Electronic Supplementary Information

Highly Efficient Synthesis of Alkylidene Cyclic Carbonates from Low Concentration CO_2usingHydroxyl and Azolate Dual Functionalized Ionic Liquids

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NMR data of ILs

[Ch][BenIm]：^{1}H NMR (400 MHz, DMSO) δ 7.77 (s, 1H), 7.38 (dd, 2H), 6.81 (dd, 2H), 3.90 (m, 2H), 3.38 (m, 2H), 3.09 (s, 9H).^{13}C NMR (101 MHz, DMSO) δ 150.61, 144.98, 117.29, 115.75, 67.35, 67.33, 67.30, 54.79, 53.25, 53.21, 53.17.

[Ch][Im]：^{1}H NMR (400 MHz, DMSO) δ 7.19 (s, 1H), 6.73 (2H), 3.84 (m, 2H), 3.35 (m, 2H), 3.09 (s, 9H).^{13}CNMR (101 MHz, DMSO) δ 141.28, 124.19, 67.50, 67.47, 67.44, 54.72, 53.23, 53.19, 53.16.

[Ch][Tetz]：^{1}H NMR (400 MHz, DMSO) δ 8.21 (s, 1H), 3.85 (m, 2H), 3.46 – 3.37 (m, 2H), 3.11 (s, 9H).^{13}CNMR (101 MHz, DMSO) δ 148.16, 67.08, 67.05, 67.02, 55.21, 53.26, 53.23, 53.19.

[Ch][Triz]：^{1}H NMR (400 MHz, DMSO) δ 7.74 (s, 2H), 3.87 (m, 2H), 3.45 – 3.40 (m, 2H), 3.12 (s, 9H).^{13}CNMR (101 MHz, DMSO) δ 148.81, 67.35, 67.32, 67.29, 54.97, 53.26, 53.22, 53.18

[N_{1111}][Triz]：^{1}H NMR (400 MHz, DMSO) δ 7.61 (s, 2H), 3.09 (s, 12H). ^{13}C NMR (101 MHz, DMSO) δ 149.20, 54.37, 54.33, 54.30

[N_{2222}][Triz]：^{1}H NMR(400 MHz, DMSO) δ 7.53 (s, 1H), 3.20 (q, J = 7.3 Hz, 8H), 1.20 – 1.06 (m, 12H).^{13}C NMR (101 MHz, DMSO) δ 148.98, 51.36, 51.33, 51.30, 7.04.

[N_{4444}][Triz]：^{1}H NMR (400 MHz, DMSO) δ 7.58 (s, 2H), 3.22 – 3.11 (m, 8H), 1.62 – 1.49 (m, 8H), 1.36 – 1.24 (m, 8H), 0.93 (t, *J* = 7.3 Hz, 12H).^{13}CNMR (101 MHz, DMSO) δ 148.98, 57.60, 23.16, 19.30, 13.59.

[P_{66614}][Triz]：^{1}H NMR (400 MHz, DMSO) δ 7.64 (s, 2H), 2.26 – 2.09 (m, 8H), 1.47 – 1.21 (m, 47H), 0.91 – 0.82 (m, 13H).^{13}CNMR (101 MHz, DMSO) δ 148.62, 31.28, 30.80, 30.38, 30.01, 29.86, 29.80, 29.65, 29.05, 29.03, 29.01, 28.99, 28.94, 28.70, 28.62, 28.06, 22.07, 21.90, 21.79, 20.52, 20.48, 20.41, 17.66, 17.57, 17.19, 17.10, 13.91, 13.82

Table S1. The effect of various metal catalysts[a] on this reaction.

Entry	Metal salt	Yield(%)[b]
1	$AgNO_3$	93
2	AgOAc	91
3	$AgCO_3$	48
4[c]	Ag_2O	78
5	$Fe(NO_3)_3$	4
6	$Cu(NO_3)_2$	1
7	$Al(NO_3)_3$	3

[a]Reaction conditions: **1a** (4 mmol), metal salt (0.4 mmol), [Ch][Tri] (0.8 mmol) and CO_2 (1 bar) for 24 h at 30 ^{o}C). [b] Determined by GC using internal standard method. [c] 0.2 mmol Ag_2O was used.

Table S2. The effect of the temperature, time and the amount of the catalyst on the synthesis of alkylidene carbonates from CO_2.[a]

Entry	$AgNO_3$ [%]	[Ch][Tri][%]	T [^{o}C]	Time [h]	Yield [%][b]
1	10	20	30	6	49
2	10	20	30	12	78
3	10	20	30	24	93
4	10	20	30	36	92
5	10	20	20	24	77
6	10	20	40	24	83
7	1	20	30	24	26
8	10	15	30	24	71
9	10	20	30	24	90

[a] Reaction conditions: **1a** (4 mmol), $AgNO_3$, [Ch][Tri] and CO_2 (1 bar).
[b] Determined by GC using internal standard method.

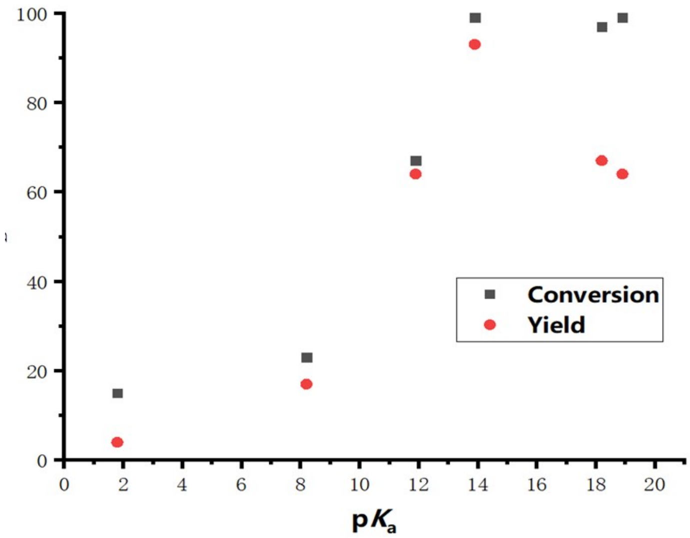

Fig. S1 The relationship between the conversion and the yield with the calculated pK_a value

Table S3 The CO_2 absorption capacity by anion-functionalized ILs[a]

Entry	Ionic liquid	Calculated pK_a	absorption capacity[b]
1	[Ch][Cl]	1.8	0.04
2	[Ch][Tetz]	8.2	0.08
3	[Ch][BenTri]	11.9	0.27
4	[Ch][Tri]	13.9	0.87
5	[Ch][BenIm]	18.2	0.89
6	[Ch][Im]	18.9	0.93

[a] The absorption was carried out at 30°C. [b] Mol CO_2 per mol IL

Table S4 The synthesis of alkylidene carbonates using $AgNO_3$ as catalyst

entry	Base/Ligand	P(MPa)	T(°C)	Yield(%)	Ref
1	[Ch][Tri]	0.1	30	93	This work
2	[Ch][Tri]	0.01	30	85	This work
3	[Ch][Tri]	0.015	30	87	This work
4	$[P_{66614}]$[Tri]	0.1	30	73	1
5	Ph_3P	0.1	25	0	2
6	Ph_3P	0.1	25	0	3
7	$(n\text{-}C_7H_{15})_4NBr$	0.1	60	0	4
9	EMImOAc	0.1	45	58	5
10	DavePhos	0.8	25	20	6

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