

Supporting Information:

Systematic Investigation of Relationship between Strength of NH···S Hydrogen Bond and Reactivity of Molybdoenzyme Models

Taka-aki Okamura, Yasuhito Ushijima, Yui Omi, and Kiyotaka Onitsuka*

Department of Macromolecular Science, Graduate School of Science, Osaka University, Toyonaka,
Osaka 560-0043, Japan

E-mail: tokamura@chem.sci.osaka-u.ac.jp

Table S1. Crystallographic Data for 2,3-(*i*-PrS)₂C₆H₃NHCON₃ (**1**) and 2,3-(*i*-PrS)₂C₆H₃NHCOR (R = CH₃ (**3a**), *t*-Bu (**3b**), CPh₃ (**3d**)))

	1	3a	3b	3d
empirical formula	C ₁₃ H ₁₈ N ₄ OS ₂	C ₁₄ H ₂₁ NOS ₂	C ₁₇ H ₂₇ NOS ₂	C ₃₂ H ₃₃ NOS ₂
formula weight	310.43	283.45	325.53	511.74
color	colorless	colorless	colorless	colorless
crystal system	orthorhombic	monoclinic	monoclinic	monoclinic
<i>a</i> , Å	17.893(5)	16.100(5)	20.503(5)	7.7754(13)
<i>b</i> , Å	9.440(2)	9.371(3)	11.373(3)	15.348(2)
<i>c</i> , Å	18.631(5)	10.051(3)	16.802(4)	45.162(6)
β, deg	90	95.505(13)	108.502(11)	92.095(5)
<i>V</i> , Å ³	3147.1(15)	1509.4(7)	3715.5(15)	5385.9(13)
space group	<i>Pbcn</i>	<i>P2</i> ₁ / <i>c</i>	<i>C2</i> / <i>c</i>	<i>P2</i> ₁ / <i>n</i>
<i>Z</i>	8	4	8	8
<i>D</i> _{calc} , g/cm ³	1.310	1.247	1.164	1.262
<i>F</i> (000)	1312	608	1408	2176
μ(MoKα), mm ⁻¹	0.340	0.342	0.286	0.224
Scan type	ω	ω	ω	ω
2θ _{max} , deg	55	55	55	55
No. of Reflections unique	3600	3451	4237	12290
No. Variables	184	167	190	655
residuals; <i>R</i> 1 ^a (<i>I</i> > 2σ(<i>I</i>)), w <i>R</i> 2 ^b (all data)	0.0497, 0.1399	0.0477, 0.1440	0.0687, 0.2148	0.0633, 0.1786
GOF	1.070	1.058	1.073	1.025

^a*R*1 = Σ||*F*_o|| - |*F*_c||/Σ|*F*_o||. ^bw*R*2 = {Σ[w(*F*_o²-*F*_c²)²]/Σ[w(*F*_o²)²]}^{1/2}

Table S2. IR Bands of v(NH) (cm⁻¹) in the Thioether (**3a–3e**) Compared with the Corresponding Disulfide, (S-2-RCONHC₆H₄)₂

	R	3-RCONHC ₆ H ₄ (S- <i>i</i> -Pr) ₂ ^a	(S-2-RCONHC ₆ H ₄) ₂ ^b	Δv(NH)
3a	CH ₃	3338	3382	-44
3b	<i>t</i> -Bu	3343	3397	-54
3c	CF ₃	3286	3358	-72
3d	CPh ₃	3293	3341	-48
3e	C(C ₆ H ₄ -4- <i>t</i> -Bu) ₃	3294	3342	-48

^a In CH₂Cl₂ (2.5 mM). ^b In CH₂Cl₂ (10 mM).

Table S3. Geometric and Electrostatic Parameters of the Optimized Structures for *trans*-**5b**, *cis*-**5b**, and **8**

	<i>trans</i> - 5b	<i>cis</i> - 5b	8
O–Mo–S1, deg	106.61	107.18	107.00
O–Mo–S2, deg	107.70	106.93	107.13
Mo=O, Å	1.7009	1.7006	1.7041
bond index ^a	1.9945	1.9952	1.9774
bond order ^b	0.9048	0.9051	0.9014
Mo–S1 ^c , Å	2.4449	2.4450	2.4497
bond index	0.7318	0.7250	0.7814
bond order	0.5659	0.5632	0.5774
Mo–S2, Å	2.4415	2.4369	2.4497
bond index	0.8027	0.8087	0.7820
bond order	0.5843	0.5867	0.5776
S1–C1, Å	1.7838	1.7841	1.7784
bond index	1.0698	1.0693	1.0872
bond order	0.8415	0.8411	0.8500
S2–C2, Å	1.7811	1.7810	1.7785
bond index	1.0794	1.0800	1.0870
bond order	0.8445	0.8447	0.8498
NH···S, Å	2.2835	2.2853	—
bond index	0.0517	0.0517	—
bond order	0.0779	0.0778	—
natural charge			
Mo	0.65480	0.65510	0.62576
O	-0.54174	-0.54118	-0.55817
S1	-0.23650	-0.24536	-0.20618
S2	-0.19451	-0.18588	-0.20616
C1	-0.20271	-0.20183	-0.18584
C2	-0.17876	-0.17967	-0.18580
energy level/a.u.			
LUMO	0.17570	0.17565	0.21272
HOMO	0.03668	0.03679	0.06563
gap/a.u. kcal·mol ⁻¹	0.13902 87.236	0.13886 87.136	0.14709 92.300
total energy			
E(RB+HF-LYP)/a.u.	-6756.638620	-6756.638465	
difference/a.u. kcal·mol ⁻¹	-0.000155 -0.097		

^aWiberg bond index. ^bAtom-atom overlap-weighted NAO bond order. ^cNumbers of the atoms are given in Figure S7.

Table S4. Geometric and Electrostatic Parameters of the Optimized Structures for **6b-A**, **6b-B**, and **9**

	6b-A	6b-B	9
O–Mo–O*, deg	103.36	102.72	103.04
O–Mo–S1, deg	88.25	88.89	88.67
O–Mo–S2, deg	109.10	110.43	109.73
O*–Mo–S1, deg	161.43	158.46	159.94
O*–Mo–S2, deg	84.18	81.06	82.28
Mo=O, Å	1.7331	1.7380	1.7383
bond index ^a	1.7714	1.7531	1.7501
bond order ^b	0.8110	0.8027	0.8040
Mo–S1 ^c , Å	2.6994	2.6543	2.6822
bond index	0.4831	0.5997	0.5580
bond order	0.4086	0.4505	0.4329
Mo–S2, Å	2.4737	2.4933	2.4874
bond index	0.7949	0.7013	0.7636
bond order	0.5512	0.5223	0.5403
difference Mo–S	0.2256	0.1610	0.1948
S1–C1, Å	1.7545	1.7498	1.7477
bond index	1.1539	1.1646	1.1759
bond order	0.9038	0.9061	0.9130
S2–C2, Å	1.7707	1.7697	1.7678
bond index	1.0921	1.0916	1.0994
bond order	0.8517	0.8554	0.8576
NH···S, Å	2.2694	2.2871	—
bond index	0.0591	0.0466	—
bond order	0.0848	0.0712	—
natural charge			
Mo	1.14817	1.13593	1.1149
O	-0.56684	-0.57310	-0.58246
S1	-0.25738	-0.18893	-0.20960
S2	-0.12336	-0.18007	-0.14145
C1	-0.20128	-0.18181	-0.18813
C2	-0.19145	-0.21464	-0.19766
total energy			
E(RB+HF-LYP)/a.u.	-6831.819597	-6831.811021	
difference/a.u.	-0.008576		
kcal·mol ⁻¹	-5.381		

^aWiberg bond index]. ^bAtom-atom overlap-weighted NAO bond order. ^cNumbers of the atoms are given in Figure S7.

Table S5. Distances (Å) and Angles (deg) of the Optimized Structures of the Me₃NO-Adducts

	8-ONMe ₃	<i>trans</i> -5b-ONMe ₃	<i>cis</i> -5b-ONMe ₃ ^a	7b-ONMe ₃	5c-ONMe ₃
Mo=O	1.6977	1.6953	1.6951	1.6932	1.6945
Mo–O(NMe ₃)	2.5314	2.4579	2.4885	2.4457	2.4383
Mo–O–N	136.24	137.23	136.29	138.10	137.70
Mo–S1	2.4938	2.4958	2.4758	2.4874	2.4992
Mo–S2	2.4713	2.4661	2.4811	2.4620	2.4659
Mo–S3	2.4971	2.4971	2.5089	2.4890	2.5000
Mo–S4	2.5046	2.5042	2.4865	2.4967	2.5042
O=Mo–S1	99.12067	97.85836	99.09066	98.00863	97.64485
O=Mo–S2	100.15185	100.03832	99.0619	99.43935	99.90749
O=Mo–S3	99.72773	98.64693	98.5268	98.72113	98.5198
O=Mo–S4	98.30788	97.554	98.01721	96.96839	97.27741

^a Mirror image of the structure shown in Figure S8 is indicated here for easy understanding in the comparison.

Scheme S1. Proposed Mechanism for the Formation of **1**

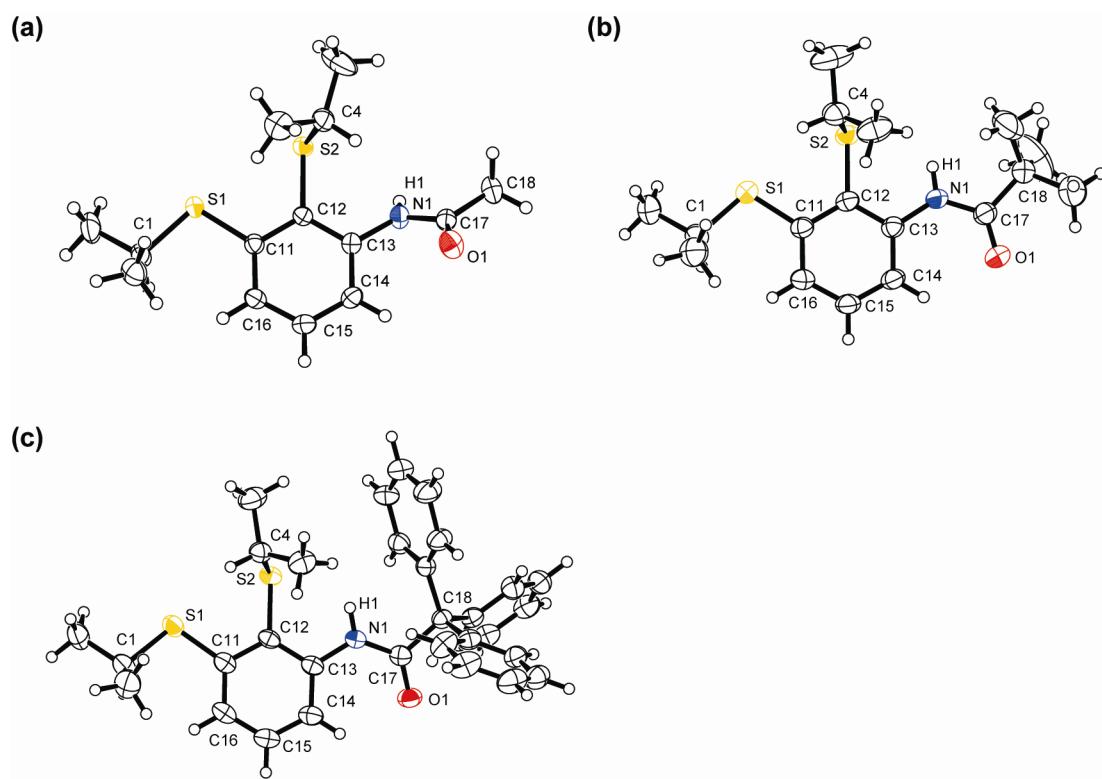
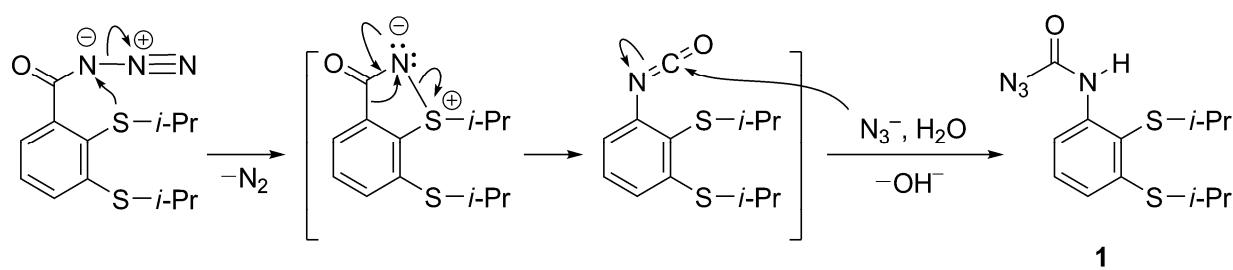


Figure S1. Molecular structure of (a) *N*-{2,3-bis(isopropylthio)phenyl}acetamide (**3a**), (b) *N*-{2,3-bis(isopropylthio)phenyl}pivalamide (**3b**), and (c) *N*-{2,3-bis(isopropylthio)phenyl}-2,2,2-triphenylacetamide (**3d**).

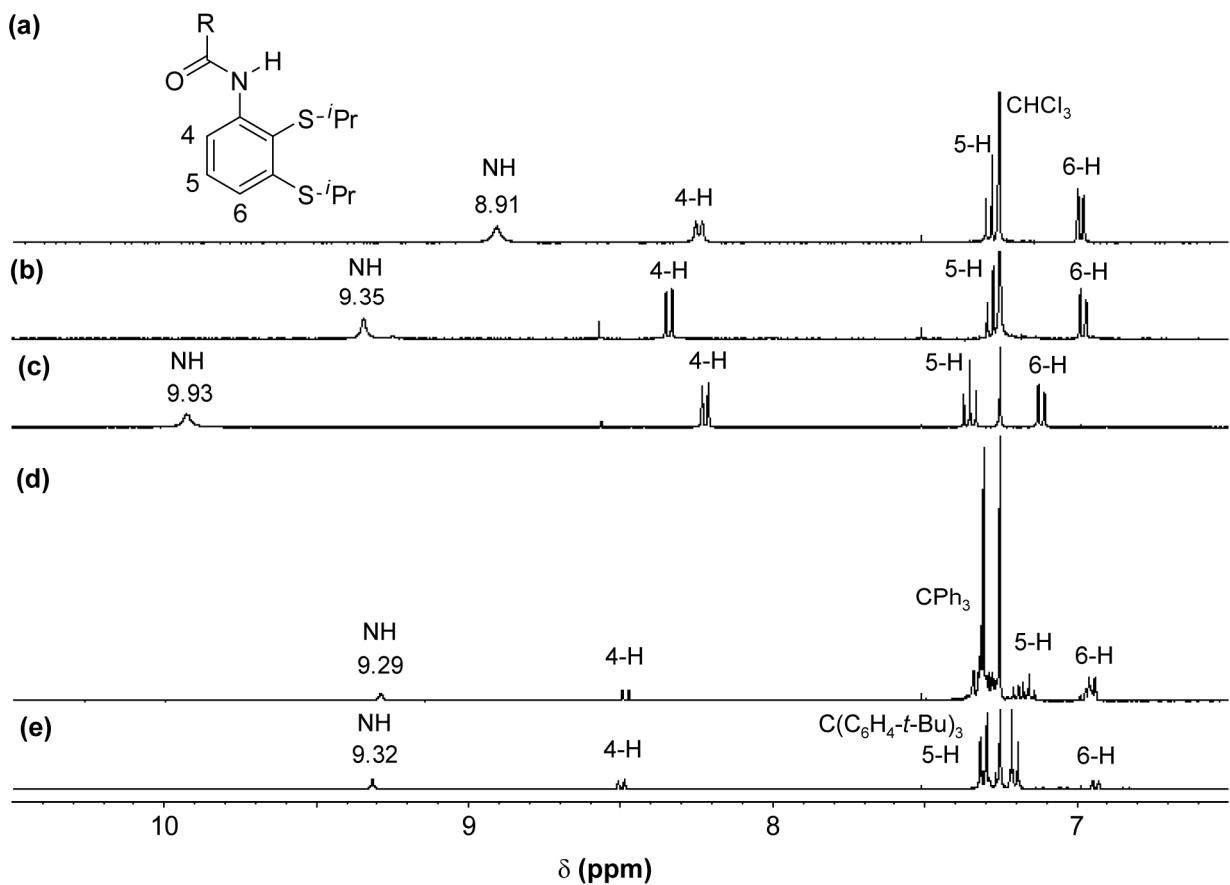


Figure S2. ^1H NMR spectra of (a) **3a**, (b) **3b**, (c) **3c**, (d) **3d**, and (e) **3e** in CDCl_3 at 30 °C.

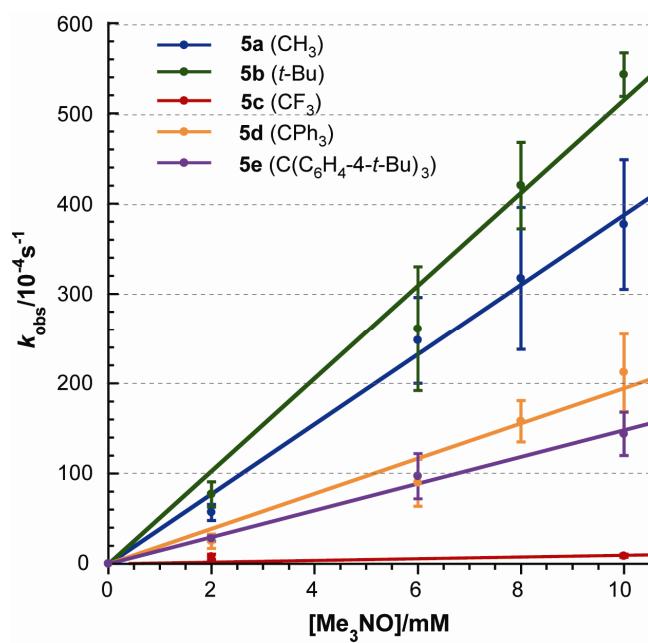


Figure S3. The dependence of k_{obs} on the concentration of the substrate Me_3NO in the reduction by **5a–5e**.

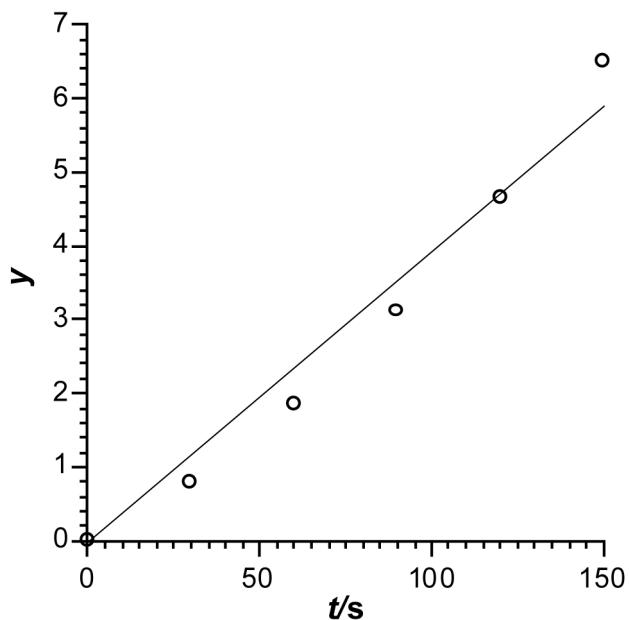


Figure S4. Second-order kinetics of the reaction between **5a** and Me₃NO to **6a** in DMF at 27 °C ([Mo] = 1 mM, [Me₃NO] = 2 mM). The fitting line is $y = 10^{-2} \cdot \{1/([Mo^{IV}O]_0 - [Me_3NO]_0)\} \cdot \ln \{([Mo^{IV}O][Me_3NO]_0)/([Mo^{IV}O]_0[Me_3NO])\} = 10^{-2} \cdot k_2 \cdot t$.

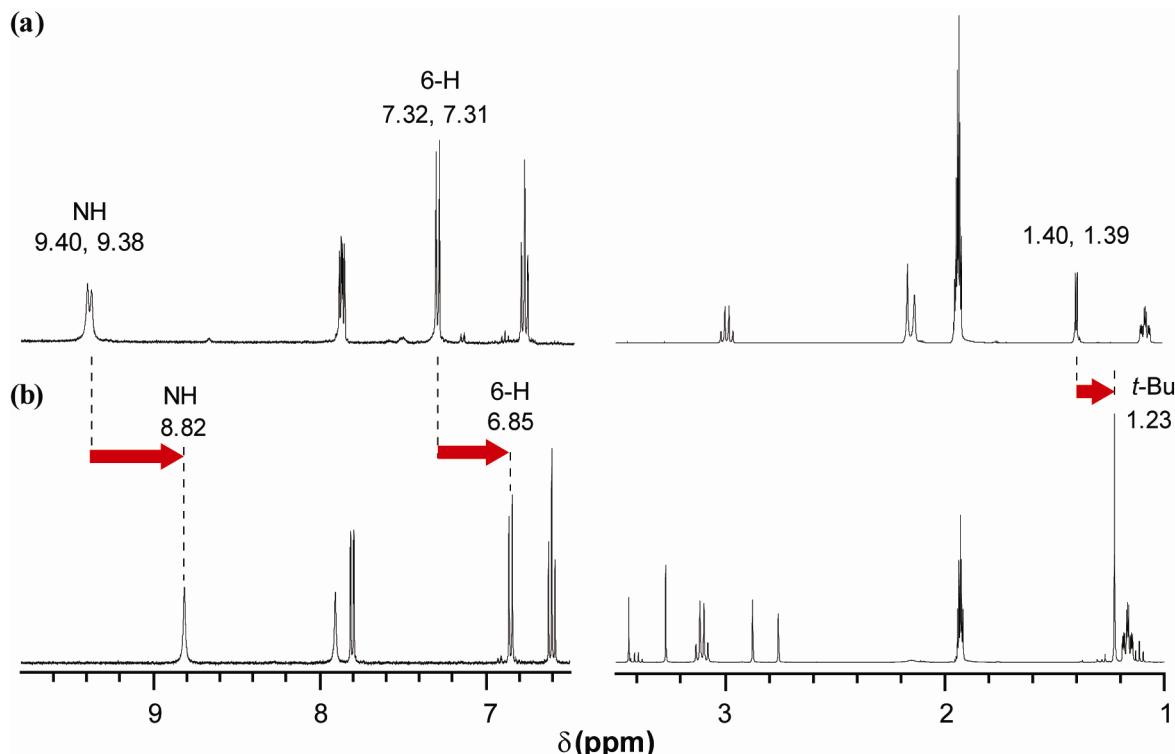


Figure S5. ¹H NMR spectra of (a) **5b** and (b) **6b** in CD₃CN at 30 °C.

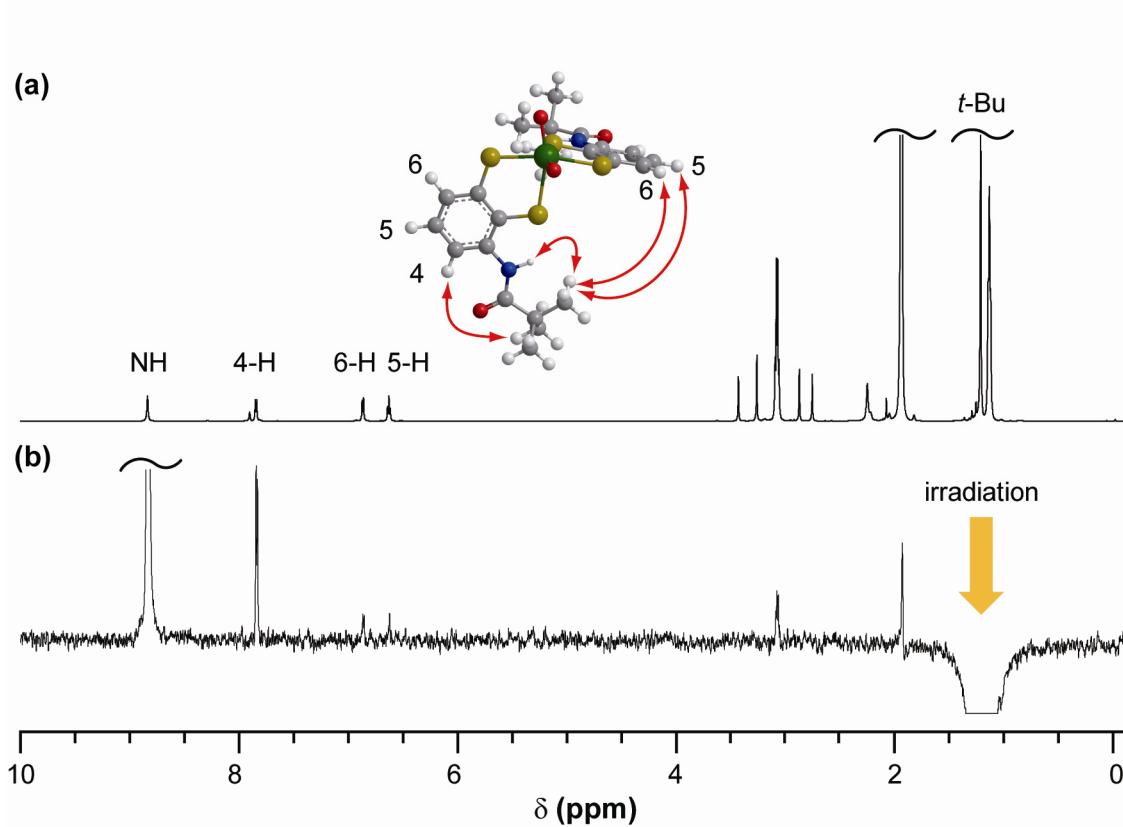


Figure S6. ^1H NMR (a) and GOESY (b) spectra of **6b** in CD_3CN at $-10\text{ }^\circ\text{C}$. The red arrows indicate the observed NOEs.

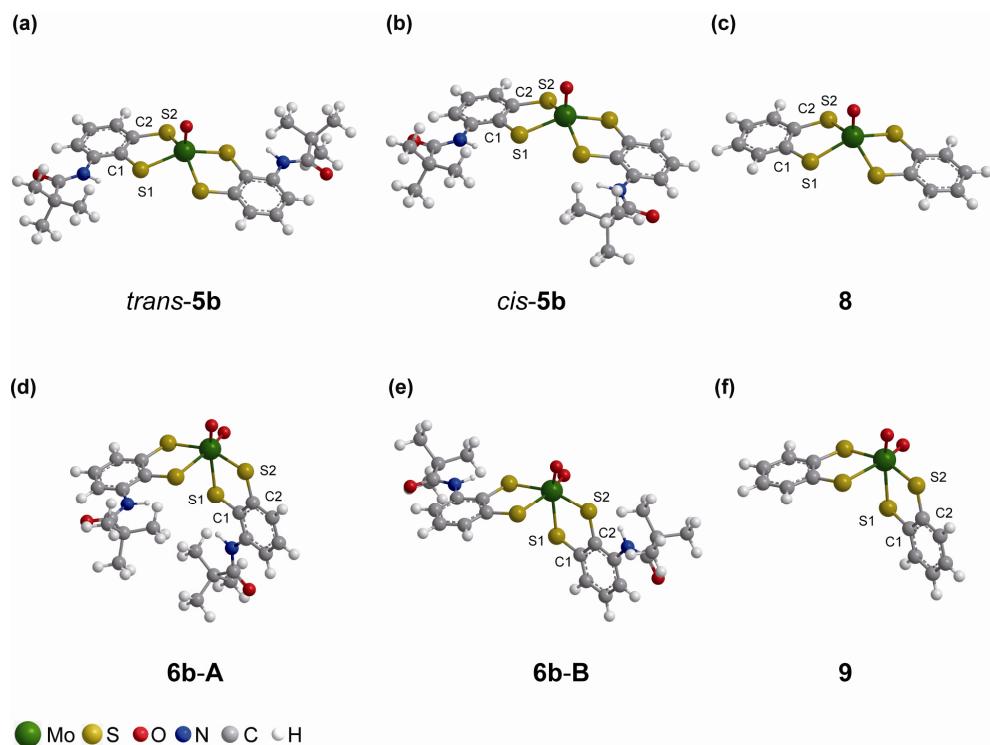


Figure S7. Optimized structures of (a) *trans*-**5b**, (b) *cis*-**5b**, (c) **8**, (d) **6b-A**, (e) **6b-B**, and (f) **9**.

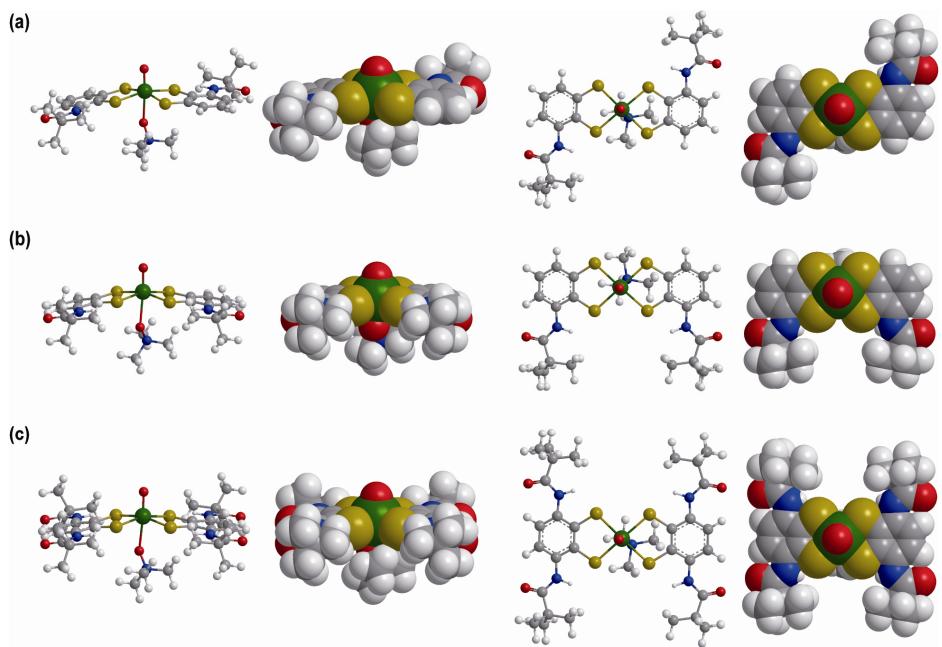


Figure S8. Optimized structures of the intermediates in the reaction between the monooxomolybdenum(IV) complexes and Me_3NO via the attack of Me_3NO molecule to the molybdenum center at the *trans* position to the oxo ligand. (a) $\text{trans}-[\text{MoO}(\text{ONMe}_3)(1,2-\text{S}_2-3-\text{t-BuCONHC}_6\text{H}_3)_2]^{2-}$ (*trans*-**5b**-ONMe₃), (b) $\text{cis}-[\text{MoO}(\text{ONMe}_3)(1,2-\text{S}_2-3-\text{t-BuCONHC}_6\text{H}_3)_2]^{2-}$ (*cis*-**5b**-ONMe₃), and (c) $[\text{MoO}(\text{ONMe}_3)\{1,2-\text{S}_2-3,6-(\text{t-BuCONH})_2\text{C}_6\text{H}_2\}_2]^{2-}$ (**7b**-ONMe₃). For each molecule, side and top views are shown using ball & stick and space filling models.

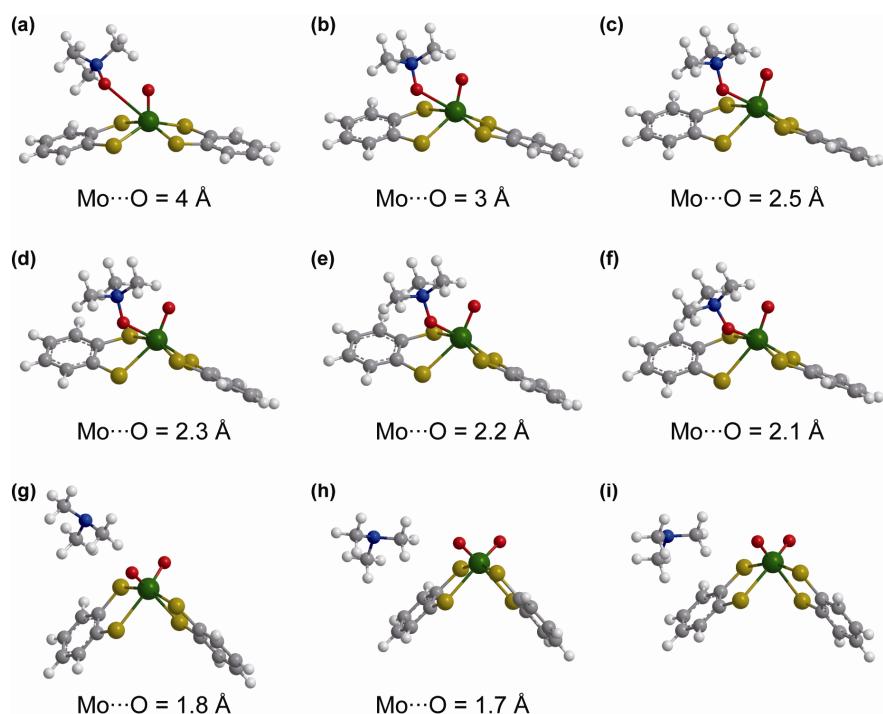


Figure S9. Optimized structures of the intermediates in the reaction between $[\text{Mo}^{\text{IV}}\text{O}(\text{bdt})_2]^{2-}$ and Me_3NO via *cis* attack of Me_3NO . The distances between Mo center and the oxygen atom ($\text{Mo}\cdots\text{O}$) of Me_3NO are shown below each molecular structure and were fixed during the optimization (a-h). The Me_3NO molecule was approached step by step from (a) to (h). (i) Re-optimized structure of (h) without constraint.