Electronic Supplementary Material (ESI) for Green Chemistry.

Supporting Information for

Selective oxidative C-C bond cleavage of a lignin model compound in presence of acetic acid with a vanadium catalyst

Yangyang Ma,[a,b] Zhongtian Du,[a] Junxia Liu,[a,b] Fei Xia[a,b] and Jie Xu*[a]

[a]*State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian National Laboratory for Clean Energy, Dalian 116023, P. R. China*

[b]*University of the Chinese Academy of Sciences, Beijing 100039, P. R. China*

**Correspondence and requests for materials should be addressed to: xujie@dicp.ac.cn*

Additional results

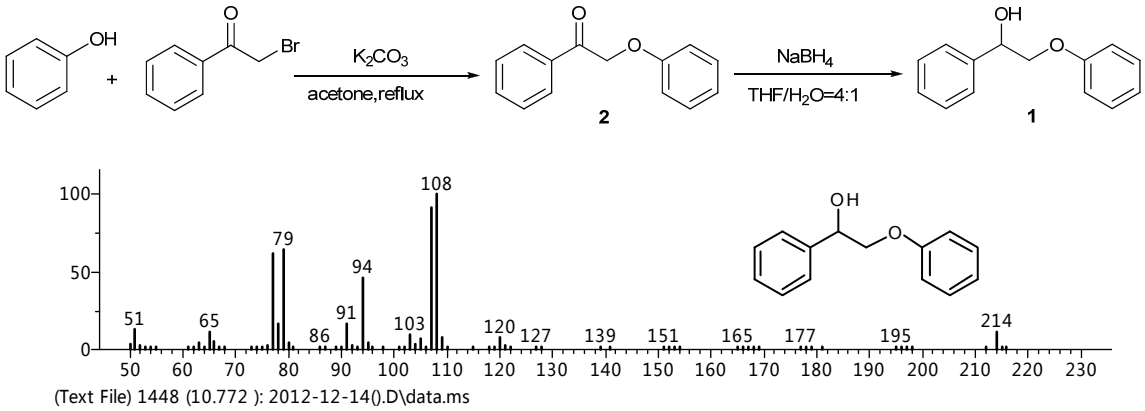

Fig. S1 Synthesis pathway for 2-phenoxy-1-phenylethanol (**1**) and its Mass spectrum..

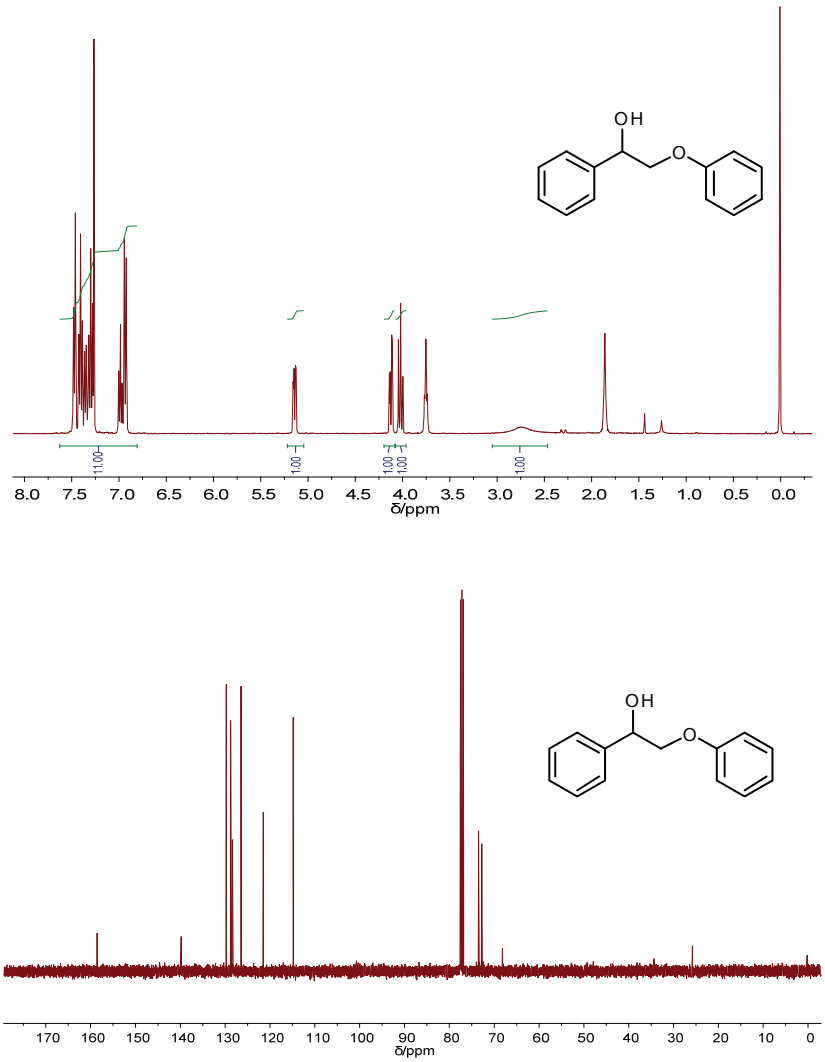

Fig. S2 ^{1}H and ^{13}C NMR spectra of 2-phenoxy-1-phenylethanol (**1**).

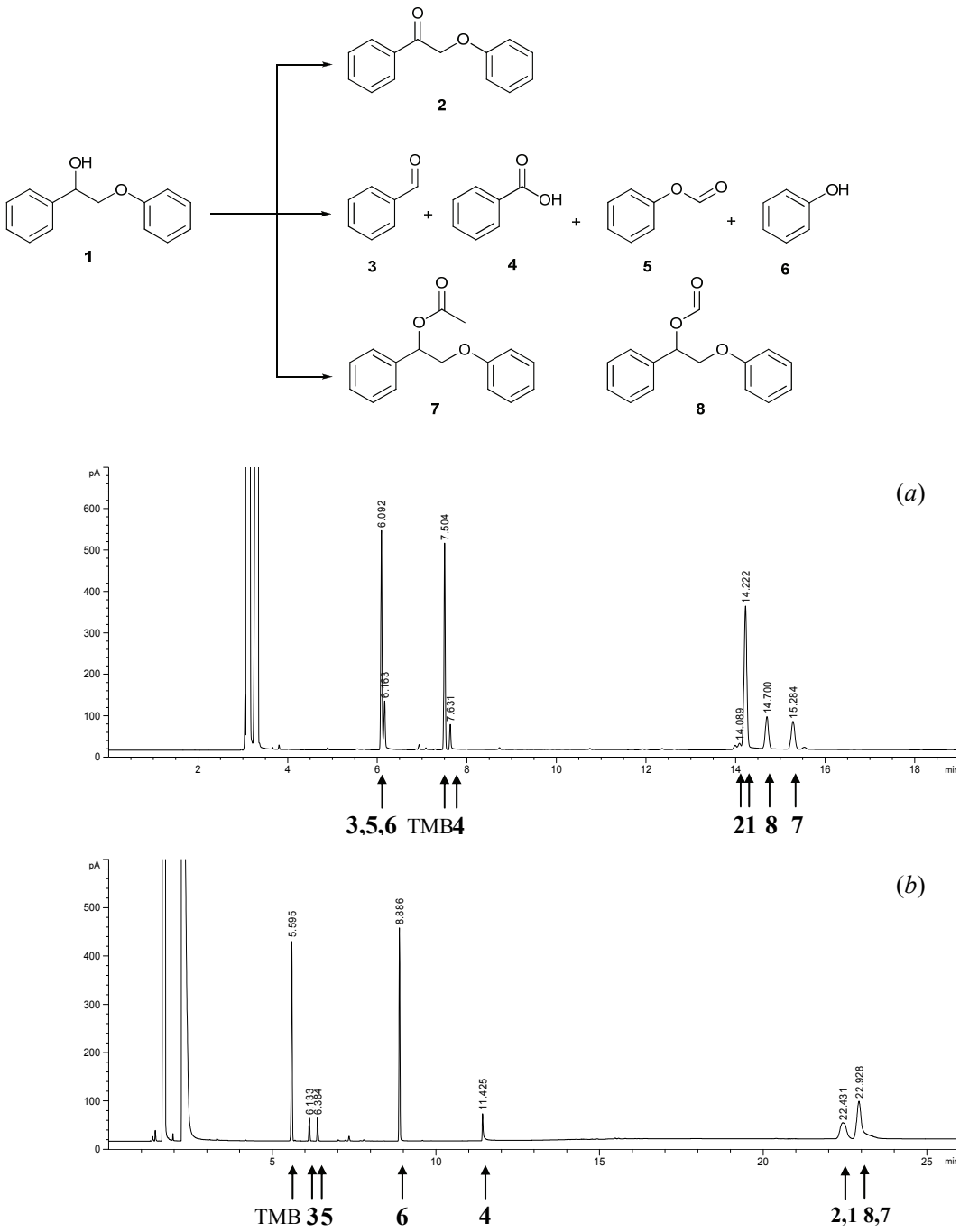

Fig. S3 The GC trace for oxidation products of 2-phenoxy-1-phenylethanol (**1**) in acetic acid (*a*: on HP-5 column; 6.0 min and 6.1 min: the mixture of **3, 5, 6**; 7.5 min: internal standard (TMB); 7.6 min: **4**; 14.0 min: **2**; 14.2 min: **1**; 14.7 min: **8**; 15.2 min: **7**; *b*: on DB-225 column; 5.5 min: internal standard (TMB); 6.1 min: **3**; 6.3 min: **5**; 8.8 min: **6**; 11.4 min: **4**; 22.4 min: the mixture of **2**, **1**; 22.9 min: the mixture of **8**, **7**). Reaction condition: 0.25 mmol model compound **1**, 0.025 mmol $VO(acac)_2$, 0.5 mL acetic acid, 80 ^{o}C, 8 h, 1 atm O_2. 1,2,4,5-tetramethylbenzene (TMB) was used as the internal standard.

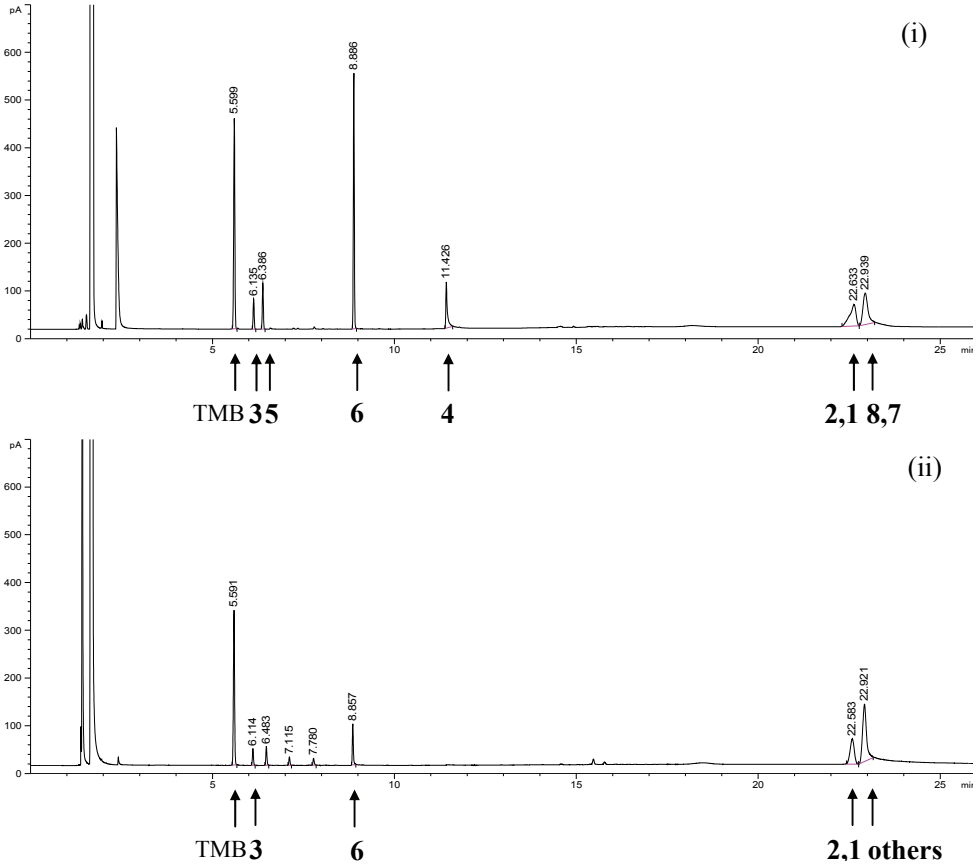

Fig. S4 The GC trace for oxidation products of 2-phenoxy-1-phenylethanol (**1**) in (i): acetonitrile/10% acetic acid. 5.5 min: internal standard (TMB); 6.1 min: **3**; 6.3 min: **5**; 8.8 min: **6**; 11.4 min: **4**; 22.4 min: the mixture of **2**, **1**; 22.9 min: the mixture of **8**, **7**; (ii) in acetonitrile/10% triethylamine. 5.5 min: internal standard (TMB); 6.1 min: **3**; 8.8 min: **6**; 22.4 min: the mixture of **2**, **1**; 22.9 min: others. (on DB-225 column). Reaction condition: 0.25 mmol model compound **1**, 0.025 mmol $VO(acac)_2$, 0.5 mL solvent, 80 ^{o}C, 8 h, 1 atm O_2.

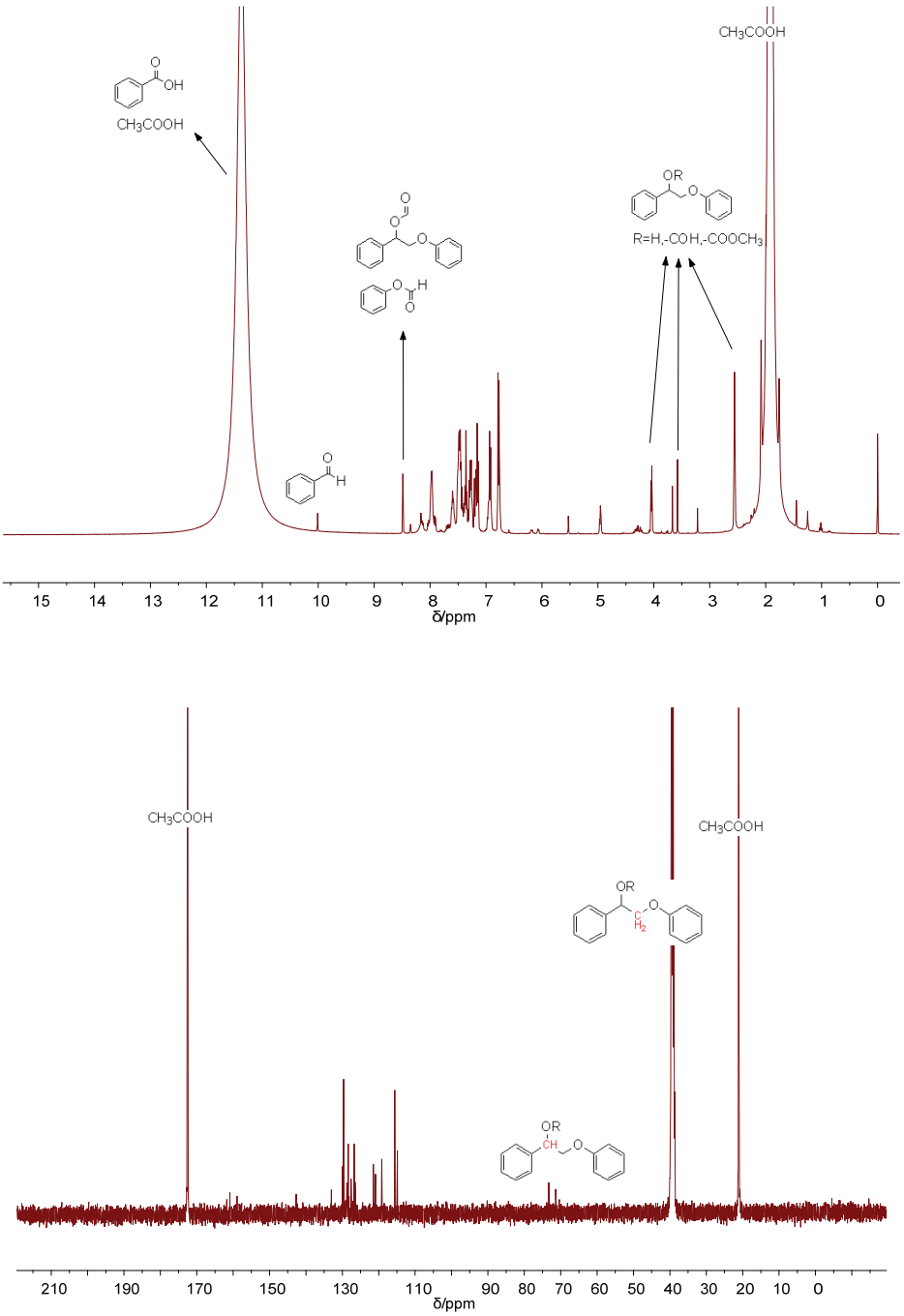

Fig. S5 ^{1}H and ^{13}C NMR spectra of oxidation products of 2-phenoxy-1-phenylethanol (**1**) in acetic acid-d_3. Reaction condition: 0.25 mmol model compound **1**, 0.025 mmol $VO(acac)_2$, 0.5 mL acetic acid-d_3, 80 ^{o}C, 8 h, 1 atm O_2.

Table S1 Catalytic oxidation of **1** with different vanadium catalysts in acetic acid. [a]

Entry	Catalyst	Conversion (mol%)	Product distribution (mol%)						Cleavage selectivity (mol%)
			2	**3**	**4**	**5**	**6**	others	
1	$VO(acac)_2$	76.0	2.3	5.6	13.7	8.8	53.7	15.9	81.8
2	$VO(mal)_2$	60.1	5.1	7.7	10.0	19.4	35.0	22.8	72.1
3	$VOSO_4 \bullet xH_2O$	39.5	5.0	8.3	10.7	18.2	31.3	26.5	68.5
4	VOC_2O_4	78.8	2.8	4.9	9.6	16.8	48.4	17.5	79.7
5	$VO(OAc)_2$	38.6	4.5	9.1	-	19.9	36.4	30.1	65.4
6	$VO(OEt)_3$	82.2	2.4	5.6	17.5	8.0	52.0	14.5	83.1
7	$VO(O^iPr)_3$	82.0	2.4	5.8	16.3	8.8	51.0	15.7	81.9

[a] Reaction conditions: 0.25 mmol model compound **1**, 0.025 mmol catalyst, 0.5 mL acetic acid, 80 ^oC, 8 h, 1 atm O_2. Cleavage selectivity was presented as the amount of (**3**+**4**+**5**+**6**) in product distribution.

Table S2 Catalytic oxidation of **1** in different solvent systems with vanadium catalysts. [a]

Entry	Catalyst	Solvent	Conversion (mol%)	Product distribution (mol%)						Cleavage selectivity (mol%)
				2	**3**	**4**	**5**	**6**	others	
1	$VO(acac)_2$	CH_3COOH	76.0	2.3	5.6	13.7	8.8	53.7	15.9	81.8
2	$VO(OAc)_2$	CH_3CN	28.3	>99	-	-	-	-	-	-
3	$VO(acac)_2$	CH_3CN[b]	<2.0	-	-	-	-	-	-	-

[a] Reaction conditions: 0.25 mmol model compound **1**, 0.025 mmol $VO(acac)_2$, 0.5 mL solvent, 80 ^oC, 8 h, 1 atm O_2. Cleavage selectivity was presented as the amount of (**3**+**4**+**5**+**6**) in product distribution. [b] 10 mol% NaOAc relative to **1** was added.

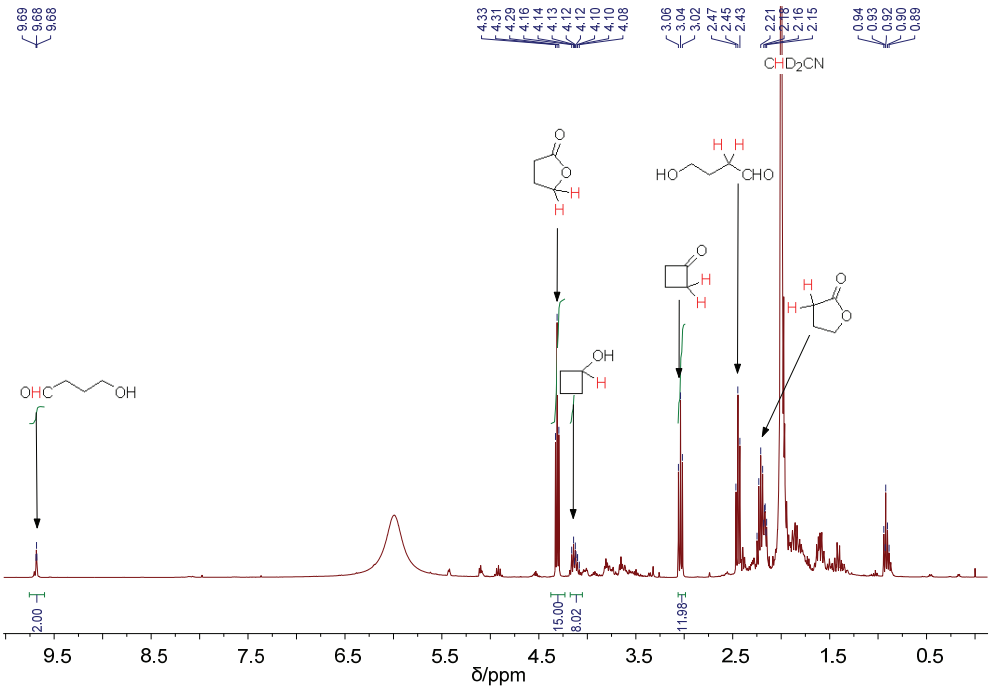

Fig. S6 The ^{1}H NMR spectra of the products of cyclobutanol oxidation in acetonitrile-d_3/10% acetic acid.

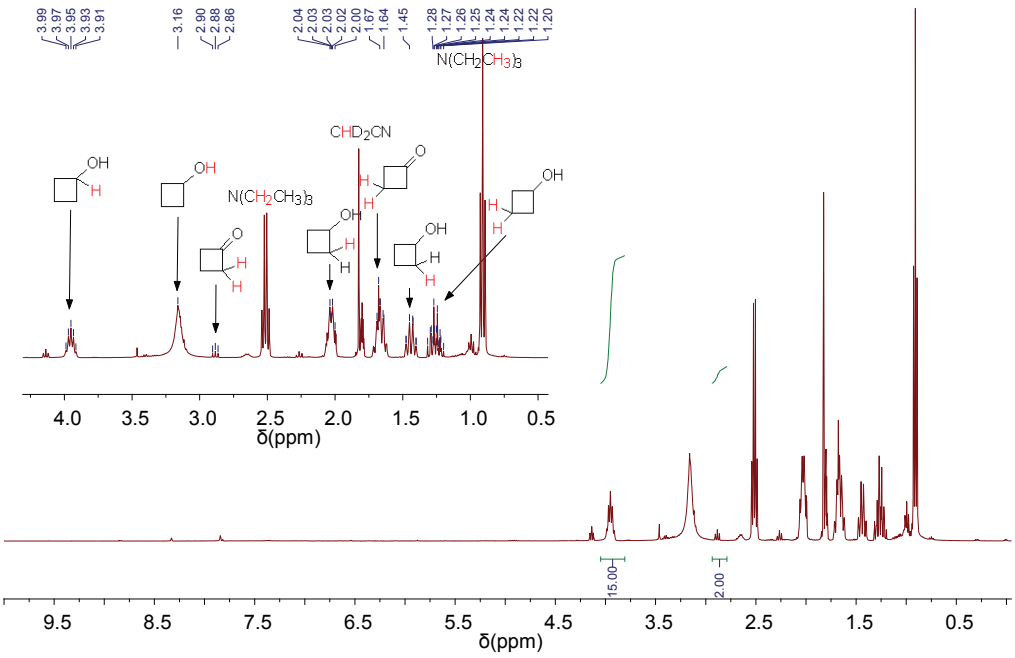

Fig. S7 The ^{1}H NMR spectra of the products of cyclobutanol oxidation in acetonitrile-d_3/10% triethylamine.

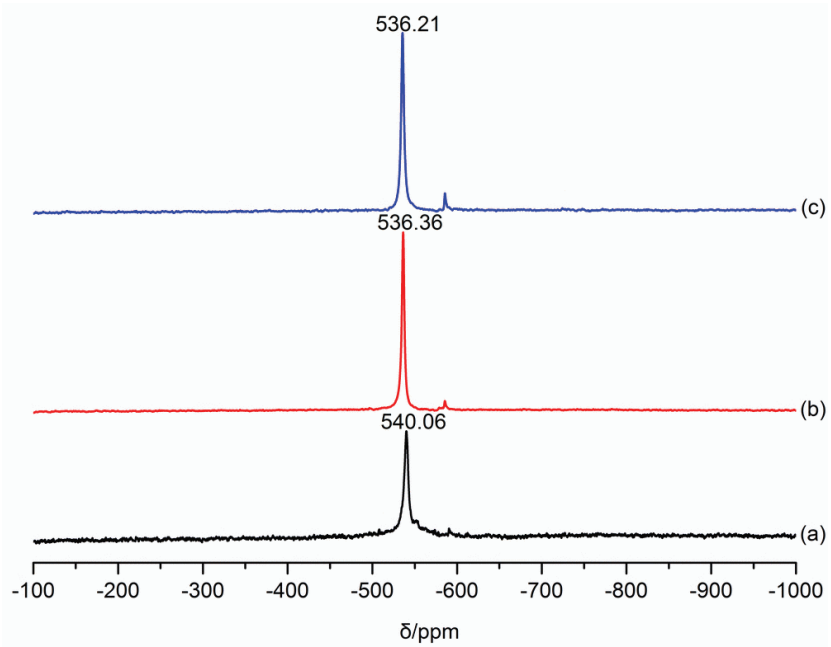

Fig. S8 ^{51}V NMR spectra of the reaction mixtures. Reaction condition: 0.05 mmol vanadium compounds, 1 mL solvent (acetonitrile/10% acetic acid), 80 ^{o}C, 16 h, 1 atm O_2. (a) $VO(acac)_2$; (b) $VO(O^iPr)_3$; (c) $VO(OEt)_3$.