

Supporting Information:

Table S1. Photo-assisted catalytic oxidation of benzene^a and cyclohexane^b.

catalyst	μmol	phenol yield		TON ^c
		mmol/l	μmol	
none	-	0.17	3	-
c-C ₅ H ₉ T ₇	50.0	0.53	11	0.2
1	50.4	0.79	16	0.3
VO(acac) ₂	49.6	3.96	79	1.6
2	50.0	5.05	101	2.0
c-C ₅ H ₉ I	56.6	7.26	145	2.6
PPh ₄ 3	49.9	8.58	171	3.4

catalyst	μmol	cyclohexanone yield		cyclohexanol yield		total TON ^d
		mmol/l	μmol	mmol/l	μmol	
none	-	0.77	15	1.21	24	-
c-C ₅ H ₉ T ₇	25.0	0.15	3	0.40	8	0.44
1	25.6	1.31	26	0.96	19	1.78
VO(acac) ₂	25.8	3.07	61	2.28	46	4.14
2	23.7	0.89	18	4.99	100	4.97
c-C ₅ H ₉ I	27.3	18.80	376	18.15	363	27.06
PPh ₄ 3	25.0 ^e	4.34	93	5.41	116	8.36

^a Catalyst 50 μmol , benzene 10 cm^3 , acetonitrile 10 cm^3 , O₂ 1.6 atm, 298 K, 6 h, 200 W Hg-medium-pressure arc lamp.

^b Catalyst 25 μmol , cyclohexane 20 cm^3 , O₂ 1.6 atm, 298 K, 6 h, 200 W Hg-medium-pressure arc lamp.

^c Turnover number (moles- phenol / moles-catalyst used).

^d Turnover number (moles-cyclohexanone and cyclohexanol / moles-catalyst used).

^e This amount was added but not dissolved, so that the entry only provided the lower limit for **3**.

Figure S2: IR spectra for NBu_4VO_3 (before and after ^{18}O -enrichment).

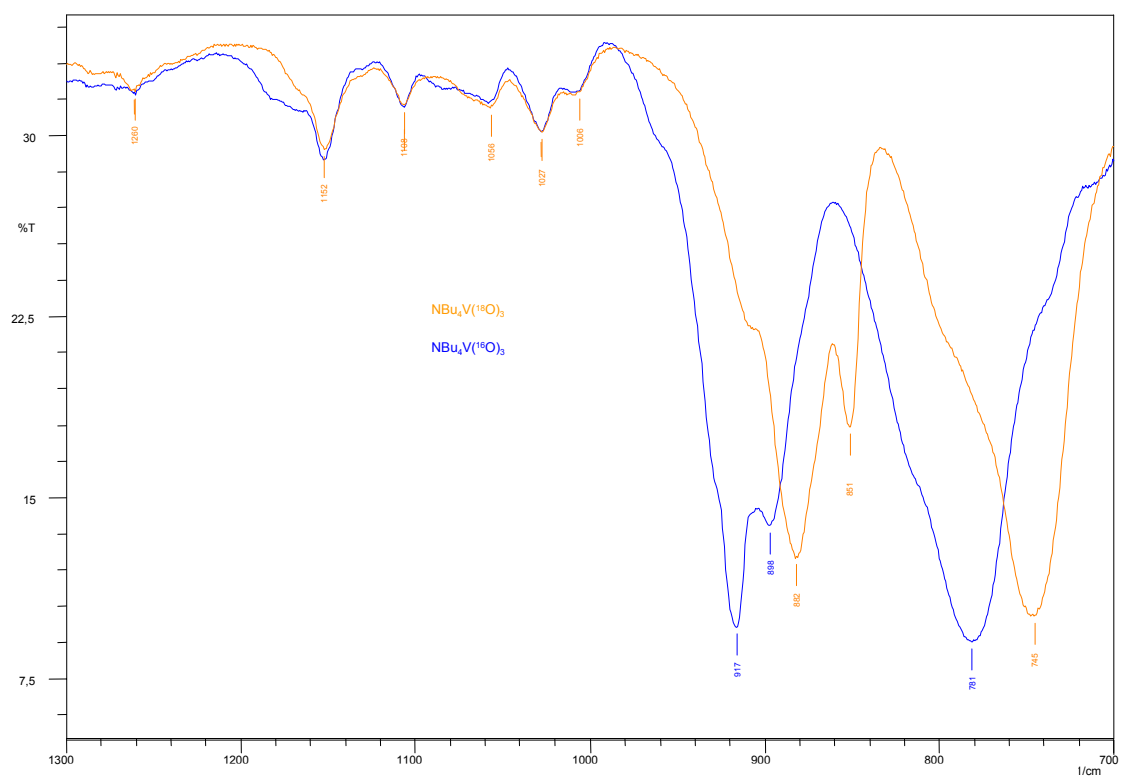


Figure S3: Raman spectra for complex 3^{NBu_4} (before and after ^{18}O -enrichment).

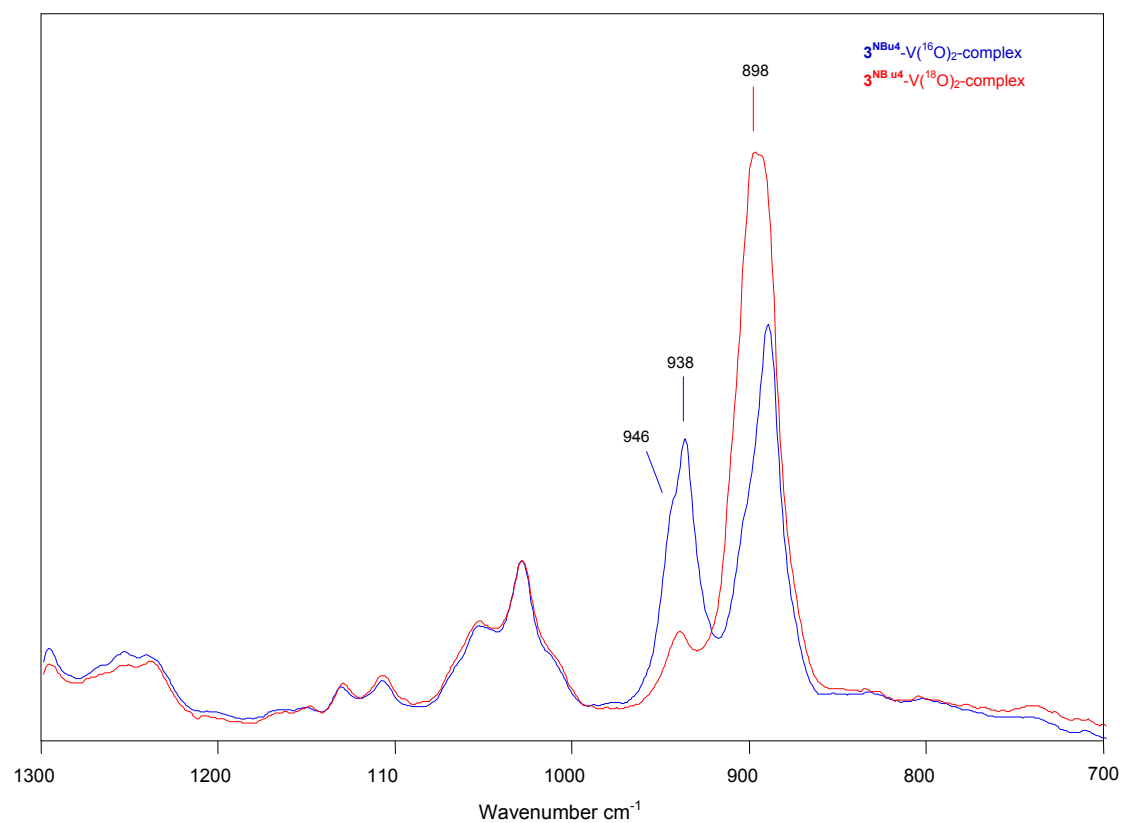


Figure S4: Raman spectra for complex 4^{NBu_4} (before and after ^{18}O -enrichment).

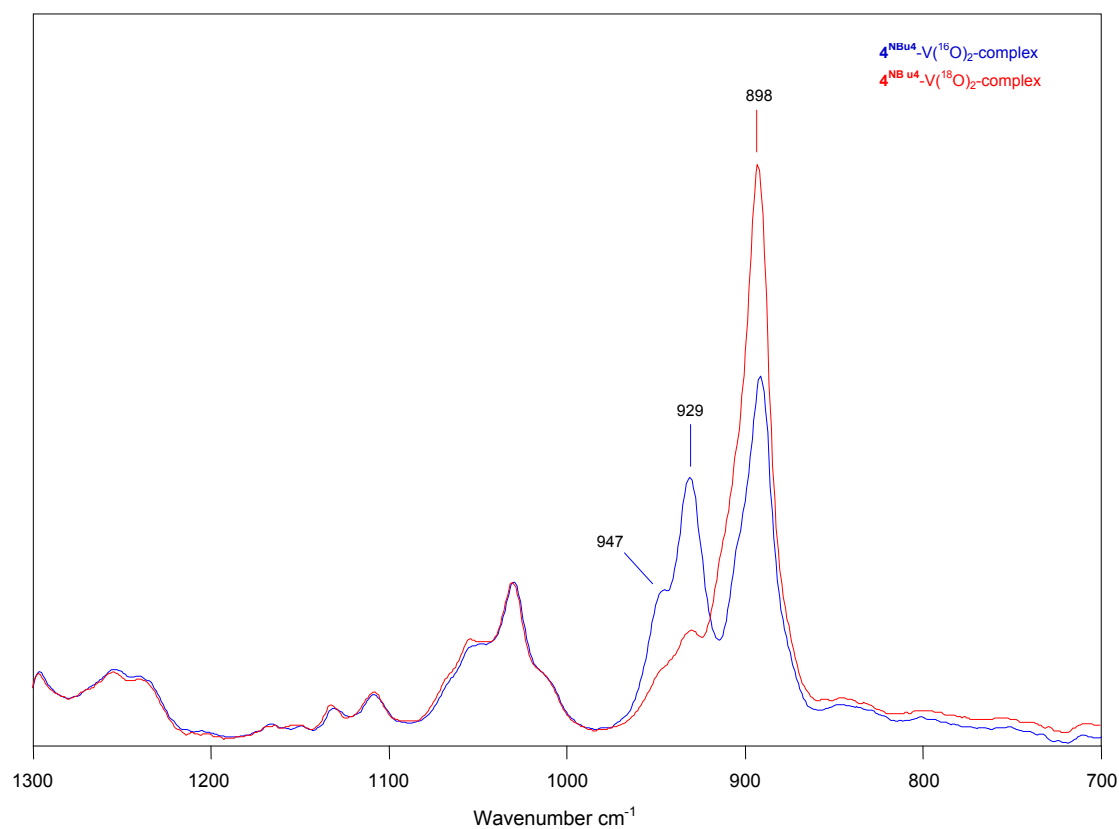


Figure S5: Raman spectra for $c\text{-C}_5\text{H}_9\text{T}_7$ and complex 3^{NBu_4} .

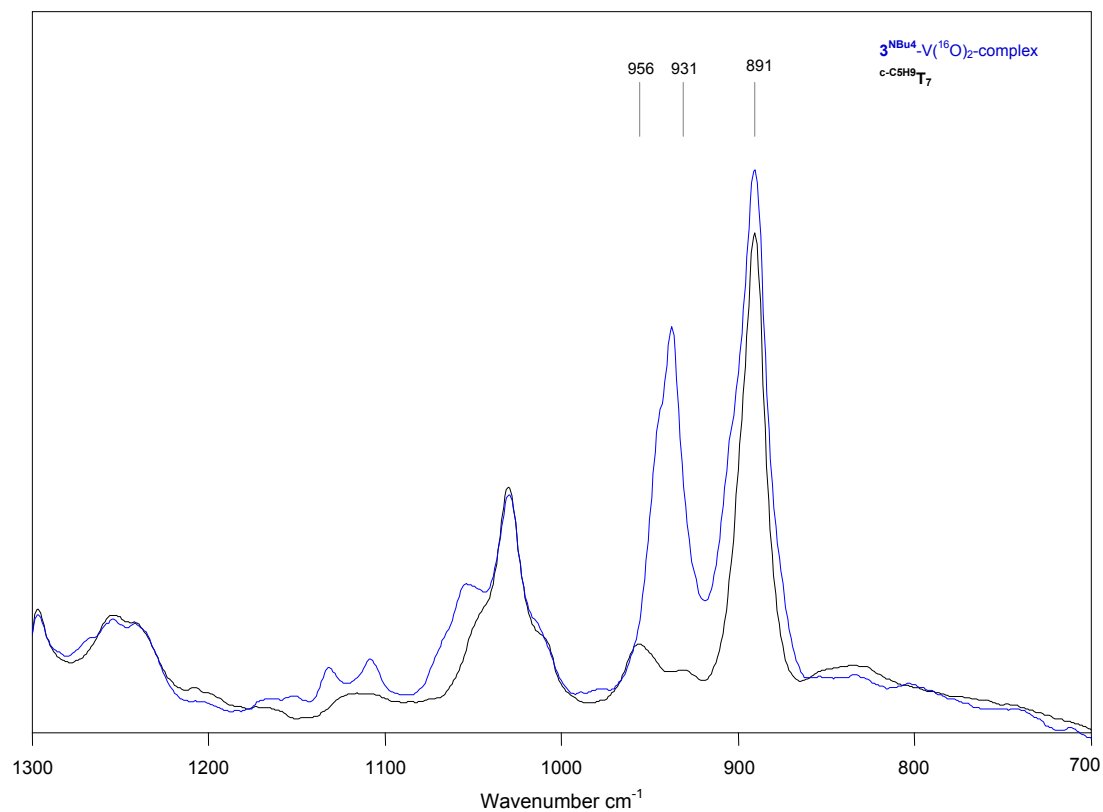


Figure S5: Raman spectra for $\text{TMS-}c\text{-C}_5\text{H}_9\text{T}_7$ and complex 4^{NBu_4} .

