Electronic Supplementary Information

Tuning the Basicity of Ionic Liquids for Efficient Synthesis of Alkylidene

Carbonates from CO₂ at Atmospheric Pressure

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1. General Information.

All chemicals used in this work were purchased from commercial and used without further purification unless otherwise stated. Methyl-1H-1,2,4-triazole-3-carboxylate (CO₂Me-Triz), Dimethyl 4,5-imidazoledicarboxylate (DEIm), 3-Methyl-1-pentyn-3-ol, 2-Phenyl-3-butyn-2-ol and 1-Ethynylcyclopentanol were purchased from J&K Scientific Ltd. 1H-Tetraazole (Tetz), Imidazole (Im), 4-Nitroimidazole (NO₂-Im) and 1-Ethynyl-1-cyclohexanol were purchased from Energy-Chemistry Co., Ltd. trihexyl(tetradecyl)phosphonium bromide ([P₆₆₆₁₄][Br]), 1,2,4-Triazole (Triz) and 2-Methyl-3-butyn-2-ol were purchased from Aladdin Ind. Co., Ltd. CO₂ (99.99%) and CO₂ (10%) were purchased from Hangzhou Jingong Special Gas Co., Ltd. ¹H NMR and ¹³C NMR spectra were recorded on a Bruker spectrometer (400 MHz) in CDCl₃, which was obtained from Adamas-beta, with tetramethylsilane as the standard. FT-IR spectra were obtained using a Perkin-Elmer Spectrum One FTIR spectrometer with diamond ATR accessory. Gas Chromatograph – Mass Spectrometer (GC-MS) were carried out using an Agilent 5973N-6890N Analyzer. Energy Dispersive X-Ray Flourescence Spectrometer (EDXRF) was carried out using a Rigaku NEX CG EDXRF instrument.

General procedure for the synthesis of alkylidene carbonates. Taking the synthesis of 2a from atmospheric pressure CO₂ as an example: The reaction was carried out in a 10 mL flask, where AgOAc (0.033 g, 0.2 mmol), $[P_{66614}]$ [DEIm] (0.267 g, 0.4 mmol), and 1a (0.168 g, 2 mmol) were added into the flask in sequence. Subsequently, the flask was attached to a balloon filled with CO₂ (99.99%). Then the mixture was stirred at 30 °C for 5 h. The resulted product was quantitatively analyzed by gas chromatography (GC) with biphenyl as the internal standard. When the reusability of the catalyst system was investigated, the reaction mixture was diluted with *n*-hexane (5x2mL), and the upper layer solution was collected. The yield of 2a can be obtained by evaporating *n*-hexane. Then the lower layer could be used in the next turn after dried in vacuum at 60 °C, which was the mixture of [P₆₆₆₁₄][DEIm] and AgOAc.

2. NMR data for ILs using in this work and products.

These anion-functionalized ILs could be easily prepared by the neutralization of azole and an ethanol solution of $[P_{66614}]OH$, which was prepared from $[P_{66614}]Br$ using an anion-exchange resin according to the literature method^[S1].

[**P**₆₆₆₁₄][**Im**]: ¹H NMR (400 MHz, CDCl₃) 7.68 (s, 1H),7.07 (s, 2H),2.36 (m, 8H),1.30-1.56 (m, 48H), 0.90 (m, 12H); ¹³C NMR (101 MHz,CDCl₃) 135.2, 121.5, 31.8, 30.9, 30.7, 30.6, 30.4, 30.2, 29.5, 29.3, 29.2,28.8, 22.5, 22.2, 21.7, 14.0, 13.8 ppm.

[**P**₆₆₆₁₄][**Triz**]: ¹H NMR (400 MHz, CDCl₃) 8.06 (s, 2H), 2.32 – 2.14 (m, 8H), 1.55- 1.20 (m, 48H), 0.97-0.84 (m, 12H) ppm; ¹³C NMR (101 MHz, CDCl₃) 149.85, 31.88, 31.02, 30.81, 30.67, 30.48, 30.34, 29.65, 29.61, 29.58, 29.48, 29.32, 29.27, 28.92, 22.66, 22.30, 21.78, 21.73, 19.17, 18.70, 14.11, 13.91 ppm.

[**P**₆₆₆₁₄] [4-CHO-Im]: ¹H NMR (400 MHz, CDCl₃) 9.68 (s, 1H), 7.83 (s, 1H), 7.65 (s, 1H), 2.20 (m, 8H), 1.22-1.43 (m, 48H), 0.86 (m, 12H); ¹³C NMR (101 MHz, CDCl₃) 183.2, 146.5, 141.8, 137.0, 31.8, 30.9, 30.4, 30.3, 29.6, 29.5, 29.3, 29.2, 28.9, 22.6, 22.3, 21.7, 19.1, 18.8, 14.1, 13.9 ppm.

[**P**₆₆₆₁₄][**CO**₂**Me-Triz**]: ¹H NMR (400 MHz, CDCl₃) 8.20 (s, 1H), 3.89 (s, 3H), 2.37 – 2.14 (m, 8H), 1.58 – 1.15 (m, 48H), 0.96 – 0.79 ppm (m, 12H); ¹³C NMR (101 MHz, CDCl₃) 162.5, 154.3, 150.0, 51.5, 31.9, 30.0, 30.8, 30.6, 30.4, 30.3, 29.6, 29.5, 29.3, 29.3, 28.9, 22.7, 22.3, 21.7, 19.1, 18.6, 14.1, 13.9ppm.

[**P**₆₆₆₁₄][**DCIm**]: ¹H NMR (400 MHz, CDCl₃) 7.39 (dd, 4.9, 1H), 3.81 (dd, 8.2, 6H), 2.20 – 1.89 (m, 8H), 1.52 – 1.13 (m, 48H), 0.98 – 0.71 (m, 12H);¹³C NMR (101 MHz, CDCl₃) 165.3, 146.2, 134.5, 50.9, 31.9, 31.0, 30.4, 30.3, 29.6, 29.5, 29.3, 29.3, 29.0, 22.7, 22.3, 21.7, 18.9, 18.5, 14.1, 13.9 ppm.

[**P**₆₆₆₁₄][**3-CN-Triz**]: ¹H NMR (400 MHz, CDCl₃) 8.04 (s, 1H), 2.30 – 2.08 (m, 8H), 1.59 – 1.17 (m, 48H), 0.89 ppm (m, 12H); ¹³C NMR (101 MHz, CDCl₃) 152.4, 137.4, 117.53, 31.9, 30.9, 30.8, 30.6, 30.4, 30.3, 29.7, 29.6, 29.5, 28.9, 22.7, 22.3, 21.6, 19.1, 18.6, 14.1, 13.9 ppm.

[**P**₆₆₆₁₄][**Tetz**]: ¹H NMR (400 MHz, CDCl₃) 8.40 (s, 1H), 2.32-2.13 (m, 8H), 1.73 – 1.19 (m, 48H), 0.96 – 0.82 ppm (m, 12H); ¹³C NMR (101 MHz, CDCl₃) 149.9, 31.88, 31.30, 30.95, 30.78, 30.64, 30.45, 30.30, 29.61, 29.48, 29.32, 29.26, 28.89, 28.26, 27.62, 22.65, 22.40, 22.29, 21.70, 19.09, 18.62, 14.10, 13.99, 13.90 ppm.

2a: ¹H NMR (400 MHz, CDCl₃) 4.77 (d, 1H), 4.33 (d, 1H), 1.62 (s, 6H); ¹³C NMR (101 MHz, CDCl₃) 158.7, 151.3, 85.3, 84.7, 27.6 ppm.

2b: ¹H NMR (400 MHz, CDCl₃) 4.82 (d, 1H), 4.28 (d, 1H), 1.92 (dq, 1H), 1.76 (dq, 1H), 1.59 (s, 3H), 0.99 (t, 3H); ¹³C NMR (101 MHz, CDCl₃) 157.4, 151.6, 87.6, 85.6, 33.4, 26.0, 7.3 ppm.

2c: ¹H NMR (400 MHz, CDCl₃) 7.51-7.45(m, 2H), 7.43-7.37(m, 3H), 4.95 (d, 1H), 4.47 (d, 1H), 1.97 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) 157.4, 151.2, 139.2, 129.2, 128.9, 124.7, 88.2, 87.2, 27.5 ppm.

2d: ¹H NMR (400 MHz, CDCl₃) 4.76 (d, 1H), 4.30 (d, 1H), 2.08-1.96 (m, 2H), 1.75-1.60 (m, 7H), 1.33-1.24 (m, 1H); ¹³C NMR (101 MHz, CDCl₃) 158.7, 151.6, 86.4, 85.6, 36.5, 24.3, 21.6 ppm.
2e: ¹H NMR (400 MHz, CDCl₃) 4.78 (d, 1H), 4.34 (d, 1H), 2.31-2.17 (m, 2H), 1.97-1.80 (m, 6H); ¹³C NMR (101 MHz, CDCl₃) 157.8, 151.7, 94.4, 85.6, 40.8, 24.4 ppm.

3. Screening of different metal catalysts

=	CO ₂ -	Metal salt [P ₆₆₆₁₄][Tri]	2a
Entry		Metal salt	Yield(%) ^[b]
1		AgOAc	76
2		AgNO ₃	73
3		AgCO ₃	53
4[c]		Ag ₂ O	72
5		CuI	3
6		CuCl	2

Table S1 Screening of various metal catalysts^[a]

[a] Reaction conditions: **1a** (2 mmol), metal salt (0.2 mmol), $[P_{66614}]$ [Tri] (0.4 mmol) and CO₂ (1 bar) for 5 h at 30 °C. [b] Determined by GC using internal standard method. [c] 0.1 mmol Ag₂O was used.

4. Optimization of the reaction condition

Table S2 The effect of the temperature and the amount of the catalyst
on the synthesis of alkylidene carbonates from atmospheric CO ₂ . ^[a]

Entry	AgOAc [%]	[P ₆₆₆₁₄][DEIm] [%]	T [ºC]	Time [h]	Yield [%] ^[b]
1	10	20	30	5	91
2	10	15	30	5	85
3	10	10	30	5	65 ^[c]
4	10	20	20	5	92
5	10	20	40	5	71 ^[d]
6	10	20	40	8	73
7	1	20	20	15	87
8	1	10	20	30	91

[a] Reaction conditions: **1a** (2 mmol), AgOAc, $[P_{66614}]$ [DEIm] and CO₂ (1 bar). [b] Determined by GC using internal standard method. [c] The conversion is 69%. [d] The conversion is 91%.

5. DFT calculation

All calculations were performed with the Gaussian 09 package.^[S2] Geometry optimizations and frequency calculations were carried out at the B3LYP/LANL2DZ level for Ag and B3LYP/6-31++G(d,p) level for other atoms. Solvation corrections were calculated by a self-consistent reaction field (SCRF) using the CPCM model with 2-Methyl-2-Propanol as solvent.

Calculated pK_a value for anions in *t*BuOH

The pK_a was calculated according to the literature method by using thermodynamic cycle.^[S3,S4] In this work, the value for $G_{gas}(H^+)$ was -6.28 kcal/mol, which could be calculated from Sackur-Tetrode equation.^[S5] The value for $\triangle G_{sol}(H^+)$, -270.39 kcal/mol, was consistent with the value in Ref. S3.

The Optimized structures for key intermediates.

The reaction mechanism of cycoaddition between CO_2 and propargylic alcohols was believed involving two competing cycles (Scheme S1)^[S6-S8]. One probable pathway may be started with the hydrogen abstraction of propargylic alcohols by the base contained in this system to give the intermediate **Ia**. Then **Ia** reacts with CO_2 to form **Ib**, which will proceed an intramolecular ring-closing reaction and snatches the hydrogen from H-Base to afford the product (Scheme S1,cycle I). On another pathway, CO_2 may be captured by the base at first to give **Ha**. After that, base-CO₂ can nucleophilic attack triple bond in **1a** to generate **Hb**. The product will be obtained through hydrogen transfer and alkoxide anion attack to carbonyl carbon in **Ha** (Scheme S1,cycle II).



Scheme S1. The plausible mechanism of cycoaddition between CO₂ and propargylic alcohol





Figure S1. DFT calculated key structures for (a) cycle I, (b) cycle II.



Scheme S2 The plausible mechanism for the synthesis of alkylidene carbonates from CO_2 and propargylic alcohol using [P₆₆₆₁₄] [DEIm] as the base.

6. The reaction at 10 mmol scale



Scheme S3. The catalytic activity at 10 mmol scale.

7. Reusability of the catalytic system



Figure S2. Recyclability of catalytic system.

8. Discussion about the cycloaddition between 1a and CO₂ with [P₆₆₆₁₄][Im] as the base.

In order to investigate why the strong basicity led to high side reaction, we carried out the cycloaddition with $[P_{66614}][Im]$ as the base, monitoring the reaction by GC-MS (Figure S4-S7). At first, the solution was clear after stirring. With the reaction went on, the reaction mixture got more and more muddy, which was agreed with the GC-MS spectrums that the trimer of **1a** appeared during 1h and increased as time went on. After the reaction accomplished, about 26 mg sediment was gotten after washed by CH_2Cl_2 3 times, which did not solve in CH_2Cl_2 , ethanol or CH_3CN . EDXRF showed that there was silver in sediment, which indicated that the catalyst was damaged at this system (Figure S8). In the IR spectrum of the sediment, the absorption band at 1622 cm⁻¹ attributable to alkene C=C stretches, and 1310 and 754 and 665 cm⁻¹attributable to alkene C-H stretches (Figure S6). When the sediment was heated to 600 °C for 2 days in muffle furnace, white solid residue about 10 mg was gotten.



Figure S3. The GC-MS spectra of reaction mixture at 0.5 h.



Figure S4. The GC-MS spectra of reaction mixture at 1 h.



Figure S5. The GC-MS spectra of reaction mixture at 3 h.



Figure S6. The GC-MS spectra of reaction mixture at 5 h.



Figure S7. EDXRF spectra of sediment with Al target.



Figure S8. IR spectra of sediment.

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