Conversion of Formic Acid into Methanol Using a Bipyridine-functionalized Molecular Heterogeneous Catalyst

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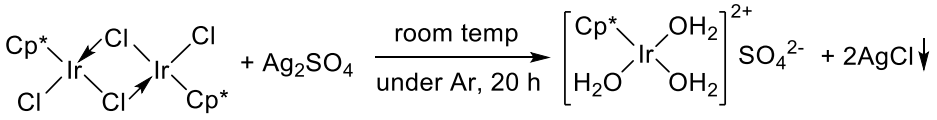
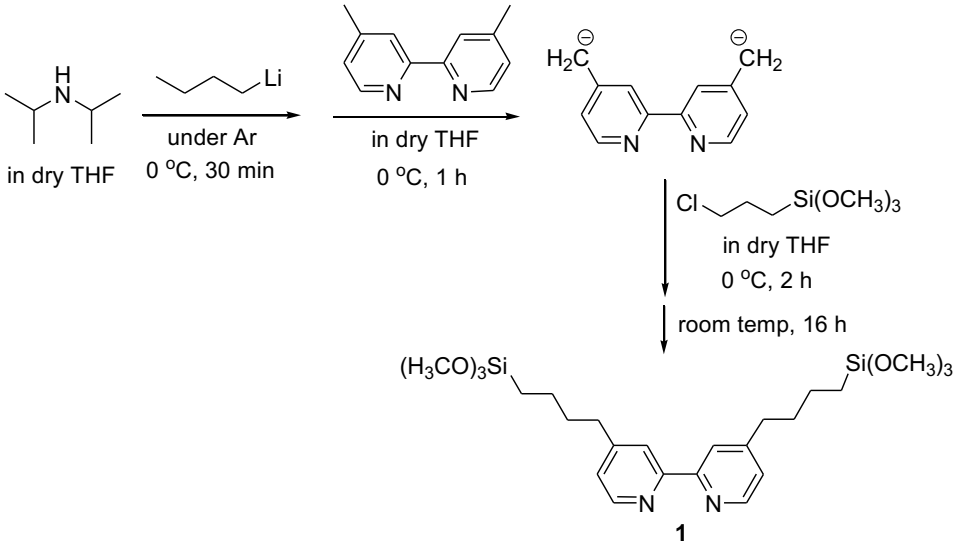
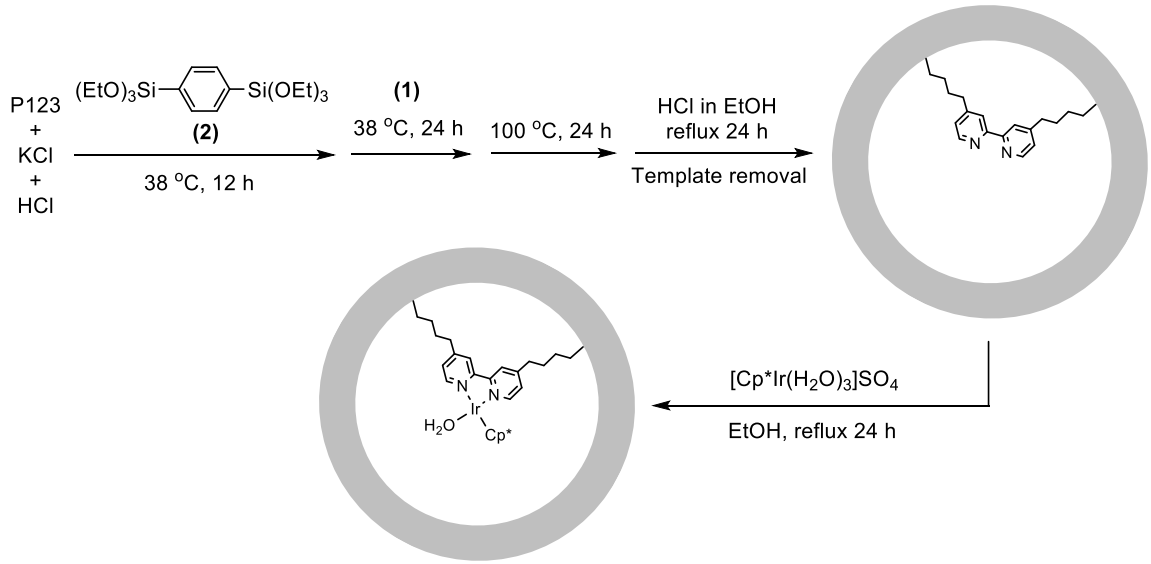


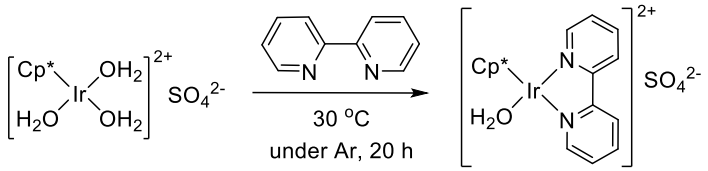
Scheme S1. Synthesis of $[Cp^*Ir(H_2O)_3]SO_4$



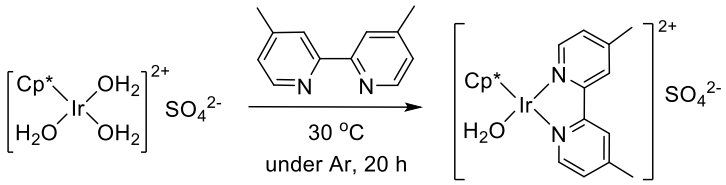
Scheme S2. Synthesis of 4,4′-[4-(Trimethoxysilanyl)butyl]-2,2′-bipyridine



Scheme S3. Synthesis of BPy-NT and Cp*Ir-BPy-NT



Scheme S4. Synthesis of $[Cp^*Ir(bpy)(H_2O)]SO_4$



Scheme S5. Synthesis of $[Cp^*Ir(dmbpy)(H_2O)]SO_4$

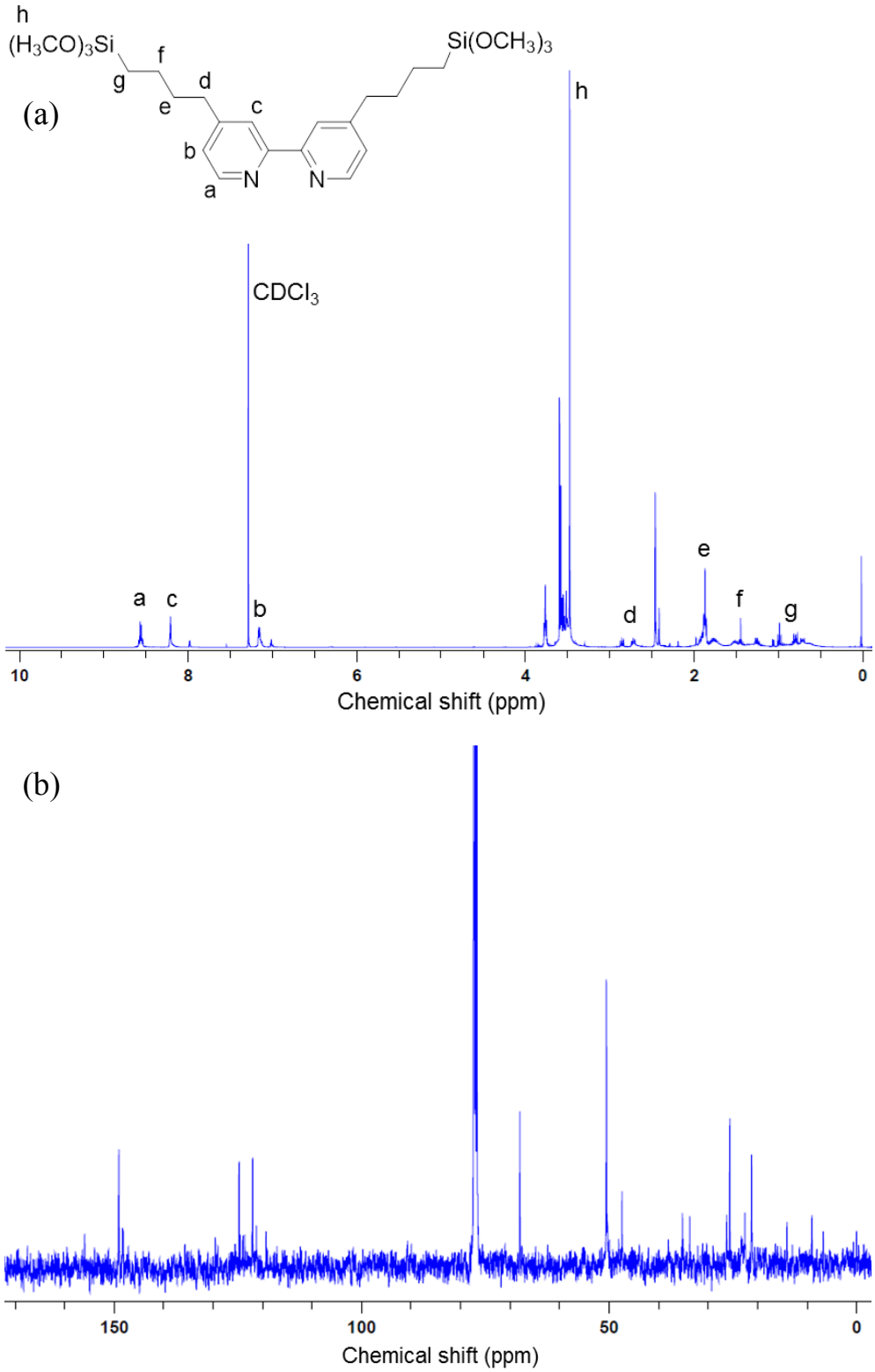


Figure S1. (a) ^{1}H NMR spectrum and (b) ^{13}C NMR spectrum of compound (1) in $CDCl_3$.

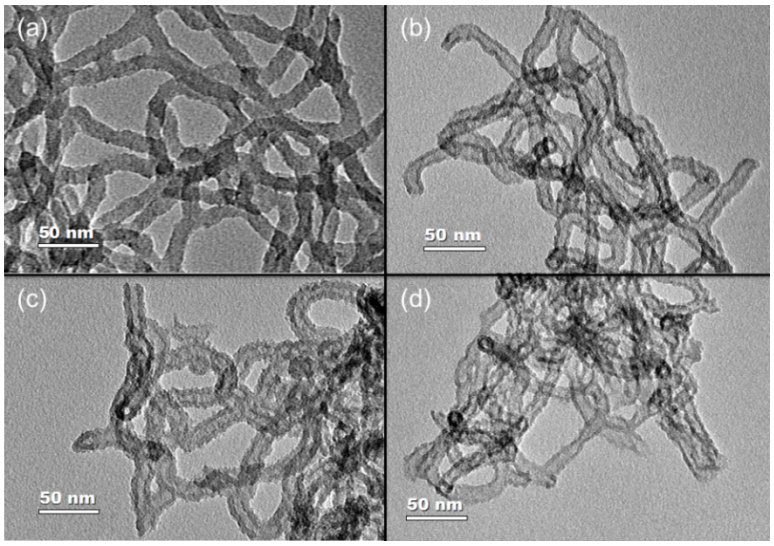


Figure S2. TEM images of (a) BPy-NT-1/3, (b) Ir-BPy-NT-1-3, (c) BPy-NT-1/9 and (b) Ir-BPy-NT-1-9.

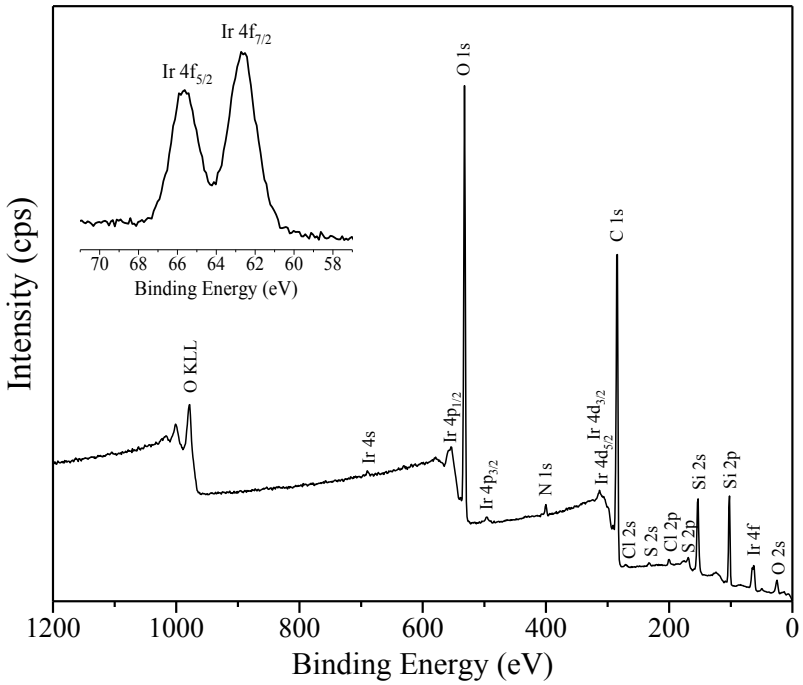


Figure S3. XPS spectrum of Ir-BPy-NT-1/6 catalyst. Ir 4f spectrum is shown in the inset.

Table S1. CHNS, XRF and ICP analyses data

Sample	C%	H%	N%	S%	Si%	Ir%	Ir/BPy
BPy-NT-1/9	41.86	4.60	0.77	–	39.64	–	–
Ir-BPy-NT-1/9	38.62	4.31	0.65	0.43	36.13	3.07	0.692
BPy-NT-1/6	41.87	4.65	0.98	–	38.79	–	–
Ir-BPy-NT-1/6	38.78	4.25	0.86	0.65	35.40	3.60	0.612
BPy-NT-1/3	40.99	4.72	1.22	–	36.25	–	–
Ir-BPy-NT-1/3	38.68	4.49	1.12	0.71	34.07	3.24	0.423

The values of carbon, hydrogen, nitrogen and sulfur contents were measured by CHNS elemental analysis. Si content was determined by XRF analysis. Ir loadings were measured by ICP analysis.

Table S2. Effect of H_2SO_4 on HCO_2H conversion and methanol selectivity

Entry	Catalyst (20 mg)	H_2SO_4 (mol%)[a]	HCO_2H conv.	MeOH yield	MeOH selectivity
1	Ir-BPy-SNT-1/9	5	78	0.5	0.6
2	Ir-BPy-SNT-1/9	10	64	1.4	2.2
3	Ir-BPy-SNT-1/9	20	43	4.1	9.5
4	Ir-BPy-SNT-1/6	20	39	4.2	10.8

Reaction conditions: 1 mL 4 M HCO_2H, T =60 °C, H_2 = 50 bar, t = 16 h. [a]H_2SO_4 concentration is w.r.t. HCO_2H.

Table S3. Effect of free nitrogen on methanol selectivity

Entry	Free N source*	HCO_2H conv.	MeOH yield	MeOH selectivity
1	-	32	7.8	24.4
2	Bipyridine	57	2.1	3.7
3	Pyridine	54	1.4	2.6
4	Aniline	55	2.8	5.1
5	Diisopropylamine	52	1.8	3.7
6	Triethylamine	63	2.2	3.5

Reaction conditions: 1 mL 4 M HCO_2H, Cp*Ir(bpy)SO_4 = 1.5 mg, CF_3SO_3H = 20 mol%, T =60 °C, H_2 = 50 bar, t = 6 h.
*Same equivalent of N was taken for all the nitrogen containing compounds.