Electronic Supplementary Information

Iron-Catalyzed Aerobic Oxidation of Alcohols in Water Selectively to Carboxylic Acids Mediated by Additives

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1. General information

All commercially available materials and solvents were used directly without further purification unless otherwise noted. \(^1\)H NMR and \(^{13}\)C NMR data were recorded with a Bruker spectrometer (500 MHz) using TMS as internal standard and reported relative to residual solvent signals as follows: chemical shift (\(\delta\) ppm), multiplicity, coupling constant (Hz), and integration. FT-IR spectra were recorded on a Thermo Fisher Nicolet 6700. XRD were explored on D/max 2200PC of Janpan. GC analyses were performed on Shimadzu GC-2014 with a flame ionization detector equipped with an Rtx-1 capillary column (internal diameter = 0.25 mm, length = 30 m) or a HP-INNOWAX (30*0.25*0.25, length = 30 m). GC mass spectra were recorded on Shimadzu GCMS-QP2010 with RTX-5MS column (0.25 mm× 30 m). Column chromatography was performed using 200-300 mesh silica gel.

**CAUTION:** The oxygen was used in the reaction, all ignition devices should be removed for that the oxygen can increase the intensity of any fire, including spark, stationary or flame sources, and so on. Pure oxygen inhalation should also be avoided. For more information, see: Cheremisinoff, N. P. *Handbook of Hazardous Chemical Properties*, Butterworth-Heinemann, Woburn, 1999.

2. Preparation of inorganic-ligand supported iron catalyst 1

![Figure S1. Preparation of (TBA)\(_3\)[FeMo\(_6\)O\(_{18}\)(OH)\(_6\)].](image)

(NH\(_4\))\(_6\)Mo\(_7\)O\(_{24}\)·4H\(_2\)O was synthesized according to a modified published procedure\(^{12}\): (NH\(_4\))\(_6\)Mo\(_7\)O\(_{24}\)·4H\(_2\)O (15.9 g) was dissolved in water (250 mL) and then heated to 100 °C. Fe\(_2\)(SO\(_4\))\(_3\) (3.8 g) was dissolved in water (60 mL), which was slowly added in the solution with stirring. The pH value of the mixture was kept to about 2.5 - 3.0. The mixture was still stirring 1h after completely adding. Then the crude ammonium salt filtrate obtained from the refluxed solution by heat filtering. The brown block crystals were filtered off after the filtrate stewed for 12 h at room temperature. The light yellow aim product (11.8 g) was collected after recrystallized in hot water (100 °C) for two times.

Preparation of (TBA)\(_3\)[FeMo\(_6\)O\(_{18}\)(OH)\(_6\)]: Tetraethylammonium bromide (TBAB, 2.9 g), (NH\(_4\))\(_3\)[FeMo\(_6\)O\(_{18}\)(OH)\(_6\)]·7H\(_2\)O (2.4 g, 2.0 mmol) were added to 50 mL of H\(_2\)O, and heated to 100 °C with stirring for 30 min. Then, a large white solid (3.9 g) appeared by adding 50 mL of acetonitrile after cooling naturally to room temperature, the target product was obtained by suction filtration and drying.

IR: \(\nu_{\text{max}}\) 3401.29 (v as NH, w), 2953.21 (vCH, s), 2782.41 (v CH, s), 1609.32 (w), 1552.24 (s CH), 1486.65 (s CH, m), 1379.43(w), 959.55 (v Mo=O, s), 929.62 (v Mo=O, s), 857.03 (v Mo=O, s), 669.83 (v Mo-O-Mo, vs), 560.94 (w) cm\(^{-1}\). \(^1\)H NMR (500 MHz, DMSO) \(\delta\) 7.12 (s, 6H), 3.25 (d, 3H), 3.15 (t, 24H), 1.61 (m, 24H), 1.28 (m, 24H), 0.95 (t, 36H).
3. FT-IR and XRD spectra of the catalyst

Figure S2. The FT-IR spectra of (TBA)$_3$[FeMo$_6$O$_{18}$(OH)$_6$].

Figure S3. The XRD spectra of (TBA)$_3$[FeMo$_6$O$_{18}$(OH)$_6$].
4. Crystal data, structure refinement and hydrogen bonds for FeMoO$_5$Cl

FeMoO$_5$Cl was synthesized according to a modified published procedure$^{[3]}$: (TBA)$_2$[FeMoO$_5$(OH)$_2$] (1.800 g, 1.0 mmol) and KCl (0.075 g, 1.0 mmol) was added into 20 mL H$_2$O and stirred for 30 minutes at 100 °C. Then the large white solid (1.223 g) appeared by adding 20 mL acetonitrile after cooling naturally to room temperature and filtered off.

| Table S1. Crystal data and structure refinement for FeMoO$_5$Cl |
|-----------------|----------------|
| Identification code | FeMoCl |
| CCDC number | 1882680 |
| Empirical formula | C$_{86}$H$_{12}$ClFeMo$_5$NO$_{15}$ |
| Formula weight | 2224.99 |
| Temperature/K | 100 |
| Crystal system | orthorhombic |
| Space group | Pbc | |
| a/Å | 48.6754(12) |
| b/Å | 17.5864(3) |
| c/Å | 23.1423(4) |
| α° | 90 |
| β° | 90 |
| γ° | 90 |
| Volume/Å$^3$ | 19810.4(7) |
| Z | 8 |
| ρ$\text{calc}$/cm$^3$ | 1.492 |
| $\mu$/mm$^{-1}$ | 0.978 |
| F(000) | 9272.0 |
| Crystal size/mm$^3$ | 0.1 x 0.1 x 0.1 |
| Radiation | MoKα (λ = 0.71073) |
| 2θ range for data collection/* | 6.67 to 59.276 |
| Index ranges | -67 ≤ h ≤ 48, -24 ≤ k ≤ 23, -23 ≤ l ≤ 31 |
| Independent reflections | 83221 |
| Final R indexes [I>2σ(I)] | 23470 [R$_{ref}$ = 0.0708, R$_{max}$ = 0.0827] |
| Final R indexes [all data] | 1.177 |
| Goodness-of-fit on F$^2$ | R$_1$ = 0.0870, wR$_2$ = 0.1479 |
| Largest diff. peak/hole / e Å$^{-3}$ | 1.10/-1.81 |

| Table S2. Hydrogen bonds for FeMoO$_6$Cl. |
|-----------------|----------------|
| D-H | d(D-H) | d(H..A) | <DHA | d(D,A) | A |
| O2-H2 | 0.980 | 2.313 | 141.83 | 3.143 | CI |
| O6-H6 | 0.980 | 1.749 | 176.34 | 2.773 | O5W |
| O1-H1 | 0.980 | 2.458 | 138.35 | 3.256 | CI |
| O4-H4 | 0.980 | 2.601 | 129.67 | 3.314 | O7W |
| O4-H4 | 0.980 | 2.345 | 129.70 | 3.065 | O8W |
| O9W-H9WA | 0.850 | 1.937 | 160.31 | 2.752 | O10W |
| O9W-H9WB | 0.850 | 1.907 | 152.77 | 2.691 | O5W |
| O3-H3 | 0.980 | 2.273 | 143.51 | 3.116 | CI |
| O5W-H5WA | 0.849 | 1.871 | 176.34 | 2.719 | O6W |
| O5W-H5WB | 0.851 | 1.944 | 150.18 | 2.715 | O4W |
| C50-H50B | 0.970 | 2.539 | 152.17 | 3.427 | O1W [-x+1/2, y-1/2, z] |
| O5-H5 | 0.970 | 1.776 | 168.21 | 2.742 | O9W |
| C9-H9A | 0.970 | 2.617 | 123.59 | 3.256 | O14 |
| C9-H9B | 0.970 | 2.652 | 134.01 | 3.398 | O8 |
| O1W-H1WA | 0.850 | 1.966 | 170.27 | 2.807 | O12 |
| O1W-H1WB | 0.851 | 2.415 | 161.54 | 3.234 | CI |
| O4W-H4WB | 0.850 | 2.076 | 151.24 | 2.850 | O23 |
| O7W-H7WA | 0.850 | 1.963 | 167.95 | 2.799 | O8W |
| O7W-H7WB | 0.850 | 2.495 | 121.53 | 3.028 | O24 |
| O7W-H7WB | 0.850 | 2.454 | 137.72 | 3.135 | O19 |
| O3W-H3WA | 0.851 | 2.570 | 146.10 | 3.331 | CI |
| O3W-H3WB | 0.850 | 1.915 | 178.22 | 2.765 | O2W |
| O8W-H8WA | 0.850 | 1.976 | 167.51 | 2.812 | O9W |
| O10W-H10C | 0.850 | 2.005 | 148.02 | 2.763 | O11W |
| O10W-H10D | 0.848 | 2.005 | 155.95 | 2.802 | O21 |
| O11W-H11C | 0.850 | 2.064 | 168.74 | 2.903 | O10W [-x, -y+1, -z+1] |
| O11W-H11D | 0.850 | 2.038 | 161.31 | 2.856 | O20 [-x, -y+1, -z+1] |
| O2W-H2WA | 0.850 | 2.231 | 149.97 | 3.086 | O1W |
| O2W-H2WB | 0.850 | 2.328 | 161.69 | 3.146 | O17 |
| O2W-H2WB | 0.850 | 2.519 | 113.23 | 2.959 | O18 |
| O6W-H6WA | 0.850 | 1.941 | 166.57 | 2.775 | O11 |
Figure S4 The BET report of FeMo₆Cl
5. Condition Optimization

**General procedure:** To a Schlenk tube were added cinnamic alcohol (134.1 mg, 1.0 mmol), Cat. 1 (19.9 mg, 0.01 mmol), KCl (14.9 mg, 0.2 mmol), and H2O (2 mL) sequentially under the atmosphere of oxygen from a O2 balloon. The Schlenk tube was then stirred at 70 °C until completion of the reaction as monitored by GC (24 h). The crude reaction mixture was extracted with ethyl acetate or ether (7.5 mL). After evaporation, the residue was purified by chromatography on silica gel to afford 2a (136.3 mg, 92%) (eluent: petroleum ether/ethyl acetate) as a white crystal. The following starting materials 3a-41 were conducted according to General Procedure.

**Cyclic voltammogram:** Cyclic voltammograms were obtained at the glassy carbon electrode and a 1.0 mM acetonitrile solution of the FeMo6 in the presence of increasing respectively amounts of KCl, MgCl₂, RbCl, NH₄Cl, NaCl, LiCl, KF, KBr, and KI at sweep rates of 100 mV s⁻¹.

*Table S3.* The effects of catalyst and additives
### Table S4. The effects of solvents and time

<table>
<thead>
<tr>
<th>Entry</th>
<th>Solvent</th>
<th>Time (h)</th>
<th>Selectivity (%)</th>
<th>Yield (%)</th>
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<tbody>
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<td>1</td>
<td>Dioxane</td>
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<td>92</td>
<td>47</td>
</tr>
<tr>
<td>2</td>
<td>Toluene</td>
<td>24</td>
<td>95</td>
<td>61</td>
</tr>
<tr>
<td>3</td>
<td>DMF</td>
<td>24</td>
<td>97</td>
<td>55</td>
</tr>
<tr>
<td>4</td>
<td>MeOH</td>
<td>24</td>
<td>90</td>
<td>74</td>
</tr>
<tr>
<td>5</td>
<td>MeCN</td>
<td>24</td>
<td>94</td>
<td>69</td>
</tr>
<tr>
<td>6&lt;sup&gt;b&lt;/sup&gt;</td>
<td>CH&lt;sub&gt;2&lt;/sub&gt;Cl&lt;sub&gt;2&lt;/sub&gt;</td>
<td>24</td>
<td>96</td>
<td>57</td>
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<tr>
<td>7&lt;sup&gt;c&lt;/sup&gt;</td>
<td>THF</td>
<td>24</td>
<td>95</td>
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<tr>
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<td>30</td>
<td>97</td>
<td>82</td>
</tr>
<tr>
<td>12&lt;sup&gt;e&lt;/sup&gt;</td>
<td>CH&lt;sub&gt;2&lt;/sub&gt;Cl&lt;sub&gt;2&lt;/sub&gt;</td>
<td>30</td>
<td>95</td>
<td>29</td>
</tr>
</tbody>
</table>

<sup>a</sup>Reaction conditions: cinnamic alcohol (1.0 mmol), I (1.0 mol%), KCl (0.2 equiv.), O<sub>2</sub> (1.0 atm), Solvent (2.0 mL), 70 °C, yields and selectivity were determined by GC and confirmed by GC-MS. <sup>b</sup>at 40 °C. <sup>c</sup>at 60 °C. <sup>d</sup>at 50 °C. <sup>e</sup>at 30 °C, air as oxidant.
Figure S7. Cyclic voltammogram experiments. Cyclic voltammograms (298 K, scan rate 100mVs⁻¹) of a 1.0 mM acetonitrile solution of the FeMo₆ in the presence of KCl, MgCl₂, RbCl, NH₄Cl, NaCl and LiCl.

Figure S8. Cyclic voltammogram experiments. Cyclic voltammograms (298 K, scan rate 100mVs⁻¹) of a 1.0 mM acetonitrile solution of the FeMo₆ in the presence of KCl, KF, KBr and KI.

6. Gram-scale reaction

To a 50 mL three-necked bottle were added cinnamic alcohol (1.34 g, 0.01 mol), Cat.1 (0.20 g, 0.0001mol), KCl (0.15 g, 0.002 mol), and H₂O (20 mL) sequentially under the atmosphere of O₂ from a gas bag with a valve. The three-necked bottle was then stirred at 70 °C until completion of the reaction as monitored by GC (24 h). The crude reaction mixture was extracted with ethyl acetate (3*20 mL). After evaporation, the residue was purified by recrystallization (water/ethanol = 3/1) to afford 2a (1.36 g, 92%) as a white crystal.
7. Recycling experiments of the catalyst

The Fe\textsuperscript{III}Mo\textsubscript{6} catalyst was precipitated by adding ethyl acetate or anhydrous ether to the reaction system after the oxidative experiments, and then recovered for reuse. The recovered catalyst was characterized by FT-IR and XRD.

![Figure S10. Recycling experiments of the catalyst.](image)

![Figure S11. The FT-IR spectra of the catalyst before and after the reaction.](image)
8. The $^1$H NMR studies for tracking the oxidation process

Figure S12. The XRD spectra of the catalyst before and after the reaction.

Figure S13. $^1$H NMR spectra of the reaction mixture at different time points.
Figure S14. $^1$H NMR Tracing of d$_1$-benzyl alcohol

Figure S15. $^1$H NMR tracing of d$_2$-benzyl alcohol (4-28 h)
Figure S16. $^1$H NMR tracing of di-benzyl alcohol (32-60 h)
9. Computational details
All DFT calculations were performed by using B3LYP-D3 hybrid functional[4] in Gaussian 09 program package.[5] The solvent effect was modeled with the conductor-like polarizable continuum model (CPCM) in water.[6] The basis sets LANL2DZ[7] and 6-31G(d, p)[8] were applied for metal atoms (Fe, Mo) and non-metal atoms (H, C, O, Cl), respectively. On the basis of optimized structure, the single-point energy was obtained at B3LYP-D3/6-311+G(d,p)/SDD level.

<table>
<thead>
<tr>
<th>α spin</th>
<th>LUMO</th>
<th>LUMO+1</th>
<th>LUMO+2</th>
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<td></td>
</tr>
<tr>
<td>β spin</td>
<td>-3.39</td>
<td>-3.29</td>
<td>-3.29</td>
</tr>
</tbody>
</table>

10. NMR data of products

Cinnamic acid (2)[9]: White crystal. $^1$H NMR (400 MHz, CDCl$_3$) δ 12.25 (s, 1H), δ 7.83 (d, $J = 16.0$ Hz, 1H), 7.62 – 7.55 (m, 2H), 7.47 – 7.42 (m, 3H), 6.49 (d, $J = 16.0$ Hz, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 172.44 (s), 147.14 (s), 134.05 (s), 130.79 (s), 128.99 (s), 128.40 (s), 117.31 (s).
4-Methylcinnamic acid (3) \([9]\): White powder. \(^1\)H NMR (400 MHz, DMSO-\(d_6\)) \(\delta\) 12.27 (s, 1H), 7.55 – 7.48 (m, 3H), 7.18 (d, \(J = 8.0\) Hz, 2H), 6.42 (d, \(J = 16.0\) Hz, 1H), 2.28 (s, 3H). \(^{13}\)C NMR (100 MHz, DMSO-\(d_6\)) \(\delta\) 168.20 (s), 144.45 (s), 140.66 (s), 132.03 (s), 130.03 (s), 128.71 (s), 118.62 (s), 21.53 (s).

4-methoxycinnamic acid (4) \([9]\): White powder. \(^1\)H NMR (400 MHz, DMSO-\(d_6\)) \(\delta\) 12.18 (s, 1H), 7.59 (d, \(J = 8.7\) Hz, 2H), 7.50 (d, \(J = 16.0\) Hz, 1H), 6.93 (d, \(J = 8.7\) Hz, 2H), 6.34 (d, \(J = 16.0\) Hz, 1H), 3.75 (s, 3H). \(^{13}\)C NMR (100 MHz, DMSO-\(d_6\)) \(\delta\) 168.36 (s), 161.46 (s), 144.27 (s), 130.46 (s), 127.35 (s), 117.02 (s), 114.87 (s), 55.83 (s).

4-fluorocinnamic acid (5) \([9]\): White crystal. \(^1\)H NMR (400 MHz, DMSO-\(d_6\)) \(\delta\) 12.35 (s, 1H), 7.72 (dd, \(J = 8.7, 5.6\) Hz, 2H), 7.55 (d, \(J = 16.0\) Hz, 1H), 7.20 (t, \(J = 8.8\) Hz, 2H), 6.45 (d, \(J = 16.0\) Hz, 1H). \(^{13}\)C NMR (100 MHz, DMSO-\(d_6\)) \(\delta\) 168.04 (s), 162.44 (d, \(J = 246.98\) Hz), 143.22 (s), 131.42 (s), 130.98 (s), 119.63 (s), 116.50 (s).

4-chlorocinnamic acid (6) \([9]\): Colorless crystal. \(^1\)H NMR (400 MHz, DMSO-\(d_6\)) \(\delta\) 12.43 (s, 1H), 7.69 (d, \(J = 8.5\) Hz, 2H), 7.54 (d, \(J = 16.0\) Hz, 1H), 7.43 (d, \(J = 8.5\) Hz, 2H), 6.52 (d, \(J = 16.0\) Hz, 1H). \(^{13}\)C NMR (100 MHz, DMSO-\(d_6\)) \(\delta\) 167.95 (s), 143.04 (s), 135.23 (s), 133.75 (s), 130.47 (s), 129.45 (s), 120.61 (s).

4-bromocinnamic acid (7) \([9]\): White crystal. \(^1\)H NMR (400 MHz, DMSO-\(d_6\)) \(\delta\) 7.57 (dt, \(J = 19.6, 12.3\) Hz, 5H), 6.53 (d, \(J = 16.0\) Hz, 1H). \(^{13}\)C NMR (100 MHz, DMSO-\(d_6\)) \(\delta\) 167.94 (s), 143.13 (s), 134.07 (s), 132.38 (s), 130.68 (s), 124.05 (s), 120.67 (s).

4-( trifluoromethyl) cinnamic acid (8) \([9]\): White powder. \(^1\)H NMR (400 MHz, DMSO-\(d_6\)) \(\delta\) 12.61 (s, 1H), 7.86 (d, \(J = 8.1\) Hz, 2H), 7.70 (d, \(J = 8.3\) Hz, 2H), 7.62 (d, \(J = 16.1\) Hz, 1H), 6.64 (d, \(J = 16.1\) Hz, 1H). \(^{13}\)C NMR (100 MHz, DMSO-\(d_6\)) \(\delta\) 167.73 (s), 142.59 (s), 138.79 (s), 130.51 (s), 129.33 (s), 126.18 (d, \(J = 3.7\) Hz), 122.68 (s).
Benzoic acid (9):
White solid. $^1$H NMR (400 MHz, CDCl$_3$) δ 10.04 (d, J = 7.8 Hz, 2H), 9.57 (d, J = 3.1 Hz, 1H), 9.43 (d, J = 2.0 Hz, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 173.90 (s), 135.88 (s), 132.07 (s), 131.23 (s), 130.54 (s).

p-Toluic acid (10):
White powder. $^1$H NMR (400 MHz, DMSO-d$_6$) δ 12.75 (s, 1H), 7.80 (d, J = 8.1 Hz, 2H), 7.24 (d, J = 8.1 Hz, 2H), 2.31 (s, 3H). $^{13}$C NMR (100 MHz, DMSO-d$_6$) δ 167.84 (s), 143.52 (s), 129.85 (s), 129.62 (s), 128.55 (s), 21.62 (s).

4-Isopropylbenzoic acid (11):
White powder. $^1$H NMR (400 MHz, CDCl$_3$) δ 8.04 (d, J = 8.4 Hz, 2H), 7.32 (d, J = 8.1 Hz, 2H), 2.98 (dt, J = 13.8, 6.9 Hz, 1H), 1.27 (d, J = 6.9 Hz, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 172.51 (s), 155.48 (s), 130.50 (s), 126.72 (s), 125.65 (s), 34.44 (s), 23.77 (s).

4-Methoxybenzoic acid (12):
White powder. $^1$H NMR (400 MHz, DMSO-d$_6$) δ 12.59 (s, 1H), 7.85 (d, J = 8.9 Hz, 2H), 6.97 (d, J = 9.0 Hz, 2H), 3.78 (s, 3H). $^{13}$C NMR (100 MHz, DMSO-d$_6$) δ 167.54 (s), 163.36 (s), 131.87 (s), 123.48 (s), 114.33 (s), 55.95 (s).

4-Fluorobenzoic acid (13):
White powder. $^1$H NMR (400 MHz, CDCl$_3$) δ 8.13 (dd, J = 8.9, 5.4 Hz, 2H), 7.14 (t, J = 8.6 Hz, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 166.89 (d, J = 253.8 Hz), 132.63 (d, J = 9.5 Hz), 116.27 (s), 116.05 (s).

4-Chlorobenzoic acid (14):
White powder. $^1$H NMR (500 MHz, DMSO-d$_6$) δ 13.16 (s, 1H), 7.93 (d, J = 8.6 Hz, 2H), 7.52 (d, J = 8.6 Hz, 2H). $^{13}$C NMR (125 MHz, DMSO-d$_6$) δ 166.91 (s), 138.25 (s), 131.55 (s), 130.07 (s), 129.10 (s).

4-Bromobenzoic acid (15):
White powder. $^1$H NMR (500 MHz, DMSO-d$_6$) δ 13.19 (s, 1H), 7.85 (s, 2H), 7.71 (s, 2H). $^{13}$C NMR (125 MHz, DMSO-d$_6$) δ 167.07 (s), 132.85 (s), 131.48 (s), 131.13 (s), 130.47 (s).
4-(trifluoromethyl)benzoic acid (16): White powder. $^1$H NMR (500 MHz, DMSO-$d_6$) δ 13.49 (s, 1H), 8.14 (d, $J = 8.4$ Hz, 2H), 7.87 (d, $J = 8.2$ Hz, 2H). $^{13}$C NMR (125 MHz, DMSO-$d_6$) δ 166.65 (s), 135.05 (s), 132.81 (s), 130.55 (s), 126.05 (s), 125.34 (s).

4-nitrobenzoic acid (17): Light yellow powder. $^1$H NMR (400 MHz, DMSO-$d_6$) δ 13.63 (s, 1H), 8.27 (d, $J = 8.8$ Hz, 2H), 8.11 (d, $J = 8.8$ Hz, 2H). $^{13}$C NMR (100 MHz, DMSO-$d_6$) δ 166.34 (s), 150.58 (s), 136.90 (s), 131.24 (s), 124.28 (s).

2,4,6-Trimethylbenzoic acid (18): White powder. $^1$H NMR (400 MHz, CDCl$_3$) δ 8.83 (s, 2H), 4.31 (s, 6H), 4.22 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 176.29 (s), 142.14 (s), 137.89 (s), 131.31 (s), 130.65 (s), 22.86 (s), 21.94 (s).

naphthoic acid (19): Light yellow powder. $^1$H NMR (400 MHz, DMSO-$d_6$) δ 13.05 (s, 1H), 8.58 (s, 1H), 8.10 – 7.93 (m, 4H), 7.64 – 7.52 (m, 2H). $^{13}$C NMR (100 MHz, DMSO-$d_6$) δ 167.98 (s), 135.46 (s), 132.67 (s), 131.05 (s), 129.80 (s), 128.71 (t, $J = 12.7$ Hz), 128.18 (s), 127.33 (s), 125.69 (s).

4-bromo-2-chlorobenzoic acid (20): White powder. $^1$H NMR (500 MHz, DMSO-$d_6$) δ 13.73 (s, 1H), 7.94 (d, $J = 2.3$ Hz, 1H), 7.74 (dd, $J = 8.6$, 2.5 Hz, 1H), 7.52 (d, $J = 8.6$ Hz, 1H). $^{13}$C NMR (125 MHz, DMSO-$d_6$) δ 135.57 (s), 133.86 (s), 133.48 (s), 133.05 (s), 131.33 (s), 120.32 (s).

3,5-dimethoxybenzoic acid (21): White powder. $^1$H NMR (500 MHz, DMSO-$d_6$) δ 12.94 (s, 1H), 6.97 (d, $J = 2.3$ Hz, 2H), 6.64 (t, $J = 2.2$ Hz, 1H), 3.69 (s, 6H). $^{13}$C NMR (125 MHz, DMSO-$d_6$) δ 167.43 (s), 160.83 (s), 133.30 (s), 107.29 (s), 105.33 (s), 55.86 (s).

4-hydroxy-3-methoxybenzoic acid (22): Liquid. $^1$H NMR (400 MHz, DMSO-$d_6$) δ 12.45 (s, 1H), 9.80 (s, 1H), 7.42 – 7.36 (m, 2H), 6.80 (d, $J = 8.5$ Hz, 1H), 3.76 (s, 3H). $^{13}$C NMR (100 MHz, DMSO-$d_6$) δ 167.73 (s), 151.60 (s), 147.72 (s), 123.98 (s), 122.10 (s), 115.53 (s), 113.19 (s), 56.03 (s).
**Salicylic acid** (23): White solid. \(^1\)H NMR (400 MHz, DMSO-\(d_6\)) \(\delta\) 13.76 (s, 1H), 11.37 (s, 1H), 7.75 (dd, \(J = 7.9, 1.7\) Hz, 1H), 7.48 – 7.44 (m, 1H), 6.92 – 6.85 (m, 2H). \(^{13}\)C NMR (100 MHz, DMSO-\(d_6\)) \(\delta\) 172.48 (s), 161.68 (s), 136.17 (s), 130.79 (s), 119.69 (s), 117.61 (s), 113.40 (s).

![Salicylic acid](image)

**Picolinic acid** (24): White powder. \(^1\)H NMR (400 MHz, DMSO-\(d_6\)) \(\delta\) 13.13 (s, 1H), 8.66 (d, \(J = 4.6\) Hz, 1H), 8.01 – 7.92 (m, 2H), 7.58 (dd, \(J = 4.9, 1.1\) Hz, 1H). \(^{13}\)C NMR (100 MHz, DMSO-\(d_6\)) \(\delta\) 166.70 (s), 149.96 (s), 148.86 (s), 138.04 (s), 127.62 (s), 125.18 (s).

![Picolinic acid](image)

**2-furoic acid** (25): Off-white powder. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 11.32 (s, 1H), 7.66 – 7.61 (m, 1H), 7.35 – 7.30 (m, 1H), 6.55 (dd, \(J = 3.6, 1.8\) Hz, 1H).

\(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 163.73 (s), 147.54 (s), 143.88 (s), 120.28 (s), 112.38 (s).

![2-furoic acid](image)

**2-thiophenecarboxylic acid** (26): Solid. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.89 (dd, \(J = 3.7, 1.2\) Hz, 1H), 7.64 (dd, \(J = 4.9, 1.1\) Hz, 1H), 7.14 (dd, \(J = 4.9, 3.8\) Hz, 1H).

\(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 167.74 (s), 135.13 (s), 134.13 (s), 132.92 (s), 128.17 (s).

![2-thiophenecarboxylic acid](image)

**2-methyl-1,3-thiazole-5-carboxylic acid** (27): Solid. \(^1\)H NMR (500 MHz, DMSO-\(d_6\)) \(\delta\) 13.29 (s, 1H), 8.07 (s, 1H), 2.60 (s, 3H).

\(^{13}\)C NMR (125 MHz, DMSO-\(d_6\)) \(\delta\) 172.21 (s), 162.54 (s), 147.99 (s), 130.50 (s), 19.78 (s).

![2-methyl-1,3-thiazole-5-carboxylic acid](image)

**Propionic acid** (28): Colorless liquid. \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 11.83 (s, 1H), 1.61 – 1.45 (m, 2H), 0.91 – 0.77 (m, 3H). \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 180.15 (s), 17.88 (s), 13.11 – 12.95 (m).

![Propionic acid](image)

**Valeric acid** (29): Colorless liquid. \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 11.60 (s, 1H), 2.13 (td, \(J = 7.6, 2.4\) Hz, 2H), 1.50 – 1.34 (m, 2H), 1.17 (pd, \(J = 7.5, 2.4\) Hz, 2H), 0.72 (td, \(J = 7.4, 2.4\) Hz, 3H). \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 180.27 (s), 33.52 (s), 26.54 (s), 21.96 (s), 13.22 (s).

![Valeric acid](image)

**Acrylic acid** (30): Clear liquid. \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 11.63 (s, 1H), 6.26 (dd, \(J = 17.3, 1.2\) Hz, 1H), 5.90 (dd, \(J = 17.3, 10.5\) Hz, 1H), 5.71 (dd, \(J = 10.4, 1.2\) Hz, 1H). \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 171.34 (s), 132.70 (s), 127.80 (s).

![Acrylic acid](image)

**3,3-dimethylacrylic acid** (31): White crystal. \(^1\)H NMR (500 MHz, DMSO-\(d_6\)) \(\delta\) 11.73 (s, 1H), 5.51 (s, 1H), 1.98 (s, 3H), 1.74 (s, 4H). \(^{13}\)C NMR (125 MHz, DMSO-\(d_6\)) \(\delta\) 167.75 (s), 155.83 (s), 116.93 (s), 27.22 (s), 20.08 (s).
Geranic acid (32): Solid. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 13.84 (s, 1H), 7.62 (d, \(J = 1.1\) Hz, 1H), 7.08 – 6.97 (m, 1H), 4.15 – 4.09 (m, 6H), 3.86 (d, \(J = 1.3\) Hz, 1H), 3.62 (s, 3H), 3.55 (s, 3H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 174.64 (s), 165.48 (s), 134.56 (s), 124.82 (s), 117.02 (s), 43.16 (s), 35.63 (s), 28.01 (s), 27.34 (s), 19.35 (s).

Levulinic acid (33): Clear yellow liquid. \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 10.02 (s, 1H), 2.34 (t, \(J = 6.5\) Hz, 2H), 2.12 (t, \(J = 6.5\) Hz, 2H), 1.73 (s, 3H).

2-chloropropionic acid (34): Colourless liquid. \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 11.13 (s, 1H), 4.30 (q, \(J = 7.0\) Hz, 1H), 1.52 (d, \(J = 7.1\) Hz, 2H).

Cyclohexanecarboxylic acid (35): White solid. \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 12.20 (s, 1H), 2.26 (d, \(J = 10.9\) Hz, 1H), 1.87 (s, 2H), 1.70 (s, 2H), 1.58 (s, 1H), 1.40 (s, 2H), 1.31 – 1.09 (m, 3H).

Indole-5-carboxylic acid (36): Light beige powder. \(^1\)H NMR (500 MHz, DMSO-d\(_6\)) \(\delta\) 12.38 (s, 1H), 11.43 (s, 1H), 8.24 (d, \(J = 0.6\) Hz, 1H), 7.71 (dd, \(J = 8.5, 1.5\) Hz, 1H), 7.49 – 7.41 (m, 2H), 6.61 – 6.55 (m, 1H). \(^{13}\)C NMR (125 MHz, DMSO-d\(_6\)) \(\delta\) 168.88 (s), 138.78 (s), 127.64 (s), 127.37 (s), 123.26 (s), 122.66 (s), 121.85 (s), 111.55 (s), 102.94 (s).

1h-indazole-6-carboxylic acid (37): White powder. \(^1\)H NMR (500 MHz, DMSO-d\(_6\)) \(\delta\) 12.38 (s, 1H), 11.43 (s, 1H), 8.24 (d, \(J = 0.6\) Hz, 1H), 7.71 (dd, \(J = 8.5, 1.5\) Hz, 1H), 7.49 – 7.41 (m, 2H), 6.61 – 6.55 (m, 1H). \(^{13}\)C NMR (125 MHz, DMSO-d\(_6\)) \(\delta\) 168.88 (s), 138.78 (s), 127.64 (s), 127.37 (s), 123.26 (s), 122.66 (s), 121.85 (s), 111.55 (s), 102.94 (s).

Piperonylic acid (38): Off-white powder. \(^1\)H NMR (400 MHz, DMSO-d\(_6\)) \(\delta\) 12.72 (s, 1H), 7.50 (dd, \(J = 8.1, 1.6\) Hz, 1H), 7.32 (d, \(J = 1.6\) Hz, 1H), 6.95 (d, \(J = 8.1\) Hz, 1H), 6.08 (s, 2H). \(^{13}\)C NMR (100 MHz, DMSO-d\(_6\)) \(\delta\) 167.15 (s), 151.65 (s), 147.99 (s), 125.48 (s), 109.31 (s), 108.58 (s), 102.46 (s).
12. NMR Spectra

11. Reference


$^1$H NMR spectra of 2 (400 MHz, CDCl₃)

$^{13}$C NMR spectra of 2 (100 MHz, CDCl₃)
$^1$H NMR spectra of 3 (500 MHz, DMSO-$d_6$)

$^{13}$C NMR spectra of 3 (125 MHz, DMSO-$d_6$)
H NMR spectra of 4 (500 MHz, DMSO-d$_6$)

$^1$H NMR spectra of 4 (500 MHz, DMSO-d$_6$)

$^1$C NMR spectra of 4 (125 MHz, DMSO-d$_6$)

$^1$C NMR spectra of 4 (125 MHz, DMSO-d$_6$)
$^1$H NMR spectra of 5 (500 MHz, DMSO-$_d_6$)

$^{13}$C NMR spectra of 5 (125 MHz, DMSO-$_d_6$)
\(^1\)H NMR spectra of 6 (500 MHz, DMSO-\(d_6\))

\(^{13}\)C NMR spectra of 6 (125 MHz, DMSO-\(d_6\))
\(^1H\) NMR spectra of 7 (500 MHz, DMSO-\(d_6\))

\(^{13}C\) NMR spectra of 7 (125 MHz, DMSO-\(d_6\))
\( ^1\text{H} \) NMR spectra of 8 (500 MHz, DMSO-\( \text{d}_6 \))

\( ^{13}\text{C} \) NMR spectra of 8 (125 MHz, DMSO-\( \text{d}_6 \))
$^1$H NMR spectra of 9 (500 MHz, CDCl$_3$)

$^{13}$C NMR spectra of 9 (125 MHz, CDCl$_3$)
H NMR spectra of 10 (500 MHz, DMSO-$d_6$)

$^{13}$C NMR spectra of 10 (125 MHz, DMSO-$d_6$)
$^1$H NMR spectra of 11 (500 MHz, CDCl$_3$)

$^{13}$C NMR spectra of 11 (125 MHz, CDCl$_3$)
$^{1}H$ NMR spectra of 12 (500 MHz, DMSO-$d_6$)

$^{13}C$ NMR spectra of 12 (125 MHz, DMSO-$d_6$)
$^1$H NMR spectra of 13 (500 MHz, CDCl$_3$)

$^{13}$C NMR spectra of 13 (125 MHz, CDCl$_3$)
1H NMR spectra of 14 (500 MHz, DMSO-d$_6$)

13C NMR spectra of 14 (125 MHz, DMSO-d$_6$)
$^1$H NMR spectra of 15 (500 MHz, DMSO-d$_6$)

$^{13}$C NMR spectra of 15 (125 MHz, DMSO-d$_6$)
$^1$H NMR spectra of 16 (500 MHz, DMSO-$d_6$)

$^{13}$C NMR spectra of 16 (125 MHz, DMSO-$d_6$)
$^1$H NMR spectra of 17 (500 MHz, DMSO-d$_6$)

$^{13}$C NMR spectra of 17 (125 MHz, DMSO-d$_6$)
$^1$H NMR spectra of 18 (500 MHz, CDCl$_3$)

$^{13}$C NMR spectra of 18 (125 MHz, CDCl$_3$)
$^1$H NMR spectra of 19 (500 MHz, DMSO-$d_6$)

$^{13}$C NMR spectra of 19 (125 MHz, DMSO-$d_6$)
$^1$H NMR spectra of 20 (500 MHz, DMSO-$d_6$)

$^{13}$C NMR spectra of 20 (125 MHz, DMSO-$d_6$)
$^1$H NMR spectra of 21 (500 MHz, DMSO-$d_6$)

$^{13}$C NMR spectra of 21 (125 MHz, DMSO-$d_6$)
$^1$H NMR spectra of 22 (500 MHz, DMSO-$d_6$)

$^{13}$C NMR spectra of 22 (125 MHz, DMSO-$d_6$)
$^1$H NMR spectra of 23 (500 MHz, DMSO-$d_6$)

$^1$C NMR spectra of 23 (125 MHz, DMSO-$d_6$)
$^1$H NMR spectra of 24 (500 MHz, DMSO-$d_6$)

$^{13}$C NMR spectra of 24 (125 MHz, DMSO-$d_6$)
$^1$H NMR spectra of 25 (500 MHz, CDCl$_3$)

$^{13}$C NMR spectra of 25 (125 MHz, CDCl$_3$)
$^1$H NMR spectra of 26 (500 MHz, CDCl$_3$)

$^{13}$C NMR spectra of 26 (125 MHz, CDCl$_3$)
$^1$H NMR spectra of 27 (500 MHz, DMSO-$d_6$)

$^{13}$C NMR spectra of 27 (125 MHz, DMSO-$d_6$)
$^1$H NMR spectra of 2 (500 MHz, CDCl$_3$)

$^{13}$C NMR spectra of 2 (125 MHz, CDCl$_3$)
$^1$H NMR spectra of 29 (500 MHz, CDCl$_3$)

$^{13}$C NMR spectra of 29 (125 MHz, CDCl$_3$)
H NMR spectra of 30 (500 MHz, CDCl₃)

$^{13}$C NMR spectra of 30 (125 MHz, CDCl₃)
H NMR spectra of 31 (500 MHz, DMSO-\textit{d}_6)

\textbf{13}C NMR spectra of 31 (125 MHz, DMSO-\textit{d}_6)
$^1$H NMR spectra of 32 (500 MHz, CDCl$_3$)

$^{13}$C NMR spectra of 32 (125 MHz, CDCl$_3$)
H NMR spectra of $3 (500 \text{ MHz, CDCl}_3)$

$^{13}$C NMR spectra of $3 (125 \text{ MHz, CDCl}_3)$
$^1$H NMR spectra of 34 (500 MHz, CDCl$_3$)

$^{13}$C NMR spectra of 34 (125 MHz, CDCl$_3$)
$^1$H NMR spectra of 35 (500 MHz, CDCl$_3$)

$^{13}$C NMR spectra of 35 (125 MHz, CDCl$_3$)
$^1$H NMR spectra of 36 (500 MHz, DMSO-$d_6$)

$^{13}$C NMR spectra of 36 (125 MHz, DMSO-$d_6$)
H NMR spectra of 37 (500 MHz, DMSO-d$_6$)

13C NMR spectra of 37 (125 MHz, DMSO-d$_6$)
$^1$H NMR spectra of 38 (500 MHz, DMSO-d$_6$)

$^{13}$C NMR spectra of 38 (125 MHz, DMSO-d$_6$)
\(^1\)H NMR spectra of 39 (500 MHz, DMSO-\textit{d}_6)

\(^{13}\)C NMR spectra of 39 (125 MHz, DMSO-\textit{d}_6)
$^1$H NMR spectra of 40 (500 MHz, DMSO-$d_6$)

$^{13}$C NMR spectra of 40 (125 MHz, DMSO-$d_6$)
H NMR spectra of 41 (500 MHz, DMSO-d$_6$)

$^{13}$C NMR spectra of 41 (125 MHz, DMSO-d$_6$)