SUPPORTING INFORMATION

Phosphorus-Alloying as a Powerful Method for Designing Highly Active and Durable Metal Nanoparticle Catalysts for the Deoxygenation of Sulfoxides: Ligand and Ensemble Effects of Phosphorus

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1. General experimental details

All organic reagents were purified by distillation or recrystallization [S1]. RuCl$_3$·nH$_2$O, RhCl$_3$·nH$_2$O, and H$_2$PtCl$_6$·nH$_2$O were obtained from N.E. Chemcat. (NH$_3$)$_2$PdCl$_2$·H$_2$O was purchased from Mitsuwa Chemicals. SiO$_2$ (CArIACT, G-6) was purchased from Fuji Silysia Chemical. NH$_4$H$_2$PO$_2$ and NaH$_2$PO$_2$·H$_2$O were purchased from Kishida Chemical and FUJIFILM Wako Pure Chemical, respectively.

Inductively coupled plasma–atomic emission spectroscopy (ICP–AES) was performed using a Perkin Elmer Optima 8300 instrument. $^1$H and $^{13}$C nuclear magnetic resonance (NMR) spectra were recorded using a JEOL JNM-ESC400 spectrometer and chemical shifts (δ) are reported in ppm relative to tetramethylsilane. Transmission electron microscopy (TEM) observations were carried out using a FEI Tecnai G2 20ST instrument operated at 200 kV. Scanning transmission electron microscopy (STEM) images with elemental maps were collected using a FEI Titan Cubed G2 60-300 instrument operated at 300 kV and equipped with Super-X energy-dispersive X-ray spectroscopy (EDX) detector. Elemental mapping based on quantification analysis of EDX spectra was carried out using Esprit. Ru K-edge X-ray absorption spectra were recorded at room temperature at the BL01B1 and BL14B2 lines, using a Si (311) monochromator at SPring-8, Japan Synchrotron Radiation Research Institute (JASRI), Harima, Japan. X-ray diffraction (XRD) studies were conducted on a Philips XPert-MPD diffractometer with Cu-Kα radiation (45 kV, 40 mA). X-ray photoelectron spectroscopy (XPS) analysis was performed on an ESCA1700R system equipped with a dual Mg/Al X-ray source and a hemispherical analyzer operating in fixed analyzer transmission mode. Spectra were obtained using a pass energy of 58.7 eV and an Al-K X-ray source operated at 350 W and 14 kV. The analysis area was 0.8 × 2 mm. The working pressure in the analysis chamber was less than 1 × 10$^{-7}$ Pa. The Si 2p peak at a binding energy (BE) of 103.3 eV was used as an internal reference. Fourier-transform infrared (FT-IR) spectra were recorded using a JASCO FT-IR 4100 spectrometer equipped with a mercury cadmium telluride detector at a spectral resolution of 4 cm$^{-1}$ with 256 scans accumulated. Thin self-supported disks was prepared by pressing the sample powder onto a stainless-steel grid. The sample disk was then placed inside an IR cell with CaF$_2$ windows to enable thermal treatment in a controlled atmosphere. The sample pellet was treated under flowing H$_2$ (ca. 40 kPa) at 473 K for 0.5 h, followed by evacuation (<1 Pa) at the same temperature for 5 min. After the pretreatment, the probe molecule was introduced to the sample disk and evacuated at 298 K. The H$_2$–D$_2$ exchange reaction was performed in a closed gas-circulation system equipped with an online quadrupole mass spectrometer (BELMass-S, BEL Japan, Inc.). The sample (10 mg) was treated under flowing H$_2$ (ca. 35 kPa) at 573 K for 1 h, followed by evacuation at the same temperature for 30 min. After the pretreatment, A mixture of H$_2$ (0.068 mmol) and D$_2$ (0.068 mmol) gases was introduced to the reaction system at 273 K and the total pressure was adjusted with Ar to 18.5
kPa. The gas phase was analyzed by monitoring the signals of m/z = 2, 3, and 4.

2. Catalyst preparation

Synthesis of SiO$_2$-supported metal phosphide catalysts

The SiO$_2$-supported metal phosphides were synthesized by the temperature-programmed reduction (TPR) of the catalyst precursors having P/Metal molar ratios of 0.86 (Ru−P and Rh−P) and 3.0 (Pd−P and Pt−P). The precursor was prepared by the sequential impregnation of SiO$_2$ with a metal precursor (RuCl$_3$, RhCl$_3$, (NH$_3$)$_4$PdCl$_2$, or H$_2$PtCl$_6$) and ammonium hypophosphite (NH$_4$H$_2$PO$_2$). SiO$_2$ (0.91 g) was added to 50 mL of an aqueous solution of a metal precursor (0.16 wt%) and the mixture was stirred magnetically for 1 h. Water was removed by rotary evaporation under reduced pressure and the obtained powder was dried at 383 K. In the case of Pd, the obtained powder was calcined in air at 773 K for 1 h. The SiO$_2$-supported metal precursor was added to 50 mL of an aqueous solution of NH$_4$H$_2$PO$_2$ and the mixture was stirred magnetically for 1 h. Water was removed by rotary evaporation under reduced pressure and the obtained powder was dried at 333 K. The obtained catalyst precursor was then reduced in a H$_2$ flow with heating from room temperature to 823 K at a rate of 5 K min$^{-1}$ followed by holding at 823 K for 1 h to yield the SiO$_2$-supported metal phosphide. SiO$_2$-supported metal precursors were used to prepare SiO$_2$-supported metal catalysts. SiO$_2$-supported metal precursors were reduced in a similar way. Elemental analysis by ICP–AES revealed that the ruthenium contents of Ru−P/SiO$_2$ and Ru/SiO$_2$ were 7.29 and 8.02 wt%, respectively. The phosphorus content of Ru−P/SiO$_2$ was 1.89 wt%.

Synthesis of bulk-Ru$_2$P

NaH$_2$PO$_2$·H$_2$O (0.30 g) and RuCl$_3$·nH$_2$O (0.145 g, Ru: 42.8 wt%) were dissolved in water (10 mL) and the mixture was stirred magnetically for 15 min. Water was removed by rotary evaporation under reduced pressure and the obtained powder was dried under vacuum at room temperature. The powder was treated at 823 K for 1 h at a rate of 5 K min$^{-1}$ in a N$_2$ atmosphere to give bulk-Ru$_2$P. After cooling to room temperature, the bulk-Ru$_2$P was washed with water and ethanol, and dried under vacuum at room temperature.

3. Typical reaction procedure

The typical reaction procedure for the deoxygenation of diphenyl sulfoxide to diphenyl sulfide using Ru−P/SiO$_2$ was as follows. Ru−P/SiO$_2$ powder and diphenyl sulfoxide (2.5 mmol) were
placed in a reaction vessel connected to a gas bag filled with 1 bar of H₂. n-dodecane (5 mL) was subsequently added. The reaction mixture was stirred vigorously at 373 K. After the reaction, naphthalene (internal standard) and 1,2-dimethoxyethane were added to the reaction mixture, and then, the catalyst was separated by centrifugation. The reaction solution was analyzed by gas chromatography–mass spectrometry (GC–MS) to determine the yield. GC–MS was performed using a Shimadzu GCMS-QP2010 SE gas chromatograph–mass spectrometer equipped with a capillary column (InertCap WAX-HT, GL Sciences, 30 m × 0.25 mm i.d., film thickness 0.25 μm). The column oven temperature started from 393 K (2-min hold) and was then increased to 513 K at a heating rate of 20 K min⁻¹. Other conditions were as follows: column flow rate (He carrier): 1.22 mL min⁻¹; split ratio: 32:1; injector temperature: 523 K; interface temperature: 523 K.

4. Recycling experiments

After the reaction, Ru−P/SiO₂ was removed by centrifugation, and the yield was determined by GC–MS analysis. The spent catalyst was washed with 1,2-dimethoxyethane followed by drying under vacuum at room temperature. The obtained powder was then reduced in a H₂ flow with heating from room temperature to 823 K at a rate of 5 K min⁻¹ followed by holding at 823 K for 1 h, after which it was reused for the next reaction.

5. Gram-scale reaction

Ru−P/SiO₂ powder, diphenyl sulfoxide (4.04 g), and n-dodecane (20 mL) were placed in a 100-mL stainless steel autoclave with a Teflon inner cylinder. The reaction mixture was stirred vigorously at 453 K under 50 bar of H₂ for 80 h. After the reaction, Ru−P/SiO₂ was filtered to separate the liquid phase from the solid catalyst. Distillation of the liquid phase gave crude diphenyl sulfide. Crude diphenyl sulfide was subjected to silica gel column chromatography (n-hexane/AcOEt) to give pure diphenyl sulfide (3.39 g), which was identified by GC–MS and ¹H and ¹³C NMR. Column chromatography on silica gel was performed on Biotage Isolera.
6. Effect of molar ratio of phosphorus to ruthenium

Scheme S1. Effect of the P/Ru molar ratio used in the preparation of Ru−P/SiO₂ on the yield of diphenyl sulfide (2a). Reaction conditions: Ru−P/SiO₂ (0.5 mol%), 1a (2.5 mmol), n-dodecane (5 mL), H₂ (1 bar), 373 K, 30 min.
7. Comparison of activity of Ru−P/SiO$_2$ with previously reported catalysts

**Table S1.** Comparison of the activity of Ru−P/SiO$_2$ with the activities of previously reported catalysts for deoxygenation of sulfoxide using H$_2$.

| Catalyst       | TON             | Reference                  |
|----------------|-----------------|----------------------------|
| Ru−P/SiO$_2$   | 12,500 ($32,000$ based on the number of surface Ru atoms$^a$) | This work                  |
| Ru−P/SiO$_2$   | 8,900 ($22,800$ based on the number of surface Ru atoms$^a$) | This work                  |
| Pt−MoO$_3$/TiO$_2$ | 4,400 (based on Pt) | A. S. Touchy et al., *Green Chem.*, 2016, 18, 2554–2560. (S2) |
| Ru/TiO$_2$     | 500             | T. Mitsudome et al., *Angew. Chem. Int. Ed.*, 2014, 53, 8348–8351. (S1) |
| PVV$_5$-Cl$_{13}$-H0l | 228 (based on Pt) | T. Uematsu et al., *Catal. Sci. Technol.*, 2017, 7, 1912–1920. (S3) |
| Ru/Zn-MOF      | 208             | P. Zhang et al., *Chem. Sci.*, 2018, 9, 1339–1343. (S4) |
| Pt/H$_2$MoO$_{3γ}$ | 159 (based on Pt) | Y. Kuwahara et al., *J. Am. Chem. Soc.*, 2018, 140, 9203–9210. (S5) |
| nano-Ni$_3$P/TiO$_2$ | 92              | S. Fujita et al., *Org. Biomol. Chem.*, 2020, 18, 8827–8833. (S6) |
| Pd/C           | 50              | K. Ogura et al., *Synthesis*, 1975, 385–387. (S7) |
| MoO$_3$Cl$_2$   | 10              | P. M. Reis et al., *Dalton Trans.*, 2008, 1727–1733. (S8) |
| Co−Mo/NC-400   | -               | K. Yao et al., *Green Chem.*, 2020, 22, 39–43. (S9) |

$^a$H$_2$ (50 bar). $^b$H$_2$ (1 bar). $^c$The ratio of the number of surface Ru atoms to the total number of Ru atoms in Ru−P/SiO$_2$ was calculated based on the model structure of a spherical Ru$_2$P nanoparticle with a mean diameter of 3.0 nm.

**Scheme S2.** The model structure of a spherical Ru$_2$P nanoparticle with a mean diameter of 3.0 nm.
8. Hot filtration experiment

Scheme S3. Hot filtration of Ru–P/\text{SiO}_2\) during the deoxygenation of diphenyl sulfoxide (1a) to diphenyl sulfide (2a). Reaction conditions: Ru–P/\text{SiO}_2\ (0.5 \text{ mol}%), 1a \ (2.5 \text{ mmol}), \text{n-dodecane} (5 \text{ mL}), \text{H}_2 \ (1 \text{ bar}), 373 \text{ K}. \text{Red spheres (●)}: catalyst retained. \text{Black spheres (●)}: catalyst removed by hot filtration at 15 min.
Figure S1. HAADF-STEM and elemental mapping images of (a–e) Ru–P/SiO$_2$, (f–j) Rh–P/SiO$_2$, (k–o) Pd–P/SiO$_2$, and (p–t) Pt–P/SiO$_2$. 

9. Characterization
**Figure S2.** TEM images and size distribution histograms of (a, e) Ru/SiO$_2$, (b, f) Rh/SiO$_2$, (c, g) Pd/SiO$_2$, and (d, h) Pt/SiO$_2$.

**Figure S3.** (a) TEM image and (b) size distribution histogram of Ru–P/SiO$_2$ after reaction.
Figure S4. $\text{H}_2$–$\text{D}_2$ exchange reaction using Ru–P/SiO$_2$ (red line) and Ru/SiO$_2$ (blue line).
Figure S5. EXAFS fitting curves in k-space (left panel) and R-space (right panel) of (a) Ru–P/SiO$_2$, (b) used Ru–P/SiO$_2$, (c) bulk-Ru$_2$P, and (d) Ru/SiO$_2$. 
Figure S6. (a) Ru $K$-edge XANES spectra and (b) Fourier transforms of the $k^3$-weighted EXAFS spectra of Ru–P/SiO$_2$ and used Ru–P/SiO$_2$.

Table S2. Curve-fitting results of Ru $K$-edge EXAFS for Ru–P/SiO$_2$ and used Ru–P/SiO$_2$.

| sample            | shell | $CN^a$ | $r$ (Å)$^b$ | D.W.$^c$         | R factor (%) |
|-------------------|-------|--------|-------------|------------------|--------------|
| Ru–P/SiO$_2$      | Ru–P  | $2.8 \pm 0.6$ | $2.30 \pm 0.010$ | $0.006 \pm 0.0015$ | 8.6          |
|                   | Ru–Ru | $2.8 \pm 0.9$ | $2.80 \pm 0.009$ | $0.008 \pm 0.0018$ |              |
| Used Ru–P/SiO$_2$ | Ru–P  | $2.5 \pm 0.6$ | $2.31 \pm 0.011$ | $0.006 \pm 0.0015$ | 9.4          |
|                   | Ru–Ru | $2.6 \pm 0.9$ | $2.79 \pm 0.011$ | $0.008 \pm 0.0018$ |              |

$^a$ Coordination number. $^b$ Bond distance. $^c$ Debye–Waller factor.
10. Kinetic study

The kinetic study on deoxygenation of a sulfoxide using H₂ was examined based on the Langmuir−Hinshelwood model as follows.

\[
\text{Sulfoxide} + \sigma \xrightleftharpoons[k_{\text{Sulfoxide}}]{k_{\text{Sulfoxide}}} \text{Sulfoxide} \cdot \sigma \tag{1}
\]

\[
\text{H}_2 + 2\sigma \xrightarrow[k_{\text{H}_2}]{k_{\text{H}_2}} 2H \cdot \sigma \tag{2}
\]

\[
\text{Sulfoxide} \cdot \sigma + H \cdot \sigma \xrightarrow[k_1]{k_{-1}} \text{Sulfoxide} - H \cdot \sigma + \sigma \tag{3}
\]

\[
\text{Sulfoxide} - H \cdot \sigma + H \cdot \sigma \xrightarrow[k_2]{k_{-2}} \text{H}_2O \cdot \sigma + \text{Sulfide} + \sigma \tag{4}
\]

\[
\text{H}_2O \cdot \sigma \xrightarrow[k_{\text{H}_2O}]{k_{\text{H}_2O}} \text{H}_2O + \sigma \tag{5}
\]

where \( \bullet \) and \( \sigma \) show the adsorbed species and a vacant active site, respectively. \( k_i \) and \( k_{-i} \) represent adsorption and desorption rate constant, respectively.

The rate determining step in the deoxygenation of sulfoxides was assumed to be the surface reaction between the sulfoxide and the hydrogen species represented in eq. (4). Under steady-state conditions, the rate of adsorption can be equated to the rate of desorption. From the above assumptions, the following kinetic equation can be obtained.

\[
r = \frac{k_1 k_2 K_{\text{Sulfoxide}} K_{\text{H}_2} [\text{H}_2] [\text{Sulfoxide}]}{k_{-1} \left( 1 + K_{\text{Sulfoxide}} [\text{Sulfoxide}] + \left( 1 + \frac{k_1 K_{\text{Sulfoxide}} [\text{Sulfoxide}]}{k_{-1}} \right) \sqrt{K_{\text{H}_2} [\text{H}_2] + K_{\text{H}_2O} [\text{H}_2O]} \right)^2} \tag{6}
\]

where \( K_i \) represents the adsorption equilibrium constant, which can be defined as the ratio of \( k_i \) to \( k_{-i} \). According to eq. (6), the initial reaction rate \( (r_0) \) is given by the following equations.
\[
\frac{1}{\sqrt{r_0}} = \frac{1 + K_{\text{Sulfoxide}}[\text{Sulfoxide}]}{\sqrt{k_1 k_2 K_{\text{Sulfoxide}} K_{\text{H}_2}[\text{Sulfoxide}][\text{H}_2]}} + \frac{k_{-1} + k_1 K_{\text{Sulfoxide}}[\text{Sulfoxide}]}{\sqrt{k_1 k_2 K_{\text{Sulfoxide}} K_{\text{H}_2}[\text{Sulfoxide}]}} 
\]

(7)

\[
\sqrt{\frac{[\text{Sulfoxide}]}{r_0}} = \left( \frac{1 + k_1 \sqrt{K_{\text{H}_2}[\text{H}_2]}}{k_{-1}} \right) \frac{[\text{Sulfoxide}]}{\sqrt{k_1 k_2 K_{\text{H}_2}[\text{Sulfoxide}]/k_{-1}} + \frac{1 + \sqrt{K_{\text{H}_2}[\text{H}_2]}}{k_{-1}} \frac{[\text{Sulfoxide}]}{\sqrt{k_1 k_2 K_{\text{Sulfoxide}} K_{\text{H}_2}[\text{Sulfoxide}]}} 
\]

(8)

Plots of \(1/\sqrt{r_0}\) versus \(1/\sqrt{[\text{H}_2]}\), and \(\sqrt{[\text{Sulfoxide}]/r_0}\) versus \([\text{Sulfoxide}]\) showed linear proportionality (Figure 5g and 5h in the manuscript). These results supported that the rate determining step in the deoxygenation of sulfoxides is the reaction process between the sulfoxide and the hydrogen species adsorbed on the catalyst surface.

11. DFT Calculation details

Density functional theory (DFT) calculations were performed using the CONQUEST program [S10, S11]. The Perdew, Burke and Ernzerhof (PBE) exchange-correlation functional [S12] was used with a norm-conserving pseudopotential and real-space pseudo atomic orbital (PAO) basis functions [S13, S14]. The double-zeta plus polarization (DZP) type PAOs were used for valence states and single-zeta PAOs were added to describe semi-core 4s and 4p electrons of Ru atoms. Thus, the PAOs of Ru, P and S atoms consist of \((3s, 2p, 2d), (2s, 2p, d)\) and \((2s, 2p, d)\) functions with the radii \((3.16, 7.93, 4.02), (3.65, 7.93), (7.93, 4.02)\), \((6.73, 3.66), (6.73, 3.66), (6.73)\), and \((6.08, 3.35), (6.08, 3.35), (6.08)\) bohr, respectively. The cutoff of the integration grid for electronic density was set to be 200 hartree. The dispersion energies were considered by using the DFT-D2 method [S15]. The basis set superposition errors (BSSEs) were corrected by the counterpoise method [S16] in adsorption energy calculations.

First, we optimized the bulk structures of orthorhombic Ru₂P and hexagonal Ru. The unit cell of Ru₂P is shown in Figure S7. 9×13×7 and 13×7×7 Monkhorst–Pack mesh of k-points were used for Ru₂P and Ru. The calculated lattice parameters \((a, b, c)\) of Ru₂P and \(a_0\) of Ru were \((5.828, 3.859, 7.068)\) Å and 2.732 Å, which are close to the experimental values of Ru₂P \((5.902, 3.859, 6.896)\) Å [S17] and \(a_0\) of Ru calculated using plane-waves, 2.733 Å [S18].

Next, we constructed the Ru₂P(210) and Ru(0001) surface slab models (Figure S8). The surface areas were 14×19 Å² for Ru₂P(210) and 14×14 Å² for Ru(0001). 3×3×1 k-points were used for both slab models. To investigate the convergence of the slab thickness, we put a sulfur atom at the on-top site to a Ru atom with certain heights \((2.0\) Å for Ru₂P and 2.2 Å for Ru) and calculated...
the adsorption energy $\Delta E$ of a sulfur atom to the surface,
\[
\Delta E = E(\text{surface-adsorbate}) - E(\text{surface}) - E(\text{adsorbate}),
\]
where the adsorbate was a sulfur atom. As in Table S3, it is found that $\Delta E$ is converged within 0.5 kcal mol$^{-1}$ with 4-layers slab thickness both for Ru$_2$P and Ru. Therefore, we used the 4-layers slab models in the subsequent $\Delta E$ calculations. In the optimized surface structures, compared to the Ru–Ru bond in Ru(0001), 2.73 Å, the Ru–Ru bond between two Ru$_1$ hollow sites (b1) was shorter, 2.65 Å, while those between a Ru$_1$ hollow site and a Ru$_2$P hollow site (b2) and between two Ru$_2$P hollow sites (b3) were longer, 2.84 Å and 2.92 Å, respectively, in Ru$_2$P(210). The elongation of the Ru–Ru bond length in Ru$_2$P was also found experimentally as written in the manuscript.

Then, we investigated the adsorptions of the dimethyl sulfide molecules. The lower two slab layers were fixed when optimizing the adsorption structures. Several adsorption sites on Ru(0001) and Ru$_2$P(210) surfaces were investigated as in Figures S9 and S10. As described in the manuscript and in Figure S10, the b1 bridge sites was more stable than the b2 and b3 bridge sites and on-top sites. The hollow sites and Ru–P bridge sites were less stable, therefore the sulfide molecules moved to the Ru–Ru bridge or on-top sites from the initial hollow and Ru–P bridge positions spontaneously. As in Figure S11, there are 8 b1 sites while there are 32 b2 sites and 24 b3 sites, therefore the rate of b1 sites among Ru–Ru bonds is 1/8 (12.5%).

**Figure S7.** Unit cell of Ru$_2$P. Gray and light blue balls indicate Ru and P, respectively.
Figure S8. Top view of (a) Ru(0001) and (b) Ru₃P(210) surfaces.
Figure S9. Initial and optimized structures of dimethyl sulfide adsorbed on Ru(0001) surface. Gray, yellow, brown, and light pink balls indicate Ru (only in the top layer), S, C, and H atoms, respectively. Blue, yellow, and red frames correspond to bridge, hollow, and on-top sites, respectively. Adsorption energies (ΔE) are also shown.
Figure S10. Initial and optimized structures of dimethyl sulfide adsorbed on Ru$_2$P(210) surface. Gray, light blue, yellow, brown, and pink balls indicate Ru, P (only in the top layer), S, C, and H atoms, respectively. Blue, yellow, and red frames correspond to bridge, hollow, and on-top sites, respectively. Adsorption energies ($\Delta E$) are also shown.
Figure S11. Occupancies of b1, b2, and b3 sites among the total Ru–Ru bridge sites in Ru₂P (210).

Table S3. Change of adsorption energies $\Delta E$ [kcal mol$^{-1}$] of a sulfur atom with respect to the slab thickness.

| # of layers | $\Delta E$  | # of layers | $\Delta E$  |
|-------------|-------------|-------------|-------------|
| 4           | -121.03     | 3           | -81.87      |
| 6           | -121.09     | 4           | -85.03      |
| 8           | -121.47     | 5           | -84.98      |
| 10          | -121.31     |             |             |
12. Product identification

All the reaction products were characterized by GC–MS and NMR. The retention times (GC–MS) and chemical shifts (1H and 13C) of the products agreed with those of authentic samples or previously reported values.

**Diphenyl sulfide [S6]**

\[ \text{S} \]

CAS registry No. [139-66-2]. 1H NMR (400 MHz, CDCl₃): \( \delta = 7.34–7.18 \text{ (m, 10H)} \); 13C NMR (100 MHz, CDCl₃): \( \delta = 135.8, 131.1, 129.2, 127.0 \).

**Bis(4-methylphenyl) sulfide [S6]**

\[ \text{S} \]

CAS registry No. [620-94-0]. 1H NMR (400 MHz, CDCl₃): \( \delta = 7.22 \text{ (d, } J=8.4 \text{ Hz, 4H), 7.09 (d, } J=8.4 \text{ Hz, 4H), 2.31 (s, 6H)} \); 13C NMR (100 MHz, CDCl₃): \( \delta = 137.0, 132.8, 131.2, 130.0, 21.1 \).

**Benzyl phenyl sulfide [S6]**

\[ \text{S} \]

CAS registry No. [831-91-4]. 1H NMR (400 MHz, CDCl₃): \( \delta = 7.31–7.14 \text{ (m, 10H), 4.10 (s, 2H)} \); 13C NMR (100 MHz, CDCl₃): \( \delta = 137.6, 136.5, 130.0, 128.9, 128.6, 127.2, 126.4, 39.2 \).

**Dibenzyl sulfide [S19]**

\[ \text{S} \]

CAS registry No. [538-74-9]. 1H NMR (400 MHz, CDCl₃): \( \delta = 7.32–7.21 \text{ (m, 10H), 3.59 (s, 4H)} \); 13C NMR (100 MHz, CDCl₃): \( \delta = 138.2, 129.1, 128.5, 127.0, 35.7 \).
**Thioanisole [S2]**

CAS registry No. [100-68-5]. $^1$H NMR (400 MHz, CDCl$_3$): $\delta =$ 7.30–7.24 (m, 4H), 7.13 (m, 1H), 2.47 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta =$ 138.5, 128.9, 126.8, 125.1, 15.9.

**4-(Methylthio)toluene [S6]**

CAS registry No. [623-13-2]. $^1$H NMR (400 MHz, CDCl$_3$): $\delta =$ 7.18 (d, $J =$ 8.4 Hz, 2H), 7.09 (d, $J =$ 8.4 Hz, 2H), 2.45 (s, 3H), 2.31 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta =$ 135.1, 134.8, 129.7, 127.5, 21.0, 16.6.

**4'-(Methylthio)acetophenone [S6]**

CAS registry No. [1778-09-2]. $^1$H NMR (400 MHz, CDCl$_3$): $\delta =$ 7.86 (d, $J =$ 8.8 Hz, 2H), 7.26 (d, $J =$ 8.8 Hz, 2H), 2.56 (s, 3H), 2.52 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta =$ 197.2, 145.9, 133.7, 128.8, 125.1, 26.5, 14.9.

**4-(Methylthio)benzaldehyde [S20]**

CAS registry No. [3446-89-7]. $^1$H NMR (400 MHz, CDCl$_3$): $\delta =$ 9.92 (s, 1H), 7.76 (d, $J =$ 8.0 Hz, 2H), 7.32 (d, $J =$ 8.0 Hz, 2H), 2.53 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta =$ 191.2, 147.9, 133.0, 130.0, 125.3, 14.7.
**4-Methoxythioanisole [S6]**

CAS registry No. [1879-16-9]. $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.27$ (d, $J = 8.8$ Hz, 2H), 6.85 (d, $J = 8.8$ Hz, 2H), 3.79 (s, 3H), 2.44 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 158.3, 130.3, 128.9, 114.7, 55.4, 18.2$.

**Bis(4-chlorophenyl) sulfide [S6]**

CAS registry No. [5181-10-2]. $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.28–7.23$ (m, 8H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 134.1, 133.6, 132.4, 129.6$.

**4-Bromo-thioanisole [S6]**

CAS registry No. [104-95-0]. $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.39$ (d, $J = 8.4$ Hz, 2H), 7.11 (d, $J = 8.4$ Hz, 2H), 2.46 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 137.8, 131.9, 128.3, 118.7, 16.0$.

**3-Bromo-thioanisole [S27]**

CAS registry No. [33733-73-2]. $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.36$ (s, 1H), 7.25 (m, 1H), 7.18–7.10 (m, 2H), 2.47 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 141.1, 130.1, 128.9, 128.0, 125.1, 123.0, 15.7$. 
2-Bromothioanisole [S22]

\[ \text{CAS registry No. [19614-16-5].} \]

\[^1^H\text{NMR (400 MHz, CDCl}_3\text{):} \ \delta = 7.51 (d, J = 8.0 \text{ Hz, 1H}), 7.29 (t, J = 8.0 \text{ Hz, 1H}), 7.13 (d, J = 8.0 \text{ Hz, 1H}), 6.99 (t, J = 8.0 \text{ Hz, 1H}), 2.47 (s, 3H); \ ^{13}\text{C NMR (100 MHz, CDCl}_3\text{):} \ \delta = 139.8, 132.8, 127.9, 125.8, 125.6, 121.9, 15.8. \]

Tetrahydrothiophene [S6]

\[ \text{CAS registry No. [110-01-0].} \]

\[^1^H\text{NMR (400 MHz, CDCl}_3\text{):} \ \delta = 2.84–2.81 (m, 4H), 1.95–1.92 (m, 4H); \ ^{13}\text{C NMR (100 MHz, CDCl}_3\text{):} \ \delta = 31.9, 31.1. \]

Dibutyl sulfide [S6]

\[ \text{CAS registry No. [544-40-1].} \]

\[^1^H\text{NMR (400 MHz, CDCl}_3\text{):} \ \delta = 2.51 (t, J = 7.4 \text{ Hz, 4H}), 1.60–1.53 (m, 4H), 1.46–1.36 (m, 4H), 0.92 (t, J = 7.4 \text{ Hz, 6H}); \ ^{13}\text{C NMR (100 MHz, CDCl}_3\text{):} \ \delta = 32.0, 22.1, 13.8. \]

Dodecyl methyl sulfide [S19]

\[ \text{CAS registry No. [3698-89-3].} \]

\[^1^H\text{NMR (400 MHz, CDCl}_3\text{):} \ \delta = 2.48 (t, J = 7.2 \text{ Hz, 2H}), 2.09 (s, 3H), 1.62–1.55 (m, 2H), 1.39–1.26 (m, 18H), 0.88 (t, J = 7.2 \text{ Hz, 3H}); \ ^{13}\text{C NMR (100 MHz, CDCl}_3\text{):} \ \delta = 34.4, 32.0, 29.7, 29.7, 29.7, 29.6, 29.4, 29.4, 29.3, 28.9, 22.8, 15.6, 14.2. \]

Bis(methyithio)methane [S23]

\[ \text{CAS registry No. [1618-26-4].} \]

\[^1^H\text{NMR (400 MHz, CDCl}_3\text{):} \ \delta = 3.61 (s, 2H), 2.14 (s, 6H); \ ^{13}\text{C NMR (100 MHz, CDCl}_3\text{):} \ \delta = 40.2, 14.4. \]
**DL-Methionine [S24]**

![DL-Methionine structure](image)

CAS registry No. [59-51-8]. $^1$H NMR (400 MHz, D$_2$O): $\delta = 3.79$ (m, 1H), 2.57 (t, $J = 7.8$ Hz, 2H), 2.06 (s, 3H), 2.18–2.00 (m, 2H); $^{13}$C NMR (100 MHz, D$_2$O): $\delta = 174.2, 53.9, 29.7, 28.9, 14.0$.

**Sulindac sulfide [S25]**

![Sulindac sulfide structure](image)

CAS registry No. [32004-67-4]. $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.43$ (d, $J = 8.4$ Hz, 2H), 7.36 (dd, $J = 8.4, 5.2$ Hz, 1H), 7.29 (d, $J = 8.4$ Hz, 2H), 7.15 (s, 1H), 6.88 (dd, $J = 8.4, 2.0$ Hz, 1H), 6.58 (ddd, $J = 8.6, 8.6, 2.0$ Hz, 1H), 3.59 (s, 2H), 2.54 (s, 3H), 2.20 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 175.1, 163.2$ (d, $J = 244.1$ Hz), 146.3 (d, $J = 8.6$ Hz) 140.1, 139.3, 138.9, 133.0, 130.3 (quat.), 130.1 (quat.), 130.0, 129.8 (quat.), 126.1, 123.9 (d, $J = 8.6$ Hz), 110.8 (d, $J = 21.9$ Hz), 105.8 (d, $J = 23.9$ Hz), 31.3, 15.5, 10.7.

**Fenbendazole [S26]**

![Fenbendazole structure](image)

CAS registry No. [43210-67-9]. $^1$H NMR (400 MHz, DMSO-d$_6$): $\delta = 11.80$ (br s, 2H), 7.54 (s, 1H), 7.47 (d, $J = 8.4$ Hz, 1H), 7.30–7.13 (m, 6H), 3.77 (s, 3H); $^{13}$C NMR (100 MHz, DMSO-d$_6$): $\delta = 154.5, 148.3, 138.4, 129.2, 127.6, 126.9, 125.8, 123.4, 52.5$. 

S26
**Fensulfothin sulfide [S23]**

CAS registry No. [3070-15-3]. $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.23$ (d, $J = 8.4$ Hz, 2H), 7.12 (d, $J = 8.4$ Hz, 2H), 4.27–4.19 (m, 4H), 2.47 (s, 3H), 1.36 (t, $J = 7.0$ Hz, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 148.6$ (d, $J = 8.6$ Hz), 135.0, 128.2, 121.6 (d, $J = 4.8$ Hz), 65.2 (d, $J = 5.7$ Hz), 16.6, 16.0 (d, $J = 7.6$ Hz).

**Ufiprazole (Omeprazole sulfide) [S27]**

CAS registry No. [73590-85-9]. $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 8.26$ (s, 1H), 7.41 (d, $J = 8.8$ Hz, 1H), 7.03 (br s, 1H), 6.82 (d, $J = 8.8$, 2.4 Hz, 1H), 4.36 (s, 2H), 3.84 (s, 3H), 3.78 (s, 3H), 2.32 (s, 3H), 2.27 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 165.1$, 156.0, 156.0, 150.7, 148.5, 126.4, 125.6, 111.1, 60.1, 55.9, 35.1, 13.5, 11.4.
13. $^1$H and $^{13}$C NMR spectra of products 2a–2v

$^1$H NMR spectrum of diphenyl sulfide

$^{13}$C NMR spectrum of diphenyl sulfide
$^1$H NMR spectrum of bis(4-methylphenyl) sulfide

$^{13}$C NMR spectrum of bis(4-methylphenyl) sulfide
$^1$H NMR spectrum of benzyl phenyl sulfide

$^{13}$C NMR spectrum of benzyl phenyl sulfide
$^1$H NMR spectrum of dibenzyl sulfide

$^{13}$C NMR spectrum of dibenzyl sulfide
$^1$H NMR spectrum of thioanisole

$^{13}$C NMR spectrum of thioanisole

S32
$^1$H NMR spectrum of (4-methylthio)toluene

$^{13}$C NMR spectrum of (4-methylthio)toluene
$^1$H NMR spectrum of 4'-/(methylthio)acetophenone

$^{13}$C NMR spectrum of 4'-/(methylthio)acetophenone
$^1$H NMR spectrum of 4-(methylthio)benzaldehyde

$^{13}$C NMR spectrum of 4-(methylthio)benzaldehyde
$^1$H NMR spectrum of 4-methoxythioanisole

$^{13}$C NMR spectrum of 4-methoxythioanisole
$^1$H NMR spectrum of bis(4-chlorophenyl) sulfide

$^{13}$C NMR spectrum of bis(4-chlorophenyl) sulfide
$^1$H NMR spectrum of 4-bromothioanisole

$^{13}$C NMR spectrum of 4-bromothioanisole

S38
$^1$H NMR spectrum of 3-bromothioanisole

$^{13}$C NMR spectrum of 3-bromothioanisole
H NMR spectrum of 2-bromothioanisole

13C NMR spectrum of 2-bromothioanisole
$^1$H NMR spectrum of tetrahydrothiophene

$^{13}$C NMR spectrum of tetrahydrothiophene
$^1$H NMR spectrum of dibutyl sulfide

$^{13}$C NMR spectrum of dibutyl sulfide
$^1$H NMR spectrum of dodecyl methyl sulfide

$^{13}$C NMR spectrum of dodecyl methyl sulfide
$^1$H NMR spectrum of bis(methylthio)methane

$^{13}$C NMR spectrum of bis(methylthio)methane
$^1$H NMR spectrum of DL-methionine

$^{13}$C NMR spectrum of DL-methionine
$^1$H NMR spectrum of sulindac sulfide

$^{13}$C NMR spectrum of sulindac sulfide
$^1$H NMR spectrum of fenbendazole

$^{13}$C NMR spectrum of fenbendazole
$^1$H NMR spectrum of fensulfothion sulfide

$^{13}$C NMR spectrum of fensulfothion sulfide
$^1$H NMR spectrum of ufiprazole

$^{13}$C NMR spectrum of ufiprazole
References

[S1] Mitsudome, T.; Takahashi, Y.; Mizugaki, T.; Jitsukawa, K.; Kaneda, K. Hydrogenation of Sulfoxides to Sulfides under Mild Conditions Using Ruthenium Nanoparticle Catalysts. *Angew. Chem. Int. Ed.* **2014**, *53*, 8348–8351.

[S2] Touchy, A. S.; Hakim Siddiki, S. M. A.; Onodera, W.; Kon, K.; Shimizu, K. Hydrodeoxygenation of Sulfoxides to Sulfides by a Pt and MoO$_x$-Co-Loaded TiO$_2$ Catalyst. *Green Chem.* **2016**, *18*, 2554–2560.

[S3] Uematsu, T.; Ogasawara, Y.; Suzuki, K.; Yamaguchi, K.; Mizuno, N. Platinum-Supporting Hollandite-Type Vanadium–Chromium Mixed Oxides as Efficient Heterogeneous Catalysts for Deoxygenation of Sulfoxides under Atmospheric H$_2$ Pressure. *Catal. Sci. Technol.* **2017**, *7*, 1912–1920.

[S4] Zhang, P.; Chen, C.; Kang, X.; Zhang, L.; Wu, C.; Zhang, J.; Han, B. In situ Synthesis of Sub-Nanometer Metal Particles on Hierarchically Porous Metal-Organic Frameworks via Interfacial Control for Highly Efficient Catalysis. *Chem. Sci.* **2018**, *9*, 1339–1343.

[S5] Kuwahara, Y.; Yoshimura, Y.; Haematsu, K.; Yamashita, H. Mild Deoxygenation of Sulfoxides over Plasmonic Molybdenum Oxide Hybrid with Dramatic Activity Enhancement under Visible Light. *J. Am. Chem. Soc.* **2018**, *140*, 9203–9210.

[S6] Fujita, S.; Yamaguchi, S.; Yamazoe, S.; Yamasaki, J.; Mizugaki, T.; Mitsudome, T. Nickel Phosphide Nanoalloy Catalyst for the Selective Deoxygenation of Sulfoxides to Sulfides under Ambient H$_2$ Pressure. *Org. Biomol. Chem.* **2020**, *18*, 8827–8833.

[S7] Ogura, K.; Yamashita, M.; Tsuchihashi, G. Catalytic Deoxygenation of Sulfoxides by Molecular Hydrogen and its Application to the Homologation of Aromatic Aldehydes. *Synthesis* **1975**, *1975*, 385–387.

[S8] Reis, P. M.; Costa, P. J.; Romao, C. C.; Fernandes, J. A.; Calhorda, M. J.; Royo, B. Hydrogen Activation by High-Valent Oxo-Molybdenum(vi) and -Rhenium(vii) and -(v) Compounds. *Dalton Trans.* **2008**, *1727–1733*.

[S9] Yao, K.; Yuan, Z.; Jin, S.; Chi, Q.; Liu, B.; Huang, R.; Zhang, Z. Hydrodeoxygenation of Sulfoxides into Sulfides under Mild Conditions using Heterogeneous Cobalt–Molybdenum Catalysts. *Green Chem.* **2020**, *22*, 39–43.

[S10] Conquest website, http://www.order-n.org, (accessed April 2021).

[S11] Nakata, A.; Baker, J.; Mujahed, S. Y.; Poulton, J. T. L.; Arapan, S.; Lin, J.; Raza, Z.; Yadav, S.; Truanider, L.; Miyazaki, T.; Bowler, D. R. Large Scale and Linear Scaling DFT with the CONQUEST Code. *J. Chem. Phys.* **2020**, *152*, 164112.

[S12] Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **1996**, *77*, 3865–3868.
[S13] Torralba, A. S.; Todorović, M.; Brázdová, V.; Choudhury, R.; Miyazaki, T.; Gillan, M. J.; Bowler, D. R. Pseudo-Atomic Orbitals as Basis Sets for the O(N) DFT Code CONQUEST. J. Phys.: Condens. Matter 2008, 20, 294206.

[S14] Bowler, D. R.; Baker, J. S.; Poulton, J. T. L.; Mujahed, S. Y.; Lin, J.; Yadav, S.; Raza, Z.; Miyazaki, T. Highly Accurate Local Basis Sets for Large-Scale DFT Calculations in Conquest. Jpn. J. Appl. Phys. 2019, 58, 100503.

[S15] Grimme, S. Semiempirical GGA-Type Density Functional Constructed with a Long-Range Dispersion Correction. J. Comp. Chem. 2006, 27, 1787–1799.

[S16] van Duijneveldt, F. B.; van Duijneveldt-van de Rijdt, J. G. C. M.; van Lenthe, J. H. State of the Art in Counterpoise Theory. Chem. Rev. 1994, 94, 1873–1885.

[S17] Liu, T.; Wang, S.; Zhang, Q.; Chen, L.; Hu, W.; Li, C. M. Ultrasmall Ru₂P Nanoparticles on Graphene: A Highly Efficient Hydrogen Evolution Reaction Electrocatalyst in Both Acidic and Alkaline Media. Chem. Commun. 2018, 54, 3343–3346.

[S18] Jain, A.; Ong, S. P.; Hautier, G.; Chen, W.; Richards, W. D.; Dacek, S.; Cholia, S.; Gunter, D.; Skinner, D.; Ceder, G.; Persson, K. A. The Materials Project: A Materials Genome Approach to Accelerating Materials Innovation. APL Materials, 2013, 1, 011002.

[S19] Takahashi, F.; Nogi, K.; Yorimitsu, H. B₂cat₂-Mediated Reduction of Sulfoxides to Sulfides. Eur. J. Org. Chem. 2020, 2020, 3009–8833.

[S20] Suzuki, T.; Morita, K.; Tsuchida, M.; Hiroi, K. Iridium-Catalyzed Oppenauer Oxidations of Primary Alcohols Using Acetone or 2-Butanone as Oxidant. J. Org. Chem. 2003, 68, 1601–1602.

[S21] Wu, X.; Wang, Y. Metal-Free S-Methylation of Diaryl Disulfides with di-tert-Butyl Peroxide. Tetrahedron Lett. 2018, 59, 1240–1243

[S22] Czyz, M. L.; Weragoda, G. K.; Monaghan, R.; Connell, T. U.; Brzozowski, M.; Scully, A. D.; Burton, J.; Lupton, D. W.; Polyzos, A. A Visible-Light Photocatalytic Thiolation of Aryl, Heteroaryl and Vinyl Iodides. Org. Biomol. Chem. 2018, 16, 1543–1551.

[S23] Clarke, A. K.; Parkin, A.; Taylor, R. J. K.; Unsworth, W. P.; Rossi-Ashton, J. A. Photocatalytic Deoxygenation of Sulfoxides using Visible Light: Mechanistic Investigations and Synthetic Applications. ACS Catal. 2020, 10, 5814–5820.

[S24] Głaszczka, R.; Jaźwiński, J.; Kamieński, B.; Kamińska, M. Adducts of Rhodium(II) Tetraacylates with Methionine and Its Derivatives: 1H and 13C Nuclear Magnetic Resonance Spectroscopy and Chiral Recognition. Tetrahedron: Asymmetry 2010, 21, 2346–2355.

[S25] Nortcliffe, A.; Ekstrom, A. G.; Black, J. R.; Ross, J. A.; Habib, F. K.; Botting, N. P.; O’Hagan, D. Synthesis and Biological Evaluation of Nitric Oxide-Donating Analogues of Sulindac for Prostate Cancer Treatment. Bioorg. Med. Chem. 2014, 22, 756–761.
[S26] Rodrigues, L. N. C.; Tavares, A. C. M.; Ferreira, B. T.; Reis, A. K. C. A.; Katiki, L. M. Inclusion Complexes and Self-Assembled Cyclodextrin Aggregates for Increasing the Solubility of Benzimidazoles. *Braz. J. Pharm. Sci.* **2019**, *55*.

[S27] Acosta-Guzmán, P.; Mahecha-Mahecha, C.; Gamba-Sánchez, D. Electrophilic Chlorine from Chlorosulfonium Salts: A Highly Chemoselective Reduction of Sulfoxides. *Chem. Eur. J.* **2020**, *26*, 10348–10354.