Supplementary Information:

Efficient uptake of dimethyl sulfoxide by desoxomolybdenum(IV) dithiolate complex containing bulky hydrophobic groups

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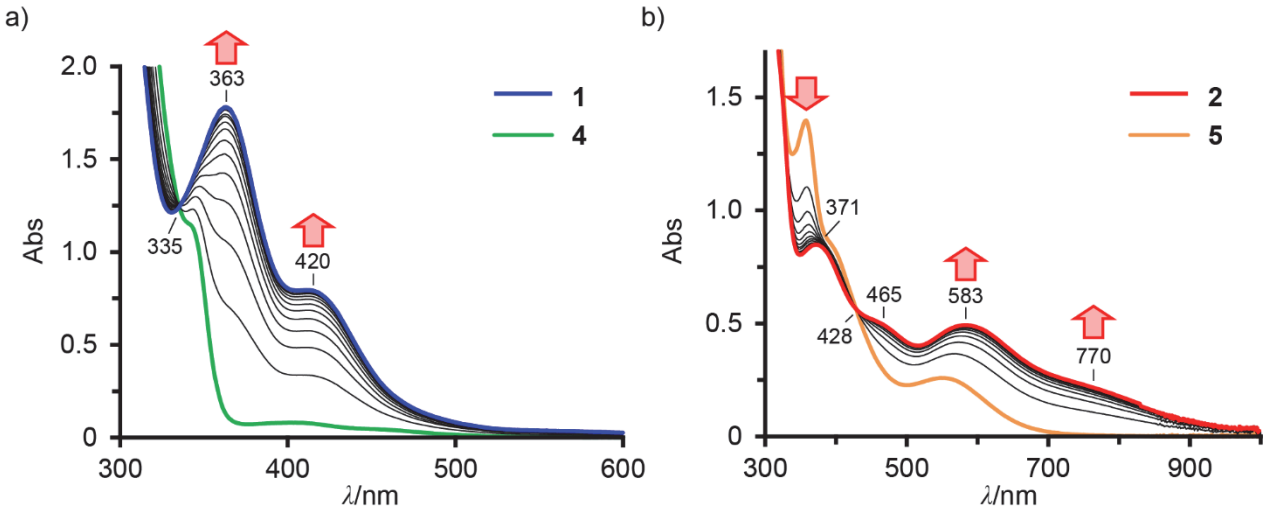

Fig. S1 UV-vis spectral change (measured every 30 min.) of the reaction of a 1 mM solution of (a) **4** (green) and (b) **5** (orange) with 1.7 eq. of ^{t}BuPh$_2$SiCl in toluene at 27 °C to afford **1** (blue) and **2** (red), respectively.

Table S1 Crystallographic Data for **1** and **3**

	1·5CH$_3$CN·2H$_2$O	**3**·7/2CH$_3$CN·5/2H$_2$O^c
empirical formula	$C_{174}H_{222}MoN_{10}O_7S_4Si$	$C_{171}H_{218.5}N_{8.5}O_{8.5}S_4SiW$
formula weight	2817.87	2869.33
color	green	dark purple
crystal system	monoclinic	triclinic
a, Å	18.8827(13)	18.246(3)
b, Å	23.9699(18)	20.495(4)
c, Å	20.0864 (14)	26.099(4)
α, deg		93.493(7)
β, deg	102.832(7)	104.138(7)
γ, deg		90.070(6)
V, Å^3	8864.4(11)	9445(3)
space group	$P2_1/c$	$P\bar{1}$
Z	2	2
D_{calc}, g/cm^3	1.056	1.009
F (000)	3024	3048
μ(MoKα), mm^{-1}	0.181	0.711
scan type	ω	ω
2θ$_{max}$, deg	50	50
No. of reflections unique	15579	33198
No. variables	1206	1790
residuals; $R1^a$ (I > 2σ(I)),w$R2^b$ (all data)	0.0908, 0.3094	0.1028, 0.2707
GOF	0.966	1.002

$^a R1 = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$. $^b wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]\}^{1/2}$. ^{c}Not all solvent was detected.

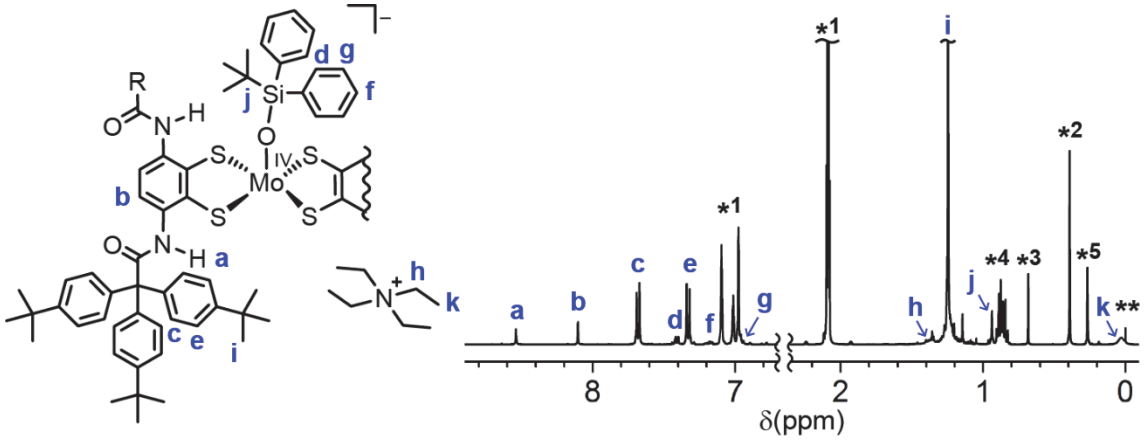

Fig. S2 ^{1}H NMR spectrum of **1** in toluene-d_8 at 30 °C. The asterisks denote solvents as a contaminant (*1: toluene; *2: water; *3: acetonitrile; *4: petroleum ether; *5: silicone grease). The double asterisk (**) denotes TMS.

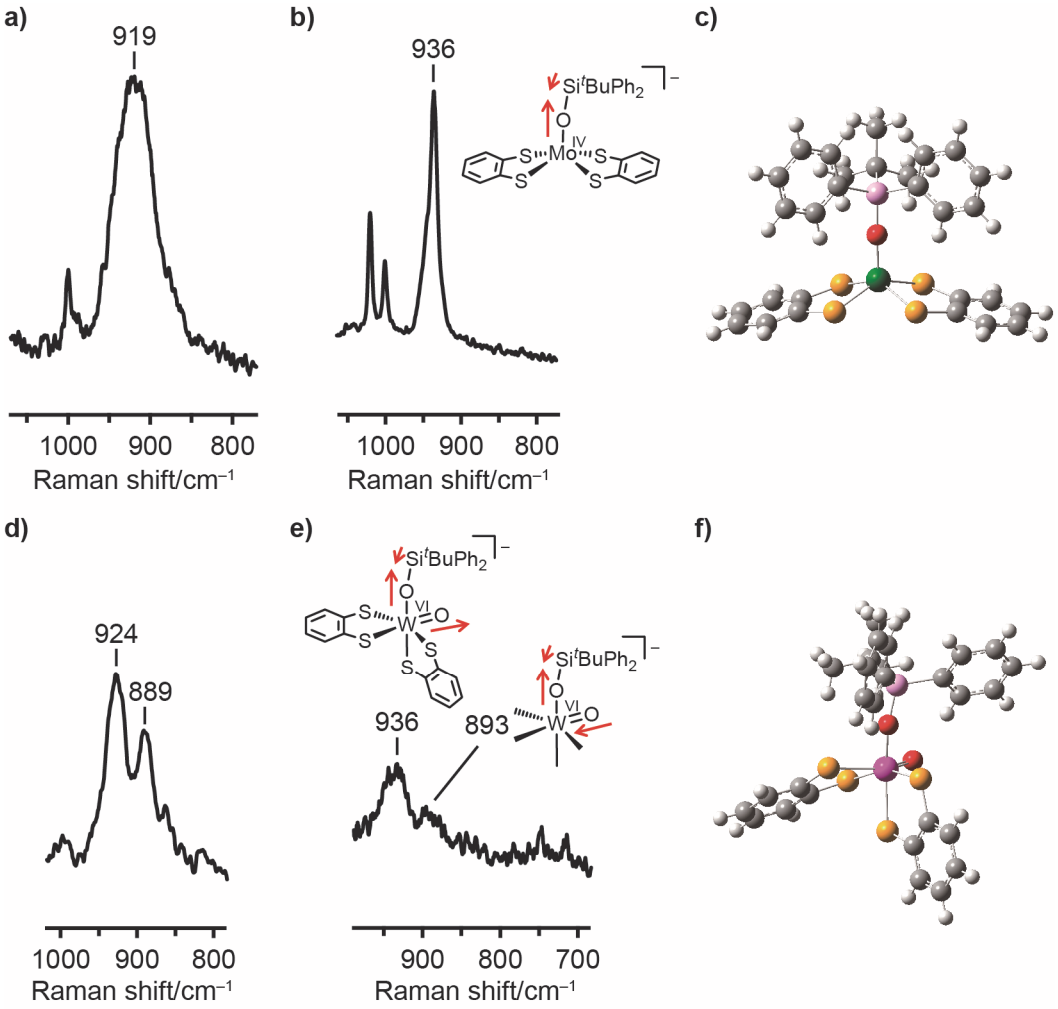

Fig. S3 Resonance Raman spectra of (a) **1**, (b) $(Et_4N)[Mo^{IV}(OSi^tBuPh_2)(bdt)_2]$, (d) **3**, (e) $(Et_4N)[W^{VI}O(OSi^tBuPh_2)(bdt)_2]$ excited at 514.5 nm in the solid state. The optimized structures using DFT calculations of (c) $(Et_4N)[Mo^{IV}(OSi^tBuPh_2)(bdt)_2]$ and (f) $(Et_4N)[W^{VI}O(OSi^tBuPh_2)(bdt)_2]$. The vibrational mode was illustrated in (b) and (e).

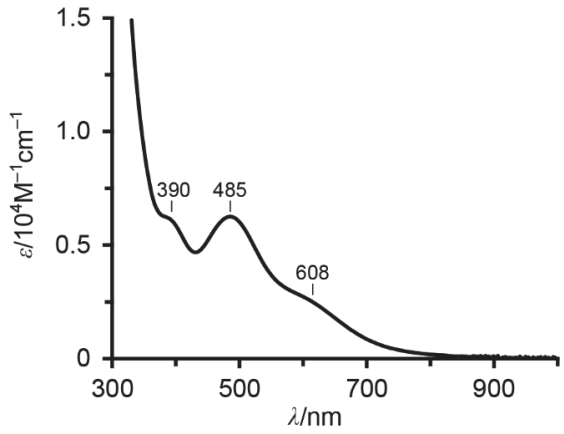

Fig. S4 UV-vis spectra of **3** in toluene at 27 °C.

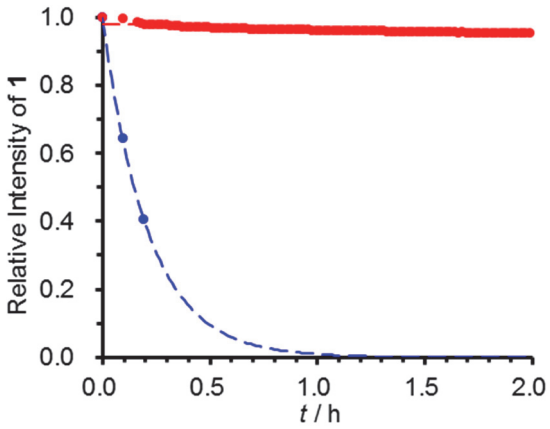

Fig. S5 Stability of **1** in an aqueous micellar solution (red) and DMF (blue) monitored by absorption at 418 nm using UV-vis spectroscopy at 27 °C.

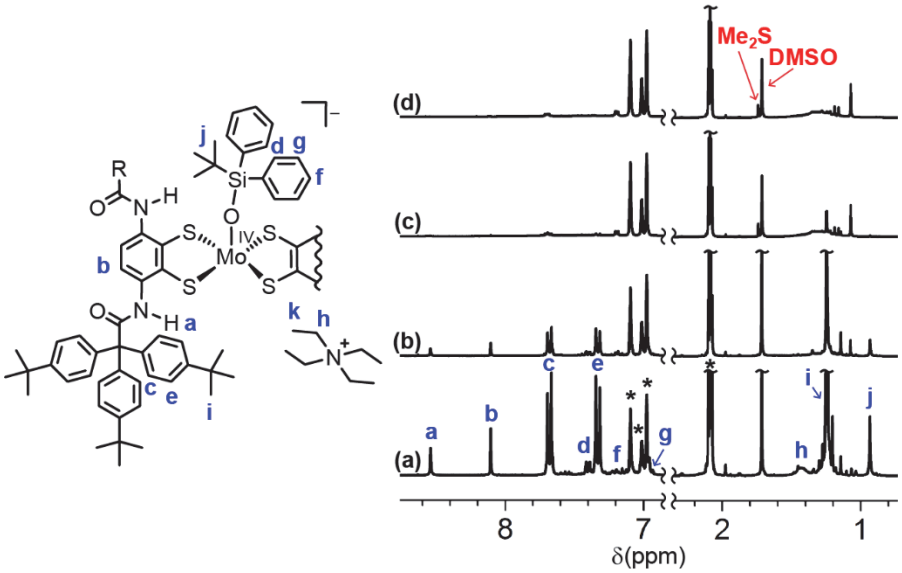

Fig. S6 NMR spectral change during the reaction of **1** and 5 eq. of DMSO in toluene-d_8. (a) 0 h, (b) 24 h, (c) 294 h, (d) 576 h. The asterisk (*) denotes toluene.

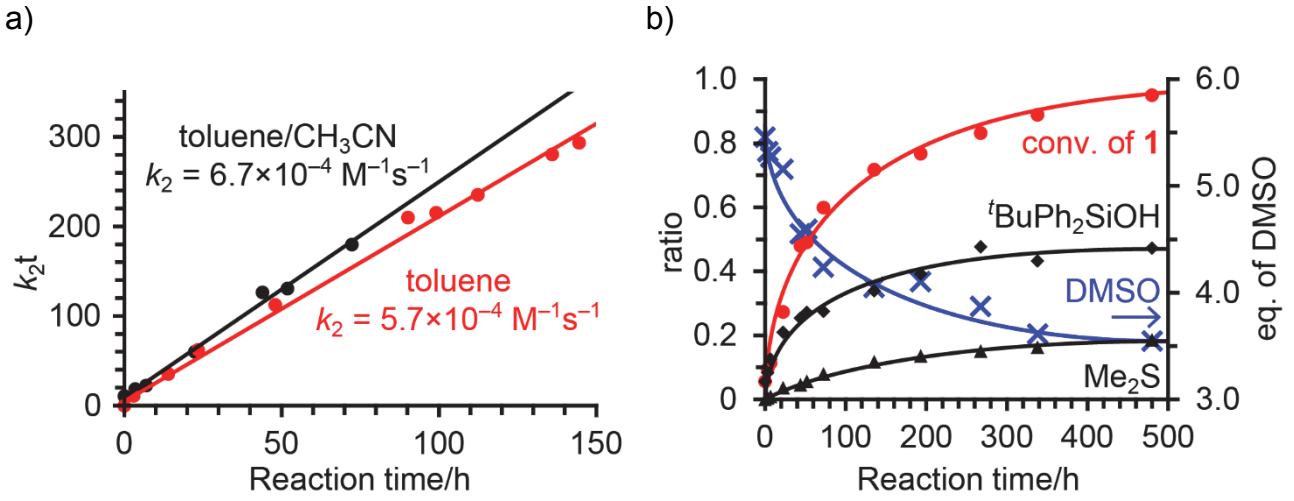

Fig. S7 (a) Kinetic plot of the reduction of DMSO. (b) Time course of the conversion of **1** during the reduction of DMSO in a mixture of toluene-d_8 and acetonitrile-d_3 (v/v = 1/1).

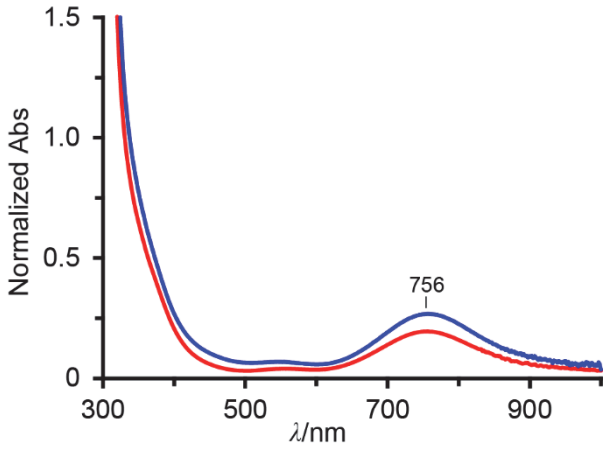

Fig. S8 UV-vis spectra of the reaction mixture of **1** and DMSO in toluene (red) and the in-situ generated monooxomolybdenum(V) complex (blue) in toluene at 27 °C.