Electronic Supplementary Information

Vanadyl complexes bearing bi-dentate phenoxyimine ligands: Synthesis, structural studies and ethylene polymerization capability

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Contents

Molecular structures of **2**, **4, 6 – 9**:

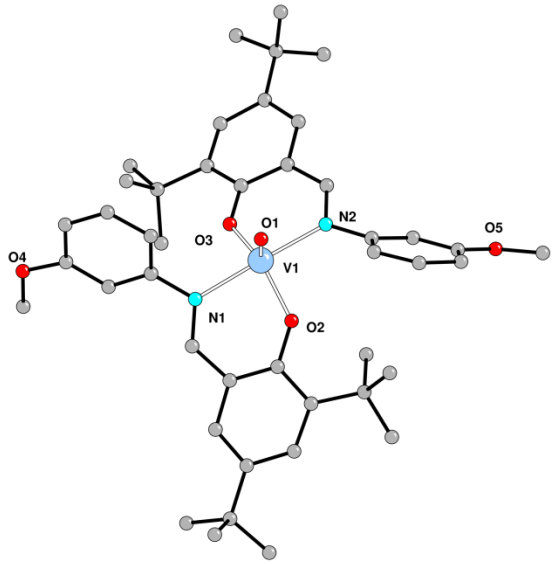

Figure S1. CAMERON representation of the one of the independent molecules of **2** in the unit cell showing spheres of arbitrary size; hydrogen atoms and molecules of MeCN have been omitted for clarity.

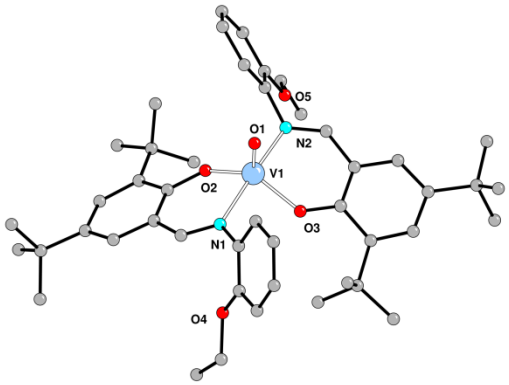

Figure S2. CAMERON representation of the one of the independent molecules of **4** in the unit cell showing spheres of arbitrary size; hydrogen atoms and molecules of MeCN have been omitted for clarity.

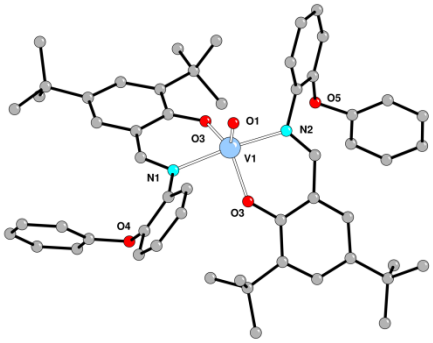

Figure S3. CAMERON representation of the one of the independent molecules of **6** in the unit cell showing spheres of arbitrary size; hydrogen atoms and molecules of MeCN have been omitted for clarity.

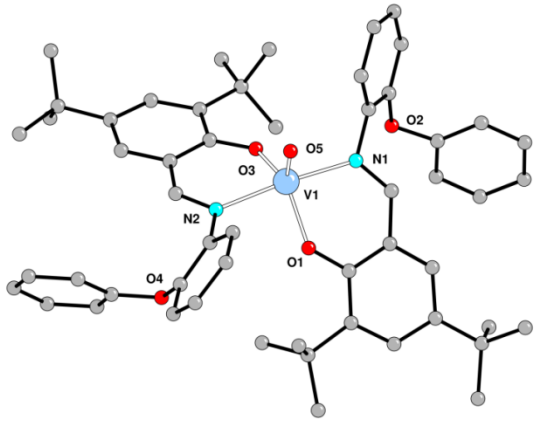

Figure S4. CAMERON representation of the one of the independent molecules of **7**·1½MeCN in the unit cell showing spheres of arbitrary size; hydrogen atoms and molecules of MeCN have been omitted for clarity.

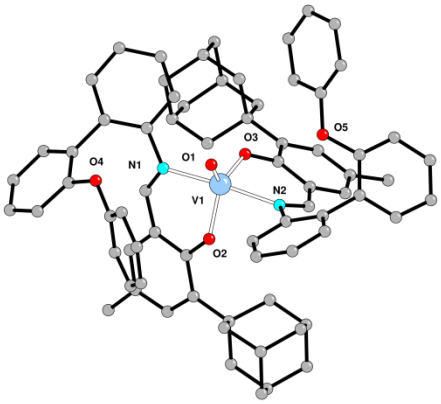

Figure S5. CAMERON representation of the one of the independent molecules of **8** in the unit cell showing spheres of arbitrary size; hydrogen atoms and molecules of MeCN have been omitted for clarity.

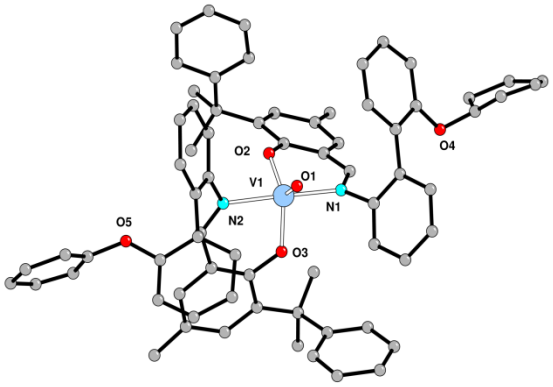

Figure S6. CAMERON representation of the one of the independent molecules of **9** in the unit cell showing spheres of arbitrary size; hydrogen atoms and molecules of MeCN have been omitted for clarity.

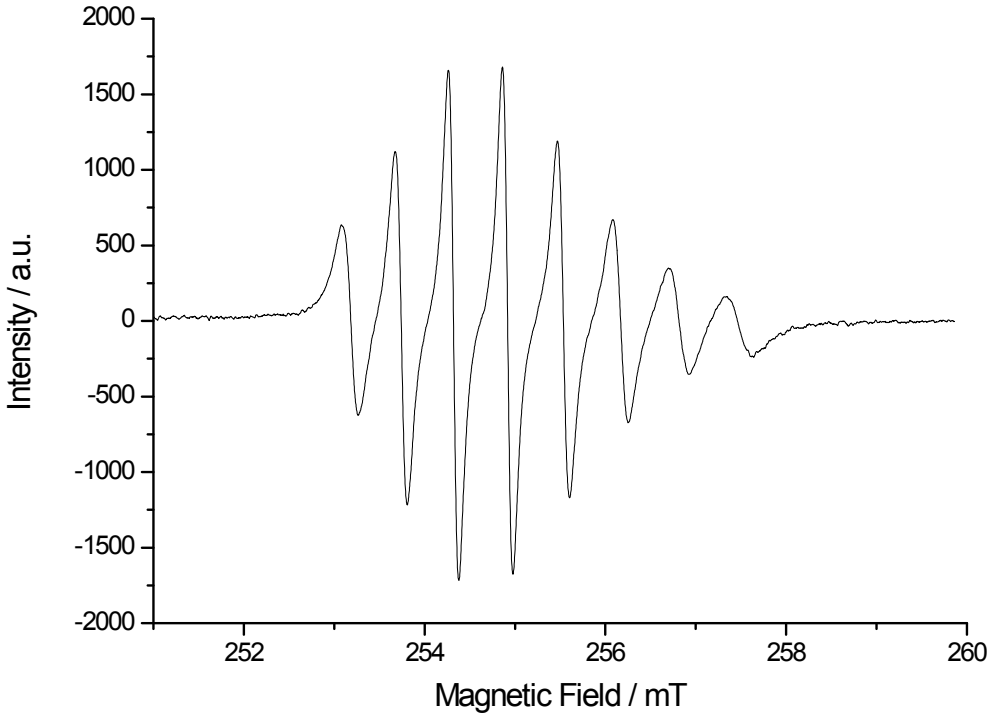

Figure S8. EPR spectra of **5** (298K) in toluene.

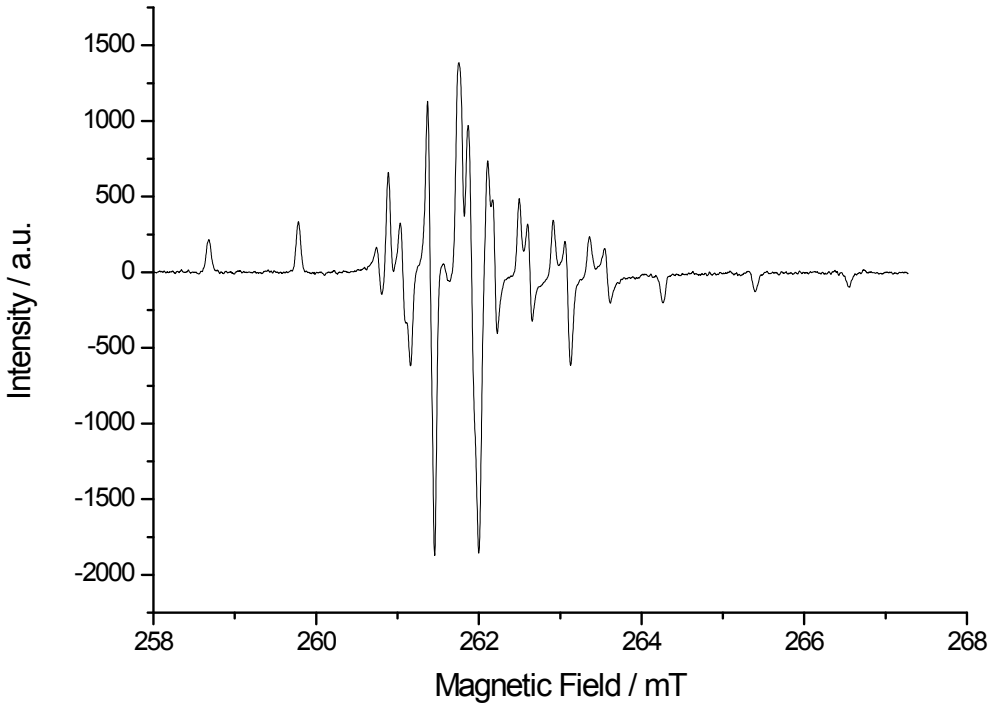

Figure S9. EPR spectra of **5** (120K) in toluene.

Table S1. Optimization of catalysis conditions using pre-catalyst **9** at 1 bar.[a]

Run	Al/V	T (℃)	T (min)	PE (g)	Activity (g/mmol.h)	M_w /10^4	M_n /10^4	PDI	T_m (℃)
1	4000	20	30	0.382	1530	10.15	5.45	1.86	137.19
2	8000	20	30	0.437	1750	11.87	6.60	1.80	134.92
3	12000	20	30	0.452	1810	12.59	6.32	1.99	135.54
4	16000	20	30	0.478	1910	13.56	7.41	1.83	135.88
5	20000	20	30	0.432	1730	10.58	5.24	2.02	135.37
6	24000	20	30	0.335	1340	11.71	6.00	1.95	136.20
7	16000	30	30	0.669	2680	1.58	0.60	2.63	130.47
8	16000	40	30	0.830	3320	0.81	0.27	3.00	127.03
9	16000	50	30	0.982	3930	0.81	0.22	3.68	126.94
10	16000	60	30	1.104	4420	0.77	0.20	3.85	125.99
11	16000	70	30	1.308	5230	0.80	0.21	3.81	126.28
12	16000	80	30	1.648	6590	1.32	0.27	4.88	128.05
13	16000	90	30	1.077	4310	2.20	0.19	11.60	126.95
14	16000	100	30	0.431	1730	0.54	0.11	4.91	128.05
15	16000	110	30	0.172	690	0.64	0.09	7.11	121.59
16	16000	80	10	0.775	9300	0.49	0.15	3.27	124.88
17	16000	80	20	1.195	7170	0.36	0.13	2.77	124.23
18	16000	80	60	2.033	4070	0.52	0.16	3.25	125.39

[a] Conditions: 0.5 μmol of [V] per run, 30 mL of toluene, 0.1ml ETA per run, 1 bar of ethylene. GPC analysis was conducted in 1,2,4-trichlorobenzene.

Table S2. Polymerization screening using pre-catalyst **10**.[a]

Run	co-catalyst	Al/V	ETA	T (°C)	t (min)	PE (g)	Activity (g/mmol.h)	M_w /10^4	M_n /10^4	PDI	T_m (°C)
1	MMAO	1000	0	40	30	0.021	40	111.05	22.51	4.93	135.4
2	MMAO	1000	0	30	30	0.055	110	125.10	61.08	2.05	134.4
3	MAO	1000	0	30	30	trace					
4	Et_2AlCl	1000	0	20	30	1.452	2900	78.96	33.46	2.36	135.4
5	Et_2AlCl	1000	0	30	30	1.213	2430	88.63	37.85	2.34	135.3
6	Et_2AlCl	1000	0	40	30	0.805	1610	53.98	14.47	3.73	135.1
7	Et_2AlCl	1000	0	50	30	0.264	530	63.94	7.41	8.63	134.9
8	Et_2AlCl	1000	0.1	20	30	2.482	4960	43.27	13.09	3.31	135.3
9	Et_2AlCl	2000	0.1	20	30	2.537	5070	55.89	14.21	3.93	135.8
10	Et_2AlCl	4000	0.1	20	30	3.526	7050	20.65	6.91	2.99	136.3
11	Et_2AlCl	8000	0.1	20	30	3.902	7800	32.24	11.23	2.87	135.8
12	Et_2AlCl	12000	0.1	20	30	4.132	8260	37.12	12.03	3.09	136.0
13	Et_2AlCl	16000	0.1	20	30	4.421	8840	31.08	10.93	2.84	135.9
14	Et_2AlCl	20000	0.1	20	30	4.218	8440	42.35	17.39	2.43	135.8
15	Et_2AlCl	24000	0.1	20	30	2.999	6000	67.28	18.53	3.63	135.9
16	Et_2AlCl	16000	0.1	20	10	2.729	16370	32.56	10.13	3.21	135.7
17	Et_2AlCl	16000	0.1	20	20	3.598	10790	35.51	12.95	2.74	136.0

[a] Conditions: 1 μmol of [V] per run, 100 mL of toluene, 10 bar of ethylene.

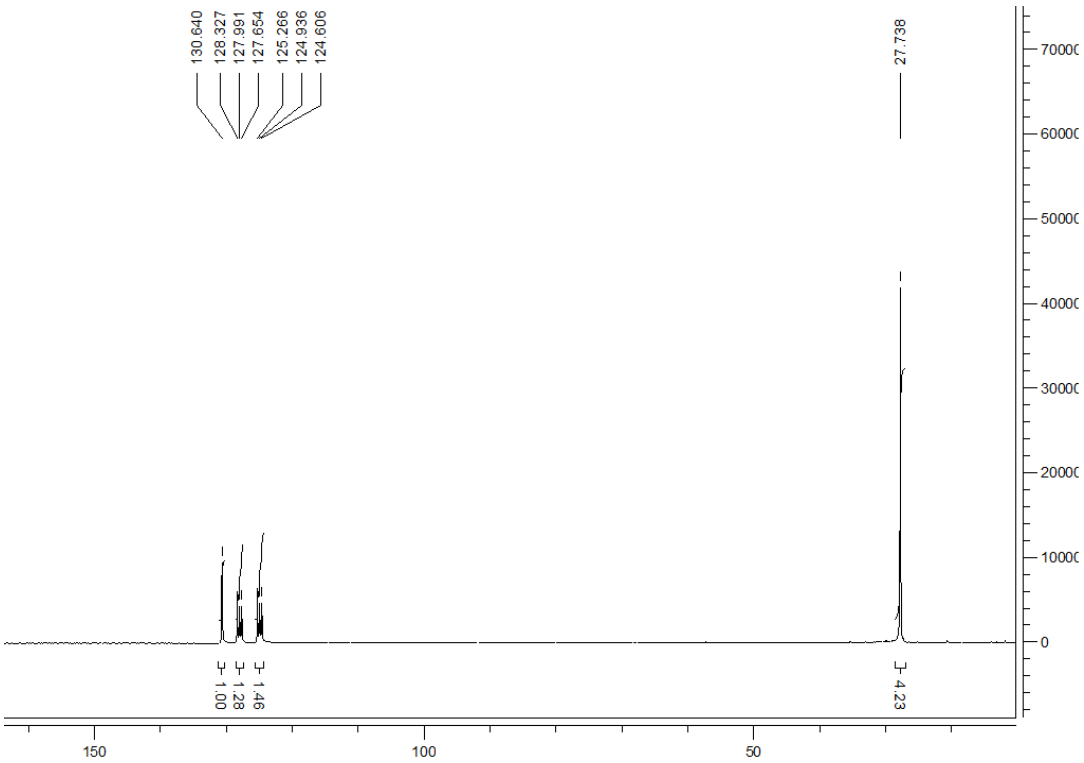

Figure S10. ^{13}C NMR of polyethylene samples from Table S1, run 7 (T_m = 130.47 °C).

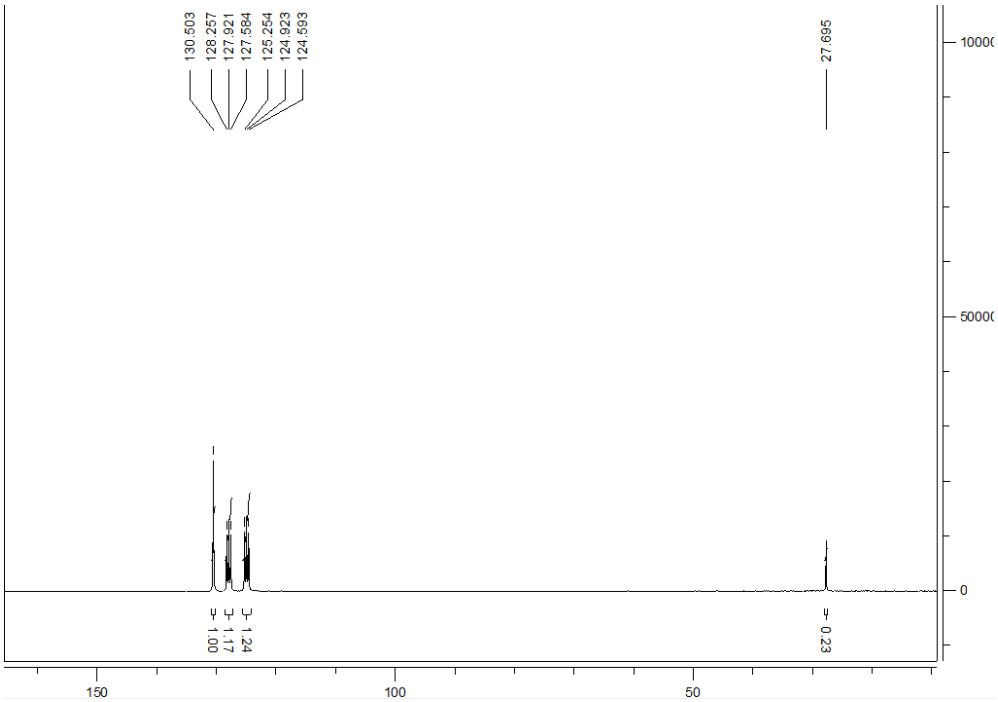

Figure S11. ^{13}C NMR of polyethylene (in 1,2-dichlorobenzene) samples from Table 5, run 11 (T_m = 122.6 ^oC).