Supplementary information for "Development of $H_3PW_{12}O_{40}/CeO_2$ catalyst for bulk ring-opening polymerization of cyclic carbonate"

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Table S1. Effect of the pre-calcination temperature of CeO_2

Pre-calcination temperature / ºC	BET surface area / $m^2\ g^{-1}$	Conv. [a] / %	Ether linkage [a] selectivity / %	$M_{n,\ theo}$ [b] / g mol^{-1}	$M_{n,\ GPC}$ [c] / g mol^{-1}	M_w/M_n [c]
400	119	12	0	3,700	3,600	1.21
500	109	18	0	5,700	5,100	1.31
600	73	20	0	6,300	6,200	1.41
700	62	15	0	4,700	4,500	1.35
800	43	4	0	1,300	1,400	1.19
900	26	0	0	-	-	-

Reaction conditions: 1 wt% $H_3PW_{12}O_{40}/CeO_2$ 20 mg (pretreated by drying under reduced pressure, 180 ºC, 0.5 h), TMC 3 mmol, methyl iodide 0.01 mmol, reaction temperature 60 ºC, reaction time 2 h.

[a] calculated by ^1H NMR, [b] calculated by $[TMC]_0/[CH_3I]_0 \times$(conv.)$\times$(molecular weight of TMC) + (molecular weight of CH_3I), [c] determined by GPC in chloroform relative to polystylene standards.

Table S2. Effect of the pretreatment temperature

Pretreatment temperature / ºC	Conversion [a] / %	Ether linkage [a] selectivity / %	$M_{n,\ theo}$ [b] / g mol^{-1}	$M_{n,\ GPC}$ [c] / g mol^{-1}	M_w/M_n [c]
-	7	0	2,100	660	1.29
100	8	0	2,700	2,000	1.30
120	8	0	2,700	3,500	1.31
140	11	0	3,500	3,400	1.33
160	15	0	4,600	4,600	1.40
180	20	0	6,300	6,200	1.41
200	8	0	2,700	2,800	1.30

Reaction conditions: 1 wt% $H_3PW_{12}O_{40}/CeO_2$ 20 mg (pretreated by drying under reduced pressure, 0.5 h), TMC 3 mmol, methyl iodide 0.01 mmol, reaction temperature 60 ºC, reaction time 2 h.

[a] calculated by ^1H NMR, [b] calculated by $[TMC]_0/[CH_3I]_0 \times$(conv.)$\times$(molecular weight of TMC) + (molecular weight of CH_3I), [c] determined by GPC in chloroform relative to polystylene standards.

Table S3. Effect of the loaded amount of $H_3PW_{12}O_{40}$ on CeO_2

Loaded amount of $H_3PW_{12}O_{40}$ / wt%	BET surface area / $m^2\ g^{-1}$	Conversion [a] / %	Ether linkage [a] selectivity / %	$M_{n,\ theo}$ [b] / g mol^{-1}	$M_{n,\ GPC}$ [c] / g mol^{-1}	M_w/M_n [c]
0.1	66	19	0	5,900	19,000	1.26
0.5	70	20	0	6,300	14,000	1.29
1	73	20	0	6,300	6,200	1.41
2	70	3	0	1,000	470	1.39
5	68	2	0	750	250	1.36

Reaction conditions: $H_3PW_{12}O_{40}/CeO_2$ 20 mg (pretreated by drying under reduced pressure, 180 ºC, 0.5 h), TMC 3 mmol, methyl iodide 0.01 mmol, reaction temperature 60 ºC, reaction time 2 h.

[a] calculated by ^1H NMR, [b] calculated by $[TMC]_0/[CH_3I]_0 \times$(conv.)$\times$(molecular weight of TMC) + (molecular

weight of CH_3I), [c] determined by GPC in chloroform relative to polystylene standards.

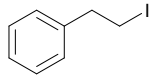
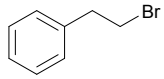
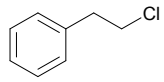
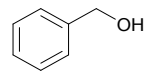
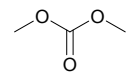
Table S4. Catalyst recycle test

Usage time	Conversion [a] / %	Ether linkage [a] selectivity / %	$M_{n,\,theo}$ [b] / g mol^{-1}	$M_{n,\,GPC}$ [c] / g mol^{-1}	M_w/M_n [c]
1	21	0	6,400	6,200	1.41
2	17	0	5,100	690	1.18
2[d]	17	0	5,100	1,300	1.23

Reaction conditions: $H_3PW_{12}O_{40}/CeO_2$ 20 mg (pretreated by drying under reduced pressure, 180 ºC, 0.5 h), TMC 3 mmol, initiator 0.01 mmol, reaction temperature 60 ºC, reaction time 2 h.

[a] calculated by ^{1}H NMR, [b] calculated by $[TMC]_0/[CH_3I]_0 \times$(conv.)$\times$(molecular weight of TMC) + (molecular weight of CH_3I), [c] determined by GPC in chloroform relative to polystylene standards, [d] calcined at 200 ºC for 0.5 h.

Table S5. Effect of initiator

Entry	Initiator	Conversion [a] / %	Ether linkage [a] selectivity / %	$M_{n,\,theo}$ [b] / g mol^{-1}	$M_{n,\,GPC}$ [c] / g mol^{-1}	M_w/M_n [c]
1		21	0	6,400	6,200	1.41
2		12	0	3,900	3,300	1.38
3		3	0	1,000	220	1.56
4		0	0	140	-	-
5		15	0	4,600	2,400	1.18
6		1	0	450	-	-
7		3	0	1,000	1,600	1.12
8		10	0	3,000	430	1.55
9		11	0	3,400	290	1.85
10		12	0	5,000	2,900	1.77
11	None	3	0	-	640	1.36

Reaction conditions: $H_3PW_{12}O_{40}/CeO_2$ 20 mg (pretreated by drying under reduced pressure, 180 ºC, 0.5 h), TMC 3 mmol, initiator 0.01 mmol, reaction temperature 60 ºC, reaction time 2 h.

[a] calculated by ^{1}H NMR, [b] calculated by $[TMC]_0/[initiator]_0 \times$(conv.)$\times$(molecular weight of TMC) + (molecular weight of initiator), [c] determined by GPC in chloroform relative to polystylene standards.

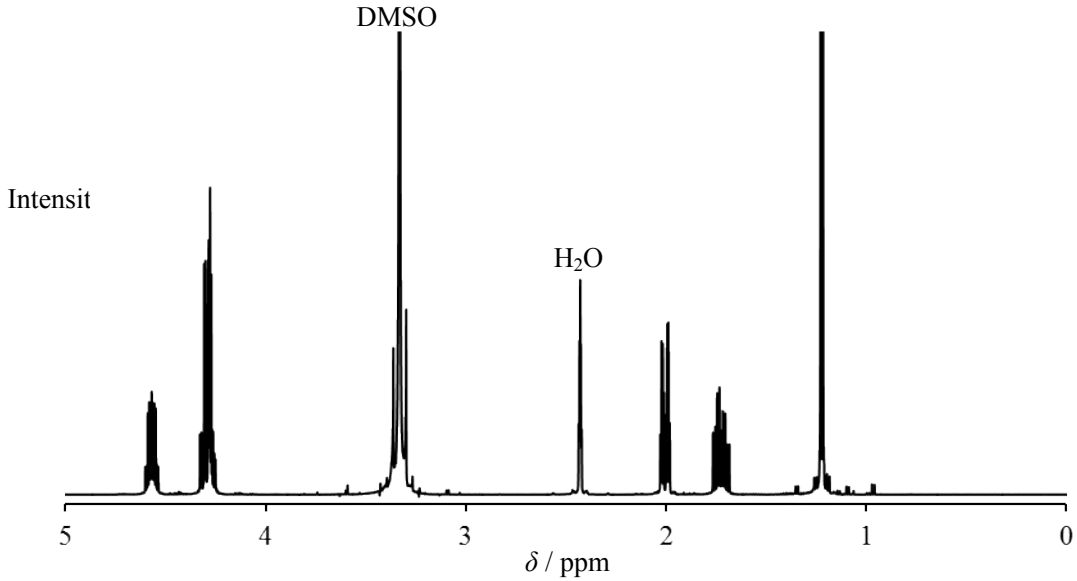


Figure S1. ^{1}H NMR spectra of 4-methyl-1,3-dioxan-2-one

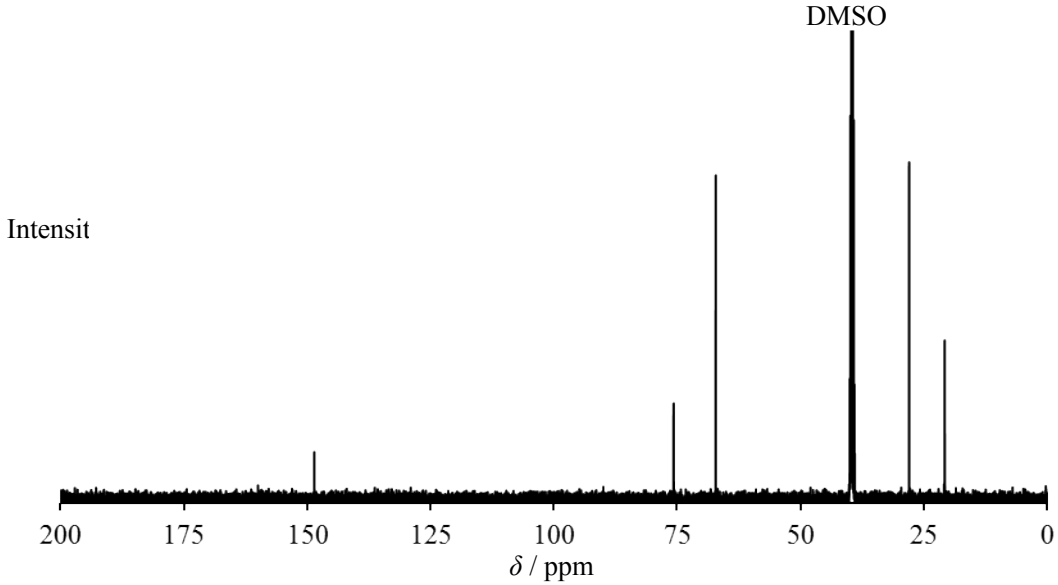


Figure S2. ^{13}C NMR spectra of 4-methyl-1,3-dioxan-2-one

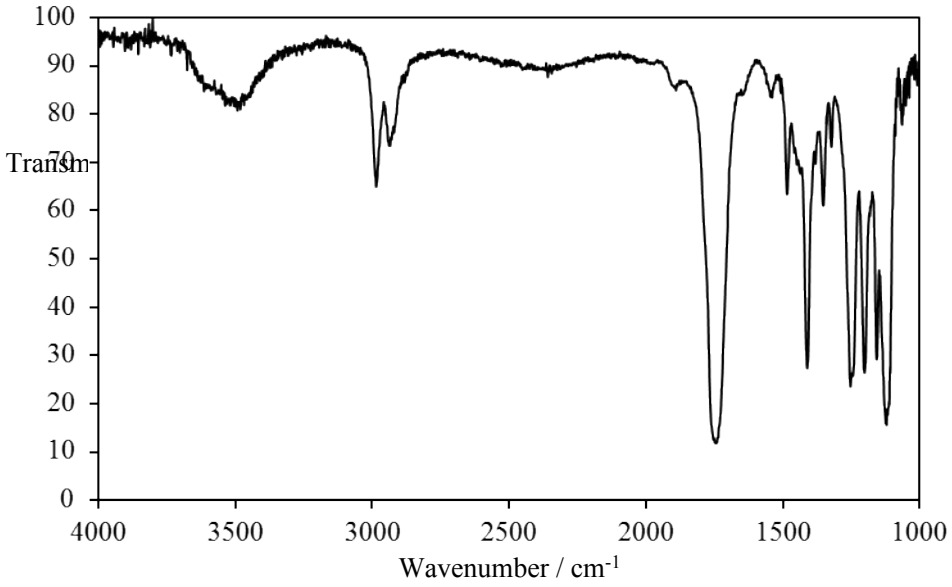


Figure S3. FTIR spectra of 4-methyl-1,3-dioxan-2-one

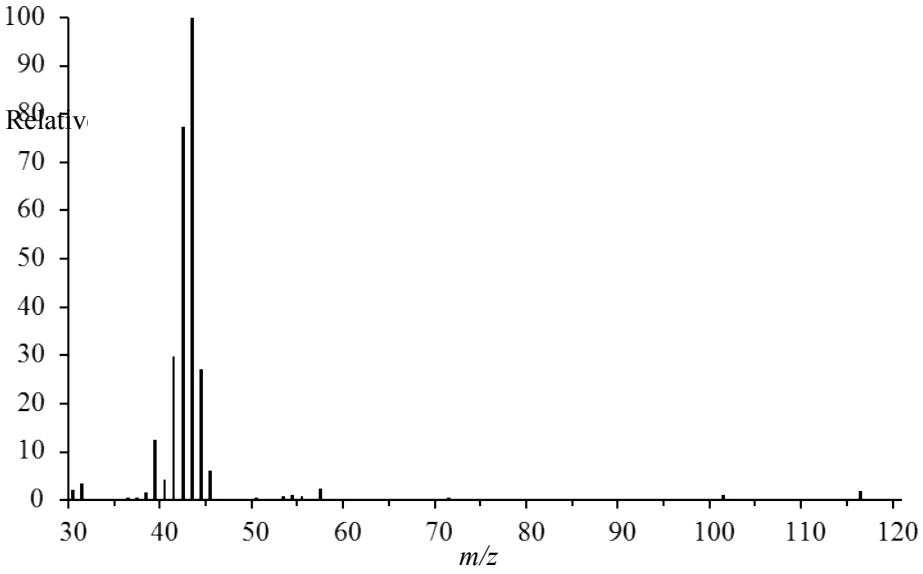


Figure S4. MS spectra of 4-methyl-1,3-dioxan-2-one

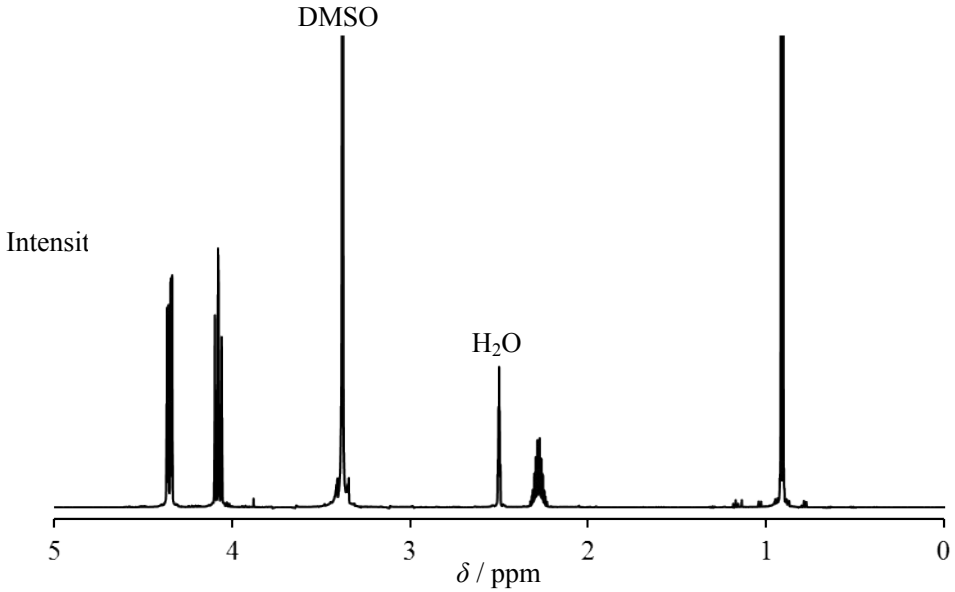


Figure S5. ^{1}H NMR spectra of 5-methyl-1,3-dioxan-2-one

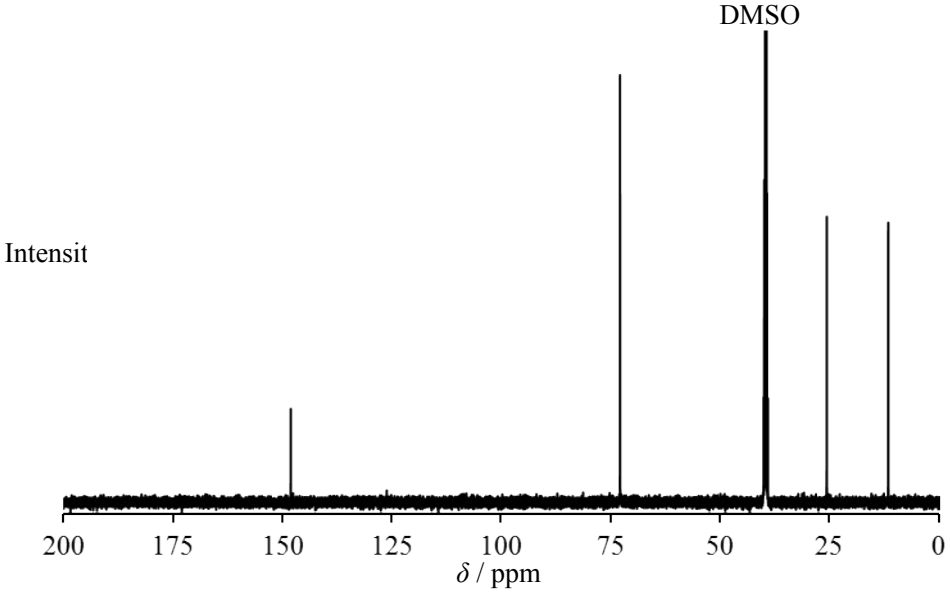


Figure S6. ^{13}C NMR spectra of 5-methyl-1,3-dioxan-2-one

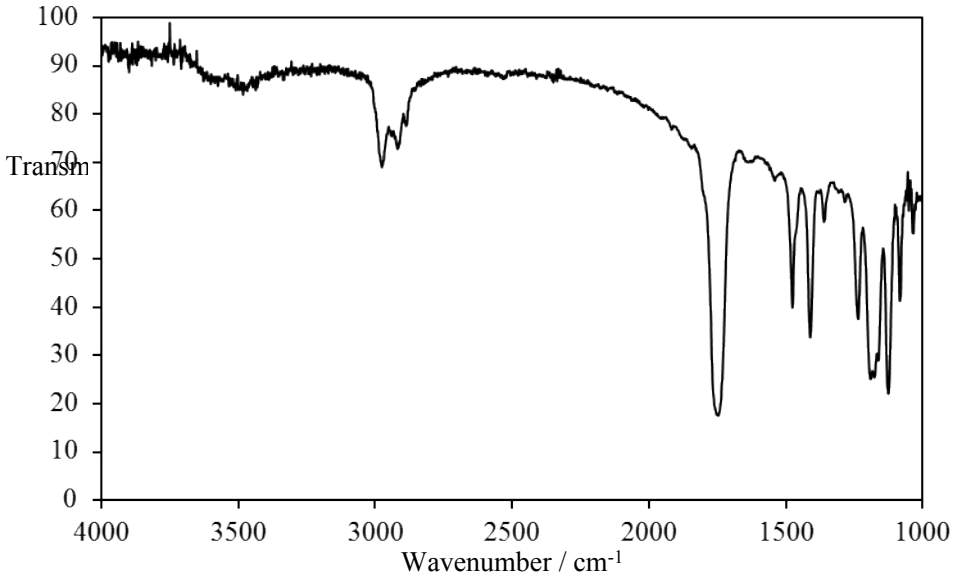


Figure S7. FTIR spectra of 5-methyl-1,3-dioxan-2-one

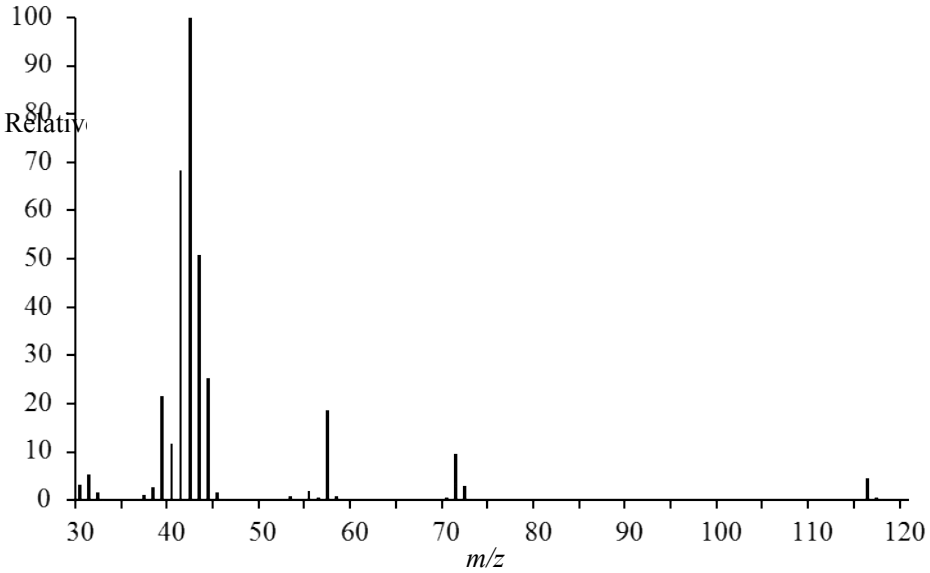


Figure S8. MS spectra of 5-methyl-1,3-dioxan-2-one

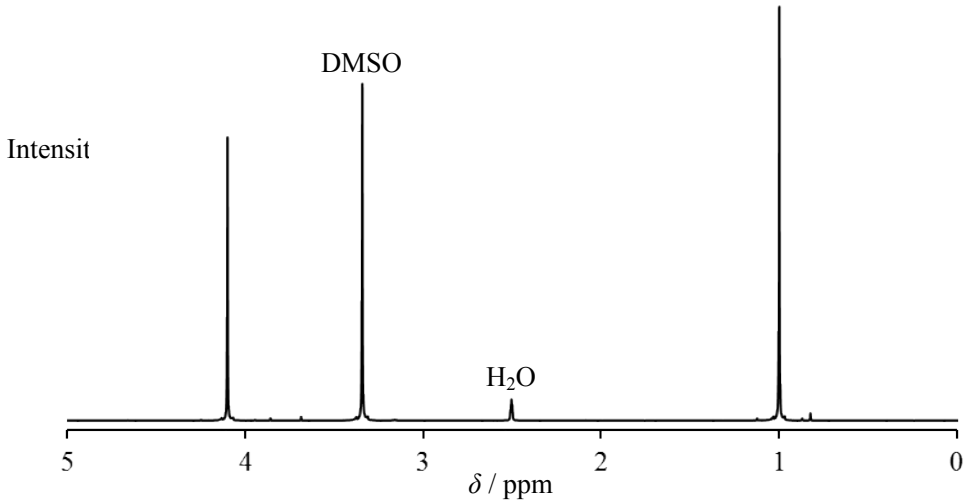


Figure S9. ^{1}H NMR spectra of 5,5-dimethyl-1,3-dioxan-2-one

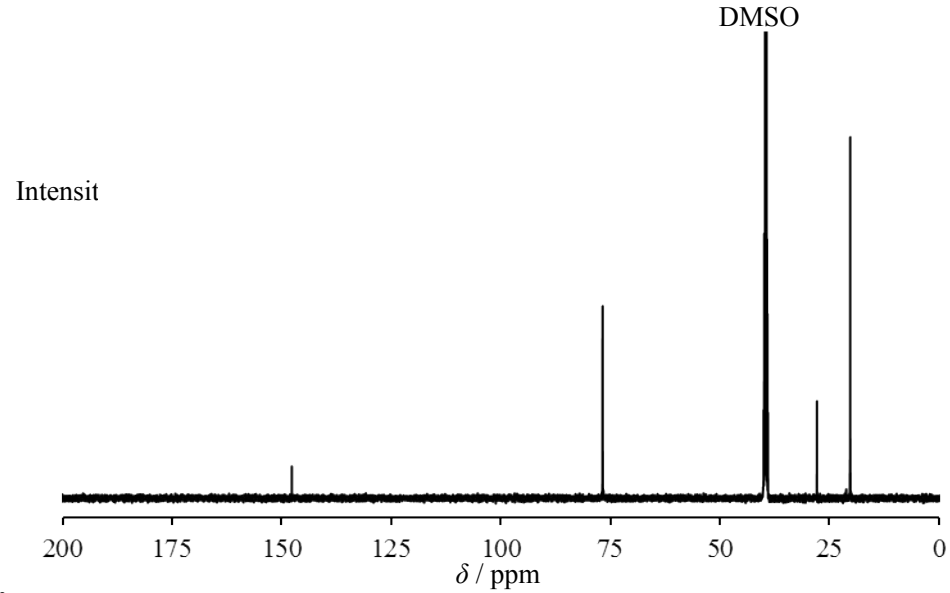


Figure S10. ^{13}C NMR spectra of 5,5-dimethyl-1,3-dioxan-2-one

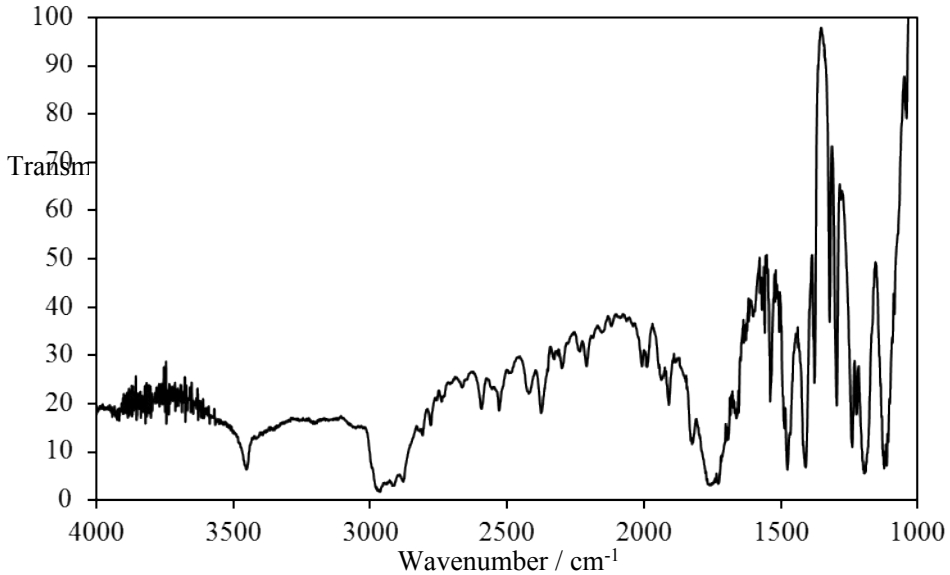


Figure S11. FTIR spectra of 5,5-dimethyl-1,3-dioxan-2-one

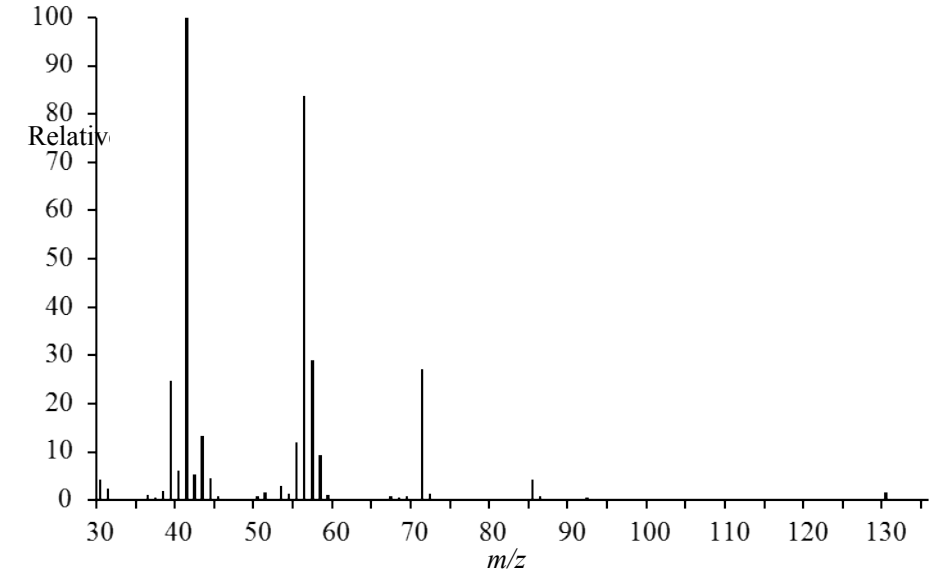


Figure S12. MS spectra of 5,5-dimethyl-1,3-dioxan-2-one

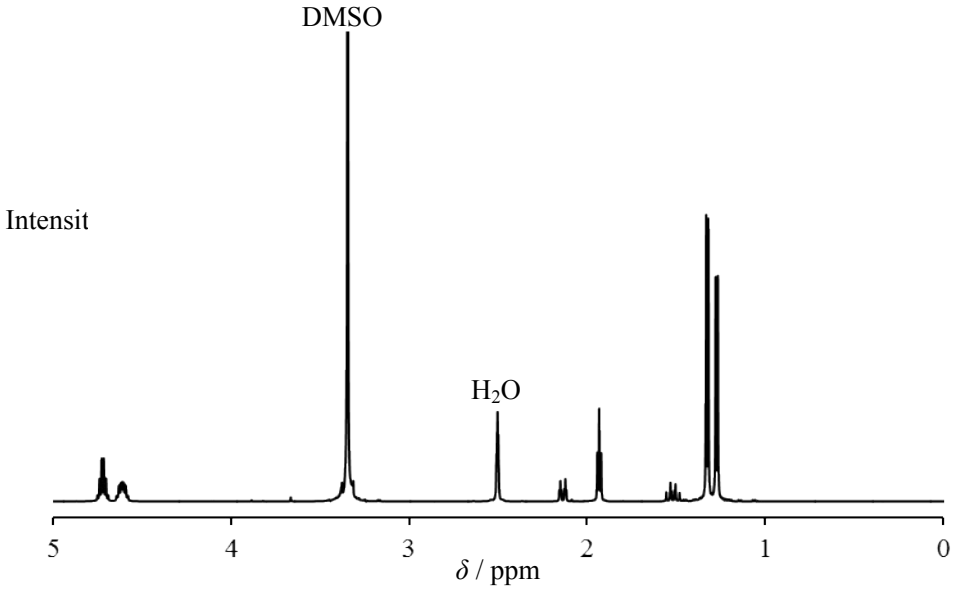


Figure S13. ^{1}H NMR spectra of 4,6-dimethyl-1,3-dioxan-2-one

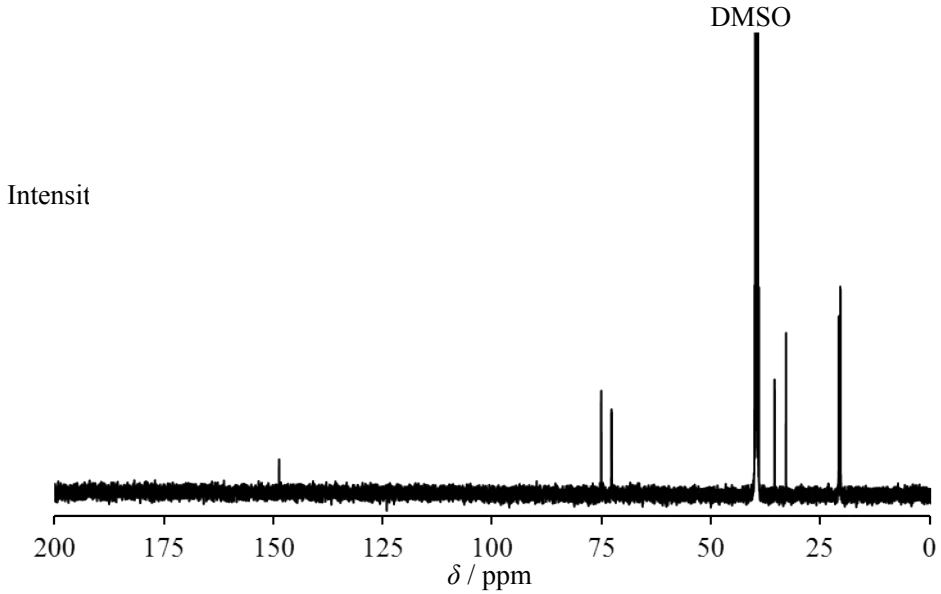


Figure S14. ^{13}C NMR spectra of 4,6-dimethyl-1,3-dioxan-2-one

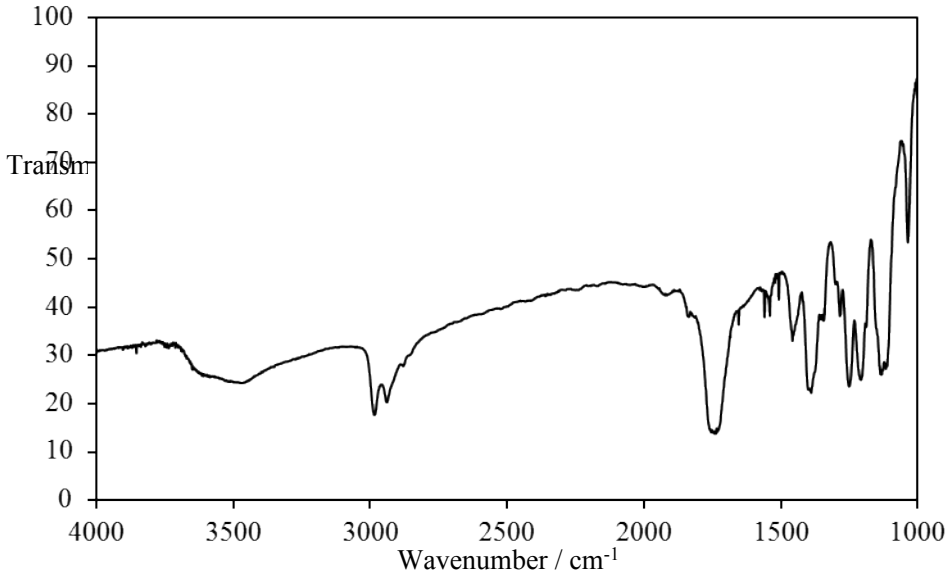


Figure S15. FTIR spectra of 4,6-dimethyl-1,3-dioxan-2-one

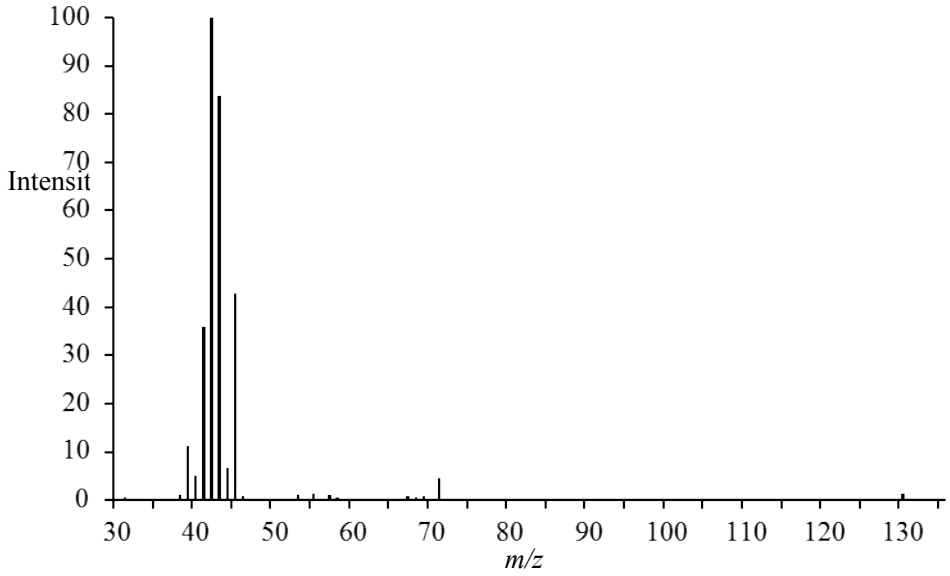


Figure S16. MS spectra of 4,6-dimethyl-1,3-dioxan-2-one

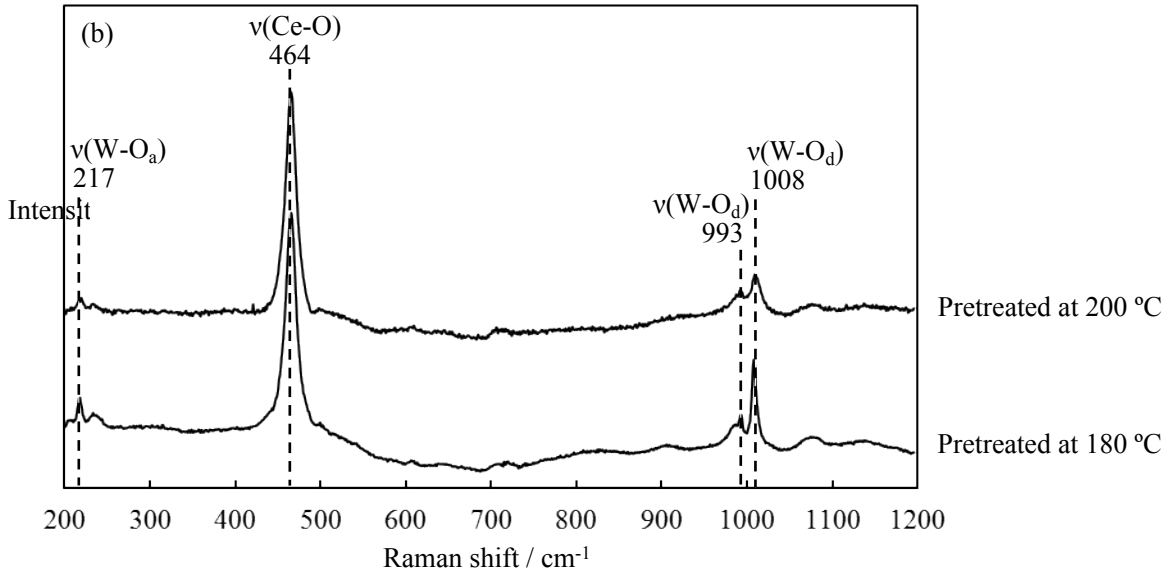


Figure S17. Raman spectra of 30 wt% $H_3PW_{12}O_{40}/CeO_2$ pretreated at different temperature

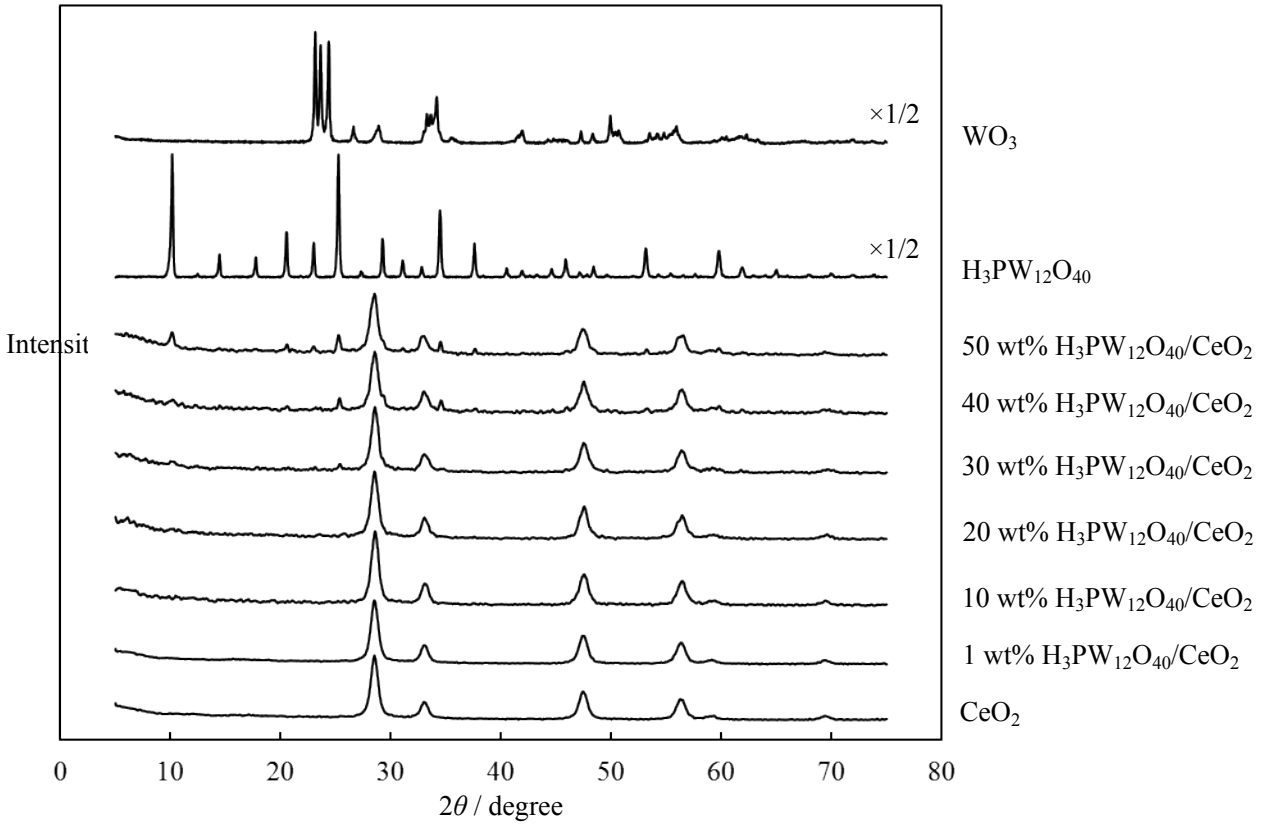


Figure S18. XRD profile of WO_3, $H_3PW_{12}O_{40}$ and $H_3PW_{12}O_{40}/CeO_2$

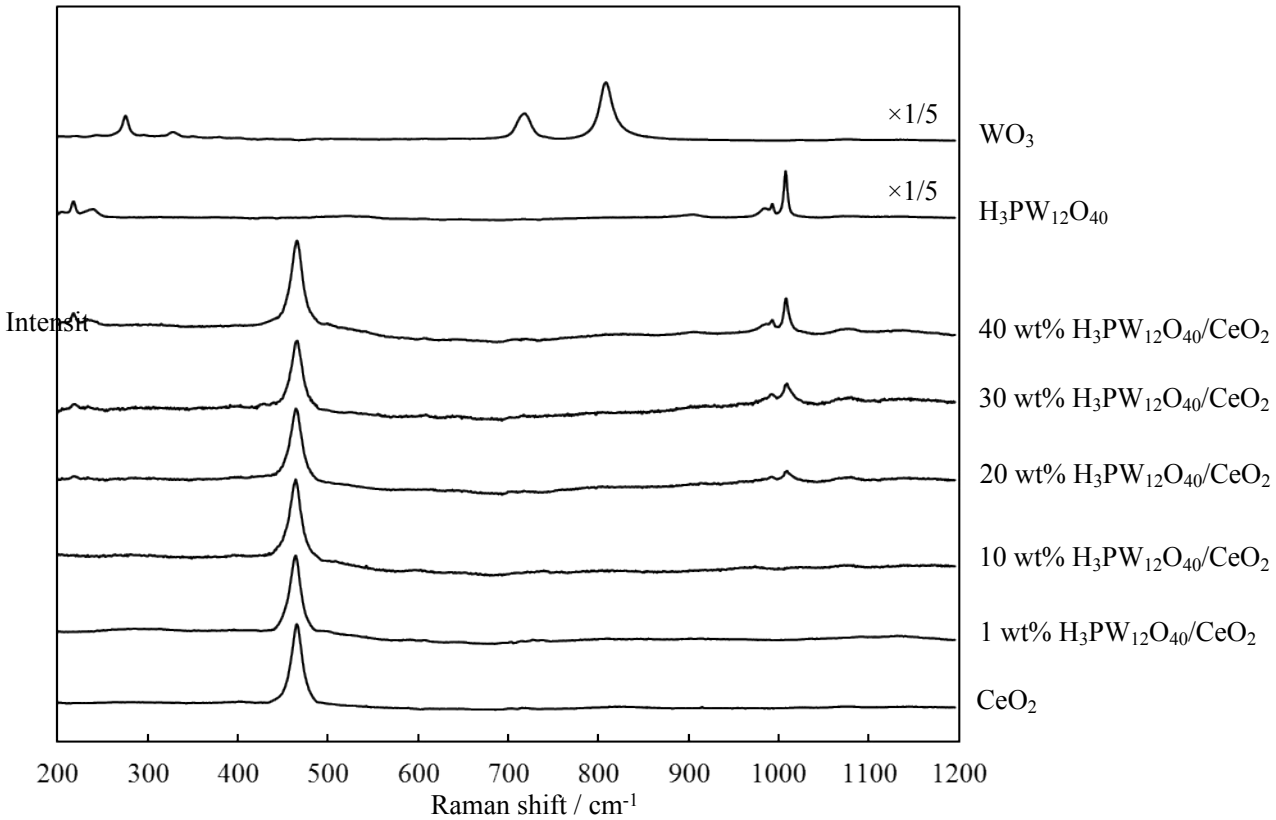


Figure S19. Raman spectra of WO_3, $H_3PW_{12}O_{40}$ and $H_3PW_{12}O_{40}/CeO_2$

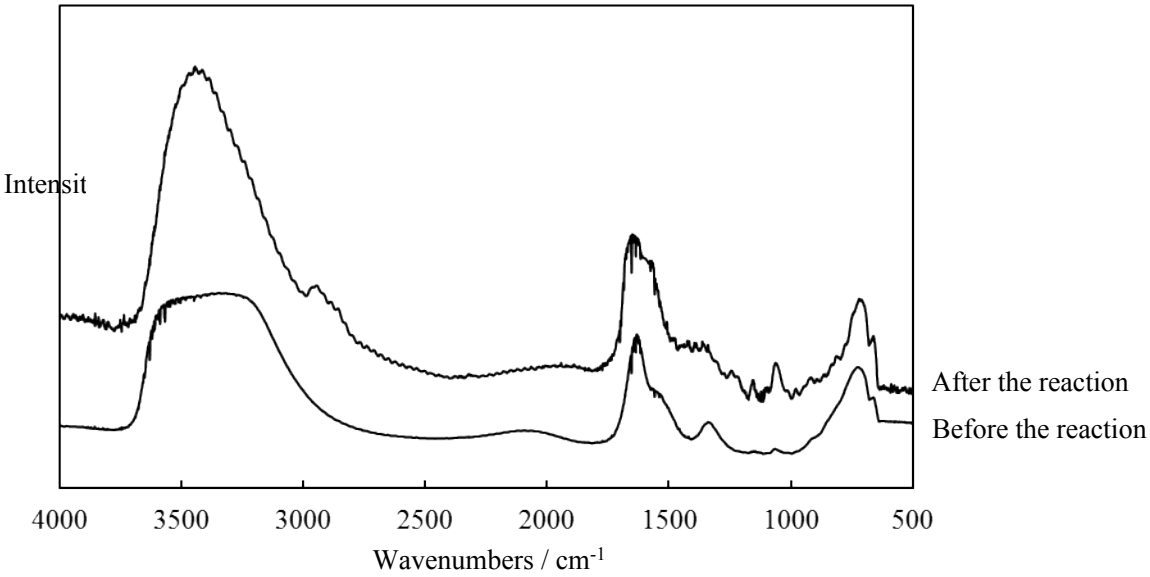


Figure S20. FTIR spectra of 1 wt% $H_3PW_{12}O_{40}/CeO_2$ catalyst before and after the reaction

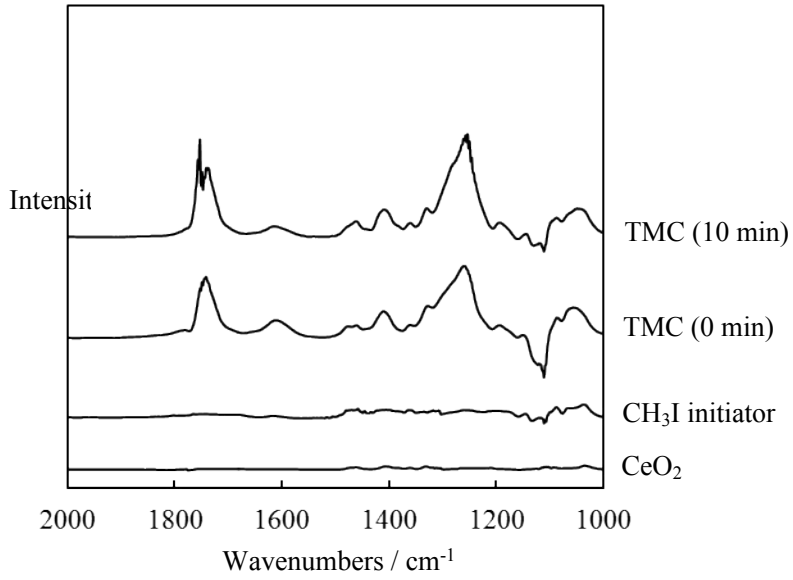


Figure S21. Differential FTIR spectra of CeO_2

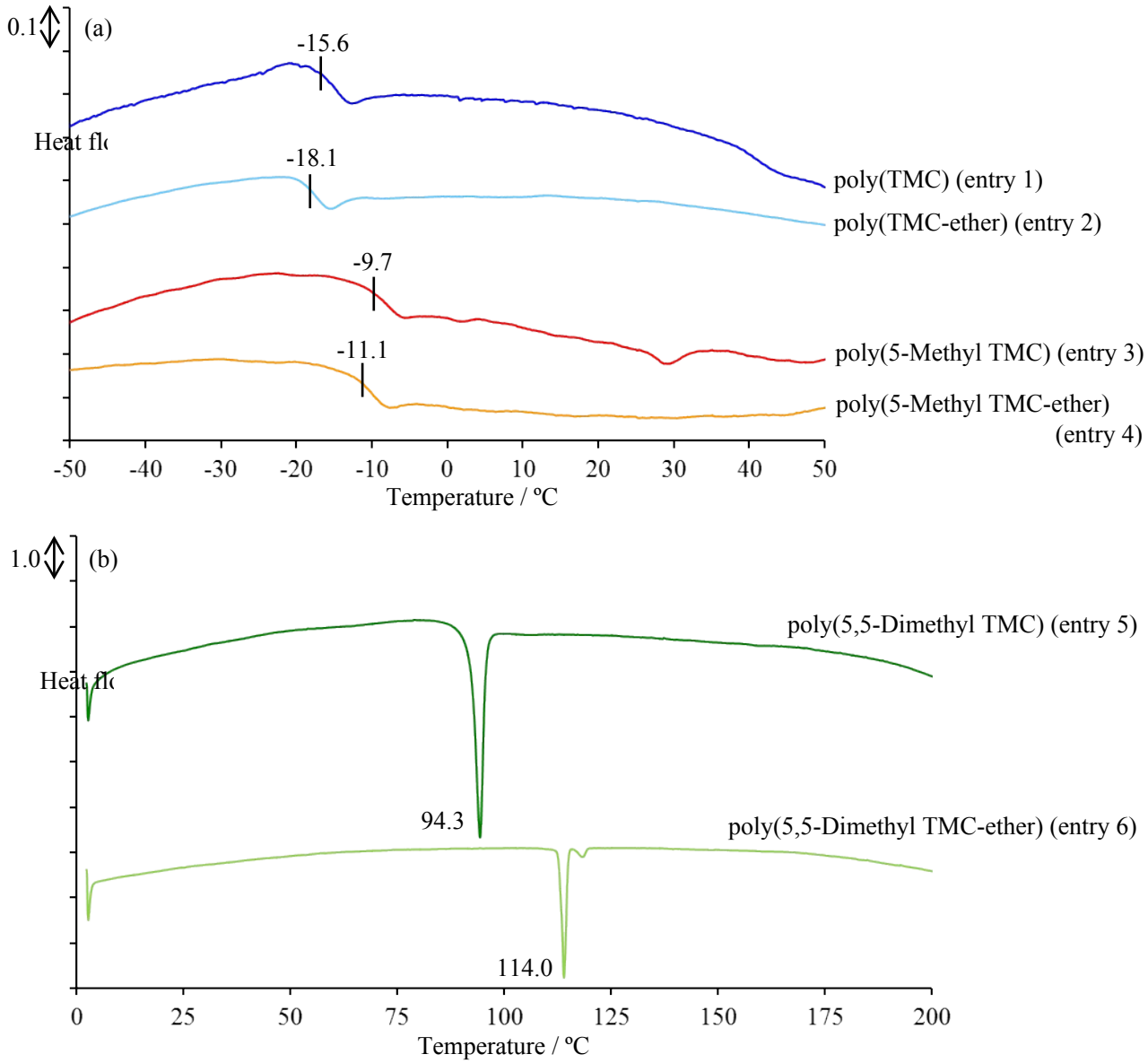


Figure S22. DSC profiles of (a) entries 1-4 (b) entries 5, 6 in Table 5

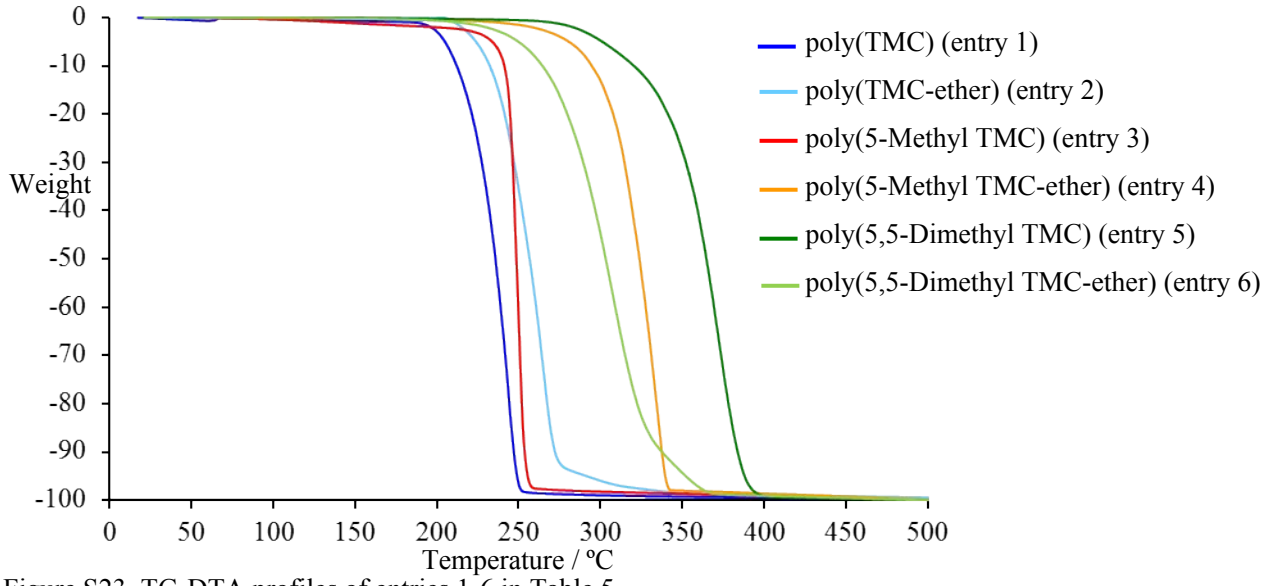


Figure S23. TG-DTA profiles of entries 1-6 in Table 5

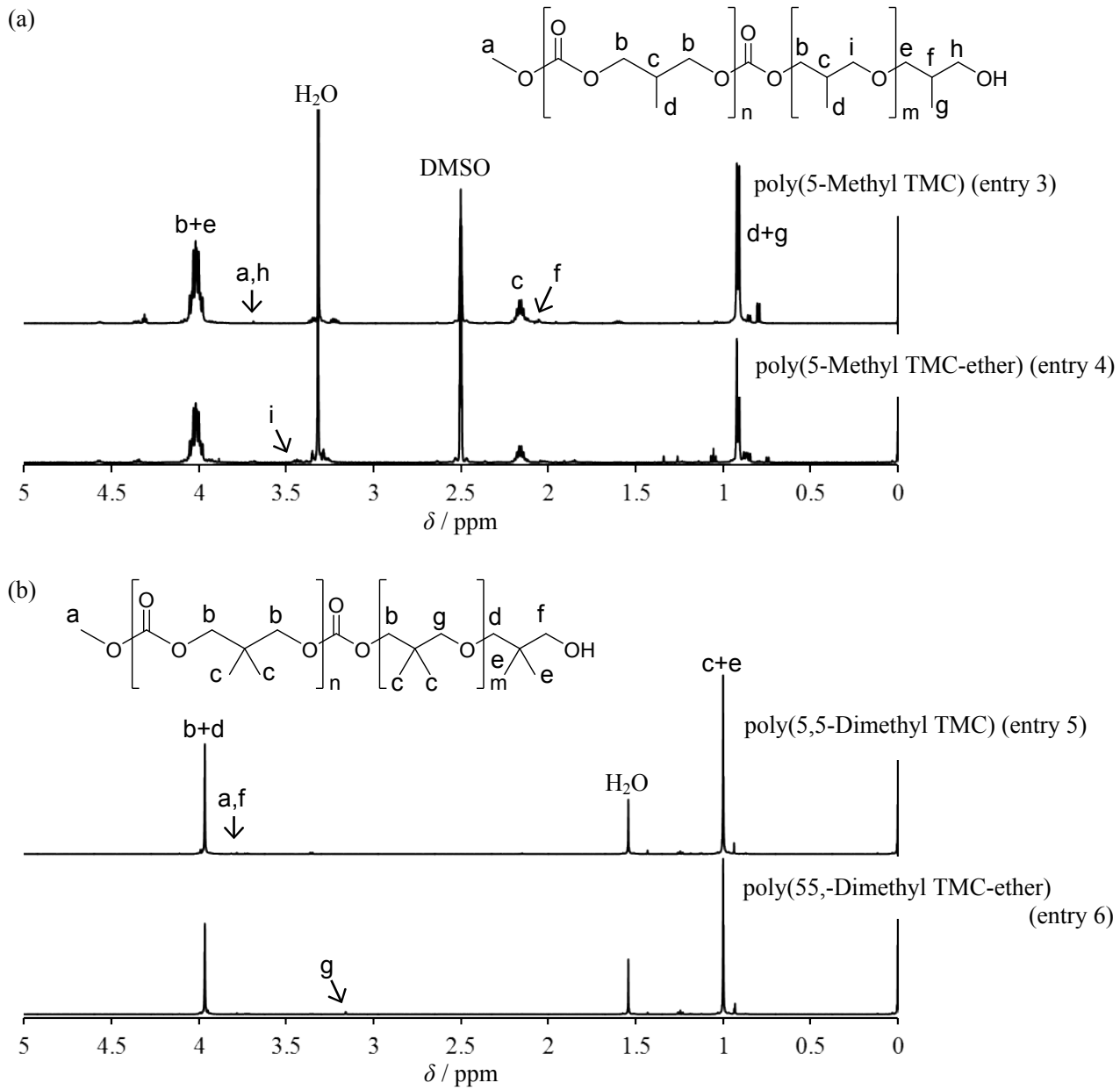


Figure S24. ^{1}H NMR spectra of (a) poly(5-Methyl TMC)s in DMSO-*d6* and (b) poly(5,5-dimethyl TMC)s in $CDCl_3$

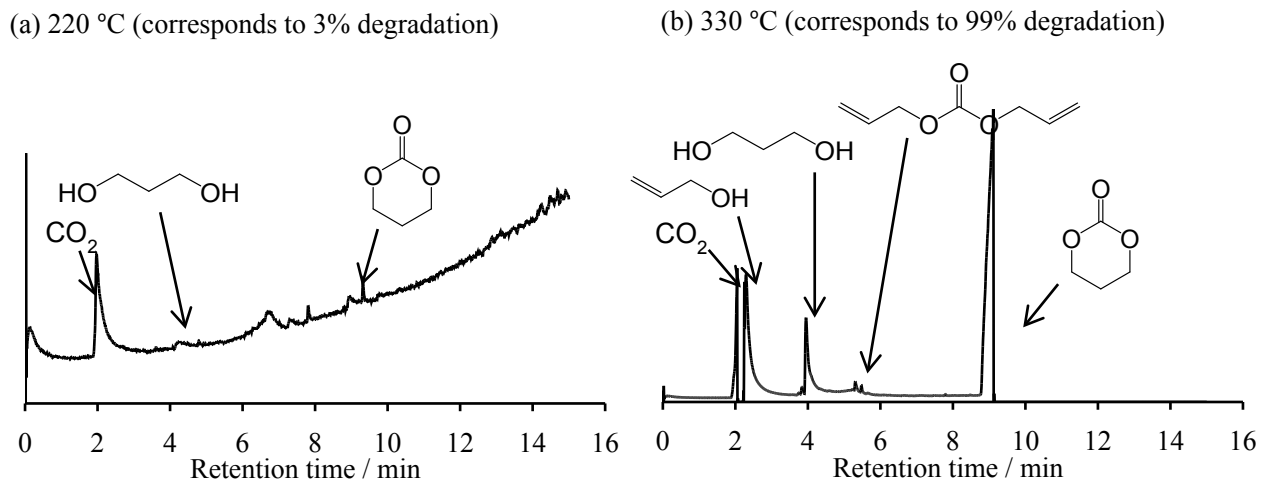


Figure S25. The chromatograms of Py-GCMS of poly(TMC-ether)