Electronic Supplementary Material (ESI) for Dalton Transactions

Supplementary Information:

Strong NH···S hydrogen bonds in molybdoenzyme models containing anilide moieties

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X-ray analysis

Single crystal of *N*-phenyl-2,3-bis(pivaloylthio)benzamide was selected carefully and mounted in a loop with Nujol, which was frozen immediately in a stream of cold nitrogen at 200 K. Data collection was made on a Rigaku RAXIS-RAPID Imaging Plate diffractometer with graphite monochromated Mo-Kα radiation (0.71075 Å). The structures were solved by SIR92[1] and expanded by Fourier technique using SHELXL-97.[2] All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed at the calculated positions using the riding model.

References

1. A. Altomare, M. C. Burla, M. Camalli, M. Cascarano, C. Giacovazzo, A. Guagliardi and G. Polidori, *J. Appl. Crystallogr.*, 1994, **27**, 435.
2. G. M. Sheldrick, *Acta Cryst.*, 2008, **A64**, 112-122.

Table S1 Crystallographic data for 2,3-(*t*-BuCOS)$_2$C$_6$H$_3$CONHPh

	2,3-(*t*-BuCOS)$_2$C$_6$H$_3$CONHPh
empirical formula	$C_{23}H_{27}NO_3S_2$
formula weight	429.58
color	colorless
crystal system	monoclinic
a, Å	14.012(5)
b, Å	11.196(3)
c, Å	17.900(5)
β, deg	123.857(13)
V, Å^3	2332(1)
space group	$P2_1/c$
Z	4
D_{calc}, g/cm^3	1.224
F (000)	912
μ (MoKα), mm^{-1}	0.251
Scan type	ω
$2\theta_{max}$, deg	55
No. of Reflections unique	5334
No. Variables	266
$R1^a$ (I > 2σ(I)), w$R2^b$ (all data)	0.0424, 0.1108
GOF	1.037
CCDC number	917686

$^aR1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. $^bwR2 = \{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$

Table S2 ^{1}H NMR chemical shifts for the anion parts of **1**–**4** in acetonitrile-d_3 at 30 °C

	1	**2**	difference	**3**	**4**	difference
4-H	7.77	7.47	0.30	7.60	7.26	0.34
5-H	6.92	6.82	0.10	6.74	6.55	0.19
6-H	7.60	7.43	0.17	7.40	7.14	0.26
NH	11.3	11.0	0.3	9.08	8.63	0.45
o-H	7.85	7.18	0.67	—	—	—
m-H	7.41	7.18	0.23	—	—	—
p-H	7.13	6.96	0.17	—	—	—
t-Bu	—	—	—	1.45	1.16	0.29

Table S3 Geometrical and electrostatic parameters of the optimized structures for *trans*-**1** and *cis*-**1**

	trans-**1**	*cis*-**1**	
Mo=O, Å	1.7002	1.7002	
bond index[a]	1.9954	1.9946	
bond order[b]	0.9056	0.9055	
Mo–S1(S3), Å	2.4329	2.4393	2.4378
bond index	0.7203	0.7106	0.7163
bond order	0.5656	0.5619	0.5637
Mo–S2(S4), Å	2.4246	2.4190	2.4203
bond index	0.8141	0.8234	0.8206
bond order	0.5909	0.5944	0.5933
S1–C1(S3–C3), Å	1.7853	1.7857	1.7857
bond index	1.0866	1.0858	1.0846
bond order	0.8449	0.8444	0.844
S2–C2(S4–C4), Å	1.7833	1.7838	1.7832
bond index	1.0761	1.0761	1.0772
bond order	0.8427	0.8422	0.8431
NH···S, Å	2.0507	2.0490	2.0605
bond index	0.1114	0.1123	0.1082
bond order	0.1498	0.1508	0.1459
natural charge			
Mo	0.65512	0.65359	
O	-0.53531	-0.5357	
S1(S3)	-0.19381	-0.20411	-0.20435
S2(S4)	-0.18424	-0.17387	-0.1742
C1(C3)	-0.18436	-0.15925	-0.16002
C2(C4)	-0.16052	-0.18551	-0.18556
energy level/a.u.			
LUMO	0.13486	0.13587	
HOMO	0.02130	0.02212	
gap/a.u.	0.11356	0.11375	
kcal·mol^{-1}	71.260	71.379	
total energy			
E(RB+HF-LYP)/a.u.	-6904.232680	-6904.231831	
difference/a.u.	-0.000851		
kcal·mol^{-1}	-0.534		

[a]Wiberg bond index. [b]Atom-atom overlap-weighted NAO bond order.

Table S4 Geometrical and electrostatic parameters of the optimized structures for **2**

	2	
O1–Mo–O2, deg	103.71	
Mo=O1(O2), Å	1.7315	1.7316
bond index[a]	1.7760	1.7754
bond order[b]	0.8134	0.8131
Mo–S1(S3), Å	2.6912	2.6896
bond index	0.4623	0.4641
bond order	0.4051	0.4060
Mo–S2(S4), Å	2.4579	2.4580
bond index	0.8021	0.8024
bond order	0.5574	0.5576
difference Mo-S, Å	0.2333	0.2316
S1–C1(S3–C3), Å	1.7530	1.7533
bond index	1.1812	1.1803
bond order	0.9112	0.9106
S2–C2(S4–C4), Å	1.7742	1.7742
bond index	1.0891	1.0892
bond order	0.8491	0.8492
NH···S, Å	2.0495	2.0514
bond index	0.1178	0.1171
bond order	0.1536	0.1528
natural charge		
Mo	1.15059	
O1(O2)	-0.56158	-0.56170
S1(S3)	-0.21082	-0.21091
S2(S4)	-0.11558	-0.11558
C1(C3)	-0.16229	-0.16223
C2(C4)	-0.19383	-0.19376

[a]Wiberg bond index|. [b]Atom-atom overlap-weighted NAO bond order.

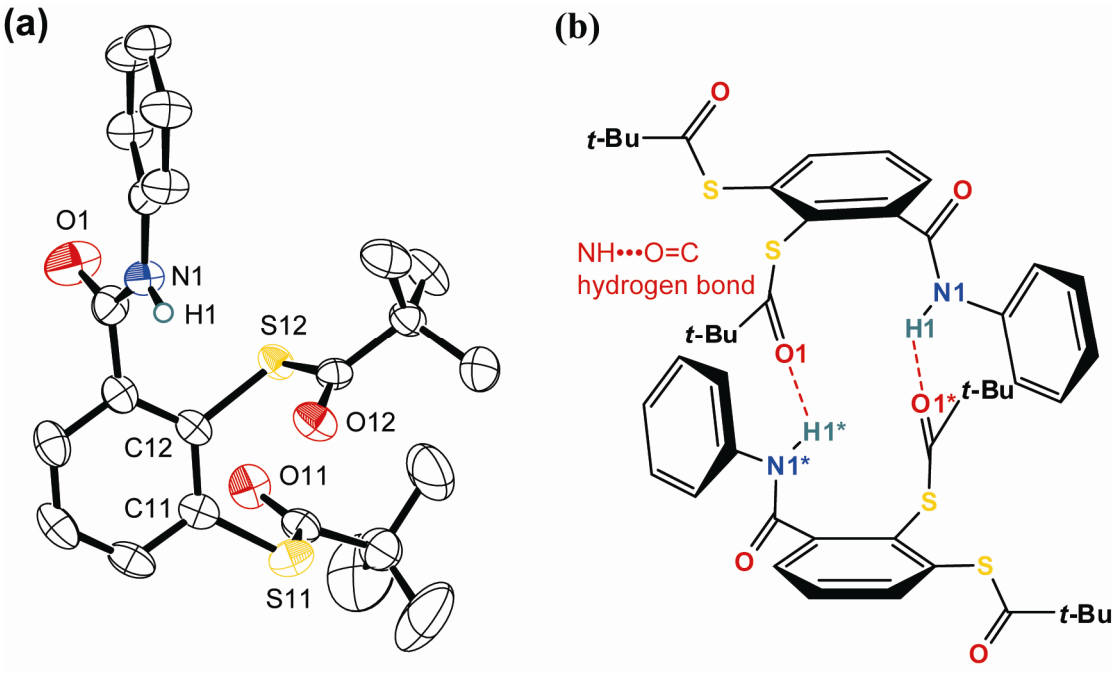

Fig. S1 Molecular structure of 2,3-(*t*-BuCOS)$_2$C$_6$H$_3$CONHPh (a) and illustration of intermolecular NH···O=C hydrogen bonds (b).

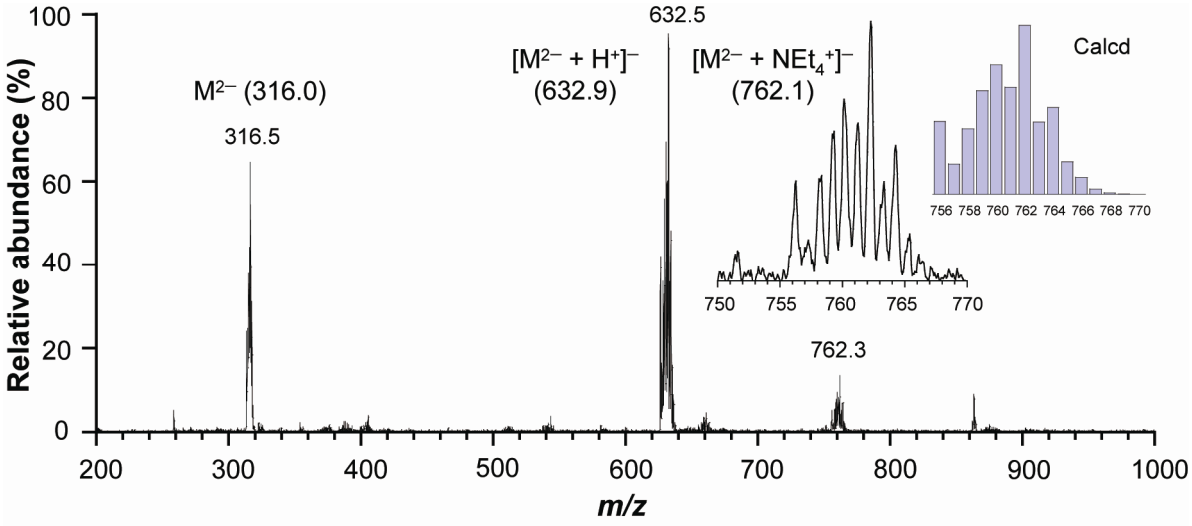

Fig. S2 ESI-MS spectrum of $(NEt_4)_2[Mo^{IV}O(1,2\text{-}S_2\text{-}3\text{-}PhNHCOC_6H_3)_2]$ (**1**) in acetonitrile, where M^{2-} = $[MoO(1,2\text{-}S_2\text{-}3\text{-}PhNHCOC_6H_3)_2]^{2-}$. Calculated values are shown in the parentheses. The enlarged spectrum is the peak at m/z 762.3, accompanying simulated isotope pattern.

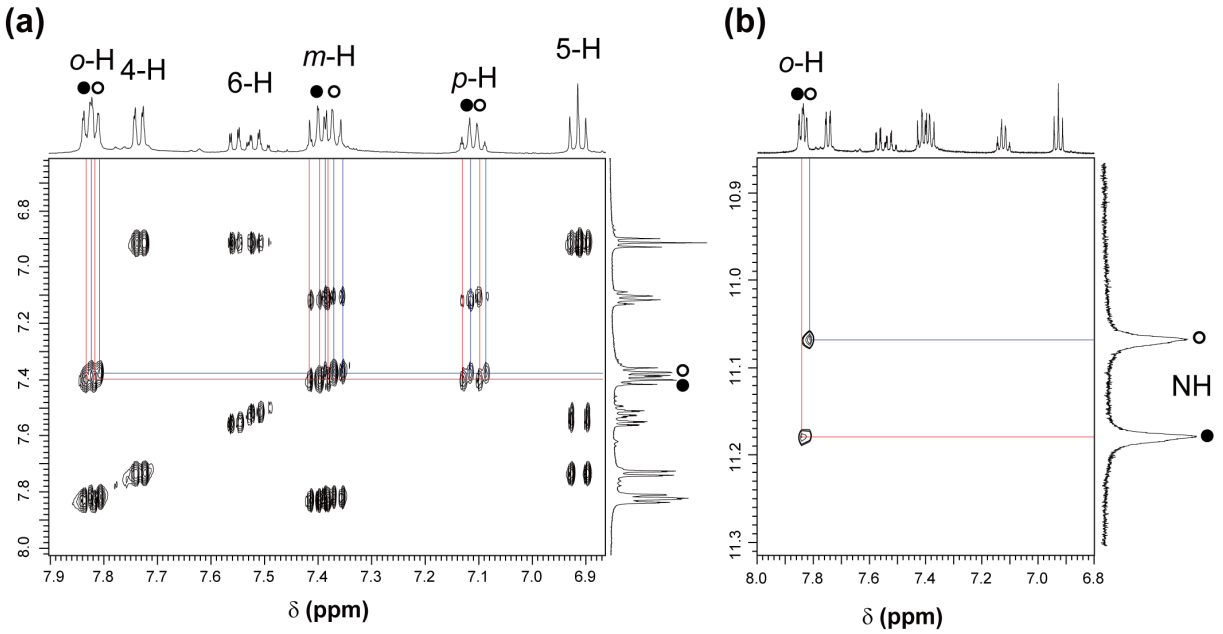

Fig. S3 (a) ^{1}H-^{1}H gCOSY and (b) NOESY spectra of **1** in acetonitrile-d_3 at −30 °C.

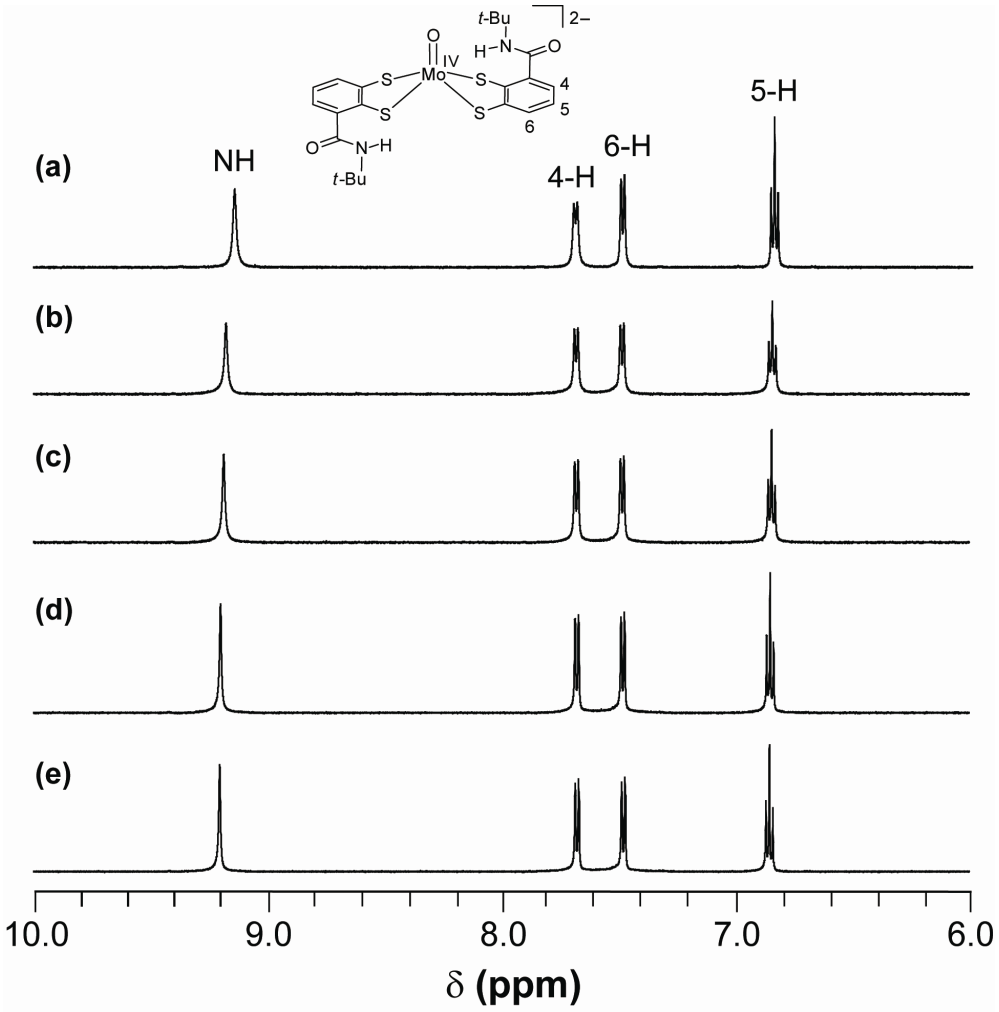

Fig. S4 ^{1}H NMR spectra of $(NEt_4)_2[Mo^{IV}O(1,2\text{-}S_2\text{-}3\text{-}t\text{-}BuNHCOC_6H_3)_2]$ (*trans*-**3**) in acetonitrile-d_3 at (a) 30, (b) 0, (c) −10, (d) −30, and (e) −40 °C.

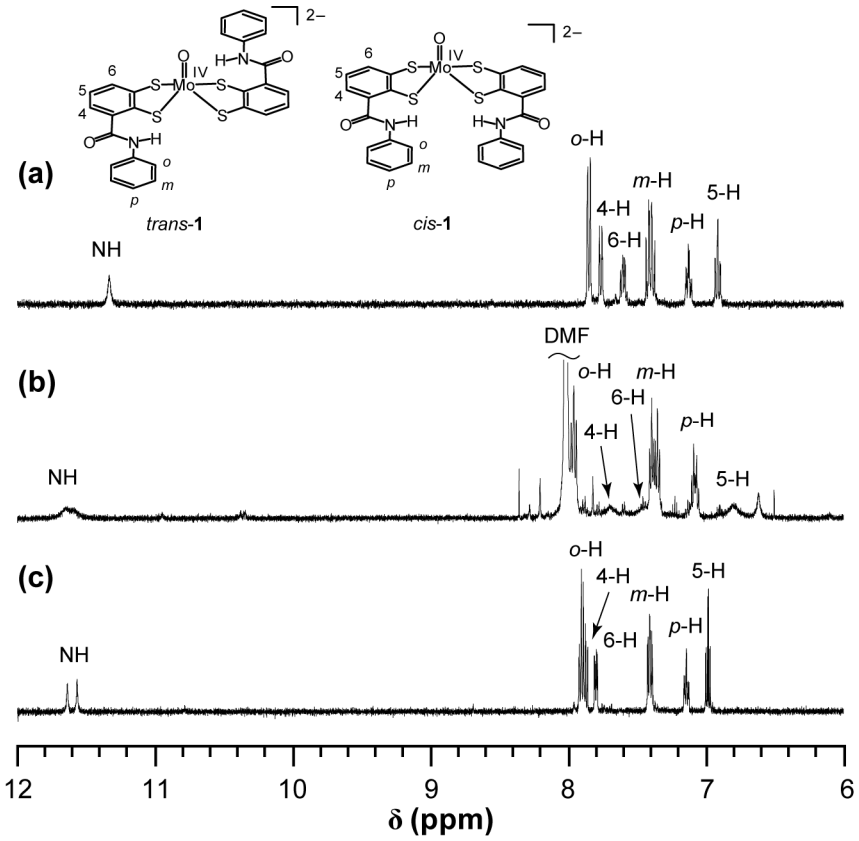

Fig. S5 ^{1}H NMR spectra of $(NEt_4)_2[Mo^{IV}O(1,2\text{-}S_2\text{-}3\text{-}PhNHCOC_6H_3)_2]$ (**1**) in (a) acetonitrile-d_3, (b) DMF-d_7, and (c) dichloromethane-d_2 at 30 °C.

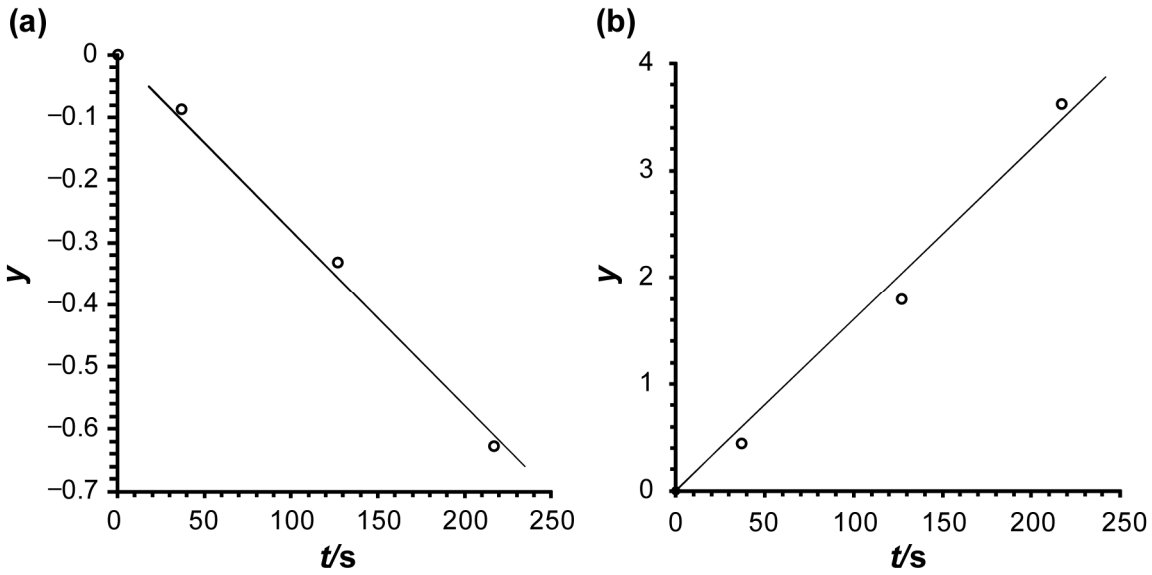

Fig. S6 (a) Pseudo-first- and (b) second-order kinetics of the reaction between **1** and Me_3NO to **2** in DMF at 27 °C ([Mo] = 1 mM, $[Me_3NO]$ = 2 mM). The fitting lines are $y = \ln(1\text{-}[Mo^{VI}O_2]/[Mo^{IV}O]_0) = -k_{obs} \cdot t$, where k_{obs} equals 31×10^{-4} s^{-1} for (a) and $y = 10^{-2}\cdot\{1/([Mo^{IV}O]_0-[Me_3NO]_0)\} \cdot\ln\{([Mo^{IV}O][Me_3NO]_0)/([Mo^{IV}O]_0[Me_3NO])\} = 10^{-2}\cdot k_2\cdot t$, where k_2 equals 2.12 for (b).

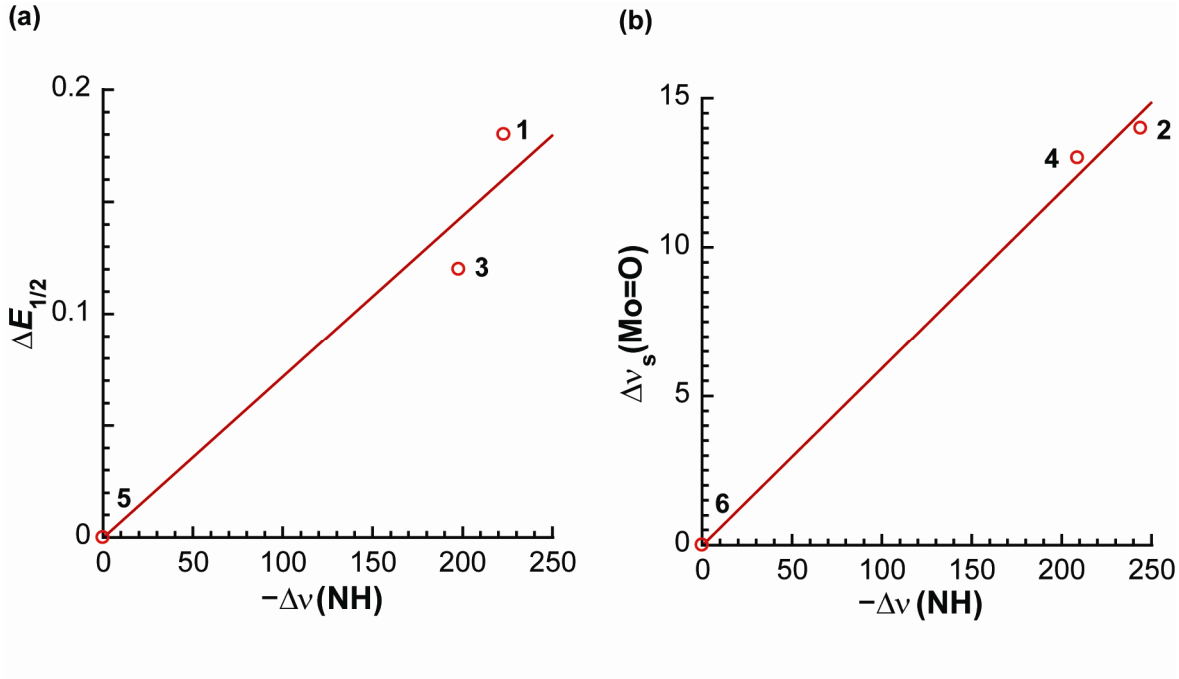

Fig. S7 Correlation (a) between Δν(NH) and $\Delta E_{1/2}$ in the monooxomolybdenum(IV) complexes and (b) between Δν(NH) and $\Delta\nu_s$(Mo=O) in the dioxomolybdenum(VI) complexes. The original data are shown in Tables 1 and 2.