

Supporting Information

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

Di Meng,[‡] Jiajun Bi,[‡] Yahao Dong, Bo Hao, Kaiwei Qin, Tao Li,* Dajian Zhu*

*Hubei Key laboratory of Material Chemistry and Service Failure; Key laboratory of Material Chemistry for Energy Conversion and Storage, Ministry of Education; School of Chemistry and Chemical Engineering, Huazhong University of Science and Technology, Wuhan 430074, China,
E-mail: taoli@hust.edu.cn(T. Li), zhudj@hust.edu.cn(D. Zhu)*

[‡]D. Meng and J. Bi contributed equally to this work.

Table of Contents

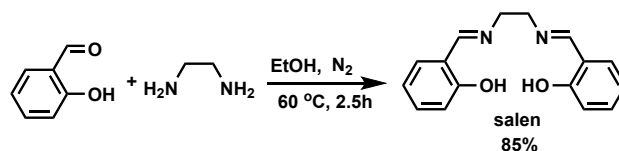
1. General Information	S2
2. Experimental Section	S2
2.1 Synthesis of salen	S2
2.2 Synthesis of poly-salen	S2
2.3 Synthesis of poly-salen-Pd	S3
2.4 Experimental Procedure for Pd-Catalyzed C–H halogenation	S3
2.5 Experimental Procedure for hot filtration	S3
2.6 Experimental Procedure for catalyst recycling experiment	S3
2.7 Experimental procedure for Pd leaching test	S3
3. Characterization of samples	S4
4. NMR Data of Products	S7
5. References	S18
6. NMR spectra of Products	S19

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. ^1H NMR spectra were recorded on Bruker 400 MHz instrument operating at 400 MHz for ^1H and 100 MHz for ^{13}C acquisitions. Chemical shifts are reported in δ ppm referenced to CDCl_3 (δ 7.26) for ^1H 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 $^{\circ}\text{C}/\text{min}$ on a PerkinElmer Diamond TG/DTA instrument. The Pd content in the poly-salen-Pd catalyst was determined using ICP-OES (iCAP7200, Thermo Fisher).

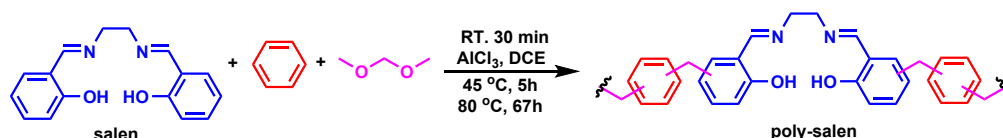
2. Experimental Section

2.1 Synthesis of salen



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 $^{\circ}\text{C}$ for 2.5 h. The resulting golden flake was washed with ethanol (30 mL) five times. The resulting product was finally dried at 60 $^{\circ}\text{C}$ under vacuum for 6 h. 2.30 g salen was obtained with yield of 85%.

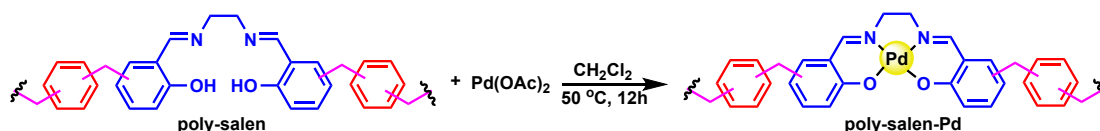
2.2 Synthesis of poly-salen



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

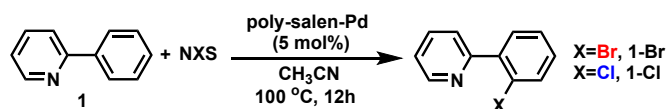
benzene (20 mmol) was added into the above solutions. The resulting mixture was stirred at room temperature for 30 min, and then 8.08 g AlCl_3 (anhydrous, 60 mmol) was added to the solution. The mixture was stirred at 45 °C for 5 h to form original network and heated at 80 °C for 67 h. The precipitate 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



0.12 g $\text{Pd}(\text{OAc})_2$ (0.5 mmol) was dissolved in 100 mL CH_2Cl_2 , then 1.29 g poly-salen was added to the above solution. The mixture was stirred at 50 °C for 12 h. The resulting solid was washed with CH_2Cl_2 , methanol, and Soxlet-extraction with CH_2Cl_2 for 48 h to remove the $\text{Pd}(\text{II})$ 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



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 CH_3CN (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, Na_2SO_4 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), CH_3CN (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 CH_3CN (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), CH₃CN (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

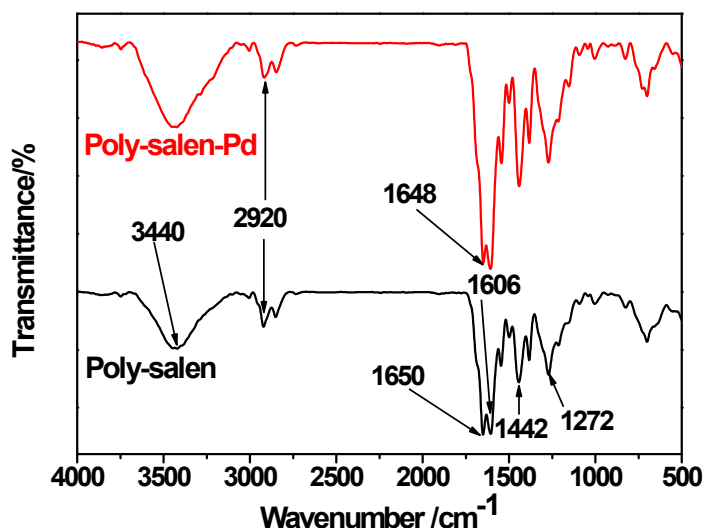


Fig. S1 The FT-IR of poly-salen and poly-salen-Pd

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 -CH₂- 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).

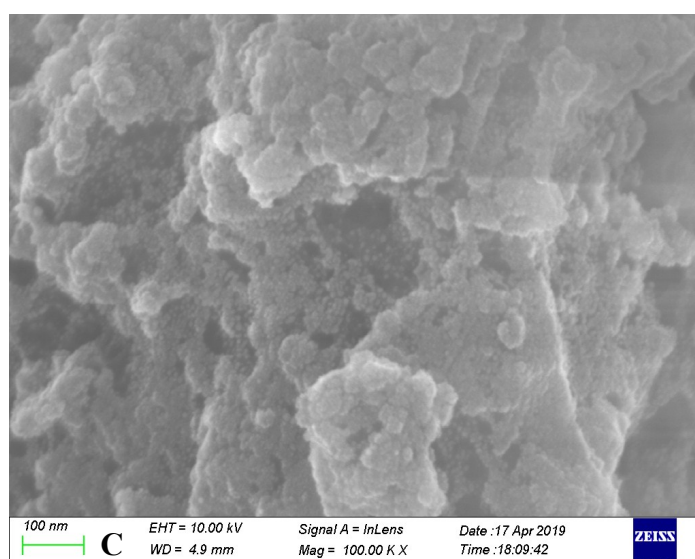
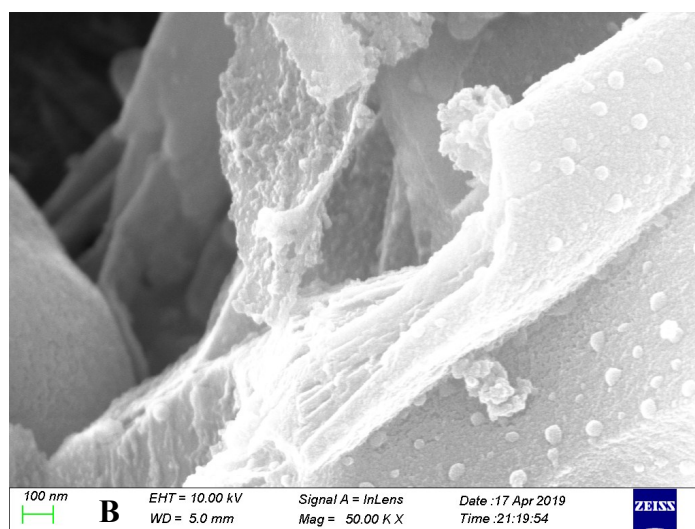
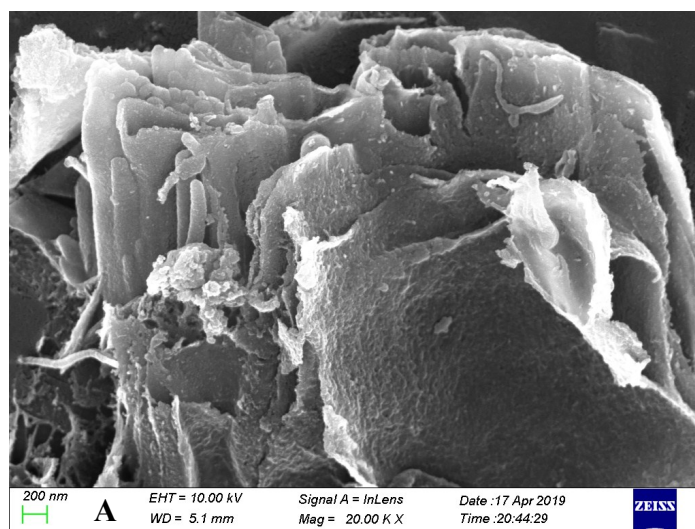


Fig. S2 SEM of poly-salen(A) and poly-salen-Pd(B:fresh, C:used)

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.

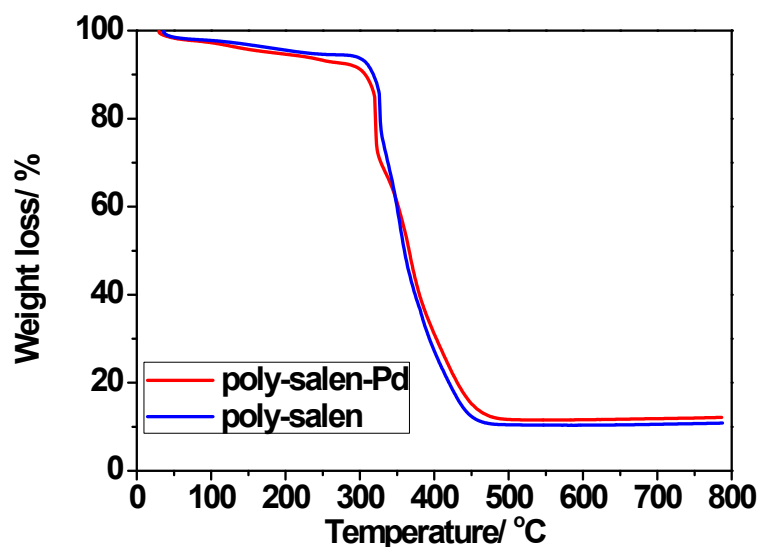


Fig. S3 TGA of poly-salen and poly-salen-Pd

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 Pd⁰ (Fig. S4). After reaction, only a pair of doublet with mainly Pd^{II} species was present in the poly-salen-Pd-used catalyst.

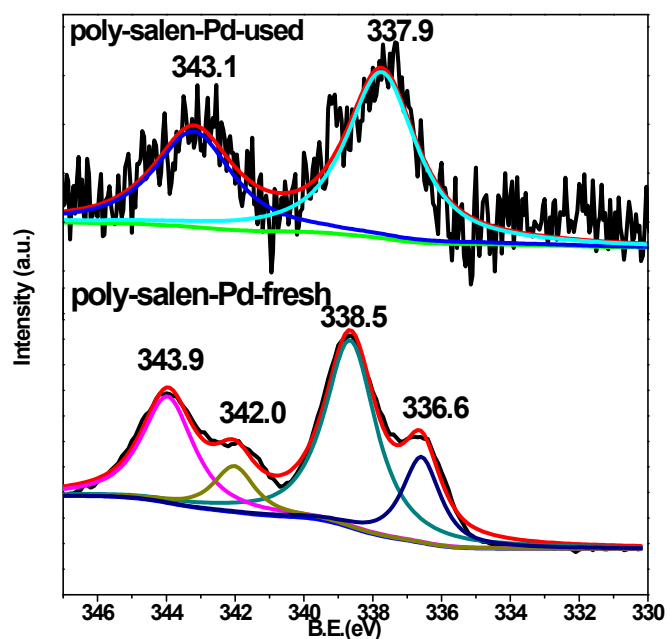
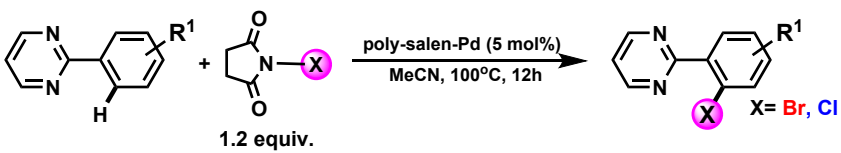
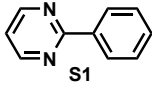
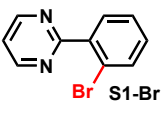
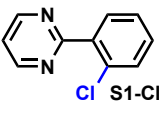
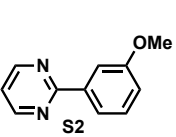
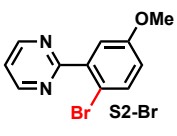
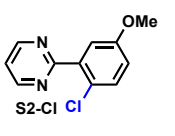
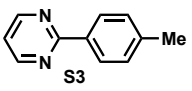
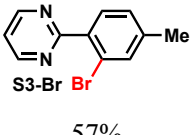
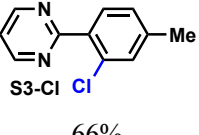
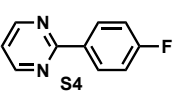
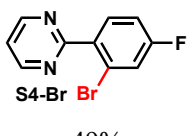
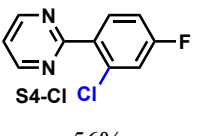
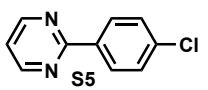
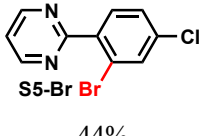
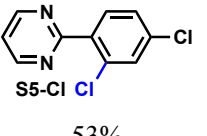
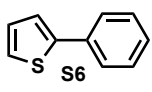
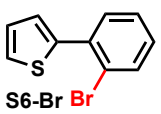
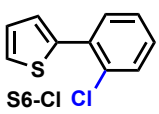


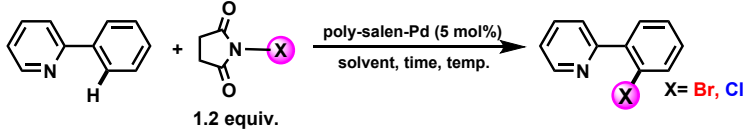
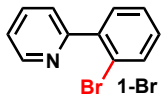
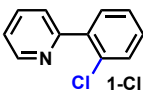
Fig. S4 XPS of poly-salen-Pd-fresh and poly-salen-Pd-used

Table S1 C–H bromination and chlorination of 2-phenylpyrimidine^a

		
Entry	Substrate	Product
1		 S1-Br 65%  S1-Cl 82%
2		 S2-Br 55%  S2-Cl 60%
3		 S3-Br 57%  S3-Cl 66%
4		 S4-Br 49%  S4-Cl 56%
5		 S5-Br 44%  S5-Cl 53%
6		 S6-Br trace  S6-Cl trace

^areaction conditions: substrate (0.2 mmol), poly-salen-Pd (5 %mol), NXS (1.2 equiv.), MeCN (2 mL), 100 °C, 12 h.

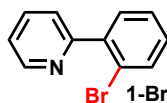
Table S2 The optimization of C–H bromination and chlorination of 2-phenylpyridine^a

					
Entry	Temp. (°C)	Solvent ^b	Time (h)	Yield (%)	
					
1	60	MeCN	12	47	43
2	80	MeCN	12	75	59
3	100	MeCN	12	90	71
4	120	MeCN	12	91	70
5	100	MeCN	8	73	55
6	100	MeCN	4	48	35
7	100	DCE	12	85	66
8	100	HFIP	12	36	32
9	100	DCM	12	trace	trace
10 ^c	100	MeCN	12	88	70

^areaction conditions: 2-phenylpyridine (0.2 mmol), poly-salen-Pd (5 %mol), NXS (1.2 equiv.), solvent (2 mL), temperature and time. ^bMeCN: acetonitrile, DCE: 1,2-dichloroethane, HFIP: hexafluoroisopropanol, DCM: dichloromethane. ^csalen-Pd (5 mol%) was used as catalyst.

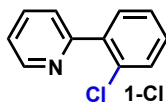
4. NMR Spectra of Products

2-(2-Bromo-phenyl)pyridine (1-Br)²:



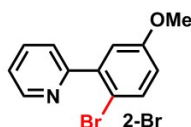
¹H NMR (400 MHz, CDCl₃): δ 8.75 (d, J = 4.8 Hz, 1H), 7.82 (td, J = 7.6, 1.6 Hz, 1H), 7.64 (d, J = 8.0 Hz, 2H), 7.36-7.33 (m, 1H), 7.31 (d, J = 7.6 Hz, 1H), 7.12 (t, J = 8.0 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 158.39, 149.43, 141.19, 136.20, 133.46, 131.59, 129.97, 127.72, 125.04, 122.71, 121.95.

2-(2-Chloro-phenyl)pyridine (1-Cl)³:



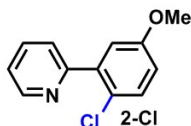
¹H NMR (400 MHz, CDCl₃): δ 8.72 (d, J = 4.4 Hz, 1H), 7.77 (td, J = 7.6, 1.6 Hz, 1H), 7.65 (d, J = 8.0 Hz, 1H), 7.59 (dd, J = 7.2, 2.0 Hz, 1H), 7.48 (dd, J = 7.6, 1.6 Hz, 1H), 7.35 (td, J = 6.8, 2.0 Hz, 1H), 7.32-7.27 (m, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 156.97, 149.60, 139.17, 136.23, 132.35, 131.73, 130.30, 129.85, 127.20, 125.17, 122.69.

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



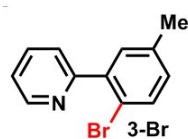
¹H NMR (400 MHz, CDCl₃): δ 8.70 (d, J = 4.4 Hz, 1H), 7.76 (td, J = 7.6, 0.8 Hz, 1H), 7.60 (d, J = 7.6 Hz, 1H), 7.53 (d, J = 8.8 Hz, 1H), 7.30 (t, J = 6.0 Hz, 1H), 7.07 (d, J = 2.8 Hz, 1H), 6.82 (dd, J = 8.8, 2.8 Hz, 1H), 3.81 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 159.16, 158.41, 149.52, 142.08, 136.07, 134.15, 124.97, 122.71, 116.53, 116.48, 112.33, 55.76.

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



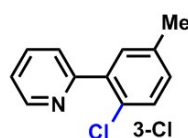
¹H NMR (400 MHz, CDCl₃): δ 8.73 (d, J = 4.4 Hz, 1H), 7.78 (td, J = 7.6, 1.2 Hz, 1H), 7.66 (d, J = 8.0 Hz, 1H), 7.36 (d, J = 8.8 Hz, 1H), 7.31 (t, J = 6.0 Hz, 1H), 7.13 (d, J = 2.8 Hz, 1H), 6.90 (dd, J = 8.8, 2.8 Hz, 1H), 3.83 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 158.61, 156.98, 149.65, 139.98, 136.11, 131.07, 125.11, 123.67, 122.70, 116.33, 116.28, 55.83.

2-(2-Bromo-5-methylphenyl)pyridine (3-Br)⁴:



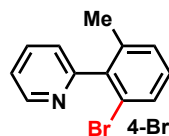
¹H NMR (400 MHz, CDCl₃): δ 8.71 (d, J = 4.0 Hz, 1H), 7.77 (t, J = 7.2 Hz, 1H), 7.61 (d, J = 7.6 Hz, 1H), 7.54 (d, J = 8.4 Hz, 1H), 7.35 (s, 1H), 7.30 (t, J = 6.2 Hz, 1H), 7.07 (d, J = 7.6 Hz, 1H), 2.35 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 158.59, 149.54, 140.99, 137.73, 136.00, 133.22, 132.30, 130.80, 125.05, 122.57, 118.53, 21.04.

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



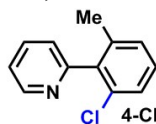
¹H NMR (400 MHz, CDCl₃): δ 8.67 (d, J = 4.4 Hz, 1H), 7.73-7.69 (m, 1H), 7.60 (d, J = 7.6 Hz, 1H), 7.36 (s, 1H), 7.30 (d, J = 8.0 Hz, 1H), 7.25-7.23 (m, 1H), 7.09 (d, J = 7.2 Hz, 1H), 2.32 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 157.14, 149.65, 138.86, 137.12, 136.03, 132.29, 130.57, 130.03, 129.20, 125.15, 122.54, 21.00.

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



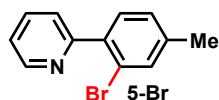
¹H NMR (400 MHz, CDCl₃): δ 8.73 (d, J = 4.8 Hz, 1H), 7.79 (td, J = 7.6 Hz, J = 2.0 Hz, 1H), 7.49 (d, J = 8.0 Hz, 1H), 7.27-7.31 (m, 2H), 7.22 (d, J = 7.6 Hz, 1H), 7.14 (t, J = 7.6 Hz, 1H), 2.09 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 159.22, 149.72, 141.22, 138.78, 136.37, 130.26, 129.54, 129.34, 124.94, 123.18, 122.56, 20.89.

2-(2-Chloro-6-methylphenyl)pyridine (4-Cl)³:



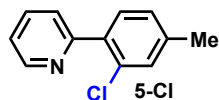
¹H NMR (400 MHz, CDCl₃): δ 8.69 (d, J = 4.4 Hz, 1H), 7.74 (td, J = 7.6 Hz, J = 1.6 Hz, 1H), 7.27-7.22 (m, 3H), 7.20-7.12 (m, 2H), 2.01 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 157.69, 149.75, 139.33, 138.75, 136.55, 133.22, 129.20, 128.76, 127.08, 125.13, 122.53, 20.44.

2-(2-Bromo-4-methylphenyl)pyridine (5-Br)⁷:



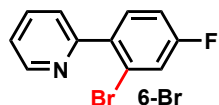
¹H NMR (400 MHz, CDCl₃): δ 8.70 (d, J = 3.6 Hz, 1H), 7.75 (t, J = 7.6 Hz, 1H), 7.60 (d, J = 8.0 Hz, 1H), 7.51 (s, 1H), 7.43 (d, J = 8.0 Hz, 1H), 7.29 (d, J = 7.2 Hz, 1H), 7.21 (d, J = 7.6 Hz, 1H), 2.38 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 158.50, 149.52, 140.25, 138.48, 136.02, 133.92, 131.38, 128.58, 125.05, 122.46, 121.64, 21.04.

2-(2-Chloro-4-methylphenyl)pyridine (5-Cl)⁵:



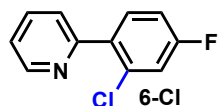
¹H NMR (400 MHz, CDCl₃): δ 8.71 (d, J = 4.0 Hz, 1H), 7.76 (td, J = 7.6, 0.8 Hz, 1H), 7.64 (d, J = 8.0 Hz, 1H), 7.49 (d, J = 8.0 Hz, 1H), 7.30-7.26 (m, 2H), 7.17 (d, J = 8.0 Hz, 1H), 2.38 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 157.05, 149.62, 140.15, 136.39, 136.05, 131.96, 131.53, 130.74, 128.06, 125.13, 122.42, 21.14.

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

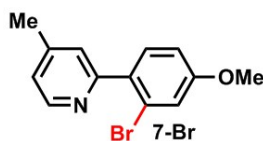


¹H NMR (400 MHz, CDCl₃): δ 8.71 (d, J = 4.0 Hz, 1H), 7.78 (td, J = 8.0, 1.2 Hz, 1H), 7.59 (d, J = 8.0 Hz, 1H), 7.53 (td, J = 6.4, 2.0 Hz, 1H), 7.43 (dd, J = 8.0, 2.0 Hz, 1H), 7.31 (td, J = 6.0, 1.2 Hz, 1H), 7.14 (td, J = 8.4, 2.4 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 163.65, 161.14 (d, J_{C-F} = 251.0 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).

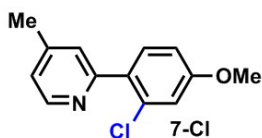
2-(2-Chloro-4-fluorophenyl)pyridine (6-Cl)⁸:



¹H NMR (400 MHz, CDCl₃): δ 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); ¹³C NMR (100 MHz, CDCl₃): δ 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} = 4.0 Hz, 1C), 133.25, 133.15 (d, J_{C-F} = 10.0 Hz, 1C), 133.03, 132.94 (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):

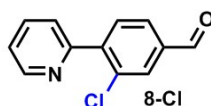
light yellow oil, ^1H NMR (400 MHz, CDCl_3): δ 8.54 (d, $J = 4.8$ Hz, 1H), 7.45 (d, $J = 8.8$ Hz, 1H), 7.39 (s, 1H), 7.20 (d, $J = 2.0$ Hz, 1H), 7.09 (d, $J = 4.4$ Hz, 1H), 6.94 (dd, $J = 8.4$ Hz, 2.4 Hz, 1H), 3.84 (s, 3H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 160.13, 158.06, 149.13, 147.22, 132.22, 131.13, 129.05, 125.94, 123.36, 118.56, 113.86, 55.83, 21.36. HRMS (ESI-TOF): calcd. For $\text{C}_{13}\text{H}_{12}\text{BrNO}$ $[\text{M}+\text{H}]^+$ 278.0181, found 278.0185.

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

light yellow oil, ^1H NMR (400 MHz, CDCl_3): δ 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), 7.01 (s, 1H), 6.90 (d, $J = 8.4$ Hz, 1H), 3.84 (s, 3H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 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 $\text{C}_{13}\text{H}_{12}\text{ClNO}$ $[\text{M}+\text{H}]^+$ 234.0686, found 234.0688.

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

light yellow oil, ^1H NMR (400 MHz, CDCl_3): δ 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): δ 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 $\text{C}_{12}\text{H}_8\text{BrNO}$ $[\text{M}+\text{H}]^+$ 261.9868, found 261.9871.

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

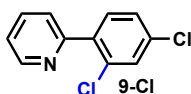
^1H NMR (400 MHz, CDCl_3): δ 10.04 (s, 1H), 8.77 (d, $J = 3.6$ Hz, 1H), 8.00 (s, 1H), 7.88 (dd, $J = 8.0, 1.2$ Hz, 1H), 7.84-7.79 (m, 2H), 7.71 (d, $J = 8.0$ Hz, 1H), 7.37 (t, $J = 6.2$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 190.82, 155.77, 150.00, 144.66, 137.36, 136.35, 133.57, 132.64, 131.37, 128.16, 125.11, 123.38.

2-(2-Bromo-4-chlorophenyl)pyridine (9-Br)¹⁰:



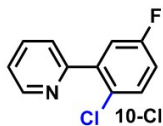
¹H NMR (400 MHz, CDCl₃): δ 8.72 (d, J = 3.6 Hz, 1H), 7.79 (t, J = 7.6 Hz, 1H), 7.70 (d, J = 1.6 Hz, 1H), 7.60 (d, J = 7.6, 1H), 7.48 (d, J = 8.0 Hz, 1H), 7.40 (dd, J = 8.0 Hz, 1.6 Hz, 1H), 7.33 (t, J = 6.4 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 157.46, 149.74, 139.91, 136.20, 135.10, 133.10, 132.43, 128.06, 124.94, 122.91, 122.32.

2-(2,4-dichlorophenyl)pyridine (9-Cl)⁵:



¹H NMR (400 MHz, CDCl₃): δ 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, 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); ¹³C NMR (100 MHz, CDCl₃): δ 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):



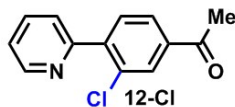
light yellow oil, ¹H NMR (400 MHz, CDCl₃): δ 8.74 (d, J = 4.4 Hz, 1H), 7.80 (td, J = 7.6, 0.8 Hz, 1H), 7.64 (d, J = 8.0 Hz, 1H), 7.38 (t, J = 7.6 Hz, 1H), 7.35-7.32 (m, 2H), 7.21 (td, J = 8.0, 0.8 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 159.95, 157.48, 155.99, 155.96 (d, J_{C-F} = 4.0 Hz, 1C), 149.86, 141.45, 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 C₁₁H₇ClFN [M+H]⁺ 208.0329, found 208.0333.

2-(2-Chloro-4-methoxyphenyl)pyridine (11-Cl)⁵:



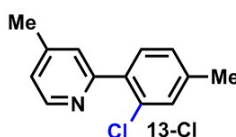
¹H NMR (400 MHz, CDCl₃): δ 8.70 (d, J = 4.4 Hz, 1H), 7.74 (td, J = 7.6, 1.2 Hz, 1H), 7.65 (d, J = 8.0 Hz, 1H), 7.55 (d, J = 8.4 Hz, 1H), 7.25 (d, J = 4.8 Hz, 1H), 7.02 (d, J = 2.0 Hz, 1H), 6.92 (dd, J = 8.8, 2.4 Hz, 1H), 3.85 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 160.34, 156.80, 149.60, 136.01, 132.96, 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)⁵:



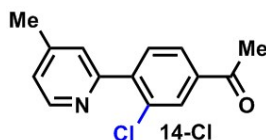
¹H NMR (400 MHz, CDCl₃): δ 8.75 (d, J = 4.0 Hz, 1H), 8.06 (s, 1H), 7.93 (d, J = 8.0 Hz, 1H), 7.80 (td, J = 7.6, 0.8 Hz, 1H), 7.73-7.68 (m, 2H), 7.34 (dd, J = 5.6, 1.2 Hz, 1H), 2.64 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 196.75, 155.96, 149.93, 143.38, 138.18, 136.28, 133.01, 132.14, 130.32, 126.89, 125.09, 123.21, 26.95.

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



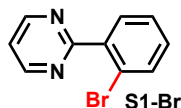
light yellow oil, ¹H NMR (400 MHz, CDCl₃): δ 8.55 (d, J = 4.8 Hz, 1H), 7.72 (dd, J = 3.6, 2.0 Hz, 1H), 7.49 (s, 1H), 7.39 (s, 1H), 7.19 (d, J = 7.6 Hz, 1H), 7.10 (d, J = 4.0 Hz, 1H), 2.42 (s, 3H), 2.38 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 158.35, 149.20, 147.19, 140.09, 133.85, 132.95, 131.30, 128.49, 125.84, 123.48, 121.66, 21.35, 21.02. HRMS (ESI-TOF): calcd. For C₁₃H₁₂ClN [M+H]⁺ 218.0737, found 208.0741.

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



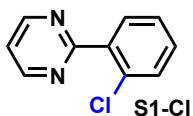
light yellow oil, ¹H NMR (400 MHz, CDCl₃): δ 8.60 (d, J = 4.8 Hz, 1H), 8.06 (d, J = 1.2, 1H), 7.92 (dd, J = 8.0, 1.2 Hz, 1H), 7.69 (d, J = 8.0 Hz, 1H), 7.49 (s, 1H), 7.16 (d, J = 4.4 Hz, 1H), 2.64 (s, 3H), 2.44 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 196.79, 155.81, 149.58, 147.54, 143.56, 138.04, 132.98, 132.05, 130.24, 126.81, 125.85, 124.18, 26.91, 21.36. HRMS (ESI-TOF): calcd. For C₁₄H₁₂ClNO [M+H]⁺ 246.0686, found 246.0689.

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



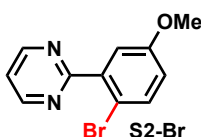
¹H NMR (400 MHz, CDCl₃): δ 8.89 (d, J = 4.8 Hz, 2H), 7.70 (t, J = 7.6 Hz, 2H), 7.43 (t, J = 7.6 Hz, 1H), 7.33-7.29 (m, 2H); ¹³C NMR (100 MHz, CDCl₃): δ 166.59, 157.09, 137.80, 134.70, 133.68, 130.46, 127.67, 120.50, 119.47. HRMS (ESI-TOF): calcd. For C₁₀H₇BrN₂ [M+H]⁺ 234.9871, found 234.9876.

2-(2-chlorophenyl)pyrimidine (S1-Cl)



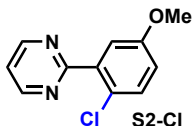
^1H NMR (400 MHz, CDCl_3): δ 8.89 (d, $J = 4.8$ Hz, 2H), 7.75-7.73 (m, 1H), 7.53-7.49 (m, 1H), 7.41-7.37 (m, 2H), 7.30 (t, $J = 4.8$ Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3): δ 165.70, 157.10, 137.80, 132.70, 131.70, 130.60, 130.51, 126.91, 119.40. HRMS (ESI-TOF): calcd. For $\text{C}_{10}\text{H}_7\text{ClN}_2$ $[\text{M}+\text{H}]^+$ 191.0376, found 191.0380.

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



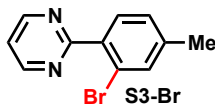
^1H NMR (400 MHz, CDCl_3): δ 8.90 (d, $J = 4.8$ Hz, 2H), 7.58 (d, $J = 8.8$ Hz, 1H), 7.32 (t, $J = 4.8$ Hz, 1H), 7.24 (d, $J = 3.2$ Hz, 1H), 6.89 (dd, $J = 8.8, 2.8$ Hz, 1H), 3.84 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 166.60, 159.10, 157.26, 140.42, 134.70, 119.70, 117.40, 116.62, 112.20, 55.83. HRMS (ESI-TOF): calcd. For $\text{C}_{11}\text{H}_9\text{BrN}_2\text{O}$ $[\text{M}+\text{H}]^+$ 264.9977, found 264.9981.

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



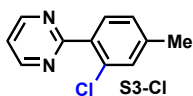
^1H NMR (400 MHz, CDCl_3): δ 8.90 (d, $J = 5.2$ Hz, 2H), 7.40 (d, $J = 8.8$ Hz, 1H), 7.32 (t, $J = 4.8$ Hz, 1H), 7.28 (d, $J = 3.2$ Hz, 1H), 6.95 (dd, $J = 8.8, 2.8$ Hz, 1H), 3.85 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 165.76, 158.47, 157.28, 138.43, 131.60, 124.22, 119.64, 117.21, 116.46, 55.87. HRMS (ESI-TOF): calcd. For $\text{C}_{11}\text{H}_9\text{ClN}_2\text{O}$ $[\text{M}+\text{H}]^+$ 221.0482, found 221.0485.

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



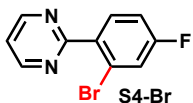
^1H NMR (400 MHz, CDCl_3): δ 8.88 (d, $J = 5.2$ Hz, 2H), 7.62 (d, $J = 7.6$ Hz, 1H), 7.55 (s, 1H), 7.29 (t, $J = 4.8$ Hz, 1H), 7.24 (d, $J = 8.0$ Hz, 1H), 2.40 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 166.69, 157.19, 141.25, 136.92, 134.48, 131.62, 128.45, 121.50, 119.40, 21.15. HRMS (ESI-TOF): calcd. For $\text{C}_{11}\text{H}_9\text{BrN}_2$ $[\text{M}+\text{H}]^+$ 249.0027, found 249.0025.

2-(2-chloro-4-methylphenyl)pyrimidine (S3-Cl)



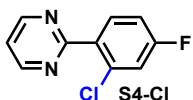
^1H NMR (400 MHz, CDCl_3): δ 8.88 (d, J = 5.2 Hz, 2H), 7.66 (d, J = 8.0 Hz, 1H), 7.34 (s, 1H), 7.28 (t, J = 4.8 Hz, 1H), 7.19 (d, J = 8.0 Hz, 1H), 2.40 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 165.84, 157.21, 141.23, 134.94, 132.54, 131.76, 131.28, 127.88, 119.33, 21.24. HRMS (ESI-TOF): calcd. For $\text{C}_{11}\text{H}_9\text{ClN}_2$ $[\text{M}+\text{H}]^+$ 205.0533, found 205.0537.

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



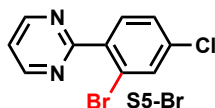
^1H NMR (400 MHz, CDCl_3): δ 8.89 (d, J = 4.8 Hz, 2H), 7.74 (dd, J = 6.0, 2.8 Hz, 1H), 7.47 (dd, J = 8.4, 2.4 Hz, 1H), 7.32 (t, J = 4.8 Hz, 1H), 7.16 (td, J = 8.0, 2.4 Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3): δ 165.86, 164.15, 161.64 (d, $J_{\text{C-F}}$ = 251 Hz, 1C), 157.29, 136.09, 136.06 (d, $J_{\text{C-F}}$ = 3 Hz, 1C), 133.21, 133.12 (d, $J_{\text{C-F}}$ = 9 Hz, 1C), 122.38, 122.29 (d, $J_{\text{C-F}}$ = 9 Hz, 1C), 121.39, 121.14 (d, $J_{\text{C-F}}$ = 25 Hz, 1C), 119.66, 115.04, 114.83 (d, $J_{\text{C-F}}$ = 21 Hz, 1C). HRMS (ESI-TOF): calcd. For $\text{C}_{10}\text{H}_6\text{BrFN}_2$ $[\text{M}+\text{H}]^+$ 252.9777, found 252.9780.

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



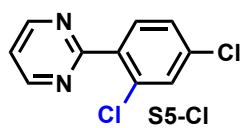
^1H NMR (400 MHz, CDCl_3): δ 8.89 (d, J = 5.2 Hz, 2H), 7.78 (dd, J = 6.0, 2.4 Hz, 1H), 7.32 (t, J = 4.8 Hz, 1H), 7.29-7.26 (m, 1H), 7.11 (td, J = 8.0, 2.4 Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3): δ 165.02, 163.78, 161.87 (d, $J_{\text{C-F}}$ = 191 Hz, 1C), 157.33, 134.17, 134.15 (d, $J_{\text{C-F}}$ = 2 Hz, 1C), 134.06, 133.94 (d, $J_{\text{C-F}}$ = 12 Hz, 1C), 133.46, 133.37 (d, $J_{\text{C-F}}$ = 9 Hz, 1C), 119.61, 118.28, 118.04 (d, $J_{\text{C-F}}$ = 24 Hz, 1C), 114.56, 114.35 (d, $J_{\text{C-F}}$ = 21 Hz, 1C). HRMS (ESI-TOF): calcd. For $\text{C}_{10}\text{H}_6\text{ClFN}_2$ $[\text{M}+\text{H}]^+$ 209.0282, found 209.0279.

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



^1H NMR (400 MHz, CDCl_3): δ 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): δ 165.78, 157.32, 138.19, 136.07, 133.68, 132.67, 127.94, 122.31, 119.79. HRMS (ESI-TOF): calcd. For $\text{C}_{10}\text{H}_6\text{BrClN}_2$ $[\text{M}+\text{H}]^+$ 268.9481, found 268.9485.

2-(2,4-dichlorophenyl)pyrimidine (S5-Cl)



^1H NMR (400 MHz, CDCl_3): δ 8.90 (d, $J = 4.8$ Hz, 2H), 7.73 (d, $J = 8.4$ Hz, 1H), 7.54 (d, $J = 1.6$ Hz, 1H), 7.38 (dd, $J = 8.4, 2.0$ Hz, 1H), 7.32 (t, $J = 4.8$ Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3): δ 164.94, 157.35, 136.28, 136.11, 133.82, 132.89, 130.66, 127.41, 119.73. HRMS (ESI-TOF): calcd. For $\text{C}_{10}\text{H}_6\text{Cl}_2\text{N}_2$ $[\text{M}+\text{H}]^+$ 224.9986, found 224.9985.

5. Reference

- 1 J. Bi, Y. Dong, D. Meng, D. Zhu and T. Li, *Polymer*, 2019, **164**, 183.
- 2 S. Mo, Y. Zhu and Z. Shen, *Org. Biomol. Chem.*, 2013, **11**, 2756.
- 3 X. Chen, X.-S. Hao, C. E. Goodhue and J.-Q. Yu, *J. Am. Chem. Soc.*, 2006, **128**, 6790.
- 4 D. Kalyani, A. R. Dick, W. Q. Anani and M. S. Sanford, *Tetrahedron*, 2006, **62**, 11483.
- 5 G. Zhang, S. Sun, F. Yang, Q. Zhang, J. Kang, Y. Wu and Y. Wu, *Adv. Synth. Catal.*, 2015, **357**, 443.
- 6 Q. Wu, C. Du, Y. Huang, X. Liu, Z. Long, F. Song and J. You, *Chem. Sci.*, 2015, **6**, 288.
- 7 A. Maity, B. L. Anderson, N. Deligonul and T. G. Gray, *Chem. Sci.*, 2013, **4**, 1175.
- 8 V. Botla, A. Akudari and C. Malapaka, *Tetrahedron Lett.*, 2019, **60**, 115.
- 9 D. Kalyani, A. R. Dick, W. Q. Anani and M. S. Sanford, *Org. Lett.*, 2006, **8**, 2523.
- 10 L. Niu, H. Yang, D. Yang and H. Fu, *Adv. Synth. Catal.*, 2012, **354**, 2211.

6. NMR Spectra of Products

