Electronic Supplementary Information For:

Metal-free imidazolium hydrogen carbonate ionic liquids as bifunctional catalyst for the one-pot synthesis of cyclic carbonates from olefins and CO2

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1. Experimental method

1.1 Materials and characterization methods

Analytical-grade 1-ethyl-3-methylimidazolium bromide ($[C_1C_2Im][Br]$), 1-buty-3-methylimidazolium bromide ($[C_1C_4Im][Br]$), and 1-hexyl-3-methylimidazolium bromide ($[C_1C_6Im][Br]$) were purchased from Shanghai Adamas-beta company. 1-methylimidazole, 1-bromododecane, potassium bicarbonate, 1,3-bis(2,4,6-trimethylpheny)imidazolinium chloride, olefins, epoxides, and TBHP were purchased from Aladdin Reagent Corporation. CO_2 (99.99%) and commercially available reagents were used without further purification. The NMR spectra were recorded by using Bruker AC-400 MHz spectrometers. The reaction solution was analyzed by using a GC2014C gas chromatograph fitted with a RTX-5 column (30 m×0.32 mm×0.25 μm) and a flame ionization detector (FID). The structures of the product and byproducts were further identified by using GC-MS (type: GC-TOF).

1.2 Synthesis of $[C_1C_{12}Im][Br]$

A 50 mL 3-necked round-bottom glass flask was charged with a mixture of 1-methylimidazole (50mmol), 1-bromododecane (50mmol), and CH_3OH (15mL). The mixture was stirred for 24 h at 80℃. After the reaction was completed, the CH_3OH was evaporated under vacuum. The final mixture was washed by hexane (3×10mL) to remove the residual substrate. Then, the product was dried at 70 ℃ under vacuum for 12 h.

1.3 Synthesis of $[C_nC_mIm][HCO_3]$ and SMes-CO_2

Imidazolium hydrogen carbonate ILs ($[C_nC_mIm][HCO_3]$) were synthesized according to

our previous work[1]. Briefly, an 50mL round bottom flask was charged with imidazolium bromide salt (0.1mol), $KHCO_3$ (0.11mol) and methanol (25mL). The mixture was stirred at room temperature for 36h. After the reaction was completed, the mixture was filtered and the filtrate was evaporated to remove methanol and dried under high vacuum. $[C_nC_mIm][HCO_3]$ was obtained as colorless or slight yellow oil.

Carbene-CO_2 adduct SMes-CO_2 were prepared according to the methods reported in the literature [2,3]. Briefly, an 50mL schlenk flask was charged with 1,3-bis(2,4,6-trimethylphenyl)imidazolinium chloride (3 mmol) and potassium bis(trimethylsilyl)amide (3.1 mmol). The reactor was purged by vaccum/dry nitrogen cycles for three times. Then, dry THF (20mL) was added and the mixture was stirred at -30℃ for 2 hours. It was then allowed to stand for 2 hours. After that, dry CO_2 was bubbled into the obtained solution. After 4 hours, the solvent was evaporated under vaccum and the residue was washed with dry THF (5×10mL). After dry under vaccum, SMes-CO_2 was obtained as white powder.

1.4 Catalytic reactions

The epoxidation of olefin was carried out in a 25 mL 3-necked round-bottom glass flask equipped with a cryogenic-liquid condenser under atmospheric pressure. Typically, catalyst (1.25 mmol), olefin (20 mmol), TBHP (40 mmol) were added into the reactor. The mixture was stirred by a magnetic stirrer and heated to desired temperature in a water bath.

The cycloaddition reaction and one-pot synthesis of cyclic carbonates were conducted in a 25 mL stainless autoclave. The catalyst (1.25 mmol) and substrates (20 mmol) were charged into the stainless autoclave equipped with magnetic stirring and heating devices. The reactor was purged with CO_2 for three times and then charged with CO_2. Next, the stainless autoclave was heated to desirable temperature and stirred for 30h. After the reaction is completed, the autoclave was cooled to room temperature, and the remaining CO_2 is slowly discharged from the reactor. The reaction solution was analyzed by using GC and GC-MS.

1.5 Procedure for the recycle of catalyst

After the catalytic reaction was completed and the remaining CO_2 was discharged from the reactor, the final mixture in the autoclave was dissolved in ethyl acetate (10 ml). Then adding diethyl ether (15 ml) to separate the catalyst and the separated catalyst was washed by diethyl ether (3×5ml). The recovered catalyst was dried 10h under vacuum and reused for the next running of catalytic reaction.

Reference:

[1] T. Zhao, X. Hu, D. Wu, R. Li, G. Yang and Y. Wu, *ChemSusChem*, 2017, **10**, 2046-2052.

[2] H. Zhou, W. Z. Zhang, C. H. Liu, J. P. Qu and X. B. Lu, *J. Org. Chem*., 2008, **73**, 8039-8044.

[3] W. Zhenhong, Z. Wenbiao, L. Guangming, X. Feng, M. Yingxuan and C. Hu, *J. Organomet. Chem*., 2016, **808**, 104-108.

2. Characterization results

The ^{1}H and ^{13}C NMR spectra of $[C_1C_2Im][HCO_3]$

^{1}H-NMR, (400 MHz, DMSO-d_6)

$[C_1C_2Im][HCO_3]$: δ1.41-1.38 (t, 3H, -CH_3), 3.88 (s, 3H, N-CH_3), 4.26-4.20 (q, 2H, N-CH_2-), 7.80 (d, 1H,-CH=C-), 7.91 (d, 1H, -C=CH-), 9.44 (s, 1H, N-CH-N)

C_1C_2Im-CO_2: δ1.33-1.29 (t, 3H, -CH_3), 3.95 (s, 3H, N-CH_3), 4.49-4.44 (q, 2H, N-CH_2-),7.68 (d, 1H, -CH=C-), 7.76 (d, 1H, -C=CH-)

^{13}C-NMR, (100 MHz, DMSO-d_6)

$[C_1C_2Im][HCO_3]$: δ 15.66 (-CH_3), 36.22 (N-CH_3), 44.46 (N-CH_2-), 122.42 (-CH=), 123.95 (=CH-), 136.80 (N-CH-N)

C_1C_2Im-CO_2: δ16.44 (-CH_3), 36.94 (N-CH_3), 44.55 (N-CH_2-), 120.99 (-CH=), 122.85 (=CH-), 142.05 (N-C-N), 154.72 (CO_2)

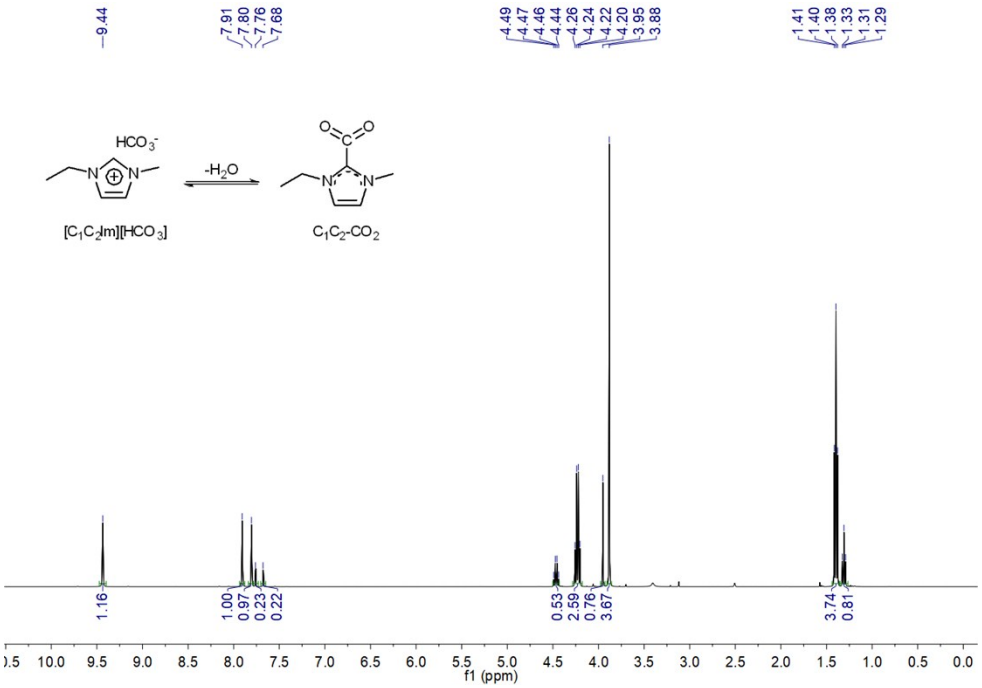


Fig. S1. ^{1}H NMR spectra of $[C_1C_2Im][HCO_3]$ in DMSO

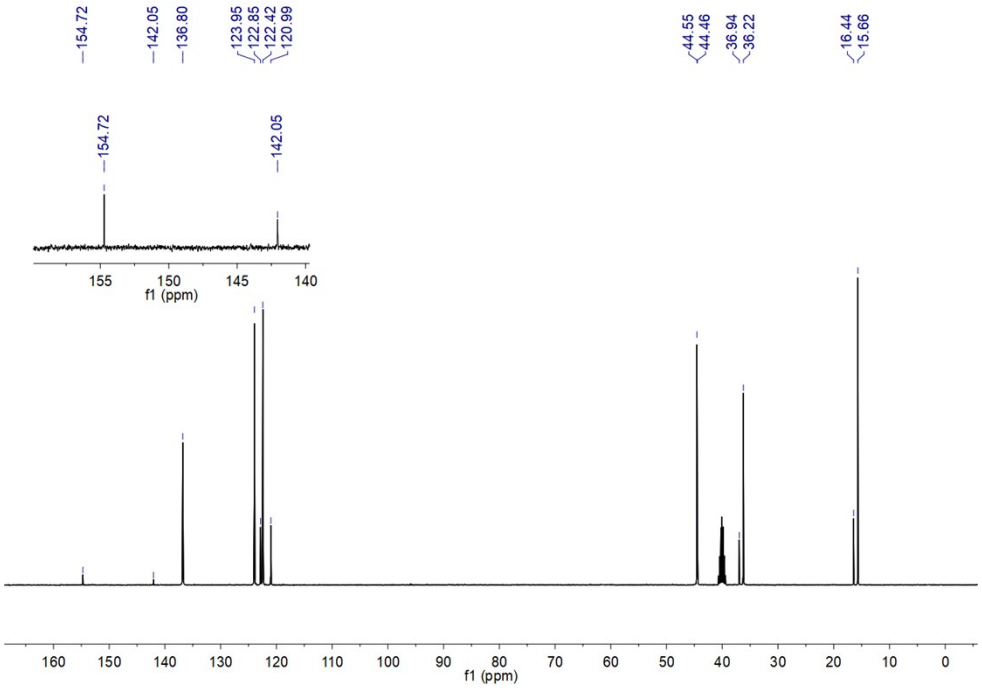


Fig. S2. ^{13}C NMR spectra of $[C_1C_2Im][HCO_3]$ in DMSO

The ^{1}H and ^{13}C NMR spectra of $[C_1C_4Im][HCO_3]$

^{1}H-NMR, (400 MHz, DMSO-d_6)

$[C_1C_4Im][HCO_3]$: δ 0.88-0.86 (t, 3H, -CH_3), 1.28-1.21 (m, 2H, -CH_2-), 1.80-1.72 (m, 2H, -

CH_2-), 3.89 (s, 3H, N-CH_3), 4.23-4.19 (t, 2H, N-CH_2-), 7.81 (d, 1H, -CH=C-), 7.89 (d, 1H, -C=CH-), 9.41 (s, 1H, N-CH-N)

C_1C_4Im-CO_2: δ 0.85-0.82 (t, 3H, -CH_3), 1.20-1.16 (m, 2H, -CH_2-), 1.71-1.65 (m, 2H, -CH_2-), 3.96 (s, 3H, N-CH_3), 4.48-4.44 (t, 2H, N-CH_2-), 7.66 (d, 1H, -CH=C-), 7.73 (d, 1H, -C=CH-)

^{13}C-NMR, (100 MHz, DMSO-d_6)

[C_1C_4Im][HCO_3]: δ 13.73 (-CH_3), 19.20 (-CH_2-), 31.85 (-CH_2-), 36.24 (N-CH_3), 48.88 (N-CH_2-), 122.73 (-CH=), 124.00 (=CH-), 137.06 (N-CH-N)

C_1C_4Im-CO_2: δ13.82 (-CH_3), 19.38 (-CH_2-), 32.60 (-CH_2-), 36.94 (N-CH_3), 48.66 (N-CH_2-), 121.39 (-CH=), 122.73 (=CH-), 142.36 (N-C-N), 154.70 (CO_2)

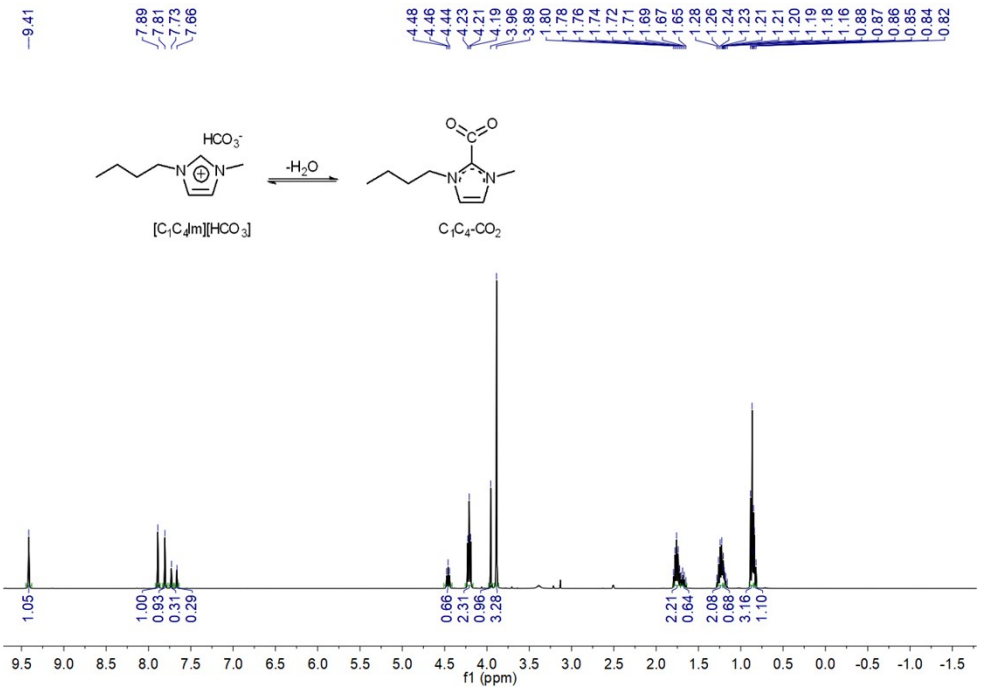


Fig. S3. ^{1}H NMR spectra of [C_1C_4Im][HCO_3] in DMSO

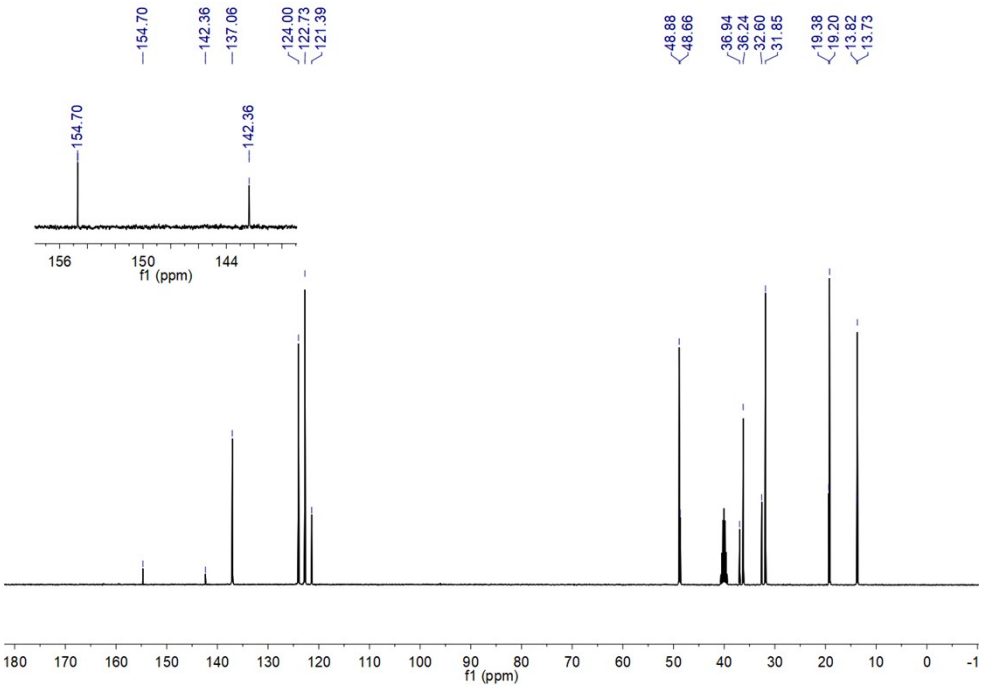


Fig. S4. ^{13}C NMR spectra of $[C_1C_4Im][HCO_3]$ in DMSO

The ^{1}H and ^{13}C NMR spectra of $[C_1C_4Im][Br]$

^{1}H-NMR, (400 MHz, DMSO-d_6)

$[C_1C_4Im][Br]$: δ 0.89-0.85 (t, 3H, $-CH_3$), 1.24-1.22 (m, 2H, $-CH_2-$), 1.77-1.74 (m, 2H, $-CH_2-$), 3.88 (s, 3H, $N-CH_3$), 4.23-4.19 (t, 2H, $N-CH_2-$), 7.81 (d, 1H, -CH=C-), 7.89 (d, 1H, -C=CH-), 9.40 (s, 1H, N-CH-N)

^{13}C-NMR, (100 MHz, DMSO-d_6)

$[C_1C_4Im][Br]$: δ 13.75 ($-CH_3$), 19.20 ($-CH_2-$), 31.85 ($-CH_2-$), 36.26 ($N-CH_3$), 48.87 ($N-CH_2-$), 122.72 (-CH=), 123.99 (=CH-), 137.01 (N-CH-N)

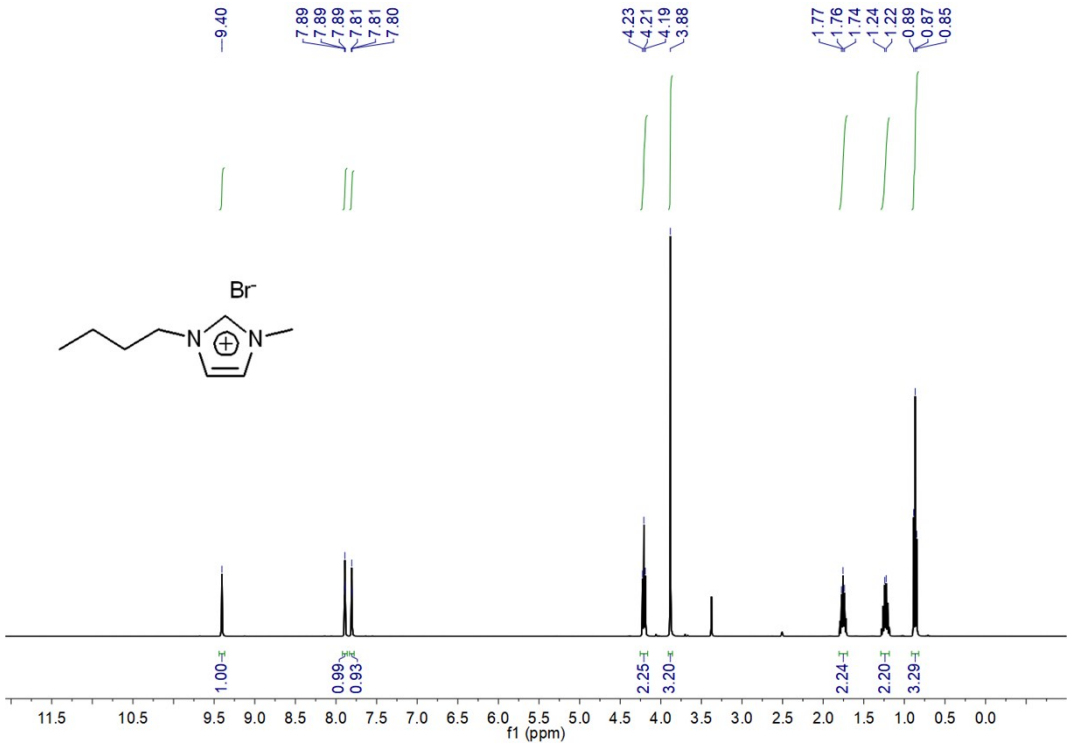


Fig. S5. ^{1}H NMR spectra of $[C_1C_4Im][Br]$ in DMSO

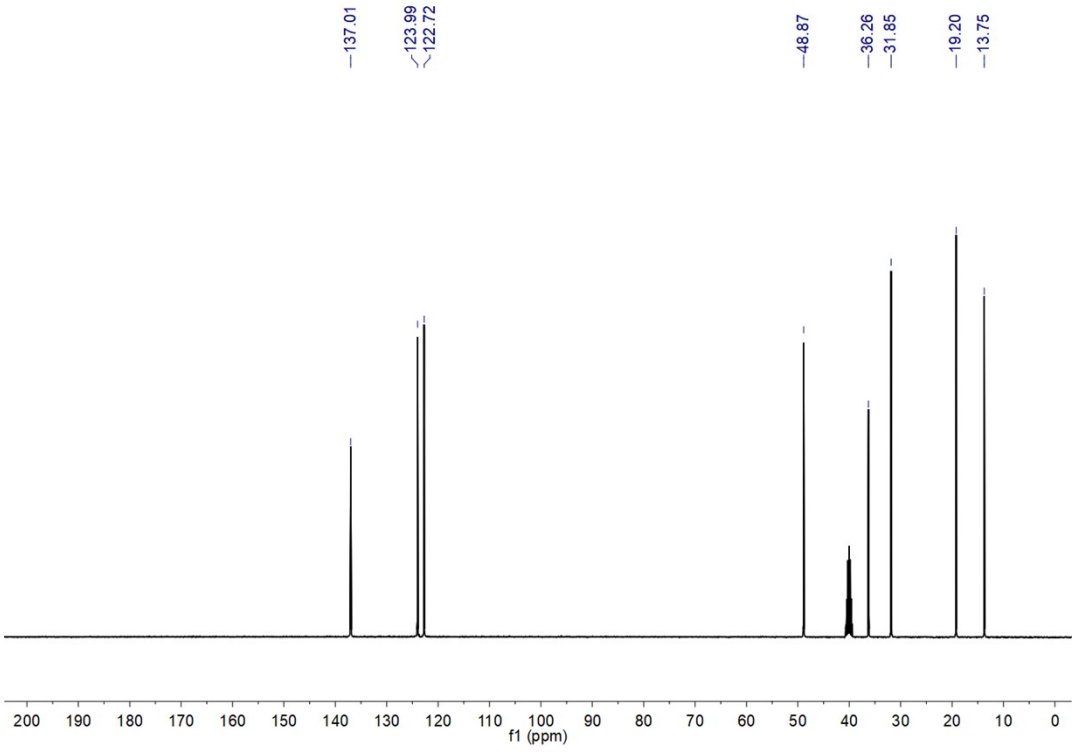


Fig. S6. ^{13}C NMR spectra of $[C_1C_4Im][Br]$ in DMSO

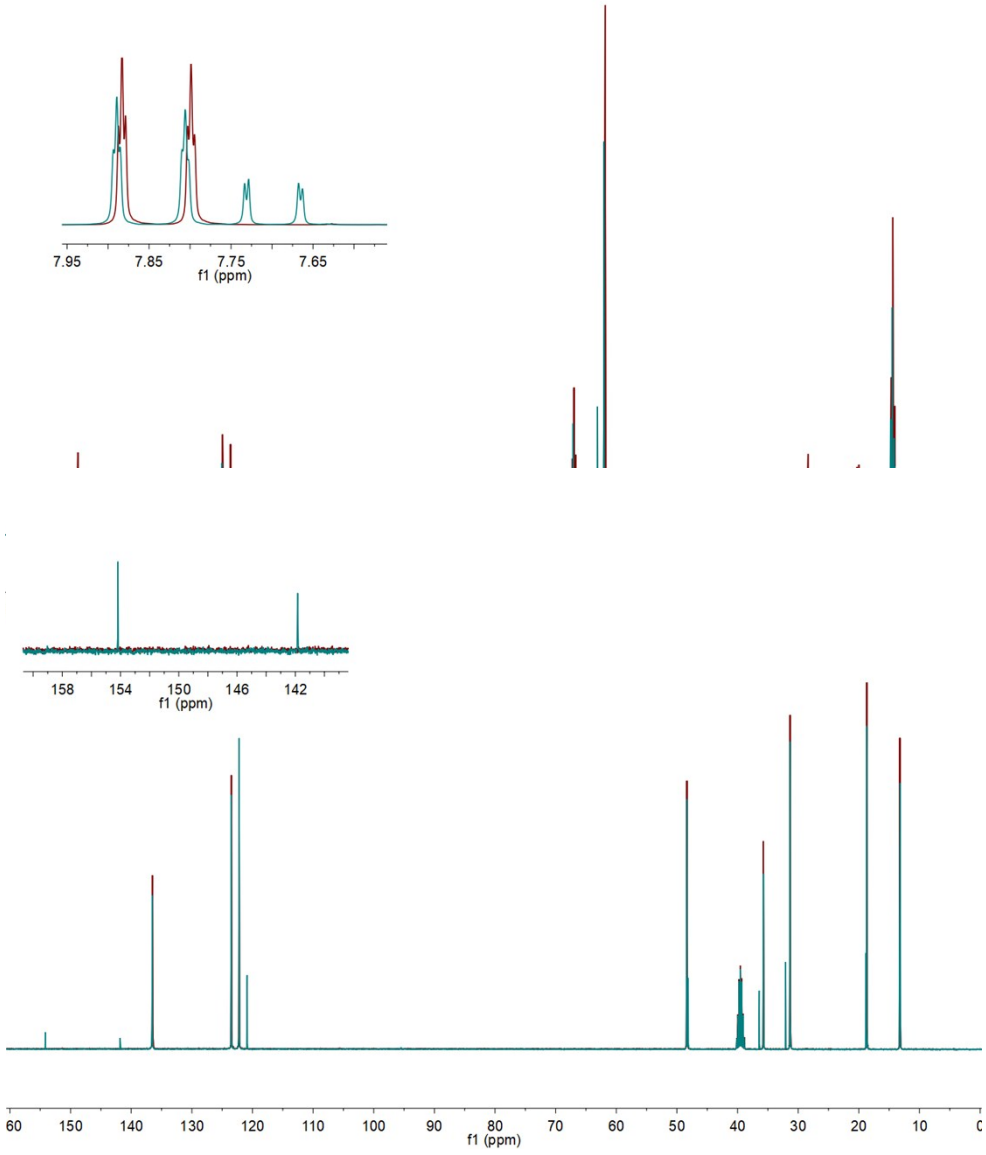


Fig. S7. ^{1}H NMR overlapped spectra of $[C_1C_4Im][Br]$ (red) and $[C_1C_4Im][HCO_3]$ (green) in DMSO

Fig. S8. ^{13}C NMR overlapped spectra of $[C_1C_4Im][Br]$ (red) and $[C_1C_4Im][HCO_3]$ (green) in DMSO

The ^{1}H and ^{13}C NMR spectra of $[C_1C_6Im][HCO_3]$

^{1}H-NMR, (400 MHz, DMSO-d_6)

$[C_1C_6Im][HCO_3]$: δ 0.76-0.73 (t, 3H, $-CH_3$), 1.17 (br, 6H, $-C_3H_6-$), 1.76-1.73 (m, 2H, $-CH_2-$), 3.91 (s, 3H, N-CH_3), 4.25-4.21 (t, 2H, N-CH_2-), 7.92 (d, 1H, -CH=C-), 8.02 (d, 1H, -C=CH-), 9.64 (s, 1H, N-CH-N)

C_1C_6Im-CO_2: δ 0.76-0.73 (t, 3H, $-CH_3$), 1.17 (br, 6H, $-C_3H_6-$), 1.68-1.65 (m, 2H, $-CH_2-$), 3.97 (s, 3H, N-CH_3), 4.49-4.45 (t, 2H, N-CH_2-), 7.83 (d, 1H, -CH=C-), 7.90 (d, 1H, - C=CH-)

^{13}C-NMR, (100 MHz, DMSO-d_6)

$[C_1C_6Im][HCO_3]$: δ 14.15 ($-CH_3$), 22.29 ($-CH_2-$), 25.54 ($-CH_2-$), 29.92 ($-CH_2-$), 30.98 ($-CH_2-$), 36.25 (N-CH_3), 49.06 (N-CH_2-), 122.69 (-CH=), 123.88 (=CH-), 137.12 (N-CH-N)

C_1C_6Im-CO_2: δ 14.15 ($-CH_3$), 22.31 ($-CH_2-$), 25.71 ($-CH_2-$), 30.61 ($-CH_2-$), 31.07 ($-CH_2-$), 37.03 (N-CH_3), 48.91 (N-CH_2-), 121.57 (-CH=), 122.81 (=CH-), 141.94 (N-C-N), 154.93 (CO_2)

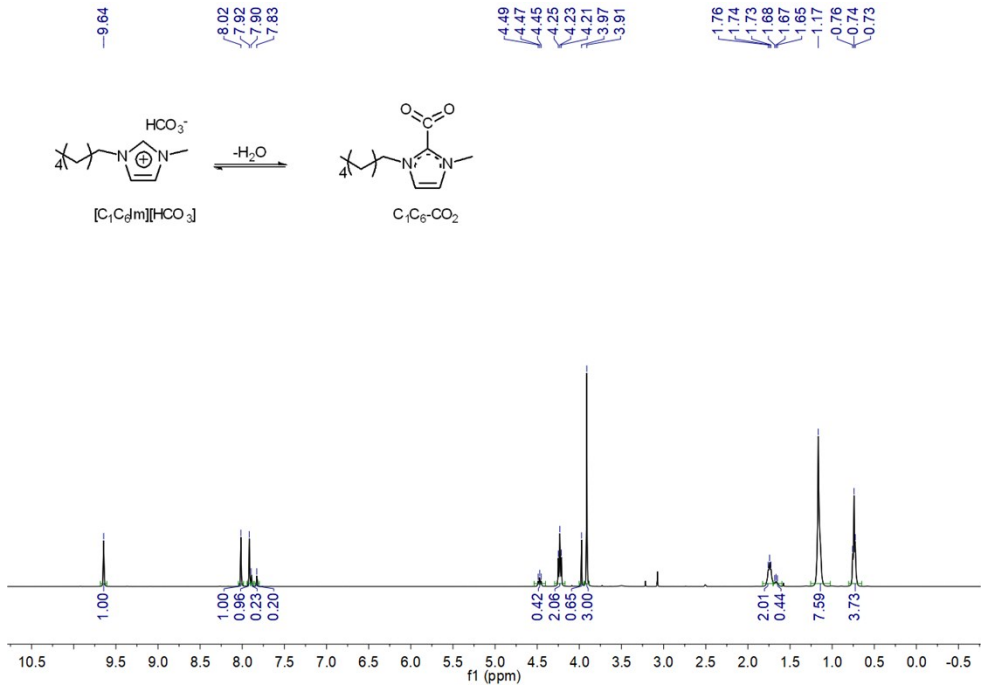


Fig. S9. ^{1}H NMR spectra of $[C_1C_6Im][HCO_3]$ in DMSO

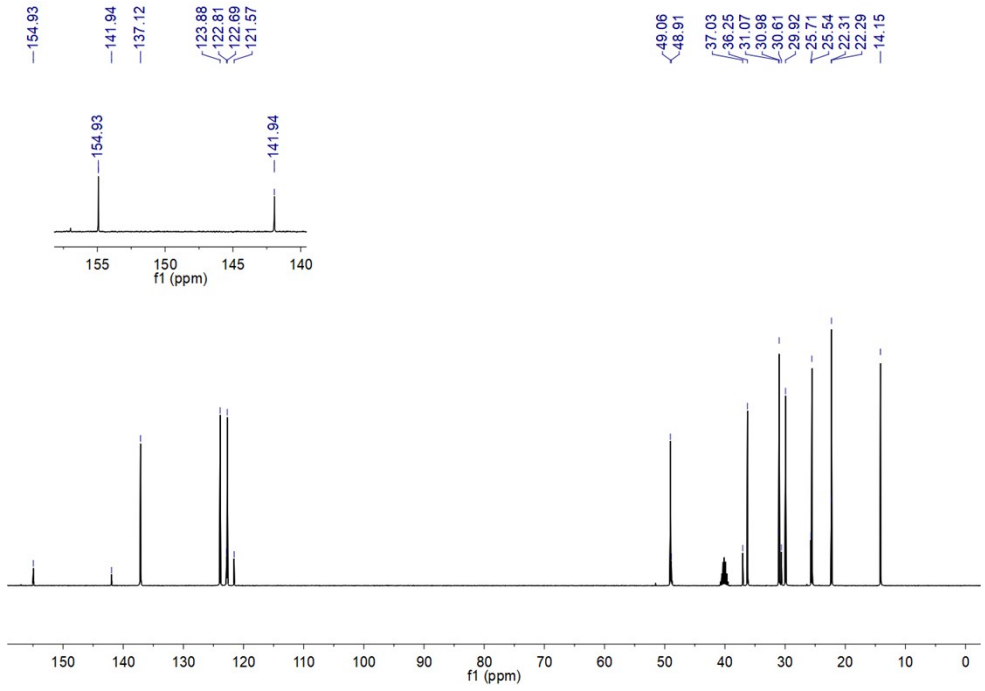


Fig. S10. ^{13}C NMR spectra of $[C_1C_6Im][HCO_3]$ in DMSO

The ^{1}H and ^{13}C NMR spectra of $[C_1C_{12}Im][Br]$

^{1}H-NMR, (400 MHz, DMSO-d_6): δ 0.85-0.82 (t, 3H, -CH_3), 1.12 (br, 18H, -C_9H_{12}-), 1.81-1.74 (m, 2H, -CH_2-), 3.88 (s, 3H, N-CH_3), 4.21-4.17 (t, 2H, N-CH_2-), 7.79 (d, 1H, -CH=C-),

7.86 (d, 1H, -C=CH-), 9.35 (s, 1H, N-CH-N)

^{13}C-NMR, (100 MHz, DMSO-d_6): δ 14.39 (-CH_3), 22.56 (-CH_2-), 25.97 (-CH_2-), 28.88 (-CH_2-), 29.19 (-CH_2-), 29.33 (- CH_2-), 29.44 (-CH_2-), 29.49 (-CH_2-), 29.51 (-CH_2-), 29.91 (-CH_2-), 31.77 (-CH_2-), 36.24 (N-CH_3), 49.16 (N-CH_2-), 122.72 (-CH=), 124.01 (=CH-), 137.00 (N-CH-N)

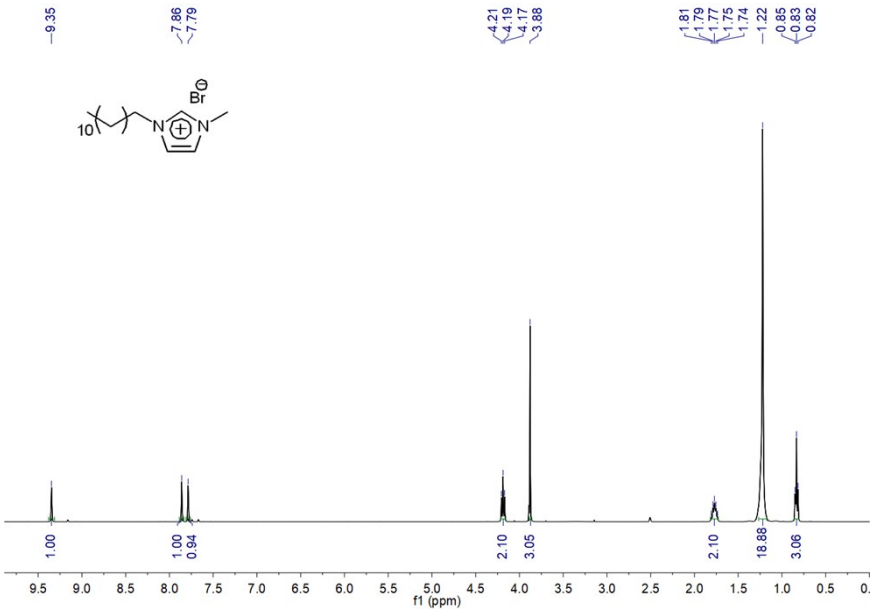


Fig. S11. ^{1}H NMR spectra of [C_1C_{12}Im][Br] in DMSO

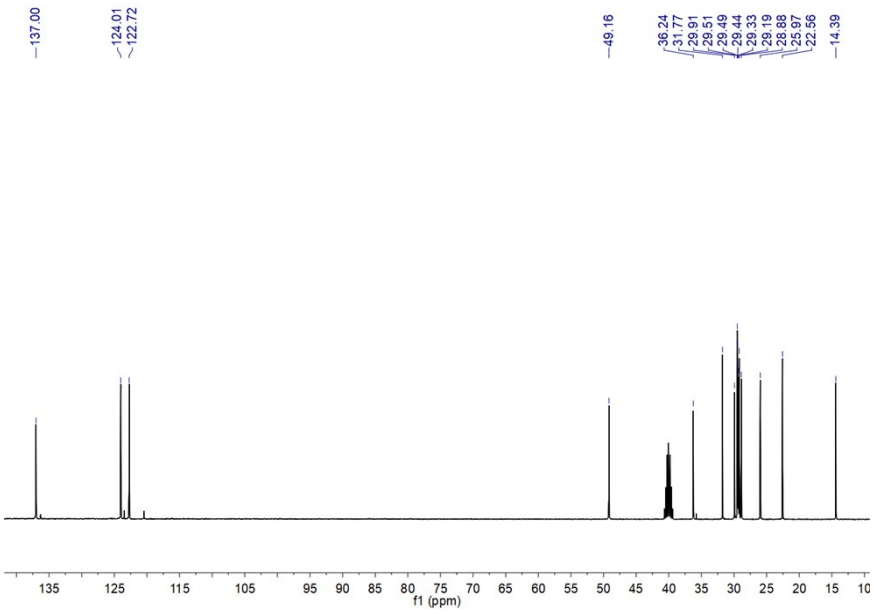


Fig. S12. ^{13}C NMR spectra of [C_1C_{12}Im][Br] in DMSO

The ^{1}H and ^{13}C NMR spectra of $[C_1C_{12}Im][HCO_3]$

^{1}H-NMR, (400 MHz, DMSO-d_6)

$[C_1C_{12}Im][HCO_3]$: δ 0.85-0.81 (t, 3H, -CH_3), 1.22 (br, 18H, -C_9H_{18}-), 1.81-1.76 (m, 2H, -CH_2-), 3.88 (s, 3H, N-CH_3), 4.21-4.17 (t, 2H, N-CH_2-), 7.79 (d, 1H, -CH=C-), 7.87 (d, 1H, -C=CH-), 9.37 (s, 1H, N-CH-N)

$C_1C_{12}Im$-CO_2: δ 0.85-0.81 (t, 3H, -CH_3), 1.22 (br, 18H, -C_9H_{18}-), 1.81-1.76 (m, 2H, -CH_2-), 3.96 (s, 3H, N-CH_3), 4.47-4.44 (t, 2H, N-CH_2-), 7.65 (d, 1H, -CH=C-), 7.71 (d, 1H, -C=CH-)

^{13}C-NMR, (100 MHz, DMSO-d_6)

$[C_1C_{12}Im][HCO_3]$: δ 14.37 (-CH_3), 22.57 (-CH_2-), 25.98 (-CH_2-), 28.90 (-CH_2-), 29.21 (-CH_2-), 29.34 (-CH_2-), 29.46 (-CH_2-), 29.51 (-CH_2-), 29.53 (-CH_2-), 29.93 (-CH_2-), 31.78 (-CH_2-), 36.23 (N-CH_3), 49.16 (N-CH_2-), 122.73 (-CH=), 124.01 (=CH-), 137.05 (N-CH-N)

$C_1C_{12}Im$-CO_2: δ 14.37 (-CH_3), 22.57 (-CH_2-), 26.18 (-CH_2-), 29.01 (-CH_2-), 29.21 (-CH_2-), 29.39 (-CH_2-), 29.46 (-CH_2-), 29.51 (-CH_2-), 29.53 (-CH_2-), 30.65 (-CH_2-), 31.78 (-CH_2-), 36.97 (N-CH_3), 48.96 (N-CH_2-), 121.39 (-CH=), 122.73 (=CH-), 142.31 (N-C- N), 154.65 (CO_2)

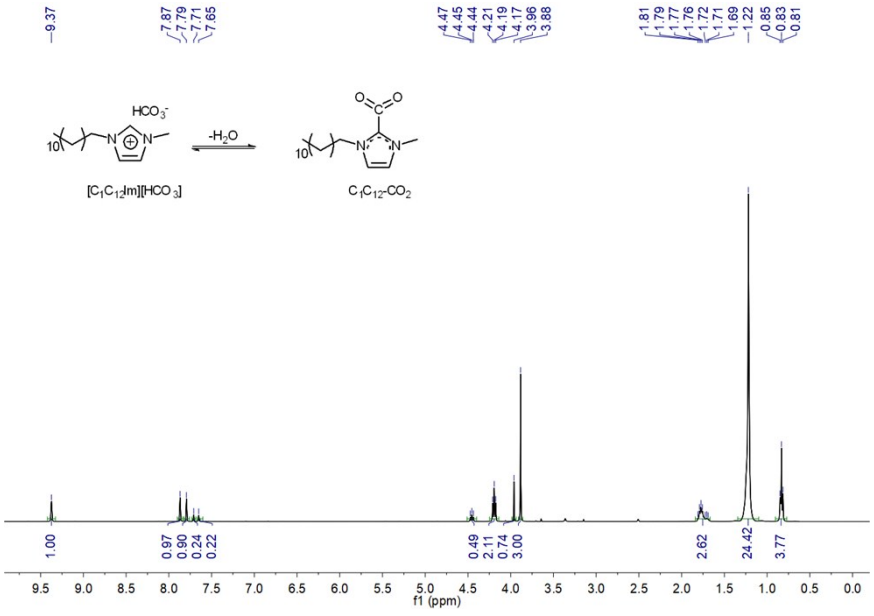


Fig. S13. ^{1}H NMR spectra of $[C_1C_{12}Im][HCO_3]$ in DMSO

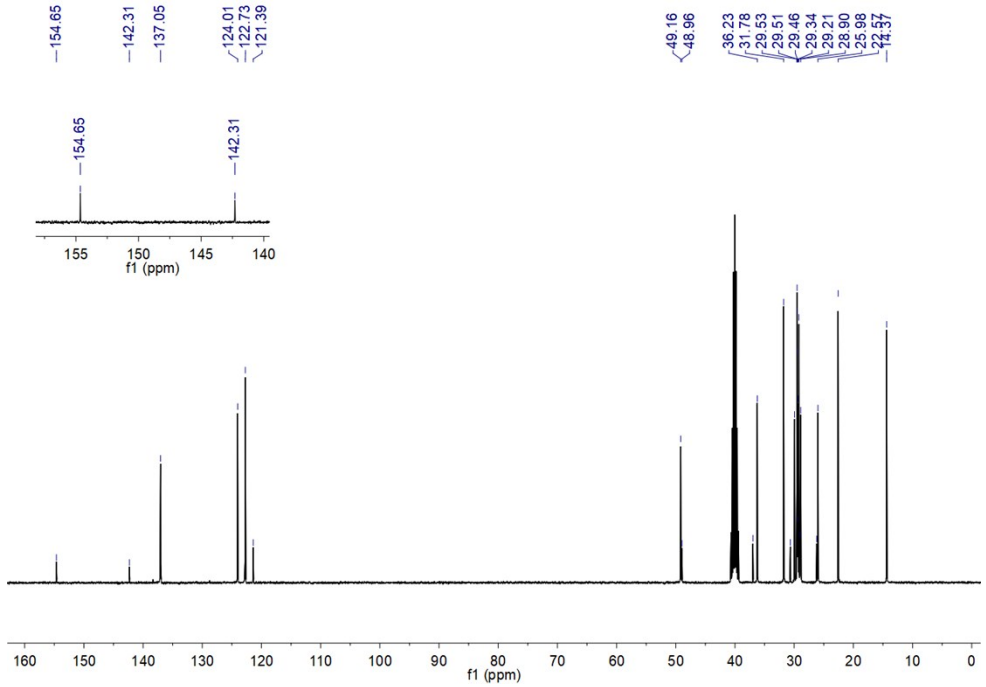
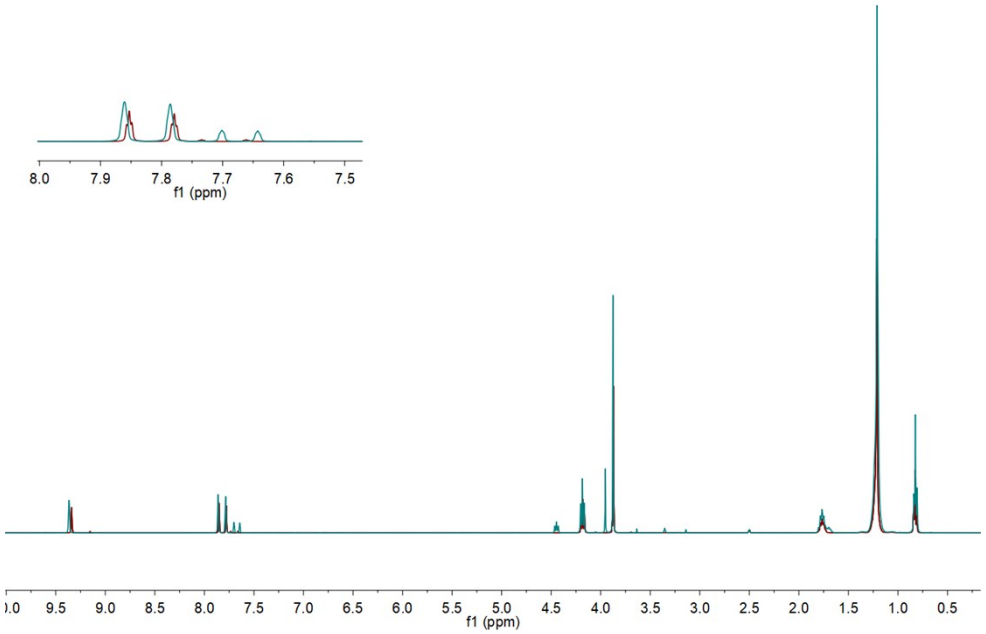


Fig. S14. ^{13}C NMR spectra of $[C_1C_{12}Im][HCO_3]$ in DMSO

Fig. S15. ^{1}H NMR overlapped spectra of $[C_1C_{12}Im][Br]$ (red) and $[C_1C_{12}Im][HCO_3]$ (green) in DMSO



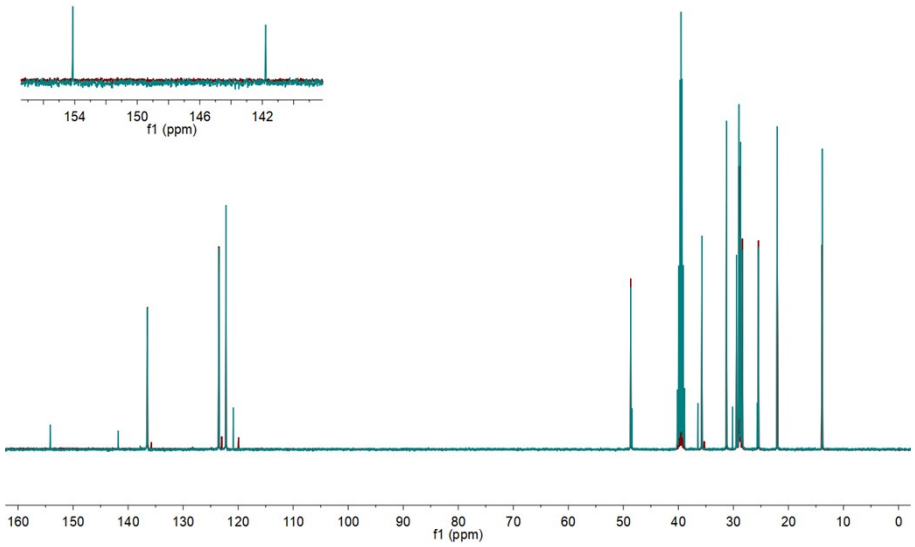


Fig. S16. ^{13}C NMR overlapped spectra of $[C_1C_{12}Im][Br]$ (red) and $[C_1C_{12}Im][HCO_3]$ (green) in DMSO

The ^{1}H and ^{13}C NMR spectra of [SMes][Cl]

^{1}H-NMR, (400 MHz, $CDCl_3$): δ 2.20 (s, 6H, $ArCH_3$), 2.29 (s, 12H, $ArCH_3$), 4.47 (s, 4H, ArH), 6.85 (s, 4H, CH_2-CH_2), 9.44 (s, 1H, N-CH-N)

^{13}C-NMR, (100 MHz, $CDCl_3$): δ 17.02, 20.04, 50.95, 128.97, 129.29, 133.97, 139.36, 159.07

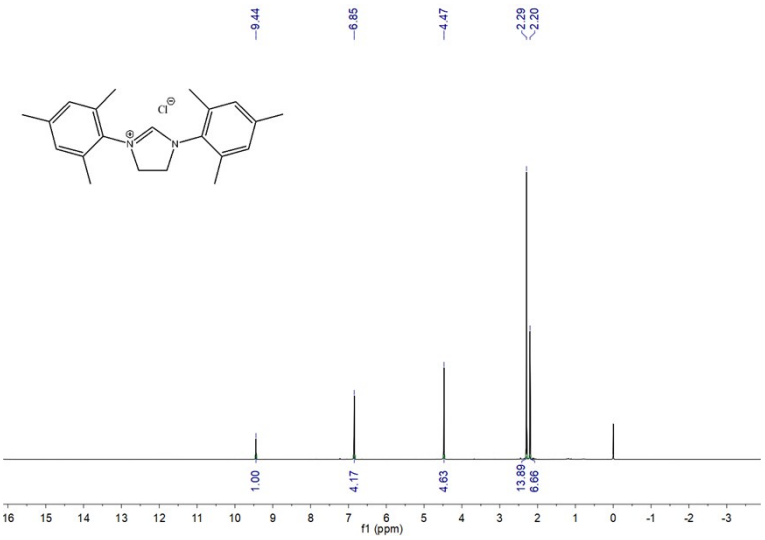


Fig. S17. ^{1}H NMR spectra of [SMes][Cl] in $CDCl_3$

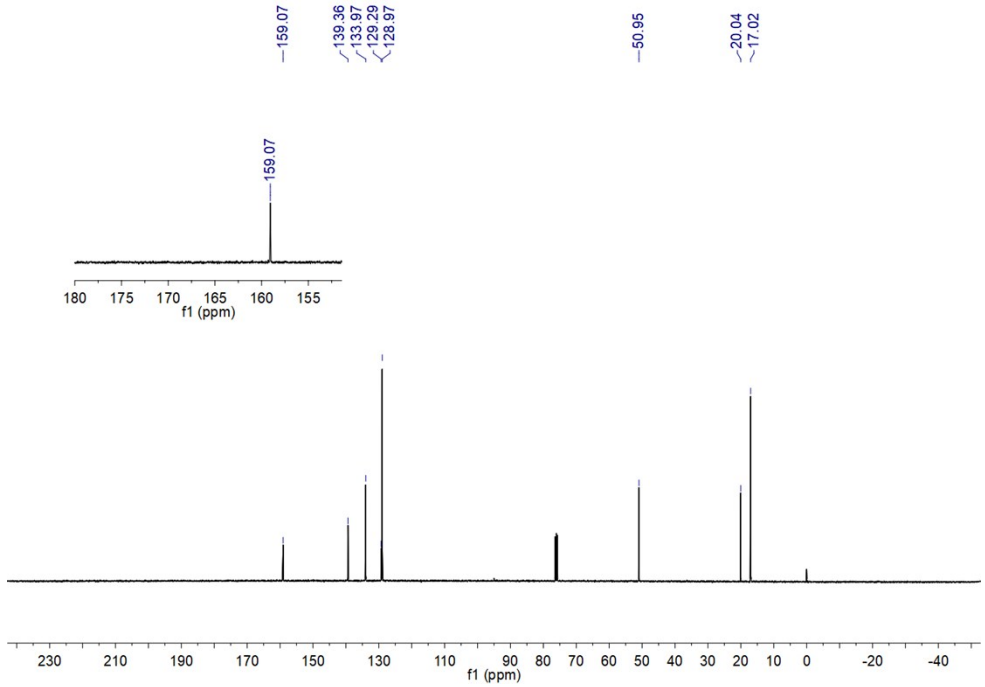


Fig. S18. ^{13}C NMR spectra of [SMes][Cl] in $CDCl_3$

The ^{1}H and ^{13}C NMR spectra of SMes-CO_2

^{1}H-NMR, (400 MHz, $CDCl_3$): δ 2.17 (s, 6H, $ArCH_3$), 2.35 (s, 12H, $ArCH_3$), 4.05 (s, 4H, ArH), 6.81 (s, 4H, CH_2-CH_2)

^{13}C-NMR, (100 MHz, $CDCl_3$):δ 16.66, 20.00, 48.59, 128.67, 129.70, 135.16, 138.92, 153.46, 164.67 (CO_2)

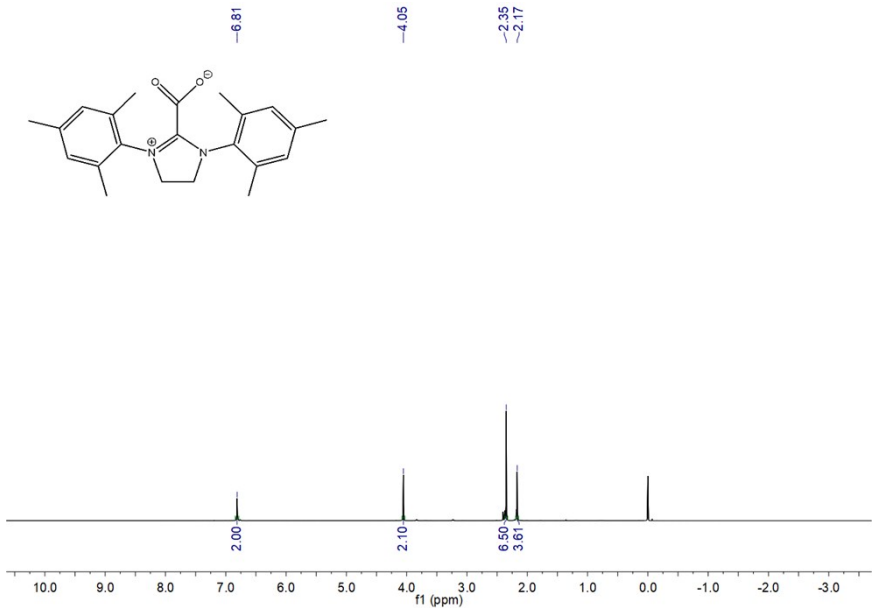


Fig. S19. ^{1}H NMR spectra of SMes-CO_2 in $CDCl_3$

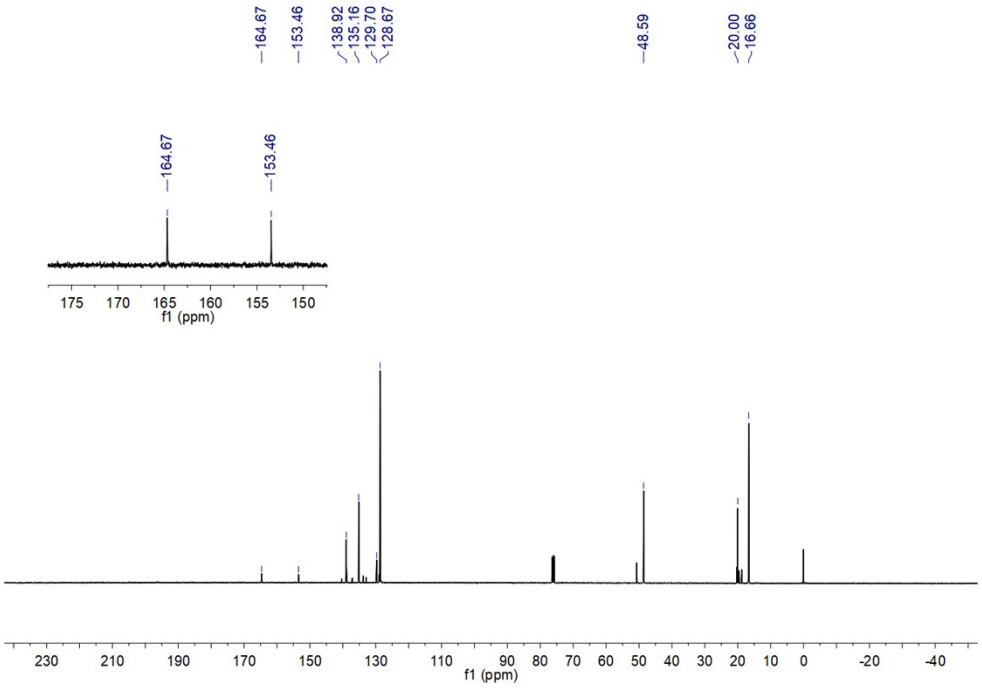


Fig. S20. ^{13}C NMR spectra of SMes-CO_2 in $CDCl_3$

3. The original GC, GC-MS and crude NMR spectrum of the reaction mixture

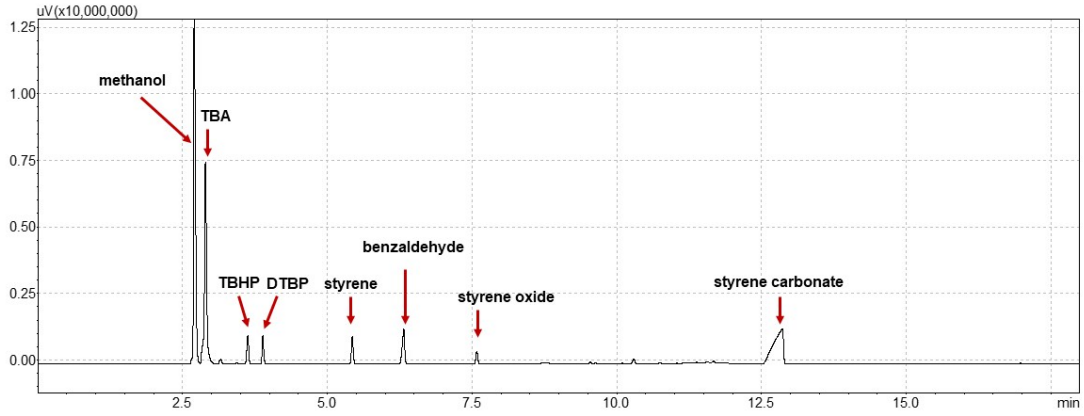


Fig. S21. The GC trace of styrene oxidative carboxylation (TBA: Tert-butyl alcohol. TBHP: Tert-butyl hydroperoxide. DTBP: Di-tert-butyl peroxide).

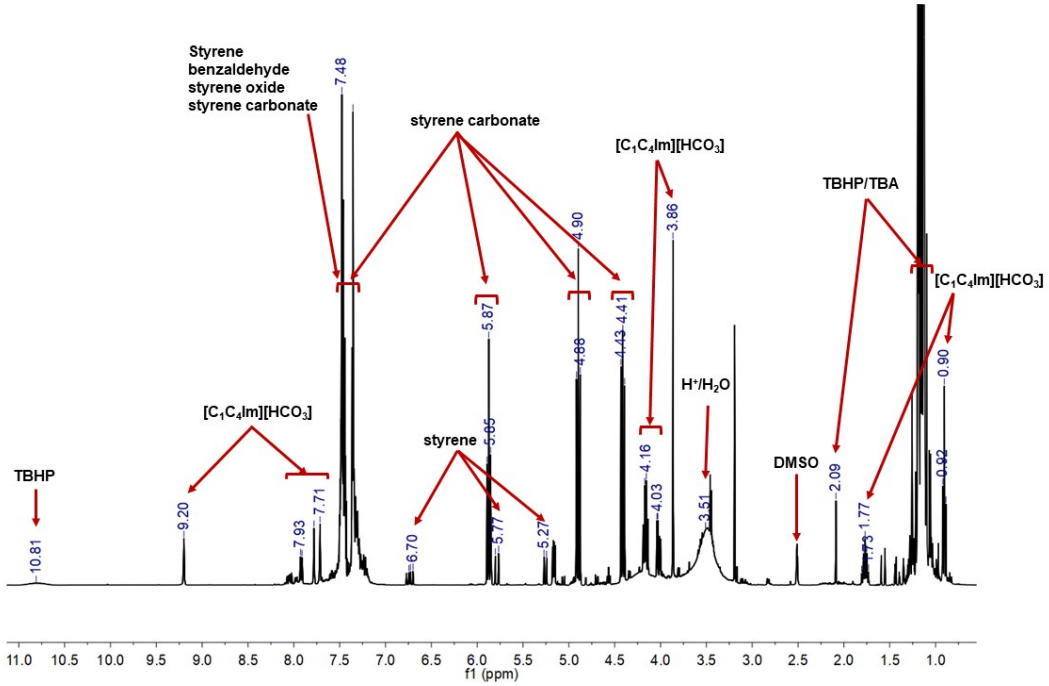


Fig. S22. ^{1}H NMR spectra of the reaction mixture of styrene oxidative carboxylation.

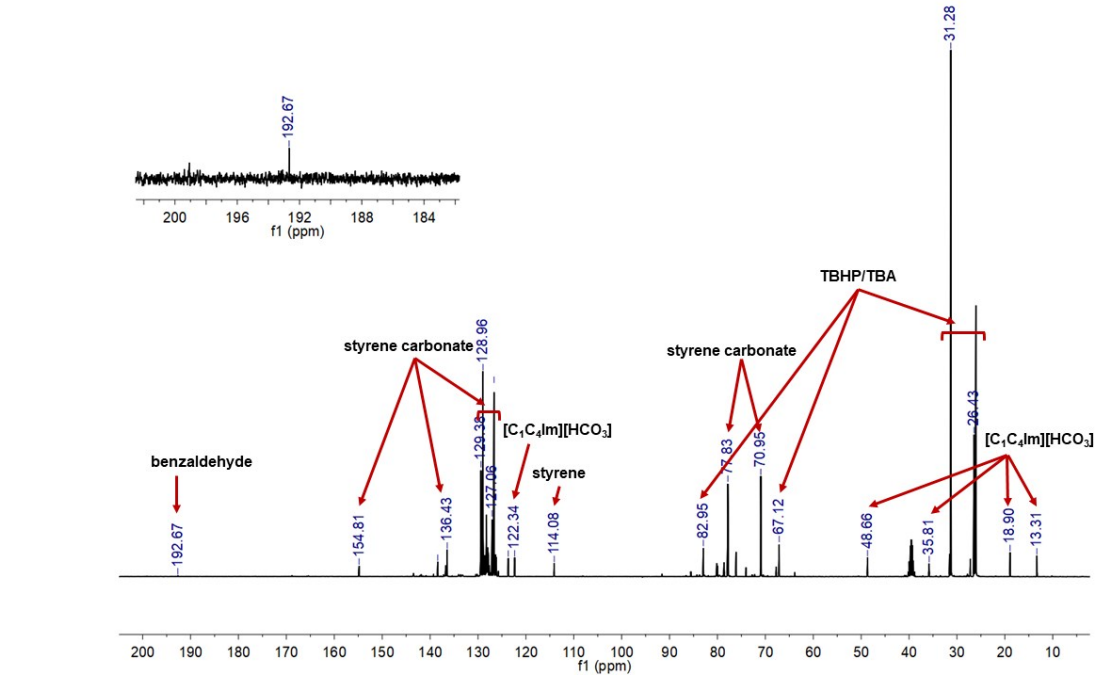
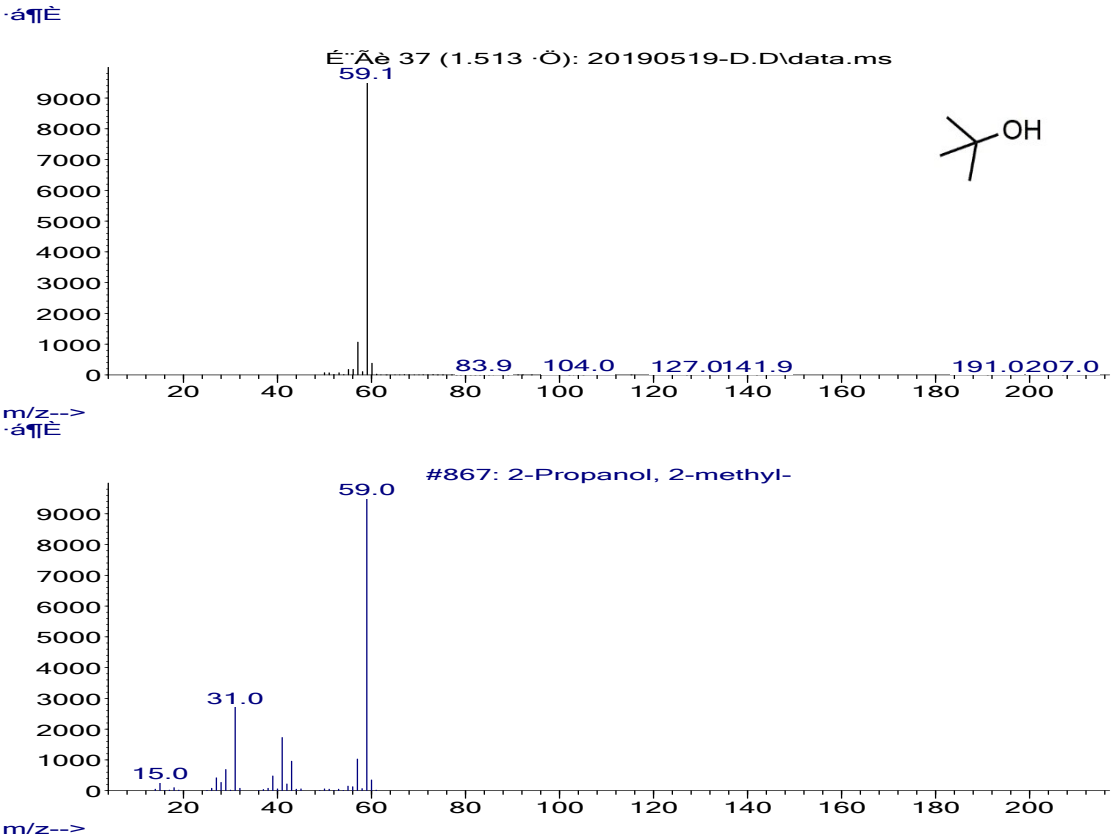


Fig. S23. ^{13}C NMR spectra of the reaction mixture of styrene oxidative carboxylation.



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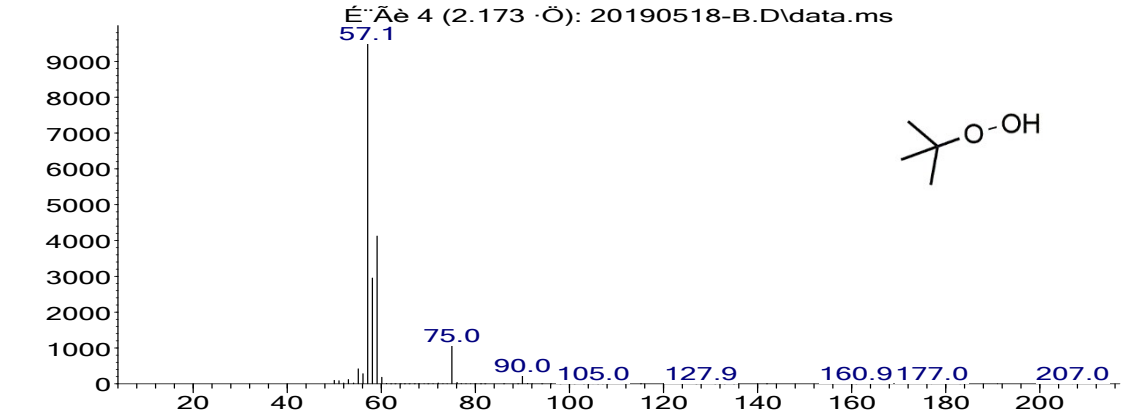
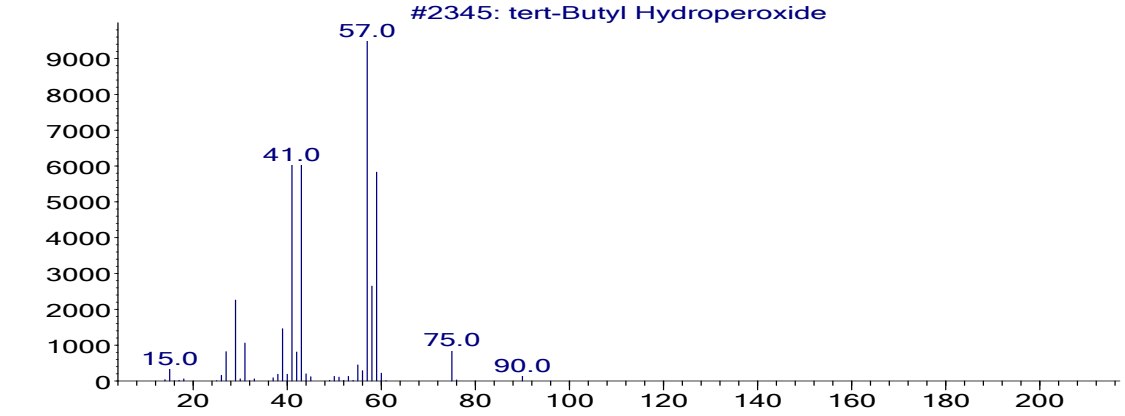
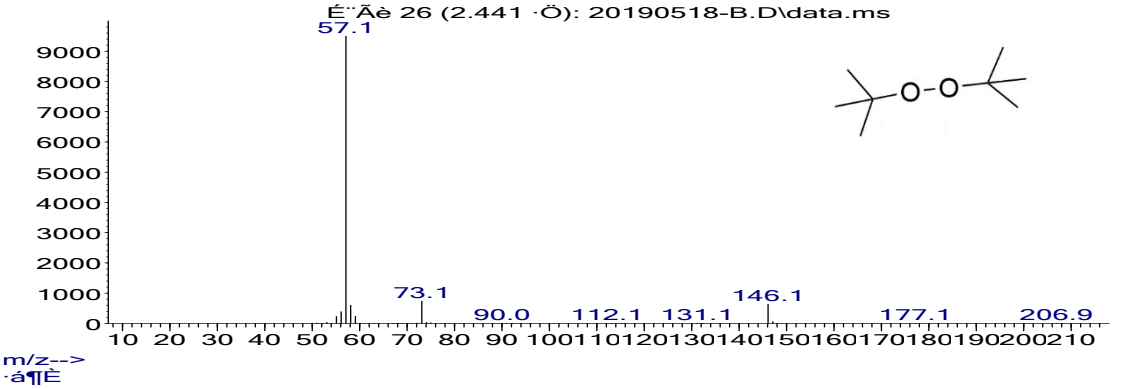

É¨Ãè 4 (2.173 ·Ö): 20190518-B.D\data.ms
57.1
75.0
90.0
105.0
127.9
160.9
177.0
207.0
O-OH
m/z-->

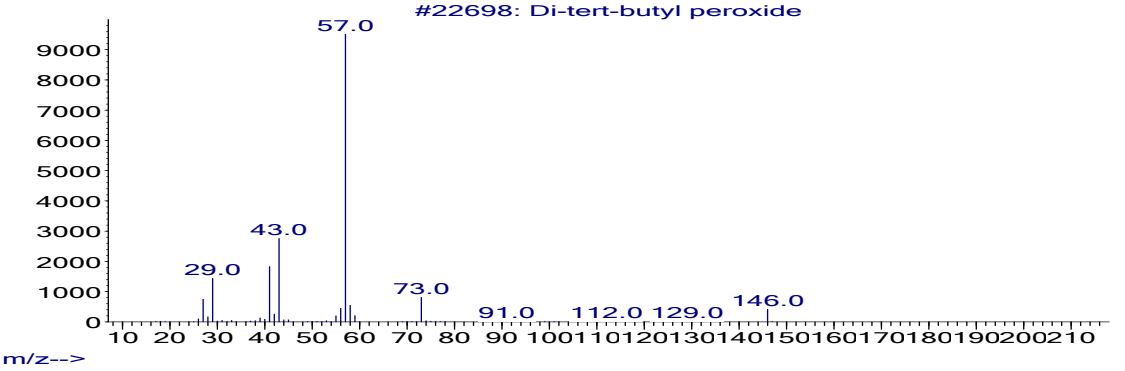
·á¶È

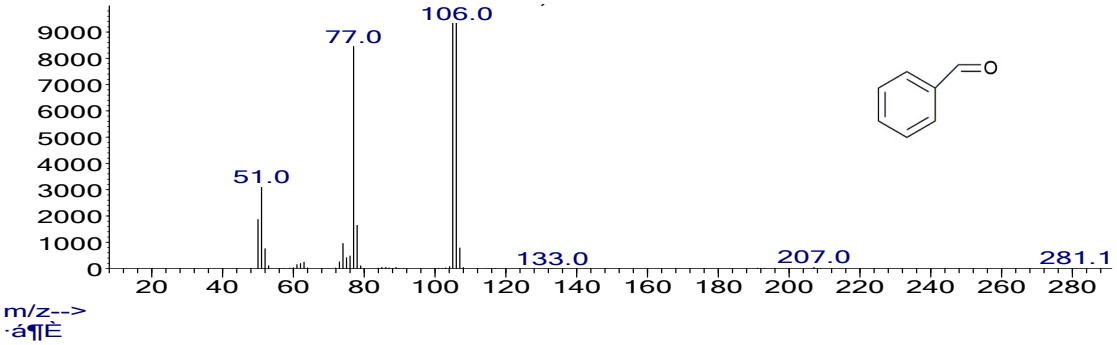

#2345: tert-Butyl Hydroperoxide
57.0
41.0
15.0
75.0
90.0
m/z-->

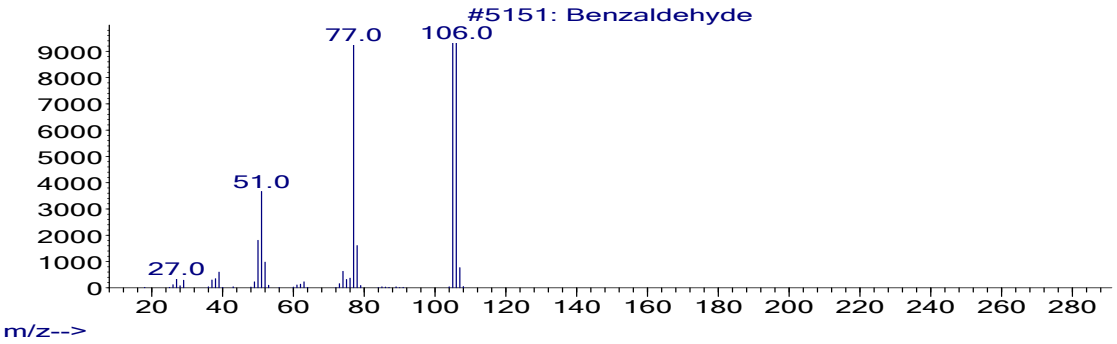
·á¶È

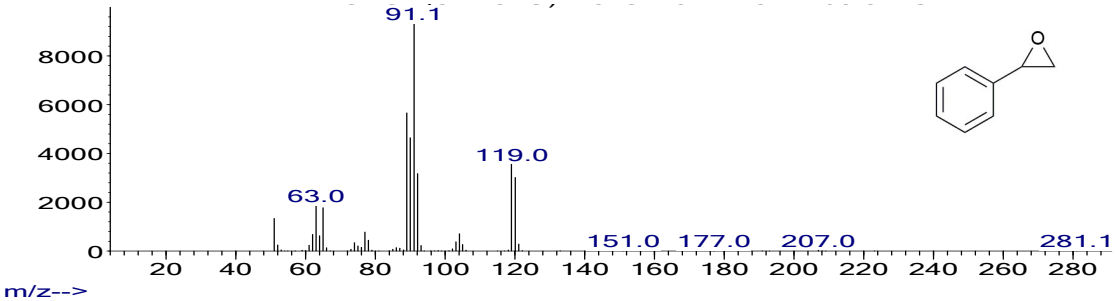

É¨Ãè 26 (2.441 ·Ö): 20190518-B.D\data.ms
57.1
73.1
90.0
112.1
131.1
146.1
177.1
206.9
O-O
m/z-->

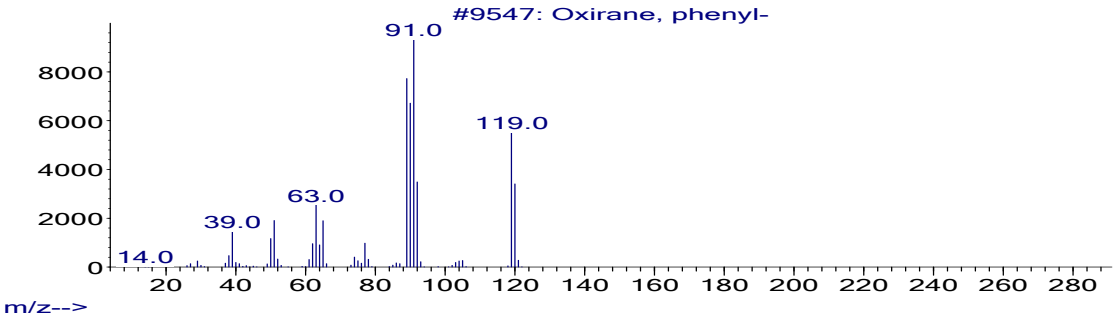
·á¶È


#22698: Di-tert-butyl peroxide
57.0
43.0
29.0
73.0
91.0
112.0
129.0
146.0
m/z-->


106.0
77.0
51.0
133.0
207.0
281.1
m/z-->


#5151: Benzaldehyde
77.0
106.0
51.0
27.0
m/z-->


91.1
119.0
63.0
151.0
177.0
207.0
281.1
m/z-->


#9547: Oxirane, phenyl-
91.0
119.0
63.0
39.0
14.0
m/z-->

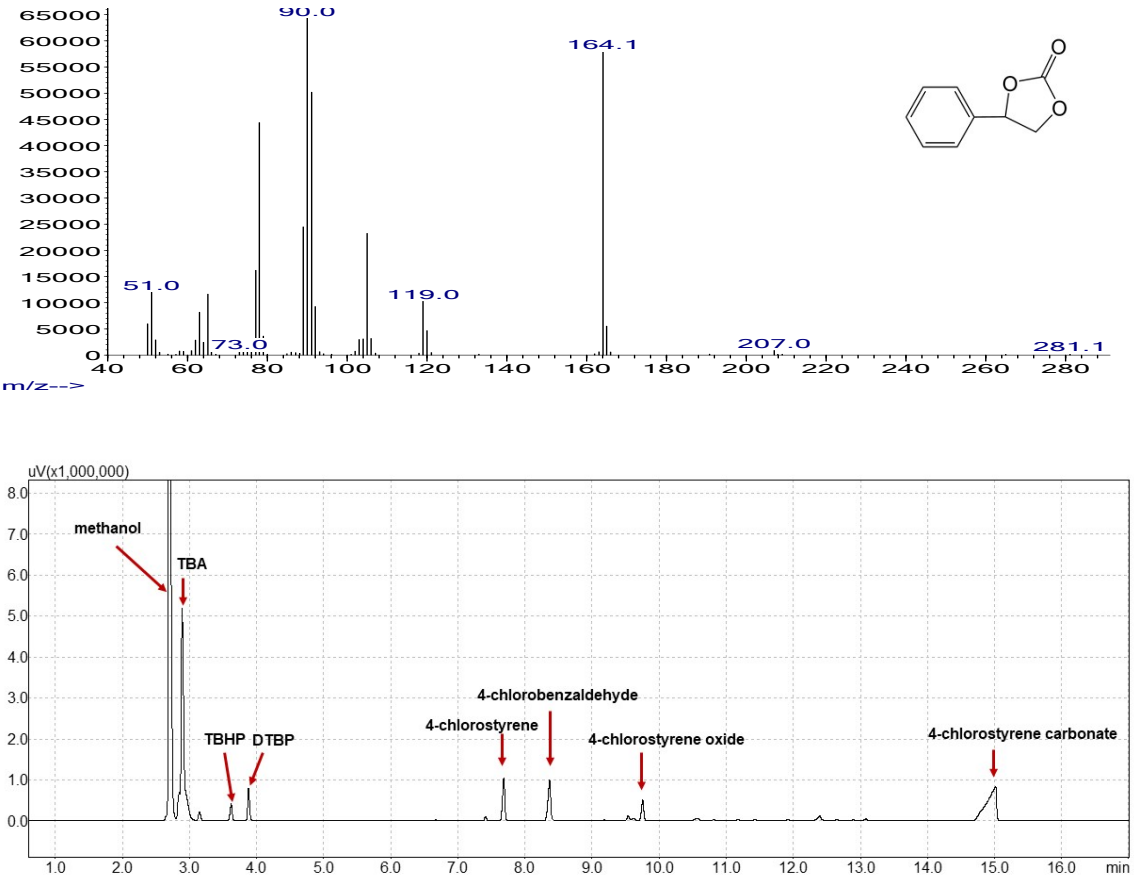
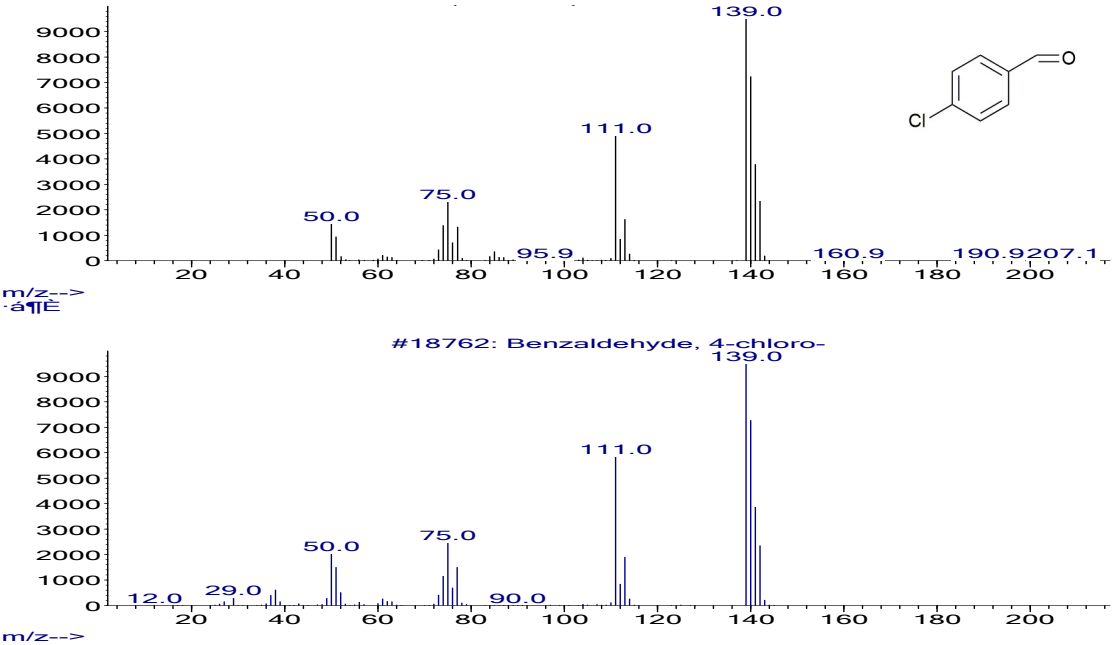
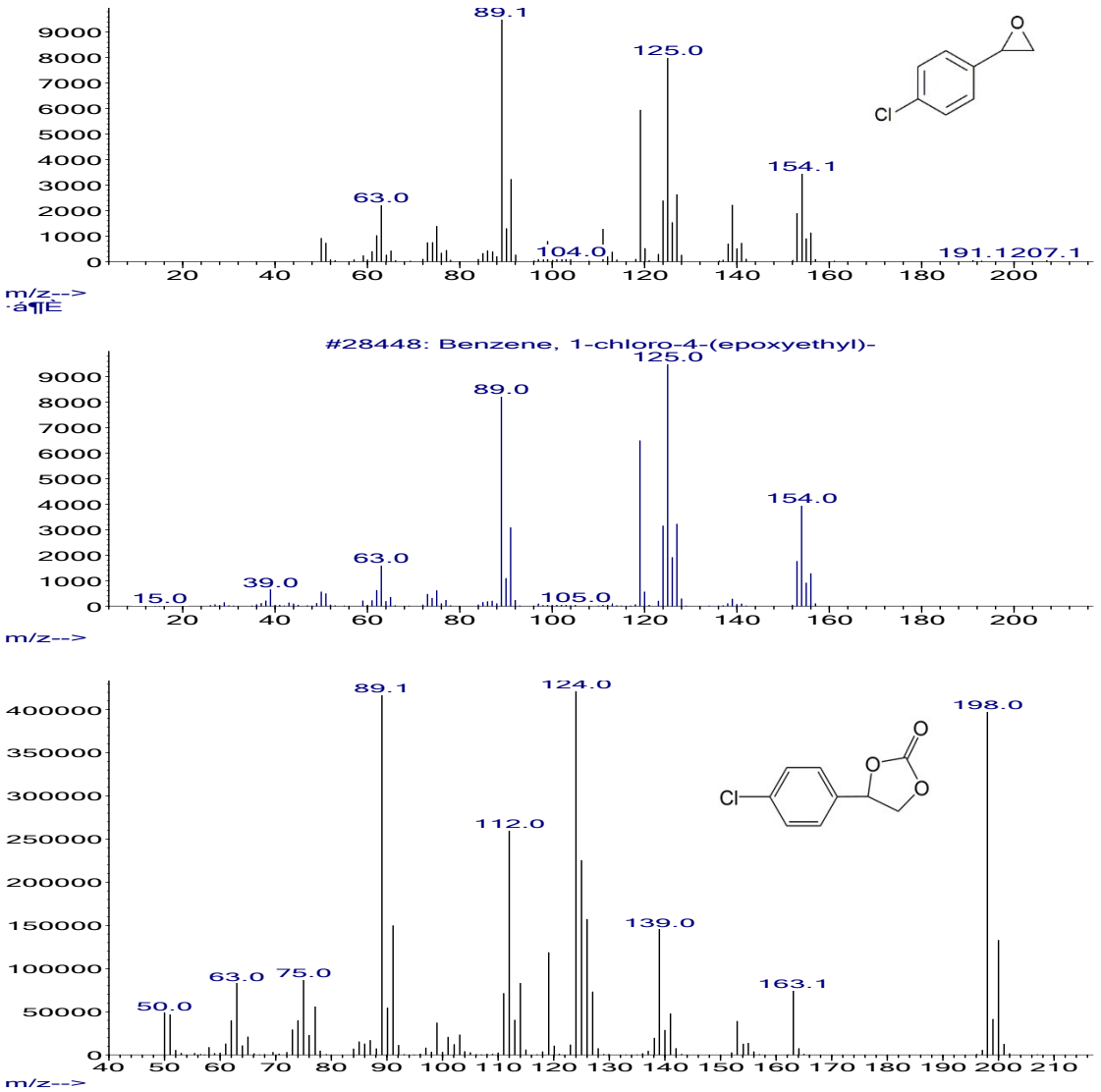


Fig. S24. The GC trace of 4-chlorostyrene oxidative carboxylation.





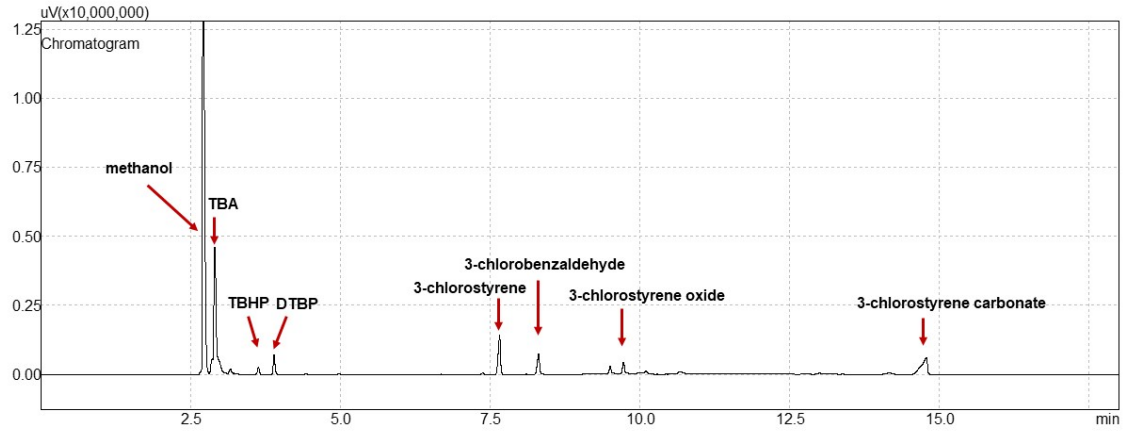
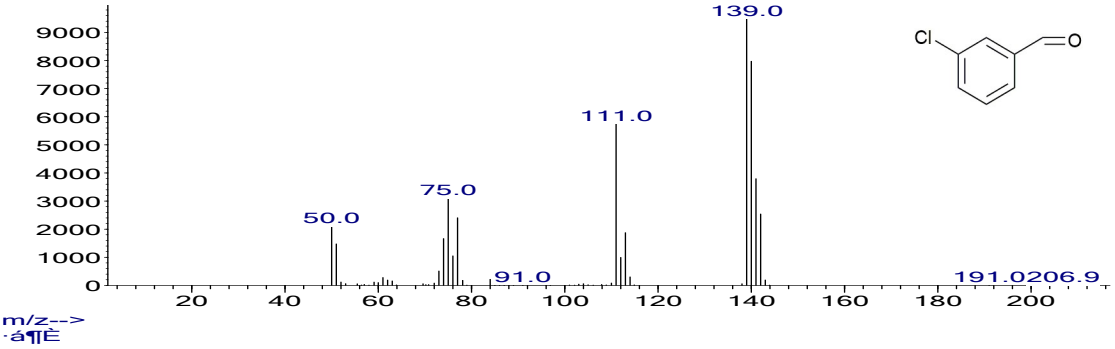
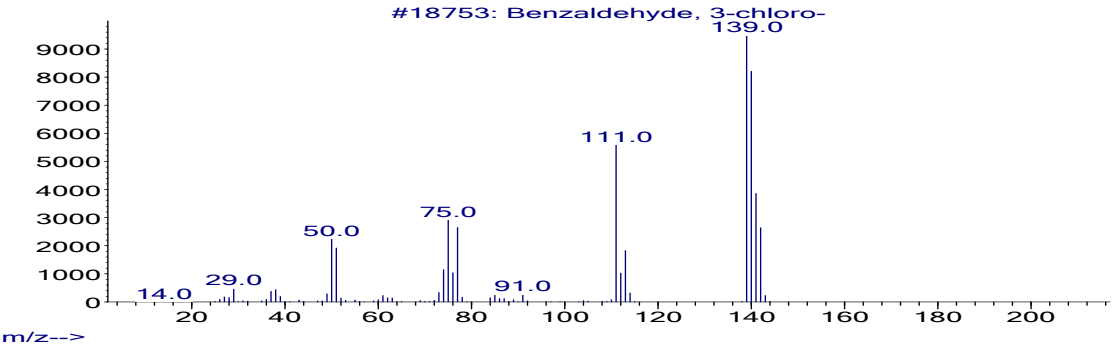
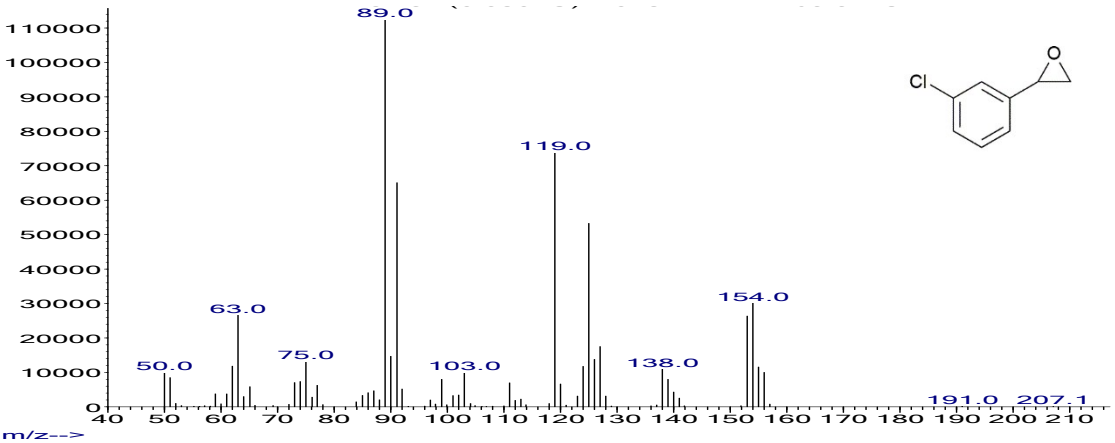
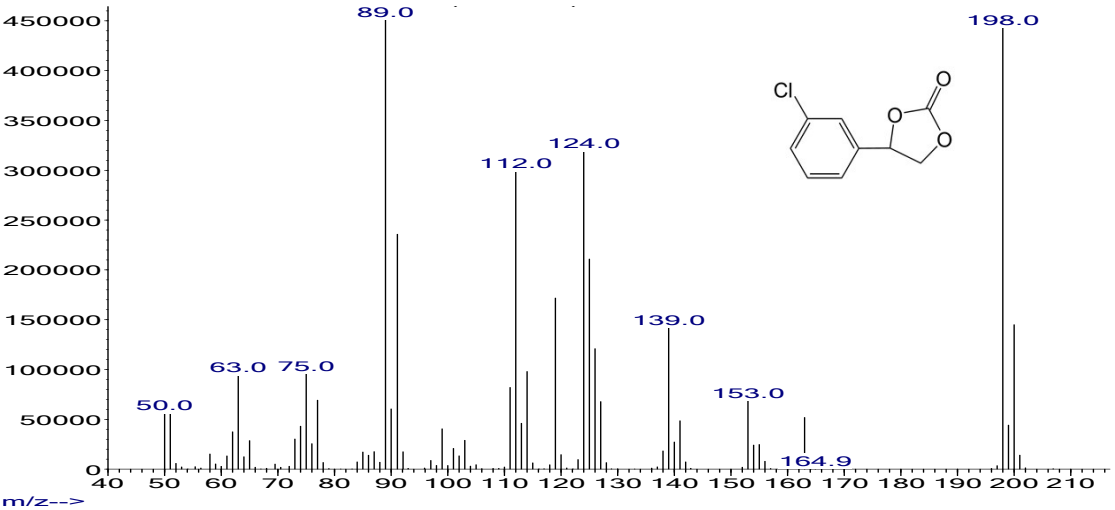


Fig. S25. The GC trace of 3-chlorostyrene oxidative carboxylation.


139.0
111.0
75.0
50.0
91.0
191.0206.9
m/z-->


#18753: Benzaldehyde, 3-chloro-
139.0
111.0
75.0
50.0
29.0
14.0
91.0
m/z-->


89.0
119.0
63.0
154.0
50.0
75.0
103.0
138.0
191.0 207.1
m/z-->


89.0
198.0
124.0
112.0
139.0
63.0
75.0
50.0
153.0
164.9
m/z-->

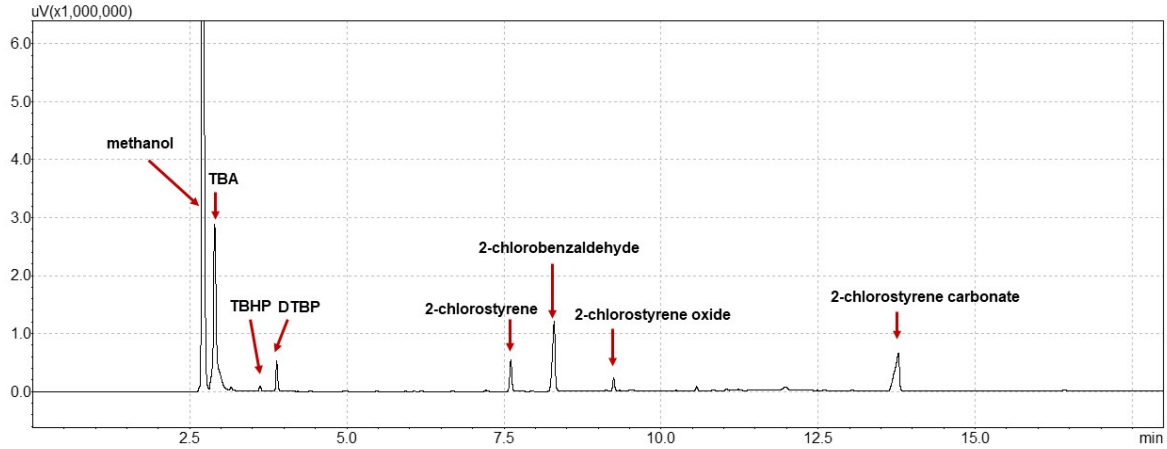
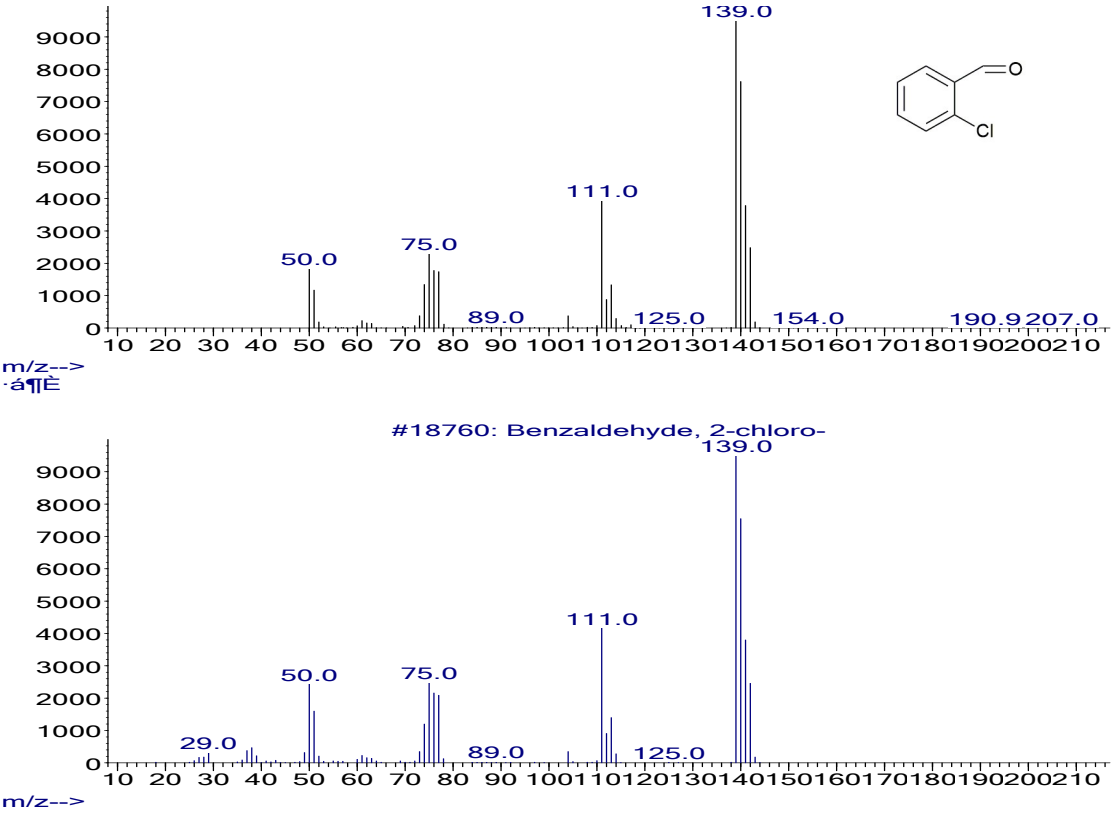
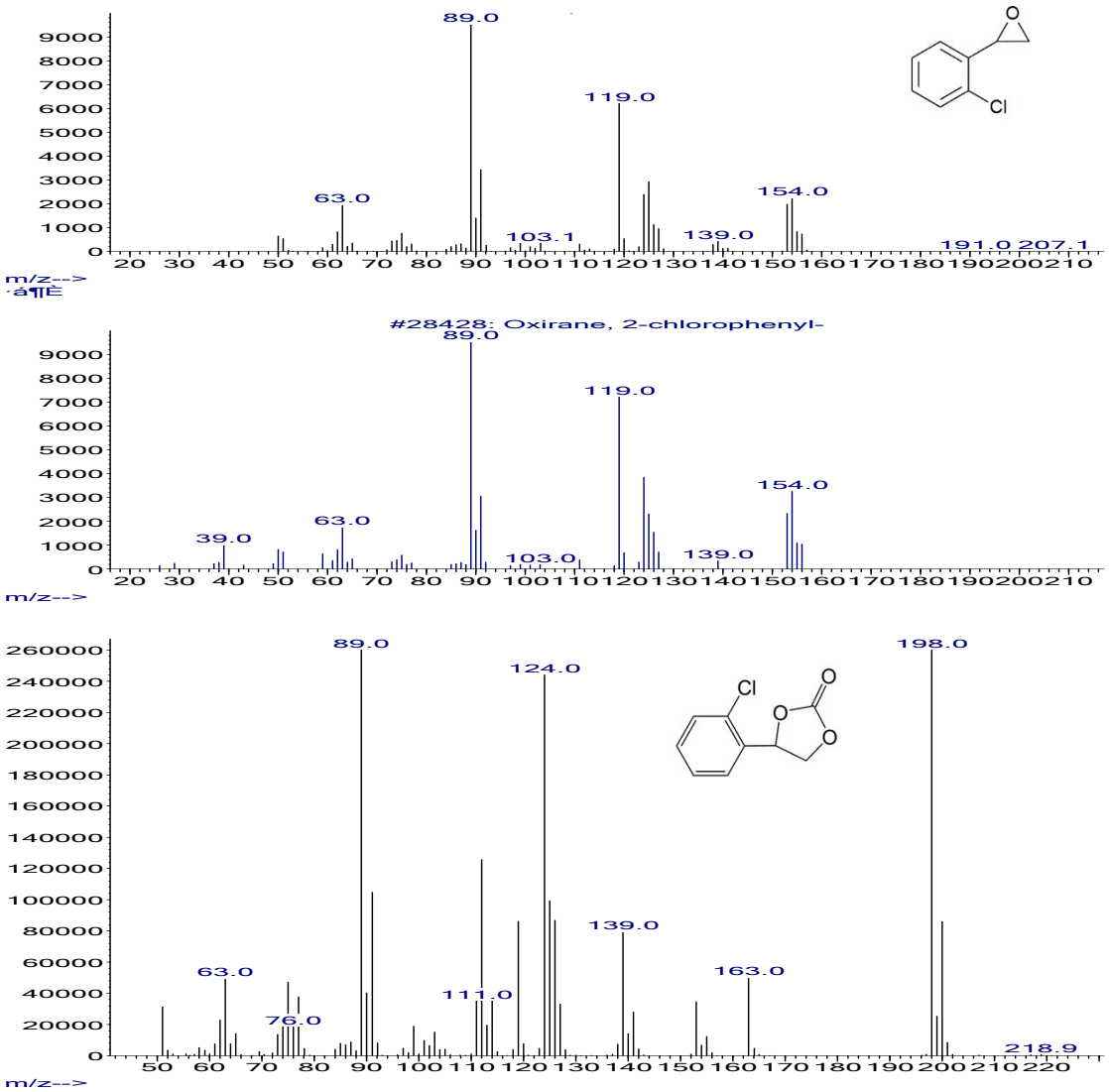


Fig. S26. The GC trace of 2-chlorostyrene oxidative carboxylation.





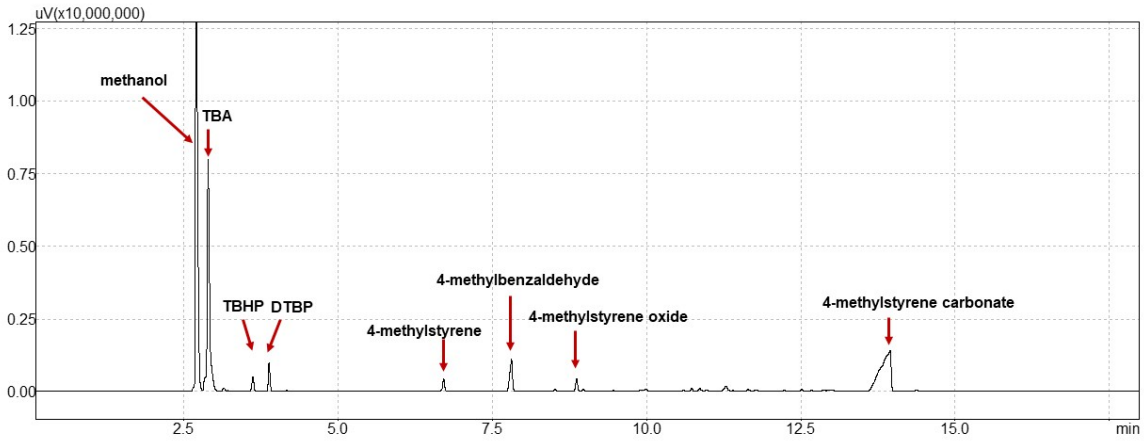
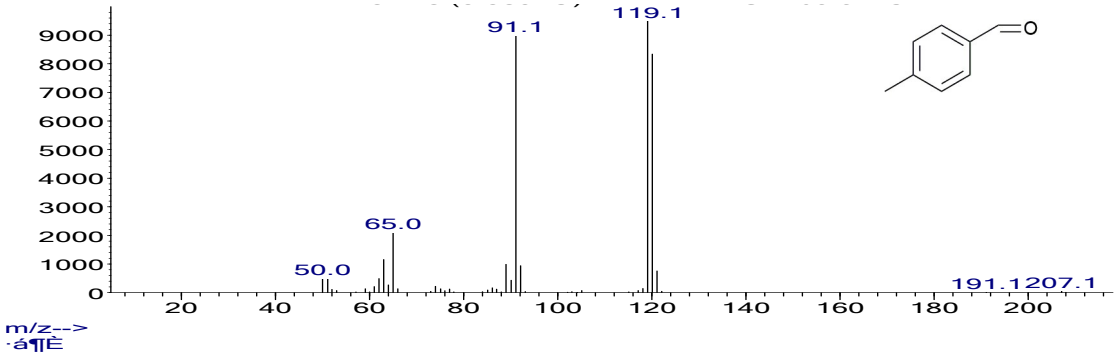
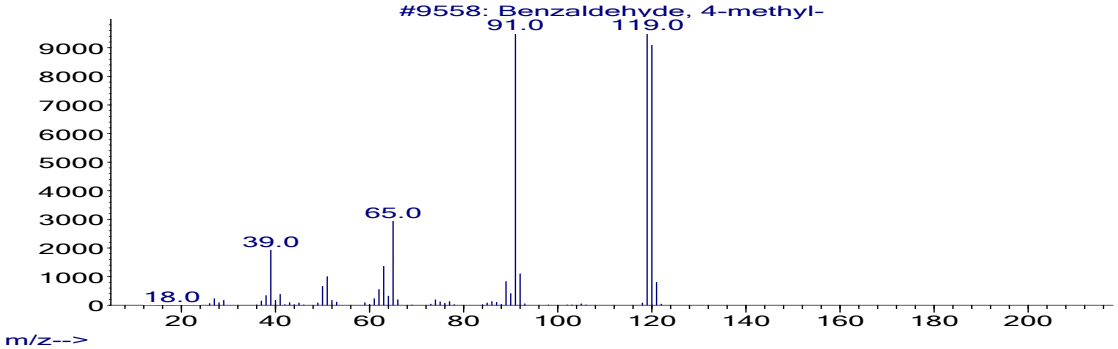
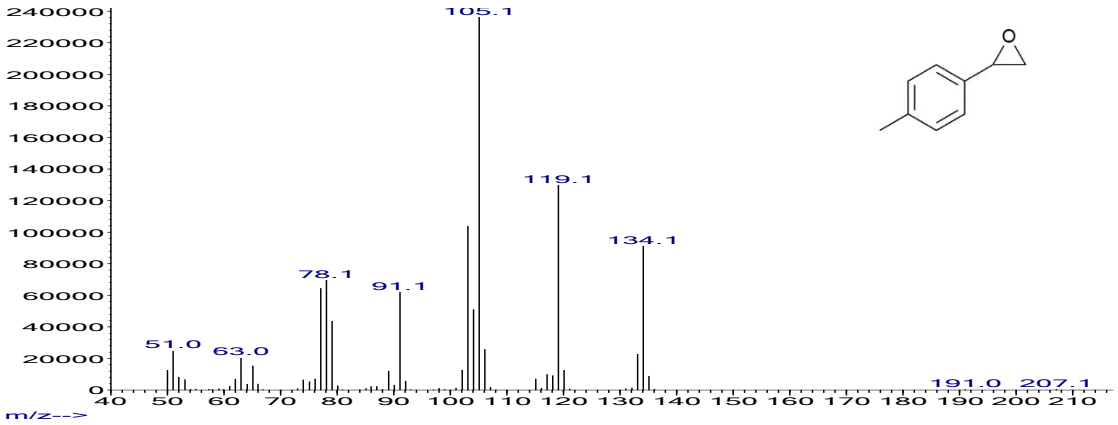


Fig. S27. The GC trace of 4-methylstyrene oxidative carboxylation.


119.1
91.1
65.0
50.0
191.1207.1
m/z-->


#9558: Benzaldehyde, 4-methyl-
91.0
119.0
65.0
39.0
18.0
m/z-->


105.1
119.1
134.1
78.1
91.1
51.0
63.0
191.0 207.1
m/z-->

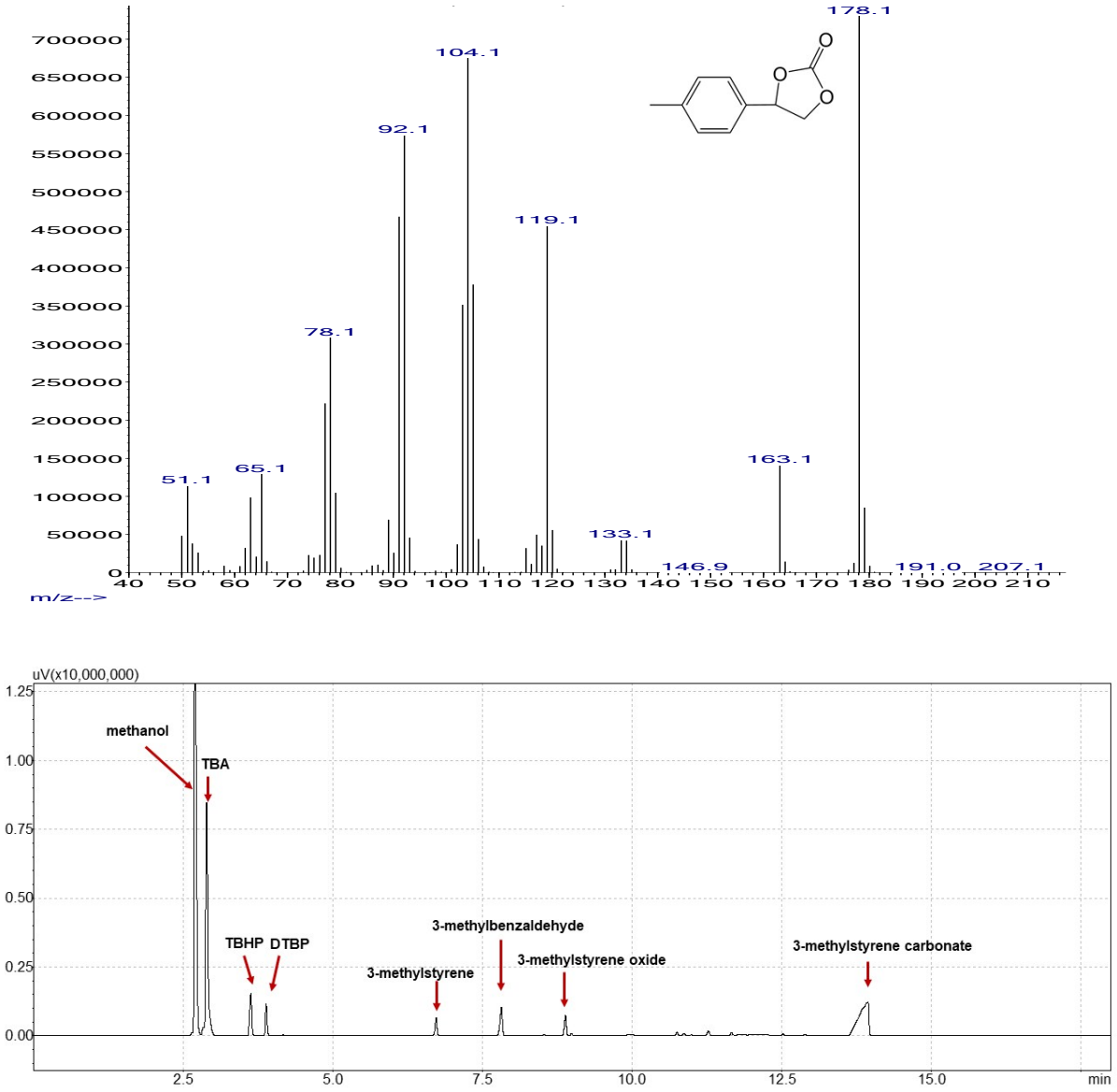
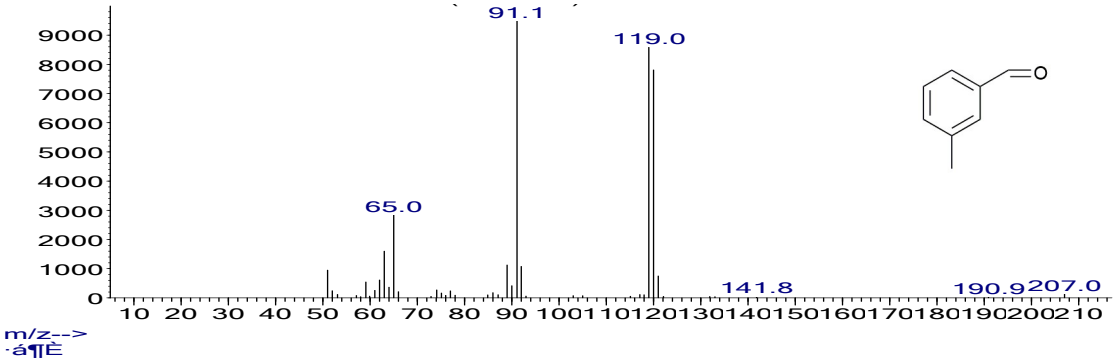
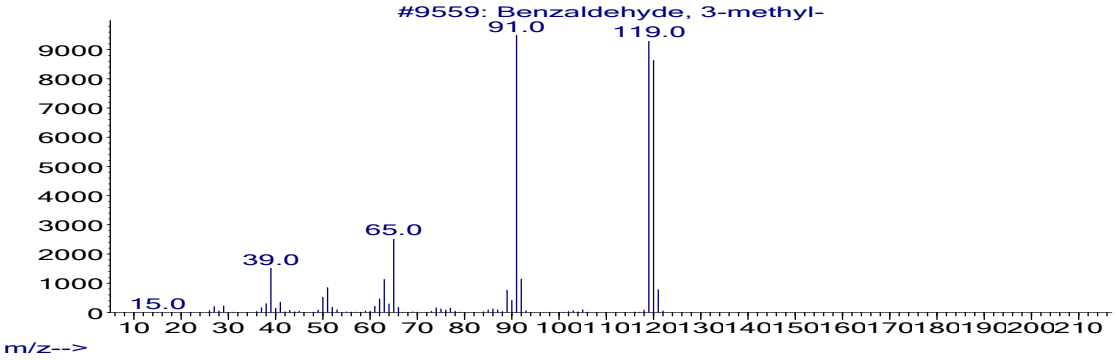
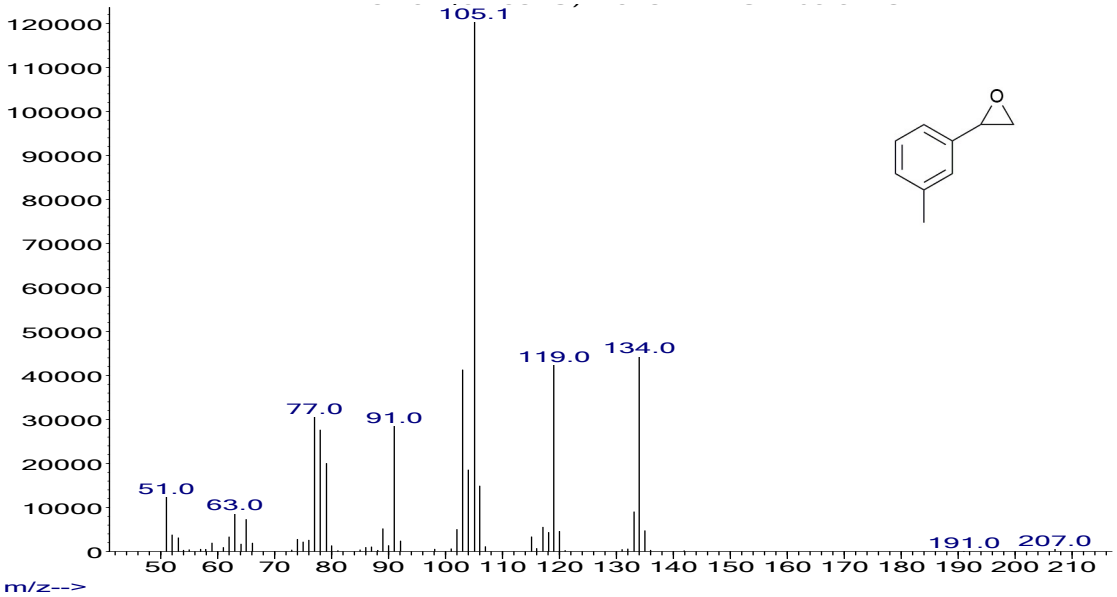
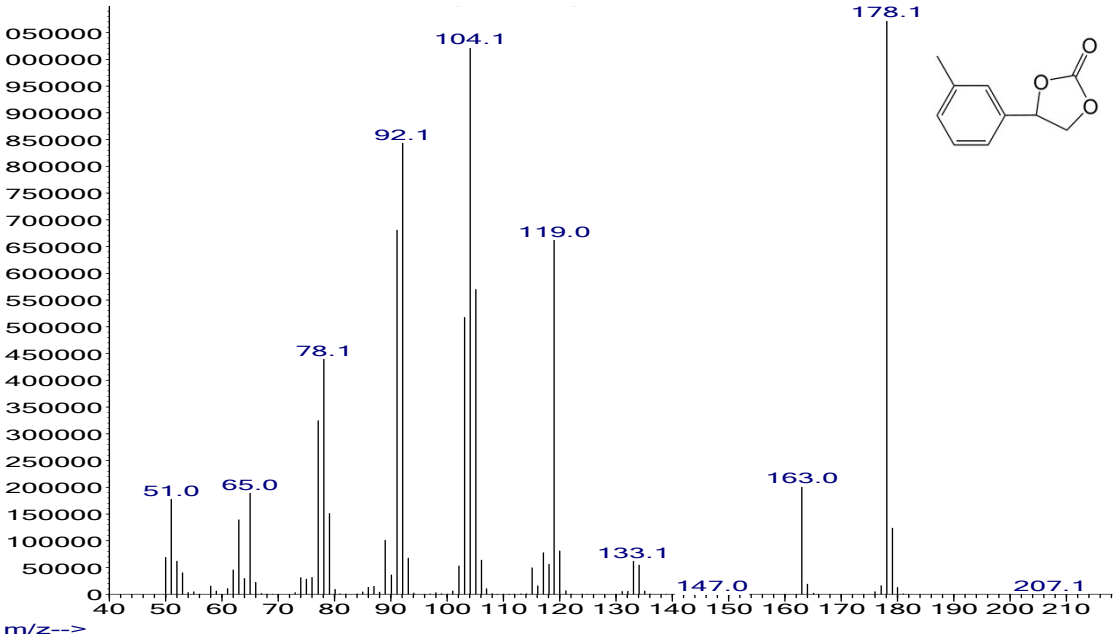


Fig. S28. The GC trace of 3-methylstyrene oxidative carboxylation.


91.1
119.0
65.0
141.8
190.9207.0
m/z-->


#9559: Benzaldehyde, 3-methyl-
91.0
119.0
65.0
39.0
15.0
m/z-->


105.1
119.0
134.0
77.0
91.0
51.0
63.0
191.0 207.0
m/z-->


178.1
104.1
92.1
119.0
78.1
51.0
65.0
163.0
133.1
147.0
207.1
m/z-->