

## Supporting Information for

### Biomass-derived $\gamma$ -valerolactone as efficient solvent and catalyst for the conversion of CO<sub>2</sub> with amines

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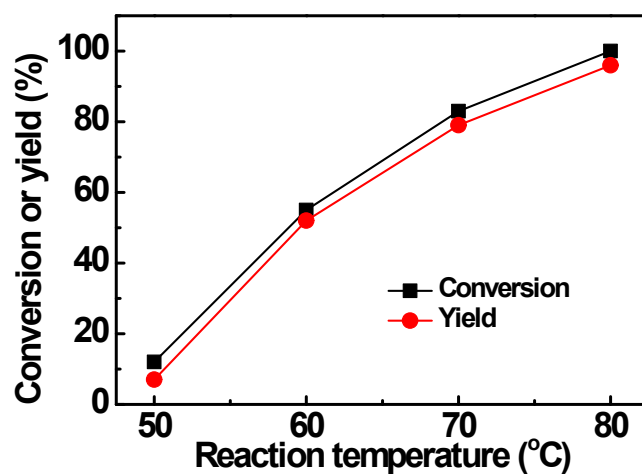
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#### 1. Experimental Section

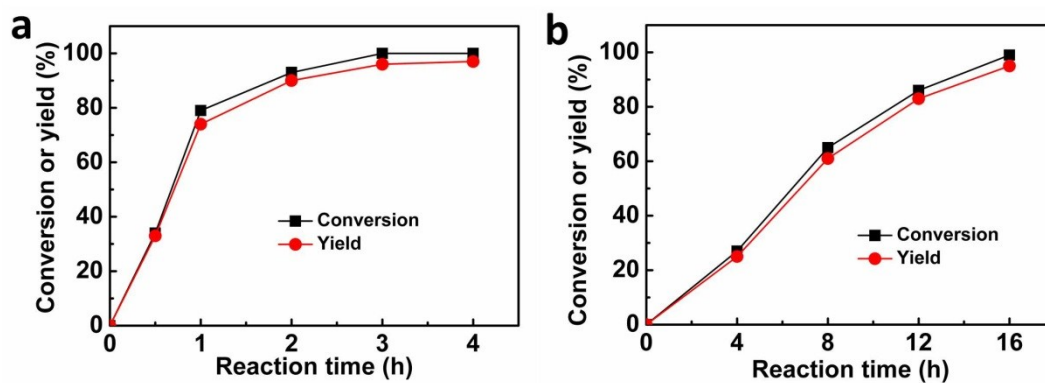
**Materials:** *N*-Methylaniline (99%), 4-methoxy-*N*-methylaniline (98%), 4-methyl-*N*-methylaniline (98%), 4-bromo-*N*-methylaniline (97%), 2-methoxy-*N*-methylaniline (97%), indoline (97%), diphenylamine (99%), dihexylamine (98%), pyrrolidine (99%), aniline (99%), 4-methoxyaniline (99%), 3,5-dimethylaniline (98%), 2,6-diisopropylaniline (95%), 2-methoxyaniline (99%), benzylamine (99%), 4-methoxybenzylamine (98%), 4-chlorobenzylamine (98%), octylamine (99%),  $\gamma$ -valerolactone (98%),  $\gamma$ -butyrolactone (99%),  $\delta$ -valerolactone (98.5%),  $\epsilon$ -Caprolactone (99%), ethyl levulinate (98%), 2-aminophenol (99%), 2-aminothiophenol (99%), *o*-phenylenediamine (99%), dimethyl carbonate (99.5%), diethyl carbonate (99%), butyl ether (99%), mesitylene (98%), *N,N*-dimethylaniline (99%), diphenylsilane (Ph<sub>2</sub>SiH<sub>2</sub>, 99%), triethylsilane (Et<sub>3</sub>SiH, 99%), and phenylsilane (PhSiH<sub>3</sub>, 97.5%) were provided by J&K Scientific Ltd. 4-Chloro-*N*-methylaniline (95%), *N*-methyl-4-nitroaniline (97%), di-*n*-propylamine (99%), morpholine (99%), and dodecane (99%) were purchased from Alfa Aesar. Ethyl acetate, tetrahydrofuran, CH<sub>2</sub>Cl<sub>2</sub>, CH<sub>3</sub>CH<sub>2</sub>OH, CH<sub>3</sub>OH, CH<sub>3</sub>CN, 1,4-dioxane, methylbenzene, chloroform, carbon tetrachloride, and acetone were A. R. grade and were obtained from Sinopharm Chemical Reagent Beijing Co., Ltd.

**Formylation of various amines using CO<sub>2</sub> as the carbon source to produce formamides:** In a typical experiment, amines (1 mmol), PhSiH<sub>3</sub> (2 mmol) and the solvent (1 g) were charged into a stainless reactor of 20 mL equipped with a magnetic stirrer. After sealing, CO<sub>2</sub> was charged into the reactor until the desired pressure was reached. Then, the reactor was put into a constant-temperature air bath at a desired temperature, and the stirrer was started. After a certain reaction time, the reactor was placed into ice water and CO<sub>2</sub> was released slowly passing through a cold trap containing the corresponding solvent to absorb the trace amounts of reactant and product entrained by CO<sub>2</sub>. After depressurization, the solvent in the cold trap and the internal standard ethylbenzene were added into the reactor. The reaction mixture was analyzed quantitatively by gas chromatography (GC, Agilent 7890), and identification of the products was done by GC-MS (Shimadzu QP2010).

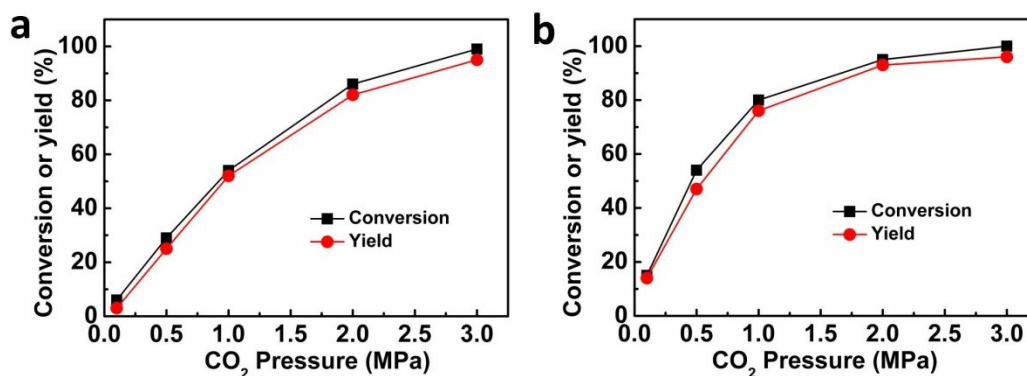
## 2. Results and Discussion



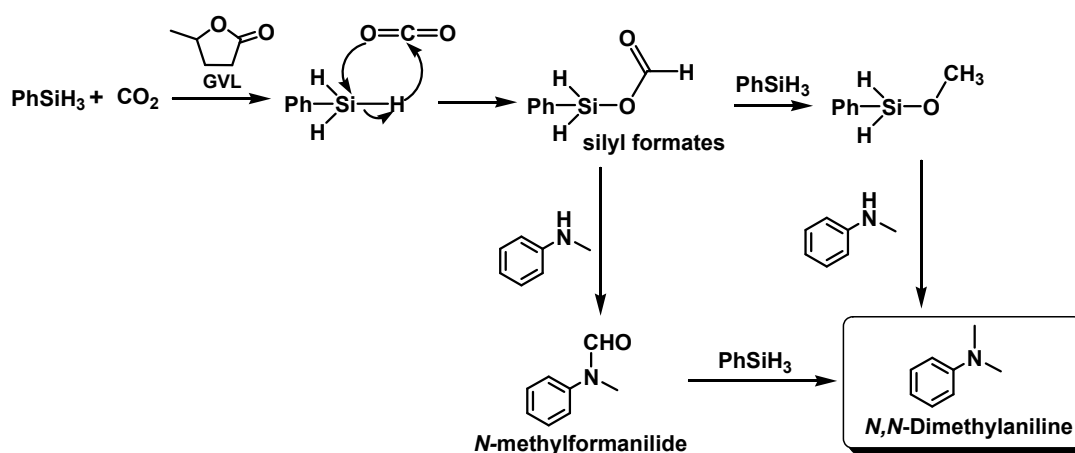
**Fig. S1.** Effect of reaction temperature on the formylation of *N*-methylaniline using CO<sub>2</sub> as the carbon source. Reaction conditions: *N*-methylaniline, 1 mmol; PhSiH<sub>3</sub>, 2 mmol; GVL, 1 g; CO<sub>2</sub>, 3 MPa; reaction time, 3 h.



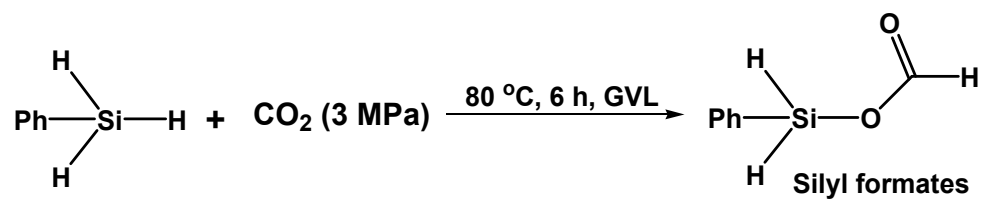
**Fig. S2.** Influence of reaction time on the formylation of *N*-methylaniline using CO<sub>2</sub> as the carbon source. Reaction conditions: *N*-methylaniline, 1 mmol; PhSiH<sub>3</sub>, 2 mmol; GVL, 1 g; CO<sub>2</sub>, 3 MPa; reaction temperature, 80 °C for a and 50 °C for b.



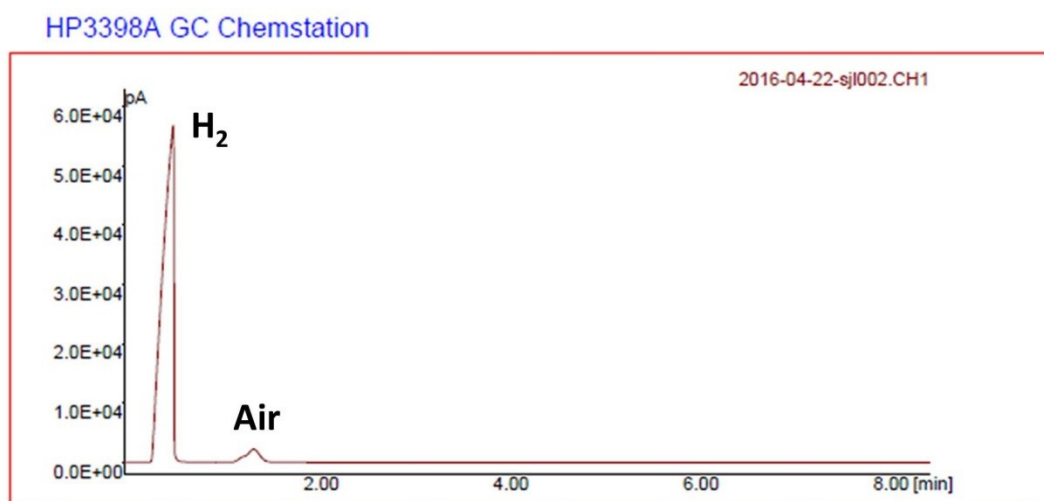
**Fig. S3.** Influence of CO<sub>2</sub> pressure on the formylation of *N*-methylaniline using CO<sub>2</sub> as the carbon source. Reaction conditions: *N*-methylaniline, 1 mmol; PhSiH<sub>3</sub>, 2 mmol; GVL, 1 g; reaction temperature, 50 °C for a and 80 °C for b; reaction time, 16 h for a and 3 h for b.



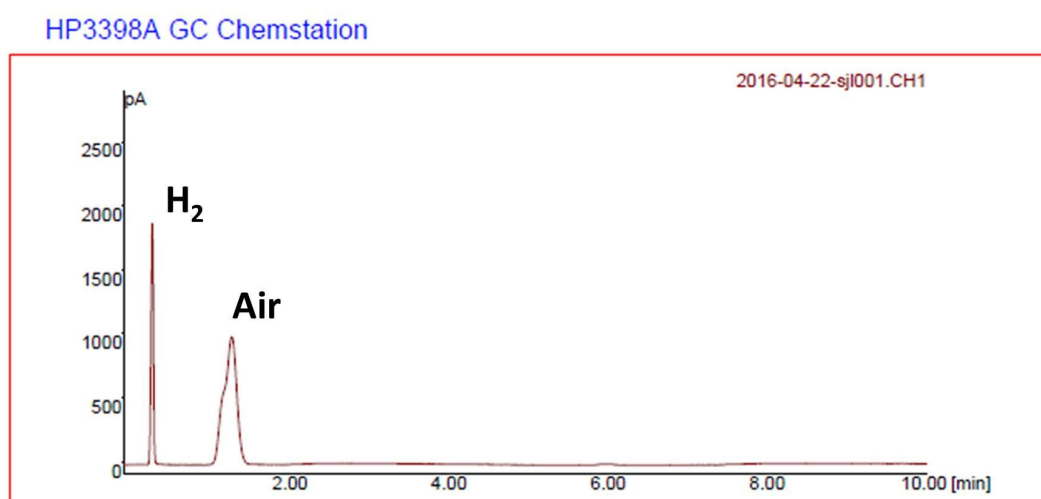
**Scheme S1.** The route for the formation of *N,N*-dimethylaniline in GVL.



**Scheme S2.** The formation of the active silyl formates in GVL.



**Fig. S4.** The GC spectra for the gas products from the mixture of dihexylamine and  $\text{PhSiH}_3$  stirred at room temperature for 2 h.



**Fig. S5.** The GC spectra for the gas products from the mixture of *N*-methylaniline and  $\text{PhSiH}_3$  stirred at room temperature for 2 h.

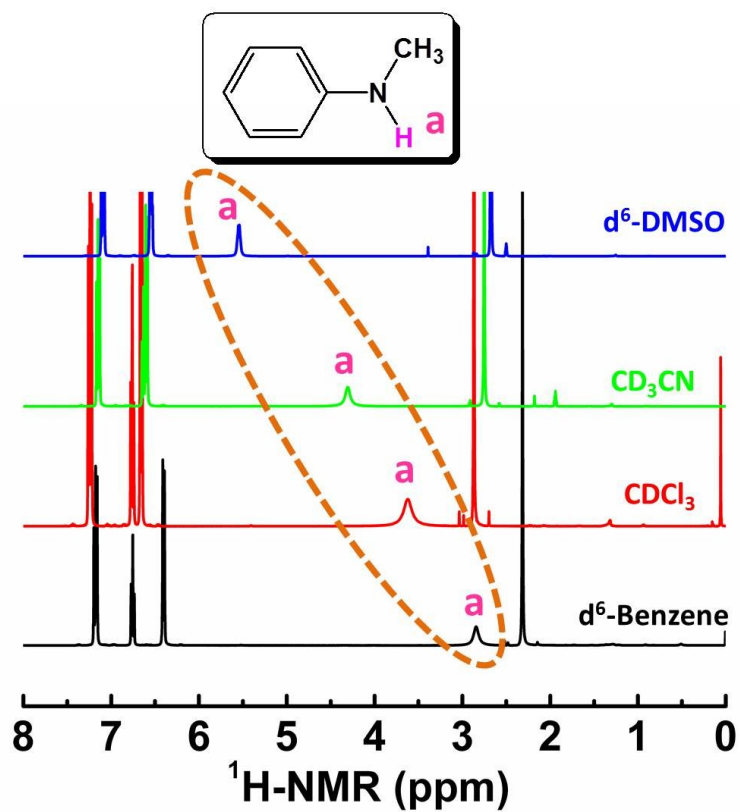


Fig. S6.  $^1\text{H}$  NMR spectra for *N*-methylaniline in different deuterated solvents.

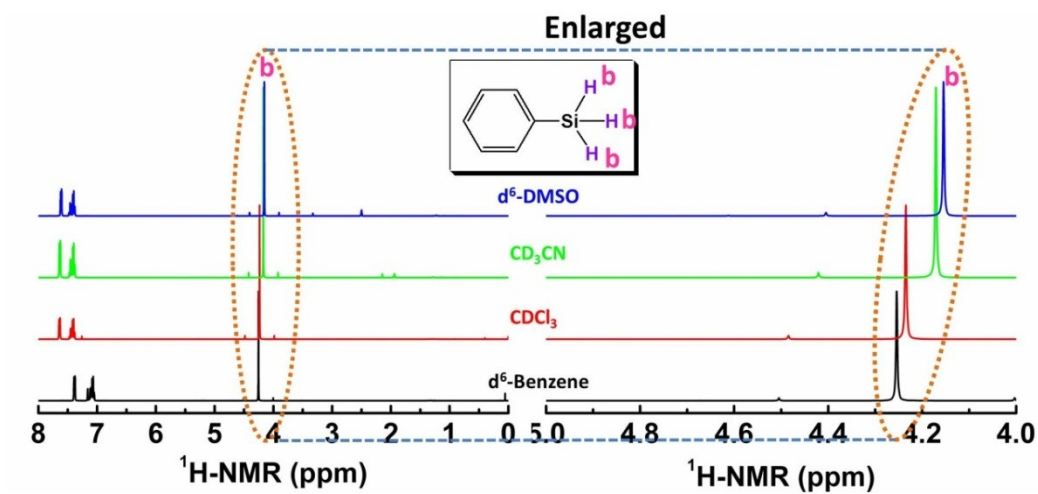
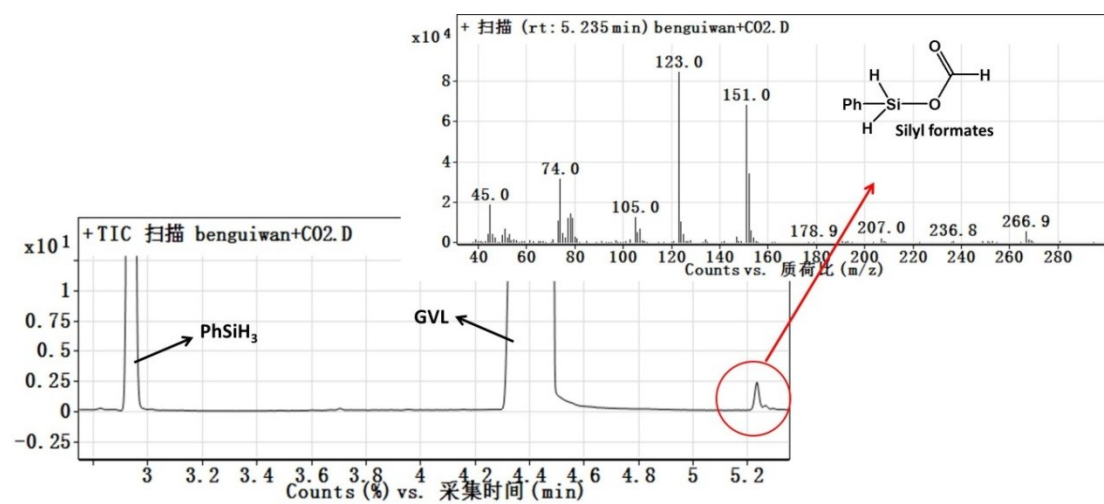


Fig. S7.  $^1\text{H}$  NMR spectra for  $\text{PhSiH}_3$  in different deuterated solvents.



**Fig. S8.** GC-MS spectra of the mixture of  $\text{PhSiH}_3$  (3 mmol), GVL (1 g) and  $\text{CO}_2$  (3 MPa) treated at  $80\text{ }^\circ\text{C}$ .