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Supplementary information for

One-Pot Asymmetric Sulfoxidation Using *in situ* Generated H_2O_2 from H_2 and O_2 Catalyzed by Rhodium and Vanadium Complexes

Takeshi Yatabe, Naoto Kanda, Mizuki Tsuji, Sho Sakogashira, Norifumi Tashiro,
Hidetaka Nakai, Seiji Ogo*

*To whom correspondence should be addressed.
E-mail: ogo.seiji.872@m.kyushu-u.ac.jp

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Experimental Section

Materials and Methods. H_2 (99.9999%) and O_2 (99.9999%) were purchased from Sumitomo Seika Chemical Co., Ltd, distilled water was purchased from Hayashi Pure Chemical Ind., Ltd, sodium sulfate, triethylamine, magnesium chrolide, hydrochloric acid, sodium chloride, sodium acetate *p*-methoxythioanisole, 2-(methylthio)naphthalene, cyclohexyl methyl sulfide, ethyl phenyl sulfide, and Wakogel® C-300 were purchased from FUJIFILM Wako Pure Chemical Corporation, paraformaldehyde, 2-phenylphenol, *N*-chlorosuccinimide, L-*tert*-leucinol, triisopropoxyvanadium(V) oxide, thioanisole, 4-chlorothioanisole, 2-methoxythioanisole, 3-methoxythioanisole, benzyl methyl sulfide, dodecyl methyl sulfide, benzyl phenyl sulfide, omeprazole sulfide, and chloroform-*d* were purchased from Tokyo Chemical Industry Co. Ltd, H_2O_2 (30% aqueous solution) and $H_2{}^{18}O_2$ (90% ^{18}O-enriched, 2-3% in $H_2{}^{16}O$) were purchased from Sigma-Aldrich, and $^{18}O_2$ (98 atm%) was purchased from SI Science Co., Ltd. These reagents were used without further purification. The Rh^{II} dimer complex $[Rh^{II}_2(L)_2(OH_2)_4](NO_3)_4$ $\{[\mathbf{1}](NO_3)_4\}$ and 2-hydroxy-3-phenylbenxaldehyde derivatives were prepared by the method described in the literature.[1–3]

NMR spectra were recorded on a Bruker Advance III 600 FT-NMR spectrometer at 25 °C. ^1H NMR experiments in $CDCl_3$ were measured using tetramethylsilane (TMS) as an internal standard. IR spectra were recorded on a PerkinElmer Spectrum Two as a solid state. Ultraviolet-visible-near-infrared (UV-vis-NIR) spectra were recorded on a JASCO V-670 UV-Visible-NIR Spectrophotometer (light pass length: 1.0 cm). Gas chromatography-mass spectrometry (GC-MS) data were recorded on an Agilent 7890B GC coupled to a 5977B MSD. High performance liquid chromatography (HPLC) was performed by using an Agilent 1260 HPLC infinity system equipped with a chiralcel OD-H or chiralcel OB-H columns (4.6 mm x 250 mm, particle size 5 mm). The absolute configuration of sulfides were determined by comparison of the literature data.[4–9] Electrospray ionization-mass spectrometry (ESI-MS) data were obtained by a JEOL JMS-T100LC AccuTOF. Elemental analysis data were obtained by a Yanaco CHN-coder MT-5.

General Procedure for Ligand Synthesis. An ethanol solution (35 mL) of 2-hydroxy-3-phenylbenxaldehyde derivatives (15.0 mmol) was added to an ethanol solution (15 mL) of L-*tert*-Leucinol (15.0 mmol) or L- Phenylalaninol (15.0 mmol) and sodium sulfate (10.7 g, 75.2 mmol), followed by stirring for 4 h at room temperature to afford orange solution. Then the reaction mixture was filtered to remove insoluble materials, and the filtrate was dried under reduced pressure. The residue was purified by silica gel column chromatography (CH_2Cl_2/methanol = 98:2).

H_2L (L = 5-chloro-3-(((3,3-dimethyl-1-oxidobutan-2-yl)imino)methyl)-[1,1'-biphenyl]-2-olate). Brown oil {yield: 63% based on 5-chloro-2-hydroxy-[1,1'-biphenyl]-3-carbaldehyde}. ^{1}H NMR (600 MHz, in $CDCl_3$, referenced to TMS, 25 °C): δ 14.05 (br, 1H, Ar-O*H*), 8.33 (s, 1H, N=C*H*), 7.61 (d, 2H, Ar-*H*), 7.45 (t, 2H, Ar-*H*), 7.38-7.34 (m, 2H, Ar-*H*), 7.27 (d, 1H, Ar-*H*), 3.95 (dd, 1H, C*H*$_2$OH), 3.70 (t, 1H, N-C*H*), 2.97 (dd, 1H, C*H*$_2$OH), 0.96 (s, 9H, C(C*H*$_3$)$_3$). ^{13}C NMR (150 MHz, in $CDCl_3$, referenced to TMS, 25 °C): Anal. Calcd for H_2L: $C_{19}H_{22}ClNO_2$: C, 68.77; H, 6.68; N, 4.22%. Found: C, 68.93; H, 6.62; N, 4.08%.

H_2L2 (L = 5-methoxy-3-(((3,3-dimethyl-1-oxidobutan-2-yl)imino)methyl)-[1,1'-biphenyl]-2-olate). Brown solid {yield: 64% based on 2-hydroxy-5-methoxy-[1,1'-biphenyl]-3-carbaldehyde}. ^{1}H NMR (600 MHz, in $CDCl_3$, referenced to TMS, 25 °C): δ 8.38 (s, 1H, N=C*H*), 7.63 (d, 2H, Ar-*H*), 7.44 (t, 2H, Ar-*H*), 7.35 (t, 1H, Ar–*H*), 7.04 (d, 1H, Ar–*H*), 6.84 (d, 1H, Ar-*H*), 3.95 (dd, 1H, C*H*$_2$OH), 3.83 (s, 3H, –OCH_3), 3.54 (t, 1H, N-C*H*), 2.97 (dd, 1H, C*H*$_2$OH), 0.97 (s, 9H, C(C*H*$_3$)$_3$).

H_2L3 (L = 3-(((3,3-dimethyl-1-oxidobutan-2-yl)imino)methyl)-[1,1'-biphenyl]-2-olate). Yellow solid {yield: 65% based on 2-hydroxy-[1,1'-biphenyl]-3-carbaldehyde}. ^{1}H NMR (600 MHz, in $CDCl_3$, referenced to TMS, 25 °C): δ 14.02 (br, 1H, Ar-O*H*), 8.40 (s, 1H, N=C*H*), 7.63 (d, 2H, Ar-*H*), 7.45-7.40 (m, 3H, Ar-*H*), 7.34 (t, 1H, Ar-*H*), 7.30 (dd, 1H, Ar–*H*), 6.98 (t, 1H, Ar–*H*), 3.93 (dd, 1H, C*H*$_2$OH), 3.70 (t, 1H, N-C*H*), 2.96 (dd, 1H, C*H*$_2$OH), 0.96 (s, 9H, C(C*H*$_3$)$_3$).

H_2L4 (L = 5-bromo-3-(((3,3-dimethyl-1-oxidobutan-2-yl)imino)methyl)-[1,1'-biphenyl]-2-olate). Brown solid {yield: 46% based on 5-bromo-2-hydroxy-[1,1'-biphenyl]-3-carbaldehyde}. ^{1}H NMR (600 MHz, in $CDCl_3$, referenced to TMS, 25 °C): δ 14.06 (br, 1H, Ar-O*H*), 8.33 (s, 1H, N=C*H*), 7.60 (dd, 2H, Ar-*H*), 7.51 (d, 1H, Ar-*H*), 7.44 (t, 2H, Ar-*H*), 7.41 (d, 1H, Ar-*H*), 7.36 (tt, 1H, Ar-*H*), 3.95 (dd, 1H, C*H*$_2$OH), 3.70 (t, 1H, N-C*H*), 2.98 (dd, 1H, C*H*$_2$OH), 0.96 (s, 9H, C(C*H*$_3$)$_3$).

H$_2$L5 (L = 5-nitroso-3-(((3,3-dimethyl-1-oxidobutan-2-yl)imino)methyl)-[1,1'-biphenyl]-2-olate). Brown powder {yield: 59% based on 2-hydroxy-5-nitroso-[1,1'-biphenyl]-3-carbaldehyde}. ^{1}H NMR (600 MHz, in CDCl$_3$, referenced to TMS, 25 °C): δ 15.33 (br, 1H, Ar-O*H*), 8.29 (s, 1H, N=C*H*), 8.24 (d, 1H, Ar-*H*), 8.20 (d, 1H, Ar-*H*), 7.62 (d, 2H, Ar-*H*), 7.46 (t, 2H, Ar-*H*), 7.39 (tt, 1H, Ar–*H*), 3.98 (d, 1H, C*H*$_2$OH), 3.69 (t, 1H, N-C*H*), 3.11 (d, 1H, C*H*$_2$OH), 1.02 (s, 9H, C(C*H*$_3$)$_3$).

H$_2$L6 (L = 5-chloro-3-(((1-oxido-3-phenylpropan-2-yl)imino)methyl)-[1,1'-biphenyl]-2-olate). Brown oil {yield: 58% based on 5-chloro-2-hydroxy-[1,1'-biphenyl]-3-carbaldehyde}. ^{1}H NMR (600 MHz, in CDCl$_3$, referenced to TMS, 25 °C): δ 13.95 (br, 1H, Ar-O*H*), 8.03 (s, 1H, N=C*H*), 7.60 (d, 2H, Ar-*H*), 7.45 (t, 2H, Ar-*H*), 7.39–7.36 (m, 2H, Ar-*H*), 7.26 (t, 2H, Ar-*H*), 7.20 (t, 1H, Ar–*H*), 7.12 (t, 2H, Ar–*H*), 7.09 (d, 1H, Ar–*H*), 3.84 (dd, 1H, C*H*$_2$OH), 3.77 (dd, 1H, –C*H*$_2$–), 3.57–3.53 (m, 1H, N–C*H*), 2.99 (dd, 1H, C*H*$_2$OH), 2.83 (dd, 1H, –C*H*$_2$–).

[V^V(O)(L)(O^{i}Pr)] (2). [V^V(O)(O^{i}Pr)$_3$] (0.24 mL, 1.0 mmol) was added to a ^{i}PrOH solution (10 mL) of H$_2$L (332 mg, 1.0 mmol), followed by stirring for 1 h at room temperature to afford dark red solution. The resulting solution was evaporated under reduced pressure to yield black solid **2** {yield: 99% based on [V^{V}O(O^{i}Pr)$_3$]}.^{1}H NMR (600 MHz, in CDCl$_3$, referenced to TMS, 25 °C): δ 8.51 (s, 1H, C*H*=N), 7.67 (d, 2H, Ar-*H*), 7.57 (d, 1H, Ar-*H*), 7.42 (m, 3H, Ar-*H*), 7.35 (t, 1H, Ar-*H*), 5.34 (m, 1H, C*H*(CH$_3$)$_2$), 5.22 (q, N-C*H*, 1H), 4.86 (d, 1H, C*H*$_2$OH), 3.99 (d, 1H, C*H*$_2$OH), 1.37 (d, 3H, CH(C*H*$_3$)$_2$), 1.30 (d, 3H, CH(C*H*$_3$)$_2$), 0.94 (s, 9H, (C*H*$_3$)$_3$). ^{13}C NMR (150 MHz, in CDCl$_3$, referenced to TMS, 25 °C): Anal. Calcd for **1**·0.5H$_2$O: $C_{22}H_{28}ClNO_{4.5}V$: C, 56.84; H, 6.07; N, 3.01%. Found: C, 56.59; H, 5.77; N, 2.83%. ESI-MS (in acetone/methanol with NaCl): *m*/*z* 534.0 {[**2**+Na+2N$_2$]$^+$, relative intensity (*I*) = 100% in the range of *m*/*z* 100 to 2000}. ATR-FTIR (cm^{-1}): 966.

[V^V(O)(L)(O$_2$)] (3). A methanol solution (1 mL) of **2** (10 mg, 22 μmol) was cooled to 10 ºC and H$_2$O$_2$ (110 μmol) in methanol (100 μL) was added. The mixture was stirred for

15 min at 10 ºC, and the resulting solution was evaporated under reduced pressure to yield black solid **3**. ATR-FTIR (cm^{-1}): 897.

Typical Procedure for Ligand Screening. A CH_2Cl_2 solution (2 mL) of $[V^{IV}(O)(acac)_2]$ (10 µmol) and ligand (15 µmol) was stirred for 5 min at room temperature. Then, thioanisole (1 mmol) and an aqueous H_2O_2 (30%, 1.1 mmol) were added into the reaction solution. After stirring (1100 rpm) for 16 h at room temperature, the solvent was evaporated under reduced pressure, and the residue was purified by silica gel column chromatography (hexane/AcOEt = 50:50 to AcOEt) to give methyl phenyl sulfoxide. The produced sulfoxide was characterized and quantified by ^1H NMR spectroscopy and its enantiomeric excess was determined by chiral HPLC.

Typical Procedure for the Asymmetric Oxidation of Thioanisole Using Authentic H_2O_2. A CH_2Cl_2 solution (4 mL) of **2** (9.1 mg, 20 µmol) and thioanisole (200 µmol) was added to an aqueous solution (4 mL) of H_2O_2 (220 µmol) and sodium acetate (2.0 mmol). After stirring (1100 rpm) for 2 h at room temperature, the biphasic mixture was separated into the organic and aqueous phases. The isolated aqueous phase was extracted with AcOEt (3 × 4 mL). The combined organic phase was dried over anhydrous Na_2SO_4 and filtered. The filtrate was evaporated under reduced pressure, and the residue was purified by silica gel column chromatography (hexane/AcOEt = 50:50 to AcOEt) to give methyl phenyl sulfoxide. The produced sulfoxide was characterized and quantified by ^1H NMR spectroscopy and its enantiomeric excess was determined by chiral HPLC.

Typical Procedure for Asymmetric Oxidation of Sulfides Using H_2 and O_2. A polypropylene tube containing an aqueous CH_3COONa solution (0.5 M, 4.0 mL) of [**1**]$(NO_3)_4$ (100 µM) was transferred to the reaction cylinder, and the reaction solution was stirred for 12 h under an H_2/O_2 (95/5) atmosphere at a pressure of 1.9 MPa at room temperature. After removing the H_2 and O_2 gases, a CH_2Cl_2 solution (4 mL) of **2** (9.1 mg, 20 µmol) and sulfide (200 µmol) was added to the reaction mixture. After stirring (1100 rpm) for 2 h at room temperature, the biphasic mixture was separated into the organic and aqueous phases. The isolated aqueous phase was extracted with AcOEt (3 × 4 mL). The combined organic phase was dried over anhydrous Na_2SO_4 and filtered. The filtrate was evaporated under reduced pressure, and the residue was purified by silica gel column chromatography (hexane/AcOEt = 50:50 to AcOEt) to give corresponding sulfoxide. The produced sulfoxide was characterized and quantified by ^{1}H NMR spectroscopy (Figs. S4–S14) and its enantiomeric excess was determined by chiral HPLC.

Isotope Labeling Experiment for the ^{18}O-labeled Methyl Phenyl Sulfoxide from the Catalytic Reaction with 1 and 2 Using H_2 and $^{18}O_2$ and Thioanisole. $^{18}O_2$ (50 mL) was injected to the Hiper glass cylinder containing an aqueous CH_3COONa solution (0.5 M, 4.0 mL) of [**1**]$(NO_3)_4$ (100 μM), and the resulting solution was stirred for 12 h under an H_2 atmosphere (1.9 MPa) at room temperature. After removing the H_2 and $^{18}O_2$ gases, a CH_2Cl_2 solution (4 mL) of **2** (9.1 mg, 20 μmol) and thioanisole (200 μmol) was added to the reaction mixture. After stirring for 2 h at room temperature, the biphasic mixture was separated into the organic and aqueous phases. The isolated aqueous phase was extracted with AcOEt (3 × 4 mL). The combined organic phase was dried over anhydrous Na_2SO_4 and filtered. The filtrate was evaporated under reduced pressure, and the residue was purified by silica gel column chromatography (hexane/AcOEt = 50:50 to AcOEt). The formed ^{18}O-labeled methyl phenyl sulfoxide was detected by GC- MS.

Yield, Enantiomeric Excess, and Spectroscopic Data of Products

(*S*)-Methyl phenyl sulfoxide. Colerless oil; 15.7 mg, 56%; 59% ee; ^{1}H NMR (600 MHz, in CDCl$_3$, referenced to TMS): δ 7.65 (d, 2H, Ar-*H*), 7.55-7.49 (m, 3H, Ar-*H*), 2.73 (s, 3H, C*H*$_3$); HPLC: t_R (*R*) = 12.0 min (minor isomer), t_R (*S*) = 13.4 min (major isomer) (Chiralcel OD-H column, *n*-hexane/^{i}PrOH = 90:10, flow rate = 0.5 mL/ min, wavelength = 254 nm).

(*S*)-*p*-Chlorophenyl methyl sulfoxide. Pale yellow oil; 17.3 mg, 50%; 58% ee; ^{1}H NMR (600 MHz, in CDCl$_3$, referenced to TMS): δ 7.60 (d, 2H, Ar-*H*), 7.52 (d, 2H, Ar-*H*), 2.72 (s, 3H, C*H*$_3$); HPLC: t_R (*R*) = 57.6 min (minor isomer), t_R (*S*) = 61.3 min (major isomer) (Chiralcel OD-H column, *n*-hexane/EtOH = 95:5, flow rate = 0.5 mL/ min, wavelength = 254 nm).

(*S*)-*p*-Methoxyphenyl methyl sulfoxide. Colerless oil; 19.8 mg, 58%; 38% ee; ^{1}H NMR (600 MHz, in CDCl$_3$, referenced to TMS): δ 7.60 (d, 2H, Ar-*H*), 7.03 (d, 2H, Ar-*H*), 3.86 (s, 3H, OC*H*$_3$), 2.70 (s, 3H, SC*H*$_3$); HPLC: t_R (*S*) = 12.7 min (major isomer), t_R (*R*) = 23.6 min (minor isomer) (Chiralcel OB-H column, *n*-hexane/^{i}PrOH = 50:50, flow rate = 0.5 mL/ min, wavelength = 254 nm).

(*S*)-*m*-Methoxyphenyl methyl sulfoxide. Pale yellow oil; 26.2 mg, 77%; 63% ee; ^{1}H NMR (600 MHz, in CDCl$_3$, referenced to TMS): δ 7.42 (t, 1H, Ar-*H*), 7.26 (s, 1H, Ar-*H*), 7.12 (d, 1H, Ar-*H*), 7.02 (d, 1H, Ar-*H*), 3.87 (s, 3H, OC*H*$_3$), 2.73 (s, 3H, SC*H*$_3$); HPLC: t_R (*S*) = 22.9 min (major isomer), t_R (*R*) = 35.4 min (minor isomer) (Chiralcel OB-H column, *n*-hexane/^{i}PrOH = 80:20, flow rate = 0.5 mL/ min, wavelength = 254 nm).

(*S*)-*o*-Methoxyphenyl methyl sulfoxide.Pale yellow oil; 22.7 mg, 67%; 39% ee; ^{1}H NMR (600 MHz, in CDCl$_3$, referenced to TMS): δ 7.82 (d, 1H, Ar-*H*), 7.46 (t, 1H, Ar-*H*), 7.19 (t, 1H, Ar-*H*), 6.93 (d, 1H, Ar-*H*), 3.89 (s, 3H, OC*H*$_3$), 2.78 (s, 3H, SC*H*$_3$); HPLC: t_R (*S*) = 19.4 min (major isomer), t_R (*R*) = 42.5 min (minor isomer) (Chiralcel OB-H column, *n*-hexane/^{i}PrOH = 80:20, flow rate = 0.5 mL/ min, wavelength = 254 nm).

(*S*)-Benzyl methyl sulfoxide. White solid; 27.0 mg, 88%; 12% ee; ^{1}H NMR (600 MHz, in CDCl$_3$, referenced to TMS): δ 7.42-7.33 (m, 3H, Ar-*H*), 7.29 (d, 2H, Ar-*H*), 4.05 (d, 1H, PhC*H*$_2$), 3.93 (d, 1H, PhC*H*$_2$), 2.45 (s, 3H, C*H*$_3$); HPLC: t_R (*S*) = 41.3 min (major isomer), t_R (*R*) = 46.9 min (minor isomer) (Chiralcel OD-H column, *n*-hexane/^{i}PrOH = 95:5, flow rate = 1.0 mL/ min, wavelength = 254 nm).

(*S*)-Methyl 2-naphthyl sulfoxide. Pale yellow solid; 12.4 mg, 33%; 42% ee; ^{1}H NMR (600 MHz, in $CDCl_3$, referenced to TMS): δ 8.22 (s, 1H, Ar-*H*), 7.99 (d, 1H, Ar-*H*), 7.95 (t, 1H, Ar-*H*), 7.91 (t, 1H, Ar-*H*), 7.62-7.58 (m, 3H, Ar-*H*), 2.80 (s, 3H, CH_3); HPLC: t_R (*R*) = 38.3 min (minor isomer), t_R (*S*) = 42.8 min (major isomer) (Chiralcel OD-H column, *n*-hexane/^{i}PrOH = 90:10, flow rate = 0.5 mL/ min, wavelength = 254 nm).

(*S*)-Benzyl phenyl sulfoxide. White solid; 20.0 mg, 38%; 69% ee; ^{1}H NMR (600 MHz, in $CDCl_3$, referenced to TMS): *δ* 7.48-7.35 (m, 5H, Ar-*H*), 7.30-7.22 (m, 3H, Ar-*H*), 6.98 (d, 2H, Ar-*H*), 4.09 (d, 1H, CH_2), 4.00 (d, 1H, CH_2); HPLC: t_R (*R*) = 14.1 min (minor isomer), t_R (*S*) = 17.0 min (major isomer) (Chiralcel OD-H column, *n*-hexane/^{i}PrOH = 90:10, flow rate = 1.0 mL/ min, wavelength = 254 nm).

(*S*)-Ethyl phenyl sulfoxide. Pale yellow oil; 16.3 mg, 53%; 57% ee; ^{1}H NMR (600 MHz, in $CDCl_3$, referenced to TMS): *δ* 7.61 (d, 2H, Ar-*H*), 7.55-7.48 (m, 3H, Ar-*H*), 2.90 (m, 1H, CH_2), 2.78 (m, 1H, CH_2), 1.20 (t, 3H, CH_3); HPLC: t_R (*R*) = 19.0 min (minor isomer), t_R (*S*) = 22.8 min (major isomer) (Chiralcel OD-H column, *n*-hexane/^{i}PrOH = 90:10, flow rate = 0.5 mL/ min, wavelength = 254 nm).

(*S*)-*n*-Dodecyl methyl sulfoxide. White solid; 117.9 mg, 59 %; 14% ee; ^{1}H NMR (600 MHz, in $CDCl_3$, referenced to TMS): *δ* 2.78-2.70 (m, 1H, SCH_2), 2.69-2.61 (m, 1H, SCH_2), 2.57 (s, 3H, SCH_3), 1.81-1.70 (m, 2H, SCH_2CH_2), 1.53-1.19 (m, 18H, CH_2), 0.88 (t, 3H, CH_3CH_2); HPLC: t_R (*R*) = 21.9 min (major isomer), t_R (*S*) = 24.5 min (minor isomer) (Chiralcel OB-H column, *n*-hexane/^{i}PrOH = 99:1, flow rate = 0.8 mL/ min, wavelength = 215 nm).

(*S*)-Cyclohexyl methyl sulfoxide. Pale yellow oil; 14.1 mg, 48%; 13% ee; ^{1}H NMR (600 MHz, in $CDCl_3$, referenced to TMS): *δ* 2.56-2.49 (m, 4H, $CHSCH_3$), 2.15 (d, 1H, Cy-*H*), 1.97-1.86 (m, 3H, Cy-*H*), 1.73 (d, 1H, Cy-*H*), 1.49-1.22 (m, 5H, Cy-*H*); HPLC: t_R (*S*) = 6.6 min (major isomer), t_R (*R*) = 8.0 min (minor isomer) (Chiralcel OB-H column, *n*-hexane/^{i}PrOH = 80:20, flow rate = 0.8 mL/ min, wavelength = 215 nm).

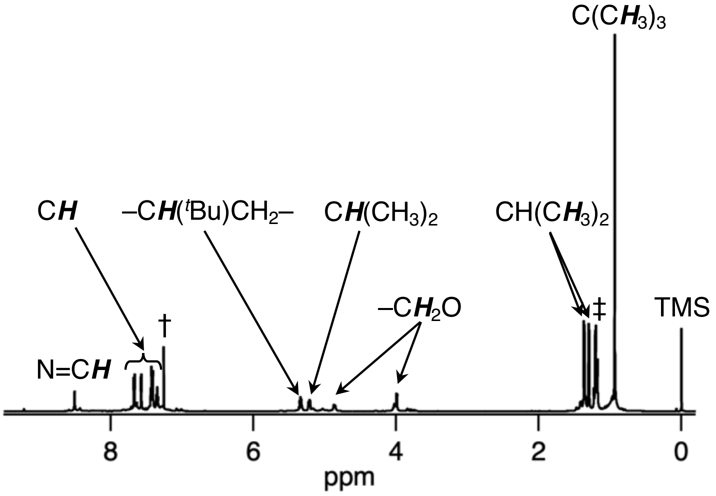


Fig. S1 NMR spectrum of **2** in $CDCl_3$. Tetramethylsilane (TMS), reference with the methyl proton resonance set at 0.00 ppm. ‡: Peak of ^{i}PrOH. †: Peak of chloroform.

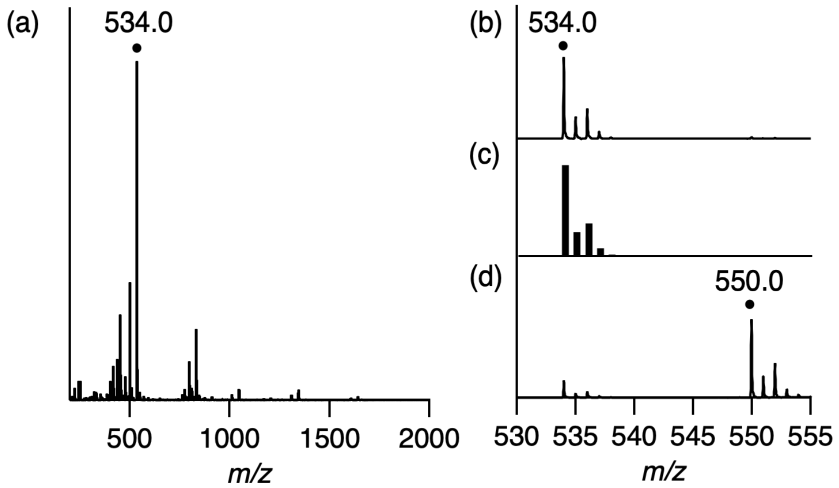


Fig. S2 (a) Positive-ion ESI-mass spectrum of **2** with NaCl in acetone/methanol. The signal at *m*/*z* 534.0 corresponds to [**2**+Na+2N$_2$]$^+$. N$_2$ is derived from nebulizer N$_2$ gas of ESI-MS. (b) The signal at *m*/*z* 534.0 for [**2**+Na+2N$_2$]$^+$. (c) The calculated isotopic distribution for [**2**+Na+2N$_2$]$^+$. (d) Positive-ion ESI-mass spectrum of **2** with KBr in acetone/methanol. The signal at *m*/*z* 550.0 corresponds to [**2**+K+2N$_2$]$^+$. N$_2$ is derived from nebulizer N$_2$ gas of ESI-MS.

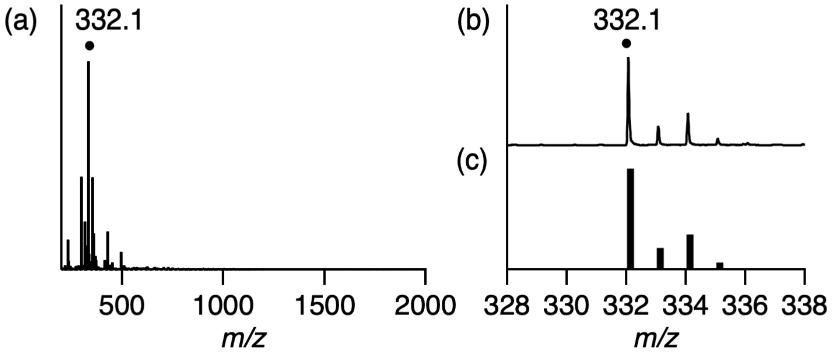


Fig. S3 (a) Positive-ion ESI-mass spectrum of **2** with sodium acetate in acetone/methanol. The signal at *m*/*z* 332.1 corresponds to $[H_2L+H]^+$ derived from the ligand L without vanadium ion. (b) The signal at *m*/*z* 332.1 for $[H_2L+H]^+$. (c) The calculated isotopic distribution for $[H_2L+H]^+$.

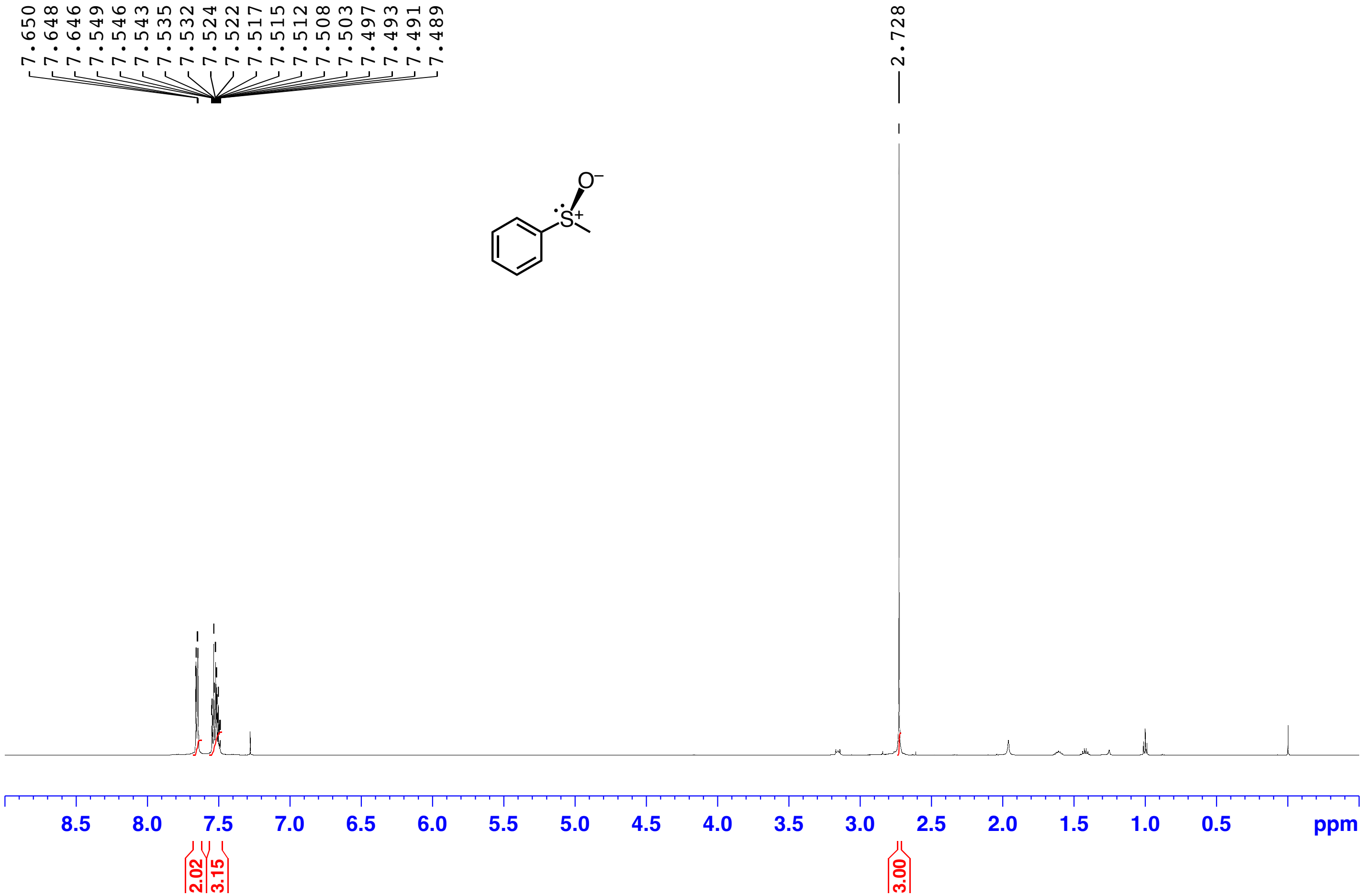


Fig. S4 ^{1}H NMR spectrum of methyl phenyl sulfoxide in $CDCl_3$.

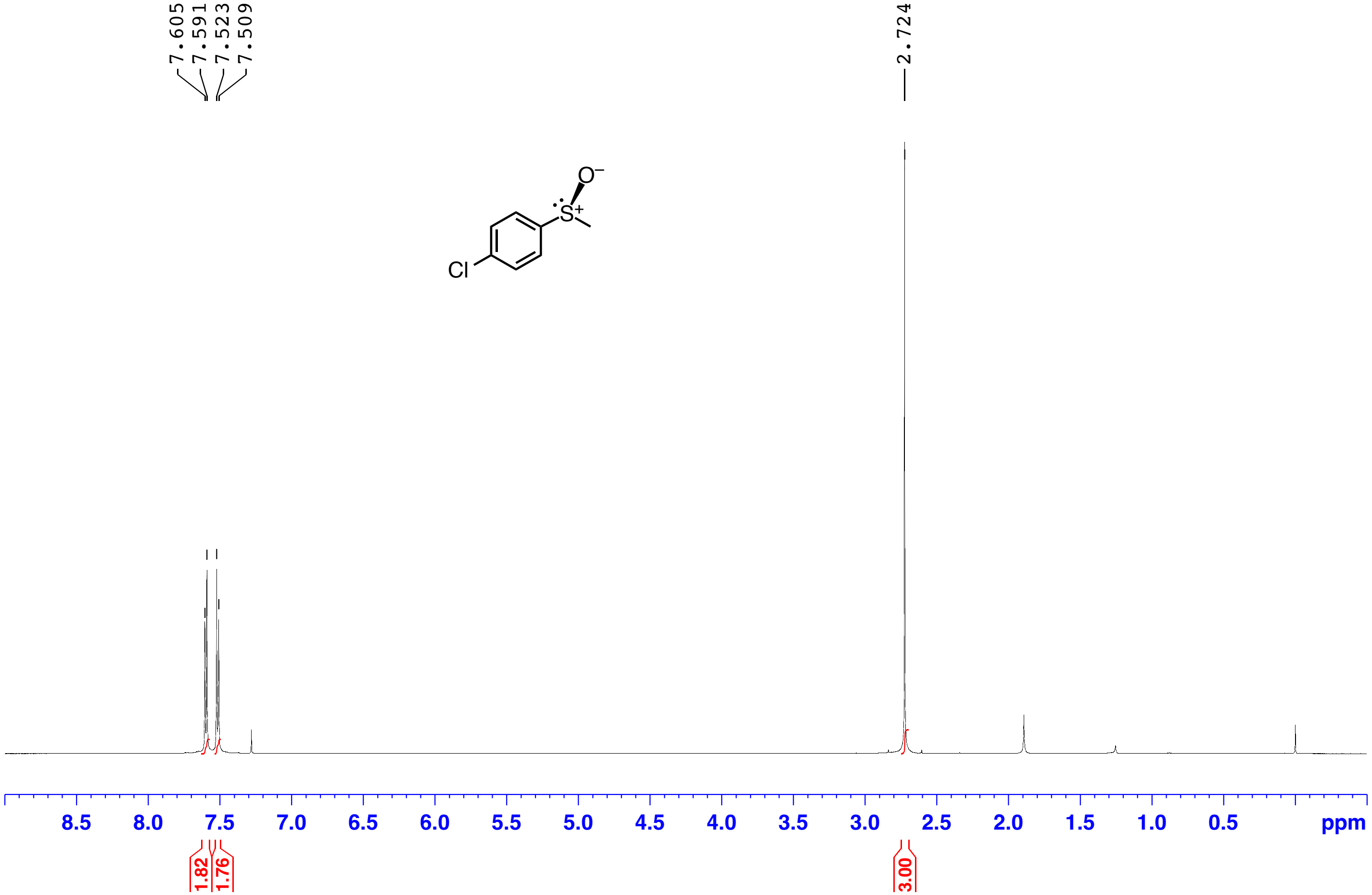


Fig. S5 ^{1}H NMR spectrum of *p*-chlorophenyl methyl sulfoxide in $CDCl_3$.

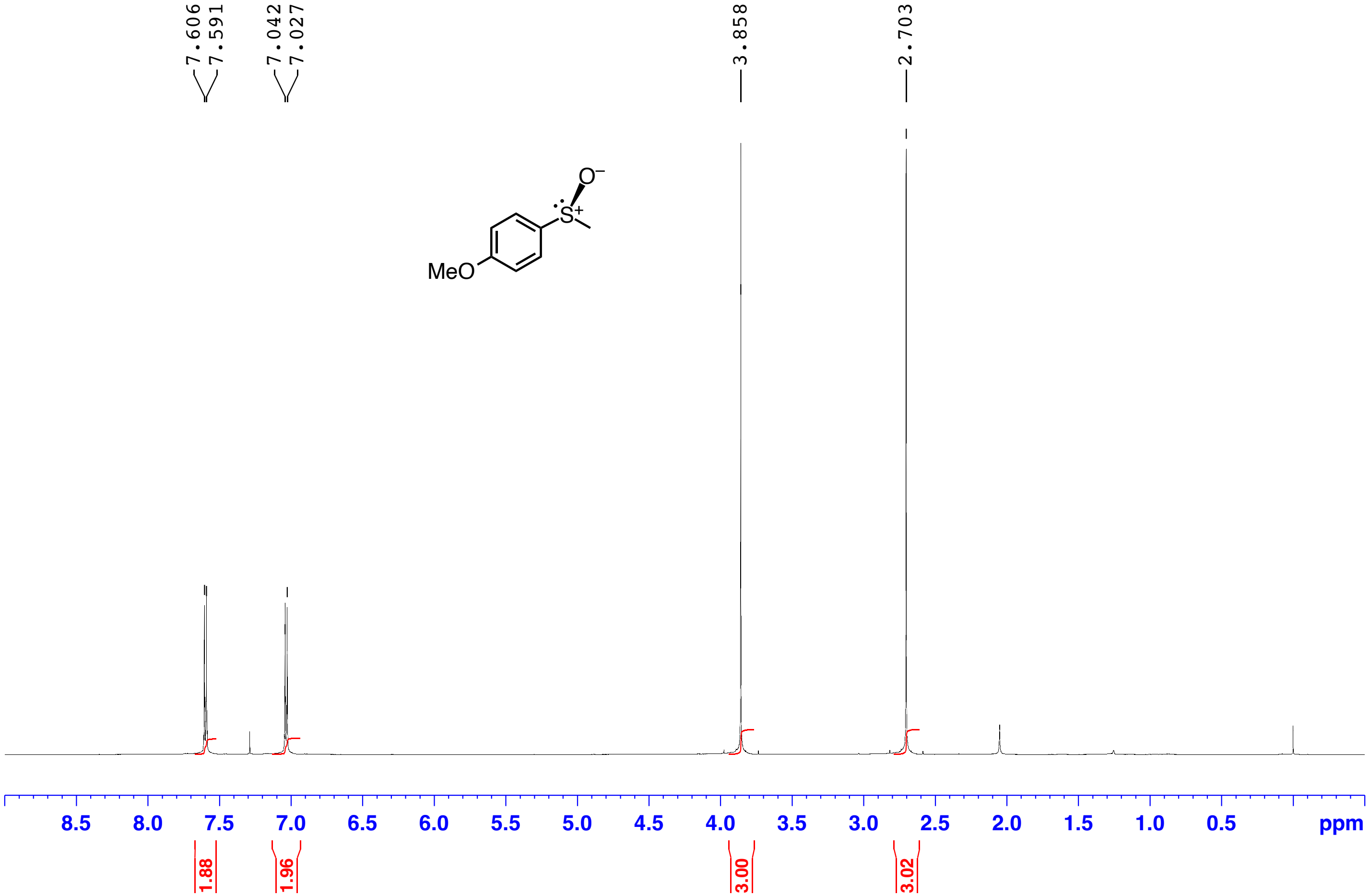


Fig. S6 ^{1}H NMR spectrum of *p*-methoxyphenyl methyl sulfoxide in $CDCl_3$.

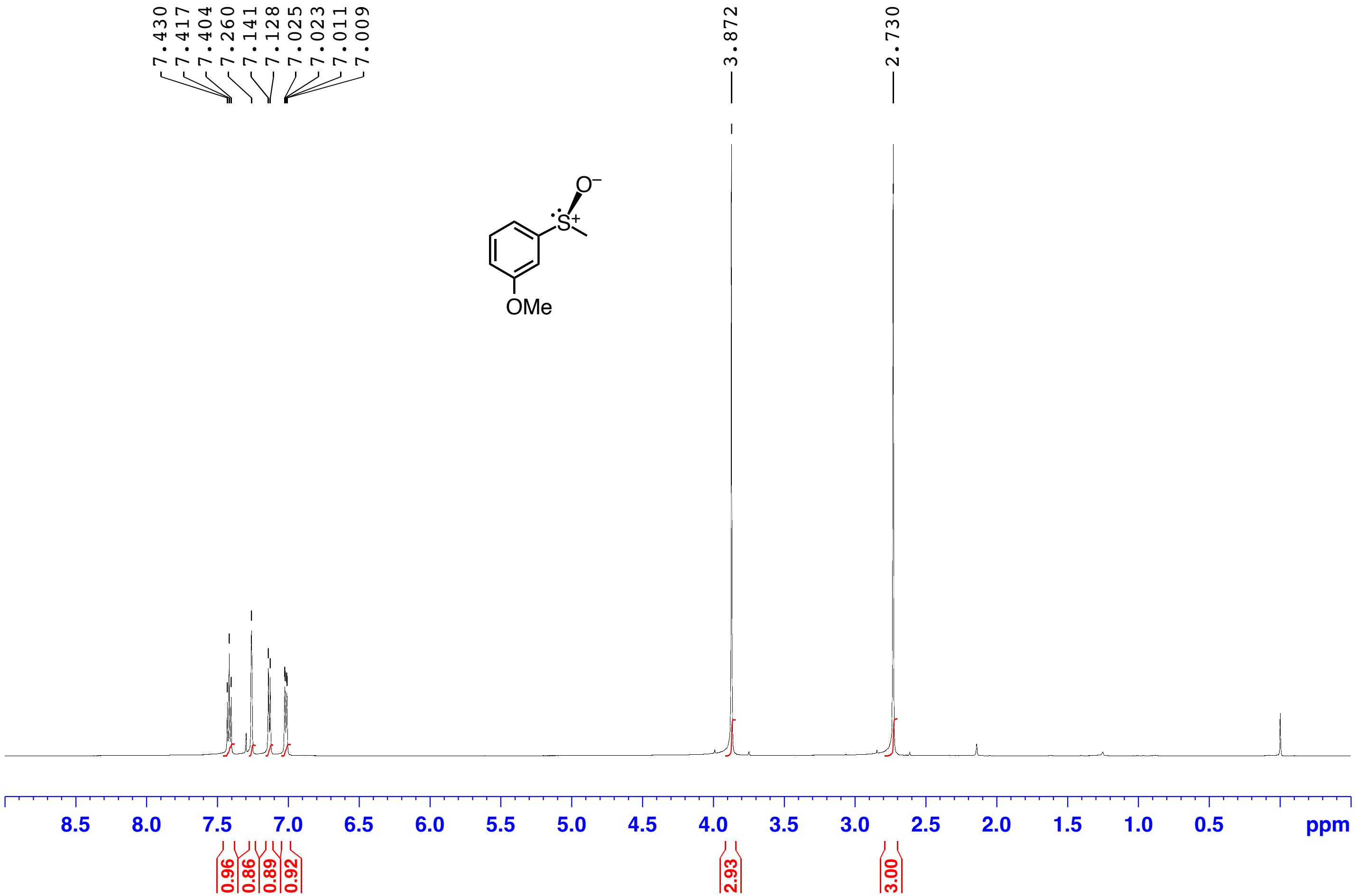


Fig. S7 ^{1}H NMR spectrum of *m*-methoxyphenyl methyl sulfoxide in $CDCl_3$.

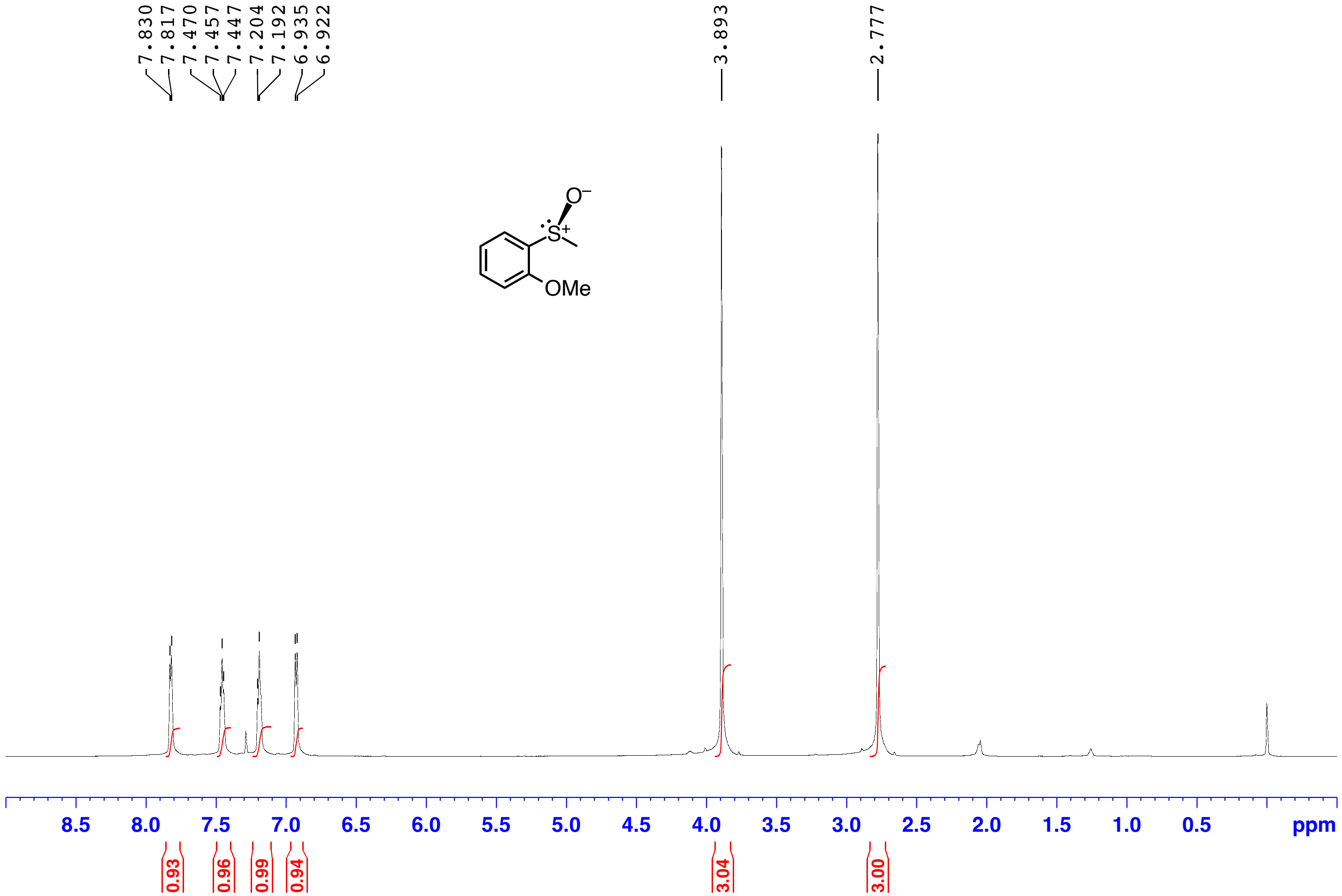


Fig. S8 ^{1}H NMR spectrum of *o*-methoxyphenyl methyl sulfoxide in $CDCl_3$.

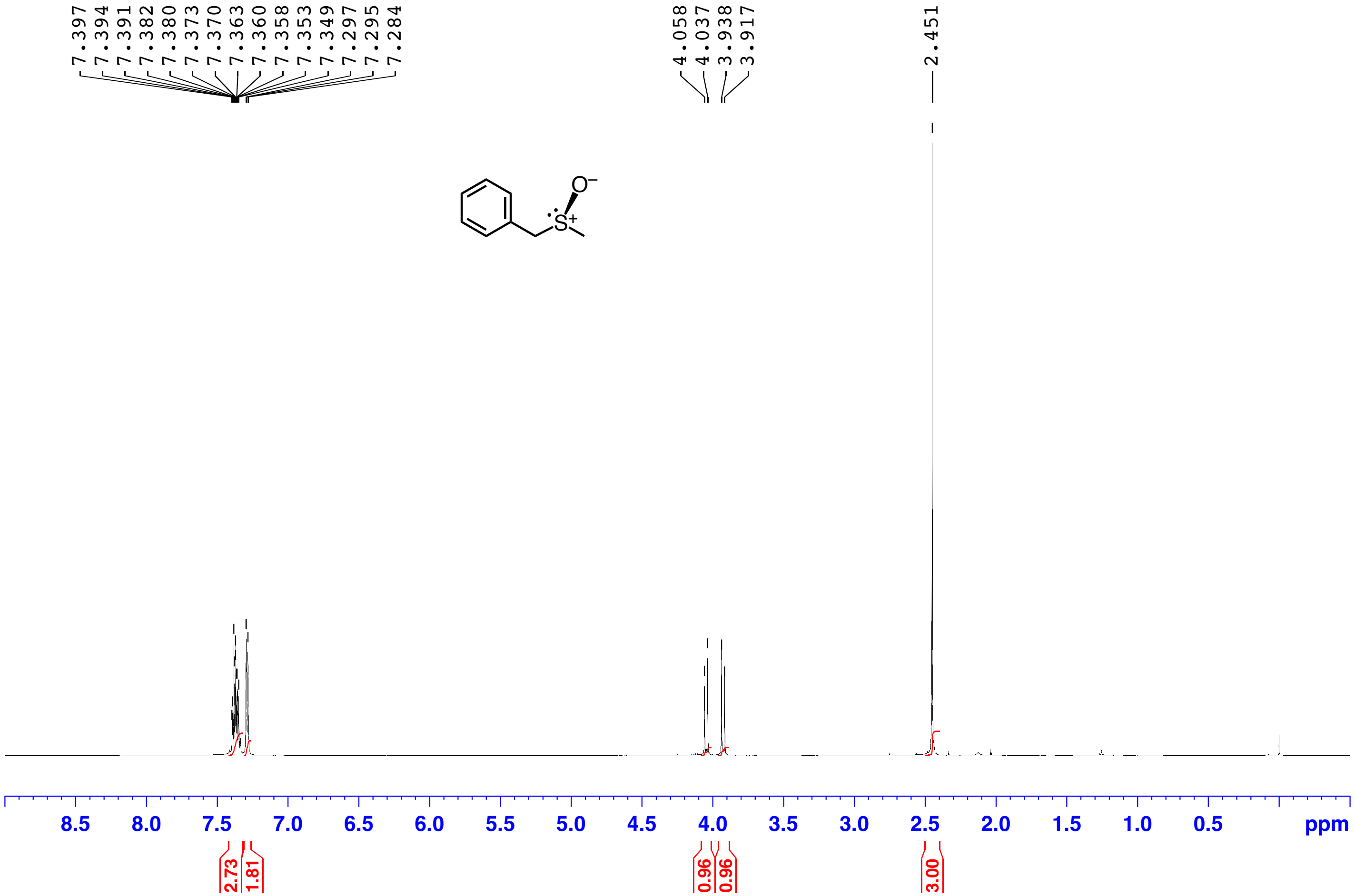


Fig. S9 ^{1}H NMR spectrum of benzyl methyl sulfoxide in $CDCl_3$.

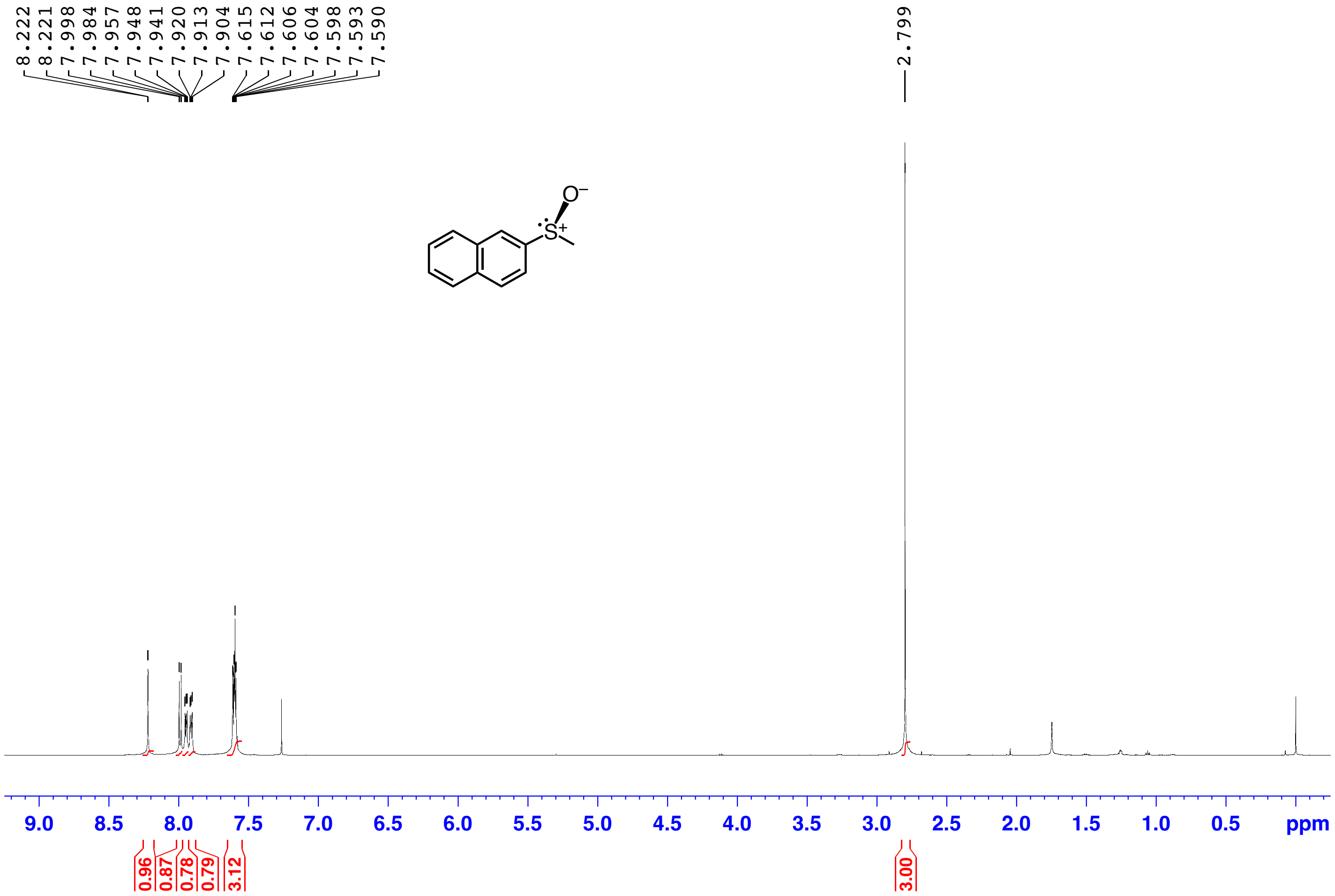


Fig. S10 ^{1}H NMR spectrum of methyl 2-naphthyl sulfoxide in $CDCl_3$.

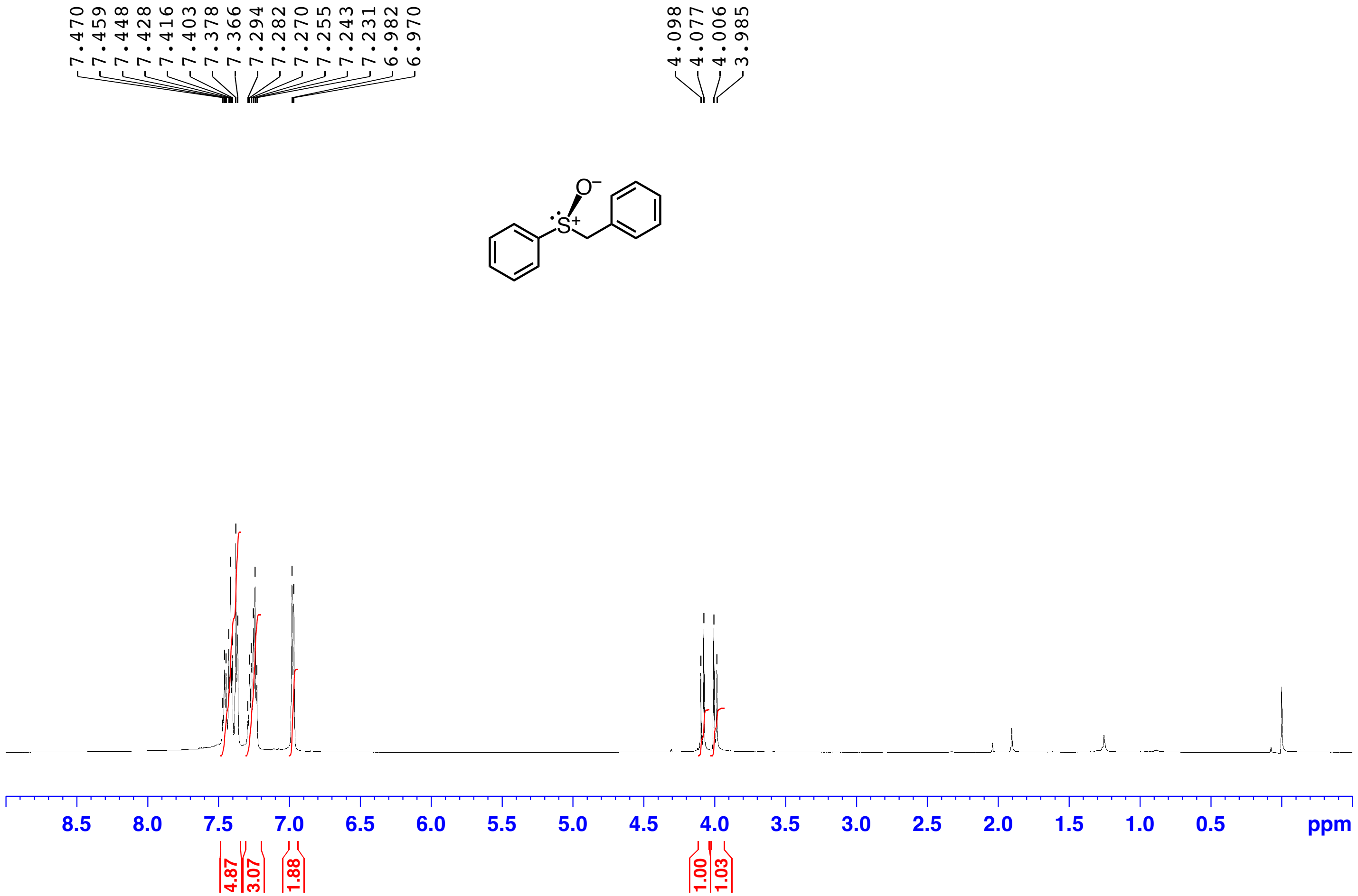


Fig. S11 ^{1}H NMR spectrum of benzyl phenyl sulfoxide in $CDCl_3$.

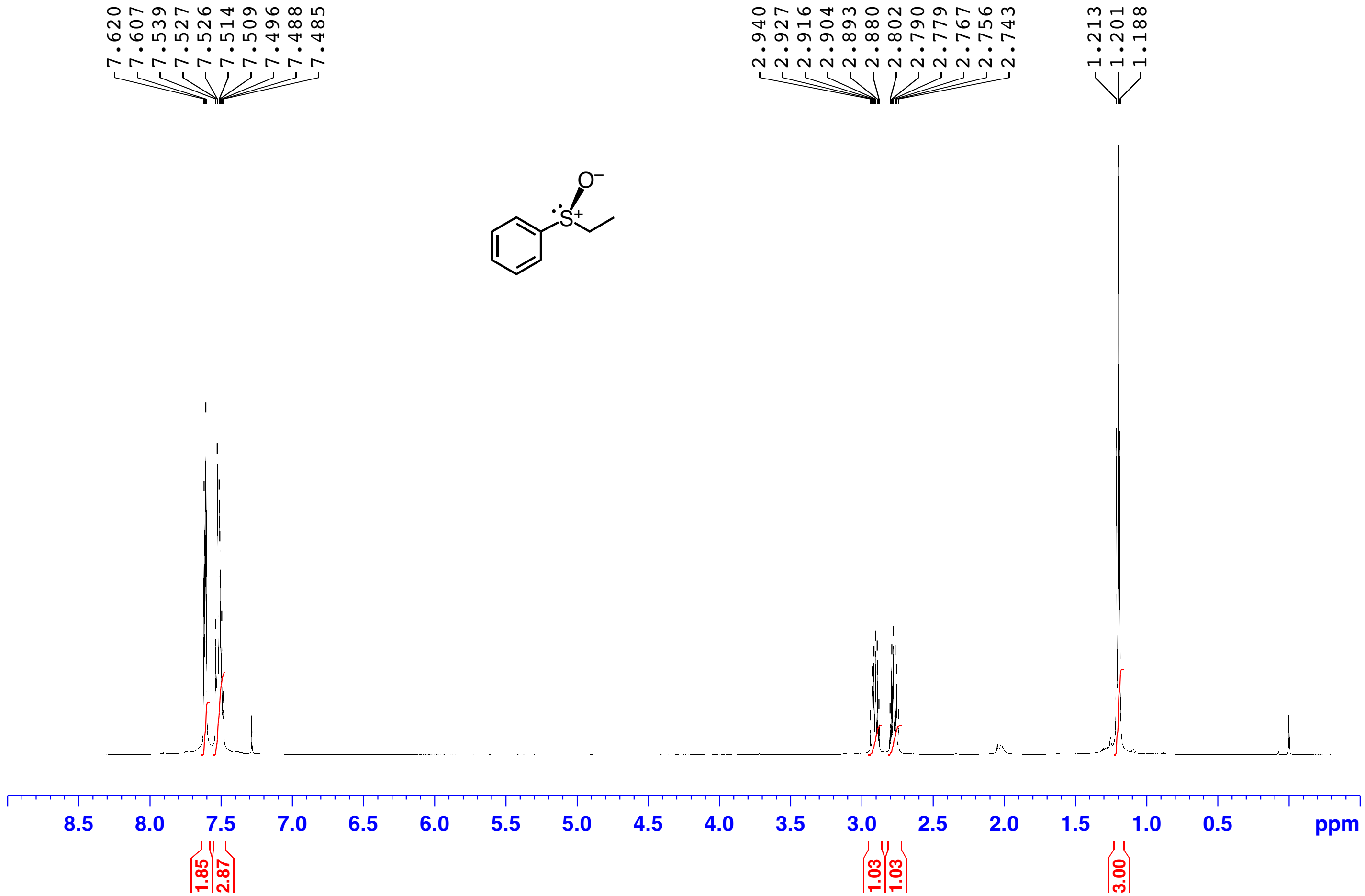


Fig. S12 ^{1}H NMR spectrum of ethyl phenyl sulfoxide in $CDCl_3$.

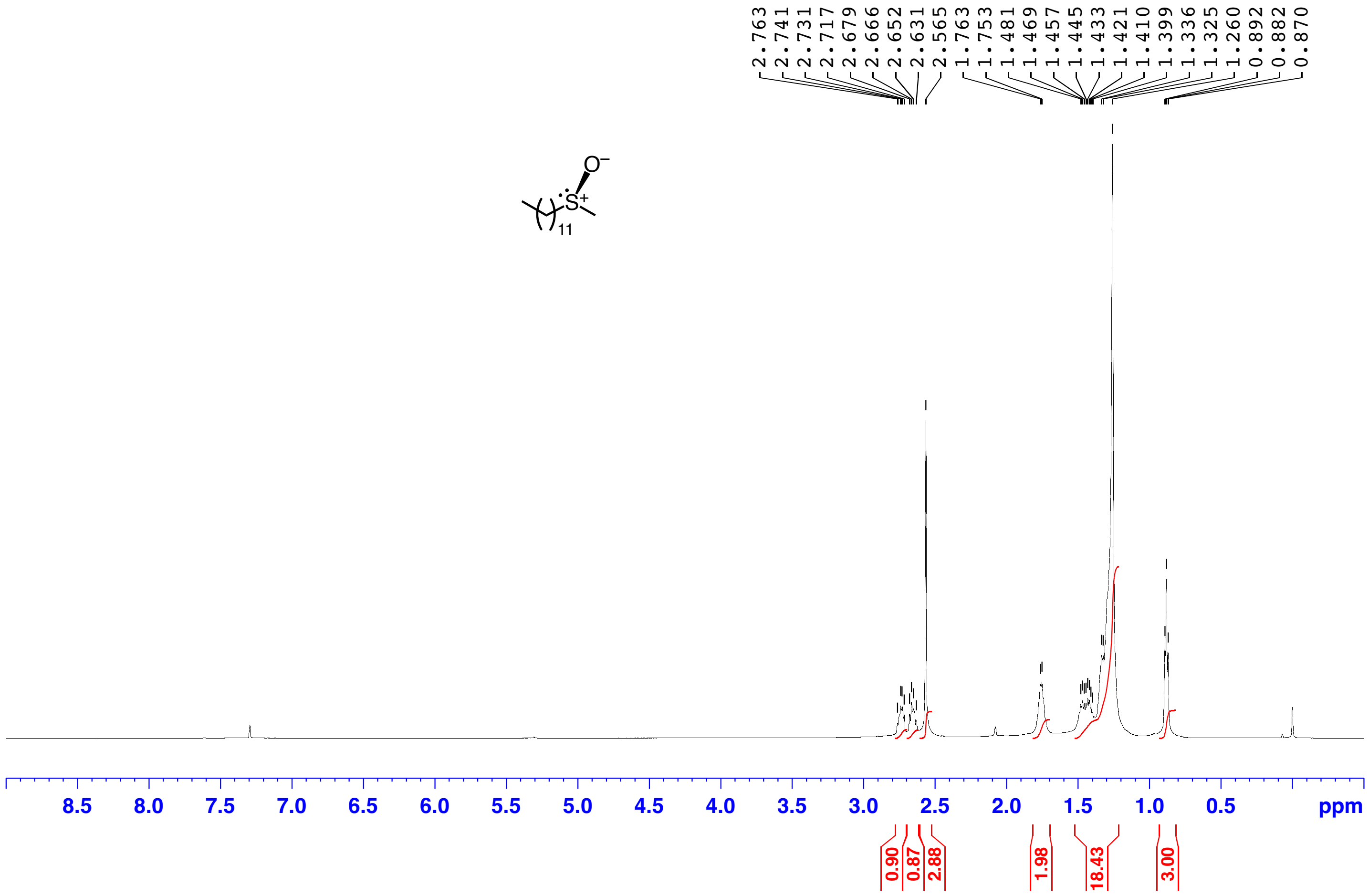


Fig. S13 ^{1}H NMR spectrum of *n*-dodecyl methyl sulfoxide in $CDCl_3$.

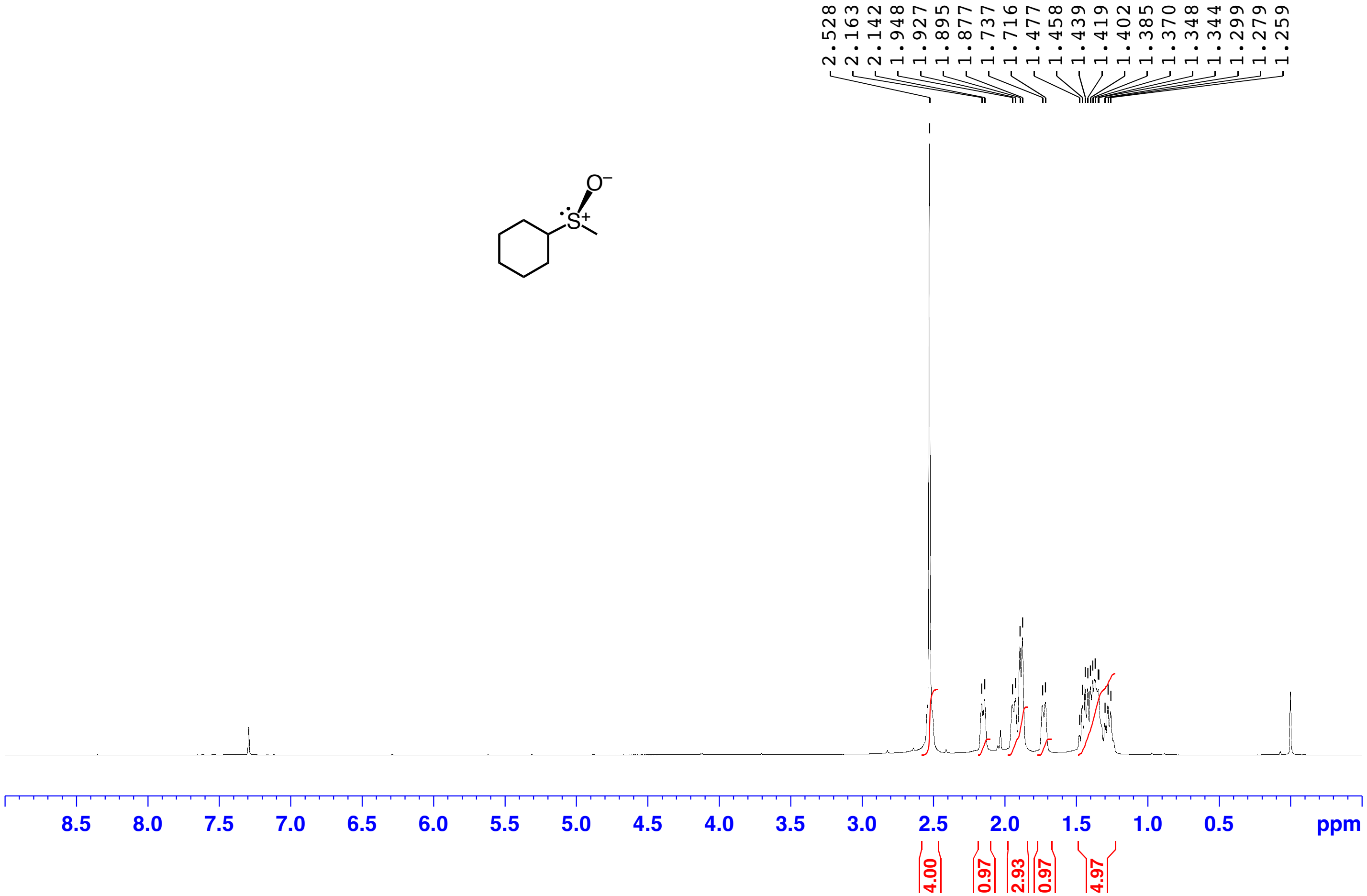


Fig. S14 ^{1}H NMR spectrum of cyclohexyl methyl sulfoxide in $CDCl_3$.

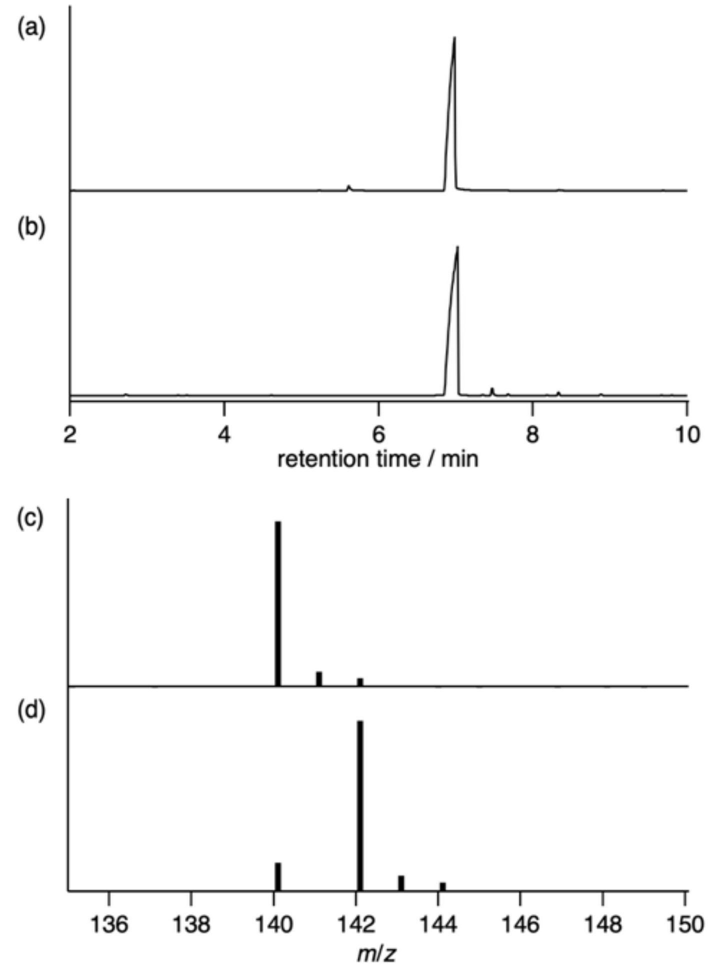
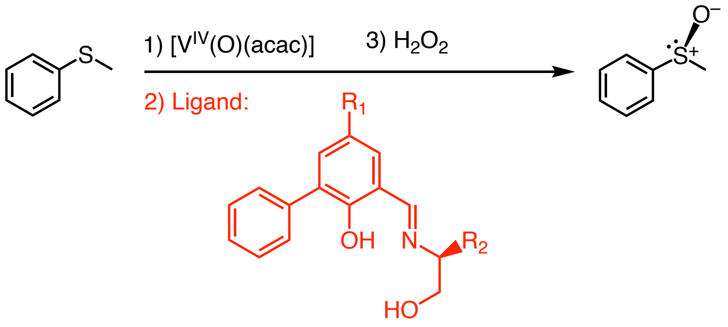


Fig. S15 Gas chromatograms of methyl phenyl sulfoxide isolated from the one-pot sulfoxidation using (a) $^{16}O_2$ and (b) $^{18}O_2$ as an oxygen source. Mass spectra of methyl phenyl sulfoxide isolated from the catalytic reaction using (c) $^{16}O_2$ and (d) $^{18}O_2$ as an oxygen source.

Table S1. Ligand screening results for vanadium catalyst optimization[a]

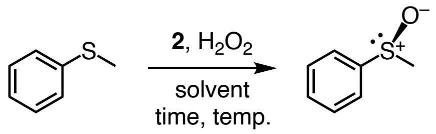


Reaction conditions: in CH_2Cl_2 for 16 h at r.t.

Entry	Ligand	R_1	R_2	Yield (%)[b]	ee(%)[c]
1	L	Cl	^{t}Bu	70	65
2	L2	MeO	^{t}Bu	69	49
3	L3	H	^{t}Bu	71	60
4	L4	Br	^{t}Bu	74	64
5	L5	NO	^{t}Bu	58	58
6	L6	Cl	Bn	85	52

[a] Reaction conditions: $[V^{IV}(O)(acac)_2]$ (10 µmol), ligand (15 µmol), thioanisole (1 mmol), H_2O_2 (30%, 1.1 mmol), and CH_2Cl_2 (2 mL). [b] Determined by ^{1}H NMR analysis. [c] Determined by chiral HPLC analysis.

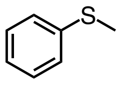
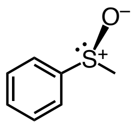
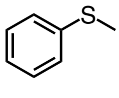
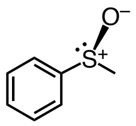
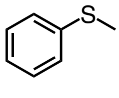
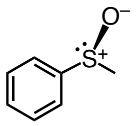
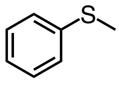
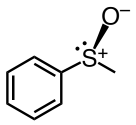
Table S2. Optimization of the reaction conditions^a



Entry	Solvent	Temp.	Time	Cat. (mol%)	Yield (%)^b (TON)^c	ee(%)^d
1	H_2O/CH_2Cl_2 (1/1)	r.t.	2	10	61 (6.1)	65
2	H_2O/CH_2Cl_2 (1/1)	r.t.	16	10	61 (6.1)	60
3	$H_2O/CHCl_3$ (1/1)	r.t.	16	10	43 (4.3)	53
4	H_2O/toluene (1/1)	r.t.	16	10	58 (5.8)	39
5	H_2O/ethyl acetate (1/1)	r.t.	16	10	18 (1.8)	29
6	H_2O/CH_2Cl_2/n-hexane (13/12/1)	r.t.	16	10	48 (4.8)	45
7	H_2O/CH_2Cl_2/n-hexane (2/1/1)	r.t.	16	10	26 (2.6)	40
8	methanol	r.t.	16	10	17 (1.7)	2
9	H_2O/CH_2Cl_2 (1/1)	r.t.	16	1	12 (12)	23
10	H_2O/CH_2Cl_2 (1/1)	r.t.	16	5	39 (7.8)	52
11	H_2O/CH_2Cl_2 (1/1)	r.t.	16	20	64 (3.2)	56
12	H_2O/CH_2Cl_2 (1/1)	0	16	10	36 (3.6)	32
13	H_2O/CH_2Cl_2 (1/1)	r.t.	1	10	51 (5.1)	50
14^e	H_2O/CH_2Cl_2 (1/1) Without H_2O_2	r.t.	2	10	0 (0)	0
15^f	H_2O/CH_2Cl_2 (1/1) Without **2**	r.t.	2	10	trace (0)	0

[a] Reaction conditions: complex **2** (20 μmol), thioanisole (200 μmol), H_2O_2 (220 μmol), sodium acetate (2 mmol) and solvent (8 mL). [b] Determined by ^1H NMR analysis. [c] Turnover numbers (TONs, mol of sulfoxide /mol of **2**) based on complex **2**. [d] Determined by chiral HPLC analysis. [e] Reaction performed without H_2O_2. [f] Reaction performed without **2**.

Table S3. Results of the control experiments[a]

Entry	Sulfide	Sulfoxide	Yield (%)[b] (TON)[c]	ee(%)[d]
1[e]	 Without **1**		0 (0)	0
2[f]	 Without H_2		0 (0)	0
3[g]	 Without O_2		0 (0)	0
4[h]	 Without **2**		trace –	0

[a] Reaction conditions for direct synthesis of H_2O_2: Complex **1** (0.4 μmol), sodium acetate (2 mmol), H_2O (4 mL), H_2 (1.9 MPa), O_2 (0.09 MPa), r.t., 12 h. Reaction conditions for asymmetric sulfoxidation: complex **2** (20 μmol), sulfide (200 μmol), H_2O/CH_2Cl_2 (1:1, v/v, 8 mL), r.t., 2 h. [b] Determined by ^1H NMR analysis. The values are isolated yields. [c] Turnover numbers (TONs, mol of sulfoxide /mol of **2**) based on complex **2**. [d] Determined by chiral HPLC analysis. [e] Reaction performed without **1**. [f] Reaction performed without H_2. [g] Reaction performed without O_2. [h] Reaction performed without **2**.

References

1 S. Ogo, T. Yatabe, T. Tome, R. Takenaka, Y. Shiota and K. Kato, *J. Am. Chem. Soc.,* 2023, **145**, 4384−4388. DOI: 10.1021/jacs.2c13149

2 E. P. Talsi, D. G. Samsonenko and K. P. Bryliakov, *Chem. Eur. J.,* 2014, **20**, 14329–14335. DOI: 10.1002/chem.201404157

3 E. Verner, B. A. Katz, J. R. Spencer, D. Allen, J. Hataye, W. Hruzewicz, H. C. Hui, A. Kolesnikov, Y. Li, C. Luong, A. Martelli, K. Radika, R. Rai, M. She, W. Shrader, P. A. Sprengeler, S. Trapp, J. Wang, W. B. Young and R. L. Mackman, *J. Med. Chem.,* 2001, **44**, 2753–2771. DOI: 10.1021/jm0100638

4 A. Jalba, N. Régnier and T. Ollevier, *Eur. J. Org. Chem.,* 2017, 1628–1637. DOI: 10.1002/ejoc.201601597

5 G. E. O'Mahony, A. Ford and A. R. Maguire, *J. Org. Chem.,* 2012, **77**, 3288−3296. DOI: 10.1021/jo2026178

6 H. Egami and T. Katsuki, *J. Am. Chem. Soc.*, 2007, **129**, 8940–8941. DOI: 10.1021/ja071916%2B

7 G. E. O'Mahony, K. S. Eccles, R. E. Morrison, A. Ford, S. E. Lawrence and A. R. Maguire, *Tetrahedron,* 2013, **69**, 10168e10184. DOI: 10.1016/j.tet.2013.08.063

8 Y. Wu, J. Liu, X. Li and A. S. C. Chan, *Eur. J. Org. Chem.,* 2009, 2607–2610. DOI: 10.1002/ejoc.200900289

9 R. M. Orlando and P. S. Bonato, *J. Chromatogr. B*, 2003, **795**, 227–235. DOI: 10.1016/S1570-0232(03)00570-1