

Electronic Supplementary Information (ESI) for

Synthesis and structural characterization of BINOL-modified chiral polyoxometalates

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Experimental Section

Materials. Acetonitrile (Kanto Chemical) and dichloromethane (Kanto Chemical) were purified by the Ultimate Solvent System (GlassContour Company) prior to use.^{S1} Thioanisole was purified according to the reported procedure.^{S2} CD₃CN (Acros), other solvents (Kanto Chemical and TCI), TBHP (5.5 M decane solution, Fluka), TiO(acac)₂ (TCI), and BINOL (Wako Chemical) were used as received. TBA₈[{ γ -SiTi₂W₁₀O₃₆(μ -OH)₂]₂(μ -O)₂] (**Ti2-dimer**)^{S3} and TBA₄[γ -SiW₁₀O₃₄(H₂O)₂] (**SiW10**)^{S4} were synthesized according to the reported procedures.

Instruments. IR spectra were measured on a Jasco FT/IR-4100 spectrometer Plus using KBr disks. NMR spectra were recorded on a JEOL ECA-500 spectrometer (¹H, 500.2 MHz; ¹³C, 125.8 MHz; ²⁹Si, 99.37 MHz; ¹⁸³W, 20.84 MHz) by using 5 mm tubes (for ¹H, ¹³C, and ²⁹Si) or 10 mm tubes (for ¹⁸³W). Chemical shifts were reported in ppm downfield from Si(CH₃)₄ (solvent, CDCl₃) for ¹H, ¹³C, and ²⁹Si NMR spectra and 2 M Na₂WO₄ (solvent, D₂O) for ¹⁸³W NMR spectra. UV-vis spectra were measured on a Jasco V-570 spectrometer. CD spectra were measured on a Jasco J-820 spectrometer. GC analyses were carried out on Shimadzu GC-2014 with a flame ionization detector equipped with an Inert Cap 5 capillary column (internal diameter = 0.25 mm, film thickness = 0.25 μ m, length = 60 m). HPLC analyses were performed on Shimadzu Prominence with a CD (Jasco CD-2095 Plus) detector equipped with a DAICEL CHIRALCEL (OD-H) column (0.46 cm ϕ \times 25 cm). Mass spectra were recorded on a Shimadzu GCMS-QP2010 equipped with a TC-5HT capillary column at an ionization voltage of 70 eV. Cold-spray ionization mass spectra were measured on a JEOL JMS-T100CS spectrometer in the positive-ion or negative-ion mode by direct infusion with a syringe pump (0.05 mL min⁻¹).

X-ray crystallography. X-ray diffraction measurements were made on a Rigaku MicroMax-007 Saturn 724 CCD detector with graphite monochromated Mo K α radiation (λ = 0.71069 Å). The data were collected using CrystalClear^{S5} at 113 or 123 K, and indexing, integration, and absorption correction were performed with HKL2000^{S6} software for Linux. Neutral scattering factors were

obtained from the standard source. In the data reduction, corrections for Lorentz and polarization effects were made. The structural analysis was performed using CrystalStructure^{S7} and Win-GX for Windows software.^{S8} The molecular structures were solved by combination of SHELXS-97 (direct methods) and SHELXH-97 (Fourier and least squares refinement).^{S9} Tungsten, silicon, oxygen, nitrogen, and carbon atoms except for solvents were refined anisotropically, and oxygen, nitrogen, and carbon atoms in solvents were refined isotropically. Detailed crystallographic data are summarized in Table S1. Selected distances and angles of **I** are shown in Table S2. CCDC 1047984 (*R-I*) and 1047985 (*S-I*) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via <https://summary.ccdc.cam.ac.uk/structure-summary-form>.

Reaction of TBA₈[{ γ -SiTi₂W₁₀O₃₆(μ -OH)₂]₂(μ -O)₂] with BINOL in the presence of acid or base.

To a solution of TBA₈[{ γ -SiTi₂W₁₀O₃₆(μ -OH)₂]₂(μ -O)₂] (**Ti2-dimer**; 53.4 mg, 7.5 μ mol) in acetonitrile (1 mL), BINOL (17.2 mg, 60 μ mol) was dissolved, followed by the addition of HClO₄ or TBAOH·30H₂O (15 μ mol). The solution was stirred at room temperature for 6 h and the solution species were confirmed by CSI-MS. After that, HClO₄ or TBAOH·30H₂O (15 μ mol) was added into the solution, the reaction mixture was stirred at room temperature for 6 h, and the solution species were again confirmed by CSI-MS. However, all the CSI-MS spectra showed that **Ti2-dimer** is not dissociated into [γ -SiTi₂W₁₀O₃₈H_{*n*}(μ -OH)₂]^{(6-*n*)⁻ (*n* = 0, 1, or 2).}

Reaction of K₈[γ -SiW₁₀O₃₆], BINOL, and titanium source. The synthesis of **I** from [γ -SiW₁₀O₃₄(H₂O)₂]⁴⁻, titanium source, and BINOL was attempted. To an aqueous solution (1 mL) of K₈[γ -SiW₁₀O₃₆] (41.6 mg, 15 μ mol), BINOL (17.2 mg, 60 μ mol) and TiO(acac)₂ (7.9 mg, 30 μ mol) or TiO(SO₄) (4.8 mg, 30 μ mol) were added and the reaction solution was stirred at room temperature for 2 days. However, the CSI-MS spectra of the reaction solution showed that introduction of titanium into the POM hardly proceeded.

Synthesis and characterization of TBA₄[γ -SiTi₂W₁₀O₃₈H₂(μ -BINOL)] (I**).** To a 1,2-dichloroethane solution (40 mL) of **SiW10** (2.06 g, 0.6 mmol) was added (*R*)-BINOL (0.687 g, 2.4 mmol), followed by the addition of TiO(acac)₂ (314.5 mg, 1.2 mmol). The resulting solution was stirred for a day at 313 K. The residue was filtered off and the filtrate was dropwisely added into a mixed solvent of diethyl ether/chloroform (400/100 mL). The resulting yellow precipitate was collected by filtration and then washed with diethyl ether (60 mL). The yellow powder was dissolved in dichloromethane (90 mL) and the resulting precipitate was collected by filtration and washed with dichloromethane (10 mL) and diethyl ether (30 mL \times 2) to afford yellow powder (1.47 g, 63.4% based on **SiW10**). The crude product (240 mg) was recrystallized in a mixture of nitromethane/diethyl ether (12/36 mL) to give yellowish single crystals (*R-I*; 194.3 mg, 81%, based on the crude product) suitable for X-ray crystallographic analysis.

¹⁸³W NMR (20.83 MHz, CD₃CN, 298 K, Na₂WO₄): δ = -101.8, -117.4, -122.7, -133.8, -135.0.

²⁹Si NMR (99.37 MHz, CD₃CN, 298 K, TMS): δ = -84.22 ($\Delta\nu_{1/2}$ = 1.9 Hz). ¹³C NMR (125.8 MHz, CD₃CN, 298 K, TMS): δ = 162.7, 135.1, 130.5, 129.5, 129.0, 126.8, 126.6, 124.3, 123.1, 117.2, 59.3, 24.3, 20.4, 13.9. ¹H NMR (500.2 MHz, CD₃CN, 298 K, TMS): δ = 7.97 (d, *J* = 9.0 Hz, 2H),

7.89 (d, $J = 8.0$ Hz, 2H), 7.72 (d, $J = 9.0$ Hz, 2H), 7.28 (ddd, $J = 1.0, 7.0,$ and 8.0 Hz, 2H), 7.15 (ddd, $J = 1.4, 6.8,$ and 8.4 Hz, 2H), 6.81 (d, $J = 8.5$ Hz, 2H), 6.24 (s, 2H), 3.09–3.04 (m, 32H), 1.60–1.53 (m, 32H), 1.39–1.30 (m, 32H), 0.95 (t, $J = 7.5$ Hz, 48H). IR (KCl): $\nu = 3510, 1591, 1483, 1466, 1379, 1334, 1272, 1244, 1075, 1002, 968, 896, 875, 791, 740, 671, 601, 568, 398, 352, 329$. UV-Vis (acetonitrile) (ϵ): 242 nm ($1.22 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$). Elemental analysis calcd (%) for $\text{C}_{84}\text{H}_{158}\text{N}_4\text{O}_{40}\text{Si}_1\text{Ti}_2\text{W}_{10}$ ($\text{TBA}_4[\text{SiTi}_2\text{W}_{10}\text{O}_{38}\text{H}_2(\mu\text{-C}_{20}\text{H}_{12}\text{O}_2)]$): C 26.37, H 4.16, N 1.46, Si 0.73, Ti 2.50, W 48.04; found: C 26.15, H 4.18, N 1.39, Si 0.76, Ti 2.56, W 48.64.

Similarly, *S*-**I** (yellowish crystals; 198.2 mg, 83%, based on the crude product) could also be synthesized with (*S*)-BINOL.

^{29}Si NMR (99.37 MHz, CD_3CN , 298 K, TMS): $\delta = -84.22$ ($\Delta\nu_{1/2} = 1.5$ Hz). ^{13}C NMR (125.8 MHz, CD_3CN , 298 K, TMS): $\delta = 162.6, 135.1, 130.5, 129.5, 129.0, 126.8, 126.6, 124.3, 123.1, 117.2, 59.3, 24.4, 20.4, 14.0$. ^1H NMR (500.2 MHz, CD_3CN , 298 K, TMS): $\delta = 7.96$ (d, $J = 9.0$ Hz, 2H), 7.89 (d, $J = 8.0$ Hz, 2H), 7.72 (d, $J = 9.0$ Hz, 2H), 7.28 (ddd, $J = 0.9, 6.9,$ and 8.1 Hz, 2H), 7.13 (ddd, $J = 1.0, 7.0,$ and 8.3 Hz, 2H), 6.81 (d, $J = 8.5$ Hz, 2H), 6.24 (s, 2H), 3.09–3.04 (m, 32H), 1.60–1.53 (m, 32H), 1.39–1.30 (m, 32H), 0.94 (t, $J = 7.3$ Hz, 48H). IR (KCl): 3518, 1591, 1483, 1467, 1379, 1335, 1272, 1001, 968, 896, 875, 792, 741, 671, 601, 569, 399, 352, 331. UV-Vis (acetonitrile) (ϵ): 242 nm ($1.22 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$).

Procedure for catalytic oxidation. A catalytic reaction was carried out with a glass tube (30 mL) that contained a magnetic stir bar. A catalyst (*R*-**I** (10 μmol , 38 mg), $\text{TiO}(\text{acac})_2/\text{BINOL}$ (20/40 μmol), or **SiW10**/BINOL (10/10 μmol)), thioanisole (0.5 mmol), and acetonitrile (3 mL) were successively placed into a 30 mL glass vessel with a magnetic stir bar, and the mixture was heated to 333 K. The reaction was initiated by the addition of TBHP (0.5 mmol), and the reaction solution was periodically analyzed by GC. All products were known compounds and identified by comparison of their retention times and mass spectra with those of authentic samples. Enantiomeric excess was determined by chiral HPLC analysis using a DAICEL CHIRALCEL (OD-H) column, and the configuration was determined by comparison of the retention times of the two enantiomers with those of literature data.^{S10}

References

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Table S1 Summary of crystallographic data for **I**

	R-I	S-I
Formula	C _{92.5} H _{179.5} N _{8.5} O ₅₀ SiTi ₂ W ₁₀	C ₉₃ H ₁₈₁ N ₉ O ₅₁ SiTi ₂ W ₁₀
Crystal system	Monoclinic	Monoclinic
Space group	<i>P2</i> ₁ (#4)	<i>P2</i> ₁ (#4)
<i>a</i> (Å)	17.9204(3)	17.8620(2)
<i>b</i> (Å)	19.8114(3)	19.7487(2)
<i>c</i> (Å)	36.8133(5)	36.5801(4)
β (°)	90.0457(6)	90.0149(4)
<i>V</i> (Å ³)	13069.8(3)	12903.0(2)
<i>Z</i>	2	2
Temp. (K)	123	113
<i>d</i> _{calcd} (g·cm ⁻³)	2.121	2.164
μ (cm ⁻¹)	8.967	9.085
No. of parameters refined	2998	2992
<i>R</i> ₁	0.0546 (for 34371 data) ^a	0.0600 (for 54350 data) ^a
<i>wR</i> ₂	0.1539 (for all 37578 data)	0.1664 (for all 59263 data)
gof	1.078	1.148
Flack parameter	0.005(8)	0.002(11)

^aFor data with $I > 2.0\sigma(I)$.

Table S2 Selected distances (Å) and angles (deg) for *R-I* and *S-I**R-I*

Ti1–O1	2.029(17)	Ti2–O1	2.043(17)	Ti1–O1–Ti2	101.8(8)
Ti1–O2	2.007(19)	Ti2–O2	2.047(18)	Ti1–O2–Ti2	102.4(8)
Ti1–O3	1.831(16)	Ti2–O4	1.815(17)	Ti1–O3–C2	129.5(15)
Ti1–O5	1.839(18)	Ti2–O7	1.840(17)	Ti2–O4–C12	133.2(16)
Ti1–O6	1.901(18)	Ti2–O8	1.88(2)	O5–Ti1–O6	96.4(8)
Ti1–O16	2.331(16)	Ti2–O19	2.302(16)	O7–Ti2–O8	95.5(8)
Ti1⋯Ti2	3.160(6)			C2–C1–C11–C12	84.47

S-I

Ti1–O1	2.002(14)	Ti2–O1	1.988(13)	Ti1–O1–Ti2	103.9(6)
Ti1–O2	2.013(13)	Ti2–O2	2.004(14)	Ti1–O2–Ti2	103.0(6)
Ti1–O3	1.814(14)	Ti2–O4	1.837(14)	Ti1–O3–C2	135.0(13)
Ti1–O5	1.831(15)	Ti2–O7	1.820(13)	Ti2–O4–C12	127.8(13)
Ti1–O6	1.865(13)	Ti2–O8	1.861(14)	O5–Ti1–O6	96.5(7)
Ti1–O16	2.273(13)	Ti2–O19	2.286(15)	O7–Ti2–O8	96.2(6)
Ti1⋯Ti2	3.143(3)			C2–C1–C11–C12	90.39

Table S3 BVS calculations for *R-I* and *S-I**R-I*

Ti1	4.09	Ti2	4.12	Si1	3.73	W1	6.12
W2	6.28	W3	5.94	W4	5.94	W5	5.97
W6	6.21	W7	5.91	W8	6.23	W9	6.38
W10	5.92	O1	1.10	O2	1.13	O3	2.13
O4	2.03	O5	1.98	O6	1.98	O7	1.98
O8	1.90	O9	1.85	O10	1.98	O11	1.93
O12	1.70	O13	1.93	O14	1.72	O15	1.93
O16	1.81	O17	1.91	O18	1.99	O19	1.81
O20	1.93	O21	1.58	O22	1.75	O23	2.03
O24	2.05	O25	2.05	O26	1.96	O27	2.06
O28	2.02	O29	1.91	O30	1.96	O31	1.89
O32	1.91	O33	2.09	O34	2.03	O35	2.13
O36	1.91	O37	1.80	O38	1.61	O39	1.81
O40	1.71						

S-I

Ti1	4.31	Ti2	4.32	Si1	3.76	W1	6.11
W2	6.27	W3	6.13	W4	6.14	W5	6.24
W6	6.24	W7	6.11	W8	6.27	W9	6.16
W10	6.17	O1	1.23	O2	1.19	O3	2.06
O4	2.00	O5	2.00	O6	1.99	O7	2.03
O8	2.05	O9	1.78	O10	1.98	O11	1.89
O12	1.72	O13	2.03	O14	1.77	O15	1.96
O16	1.86	O17	2.01	O18	1.96	O19	1.86
O20	1.98	O21	1.81	O22	1.80	O23	2.05
O24	2.09	O25	1.97	O26	2.04	O27	2.07
O28	2.08	O29	1.98	O30	1.99	O31	1.93
O32	1.94	O33	2.13	O34	1.99	O35	2.08
O36	1.99	O37	1.71	O38	1.88	O39	1.74
O40	1.72						

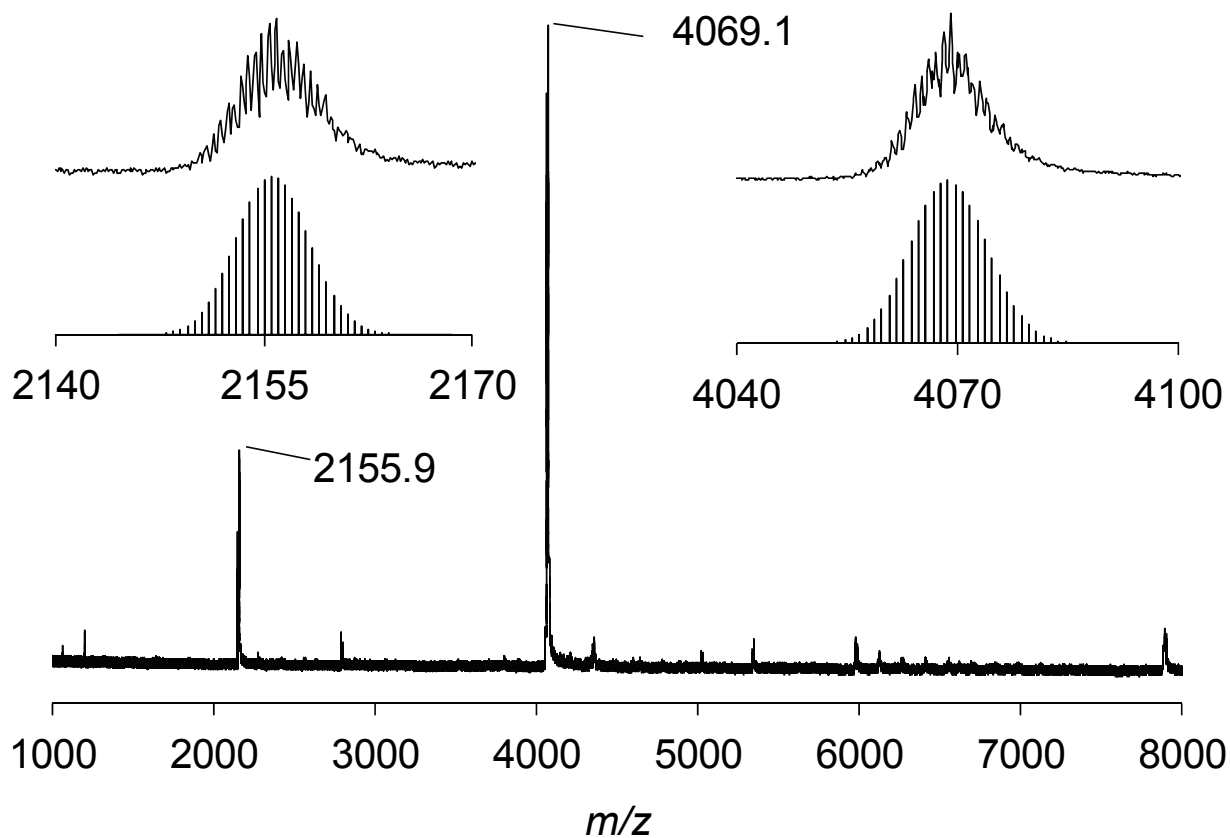


Fig. S1 Positive-ion CSI-MS spectrum of the reaction solution of **SiW10**, (*R*)-BINOL, and $\text{TiO}(\text{acac})_2$ (for 24 h) in 1,2-dichloroethane. The signal sets at $m/z = 2155.9$ and 4069.1 were assignable to $[\text{TBA}_6\text{SiTi}_2\text{W}_{10}\text{O}_{38}\text{H}_2(\text{BINOLate})]^{2+}$ and $[\text{TBA}_5\text{SiTi}_2\text{W}_{10}\text{O}_{38}\text{H}_2(\text{BINOLate})]^+$, respectively.

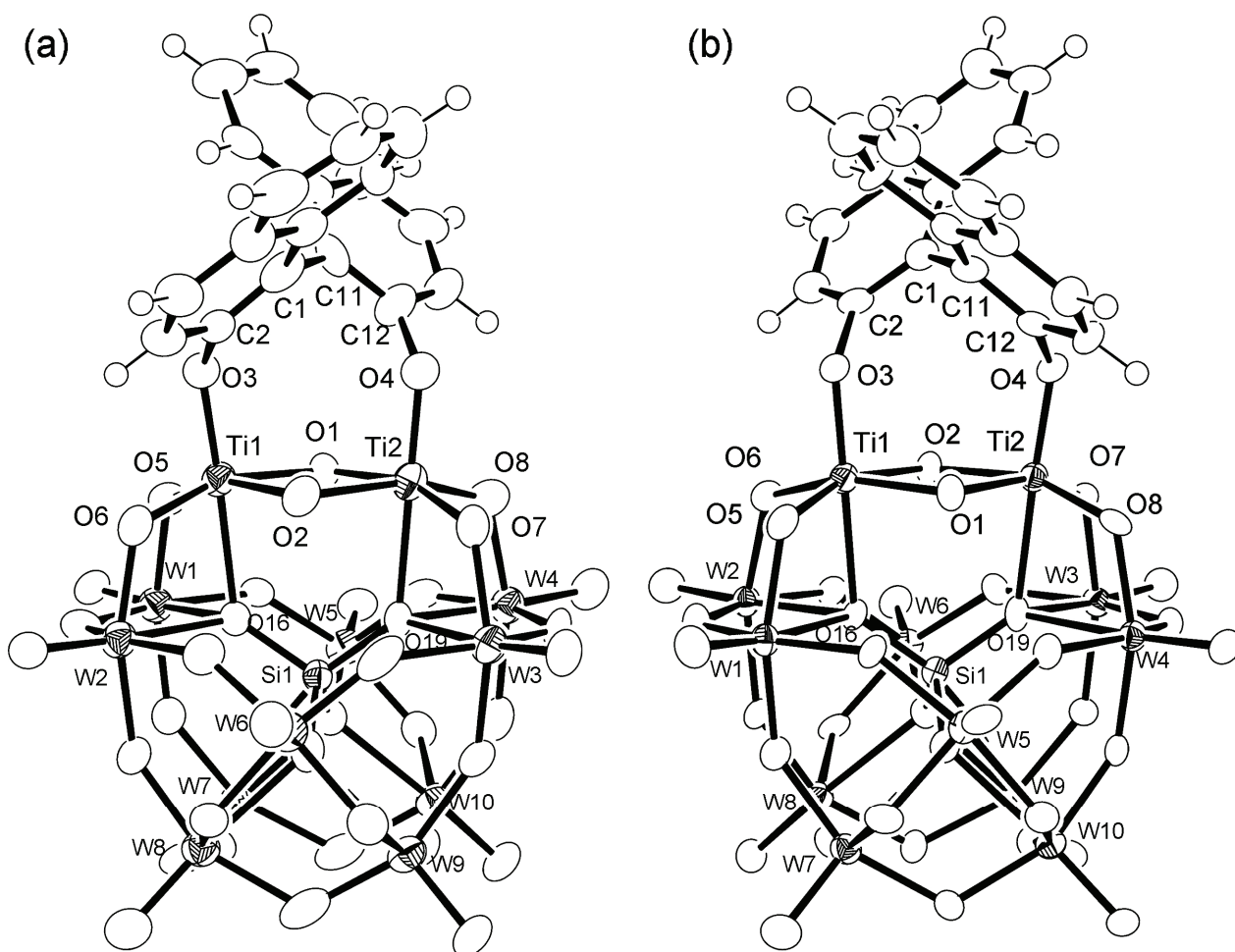


Fig. S2 ORTEP representations of the anion parts of (a) *R*-I and (b) *S*-I with thermal ellipsoids at 50% probability level.

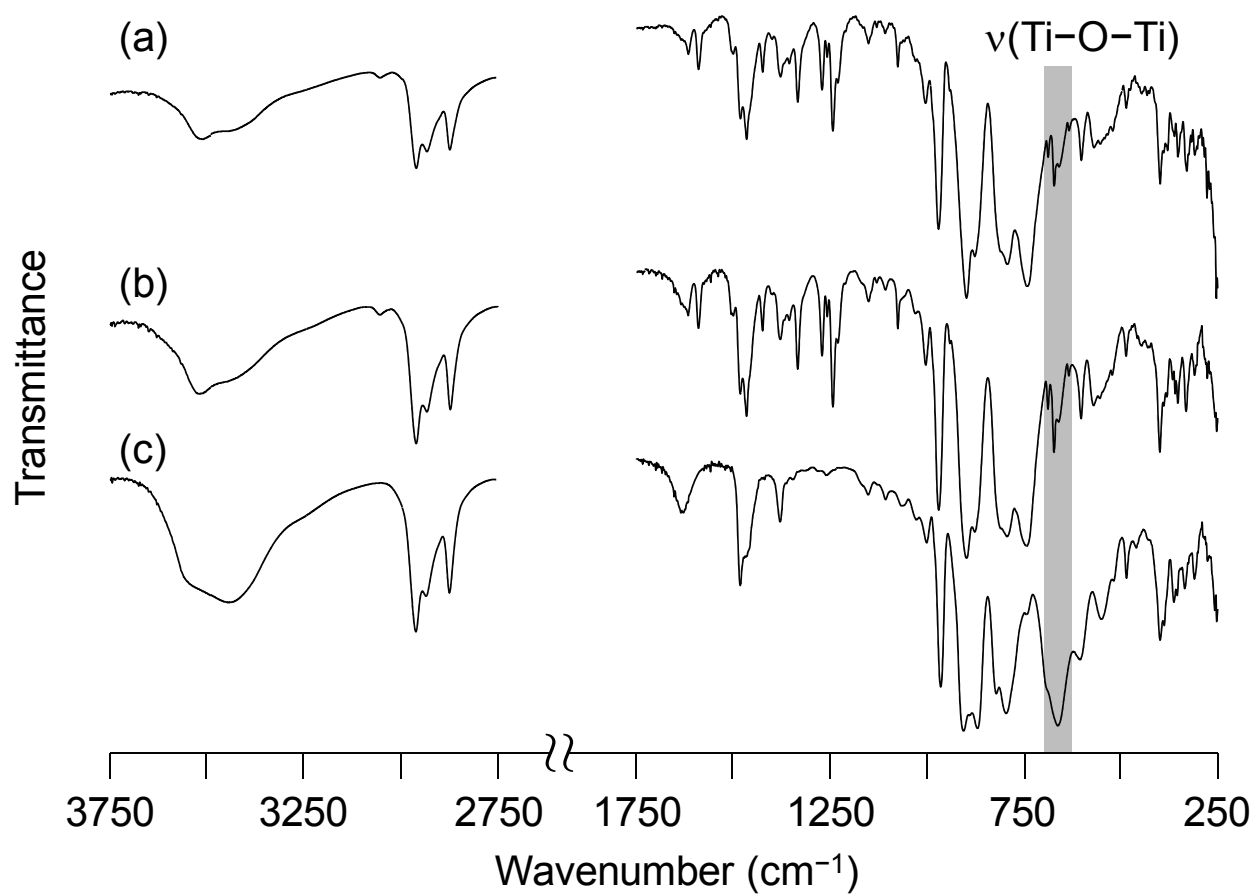


Fig. S3 IR spectra of (a) *R-I*, (b) *S-I*, and (c) **Ti2-dimer**.

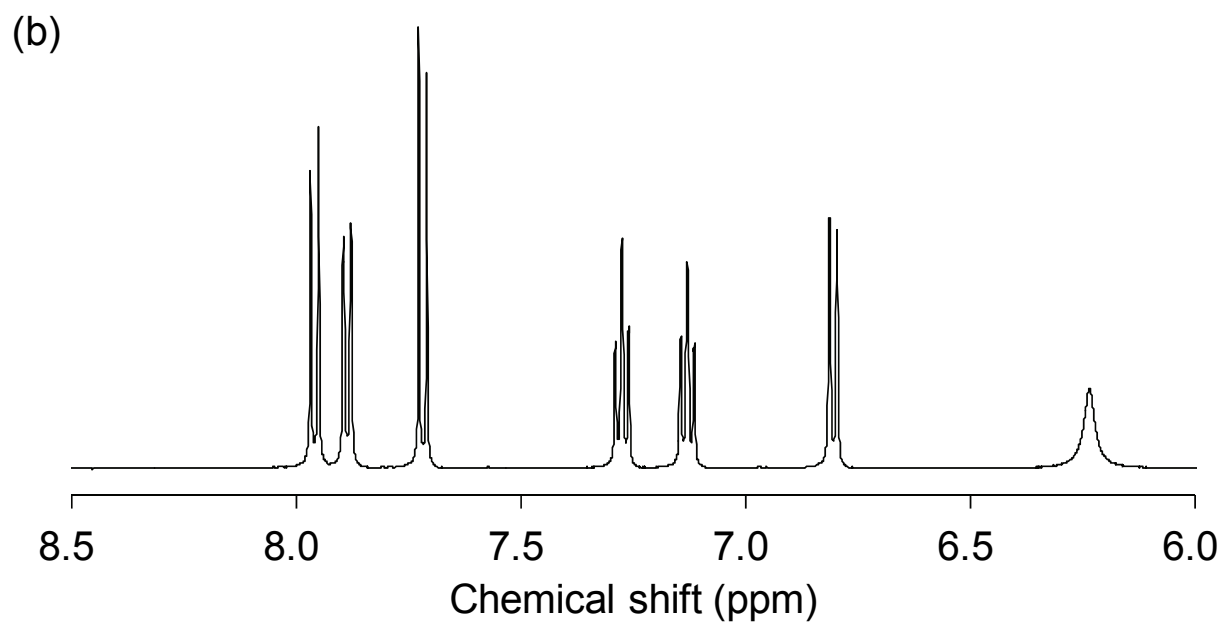
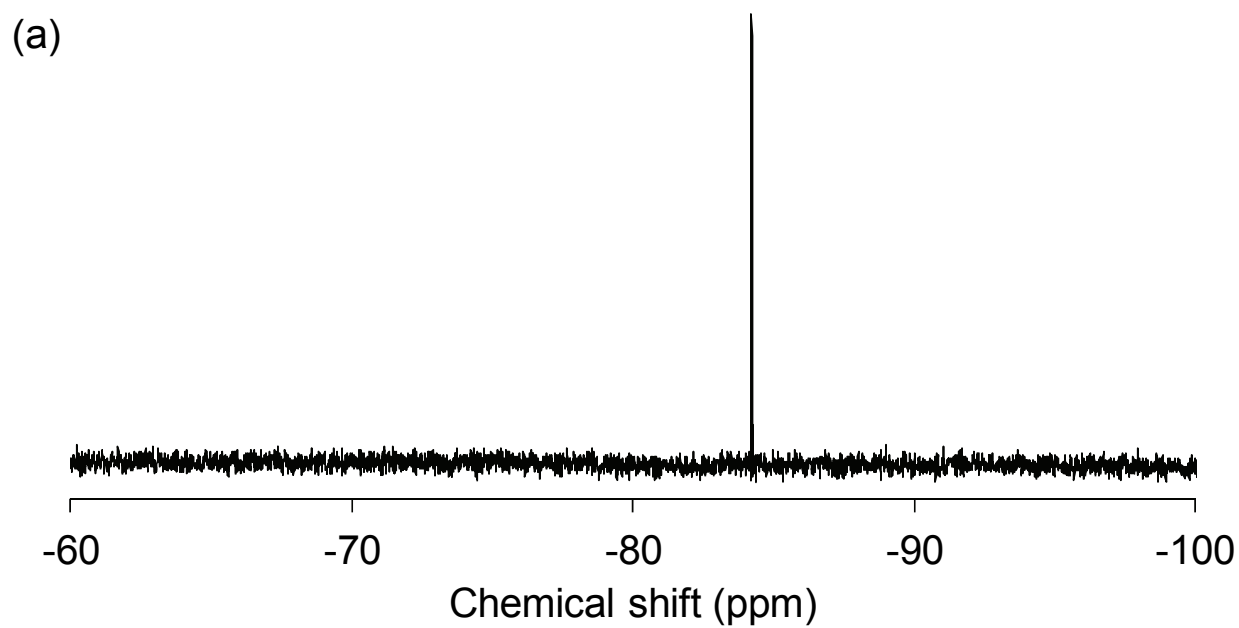


Fig. S4 (a) ^{29}Si and (b) ^1H NMR spectra of *S-I*.

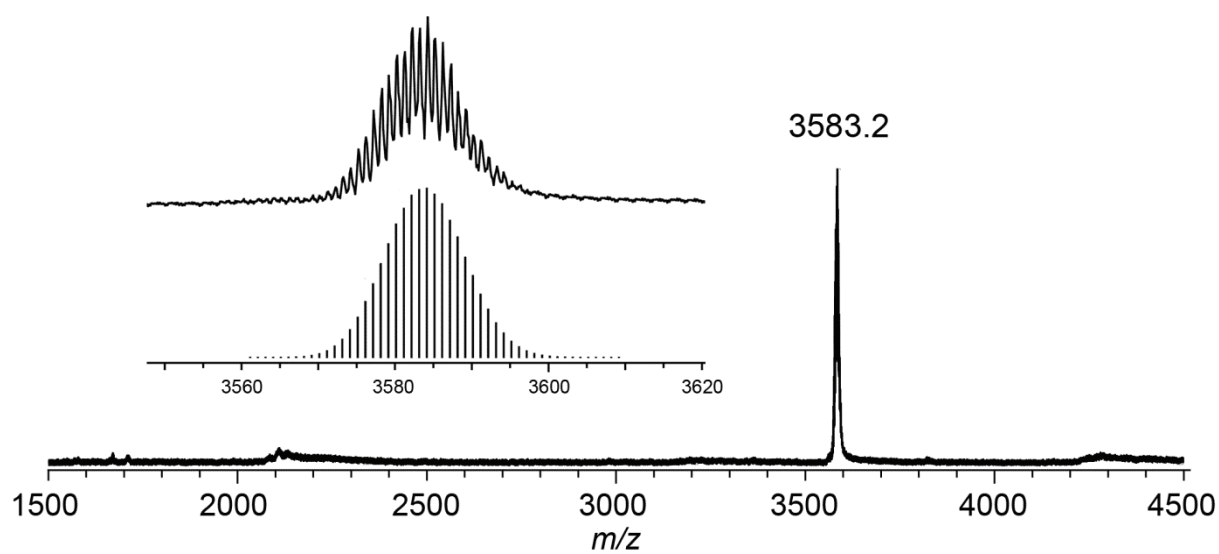


Fig. S5 Negative-ion CSI-MS spectrum of *R-I* (0.25 mM) in acetonitrile. Inset: calculated patterns for [TBA₃SiTi₂W₁₀O₃₈H₂(BINOLate)]⁻.

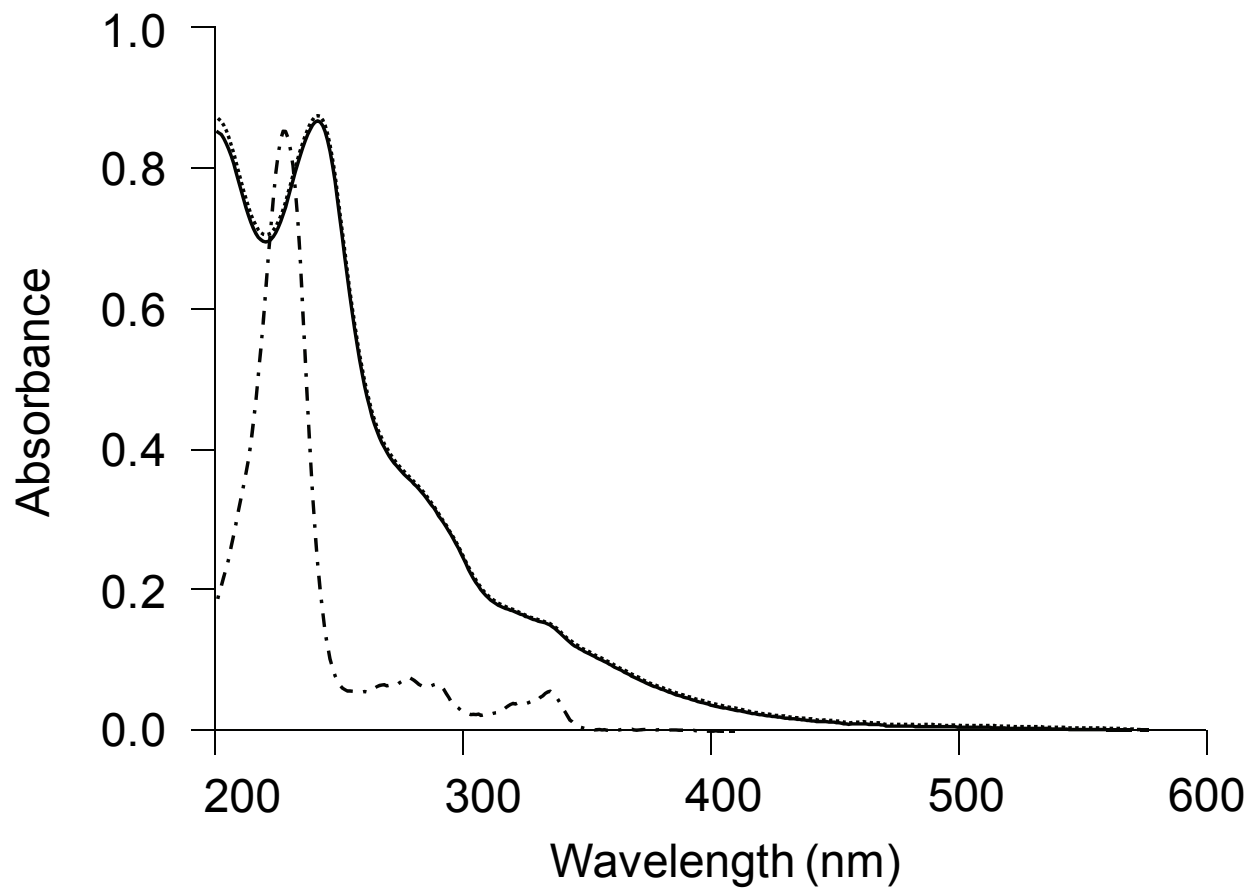


Fig. S6 UV-vis spectra of *R-I* (solid line), *S-I* (dotted line), and (*R*)-BINOL (dashdot line). Conditions: *R-I*, *S-I*, or (*R*)-BINOL (0.0725 mM) in acetonitrile.

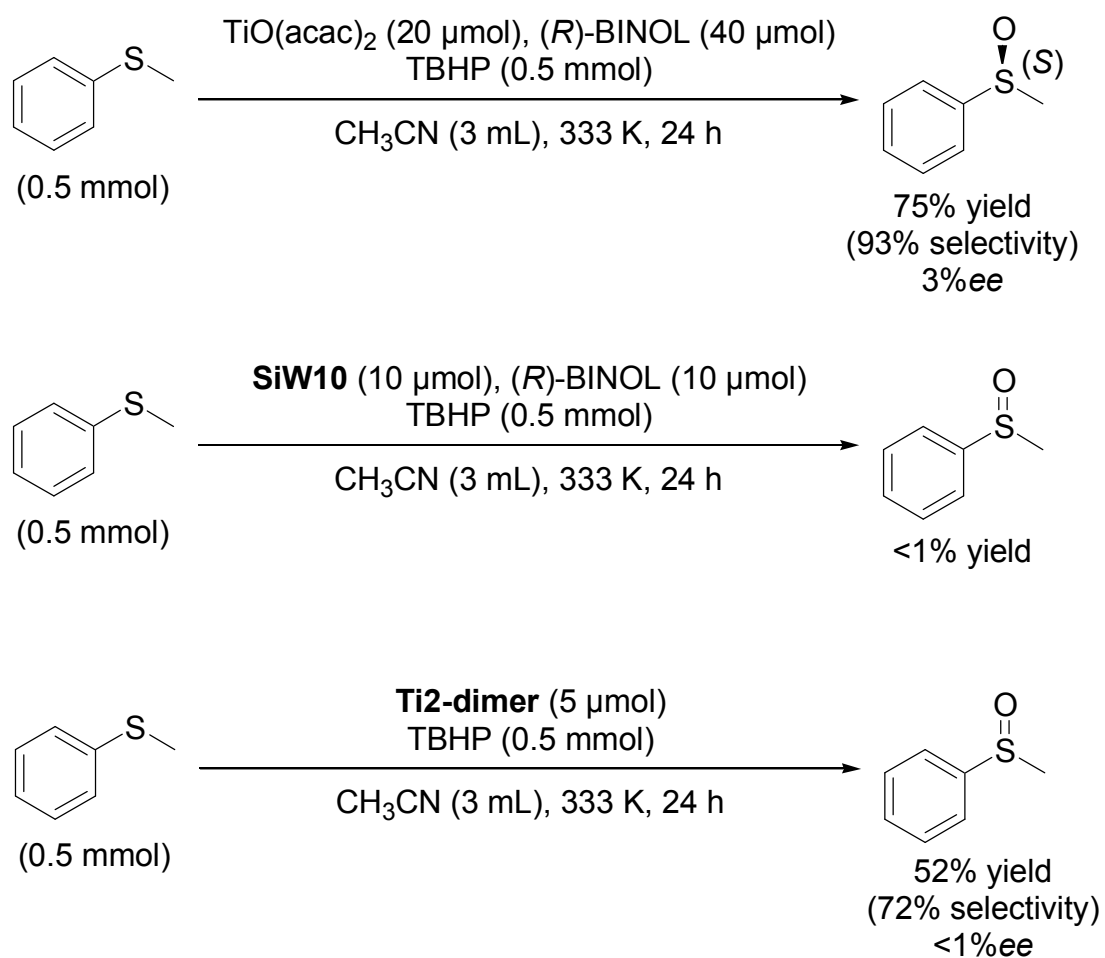


Fig. S7 Enantioselective oxidation of thioanisole catalyzed by $\text{TiO}(\text{acac})_2$ /*(R)*-BINOL, **SiW10**/*(R)*-BINOL, or **Ti2-dimer**.

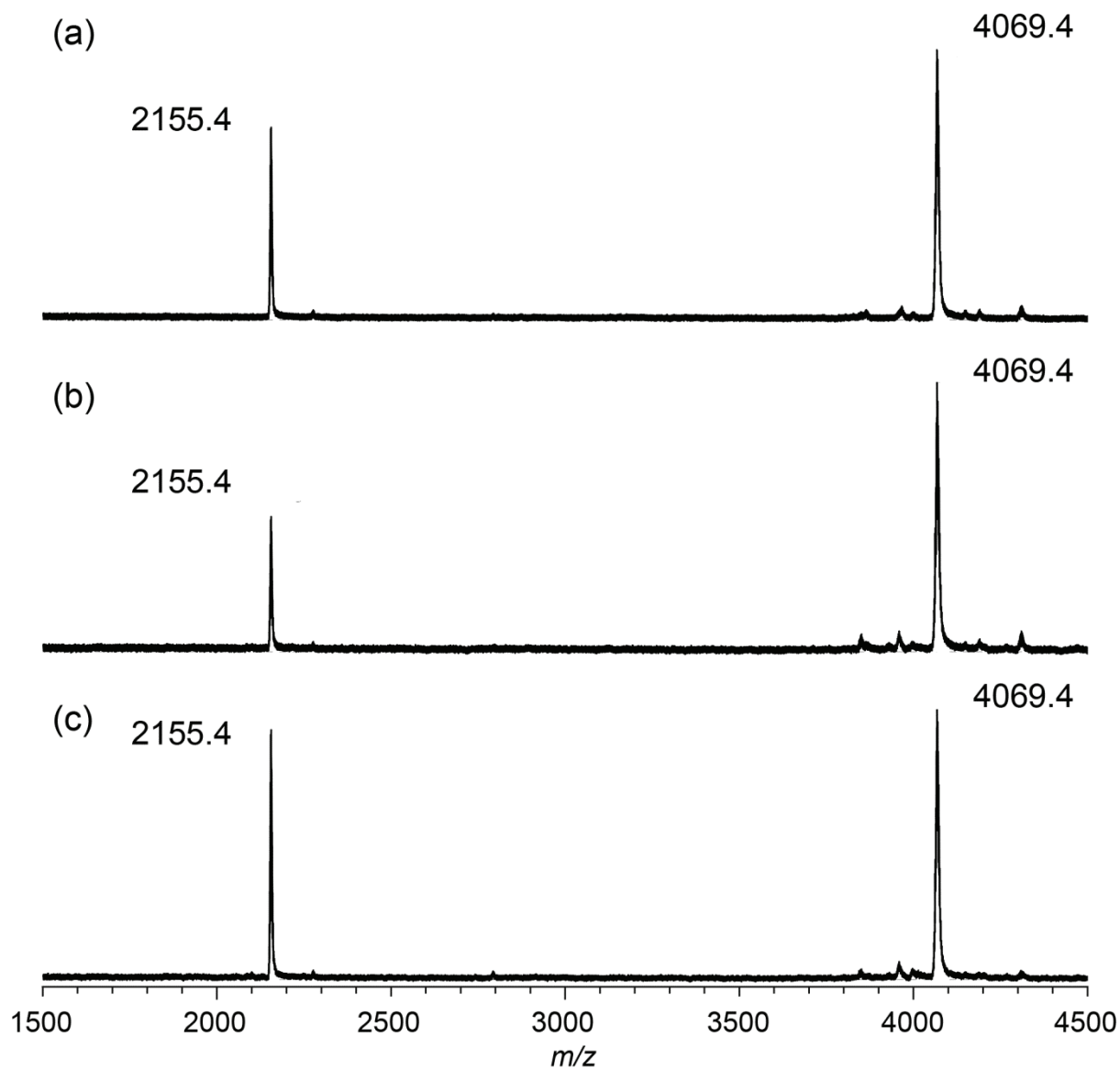


Fig. S8 Positive-ion CSI-MS spectra of (a) fresh *R-I* (before the reaction), (b) *R-I* during the catalytic oxidation of thioanisole (at 3 h), and (c) *R-I* recovered after the catalytic oxidation of thioanisole. The signal sets at $m/z = 2155.4$ and 4069.4 were assignable to $[\text{TBA}_6\text{SiTi}_2\text{W}_{10}\text{O}_{38}\text{H}_2(\text{BINOLate})]^{2+}$ and $[\text{TBA}_5\text{SiTi}_2\text{W}_{10}\text{O}_{38}\text{H}_2(\text{BINOLate})]^+$, respectively.