Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Supporting Information

CO_2 hydrogenation into formate and methyl formate using Ru molecular catalysts supported on NNN pincer porous organic polymers

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Table S1. Comparison of activity with catalysts reported in literature

Catalyst	Temperature (°C)	Time (h)	Pressure (bar)	TON of MF	TOF (h-1)	ref
Cu/ZnO/alumina	150	25	60	771.25	30.85	S1
1 % Ru-Cu/AnO/alumina	150	25	60	840.5	33.62	S1
1 % Ni-Cu/ZnO/alumina	150	25	60	931.75	37.27	S1
1 % Au-Cu/ZnO/alumina	150	25	60	335.5	13.42	S1
1 % Pd-Cu/ZnO/alumina	150	25	60	953.75	38.15	S1
Au-ZrO2-9.0	200	1	80	534	534	S2
Au/Al2O3	70	9.22	40	1088	118	S3
Au/Al2O3	100	1.24	40	118	95	S3
1 wt% Ru@pDPPE	160	1	80	1079	1079	S4
1 wt% Ru/N-Me-3-bpp-POP	160	2	80	1726	863	this

Ref S1: Journal of the American Chemical Society 129. (2007), 6346-6662 DOI: https://doi.org/10.1021/ja0706302

Ref S2: Green Chemistry 17, (2015), 1467-1472 DOI: https://doi.org/10.1039/C4GC01818D

Ref S3: Journal of CO2 utilization 17, (2017), 273-283 DOI: https://doi.org/10.1016/j.jcou.2016.11.016

Ref S4: ChemSusChem 12, (2019), 3278-3285 DOI: https://doi.org/10.1002/cssc.201900808

Table S2. Porosity parameters of materials by BET analysis

Material	BET plot					
	Correlation coefficient	V_m [cm^3(STP) g^{-1}]	$a_{S, BET}$ [m^2 g^{-1}]	C	Total pore volume [cm^3 g^{-1}]	Mean pore diameter [nm]
3-bpp-POP	1	129.72	564.59	787.53	0.2926	2.0731
Ru/3-bpp-POP	1	140.95	613.47	735.72	0.3152	2.0553
N-Me-3-bpp-POP	1	127.87	556.54	265.54	0.2901	2.167
Ru/N-Me-3-bpp-POP	1	137.44	598.19	213.59	0.3041	2.0335

Table S3. Remaining of Ru amount of fresh and used catalyst

Sample	Ru / wt %
Fresh N-Me-3-bpp-POP	1.1
Spent N-Me-3-bpp-POP (after 5th run)	0.62

Table S4. Leaching Ru content of every cycle[a]

Filtrate	Filtrate vol. (mL)	Ru conc. (mg/L)	Leached Ru (wt %)
1st run	33.3	2.53	0.421
2nd run	44	0.26	0.057
3rd run	32.8	0.15	0.025
4th run	32.5	0.12	0.020
5th run	32.3	0.05	0.008

[a]determined by ICP-OES,

Figure S1. Electron dispersive X-ray spectroscopy (EDX) of supports (3-bpp-POP and N-Me-bpp-POP)

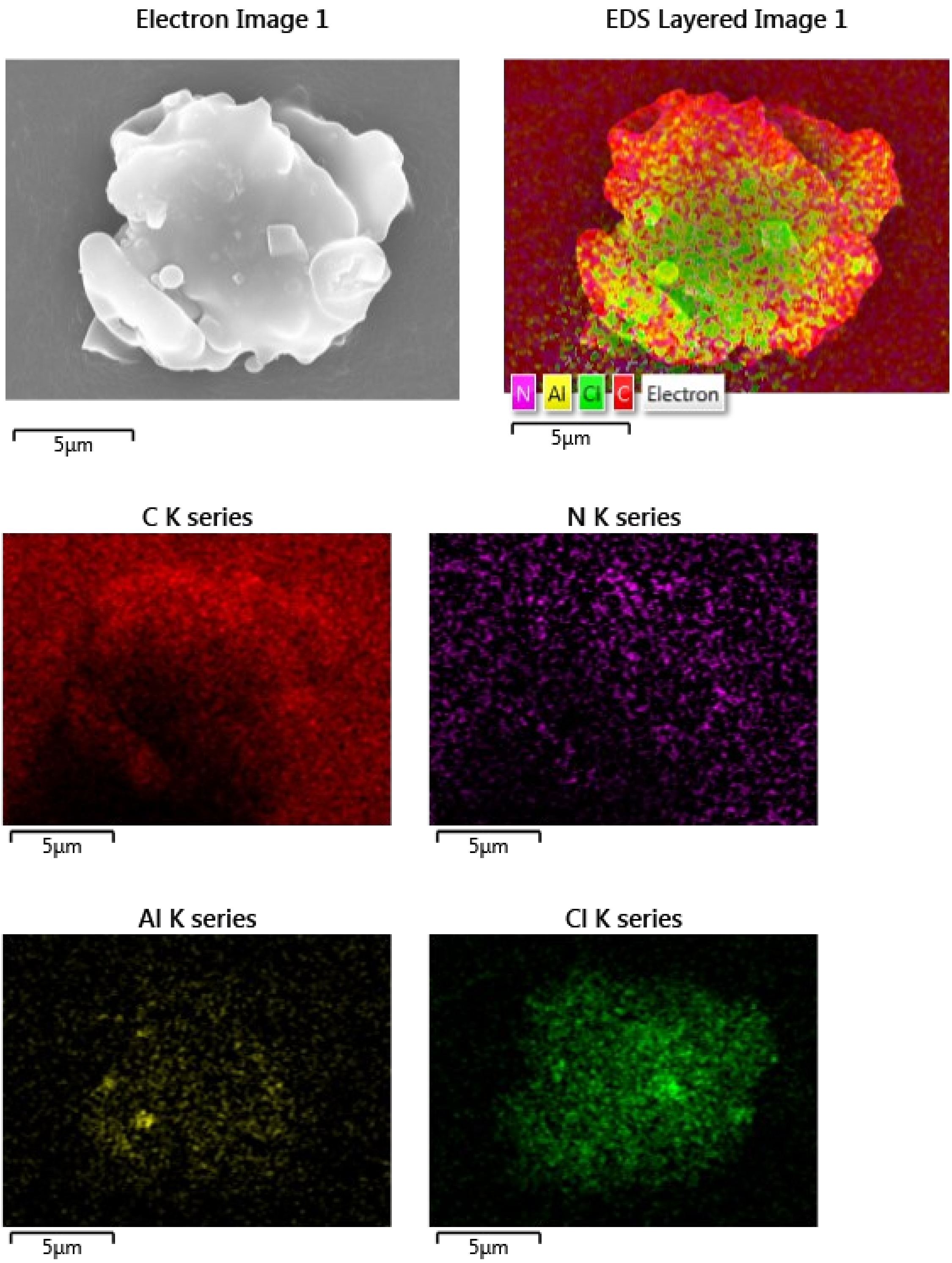


Figure S1, a, EDX of 3-bpp-POP

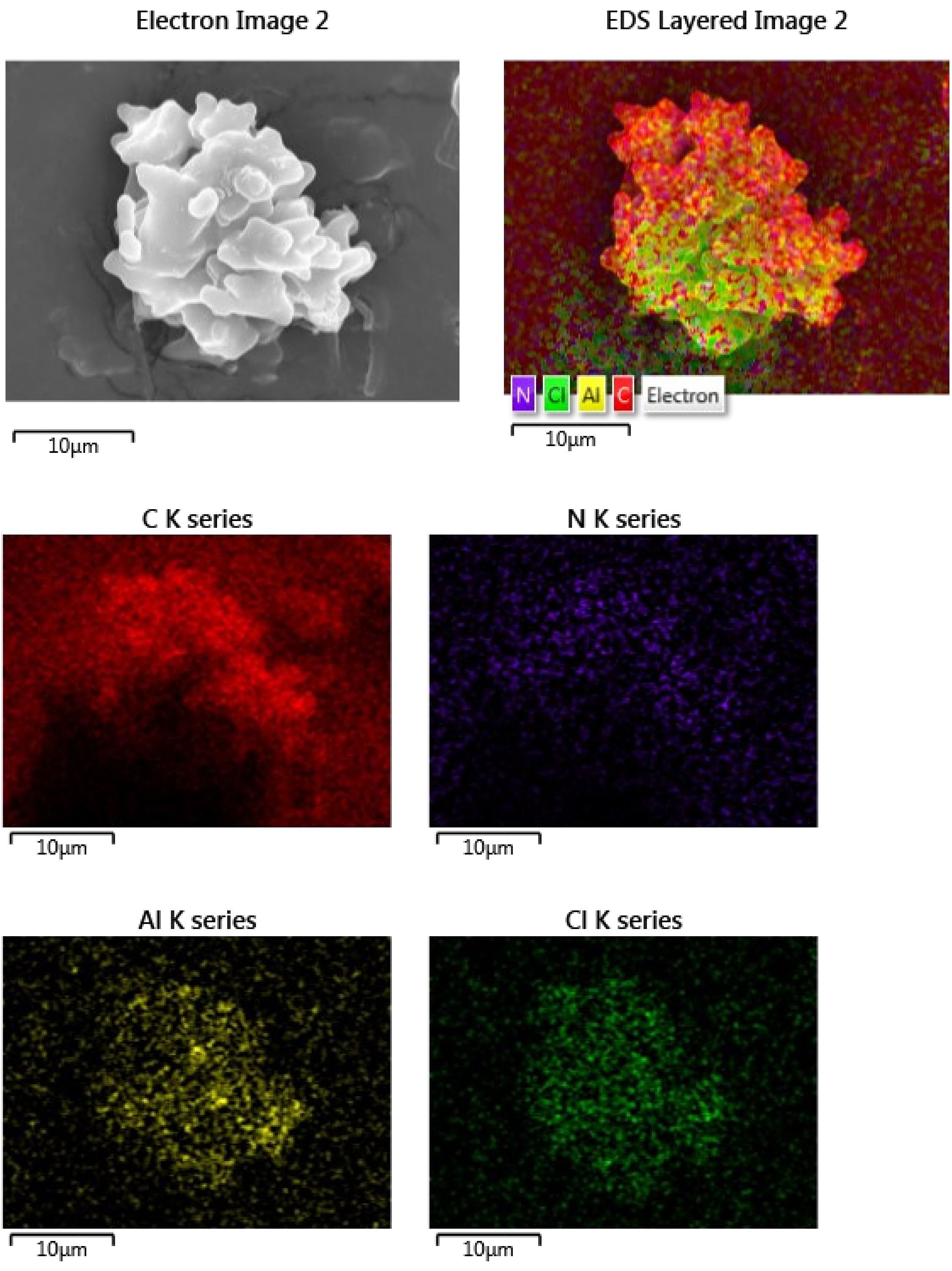


Figure S1, b, EDX of N-Me-3-bpp-POP

Figure S2. FT-IR spectrum of 3-bpp monomer and N-Me-bpp monomer

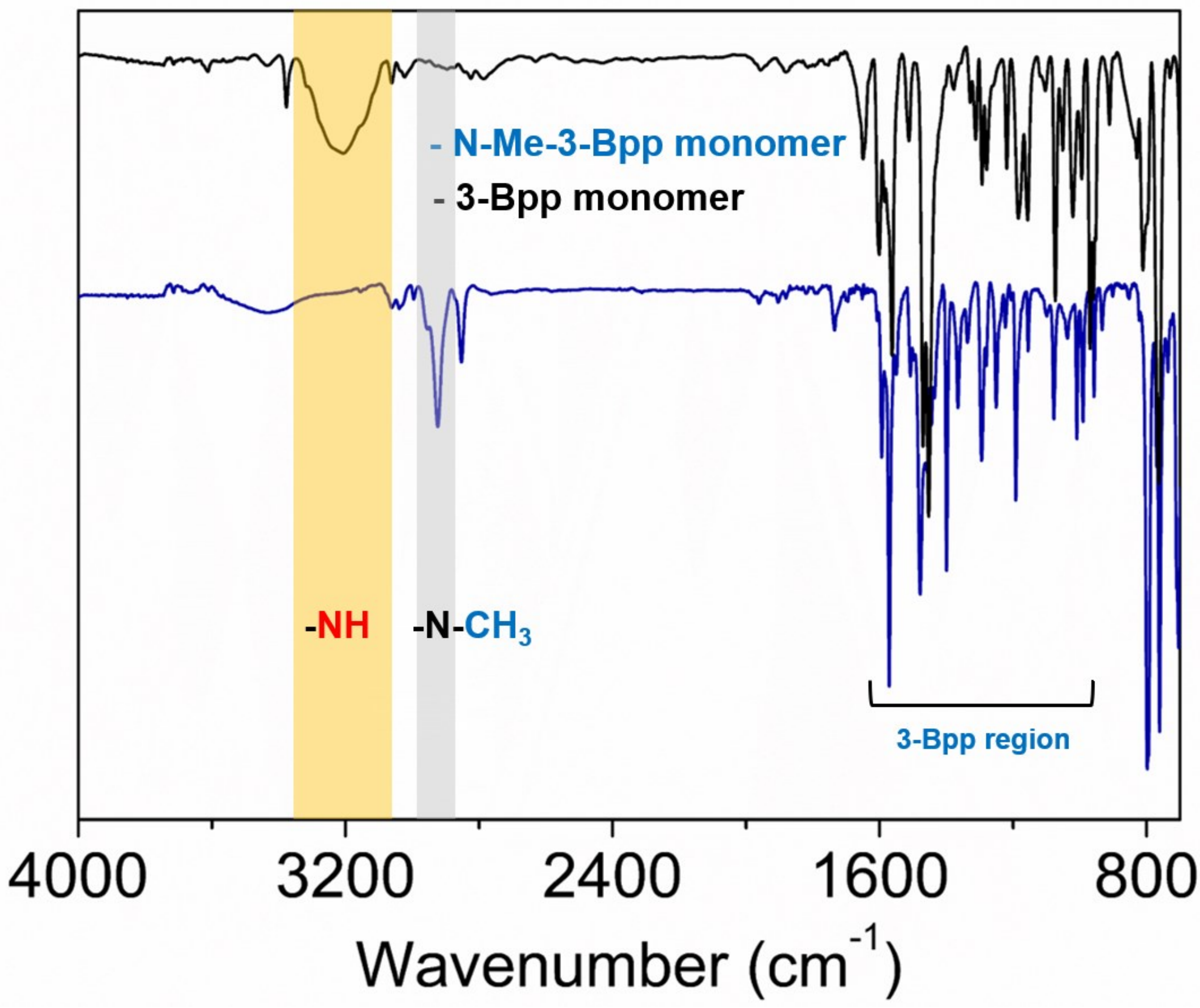


Figure S3. Electron dispersive X-ray spectroscopy (EDX) of catalysts (Ru/3-bpp-POP and N-Me-3-bpp-POP

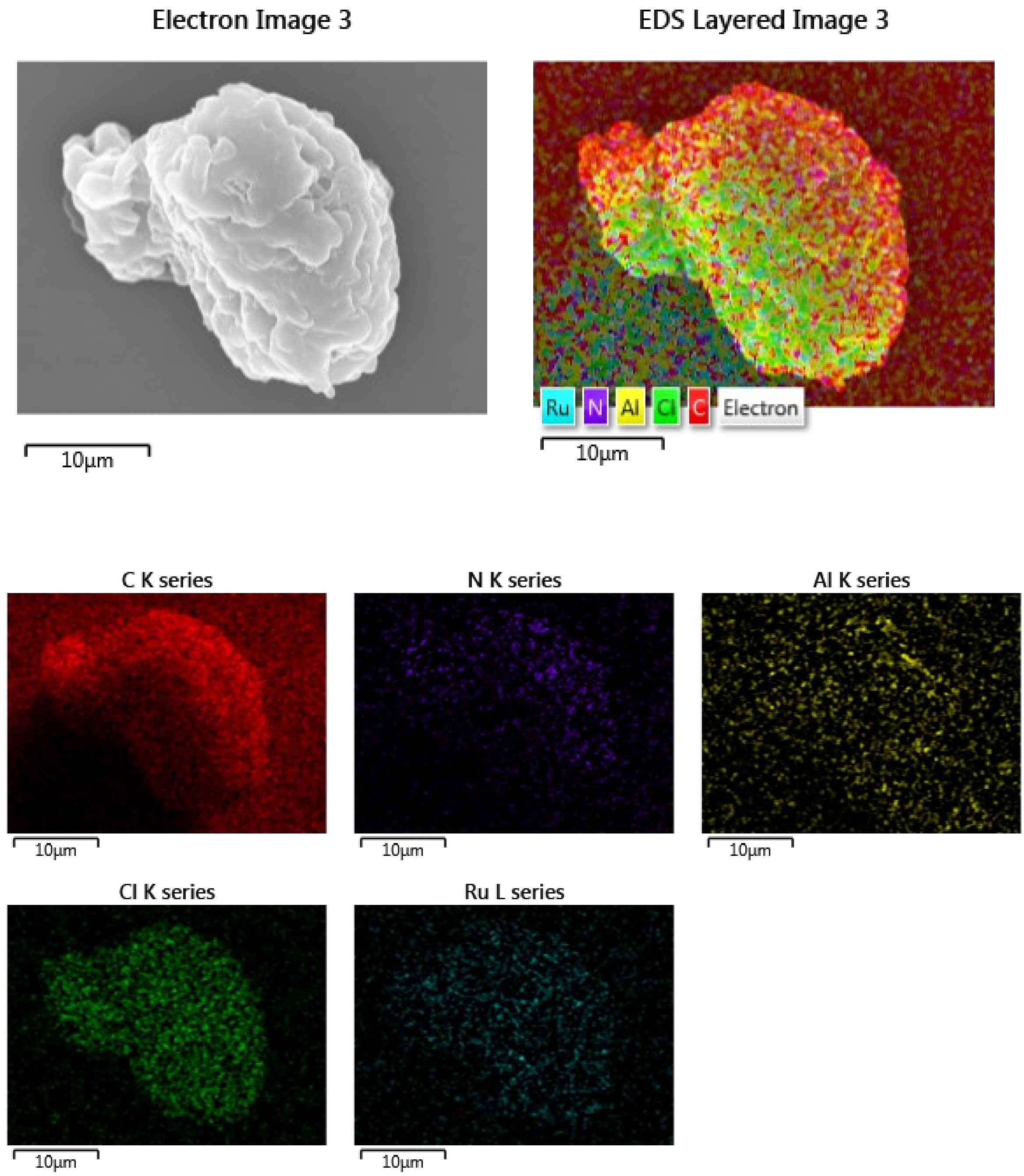


Figure S3, a, EDX of Ru/3-bpp-POP

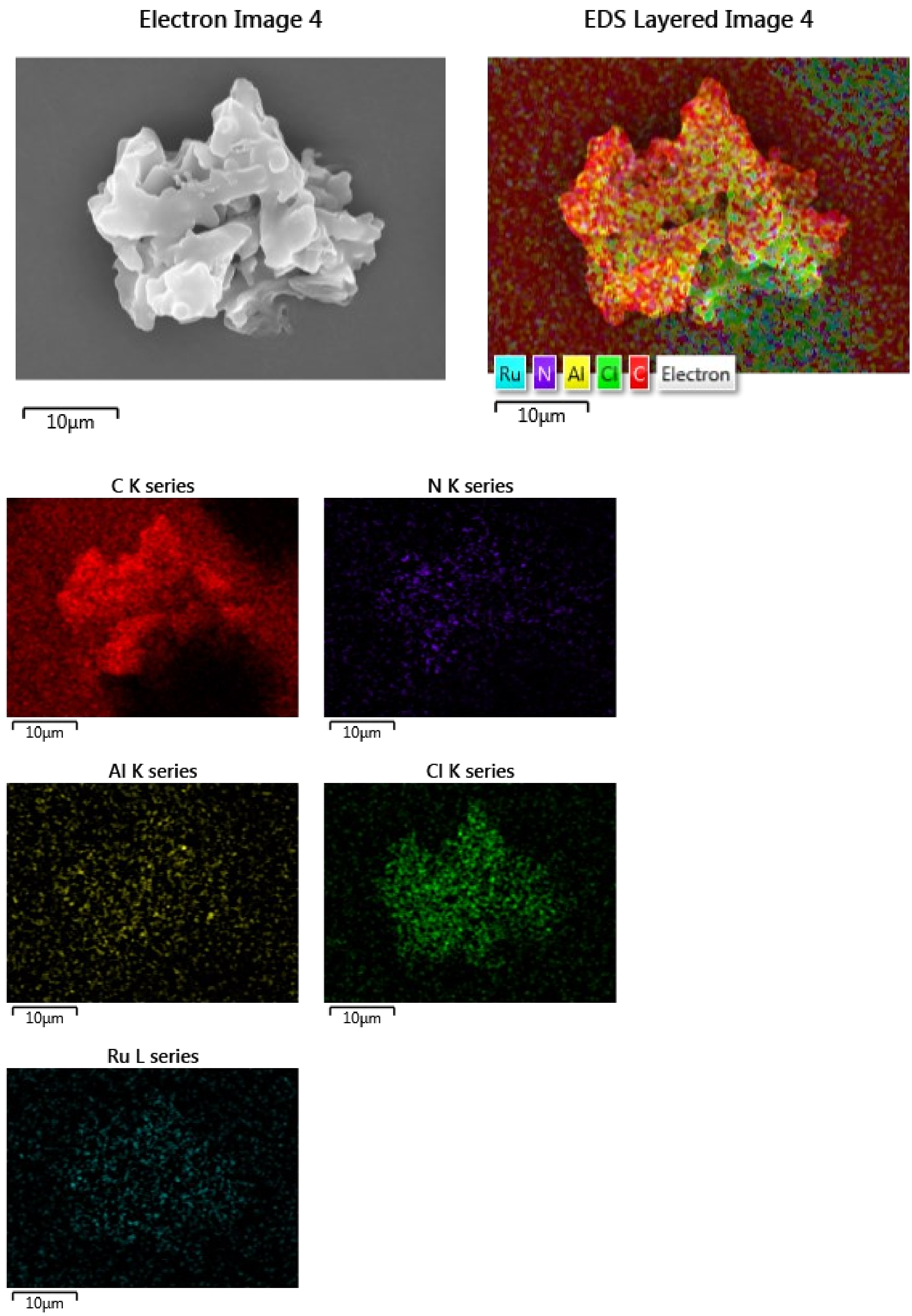


Figure S3, b, EDX of Ru/3-Me-bpp-POP

Figure S4. X-ray photoelectron spectroscopy (XPS) of catalysts (Ru $3d_{3/2}$ and $3d_{1/2}$ peaks of Ru/3-bpp-POP

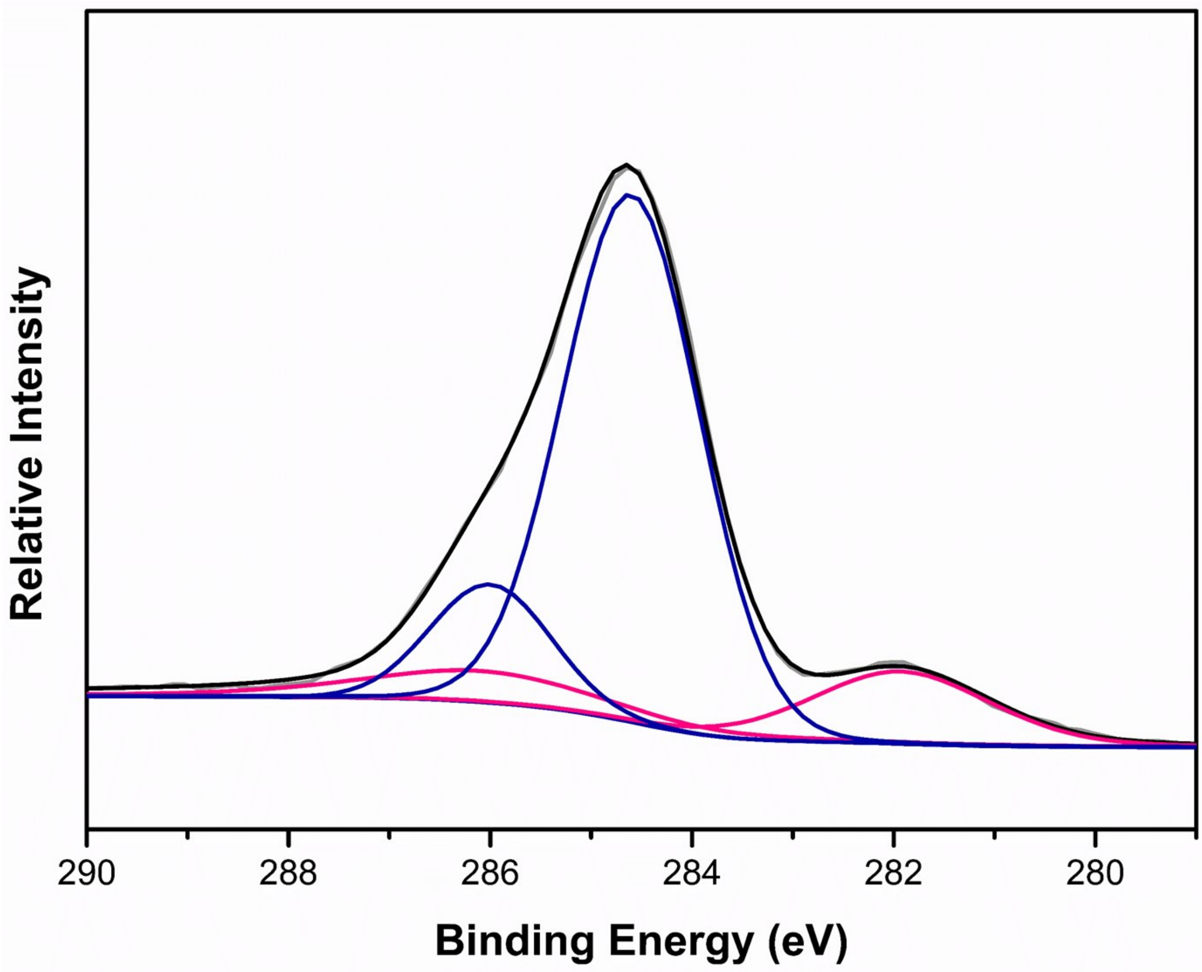


Figure S5. X-ray photoelectron spectroscopy (XPS) of catalysts (Ru $3d_{3/2}$ and $3d_{1/2}$ peaks of Ru/N-Me-3-bpp-POP

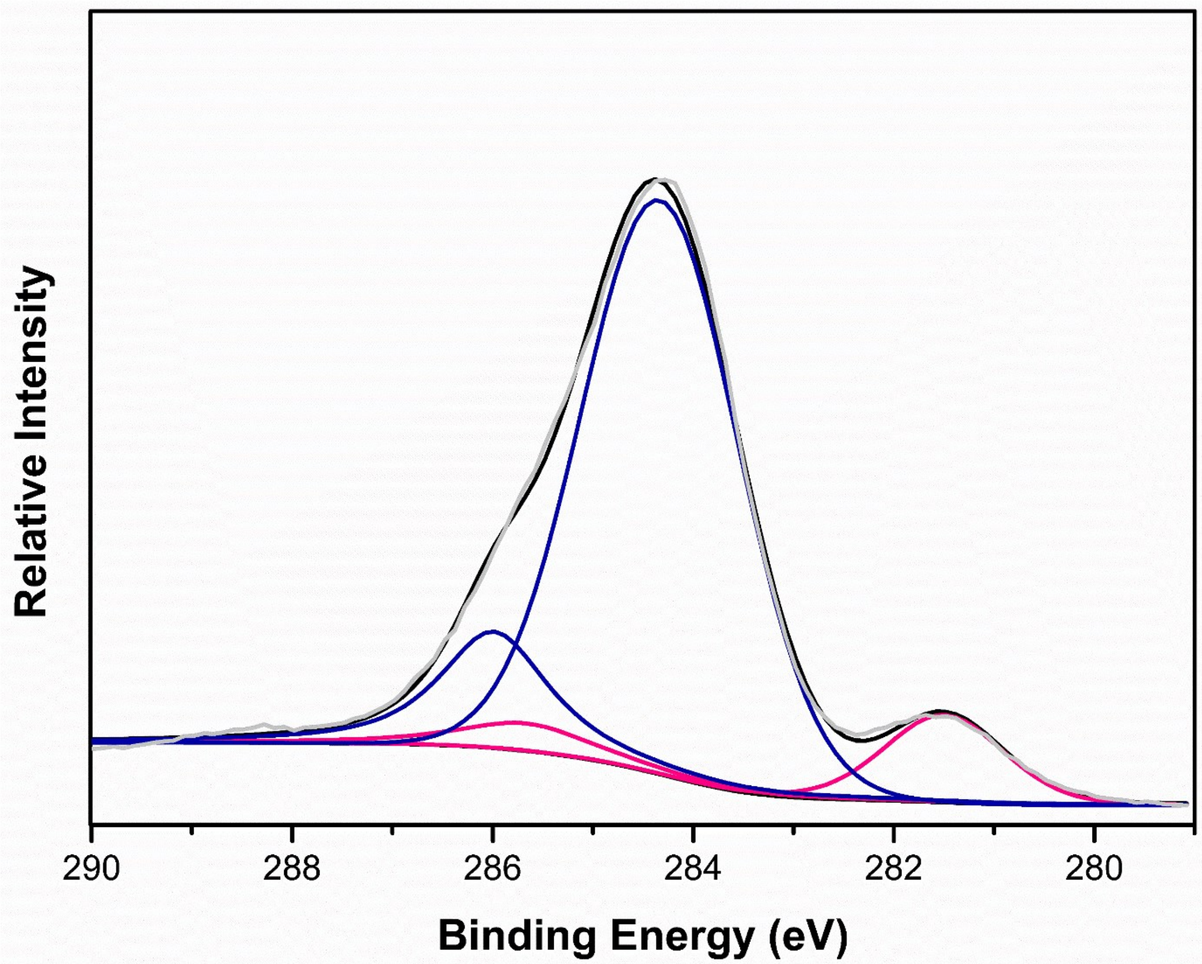
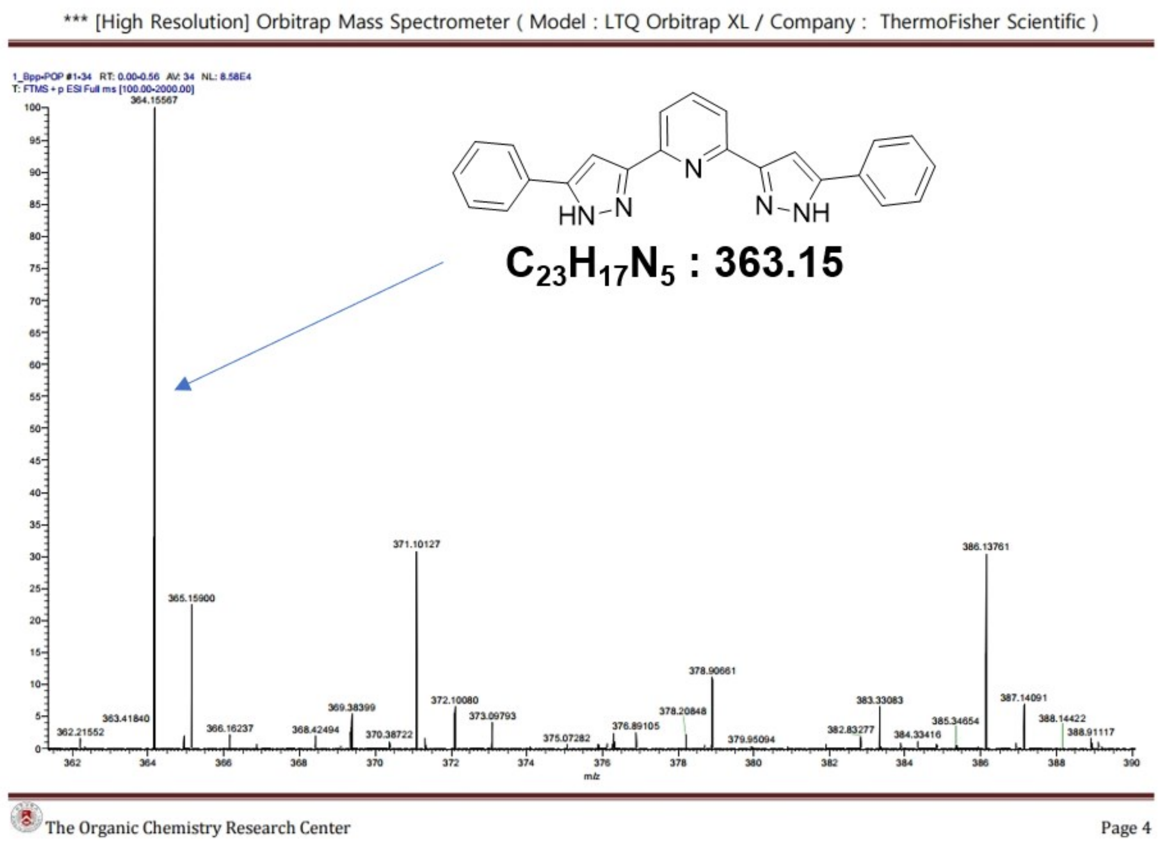


Figure S6. MASS spectra of 3-bpp and N-Me-3-bpp monomer



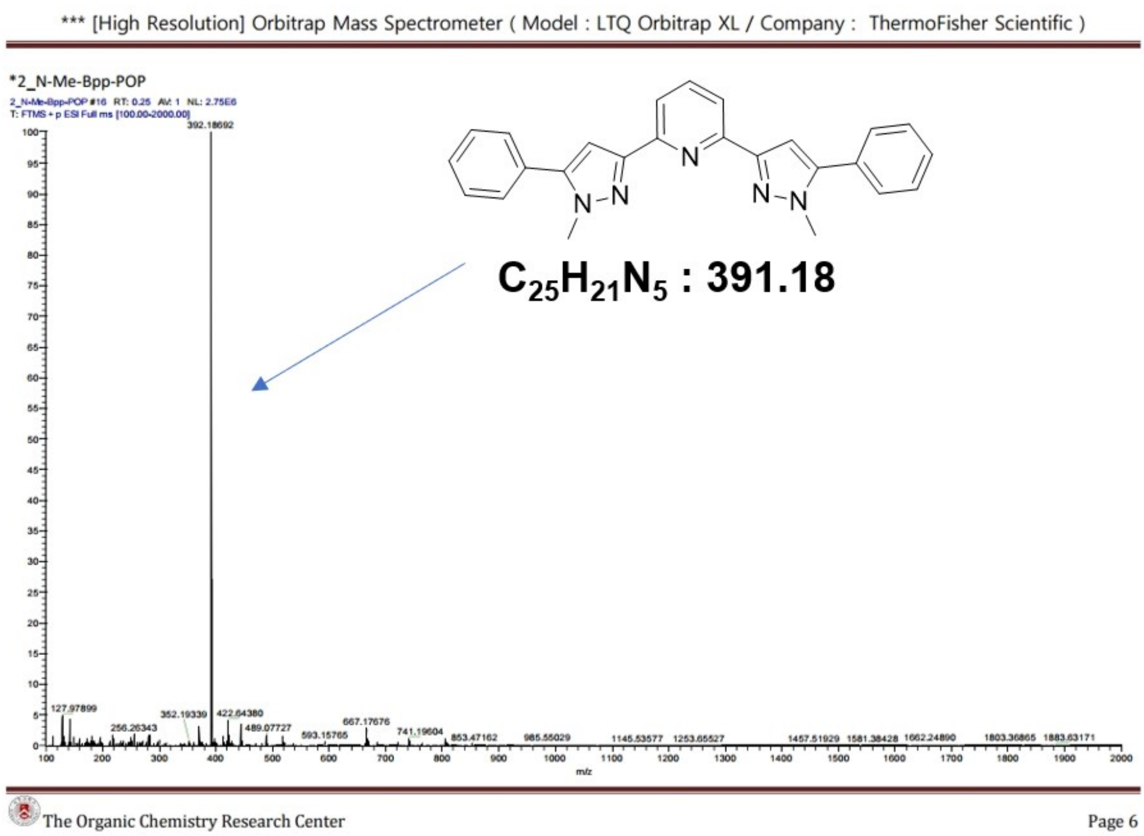


Figure S7. TGA of 3-bpp-POP and N-Me-bpp-POP

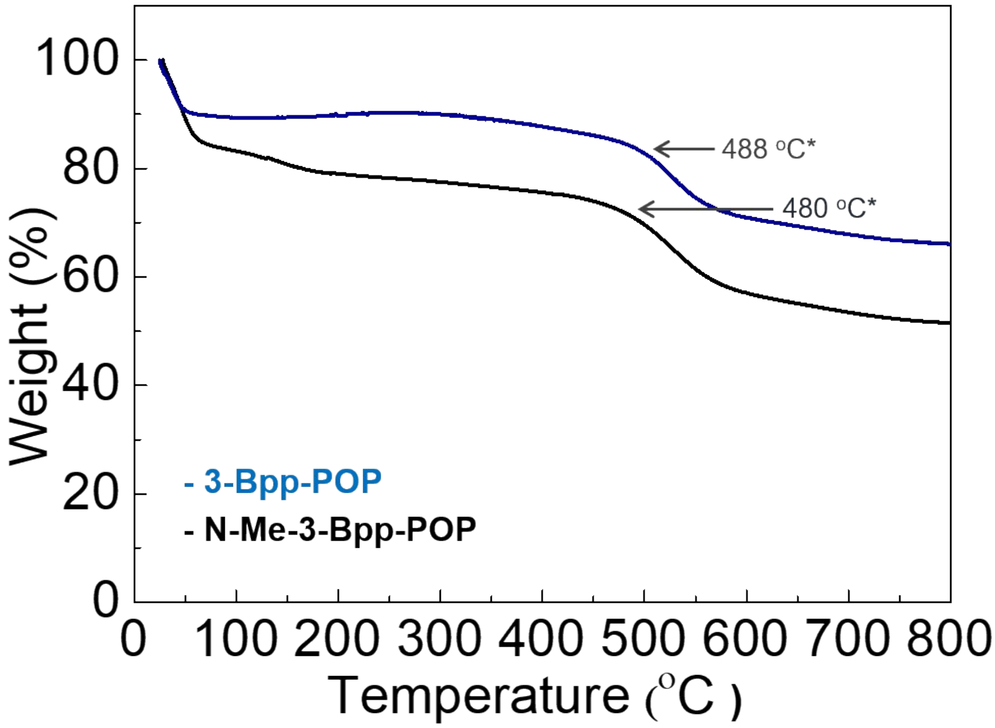
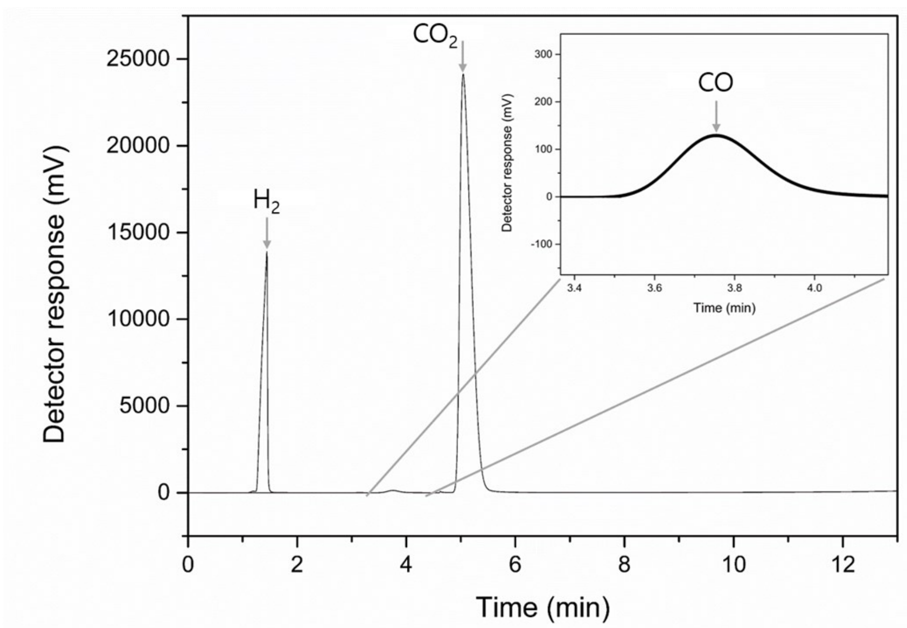


Figure S8. Performing GC analysis for detecting of CO



Gas	Retention time (min)
H_2	1.44
CO	3.75
CO_2	5.04

CO amount = 1406.477 ppm