Supporting Information Tungsten-Dioxo Single-Site Heterogeneous Catalyst on Carbon: Synthesis, Structure, and Catalysis

Amol Agarwal,^[a] Yiqi Liu,^[b] Miyuki Hanazawa,^[c] Jiaqi Li,^[b] Takayuki Nakamuro,^[c] Eiichi Nakamura,^[c] Yosi Kratish,^{*[b]} and Tobin J. Marks^{*[b]}

[a]	A. Agarwal		
	Department of Materials Science and Engineering, and the Trienens Institute for Sustainability and Energy		
	Northwestern University		
	2145 Sheridan Road, Evanston Illinois 60208 (USA)		
[b]	Dr. Y. Liu, Dr. J. Li, Prof. Y. Kratish, Prof. T. J. Marks		
	Department of Chemistry, and the Trienens Institute for Sustainability and Energy		
	Northwestern University		
	2145 Sheridan Road, Evanston Illinois 60208 (US)A		
[c]	Miyuki Hanazawa, Prof. Eiichi Nakamura, Prof. Takayuki Nakamuro,		
	Department of Chemistry		
	The University of Tokyo		
	Tokyo 113-0033, Japan		
	Email: <u>muro@chem.s.u-tokyo.ac.jp</u> .		
	nakamura@chem.s.u-tokyo.ac.jp.		

Table of Contents

Experimental Details	S1
Physical and Analytical Measurements	S3
Spectroscopic Data for Products	S5
SMART-EM Imaging	S7
DFT Coordinates	S11
References	S12

Experimental Details

General Considerations

All other starting materials and solvents were purchased from Sigma-Aldrich unless specified otherwise. Carbon nanohorns (CNHs) were purchased from NEC (Lot No. 181-3-2; assay: 90%). All reagents were used without further purification unless otherwise noted.

(DME)WO₂Cl₂ Preparation

This tungsten precursor was synthesized by modifying a previously published procedure (Scheme 1 in MS).¹ In the glove box, WOCl₄ (0.64 g, 1.9 mmol) was weighed into a Schlenk flask with a stir bar. The flask was removed from the glove box, attached to a Schlenk line under N₂, and anhydrous DCM (10 mL) and hexamethyldisiloxane (0.42 mL, 1.9 mmol) were added by syringe. The mixture was stirred at room temperature for 90 min, and dry dimethoxyethane (0.29 mL) was added. The solution was stirred at room temperature overnight. The solvent was next removed under vacuum, and the solid obtained was washed with distilled ether and stored at - 30 °C in the glovebox to yield (DME)WO₂Cl₂ as a white solid. From NMR, ¹H : 4.10 (s, O-CH₃) and ¹H : 4.04 (s, CH₂-O) were identified that match with reported values.¹

AC/WO₂ Preparation

The supported tungsten catalyst was synthesized following an analogous procedure for AC/MoO₂.² Activated carbon (5.0 g) was weighted into a Schlenk flask with a Tefloncoated magnetic stirring bar and dried under vacuum overnight at 250 °C. Dry dichloromethane (100 mL) was added to disperse the activated carbon. A second Schlenk flask was charged with (DME)WO₂Cl₂ (0.41 g, 1.2 mmol) in a glovebox and dichloromethane (50 mL) was added to it under an N₂ flow outside the glovebox to form a colorless solution. The contents of the second Schlenk were then canula filtered and transferred to the carbon Schlenk under an N₂ flow. The solution was allowed to stir overnight at room temperature. The supernatant solution was then removed by cannula. The solid product was washed with dichloromethane (3 \times 150 mL). The residual solvent was removed under vacuum and the resulting product was dried under vacuum. From ICP-OES analysis, the catalyst was found to have 2.8 wt% W. The W 4f_{7/2} XPS peak at 35.9 eV indicates the presence of bound W(VI) species. The W L_{III}-edge energy at 10.208 keV from X-Ray Absorption Near Edge Spectroscopy (XANES) further confirms the W oxidation state as +6. The structural architecture, including the bond distances and bond orders, have been experimentally determined using extended X-ray absorption fine structure (EXAFS) and validated with DFT (See Table 1 and discussion in text for more details.).

Catalytic Dehydration Procedure

In a typical experiment, the alcohol substrate (1 mmol), mesitylene (1 mmol), decalin (1.0 mL), AC/MoO₂ (1 mol% Mo; 25 mg of 3.82 wt% Mo catalyst) or AC/WO₂ (1 mol% W; 66 mg of 2.80 wt% W catalyst), and a PTFE coated magnetic stir bar were added to a 25 mL J-Young reaction flask in air. The solution was freeze-thaw degassed, then placed under Ar, and kept sealed throughout the reaction. While stirring at 400 rpm, the flask was lowered into an oil bath (for temperatures below 150 °C) or an aluminum block heater (for temperatures above 150 °C) at the desired temperature behind a blast shield. Samples were periodically withdrawn and analyzed via NMR spectroscopy to monitor the course of the reaction. Conversion and selectivity were calculated from ¹H-NMR spectra by integration against the mesitylene internal standard. All reported products are known compounds and were compared to published ¹H/¹³C NMR values when possible and verified by GC/MS when appropriate.

Epoxidation Procedure

In a typical reaction, the olefin substrate (2.25 mmol), TBHP (4.8 mmol of a 5–6 M solution in decane), mesitylene (0.4 mL, 2.88 mmol), decane (2.3 mL), AC/MO₂ (1.5 mol% M; M = Mo, W), and a Teflon-coated magnetic stirring bar were added to a glass reaction tube. The test tube was sealed using a rubber septum throughout the reaction and NMR aliquots were withdraw by puncturing the septum using a metal syringe. While stirring at 400 rpm, the test tube was lowered into an oil bath (80 °C or 130 °C). NMR samples were collected at various time points to monitor the progress of the reaction. Conversion and selectivity were assayed by ¹H-NMR spectroscopy by integration against the mesitylene internal standard. All reported products are known compounds and were compared to published ¹H/¹³C NMR values when possible.

PET Hydrogenolysis Procedure

A dry cylindrical reactor (tube) was charged with PET and 5 mol % of AC/MoO₂ (based on Mo). The reaction tube was sealed with a rubber septum and pierced with a needle connected to a gas delivery balloon suitable for chemical reactions (Sigma-Aldrich). The tube and gas delivery balloon were then carefully purged with Ar, five times, charged with H₂, and then heated at 260 °C using a heating block. During the reaction crystalline terephthalic acid sublimes from the reaction zone and crystallizes near the top of the reaction tube. After the reaction is complete, 2 mL of d₆-DMSO and mesitylene as an internal standard, were added and 0.5 mL of the reaction mixture solution was charged into an NMR tube. Conversion and selectivity were assayed by ¹H-NMR spectroscopy by integration against the mesitylene internal standard.

Catalyst Recycling Procedure

The typical dehydration procedure with 5-nonanol was upscaled 2 times to start with 130 mg of AC/WO₂. After every run, the catalyst was filtered, washed with ~5 mL hexane and dried in a Schlenk flask overnight. With every subsequent run, the amount of recovered catalyst decreased due to losses during filtration and transfer and hence the amounts of the other reagents (5-nonanol, decalin) were stoichiometrically adjusted to maintain catalytic loading. This procedure was adopted from previously reported recyclability tests performed for other carbon-supported heterogeneous catalysts.^{2, 3}

Grid Preparation for Transmission Electron Microscopy (TEM)

CNH/WO₂ was prepared according to the above procedure using instead of an amorphous carbon. A black powder of CNH/WO₂ and a small amount of dry toluene (0.5 mg/mL) were ground for 3 min in an agate mortar under dry N₂ flow. The mixture was deposited on a TEM grid (NS-C15, pore size $1.5 - 8 \mu m$, Okenshoji Co., Ltd.) placed on a paper that absorbs excess toluene. The TEM grid was dried in vacuo (60 Pa) to remove solvent for 1 h.

Physical and Analytical Measurements

Nuclear Magnetic Resonance Spectroscopy

NMR spectra were recorded at the Integrated Molecular Structure Education and Research Center (IMSERC) at Northwestern University with a 500 MHz Bruker Avance III HD system equipped with a TXO Prodigy probe.

X-Ray Photoelectron Spectroscopy

XPS spectra were recorded at the Keck-II facility at Northwestern University with a Thermo Scientific ESCALAB 250 Xi spectrometer, equipped with an AI K alpha radiation source and electron flood-gun, at a pressure of 8×10^{-8} mbar with a pass energy of 50 eV. Typically, a 50 ms dwell time and 10 scans were used for each spectrum. All spectra were calibrated according to the asymmetric graphitic peak at 284.8 eV. Spectra were normalized using Origin.

Inductively Coupled Plasma

Inductively coupled plasma analysis of the catalyst metal loading was performed by Galbraith Labs (Knoxville, TN).

X-Ray Absorption Spectroscopy

XANES and EXAFS measurements at Mo K-edge (20.000 KeV) and W L-III edge (10.205 KeV) were performed at the 5 BM-D beamline of the DND-CAT at the Advanced Photon Source. A double Si (111) monochromator was used for energy selection with energy resolution of $\Delta E/E = 1.4 \times 10^{-4}$. The X-ray energy was calibrated using metallic Mo/W foils. The incident X-ray intensity was measured by a spectroscopy-grade ionization chamber (FMB-Oxford) filled with 600 He/100 N₂ (Torr) and was detuned to 60 % of its maximum for harmonic rejection. The powder catalysts were uniformly spread on a 6-inch piece of Scotch tape and folded 3 times for the EXAFS measurements. The EXAFS spectra were collected in fluorescence mode using a passivated implanted planar silicon (PIPS) detector (Canberra). The sample and the detector were positioned 45 deg and 90 deg, respectively, to the X-ray beam direction. For data analyses, three standard reference materials were used: WO₂, WO₃, and (dme)WO₂Cl₂, which were measured in transmission mode. The transmitted intensity was measured using an identical ionization chamber filled with 1150 He/250 N₂ (Torr) placed behind the sample. Energy scans were executed from 260 eV below to 750 eV above the edge which produces the EXAFS spectra up to the wavenumber of 14 Å⁻¹. The reference foil spectra were collected simultaneously for each energy scan using a third ionization chamber filled with 760 Torr Ar. The XAS measurements were carried out under an inert argon environment. The XANES spectra of WO₂, WO₃, and (dme)WO₂Cl₂, and the AC/WO₂ are shown in Figure 2a. XANES data extraction, normalization, and background subtraction were performed using the software Athena. EXAFS data analysis was done using the software Artemis. The EXAFS analysis fitted results are shown in Table S1. The bond lengths (R) and coordination number (N) were obtained by a least-square fit in the R-space of the nearest neighbors using k²-weighted Fourier transform fitting parameter. The standard deviations in the EXAFS-determined bond lengths came from the standard python error analysis procedure and are given in parentheses accompanying each bond length where (1) signifies +/- 0.01 Å.

Transmission Electron Microscopy⁴

Atomic-resolution TEM observation was carried out on a JEOL JEM-ARM200F instrument equipped with an aberration corrector and at an acceleration voltage of 80 kV, under 1 × 10^{-5} Pa in the specimen chamber using a double-tilt holder (JEOL EM-01030RSTH) at 298 K. The accuracy of the grid temperature is ± a few degrees according to the instrumental specification. A series of images were continuously recorded at a frame rate of 50 fps (frames per second) on a CMOS camera (Gatan OneView, In situ mode, 4096 × 4096 pixels) operating on a binning 4 mode (output image size: 1024×1024 pixels, pixel resolution 0.02 nm at × 2,000,000) at room temperature with an electron dose rate (EDR) = $10^6 - 10^7 e^{-nm^{-2}} s^{-1}$. All images were automatically processed on Gatan Digital Micrograph software. To record the atomic-resolution images of the specimens, we first surveyed the whole CNH aggregates on the grid at \times 100,000 magnifications to find CNHs suitable for careful analysis. To analyze them in depth, we increased the magnification to \times 2,000,000 and started the recording. We adjusted the defocus value during image collection. The images were recorded at under-focus conditions (defocus value: 10 - 20 nm). The images were recorded in a .dm4 format using the Gatan Digital Micrograph software. The images taken in a .dm4 format were transformed into 8-bit or 32-bit .tiff format files by Gatan Digital Micrograph and Fiji software. The images were analyzed as they are, or aligned to minimize specimen drift and rotation by checking the cross-correlation of each image and filtered by a bandpass filter (filtering structures smaller than 2 pixels and larger than 40 pixels, tolerance of direction: 5%). Linear adjustment of brightness and contrast was applied as required for analyses.

The TEM image simulation was performed by using a multi-slice procedure implemented in a Bionet elbis software. We used the experimental TEM conditions including total electron dose as the parameters for the simulation. The molecular models were generated on a Materials Studio package version 2019 software. The coordinates of W species were calculated with density functional theory (DFT) using B3LYP hybrid functional with a basis set 6-31G* in the gas phase, which was used as the initial structure of Mo for further modeling.

DFT calculations

All quantum chemical calculations were performed using the ORCA 4.1.0 software package.⁵ Geometry optimizations of AC/WO₂ were carried out at the CAM-B3LYP/Def2-SVP level of theory. Frequency calculations at the same level were performed to validate the structure as a minimum. The relativistic effective core potential of W was described with def2-ECP.⁶

Spectroscopic Data

¹H NMR (CDCl₃) δ ppm 5.39 (2H), 1.98 (4H), 1.36-1.32 (8H), 0.88 (6H)⁷

¹H NMR (CDCl₃) δ ppm 7.37-7.20 (5H), 6.45-6.40 6.31-6.26 (1H), 1.92-1.89 (3H)⁸

¹H NMR (CDCl₃) δ ppm 5.61 (2H), 2.14 (4H), 1.49 (8H)⁹



¹H NMR (CDCl₃) δ ppm 5.66 (2H), 1.98 (4H), 1.61 (4H)¹⁰



¹H NMR (CDCl₃) δ ppm 7.79-7.77 (3H), 7.73(1H), 7.62 (1H), 7.43 (1H), 6.87 (1H), 5.86 (1H), 5.32 (1H)¹¹

¹H NMR (CDCl₃) δ ppm 5.8 (1H), 5.0-4.9 (2H), 2.0 (2H), 1.5-1.0 (8H), 0.9 (3H)¹² ¹³C NMR (CDCl₃) δ ppm 139.2, 114.1, 33.9, 31.9, 29.1, 29.0, 22.7, 14.1 ¹²

$\sim \sim \sim$

¹H NMR (CDCl₃) δ ppm 5.5-5.3 (2H), 1.9 (2H), 1.6 (1H), 1.5-1.0 (6H), 0.9 (3H)¹³ (¹³C NMR (CDCl₃) δ ppm 131.0, 123.7, 31.8, 29.5, 27.0, 22.8, 14.1, 12.7 ¹³

¹H NMR (CDCl₃) δ ppm 5.39 (2H), 1.96 (4H), 1.36 (4H), 0.89 (6H) ¹⁴ ¹³C NMR (CDCl₃) δ ppm 130.5, 34.9, 22.9, 13.7 ¹⁴



¹H NMR (CDCl₃) δ ppm 3.38 (4H), 1.56 (4H), 1.28 (24H), 0.89 (6H) ¹⁵ ¹³C NMR (CDCl₃) δ ppm 71.0, 31.9, 29.9, 29.6, 29.4, 26.4, 22.8, 14.1 ¹⁵



¹H NMR (CDCl₃) δ ppm 3.98 (2H), 2.22 (2H), 1.62-1.47 (4H), 1.34-1.10 (18H), 0.89-0.73(6H) ¹⁶ ¹³C NMR (CDCl₃) δ ppm 174, 64, 34, 32, 29, 26, 22, 14 ¹⁶

0/

¹H NMR (CDCl₃) δ ppm 9.76 (1H), 2.41 (2H), 1.63 (2H), 1.3 (8H), 0.88 (3H) ¹⁷

¹H NMR (CDCl₃) δ ppm 5.4 (2H), 2.0 (4H), 1.4 (4H), 0.9 (6H) ¹⁸ ¹³C NMR (CDCl₃) δ ppm 129.9, 29.5, 23.0, 13.8 ¹⁸

¹H NMR (CDCl₃) δ ppm 5.35 (2H), 2.0 (4H), 1.3 (4H), 0.9 (6H) ¹⁹ ¹³C NMR (CDCl₃) δ ppm 131.6, 129.4, 32.2, 27.0, 22.5, 20.7, 14.5, 14.0 ¹⁹

¹H NMR (CDCl₃) δ ppm 5.8 (1H), 5.0-4.9 (2H), 2.0 (2H), 1.5-1.0 (16H), 0.9 (3H) ²⁰ ¹³C NMR (CDCl₃) δ ppm 139.2, 114.1, 44.0, 32.1, 29.8, 29.7, 29.5, 29.3, 29.1, 22.8, 14.2 ²⁰



¹H NMR (CDCl₃): 2.89 (2H), 2.16 (2H), 1.7-1.2 (10H).²¹



¹H NMR (DMSO-d₆) δ ppm 13.3 (2H), 8.1 (4H) ²²

<u>Single-molecule atomic-resolution time-resolved electron microscopy</u> (SMART-EM) imaging

The following is a series of TEM images taken at 50 fps (Figure S1). The signal-to-noise ratio was poor, making it difficult to extract structural information, so Figure 3a was generated by stacking 20 images taken between 0-0.38 s, where image blur was minimal.



Figure S1. Representative TEM images of Figure 3a. Scale bar 1 nm. Single sites are highlighted in white arrows. EDR = 5.7×10^6 e⁻ nm⁻² s⁻¹.

Based on the data in Table 1, constructing a hypothetical oligomer structure yields an estimated W–W distance of approximately 0.30 nm. This result differs from the 0.23-0.24 nm distance observed between high-contrast regions in the TEM images (Figure S2). This discrepancy suggests that the plane containing W–O–W is not perpendicular to the electron beam.



Figure S2. Average distances in dark spots at CNH edge in Figure 3a. Scale bar 1 nm.

Statistical analysis of WO₂ supported on CNH was conducted using the method reported in ref 4. Examination of 400 CNHs, carefully selected to avoid overlap with other objects, revealed strong contrast spots corresponding to W in 27 CNHs. As shown in Figure S3, 44% of the W sites were identified as single sites, clearly determined through SMART-EM observations. No data strongly supporting an in-plane binding mode was observed, supporting with findings from our previous CNH/MoO₂ study (Figure S4).

The remaining 56% of W sites were observed in an aggregated form, classified as multimetallic sites, consistent with results from the CNH/MoO₂ study. Figure S3 presents a trinuclear structure with nominal atomic distances ranging from 0.29 to 0.33 nm. This value supports the presence of multi-sites containing W–O–W linkages.



Figure S3. Representative TEM snapshots of CNH/WO₂. White arrows and circle indicate single and multiple sites (a few to several W's), respectively. Scale bars 1 nm. EDR = 10^{6} – 10^{7} e⁻ nm⁻² s⁻¹.



Figure S4. Representative TEM snapshots of out-of-plane binding of CNH/WO₂. White arrows indicate single site. Scale bars 1 nm. EDR = 10^{6} - 10^{7} e⁻ nm⁻² s⁻¹.

DFT-optimized Cartesian coordinates for AC/WO₂



С	0.596930000	-0.956901000	-0.572684000
С	-0.430795000	0.152495000	-0.469546000
С	-1.850352000	-0.365257000	-0.508574000
С	-2.134598000	-1.610754000	0.019263000
С	-1.020518000	-2.432700000	0.626470000
С	0.315078000	-2.192833000	-0.048601000
С	-3.474955000	-2.057208000	0.141352000
С	-3.731038000	-3.357630000	0.662289000
С	-2.720558000	-4.236026000	0.962157000
С	-1.361529000	-3.890747000	0.807453000
С	-0.326530000	-4.804895000	0.867754000
С	0.987230000	-4.467909000	0.520817000
С	1.324695000	-3.207644000	0.025549000
С	2.632707000	-2.885049000	-0.446827000
С	2.912436000	-1.658261000	-0.967731000
С	1.908688000	-0.647399000	-1.060824000
С	2.144337000	0.603867000	-1.632090000
С	1.120947000	1.539462000	-1.824777000
С	-0.174421000	1.311852000	-1.399650000
С	-1.266349000	2.136756000	-1.742303000
С	-2.564066000	1.757154000	-1.508806000
С	-2.893008000	0.493368000	-0.940587000
С	-4.226771000	0.041803000	-0.816354000
С	-4.509227000	-1.196083000	-0.291065000
W	0.061370000	-0.326289000	2.419329000
0	-0.291710000	0.733835000	0.891789000
0	-0.893955000	-1.908394000	2.011716000
0	1.735393000	-0.619798000	2.622572000
Н	3.917161000	-1.426678000	-1.327197000
Н	3.410938000	-3.648618000	-0.383086000
Н	1.764276000	-5.233872000	0.572970000

Н	-0.555754000	-5.837819000	1.140707000
Н	-2.962068000	-5.255284000	1.272673000
Н	-4.771094000	-3.675603000	0.764053000
Н	-5.544599000	-1.532422000	-0.202640000
Н	-5.036303000	0.695434000	-1.148485000
Н	-3.382371000	2.409695000	-1.821308000
Н	-1.060588000	3.074864000	-2.263188000
Н	1.336223000	2.455547000	-2.380103000
Н	3.147105000	0.828032000	-2.002195000
0	-0.532603000	0.409397000	3.839864000

References

(1) Dreisch, K.; Andersson, C.; St, C. Synthesis and structure of dimethoxyethane-dichlorodioxotungsten (VI)—a highly soluble derivative of tungsten dioxodichloride. *Polyhedron* **1991**, *10* (20-21), 2417-2421.

(2) Liu, Y.; Li, J.; Das, A.; Kim, H.; Jones, L. O.; Ma, Q.; Bedzyk, M. J.; Schatz, G. C.; Kratish, Y.; Marks, T. J. Synthesis and Structure–Activity Characterization of a Single-Site MoO2 Catalytic Center Anchored on Reduced Graphene Oxide. *J. Am. Chem. Soc.* **2021**, *143* (51), 21532-21540. DOI: 10.1021/jacs.1c07236.

(3) Liu, Y.; Agarwal, A.; Ye, L.; Kratish, Y.; Marks, T. J. Aldehyde and Ketone Hydroboration

Mediated by a Heterogeneous Single - Site Molybdenum - Dioxo Catalyst: Scope and Mechanistic Implications. *ChemCatChem* **2023**, e202301417.

(4) Kratish, Y.; Nakamuro, T.; Liu, Y.; Li, J.; Tomotsuka, I.; Harano, K.; Nakamura, E.; Marks, T. J. Synthesis and characterization of a well-defined carbon nanohorn-supported molybdenum dioxo catalyst by SMART-EM imaging. Surface structure at the atomic level. *Bulletin of the Chemical Society of Japan* **2021**, *94* (2), 427-432.

(5) Calculations were carried out using the ORCA 4.1.0 software; F. Neese, The ORCA program system, Wiley Interdiscip. Rev.: Comput. Mol. Sci., **2012**, *2*, 73-78.

(6) Weigend, F.; Ahlrichs, R. Balanced basis sets of split valence, triple zeta valence and quadruple zeta valence quality for H to Rn: Design and assessment of accuracy. *Phys. Chem. Chem. Phys.*, **2005**, *7* (18), 3297-3305, 10.1039/B508541A. DOI: 10.1039/B508541A.

(7) H-NMR spectrum, SDBS No. 2198-23-4. *Spectral Database for Organic Compounds (SDBS)*. <u>https://sdbs.db.aist.go.jp</u> (accessed October 17th 2024).

(8) Keskiväli, J.; Parviainen, A.; Lagerblom, K.; Repo, T. Transition metal triflate catalyzed conversion of alcohols, ethers and esters to olefins. *RSC advances* **2018**, *8* (27), 15111-15118.
(9) SDBS No. 2051HSP-03-574. Spectral Database for Organic Compounds (SDBS) H-NMR spectrum. <u>https://sdbs.db.aist.go.jp</u> (accessed October 17th 2024).

(10) SDBS No. 110-83-8. Spectral Database for Organic Compounds (SDBS) H-NMR spectrum. <u>https://sdbs.db.aist.go.jp/</u> (accessed December 4th 2024).

(11) SDBS No. 827-54-3. Spectral Database for Organic Compounds (SDBS) H-NMR spectrum. <u>https://sdbs.db.aist.go.jp/</u> (accessed December 12th 2024). (12) SDBS No. 788HSP-00-085. *Spectral Database for Organic Compounds (SDBS) H-NMR spectrum*. <u>https://sdbs.db.aist.go.jp</u> (accessed October 17th 2024).

(13) SDBS No. 281HSP-03-379. *Spectral Database for Organic Compounds (SDBS) H-NMR spectrum*. <u>https://sdbs.db.aist.go.jp</u> (accessed October 17th 2024).

(14) SDBS No. 278CDS-00-026. *Spectral Database for Organic Compounds (SDBS) H-NMR spectrum*. <u>https://sdbs.db.aist.go.jp</u> (accessed October 17th 2024).

(15) SDBS No. 7770HSP-02-236. *Spectral Database for Organic Compounds (SDBS) H-NMR spectrum*. <u>https://sdbs.db.aist.go.jp</u> (accessed October 17th 2024).

(16) Gowrisankar, S.; Neumann, H.; Beller, M. General and Selective Palladium - Catalyzed Oxidative Esterification of Alcohols. *Angewandte Chemie International Edition* **2011**, *22* (50), 5139-5143.

(17) SDBS No. 4269HSP-02-548. *Spectral Database for Organic Compounds (SDBS) H-NMR spectrum*. <u>https://sdbs.db.aist.go.jp</u> (accessed October 17th 2024).

(18) SDBS No. 277HSP-03-378. *Spectral Database for Organic Compounds (SDBS) H-NMR spectrum*. <u>https://sdbs.db.aist.go.jp</u> (accessed October 17th 2024).

(19) SDBS No. 279HSP-03-385. *Spectral Database for Organic Compounds (SDBS) H-NMR spectrum*. <u>https://sdbs.db.aist.go.jp</u> (accessed October 17th 2024).

(20) SDBS No. 2252. *Spectral Database for Organic Compounds (SDBS) H-NMR spectrum*. <u>https://sdbs.db.aist.go.jp</u> (accessed October 17th 2024).

(21) 9-oxabicyclo[6.1.0]nonane. *Spectral Database for Organic Compounds*. 2003-09-30. <u>https://sdbs.db.aist.go.jp/sdbs/cgi-bin/direct_frame_disp.cgi?sdbsno=41174</u> (accessed 2024-3-27).

(22) SDBS No. 2912. *Spectral Database for Organic Compounds (SDBS) H-NMR spectrum*. <u>https://sdbs.db.aist.go.jp</u> (accessed October 17th 2024).