Supporting Information

Salen-based hypercrosslinked polymer-supported Pd as an efficient and recyclable catalyst for C−H halogenation†

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1. General Information

All commercially available reagents were purchased from Sa-en Chemical Technology Co., Ltd. Sigma-Aldrich, Alfa Aesar, TCI, Acros, and Sinopharm Chemical Reagent Co., Ltd in the highest purity grade and used without further purification. Palladium (II) acetate (Pd content: >47.4%, reagent grade) was purchased from Shanxi Kaida Chemical Engineering Co., Ltd. All the analytical thin layer chromatography was performed on silica gel GF-254 (Qingdao Haiyang Chemical Co., Ltd, China). Visualization was carried out with UV light and Vogel’s permanganate. Unless otherwise noted, all reactions were run under air and the indicated reaction temperature was that of the oil bath. \(^1\)H NMR spectra were recorded on Bruker 400 MHz instrument operating at 400 MHz for \(^1\)H and 100 MHz for \(^{13}\)C acquisitions. Chemical shifts are reported in \(\delta\) ppm referenced to CDCl\(_3\) (\(\delta\) 7.26) for \(^1\)H NMR and CDCl\(_3\) (the center peak of a triplet at 77.0 ppm) for \(^{13}\)C NMR. The following abbreviations were used to explain multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet and br = broad. High-resolution mass spectra (HRMS) were recorded on a Bruker Daltonics microTOF II Mass Spectrometer. FT-IR spectra were obtained under ambient conditions in the wave number range of 4000-400 cm\(^{-1}\) using a Bruker VERTEX 70 FT-IR Spectrometer. The X-ray photoelectron spectroscopy (XPS) analysis was performed on a Thermo Fisher Scientific ESCALAB 250 using a monochromatic Al KR X-ray. Scanning electron microscopy (SEM) images were obtained on a GeminiSEM 300 at 10.0 kV. Thermogravimetric (TGA) data were recorded under air atmosphere with a heating rate of 10 °C/min on a PerkinElmer Diamond TG/DTA instrument. The Pd content in the poly-salen-Pd catalyst was determined using ICP-OES (iCAP7200, Thermo Fisher).

2. Experimental Section

2.1 Synthesis of salen

\[
\begin{align*}
&\text{Ethanol, } \text{N}_2 \\
&60 \degree C, 2.5h
\end{align*}
\]

The salen was prepared according to the reference.\(^1\) 0.61 g Ethylenediamine (10 mmol) and 2.49 g salicylaldehyde (20 mmol) were dissolved in 20 mL ethanol, respectively. Then, ethylenediamine solution was added to salicylaldehyde solution under N\(_2\) atmosphere. The mixture was stirred at 60 °C for 2.5 h. The resulting golden flake was washed with ethanol (30 mL) five times. The resulting product was finally dried at 60 °C under vacuum for 6 h. 2.30 g salen was obtained with yield of 85%.

2.2 Synthesis of poly-salen

\[
\begin{align*}
&\text{RT, 30 min} \\
&\text{AlCl}_3, \text{DCE}
\end{align*}
\]

The poly-salen was prepared according to the reference.\(^1\) 1.08 g salen (4 mmol) and 4.66 g dimethoxymethane (60 mmol) were dissolved in 10 mL 1,2-dichloroethane (DCE). Then, 1.58 g
benzene (20 mmol) was added into the above solutions. The resulting mixture was stirred at room temperature for 30 min, and then 8.08 g AlCl₃ (anhydrous, 60 mmol) was added to the solution. The mixture was stirred at 45 °C for 5 h to form original network and heated at 80 °C for 67 h. The precipitate was filtered and washed with methanol (50 mL), then the solid was washed with methanol in a Soxhlet for 24 h and dried under vacuum at 60 °C for 24 h (denoted as poly-salen).

### 2.3 Synthesis of poly-salen-Pd

![Poly-salen-Pd Synthesis Reaction](image)

0.12 g Pd(OAc)₂ (0.5 mmol) was dissolved in 100 mL CH₂Cl₂, then 1.29 g poly-salen was added to the above solution. The mixture was stirring at 50 °C for 12 h. The resulting solid was washed with CH₂Cl₂, methanol, and Soxlet-extration with CH₂Cl₂ for 48 h to remove the Pd(II) species that physisorbed on the support. The solid was dried at 60 °C under vacuum and poly-salen-Pd was obtained. The Pd content of poly-salen-Pd was 4.0 wt% as measured by ICP-OES.

### 2.4 Experimental procedure for Pd-catalyzed C−H halogenation

![Experimental Procedure for C−H Halogenation](image)

NBS (43.2 mg, 0.24 mmol) and poly-salen-Pd (26.6 mg, 5 mol%) were added to a solution of 2-phenylpyridine (31.4 mg, 0.2 mmol) in CH₃CN (2 mL). The reaction was heated at 100 °C for 12 h. After cooling to room temperature, it was diluted with EtOAc and washed with brine. The organic layer was filtered through celite, Na₂SO₄ and dried. The crude product was purified by flash chromatography (silica gel, 20% EtOAc/n-hexane) to give the product in isolated yield.

### 2.5 Experimental procedure for hot filtration

In order to determine whether the poly-salen-Pd was behaving in a truly heterogeneous pattern, or whether it is merely a reservoir for more active soluble Pd species, hot filtration test was adopted. In a typical run, poly-salen-Pd (26.6 mg), 2-phenylpyridine (31.4 mg, 0.2 mmol), NBS (43.2 mg, 0.24 mmol), CH₃CN (2 mL) were loaded in a sealed vial and stirred at 100 °C for 1 h. The solid catalyst was removed by filtration and the filtrate was continued to react for another 12 h under similar conditions. The amount of Pd content in filtrate was determined to be < 0.1 ppm. No significant increase in the product concentration was observed, indicating that the < 0.1 ppm of residual Pd that remains in reaction liquor is not adequate to catalyze the C−H halogenation. It is confirmed the heterogeneous nature of the catalytically active species.

### 2.6 Experimental procedure for catalyst recycling experiment

To a solution of 2-phenylpyridine (31.4 mg, 0.2 mmol) in CH₃CN (2 mL) reaction vial, was added NBS (43.2 mg, 0.24 mmol) and poly-salen-Pd (26.6 mg, 5 mol%). The vial was sealed and the reaction mixture was heated at 100 °C for 12 h. Upon the completion of the
reaction period, the mixture was diluted with 2 mL acetonitrile and shaken. The entire mixture was centrifuged and the solvent above the poly-salen-Pd was decanted. The washing and centrifugation were repeated for three additional times to ensure the removal of the organic products from the surface of the catalyst. The poly-salen-Pd was then reused for the subsequent reaction with the loading of fresh reagents (2-phenylpyridine, NBS, and acetonitrile). This procedure was applied for each recycling experiment and the isolated yield of the product was determined by flash chromatography.

2.7 Experimental procedure for Pd leaching test
Poly-salen-Pd (26.6 mg), 2-phenylpyridine (31.4 mg, 0.2 mmol), NBS (43.2 mg, 0.24 mmol), CH$_3$CN (2 mL) were loaded in a sealed vial and stirred at 100 °C for 12 h. Upon the completion of the reaction, the reaction mixture was then hot filtered over celite and the filtrate was subjected to ICP-OES analysis. The amount of Pd content was determined to 98 ppb. This means that the Pd leaching during the reaction period is negligible.

3. Characterization of poly-salen and poly-salen-Pd

![FT-IR spectra](image)

**Fig. S1** The FT-IR of poly-salen and poly-salen-Pd

The FT-IR spectra of poly-salen and poly-salen-Pd were displayed in Fig. S1. The peaks at 1442 cm$^{-1}$ and 1650 cm$^{-1}$ are the C=C stretching vibration of aromatic ring. The typical bands at 1272 cm$^{-1}$, 1606 cm$^{-1}$, 3440 cm$^{-1}$ are assigned for the C–O group, the C=N group and the O–H group in salen backbone, respectively. The FT-IR spectra of both the samples show the characteristic peak at 2920 cm$^{-1}$ due to the -CH$_2$- stretching vibration, which is the direct evidence for the successful formation of methylene crosslinking bridges throughout the poly-salen frameworks.

The morphology of the three samples was displayed in Fig. S2. The scanning electron micrograph (SEM) images exhibit that the poly-salen (Fig. S2 A) and poly-salen-Pd-fresh (Fig. S2 B) possesses abundant nanosheets. After tenth reaction cycle, some of the nanosheets have been broken and accumulated to form porous structure (Fig. S2 C).
Fig. S2 SEM of poly-salen(A) and poly-salen-Pd(B: fresh, C: used)
TGA was performed to test the stability of the sample under air atmosphere with a heating rate of 10 °C/min. According to Fig. S3, there is a slight weight loss about 5% below 300 °C for both poly-salen and poly-salen-Pd, which may be attributed to the release of physical absorbed water. The sharp weight loss of both had occurred around 320 °C, which means that the poly-salen-Pd has possessed excellent thermal stability.

Fig. S3 TGA of poly-salen and poly-salen-Pd

The XPS measure was used to probe the Pd oxidation state. The Pd 3d XPS of fresh catalyst could be deconvoluted into two pairs of doublets, which showed a mixture of Pd$^{II}$ and Pd$^{0}$ (Fig. S4). After reaction, only a pair of doublet with mainly Pd$^{II}$ species was present in the poly-salen-Pd-used catalyst.

Fig. S4 XPS of poly-salen-Pd-fresh and poly-salen-Pd-used
**Table S1** C–H bromination and chlorination of 2-phenylpyrimidine

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<td><img src="image17" alt="S=S S6-Br" /> <img src="image18" alt="S=S S6-Cl" /></td>
</tr>
</tbody>
</table>

*a*reaction conditions: substrate (0.2 mmol), poly-salen-Pd (5 %mol), NXS (1.2 equiv.), MeCN (2 mL), 100 °C, 12 h.
Table S2 The optimization of C–H bromination and chlorination of 2-phenylpyridine\textsuperscript{a}

\[
\text{poly-salen-Pd (5 mol\%)} \quad \text{solvent, time, temp.}
\]

<table>
<thead>
<tr>
<th>Entry</th>
<th>Temp. (°C)</th>
<th>Solvent \textsuperscript{b}</th>
<th>Time (h)</th>
<th>Yield (%)</th>
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<td>100</td>
<td>MeCN</td>
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</table>

\textsuperscript{a}reaction conditions: 2-phenylpyridine (0.2 mmol), poly-salen-Pd (5 %mol), NXS (1.2 equiv.), solvent (2 mL), temperature and time. \textsuperscript{b}MeCN: acetonitrile, DCE: 1,2-dichloroethane, HFIP: hexafluoroisopropanol, DCM: dichloromethane. \textsuperscript{c}salen-Pd (5 mol\%) was used as catalyst.
4. NMR Spectra of Products

2-(2-Bromo-phenyl)pyridine (1-Br)²:

\[
\begin{align*}
\text{H NMR (400 MHz, CDCl}_3\text{)): } & \delta 8.75 (d, J = 4.8 Hz, 1H), 7.82 (td, J = 7.6, 1.6 Hz, 1H), 7.64 (d, J = 8.0 Hz, 2H), 7.36-7.33 (m, 1H), 7.31 (d, J = 7.6 Hz, 1H), 7.12 (t, J = 8.0 Hz, 1H); \text{ } ^{13}\text{C NMR (100 MHz, CDCl}_3\text{)): } & \delta 158.39, 149.43, 141.19, 136.20, 133.46, 131.59, 129.97, 127.72, 125.04, 122.71, 121.95.
\end{align*}
\]

2-(2-Chloro-phenyl)pyridine (1-Cl)²:

\[
\begin{align*}
\text{H NMR (400 MHz, CDCl}_3\text{)): } & \delta 8.72 (d, J = 4.4 Hz, 1H), 7.77 (td, J = 7.6, 1.6 Hz, 1H), 7.65 (d, J = 8.0 Hz, 1H), 7.59 (dd, J = 7.2, 2.0 Hz, 1H), 7.48 (dd, J = 7.6, 1.6 Hz, 1H), 7.35 (td, J = 6.8, 2.0 Hz, 1H), 7.32-7.27 (m, 1H); \text{ } ^{13}\text{C NMR (100 MHz, CDCl}_3\text{)): } & \delta 156.97, 149.60, 139.17, 136.23, 132.35, 131.73, 130.30, 129.85, 127.20, 125.17, 122.69.
\end{align*}
\]

2-(2-Bromo-5-methoxyphenyl)pyridine (2-Br)⁴:

\[
\begin{align*}
\text{H NMR (400 MHz, CDCl}_3\text{)): } & \delta 8.70 (d, J = 4.4 Hz, 1H), 7.76 (td, J = 7.6, 0.8 Hz, 1H), 7.60 (d, J = 7.6 Hz, 1H), 7.53 (d, J = 8.8 Hz, 1H), 7.30 (t, J = 6.0 Hz, 1H), 7.07 (d, J = 2.8 Hz, 1H), 6.82 (dd, J = 8.8, 2.8 Hz, 1H), 3.81 (s, 3H); \text{ } ^{13}\text{C NMR (100 MHz, CDCl}_3\text{)): } & \delta 159.16, 158.41, 149.52, 136.07, 134.15, 124.97, 122.71, 116.53, 116.48, 112.33, 55.76.
\end{align*}
\]

2-(2-Chloro-5-methoxyphenyl)pyridine (2-Cl)⁵:

\[
\begin{align*}
\text{H NMR (400 MHz, CDCl}_3\text{)): } & \delta 8.73 (d, J = 4.4 Hz, 1H), 7.78 (td, J = 7.6, 1.2 Hz, 1H), 7.66 (d, J = 8.0 Hz, 1H), 7.36 (d, J = 8.8 Hz, 1H), 7.31 (t, J = 6.0 Hz, 1H), 7.13 (d, J = 2.8 Hz, 1H), 6.90 (dd, J = 8.8, 2.8 Hz, 1H), 3.83 (s, 3H); \text{ } ^{13}\text{C NMR (100 MHz, CDCl}_3\text{)): } & \delta 158.61, 156.98, 149.65, 139.98, 136.11, 131.07, 125.11, 123.67, 122.70, 116.33, 116.28, 55.83.
\end{align*}
\]
2-(2-Bromo-5-methylphenyl)pyridine (3-Br):

\[
\text{H NMR (400 MHz, CDCl}_3\text{): } \delta 8.71 (d, J = 4.0 \text{ Hz, 1H}), 7.77 (t, J = 7.2 \text{ Hz, 1H}), 7.61 (d, J = 7.6 \text{ Hz, 1H}), 7.54 (d, J = 8.4 \text{ Hz, 1H}), 7.35 (s, 1H), 7.30 (t, J = 6.2 \text{ Hz, 1H}), 7.07 (d, J = 7.6 \text{ Hz, 1H}), 2.35 \text{ (s, 3H); } ^{13}\text{C NMR (100 MHz, CDCl}_3\text{): } \delta 158.59, 149.54, 140.99, 137.73, 136.00, 133.22, 132.30, 130.80, 125.05, 122.57, 118.53, 21.04.\]

2-(2-Chloro-5-methylphenyl)pyridine (3-Cl):

\[
\text{H NMR (400 MHz, CDCl}_3\text{): } \delta 8.67 (d, J = 4.4 \text{ Hz, 1H}), 7.73-7.69 \text{ (m, 1H), 7.60 (d, J = 7.6 \text{ Hz, 1H}), 7.36 (s, 1H), 7.30 (d, J = 8.0 \text{ Hz 1H}), 7.25-7.23 \text{ (m, 1H), 7.09 (d, J = 7.2 Hz, 1H), 2.32 (s, 3H); } ^{13}\text{C NMR (100 MHz, CDCl}_3\text{): } \delta 157.14, 149.65, 138.86, 137.12, 136.03, 132.29, 130.57, 130.03, 129.20, 125.15, 122.54, 21.00.\]

2-(2-Bromo-6-methylphenyl)pyridine (4-Br):

\[
\text{H NMR (400 MHz, CDCl}_3\text{): } \delta 8.73 (d, J = 4.8 \text{ Hz, 1H}), 7.79 (td, J = 7.6 \text{ Hz, J = 2.0 Hz, 1H}), 7.49 (d, J = 8.0 \text{ Hz, 1H}), 7.27-7.31 \text{ (m, 2H), 7.22 (d, J = 7.6 Hz, 1H), 7.14 (t, J = 7.6 Hz, 1H), 2.09 (s, 3H); } ^{13}\text{C NMR (100 MHz, CDCl}_3\text{): } \delta 159.22, 149.72, 141.22, 138.78, 136.37, 130.26, 129.54, 129.34, 124.94, 123.18, 122.56, 20.89.\]

2-(2-Chloro-6-methylphenyl)pyridine (4-Cl):

\[
\text{H NMR (400 MHz, CDCl}_3\text{): } \delta 8.69 (d, J = 4.4 \text{ Hz, 1H}, 7.74 \text{ (td, J = 7.6 Hz, J = 1.6 Hz, 1H), 7.27-7.22 \text{ (m, 3H), 7.20-7.12 \text{ (m, 2H), 2.01 (s, 3H); } ^{13}\text{C NMR (100 MHz, CDCl}_3\text{): } \delta 157.69, 149.75, 139.33, 138.75, 136.55, 133.22, 129.20, 128.76, 127.08, 125.13, 122.53, 20.44.\]
2-(2-Bromo-4-methylphenyl)pyridine (5-Br)\(^7\): [Chemical structure image]

\(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta 8.70\) (d, \(J = 3.6\) Hz, 1H), \(7.75\) (t, \(J = 7.6\) Hz, 1H), \(7.60\) (d, \(J = 8.0\) Hz, 1H), \(7.51\) (s, 1H), \(7.43\) (d, \(J = 8.0\) Hz, 1H), \(7.29\) (d, \(J = 7.2\) Hz, 1H), \(7.21\) (d, \(J = 7.6\) Hz, 1H), \(2.38\) (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta 158.50, 149.52, 140.25, 138.48, 136.02, 133.92, 131.38, 128.58, 125.05, 122.46, 121.64, 21.04\).

2-(2-Chloro-4-methylphenyl)pyridine (5-Cl)\(^5\): [Chemical structure image]

\(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta 8.71\) (d, \(J = 4.0\) Hz, 1H), \(7.76\) (td, \(J = 7.6, 0.8\) Hz, 1H), \(7.64\) (d, \(J = 8.0\) Hz, 1H), \(7.49\) (d, \(J = 8.0\) Hz, 1H), \(7.30-7.26\) (m, 2H), \(7.17\) (d, \(J = 8.0\) Hz, 1H), \(2.38\) (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta 157.05, 149.62, 140.15, 136.39, 136.05, 131.96, 131.53, 130.74, 128.06, 125.13, 122.42, 21.14\).

2-(2-Bromo-4-florophenyl)pyridine (6-Br)\(^2\): [Chemical structure image]

\(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta 8.71\) (d, \(J = 4.0\) Hz, 1H), \(7.78\) (td, \(J = 7.6, 0.8\) Hz, 1H), \(7.59\) (d, \(J = 8.0\) Hz, 1H), \(7.53\) (td, \(J = 6.4, 2.0\) Hz, 1H), \(7.43\) (dd, \(J = 8.0, 2.0\) Hz, 1H), \(7.31\) (td, \(J = 6.0, 1.2\) Hz, 1H), \(7.14\) (td, \(J = 8.4, 2.4\) Hz, 1H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta 163.65, 161.14\) (d, \(J_{C-F} = 251.0\) Hz), \(157.60, 149.64, 137.70, 137.67\) (d, \(J_{C-F} = 3.0\) Hz, 1C), \(136.19, 132.77, 132.68\) (d, \(J_{C-F} = 9.0\) Hz, 1C), \(125.02, 122.78, 122.23\) (d, \(J_{C-F} = 55.0\) Hz, 1C), \(120.74, 120.50\) (d, \(J_{C-F} = 24.0\) Hz, 1C), \(115.14, 114.93\) (d, \(J_{C-F} = 21.0\) Hz, 1C).

2-(2-Chloro-4-florophenyl)pyridine (6-Cl)\(^8\): [Chemical structure image]

\(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta 8.72\) (d, \(J = 4.8\) Hz, 1H), \(7.78\) (td, \(J = 8.0, 0.8\) Hz, 1H), \(7.64-7.57\) (m, 2H), \(7.31\) (t, \(J = 6.2, 1H\)), \(7.23\) (dd, \(J = 8.4, 2.0\) Hz, 1H), \(7.10\) (td, \(J = 8.0, 2.0\) Hz, 1H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta 163.82, 161.32\) (d, \(J_{C-F} = 250.0\) Hz), \(156.12, 149.75, 136.21, 135.65, 135.61\) (d, \(J_{C-F} = 3.0, 1C\)), \(133.25, 133.15\) (d, \(J_{C-F} = 10.0\) Hz, 1C), \(133.03, 122.42\) (d, \(J_{C-F} = 9.0\) Hz, 1C), \(125.08, 122.72, 117.63, 117.39\) (d, \(J_{C-F} = 24.0\) Hz, 1C), \(114.69, 114.48\) (d, \(J_{C-F} = 21.0\) Hz, 1C).
2-(2-Bromo-4-methoxyphenyl)-4-methylpyridine (7-Br):

Light yellow oil, \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 8.54 (d, \(J = 4.8\) Hz, 1H), 7.45 (d, \(J = 8.8\) Hz, 1H), 7.39 (s, 1H), 7.20 (d, \(J = 2.0\) Hz, 1H), 7.09 (d, \(J = 4.4\) Hz, 1H), 6.94 (dd, \(J = 8.4, 2.4\) Hz, 1H), 3.84 (s, 3H), 2.41 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 160.13, 158.06, 149.13, 147.22, 132.22, 131.13, 129.05, 125.94, 123.36, 118.56, 113.86, 55.83, 21.36. HRMS (ESI-TOF): calcd. For C\(_{13}\)H\(_{12}\)BrNO [M+H]\(^+\) 278.0181, found 278.0185.

2-(2-Chloro-4-methoxyphenyl)-4-methylpyridine (7-Cl):

Light yellow oil, \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 8.54 (d, \(J = 4.8\) Hz, 1H), 7.51 (d, \(J = 6.4\) Hz, 1H), 7.44 (s, 1H), 7.08 (d, \(J = 4.4\) Hz, 1H), 2.41 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 160.22, 156.69, 149.33, 147.11, 132.93, 132.47, 132.04, 125.90, 123.25, 115.38, 113.37, 55.79, 21.35. HRMS (ESI-TOF): calcd. For C\(_{13}\)H\(_{12}\)ClNO [M+H]\(^+\) 234.0686, found 234.0688.

3-Bromo-4-(pyridine-2-yl)benzaldehyde (8-Br):

Light yellow oil, \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 10.03 (s, 1H), 8.76 (d, \(J = 3.6\) Hz, 1H), 8.20 (s, 1H), 7.92 (d, \(J = 7.6\) Hz, 1H), 7.85-7.81 (m, 1H), 7.72 (d, \(J = 7.6\) Hz, 1H), 7.65 (d, \(J = 7.2\) Hz, 1H), 7.37 (t, \(J = 6.0\) Hz, 1H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 190.70, 157.26, 149.82, 146.65, 137.42, 136.40, 134.68, 132.42, 128.66, 124.94, 123.40, 122.88. HRMS (ESI-TOF): calcd. For C\(_{12}\)H\(_8\)BrNO [M+H]\(^+\) 261.9868, found 261.9871.

3-Chloro-4-(pyridine-2-yl)benzaldehyde (8-Cl):

\(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 10.04 (s, 1H), 8.77 (d, \(J = 3.6\) Hz, 1H), 8.00 (s, 1H), 7.88 (dd, \(J = 8.0, 1.2\) Hz, 1H), 7.84-7.79 (m, 2H), 7.71 (d, \(J = 8.0\) Hz, 1H), 7.37 (t, \(J = 6.2\) Hz, 1H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 190.82, 155.77, 150.00, 144.66, 137.36, 136.35, 133.57, 132.64, 131.37, 128.16, 125.11, 123.38.
2-(2-Bromo-4-chlorophenyl)pyridine (9-Br): 

![Image of 2-(2-Bromo-4-chlorophenyl)pyridine (9-Br)]

\(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 8.72 (d, \(J = 3.6\) Hz, 1H), 7.79 (t, \(J = 7.6\) Hz, 1H), 7.70 (d, \(J = 1.6\) Hz, 1H), 7.60 (d, \(J = 7.6\) Hz, 1H), 7.48 (d, \(J = 8.0\) Hz, 1H), 7.40 (dd, \(J = 8.0\) Hz, 1.6 Hz, 1H), 7.33 (t, \(J = 6.4\) Hz, 1H); \(^1\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 157.46, 149.74, 139.91, 136.20, 135.10, 133.10, 132.43, 128.06, 124.94, 122.91, 122.32.

2-(2,4-dichlorophenyl)pyridine (9-Cl): 

![Image of 2-(2,4-dichlorophenyl)pyridine (9-Cl)]

\(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 8.72 (d, \(J = 4.0\) Hz, 1H), 7.78 (td, \(J = 7.6\) Hz, 1.2 Hz, 1H), 7.64 (d, \(J = 8.0\) Hz, 1H), 7.55 (d, \(J = 8.4\) Hz, 1H), 7.50 (d, \(J = 2.0\) Hz, 1H), 7.36 (dd, \(J = 8.0\) Hz, 1.6 Hz, 1H), 7.32 (t, \(J = 5.6\) Hz, 1H); \(^1\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 155.97, 149.85, 137.83, 136.24, 135.08, 133.10, 132.65, 130.10, 127.59, 125.05, 122.90.

2-(2-Chloro-5-fluorophenyl)pyridine (10-Cl): 

light yellow oil, \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 8.74 (d, \(J = 4.4\) Hz, 1H), 7.80 (td, \(J = 7.6\) Hz, 0.8 Hz, 1H), 7.64 (d, \(J = 8.0\) Hz, 1H), 7.38 (t, \(J = 7.6\) Hz, 1H), 7.35-7.32 (m, 2H), 7.21 (td, \(J = 8.0\) Hz, 0.8 Hz, 1H); \(^1\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 159.95, 157.48, 155.99, 155.96 (d, \(J_{C,F} = 4.0\) Hz, 1C), 149.86, 141.45, 136.28, 127.90, 127.82 (d, \(J_{C,F} = 8.0\) Hz, 1C), 126.86, 126.83 (d, \(J_{C,F} = 3.0\) Hz, 1C), 125.06, 123.02, 116.63, 116.42 (d, \(J_{C,F} = 21.0\) Hz, 1C). HRMS (ESI-TOF): calcd. For \(\text{C}_{11}\text{H}_{7}\text{ClF} \ [\text{M+H}]^+\) 208.0329, found 208.0333.

2-(2-Chloro-4-methoxyphenyl)pyridine (11-Cl): 

![Image of 2-(2-Chloro-4-methoxyphenyl)pyridine (11-Cl)]

\(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 8.70 (d, \(J = 4.4\) Hz, 1H), 7.74 (td, \(J = 7.6\) Hz, 1H), 7.65 (d, \(J = 8.0\) Hz, 1H), 7.55 (d, \(J = 8.4\) Hz, 1H), 7.25 (d, \(J = 4.8\) Hz, 1H), 7.02 (d, \(J = 2.0\) Hz, 1H), 6.92 (dd, \(J = 8.8\), 2.4 Hz, 1H), 3.85 (s, 3H); \(^1\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 160.34, 156.80, 149.60, 136.01, 132.96, 132.55, 131.86, 125.10, 122.20, 115.43, 113.46, 55.81.
1-(3-Chloro-4-(pyridin-2-yl)phenyl)ethanone (12-Cl):

![Diagram of 1-(3-Chloro-4-(pyridin-2-yl)phenyl)ethanone]

\[\text{H NMR (400 MHz, CDCl}_3\text{): } \delta 8.75 \text{ (d, } J = 4.0 \text{ Hz, 1H), 8.06 (s, 1H), 7.93 (d, } J = 8.0 \text{ Hz, 1H), 7.80 (td, } J = 7.6, 0.8 \text{ Hz, 1H), 7.73-7.68 (m, 2H), 7.34 (dd, } J = 5.6, 1.2 \text{ Hz, 1H), 2.64 (s, 3H); }\]

\[\text{13C NMR (100 MHz, CDCl}_3\text{): } \delta 196.75, 155.96, 149.93, 143.38, 138.18, 136.28, 133.01, 132.14, 130.32, 126.89, 125.09, 123.21, 26.95.\]

2-(2-Chloro-4-methylphenyl)-4-methylpyridine (13-Cl):

light yellow oil, \[\text{H NMR (400 MHz, CDCl}_3\text{): } \delta 8.55 \text{ (d, } J = 4.8 \text{ Hz, 1H), 7.72 (dd, } J = 3.6, 2.0 \text{ Hz, 1H), 7.49 (s, 1H), 7.39 (s, 1H), 7.19 (d, } J = 7.6 \text{ Hz, 1H), 7.10 (d, } J = 4.0 \text{ Hz, 1H), 2.42 (s, 3H), 2.38 (s, 3H); }\]

\[\text{13C NMR (100 MHz, CDCl}_3\text{): } \delta 158.35, 149.20, 147.19, 140.09, 133.85, 132.95, 131.30, 128.49, 125.84, 123.48, 121.66, 21.35, 21.02. \text{ HRMS (ESI-TOF): calcd. For C}_{13}\text{H}_{12}\text{ClN } [M+H]^+ 218.0737, \text{ found 208.0741.}\]

1-(3-Chloro-4-(4-methylpyridin-2-yl)phenyl)ethan-1-one (14-Cl):

light yellow oil, \[\text{H NMR (400 MHz, CDCl}_3\text{): } \delta 8.60 \text{ (d, } J = 4.8 \text{ Hz, 1H), 8.06 (d, } J = 1.2 \text{, 1H), 7.92 (dd, } J = 8.0, 1.2 \text{ Hz, 1H), 7.69 (d, } J = 8.0 \text{ Hz, 1H), 7.49 (s, 1H), 7.16 (d, } J = 4.4 \text{ Hz, 1H), 2.64 (s, 3H), 2.44(s, 3H); }\]

\[\text{13C NMR (100 MHz, CDCl}_3\text{): } \delta 196.79, 155.81, 149.58, 147.54, 143.56, 138.04, 132.98, 132.05, 130.24, 126.81, 125.85, 124.18, 26.91, 21.36. \text{ HRMS (ESI-TOF): calcd. For C}_{14}\text{H}_{12}\text{ClNO } [M+H]^+ 246.0686, \text{ found 246.0689.}\]

2-(2-bromophenyl)pyrimidine (S1-Br)

\[\text{H NMR (400 MHz, CDCl}_3\text{): } \delta 8.89 \text{ (d, } J = 4.8 \text{ Hz, 2H), 7.70 (t, } J = 7.6 \text{ Hz, 2H), 7.43 (t, } J = 7.6 \text{ Hz, 1H), 7.33-7.29 (m, 2H); }\]

\[\text{13C NMR (100 MHz, CDCl}_3\text{): } \delta 166.59, 157.09, 137.80, 134.70, 133.68, 130.46, 127.67, 120.50, 119.47. \text{ HRMS (ESI-TOF): calcd. For C}_{10}\text{H}_{7}\text{BrN}_2 [M+H]^+ 234.9871, \text{ found 234.9876.}\]
2-(2-chlorophenyl)pyrimidine (S1-Cl)

\[
\begin{align*}
\text{H NMR (400 MHz, CDCl}_3\text{): } & \delta 8.89 (d, J = 4.8 \text{ Hz}, 2\text{H}), 7.75-7.73 (m, 1\text{H}), 7.53-7.49 (m, 1\text{H}), \\
& 7.41-7.37 (m, 2\text{H}), 7.30 (t, J = 4.8 \text{ Hz}, 1\text{H}). \\
\text{C NMR (100 MHz, CDCl}_3\text{): } & \delta 165.70, 157.10, 137.80, 132.70, 131.70, 130.60, 130.51, 126.91, 119.40. \\
\text{HRMS (ESI-TOF): calcd. For C}_{10}\text{H}_7\text{ClN}_2\text{ [M+H]}^+ 191.0376, found 191.0380. 
\end{align*}
\]

2-(2-bromo-5-methoxyphenyl)pyrimidine (S2-Br)

\[
\begin{align*}
\text{H NMR (400 MHz, CDCl}_3\text{): } & \delta 8.90 (d, J = 4.8 \text{ Hz}, 2\text{H}), 7.58 (d, J = 8.8 \text{ Hz}, 1\text{H}), 7.32 (t, J = 4.8 \\
& \text{Hz}, 1\text{H}), 7.24 (d, J = 3.2 \text{ Hz}, 1\text{H}), 6.89 (dd, J = 8.8, 2.8 \text{ Hz}, 1\text{H}), 3.84 (s, 3\text{H}). \\
\text{C NMR (100 MHz, CDCl}_3\text{): } & \delta 166.60, 159.10, 157.26, 140.42, 134.70, 119.70, 117.40, 116.62, 112.20, 55.83. \\
\text{HRMS (ESI-TOF): calcd. For C}_{11}\text{H}_9\text{BrN}_2\text{O [M+H]}^+ 264.9977, found 264.9981. 
\end{align*}
\]

2-(2-chloro-5-methoxyphenyl)pyrimidine (S2-Cl)

\[
\begin{align*}
\text{H NMR (400 MHz, CDCl}_3\text{): } & \delta 8.90 (d, J = 5.2 \text{ Hz}, 2\text{H}), 7.40 (d, J = 8.8 \text{ Hz}, 1\text{H}), 7.32 (t, J = 4.8 \\
& \text{Hz}, 1\text{H}), 7.28 (d, J = 3.2 \text{ Hz}, 1\text{H}), 6.95 (dd, J = 8.8, 2.8 \text{ Hz}, 1\text{H}), 3.85 (s, 3\text{H}). \\
\text{C NMR (100 MHz, CDCl}_3\text{): } & \delta 165.76, 158.47, 157.28, 138.43, 131.60, 124.22, 119.64, 117.21, 116.46, 55.87. \\
\text{HRMS (ESI-TOF): calcd. For C}_{11}\text{H}_9\text{ClN}_2\text{O [M+H]}^+ 221.0482, found 221.0485. 
\end{align*}
\]

2-(2-bromo-4-methylphenyl)pyrimidine (S3-Br)

\[
\begin{align*}
\text{H NMR (400 MHz, CDCl}_3\text{): } & \delta 8.88 (d, J = 5.2 \text{ Hz}, 2\text{H}), 7.62 (d, J = 7.6 \text{ Hz}, 1\text{H}), 7.55 (s, 1\text{H}), \\
& 7.29 (t, J = 4.8 \text{ Hz}, 1\text{H}), 7.24 (d, J = 8.0 \text{ Hz}, 1\text{H}), 2.40 (s, 3\text{H}). \\
\text{C NMR (100 MHz, CDCl}_3\text{): } & \delta 166.69, 157.19, 141.25, 136.92, 134.48, 131.62, 128.45, 121.50, 119.40, 21.15. \\
\text{HRMS (ESI-TOF): calcd. For C}_{11}\text{H}_9\text{BrN}_2\text{ [M+H]}^+ 249.0027, found 249.0025. 
\end{align*}
\]
2-(2-chloro-4-methylphenyl)pyrimidine (S3-Cl)

\[
\text{N} \quad \begin{array}{c}
\text{Cl} \\
\text{Me}
\end{array} \\
\text{S3-Cl}
\]

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.88 (d, $J = 5.2$ Hz, 2H), 7.66 (d, $J = 8.0$ Hz, 1H), 7.34 (s, 1H), 7.28 (t, $J = 4.8$ Hz, 1H), 7.19 (d, $J = 8.0$ Hz, 1H), 2.40 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 165.84, 157.21, 141.23, 134.94, 132.54, 131.76, 131.28, 127.88, 119.33, 21.24. HRMS (ESI-TOF): calcd. For C$_{11}$H$_9$ClN$_2$ [M+H]$^+$ 205.0533, found 205.0537.

2-(2-bromo-4-fluorophenyl)pyrimidine (S4-Br)

\[
\text{N} \quad \begin{array}{c}
\text{Br} \\
\text{F}
\end{array} \\
\text{S4-Br}
\]

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.89 (d, $J = 4.8$ Hz, 2H), 7.74 (dd, $J = 6.0$, 2.8 Hz, 1H), 7.47 (dd, $J = 8.4$, 2.4 Hz, 1H), 7.32 (t, $J = 4.8$ Hz, 1H), 7.16 (td, $J = 8.0$, 2.4 Hz, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 165.86, 164.15, 161.64 (d, $J_{C-F} = 251$ Hz, 1C), 157.29, 136.09, 136.06 (d, $J_{C-F} = 3$ Hz, 1C), 133.21, 133.12 (d, $J_{C-F} = 9$ Hz, 1C), 122.38, 122.29 (d, $J_{C-F} = 9$ Hz, 1C), 121.39, 121.14 (d, $J_{C-F} = 25$ Hz, 1C), 119.66, 115.04, 114.83 (d, $J_{C-F} = 21$ Hz, 1C). HRMS (ESI-TOF): calcd. For C$_{10}$H$_6$BrFNN$_2$ [M+H]$^+$ 252.9777, found 252.9780.

2-(2-chloro-4-fluorophenyl)pyrimidine (S4-Cl)

\[
\text{N} \quad \begin{array}{c}
\text{Cl} \\
\text{F}
\end{array} \\
\text{S4-Cl}
\]

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.89 (d, $J = 5.2$ Hz, 2H), 7.78 (dd, $J = 6.0$, 2.4 Hz, 1H), 7.32 (t, $J = 4.8$ Hz, 1H), 7.29-7.26 (m, 1H), 7.11 (td, $J = 8.0$, 2.4 Hz, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 165.02, 163.78, 161.87 (d, $J_{C-F} = 191$ Hz, 1C), 157.33, 134.17, 134.15 (d, $J_{C-F} = 2$ Hz, 1C), 134.06, 133.94 (d, $J_{C-F} = 12$ Hz, 1C), 133.46, 133.37 (d, $J_{C-F} = 9$ Hz, 1C), 119.61, 118.28, 118.04 (d, $J_{C-F} = 24$ Hz, 1C), 114.56, 114.35 (d, $J_{C-F} = 21$ Hz, 1C). HRMS (ESI-TOF): calcd. For C$_{10}$H$_6$ClFN$_2$ [M+H]$^+$ 209.0282, found 209.0279.

2-(2-bromo-4-chlorophenyl)pyrimidine (S5-Br)

\[
\text{N} \quad \begin{array}{c}
\text{Br} \\
\text{Cl}
\end{array} \\
\text{S5-Br}
\]

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.90 (d, $J = 5.2$ Hz, 2H), 7.74 (d, $J = 1.6$ Hz, 1H), 7.69 (d, $J = 8.4$ Hz, 1H), 7.43 (dd, $J = 8.4$, 2.0 Hz, 1H), 7.33 (t, $J = 4.8$ Hz, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 165.78, 157.32, 138.19, 136.07, 133.68, 132.67, 127.94, 122.31, 119.79. HRMS (ESI-TOF): calcd. For C$_{10}$H$_6$BrClN$_2$ [M+H]$^+$ 268.9481, found 268.9485.
2-(2,4-dichlorophenyl)pyrimidine (S5-Cl)

\[
\begin{align*}
\text{H NMR (400 MHz, CDCl}_3\text{): } & \delta 8.90 (d, J = 4.8 \text{ Hz}, 2\text{H}), 7.73 (d, J = 8.4 \text{ Hz}, 1\text{H}), 7.54 (d, J = 1.6 \text{ Hz}, 1\text{H}), 7.38 (dd, J = 8.4, 2.0 \text{ Hz}, 1\text{H}), 7.32 (t, J = 4.8 \text{ Hz}, 1\text{H}). \\
\text{C NMR (100 MHz, CDCl}_3\text{): } & \delta 164.94, 157.35, 136.28, 136.11, 133.82, 132.89, 130.66, 127.41, 119.73. 
\end{align*}
\]

HRMS (ESI-TOF): calcd. For C\textsubscript{10}H\textsubscript{6}Cl\textsubscript{2}N\textsubscript{2}[M+H]+ 224.9986, found 224.9985.
5. Reference

6. NMR Spectra of Products

[Diagram of NMR spectra with assignments]

[Spectra showing chemical shifts and assignments for 1-Br]