Supporting Information

PCCP **Sept. 2016**

Carbonate Based Ionic Liquid Synthesis (CBILS®): Thermodynamic Analysis

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Materials. The samples of vinylene carbonate [CAS-number 872-36-6], 4-vinyl ethylene carbonate [CAS-number 4427-96-7] (purchased from Sigma-Aldrich), and methyl phenyl carbonate [CAS-number 13509-27-8] (purchased from Alfa Aesar) having a mass-fraction purity of 97-99% were purified by repeated distillation in vacuum. Gas chromatography (GC) showed no traceable amounts of impurities in carbonates after they were purified. The samples were analysed with a Hewlett Packard gas chromatograph 5890 Series II with a flame ionization detector and Hewlett Packard 3390A integrator. The dimensions of the capillary column HP-5 (stationary phase crosslinked 5% PH ME silicone) were the following: the column length, inside diameter, and film thickness were 25 m, 0.32 mm and 0.25 μm, respectively. The flow rate of a carrier gas (nitrogen) was 12.1 $cm^3 \cdot s^{-1}$. The starting point for the GC temperature program was 323 K with a heating rate of 0.167 $K \cdot s^{-1}$ up until reaching 523 K temperature.

Vapour Pressure Measurements of Carbonates. Vapour pressures of carbonates were determined using the method of transpiration in a saturated nitrogen stream. About 0.5 g of the sample was mixed with small glass beads and placed in a thermostated U-shaped saturator. A well-defined nitrogen stream was passed through the saturator at a constant temperature (± 0.1 K), and the transported material was collected in a cold trap. The amount of condensed sample of each compound was determined by GC analysis using an external standard n-$C_{13}H_{28}$. The absolute vapor pressure p_i at each temperature T_i was calculated from the amount of the product collected within a definite period. Assuming validity of the Dalton's law applied to the nitrogen stream saturated with the substance i, values of p_i were calculated with equation:

$$p_i = m_i \cdot R \cdot T_a / V \cdot M_i \, ; \qquad V = V_{N2} + V_i \, ; \qquad (V_{N2} \gg V_i) \qquad (1)$$

where R = 8.314462 J·K^{-1}·mol^{-1}; m_i is the mass of the transported compound, M_i is the molar mass of the compound, and V_i its volume contribution to the gaseous phase. V_{N2} is the volume of the carrier gas and T_{a} is the temperature of the soap bubble meter used for measurement of the gas flow. The volume of the carrier gas V_{N2} was determined from the flow rate and the time measurement. Experimental results are given in Table S1. It was established that the total uncertainty of the data for this experimental technique was within the range from 1 to 3 % with the main source of errors attributed to the reproducibility of GC measurements.

Temperature dependence of vapor pressures p_i measured for vinylene carbonate, 4-vinyl ethylene carbonate, and methyl phenyl carbonate were fit with the following equation:

$$R \cdot \ln p_i = a + \frac{b}{T} + \Delta_{\mathrm{l}}^{\mathrm{g}} C_{p,m}^{\mathrm{o}} \cdot \ln\left(\frac{T}{T_0}\right) \qquad (2),$$

where a and b are adjustable parameters and $\Delta_{\mathrm{l}}^{\mathrm{g}} C_{p,m}^{\mathrm{o}}$ is difference between isobaric molar heat capacities of the gas, $C_{p,m}^{\mathrm{o}}$(g), and the liquid, $C_{p,m}^{\mathrm{o}}$(liq) given in Table 1 (see main text). Value T_0 appearing in equation (2) is an arbitrarily chosen reference temperature (which has been chosen to be 298 K) and R is the molar gas constant.

Vaporization enthalpies at temperature T were derived from the temperature dependence of vapor pressures using equation (3):

$$\Delta_{\mathrm{l}}^{\mathrm{g}} H_m^{\mathrm{o}}(T) = -b + \Delta_{\mathrm{l}}^{\mathrm{g}} C_{p,m}^{\mathrm{o}} \cdot T \qquad (3)$$

Vaporization entropies at temperature T were also derived from the temperature dependence of vapor pressures using equation (4):

$$\Delta_{\mathrm{l}}^{\mathrm{g}} S_m^{\mathrm{o}}(T) = \Delta_{\mathrm{l}}^{\mathrm{g}} H_m^{\mathrm{o}} / T + R \ln(p_i / p^{\mathrm{o}}) \qquad (4)$$

Experimental absolute vapor pressures measured by the transpiration method, coefficients a and b of equation (2), as well as values of $\Delta_{\mathrm{l}}^{\mathrm{g}} H_m^{\mathrm{o}}(T)$ and $\Delta_{\mathrm{l}}^{\mathrm{g}} S_m^{\mathrm{o}}(T)$ are given in Table S1. Procedure for calculation of the combined uncertainties of the vaporization enthalpy was described elsewhere.[1] It includes uncertainties from the transpiration experimental conditions, uncertainties in vapor pressure, and uncertainties in the temperature adjustment to T = 298 K.

Table S1. Absolute Vapor Pressures p, Vaporization Enthalpies, $\Delta_l^g H_m^\circ$, and Vaporization Entropies, $\Delta_l^g S_m^\circ$, Obtained by the Transpiration Method.

T/ K[a]	m/ mg[b]	$V(N_2)$[c] / dm^3	T_a/ K[d]	Flow/ dm^3·h^{-1}	p/ Pa[e]	$u(p)$/ Pa[f]	$\Delta_l^g H_m^\circ$/ kJ·mol^{-1}	$\Delta_l^g S_m^\circ$/ J·K^{-1}·mol^{-1}
vinylene carbonate: $\Delta_l^g H_m^\circ$(298.15 K) = (49.5±0.3) kJ·mol^{-1}								
$\ln(p/p^\circ) = \frac{257.4}{R} - \frac{63244.9}{R\cdot(T,\mathrm{K})} - \frac{45.8}{R}\ln\left(\frac{T,\mathrm{K}}{298.15}\right)$								
298.2	3.64	0.460	296.7	0.92	229.2	5.8	49.59	115.8
299.6	4.08	0.456	293.0	0.91	256.0	6.4	49.53	115.7
301.1	3.09	0.321	296.7	0.92	278.9	7.0	49.46	115.4
302.5	9.47	0.895	294.2	0.89	303.3	7.6	49.39	115.1
303.1	2.25	0.204	296.7	0.91	319.5	8.0	49.37	115.1
304.5	4.81	0.393	294.7	1.00	350.9	8.8	49.30	114.9
305.5	4.65	0.357	295.5	0.89	374.7	9.4	49.26	114.8
305.9	6.21	0.460	296.7	0.92	389.4	9.8	49.24	114.9
306.3	11.51	0.833	296.6	1.00	398.3	10.0	49.22	114.8
307.5	5.05	0.334	294.2	1.00	431.5	10.8	49.16	114.6
307.9	3.83	0.258	296.7	0.91	428.0	10.7	49.14	114.3
308.5	5.13	0.325	295.5	0.89	453.8	11.4	49.12	114.4
310.4	5.71	0.324	294.2	1.02	503.2	12.6	49.03	114.0
310.9	5.03	0.281	296.7	0.91	516.4	12.9	49.01	113.9
311.4	17.37	0.921	295.5	0.89	541.1	13.6	48.99	113.9
312.8	4.77	0.237	296.7	0.91	579.6	14.5	48.92	113.6
313.4	5.35	0.258	294.2	1.03	591.0	14.8	48.89	113.4
314.3	12.50	0.560	295.8	0.88	640.7	16.0	48.85	113.5
315.3	8.02	0.341	296.9	1.00	676.6	16.9	48.81	113.3
316.3	8.54	0.338	294.8	1.01	723.1	18.1	48.76	113.2
317.3	10.55	0.399	295.8	0.89	758.1	19.0	48.71	113.0
317.3	10.78	0.408	296.6	1.02	759.4	19.0	48.71	113.0
317.8	6.36	0.232	296.7	0.92	787.6	19.7	48.69	113.0
319.3	10.01	0.337	294.8	1.01	848.5	21.2	48.62	112.6
320.3	8.14	0.264	296.5	0.88	886.2	22.2	48.58	112.4
322.2	14.20	0.404	295.8	1.01	1006.4	25.2	48.49	112.3
322.9	16.45	0.449	295.2	2.25	1047.2	26.2	48.46	112.2
323.2	9.14	0.243	295.4	0.89	1076.1	26.9	48.44	112.2
323.4	10.36	0.270	296.8	1.01	1103.3	27.6	48.44	112.3
325.2	12.05	0.285	295.8	1.01	1209.6	30.3	48.35	112.0
326.2	8.43	0.190	295.3	0.88	1266.6	31.7	48.31	111.8
4-vinyl ethylene carbonate: $\Delta_l^g H_m^\circ$(298.15 K) = (63.5±0.4) kJ·mol^{-1}								
$\ln(p/p^\circ) = \frac{285.3}{R} - \frac{81484.1}{R\cdot(T,\mathrm{K})} - \frac{60.5}{R}\ln\left(\frac{T,\mathrm{K}}{298.15}\right)$								
295.2	2.03	13.76	293.9	3.11	3.2	0.1	63.63	129.5
298.2	1.76	9.06	294.7	5.78	4.2	0.1	63.45	129.0
303.0	2.12	7.02	292.7	5.54	6.4	0.2	63.15	128.2
308.0	0.55	1.29	296.3	3.08	9.3	0.3	62.85	126.9
308.0	1.89	4.26	294.9	3.20	9.5	0.3	62.85	127.1
310.9	2.03	3.63	293.4	2.98	12.0	0.3	62.68	126.5
312.9	1.95	2.99	295.0	5.37	14.0	0.4	62.56	126.2
315.9	1.85	2.23	297.0	1.29	18.0	0.5	62.38	125.8
317.9	2.94	3.13	296.5	3.08	20.3	0.5	62.25	125.2

322.8	2.05	1.49	297.4	5.27	29.8	0.8	61.96	124.5
327.8	2.14	1.10	296.3	1.30	41.9	1.1	61.66	123.4
330.7	1.82	0.783	295.3	2.94	50.1	1.3	61.48	122.8
332.7	1.70	0.651	295.8	1.30	56.4	1.4	61.36	122.3
335.2	1.91	0.617	295.4	1.09	66.7	1.7	61.21	121.8
335.2	2.66	0.825	296.3	1.05	69.7	1.8	61.21	122.2
337.7	1.93	0.545	295.2	1.36	76.1	1.9	61.06	121.1
339.2	2.07	0.505	295.8	1.08	88.4	2.2	60.97	121.3
342.6	1.81	0.371	294.0	1.39	104.8	2.6	60.76	120.3
345.1	2.44	0.409	296.1	1.07	128.5	3.2	60.60	120.3
347.6	4.61	0.652	294.1	3.13	151.5	3.8	60.46	120.0

methyl phenyl carbonate: $\Delta_{\mathrm{l}}^{\mathrm{g}}H_{m}^{\circ}$ (298.15 K) = (63.8±0.3) kJ·mol^{-1}

$$\ln(p/p^{\circ}) = \frac{312.7}{R} - \frac{86644.8}{R\cdot(T,\mathrm{K})} - \frac{76.6}{R}\ln\left(\frac{T,\mathrm{K}}{298.15}\right)$$

283.5	1.48	6.49	295.3	5.49	3.7	0.1	64.93	144.2
288.4	1.57	4.32	295.6	5.29	5.9	0.2	64.55	142.9
293.3	1.46	2.53	294.1	1.01	9.3	0.3	64.18	141.7
298.2	1.63	1.82	296.0	0.99	14.5	0.4	63.81	140.5
303.2	1.87	1.37	295.2	1.55	22.0	0.6	63.42	139.2
308.0	1.77	0.862	295.9	1.03	33.2	0.9	63.06	138.2
312.9	1.98	0.660	295.3	1.04	48.4	1.2	62.68	136.9
317.8	1.58	0.379	295.6	1.03	67.4	1.7	62.31	135.4
322.8	1.53	0.259	295.4	1.04	95.5	2.4	61.92	134.0
327.7	1.77	0.213	295.3	0.91	134.4	3.4	61.55	132.9
328.3	6.63	0.743	295.2	2.41	144.0	3.6	61.50	133.0
333.3	6.49	0.528	295.4	2.44	198.6	5.0	61.12	131.7
338.2	5.21	0.304	295.3	0.91	276.3	6.9	60.74	130.6
347.2	6.73	0.213	295.3	0.91	510.3	12.8	60.05	129.1
353.2	16.35	0.371	295.2	2.48	710.2	17.8	59.59	127.6

[a] Saturation temperature ($u(T)$ = 0.1 K). [b] Mass of transferred sample condensed at T = 243 K. [c] Volume of nitrogen ($u(V)$ = 0.005 dm^3) used to transfer m ($u(m)$ = 0.0001 g) of the sample. [d] T_a is the temperature of the soap bubble meter used for measurement of the gas flow. [e] Vapor pressure at temperature T calculated from the m and the residual vapor pressure at T = 243 K estimated by iteration. [f] Standard uncertainty in p calculated with $u(p/\mathrm{Pa}) = 0.005 + 0.025(p/\mathrm{Pa})$ for $p < 5$ Pa and $u(p/\mathrm{Pa}) = 0.025 + 0.025(p/\mathrm{Pa})$ for $p > 5$ to 3000 Pa.

Table S2. G3MP2 calculated thermodynamic functions, $\Delta_{\mathrm{r}}G_m^{\mathrm{o}}$ $\Delta_r H_m^{\circ}$ and $\Delta_r S_m^{\circ}$ and thermodynamic equilibrium constants of the reactions (1-16) in the gas phase (K_P) and in the liquid phase (K_x) at 298 K

Reaction	$\Delta_{\mathrm{r}}G_m^{\mathrm{o}}$	$\Delta_r H_m^{\circ}$	$\Delta_r S_m^{\circ}$	K_P	K_x
	kJ·mol^{-1}		J·mol^{-1} K^{-1}		
R1	39.8	-1.2	-137.6	1×10^{-7}	1.5×10^{7}
R2	45.1	3.3	-140.1	1×10^{-8}	3.9×10^{5}
R3	42.7	2.4	-134.9	3×10^{-8}	1.3×10^{5}
R4	90.2	47.7	-142.9	2×10^{-16}	1×10^{-6}
R5	61.4	11.3	-168.0	2×10^{-11}	1.9
R6	29.3	6.3	-77.2	7.3×10^{-6}	3×10^{7}
R7	98.5	48.2	-169.0	5.1×10^{-18}	4×10^{-7}
R8	93.2	39.6	-179.9	5.1×10^{-17}	8×10^{-9}
R9	38.5	-9.3	-160.2	1.8×10^{-7}	5×10^{4}
R10	22.4	-24.9	-158.4	1.2×10^{-4}	1.4×10^{5}
R11	25.9	-19.7	-152.9	3×10^{-5}	2.4×10^{3}
R12	45.2	4.4	-136.8	1×10^{-8}	3×10^{5}
R13	35.6	-7.0	-143.1	6×10^{-7}	2.5×10^{6}
R14	74.8	25.3	-166.1	8×10^{-14}	3.8×10^{3}
R15	106.9	65.7	-138.3	2×10^{-19}	8.7×10^{-3}
R16	114.9	71.4	-145.7	7.1×10^{-21}	9.6×10^{-5}

Table S3. G3MP2 calculated thermodynamic functions, $\Delta_{\mathrm{r}}G_m^{\mathrm{o}}$ $\Delta_r H_m^{\circ}$ and $\Delta_r S_m^{\circ}$ and thermodynamic equilibrium constants of the reactions (1-16) in the gas phase (K_P) and in the liquid phase (K_x) at 393 K

Reaction	$\Delta_{\mathrm{r}}G_m^{\mathrm{o}}$	$\Delta_r H_m^{\circ}$	$\Delta_r S_m^{\circ}$	K_P	K_x [a]
	kJ·mol^{-1}		J·mol^{-1} K^{-1}		
R1	19.5	12.2	-16.1	3×10^{-3}	6.4×10^{10}
R2	23.7	16.7	-18.6	7×10^{-4}	5.8×10^{9}
R3	55.3	3.9	-130.7	4×10^{-8}	1.1×10^{5}
R4	103.6	49.0	-139.0	2×10^{-14}	1.2×10^{-2}
R5	43.1	24.8	-46.5	2×10^{-6}	2×10^{5}
R6	36.3	9.0	-69.3	1.5×10^{-5}	3×10^{6}
R7	114.4	49.2	-164.8	6×10^{-16}	6×10^{-5}
R8	110.1	40.7	-176.6	2×10^{-15}	5×10^{-6}
R9	53.5	-8.0	-156.5	8×10^{-8}	3×10^{4}
R10	3.1	-11.6	-37.4	4×10^{-1}	3.5×10^{9}
R11	6.1	-6.3	-31.7	2×10^{-1}	3×10^{8}
R12	23.8	17.7	-15.6	7×10^{-4}	5.8×10^{9}
R13	14.8	6.4	-21.5	1×10^{-2}	2.7×10^{10}
R14	90.5	26.5	-162.9	9×10^{-13}	5.7×10^{2}
R15	117.6	67.5	-127.4	2×10^{-16}	1.2×10^{-4}
R16	126.2	73.2	-134.7	2×10^{-17}	5×10^{-6}

Table S4. Vapor pressures of Precursors Used for the CBILS® Process (in Pa)[a]

Precursor	Vapor pressure at 298 K	Vapor pressure at 393 K	Ref.
1-ethyl-imidazole	26	6658	S1
di-methyl carbonate	7274	256107	S2
di-ethyl carbonate	1516	115960	S3
di-isopropyl carbonate	209	38260	S3
di-tertbutyl carbonate	24	8588	S3
ethylene carbonate	4.7	1442	S4
vinylene carbonate	229	2700	this work
4-vinyl ethylene carbonate	4.2	1500	this work
glycerol carbonate	0.01	34.5	S3
methyl phenyl carbonate	14.5	5000	this work
diphenyl carbonate	0.07	121	S5
dibenzyl carbonate	0.004	21	S5
diethenyl carbonate	1516	115690	S3
diallyl carbonate	209	38260	S3
trimethylamine	8500	230000	S6
diethyl sulfide	7781	217515	S7
tetrahydrothiophene	2448	97803	S7

[a] As the reference IL was taken $[C_2mim][NTf_2]$ where reliable data on vapor pressures are available from ref. [S8]: 1.3×10^{-9} at 298 K and 9.3×10^{-5} at 298 K

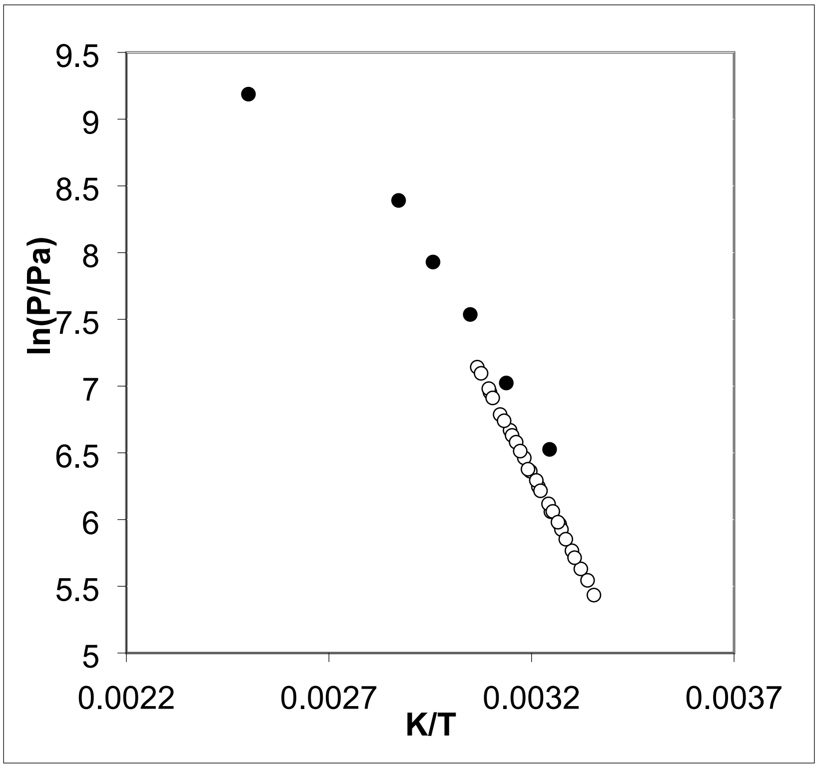

Figure S2. Experimental vapor pressures of the vinylene carbonate:
● - from ref. [S9] and ○ - from this work

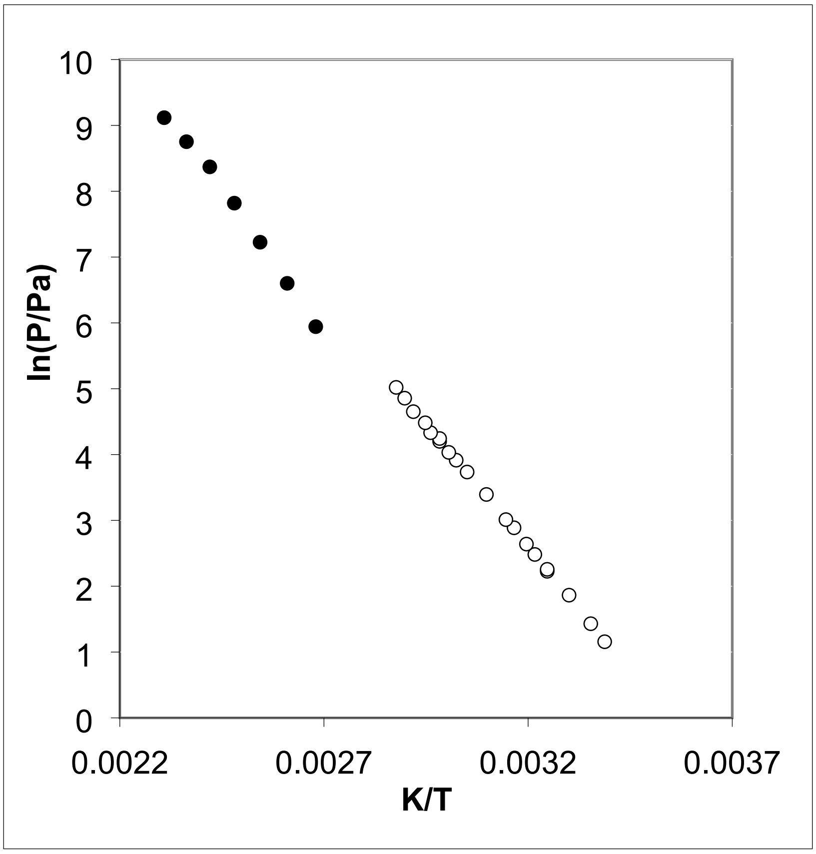

Figure S3. Experimental vapor pressures of the 4-vinyl ethylene carbonate:
● - from ref. [S10] and ○ - from this work

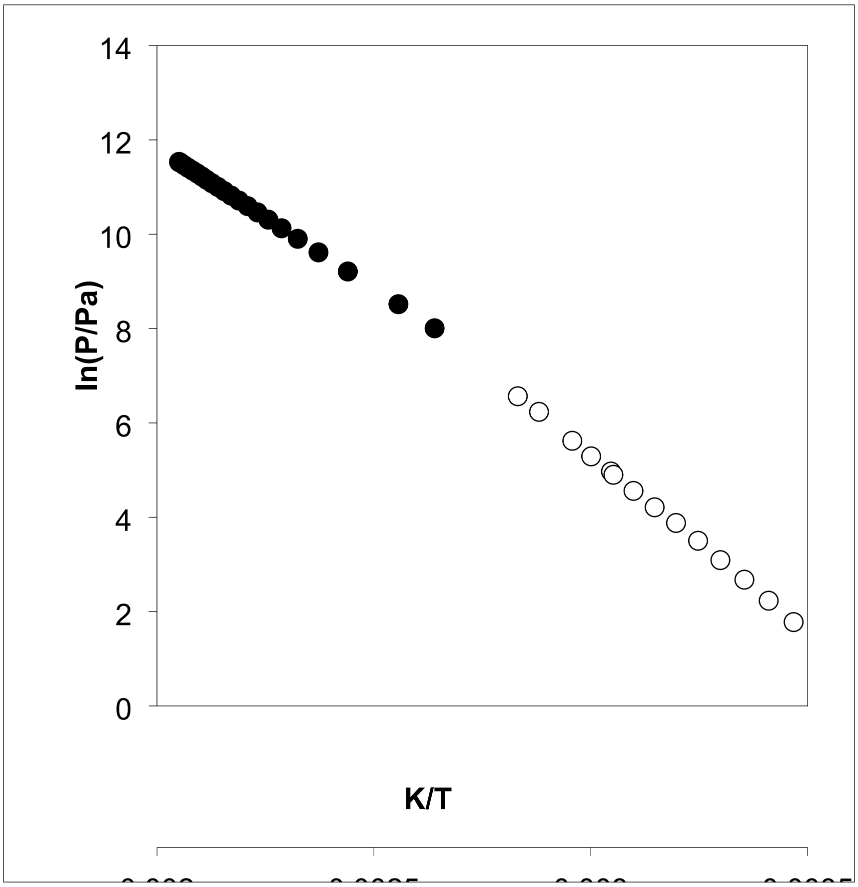

Figure S4. Experimental vapor pressures of the methyl phenyl carbonate:
● - from ref. [S11] and ○ - from this work

General Experimental Procedure for Screening of CBILS® reactions. All chemicals were purchased from commercial sources with a purity >99%wt and used without further purification. Reaction screening and small scale synthesis was performed in 4 mL screw-capped vials equipped with a PTFE stir bar. The vessels were sealed with PTFE seals and PEEK screw caps to resist pressures up to 20 bar. Heating occurred in a massive aluminum block, that was thermostated with an error of ± 1 K on a standard hotplate/stirrer under thermal control using an external contact thermometer.

Model reaction (1-Ethyl-3-methylimidazolium methylcarbonate synthesis): 288 mg (3 mmol, 290 μL) 1-Ethylimidazole (nucleophile) was mixed with 432 mg (4.8 mmol, 404 μL) dimethyl carbonate and 1081 mg (60 %wt, 1369 μL) methanol. The reaction mixture was heated for 3 days at 140°C to yield full conversion of 1-Ethylimidazole to 1-Ethyl-3-methylimidazolium methylcarbonate. Other nucleophiles were accordingly reacted at 80°C to 140°C with 1 to 2 molar equivalent of a carbonic acid dialkyl- or diarylester and 0%wt to 75%wt of an alcohol, which is conjugated to the alkyl- or aryl-group of the carbonic acid ester, to prevent transesterification.

Analysis

Analytical HPLC analysis was performed using a Dionex Ultimate 3000 system that is combined with an Ultimate 3000 RS variable wavelength detector and a Corona Ultra RS charged aerosol detector. Measurements were carried out on a reversed-phase analytical column (SIELC, Primesep 200, 3.2 × 250 mm, particle size 5 μm) using a mobile phase consisting of 60%wt water and 40%wt acetonitrile, under subsequent addition of 0.22%wt trifluoroacetic acid to the eluent mixture. Samples were analyzed applying isocratic elution, a flow rate of 0.5 mL/min and a detection wavelength of 210 nm and/or charged aerosol detection. The formed methylcarbonate, alkyl- or arylcarbonate anion was quantified using standard aqueous acidimetric titration as well.

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