## **Bifunctional Ru-loaded Porous Organic Polymers with Pyridine Functionality: Recyclable Catalysts for N-Formylation of Amines** with CO<sub>2</sub> and H<sub>2</sub>

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Abstract: A series of pyridine functionalized porous organic polymers (POPs-Py&PPh<sub>3</sub>) have been synthesized by polymerizing tris(4-vinylphenyl) phosphane and 4-vinylpyridine. The pyridine moieties in the copolymer materials contribute to CO<sub>2</sub> adsorption and promote the subsequent conversion of CO<sub>2</sub>. The POP supported Ru catalyst (Ru/POP<sub>3</sub>-Py&PPh<sub>3</sub>) shows a high catalytic activity (TON up to 710) in the N-formylation of various primary and secondary amines with CO<sub>2</sub>/H<sub>2</sub>, affording the corresponding formamides in good yields (55-95%) under mild reaction conditions. The heterogeneous catalyst can be easily separated from the reaction system and reused for at least eight cycles in the Nformylation of morpholine.

Keywords: porous organic polymers; N-formylation; formamides; ruthenium; heterogeneous catalysis

Formamide compounds are important chemicals with widespread applications in the industry, which not only can be used as solvents and raw materials for the synthesis of high value-added fine chemicals, biological intermediates, and pharmaceuticals,<sup>[1]</sup> but also can be used as Lewis base organocatalysts in synthetic transformations.<sup>[2]</sup> Among the methods for the synthesis of formamides, N-formylation of amines with gas carbonyl sources (such as  $CO_2$  and  $CO^{[3]}$ ) and reducing reagents in the presence of catalysts has attracted long-term interest owing to high atom efficiency. As an abundant and cheap C1 building block, CO<sub>2</sub> is nontoxic and exhibits higher security than CO in organic synthesis. Furthermore, compared with the expensive reducing reagents of organic silicones,<sup>[4]</sup> hydrogen is more abundant and economical. Therefore, catalyzed N-formylation of amines with CO<sub>2</sub>/H<sub>2</sub> as the formylating reagent afforded a green route for the synthesis of formamides. Since Haynes first reported the preparation of dimethylformamide from dimethylamine and CO2/H2 in 1970,<sup>[5]</sup> a series of homogeneous catalysts based on the complex of Ru,<sup>[6]</sup> Fe,<sup>[7]</sup> Co,<sup>[8]</sup> Pd,<sup>[9]</sup> and Pt<sup>[10]</sup> have been developed for the N-formylation of amines with CO<sub>2</sub>/ H<sub>2</sub>.

However, heterogeneous catalysts generally possess significant advantages in terms of recyclability and catalyst separation, and thus, they are more desirable for industrial applications. Inorganic materials (e.g., metallic oxides, carbon)-supported metal catalysts have been reported, such as Cu/ZnO,<sup>[11]</sup> Ir/HSA-TiO<sub>2</sub> surface area),<sup>[12]</sup> Au/TiO<sub>2</sub>,<sup>[13]</sup> (HAS, high Pd/ Al<sub>2</sub>O<sub>3</sub>–NR–RD (NR, nanorod; RD, reductive deposition),<sup>[14]</sup> Pd/NC (NC, N-doped carbons),<sup>[15]</sup> Pd/ Palygorskite,<sup>[16]</sup> and Pd/Mg–Al LDH (Mg–Al layered double hydroxide).<sup>[17]</sup> In addition, composite material and metal-organic framework material-immobilized catalysts have also been developed for the N-formylation of amines with  $CO_2/H_2$ .<sup>[18]</sup> In recent years, porous organic polymers (POPs) have received great attention for their application as the supporting materials of catalysts in heterogeneous reaction systems owing to the high surface areas, excellent thermal stabilities, and structural diversities.<sup>[19]</sup> Mesoporous imine-functionalized POP-supported Pd catalyst (Imine-POP@Pd)<sup>[20]</sup> and pyridine-functionalized POP-immobilized Ru (CarPy-CMP@Ru)<sup>[21]</sup> were developed for the N-formylation of amines with  $CO_2/H_2$  by Liu's group. More recently, Ding and Yan reported а Ru-PPh<sub>3</sub>-SO<sub>3</sub>Na@POP catalyst that incorporated SO<sub>3</sub>Na as the base for the N-formylation of amines, which was mainly effective for the N-formylation of secondary aliphatic amines.<sup>[22]</sup> Alkali is generally required as a co-catalyst in the N-formylation of



amines with CO<sub>2</sub>/H<sub>2</sub>, and it is difficult to be recovered in a homogeneous reaction. It seems that the alkali not only can be reused in a heterogeneous system, but also the species and amount of alkali in supporting materials affect the catalytic activity and substrate scope. Herein, we report a series of pyridine-doped PPh<sub>3</sub>-based POPs (POPs-Py&PPh<sub>3</sub>), in which both the doped "CO<sub>2</sub>-philic" pyridine moieties and the PPh<sub>3</sub> based porous framework could increase the CO<sub>2</sub> adsorption.<sup>[23]</sup> The alkaline pyridine moieties further facilitate the subsequent conversion of CO<sub>2</sub> to formic acid salt by shifting the thermodynamic equilibrium of the CO<sub>2</sub> hydrogenation.<sup>[6a,24]</sup> The copolymer supported Ru catalyst (Ru/POP<sub>3</sub>-Py&PPh<sub>3</sub>) exhibited high activities (TON up to 710) in the N-formylation of primary and secondary amines under relatively mild CO<sub>2</sub> and  $H_2$  pressures (2/2 MPa) to afford the formamides with good yields (55-95%).

As shown in Scheme 1, a series of POPs-Py&PPh<sub>3</sub> including different molar ratios of PPh<sub>3</sub> and pyridine moieties (m:n=1:1, 3:1, and 5:1), were prepared by the free radical copolymerization of tris(4-vinylphenyl)



**Scheme 1.** Synthesis of POPs-Py&PPh<sub>3</sub>, POP-PPh<sub>3</sub> and Poly(4-vPy).



Figure 1. FT-IR spectra of supported Ru catalysts and porous polymer.

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phosphane (vPPh<sub>3</sub>) and 4-vinylpyridine (4-vPy) with AIBN (azobisisobutyronitrile) as the initiator in tetrahydrofuran. The treatment of the copolymers, POPs-Py&PPh<sub>3</sub>, with RuCl<sub>3</sub> in toluene readily afforded the Ru/POPs-Py&PPh<sub>3</sub> as dark solids (for details, see the Supporting Information). In addition, to further understand the relationship between the catalytic activity and compositions of POPs, POP-PPh<sub>3</sub>, and Poly(4vPy) were also prepared for the N-formylation of amines with CO<sub>2</sub>/H<sub>2</sub> (see SI).

The FT-IR (Fourier-transform infrared) spectra of various Ru-based catalysts are presented in Figure 1 (for details, see Figure S1–6, SI). The peaks at 2925 and 1404 cm<sup>-1</sup> are attributed to the stretching vibration of C–H and bending vibration of newly formed cross-linking bridges (–CH–CH<sub>2</sub>–). The peak at 1599 cm<sup>-1</sup> was assigned to the –C=N– bond stretching vibration of pyridine ring. Compared with that of POP<sub>3</sub>-Py&PPh<sub>3</sub> (Figure S6, SI), the characteristic peak of the phenyl-phosphorus group at 1016 cm<sup>-1</sup> was weakened dramatically in the spectrum of Ru/POP<sub>3</sub>-Py&PPh<sub>3</sub> (Figure S3, SI),<sup>[25]</sup> which was attributed to the coordination of Ru with the PPh<sub>3</sub> moieties.

The porosities of various supported Ru catalysts were investigated (Figure S7-S12, SI), and the result is summarized in Table 1. Ru/POP-PPh<sub>3</sub> catalyst has the highest BET surface area and pore volume in these catalysts (entry 4), while the Ru/Poly(4-vPy) catalyst afforded the lowest results (entry 5). Increasing the molar ratio of PPh<sub>3</sub>/pyridine moieties from 1:1 to 5:1 in copolymers led to the enhancements of both surface area and pore volume. The results indicated that PPh<sub>3</sub> moiety was crucial for the synthesis of the porous organic framework. The nitrogen sorption isotherms of Ru/POPs-Py&PPh<sub>3</sub> exhibit a combined curve of type-I and type-IV (Figure S7–S9, SI). The rise sorption at P/ $P_0 < 0.1$  indicates the filling of micropore, and the hysteresis loops at a relatively high pressure (0.4 < P/ $P_0 < 1.0$ ) suggests the presence of mesopores. Based on the calculations of the nonlocal density functional theory (NLDFT), the pore sizes of Ru/POPs-Py&PPh<sub>3</sub> are mainly distributed at 1-2 nm and 2-30 nm. As a representative catalyst, Ru/POP<sub>3</sub>-Py&PPh<sub>3</sub> exhibits a

 Table 1. Textural parameters of the various supported Ru catalysts and porous polymer.<sup>[a]</sup>

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entry	sample	surface area $[m^2g^{-1}]$	pore volume $[cm^3 g^{-1}]$
1	Ru/POP <sub>1</sub> -Py&PPh <sub>3</sub>	254.1	0.3
2	Ru/POP <sub>2</sub> -Py&PPh <sub>3</sub>	430.4	0.5
3	Ru/POP <sub>3</sub> -Py&PPh <sub>3</sub>	583.3	0.8
4	Ru/POP-PPh <sub>3</sub>	690.7	0.9
5	Ru/Poly(4-vPy)	0.4	$6.5 \times 10^{-4}$
6	POP <sub>3</sub> -Py&PPh <sub>3</sub>	618.6	0.7

<sup>[a]</sup> Analysed by BET (Brunauer-Emmett-Teller) method.



high BET surface area of 583.3  $m^2 g^{-1}$  and pore volume of  $0.8 \text{ cm}^3 \text{g}^{-1}$  (Figure S9, SI), which is lower than those of POP<sub>3</sub>-Py&PPh<sub>3</sub> (Figure S12, SI), due to the load of RuCl<sub>3</sub>. The SEM (scanning electron microscopy) and TEM (transmission electron microscopy) images in Figures 2a and 2b display rough morphologies with abundant pores on the surface and in the internal structure, which further demonstrate the porosity of Ru/POP<sub>3</sub>-Py&PPh<sub>3</sub>. In addition, Ru/POP<sub>3</sub>- $Py\&PPh_3$  had a good  $CO_2$  uptake capacity (up to 41.5 mg  $g^{-1}$  under 1 bar at 298 k), and the result was similar to those of the phosphine-rich polymerssupported catalysts in the literature.<sup>[22,23]</sup> The CO<sub>2</sub> uptake capacity of Ru/POP-PPh<sub>3</sub> was also detected and exhibited a slightly higher capacity  $(45.2 \text{ mg g}^{-1})$  than Ru/POP<sub>3</sub>-Py&PPh<sub>3</sub>, which may be owing to the relatively high surface area of the catalyst.

X-ray photoelectron energy spectroscopy (XPS) was carried out to analyze the catalyst of Ru/POP<sub>3</sub>-Py&PPh<sub>3</sub>. The binding energies of P2p for Ru/POP<sub>3</sub>-Py&PPh<sub>3</sub> at 132.3 and 130.5 eV are observed in Figure 2c, which are higher than those of POP<sub>3</sub>-Py&PPh<sub>3</sub> (132.2 and 130.4 eV, Figure S16, SI).<sup>[22]</sup> The binding energies of Ru3p<sub>1/2</sub> and Ru3p<sub>3/2</sub> moved from 484.4 and 462.2 eV for RuCl<sub>3</sub> (Figure S15, SI) to 486.2 and 463.4 eV for Ru/POP<sub>3</sub>-Py&PPh<sub>3</sub> (Figure 2d). In addition, POP<sub>3</sub>-Py&PPh<sub>3</sub> and Ru/POP<sub>3</sub>-Py&PPh<sub>3</sub> show the same binding energies of N1s (399.4 eV,



Figure 2. (a) SEM image, (b) TEM image, (c) P 2p XPS spectra, (d) Ru 3p XPS spectra, (e) <sup>31</sup>P MAS NMR spectrum (MAS, Magic Angle Spinning), (f) <sup>13</sup>C MAS NMR spectrum of Ru/POP<sub>3</sub>-Py&PPh<sub>3</sub>.

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Figure S17 and S20, SI). The results revealed that Ru coordinated with PPh<sub>3</sub> moieties, but not with pyridine moieties in Ru/POP<sub>3</sub>-Py&PPh<sub>3</sub> catalyst. In the solidstate <sup>31</sup>P NMR spectrum of Ru/POP<sub>3</sub>-Py&PPh<sub>3</sub> (Figure 2e), the peak observed at 20.8 ppm can be attributed to the P atoms of the polymerized vPPh<sub>3</sub> coordinated to Ru, which is consistent with the literature.<sup>[26]</sup> The peak at -12.7 ppm is assignable to the phosphorus signals of PPh<sub>3</sub> moieties. The <sup>13</sup>C MAS NMR spectrum exhibited two peaks at 179.7 and 126.5 ppm, corresponding to the carbon signals of the pyridine and benzene ring (Figure 2f). In addition, the peak centered at 38.6 ppm could be ascribed to the polymerized vinyl groups. The thermal stability of Ru/ POP<sub>3</sub>-Py&PPh<sub>3</sub> was characterized by thermogravimetric analysis (TGA). The first weight loss of 5% was observed starting from 100°C. Additional heating up to 373 °C, revealed the high thermostability of Ru/ POP<sub>3</sub>-Py&PPh<sub>3</sub> (Figure S14, SI). Inductively coupled plasma-mass spectrometry (ICP-MS) indicated a Ru loading of 2.73 wt% in Ru/POP<sub>3</sub>-Py&PPh<sub>3</sub>. The elemental analysis showed that the content of nitrogen and phosphine in the catalyst was consistent with the stoichiometric relationship of the monomers.

We initiated the study of N-formylation with  $CO_2/$  $H_2$  using morpholine as the model substrate and Ru/ POP<sub>3</sub>-Py&PPh<sub>3</sub> as the catalyst. Various reaction conditions, including solvent, temperature, and pressure of CO<sub>2</sub>/H<sub>2</sub>, were investigated, and the results are summarized in Table S1 (for details, see SI). N-formylation of morpholine was best performed in NMP (N-methyl-2pyrrolidone) at 100 °C under at 2/2 MPa for  $CO_2/H_2$ , affording N-formylmorpholine in excellent yield (93%, entry 1, Table S1). Under the optimized reaction conditions, a variety of catalysts were evaluated, as shown in Table 2. In the comparative experiment with Ru/POP<sub>s</sub>-Py&PPh<sub>3</sub> (entries 1–3, Table 2), Ru/POP<sub>3</sub>-Py&PPh<sub>3</sub> exhibited the best catalytic activity while Ru/ POP<sub>1</sub>-Py&PPh<sub>3</sub> was less reactive (entry 1). When using RuCl<sub>3</sub> as a precatalyst in the absence of ligands and basic additives, a 55% yield was obtained (entry 4). Moreover, the POP-PPh<sub>3</sub>-supported RuCl<sub>3</sub> catalyst (Ru/POP-PPh<sub>3</sub>) showed a better performance than RuCl<sub>3</sub> (83%, entry 5), but an inverse result was observed when using Ru/Poly(4-vPy) as the catalyst (28%, entry 6). Ru/POP<sub>3</sub>-Py&PPh<sub>3</sub> showed a higher catalytic activity than Ru/POP-PPh<sub>3</sub>, although the latter had higher CO<sub>2</sub> uptake capacity, proving that pyridine moieties could promote the conversion rate of Nformylation. Based on these results, we concluded that the catalytic activity of the catalyst depended on the molar ratio of PPh<sub>3</sub> and pyridine moieties in copolymers. A proper ratio of pyridine and PPh<sub>3</sub> moieties was favorable for improving the catalytic activity, whereas excessive pyridine moieties in the copolymer resulted in decreased catalytic activity due to the coordination effect of Ru with pyridine. Additionally, the heteroge-

**Table 2.** Catalytic activities of various Ru-based catalysts for the N-formylation of morpholine with  $CO_2/H_2$ .<sup>[a]</sup>

	$O NH + CO_2 + H_2 - Cat$	→ ОN-СНО
entry	catalyst	yield <sup>[b]</sup> (%)
1 <sup>[c]</sup>	Ru/POP <sub>1</sub> -Py&PPh <sub>3</sub>	66
$2^{[d]}$	Ru/POP <sub>2</sub> -Py&PPh <sub>3</sub>	77
3 <sup>[e]</sup>	Ru/POP <sub>3</sub> -Py&PPh <sub>3</sub>	93
4 <sup>[f]</sup>	RuCl <sub>3</sub>	55
5 <sup>[g]</sup>	Ru/POP-PPh <sub>3</sub>	83
6 <sup>[h]</sup>	Ru/Poly(4-vPy)	28
7 <sup>[i]</sup>	Ru/PPh <sub>3</sub> /Py	90
8 <sup>[j]</sup>	Ru/POP <sub>3</sub> -Py&PPh <sub>3</sub>	64

<sup>[a]</sup> Reaction conditions: morpholine (1 mmol), S/C=222, CO<sub>2</sub>/ $H_2=2/2$  MPa, NMP (1.0 mL), 100 °C, 24 h, decane as the internal standard.

<sup>[b]</sup> Yields were determined on the basis of GC analysis.

<sup>[c]</sup> 20.1 mg of Ru/POP<sub>1</sub>-Py&PPh<sub>3</sub> (Ru loading at 2.27 wt%).

<sup>[d]</sup> 17.2 mg of Ru/POP<sub>2</sub>-Py&PPh<sub>3</sub> (Ru loading at 2.64 wt%).

<sup>[e]</sup> 16.5 mg of Ru/POP<sub>3</sub>-Py&PPh<sub>3</sub> (Ru loading at 2.73 wt%).

<sup>[f]</sup> 0.93 mg of RuCl<sub>3</sub>.

<sup>[g]</sup> 12.4 mg of Ru/POP-PPh<sub>3</sub> (Ru loading at 3.67 wt%).

 $^{[h]}$  6.33 mg of Ru/Poly(4-vPy) (Ru loading at 7.19 wt%).

<sup>[i]</sup> 0.93 mg of RuCl<sub>3</sub>, RuCl<sub>3</sub>:PPh<sub>3</sub>:Py = 1:10:2.

<sup>[j]</sup> S/C = 1110.

neous Ru/POP<sub>3</sub>-Py&PPh<sub>3</sub> gave a similar yield to that of the homogeneous Ru/PPh<sub>3</sub>/Py system (entries 3 vs 7). The catalyst loading of 0.111 mol% (S/C=1110) was tested, affording the N-formylmorpholine in 64% yield (TON=710, entry 8). Compared with the reported heterogeneous Ru catalysts of CarPy-CMP@Ru (TON=188,  $CO_2/H_2=4/4$  MPa)<sup>[21]</sup> and Ru-PPh<sub>3</sub>-SO<sub>3</sub>Na@POPs (TON=216,  $CO_2/H_2=3/3$  MPa),<sup>[22]</sup> Ru/POP<sub>3</sub>-Py&PPh<sub>3</sub> showed the highest catalytic activity under a relatively low pressure of  $CO_2/H_2$ .

Under optimal reaction conditions, various amines were investigated as substrates for Ru/POP<sub>3</sub>-Py&PPh<sub>3</sub>catalyzed N-formylation. As shown in Table 3, cyclic secondary amines, such as morpholine, pyrrolidine, and piperidine, are readily amenable to the Nformylation procedure, affording the corresponding formamides 2 a-2 c in excellent yields (93-99%, entries 1-3). When using linearly aliphatic amines dimethylamine (1d) and dibutylamine (1e) as the substrates, products of 2d and 2e were obtained with good yields, respectively (60% and 68%, entries 4 and 5). The N-methylbenzylamine (1 f) also worked well in this catalytic system with an excellent yield (95%, entry 6). Moreover, its derivatives, bearing electrodonating or electro-withdrawing substituents on benzene ring, proceeded smoothly and formed the desired corresponding products (2g-2i) in excellent vields (92–97%, entries 7–9). Encouraged by these **Table 3.** N-formylation of amines catalyzed by  $Ru/POP_3$ -Py&PPh<sub>3</sub> with  $CO_2/H_2$ .<sup>[a]</sup>

R <sup>1</sup> N H	$^{R^{2}}_{+} CO_{2} + H_{2} - \frac{Ru}{-}$	ı/POP <sub>3</sub> -Py&PPh	$3 \rightarrow H N^{-R^2}$
entry	substrate	product	yield <sup>[b]</sup> (%)
1	ONH 1a	oH 2a	93(90) <sup>c</sup>
2	NH 1b		99(95) <sup>c</sup>
3	NH 1c	N H 2c	99(95) <sup>c</sup>
4	NH 1d	N-( P-( 2d	60(55) <sup>c</sup>
5	H N 1e		68 (62) <sup>c</sup>
6	NH 1f	2f	H 95 (90) <sup>c</sup> O
7	NH 1g	O 2g	96 (92) <sup>c</sup> O
8	NH Ih	2h	⊣ 92 (90) <sup>c</sup>
9	F NH		U H 97 (92) <sup>c</sup> O
10	1j	21 H 2j	Щ Н 70 (62) <sup>с</sup>
11	→−NH₂ 1k		`H 67(60) <sup>c</sup>
12	NH <sub>2</sub>	N 2I	H 72 (70)°
13	F 1m	F 2m	<sup>⊥</sup> H 75(71) <sup>c</sup>

<sup>[a]</sup> Reaction conditions: amines **1 a–m** (1 mmol), 16.5 mg of Ru/ POP<sub>3</sub>-Py&PPh<sub>3</sub> (Ru loading at 2.73 wt%), S/C=222, CO<sub>2</sub>/ $H_2=2/2$  MPa, NMP (1.0 mL), 100 °C, 24 h, decane as the internal standard.

<sup>[b]</sup> Yields were determined by GC analysis.

<sup>[c]</sup> Yields of isolated products.



results, the N-formylation of primary amines was then investigated in the presence of Ru/POP<sub>3</sub>-Py&PPh<sub>3</sub> as the catalyst. For linear primary amine (**1j**) and cyclohexanamine (**1k**), 70% and 67% yields of the corresponding formamide products were obtained, respectively, (entries 10 and 11). Benzylamine and the derivative were good reaction partners, delivering the desired formamides with good yields (entries 12 and 13).

The reusability of the Ru/POP<sub>3</sub>-Py&PPh<sub>3</sub> catalyst in the N-formylation was investigated. As shown in Figure 3, with the morphine as the substrate for reaction time of 12 h, the catalyst was at least reused eight times and the yield of **2a** was considerably retained (Table S2, SI). Additionally, 1.4 ppm Ru species were detected in the residual liquids by ICP-MS analysis. Further, the recovered catalyst was characterized by N<sub>2</sub> adsorption-desorption analysis and XPS. The used catalyst also had a high surface area (569.9  $m^2g^{-1}$ , Figure S13, SI), and the XPS spectra (Figure S21–23, SI) was similar to that of the fresh Ru/ POP<sub>3</sub>-Py&PPh<sub>3</sub> catalyst. Finally, a hot filtration test was carried out using Ru/POP<sub>3</sub>-Py&PPh<sub>3</sub>. After 12 h of the initial reaction, the mixture was immediately filtered and the resultant filtrate was conducted for an additional 12 h. After the removal of the solid catalyst. the reaction stopped, and the conversion of morpholine remained constant (69%). The results indicated the stability of the polymeric framework and the strong coordination ability of Ru with the copolymer support, which resulted in the excellent recyclability of the Ru/ POP<sub>3</sub>-Py&PPh<sub>3</sub> catalyst.

In summary, a series of porous copolymers (POPs- $Py\&PPh_3$ ) were synthesized by polymerizing the vinyl-functionalized PPh<sub>3</sub> and pyridine. Among the Ru species-loaded porous polymers, Ru/POP<sub>3</sub>-Py&PPh<sub>3</sub> catalyst showed the best catalytic activity in the N-formylation of amines with CO<sub>2</sub>/H<sub>2</sub>. Various primary



**Figure 3.** Recycling studies of the Ru/POP<sub>3</sub>-Py&PPh<sub>3</sub> in the N-formylation of morpholine with  $CO_2/H_2$ . Reaction condition: Ru/POP<sub>3</sub>-Py&PPh<sub>3</sub> (40 mg), **1a** (2.42 mmol), S/C=222, CO<sub>2</sub>/ $H_2=2/2$  MPa, NMP (1.0 mL), 100 °C for 12 h.

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and secondary amines are amenable to the procedure, affording the corresponding formamides in good yields and excellent recyclability under relatively mild reaction conditions. Moreover, through multiple comparing experimental studies, it was confirmed that the catalytic activities of the catalysts depended on the molar ratios of PPh<sub>3</sub> and pyridine moieties in copolymers.

### **Experimental Section**

# General Procedure for the N-Formylation of Amines

In a glove box, an autoclave with a magnetic stirring bar was successively charged with Ru/POP<sub>3</sub>-Py&PPh<sub>3</sub> (16.5 mg), the corresponding amines (1 mmol), N-methyl pyrrolidone (1.0 mL), and decane (10  $\mu L,$  0.05 mmol) as the internal standard. The autoclave was sealed and purged with CO<sub>2</sub> three times and subsequently charged with CO<sub>2</sub> (20 atm) and H<sub>2</sub> (20 atm) at room temperature. The autoclave was moved to an oil bath of 100°C and stirred for 24 h. The autoclave was cooled in ice water, and the gas was carefully released in a well-ventilated hood. The mixture was subsequently analyzed by gas chromatography (GC). After the reaction, the catalyst was removed by centrifugation. The supernatant was washed with H<sub>2</sub>O, and the mixture was extracted by ethyl acetate. Afterward, the ethyl acetate solution of the product was gathered and dried by MgSO<sub>4</sub>. The solvent was removed by rotary evaporation and the residue was directly purified by silica gel column chromatography to give the desired product.

GC analysis condition: SE-54, 30 m×0.32 mm×0.33 mm, flow rate 2.0 mL min<sup>-1</sup>, method: 50 °C was maintained for 5 min, and then ramped from 50 °C to 250 °C at a rate of 20 °C min<sup>-1</sup>, 250 °C was maintained for 10 min.

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