

Supporting Information

**Syntheses of Cyclic Carbonates with Amidinium Halide Catalysts in
Reusable, Reversible, Room-Temperature Ionic Liquids or
Acetonitrile**

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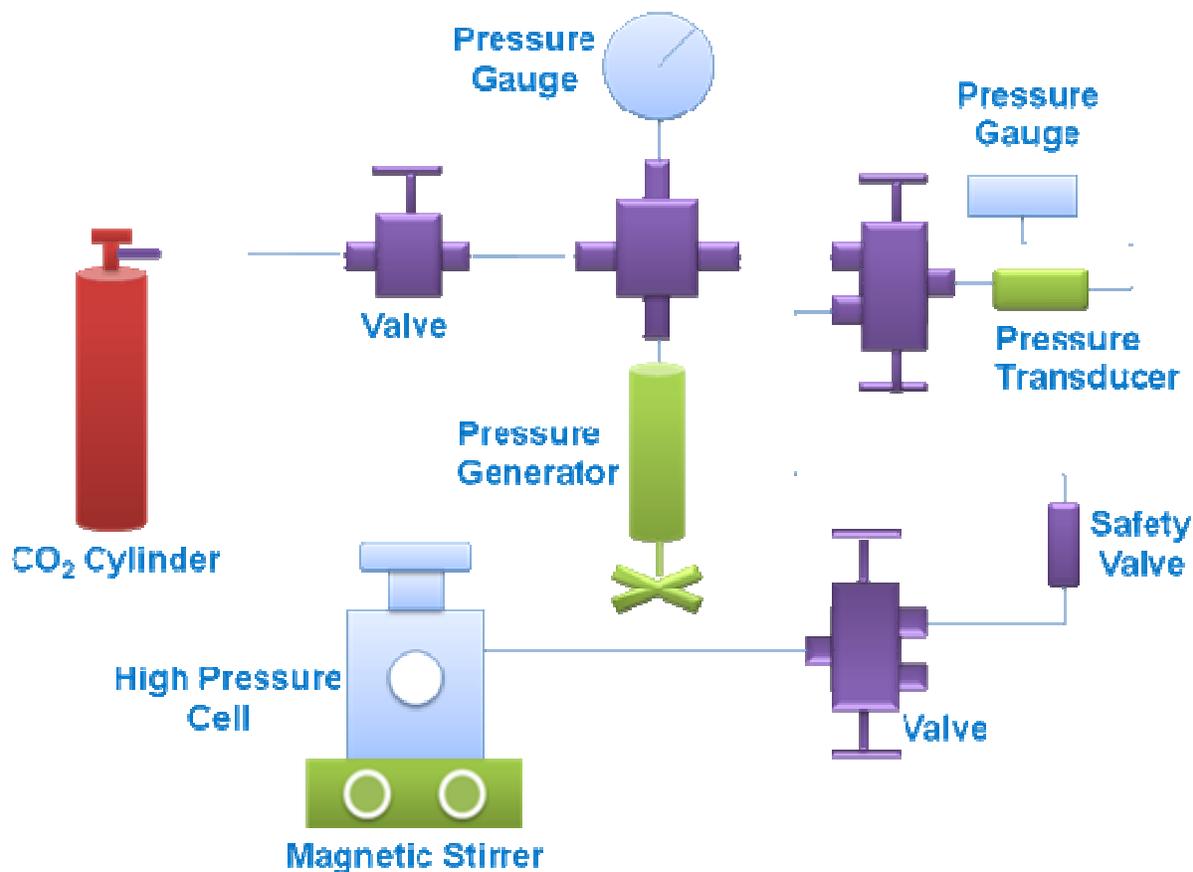


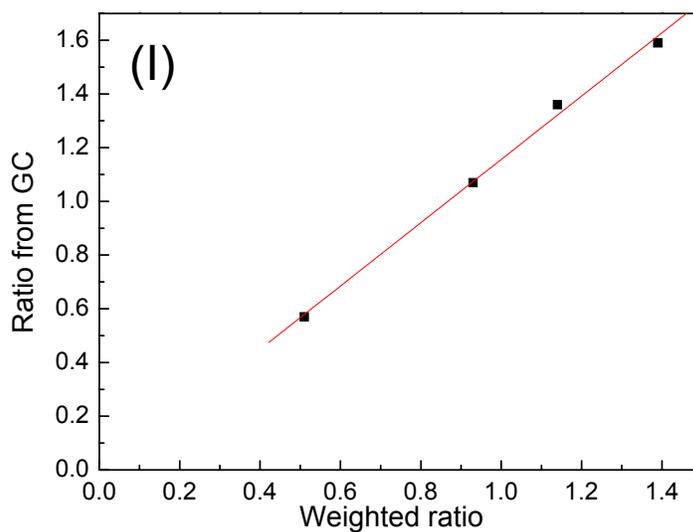
Figure S1. High pressure CO₂ generator and reaction cell (upper left) and temperature control setup (upper right). The reaction cell is indicated by the arrow in both figures. The layout of the components of the high pressure instrument is shown in the diagram at the bottom.

The stainless steel reaction cell, with three quartz windows, was designed and manufactured at the University of Buenos Aires (Argentina). Super-ambient temperatures were achieved with four cartridge electric heating elements and a rheostat in a system. Temperature was monitored by an Omega HH503 microprocessor thermometer connected to a J-K-T thermocouple. High pressure generators (Model: 50-6-15; Pressure rating: 15,000 psi; capacity per stroke: 20 mL), valves and tubings were purchased from High Pressure Equipment Company (HIP), Pennsylvania. The 0-25000 psi pressure gauge was purchased from McDaniel Controls, Inc.

GC response factor calculations

$$F_i(\mathbf{R}\text{-molar}) = (\text{area}_{\text{refer}}/\text{mol}_{\text{refer}})/(\text{area}_{\text{comp}}/\text{mol}_{\text{comp}}) \quad (\text{S1})$$

The response factor ($F_i(\mathbf{R}\text{-molar})$) was calculated according to eq S1.¹ Here, $\text{area}_{\text{refer}}$ and $\text{area}_{\text{comp}}$ are the areas of the peaks of a reference compound (biphenyl) and an **a** epoxide or a **b** product, respectively. $\text{mol}_{\text{refer}}$ and mol_{comp} are the known (by preparation) concentrations of the biphenyl and **a** or **b**, respectively. From a plot of area ratios versus composition ratios in samples with known amounts of each, $F_i(\text{biphenyl}/\mathbf{b})$ and $F_i(\text{biphenyl}/\mathbf{a})$ were calculated; see Figure S2 for **2a** and **2b**, for example, where $F_i(\text{biphenyl}/\mathbf{2b}) = 1.18$ ($R^2 = 0.998$) and $F_i(\text{biphenyl}/\mathbf{2a}) = 1.20$ ($R^2 = 0.999$). Response factors for the other epoxides and cyclic carbonates are collected in Table S1.



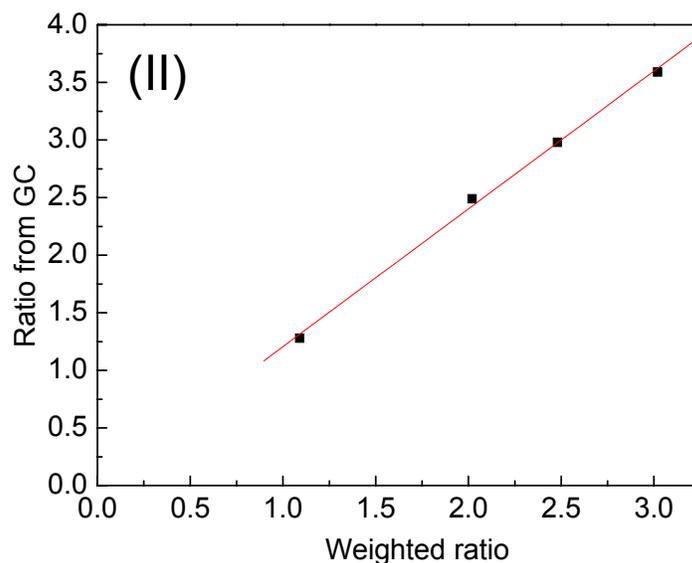


Figure S2. Linear fit of weight and GC peak ratios for biphenyl/**2b** (I) and biphenyl/**2a** (II). The respective formulas are: $Y = -0.02 + 1.18X$ for **2a** and $Y = 0.01 + 1.20X$ for **2b**.

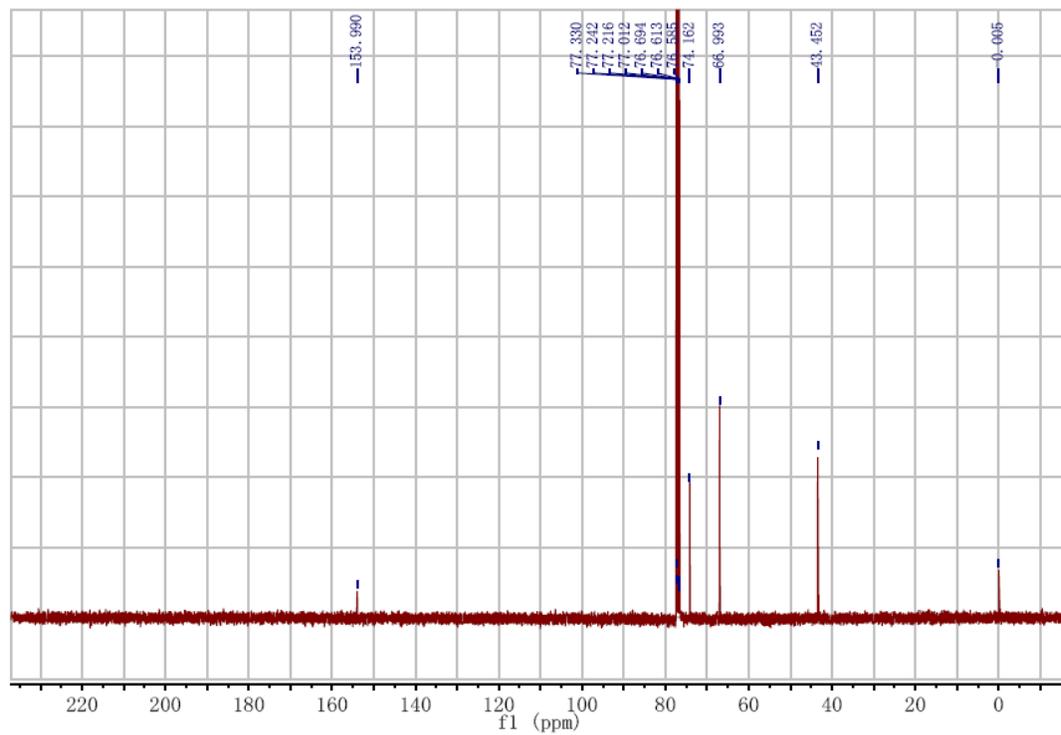
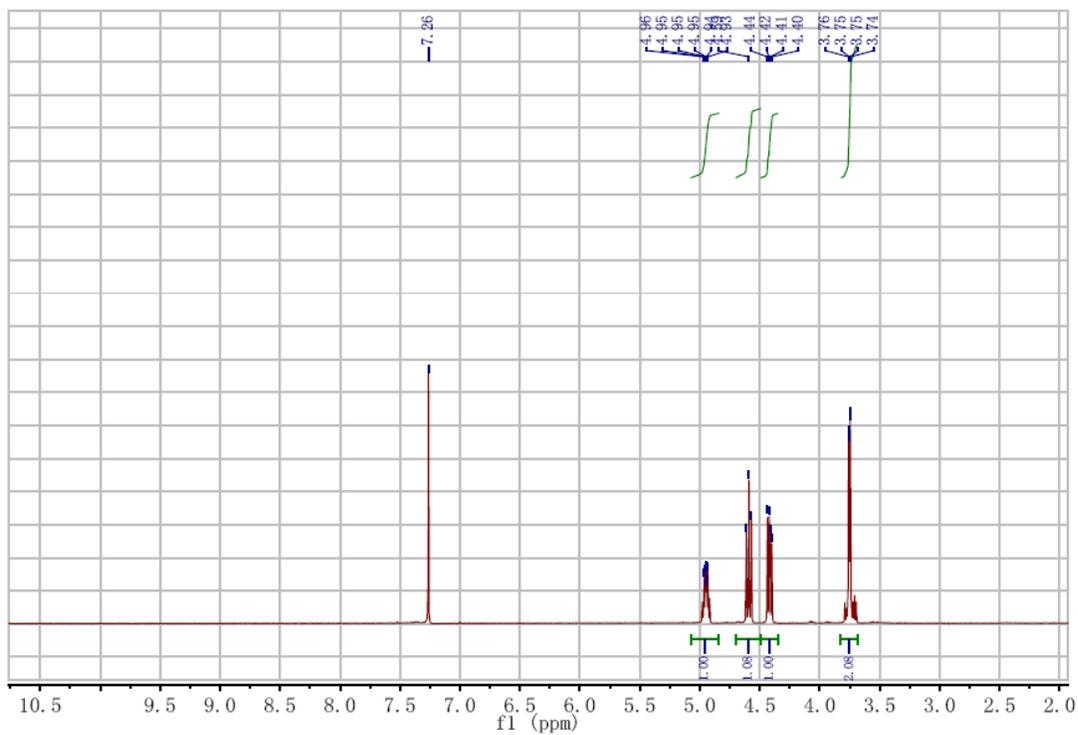
Table S1. GC response factors of **1a-4a** and **1b-4b**.

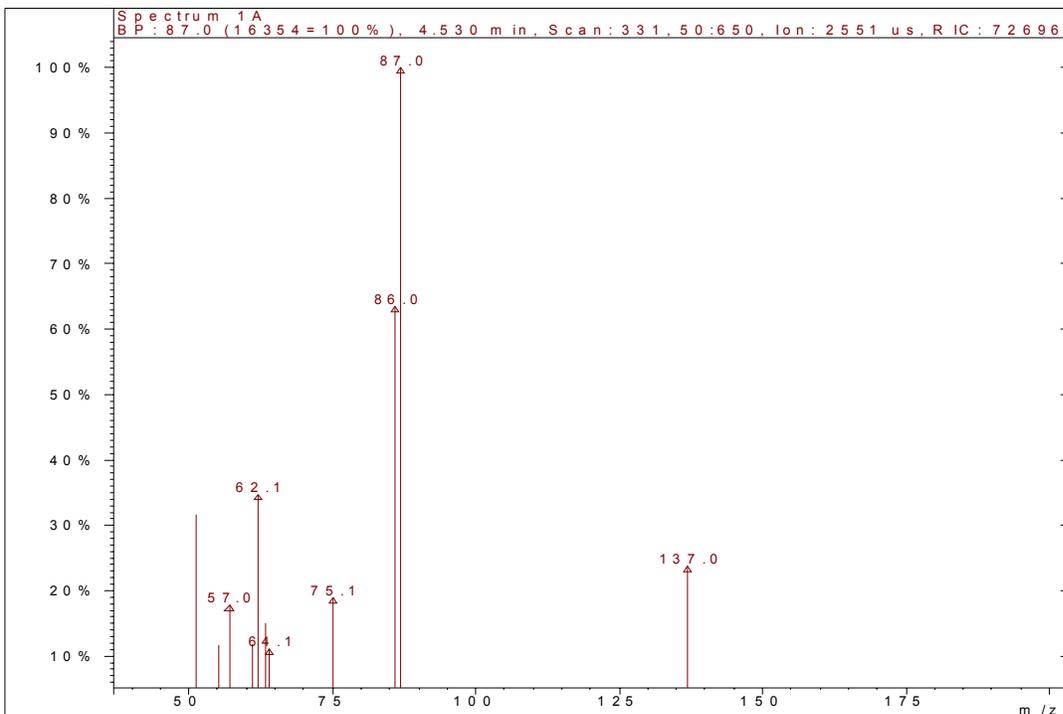
Substrate	Response Factor	Substrate	Response Factor
1a	1.16	1b	1.15
2a	1.20	2b	1.18
3a	1.12	3b	1.14
4a	1.08	4b	1.09

Characterizations of cyclic carbonates

4-Chloromethyl-1,3-dioxolan-2-one (**1b**): ^1H NMR: d = 3.75 - 3.81 (m, 2 H, ClCH_2), 4.41 (dd, $J = 6.0, 9.0$ Hz, 1 H, OCH_2), 4.59 (dd, $J = 8.4, 9.0$ Hz, 1H, OCH_2), 4.93 - 4.96 (m, 1 H, CHO); ^{13}C NMR: δ 43.71, 66.90, 74.35, 154.30 ppm; IR: 1786 cm^{-1} (C=O); MS (m/z 137 M^+).

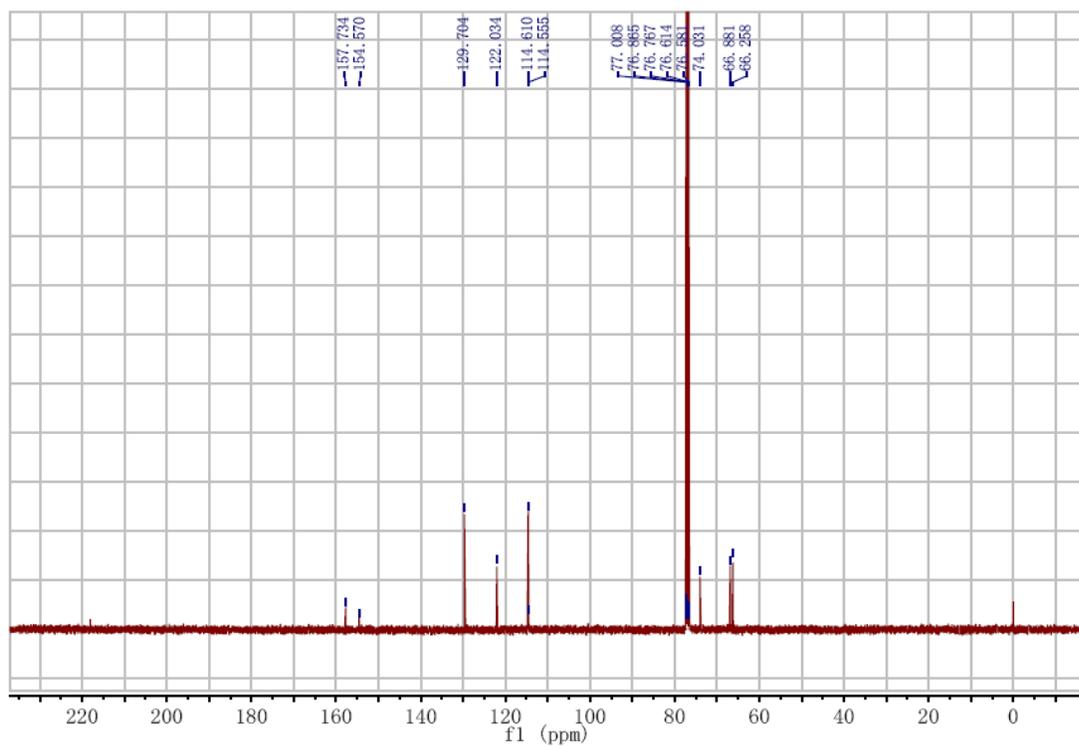
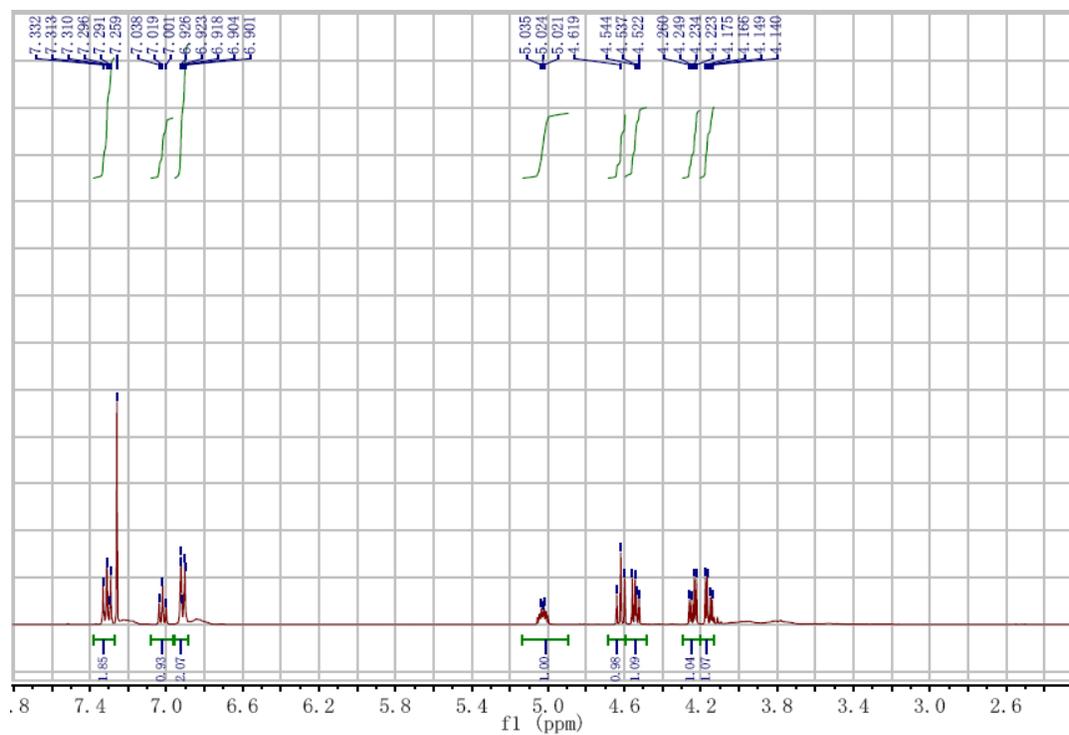
^1H NMR, ^{13}C NMR and mass spectra of 4-chloromethyl-1,3-dioxolan-2-one (**1b**)

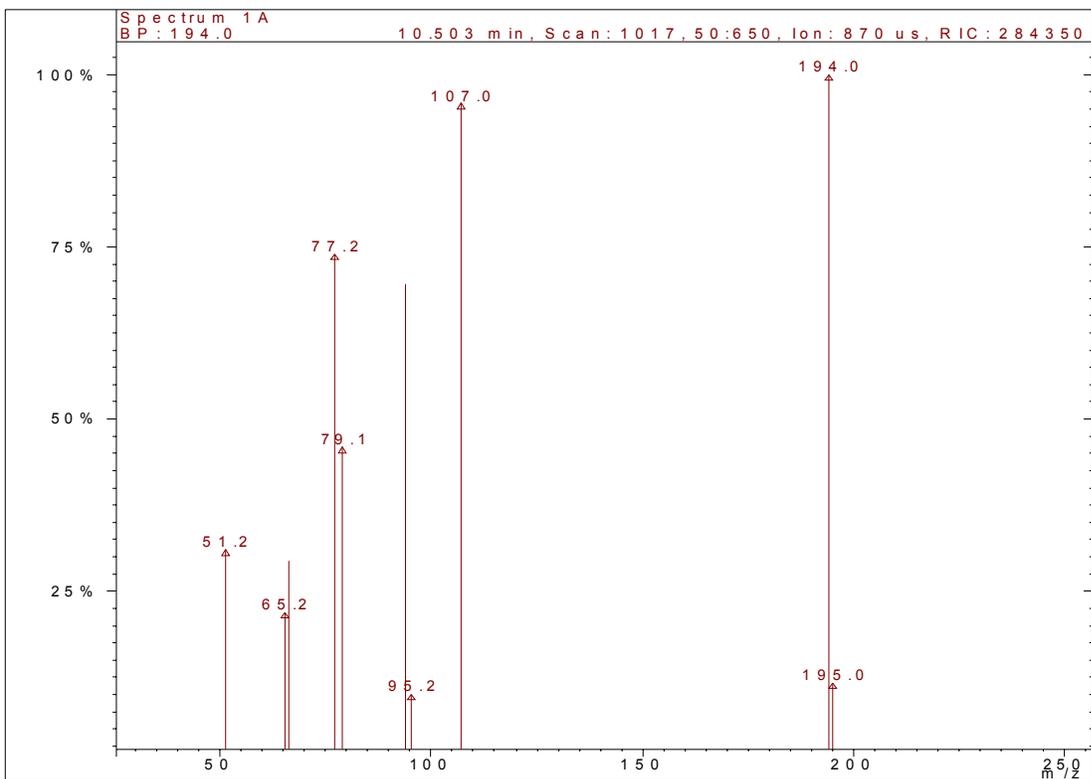




4-Phenoxymethyl-1,3-dioxolan-2-one (**2b**): ^1H NMR: 4.15 (dd, $J = 3.6, 3.6$ Hz 1H, OCH_2), 4.24 (dd, $J = 4.4, 4.4$ Hz 1H, OCH_2), 4.55 (dd, 1H, PhOCH_2), 4.62 (t, $J = 8.4$ Hz, 1H, PhOCH_2), 5.03 (m, 1H, OCH), 6.91 (d, $J = 8.8$ Hz, 2H, Ph), 7.02 (t, $J = 8.0$ Hz, 1H, Ph), 7.31 (t, $J = 8.0$ Hz, 2H, Ph); ^{13}C NMR: δ 66.25, 66.88, 74.03, 114.55, 122.03, 129.70, 154.57, 157.73 ppm; IR: 1786 cm^{-1} ($\text{C}=\text{O}$); MS (m/z 194, M^+).

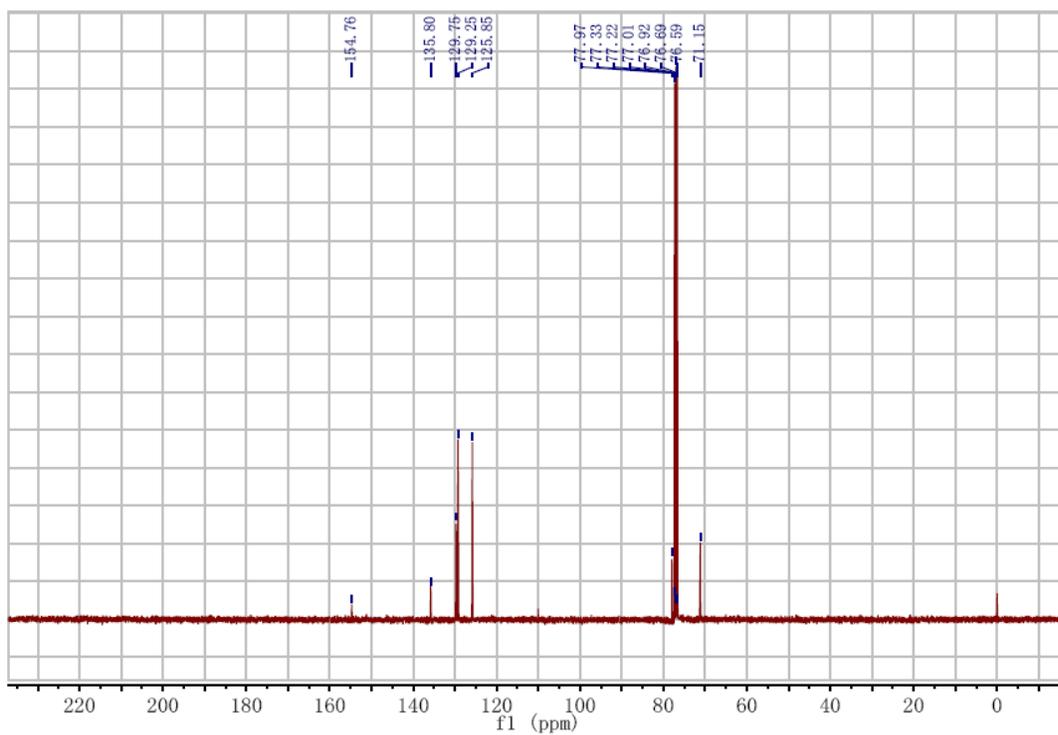
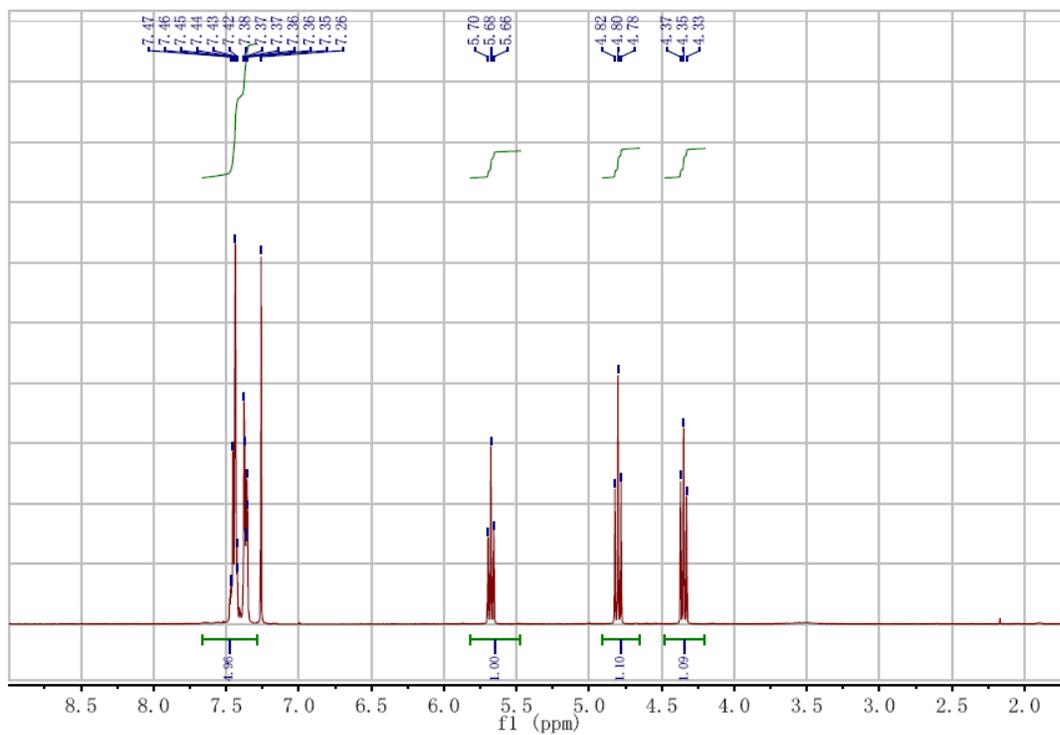
^1H NMR, ^{13}C NMR and mass spectra of 4-phenoxymethyl-1,3-dioxolan-2-one (**2b**)

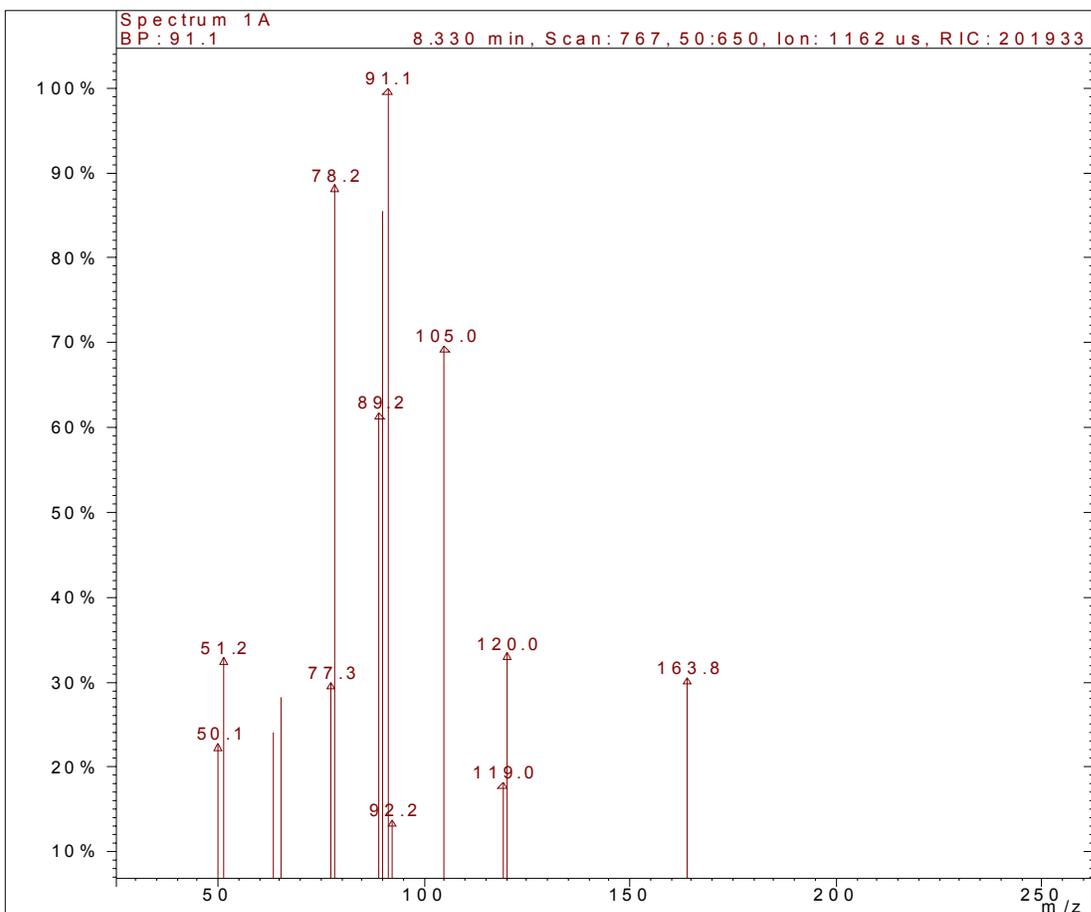




4-Phenyl-1,3-dioxolan-2-one (**3b**): ^1H NMR: δ = 4.36 (t, J = 8.4 Hz, 1 H, OCH_2), 4.82 (t, J = 8.4 Hz, 1 H, OCH_2), 5.72 (t, J = 8.4 Hz, 1 H, OCH), 7.36 (m, 2 H, Ph), 7.44 (m, 3 H, Ph); ^{13}C NMR: δ 71.15, 77.97, 125.85, 129.25, 129.75, 135.80, 154.76 ppm; IR: 1780 cm^{-1} ($\text{C}=\text{O}$); MS (m/z 164 M^+).

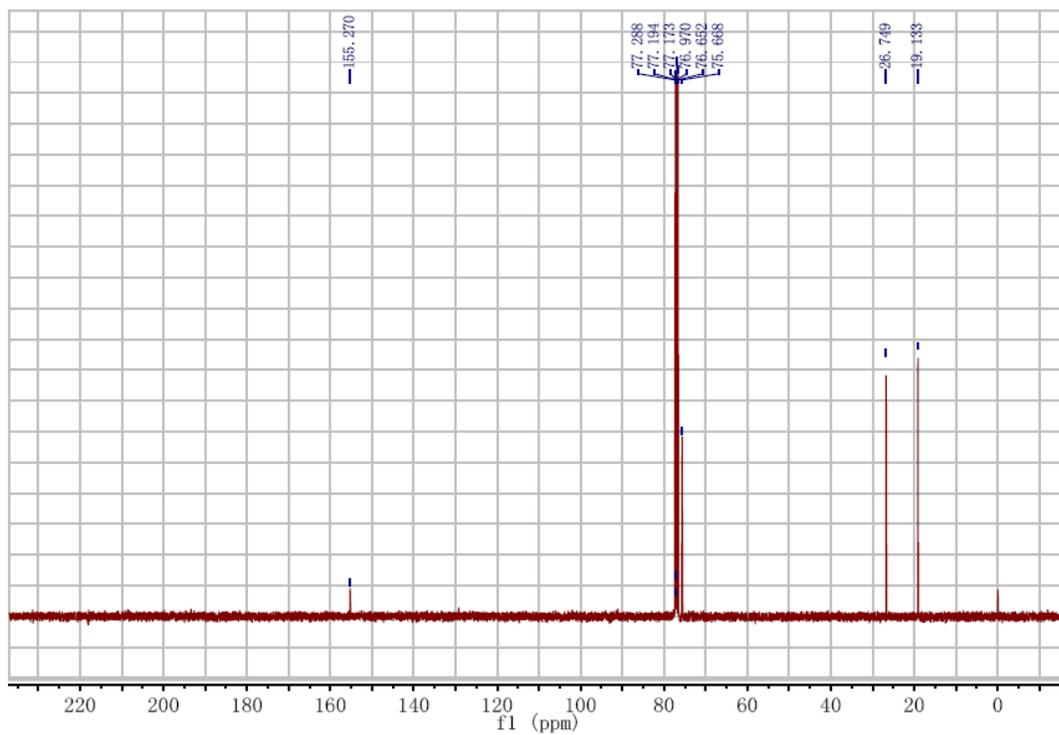
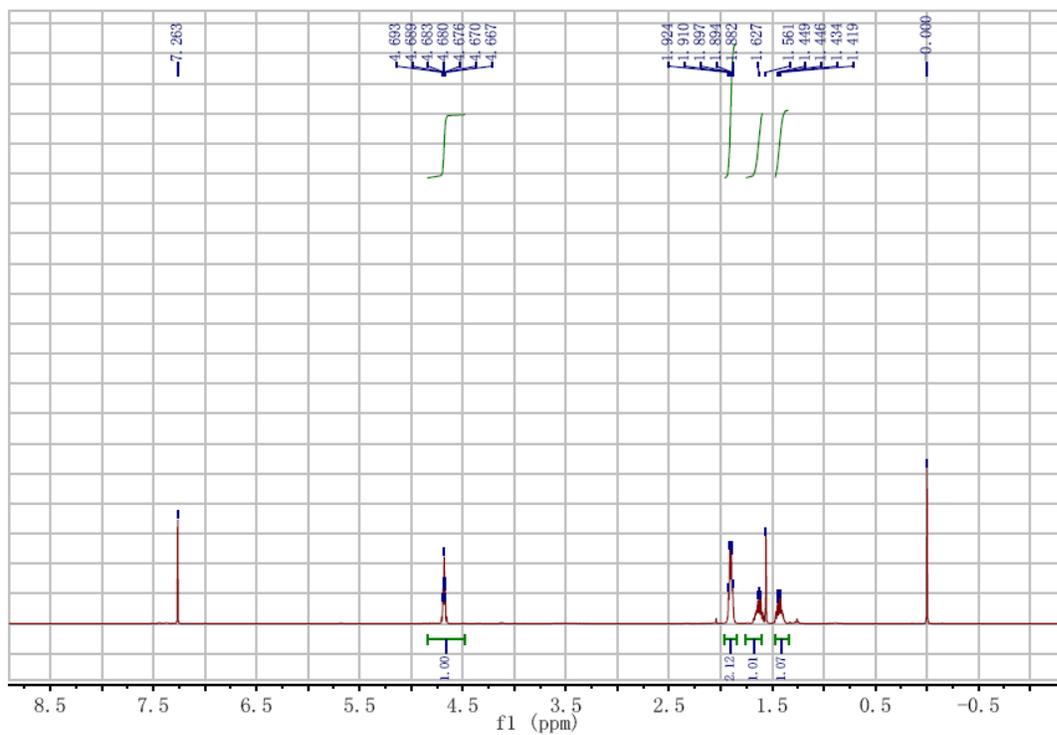
^1H NMR, ^{13}C NMR and mass spectra of 4-phenyl-1,3-dioxolan-2-one (**3b**)

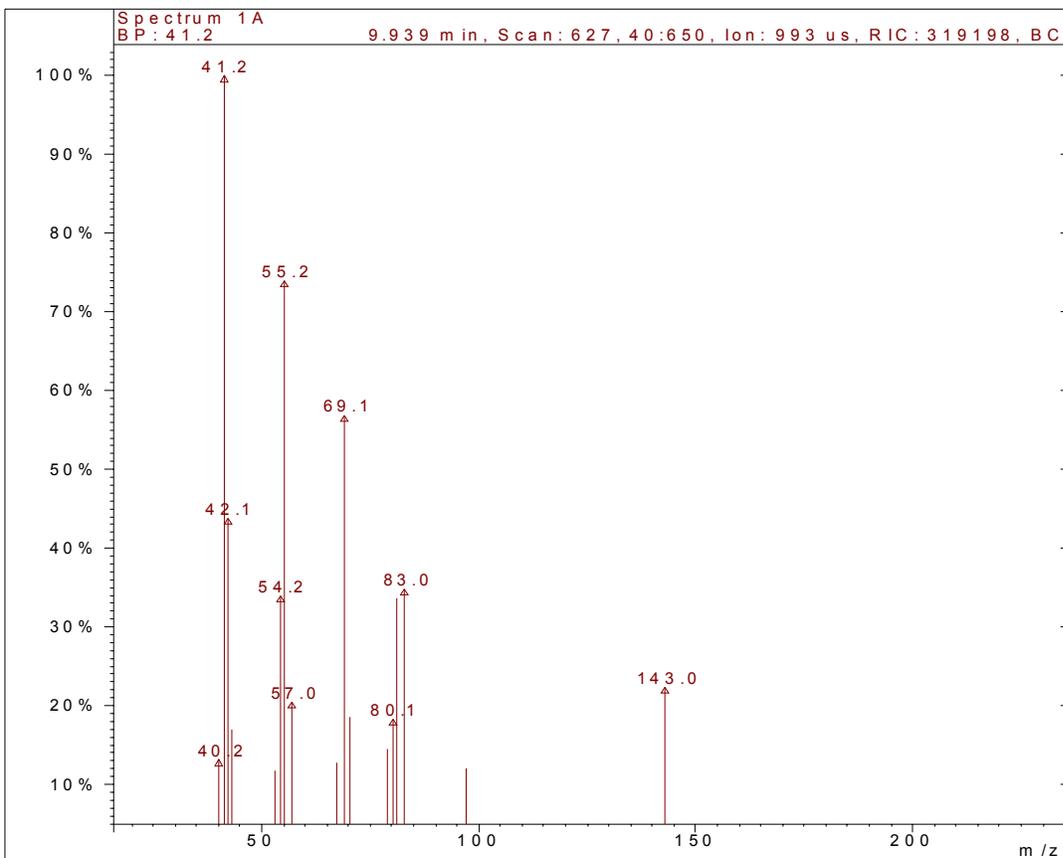




4,5-Tetramethylene-1,3-dioxolan-2-one (**4b**): ^1H NMR: d = 4.65 – 4.70 (m, 2 H, CHO), 1.86 – 1.90 (m, 4 H, CH_2CHO), 1.58–1.64 (m, 2 H, CH_2CH_2), 1.38–1.44 (m, 2 H, CH_2CH_2); ^{13}C NMR: δ 19.13, 26.75, 75.67, 155.27 ppm; IR: 1790 cm^{-1} ; MS (m/z 142 M^+).

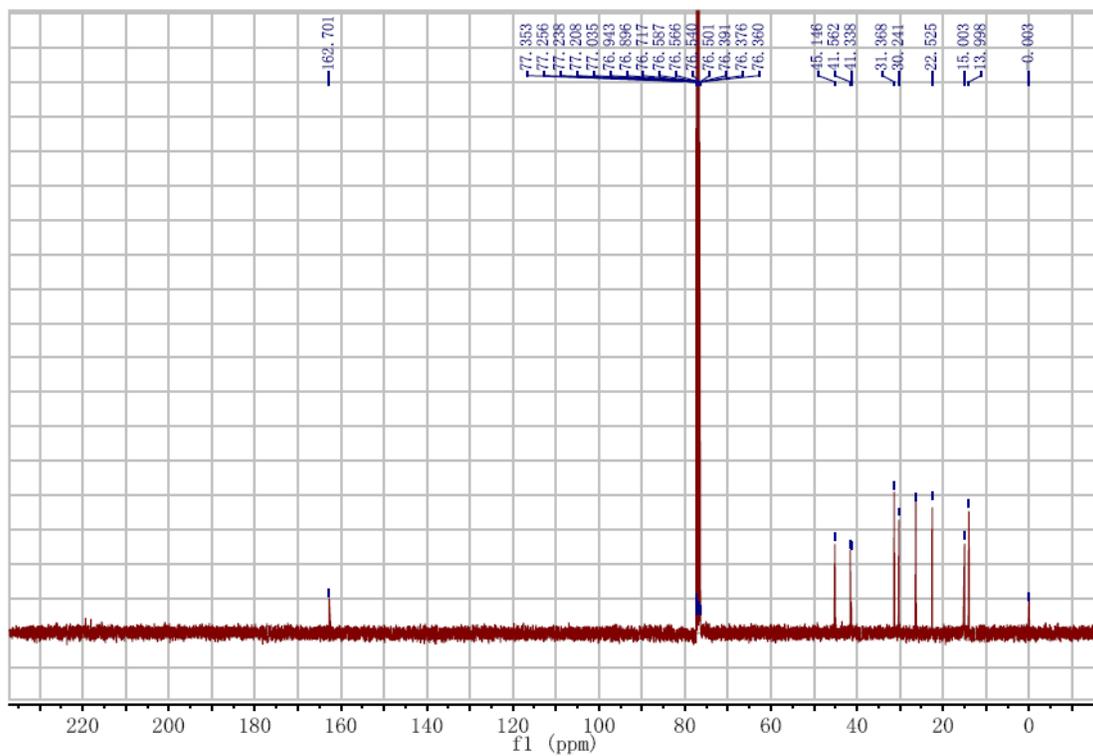
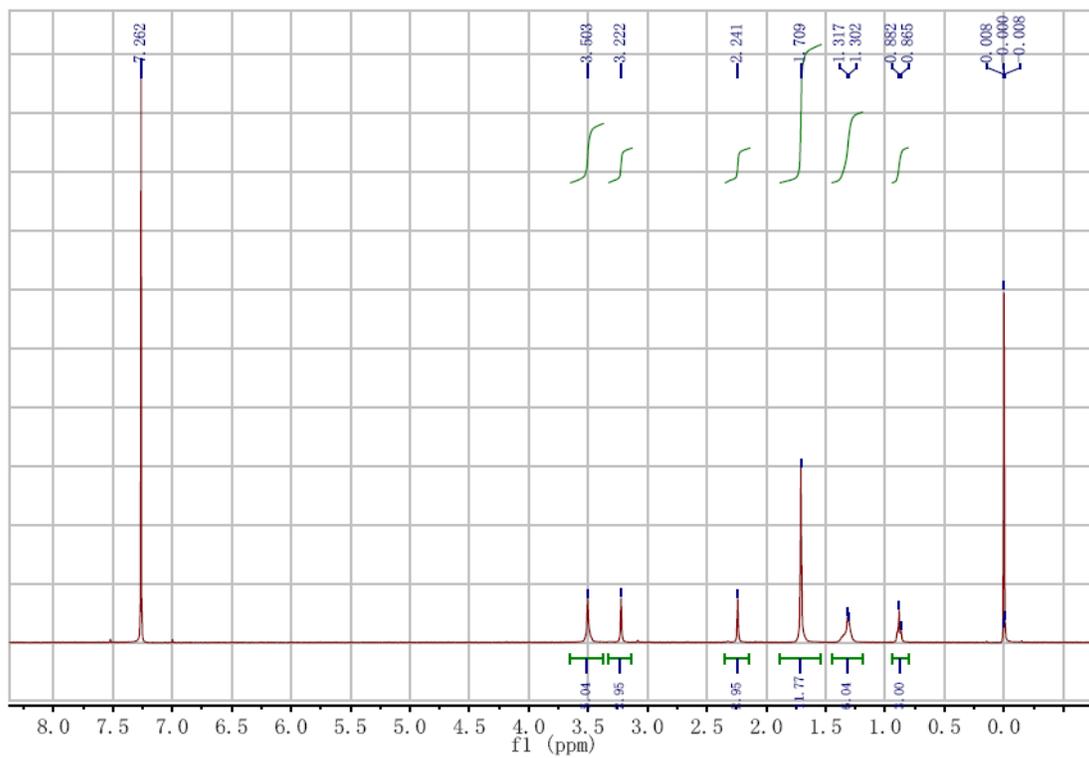
^1H NMR, ^{13}C NMR and mass spectra of 4,5-tetramethylene-1,3-dioxolan-2-one (**4b**)

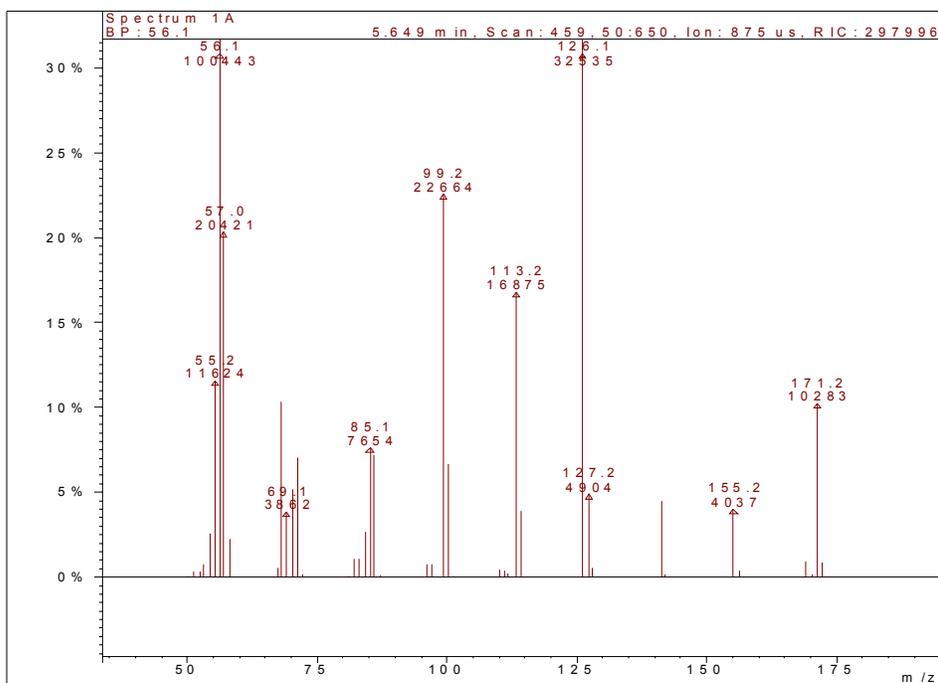
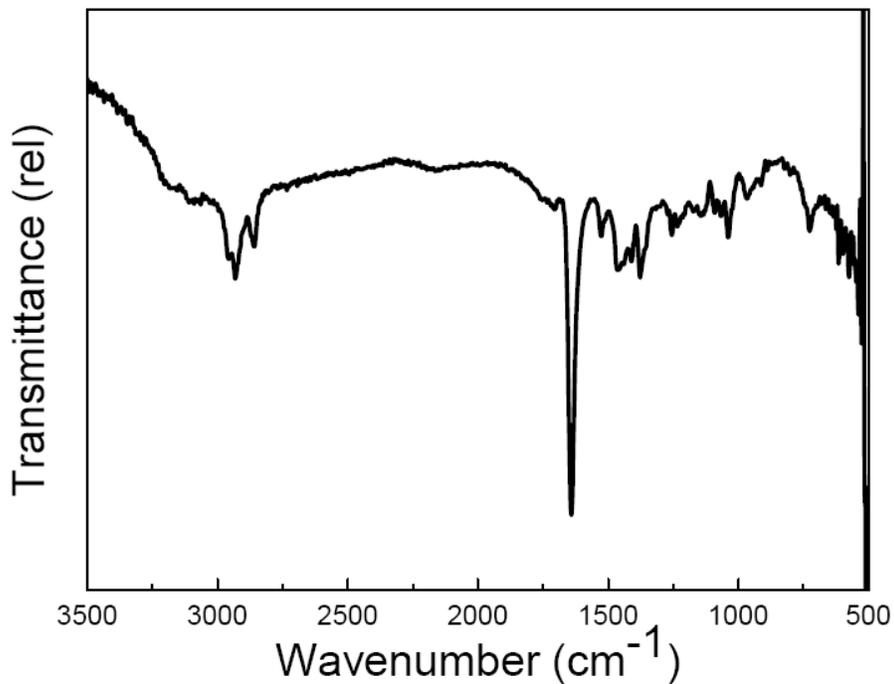




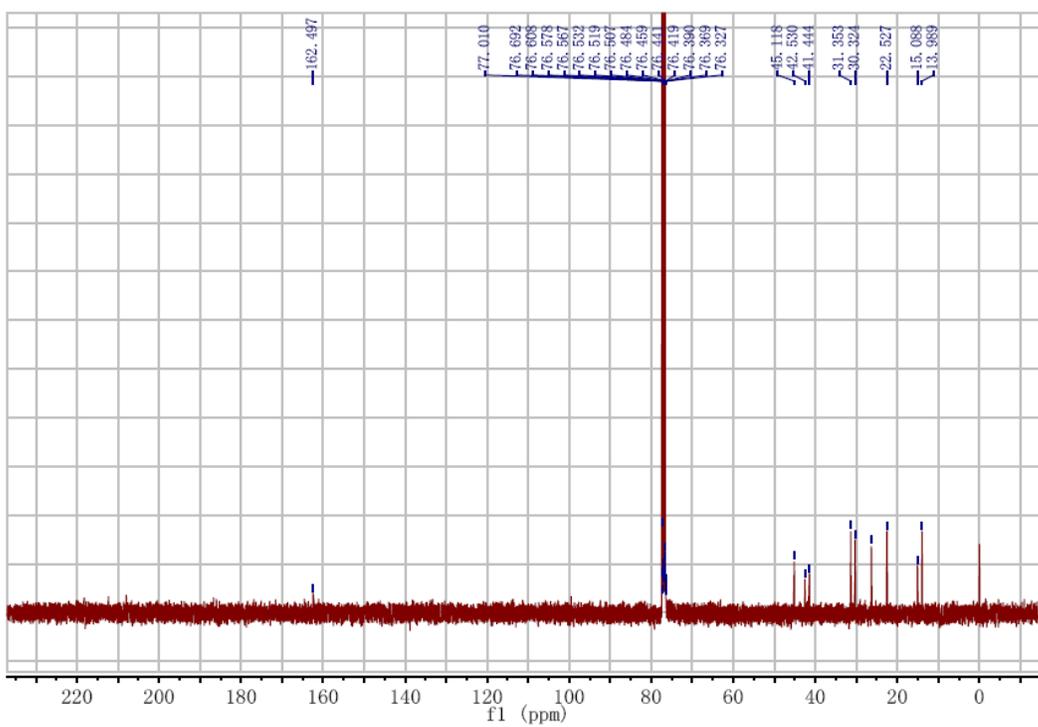
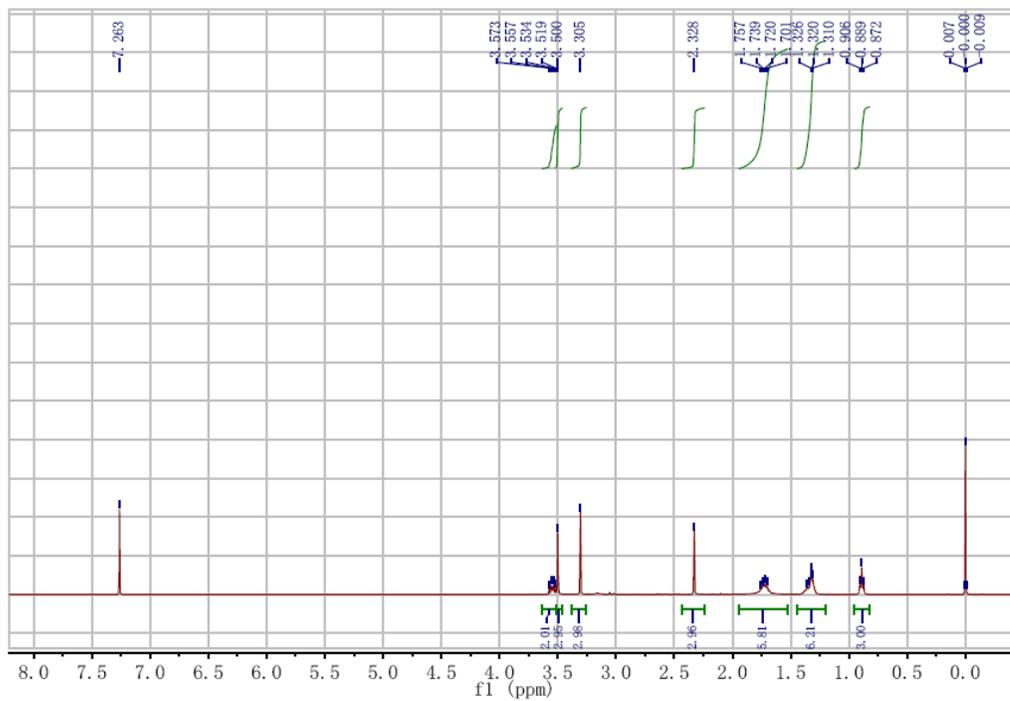
Characterization of amidinium halide catalysts

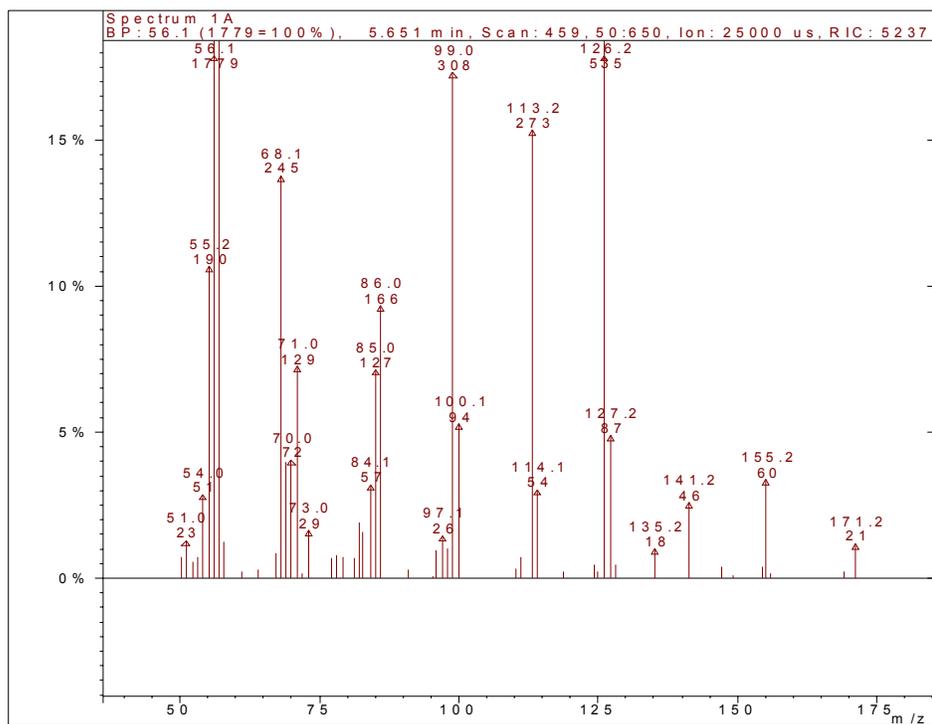
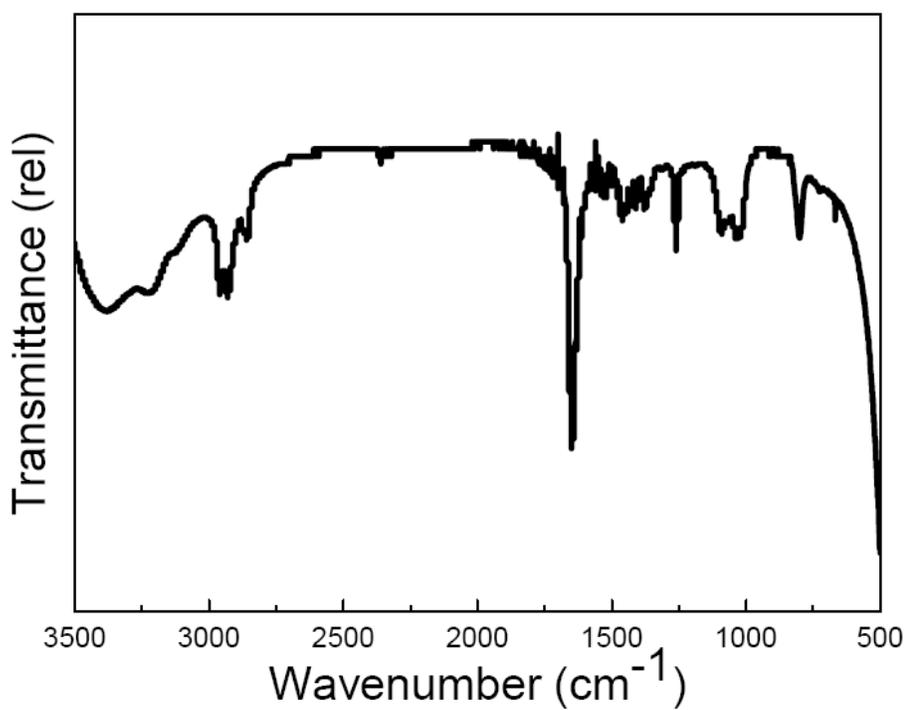
^1H NMR, ^{13}C NMR MS and FT-IR spectra of C6-HCl



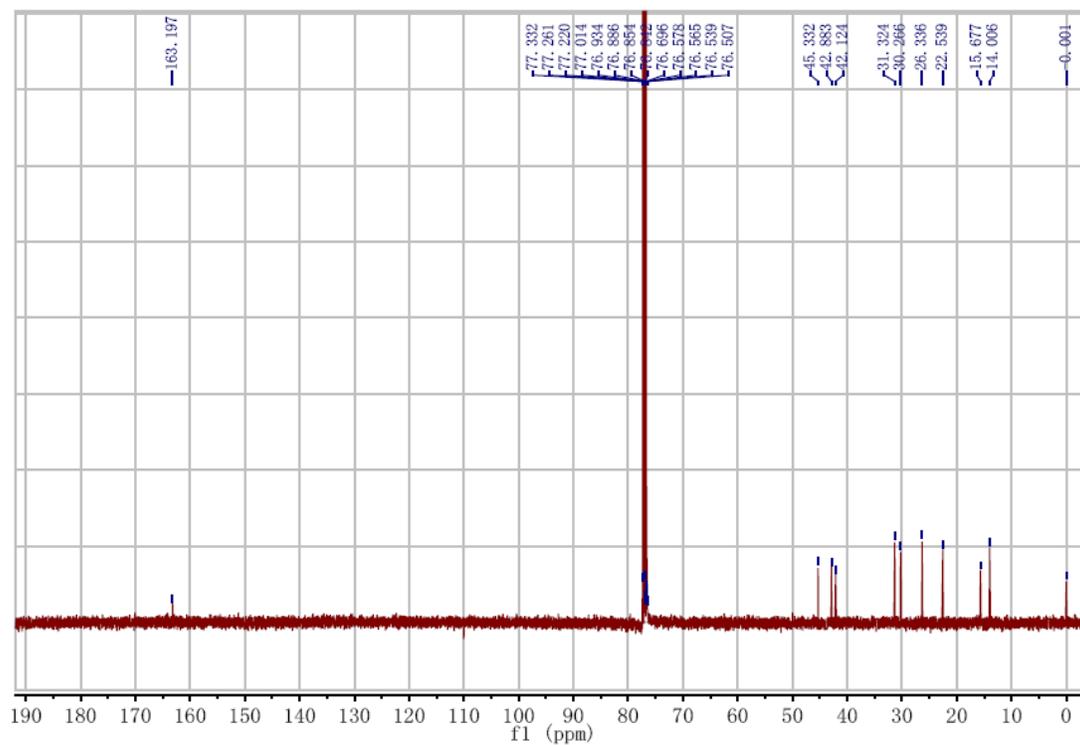
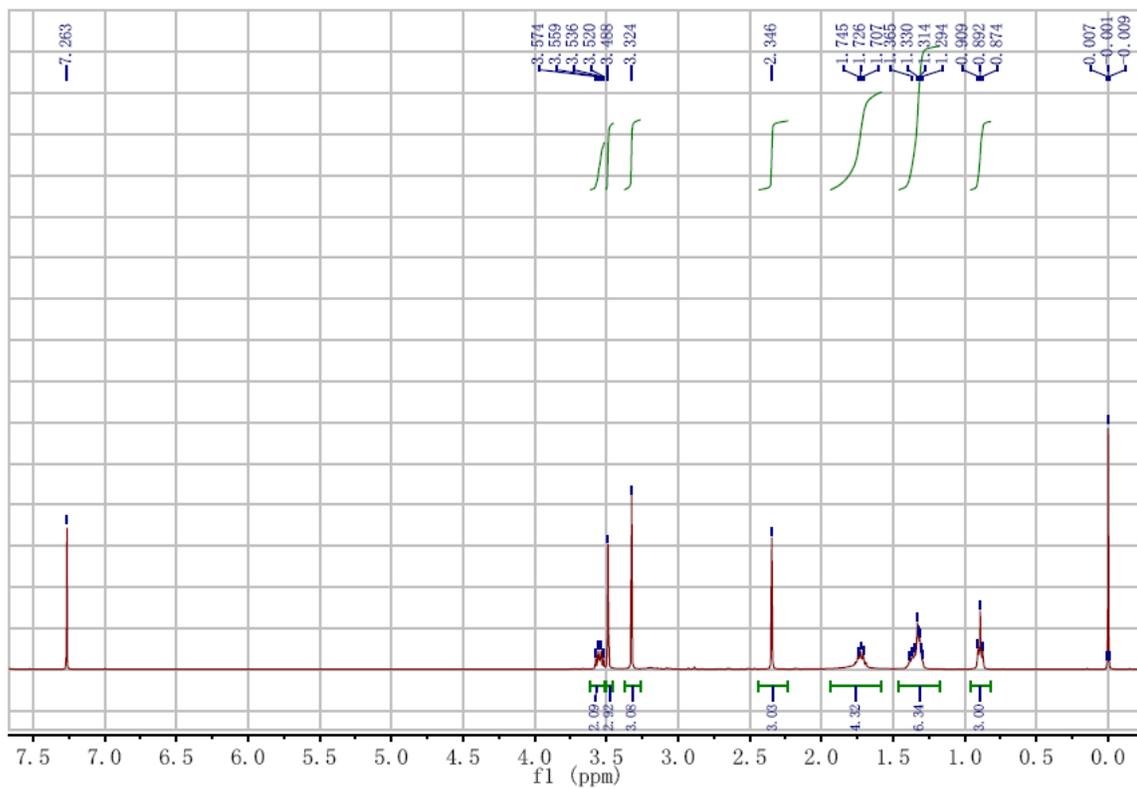


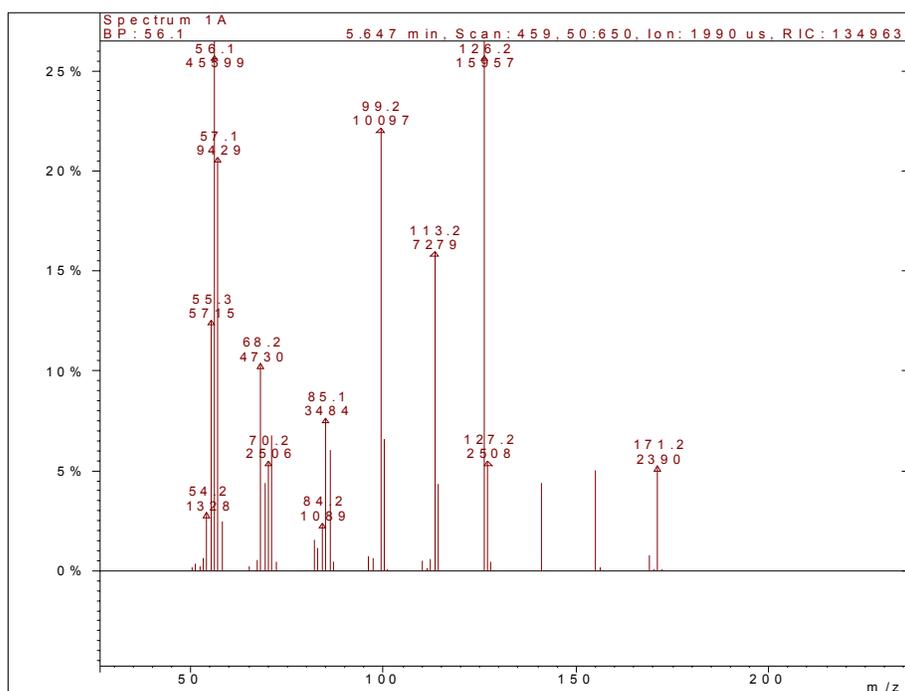
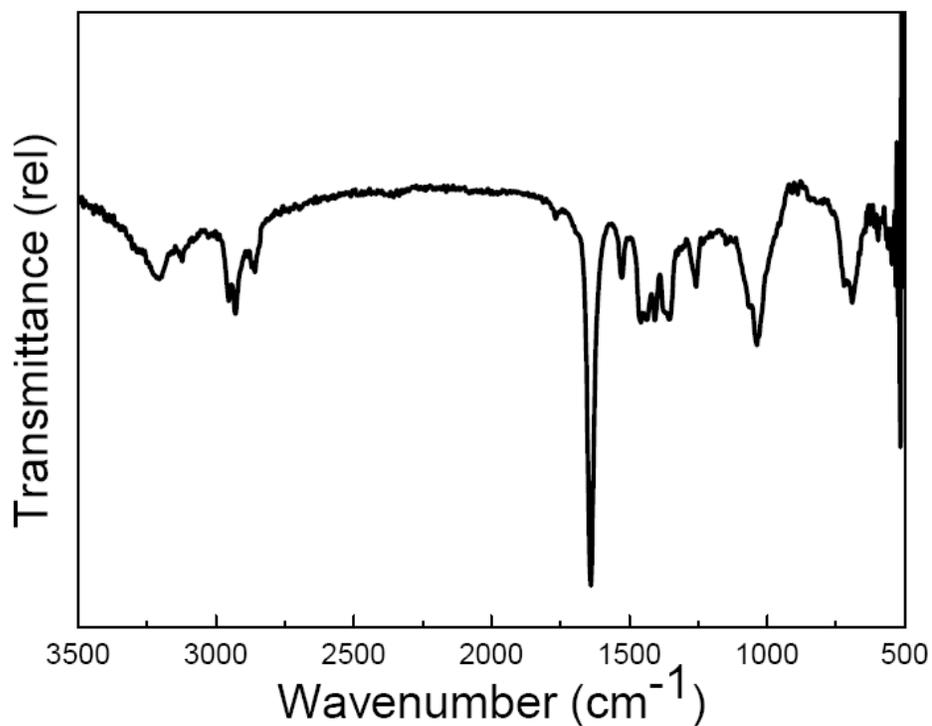
¹H NMR, ¹³C NMR, MS and FT-IR spectra of C6-HBr





¹H NMR, ¹³C NMR, MS and FT-IR spectra of C6-HI





Reactions at 1 atm pressure of CO₂

(1) C6 amidine (0.34 g, 2.0 mmol), and LiBr (0.44 g, 5.0 mmol) were added to a solution of

cyclohexene oxide (**3a**) (2.0 g, 20 mmol) in 5.0 mL of DMF in a flask with a 1 cm teflon stir bar. CO₂ (g) from a gas balloon was attached to the flask through a rubber stopper and the reaction was allowed to stir at room temperature under CO₂ atmosphere for 72 h.

(2) C6 amidine (0.34 g, 2.0 mmol), and LiBr (0.44 g, 5.0 mmol) were added to a solution of cyclohexene oxide (**3a**) (2.0 g, 20 mmol) in a flask with a 1 cm teflon stir bar. CO₂ (g) from a gas balloon was attached to the flask through a rubber stopper and the reaction was allowed to vigorously stir at room temperature under CO₂ atmosphere for 24 h.

(3) C6 amidine (0.34 g, 2.0 mmol), and C6-HBr (1.25 g, 5.0 mmol) were added to a solution of cyclohexene oxide (**3a**) (2.0 g, 20 mmol) in a flask with a 1 cm teflon stir bar. CO₂ (g) from a gas balloon was attached to the flask through a rubber stopper and the reaction was allowed to vigorously stir at room temperature under CO₂ atmosphere for 24 h.

References

- (1) J. Slemr, F. Slemr, H. D'Souzac and R. Partridge, *J. Chromatogr. A* 2004, **1061**, 75–84.