Electronic supplementary information (ESI)

Eco-friendly acetylcholine-carboxylate bio-ionic liquids for controllable *N*-methylation and *N*-formylation using ambient CO_2 at low temperatures

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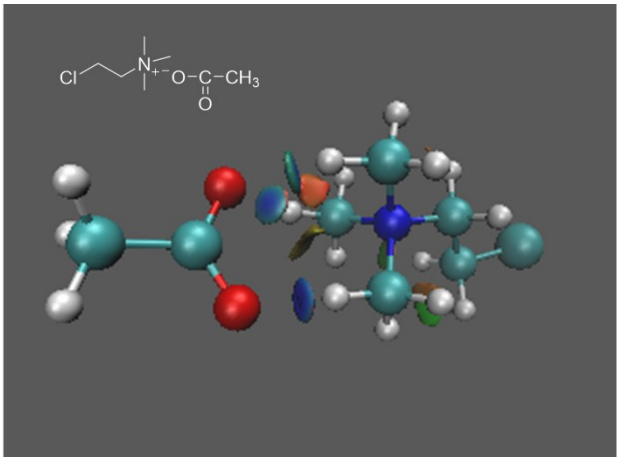


Figure S1 Calculated/simulated representative atomic diagram of CC-AA catalyst. Fairly strong hydrogen-bond interaction between anion and cation of the bio-IL CC-AA was observed.

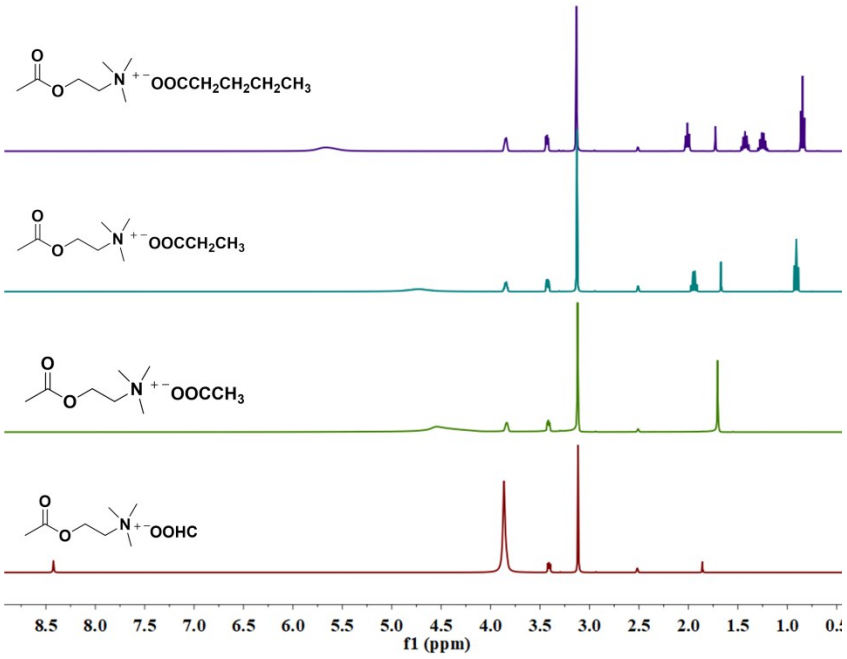


Figure S2 ^{1}H NMR spectra of ionic liquid catalysts: acetylcholine formate (ACH-FA), acetylcholine acetate (ACH-AA), acetylcholine propionate (ACH-PA) and acetylcholine valerate (ACH-VA) with d_6-DMSO as deuterated solvent.

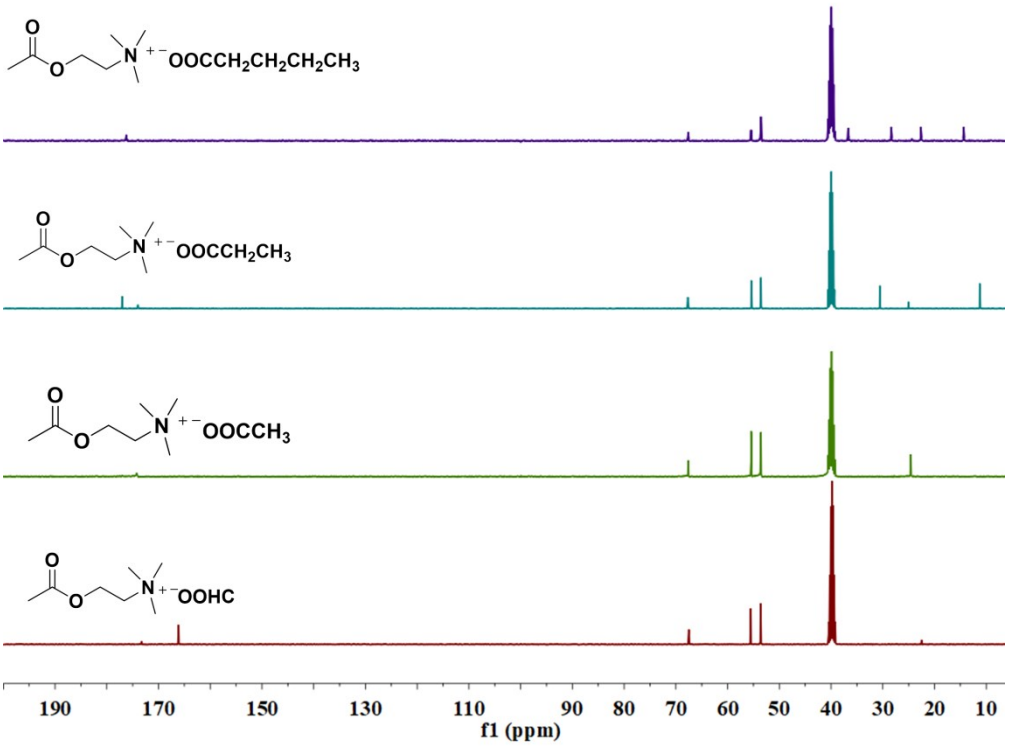


Figure S3 ^{13}C NMR spectra of ionic liquid catalysts: acetylcholine formate (ACH-FA), acetylcholine acetate (ACH-AA), acetylcholine propionate (ACH-PA), and acetylcholine valerate (ACH-VA) with d_6-DMSO as deuterated solvent

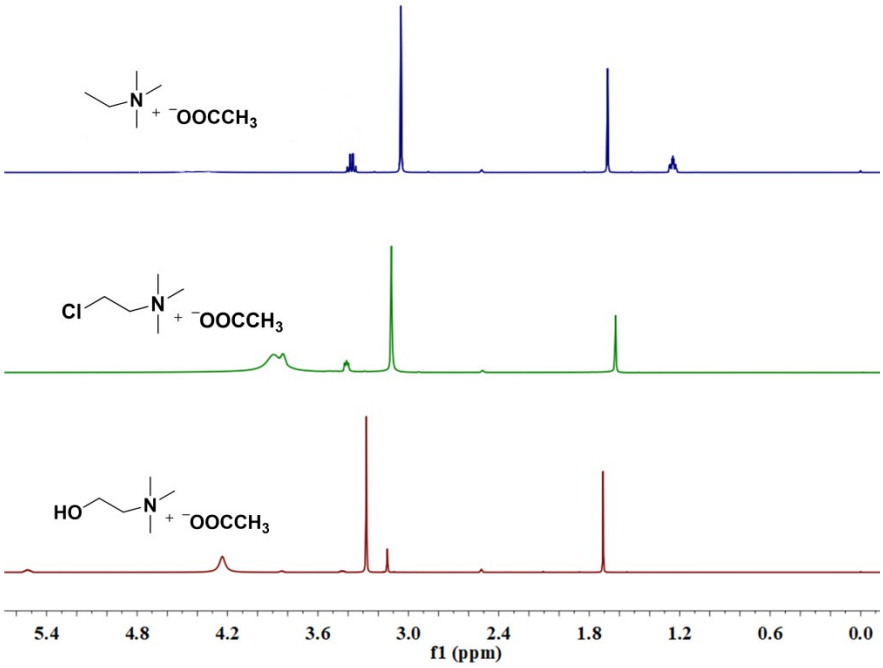


Figure S4 ^{1}H NMR spectra of ionic liquid catalysts: thyltrimethylammonium (ETA-AA), choline (CH-AA) and chlormequat (CC-AA) acetate with d_6-DMSO as deuterated solvent

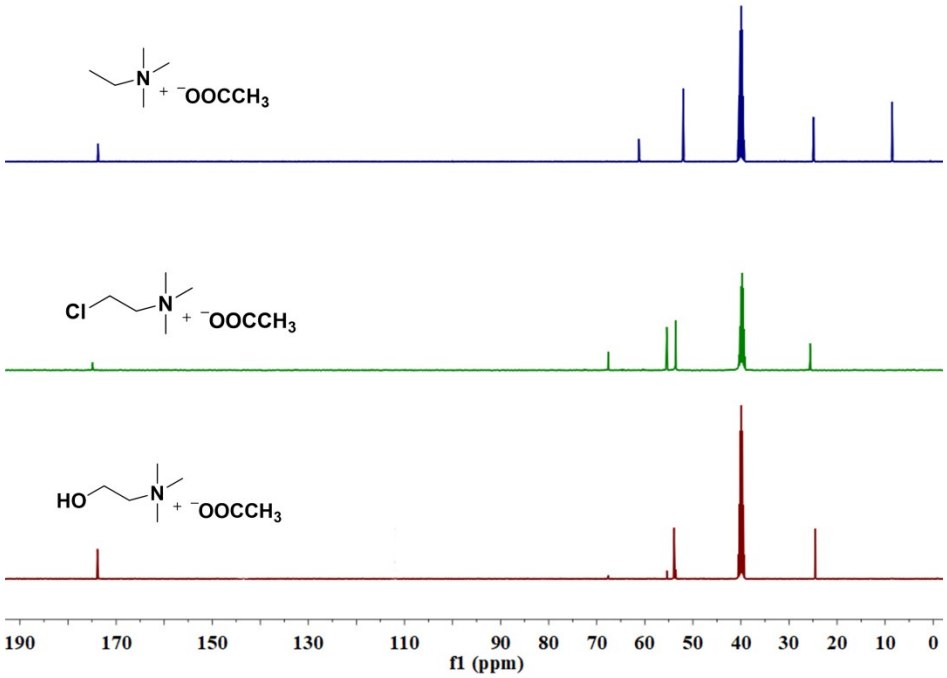
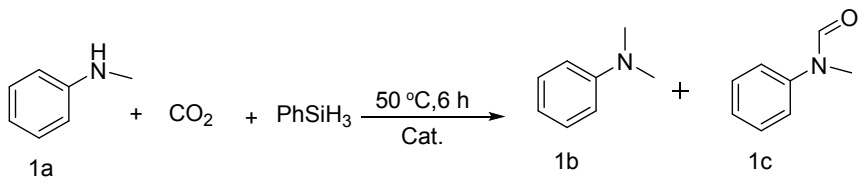


Figure S5 ^{13}C NMR spectra of ionic liquid catalysts: thyltrimethylammonium (ETA-AA), choline (CH-AA) and chlormequat (CC-AA) acetate with d_6-DMSO as deuterated solvent

Table S1 Effect of solvent species on catalytic performance of methylation of *N*-methylaniline using CO_2



Entry	Solvent	Conv. (**1a**, %)	Yield (**1b**, %)	Yield (**1c**, %)
1	CH_3CN	100	96	2
2	DMF	98	86	11
3	EtOH	0	0	0
4	EA	53	38	3
5	THF	76	65	2
6	*n*-hexane	0	0	0
7	Solvent-free	85	24	45

Reaction conditions: 0.25 mmol **1a**, 0.75 mmol $PhSiH_3$, 6 mol% ACH-AA, 2.0 mL solvent, 1 bar CO_2, 50 °C and 6 h. Conversion of **1a**, and yield of **1b** and **1c** were determined by GC using naphthalene as internal standard.

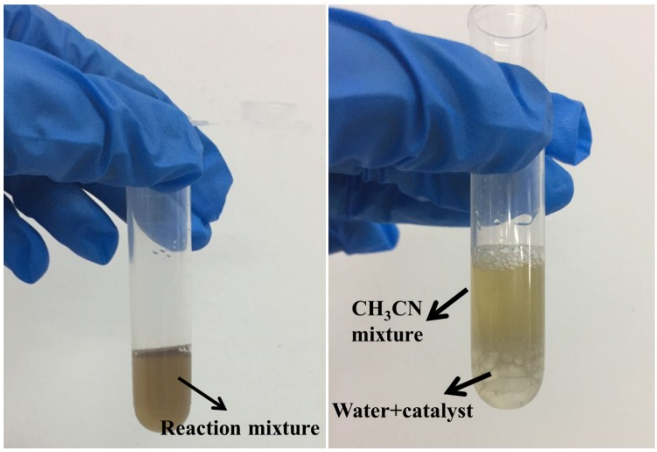


Figure S6 Images of the reaction mixture treated by adding wate and diethyl ether after the reaction for isolating the used ACH-AA IL

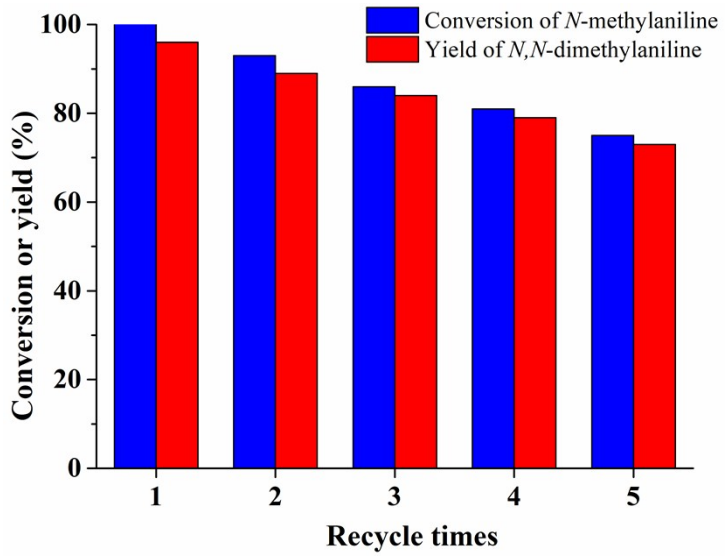


Figure S7 Catalyst recycling study. Reaction conditions: 0.25 mmol *N*-methylaniline, 6% mol ACH-AA, 0.75 mmol $PhSiH_3$, 2 mL CH_3CN, 1.0 bar CO_2, 50 °C and 6 h. Recycling process: the extracted ionic liquid mixed with water, and activated carbon was added; the resulting slurry was stirred (200 rpm) at room temperature for 24 h, and the activated carbon was subsequently separated by filtration.

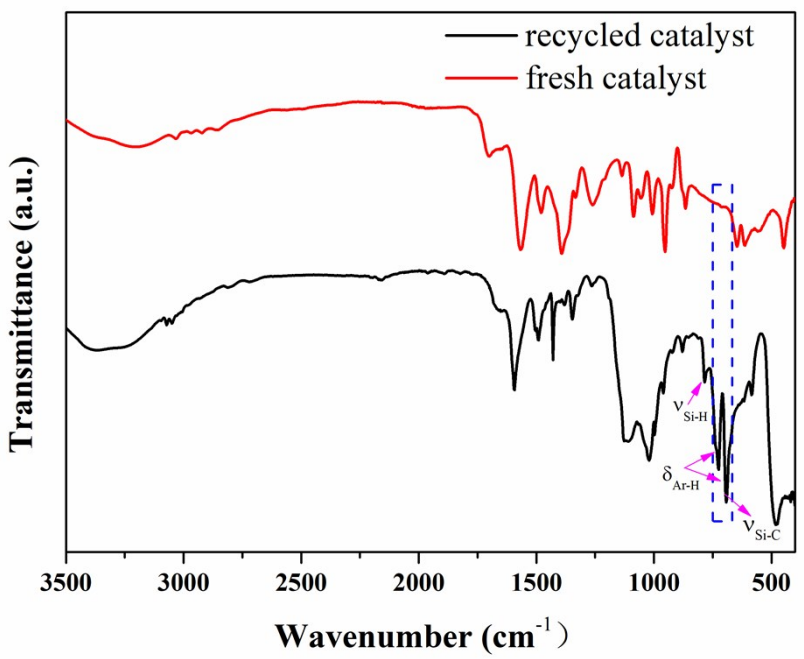


Figure S8 The FT-IR spectra of reused and fresh ACH-AA catalysts

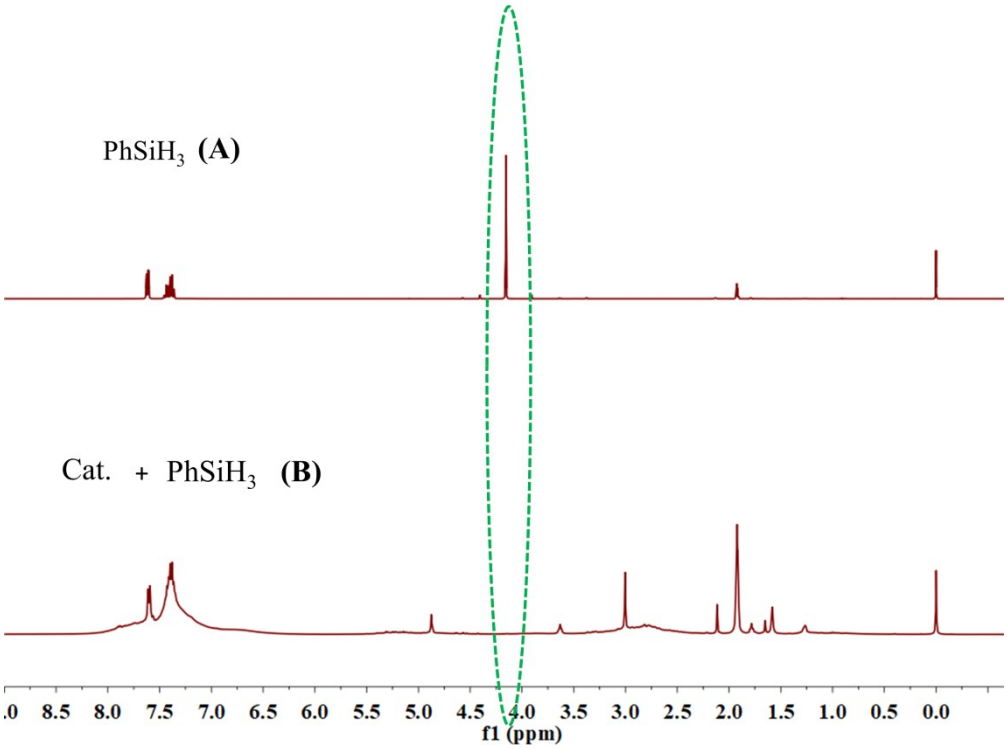


Figure S9 ^{1}H NMR spectra of $PhSiH_3$ (A) and its mixture with ACH-AA (B) (Solvent: CD_3CN, 25 ºC)

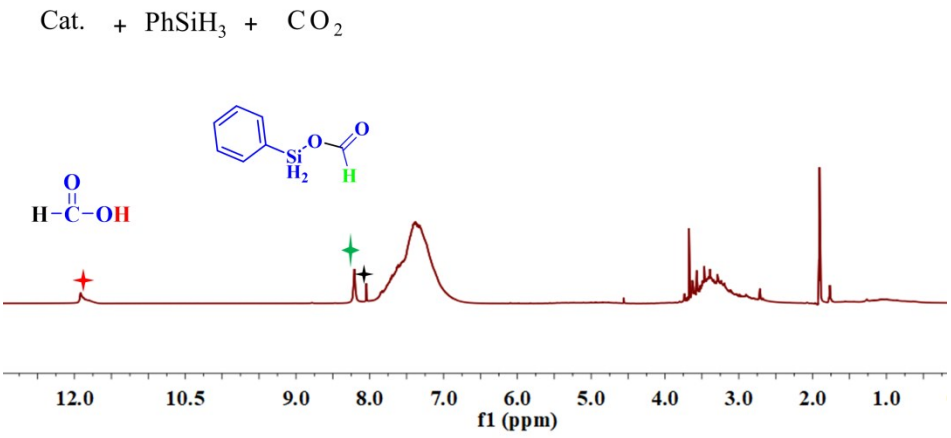


Figure S10 ^{1}H NMR spectra of silyl formate formed from $PhSiH_3$, ACH-AA and 1 bar CO_2 in CD_3CN under 50 °C for 6 h

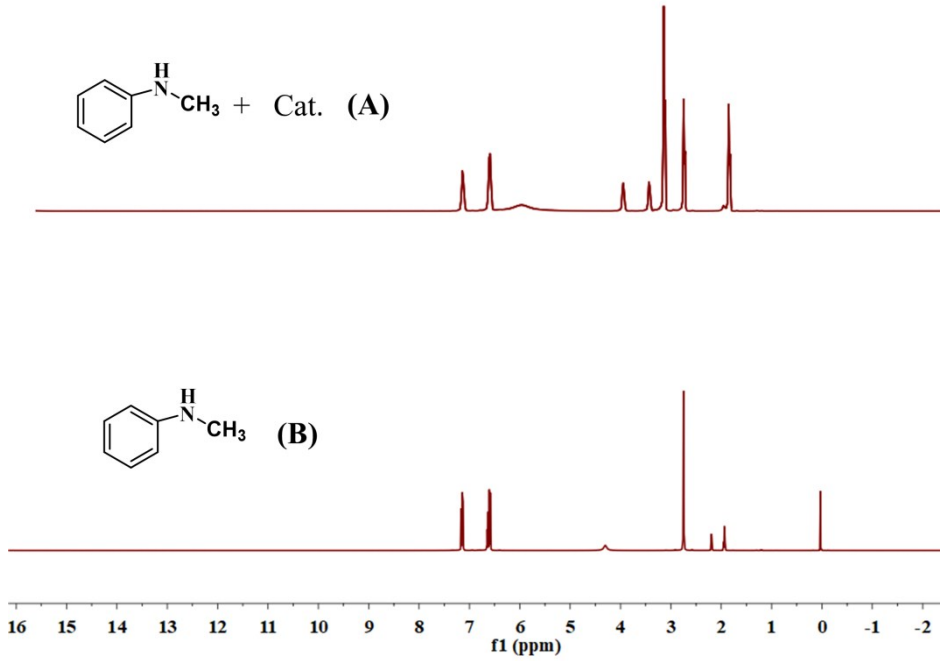


Figure S11 ^{1}H NMR spectra of the mixture of *N*-methylaniline and ACH-AA (A), and *N*-methylaniline (B) (Solvent: CD_3CN, 25 ºC)

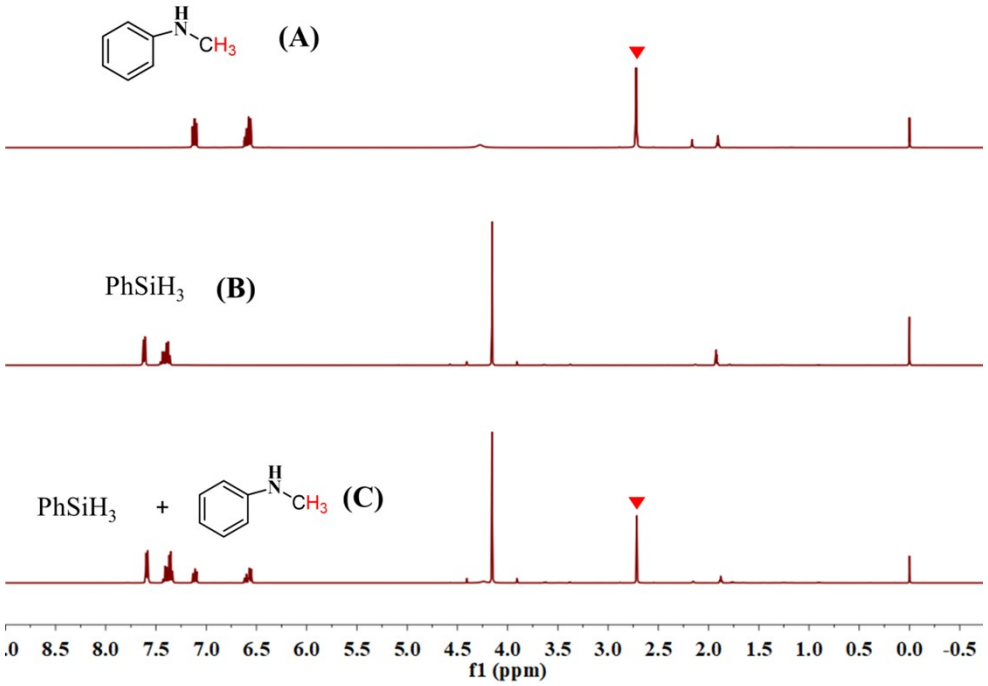


Figure S12 ^{1}H NMR spectra of *N*-methylaniline (A), $PhSiH_3$ (B) and their mixture (C) (Solvent: CD_3CN, 25 ºC)

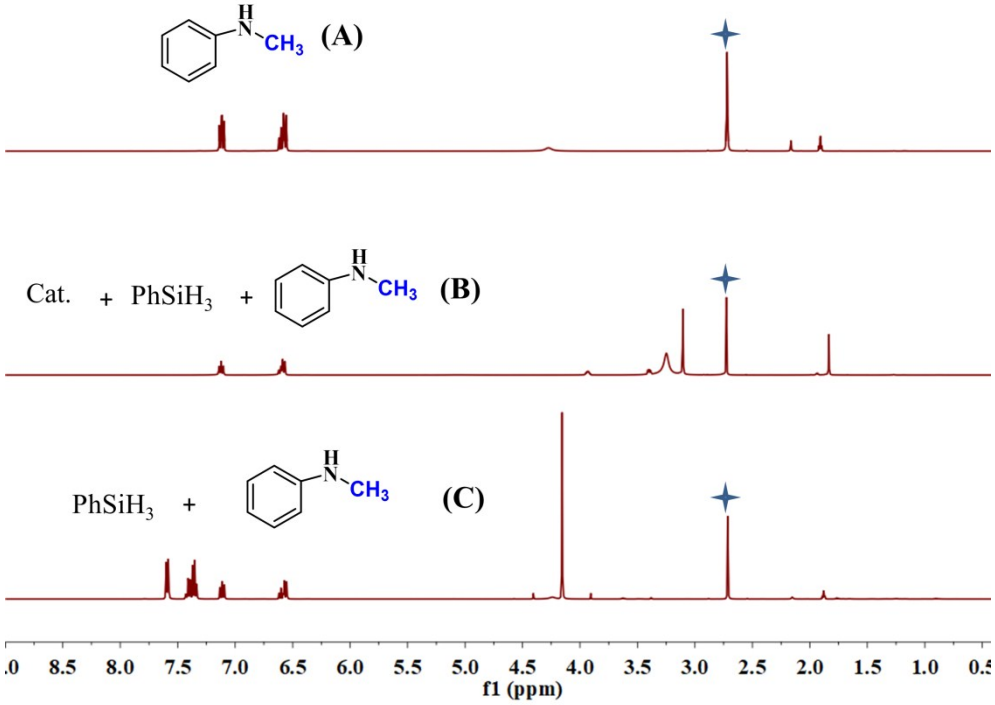
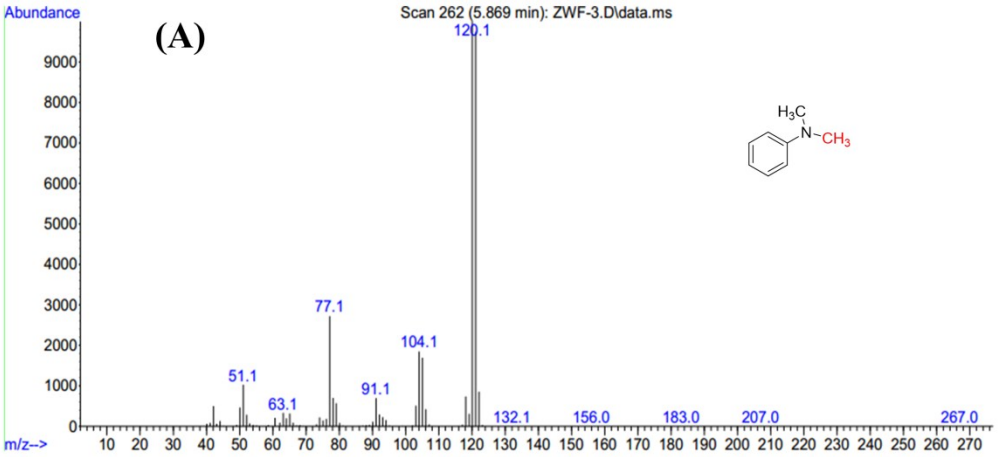


Figure S13 ^{1}H NMR spectra of *N*-methylaniline (A), its mixture of $PhSiH_3$ under room condition in CD_3CN (B), and standard reaction in the absence of CO_2 (C).



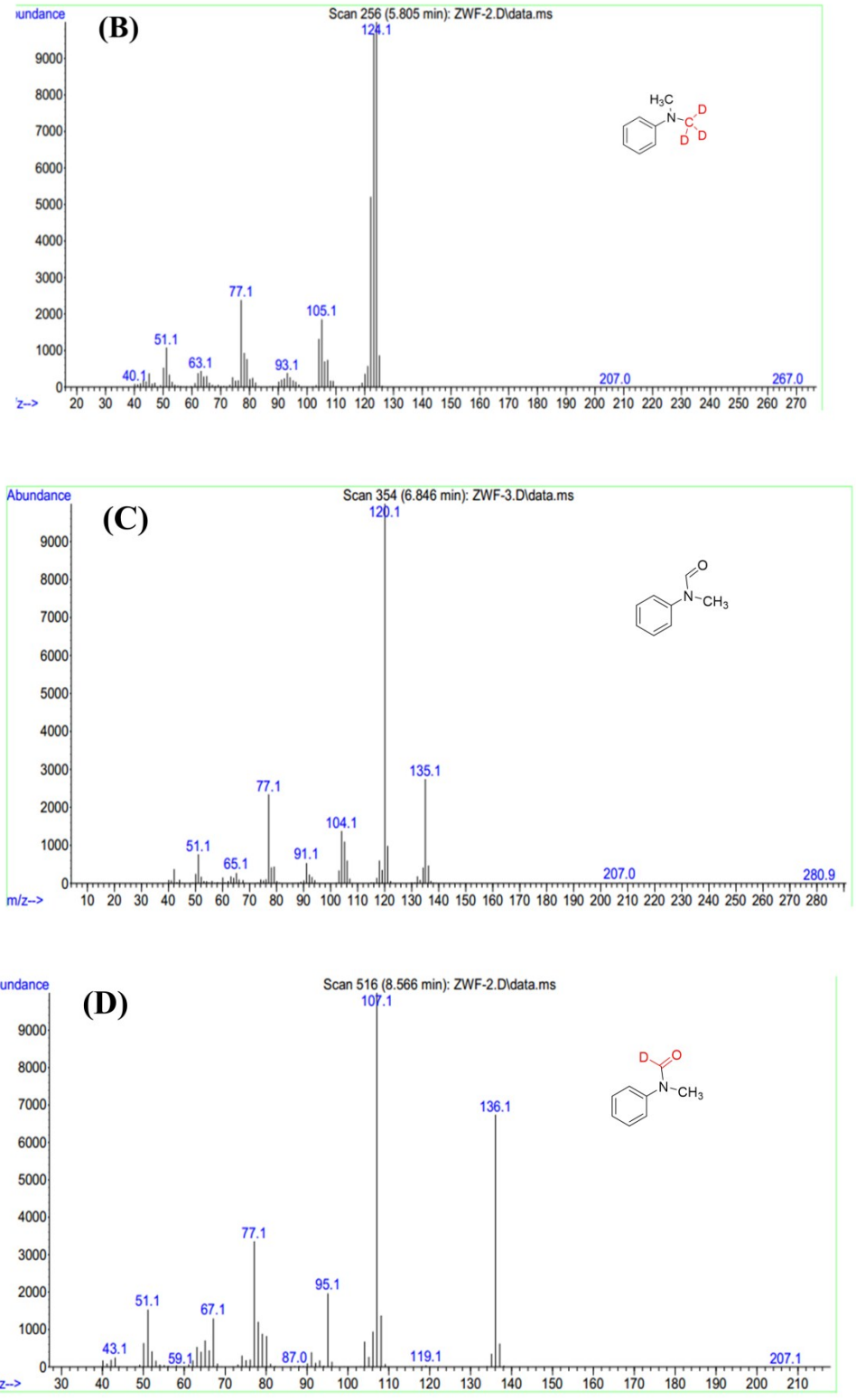


Figure S14 Representative GC-MS spectra for producing *N, N*-dimethylaniline and *N*-methylformylaniline from *N*-methylaniline using different H-donors under standard reaction conditions: (A) and (B) with $PhSiH_3$ in CD_3CN; (C) and (D) with Ph_2SiD_2 in CD_3CN.

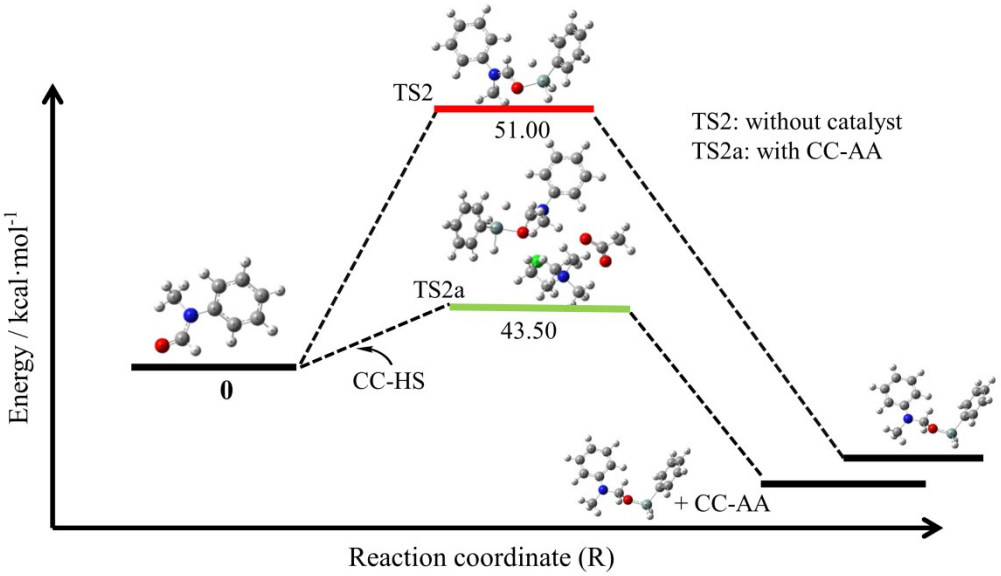


Figure S15 The reaction energy profiles (in kcal/mol) for the hydrosilylation of *N*-methylformanilide with or without CC-AA.