Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Chemical Vapor Deposition of Ruthenium-based Layers by the Single-Source Approach

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Supporting Information

Contents

Crystallographic Data

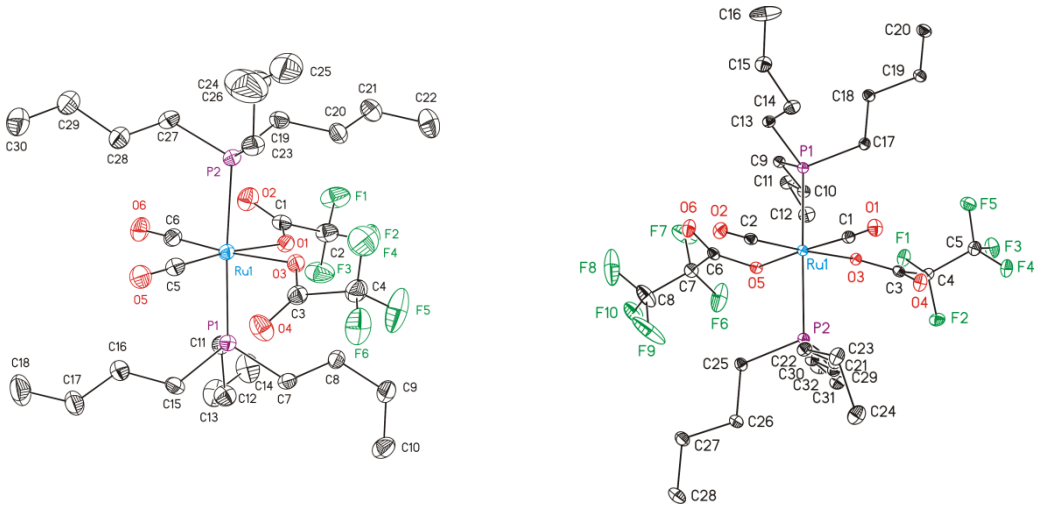


Figure S1. ORTEP diagram (30 % probability level) of the molecular structures of **4f** (left) and **4g** (right) with the atom numbering scheme. All hydrogen and disordered atoms have been omitted for clarity.

Selected Bond Lengths and Angles

Table S2. Selected bond distances (Å) and angles (°) for complexes **4b**,**c** and **4e**–**g**.

	4b	**4c**	**4e**	**4f**	**4g**
Ru–O	2.1018(14)	2.1010(13)	2.100(2)	2.1046(17)	2.1099(15)
		2.1037(12)		2.0937(17)	2.1074(15)
Ru–C	1.873(2)	1.866(2)	1.892(3)	1.866(3)	1.877(2)
		1.873(2)		1.862(3)	1.869(2)
Ru–P	2.3906(5)	2.3856(5)	2.3844(8)	2.4063(7)	2.4102(6)
		2.3910(5)		2.4096(7)	2.3993(6)
C≡O	1.143(3)	1.144(2)	1.134(4)	1.140(3)	1.143(3)
		1.141(2)		1.141(3)	1.144(3)
C–O	1.230(3)	1.230(2)	1.221(4)	1.268(3)	1.224(3)
	1.291(3)	1.280(2)	1.294(4)	1.214(3)	1.267(3)
		1.231(2)		1.204(3)	1.220(3)
		1.290(2)		1.274(3)	1.269(3)
P–Ru–P	173.03(3)	173.041(18)	173.04(4)	176.23(3)	171.11(2)
P–Ru–C	92.93(7)	92.70(6)	92.44(9)	91.68(9)	93.57(7)
	92.05(7)	92.90(6)	92.60(9)	91.27(9)	93.86(7)
		92.87(6)		91.07(9)	92.58(7)
		91.48(6)		91.31(9)	92.82(7)
P–Ru–O	84.58(4)	90.20(4)	85.20(6)	91.99(5)	89.16(4)
	90.17(4)	84.70(4)	89.44(6)	84.46(5)	84.00(4)
		85.23(4)		85.23(5)	83.95(4)
		89.57(4)		92.55(5)	89.66(4)
C–Ru–C	88.83(13)	87.65(8)	87.13(19)	89.94(13)	87.34(9)
O–Ru–O	82.27(8)	83.55(5)	79.27(11)	80.24(7)	83.75(6)
C–Ru–O	175.90(7)	176.19(7)	175.53(10)	174.50(10)	176.28(8)
	94.50(8)	94.44(7)	96.84(12)	94.40(10)	94.64(8)
		176.70(7)		173.25(10)	177.09(8)
		94.51(7)		95.67(10)	94.40(8)
Ru–C–O	175.11(19)	173.12(18)	174.8(3)	178.0(3)	175.0(2)
		174.12(17)		177.2(3)	174.9(2)

TG Studies

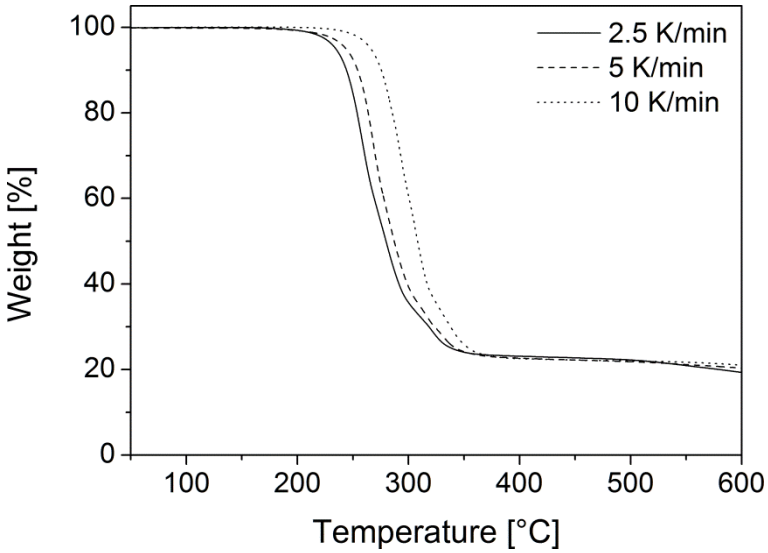
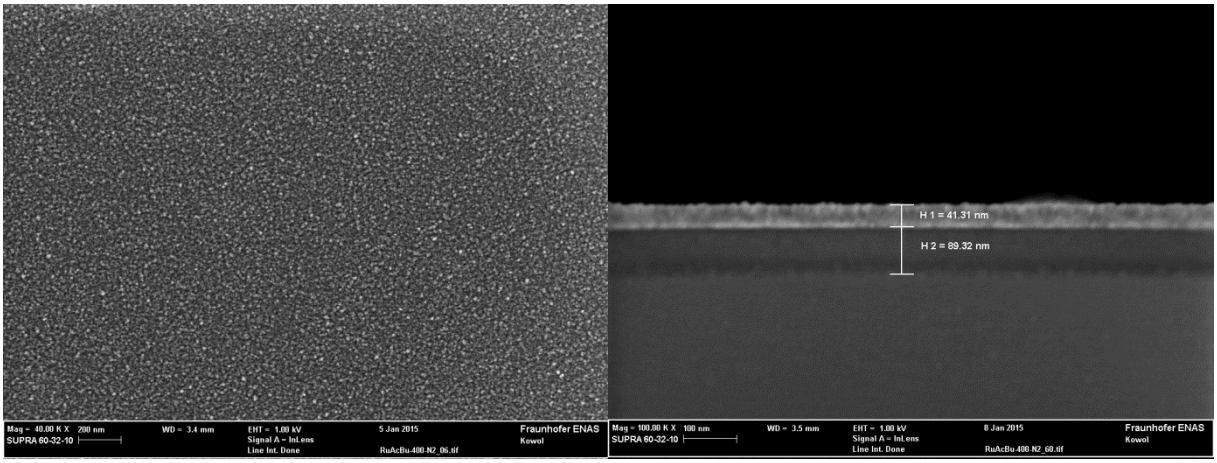


Figure S3. TG traces of **4e** at varying heating rates; gas flow N_2 60 mL·min^{-1}.

SEM Images

Layer A



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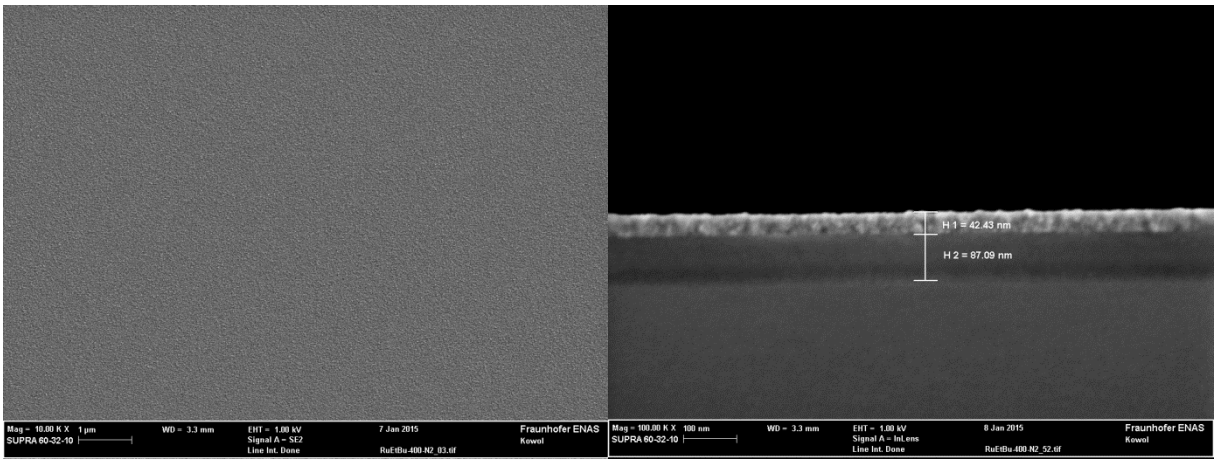

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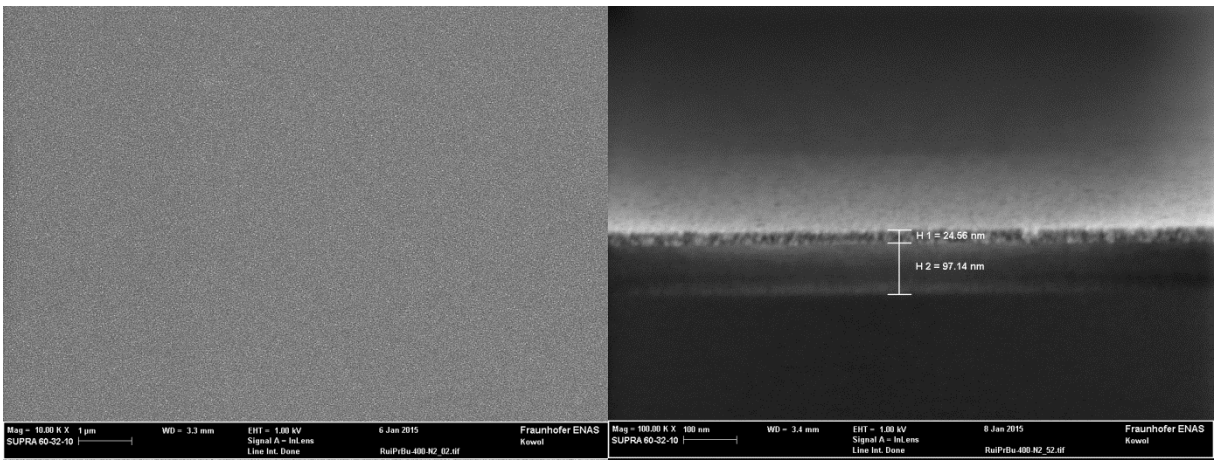

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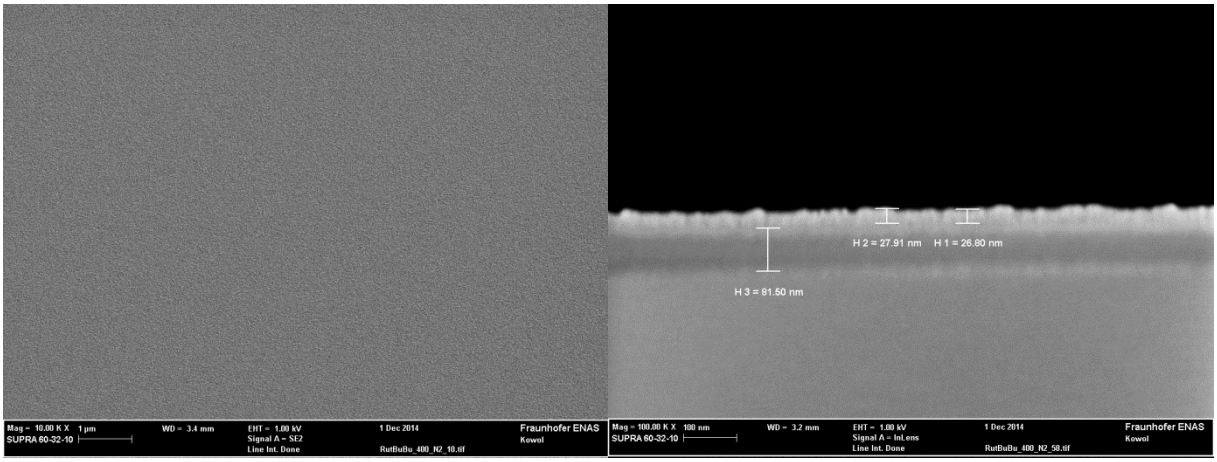
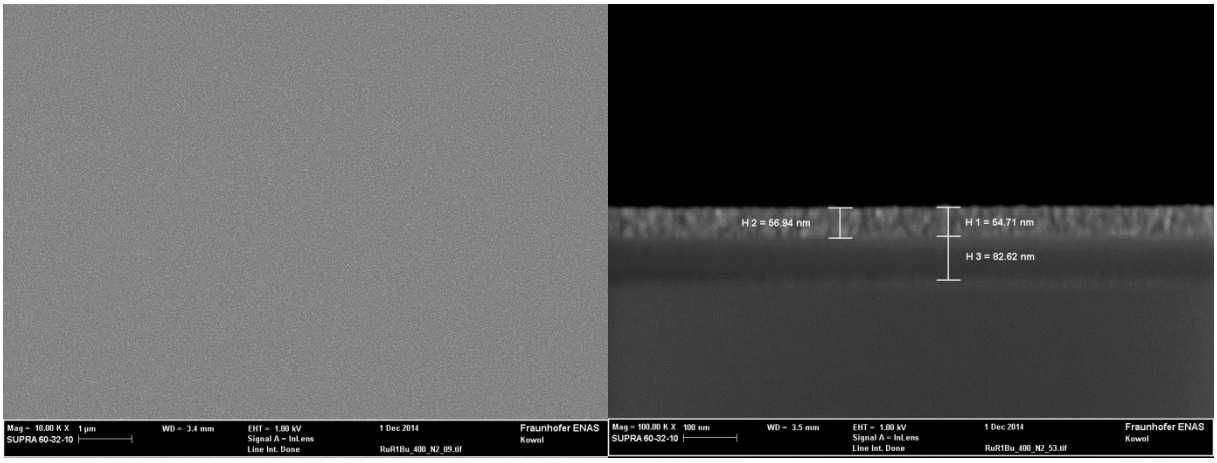


Layer E



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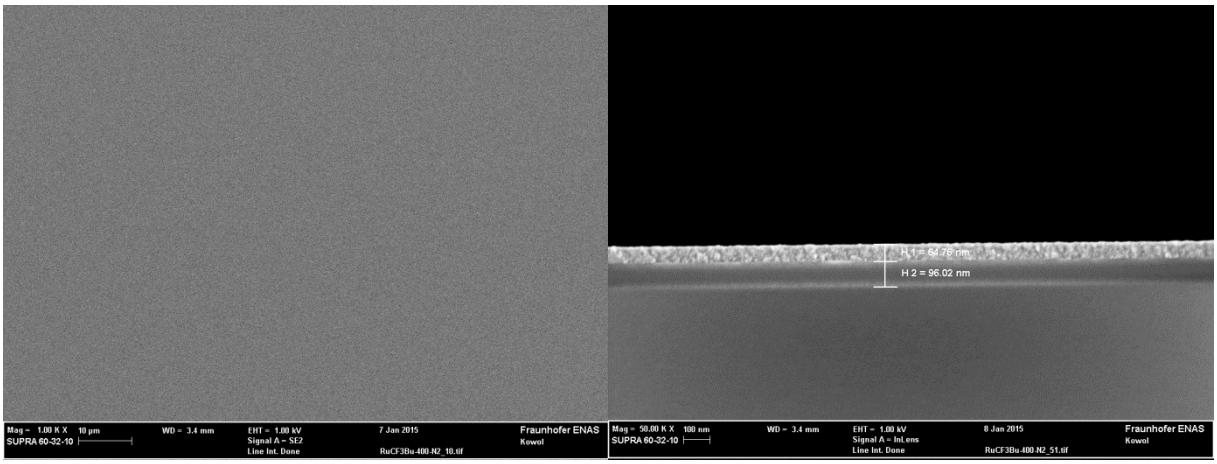

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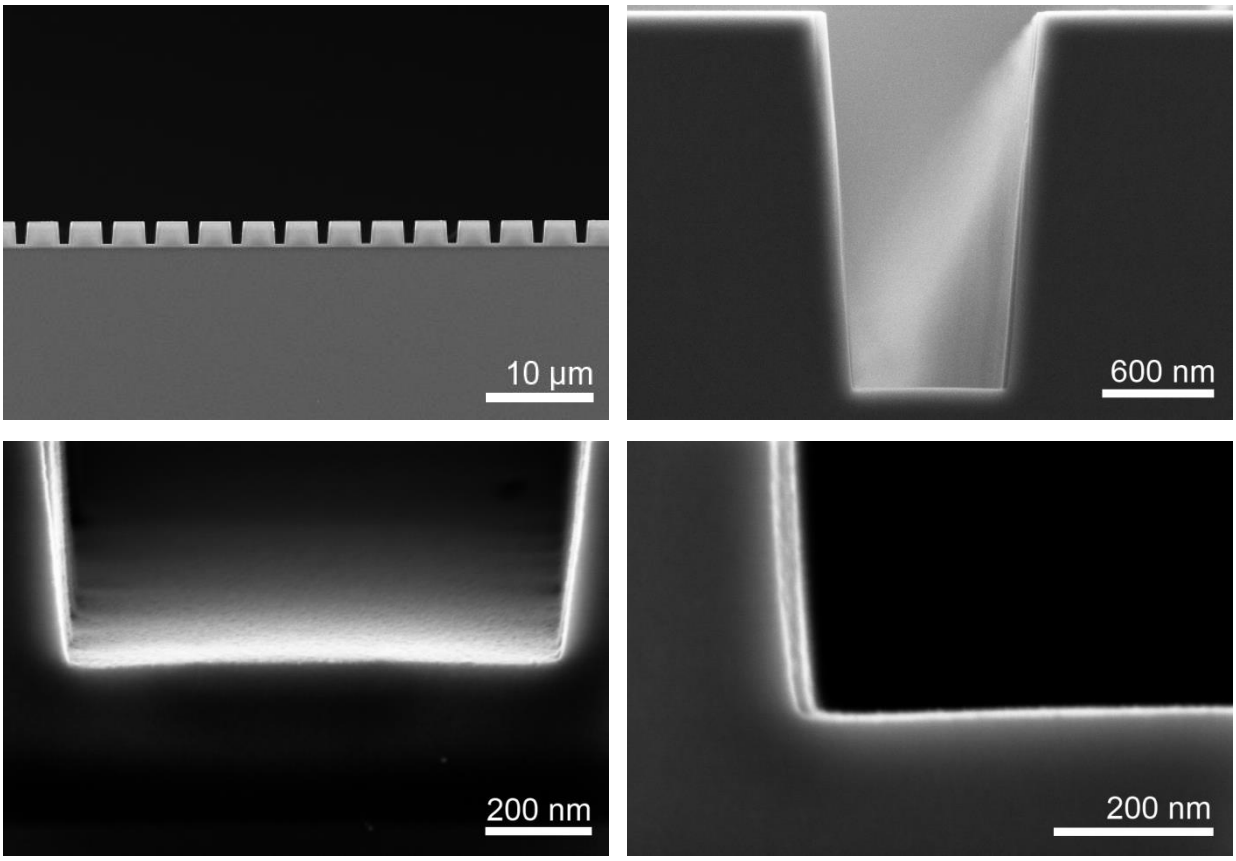


EDX Spectra

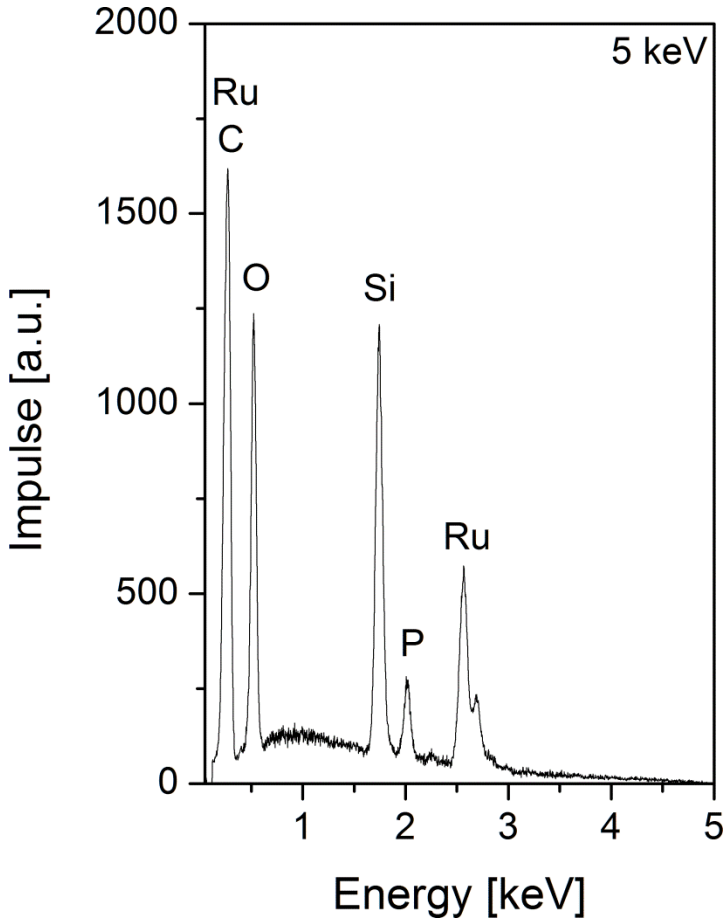


Figure S4. Representative EDX spectra obtained from layer E (Table 2) showing the characteristic pattern of ruthenium and the presence of phosphorus, silicon, oxygen and carbon.

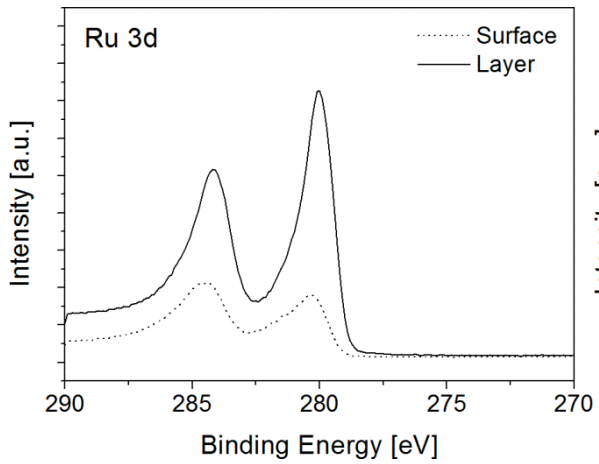
XPS Data

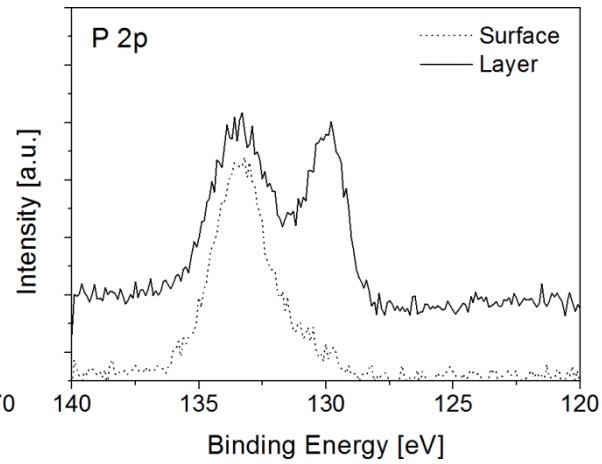
Table S5. Applied parameters for the peak deconvolution in XPS analyses.

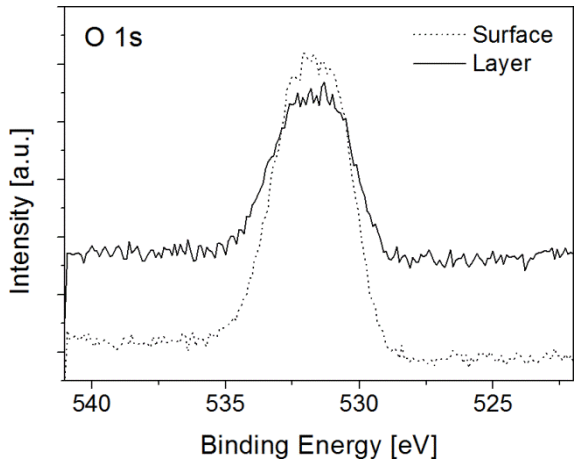
Peak	Ru 3d 5/2	Ru 3d 3/2	RuO_2 3d 5/2	RuO_2 3d 3/2	C 1s
Line shape	Gaussian-Lorentzian, GL(25) + exponential tail				GL(25)
Pos. [eV]	280.5-279.5	Ru 3d 5/2 + 4.2	282.0-280.6	RuO_2 3d 5/2 + 4.2	285.5 – 284.5

XPS detail spectra

Layer A







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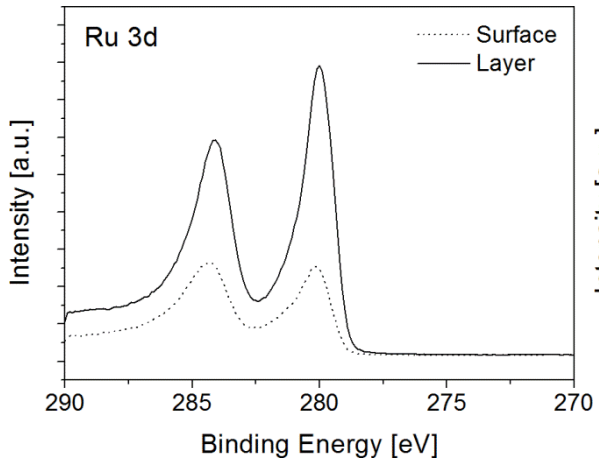

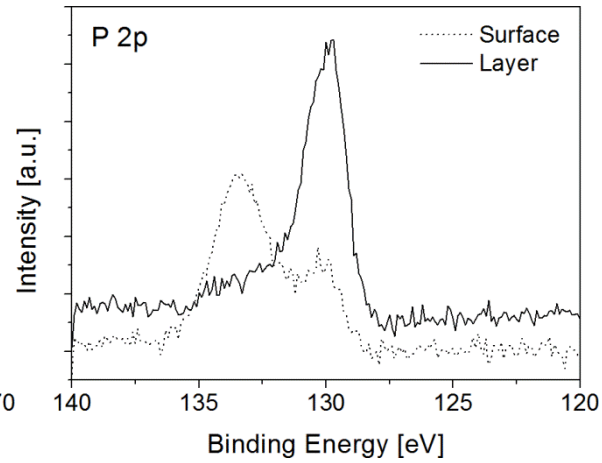

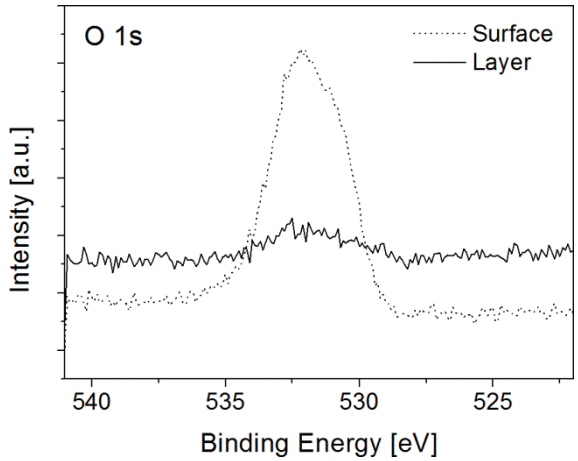

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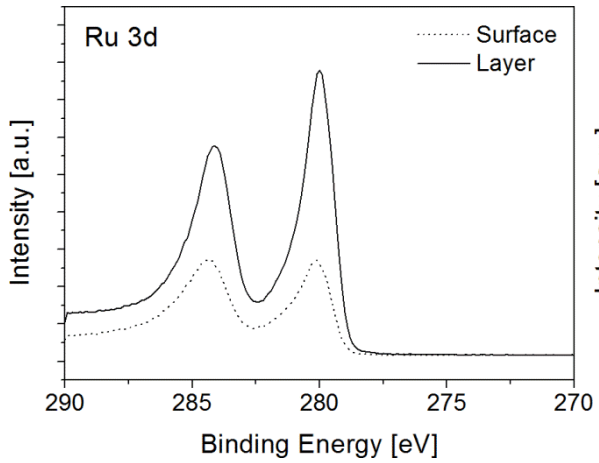
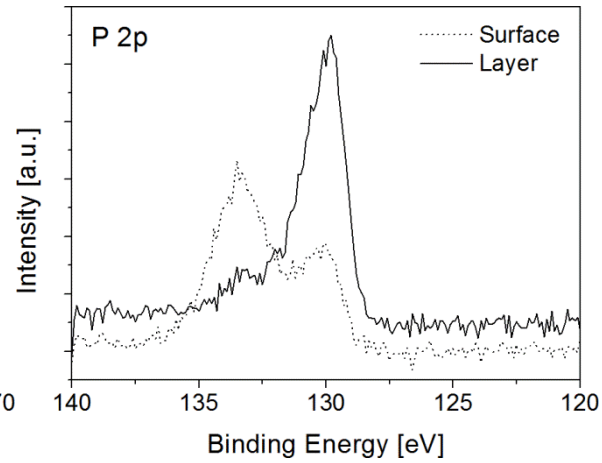
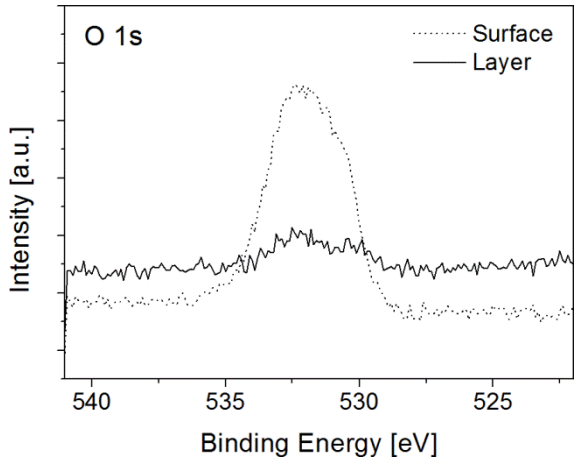
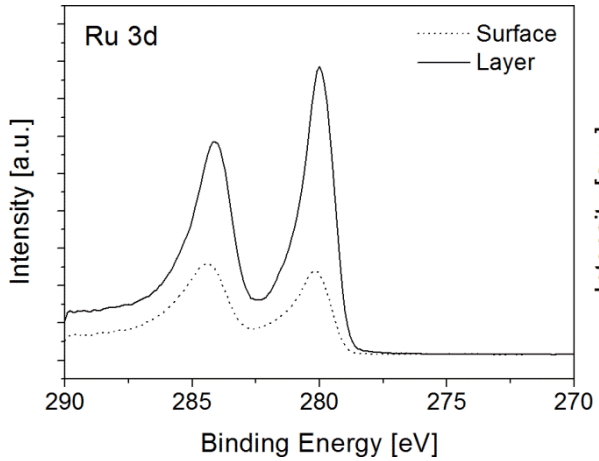





O 1s
Surface
Layer
Intensity [a.u.]
540
535
530
525
Binding Energy [eV]

Layer D


Ru 3d
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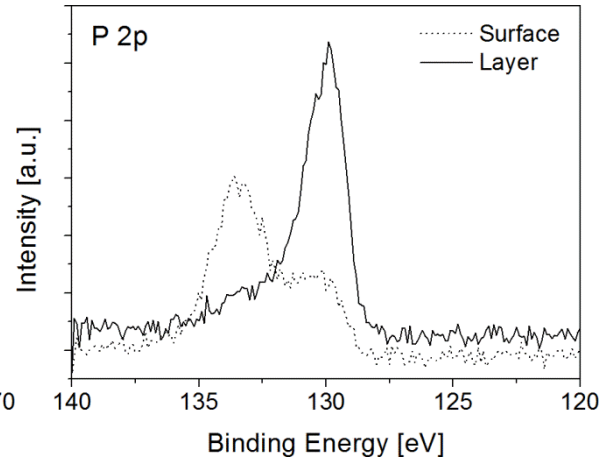
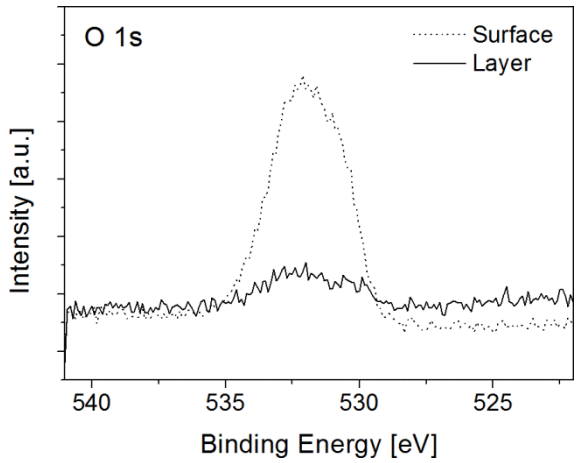
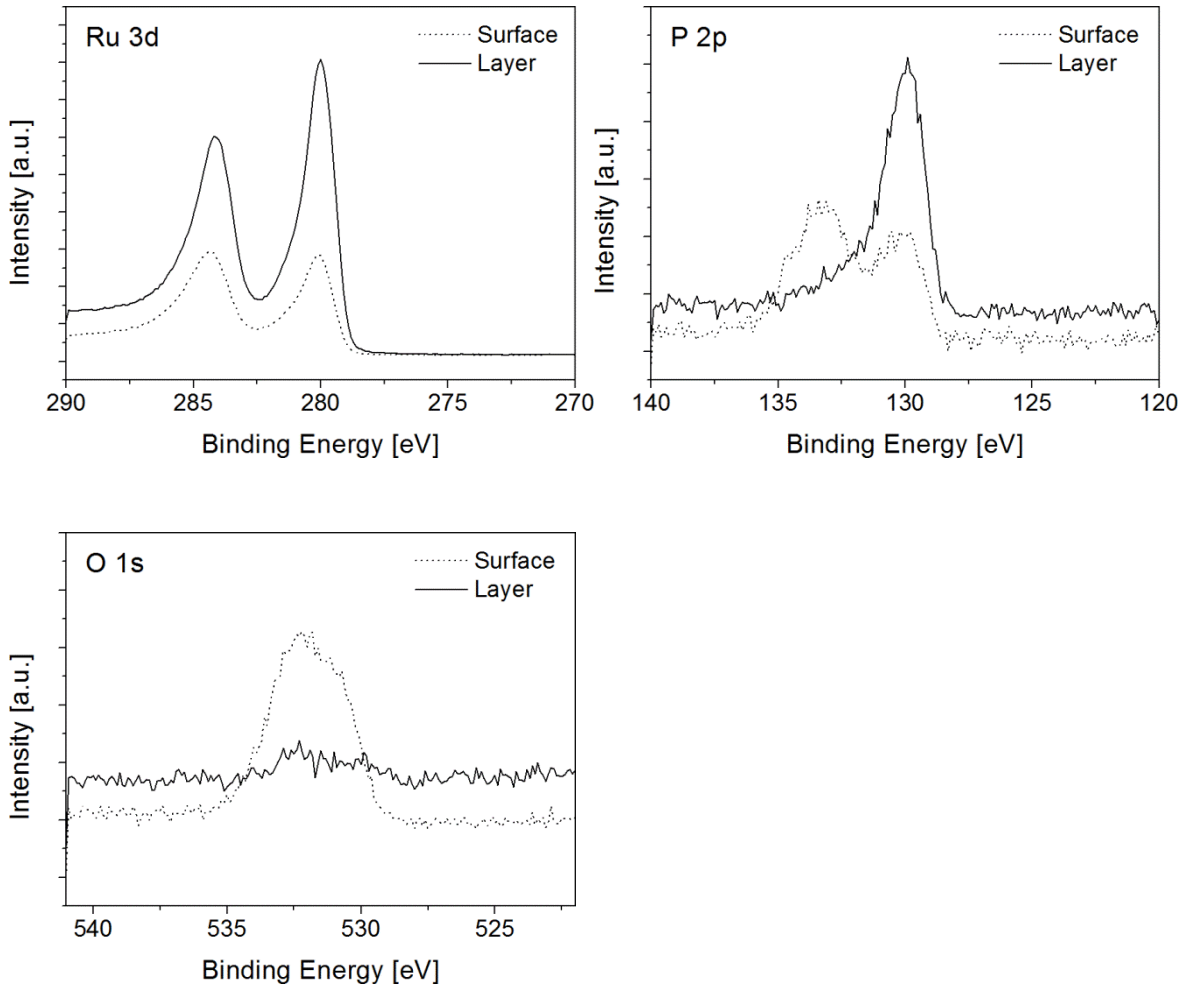
Layer
Intensity [a.u.]
290
285
280
275
270
Binding Energy [eV]


P 2p
Surface
Layer
Intensity [a.u.]
140
135
130
125
120
Binding Energy [eV]


O 1s
Surface
Layer
Intensity [a.u.]
540
535
530
525
Binding Energy [eV]

Layer F


Ru 3d
Surface
Layer
Intensity [a.u.]
290
285
280
275
270
Binding Energy [eV]
P 2p
Surface
Layer
Intensity [a.u.]
140
135
130
125
120
Binding Energy [eV]
O 1s
Surface
Layer
Intensity [a.u.]
540
535
530
525
Binding Energy [eV]

XRPD

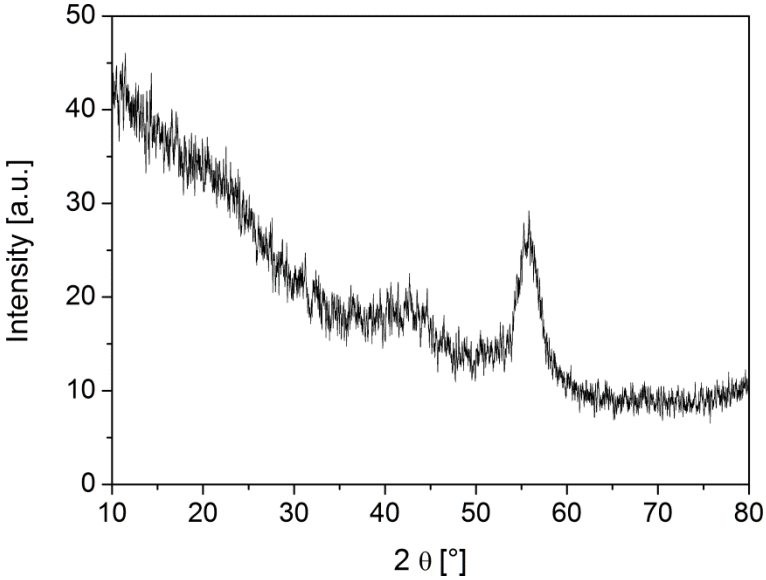
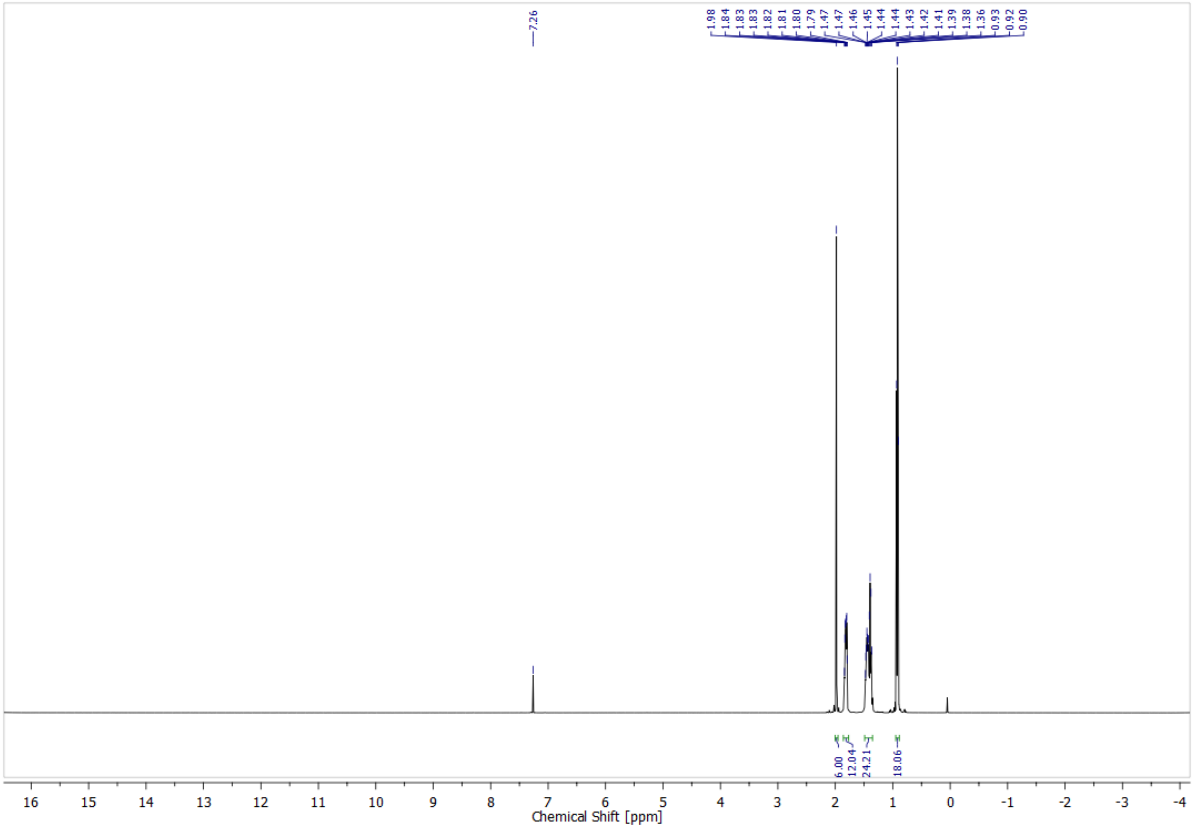
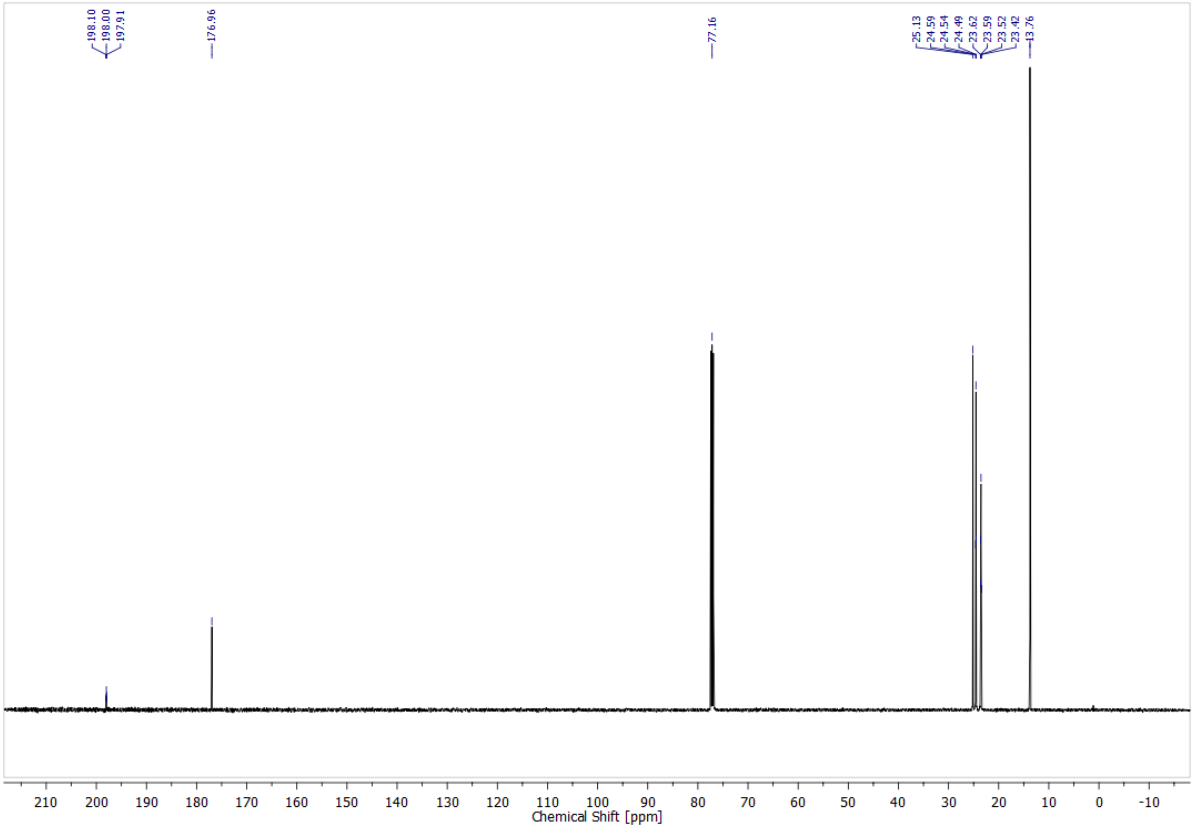


Figure S6. Representative diffractogram of layer E (Table 2) measured under grazing incidence. The diffractogram was recorded using Cu-$K_{\alpha 1}$ radiation (λ = 1.5405 Å) with a Ge(111) monochromator.

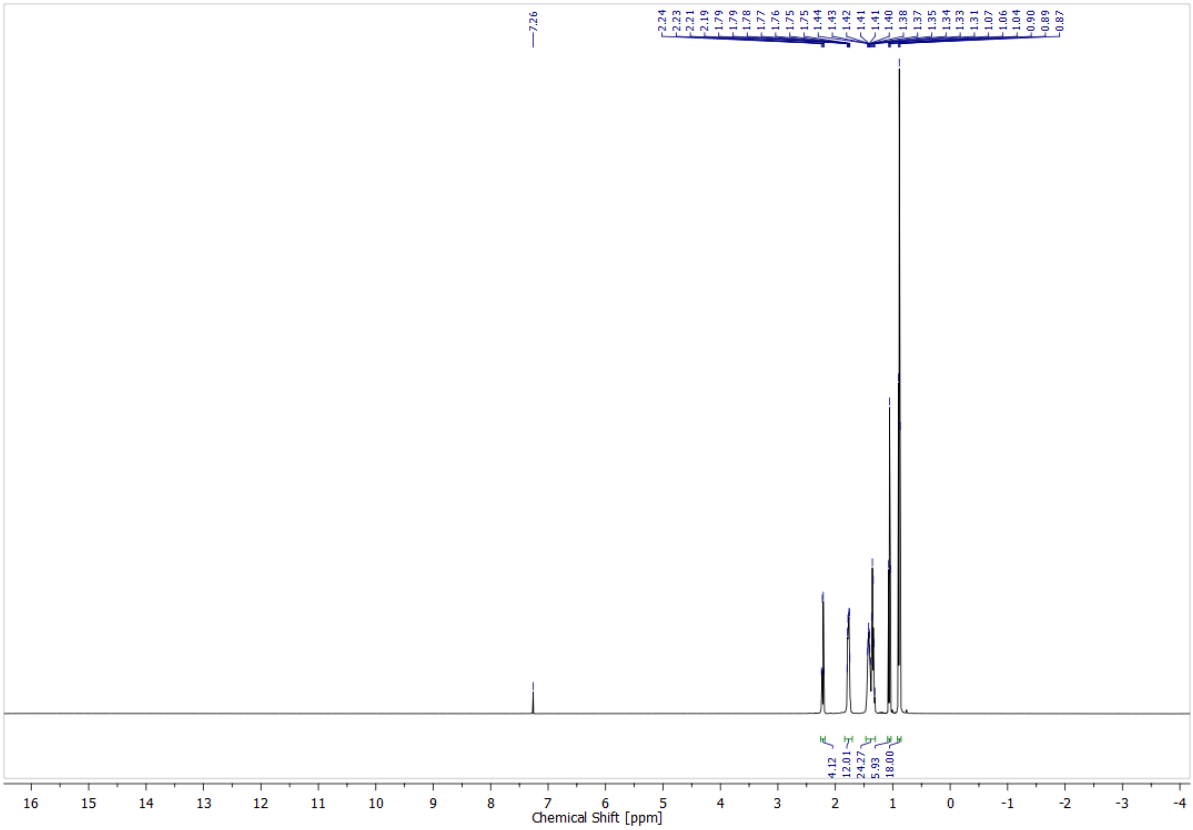
^{1}H and ^{13}C{^{1}H} NMR Spectra of Ruthenium Complexes 4a–g in $CDCl_3$

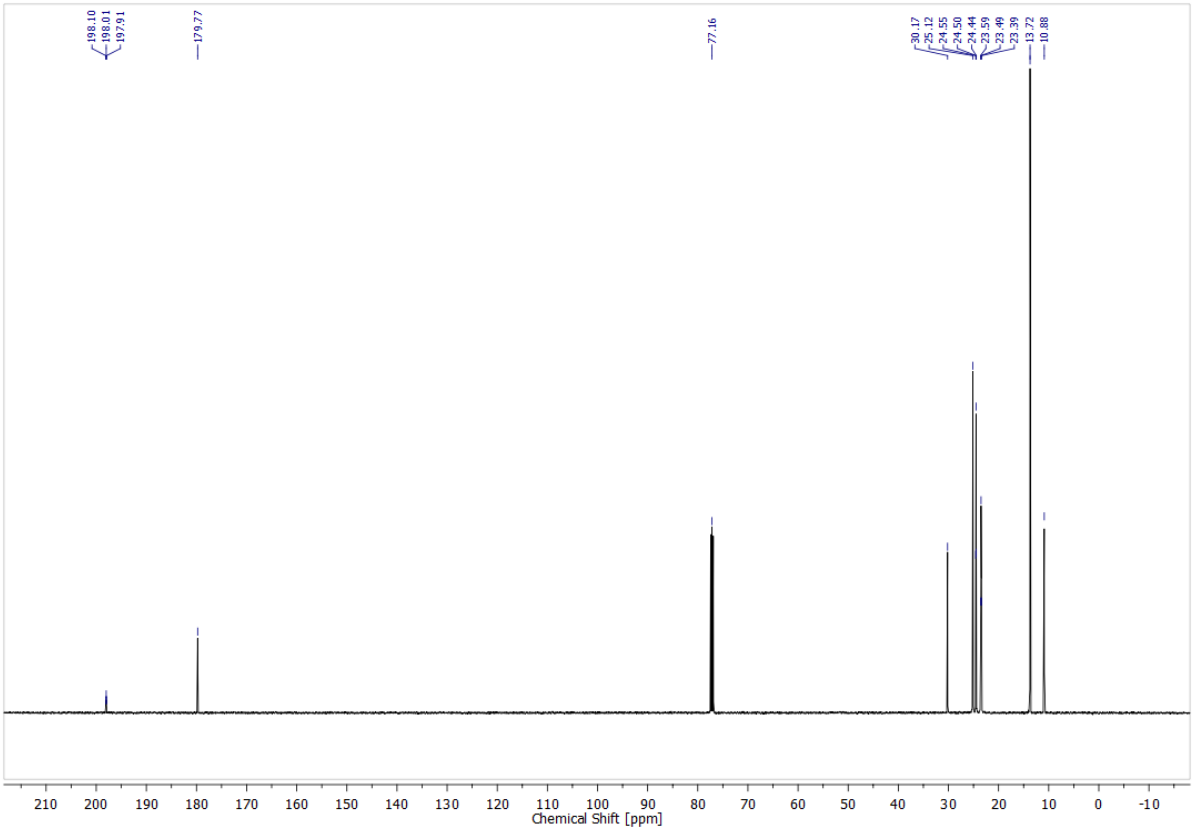
$Ru(CO)_2(P^nBu_3)_2(O_2CCH_3)_2$ (**4a**)



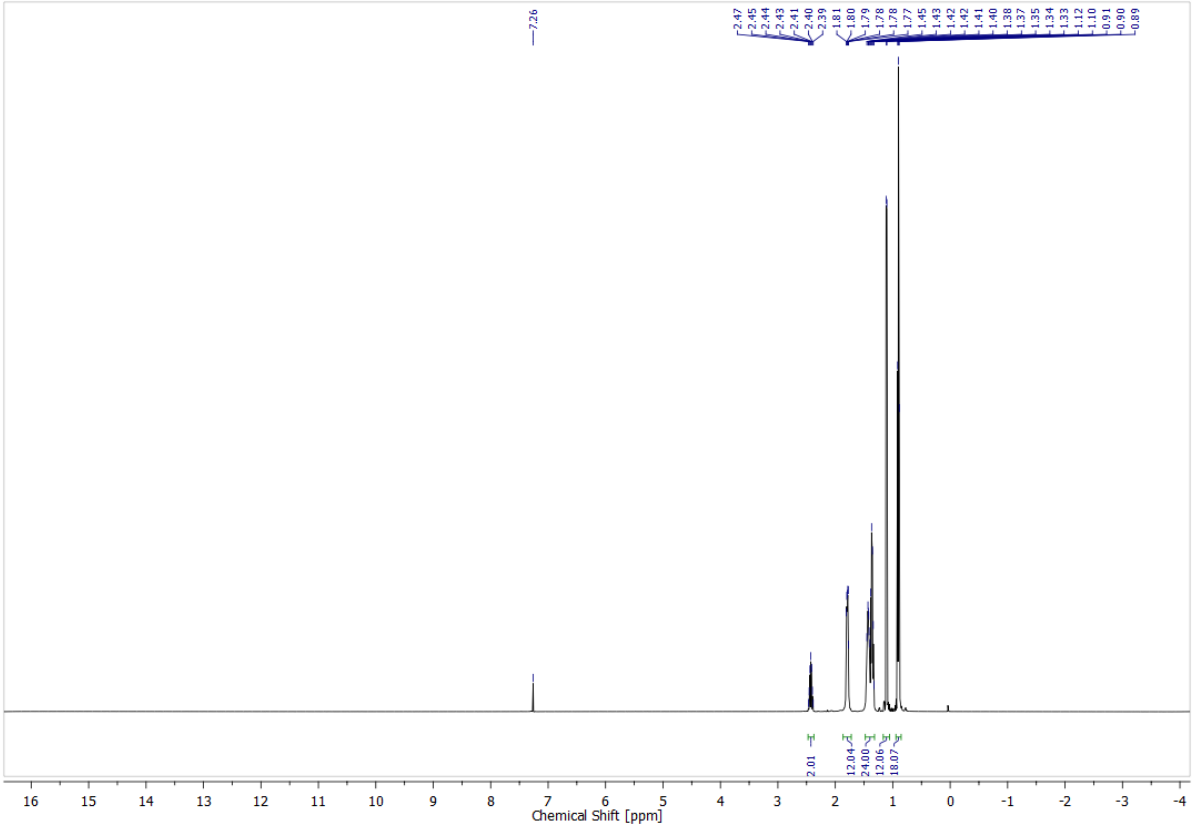


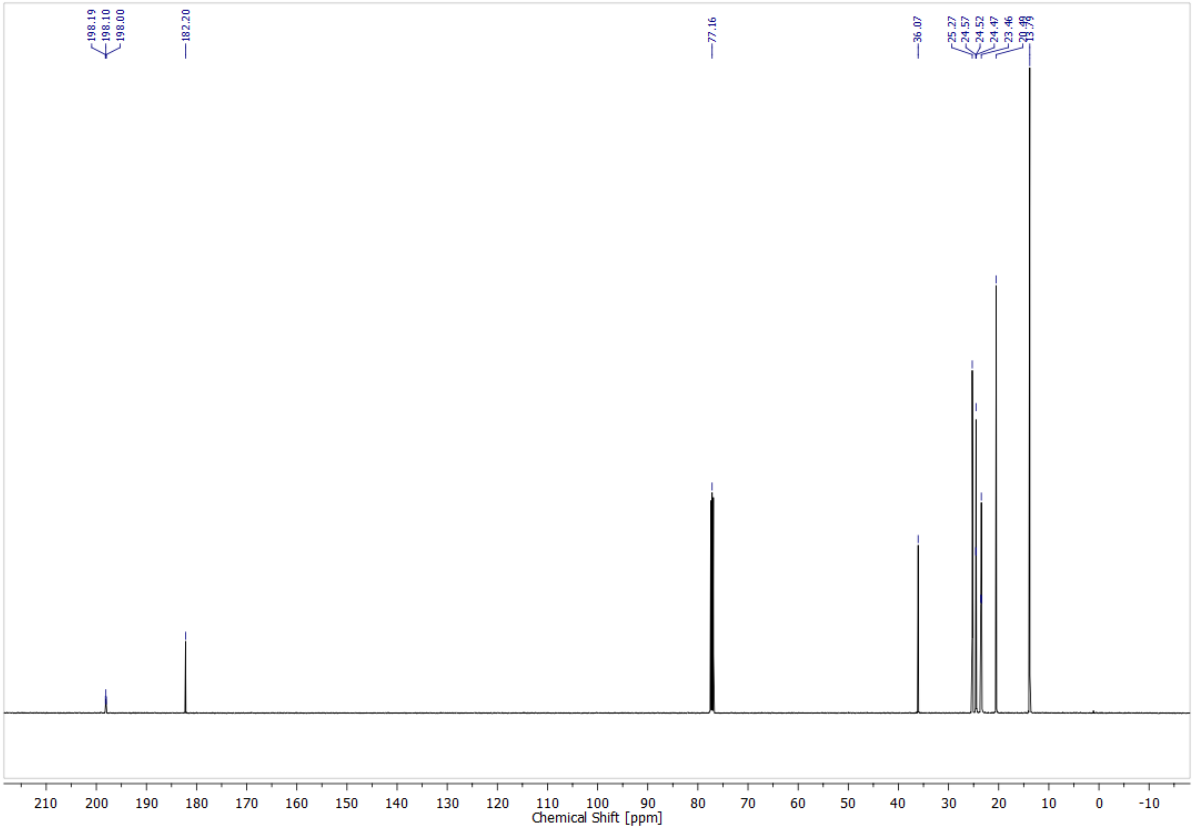
$Ru(CO)_2(P^nBu_3)_2(O_2CCH_2CH_3)_2$ (**4b**)



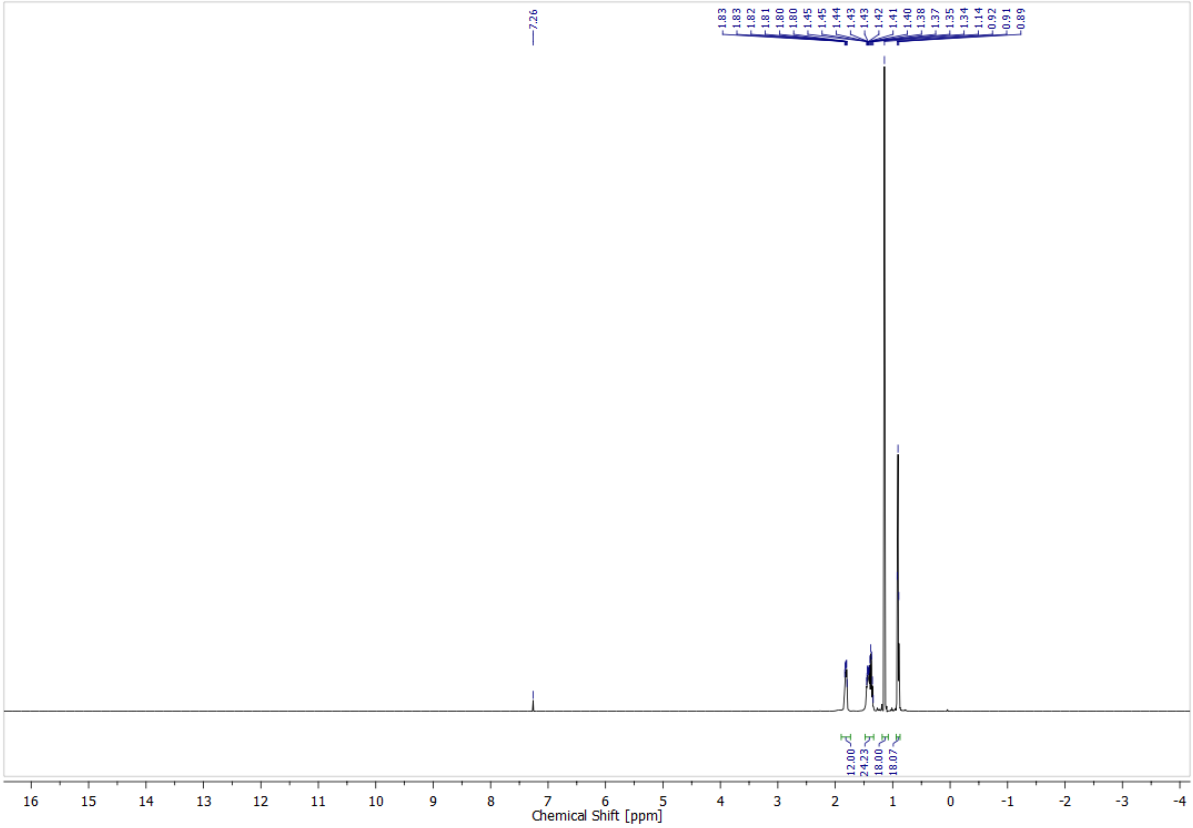


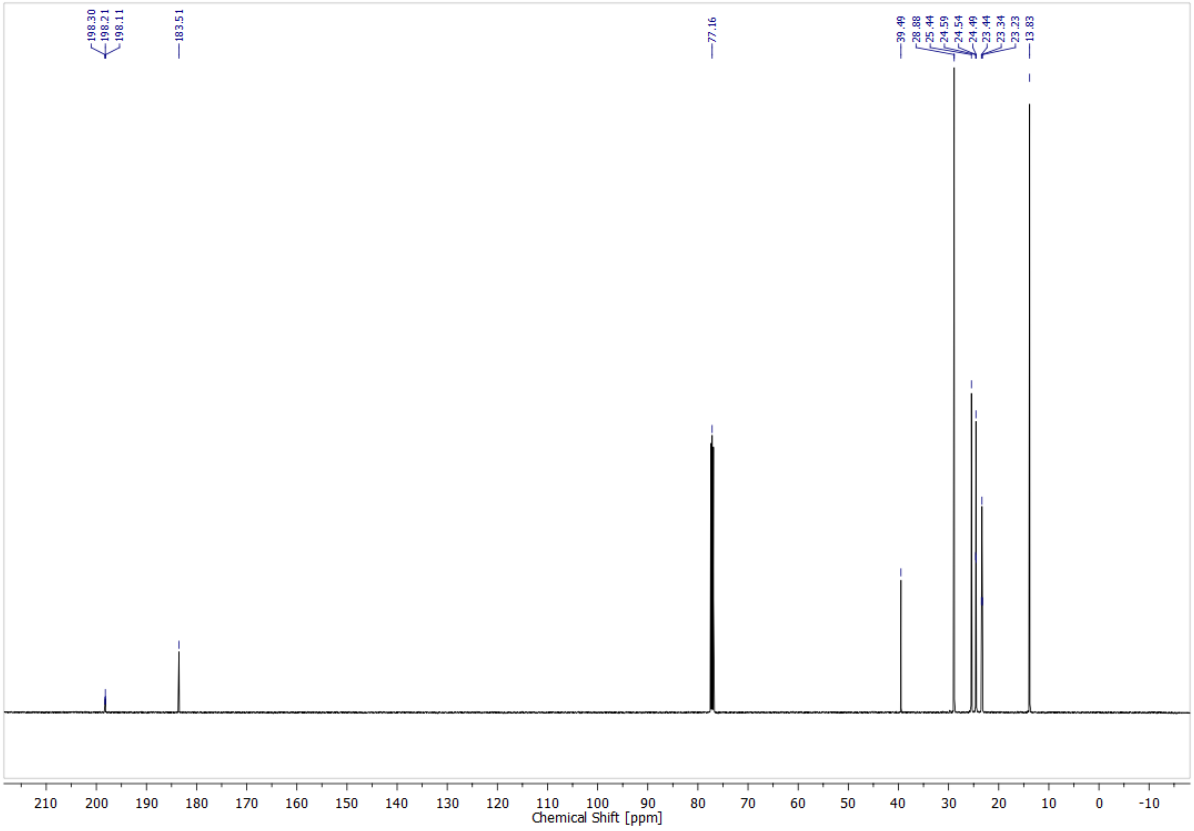
$Ru(CO)_2(P^nBu_3)_2(O_2CCH(CH_3)_2)_2$ (**4c**)



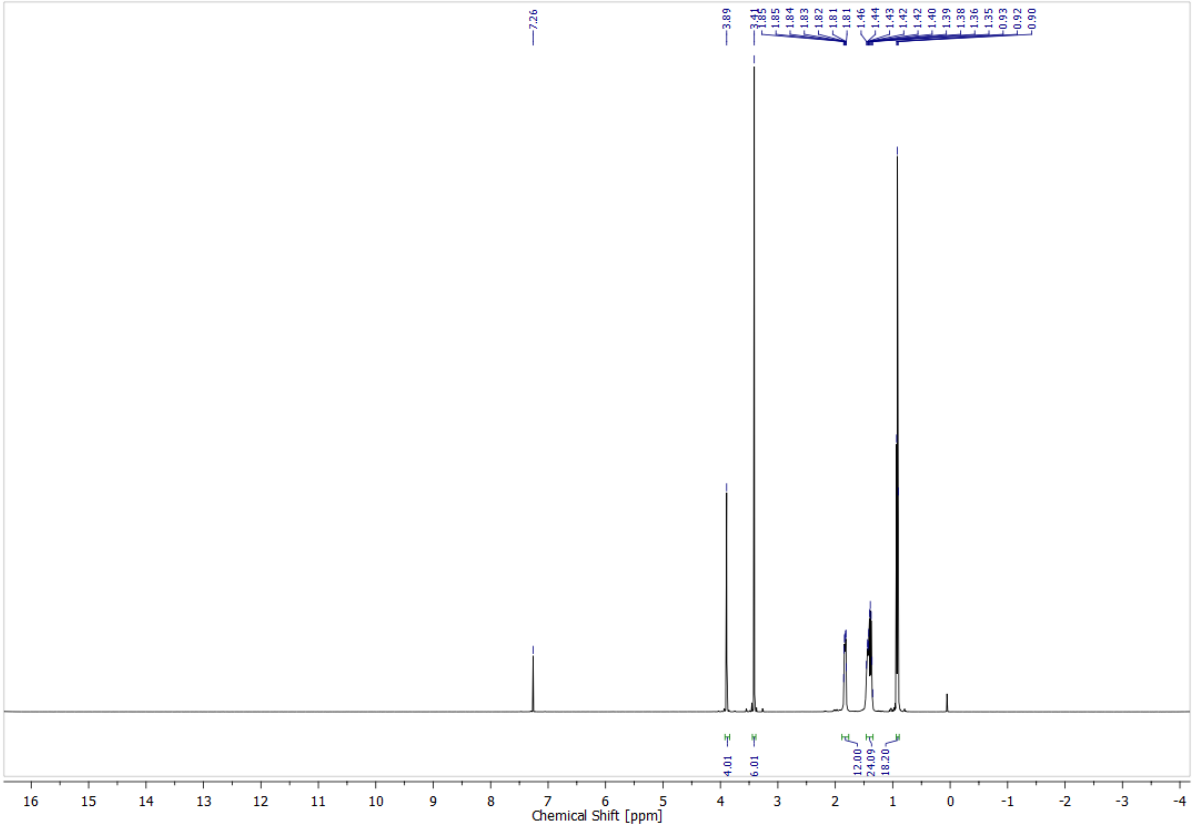


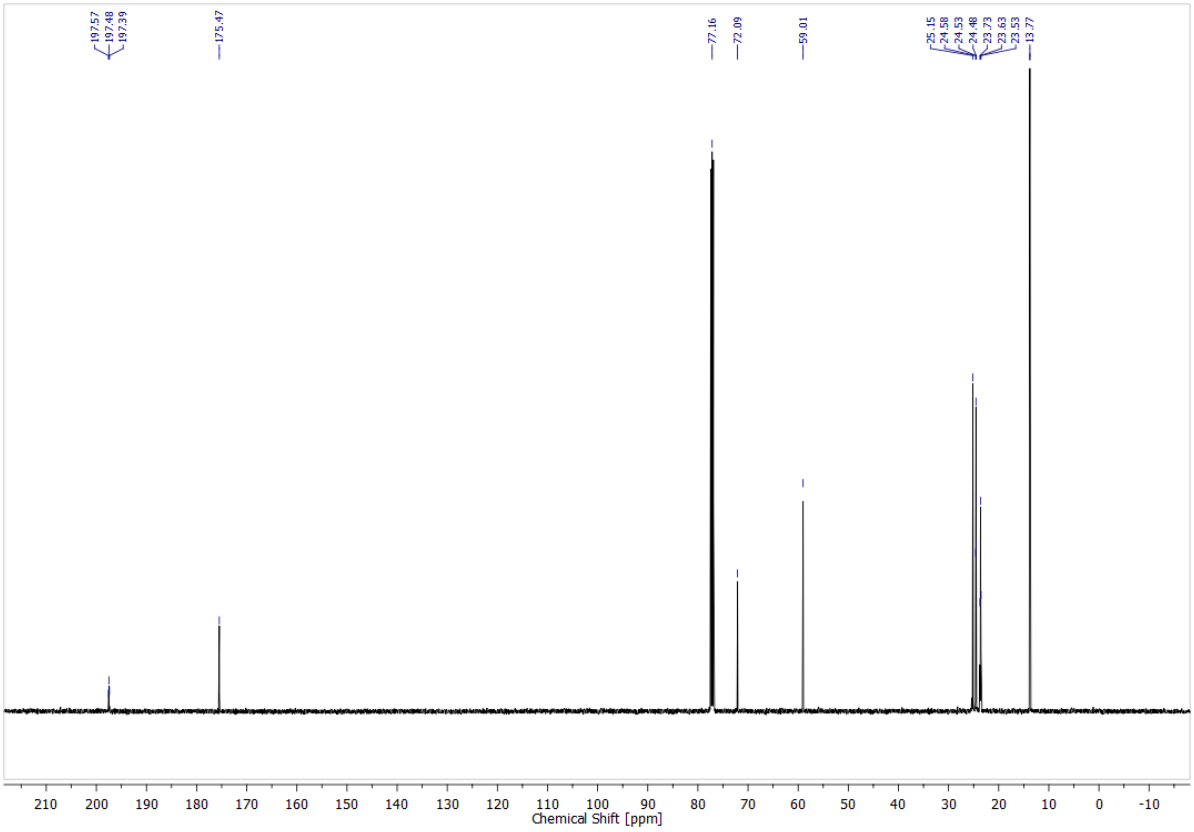
$Ru(CO)_2(P^nBu_3)_2(O_2CC(CH_3)_3)_2$ (**4d**)



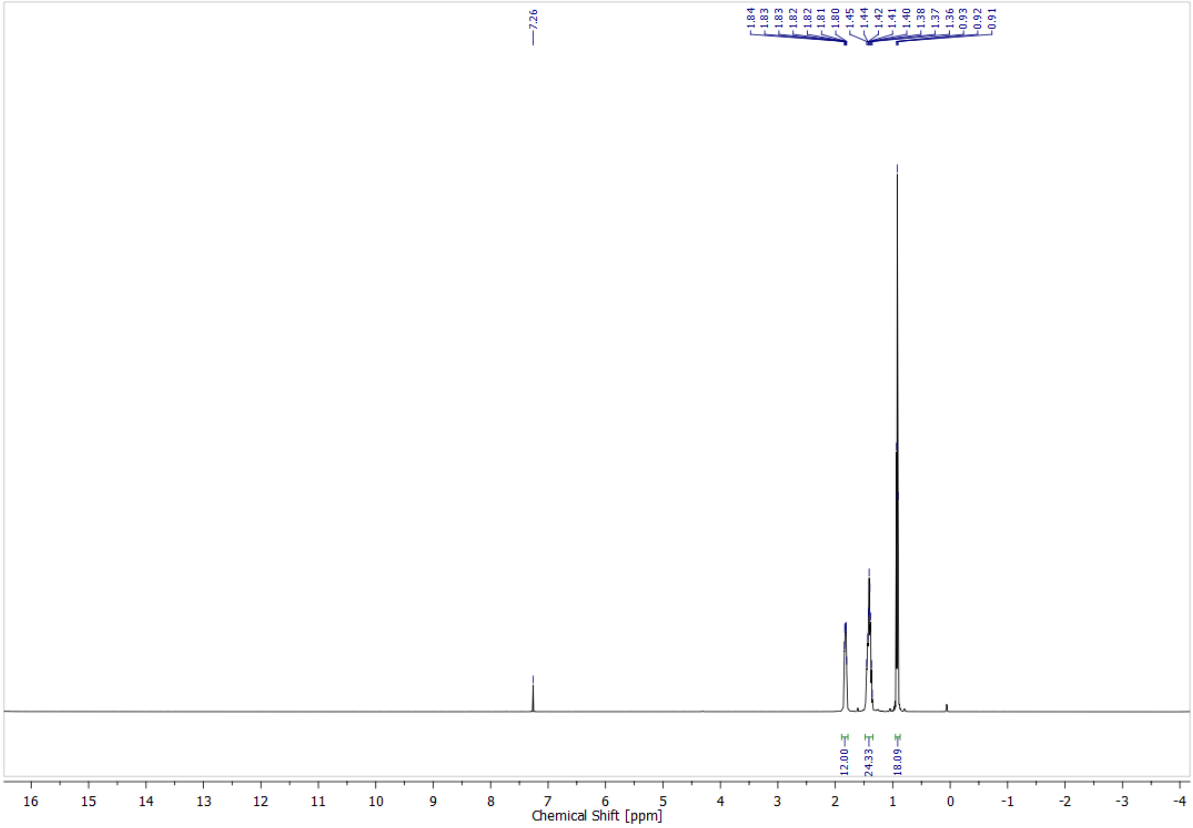


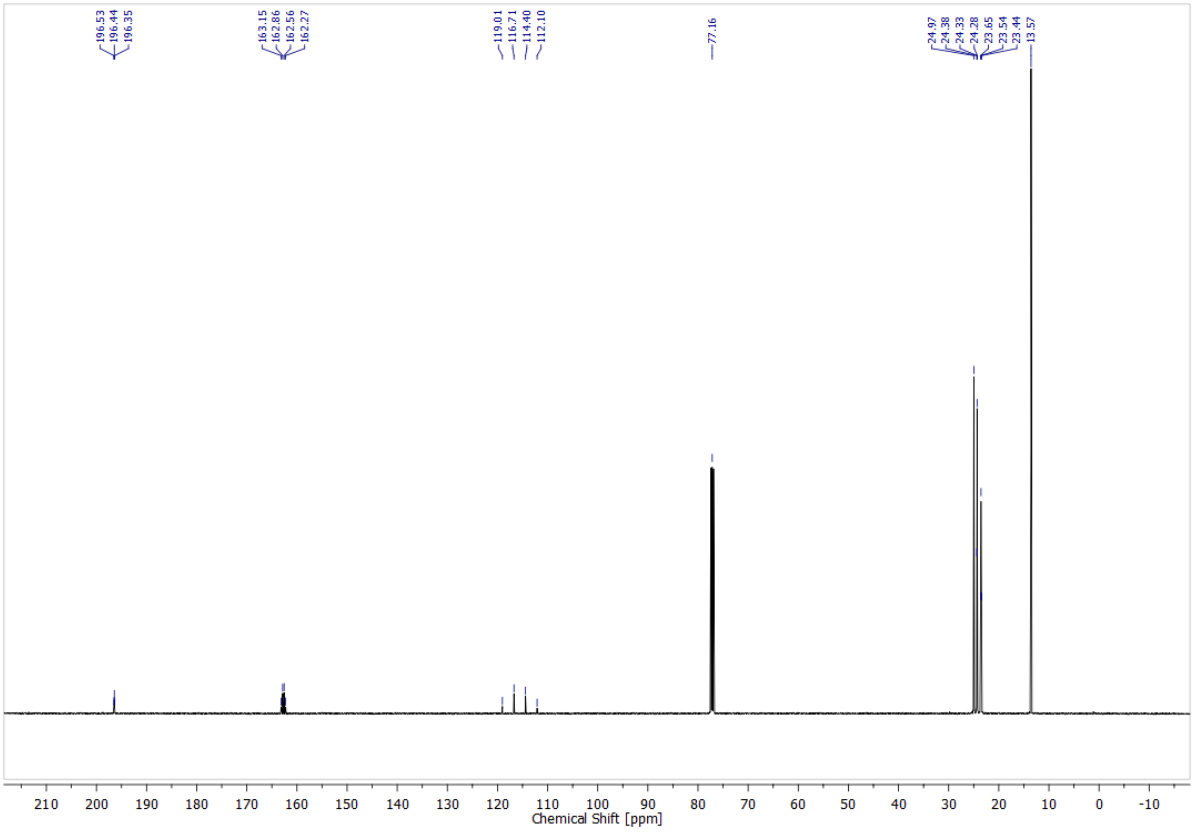
$Ru(CO)_2(P^nBu_3)_2(O_2CCH_2OCH_3)_2$ (**4e**)





$Ru(CO)_2(P^nBu_3)_2(O_2CCF_3)_2$ (**4f**)





$Ru(CO)_2(P^nBu_3)_2(O_2CCF_2CF_3)_2$ (**4g**)