Supporting Information for:

Partially Fluorinated Oxo-alkoxide Tungsten (VI) Complexes as Precursors for Deposition of WO_x Nanomaterials

Richard O. Bonsu,[a] *Hankook Kim,*[b] *Christopher O'Donohue,*[b] *Roman Y. Korotkov,*[c] *K. Randall McClain,*[a] *Khalil A. Abboud,*[a] *Ashley A. Ellsworth,*[d] *Amy V. Walker,*[d] *Timothy J. Anderson*[b] *and Lisa McElwee-White*[*,a]

[a]Department of Chemistry, University of Florida, Gainesville, Florida, 32611-7200 USA. Email: lmwhite@chem.ufl.edu

[b]Department of Chemical Engineering, University of Florida, Gainesville, Florida, 32611-6005 USA

[c]Arkema Inc., 900 First Ave., King of Prussia, PA 19406 USA

[d]Department of Materials Science and Engineering RL10, University of Texas at Dallas, 800 W. Campbell Rd, Richardson, Texas 75080 USA

lmwhite@chem.ufl.edu
tim@ufl.edu

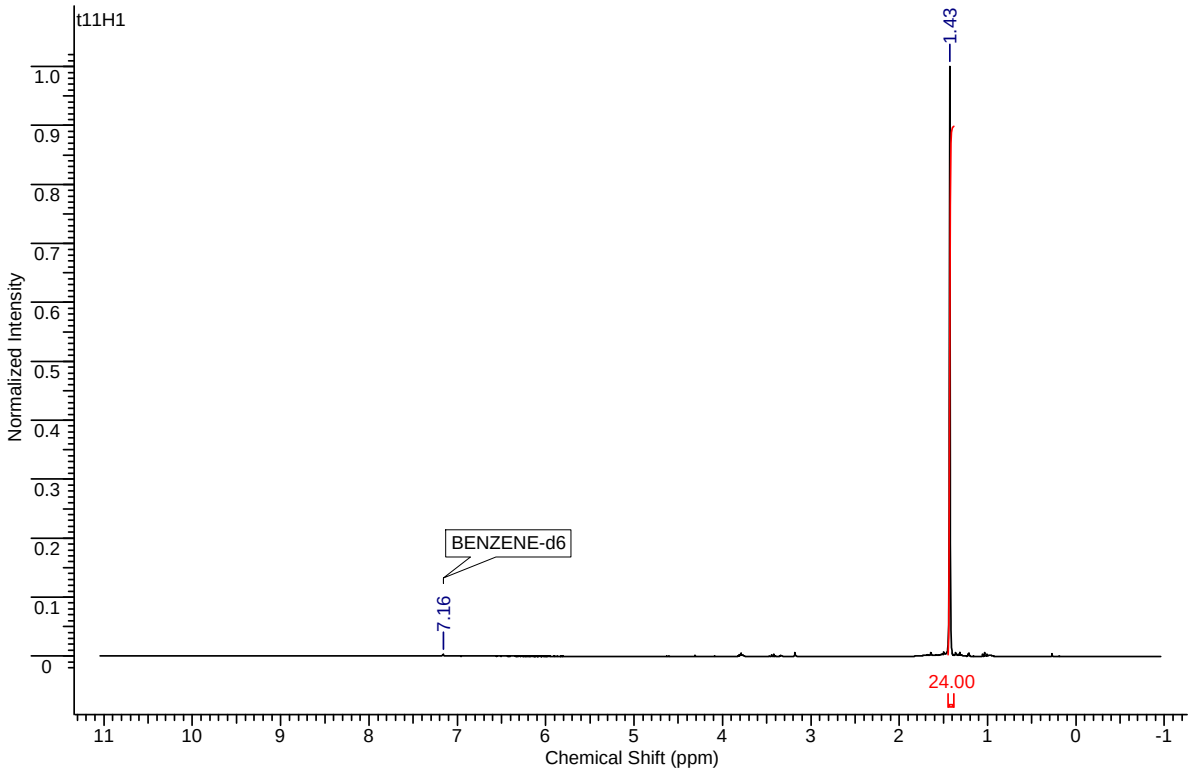

Figure S-1: Room Temperature ^{1}H NMR of **4** in benzene-d_6.

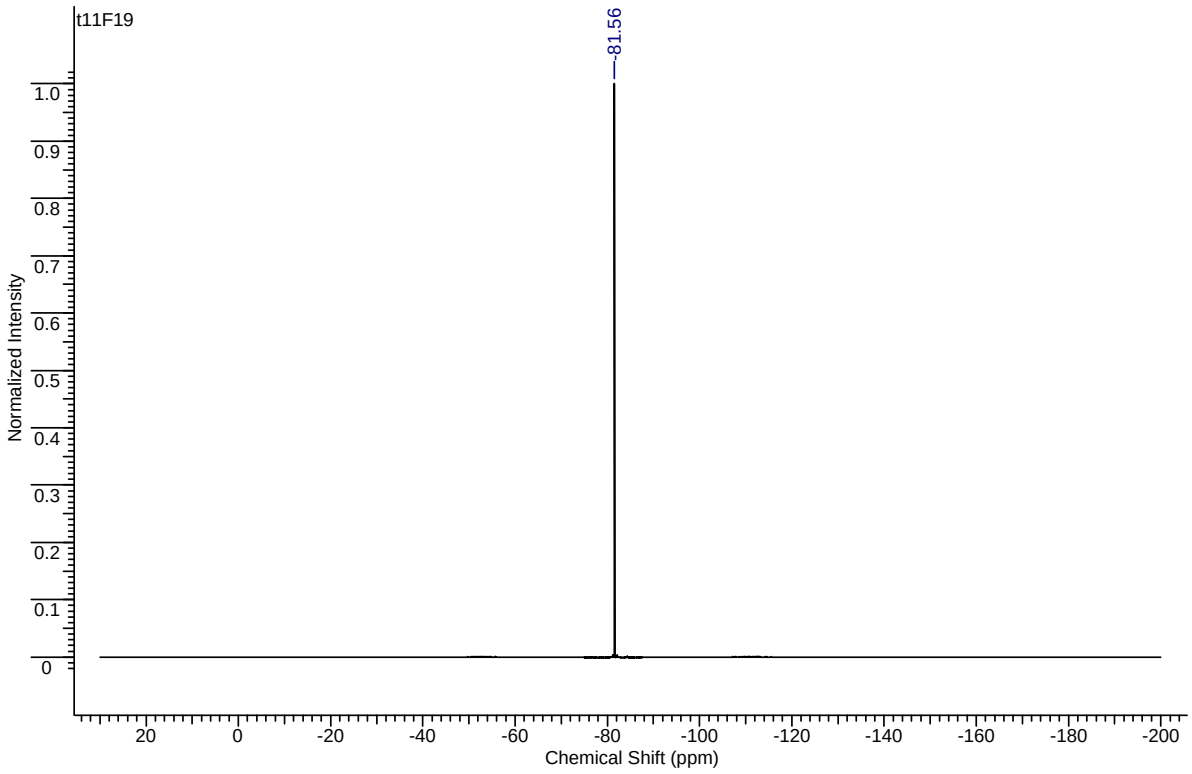

Figure S-2: Room Temperature ^{19}F NMR of **4** in benzene-d_6.

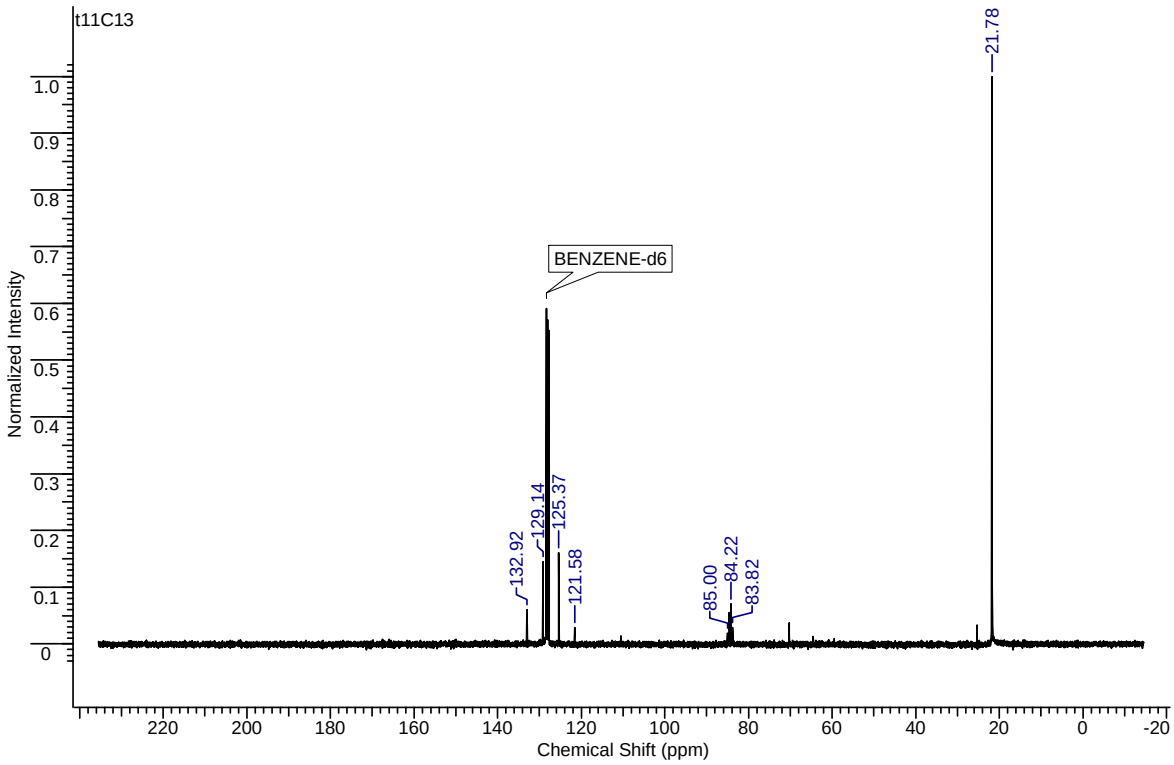

Figure S-3: Room Temperature ^{13}C NMR of **4** in benzene-d_6.

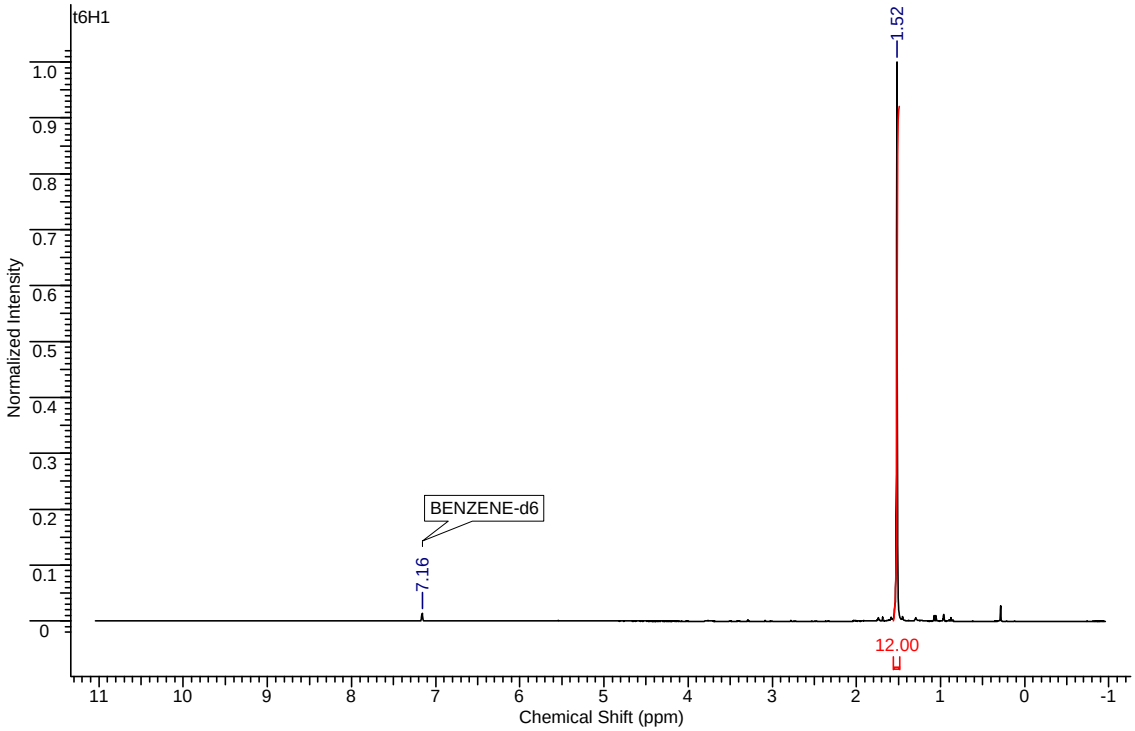

Figure S-4: Room Temperature ^{1}H NMR of **5** in benzene-d_6.

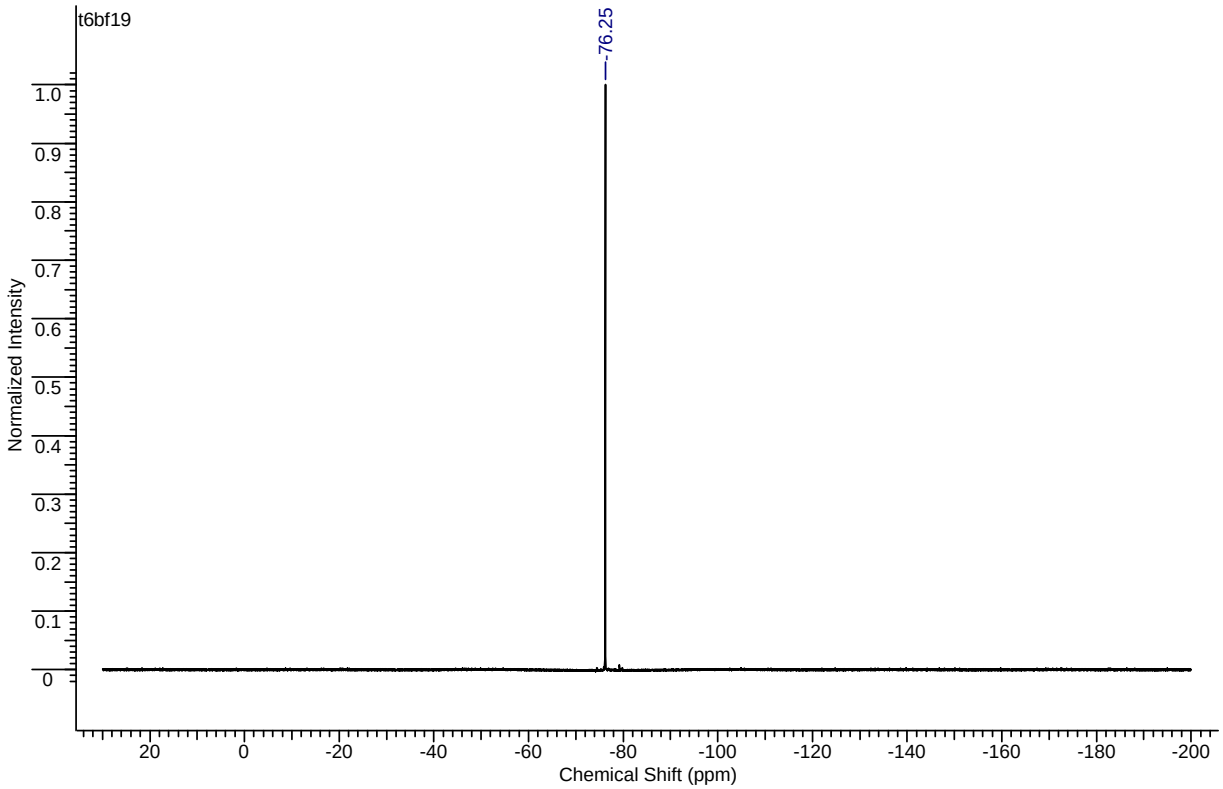

Figure S-5: Room Temperature ^{19}F NMR of **5** in benzene-d_6.

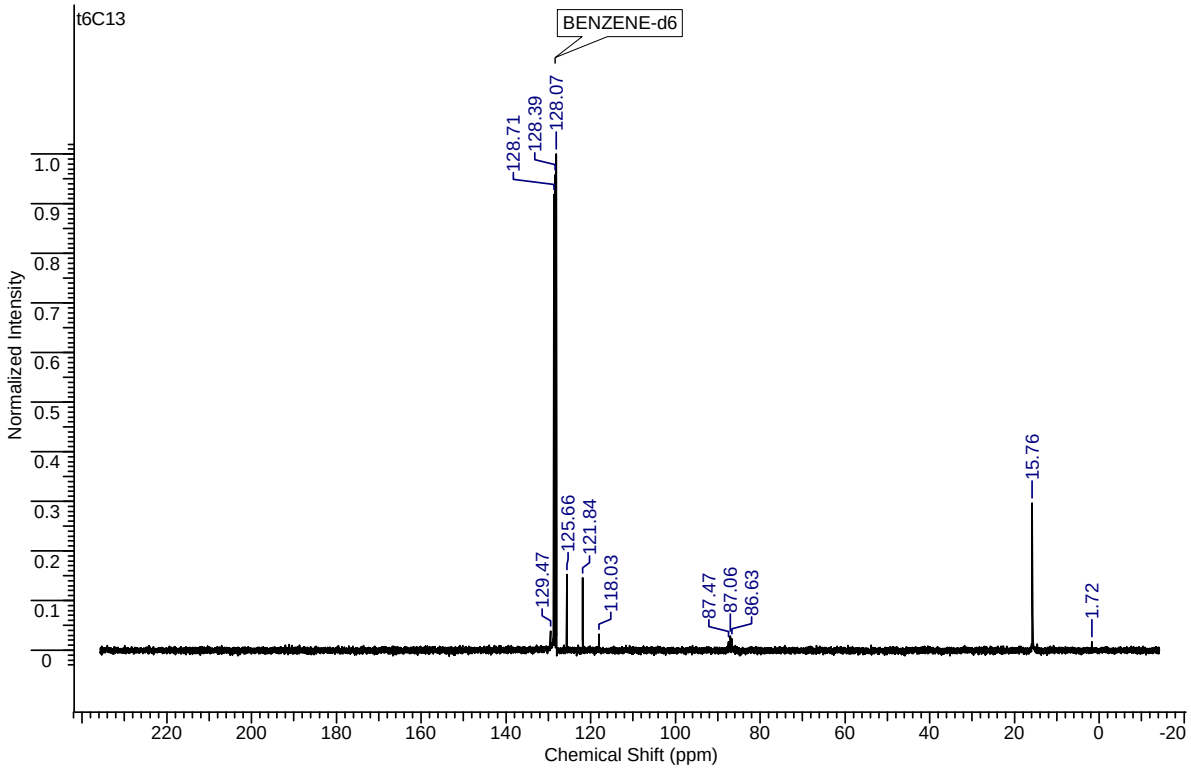

Figure S-6: Room Temperature ^{13}C NMR of **5** in benzene-d_6.

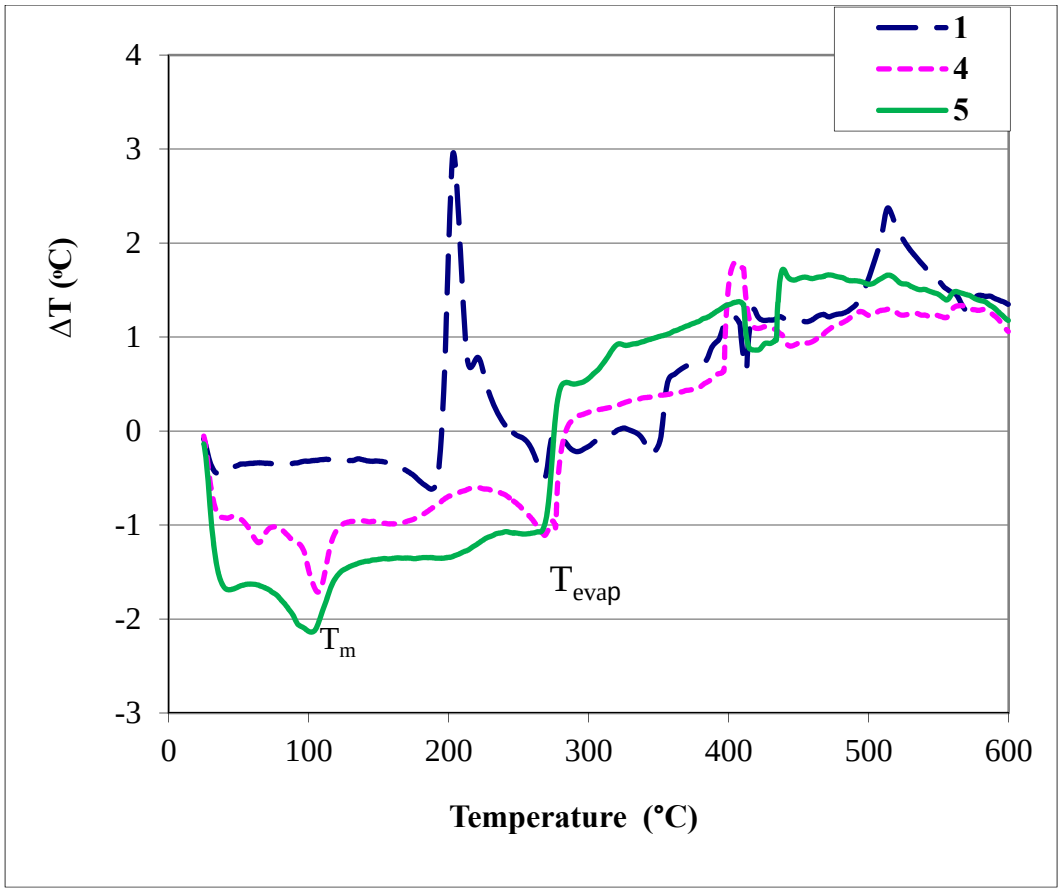

Figure S-7: DTA measurements of compounds **1**, **4** and **5**.

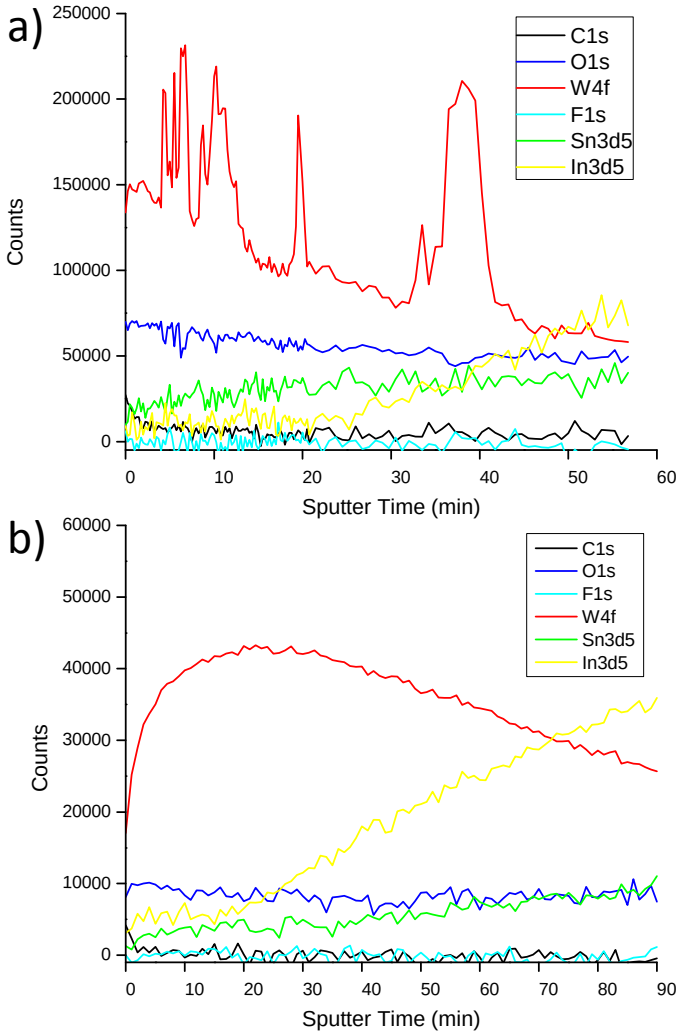

Figure S-8. XPS depth profiles of the films grown at (a) 450 °C and (b) 550 °C. Sputtering performed using 1 keV Ar^+. No F is detected in the film. The variation of the W4f intensity in (a) is most likely due to variations in the densities of the nanorod bundles.

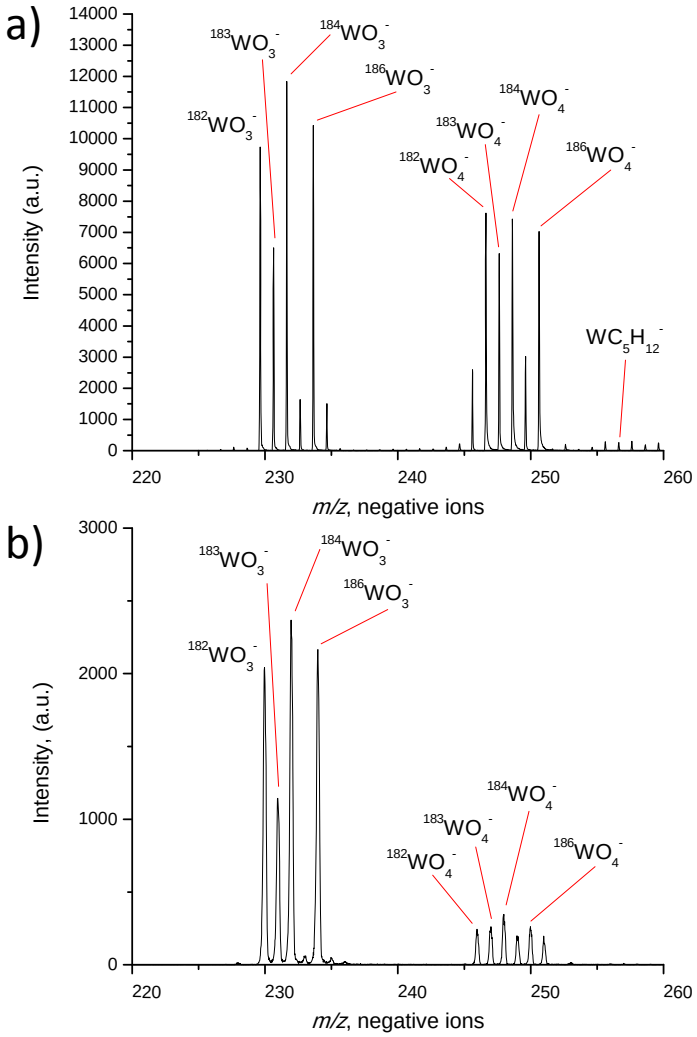

Figure S-9. High mass resolution negative ion spectra centered at m/z 240 for films deposited at 450 °C (a) before and (b) after sputtering for 30s. The data indicate that there are some hydrocarbon species present at the surface.

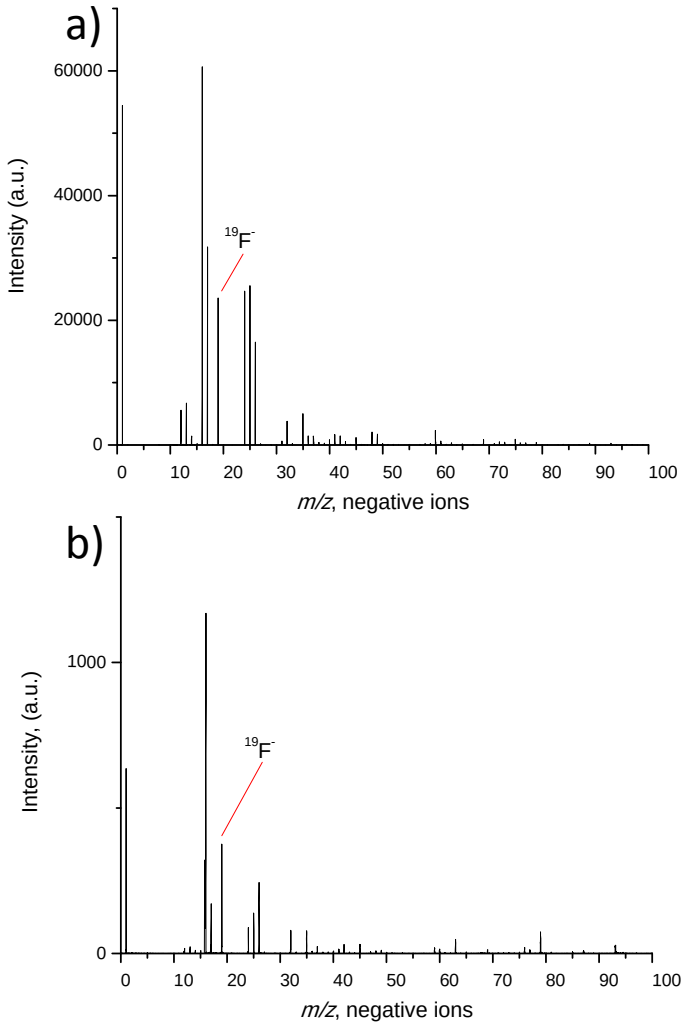

Figure S-10. High mass resolution negative ion spectra *m/z* 0-100 for films deposited at 450 °C (a) before and (b) after sputtering for 30s. The data indicate that there is negligible F present in the deposited films.

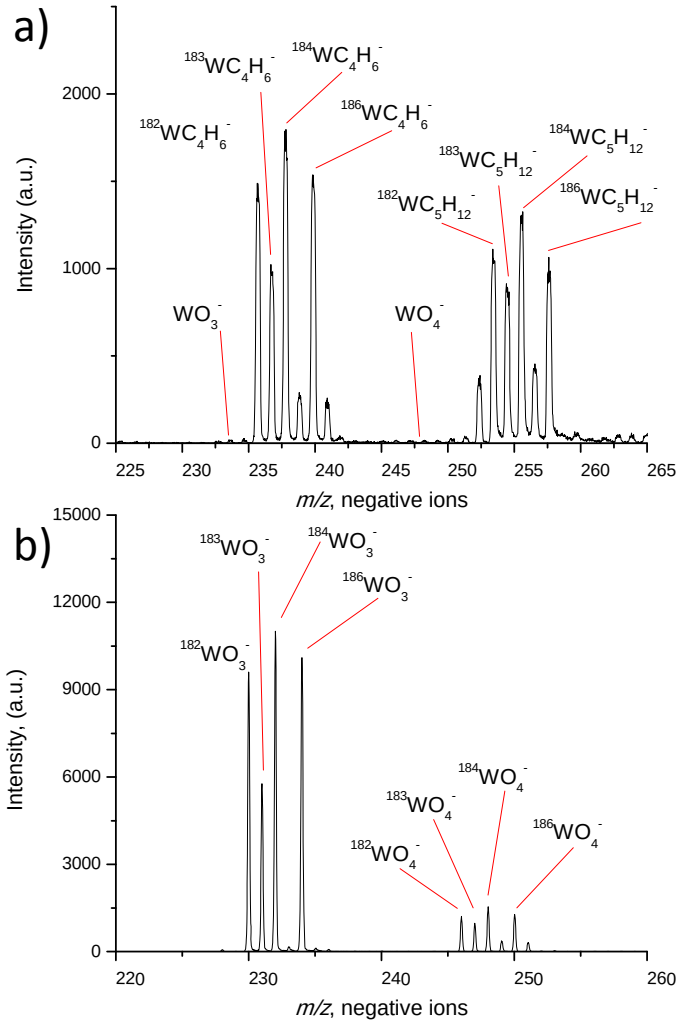

Figure S-11. High mass resolution negative ion spectra centered at *m/z* 240 for films deposited at 550 °C (a) before and (b) after sputtering for 30s. The data indicate that there are hydrocarbon species present at the surface.

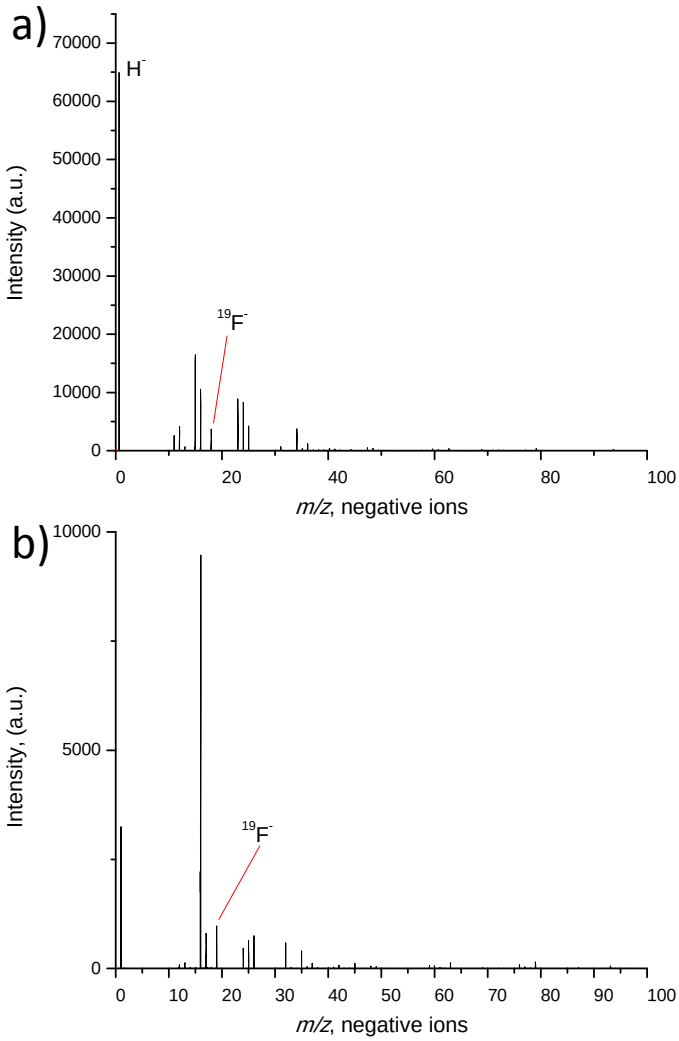

Figure S-12. High mass resolution negative ion spectra m/z 0-100 for films deposited at 550 °C (a) before and (b) after sputtering for 30s. The data indicate that there is negligible F present in the deposited films.

Table S-1: Thermal Behaviors of **1**, **4** and **5** Based on TGA/DTA Measurements.

Compound	Compound Name	T_m, °C	5 % Mass Loss	10 % Mass Loss	% Residue at 600 °C
1	$WOCl_4$	-	173.3	190	15.3
4	$[CF_3(CH_3)_2CO]_4WO$	105.0	172.6	202.5	14.2
5	$[(CF_3)_2CH_3CO]_4WO$	100.5	166.2	199.81	13.6

Table S-2: Relative Abundances for Positive Ion DIPCI Mass Spectra of Complexes **4** and **5**.

Compound	Ion	m/z	rel. abundance (%)[a]
4	$[M]^+$	708	0.05
	$[WO(OC(CH_3)_2CF_3)_3]^+$	581	2
	$[WO(OC(CH_3)_2CF_3)_2(OH)(H_2O)]^+$	489	1
	$[WO(OH)_3(H_2O)+H]^+$	270	1
	$[HOC(CH_3)_2CF_3+H]^+$	129	33
	$[HOC(CH_3)_2CF_3]^+$	128	18
	$[OC(CH_3)_2CF_3]^+$	127	9
	$[HC(CH_3)_2CF_3+H]^+$	113	10
	$[OCH_3CF_3+H]^+$	113	9
	$[OCCH_3CF_3]^+$	112	6
	$[C(CH_3)_2CF_3]^+$	111	12
	$[H_2CCCH_3CF_3]^+$	110	9
	$[HCCCH_3CF_3]^+$	109	100
5	$[M+H]^+$	925	1
	$[M]^+$	924	9
	$[WO(OCCH_3(CF_3)_2)_3]^+$	743	9
	$[WO(OCCH_3(CF_3)_2)_3+2H]^+$	745	1
	$[WO(OCCH_3(CF_3)_2)_2(OH)]^+$	579	12
	$[WO(OH)_3(H_2O)+H]^+$	270	1
	$[HOC_4H_3F_6+H]^+$	183	100
	$[OCCH_3(CF_3)_2]^+$	181	77
	$[H_2CC(CF_3)_2]^+$	164	5
	$HCC(CF_3)_2]^+$	163	51
	$[H_2C(CF_3)_2]^+$	152	39
	$[OCCH_3CF_3+H]^+$	113	28

[a] Relative abundances were predicted by adjusting peak intensities relative to the highest peak normalized to 100 %.

Table S-3: Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **4**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
W1	0	2660(1)	2500	11(1)
F1	-260(1)	-191(3)	4148(1)	26(1)
F2	-283(1)	3103(3)	4553(1)	24(1)
F3	-1196(1)	920(3)	4322(1)	26(1)
F4	1904(1)	6888(4)	3397(1)	33(1)
F5	2333(1)	3599(4)	3672(1)	30(1)
F6	2408(1)	5963(3)	4479(1)	26(1)
O1	0	-167(5)	2500	21(1)
O2	-405(1)	3138(3)	3185(1)	15(1)
O3	867(1)	3713(4)	3159(1)	22(1)
C1	-1004(1)	2473(5)	3350(1)	15(1)
C2	-679(2)	1571(5)	4098(1)	16(1)
C3	-1454(2)	4527(6)	3330(2)	25(1)
C4	-1437(2)	636(6)	2864(2)	22(1)
C5	1256(1)	4434(5)	3859(1)	14(1)
C6	1976(2)	5221(5)	3851(2)	18(1)
C7	1384(2)	2516(5)	4364(2)	26(1)
C8	877(2)	6383(5)	4037(2)	21(1)

Table S-4: Bond lengths [Å] and angles [°] for **4**.

W1-O1	1.700(3)
W1-O3	1.8718(19)
W1-O3#1	1.8718(19)
W1-O2	1.8995(18)
W1-O2#1	1.8995(18)
F1-C2	1.335(3)
F2-C2	1.342(3)
F3-C2	1.347(3)
F4-C6	1.341(4)
F5-C6	1.342(3)
F6-C6	1.335(3)
O2-C1	1.429(3)
O3-C5	1.425(3)
C1-C4	1.523(4)
C1-C3	1.523(4)
C1-C2	1.529(4)
C3-H3A	0.9800
C3-H3B	0.9800
C3-H3C	0.9800
C4-H4A	0.9800
C4-H4B	0.9800
C4-H4C	0.9800
C5-C7	1.508(4)
C5-C8	1.517(4)
C5-C6	1.531(4)
C7-H7A	0.9800
C7-H7B	0.9800
C7-H7C	0.9800
C8-H8A	0.9800
C8-H8B	0.9800
C8-H8C	0.9800
O1-W1-O3	109.74(7)
O1-W1-O3#1	109.74(7)

O3-W1-O3#1	140.51(15)
O1-W1-O2	98.70(6)
O3-W1-O2	87.33(8)
O3#1-W1-O2	86.82(8)
O1-W1-O2#1	98.70(6)
O3-W1-O2#1	86.82(8)
O3#1-W1-O2#1	87.33(8)
O2-W1-O2#1	162.60(13)
C1-O2-W1	140.54(17)
C5-O3-W1	147.55(17)
O2-C1-C4	111.8(2)
O2-C1-C3	108.3(2)
C4-C1-C3	112.5(2)
O2-C1-C2	105.1(2)
C4-C1-C2	109.1(2)
C3-C1-C2	109.8(2)
F1-C2-F2	107.4(2)
F1-C2-F3	107.0(2)
F2-C2-F3	106.9(2)
F1-C2-C1	112.1(2)
F2-C2-C1	112.2(2)
F3-C2-C1	110.9(2)
C1-C3-H3A	109.5
C1-C3-H3B	109.5
H3A-C3-H3B	109.5
C1-C3-H3C	109.5
H3A-C3-H3C	109.5
H3B-C3-H3C	109.5
C1-C4-H4A	109.5
C1-C4-H4B	109.5
H4A-C4-H4B	109.5
C1-C4-H4C	109.5
H4A-C4-H4C	109.5
H4B-C4-H4C	109.5
O3-C5-C7	110.6(2)

O3-C5-C8	110.1(2)
C7-C5-C8	113.2(2)
O3-C5-C6	104.1(2)
C7-C5-C6	109.2(2)
C8-C5-C6	109.2(2)
F6-C6-F4	106.7(2)
F6-C6-F5	106.7(2)
F4-C6-F5	106.2(2)
F6-C6-C5	111.4(2)
F4-C6-C5	112.6(2)
F5-C6-C5	112.7(3)
C5-C7-H7A	109.5
C5-C7-H7B	109.5
H7A-C7-H7B	109.5
C5-C7-H7C	109.5
H7A-C7-H7C	109.5
H7B-C7-H7C	109.5
C5-C8-H8A	109.5
C5-C8-H8B	109.5
H8A-C8-H8B	109.5
C5-C8-H8C	109.5
H8A-C8-H8C	109.5
H8B-C8-H8C	109.5

Symmetry transformations used to generate equivalent atoms:

#1 -x,y,-z+1/2

Table S-5: Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **5**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
W(1)	8930(1)	1423(1)	2474(1)	12(1)
S(1)	8077(3)	-756(2)	2261(1)	57(1)
F(1)	7786(4)	773(3)	347(2)	36(1)
F(2)	6791(5)	1843(3)	-159(2)	42(1)
F(3)	5954(5)	1149(3)	736(2)	33(1)
F(4)	6749(5)	3394(3)	556(2)	42(1)
F(5)	5703(4)	2707(3)	1378(2)	31(1)
F(6)	7393(4)	3401(3)	1669(2)	31(1)
F(7)	12507(4)	1329(3)	2120(2)	35(1)
F(8)	13155(5)	587(5)	1212(3)	64(2)
F(9)	11864(6)	1644(4)	1053(3)	49(2)
F(10)	11617(5)	-627(3)	643(3)	50(1)
F(11)	10443(4)	460(3)	357(2)	28(1)
F(12)	9680(5)	-599(3)	968(3)	44(1)
F(13)	5935(5)	3072(3)	2900(2)	42(1)
F(14)	4812(4)	2646(4)	3800(3)	46(1)
F(15)	6759(6)	2976(4)	3957(3)	41(1)
F(16)	4980(4)	993(3)	4220(3)	44(1)
F(17)	6804(4)	1387(4)	4590(2)	35(1)
F(18)	6606(5)	259(3)	3903(2)	40(1)
F(19)	8997(4)	278(3)	4537(2)	39(1)
F(20)	10642(4)	626(3)	5139(2)	42(1)
F(21)	10771(5)	-255(3)	4232(3)	41(1)
F(22)	12326(4)	1704(3)	4496(2)	33(1)
F(23)	12453(4)	790(3)	3606(2)	31(1)
F(24)	11941(4)	2132(3)	3403(2)	31(1)
O(1)	9603(4)	2433(2)	2465(3)	21(1)
O(2)	7797(4)	1613(3)	1667(2)	16(1)
O(3)	10028(5)	831(4)	1829(3)	22(1)
O(4)	7590(4)	1664(3)	3121(2)	23(1)
O(5)	9896(4)	982(3)	3285(3)	16(1)

O(6)	7988(5)	108(3)	2542(3)	41(1)
C(1)	7696(6)	2088(4)	1016(3)	19(1)
C(2)	8950(7)	2388(4)	701(3)	23(1)
C(3)	7040(7)	1461(6)	481(3)	26(2)
C(4)	6874(8)	2900(5)	1154(4)	27(2)
C(5)	11064(6)	340(4)	1612(3)	19(1)
C(6)	11438(6)	-347(4)	2164(4)	27(2)
C(7)	12156(7)	977(6)	1491(4)	28(2)
C(8)	10710(8)	-105(5)	882(4)	28(2)
C(9)	6324(5)	1635(5)	3329(3)	21(1)
C(10)	5447(6)	1272(5)	2734(3)	28(2)
C(11)	5975(8)	2591(5)	3501(4)	29(2)
C(12)	6176(7)	1056(5)	4019(4)	28(2)
C(13)	10381(6)	1256(4)	3961(3)	16(1)
C(14)	9737(6)	2069(4)	4273(3)	22(1)
C(15)	10204(7)	460(5)	4474(4)	25(2)
C(16)	11781(6)	1460(6)	3869(3)	23(1)
C(17)	7390(12)	-1457(6)	2915(5)	63(3)
C(18)	7001(14)	-833(9)	1494(8)	90(4)

Table S-6: Bond lengths [Å] and angles [°] for **5**.

W(1)-O(1)	1.695(4)
W(1)-O(4)	1.888(5)
W(1)-O(3)	1.888(5)
W(1)-O(5)	1.924(5)
W(1)-O(2)	1.927(4)
W(1)-O(6)	2.242(4)
S(1)-O(6)	1.415(6)
S(1)-C(17)	1.762(8)
S(1)-C(18)	1.814(13)
F(1)-C(3)	1.335(9)
F(2)-C(3)	1.334(8)
F(3)-C(3)	1.331(9)
F(4)-C(4)	1.334(8)
F(5)-C(4)	1.341(10)
F(6)-C(4)	1.332(9)
F(7)-C(7)	1.324(8)
F(8)-C(7)	1.318(9)
F(9)-C(7)	1.330(9)
F(10)-C(8)	1.322(9)
F(11)-C(8)	1.320(9)
F(12)-C(8)	1.337(9)
F(13)-C(11)	1.324(8)
F(14)-C(11)	1.353(9)
F(15)-C(11)	1.317(10)
F(16)-C(12)	1.324(8)
F(17)-C(12)	1.337(8)
F(18)-C(12)	1.314(9)
F(19)-C(15)	1.315(8)
F(20)-C(15)	1.327(8)
F(21)-C(15)	1.321(9)
F(22)-C(16)	1.338(7)
F(23)-C(16)	1.334(9)
F(24)-C(16)	1.343(9)
O(2)-C(1)	1.399(7)

O(3)-C(5)	1.387(8)
O(4)-C(9)	1.396(7)
O(5)-C(13)	1.404(7)
C(1)-C(2)	1.521(9)
C(1)-C(4)	1.535(10)
C(1)-C(3)	1.536(9)
C(2)-H(2A)	0.9800
C(2)-H(2B)	0.9800
C(2)-H(2C)	0.9800
C(5)-C(6)	1.507(8)
C(5)-C(7)	1.528(10)
C(5)-C(8)	1.544(9)
C(6)-H(6A)	0.9800
C(6)-H(6B)	0.9800
C(6)-H(6C)	0.9800
C(9)-C(11)	1.533(10)
C(9)-C(10)	1.536(8)
C(9)-C(12)	1.550(9)
C(10)-H(10A)	0.9800
C(10)-H(10B)	0.9800
C(10)-H(10C)	0.9800
C(13)-C(14)	1.525(9)
C(13)-C(16)	1.527(8)
C(13)-C(15)	1.546(9)
C(14)-H(14A)	0.9800
C(14)-H(14B)	0.9800
C(14)-H(14C)	0.9800
C(17)-H(17A)	0.9800
C(17)-H(17B)	0.9800
C(17)-H(17C)	0.9800
C(18)-H(18A)	0.9800
C(18)-H(18B)	0.9800
C(18)-H(18C)	0.9800
O(1)-W(1)-O(4)	98.5(2)

O(1)-W(1)-O(3)	99.6(2)
O(4)-W(1)-O(3)	161.9(2)
O(1)-W(1)-O(5)	95.8(2)
O(4)-W(1)-O(5)	89.2(2)
O(3)-W(1)-O(5)	89.3(2)
O(1)-W(1)-O(2)	96.8(2)
O(4)-W(1)-O(2)	89.0(2)
O(3)-W(1)-O(2)	88.6(2)
O(5)-W(1)-O(2)	167.42(19)
O(1)-W(1)-O(6)	177.0(2)
O(4)-W(1)-O(6)	78.6(2)
O(3)-W(1)-O(6)	83.3(2)
O(5)-W(1)-O(6)	83.3(2)
O(2)-W(1)-O(6)	84.1(2)
O(6)-S(1)-C(17)	106.7(4)
O(6)-S(1)-C(18)	107.4(5)
C(17)-S(1)-C(18)	103.1(6)
C(1)-O(2)-W(1)	141.2(4)
C(5)-O(3)-W(1)	157.7(4)
C(9)-O(4)-W(1)	152.8(4)
C(13)-O(5)-W(1)	140.5(4)
S(1)-O(6)-W(1)	141.3(4)
O(2)-C(1)-C(2)	114.3(5)
O(2)-C(1)-C(4)	108.7(5)
C(2)-C(1)-C(4)	108.5(6)
O(2)-C(1)-C(3)	104.9(5)
C(2)-C(1)-C(3)	110.0(5)
C(4)-C(1)-C(3)	110.3(6)
C(1)-C(2)-H(2A)	109.5
C(1)-C(2)-H(2B)	109.5
H(2A)-C(2)-H(2B)	109.5
C(1)-C(2)-H(2C)	109.5
H(2A)-C(2)-H(2C)	109.5
H(2B)-C(2)-H(2C)	109.5
F(3)-C(3)-F(2)	107.0(6)

F(3)-C(3)-F(1)	107.3(7)
F(2)-C(3)-F(1)	107.4(6)
F(3)-C(3)-C(1)	113.0(5)
F(2)-C(3)-C(1)	112.3(7)
F(1)-C(3)-C(1)	109.6(5)
F(6)-C(4)-F(4)	107.4(6)
F(6)-C(4)-F(5)	107.0(6)
F(4)-C(4)-F(5)	106.5(6)
F(6)-C(4)-C(1)	110.0(6)
F(4)-C(4)-C(1)	112.1(6)
F(5)-C(4)-C(1)	113.6(6)
O(3)-C(5)-C(6)	113.0(5)
O(3)-C(5)-C(7)	107.5(5)
C(6)-C(5)-C(7)	109.8(6)
O(3)-C(5)-C(8)	107.0(6)
C(6)-C(5)-C(8)	109.9(5)
C(7)-C(5)-C(8)	109.6(5)
C(5)-C(6)-H(6A)	109.5
C(5)-C(6)-H(6B)	109.5
H(6A)-C(6)-H(6B)	109.5
C(5)-C(6)-H(6C)	109.5
H(6A)-C(6)-H(6C)	109.5
H(6B)-C(6)-H(6C)	109.5
F(8)-C(7)-F(7)	107.0(6)
F(8)-C(7)-F(9)	107.3(7)
F(7)-C(7)-F(9)	106.3(6)
F(8)-C(7)-C(5)	112.4(7)
F(7)-C(7)-C(5)	110.1(6)
F(9)-C(7)-C(5)	113.3(6)
F(11)-C(8)-F(10)	107.8(6)
F(11)-C(8)-F(12)	106.0(6)
F(10)-C(8)-F(12)	107.2(6)
F(11)-C(8)-C(5)	113.4(6)
F(10)-C(8)-C(5)	111.9(6)
F(12)-C(8)-C(5)	110.1(6)

O(4)-C(9)-C(11)	105.0(6)
O(4)-C(9)-C(10)	113.7(5)
C(11)-C(9)-C(10)	110.0(6)
O(4)-C(9)-C(12)	109.7(5)
C(11)-C(9)-C(12)	110.3(5)
C(10)-C(9)-C(12)	108.2(5)
C(9)-C(10)-H(10A)	109.5
C(9)-C(10)-H(10B)	109.5
H(10A)-C(10)-H(10B)	109.5
C(9)-C(10)-H(10C)	109.5
H(10A)-C(10)-H(10C)	109.5
H(10B)-C(10)-H(10C)	109.5
F(15)-C(11)-F(13)	107.5(7)
F(15)-C(11)-F(14)	107.0(6)
F(13)-C(11)-F(14)	105.8(7)
F(15)-C(11)-C(9)	113.6(6)
F(13)-C(11)-C(9)	111.2(5)
F(14)-C(11)-C(9)	111.2(7)
F(18)-C(12)-F(16)	108.1(7)
F(18)-C(12)-F(17)	107.5(6)
F(16)-C(12)-F(17)	106.8(6)
F(18)-C(12)-C(9)	111.0(6)
F(16)-C(12)-C(9)	111.4(6)
F(17)-C(12)-C(9)	111.9(6)
O(5)-C(13)-C(14)	114.0(5)
O(5)-C(13)-C(16)	108.6(5)
C(14)-C(13)-C(16)	108.3(6)
O(5)-C(13)-C(15)	105.0(5)
C(14)-C(13)-C(15)	110.8(5)
C(16)-C(13)-C(15)	110.2(5)
C(13)-C(14)-H(14A)	109.5
C(13)-C(14)-H(14B)	109.5
H(14A)-C(14)-H(14B)	109.5
C(13)-C(14)-H(14C)	109.5
H(14A)-C(14)-H(14C)	109.5

H(14B)-C(14)-H(14C)	109.5
F(19)-C(15)-F(21)	107.4(7)
F(19)-C(15)-F(20)	107.6(6)
F(21)-C(15)-F(20)	107.8(6)
F(19)-C(15)-C(13)	109.7(6)
F(21)-C(15)-C(13)	112.7(6)
F(20)-C(15)-C(13)	111.4(6)
F(23)-C(16)-F(22)	106.9(6)
F(23)-C(16)-F(24)	106.7(5)
F(22)-C(16)-F(24)	106.2(6)
F(23)-C(16)-C(13)	113.9(6)
F(22)-C(16)-C(13)	112.4(5)
F(24)-C(16)-C(13)	110.3(6)
S(1)-C(17)-H(17A)	109.5
S(1)-C(17)-H(17B)	109.5
H(17A)-C(17)-H(17B)	109.5
S(1)-C(17)-H(17C)	109.5
H(17A)-C(17)-H(17C)	109.5
H(17B)-C(17)-H(17C)	109.5
S(1)-C(18)-H(18A)	109.5
S(1)-C(18)-H(18B)	109.5
H(18A)-C(18)-H(18B)	109.5
S(1)-C(18)-H(18C)	109.5
H(18A)-C(18)-H(18C)	109.5
H(18B)-C(18)-H(18C)	109.5