Supporting Information

Bifunctional heterogeneous Ru/POPs catalyst embedded with alkali for the N-formylation of amine and CO_2

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1. Supplementary Figure

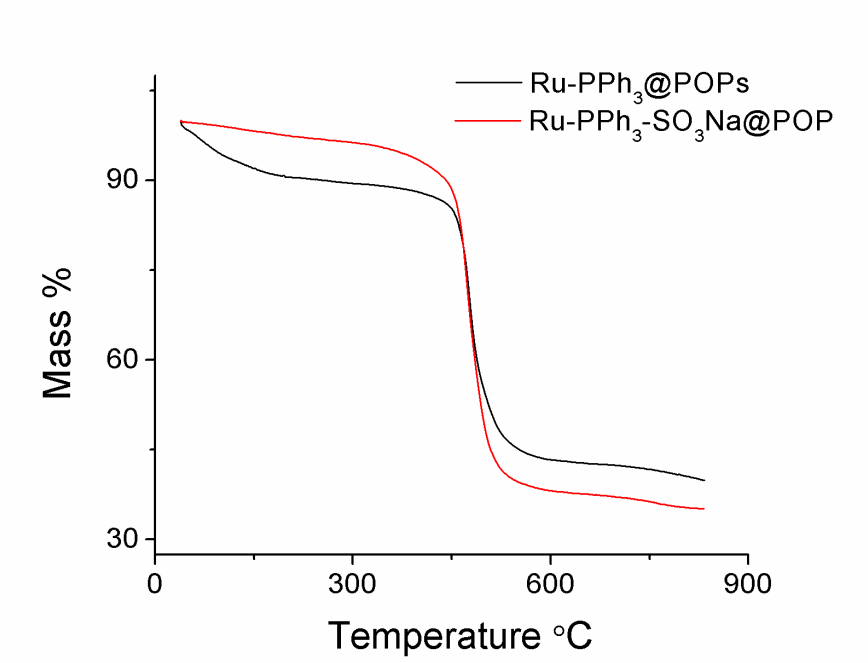


Figure S1. TG curves of Ru-PPh_3@POPs (black) and Ru-PPh_3-SO_3Na@POPs (red).

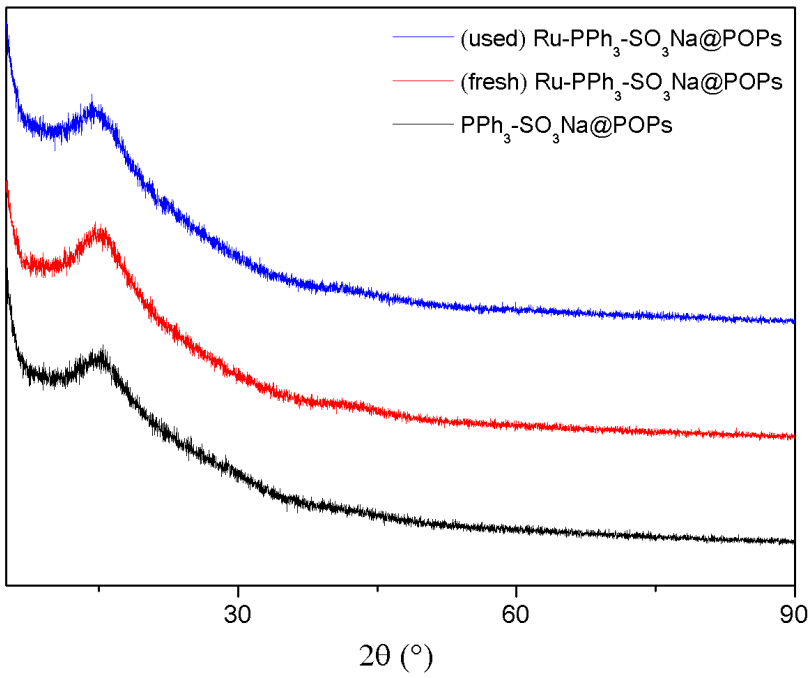


Figure S2. The XRD patterns of PPh_3-SO_3Na@POPs (black), (fresh) Ru-PPh_3-SO_3Na@POPs (red), (used) Ru-PPh_3-SO_3Na@POPs (blue)

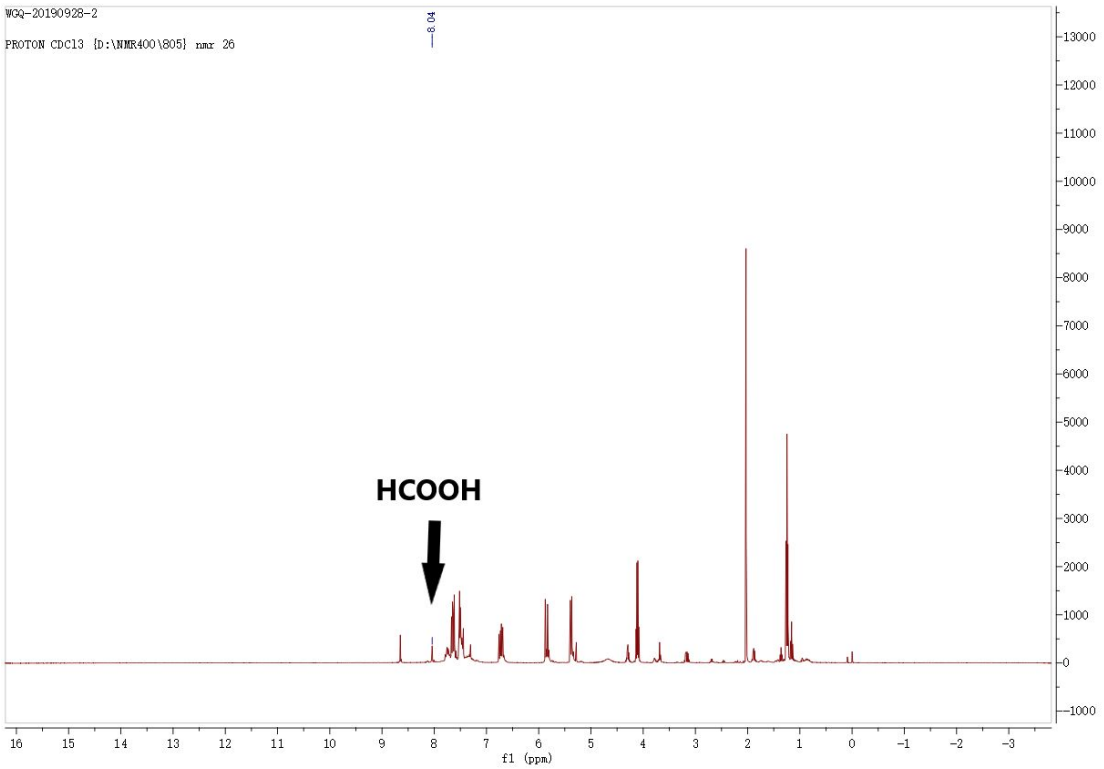
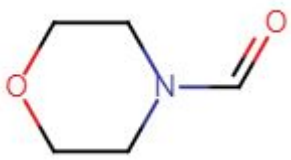


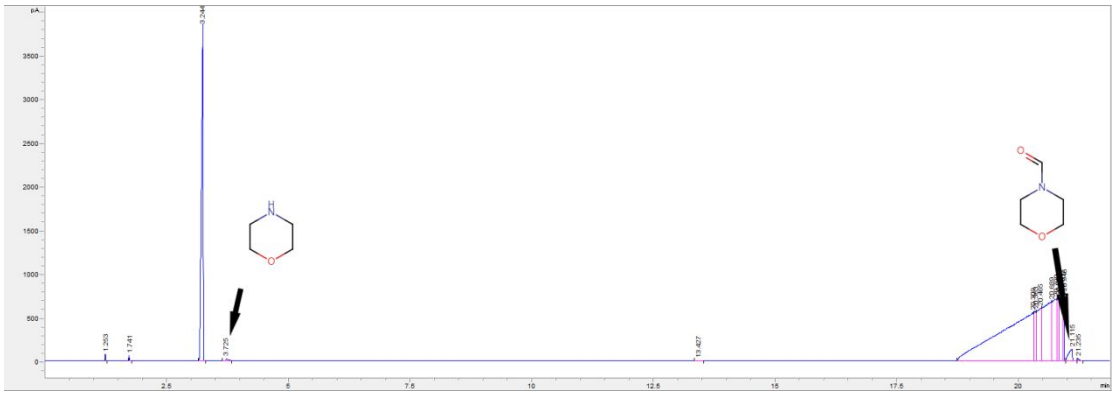
Figure S3. The NMR spectrum of control experiment for mechanism study. Reaction conditions: Ru/POPs-SO_3Na, 0.0923g (Ru 0.368 mol%); CO_2, 3 MPa; H_2, 3 MPa; DMI, 4 mL; 100 ℃, 24 h.

2. Determination of the product yields

The structure of 1a was characterized by comparing the retention time with the authentic compound and GC-MS. The yield was determined by GC using toluene as the internal standard. For 2b-10b, NMR yields were given. The ^1H NMR ($CDCl_3$, 400 MHz) spectra of the reaction mixture and MS spectra of the product were shown below.



1b



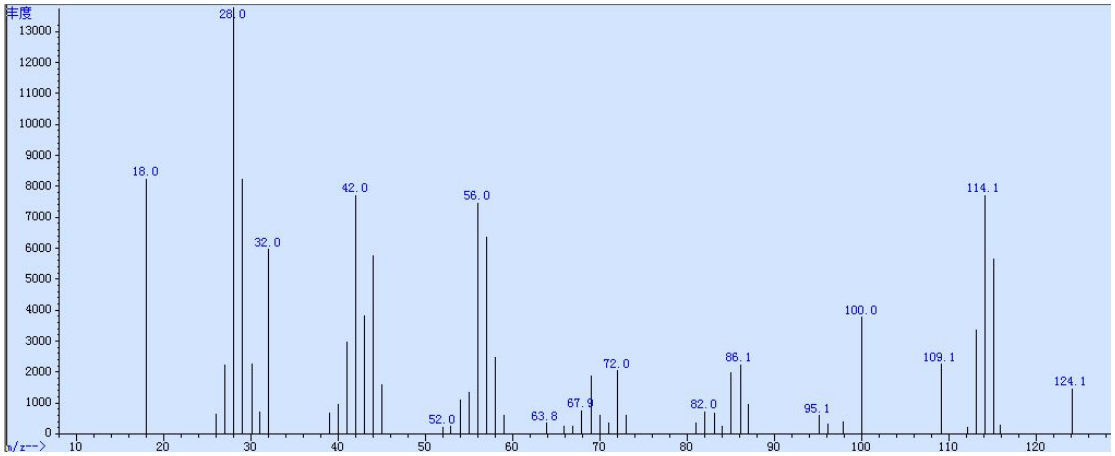
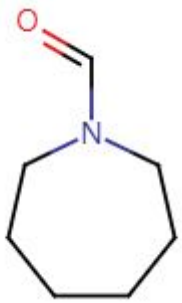


Figure S4 GC spectra of reaction solution of morpholine (1a) reacting with CO_2/H_2 and MS spectrum of 1b.



2b

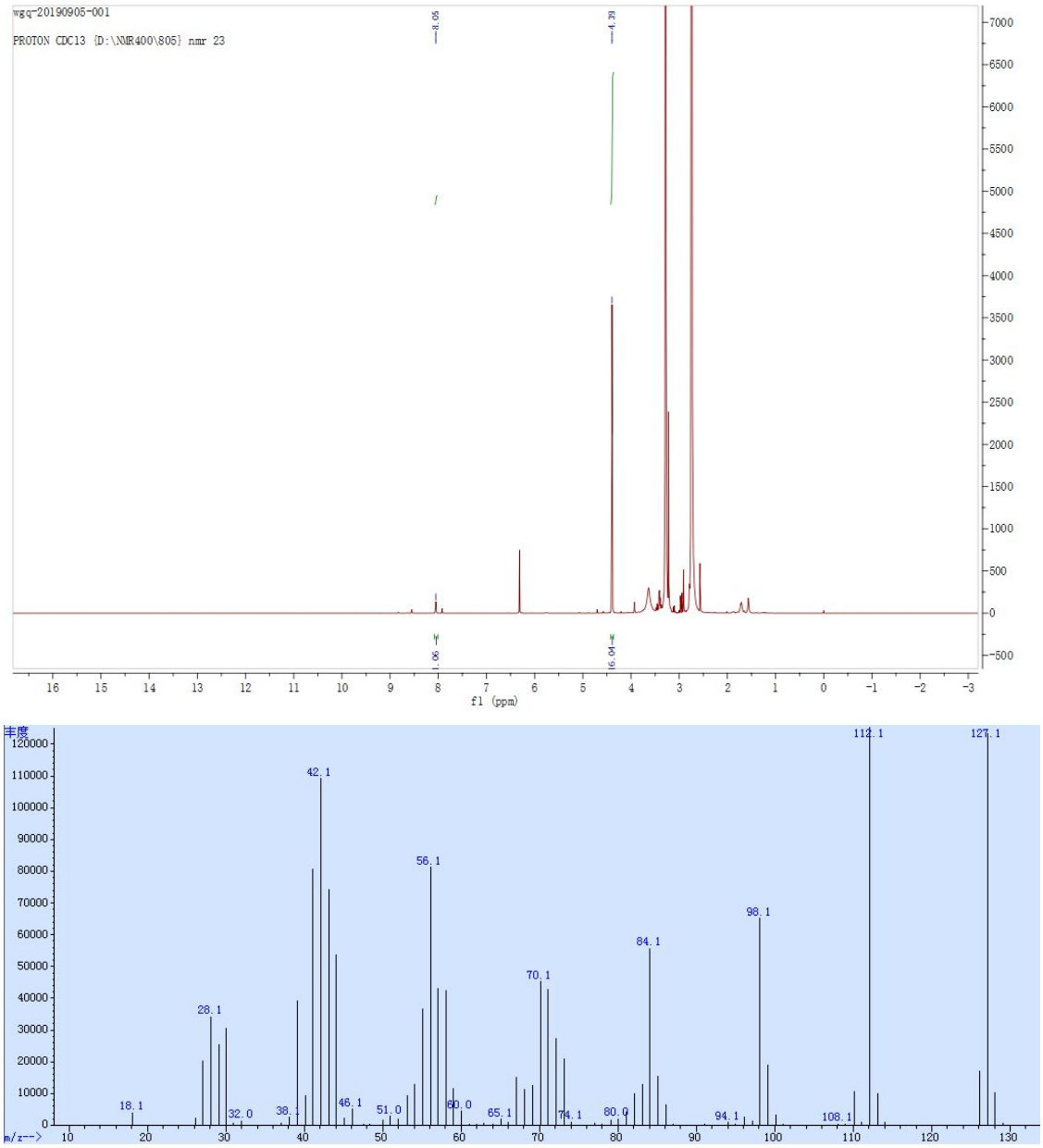
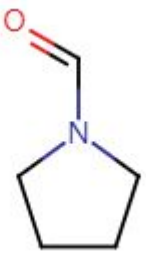


Figure S5 NMR spectrum of reaction solution of 2a reacting with CO_2/H_2 (CH_3NO_2: 0.0241 g) and MS spectrum of 2b.



3b

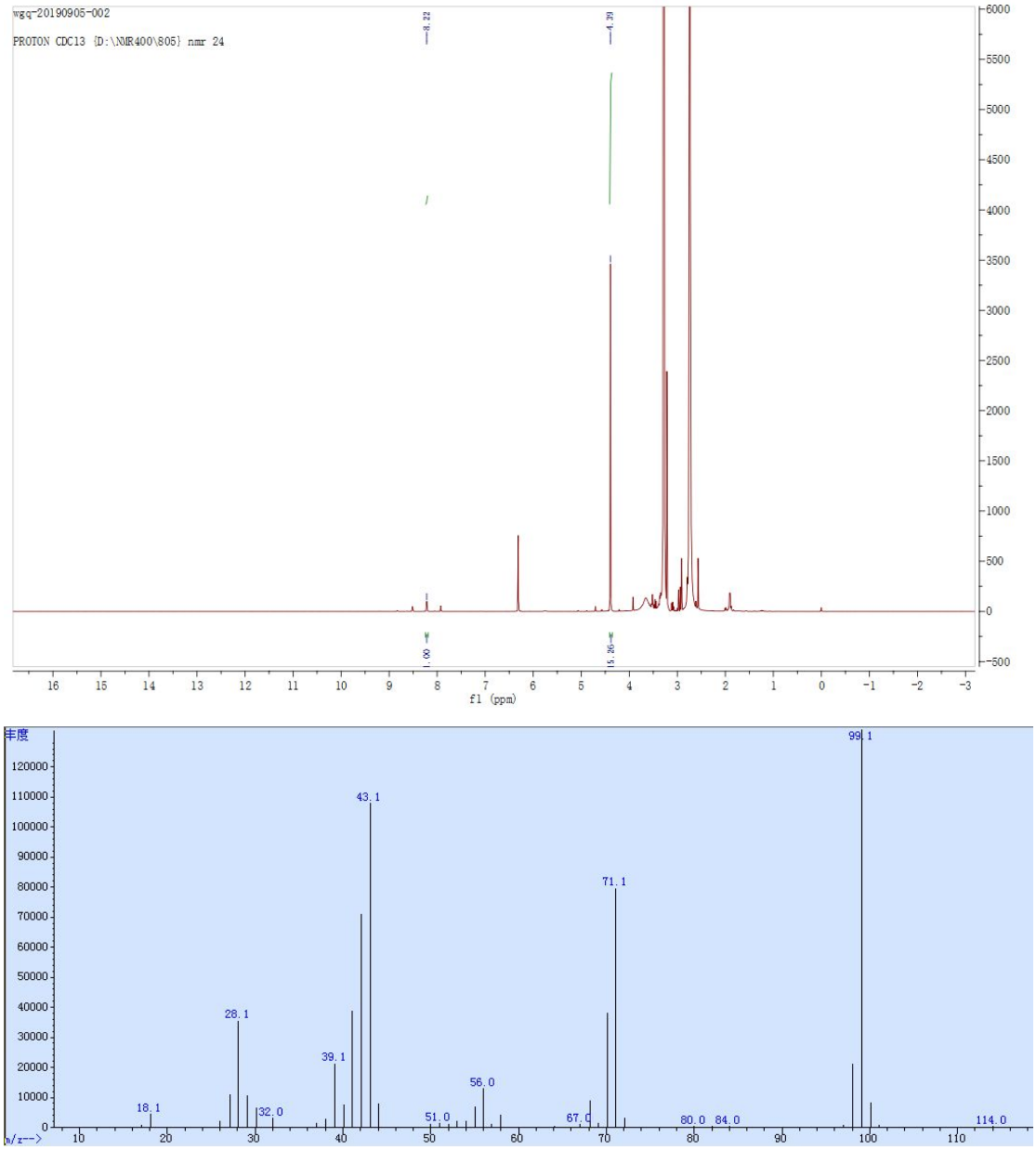
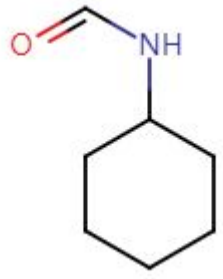


Figure S6 NMR spectrum of reaction solution of 3a reacting with CO_2/H_2 (CH_3NO_2: 0.0226 g) and MS spectrum of 3b.



4b

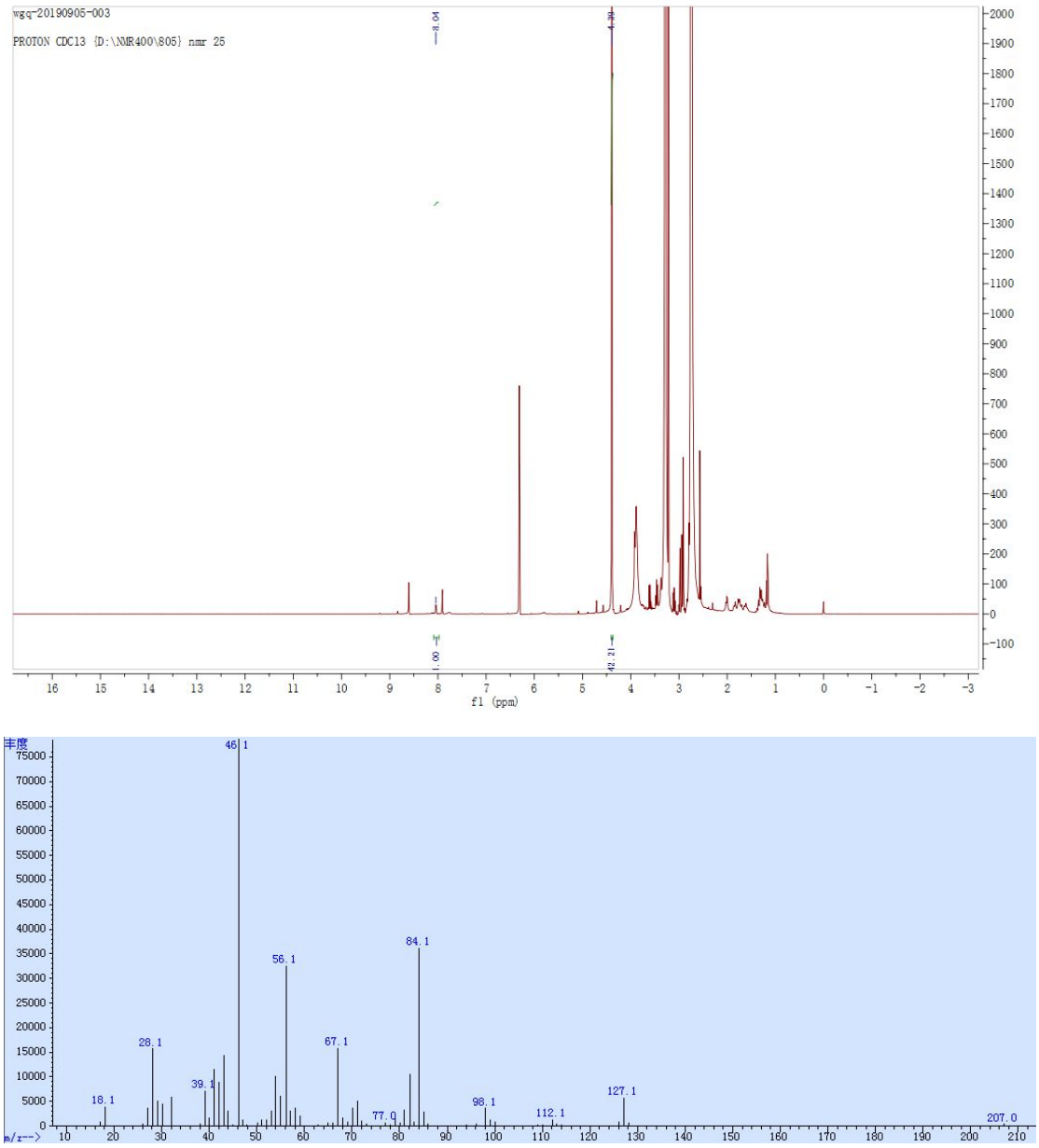
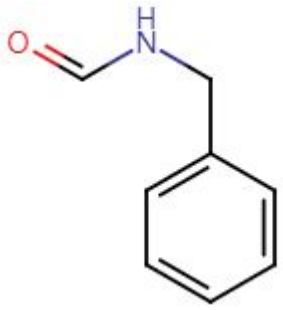


Figure S7 NMR spectrum of reaction solution of 4a reacting with CO_2/H_2 (CH_3NO_2: 0.0283 g) and MS spectrum of 4b.



5b

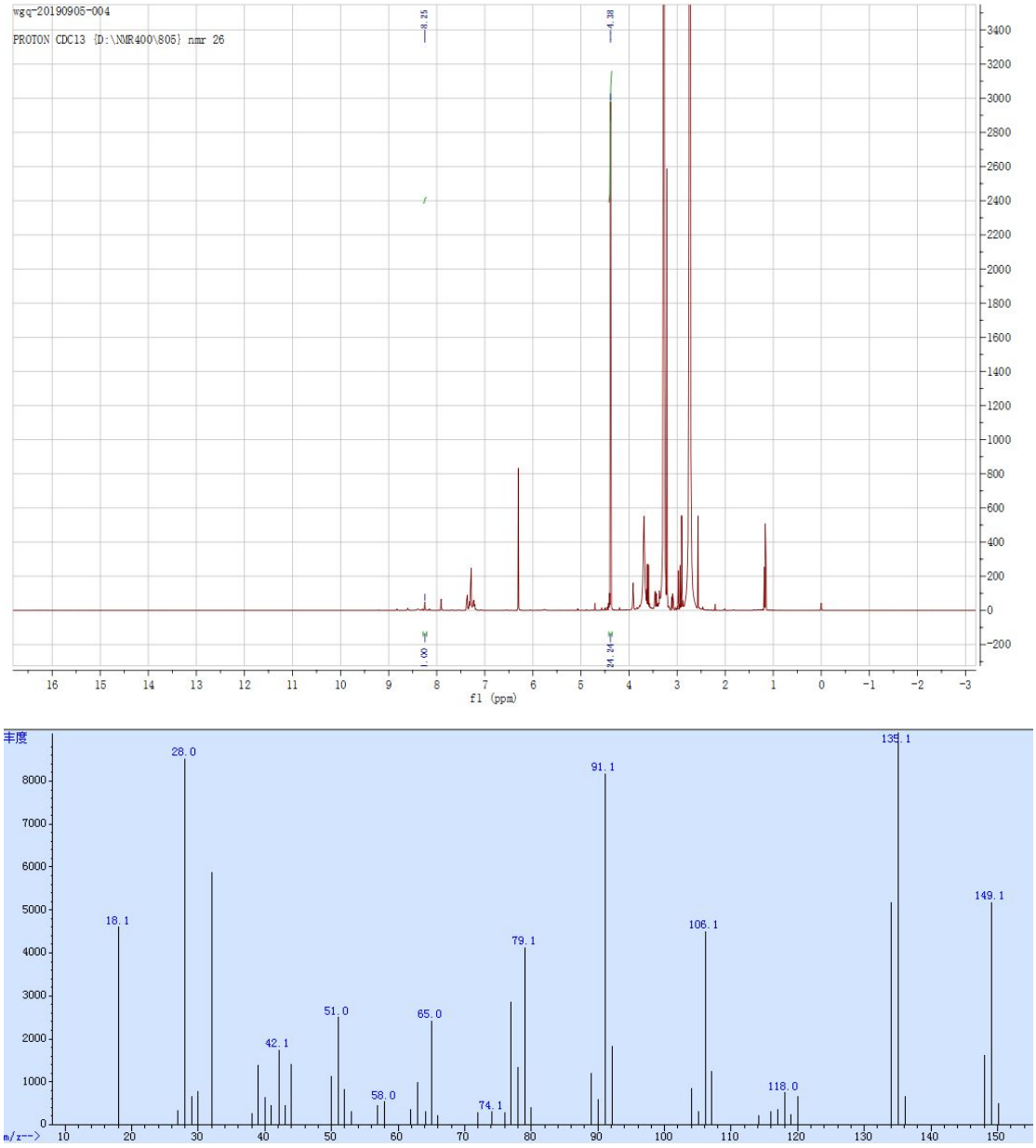
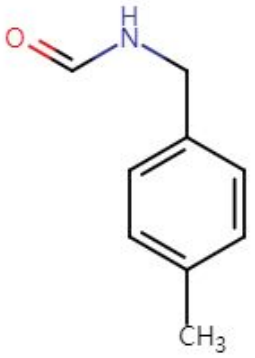


Figure S8 NMR spectrum of reaction solution of 5a reacting with CO_2/H_2 (CH_3NO_2: 0.0241 g) and MS spectrum of 5b.



6b

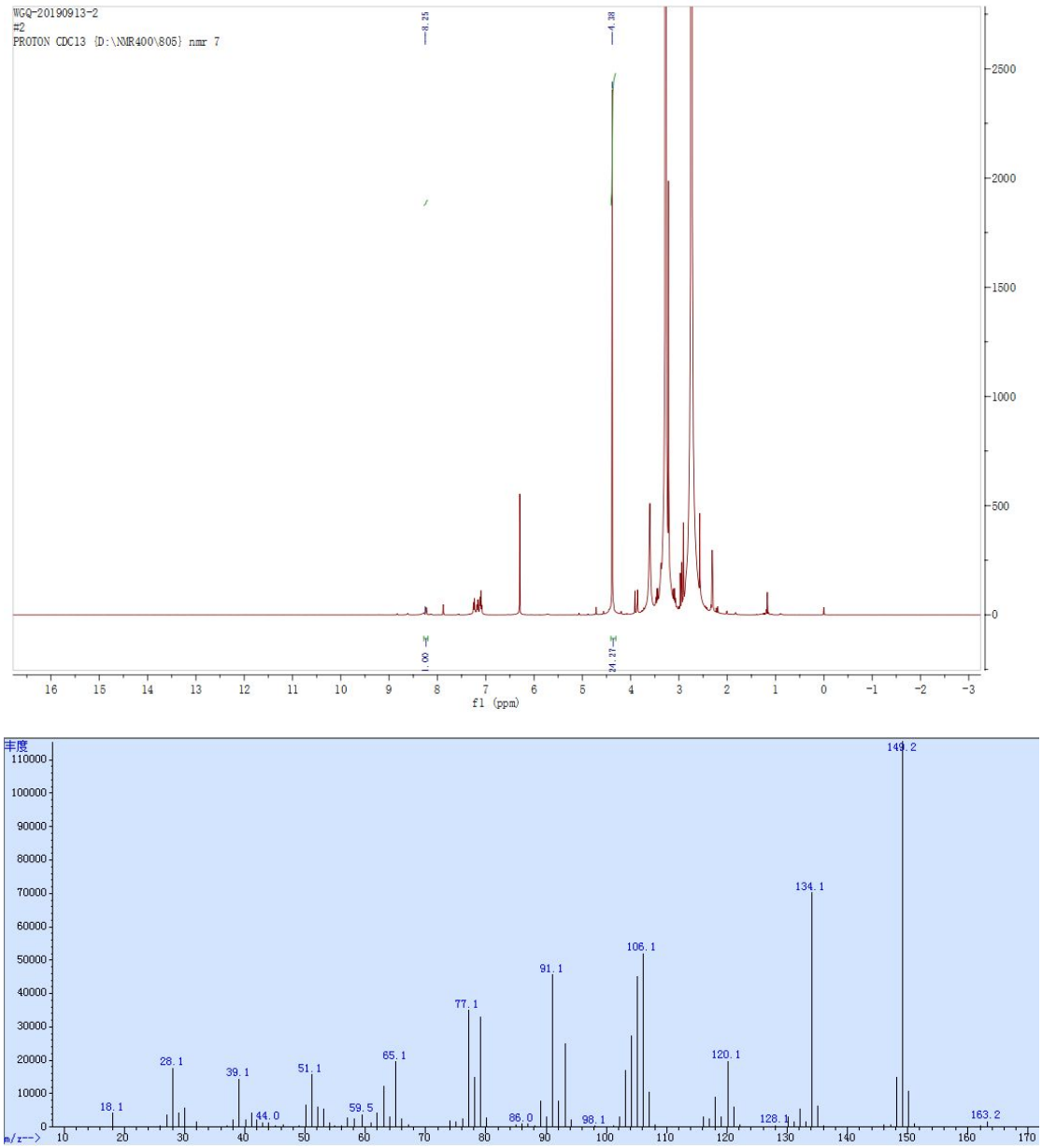
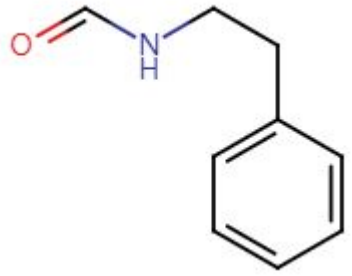


Figure S9 NMR spectrum of reaction solution of 6a reacting with CO_2/H_2 (CH_3NO_2: 0.0209 g) and MS spectrum of 6b.



7b

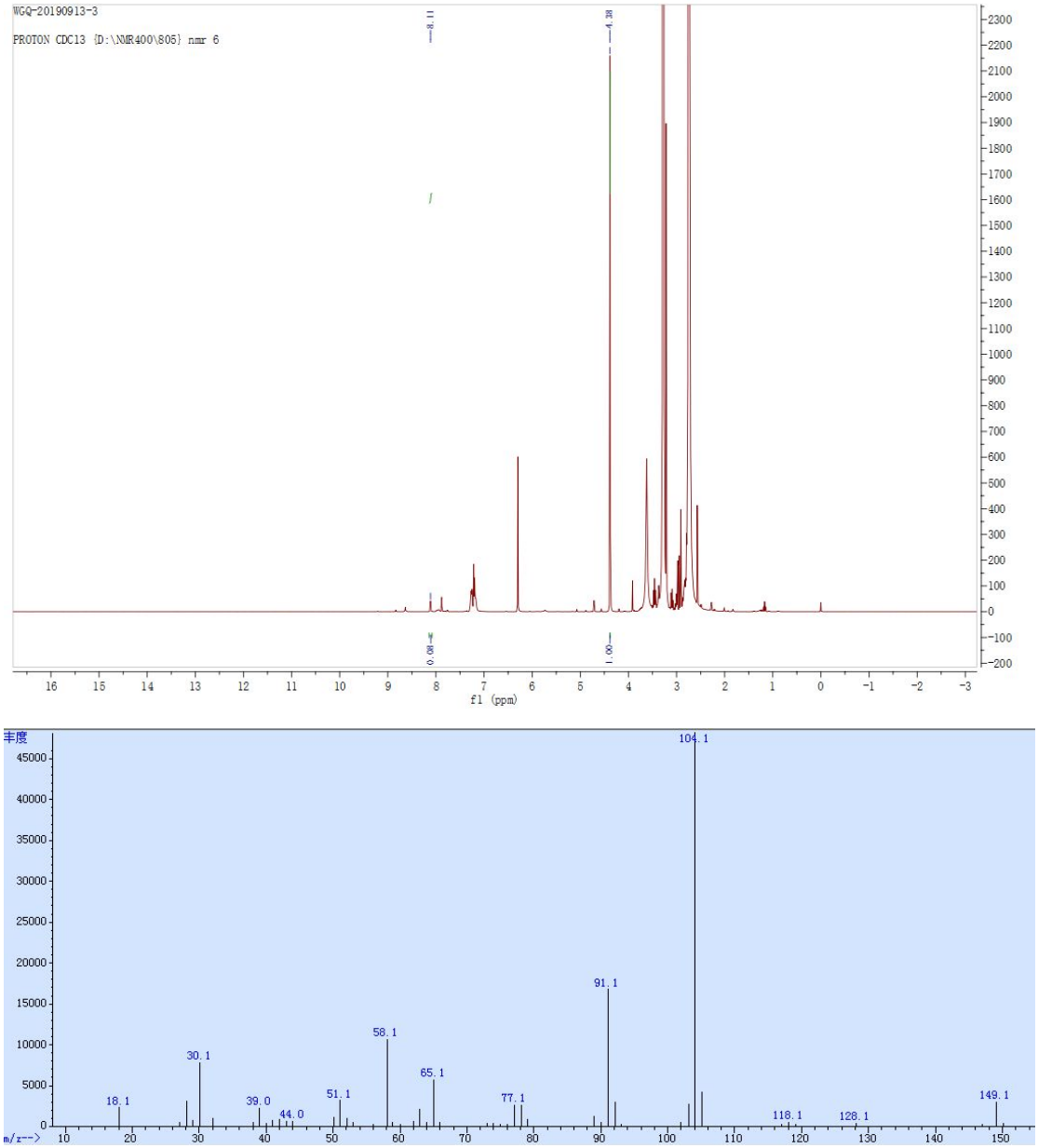
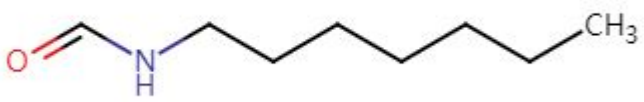


Figure S10 NMR spectrum of reaction solution of 7a reacting with CO_2/H_2 (CH_3NO_2: 0.0166 g) and MS spectrum of 7b.



8b

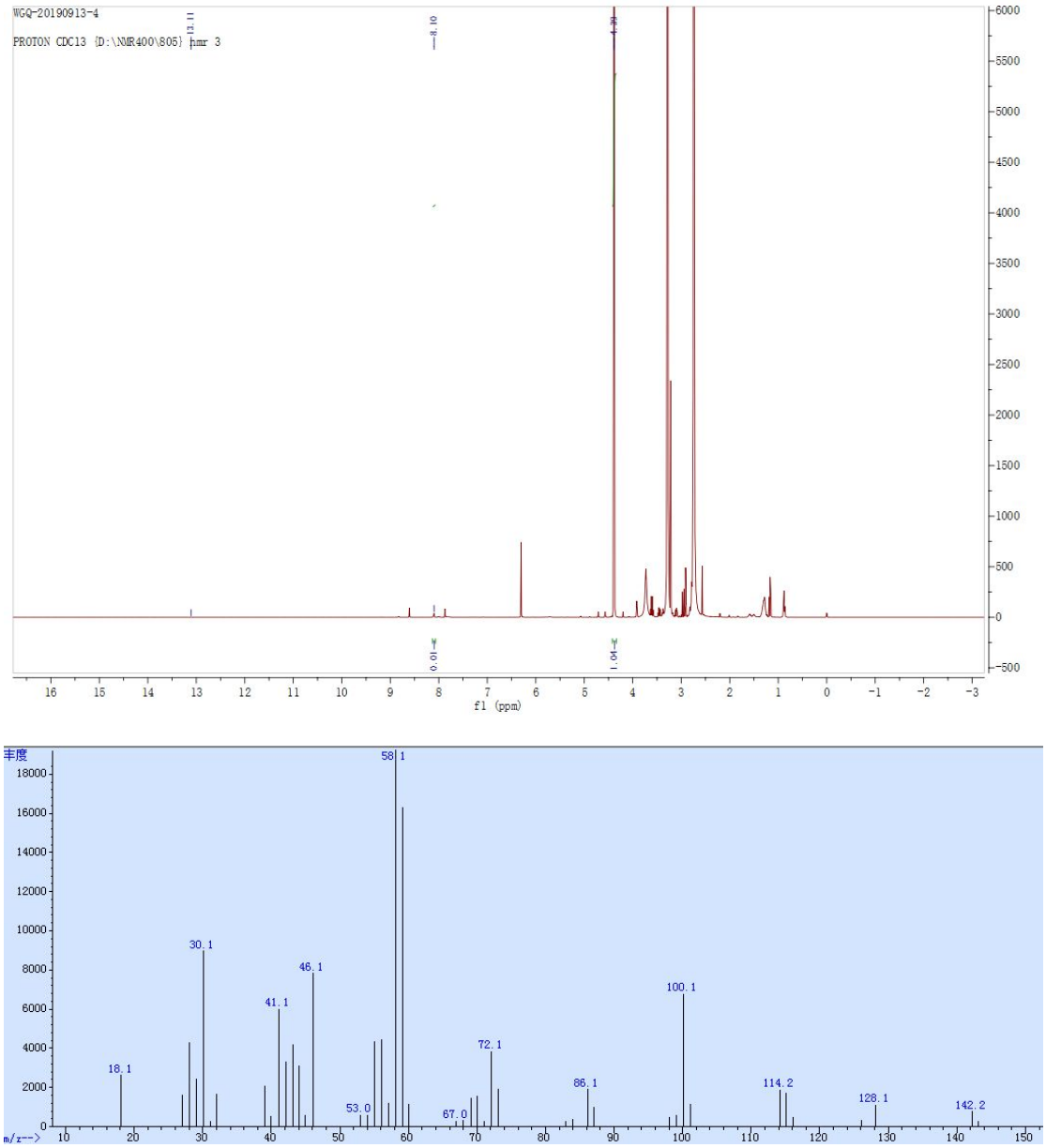
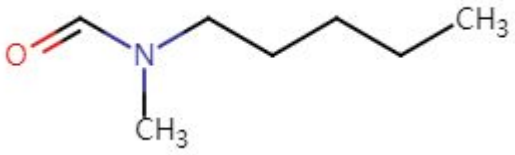


Figure S11 NMR spectrum of reaction solution of 8a reacting with CO_2/H_2 (CH_3NO_2: 0.0647 g) and MS spectrum of 8b.



9b

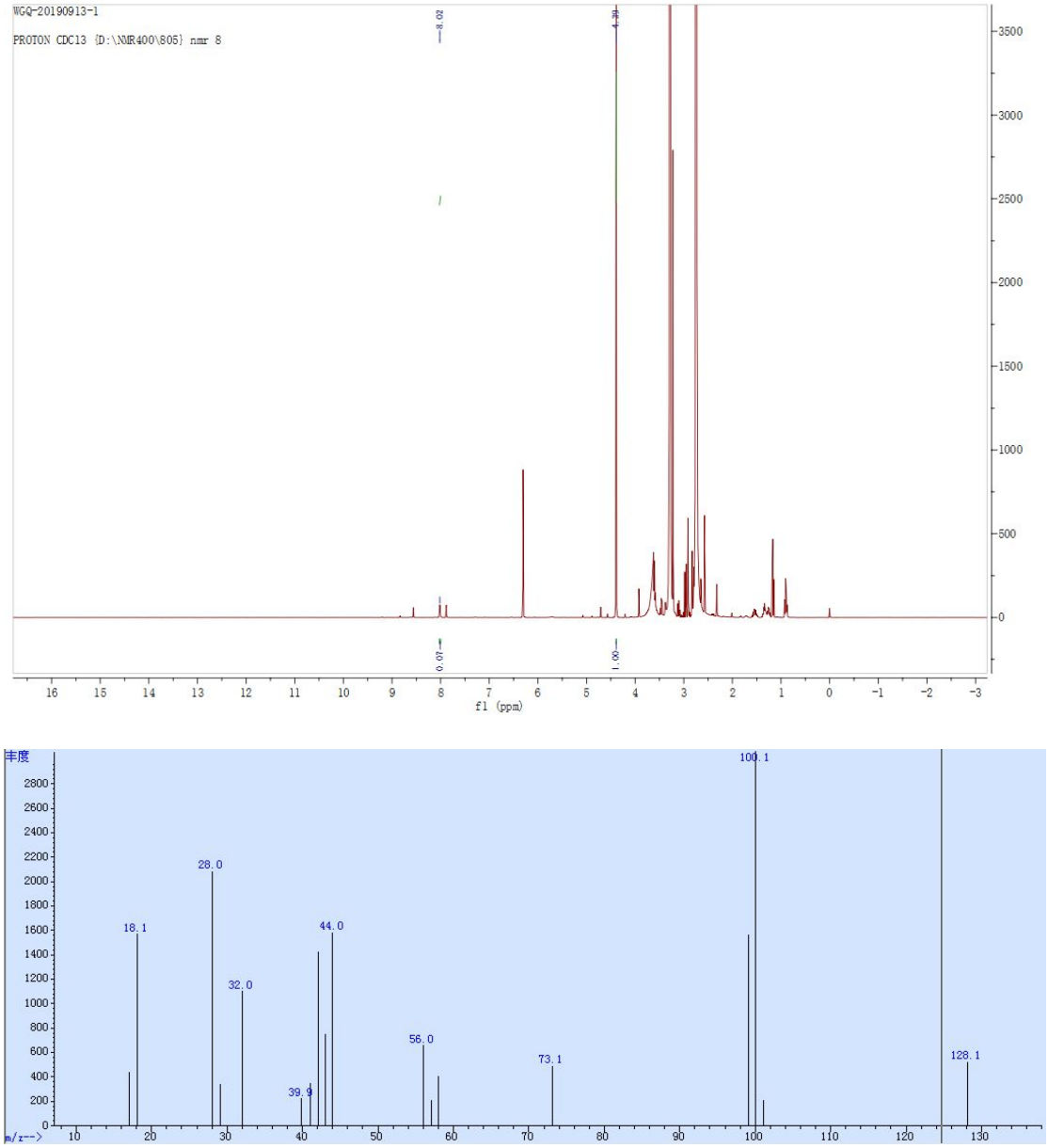
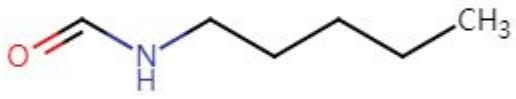


Figure S12 NMR spectrum of reaction solution of 9a reacting with CO_2/H_2 (CH_3NO_2: 0.0221 g) and MS spectrum of 9b.



10b

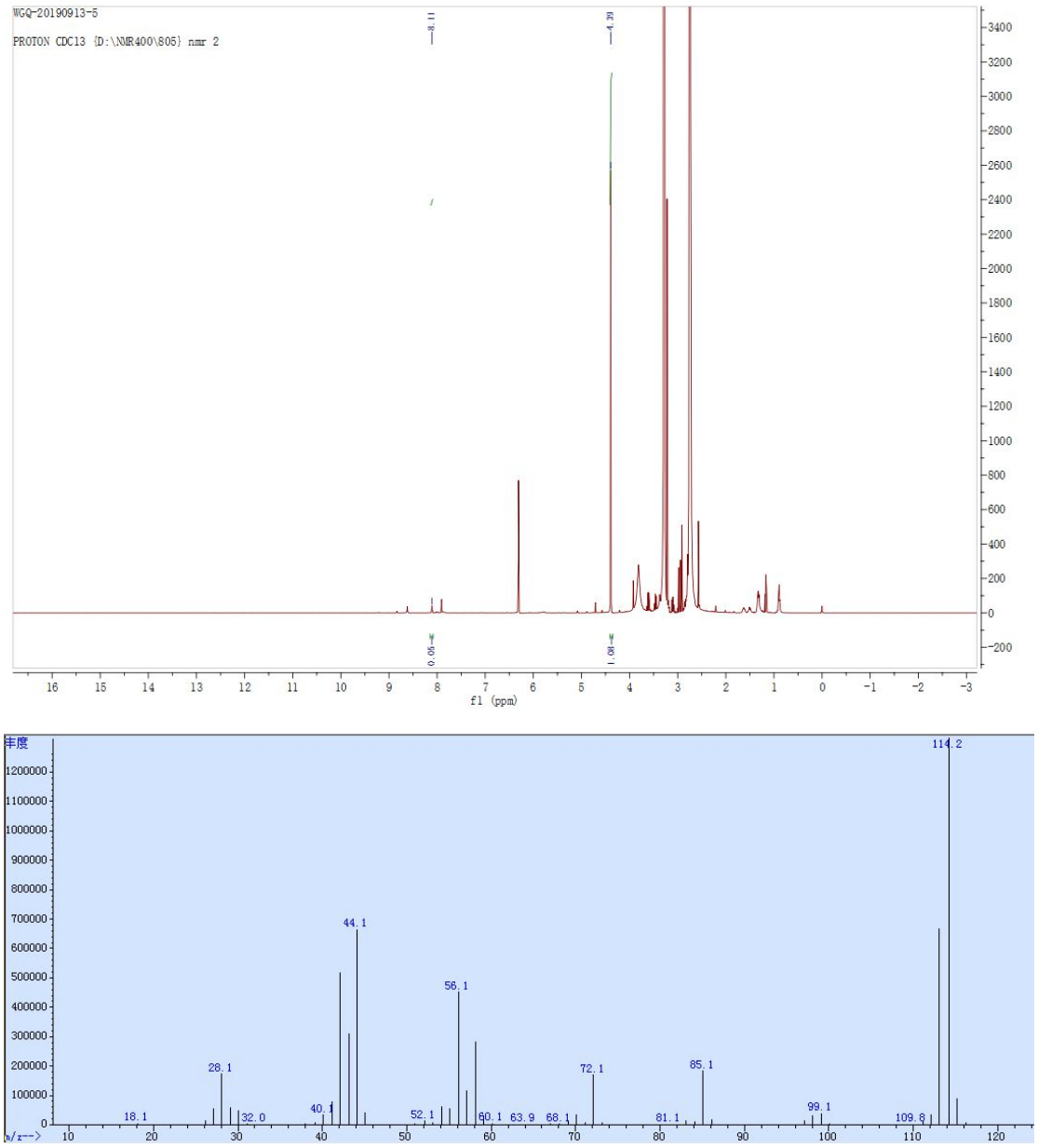
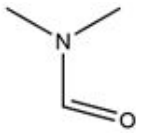


Figure S13 NMR spectrum of reaction solution of 10a reacting with CO_2/H_2 (CH_3NO_2: 0.0167 g) and MS spectrum of 10b.



11b

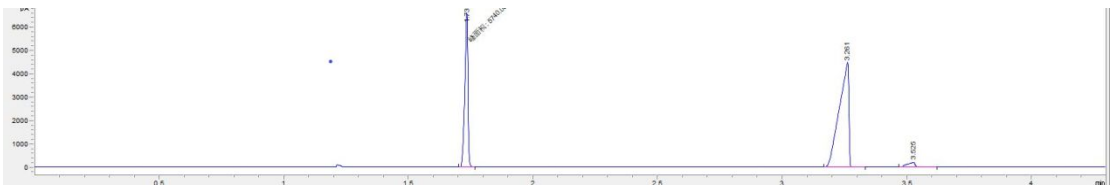


Figure S14 GC spectrum of reaction solution: the aqueous solution of dimethylamine reacting

with CO_2/H_2 (toluene: 0.0643g about 3.25min. DMF about 3.5min)

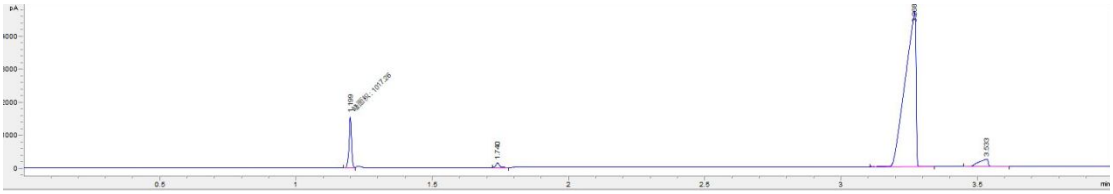


Figure S15 GC spectrum of reaction solution: the THF solution of dimethylamine reacting with CO_2/H_2 (toluene: 0.0702g about 3.25min. DMF about 3.5min)

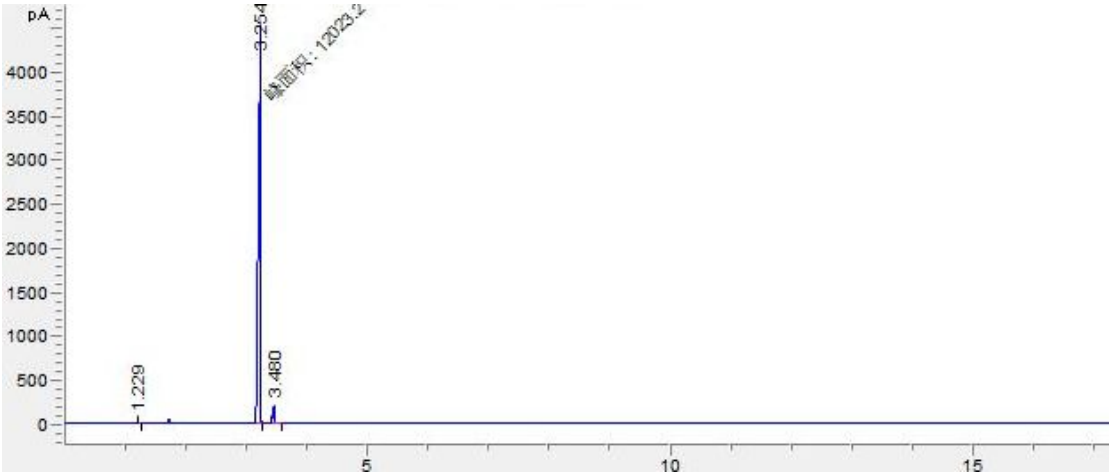


Figure S16 GC spectrum of reaction solution: the methanol solution of dimethylamine reacting with CO_2/H_2 (toluene: 0.0723g about 3.25min. DMF about 3.5min)

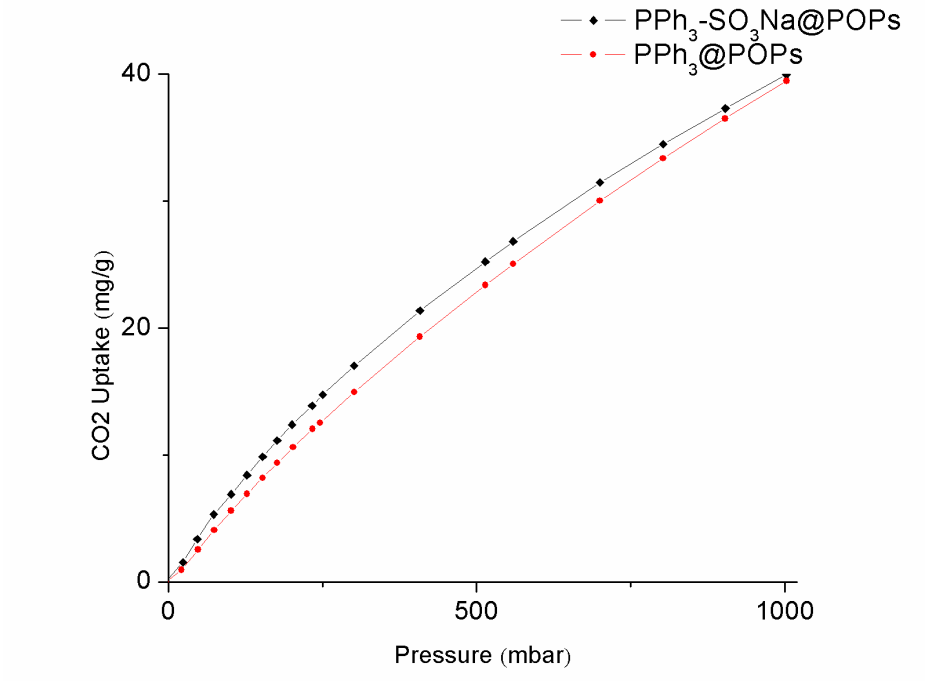


Figure S17 The first-time measurement of CO_2 uptake by IGA

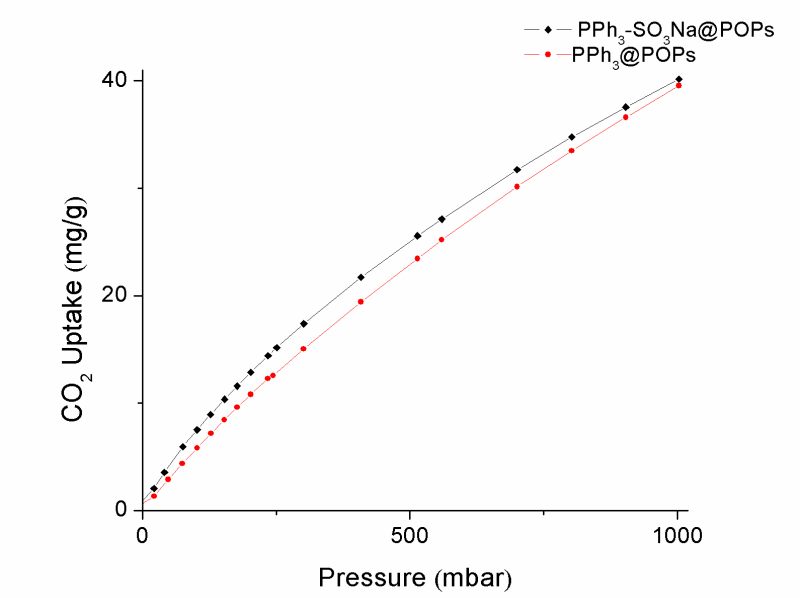


Figure S18 The second time measurement of CO_2 uptake by IGA

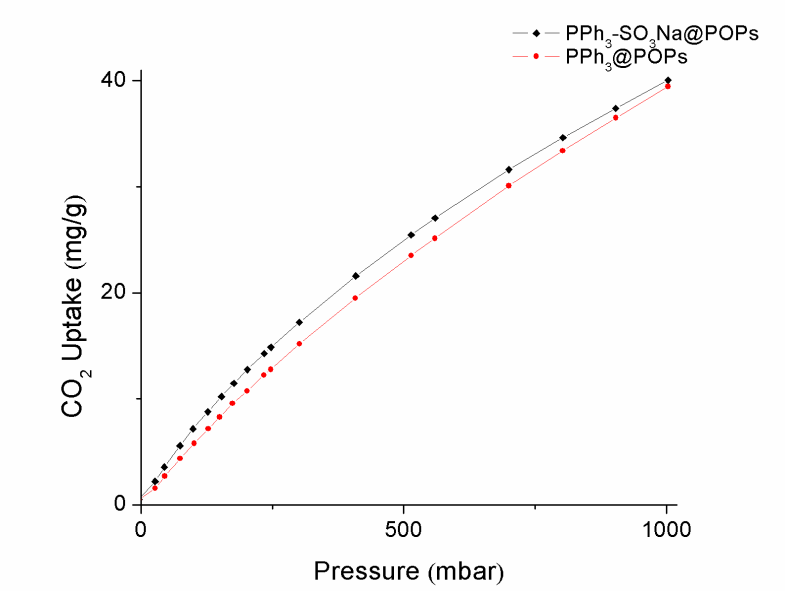


Figure S19 The third time measurement of CO_2 uptake by IGA

Table S1 The CO_2 uptake and pore volume of PPh_3-SO_3Na@POPs and PPh_3@POPs

Entry	CO_2 uptake of PPh_3-SO_3Na@POPs	CO_2 uptake of PPh_3@POPs
1	39.94 mg/g	39.46 mg/g
2	40.15 mg/g	39.55 mg/g
3	40.06 mg/g	39.46 mg/g
pore volume cm^3/g	0.921	1.075

Table S2 The ICP-OES results of fresh Ru-PPh_3-SO_3Na@POPs and used Ru-PPh_3-SO_3Na@POPs

Element	fresh Ru-PPh_3-SO_3Na@POPs/wt%	used Ru-PPh_3-SO_3Na@POPs/wt%
P	5.45	5.59
S	1.06	1.1
Ru	0.4515	0.4605