Supporting Information

Clever Use of Natural Clay Materials in Synthesis of Non-symmetric Carbonates by Utilizing CO_2 as a Feedstock: Ag/Attapulgite Nano-Catalyst

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1. Catalyst characterization

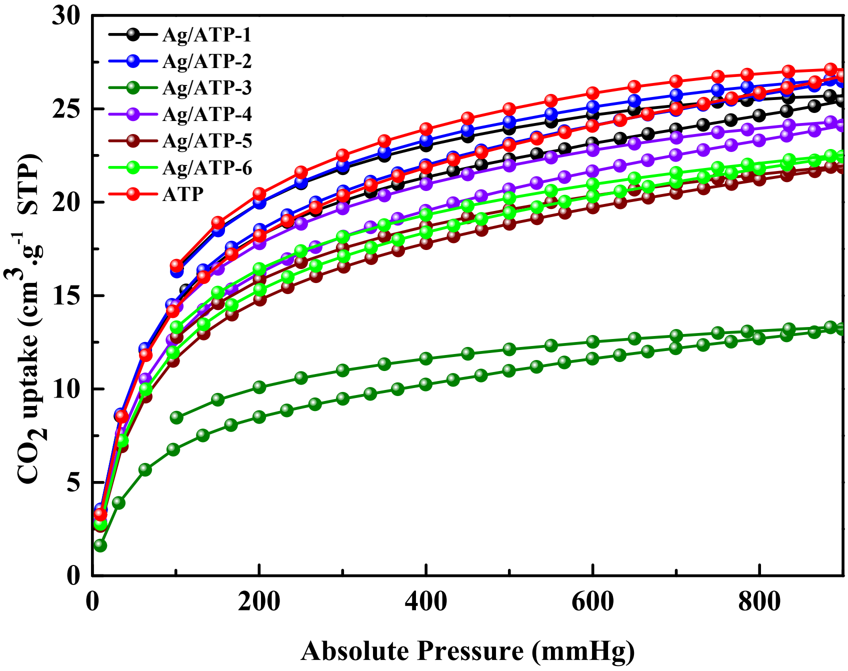


Figure S1. CO_2 adsorption-desorption isotherm curves of Ag/ATP (298K)

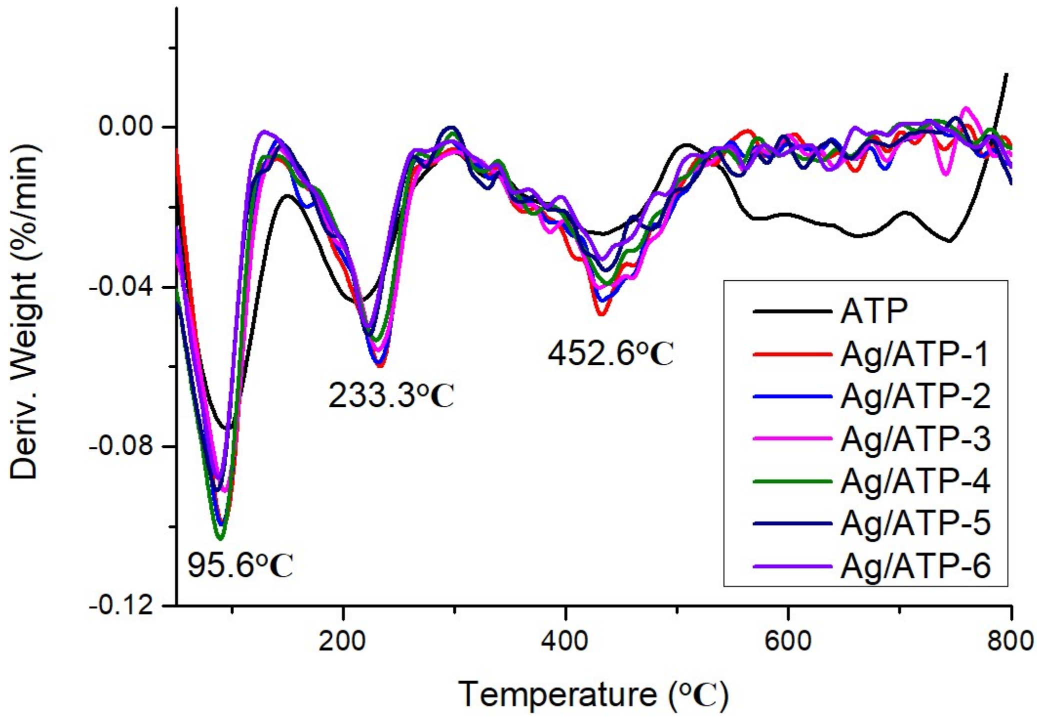


Figure S2. Derivative Thermogravimetry (DTG) curves of ATP and Ag/ATP catalysts

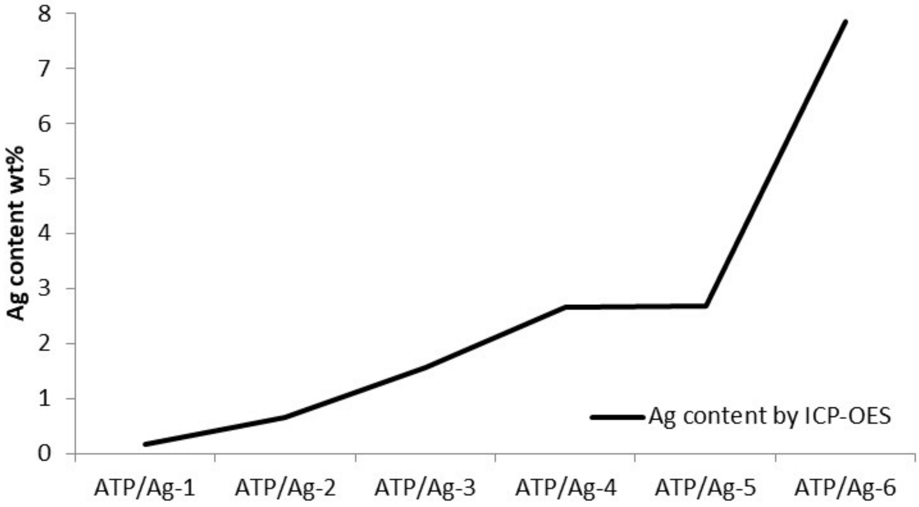


Figure S3. Ag content of Ag/ATP catalysts

2. Catalysis details

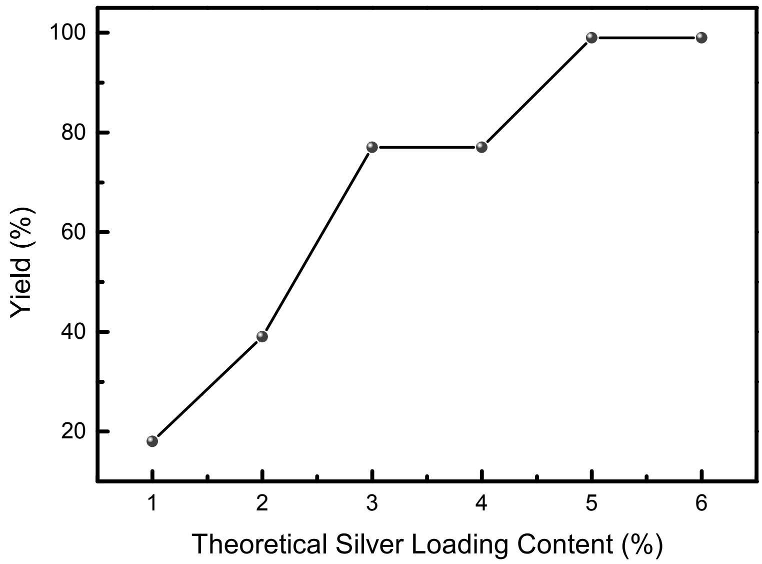


Figure S4. Effect of theoretical silver loading content on the yield. Reaction conditions: 3 mmol 1a, 2 mmol 2a, 10mg Ag/ATP, 0.3 mmol DBN, 1 mL DMF, 6 h, 60 °C, 1 MPa CO_2.

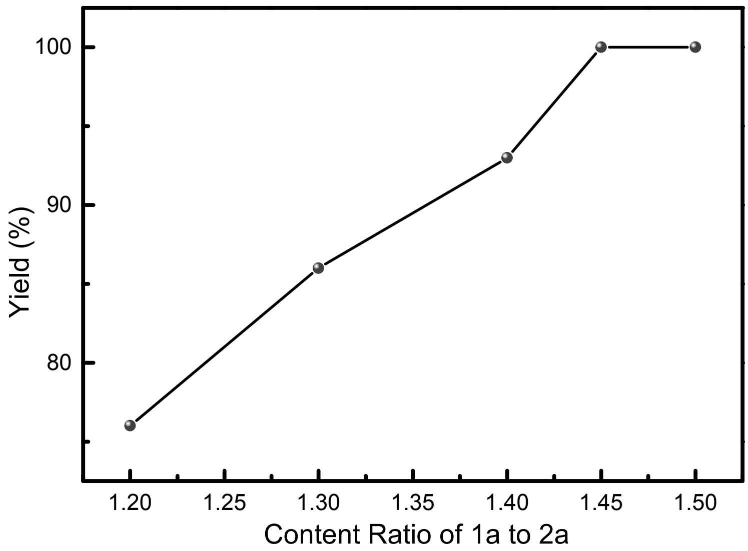


Figure S5. Effect of content ratio of 1a to 2a on the yield. Reaction conditions: 10mg Ag/ATP-5, 0.3 mmol DBN, 1 mL DMF, 6 h, 60 °C, 1 MPa CO_2.

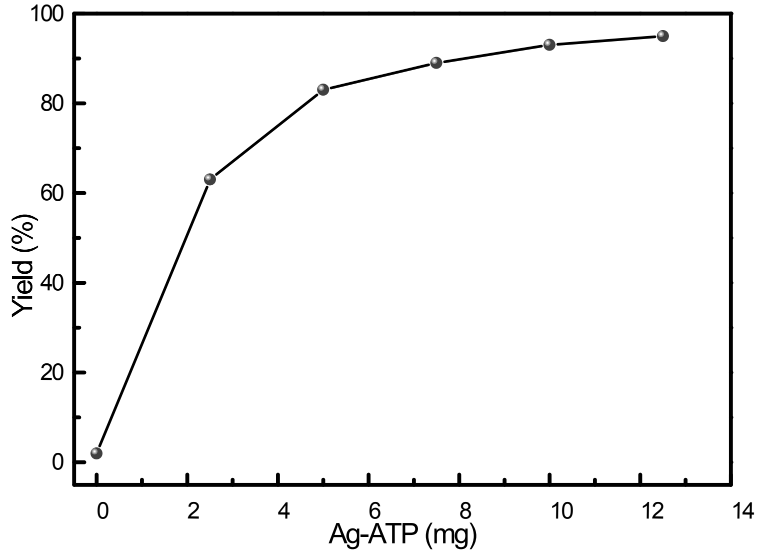


Figure S6. Effect of catalyst content on the yield. Reaction conditions: 2.8 mmol 1a, 2 mmol 2a, 0.3 mmol DBN, 1 mL DMF, 6 h, 60 °C, 1 MPa CO_2.

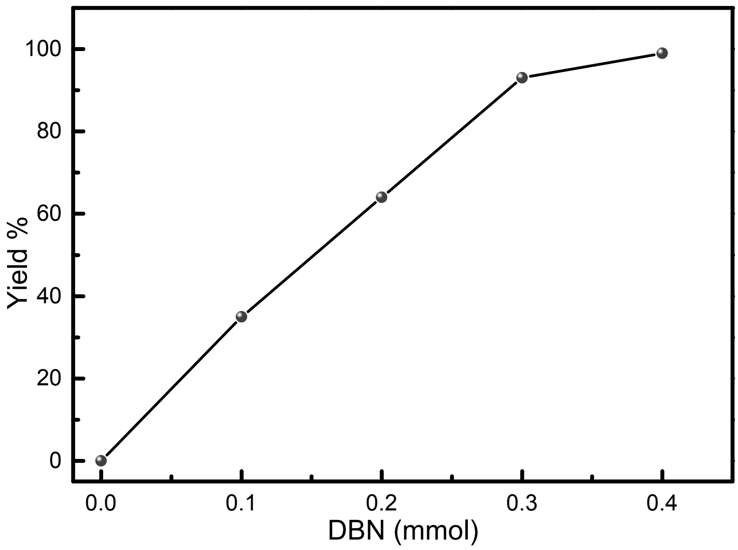


Figure S7. Effect of cocatalyst content on the yield. Reaction conditions: 2.8 mmol 1a, 2 mmol 2a, 10mg Ag/ATP-5, 1 mL DMF, 6 h, 60 °C, 1 MPa CO_2.

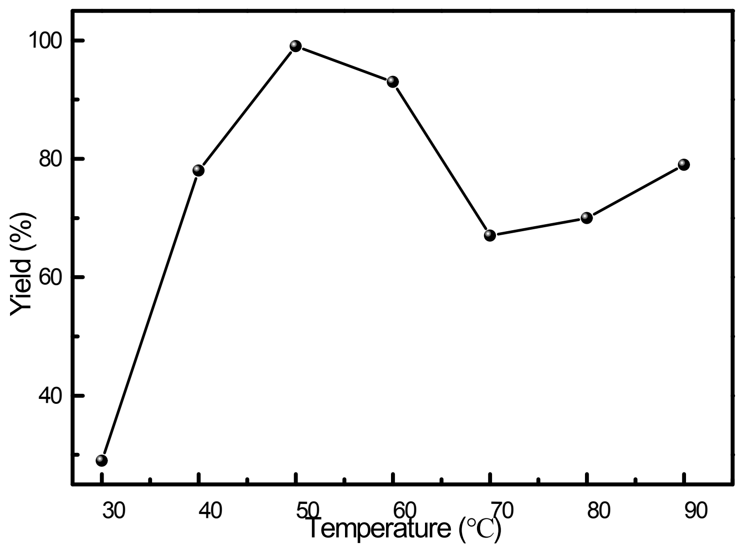


Figure S8. Effect of temperature on the yield. Reaction conditions: 2.8 mmol 1a, 2 mmol 2a, 10mg Ag/ATP-5, 0.3 mmol DBN, 1 mL DMF, 6 h, 1 MPa CO_2.

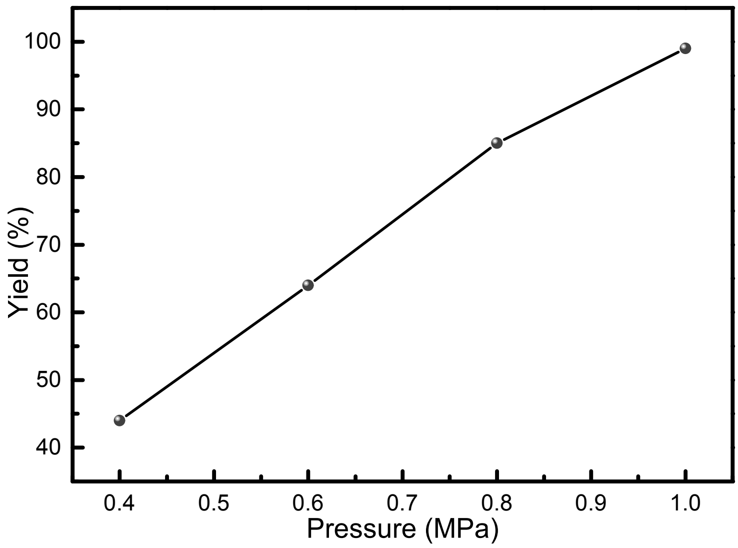


Figure S9. Effect of pressure on the yield. Reaction conditions: 10mg Ag/ATP-5, 0.3 mmol DBN, 1 mL DMF, 6 h, 50 °C.

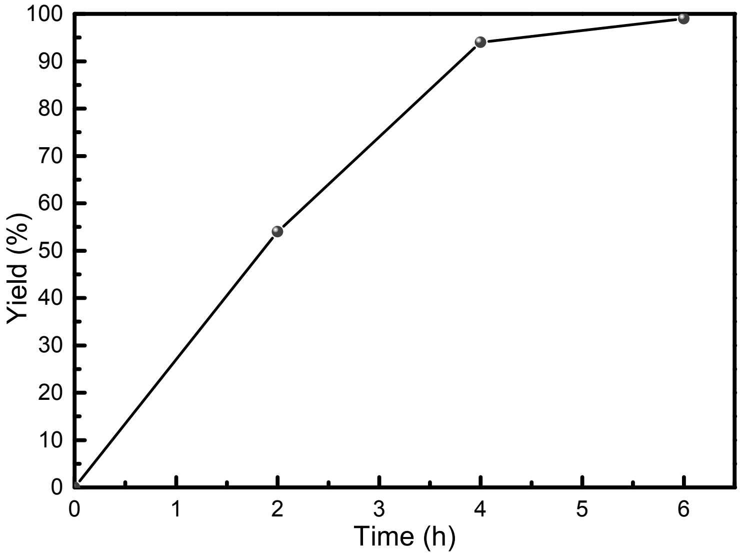


Figure S10. Effect of time on the yield. Reaction conditions: 3 mmol 1a, 2 mmol 2a, 10mg Ag/ATP, 0.3 mmol DBN, 1 mL DMF, 50 °C, 1 MPa CO_2.

Table S1 Effect of the cocatalyst time on the yield [a].

Entry	Catalyst	Co-catalyst	Solvent	T (°C)	Yield (%)
1	Ag/ATP-5	DBN	DMF	60	99
2	Ag/ATP-5	K_2CO_3	DMF	60	-
3	Ag/ATP-5	Cs_2CO_3	DMF	60	-

4	Ag/ATP-5	TBAB	DMF	60	-
5	Ag/ATP-5	PPNCl	DMF	60	-
6	Ag/ATP-5	PPh_3	DMF	60	1
7	Ag/ATP-5	TMEDA	DMF	60	33
8	Ag/ATP-5	DMAP	DMF	60	19
9	Ag/ATP-5	DBU	DMF	60	71

[a] Reaction conditions: 3 mmol 1a, 2 mmol 2a, 10mg catalyst, 0.3 mmol cocatalyst, 1 mL solvent, 6 h, 1 MPa CO_2.

Table S2 Effect of the cocatalyst time on the yield [a].

Entry	Catalyst	Cocatalyst	Solvent	T (°C)	Yield (%)
1	Ag/ATP-5	DBN	DMF	50	99
2	Ag/ATP-5	DBN	Dioxane	50	27
3	Ag/ATP-5	DBN	THF	50	27
4	Ag/ATP-5	DBN	tert-Butanol	50	22
5	Ag/ATP-5	DBN	ACN	50	47

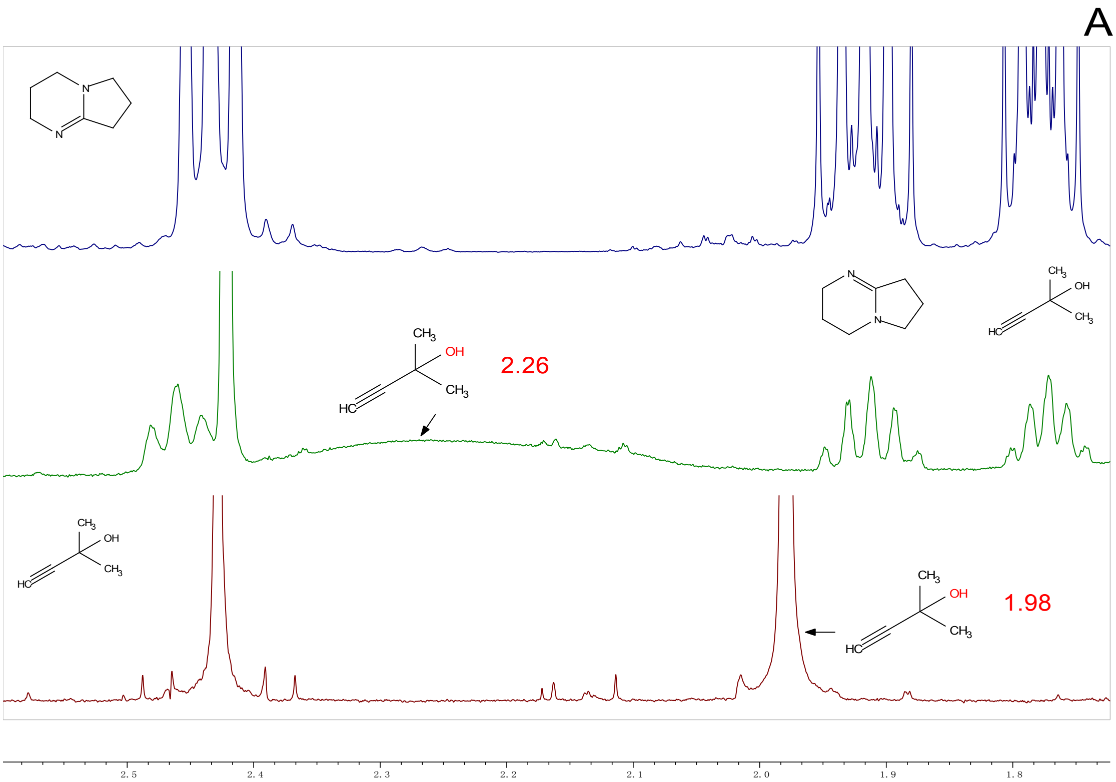
[a] Reaction conditions: 2.8 mmol 1a, 2 mmol 2a, 10mg catalyst, 0.3 mmol cocatalyst, 1 mL solvent, 6 h, 1 MPa CO_2.

Table S3 Performance of selected catalytic systems in the reaction of CO_2 with 1a and 2a.

Entry	1a (mmol)	2a (mmol)	Catalyst (mmol)	CO_2 (MPa)	t (h)	T (°C)	Yield (%)	Tof (h^{-1})
1 [1]	1.5	1	$ZnCl_2$ 0.5	1	24	80	94	0.083
2 [2]	1.5	1	Silver sulfadiazine 0.05	0.1	24	80	98	0.817
3 [3]	1.5	1	Ag_2CO_3 0.05	1	12	80	98	1.633
4 [a]	2.8	2	Ag/ATP-5 10mg [b]	1	6	50	99	132.1

[a] The current work; [b]. 2.68 wt% of the silver content, by ICP test (Figure S3).

3. ^{1}H NMR spectra



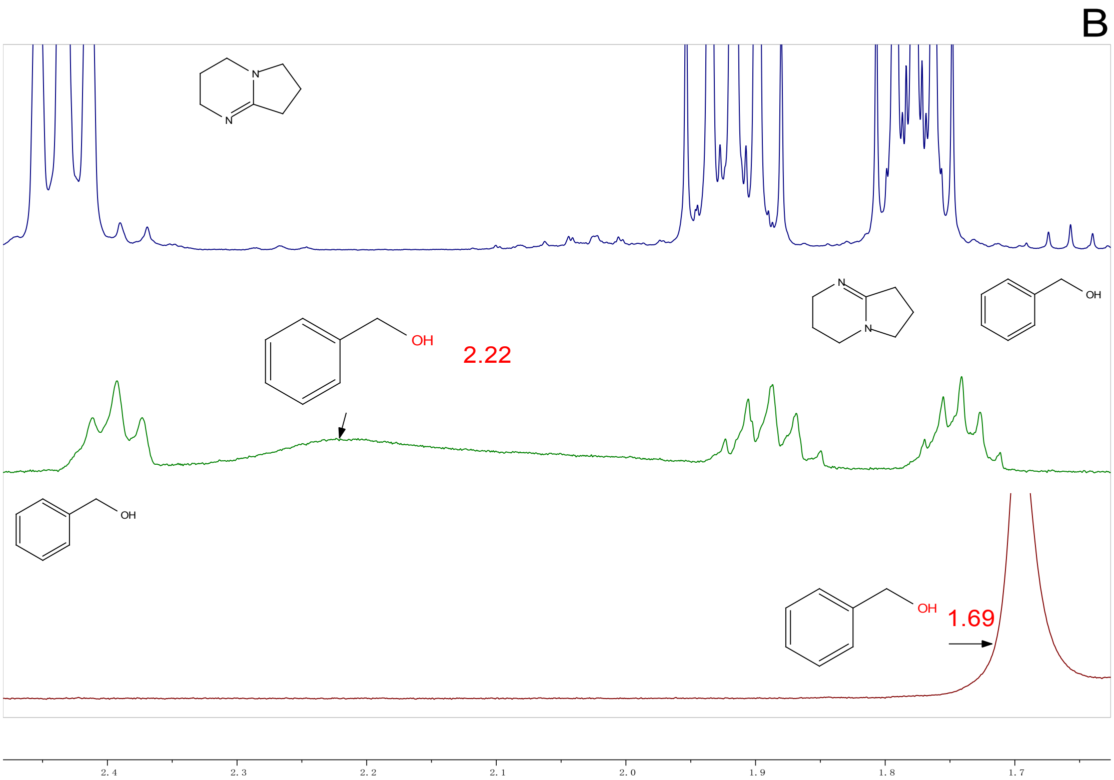
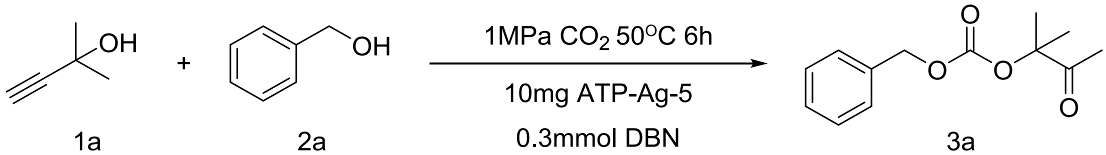


Figure S11. Figure A: ^{1}H NMR spectra of DBN (blue), 1a/DBN (green) and 1a (red). ([D6] DMSO, 298 K). Figure B: ^{1}H NMR spectra of DBN (blue), 2a/DBN (green) and 2a (red). ([D6] DMSO, 298 K).Experiment conditions: Figure A (green) 2.8 mmol (0.2352 g) 1a and 0.3 mmol (0.0373 g) DBN were added into a 10 mL test tubes. the mixture was determined by ^{1}H NMR; Figure B (green) 2.0 mmol (0.2163 g) 1a and 0.3 mmol (0.0373 g) DBN were added into a 10 mL test tubes. the mixture was determined by ^{1}H NMR.



1a 2a 3a

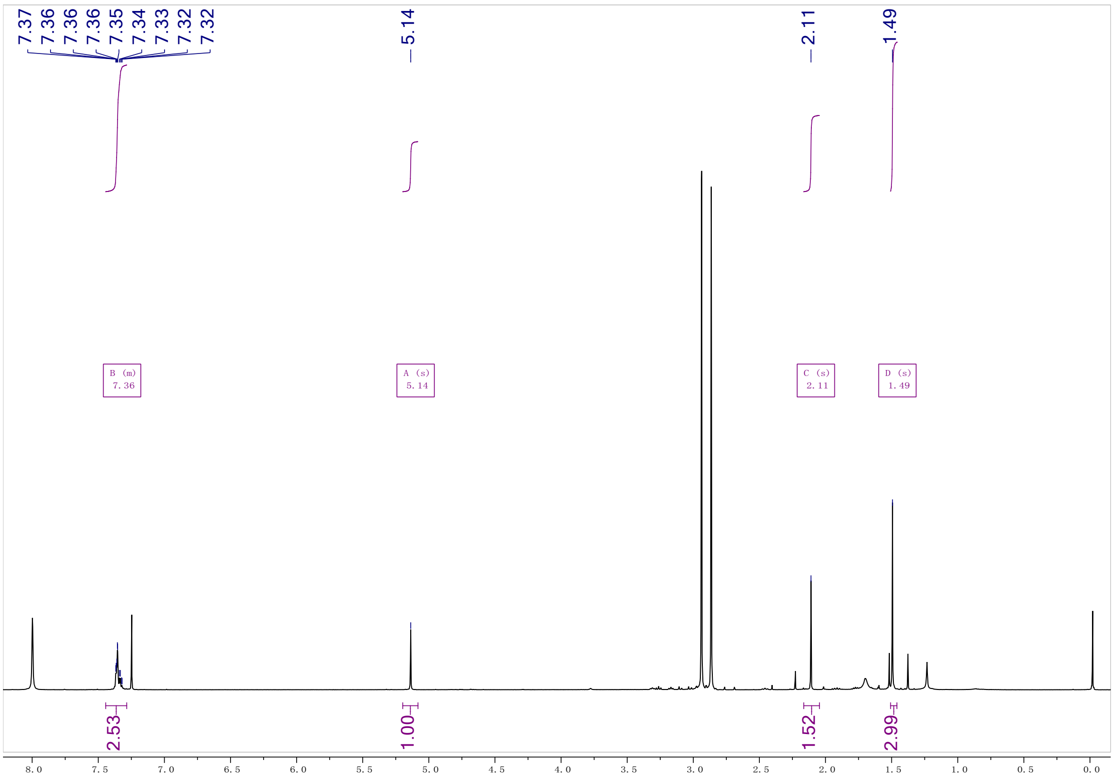


Figure S12. ^{1}H NMR spectra of the main reaction

Main product-3a:

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.44 – 7.28 (m, 5H), 5.14 (s, 2H), 2.11 (s, 3H), 1.49 (s, 6H).

4. Reaction cycles

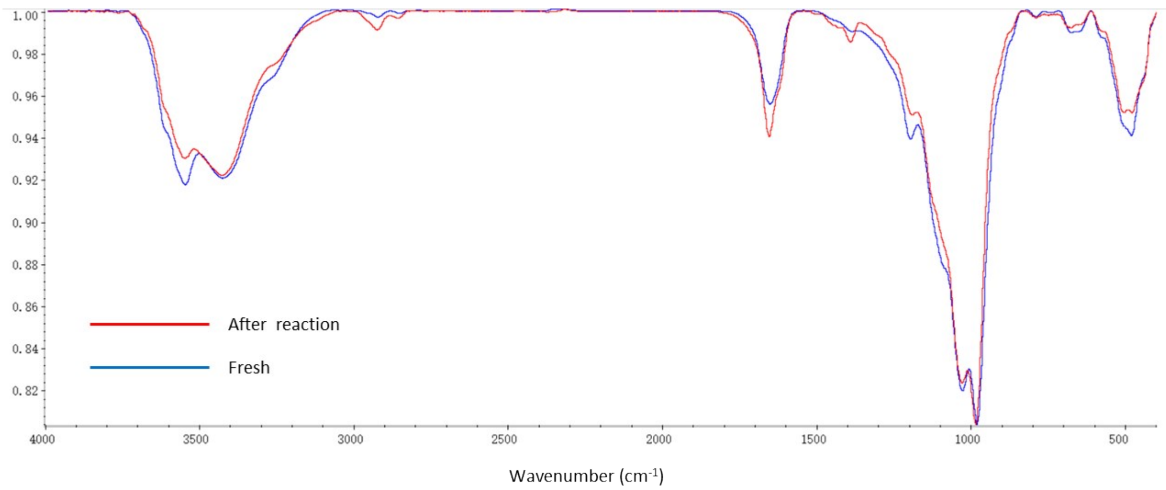


Figure S13. IR spectra of Ag/ATP and its sample after recycled reaction

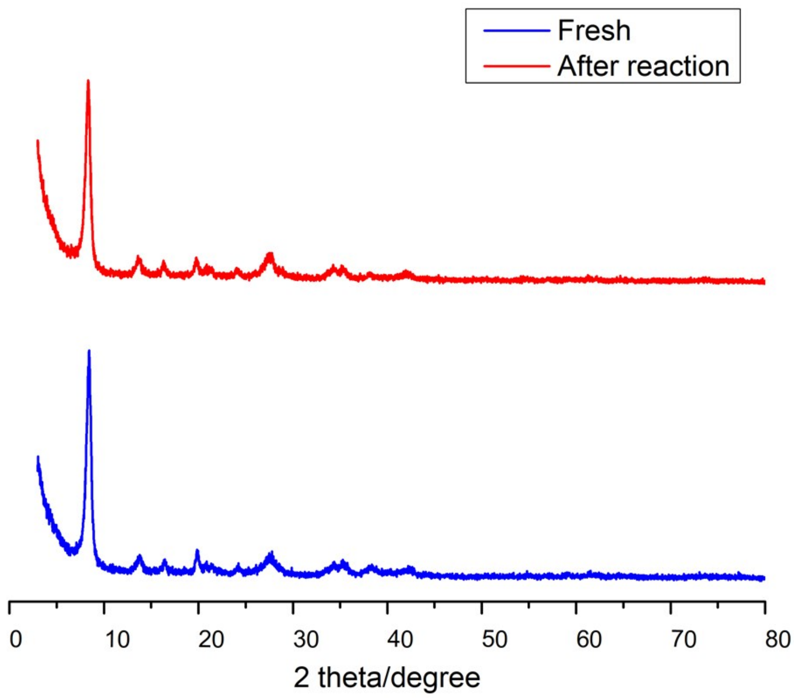


Figure S14. XRD spectra of Ag/ATP and the recycled catalyst after reaction

References

1. P. Liu, Q.-W. Song, Q.-N. Zhao, J.-Y. Li and K. Zhang, *Synthesis*, 2018, **51**, 739-746.
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3. Z. H. Zhou, Q. W. Song, J. N. Xie, R. Ma and L. N. He, *Chemistry, an Asian journal*, 2016, **11**, 2065-2071.