Supplementary Information:

Comparative studies on the contribution of NH···S hydrogen bonds in tungsten and molybdenum benzenedithiolate complexes

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Table S1 Crystallographic data

	1b-W·CH_3CN	**3-W**·5/2CH_3CN	**3-Mo**·5/2CH_3CN	**6**·CH_3CN
formula	$C_{40}H_{69}N_5O_3S_4W$	$C_{53}H_{91.5}N_{8.5}O_5S_4W$	$C_{53}H_{91.5}MoN_{8.5}O_5S_4$	$C_{51}H_{82}N_6O_3S_6W$
fw	980.09	1239.93	1152.02	3378.34
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$	$C2/c$	$C2/c$	$P2_1/c$
a, Å	17.7336(12)	36.772(6)	36.769(6)	11.4233(4)
b, Å	17.9441(5)	16.687(2)	16.624(3)	28.3088(11)
c, Å	15.2516(4)	26.502(4)	26.525(4)	18.3378(13)
α, deg	90	90	90	90
β, deg	110.304(7)	127.642(4)	127.696(5)	95.752(7)
γ, deg	90	90	90	90
V, Å^3	4551.7(4)	12877(3)	12829(4)	5900.2(5)
Z	4	8	8	4
d_{calc}, g cm^{-3}	1.430	1.279	1.193	1.355
μ, mm^{-1}	2.762	1.971	0.382	2.213
GOF	1.097	1.031	1.037	1.116
$R1^a$ [I > 2σ(I)]	0.0491	0.0520	0.0599	0.0584
w$R2^b$ (all data)	0.1118	0.1374	0.1743	0.1401

$^a R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. $^b wR2 = \{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$

Table S2 ^{1}H NMR signals of **1a-M**—**1c-M** (**M** = **W**, **Mo**[a]) in acetonitrile-d_3 at 30 °C

	NH		4-H		6-H		5-H	
1a-W	9.00	8.98	7.76	7.75	7.51	7.50	6.85	6.85
1a-Mo[b]	8.93		7.72		7.23		6.71	
1b-W	9.41	9.39	7.87	7.86	7.51	7.51	6.86	6.86
1b-Mo	9.40	9.38	7.89	7.88	7.32	7.31	6.80	6.79
1c-W[c]	10.00		7.71		7.64		6.94	
1c-Mo	10.02[b]		7.75	7.75	7.47	7.46	6.88	6.88

[a]Ref. 28. [b]Broad signals including *trans*- and *cis*-isomers. [c]Single isomer.

Table S3 ^{1}H NMR signals of **2a-M**—**2c-M** (**M** = **W**, **Mo**[a]) in acetonitrile-d_3 at 30 °C

	NH	4-H	6-H	5-H
2a-W	8.37	7.67	6.86	6.64
2a-Mo	8.43	7.70	6.87	6.60
2b-W	8.75	7.78	6.86	6.66
2b-Mo	8.82	7.81	6.86	6.61
2c-W	9.44	7.64	7.01	6.73
2c-Mo	9.54	7.68	7.02	6.69

[a]Ref. 28.

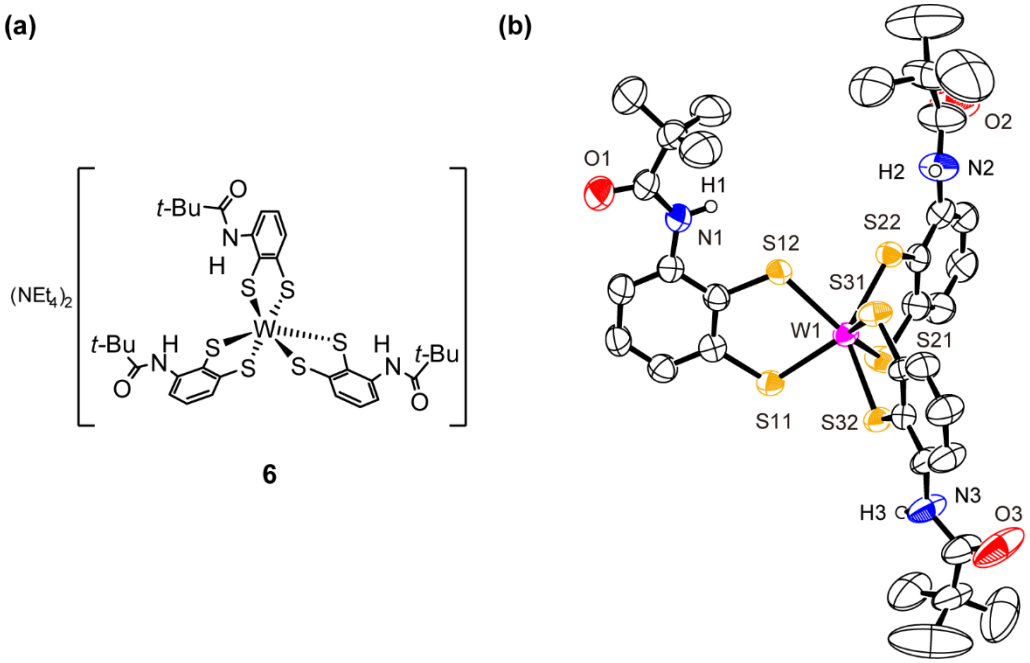

Fig. S1 (a) Schematic drawing of **6.** (b) Molecular structure (anion part) of **6** showing a unique up-up-down orientation of the three *t*-BuCONH substituent groups. Solution ^{1}H-NMR spectra showed only one set of broad signals for the ligand in acetonitrile-d_3, suggesting that rapid conformational change occurs in solution on the NMR timescale.

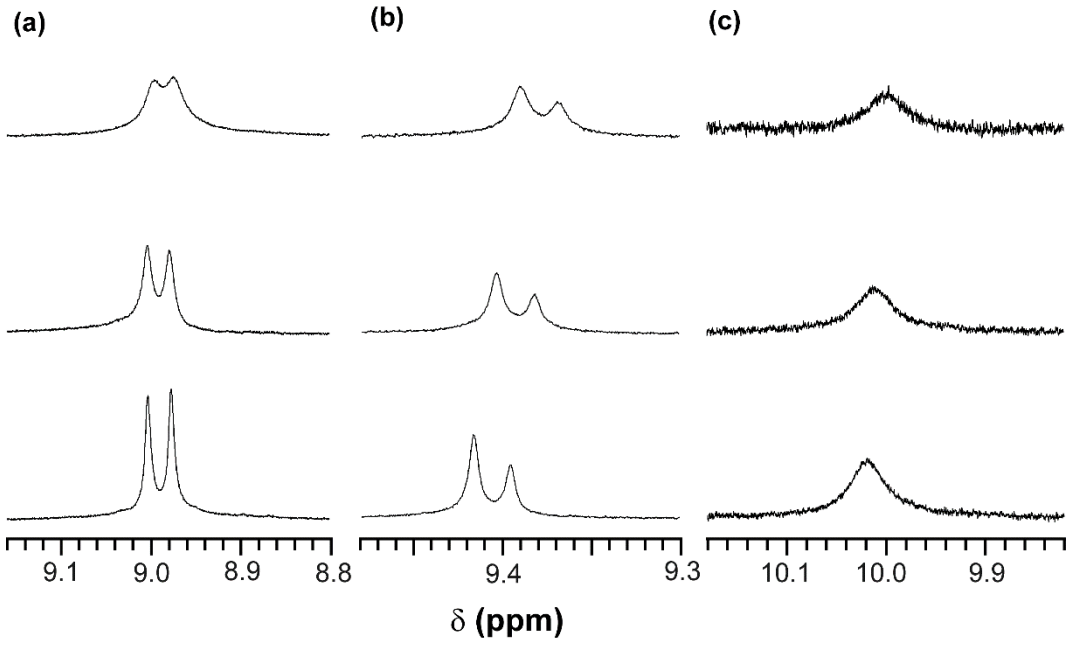

Fig. S2 ^{1}H NMR NH signals of (a) **1a-W**, (b) **1b-W** (powder), and (c) **1c-W** in acetonitrile-d_3 at 30 (top), 0 (middle), and −30 °C (bottom).

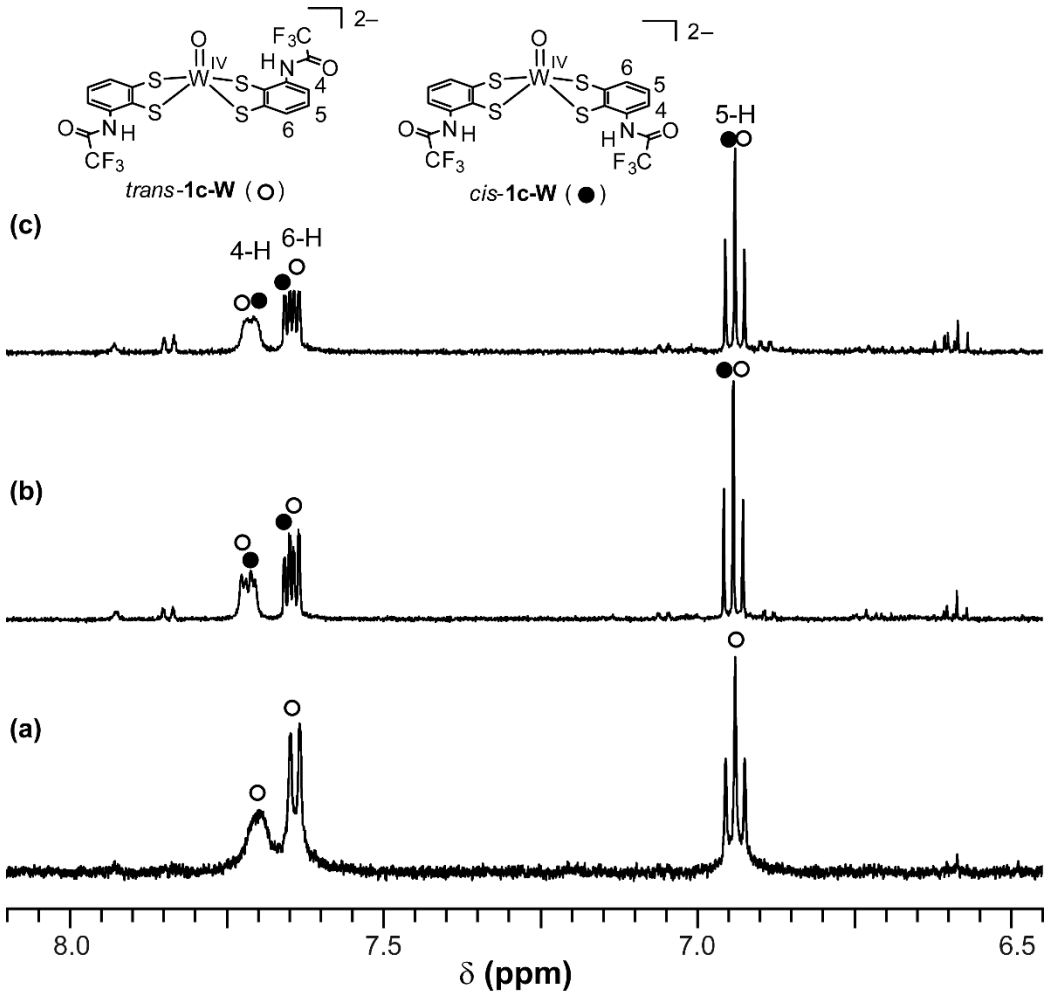

Fig. S3 ^{1}H NMR spectra of **1c-W** in acetonitrile-d_3 at 30 °C: (a) *trans*-**1c-W** (isolated microcrystals), (b) heated at 50 °C for 6.5 h, and (c) heated at 50 °C for 24 h.