Supporting Information

Hydroxy Acids-Functionalized Ionic Liquids as Efficient Catalysts for Carbonate Synthesis from Carbon Dioxide and Epoxide under Solvent and Cocatalyst-Free Conditions

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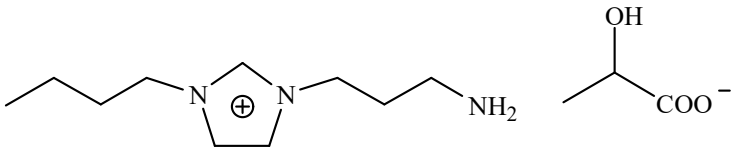
Characteristic data:

Ionic liquid 1:



[APbim][LAc]: ^{1}H NMR (300 MHz, D_2O): δ(ppm) 7.54(2H, d), 4.21(4H, m), 4.10(1H, m), 2.72(2H, t), 2.08(2H, m), 1.84(2H, m), 1.33(5H, m), 0.92(3H, t); ^{13}C NMR (75.5MHz, D_2O): δ(ppm) 182.10, 135.47, 122.75, 122.43, 68.57, 49.62, 46.98, 36.95, 31.37, 29.71, 20.60, 18.97, 13.02. IR(KBr): ν(C=O) 1587.43 cm^{-1}. TOF-MS m/z: $[APbim]^{+}$=182.0, $[LAc]^{-}$=89.0.

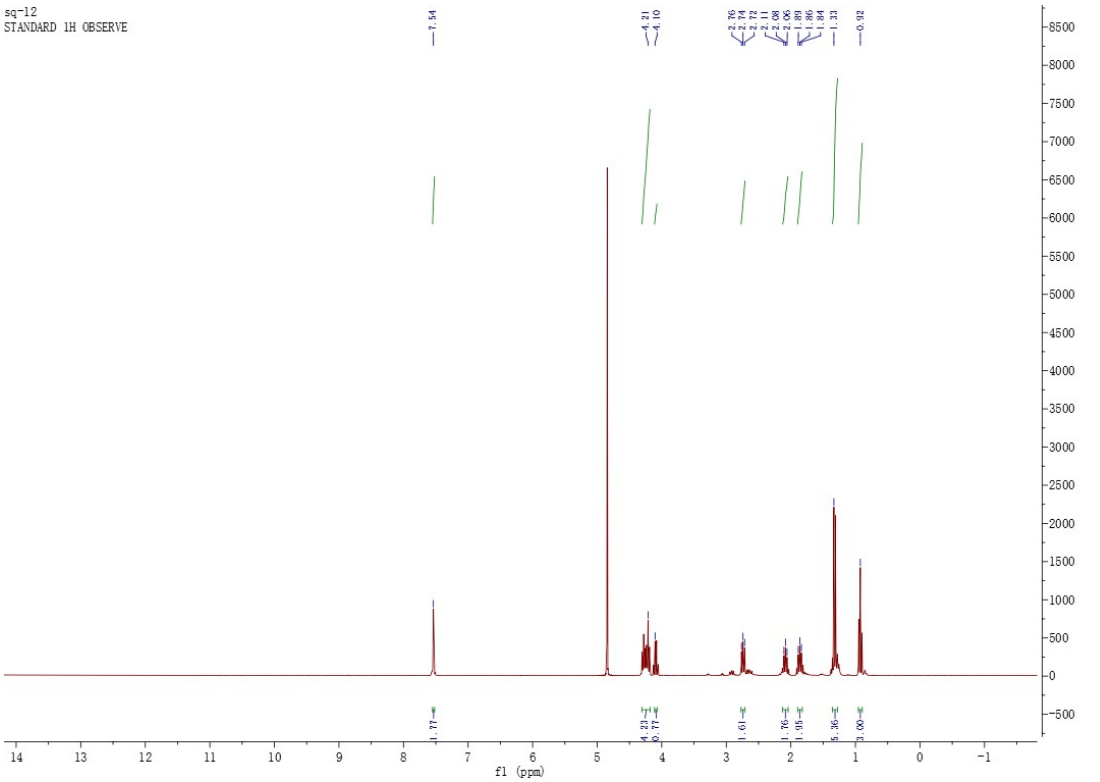


Fig. S1-1 ^{1}H NMR spectrum of [APbim][LAc]

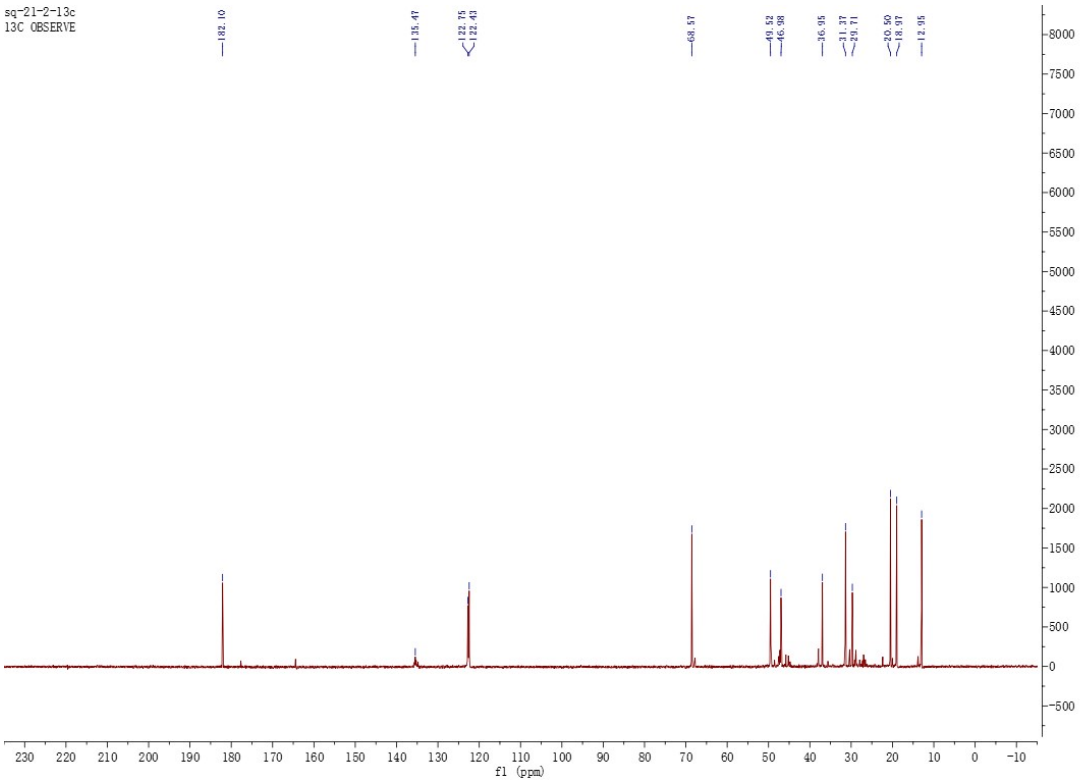


Fig. S1-2 ^{13}C NMR spectrum of [APbim][LAc]

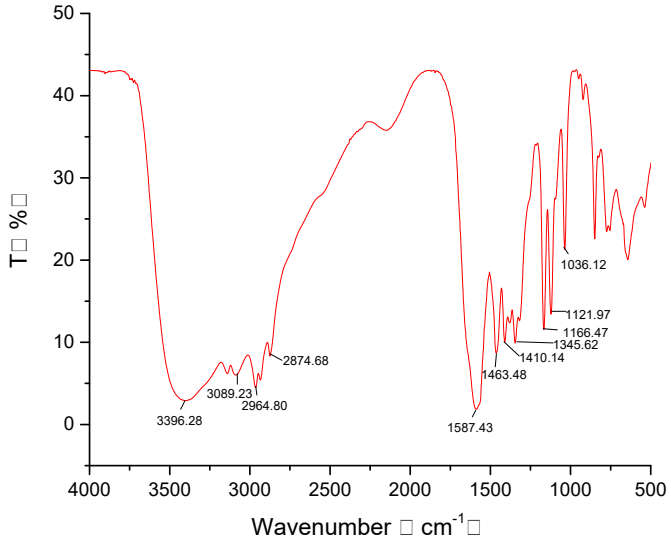


Fig. S1-3 IR spectrum of [APbim][LAc]

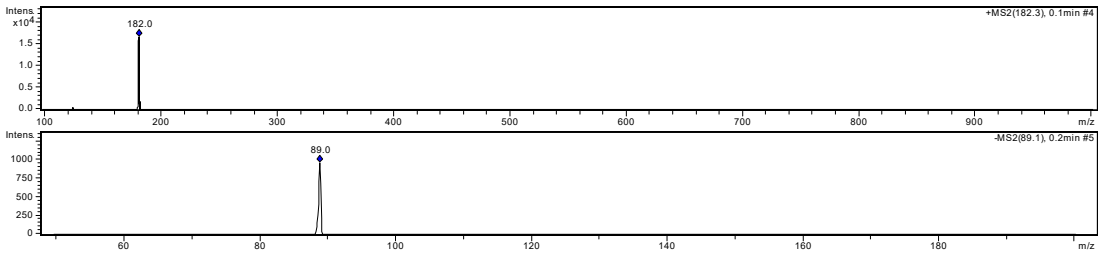


Fig. S1-4 TOF-MS of [APbim][LAc]

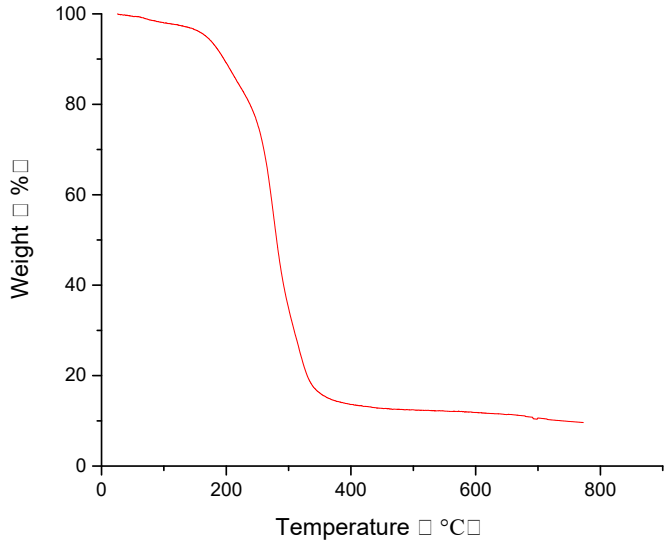
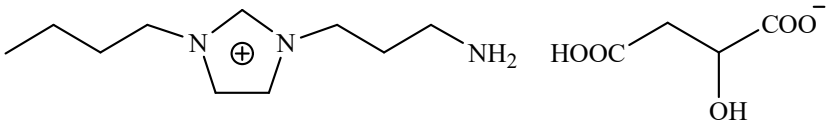


Fig. S1-5 Degradation of [APbim][LAc] measured by temperature-ramped TGA (10 K min^{-1}, 25-800 °C,

N_2 flow).

Ionic liquid 2:



[APbim][MA]: ^{1}H NMR (300 MHz, D_2O): δ(ppm) 7.56(2H, d), 4.29(5H, m), 3.06(2H, t), 2.69(1H, m), 2.29(3H, m), 1.87(2H, m), 1.36(2H, m), 0.94(3H, t); ^{13}C NMR (75.5MHz, D_2O): δ(ppm) 180.93, 179.71, 135.30, 122.82, 122.33, 70.62, 49.66, 46.60, 42.88, 36.60, 31.20, 27.98, 18.92, 12.81. IR(KBr): ν(C=O) 1584.97 cm^{-1}. TOF-MS m/z: $[APbim]^+$=182.0, $[MA]^-$=132.8.

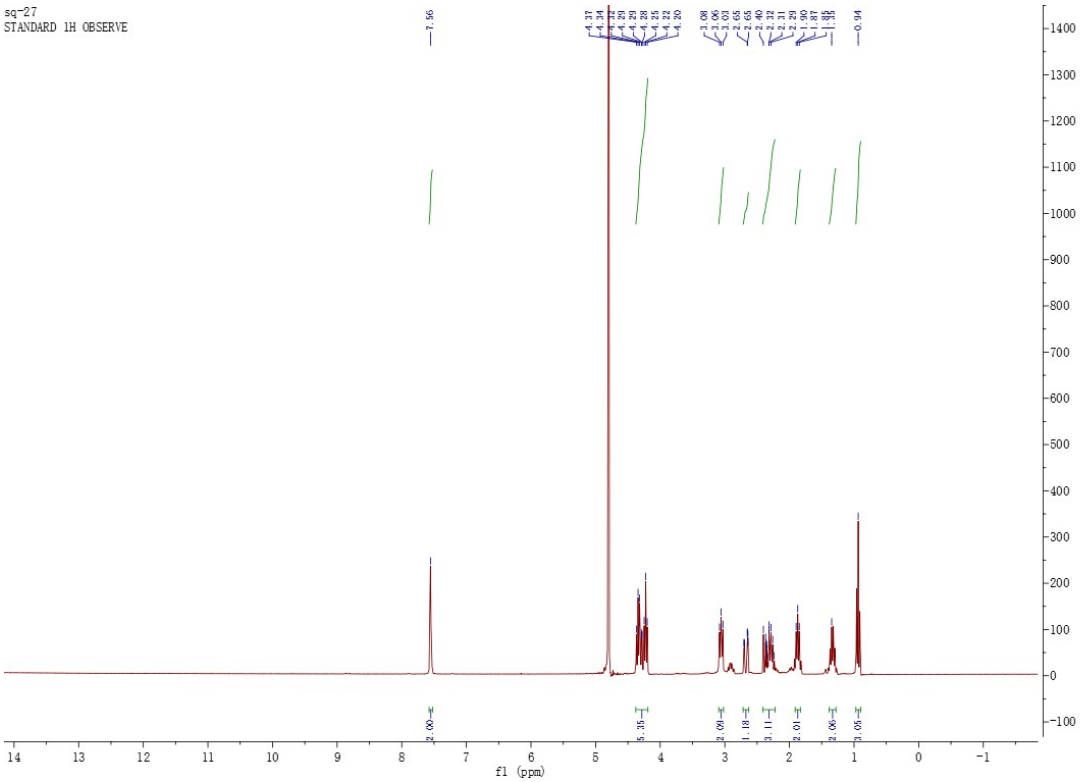


Fig. S2-1 ^{1}H NMR spectrum of [APmim][MA]

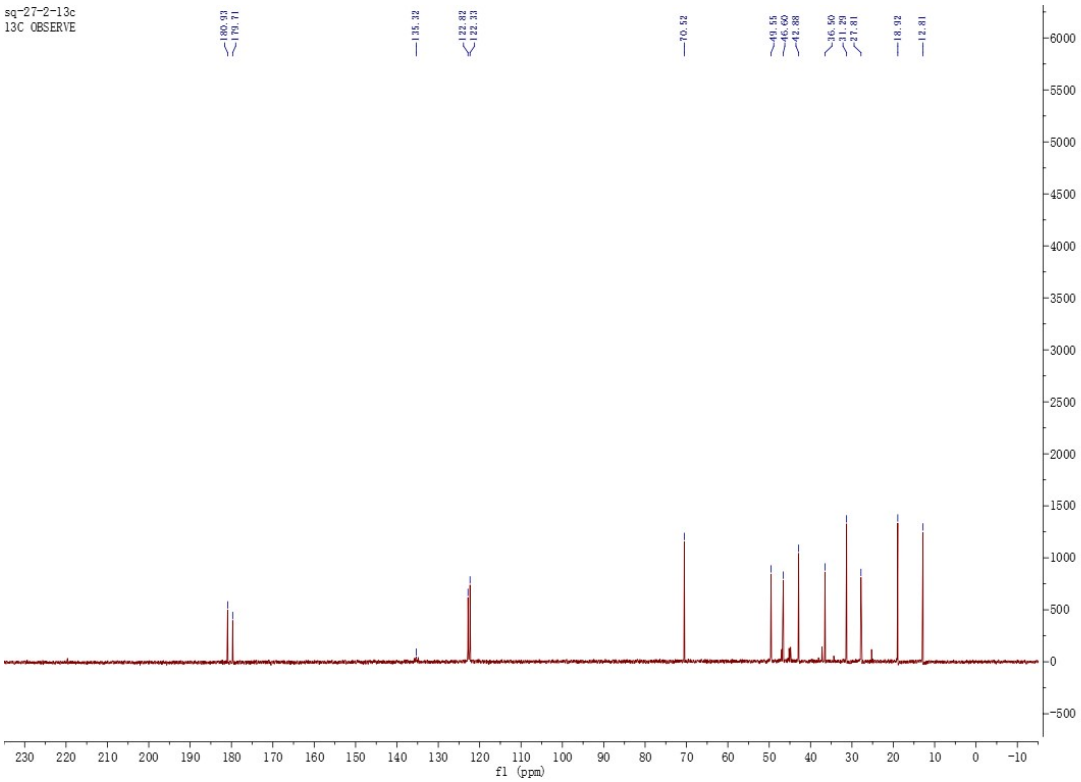


Fig. S2-2 ^{13}C NMR spectrum of [APmim][MA]

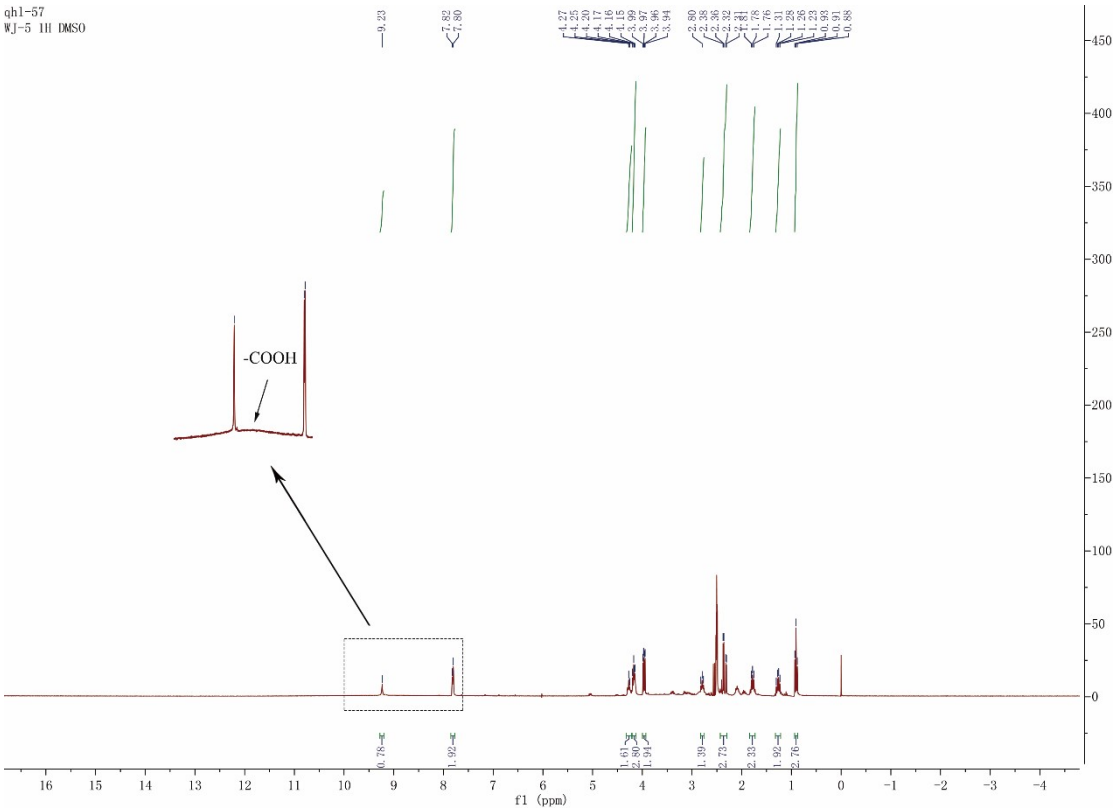


Fig. S2-3 ^{1}H NMR spectrum of [APmim][MA] in DMSO

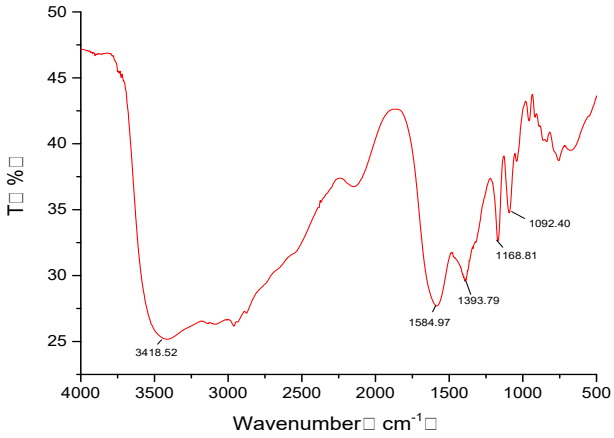


Fig. S2-4 IR spectrum of [APmim][MA]

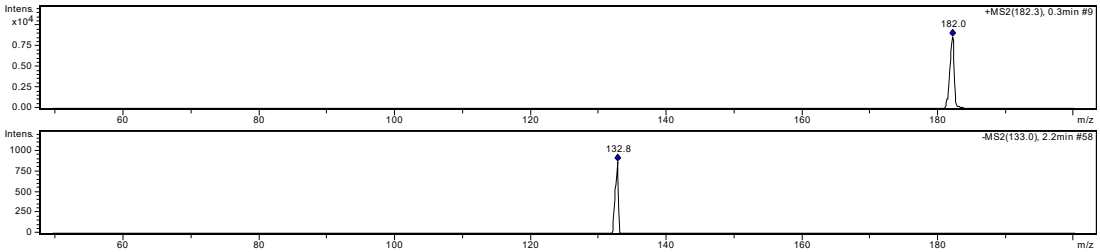
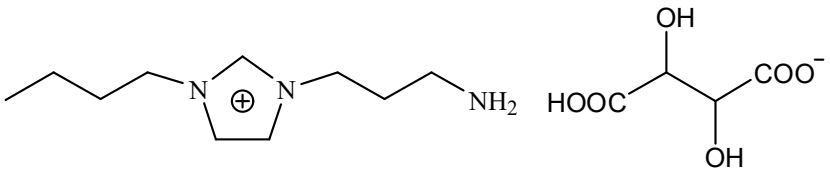


Fig. S2-5 TOF-MS of [APbim][MA]

Ionic liquid 3:



[APbim][Tar]: ^{1}H NMR (300 MHz, D_2O): δ(ppm) 7.54(2H, d), 4.32(4H, m), 4.21(2H, m), 2.98(2H, m), 2.25(2H, m), 1.88(2H, m), 1.32(2H, m), 0.92(3H, t); ^{13}C NMR (75.5MHz, D_2O): δ(ppm) 178.38, 135.54, 122.77, 122.37, 49.51, 42.88, 36.68, 31.30, 28.06, 18.92, 12.81. IR(KBr): ν(C=O) 1602.01 cm^{-1}. TOF-MS m/z: $[APbim]^+$=182.0, $[Tar]^-$=148.7.

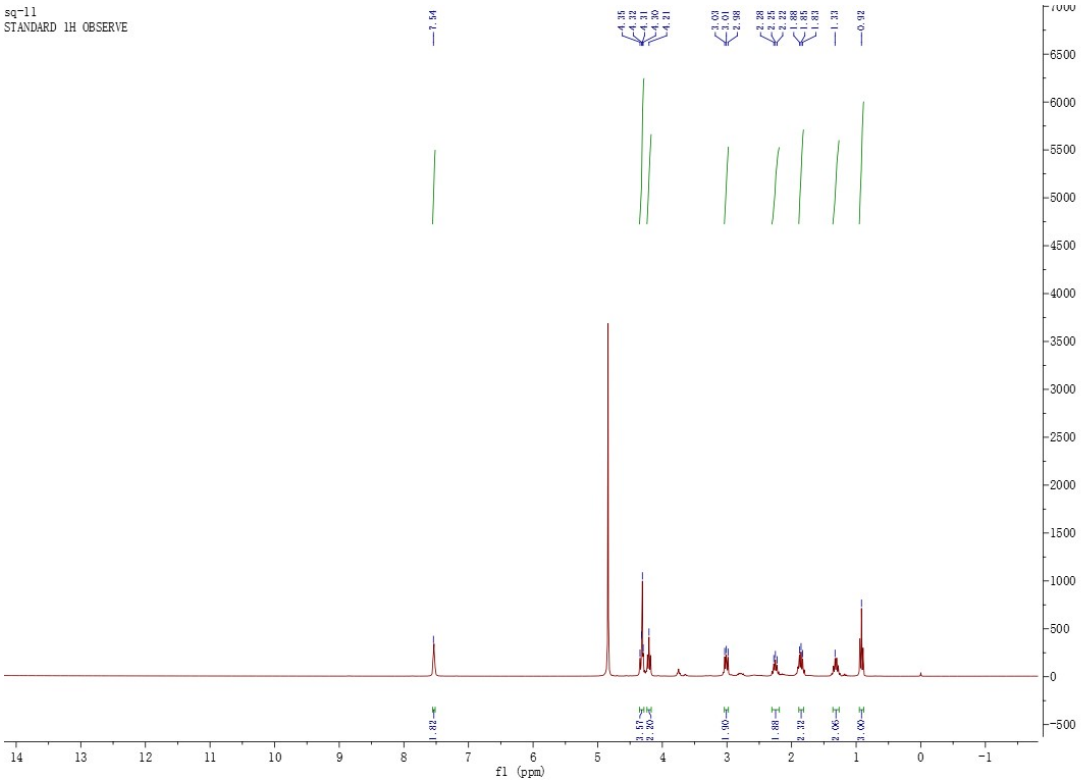


Fig. S3-1 ^{1}H NMR spectrum of [APmim][Tar]

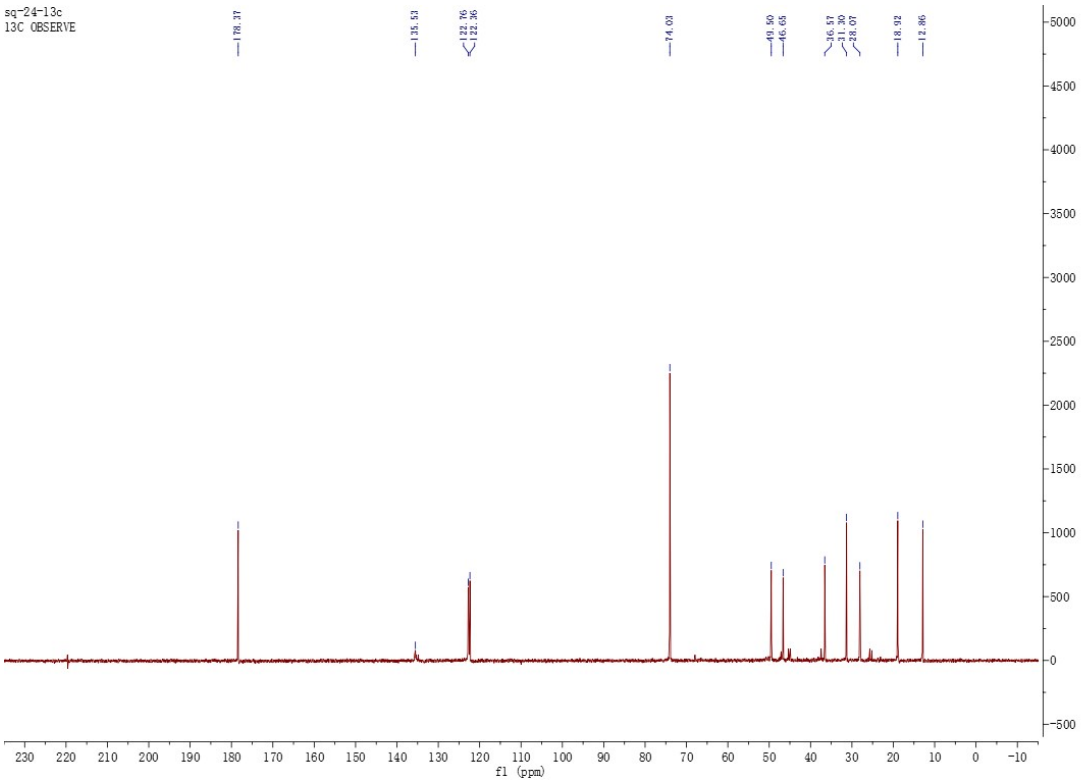


Fig. S3-2 ^{13}C NMR spectrum of [APmim][Tar]

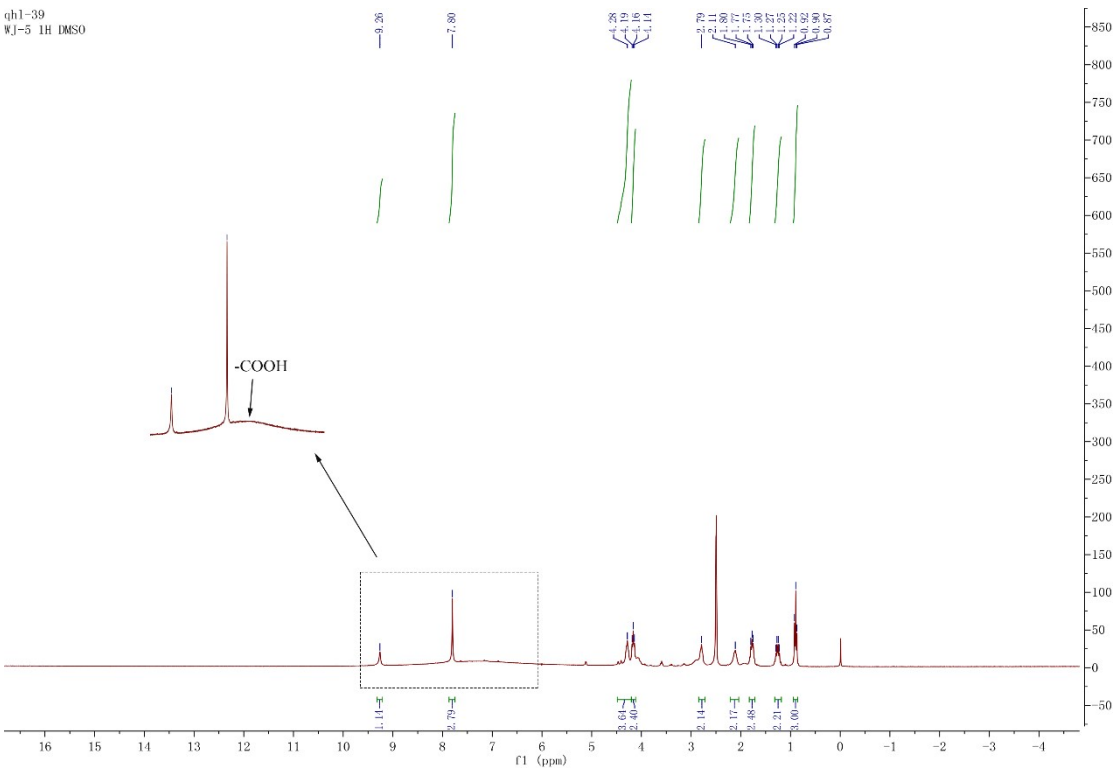


Fig. S3-3 ^{1}H NMR spectrum of [APmim][Tar] in DMSO

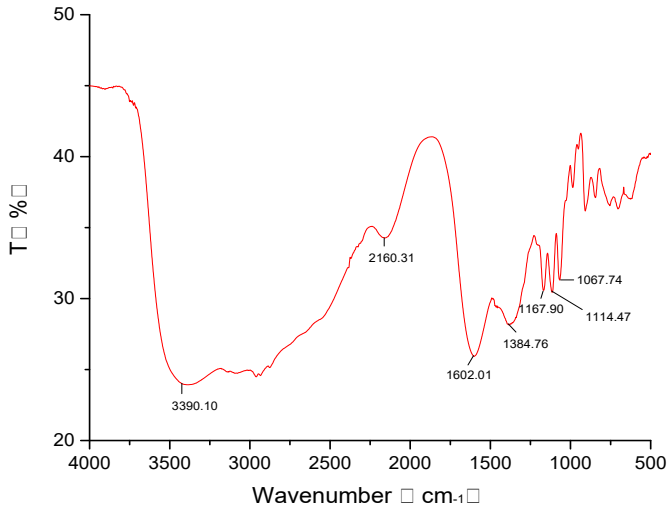


Fig. S3-4 IR spectrum of [APmim][Tar]

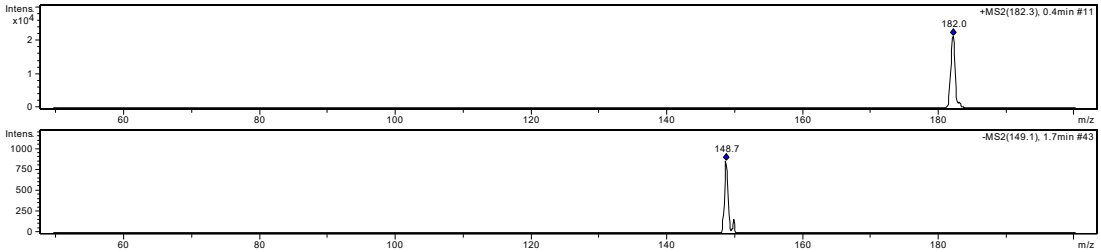
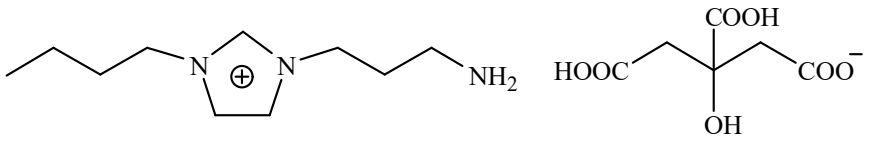


Fig. S3-5 TOF-MS of [APbim][Tar]

Ionic liquid 4:



[APbim][CA]: ^{1}H NMR (300 MHz, D_2O): δ(ppm) 8.91(1H, s), 7.57(2H, d), 4.41(2H, m), 4.22(2H, m), 3.10(2H, m), 2.62(4H, m), 2.33(2H, m), 1.92(2H, m), 0.92(3H, t); ^{13}C NMR (75.5MHz, D_2O): δ(ppm) 181.41, 178.62, 176.68, 135.66, 122.77, 122.32, 76.12, 49.61, 46.62, 45.65, 36.38, 31.27, 27.48, 18.89, 12.81. IR(KBr): ν(C=O) 1601.72 cm^{-1}. TOF-MS m/z: $[APbim]^+$=182.0, $[CA]^-$=190.7.

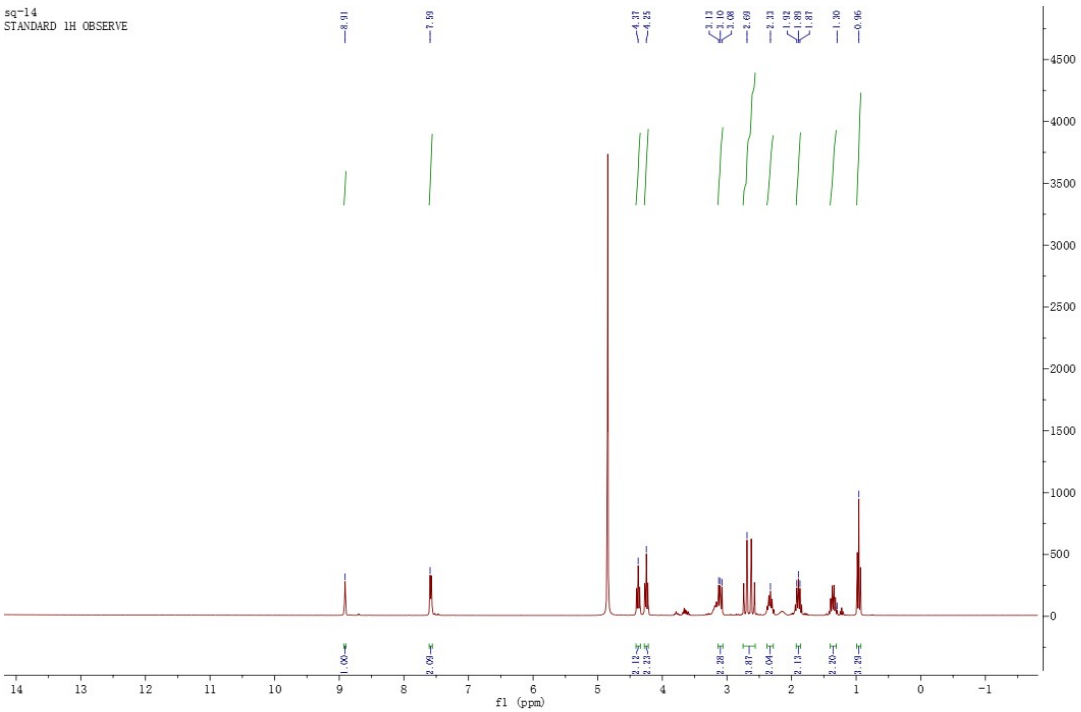


Fig. S4-1^{1}H NMR spectrum of [APmim][CA]

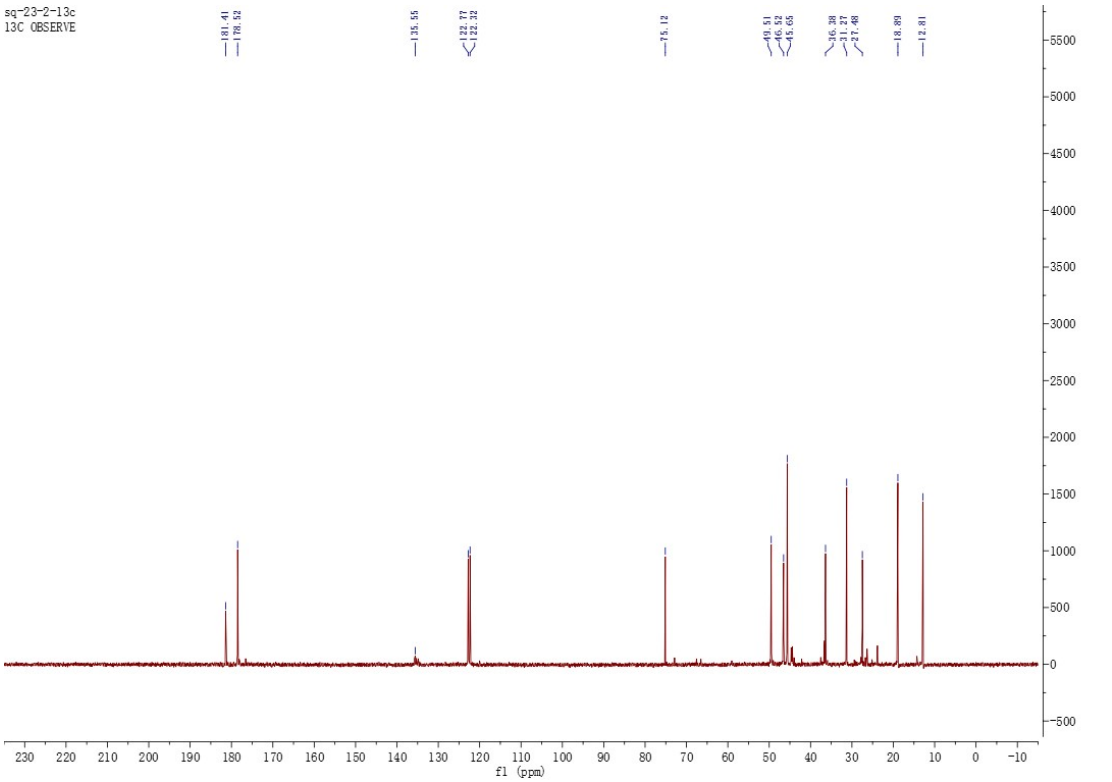


Fig. S4-2 ^{13}C NMR spectrum of [APmim][CA]

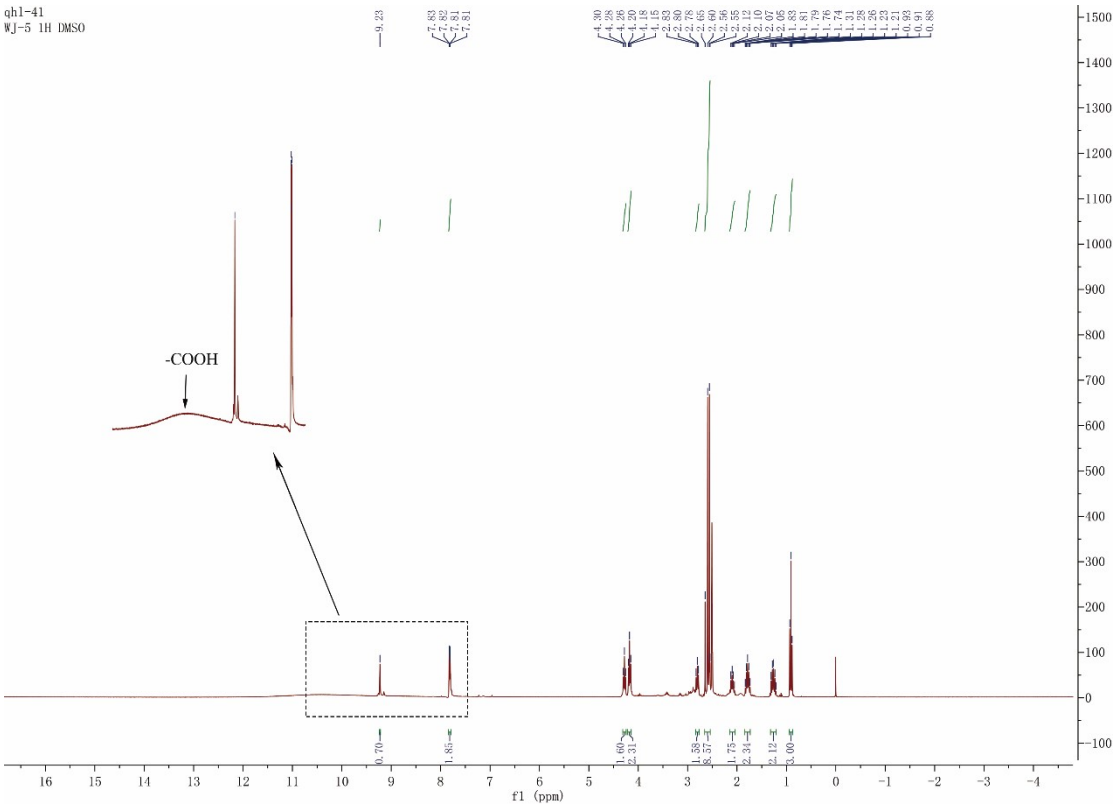


Fig. S4-3 ^{1}H NMR spectrum of [APmim][CA] in DMSO

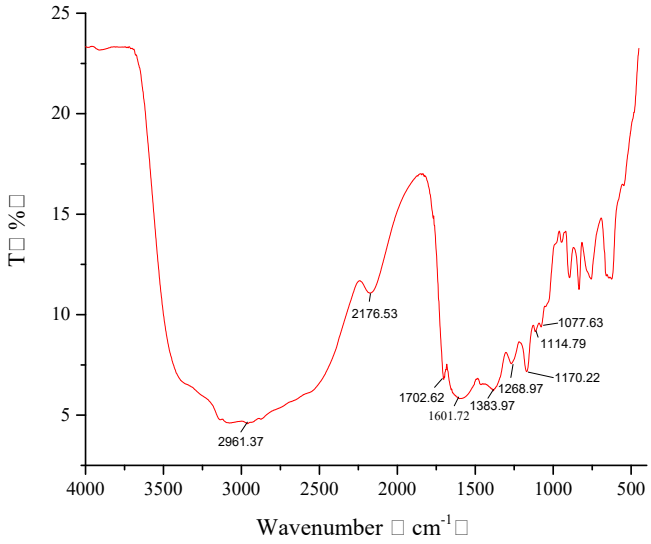


Fig. S4-4 IR spectrum of [APmim][CA]

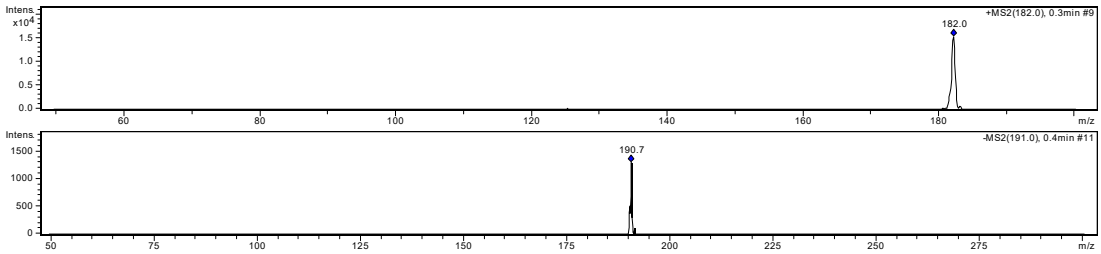
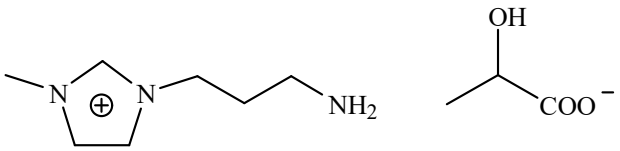


Fig. S4-5 TOF-MS of [APbim][CA]

Ionic liquid 5:



[APmim][LAc]: ^{1}H NMR (300 MHz, D_2O): δ(ppm) 7.49(2H, d), 4.27(2H, m), 4.21(1H, m), 3.88(3H, m), 3.04(1H, m), 2.84(1H, m), 2.15(2H, m), 1.31(3H, t); ^{13}C NMR (75.5MHz, D_2O): δ(ppm) 182.16, 136.19, 123.84, 122.24, 68.66, 46.97, 37.86, 36.98, 30.11, 20.42. IR(KBr): ν(C=O) 1601.43 cm^{-1}. TOF-MS m/z: $[APmim]^+$=132.8, $[LAc]^-$=89.0.

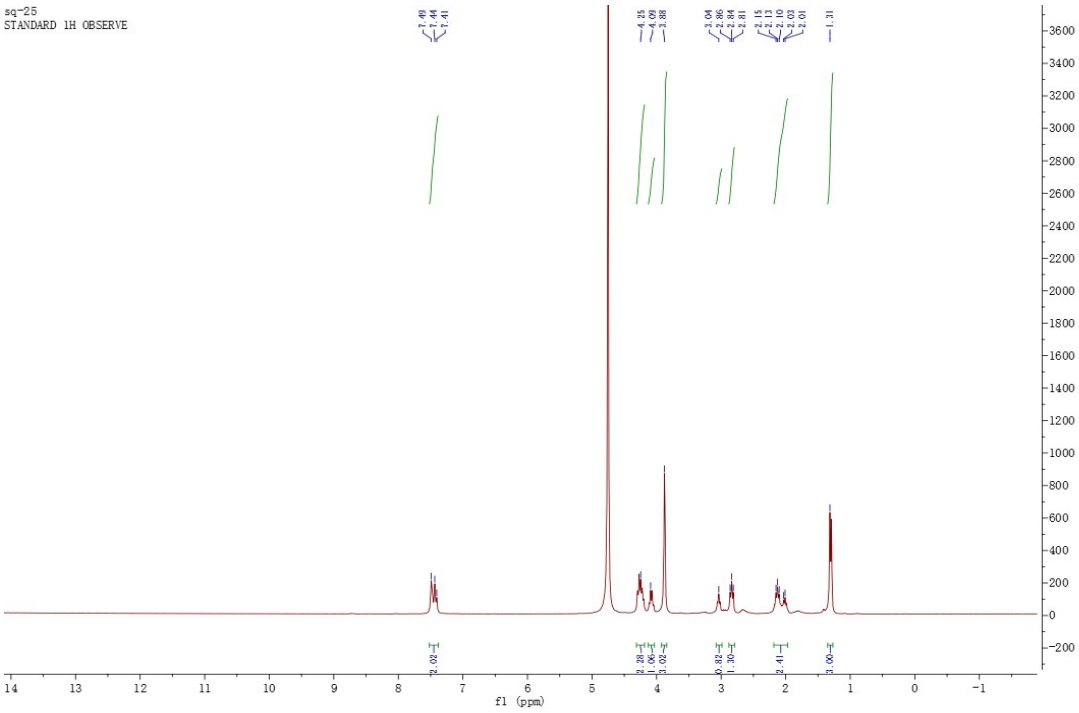


Fig. S5-1 ^{1}H NMR spectrum of [APmim][LAc]

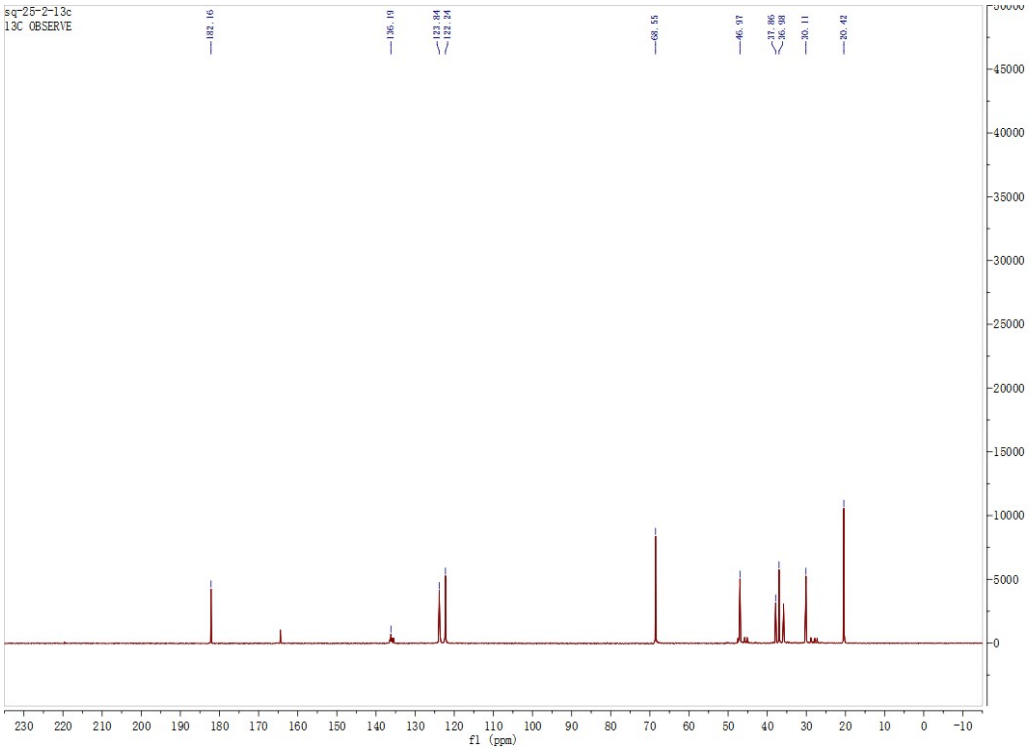


Fig. S5-2 ^{13}C NMR spectrum of [APmim][LAc]

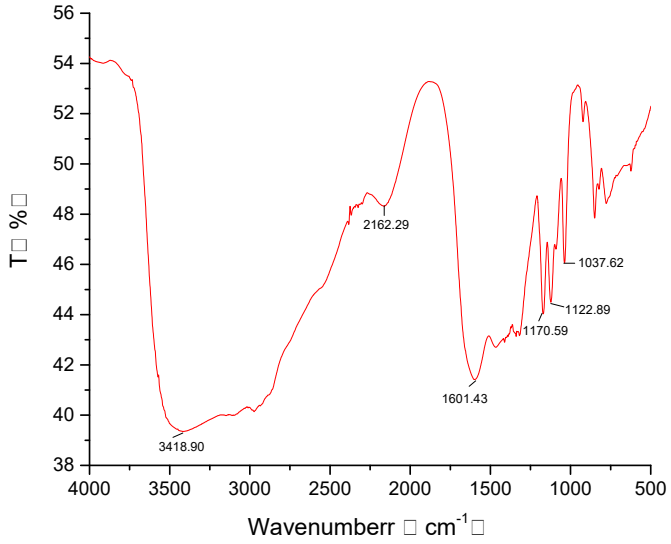


Fig. S5-3 IR spectrum of [APmim][LAc]

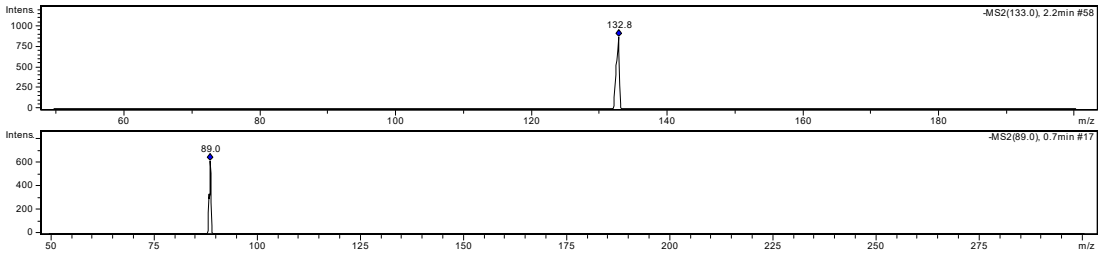
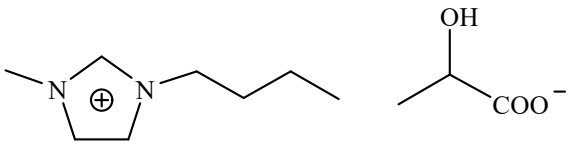


Fig. S5-4 TOF-MS of [APmim][LAc]

Ionic liquid 6:



[Bmim][LAc]: ^{1}H NMR (300 MHz, D_2O): δ(ppm) 7.48(1H, d), 7.44(1H, d), 4.21(2H, t), 4.13(1H, t), 3.90(3H, s), 1.86(2H, m), 1.36(5H, m), 0.94(3H, t); ^{13}C NMR (75.5MHz, D_2O): δ(ppm) 181.90, 136.03, 123.69, 122.39, 68.60, 49.39, 37.86, 35.84, 30.11, 20.60, 18.96. IR(KBr): ν(C=O) 1593.68 cm^{-1}. TOF-MS m/z: $[Bmim]^+$=139.1, $[LAc]^-$=89.0.

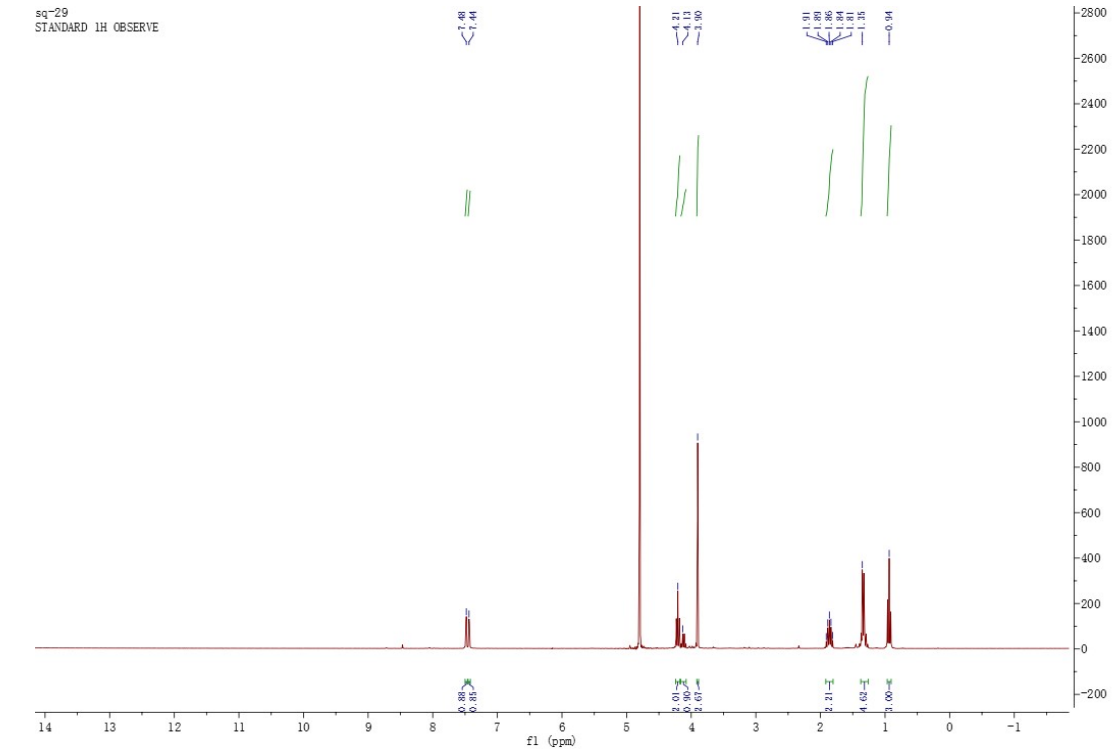


Fig. S6-1 ^{1}H NMR spectrum of [Bmim][LAc]

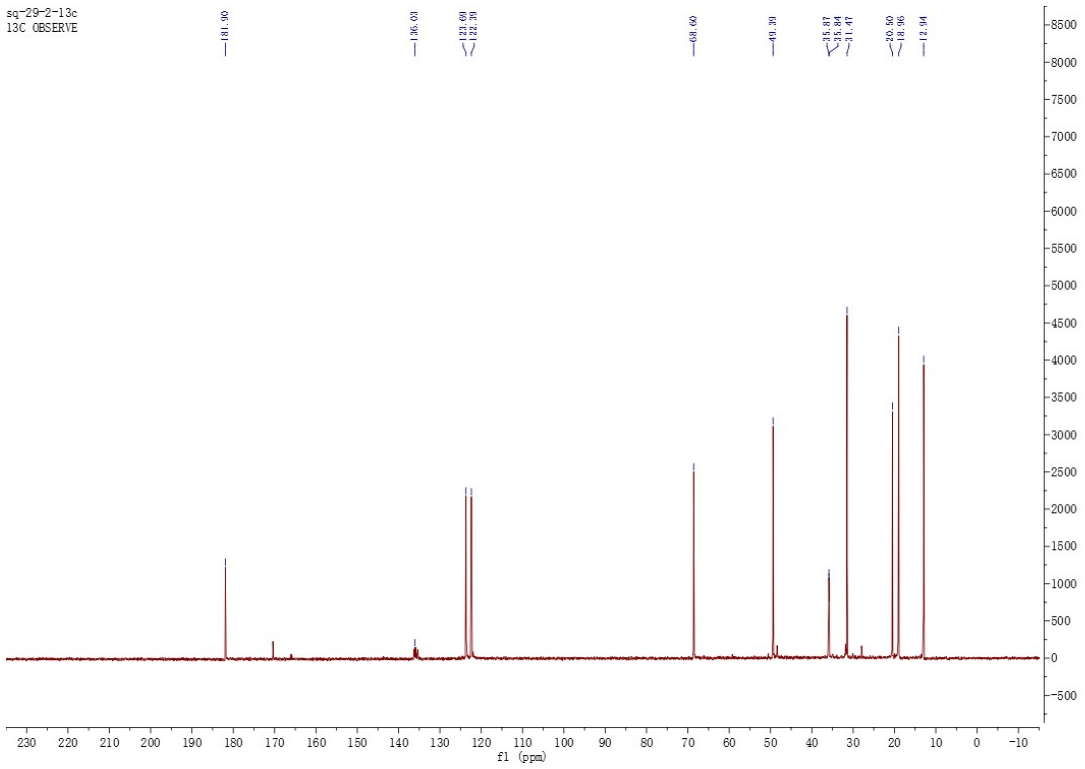


Fig. S6-2 ^{13}C NMR spectrum of [Bmim][LAc]

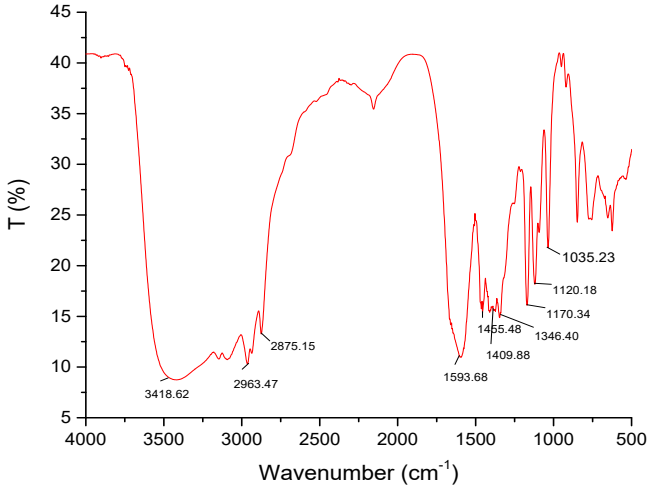


Fig. S6-3 IR spectrum of [Bmim][LAc]

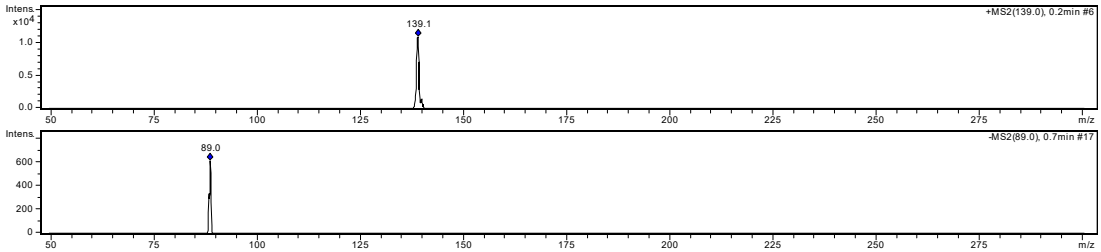


Fig. S6-4 TOF-MS of [Bmim][LAc]

[APbim][LAc]: ^{1}H NMR (300 MHz, DMSO) δ 9.37 (s, 1H), 7.82 (s, 2H), 4.96 (s, 3H), 4.30 (t, 2H), 4.17 (t, 2H), 3.65 (m, 1H), 2.72 (t, 2H), 2.10 (m, 2H), 1.82 (m, 2H), 1.25 (m, 2H), 1.12 (d, 3H), 0.90 (t, 3H).

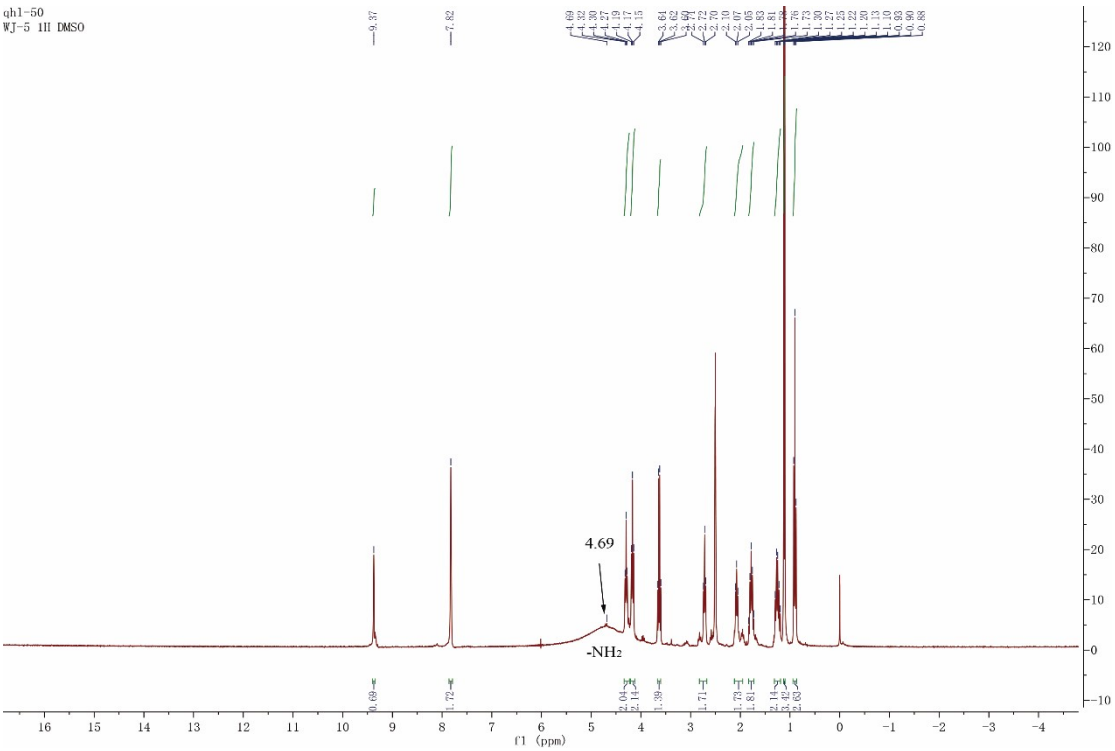


Fig. S7-1 ^{1}H NMR spectrum of [APbim][LAc] in DMSO

[APbim][LAc]: ^{1}H NMR (300 MHz, DMSO) δ 9.43 (s, 1H), 7.83 (m, 2H), 4.69 (s, 3H), 4.31 (t, 2H), 4.17 (t, 2H), 3.65 (d, J = 6.8 Hz, 1H), 2.72 (t, 2H), 2.09 (t, 2H), 1.79 (m, 2H), 1.26 (m, 2H), 1.12 (d, 3H), 0.90 (t, 3H). epichlorohydrin: 3.90 (m, 1H),3.54 (m, 1H), 3.24 (m, 1H), 2.85 (m, 1H), 2.78 (m, 1H).

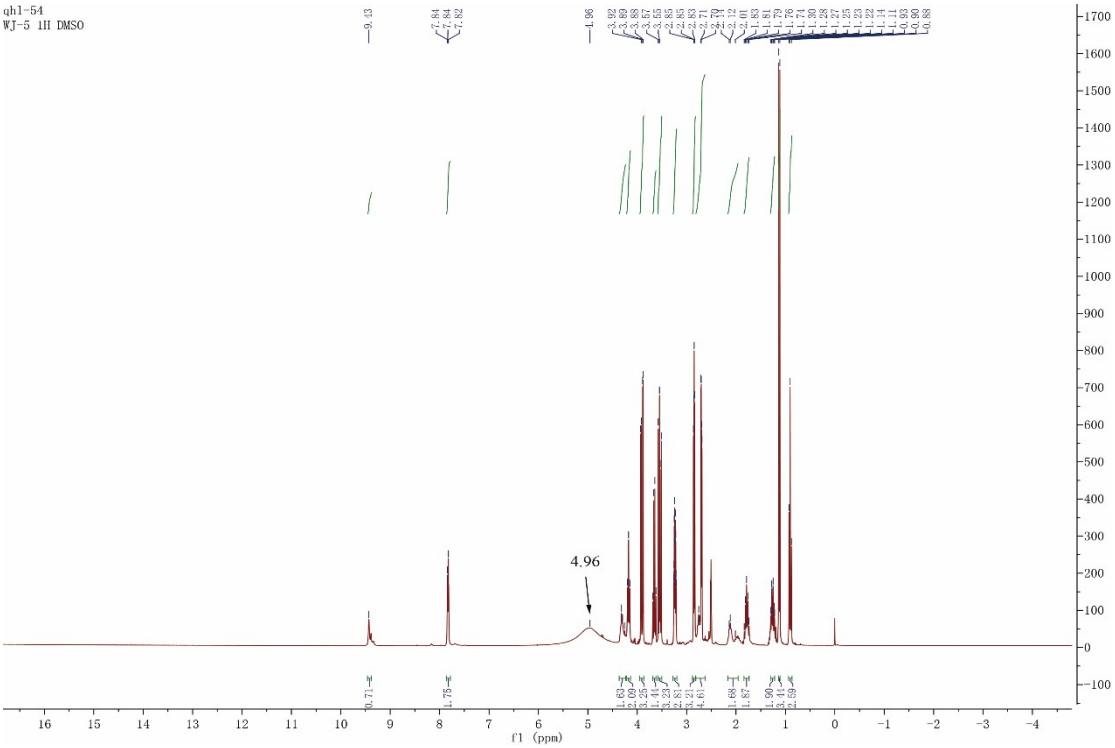


Fig. S7-2 ^{1}H-NMR spectrum for [APbim][LAc] + epichlorohydrin + CO_2 at 30 ℃ and t = 0.5 h in DMSO

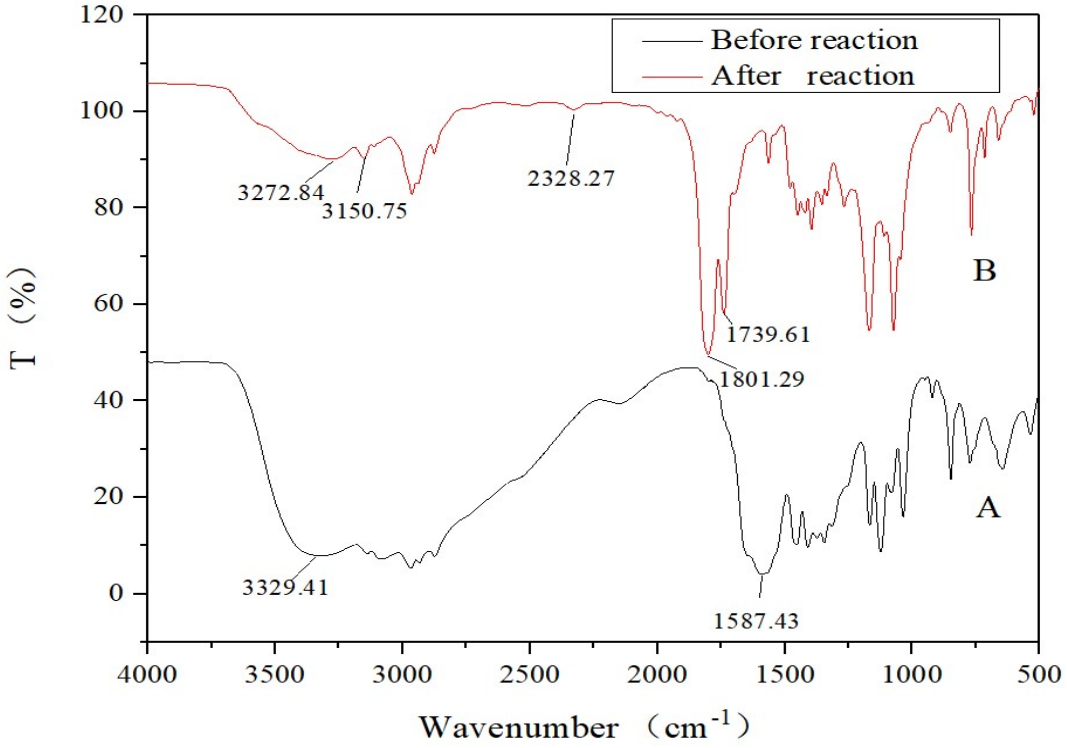
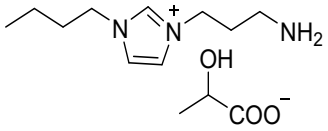
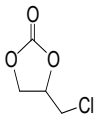
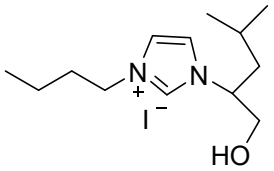
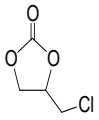
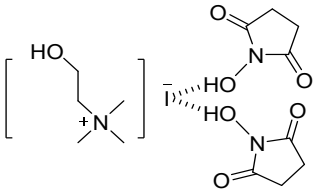
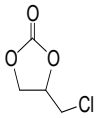
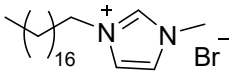
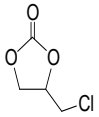
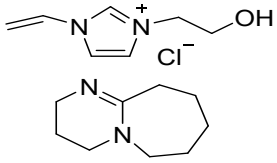
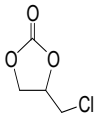
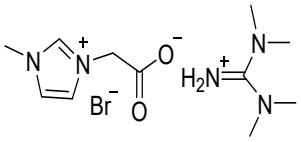
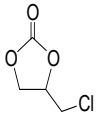
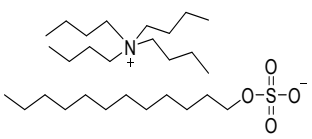
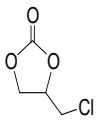
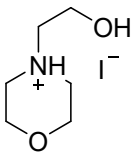
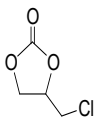
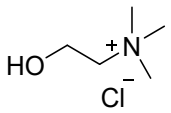
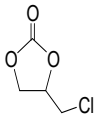
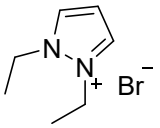
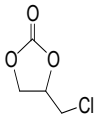
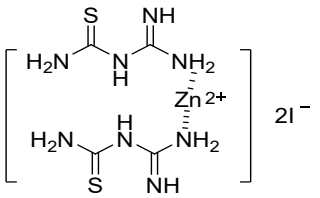
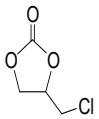
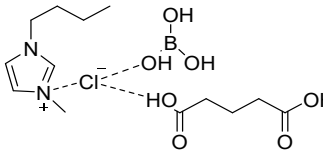
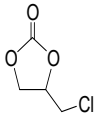
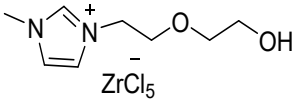
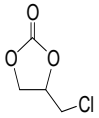
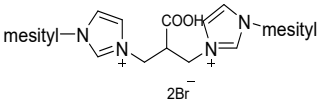
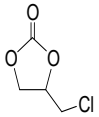


Fig. S8 FT-IR spectra of catalyst: A: Before reaction, B: After reaction.

Table S1 Summary of data for cycloaddition reactions between CO_2 and the epoxides.

Reference	Catalyst	Co-Catalyst	Epoxide	Reaction conditions	Yield (%)
Our work				Epichlorohydrin (0.06383 mol), IL (0.5 mol%), CO_2 0.5 MPa, 80 ℃, 12 h	97
Denizaltı S1				Epichlorohydrin (0.01 mol), IL (2.0 mol%), CO_2 0.5 MPa, 60 ℃, 8 h	>99
Liu et al. S2				Epichlorohydrin (0.015 mol), IL (6.0 mol%), CO_2 1.0 MPa, 30 °C, 10 h	99
Byun et al. S3				Epichlorohydrin (0.01 mol), IL (1.0 mol%), CO_2 0.1 MPa, 90 ℃, 24 h	99
Mujmule et al. S4				Epichlorohydrin (0.3443 mol), [EvimOH][Cl]/DBU 1.66:1.9 mol % (1:1), CO_2 2 MPa, 120 ℃, 1 h	99
Hu et al. S5				Epichlorohydrin (0.002 mol), IL (0.05 mol%), CO_2 0.1 MPa, 30 ℃, 20 h	99
Vieira et al. S6		$ZnBr_2$		Epichlorohydrin (0.1 mol), IL (0.1 mol%), $ZnBr_2$ (0.015 mol%), CO_2 3 MPa, 120 ℃, 2 h	92
Li et al. S7				Epichlorohydrin (0.01 mol), IL (10 mol%), CO_2 0.1 MPa, 60 ℃, 24 h	78

Vagnoni et al. S8		Malic Acid		Epichlorohydrin (0.0013 mol), IL (5 mol%), CO_2 0.4 MPa, 80 °C, 7 h	80
Ma et al. S9		KBr and alkaline		Epichlorohydrin (0.1 mol), IL (1.0 mol%), CO_2 2.0 MPa, 130 °C, 4 h	86
Yang et al. S10				Epichlorohydrin (34.5 mol), IL (0.018 mol%), CO_2 1.0 MPa, 110 °C, 4 h	96
				Epichlorohydrin (34.5 mol), IL (0.018 mol%), CO_2 1.0 MPa, 90 °C, 6 h	94
Wang et al. S11				Epichlorohydrin (0.0286 mol), IL (0.2 mol%), CO_2 0.8 MPa, 70 °C, 7 h	99
Hu et al. S12				Epichlorohydrin (0.01 mol), IL (0.2 mol%), CO_2 1 MPa, 120 °C, 3 h	97
Li et al. S13				Epichlorohydrin (0.01 mol), IL (5 mol%), CO_2 0.4 MPa, 70 °C, 16 h	99

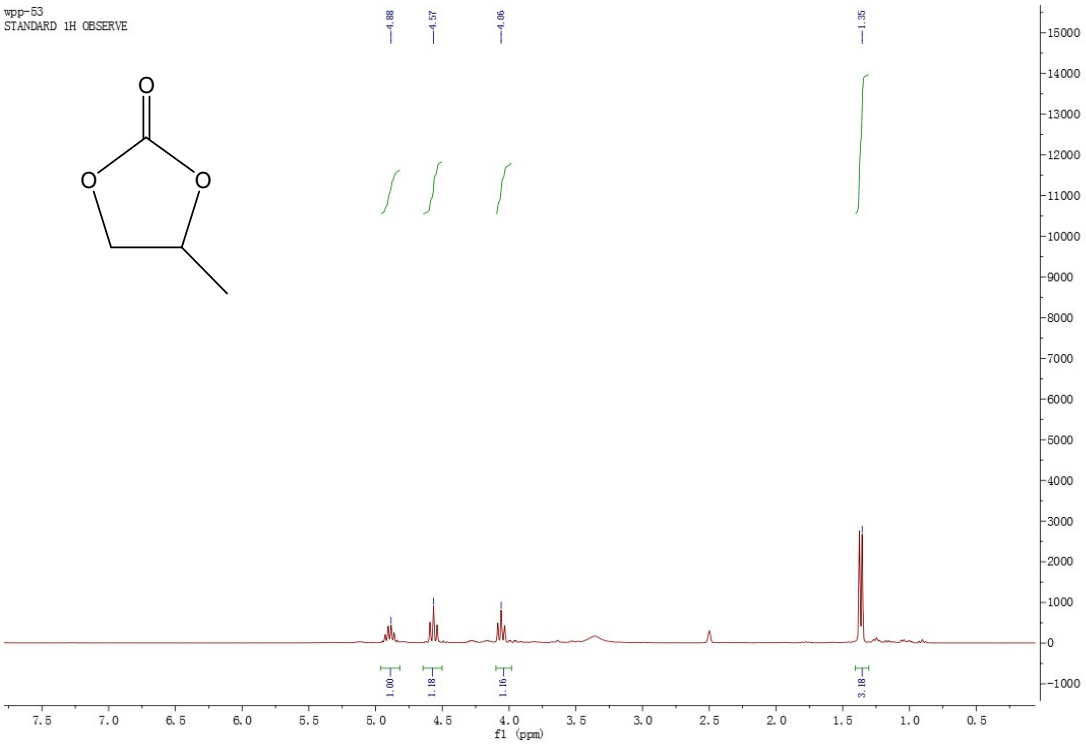


Fig. S9 ^{1}H NMR spectrum of 4-methyl-1,3-dioxolan-2-one

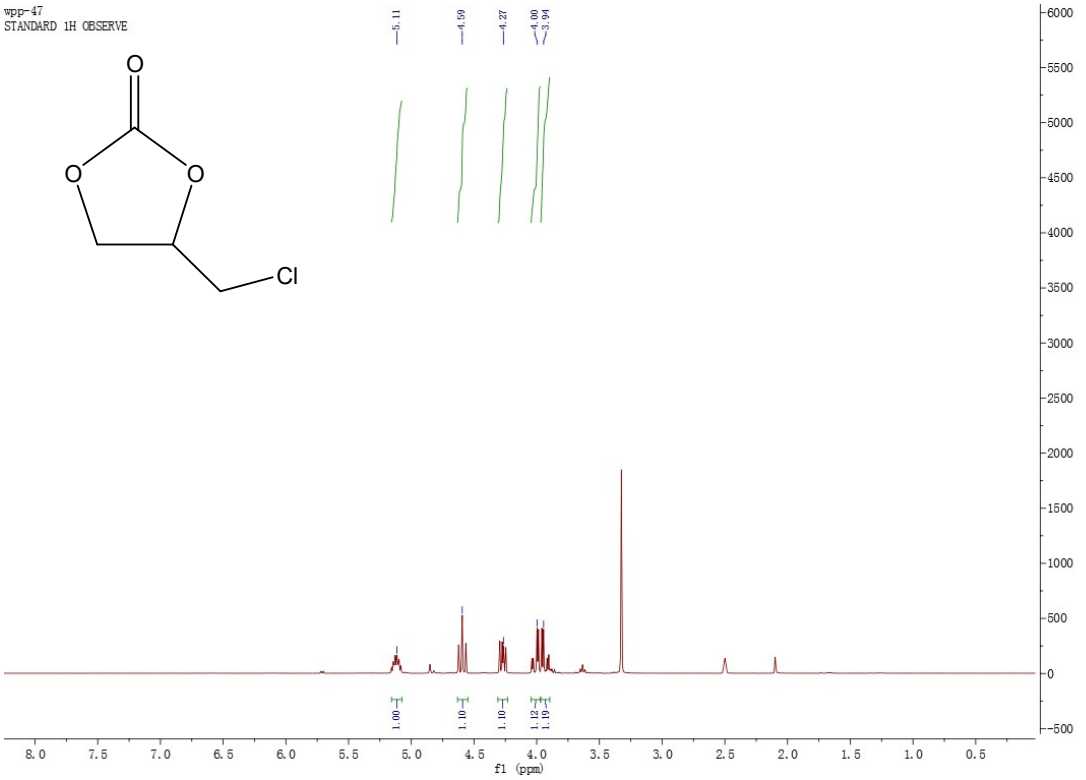


Fig. S10 ^{1}H NMR spectrum of 4-(chloromethyl)-1,3-dioxolan-2-one

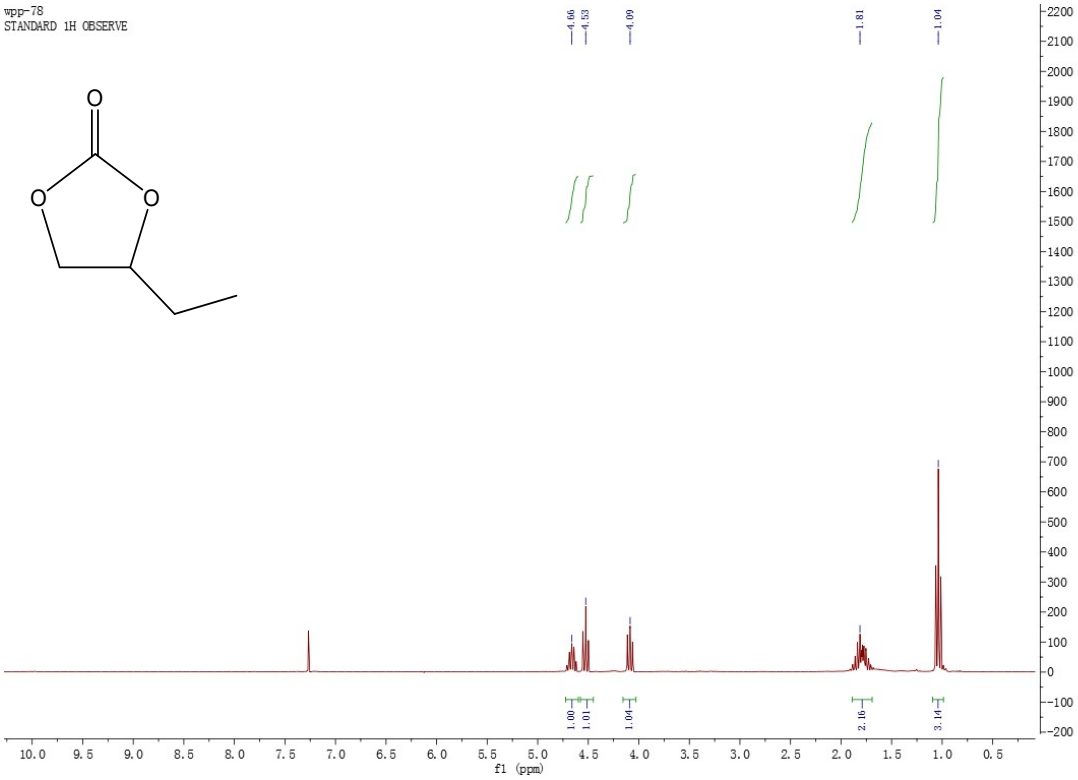


Fig. S11 [1]H NMR spectrum of 4-ethyl-1,3-dioxolan-2-one

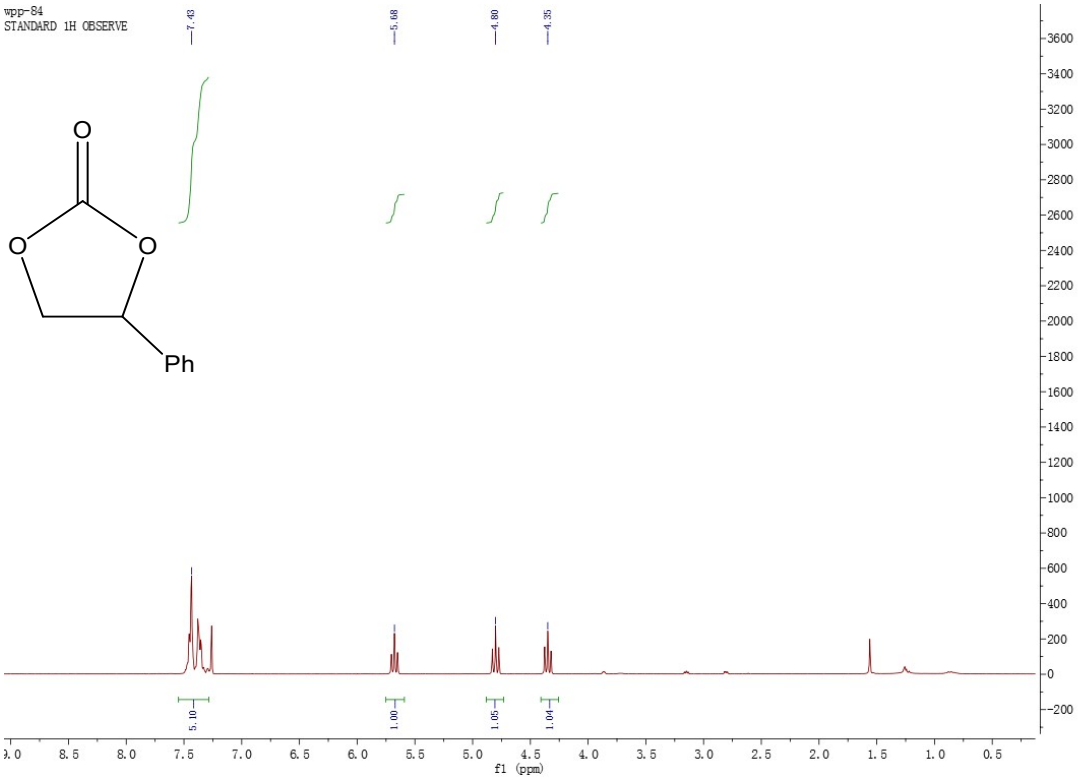


Fig. S12 [1]H NMR spectrum of 4-phenyl-1,3-dioxolan-2-one

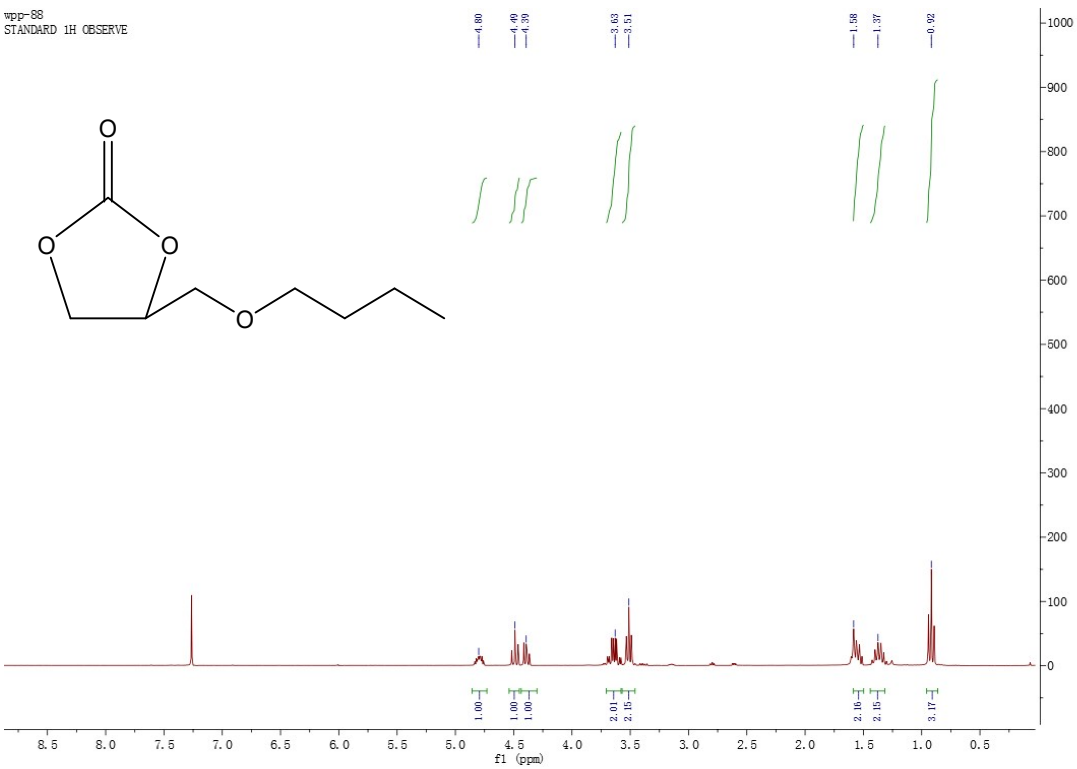


Fig. S13 [1]H NMR spectrum of 4-butoxymethyl-1,3-dioxolan-2-one

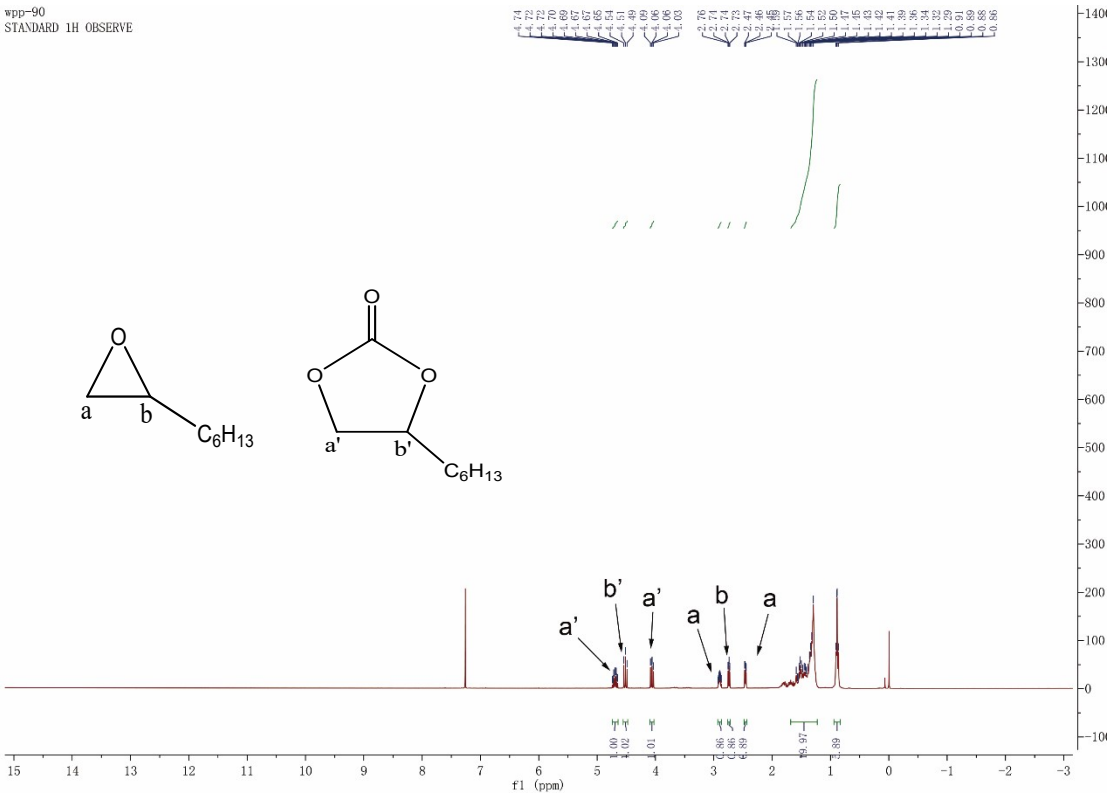


Fig. S14 [1]H NMR spectrum of 4-Hexyl-1,3-dioxolan-2-one

Table S2 Kinetic Equations and Kinetic Parameters at Different Temperature

T/(℃)	Kinetic equation	R’	*k*(min-1)	1/T(k-1)	In *k*
70	y=0.0017x-0.0224	0.9996	0.0017	0.00291	-6.3538
75	y=0.0024x-0.0405	0.9975	0.0024	0.00287	-5.9994
80	y=0.0033x-0.0481	0.9983	0.0033	0.00283	-5.7138
85	y=0.0046x-0.0579	0.9934	0.0046	0.00279	-5.3751

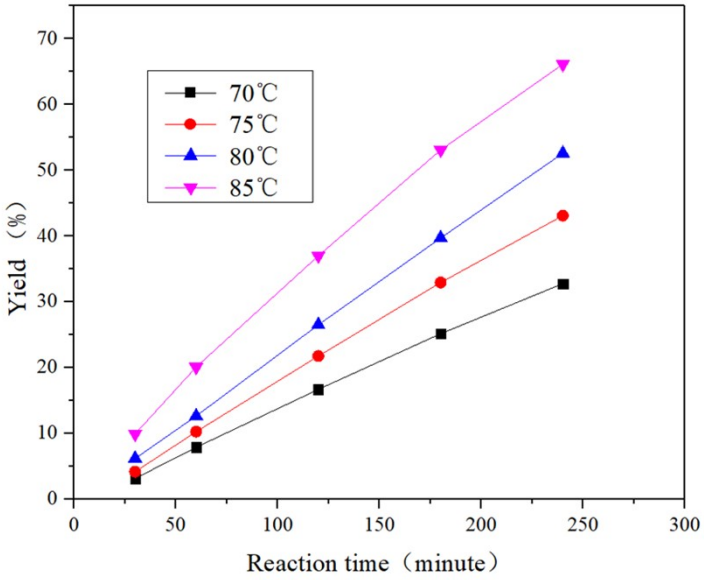


Fig. S15 The chloropropene carbonate yield-time profile at different temperatures catalyzed by IL **1** as catalyst. Reaction conditions: n[epichlorohydrin] = 0.06383 mol, CO_2 0.5 MPa, IL **1** 0.5 mol%.

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