Supporting Information for

Growth of WO_x Materials from Tungsten (VI) Oxo-Fluoroalkoxide Complexes with Partially Fluorinated β-diketonate/β-ketoesterate Ligands: Comparison of Chemical Vapor Deposition to Aerosol-Assisted CVD

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Experimental Section

General procedures

All reactions were carried out under an atmosphere of dry nitrogen gas utilizing either glovebox or Schlenk techniques. All chemicals used were reagent grade. Solvents used were air-free and dried using standard procedures: CH_2Cl_2 using an MBraun MB-SP solvent purification system and diethyl ether by distillation from sodium/benzophenone ketyl. Hexamethyldisiloxane (Sigma-Aldrich), 1,1,1-trifluoro-2-methyl-2-propanol (Synquest Laboratories), 1,1,1,3,3,3-hexafluoro-2-methyl-2-propanol (Synquest Laboratories), 1,1,1,3,3,3-hexafluoro-2-propanol (Synquest Laboratories), acetylacetone (Hacac, Sigma-Aldrich), hexafluoroacetylacetone (Hhfac), ethyl 4,4,4-trifluoro(acetoacetate) (Hetfac, Synquest Laboratories), and chloroform-d_1 (Cambridge Isotopes) were stored over 3 Å molecular sieves for 24 h prior to use. All other reagents were used as received. $WOCl_4$,[30] $NaOCH(CF_3)_2$,[31] $WO(OC(CH_3)_2CF_3)_4$,[32] $WO(OC(CF_3)_2CH_3)_4$,[32] and compounds **1** and **4** were synthesized[27] and characterized according to literature procedures. Elemental analyses were obtained from Robertson Microlit Laboratories (Ledgewood, NJ). NMR spectra were recorded on a Varian Mercury 300BB (300 MHz) spectrometer. The chemical shifts

for ^{1}H and ^{13}C NMR spectra are reported using residual solvent protons as reference, and are reported on the $CFCl_3$ scale for ^{19}F NMR spectra. Thermogravimetric analysis (TGA, TA Discovery5500) was performed under N_2 gas with a heating rate of 10 °C/min.

ESI mass spectra were obtained using a Bruker Daltonics Impact II-Qq-TOF instrument with electrospray as the source of ionization in positive mode. In a nitrogen-filled glovebox, a 4 mL (100 μM) solution of sample was prepared using anhydrous, deoxygenated GC-MS-grade acetonitrile and added to a Hamilton 10 mL gas-tight syringe. The operation parameters were: gas temperature 200 °C, drying gas 4 L/min, nebulizer 1.0 bar, capillary voltage 4500 V in positive mode. The parent mass was further fragmented with a collision energy of 40 eV. The samples were injected using a syringe pump at a steady flow rate of 100 μL/min.

For GC-MS, the mass spectrometry was performed using a ThermoScientific DSQ II with electron impact ionization (70 eV) with an ion source temperature of 250 °C. The gas chromatograph was a ThermoScientific Trace GC Ultra equipped with a Restek Corp., Rxi-5MS column, 30 m x 0.25 mm i.d. x 0.25 μm df. The operation parameters were: MS transfer line of 240 °C with GC helium used as a carrier gas with constant flow of 1 mL/min. All samples were injected in split mode with a 10 μL GC-type syringe with a flow rate of 10 mL/min. The NIST Mass Spectral Search Program library was used to compare fragmentation patterns of selected peaks.

Synthesis of $WO(OC(CH_3)_2CF_3)_3(hfac)$ (2)

In a Schlenk flask, $WO(OC(CH_3)_2CF_3)_4$ (0.927 mmol, 0.656 g) was dissolved in diethyl ether (40 mL) and chilled in an ice bath for 30 min. Hhfac (1.05 mmol, 0.22 g), dissolved in diethyl ether (10 mL), was added dropwise to the $WO(OC(CH_3)_2CF_3)_4$ solution. Then the reaction was warmed to room temperature and allowed to stir for 15 h. Volatiles were removed *in vacuo*

to afford a white solid. The solid was distilled under vacuum (30 mTorr) using a flask equipped with a drip-tip cold finger at 36 °C whereupon liquid droplets condensed on the cold finger. After 15 h, the droplets solidified to yield a solid white sublimate. Yield: 0.35 g (48 %). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ 6.36 (s, 1H, OC(CF_3)C*H*), 1.65 (s, 6H, OC(C*H*$_3$)$_2$CF$_3$), 1.61 (s, 6H, OC(C*H*$_3$)$_2$CF$_3$), 1.53 (s, 6H, OC(C*H*$_3$)$_2$CF$_3$). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, 25 °C): 179.9 (q, O*C*(CF_3)CH), $J_{C\text{-}F}$ = 37.8 Hz), 173.6 (q, O*C*(CF_3)CH), $J_{C\text{-}F}$ = 36.5 Hz), 125.9 (q, OC(CH_3)$_2$*C*F$_3$, $J_{C\text{-}F}$ = 286.0 Hz), 125.6 (q, OC(CH_3)$_2$*C*F$_3$, $J_{C\text{-}F}$ = 284.7 Hz), 117.5 (q, OC(*C*F$_3$)CH, $J_{C\text{-}F}$ = 282.2 Hz), 116.3 (q, OC(*C*F$_3$)CH, $J_{C\text{-}F}$ = 286.0 Hz), 94.5 (s, OC(CF_3)*C*H), 87.8 (q, O*C*(CH_3)$_2$CF$_3$, $J_{C\text{-}F}$ = 31.5 Hz), 84.9 (q, O*C*(CH_3)$_2$CF$_3$, $J_{C\text{-}F}$ = 30.2 Hz), 22.8 (s, OC(*C*H$_3$)$_2$CF$_3$), 22.4 (s, OC(*C*H$_3$)$_2$CF$_3$), 21.9 (s, OC(*C*H$_3$)$_2$CF$_3$). ^{19}F{^{13}C} NMR (282 MHz, $CDCl_3$, 25 °C): δ -75.2 (s, 3F, OCC*F*$_3$CH), -77.0 (s, 3F, OCC*F*$_3$CH), -82.5 (s, 3F, OC(CH_3)$_2$C*F*$_3$), -83.0 (s, 6F, OC(CH_3)$_2$C*F*$_3$). MS (ESI): calc'd for [M + Na]$^{+}$ 811.0347, found 811.0355.

Synthesis of WO(OC(CH_3)$_2$CF$_3$)$_3$(etfac) (3)

Compound **3** was synthesized using the same procedure as **2**. In a Schlenk flask, WO(OC(CH_3)$_2$CF$_3$)$_4$ (1.54 mmol, 1.09 g) was dissolved in diethyl ether (40 mL) and chilled in an ice bath for 30 min. Hetfac (1.64 mmol, 0.301 g), dissolved in diethyl ether (10 mL), was added dropwise to the WO(OC(CH_3)$_2$CF$_3$)$_4$ solution. Then the reaction was warmed to room temperature and allowed to stir for 15 h. Volatiles were removed *in vacuo* to afford a yellow green oily residue. This residue was vacuum distilled (120 mTorr) at 55 °C for 15 h to yield a colorless, clear liquid. Yield: 0.25 g (21 %). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ 5.61 (s, 1H, OC(CF_3)C*H*), 4.29 (q, 2H, OC(OC*H*$_2$CH$_3$)CH, $J_{H\text{-}H}$ = 6 Hz), 1.63 (s, 12H, OC(C*H*$_3$)$_2$CF$_3$), 1.48 (s, 6H, OC(C*H*$_3$)$_2$CF$_3$), 1.33 (t, 3H, OC(OCH$_2$C*H*$_3$)CH, $J_{H\text{-}H}$ = 6 Hz). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, 25 °C): δ 172.8 (s, O*C*(OCH$_2$CH$_3$), 163.9 (q, O*C*(CF_3)CH, $J_{C\text{-}F}$ = 35 Hz), 126.6 (q, OC(CH_3)$_2$*C*F$_3$, $J_{C\text{-}F}$ = 283.8 Hz), 126.0 (q, OC(CH_3)$_2$*C*F$_3$, $J_{C\text{-}F}$ = 282.5 Hz), 119.4 (q, OC(*C*F$_3$)CH, $J_{C\text{-}F}$ = 278.8 Hz), 91.71 (s, OC(CF_3)*C*H), 85.9 (q, O*C*(CH_3)$_2$CF$_3$, $J_{C\text{-}F}$ = 31.3 Hz), 83.9 (q, O*C*(CH_3)$_2$CF$_3$, $J_{C\text{-}F}$ = 30 Hz), 63.6

(s, OC(O*C*H$_2$CH$_3$), 22.3 (s, OC(*C*H$_3$)CF$_3$) 22.2 (s, OC(*C*H$_3$)CF$_3$), 22.0 (s, OC(*C*H$_3$)CF$_3$), 14.03 (s, OC(OCH$_2$*C*H$_3$). ^{19}F{^{13}C} NMR (282 MHz, CDCl$_3$, 25 °C): δ -74.67 (s, 3F, OC(C*F*$_3$)CH), -82.67 (s, 3F, OC(CH$_3$)$_2$C*F*$_3$), -82.94 (s, 6F, OC(CH$_3$)$_2$C*F*$_3$). MS (ESI) calc'd for [M + Na]$^+$ 787.0735, found 787.0762.

Synthesis of WO(OC(CF$_3$)$_2$CH$_3$)$_3$(hfac) (5)

Compound **5** was synthesized following the same procedure as **2**. In a Schlenk flask, WO(OC(CF$_3$)$_2$CH$_3$)$_4$ (0.693 mmol, 0.491 g) was dissolved in diethyl ether (40 mL) and chilled in an ice bath for 30 min. Hhfac (0.843 mmol, 0.175 g), dissolved in diethyl ether (10 mL), was added dropwise to the WO(OC(CF$_3$)$_2$CH$_3$)$_4$ solution. Then the reaction was warmed to room temperature and allowed to stir for 15 h. Volatiles were removed *in vacuo* to afford a yellowish solid. The solid was sublimed under vacuum (30 mTorr) at 36 °C for 15 h to yield a solid yellowish-white sublimate. Yield: 0.45 g (68 %). ^{1}H NMR (300 MHz, CDCl$_3$, 25 °C): δ 6.49 (s, 1H, OC(CF$_3$)C*H*), 1.88 (s, 6H, OC(CF$_3$)$_2$C*H*$_3$), 1.85 (s, 3H, OC(CF$_3$)$_2$C*H*$_3$). ^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$, 25 °C): δ 182.5 (q, O*C*(CF$_3$)CH, $J_{C\text{-}F}$ = 39.1 Hz), 174.0 (q, O*C*(CF$_3$)CH, $J_{C\text{-}F}$ = 37.8 Hz), 122.9 (q, OC(*C*F$_3$)$_2$CH$_3$, $J_{C\text{-}F}$ = 288.5 Hz), 122.8 (q, OC(*C*F$_3$)$_2$CH$_3$, $J_{C\text{-}F}$ = 286.0 Hz), 122.3 (q, OC(*C*F$_3$)$_2$CH$_3$, $J_{C\text{-}F}$ = 288.5 Hz), 117.8 (q, OC(*C*F$_3$)CH, $J_{C\text{-}F}$ = 286.0 Hz), 116.2 (q, OC(*C*F$_3$)CH, $J_{C\text{-}F}$ = 282.2 Hz), 96.6 (s, OC(CF$_3$)*C*H), 88.6 (sp, O*C*(CF$_3$)$_2$CH$_3$, $J_{C\text{-}F}$ = 31.5 Hz), 86.2 (sp, O*C*(CF$_3$)$_2$CH$_3$, $J_{C\text{-}F}$ = 31.5 Hz), 15.9 (s, OC(CF$_3$)$_2$*C*H$_3$), 15.6 (s, OC(CF$_3$)$_2$*C*H$_3$). ^{19}F{^{13}C} NMR (282 MHz, CDCl$_3$, 25 °C): δ -74.71 (s, 3F, OC(C*F*$_3$)CH), -76.72 (s, 6F, OC(C*F*$_3$)$_2$CH$_3$), -77.10 (s, 3F, OC(C*F*$_3$)CH), -77.29 (m, 6F, OC(CF$_3$)$_2$CH$_3$), -77.47 (m, 6F, OC(CF$_3$)$_2$CH$_3$). Anal. Calc'd for WO$_6$C$_{17}$H$_{10}$F$_{24}$: C: 21.49; H: 1.06%. Found: C: 21.66; H: 0.82%.

Synthesis of WO(OC(CF$_3$)$_2$CH$_3$)$_3$(etfac) (6)

Compound **6** was synthesized using the same procedure as **2**. In a Schlenk flask, WO(OC(CF$_3$)$_2$CH$_3$)$_4$ (0.914 mmol, 0.845 g) was dissolved in diethyl ether (40 mL) and chilled in

an ice bath for 30 min. Hetfac (1.06 mmol, 0.185 g), dissolved in diethyl ether (10 mL), was added dropwise to the $WO(OC(CF_3)_2CH_3)_4$ solution. Then the reaction was warmed to room temperature and allowed to stir for 15 h. Volatiles were removed *in vacuo* to afford a yellow oily residue. This residue was vacuum distilled (60 mTorr) at 41 °C for 15 h to yield a yellowish distillate. Yield: 0.35 g (41 %). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ 5.74 (s, 1H, $OC(CF_3)CH$), 4.35 (q, 2H, $OC(OCCH_2CH_3)CH$, J_{H-H} = 9 Hz), 1.86 (s, 6H, $OC(CF_3)_2CH_3$), 1.82 (s, 3H, $OC(CF_3)_2CH_3$), 1.34 (t, 3H, $OC(OCCH_2CH_3)CH$, J_{H-H} = 6 Hz). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$, 25 °C): δ 173.0 (s, $OC(OCH_2CH_3)$), 162.8 (q, $OC(CF_3)CH$, J_{C-F} = 36.5 Hz), 123.3 (q, $OC(CF_3)_2CH_3$, J_{C-F} = 287.3 Hz), 123.1 (q, $OC(CF_3)_2CH_3$, J_{C-F} = 287.3 Hz), 122.8 (q, $OC(CF_3)_2CH_3$, J_{C-F} = 286.0 Hz), 119.5 (q, $OC(CF_3)CH$, J_{C-F} = 279.7 Hz), 94.8 (s, $OC(CF_3)CH$), 86.8 (sp, $OC(CF_3)_2CH_3$, J_{C-F} = 30.2 Hz), 85.0 (sp, $OC(CF_3)_2CH_3$, J_{C-F} = 30.2 Hz), 64.9 (s, $OC(OCCH_2CH_3)$), 15.9 (s, $OC(CF_3)_2CH_3$), 15.6 (s, $OC(CF_3)_2CH_3$) 13.9 (s, $OC(OCCH_2CH_3)$). $^{19}F\{^{13}C\}$ NMR (282 MHz, $CDCl_3$, 25 °C): δ -74.36 (s, 3F, $OC(CF_3)CH$), -77.21 (s, 6F, $OC(CF_3)_2CH_3$), -77.25 (s, 6F, $OC(CF_3)_2CH_3$), -77.86 (m, 6F, $OC(CF_3)_2CH_3$). MS (ESI): calc'd for $[M + Na]^+$ 948.9887, found 948.9909.

Synthesis of $WO(OCH(CF_3)_2)_4(Et_2O)$

In a Schlenk flask, $WOCl_4$ (3.97 mmol, 1.36 g) was dissolved in diethyl ether (40 mL) and chilled in an ice bath for 30 min. $NaOCH(CF_3)_2$ (16.2 mmol, 3.09 g), dissolved in diethyl ether (40 mL), was added dropwise to the $WOCl_4$ solution and a progressive color change from orange to dark blue was observed. The reaction was then warmed to room temperature and allowed to stir for 15 h after which volatiles were removed *in vacuo* to afford a sticky dark blue residue. The residue was sublimed under vacuum (60 mTorr) at room temperature for 15 h to yield a solid yellow sublimate. Yield: 1.26 g (36.5 %). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ 5.35 (sp, 4H, $OCH(CF_3)_2$, J_{H-F} = 6 Hz), 3.92 (q, 4H, $(CH_3CH_2)_2O$, J_{H-H} = 6 Hz), 1.21 (t, 6H, $(CH_3CH_2)_2O$, J_{H-H} = 6 Hz). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$, 25 °C): δ 122.0 (q, $OCH(CF_3)_2$, J_{C-F} = 273.4 Hz), 80.5 (sp, $OCH(CF_3)_2$, J_{C-F} = 34.0 Hz), 65.1 (s, $(CH_3CH_2)_2O$), 12.3 (s, $(CH_3CH_2)_2O$). $^{19}F\{^{13}C\}$ NMR

(282 MHz, $CDCl_3$, 25 °C): δ -73.72 (d, 24F, OCH(C*F*$_3$)$_2$, J_{F-H} = 5.6 Hz). MS (DART): calc'd for [M - Et_2O - H]$^-$ 866.9103, found 866.9088.

Synthesis of WO(OCH(CF$_3$)$_2$)$_3$(acac) (7)

Compound **7** was synthesized using the same procedure as **2**. In a Schlenk flask, WO(OCH(CF$_3$)$_2$)$_4$(Et_2O) (1.27 mmol, 1.10 g) was dissolved in diethyl ether (40 mL) and in an additional funnel, Hacac (1.27 mmol, 0.128 g) was dissolved in diethyl ether (30 mL). The flask was chilled in an ice bath for 30 minutes. Hacac was added dropwise to the WO(OCH(CF$_3$)$_2$)$_4$(Et_2O) solution. The reaction was warmed to room temperature and allowed to stir for 15 h. The volatiles were removed *in vacuo* to afford a yellow solid. The crude product was sublimed (300 mTorr) at 40 °C to yield a yellow sublimate. Yield 0.46 g (45 %). ^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ 5.73 (sp, 1H, OC*H*(CF$_3$)$_2$, J_{H-F} = 6 Hz), 5.22 (sp, 2H, OC*H*(CF$_3$)$_2$, J_{H-F} = 6 Hz), 4.82 (s, 1H, OC(CH$_3$)C*H*), 1.40 (s, 3H, OC(C*H*$_3$)), 1.20 (s, 3H, OC(C*H*$_3$)). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, 25 °C): δ 197.72 (s, O*C*(CH$_3$)CH), 185.46 (s, O*C*(CH$_3$)CH), 121.71 (q, OCH(*C*F$_3$)$_2$, J_{C-F} = 284.3 Hz), 121.48 (q, OCH(*C*F$_3$)$_2$, J_{C-F} = 282.8 Hz), 108.27 (s, *C*H), 81.37 (sp, O*C*H(CF$_3$)$_2$, J_{C-F} = 33.8 Hz), 77.98 (sp, O*C*H(CF$_3$)$_2$, J_{C-F} = 34.5 Hz), 27.46 (s, C(*C*H$_3$)), 25.16 (s, C(*C*H$_3$)). ^{19}F{^{13}C} NMR (282 MHz, C_6D_6 25 °C): δ -73.34 (s, 6F, OCH(C*F*$_3$)$_2$), -74.18 (m, 6F, OCH(C*F*$_3$)$_2$, J_{F-F} = 8.5 Hz), -74.31 (q, 6F, OCH(C*F*$_3$)$_2$, J_{F-F} = 8.5 Hz). Anal. Calc'd for $WO_6C_{14}H_{10}F_{18}$: C, 21.02; H, 1.21. Found: C, 21.21; H, 0.99 %.

Synthesis of WO(OCH(CF$_3$)$_2$)$_3$(hfac) (8)

Compound **8** was synthesized using the same procedure as **2**. In a Schlenk flask, WO(OCH(CF$_3$)$_2$)$_4$(Et_2O) (0.494 mmol, 0.429 g) was dissolved in diethyl ether (40 mL) and chilled in an ice bath for 30 min. Hhfac (0.632 mmol, 0.131 g), dissolved in diethyl ether (10 mL), was added dropwise to the WO(OCH(CF$_3$)$_2$)$_4$ solution. Then the reaction was warmed to room temperature and allowed to stir for 15 h. Volatiles were removed *in vacuo* to afford an oily dark

green residue. This residue was vacuum distilled (60 mTorr) at room temperature for 15 h to afford an orange distillate. Yield: 0.11 g (25 %). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ 6.65 (s, 1H, OC(CF_3)C*H*), 5.59 (sp, 1H, OC*H*(CF_3)$_2$, J_{H-F} = 6 Hz). 5.47 (sp, 2H, OC*H*(CF_3)$_2$, J_{H-F} = 6 Hz). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, 25 °C): δ 182.9 (q, O*C*(CF_3)CH, J_{C-F} = 39.1 Hz), 174.3 (q, O*C*(CF_3)CH, J_{C-F} = 39.1 Hz), 120.4 (q, OCH(*C*F$_3$)$_2$, J_{C-F} = 284.7 Hz), 120.5 (q, OCH(*C*F$_3$)$_2$, J_{C-F} = 283.5 Hz), 120.2 (q, OCH(*C*F$_3$)$_2$, J_{C-F} = 283.5 Hz), 117.4 (q, OC(*C*F$_3$)CH, J_{C-F} = 284.8 Hz), 116.5 (q, OC(*C*F$_3$)CH, J_{C-F} = 282.2 Hz), 98.0 (s, OC(CF_3)*C*H), 81.1 (sp, O*C*H(CF_3)$_2$, J_{C-F} = 34.0 Hz), 80.0 (sp, O*C*H(CF_3)$_2$, J_{C-F} = 35.3 Hz). ^{19}F{^{13}C} NMR (282 MHz, $CDCl_3$, 25 °C): δ -73.79 (s, 6F, OCH(C*F*$_3$)$_2$), -74.12 (s, 6F, OCH(C*F*$_3$)$_2$), -74.57 (s, 6F, OCH(C*F*$_3$)$_2$), -74.78 (s, 3F, OC(C*F*$_3$)CH), -76.95 (s, 3F, OC(C*F*$_3$)CH). MS (DART): calc'd for $[M + H]^+$ 908.9212, found 908.9209.

Synthesis of WO(OCH(CF_3)$_2$)$_3$(etfac) (9)

Compound **9** was synthesized using the same procedure as **2**. In a Schlenk flask, WO(OCH(CF_3)$_2$)$_4$ (0.881 mmol, 0.624 g) was dissolved in diethyl ether (10 mL) and chilled in an ice bath for 30 min. Hetfac (0.934 mmol, 0.172 g), dissolved in diethyl ether (10 mL), was added dropwise to the WO(OCH(CF_3)$_2$)$_4$ solution. Then the reaction was warmed to room temperature and allowed to stir for 15 h. Volatiles were removed *in vacuo* to afford a dark green oily residue. This residue was vacuum distilled (120 mTorr) at 55 °C for 15 h to yield a dark green distillate. Yield: 0.10 g (12 %). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ 5.88 (s, 1H, OC(CF_3)C*H*), 5.42 (sp, 1H, OCC*H*(CF_3)$_2$, J_{H-F} = 6 Hz), 5.38 (sp, 2H, OCC*H*(CF_3)$_2$, J_{H-F} = 6 Hz), 4.42 (q, 2H, OC(OC*H*$_2$CH$_3$), J_{H-H} = 3 Hz), 1.38 (t, 3H, OC(OCH$_2$C*H*$_3$), J_{H-H} = 3 Hz). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, 25 °C): 173.4 (s, O*C*(OCH$_2$CH$_3$)), 162.9 (q, O*C*(CF_3)CH, J_{C-F} = 37.5 Hz), 121.8 (q, OCH(*C*F$_3$)$_2$, J_{C-F} = 282.5 Hz), 121.5 (q, OCH(*C*F$_3$)$_2$, J_{C-F} = 282.5 Hz), 121.5 (q, OCH(*C*F$_3$)$_2$, J_{C-F} = 280.0 Hz), 121.0 (q, OC(*C*F$_3$)CH, J_{C-F} = 276.2 Hz), 96.6 (s, OC(CF_3)*C*H), 81.2 (sp, O*C*CH(CF_3)$_2$, J_{C-F} = 33.8), 80.4 (sp, O*C*CH(CF_3)$_2$, J_{C-F} = 33.8 Hz), 66.0 (s, OC(O*C*H$_2$CH$_3$)), 13.8

(s, OC(OCH$_2$*C*H$_3$)). ^{19}F{^{13}C} NMR (282 MHz, $CDCl_3$, 25 °C): δ -73.91 (s, 6F, OCH(C*F*$_3$)$_2$), -74.06 (m, 6F, OCH(C*F*$_3$)$_2$), -74.61 (s, 3F, OC(C*F*$_3$)CH), -74.76 (m, 6F, OCH(C*F*$_3$)$_2$). MS (DART): calc'd for [M – OR]$^-$ 716.9591 found 716.9634

NMR spectra of 2

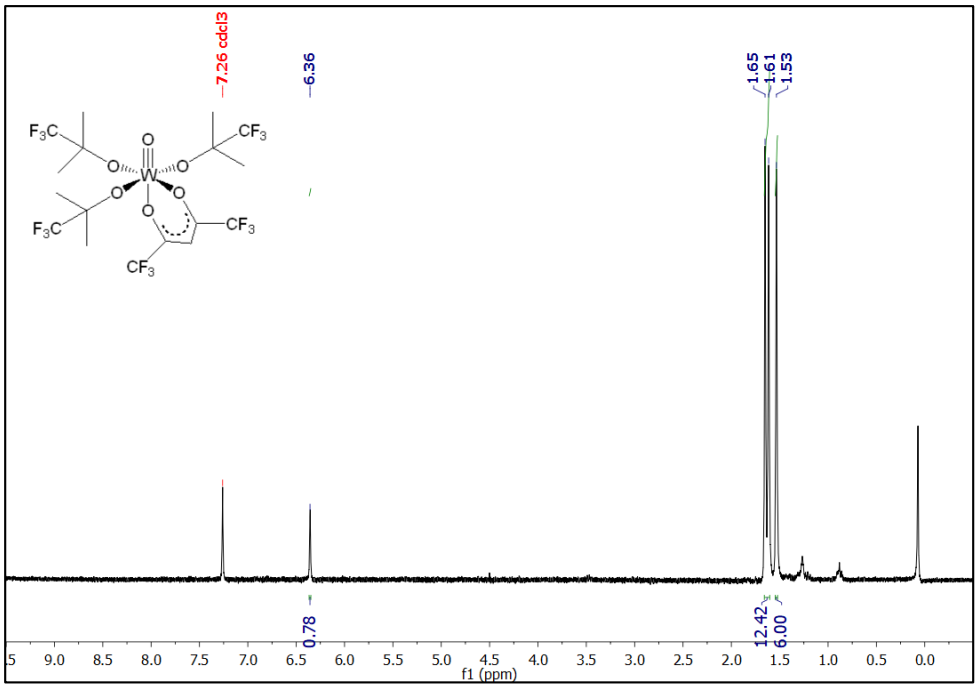

Figure S1. ^{1}H NMR of **2** in $CDCl_3$

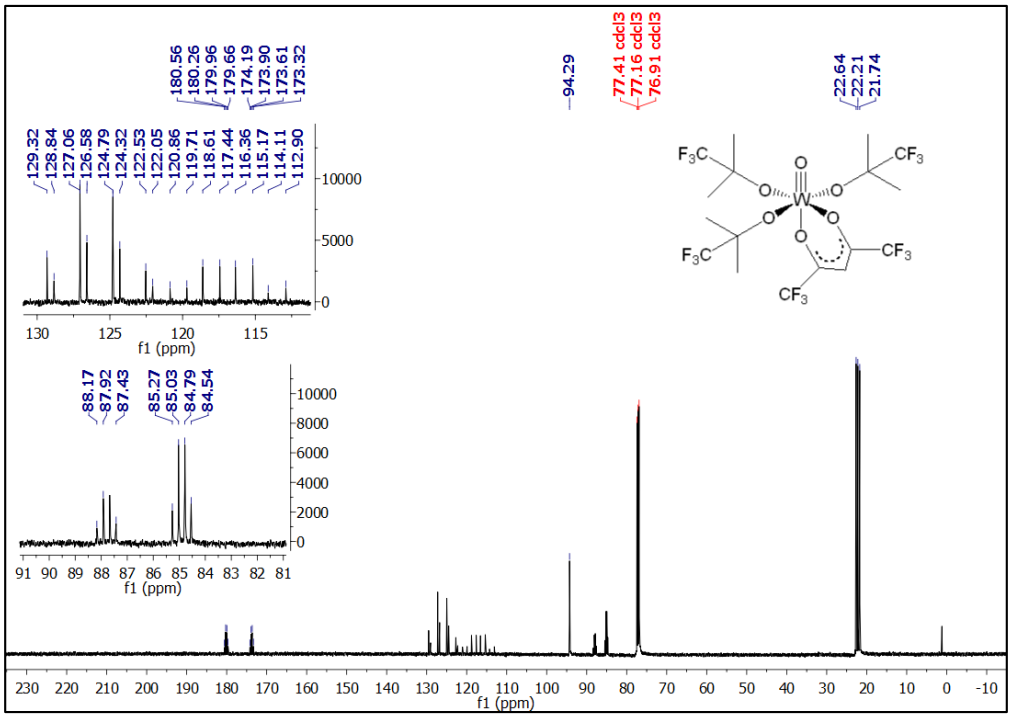

Figure S2. ^{13}C NMR of **2** in $CDCl_3$

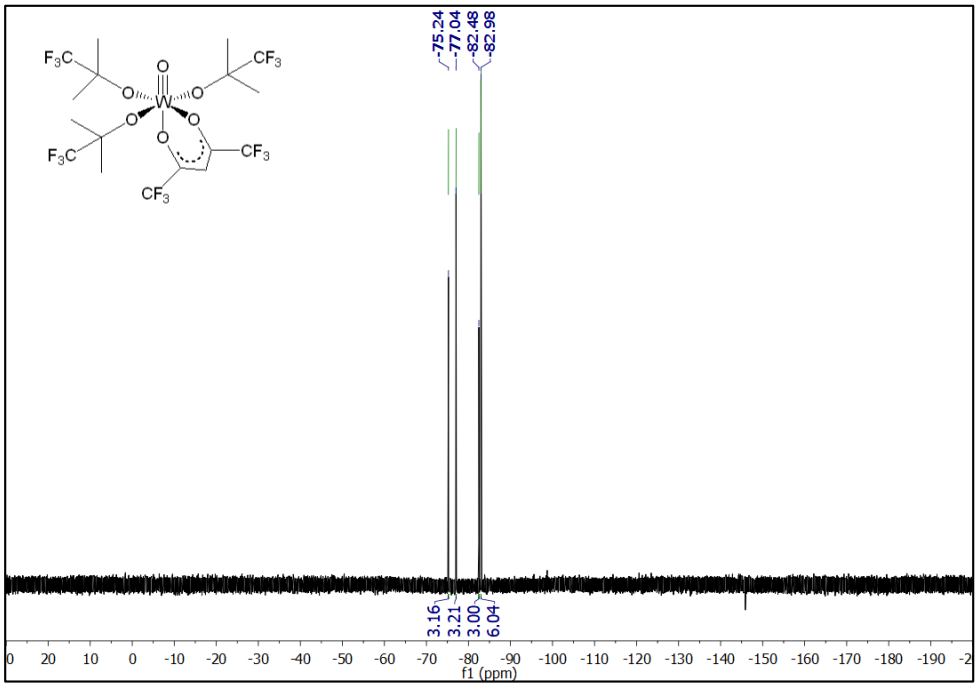

Figure S3. ^{19}F NMR of **2** in $CDCl_3$

NMR spectra of 3

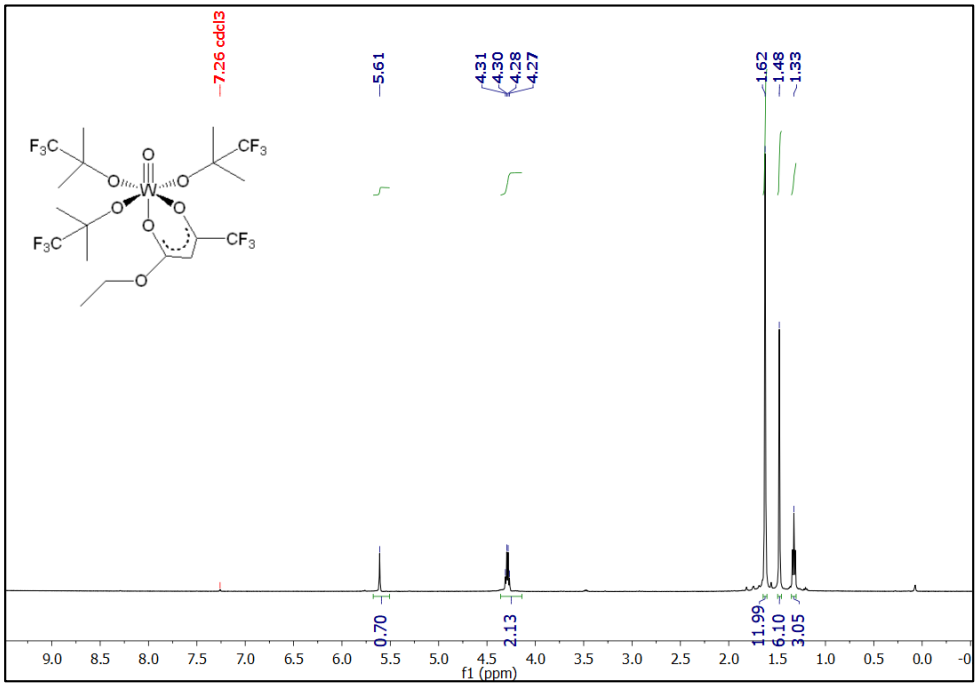

Figure S4. ^{1}H NMR of **3** in $CDCl_3$

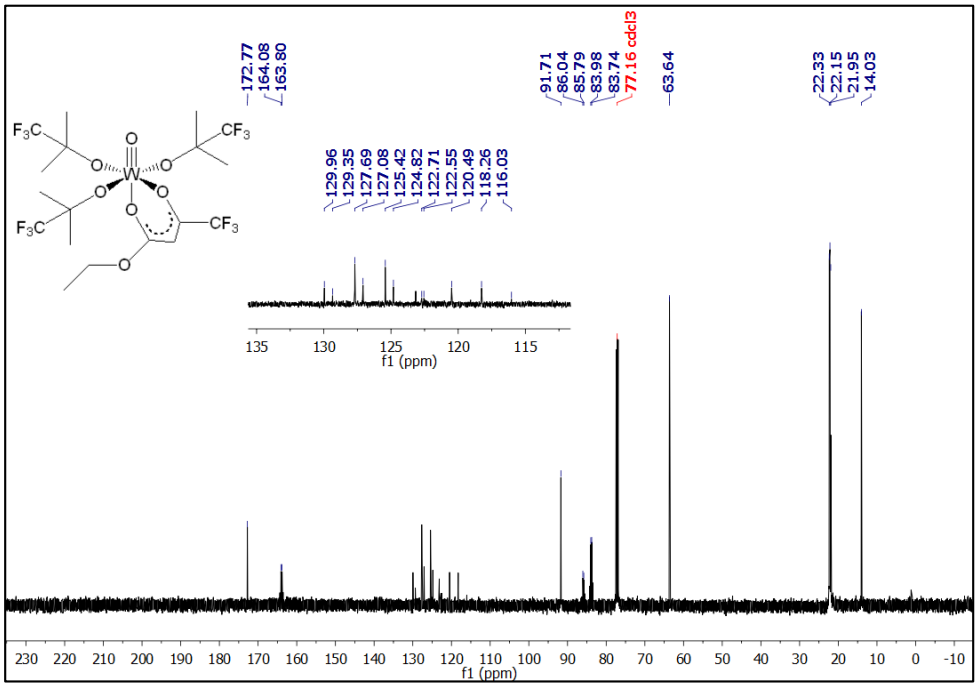

Figure S5. ^{13}C NMR of **3** in $CDCl_3$

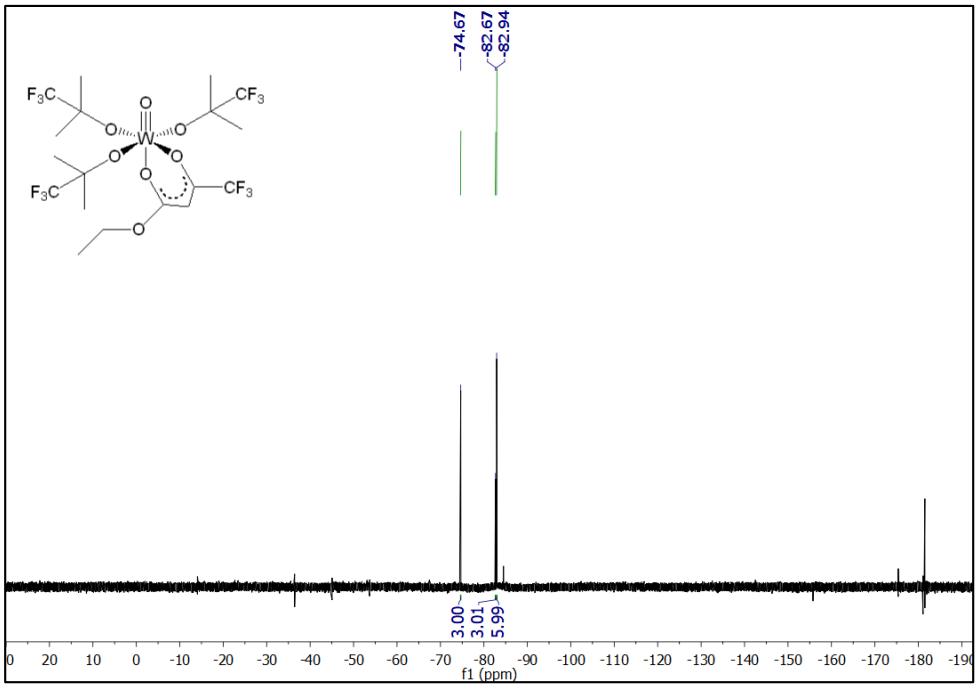

Figure S6. ^{19}F NMR of **3** in $CDCl_3$

NMR spectra of 5

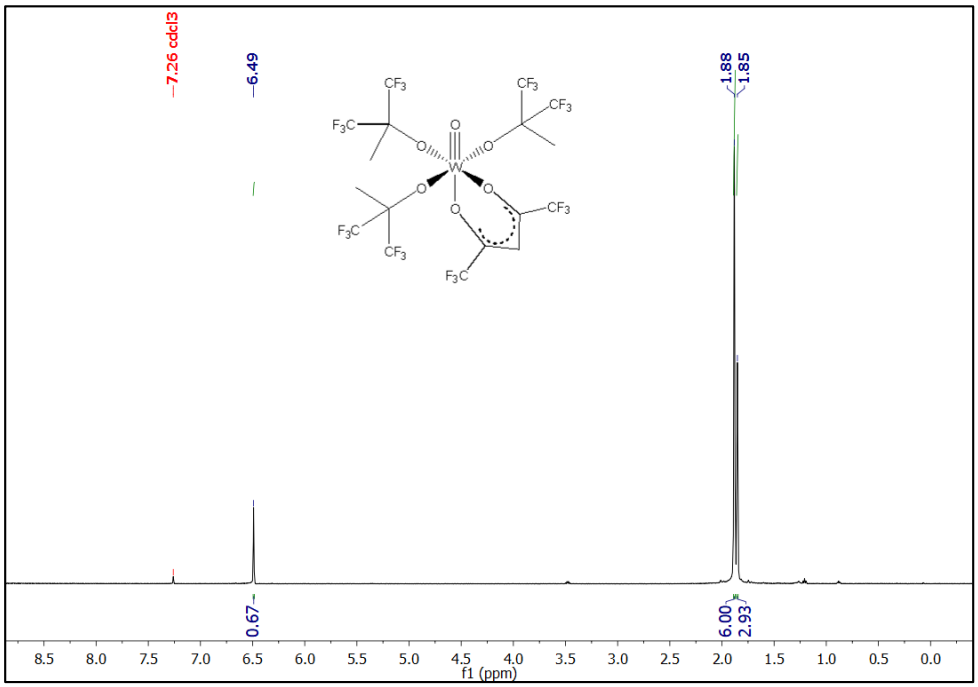

Figure S7. ^{1}H NMR of **5** in $CDCl_3$

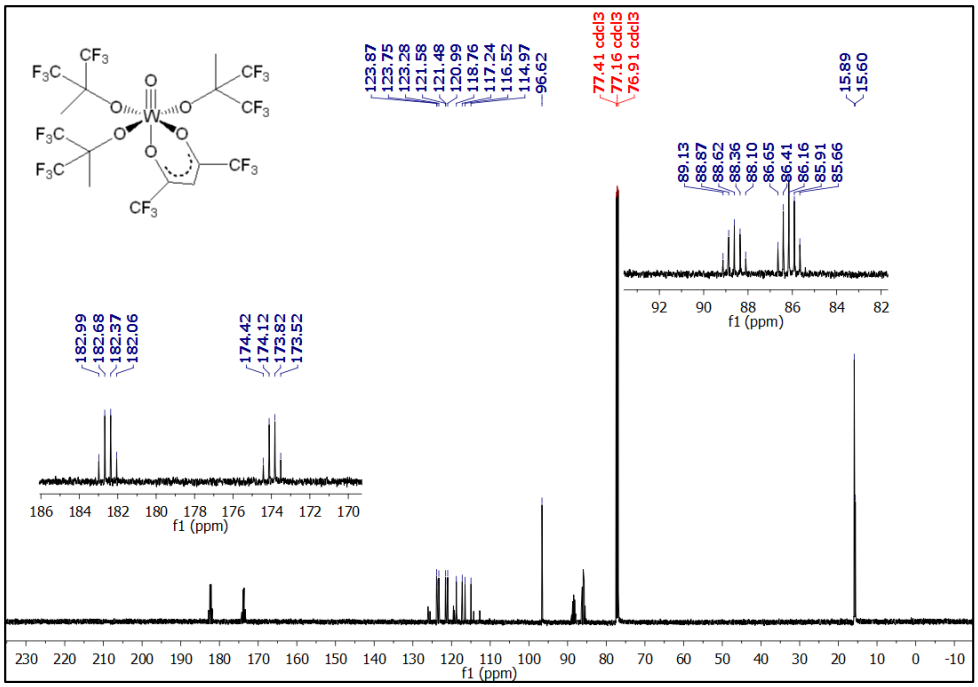

Figure S8. ^{13}C NMR of **5** in $CDCl_3$

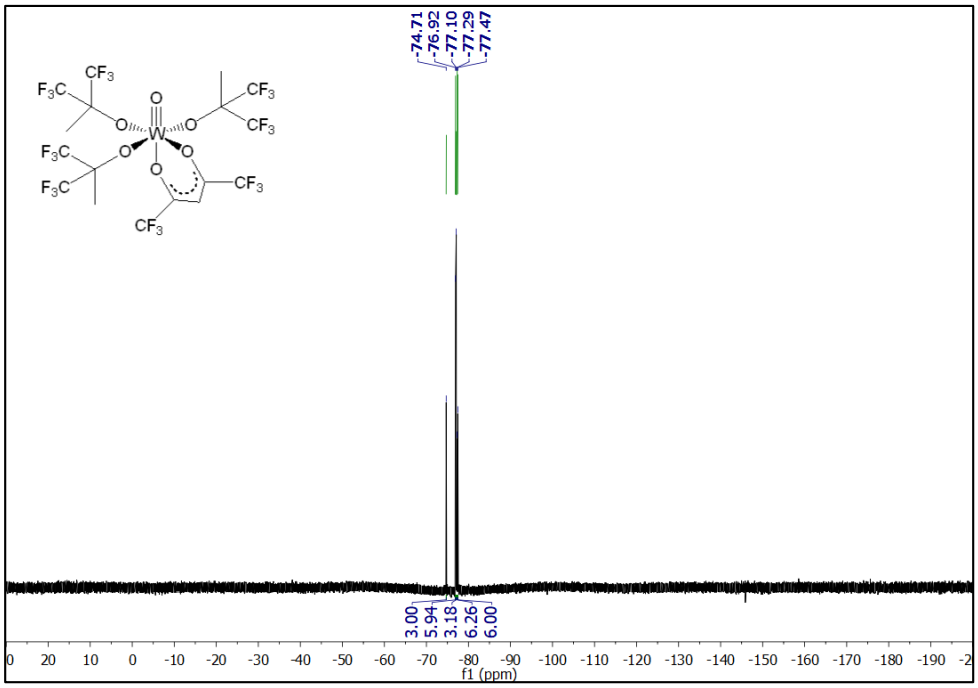

Figure S9. ^{19}F NMR of **5** in $CDCl_3$

NMR spectra of 6

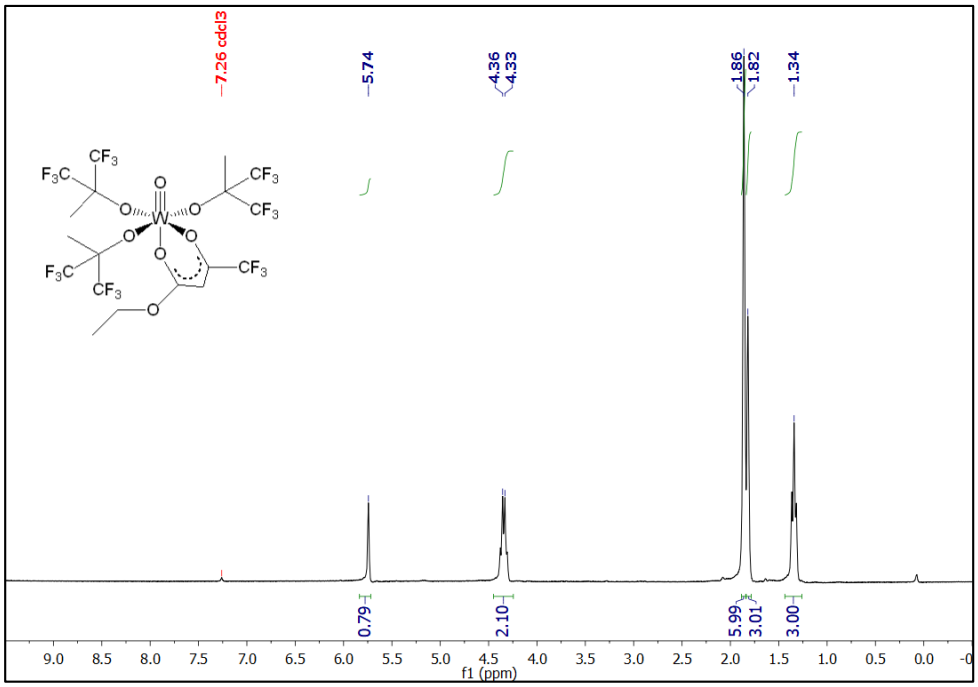

Figure S10. ^{1}H NMR of **6** in $CDCl_3$

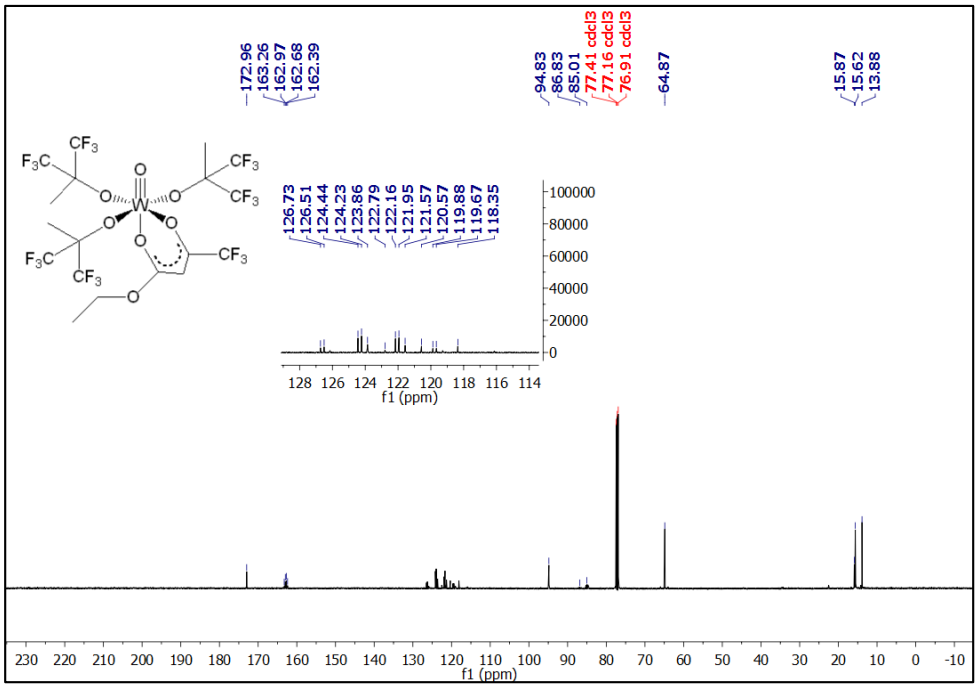

Figure S11. ^{13}C NMR of **6** in $CDCl_3$

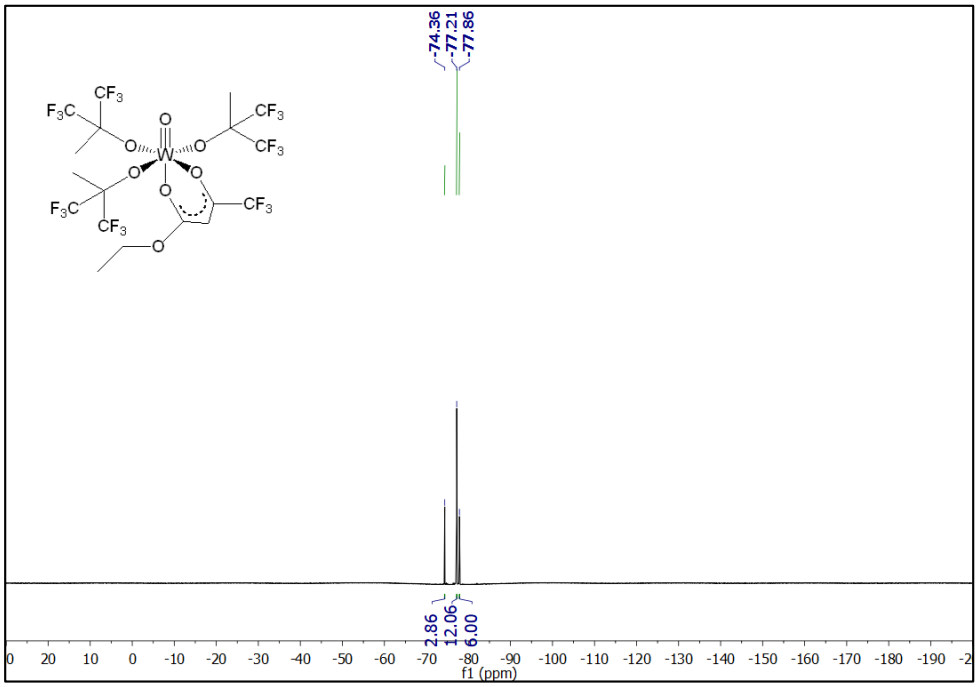

Figure S12. ^{19}F NMR of **6** in $CDCl_3$

NMR spectra of 7

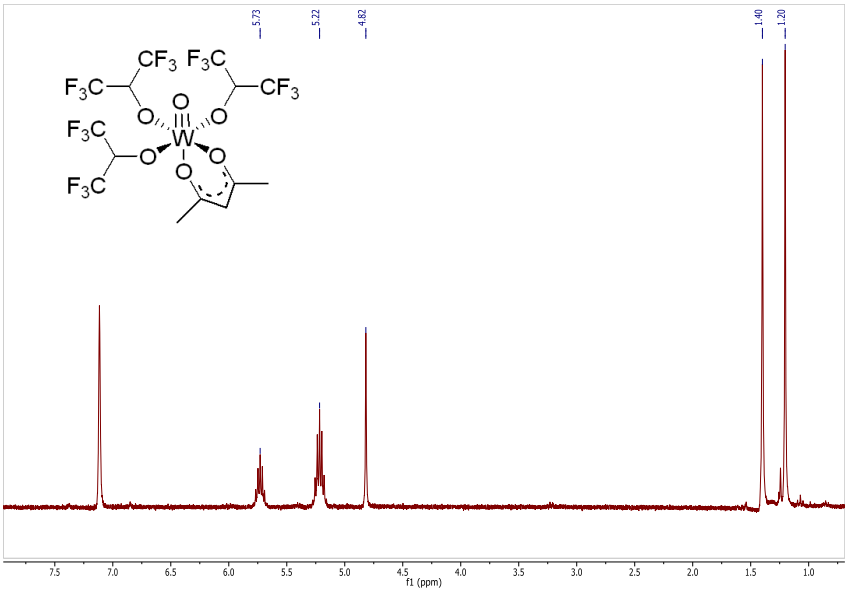

Figure S13. ^{1}H NMR of **7** in C_6D_6

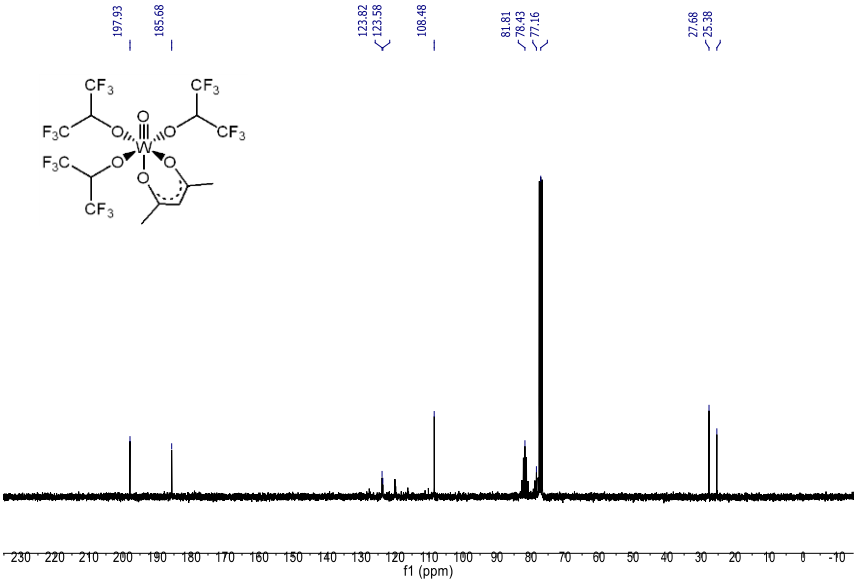

Figure S14. ^{13}C NMR of **7** in C_6D_6

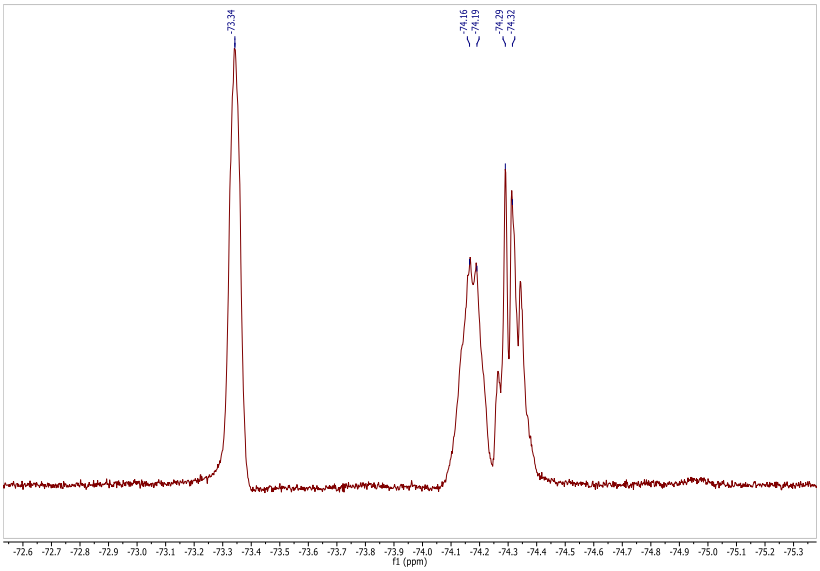

Figure S15. ^{19}F NMR of **7** in C_6D_6

NMR spectra of 8

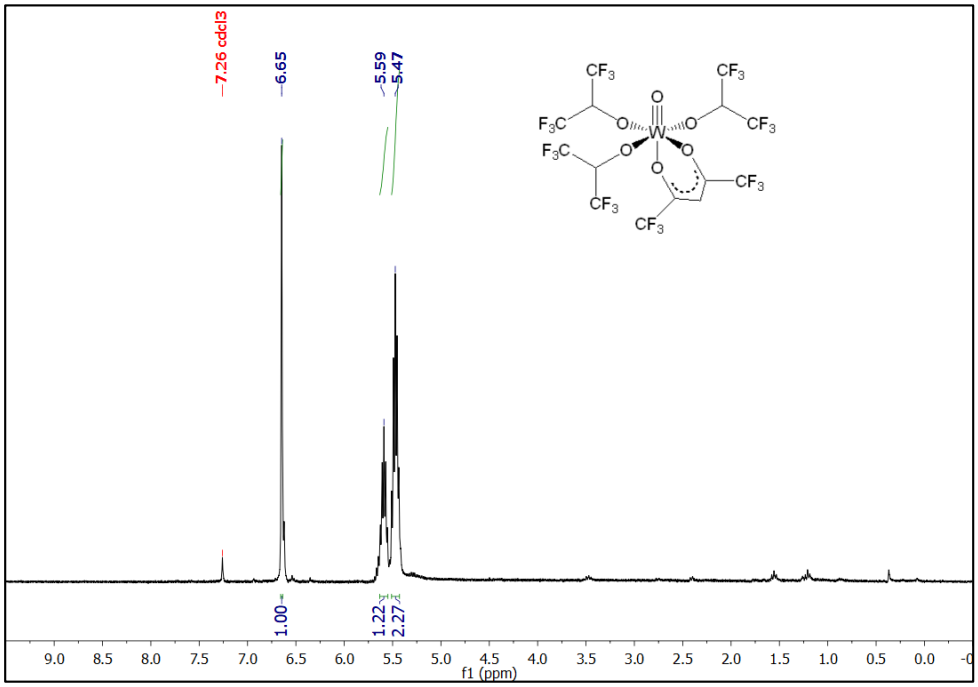

Figure S16. ^{1}H NMR of **8** in $CDCl_3$

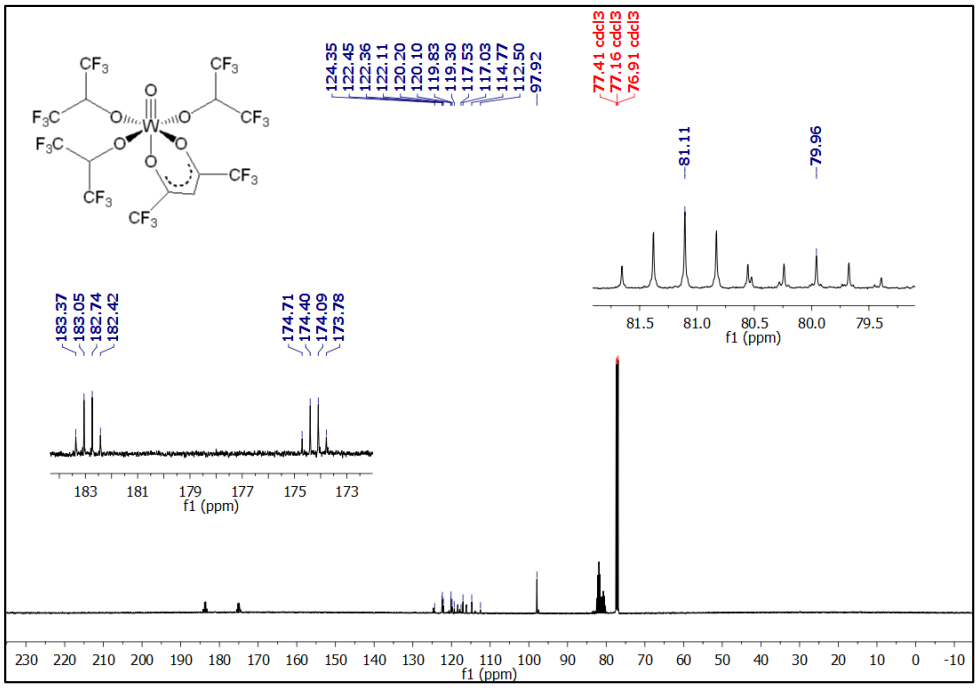

Figure S17. ^{13}C NMR of **8** in $CDCl_3$

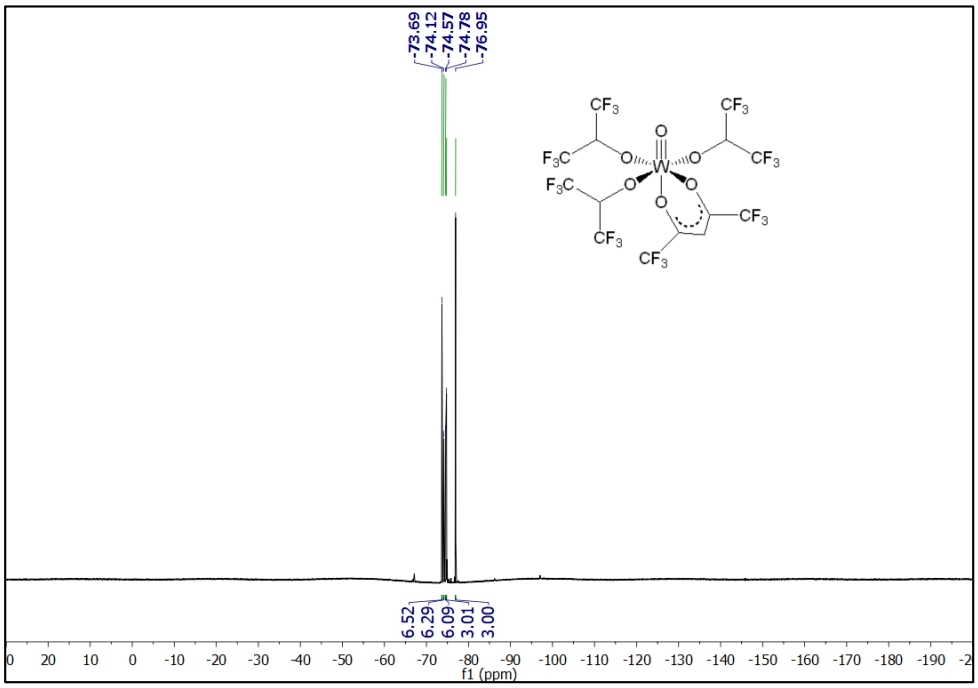

Figure S18. ^{19}F NMR of **8** in $CDCl_3$

NMR spectra of 9

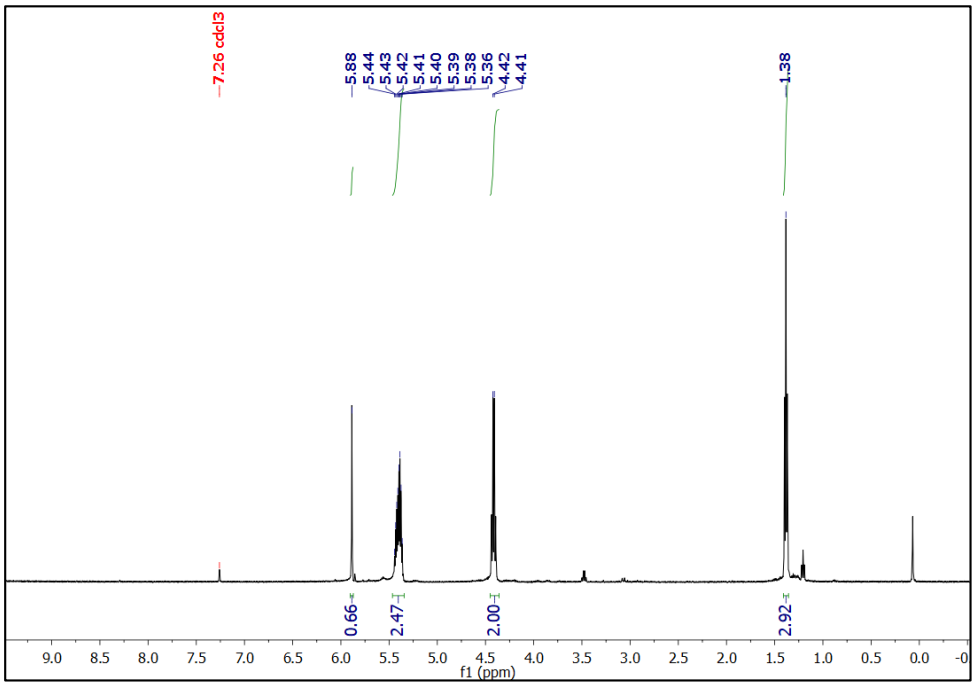

Figure S19. ^{1}H NMR of **9** in $CDCl_3$

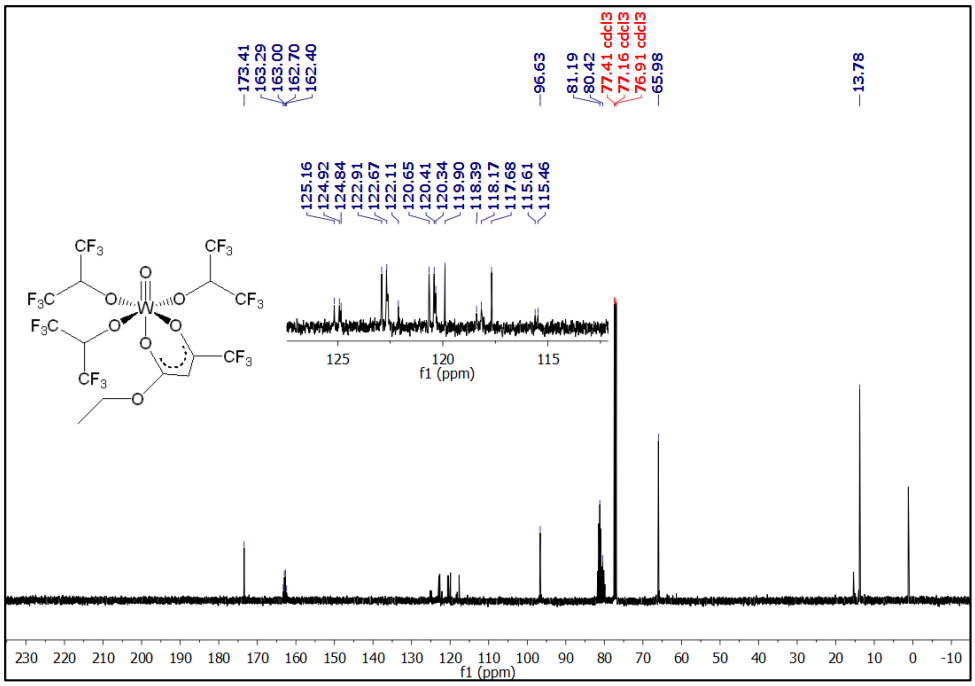

Figure S20. ^{13}C NMR of **9** in $CDCl_3$

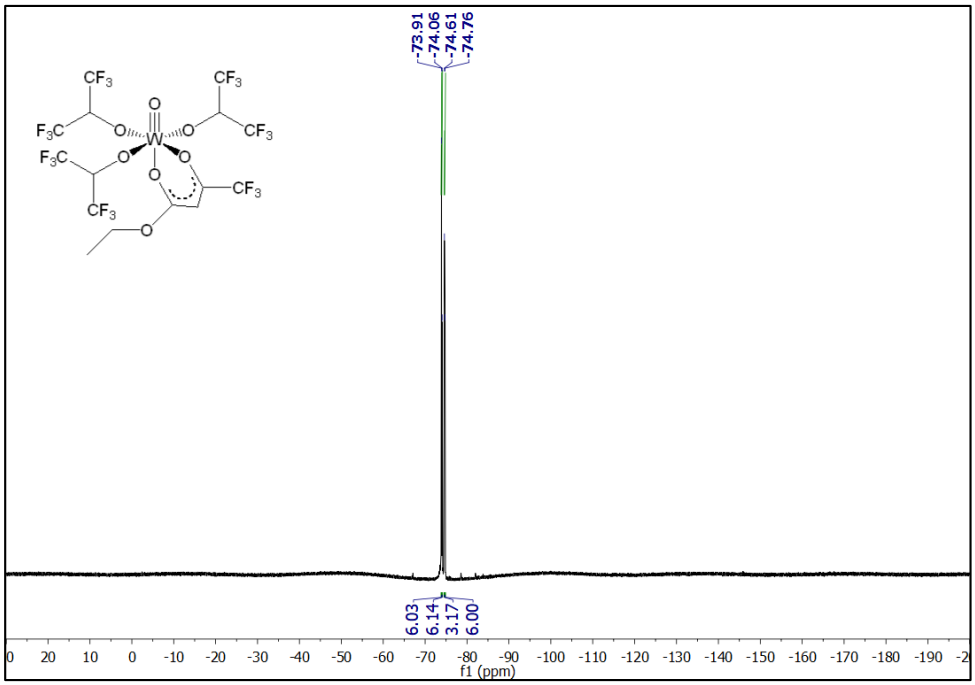

Figure S21. ^{19}F NMR of **9** in $CDCl_3$

NMR spectra of $WO(OCH(CF_3)_2)_4(Et_2O)$

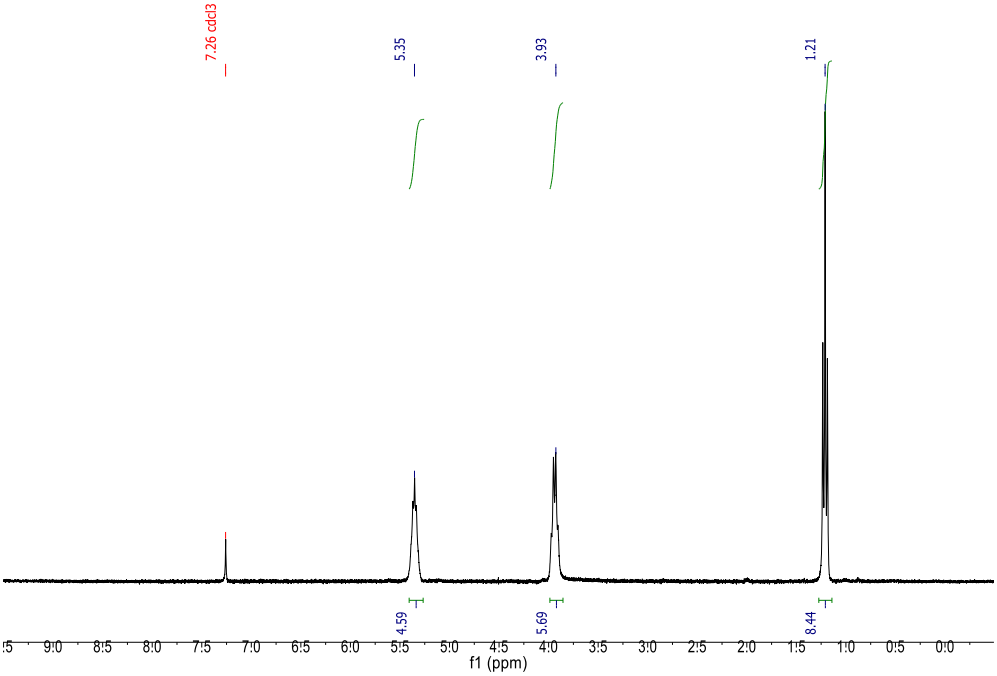

Figure S22. ^{1}H NMR of $WO(OCH(CF_3)_2)_4(Et_2O)$ in $CDCl_3$

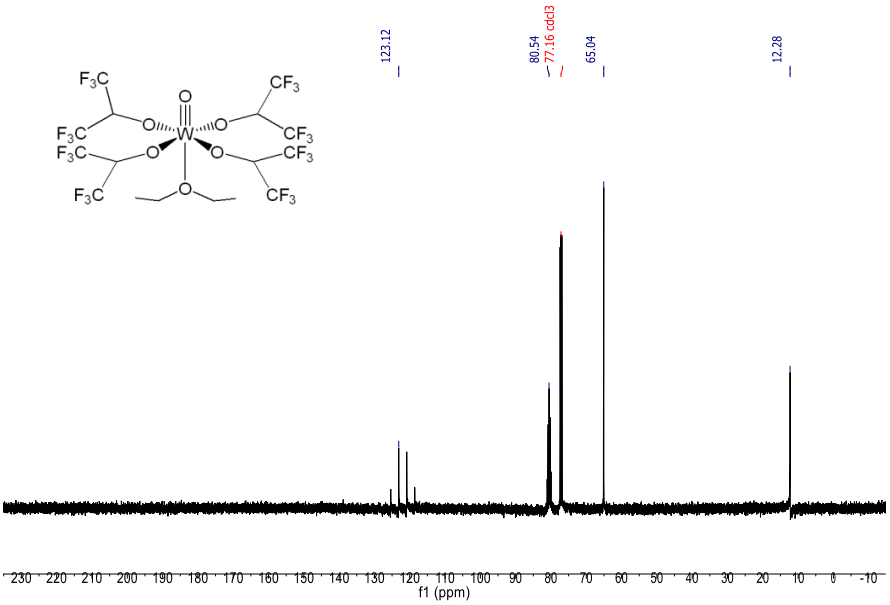

Figure S23. ^{13}C NMR of $WO(OCH(CF_3)_2)_4(Et_2O)$ in $CDCl_3$

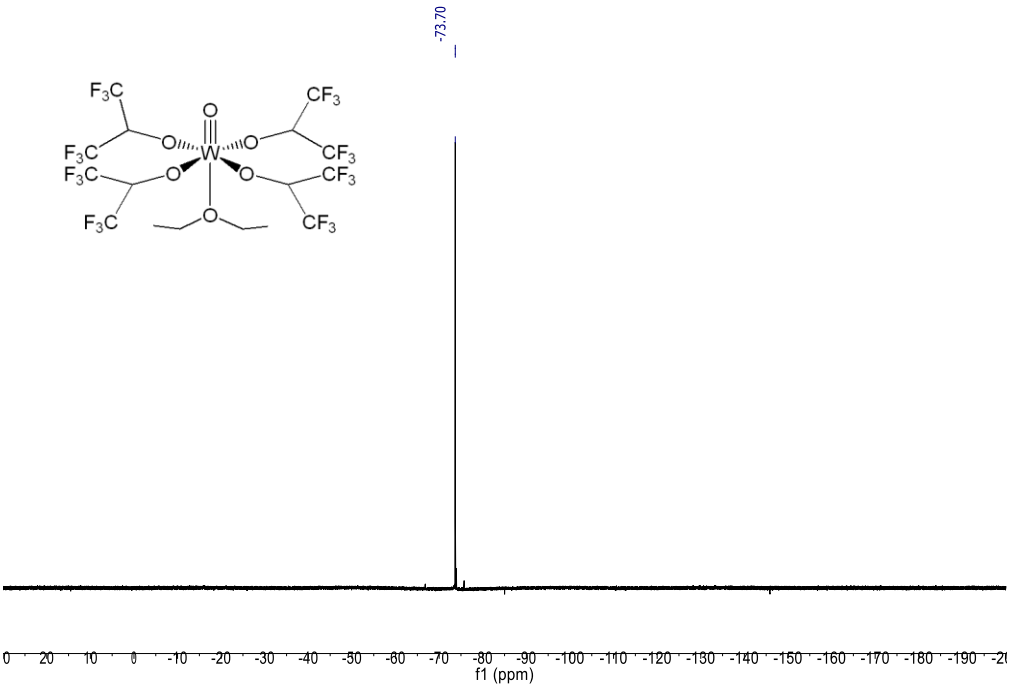

Figure S24. ^{19}F NMR of $WO(OCH(CF_3)_2)_4(Et_2O)$ in $CDCl_3$

NMR spectra of thermolysis products from 5

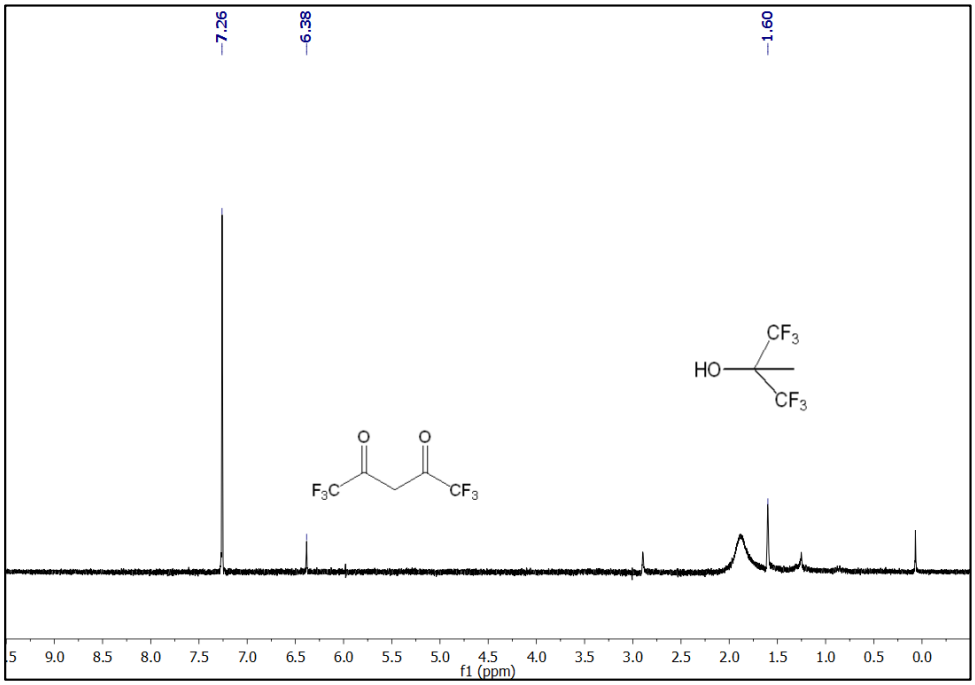

Figure S25. ^{1}H NMR of thermolysis products from **5** in $CDCl_3$

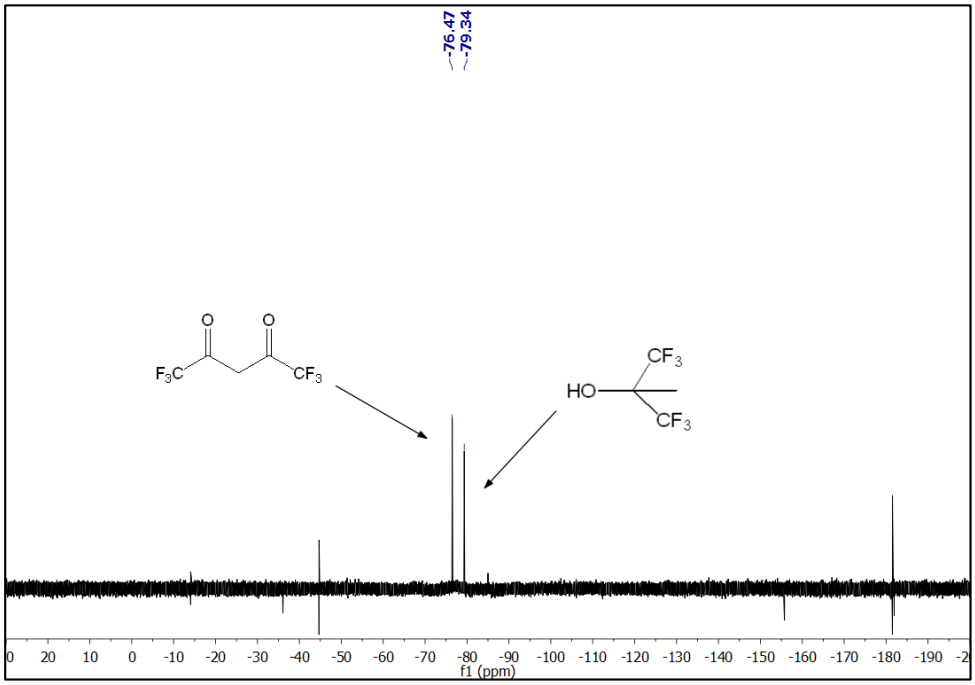

Figure S26. ^{19}F NMR of thermolysis products from **5** in $CDCl_3$

GC-MS Spectra of thermolysis products from 5

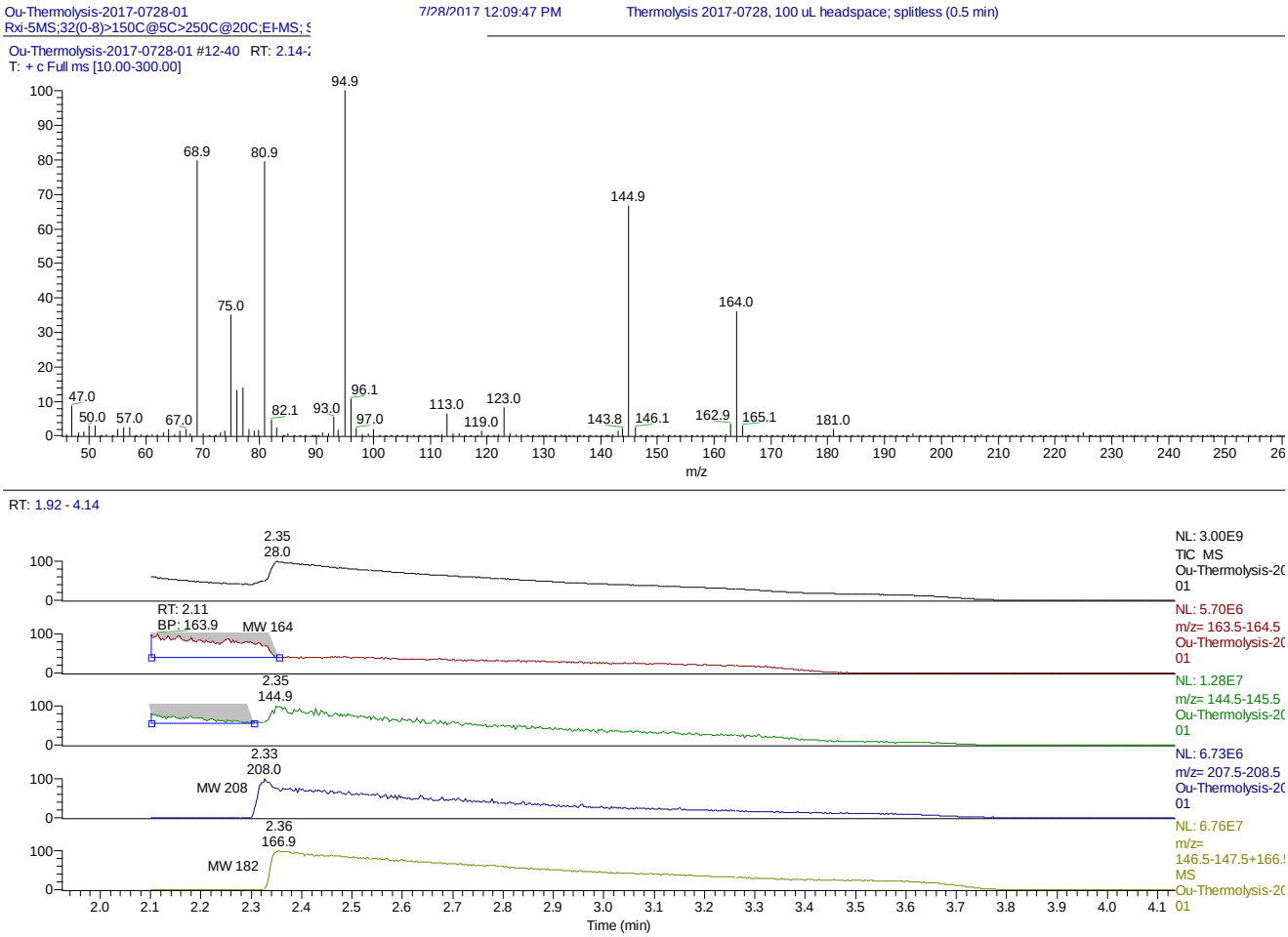

Figure S27. Mass spectra and chromatograms of thermolysis products from **5** showing patterns attributed to hexafluoroisobutene

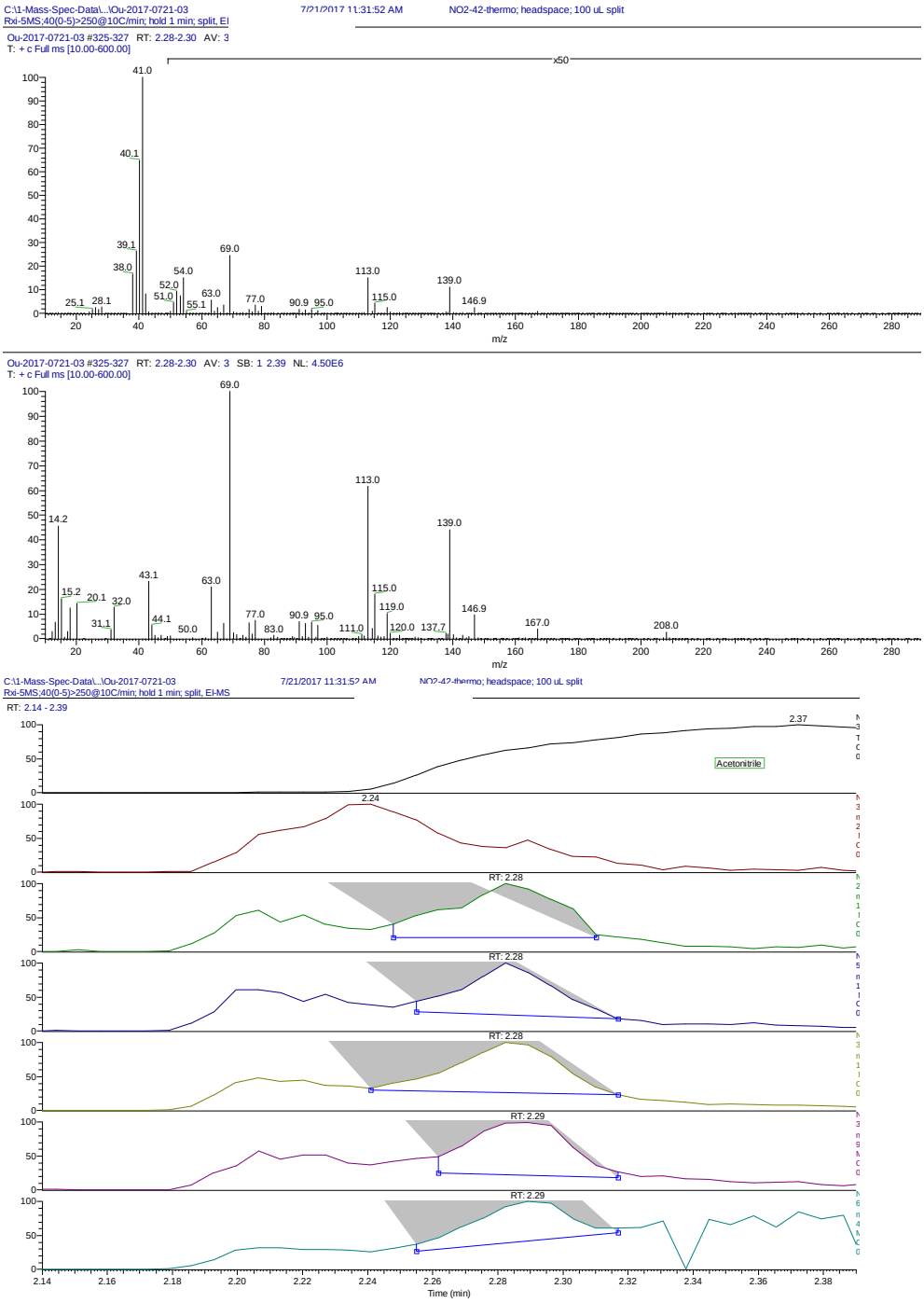

Figure S28. Mass spectrum and chromatograms of thermolysis products from **5** showing fragmentation patterns attributed to hexafluoroacetylacetone and hexafluoro-*tert*-butanol.

GC-MS Spectra of thermolysis products from 8

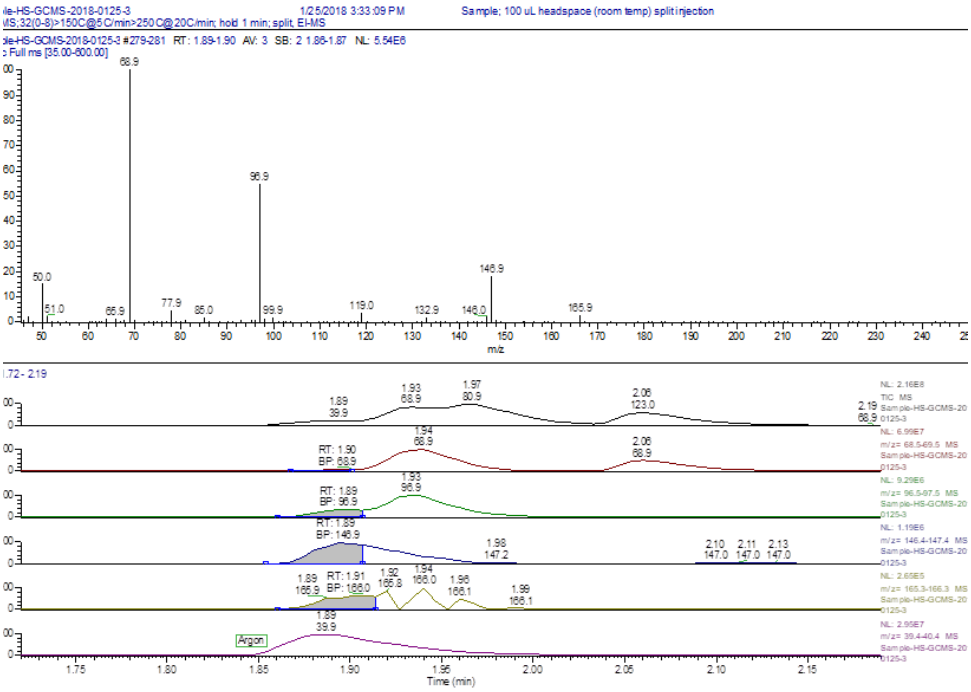

Figure S29. Mass spectra and chromatograms of thermolysis products from **8** showing patterns attributed to hexafluoroacetone

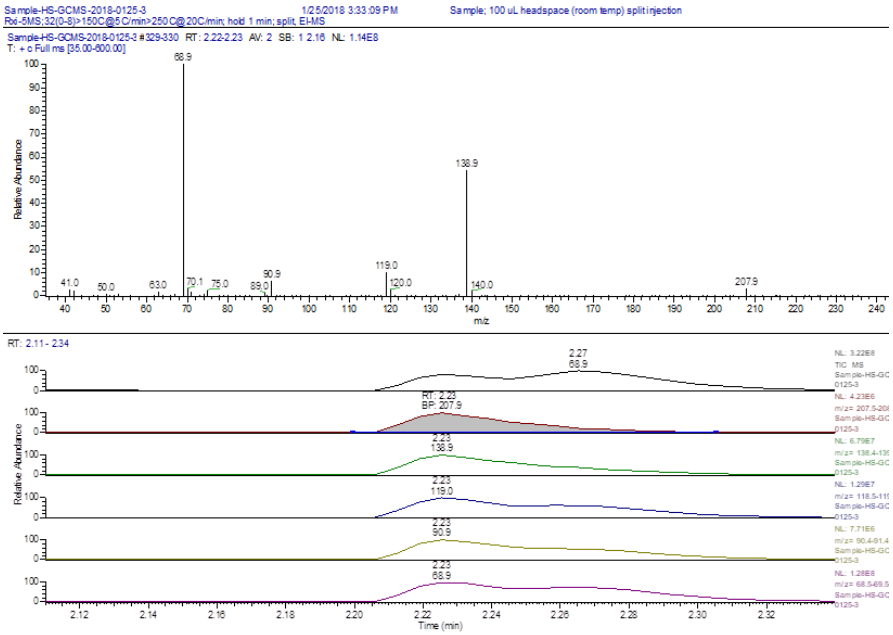

Figure S30. Mass spectrum and chromatograms of thermolysis products from **8** showing fragmentation patterns attributed to hexafluoroacetylacetone

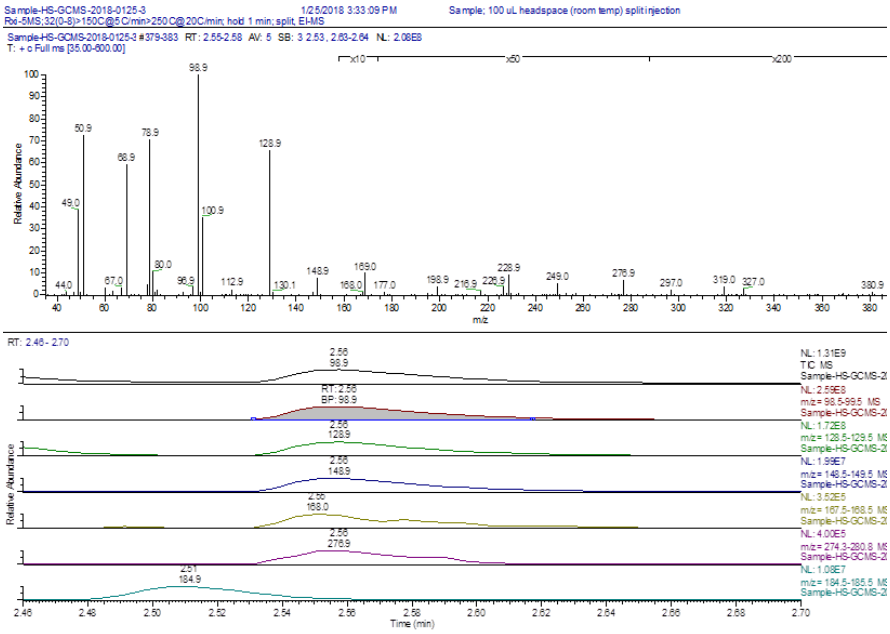

Figure S31. Mass spectrum and chromatograms of thermolysis products from **8** showing fragmentation patterns attributed to hexafluoroisopropanol

ESI MS/MS Spectra of 2-3, and 5-6

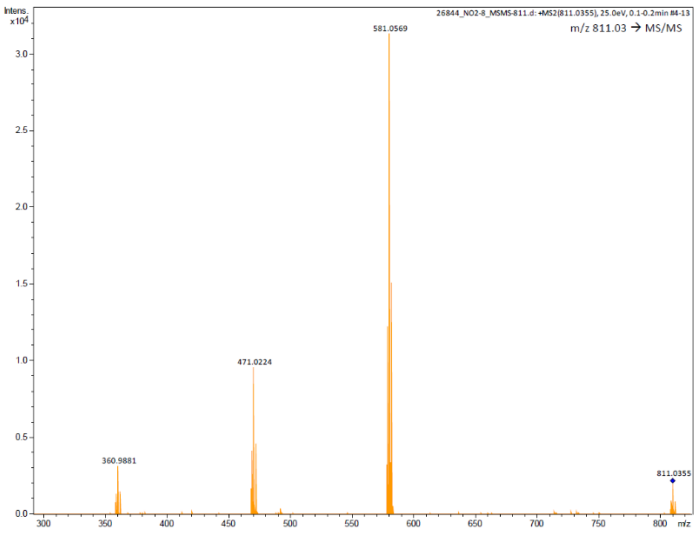

Figure S32. ESI MS/MS of **2**

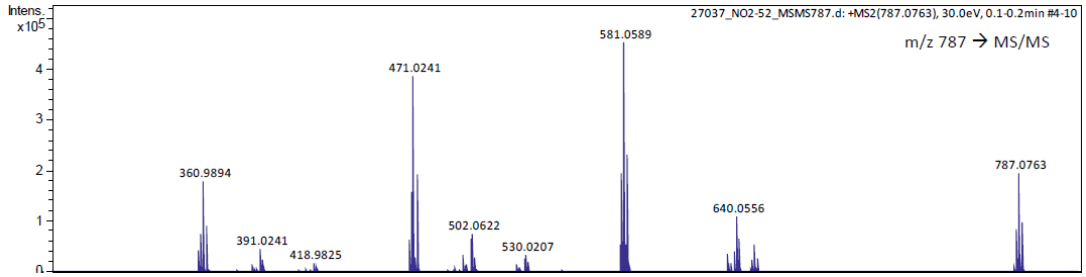

Figure S33. ESI MS/MS of **3**

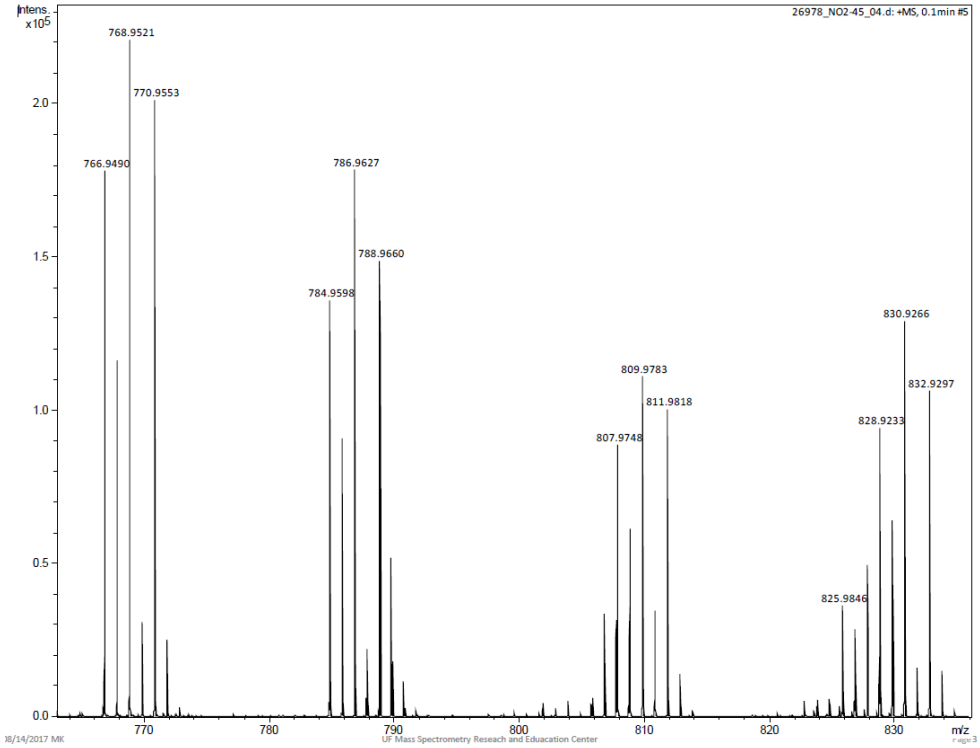

Figure S34. ESI MS/MS of **5**.

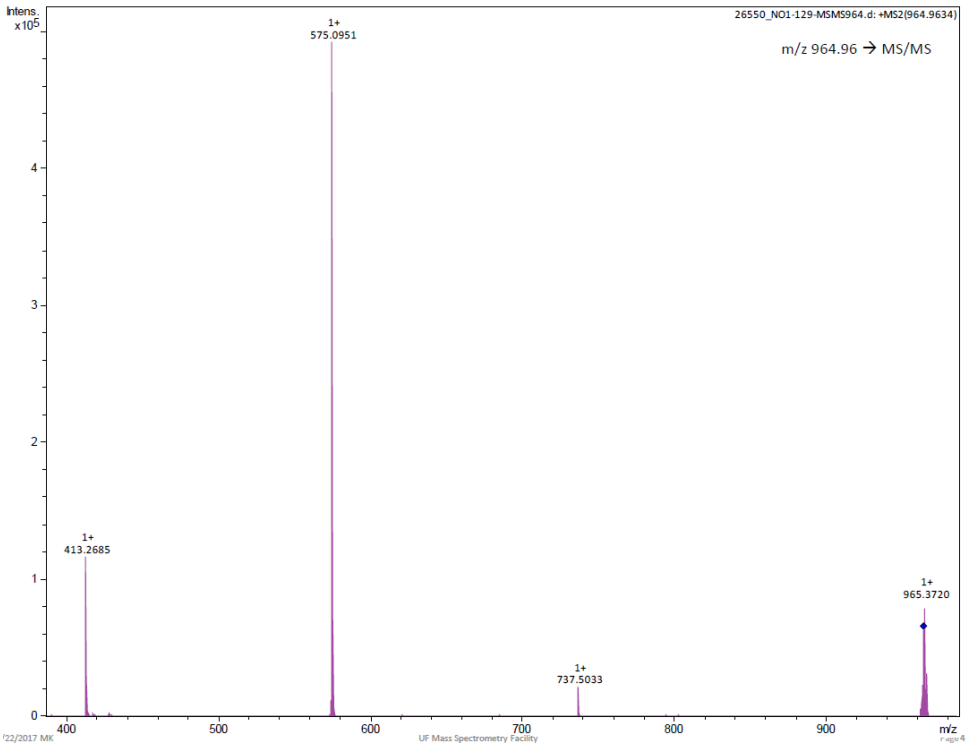

Figure S35. ESI MS/MS of **6**

XPS of WO_x deposition of $WO(OC(CF_3)_3CH_3)_3$(hfac)

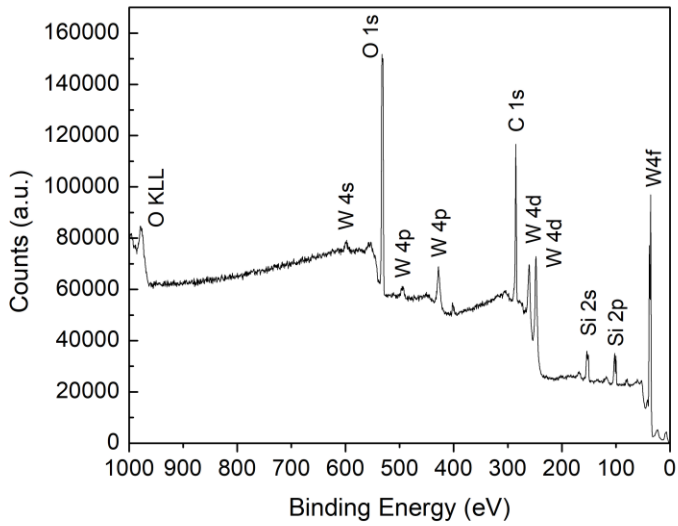

Figure S36. Survey of as-deposited film by AACVD grown from **5**

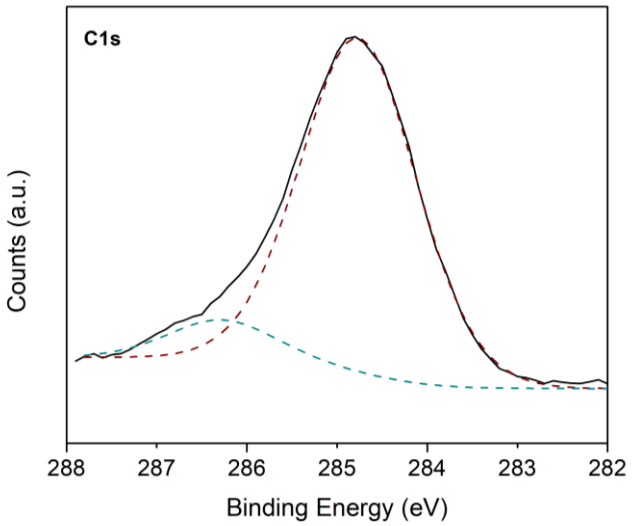

Figure S37. As-deposited C 1s of AACVD deposit grown at 500 °C from **5**

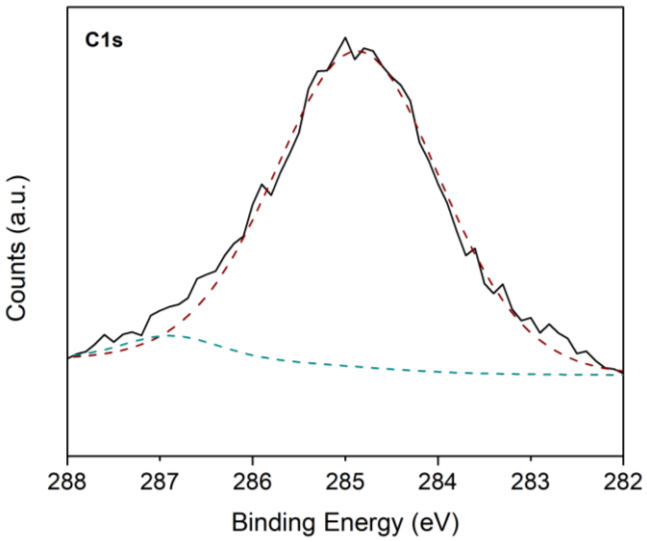

Figure S38. C 1s of AACVD deposit grown at 500 °C from **5** acquired after gentle sputtering (500 eV) the surface for 2 min

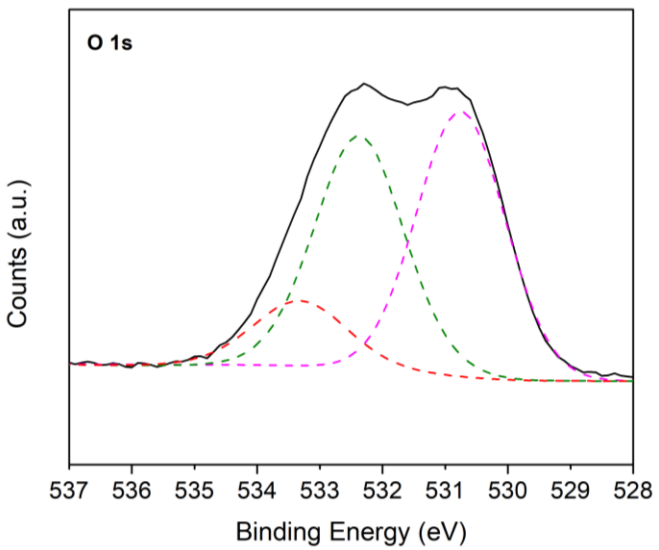

Figure S39. As-deposited O 1s high resolution spectrum of AACVD deposit grown at 500 °C from **5**. The peak located at 530.2 eV is from O^{2-} in WO_3 lattice, the peak located at 532.3 eV is from C-O-C and C-O-H oxygen atoms, while the one located at 533.5 eV is from H_2O

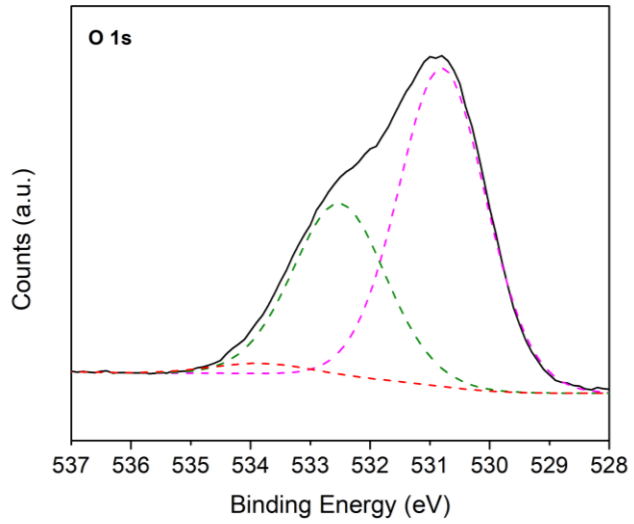

Figure S40. Sputtered O 1s of AACVD deposit grown at 500 °C from **5**. The O 1s core level peaks corresponding to H_2O and C-O-C or C-O-H strongly decreased in intensity (surface contaminants) while that corresponding to WO_3 increased.

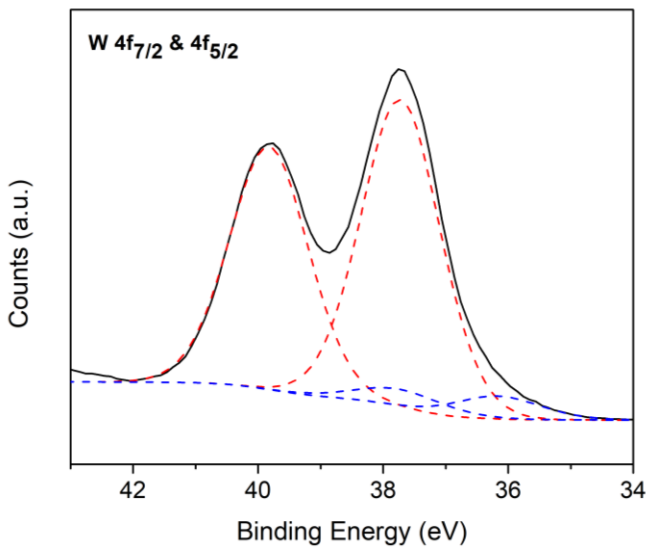

Figure S41. As-deposited W 4f of AACVD deposit grown at 500 °C from **5**. The deconvolution process identified mostly WO_3 and a small fraction (around 5%) of WO_{3-x}.

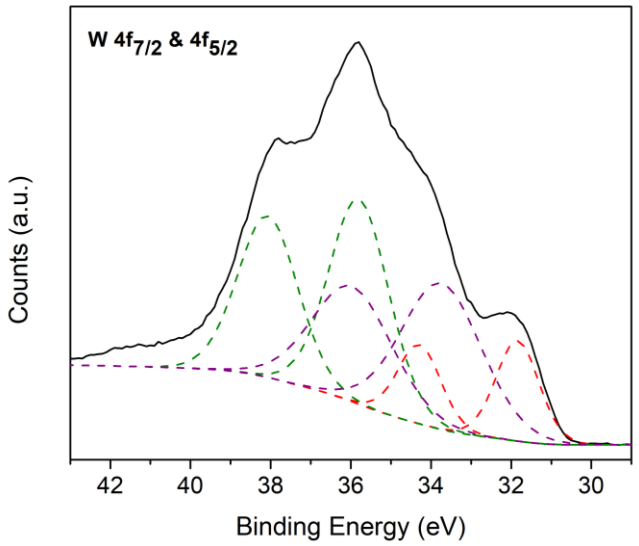

Figure S42. Sputtered W 4f of AACVD deposit grown at 500 °C from **5**. After sputtering, the deconvolution process for the W 4f core level peak identified the presence of three peaks: WO_3 (35.8 eV), WO_x (33.8 eV) and metallic W (31.8 eV).

Rutherford Backscattering of WO_x deposition of $WO(OC(CF_3)_3CH_3)_3$(hfac)

Sample	Beam spot position	Characterization			
		Layers	Thickness (Å)	Composition	
CVD, 500 °C	First point	1	2350	W 1.000	O 3.000
		*2	100000	Si 1.000	
	Second point	1	2300	W 1.000	O 3.000
		*2	100000	Si 1.000	

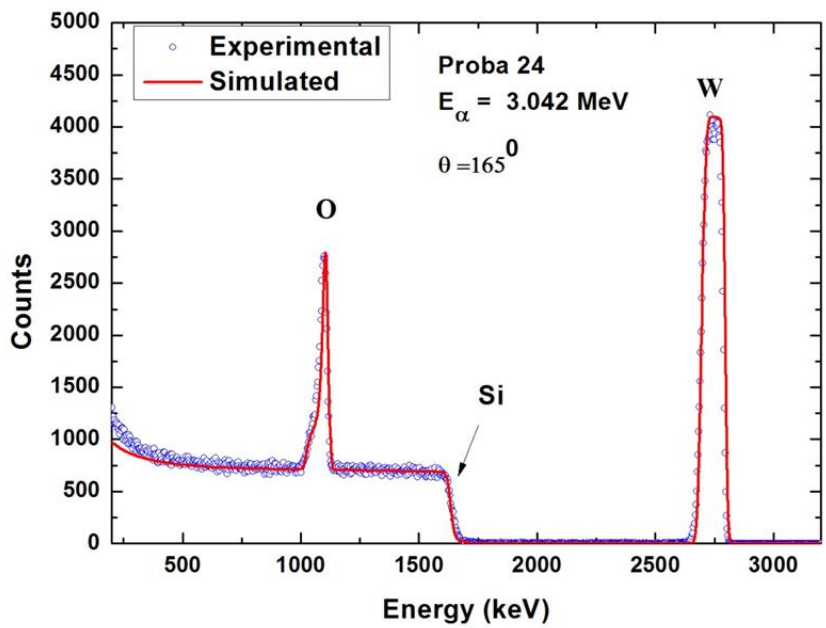

Figure S43. RBS spectrum obtained from CVD deposit grown at 500 °C from **5**. The Rutherford scattering cross-section is proportional to the square of the nuclear charge of the target nucleus. Therefore, the scattering peaks from light elements such as C, N and O are superimposed on a relatively high background due to backscattering from heavy elements in the sample. In recent years, high energy $_1$H and $_4$He backscattering has been utilized to overcome this difficulty and to quantify the stoichiometry or to profile the light elements in the heavy bulk samples. In the high energy backscattering experiments, $_1$H and $_4$He ions of *3–9 MeV* (or even more) are used as incident projectiles. The elastic scattering cross section for light elements becomes a nuclear rather than a Rutherford interaction, called non–Rutherford backscattering or nuclear resonance elastic scattering. The non–Rutherford backscattering can be used to enhance the sensitivity for light elements. For example, at $_4$He energy of *3.042 MeV* the elastic backscattering cross section for O is 25 times larger than that corresponding to Rutherford cross sections. An example of this type of non-Rutherford scattering is presented in Fig. S43 for a thin WO_3 film deposited on a Si substrate.

Particle size distribution histograms of WO_x deposits by AACVD and CVD

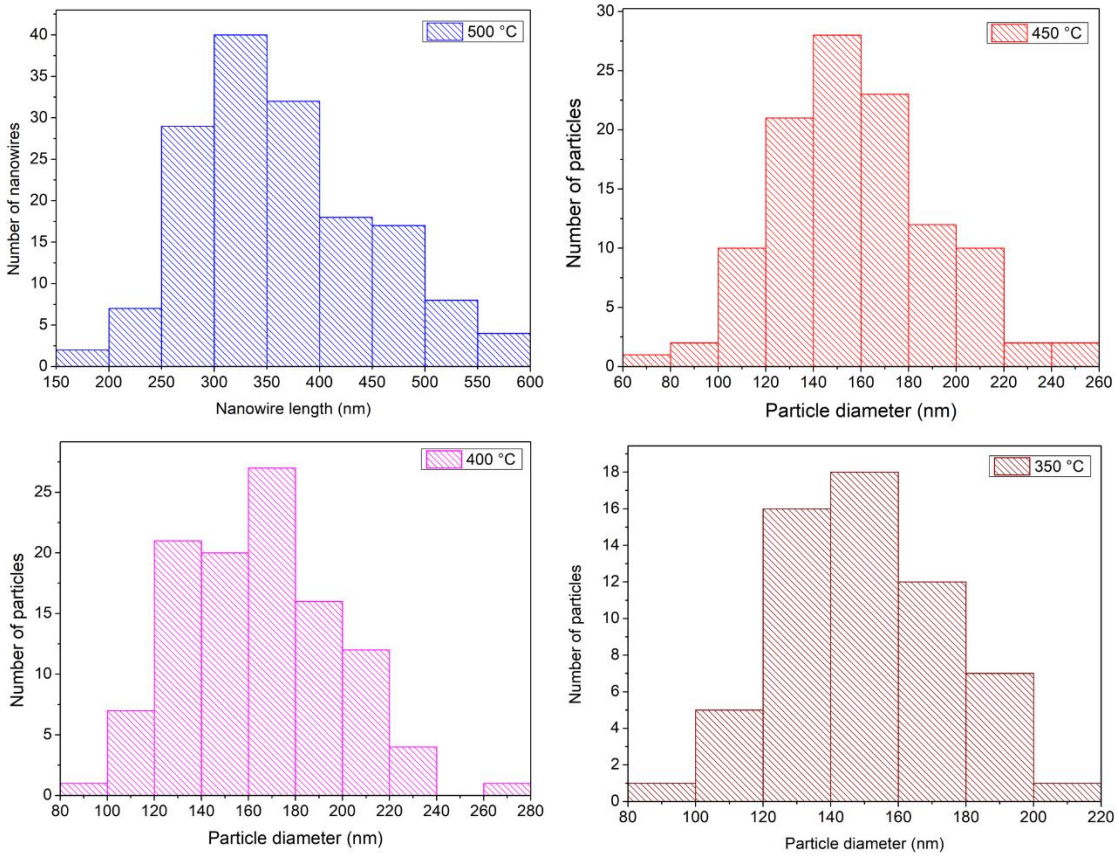

Figure S44. Particle size distribution histograms for AACVD deposits

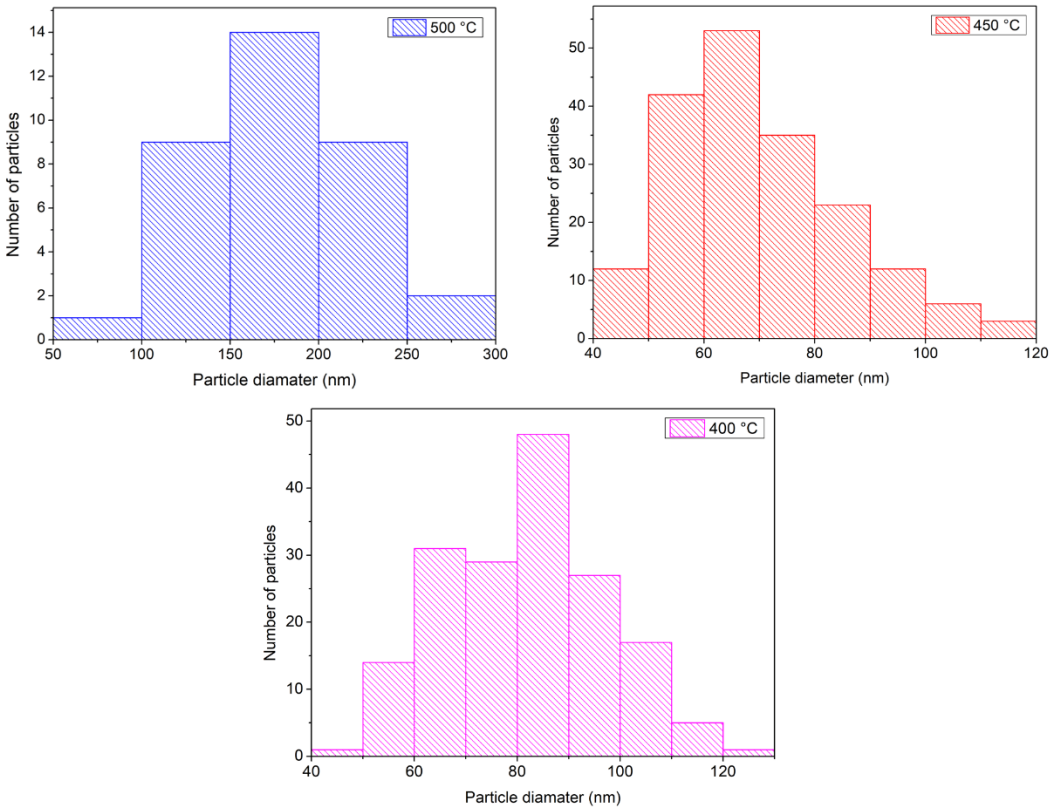

Figure S45. Particle size distribution histograms for CVD deposits