Reductive Transformation of V(III) - Precursors into Vanadium (II) oxide Nanowires

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Keywords: vanadium complexes, electrocatalysts, cyclovoltammetry, nanowire, XRD.

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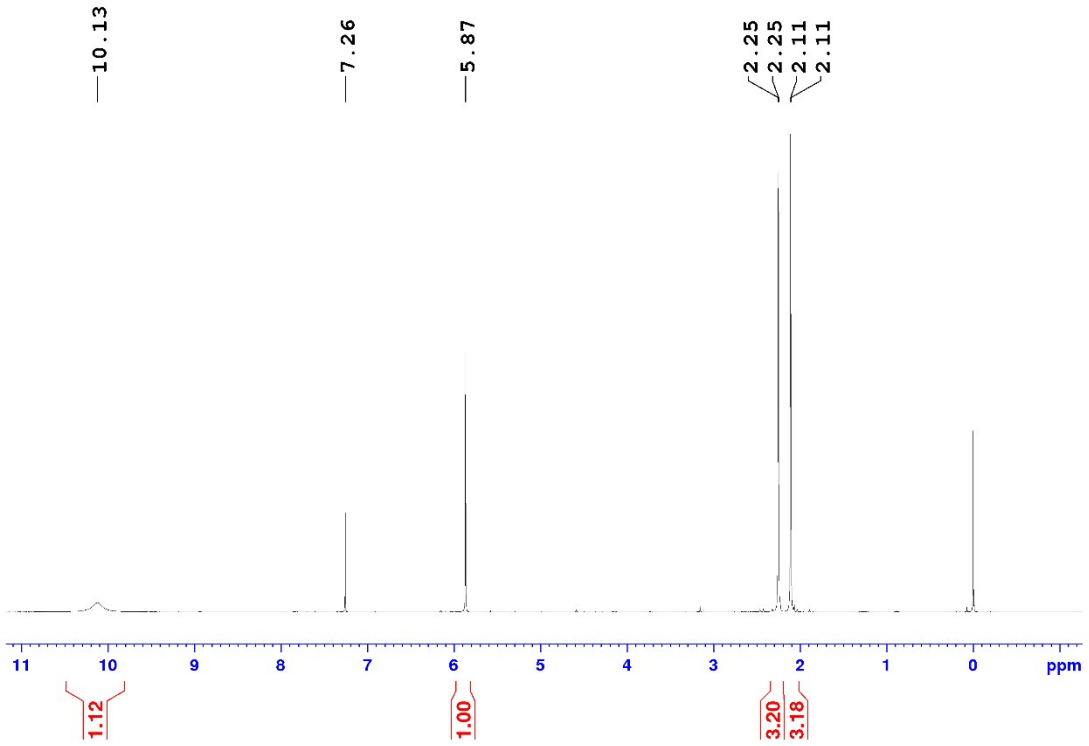
Ligand Synthesis

3,3,3-Trifluoro-1-(4,5-dimethyloxazole-2-yl) propen-2-ol (**1**)

In a 1 l flask 2,4,5-trimethyloxazole (9.00 ml, 8.68 g, 78.06 mmol) was mixed with pyridine (18 ml, 17.60 g, 222.55 mmol) and toluene (80 ml). The mixture was cooled with an ice bath (0°C) and while stirring, trifluoroacetic anhydride (22 ml, 33.07 g, 157.43 mmol), was added via a dropping funnel. After stirring for 12 h at ambient temperature 300 ml Na_2CO_3 solution (3%) was added. The desired product was extracted with ethyl acetate (3x250 ml). The combined organic layers were washed with brine solution (1x250ml) and dried over Na_2SO_4. After the removal of solvents under reduced pressure the brown raw product was sublimed (45°C, 10^{-3} mbar) to yield a colorless product in a yield of 75% (12.11 g, 58.49 mmol).

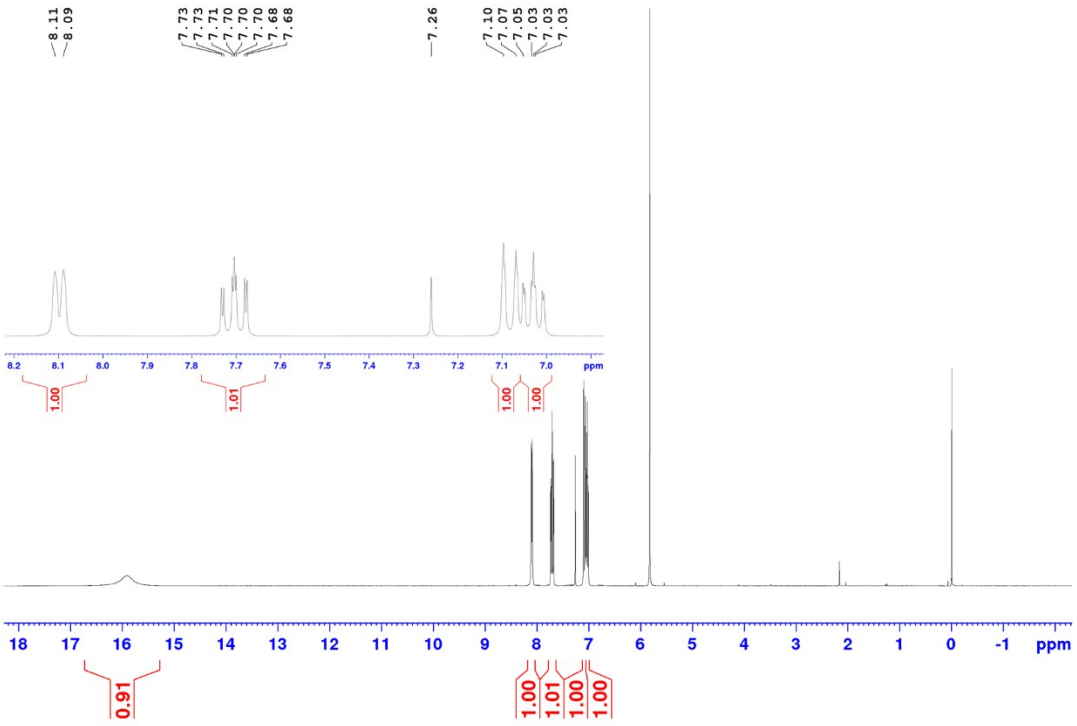
^{1}H NMR: (300.1 MHz, 25°C, $CDCl_3$) δ [ppm] = 10.13 (s, 1 H, HO-H), 5.87 (s, 1 H, 6-H), 2.25 (s, 3 H, 4-H), 2.11 (s, 3 H, 5-H). ^{13}C NMR: (75.5 MHz, 25°C, $CDCl_3$) δ [ppm] = 160.1 (1-C), 157.3 (7-C), 141.0 (3-C), 125.8 (2-C), 119.0 (8-C), 83.3 (6-C), 9.7 (5-C), 9.5 (4-C). ^{19}F NMR: (282.4 MHz, 25°C, $CDCl_3$) δ [ppm] = -74:2 (s).



1,1,1-trifluoro-3-(pyridin-2-yl) propan-2-one (**2**)

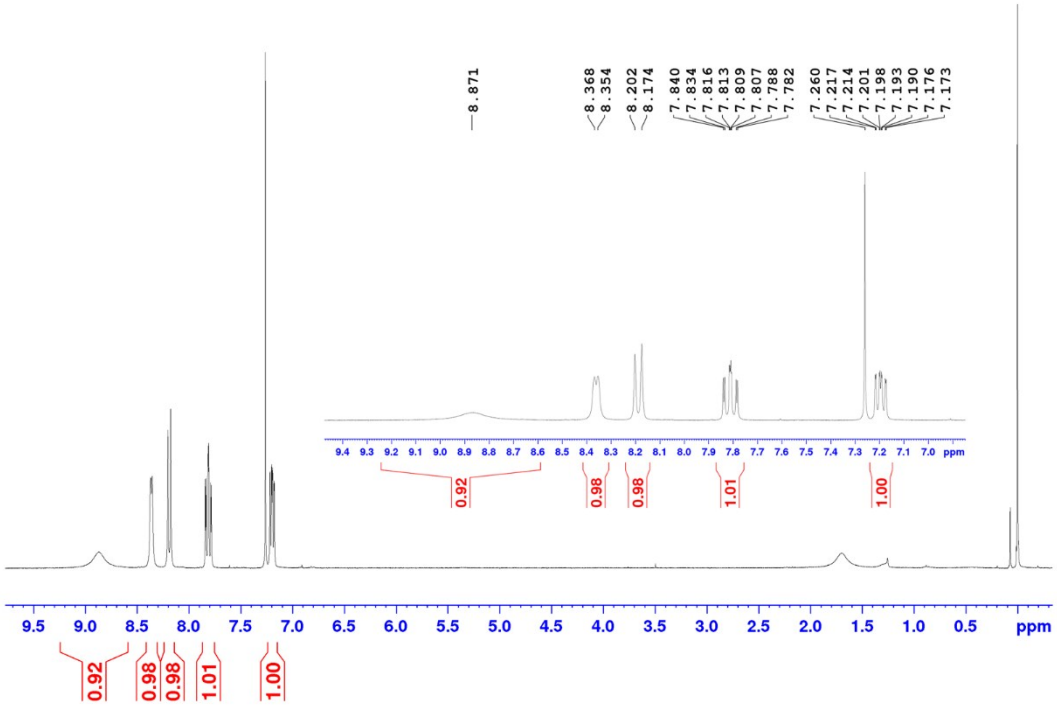
In a 500mL round-bottom flask 4.62mL (4.36 g; 46.78 mmol; 1.0 eq.) of 2-Picolin and 18.46mL (18.13 g; 229.15 mmol; 4.9 eq.) of Pyridine were added to 100mL toluene. The reaction mixture was cooled to 0°C and 20.0mL (29.8 g; 141.88 mmol; 3.0 eq.) of trifluoroacetic anhydride were added dropwise. The mixture was stirred for 16 h at room temperature. The solution was added to 300mL of 3% $Na2CO_3$ (aq) and subsequently extracted seven times with 100mL of Ethylacetate. The collected organic phases were washed with 300 ml of brine and dried over $MgSO_4$. The solvent was removed under reduced pressure and the remaining crude product was sublimed in a dynamic vacuum (50°C, 10^{-3} mbar). The product was obtained as a crystalline, bright yellow solid in a yield of 48% (4.24 g, 22.45 mmol).

^{1}H NMR (300.1 MHz, 25°C, $CDCl_3$) δ [ppm] = 15.86 (br, 1 H, HOH), 8.10 (d, 1 H, 5-H), 7.70 (td, 1 H, 3-H), 7.10 (d, 1 H, 2-H), 7.03 (td, 1 H, 4-H), 5.76 (s, 1 H, 6-H). ^{13}C NMR (75.5 MHz, 25°C, $CDCl_3$) δ [ppm] = 163.8 (7-C), 155.7 (1-C), 139.4 (3-C), 138.6 (5-C), 122.4 (2-C), 117.7 (8-C), 117.3 (4-C), 89.1 (6-C). ^{19}F NMR (282.4 MHz, 25°C, $CDCl_3$) δ [ppm] = -74.9 (s).



1,1,1-trifluoro-*N*-(pyridin-2-yl) acetamide (**3**)

In a 250mL round-bottom flask 3.31 g (35.32 mmol; 1.0 eq.) of 2-aminopyridine were suspended in 7.0mL (6.8 g; 542.63 mmol; 15.3 eq.) of Pyridine and cooled to 0°C. 7.0mL (10.43 g; 49.66 mmol; 1.4 eq.) of trifluoroacetic anhydride were added dropwise. The reaction mixture was stirred for 3 h at room temperature. 25mL of water were slowly added to stop the reaction and the solution was extracted three times with 25mL of Ethylacetate. The collected organic phases were washed three times with 25mL of water and dried over $MgSO_4$. The solvents were removed under reduced pressure and the remaining crude product was sublimed in a dynamic vacuum, to yield a colorless, crystalline solid in a yield of 60% (4.05 g 21.3 mmol) ^{1}H NMR (300.1 MHz, 25°C, $CDCl_3$) δ [ppm] = 8.87 (br, 1 H, HNH), 8.36 (d, 1 H, 5-H), 8.19 (d, 1 H, 2-H), 7.81 (td, 1 H, 3-H), 7.20 (dd, 1 H, 4-H). ^{13}C NMR (75.5 MHz, 25°C, $CDCl_3$) δ [ppm] = 148.2 (1-C), 139.0 (3-C), 121.7 (4-C), 114.7 (2-C). ^{19}F NMR (282.4 MHz, 25°C, $CDCl_3$) δ [ppm] = -75.9 (s).



IR spectroscopy

The IR spectra (4000-400 cm^{-1}) showed the hydroxyl -OH mode in the ligand to be absent in the complex, thereby suggesting the deprotonation of hydroxyl-oxygen. The absorption bands due to υ(C-O) mode occurring at 1320 cm^{-1} in uncoordinated ligand shifted to higher wave numbers (1354 cm^{-1}) due to the coordination to electrophilic metal centre. Also, the absorption bands of the conjugated olefin υ(C=C) mode occurring at 1566 cm^{-1} in uncoordinated ligand shifted to higher wave numbers (1618 cm^{-1}) in the complex, due to formation of a metallacycle (Figure 1).

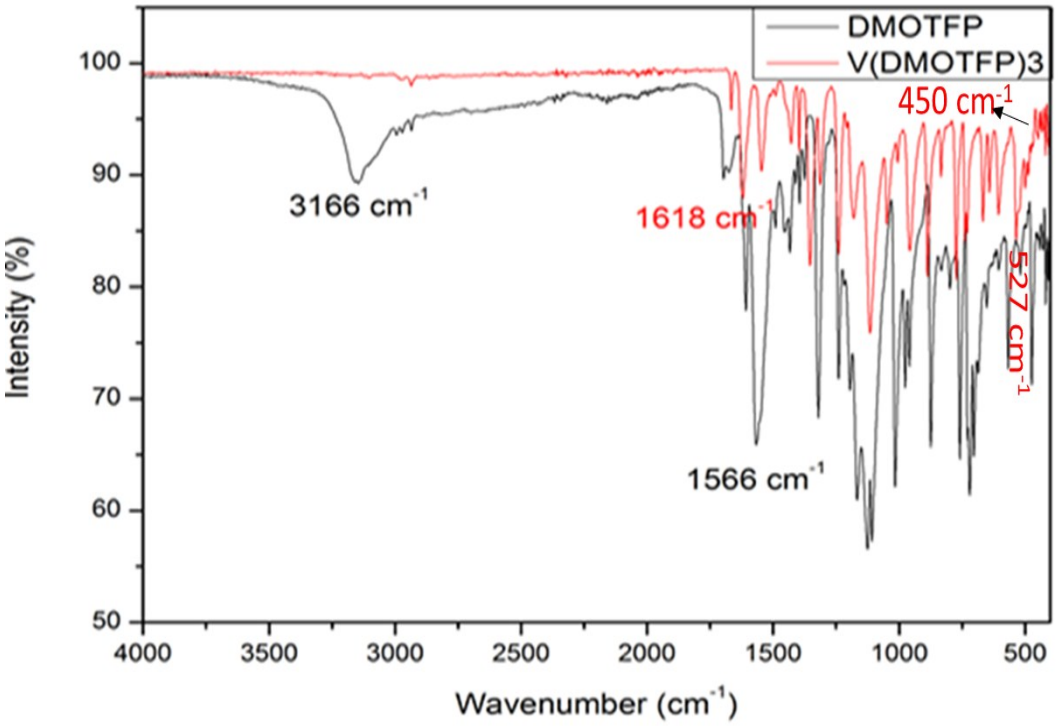


Figure S1: FT-IR spectrum of [V(DmoxCH=$COCF_3$)$_3$] (**4**).

Table S1: Details on crystal and structure refinement of (**4**), (**5**) & (**6**).

	[V(DmoxCH=$COCF_3$)$_3$] (**4**)	[V(PyCH=$COCF_3$)$_3$] (**5**)	[V(PyN=$COCF_3$)$_3$] (**6**)
Empirical formula	$C_{24}H_{21}F_9N_3O_6V$	$C_{24}H_{15}F_9N_3O_3V$	$C_{21}H_{12}F_9N_6O_3V$
Formula weight / g mol^{-1}	669.07	615.15	618.31
T / K	293(2)	293(2)	170(2)
Crystal system	monoclinic	triclinic	triclinic
Space group	P 2_1/c	$P\bar{1}$	$P\bar{1}$
a /Å	8.136(3)	9.394(1)	9.558(2)
b /Å	17.747(9)	10.639(1)	10.243(2)
c /Å	20.044(9)	13.475(2)	14.555(3)
α / °	90.00 (3)	87.461(9)	73.757(15)
β / °	99.59(3)	73.130(9)	88.851(15)
γ / °	90.00 (3)	82.194(9)	66.864(14)
V / $Å^3$	2854.1(2)	1277.0(3)	1251.6(4)
Z	4	2	2
goodness of fit	1.023	1.094	1.236
final *R* indices [I > 2σ(I)]: R_1, wR_2	0.0887, 0.0504	0.1066, 0.0745	0.2513, 0.1362
R indices (all data): R_1, wR_2	0.1559, 0.1346	0.2285, 0.3039	0.4433, 0.3886

Table S2: Selected bond distances (Å) and angles (°) of compounds (**4**), (**5**) & (**6**).

[V(DmoxCH=$COCF_3$)$_3$] **(4)**		[V(PyCH=$COCF_3$)$_3$] **(5)**		[V(PyN=$COCF_3$)$_3$] **(6)**	
V1-N1	2.12 Å	V1-N1	2.14 Å	V1-N1	2.12 Å
V1-N2	2.12 Å	V1-N2	2.13 Å	V1-N4	2.13 Å
V1-N3	2.10 Å	V1-N3	2.18 Å	V1-N5	2.11 Å
V1-O2	1.95 Å	V1-O1	1.92 Å	V1-O1	1.92 Å
V1-O4	1.93 Å	V1-O2	1.93 Å	V1-O2	1.89 Å
V1-O6	1.96 Å	V1-O3	1.94 Å	V1-O3	1.97 Å
Bond angle		**Bond angle**		**Bond angle**	
N1-V1-N2	88.9°	N1-V1-N3	91.3°	N4-V1-N5	91.2°
O2-V1-N3	89.5°	N2-V1-O3	90.1°	N1-V1-O2	90.9°
O4-V1-O6	94.4°	O1-V1-O2	97.1°	O1-V1-O3	96.6°
N2-V1-N3	172.7°	N1-V1-N2	176.8°	N1-V1-N5	175.9°
N1-V1-O6	170.2°	O2-V1-N3	173.2°	O1-V1-N4	169.3°
O2-V1-O4	176.8°	O1-V1-O3	172.9°	O2-V1-O3	174.9°

UV-Vis Spectroscopy

The UV-vis spectral data (200-900 nm) of [V(DmoxCH=$COCF_3$)$_3$] (**4**) recorded in acetone showed two bands corresponding to d-d and charge-transfer transitions (Figure SI 3). In the visible region two moderately intense absorption maxima were observed at 616 nm (ε = 200 lmol-1cm -1) and 756 nm (ε = 183 lmol-1cm -1) assignable to d-d transitions (3T1g(F) →3T1g(P) and 3T1g(F) →3T2g) respectively. The absorbance of the concentrated sample was too high to determine the absorption maxima of the intra-ligand charge transfer. However, upon dilution, a decrease in absorbance was observed with new absorption maxima at 327 nm (ε = 10,000 lmol-1cm -1) and 211 nm (ε = 7,400 lmol-1cm -1) corresponding to intra-ligand n → π* and π → π* charge transfer transitions.

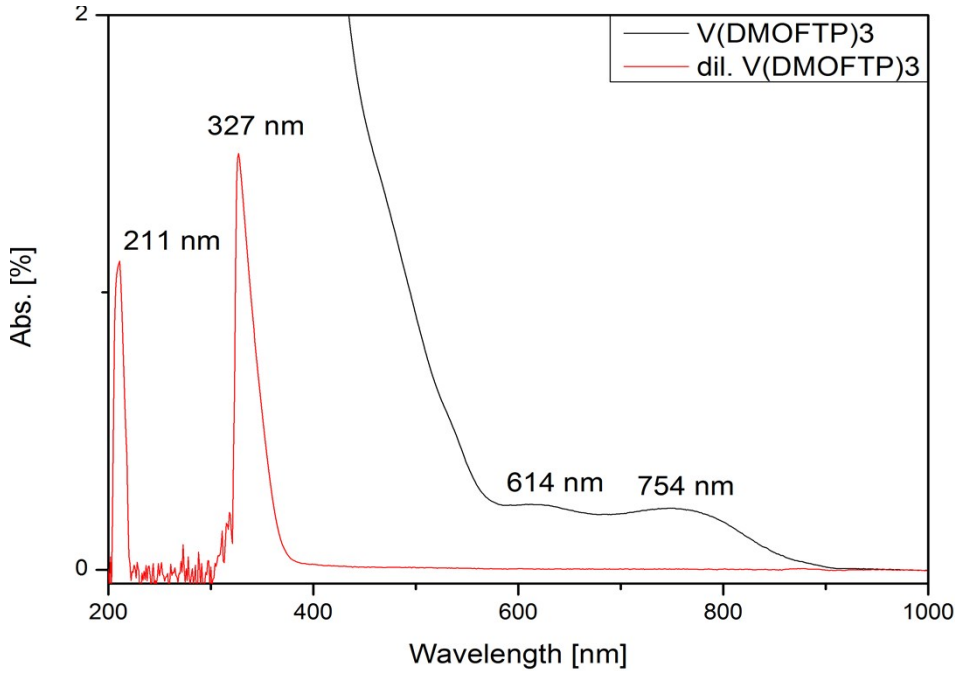


Figure S3: UV- VIS spectrum of [V(DmoxCH=$COCF_3$)$_3$] (**4**)

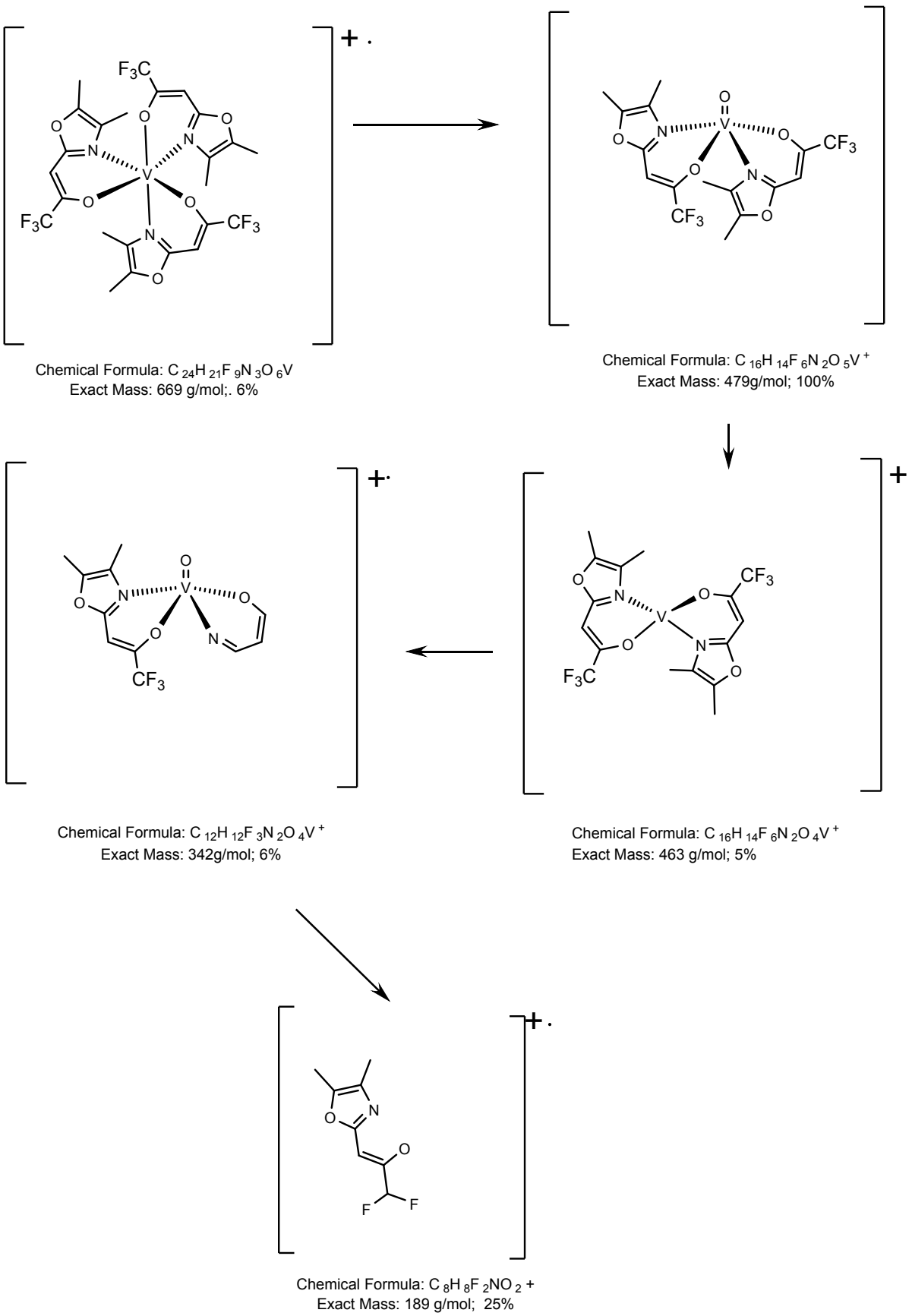


Figure S4: Schematic fragmentation pathway of compound (**4**) during electron ionization mass spectra recorded with energy of 20 eV.