Supplementary Information

A highly active copper catalyst for the hydrogenation of Carbon Dioxide to formate under ambient conditions

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Table 1. Effect of solvent on the hydrogenation

Entry	solvent	Yield [%][b]	TON[c]
1.	1,4-dioxane	20	92
2.	THF	18	83
3.	CH_3CN	11	51
4.	CH_3OH	<1	<1
5.	DMF	30	138
6.	DME	15	69
7.	Toluene	10	46
8.	2-propanol	<1	<1

[a]Reaction conditions: catalyst (0.02 mmol), DBU (10 mmol), Dimethylformamide (5.0 mL), CO_2 (1 atm), H_2 (1 atm), 25°C, 12 h.
[b]Molar ratio of the product/initial DBU determined by ^1H NMR spectroscopy.
[c] TON: turnover number.

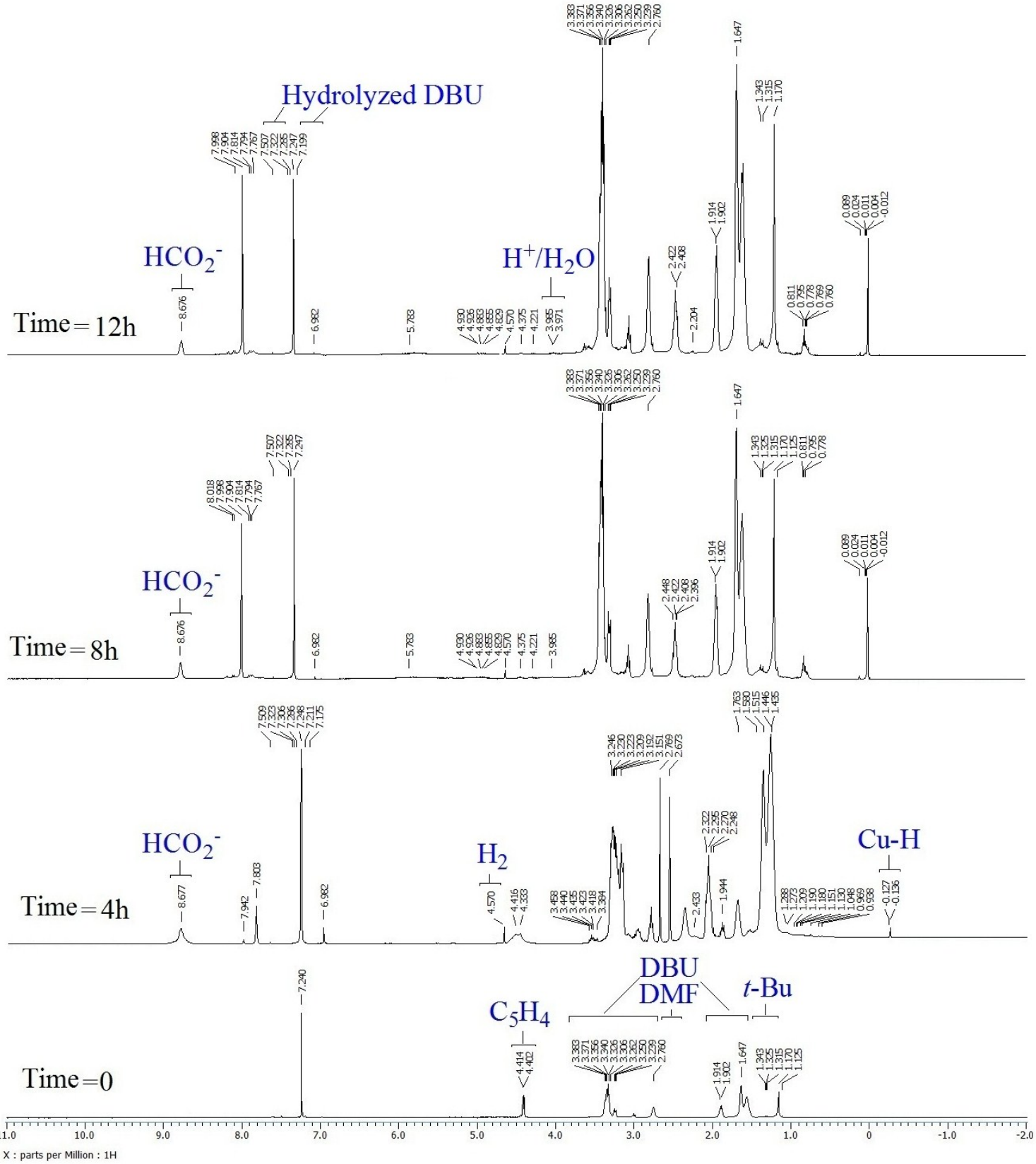

Figure S1. Time-resolved ^{1}H NMR spectra for a representative CO_2 hydrogenation using DBU. Conditions: 1.0 atm H_2/CO_2, 25°C, [CuI(dtbpf)] (0.02 mmol), DBU (10 mmol) was run in 5mL DMF and 0.25 mL of the reaction mixture was dissolved into 1.0 mL of $CDCl_3$ for analysis by NMR spectroscopy (Table 1, entry 6). The region from -2.0 to 11 ppm showing formate and catalyst 1,1′-bis(di-*tert*-butylphosphino) ferrocene signals is shown, and diagnostic peaks are labeled. Spectra were acquired at room temperature in $CDCl_3$ solvent.

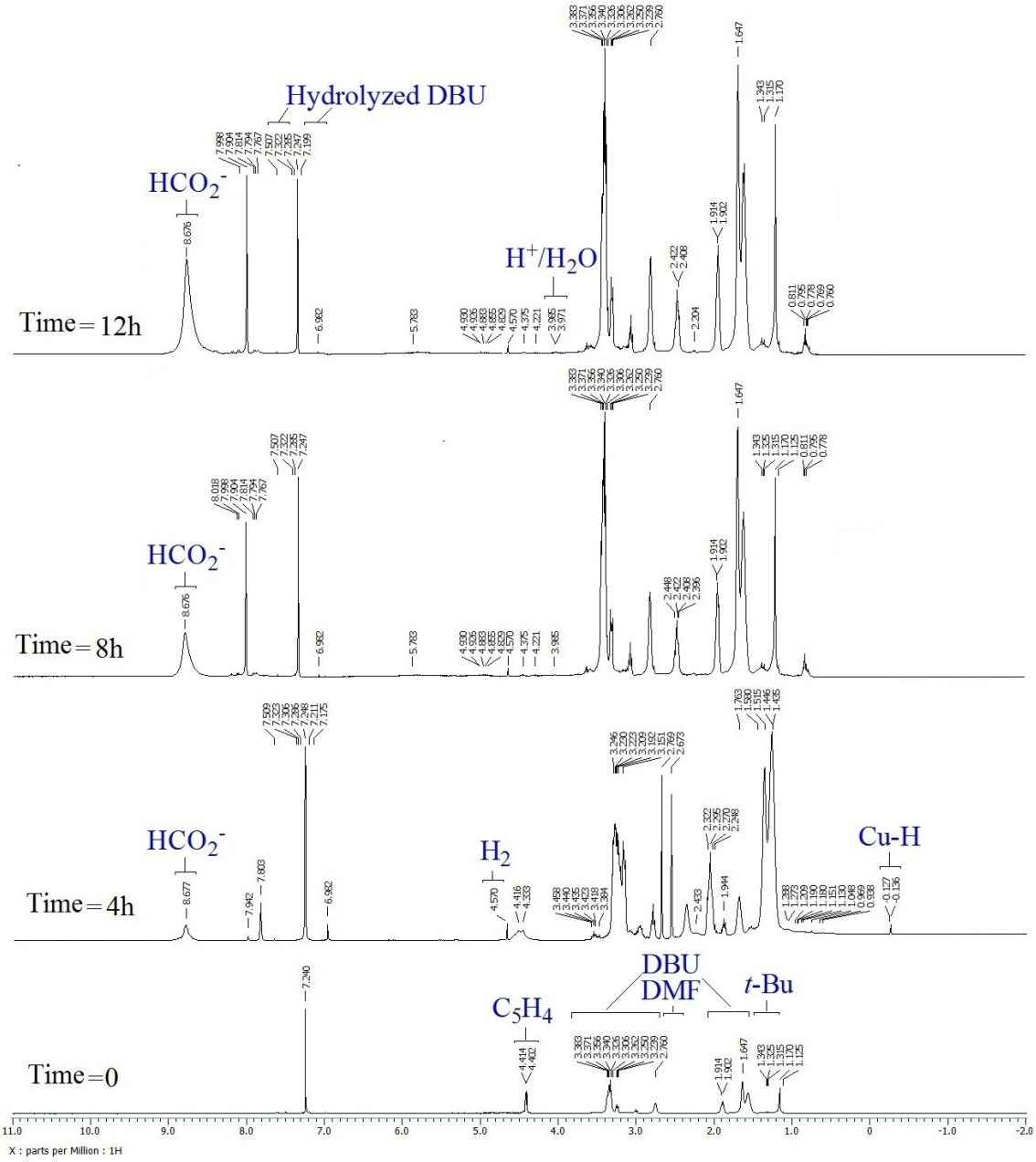

Figure S2. Time-resolved ^{1}H NMR spectra for a representative CO_2 hydrogenation using DBU. Conditions: 1.0 atm H_2/CO_2, 80°C, [CuI(dtbpf)] (0.02 mmol), DBU (10 mmol), in 5 mL DMF (Table 3, entry 5). The region from -2.0 to 11 ppm showing formate and catalyst 1,1′-bis(di-*tert*-butylphosphino) ferrocene signals is shown, and diagnostic peaks are labeled. Spectra were acquired at room temperature in $CDCl_3$ solvent.

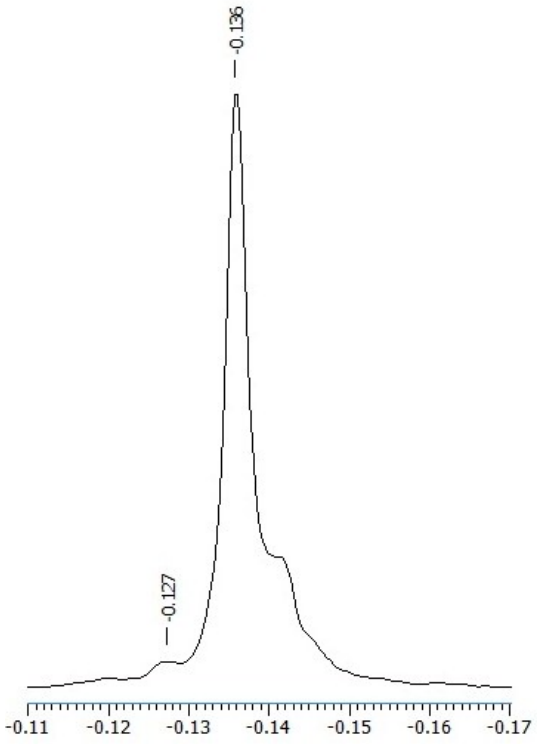

Figure S3. ^{1}H NMR spectrum for a representative CO_2 hydrogenation using DBU in $CDCl_3$ solvent. Conditions: 1.0 atm H_2/CO_2, 80°C, [CuI(dtbpf)] (0.02 mmol), DBU (10 mmol), in 5 mL DMF. The region from -0.11 to -0.17 ppm showing Cu-H signal.

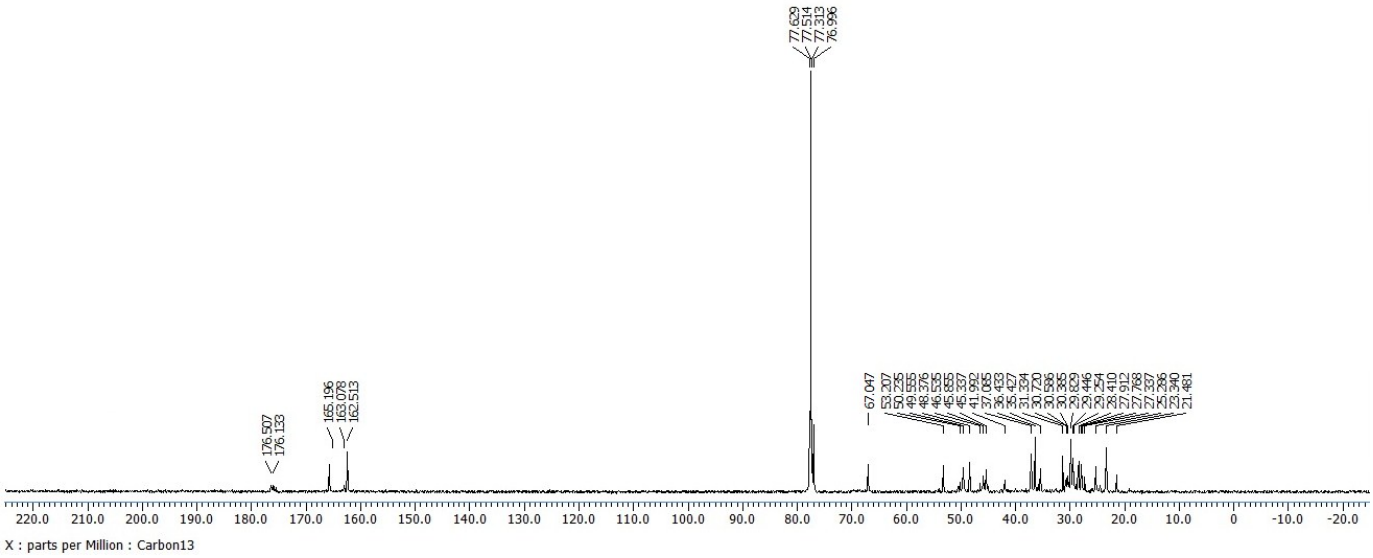

Figure S4. ^{13}C NMR spectrum of reaction mixture for a representative CO_2 hydrogenation using DBU in $CDCl_3$ solvent. Conditions: 1.0 atm H_2/CO_2, 80°C, [CuI(dtbpf)] (0.02 mmol), DBU (10 mmol), in 5 mL DMF after 4 hour.

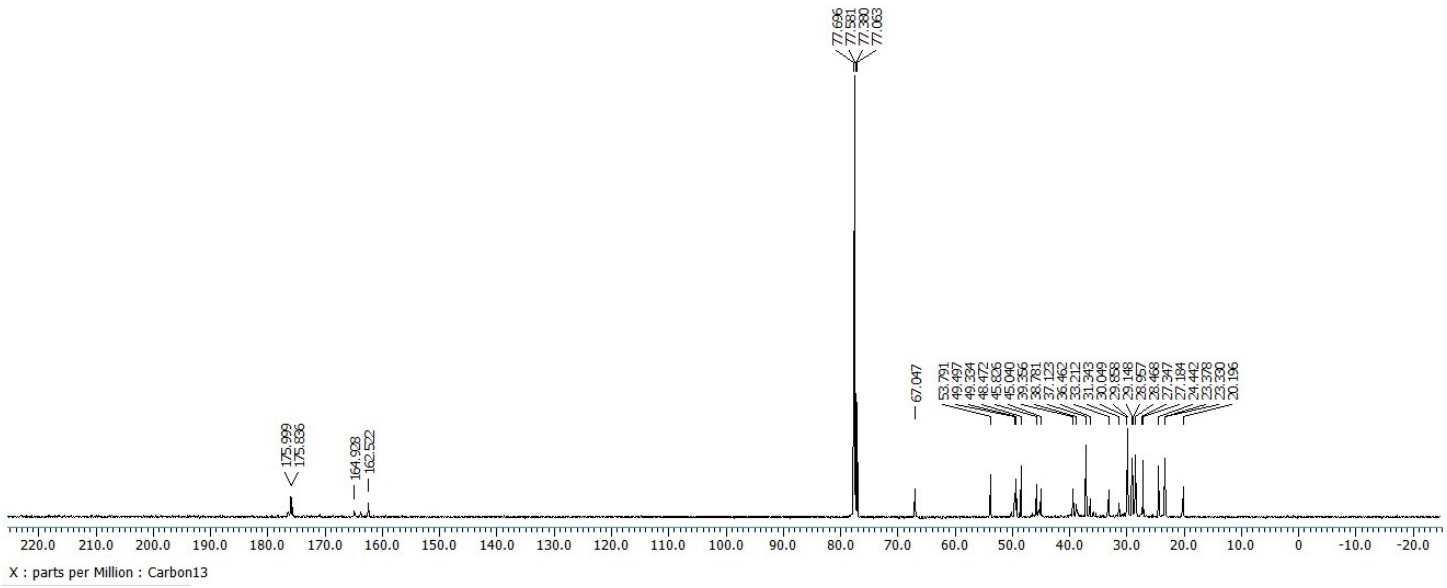

Figure S5. ^{13}C NMR spectrum of reaction mixture for a representative CO_2 hydrogenation using DBU in $CDCl_3$ solvent. Conditions: 1.0 atm H_2/CO_2, 80°C, [CuI(dtbpf)] (0.02 mmol), DBU (10 mmol), in 5 mL DMF after 12 hour.

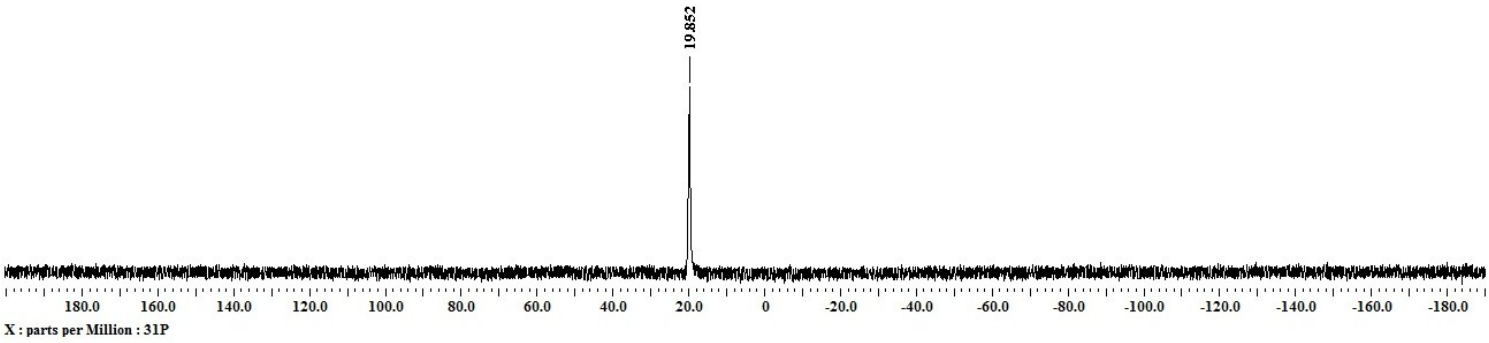

Figure S6. $^{31}P\{^{1}H\}$-NMR spectrum of [CuI(dtbpf)] at room temperature (400 MHz, in $CDCl_3$).

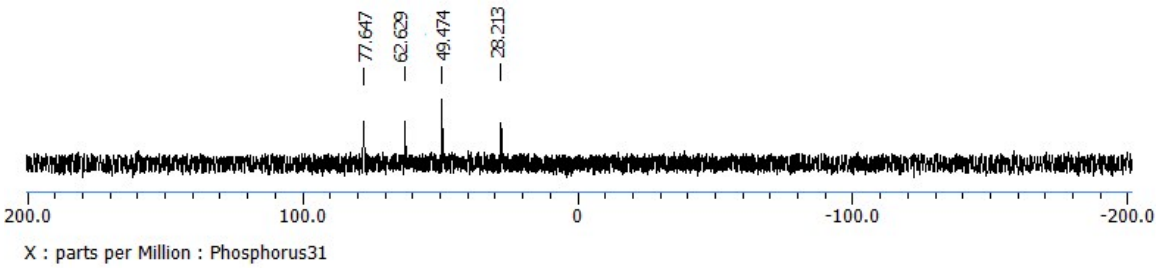

Figure S7. $^{31}P\{^{1}H\}$-NMR *in-situ* spectrum of a post catalytic mixture in $CDCl_3$.

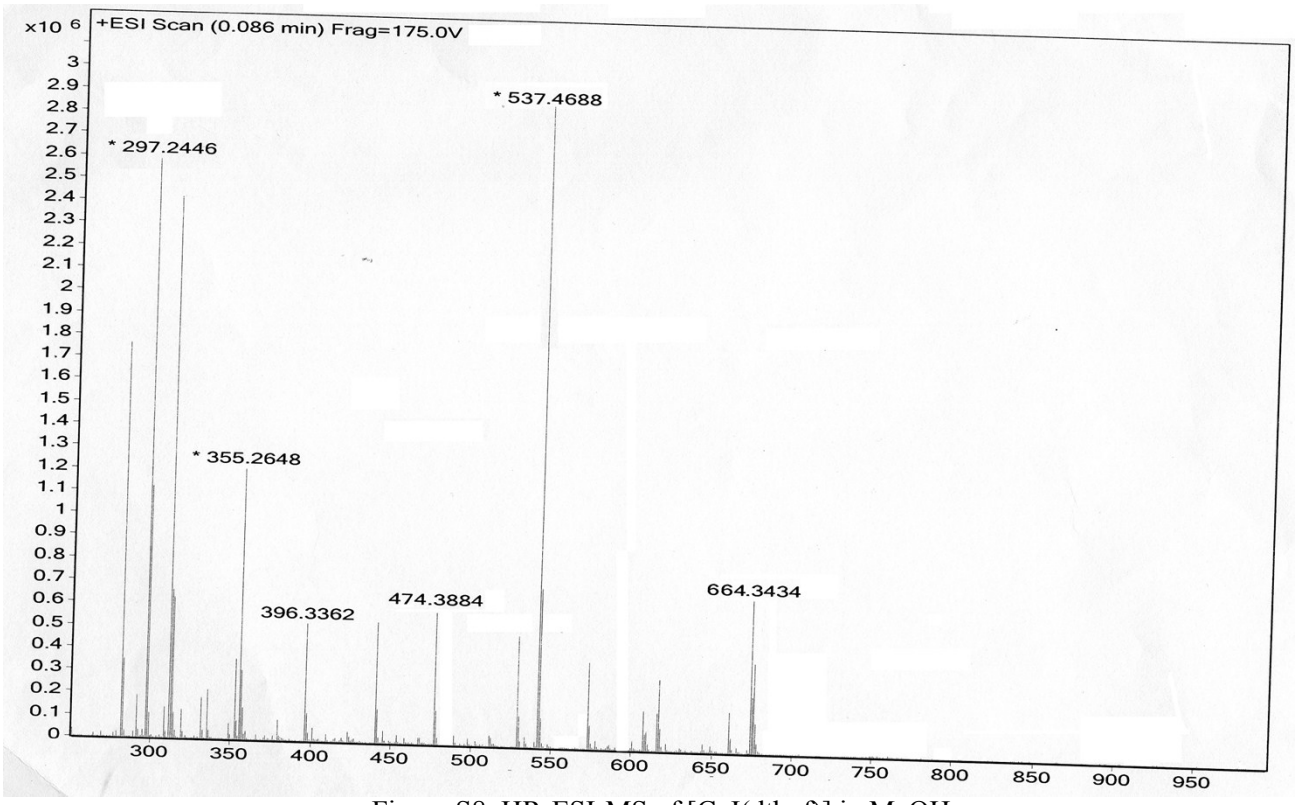

Figure S8. HR-ESI-MS of [CuI(dtbpf)] in MeOH.

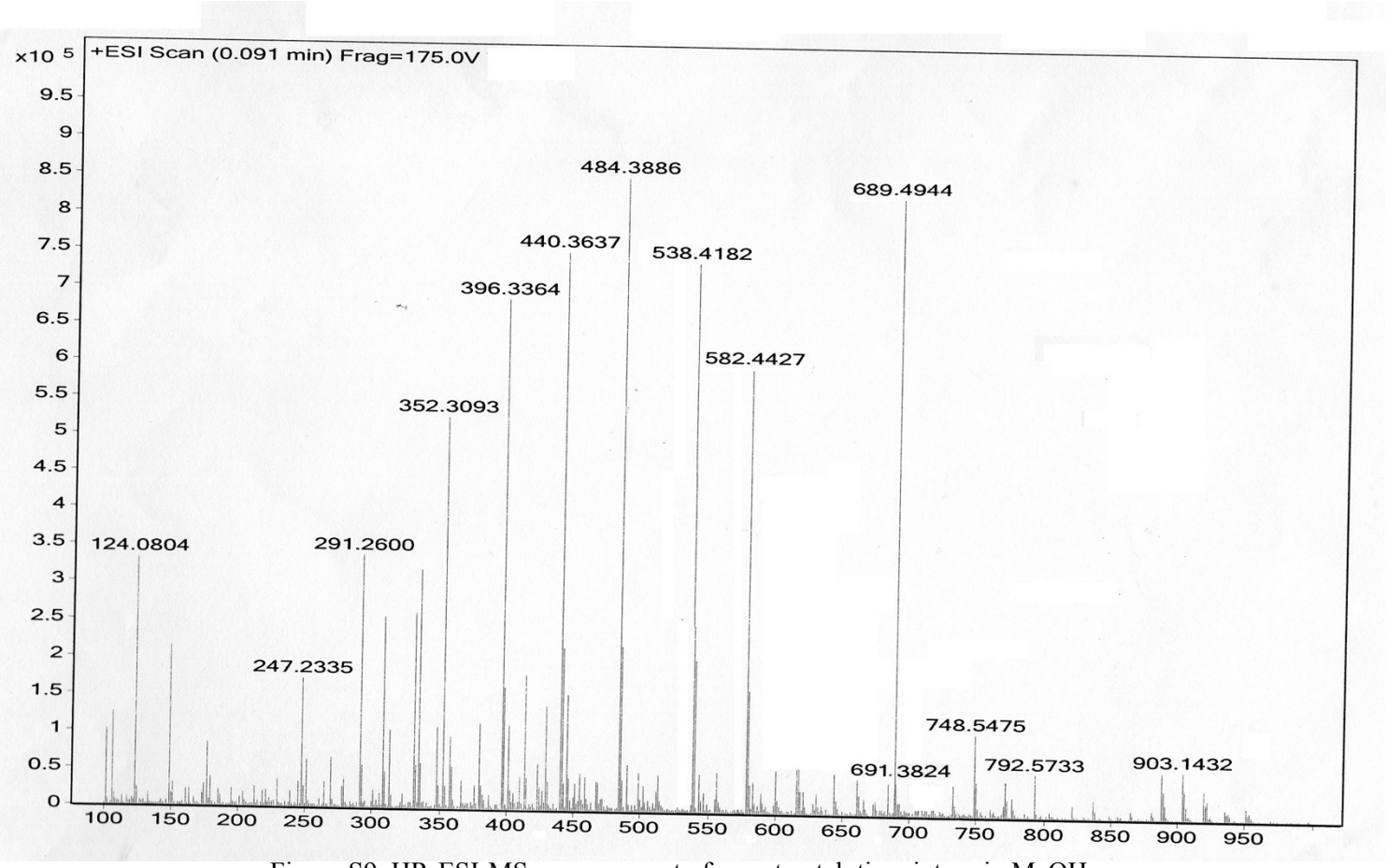

Figure S9. HR-ESI-MS measurement of a post-catalytic mixture in MeOH.

Synthesis of [CuH(dtbpf)]: A 100 mL two neck round-bottom (RB) flask was charged with [CuI(dtbpf)] (166 mg, 0.25 mmol) in 5 ML of CH_3OH:CH_3CN (50:50 V/V). This two neck round-bottom was connected to three neck round-bottom (RB) containing granulated tin metal through tube. Concentrated HCl was added to three neck round-bottom (RB) containing granulated tin metal in part wise to generate H_2 gas *in-situ* and this generate H_2 gas was passed to 100 mL two neck round-bottom (RB) flask through tube. The resulting solution was stirred for 12 hour. The solution turned bright yellow and pale and cloudy yellow precipitate appeared. This was separated and washed with small amount of diethyl ether and dried under vacuum. Yield: (67 mg, 50%).

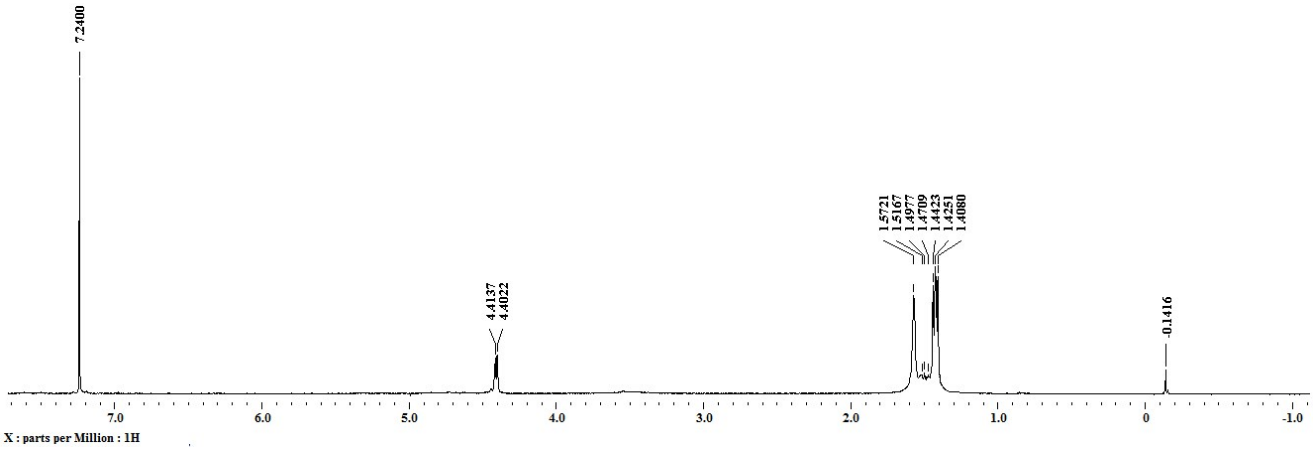

Figure S10. $^{1}H\{^{31}P\}$decoupled NMR spectrum of [CuH(dtbpf)] at room temperature (400 MHz, in $CDCl_3$).

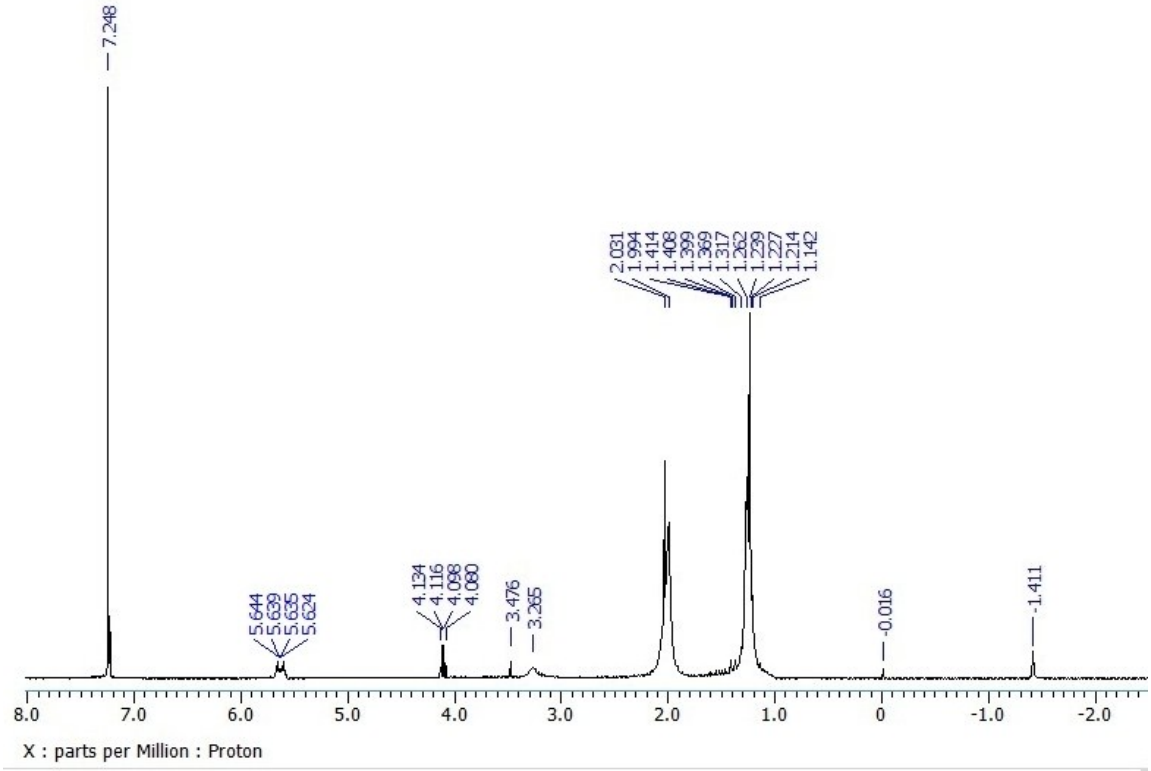

Figure S11. $^{1}H\{^{31}P\}$coupled NMR spectrum of [CuH(dtbpf)] at room temperature (400 MHz, in $CDCl_3$).

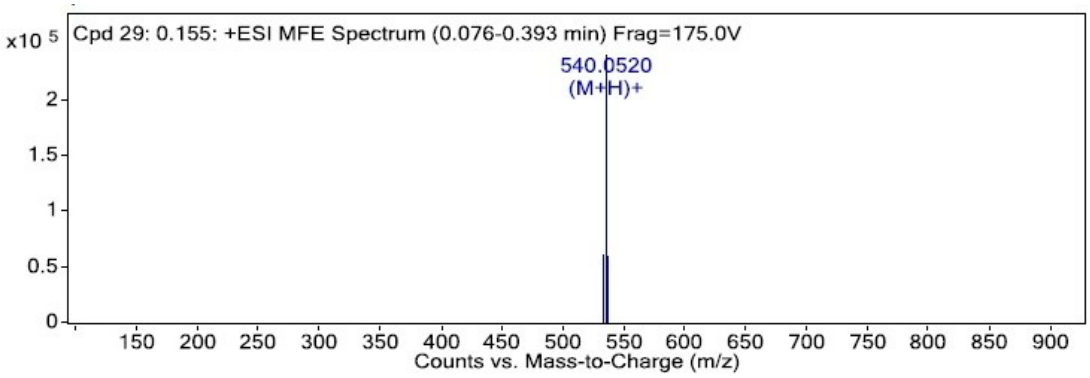

Figure S12. HR-ESI-MS measurement of [CuH(dtbpf)] in MeOH.