Supporting Information

Tandem reaction of olefins and CO_2 to cyclic carbonates over polyetheretherketone fiber-supported ionic liquids via relay catalysis in the spinning basket reactor

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Experimental details

Materials

Commercially available PEEK fiber with a length of 10 cm and a diameter of 30 ± 0.5 μm (from the Changzhou Co-win New Material Technology Co., Ltd.) was used after dried (In order to avoid the possible impacts of water absorption on the subsequent reactions and the consequent possible sources for experimental errors, all the fiber samples before use were dried fully at 60 °C under vacuum in this study). Tert-butyl hydroperoxide (TBHP) was 70 wt% aqueous solution, 1-methylimidazole and all the others chemicals or solvents used were analytical grade and employed without further purification or desiccation. CO_2 (99.99%) was used without further purification. Water was deionized.

Apparatus and instruments

A scanning electron microscope (Germany, model Merlin Compact) was used to characterize the surface morphology of the fibers. X-rays diffraction (XRD) spectroscopies were obtained with X-ray diffractometer (Germany, D8ADVANCE). The mechanical properties of different fiber samples were tested with an electronic single fiber strength tester (Quanzhou Meibang Instrument Co., Ltd of China, model YG001E). Elemental analyses were performed on a thermo scientific flash 2000 auto-analyzer. Fourier transform infrared (FTIR) spectra were obtained with an AVATAR 360 FTIR spectrometer (Thermo Nicolet), KBr disc. The X-ray photoelectron spectroscopy (XPS) of the fiber samples was detected on a Thermo Fisher Scientific K-Alpha XPS system. The quantitative analyses of product during the conditions optimizing were performed on a GC analyzer (SP-3420A) equipped with a FID hydrogen flame detector. ^1H NMR spectra were recorded on an AVANCE III

(Bruker, 400 MHz) instrument using TMS as the internal standard. ^{13}C NMR spectra were recorded on an AVANCE III (Bruker, 101 MHz) instrument with complete proton decoupling.

The analytical method of gas chromatography (GC)

The GC analyzer fitted with a HP-5 column (30 m×0.25 mm×0.25 μm) and a flame ionization detector (FID) was used for quantitative analyzing of the product of 4-phenyl-1,3-dioxolan-2-one.

Analytical method: High purity N_2 was used as carrier gas with a flow rate of 1 mL min^{-1}, the temperature of detector was 300 °C and the temperature of inlet was 280 °C, the injection volume was 0.1 μL with anisole as the internal standard, and the split ratio was 50: 1. The initial temperature of the column box was set at 80 °C, the retention time was 1 min, and the temperature was heated to 250 °C at a rate of 10 °C min^{-1}.

Experimental details

Molecular geometry was optimized without constraints via DFT calculations using the Becke3LYP (B3LYP) functional,[1] as implemented in the Gaussian 09 suite of programs.[2] The 6-31++G** basis set[3] was used for all atoms. Natural Bond Orbital (NBO) analysis was also performed at the same level of theory.

Additional experimental results

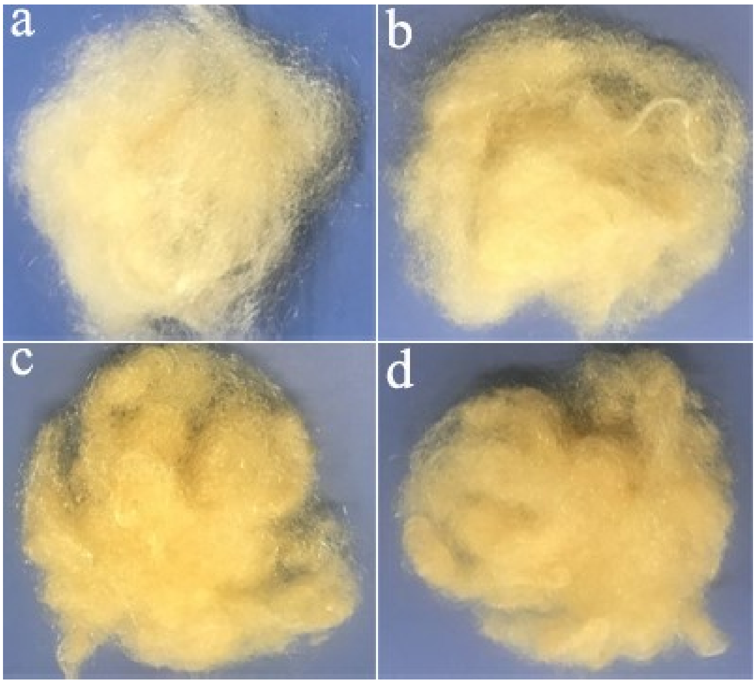


Figure S1. Photographs of (a) PEEK-MIMCl, (b) PEEK-MIMHCO$_3$, (c) PEEK-MIMHCO$_3$-1 , and (d) PEEK-MIMHCO$_3$-10.

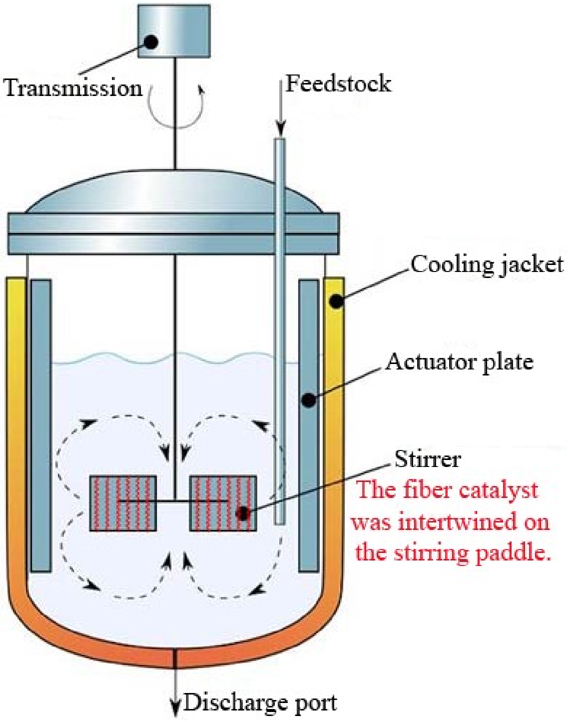
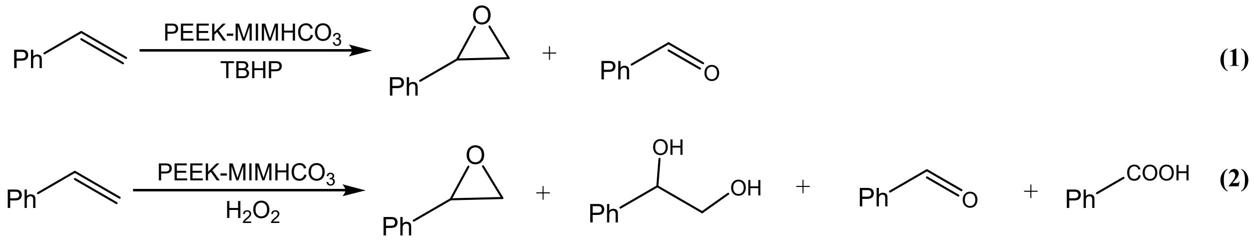


Figure S2. A diagrammatic sketch of the spinning basket reactor with the fiber catalyst in impellers.



Scheme S1, The oxidation reactions of styrene catalyzed by PEEK-MIMHCO$_3$ with TBHP or H_2O_2.

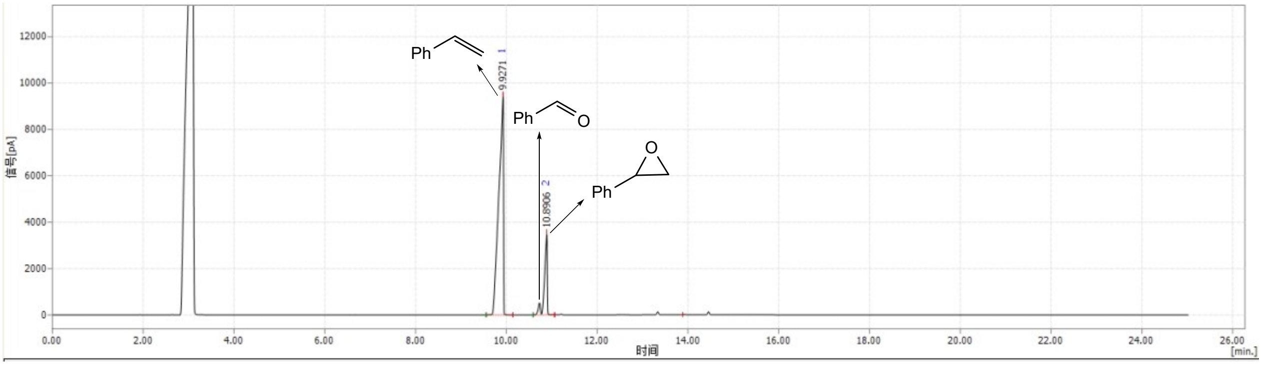


Figure S3. GC detection result of styrene epoxidation catalyzed by PEEK-MIMHCO$_3$ using H_2O_2 as the oxidant.

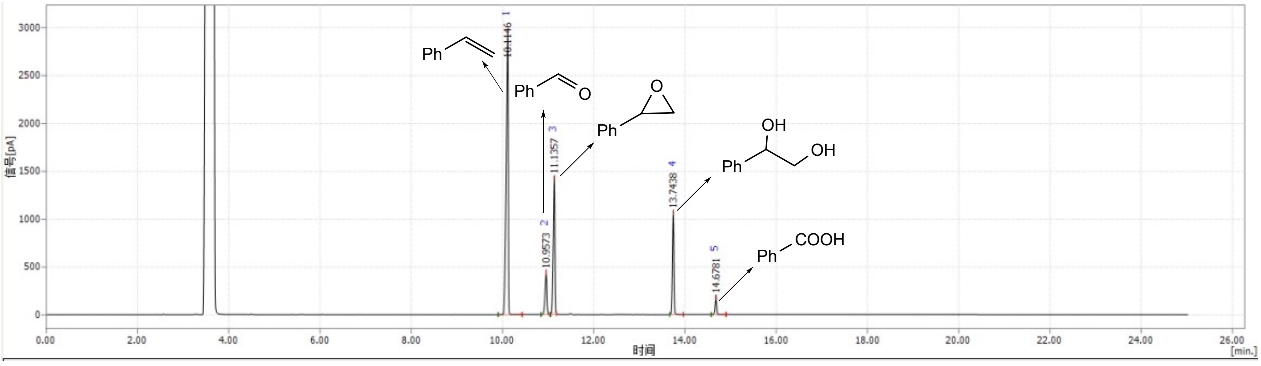
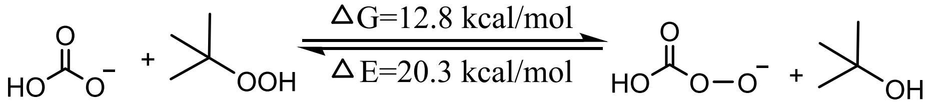


Figure S4. GC detection result of styrene epoxidation catalyzed by PEEK-MIMHCO$_3$ using TBHP as the oxidant.



Scheme S2. The energy analysis for the formation of peroxymonocarbonate anions from HCO_3^- and TBHP.

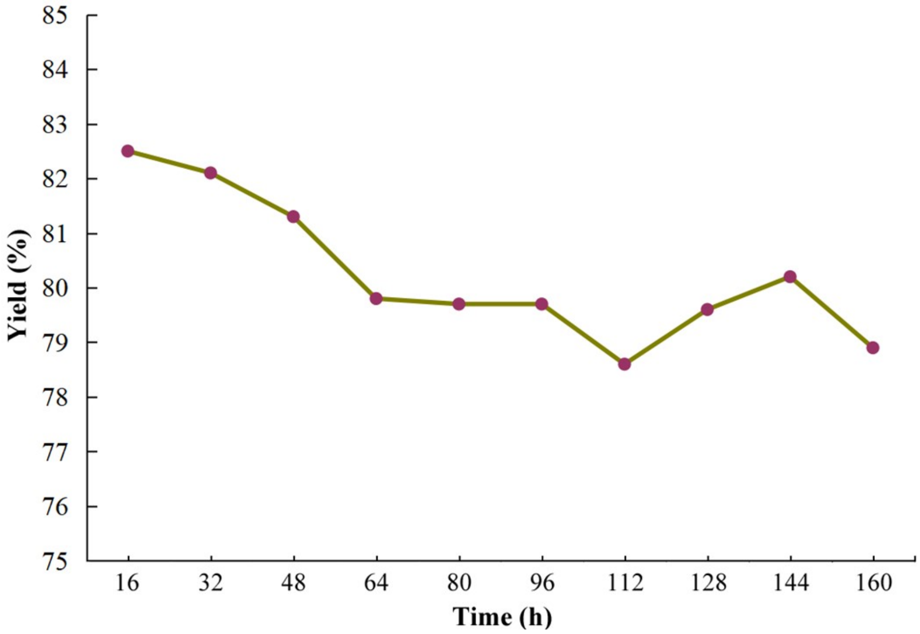


Figure S5. Time-conversion plot of the tandem reaction for direct conversion of styrene and CO_2 to cyclic carbonate catalyzed by PEEK-MIMHCO$_3$ (Yields detected by GC).

Cartesian coordinates for all of the species calculated in this study

HCO_3^-

E = -264.47669666

C	0.15718000	0.06693600	0.00003500
O	1.22562900	-0.56478400	-0.00000800
O	-1.02567700	-0.76897800	-0.00001100
H	-1.74128000	-0.11789900	0.00002900
O	-0.10017700	1.29829700	-0.00001100

t-Butyl Hydroperoxide (TBHP)

E = -308.83399979

C	-0.39103500	0.00003500	0.03168700
O	0.73920500	-0.00056700	-0.87323500
O	1.96705200	0.00000800	-0.05856300
H	2.61315700	-0.00095200	-0.78135200
C	-0.38204000	-1.26954700	0.89182800
H	-1.28059100	-1.30762600	1.51675300
H	-0.36208700	-2.16047000	0.25656800
H	0.49343200	-1.29100400	1.54494000
C	-1.57017400	-0.00174600	-0.94958300
H	-2.51047900	-0.00001300	-0.38962700
H	-1.54608500	0.88567600	-1.58902600
H	-1.54686100	-0.89201000	-1.58506800
C	-0.38304300	1.27182600	0.88856800
H	-0.36631600	2.16125200	0.25111300
H	-1.28029300	1.30960000	1.51537900
H	0.49381500	1.29661100	1.53971000

H_2O_2

E = -151.55727074

O	0.00000000	0.73332800	-0.00028100
H	0.95842700	0.88327900	0.00224500
O	0.00000000	-0.73332800	-0.00028100
H	-0.95842700	-0.88327900	0.00224500

Styrene

E = -309.67404959

C	-1.78272800	-1.04733800	-0.00000300
C	-0.40653500	-1.28263700	-0.00000400
C	0.51567800	-0.22049600	0.00000100
C	0.00890700	1.09336200	0.00000300
C	-1.36387300	1.33086900	-0.00000300
C	-2.26807000	0.26197600	0.00000200
H	-2.47348500	-1.88573900	0.00000200
H	-0.03595700	-2.30486100	-0.00000300
H	0.69222400	1.93691000	0.00001300
H	-1.73191700	2.35306000	0.00000900
H	-3.33764400	0.45042200	0.00000100
C	1.95657800	-0.52979800	0.00000800
H	2.18899900	-1.59445500	0.00001800
C	2.98133000	0.33583900	-0.00000500
H	2.84338200	1.41322900	-0.00002600
H	4.00667800	-0.01922300	0.00000200

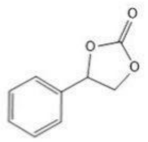
TBHP---HCO_3^-

E = -573.34283440

C	-2.61258000	0.19220500	0.00125400
O	-2.13207500	1.32767700	0.07818000
O	-4.02884500	0.12256700	-0.03174500
H	-4.20941700	-0.82617900	-0.09552000
O	-2.05712600	-0.95110100	-0.05259600
O	1.18548900	-0.64509600	-0.85391100
C	1.96786200	0.20051900	0.01534300
C	3.09728600	-0.62612500	0.65066300
H	2.66622200	-1.44650100	1.23101200
H	3.74505800	-1.05254700	-0.12421100
H	3.70902200	-0.00591300	1.31819200
C	1.09222600	0.86933900	1.08255300
H	1.66546300	1.64960200	1.60067300
H	0.19493500	1.30810900	0.63361600
H	0.76295800	0.13529100	1.82287800
C	2.52732400	1.24193400	-0.96390700
H	3.07377300	0.75031700	-1.77674100
H	1.71232400	1.82975500	-1.39663000
H	3.21302700	1.92030300	-0.44325700
O	0.47151100	-1.63552900	-0.06428700
H	-0.47771200	-1.27762200	-0.09056800

Copies of ^{1}H NMR and ^{13}C NMR spectra of the synthesized compounds

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.49-7.42 (m, 3H), 7.40-7.33 (m, 2H), 5.68 (t, J = 8.1 Hz, 1H), 4.81(t, J = 8.4 Hz, 1H), 4.35 (t, J = 8.1 Hz, 8.7 Hz, 1H).



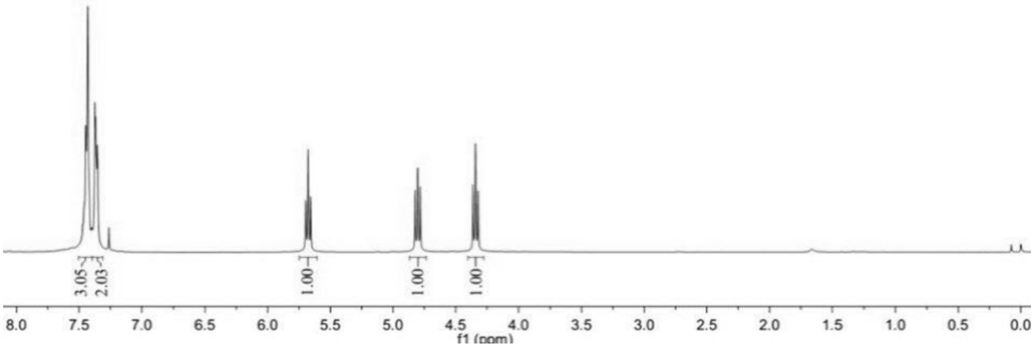
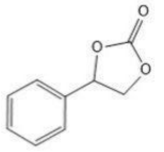


Figure S3. The ^{1}H NMR spectrum of 4-phenyl-1,3-dioxolan-2-one (3a).

^{13}C NMR (101 MHz, $CDCl_3$): δ 154.9, 135.8, 129.7, 129.2, 125.9, 78.0, 71.2.



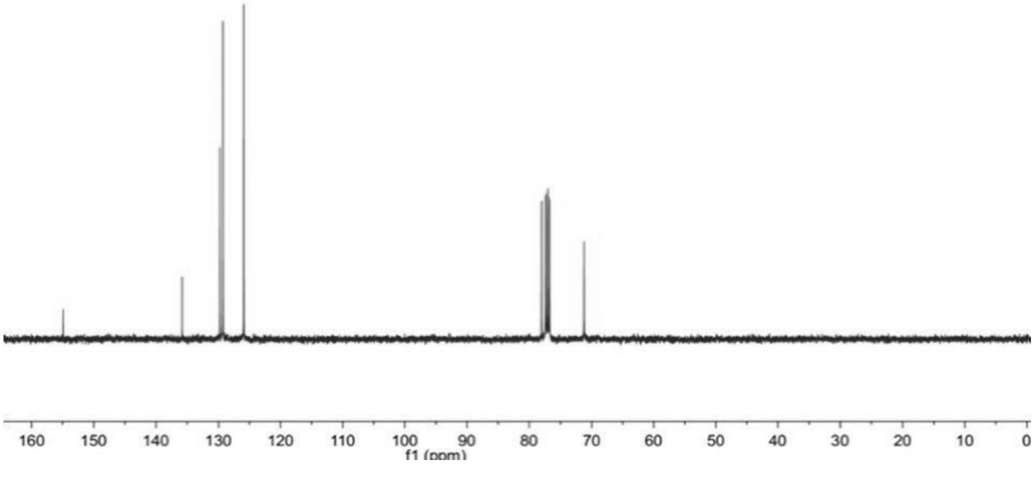
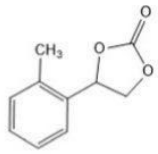


Figure S4. The ^{13}C NMR spectrum of 4-phenyl-1,3-dioxolan-2-one (3a).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.49-7.03 (m, 4H), 5.86 (m, 1H), 4.79 (m, 1H), 4.35-4.09 (m, 1H), 2.27 (s, 3H).



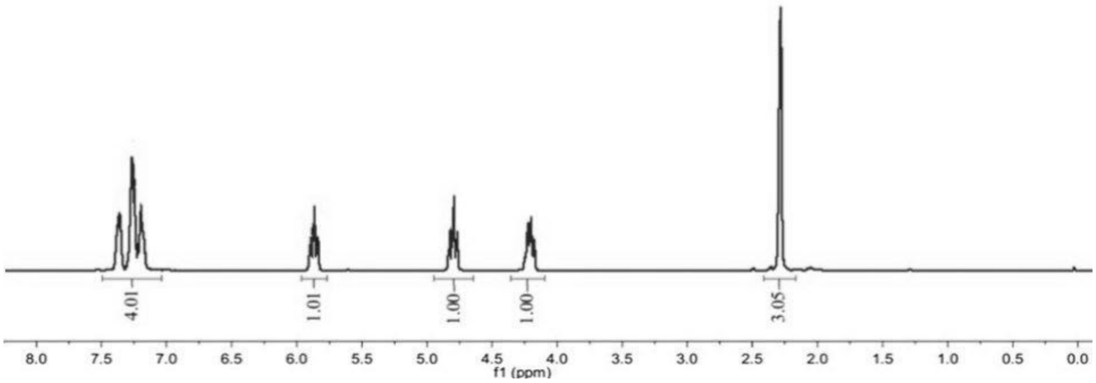
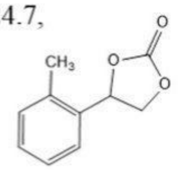


Figure S5. The ^{1}H NMR spectrum of 4-o-tolyl-1,3-dioxolan-2-one (3b).

^{13}C NMR (101 MHz, $CDCl_3$): δ 155.3, 135.0, 134.3, 131.1, 129.2, 126.7, 124.7, 75.7, 70.5, 18.8.



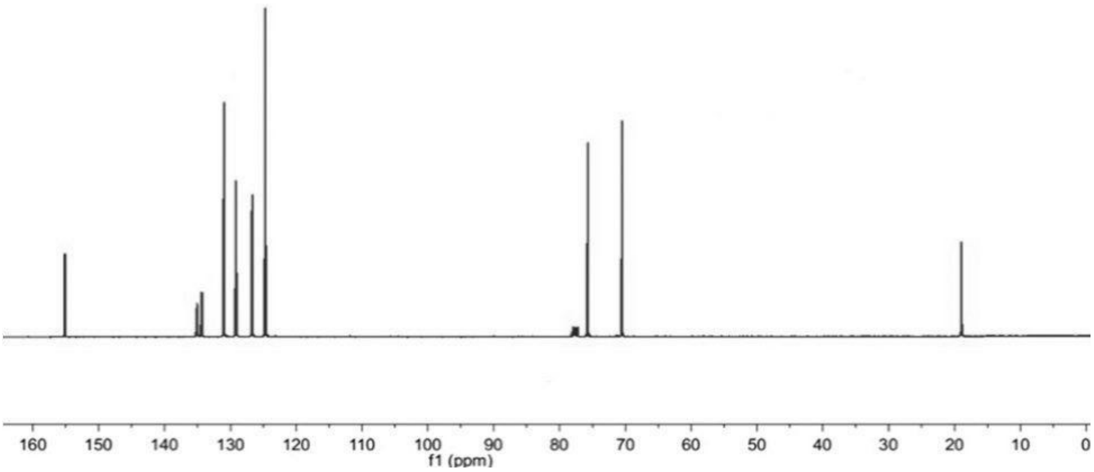
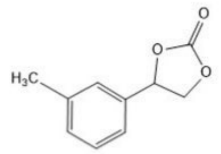


Figure S6. The ^{13}C NMR spectrum of 4-o-tolyl-1,3-dioxolan-2-one (4b).

^{1}H NMR (400 MHz, CDCl$_3$): δ 7.35-7.05 (m, 4H), 5.70-5.54 (m, 1H), 4.84-4.64 (m, 1H), 4.35-4.13 (m, 1H), 2.21 (s, 3H).



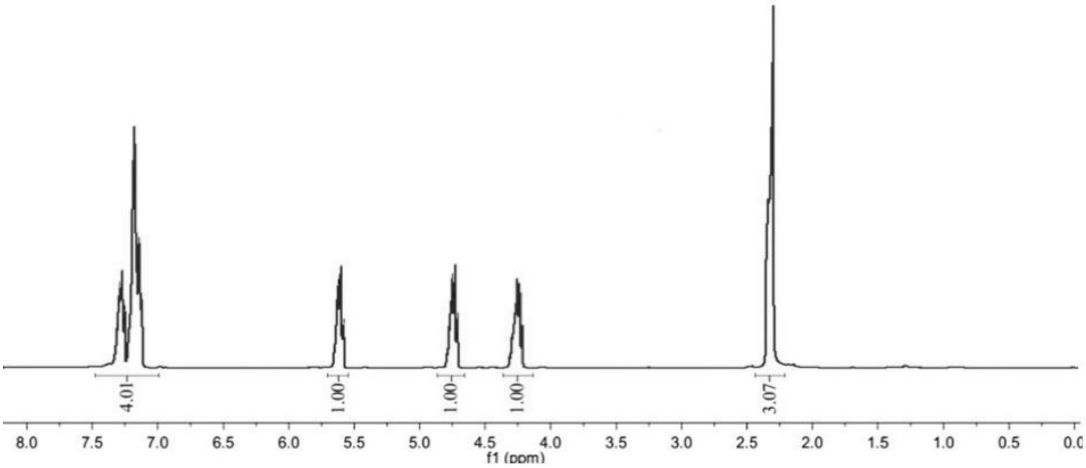
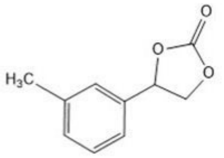


Figure S7. The ^{1}H NMR spectrum of 4-m-tolyl-1,3-dioxolan-2-one (4c).

^{13}C NMR (101 MHz, CDCl$_3$): δ 155.2, 139.0, 136.1, 130.3, 129.0, 126.7, 123.2, 78.2, 71.2, 21.2.



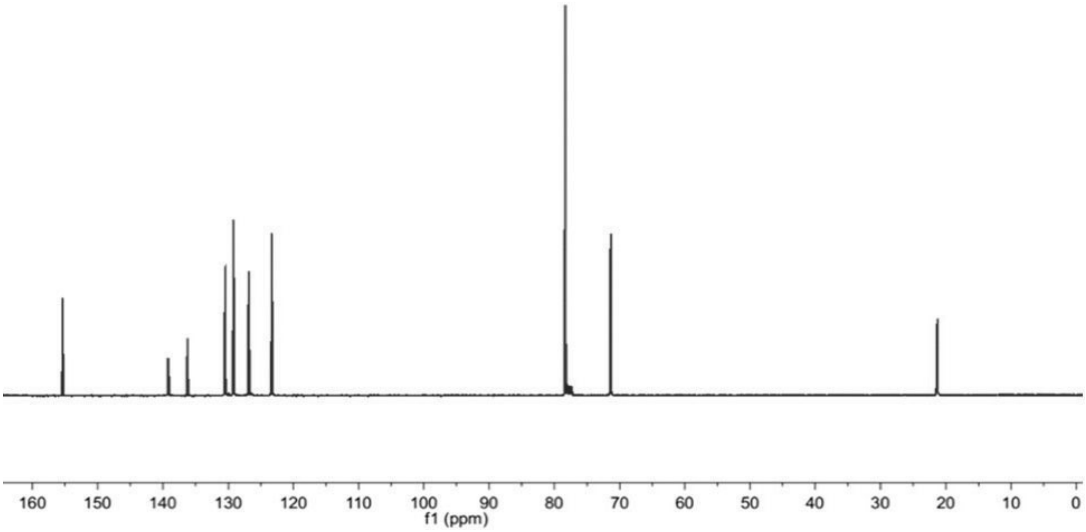


Figure S8. The ^{13}C NMR spectrum of 4-m-tolyl-1,3-dioxolan-2-one (4c).

^{1}H NMR (400 MHz, CDCl$_3$): δ 7.25 (s, 4H), 5.64 (t, J = 8.0 Hz, 1H), 4.77 (t, J = 8.3 Hz, 1H), 4.34 (t, J = 8.6 Hz, 7.9 Hz, 1H), 2.39 (s, 3H)

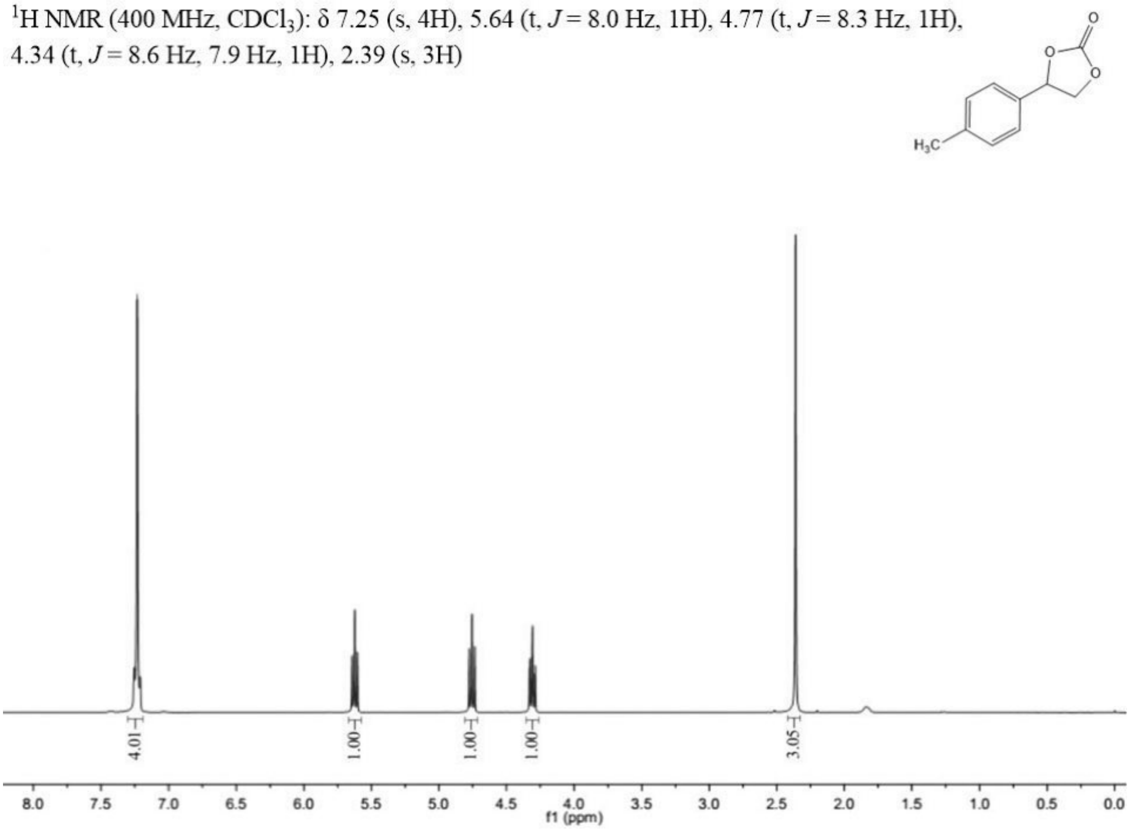


Figure S9. The ^{1}H NMR spectrum of 4-p-tolyl-1,3-dioxolan-2-one (4d).

^{13}C NMR (101 MHz, CDCl$_3$): δ 154.9, 139.9, 132.7, 129.9, 126.0, 78.1, 71.2.

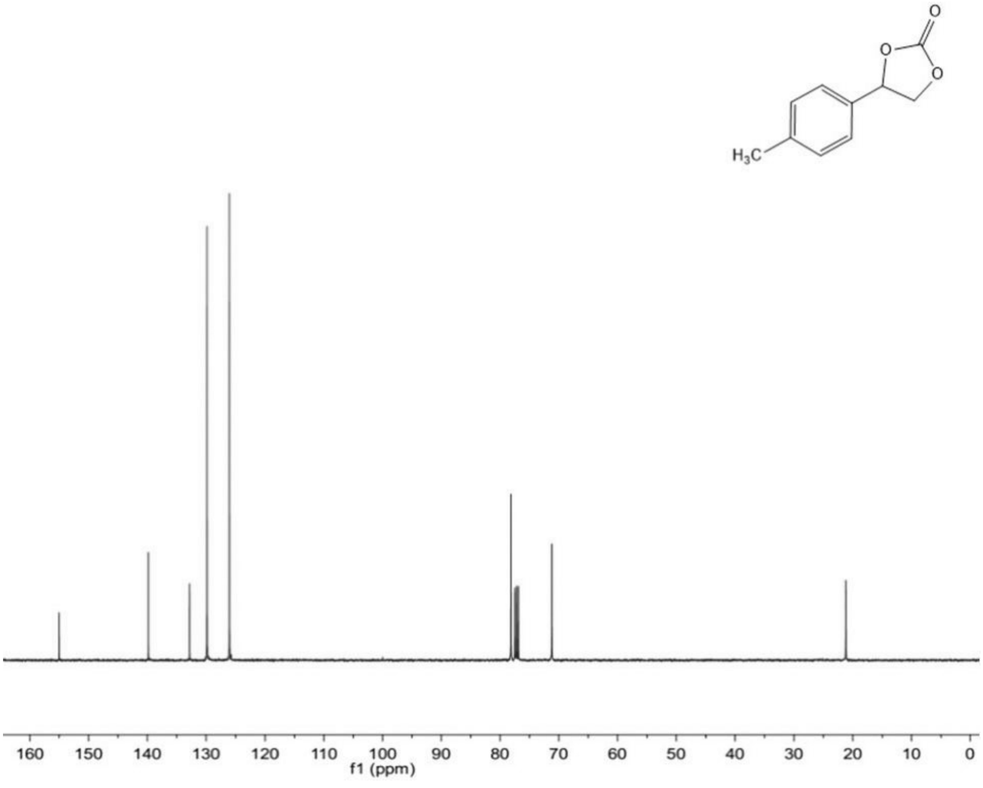
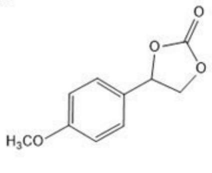


Figure S10. The ^{13}C NMR spectrum of 4-p-tolyl-1,3-dioxolan-2-one (4d).

^{1}H NMR (400 MHz, CDCl$_3$): δ 7.34-7.27 (m, 2H), 6.99-6.92 (m, 2H), 5.62 (m, 1H), 4.75 (m, 1H), 4.35 (m, 3H), 3.83 (s, 3H)



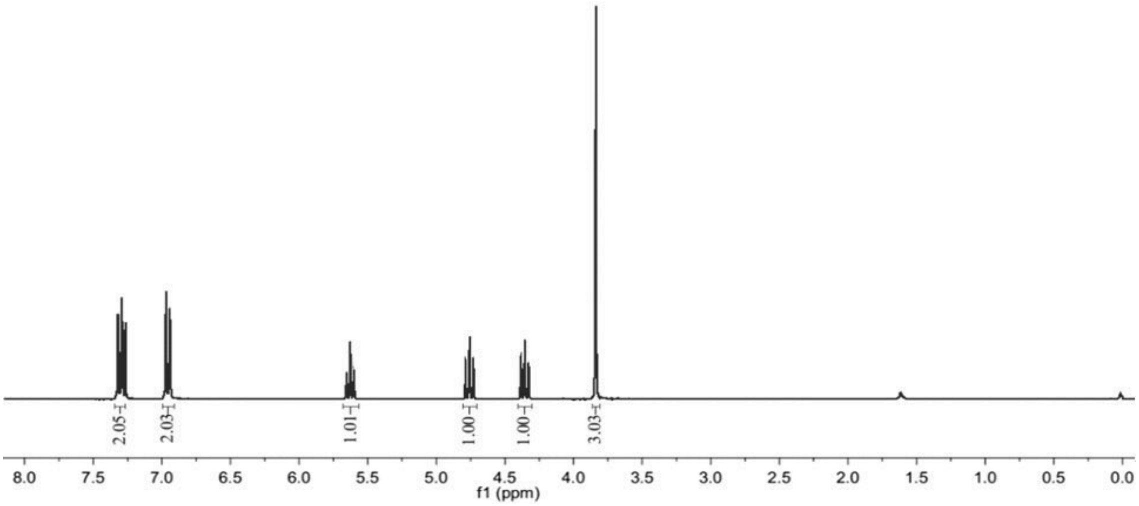
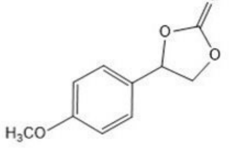


Figure S11. The ^{1}H NMR spectrum of 4-(4-methoxyphenyl)-1,3-dioxolan-2-one (4e).

^{13}C NMR (101 MHz, CDCl$_3$): δ 161.2, 154.9, 127.8, 127.4, 114.6, 78.2, 71.1, 55.4.



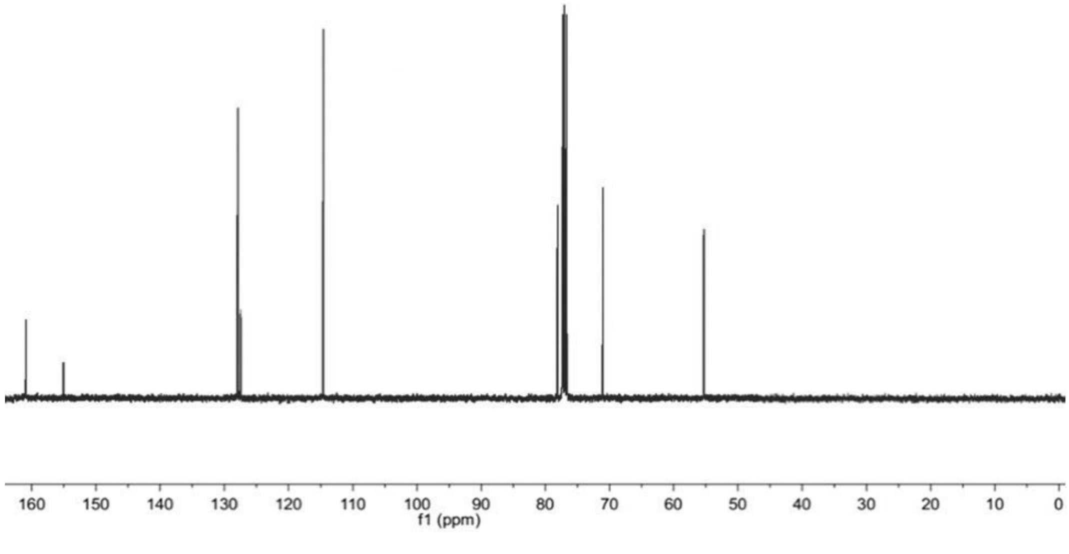
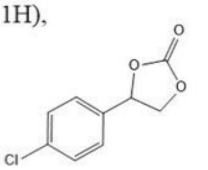


Figure S12. The ^{13}C NMR spectrum of 4-(4-methoxyphenyl)-1,3-dioxolan-2-one (4e).

^{1}H NMR (400 MHz, CDCl$_3$): δ 7.49-7.38 (m, 2H), 7.37-7.28 (m, 2H), 5.69 (t, *J* = 8.0 Hz, 1H), 4.82 (t, *J* = 8.4 Hz, 1H), 4.33 (t, *J* = 8.7 Hz, 1H) .



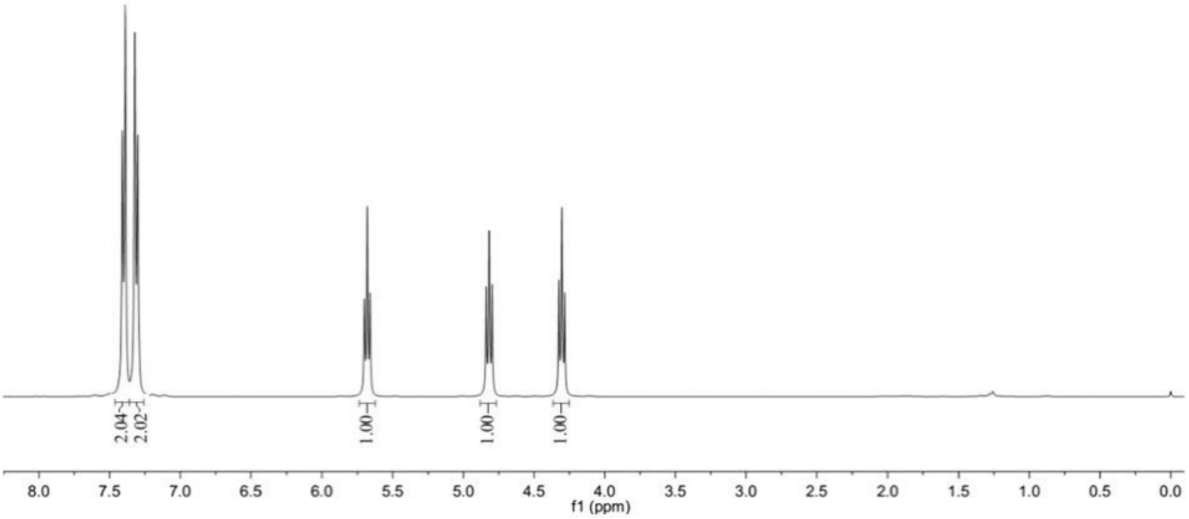
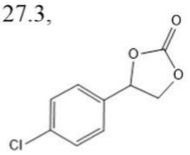


Figure S13. The ^{1}H NMR spectrum of 4-(4-chlorophenyl)-1,3-dioxolan-2-one (4f).

^{13}C NMR (101 MHz, CDCl$_3$): δ 154.5, 135.8, 134.3, 129.5, 127.3, 77.2, 71.0.



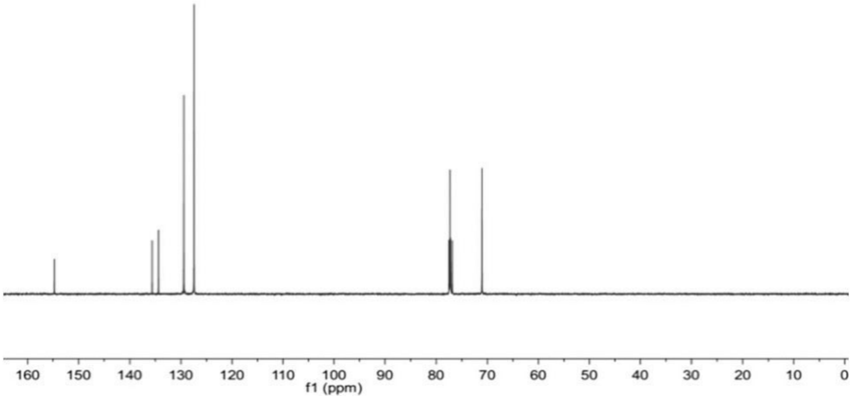


Figure S14. The ^{13}C NMR spectrum of 4-(4-chlorophenyl)-1,3-dioxolan-2-one (4f).

References

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3. (a) Krishnan, R.; Binkley, J. S.; Seeger, R.; Pople, J. A., Self-consistent molecular orbital methods. XX. A basis set for correlated wave functions. *J. Chem. Phys.* **1980,** *72* (1), 650-654; (b) Pople, J. A.; Binkley, J. S.; Seeger, R., Theoretical models incorporating electron correlation. *Int. J. Quantum Chem*. **1976,** *10* (1-19); (c) Huzinaga, S.; Andzelm, J.; Klobukowski, M.; Radzio-Andzelm, E.; Sakai, Y.; Tatewaki, H., *Gaussian Basis Sets for Molecular Calculations*. **1984**.