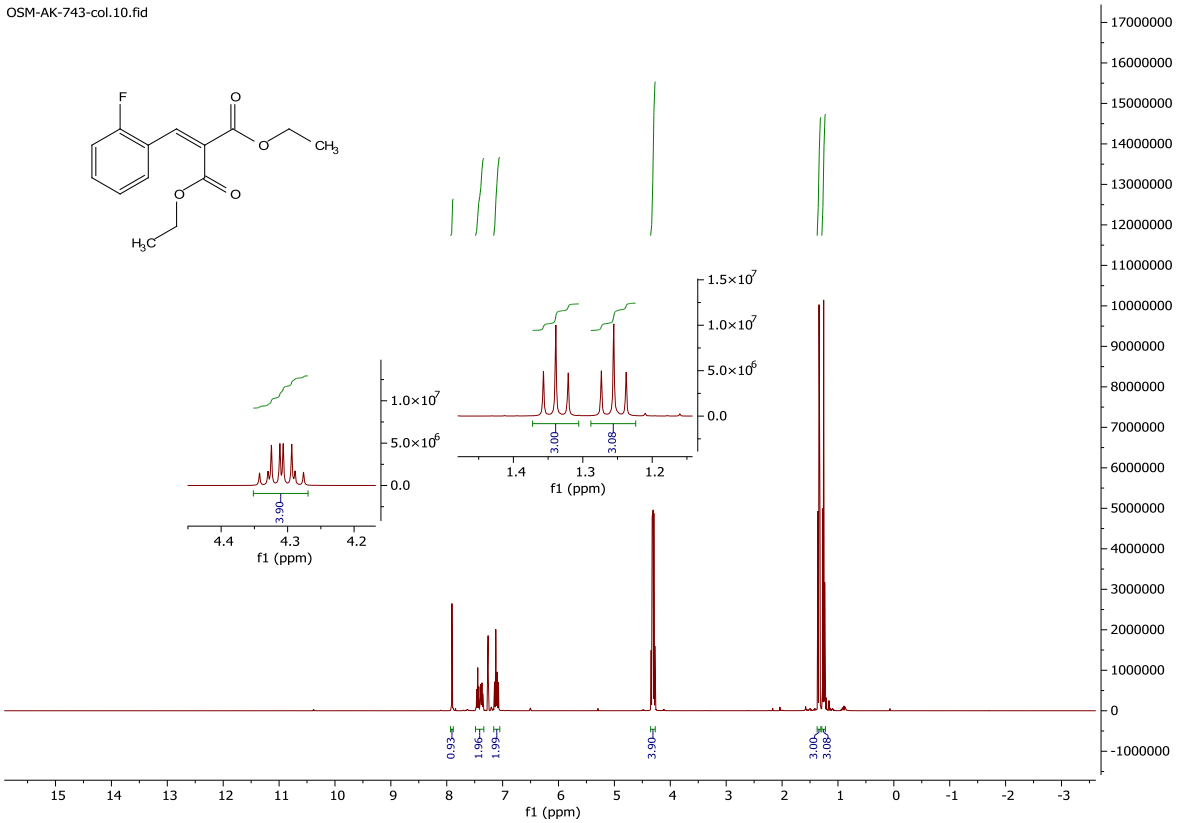
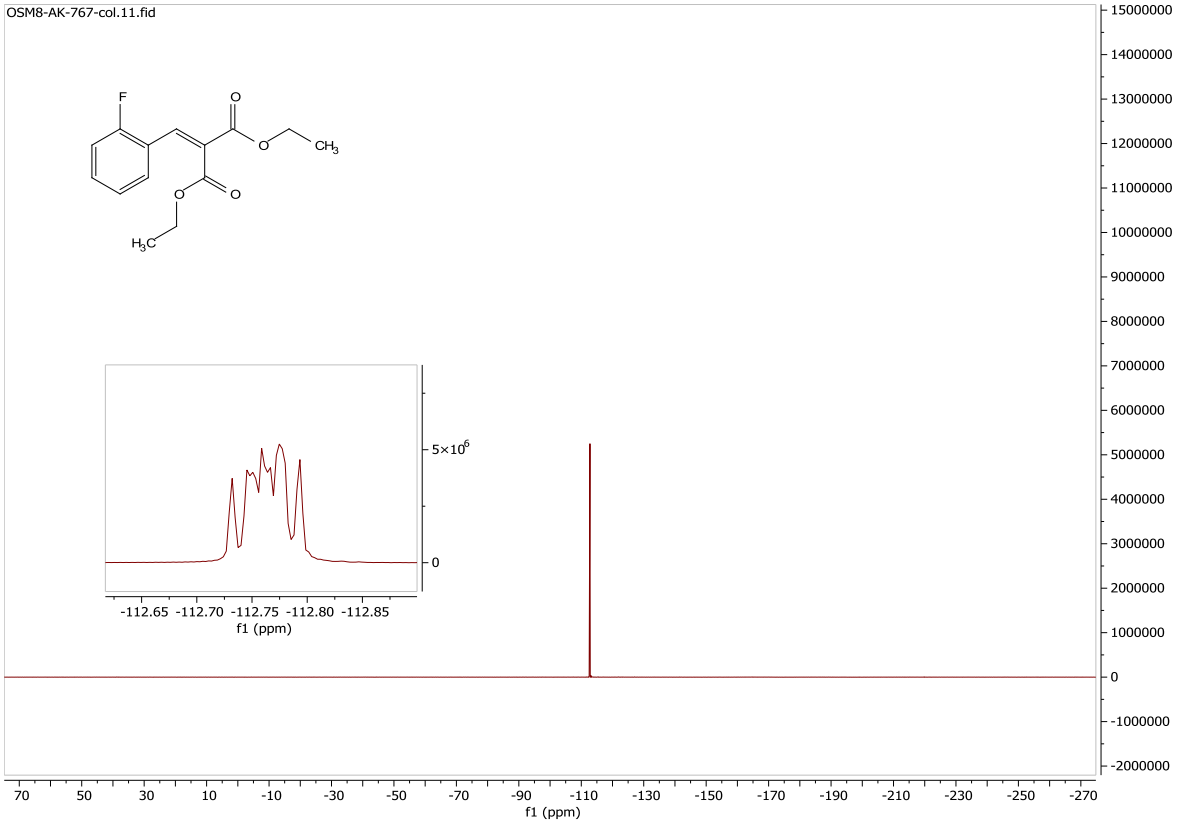


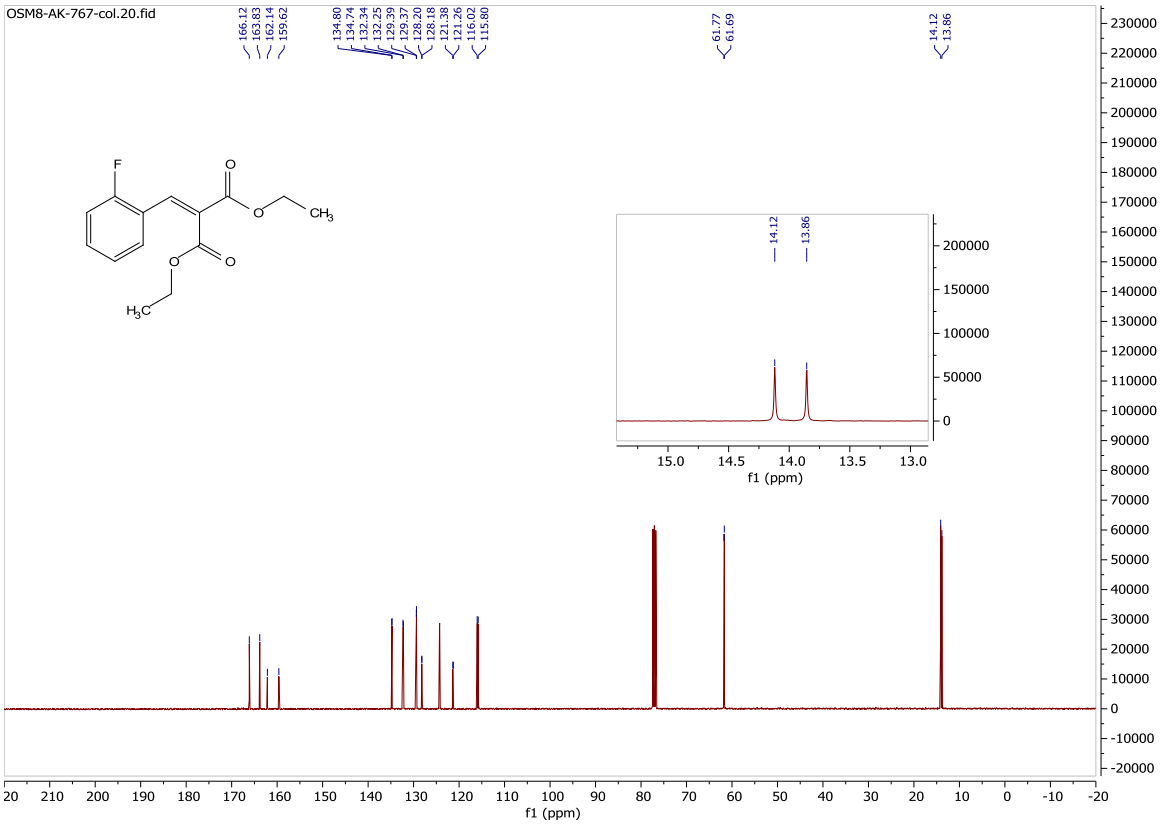
Compound **4l** ^{1}H NMR (400 MHz, $CDCl_3$)



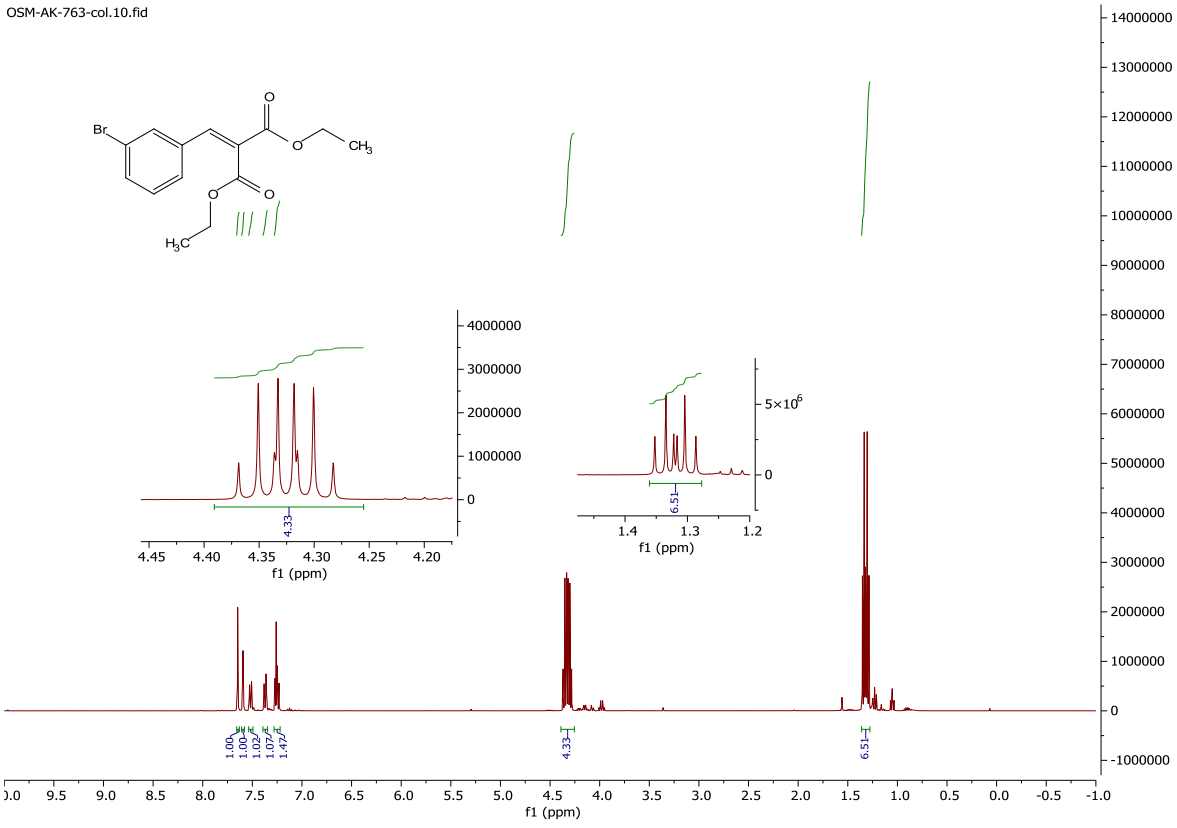
Compound **4l** ^{19}F NMR (400 MHz, $CDCl_3$)



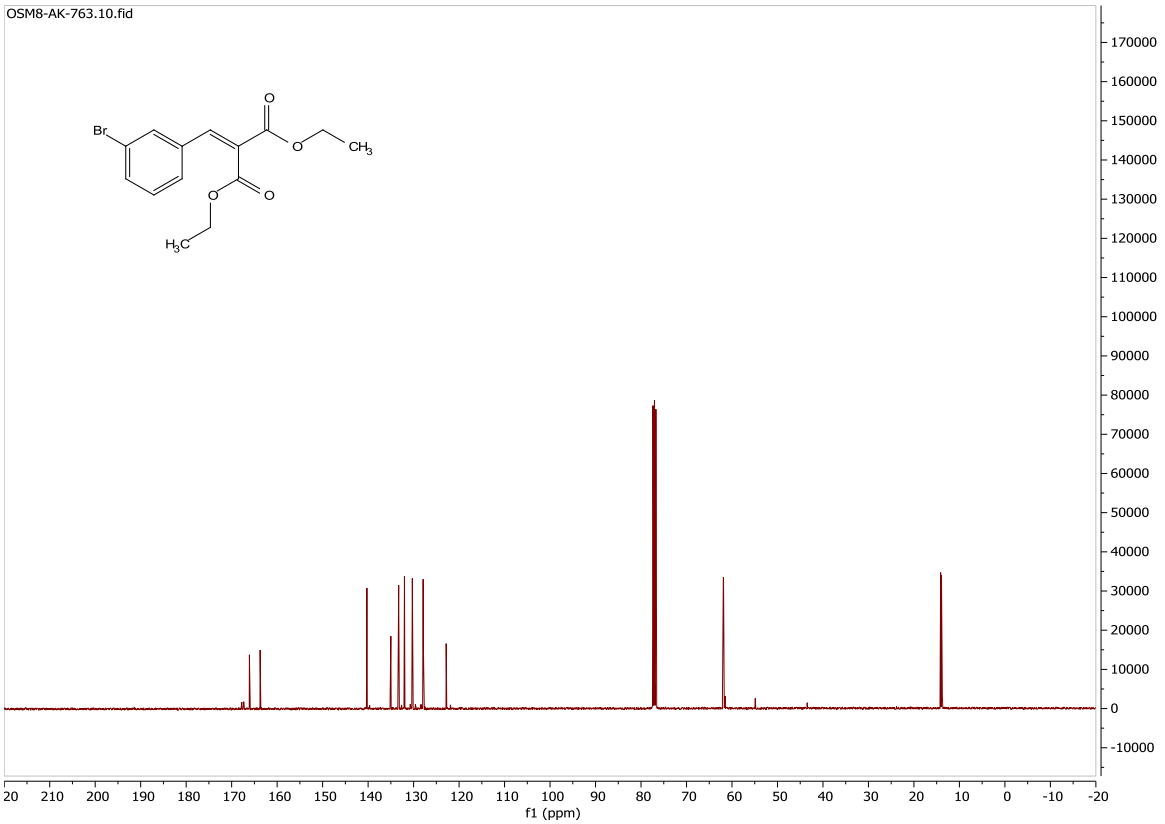
Compound **4l** ^{13}C NMR (400 MHz, $CDCl_3$)



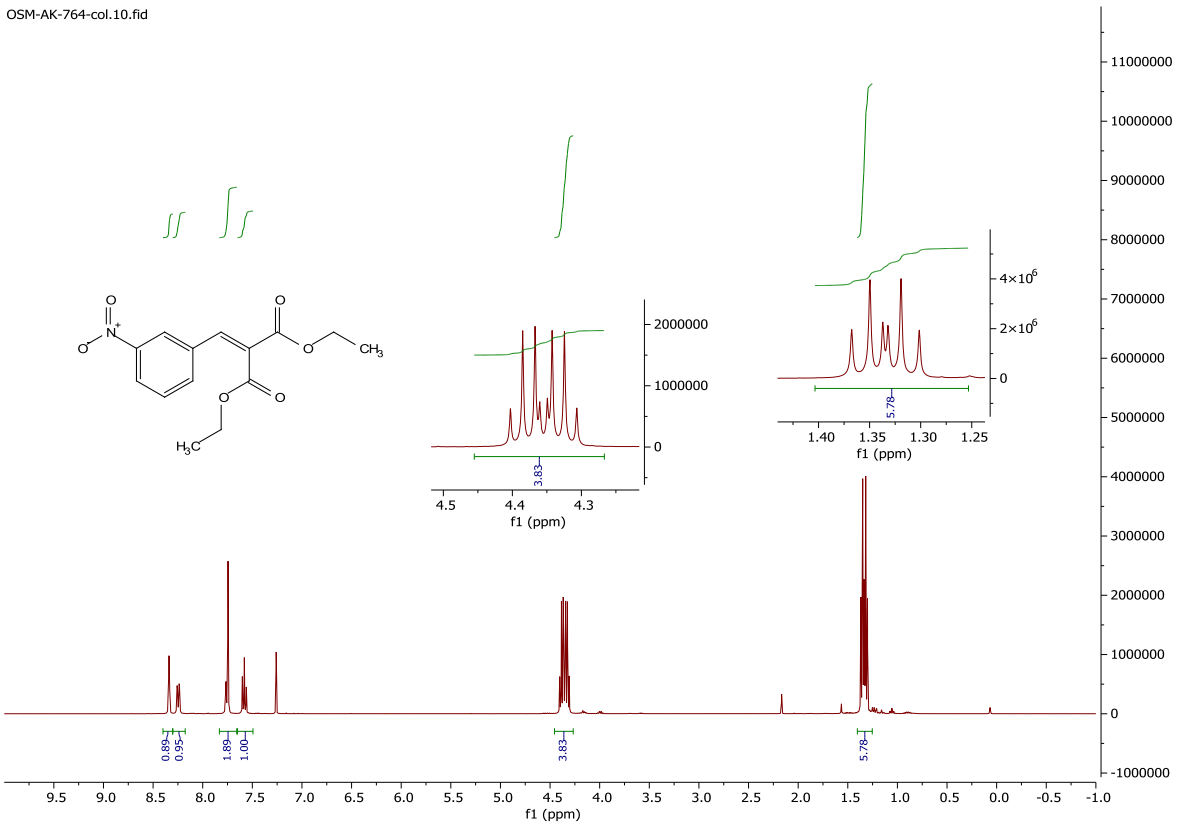
Compound **4m** ^{1}H NMR (400 MHz, $CDCl_3$)



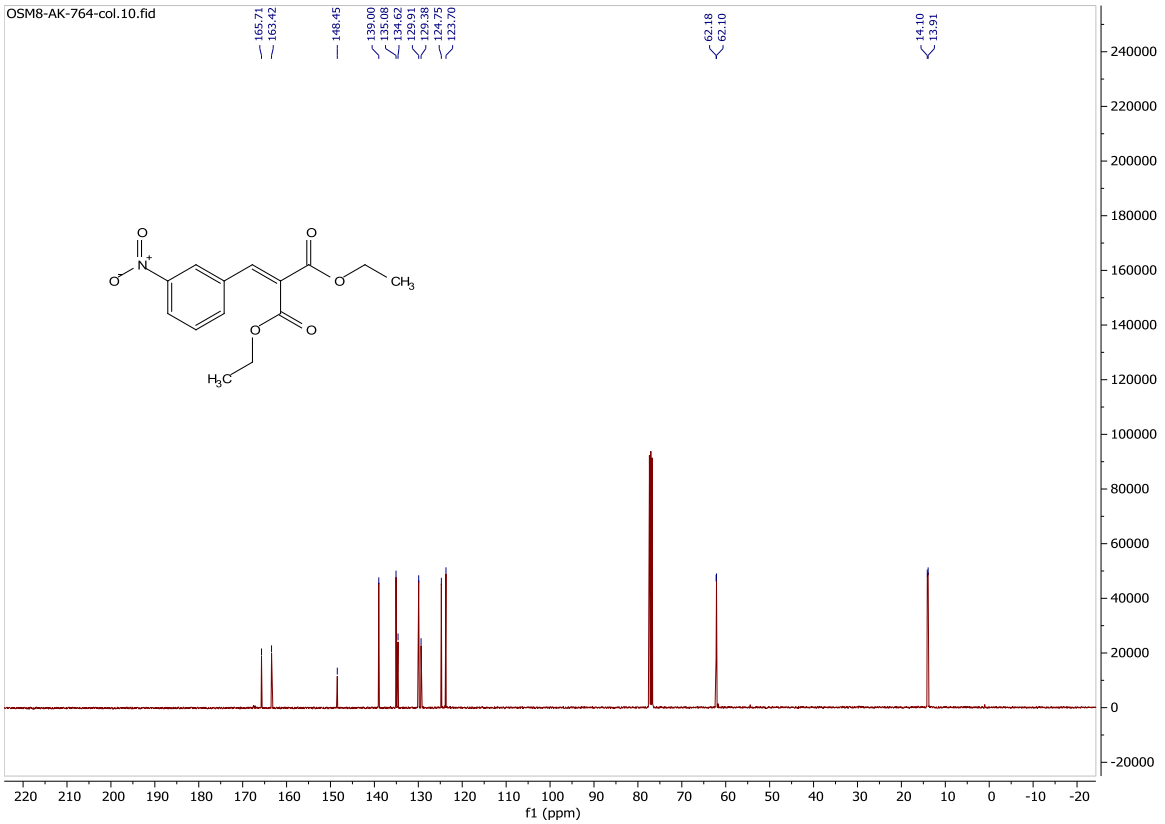
Compound **4m** ^{13}C NMR (400 MHz, $CDCl_3$)



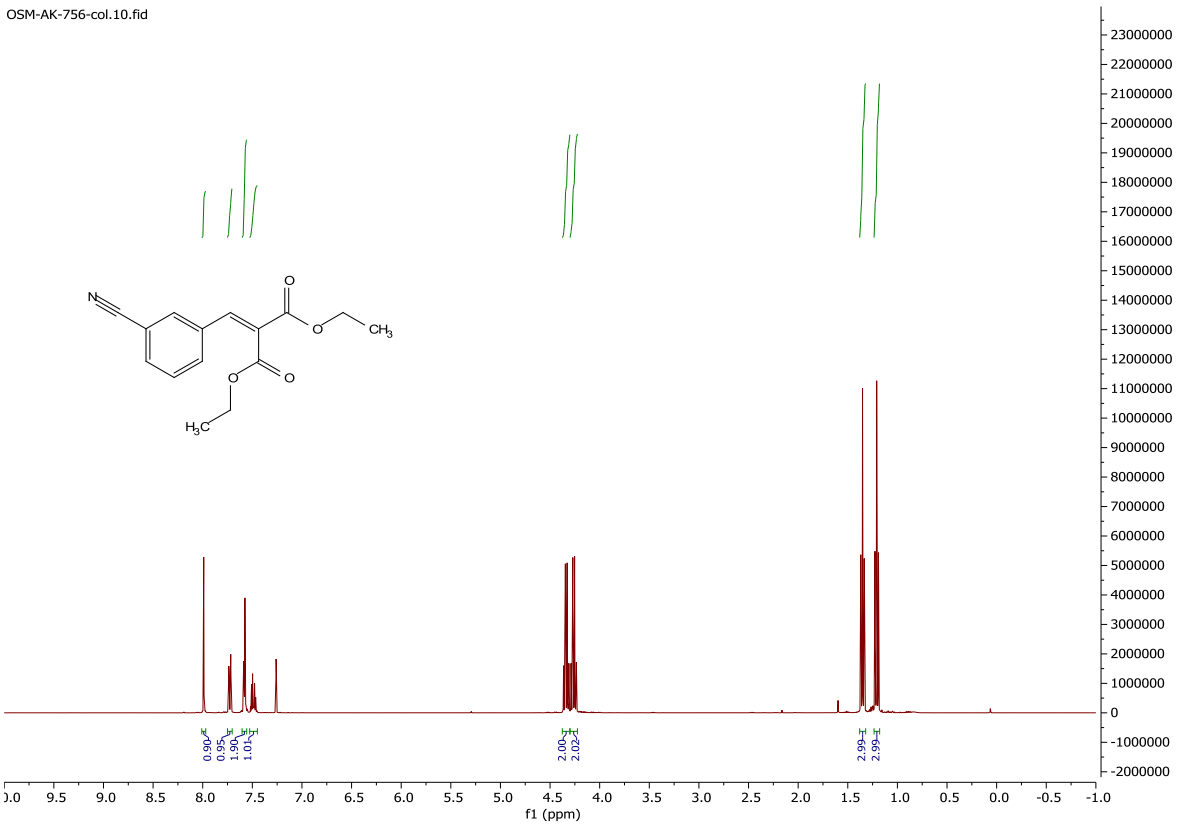
Compound **4n** ^{1}H NMR (400 MHz, $CDCl_3$)



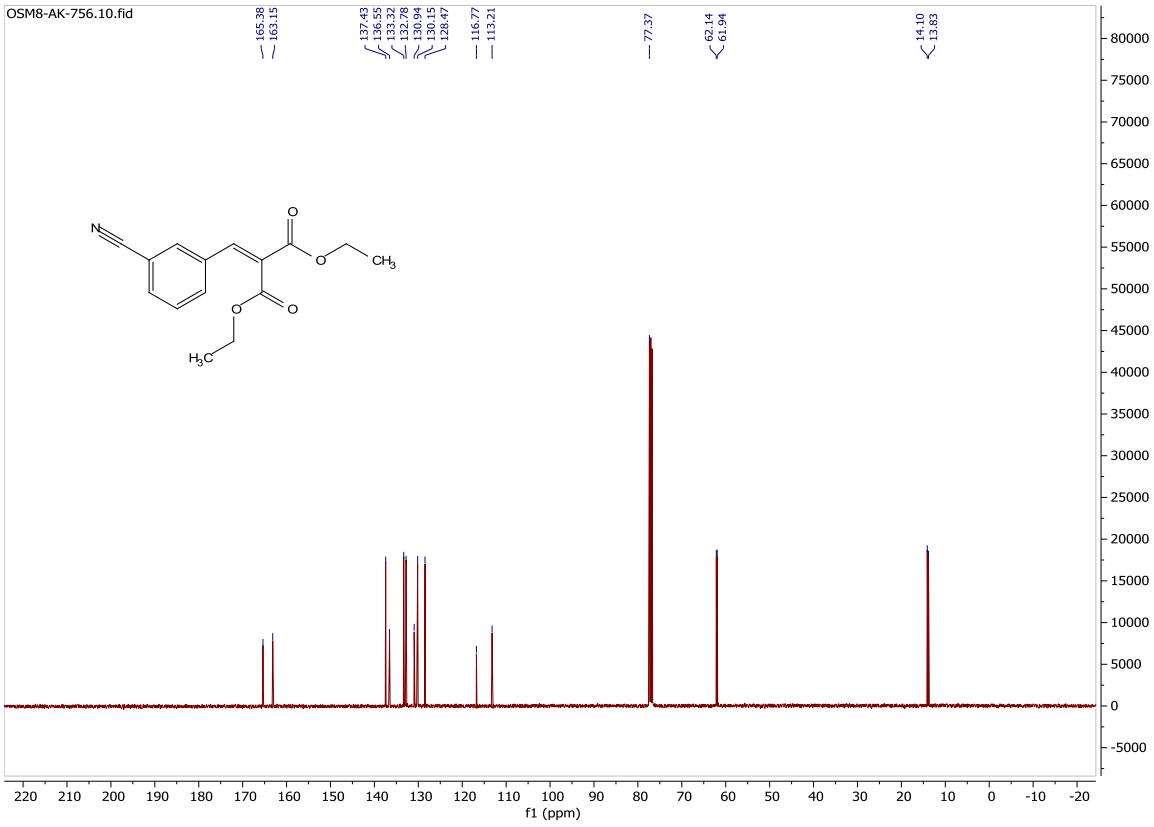
Compound **4n** ^{1}H NMR (400 MHz, $CDCl_3$)



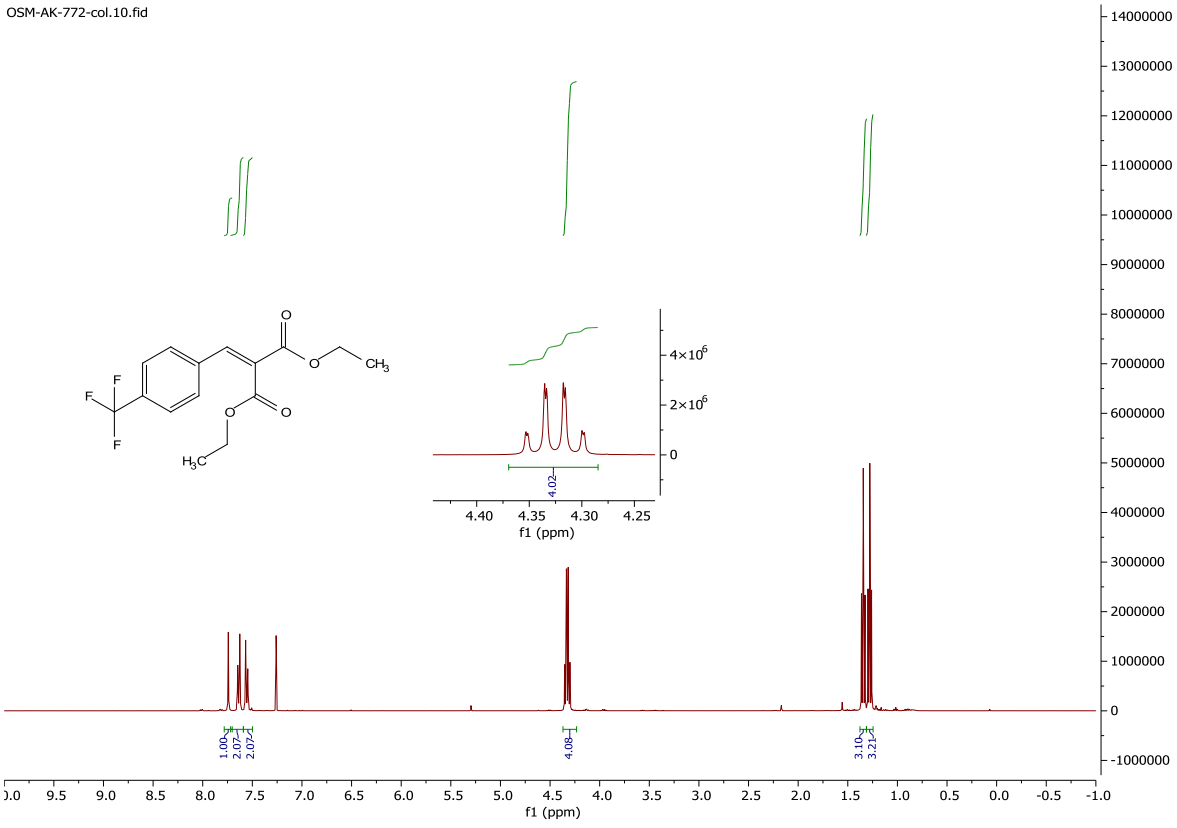
Compound **4o** ^{1}H NMR (400 MHz, $CDCl_3$)



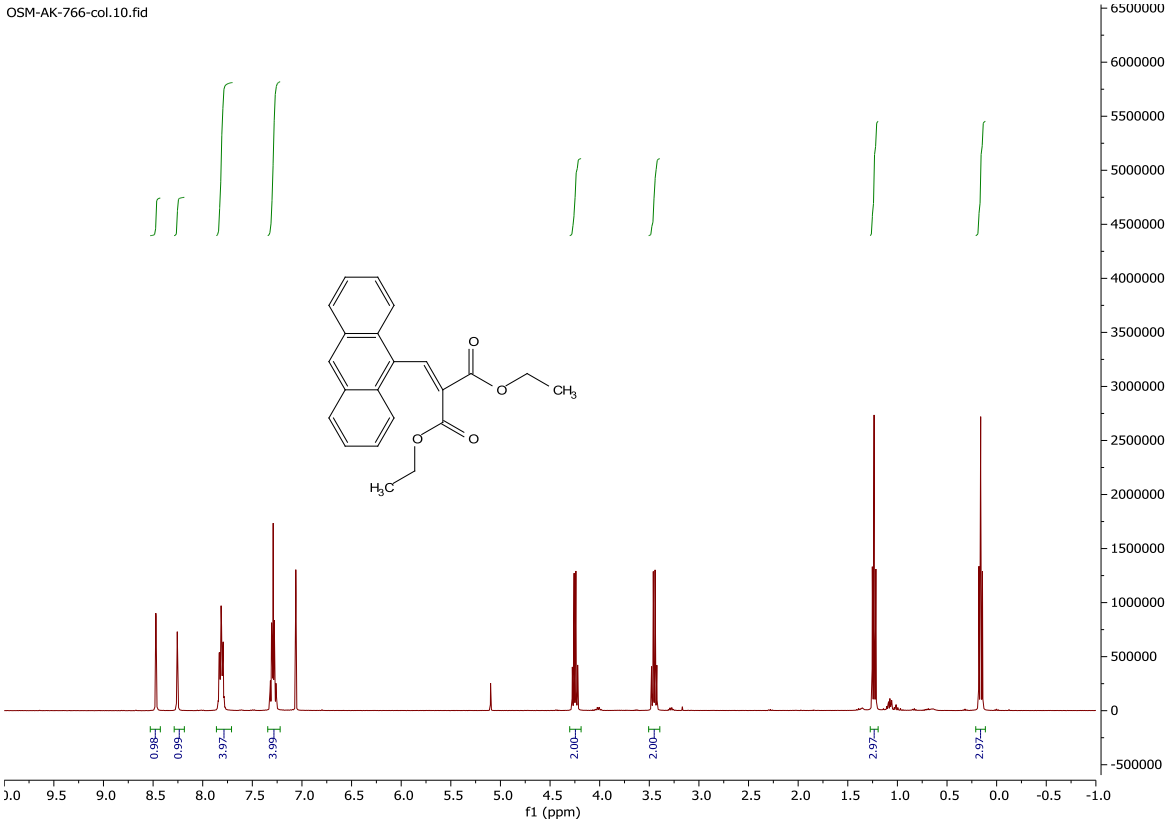
Compound **4o** ^{13}C NMR (400 MHz, $CDCl_3$)



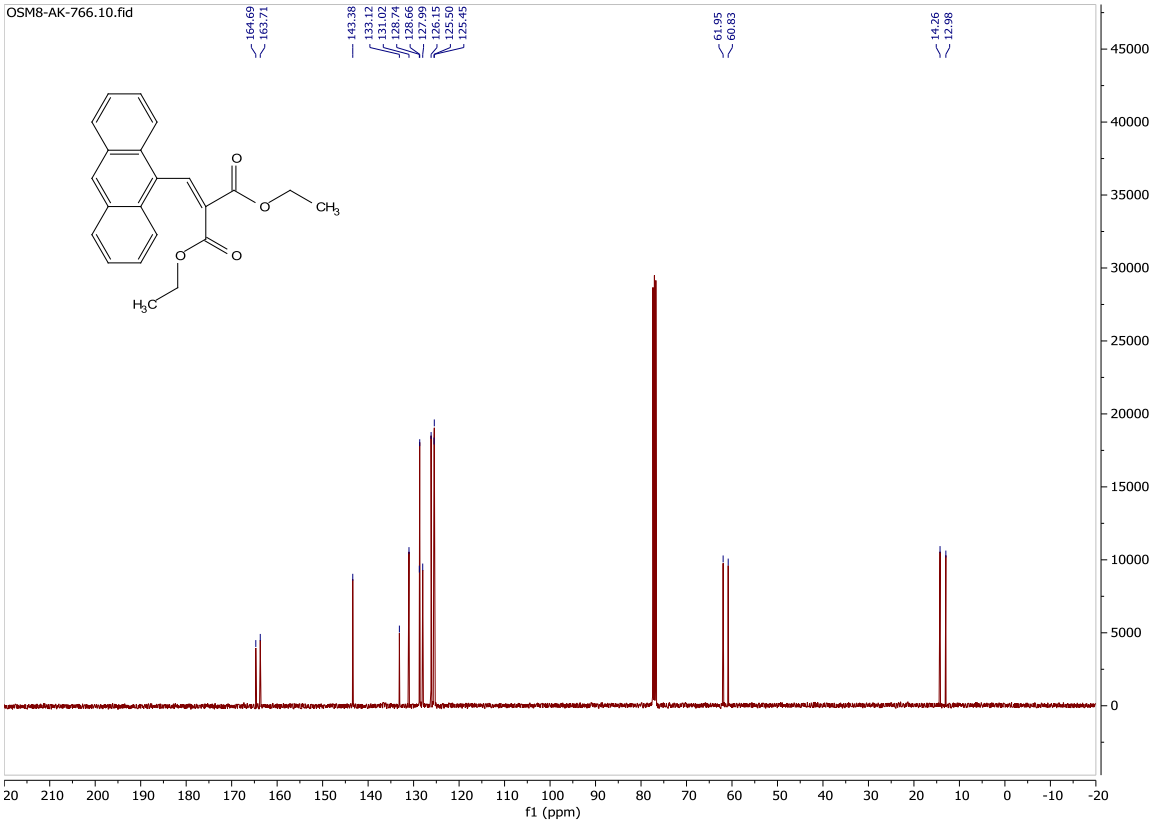
Compound **4p** ^{1}H NMR (400 MHz, $CDCl_3$)



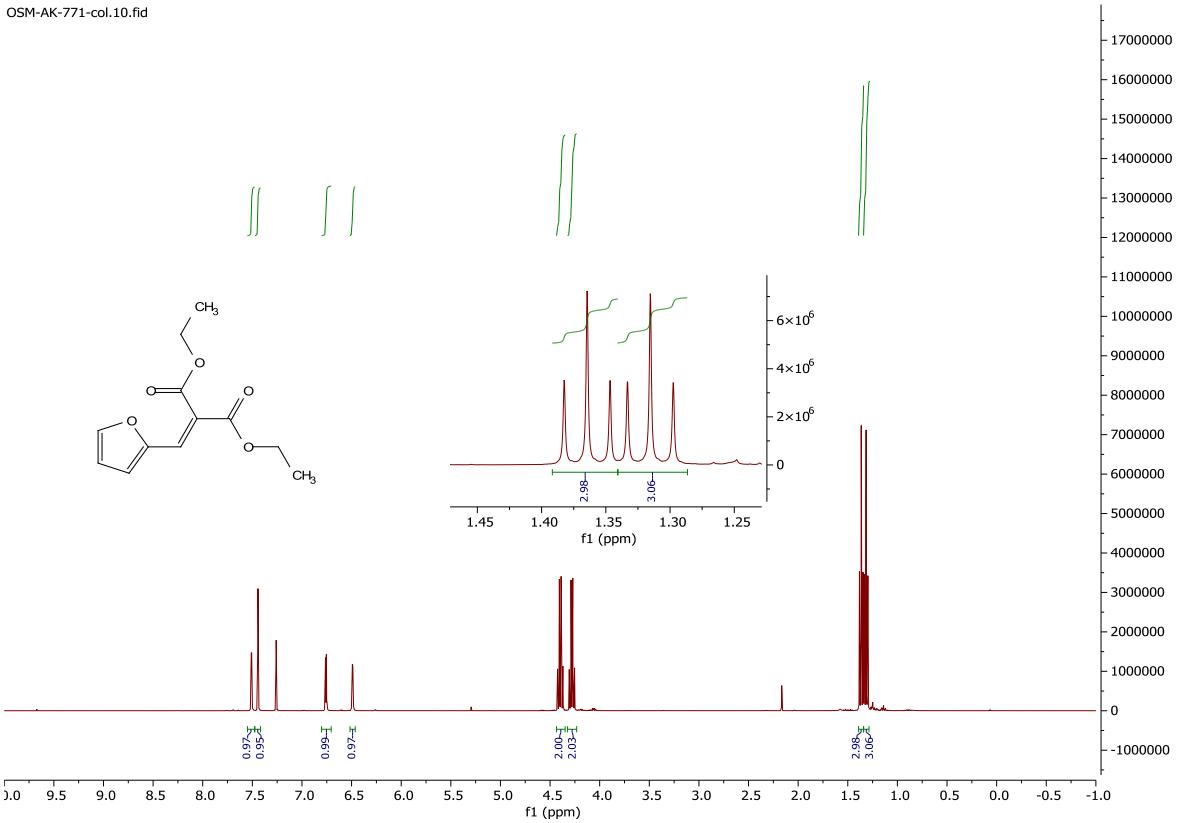
Compound **4r** ^{1}H NMR (400 MHz, $CDCl_3$)



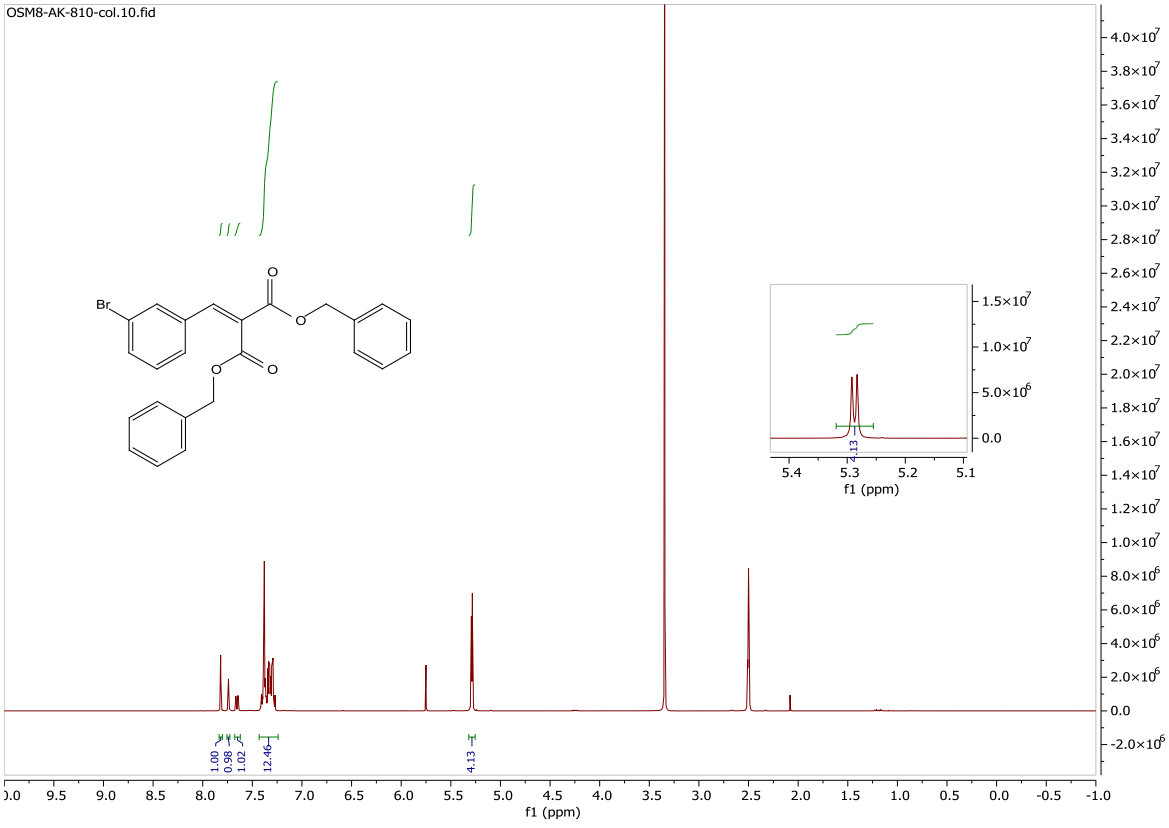
Compound **4r** ^{13}C NMR (400 MHz, $CDCl_3$)



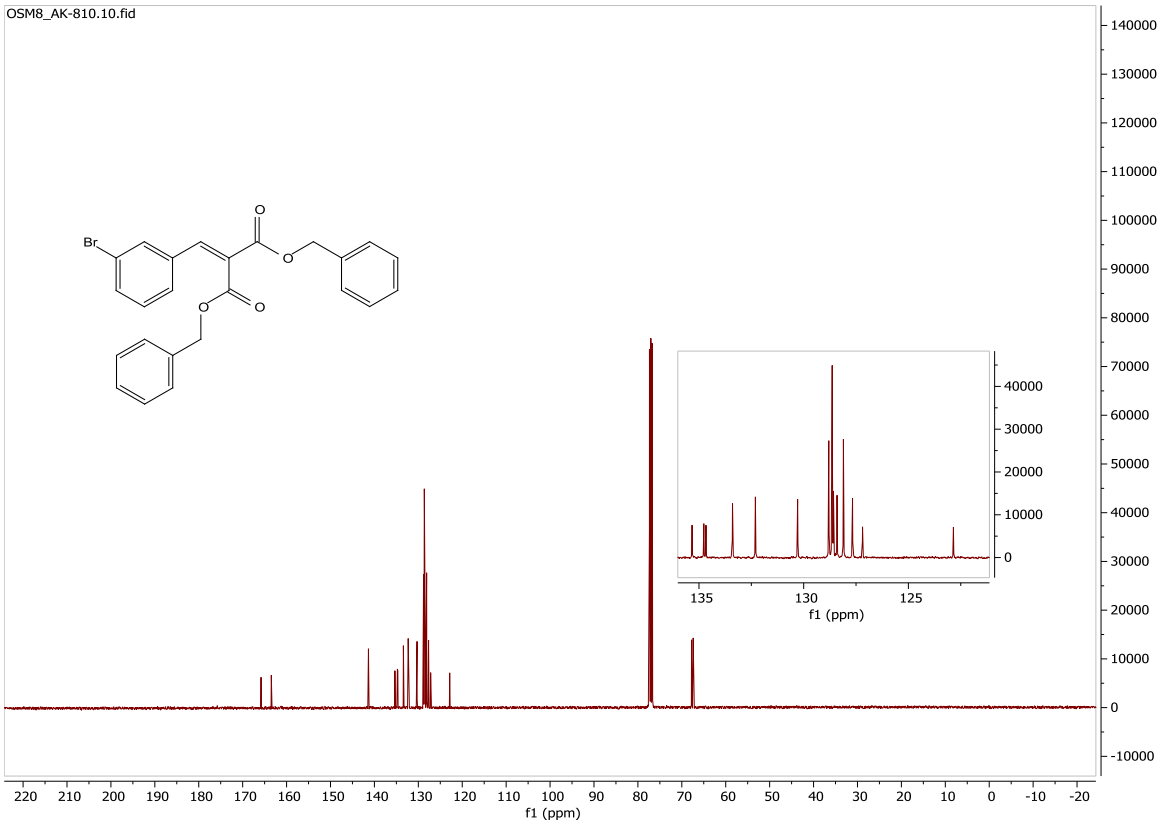
Compound **4s** ^{1}H NMR (400 MHz, $CDCl_3$)



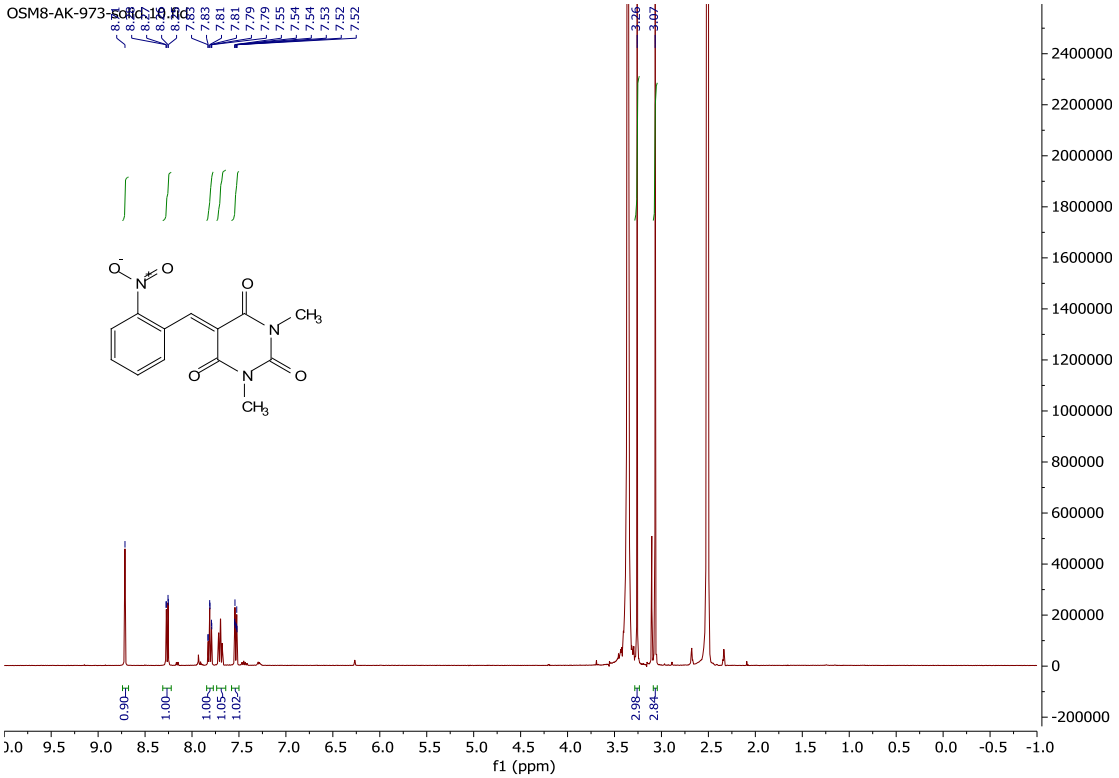
Compound **4t** ^{1}H NMR (400 MHz, DMSO-*d6*)



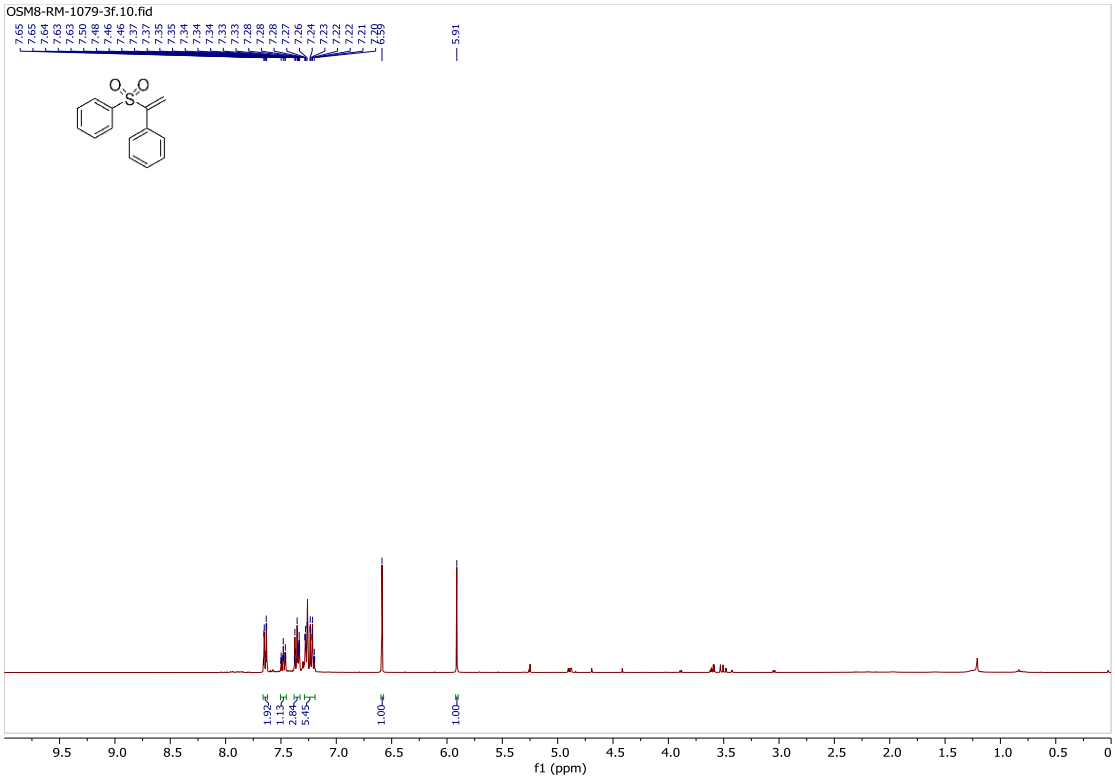
Compound **4t** ^{13}C NMR (400 MHz, DMSO-*d6*)



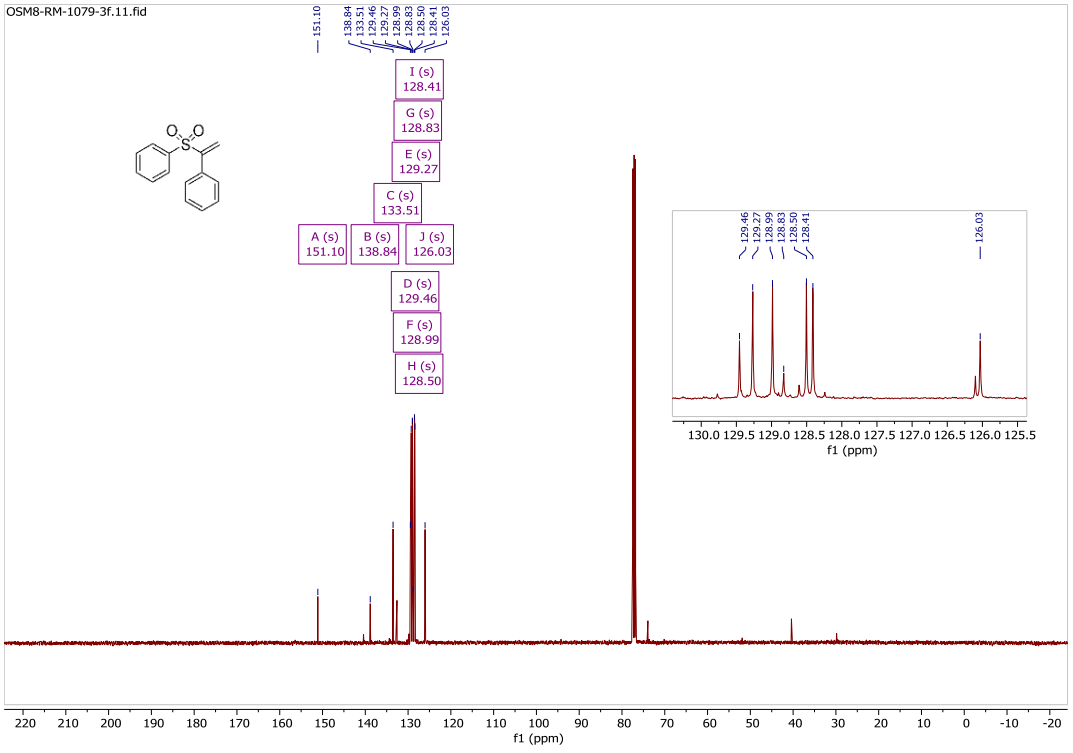
Compound **4u** ^{1}H NMR (400 MHz, DMSO-*d6*)



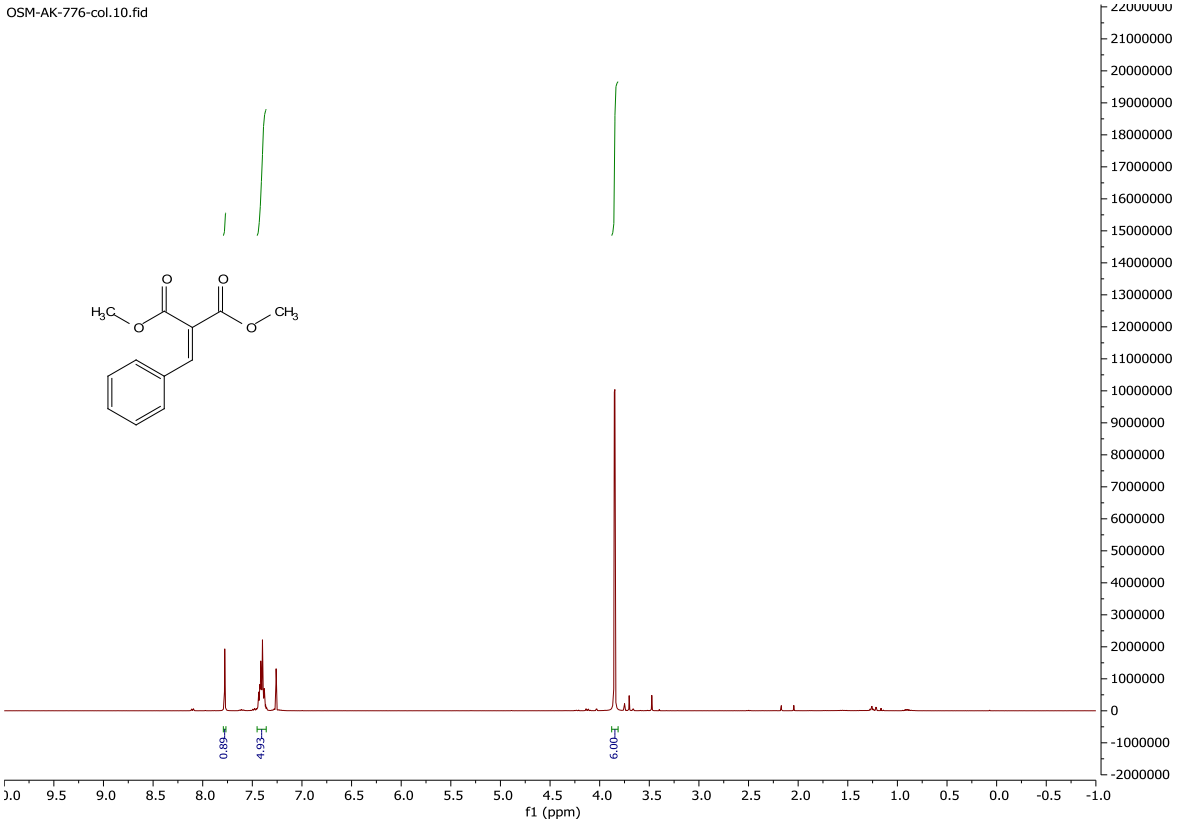
Compound **4x** ^{1}H NMR (400 MHz, $CDCl_3$)



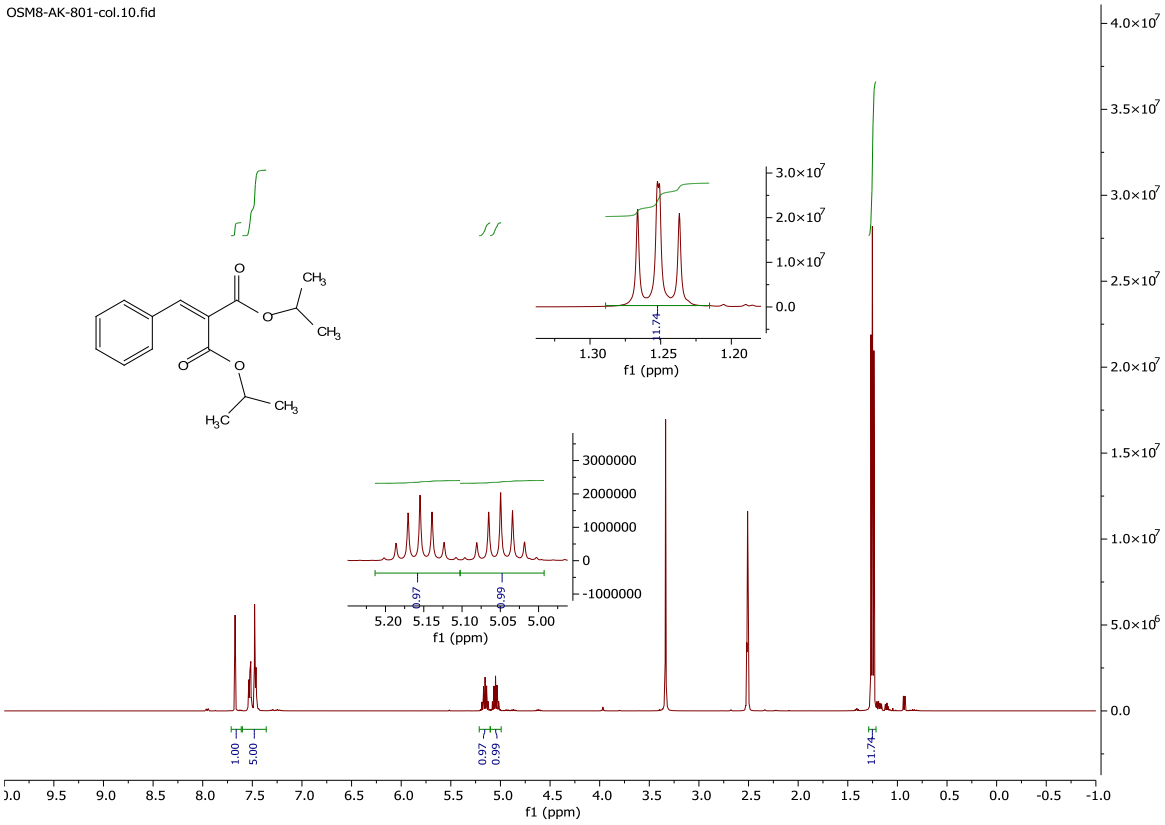
Compound **4x** ^{13}C NMR (400 MHz, $CDCl_3$)



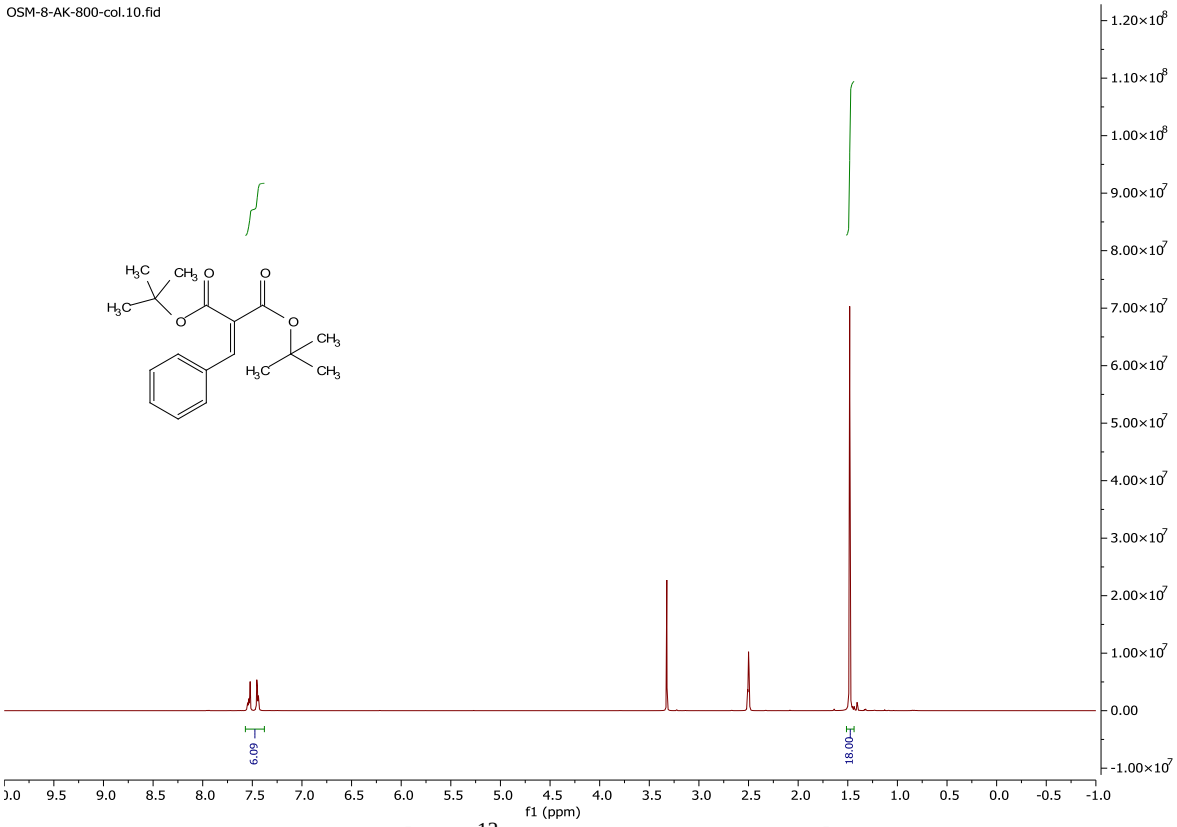
Compound **4y** ^{1}H NMR (400 MHz, $CDCl_3$)



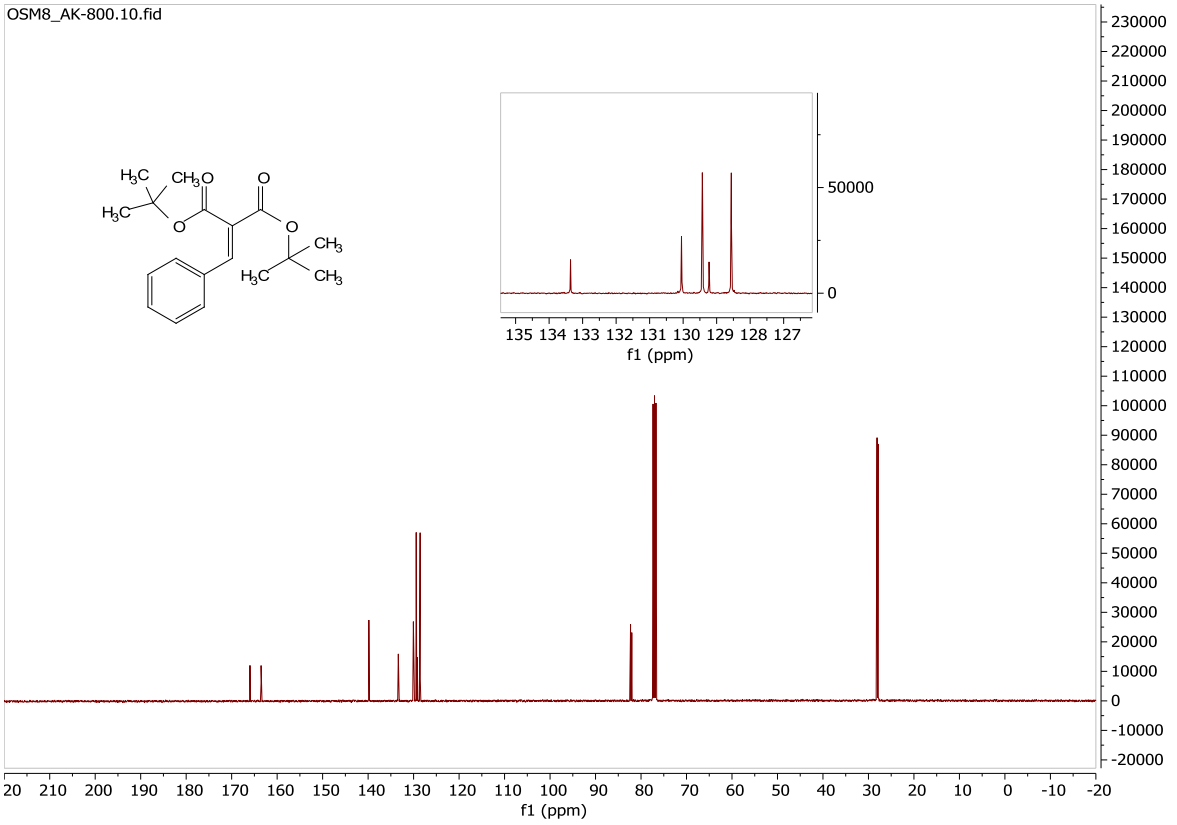
Compound **4z** ^{1}H NMR (400 MHz, DMSO-*d6*)



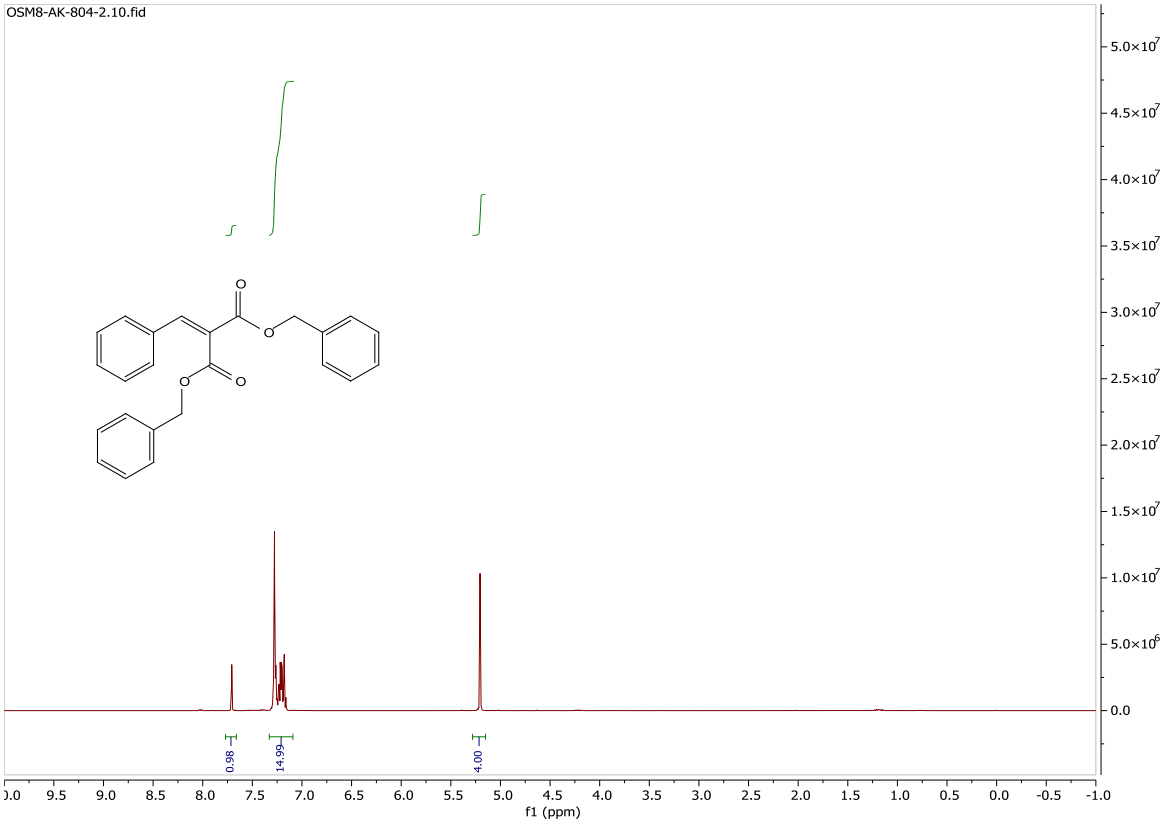
Compound **4aa** ^{1}H NMR (400 MHz, DMSO-*d6*)



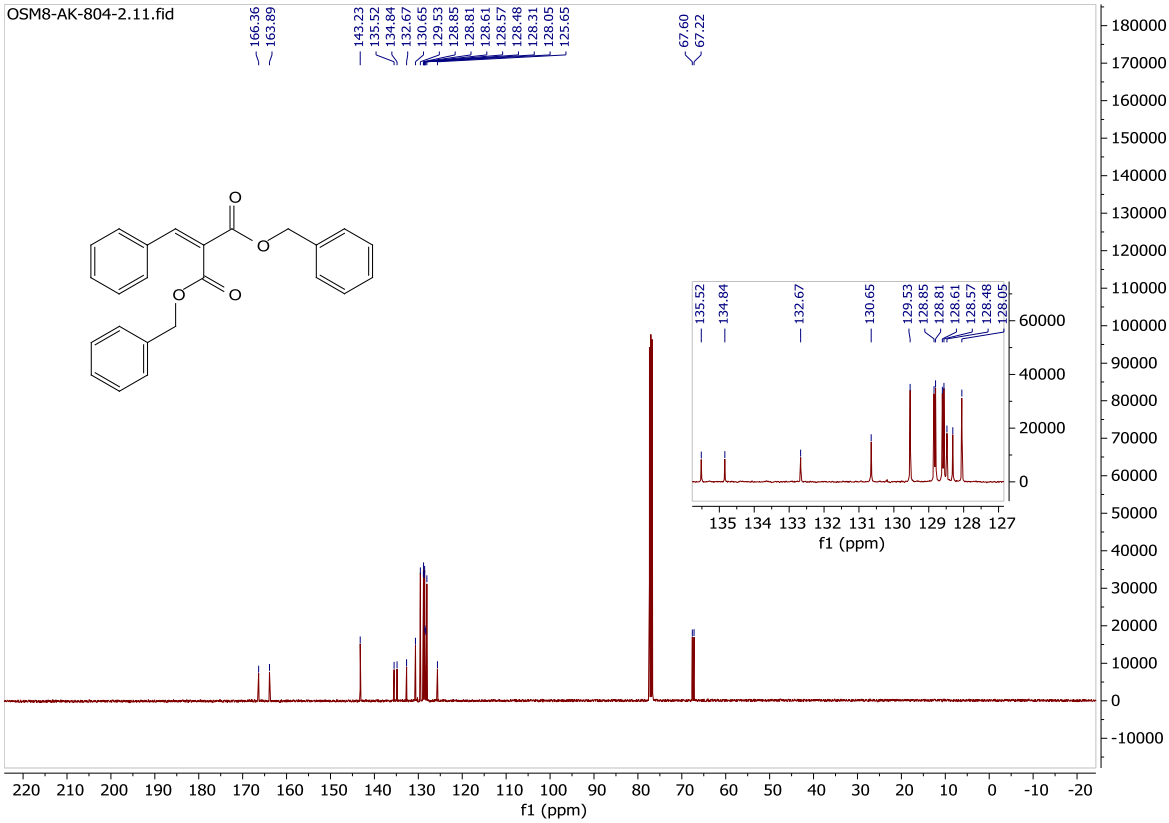
Compound **4aa** ^{13}C NMR (400 MHz, $CDCl_3$)



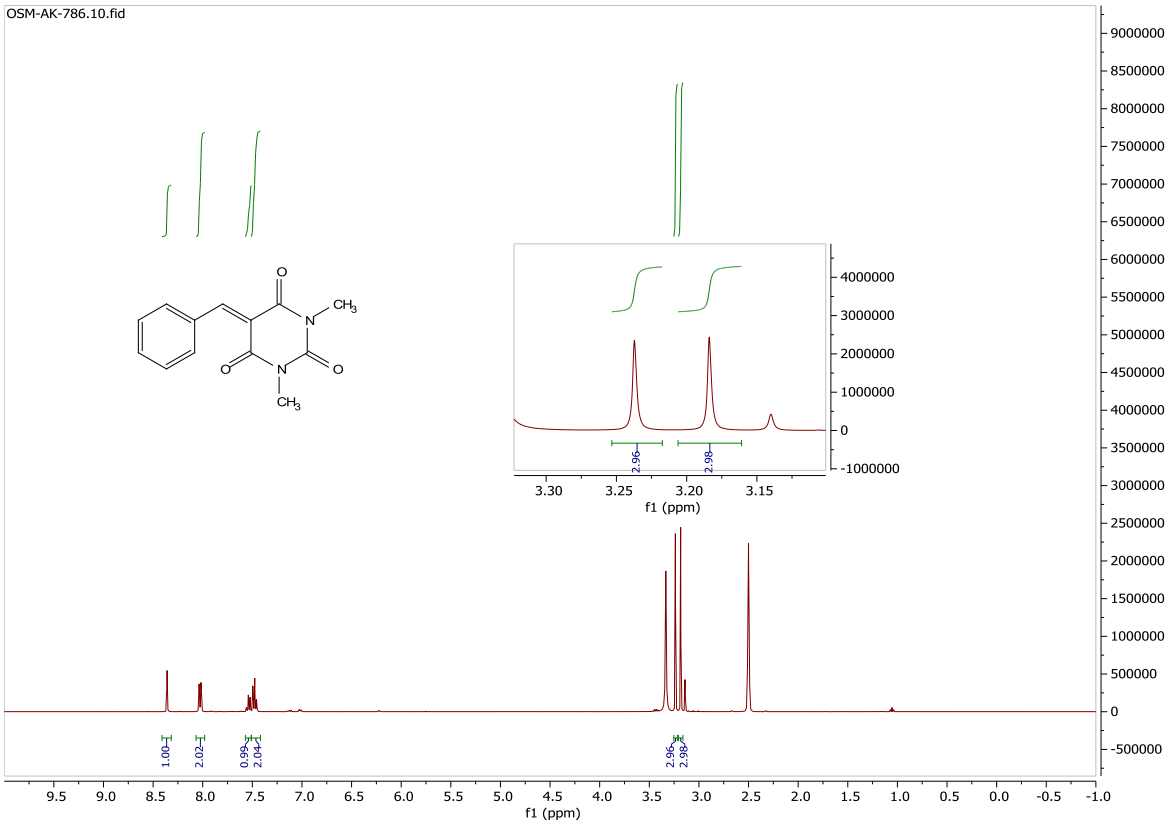
Compound **4ab** ^{1}H NMR (400 MHz, $CDCl_3$)



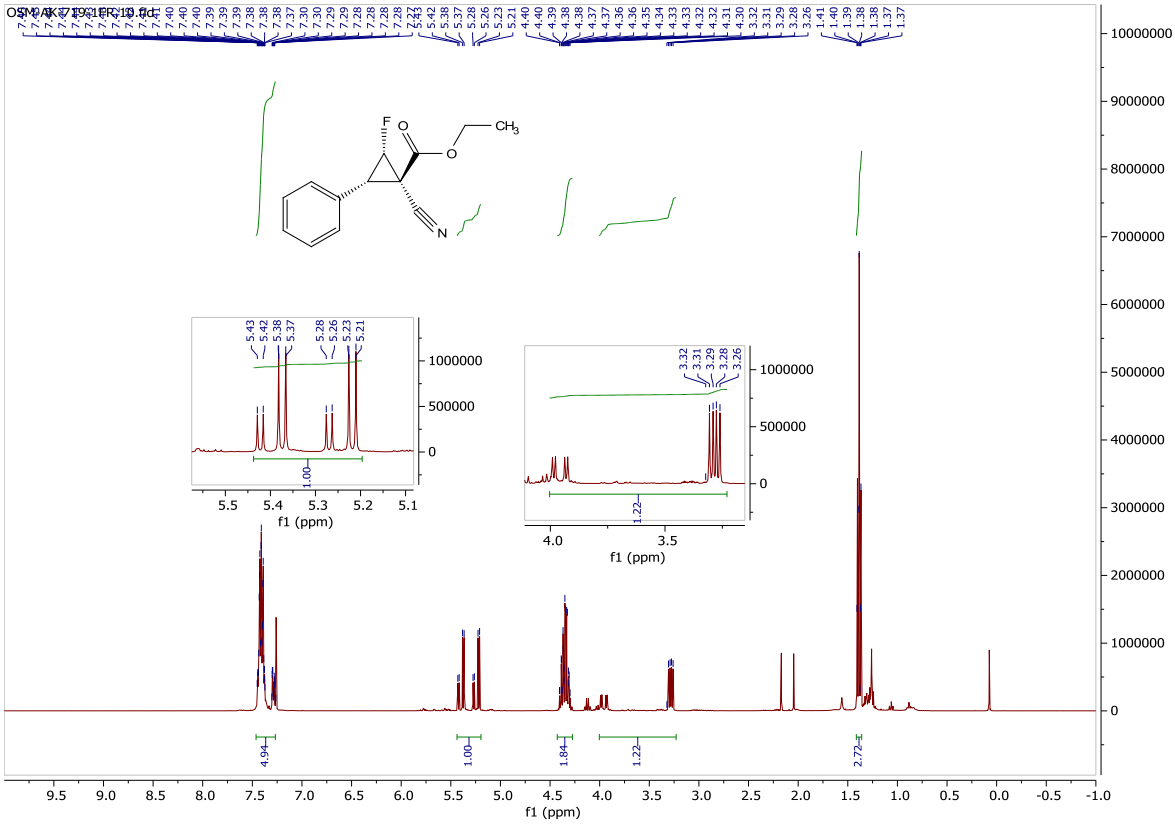
Compound **4ab** ^{13}C NMR (400 MHz, $CDCl_3$)



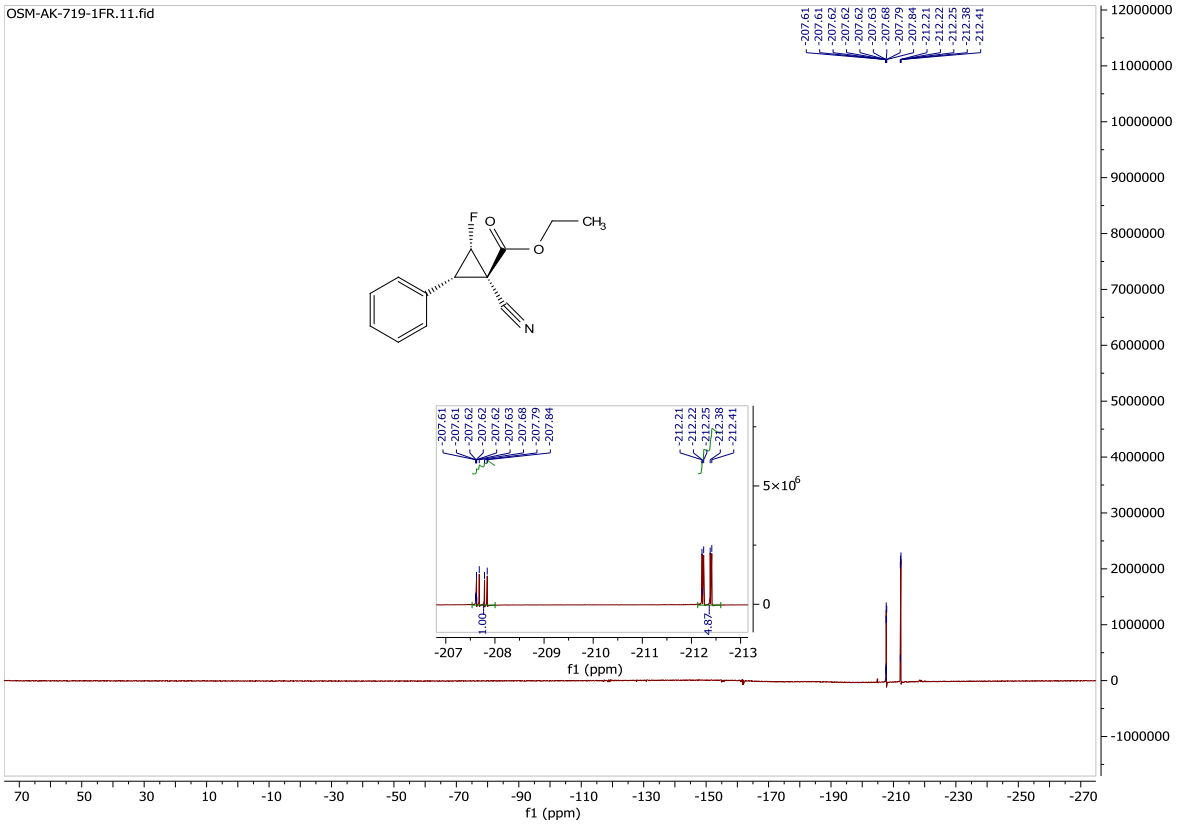
Compound **4ac** ^{1}H NMR (400 MHz, DMSO-*d6*)



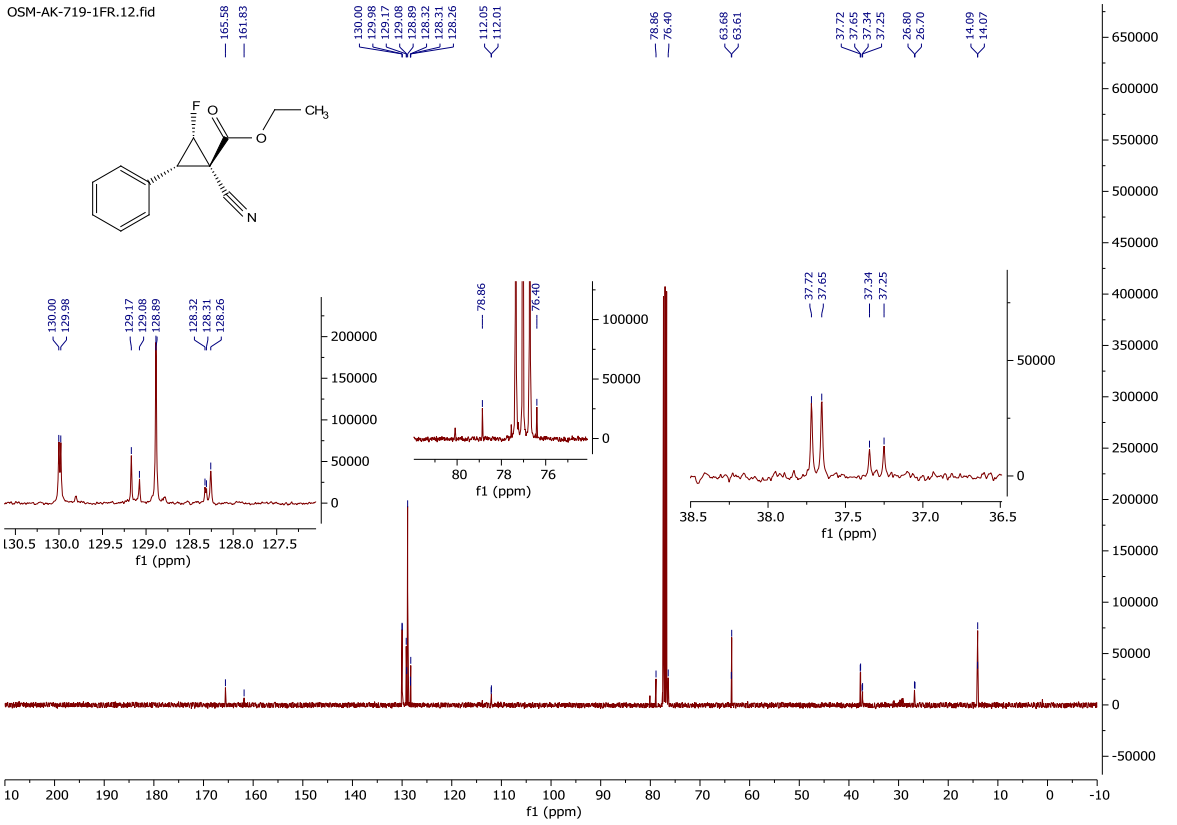
Enriched (1S*,2S*,3S*)-**5a** ^{1}H NMR (400 MHz, $CDCl_3$)



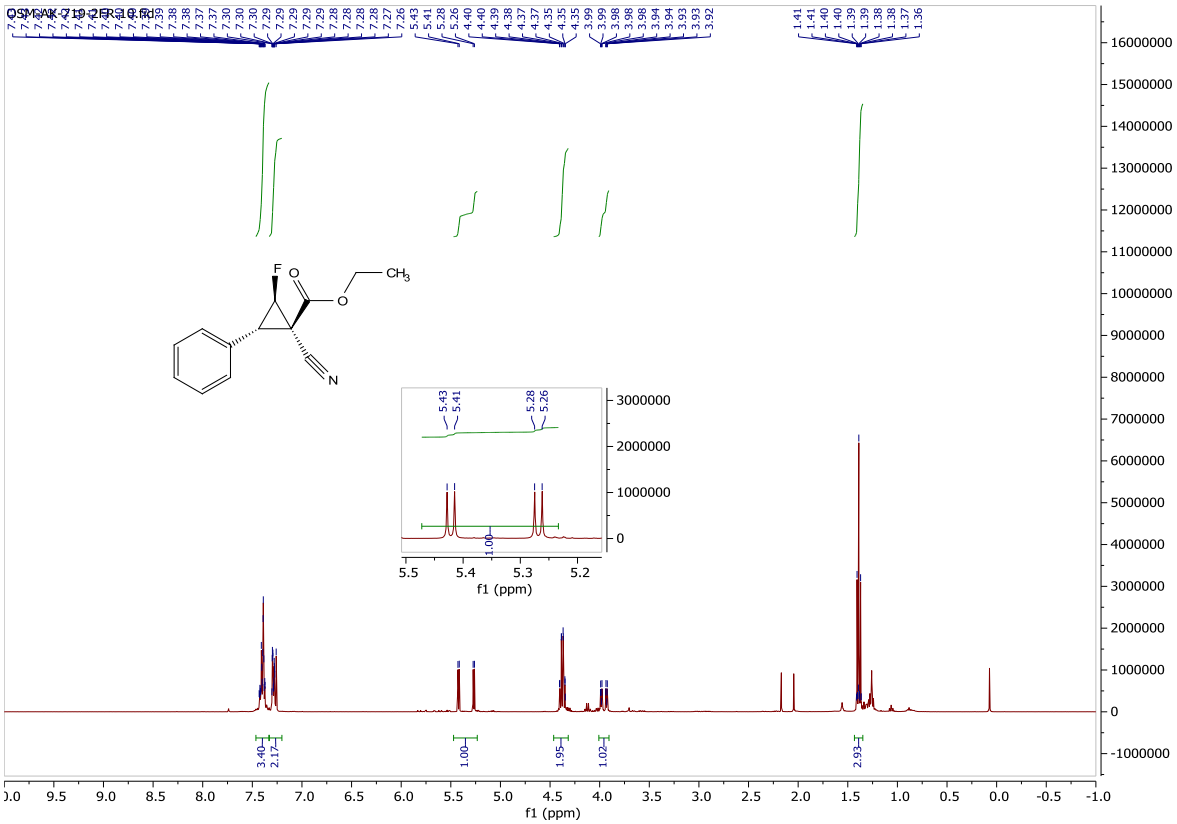
Enriched (1S*,2S*,3S*)-**5a** ^{19}F NMR (400 MHz, $CDCl_3$)



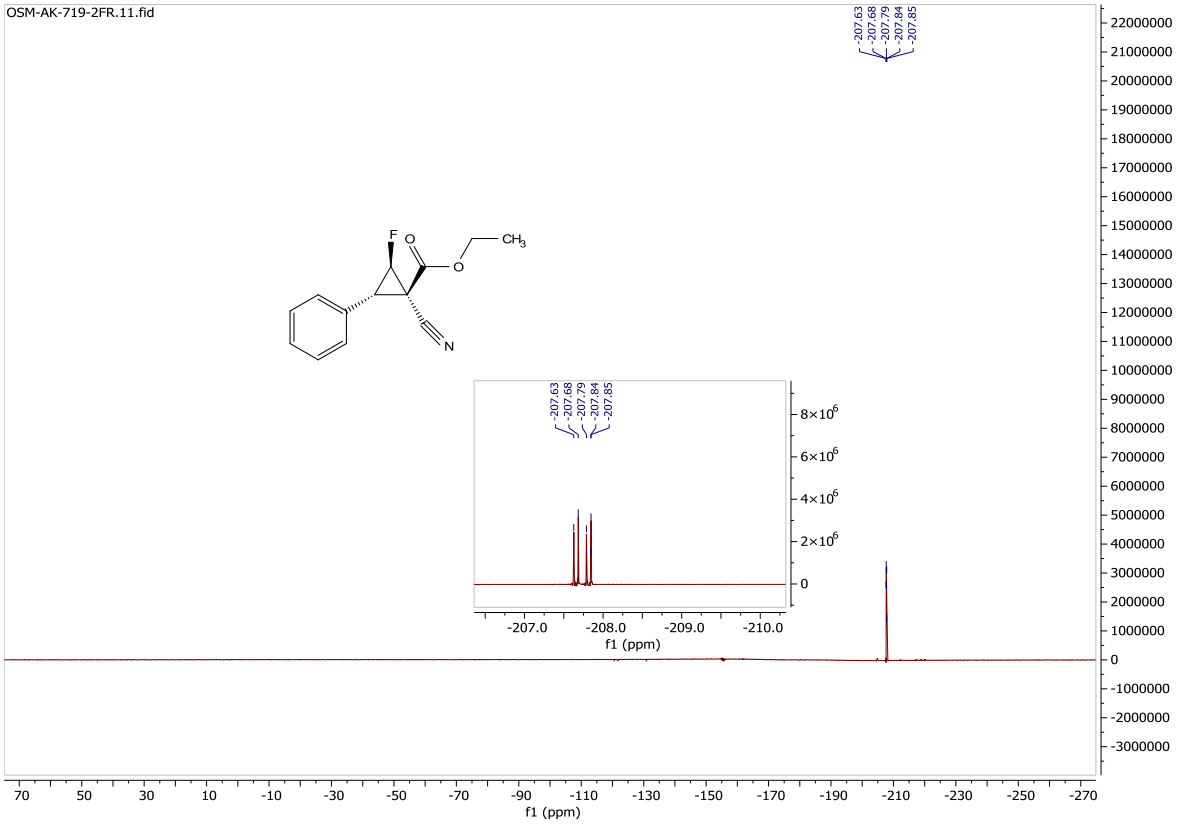
Enriched (1S*,2S*,3S*)-**5a** ^{13}C NMR (400 MHz, $CDCl_3$)



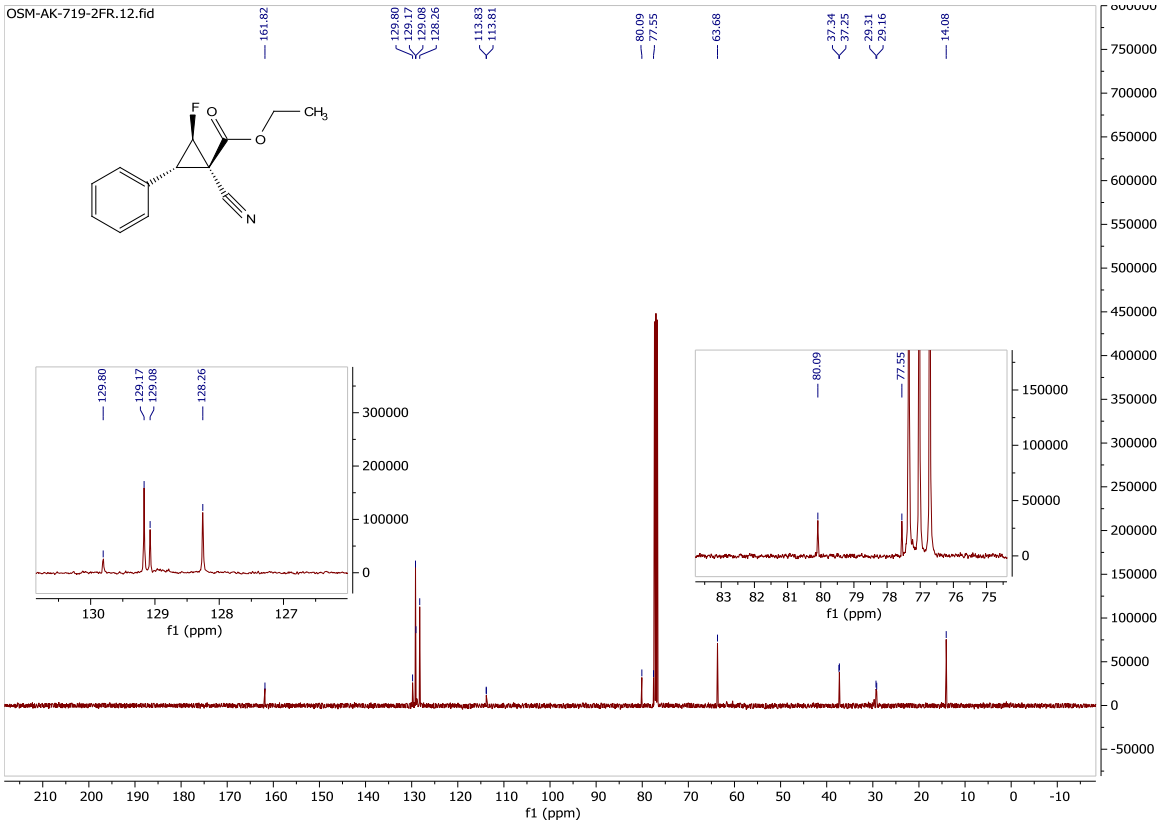
Compound (1S*,2R*,3S*)-**5a** ^{1}H NMR (400 MHz, $CDCl_3$)



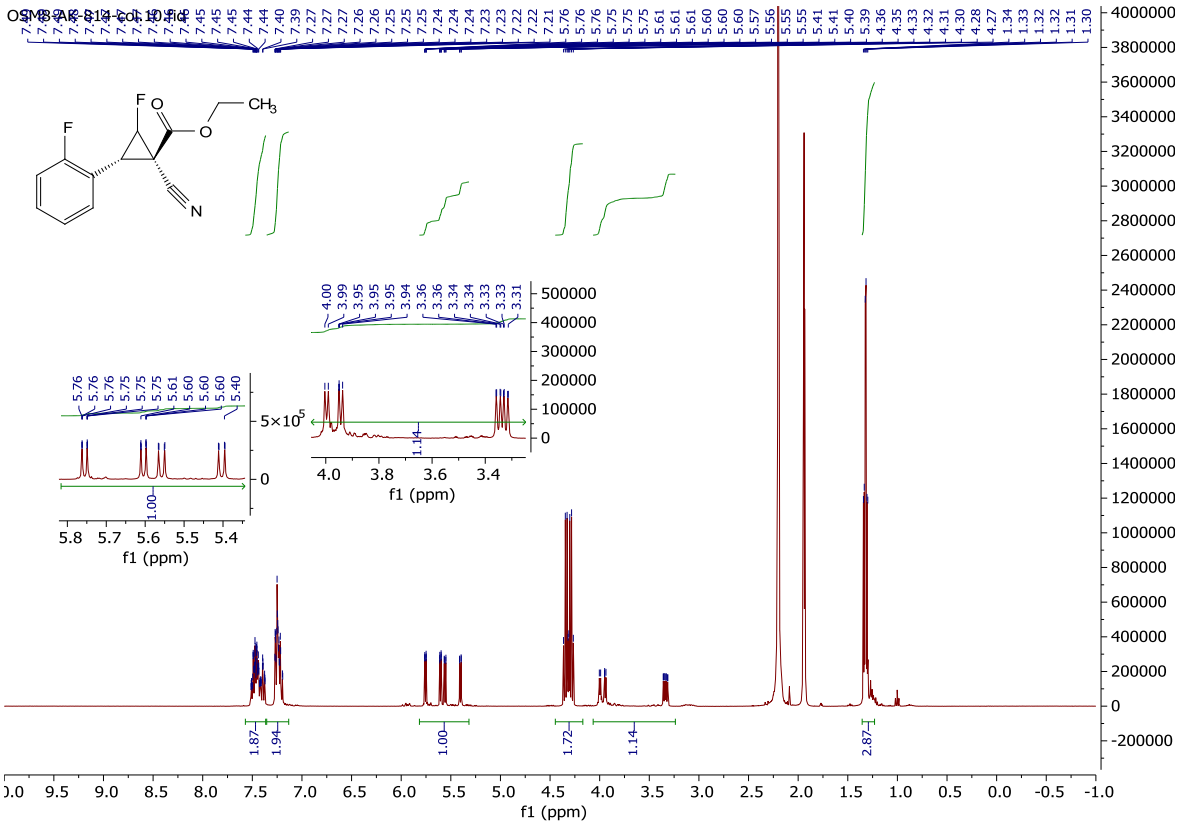
Compound (1S*,2R*,3S*)-**5a** ^{19}F NMR (400 MHz, $CDCl_3$)



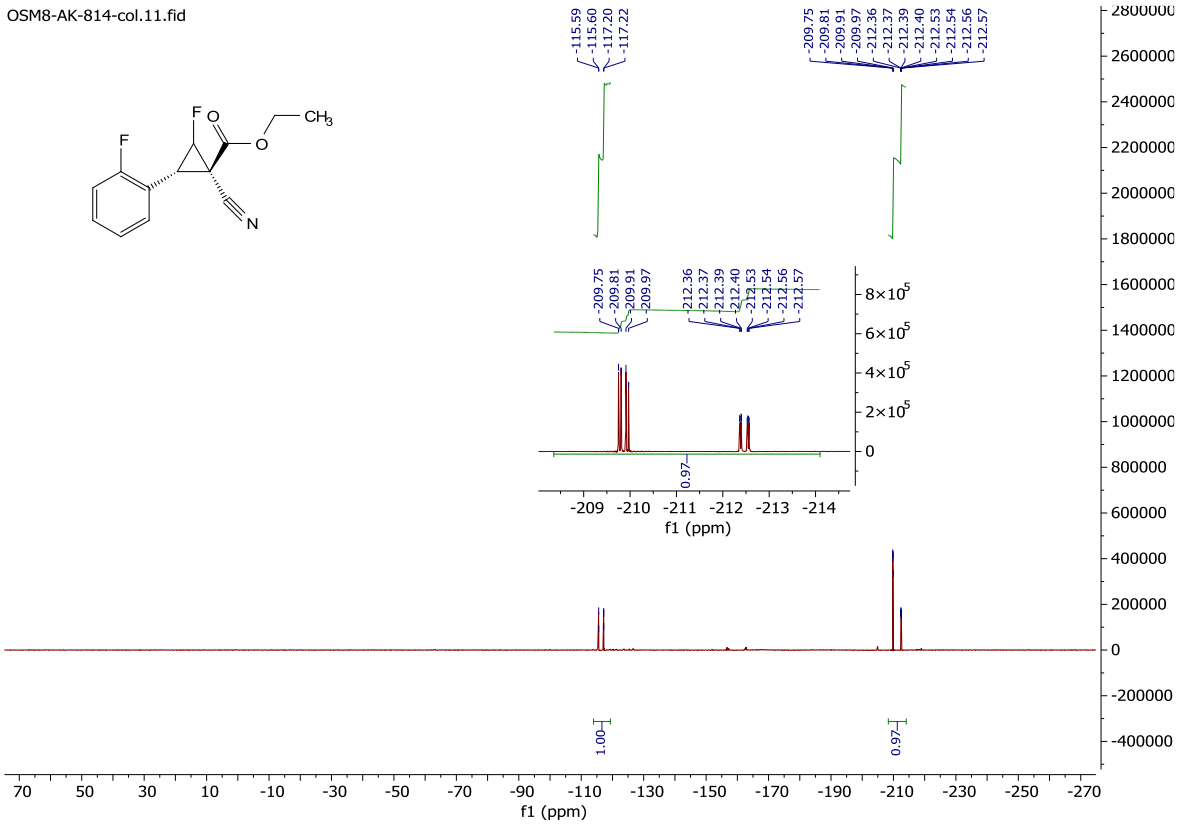
Compound (1S*,2R*,3S*)-**5a** ^{13}C NMR (400 MHz, $CDCl_3$)



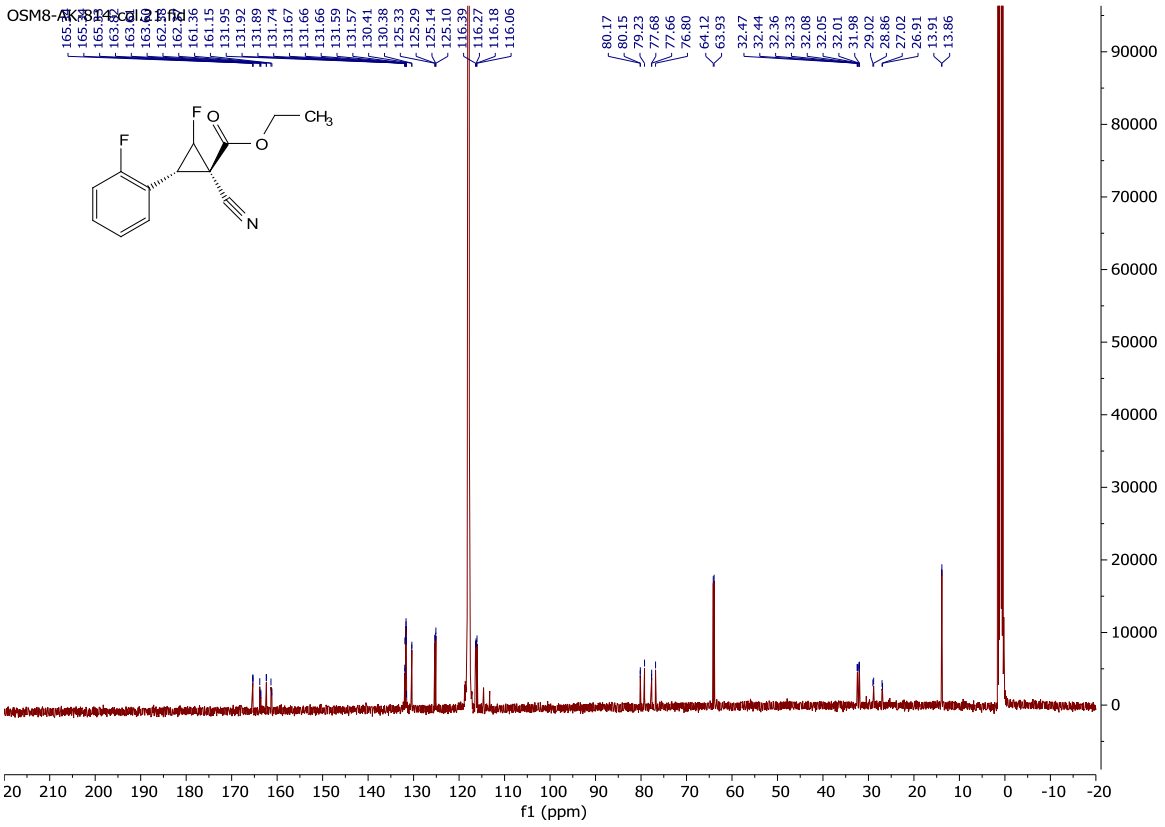
Compound **5b** ^{1}H NMR (400 MHz, MeCN-*d3*)



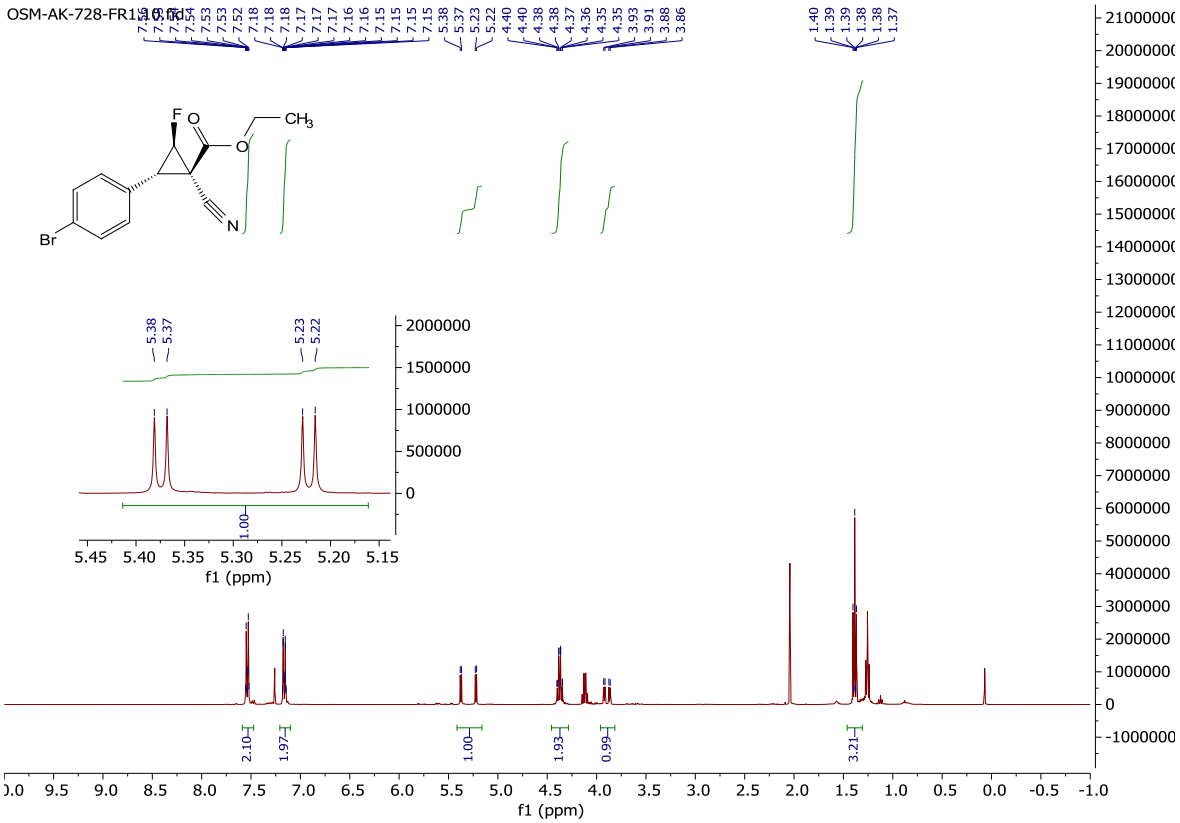
Compound **5b** ^{19}F NMR (400 MHz, MeCN-*d3*)



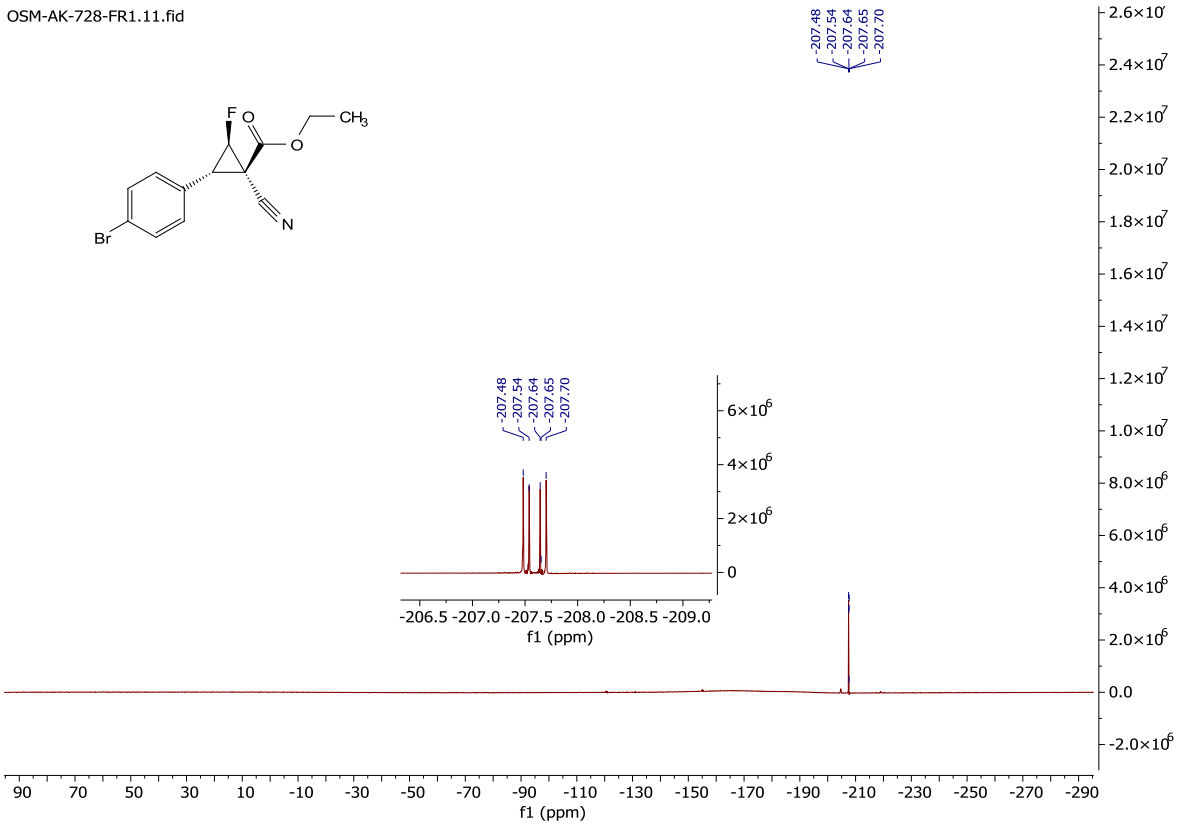
Compound **5b** ^{13}C NMR (400 MHz, MeCN-*d3*)



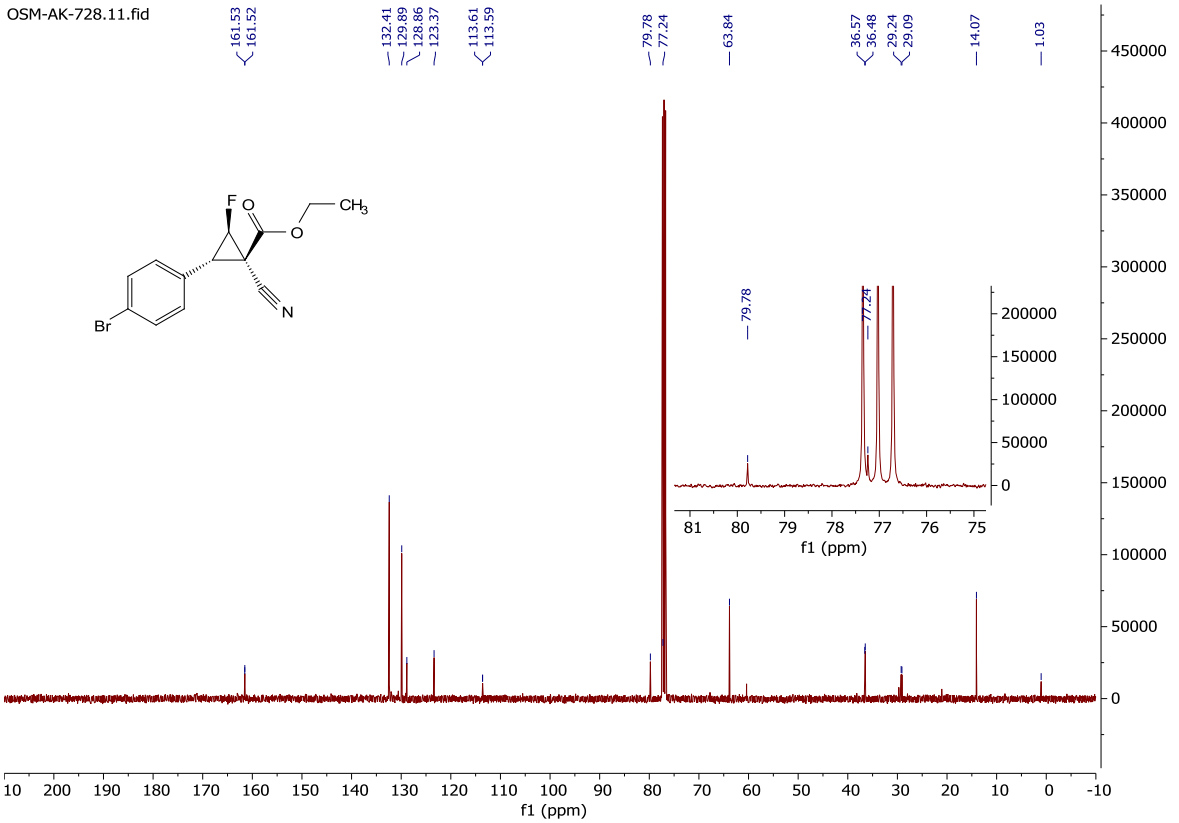
Compound (1S*,2S*,3R*)-**5c** ^{1}H NMR (400 MHz, $CDCl_3$)



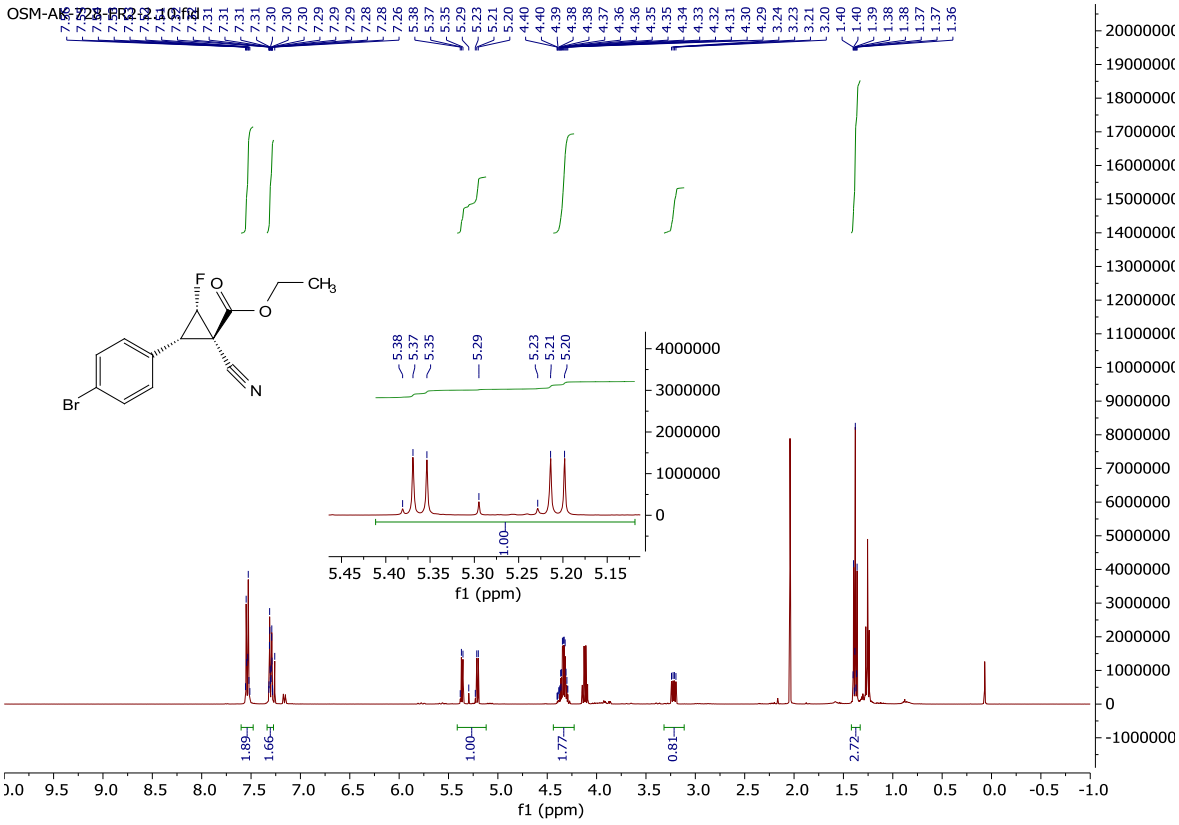
Compound (1S*,2S*,3R*)-**5c** ^{19}F NMR (400 MHz, $CDCl_3$)



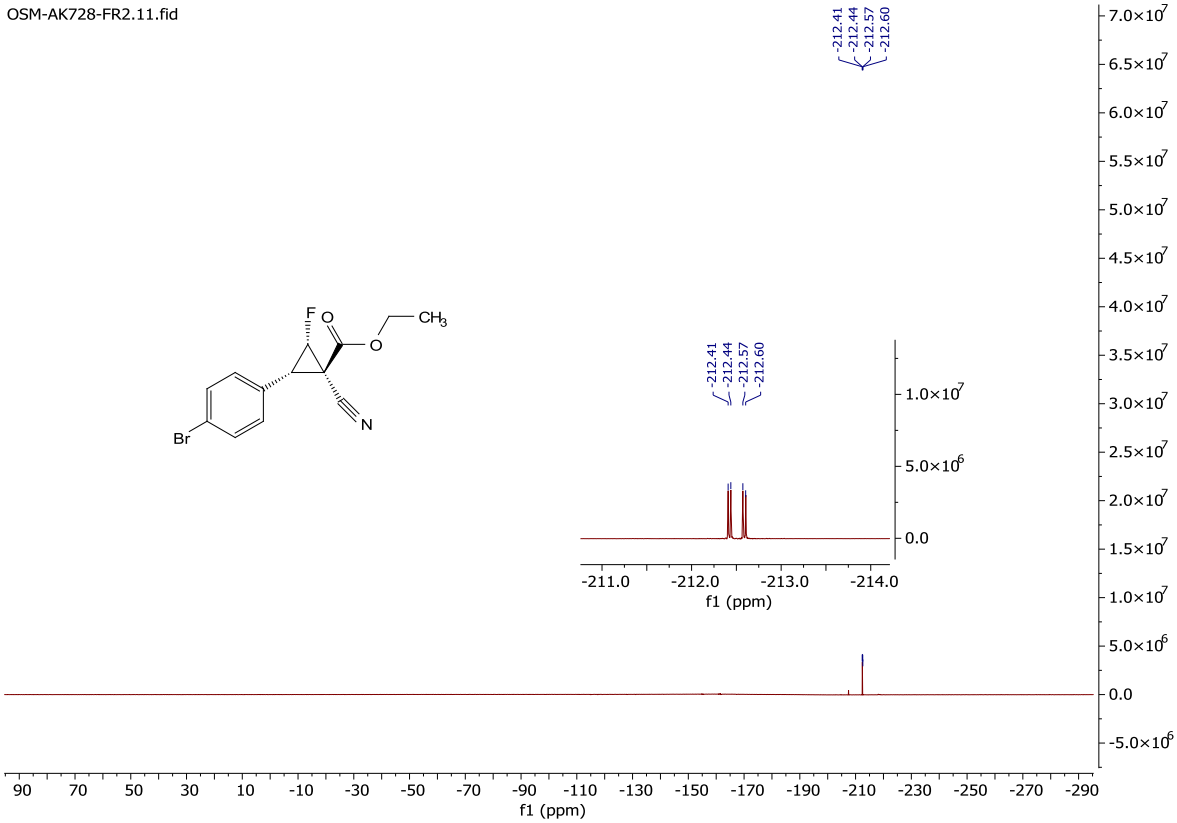
Compound (1S*,2S*,3R*)-**5c** ^{13}C NMR (400 MHz, $CDCl_3$)



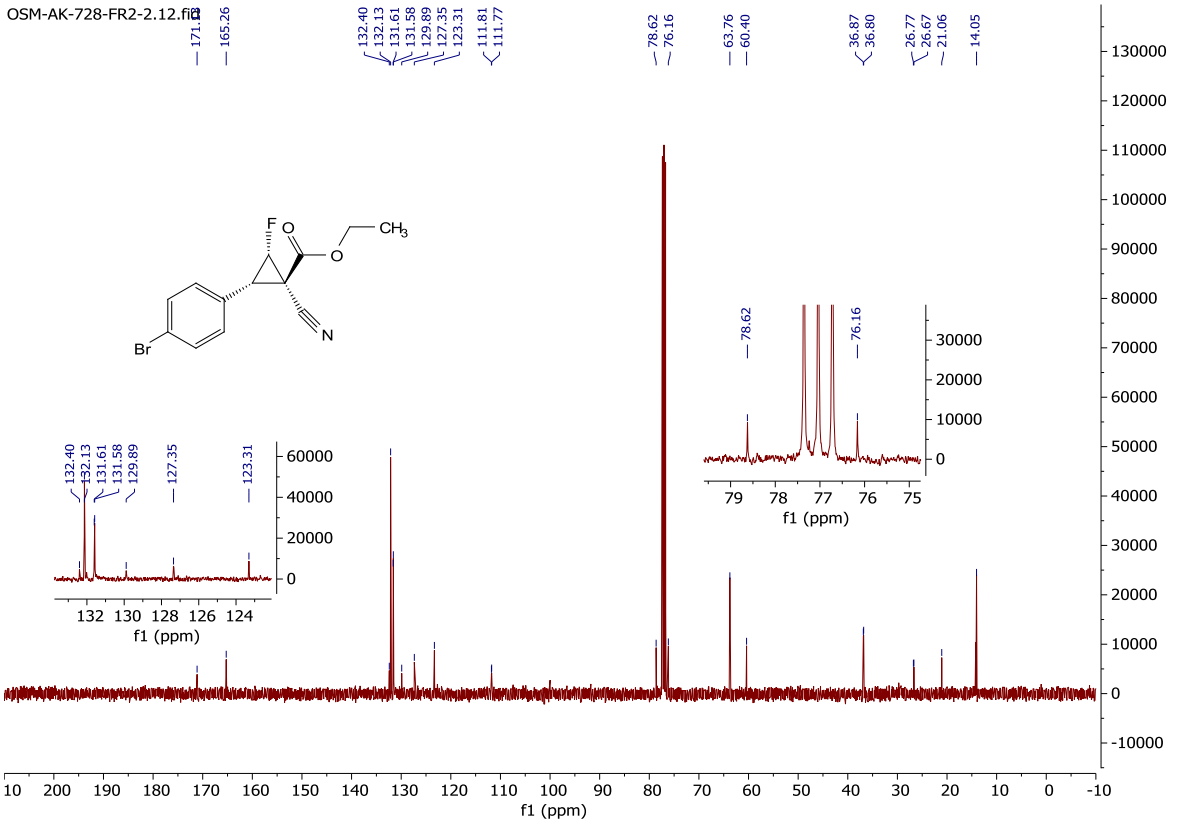
Compound (1S*,2S*,3S*)-**5c** ^{1}H NMR (400 MHz, $CDCl_3$)



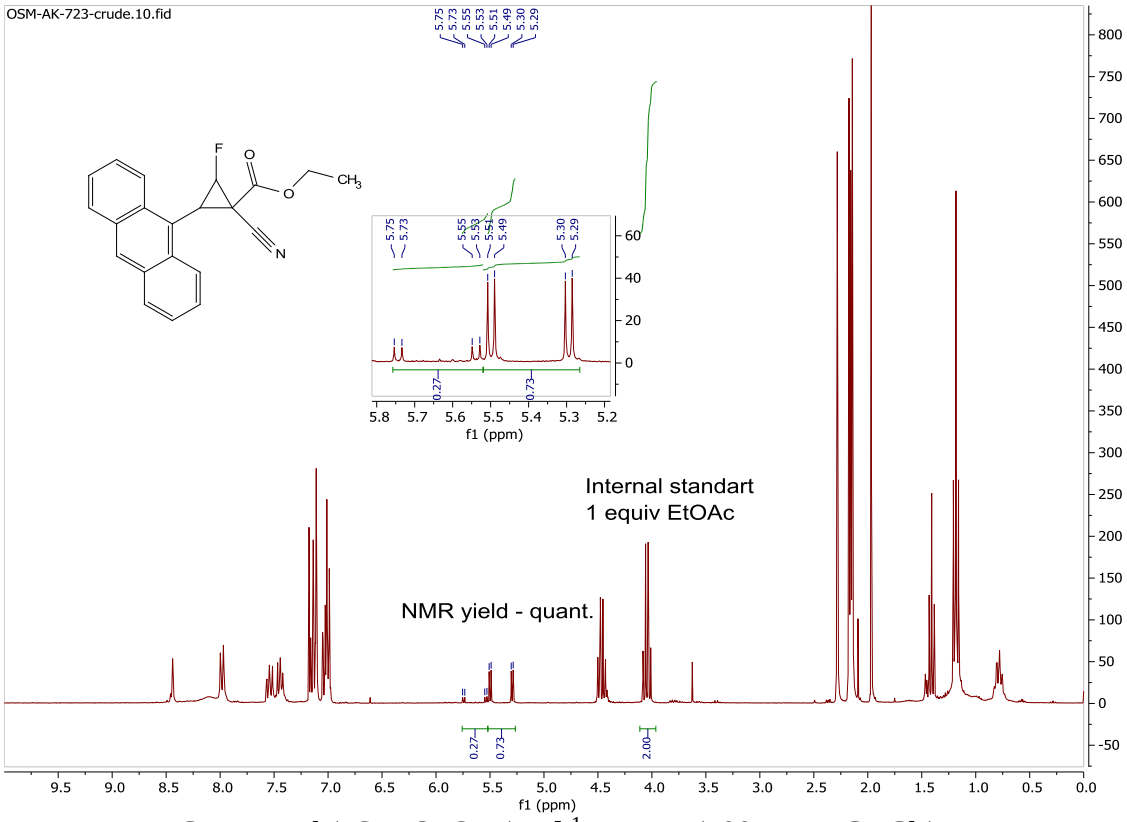
Compound (1S*,2S*,3S*)-**5c** ^{19}F NMR (400 MHz, $CDCl_3$)



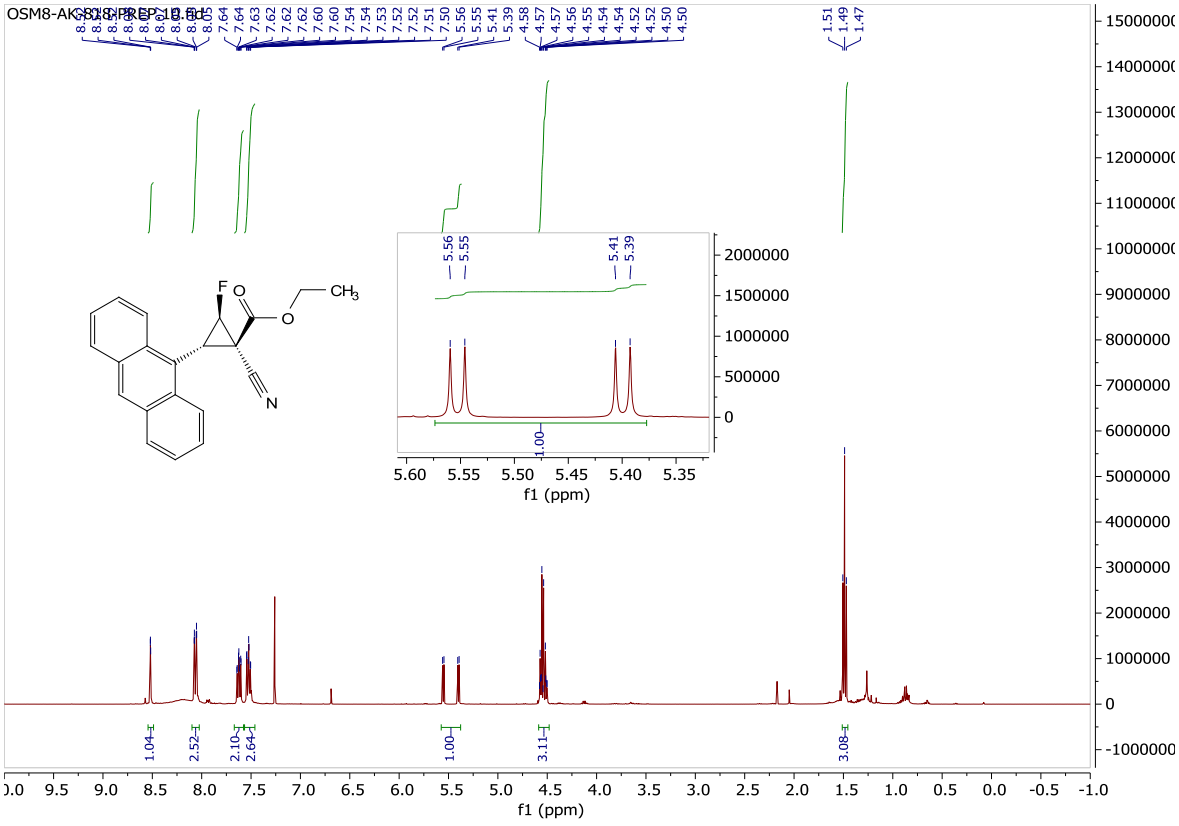
Compound (1S*,2S*,3S*)-**5c** ^{13}C NMR (400 MHz, $CDCl_3$)



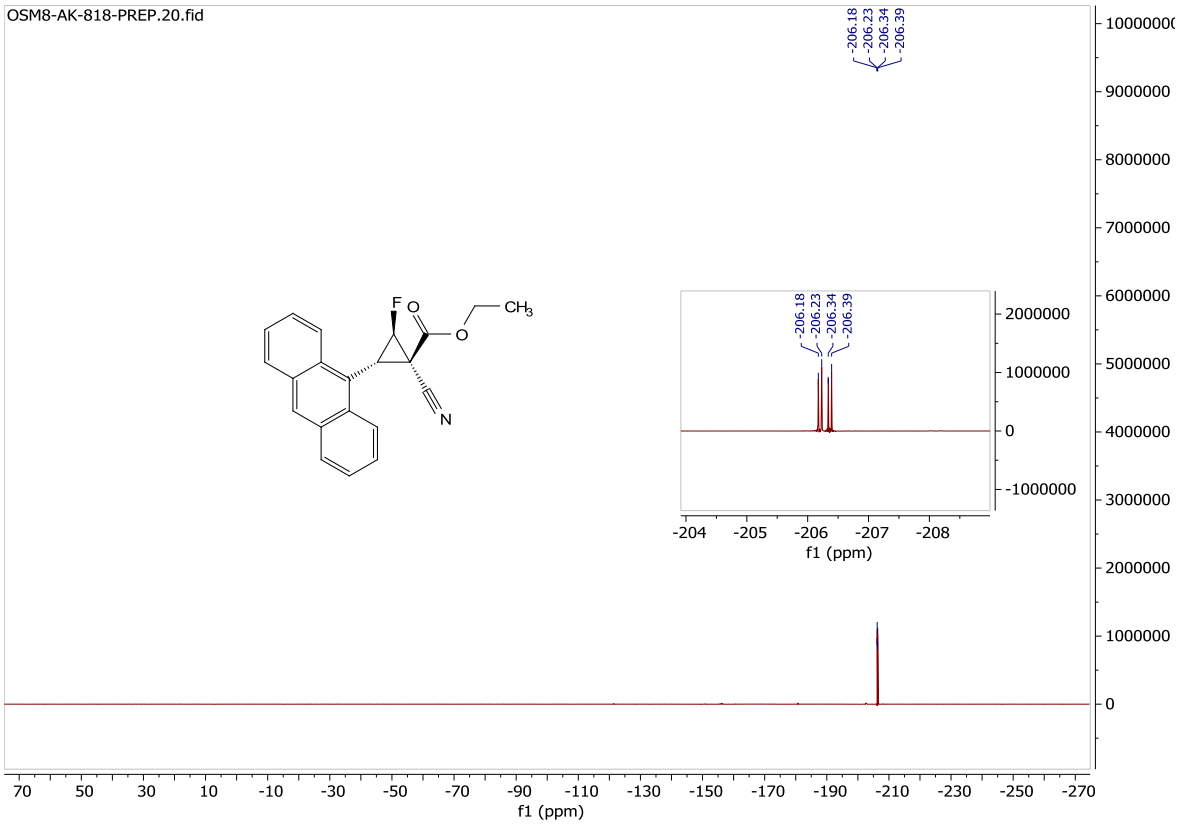
Compound **5d** crude ^{1}H NMR (400 MHz, $CDCl_3$)



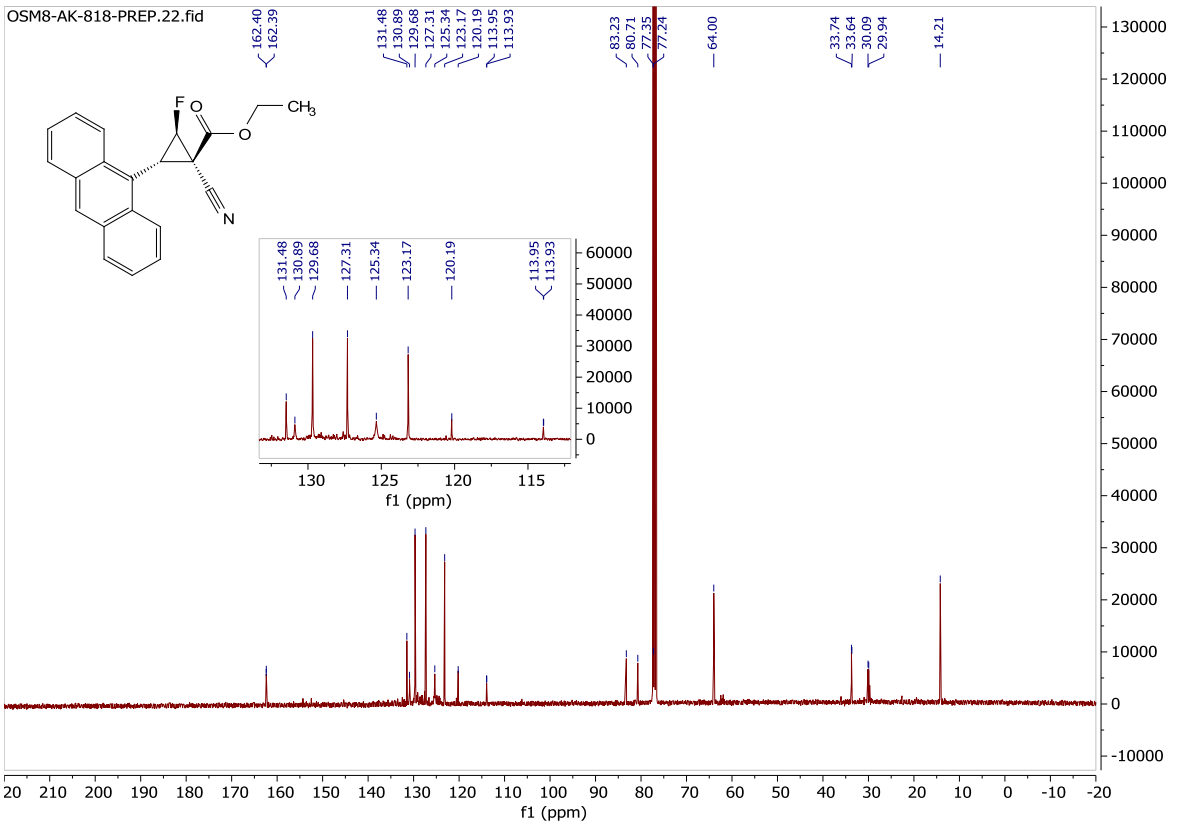
Compound (1S*,2S*,3R*)-**5d** ^{1}H NMR (400 MHz, $CDCl_3$)



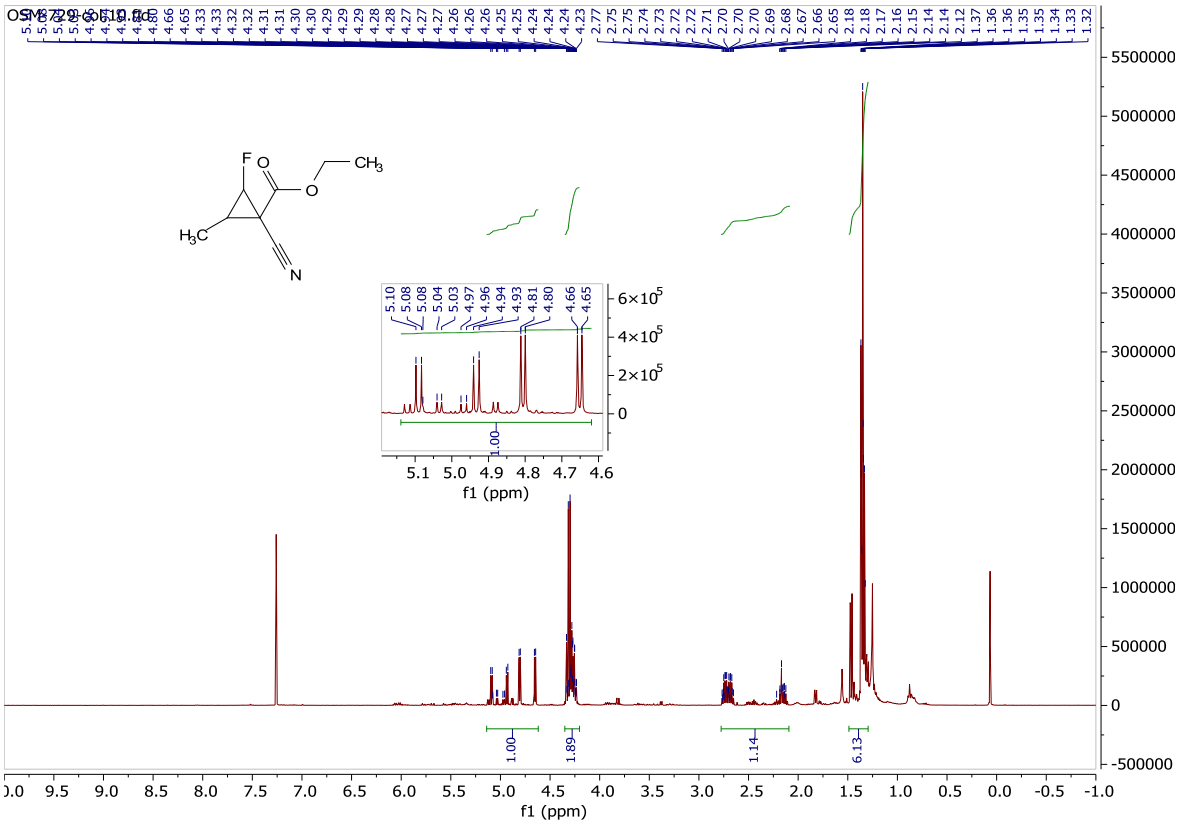
Compound (1S*,2S*,3R*)-**5d** ^{19}F NMR (400 MHz, $CDCl_3$)



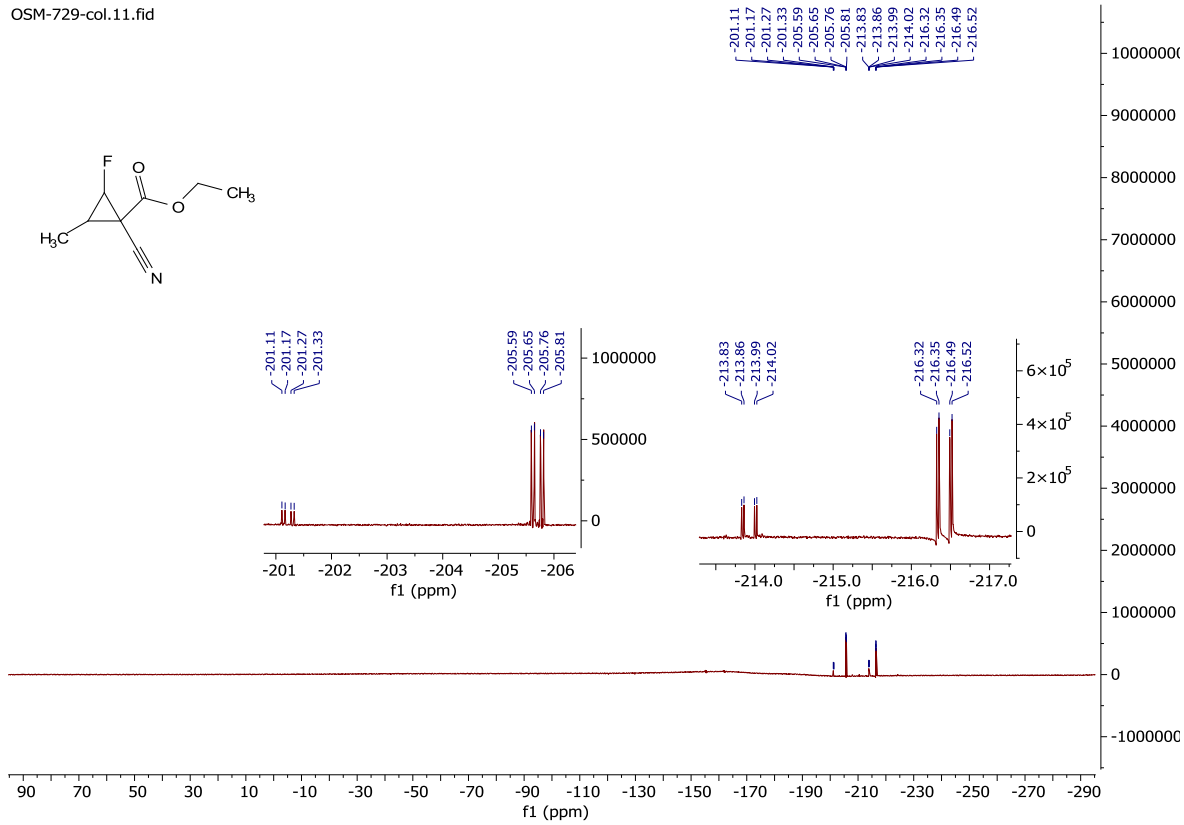
Compound (1S*,2S*,3R*)-**5d** ^{13}C NMR (400 MHz, $CDCl_3$)



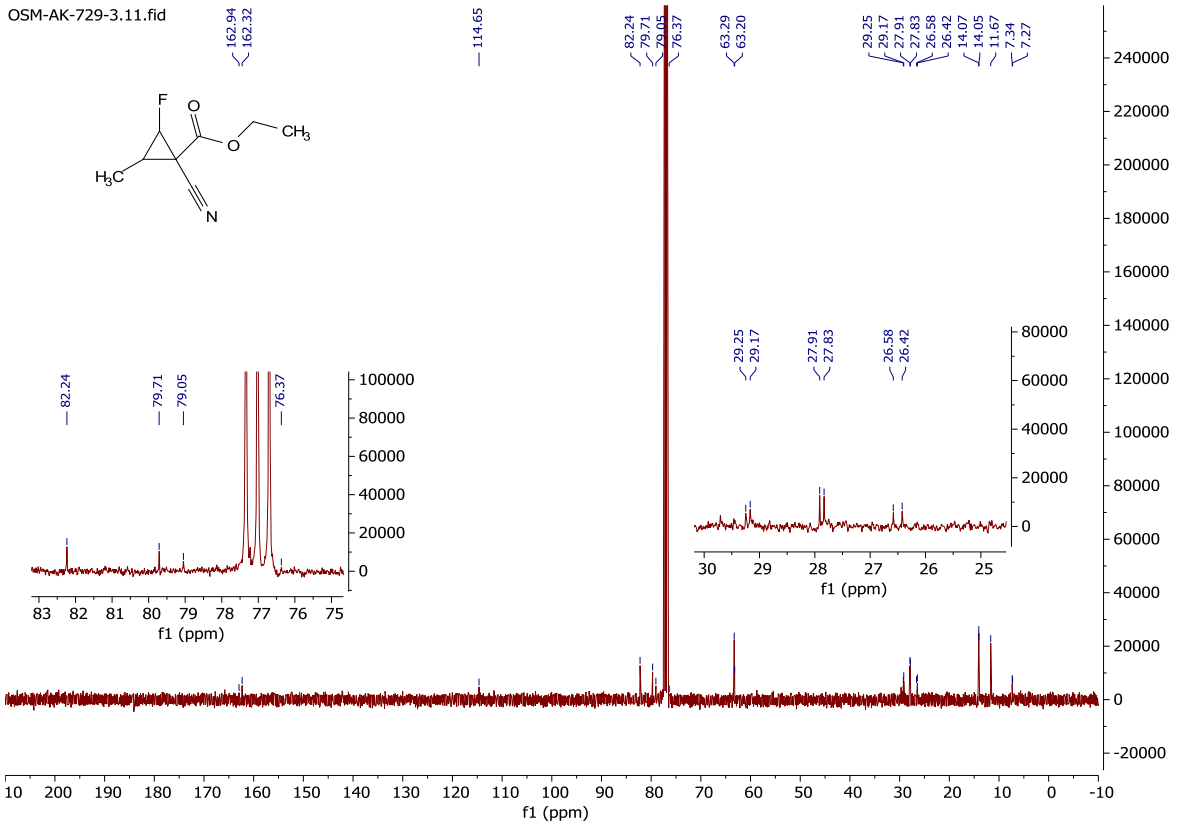
Compound **5e** ^{1}H NMR (400 MHz, $CDCl_3$)



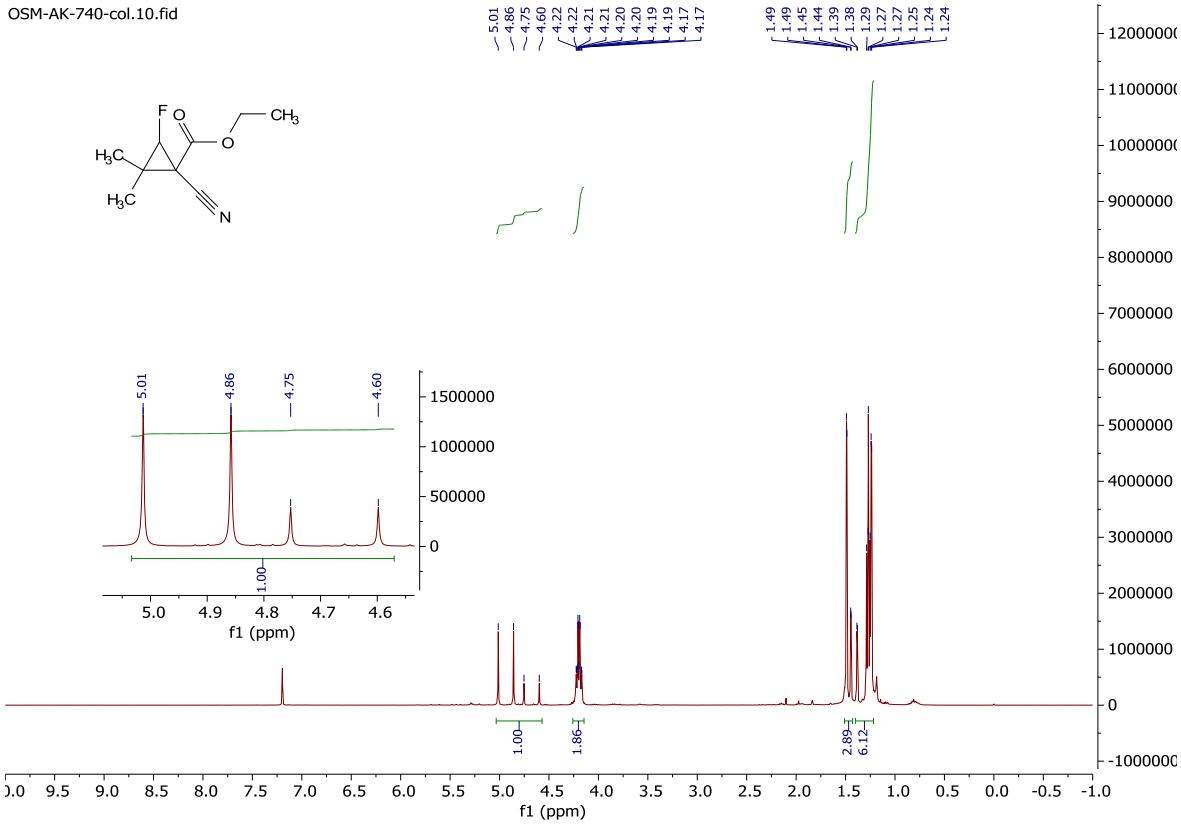
Compound **5e** ^{19}F NMR (400 MHz, $CDCl_3$)



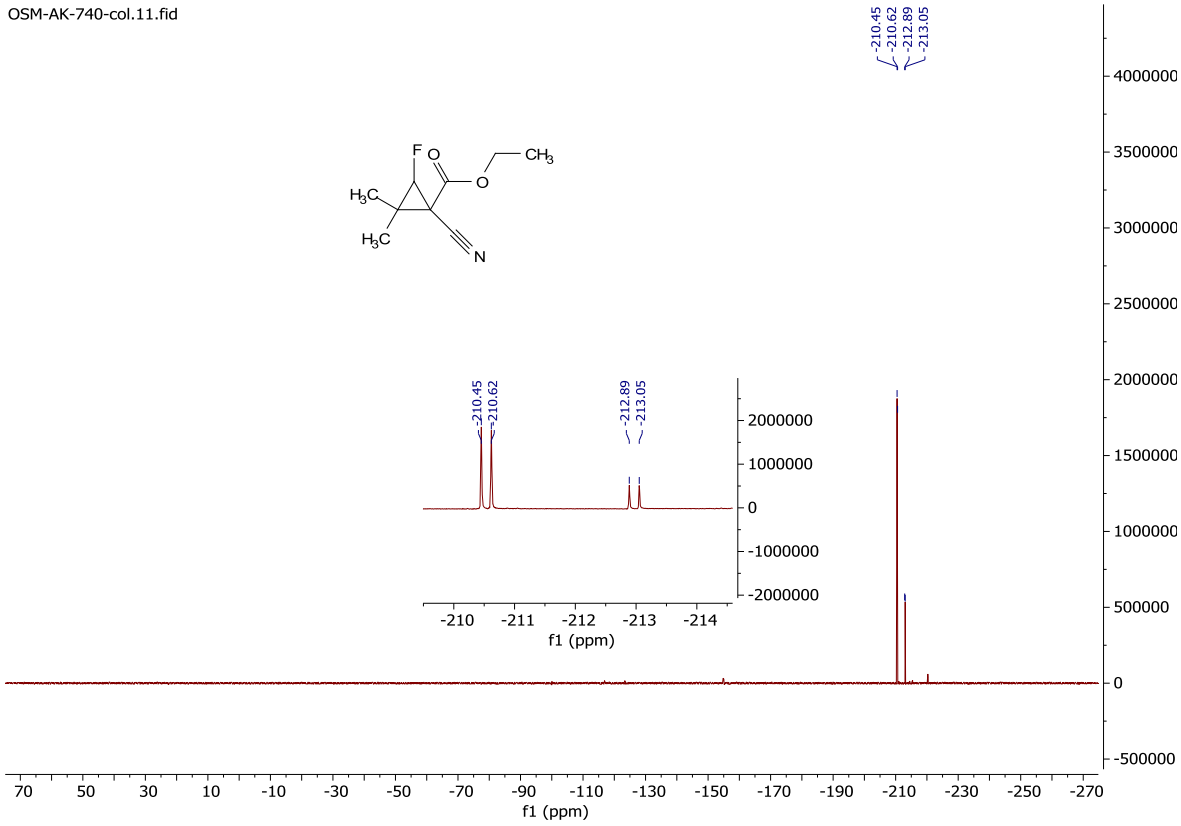
Compound **5e** ^{13}C NMR (400 MHz, $CDCl_3$)



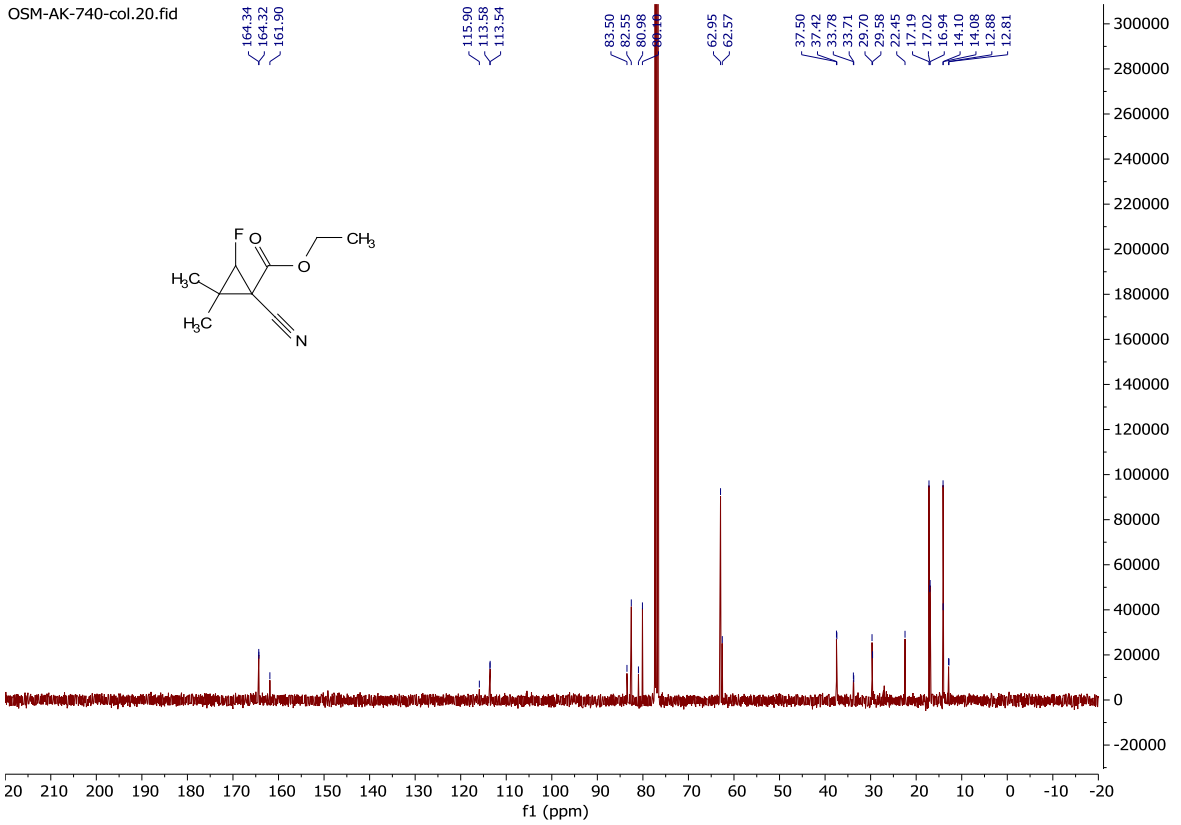
Compound **5f** ^{1}H NMR (400 MHz, $CDCl_3$)



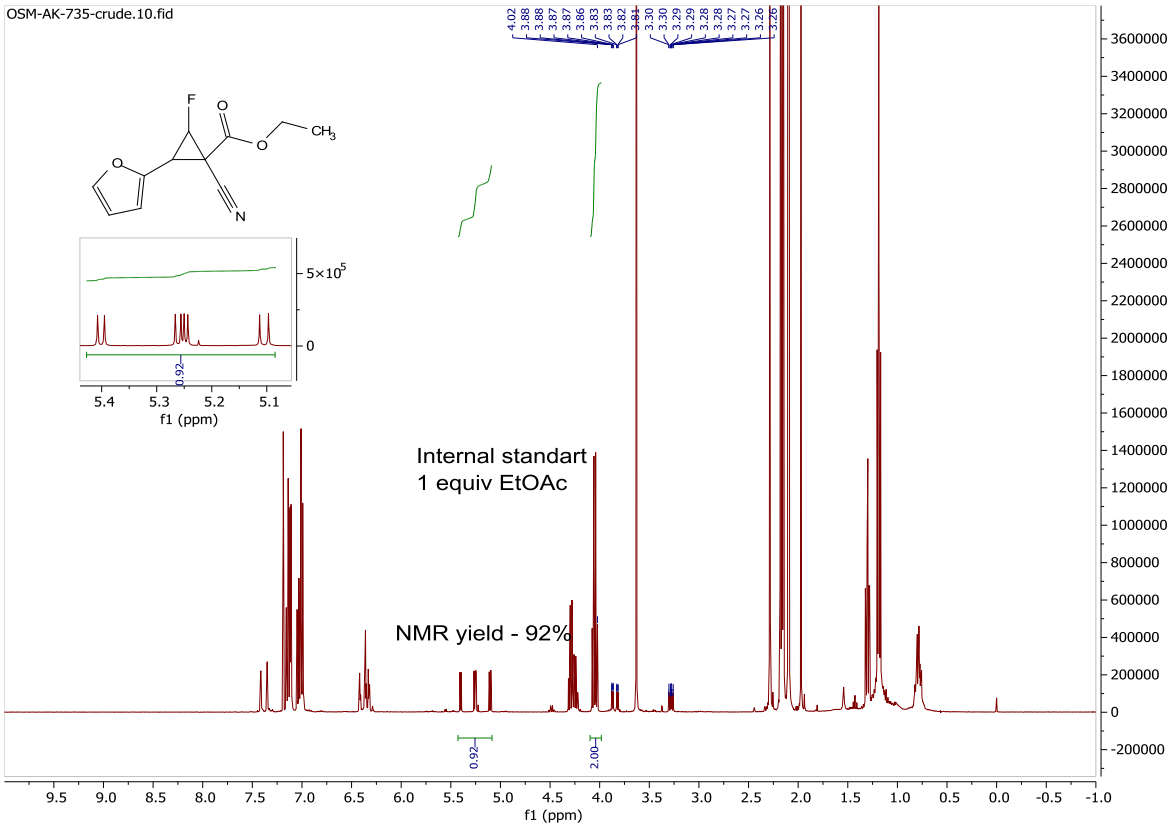
Compound **5f** ^{19}F NMR (400 MHz, $CDCl_3$)



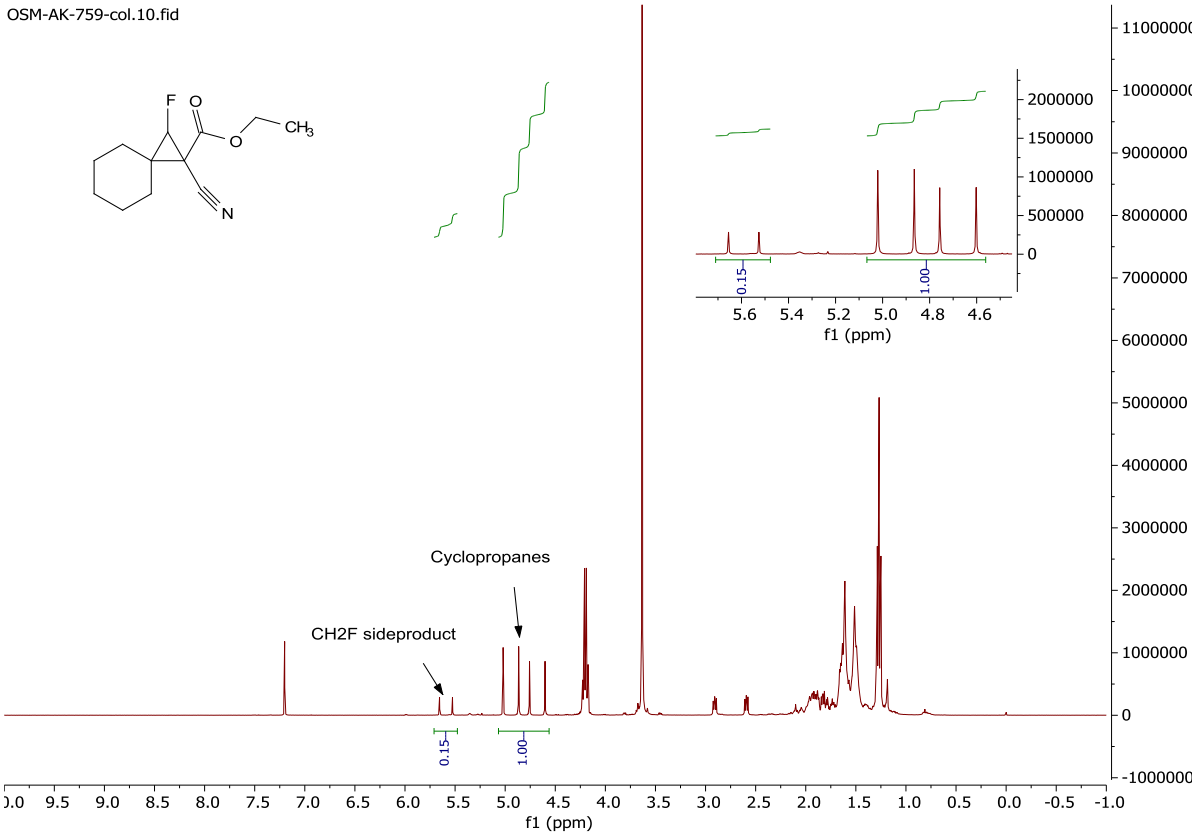
Compound **5f** ^{13}C NMR (400 MHz, $CDCl_3$)



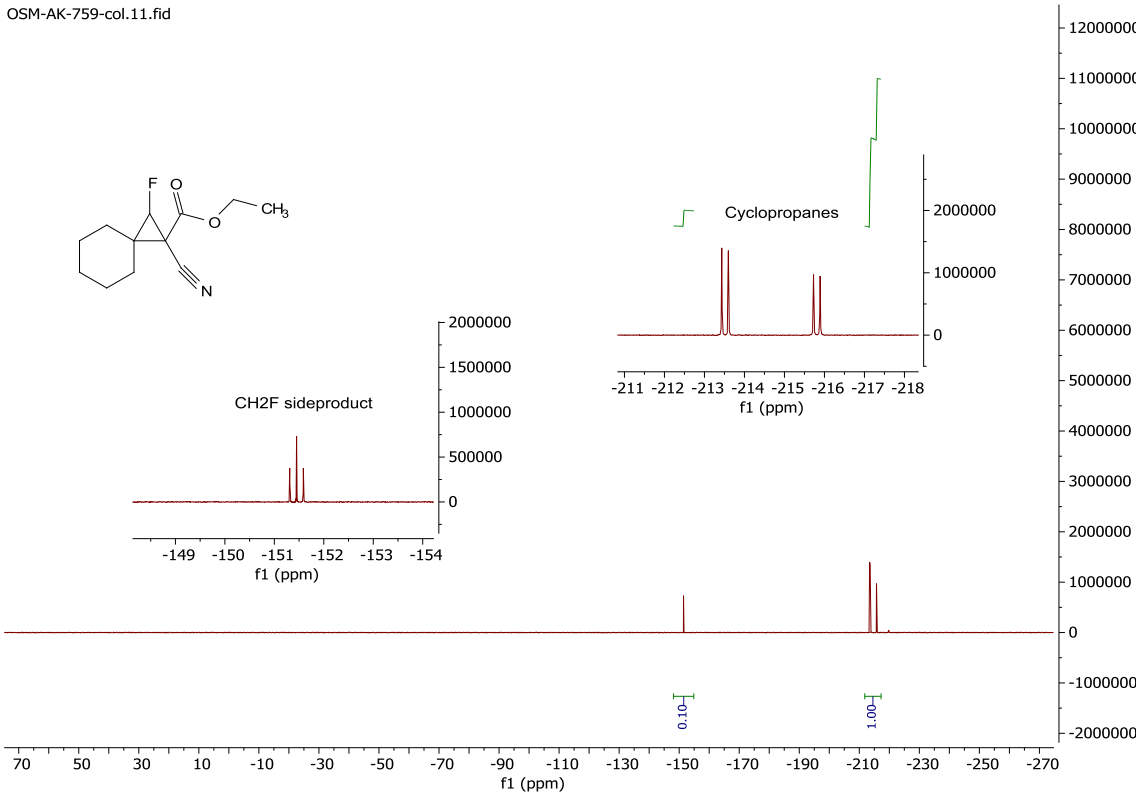
Compound **5h** crude ^{1}H NMR (400 MHz, $CDCl_3$)



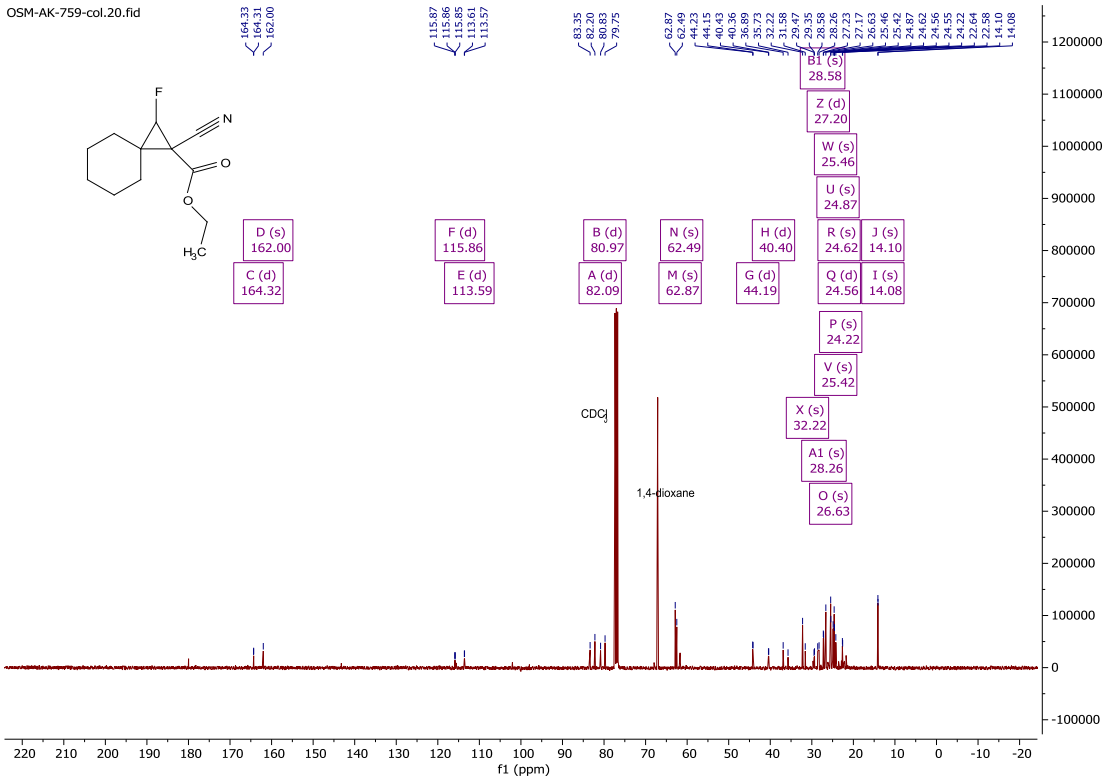
Compound **5j** + CH_2F sideproduct ^{1}H NMR (400 MHz, $CDCl_3$)



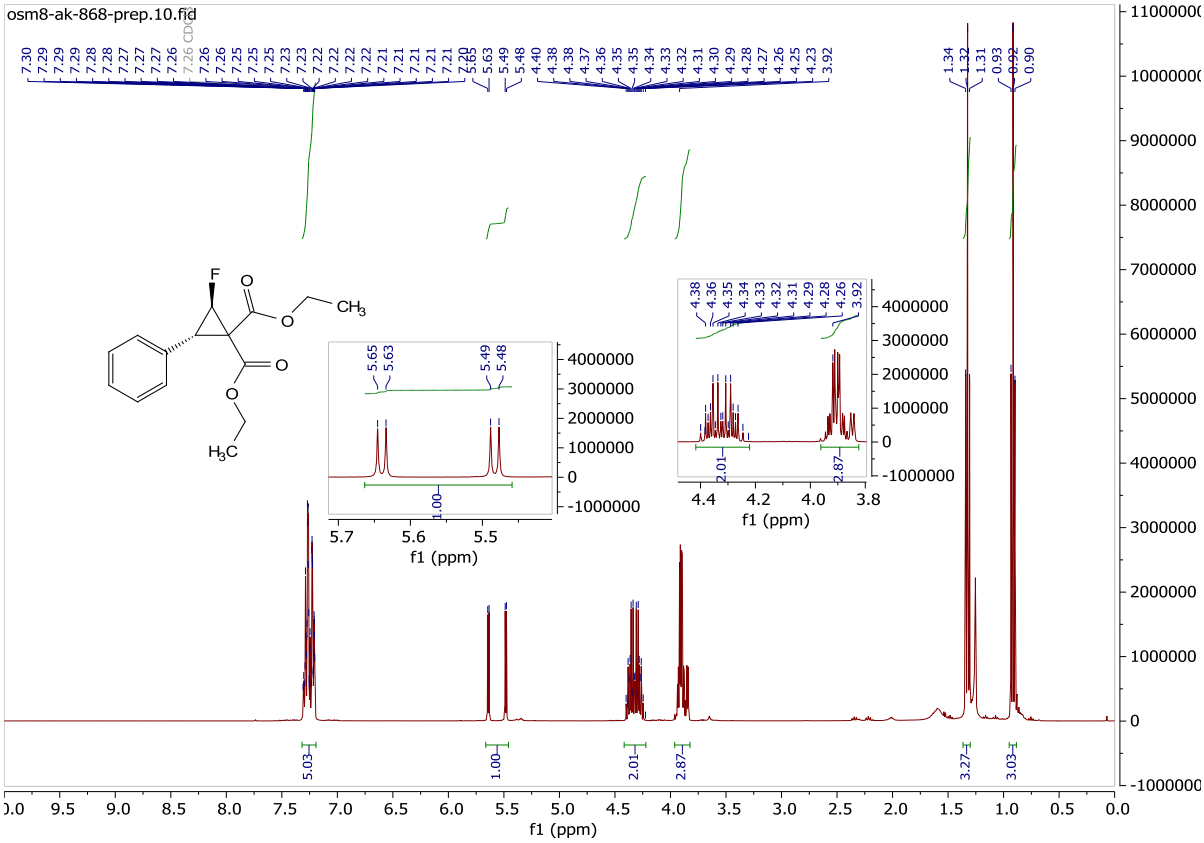
Compound **5j** + CH_2F sideproduct ^{19}F NMR (400 MHz, $CDCl_3$)



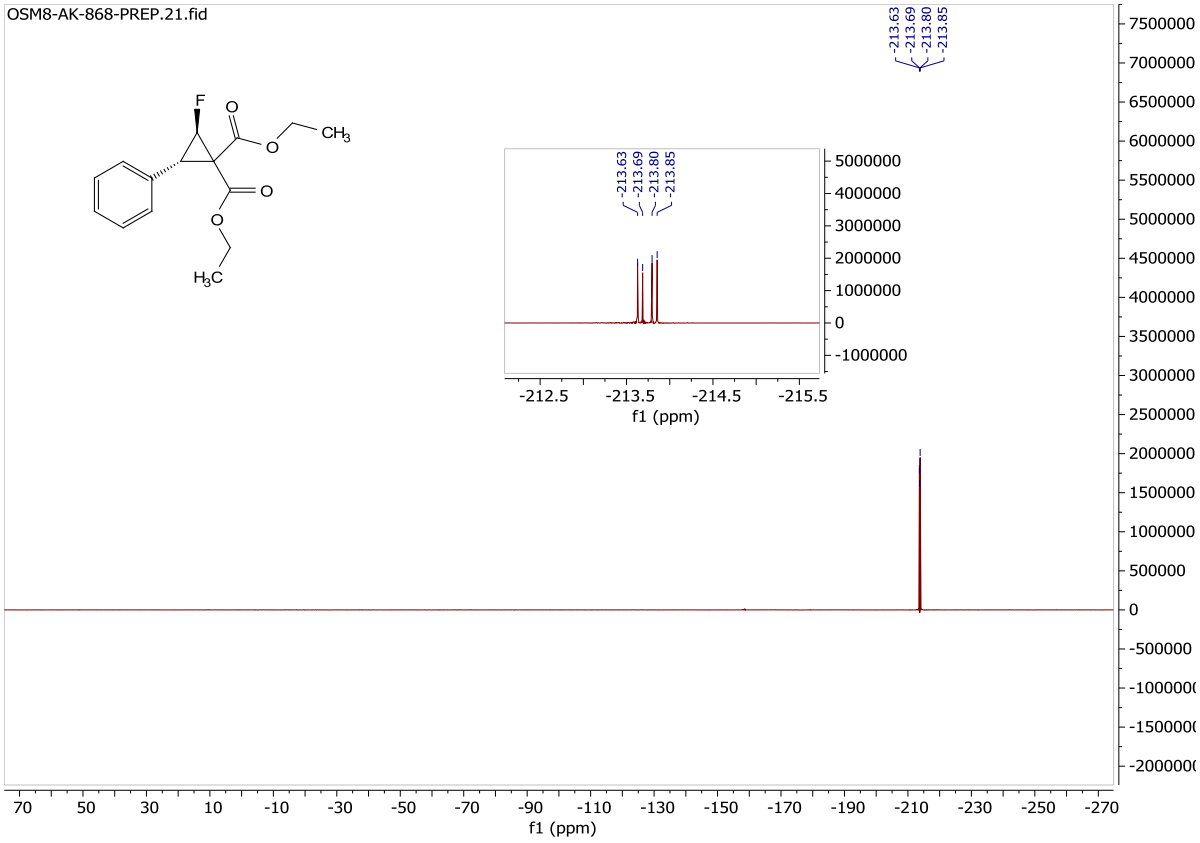
Compound **5j** + CH_2F sideproduct ^{13}C NMR (400 MHz, $CDCl_3$)



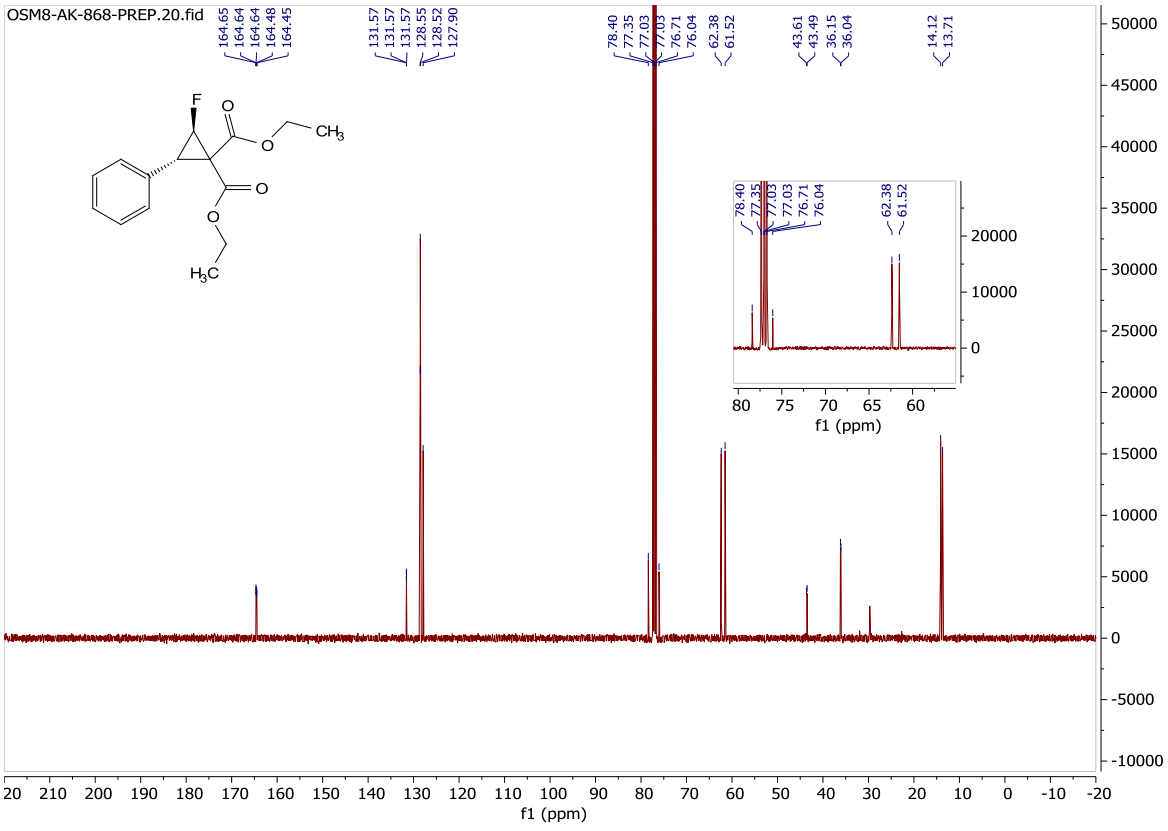
Compound (2*R**,3*S**)-**5k** ^1H NMR (400 MHz, $CDCl_3$)



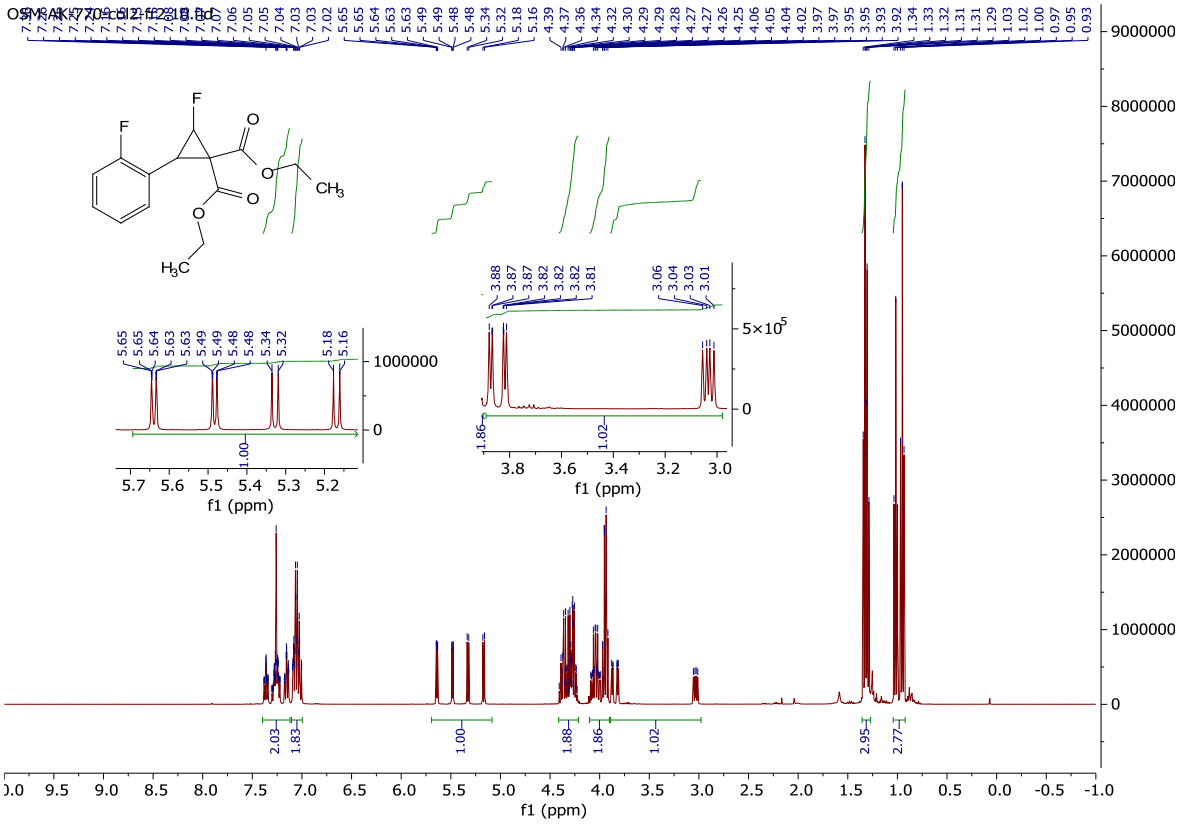
Compound (2*R**,3*S**)-**5k** ^{19}F NMR (400 MHz, $CDCl_3$)



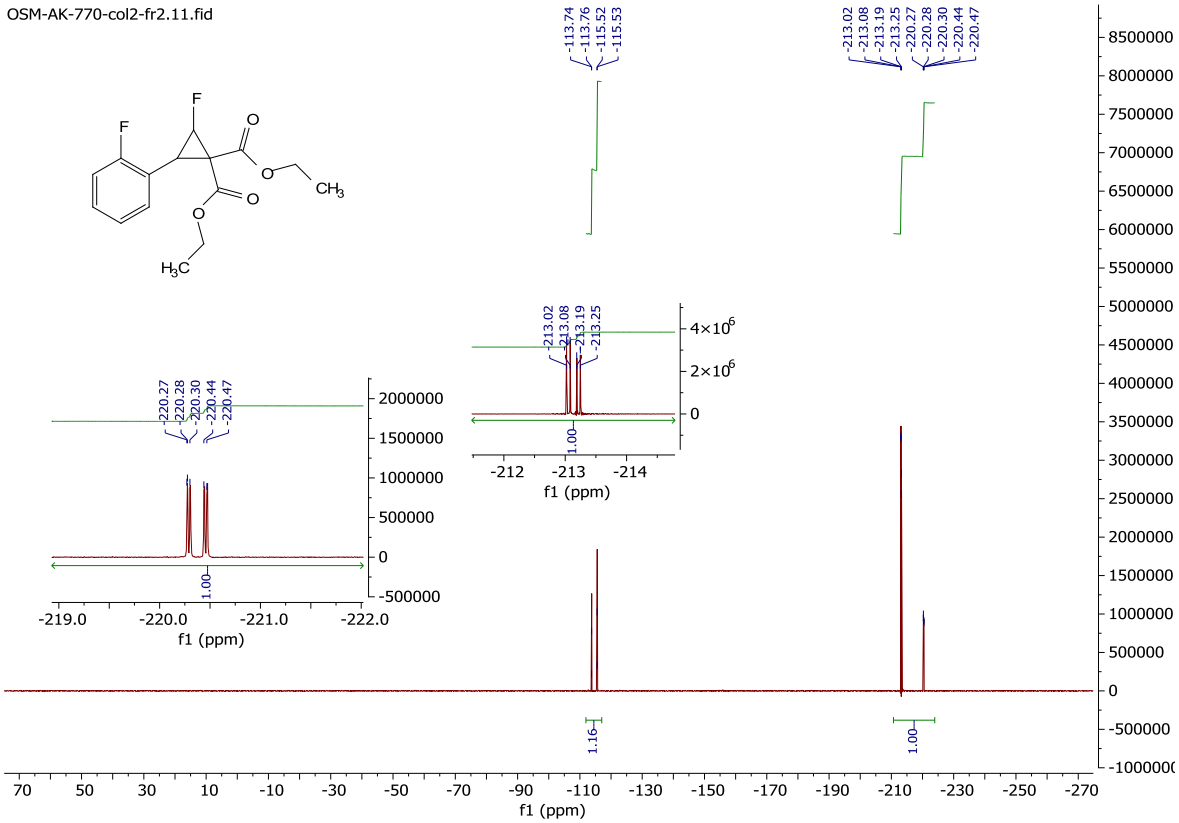
Compound (2*R**,3*S**)-**5k** ^{13}C NMR (400 MHz, $CDCl_3$)



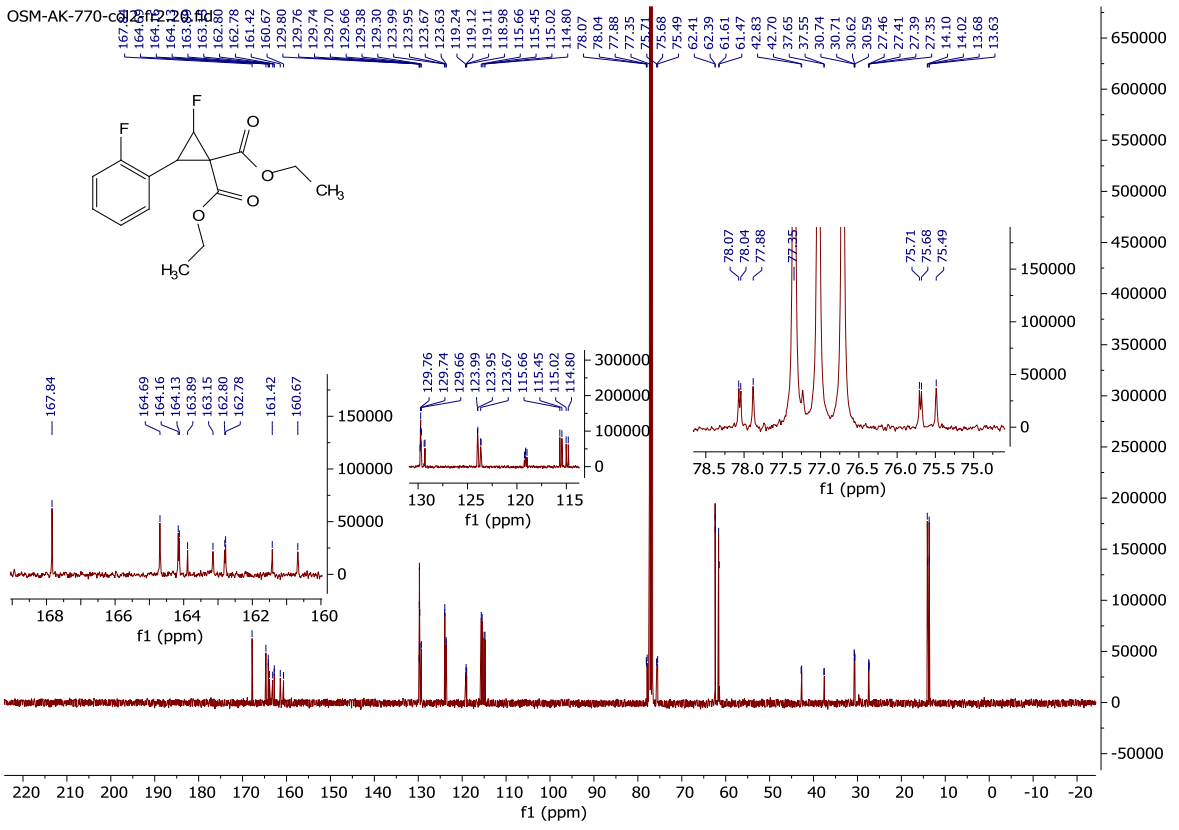
Compound **5l** ^{1}H NMR (400 MHz, $CDCl_3$)


F
F
O
O
O
O
CH3
H3C
f1 (ppm)
f1 (ppm)
f1 (ppm)

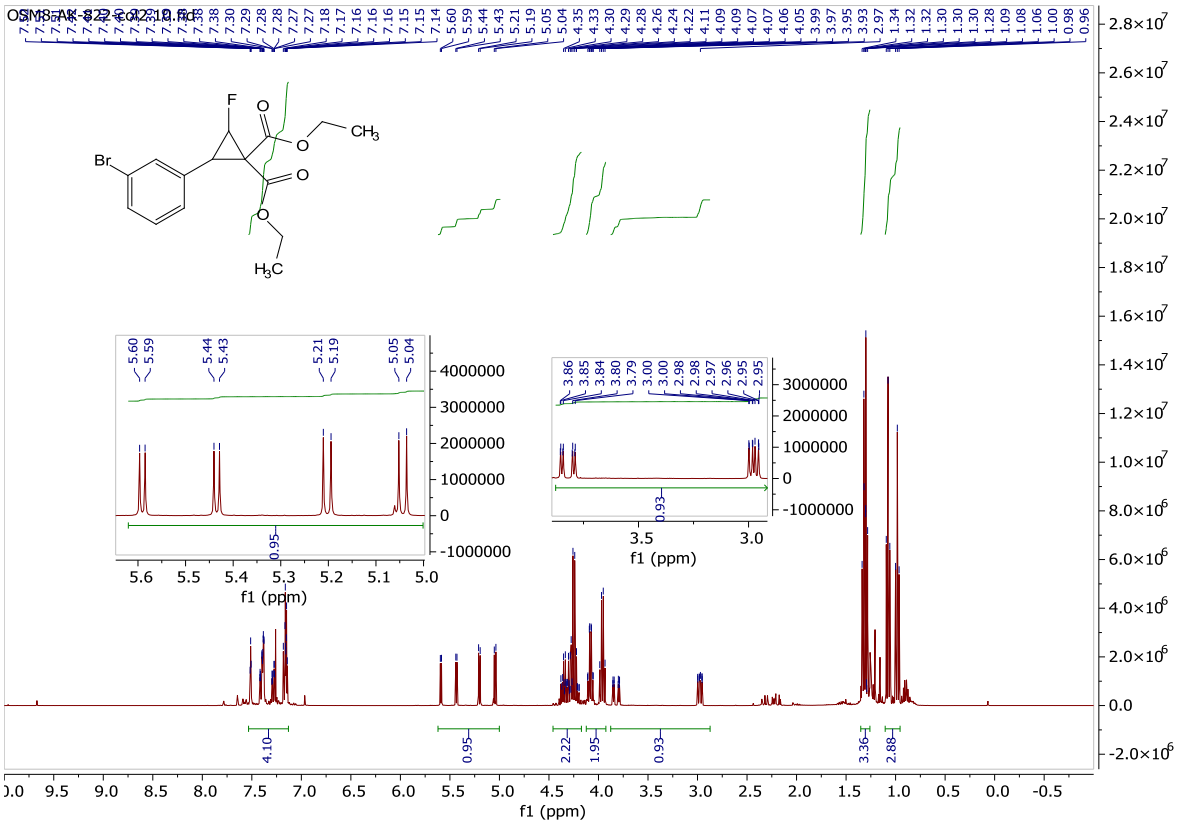
Compound **5l** ^{19}F NMR (400 MHz, $CDCl_3$)



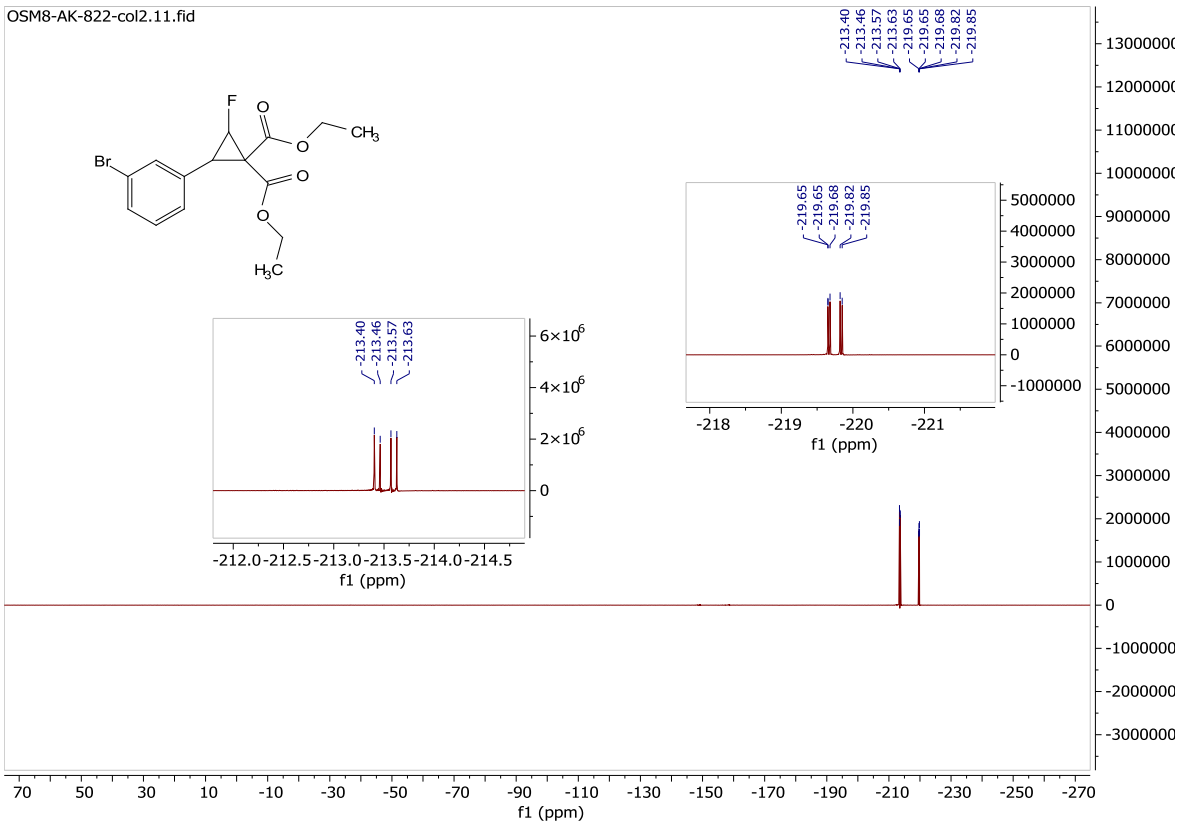
Compound **5l** ^{13}C NMR (400 MHz, $CDCl_3$)



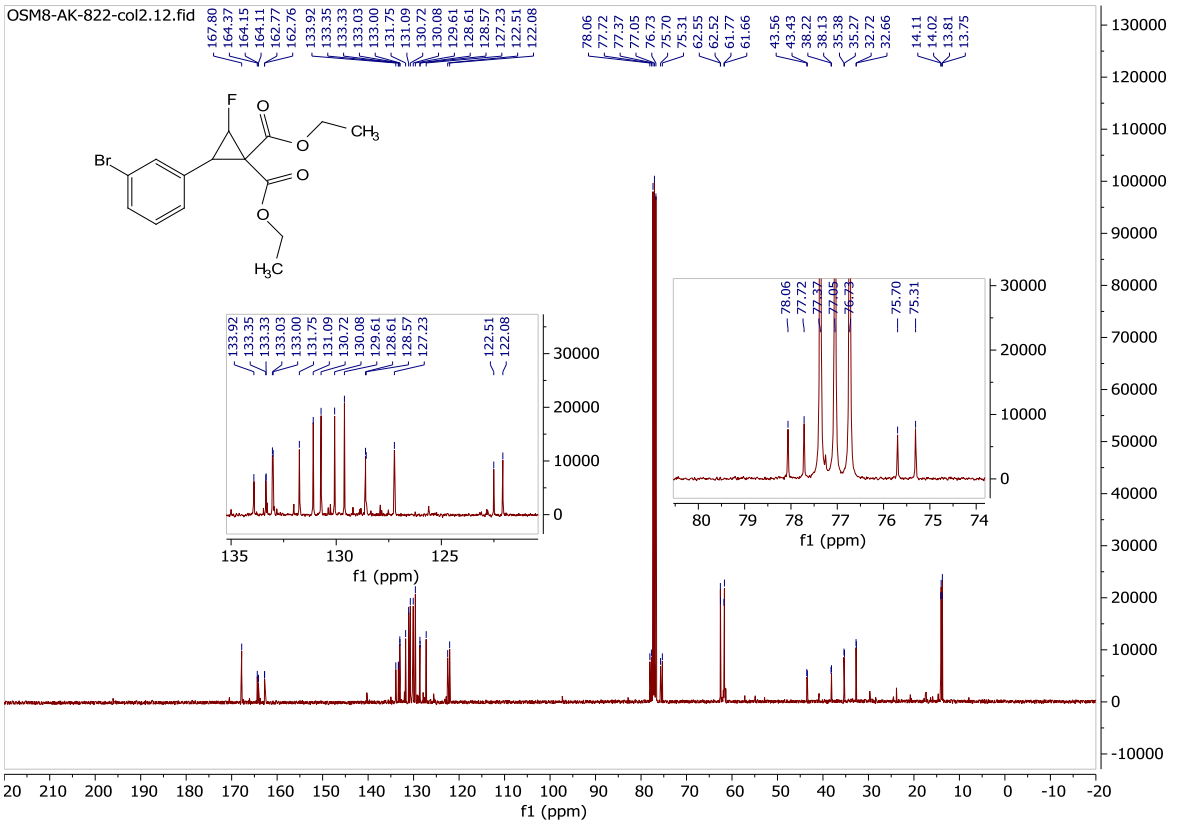
Compound **5m** ^{1}H NMR (400 MHz, $CDCl_3$)



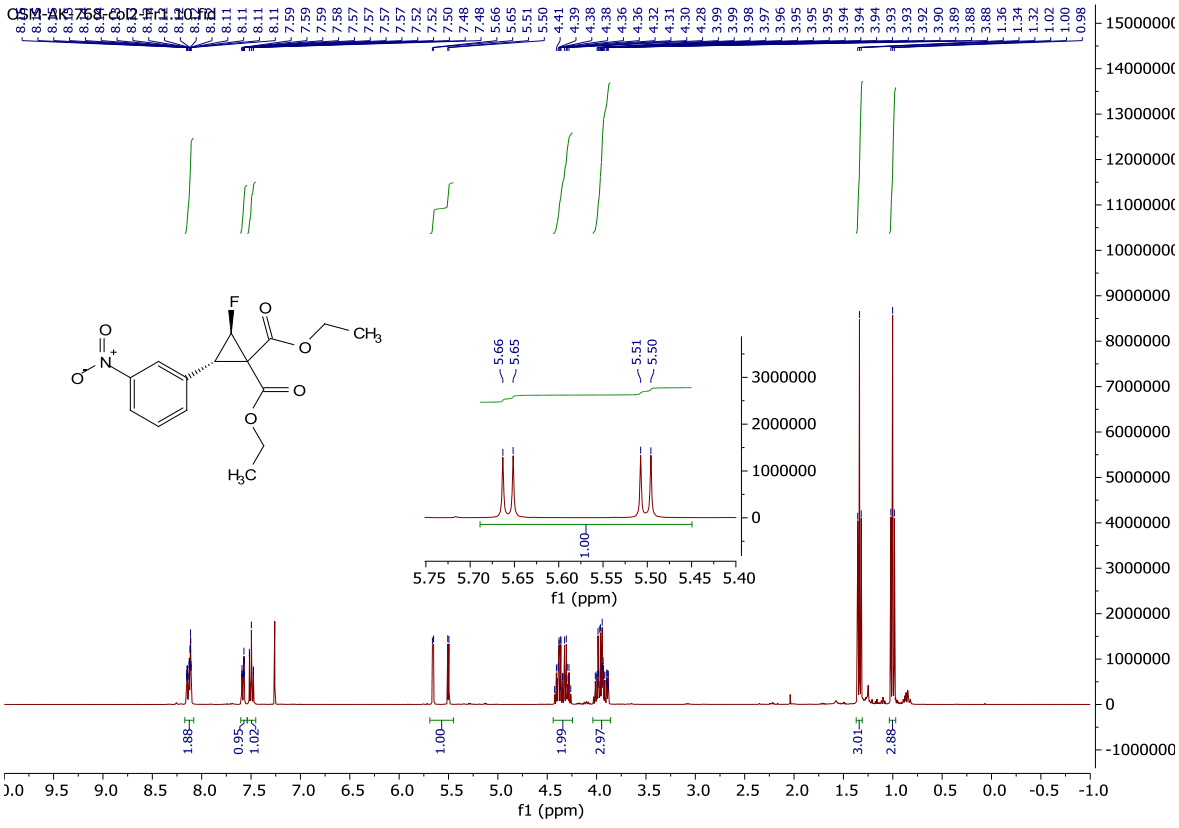
Compound **5m** ^{19}F NMR (400 MHz, $CDCl_3$)



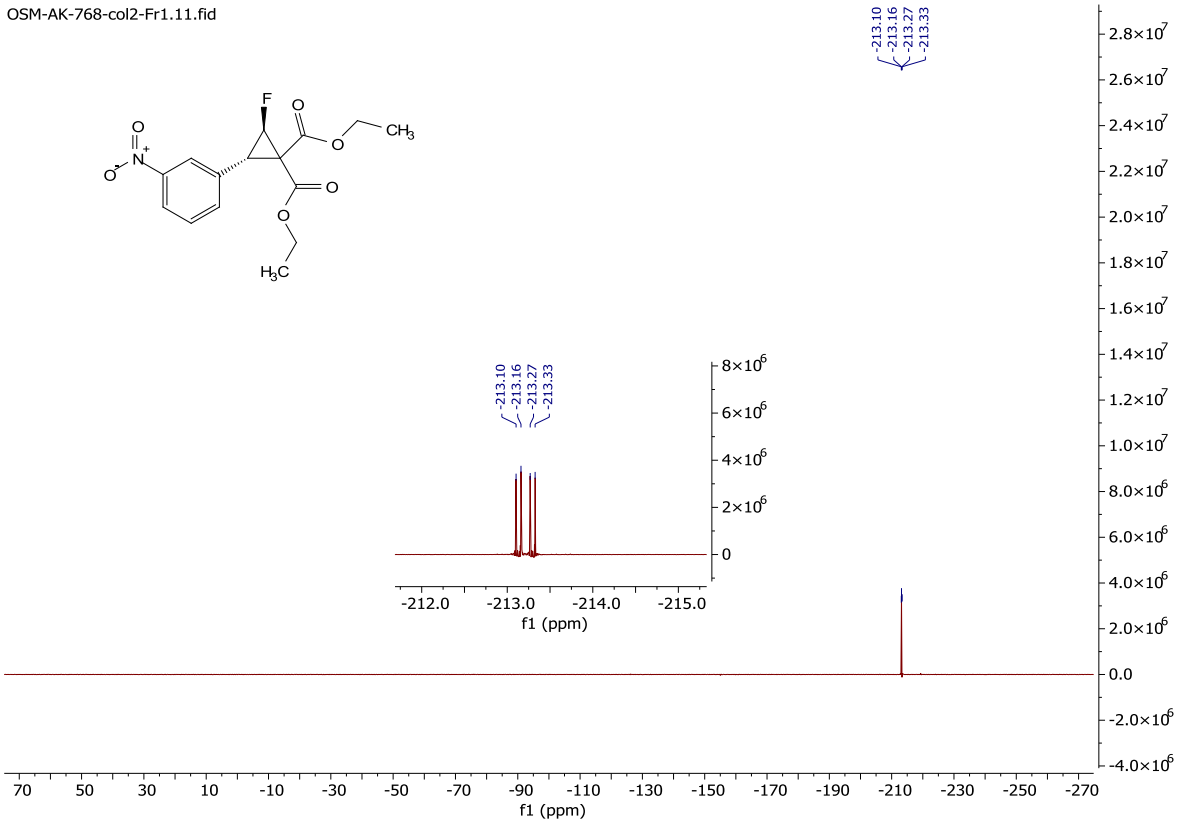
Compound **5m** ^{13}C NMR (400 MHz, $CDCl_3$)



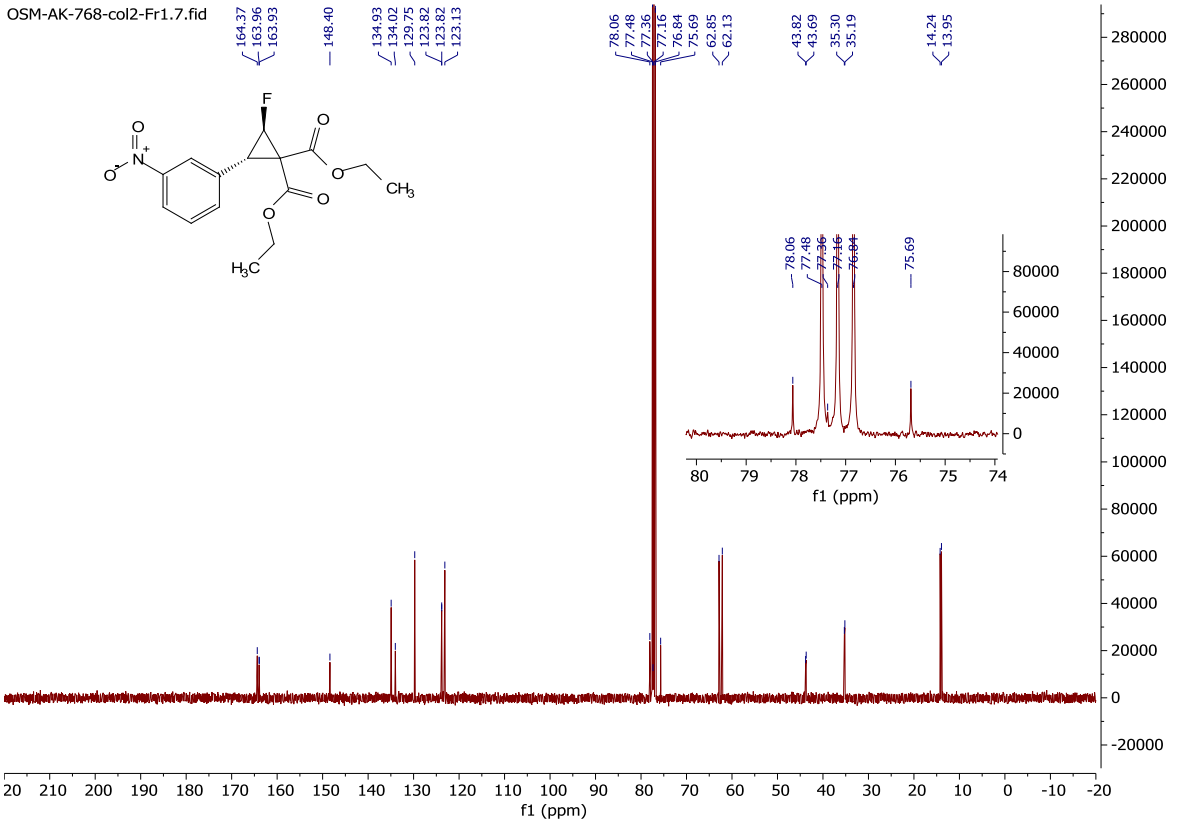
Compound (2R*,3S*)-**5n** ^{1}H NMR (400 MHz, $CDCl_3$)



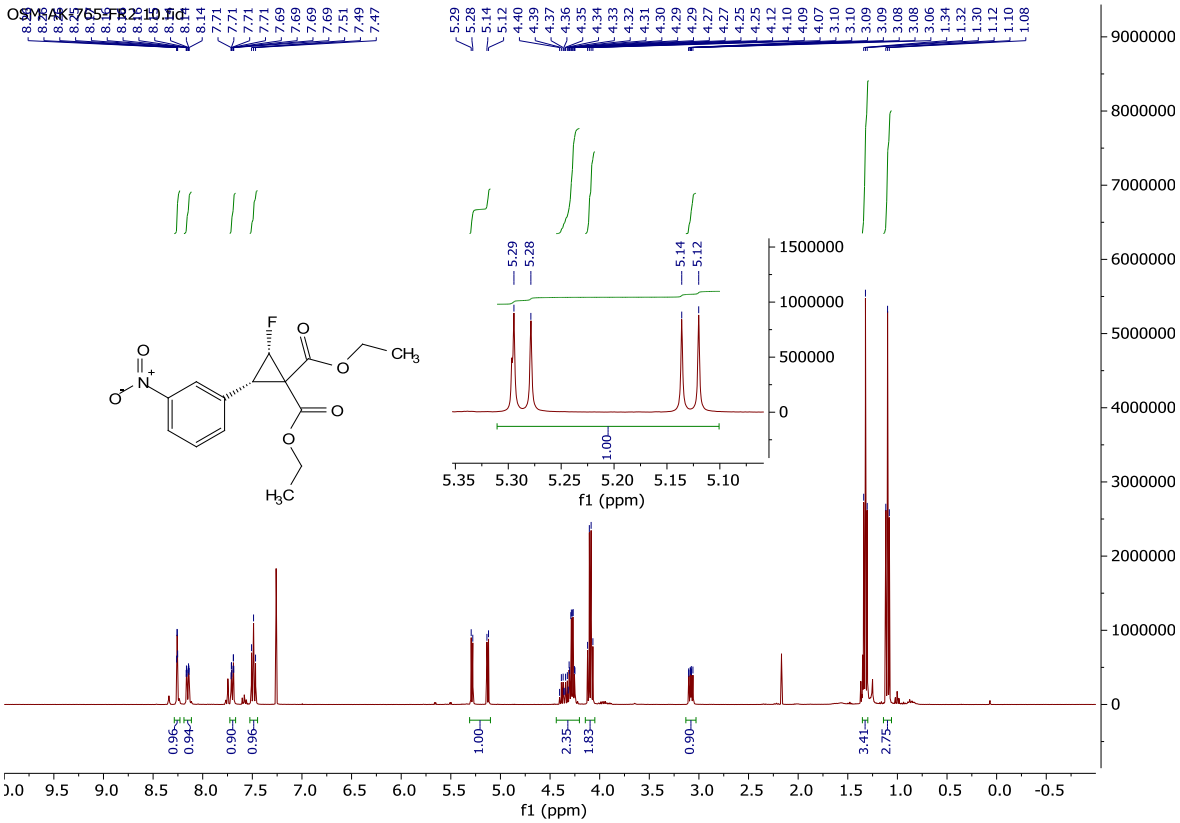
Compound (2R*,3S*)-**5n** ^{19}F NMR (400 MHz, $CDCl_3$)



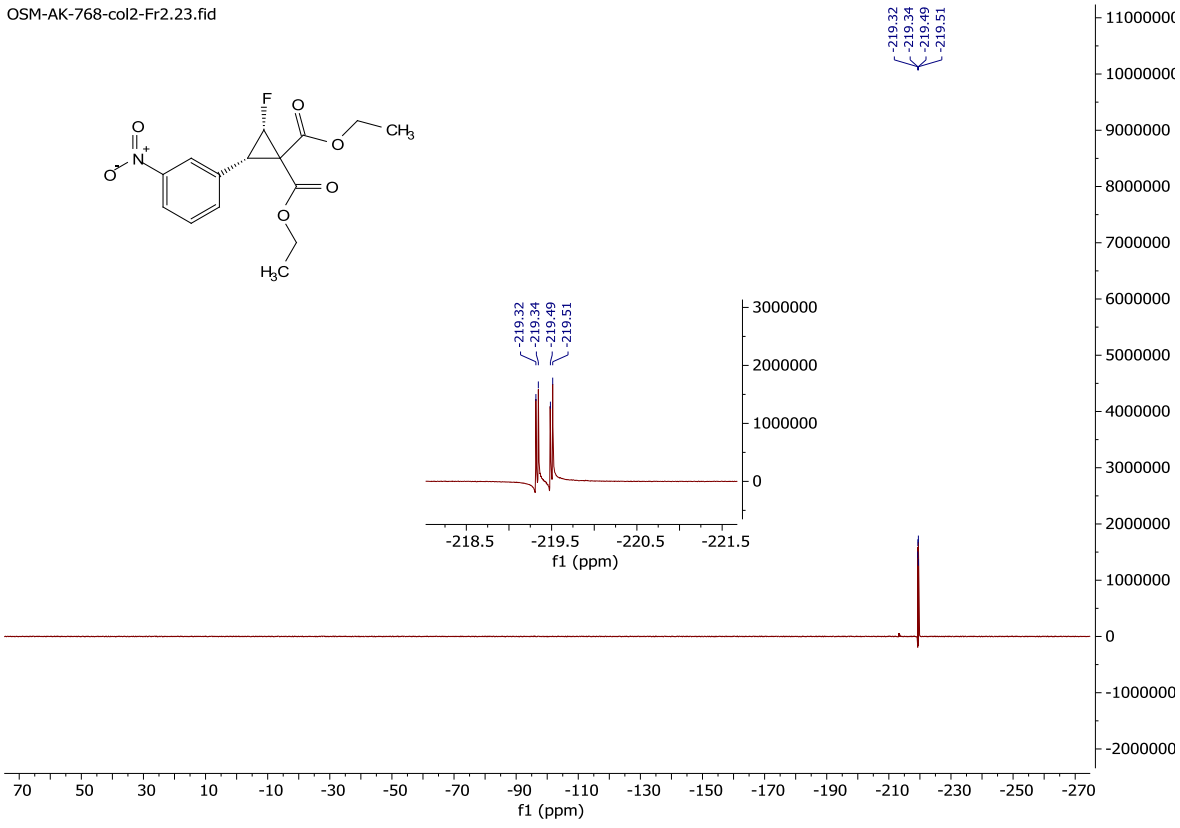
Compound (2R*,3S*)-**5n** ^{13}C NMR (400 MHz, $CDCl_3$)



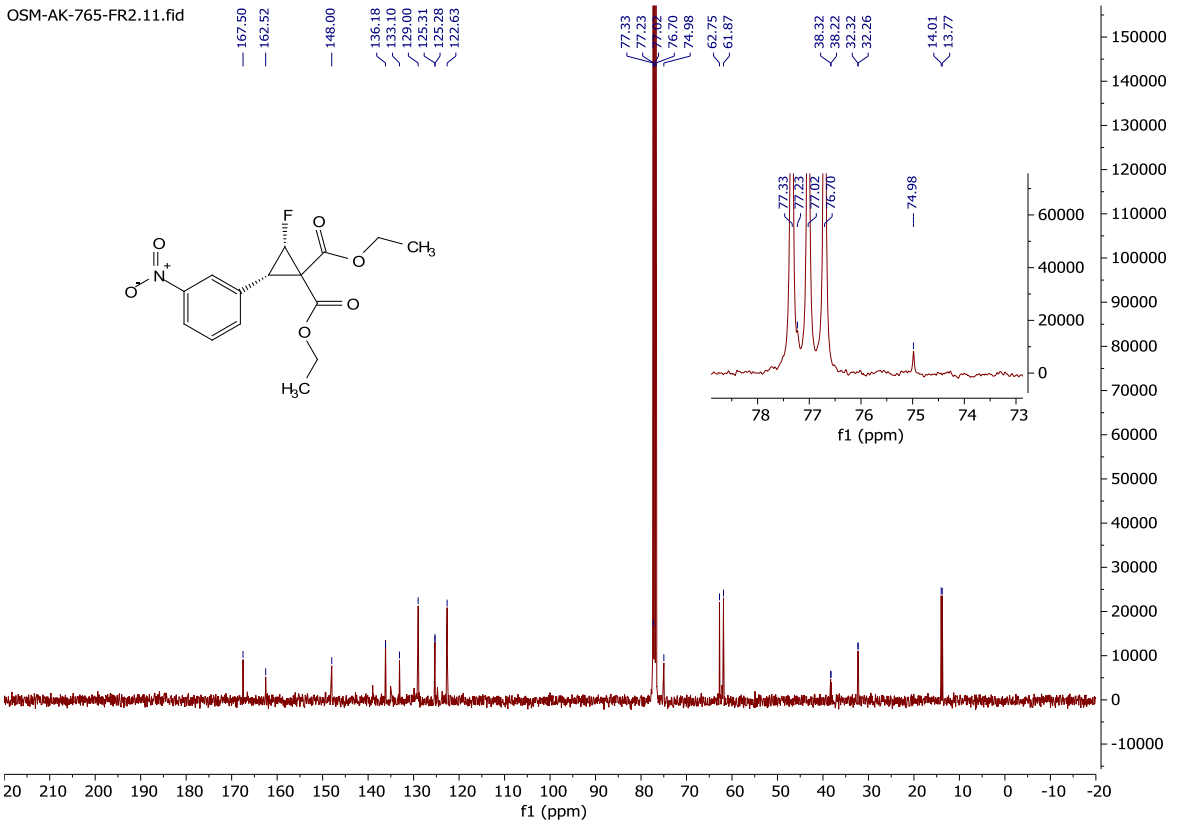
Compound (2S*,3S*)-**5n** ^{1}H NMR (400 MHz, $CDCl_3$)



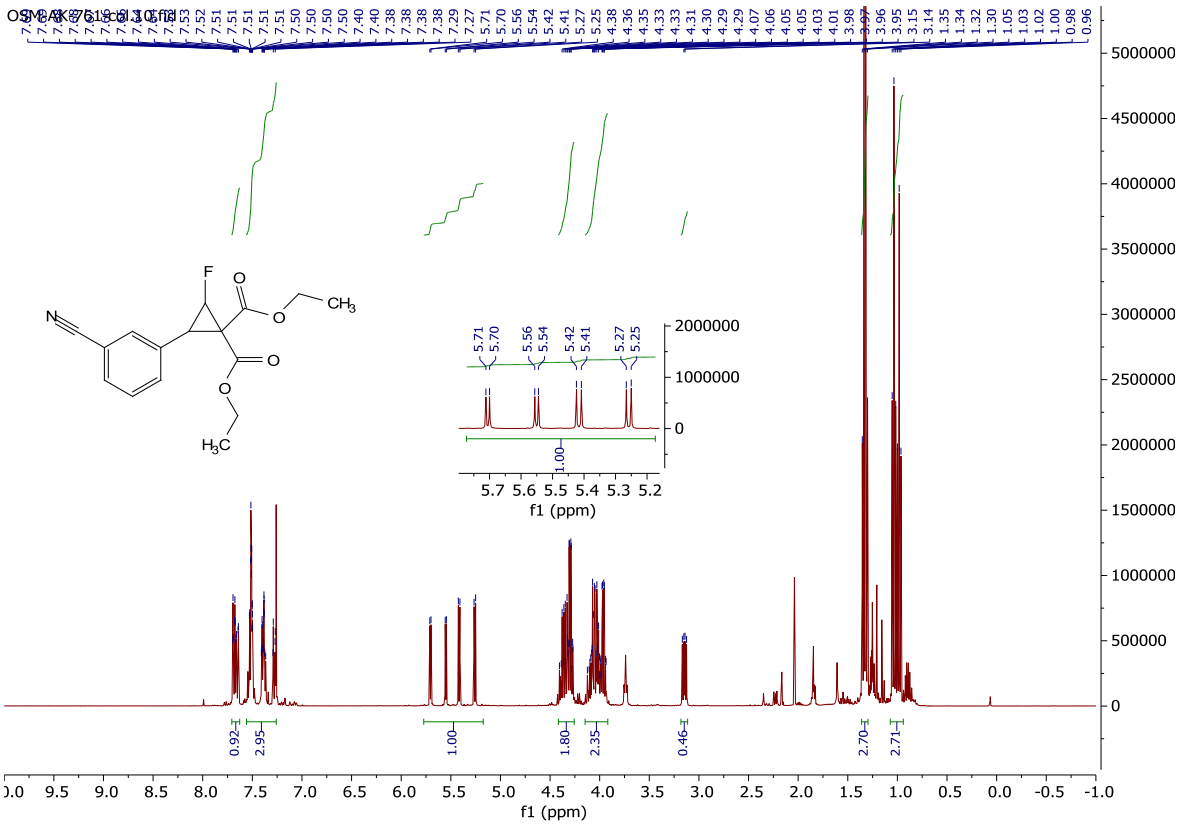
Compound (2S*,3S*)-**5n** ^{19}F NMR (400 MHz, $CDCl_3$)



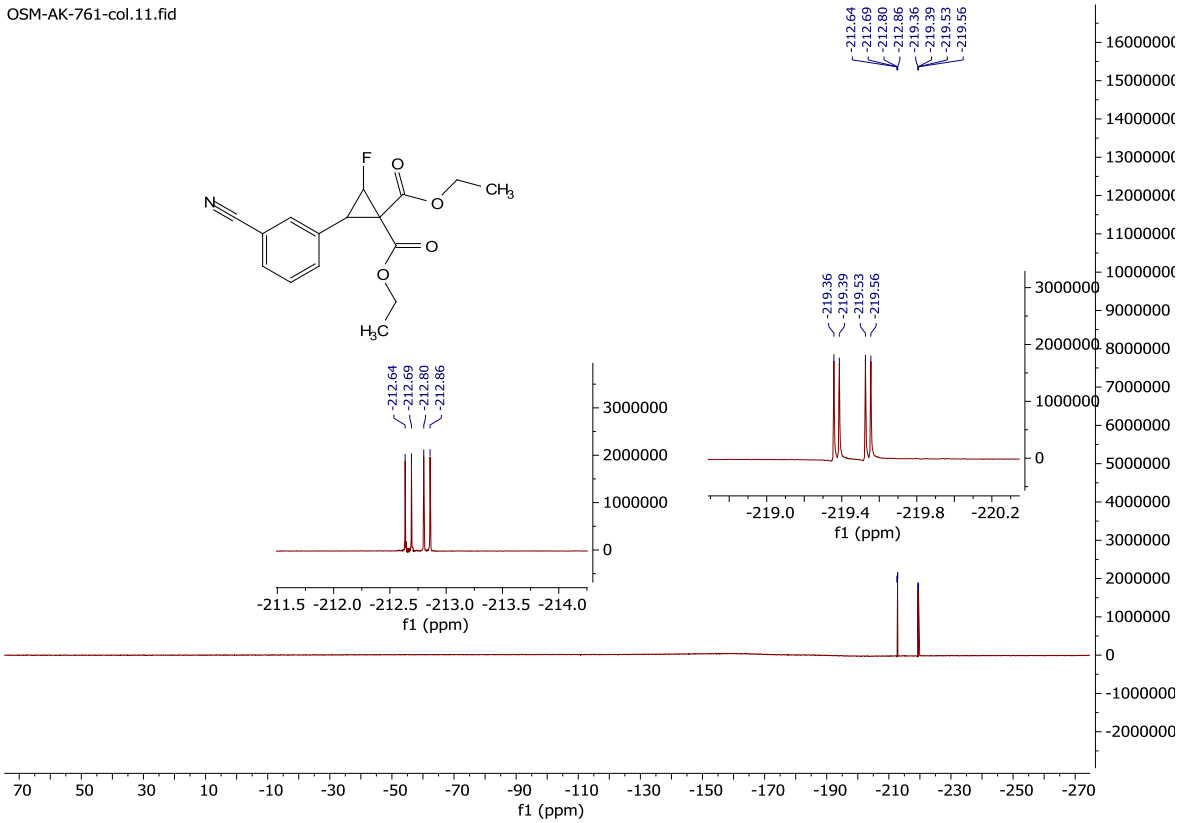
Compound (2S*,3S*)-**5n** ^{13}C NMR (400 MHz, $CDCl_3$)



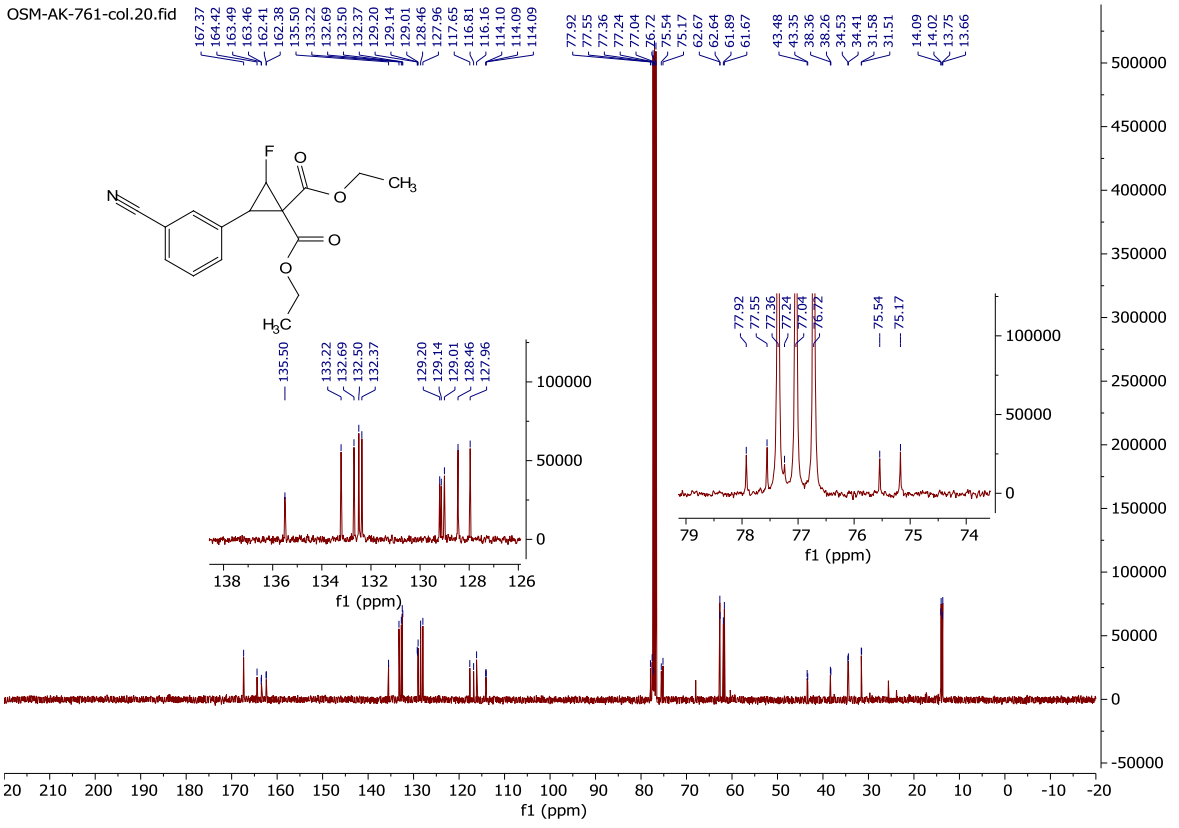
Compound **5o** ^{1}H NMR (400 MHz, $CDCl_3$)



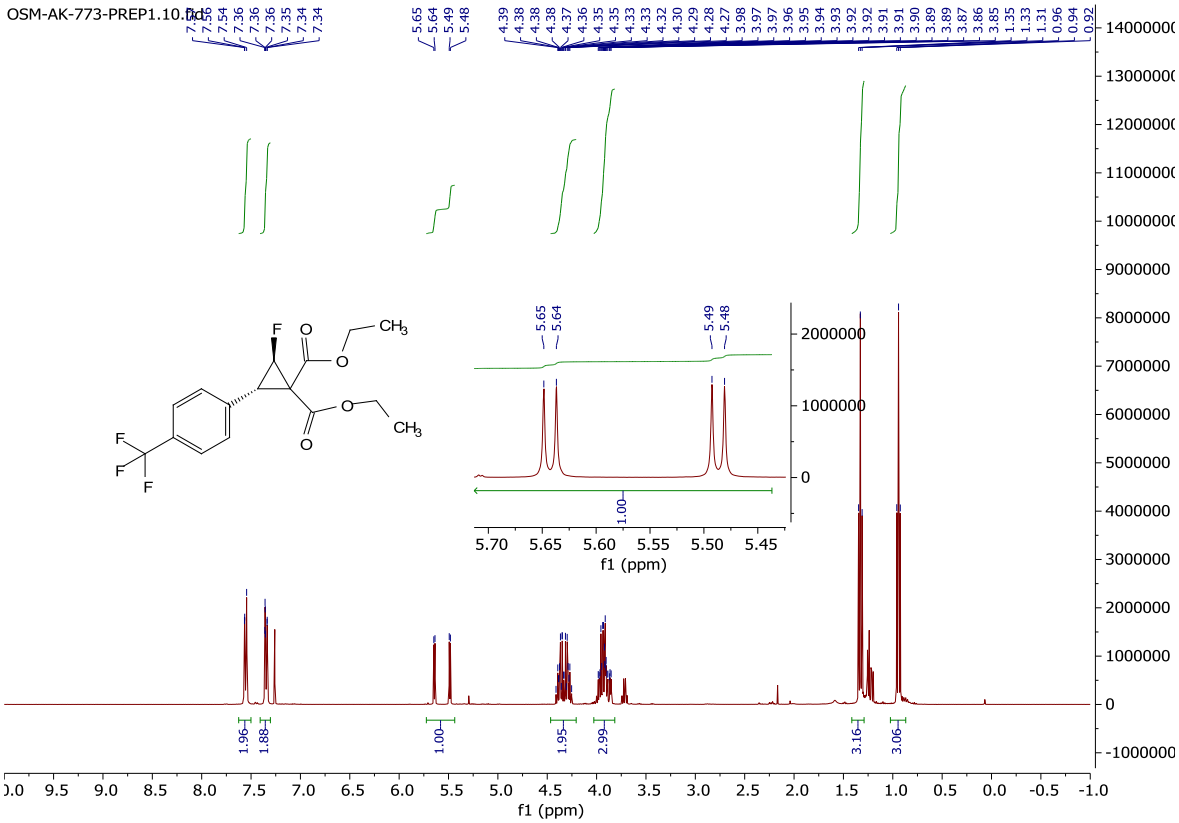
Compound **5o** ^{19}F NMR (400 MHz, $CDCl_3$)



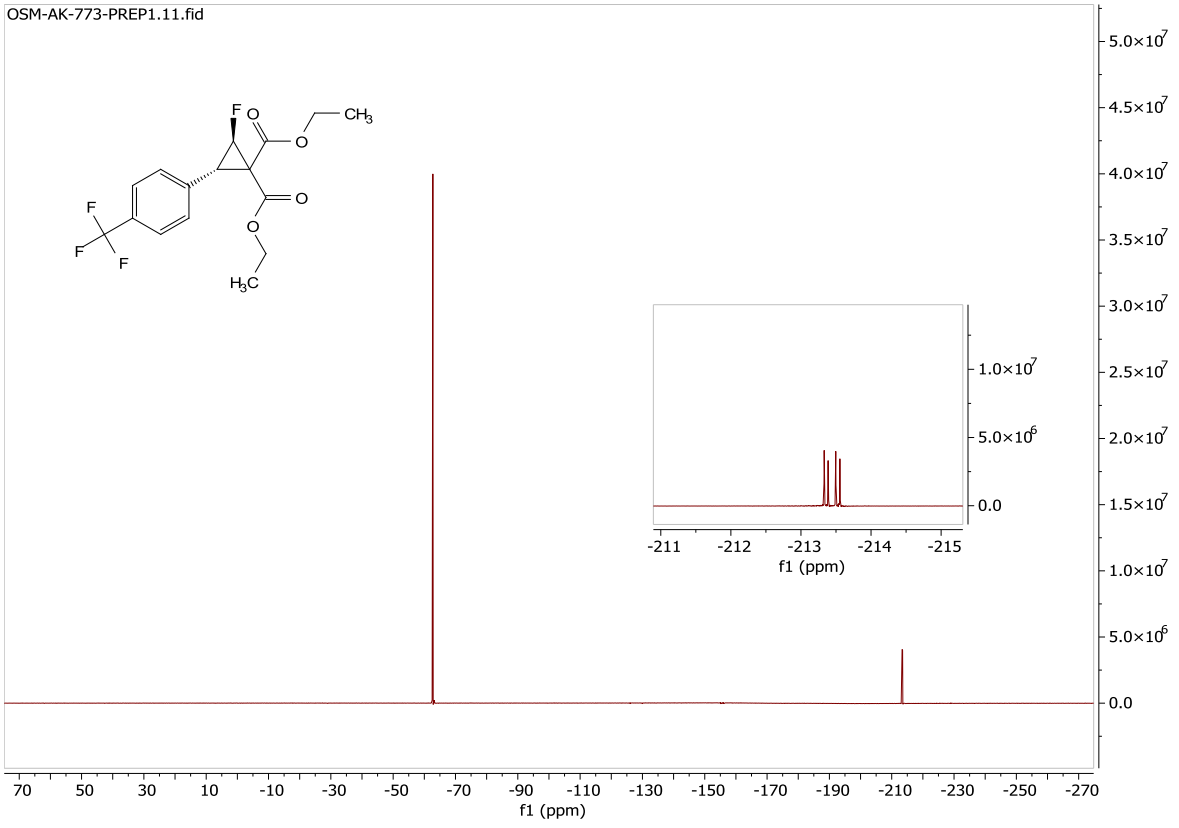
Compound **5o** ^{13}C NMR (400 MHz, $CDCl_3$)



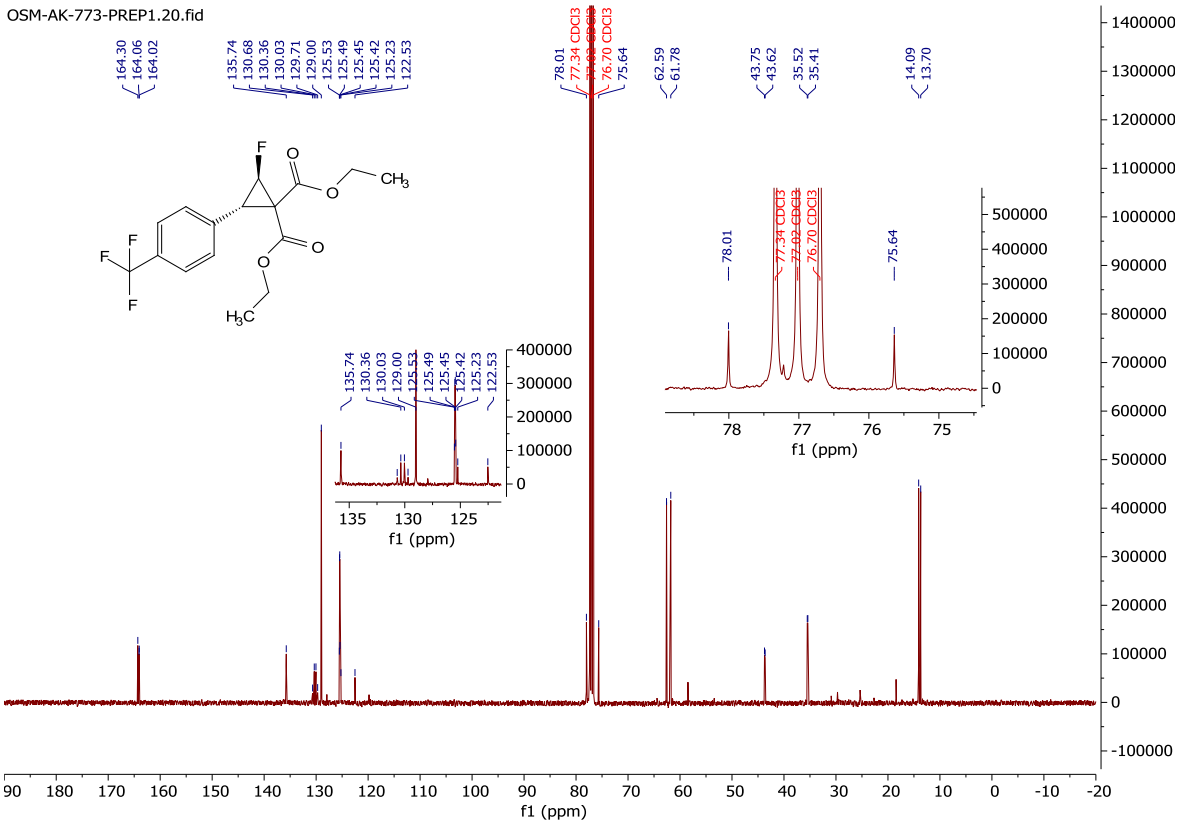
Compound (2R*,3S*)-**5p** ^{1}H NMR (400 MHz, $CDCl_3$)



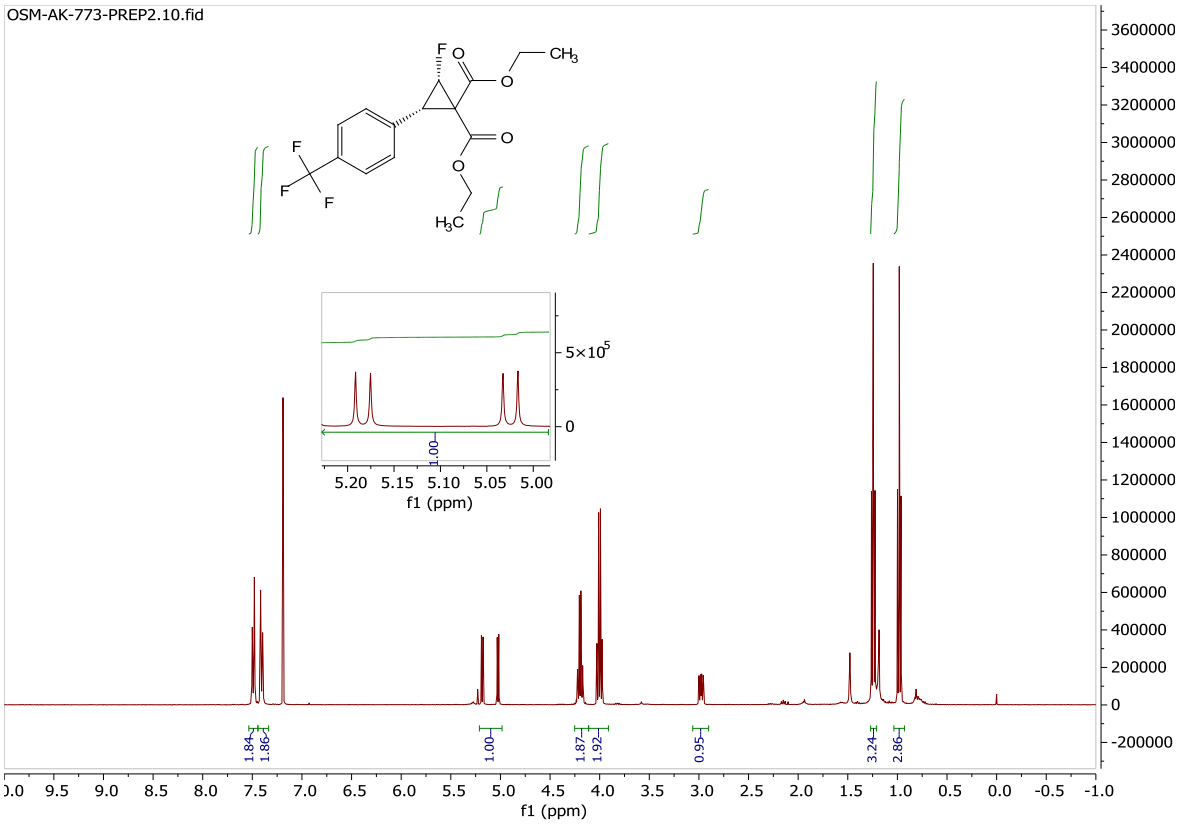
Compound (2R*,3S*)-**5p** ^{19}F NMR (400 MHz, $CDCl_3$)



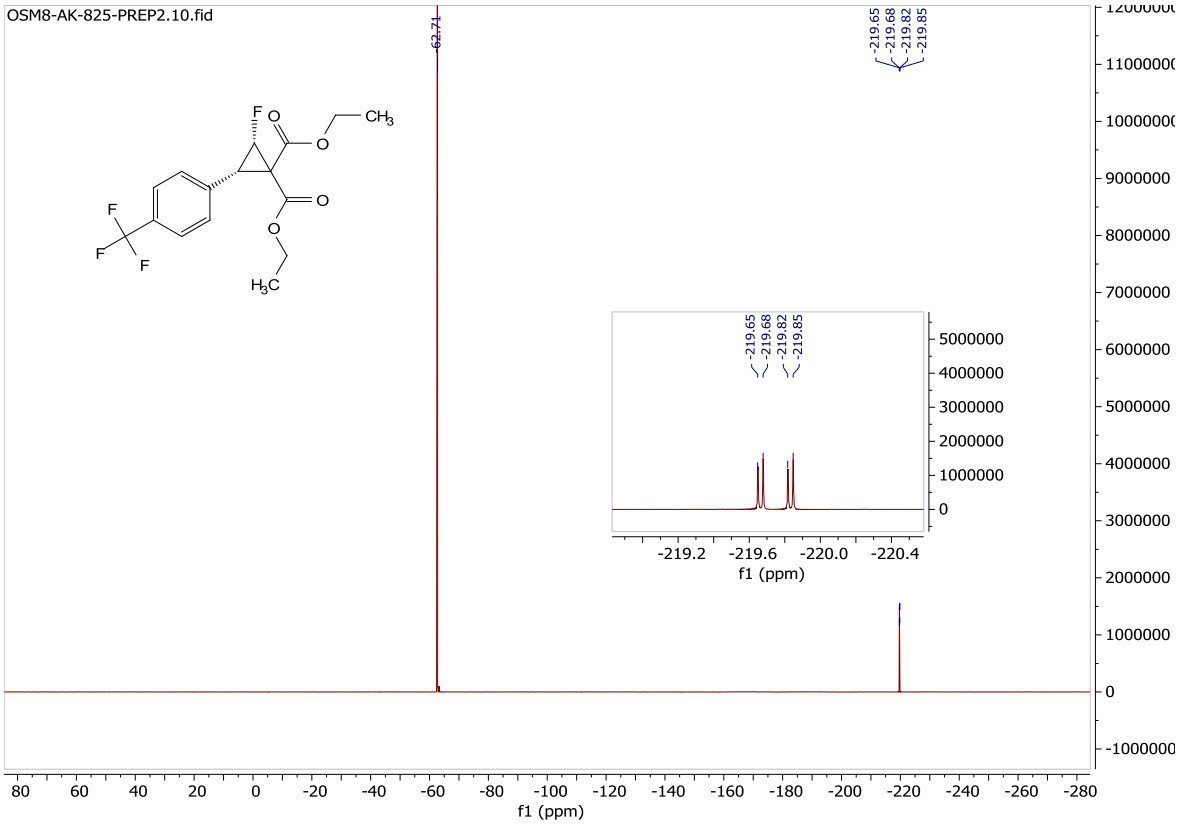
Compound (2R*,3S*)-**5p** ^{13}C NMR (400 MHz, $CDCl_3$)



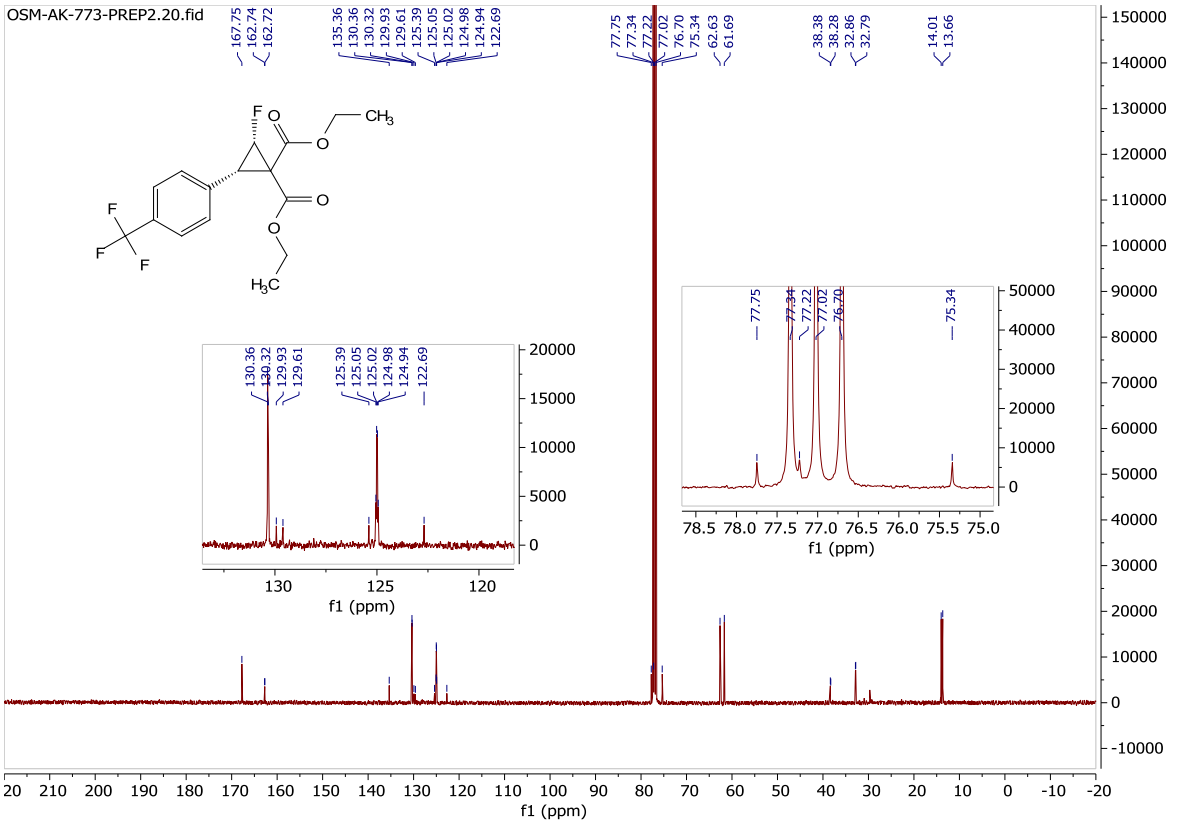
Compound (2S*,3S*)-**5p** ^{1}H NMR (400 MHz, $CDCl_3$)



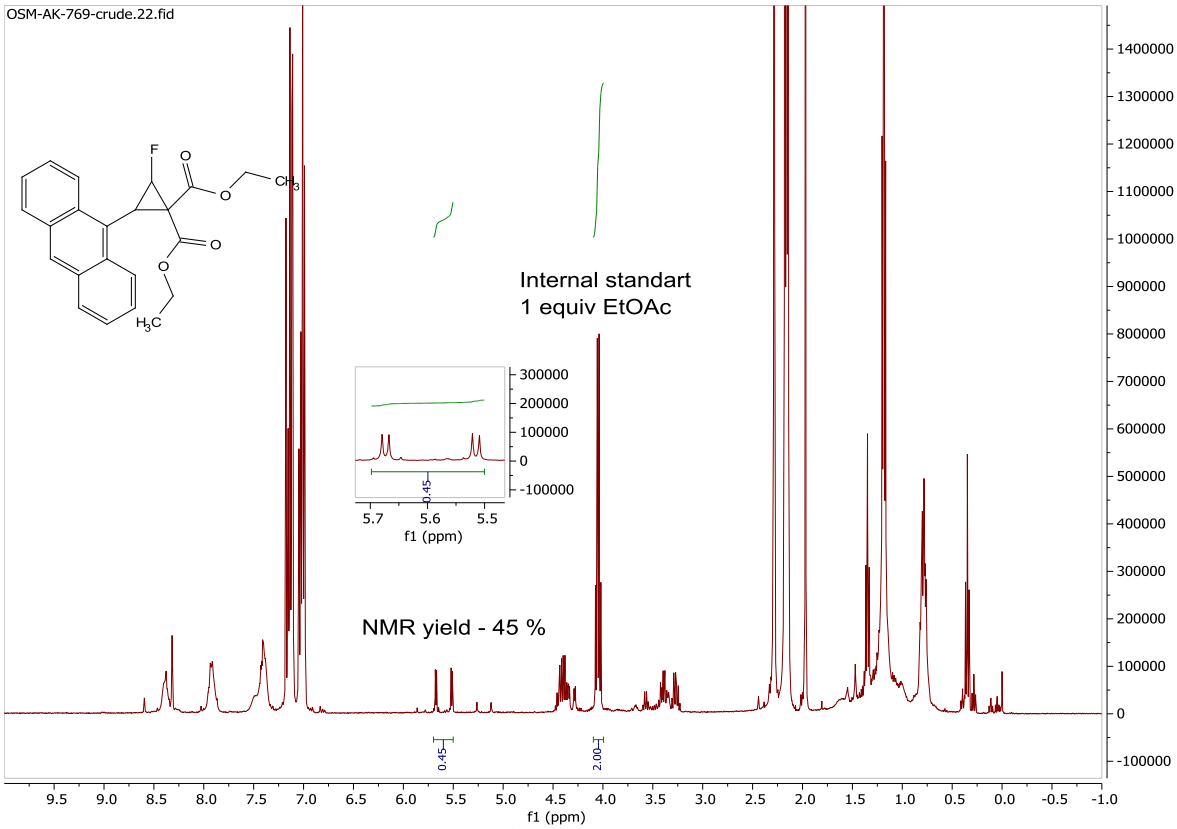
Compound (2S*,3S*)-**5p** ^{19}F NMR (400 MHz, $CDCl_3$)



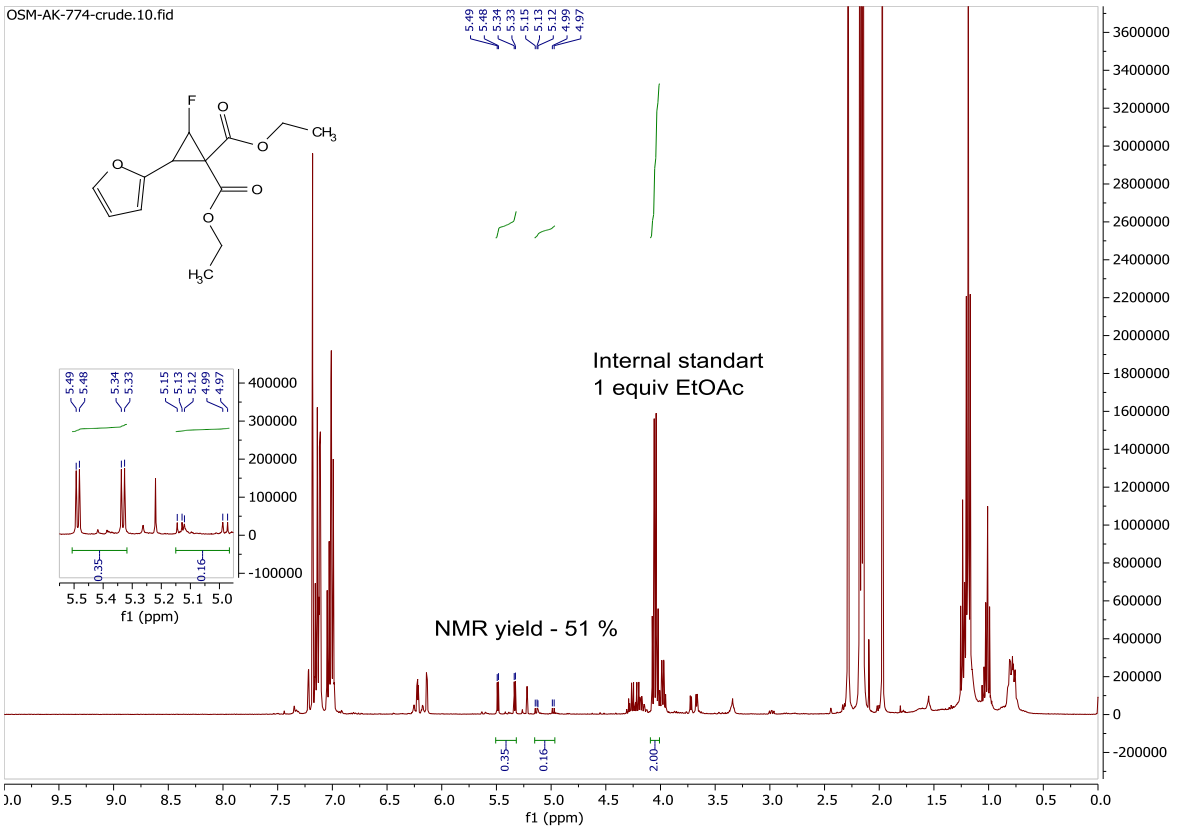
Compound (2S*,3S*)-**5p** ^{13}C NMR (400 MHz, $CDCl_3$)



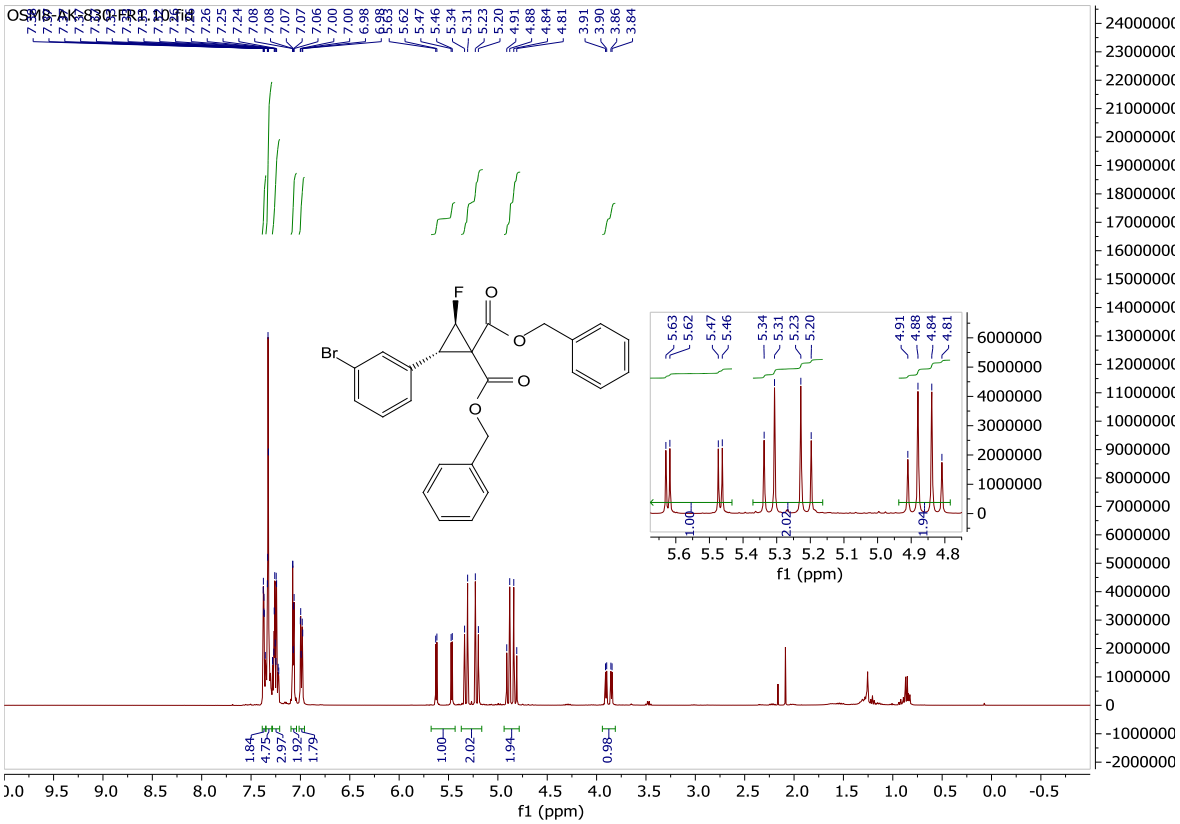
Compound **5r** crude ^{1}H NMR (400 MHz, $CDCl_3$)



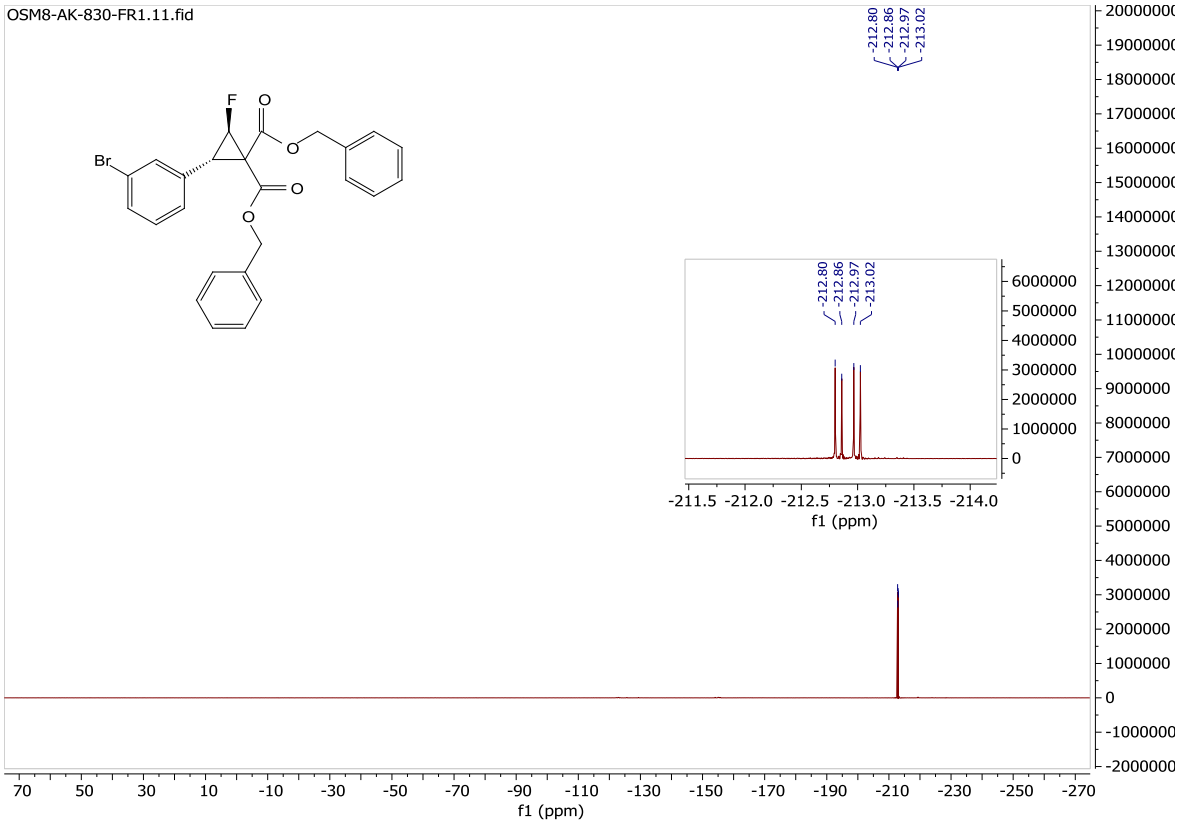
Compound **5s** crude ^{1}H NMR (400 MHz, $CDCl_3$)



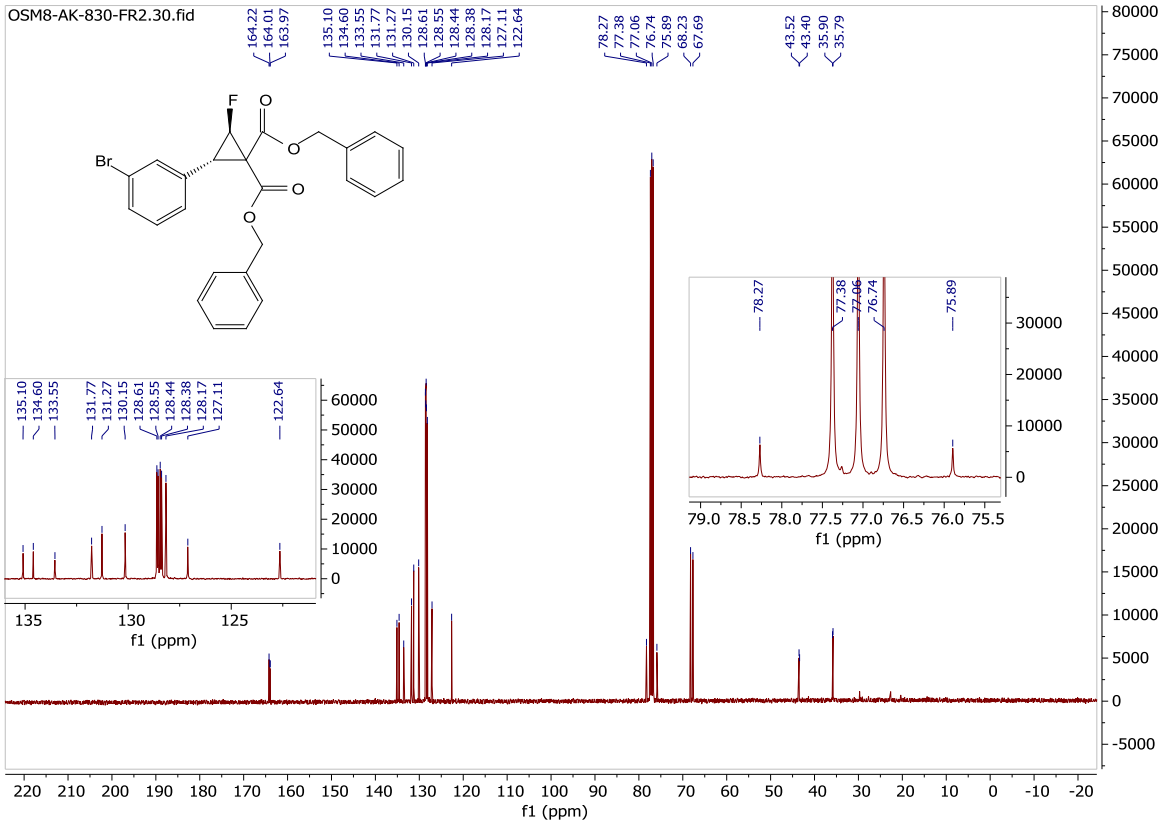
Compound (2*S**,3*R**)-**5t** ^{1}H NMR (400 MHz, $CDCl_3$)



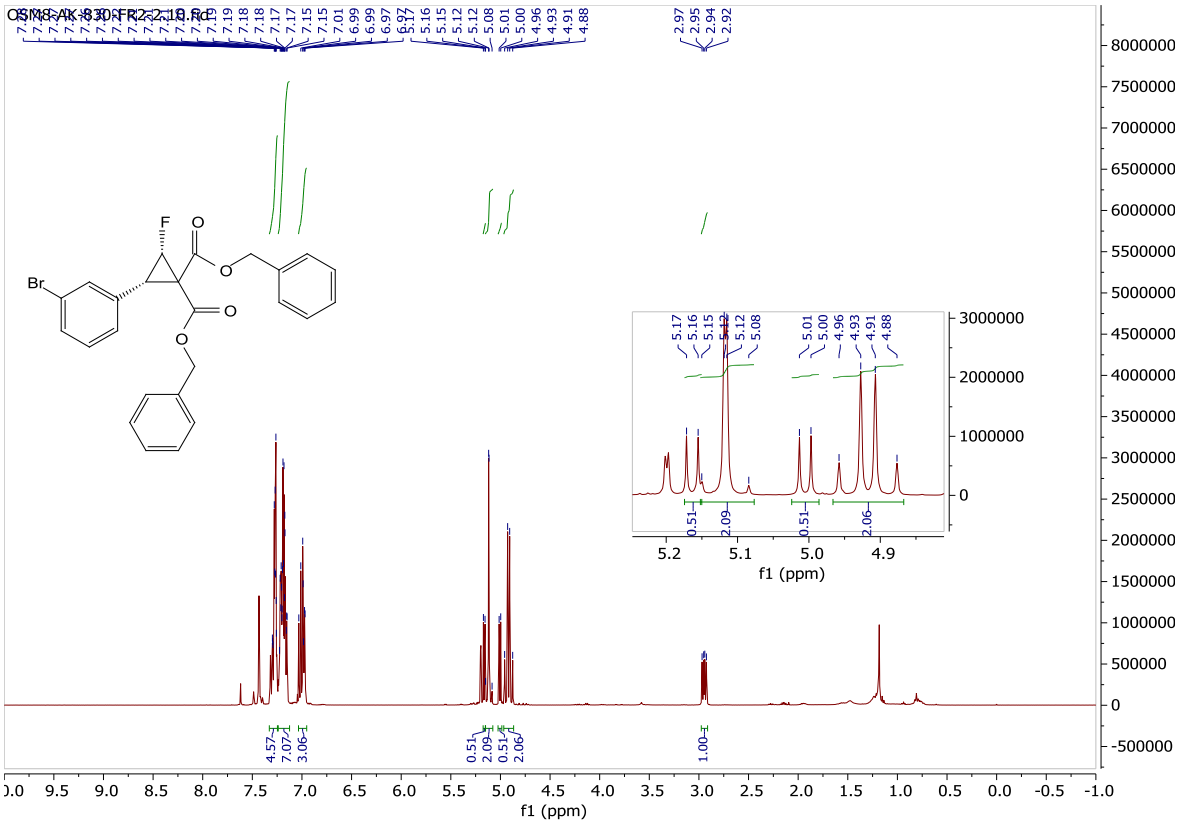
Compound (2*S**,3*R**)-**5t** ^{19}F NMR (400 MHz, $CDCl_3$)



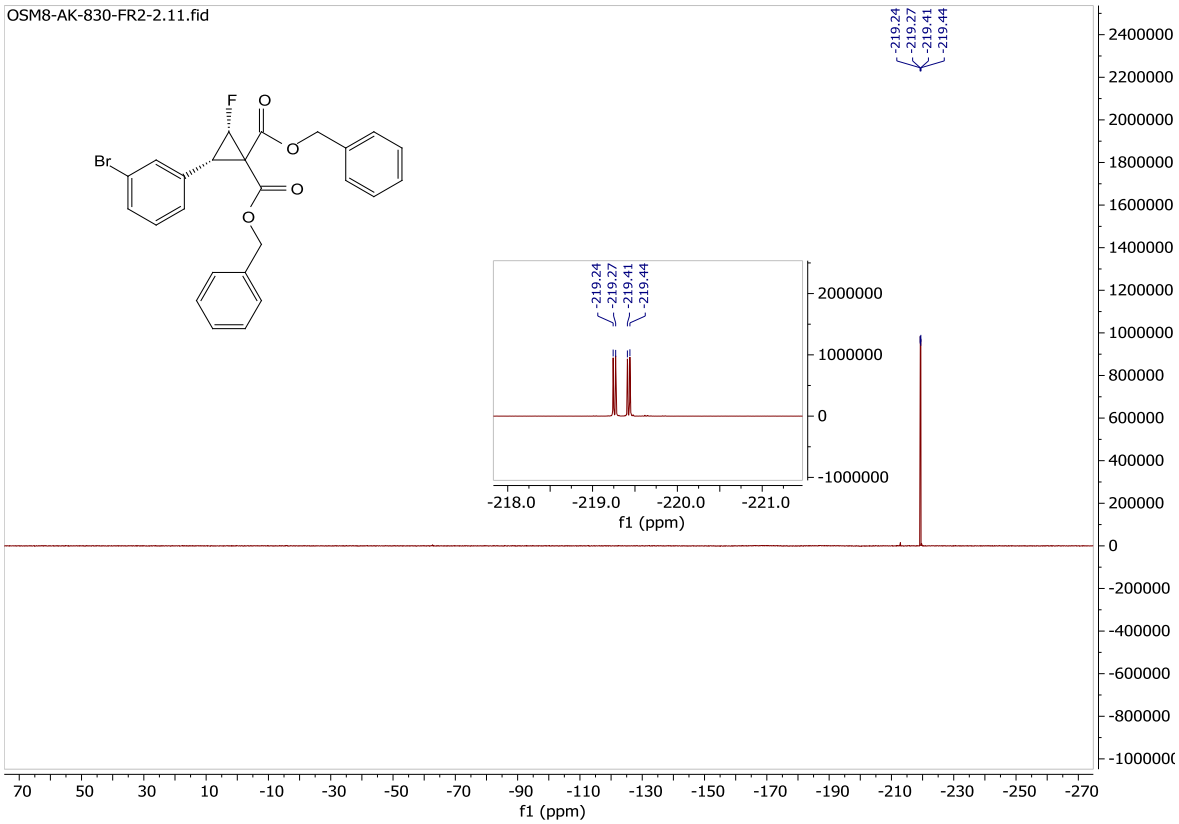
Compound (2*S**,3*R**)-**5t** ^{13}C NMR (400 MHz, $CDCl_3$)



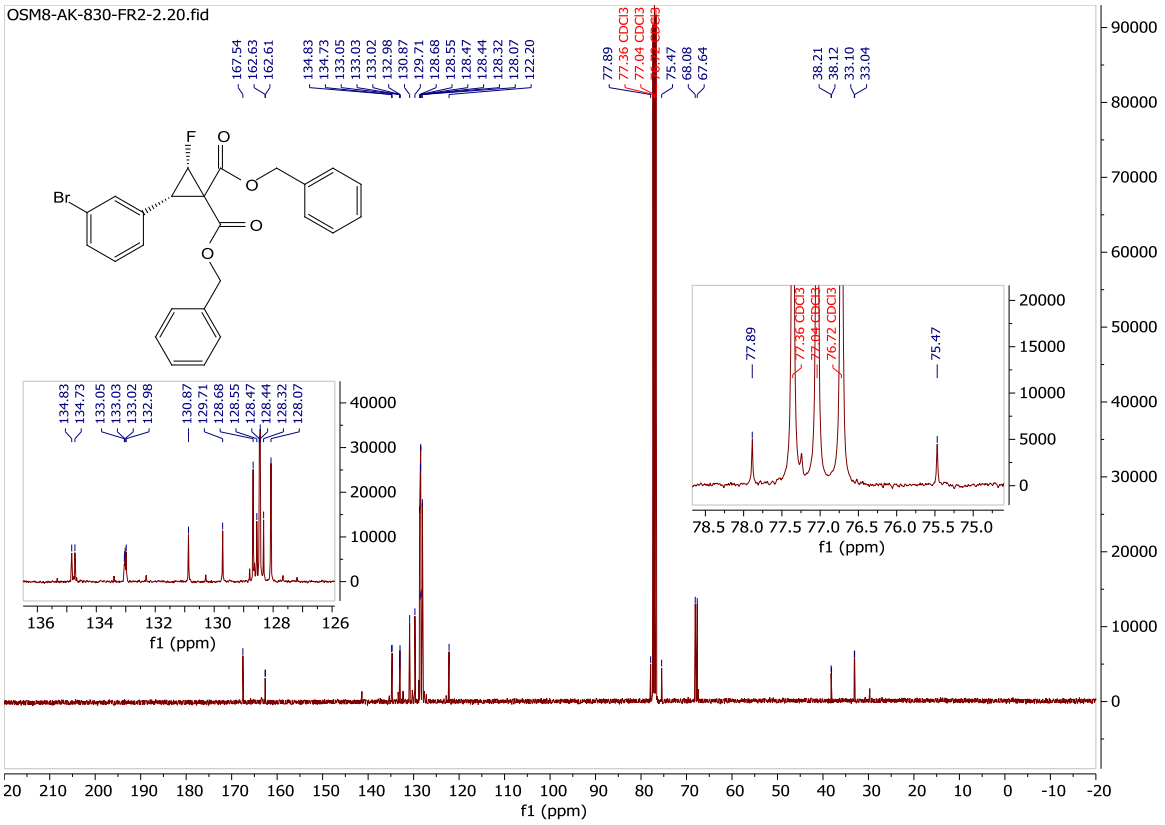
Compound (2*S**,3*S**)-**5t** ^{1}H NMR (400 MHz, $CDCl_3$)



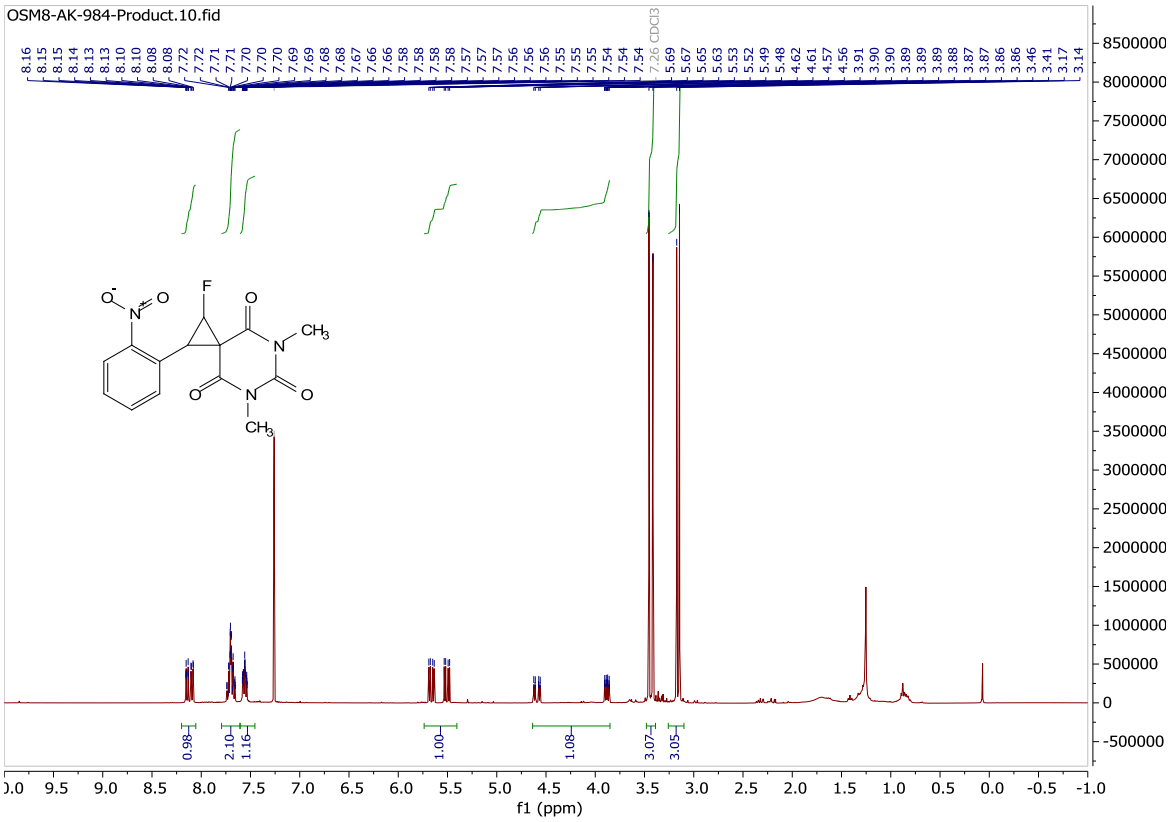
Compound (2*S**,3*S**)-**5t** ^{19}F NMR (400 MHz, $CDCl_3$)



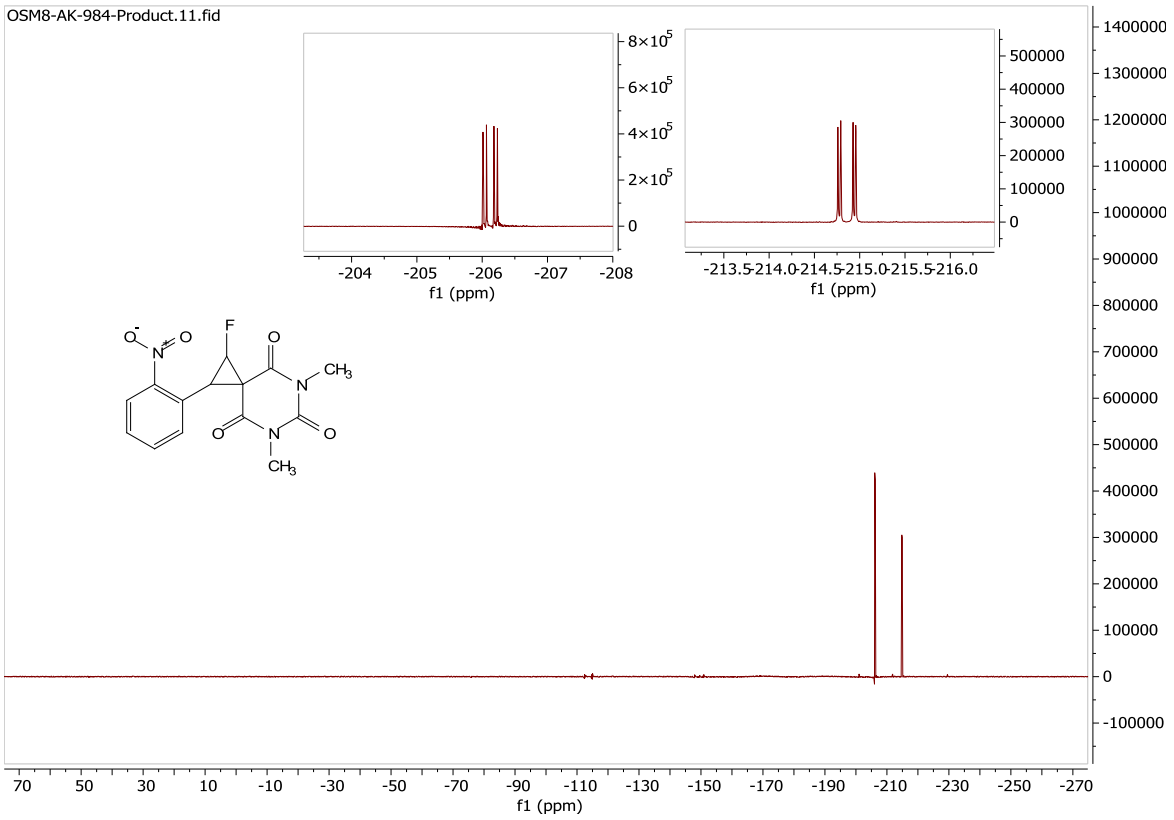
Compound (2*S**,3*S**)-**5t** ^{13}C NMR (400 MHz, $CDCl_3$)



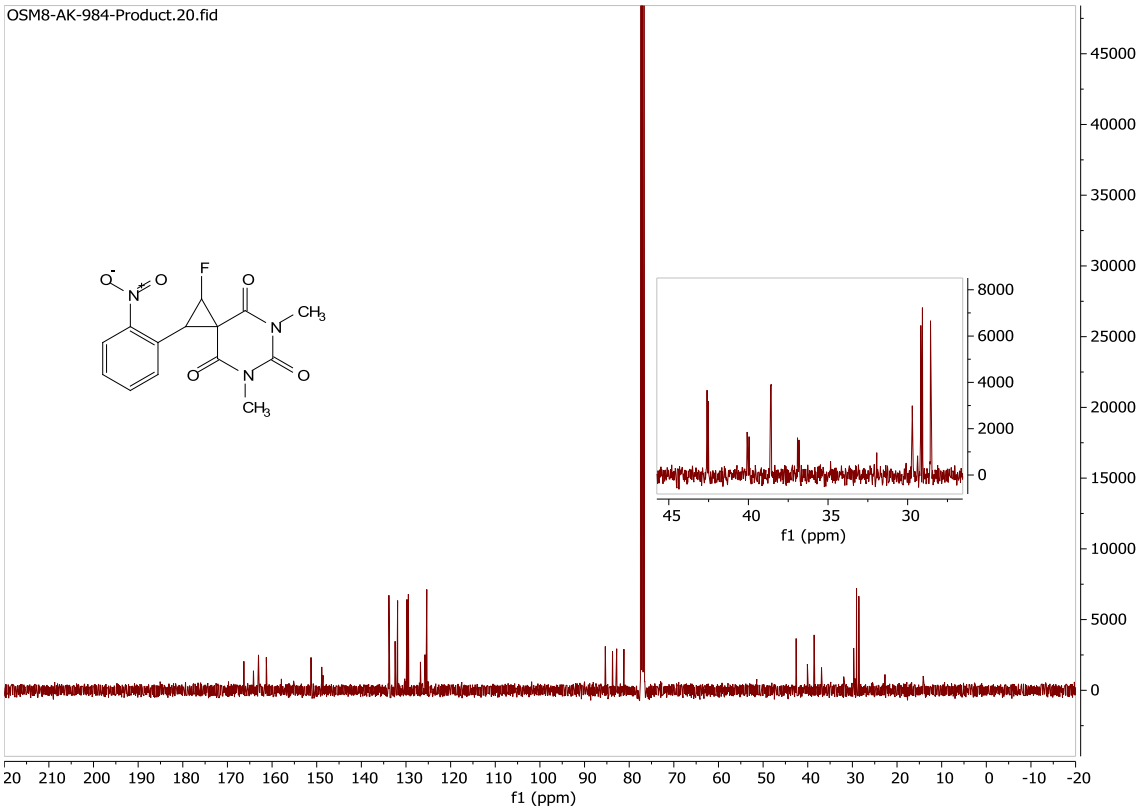
Compound **5u** ^{1}H NMR (400 MHz, $CDCl_3$)



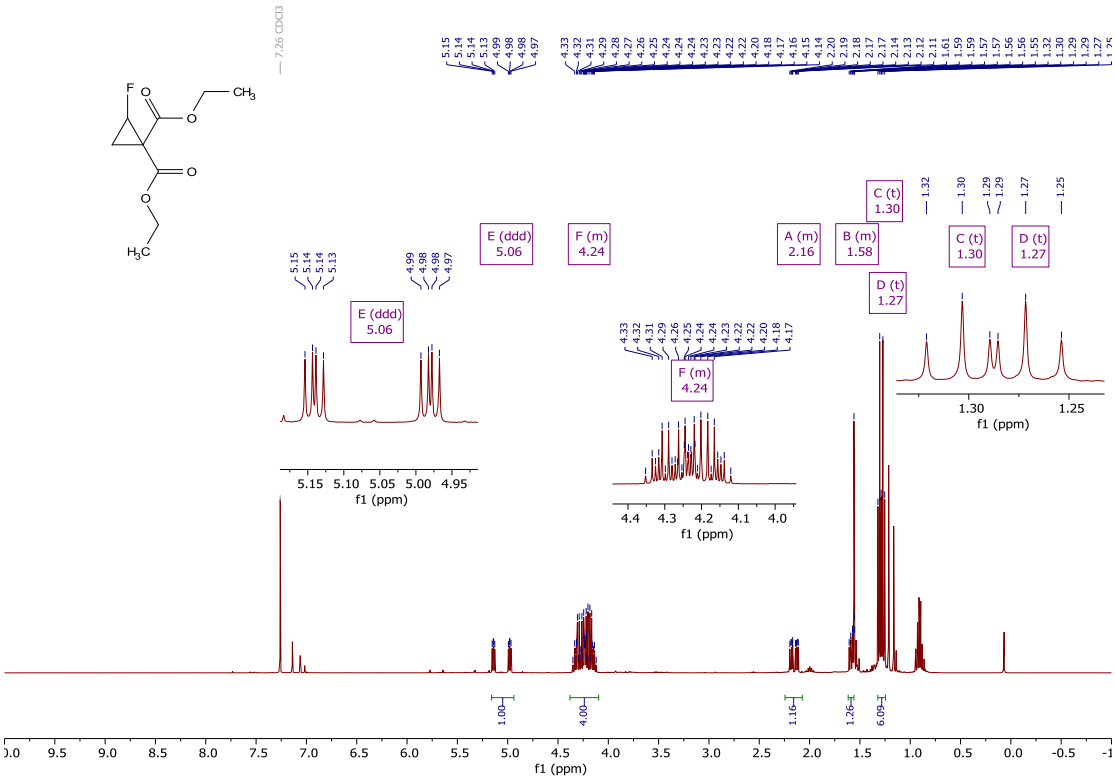
Compound **5u** ^{19}F NMR (400 MHz, $CDCl_3$)



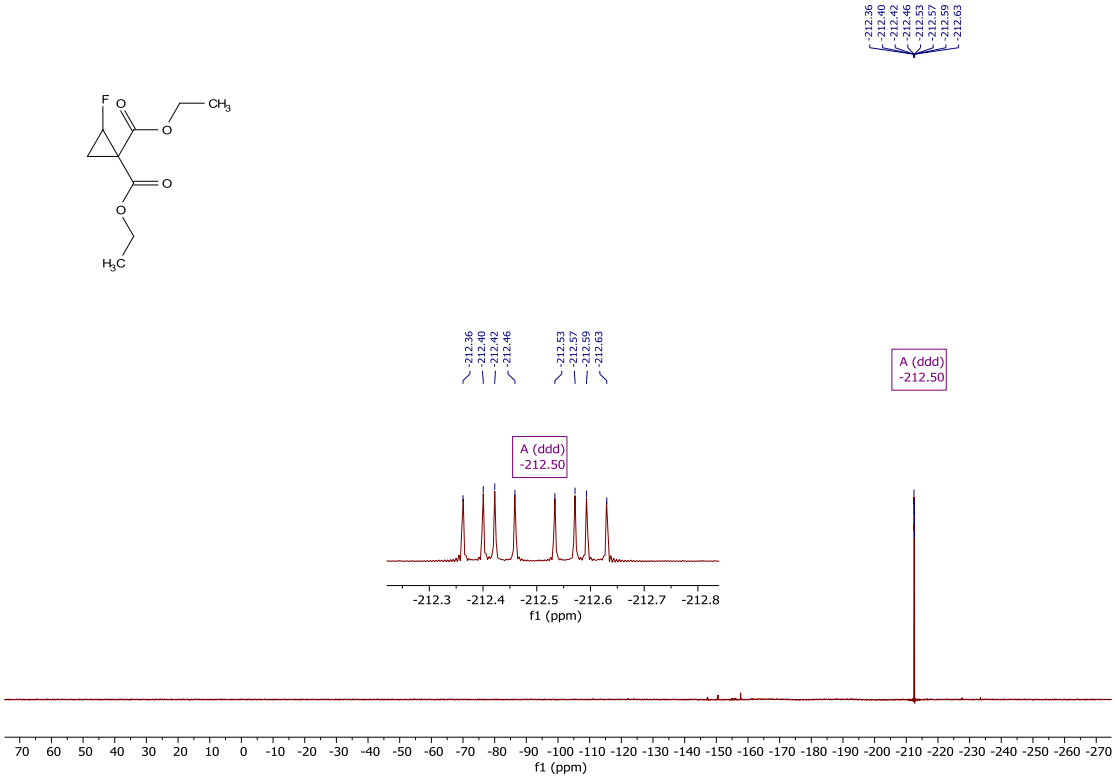
Compound **5u** ^{13}C NMR (400 MHz, $CDCl_3$)



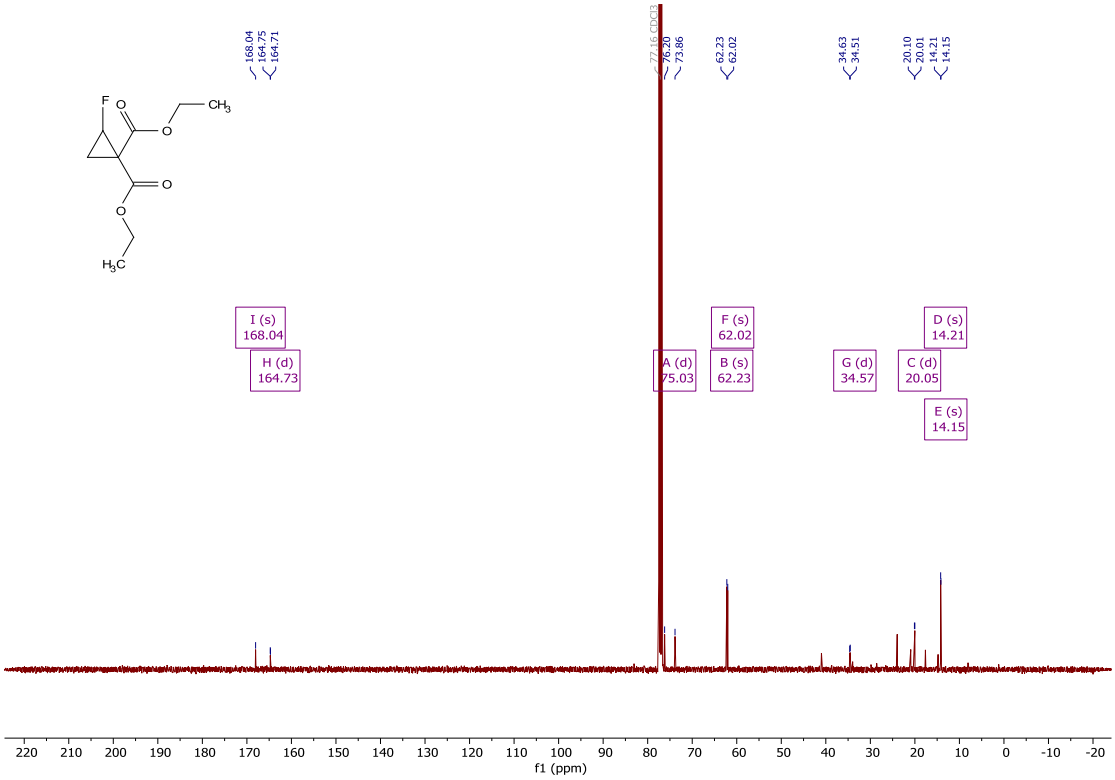
Compound **5v** ^{1}H NMR (400 MHz, $CDCl_3$)



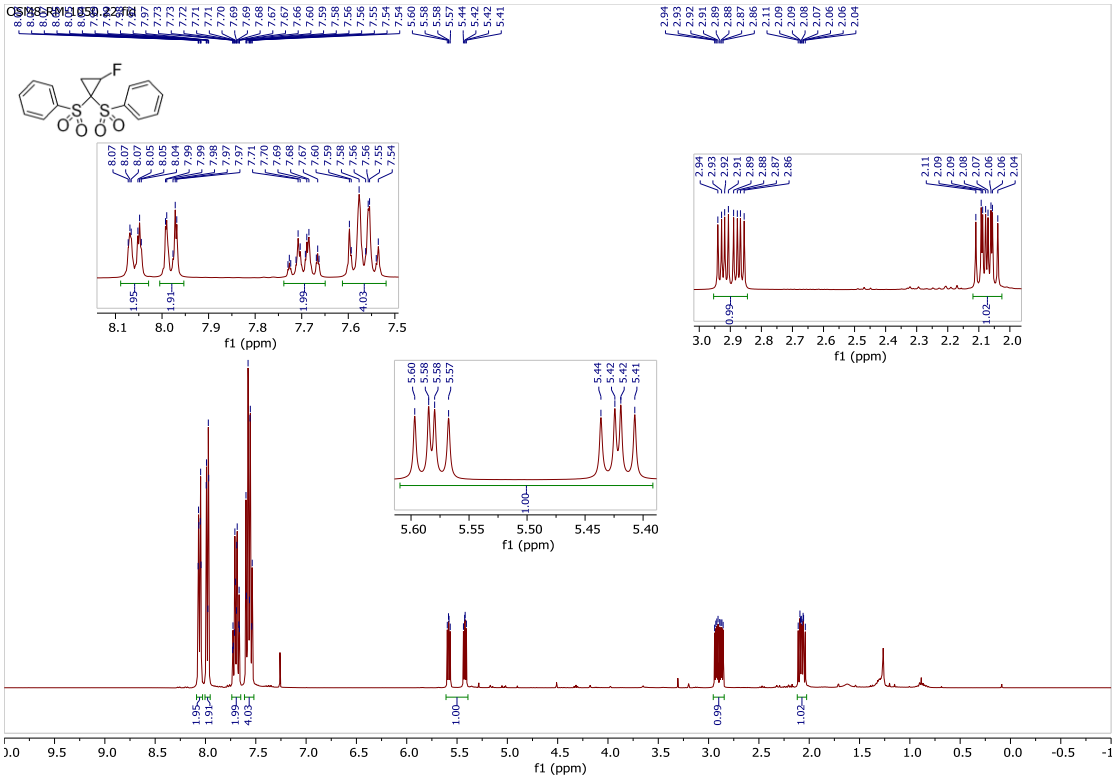
Compound **5v** ^{19}F NMR (400 MHz, $CDCl_3$)



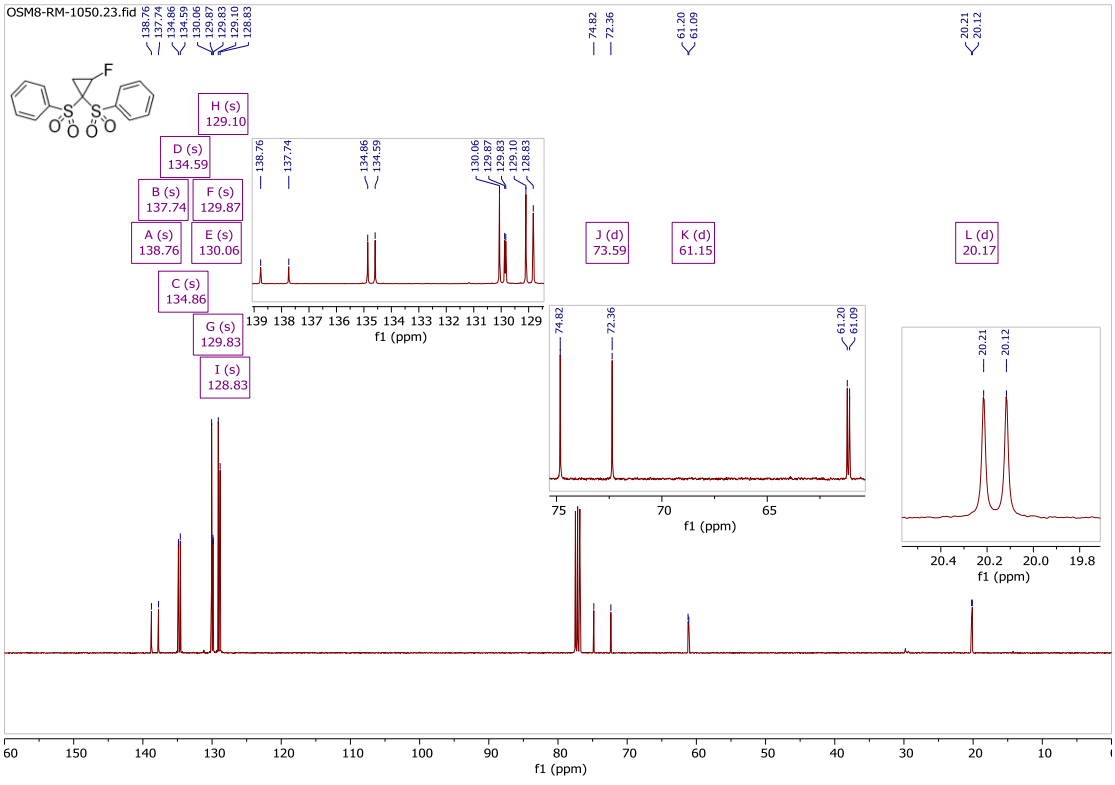
Compound **5v** ^{13}C NMR (400 MHz, $CDCl_3$)



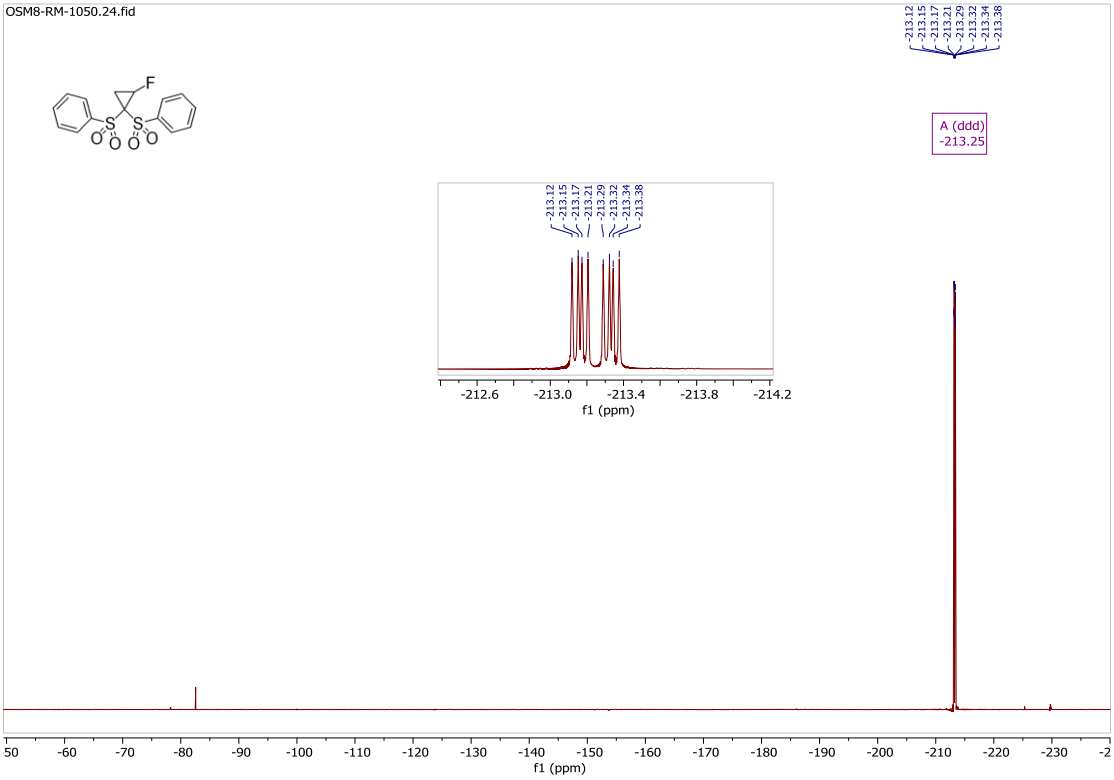
Compound **5w** ^{1}H NMR (400 MHz, $CDCl_3$)



Compound **5w** ^{13}C NMR (400 MHz, $CDCl_3$)



Compound **5w** ^{19}F NMR (400 MHz, $CDCl_3$)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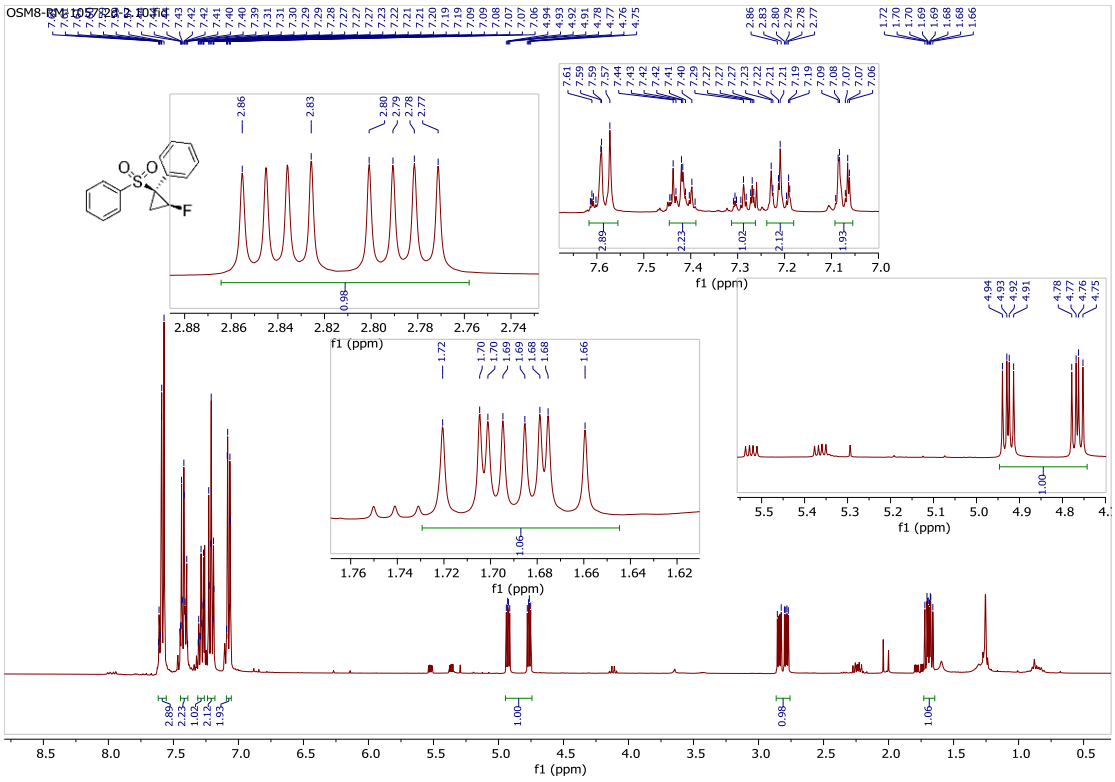
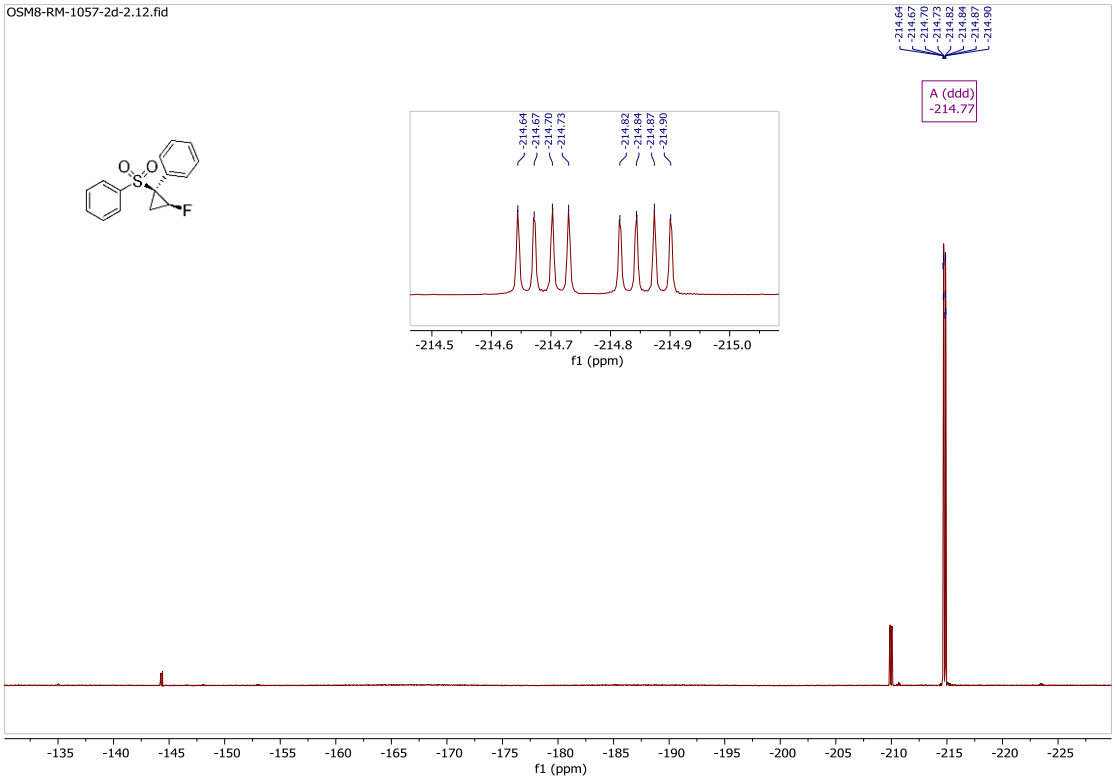
-213.15
-213.17
-213.21
-213.29
-213.32
-213.34
-213.38
A (ddd)
-213.25
-212.6
-213.0
-213.4
-213.8
-214.2
f1 (ppm)
50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
-220
-230
f1 (ppm)

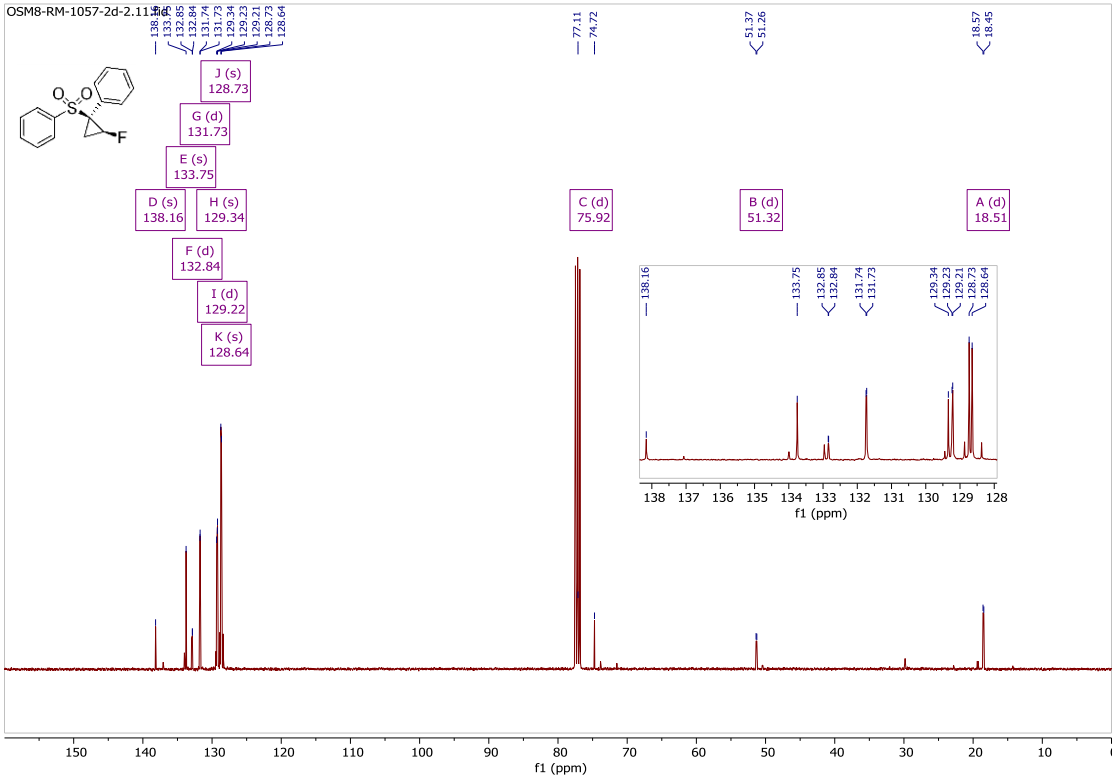
Compound *trans*-**5x** ^{1}H NMR (400 MHz, $CDCl_3$)



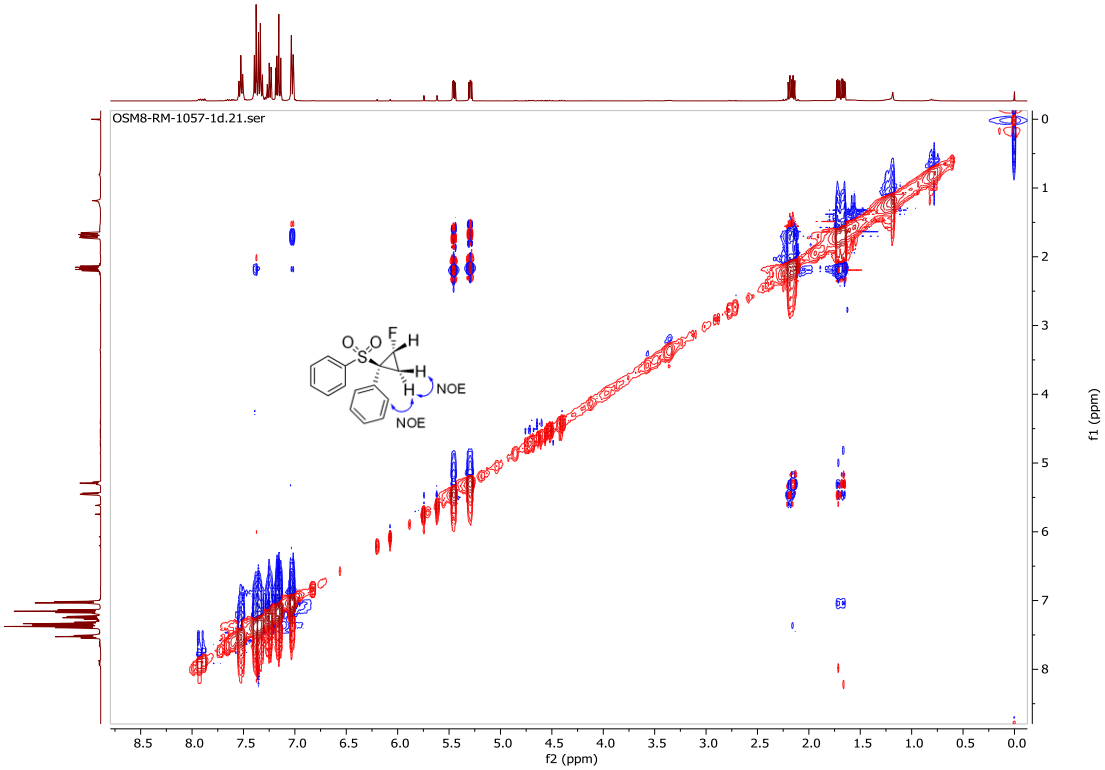
Compound *trans*-**5x** ^{19}F NMR (400 MHz, $CDCl_3$)



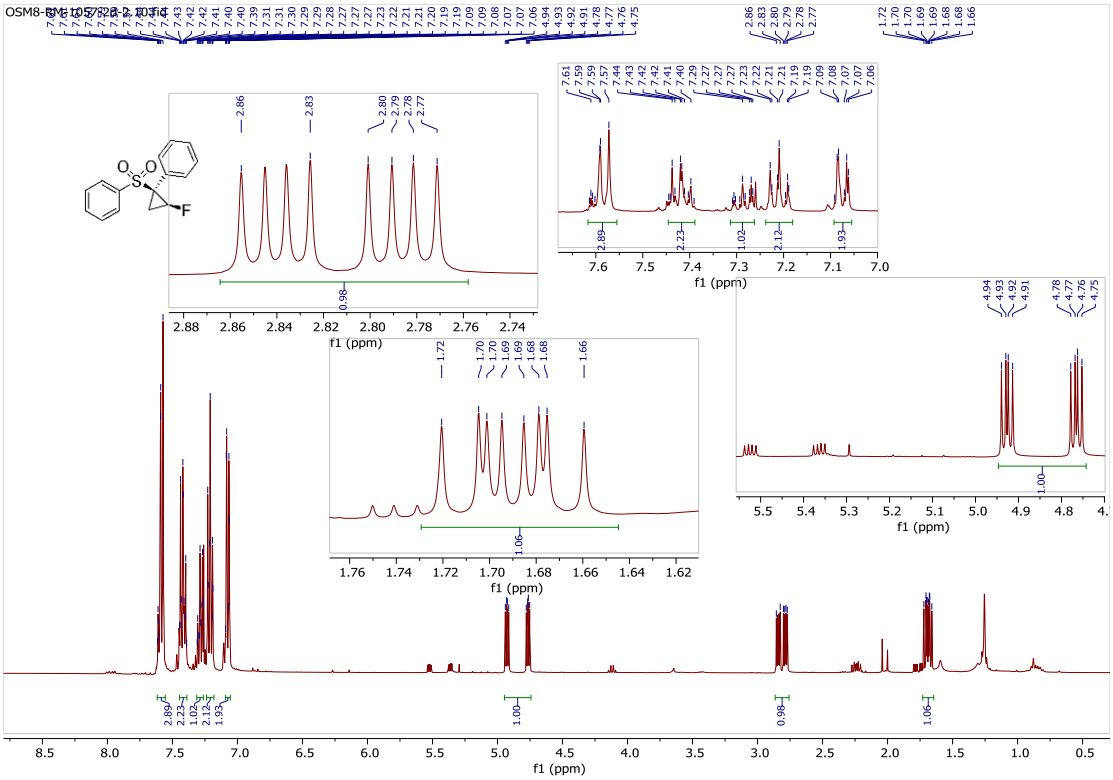
Compound *trans*-**5x** ^{13}C NMR (400 MHz, $CDCl_3$)



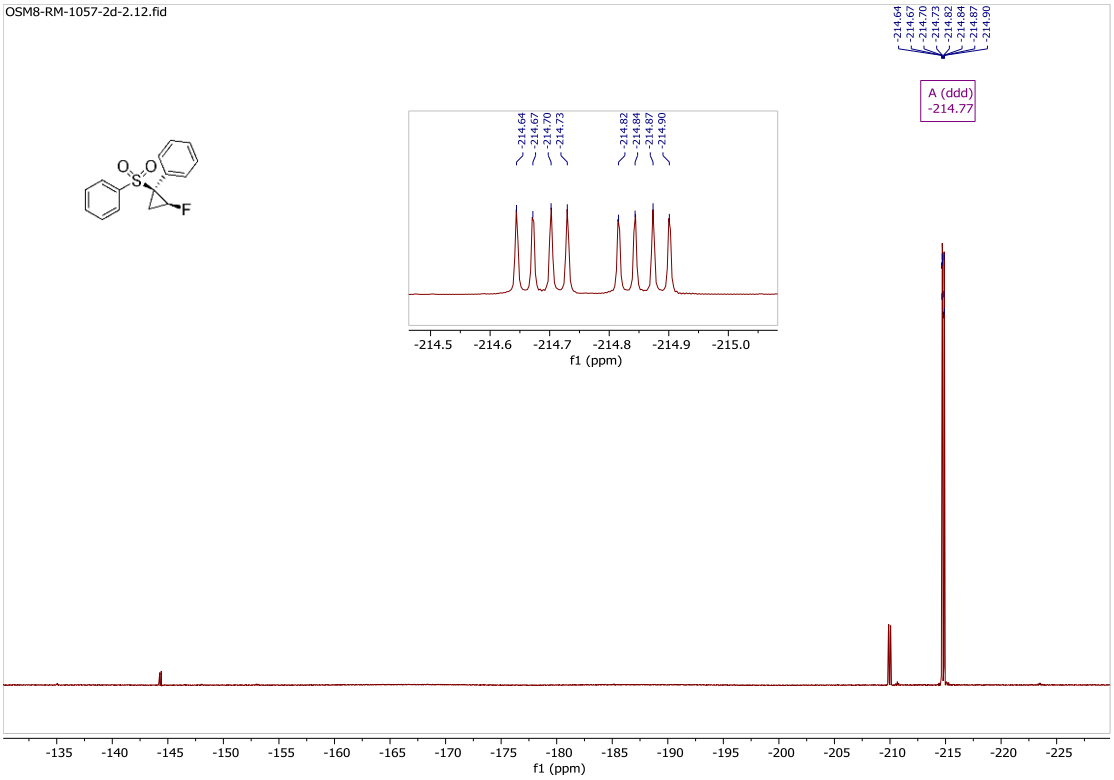
Compound *trans*-**5x** NOESY(400 MHz, $CDCl_3$)



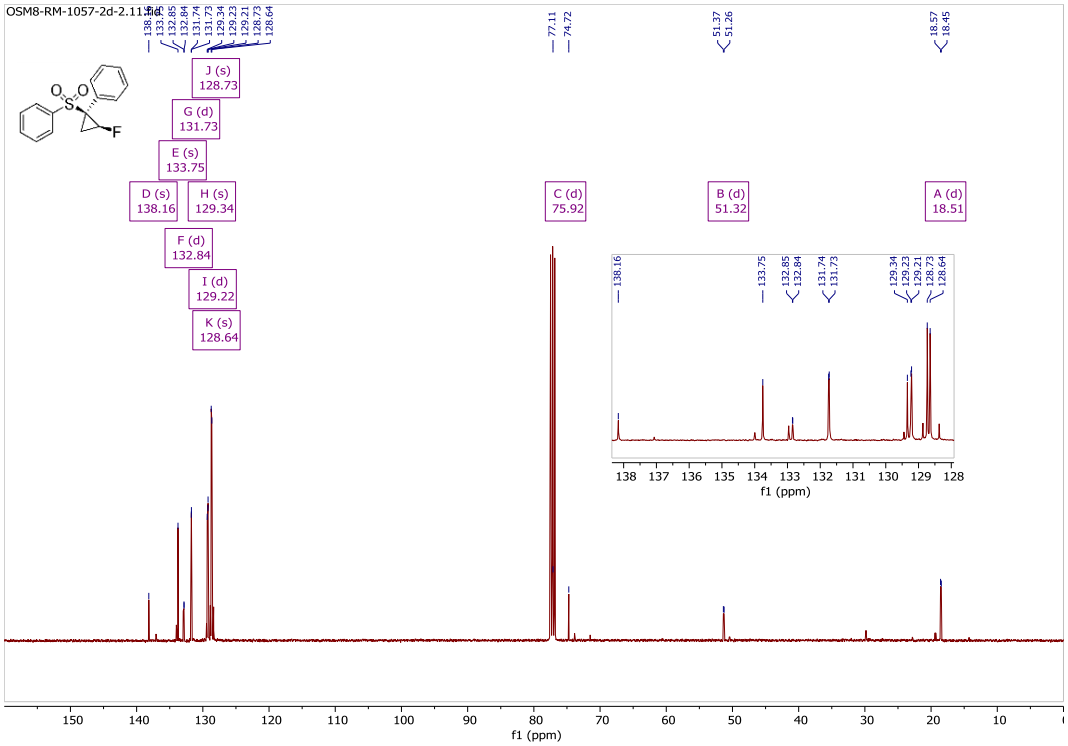
Compound *cis*-**5x** ^{1}H (400 MHz, $CDCl_3$)



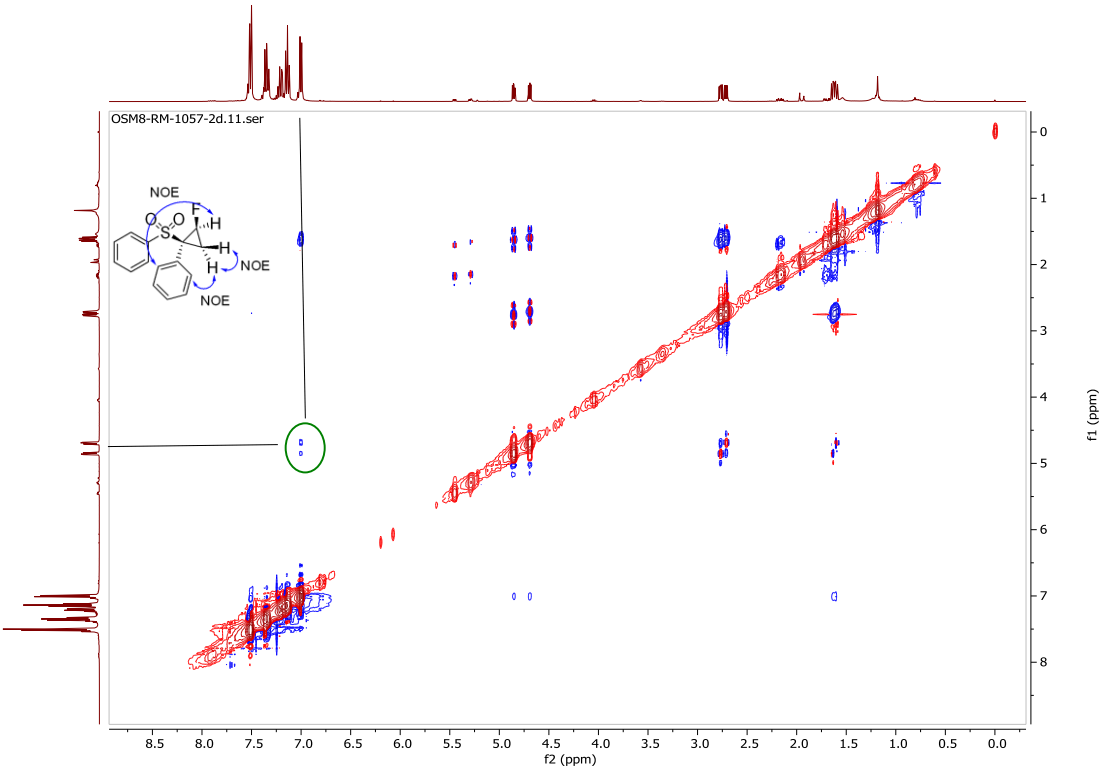
Compound *cis*-**5x** ^{19}F (400 MHz, $CDCl_3$)



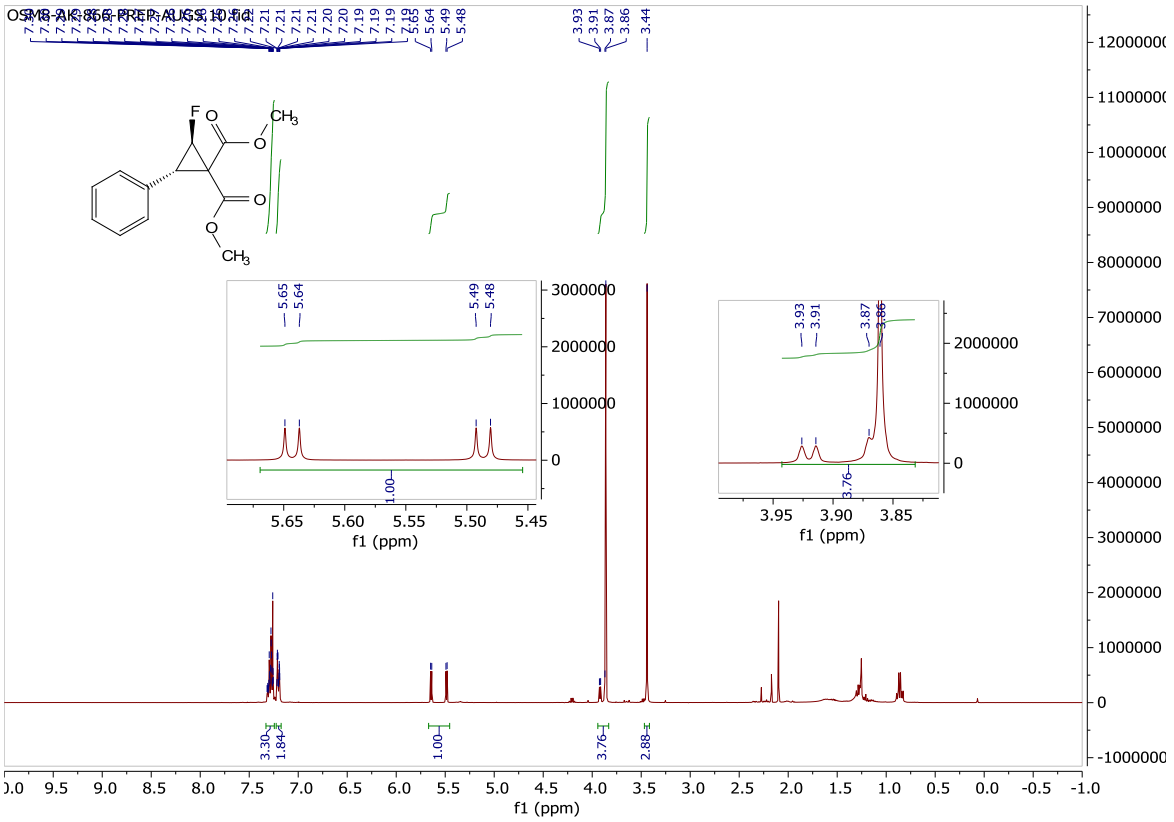
Compound *cis*-**5x** ^{13}C (400 MHz, $CDCl_3$)



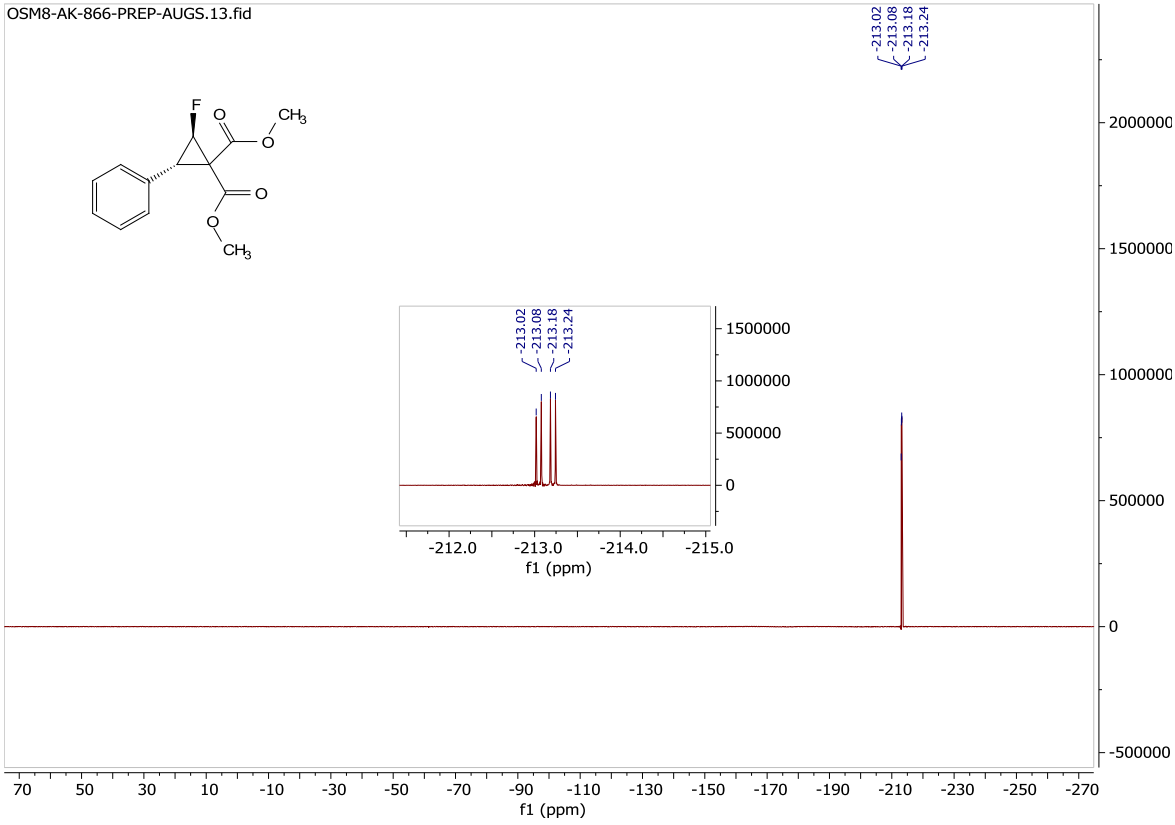
Compound *cis*-**5x** NOESY (400 MHz, $CDCl_3$)



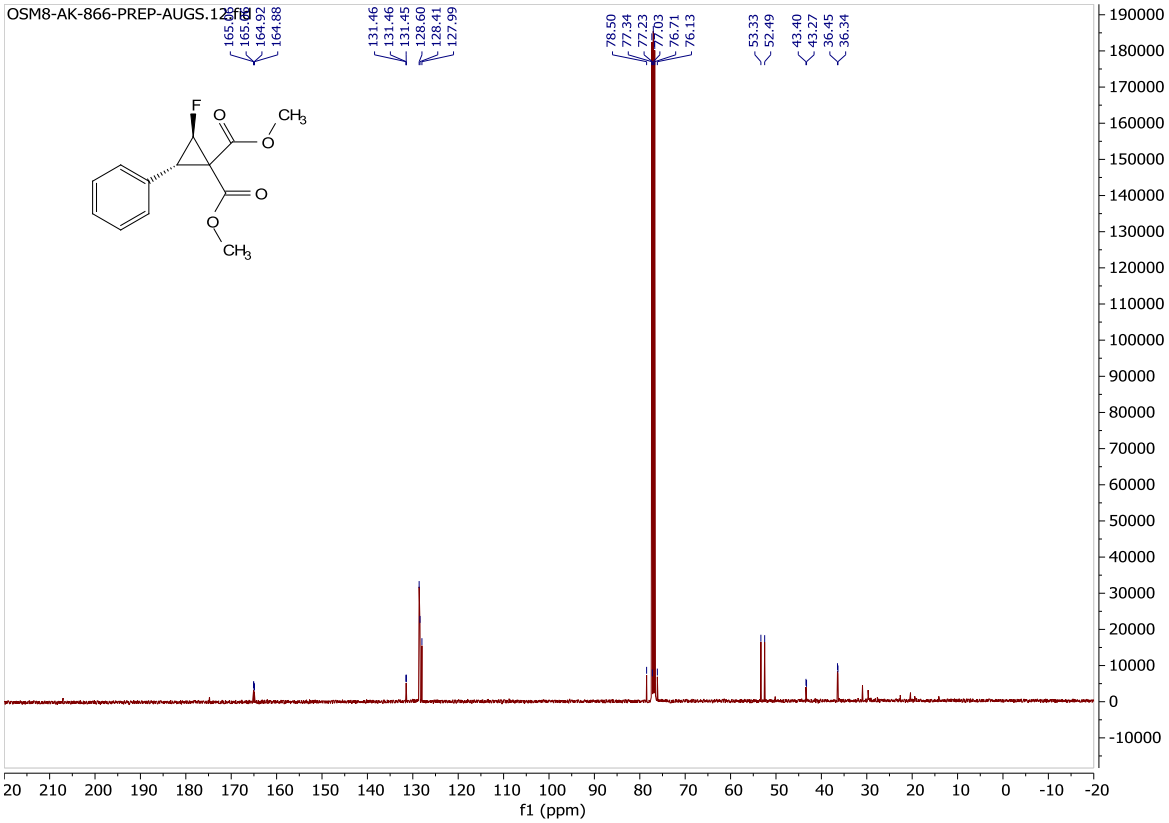
Compound (2*R**,3*S**)-**5y** ^{1}H NMR (400 MHz, $CDCl_3$)



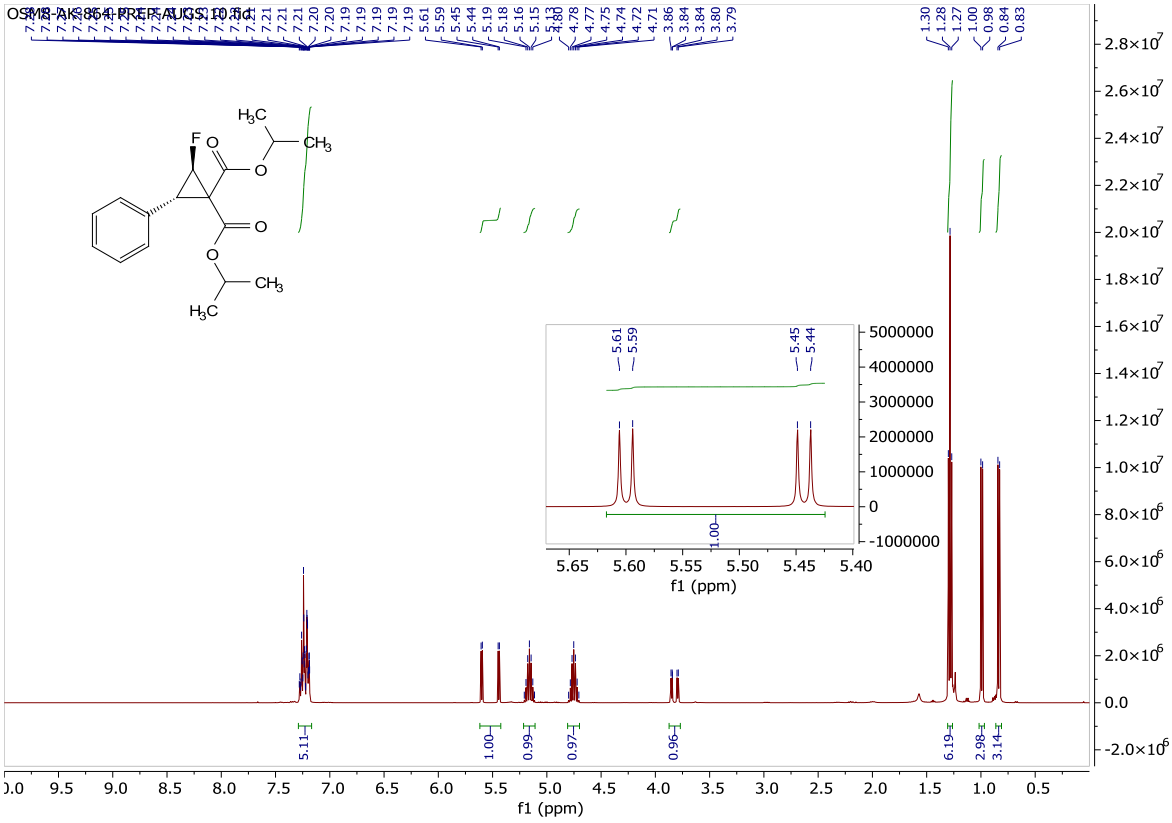
Compound (2*R**,3*S**)-**5y** ^{19}F NMR (400 MHz, $CDCl_3$)



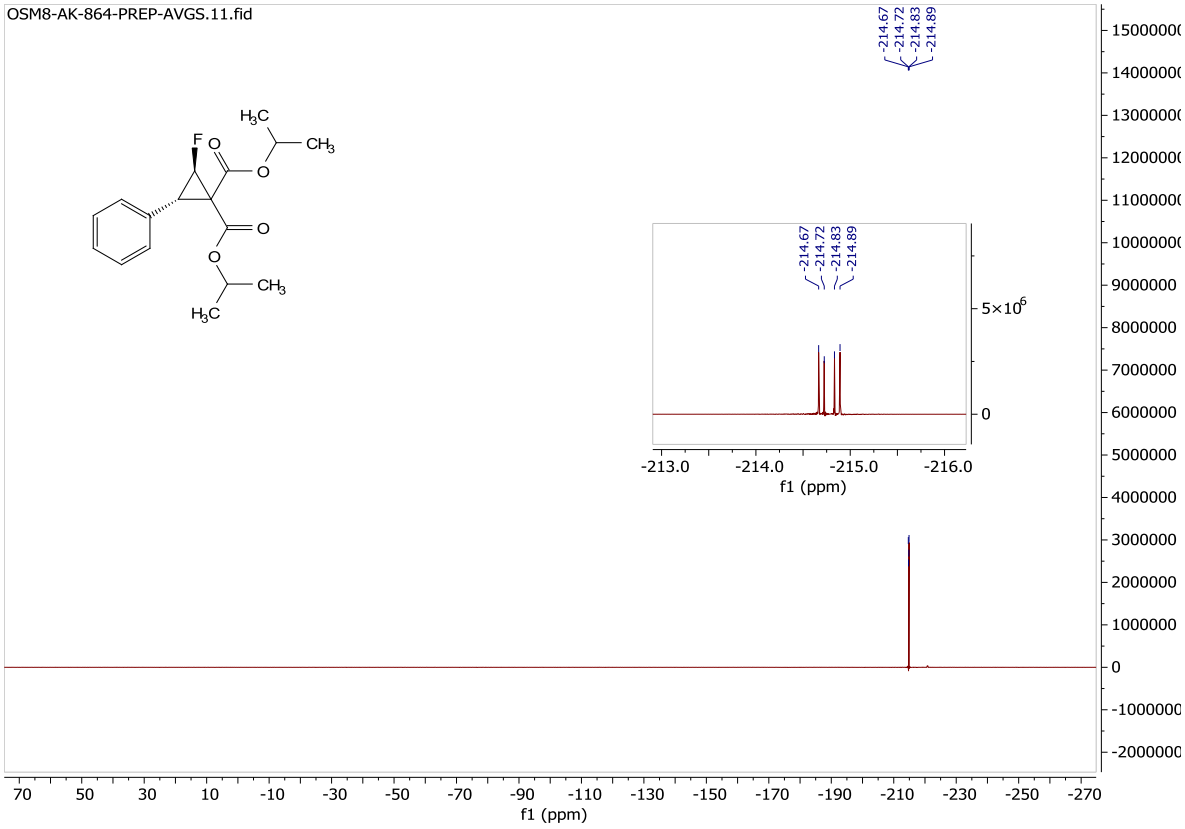
Compound (2*R**,3*S**)-**5y** ^{13}C NMR (400 MHz, $CDCl_3$)



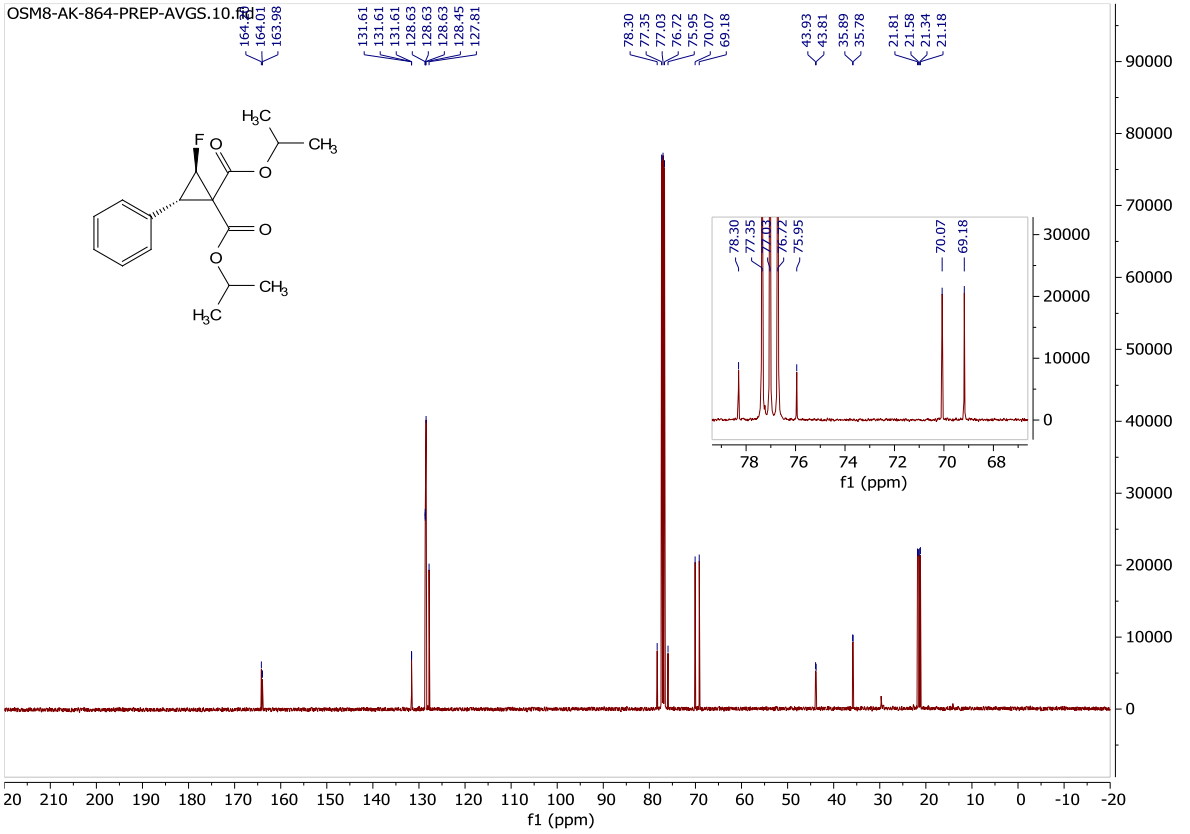
Compound (2*R**,3*S**)-**5z** ^{1}H NMR (400 MHz, $CDCl_3$)



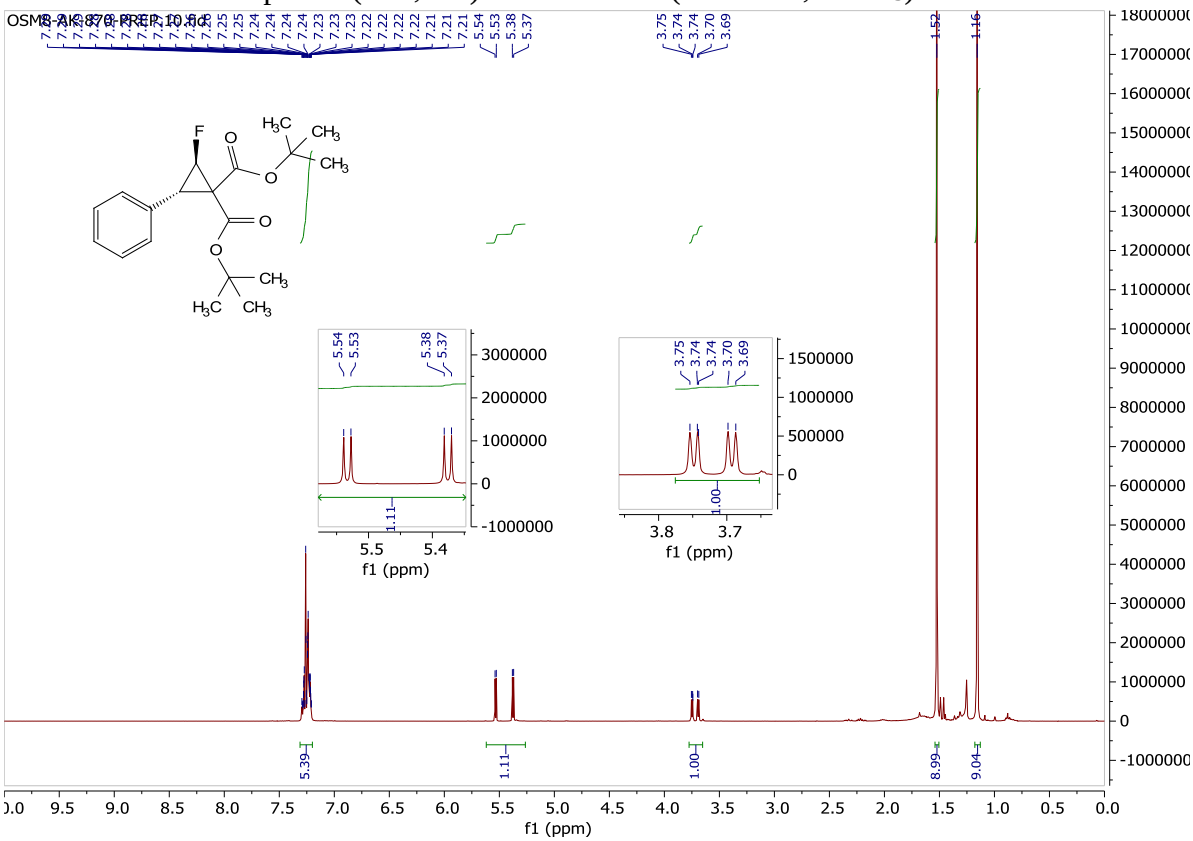
Compound (2*R**,3*S**)-**5z** ^{19}F NMR (400 MHz, $CDCl_3$)


OSM8-AK-864-PREP-AVGS.11.fid
-214.67
-214.72
-214.83
-214.89
F
O
O
O
O
O
H3C
CH3
CH3
H3C
5×10^6
0
-213.0
-214.0
-215.0
-216.0
f1 (ppm)
70
50
30
10
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
-230
-250
-270
f1 (ppm)

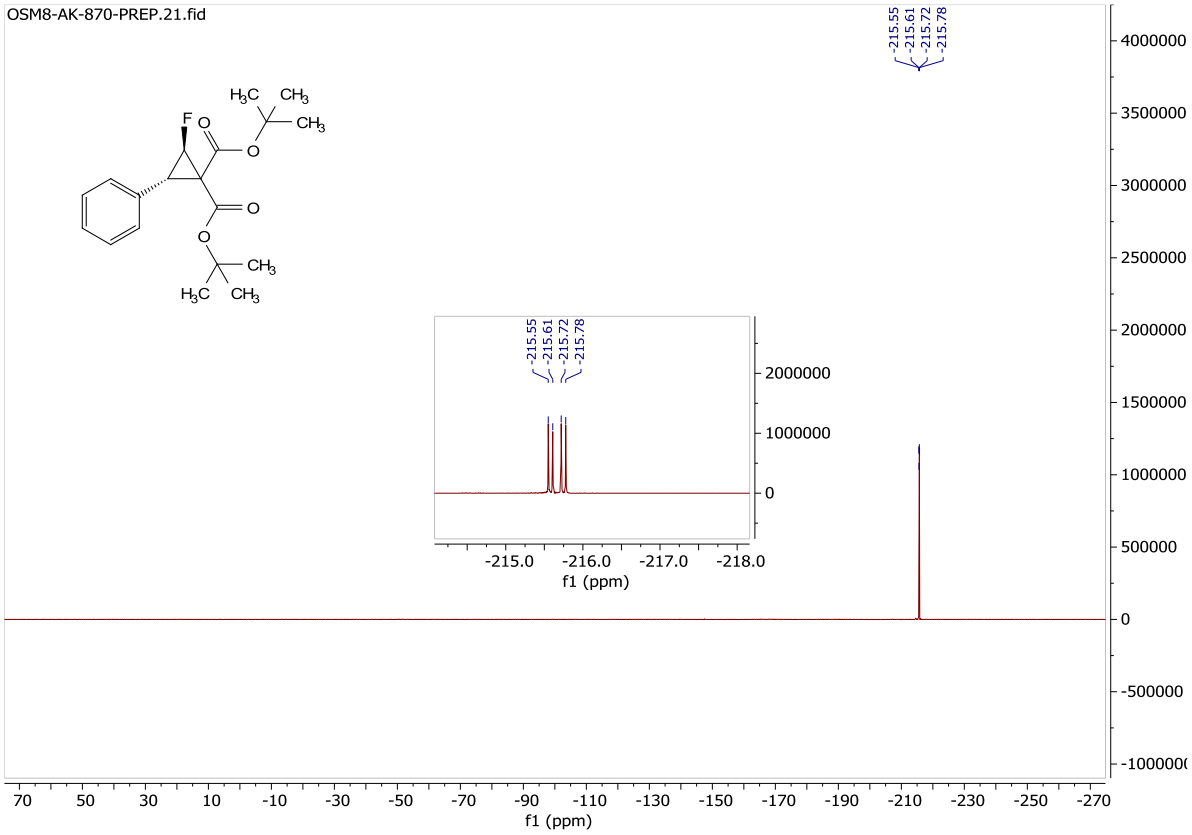
Compound (2*R**,3*S**)-**5z** ^{13}C NMR (400 MHz, $CDCl_3$)



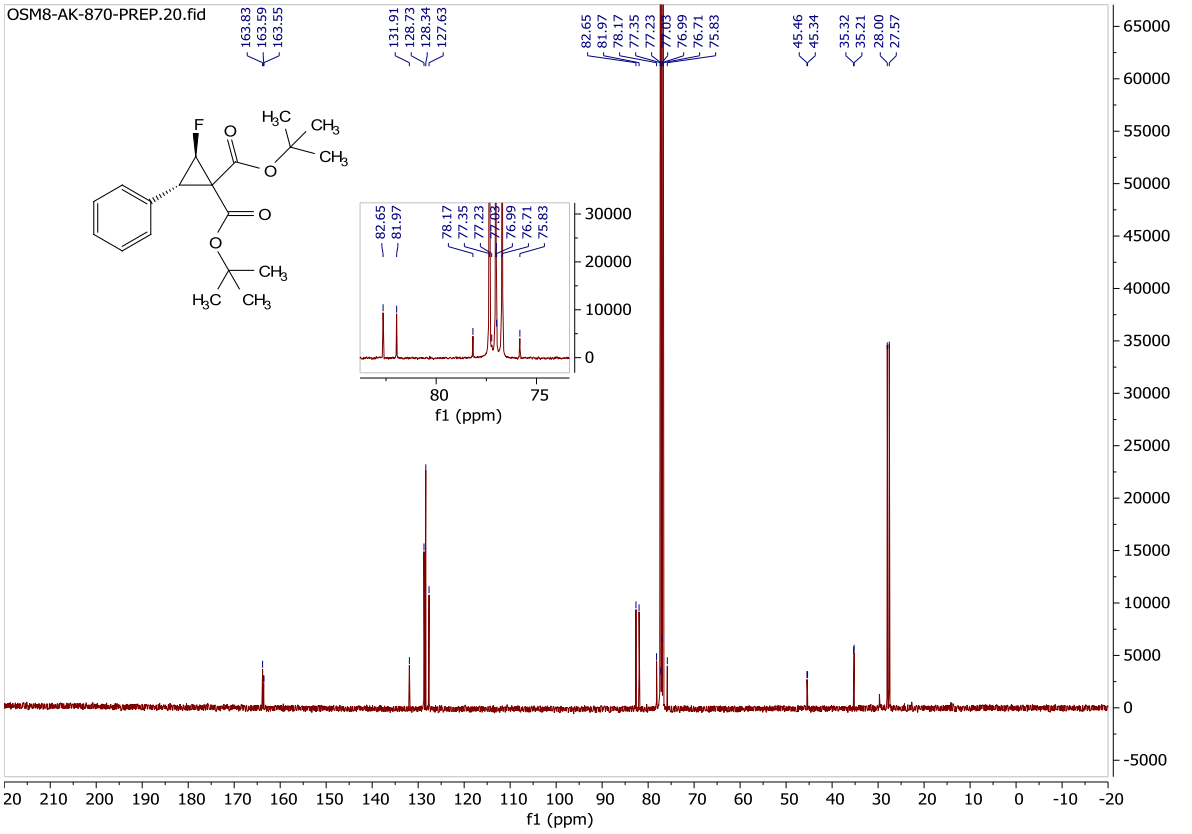
Compound (2*R**,3*S**)-**5aa** ^{1}H NMR (400 MHz, $CDCl_3$)



Compound (2*R**,3*S**)-**5aa** ^{19}F NMR (400 MHz, $CDCl_3$)

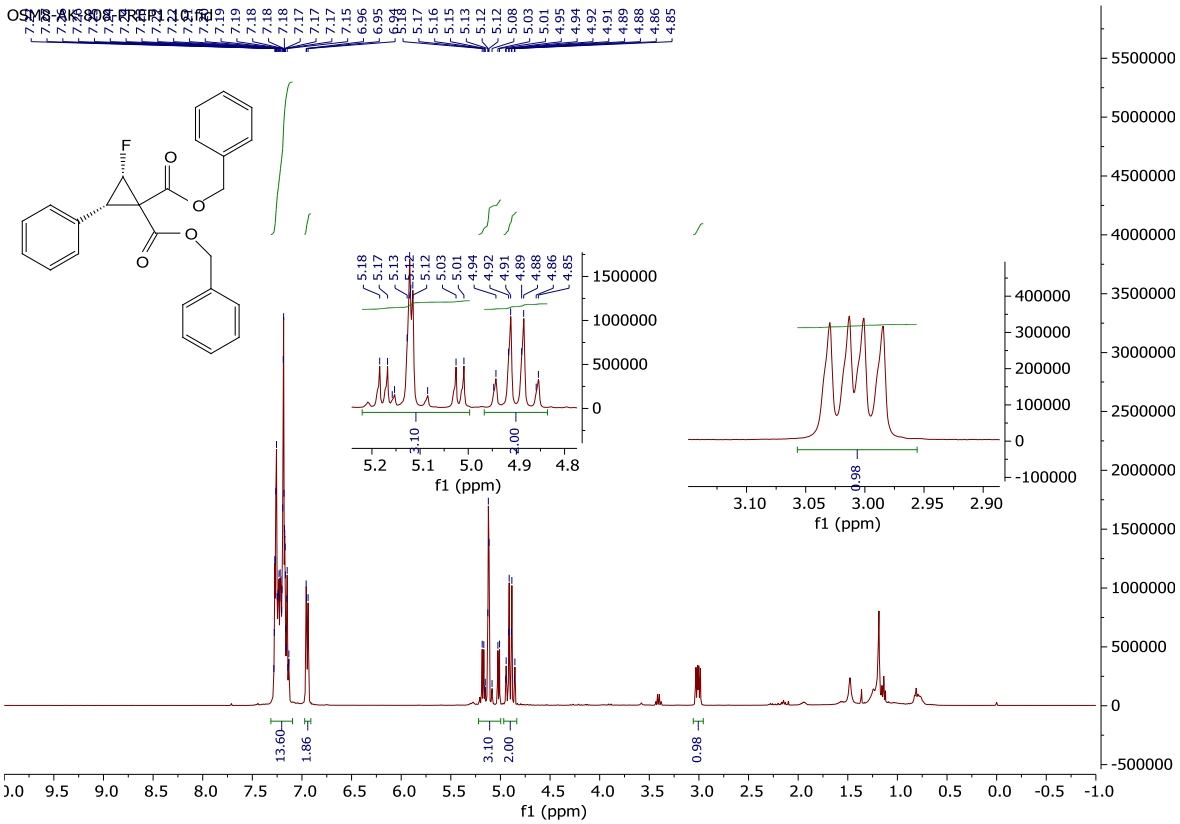


Compound (2*R**,3*S**)-**5aa** ^{13}C NMR (400 MHz, $CDCl_3$)

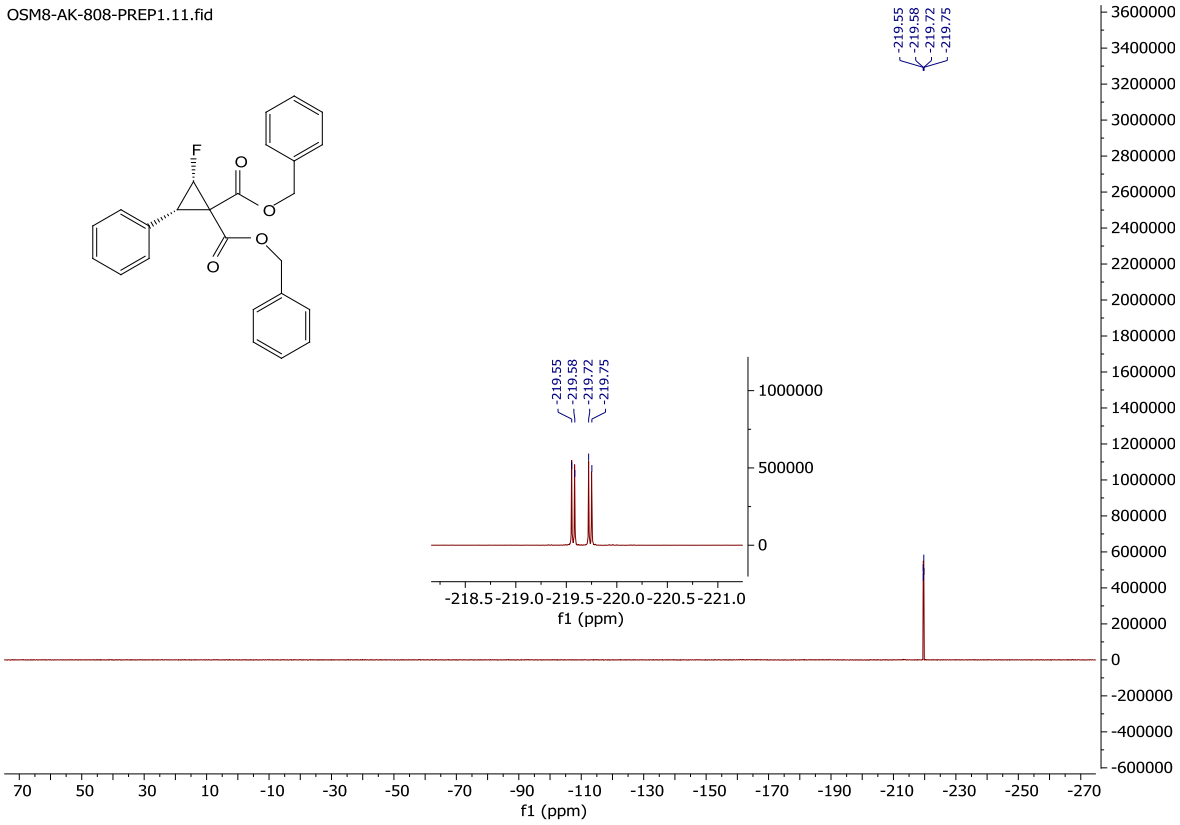


Compound (xx)

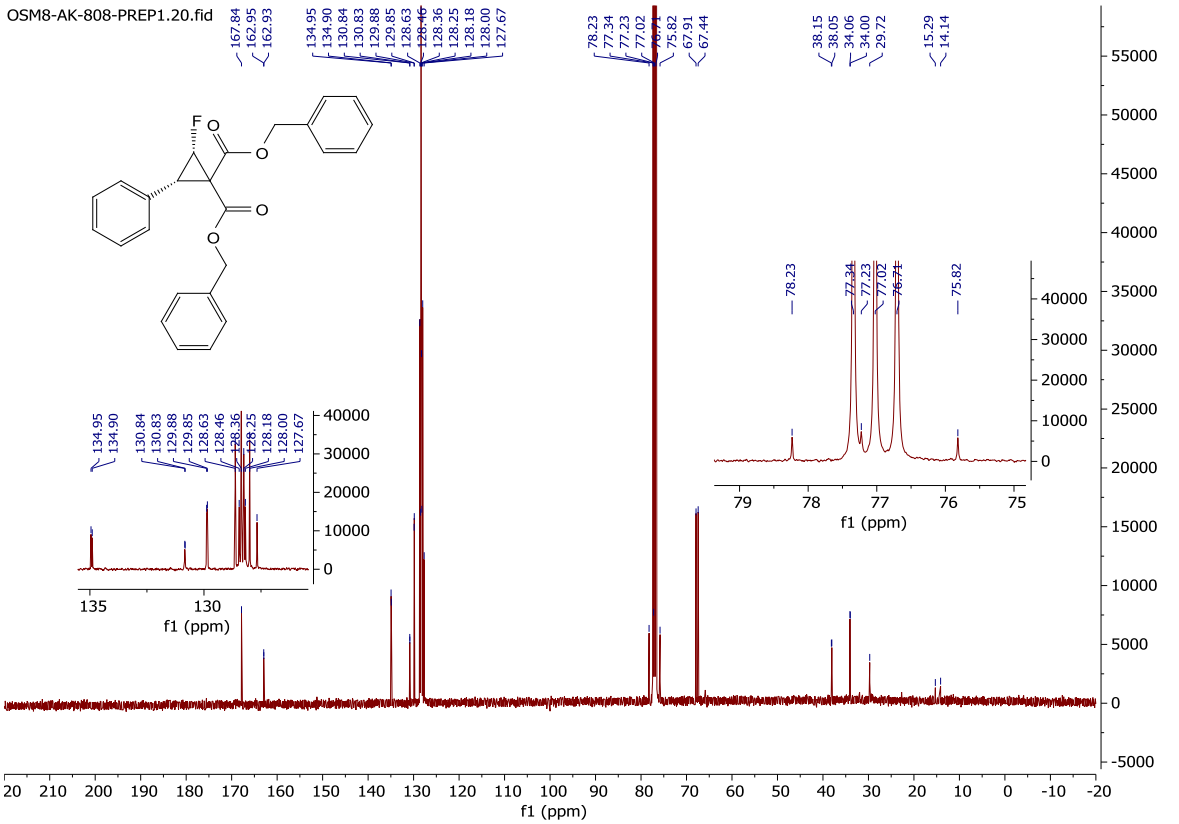
Compound (2S*,3S*)-**5ab** ^{1}H NMR (400 MHz, $CDCl_3$)



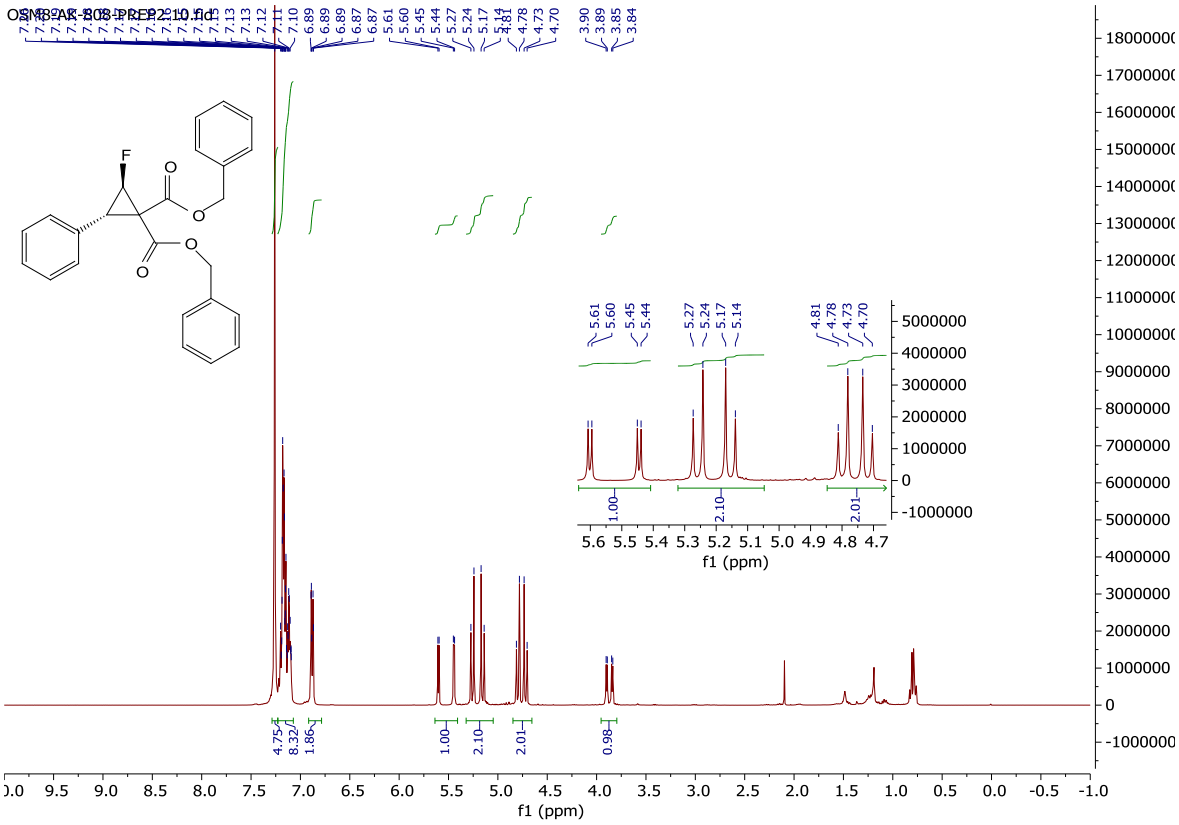
Compound (2S*,3S*)-**5ab** ^{19}F NMR (400 MHz, $CDCl_3$)



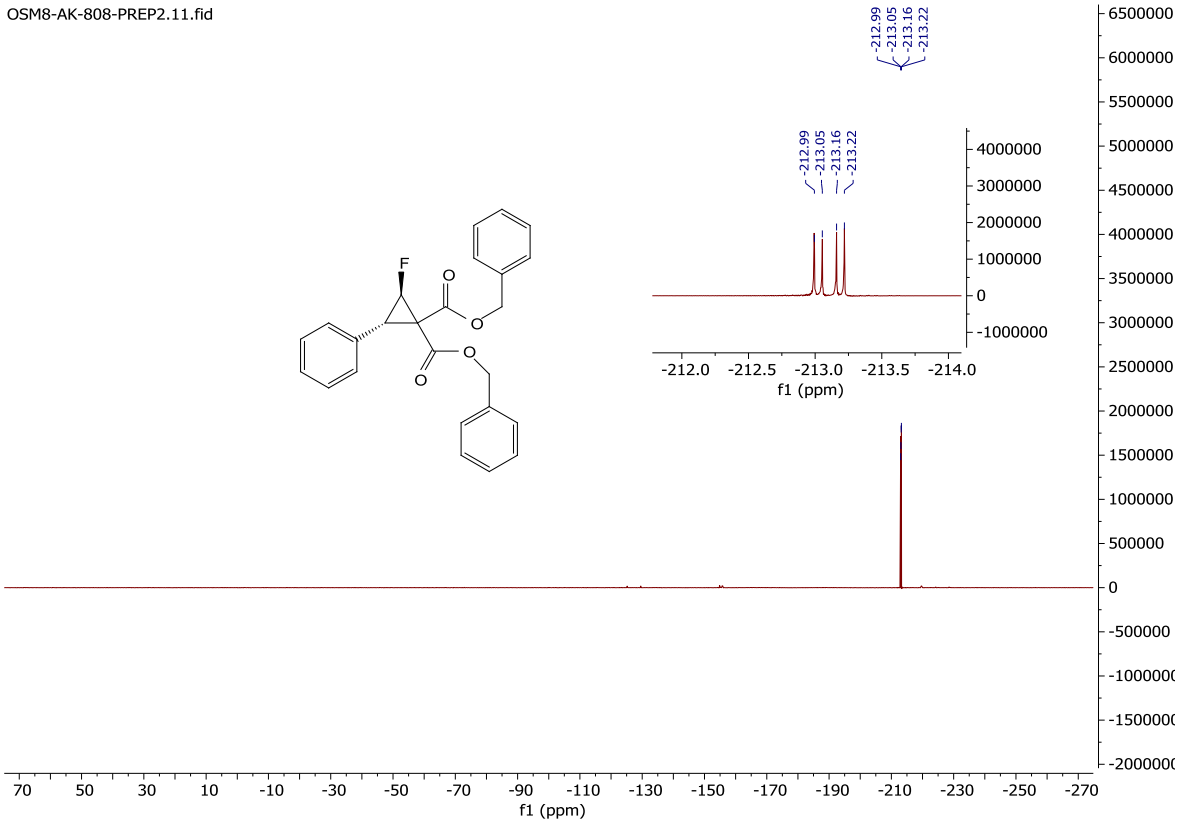
Compound **(2S*,3S*)-5ab** ^{13}C NMR (400 MHz, $CDCl_3$)



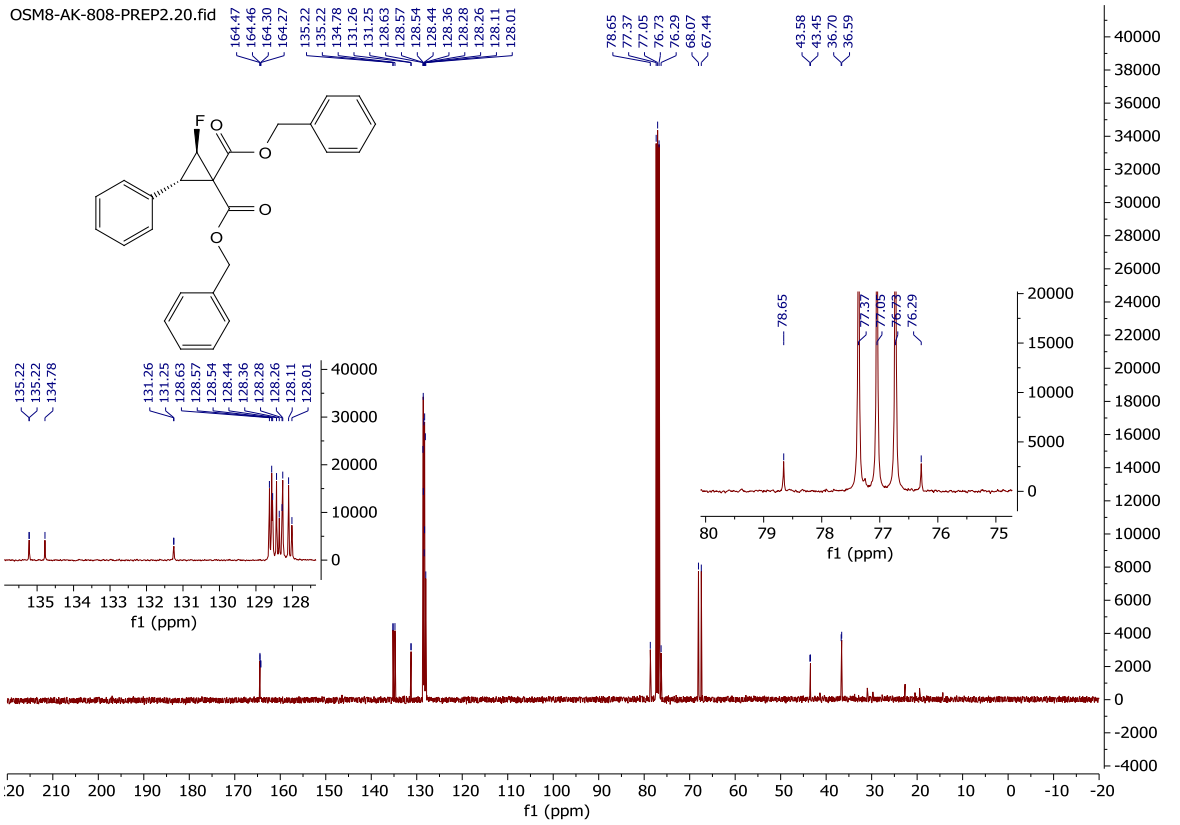
Compound (2R*,3S*)-**5ab** ^{1}H NMR (400 MHz, $CDCl_3$)



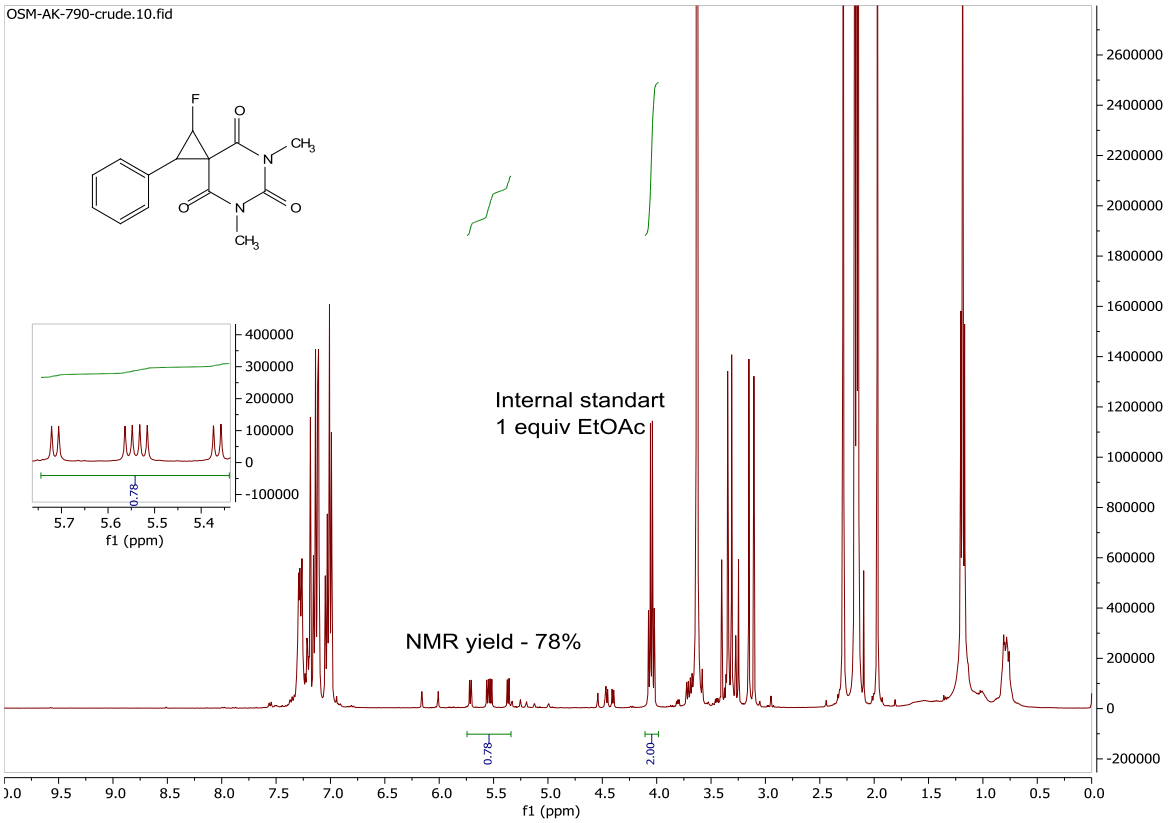
Compound (2R*,3S*)-**5ab** ^{19}F NMR (400 MHz, $CDCl_3$)



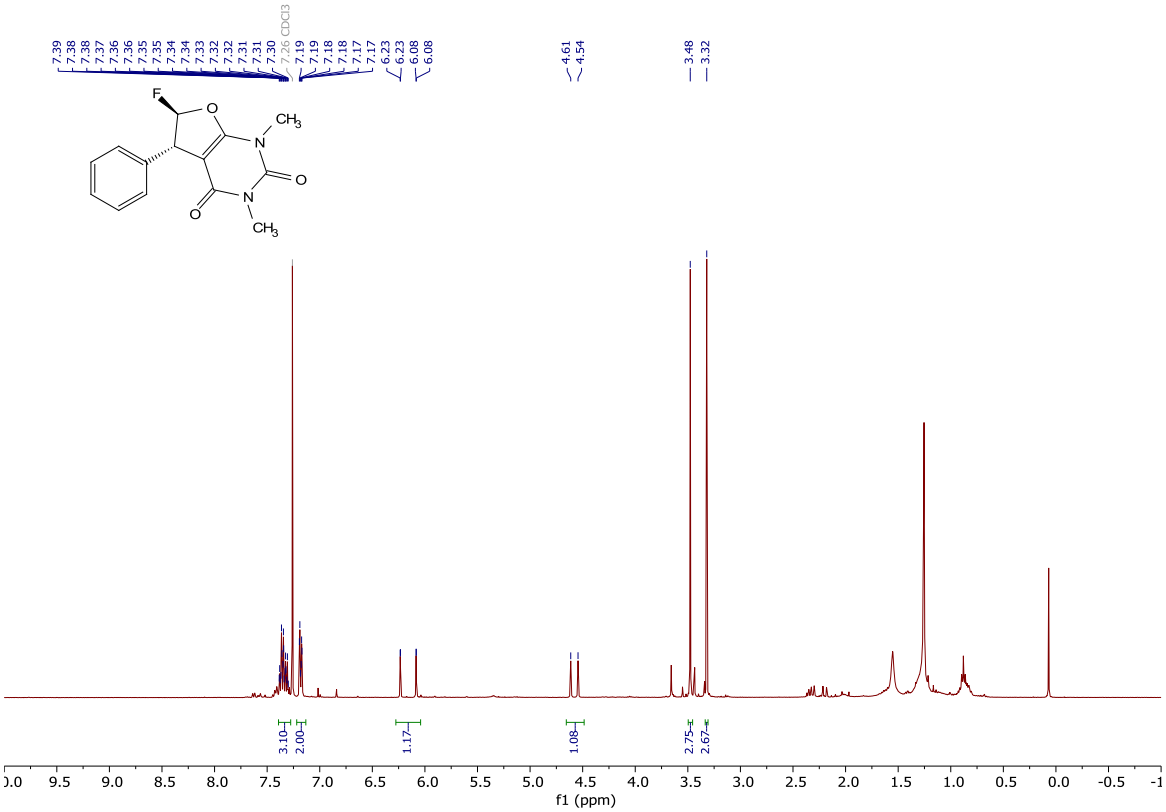
Compound (2R*,3S*)-**5ab** ^{13}C-KMR spektrs (400 MHz, $CDCl_3$)



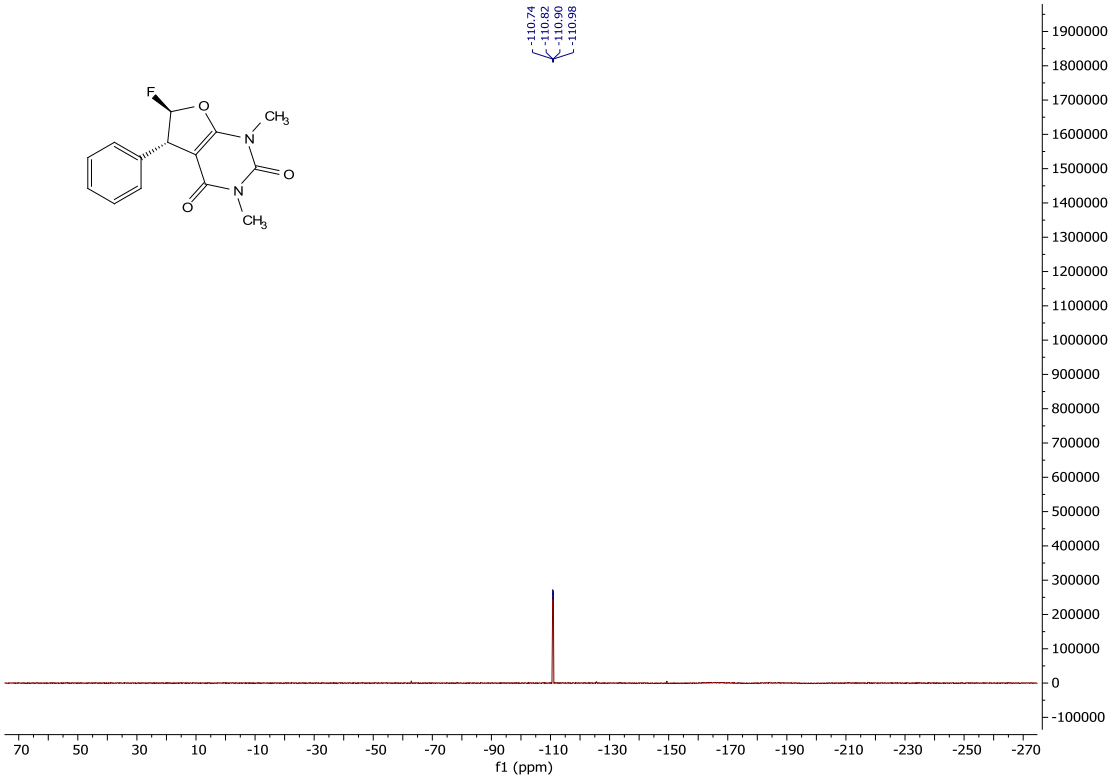
Compound **5ac** crude ^{1}H NMR (400 MHz, $CDCl_3$)



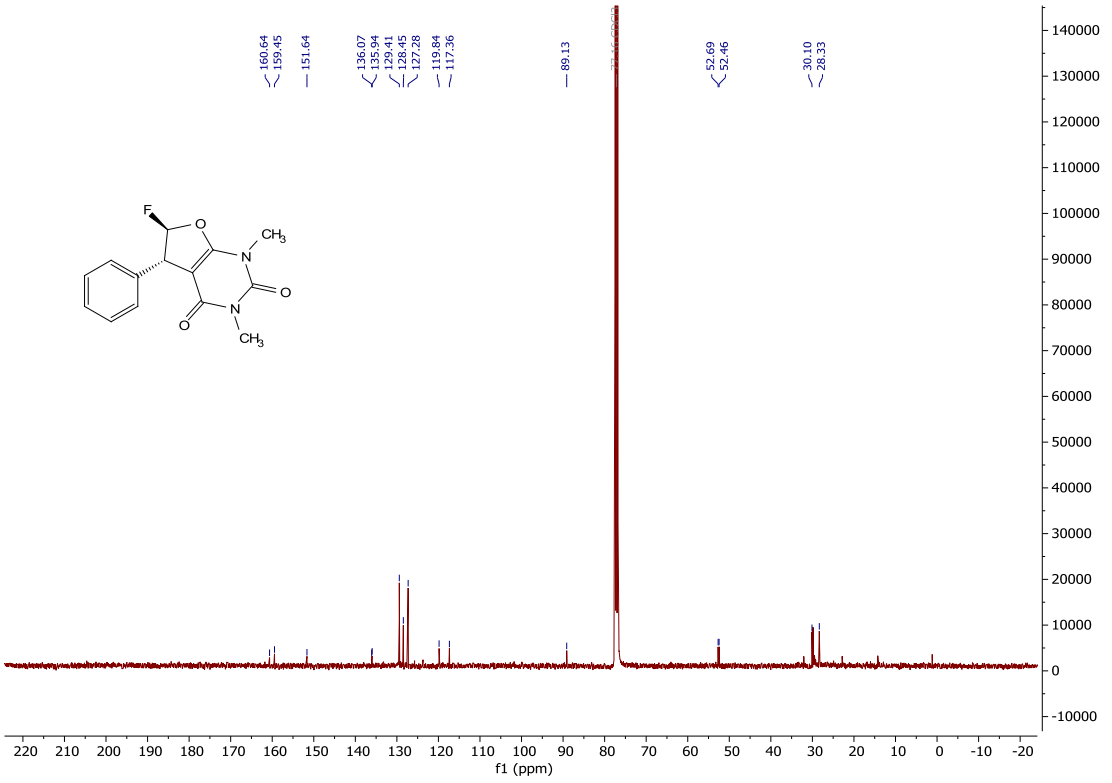
Compound **6ac** ^{1}H NMR



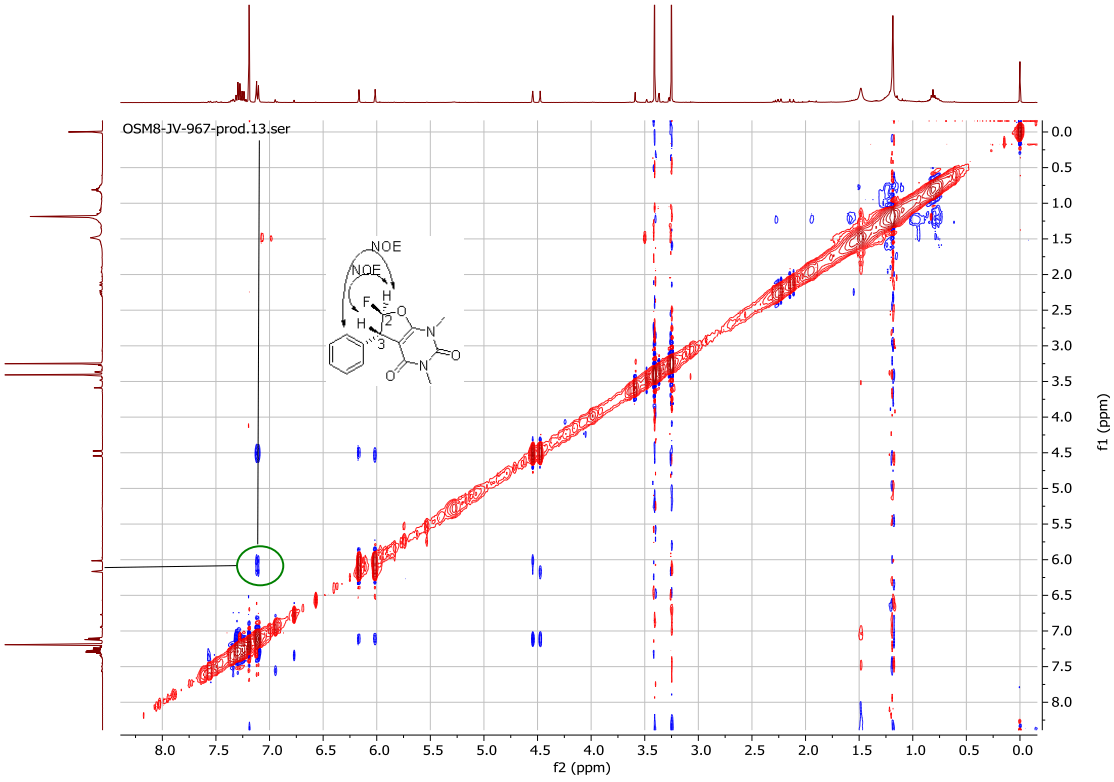
Compound **6ac** ^{19}F NMR



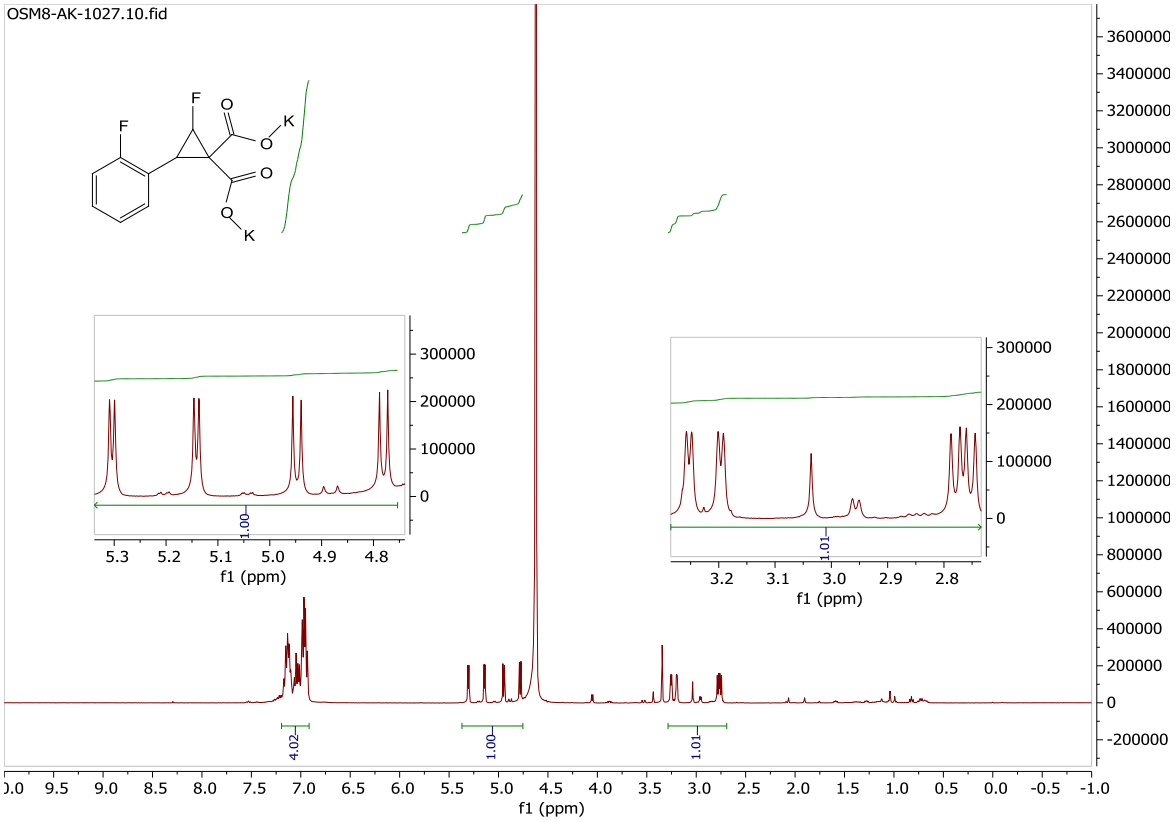
Compound **6ac** ^{13}C NMR



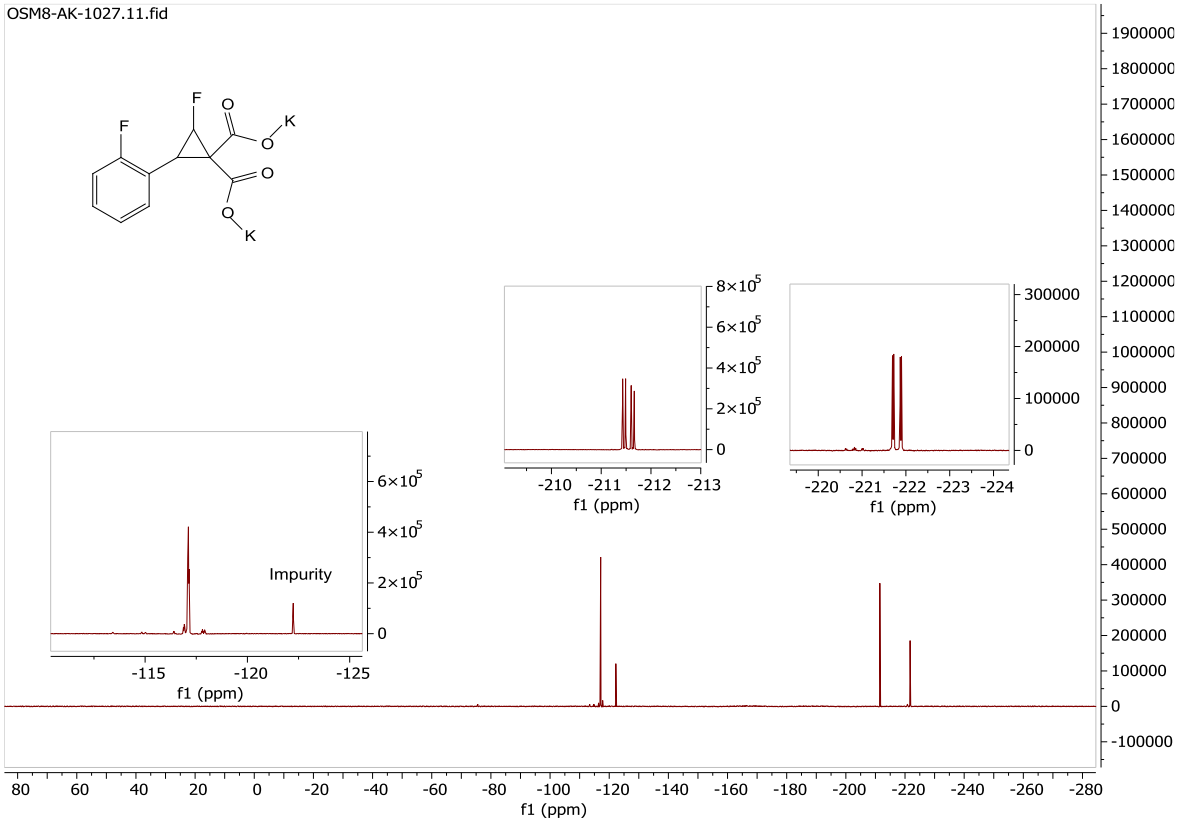
Compound **6ac** NOESY



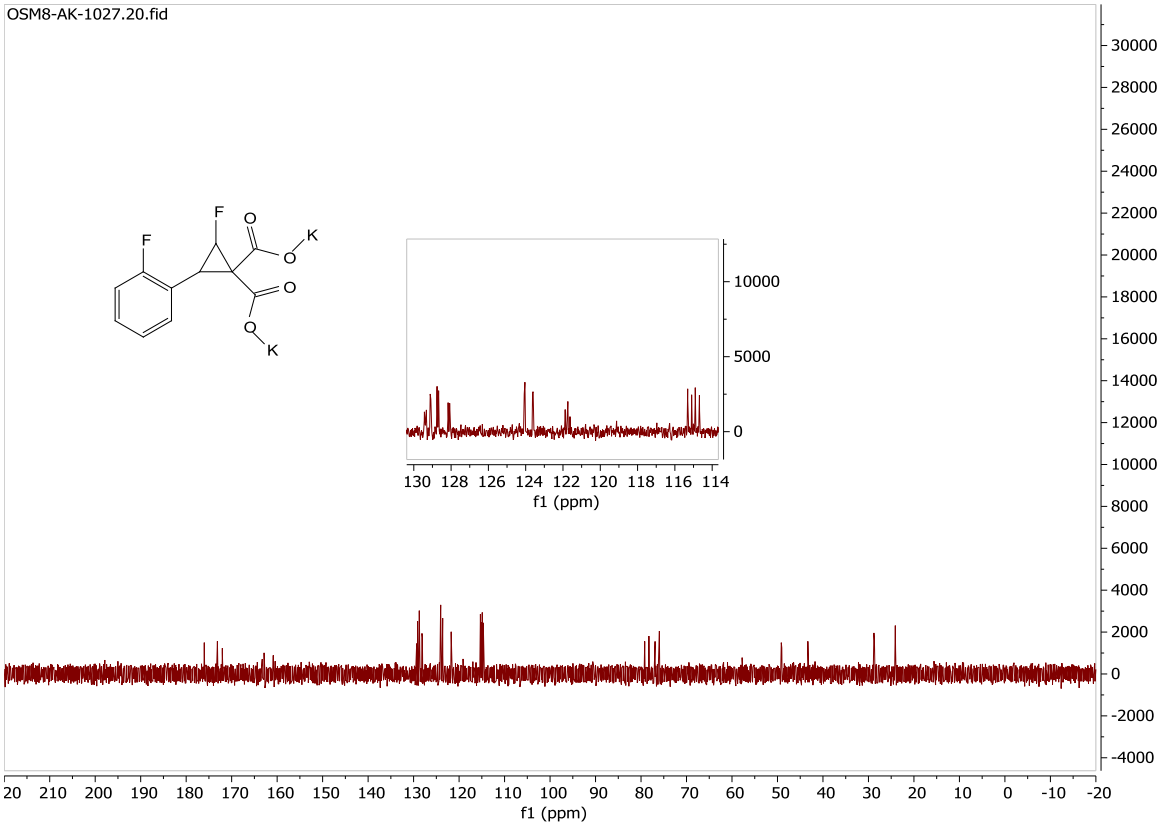
Compound **7l** ^{1}H NMR (400 MHz, D_2O)



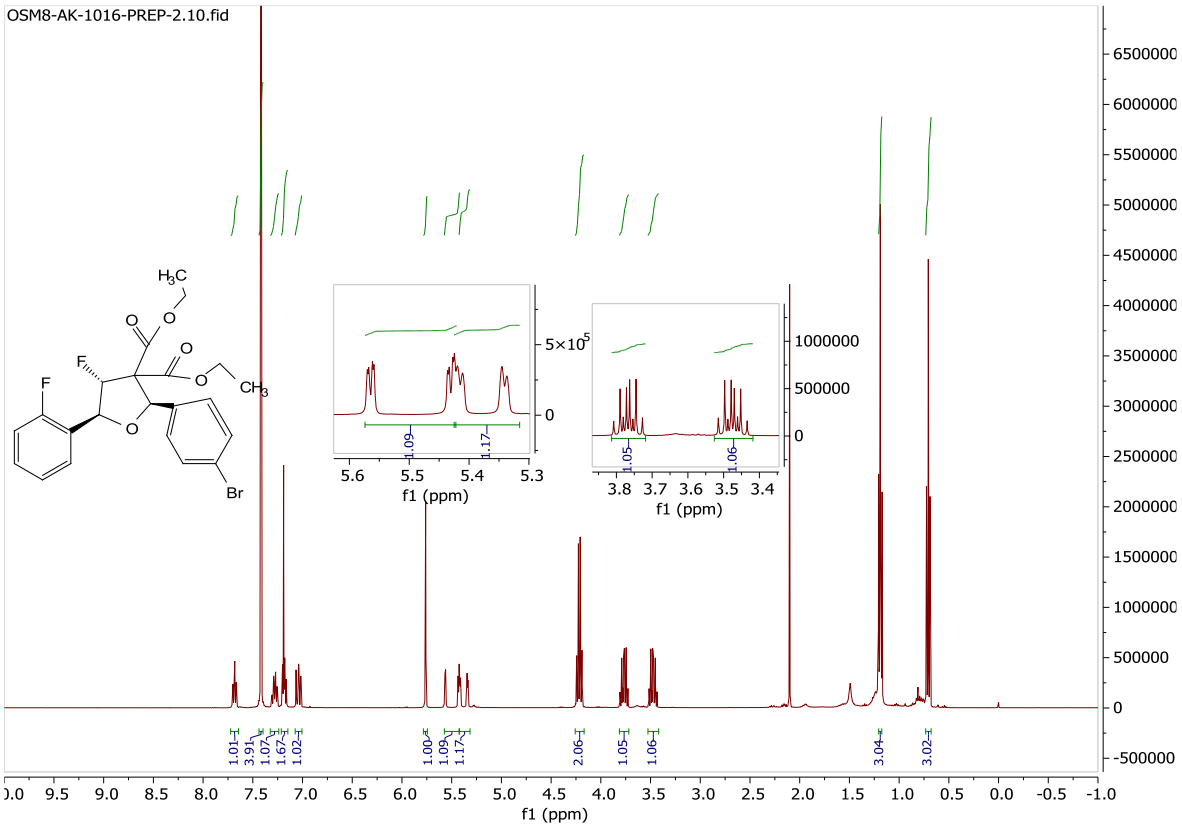
Compound **7l** ^{19}F NMR (400 MHz, D_2O)



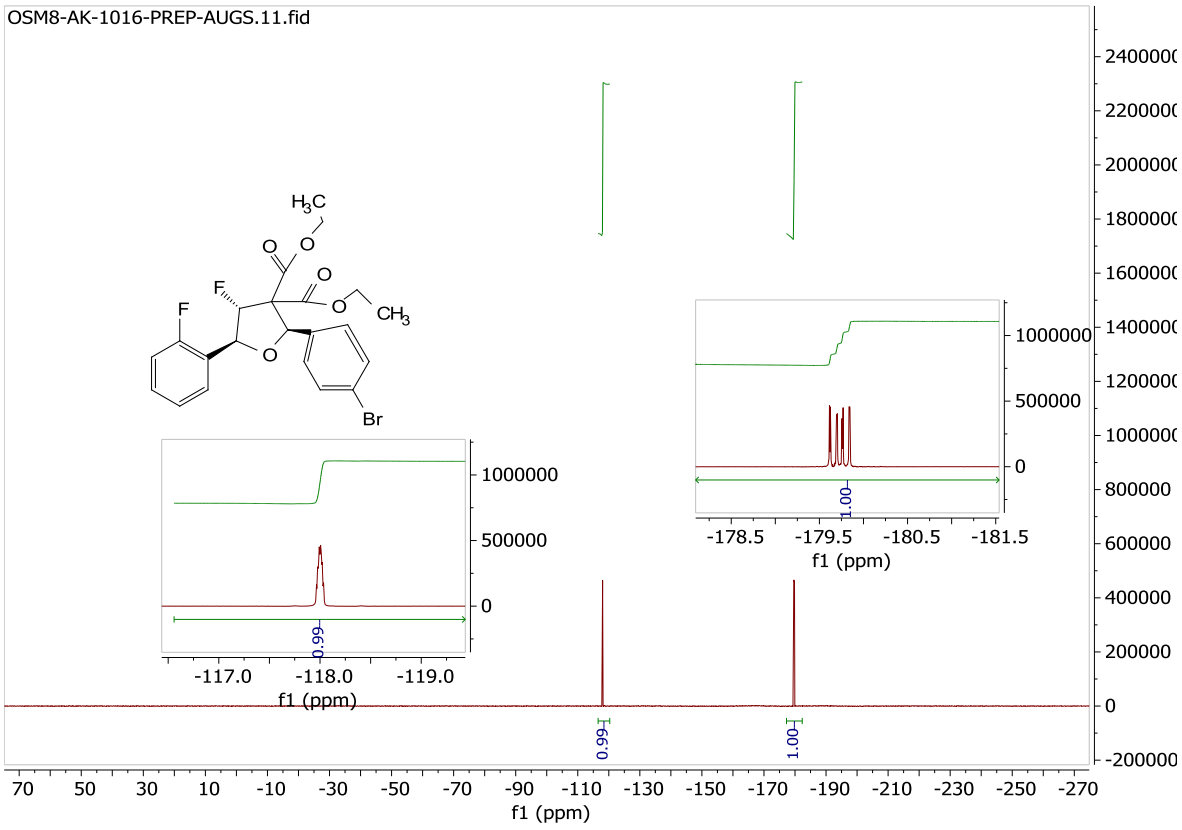
Compound **7l** ^{13}C NMR (400 MHz, D_2O)



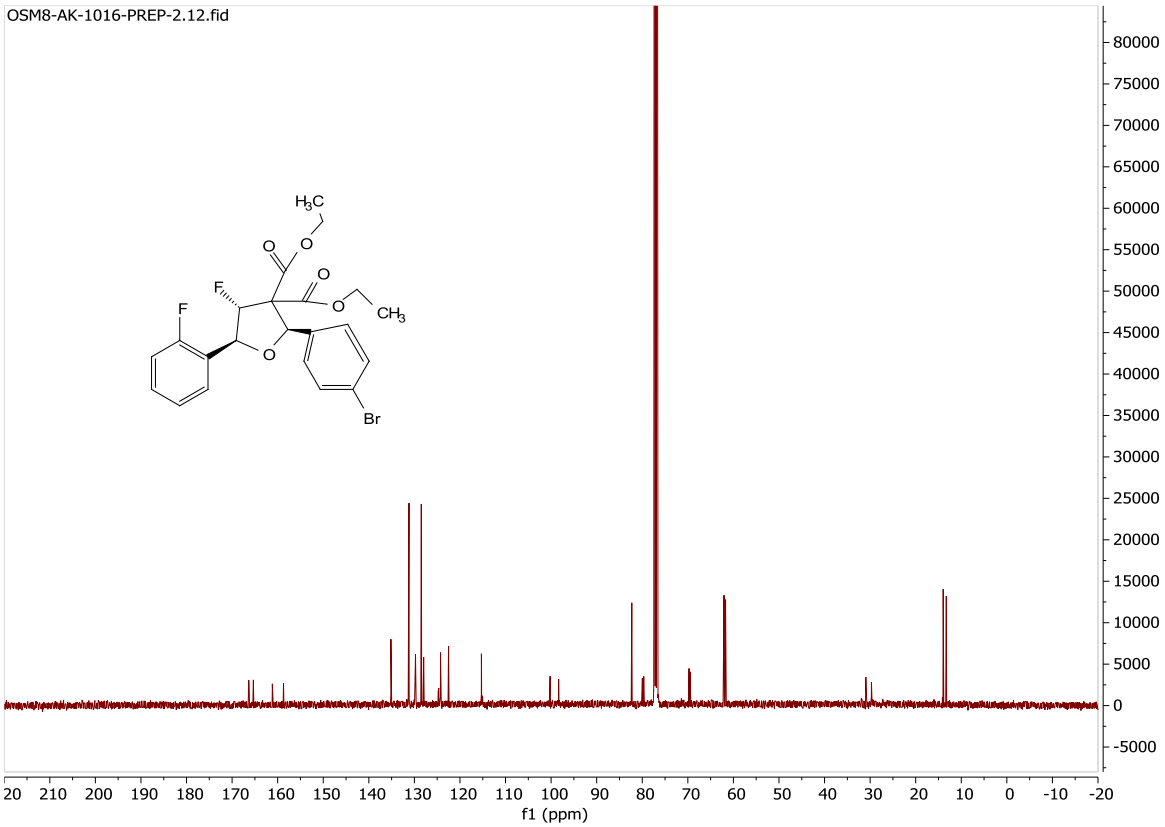
Compound *trans,cis* or (2*R**,4*R**,5*S**)-**8l** ^{1}H NMR (400 MHz, $CDCl_3$)



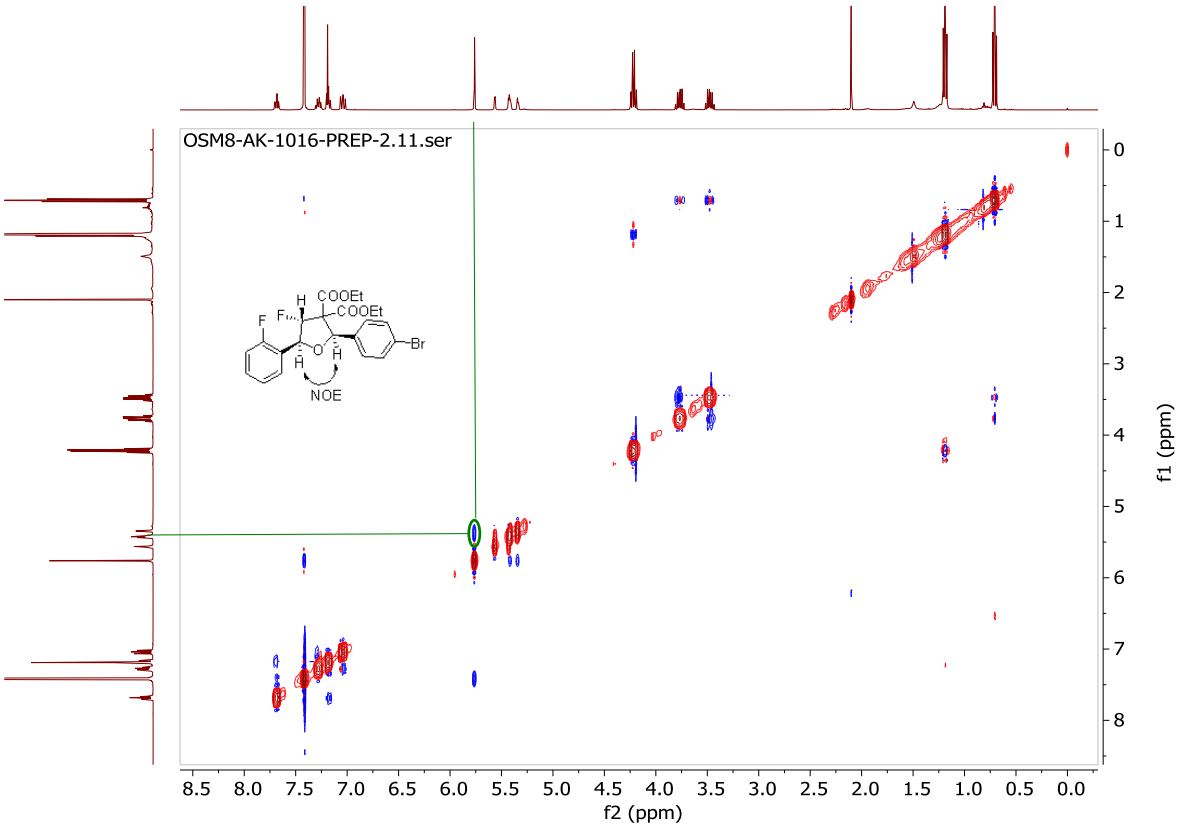
Compound *trans,cis* or (2*R**,4*R**,5*S**)-**8l** ^{19}F NMR (400 MHz, $CDCl_3$)



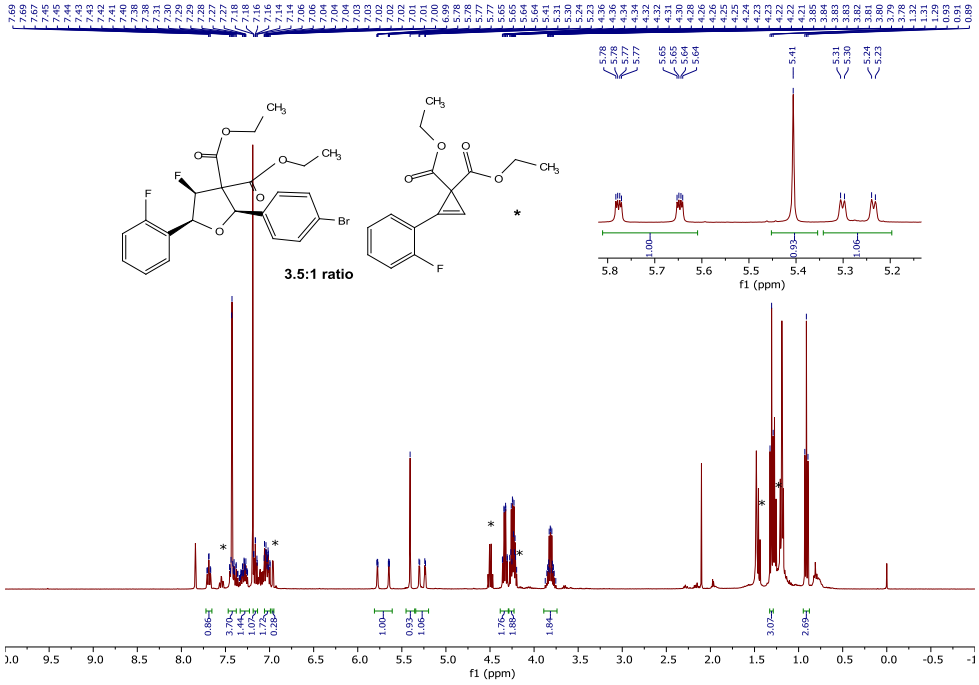
Compound *trans*,*cis* or (2*R**,4*R**,5*S**)-**8l** ^{13}C NMR (400 MHz, $CDCl_3$)



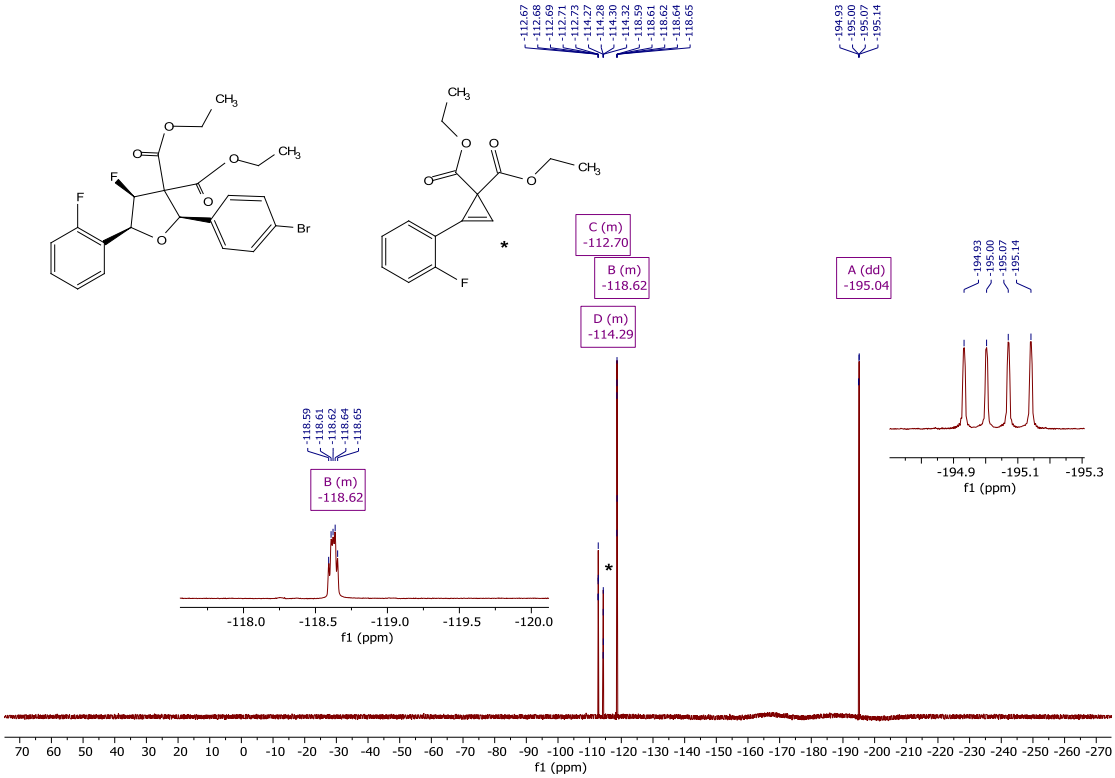
Compound *trans*,*cis* or (2*R**,4*R**,5*S**)-**8l** NOESY NMR (400 MHz, $CDCl_3$)



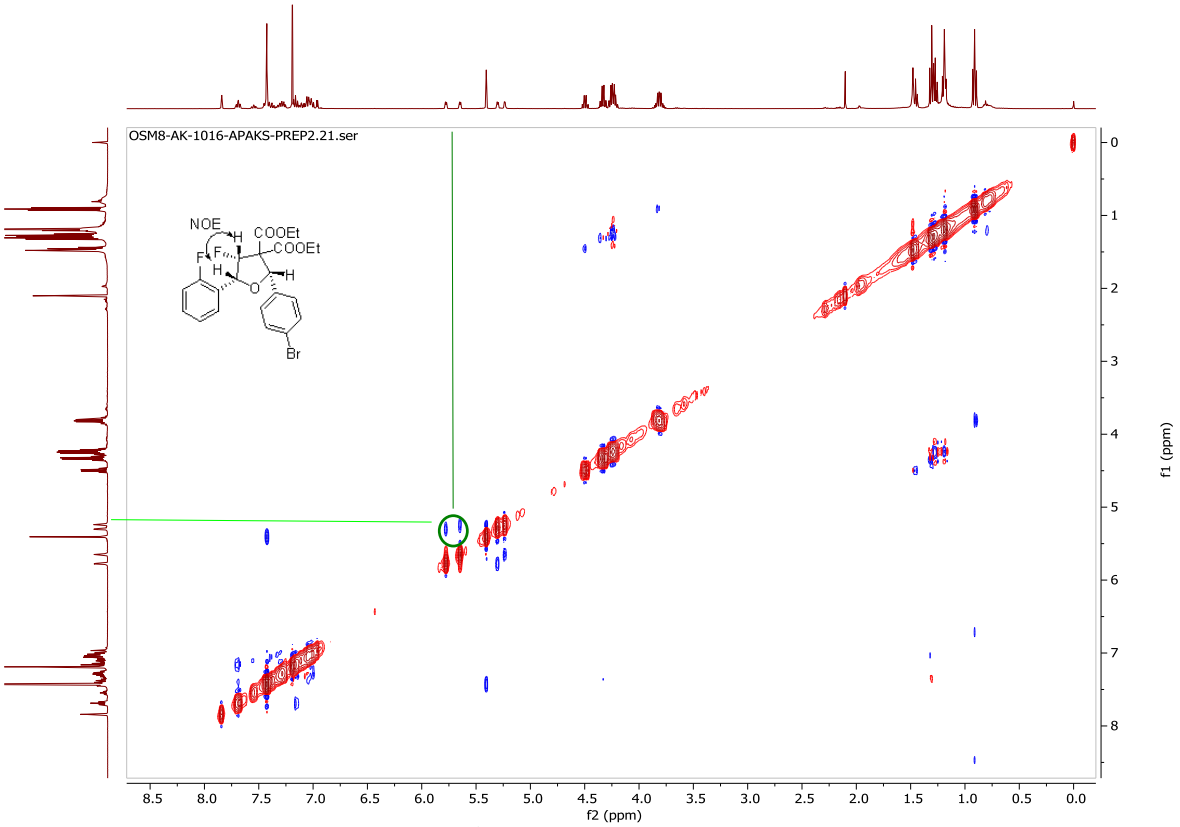
Compound *cis,cis* or (2*R**,4*R**,5*R**)-**8l** ^{1}H NMR (400 MHz, $CDCl_3$)



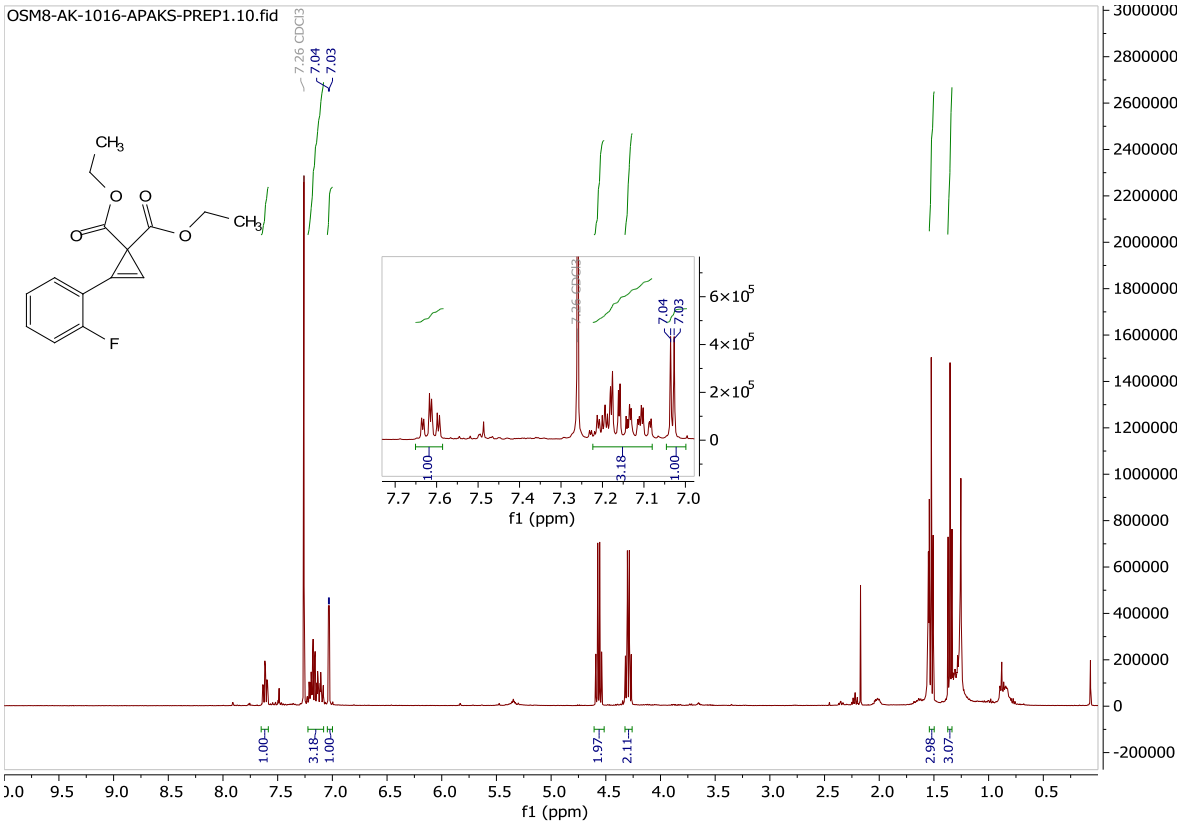
Compound *cis,cis* or (2*R**,4*R**,5*R**)-**8l** ^{19}F NMR (400 MHz, $CDCl_3$)



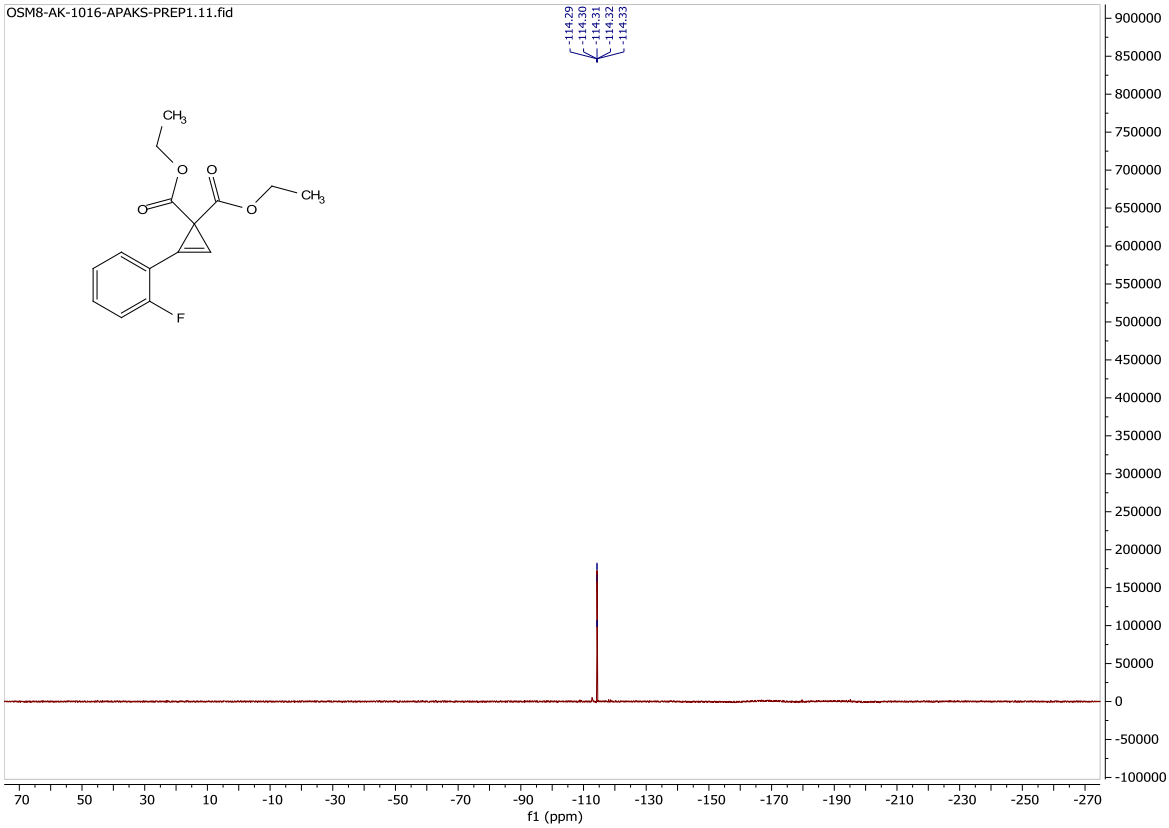
Compound *cis*,*cis* or (2*R**,4*R**,5*R**)-**8l** NOESY NMR (400 MHz, $CDCl_3$)



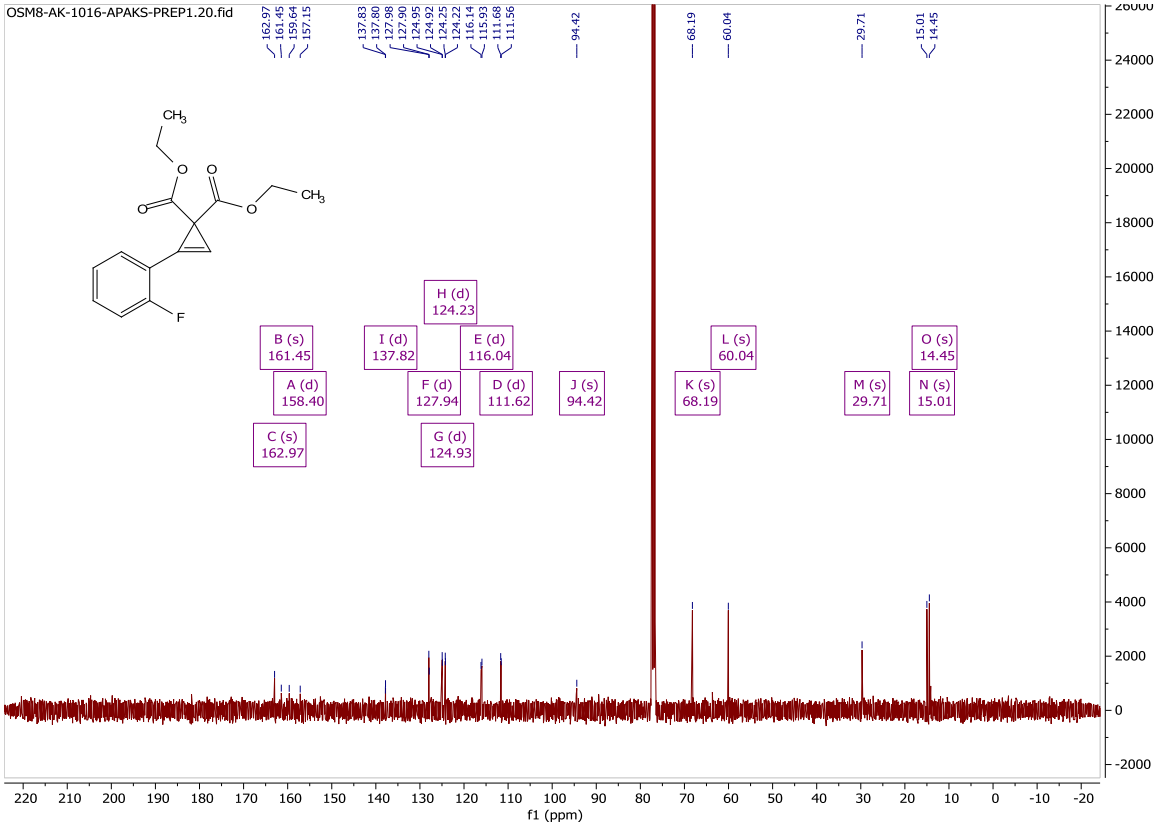
Sideproduct **9l** ^{1}H NMR (400 MHz, $CDCl_3$)



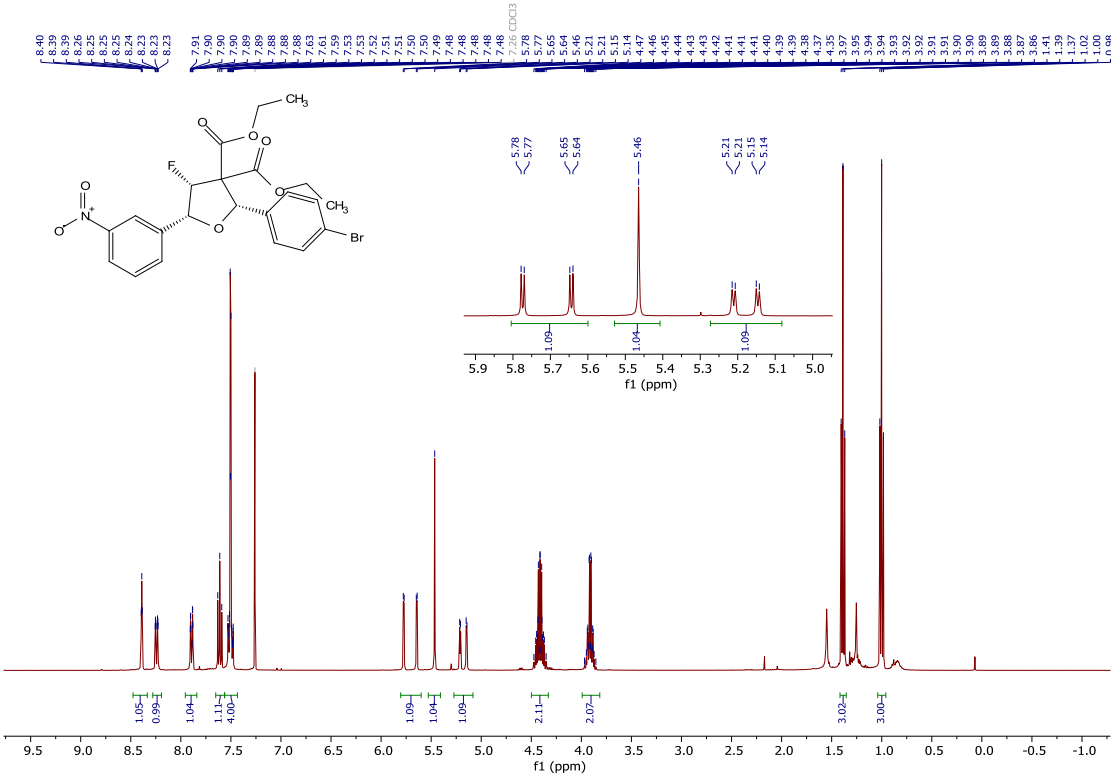
Sideproduct **9l** ^{19}F NMR (400 MHz, $CDCl_3$)



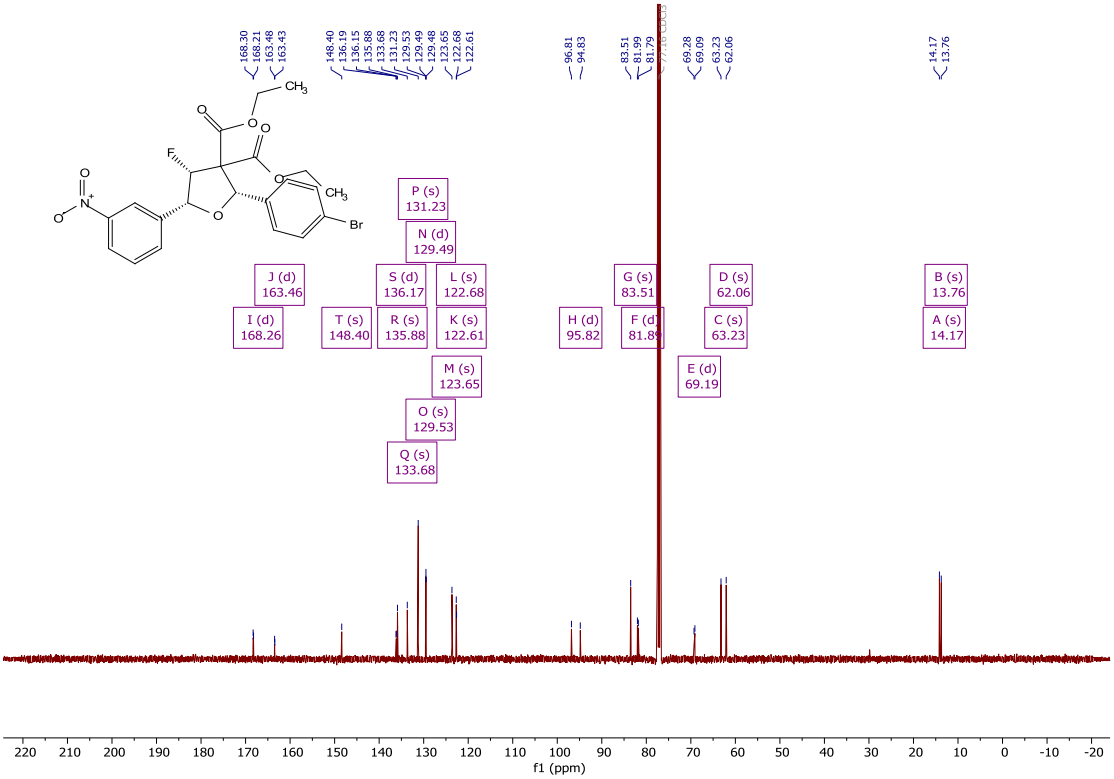
Sideproduct **9l** ^{13}C NMR (400 MHz, $CDCl_3$)



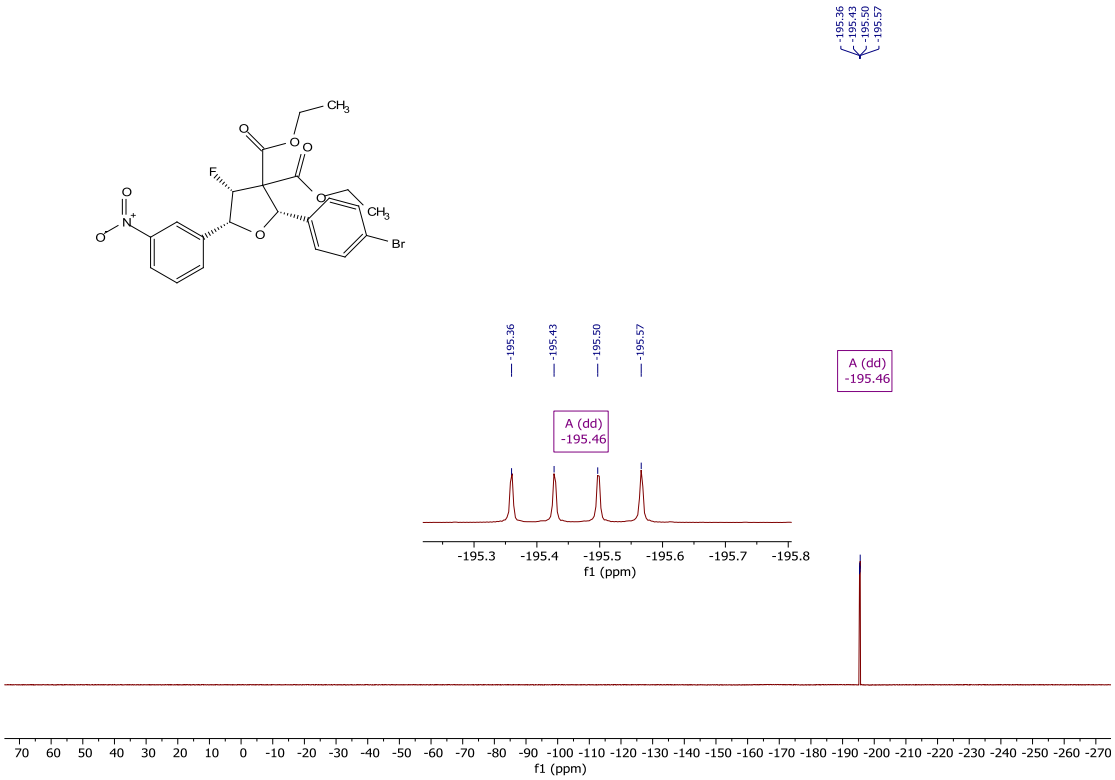
Compound *cis*,*cis* or (*2S**,*4R**,*5R**)-**8n** ^{1}H NMR (400 MHz, $CDCl_3$)



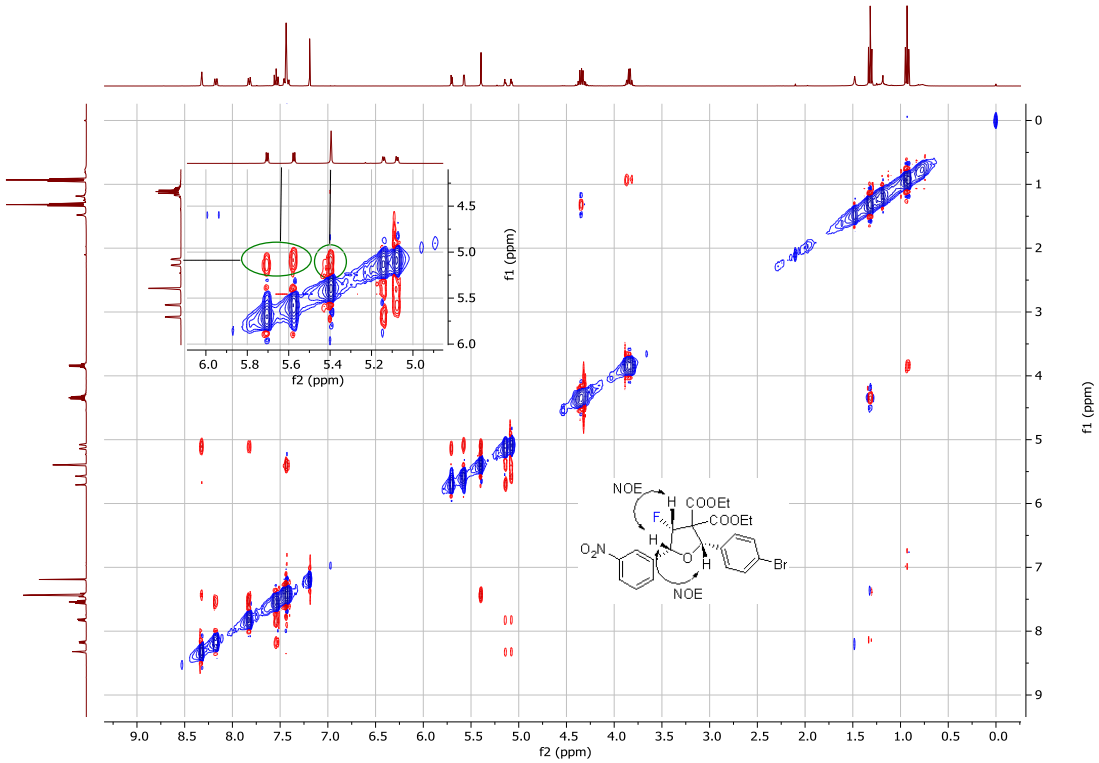
Compound *cis*,*cis* or (*2S**,*4R**,*5R**)-**8n** ^{1C}H NMR (400 MHz, $CDCl_3$)



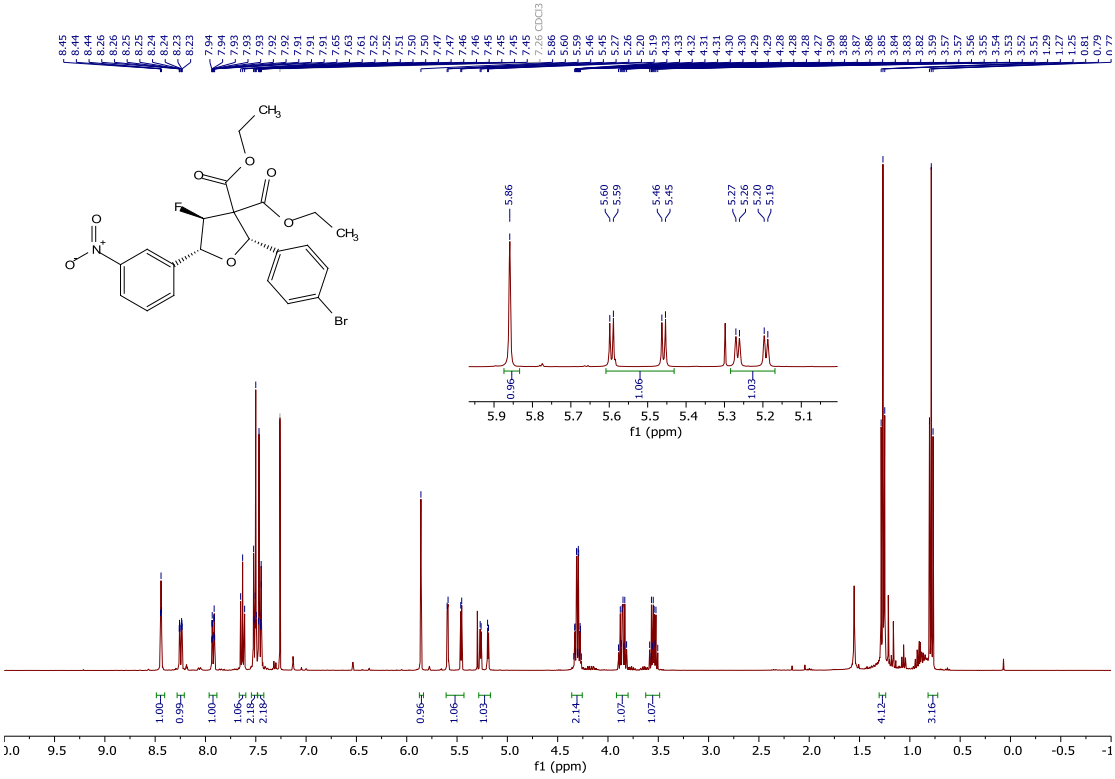
Compound *cis,cis* or (*2S**,*4R**,*5R**)-**8n** ^{19}F NMR (400 MHz, $CDCl_3$)



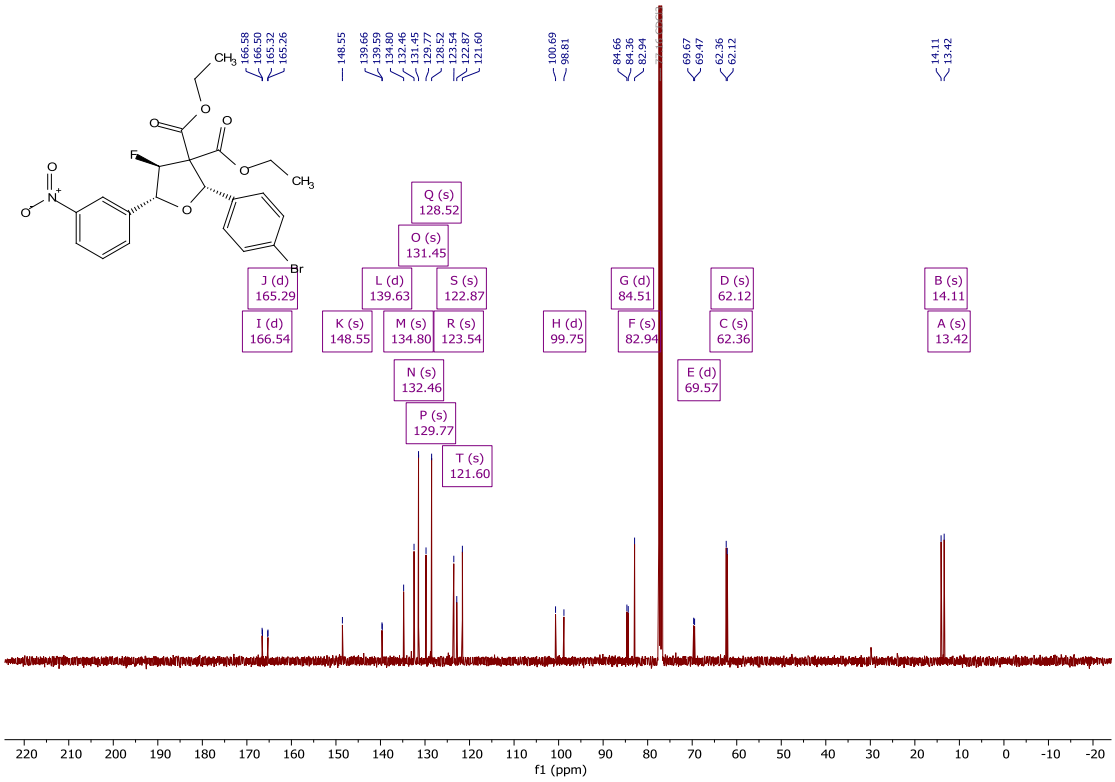
Compound *cis,cis* or (*2S**,*4R**,*5R**)-**8n** NOESY (400 MHz, $CDCl_3$)



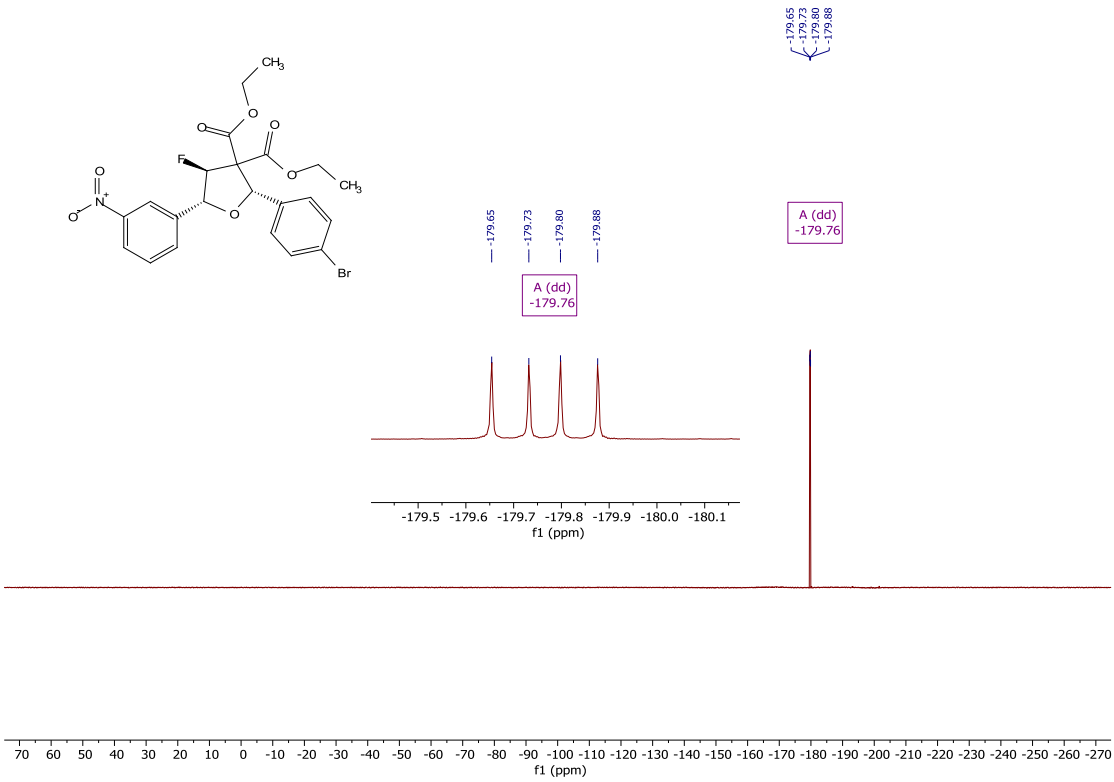
Compound *trans,cis* or (*2S*,4S*,5R**)-**8n** ^{1}H NMR (400 MHz, $CDCl_3$)



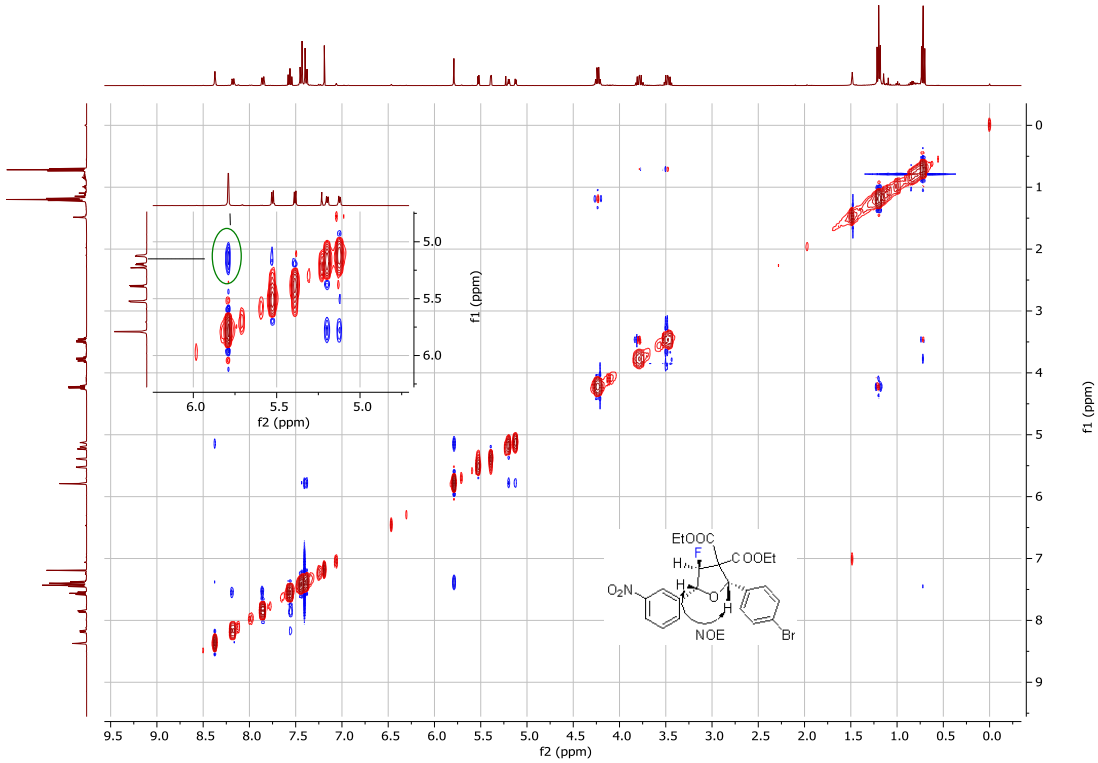
Compound *trans,cis* or (*2S*,4S*,5R**)-**8n** ^{13}C NMR (400 MHz, $CDCl_3$)



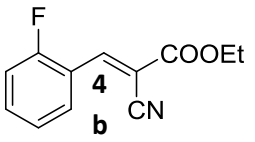
Compound *trans*,*cis* or (*2S*,4S*,5R**)-**8n** ^{19}F NMR (400 MHz, $CDCl_3$)

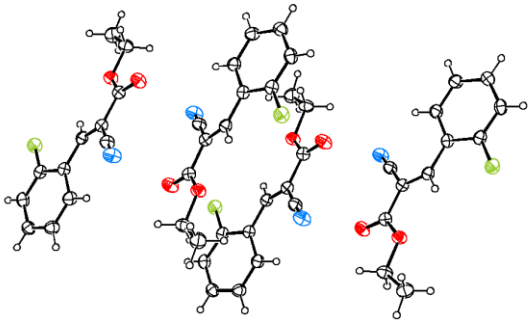


Compound *trans*,*cis* or (*2S*,4S*,5R**)-**8n** NOESY (400 MHz, $CDCl_3$)



X-Ray structure of **4b**





Electronic supplementary information

Crystal data, data collection and structure refinement details are summarized in Table 1.

Table 1 *Experimental details*

Crystal data	
Chemical formula	$C_{12}H_{10}FNO_2$
M_r	219.21
Crystal system, space group	Triclinic, $P\bar{1}$
Temperature (K)	170
a, *b*, *c* (Å)	9.3585 (1), 13.5874 (1), 17.4681 (1)
α, β, γ (°)	103.374 (1), 91.665 (1), 93.433 (1)
V (Å^3)	2154.98 (3)
Z	8
Radiation type	Cu *K*α
μ (mm^{-1})	0.88
Crystal size (mm)	0.2 × 0.12 × 0.08
Data collection	
Diffractometer	XtaLAB Synergy, Dualflex, HyPix
Absorption correction	Multi-scan *CrysAlis PRO* 1.171.40.53 (Rigaku Oxford Diffraction, 2019) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.
T_{min}, T_{max}	0.795, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	46760, 9086, 8154

R_{int}	0.054
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.633
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.051, 0.163, 1.06
No. of reflections	9086
No. of parameters	582
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.34, -0.33

Computer programs: *CrysAlis PRO* 1.171.40.35a (Rigaku OD, 2018), SHELXT 2014/4 (Sheldrick, 2014), *SHELXL2017*/1 (Sheldrick, 2017).

References

Document origin: *publCIF* [Westrip, S. P. (2010). *J. Apply. Cryst.*, **43**, 920-925].

Computing details

Data collection: *CrysAlis PRO* 1.171.40.35a (Rigaku OD, 2018); cell refinement: *CrysAlis PRO* 1.171.40.35a (Rigaku OD, 2018); data reduction: *CrysAlis PRO* 1.171.40.35a (Rigaku OD, 2018); program(s) used to solve structure: SHELXT 2014/4 (Sheldrick, 2014); program(s) used to refine structure: *SHELXL2017*/1 (Sheldrick, 2017).

(ak717b)

Crystal data

$C_{12}H_{10}FNO_2$	$Z = 8$
$M_r = 219.21$	$F(000) = 912$
Triclinic, $P\bar{1}$	$D_x = 1.351$ Mg m^{-3}
$a = 9.3585$ (1) Å	Cu $K\alpha$ radiation, $\lambda = 1.54184$ Å
$b = 13.5874$ (1) Å	Cell parameters from 34979 reflections
$c = 17.4681$ (1) Å	$\theta = 3.7$–$77.2°$
$\alpha = 103.374$ (1)°	$\mu = 0.88$ mm^{-1}
$\beta = 91.665$ (1)°	$T = 170$ K
$\gamma = 93.433$ (1)°	Block, colourless
$V = 2154.98$ (3) Å^3	0.2 × 0.12 × 0.08 mm

Data collection

XtaLAB Synergy, Dualflex, HyPix diffractometer	8154 reflections with $I > 2\sigma(I)$
Radiation source: micro-focus sealed X-ray tube	$R_{int} = 0.054$
ω scans	$\theta_{max} = 77.2°$, $\theta_{min} = 3.7°$
Absorption correction: multi-scan *CrysAlis PRO* 1.171.40.53 (Rigaku Oxford Diffraction, 2019) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.	$h = -11 \rightarrow 10$
$T_{min} = 0.795$, $T_{max} = 1.000$	$k = -16 \rightarrow 17$
46760 measured reflections	$l = -22 \rightarrow 22$
9086 independent reflections	

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.051$	$w = 1/[\sigma^2(F_o^2) + (0.1028P)^2 + 0.2925P]$ where $P = (F_o^2 + 2F_c^2)/3$

$wR(F^2)$ = 0.163	$(\Delta/\sigma)_{max}$ = 0.001
S = 1.06	$\Delta\rangle_{max}$ = 0.34 e Å^{-3}
9086 reflections	$\Delta\rangle_{min}$ = -0.33 e Å^{-3}
582 parameters	Extinction correction: *SHELXL2017*/1 (Sheldrick 2017), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
0 restraints	Extinction coefficient: 0.0025 (3)

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2) for (ak717b)

	x	*y*	*z*	U_{iso}*/U_{eq}
F16	0.00461 (8)	0.71535 (6)	0.27873 (4)	0.0469 (2)
F32	-0.42462 (8)	0.20387 (6)	0.29971 (4)	0.0495 (2)
F48	1.21004 (8)	1.04229 (6)	0.21133 (4)	0.0477 (2)
F64	0.71213 (8)	0.53654 (6)	0.21025 (4)	0.0477 (2)
O42	0.75308 (9)	0.98250 (6)	0.12329 (5)	0.0398 (2)
O26	0.03073 (9)	0.26287 (6)	0.38822 (5)	0.0410 (2)
O58	0.25524 (9)	0.49397 (7)	0.12256 (5)	0.0415 (2)
O29	0.22224 (9)	0.27130 (7)	0.31470 (5)	0.0461 (2)
O10	0.46228 (9)	0.76243 (7)	0.36636 (5)	0.0412 (2)
O45	0.56274 (9)	0.97598 (7)	0.19806 (5)	0.0456 (2)
O61	0.06364 (9)	0.49424 (7)	0.19722 (5)	0.0488 (2)
O13	0.65252 (10)	0.75677 (7)	0.29023 (5)	0.0486 (2)
N47	0.67946 (12)	1.00197 (9)	0.39070 (6)	0.0490 (3)
N15	0.53453 (12)	0.72961 (9)	0.09728 (6)	0.0495 (3)
N31	0.10708 (12)	0.24712 (10)	0.12149 (7)	0.0509 (3)
N63	0.18050 (12)	0.52068 (10)	0.39066 (6)	0.0515 (3)
C8	0.41883 (12)	0.75630 (8)	0.23236 (6)	0.0341 (2)
C41	0.69051 (12)	0.98103 (8)	0.19041 (7)	0.0351 (2)
C34	1.19562 (13)	1.01955 (8)	0.28210 (6)	0.0355 (2)
C56	0.29701 (12)	0.49676 (8)	0.25597 (6)	0.0349 (2)
C33	1.05773 (12)	0.99310 (8)	0.30291 (6)	0.0333 (2)
C17	-0.27197 (12)	0.25415 (8)	0.20874 (7)	0.0350 (2)
C39	0.93903 (13)	0.98892 (8)	0.24626 (6)	0.0343 (2)

H39	0.965049	0.986962	0.194976	0.041*
C7	0.27808 (13)	0.76263 (8)	0.24431 (6)	0.0344 (2)
H7	0.252086	0.768923	0.296116	0.041*
C1	0.16033 (12)	0.76097 (8)	0.18717 (6)	0.0333 (2)
C22	-0.41014 (13)	0.22823 (8)	0.22950 (7)	0.0365 (3)
C54	0.69452 (13)	0.51358 (8)	0.28070 (7)	0.0368 (3)
C9	0.52515 (13)	0.75881 (8)	0.29870 (7)	0.0363 (2)
C57	0.19130 (13)	0.49468 (8)	0.18949 (7)	0.0364 (3)
C49	0.55525 (12)	0.48976 (8)	0.30086 (6)	0.0342 (2)
C6	0.02143 (13)	0.73622 (8)	0.20755 (7)	0.0361 (3)
C23	-0.15324 (13)	0.25736 (8)	0.26513 (7)	0.0355 (2)
H23	-0.179468	0.258256	0.316224	0.043*
C2	0.17414 (13)	0.78527 (9)	0.11390 (7)	0.0381 (3)
H2	0.264182	0.803945	0.098593	0.046*
C25	0.09436 (13)	0.26521 (8)	0.32159 (7)	0.0354 (2)
C14	0.48167 (12)	0.74235 (9)	0.15702 (7)	0.0381 (3)
C40	0.79715 (12)	0.98746 (8)	0.25712 (6)	0.0333 (2)
C46	0.73320 (12)	0.99497 (9)	0.33175 (7)	0.0376 (3)
C24	-0.01125 (13)	0.25924 (8)	0.25466 (7)	0.0347 (2)
C38	1.04710 (13)	0.96826 (9)	0.37630 (7)	0.0388 (3)
H38	0.957910	0.949017	0.392336	0.047*
C55	0.43814 (13)	0.49034 (8)	0.24435 (6)	0.0349 (2)
H55	0.464539	0.485592	0.192770	0.042*
C50	0.54065 (13)	0.46401 (9)	0.37369 (7)	0.0398 (3)
H50	0.450191	0.446172	0.388955	0.048*
C36	1.30180 (13)	0.99938 (9)	0.40175 (7)	0.0391 (3)
H36	1.382074	1.001669	0.434938	0.047*
C30	0.05321 (13)	0.25304 (9)	0.18026 (7)	0.0393 (3)
C37	1.16722 (13)	0.97199 (9)	0.42503 (7)	0.0411 (3)
H37	1.158013	0.956085	0.473733	0.049*
C5	-0.09801 (13)	0.73216 (8)	0.15909 (7)	0.0394 (3)
H5	-0.188426	0.714515	0.174511	0.047*
C3	0.05547 (13)	0.78180 (9)	0.06415 (7)	0.0408 (3)
H3	0.066308	0.797399	0.015445	0.049*
C35	1.31685 (12)	1.02328 (9)	0.32931 (7)	0.0395 (3)
H35	1.406462	1.041322	0.313104	0.047*
C4	-0.08002 (13)	0.75509 (9)	0.08657 (7)	0.0401 (3)
H4	-0.159234	0.752603	0.052606	0.048*
C53	0.81413 (13)	0.51457 (9)	0.32853 (7)	0.0416 (3)
H53	0.904957	0.531178	0.313080	0.050*

C62	0.23360 (12)	0.50940 (9)	0.33126 (7)	0.0391 (3)
C51	0.65890 (14)	0.46485 (9)	0.42286 (7)	0.0432 (3)
H51	0.647512	0.448476	0.471251	0.052*
C20	-0.51618 (13)	0.25149 (9)	0.11079 (7)	0.0418 (3)
H20	-0.596558	0.250644	0.077997	0.050*
C18	-0.26120 (13)	0.28017 (9)	0.13577 (7)	0.0415 (3)
H18	-0.171852	0.299221	0.119807	0.050*
C21	-0.53141 (13)	0.22642 (9)	0.18284 (8)	0.0424 (3)
H21	-0.621197	0.208866	0.199104	0.051*
C19	-0.38124 (14)	0.27791 (10)	0.08734 (8)	0.0447 (3)
H19	-0.371811	0.294145	0.038767	0.054*
C43	0.65758 (14)	0.97965 (10)	0.05560 (7)	0.0439 (3)
H43A	0.597491	1.036577	0.066451	0.053*
H43B	0.596286	0.917421	0.043647	0.053*
C27	0.12536 (15)	0.26631 (10)	0.45643 (7)	0.0450 (3)
H27A	0.184352	0.329571	0.469468	0.054*
H27B	0.187707	0.210667	0.445569	0.054*
C52	0.79530 (13)	0.49009 (9)	0.40043 (7)	0.0424 (3)
H52	0.874402	0.490508	0.434007	0.051*
C11	0.55695 (15)	0.76191 (10)	0.43404 (7)	0.0443 (3)
H11A	0.626032	0.820049	0.444216	0.053*
H11B	0.608469	0.700679	0.424394	0.053*
C59	0.16142 (15)	0.49212 (10)	0.05442 (7)	0.0451 (3)
H59A	0.104771	0.550891	0.064142	0.054*
H59B	0.096929	0.431450	0.042927	0.054*
C12	0.46372 (17)	0.76624 (12)	0.50249 (8)	0.0553 (4)
H12A	0.389162	0.712690	0.489307	0.083*
H12B	0.421786	0.830484	0.515047	0.083*
H12C	0.520263	0.758323	0.547146	0.083*
C44	0.74862 (17)	0.98499 (12)	-0.01207 (8)	0.0552 (4)
H44A	0.688675	0.987070	-0.057132	0.083*
H44B	0.803490	0.926302	-0.024188	0.083*
H44C	0.812358	1.045030	0.001495	0.083*
C60	0.25604 (18)	0.49319 (12)	-0.01287 (8)	0.0575 (4)
H60A	0.198572	0.495923	-0.058660	0.086*
H60B	0.307425	0.432782	-0.023701	0.086*
H60C	0.322896	0.551571	0.000534	0.086*
C28	0.03274 (17)	0.25791 (12)	0.52297 (8)	0.0562 (4)
H28A	-0.026588	0.195763	0.508891	0.084*
H28B	-0.026711	0.314246	0.533976	0.084*

H28C	0.091891	0.258310	0.568888	0.084*

Atomic displacement parameters (Å^2) for (ak717b)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
F16	0.0433 (4)	0.0630 (4)	0.0356 (4)	-0.0023 (3)	0.0117 (3)	0.0139 (3)
F32	0.0450 (4)	0.0666 (5)	0.0389 (4)	-0.0048 (3)	0.0121 (3)	0.0173 (3)
F48	0.0420 (4)	0.0659 (5)	0.0379 (4)	-0.0037 (3)	0.0100 (3)	0.0187 (3)
F64	0.0435 (4)	0.0640 (5)	0.0368 (4)	-0.0015 (3)	0.0121 (3)	0.0144 (3)
O42	0.0372 (4)	0.0519 (5)	0.0315 (4)	0.0054 (4)	0.0031 (3)	0.0114 (3)
O26	0.0384 (5)	0.0524 (5)	0.0329 (4)	0.0037 (4)	0.0045 (3)	0.0108 (3)
O58	0.0408 (5)	0.0528 (5)	0.0308 (4)	0.0025 (4)	0.0010 (3)	0.0096 (3)
O29	0.0346 (5)	0.0593 (5)	0.0432 (5)	0.0067 (4)	0.0058 (4)	0.0081 (4)
O10	0.0400 (5)	0.0529 (5)	0.0312 (4)	0.0051 (4)	0.0028 (3)	0.0105 (3)
O45	0.0335 (5)	0.0619 (5)	0.0391 (5)	0.0049 (4)	0.0034 (3)	0.0064 (4)
O61	0.0368 (5)	0.0671 (6)	0.0415 (5)	0.0132 (4)	0.0032 (4)	0.0076 (4)
O13	0.0364 (5)	0.0681 (6)	0.0397 (5)	0.0125 (4)	0.0037 (4)	0.0068 (4)
N47	0.0372 (5)	0.0733 (7)	0.0377 (5)	0.0114 (5)	0.0078 (4)	0.0126 (5)
N15	0.0394 (6)	0.0733 (7)	0.0365 (5)	0.0123 (5)	0.0074 (4)	0.0111 (5)
N31	0.0402 (6)	0.0751 (8)	0.0406 (6)	0.0140 (5)	0.0108 (5)	0.0166 (5)
N63	0.0415 (6)	0.0767 (8)	0.0387 (6)	0.0147 (5)	0.0088 (5)	0.0146 (5)
C8	0.0370 (6)	0.0337 (5)	0.0312 (5)	0.0032 (4)	0.0042 (4)	0.0061 (4)
C41	0.0361 (6)	0.0350 (5)	0.0332 (6)	0.0047 (4)	0.0048 (4)	0.0049 (4)
C34	0.0379 (6)	0.0362 (5)	0.0320 (5)	0.0012 (4)	0.0090 (4)	0.0067 (4)
C56	0.0375 (6)	0.0345 (5)	0.0330 (5)	0.0040 (4)	0.0040 (4)	0.0075 (4)
C33	0.0321 (6)	0.0336 (5)	0.0330 (5)	0.0020 (4)	0.0055 (4)	0.0046 (4)
C17	0.0336 (6)	0.0345 (5)	0.0365 (6)	0.0032 (4)	0.0066 (4)	0.0064 (4)
C39	0.0372 (6)	0.0333 (5)	0.0321 (5)	0.0009 (4)	0.0057 (4)	0.0067 (4)
C7	0.0379 (6)	0.0338 (5)	0.0312 (5)	0.0014 (4)	0.0050 (4)	0.0068 (4)
C1	0.0336 (6)	0.0333 (5)	0.0322 (5)	0.0025 (4)	0.0059 (4)	0.0053 (4)
C22	0.0395 (6)	0.0368 (5)	0.0331 (5)	0.0018 (4)	0.0103 (4)	0.0070 (4)
C54	0.0387 (6)	0.0378 (5)	0.0330 (5)	0.0023 (4)	0.0090 (4)	0.0055 (4)
C9	0.0379 (6)	0.0370 (5)	0.0330 (6)	0.0059 (4)	0.0054 (4)	0.0049 (4)
C57	0.0387 (6)	0.0360 (5)	0.0339 (6)	0.0067 (4)	0.0048 (5)	0.0055 (4)
C49	0.0337 (6)	0.0341 (5)	0.0340 (6)	0.0027 (4)	0.0043 (4)	0.0062 (4)
C6	0.0385 (6)	0.0363 (5)	0.0323 (5)	0.0018 (4)	0.0093 (4)	0.0045 (4)
C23	0.0396 (6)	0.0326 (5)	0.0345 (5)	0.0009 (4)	0.0082 (4)	0.0080 (4)
C2	0.0335 (6)	0.0439 (6)	0.0383 (6)	0.0019 (4)	0.0057 (5)	0.0121 (5)
C25	0.0370 (6)	0.0336 (5)	0.0349 (6)	0.0056 (4)	0.0058 (4)	0.0056 (4)
C14	0.0319 (5)	0.0466 (6)	0.0354 (6)	0.0053 (4)	0.0028 (4)	0.0079 (5)
C40	0.0353 (6)	0.0331 (5)	0.0312 (5)	0.0030 (4)	0.0043 (4)	0.0061 (4)

C46	0.0312 (5)	0.0467 (6)	0.0350 (6)	0.0061 (4)	0.0036 (4)	0.0085 (5)
C24	0.0370 (6)	0.0332 (5)	0.0341 (5)	0.0038 (4)	0.0058 (4)	0.0074 (4)
C38	0.0321 (6)	0.0485 (6)	0.0368 (6)	0.0008 (5)	0.0061 (4)	0.0119 (5)
C55	0.0388 (6)	0.0340 (5)	0.0319 (5)	0.0013 (4)	0.0049 (4)	0.0079 (4)
C50	0.0356 (6)	0.0457 (6)	0.0409 (6)	0.0024 (5)	0.0063 (5)	0.0154 (5)
C36	0.0336 (6)	0.0410 (6)	0.0407 (6)	0.0028 (4)	-0.0004 (4)	0.0058 (5)
C30	0.0329 (6)	0.0476 (6)	0.0389 (6)	0.0077 (5)	0.0060 (5)	0.0115 (5)
C37	0.0388 (6)	0.0488 (6)	0.0370 (6)	0.0036 (5)	0.0034 (5)	0.0124 (5)
C5	0.0310 (6)	0.0399 (6)	0.0455 (6)	0.0021 (4)	0.0087 (5)	0.0057 (5)
C3	0.0414 (6)	0.0463 (6)	0.0371 (6)	0.0047 (5)	0.0039 (5)	0.0137 (5)
C35	0.0295 (6)	0.0419 (6)	0.0454 (6)	-0.0002 (4)	0.0079 (5)	0.0069 (5)
C4	0.0362 (6)	0.0398 (6)	0.0426 (6)	0.0045 (5)	-0.0003 (5)	0.0059 (5)
C53	0.0323 (6)	0.0436 (6)	0.0467 (7)	0.0022 (5)	0.0068 (5)	0.0053 (5)
C62	0.0337 (6)	0.0481 (6)	0.0368 (6)	0.0075 (5)	0.0038 (5)	0.0106 (5)
C51	0.0451 (7)	0.0476 (6)	0.0400 (6)	0.0059 (5)	0.0022 (5)	0.0156 (5)
C20	0.0375 (6)	0.0433 (6)	0.0430 (6)	0.0044 (5)	0.0003 (5)	0.0068 (5)
C18	0.0349 (6)	0.0502 (6)	0.0430 (6)	0.0035 (5)	0.0097 (5)	0.0175 (5)
C21	0.0334 (6)	0.0444 (6)	0.0468 (7)	-0.0007 (5)	0.0070 (5)	0.0054 (5)
C19	0.0443 (7)	0.0508 (7)	0.0417 (6)	0.0063 (5)	0.0049 (5)	0.0155 (5)
C43	0.0457 (7)	0.0525 (7)	0.0338 (6)	0.0082 (5)	-0.0018 (5)	0.0099 (5)
C27	0.0483 (7)	0.0515 (7)	0.0344 (6)	0.0079 (5)	0.0004 (5)	0.0071 (5)
C52	0.0379 (6)	0.0429 (6)	0.0448 (6)	0.0058 (5)	-0.0022 (5)	0.0066 (5)
C11	0.0510 (7)	0.0490 (6)	0.0329 (6)	0.0074 (5)	-0.0033 (5)	0.0093 (5)
C59	0.0525 (7)	0.0494 (6)	0.0319 (6)	0.0069 (5)	-0.0040 (5)	0.0063 (5)
C12	0.0669 (9)	0.0631 (8)	0.0366 (7)	-0.0051 (7)	0.0018 (6)	0.0160 (6)
C44	0.0620 (9)	0.0685 (9)	0.0372 (7)	-0.0018 (7)	0.0027 (6)	0.0182 (6)
C60	0.0738 (10)	0.0618 (8)	0.0351 (6)	-0.0109 (7)	-0.0005 (6)	0.0120 (6)
C28	0.0656 (9)	0.0653 (8)	0.0379 (7)	-0.0041 (7)	0.0041 (6)	0.0144 (6)

Geometric parameters (Å, º) for (ak717b)

F16—C6	1.3491 (13)	C24—C30	1.4356 (15)
F32—C22	1.3507 (12)	C38—C37	1.3816 (17)
F48—C34	1.3504 (12)	C38—H38	0.9300
F64—C54	1.3498 (13)	C55—H55	0.9300
O42—C41	1.3293 (13)	C50—C51	1.3789 (17)
O42—C43	1.4531 (14)	C50—H50	0.9300
O26—C25	1.3287 (13)	C36—C35	1.3862 (16)
O26—C27	1.4539 (14)	C36—C37	1.3906 (16)
O58—C57	1.3271 (13)	C36—H36	0.9300
O58—C59	1.4530 (14)	C37—H37	0.9300

O29—C25	1.2061 (14)	C5—C4	1.3852 (16)
O10—C9	1.3275 (13)	C5—H5	0.9300
O10—C11	1.4583 (14)	C3—C4	1.3901 (16)
O45—C41	1.2067 (14)	C3—H3	0.9300
O61—C57	1.2060 (14)	C35—H35	0.9300
O13—C9	1.2066 (14)	C4—H4	0.9300
N47—C46	1.1458 (15)	C53—C52	1.3849 (17)
N15—C14	1.1490 (15)	C53—H53	0.9300
N31—C30	1.1453 (15)	C51—C52	1.3926 (18)
N63—C62	1.1458 (15)	C51—H51	0.9300
C8—C7	1.3443 (16)	C20—C21	1.3869 (17)
C8—C14	1.4341 (14)	C20—C19	1.3911 (17)
C8—C9	1.4982 (15)	C20—H20	0.9300
C41—C40	1.4955 (15)	C18—C19	1.3811 (18)
C34—C35	1.3745 (17)	C18—H18	0.9300
C34—C33	1.3995 (15)	C21—H21	0.9300
C56—C55	1.3470 (16)	C19—H19	0.9300
C56—C62	1.4368 (15)	C43—C44	1.4897 (17)
C56—C57	1.4976 (16)	C43—H43A	0.9700
C33—C38	1.4038 (15)	C43—H43B	0.9700
C33—C39	1.4557 (16)	C27—C28	1.4911 (17)
C17—C22	1.3998 (15)	C27—H27A	0.9700
C17—C18	1.4041 (16)	C27—H27B	0.9700
C17—C23	1.4552 (16)	C52—H52	0.9300
C39—C40	1.3464 (16)	C11—C12	1.4929 (17)
C39—H39	0.9300	C11—H11A	0.9700
C7—C1	1.4609 (15)	C11—H11B	0.9700
C7—H7	0.9300	C59—C60	1.4941 (18)
C1—C6	1.3998 (15)	C59—H59A	0.9700
C1—C2	1.4012 (15)	C59—H59B	0.9700
C22—C21	1.3735 (17)	C12—H12A	0.9600
C54—C53	1.3748 (17)	C12—H12B	0.9600
C54—C49	1.3987 (16)	C12—H12C	0.9600
C49—C50	1.4035 (15)	C44—H44A	0.9600
C49—C55	1.4551 (16)	C44—H44B	0.9600
C6—C5	1.3730 (17)	C44—H44C	0.9600
C23—C24	1.3461 (16)	C60—H60A	0.9600
C23—H23	0.9300	C60—H60B	0.9600
C2—C3	1.3818 (17)	C60—H60C	0.9600
C2—H2	0.9300	C28—H28A	0.9600

C25—C24	1.4932 (16)	C28—H28B	0.9600
C40—C46	1.4350 (14)	C28—H28C	0.9600
C41—O42—C43	116.08 (9)	C6—C5—C4	118.12 (10)
C25—O26—C27	116.04 (9)	C6—C5—H5	120.9
C57—O58—C59	116.10 (9)	C4—C5—H5	120.9
C9—O10—C11	116.08 (9)	C2—C3—C4	120.30 (11)
C7—C8—C14	124.87 (11)	C2—C3—H3	119.9
C7—C8—C9	121.57 (10)	C4—C3—H3	119.9
C14—C8—C9	113.50 (9)	C34—C35—C36	118.14 (10)
O45—C41—O42	124.85 (11)	C34—C35—H35	120.9
O45—C41—C40	122.92 (10)	C36—C35—H35	120.9
O42—C41—C40	112.23 (9)	C5—C4—C3	120.54 (11)
F48—C34—C35	118.27 (10)	C5—C4—H4	119.7
F48—C34—C33	117.90 (11)	C3—C4—H4	119.7
C35—C34—C33	123.83 (11)	C54—C53—C52	118.00 (11)
C55—C56—C62	124.70 (11)	C54—C53—H53	121.0
C55—C56—C57	121.62 (10)	C52—C53—H53	121.0
C62—C56—C57	113.65 (10)	N63—C62—C56	178.36 (13)
C34—C33—C38	116.33 (11)	C50—C51—C52	120.35 (11)
C34—C33—C39	118.21 (10)	C50—C51—H51	119.8
C38—C33—C39	125.39 (10)	C52—C51—H51	119.8
C22—C17—C18	116.27 (11)	C21—C20—C19	120.31 (12)
C22—C17—C23	118.32 (10)	C21—C20—H20	119.8
C18—C17—C23	125.32 (10)	C19—C20—H20	119.8
C40—C39—C33	129.57 (10)	C19—C18—C17	121.02 (11)
C40—C39—H39	115.2	C19—C18—H18	119.5
C33—C39—H39	115.2	C17—C18—H18	119.5
C8—C7—C1	128.95 (10)	C22—C21—C20	118.13 (11)
C8—C7—H7	115.5	C22—C21—H21	120.9
C1—C7—H7	115.5	C20—C21—H21	120.9
C6—C1—C2	116.75 (11)	C18—C19—C20	120.38 (11)
C6—C1—C7	117.95 (10)	C18—C19—H19	119.8
C2—C1—C7	125.27 (10)	C20—C19—H19	119.8
F32—C22—C21	118.27 (10)	O42—C43—C44	107.39 (11)
F32—C22—C17	117.85 (11)	O42—C43—H43A	110.2
C21—C22—C17	123.88 (11)	C44—C43—H43A	110.2
F64—C54—C53	118.34 (10)	O42—C43—H43B	110.2
F64—C54—C49	118.04 (11)	C44—C43—H43B	110.2
C53—C54—C49	123.62 (11)	H43A—C43—H43B	108.5

O13—C9—O10	124.89 (11)	O26—C27—C28	107.16 (11)
O13—C9—C8	123.04 (10)	O26—C27—H27A	110.3
O10—C9—C8	112.07 (9)	C28—C27—H27A	110.3
O61—C57—O58	124.97 (11)	O26—C27—H27B	110.3
O61—C57—C56	123.08 (10)	C28—C27—H27B	110.3
O58—C57—C56	111.94 (10)	H27A—C27—H27B	108.5
C54—C49—C50	116.72 (11)	C53—C52—C51	120.55 (12)
C54—C49—C55	118.04 (10)	C53—C52—H52	119.7
C50—C49—C55	125.20 (10)	C51—C52—H52	119.7
F16—C6—C5	118.49 (10)	O10—C11—C12	106.60 (11)
F16—C6—C1	117.99 (10)	O10—C11—H11A	110.4
C5—C6—C1	123.52 (10)	C12—C11—H11A	110.4
C24—C23—C17	129.88 (10)	O10—C11—H11B	110.4
C24—C23—H23	115.1	C12—C11—H11B	110.4
C17—C23—H23	115.1	H11A—C11—H11B	108.6
C3—C2—C1	120.74 (10)	O58—C59—C60	106.63 (11)
C3—C2—H2	119.6	O58—C59—H59A	110.4
C1—C2—H2	119.6	C60—C59—H59A	110.4
O29—C25—O26	124.85 (11)	O58—C59—H59B	110.4
O29—C25—C24	123.00 (10)	C60—C59—H59B	110.4
O26—C25—C24	112.15 (9)	H59A—C59—H59B	108.6
N15—C14—C8	178.22 (13)	C11—C12—H12A	109.5
C39—C40—C46	124.80 (11)	C11—C12—H12B	109.5
C39—C40—C41	121.65 (10)	H12A—C12—H12B	109.5
C46—C40—C41	113.53 (9)	C11—C12—H12C	109.5
N47—C46—C40	178.39 (13)	H12A—C12—H12C	109.5
C23—C24—C30	124.71 (11)	H12B—C12—H12C	109.5
C23—C24—C25	121.50 (10)	C43—C44—H44A	109.5
C30—C24—C25	113.77 (10)	C43—C44—H44B	109.5
C37—C38—C33	120.95 (11)	H44A—C44—H44B	109.5
C37—C38—H38	119.5	C43—C44—H44C	109.5
C33—C38—H38	119.5	H44A—C44—H44C	109.5
C56—C55—C49	129.33 (10)	H44B—C44—H44C	109.5
C56—C55—H55	115.3	C59—C60—H60A	109.5
C49—C55—H55	115.3	C59—C60—H60B	109.5
C51—C50—C49	120.74 (11)	H60A—C60—H60B	109.5
C51—C50—H50	119.6	C59—C60—H60C	109.5
C49—C50—H50	119.6	H60A—C60—H60C	109.5
C35—C36—C37	120.30 (11)	H60B—C60—H60C	109.5
C35—C36—H36	119.8	C27—C28—H28A	109.5

C37—C36—H36	119.8	C27—C28—H28B	109.5
N31—C30—C24	178.51 (13)	H28A—C28—H28B	109.5
C38—C37—C36	120.44 (11)	C27—C28—H28C	109.5
C38—C37—H37	119.8	H28A—C28—H28C	109.5
C36—C37—H37	119.8	H28B—C28—H28C	109.5

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