# Supporting Information

# Multi-step Engineering of Synergistic Catalysts in a Metal-Organic Framework for Tandem C-O Bond Cleavage

Yang Song,<sup>†</sup> Xuanyu Feng,<sup>†</sup> Justin S. Chen, Carter Brzezinski, Ziwan Xu, and Wenbin Lin\*

Department of Chemistry, The University of Chicago, 929 E 57th St, Chicago, IL 60637, USA

E-mail: wenbinlin@uchicago.edu

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#### **1. Materials and Methods**

All the reactions and manipulations were carried out under  $N_2$  with the use of a glovebox or Schlenk technique, unless otherwise indicated. Tetrahydrofuran and toluene were purified by passing through a neutral alumina column under  $N_2$ . Benzene,  $d_6$ -benzene, and *n*-octane were distilled over CaH<sub>2</sub>. Substrates including alcohols, ethers and esters were purchased from Fisher or Aldrich, and dried over freshly activated 4Å molecular sieves and degassed by freeze-pump-thaw methods before storage in a glovebox for further use.

Powder X-ray diffraction (PXRD) data was collected on a Bruker D8 Venture diffractometer using Cu K $\alpha$  radiation source ( $\lambda = 1.54178$  Å). N<sub>2</sub> sorption experiments were performed on a Micrometrics TriStar II 3020 instrument. Thermogravimetric analysis (TGA) was performed in air using a Shimazu TGA-50 equipped with a platinum pan and heated at a rate of 1.5 °C per min. Fourier-transform infrared (FT-IR) spectra were collected using a Nexus 870 spectrometer (Thermo Nicolet) installed with Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) system. Transmission electron microscopy (TEM) images were taken on a TECNAI F30 HRTEM. Scanning electron microscopy (SEM) images were take on the Carl Zeiss Merlin, with the detectors of In-Lens, EsB, AsB, & SE2. Ozonolysis was performed on an Azcozon RMU-DG3 ozone generator, which produces up to  $\sim 0.42$  mol/h ozone at a 6 L/min O<sub>2</sub> gas flow rate. Inductively coupled plasma-mass spectrometry (ICP-MS) data was obtained with an Agilent 7700x ICP-MS and analyzed using ICP-MS MassHunter version B01.03. Samples were diluted in a 2% HNO3 matrix and analyzed with a <sup>159</sup>Tb internal standard against a 12-point standard curve over the range from 0.1 ppb to 500 ppb. The correlation was >0.9997 for all analyses of interest. Data collection was performed in Spectrum Mode with five replicates per sample and 100 sweeps per replicate. EPR spectra were recorded on a Bruker Elexsys 500 X-band EPR spectrometer under irradiation of a white-light lamp (Fiber-Lite MI-150) by focusing the lamp on the sample cell in the ESR

cavity at 15 K. Fluorescence measurement was performed using a Shimazu RF-5301PC spectrofluorophotometer.

<sup>1</sup>H NMR spectra were recorded on a Bruker NMR 500 DRX spectrometer at 500 MHz and referenced to the proton resonance resulting from incomplete deuteration of CDCl<sub>3</sub> ( $\delta$  7.26), DMSO-*d*<sub>6</sub> ( $\delta$  2.50), or C<sub>6</sub>D<sub>6</sub> ( $\delta$  7.16). The following abbreviations are used herein: s: singlet, d: doublet, t: triplet, q: quartet, m: multiplet, br: broad, app: apparent. The conversions of reactions were determined by gas chromatography-mass spectrometry (GC-MS) using a Shimadzu GCMS-QP2010 Ulta equipped with SH-Rxi-5Sil MS 30 m × 0.5 mm × 0.25 µm column.

# 2. Synthesis Procedures and MOF Characterization after Post-synthetic Transformations

# 2.1 Synthesis and Characterization of MOF 1.

# 2.1.1 Synthesis of MOF 1.

The synthetic procedure was based on literature reports for DUT-5 and MOF-253.<sup>1-2</sup> In a typical synthesis, 2,2'-bipyridine-5,5'-dicarboxylic acid (dcbpy, 19.5 mg, 0.08 mmol) and 1,4-benzenediacrylic acid (pdac, 4.4 mg, 0.02 mmol) were dissolved in 3 mL DMF. Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O (52 mg, 0.14 mmol) was added. The mixture was transferred to an 8-mL vial and heated at 120 <sup>°</sup>C for 12 h under stirring. After cooling to room temperature, the white solid was recovered by centrifugation and then sequentially washed with DMF three times, THF three times, and benzene three times. This solid was then freeze-dried in benzene. After that, the white powder was further heated at 100 <sup>°</sup>C under vacuum to remove the trapped solvents in the pores.



Scheme S1. Synthetic procedure for MOF 1.



Figure S1. SEM micrograph (a) and TEM image (b) of as-synthesized 1.

# 2.1.2 <sup>1</sup>H NMR Analysis of Digested 1.

To determine the formula of as-synthesized **1**, 2 mg of **1** was dried under vacuum and then digested in 50  $\mu$ L D<sub>3</sub>PO<sub>4</sub>. The mixture was sonicated for 10 min, followed by the addition of 500  $\mu$ L DMSO*d*<sub>6</sub> and 50  $\mu$ L D<sub>2</sub>O, and analyzed by <sup>1</sup>H NMR. The ratio between dcbpy and pdac was determined to be about 4:1. The formula of **1** was thus determined to be Al(OH)(dcbpy)<sub>0.81</sub>(pdac)<sub>0.19</sub>.



**Figure S2.** <sup>1</sup>H NMR spectrum of digested **1** in DMSO- $d_6$ . Red and blue circles correspond to dcbpy and pdac ligands, respectively.

# 2.1.3 Thermogravimetric Analysis of 1

The first weight loss (7.9%) in the 25 to 230 °C temperature range corresponds to the removal of adsorbed solvents in the MOF. The second weight loss (82.0%) in the 230 - 800 °C temperature range corresponds to decomposition of the MOF to metal oxides, consistent with a calculated weight loss of 81.8% based on the conversion of Al(OH)(dcbpy)<sub>0.81</sub>(pdac)<sub>0.19</sub> to 0.5 Al<sub>2</sub>O<sub>3</sub>.



Figure S3. TGA curve of freshly prepared 1 in the 25-800 °C range.

# 2.2 Synthesis and Characterization of 1-OH.

2.2.1 Synthesis of 1-OH.



Scheme S2. Synthetic procedure for 1-OH.

We used ozonolysis to selectively cleave and remove the pdac ligand.<sup>3</sup> To ensure a continuous flow of ozone through the sample, we first mixed **1** (200 mg) with 2 g Ottawa sand (20-30 mesh) to improve O<sub>3</sub> permeability. We then pack the solid mixture into a thin glass column, which was later connected to the ozonator with a gas flow. The excess O<sub>3</sub> was quenched by KI aqueous solution. The reaction was run at room temperature for 15 min to ensure complete cleavage of pdac ligands. The resulted sample was washed with DMF/HCl (1M) (10:1, v:v) three times to remove the organic and inorganic fragments trapped in the pores of ozonized **1**, and washed with THF three times and benzene three times, followed by freeze-drying in benzene, and stored in a glovebox for further use.



**Figure S4.** (a) Schematic representation of ozonolysis treatment for the removal of pdac ligands. SEM micrograph (b) and TEM image (c) of **1**-OH.

# 2.2.2 <sup>1</sup>H NMR Analysis of Digested 1-OH.

To determine the formula of 1-OH, 2 mg of 1-OH was dried under vacuum and then digested in 50  $\mu$ L of D<sub>3</sub>PO<sub>4</sub>. The mixture was sonicated for 10 min followed by the addition of 500  $\mu$ L DMSO-*d*<sub>6</sub> and 50  $\mu$ L D<sub>2</sub>O and analyzed by <sup>1</sup>H NMR.



**Figure S5.** <sup>1</sup>H NMR spectrum of digested **1**-OH in DMSO-*d*<sub>6</sub>. Red circles correspond to dcbpy ligands. No signals corresponding to pdac ligand are seen in the <sup>1</sup>H NMR spectrum, indicating complete removal of pdac ligands during ozonolysis.

# 2.2.3 Thermogravimetric Analysis of 1-OH.

The first weight loss (23.3%) in the 25 to 220 °C temperature range corresponds to the removal of adsorbed solvents in **1**-OH. The second weight loss (78.7%) in the 220 - 800 °C temperature range corresponds to the decomposition of **1**-OH to metal oxides, consistent with a calculated weight loss of 79.5% based on the conversion of Al(OH)(dcbpy)<sub>0.81</sub>(OH)<sub>0.38</sub>(H<sub>2</sub>O)<sub>0.38</sub> to 0.5 Al<sub>2</sub>O<sub>3</sub>.



Figure S6. TGA curve of 1-OH in the 25-800 °C range.

# 2.2.4 N<sub>2</sub> Sorption Isotherms of 1 and 1-OH.

BET surface areas of **1** and **1**-OH were determined to be 1499  $m^2/g$  and 1190  $m^2/g$ , respectively. The pore size distributions are also shown below. After ozonolysis, **1**-OH showed the evolution of mesoporosity when compared to **1**, featuring larger pore width in the pore size distribution.



Figure S7. Pore size distributions of 1 (a) and 1-OH (b).

# 2.3 Synthesis and Characterization of 1-OTf.

# 2.3.1 Synthesis of 1-OTf.



Scheme S3. Synthetic procedure for 1-OTf.

In a N<sub>2</sub>-filled glovebox, **1**-OH (0.10 mmol of -OH/OH<sub>2</sub>) was weighed out in a 20 mL glass vial and dispersed in 10 mL of benzene. Trimethylsilyl trifluoromethanesulfonate (Me<sub>3</sub>SiOTf, 0.18 mL, 1.0 mmol) was then added slowly to the suspension. The vessel was sealed with a Teflon cap and stir at room temperature for 12 h. The suspension was then washed with dry toluene 5 times. The

resultant MOF was further extracted with hexane in a Sohxlet extractor to remove the trapped HOTf inside the MOF channels. 10 equiv. of LiCH<sub>2</sub>SiMe<sub>3</sub> was added to the receiving flask to quench extracted HOTf during the Sohxlet extraction.<sup>4</sup> After solvent exchange with dry benzene, **1**-OTf was freeze-dried under vacuum overnight and stored inside a glovebox for further use.

# 2.3.2 Quantification of the (Me<sub>3</sub>Si)<sub>2</sub>O Byproduct.

As shown in Scheme S3, after treating 1-OTf with Me<sub>3</sub>SiOTf in benzene- $d_6$  for 12 h, 8.0 equiv. of mesitylene (w.r.t Al-OH/OH<sub>2</sub> sites) was added to the mixture as the internal standard. The supernatant was then analyzed by <sup>1</sup>H NMR. The chemical shifts of authentic (Me<sub>3</sub>Si)<sub>2</sub>O, Me<sub>3</sub>SiOTf, and mesitylene CH<sub>3</sub> groups are  $\delta = 0.12$ , -0.04, and 2.16 ppm, respectively. The amount of (Me<sub>3</sub>Si)<sub>2</sub>O was determined to be 1.93 equiv. w.r.t Al-OH/H<sub>2</sub>O sites, matching well with the expected value of 2.0 equiv.



**Figure S8.** <sup>1</sup>H NMR spectrum of the supernatant from **1**-OH activation with Me<sub>3</sub>SiOTf. The amount of (Me<sub>3</sub>Si)<sub>2</sub>O was determined to be 1.93 equiv. w.r.t. to the Al<sub>2</sub>(OH)(OH<sub>2</sub>) sites.

# 2.3.3 DRIFTS of 1, 1-OH, and 1-OTf.

FT-IR was used to support the successful preparation of **1**-OH and **1**-OTf. As shown in Figure S9, the increased absorption at  $1231 - 1266 \text{ cm}^{-1}$  in **1**-OTf corresponds to the  $v(S=O^{OTf})$  band (Figure S9a). The sharp stretching band at 3708 cm<sup>-1</sup> was observed for bridging  $\mu_2$ -OH groups in both **1** and **1**-OH (Figure S9b). A significant red shift of  $v(\mu_2$ -OH) stretching band from 3708 cm<sup>-1</sup> to 3687 cm<sup>-1</sup> was found in **1**-OTf after triflation, which can be attributed to the acidity increase of the  $\mu_2$ -OH groups owing to the electron withdrawing -OTf groups. The broad peak centered at 3689 cm<sup>-1</sup> in **1**-OH was attributed to hydrogen bonding between neighboring Al-OH and Al-OH<sub>2</sub> moieties.



**Figure S9**. (a) DRIFT spectra of **1** (blue), **1**-OH (red), and **1**-OTf (black). (b) Zoomed-in view of the DRIFT spectra show a significant red shift of  $v(\mu_2$ -OH) from 3708 cm<sup>-1</sup> in **1** (blue) and **1**-OH (red) to 3687 cm<sup>-1</sup> in **1**-OTf (black).

# 2.4 Synthesis and Characterization of 1-OTf-PdCl<sub>2</sub>.

# 2.4.1 Synthesis of 1-OTf-PdCl<sub>2</sub>.



Scheme S4. Synthetic procedure for 1-OTf-PdCl<sub>2</sub>.

In a N<sub>2</sub>-filled glovebox, **1**-OTf (0.2 mmol of bpy) was weighed out in a 20 mL glass vial. 10 mL of Pd(MeCN)<sub>2</sub>Cl<sub>2</sub> solution in THF (20 mM) was then added. The mixture was stirred at room temperature for 12 h. The brown solid was then centrifuged and washed with THF three times and benzene three times. **1**-OTf-PdCl<sub>2</sub> was then freeze-dried in benzene and stored in a glovebox for further use. ICP-MS analysis showed a Al/Pd molar ratio of 2.10, indicating ~60% of dcbpy ligands were metalated.



Figure S10. TEM image of 1-OTf-PdCl<sub>2</sub>.

# 2.4.2 Thermogravimetric Analysis of 1-OTf-PdCl<sub>2</sub>.

The first weight loss (17.2%) in the 25 to 210 °C temperature range corresponds to the removal of adsorbed solvents in **1**-OTf-PdCl<sub>2</sub>. The second weight loss (72.2%) in the 210 - 800 °C temperature range corresponds to the decomposition of **1**-OH to metal oxides, consistent with a calculated weight loss of 71.4% based on the conversion of Al(OH)(dcbpy)<sub>0.81</sub>[PdCl<sub>2</sub>(MeCN)<sub>2</sub>]<sub>0.48</sub>(OTf)<sub>0.38</sub> to 0.5 Al<sub>2</sub>O<sub>3</sub> and 0.48 PdO.



Figure S11. TGA curve of 1-OTf-PdCl<sub>2</sub> in the 25-800 °C range.

# 3. X-ray Absorption Study.

# 3.1 Data Collection.

X-ray absorption data of 1-OTf-PdCl<sub>2</sub> were collected at Beamline 10-BM at the Advanced Photon Source (APS) at Argonne National Laboratory. Spectra were collected at the palladium K-edge (24350 eV) in the transmission mode. The X-ray beam was monochromatized by a Si(111) monochromator and detuned by 15% to reduce the contribution of higher-order harmonics below the level of noise. A metallic palladium foil standard was used as a reference for energy calibration and was measured simultaneously with experimental samples. The incident beam intensity (I<sub>0</sub>), transmitted beam intensity (I<sub>1</sub>), and reference (I<sub>r</sub>) were measured by 20 cm ionization chambers with gas compositions of 38% N<sub>2</sub> and 62% Ar, 5% N<sub>2</sub> and 95% Ar, and 100% N<sub>2</sub>, respectively. Data were collected over three regions: -200 to -50 eV (5 eV step size, dwell time of 1 s), -50 to 100 eV (1 eV step size, dwell time of 2 s), 100 to 850 eV (0.05 eV step size, dwell time of 6 s). Multiple X-ray absorption spectra were collected at room temperature for each sample. Samples were grounded and mixed with polyethylene glycol (PEG) and packed in a 6-shooter sample holder to achieve adequate absorption length.

# **3.2 Data Processing.**

Data was processed using the Athena and Artemis programs of the IFEFFIT package based on FEFF 6.<sup>5-6</sup> Prior to merging, spectra were calibrated against the reference spectra and aligned to the first peak in the smoothed first derivative of the absorption spectrum, the background noise was removed, and the spectra were processed to obtain a normalized unit edge step.

# **3.3 EXAFS Fitting of 1-OTf-PdCl<sub>2</sub>.**

Fitting of the EXAFS region was performed using the Artemis program of the IFEFFIT package. Fitting was performed in R space, with a *k*-weight of 3 for palladium samples. Refinement was performed by optimizing an amplitude factor  $S_0^2$  and energy shift  $\Delta E_0$  which are common to all paths, in addition to parameters for bond length ( $\Delta R$ ) and Debye-Waller factor ( $\sigma^2$ ). The fitting model for **1**-OTf-PdCl<sub>2</sub> was based on the single crystal structure JIPGAR obtained from CCDC.<sup>7</sup>

<b>1</b> -OT	f-PdCl <sub>2</sub>	Fitting Range	k: 3.0 – 12.0 Å <sup>-1</sup> R: 1.0 - 3.0 Å
Independent Points	11.2	Variables	7.0
Reduced chi- square	579.6	<b>R-factor</b>	0.005
ΔE <sub>0</sub> (eV)	6.04	${ m S_0}^2$	1.0
R(Pd-N <sup>bpy</sup> ) (2)	$2.04 \pm 0.01 \text{ Å}$	$\sigma^2(Pd-N^{bpy})$	$0.002 \pm 0.001$
<b>R(Pd-Cl) (2)</b>	$2.30\pm0.02~\text{\AA}$	$\sigma^2$ (Pd-Cl)	$0.002\pm0.000$
$\mathbf{R}(\mathbf{Pd}\textbf{-}\mathbf{C}_{1}^{\mathbf{bpy}}) (2)$	$2.91 \pm 0.03$ Å	$\sigma^2$ (Pd-C <sub>1</sub> <sup>bpy</sup> )	$0.006 \pm 0.004$
$\mathbf{R}(\mathbf{Pd}\text{-}\mathbf{C}_{2}^{\mathbf{bpy}}) (2)$	$3.05\pm0.03~\text{\AA}$	$\sigma^2$ (Pd-C <sub>2</sub> <sup>bpy</sup> )	$0.006 \pm 0.004$

Table S1. EXAFS fitting parameters of 1-OTf-PdCl<sub>2</sub>.

# 3.4 XANES Analysis of 1-OTf-Pd<sup>NP</sup>.

XANES spectra at Pd K-edge of 1-OTf-PdCl<sub>2</sub>, 1-OTf-Pd<sup>NP</sup>, PdCl<sub>2</sub>, and Pd foil are shown in Figure S12. The first oscillations of Pd metal appear immediately after the edge, positioned at 24367 and 24391 eV, correspond to  $1s \rightarrow 5p$  and  $1s \rightarrow 4f$  electronic transitions, respectively.<sup>8</sup> PdCl<sub>2</sub> features the absorption peak at 24380 eV.<sup>9</sup> As compared to the peak positions of Pd(0) in Pd foil and Pd(II) in PdCl<sub>2</sub>, XANES spectrum of 1-OTf-Pd<sup>NP</sup> contained features of both Pd(0) and Pd(II).

We conducted the linear combination fitting of the XANES spectrum of **1**-OTf-Pd<sup>NP</sup> (the Pd-K edge: -20 eV to 60 eV) using the spectra of Pd foil and PdCl<sub>2</sub> as basis functions. The fitting gave ~48% of Pd(0) and ~52% of Pd(II).



Figure S12. XANES Spectra of 1-OTf-PdCl<sub>2</sub>, 1-OTf-Pd<sup>NP</sup>, Pd foil, and PdCl<sub>2</sub>.

#### 4. Quantification of MOF Lewis Acidity.

# 4.1 Quantification of Lewis Acidity via EPR of MOF-bound Superoxide Species.

Dimeric 1-benzyl-1,4-dihydronicotinamide [(BNA)<sub>2</sub>] was synthesized using the literature procedure.<sup>10</sup> Superoxide radical anions were generated in situ through the photoreduction of oxygen by (BNA)<sub>2</sub> in an oxygen-saturated MeCN/toluene mixture solvent. In a typical experiment, 20% MeCN in toluene was used as a mixed solvent to dissolve (BNA)<sub>2</sub> in 4.0 mM concentration (1.7 mg in 1.0 mL). After brief sonication, the (BNA)<sub>2</sub> solution was bubbled with oxygen for 10 min to saturation. Afterwards, **1**-OH or **1**-OTf [20  $\mu$ mol of Al<sub>2</sub>(OH)(OH<sub>2</sub>) or Al<sub>2</sub>(OTf)] was dispersed in 1.0 mL of the O<sub>2</sub>/(BNA)<sub>2</sub> solution via sonication. The mixture was then transferred to an EPR tube for EPR analysis. EPR spectra were recorded on a Bruker Elexsys 500 X-band EPR spectrometer under irradiation of a white-light lamp (Fiber-Lite MI-150) by focusing the lamp on the sample cell in the ESR cavity at 15 K. The sample was loaded into the cavity and held for 10 minutes to ensure superoxide generation and coordination to the MOF and the freezing of the dispersion. The EPR spectrum was collected at 9.632 GHz.

For **1**-OTf, the coordinated superoxide showed a typical anisotropic signal with  $g_{zz} = 2.0320$ . The superoxide binding energy to Al centers can be calculated using the following equation adopted from literature reports to be 0.94 eV.<sup>11-12</sup>

$$g_{zz} = g_e + 2\sqrt{\frac{\lambda^2}{\lambda^2 + \Delta E^2}}$$

where the free spin value  $g_e = 2.0023$ ,  $\lambda$  is the spin-orbit coupling constant of oxygen that is known to be 0.014 eV, and  $\Delta E$  is the energy splitting of  $\pi_g$  levels due to superoxide coordination to Al.



**Figure S13.** (a) EPR spectra of 1-OTf- $(O_2^{\bullet-})$  (black) and 1-OH- $O_2^{\bullet-}$  (red) show different  $g_{zz}$  values due to the different Lewis acidity of 1-OTf and 1-OH. (b) Proposed structures for superoxide-coordinated 1-X (X = -OH or -OTf).

# 4.2 Quantification of Lewis Acidity by *N*-methylacridone Fluorescence.

The fluorescent indicator *N*-methylacridone (NMA) was purchased from Sigma-Aldrich. The fluorescence measurement was performed using a Shimazu RF-5301PC spectrofluorophotometer with an excitation wavelength of 413 nm. NMA was dissolved in MeCN to form an NMA solution with a concentration of 10  $\mu$ M to give a reference emission wavelength that was measured to be 433 nm (Figure S14, dashed line). For the measurement of MOF Lewis acidity, 0.1 mmol of **1**-OH or **1**-OTf [by the amount of Al<sub>2</sub>(OH)(OH<sub>2</sub>) or Al<sub>2</sub>(OTf)] was added to a 2-dram vial in an N<sub>2</sub>-filled glovebox. 4 mL of NMA solution (10  $\mu$ M in MeCN) was then added to the vial. The resulting mixture was sonicated for 2 min until the MOF was well suspended, and then the suspension was transferred to a fluorescence cuvette for measurement using an excitation wavelength of 413 nm. The emission maxima for NMA-bound **1**-OH and **1**-OTf were measured to be 463 nm and 470 nm, respectively, which are correspond to  $\Delta$ E values of 0.84 eV and 0.93 eV, respectively (Figure S14).<sup>11, 13</sup>



**Figure S14.** (a) Fluorescence spectra of **1**-OTf (black), **1**-OH (red), and free NMA (dashed). (b) Proposed structures for NMA-coordinated **1**-X (X = -OH or -OTf).

# 4.3 Quantification of Lewis Acidity of 1-OTf-Pd<sup>NP</sup> after Catalysis

To determine whether Lewis acidity of **1**-OTf-Pd<sup>NP</sup> was maintained after catalysis, we carried out NMA fluorescence measurement on the MOF catalyst after catalytic reaction. The NMA fluorescence spectra indicated that the MOF recovered from C-O cleavage reaction of 1-methylcyclohexanol showed nearly the same emission maxima as **1**-OTf at ~470 nm (Figure S15). This result indicates the maintenance of Lewis acidity of the MOF catalyst throughout the catalytic reaction.



**Figure S15.** NMA fluorescence spectra upon binding to **1**-OTf (black) and **1**-OTf-Pd<sup>NP</sup> recovered from C-O bond cleavage of 1-methylcyclohexanol (red).

# 5. 1-OTf-PdCl<sub>2</sub> Catalyzed Tandem Ether/Alcohol C-O Bond Cleavage.

# 5.1 A typical procedure for 1-OTf-PdCl<sub>2</sub> catalyzed tandem ether/alcohol C-O bond cleavage.



In a nitrogen-filled glovebox, **1**-OTf-PdCl<sub>2</sub> (2.0 mg, 1.2  $\mu$ mol Al<sub>2</sub>( $\mu$ <sub>2</sub>-OTf) sites), 1,8-cineole (100  $\mu$ L, 0.6 mmol), and 1.0 mL of 1,2-dichloroethane were transferred to a Parr reactor to make an even suspension. The Parr reactor was then sealed under nitrogen, purged with hydrogen several times and charged with hydrogen to 20 bar. After stirring at 100 °C for 24 hours, the pressure was released, and the MOF catalyst was removed from the reaction mixture via centrifugation. The supernatant was analyzed by GC-MS to give menthane (a mixture of cis/trans isomers) in >99% yield with 100% conversion of 1,8-cineole. After one reaction run, ICP-MS analysis showed the leaching of 0.6% Al and 0.02% Pd into the solution.



**Figure S16.** GC-MS spectrum of **1**-OTf-PdCl<sub>2</sub> catalyzed tandem ether/alcohol C-O bond cleavage of 1,8-cineole (The two MS spectra correspond to the cis/trans isomer of menthane).

# 5.2 Condition optimization for 1-OTf-PdCl<sub>2</sub> catalyzed tandem ether/alcohol C-O bond cleavage.

Early trials of **1**-OTf-PdCl<sub>2</sub> catalyzed tandem ether/alcohol C-O bond cleavage were conducted using 1,8-cineole as the substrate at 0.5 mol% of catalyst loading (w.r.t. Al<sub>2</sub>( $\mu_2$ -OTf) sites), 20 bar of H<sub>2</sub> pressure, and 130 °C for 24 h. Several different kinds of solvents, including n-octane, n-hexane, 1,2-dichloroethane, 1,4-dichlorobutane, THF and neat conditions, were tested. 1,2-dichloroethane and 1,4-dichlorobutane outperformed other solvents, with quantitative substrate conversions and >99% yield of menthane by GC-MS. Further lowering the catalyst loading to 0.2 mol% and reaction temperature to 100 °C in 1,2-dichloroethane still gave quantitative conversion (Table S2, Entry 4). The maximum TON at 100 °C was achieved at 0.1 mol% catalyst loading, with a TON of 800 (Table S2, Entry 5).

	4	Catalyst -H <sub>2</sub> O	✓ ☐ Catalyst H <sub>2</sub>	•	
Entry	Cat. Loading / %	Solvent	$p(H_2) / bar$	Temp./ °C	Yield / %
1	0.5	Octane	20	130	74
2	0.5	Hexane	20	130	61
3	0.5	1,2-dichloroethane	20	130	>99
4	0.5	1,4-dichlorobutane	20	130	>99
5	0.2	1,2-dichloroethane	20	100	>99
6	0.1	1,2-dichloroethane	20	100	80
7	0.5	THF	20	130	31
8	0.1	neat	20	130	40

**Table S2.** Condition optimization for **1**-OTf-PdCl<sub>2</sub> catalyzed tandem ether/alcohol C-O bond cleavage of 1,8-cineole.

Reaction conditions: **1**-OTf-PdCl<sub>2</sub> (catalyst loading w.r.t. Al<sub>2</sub>( $\mu$ <sub>2</sub>-OTf)), 0.6 mmol 1,8-cineole, 20 bar H<sub>2</sub>, 1 mL solvent or neat condition, 24 h; Yield was determined by GC-MS analysis.

#### 5.3 Background reactions and control experiments.

Several additional experiments were carried out to compare the catalytic performance of homogeneous analogues and determine tandem reaction pathways of **1**-OTf-PdCl<sub>2</sub> catalyzed C-O bond cleavage.

Both HOTf acid and Al(OTf)<sub>3</sub> were tested together with Pd source [Pd(MeCN)<sub>2</sub>Cl<sub>2</sub>] in tandem C-O bond cleavage of 1,8-cineole, with the same active site loadings as **1**-OTf-PdCl<sub>2</sub>. Strong Brönsted acid (HOTf) produced 3% menthane along with significant amounts of unsaturated alkenes isomers (Table S3, Entry 2), while homogeneous metal triflates gave a slightly better menthane yield of 9% (Table S3, Entry 3). Additionally, a combination of Pd/C (10 %) and Al(OTf)<sub>3</sub> gave only slightly higher yield than [Pd(MeCN)<sub>2</sub>Cl<sub>2</sub>] plus Al(OTf)<sub>3</sub> (Table S3, Entry 4). These results indicated undesired deactivation of homogeneous species and possible interference between the homogeneous acids and Pd sources [Pd(MeCN)<sub>2</sub>Cl<sub>2</sub>]. While 0.2 mol% of **1**-OTf-PdCl<sub>2</sub> catalyzed nearly quantitative conversion of 1,8-cineole to menthane, no target product was detected without adding the MOF catalyst (Table S3, entry 1) or using the same loading of **1**-OTf (MOF catalyst with only strong Lewis acidic Al<sub>2</sub>(µ<sub>2</sub>-OTf) sites but no Pd sites, Table S3, entry 4). However, unsaturated alkenes isomers were detected with the **1**-OTf catalyst, demonstrating the ability of Lewis acidic sites to catalyze the reverse reaction of the alkene hydroalkoxylation process. When combined with the hydrogenation catalyst (Pd NPs in the MOF), such C-O cleavage proceeded smoothly (Table S3, entry 7). Furthermore, when **1**-OH-PdCl<sub>2</sub> catalyst (MOF catalyst with weak Lewis acidic Al<sub>2</sub>(OH)(OH<sub>2</sub>) sites and Pd sites, see below for detailed synthesis and characterization) was used (Table S3, entry 6), menthane was detected in a much lower yield (22%), indicating the significant contribution of Lewis acidity to C-O bond cleavage.

		-H <sub>2</sub> O	$\left  \begin{array}{c} Catalyst \\ H_2 \end{array} \right $	
Entry	Cat. & Loading / %	Temp./ °C	Yield of menthane	Other Products
1 <sup>b</sup>	-	100	N.D.	3% (iso) OH 2%
2°	$\begin{array}{l} 0.2 \ mol\% \ of \ HOTf + 0.25 \\ mol\% \ PdCl_2(MeCN)_2 \end{array}$	100	3%	9% 42% (iso) (iso)
3 <sup>d</sup>	0.2 mol% of Al(OTf) <sub>3</sub> + 0.25 mol% PdCl <sub>2</sub> (MeCN) <sub>2</sub>	100	9%	28% (iso)
4 <sup>e</sup>	0.2 mol% of Al(OTf) <sub>3</sub> + 0.25 mol% Pd/C	100	20%	1% OH 3% (iso)
5 <sup>f</sup>	0.2 mol% of <b>1</b> -OTf	100	<1%	48% 44% (iso) (iso)
6 <sup>g</sup>	0.2 mol% of 1-OH-PdCl <sub>2</sub>	100	22	ОН 2%

**Table S3.** Background and control experiments for 1-OTf-PdCl<sub>2</sub> catalyzed tandem ether/alcoholC-O bond cleavage of 1,8-cineole.<sup>a</sup>

<sup>a</sup>Reaction conditions: 0.6 mmol 1,8-cineole, 20 bar H<sub>2</sub>, 1 mL 1,2-dichloroethane, 100 °C, 24 h; Yields of different product and related isomers(iso) were determined by GC-MS analysis. <sup>b</sup>Reaction was conduct w/o. catalyst. <sup>c</sup>0.2 mol% of Al(OTf)<sub>3</sub> + 0.25 mol% PdCl<sub>2</sub>(MeCN)<sub>2</sub> was used as catalysts. <sup>d</sup>Catalysts: 0.2 mol% of HOTf + 0.25 mol% PdCl<sub>2</sub>(MeCN)<sub>2</sub> was used as catalysts. <sup>e</sup>0.2 mol% of Al(OTf)<sub>3</sub> + 0.25 mol% Pd/C (10%) was used as catalysts. <sup>f</sup>1-OTf was used as catalyst, 0.2 mol% loading (w.r.t. Al<sub>2</sub>( $\mu$ 2-OTf) sites). <sup>g</sup>1-OH-PdCl<sub>2</sub> (synthesized by Pd metalation of 1-OH, similar Pd loading with 1-OTf-PdCl<sub>2</sub>) was used as catalyst, 0.2 mol% loading (w.r.t. Al<sub>2</sub>(OH)(OH<sub>2</sub>) sites).

# **5.4 Supplementary Table for Substrate Scope Evaluation.**

Entry	Substrate	Loading / Temp.	Product	Conversion (Yield/isolated Yield) <sup>b</sup>
1	OH	0.1 mol% / 100 °C	$\bigcup$	100% (>99%/89%)
2	A	0.2 mol% / 100 °C	$\sum$	100% (>99%/93%)
3	40	0.1 mol% / 100 °C	$\checkmark$	80% (80%)
4	OH	0.1 mol% / 150 °C	$\bigcirc$	100% (>99%)
5	$\bigcirc^{\circ}\bigcirc$	0.1 mol% / 150 °C	$\bigcirc$	100% (97%)
6 <sup>c</sup>		0.1 mol% / 150 °C	$\bigcirc$	94% (89%)
7	ОН	0.2 mol% / 150 °C	$\sim$	100% (>99%/90%)
8	<b></b>	0.2 mol% / 150 °C	R = H, n-Hexyl	64% (55%) (alcohol : ether = 1 : 2)
9 <sup>d</sup>	<u>≻</u> °≻−	0.2 mol% / 150 °C	$\sim$	67% (67%)
10	но	0.5 mol% / 200 °C	$\sim$	100% (92%/78%)
11 <sup>e,<u>f</u></sup>		0.2 mol% / 150 °C		100% (89%)
12 <sup>e</sup>		0.2 mol% / 130 °C		70% (61%/55%)

Table S4. Substrate scope for 1-OTf-PdCl<sub>2</sub> catalyzed tandem etheric/alcoholic C-O bond cleavage<sup>a</sup>

<sup>a</sup>Unless noted, all reactions performed with indicated amount of **1**-OTf- PdCl<sub>2</sub>, 0.6 mmol of substrate, and 20 bar  $H_2$  in 1.0 mL of 1,2-dichloroethane for 24 h. <sup>b</sup>Conversions and yields determined by GC-MS integrals

with mesitylene as the internal standard. Isolated yield provided in the parenthesis for select entries. <sup>c</sup>Phenol detected as cleavage by-product. <sup>d</sup>Reaction performed in 1,4-dichlorobutane. <sup>e</sup>Reaction performed in 1 bar H<sub>2</sub>. <sup>f</sup>Phenol, cyclohexanone, and cyclohexane (1.5:1:1, mol ratio based on GC/MS) detected as cleavage by-product.



5.5 Synthesis and Characterization of 1-OH-PdCl<sub>2</sub> and 1-OH-Pd<sup>NP</sup>.

Scheme S5. Synthetic procedure for 1-OH-Pd<sup>NP</sup>.

In order to test the effects of Lewis acidity on C-O bond cleavage, **1**-OH (0.1 mmol of bpy) was weighed out in a 20 mL glass vial in a N<sub>2</sub>-filled glovebox. 5 mL Pd(MeCN)<sub>2</sub>Cl<sub>2</sub> solution in THF (20 mM) was then added. The mixture was stirred under room temperature for 12 h. The brown solid was then centrifuged and washed with THF three times and benzene three times. **1**-OH-PdCl<sub>2</sub> was then freeze-dried in benzene and stored in a glovebox for further use. In situ hydrogenation further afforded **1**-OH-Pd<sup>NP</sup>.



**Figure S17.** (a) PXRD patterns of 1-OH-PdCl<sub>2</sub> and 1-OH-Pd<sup>NP</sup>, matching well with the simulated PXRD pattern of DUT-5. (b) TEM image of 1-OH-Pd<sup>NP</sup> shows the evenly distributed Pd NPs in the MOF matrix after in situ reduction in catalytic reactions.

# 5.6 "Hot filtration" test.

"Hot filtration" test was performed to rule out the possibility of leached Lewis acidic metal species, soluble Brönsted acidic species, and homogeneous metal species contributing to the tandem C-O bond cleavage activity. Specifically, 0.2 mol% of **1**-OTf-PdCl<sub>2</sub> was first used to catalyze tandem C-O cleavage of 1,8-cineole to give menthane (a mixture of cis/trans isomers) in 97% yield in 10 hours. Then, under inert atmosphere, the MOF and supernatant were separated via centrifugation and used as catalysts, respectively, for the tandem C-O bond cleavage reaction of cyclohexanol without further treatment. The recovered **1**-OTf-PdCl<sub>2</sub> catalyst afforded cyclohexane in 99% yield in 10 hours, while less than 0.5% of the C-O cleavage product was detected in the reaction catalyzed by the supernatant. This result excludes the possibility of leached metal species or soluble acids contributing to the catalytic reactivity.



Figure S18. The "hot filtration" test of 1-OTf-PdCl<sub>2</sub> catalyzed tandem C-O bond cleavage reaction.

# 5.7 Leaching test of OTf groups

In order to check the amount of leached OTf groups, we separated the MOF from the supernatant after **1**-OTf-PdCl<sub>2</sub> catalyzed C-O cleavage of 1-methylcyclohexanol. We performed <sup>19</sup>F NMR analysis of both the supernatant and the digested MOF (digested with D<sub>3</sub>PO<sub>4</sub>). As shown in Figure S19, the supernatant showed no <sup>19</sup>F peak (maroon) while the digested MOF gave an OTf <sup>19</sup>F signal at -78 ppm (green). The result indicates negligible leaching of OTf groups during the catalytic reaction.





Figure S19. <sup>19</sup>F NMR spectra of the supernatant (maroon) and the digested MOF (green).

# 5.8 Recycle and reuse experiments in 1-OTf-PdCl<sub>2</sub> catalyzed tandem C-O bond cleavage.

In a N<sub>2</sub>-filled glovebox, **1**-OTf-PdCl<sub>2</sub> (2.0 mg, 1.2  $\mu$ mol Al<sub>2</sub>( $\mu$ <sub>2</sub>-OTf) sites), 1-methylcyclohexnaol (75  $\mu$ L, 0.6 mmol), and 1.0 mL of 1,2-dichloroethane was transferred into a Parr reactor to make an even suspension. The Parr reactor was then sealed under nitrogen, purged with hydrogen several times and charged with hydrogen to 20 bar. The reaction was stopped after stirring at 100 °C for 3 h to ensure an incomplete substrate conversion with a kinetic yield. The pressure was released, and the reaction slurry was then centrifugated to recover the MOF catalyst. The supernatant was analyzed by GC-MS to give menthane (a mixture of cis/trans isomers) in 84% yield.

The recovered MOF was washed with 1,2-dichloroethane 3 times before being used for another catalytic round. A new solution of 1-methylcyclohexnaol (75  $\mu$ L, 0.6 mmol) in 1,2-dichloroethane (1.0 mL) was then added. The reaction mixture was stirred at 100 °C for another 3 h, and then

worked up and recycled using the same procedure. The catalyst was recycled and reused for at least 5 times without a significant drop in catalytic activity.



**Figure S20.** The recycle experiment of **1**-OTf-PdCl<sub>2</sub> catalyzed tandem C-O bond cleavage reaction. Plots of yields (%) for the methylcyclohexane products in six consecutive runs

# 5.9 1-OTf-PdCl<sub>2</sub> catalyzed tandem C-O bond cleavage at 20 times larger scale.



In a nitrogen-filled glovebox, **1**-OTf-PdCl<sub>2</sub> (40.0 mg, 24  $\mu$ mol Al<sub>2</sub>( $\mu$ <sub>2</sub>-OTf) sites), 1,8-cineole (2.0 mL, 12 mmol), and 10.0 mL of 1,2-dichloroethane were transferred to a Parr reactor to make an even suspension. The Parr reactor was then sealed under nitrogen, purged with hydrogen several times and charged with hydrogen to 20 bar. After stirring at 100 °C for 24 hours, the pressure was released, and the MOF catalyst was removed from the reaction mixture via centrifugation. GC-MS analysis of the supernatant gave menthane (a mixture of cis/trans isomers) in 75% yield and 25% 1,8-cineole starting material.

5.10 Demonstration of 1-OTf-PdCl<sub>2</sub> catalyzed tandem C-O bond cleavage in biomass conversion.



As a key intermediate in biomass conversion, 5-(Hydroxymethyl)furfural (5-HMF) is obtained by dehydration of some sugars. The conversion of 5-HMF to biofuel or value-added chemical feedstocks is of great interest. 1-OTf-PdCl<sub>2</sub> at 0.2 mol% loading converted 5-HMF to 2,5-dimethylfuran (DMF) in 71% yield at 150 °C.

# 6. 1-OTf-PdCl<sub>2</sub> Catalyzed Tandem Ester C-O Bond Cleavage

# 6.1 A typical procedure for 1-OTf-PdCl<sub>2</sub> catalyzed tandem ester C-O bond cleavage.



In a N<sub>2</sub>-filled glovebox, 1-OTf-PdCl<sub>2</sub> (5.0 mg, 3.0  $\mu$ mol Al<sub>2</sub>( $\mu$ <sub>2</sub>-OTf) sites), terpinyl acetate (123  $\mu$ L, 0.6 mmol), and 1.0 mL of 1,2-dichloroethane was transferred to a Parr reactor to make an even suspension. The Parr reactor was then sealed under nitrogen, purged with hydrogen several times and charged with hydrogen to 20 bar. After stirring at 100 °C for 24 hours, the pressure was released, and the MOF catalyst was removed from the reaction mixture via centrifugation. The supernatant was analyzed by GC-MS to give menthane (a mixture of cis/trans isomers) in 88% yield with 100% substrate conversion. After one reaction run, 0.6% of Al and 0.15% of Pd are detected in the solution by ICP-MS analysis.



**Figure S21.** GC-MS spectra of **1**-OTf-PdCl<sub>2</sub> catalyzed tandem ester C-O bond cleavage of terpinyl acetate (The two MS spectra correspond to the cis/trans isomers of menthane).

# 6.2 Supplementary Table for Substrate Scope Evaluation.

Entry	Substrate	Loading / Temp.	Product	Conversion (Yield/isolated Yield) <sup>b</sup>
1°	i X	0.2 mol% / 100 °C	$\bigcup_{i \in \mathcal{I}}$	100% (88%)
2		0.5 mol% / 150 °C	$\searrow$	100% (>99%/95%)
3		0.1 mol% / 150 °C	$\bigvee \downarrow$	45% (45%)
4 <sup>c</sup>		0.5 mol% / 150 °C	$\bigcirc$	91% (84%)
5°	$\bigcup^{\circ} \bigcup^{\circ}$	0.5 mol% / 150 °C	$\bigcirc$	87% (62%)
6		0.5 mol% / 200 °C	$\sim$	100% (79%)
7 <sup>d</sup>		0.2 mol% / 130 °C		100% (94%/90%)
8		0.2 mol% / 130 °C	HOO	100% (61%/55%)

Table S5. Substrate scope for 1-OTf-PdCl<sub>2</sub> catalyzed ester C-O bond cleavage<sup>a</sup>

<sup>a</sup>Unless noted, all reactions performed with indicated amount of **1**-OTf-PdCl<sub>2</sub>, 0.6 mmol of substrate, and 20 bar H<sub>2</sub> in 1.0 mL of 1,2-dichloroethane for 24 h. <sup>b</sup>Conversions and yields determined by GC-MS integrals with mesitylene as the internal standard. Isolated yield provided in the parenthesis for select entries. <sup>c</sup>Reaction performed for 36 h. <sup>d</sup>Reaction performed in 1 bar H<sub>2</sub> for 6 h.

# 7. GC Retention Times

The conversions of reactions were determined by GC-MS using a Shimadzu GCMS-QP2010 Ulta. Column: SH-Rxi-5Sil MS column, 30.0 m in length, 0.25 mm in diameter, 0.25  $\mu$ m in thickness. GC conditions: Injection temperature, 220 °C; Column temperature program, 30 °C hold for 5 min, followed by a ramp of 5 °C/min to 60 °C then a ramp of 20 °C/min to 300 °C; Column flow, 1.21 mL/min.

**Table S6.** The retention times of GC traces for C-O cleavage products of ethers and alcohols (some compounds have multiple stereoisomers, thus showing more than one peak with the expected molecular mass).

Compound	<b>Retention Time</b>	Compound	<b>Retention Time</b>
OH	11.488 min	$\bigcirc$	4.646 min
A.X	14.064 min		13.255 min (trans) 13.474 min (cis)
ОН	11.058 min	$\bigcirc$	3.135 min
	17.050 min	$\bigcirc$	3.115 min
	17.600 min	$\bigcirc$	3.115 min
ОН	N.D.	$\sim$	7.632 min
ОН	10.453 min		16.365 min

<u> </u>	3.885 min 4.170 min	2.273 min
но	13.134 min	3.934 min
	19.163 min	9.977 min
	14.656 min	9.966 min
₹¢~	4.047 min	12.896 min

**Table S5.** The retention times of GC traces for ester C-O cleavage products (some compounds have multiple stereoisomers, thus showing more than one peak with the expected molecular mass).

Compound	<b>Retention Time</b>	Compound	<b>Retention Time</b>
<sup>1</sup> ×	N.D.		13.265 min (trans) 13.485 min (cis)
	16.569 min	- Martin	13.253 min (trans) 13.475 min (cis)
Û,₀Ĩ	14.157 min	$\bigcirc$	3.140 min
	15.212 min	$\bigcirc$	3.141 min
	15.874 min	$\sim$	7.612 min

16.288 min		9.986 min
14.756 min	HOO	13.538 min

# 8. NMR and MS Spectra of Select Products

lH NMR (500 MHz, Chloroform-d)  $\delta$  1.70 – 1.60 (m, 5H), 1.33 (dddq, J = 14.4, 11.1, 6.6, 3.2 Hz, 1H), 1.27 – 1.17 (m, 2H), 1.16 – 1.07 (m, 1H), 0.93 – 0.82 (m, 5H).

# **Methyl Cyclohexane** (CAS: 82166-21-0). Purfied by silica gel chromatography eluting with pentane as a colorless liquid. <sup>1</sup>H NMR (500 MHz, Chloroform-*d*) $\delta$ 1.70 – 1.60 (m, 5H), 1.33 (dddq, *J* = 14.4, 11.1, 6.6, 3.2 Hz, 1H), 1.27 – 1.17 (m, 2H), 1.16 – 1.07 (m, 1H), 0.93 – 0.82 (m, 5H). GC-MS (positive mode): *m/z* calc'd for C<sub>7</sub>H<sub>14</sub> [M]<sup>+</sup> :98.1, found 98.1.

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**Menthane** (CAS: 99-82-1). Purfied by silica gel chromatography eluting with hexane to get a colorless liquid. <sup>1</sup>H NMR (500 MHz, Chloroform-*d*)  $\delta$  1.72 – 1.65 (m, 4H), 1.53 – 1.42 (m, 1H), 1.41 – 1.35 (m, 2H), 1.28 – 1.21 (m, 1H), 0.98 – 0.93 (m, 2H), 0.92 – 0.88 (m, 1H), 0.87 – 0.83 (m, 9H). GC-MS (positive mode): *m/z* calc'd for C<sub>10</sub>H<sub>20</sub> [M]<sup>+</sup> :140.2, found 140.1.



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**n-Heptane** (CAS: 142-82-5). Purfied by silica gel chromatography eluting with pentane as a colorless liquid. <sup>1</sup>H NMR (500 MHz, Chloroform-*d*)  $\delta$  1.36 – 1.20 (m, 10H), 0.88 (t, *J* = 7.0 Hz, 6H). GC-MS (positive mode): *m*/*z* calc'd for C<sub>2</sub>H<sub>16</sub> [M]<sup>+</sup> :100.1, found 100.1.

H NMR (500 MHz, Chloroform-d) ō 1.36 - 1.20 (m, 10H), 0.88 (r. J= 7.0 Hz, 6H).



**n-Octane** (CAS: 111-65-9). Purfied by silica gel chromatography eluting with pentane as a colorless liquid. <sup>1</sup>H NMR (500 MHz, Chloroform-*d*)  $\delta$  1.33 – 1.24 (m, 12H), 0.88 (t, *J* = 6.9 Hz, 6H). GC-MS (positive mode): *m*/*z* calc'd for C<sub>8</sub>H<sub>18</sub> [M]<sup>+</sup> :114.1, found 114.1.



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**Ethylbenzene** (CAS: 100-41-4). Purfied by silica gel chromatography eluting with hexane/diethyl ether as a colorless liquid. <sup>1</sup>H NMR (500 MHz, Chloroform-*d*)  $\delta$  7.30 (td, *J* = 7.3, 1.3 Hz, 2H), 7.24 – 7.17 (m, 3H), 2.67 (q, *J* = 7.6 Hz, 2H), 1.26 (t, *J* = 7.6 Hz, 3H). HR-MS (ESI, positive mode): *m/z* calc'd for C<sub>8</sub>H<sub>11</sub> [M+H]<sup>+</sup> : 107.0861, found 107.0849.





Hexanoic acid (CAS: 142-62-1). Purfied by silica gel chromatography eluting with ethyl acetate/methanol as a colorless liquid. <sup>1</sup>H NMR (500 MHz, Chloroform-*d*)  $\delta$  11.36 (br, 1H), 2.35 (t, *J* = 7.5 Hz, 2H), 1.67 – 1.60 (m, 2H), 1.37 – 1.28 (m, 4H), 0.93 – 0.87 (m, 3H). HR-MS (ESI, positive mode): *m*/*z* calc'd for C<sub>6</sub>H<sub>13</sub>O<sub>2</sub> [M+H]<sup>+</sup> :117.0916, found 117.0909.

lH NMR (500 MHz, Chloroform-d)  $\delta$ 11.36 (br, 1H), 2.35 (t, J = 7.5 Hz, 2H), 1.67 – 1.60 (m, 2H), 1.37 – 1.28 (m, 4H), 0.93 – 0.87 (m, 3H).

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