Supporting Information

A new superacid hafnium-based metal-organic framework as a highly active heterogeneous catalyst for the synthesis of benzoxazoles under solvent-free condition

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Section S1: Materials and General Methods

Materials.

Methyl 4-iodobenzoate (purity > 97%), 1,4-diethynylbenzene (purity > 96%), copper(I) iodide (purity ≥ 99.5%), 1,3,5-Benzenetricarboxylic acid (H$_3$BTC, purity > 95%), 1,4-benzenedicarboxylic acid (H$_2$BDC, purity > 98%), hafnium chloride (HfCl$_4$, purity >98%), sulfuric acid (H$_2$SO$_4$, purity ≥ 95%), hydrofluoric acid (HF, 48 wt% in water), anhydrous benzene (C$_6$H$_6$, purity > 99%), anhydrous chloroform a with amylenes as stabilizer (CHCl$_3$, purity > 99%), (-)-isopulegol (C$_{10}$H$_{18}$O, purity > 99%), camphene (C$_{10}$H$_{16}$, analytical standard), (R)-(+)limonene (C$_{10}$H$_{16}$, analytical standard), benzaldehyde (purity ≥ 99%), 4-methylbenzaldehyde (purity ≥ 97%), 4-methoxybenzaldehyde (purity ≥ 98%), 4-tert-butylbenzaldehyde (purity ≥ 97%), 4-fluorobenzaldehyde (purity ≥ 98%), 4-chlorobenzaldehyde (purity ≥ 97%), 4-bromobenzaldehyde (purity ≥ 99%), 4-hydroxybenzaldehyde (purity ≥ 98%), anhydrous aluminum chloride (AlCl$_3$, purity ≥ 99%), anhydrous iron(III) chloride (FeCl$_3$, purity ≥ 97%), anhydrous copper(II) acetate (Cu(CH$_3$COO)$_2$, purity ≥ 98%), anhydrous zinc chloride (ZnCl$_2$, purity ≥ ≥97%), HKUST-1 (Basolite C300), MOF-177 (Basolite Z377), and ZIF-8 (Basolite Z1200), and sigmacote® siliconizing reagent for glass and other surfaces were obtained from Sigma-Aldrich Chemical Company.

Zirconium oxychloride octahydrate (ZrOCl$_2$·8H$_2$O, purity ≥ 99.5%), hafnium oxychloride octahydrate (HfOCl$_2$·8H$_2$O, purity ≥ 99.5%) were obtained from Alfa Aesar.

N,N-Dimethylformamide (DMF, purity > 99%), ammonium chloride (NH$_4$Cl, purity 99.5%, bis(triphenylphosphine)palladium dichloride (purity ≥ 99%), potassium hydroxide (purity > 99%), sodium chloride (NaCl, purity ≥ 99%), 2-aminophenol (purity ≥ 99%), 2-amino-4-methylphenol (purity ≥ 97%), 2-amino-4-chlorophenol (purity ≥ 97%), and 2-amino-4-nitrophenol (purity ≥ 99%) were obtained from Acros Organics.

Formic acid (HCOOH, purity > 98%), triethylamine (TEA, purity ≥ 99.5%), methanol (MeOH, purity ≥ 99.8%), and silica gel 230–400 mesh for flash chromatography, TLC plates (silica gel 60 F254), anhydrous 1,4-dioxane (purity ≥ 99.9%), anhydrous ethanol (EtOH, purity ≥ 99%), anhydrous toluene (purity ≥ 99%), anhydrous dichloromethane (CH$_2$Cl$_2$, 99%), anhydrous $n$-butanol (purity ≥ 99.8%), anhydrous tetrahydrofuran (THF, purity ≥ 99.5%), anhydrous ethyl acetate (EtOAc, purity ≥ 99%), acetone, and $n$-hexane (purity ≥ 99.5%) were obtained from Merck.
Deuterated solvents, CDCl$_3$, acetone-$d_6$ and DMSO-$d_6$, were purchased from Cambridge Isotope Laboratories (Andover, MA).

Hammett Indicators: 4-Phenylazoaniline (analytical standard), 4-nitrodiphenylamine (purity ≥ 99%), 9,10-anthraquinone (purity ≥ 97%), 4-fluoronitrobenzene (purity ≥ 99%), 2,4-dichloro-6-nitroaniline (purity > 98%), 2-benzoylnaphthalene (purity ≥ 98%), and 2-bromo-4,6-dinitroaniline (purity ≥ 98.0%) were obtained from Sigma-Aldrich Co. 2,4-dinitrofluorobenzene (purity 98%) was obtained from Acros Co. All chemicals were used without further purification.

**General Methods.**

Single-crystal X-ray diffraction (SXRD) data were collected using synchrotron radiation in beamline 11.3.1 of the Advanced Light Source, Lawrence Berkeley National Laboratory (LBNL). Powder X-ray diffraction (PXRD) patterns were recorded using a D8 Advance diffractometer equipped with a LYNXEYE detector (Bragg-Brentano geometry, Cu Kα radiation $\lambda = 1.54056$ Å. Fourier transform infrared (FT-IR) spectra were measured on a Bruker E400 FT-IR spectrometer using potassium bromide pellets. Scanning electron microscope (SEM) images were obtained using a Hitachi's S-4800 FE-SEM. Transmission Electron Microscopy (TEM) images were performed on a JEOL JEM-2100F. Low-pressure N$_2$ and CO$_2$ adsorption measurements were carried out on a Quantachrome Autosorb iQ volumetric gas adsorption analyzer. A liquid N$_2$ bath was used for measurements at 77 K. Helium was used as estimation of dead space. Ultrahigh-purity-grade N$_2$, and He (99.999% purity) were used throughout adsorption experiments. Solution NMR spectra were acquired on a Bruker Advance-500 MHz NMR spectrometer. For NMR measurements of MOF, 10 mg of MOF sample was digested in a mixture containing 580 μL of DMSO-$d_6$ and 20 μL of hydrofluoric acid (48 wt% in water) and sonicated for 15 min. Carbon, hydrogen, nitrogen and sulfur elemental microanalyses (EA) were performed in the Microanalytical Laboratory of the College of Chemistry at UC Berkeley, using a Perkin Elmer 2400 Series II CHNS elemental analyzer. ICP-MS analyses were performed on a PerkinElmer NexION 350X.
Section S2: Synthesis and Preparation of MOFs
HKUST-1 (Basolite C300), MOF-177 (Basolite Z377), and ZIF-8 (Basolite Z1200) were obtained from Sigma-Aldrich Chemical Co. Before HKUST-1, MOF-177, and ZIF-8 were used as heterogeneous catalysts in the reaction, the materials were activated under vacuum (30 mTorr) for 24 h at 120, 150, 100 °C, respectively.

Microcrystalline powder sample of VNU-11-P. A mixture of H$_3$BTC (2.50 mmol, 537 mg) and HfOCl$_2$·8H$_2$O (7.50 mmol, 3.10 g) were dissolved in DMF/formic acid (160 mL/160 mL) and placed in a 500 mL screw-capped glass jar, which was heated to 120 °C for three days. A white precipitate was collected by filtration and washed three times with 100 mL of fresh DMF and immersed in 100 ml DMF for three days, during which time the DMF was replaced three times per day. The DMF-exchanged compound was filtrated off and immersed in 100 mL of water for three days, during which time the water was replaced three times per day. Water exchanged material was then immersed in 100 mL of anhydrous acetone for three days, during which time the acetone was replaced three times per day. The acetone-exchanged sample was then evacuated at room temperature for 24 h and at 150 °C for 24 h to yield activated sample (Yield: 2.30 g, 74 % based on HfOCl$_2$·8H$_2$O). Digested $^1$H-NMR of activated sample (500 MHz, DMSO-$d_6$, ppm): 8.64 (s, BTC), 8.12 (s, HCOOH), peak area ratio (BTC:HCOOH) = 6.0:5.0. Anal. Calcd for Hf$_6$C$_{23}$H$_{14}$O$_{30}$ = [Hf$_6$O$_5$(OH)$_3$(C$_9$H$_3$O$_6$)$_2$(HCOO)$_5$]: Hf, C, 15.00; H, 0.76%. Found: C, 14.95; H, 0.89%.

Single crystal sample of VNU-11-SC. A mixture of H$_3$BTC (0.0125 mmol, 2.62 mg) and HfOCl$_2$·8H$_2$O (0.0125 mmol, 5.11 mg) were dissolved in DMF/formic acid (6.4 mL/6.4 mL) and placed in a 20 mL screw-capped glass jar, which was heated to 110 °C for seven days. Octahedral colorless crystals were collected and washed three times with 10 mL of fresh DMF. Digested $^1$H-NMR of as-synthesized sample (500 MHz, DMSO-$d_6$, ppm): 8.64 (s, BTC), 8.12 (s, HCOOH), peak area ratio (BTC:HCOOH) = 6.0:5.0. Anal. Calcd for Hf$_6$C$_{23}$H$_{14}$O$_{30}$ = [Hf$_6$O$_5$(OH)$_3$(C$_9$H$_3$O$_6$)$_2$(HCOO)$_5$]: C, 15.00; H, 0.76%. Found: C, 15.07; H, 0.83%.

Microcrystalline powder sample of VNU-11-P-SO$_4$. Activated VNU-11-P microcrystalline powder (200 mg, 0.109 mmol) was immersed in 20 mL of 0.1 M sulfuric acid (2.00 mmol) for 24 h during which time the mixture was stirred about once every two hours. The solid material was thoroughly washed with deionized water (3 x 20 ml per day for three days total), quickly
exchanged with 5 x 20 ml anhydrous acetone. To obtain guest-free material, VNU-11-P-2.5SO₄ was immersed in anhydrous chloroform (3 x 20 ml per day over a total of three days). The solvent exchanged sample was activated under vacuum for 24 h at room temperature and 24 h at 150 °C to get activated VNU-11-P-2.5SO₄ (Yield 195 mg). Digested ¹H-NMR of activated sample (500 MHz, DMSO-d₆, ppm): 8.64 (s, BTC), 8.12 (s, HCOOH), peak area ratio (BTC:HCOOH) = 6.0:0.06. Anal. Calcd for Hf₆C₁₈O₆H₁₁O₃₁S₂.25 = [Hf₆O₅(OH)₂.₉₄(C₉H₅O₆)₂(SO₄)₂.₅(HCOO)₀.₀₆](H₂O): C, 11.56; H, 0.59; S, 4.27%. Found: C, 11.89; H, 0.68; S, 4.05%.

**Single crystal sample of VNU-11-SC-SO₄:** Octahedral colorless crystals VNU-11 were collected and washed three times with 10 mL of fresh DMF and immersed in deionized water (3 x 20 ml per day for three days total). Roughly 50.0 mg VNU-11-SC was immersed in 5 mL of 0.1 M sulfuric acid (2.00 mmol) for 24 h during which time the mixture was stirred about once every two hours. The single crystals was thoroughly washed with deionized water (3 x 20 ml per day for three days total), quickly exchanged with 5 x 20 ml anhydrous acetone. To obtain guest-free material, VNU-11-SC-2.3SO₄ was immersed in anhydrous chloroform (3 x 20 ml per day over a total of 3 days). The solvent exchanged crystals was activated under vacuum for 24 h at room temperature and 24 h at 150 °C to get activated VNU-11-SC-2.3SO₄ (Yield 48.5 mg). Digested ¹H-NMR of activated sample (500 MHz, DMSO-d₆, ppm): 8.64 (s, BTC), 8.12 (s, HCOOH), peak area ratio (BTC:HCOOH) = 6.0:0.08. Anal. Calcd for Hf₆C₁₈H₁₁O₃₁S₂.₃ S = [Hf₆O₅.₄(OH)₂.₅₂(C₉H₅O₆)₂(SO₄)₂.₃(HCOO)₀.₀₈](H₂O): C, 10.95; H, 1.25; S, 3.72%. Found: C, 11.20; H, 1.18; S, 4.04%.

**Microcrystalline powder sample of MOF-808-P:** Synthesis of MOF-808-P was slightly modified from reported literature.¹ A mixture of H₃BTC (2.50 mmol, 537 mg) and ZrOCl₂·8H₂O (7.50 mmol, 2.42 g) were dissolved in DMF/formic acid (160 mL/160 mL) and placed in a 500 ml screw-capped glass jar, which was heated to 120 °C for three days. A white precipitate was collected by filtration and washed three times with 100 mL of fresh DMF and immersed in 100 ml DMF for three days, during which time the DMF was replaced three times per day. The DMF-exchanged compound was filtrated off and immersed in 100 mL of water for three days, during which time the water was replaced three times per day. Water exchanged material was then immersed in 100 mL of anhydrous acetone for three days, during which time the acetone
was replaced three times per day. The acetone-exchanged sample was then evacuated at room temperature for 24 h and at 150 °C for 24 h to yield activated sample.

**Microcrystalline powder MOF-808-P-2.5SO$_4$:** Synthesis of MOF-808-P-2.5SO$_4$ was slightly modified from reported literature. Activated MOF-808-P microcrystalline powder (200 mg, 0.151 mmol) was immersed in 20 mL of 0.1 M sulfuric acid (2.00 mmol) for 24 h during which time the mixture was stirred about once every two hours. The solid material was thoroughly washed with deionized water (3 x 20 ml per day for three days total), quickly exchanged with 5 x 20 ml anhydrous acetone. To obtain guest-free material, MOF-808-P-2.5SO$_4$ was immersed in anhydrous chloroform (3 x 20 ml per day over a total of 3 days). The solvent exchanged sample was activated under vacuum for 24 h at room temperature and 24 h at 150 °C to get MOF-808-P-2.5SO$_4$ (Yield 195 mg).

**Microcrystalline powder sample of UiO-66.** Synthesis of UiO-66 was modified from reported literature. ZrOCl$_2$·8H$_2$O (109 mg, 0.340 mmol) and 1,4-benzenedicarboxylic acid (56.5 mg, 0.340 mmol) in 40 mL solvent mixture of DMF and acetic acid (v/v = 39:1) in 100-mL capped bottle was heated in an oven at 120 °C for 24 h under static conditions. After cooling the vial to room temperature, the white precipitate product, UiO-66, was separated from the mother liquor via centrifugation. The as-synthesized sample of UiO-66 was washed with 10 mL of DMF three times per day over the course of three days. Then UiO-66 was immersed in 10 mL chloroform, which was replaced three times per day for a total of three days. After the solvent-exchange process was completed, UiO-66 was activated under reduced pressure at 120 °C for 24 h.

**Preparation of 1,4-bis(2-[4-carboxyphenyl]ethynyl)benzene (H$_2$CPEB).** 1,4-Bis(2-[4-carboxyphenyl]ethynyl)benzene was prepared following a literature procedure. The Sonogashira coupling of methyl 4-iodobenzoate (0.524 g, 2.00 mmol) and 1,4-diethynylbenzene (0.126 g, 1.00 mmol) was catalyzed by bis(triphenylphosphine)palladium dichloride (35.2 mg, 0.0500 mmol) and copper(I) iodide (2.0 mg, 10 µmol) in 10 mL mixture of triethylamine and toluene (v/v = 1:1) under nitrogen atmosphere. The solution was stirred at room temperature for 24 h. After the reaction, the solid was filtered, thoroughly washed with hexane, a saturated solution of NH$_4$Cl, and a saturated solution of NaCl, and dried under vacuum to afford pink product. Then the precursor (0.985 g, 0.250 mmol) was hydrolyzed by potassium hydroxide (0.420 g, 7.50 mmol) in mixture of methanol (3 mL), THF (3 mL) and water (1.5 mL) at room temperature for
12 h. After 12 h, the solvents were evaporated under reduced pressure and the remaining solution was added dropwise of concentrated HCl. The final product was recovered as a yellow powder, which was thoroughly washed with water and dried at 80 °C under vacuum overnight. Yield: 0.0780 g.

**Microcrystalline powder sample of VNU-1.** VNU-1 microcrystalline powder sample was prepared following the reported procedure. ZrOCl₂·8H₂O (10.9 mg, 0.0340 mmol) and H₂CPEB (12.4 mg, 0.0340 mmol) were dissolved in a solvent mixture of DMF (3.86 mL), acetic acid (0.042 mL), and water (0.10 mL) in a 10 mL capped vial. The solution was subsequently heated at 120 °C for 1 day in an isothermal oven to yield yellow precipitate. After cooling the vial to room temperature, the yellow precipitate product, VNU-1, was separated from the mother liquor via centrifugation. The as-synthesized sample of VNU-1 was washed with 10 mL of DMF three times per day over the course of three days. Following this, VNU-1 was immersed in 10 mL chloroform, which was replaced three times per day for a total of three days. After the solvent-exchange process was completed, VNU-1 was activated under reduced pressure at 120 °C for 24 h.

**Microcrystalline powder sample of VNU-2.** VNU-2 microcrystalline powder sample was prepared following the reported procedure. HfCl₄ (10.9 mg, 0.0340 mmol) and H₂CPEB (12.4 mg, 0.0340 mmol) were dissolved in a solvent mixture of DMF (3.80 mL), acetic acid (0.10 mL), and water (0.10 mL) in a 10 mL capped vial. The solution was subsequently heated at 120 °C for 3 days in an isothermal oven to yield light yellow microcrystalline powder. After cooling the vial to room temperature, the light yellow solid product, VNU-2, was separated from the mother liquor via centrifugation. The as-synthesized sample of VNU-2 was washed with 10 mL of DMF three times per day over the course of three days. Following this, VNU-2 was immersed in 10 mL chloroform, which was replaced three times per day for a total of three days. After the solvent-exchange process was completed, VNU-2 was activated under reduced pressure at 120 °C for 24 h.
Fig. S1. PXRD analysis of VNU-11-P. The calculated pattern from single crystal data (black) is compared to the experimental patterns from the as-synthesized powder sample (blue) and activated powder sample (red).

Fig. S2. PXRD analysis of VNU-11-P-SO$_4$ . The calculated pattern from single crystal data (black) is compared to the experimental patterns from the as-synthesized powder sample (blue) and activated powder sample (red).
**Fig. S3.** PXRD analysis of MOF-808-P. The calculated pattern from single crystal data (black) is compared to the experimental patterns from the as-synthesized powder sample (blue) and activated powder sample (red).

**Fig. S4.** PXRD analysis of MOF-808-P-2.5SO₄. The calculated pattern from single crystal data (black) is compared to the experimental patterns from the as-synthesized powder sample (blue) and activated powder sample (red).
**Fig. S5.** PXRD analysis of UiO-66. The calculated pattern from single crystal data (black) is compared to the experimental patterns from the as-synthesized powder sample (blue) and activated powder sample (red).

**Fig. S6.** PXRD analysis of VNU-1. The calculated pattern from single crystal data (black) is compared to the experimental patterns from the as-synthesized powder sample (blue) and activated powder sample (red).
**Fig. S7.** PXRD analysis of VNU-2. The calculated pattern from single crystal data (black) is compared to the experimental patterns from the as-synthesized powder sample (blue) and activated powder sample (red).
**Section S3: Single Crystal X-ray Diffraction Analyses**

The X-ray diffraction data for VNU-11 and VNU-11-SO$_4$ was collected on a Bruker D8 Venture diffractometer outfitted with a PHOTON-100 CMOS detector using monochromatic microfocus MoKα radiation ($\lambda = 0.71073$ Å) that was operated at 50 kV and 1.0 mA. The data was collected at 100 K by chilled nitrogen flow controlled by a Kryoflex II system. Unit cell determination was performed in the Bruker SMART APEX II software suite. The data sets were reduced and a multi-scan spherical absorption correction was implemented in the SCALE interface. The structures were solved with direct methods and refined by the full-matrix least-squares method in the SHELXL-97 program package. Once the framework atoms were located in the difference Fourier maps, the SQUEEZE routine in PLATON was performed to remove scattering from disordered guest molecules residing in the pores. The detail of single crystal refinement for VNU-11 and VNU-11-SO$_4$ was found in Table S1 and Table S2. VNU-11 and VNU-11-SO$_4$ contain more void space, high electron density atoms, and high vibration atoms (SO$_4^{2-}$), leading to obtain low resolution to fully refinement. These factors cause few level A and B alerts in the check cif files, which are fully explained in the CIF file. CCDC numbers for VNU-11 and VNU-11-SO4 are 1560539 and 1560540, respectively.

**Table S1.** Crystal structure data and refinement of VNU-11 single crystal

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<td>Wavelength</td>
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<td>Crystal system</td>
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<td>Space group</td>
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\[ \alpha = 90^\circ \]
\[ \beta = 90^\circ \]
\[ \gamma = 90^\circ \]
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<td>Final $R$ indices [$I &gt; 2\sigma(I)$]</td>
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<td>$R$ indices (all data)</td>
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<td>Largest diff. peak and hole</td>
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Fig. S8. Fragment unit of VNU-11 drawn by ORTEP with thermal ellipsoids style at 50% probability.
Table S2. Crystal structure data and refinement of VNU-11-SO$_4$ single crystal

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<tr>
<td>Goodness-of-fit on $F^2$</td>
<td>1.383</td>
</tr>
<tr>
<td>Final $R$ indices [$I &gt; 2\sigma(I)$]</td>
<td>$R_1 = 0.062$, $wR_2 = 0.1518$</td>
</tr>
<tr>
<td>$R$ indices (all data)</td>
<td>$R_1 = 0.0491$, $wR_2 = 0.1461$</td>
</tr>
<tr>
<td>Largest diff. peak and hole</td>
<td>2.007 and -1.498 e·Å⁻³</td>
</tr>
</tbody>
</table>

**Fig. S9.** Fragment unit of VNU-11-SO₄ drawn by ORTEP with thermal ellipsoids style at 50% probability.
Section S4: N$_2$ Adsorption Measurements

Fig. S10. N$_2$ isotherm at 77 K for activated VNU-11-P (blue) and VNU-11-P-SO$_4$ (red). Closed and open circles represent the adsorption and desorption branches, respectively.

Section S5: Infrared Spectra

Fig. S11. Infrared spectra of activated VNU-11-P (blue) and VNU-11-P-SO$_4$ (red) in dry KBr.
Section S6: Hammett Indicator Tests

Hammett Indicators solutions was prepared following the reported procedure. In an inert atmosphere, 5.0 mg of activated VNU-11-P-SO$_4$ was added in Hammett indicators solutions (Table S3), which were prepared by dissolving 1.0 mmol of indicators in 5 mL anhydrous benzene. The mixture was shaken for each 30 min, after 4 hours the color of the solid was then recorded (Table S3)

Table S3. Hammett Indicator tests of VNU-11-P-SO$_4$.

<table>
<thead>
<tr>
<th>Indicators</th>
<th>Color</th>
<th>pK$_a$</th>
<th>Hammett Indicator Tests</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Acid Form</td>
<td>Base Form</td>
<td>VNU-11-P</td>
</tr>
<tr>
<td>4-Phenylazoaniline</td>
<td>Red</td>
<td>Orange</td>
<td>+2.8</td>
</tr>
<tr>
<td>4-Nitrodiphenylamine</td>
<td>Red</td>
<td>Yellow</td>
<td>-2.4</td>
</tr>
<tr>
<td>2,4-Dichloro-6-nitroaniline</td>
<td>Red</td>
<td>Yellow</td>
<td>-3.2</td>
</tr>
<tr>
<td>2-Benzoylnaphthalene</td>
<td>Yellow</td>
<td>Colorless</td>
<td>-5.9</td>
</tr>
<tr>
<td>2-Bromo-4,6-dinitroaniline</td>
<td>Red</td>
<td>Yellow</td>
<td>-6.6</td>
</tr>
<tr>
<td>Anthraquinone</td>
<td>Yellow</td>
<td>Colorless</td>
<td>-8.1</td>
</tr>
<tr>
<td>4-Fluoronitrobenzene</td>
<td>Yellow</td>
<td>Colorless</td>
<td>-12.4</td>
</tr>
<tr>
<td>2,4-Dinitrofluorobenzene</td>
<td>Yellow</td>
<td>Colorless</td>
<td>-14.5</td>
</tr>
</tbody>
</table>

Results of Hammett indicator tests are denoted as color change observed (+) and color change not observed (-).
Section S7: Scanning Electron Microscopy and Energy-Dispersive X-ray Spectroscopy

Fig. S12. Scanning electron microscopy (SEM) image and Energy-dispersive X-ray (EDX) spectrum of VNU-11-P.

Fig. S13. Scanning electron microscopy (SEM) image and Energy-dispersive X-ray (EDX) spectrum of VNU-11-P-SO$_4$. 
Section S8: Transmission Electron Microscopy

Fig. S14. Transmission electron microscopy (TEM) images of VNU-11-P.

Fig. S15. Transmission electron microscopy (TEM) images of VNU-11-P-SO₄.
Section S9: Catalytic study

An 2-aminophenol (0.119 g, 1 mmol) and benzaldehyde (0.106 g, 1 mmol) were added into a flask pre-charged with VNU-11-P-SO$_4$(0.018 g, 0.01 mmol). The reaction was then stirred under solvent-free condition at 140 °C for 6 hour and monitored by TLC. After completion of reaction, the reaction mixture was dissolved in 5 mL acetone, and VNU-11-P-SO$_4$ catalyst was separated out by centrifugation and washed further with anhydrous acetone (2 × 10 mL) and ethanol (2 × 10 mL). The combined organic layers were evaporated under reduced pressure to obtain the crude product. The crude product was purified by silica gel column chromatography (90:10 acetone/petroleum ether) in order to afford the pure product, which was confirmed via FTIR, $^1$H-NMR, $^{13}$C-NMR, and GC-MS.

Optimization of Catalytic Reaction Conditions

![Reaction Diagram]

Table S4. Optimization of temperature on the synthesis of 2-phenylbenzoxazole.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Temperature (°C)</th>
<th>Isolated yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>80</td>
<td>25</td>
</tr>
<tr>
<td>2</td>
<td>100</td>
<td>29</td>
</tr>
<tr>
<td>3</td>
<td>120</td>
<td>62</td>
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<tr>
<td>4</td>
<td>130</td>
<td>78</td>
</tr>
<tr>
<td>5</td>
<td>140</td>
<td>99</td>
</tr>
</tbody>
</table>
Table S5. Optimization of reaction time on the synthesis of 2-phenylbenzoxazole.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Time (h)</th>
<th>Isolated yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>19</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>40</td>
</tr>
<tr>
<td>3</td>
<td>3</td>
<td>57</td>
</tr>
<tr>
<td>4</td>
<td>4</td>
<td>71</td>
</tr>
<tr>
<td>5</td>
<td>5</td>
<td>83</td>
</tr>
<tr>
<td>6</td>
<td>6</td>
<td>99</td>
</tr>
<tr>
<td>7</td>
<td>7</td>
<td>99</td>
</tr>
</tbody>
</table>

Table S6. Optimization of catalyst ratio on the synthesis of 2-phenylbenzoxazole.

<table>
<thead>
<tr>
<th>Entry</th>
<th>VNU-11-P-SO₄ (mol%)</th>
<th>Isolated yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.25</td>
<td>50</td>
</tr>
<tr>
<td>2</td>
<td>0.50</td>
<td>62</td>
</tr>
<tr>
<td>3</td>
<td>0.75</td>
<td>76</td>
</tr>
<tr>
<td>4</td>
<td>1.00</td>
<td>99</td>
</tr>
<tr>
<td>5</td>
<td>1.25</td>
<td>98</td>
</tr>
<tr>
<td>6</td>
<td>1.50</td>
<td>99</td>
</tr>
</tbody>
</table>

*Reaction conditions: A mixture of 2-aminophenol (1 mmol), benzaldehyde (1 mmol), and VNU-11-P-SO₄ was stirred at 140 °C for 6 h. Yield of 2-phenylbenzoxazole was isolated by column chromatography (acetone/hexane).
Table S7. Optimization of solvents condition on the synthesis of 2-phenylbenzoxazole.

<table>
<thead>
<tr>
<th>Entry&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Type of solvent</th>
<th>Solvents</th>
<th>Isolated yield (%)&lt;sup&gt;b&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Polar protic</td>
<td>Ethanol</td>
<td>85</td>
</tr>
<tr>
<td>2</td>
<td>Polar protic</td>
<td>1-Butanol</td>
<td>62</td>
</tr>
<tr>
<td>3</td>
<td>Polar aprotic</td>
<td>DMF</td>
<td>71</td>
</tr>
<tr>
<td>4</td>
<td>Polar aprotic</td>
<td>THF</td>
<td>37</td>
</tr>
<tr>
<td>5</td>
<td>Polar aprotic</td>
<td>Dichloromethane</td>
<td>40</td>
</tr>
<tr>
<td>6</td>
<td>Polar aprotic</td>
<td>Toluene</td>
<td>49</td>
</tr>
<tr>
<td>7</td>
<td>Polar aprotic</td>
<td>1,4-Dioxane</td>
<td>95</td>
</tr>
<tr>
<td>8</td>
<td>Free-solvent</td>
<td>-</td>
<td>99</td>
</tr>
</tbody>
</table>

<sup>a</sup>Reaction conditions: A mixture of 2-aminophenol (1 mmol), benzaldehyde (1 mmol), and VNU-11-P-SO₄ (0.01 mmol) was stirred at 140 °C for 6 h. <sup>b</sup>Yield of 2-phenylbenzoxazole was isolated by column chromatography (acetone/hexane).
Leaching test for VNU-11-P-SO$_4$

<table>
<thead>
<tr>
<th>Reaction time</th>
<th>2.0 h</th>
<th>4.0 h</th>
<th>6.0 h</th>
</tr>
</thead>
<tbody>
<tr>
<td>Isolated yield (%)</td>
<td>40</td>
<td>71</td>
<td>99</td>
</tr>
<tr>
<td>Hf$^{4+}$ leaching (ppb)</td>
<td>28</td>
<td>44</td>
<td>48</td>
</tr>
</tbody>
</table>

Fig. S16. Leaching test for VNU-11-P-SO$_4$-catalyzed synthesis of 2-phenylbenzoxazole: after 3 h, the reaction mixture was split in two parts and the catalyst was withdrawn from one sample (red hollow).
Table S8. Comparison of catalysts on the synthesis of 2-phenylbenzoxazole.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Type of catalysts</th>
<th>Catalyst</th>
<th>Chemical formula</th>
<th>Isolated yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Free-catalyst</td>
<td>-</td>
<td>-</td>
<td>5</td>
</tr>
<tr>
<td>2</td>
<td>VNU-11-P-SO₄</td>
<td>Hf₆O₅(OH)₃(BTC)₂(SO₄)₂.₅&lt;sup&gt;a&lt;/sup&gt;</td>
<td>99</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>VNU-11-P</td>
<td>Hf₆O₅(OH)₃(BTC)₂(HCOO)₅</td>
<td>78</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>VNU-1</td>
<td>Zr₆O₄(OH)₄(CPEB)&lt;sub&gt;b&lt;/sub&gt;</td>
<td>68</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>VNU-2</td>
<td>Hf₆O₄(OH)₄(CPEB)&lt;sub&gt;b&lt;/sub&gt;</td>
<td>69</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>MOFs</td>
<td>UiO-66</td>
<td>Zr₆O₄(OH)₄(BDC)&lt;sub&gt;c&lt;/sub&gt;</td>
<td>49</td>
</tr>
<tr>
<td>7</td>
<td>MOF-808-2.5SO₄</td>
<td>Zr₆O₅(OH)₃(BTC)₂(SO₄)₂.₅</td>
<td>83</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>MOF-808-P</td>
<td>Zr₆O₅(OH)₃(BTC)₂(HCOO)₅</td>
<td>79</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>MOF-177</td>
<td>Zn₄O(BTB)&lt;sub&gt;d&lt;/sub&gt;</td>
<td>63</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>HKUST-1</td>
<td>Cu₃(BTC)&lt;sub&gt;2&lt;/sub&gt;</td>
<td>63</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>ZIF-8</td>
<td>Zn(mIm)&lt;sub&gt;2&lt;/sub&gt;&lt;sup&gt;e&lt;/sup&gt;</td>
<td>34</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>Metal salts</td>
<td>Aluminium chloride</td>
<td>AlCl₃</td>
<td>53</td>
</tr>
<tr>
<td>13</td>
<td>Iron(III) chloride</td>
<td>FeCl₃</td>
<td>41</td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>Zinc chloride</td>
<td>ZnCl₂</td>
<td>51</td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>Copper acetate</td>
<td>Cu(CH₃COO)&lt;sub&gt;2&lt;/sub&gt;</td>
<td>36</td>
<td></td>
</tr>
<tr>
<td>16</td>
<td>Hafnium chloride</td>
<td>HfCl₄</td>
<td>12</td>
<td></td>
</tr>
<tr>
<td>17</td>
<td>Sulfuric acid</td>
<td>H₂SO₄</td>
<td>35</td>
<td></td>
</tr>
<tr>
<td>18</td>
<td>Hydrochloric acid</td>
<td>HCl</td>
<td>22</td>
<td></td>
</tr>
<tr>
<td>19</td>
<td>Phosphoric acid</td>
<td>H₃PO₄</td>
<td>25</td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>Trifluoroacetic acid</td>
<td>CF₃COOH</td>
<td>33</td>
<td></td>
</tr>
<tr>
<td>21</td>
<td>Triflic acid</td>
<td>TsOH</td>
<td>44</td>
<td></td>
</tr>
</tbody>
</table>

<sup>a</sup>BTC = 1,3,5-benzenetricarboxylic; <sup>b</sup>CPEB = 1,4-bis(2-[4-carboxyphenyl]ethynyl)benzene; <sup>c</sup>BDC = 1,4-benzenedicarboxylate; <sup>d</sup>BTB = benzene-1,3,5-tribenzoate; <sup>e</sup>mIm = N-methylimidazolate.
Recyclability study

For the recycling experiment, the recovered catalyst was washed with anhydrous acetone (3 × 5 mL) and ethanol (3 × 5 mL) before being isolated by centrifugation. The catalyst was then dried under reduced pressure and re-applied to the next cycle.

**Fig. S17.** The recycling experiments of VNU-11-P-SO₄-catalyzed synthesis of 2-phenylbenzoxazole over five cycles.

**Fig. S18.** Infrared spectra of VNU-11-P-SO₄ before (blue) and after (red) synthesis of 2-phenylbenzoxazole.
**Fig. S19.** PXRD analysis of VNU-11-P-SO$_4$ before (blue) and after (red) synthesis of 2-phenylbenzoxazole in comparison to the simulated pattern.

**Fig. S20.** Scanning electron microscopy (SEM) image and Energy-Dispersive X-ray (EDX) spectrum of VNU-11-P-SO$_4$ after synthesis of 2-phenylbenzoxazole.
**Fig. S21.** Transmission electron microscopy (TEM) images of VNU-11-P-SO$_4$ after synthesis of 2-phenylbenzoxazole.
Table S9. The solvent-free synthesis of benzoxazoles from 2-aminophenols and arylaldehydes catalyzed by VNU-11-P-SO$_4$ at 140 °C.

An 2-aminophenol (0.119 g, 1 mmol) and a benzaldehyde derivative (0.106 g, 1 mmol) were added into a flask pre-charged with VNU-11-P-SO$_4$ (0.018 g, 0.01 mmol). The reaction was then stirred under solvent-free conditions at 140 °C for 6-7 hours and monitored by TLC. After completion of reaction, the reaction mixture was dissolved in 5 mL acetone, and VNU-11-P-SO$_4$ catalyst was separated out by centrifugation and washed further with acetone (2 × 10 mL) and ethanol (2 × 10 mL). The combined organic layers were evaporated under reduced pressure to obtain the crude product. The crude product was purified by silica gel column chromatography (90:10 acetone/petroleum ether) in order to afford the pure product, which was confirmed via FTIR, $^1$H-NMR, $^{13}$C-NMR, and GC-MS.

<table>
<thead>
<tr>
<th>Entry</th>
<th>2-Aminophenol</th>
<th>Benzaldehyde</th>
<th>Products</th>
<th>Conditions</th>
<th>Isolated yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>OH NH$_2$</td>
<td>CHO</td>
<td><img src="image1" alt="Structure1" /></td>
<td>140 °C 6 h</td>
<td>95</td>
</tr>
<tr>
<td>2</td>
<td>OH NH$_2$</td>
<td>CHO</td>
<td><img src="image2" alt="Structure2" /></td>
<td>140 °C 6 h 30 m</td>
<td>91</td>
</tr>
<tr>
<td>3</td>
<td>OH NH$_2$</td>
<td>CHO CH$_3$</td>
<td><img src="image3" alt="Structure3" /></td>
<td>140 °C 6 h</td>
<td>90</td>
</tr>
<tr>
<td>4</td>
<td>OH NH$_2$</td>
<td>CHO OCH$_3$</td>
<td><img src="image4" alt="Structure4" /></td>
<td>140 °C 6 h</td>
<td>88</td>
</tr>
</tbody>
</table>
5  

\[
\begin{array}{c}
\text{OH} \\
\text{NH}_2 \\
\text{CHO} \\
\text{Cl} \\
\end{array}
\quad
\begin{array}{c}
\text{Cl} \\
\text{OH} \\
\text{NH}_2 \\
\text{CHO} \\
\end{array}
\quad
\begin{array}{c}
\text{N} \\
\text{O} \\
\text{Cl} \\
\end{array}
\quad
140 \text{ °C} \\
7 \text{ h} \\
85
\end{array}
\]

6  

\[
\begin{array}{c}
\text{OH} \\
\text{NH}_2 \\
\text{CHO} \\
\text{NO}_2 \\
\end{array}
\quad
\begin{array}{c}
\text{NO}_2 \\
\text{OH} \\
\text{NH}_2 \\
\text{CHO} \\
\end{array}
\quad
\begin{array}{c}
\text{N} \\
\text{O} \\
\text{Cl} \\
\end{array}
\quad
140 \text{ °C} \\
5.5 \text{ h} \\
89
\end{array}
\]

7  

\[
\begin{array}{c}
\text{OH} \\
\text{NH}_2 \\
\text{CHO} \\
\text{F} \\
\end{array}
\quad
\begin{array}{c}
\text{F} \\
\text{OH} \\
\text{NH}_2 \\
\text{CHO} \\
\end{array}
\quad
\begin{array}{c}
\text{N} \\
\text{O} \\
\text{F} \\
\end{array}
\quad
140 \text{ °C} \\
5.5 \text{ h} \\
87
\end{array}
\]

8  

\[
\begin{array}{c}
\text{OH} \\
\text{NH}_2 \\
\text{CHO} \\
\text{F} \\
\end{array}
\quad
\begin{array}{c}
\text{F} \\
\text{OH} \\
\text{NH}_2 \\
\text{CHO} \\
\end{array}
\quad
\begin{array}{c}
\text{N} \\
\text{O} \\
\text{F} \\
\end{array}
\quad
140 \text{ °C} \\
5 \text{ h} \\
90
\end{array}
\]

9  

\[
\begin{array}{c}
\text{OH} \\
\text{NH}_2 \\
\text{CHO} \\
\text{F} \\
\end{array}
\quad
\begin{array}{c}
\text{F} \\
\text{OH} \\
\text{NH}_2 \\
\text{CHO} \\
\end{array}
\quad
\begin{array}{c}
\text{N} \\
\text{O} \\
\text{F} \\
\end{array}
\quad
140 \text{ °C} \\
5 \text{ h} \\
92
\end{array}
\]

10  

\[
\begin{array}{c}
\text{OH} \\
\text{NH}_2 \\
\text{CHO} \\
\text{H}_3 \\
\end{array}
\quad
\begin{array}{c}
\text{H}_3 \\
\text{OH} \\
\text{NH}_2 \\
\text{CHO} \\
\end{array}
\quad
\begin{array}{c}
\text{N} \\
\text{O} \\
\text{H}_3 \\
\end{array}
\quad
140 \text{ °C} \\
5 \text{ h} \\
87
\end{array}
\]

11  

\[
\begin{array}{c}
\text{OH} \\
\text{NH}_2 \\
\text{CHO} \\
\text{H}_3 \\
\end{array}
\quad
\begin{array}{c}
\text{H}_3 \\
\text{OH} \\
\text{NH}_2 \\
\text{CHO} \\
\end{array}
\quad
\begin{array}{c}
\text{N} \\
\text{O} \\
\text{H}_3 \\
\end{array}
\quad
140 \text{ °C} \\
6.5 \text{ h} \\
90
\end{array}
\]

12  

\[
\begin{array}{c}
\text{OH} \\
\text{NH}_2 \\
\text{CHO} \\
\text{CH}_3 \\
\end{array}
\quad
\begin{array}{c}
\text{CH}_3 \\
\text{OH} \\
\text{NH}_2 \\
\text{CHO} \\
\end{array}
\quad
\begin{array}{c}
\text{N} \\
\text{O} \\
\text{CH}_3 \\
\end{array}
\quad
140 \text{ °C} \\
5.5 \text{ h} \\
92
\end{array}
\]

13  

\[
\begin{array}{c}
\text{OH} \\
\text{NH}_2 \\
\text{CHO} \\
\text{OCH}_3 \\
\end{array}
\quad
\begin{array}{c}
\text{OCH}_3 \\
\text{OH} \\
\text{NH}_2 \\
\text{CHO} \\
\end{array}
\quad
\begin{array}{c}
\text{N} \\
\text{O} \\
\text{OCH}_3 \\
\end{array}
\quad
140 \text{ °C} \\
5.5 \text{ h} \\
85
\end{array}
\]
<table>
<thead>
<tr>
<th></th>
<th>Structure 1</th>
<th>Structure 2</th>
<th>Reaction Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>14</td>
<td>OH-(\text{NH}_2)-(\text{NO}_2) CHO</td>
<td>(\text{O}_2\text{N}-\text{N}-\text{O})</td>
<td>140 °C 6 h 90</td>
</tr>
<tr>
<td>15</td>
<td>OH-(\text{NH}_2)-(\text{NO}_2) CHO</td>
<td>(\text{O}_2\text{N}-\text{N}-\text{O})</td>
<td>140 °C 6.5 h 87</td>
</tr>
<tr>
<td>16</td>
<td>OH-(\text{NH}_2)-(\text{NO}_2) CHO</td>
<td>(\text{O}_2\text{N}-\text{N}-\text{O})</td>
<td>140 °C 6 h 87</td>
</tr>
<tr>
<td>17</td>
<td>OH-(\text{NH}_2)-(\text{NO}_2) CHO</td>
<td>(\text{O}_2\text{N}-\text{N}-\text{O})</td>
<td>140 °C 5 h 91</td>
</tr>
<tr>
<td>18</td>
<td>OH-(\text{NH}_2)-Cl CHO</td>
<td>(\text{Cl}-\text{N}-\text{O})</td>
<td>140 °C 6 h 90</td>
</tr>
<tr>
<td>19</td>
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<td>(\text{Cl}-\text{N}-\text{O})</td>
<td>140 °C 6 h 95</td>
</tr>
<tr>
<td>20</td>
<td>OH-(\text{NH}_2)-Cl CHO</td>
<td>(\text{Cl}-\text{N}-\text{O})</td>
<td>140 °C 5 h 86</td>
</tr>
<tr>
<td>21</td>
<td>OH-(\text{NH}_2)-Cl CHO</td>
<td>(\text{Cl}-\text{N}-\text{O})</td>
<td>140 °C 5 h 85</td>
</tr>
</tbody>
</table>
Section S10: Characterization of 2-Aryl Substituted Benzoxazoles

2-Phenylbenzoxazole

Melting point: 102-103.5 ºC
FT-IR (KBr, 4000-400 cm⁻¹): 3059, 2925, 2854, 1775, 1615, 1551, 1475, 1448, 1285, 1240.
¹H NMR (500 MHz, CDCl₃) δ 8.31-8.22 (m, 2H), 7.82-7.75 (m, 1H), 7.61-7.56 (m, 1H), 7.55-7.50 (m, 3H), 7.40-7.33 (m, 2H).
¹³C NMR (125 MHz, CDCl₃) δ 163.2, 150.9, 142.2, 131.7, 129.0, 127.8, 127.3, 125.3, 124.7, 120.1, 110.7.

2-(4-tert-Butylphenyl)benzoxazole

Melting point: 107-108 ºC
FT-IR (KBr, 4000-400 cm⁻¹): 3059, 2927, 1728, 1547, 1452, 1429, 1287, 1239.
¹H NMR (500 MHz, CDCl₃) δ 8.21-8.16 (m, 2H), 7.75-7.78 (m, 1H), 7.60-7.56 (m, 1H), 7.56-7.54 (m, 2H), 7.37-7.32 (m, 2H), 1.38 (s, 9H).
¹³C NMR (125 MHz, CDCl₃) δ 163.4, 155.4, 150.8, 142.1, 127.7, 126.1, 125.1, 124.7, 124.4, 120.0, 110.7, 35.2, 31.3.

2-(p-Tolyl)benzoxazole

Melting point: 113-114.5 ºC
FT-IR (KBr, 4000-400 cm⁻¹): 3056, 2920, 2854, 1728, 1620, 1554, 1499, 1450, 1242.
¹H NMR (500 MHz, CDCl₃) δ 8.17-8.13 (m, 2H), 7.74-7.77 (m, 1H), 7.50-7.58 (m, 1H), 7.35-7.31 (m, 4H), 2.44 (s, 3H).
¹³C NMR (125 MHz, CDCl₃) δ 163.5, 150.8, 142.3, 142.2, 129.8, 127.8, 125.1, 124.7, 124.5, 120.0, 110.6, 21.8.
2-(4-Methoxyphenyl)benzoxazole

![Chemical structure of 2-(4-Methoxyphenyl)benzoxazole](image)

Melting point: 103-104.5 °C

FT-IR (KBr, 4000-400 cm\(^{-1}\)): 3050, 2924, 2849, 1615, 1501, 1450, 1420, 1244.

\(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 8.23-8.17 (m, 2H), 7.75-7.73 (m, 1H), 7.54-7.56 (m, 1H), 7.35-7.29 (m, 2H), 7.05-7.01 (m, 2H), 3.89 (s, 3H).

\(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 163.3, 162.6, 150.8, 142.1, 129.7, 124.8, 124.7, 119.7, 119.7, 114.6, 110.6, 55.6.

2-(4-Chlorophenyl)benzoxazole

![Chemical structure of 2-(4-Chlorophenyl)benzoxazole](image)

Melting point: 148-150 °C

FT-IR (KBr, 4000-400 cm\(^{-1}\)): 3067, 2922, 1725, 1607, 1451, 1428, 1237.

\(^1\)H NMR (500 MHz, CD\(_3\)CO) \(\delta\) 8.26-8.22 (m, 2H), 7.77-7.75 (m, 1H), 7.70-7.69 (m, 1H), 7.65-7.62 (m, 2H), 7.42 (pd, \(J = 7.5, 2.0\) Hz, 2H).

\(^{13}\)C NMR (125 MHz, CD\(_3\)CO) \(\delta\) 161.7, 150.8, 142.1, 137.2, 129.3, 129.0, 125.9, 125.6, 124.9, 120.0, 110.7.

2-(4-Nitrophenyl)benzoxazole

![Chemical structure of 2-(4-Nitrophenyl)benzoxazole](image)

Melting point: 156-157 °C

FT-IR (KBr, 4000-400 cm\(^{-1}\)): 2925, 2854, 1678, 1610, 1534, 1449, 1237.

\(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 8.15 (dd, \(J = 8.0, 1.0\) Hz, 1H), 7.89 (dd, \(J = 8.0, 1.0\) Hz, 1H), 7.83-7.80 (m, 1H), 7.74 (td, \(J = 8.0, 1.0\) Hz, 1H), 7.69 (td, \(J = 8.0, 1.0\) Hz, 1H), 7.59-7.57 (m, 1H), 7.42-7.37 (m, 2H).

\(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 158.9, 151.2, 141.7, 132.4, 132.0, 131.6, 126.2, 125.1, 124.3, 121.7, 120.9, 111.1.
2-(4-Fluorophenyl)benzoxazole

![2-(4-Fluorophenyl)benzoxazole](image)

Melting point: 99-99.5 °C
FT-IR (KBr, 4000-400 cm⁻¹): 3061, 2925, 1619, 1584, 1582, 1473, 1448, 1247, 1225.

¹H NMR (500 MHz, CDCl₃) δ 8.30-8.22 (m, 2H), 7.80-7.72 (m, 1H), 7.60-7.53 (m, 1H), 7.40-7.32 (m, 2H), 7.23-7.17 (m, 2H).

¹³C NMR (125 MHz, CDCl₃) δ 165.98 (s), 163.97 (s), 162.32 (s), 150.94 (s), 142.22 (s), 131.03 (s), 129.99 (d, J = 8.8 Hz), 128.99 (s), 125.28 (s), 124.81 (s), 123.67 (d, J = 3.2 Hz), 120.14 (s), 116.41 (s), 116.24 (s), 110.70 (s).

2-(3-Fluorophenyl)benzoxazole

![2-(3-Fluorophenyl)benzoxazole](image)

Melting point: 99-100 °C
FT-IR (KBr, 4000-400 cm⁻¹): 3073, 2925, 2855, 1591, 1552, 1480, 1449, 1341, 1269, 1242.

¹H NMR (500 MHz, CDCl₃) δ 8.05 (dd, J = 8.0, 1.0 Hz, 1H), 7.95 (dd, J = 8.5, 1.0 Hz, 1H), 7.79-7.77 (m, 1H), 7.59-7.58 (m, 1H), 7.49 (dd, J = 13.5, 8.0 Hz, 1H), 7.40-7.35 (m, 2H), 7.25-7.20 (m, 1H).

¹³C NMR (125 MHz, CDCl₃) δ 164.1 (s), 162.1 (s), 150.9 (s), 142.1 (s), 130.76 (d, J = 8.1 Hz), 129.35 (d, J = 8.6 Hz), 125.6 (s), 124.9 (s), 123.5 (d, J = 3.0 Hz), 120.4 (s), 118.63 (d, J = 21.3), 114.70 (d, J = 23.9), 110.8 (s).

2-(2-Fluorophenyl)benzoxazole

![2-(2-Fluorophenyl)benzoxazole](image)

Melting point: 93-95 °C
FT-IR (KBr, 4000-400 cm⁻¹): 2923, 1664, 1582, 1550, 1447, 1245.
$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.24 (td, $J = 7.5$, 2.0 Hz, 1H), 7.85-7.81 (m, 1H), 7.63-7.59 (m, 1H), 7.54-7.49 (m, 1H), 7.41-7.36 (m, 2H), 7.32-7.25 (m, 2H).

$^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 162.0 (s), 156.0 (s), 150.7 (s), 141.9 (s), 133.25 (d, $J = 8.6$ Hz), 130.7 (d, $J = 1.1$ Hz), 125.6 (s), 124.8 (s), 124.63 (d, $J = 3.8$ Hz), 120.52 (s), 117.32 (d, $J = 21.3$ Hz), 115.7 (d, $J = 10.4$ Hz), 110.8 (s).

5-Methyl-2-phenylbenzoxazole

Melting point: 112-115 °C
FT-IR (KBr, 4000-400 cm$^{-1}$): 2918, 1626, 1552, 1445, 1263.

$^1$H NMR (500 MHz, (CD$_3$)$_2$CO) $\delta$ 8.25-8.23 (m, 2H), 7.62-7.59 (m, 3H), 7.57-7.56 (m, 2H), 7.24 (d, $J = 8.5$, 1H), 2.47 (s, 3H).

$^{13}$C NMR (125 MHz, (CD$_3$)$_2$CO) $\delta$ 163.3, 149.2, 142.5, 134.5, 131.5, 129.0, 127.7, 127.5, 126.4, 120.1, 110.1, 21.6.

5-Methyl-2-(4-tert-butylphenyl)benzoxazole

Melting point: 137-140 °C
FT-IR (KBr, 4000-400 cm$^{-1}$): 3107, 2963, 2930, 2871, 1729, 1621, 1532, 1460, 1269.

$^1$H NMR (500 MHz, (CD$_3$)$_2$CO) $\delta$ 8.56 (d, $J = 2.0$ Hz, 1H), 8.34 (dd, $J = 9.0$, 2.0 Hz, 1H), 8.20 (d, $J = 8.5$ Hz, 2H), 7.92 (d, $J = 9.0$ Hz, 1H), 7.69 (d, $J = 9.0$ Hz, 2H), 2.81 (s, 3H), 1.39 (s, 9H).

$^{13}$C NMR (125 MHz, (CD$_3$)$_2$CO) $\delta$ 162.9, 155.0, 149.0, 142.5, 134.3, 127.2, 126.1, 126.0, 124.6, 119.7, 109.9, 34.7, 30.5, 20.5.

5-Methyl-2-(p-tolyl)benzoxazole

Melting point: 135 °C.
FT-IR (KBr, 4000 − 400 cm$^{-1}$): 3304, 2921, 2856, 1616, 1555, 1499, 1332, 1262.
$^1$H NMR (500 MHz, (CD$_3$)$_2$CO) δ 8.11 (d, $J = 8.0$ Hz, 2H), 7.53 – 7.51 (m, 2H), 7.39 (d, $J = 8.0$ Hz, 2H), 7.22 – 7.19 (m, 1H), 2.46 (s, 3H), 2.43 (s, 3H).

$^{13}$C NMR (125 MHz, (CD$_3$)$_2$CO) δ 163.2, 149.2, 142.7, 142.3, 134.5, 129.9, 127.5, 126.3, 124.8, 119.9, 110.1, 20.9, 20.8.

**5-Methyl-2-(4-methoxyphenyl)benzoxazole**

![Structure of 5-Methyl-2-(4-methoxyphenyl)benzoxazole]

Melting point: 112 °C

FT-IR (KBr, 4000 – 400 cm$^{-1}$): 2924, 2854, 1730, 1608, 1499, 1420, 1254.

$^1$H NMR (500 MHz, DMSO) δ 8.12 (d, $J = 9.0$ Hz, 2H), 7.61 (d, $J = 8.0$ Hz, 1H), 7.55 (s, 1H), 7.20 (d, $J = 8.5$ Hz, 1H), 7.15 (d, $J = 9.0$ Hz, 2H), 3.87 (s, 3H), 2.44 (s, 3H).

$^{13}$C NMR (125 MHz, DMSO) δ 163.0, 162.5, 148.7, 142.1, 134.7, 129.5, 126.5, 119.6, 119.5, 119.2, 115.2, 110.6, 110.5, 55.9, 21.3.

**5-Nitro-2-phenylbenzoxazole**

![Structure of 5-Nitro-2-phenylbenzoxazole]

Melting point: 166-169 °C.

FT-IR (KBr, 4000-400 cm$^{-1}$): 3105, 2925, 2853, 1709, 1604, 1526, 1463, 1348, 1286.

$^1$H NMR (500 MHz, DMSO-$d_6$) δ 8.68 (d, $J = 2.5$ Hz, 1H), 8.35 (dd, $J = 9.0$, 2.0 Hz, 1H), 8.26-8.24 (m, 2H), 8.06 (d, $J = 9.0$ Hz, 1H), 7.71-7.65 (m, 3H).

$^{13}$C NMR (125 MHz, CDCl$_3$) δ 165.4 (s), 154.0 (s), 145.1 (s), 141.9 (s), 132.9 (s), 129.5 (s), 127.8 (d, $J = 14.3$ Hz), 125.5 (s), 121.5 (d, $J = 16.8$ Hz), 115.7 (d, $J = 12.5$ Hz), 111.8 (s).

**5-Nitro-2-(4-tert-butylphenyl)benzoxazole**

![Structure of 5-Nitro-2-(4-tert-butylphenyl)benzoxazole]

Melting point: 137 °C.

FT-IR (KBr, 4000-400 cm$^{-1}$): 3106, 2964, 2869, 1724, 1619, 1531, 1496, 1462, 1343, 1267.
$^1$H NMR (500 MHz, (CD$_3$)$_2$CO) $\delta$ 8.18-8.16 (m, 2H), 7.66-7.63 (m, 2H), 7.56-7.54 (m, 2H), 7.23-7.21 (m, 1H), 1.38 (s, 9H).

$^{13}$C NMR (125 MHz, (CD$_3$)$_2$CO) $\delta$ 166.9, 157.3, 155.3, 146.4, 143.6, 132.1, 129.7, 128.7, 127.2, 124.2, 122.0, 116.4, 112.1, 35.8, 31.4.

5-Nitro-2-(p-tolyl)benzoxazole

![5-Nitro-2-(p-tolyl)benzoxazole structure]

Melting point: 125-126 °C.

FT-IR (KBr, 4000-400 cm$^{-1}$): 2923, 2850, 1695, 1628, 1515, 1416, 1328, 1250.

$^1$H NMR (500 MHz, (CD$_3$)$_2$CO) $\delta$ 8.31-8.27 (m, 2H), 7.57-7.55 (m, 2H), 7.40-7.35 (m, 2H), 7.24 (d, $J=9.0$ Hz, 1H), 2.47 (s, 3H).

$^{13}$C NMR (125 MHz, (CD$_3$)$_2$CO) $\delta$ 166.7, 164.7, 150.0, 143.3, 135.5, 130.8, 130.7, 127.30, 124.8, 120.7, 117.2, 117.0, 110.9, 21.4.

5-Nitro-2-(4-methoxyphenyl)benzoxazole

![5-Nitro-2-(4-methoxyphenyl)benzoxazole structure]

Melting point: 182-186 °C.

FT-IR (KBr, 4000-400 cm$^{-1}$): 2923, 2854, 1620, 1628, 1524, 1460, 1343, 1251.

$^1$H NMR (500 MHz, (CD$_3$)$_2$CO) $\delta$ 8.55 (d, $J=2.5$ Hz, 1H), 8.34 (dd, $J=9.0, 2.5$ Hz, 1H), 8.25-8.23 (m, 2H), 7.91 (d, $J=9.0$ Hz, 1H), 7.20-7.18 (m, 2H), 3.95 (s, 3H).

$^{13}$C NMR (125 MHz, (CD$_3$)$_2$CO) $\delta$ 163.5, 154.4, 142.8, 129.8, 120.8, 118.3, 115.2, 114.8, 111.0, 55.2.

5-Chloro-2-phenylbenzoxazole

![5-Chloro-2-phenylbenzoxazole structure]

Melting point: 102-104 °C.

FT-IR (KBr, 4000-400 cm$^{-1}$): 3061, 1612, 1551, 1443, 1333, 1265.
$^1$H NMR (500 MHz, (CD$_3$)$_2$CO) $\delta$ 8.23 (d, $J = 7.5$ Hz, 2H), 7.77 (d, $J = 1.5$ Hz, 1H), 7.70 (d, $J = 7.5$ Hz, 1H), 7.59-7.64 (m, 3H), 7.42 (dd, $J = 9.0$, 1.5 Hz, 1H).

$^{13}$C NMR (125MHz, (CD$_3$)$_2$CO) $\delta$ 165.3, 150.6, 144.5, 133.1, 130.7, 130.2, 128.6, 127.7, 126.4, 120.7, 112.9.

**5-Chloro-2-(4-tert-butylphenyl)benzoxazole**

![Structure of 5-Chloro-2-(4-tert-butylphenyl)benzoxazole](image)

Melting point: 138 °C
FT-IR (KBr, 4000-400 cm$^{-1}$): 2957, 2902, 2866, 1611, 1552, 1493, 1457, 1262.

$^1$H NMR (500 MHz, (CD$_3$)$_2$CO) $\delta$ 8.17 (d, $J = 8.5$ Hz, 2H), 7.76 (s, 1H), 7.70 (d, $J = 8.5$ Hz, 1H), 7.66 (d, $J = 8.5$ Hz, 2H), 7.41 (dd, $J = 8.5$, 2.0 Hz, 1H), 1.38 (s, 9H).

$^{13}$C NMR (126 MHz, (CD$_3$)$_2$CO) $\delta$ 165.5, 150.6, 144.6, 130.6, 128.6, 127.2, 126.2, 125.0, 120.5, 112.8, 35.9, 31.5.

**5-Chloro-2-(p-tolyl)benzoxazole**

![Structure of 5-Chloro-2-(p-tolyl)benzoxazole](image)

Melting point: 148-150 °C
FT-IR (KBr, 4000-400 cm$^{-1}$): 1610, 1551, 1479, 1448, 1258.

$^1$H NMR (500 MHz, (CD$_3$)$_2$CO) $\delta$ 8.13 (d, $J = 8.0$ Hz, 2H), 7.75 (d, $J = 2.0$ Hz, 1H), 7.70 (d, $J = 9.0$ Hz, 1H), 7.40-7.33 (m, 4H), 2.44 (s, 3H).

$^{13}$C NMR (125 MHz, (CD$_3$)$_2$CO) $\delta$ 165.6, 150.5, 144.6, 143.8, 130.8, 130.6, 128.6, 126.2, 125.0, 120.5, 112.8, 21.7.

**5-Chloro-2-(4-methoxyphenyl)benzoxazole**

![Structure of 5-Chloro-2-(4-methoxyphenyl)benzoxazole](image)

Melting point: 153-155 °C
FT-IR (KBr, 4000-400 cm$^{-1}$): 2962, 1609, 1554, 1496, 1451, 1417, 1251.
$^1$H NMR (500 MHz, (CD$_3$)$_2$CO) δ 8.19-8.17 (m, 2H), 7.72 (d, $J$ = 2.0 Hz, 1H), 7.67 (d, $J$ = 8.5 Hz, 1H), 7.38 (dd, $J$ = 8.5, 2.0 Hz, 1H), 7.16-7.14 (m, 2H), 3.92 (s, 3H).

$^{13}$C NMR (125 MHz, (CD$_3$)$_2$CO) δ 165.52, 164.09, 150.53, 144.79, 130.52, 126.57, 125.84, 120.28, 120.04, 115.66, 112.61, 56.16.
Fig. S22. $^1$H (top) and $^{13}$C (bottom) NMR spectra of 2-phenylbenzoxazole.
Fig. S23. $^1$H (top) and $^{13}$C (bottom) NMR spectra of 2-(4-tert-butylphenyl)benzoxazole.
Fig. S24. $^1$H (top) and $^{13}$C (bottom) NMR spectra of 2-(p-tolyl)benzoxazole.
Fig. S25. $^1$H (top) and $^{13}$C (bottom) NMR spectra of 2-(4-methoxyphenyl)benzoxazole.
Fig. S26. $^1$H (top) and $^{13}$C (bottom) NMR spectra of 2-(4-chlorophenyl)benzoxazole.
Fig. S27. $^1$H (top) and $^{13}$C (bottom) NMR spectra of 2-(4-nitrophenyl)benzoxazole.
Fig. S28. $^1$H (top) and $^{13}$C (bottom) NMR spectra of 2-(4-fluorophenyl)benzoxazole.
Fig. S29. $^1$H (top) and $^{13}$C (bottom) NMR spectra of 2-(3-fluorophenyl)benzoxazole.
Fig. S30. $^1$H (top) and $^{13}$C (bottom) NMR spectra of 2-(2-fluorophenyl)benzoxazole.
Fig. S31. $^1$H (top) and $^{13}$C (bottom) NMR spectra of 5-methyl-2-phenylbenzoxazole.
Fig. S32. $^1$H (top) and $^{13}$C (bottom) NMR spectra of 5-methyl-2-(4-tert-butylphenyl)benzoxazole.
Fig. S33. $^1$H (top) and $^{13}$C (bottom) NMR spectra of 5-methyl-2-($p$-tolyl)benzoxazole.
Fig. S34. $^1$H (top) and $^{13}$C (bottom) NMR spectra of 5-methyl-2-(4-methoxyphenyl)benzoxazole.
Fig. S35: $^1$H (top) and $^{13}$C (bottom) NMR spectra of 5-nitro-2-phenylbenzoxazole.
Fig. S36. $^1$H (top) and $^{13}$C (bottom) NMR spectra of 5-nitro-2-(4-tert-butylphenyl)benzoxazole.
Fig. S37. $^1$H (top) and $^{13}$C (bottom) NMR spectra of 5-nitro-2-(p-tolyl)benzoxazole.
Fig. S38. $^1$H (top) and $^{13}$C (bottom) NMR spectra of 5-nitro-2-(4-methoxyphenyl)benzoxazole.
Fig. S 39. $^1$H (top) and $^{13}$C (bottom) NMR spectra of 5-chloro-2-phenylbenzoxazole.
Fig. S40. $^1$H (top) and $^{13}$C (bottom) NMR spectra of 5-chloro-2-(4-tert-butylphenyl)benzoxazole.
Fig. S41. $^1$H (top) and $^{13}$C (bottom) NMR spectra of 5-chloro-2-(p-tolyl)benzoxazole.
Fig. S42. $^1$H (top) and $^{13}$C (bottom) NMR spectra of 5-chloro-2-(4-methoxyphenyl)benzoxazole.
References

