ESI: Diverse Structure and Reactivity of Pentamethylcyclopentadienyl Antimony(III) Cations

Omar Coughlin,[a] Tobias Krämer[b] and Sophie L. Benjamin[a]

a) School of Science and Technology, Nottingham Trent University, Clifton Lane, NG11 8NS, Nottingham, United Kingdom.
b) Department of Chemistry, Maynooth University, Maynooth, Co Kildare, Ireland.

Experimental Methods

Caution: All antimony containing compounds should be treated as toxic. Cp*Li is pyrophoric. All manipulations were performed under an atmosphere of dry N_2 using standard Schlenk or glovebox (Mbraun Unilab 2000) techniques unless otherwise stated. All glassware was dried in an oven at 150^{o}C and cooled under vacuum before use. Tetrahydrofuran (THF), CH_2Cl_2, toluene, and n-hexane were dried using an Mbraun MB SPS5. All deuterated solvents were dried and stored over 4 Å molecular sieves. $SbCl_3$ was sublimed *in vacuo* at 40-65^{o}C before use. Triethylsilane was distilled over $CaH_{2,}$ degassed by freeze/pump/thaw and stored over 4 Å moleuclar sieves. ααα-trichlorotoluene, and 1,2-diflurorobenzene (DFB) were degassed by freeze/pump/thaw and dried over 4 Å moleuclar sieves. All other reagents were used as received unless otherwise stated. $[Et_3Si(C_7H_8)][B(C_6F_5)_4]$ was synthesised according to literature methods,[1,2] and recrystalised in toluene at -10 ^{o}C or by the addition of Et_3SiH to a solution of $[Ph_3C][B(B(C_6F_5)_4)]$ in toluene. $Cp^*{}_2SbCl$ was synthesised according to literature methods.[3] IMes was synthesised using a modified literature procedure.[4] Elemental analysis was performed by Stephen Boyer at London Metropolitan University.

Synthesis of Cp*Li

1.6 M n-BuLi in hexane (9.0 mL, 14 mmol) was added dropwise to a solution of pentamethylcyclopentadiene (1.74 g, 12.77 mmol) in THF (50 mL) at -78 ^{o}C. A slightly off white suspension formed on warming to room temperature. The suspension was stirred at room temperature for 2h. The solution was removed by cannula filtration and the resulting powder was washed with hexane (3x20 mL). The solid was dried *in vacuo* to yield a white powder (1.168 g, 8.22 mmol, 64%). The product was suspended in $CDCl_3$ and a ^{1}H NMR spectrum was obtained to confirm absences of any starting material.

Synthesis of Cp^*SbCl_2

To a suspension of Cp*Li (0.408 g, 2.86 mmol) in THF (30 mL) was added a solution of $SbCl_3$ (0.652 g, 2.86 mmol) in THF (20 mL) at 0 ^{o}C. A deep red solution formed initially, this turned to a light yellow when the addition of $SbCl_3$ was complete. A white precipitate formed. The suspension was stirred at room temperature overnight. The solvent was removed *in vacuo* and the resulting yellow oil was extracted in CH_2Cl_2 (15 mL). The CH_2Cl_2 was removed *in vacuo.* This yielded a yellow solid (0.405 g, 1.23 mmol, 44 %). ^{1}H NMR (400 MHz, C_6D_6): δ ppm 1.69 (s, 30 H, Me-H) ^{13}C{^{1}H}NMR (101 MHz, C_6D_6): δ ppm 10.6 (s, Me-C) 124.0 (s, Cp-C). Screening crystals from the a sample sublimed at 90 ^{o}C *in vacuo* yielded a unit cell which confirmed the identity as Cp^*SbCl_2.[5]

Synthesis of $[Cp^*_2Sb][B(C_6F_5)_4]$ **(1)**

A suspension of $[(Et_3Si)C_7H_8][B(C_6F_5)_4]$ (0.262 g, 0.29 mmol) in toluene (10 mL) was added dropwise to a solution of Cp^*_2SbCl (0.122 g, 0.29 mmol) in toluene (20 mL) at room temperature. A red oil formed immediately from the deep red solution. The oily suspension was stirred for 30 mins and then left to settle. The solution was decanted and hexane (10 mL) was added to precipitate an orange crystalline solid. The resulting solid was dried *in vacuo.* This gave an orange powder (0.1336 g, 0.12 mmol, 43%). ^{1}H NMR (400 MHz, CD_2Cl_2): δ ppm 2.18 (s, 30 H, Me-H). $^{13}C\{^{1}H\}$ NMR (101 MHz, CD_2Cl_2) δ ppm 10.2 (s, Cp-Me) 127.7 (s, Cp-C). ^{19}F NMR (376 MHz, CD_2Cl_2): δ ppm -167.31 (br t, J=17.34 Hz,) -163.46 (br t, J=20.23 Hz) -132.96 (s). Crystals suitable for XRD were grown by layering a CH_2Cl_2 solution with hexane. Elemental Analysis Found (Cal): C: 49.47% (49.33%) H: 2.74% (2.82%).

Synthesis of Cp^*_2SbOTf **(1a)**

A suspension of AgOTf (0.027 g, 0.10 mmol) in CH_2Cl_2 (5 mL) was added to a solution of Cp^*_2SbCl (0.043 g, 0.10 mmol) in CH_2Cl_2 (5 mL) in the dark. The resulting suspension was stirred overnight then filtered to yield a red solution. Solvent was removed *in vacuo* to yield a red powder (0.030 g, 0.057 mmol, 57%). ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 2.21 (s, 30 H, Me-H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ ppm 10.1 (s, 5 C) 126.2 (s, C). ^{19}F NMR (376 MHz, $CDCl_3$): δ ppm -77.58 (s). Crystals suitable for XRD were grown by layering a CH_2Cl_2 solution with hexane. Elemental Analysis Found (Cal): C: 46.48 % (46.60%) H: 5.38% (5.58%).

Synthesis of $[Cp^*SbCl][B(C_6F_5)_4]$ **(2)**

A suspension of $[(Et_3Si)C_7H_8][B(C_6F_5)_4]$ (0.4000 g, 0.45 mmol) in toluene (30 mL) was added dropwise to a solution of Cp^*SbCl_2 (0.1470 g, 0.45 mmol) in toluene (30 mL) at room temperature. A red oil formed immediately. The oily suspension was stirred for 30 mins and then left to settle. The solution was decanted and the resulting oil was dried *in vacuo.* The resulting yellow solid was washed with hexane (3x5 mL) and dried *in vacuo.* This gave a yellow powder (0.1850 g, 0.17 mmol, 38 %). ^{1}H NMR (400 MHz, CD_2Cl_2): δ ppm 2.33 (s, 15 H, Me-H). $^{13}C\{^{1}H\}$ NMR (101 MHz, CD_2Cl_2): δ ppm 10.7 (s, Me-C) 131.3 (s, Cp-C). ^{19}F NMR (376 MHz, CD_2Cl_2): δ ppm -167.51 (br t, J=17.34 Hz) -163.68 (br t, J=20.23 Hz -133.03 (s). Crystals suitable for XRD were grown by layering a CH_2Cl_2 solution with hexane. Elemental Analysis Found (Cal): C: 42.24 % (42.04%) H: 1.41 % (1.56 %).

Gutmann-Beckett Analysis of **2**

A NMR tube was loaded with **2** (0.010 g, 0.01 mmol), Et_3PO (0.001 mg, 0.01 mmol) and CD_2Cl_2 (0.6 mL)**.** ^{1}H NMR (400 MHz, CD_2Cl_2) δ ppm 0.99 - 1.44 (m, CH_3-Et_3PO) 1.98 - 2.17 (m, CH_2 + Me-**2**) (Due to overlapping signals, integrals are not reported). ^{19}F NMR (376 MHz, CD_2Cl_2) δ ppm -168.93 to -166.49 (m) -163.63 (br t, *J*=20.23 Hz) -133.06 (br d, *J*=2.89 Hz). ^{31}P NMR (162 MHz, CD_2Cl_2) δ ppm 80.65 (br s). Layering the NMR solution with hexane produced a white powder which was not suitable for SCXRD analysis.

NMR Scale Synthesis of **2**/Pyridine

A NMR tube was loaded with **2** (10 mg, 0.01 mmol), pyridine (2 mg, 0.02 mmol) and CD_2Cl_2 (0.6 mL), forming a clear solution**.** ^{1}H NMR (400 MHz, CD_2Cl_2) δ ppm 2.04 (s, 15 H, Me-H) 7.84 (br t, J=6.1 Hz, 2 H) 8.26 (br t, J=7.4 Hz, 1 H) 8.63 (br d, J=3.4 Hz, 2 H). ^{19}F NMR (376 MHz, CD_2Cl_2) δ ppm -167.41 (br t, J=17.3 Hz) -163.56 (br t, J=20.2 Hz) -133.01 (s).

Diels-Alder Dimerisation of 1,1-Diphenylethylene by **2**

A NMR tube was loaded with **2** (5 mg, 0.005 mmol) in CD_2Cl_2 (0.075 mL) to which 1,1-diphenylethylene (16.8 mg, 0.082 mmol) in CD_2Cl_2 (0.075 mL) was added. A red colour formed instantly. The solution was stood for 2h. CD_2Cl_2 (0.5 mL) was added before obtaining NMR spectra. Relative integration of the product vs residual starting material gave a conversion of 86%.

Mukaiyama Aldol Addition of Methyl Trimethylsilyl Dimethylketene Acetal to Benzaldehyde

A NMR tube was loaded with **2** (0.005 g, 0.005 mmol), Methyl trimethylsilyl dimethylketene acetal (0.017 g, 0.1 mmol) and benzaldehyde (0.010 mg, 0.1 mmol) in CD_2Cl_2 (0.7 mL). The reaction solution turned orange after 5 minutes then purple over the course of 2 hours. Mesitylene (2.4 mg, 0.019 mmol) was added as an internal standard and NMR spectra were obtained. Yield by relative integration of mesitylene vs product proton (4.89 ppm): 0.01425 mmol, 14%.[6]

The reaction was repeated with the omission of **2** which yielded no reactivity.

Synthesis of Cp^*SbF_2 **(3)**

To a suspension of SbF_3 (0.520 g, 2.90 mmol) in THF (15 mL) was added a suspension of Cp*Li (0.4067 g, 2.81 mmol) in THF (15 mL) at room temperature. On addition, a red solution formed which rapidly dissipated to give a light yellow solution and a white precipice. The solution was stirred at room temperature overnight. The solvent was removed *in vacuo* and the resulting yellow oil was extracted in CH_2Cl_2 (15 mL). The CH_2Cl_2 was removed *in vacuo.* This yielded a yellow solid (0.362 g, 1.23 mmol, 44 %). ^1H NMR (400 MHz, CD_2Cl_2): δ ppm 2.03 (s, 30 H, Me-H) $^{13}C\{^1H\}$ NMR (101 MHz, C_6D_6): 10.3 (s, Me-C), 122.8 (s, Cp-C). ^{19}F NMR (376 MHz, CD_2Cl_2): δ ppm -60.56 (br s) . Crystals suitable for SC-XRD analysis were grown by sublimation at 90^{o}C *in vacuo*. Elemental Analysis Found (Cal): C: 40.60% (40.72%) H: 5.06% (5.13%).

Synthesis of $[Cp^*SbF][B(C_6F_5)_4]$ **(4)**

A solution of Cp^*_2SbCl (0.1216 g, 0.29 mmol) in toluene (15 mL) was added dropwise to a suspension of $[(Et_3Si)C_7H_8][B(C_6F_5)_4]$ (0.2620 g, 0.29 mmol) in toluene (15 mL) at -78^{o}C. A deep yellow solution formed instantly. On warming to room temperature the reaction solution yielded a dark yellow oil (crude **4**) which was stirred at room temperature for 1 hour. ^{19}F NMR (400 MHz, $PhCCl_3/C_6D_6$): δ ppm -166.18 (t), -162.32 (t) and -131.72 (s) ($B(C_6F_5)_4$), 18.08 (s, Sb-F).

Decomposition of **4** in CD_2Cl_2

Crude **4** was washed with hexane (15 mL) and dissolved in CH_2Cl_2 (15 mL). The resulting black precipitate was removed by filtration through celite to give a yellow solution which was layered with hexane (15 mL). The resulting yellow crystalline solid was dried *in vacuo.* NMR and SCXRD from a sample from the bulk confirmed the identity as a mixture of **2** and $[Cp^*H_2][B(C_6F_5)_4]$**.**

Decomposition of **4** in $PhCCl_3$

Crude **4** was synthesised as above from Cp^*SbF_2 (0.028 mmol) and $[(Et_3Si)C_7H_8][B(C_6F_5)_4]$ (0.2620 g, 0.29 mmol) without purification except washing with toluene (3 x 5mL). The crude oil was dissolved in $PhCCl_3$ (0.3 mL) to give a dark solution and stood for 2 hours. C_6D_6 (0.4 mL) was added. A small sample of this solution was removed and CD_2Cl_2 (0.5 mL) was added. Both solutions was then heated at 40^{o}C for 96 hours with NMR spectra taken intermittently (see figures 19-21), showing a diminishing Sb-F resonance at around 18 ppm and an increasing $PhCFCl_2$ resonance at around -53 ppm over this period.

Synthesis of $[Cp^*SbF/IMes][B(C_6F_5)_4]$ **(5)**

Cp^*SbF_2 (0.030 g, 0.033 mmol) and IMes (0.009 g, 0.029 mmol) were mixed in toluene (10 mL) for 5 minutes to give a deep yellow solution. A suspension of $[(Et_3Si)C_7H_8][B(C_6F_5)_4]$ (0.030 g, 0.33 mmol) in toluene (15 mL) was added to the reaction solution dropwise. A small amount of yellow oil formed. The solution was stirred at room temperature for 1 hour, then hexane (15 mL) was added to precipitate a yellow solid. The yellow solid was washed with hexane (3 x 15 mL), then dissolved in 1,2-DFB (15 mL) and layered with hexane (15 mL) to form yellow crystals which were dried *in vacuo* (0.020 g, 0.016 mmol, 55%). ^1H NMR (400 MHz, CD_2Cl_2) δ ppm: 2.12 (m, 33 H, Cp*+Ar-CH_3) 7.56 (d, J=1.37 Hz, 4 H, Ar-H) 8.22 - 8.27 (m, 2 H, IMes H). ^{19}F NMR (376 MHz, CD_2Cl_2) δ ppm -167.52 (br t, J=17.34 Hz) -163.67 (br t, J=20.23 Hz) -133.07 (m), 115.14(s) Elemental Analysis Found (Cal): C: 52.18% (52.45%), H 2.93% (3.12%), N 1.96% (2.22%).

Synthesis of $Cp^*Sb(OTf)_2$ **(6)**

TMSOTf (0.044 g, 0.2 mmol) in CH_2Cl_2 (5 mL) was added to a solution of Cp^*SbF_2 (0.030 g, 0.1 mmol) in CH_2Cl_2 (5 mL) which formed a deep red solution. The solution was stirred for 2 hours at room temperature then hexane (30 mL) was added to precipitate a pink powder. The solution was decanted and the powder was washed with hexane (3 x5 mL) then dried in vacuo to yield a pink powder (0.018 g, 0.03 mmol, 30%). ^1H NMR (400 MHz, $CDCl_3$) δ ppm 2.09 (s, 15 H) . $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ ppm 10.4 (s, Cp*-Me) 124.5 (s, Cp*-C). ^{19}F NMR (376 MHz, $CDCl_3$) δ ppm -77.53 (s, v minor) -76.80 (s, CF_3). Due to the highly sensitive nature of **6**, microanalysis could not be obtained.

Attempted Synthesis of $[Cp^*Sb][B(C_6F_5)_4]_2$

A solution of Cp^*SbF_2 (0.009 g, 0.03 mmol) in C_6D_6 (0.5 mL) was added dropwise to a suspension of $[(Et_3Si)C_7H_8][B(C_6F_5)_4]$ (0.053 g, 0.06 mmol) in C_6D_6 (0.5 mL) to give a dark yellow oil and a yellow solution. The solution was decanted and CD_2Cl_2 (0.7mL) was added to the oil which partially solubilised it. 1,2-DFB (1 mL) was added to fully solubilise the oil and the resulting solution was layered with hexane (5 mL) to yield light yellow crystals of **2** and **2/4**.

Spectroscopy

NMR spectra were recorded on a JEOL Eclipse 400 spectrometer or JEOL ECZ400 YH spectrometer at 298 K (399.60 MHz for ^1H, 376.01 MHz for ^{19}F, 161.76 MHz for ^{31}P and 100.48 MHz for $^{13}C\{^1H\}$).

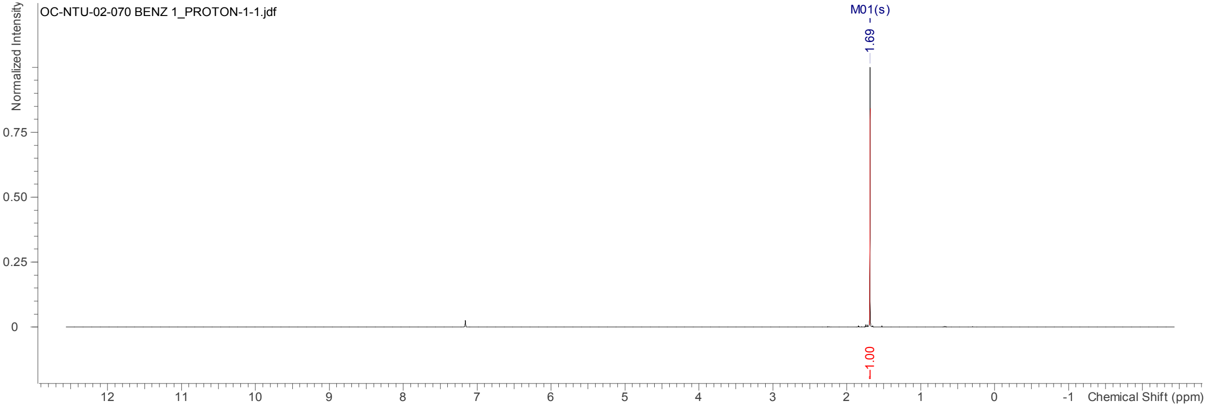

*Figure 1. ^1H NMR Spectrum of Cp*SbCl2*

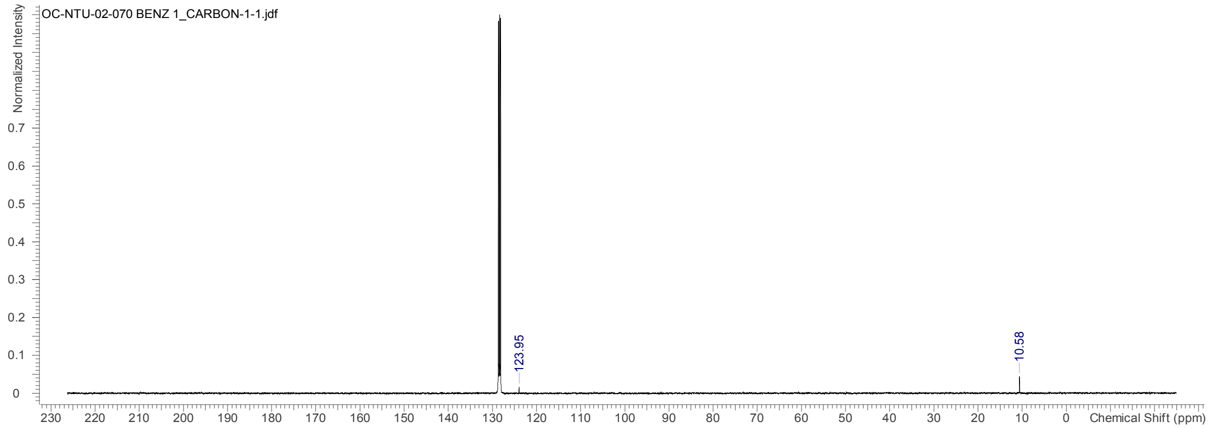

Figure 2. $^{13}C\{^1H\}$ NMR Spectrum of Cp^*SbCl_2

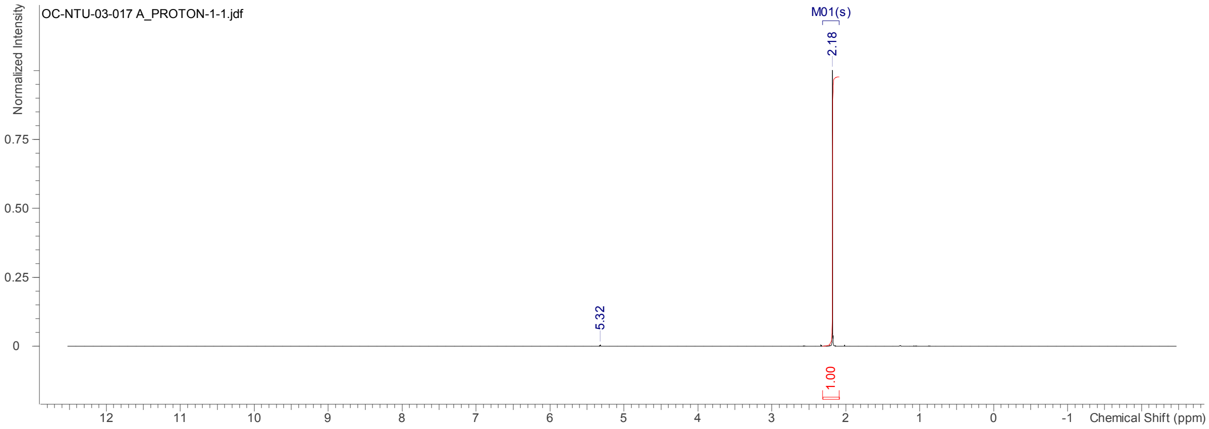

*Figure 3. ^1H NMR Spectrum of **1***

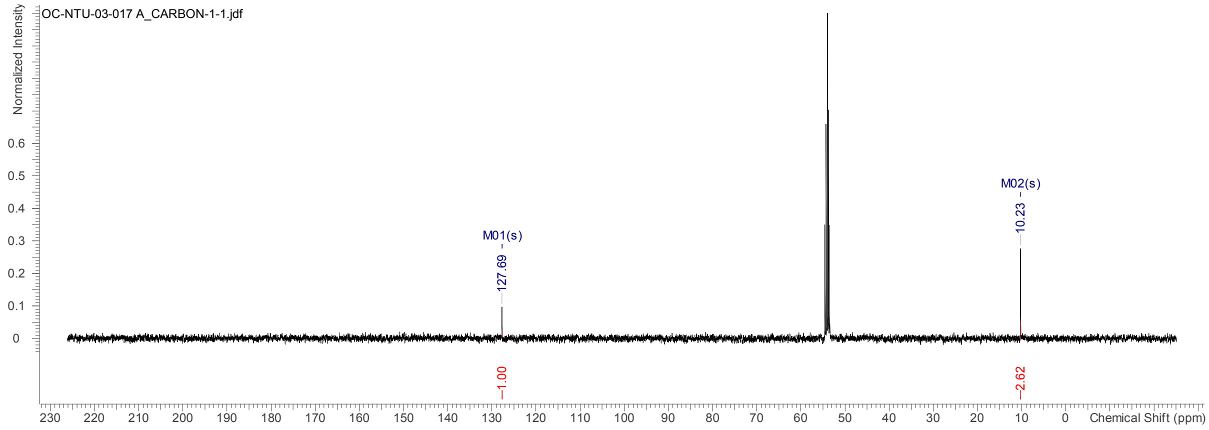

*Figure 4. $^{13}C\{^1H\}$ NMR Spectrum of **1***

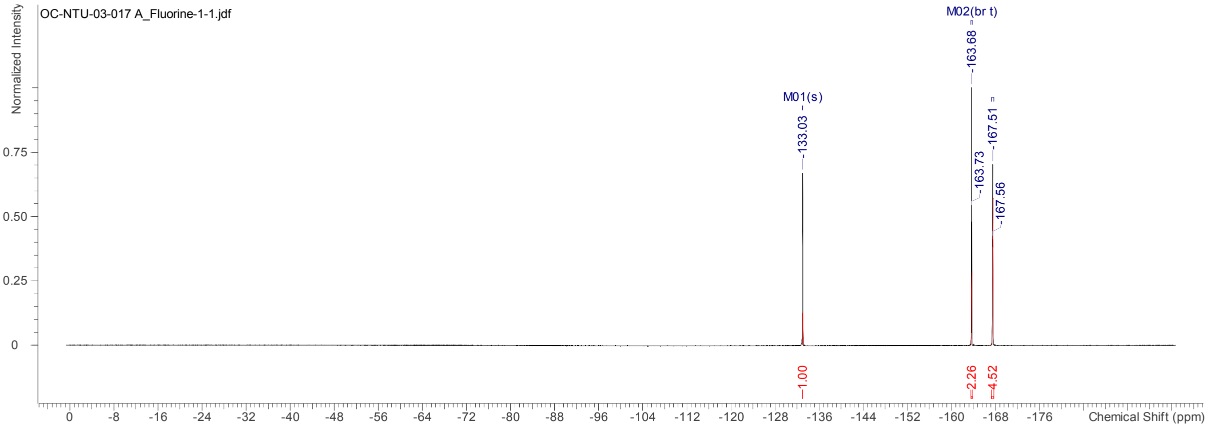

Figure 5. ^{19}*F NMR Spectrum of* ***1***

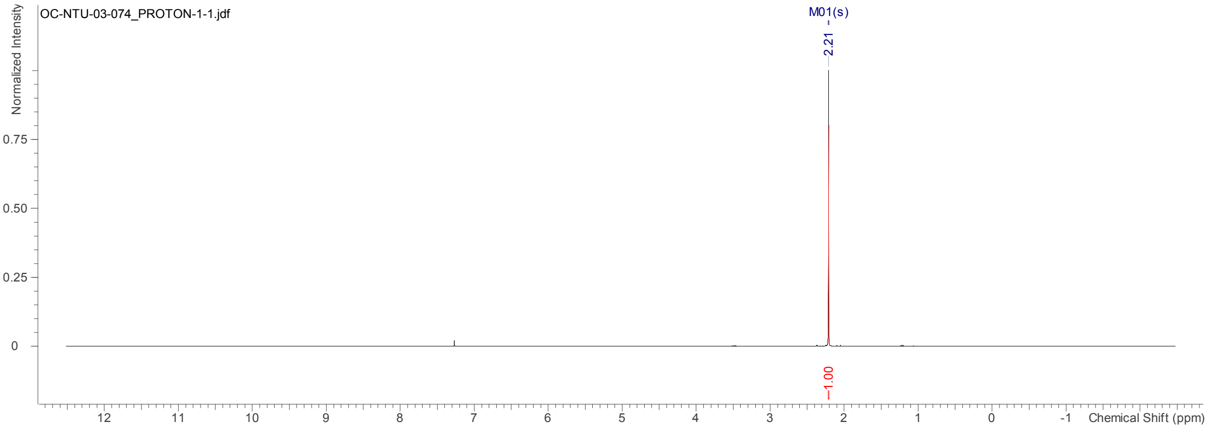

Figure 6. ^{1}*H NMR Spectrum of* ***1a***

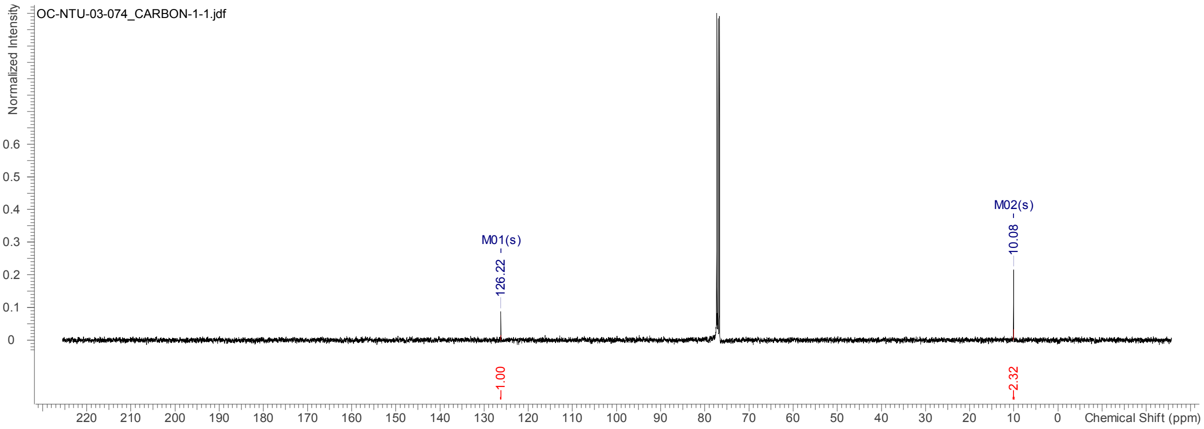

Figure 7. ^{13}*C{*^{1}*H} NMR Spectrum of* ***1a***

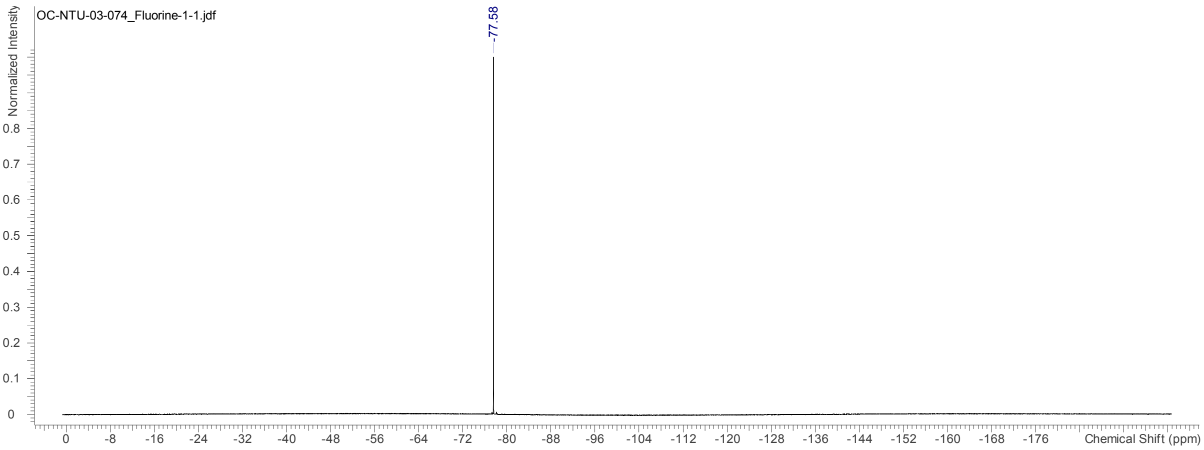

*Figure 8. ^{19}F NMR Spectrum of **1a***

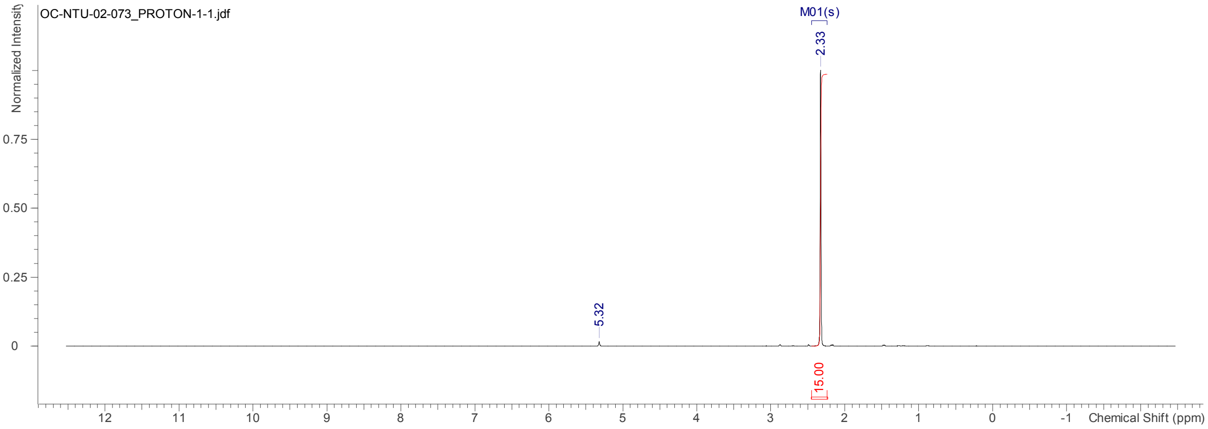

*Figure 9. ^{1}H NMR Spectrum of **2***

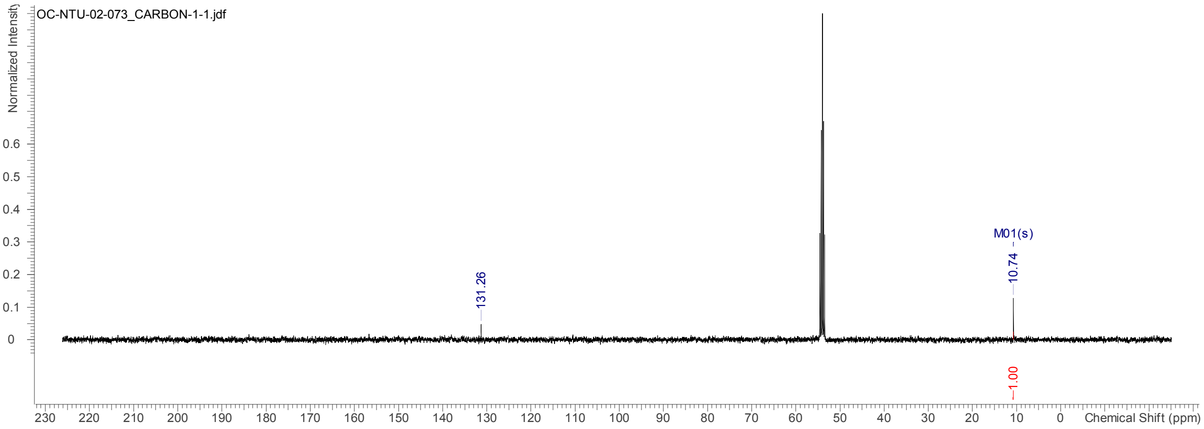

*Figure 10. ^{13}C{^{1}H} NMR Spectrum of **2***

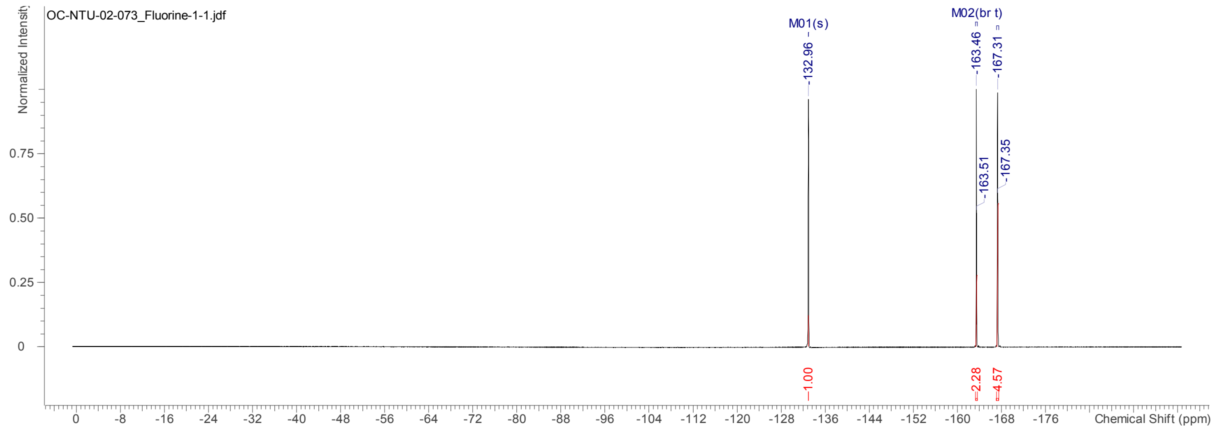

*Figure 11. ^{19}F NMR Spectrum of **2***

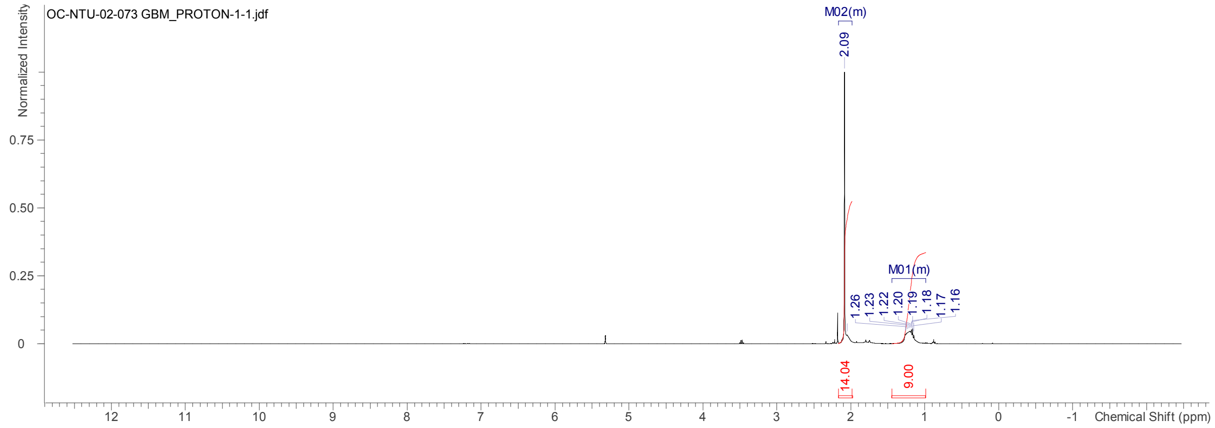

*Figure 12. ^{1}H NMR Spectrum of **2**/Et$_3$PO*

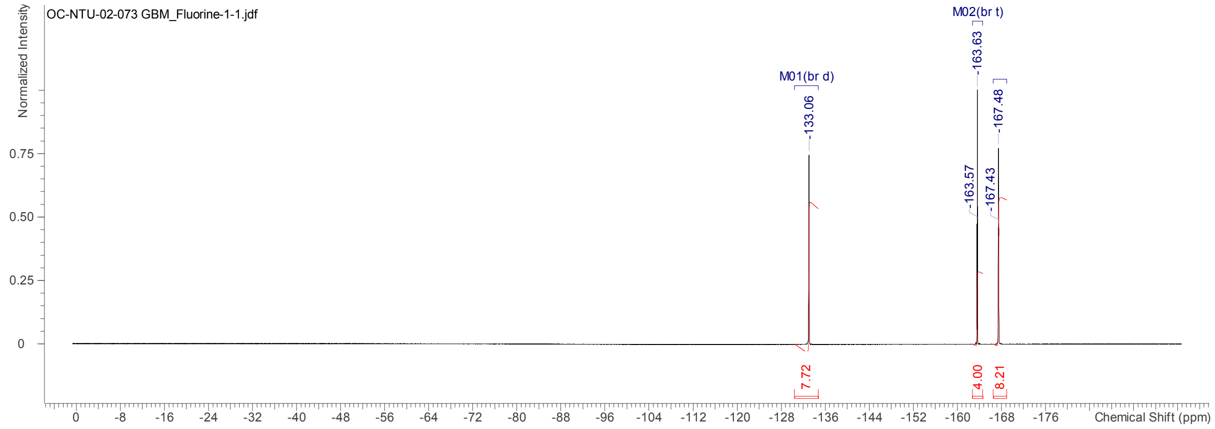

*Figure 13. ^{19}F NMR Spectrum of **2**/Et$_3$PO*

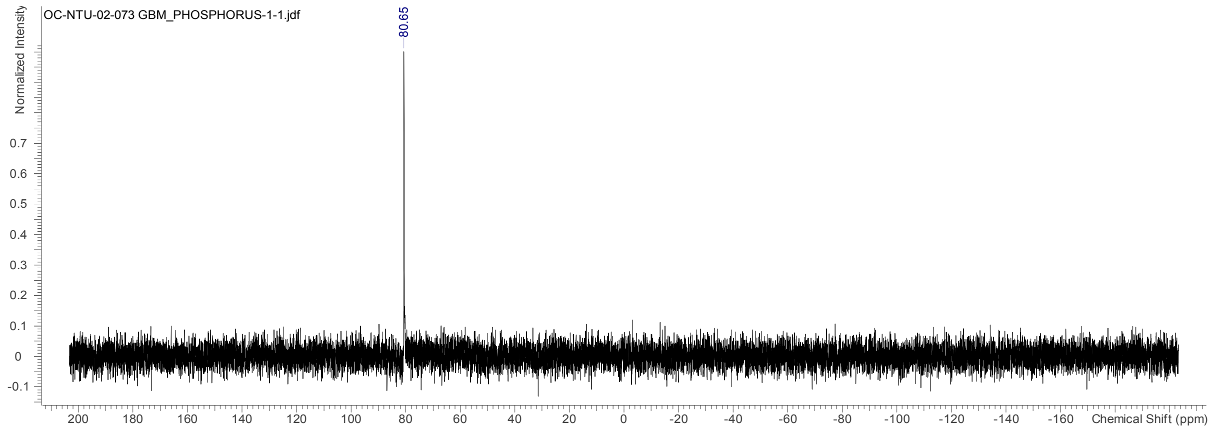

*Figure 14. ^{31}P NMR Spectrum of **2**/Et$_3$PO*

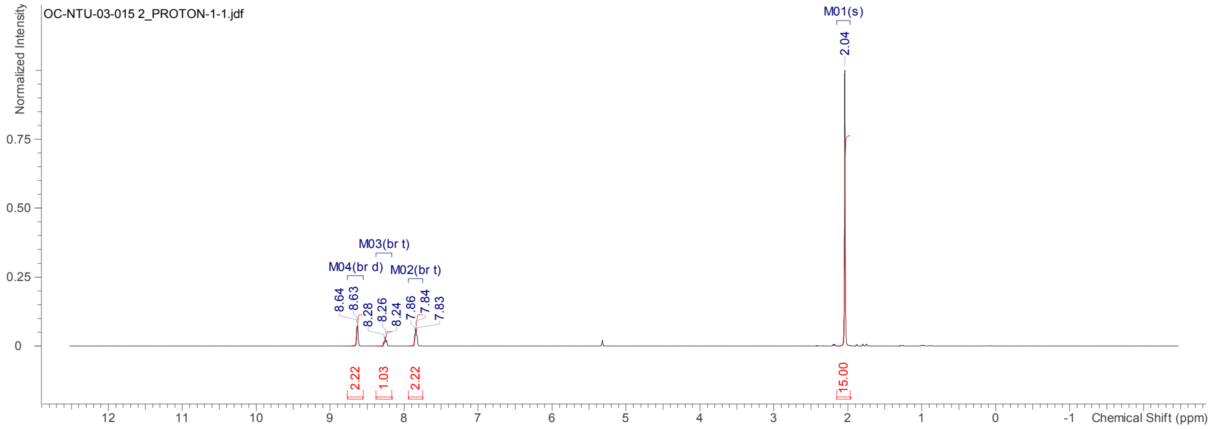

*Figure 15. ^{1}H NMR Spectrum of **2**/Pyridine*

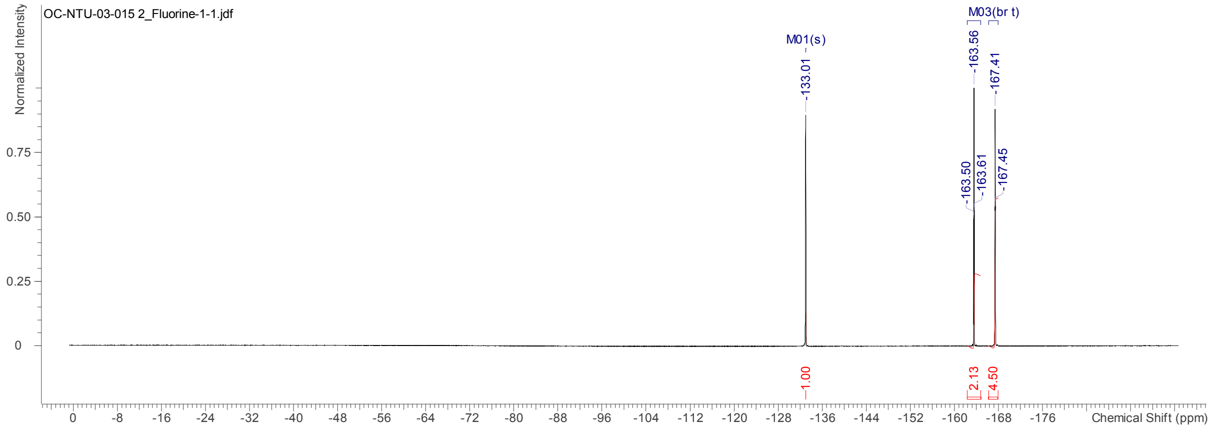

*Figure 16. ^{19}F NMR Spectrum of **2**/Pyridine*

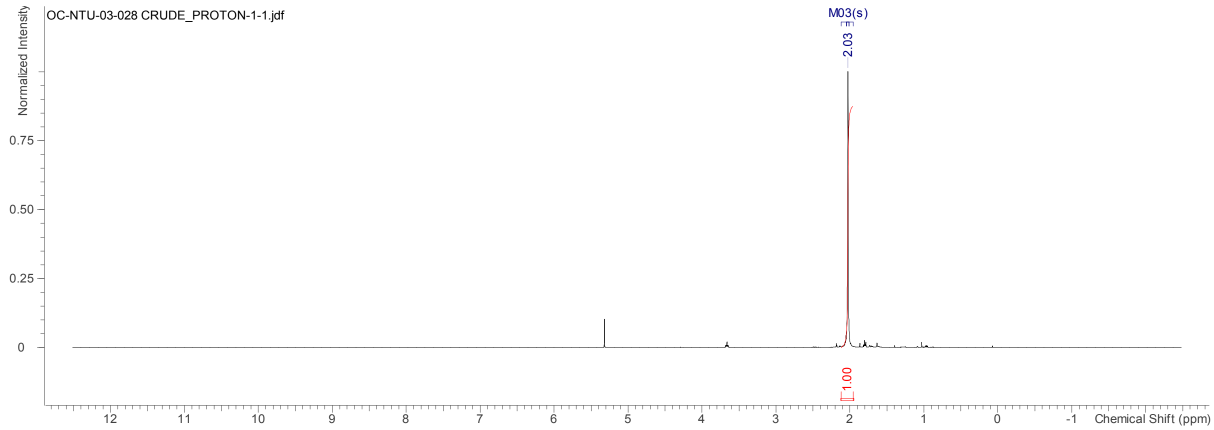

Figure 17. ^{1}H NMR Spectrum of ***3***

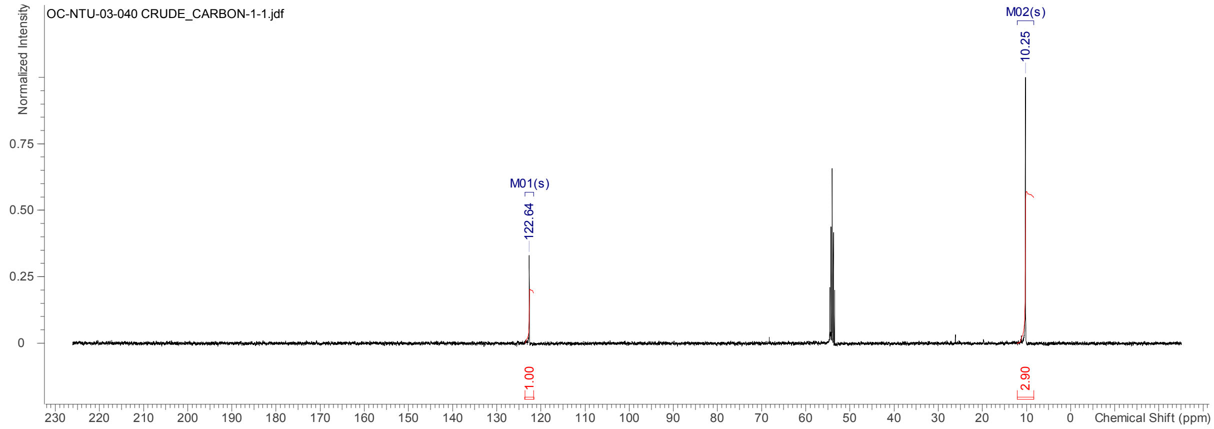

Figure 18. ^{13}C{^{1}H} NMR Spectrum of ***3***

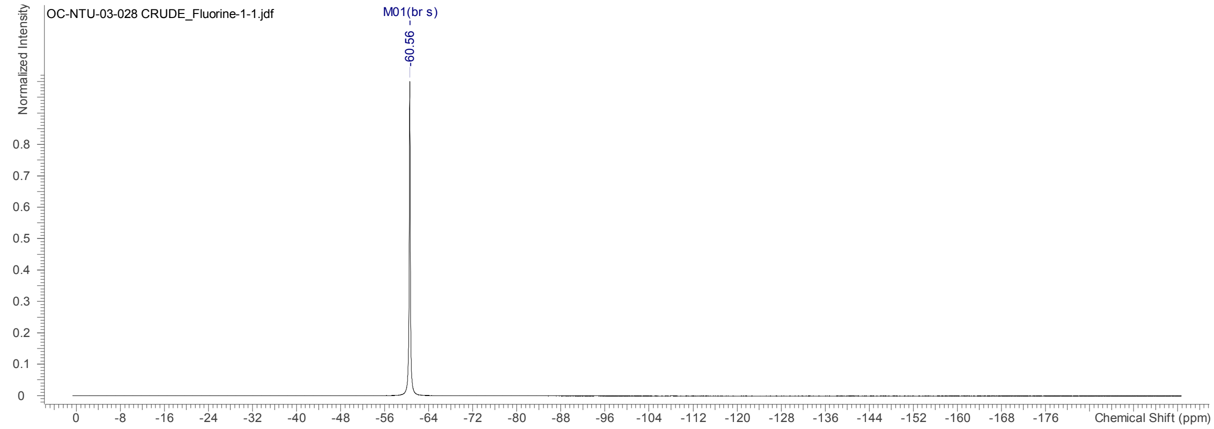

Figure 19 ^{19}F NMR Spectrum of ***3***

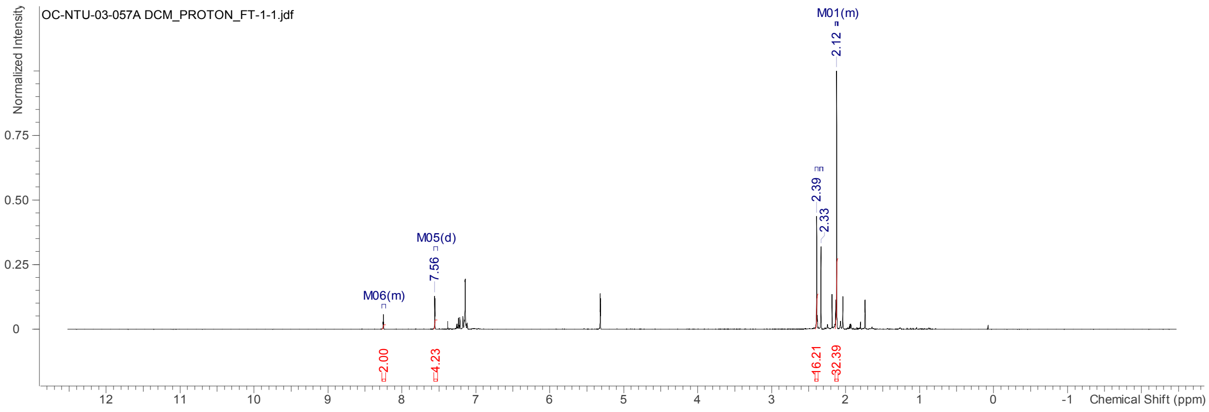

*Figure 20. ^{1}H NMR Spectrum of **5**. Some minor impurities are observed. This is likely the result of **5** decomposing in CD_2Cl_2. **5** visibly decomposes in CH_2Cl_2 overnight.*

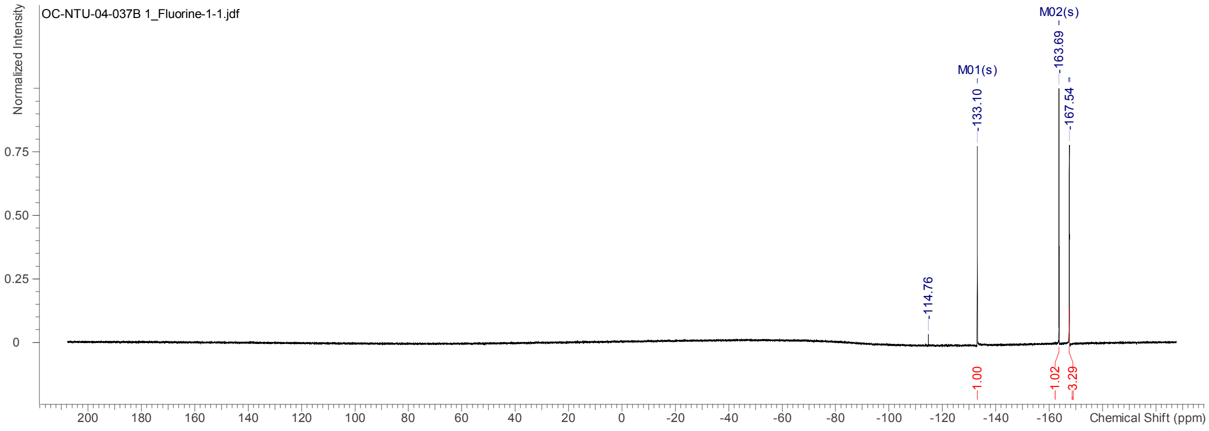

*Figure 21. ^{19}F NMR Spectrum of **5***

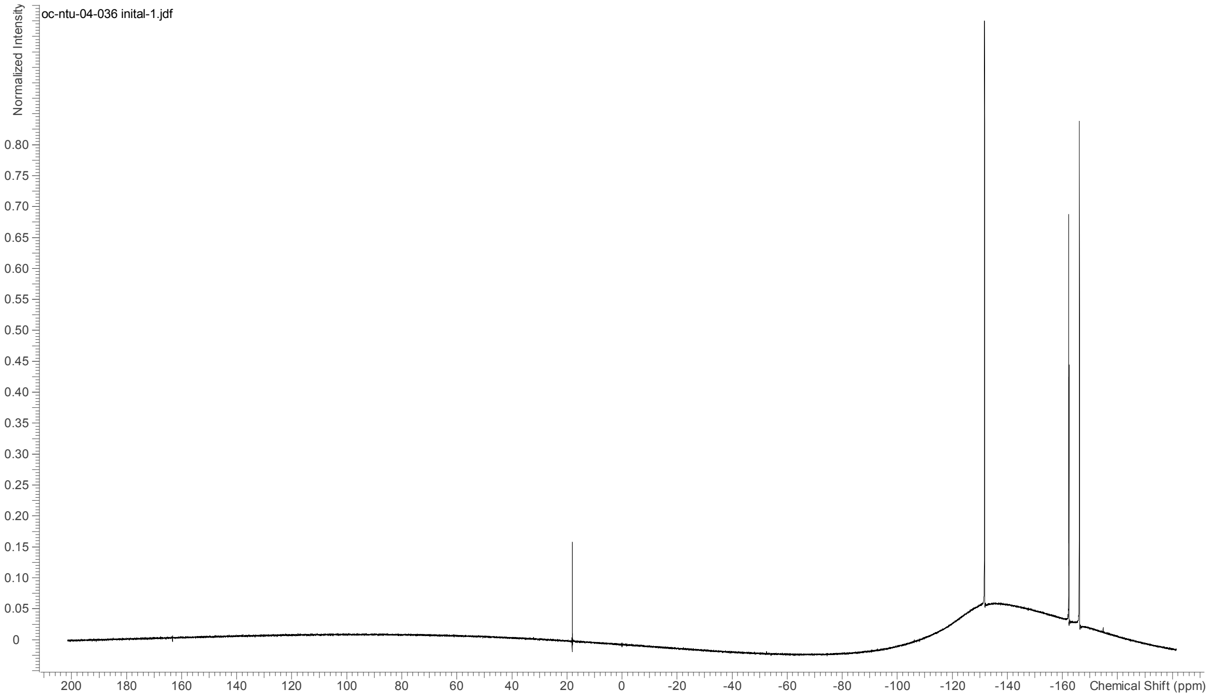

*Figure 22 Inital ^{19}F NMR Spectrum of **4** in $PhCCl_3/C_6D_6$ The signal at 18 ppm has been assigned as Sb-F.*

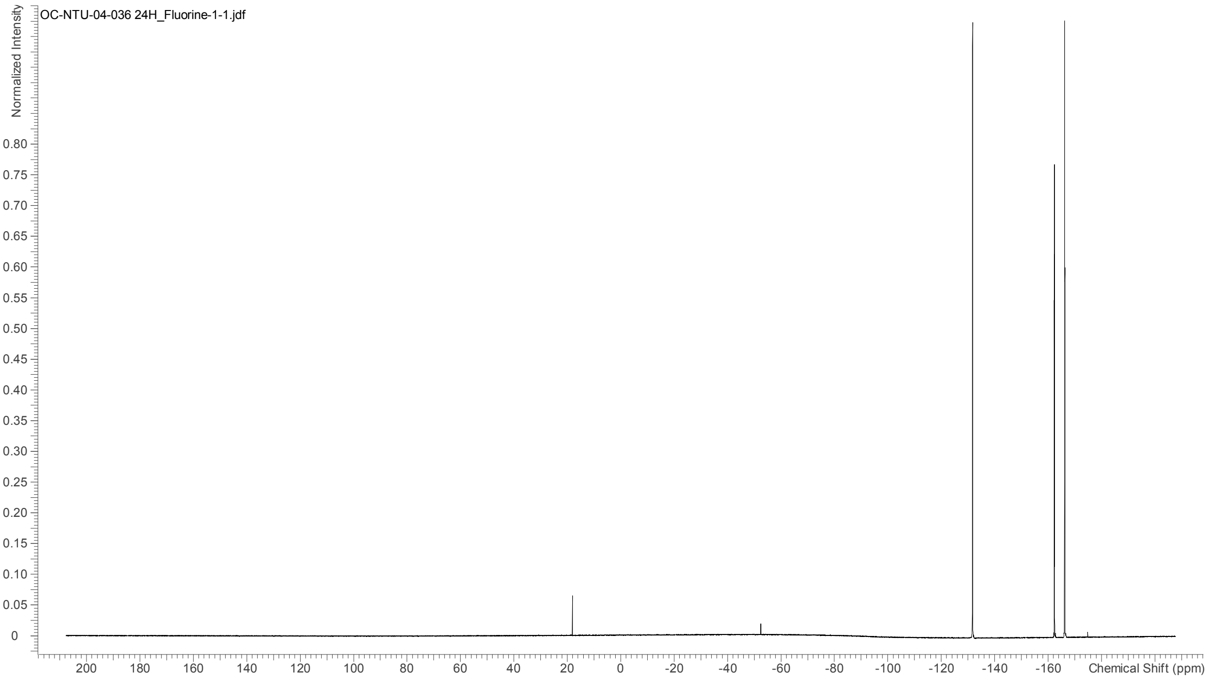

*Figure 23. ^{19}F NMR Spectrum of **4** in $PhCCl_3/C_6D_6$ after 24hours. The signal at -53 ppm has been assigned as the $PhCFCl_2$.*

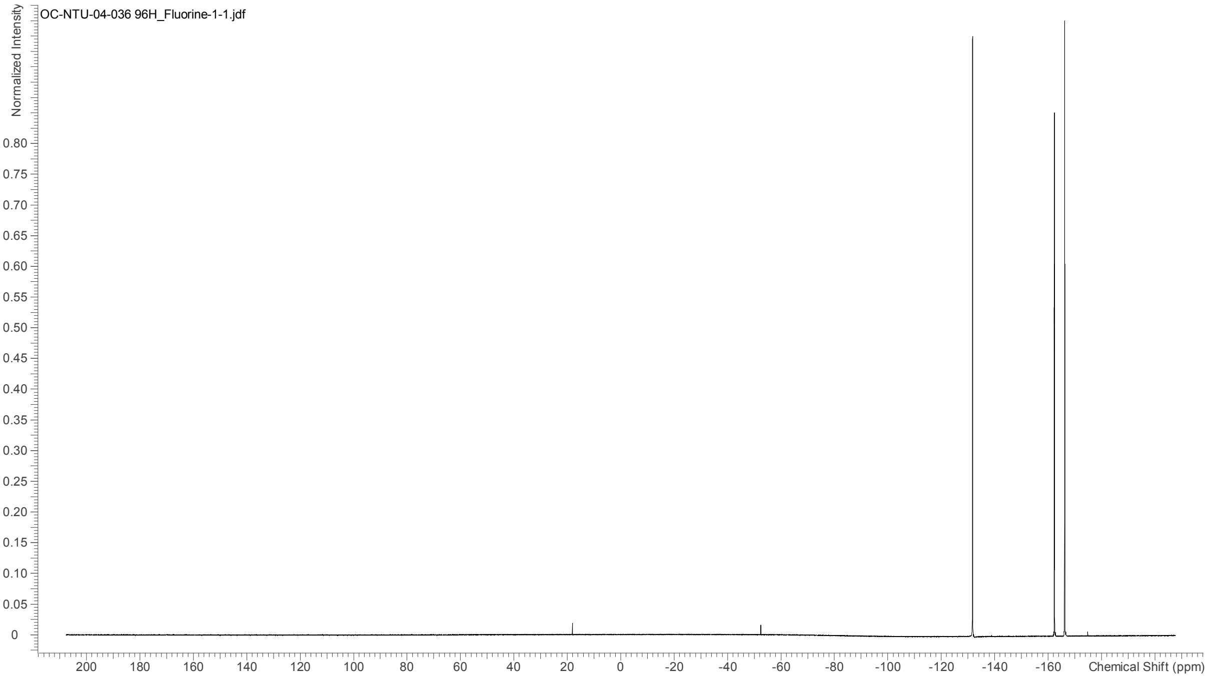

*Figure 24. ^{19}F NMR Spectrum of **4** in $PhCCl_3/C_6D_6$ after 96 hours.*

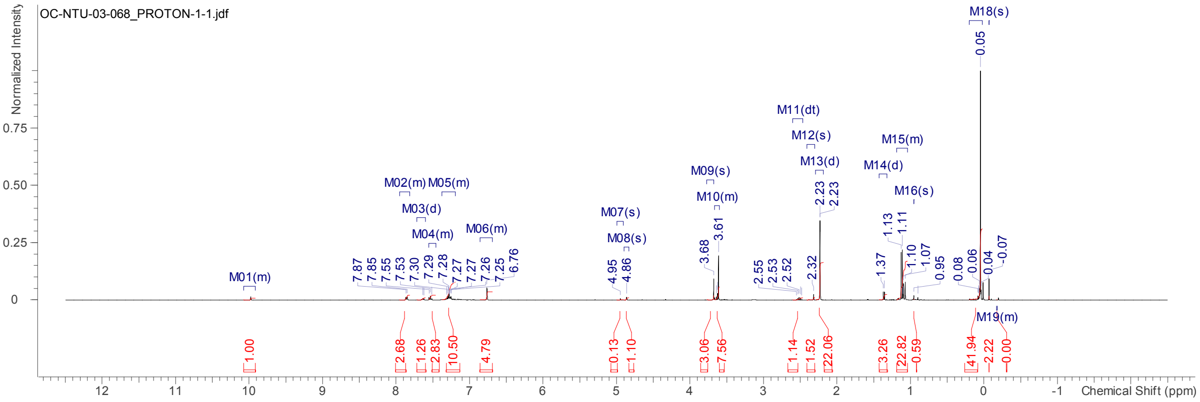

*Figure 25. Mukaiyama Aldol Addition of Methyl Trimethylsilyl Dimethylketene Acetal to Benzaldehyde by **2***

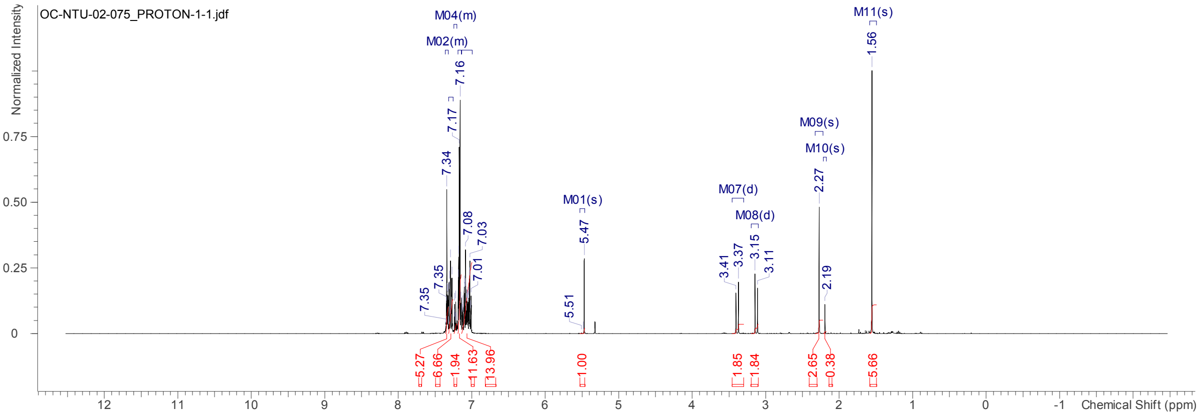

*Figure 26. Dimerisation of 1,1 diphenylethylene by **2**.*

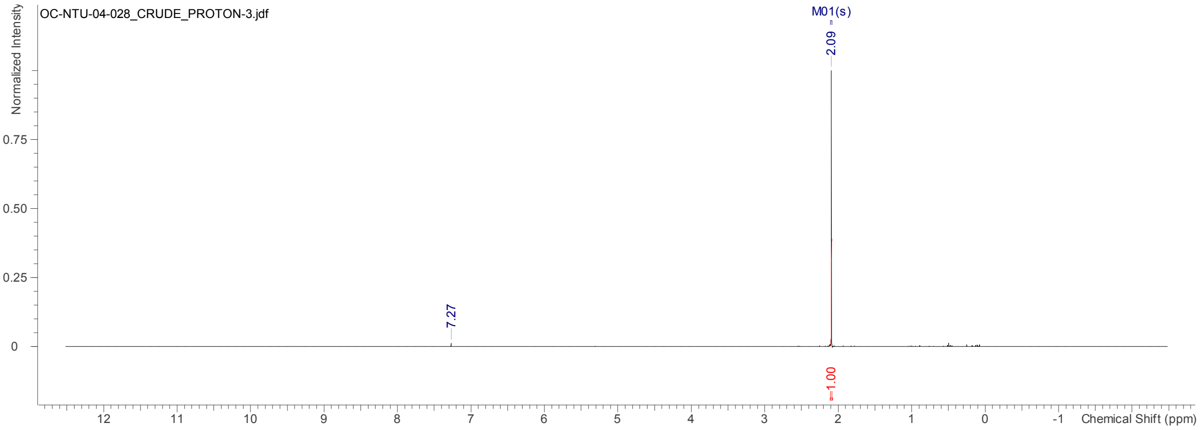

*Figure 27. ^{1}H NMR Spectrum of **6***

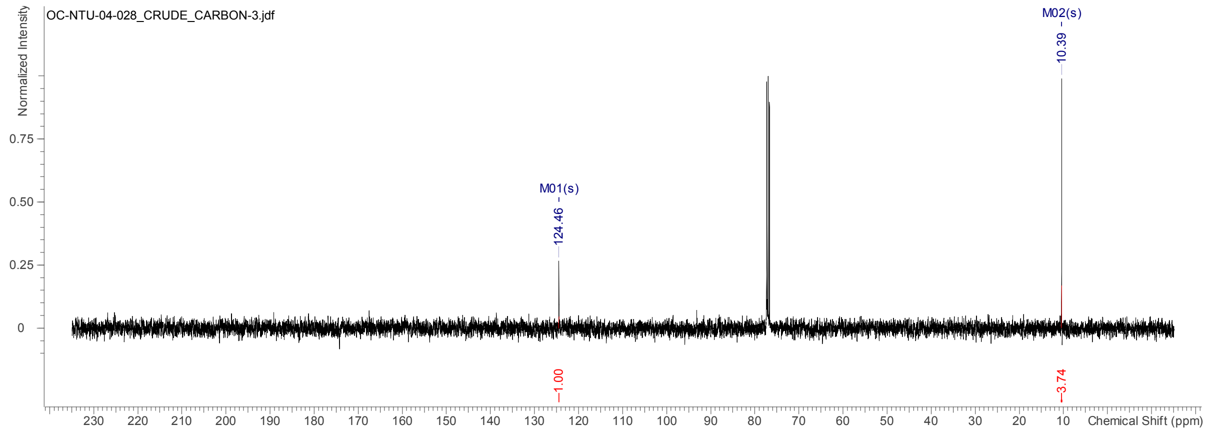

*Figure 28. $^{13}C\{^{1}H\}$ spectrum of **6***

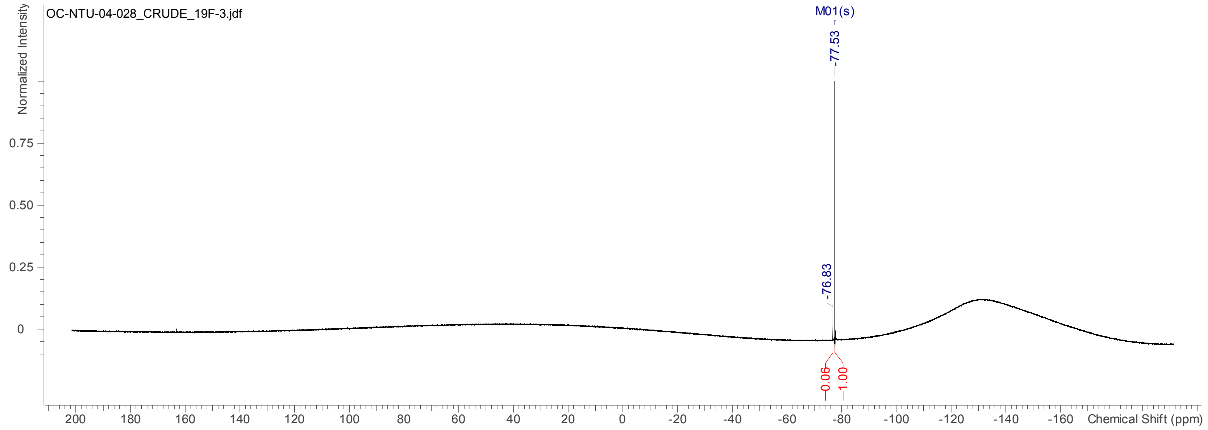

*Figure 29. ^{19}F spectrum of **6***

Assignment of Hapticity

Assignment of hapticity was based on ring slippage. The carbon with the shortest Sb-C bond length was assigned as C_{α}. The ring slippage was considered as the distance from the centroid to intersection of a vector between the Cp* ring and Sb, normal to the centroid-C_{α} distance, and the centroid-C_{α} vector (A). Using the fact that the angles of a triangle sum to 180^{o}, the centroid-Sb-A angle was calculated. The ring slippage was calculated using ring slippage = sin(∠A-Sb-centroid)*Sb-centroid. Hapcticity was then assigned as per ref 7.

Crystallography

All crystallographic measurements were performed at 150 K using an Oxford Diffraction Single Crystal Diffractometer with a Sapphire 3 CCD plate (graphite-monochromated Mo Kα radiation, λ = 0.71073 Å or Cu Kα radiation λ = 1.54184 Å). In each case, a specimen of suitable size and quality was selected, coated with Fomblin® Y oil, and mounted onto a nylon loop. Unit cell finding, data collection, data reduction and space group determination was performed using Crysalis Pro.[8] The Analytical numeric absorption correction using a multifaceted crystal model was implemented.[9] Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm was applied for absorption correction.[10] Using Olex2,[11] the structure was solved with the ShelXT structure solution program using Intrinsic Phasing and refined with the ShelXL refinement package using Least Squares minimisation.[12,13] All hydrogen atoms were geometrically placed and refined using the riding model approximation.

*Table 1 Crystal data and structure refinement for **1***

Identification code	**1**
CCDC deposition number	1967954
Empirical formula	$C_{44}H_{30}BF_{20}Sb$
Formula weight	1071.24
Temperature/K	150.00(10)
Crystal system	triclinic
Space group	P-1
a/Å	12.4426(4)
b/Å	12.7883(4)
c/Å	15.2203(5)
α/°	108.476(3)
β/°	104.868(3)
γ/°	103.354(3)
Volume/Å3	2087.32(13)
Z	2
ρcalcg/cm3	1.704
μ/mm-1	0.784
F(000)	1060.0
Crystal size/mm3	0.267 × 0.141 × 0.125
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.552 to 61.594
Index ranges	-17 ≤ h ≤ 16, -18 ≤ k ≤ 18, -21 ≤ l ≤ 21
Reflections collected	43455
Independent reflections	11878 [Rint = 0.0554, Rsigma = 0.0633]
Data/restraints/parameters	11878/0/605
Goodness-of-fit on F2	1.039
Final R indexes [I>=2σ (I)]	R1 = 0.0452, wR2 = 0.0853
Final R indexes [all data]	R1 = 0.0714, wR2 = 0.0978
Largest diff. peak/hole / e Å-3	0.57/-0.57

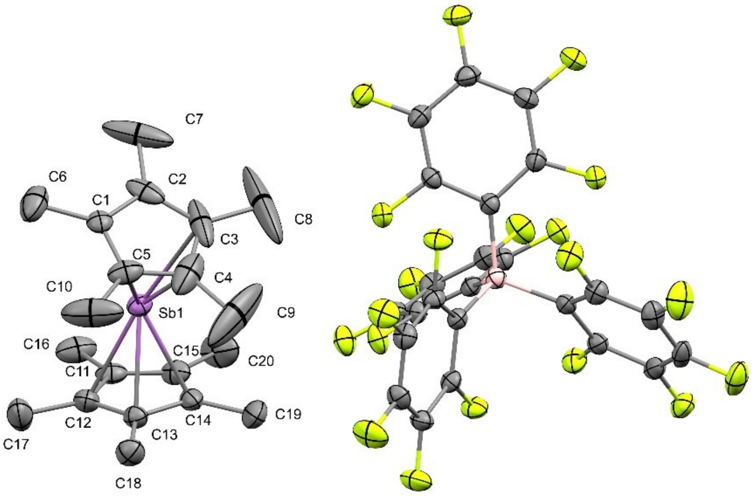

*Figure 30. Asymmetric unit of **1**. Hydrogen atoms and labels on the counteranion have been omitted. Ellipsoids are shown at 50% probability.*

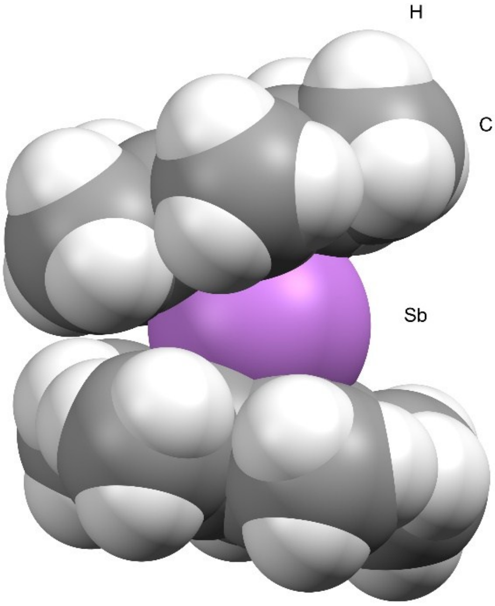

*Figure 31. Space filling model of **1**. Counteranion omitted.*

Table 2. Crystal data and structure refinement for ***2***

Identification code	**2**
CCDC deposition number	1967956
Empirical formula	$C_{34}H_{15}BClF_{20}Sb$
Formula weight	971.47
Temperature/K	150.00(10)
Crystal system	triclinic
Space group	P-1
a/Å	10.5921(7)
b/Å	12.6396(8)
c/Å	12.8627(8)
α/°	90.679(5)
β/°	96.606(5)
γ/°	104.469(5)
Volume/Å^3	1654.89(19)
Z	2
ρ_{calc}g/cm^3	1.950
μ/mm^{-1}	1.056
F(000)	944.0
Crystal size/mm^3	0.354 × 0.203 × 0.161
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.664 to 59.148
Index ranges	$-13 \le h \le 14$, $-17 \le k \le 17$, $-17 \le l \le 17$
Reflections collected	17501
Independent reflections	8897 [R_{int} = 0.0655, R_{sigma} = 0.1266]
Data/restraints/parameters	8897/0/519
Goodness-of-fit on F^2	1.011
Final R indexes [I>=2σ (I)]	R_1 = 0.0683, wR_2 = 0.0966
Final R indexes [all data]	R_1 = 0.1196, wR_2 = 0.1178
Largest diff. peak/hole / e Å^{-3}	1.03/-0.70

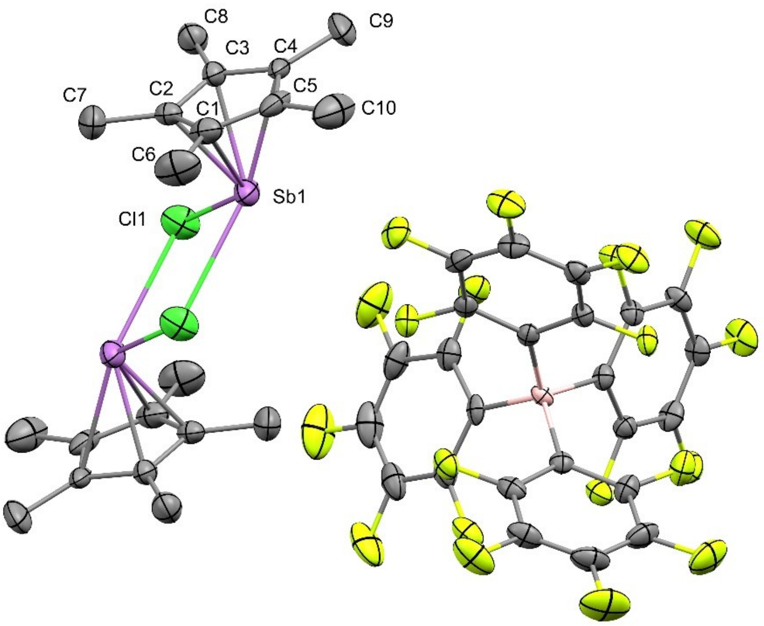

*Figure 32. Asymmetric unit of **2** with selected symmetry(-x,-y,-z). Hydrogen atoms, labels on the counteranion and selected symmetry have been omitted. Ellipsoids are shown at 50% probability.*

Table 3. Crystal data and structure refinement for 3

Identification code	**3**
CCDC deposition number	1967957
Empirical formula	$C_{10}H_{15}F_2Sb$
Formula weight	294.97
Temperature/K	150.00(10)
Crystal system	orthorhombic
Space group	Pnma
a/Å	10.2120(2)
b/Å	13.0608(4)
c/Å	8.1901(2)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	1092.37(5)
Z	4
ρ_{calc}g/cm^3	1.794
μ/mm^{-1}	2.507
F(000)	576.0
Crystal size/mm^3	0.238 × 0.138 × 0.088
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	7.1 to 61.53
Index ranges	$-14 \le h \le 13$, $-18 \le k \le 16$, $-11 \le l \le 11$
Reflections collected	7856
Independent reflections	1620 [R_{int} = 0.0326, R_{sigma} = 0.0283]
Data/restraints/parameters	1620/0/67
Goodness-of-fit on F^2	1.044
Final R indexes [I>=2σ (I)]	R_1 = 0.0222, wR_2 = 0.0403
Final R indexes [all data]	R_1 = 0.0321, wR_2 = 0.0428
Largest diff. peak/hole / e Å^{-3}	0.51/-0.48

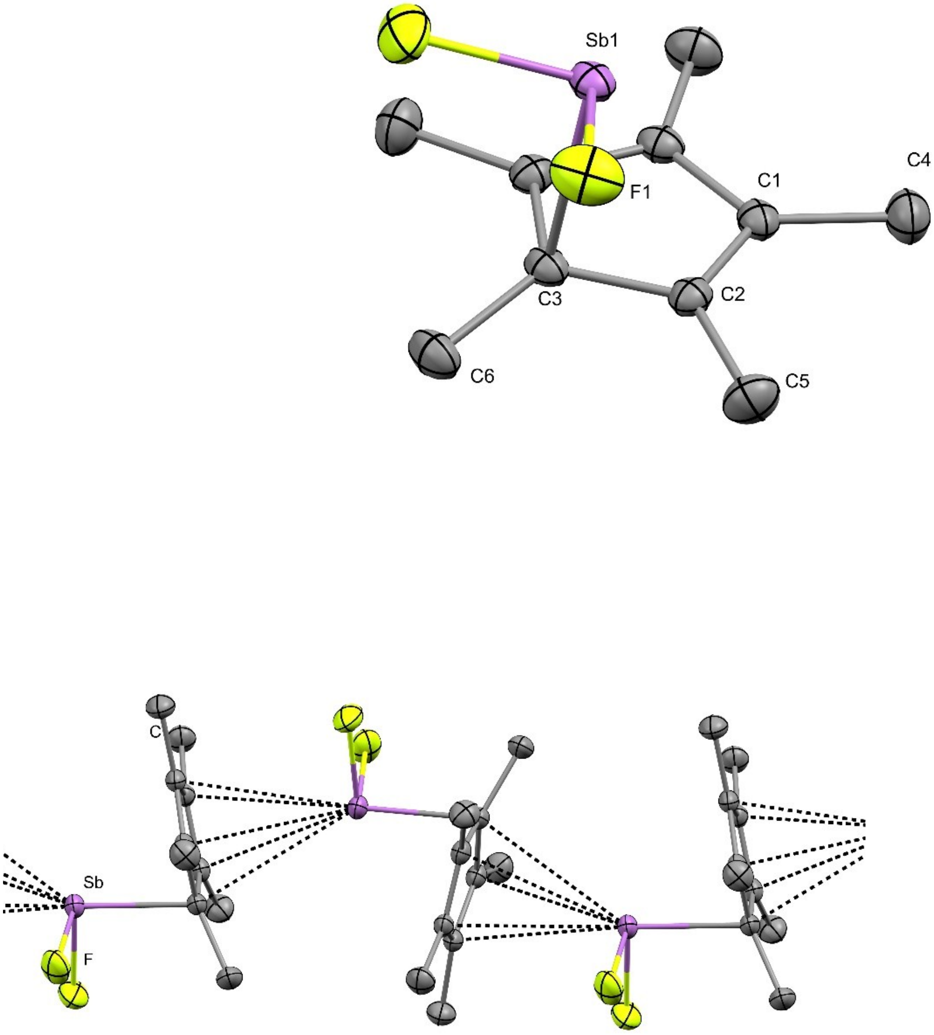

*Figure 33. Asymmetric unit of **3** with selected symmetry(x,1/2-y,z) (top) and solid state structure of **3** showing the chains via via an intermolecular Sb-Cp* interaction (represented by a dotted line) (bottom). Hydrogen atoms and labels for selected symmetry have been omitted. Ellipsoids are shown at 50% probability.*

Table 4. Crystal data and structure refinement for 2/4

Identification code	**2/4**
CCDC deposition number	1967958
Empirical formula	$C_{34}H_{15}BCl_{0.4}F_{20.6}Sb$
Formula weight	961.60
Temperature/K	150.01(10)
Crystal system	triclinic
Space group	P-1
a/Å	10.6582(3)
b/Å	12.6174(4)
c/Å	12.8229(3)
α/°	90.784(2)
β/°	95.717(2)
γ/°	105.278(3)
Volume/Å^3	1653.76(8)
Z	2
ρ_{calc}g/cm^3	1.931
μ/mm^{-1}	1.011
F(000)	934.0
Crystal size/mm^3	0.162 × 0.161 × 0.099
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.392 to 61.646
Index ranges	$-14 \le h \le 15$, $-18 \le k \le 18$, $-18 \le l \le 18$
Reflections collected	42866
Independent reflections	9520 [R_{int} = 0.0705, R_{sigma} = 0.0870]
Data/restraints/parameters	9520/0/528
Goodness-of-fit on F^2	1.158
Final R indexes [I>=2σ (I)]	R_1 = 0.0813, wR_2 = 0.1308
Final R indexes [all data]	R_1 = 0.1352, wR_2 = 0.1464
Largest diff. peak/hole / e Å^{-3}	0.95/-1.15

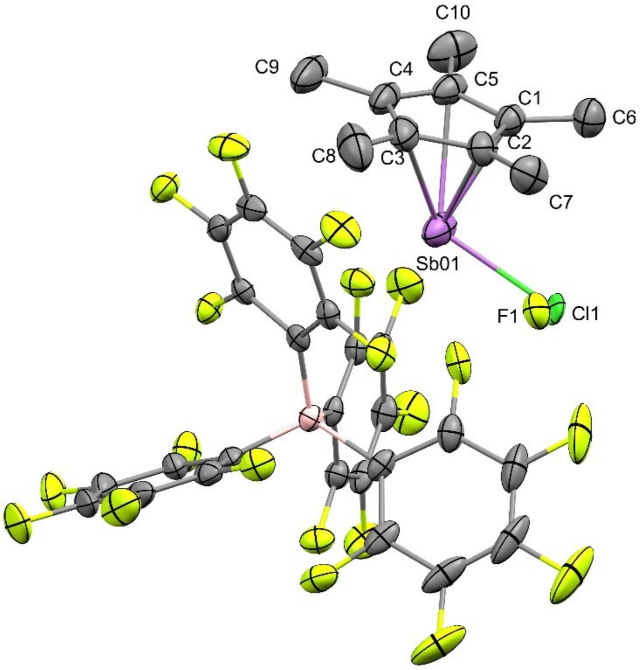

*Figure 34 Asymmetric unit of **2/4**. Hydrogen atoms and labels on the counteranion omitted. Ellipsoids are shown at 50% probability.*

Table 5. Crystal data and structure refinement for 1a

Identification code	**1a**
CCDC deposition number	1967955
Empirical formula	$C_{21}H_{30}F_3O_3SSb$
Formula weight	541.26
Temperature/K	150.01(10)
Crystal system	orthorhombic
Space group	$Pca2_1$
a/Å	17.1165(3)
b/Å	15.8699(3)
c/Å	16.6561(3)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	4524.42(14)
Z	8
ρ_{calc}g/cm^3	1.589
μ/mm^{-1}	1.355
F(000)	2192.0
Crystal size/mm^3	0.223 × 0.214 × 0.148
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.826 to 61.852
Index ranges	$-23 \leq h \leq 23$, $-22 \leq k \leq 21$, $-23 \leq l \leq 23$
Reflections collected	45019
Independent reflections	12853 [R_{int} = 0.0591, R_{sigma} = 0.0765]
Data/restraints/parameters	12853/1/544
Goodness-of-fit on F^2	1.018
Final R indexes [I>=2σ (I)]	R_1 = 0.0490, wR_2 = 0.0674
Final R indexes [all data]	R_1 = 0.0869, wR_2 = 0.0807
Largest diff. peak/hole / e Å^{-3}	0.72/-0.50
Flack parameter	0.02(3)

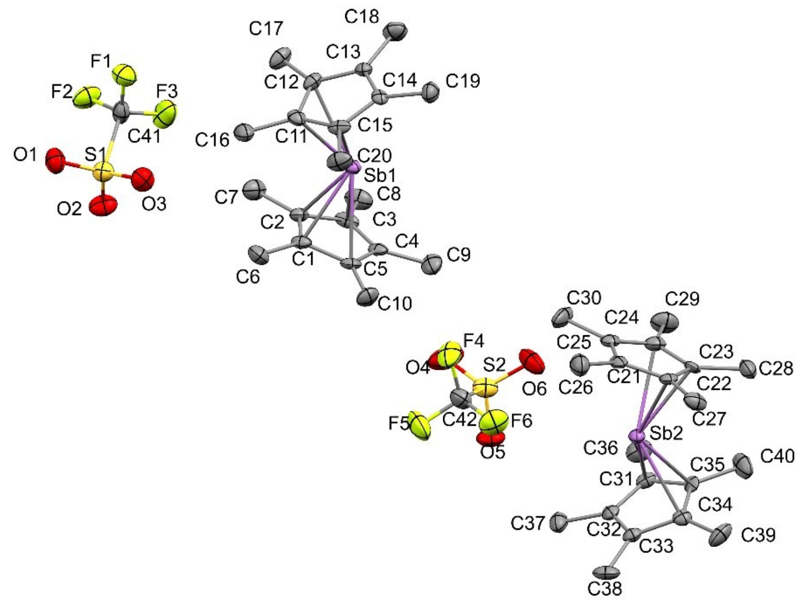

Figure 35. Asymmetric unit of 1a. Hydrogen atoms have been omitted. Ellipsoids are shown at 50% probability.

A TWIN and BASF correction was applied (-1.0, 0.0, 0.0, 0.0, 1.0, 0.0, 0.0, 0.0, -1.0), BASF [0.50(4)]

Table 6. Crystal data and structure refinement for 5

Identification code	**5**
CCDC deposition number	1967959
Empirical formula	$C_{58}H_{41}BF_{22.11}N_2Sb$
Formula weight	1318.58
Temperature/K	150.01(10)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	18.2924(2)
b/Å	17.8036(2)
c/Å	17.4223(2)
α/°	90
β/°	113.5290(10)
γ/°	90
Volume/Å^3	5202.19(11)
Z	4
ρ_{calc}g/cm^3	1.684
μ/mm^{-1}	5.316
F(000)	2632.0
Crystal size/mm^3	0.248 × 0.147 × 0.101
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	7.242 to 143.982
Index ranges	$-22 \le h \le 21$, $-16 \le k \le 21$, $-21 \le l \le 21$
Reflections collected	38975
Independent reflections	10089 [R_{int} = 0.0326, R_{sigma} = 0.0314]
Data/restraints/parameters	10089/144/805
Goodness-of-fit on F2	1.096
Final R indexes [I>=2σ (I)]	R_1 = 0.0821, wR_2 = 0.2419
Final R indexes [all data]	R_1 = 0.0881, wR_2 = 0.2455
Largest diff. peak/hole / e Å-3	1.24/-2.60

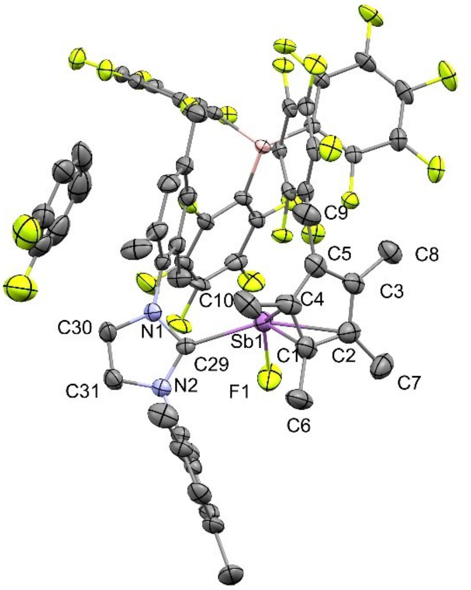

Figure 36.. Asymmetric unit of 5. Hydrogen atoms and labels on the counteranion, disordered solvent and mesityl groups have been omitted. Ellipsoids are shown at 50% probability.

N.B. There is a moderate negative electron density peak (-2.6 eA^{-3}) at the Sb centre. This is commonly observed in heavy metals.[14] Correct microanalysis, spectroscopic evidence and close inspection of the geometry suggests that the proposed assignment is correct and that the negative electron density is an artefact.

Table 7. Selected Structural parameters for Cp^*_2Sb cation. There are two crystallographically inequivalent cations in the asymmetric unit of 1a. Both Cp rings in $[Cp^*_2Sb][AlCl_4]$ are crystallographically inequivalent (indicated by ~).*

Parameter	**1**	**1a**	**$[Cp^*_2Sb][AlCl_4]$**	**$[Cp^*_2Sb][AlI_4]$**
Sb-C1 ()	2.455(5)	2.46(1)/2.44(1)	2.484	2.45(1)
Sb-C2	2.521(4)	2.521(7)/2.518(9)	2.51	2.49(1)
Sb-C3	2.573(6)	2.597(8)/2.556(7)	2.613	2.61(1)
Sb-C4	2.673(2)	2.684(6)/2.692(6)	2.653	2.66(1)
Sb-C5	2.706(3)	2.733(7)/2.727(7)	2.728	2.74(1)
Sb-C6	2.459(3)	2.44(1)/2.45(1)	2.484~	2.48(1)
Sb-C7	2.486(2)	2.520(8)/2.513(7)	2.51~	2.52(1)
Sb-C8	2.601(4)	2.535(8)/2.545(7)	2.613~	2.592(8)
Sb-C9	2.634(2)	2.701(7)/2.690(7)	2.653~	2.67(1)
Sb-C10	2.705(4)	2.703(7)/2.717(7)	2.728~	2.71(1)
Centroid-Sb-Centroid	162.48	158.79/158.90	161.10	157.37
Centroid-Sb	2.292/2.634	2.203/2.279 2.290/2.287	2.299	2.291/2.299

Computational Methods

All calculations were performed using Gaussian 09 Revision E0.01.[15] All geometries were optimised in vacuum without imposing symmetry constraints at the M062X/def2-SVP level of theory with the GD3 empirical dispersion correction.[16–18] Counteranions were omitted from all calculations. Subsequent analytical IR frequency calculations on optimised geometries were utilised to confirm the nature of stationary points (zero and exactly one imaginary mode for minima and transition states, respectively). Moreover, within the ideal gas/rigid rotor/harmonic approximation (RRHO) these calculations also provided thermal and entropic corrections to the Gibbs Free Energy at 1 atm and 298.15 K. Electronic energies were obtained from single-point calculations at the M062X-D3/def2-TZVPP level of theory including a polarisable continuum model (SMD) to account for solvent effects.[19] In the absence of parameters for $PhCCl_3$, the chosen dielectric constant ($\varepsilon = 6.72$) corresponded to α-chlorotoluene. The Kohn-Sham orbitals were visualised using Chemcraft.[20] The analysis of molecular orbitals (MOs) in terms of fragment contributions were carried out using the AOMix program.[21,22] FIAs were calculated following a reported procedure from the literature.[23] Single point energies for FIA were calculated in the gas phase and including a polarisable continuum model (dichloromethane) using M062X-D3/aug-cc-PTZ-pp (for Sb) and 6-331G** (for C, H, Cl and F). [24,25] The FIA was calculated using the enthalpy of a free fluoride calculated at the same level of theory (-99.840107 E_h (gas phase) or -99.963301 E_h (dichloromethane)).

Table 8. calculation of FIA for 1,2 and 4 in gas phase and dichloromethane

Gas Phase	**SPE**	**Thermal Correction**	**Corrected Energy**			**SPE**	**Thermal Correction**	**Corrected Energy**		**FIA(Hartree)**	**FIA (kj/mol)**
Cp*SbCl	-1090.209219	0.240029	-1089.96919		Cp*SbCl-F	-1190.332428	0.243756	-1190.088672		0.27937484	733.4986424
Cp*2Sb	-1020.019411	0.47279	-1019.546621		Cp*2Sb-F	-1120.102307	0.476119	-1119.626188		0.23945917	628.7000508
Cp*SbF	-729.8429975	0.240619	-729.6023785		Cp*SbF-F	-829.9690949	0.244207	-829.7248879		0.28240233	741.4473174
SbF5	-739.4926642	0.019773	-739.4728912		SbF6	-839.5385792	0.023076	-839.5155032		0.20250492	531.6766675

DCM correction	**SPE**	**Thermal Correction**	**Corrected Energy**			**SPE**	**Thermal Correction**	**Corrected Energy**		**FIA(Hartree)**	**FIA (kj/mol)**
Cp*SbCl	-1090.274041	0.240029	-1090.034012		Cp*SbCl-F	-1190.339371	0.243756	-1190.095615		0.09830186	258.0915334
Cp*2Sb	-1020.070795	0.47279	-1019.598005		Cp*2Sb-F	-1120.106921	0.476119	-1119.630802		0.06949543	182.4602515
Cp*SbF	-729.9097828	0.240619	-729.6691638		Cp*SbF-F	-829.9766828	0.244207	-829.7324758		0.10001101	262.5789068
SbF5	-739.4995054	0.019773	-739.4797324		SbF6	-839.6095896	0.023076	-839.5865136		0.14348021	376.7072914

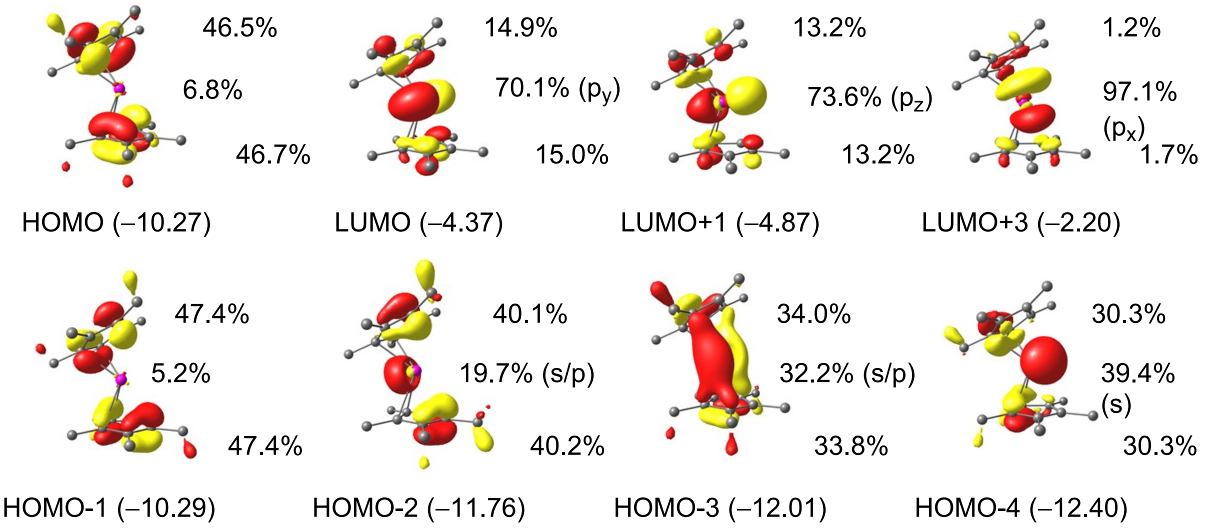

Figure 37. Kohn-Sham Orbitals of $Cp^*_2Sb^+$

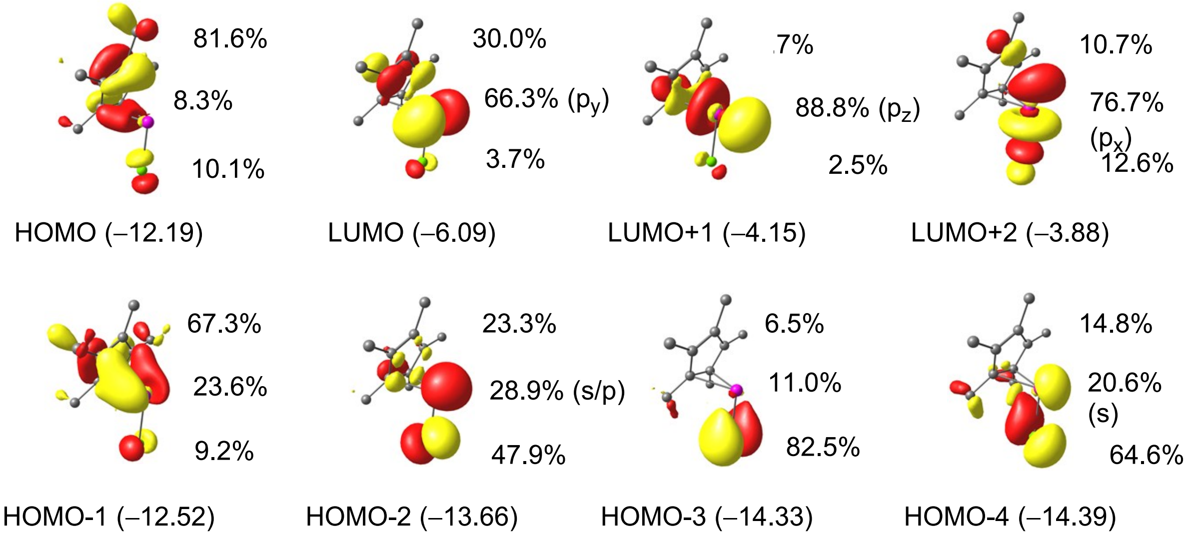

Figure 38. Kohn-Sham Orbitals of Cp^*SbCl^+

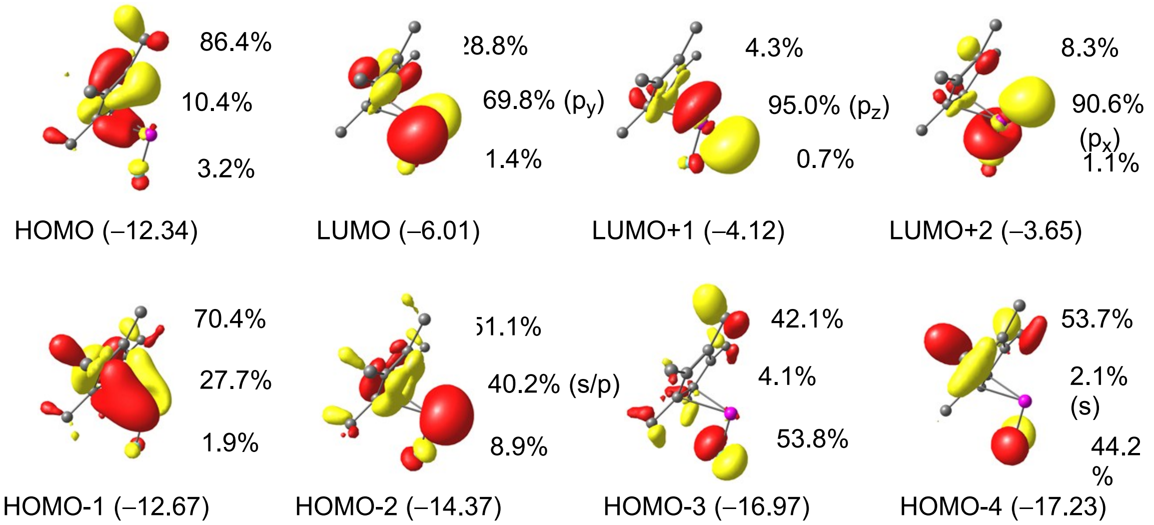

*Figure 39. Kohn-Sham Orbitals of Cp*SbF⁺*

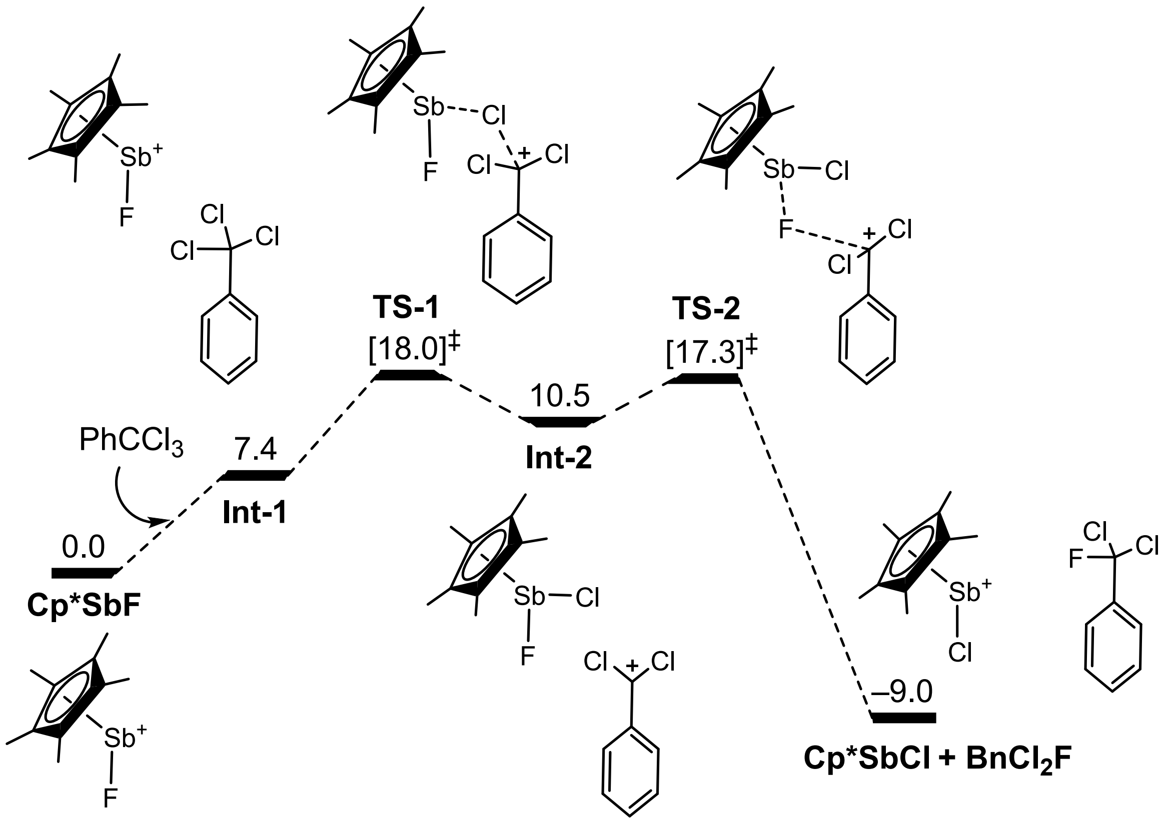

*Figure 40. Computed reaction profile (M062X-D3/def2-TZVPP) for the fluorination of $BnCl_3$ by **4**. Relative Gibbs free energies (1 atm, 298 K, kcal mol^{-1}) corrected for benzyl chloride solvent are given.*

Solution Chemistry Investigation

a)

Cp*SbCl+		
	Monomer	Dimer
GFE Correction	0.180617	0.383529
	-1090.320258	-2180.648017
Corrected (kcal/mol)	-1368125.25	-1368115.966
Difference (Dimer as product)	**9.283843675**	

b)

Cp*SbF+		
	Monomer	Dimer
GFE Correction	0.18261	0.391082
	-729.9661143	-1459.945981
Corrected (kcal/mol)	-915878.2979	-915870.6992
Difference (Dimer as product)	**7.59863595**	

*Figure 41. Calculation of free energy of dimerisation of Cp*SbCl$^+$ (a) and Cp*SbF$^+$ (b) at the M062X-D3/def2-TZVPP level of theory corrected for benzyl chloride solvent.*

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