Unexpected α,α'-difluoroethers from Ag(I)F and N-bromosuccinimide reactions of dibenzo[a,e]cyclooctatetraene

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Contents

General information

All chemicals were purchased from Sigma-Aldrich or Fluorochem except the starting material dibenzo[a,e]cyclooctatetraene, which was purchased from Tokyo Chemical Industry UK Ltd. All the reactions were carried out in oven-dried PTFE flask under the atmosphere of argon. DCM, Et_2O, THF and toluene were dried and deoxygenated using a MBraun SPS-800 solvent system. Acetonitrile HPLC grade was bought from Fisher Scientific.

The progress of reactions was followed by thin-layer chromatography (TLC) using aluminium plates coated with silica gel ($60F_{245}$ Merck). TLC plates were examined under UV light at 254 and 266 nm. Column chromatography was performed on Merck Geduran silica gel (250-400 mesh) under a positive pressure of compressed air eluting with solvents as supplied.

Proton (^{1}H) and proton-decoupled nuclear magnetic resonance spectra (^{19}F{^{1}H}, ^{13}C{^{1}H}) were recorded on a Bruker AV 300, Bruker AV 400, Bruker AVII 400, Bruker AVIII-HD 500 or Bruker AVIII 500 instrument. Chemical shifts are reported in parts per million (ppm). Tetramethylsilane (δ = 0 ppm) functioned as an internal standard for **^{1}H** and **^{13}C NMR** experiments. $CFCl_3$ was used as an external standard for **^{19}F NMR** experiments. Coupling constants (*J*) are reported in Hz. When necessary, two-dimensional spectra (HSQC, HMBC) were used for the assignments of otherwise challenging signals.

High resolution mass spectra were recorded on a Waters Micromass GCT time of flight mass spectrometer or on a Thermo Scientific Exactive orbitrap mass spectrometer by the University of St Andrews or a Waters Xevo G2-S ASAP by the EPSRC UK National Mass Spectrometry Facility at Swansea University, UK. X-ray crystal structures were obtained on a Rigaku XtaLAB P200 diffractometer, using multi-layer mirror monochromated Mo-Kα radiation, at the University of St Andrews by Prof. Alexandra Slawin and Dr David Cordes. Data was analysed by using CrystalMaker.

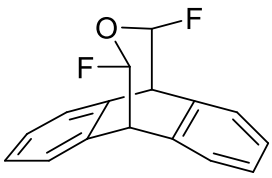
Synthetic procedure and analytical data

General procedure[1,2]

NBS (2 equiv.) was added to a solution of starting material (1 equiv.) and dry solvent (DCM, Et_2O, THF, Toluene, Acetonitrile) in an oven-dried PTFE flask. The flask was then sealed, evacuated and backfilled with argon, followed by addition of HF·Py (70 %) *via* syringe. The mixture was stirred for 2 hours at RT, then AgF (2 equiv.) was added and reaction left to stir for overnight. After completion, the reaction mixture was quenched with sodium hydrogen carbonate. The resulting mixture was extracted with dichloromethane and the combined organic phases were washed with water, followed by drying over Na_2SO_4. After filtration, solvent was removed in *vacuo*. Purification by flash column chromatography afforded the compound.

1. G. A. Olah, J. T. Welch, Y. D. Vankar, M. Nojima, I. Kerekes and J. A. Olah, *J. Org. Chem.*, **1979**, *44*, 3872-3881.
2. M. Schüler, D. O'Hagan, A. M. Z. Slawin. *Chem. Commun.,* **2005**, *34*, 4324-4326.

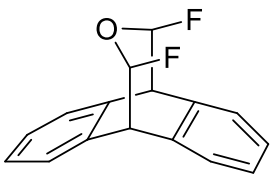
(9*R*,10*R*,11*S*,13*S*)-11,13-difluoro-9,10-dihydro-9,10-(methanooxymethano)anthracene 10



The product was prepared by following the general procedure, using DCM as the solvent. The product was purified by column chromatography (PE : Ether = 10 : 1) and obtained as a white solid (Rf = 0.3, 34 %). **M.p**. = 159-160 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 7.41-7.36 (m, 4H), 7.31-7.28 (m, 4H), 5.85-5.68 (m, 2H), 4.34-4.28 (m, 2H); **^{19}F {^{1}H}NMR** (376 MHz, $CDCl_3$) δ_F -123.2 (s, CHF); **^{19}F NMR** (376 MHz, $CDCl_3$) δ_F -123.2 (m, CHF); **^{13}C NMR** (126 MHz, $CDCl_3$) δ_c 136.6 (x2), 136.3 (x2), 128.4 (x2), 127.8 (x2), 127.7 (x2), 126.5 (x2), 104.7(d, $^1J_{CF}$ = 223.6 Hz), 104.3 (d, $^1J_{CF}$ = 223.9 Hz), 52.3 (d, $^2J_{CF}$ = 26.2 Hz, (x2)). **HRMS** (ESI$^+$) m/z calcd for $C_{16}H_{12}F_2ONa$ $[M+Na]^+$ 281.0748, found 281.0741.

Product **10** can also be efficiently prepared by adding NBS (2 equiv.) and AgF (2 equiv.) to a solution of starting material (1 equiv.) and dry DCM in the flask at RT. The reaction mixture was stirred at RT for overnight and the progress of the reaction was monitored by ^{1}H NMR. Upon completion of the reaction, the mixture was extracted with DCM, dried and concentrated under reduced pressure followed by silica gel column chromatography purification.

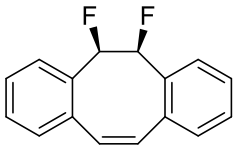
(9*R*,10*R*,11*S*,13*R*)-11,13-difluoro-9,10-dihydro-9,10-(methanooxymethano)anthracene 11



The product was prepared by following the general procedure, using DCM as the solvent. The product was purified by column chromatography (PE : Ether = 10 : 1) and obtained as a white solid (Rf = 0.2, 38 %). **M.p**. = 177-179 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ_H 7.41 (dd, *J* = 5.4, 3.3 Hz, 2H), 7.37 (dd, *J* = 5.4, 3.2 Hz, 2H), 7.30 (dd, *J* = 5.5, 3.2 Hz, 2H), 7.27-7.25 (m, 2H), 5.91-5.43 (m, 2H), 4.38 (d, *J* = 5.1 Hz, 2H); **^{19}F {^{1}H}NMR** (470 MHz, $CDCl_3$) δ_F -117.3 (s, CHF); **^{19}F NMR** (470 MHz, $CDCl_3$) δ_F -117.3 (m, CHF); **^{13}C NMR** (126 MHz, $CDCl_3$) δ_c 137.2 (t,$^3J_{CF}$ = 3.4 Hz), 136.6, 127.9, 127.7, 127.3, 127.1, 103.9 (d, $^1J_{CF}$ = 223.9 Hz), 51.8 (dt, J_{CF} = 24.3, 7.2 Hz). **HRMS** (ESI$^+$) m/z calcd for $C_{16}H_{12}F_2ONa$ $[M+Na]^+$ 281.0748, found 281.0746.

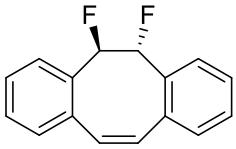
Product **11** can also be efficiently prepared by adding NBS (2 equiv.) and AgF (2 equiv.) to a solution of starting material (1 equiv.) and dry DCM in the flask at RT. The reaction mixture was stirred at RT for overnight and the progress of the reaction was monitored by ^{1}H NMR. Upon completion of the reaction, the mixture was extracted with DCM, dried and concentrated under reduced pressure followed by silica gel column chromatography purification.

(5*R*,6*S*,*Z*)-5,6-difluoro-5,6-dihydrodibenzo[a,e][8]annulene 13



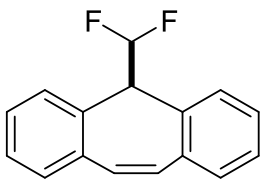
The product was prepared by following the general procedure, using ether as the solvent. The product was purified by column chromatography (PE) and obtained as a white solid (Rf = 0.15, 14 %). **M.p**. = 145-146 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 7.66 (m, 2H), 7.30 (m, 4H), 7.17 (m, 2H), 6,86 (s, 2H, CH=CH), 6.29 (m, 2H, CHF); **^{19}F {^{1}H}NMR** (376 MHz, $CDCl_3$) δ_F -182.0 (s, CHF); **^{19}F NMR** (376 MHz, $CDCl_3$) δ_F -182.0 (m, CHF); **^{13}C NMR** (126 MHz, $CDCl_3$) δ_c 133.4, 132.9 (m), 131.8, 129.5, 128.6 (t, J = 5.6 Hz), 128.1, 127.5, 91.5 (dd, $^{1}J_{CF}$ = 178.0 Hz, $^{2}J_{CF}$ = 21.4 Hz). **HRMS** (ASAP^{+}) m/z calcd for $C_{16}H_{12}F_2$ $[M]^+$ 242.0907, found 242.0909.

(5*R*,6*R*,*Z*)-5,6-difluoro-5,6-dihydrodibenzo[a,e][8]annulene 14.



The product was prepared by following the general procedure, using ether as the solvent. The product was purified by column chromatography (PE) and obtained as a white solid (Rf = 0.1, 55 %). **M.p**. = 137-138 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 7.46 (m, 2H), 7.27 (m, 4H), 7.16 (m, 2H), 7.05 (s, 2H, CH=CH), 6.01 (m, 2 H, CHF); **^{19}F {^{1}H}NMR** (376 MHz, $CDCl_3$) δ_F -182.0 (s, CHF); **^{19}F NMR** (376 MHz, $CDCl_3$) δ_F -182.0 (m, CHF); **^{13}C NMR** (126 MHz, $CDCl_3$) δ_c 134.5 (d, $^{3}J_{CF}$ = 4.4 Hz), 133.4 (dd, $^{2}J_{CF}$ = 19.4, $^{3}J_{CF}$ = 8.5 Hz), 132.2, 128.9, 128.8 (d, J = 6.2 Hz), 128.5 (d, J = 2.5 Hz), 127.8, 95.3 (dd, $^{1}J_{CF}$ = 176.5 Hz, $^{2}J_{CF}$ = 27.3 Hz). **HRMS** (ASAP^{+}) m/z calcd for $C_{16}H_{12}F_2$ $[M]^+$ 242.0907, found 242.0911.

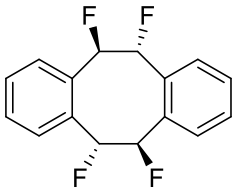
5-(difluoromethyl)-5*H*-dibenzo[a,d][7]annulene 12



The product was prepared by following the general procedure, using toluene as the solvent. The product was purified by preparative thin-layer chromatography (PE) and obtained as a yellow solid (Rf = 0.25, 10 %). **M.p**. = 84-86 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ_H 7.35 (m, 8H), 6.95 (s, 2H, CH=CH), 6.13 (td, J = 57.5, 7.8, 1 Hz, 1H, CHF_2), 4.30 (m, 1H, CH); **^{19}F {^{1}H}NMR** (470 MHz, $CDCl_3$) δ_F -116.2 (s, CHF_2); **^{19}F NMR** (470 MHz, $CDCl_3$) δ_F -116.2 (dd, J_{CF} = 57.5 Hz, $^{2}J_{CF}$ = 11.9 Hz, CHF_2); **^{13}C NMR** (126 MHz, $CDCl_3$) δ_c 134.1, 133.9 (t, ^{3}J = 4.0 Hz), 131.0, 130.9,

129.6, 129.3, 127.8, 113.1 (t, $^{1}J_{CF}$ = 242.8 Hz), 58.9 (t, $^{2}J_{CF}$ = 23.7 Hz). **HRMS** (EI^{+}) m/z calcd for $C_{16}H_{12}F_2$ 242.0901, found 242.0891.

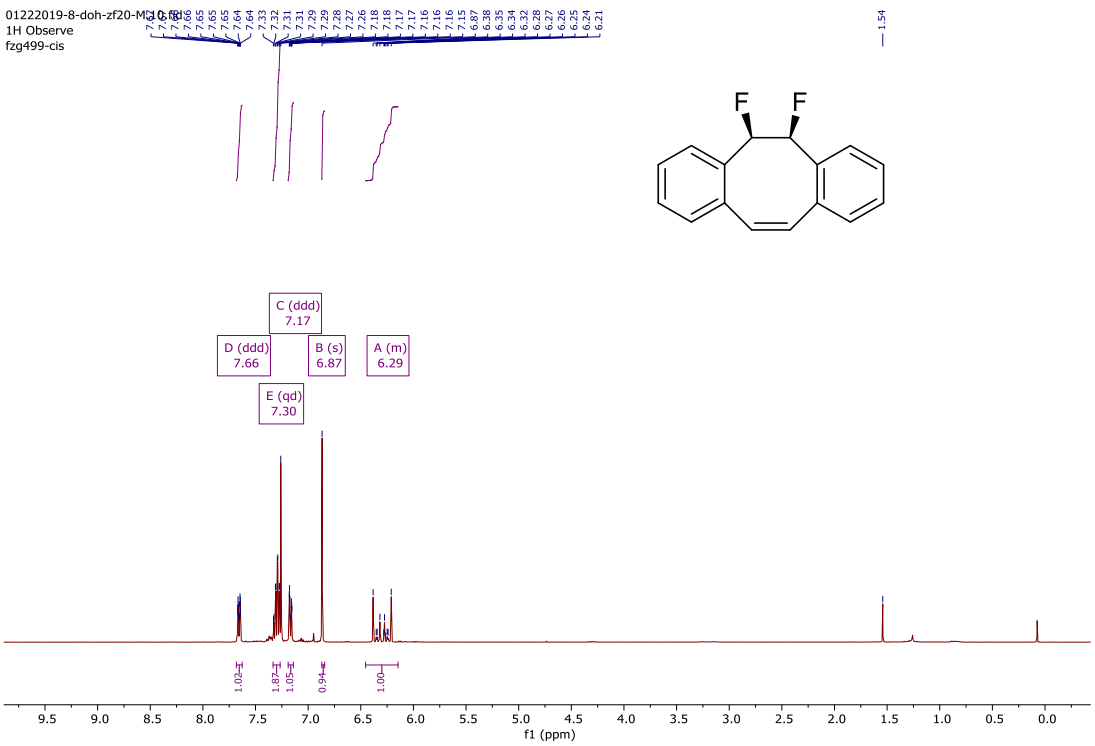
(5R,6R,11R,12R)-5,6,11,12-tetrafluoro-5,6,11,12-tetrahydrodibenzo[a,e][8]annulene 15



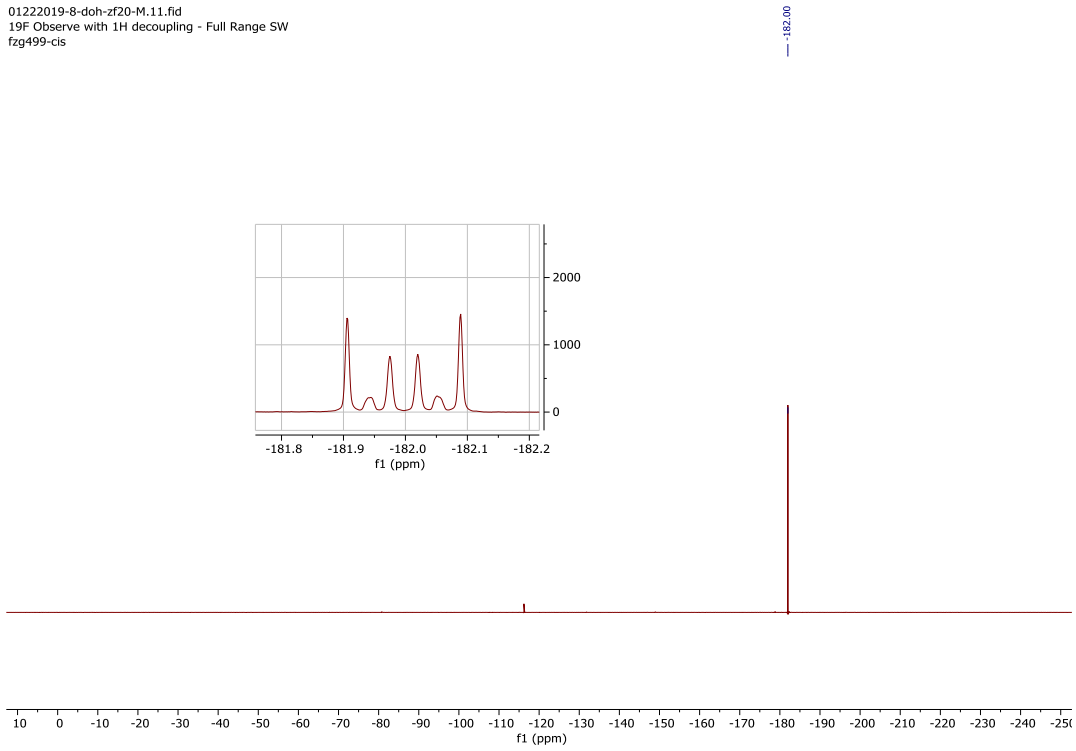
The product was prepared by following the general procedure, using DCM as the solvent. The product was purified by preparative thin-layer chromatography (PE : Ether = 10 : 1) and obtained as a white solid (Rf = 0.35, 4 %). **M.p.** = 154-156 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ_H 7.52 (d, *J* = 7.8 Hz, 2H), 7.33 (t, *J* = 7.8 Hz, 2H), 7.18 (t, *J* = 7.6 Hz, 2H), 7.06 (d, *J* = 7.6 Hz, 2H), 6.43 (ddd, *J* = 47.0, 18.7, 6.4 Hz, 2H), 5.58 (ddd, *J* = 48.4, 25.4, 6.4 Hz, 2H); **^{19}F {^{1}H}NMR** (470 MHz, $CDCl_3$) δ_F -164.1 (d, *J* = 9.8 Hz, CHF), -180.4 (d, *J* = 9.8 Hz, CHF) ; **^{19}F NMR** (470 MHz, $CDCl_3$) δ_F -164.1 (ddd, *J* = 48.4, 18.7, 9.8 Hz, CHF), -180.4 (ddd, *J* = 47.0, 25.4, 9.8 Hz, CHF); **^{13}C NMR** (126 MHz, $CDCl_3$) δ_c 134.2, 132.1, 131.0, 130.4, 129.3, 124.8, 99.5, 93.4. **HRMS** (ESI^{+}) m/z calcd for $C_{16}H_{12}F_4Na$ $[M+Na]^{+}$ 303.0767, found 303.0766.

NMR spectra

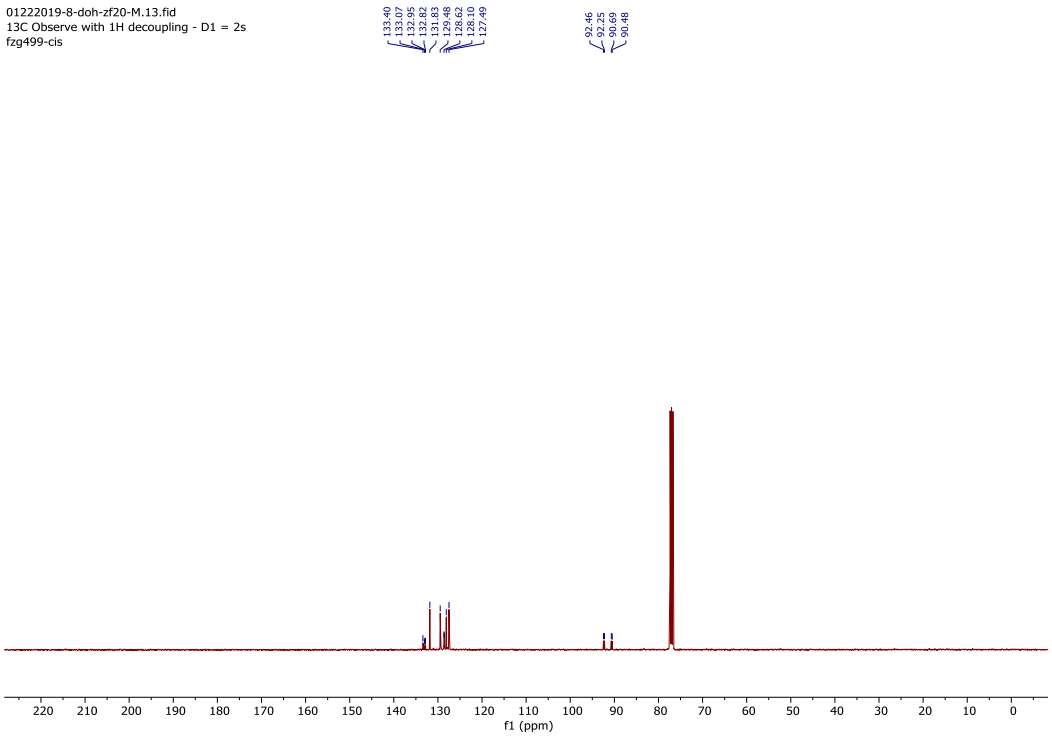
^{1}H NMR 13



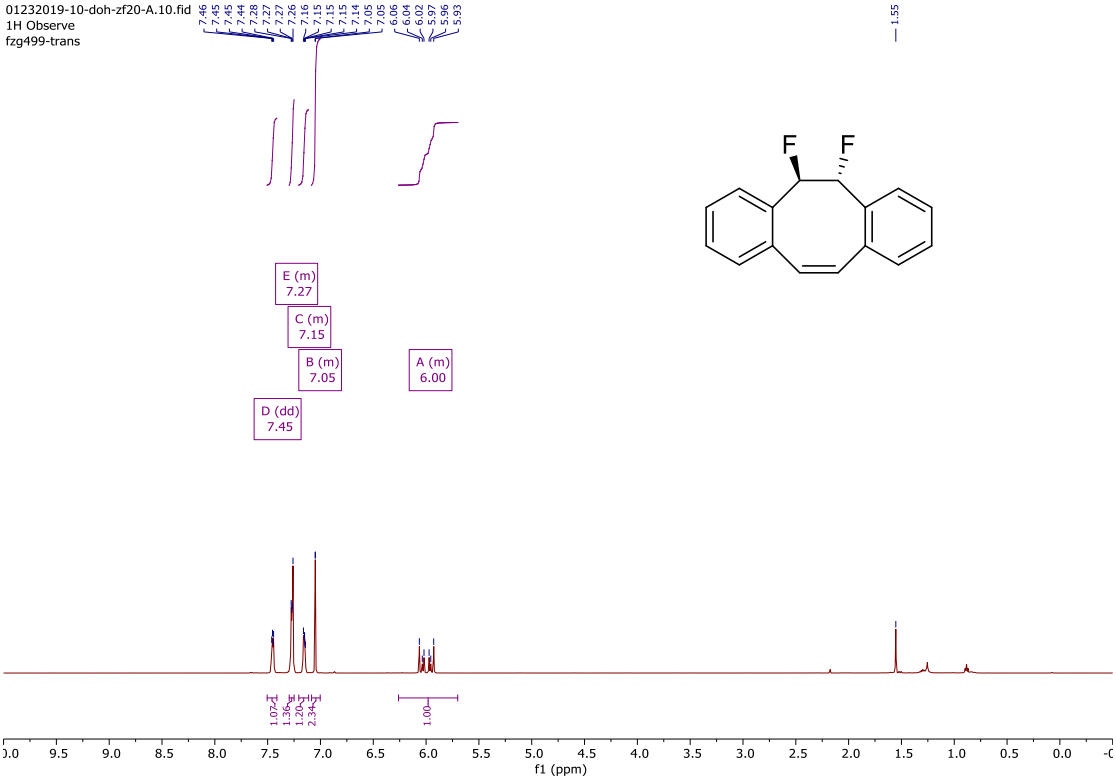
^{19}F {^{1}H} NMR 13



^{13}C NMR 13


01222019-8-doh-zf20-M.13.fid
13C Observe with 1H decoupling - D1 = 2s
fzg499-cis
133.40
133.07
132.95
132.82
131.83
129.48
129.42
128.10
127.49
92.46
92.25
90.69
90.48
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

^{1}H NMR 14



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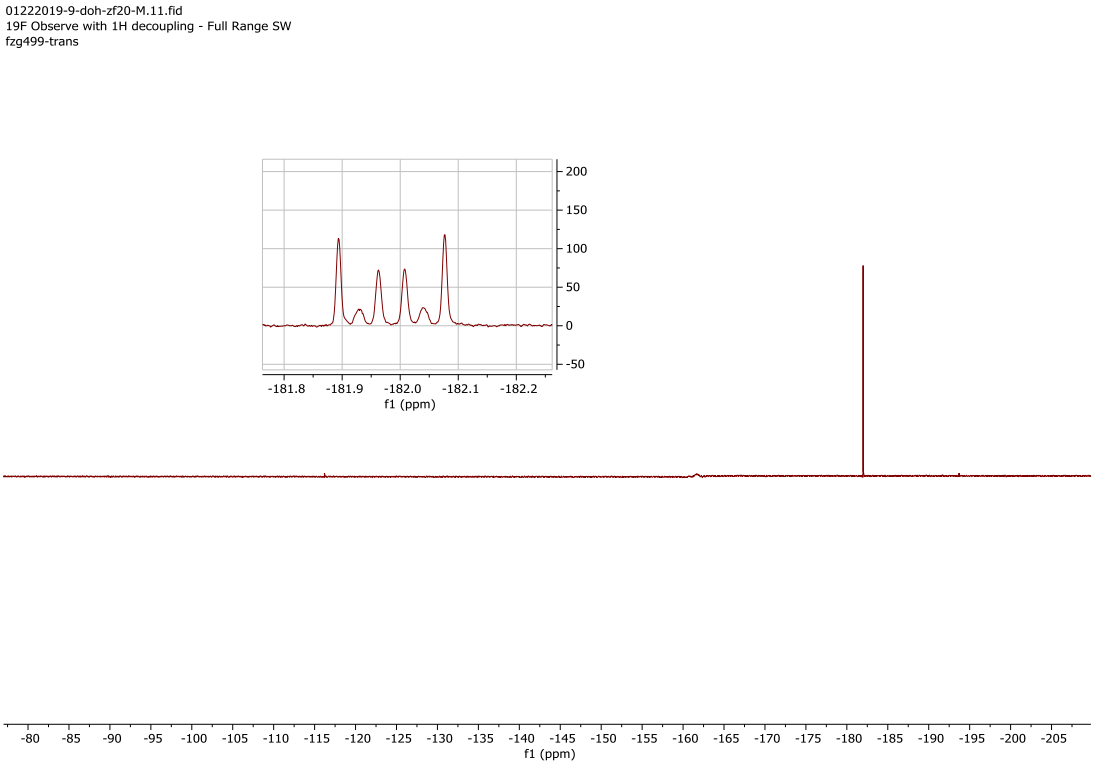

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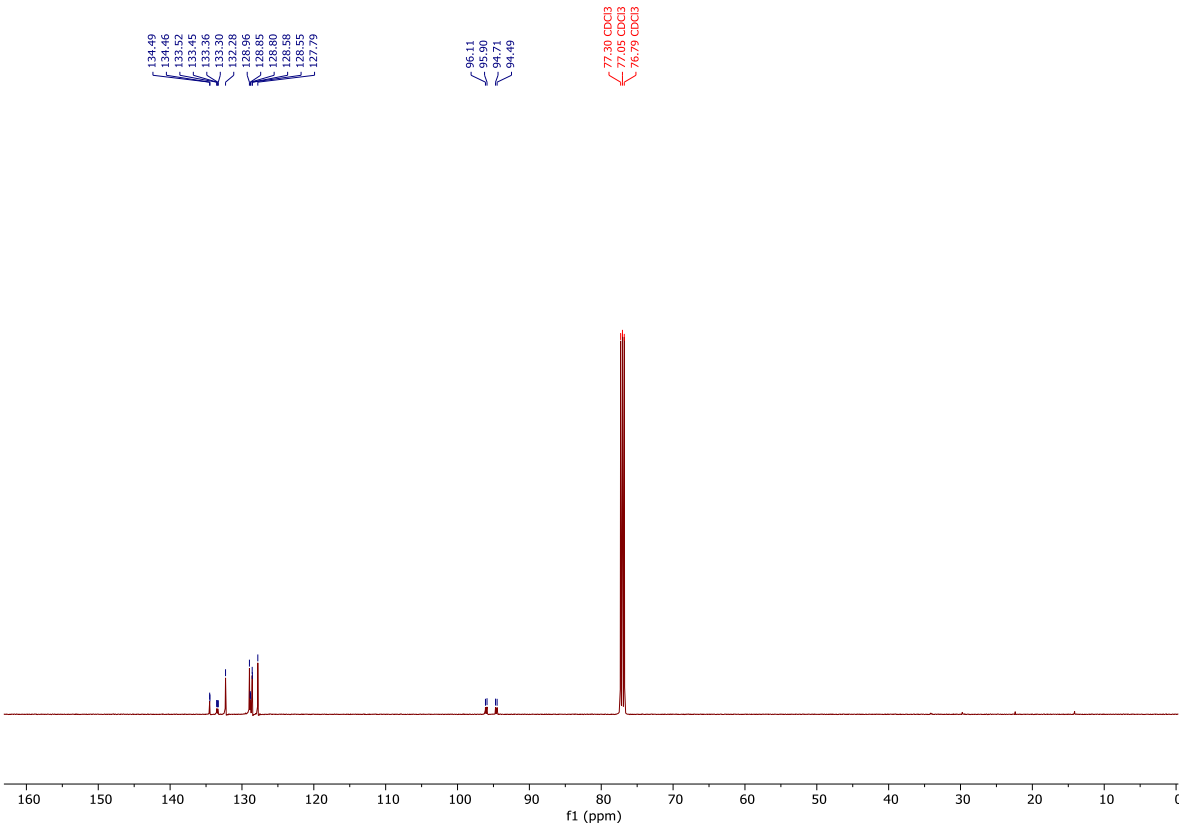
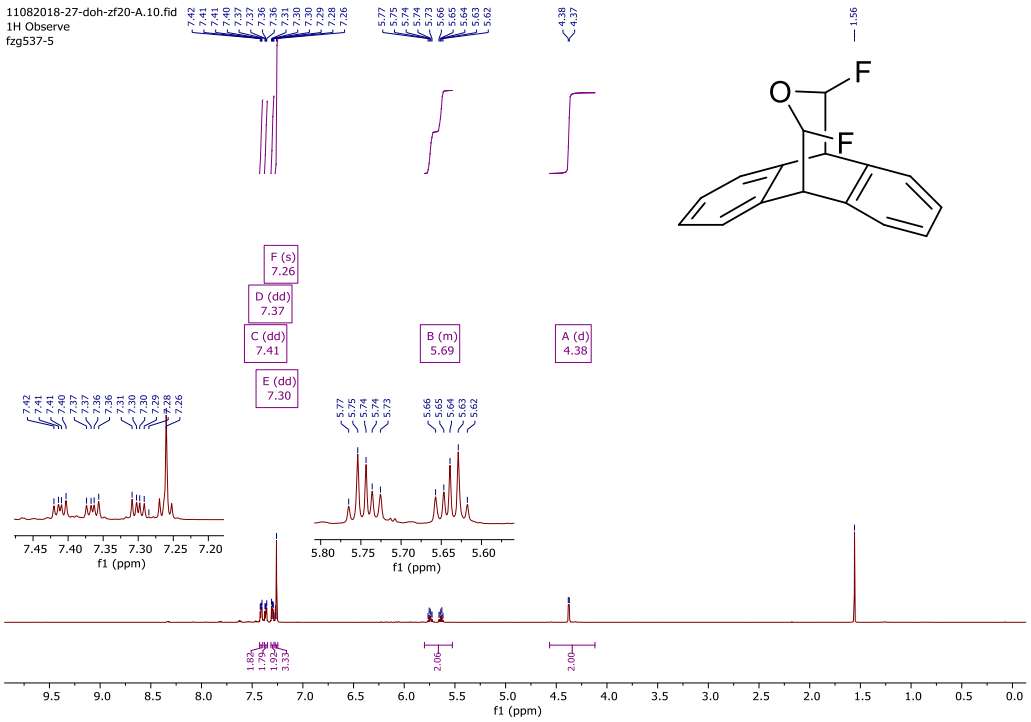
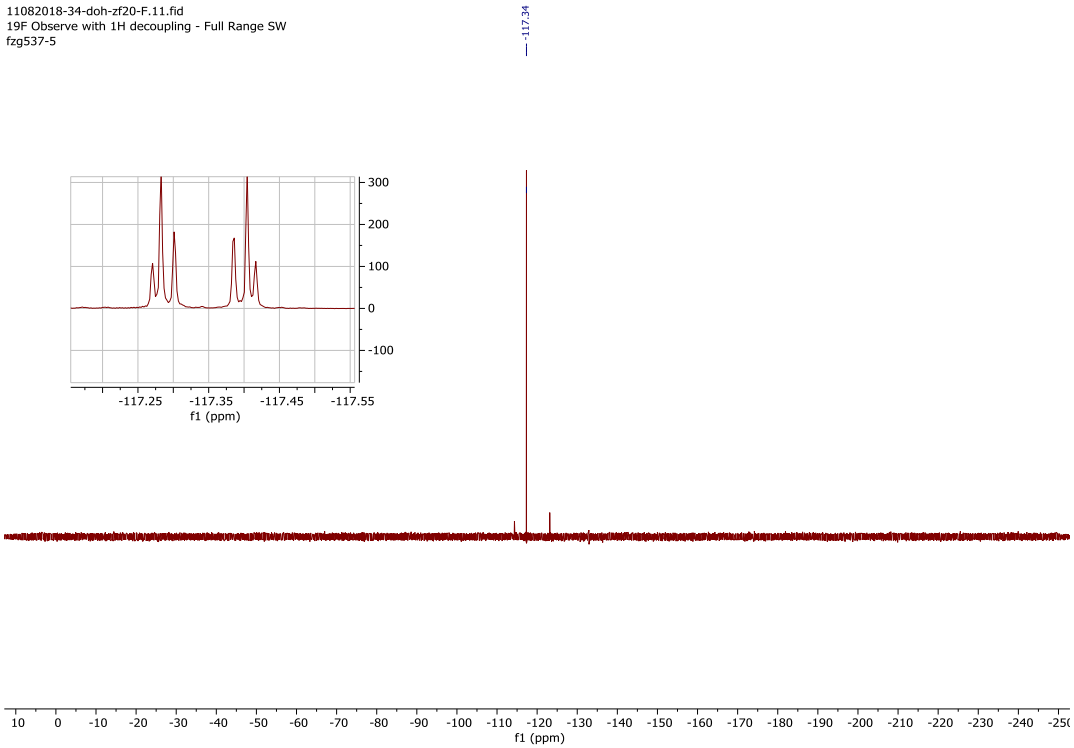

134.49
134.46
133.52
133.45
133.36
133.30
132.28
128.96
128.85
128.80
128.58
128.55
127.79
96.11
95.90
94.71
94.49
77.30 CDCl3
77.05 CDCl3
76.79 CDCl3
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

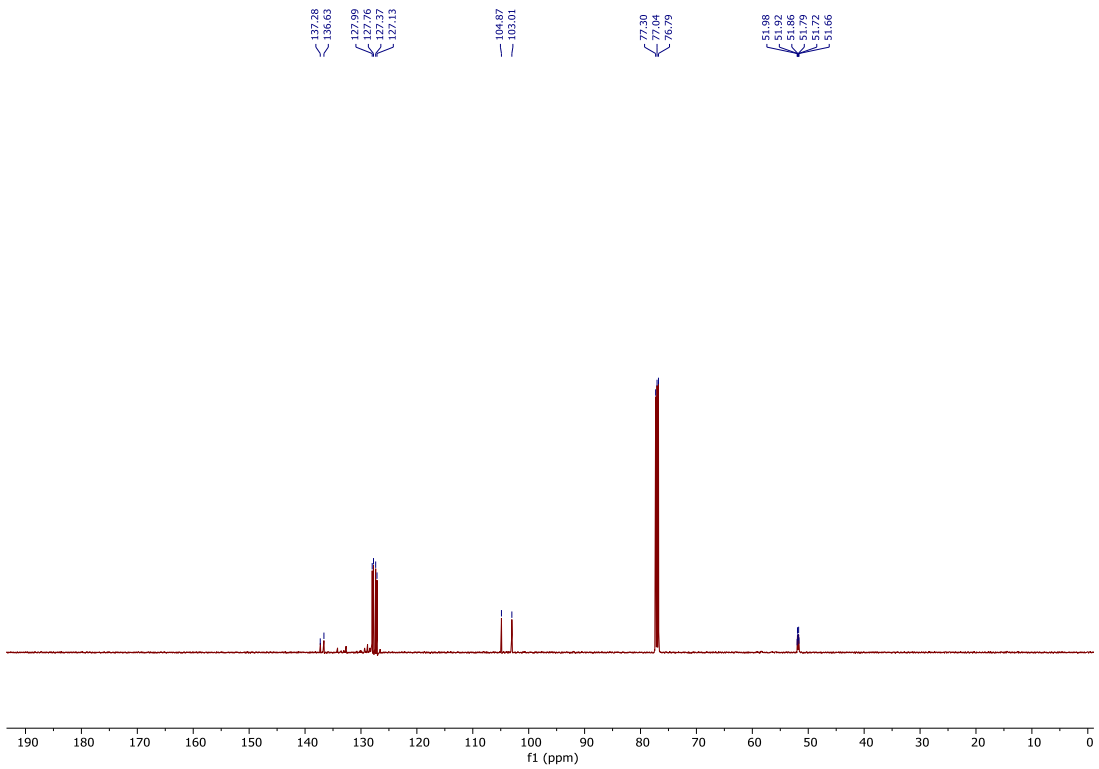
^{1}H NMR 11



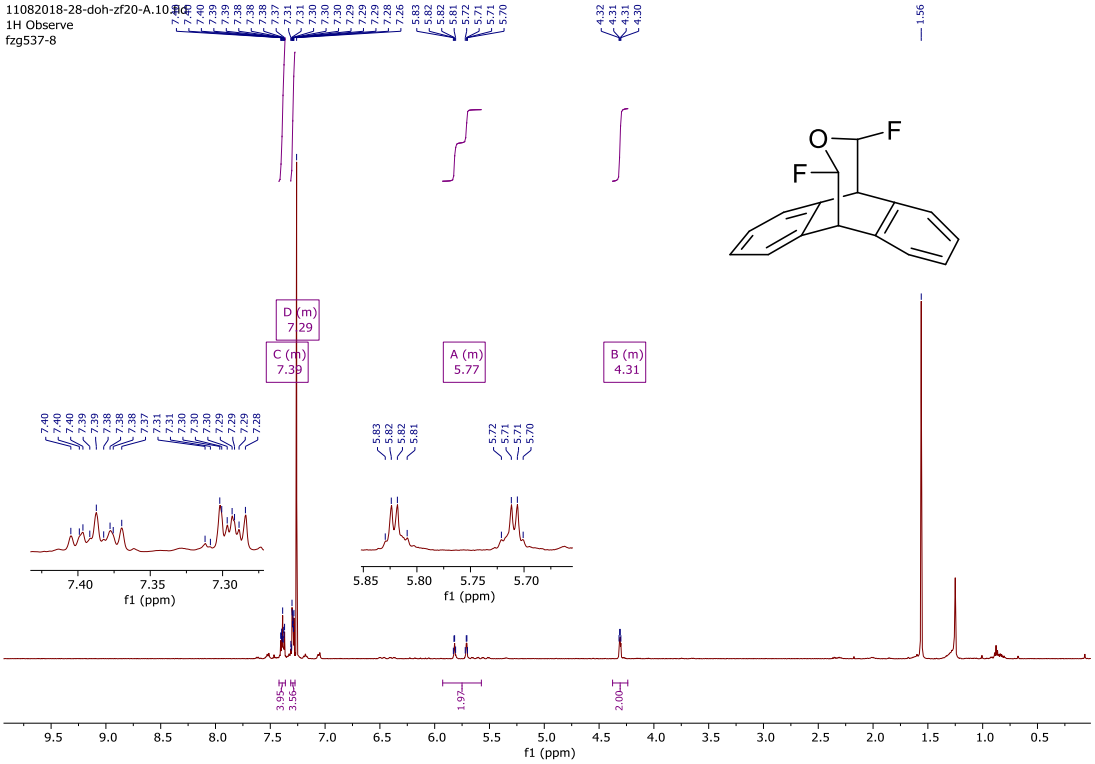
^{19}F {^{1}H} NMR 11



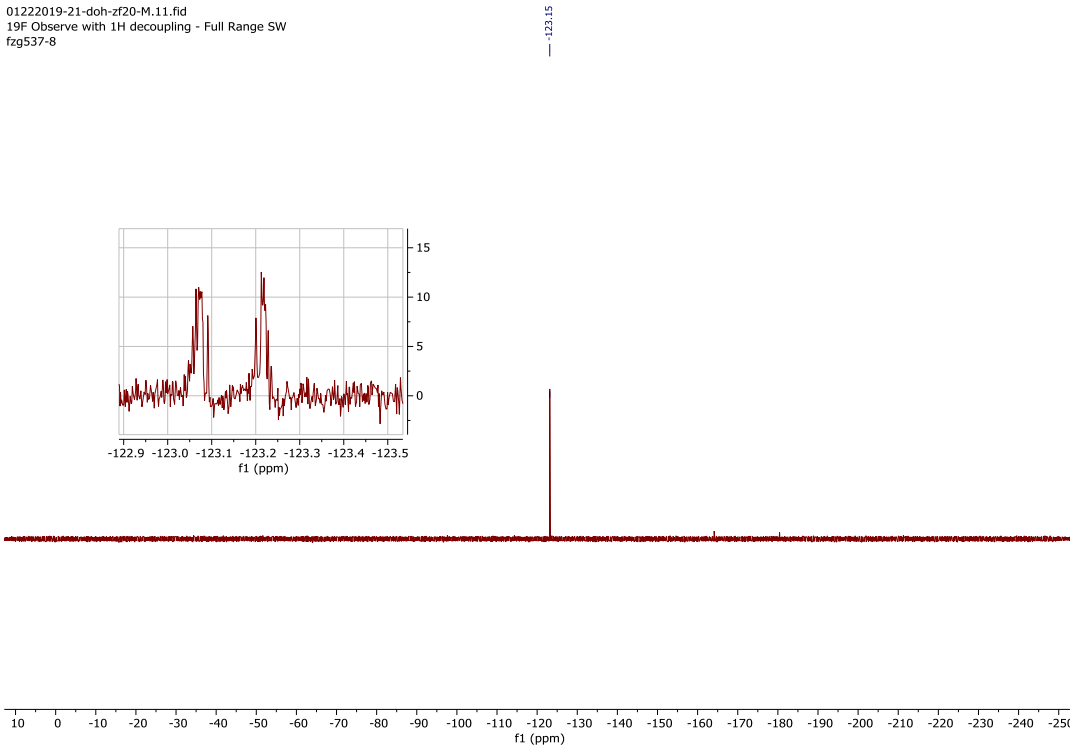
^{13}C NMR 11


137.28
136.63
127.99
127.76
127.37
127.13
104.87
103.01
77.30
77.04
76.79
51.98
51.92
51.86
51.79
51.72
51.66
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

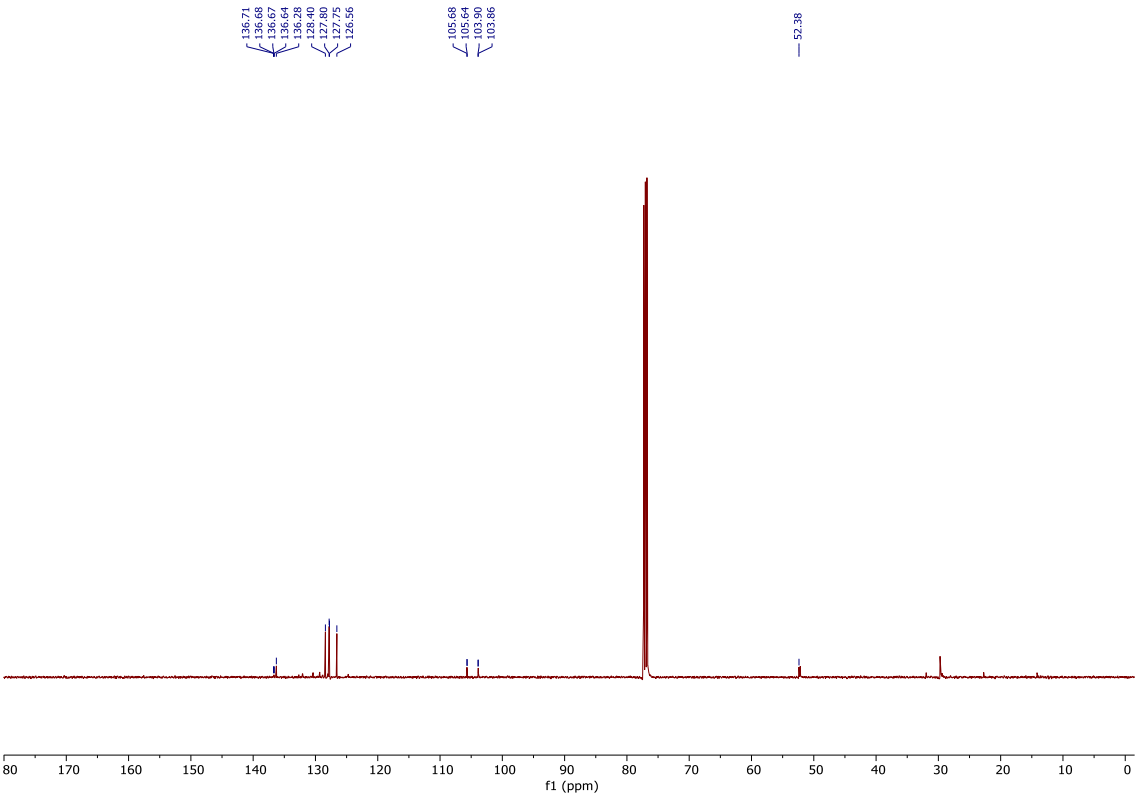
^{1}H NMR 10



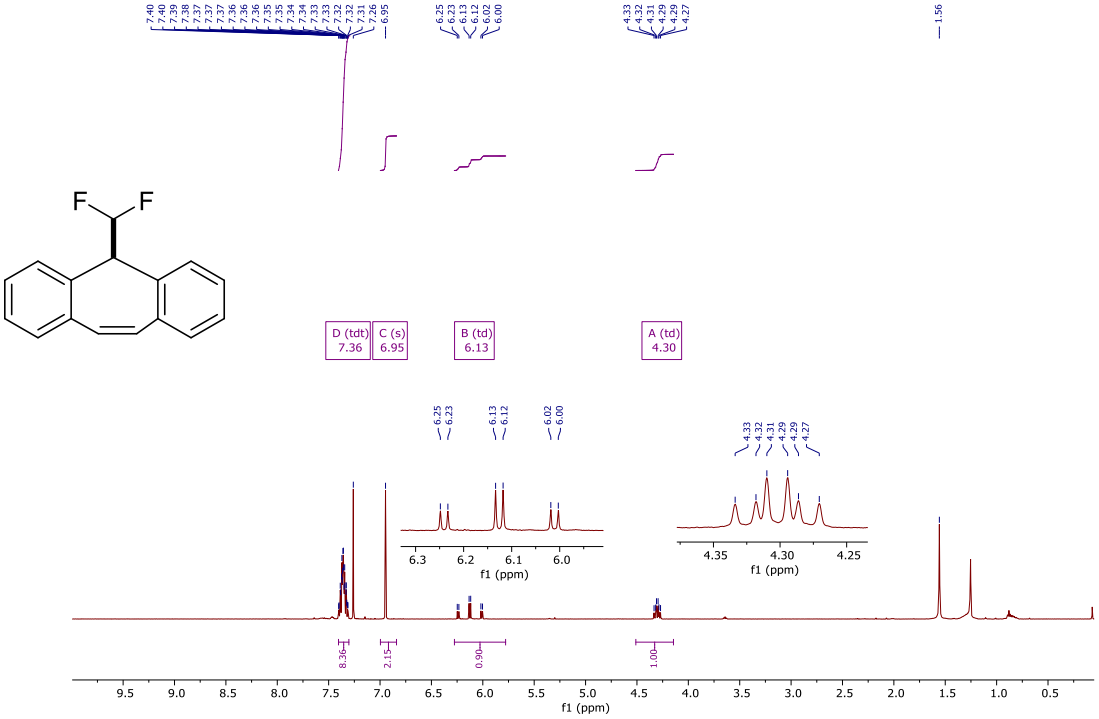
^{19}F {^{1}H} NMR 10



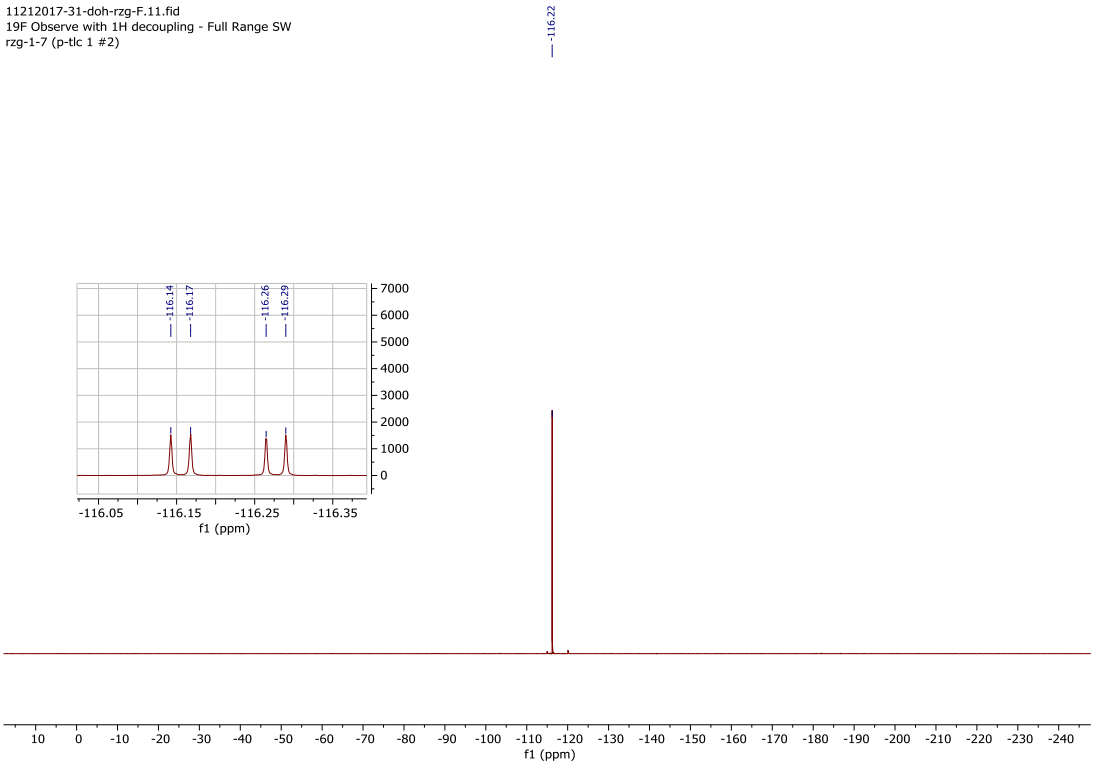
^{13}C NMR 10


136.71
136.68
136.67
136.64
136.28
128.40
127.80
127.75
126.56
105.68
105.64
103.90
103.86
52.38
80
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

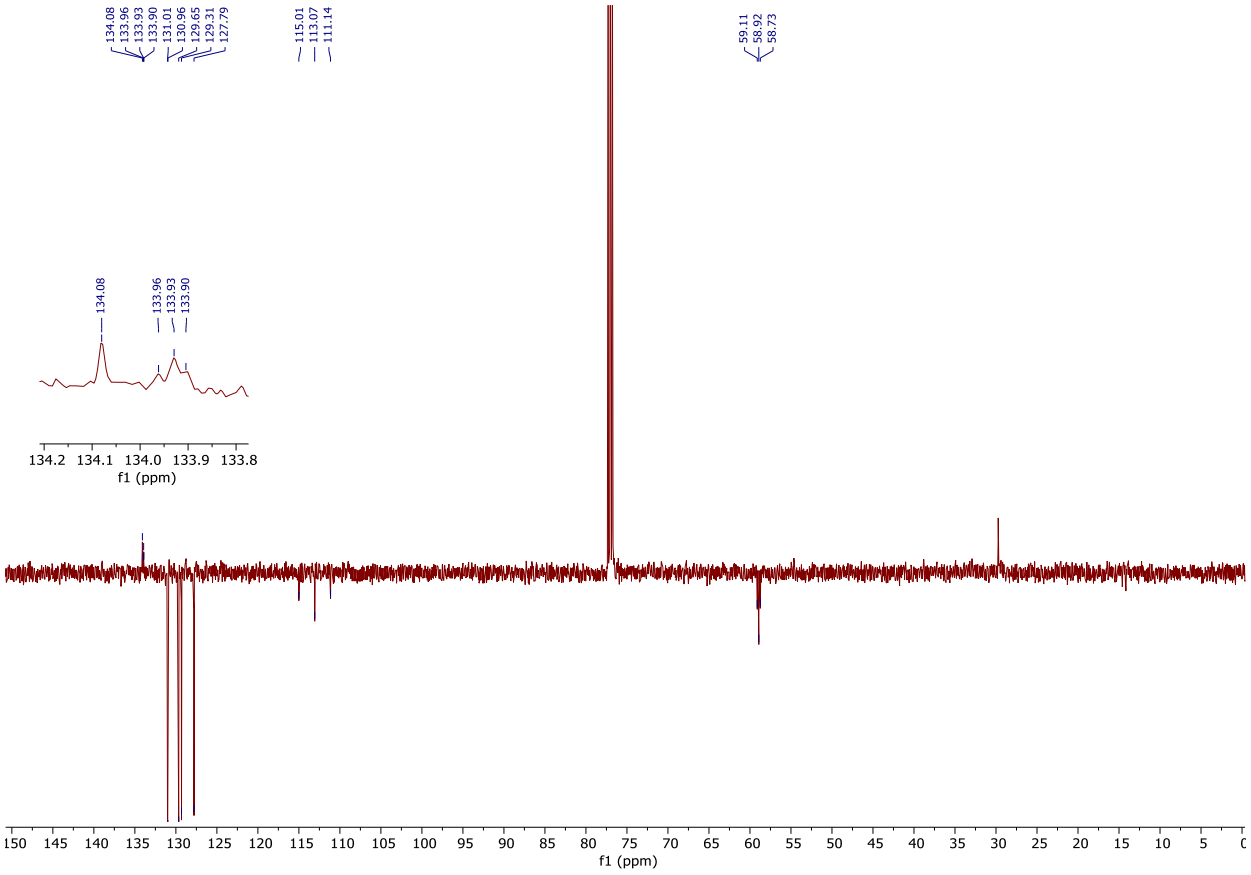
^{1}H NMR 12



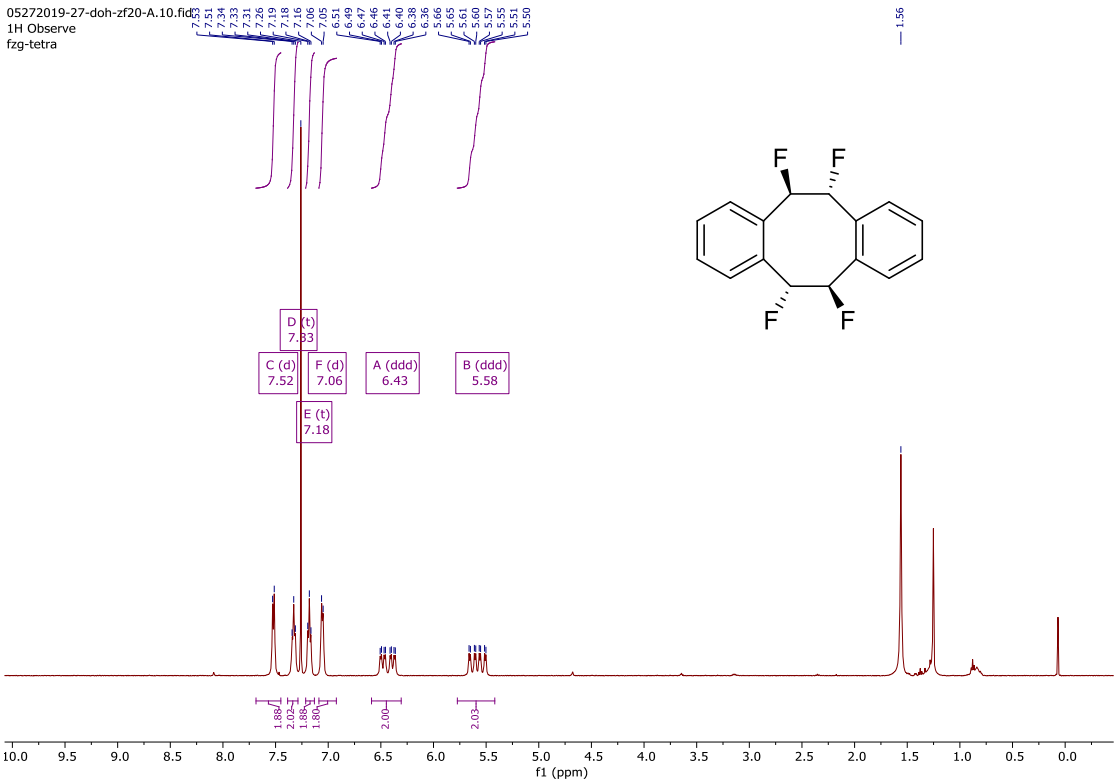
^{19}F {^{1}H} NMR 12



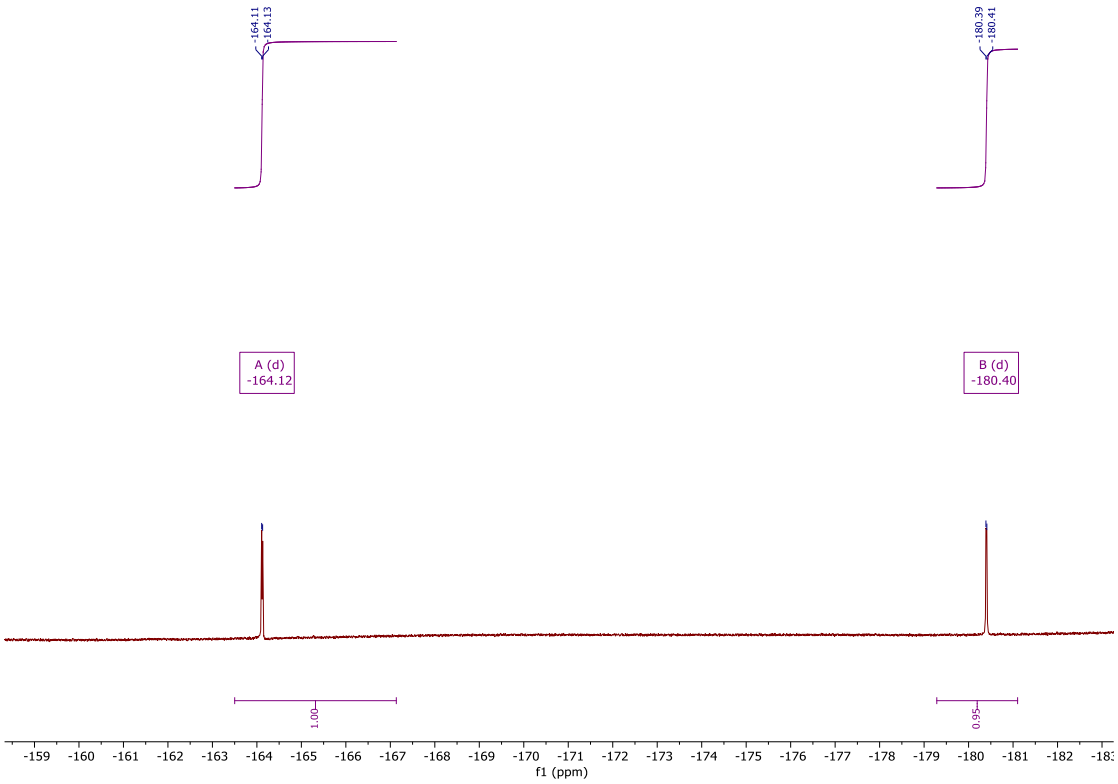
^{13}C NMR 12


134.08
133.96
133.93
133.90
131.01
130.96
129.65
129.31
127.79
115.01
113.07
111.14
59.11
58.92
58.73
134.2 134.1 134.0 133.9 133.8
f1 (ppm)
150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5
f1 (ppm)

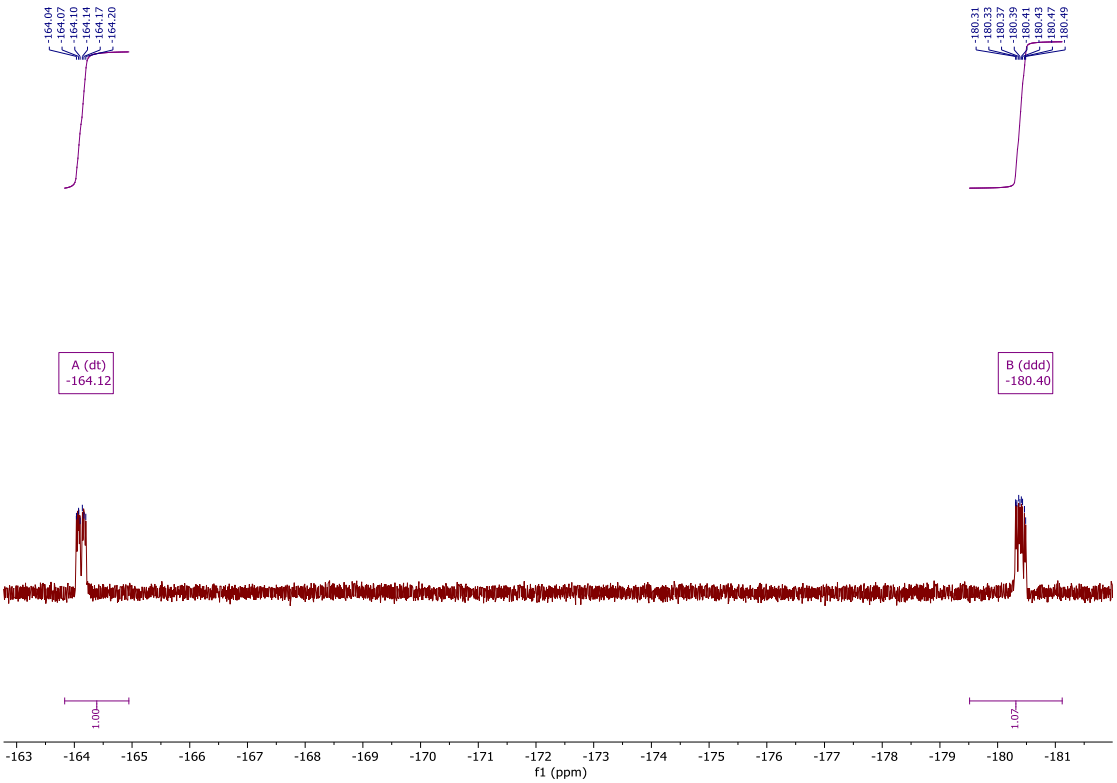
^{1}H NMR 15



^{19}F {^{1}H} NMR 15



^{19}F NMR 15



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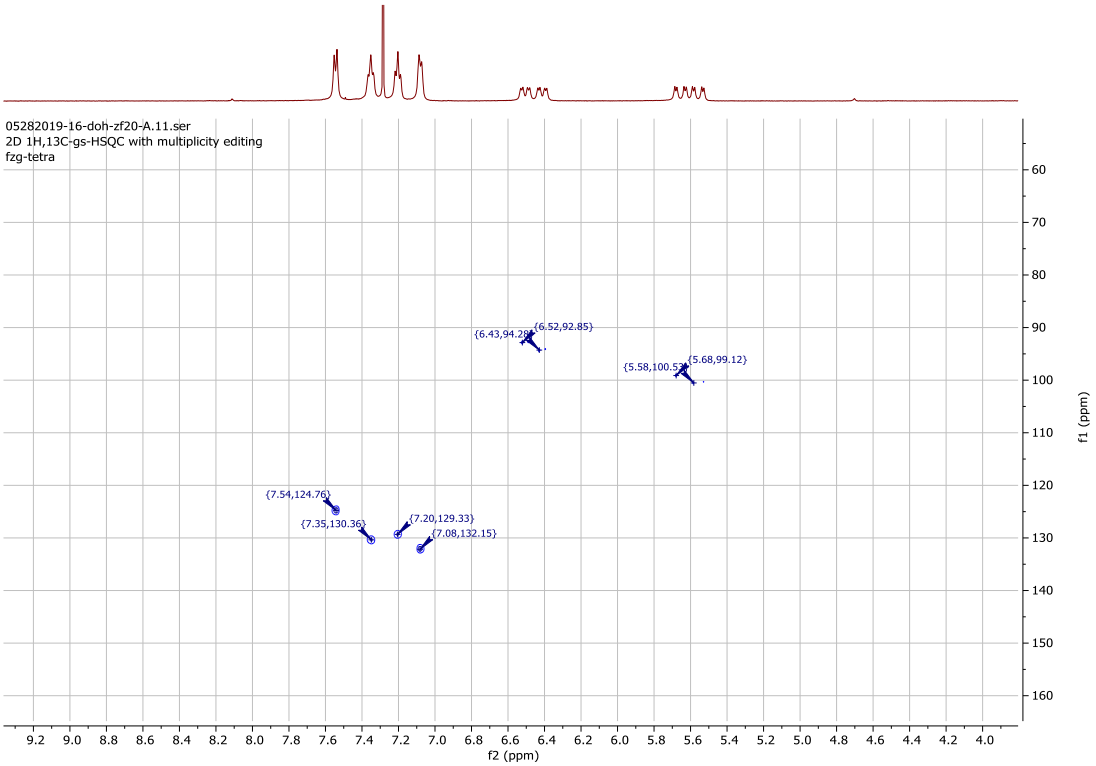

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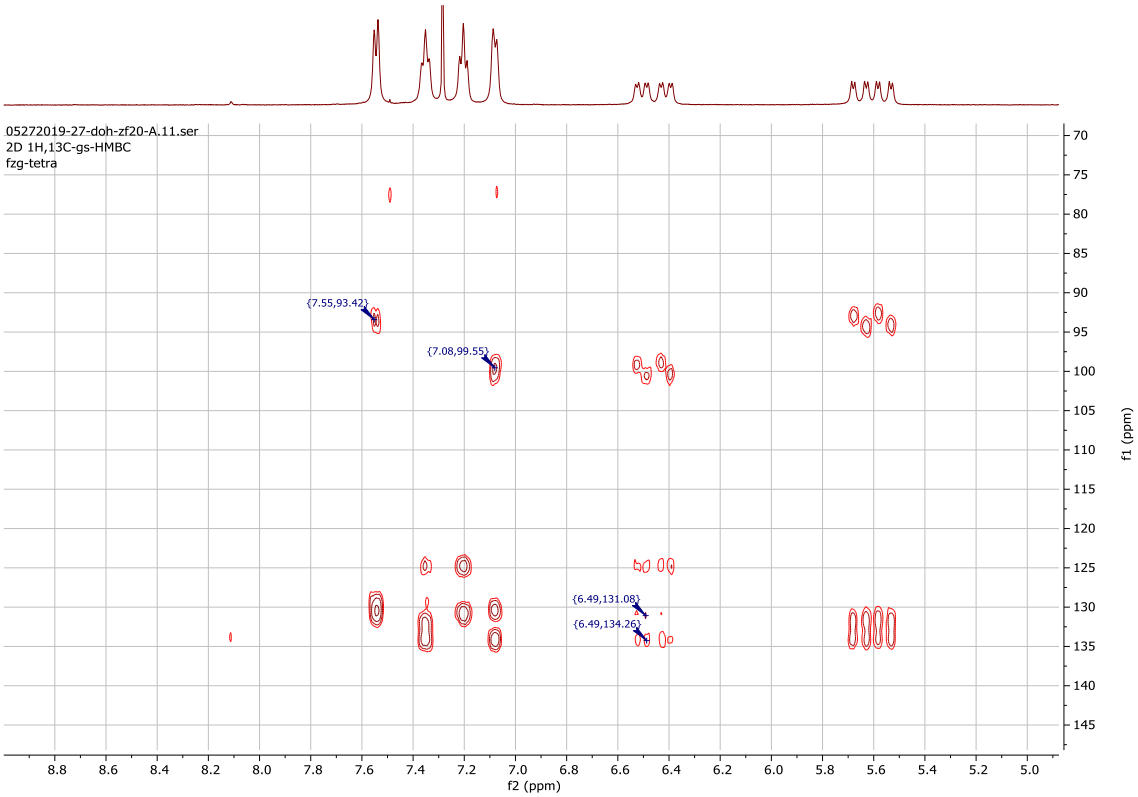
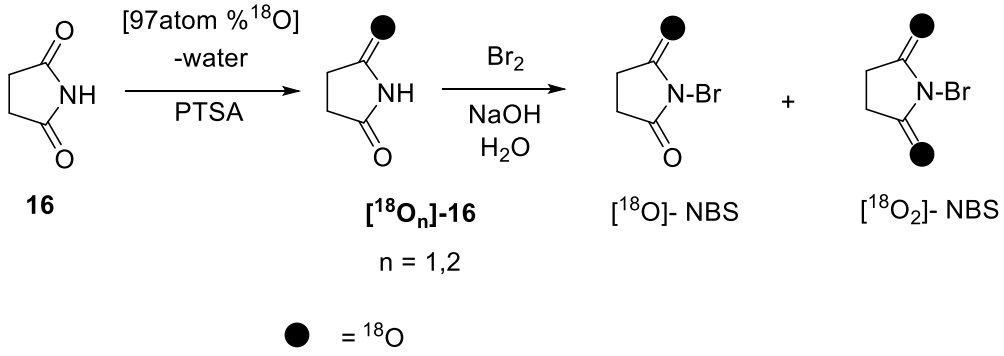

05272019-27-doh-zf20-A.11.ser
2D 1H,13C-gs-HMBC
fzg-tetra
{7.55,93.42}
{7.08,99.55}
{6.49,131.08}
{6.49,134.26}
f1 (ppm)
f2 (ppm)

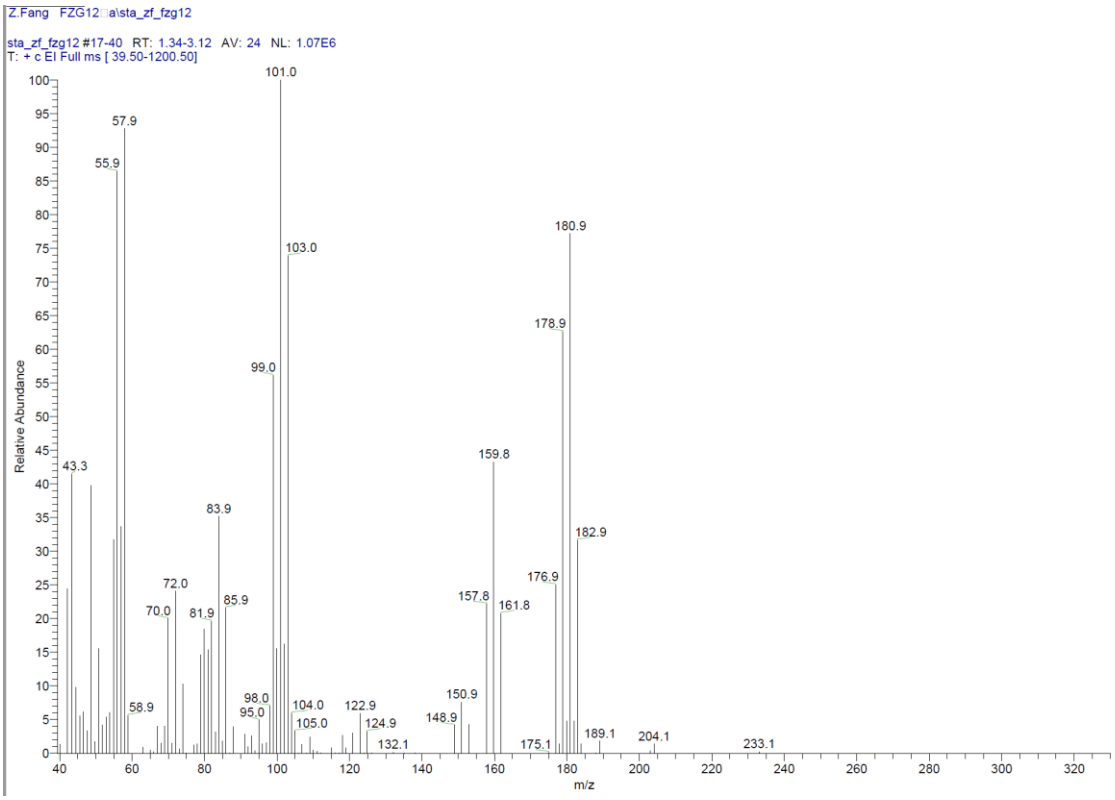
^{18}O labelled NBS

Preparation of ^{18}O labelled NBS



Succinimide (150 mg, 1.5 mmol) and *p*-Toluenesulfonic acid monohydrate (catalytic amount, 5 mg) were added into ^{18}O-water (97 atom % ^{18}O, 500 µL) in a Schlenk flask. The mixture was stirred at 60°C for overnight. After reaction, the mixture was extracted with DCM and the combined organic phase was removed *in vacuo* to get the pure ^{18}O labelled succinimide (128 mg) without further purification. ^{18}O labelled succinimide **16** (128 mg) was then dissolved in a mixture of NaOH (56.9 mg, 1.4 mmol) and water (2 mL). Cooled the mixture in an ice bath and added Br_2 (223.7 mg, 71.7 µL, 1.4 mmol) at once while stirring violently. The colour of mixture became orange and the NBS was precipitated immediately. Stir for 10 minutes, then filter the precipitated product and wash with ice water. The ^{18}O labelled NBS (154 mg, yield around 68 %) was dried in a desiccator. **HRMS** (EI^+) m/z calcd. for $C_4H_4O_2N^{79}Br$ $[M]^+$ 176.9420, found 176. 9425; $C_4H_4O_1{}^{18}O_1N^{79}Br$ $[M]^+$ 178.9462, found 178.9459.

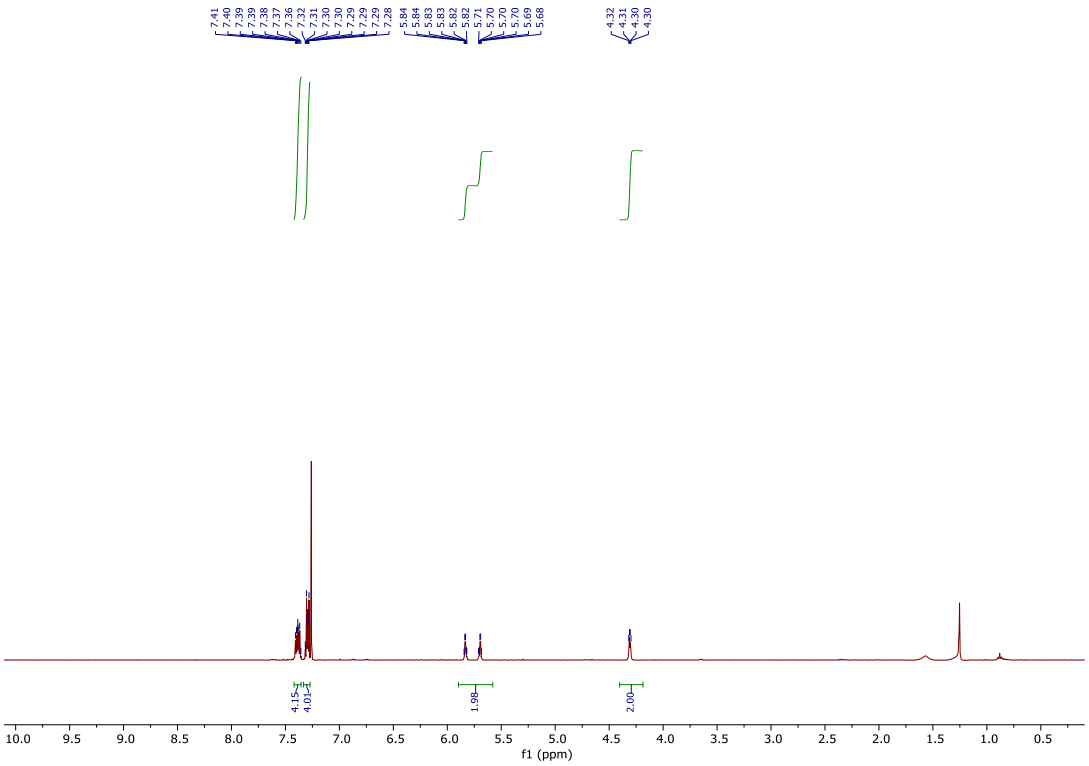
MS result for ^{18}O labelled NBS



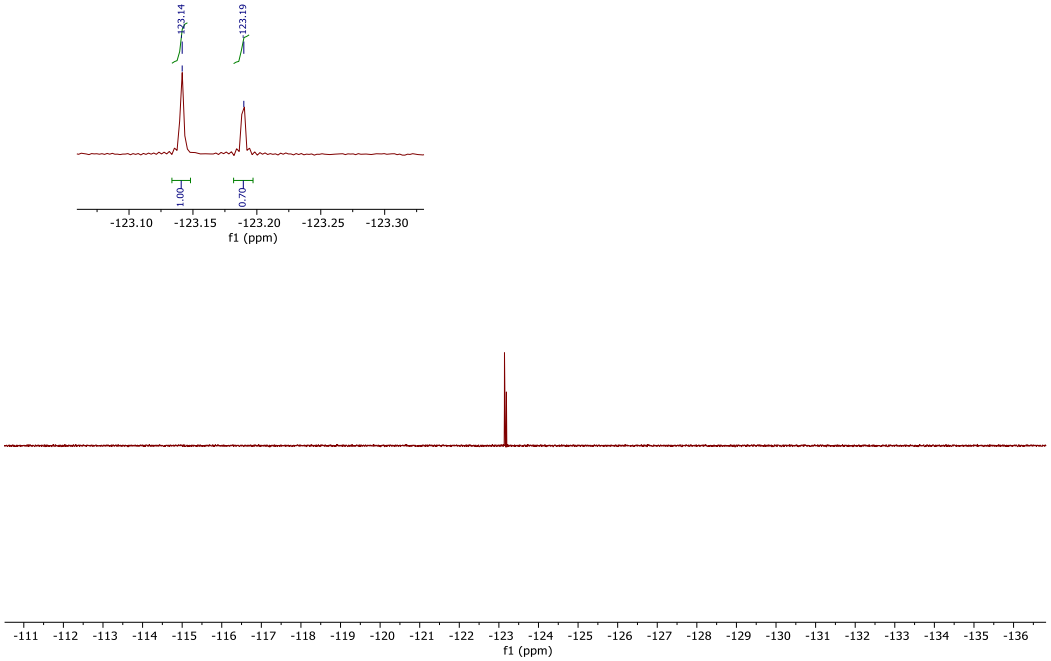
NMR and MS results for ^{18}O labelled 10 and 11

The preparation of ^{18}O labelled **10** and **11** is through the general procedure with an aliquot (100 µL) of [97%-atom-^{18}O]-water.

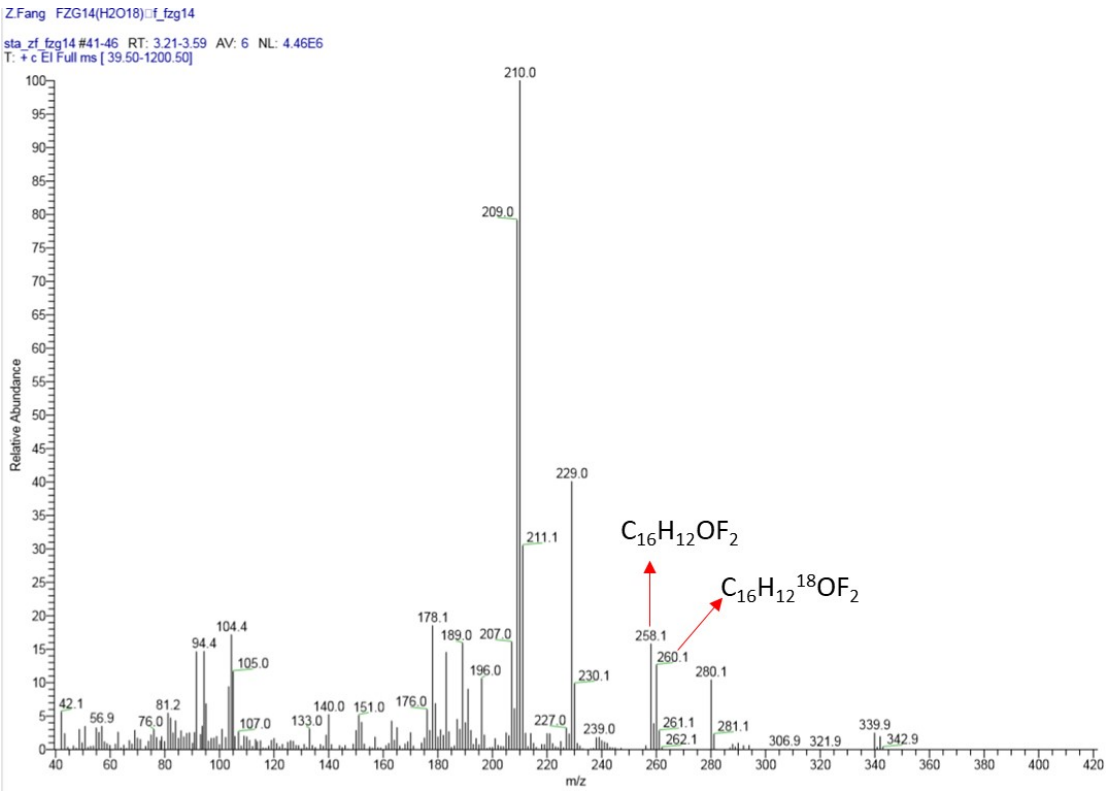
^{1}H NMR of ^{18}O labelled 10



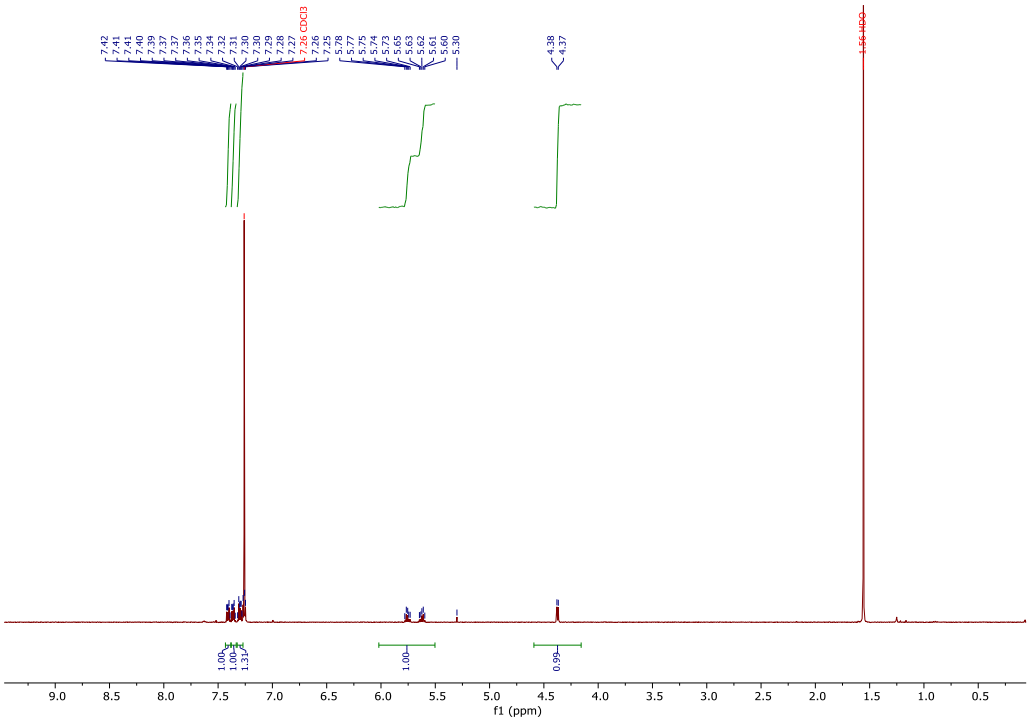
^{19}F {^{1}H} NMR of ^{18}O labelled 10



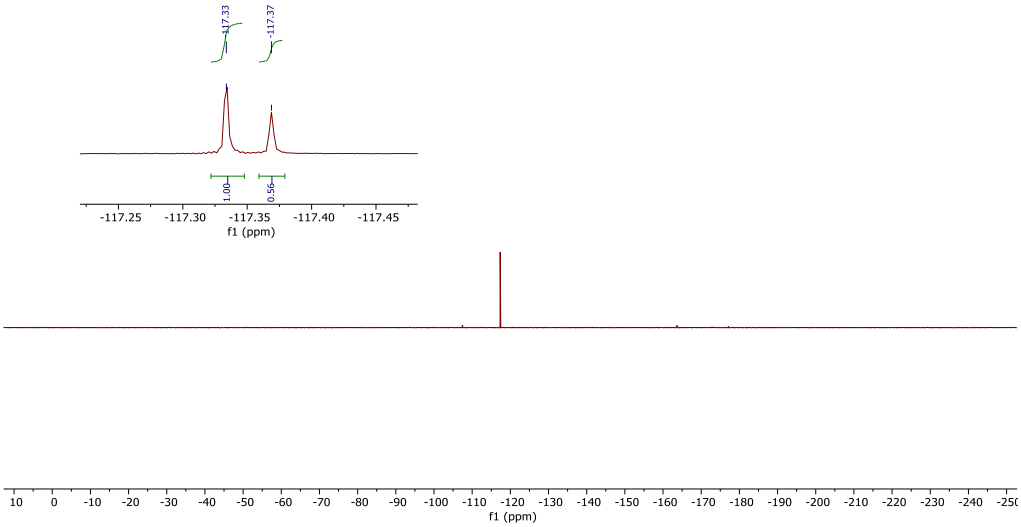
MS result for ^{18}O labelled NBS 10



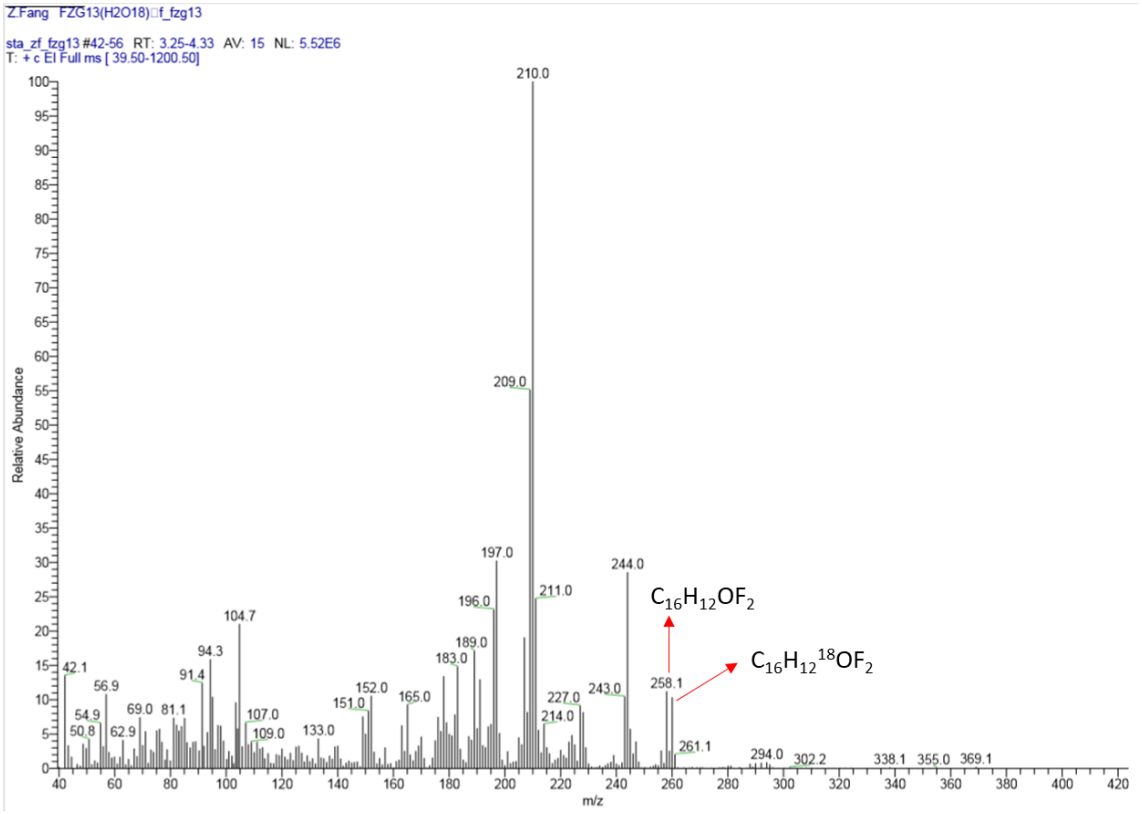
^{1}H NMR of ^{18}O labelled 11



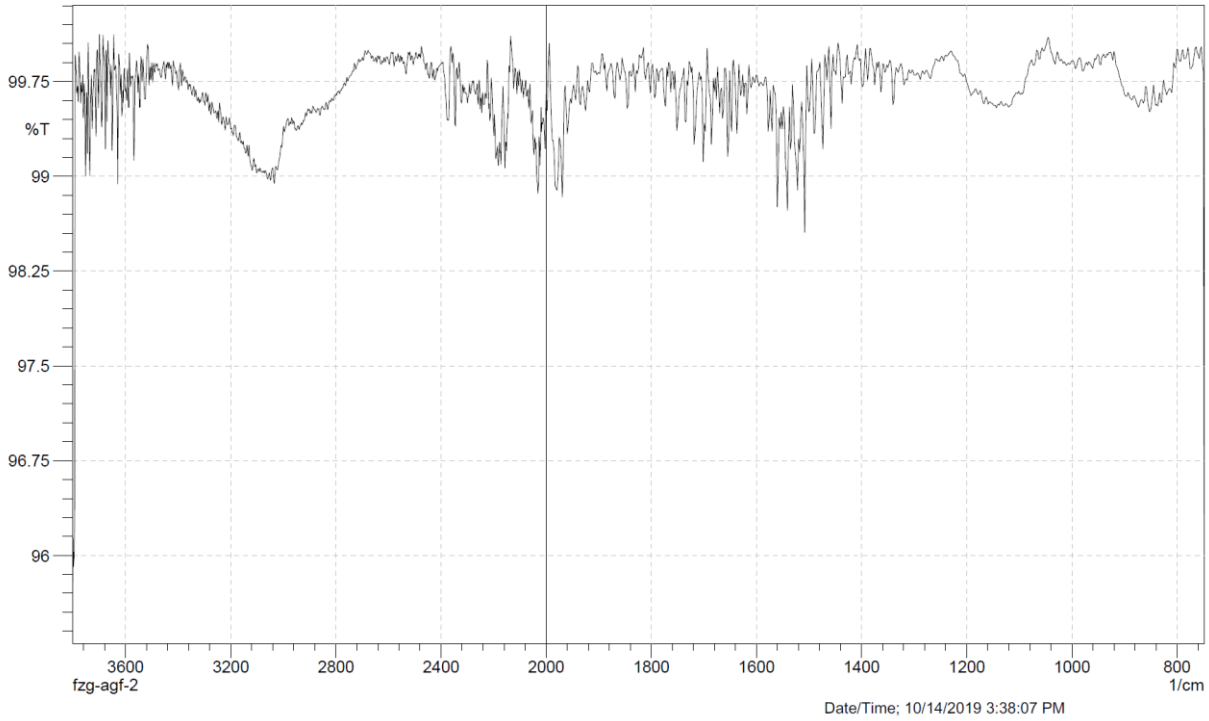
^{19}F {^{1}H} NMR of ^{18}O labelled 11



MS result for ^{18}O labelled NBS 11



IR of commercially applied AgF



X-Ray Diffraction

X-ray diffraction data for all compounds were collected at either 178, 173 or 125 K using a Rigaku MM-007HF High Brilliance RA generator/confocal optics with XtaLAB P100, or P200 diffractometer [Cu Kα radiation (λ = 1.54187 Å)]. Intensity data were collected using either ω steps or both ω and ϕ steps accumulating area detector images spanning at least a hemisphere of reciprocal space. Data for all compounds analysed were collected using CrystalClear[1] and processed (including correction for Lorentz, polarization and absorption) using CrysAlisPro.[2] Structures were solved by direct (SIR2004[3] SIR2011[4] or dual-space (SHELXT[5] methods and refined by full-matrix least-squares against F^2 (SHELXL-2018/3[5]. Non-hydrogen atoms were refined anisotropically, and hydrogen atoms were refined using a riding model. The structure of **10** showed disorder in the orientation of the –CHF-O-CHF- bridge. The atoms of the minor component were refined isotropically, with restraints to C-F distances and similarity of thermal motion. The structure of **11** shows larger thermal ellipsoids than expected, even given it was run at the highest temperature of the series. Diffraction images show some smearing at low angles, which may partially explain this. The structure is unambiguously determined, however care should be taken when considering bond distances or angles. Two of the structures (**12** and **14**) showed narrow (~5 Å) channels running down the *c*-axis containing diffuse electron density (**12**: 340 $Å^3$, **14**: 360 $Å^3$) and the SQUEEZE[6] routine implemented in PLATON[7] as used to remove the contribution to the diffraction pattern of the unordered electron density in the void spaces. All calculations except SQUEEZE were performed using either the CrystalStructure[8] Olex2[9] interface. Figures were prepared using Mercury[10] or CrystalMaker.[11] Selected crystallographic data are presented in Table 1. Thermal ellipsoid plots of the structures are presented in figures S1-S6 CCDC 1947537-1947542 contains the supplementary crystallographic data for this paper. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures.

Table 1. Selected crystallographic data.

	10	**11**	**12**	**13**	**14**	**15**
empirical formula	$C_{16}H_{12}F_2O$	$C_{16}H_{12}F_2O$	$C_{16}H_{12}F_2$	$C_{16}H_{12}F_2$	$C_{16}H_{12}F_2$	$C_{16}H_{12}F_4$
fw	258.27	258.27	242.27	242.27	242.27	280.26
crystal description	Colourless plate	Colourless prism	Colourless needle	Colourless needle	Colourless needle	Colourless plate
crystal size [mm^3]	0.09×0.03×0.01	0.30×0.06×0.04	0.14×0.03×0.01	0.02×0.01×0.01	0.16×0.02×0.02	0.12×0.10×0.03
space group	*Iba*2	$P3_1$	$R\bar{3}$	$P2_1/c$	$R\bar{3}$	$P2_1/c$
a [Å]	14.2552(3)	8.8519(6)	34.4377(4)	10.4484(5)	35.747(2)	12.7703(4)
b [Å]	22.1202(7)			12.8848(4)		7.4822(2)
c [Å]	7.4973(2)	13.9613(10)	5.42477(7)	8.6234(4)	4.9460(4)	13.8047(5)
α [°]						
β [°]				100.333(4)		110.433(4)
γ [°]						
vol $[Å]^3$	2364.11(11)	947.39(15)	5571.60(12)	1142.10(9)	5473.5(6)	1236.05(8)
Z	8	3	18	4	18	4
ρ (calc) [g/cm^3]	1.451	1.358	1.300	1.409	1.323	1.506
μ [mm^{-1}]	0.930	0.870	0.790	0.856	0.804	1.113
F(000)	1072	402	2268	504	2268	576
reflections collected	13323	9709	22504	12689	19054	13407
independent reflections (R_{int})	2383 (0.1145)	2225 (0.0690)	2550 (0.0421)	2325 (0.0864)	2212 (0.1080)	2524 (0.0391)
data/restraints/parameters	2383/27/185	2225/1/172	2550/0/163	2325/0/164	2212/0/163	2524/0/181

GoF on F^2	1.043	1.058	1.062	1.075	1.036	1.031
R_1 [$I > 2\sigma(I)$]	0.0531	0.0695	0.0445	0.0578	0.0527	0.0625
wR_2 (all data)	0.1362	0.2084	0.1235	0.1781	0.1392	0.1869
largest difference peak/hole [e/Å^3]	0.24, -0.30	0.44, -0.19	0.55, -0.35	0.28, -0.25	0.42, -0.23	0.54, -0.32
Flack parameter[12]	0.07(18)	0.1(3)	-	-	-	-

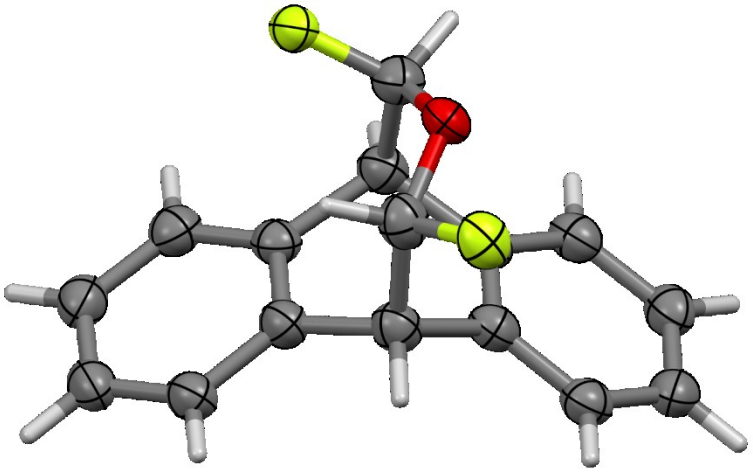


Figure S1. Thermal ellipsoid plot (50 % probability ellipsoids) of **10**. Minor component of disorder omitted for clarity.

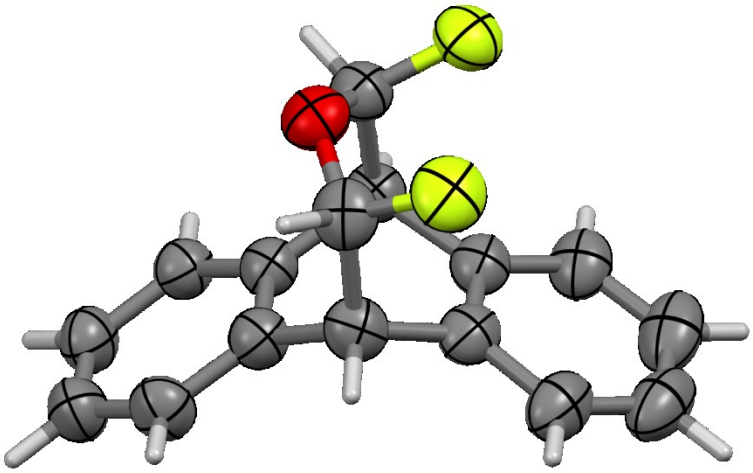


Figure S2. Thermal ellipsoid plot (30 % probability ellipsoids) of **11**.

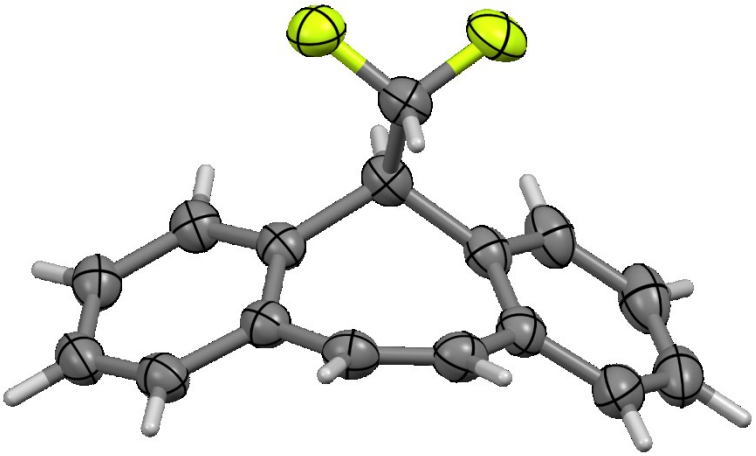


Figure S3. Thermal ellipsoid plot (50 % probability ellipsoids) of **12**.

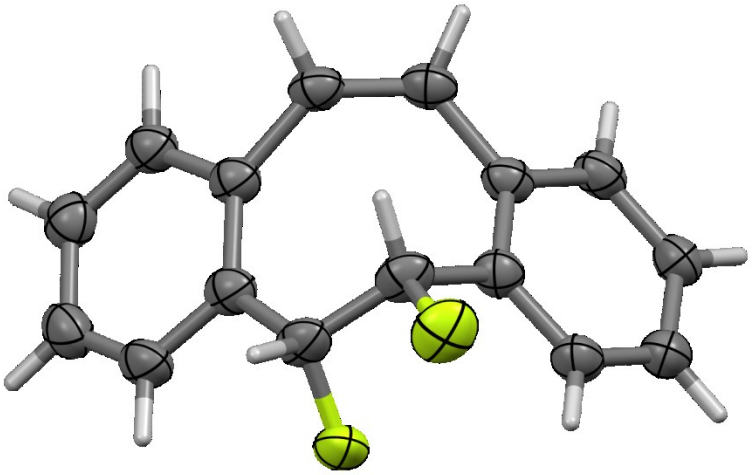


Figure S4. Thermal ellipsoid plot (50 % probability ellipsoids) of **13**.

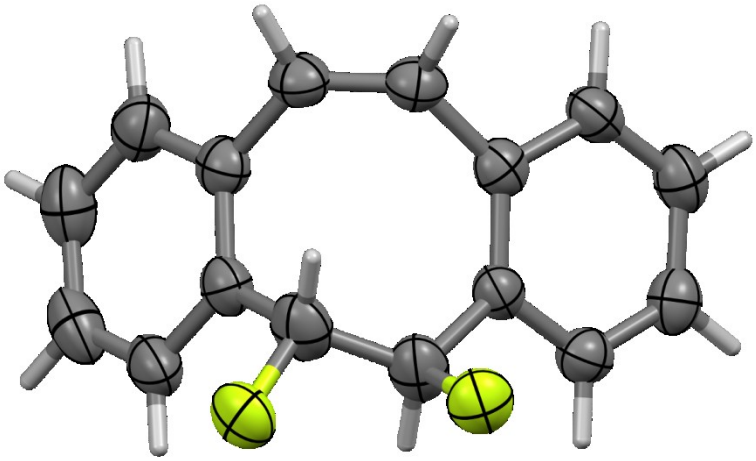


Figure S5. Thermal ellipsoid plot (50 % probability ellipsoids) of **14**.

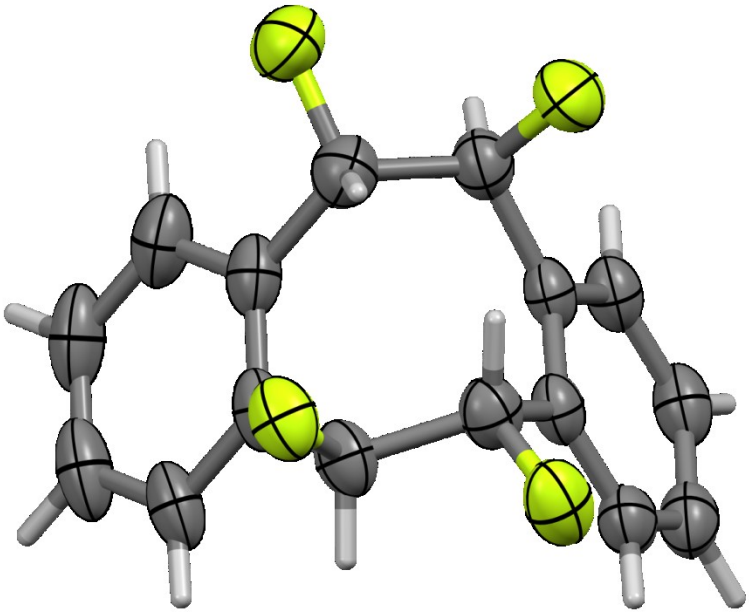


Figure S6. Thermal ellipsoid plot (50 % probability ellipsoids) of **15**.

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