Supplementary Material (ESI) for Green Chemistry

Selective Production of Cyclic Carbonate over Polycarbonate using Double Metal Cyanide-Quaternary ammonium Salt Catalyst System

Manju Mamparambath Dharman, Jeong-In Yu, Ji-Yeon Ahn and Dae-Won Park*

Department of Chemical Engineering, Pusan National University, Busan 609-735, Korea.

Fax: +82-51-512-8563; Tel: +82-51-510-2399; E-mail: dwpark@pusan.ac.kr

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1. Experimental details

1.1 Materials

Zinc chloride (≥98%), potassium hexacyanocobaltate(III) (K_3 $Co(CN)_6$), tertiary butyl alcohol (99+%) and Poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol) (PEG-PPGPEG; *M*n = 1,100)were purchased from Aldrich and used without further purification. All quaternary ammonium salts are kept in a glove box under argon atmosphere and used without further purification. Tetrapropylammonium chloride ($n$$Pr_4NCl$, 98%) and tetrahexylammonium chloride ($n$$Hex_4NCl$, 96%) were obtained from Aldrich. Tetrabutylammonium chloride ($n$$Bu_4NCl$, ≥ 97%), tetraoctylammonium chloride ($n$$Oct_4NCl$, ≥ 97%), tetradodecylammonium chloride ($n$$Dodec_4NCl$, ≥ 99%) and tetrabutylammonium bromide ($n$$Bu_4NBr$, ≥ 99%) were purchased from Fluka chemicals. Carbon dioxide of 99.999% purity was used without further purification.

1.2Catalyst synthesis

The synthetic procedure for the double metal cyanide complexes and its characterizations are well explained in our previous report.[R1] The catalyst for the present study is denoted as DMC-1.

1.3 General procedure for the cycloaddition reaction

Representative procedure for the cycloaddition reaction is detailed in the manuscript. All cyclic carbonates were isolated by column chromatography and analyzed through FT-IR (IR spectra were recorded on Shimadzu Fourier Transform Infrared spectrometer IRPrestige-21), GC/MS

(Agilent 5975C) and ^{1}H-NMR spectroscopy (Varian Gemini 2000, 300 MHz using $CDCl_3$ as solvent).

1.4 Recycling tests

After the reaction the catalyst is removed by filtration and washed with methylene chloride, dried in vacuum for 10 h. The reaction is performed by the previously described procedure. The results are given below.

Table S-1 Recycling test of DMC catalyst[a]

Recycle	Conversion (%)	Yield (%)
Fresh	47.8	47.6
1	44.9	43.8
2	44.5	44.1
3	42.0	41.8
4	40.1	39.8

[a]Reaction conditions: styrene oxide **1a** (20 ml, 184 mmol), Catalyst (40 mg, 0.184 mmol Zn), quaternary salt (2 mmol), time: 2 h, 100 ^{o}C CO_2 pressure: 0.34 MPa.

1.4 Product characterization

1. 4-Phenyl-[1,3]dioxolan-2-one (1b): Yield: 94% (GC); 87% (isolated) after purification by column chromatography (hexane / EtOAc 2:3).[R2]

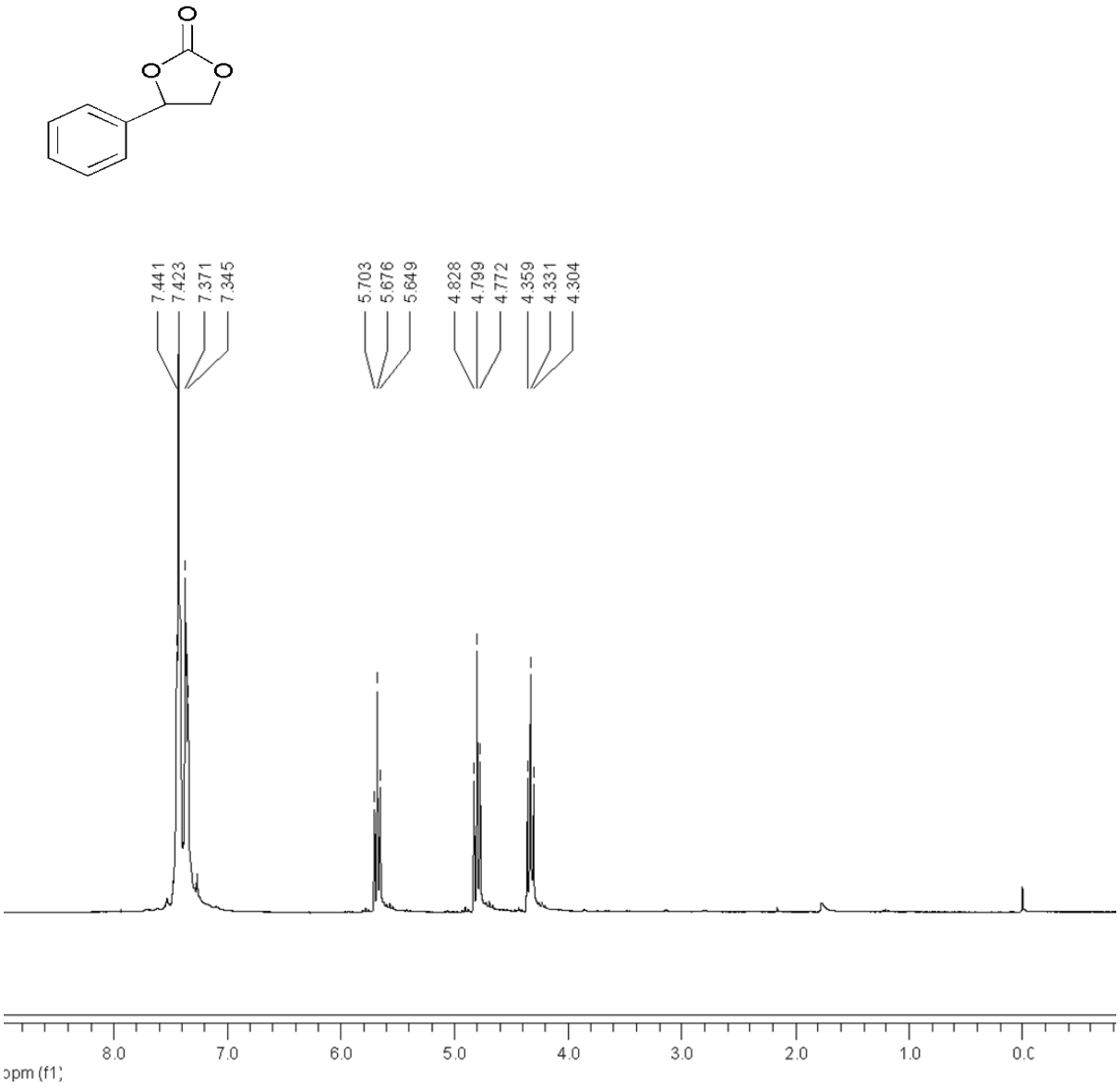


Fig. S1. ^{1}H-NMR spectra of **1b**

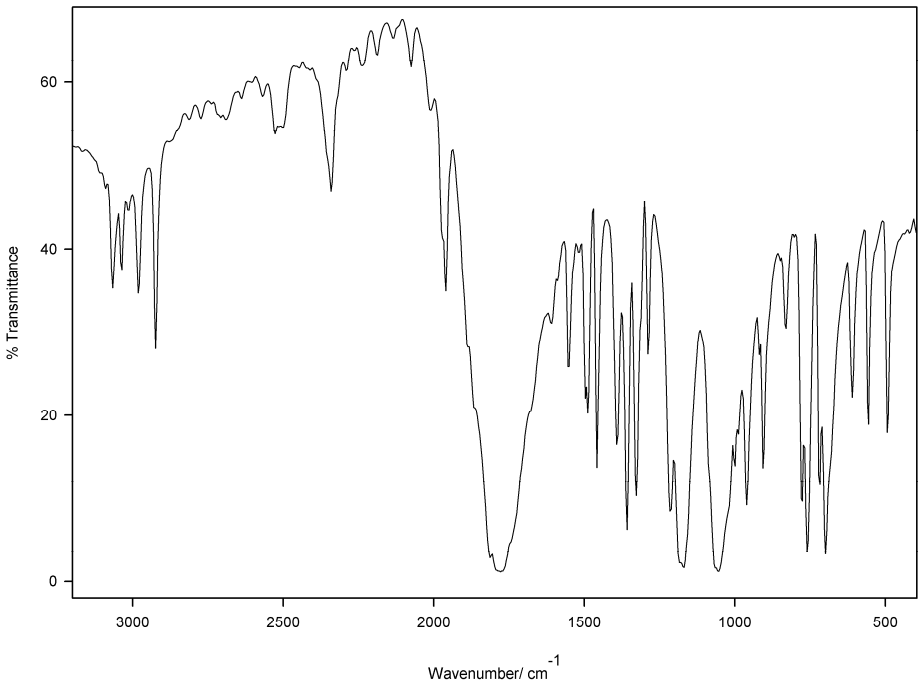


Fig. S2. FT-IR spectra of **1b**

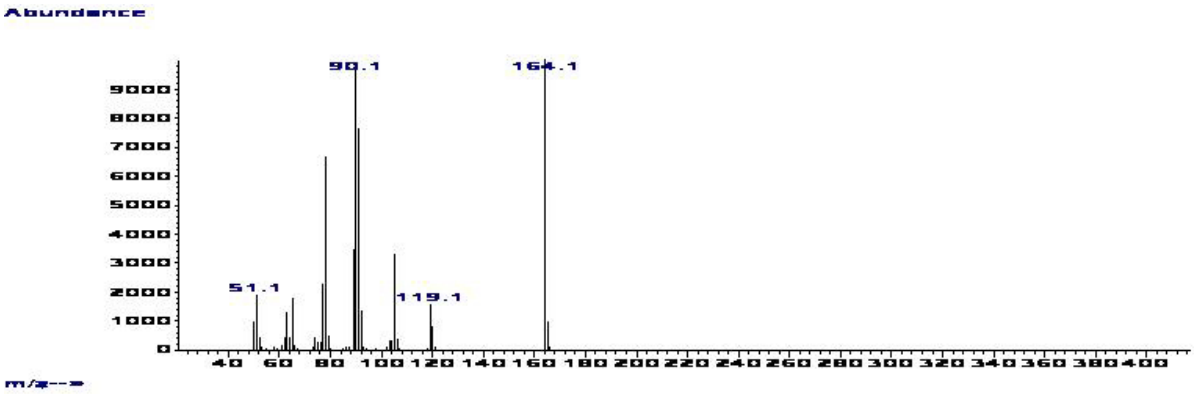
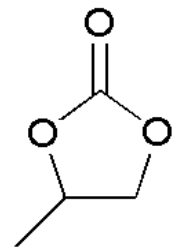


Fig. S3. Mass spectrum of **1b**

2. 4-Methyl-[1,3]dioxolan-2-one (2b): Yield: 95% (GC); 90% (isolated) after purification by column chromatography (hexane / EtOAc 4:1).[R3]



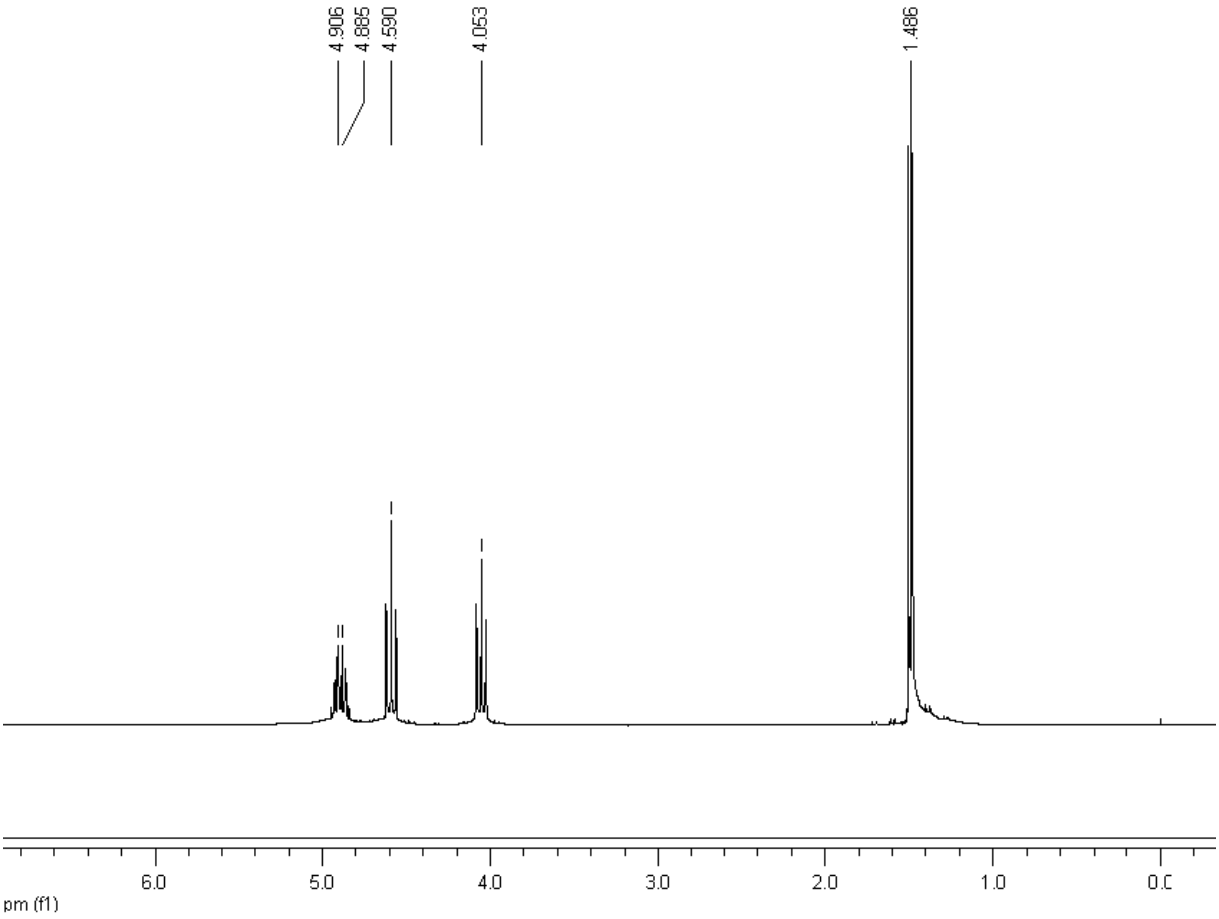


Fig. S4. ^{1}H-NMR spectra of **2b**

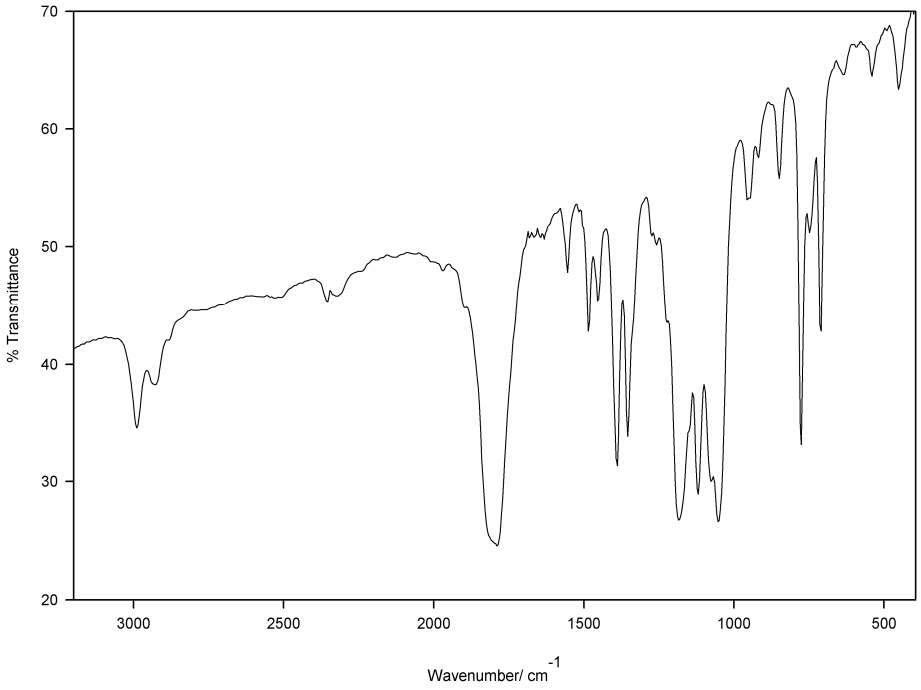


Fig. S5. FT-IR spectra of **2b**

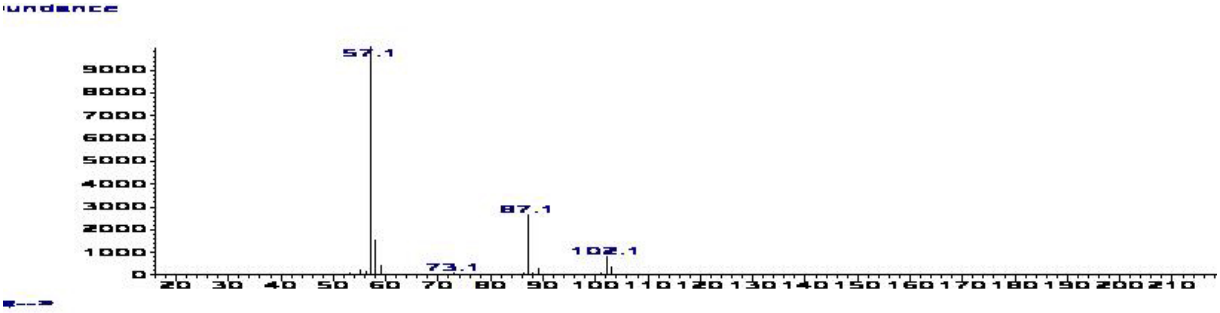


Fig. S6. Mass spectrum of **2b**

3. 4-Butyl-[1,3]dioxolan-2-one (3b): Yield: 99% (GC); 95% (isolated) after purification by column chromatography (hexane / EtOAc 2:3).[R2a; R3(a),(b); R4]

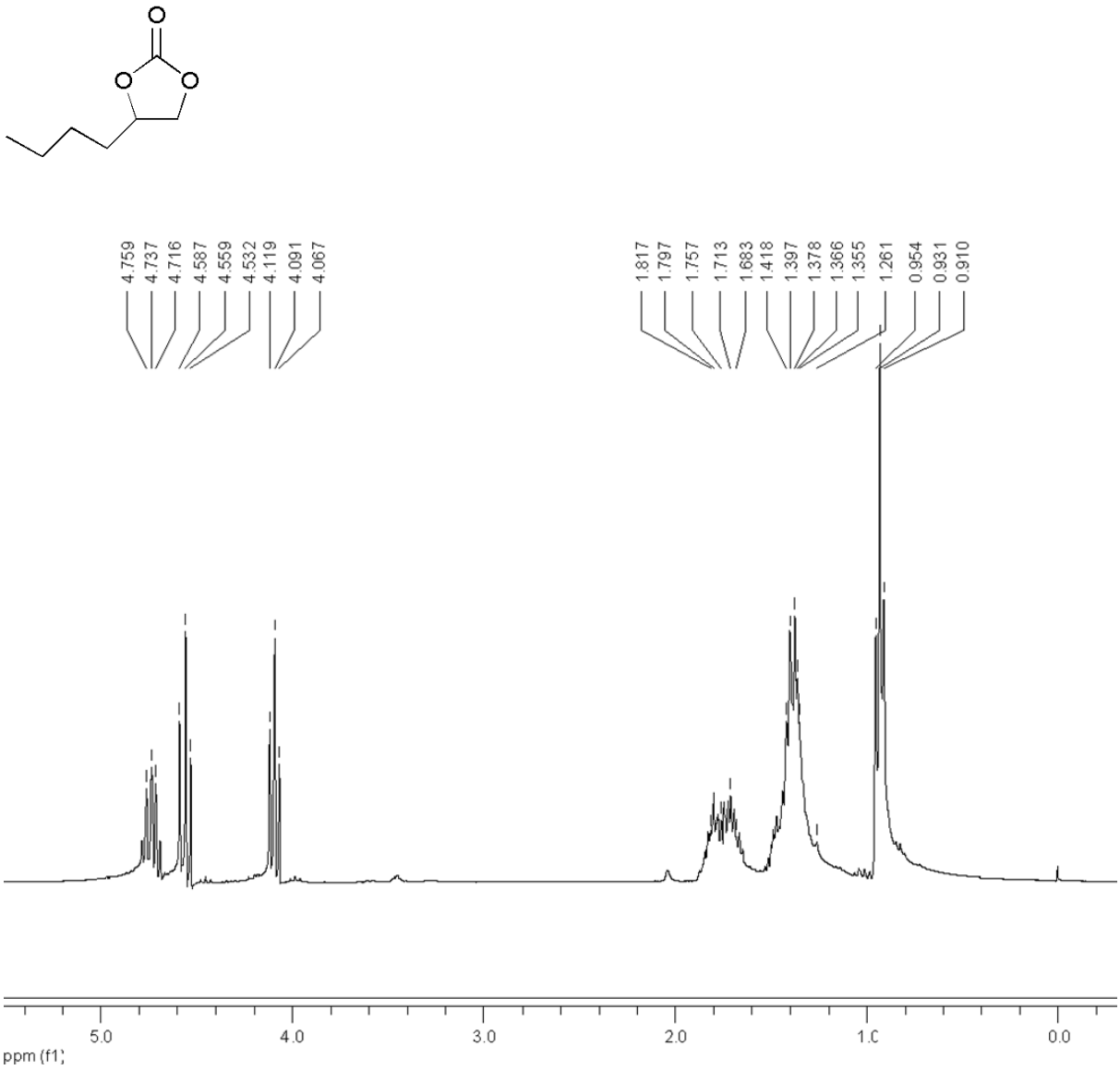


Fig. S7. ^{1}H-NMR spectra of **3b**

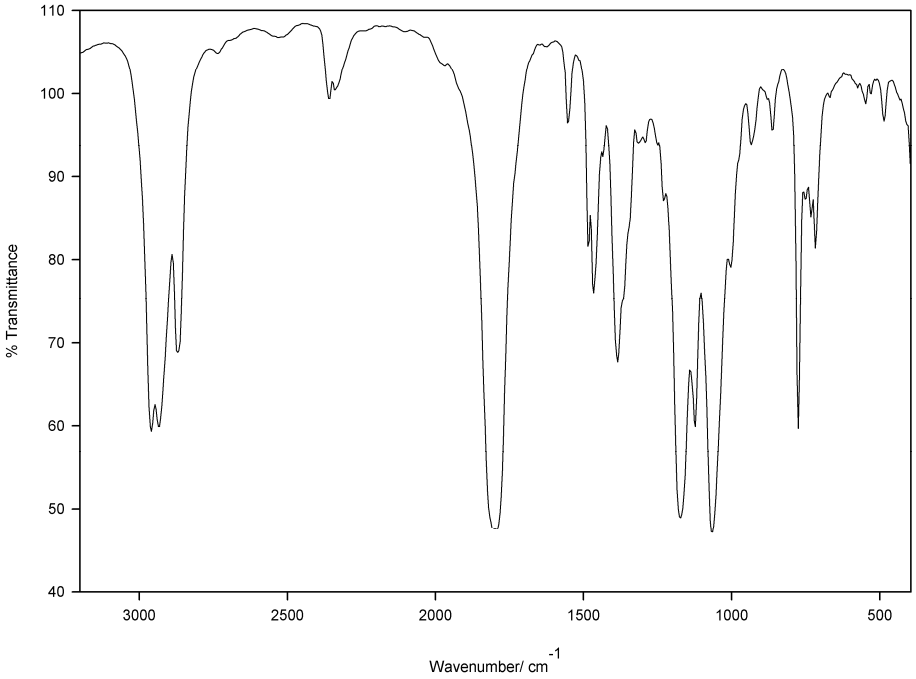


Fig. S8. FT-IR spectra of **3b**

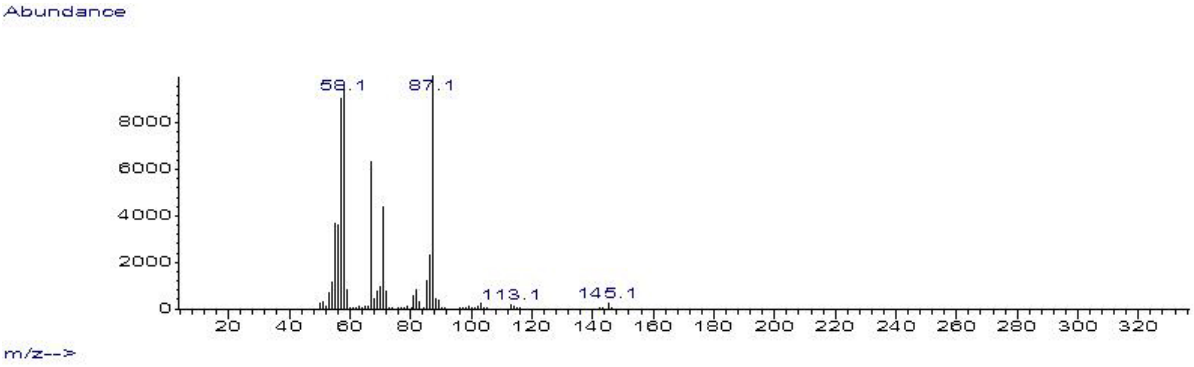


Fig. S9. Mass spectrum of **3b**

4. 4-Chloromethyl-[1,3]dioxolan-2-one(4b): Yield: 95% (GC); 92% (isolated) after purification by column chromatography (hexane / EtOAc 2:3).[R2(a),(b); R3b; R4(a),(f),(g); R5]

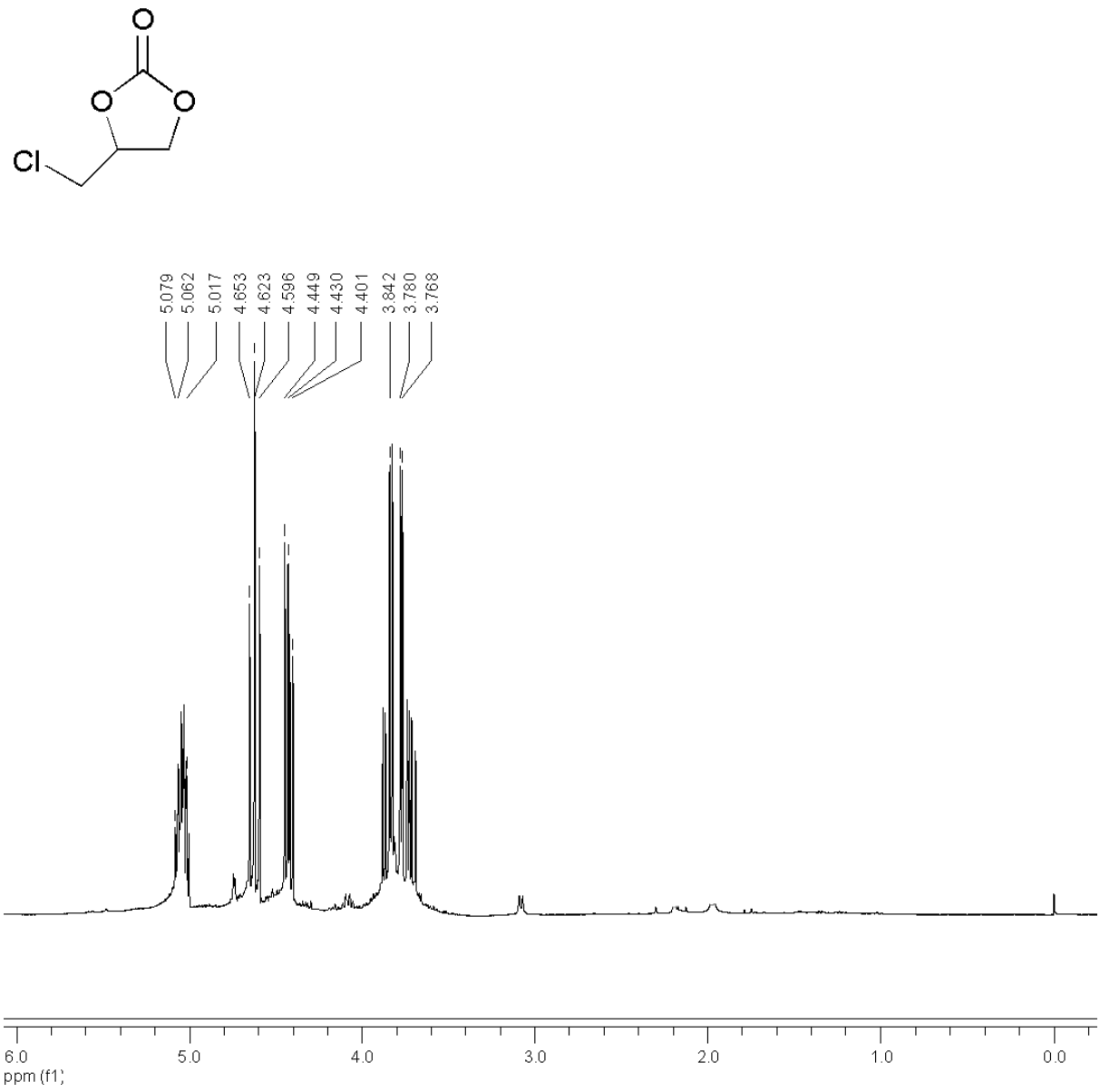


Fig. S10. ^{1}H-NMR spectra of **4b**

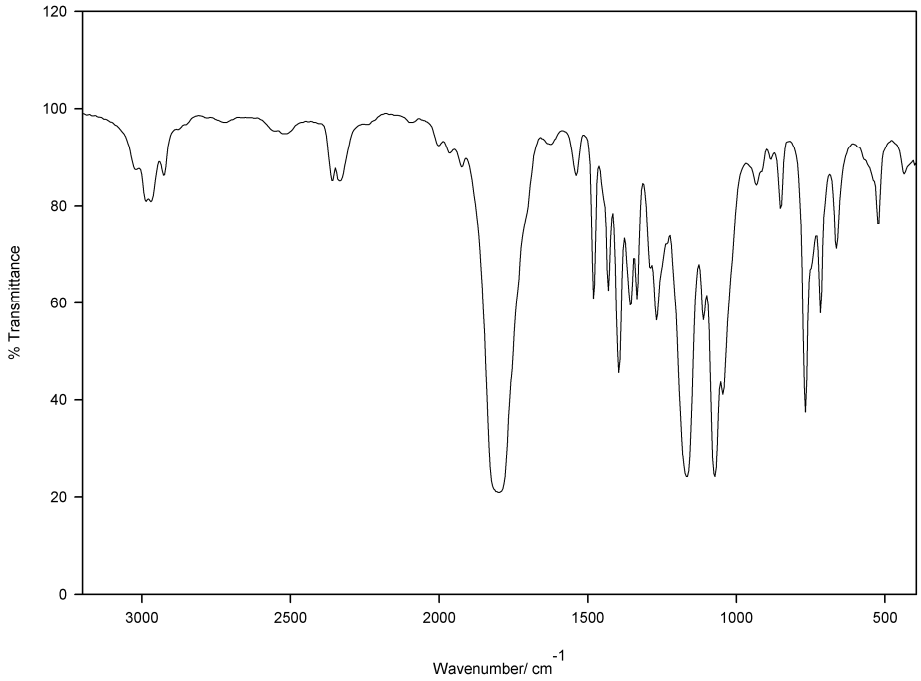


Fig. S11. FT-IR spectra of **4b**

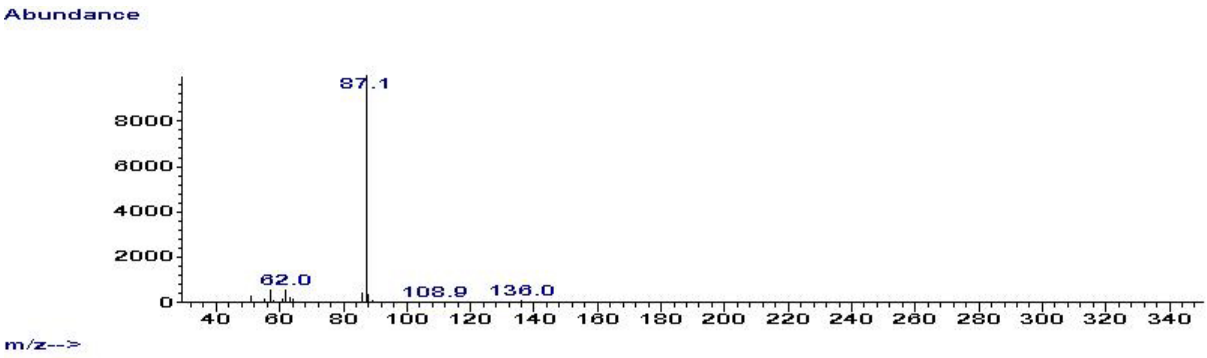
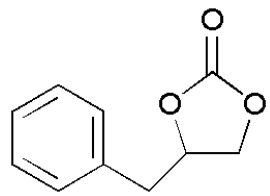


Fig. S12. Mass spectrum of **4b**

5. 4-Benzyl-[1,3]dioxolan-2-one(5b): Yield: 96% (GC); 93% (isolated) after purification by column chromatography (hexane / EtOAc 2:3).[R3(a); R4(b),(c)]



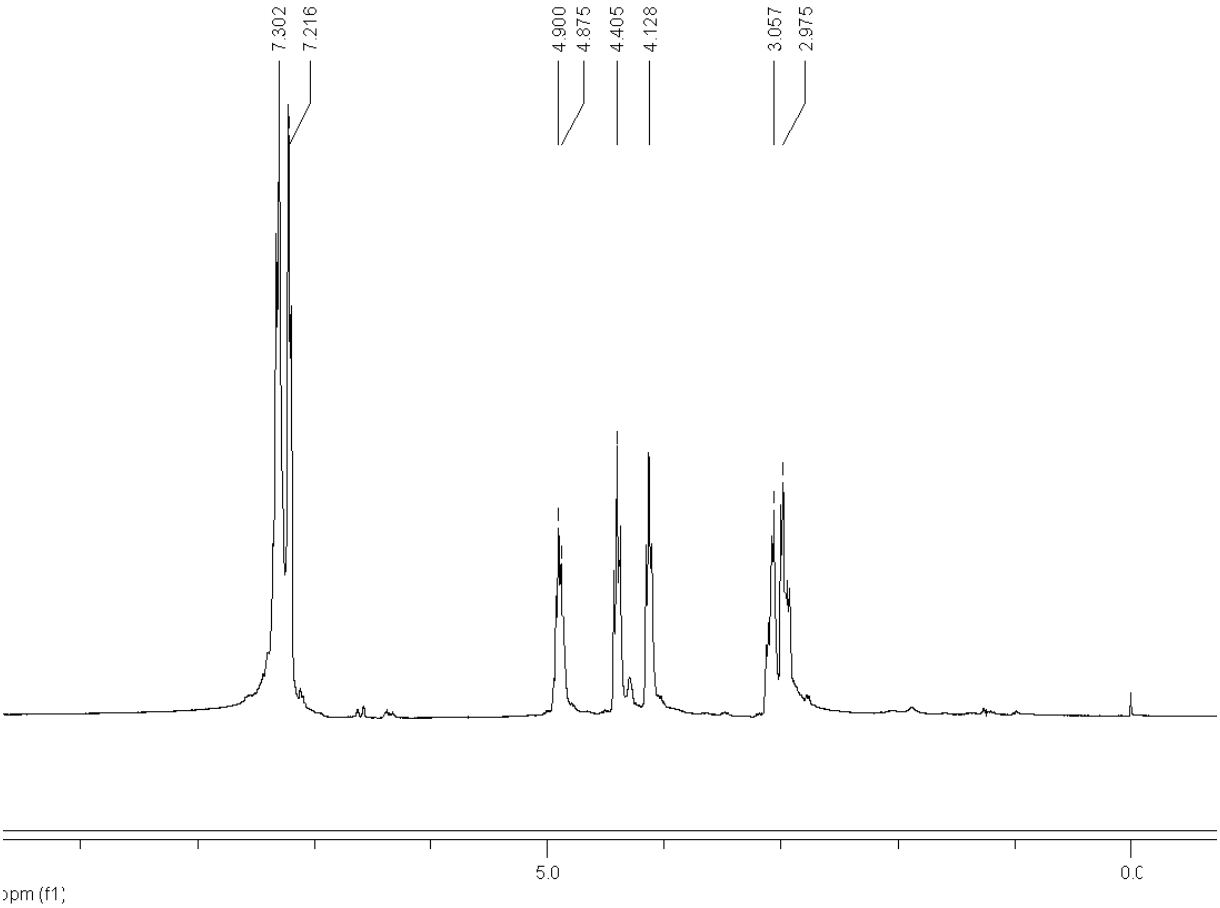


Fig. S13. ^{1}H-NMR spectra of **5b**

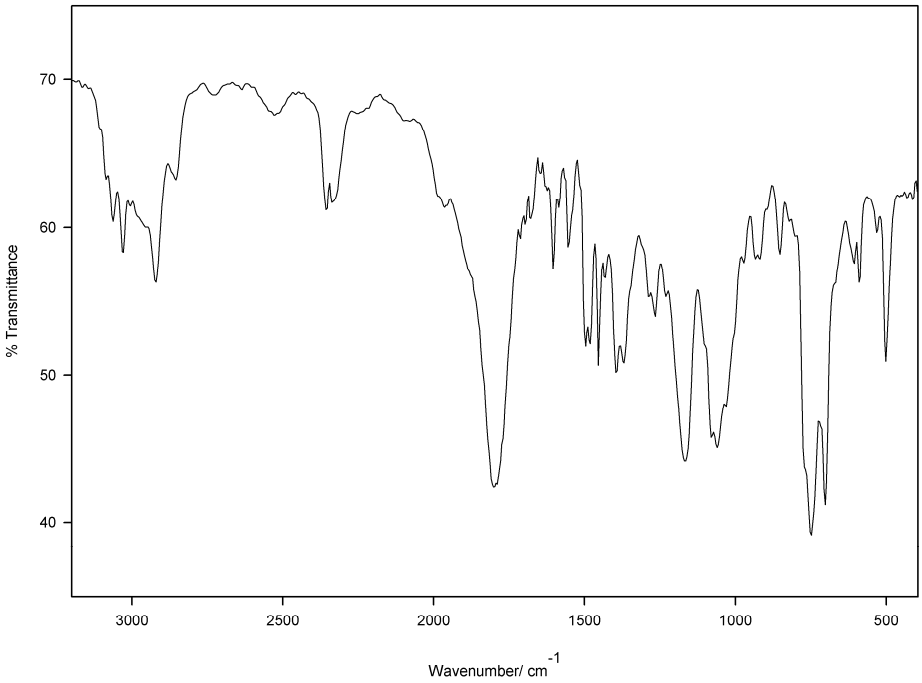


Fig. S14. FT-IR spectra of **5b**

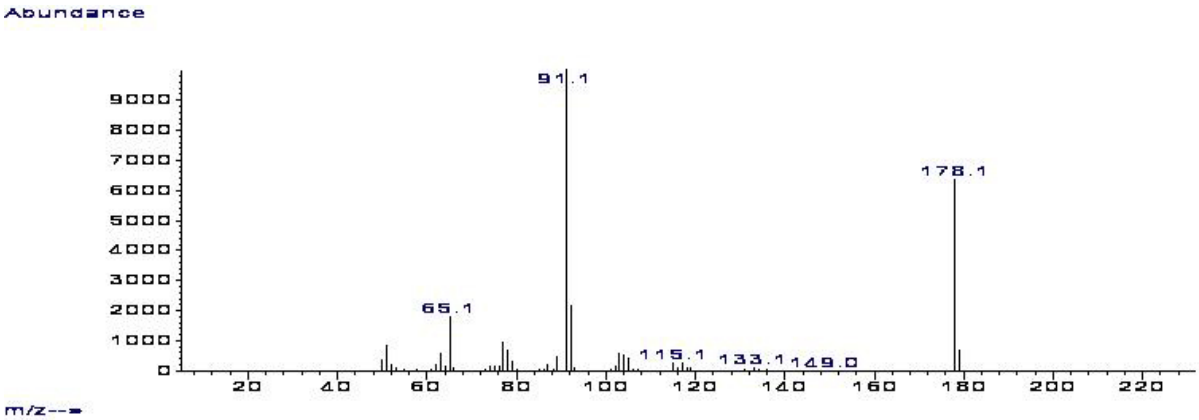
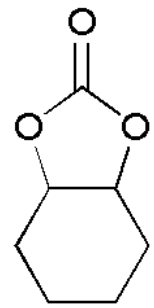


Fig. S15. Mass spectrum of **5b**

6. Hexahydro-benzo[1,3]dioxol-2-one(6b): Yield: 75% (GC); 70% (isolated) after purification by column chromatography (hexane / EtOAc 4:1).[R4(a),(e)]



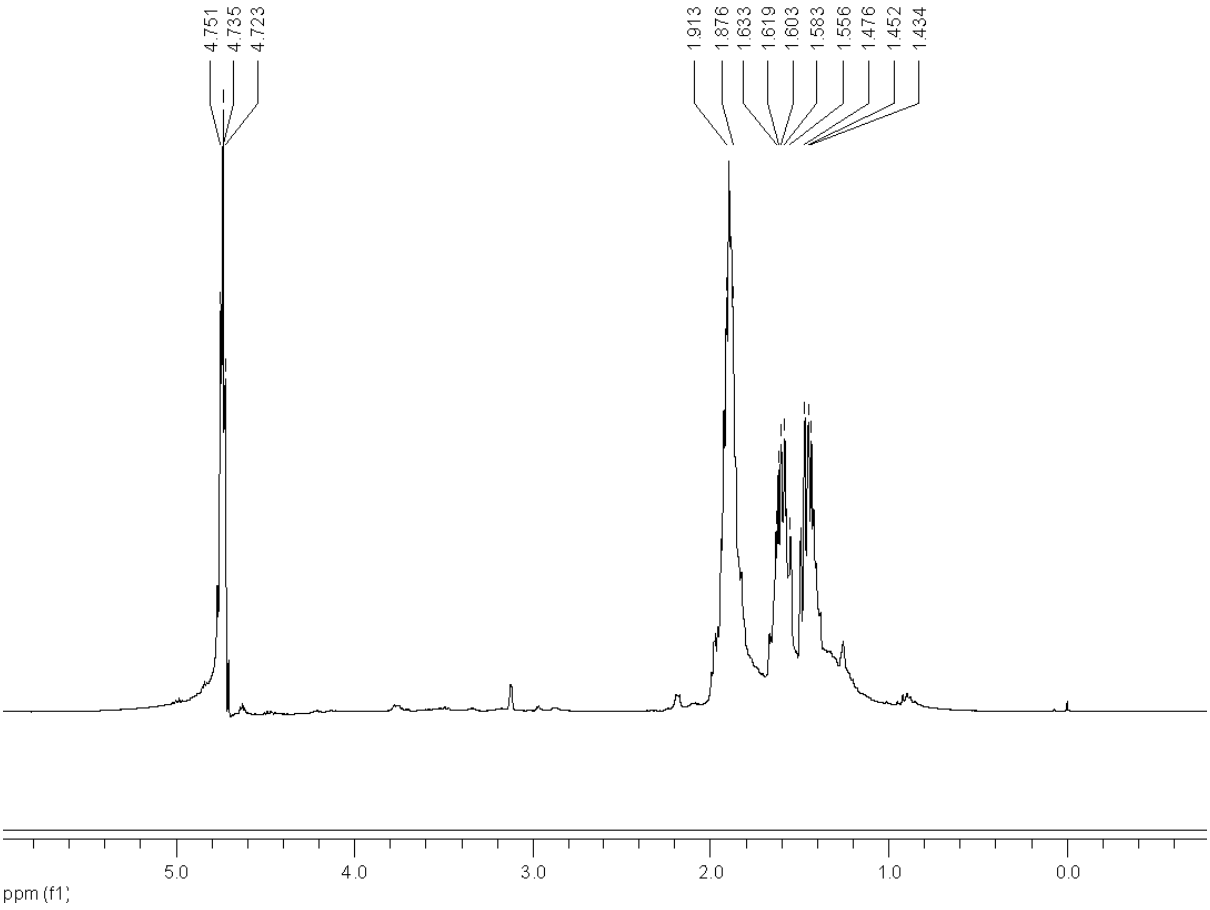


Fig. S16. ^{1}H-NMR spectra of **6b**

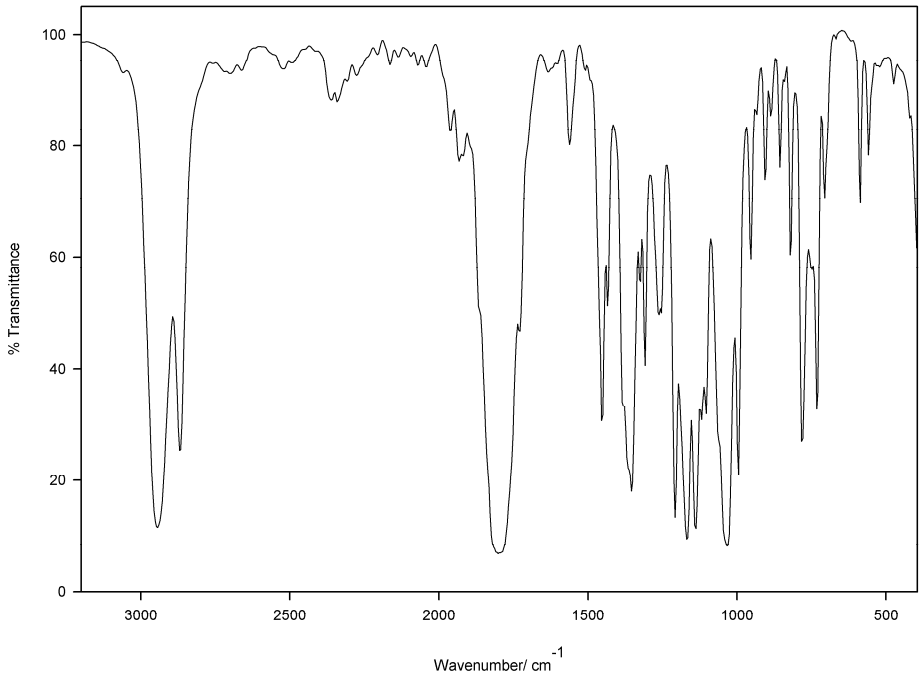


Fig. S17. FT-IR spectra of **6b**

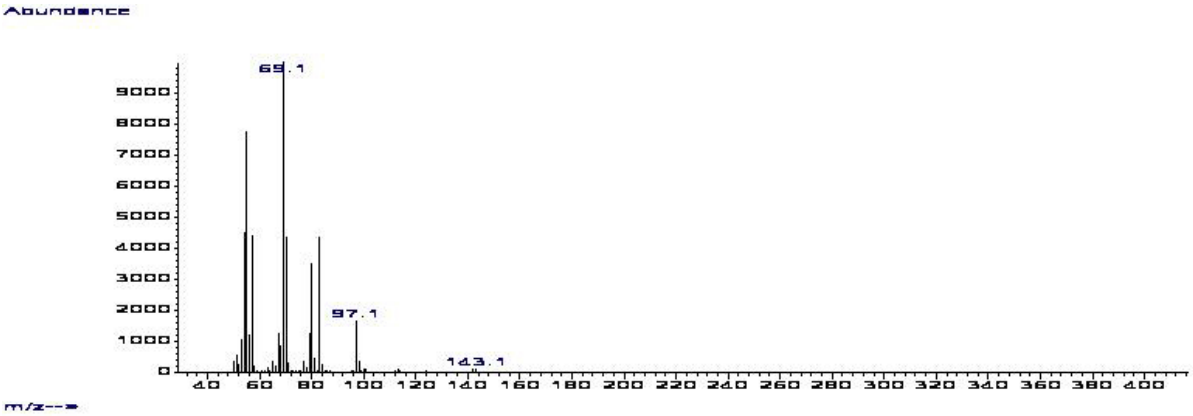


Fig. S18. Mass spectrum of **6b**

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