Polyoxometalates

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A Basic Germanodecatungstate with a −7 Charge: Efficient Chemoselective Acylation of Primary Alcohols**

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Abstract: *The synthesis of highly negatively charged polyoxometalates with electrically and structurally controlled uniform basic sites can lead to the unique base catalysis. In this work, a γ-Keggin germanodecatungstate, $[\gamma\text{-}HGeW_{10}O_{36}]^{7-}$ (**A**), having a −7 charge was, for the first time, successfully synthesized by the reaction of $[\gamma\text{-}H_2GeW_{10}O_{36}]^{6-}$ with one equivalent of $[(n\text{-}C_4H_9)_4N]OH$ under non-aqueous conditions. The activities of germanodecatungstates for base-catalyzed reactions dramatically increased with increase in the number negative charges from −6 to −7. In the presence of **A**, various combinations of acylating agents and primary alcohols including those with acid-sensitive functional groups chemoselectively gave the desired acylated products in high yields even under the stoichiometric conditions.*

Polyoxometalates (POMs), which are a class of anionic metal–oxygen clusters of early transition metals, have stimulated many current research activities in many fields including catalysis, medicine, and materials science.[1,2] While various POM catalysts have been developed for acid-catalyzed, photocatalytic, and oxidation reactions, base catalysis has scarcely been investigated. We have, for the first time, discovered a unique POM for base catalysis by focusing on the following properties:[3] 1) Construction of uniform electrically and structurally controlled basic sites, which is in contrast to that of solid bases, 2) their thermal and oxidative stabilities, which are higher than those of organic bases (e.g., trialkyl phosphine), and 3) the metal-oxo moiety, which specifically activates nucleophilic substrates. The basicities of POMs can be increased by increasing the number of negative charges and the deprotonated oxygen atoms can work as structurally well-defined active sites. Monomeric fully-occupied and lacunary Keggin-type POMs have extensively been investigated (see Table S1 in the Supporting Information), and highly negatively charged ones have typically been synthesized as alkali-metal salts. They are intrinsically insoluble in common organic solvents, and their basic oxygen atoms are coordinated to alkali metal cations. In contrast, organic-solvent-soluble alkylammonium salts of monomeric Keggin-type POMs with less than a −7 charge have not been isolated.[4,5] In this context, strict control of highly negatively charged (≤ -7) organic-solvent-soluble POMs has not yet been accomplished.

Acylation of alcohols is an important and frequently used transformation in organic synthesis because esters are valuable chemicals for solvents, plasticizing agents, perfumes, medicines, and lubricants. The synthesis of esters from carboxylic acids and alcohols usually requires harsh reaction conditions. In contrast, the acid- and base-catalyzed acylation of alcohols with acid anhydrides, acyl chlorides, and esters as acylating agents is promising for the synthesis of esters under mild reaction conditions. While efficient catalytic systems for transesterification with enol esters have been reported, the development of catalytic systems with high activity, high selectivity, and a wide substrate scope under stoichiometric conditions (alcohol/enol ester = 1:1) are still desirable (see Table S2).[6–8] Herein, we report: 1) the stepwise synthesis of a tetra-*n*-butylammonium (TBA) salt of germanodecatungstate, $[\gamma\text{-}HGeW_{10}O_{36}]^{7-}$ (**A**, Figure 1), by the reaction of isolated $[\gamma\text{-}H_2GeW_{10}O_{36}]^{6-}$ with one equivalent of TBAOH under non-aqueous conditions, 2) the significant increase in the catalytic activity for base-catalyzed reactions with an increase in the negative charge (from −6 to −7), and 3) efficient and chemoselective acylation of various primary alcohols, having acid-sensitive functional groups, even under stoichiometric conditions.

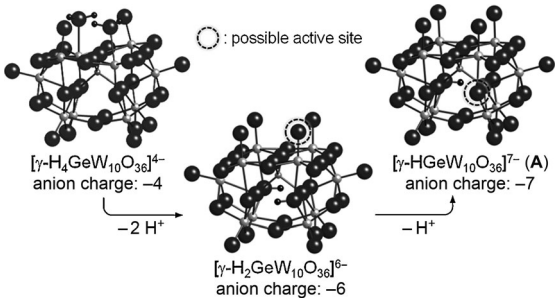

Figure 1. Increase in the number of negative charges and construction of active site(s) by the deprotonation of lacunary germanodecatungstates.

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The direct synthesis of **A** was attempted by the reaction of $[\gamma\text{-}H_4GeW_{10}O_{36}]^{4-}$ with three equivalents of TBAOH·30H_2O and was unsuccessful: Only a mixture of $[\gamma\text{-}HGeW_{10}O_{36}]^{7-}$ and $[\gamma\text{-}H_2GeW_{10}O_{36}]^{6-}$ was obtained, probably because of the coexistence of a large amount of water (see the details in the Supporting Information). Therefore, the synthetic conditions were improved by reducing the water content in the solution as follows: 1) The starting material was changed from $[\gamma\text{-}H_4GeW_{10}O_{36}]^{4-}$ to $[\gamma\text{-}H_2GeW_{10}O_{36}]^{6-}$ and 2) a methanol solution of TBAOH was used instead of TBAOH·30H_2O. Upon addition of one equivalent of TBAOH (methanol solution) with respect to $[\gamma\text{-}H_2GeW_{10}O_{36}]^{6-}$, the ^{1}H NMR spectrum showed one signal at $\delta = 6.96$ ppm (**A**) with the disappearance of the signal at $\delta = 5.32$ ppm which is representative of $[\gamma\text{-}H_2GeW_{10}O_{36}]^{6-}$, suggesting that **A** is a single species in the non-aqueous solution (see Figure S1). The analytically pure **A** could be synthesized as a white powder by the reaction of $TBA_6[\gamma\text{-}H_2GeW_{10}O_{36}]$ with one equivalent of TBAOH (methanol solution) in acetonitrile followed by the evaporation to dryness. The elemental analysis data revealed that the respective molar ratio of TBA/Ge/W was 7:1:10. The positive-ion cold-spray ionization mass (CSI-MS) spectrum of **A** in DMSO exhibited the most intense peak (centered at m/z 4426) with an isotopic distribution which agreed with the pattern calculated for $[TBA_8HGeW_{10}O_{36}]^+$ (Figure 2a and Figure S2). The ^{1}H NMR spectrum of **A** in [D_6]DMSO showed one signal at $\delta = 7.00$ ppm, which was assignable to the hydroxo proton (Figure 2b). The ^{183}W NMR spectrum of **A** in [D_6]DMSO showed five signals at $\delta = -51.0$, -101.5, -103.2, -105.1, and -149.6 ppm with the respective intensity ratio of 1:1:1:1:1 (Figure 2c). All these NMR results suggest that **A** is a monoprotonated species with C_s symmetry. To investigate the protonation site in more detail, DFT calculations were carried out, taking into account the solvation in DMSO, using the conductor-like polarizable continuum model (CPCM) and the parameters of the united atom topological model (UAHF). The structures of monoprotonated $[\gamma\text{-}HGeW_{10}O_{36}]^{7-}$ were optimized and the relative energies were compared (see Figure S3). The POM $[\gamma\text{-}HGeW_{10}O_{36}]^{7-}$ protonated at the bridging oxygen atom O_H and was calculated to be more stable, than species derived from protonation on at other sites, by 4–75 kJ mol^{-1}, showing that O_H is the most favorable monoprotonation site, and is in accord with the results reported for the calculated $[\gamma\text{-}HSiW_{10}O_{36}]^{7-}$.[4c] The deprotonated bridging oxygen atom is a possible active site (Figure 1). To the best of our knowledge, the isolation of TBA salts of single monomeric Keggin-type POMs having a -7 charge has not been reported.

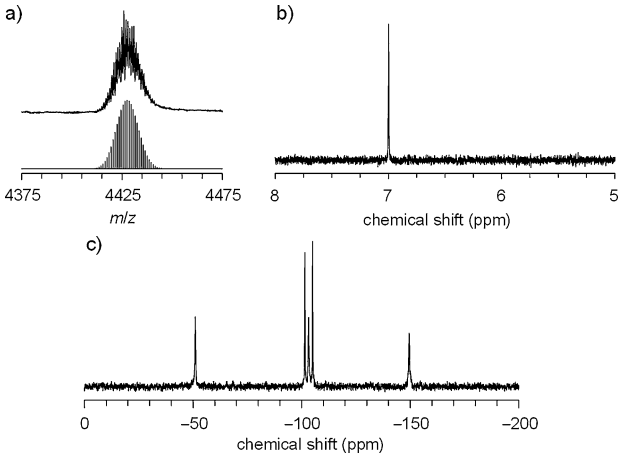
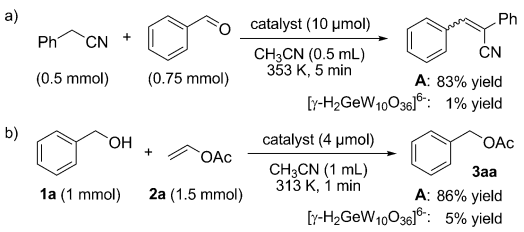


Figure 2. a) Positive-ion CSI-MS spectrum (m/z 4375–4475) of **A** (solvent: DMSO) and calculated pattern of $[TBA_8HGeW_{10}O_{36}]^+$ (m/z 4428). b) ^{1}H and c) ^{183}W NMR spectra of **A** (solvent: [D_6]DMSO, 298 K).

To compare the activity of **A** for base-catalyzed reactions with that of $[\gamma\text{-}H_2GeW_{10}O_{36}]^{6-}$,[3f] the Knoevenagel condensation of phenylacetonitrile with benzaldehyde was carried out under the reaction conditions given in Scheme 1a. The **A**-catalyzed condensation gave α-phenylcinnamonitrile in 83% yield, whereas the condensation hardly proceeded in the presence of $[\gamma\text{-}H_2GeW_{10}O_{36}]^{6-}$ (1% yield), thus suggesting that the increase in number of negative charges of germanodecatungstates from -6 to -7 significantly enhances the catalytic activity.

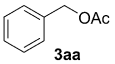
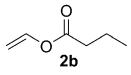
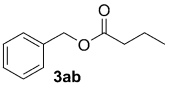
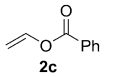
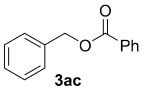
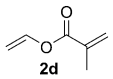
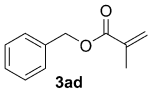


Scheme 1. a) Knoevenagel condensation of phenylacetonitrile with benzaldehyde. b) Acylation of **1a** with **2a**.

Next, we applied the **A**-catalyzed system to the acylation of benzyl alcohol (**1a**) with vinyl acetate (**2a**). The **A**-catalyzed acylation efficiently proceeded to give benzyl acetate (**3aa**) in 86% yield (Scheme 1b). In contrast, the yield of **3aa** was only 5% in the presence of $[\gamma\text{-}H_2GeW_{10}O_{36}]^{6-}$. The present system was also applicable to the 10 mmol scale acylation of **1a** with **2a** under the stoichiometric conditions (**1a**/**2a** = 1:1) at 303 K. The reaction was completed within only 1 minute, even with a low catalyst loading (0.2 mol%), to give **3aa** in 84% yield (see the details in the Supporting Information). In this case, the turnover number (TON) reached up to 421, and the turnover frequency (TOF) was 25200 h^{-1}. The TOF value was at least four times higher than those (1–6000 h^{-1}) reported for other catalytic systems, which need excess amounts (1.1–5.0 equivalents) of esters (see Table S2). The effect of catalysts on acylation of **1a** with **2a** was investigated (see Table S3). Other POMs such as the less negatively charged $TBA_4[\gamma\text{-}H_4GeW_{10}O_{36}]$, the fully occupied $TBA_4[\alpha\text{-}SiW_{12}O_{40}]$, and $TBA_8H_2[(SiREW_{10}O_{36})_2]$ (RE = Y^{3+} and Nd^{3+}) were almost inactive.[3] The catalytic activities of $TBA_2[WO_4]$, $TBA_3[PO_4]$, and strong bases (TBAOH and *t*BuOK) were lower than that of **A**. In the presence of N bases such as DABCO, DBU, Et_3N, and pyridine, the reactions hardly proceeded.

The scope of the **A**-catalyzed system with regard to various kinds of acylating agents and alcohols was investigated (Tables 1 and 2, respectively). The acylations of **1a** with various acylating agents in the presence of **A** efficiently proceeded. Not only aliphatic [**2a** and vinyl butyrate (**2b**)], but also aromatic [vinyl benzoate (**2c**)] vinyl esters gave the corresponding benzyl esters (**3aa**–**ac**) in high yields (Table 1, entries 1–3). In the case of vinyl methacrylate (**2d**), benzyl methacrylate (**3ad**) was obtained in 91% yield without the significant decomposition, isomerization, or polymerization of **2d** (entry 4). The sterically hindered isopropenyl acetate (**2e**) also gave **3aa** in 75% yield (entry 5). The **A**-catalyzed system was applicable of acylating **1a** with methyl ester instead of enol esters. The reaction of **1a** with 1.5 equivalents of methyl acetate in the presence of 4 Å molecular sieves (4 Å M.S.) gave **3aa** in 81% yield (entry 6) without using a large excess of methyl acetate.[8c,d,i,9]

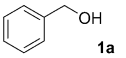
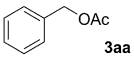
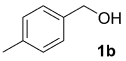
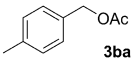
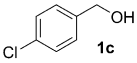
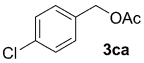
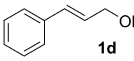
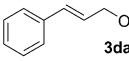
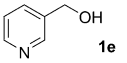
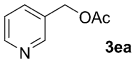
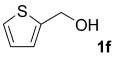
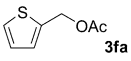
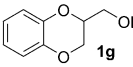
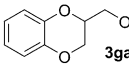
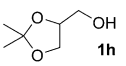
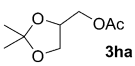
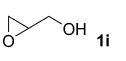
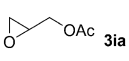
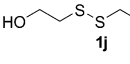
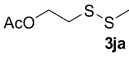
Table 1: Acylation of **1a** with various acylating agents catalyzed by **A**.[a]

Entry	Enol ester	Product	Yield [%]
1	 **2a**	 **3aa**	86 (78)
2	 **2b**	 **3ab**	75 (70)
3	 **2c**	 **3ac**	86 (76)
4	 **2d**	 **3ad**	91 (83)
5[b]	 **2e**	**3aa**	75
6[c]	MeOAc (**2f**)	**3aa**	81

[a] Reaction conditions: **A** (0.4 mol% with respect to **1a**), **1a** (1 mmol), acylating agents (1.5 mmol), CH_3CN (1 mL), 313 K, 1 min. The values within parentheses are the yields of the isolated products. [b] **A** (1 mol% with respect to **1a**), 333 K. [c] **A** (2 mol% with respect to **1a**), THF (1 mL), 4 Å M.S. (0.50 g), 293 K, 150 min.

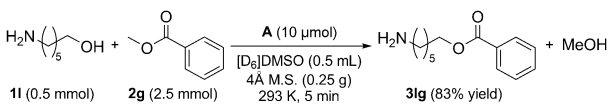
POM **A** also efficiently catalyzed the acylation of various primary alcohols with **2a**. Benzyl alcohols with electron-donating as well as electron-withdrawing *para*-substituents (**1b** and **1c**) gave the corresponding acylated products **3ba** and **3ca** in high yields (Table 2, entries 3 and 5). The reactions of alcohols containing a double bond (**1d**) and heteroatoms such as nitrogen and sulfur atoms (**1e** and **1f**) also proceeded smoothly to afford the acylated products **3da**–**fa** in the corresponding yields of 85, 97, and 97% (entries 7, 9, and 11). Alcohols with acid-sensitive functional groups such as an acetal, an epoxide, and a disulfide (**1g**–**j**) could selectively be acylated to give the corresponding acetates **3ga**–**ja** in excellent yields without the cleavage of C–O and S–S bonds (entries 13, 15, 17, and 19). In the case of an aliphatic alcohol (**1k**), octyl acetate (**3ka**) was obtained in high yield (entry 21). Even under the stoichiometric conditions (alcohol/enol ester = 1:1) at 293 K, the **A**-catalyzed acylations of various alcohols were completed within 1–20 minutes, when using a low catalyst loading (0.4–2.0 mol%), to give the corresponding esters in 81–97% yield (entries 2, 4, 6, 8, 10, 12, 16, 18, and 20).

Table 2: Acylation of various primary alcohols with **2a** catalyzed by **A**.[a]

Entry	Alcohol	Product	Cond.	Yield [%]
1	 **1a**	 **3aa**	A	86 (78)
2			B	81
3	 **1b**	 **3ba**	A	85 (75)
4			B	85
5	 **1c**	 **3ca**	A	97 (91)
6			B	97
7[b]	 **1d**	 **3da**	A	85 (83)
8[b]			B	84
9	 **1e**	 **3ea**	A	97 (83)
10			B	94
11[c]	 **1f**	 **3fa**	A	97 (82)
12[c]			B	93
13[c]	 **1g**	 **3ga**	A	90 (84)
14[d]			B	85
15	 **1h**	 **3ha**	A	85 (74)
16			B	85
17	 **1i**	 **3ia**	A	98 (86)
18			B	93
19[e]	 **1j**	 **3ja**	A	83 (82)
20[e]			B	83
21	*n*-C_8H_{17}–OH (**1k**)	*n*-C_8H_{17}–OAc (**3ka**)	C	93

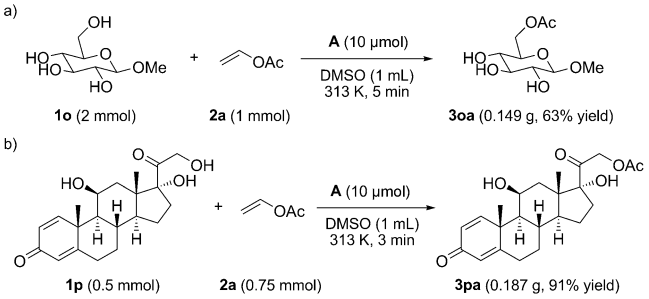
[a] Reaction conditions A: **A** (0.4 mol% with respect to alcohol), alcohol (1 mmol), **2a** (1.5 mmol), CH_3CN (1 mL), 313 K, 1 min. The values within parentheses are the yields of the isolated products. Reaction conditions B: **A** (0.4 mol% with respect to alcohol), alcohol (1 mmol), **2a** (1 mmol), CH_3CN (1 mL), 293 K, 1 min. Reaction conditions C: **A** (2 mol% with respect to **2a**), **1k** (3 mmol), **2a** (1 mmol), 353 K, 30 min. [b] **A** (1 mol% with respect to **1d**). [c] 20 min. [d] 313 K, 60 min. [e] **A** (2 mol% with respect to **1j**), **1j** (0.5 mmol).

Next, chemoselectivities of the **A**-catalyzed intra- and intermolecular competitive acylation were investigated. The acylation of 6-amino-1-hexanol (**1l**) with methyl benzoate (**2g**) chemoselectively proceeded to give the corresponding aminoester, similar to reaction employing an enzyme, $[Zn_4(OCOCF_3)_6O]$, $La(OiPr)_3$/2-(2-methoxyethoxy)ethanol, and $[Co_2(OCOtBu)_2(bpy)_2(\mu_2\text{-}OCH_2\text{-}C_6H_4\text{-}4\text{-}CH_3)_2]$ (Scheme 2).[10] For the intermolecular competitive acylation of a primary alcohol (**1a**) and secondary alcohols [2-butanol (**1m**) or 1-phenylethanol (**1n**)] with **2a**, only **1a** was selectively acylated without formation of the esters from the secondary alcohols. The present selectivity ratios for esters



Scheme 2. Chemoselective acylation of 6-amino-1-hexanol (**1l**) with methyl benzoate (**2g**) catalyzed by **A**.

from primary alcohols to those from secondary ones were >99:1, and the values were higher than those (primary/secondary = 65:35–95:5) reported for other systems using enol esters, and comparable to that (primary/secondary = 99:1) of distannoxane which achieved the highest selectivity (see Table S4).[8a–d,j] To confirm the applicability to complex and synthetically relevant substrates, we applied the **A**-catalyzed selective acylation to the reaction of methyl β-D-glucopyranoside (**1o**) with **2a**. The primary hydroxy group at C6 was selectively acylated to give the corresponding 6-O-acylated product in 79% yield (GC) and the product was isolated in 63% yield (Scheme 3a). The selective acylation was also applicable to a steroid derivative.[11] The primary alcohol in prednisolone (**1p**) was chemoselectively acylated to give the monoacylated product in 91% yield (Scheme 3b).



Scheme 3. Selective acylation of a) methyl β-D-glucopyranoside (**1o**) and b) prednisolone (**1p**) with **2a** catalyzed by **A**.

While prednisolone has been acylated with acetic anhydride in the presence of an excess amount of triethylamine, the catalytic systems for acylation with vinyl acetate have not been reported. This study provides the first example of POM catalysts efficient for chemoselective acylation of various primary alcohols with enol esters.

The reactivities of **A** with **1a** and **2a** were investigated by ^{1}H NMR spectroscopy. Upon addition of one equivalent of **A**, with respect to **2a**, the ^{1}H NMR spectrum of **2a** did not change. In contrast, the ^{1}H NMR spectrum of **1a** showed the downfield shift of the signal of hydroxy protons from $\delta = 3.42$ to 5.84 ppm upon addition of one equivalent of **A** (with respect to **1a**; see Figure S4). Such downfield shifts have been reported for hydrogen-bonded N-heterocyclic carbene/alcohol complexes.[8i,12] The $\delta = 5.18$ ppm signal of [γ-$H_2GeW_{10}O_{36}$]$^{6-}$ was not observed and the intensity of the signal at $\delta = 6.67$ ppm, representing **A**, remained unchanged. These NMR results suggest a hydrogen-bonding interaction between **A** and **1a**.[13–15] Upon addition of **2a** to the solution, the $\delta = 5.84$ ppm signal, representing the hydrogen-bonded complex of **A** and **1a**, disappeared and signals for **3aa** and acetaldehyde appeared, thus suggesting the activation of **1a** by **A** facilitates the nucleophilic attack of the hydroxy group in **1a** on the carbonyl carbon atom in **2a**. The Hammett plots ($\log(k_X/k_H)$ versus σ_P; see Figure S7) for the competitive acylation of **1a** and *para*-substituted benzyl alcohols with **2a** showed the good linearity with the positive ρ value (+0.98), thus supporting the reaction mechanism (see Figure S8).

In conclusion, a γ-Keggin germanodecatungstate (**A**) having a −7 charge was, for the first time, successfully synthesized under non-aqueous conditions. The activities for base-catalyzed reactions significantly increased with an increase in the number of negative charges of germanodecatungstates. POM **A** efficiently catalyzed the acylation of various alcohols having acid-sensitive functional groups such as an acetal, an epoxide, and a disulfide even under the stoichiometric conditions.

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[5] The isolation of single −7-charged γ-Keggin POMs, [γ-$HXW_{10}O_{36}$]$^{7-}$ (X = Si and Ge), was not possible by using the previously reported methods:[4c] A powder mixture of [γ-$HSiW_{10}O_{36}$]$^{7-}$ (60%) and [γ-$H_2SiW_{10}O_{36}$]$^{6-}$ (40%) was obtained by addition of an excess amount of diethyl ether into the acetonitrile solution containing [γ-$SiW_{10}O_{34}(H_2O)_2$]$^{4-}$ with three equivalents of TBAOH·30H_2O, while the in situ formation of single [γ-$HSiW_{10}O_{36}$]$^{7-}$ was confirmed by the ^{1}H, ^{29}Si, and ^{183}W NMR spectroscopies.

[6] The transesterification with enol esters efficiently proceeds because the conversion of the resultant enolates to aldehydes or ketones shifts the equilibrium in the desired direction. Various

catalysts such as [Cp*$_2$Sm(thf)$_2$], distannoxane, iminophosphorane, I_2, N-heterocyclic carbenes (NHC), $PdCl_2$, Et_2Zn/*N*-phenyldiethanolamine, lipase, [$Y_5(O)(OiPr)_{13}$], and nucleophilic Fe(−II) complexes have been developed for transesterification of alcohols with enol esters.[7,8] However, most of them have some disadvantages (see Table S2): 1) long reaction times, 2) need of excess amounts of enol esters with respect to alcohols, 3) low TONs, 4) inapplicability to acid-sensitive alcohols containing acetals and epoxides, and/or 5) insufficient selectivity between primary and secondary alcohols.

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[13] Upon addition of **A**, the ^{1}H NMR signals of the aromatic protons in **1a** (multiplet at $\delta = 7.31$–7.21 ppm) became clearly separated into three multiplets at $\delta = 7.27$–7.25, 7.20–7.15, and 7.09–7.04 ppm assignable to *ortho*-, *meta*-, and *para*-hydrogen atoms, respectively, thus suggesting a hydrogen-bonding interaction between **A** and **1a**.[14]

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[15] Upon addition of one equivalent of **1a** with respect to **A**, the ^{183}W NMR spectrum of **A** showed the upfield shifts from $\delta = -56.2$, -107.8, -109.2, -113.3, and -153.8 ppm to $\delta = -57.1$, -110.5, -110.1, -114.9, and -154.2 ppm, respectively (see Figure S5). In addition, only two signals at $\delta = -107.8$ and -113.3 ppm corresponding to four tungsten atoms shifted more largely than the other three signals possibly because of the hydrogen-bonding interaction between **1a** and the bridging oxygen atoms (O1; see Figure S6), which are supposed to be the most basic sites in **A**. To assign the ^{183}W NMR signals of **A**, DFT calculations were carried out. The structure of **A** with C_s symmetry was optimized at the TPSSh level of theory (Figure S6) and respective chemical shifts were calculated with the individual gauge localized orbital method (SO-IGLO) taking the spin–orbit interaction into account (see Table S5). The largely shifted two signals were assignable to W1 and W3, thus supporting the proposed mechanism.

