Supporting Information

Preparations of SF_5- and CF_3-Substituted Arenes Utilizing the 7-oxabicyclo[2.2.1]hept-2-ene Synthones

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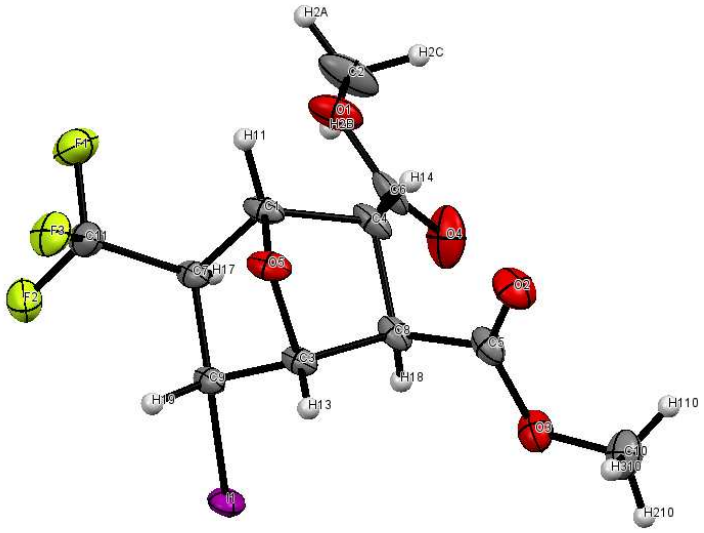


Figure 1. X-ray crystal structures of **8** (CCDC 951078).

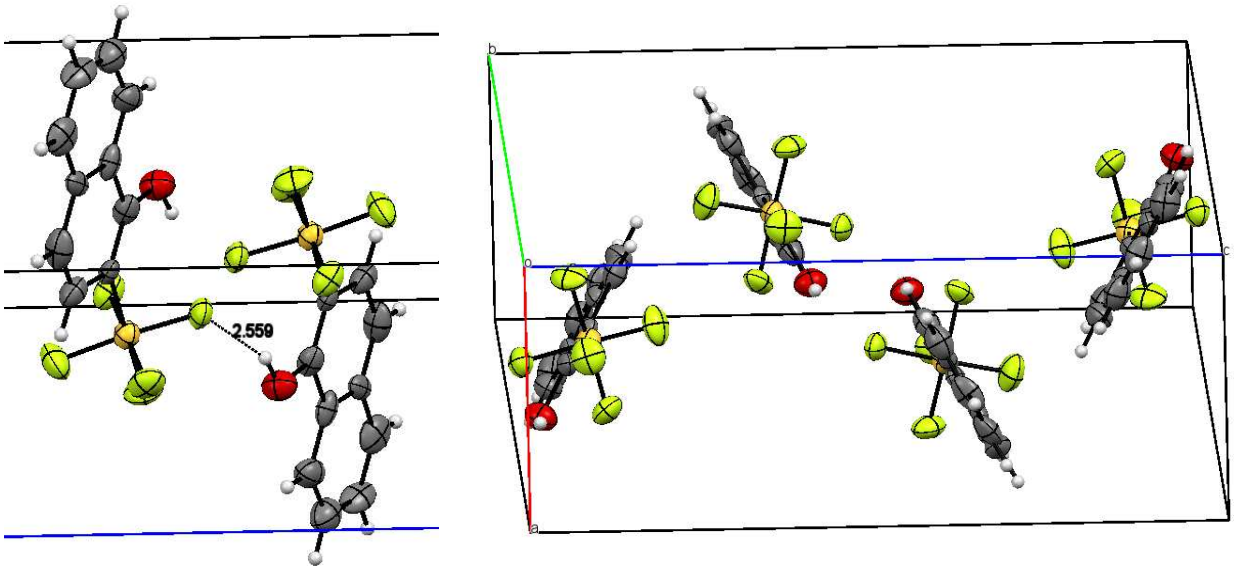


Figure 2. X-ray packing diagram for the solid state of **10a** (the F---HO bond distance in Å).

Table S1: Crystallographic data for compound **10a** (CCDC 951079)

Empirical formula	C20H14F10O2S2
Formula Weight	540.43
crystal system	Triclinic
space group	Pī
a (Å)	6.337(3)
b (Å)	10.385(5)
c (Å)	15.832(8)
α (deg)	96.304(11)
β (deg)	90.560(11)
γ (deg)	99.260(11)
volume (Å3)	1021.7(9)
Z	2
D_{calcd} (g/cm3)	1.757
abs coeff	0.369
F(000)	544
crystal size, mm^3	0.4 x 0.37 x 0.12
θ range for data collection (deg)	3.45 – 20.81
reflections collected	4875
Independent reflections	2028
R_{int}	0.0497
observed (I > 2 σ (I))	1593
goodness-of-fit on F2	1.002
R_1[I > 2σ(I)]a	0.0731
R_w (all data)b	0.2060

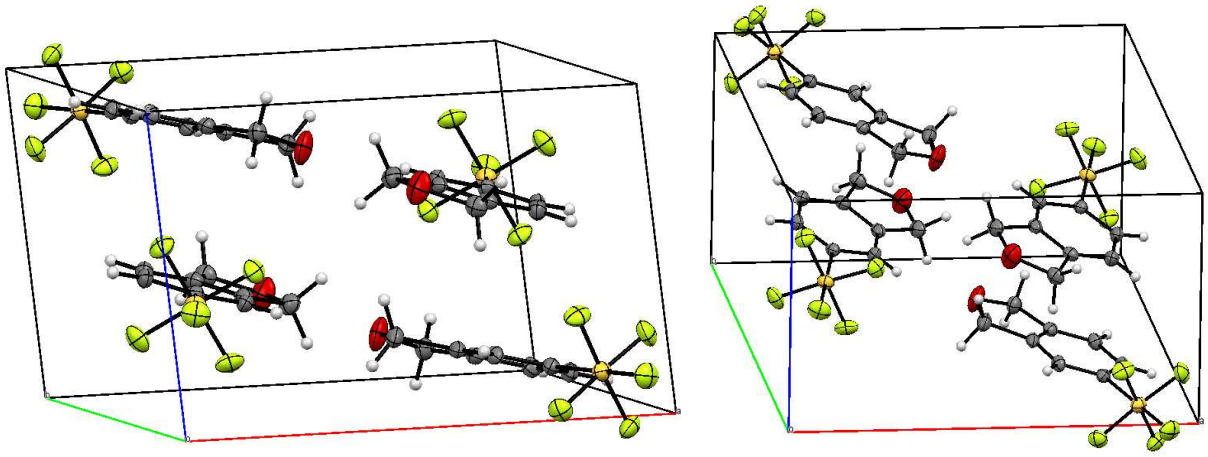


Figure 3. X-ray packing diagram for the solid state of **14c** (CCDC 951080)**.**

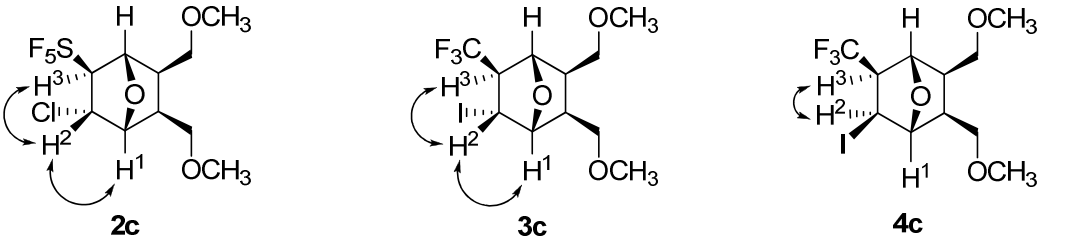
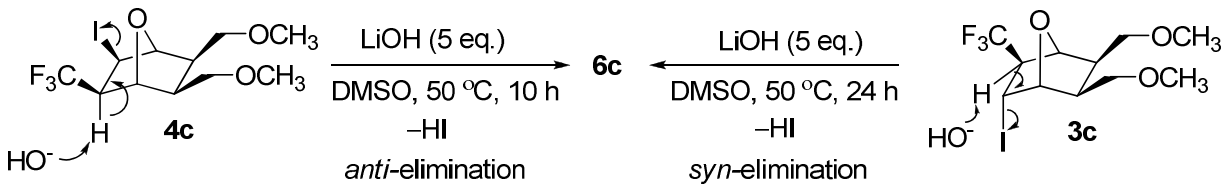


Figure 4. The appearance of the $H^{exo/endo}$ protons of **2c, 3c, 4c** in ^1H NMR (400 MHz, $CDCl_3$) spectra.



Scheme 1. *Anti*- and *syn*-elimination of HI from **4c** and **3c**.

XYZ coordinates of MP2/cc-pVDZ optimized molecules

Cation **F**

MP2=-796.3237724
C -0.07117 0.00112 -1.07772
C -1.35643 -0.06428 -0.59590
C -1.62609 -0.35915 0.84313
C -0.47089 -0.12068 1.77149
C 0.86141 -0.07700 1.22809
C 1.02626 -0.01519 -0.16687
C -0.64883 -0.02194 3.15523
C 0.47592 0.11742 3.98855
C 1.79508 0.13360 3.46586
C 1.99651 0.04311 2.09414
C 0.23247 0.15732 -2.55736
H 3.00263 0.06583 1.66190
H 2.64740 0.23264 4.14424
H 0.32887 0.21804 5.06960
H -1.65893 -0.02946 3.57232
H -2.21098 -0.01617 -1.28178
O -2.79857 0.19468 1.37596
H -1.67159 -1.48691 0.80268
H -3.56188 -0.28947 1.02424
F 0.89493 -0.92199 -2.99513
F -0.88739 0.29887 -3.26990
F 1.01095 1.23131 -2.74656
H 2.04434 0.05793 -0.57309

Cation **E**

MP2=-796.3265143
C -0.97436 0.28785 -0.05954
C -0.58146 1.60823 -0.05961
C 0.80409 1.92419 0.03075
C 1.81509 0.94578 0.10087
C 1.43998 -0.44345 0.08482
C -0.00436 -0.81492 0.24955
C 3.19488 1.32685 0.05332
C 4.16840 0.33863 -0.02838
C 3.78597 -1.02702 -0.07299
C 2.43724 -1.42045 -0.00370
C -2.43279 -0.09903 -0.22875
H 2.15724 -2.47604 -0.04262
H 4.56085 -1.79593 -0.16627
H 5.22751 0.60840 -0.07335
H 3.46084 2.38905 0.07661
H -1.31841 2.40819 -0.17044
F -2.75175 -1.03333 0.69317
F -3.24550 0.94592 -0.07382
F -2.61986 -0.62140 -1.44198
H -0.11587 -0.85231 1.37177
O -0.25492 -2.05927 -0.34028
H -1.02099 -2.46250 0.09863
H 1.10209 2.98113 0.01254

Cation **H**

MP2=-1355.1024331
C -0.14607 0.09561 0.40379
C -1.42114 0.09384 -0.10055
C -1.66484 0.34063 -1.55516
C -0.48053 0.11660 -2.44853
C 0.83716 0.13897 -1.87131
C 0.97730 0.12732 -0.47253
C -0.61915 -0.02807 -3.83230
C 0.53169 -0.14935 -4.63273
C 1.83653 -0.10040 -4.07717
C 1.99890 0.03796 -2.70428
S 0.14411 -0.02728 2.20238
H 2.99326 0.06593 -2.24597
H 2.70930 -0.18705 -4.73080
H 0.41666 -0.28686 -5.71360
H -1.61761 -0.06996 -4.27470
H -2.29285 0.03333 0.56083
O -2.80339 -0.27151 -2.09493
H -1.75293 1.46634 -1.54460
H -3.59203 0.19811 -1.78096
F 1.29446 1.12873 2.09039
F 1.27567 -1.17615 1.94143
H 1.98618 0.11398 -0.04450
F -0.97906 1.11904 2.48418
F 0.42078 -0.13068 3.77808
F -0.99792 -1.18064 2.33571

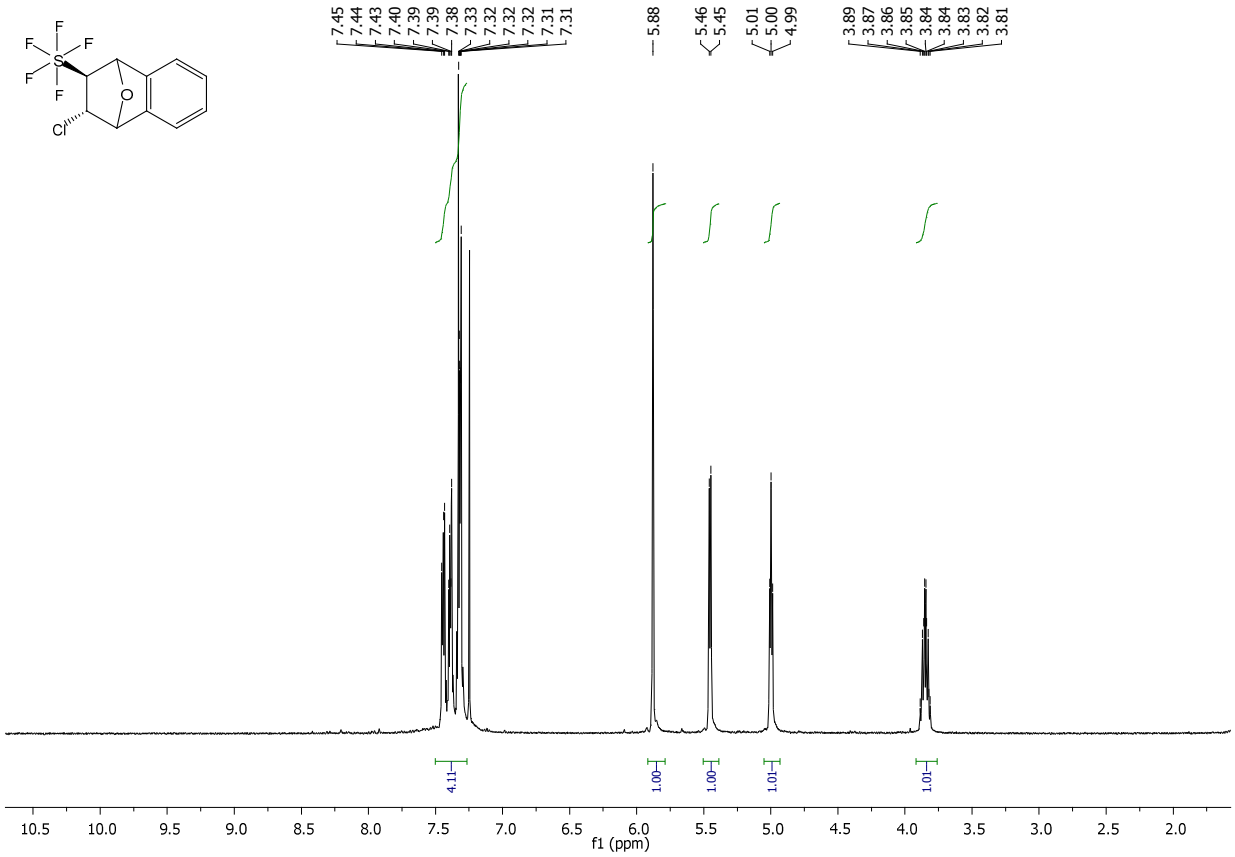
Cation **G**

MP2=-1355.1034455
C -0.35403 -0.01441 -0.31558
C -1.66415 0.03403 0.11483
C -1.94874 0.00711 1.50854
C -0.95336 -0.07079 2.49892
C 0.42368 -0.11679 2.08667
C 0.77162 -0.33215 0.63944
C -1.29948 0.02666 3.88529
C -0.28506 0.09326 4.83206
C 1.07117 0.07485 4.41406
C 1.42837 -0.04007 3.05846
S -0.03622 0.02491 -2.12537
H 2.47737 -0.04932 2.75386
H 1.86310 0.15465 5.16706
H -0.52543 0.17418 5.89611
H -2.35518 0.05189 4.17572
H -2.48730 0.12969 -0.59633
F 1.20435 -1.04575 -1.92689
F -1.05776 -1.22519 -2.35125
F -1.25285 1.07729 -2.35894
H 0.75513 -1.45824 0.55426
O 2.03934 0.19217 0.40026
H 2.38358 -0.19509 -0.42007
H -2.99916 0.07021 1.82307
F 0.27288 0.04129 -3.69800
F 1.00010 1.26074 -1.91652

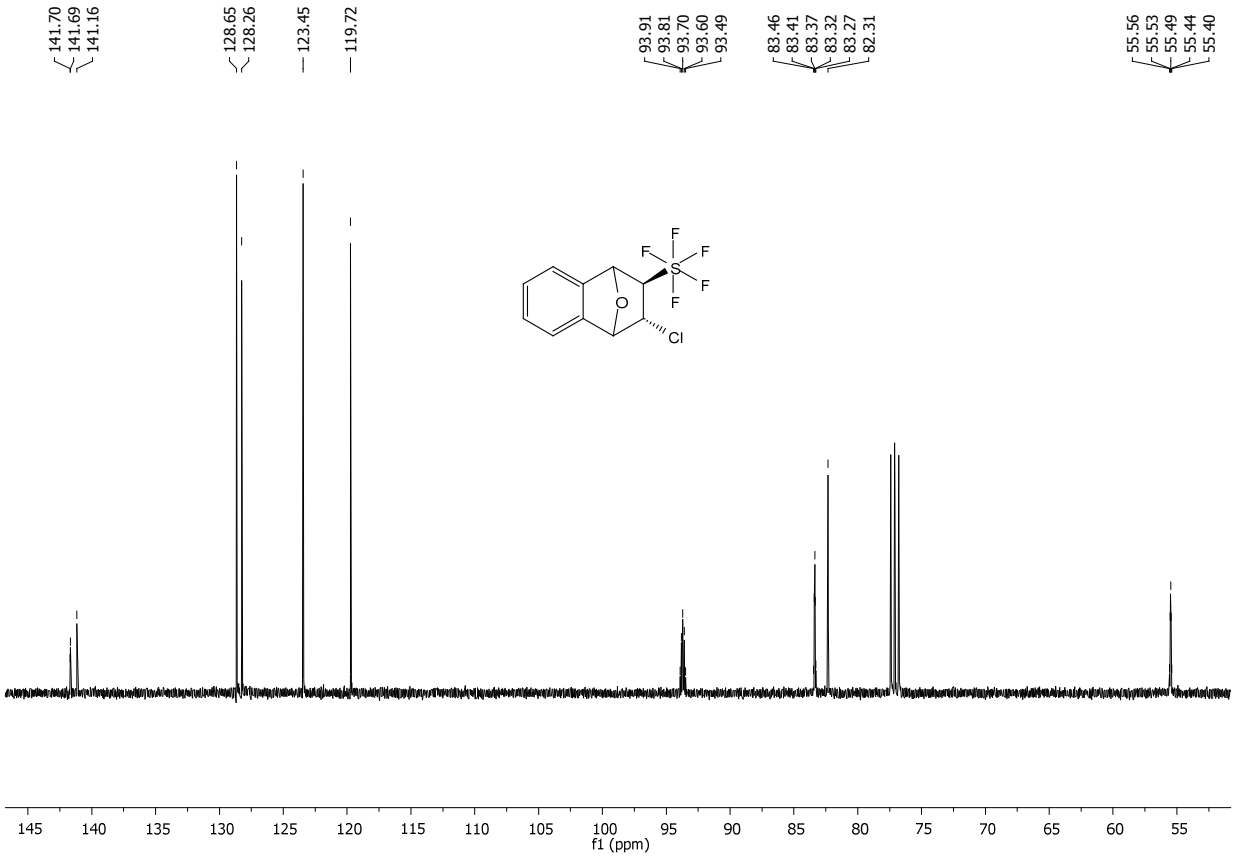
Product **10a**

MP2=-1354.8300681
C -0.31204 0.00892 0.26560
C -1.67816 0.00548 -0.14451
C -2.00151 -0.01054 -1.48730
C -0.97640 -0.02296 -2.47788
C 0.39764 -0.01220 -2.06633
C 0.73240 0.00654 -0.66582
C -1.27699 -0.04248 -3.87076
C -0.26167 -0.05112 -4.81878
C 1.09659 -0.03903 -4.40296
C 1.42648 -0.01916 -3.05244
S -0.00909 0.00557 2.04574
H 2.47057 -0.00914 -2.73194
H 1.89392 -0.04471 -5.15362
H -0.50712 -0.06651 -5.88577
H -2.32801 -0.05070 -4.18145
H -2.46517 0.01312 0.61066
F 1.18150 1.15048 1.90715
F -1.10944 1.18430 2.31082
F -1.14221 -1.13877 2.31613
O 2.06338 0.01491 -0.41125
H 2.20859 0.10531 0.54175
H -3.05234 -0.01433 -1.79532
F 0.28637 0.00751 3.64713
F 1.14598 -1.16507 1.91028

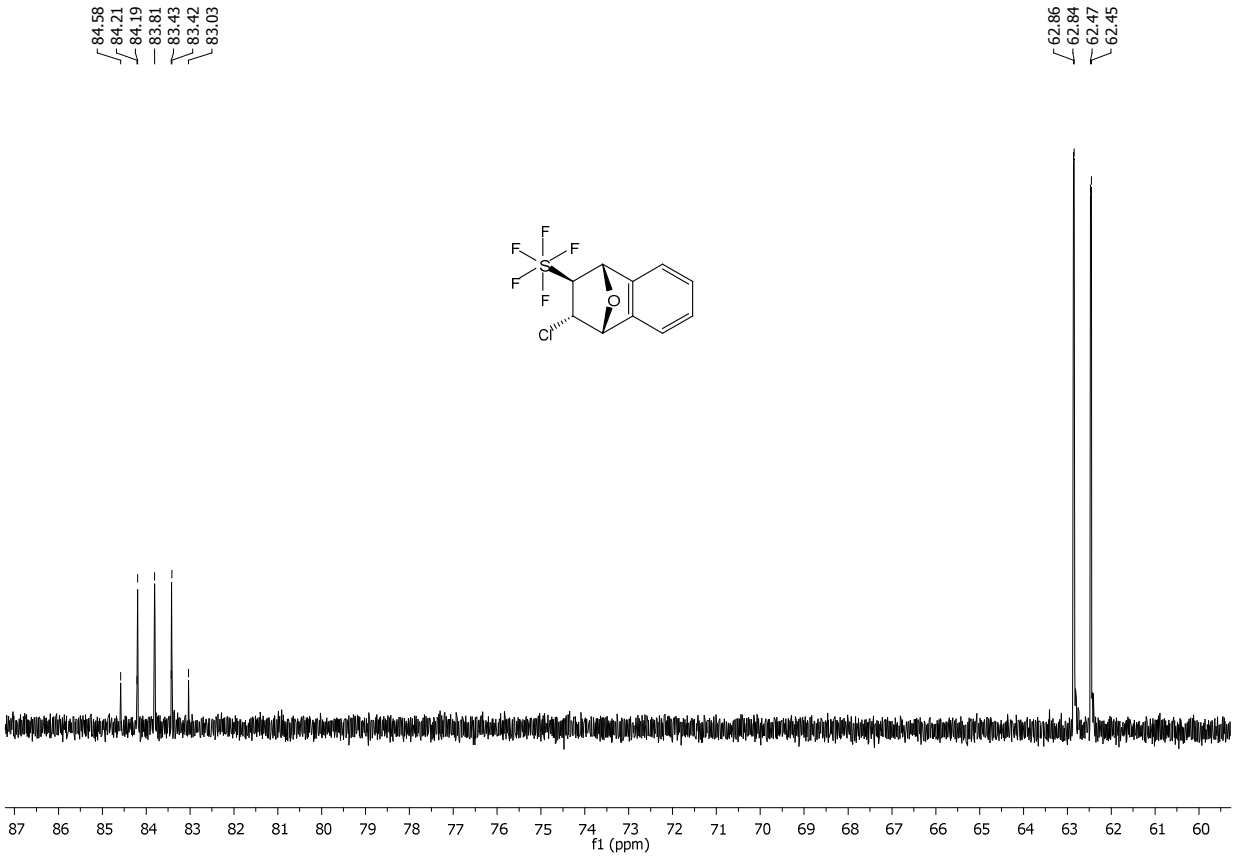
2a ^{1}H NMR (400 MHz, $CDCl_3$)



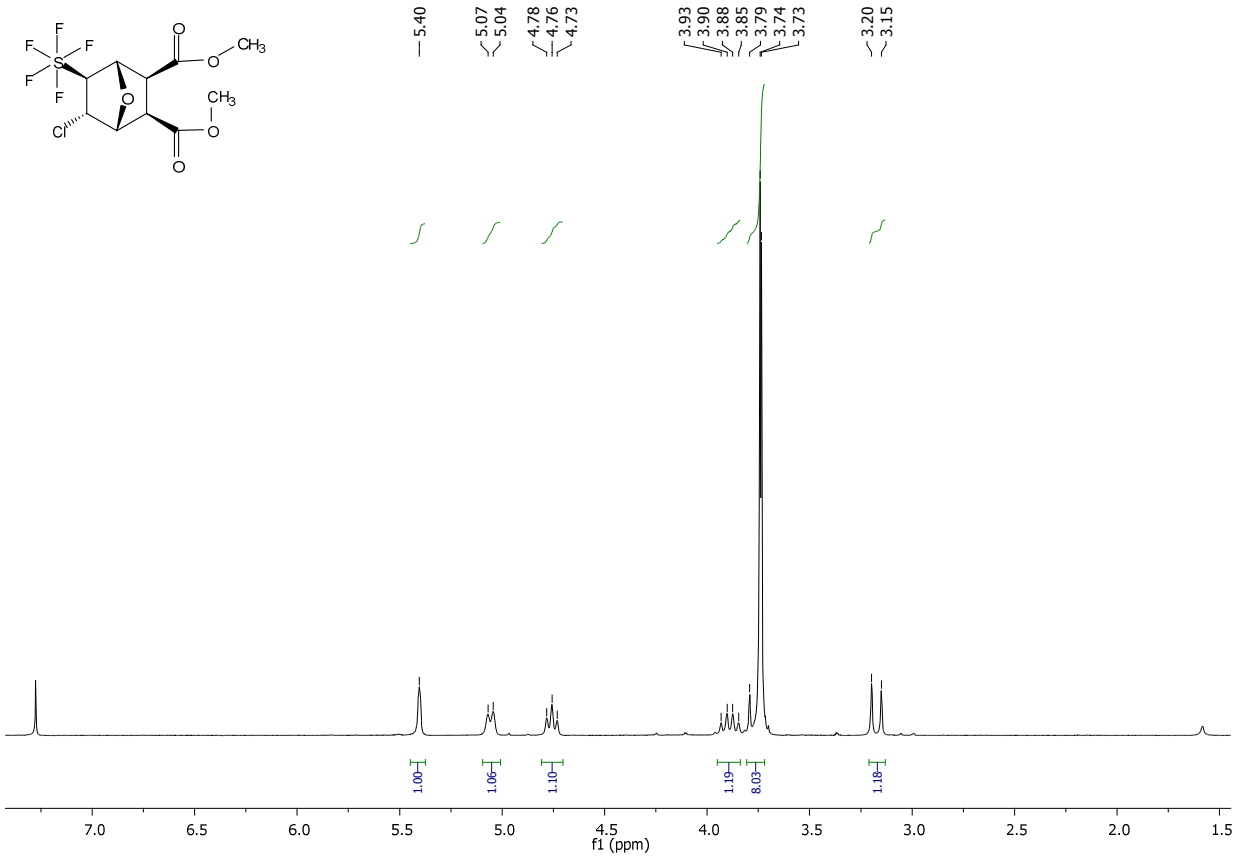
2a ^{13}C NMR (101 MHz, $CDCl_3$)



2a ^{19}F NMR (376 MHz, $CDCl_3$)



2b ^{1}H NMR (400 MHz, $CDCl_3$)



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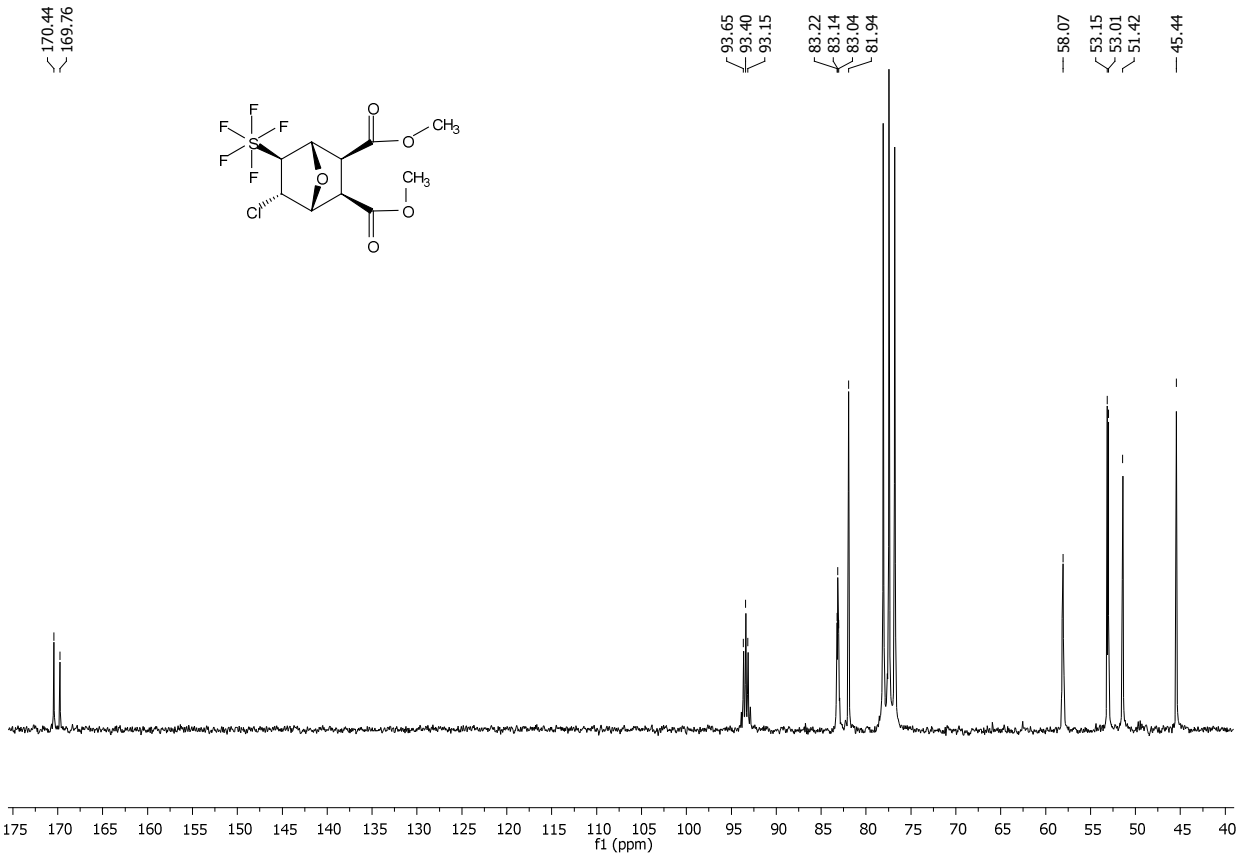
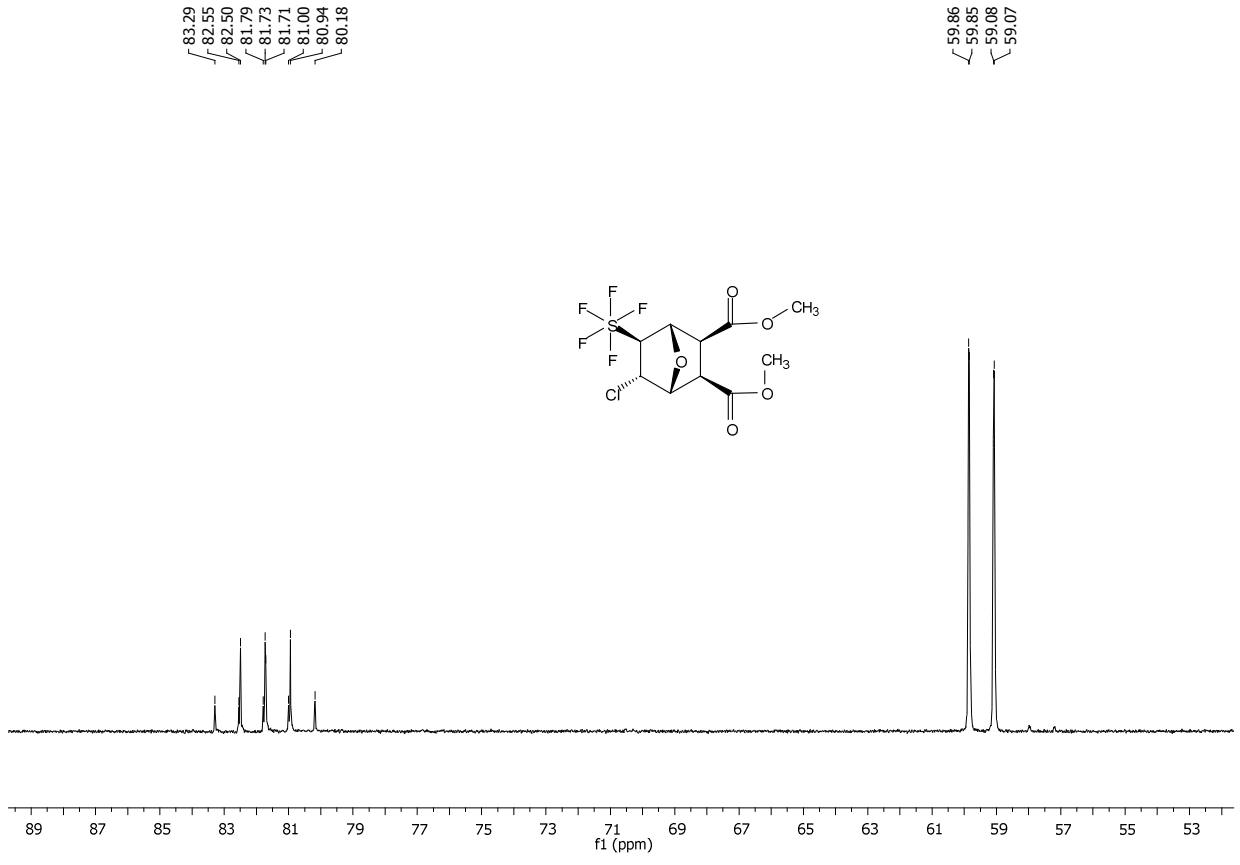
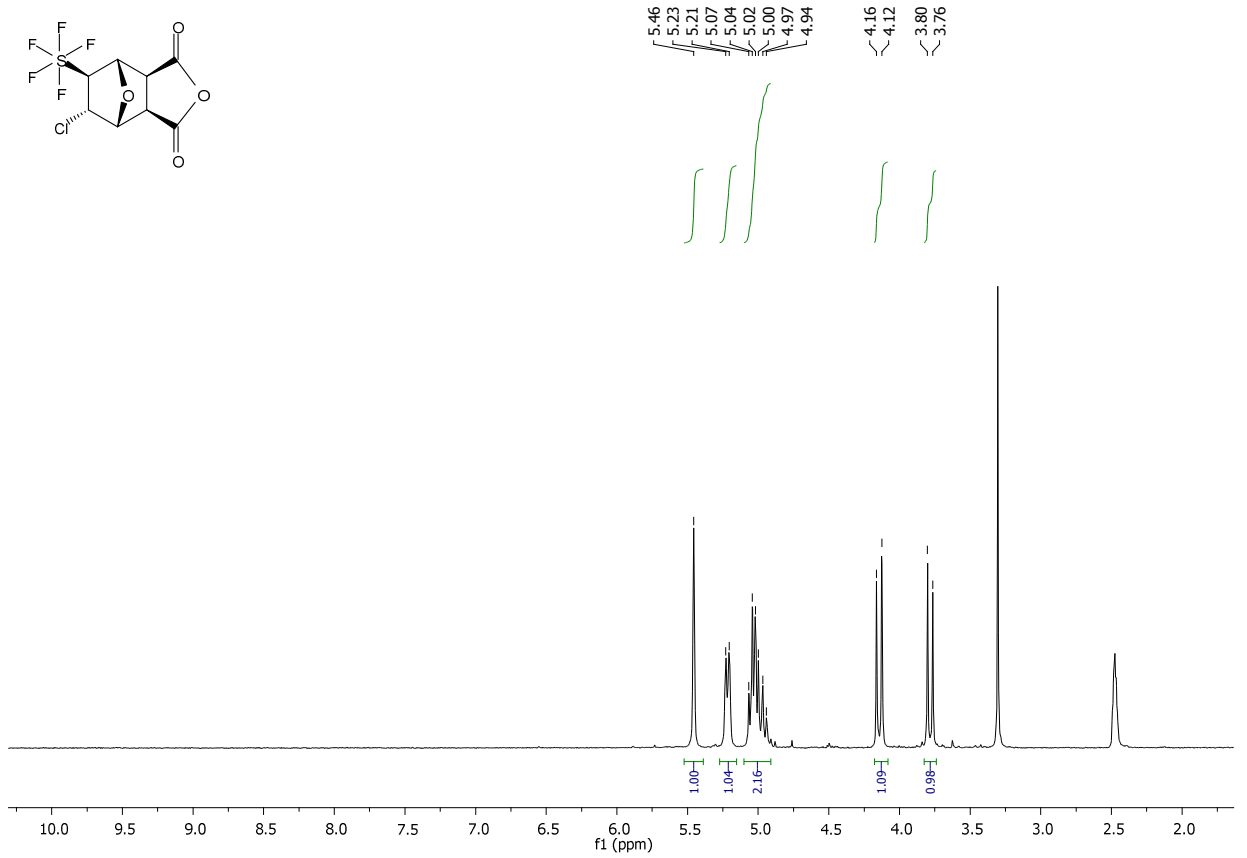


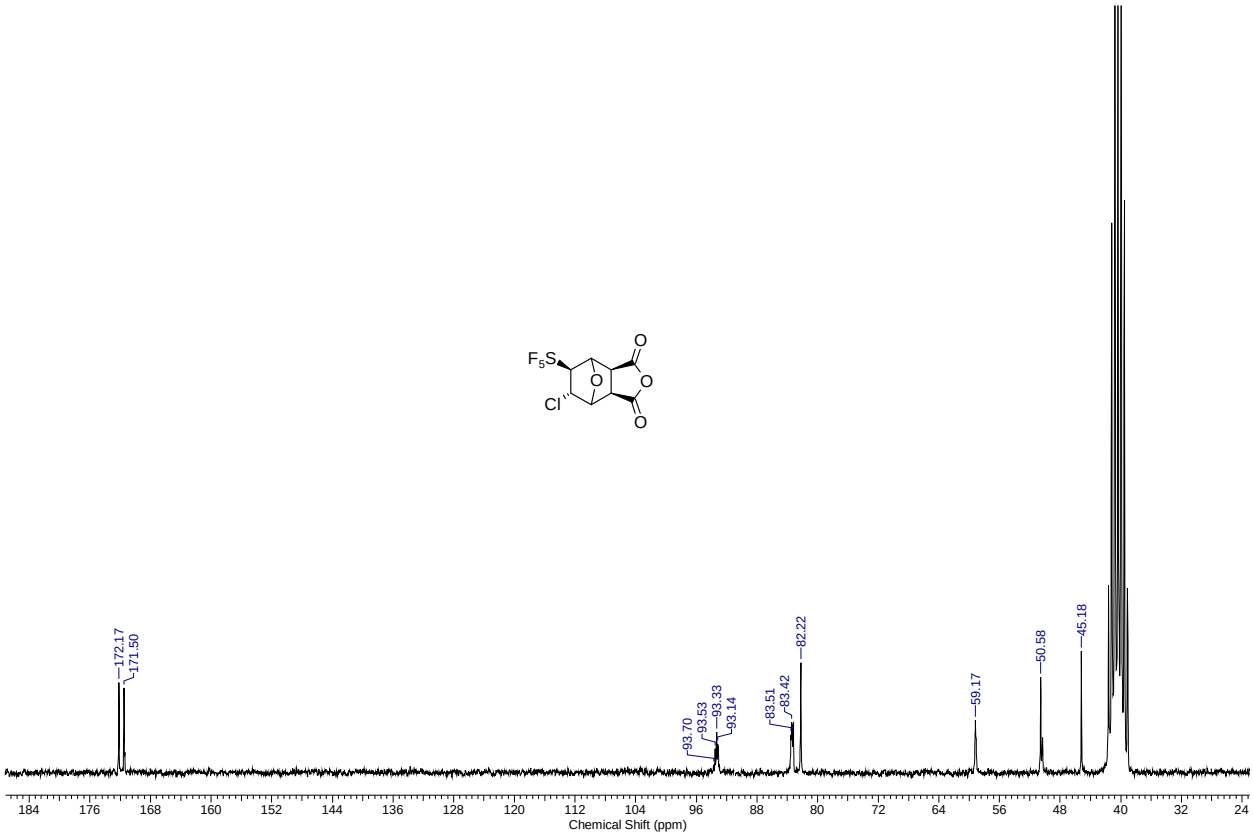
2b ^{19}F NMR (376 MHz, $CDCl_3$)



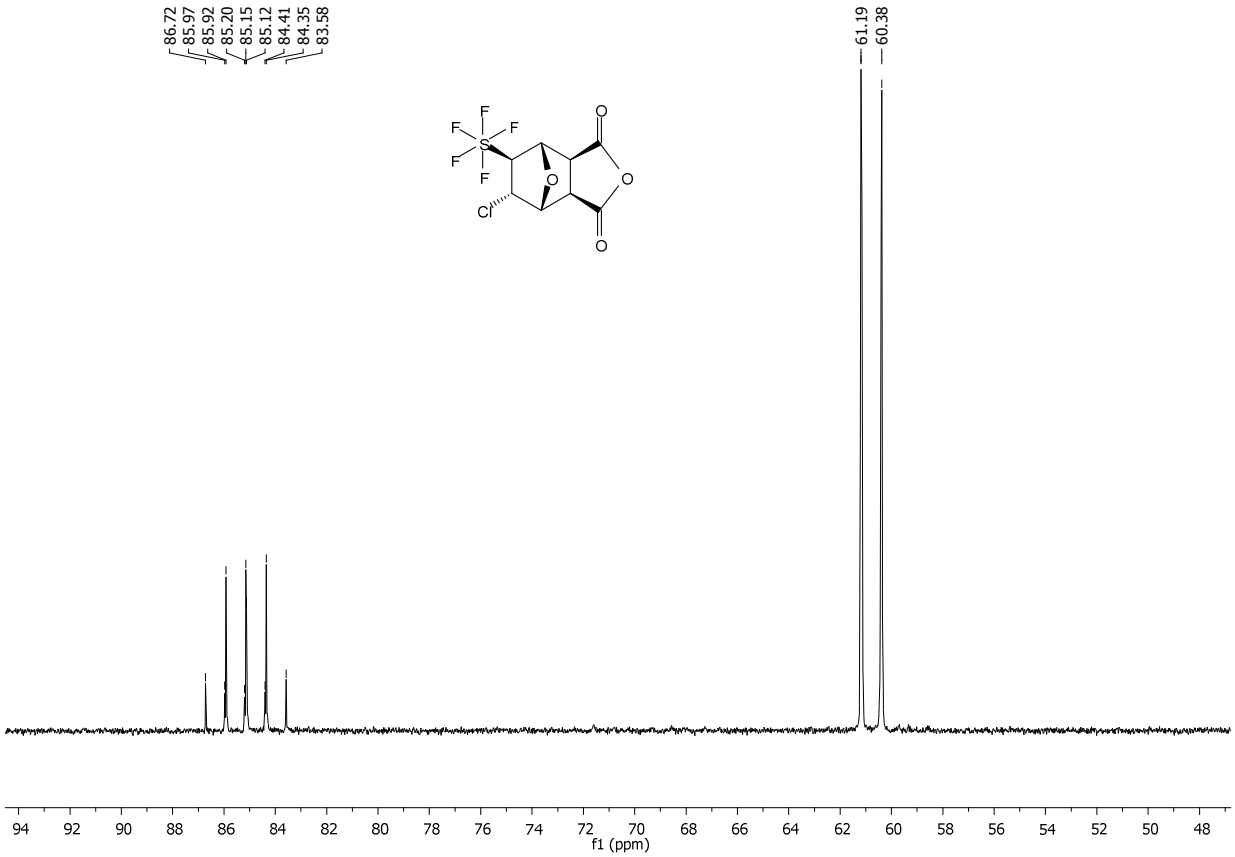
2d ^{1}H NMR (200 MHz, DMSO-d_6)



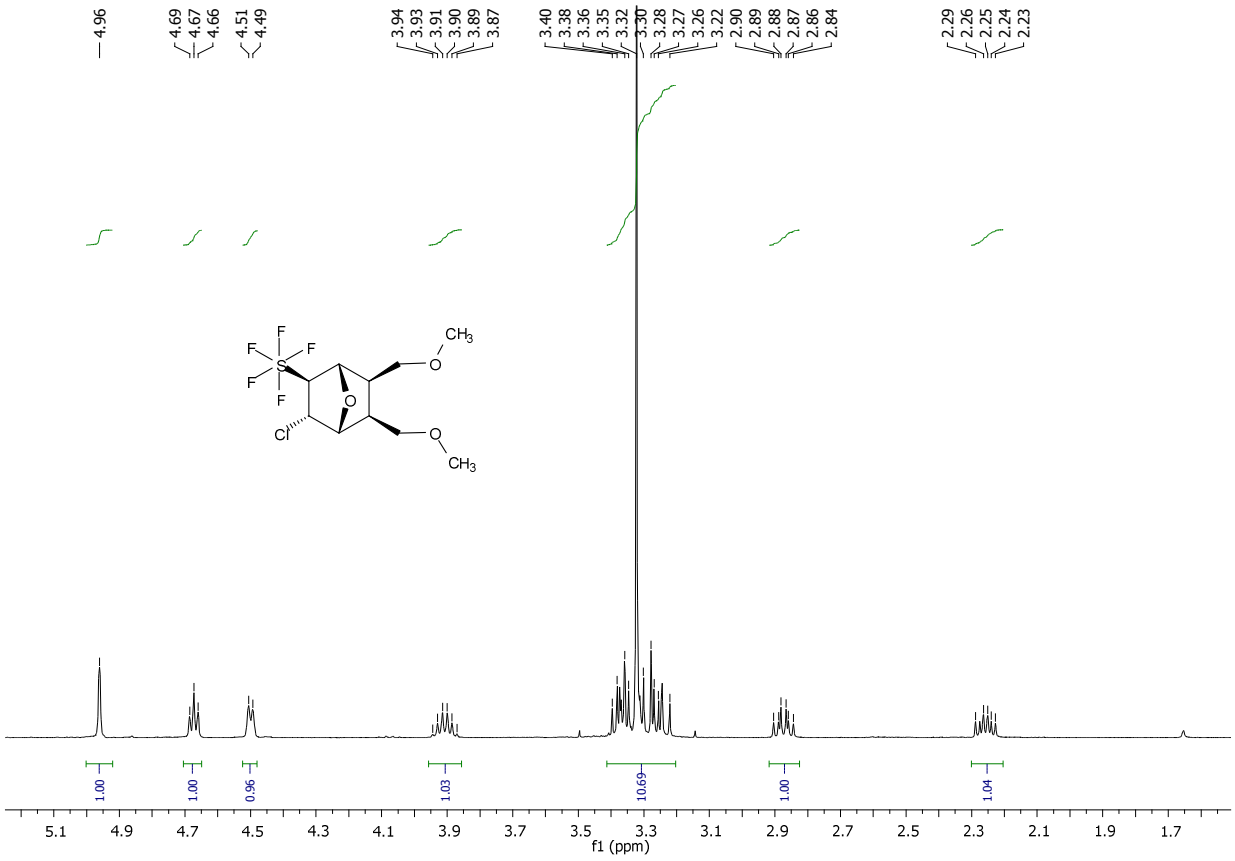
2d ^{13}C NMR (50 MHz, DMSO-d_6)



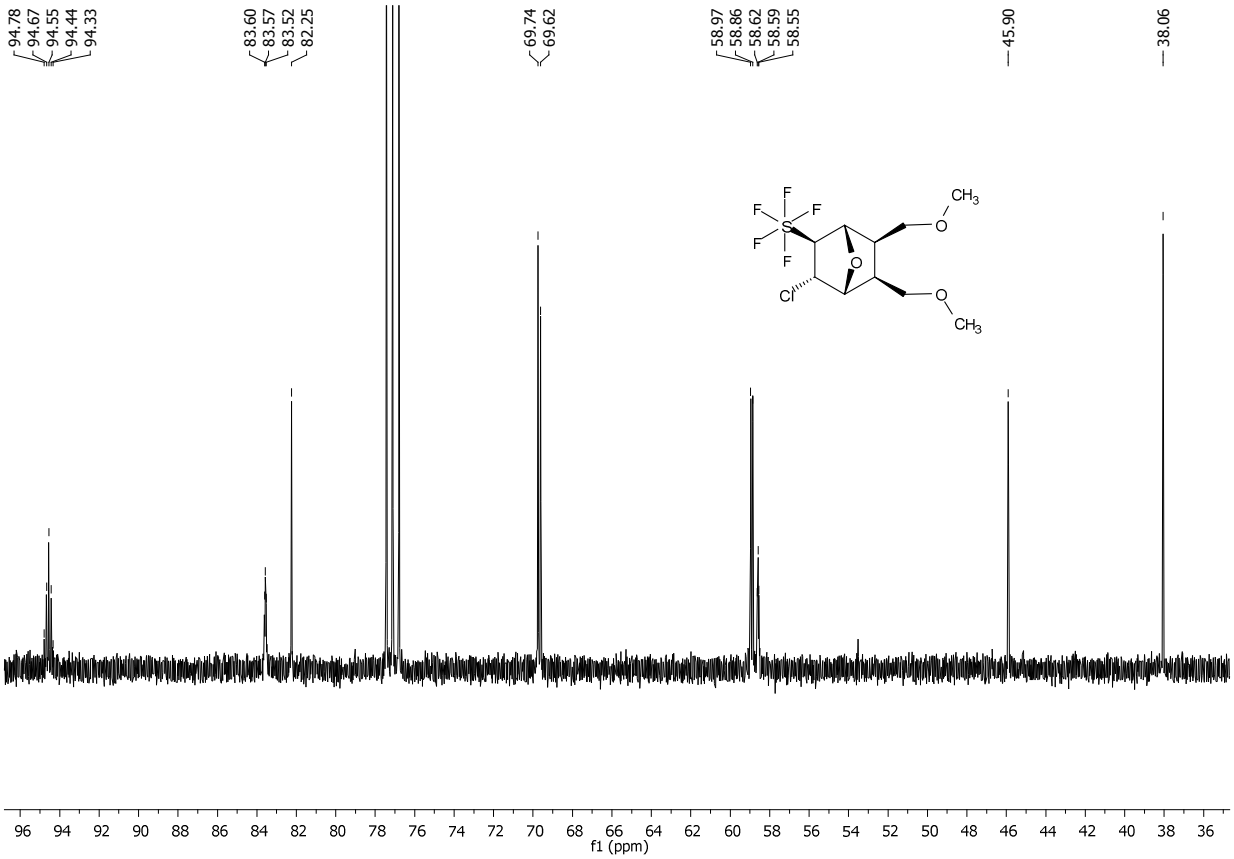
2d ^{19}F NMR (188 MHz, DMSO-d_6)



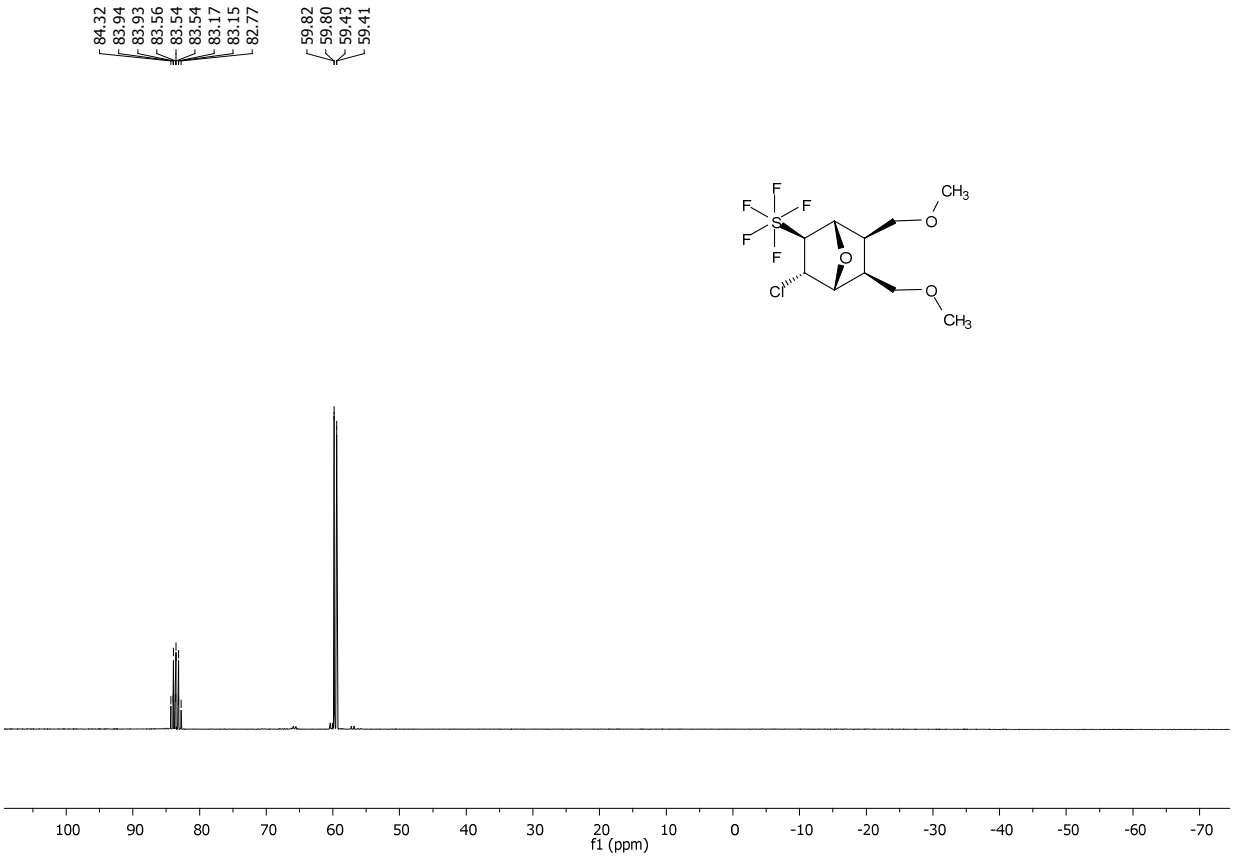
2c ^{1}H NMR (400 MHz, $CDCl_3$)

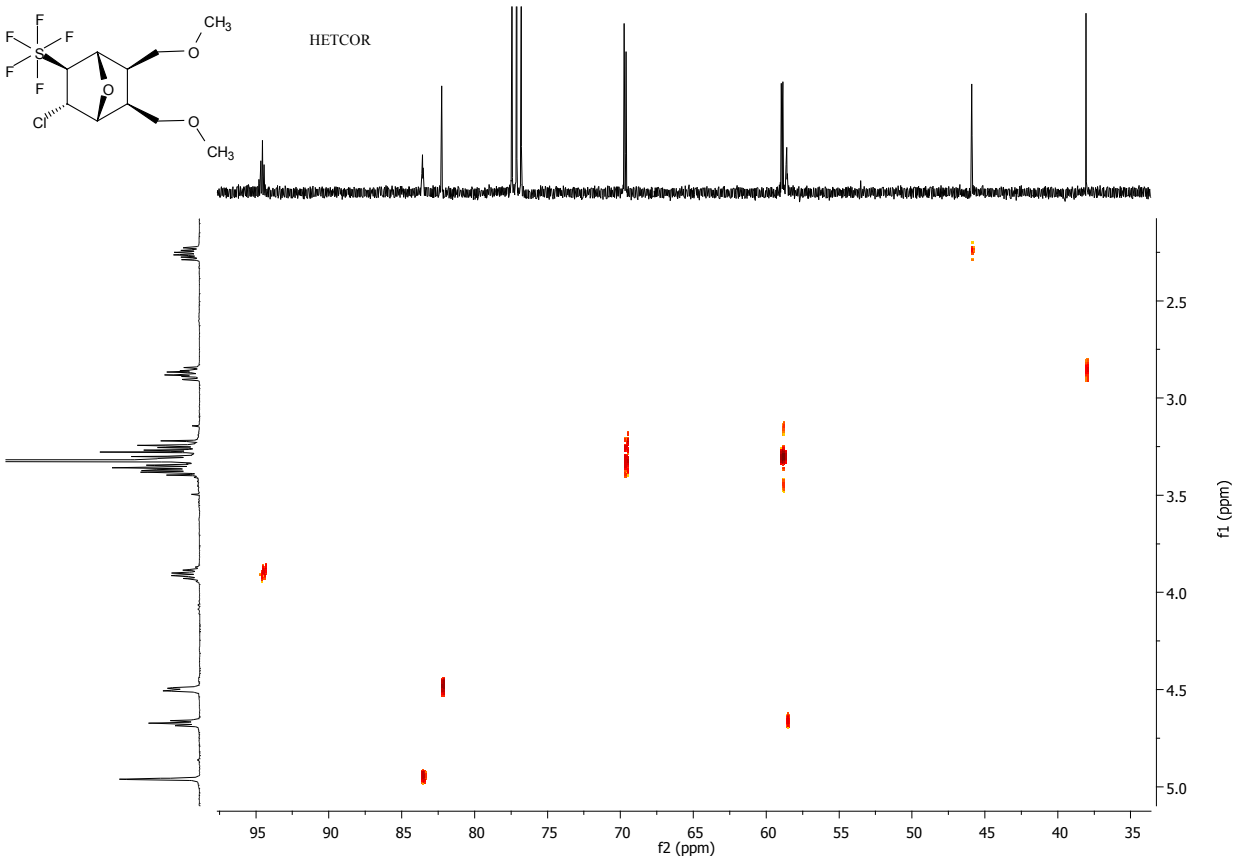


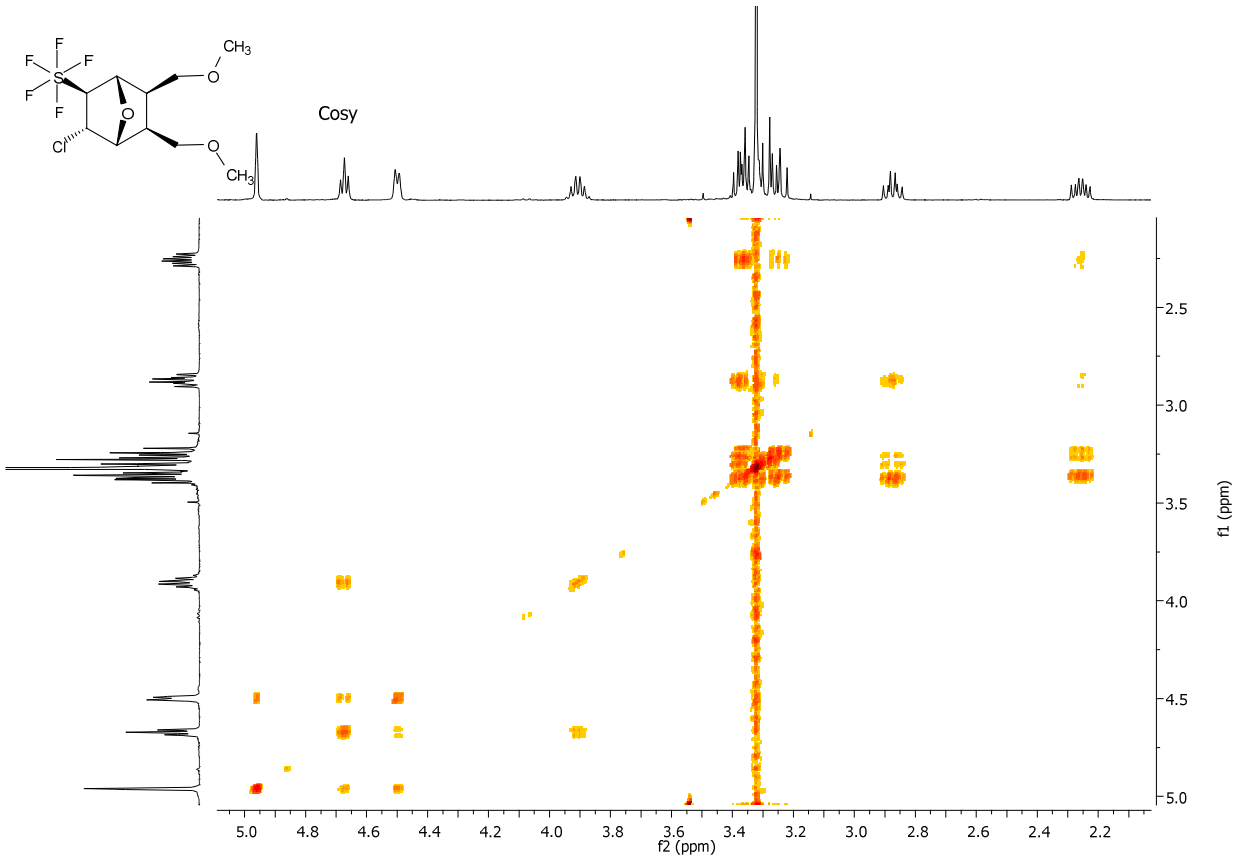
2c ^{13}C NMR (101 MHz, $CDCl_3$)

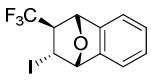


2c ^{19}F NMR (376 MHz, $CDCl_3$)

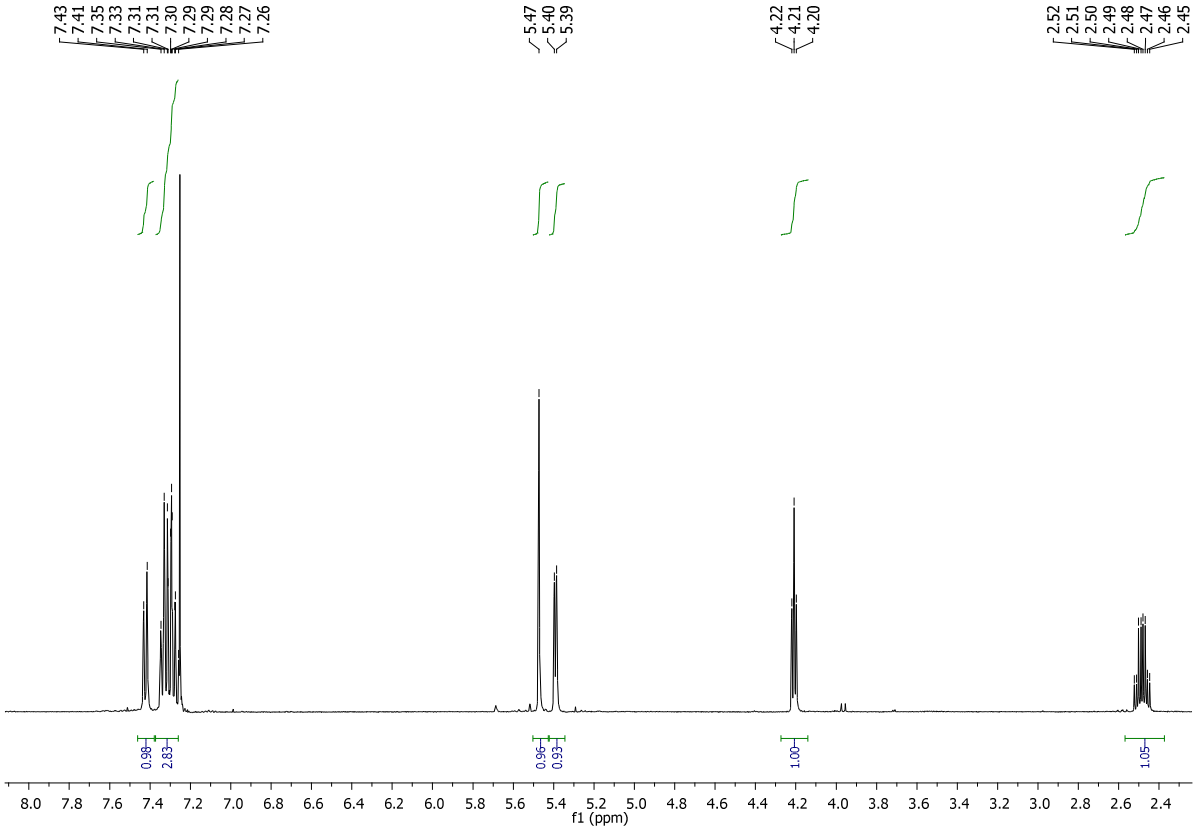


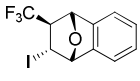




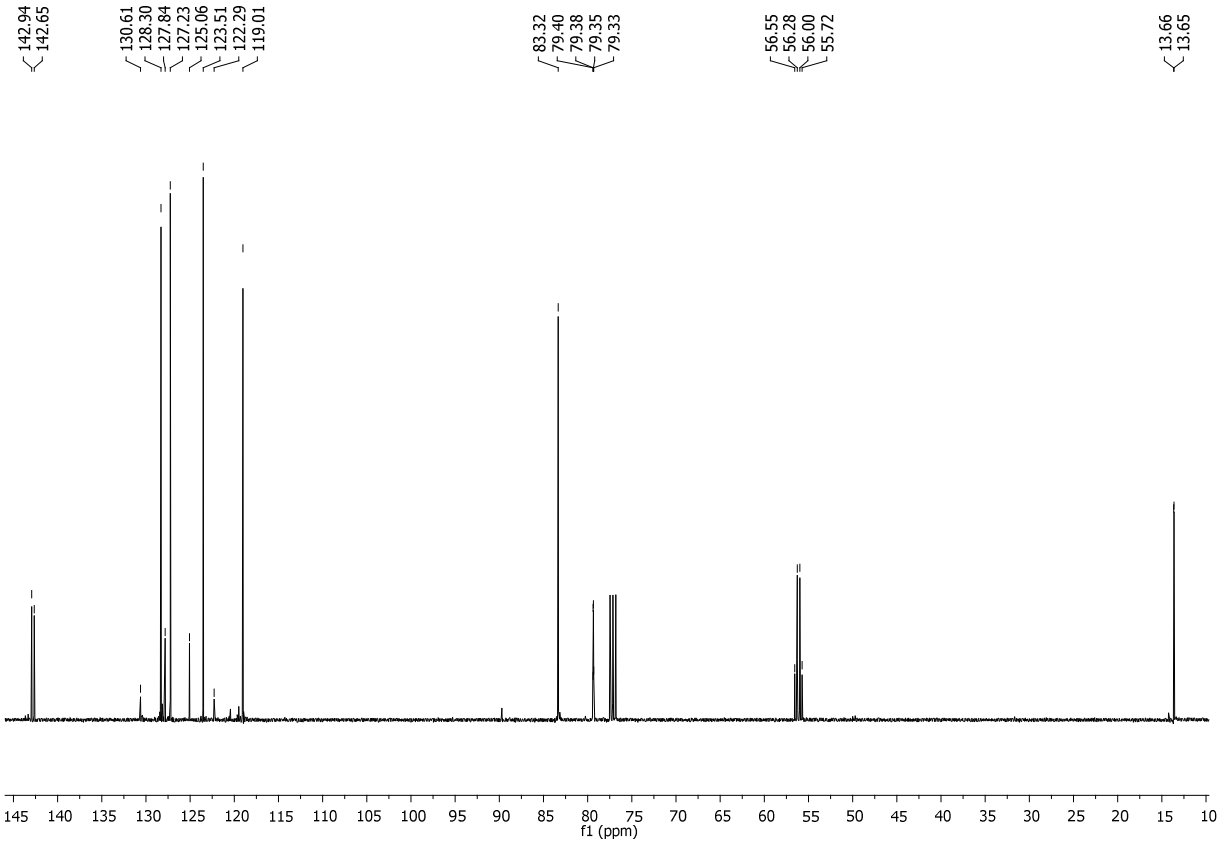


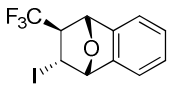
3a ^{1}H NMR (400 MHz, $CDCl_3$)



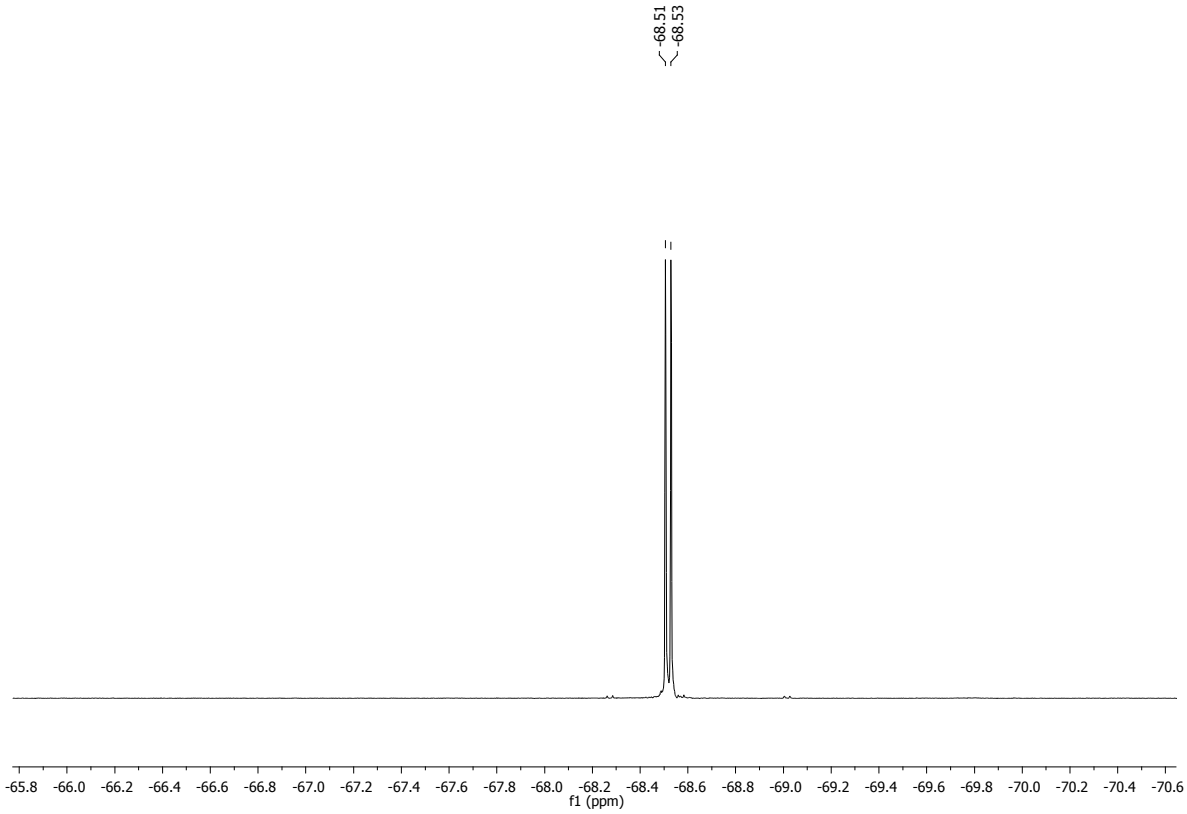


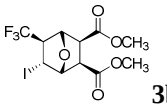
3a ^{13}C NMR (101 MHz, $CDCl_3$)





3a ^{19}F NMR (376 MHz, $CDCl_3$)





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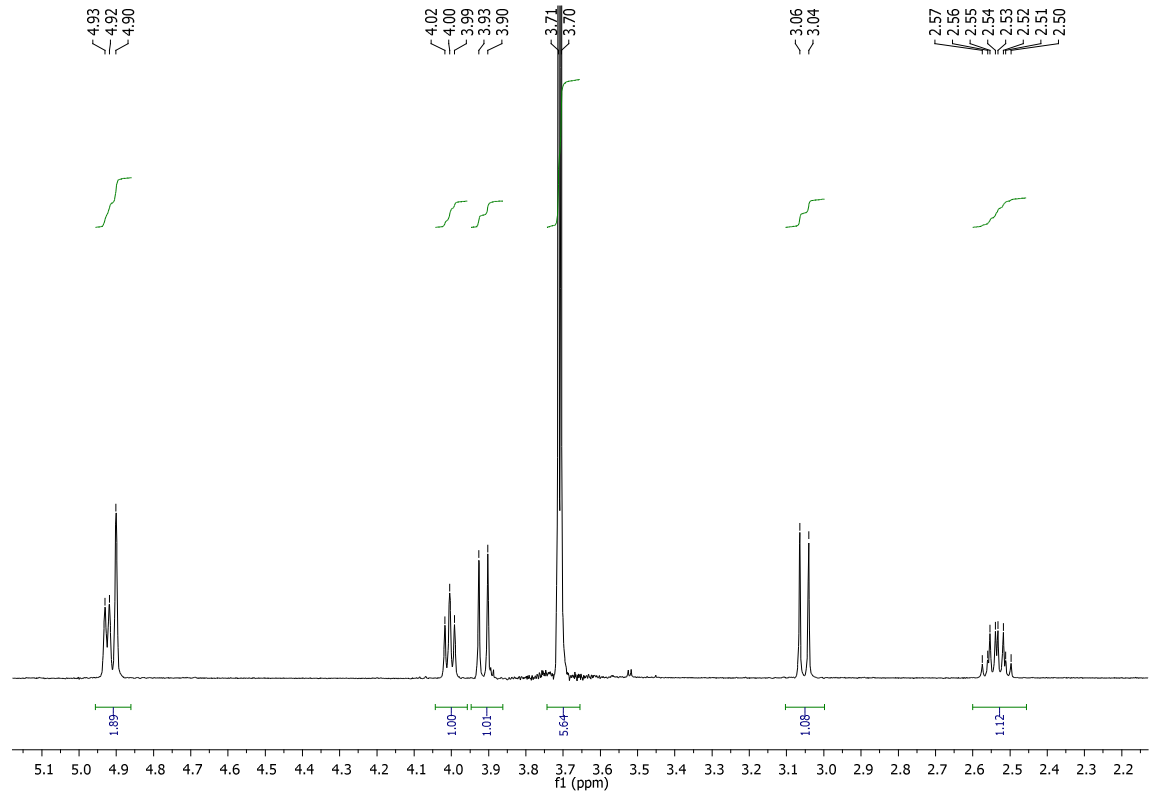

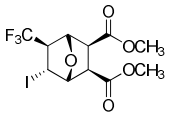

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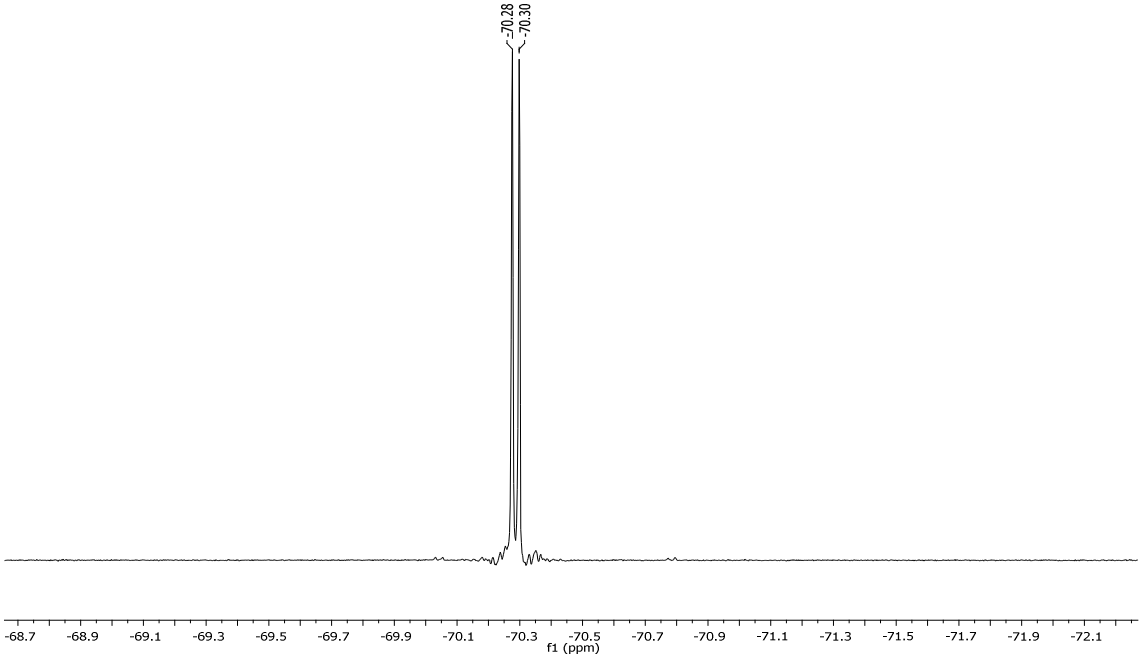
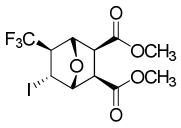
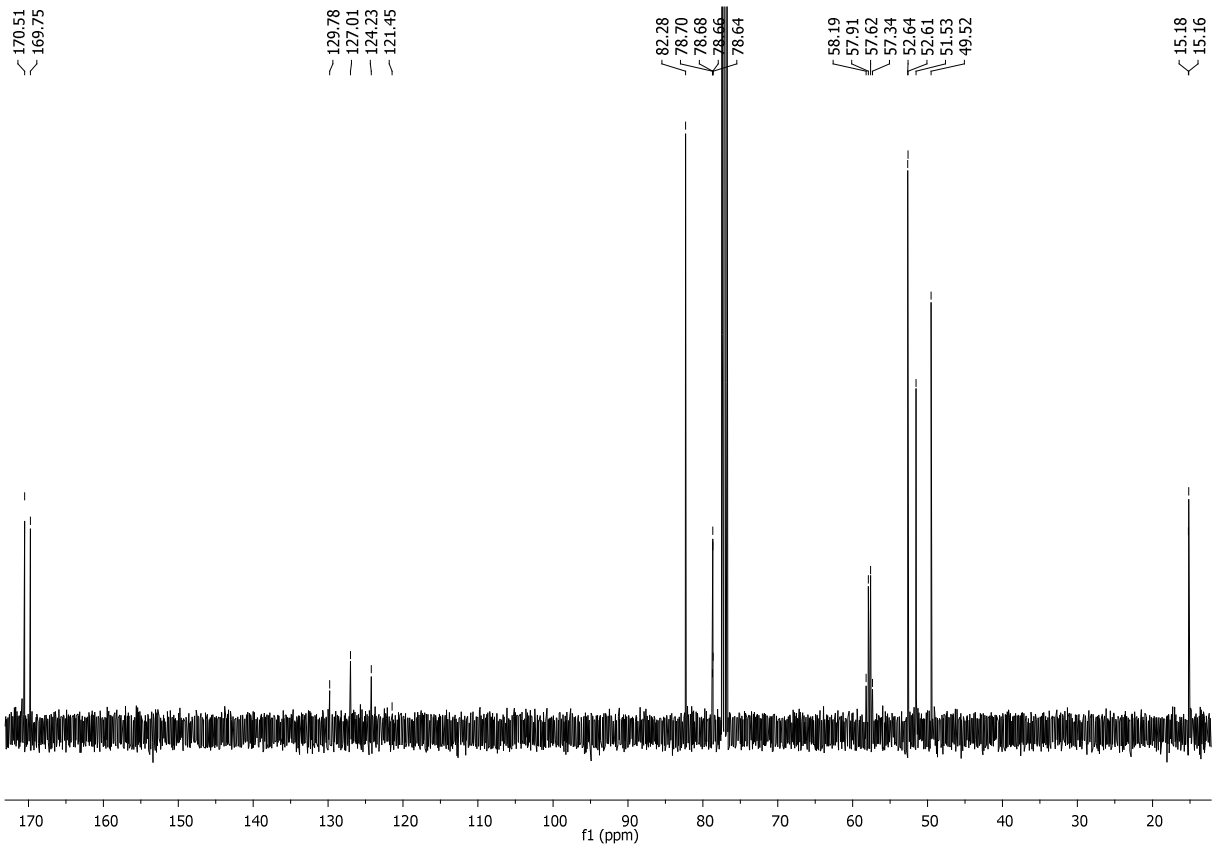
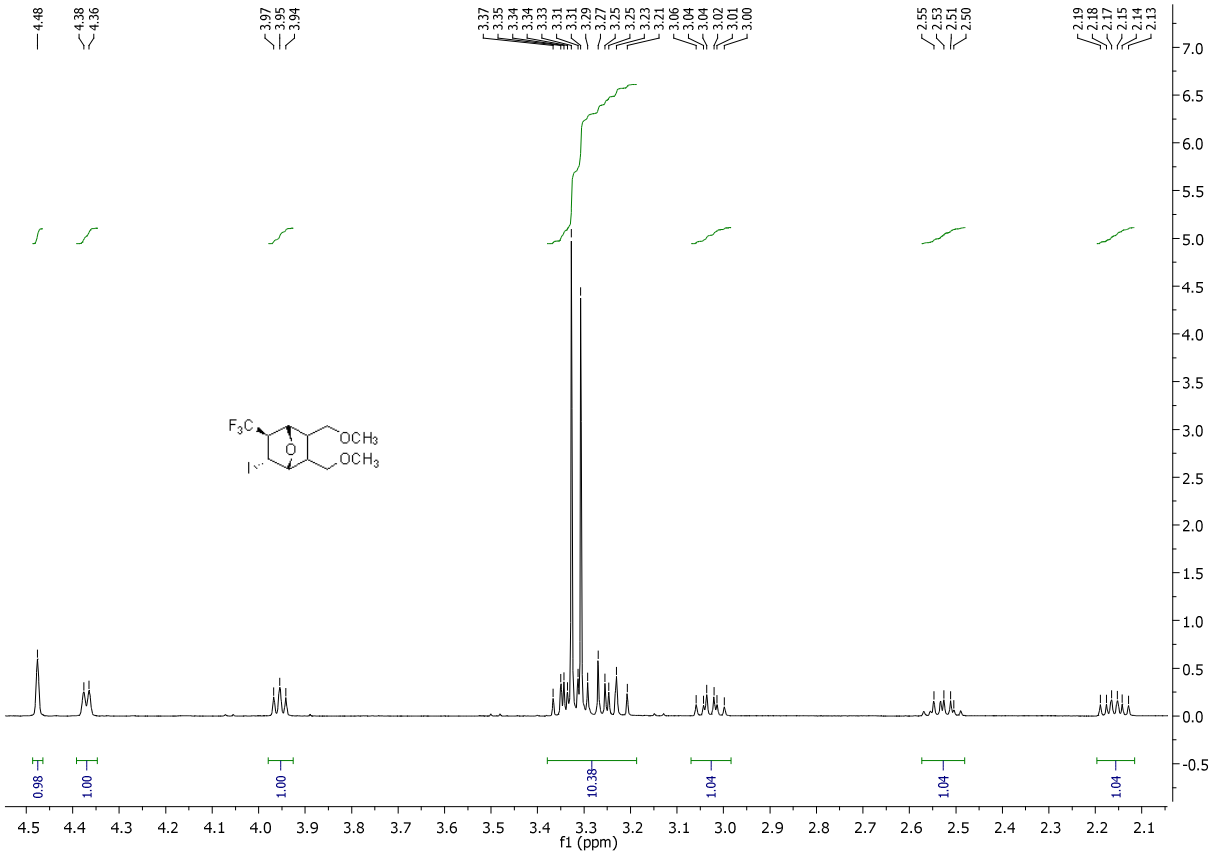




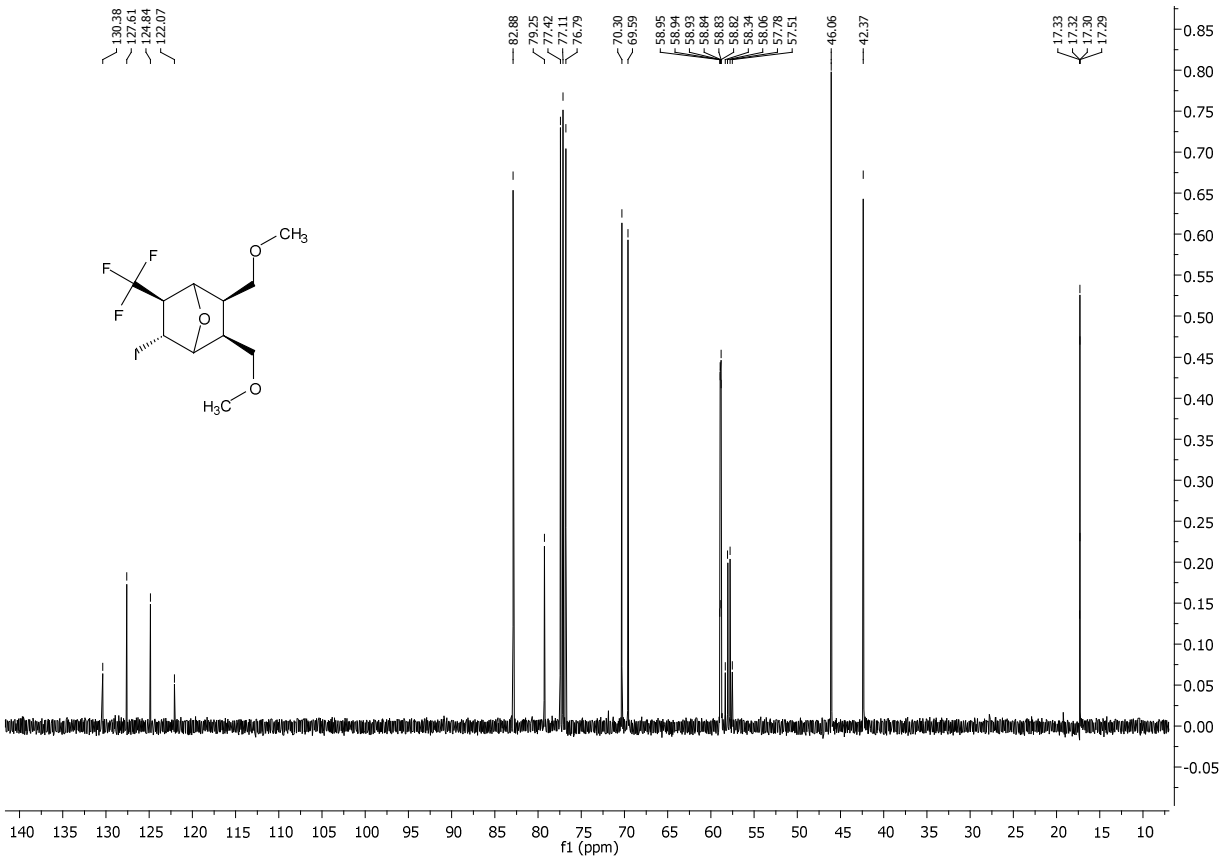
3b ^{13}C NMR (101 MHz, $CDCl_3$)

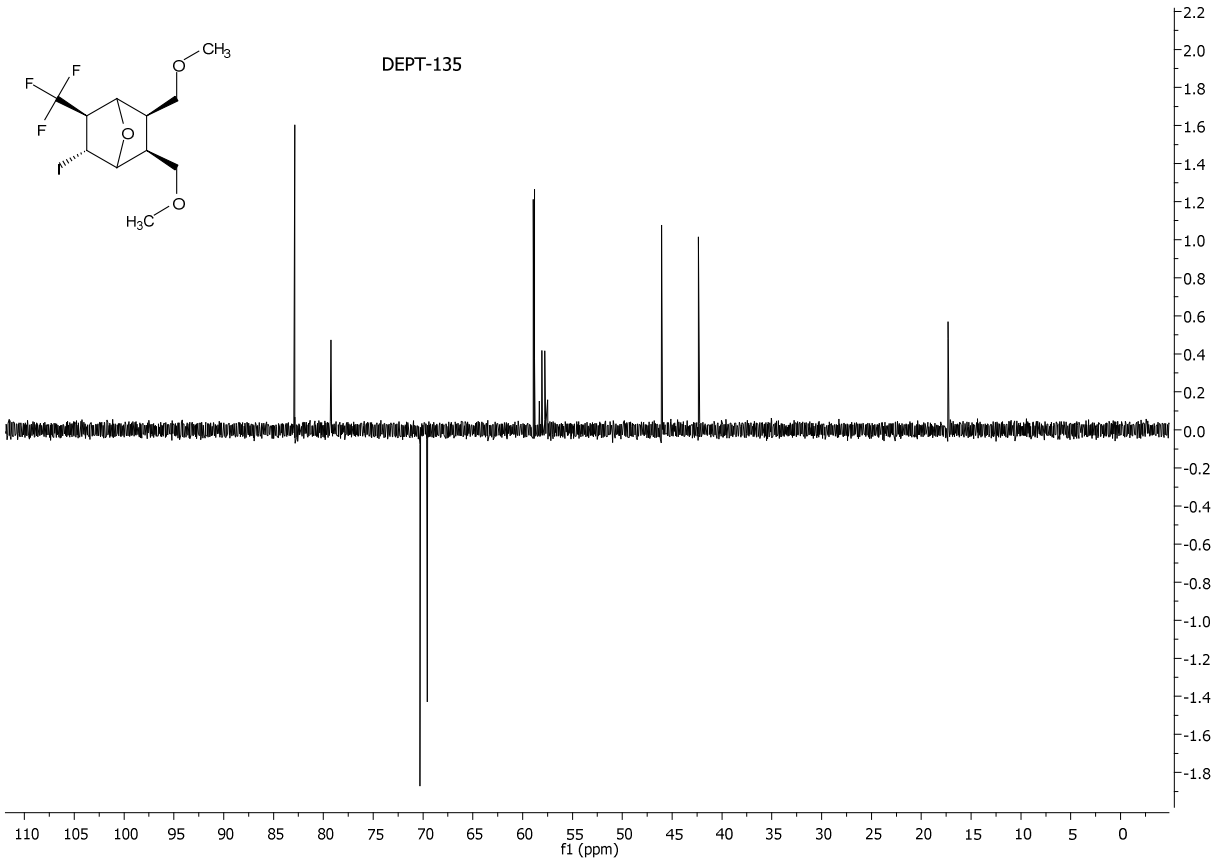


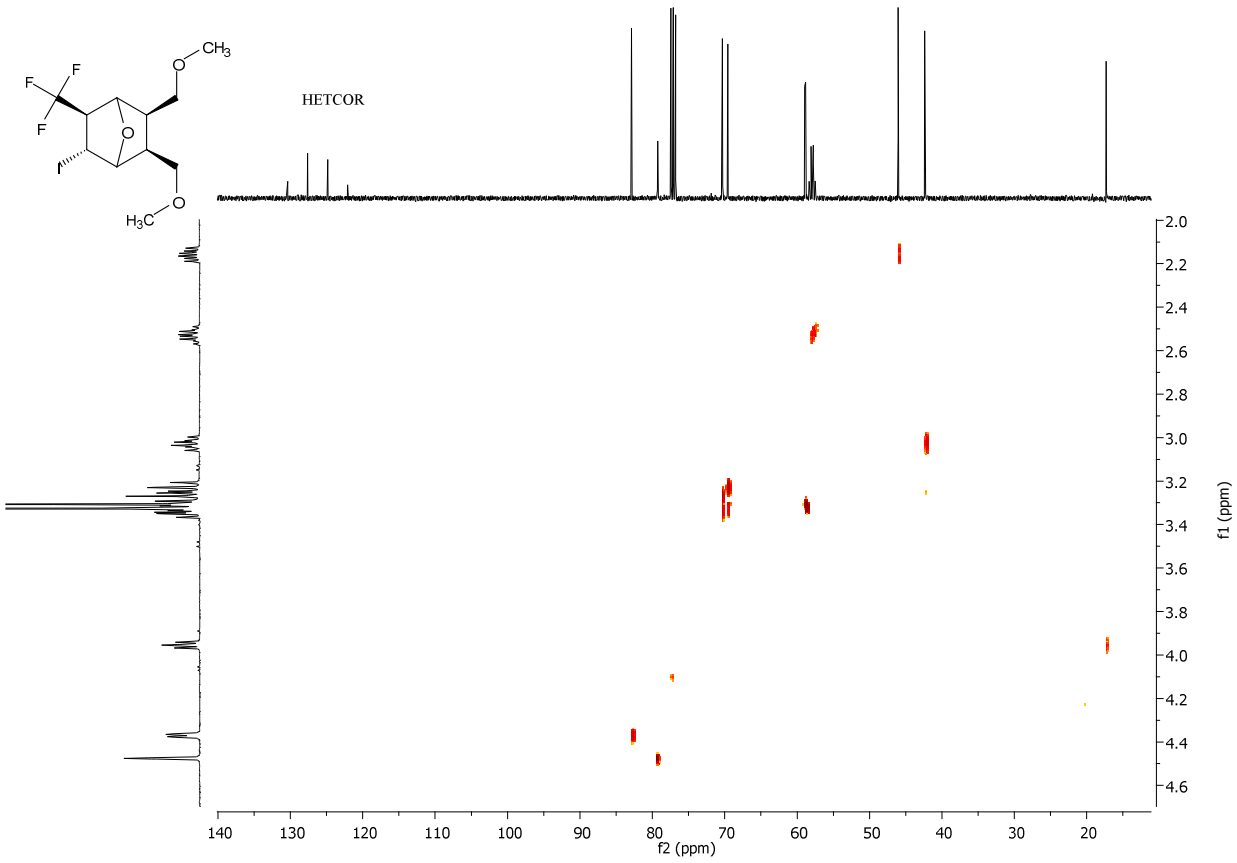
3c ^{1}H NMR (400 MHz, $CDCl_3$)

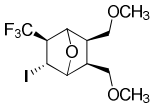


3c ^{13}C NMR (101 MHz, $CDCl_3$)

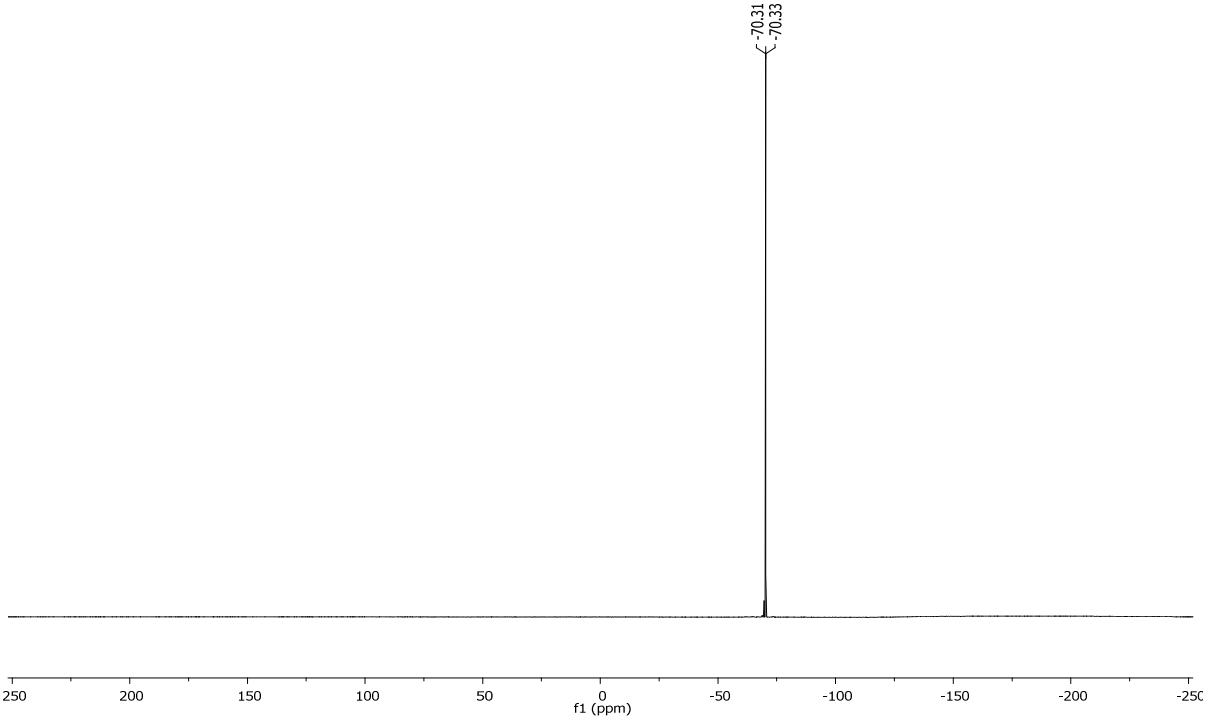




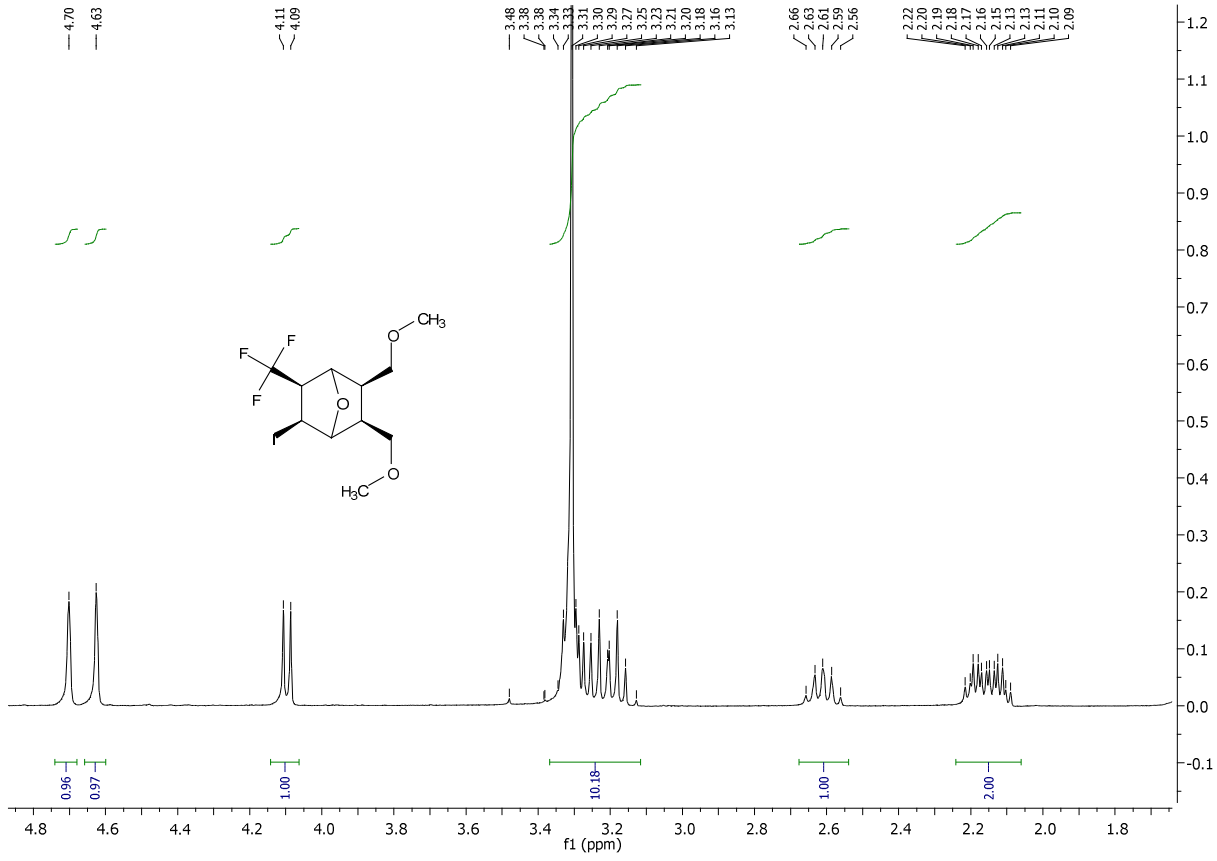




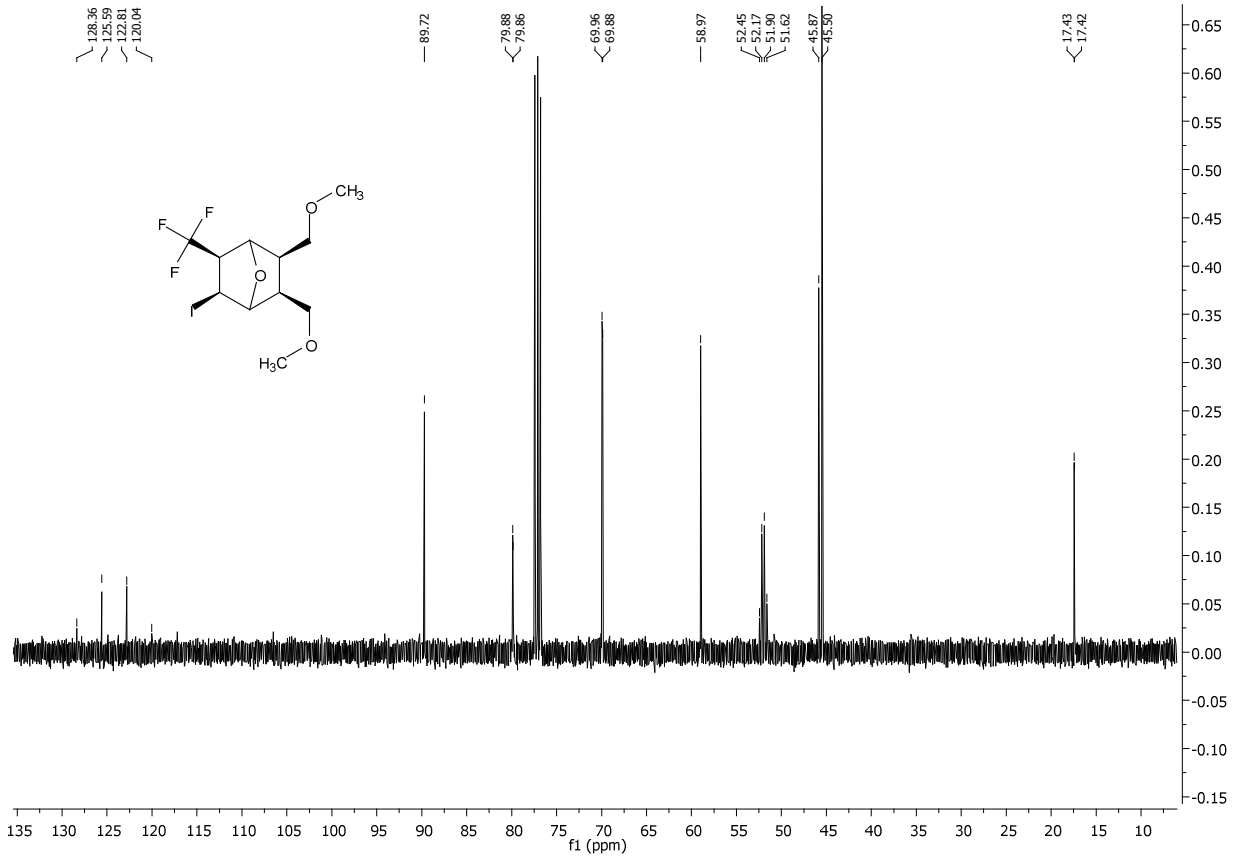
3c ^{19}F NMR (376 MHz, $CDCl_3$)

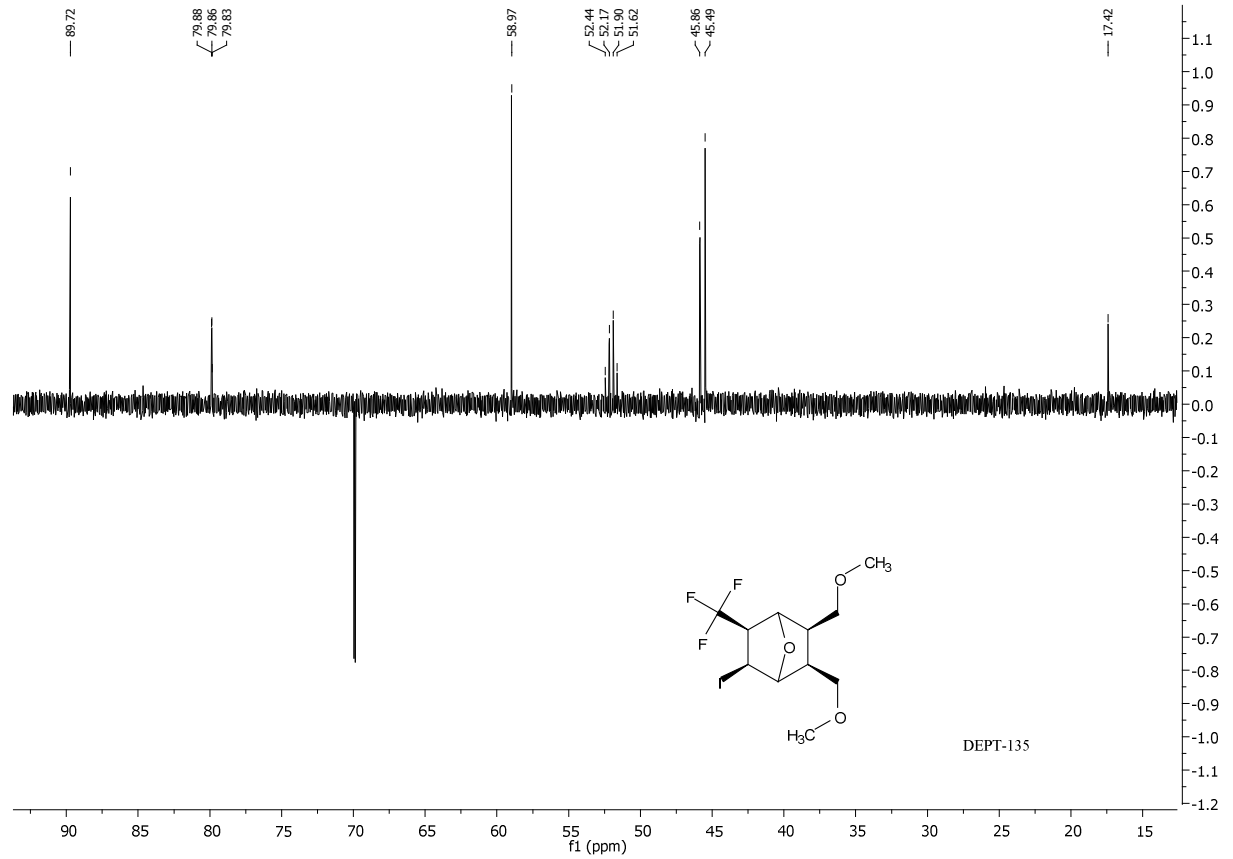


4c ^{1}H NMR (400 MHz, $CDCl_3$)

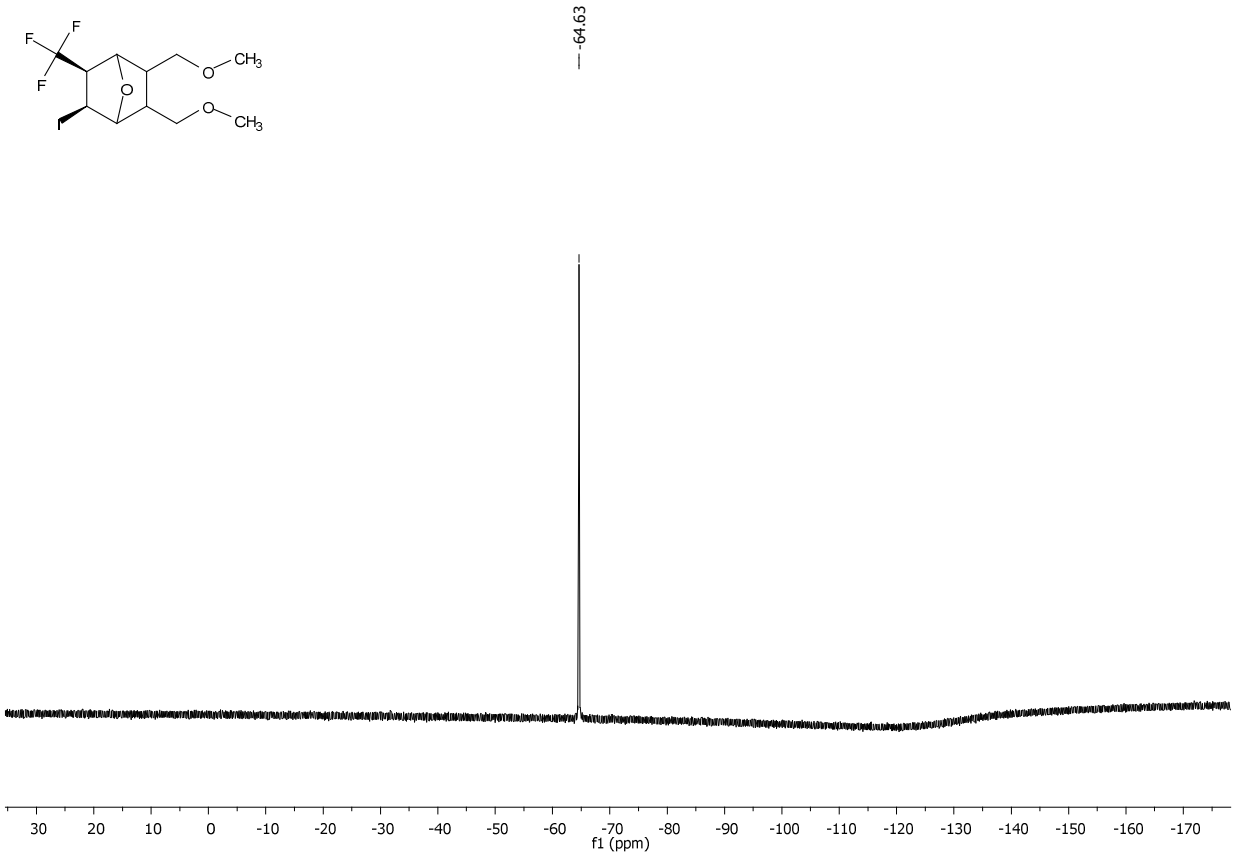


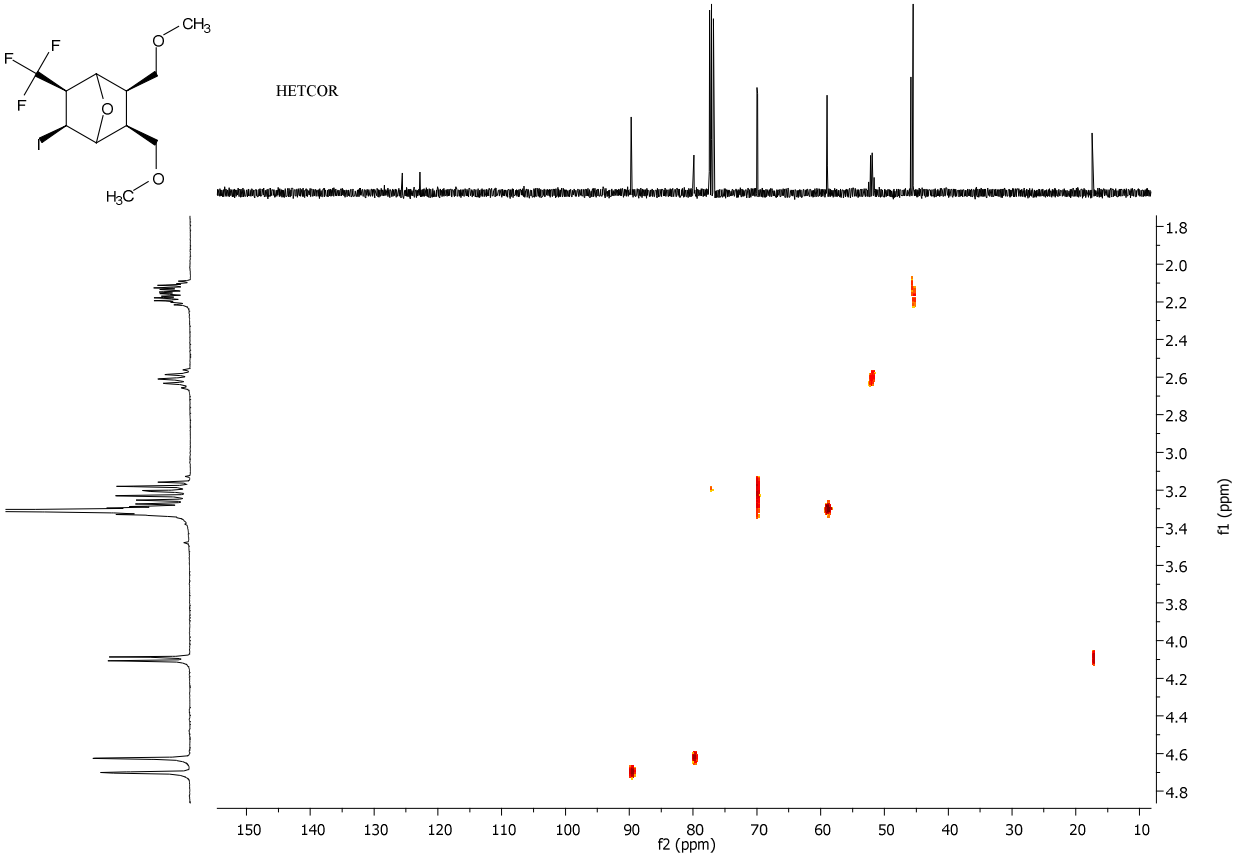
4c ^{13}C NMR (101 MHz, $CDCl_3$)



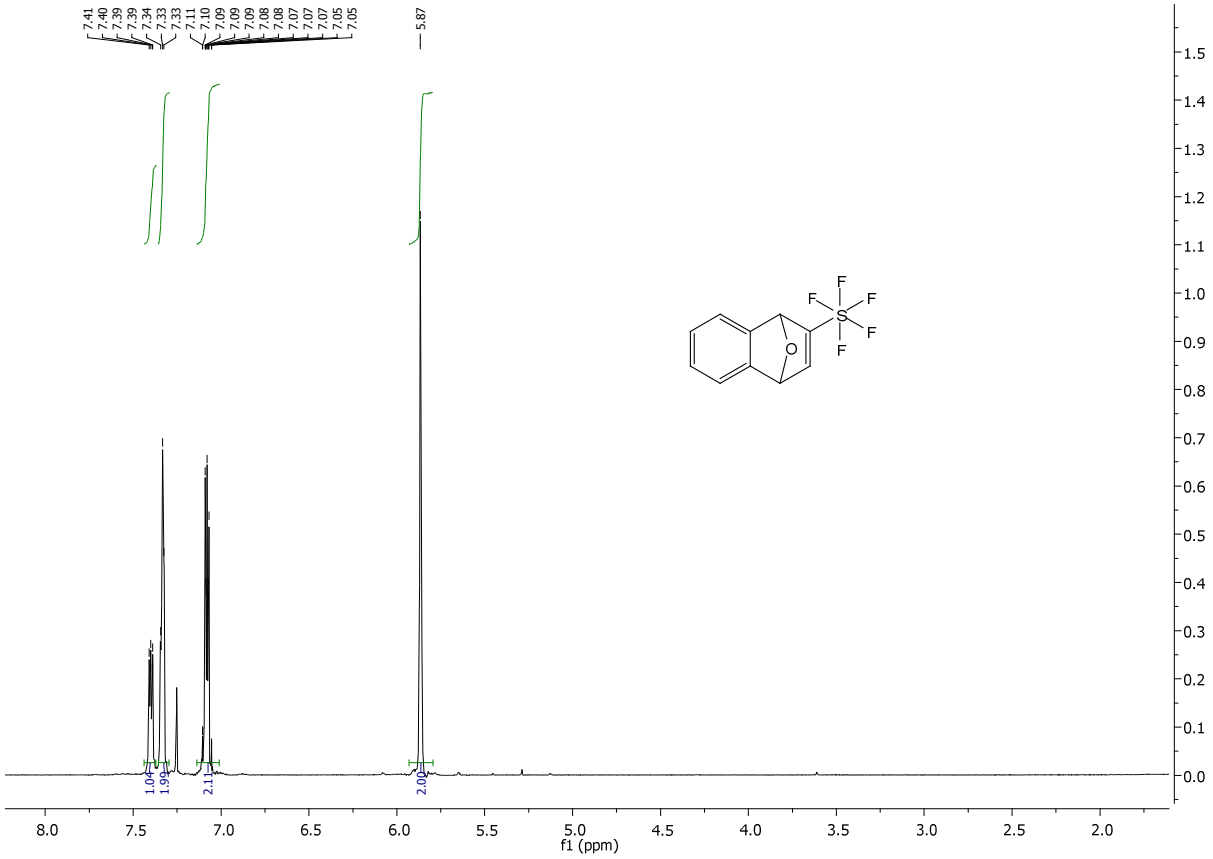


4c ^{19}F NMR (376 MHz, $CDCl_3$)

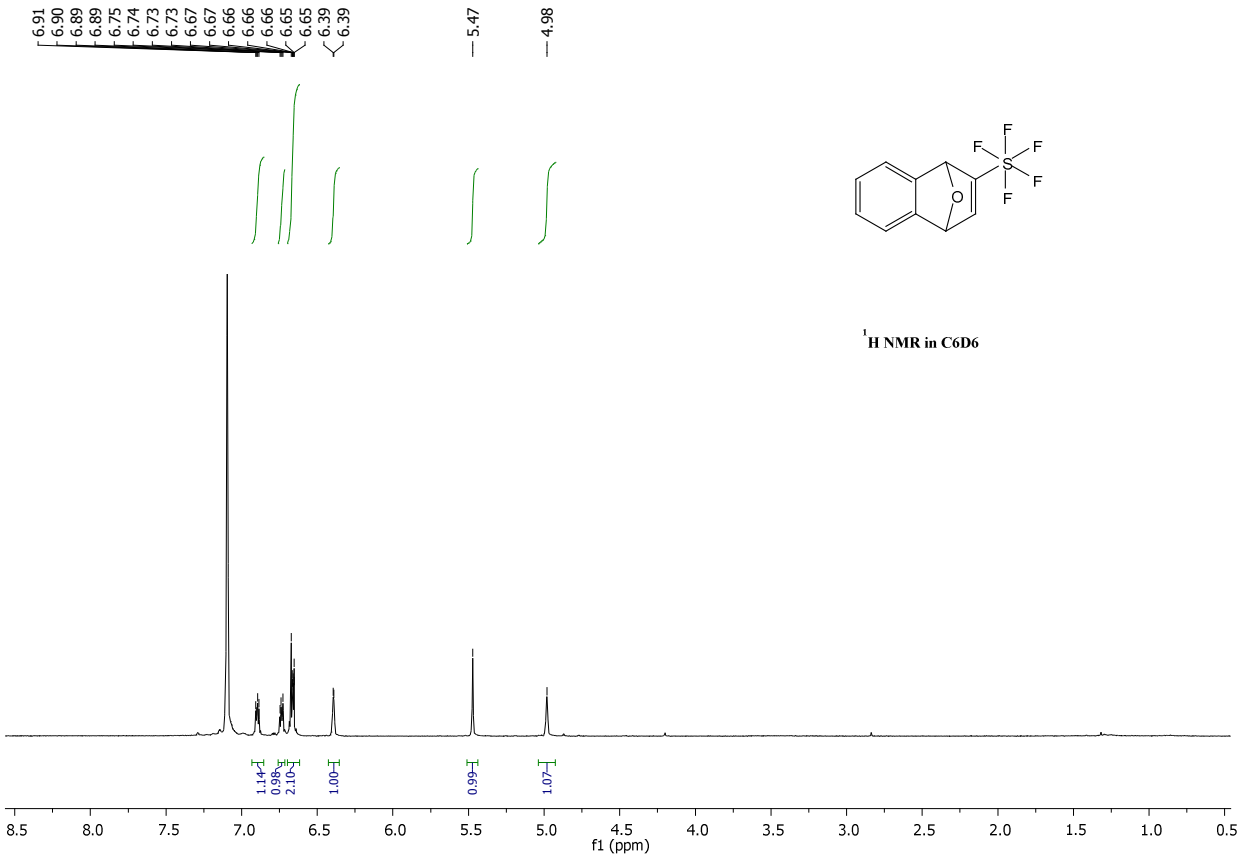




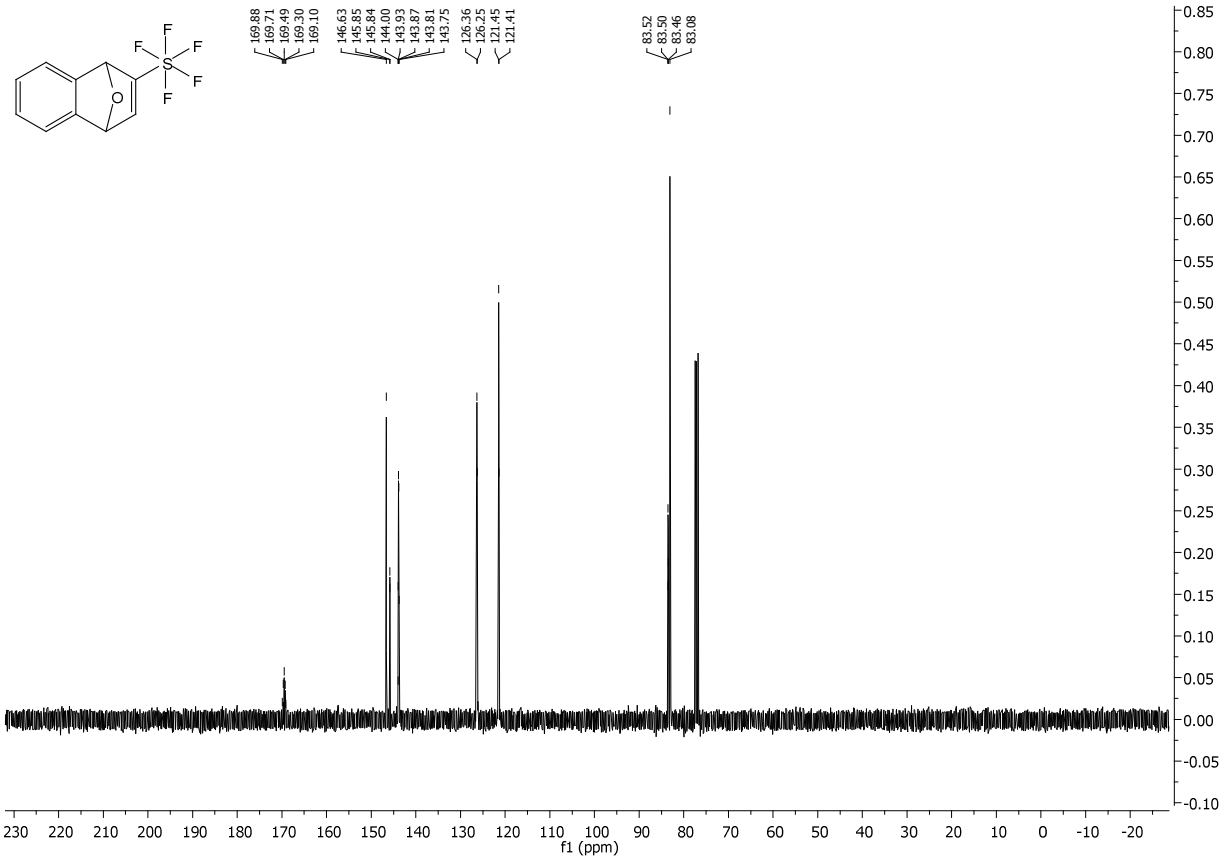
5a ^{1}H NMR (400 MHz, $CDCl_3$)



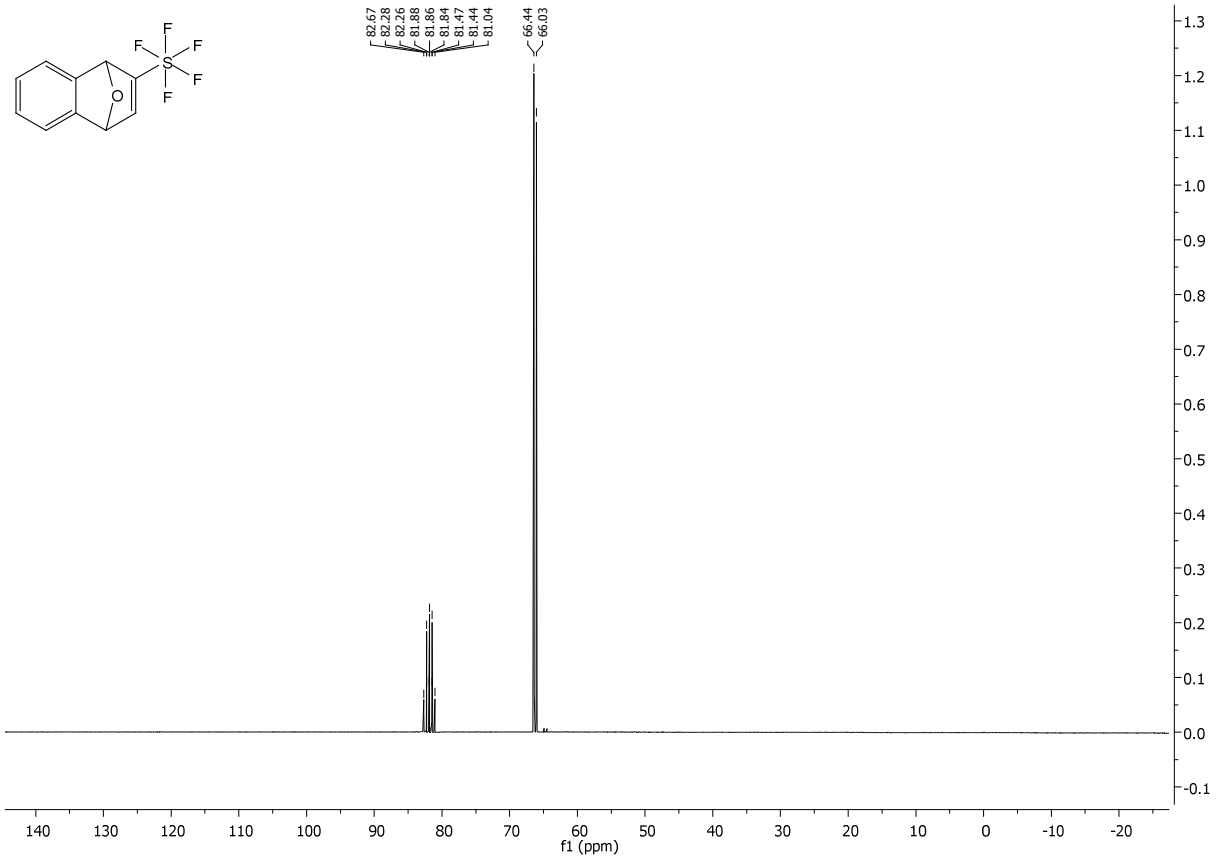
5a ^{1}H NMR (400 MHz, C_6D_6)



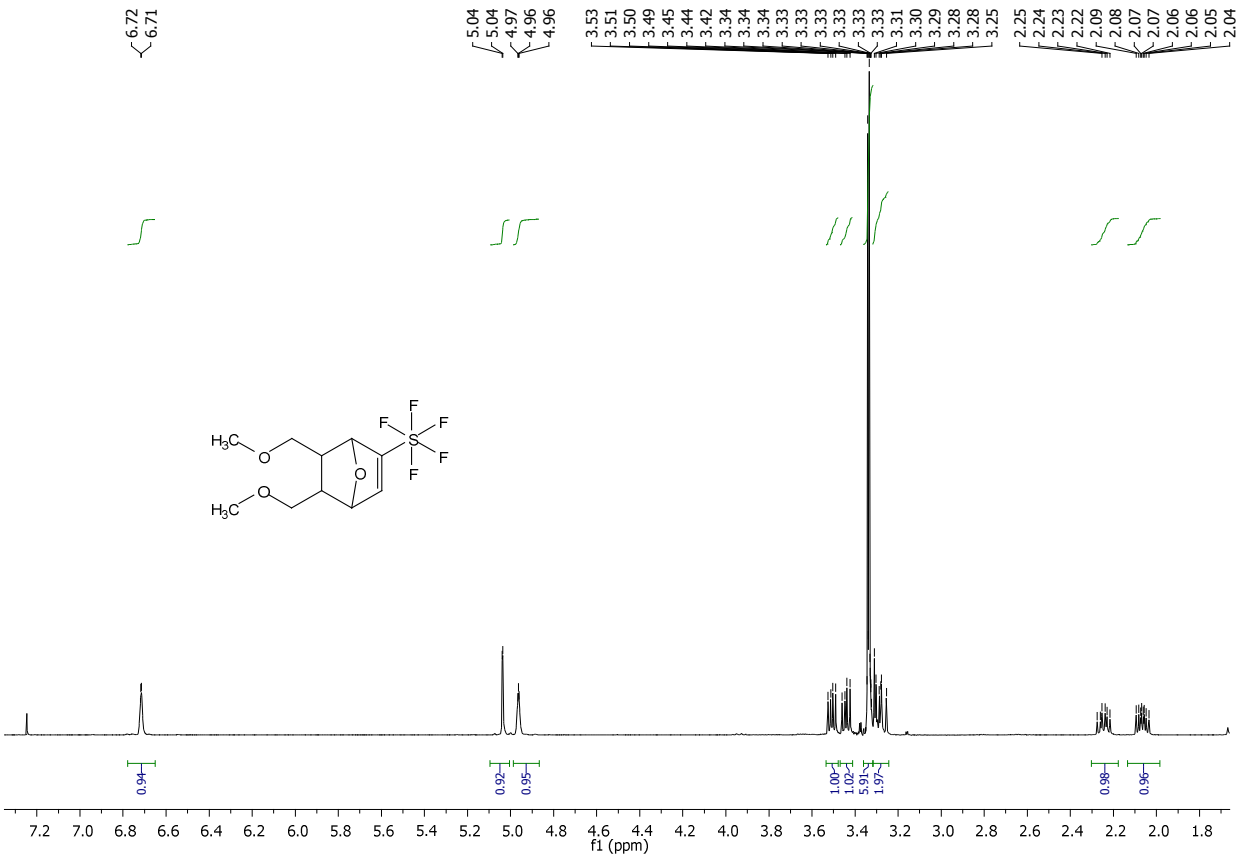
5a ^{13}C NMR (101 MHz, $CDCl_3$)



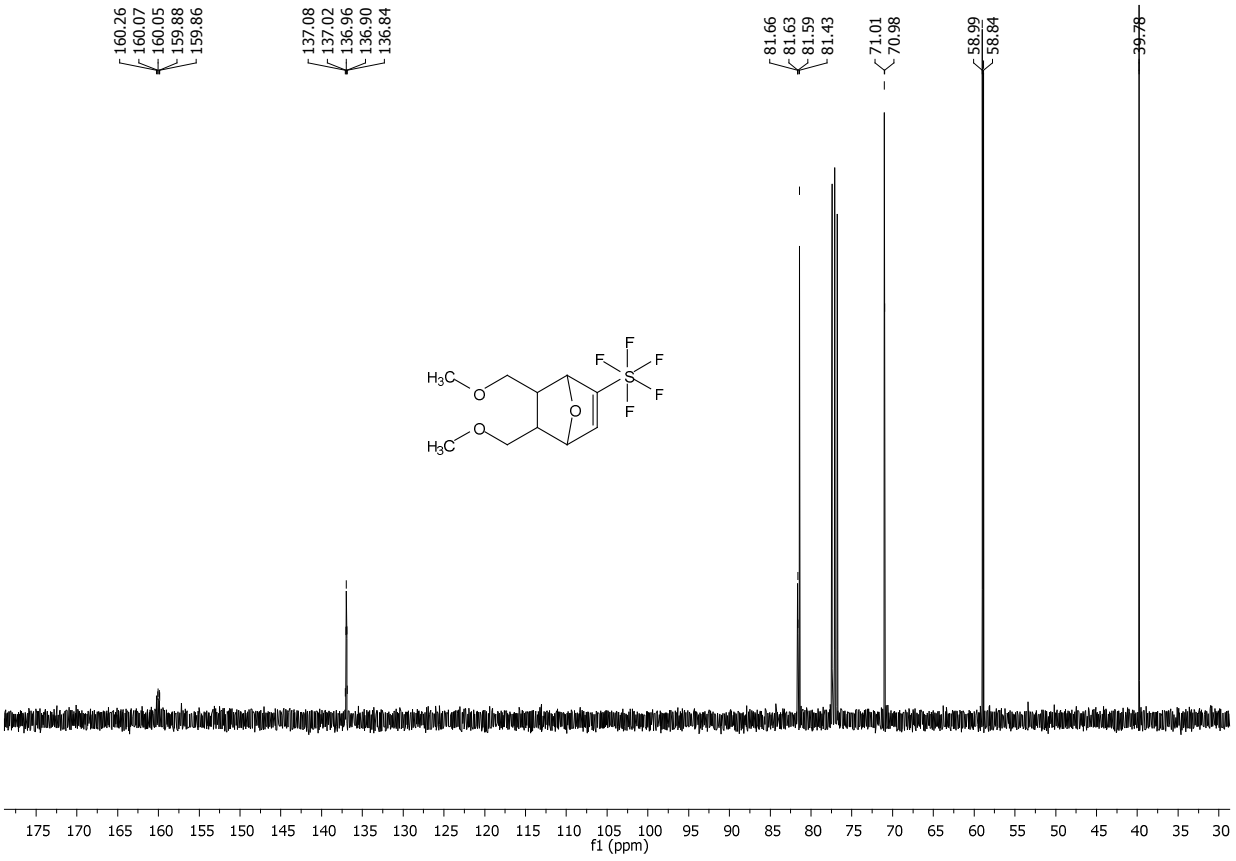
5a ^{19}F NMR (376 MHz, $CDCl_3$)

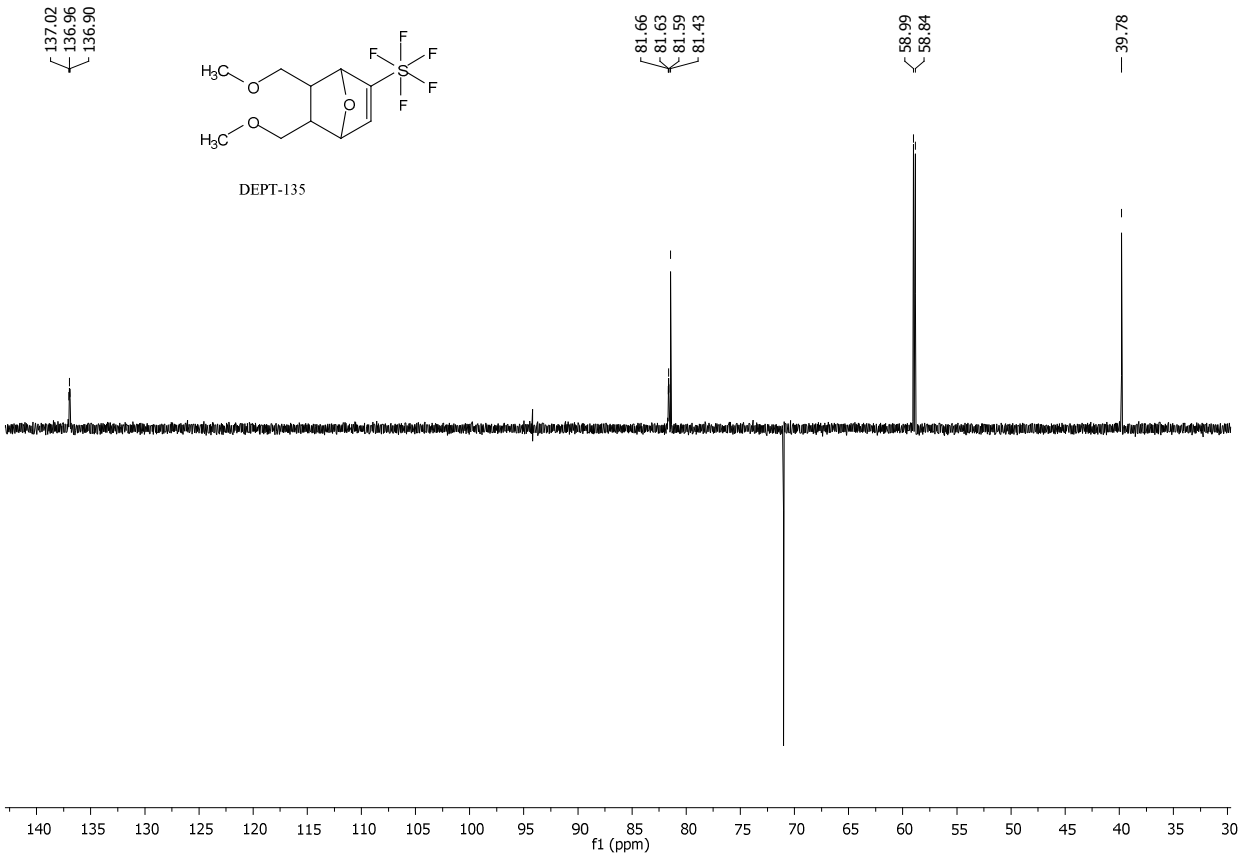


5c ^{1}H NMR (400 MHz, $CDCl_3$)

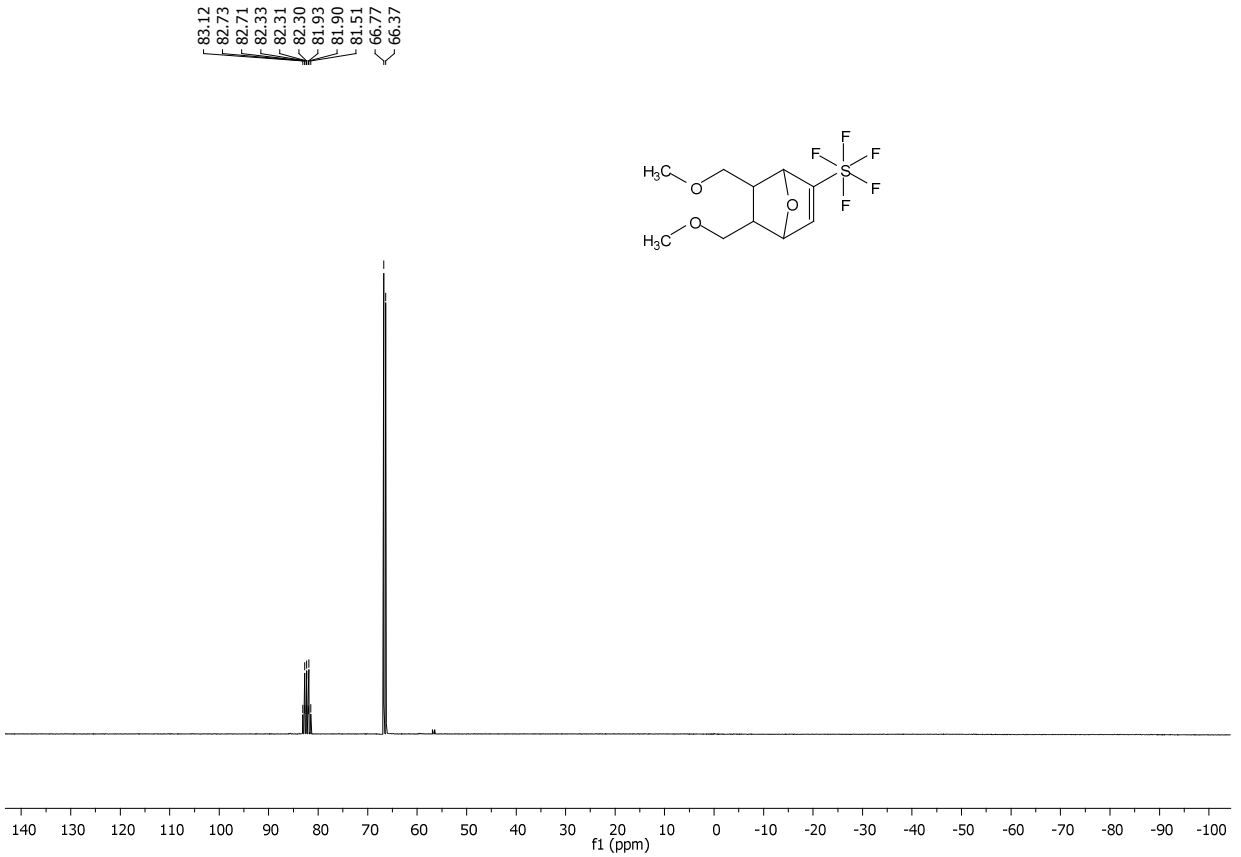


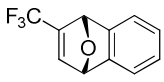
5c ^{13}C NMR (101 MHz, $CDCl_3$)



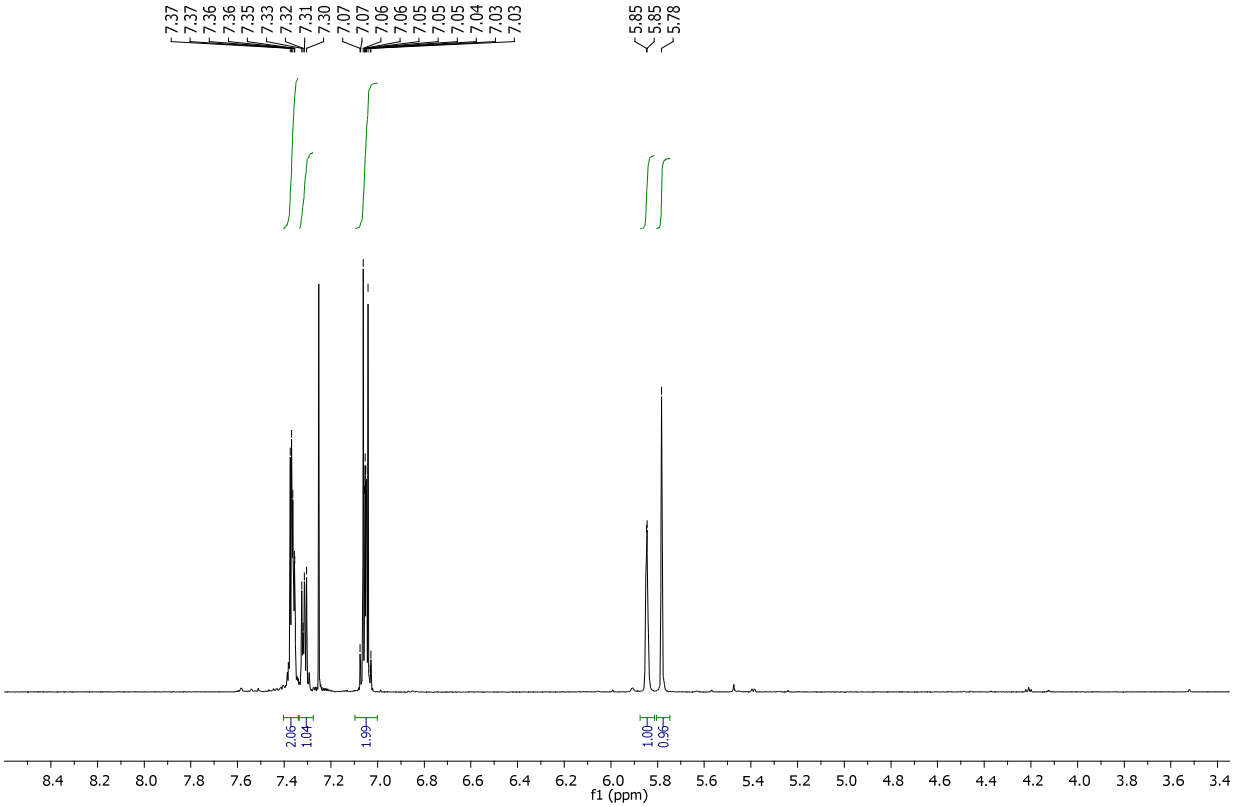


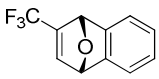
5c ^{19}F NMR (376 MHz, $CDCl_3$)



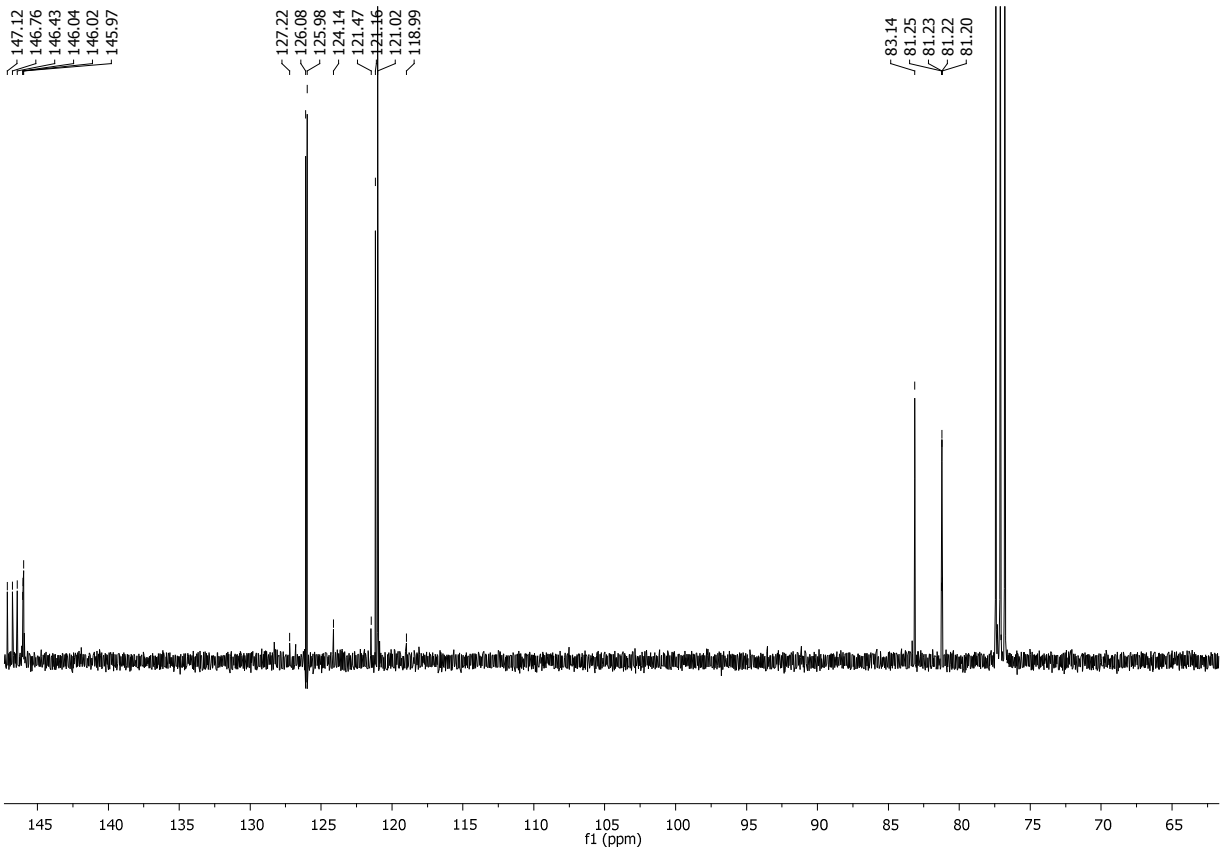


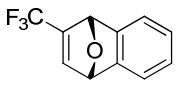
6a ^{1}H NMR (400 MHz, $CDCl_3$)



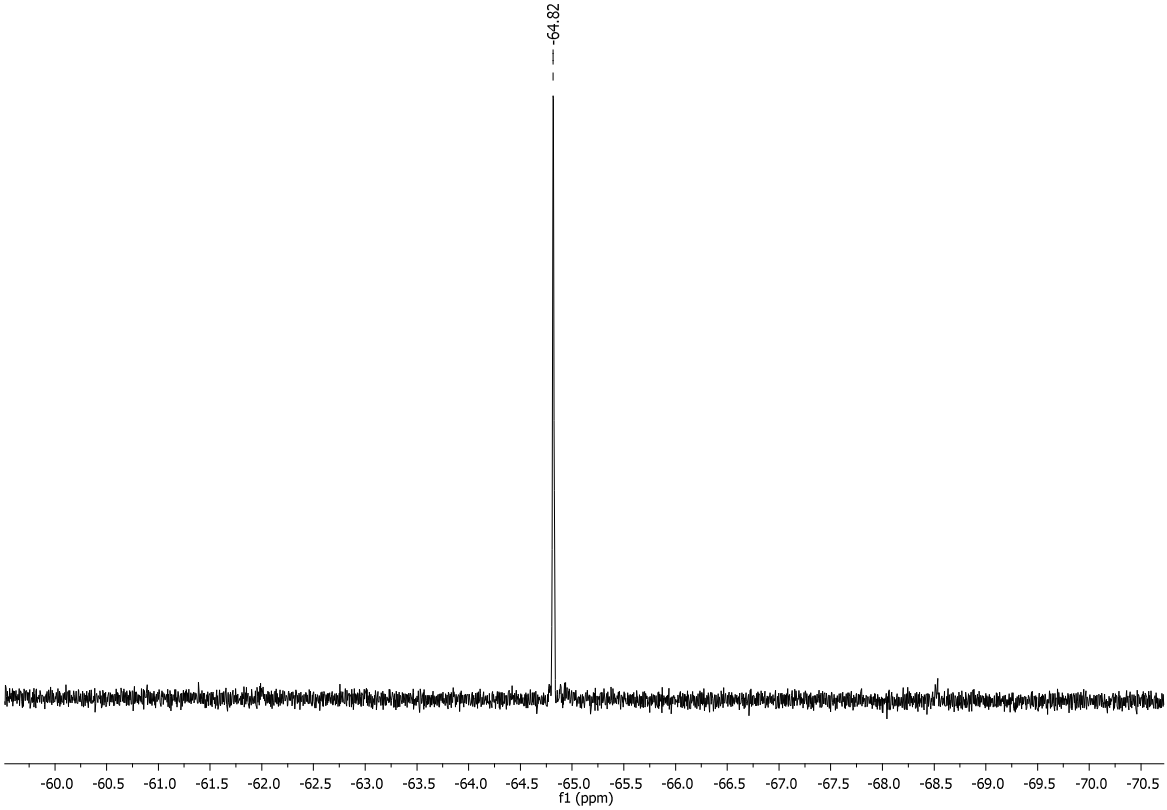


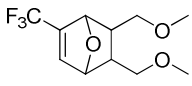
6a ^{13}C NMR (101 MHz, $CDCl_3$)



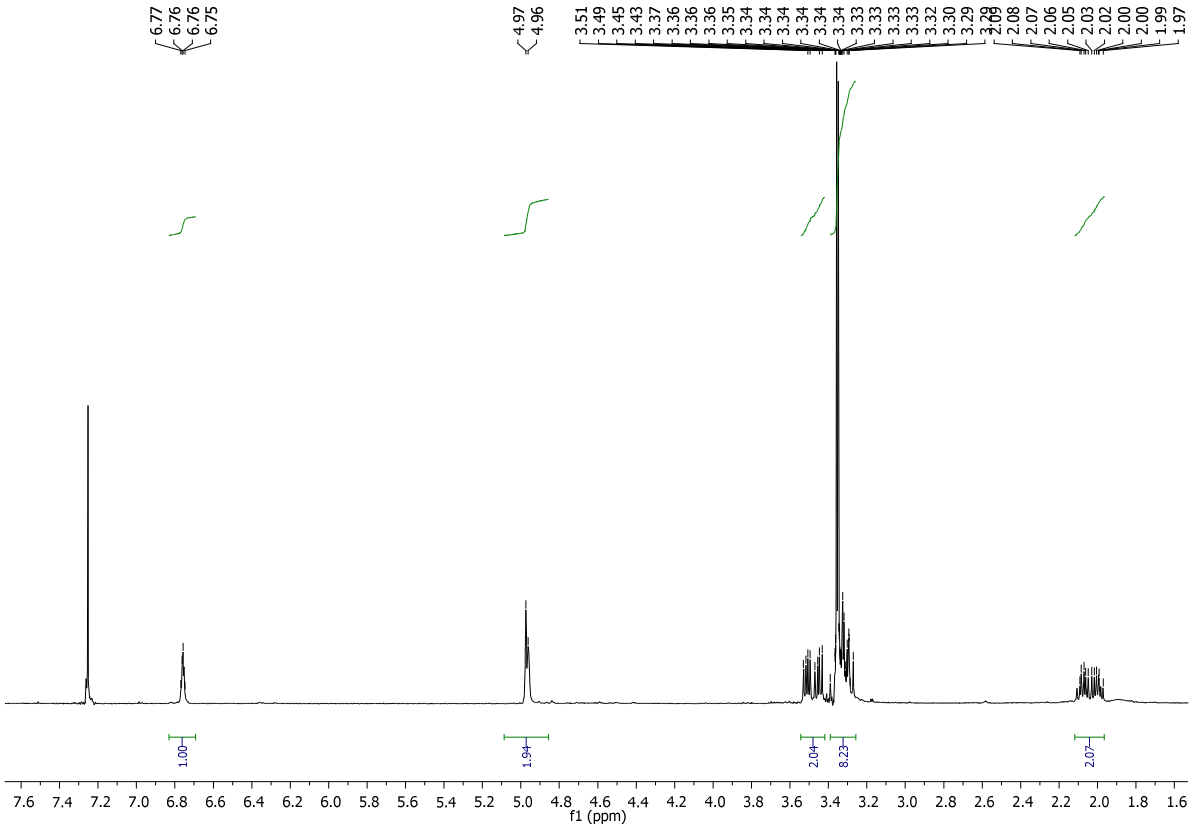


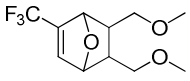
6a ^{19}F NMR (376 MHz, $CDCl_3$)



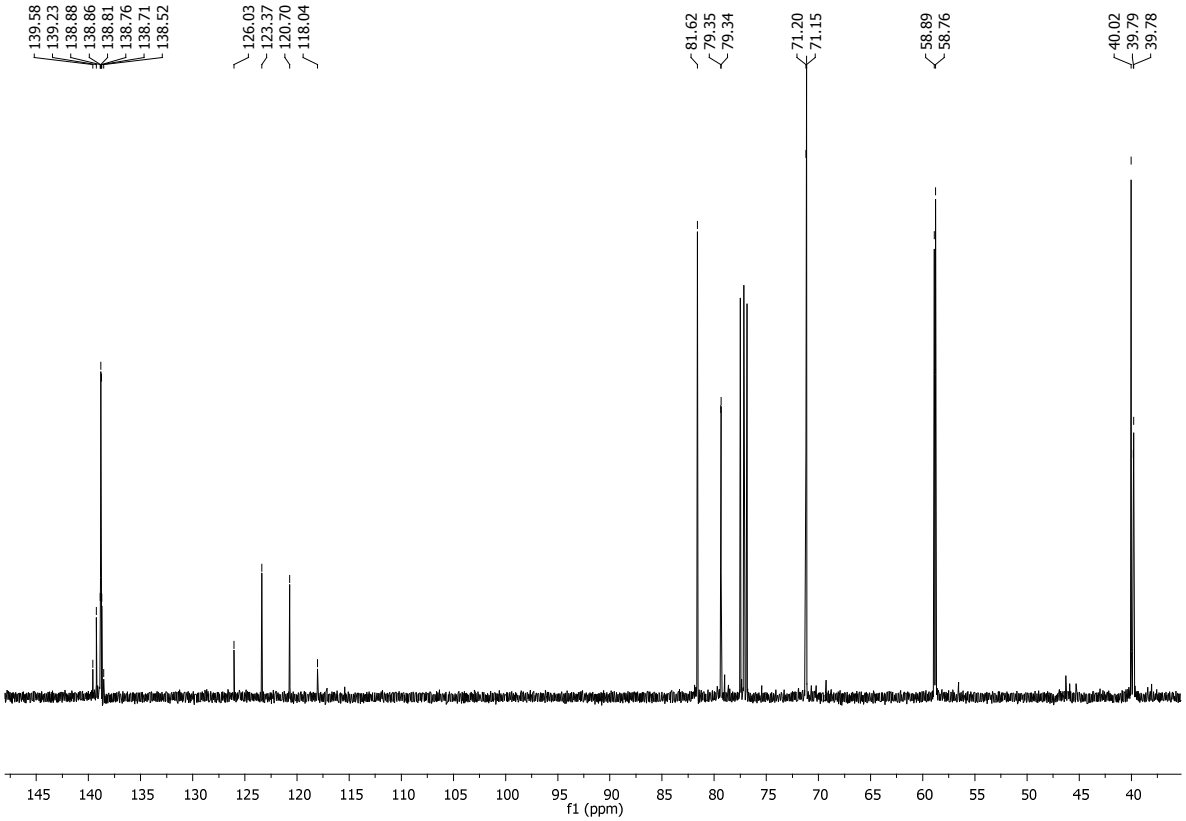


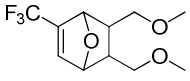
6c ^{1}H NMR (400 MHz, $CDCl_3$)



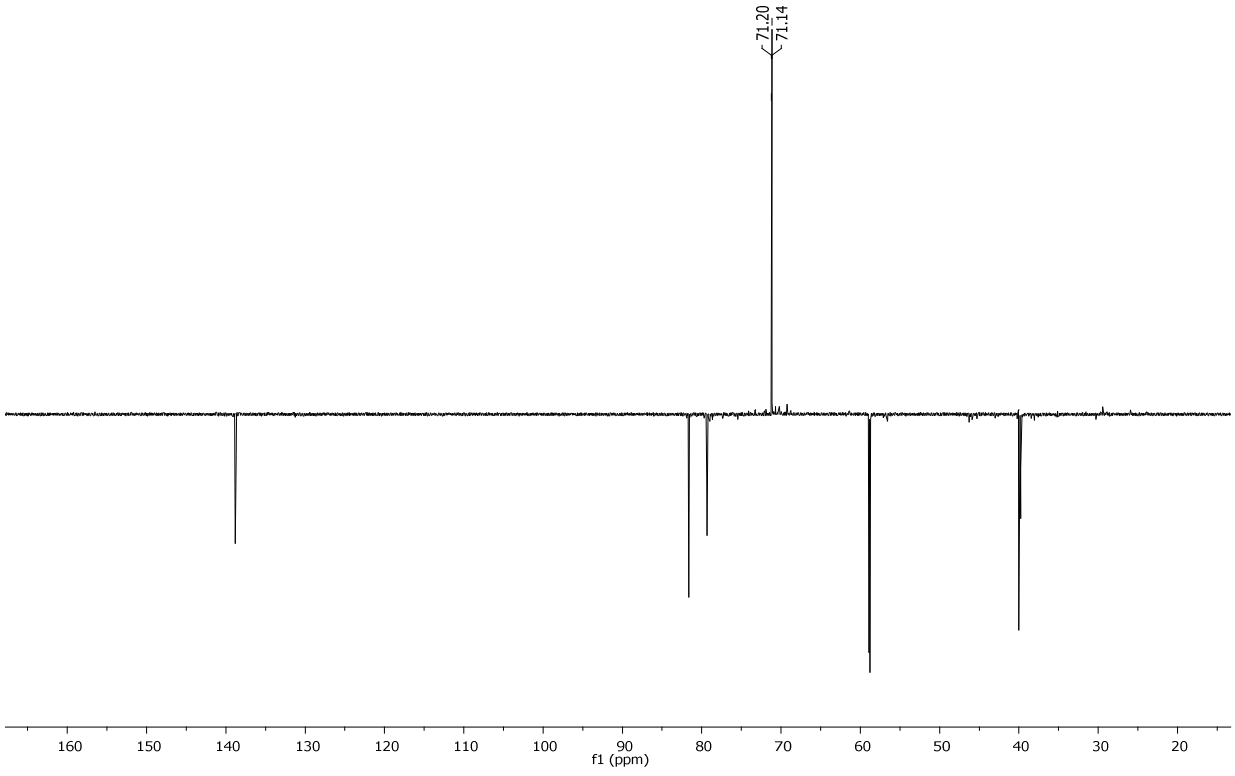


6c ^{13}C NMR (101 MHz, $CDCl_3$)

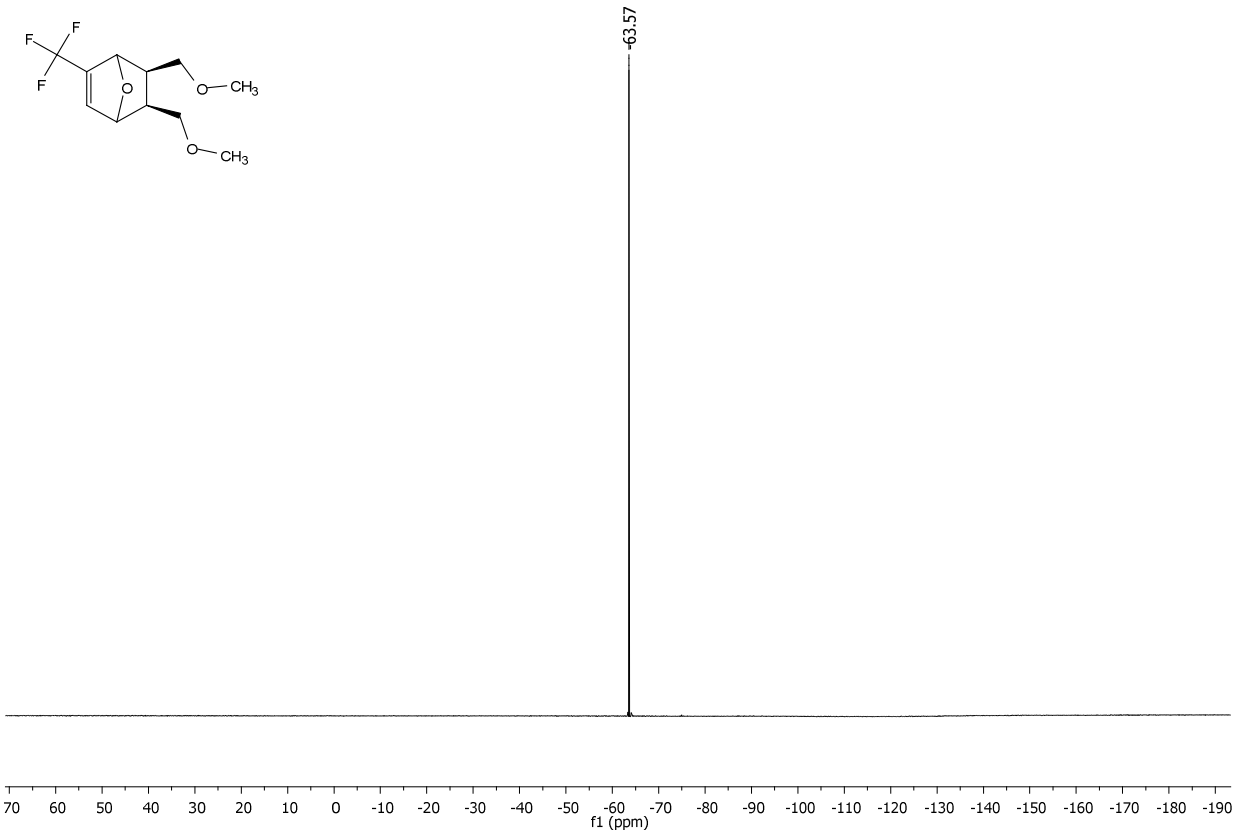




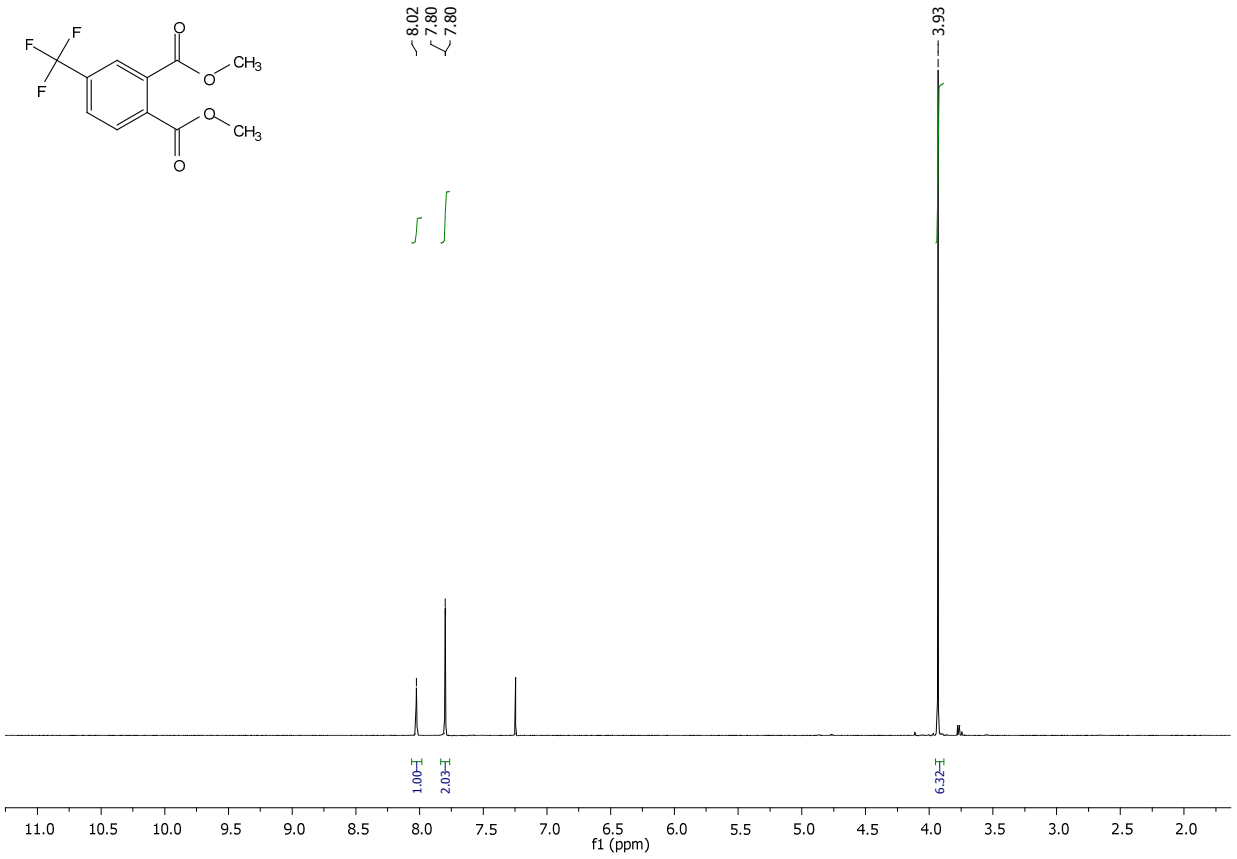
6c DEPT-135



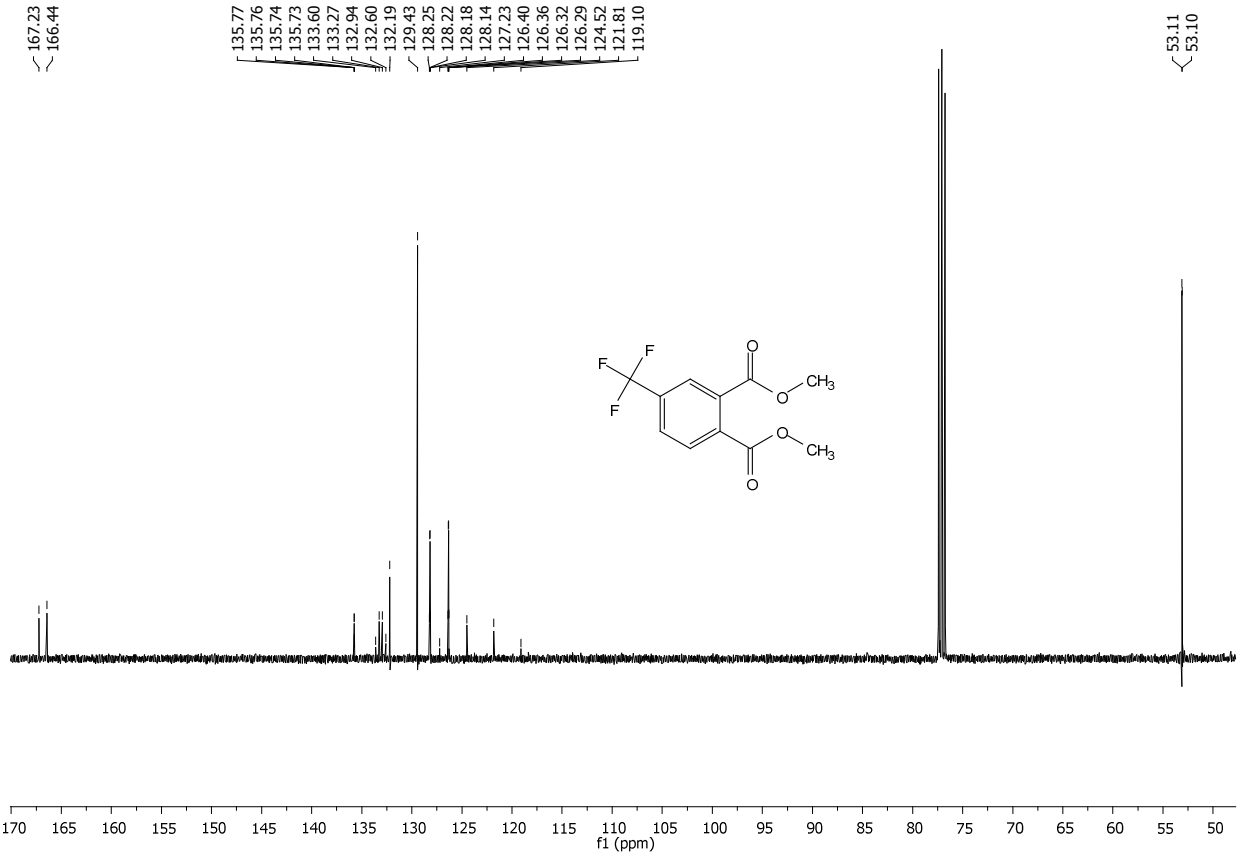
6c ^{19}F NMR (376 MHz, $CDCl_3$)



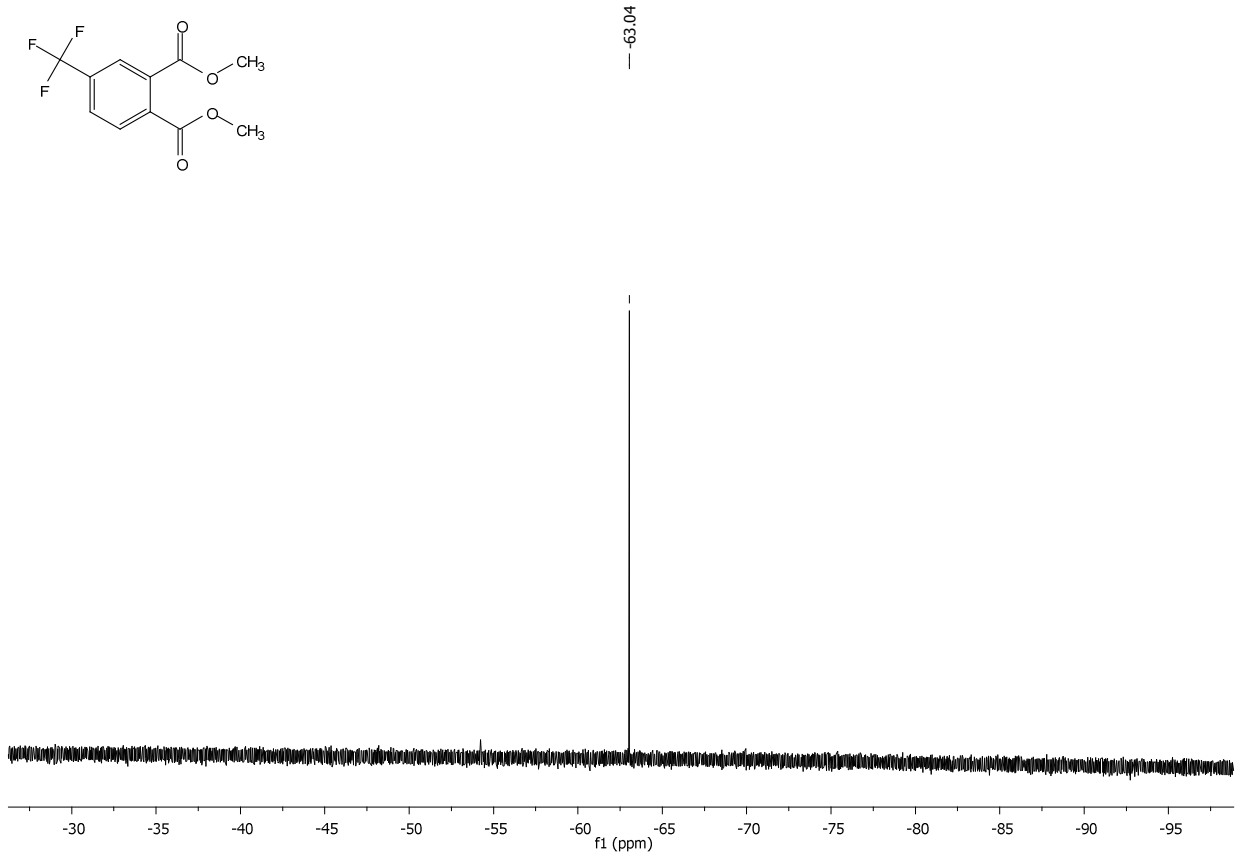
7b ^{1}H NMR (400 MHz, $CDCl_3$)



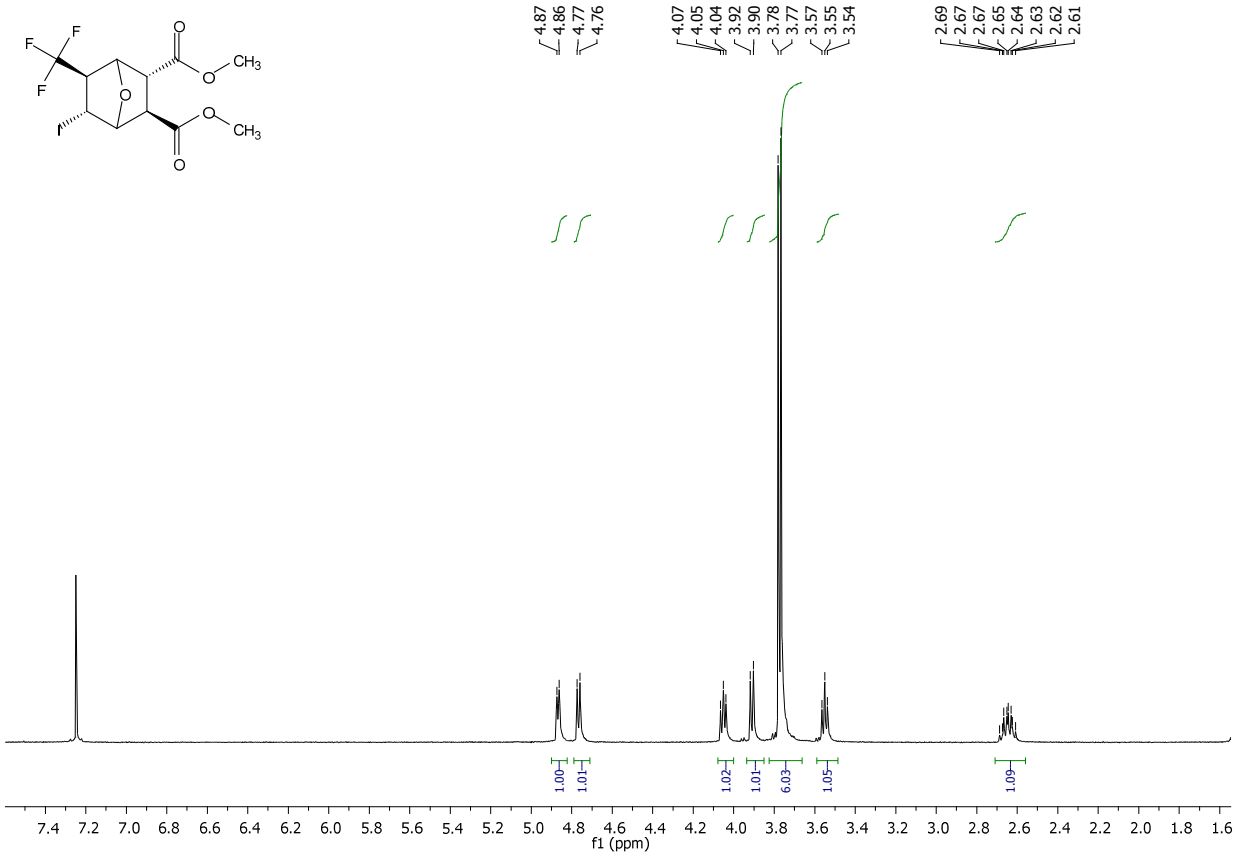
7b ^{13}C NMR (101 MHz, $CDCl_3$)



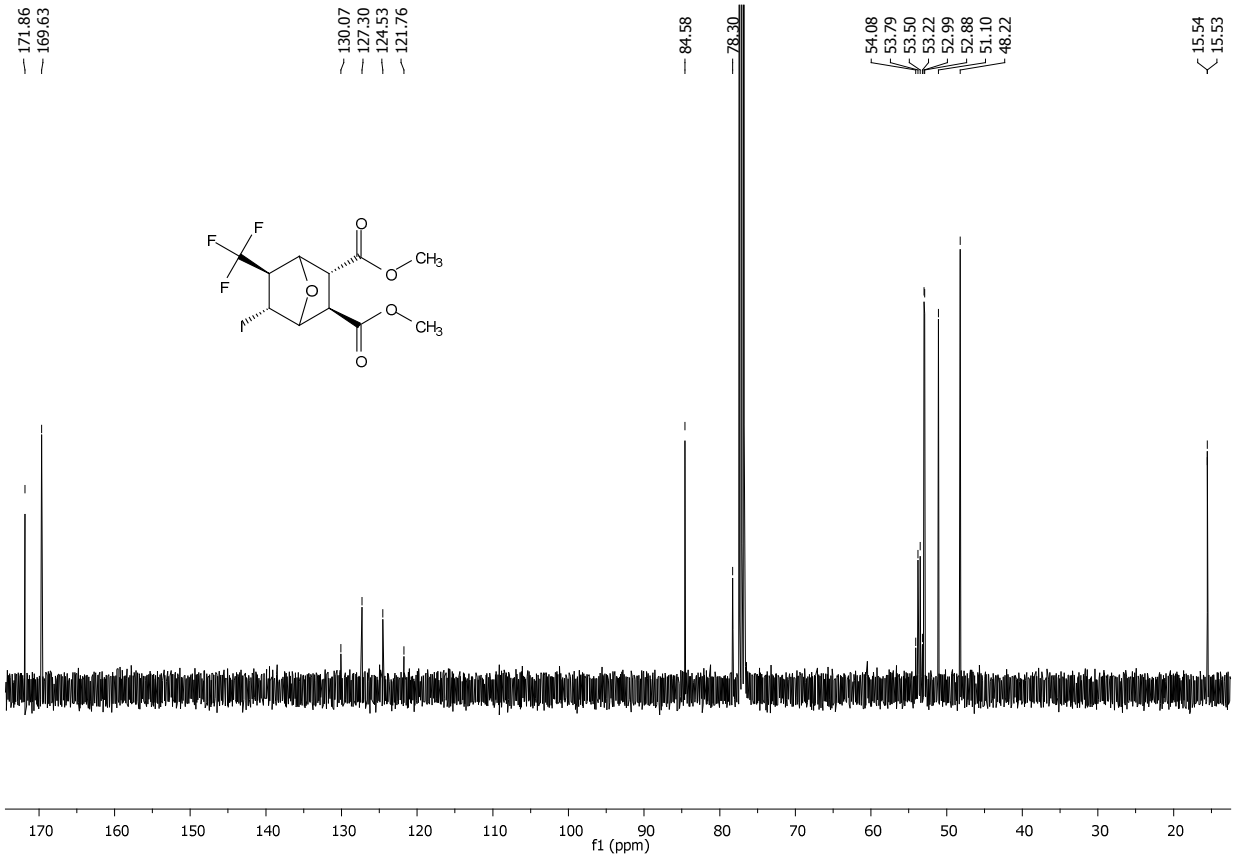
7b ^{19}F NMR (376 MHz, $CDCl_3$)

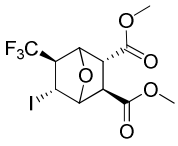


8 ^{1}H NMR (400 MHz, $CDCl_3$)

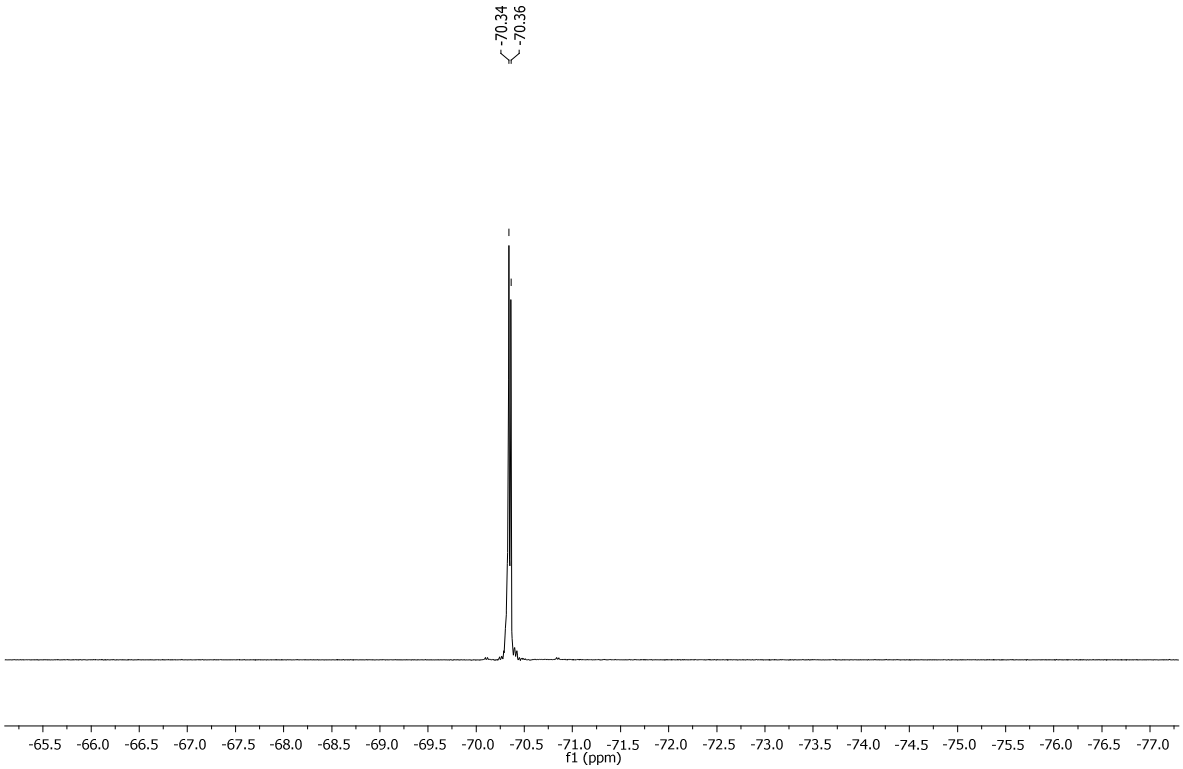


8 ^{13}C NMR (101 MHz, $CDCl_3$)

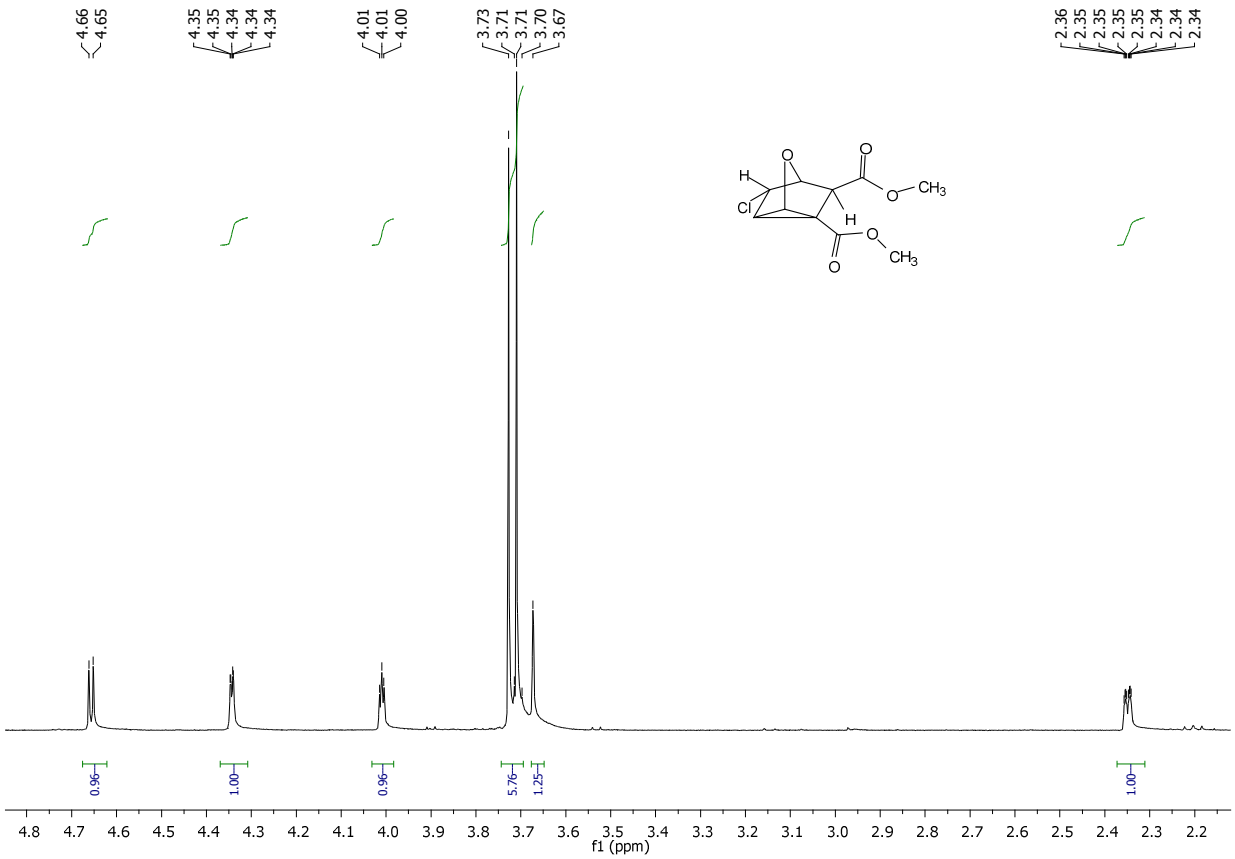




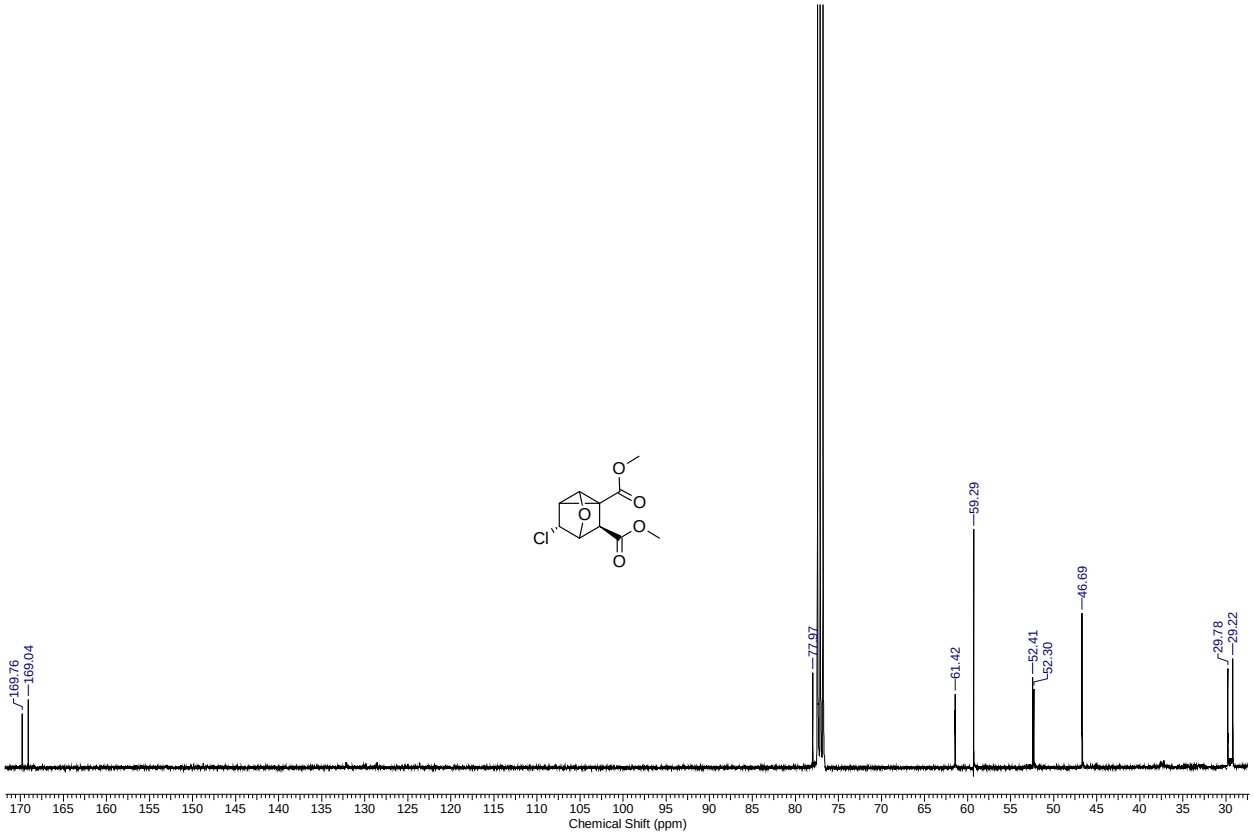
8 ^{19}F NMR (376 MHz, $CDCl_3$)

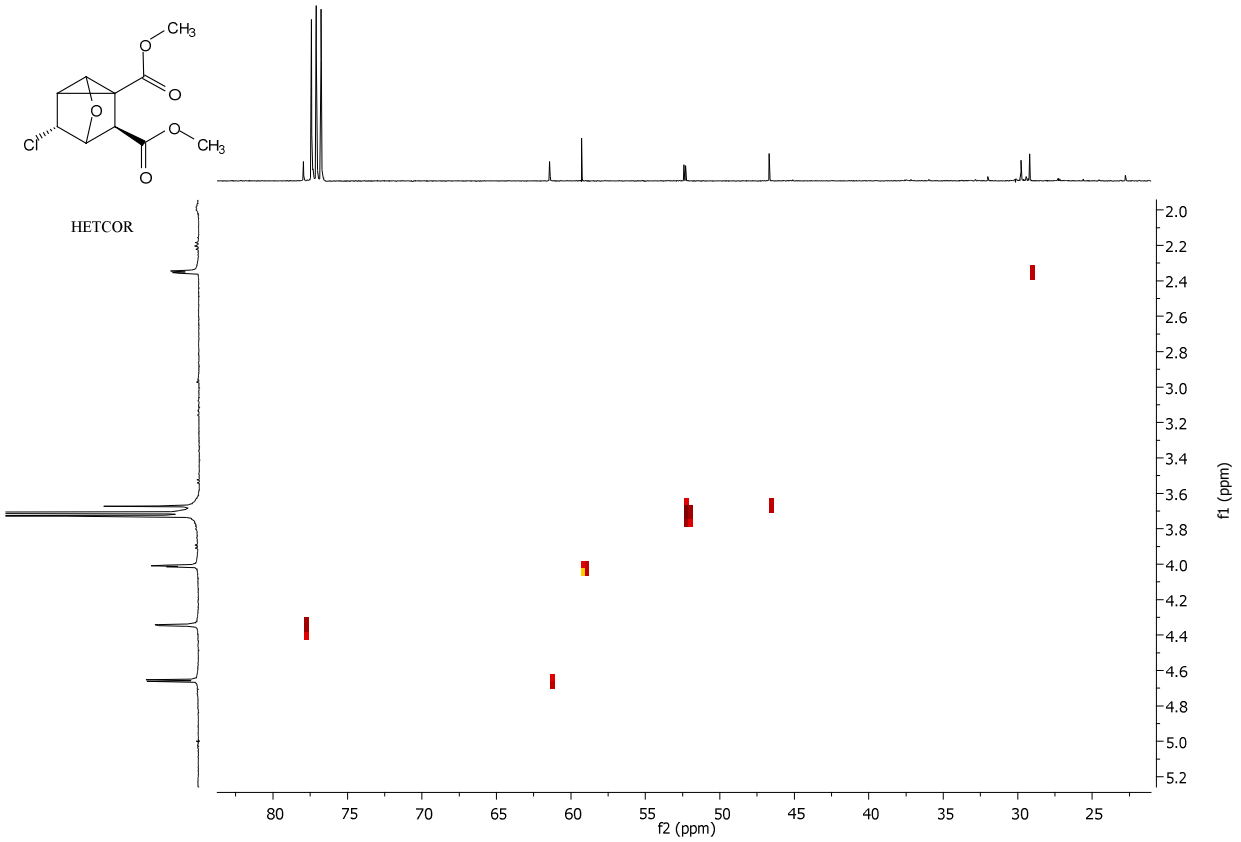


9 ^{1}H NMR (400 MHz, $CDCl_3$)

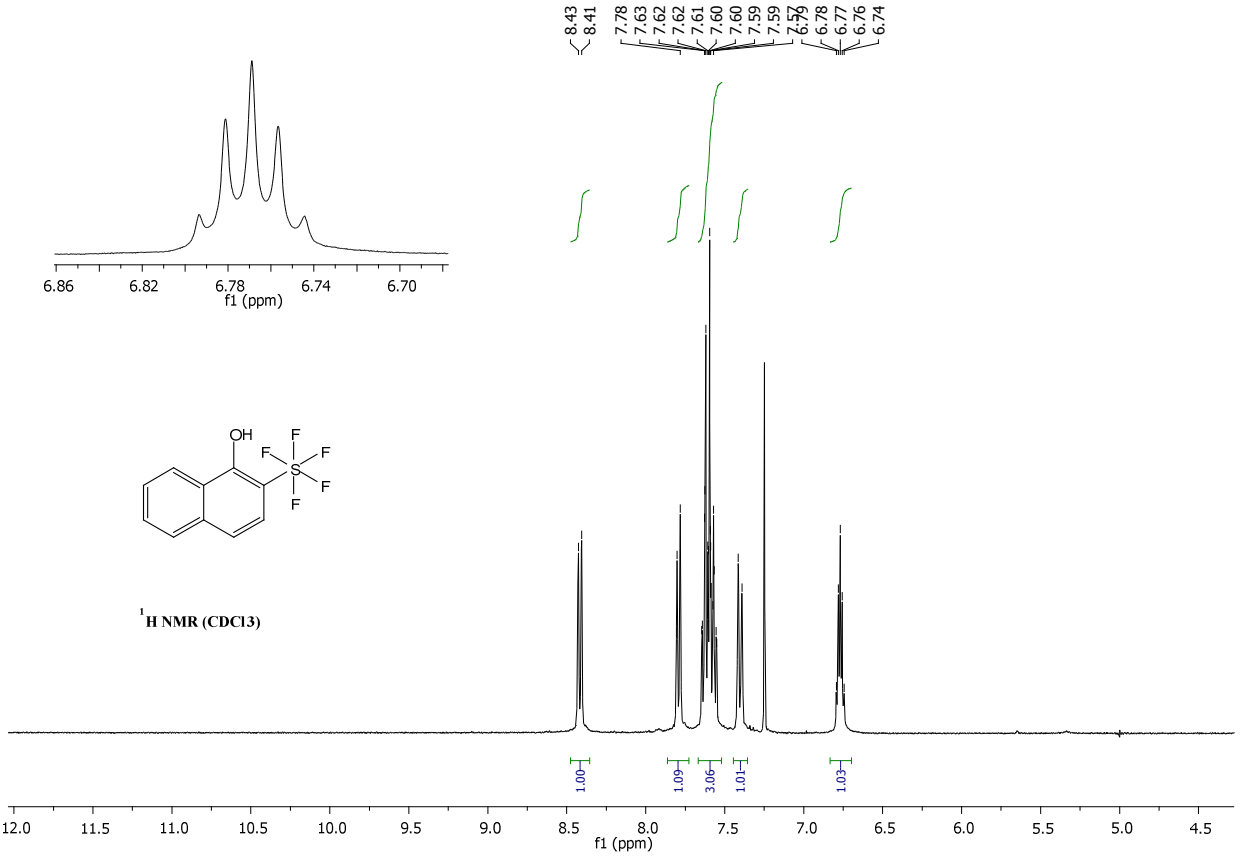


9 ^{13}C NMR (101 MHz, $CDCl_3$)

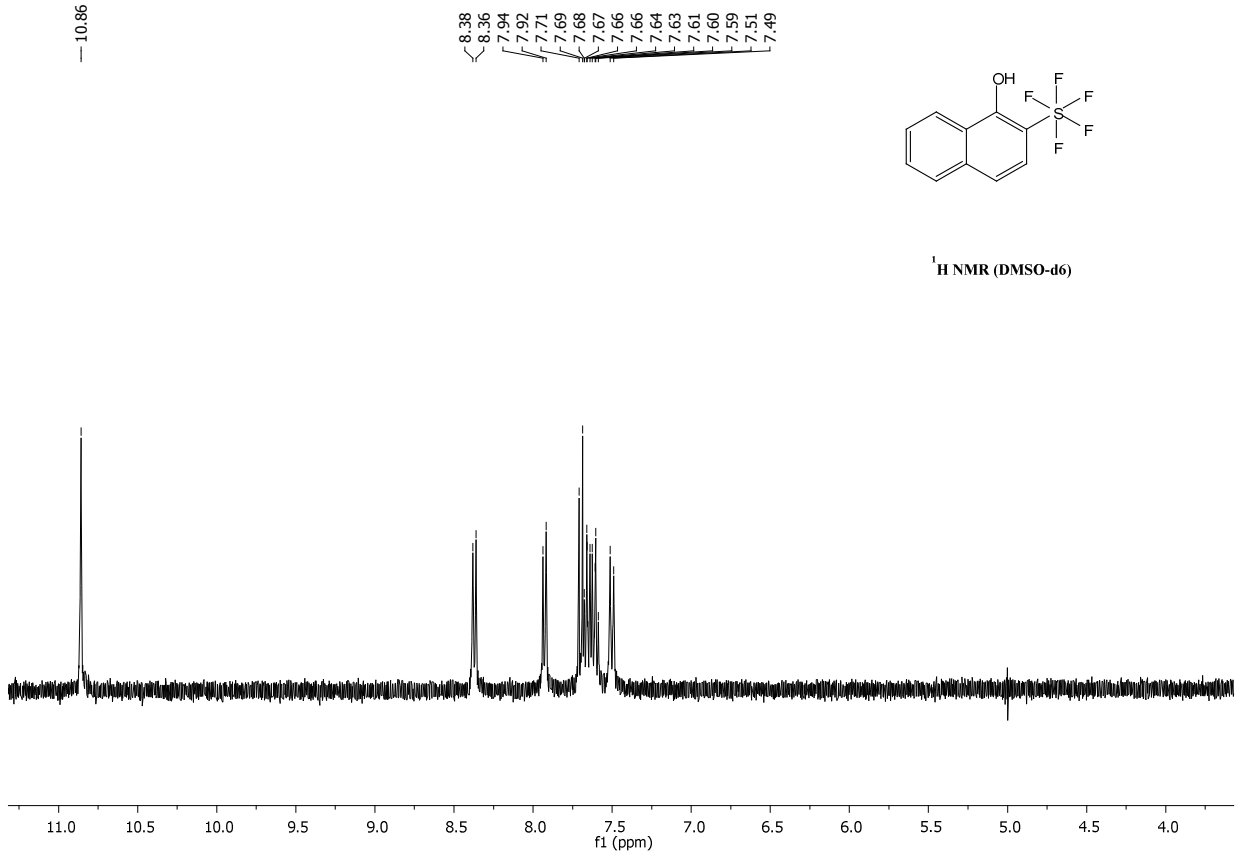




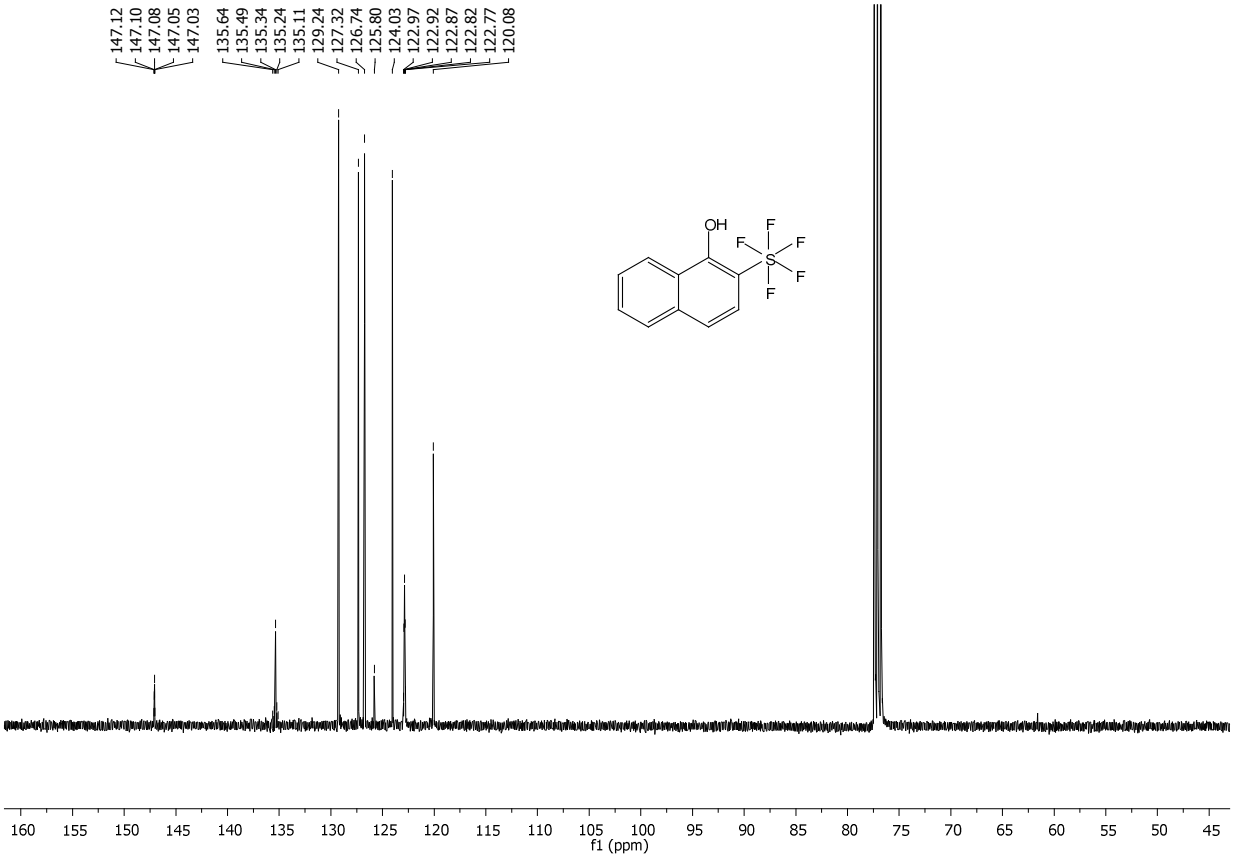
10a ^{1}H NMR (400 MHz, $CDCl_3$)

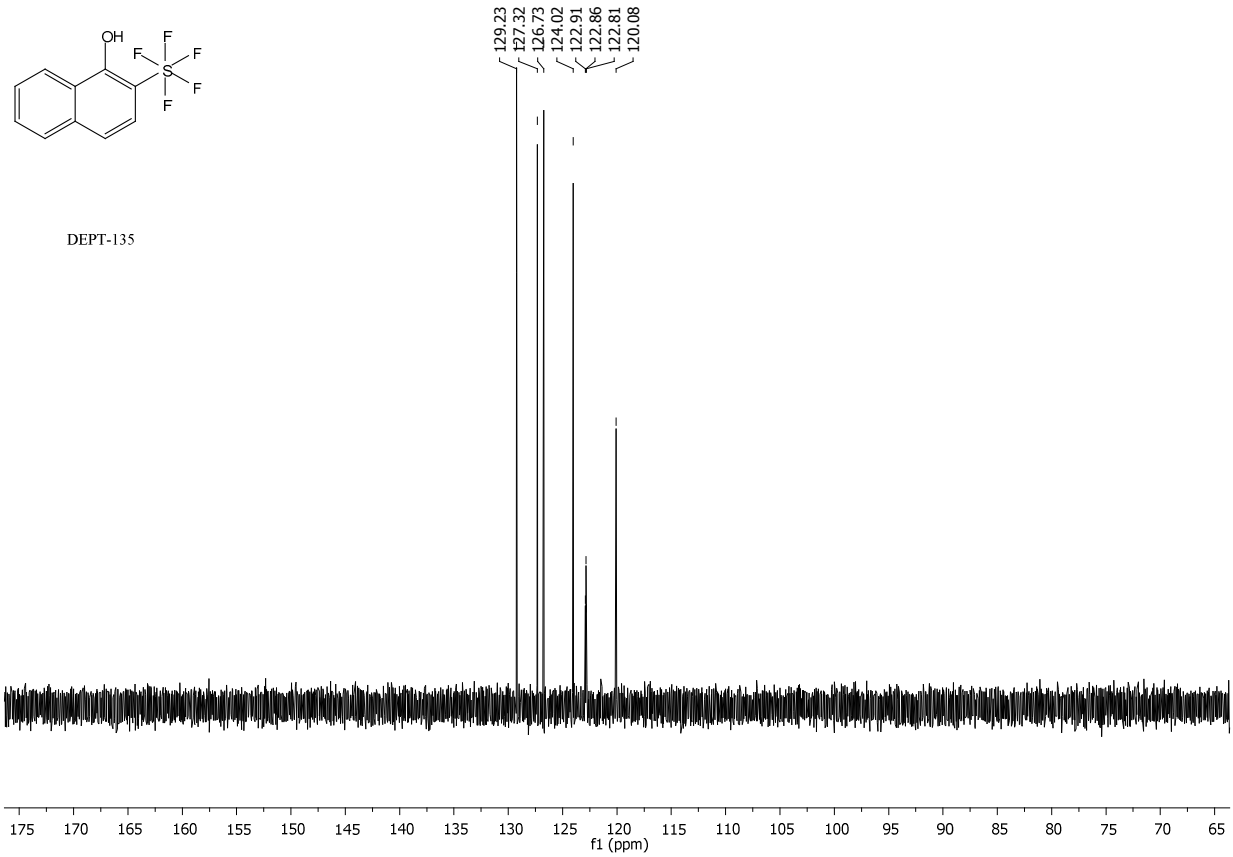


10a ^{1}H NMR (400 MHz, DMSO-d_6)



10a ^{13}C NMR (101 MHz, $CDCl_3$)





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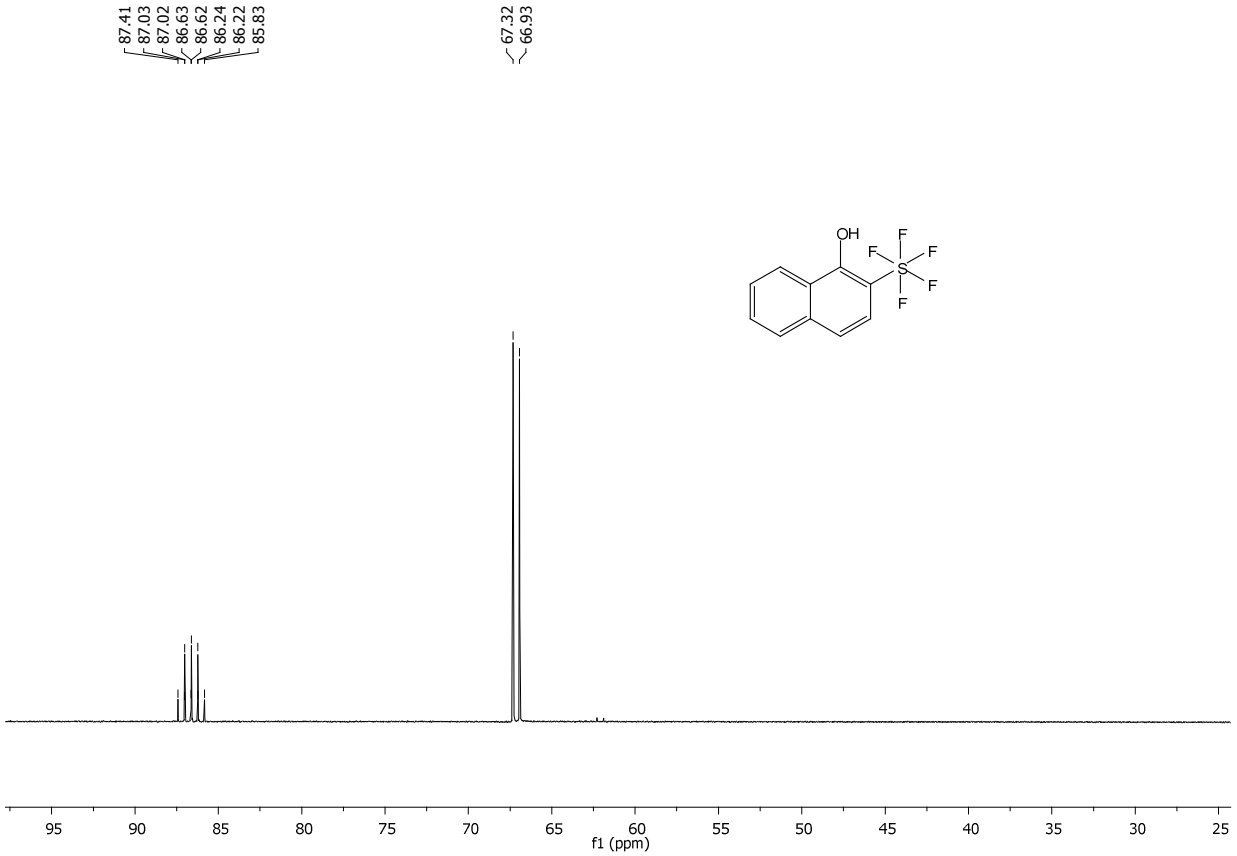
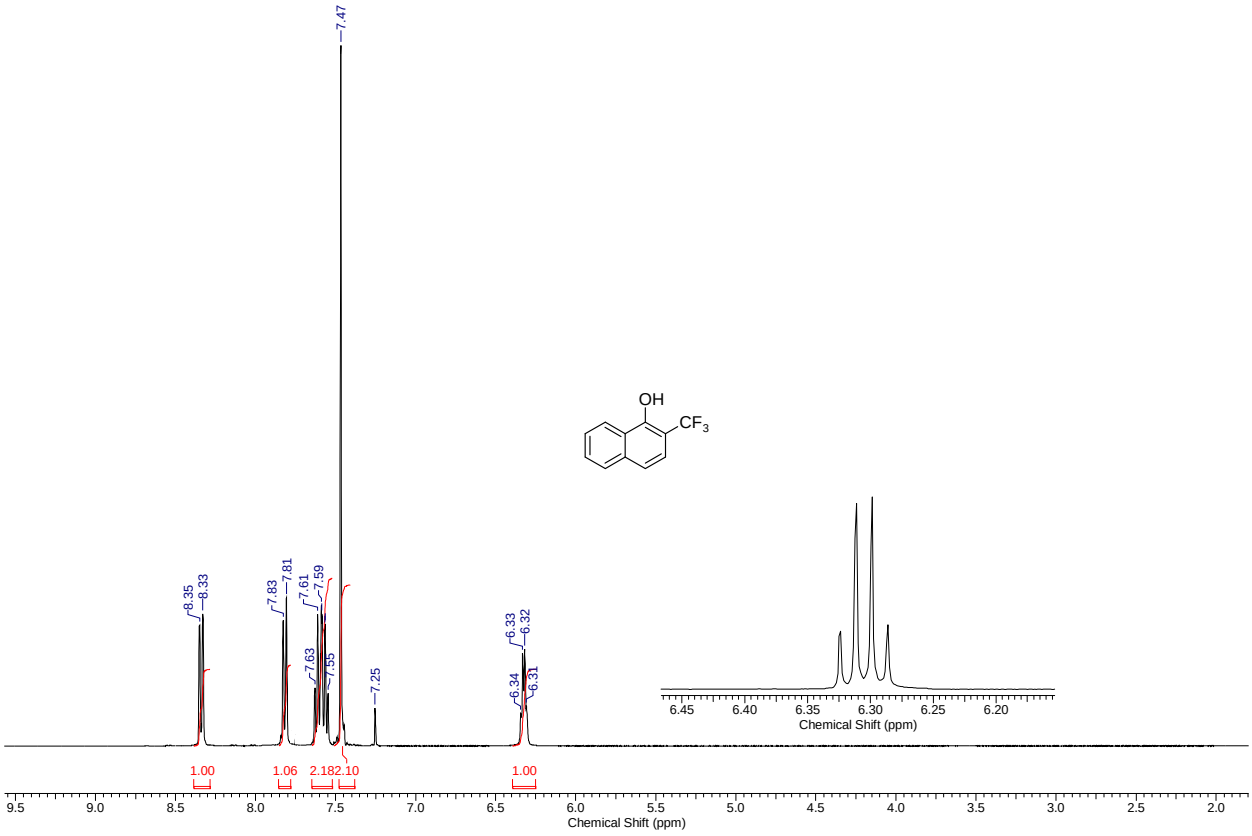
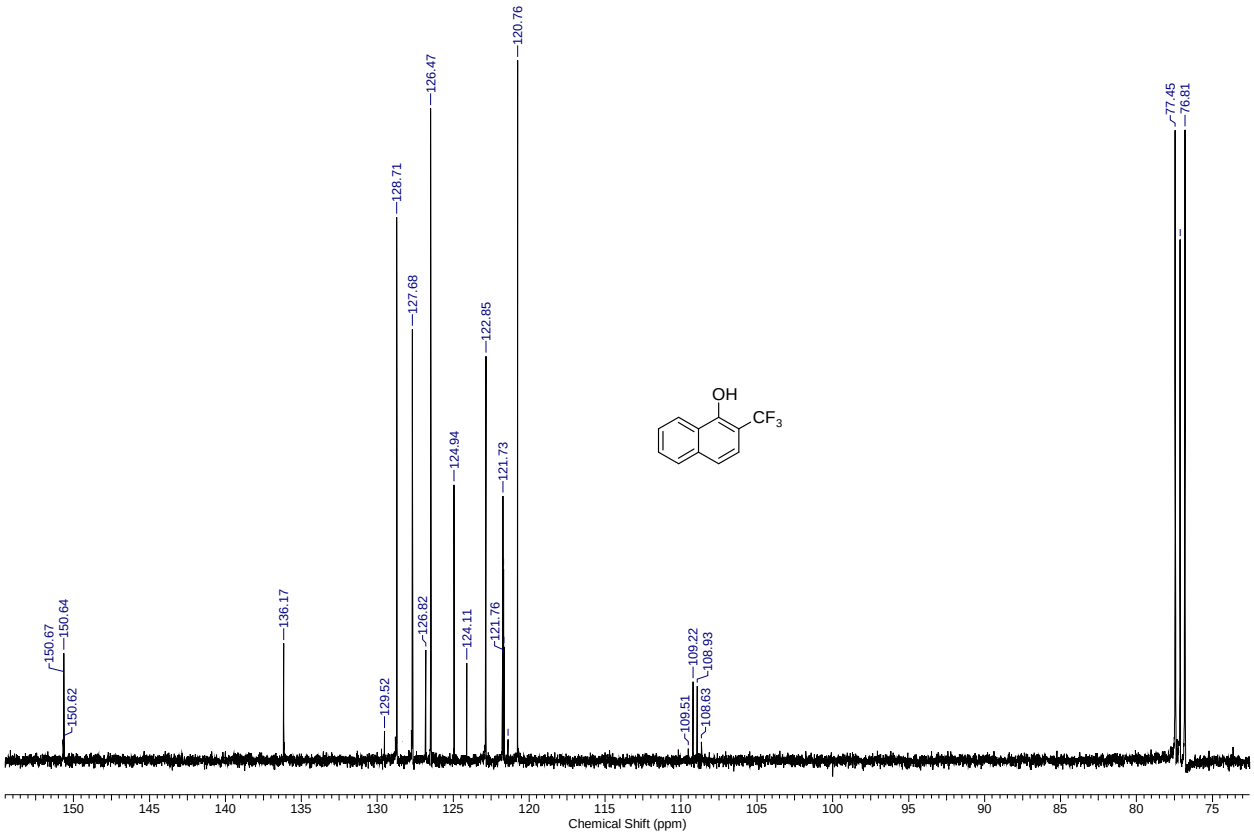
10a ^{19}F NMR (376 MHz, $CDCl_3$)

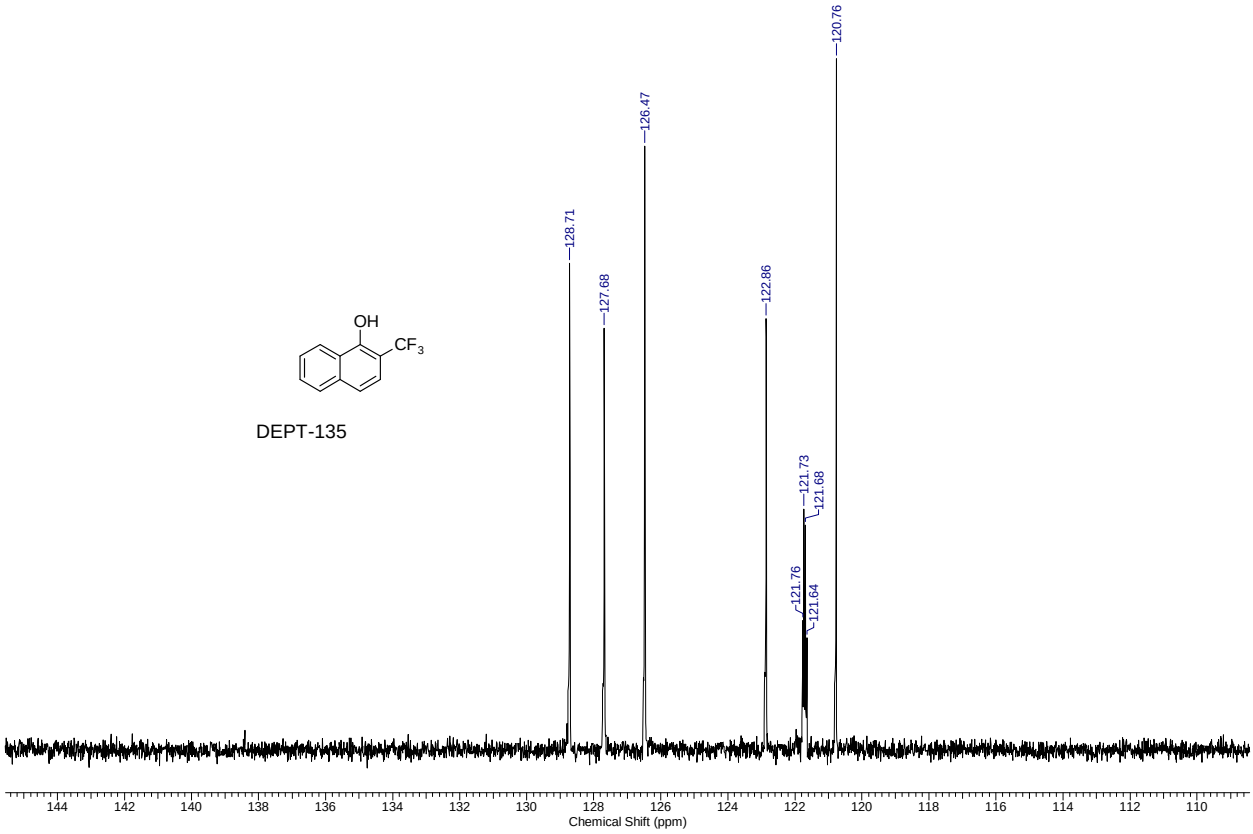


11a ^{1}H NMR (400 MHz, $CDCl_3$)

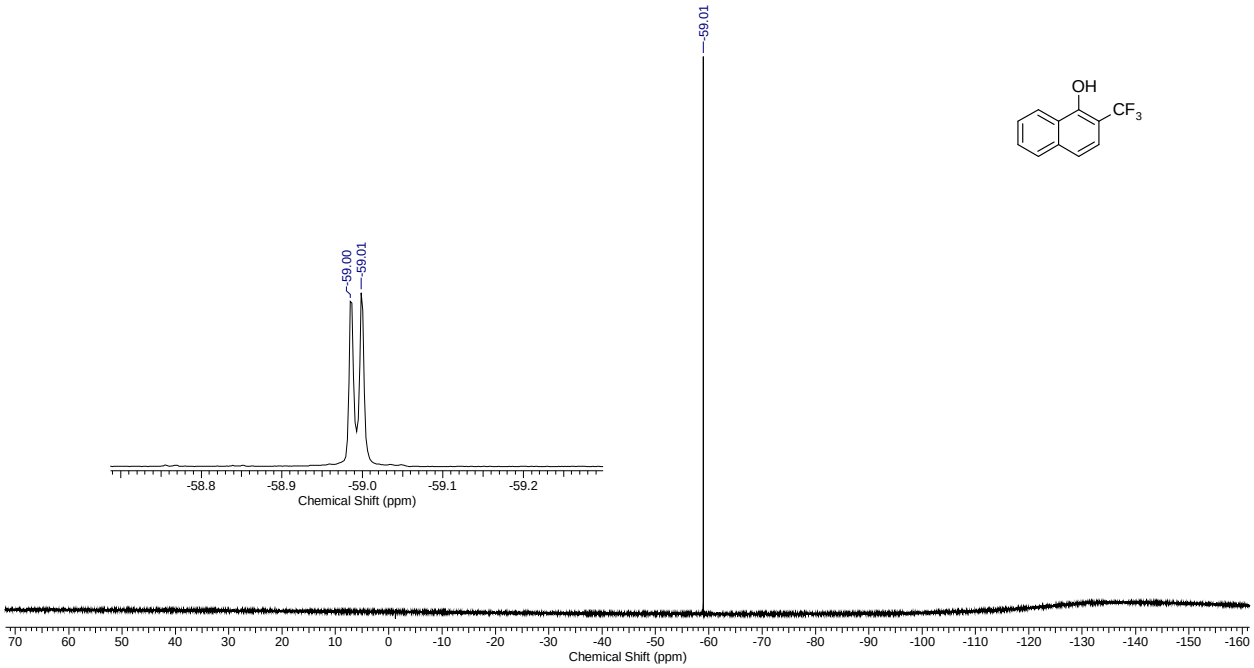


11a ^{13}C NMR (101 MHz, $CDCl_3$)

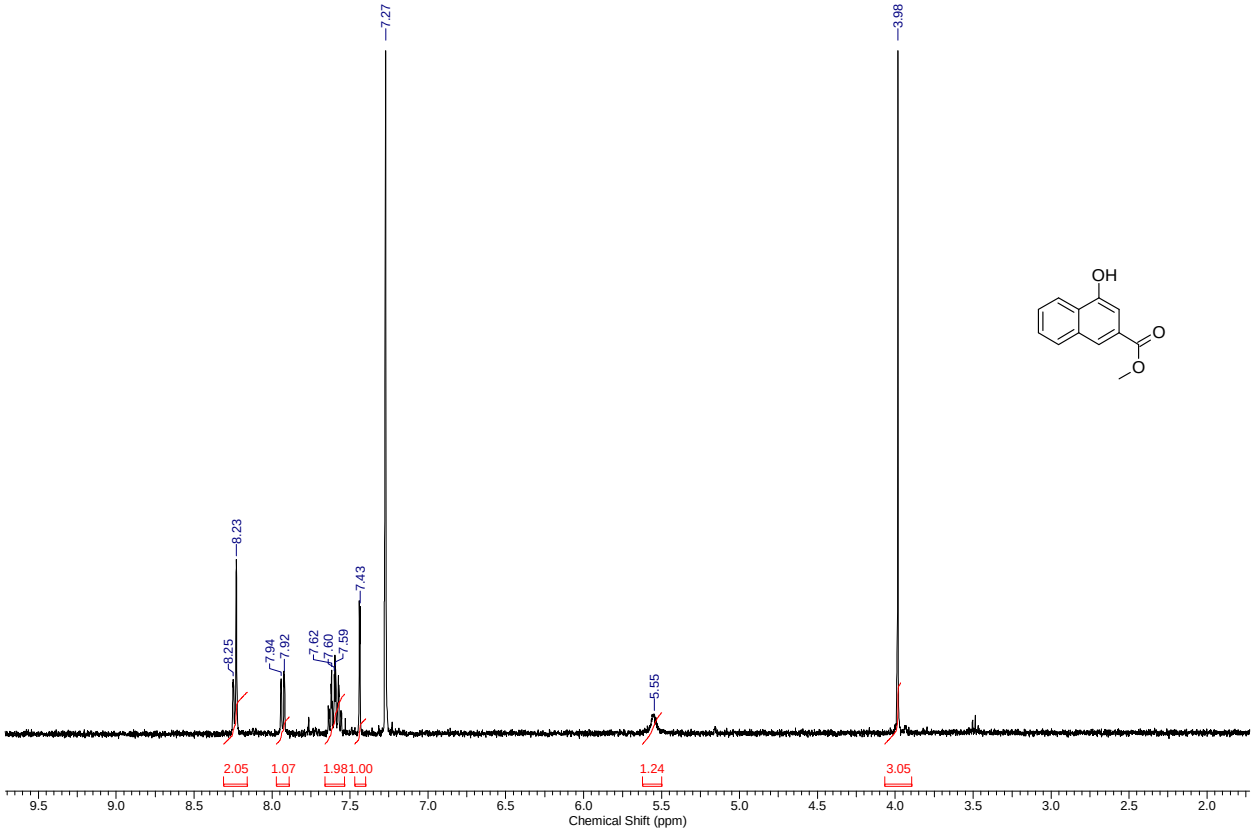




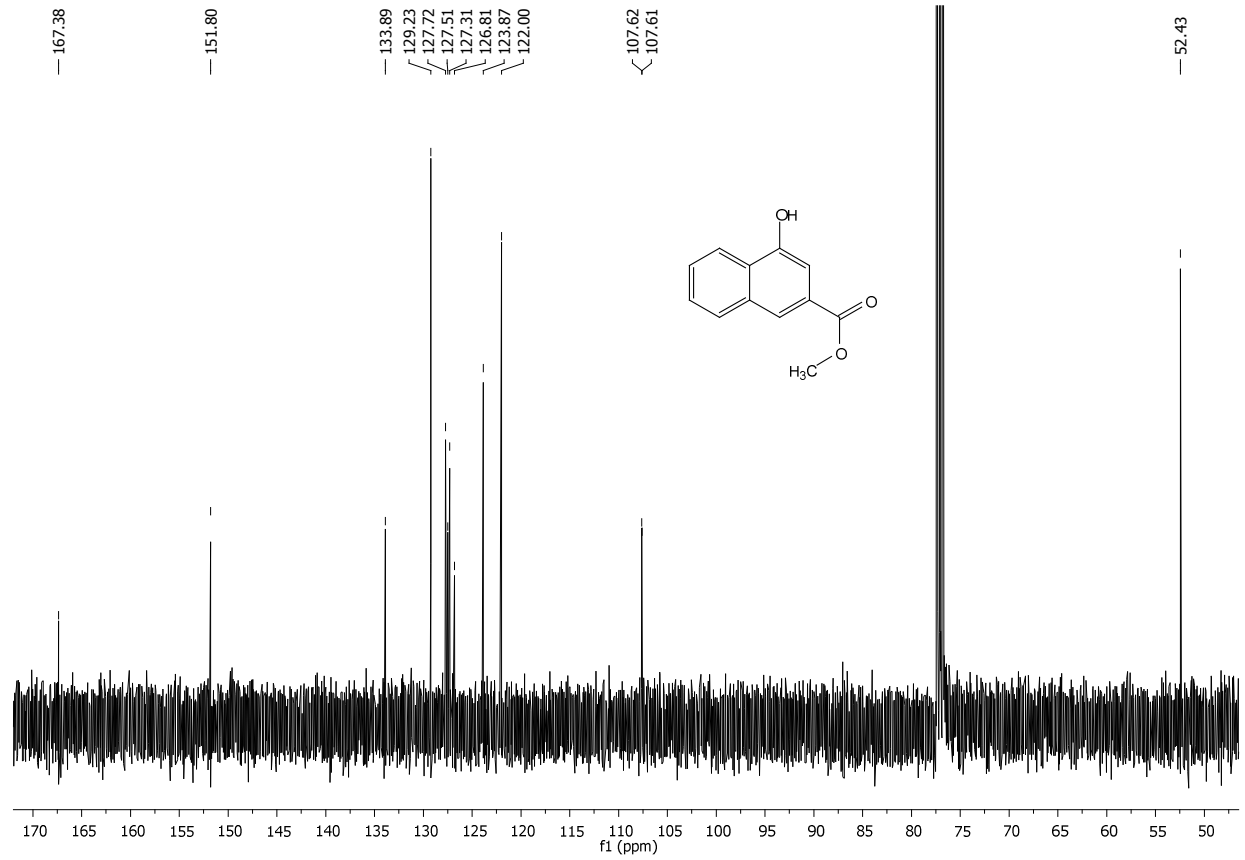
11a ^{19}F NMR (376 MHz, $CDCl_3$)

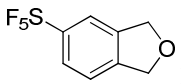


12 ^{1}H NMR (400 MHz, $CDCl_3$)

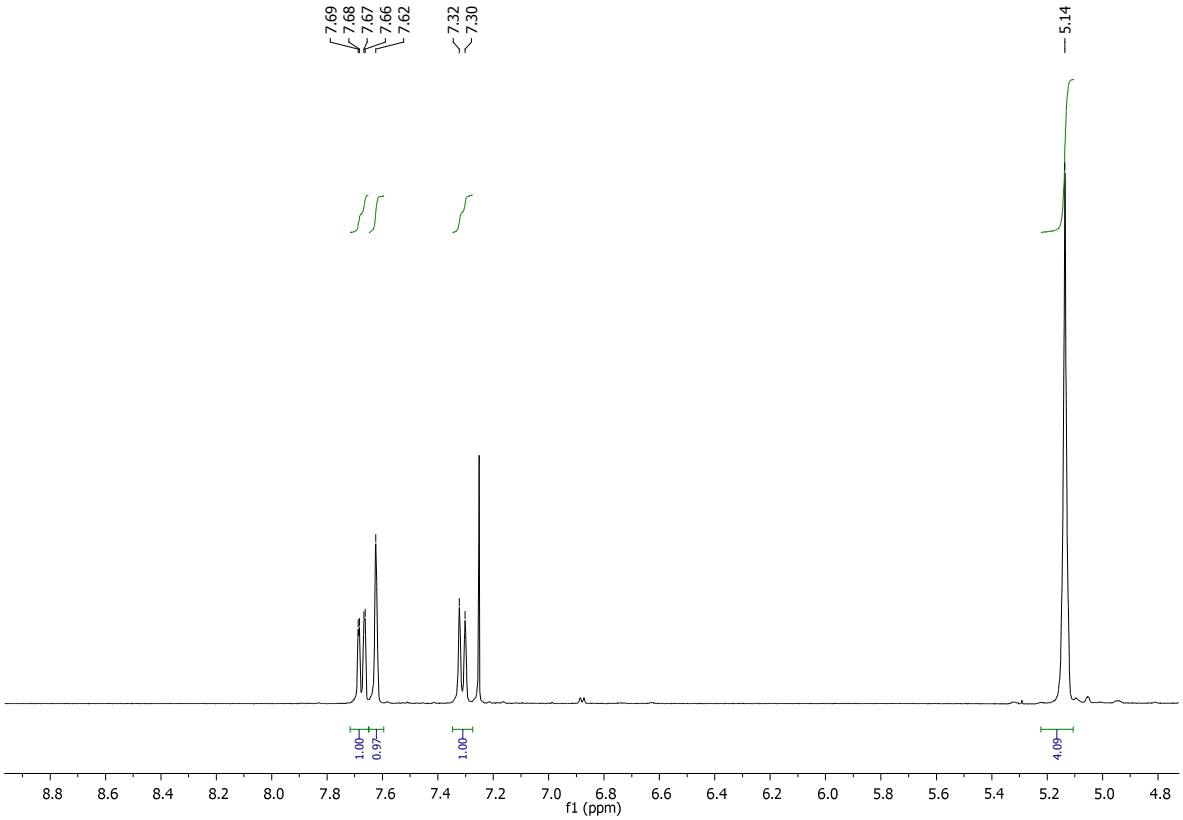


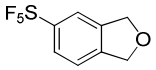
12 ^{13}C NMR (101 MHz, $CDCl_3$)



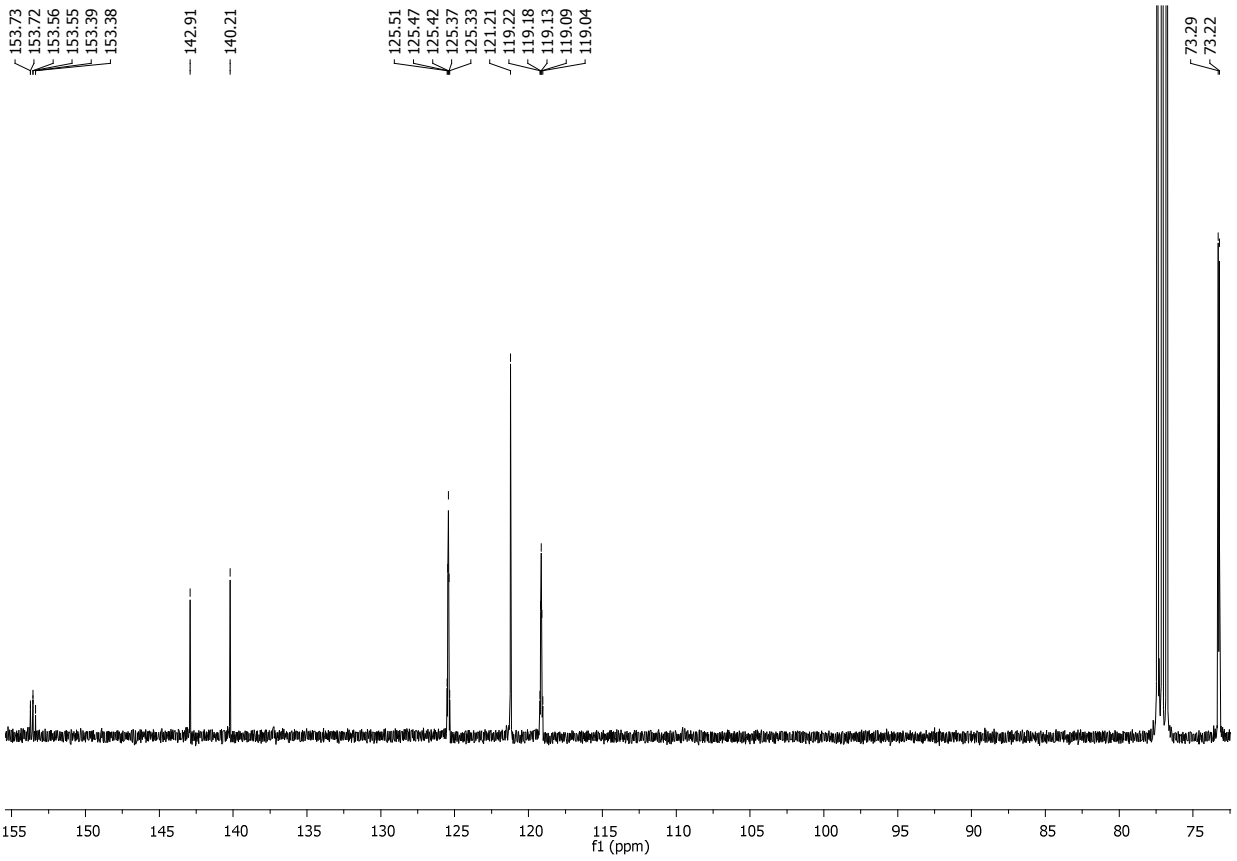


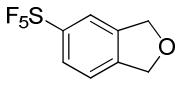
14c ^{1}H NMR (400 MHz, $CDCl_3$)



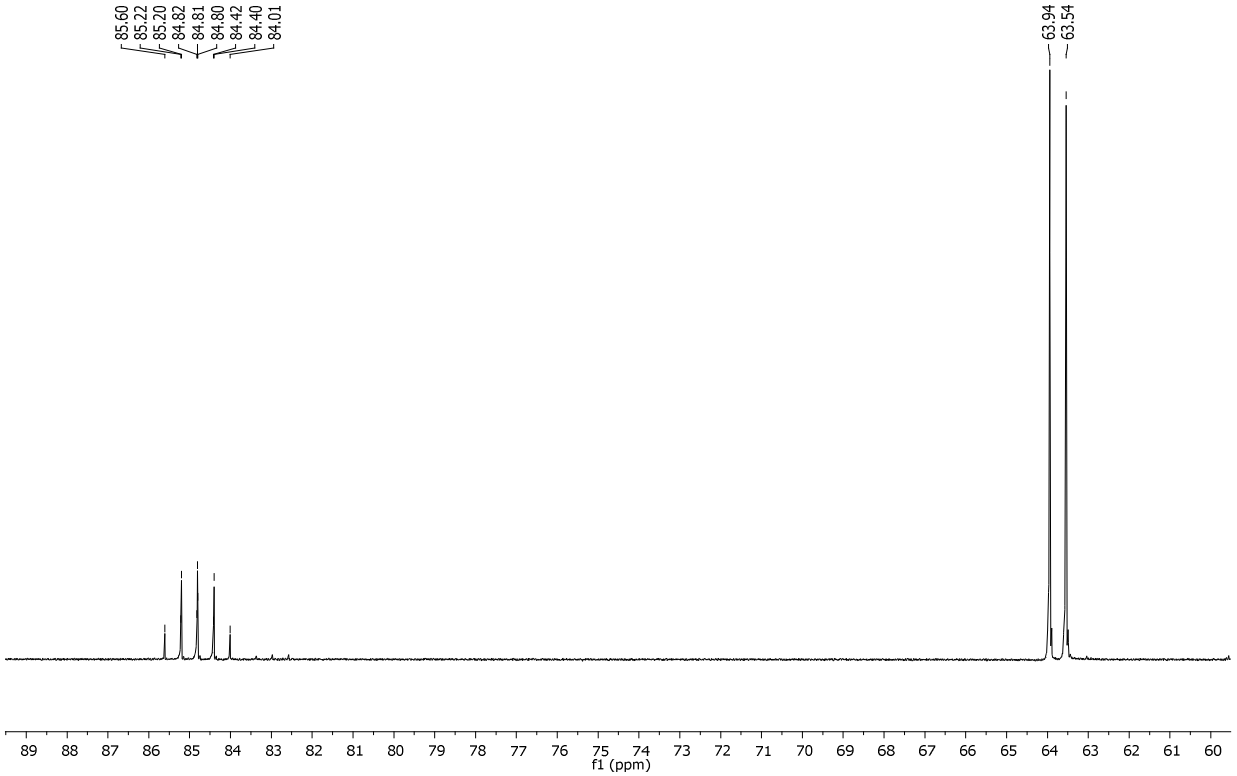


14c ^{13}C NMR (101 MHz, $CDCl_3$)

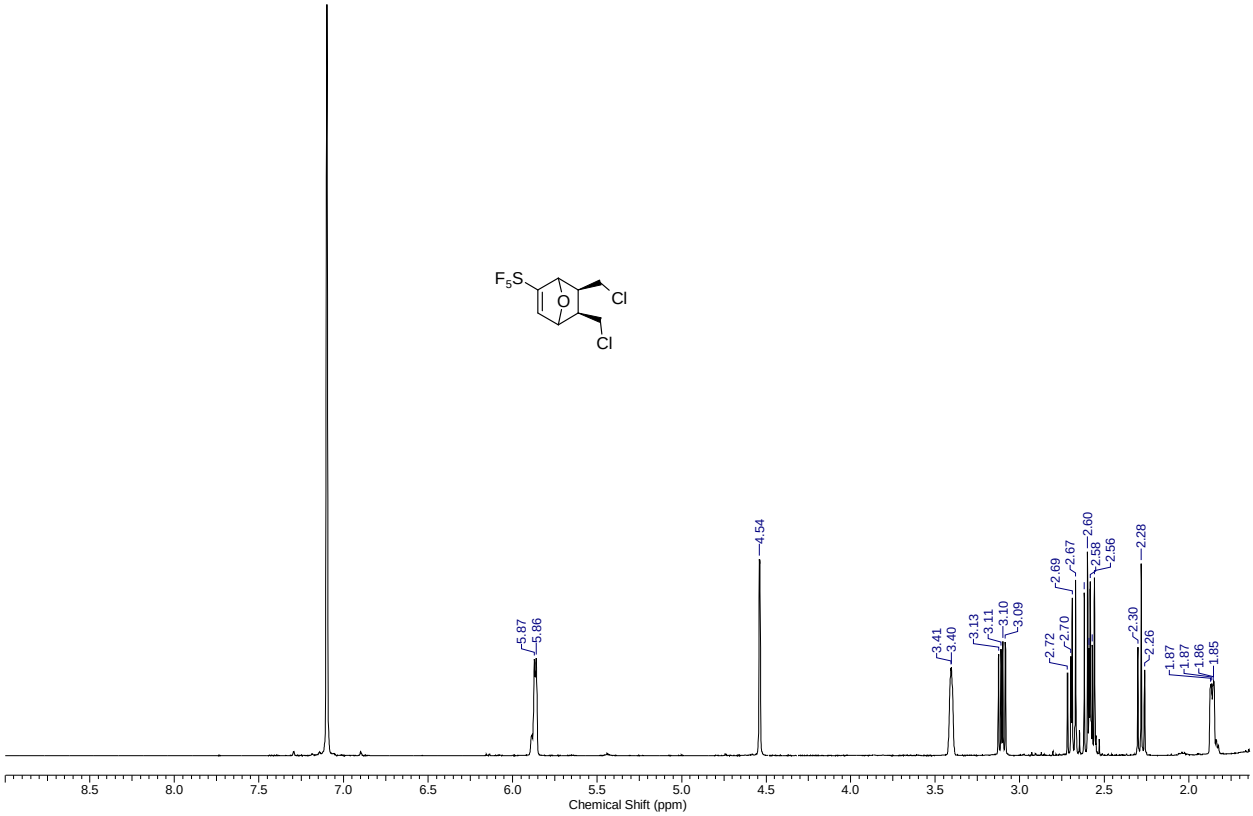




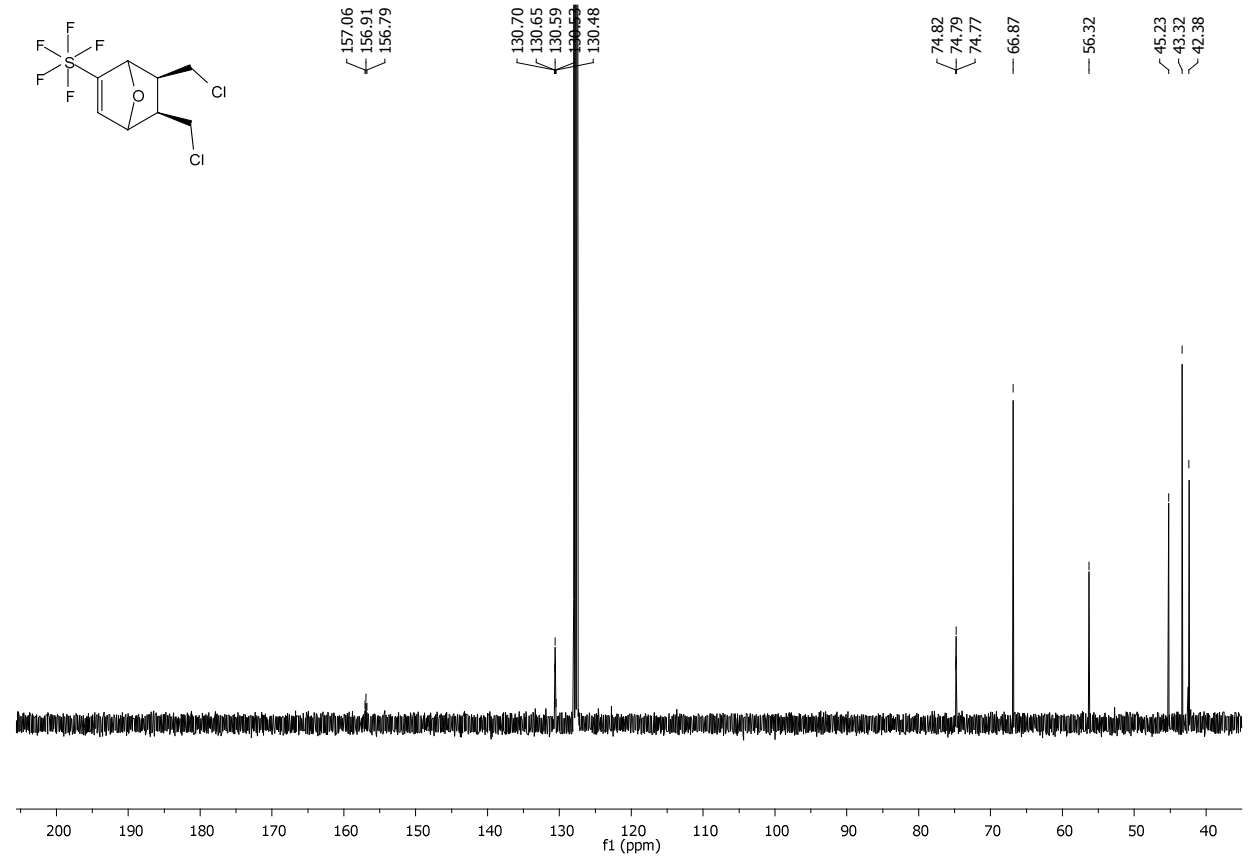
14c ^{19}F NMR (376 MHz, $CDCl_3$)

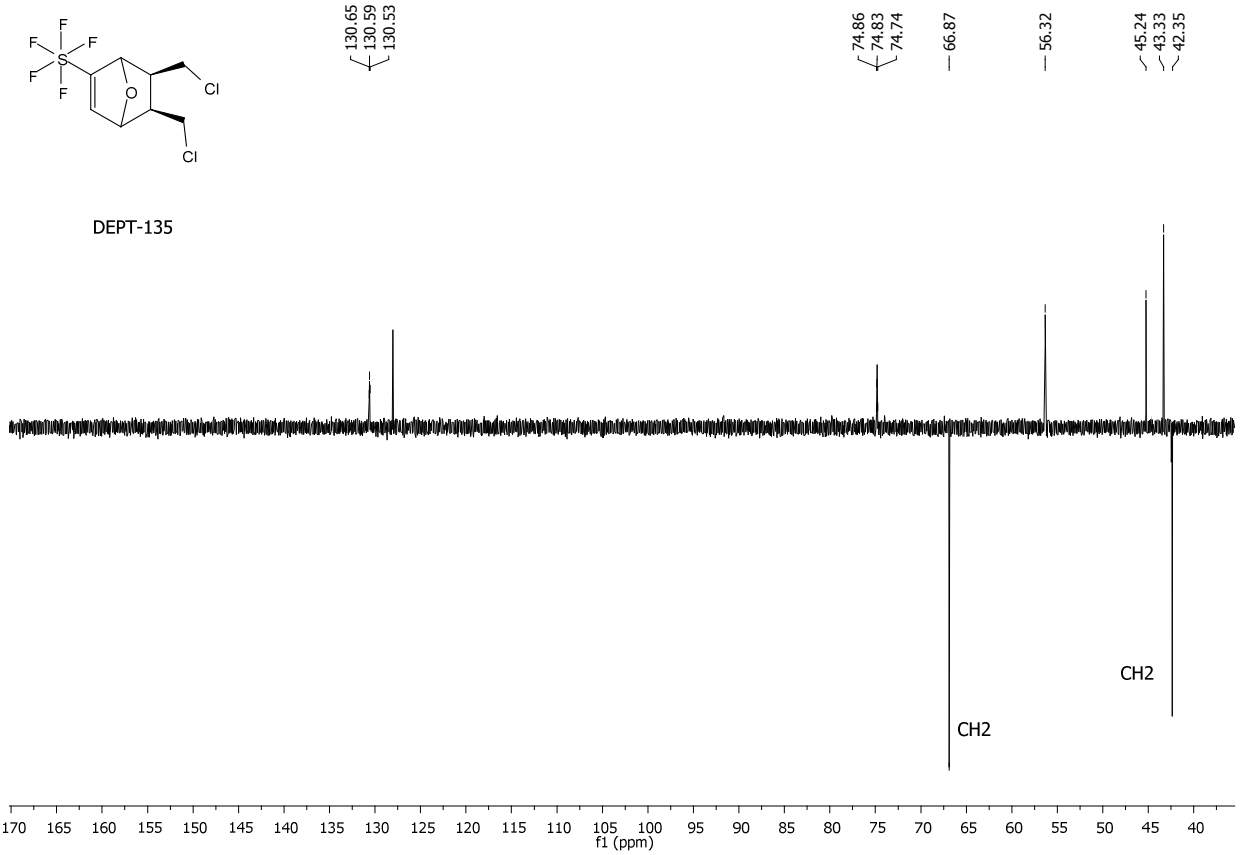


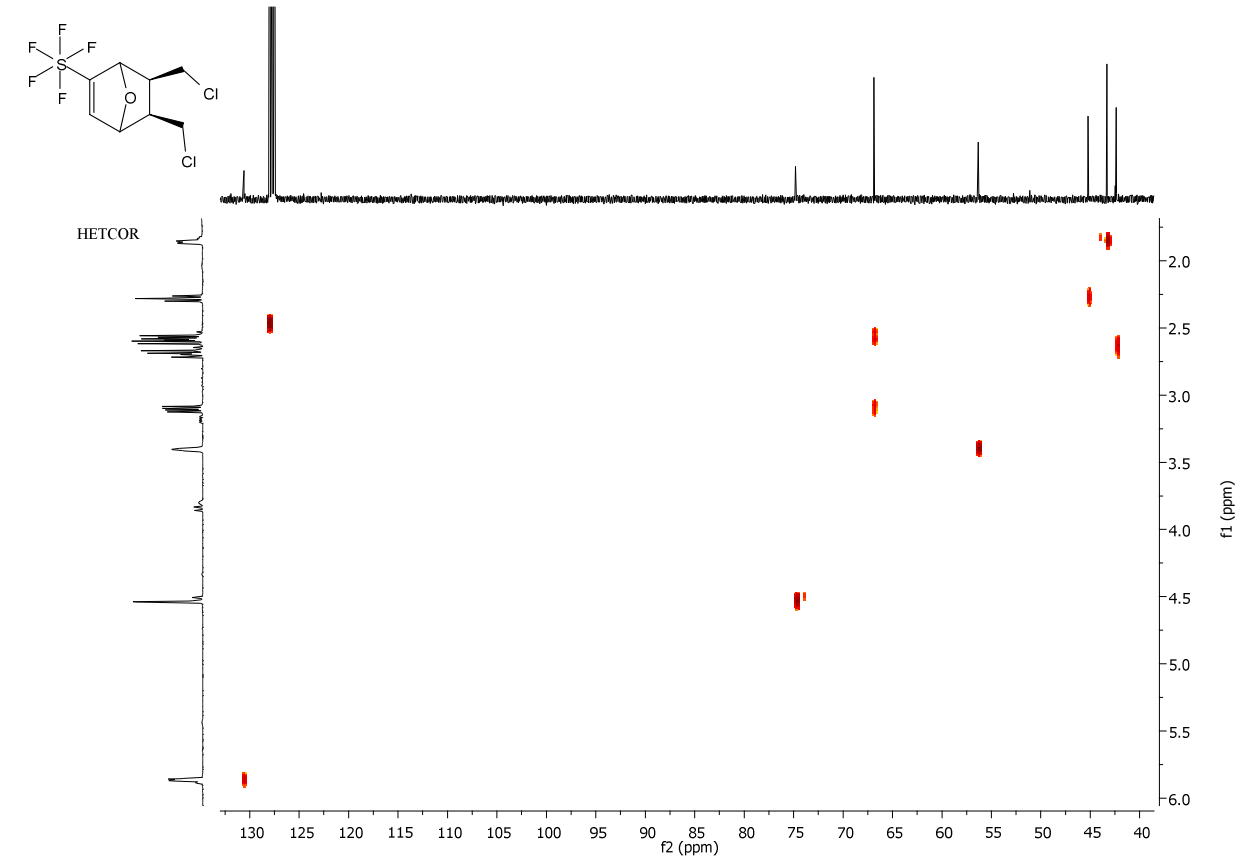
15 ^{1}H NMR (400 MHz, C_6D_6)



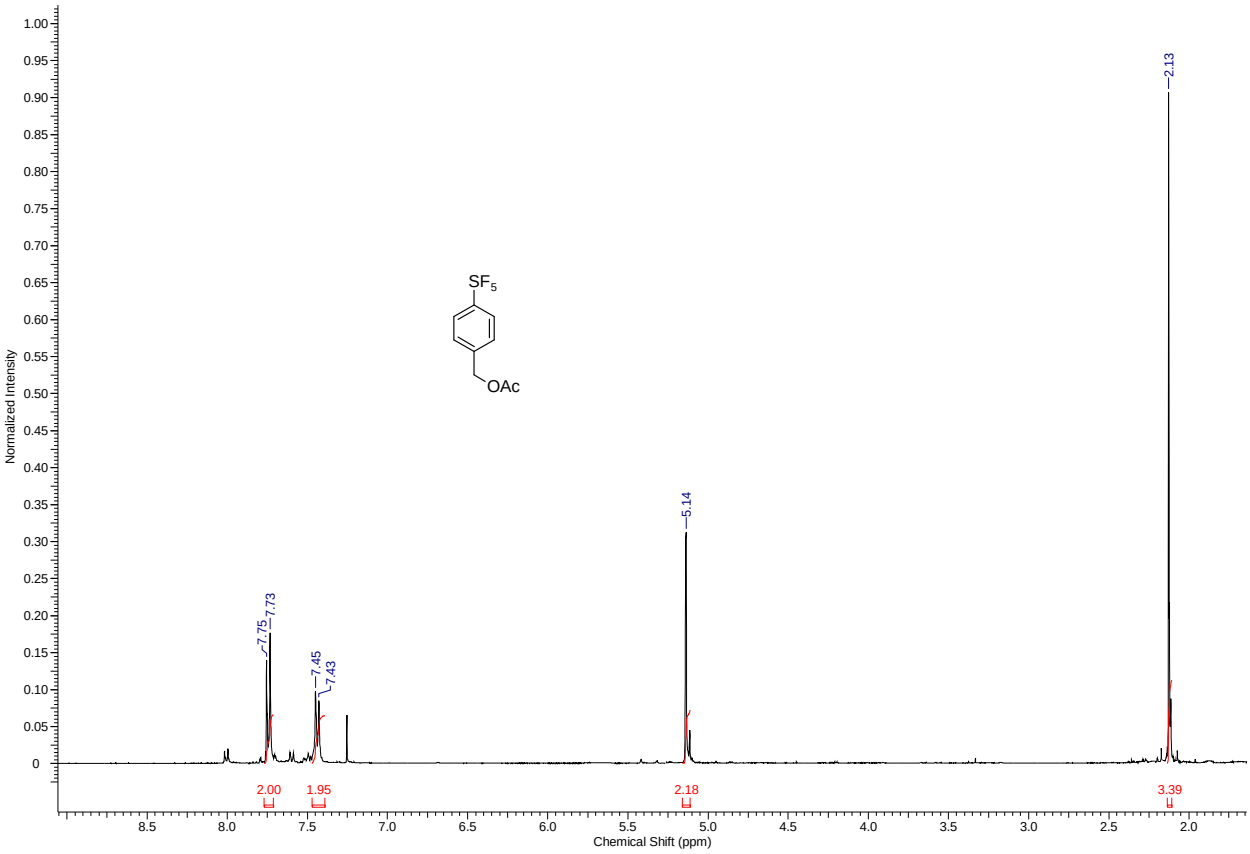
15 ^{13}C NMR (101 MHz, C_6D_6)



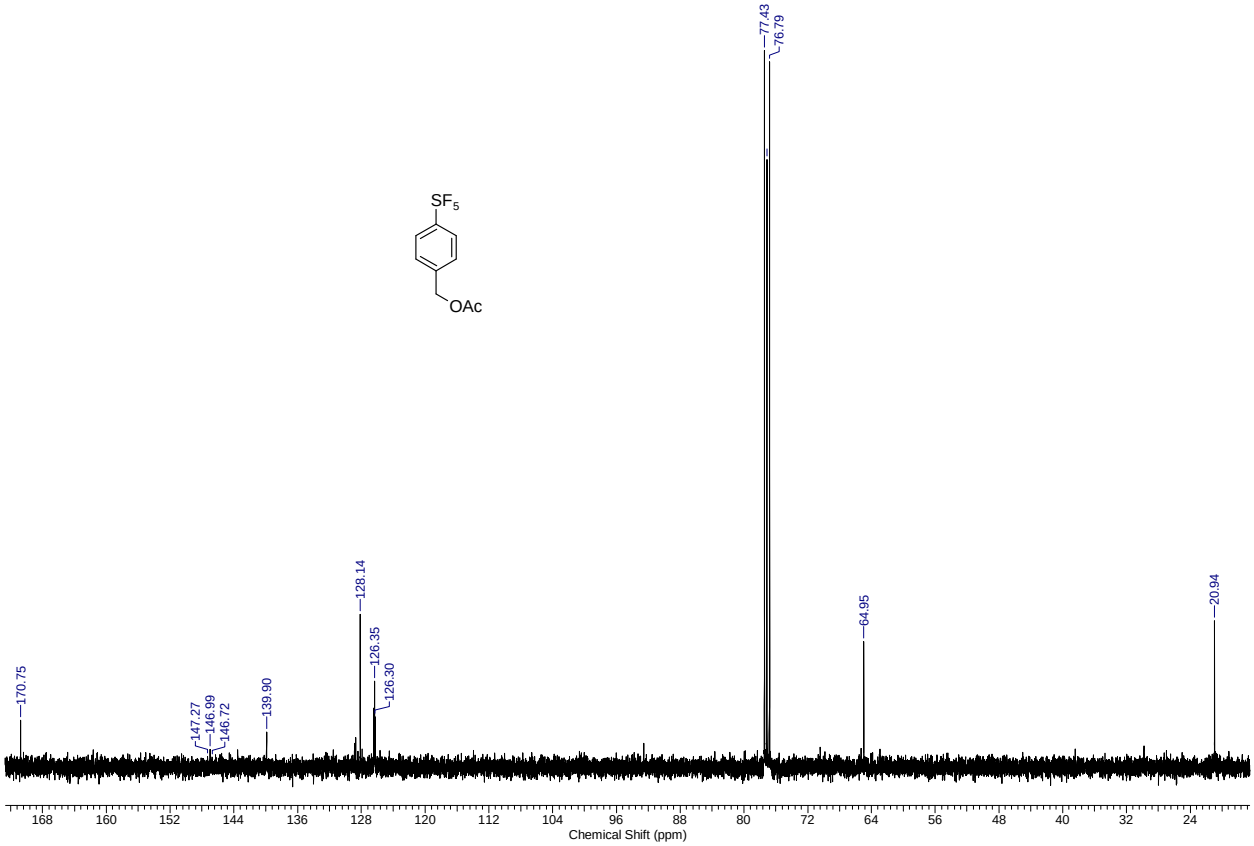




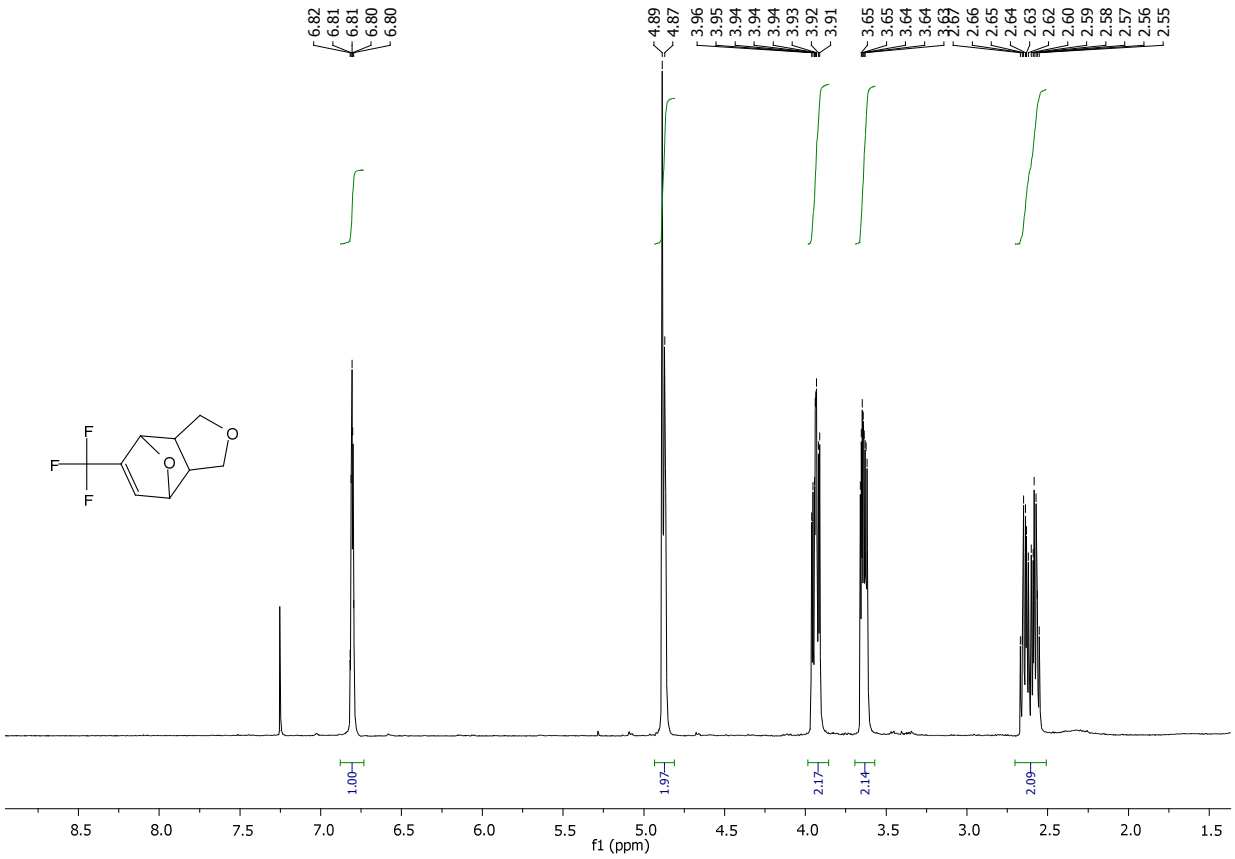
13 ^{1}H NMR (400 MHz, $CDCl_3$)



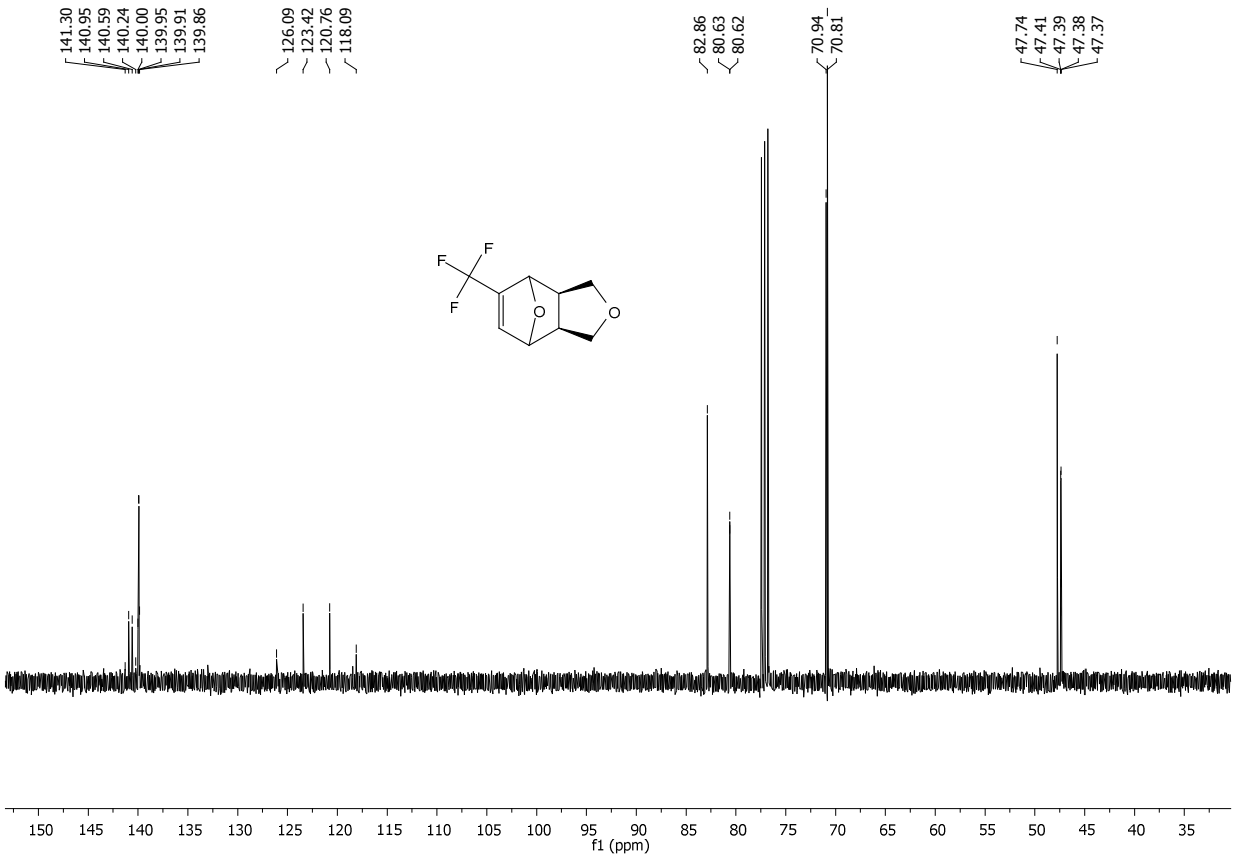
13 ^{13}C NMR (101 MHz, $CDCl_3$)

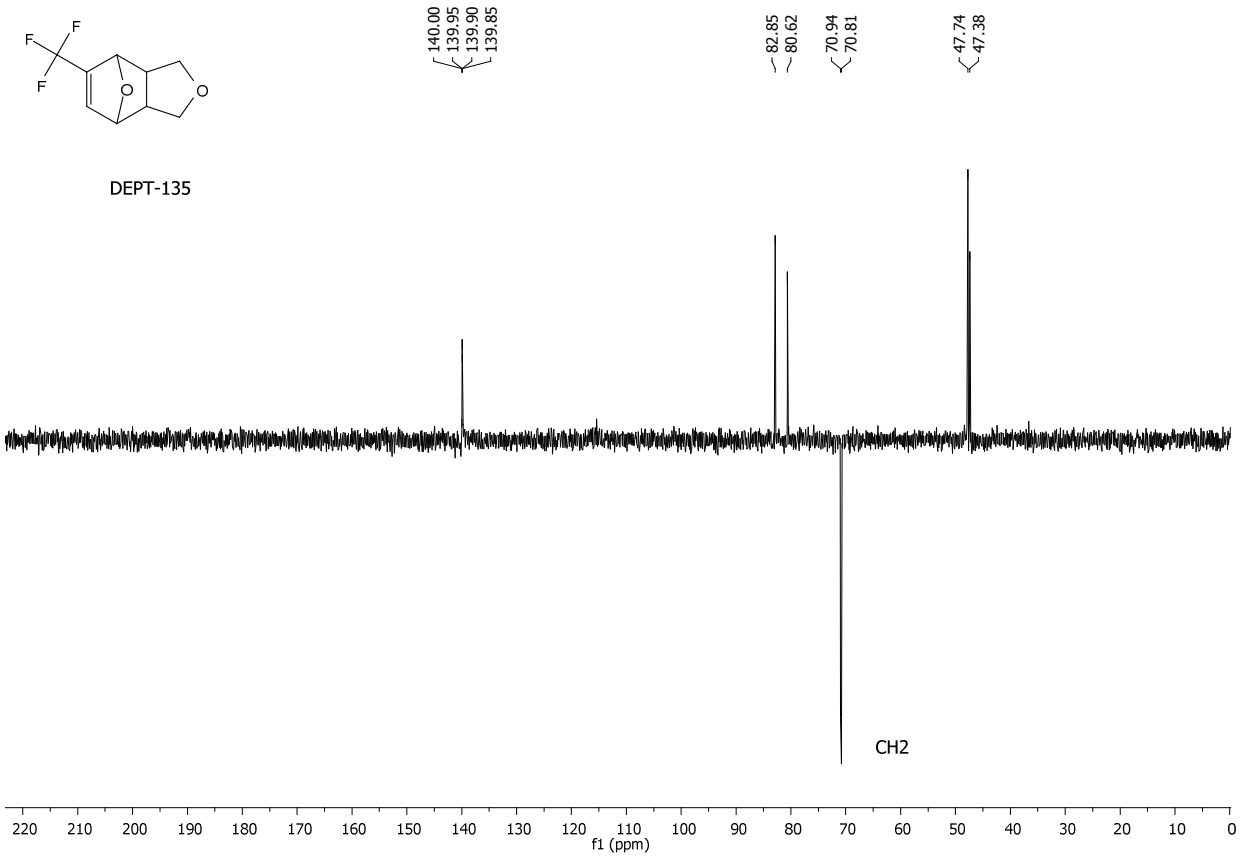


17 ^{1}H NMR (400 MHz, $CDCl_3$)



17 ^{13}C NMR (101 MHz, $CDCl_3$)





17 ^{19}F NMR (376 MHz, $CDCl_3$)