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Photochemical Activation of SF_6 by *N*-Heterocyclic Carbenes to Provide a Deoxyfluorinating Reagent

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Supporting Information

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Experimental Section

1. Instruments and Methods

All reactions were carried out under inert conditions using standard Schlenck technique or in a glove box under argon atmosphere. Toluene-d_8 , toluene, *n*-hexane ,THF were stored over Solvona® and CD_2Cl_2 was dried over CaH_2. Solvents were distilled and degassed prior to use. Other reagents were bought either from Sigma-Aldrich or abcr. The NMR spectra were recorded at 298 K on a Bruker DPX 300, a Bruker Avance III 300, or a Bruker Avance II 500. The ^1H NMR chemical shifts were referenced to residual toluene-d_7 at δ = 7.09 ppm, C_6D_5H at δ = 7.16 . The ^{19}F NMR spectra was referenced to external $CFCl_3$ at δ = 0.0 ppm and 1,2-difluorobenzene at δ = -138.1 ppm was used as a reference and external standard for quantification.

Mass spectra were recorded on a Micromass Q-Tof-2 instrument equipped with a Linden LIFDI source (Linden CMS GmbH).

The UV irradiation experiments were carried out in a photo multirays reactor (Helios Italquartz) equipped with ten light sources (each 15 W) with an emission maximum at 311 nm

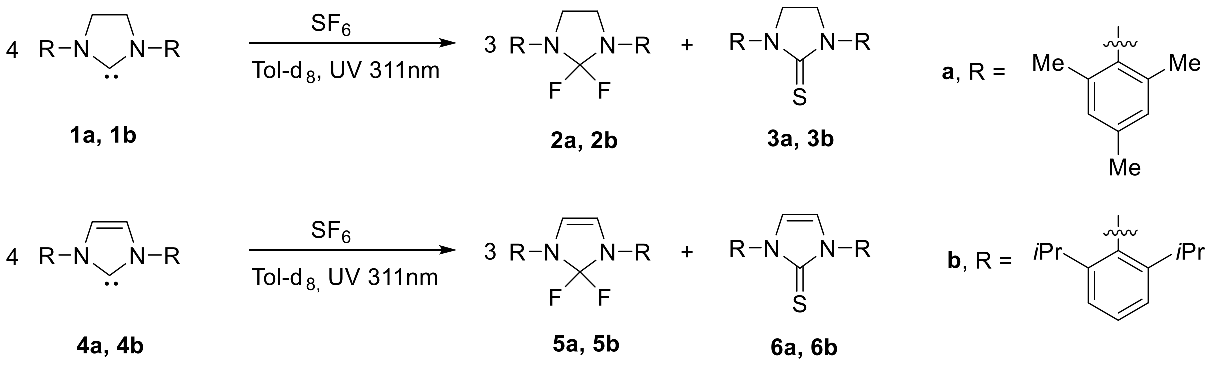
UV-vis spectra were recorded at room temperature by an Agilent 8453 diode array spectrometer connected with a cryostat from Unisoku Scientific Instruments, Japan using 10mm quartz cuvette.

Cyclic Voltammograms (CVs) were measured in THF containing 0.1 M TBAP (tetrabutylammonium hexafluorophosphate) and 1mM of the carbene under an argon atmosphere at room temperature. A potentiostat/galvanostat Reference 600 from Gamry Instruments was used for voltammetry. A conventional one-compartment three electrode cell was equipped with glassy carbon disk as working electrode, a platinum plate as the counter electrode, and Ag/Ag^+ wire in (0.1 M, TBAP + 0.01 M $AgNO_3$ in acetonitrile) solution used as a reference electrode. CVs were recorded at scan rates of 200 mV s^{-1} . All data were referenced to the Fc^0/Fc^+ couple at $E_{1/2}$ = +0.242 V in THF.

Emission spectra were recorded with a FluoroMax-4P from Horiba Jobin Yvon in 10 mm quartz cuvettes at room temperature.

1,3-Bis(2,4,6-trimethylphenyl)-imidazolidin-2-ylidene (SIMes) was synthesized by following the procedure mentioned in the literature.[1] Other carbenes , 1,3-Bis(2,6-di-*i*-propylphenyl)-imidazolidin-2-ylidene (SIPr)**,** 1,3-Bis(2,4,6-trimethylphenyl)-imidazolin-2-ylidene (IMes) and 1,3-Bis(2,6-diisopropylphenyl)-imidazolin-2-ylidene (IPr) were used as purchased from Sigma Aldrich.

2. *General procedure for the activation of SF_6*



Scheme 1: Reduction of SF_6 by *N*-hetrocyclic carbenes.

A solution of the carbene (0.05 mmol) in toluene-d_8 (0.5mL) was prepared in a *J* Young NMR tube. The solution was then freezed to -180 °C, degassed under vaccum followed by a condensation of SF_6 (0.012 mmol, 35 mbar) into it. The reaction sample was brought to room temperature and then irradiated with UV at 311nm for 15 h. A color change of reaction solution was observed from pale yellow to brown. Full conversion of the carbene was observed after 15 h in case of SIMes, other carbenes took 20-24 h for the completion of the reaction. Reaction products obtained after 15 h were characterized and quantified with NMR spectroscopy. NMR yield of fluorinated compounds in reaction mixture were calculated by using 1,2 difluorobenzene (0.2 M in C_6D_6) as an external standard and are based upon the assumption that three equivalents of 2,2-difluoroimidazolidine or 2,2-difluoroimidazoline and one equivalent of respective sulfide were formed. A signal for unreacted SF_6 was observed in the ^{19}F NMR spectrum at δ = 58.7 ppm in each case even after 48 h. Characterization of the 2,2-difluoroimidazolidines and 2,2-difluoroimidazolines by ^1H NMR was hard because signals were overlapping with the signals of respective 2-thio carbene .

To confirm the formation of imidazolidine or imidazoline sulfide it was synthesized separately (Scheme 2-5) and chemical shifts agreed well with the ones obtained for 2-thio carbene obtained during the SF_6 activation reaction.[2]

Analytical Data

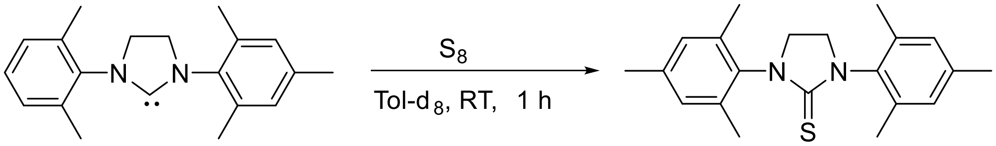
2a: ^1H NMR (300.1MHz, toluene-d_8): δ = 6.77 (s, 4H, *m*-Ar*H*), 3.29 (s, 4H, N*CH*), 2.42 (s, 12H, *o*-C*H*$_3$), 2.25 (s, 6H, *p-CH*$_3$) ppm. ^{19}F NMR (282.4MHz, toluene-d_8): δ = -55.8 ppm, Yield = 82 %.

2b: ^1H NMR (300.1MHz, toluene-d_8) : δ = 7.22-6.96 (m, 6H, Ar-*H*), 3.49 (s, 4H, N*CH*), 3.66 (sept, 4H, *o-CH*(CH_3)$_2$), 1.28 (dd, 24H, *o*-CH(*CH*$_3$)$_2$) ppm, ^{19}F NMR (282.4MHz, toluene-d_8): δ = -55.6 ppm, Yield = 75 %.[3]

5a: ^1H NMR (300.1MHz, toluene-d_8): δ = 6.70 (s, 4H, *m*-Ar-*H),* 5.43 (s, 2H, N*CH*), 2.38 (s, 12H, *o-CH*$_3$), 2.14 (s, 6H, *p-CH*$_3$) ppm ^{19}F NMR (282.4MHz, toluene-d_8): δ = -34.2 ppm, Yield = 62 %. There were signals of side products observed in the ^{19}F NMR spectrum, which are unidentified but the signals indicate the presence of sp^2 - C fluorination products. The amount of side product formed is 5% of **5a.**[4]

5b: ^{1}H NMR (300.1MHz, toluene-d$_8$): δ = 7.25 (m, 2H, *p*-Ar-*H*), 7.14 (d, 4H, *m*-Ar-*H*), 6.64 (s, 2H, N*CH*), 2.92 (sept, 4H, *o-CH*(CH$_3$)$_2$), 1.20 (dd, 24H, *o*-CH(*CH$_3$*)$_2$) ppm; ^{19}F NMR (282.4MHz, toluene-d$_8$): δ = -33.9 ppm, Yield = 15 %. There were signals of side products observed in ^{19}F NMR spectrum, which are unidentified, but the signals indicate the presence of sp^2 - C fluorination products. The amount of side products formed at δ = -95.37 ppm is the same as of **5b**.[3-4]

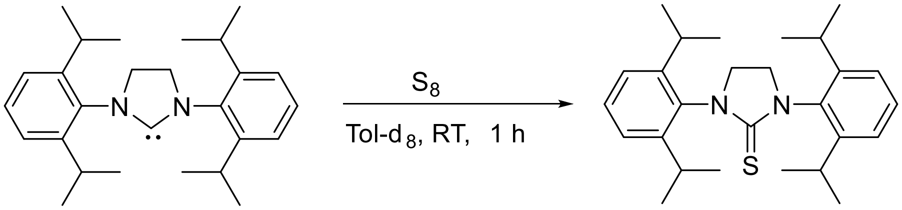
3. *Alternative routes for the formation of 2-thio carbenes.*



1a **3a**

Scheme 2 : Formation of the 1,3-Bis(2,4,6-trimethylphenyl)-imidazolidin-2-sulfide **(3a)**.

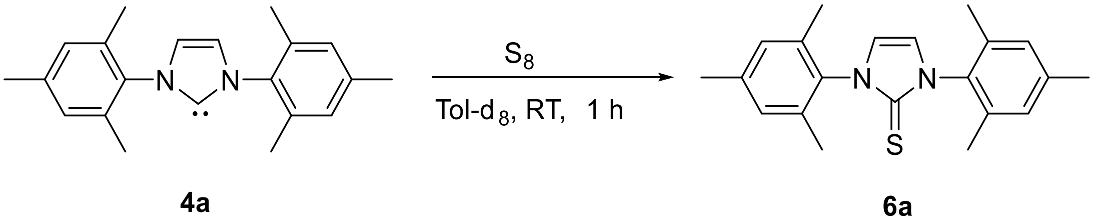
S$_8$ (0.020g, 0.05 mmol) was added into a solution of **1a** (0.015g 0.05 mmol) in toluene-d$_8$ (0.5mL) in a NMR tube. After 1h the reaction mixture was separated from the excess of S$_8$ by filtration and analyzed by NMR spectroscopy. ^{1}H NMR (300.1MHz, toluene-d$_8$): δ = 6.73 (s, 4H, *m*-Ar-*H*), 3.27 (s, 4H, N*CH$_2$*), 2.24 (s, 12H, *o-CH$_3$*), 2.09 (s, 6H, *p-CH$_3$*) ppm. ^{13}C (125.7 MHz, toluene-d$_8$): δ = 181.51 (C=S), 137.61, 136.94, 135.66, 129.57, 47.36 (NCH$_2$), 21.04, 17.94 ppm.[2b]



1b **3b**

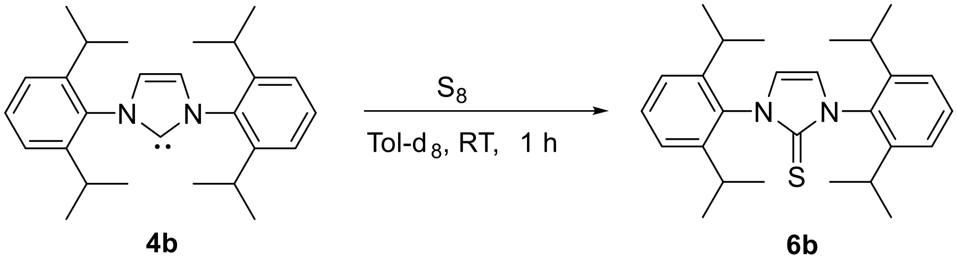
Scheme 3: Formation of 1,3-Bis(2,6-diisopropylphenyl)-imidazolidin-2-sulfide **(3b).**

S$_8$ (0.020g, 0.05 mmol) was added into a solution of **1b** (0.015g 0.05 mmol) in toluene-d$_8$ (0.5mL) in a NMR tube. After 1h, the reaction mixture was separated from the excess of S$_8$ by filtration and analyzed by NMR spectroscopy. ^{1}H NMR (300.1MHz, toluene-d$_8$): δ = 7.17 (m, 2H, *p*-Ar-*H*), 7.05 (d, 4H, *m*-Ar-*H*), 3.47 (s, 4H, N*CH$_2$*), 3.11 (sept, 4H, *o-CH(*CH$_3$)$_2$), 1.32 (dd, 24H, *o*-CH(*CH$_3$)$_2$*) ppm. ^{13}C (125.7 MHz, toluene-d$_8$): δ = 184.94 (C=S), 147.80, 135.69, 129.31, 124.40, 50.29 (NCH$_2$), 29.38, 24.77, 24.55 ppm.[2b]



Scheme 4: Synthesis of 1,3-Bis(2,4,6-trimethylphenyl)-imidazolin-2-sulfside **(6a)**.

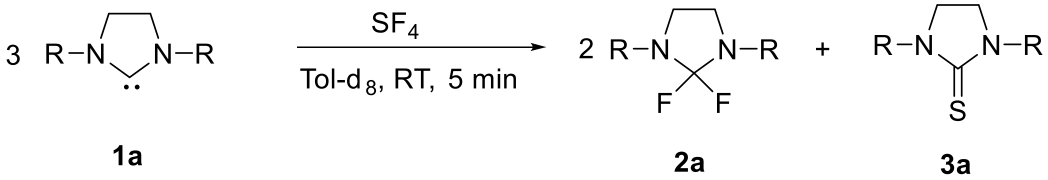
S_8 (0.020g, 0.05 mmol) was added into a solution of **4a** (0.015g 0.05 mmol) in toluene-d_8 (0.5mL) in a NMR tube. After 1h, the reaction mixture was separated from the excess of S_8 by filtration and analyzed by NMR spectroscopy. ^{1}H NMR (300.1MHz, toluene-d_8): δ = 6.70 (s, 4H, *m*-Ar-*H*), 5.91 (s, 2H, N*CH*), 2.09-2.05 (m, 18H, Ar-*CH₃*) ppm. ^{13}C (125.7 MHz, toluene-d_8): δ = 165.17 (C=S), 138.59, 136.13, 134.23, 129.30, 117.2 (NCH), 21.07, 18.10 ppm.[2a]



Scheme 5: Synthesis of 1,3-Bis(2,6-diisopropylphenyl)-imidazolin-2-sulfide (**6b**).

S_8 (0.020g, 0.05 mmol) was added into a solution of 4b (0.015g 0.05 mmol) in toluene-d_8 (0.5mL) in a NMR tube. After 1h, the reaction mixture was separated from the excess of S_8 by filtration and analyzed by NMR spectroscopy. ^{1}H NMR (300.1MHz, toluene-d8) : δ = 7.20 (m, 2H, *p*-Ar-*H*), 7.07 (d, 4H, *m*-Ar-*H*), 6.21 (s, 2H, N*CH*), 2.86 (sep, 4H, *o-CH(*$CH_3)_2$), 1.26 (dd, 24H, *o*-CH(*CH_3*)$_2$) ppm. ^{13}C (125.7 MHz, toluene-d_8): δ = 168.45 (C=S), 146.88, 134.66, 130.08, 124.20, 118.59 (NCH), 29.24, 24.16, 23.81 ppm.[2c]

4. Reaction of SF_4 with SIMes

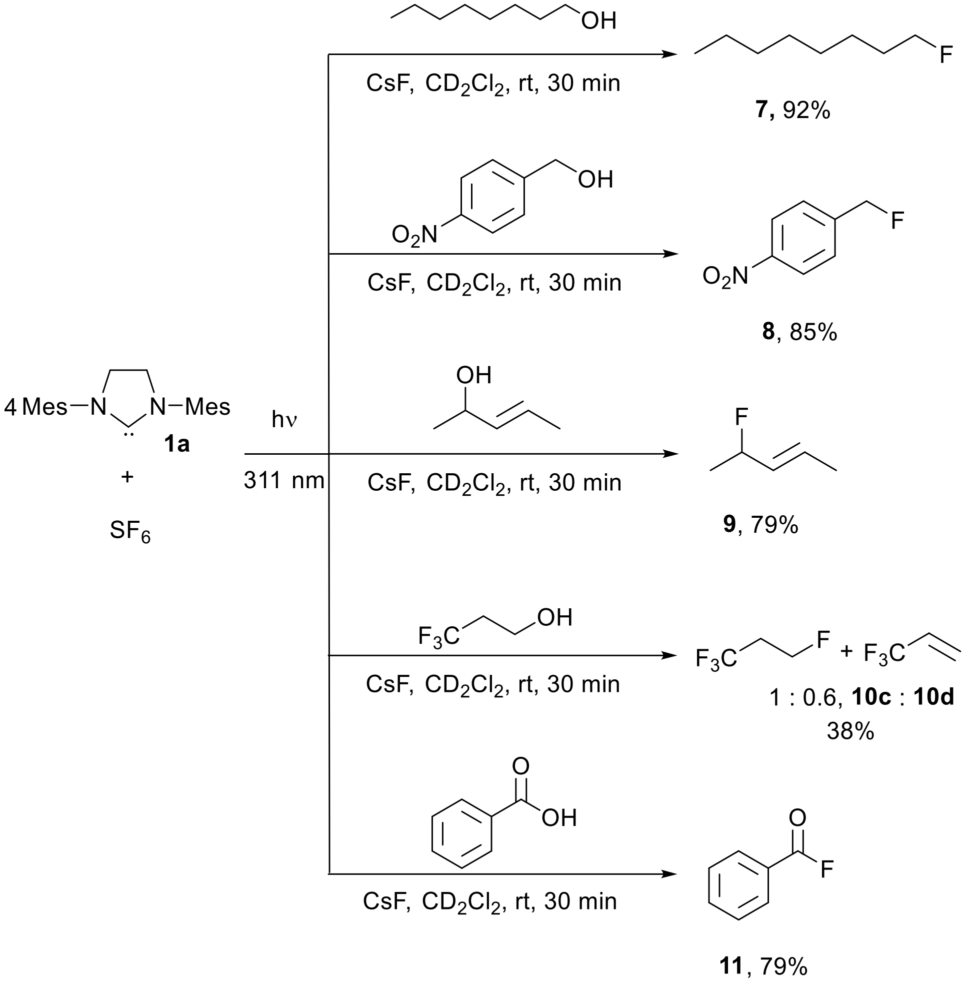


Scheme 6. Reaction of SF_4 with a *N*-hetrocyclic carbene.

A solution of SIMes (0.015g, 0.05 mmol) in toluene-d_8 (0.5mL) was prepared in a *J* Young NMR tube. The solution was then freezed to -180 °C, degassed under vaccum followed by condensation of SF_4 (0.016 mmol, 60 mbar) into it. A change in color from pale yellow to brown was observed as soon as the sample was brought to room temperature.

NMR data: **2a**: ^{1}H NMR (300.1MHz, toluene-d_8) : δ = 6.77 (s, 4H, *m*-Ar-*H*), 3.29 (s, 4H, N*CH*), 2.42 (s, 12H, *o-CH₃*), 2.25 (s, 6H, *p-CH₃*) ppm; ^{19}F NMR (282.4MHz, toluene-d8) : δ = -55.8 ppm; **3a** : ^{1}H NMR (300.1MHz, toluene-d_8): δ = 6.73 (s, 4H, *m*-Ar-*H*), 3.27 (s, 4H, N*CH*), 2.24 (s, 12H, *o-CH₃*), 2.09 (s, 6H, *p-CH₃*) ppm.

5. *General procedure for the deoxyfluorination reactions with SF₆*



Scheme 7. Deoxyfluorination reactions with SF_6

A solution of **1a** (0.05 mmol) in toluene-d_8 (0.5mL) was prepared in a *J* Young NMR tube. The solution was then freezed to -180 °C, degassed under vaccum followed by a condensation of SF_6 (0.012 mmol, 35 mbar) into it. The reaction sample was brought to room temperature and then irradiated with UV at 311nm for 15 h. The product mixture **(2a** and **3a)** obtained by the reaction of SIMes and SF_6 was degassed under vaccum and filtered to a NMR tube. The filtrate was evaporated and the residue dissolved in CD_2Cl_2. To this solution 0.025 mmol of alcohol and CsF (0.01g , 0.075 mmol) were added. Products were quantified and characterized by ^{19}F NMR spectroscopy. The yields of the fluorinated compounds were calculated by using 1,2 difluorobenzene (0.2M in C_6D_6) as an external standard. Since products obtained with fluorination of trifluoropropanol are gaseous, the conversion of trifluoropropanol was determined to quantify the reaction. NMR data:

7: ^{19}F NMR (282.4MHz, CD_2Cl_2): δ = -218.0 (tt, $^2J_{FH}$ = 47.3 Hz, $^3J_{FH}$ = 24.5 Hz) ppm.[5]

8: ^{19}F NMR (282.4MHz, CD_2Cl_2): δ = -215.4 (t, $^2J_{FH}$ = 44.8 Hz) ppm.[6]

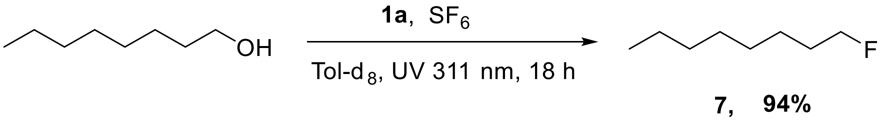
9: ^{19}F NMR (282.4MHz, CD_2Cl_2): δ = -162.3 (m) ppm.[7]

10c: ^{19}FNMR (282.4MHz, CD_2Cl_2): δ = -65.0 (m, 3F, $^4J_{FF}$ = 6.3 Hz), -221.8 (m, 1F, $^4J_{FF}$ = 6.3 Hz) ppm.

10d: ^{19}F (282.4MHz, CD_2Cl_2): δ = -66.1 (d, $^3J_{FH}$ = 7.08 Hz) ppm.[8]

11: ^{19}F (282.4MHz, CD_2Cl_2): δ = 17.7 (s) ppm.[9]

6. One pot fluorination of 1- octanol



Scheme 8. One pot approach for deoxyfluorination of octanol. The yield was calculated by using 1,2 diluorobenzene (0.2M in C_6D_6) as an external standard.

A *J* Young NMR tube was filled with SIMes (0.015g, 0.05 mmol), 1-octanol (4µL, 0.025 mmol) and toluene d_8 (0.5ml). The reaction mixture solution was freezed at -180 °C and degassed under vaccum. SF_6 (0. 012 mmol, 35 mbar) was condensed on it and the reaction sample was brought to room temperature and irradiated with UV at 311 nm for 18 h. The signal for 2,2-difluoroimidazolidin (2a) was observed at δ = -55.8 ppm when an ^{19}F NMR spectrum was recorded after 8 h. The resonance disappeared and a signal which revealed the volution of 1-fluorooctane at δ = -218.0 ppm after 18 h appeared.

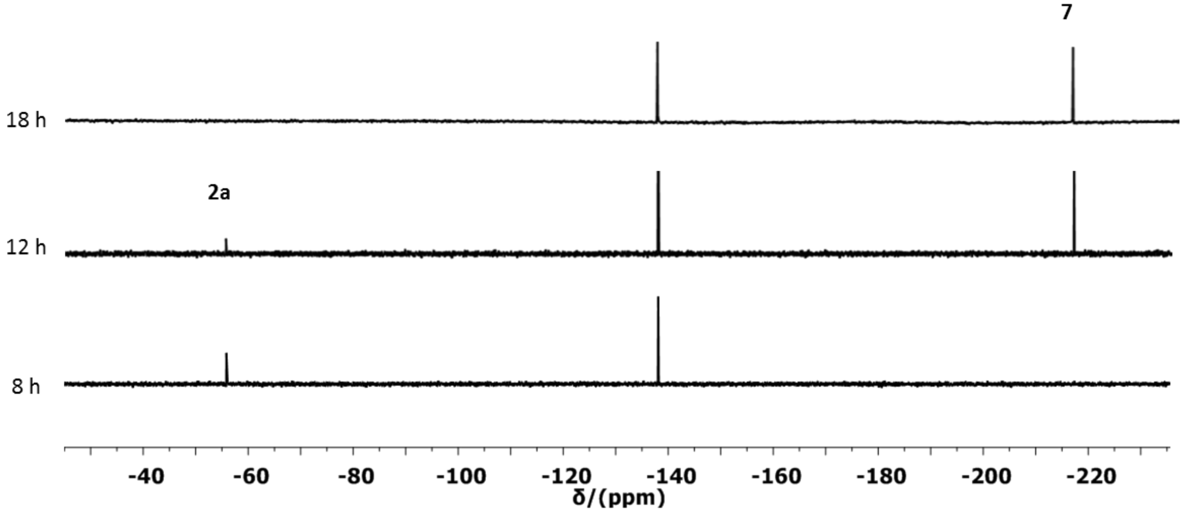


Figure 1: ^{19}F NMR (282.4 MHz, toluene-d_8) of the one pot fluorination reaction measured after different time intervals. 1,2 difluorobenzene at δ = -138.1 ppm used as an external standard

7. UV-Vis spectroscopy of carbenes

Figures 2-5 depict UV-vis spectra for 1mM solution of carbenes in THF. It was observed that the saturated carbenes **1a** and **1b** show absorbance maxima at 247 nm and 252 nm respectively, and the unsaturated carbenes **4a** and **4b** have absorbance maxima at 269 nm for both. These maxima can be attributed to absorption processes based on the inner imidazolyl unit, while maxima at 220 nm or 221 nm can be attributed to the aromatic substituents at the N-atoms.

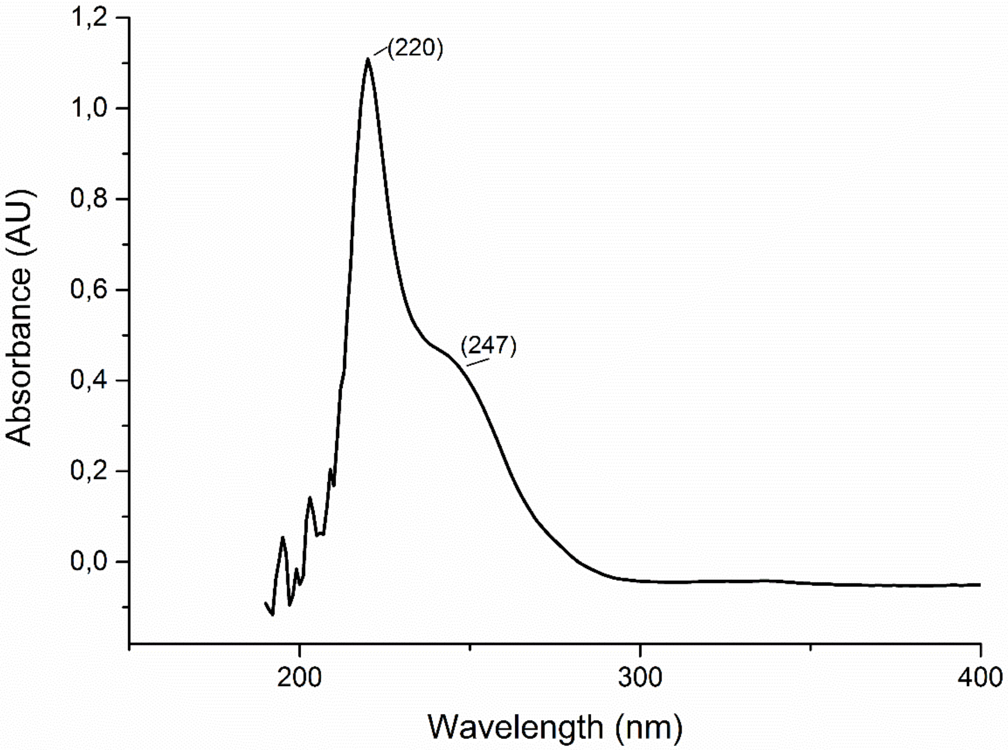


Figure 2 : UV-vis spectum of SIMes **(1a)** in THF showing maxima at 220 nm and 247 nm.

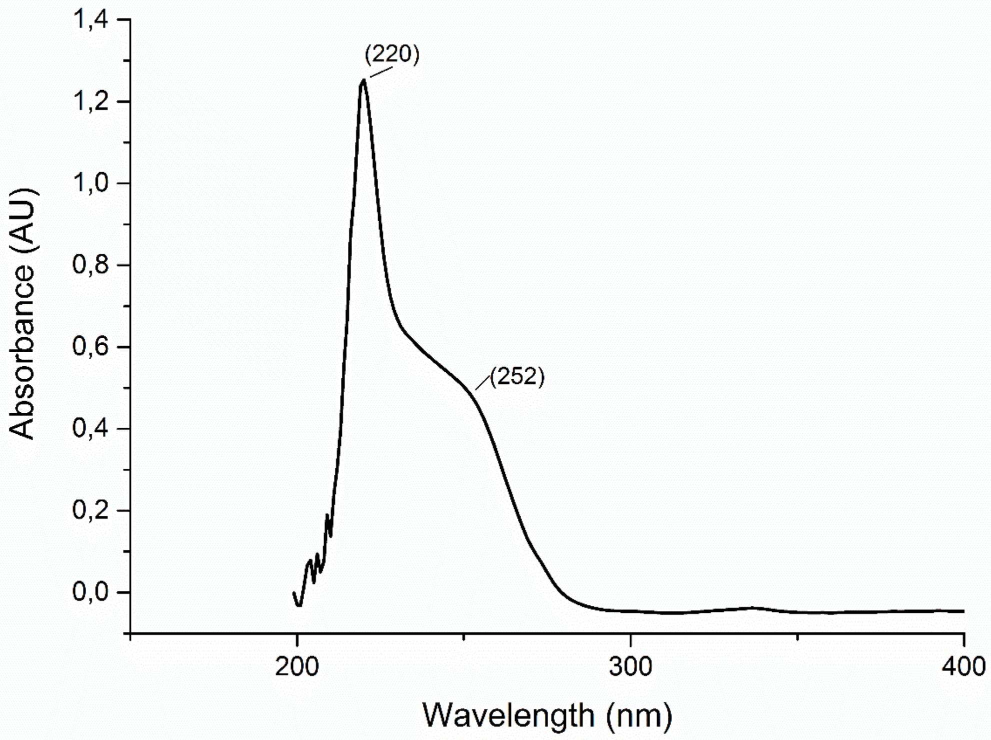


Figure 3 : UV-vis spectum of SIPr **(1b)** in THF showing maxima at 220 nm and 252 nm.

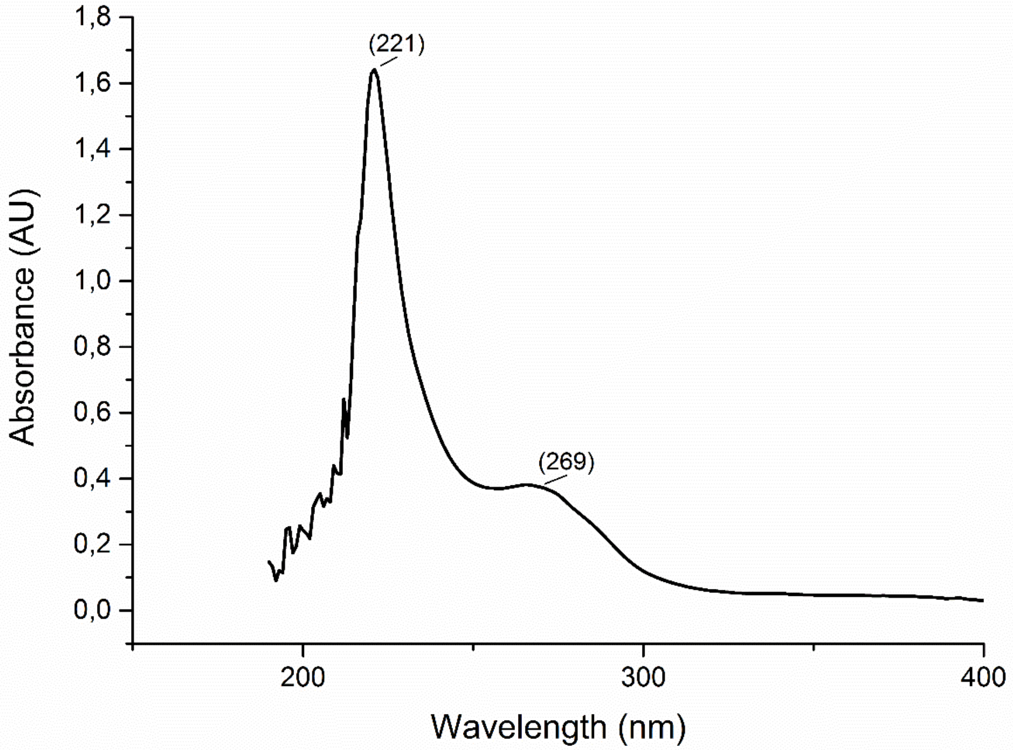


Figure 4 : UV-vis spectrum of IMes **(4a)** in THF showing maximas at 221 nm and 252 nm.

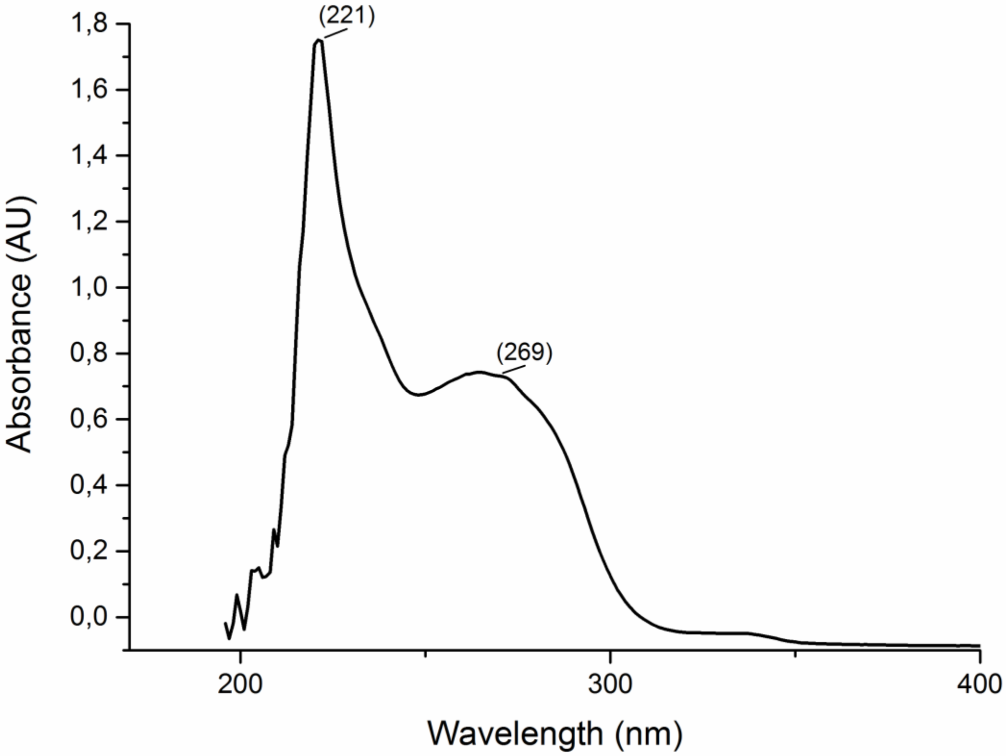


Figure 5 : UV-vis spectrum of IPr **(4b)** in THF showing maxima at 221 nm and 269 nm.

8. Cyclic voltammetry measurements for NHC carbenes

Figures 6-10 depict cyclic voltammograms for 1mM solutions of carbenes in THF. As observed from the **Figure 6**, SIMes showed a typical single electron transfer kind of cyclic voltammogram with an anodic peak potential **(E_P^{ox}) at 1.024 V vs Fc^0/Fc^+** and no redox event appearing in the negative region. Similar irreversible type of voltammograms were observed for the other investigated carbenes. Therefore, only the area of oxidation is shown in **Figures 7 - 10.** Oxidation potential (E_P^{ox}) was re-calculated v/s SCE as well by taking Fc^0/Fc^+ v/s SCE at 0.56 V.[10,11]

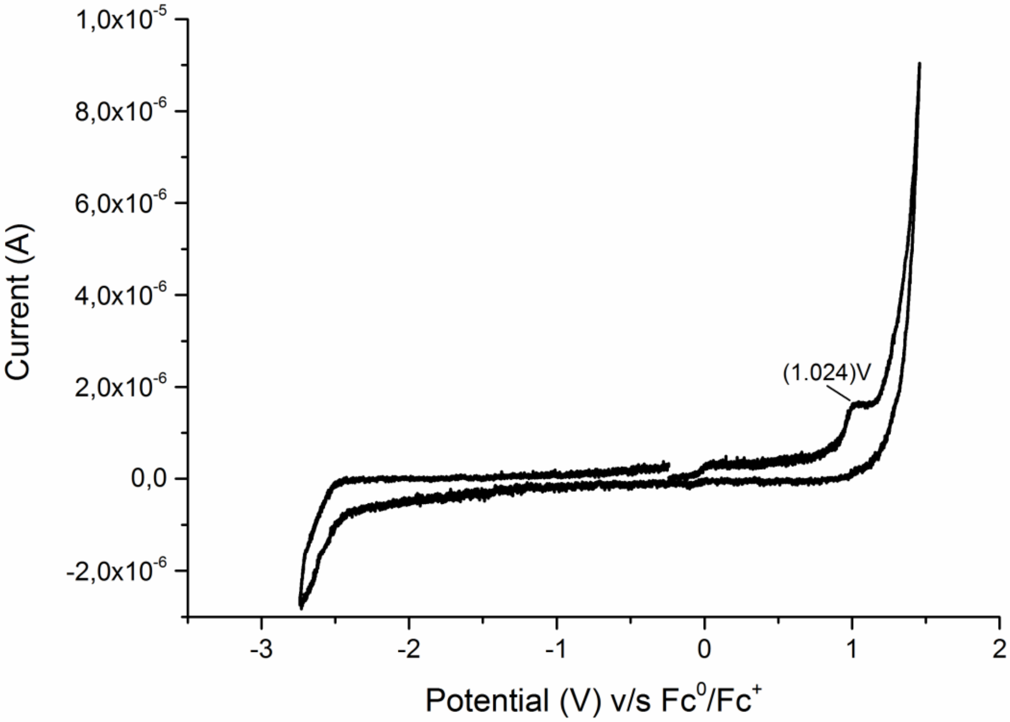


Figure 6: Cyclic voltammogram obtained from a solution of SIMes **(1a)** in THF. E_P^{ox} = 1.024 V v/s Fc^0/Fc^+ and E_P^{ox} = 1.584 V v/s SCE; measured with a scan rate of 200 mV/s.

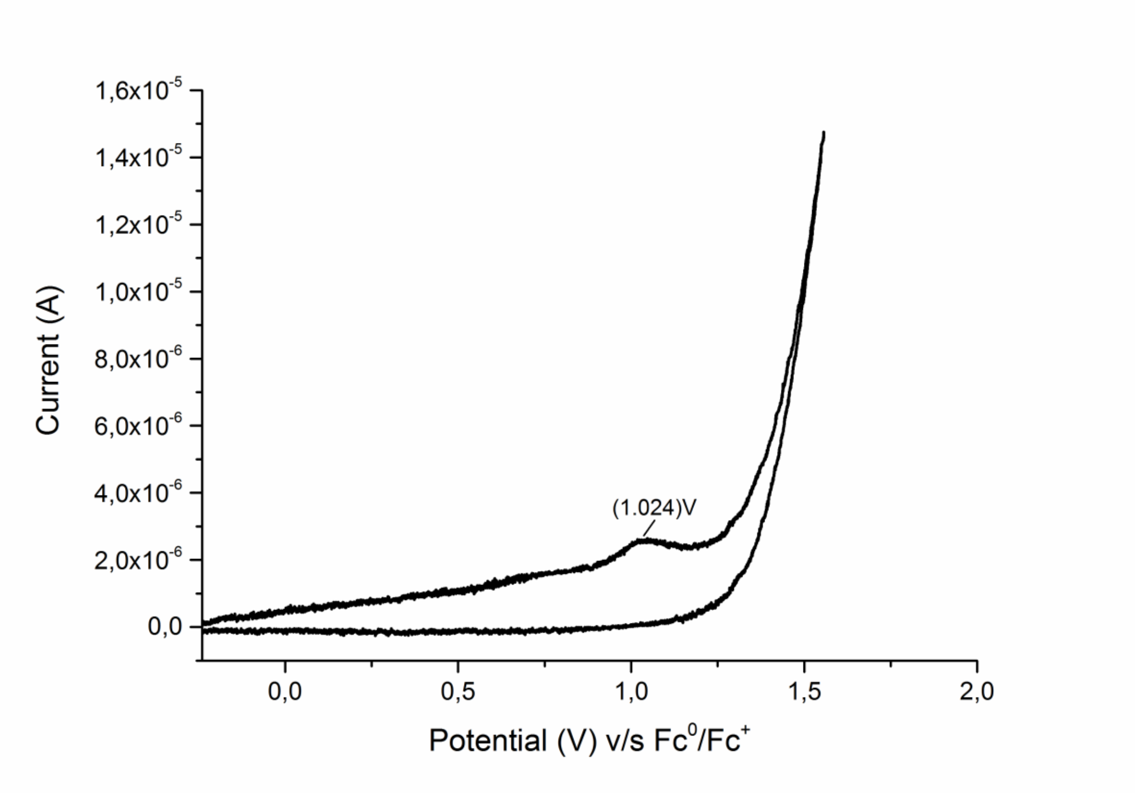


Figure 7: Cyclic voltammogram obtained from a solution of SIMes **(1a)** in THF. E_P^{ox} = 1.024 V v/s Fc^0/Fc$^+$ and E_P^{ox} = 1.584 V v/s SCE ; measured with a scan rate of 200 mV/s.

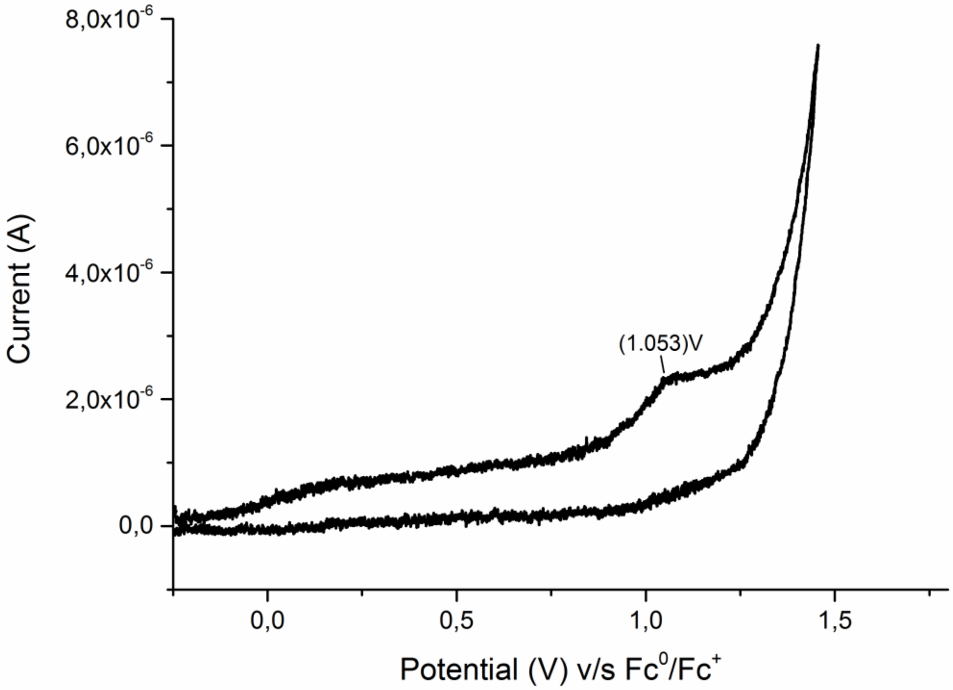


Figure 8: Cyclic voltammogram obtained from a solution of SIPr **(1b)** in THF. E_P^{ox} = 1.053 V v/s Fc^0/Fc^+ and E_P^{ox} = 1.613 V v/s SCE; measured with a scan rate of 200 mV/s.

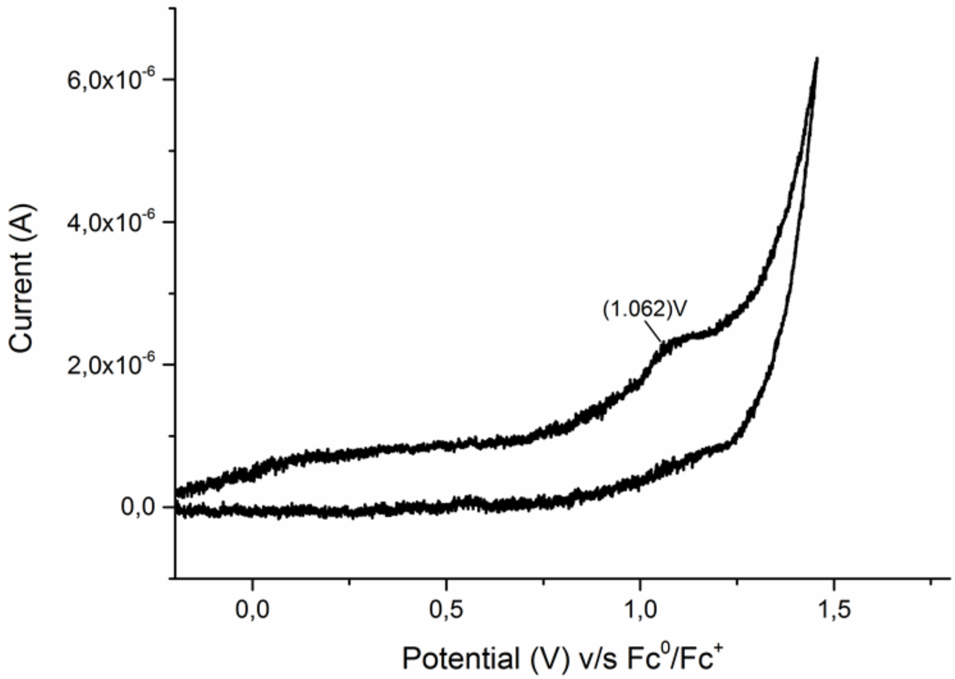


Figure 9: Cyclic voltammogram obtained from a solution of IMes **(4a)** in THF. E_P^{ox} = 1.062 V v/s Fc^0/Fc^+ and E_P^{ox} = 1.622 V v/s SCE; measured with a scan rate of 200 mV/s.

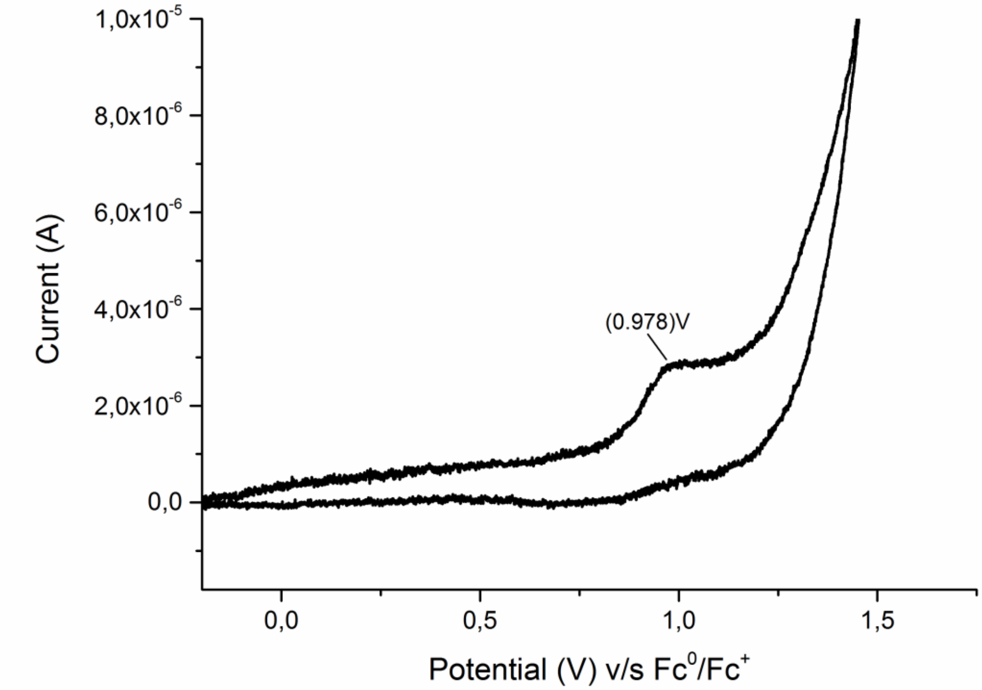


Figure 10 : Cyclic voltammogram obtained from a solution of IPr **(4b)** in THF. E_P^{ox} = 0.978 V v/s Fc^0/Fc^+ and E_P^{ox} = 1.538 V v/s SCE ; measured with a scan rate of 200 mV/s.

9. Emission spectroscopy for carbenes

Figures 11-14 depict emission spectra which were recorded for 1mM solution of carbenes in THF at room temperature. Samples first were scanned at a fixed emission wavelength (350 nm) and the excitation wavelength was chosen to be where maximum absorbance was observed for the different carbenes. SIMes showed an emission maximum at 327 nm when excited at 298 nm and the other carbenes (SIPr, IMes, IPr) showed emission maxima at 349 nm when excited at 318 nm. SIMes behaved differently as it did not show an emission maximum at 349 nm when excited at 318 nm.

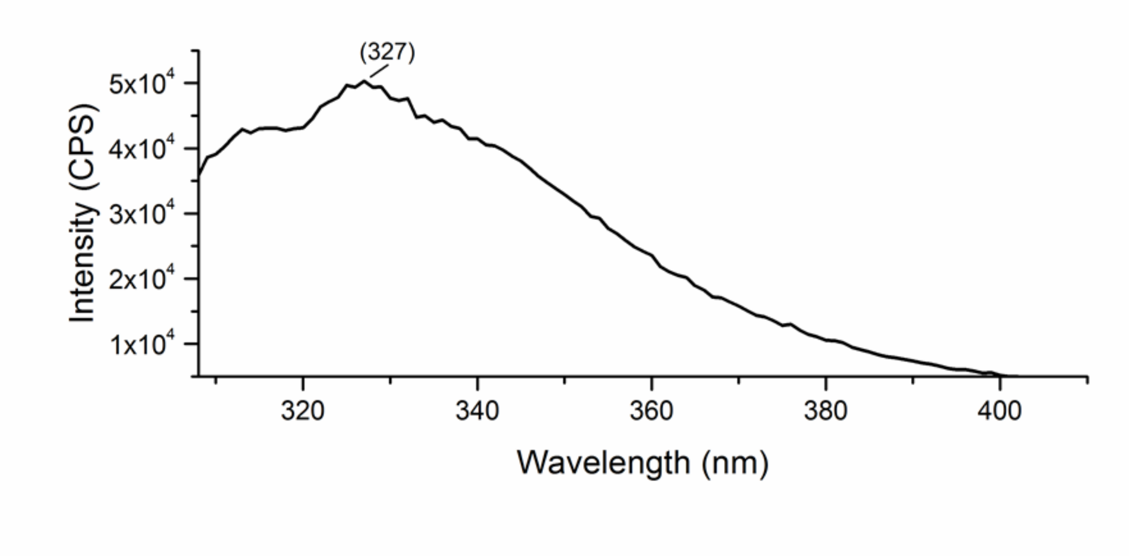


Figure 11: Emission spectrum obtained for a solution of SIMes (1mM) (**1a**) in THF. Excitation at 298 nm , slit width = 5.00 nm; emission maxima at 327 nm, slit width = 2.00 nm.

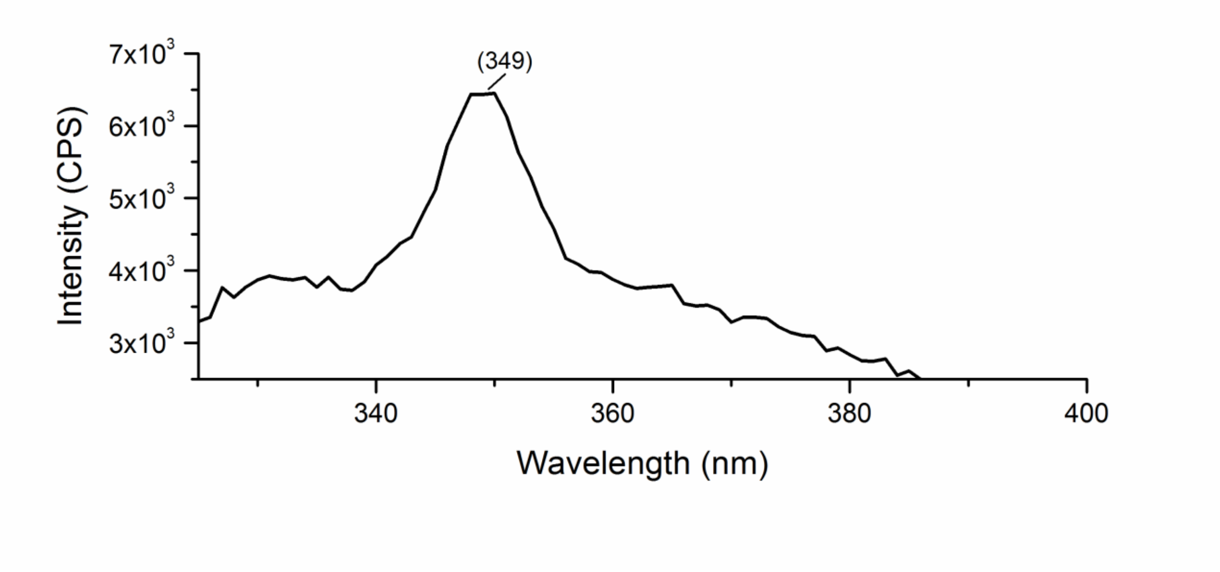


Figure 12: Emission spectrum obtained for a solution of SIPr (1mM) (**1b**) in THF. Excitation at 318 nm, slit width = 5.00 nm; emission maxima at 349 nm, slit width = 2.00 nm.

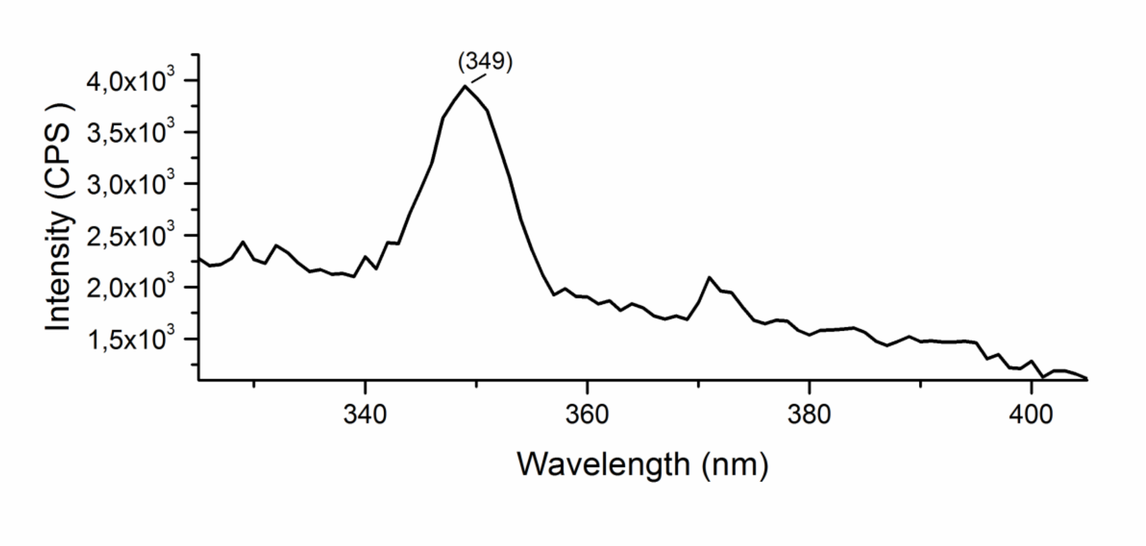


Figure 13: Emission spectrum obtained for a solution of IMes (1mM) (**4a**) in THF. Excitation at 318 nm, slit width = 5.00 nm; emission maxima at 349 nm, slit width = 2.00 nm

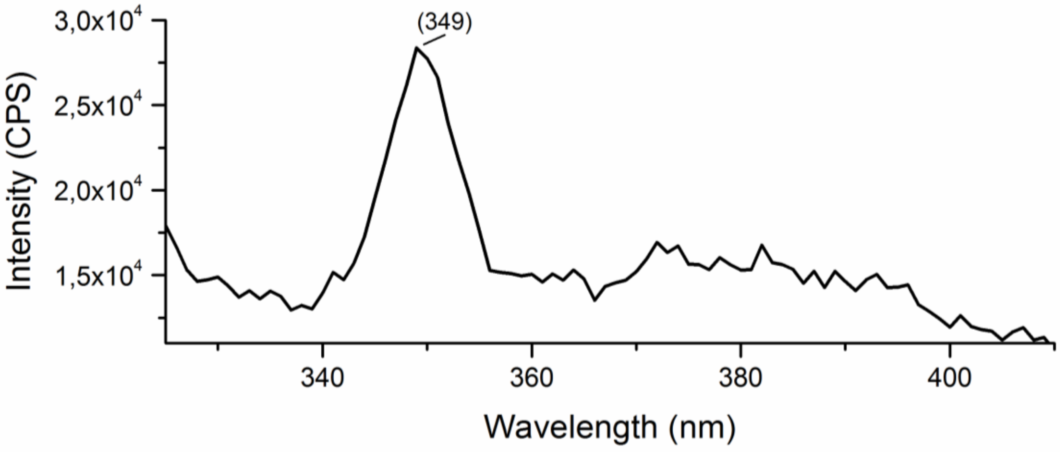


Figure 14 : Emission spectrum obtained for a solution of IPr (1mM) (**4b**) in THF. Excitation at 318 nm , slit width = 5.00 nm; emission maxima at 349 nm, slit width = 2.00 nm

10. Reactivity Trend

To understand the reactivity trend of different carbenes for the reduction of SF_6 when irradiated at 311 nm, we estimated the redox potential in the excited state of different carbenes using the formula.[12]

$E\ (A^+/A^*) \approx E\ (A^+/A) - E^{0\text{–}0}$ for oxidative electron transfer ($A^* + B \longrightarrow A^+ + B^-$)

where E(A+/A*) = potential of the excited-state couples
$E\ (A^+/A)$ = potentials of the ground-state couples
$E^{0\text{–}0}$ = one-electron potential corresponding to the zero–zero excited-state energy

$E\ (A^+/A)$ was estimated from the cyclic voltammetry, for simplicity the peak potential (E_p^{ox} v/s SCE) was used, and $E^{0\text{–}0}$ was estimated from maxima in the emission maxima. Therefore $E\ (A^+/A^*)$ for different carbenes were calculated as depicted in Table 1.

Table 1. Calculated excited state potential of carbenes v/s SCE

Carbene	E_p^{ox} V vs SCE	Emiss. Max (nm)	$E^{0\text{-}0}$ (eV)	$E\ (A^+/A^*)$ V vs SCE
SIMes	1.584	327	3.792	-2.208
SIpr	1.613	349	3.553	-1.940
IMes	1.622	349	3.553	-1.931
IPr	1.538	349	3.553	-2.015

11. References

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12. NMR Spectra

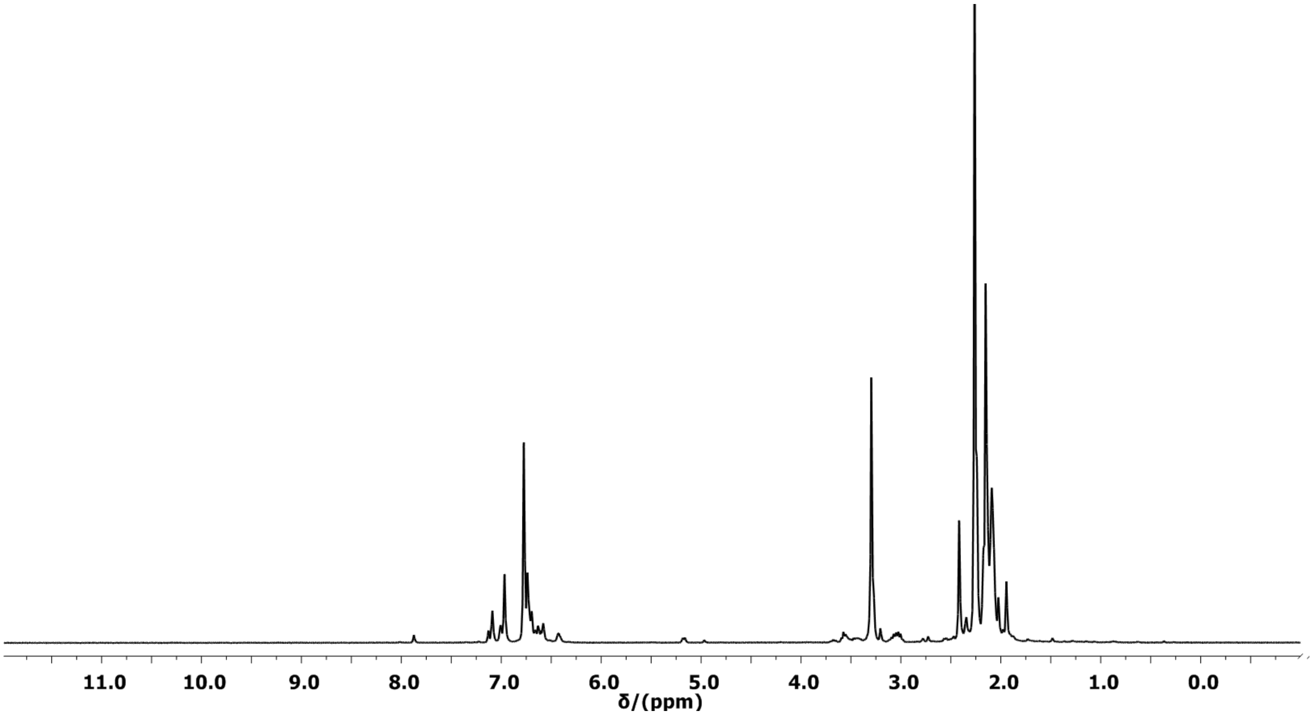

Figure 15: ^{1}H NMR spectrum (300.1 MHz, toluene-d$_8$) for the activation of SF$_6$ with SIMes (**1a**).

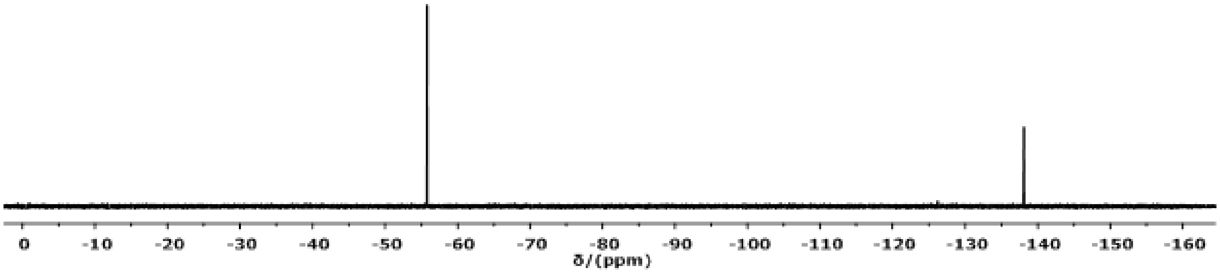

Figure 16: ^{19}F NMR spectrum (282.4 MHz, toluene-d^8) for the activation of SF$_6$ with SIMes (**1a**). 1,2-difluorobenzene (δ = -138.1 ppm) was used as an external standard.

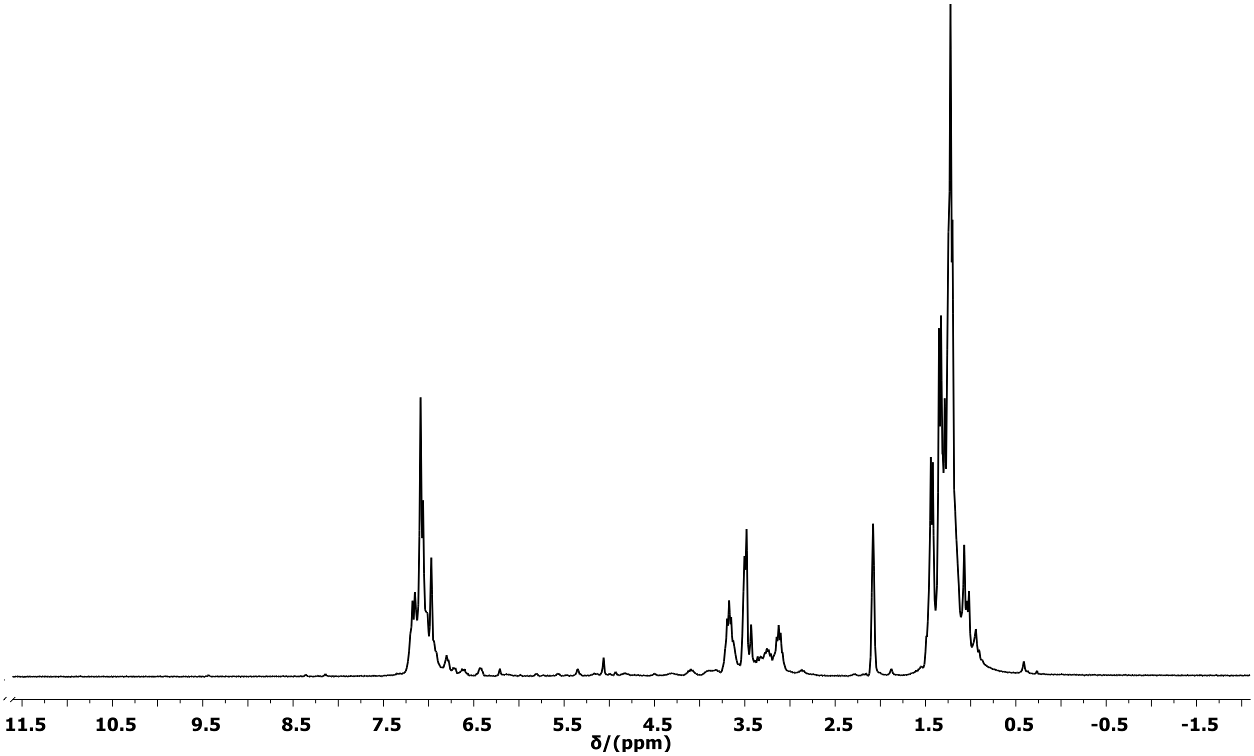

Figure 17: ^{1}H NMR spectrum (300.1 MHz, toluene-d_8) for the activation of SF_6 with SIPr (**1b**).

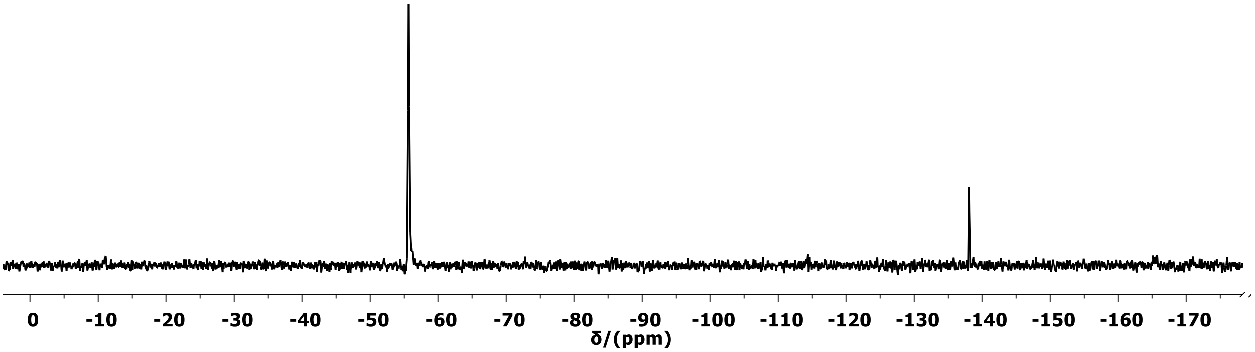

Figure 18: ^{19}F NMR spectrum (282.4 MHz, toluene-d^8) for the activation of SF_6 with SIPr (**1b**). 1,2-difluorobenzene (δ = -138.1 ppm) was used as an external standard.

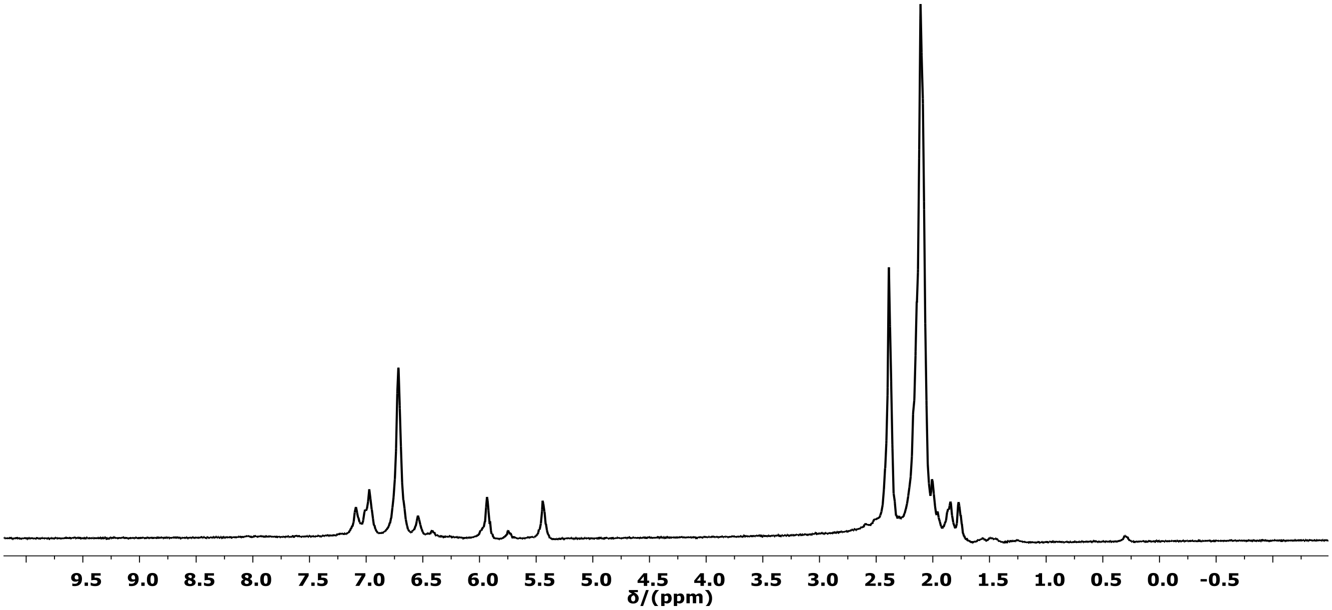

Figure 19: ^{1}H NMR spectrum (300.1 MHz, toluene-d_8) for the activation of SF_6 with IMes (**4a**).

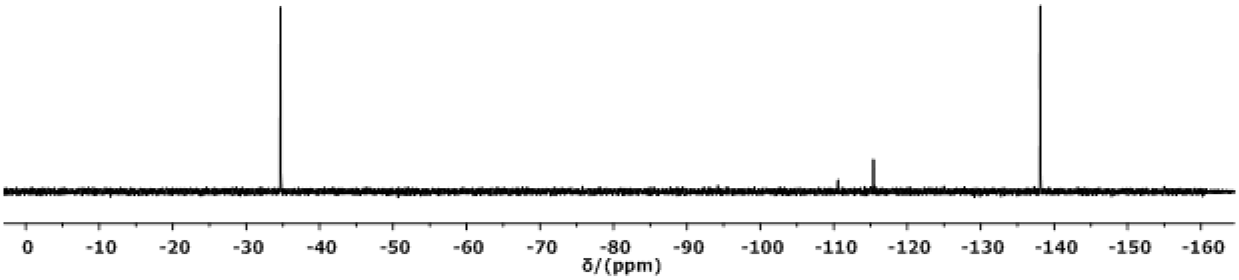

Figure 20: ^{19}F NMR spectrum (282.4 MHz, toluene-d_8) for the activation of SF_6 with IMes (**4a**). 1,2-difluorobenzene (δ = -138.1 ppm) was used as an external standard.

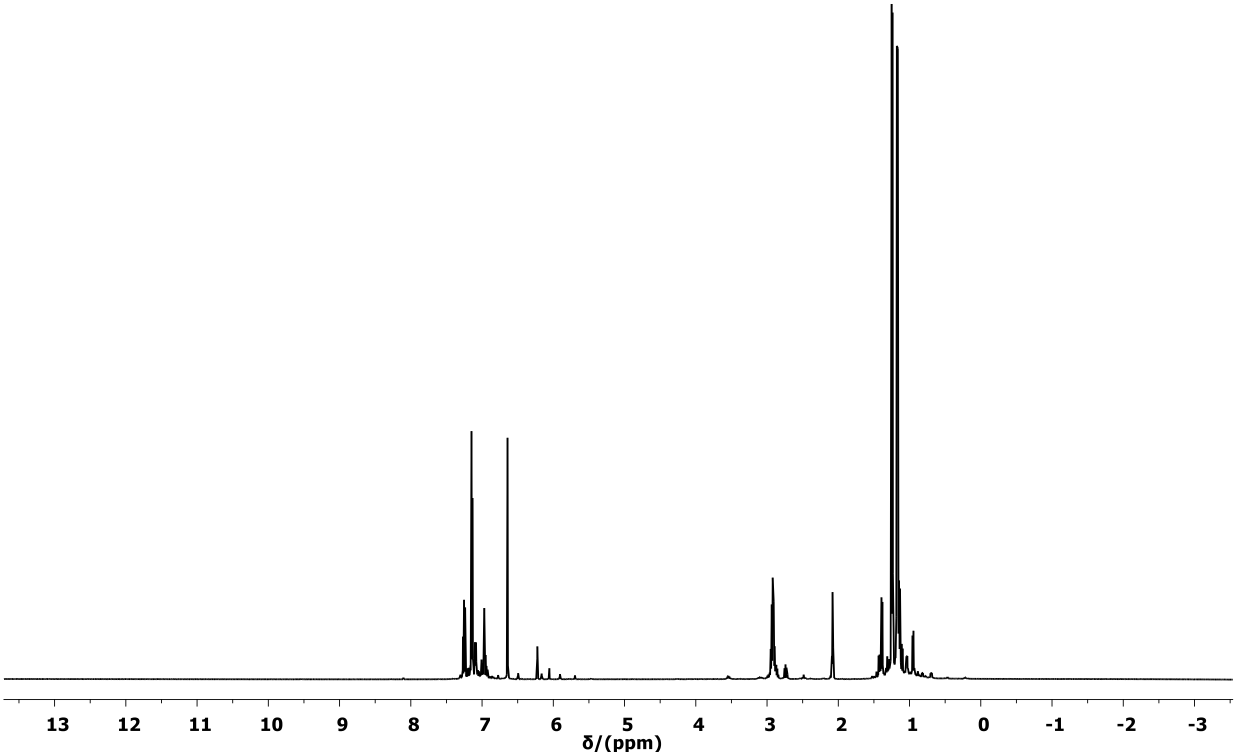

Figure 21: ^{1}H NMR spectrum (300.1 MHz, toluene-d_8) for the activation of SF_6 with IPr (**4b**).

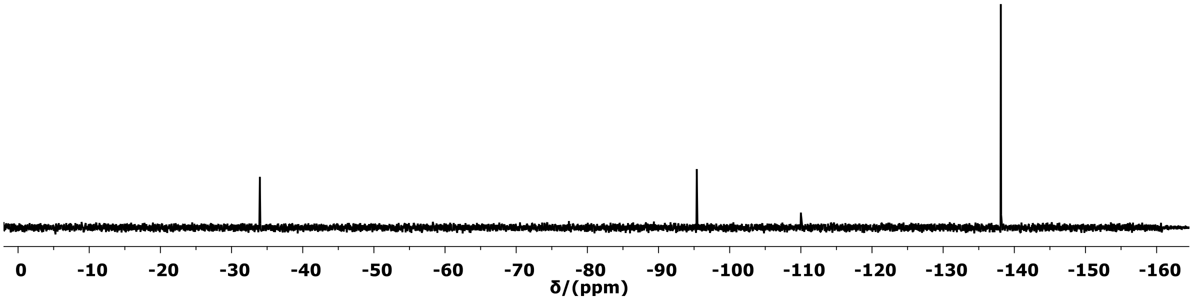

Figure 22 : ^{19}F NMR spectrum (282.4 MHz, toluene-d_8) for the activation of SF_6 with IPr (**4b**). 1,2-difluorobenzene (δ = -138.1 ppm) was used as an external standard.

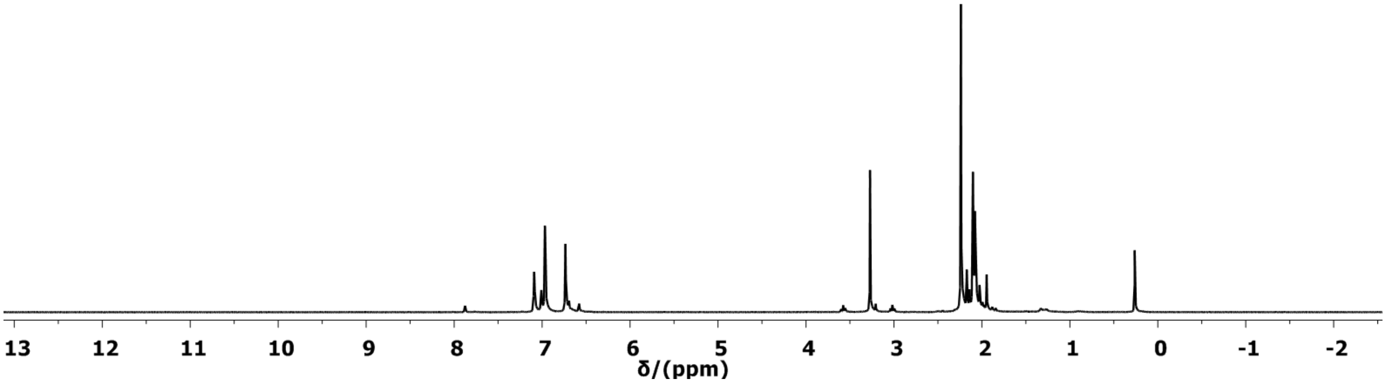

Figure 23: ^{1}H NMR spectrum (300.1 MHz, toluene-d$_8$) for the synthesis of **3a**.

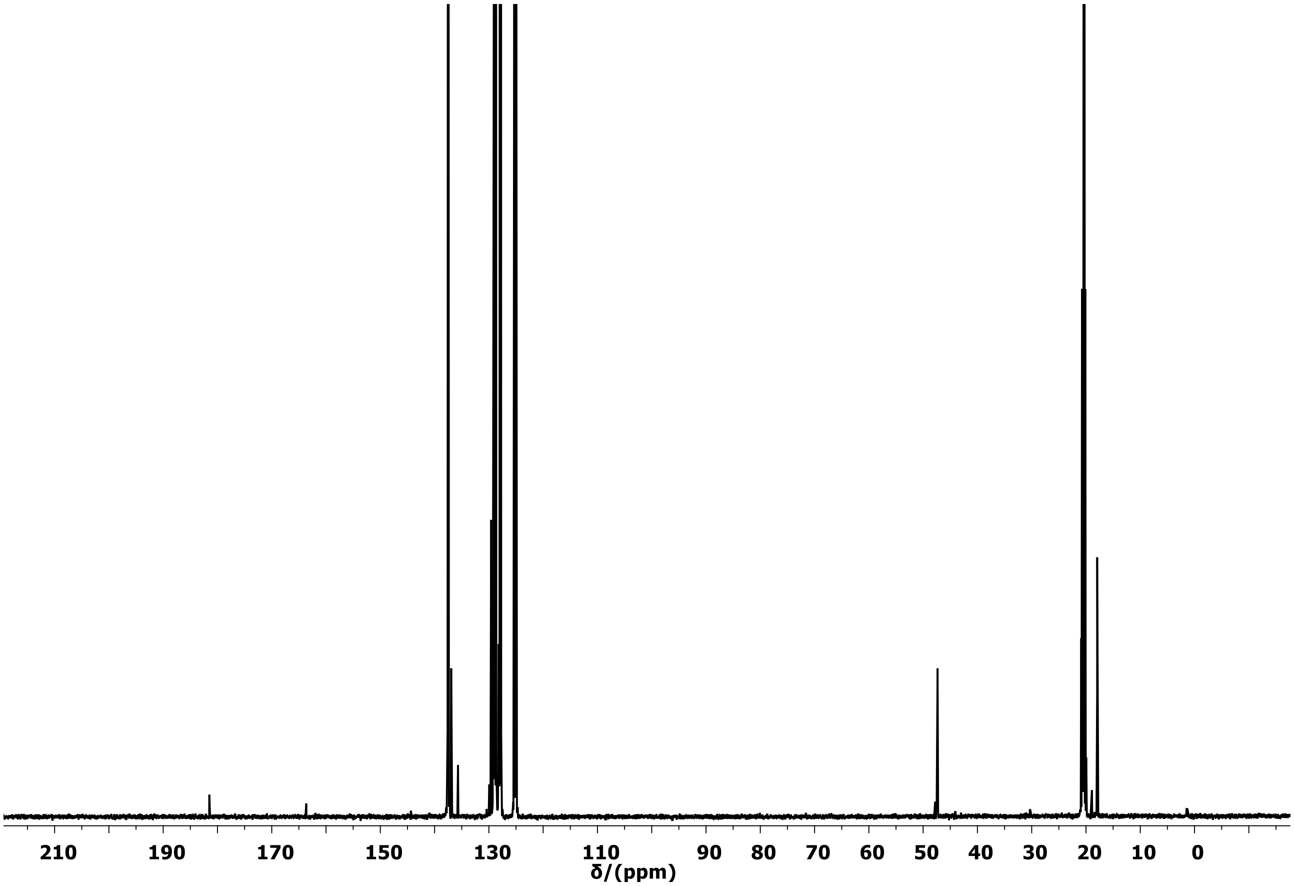

Figure 24: ^{13}C NMR spectrum (125.7.1 MHz, toluene-d$_8$) for the synthesis of **3a**.

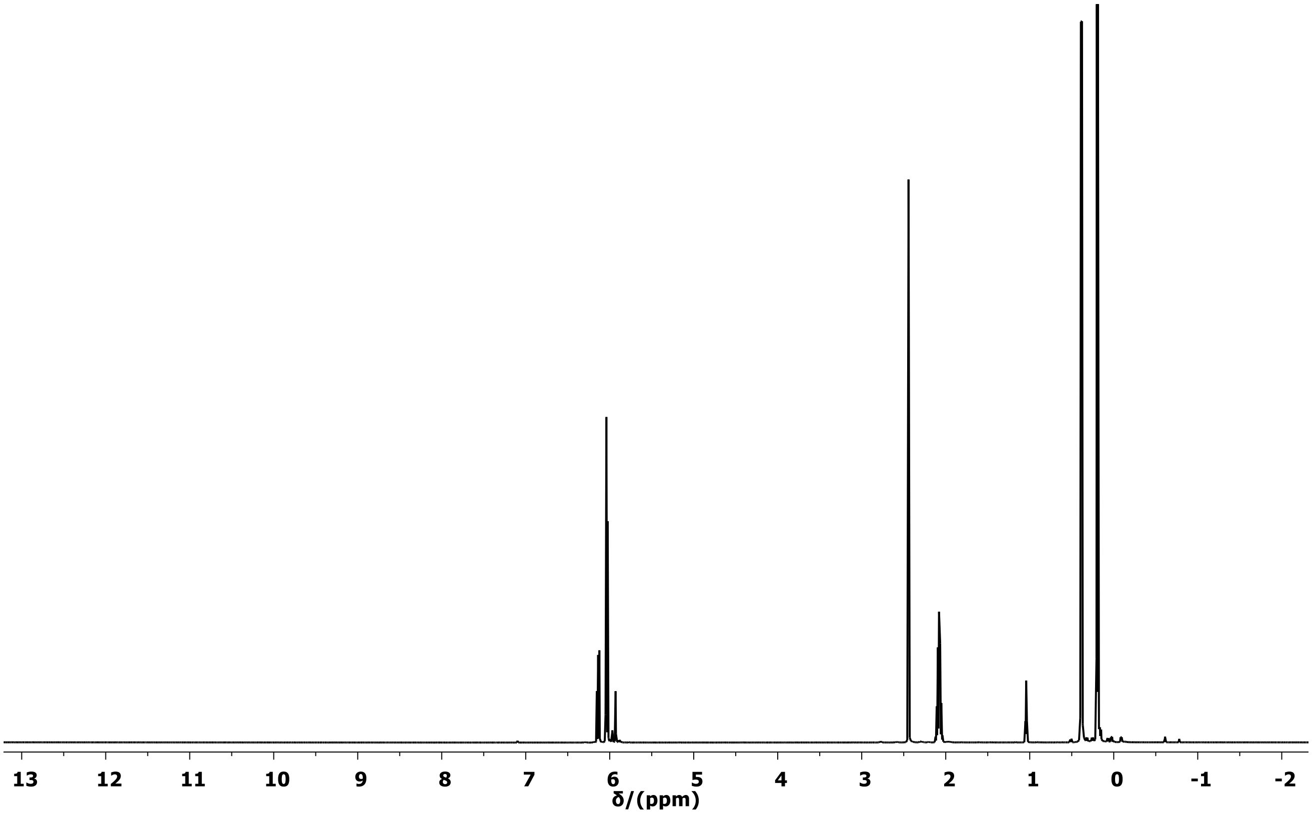

Figure 25: ^{1}H NMR spectrum (300.1 MHz, toluene-d$_8$) for the synthesis of **3b**.

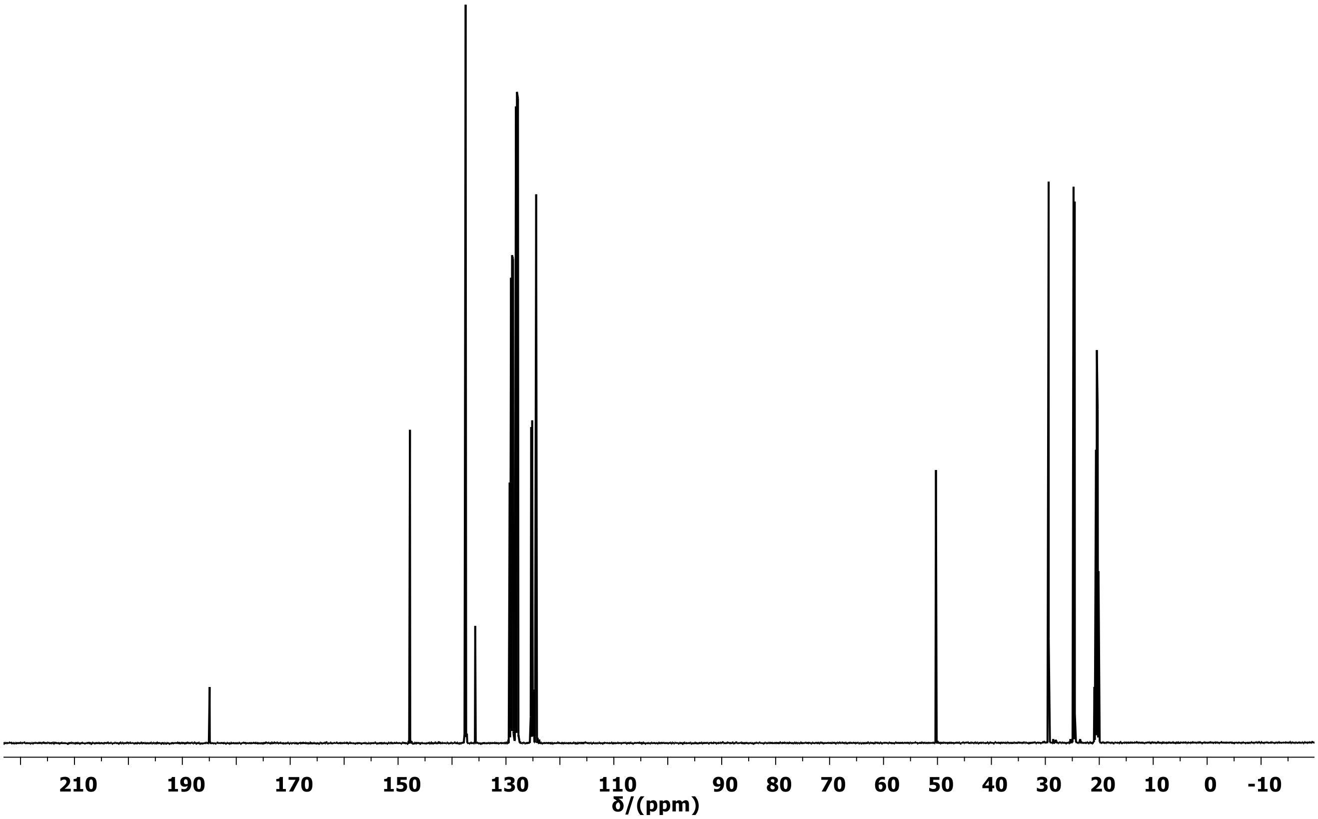

Figure 26: ^{13}C NMR spectrum (125.7.1 MHz, toluene-d$_8$) for the synthesis of **3b**.

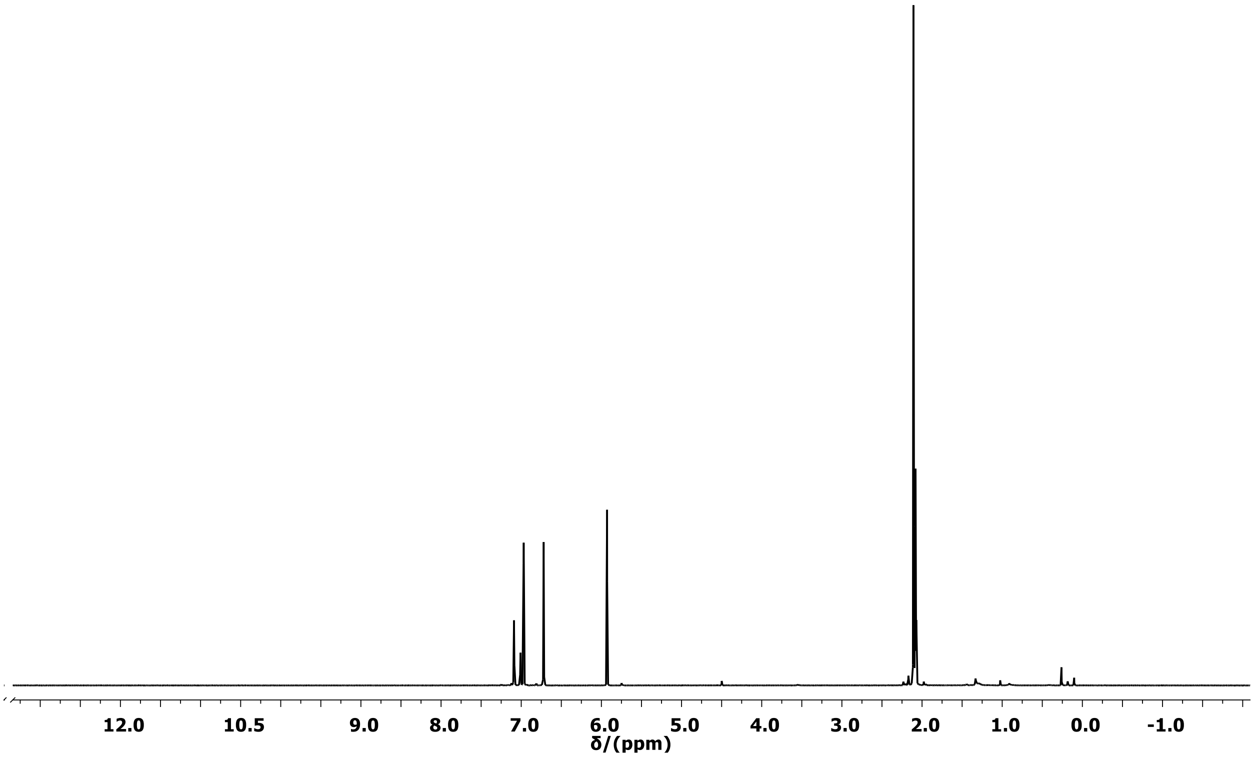

Figure 27: ^{1}H NMR spectrum (300.1 MHz, toluene-d_8) for the synthesis of **6a**.

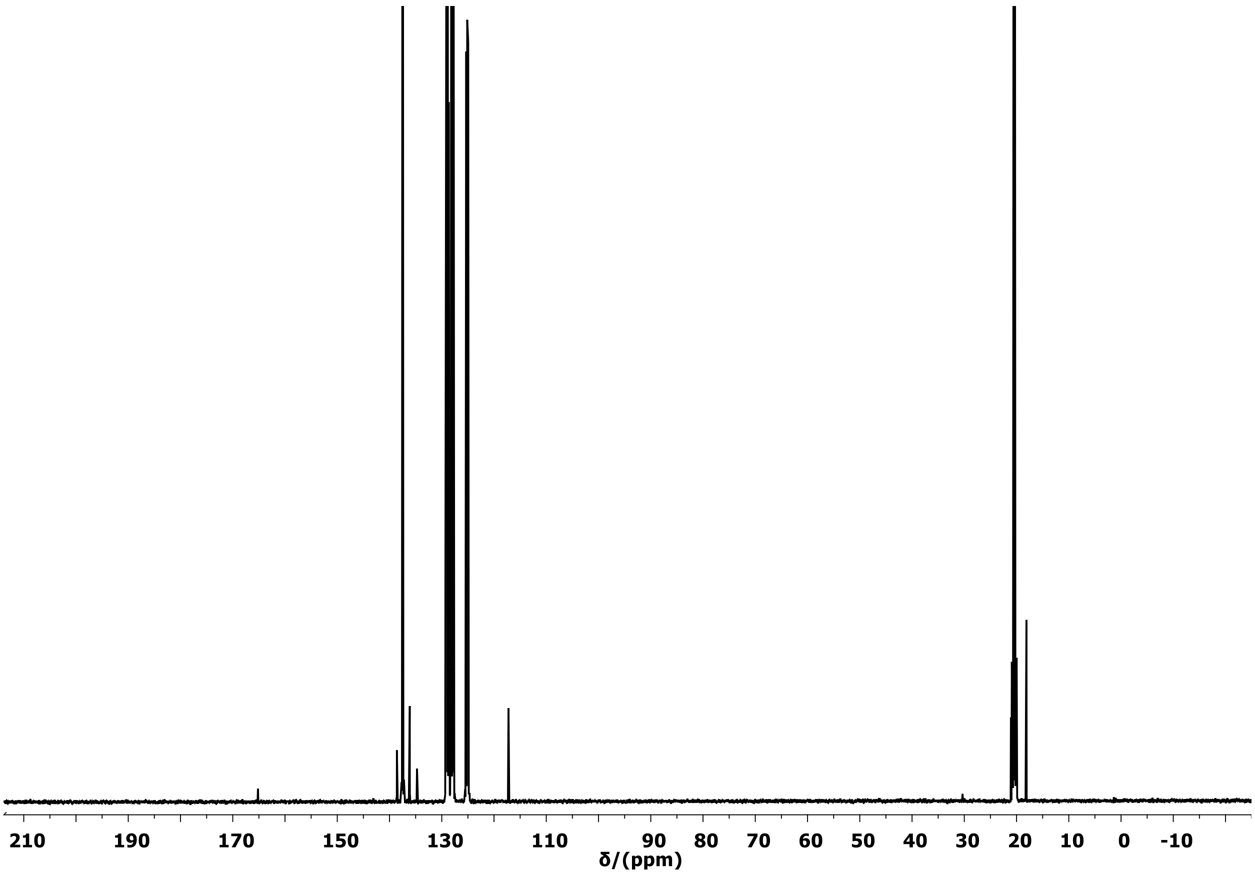

Figure 28: ^{13}C NMR spectrum (125.7.1 MHz, toluene-d$_8$) for the synthesis of **6a**.

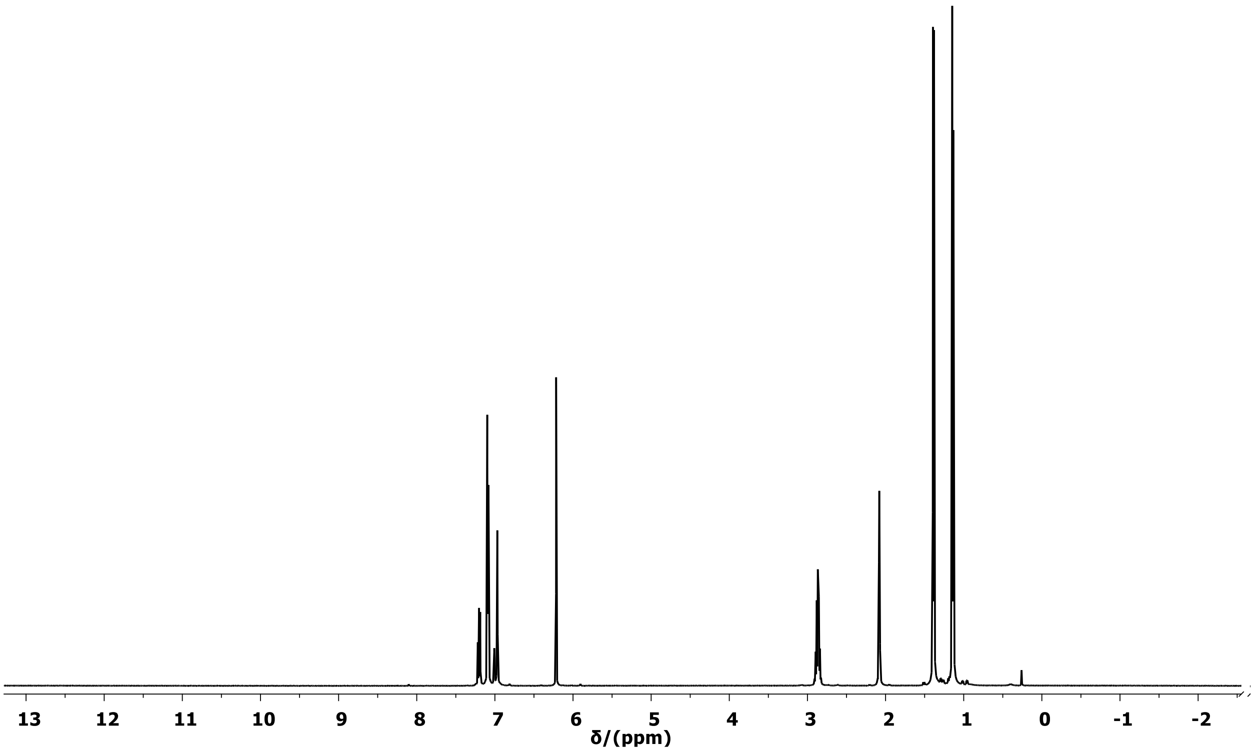

Figure 29: ^{1}H NMR spectrum (300.1 MHz, toluene-d$_8$) for the synthesis of **6b**.

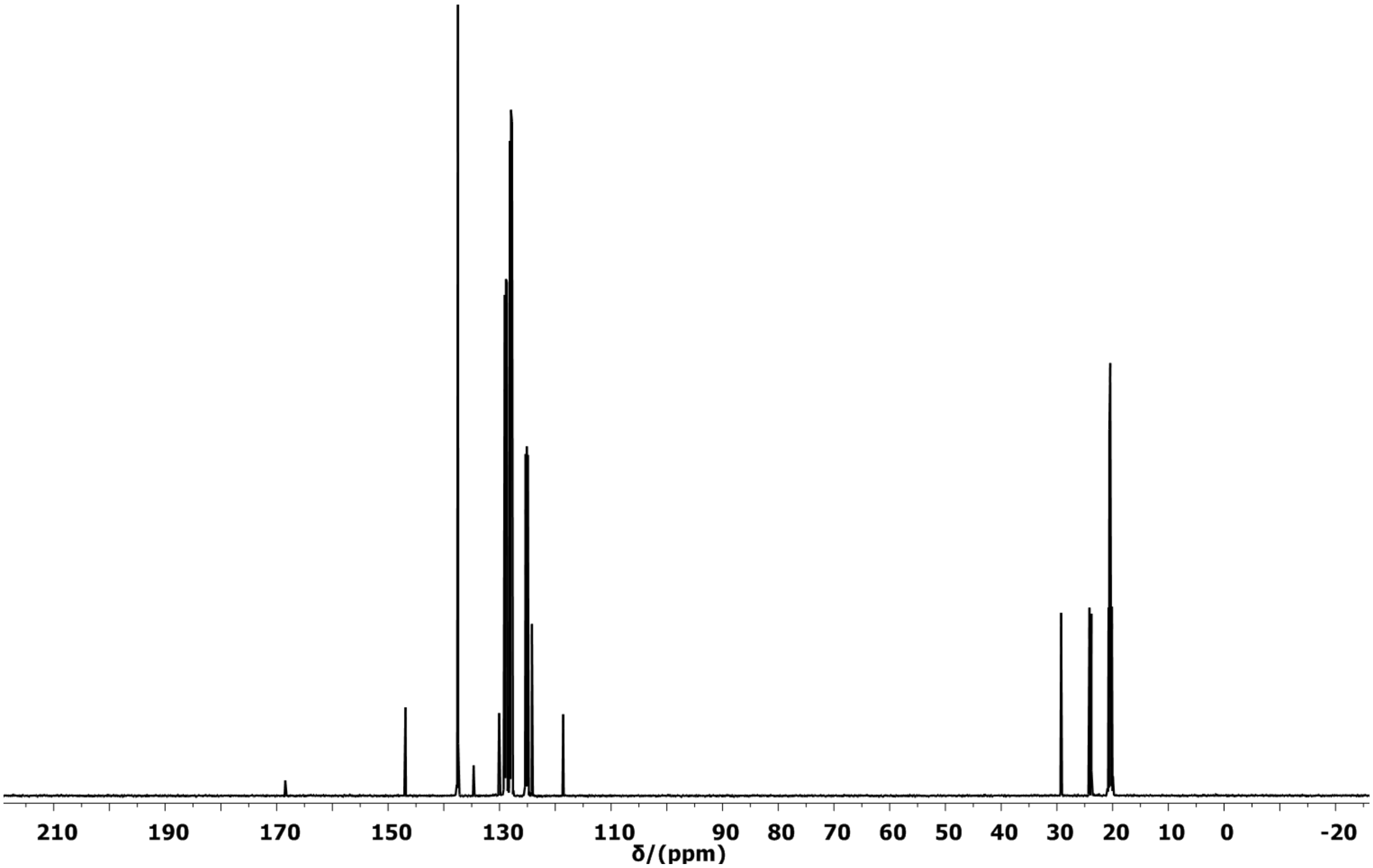

Figure 30: ^{13}C NMR spectrum (125.7.1 MHz, toluene-d$_8$) for the synthesis of **6b**.

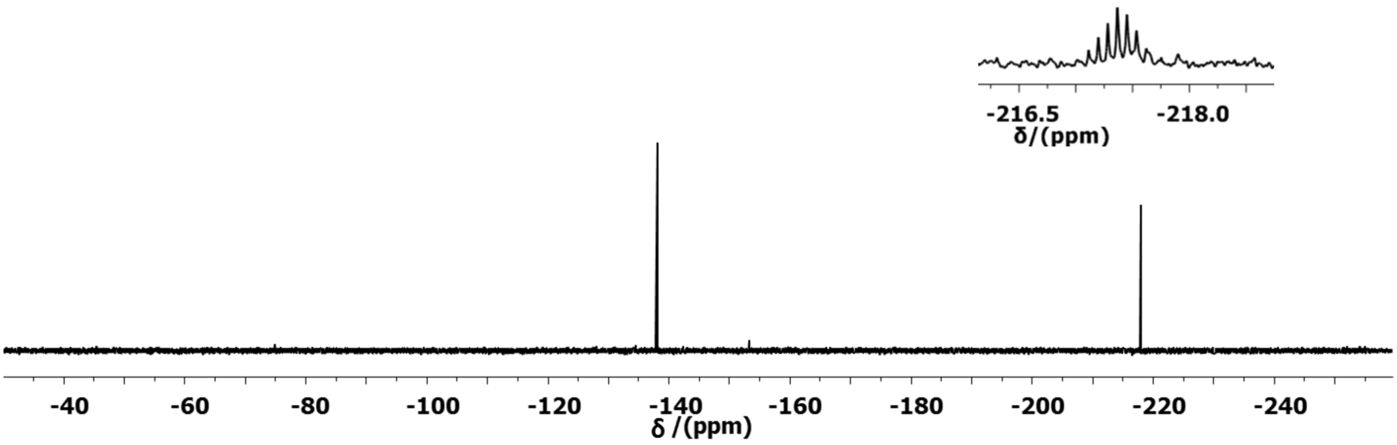

Figure 31: ^{19}F NMR spectrum (282.4 MHz, toluene-d_8) for the deoxyfluorination of 1-fluorooctane. 1,2-difluorobenzene (δ = -138.1 ppm) was used as an external standard.

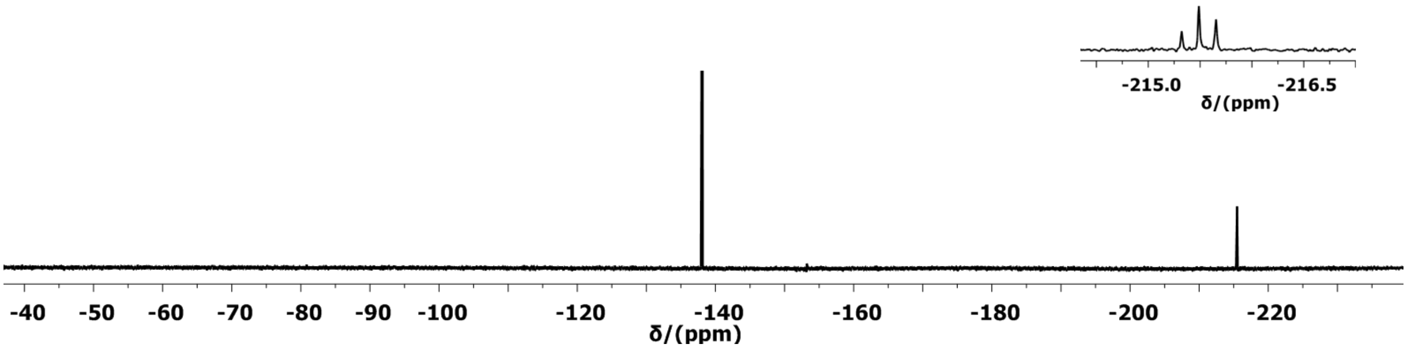

Figure 32: ^{19}F NMR spectrum (282.4 MHz, toluene-d_8) for the deoxyfluorination of 4-NO_2-benzylalcohol. 1,2-difluorobenzene (δ = -138.1 ppm) was used as an external standard.

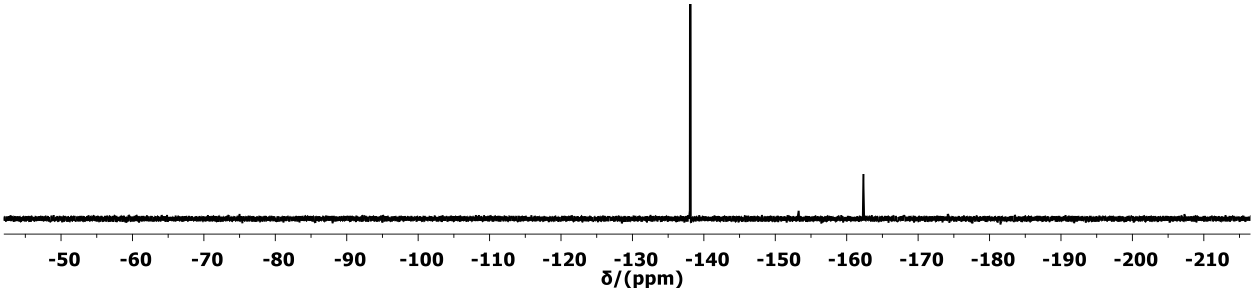

Figure 33: ^{19}F NMR spectrum (282.4 MHz, toluene-d$_8$) for the deoxyfluorination of 3-penten-2-ol. 1,2-difluorobenzene (δ = -138.1 ppm) was used as an external standard.

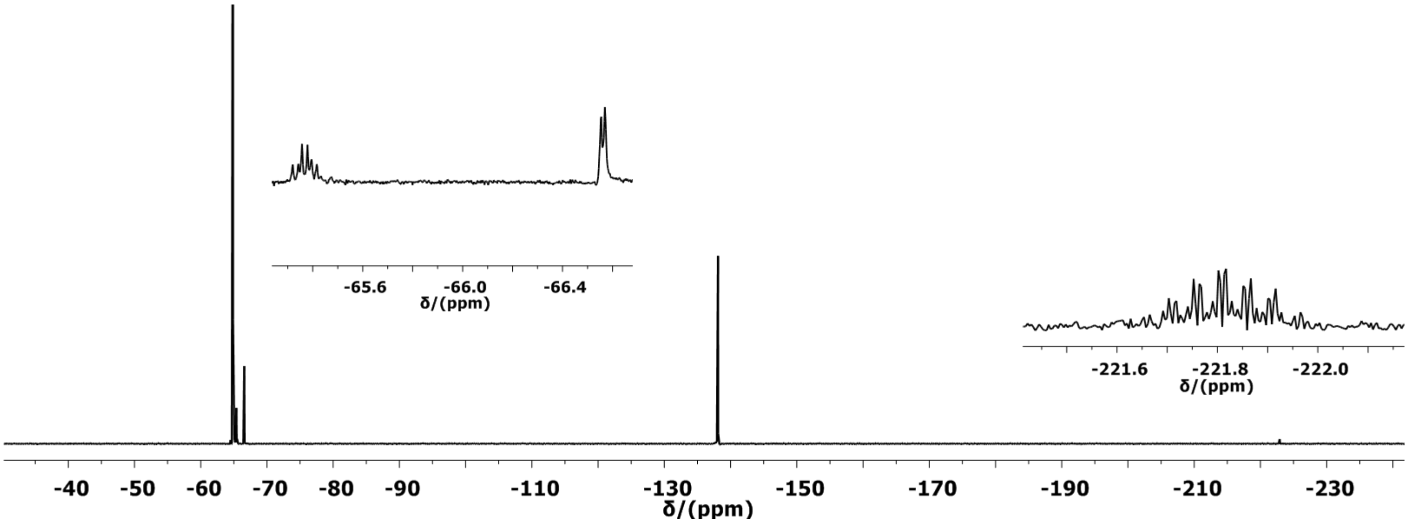

Figure 34: ^{19}F NMR spectrum (282.4 MHz, toluene-d$_8$) for the deoxyfluorination of 3,3,3-trifluoropropanol. 1,2-difluorobenzene (δ = -138.1 ppm) was used as an external standard.

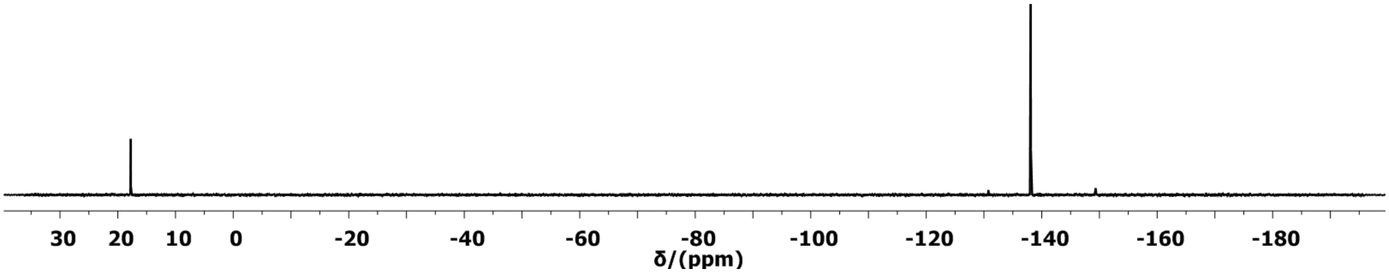

Figure 35: ^{19}F NMR spectrum (282.4 MHz, toluene-d_8) for the deoxyfluorination of benzoic acid. 1,2-difluorobenzene (δ = -138.1 ppm) was used as an external standard.