Highly conversion of CO_2 into cyclic carbonates under solvent free and ambient pressure conditions by Fe complex cyanide

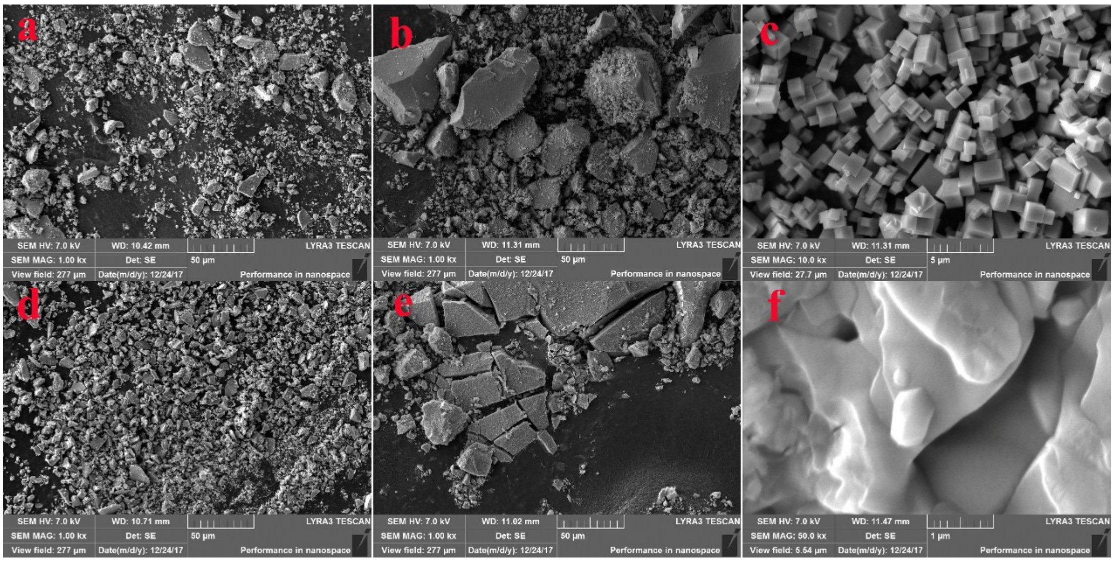


Figure S1 SEM of (a) $Fe^{III}_4(Fe(CN)_6)_3$, (b) $KNi_4(Fe^{III}(CN)_6)_3$, (c) $Fe^{III}_4(Fe(CN)_6)_3$-cube (d) after recycle 5 times of $Fe^{III}_4(Fe(CN)_6)_3$, (e) $KCo_4(Fe^{III}(CN)_6)_3$, (f) $KZn_4(Fe^{III}(CN)_6)_3$

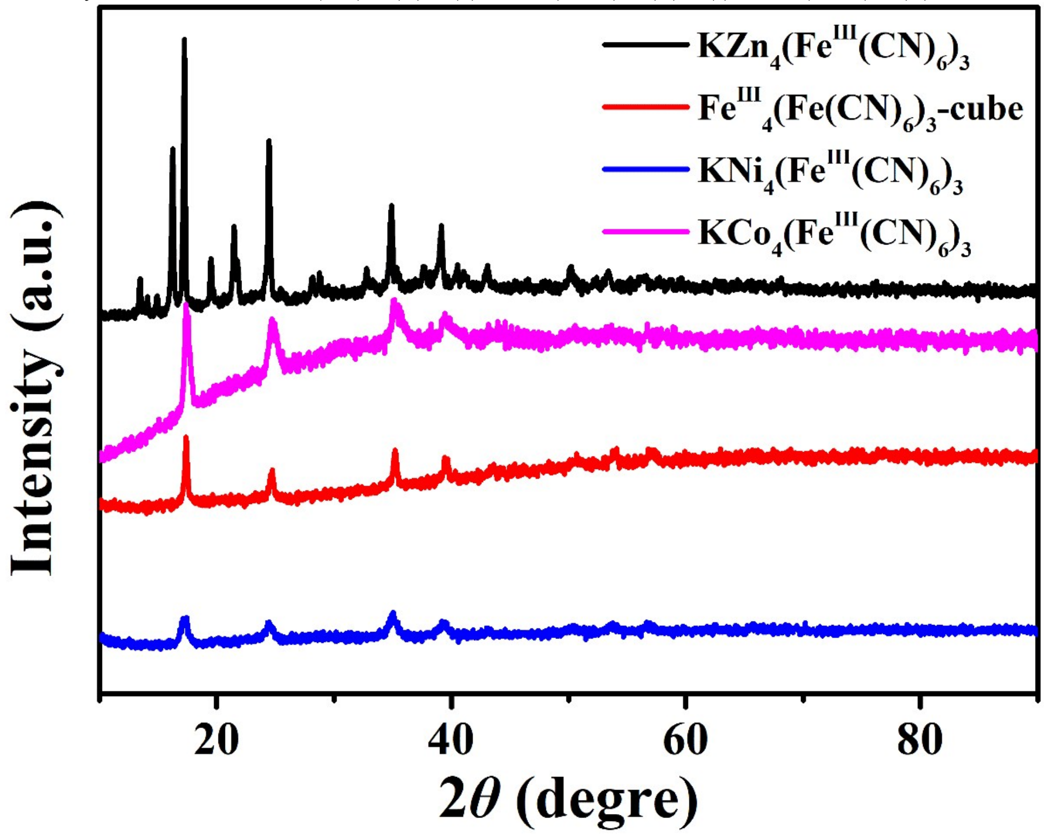


Figure S2 XRD of $KCo_4(Fe^{III}(CN)_6)^3$, $KZn_4(Fe^{III}(CN)_6)^3$, $KNi_4(Fe^{III}(CN)_6)^3$ and $Fe^{III}_4(Fe(CN)_6)_3$-cube

General experimental details

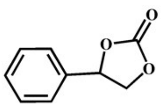
^{1}H-NMR spectra were recorded at 400 MHz. Chemical shifts (in ppm) were referenced to $CDCl_3$ (δ = 7.26 ppm) in as an internal standard. ^{13}C-NMR spectra were obtained at 100 MHz and were calibrated with $CDCl_3$ (δ = 77.0 ppm). Products were purified by flash chromatography on 200–300 mesh silica gels.

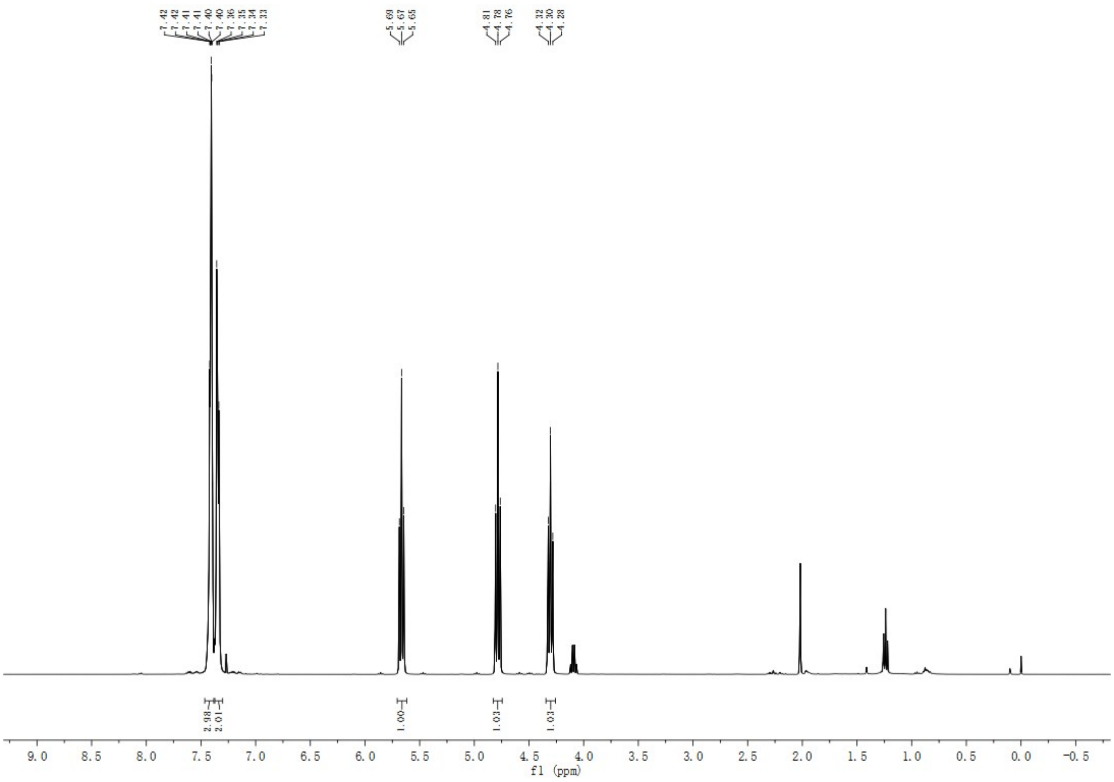
Analytical data for product of carbonic acid 1-phenylethylene ester

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (m, 3H), 7.34 (m, 2H), 5.67 (t, *J* = 8.0 Hz, 1H), 4.78 (t, *J* = 8.4 Hz, 1H), 4.30 (t, *J* = 8.3 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 155.08 (s), 135.87 (s), 129.72 (s), 129.22 (s), 126.04 (s), 78.12 (s), 71.28 (s).

NMR spectra of compound





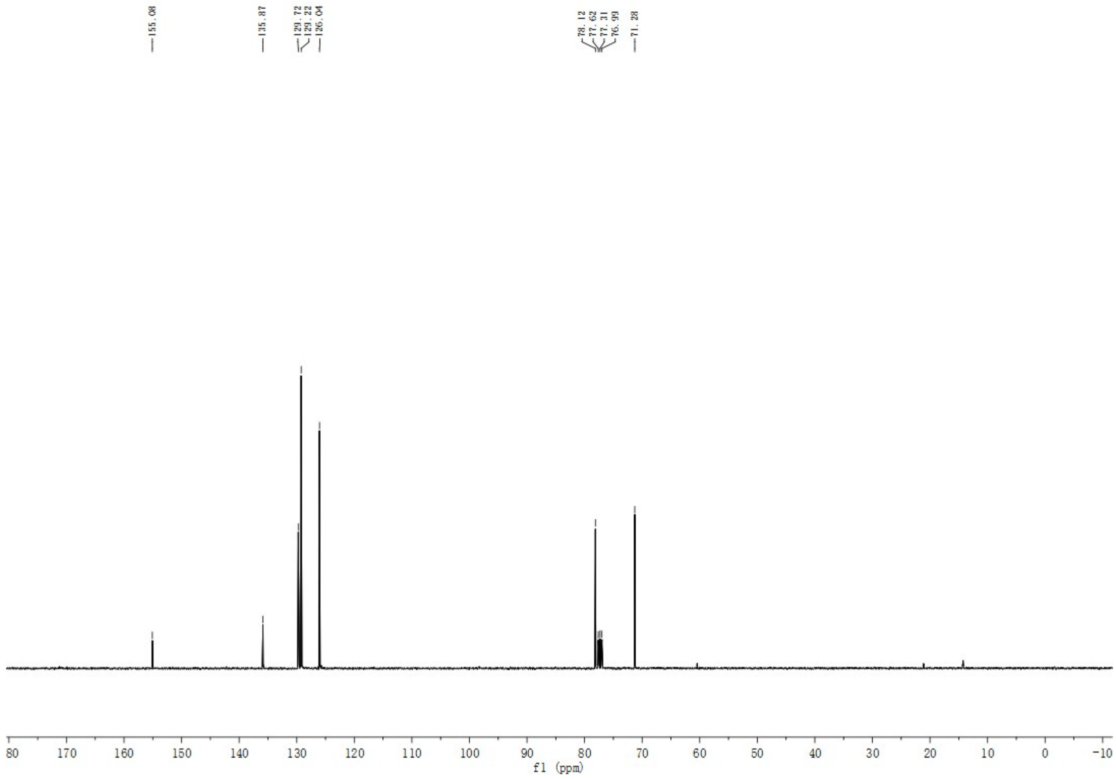


Table S1 Comparison with different reported metal cyanides as high-efficiency catalyst for cycloaddition reaction.

Catalysts and mass/(mg)	Epoxide (mL)	The pressure of CO_2/(bar)	Reaction temperature/(°C)	Reaction time/(h)	TOF h^{-1}	Yield (%)	Reference
$Fe^{III}_4(Fe(CN)_6)_3$/(10)	0.5	1	100	3	20.8	99	This work
DMC-Br/(20)	5	9.6	50	24	21.47	-	Catalysis Today 111 (2006) 292–296
$Zn_3Co(CN)_6$ x$ZnCl_2$ yH2O zCA (20)	5	9.6	80	24	22.76	-	Macromol. Symp. 2005, 224, 181-191
$Zn_3[Co(CN)_6]_2$.	-	45	110	10	38	-	Catal. Lett. Vol. 91, No. 1, 69−75 (2007)
$Zn_3[Co(CN)_6]_2 2.2H_2O$	-	-	90	8	3.75	57	Applied Catalysis A: General 325 (2007) 91–98
$Zn_3[Co(CN)_6]_2$/(20)	1.8	11.7	140	6	581	92	Applied Catalysis A: General 419–420 (2012) 178– 184

Table S2 The data of the active energy of $Fe^{III}_4(Fe(CN)_6)_3$-cube

Entry	T (K)	Slope	y intercept	r^2	K min^{-1}	Eact kJ/mol
1	343	-0.00215	0.00197	0.9991	0.00215	61.05
2	353	-0.00422	0.00775	0.9988	0.00422	
3	363	-0.00740	0.02267	0.9963	0.00740	
4	373	-0.01205	0.05615	0.9902	0.01205	

Table S3 The data of the active energy of $Fe^{Ⅲ}_4(Fe\,(CN)_6)_3$

Entry	T (K)	Slope	y intercept	r^2	K min^{-1}	Eact kJ/mol
1	343	-0.00206	0.00047	0.9859	0.00206	56.03
2	353	-0.00400	0.00654	0.9990	0.00400	
3	363	-0.00661	0.01830	0.9971	0.00661	
4	373	-0.01003	0.04007	0.9932	0.01003	

Table S4 The data of the active energy of $KNi_4(Fe^{Ⅲ}(CN)_6)_3$

Entry	T (K)	Slope	y intercept	r^2	K min^{-1}	Eact kJ/mol
1	343	-0.00315	0.00445	0.9993	0.00315	39.49
2	353	-0.00468	0.0099	0.9982	0.00468	
3	363	-0.00712	0.0210	0.9965	0.00712	
4	373	-0.00943	0.0358	0.9937	0.00943	

Table S5 The data of the active energy of $KZn_4(Fe^{III}(CN)_6)_3$

	T (K)	Slope	y intercept	r^2	K min^{-1}	Eact kJ/mol
1	343	-0.00121	0.00072	0.9998	0.00121	78.34
2	353	-0.00196	0.0018	0.9997	0.00196	
3	363	-0.00558	0.0139	0.9964	0.00558	
4	373	-0.01002	0.0403	0.9926	0.01002	