

Supporting information

In-depth study on the effect of oxygen- containing functional groups in pyrolysis oil by P-31 NMR

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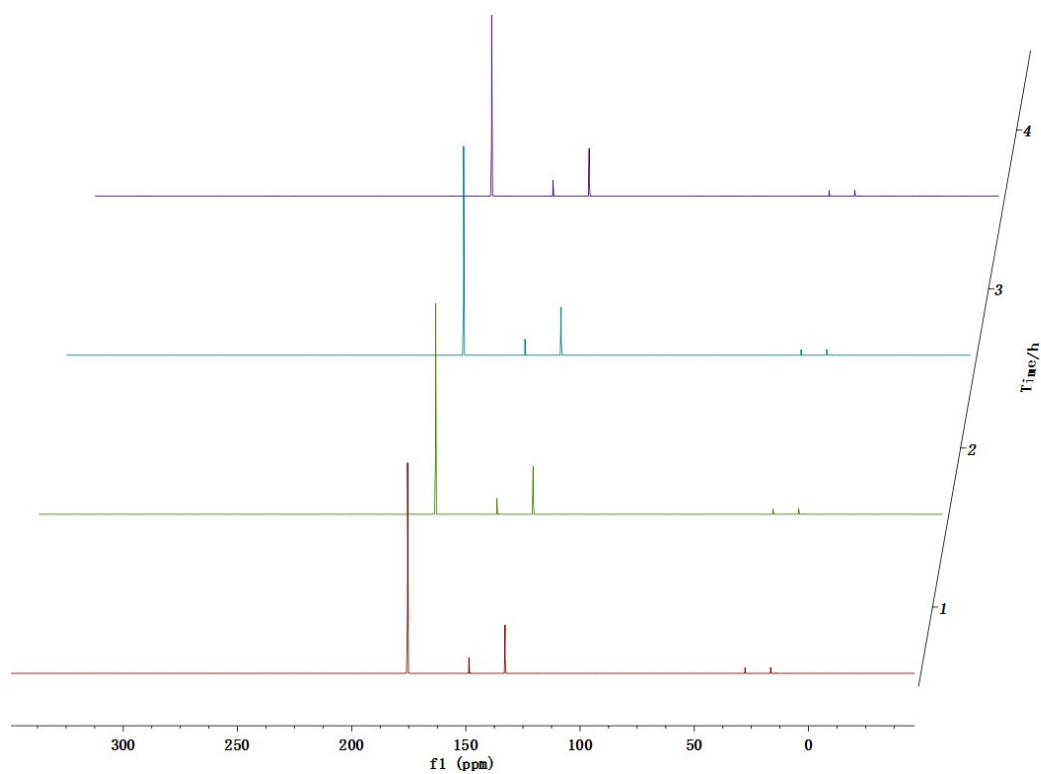
² Key Laboratory of Energy Thermal Conversion and Control of Ministry of
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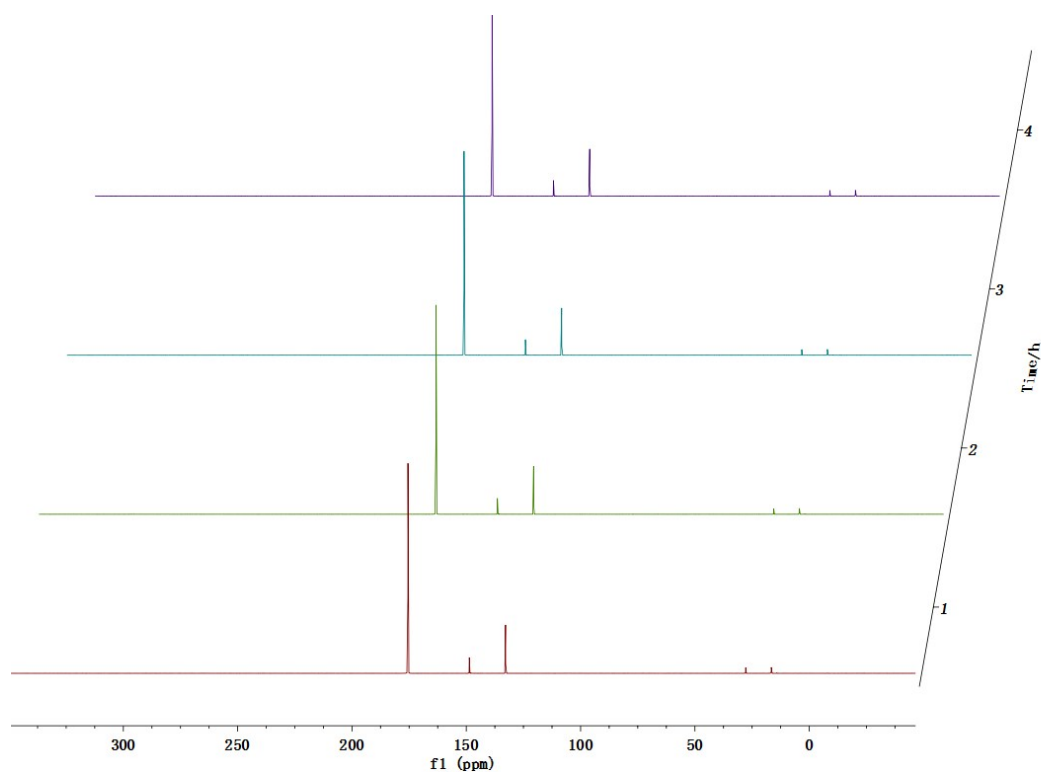
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a



b

Fig. S1 In situ monitoring for the stability of formic acid with different D1 in ^{31}P NMR (a: D1=25s; b: D1=100s).

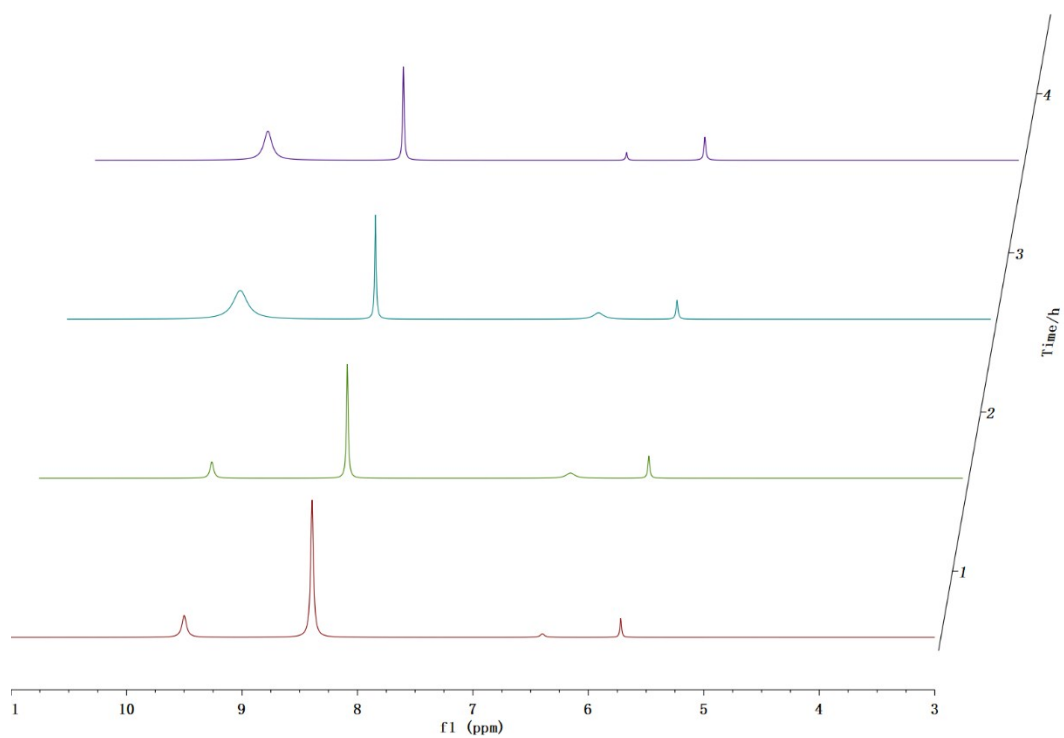


Fig. S2 In situ monitoring for the stability of formic acid in ^1H NMR.

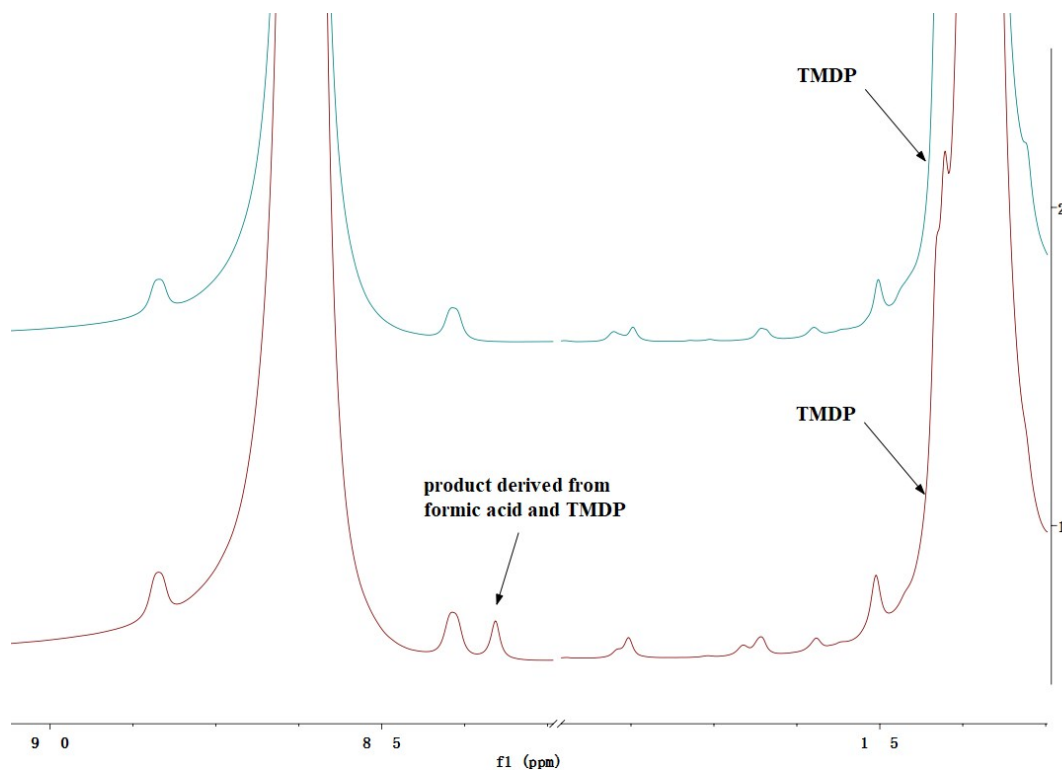
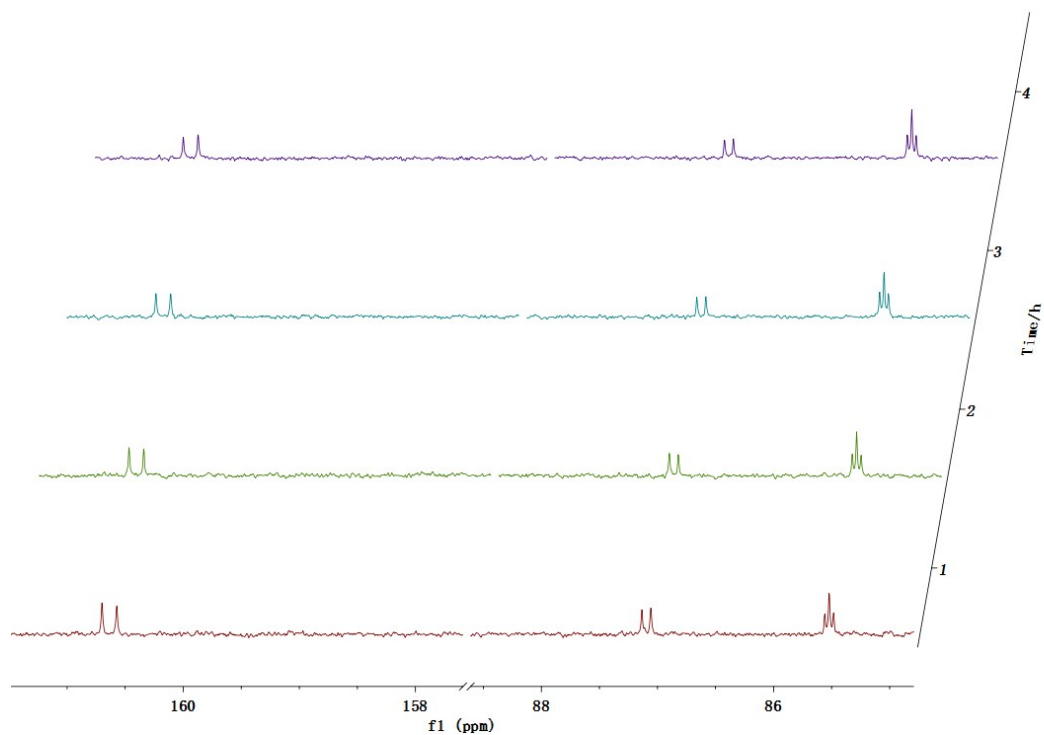


Fig. S3 Comparison before(bottom) and after(top) 14 days of ex situ monitoring of formic acid in ^1H NMR.



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ig. S4 The peak of formic acid and some growing peaks during the in situ monitoring in ^{13}C NMR with TPPO as internal standard.

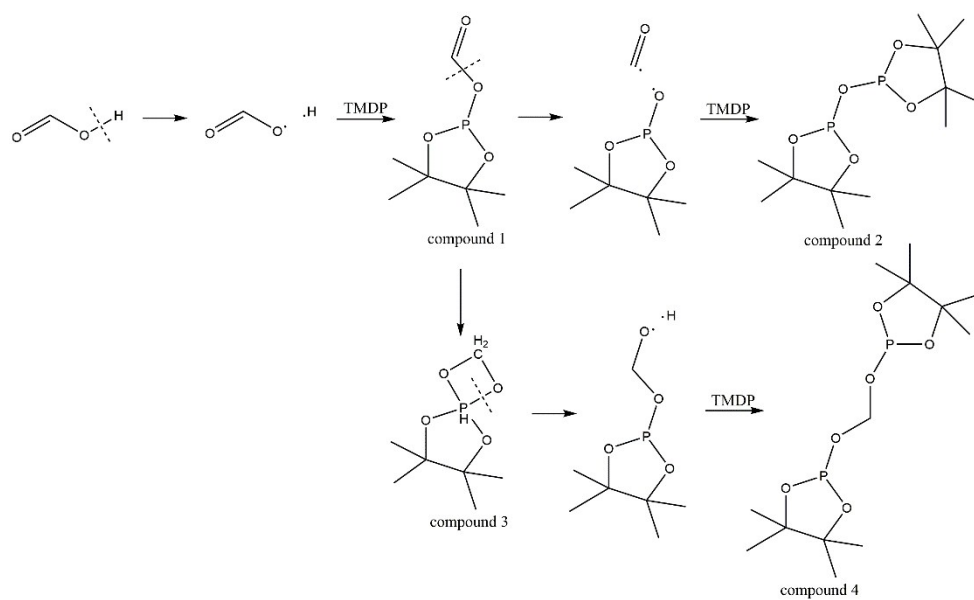


Fig S5. Two possible decomposition pathway for formic acid in ^{31}P NMR.

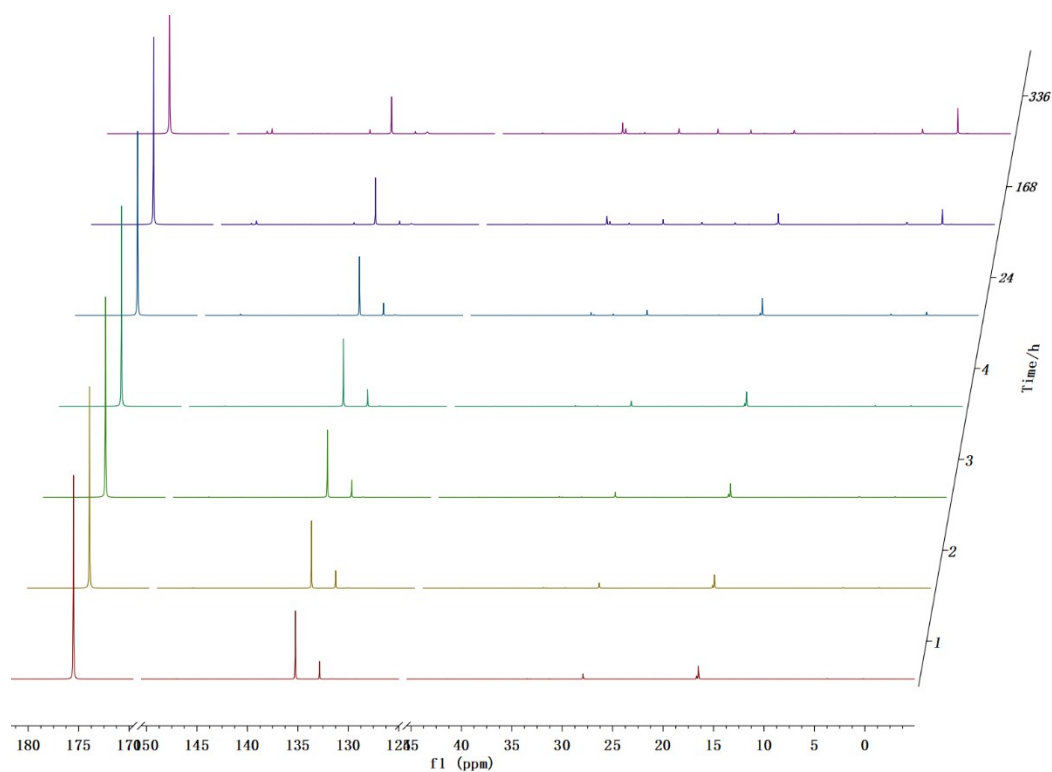


Fig. S6 In situ and ex situ monitoring for the stability of acetic acid during ^{31}P NMR with TPPO as internal standard.

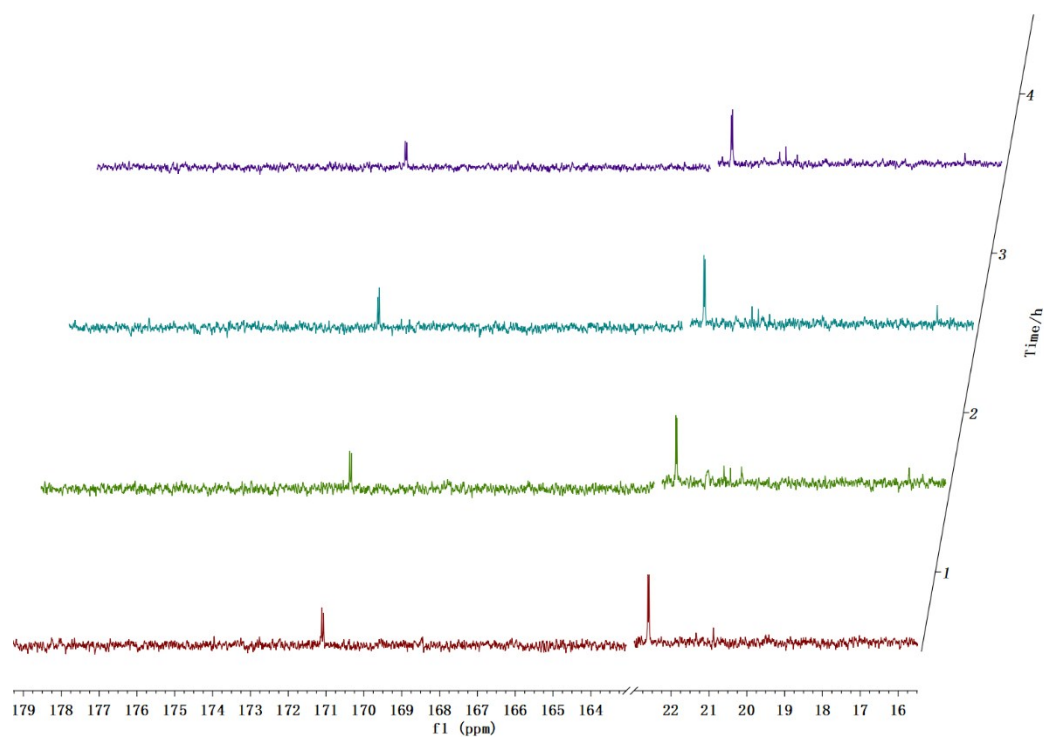


Fig. S7 The peak of acetic acid during the in situ monitoring in ^{13}C NMR with TPPO as internal standard.

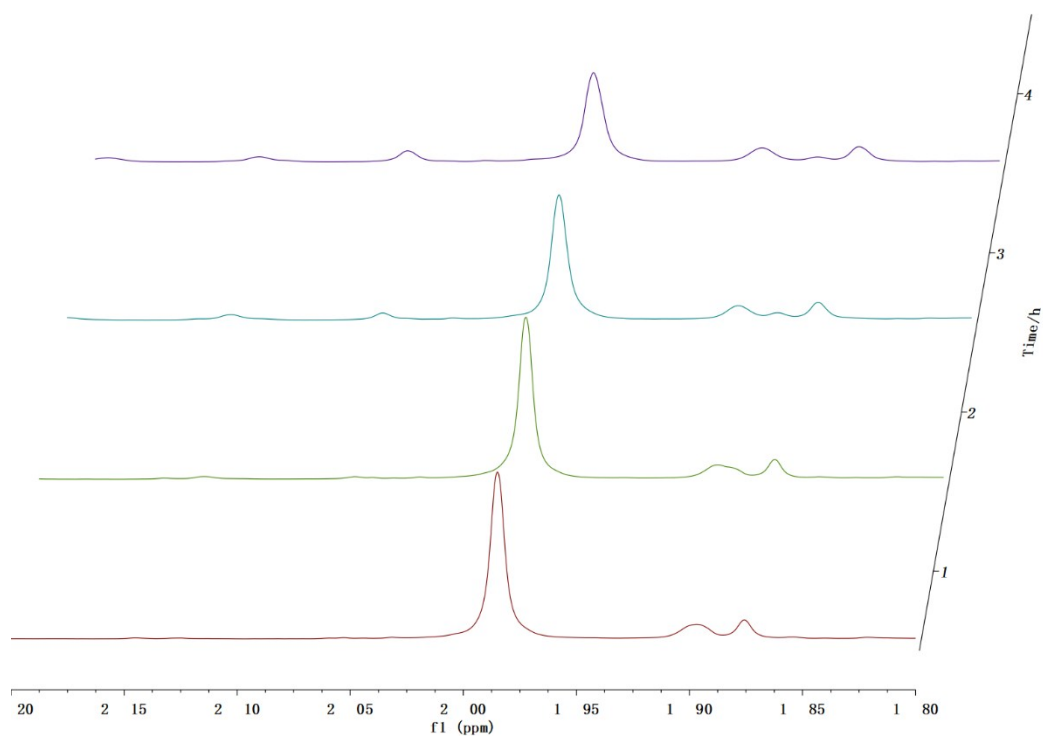
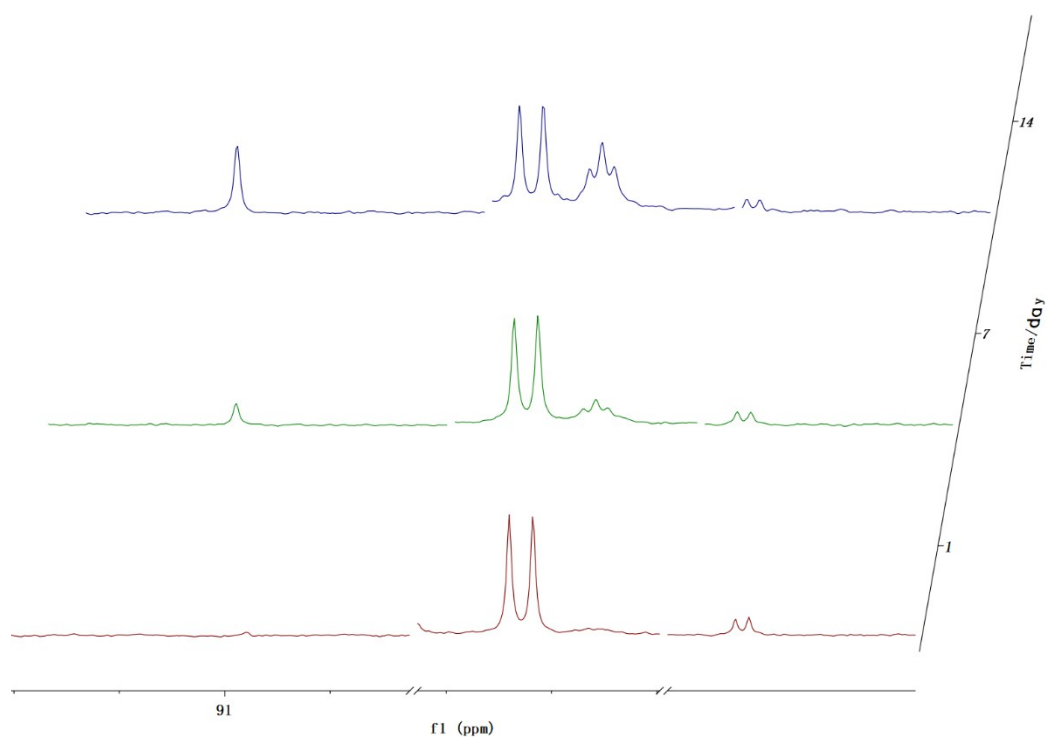


Fig. S8 In situ monitoring for the stability of acetic acid in ^1H NMR.



ig. S9 Ex situ monitoring for the stability of acetic acid in ^{13}C NMR.

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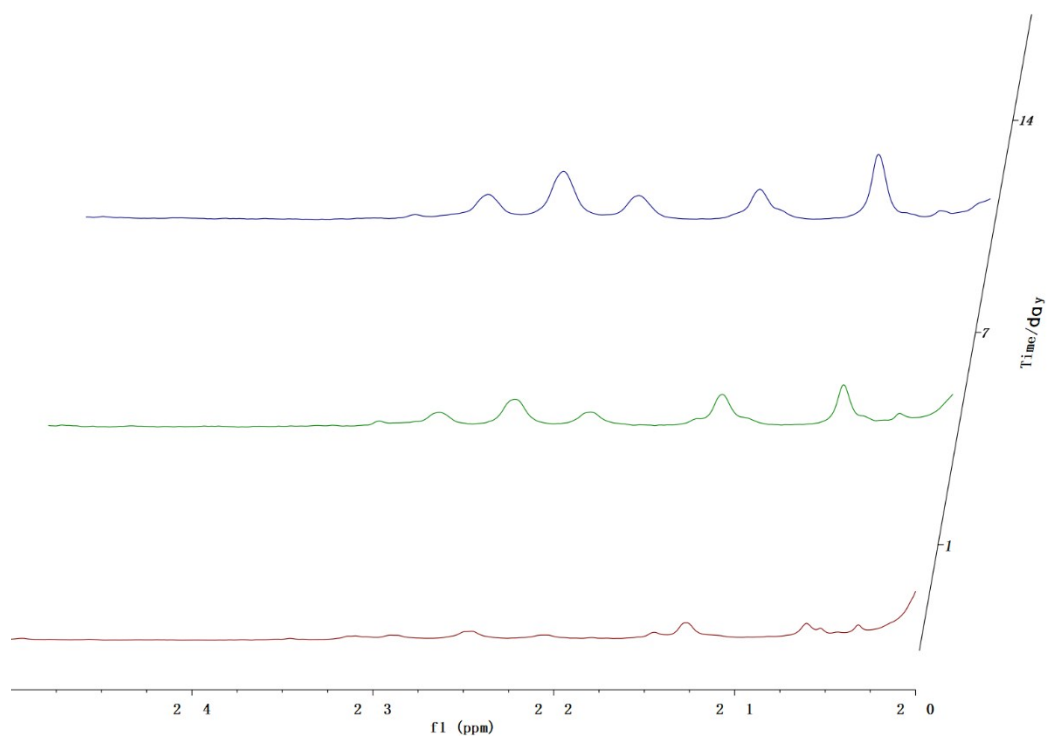


Fig. S10 Ex situ monitoring for the stability of acetic acid in ^1H NMR.

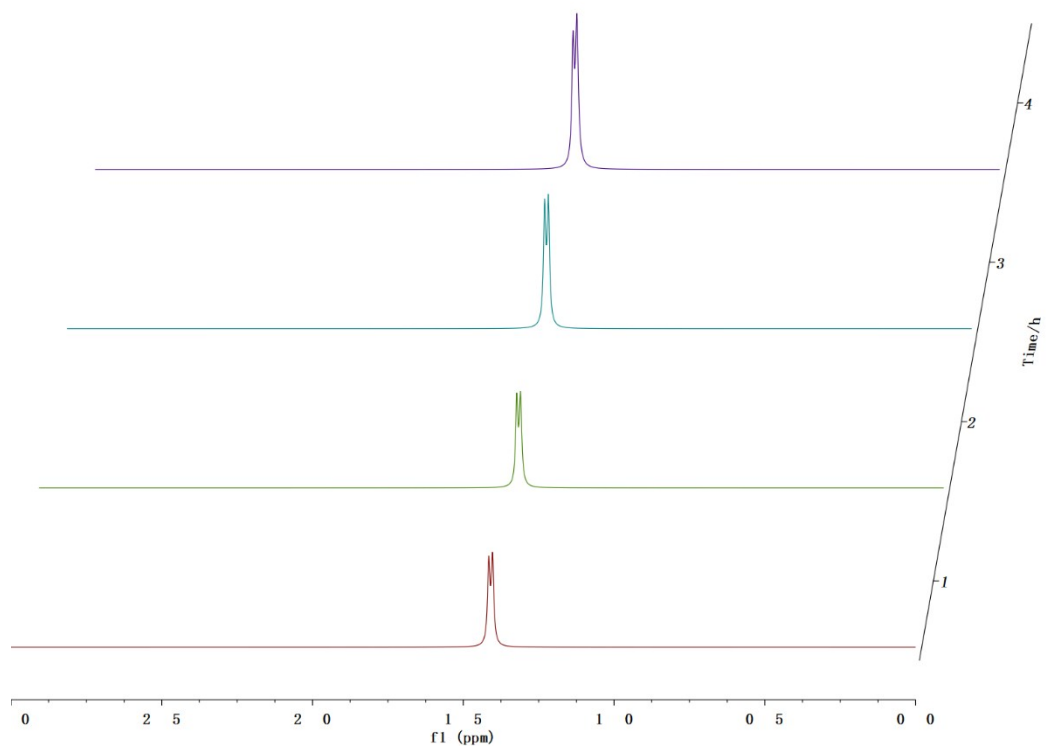
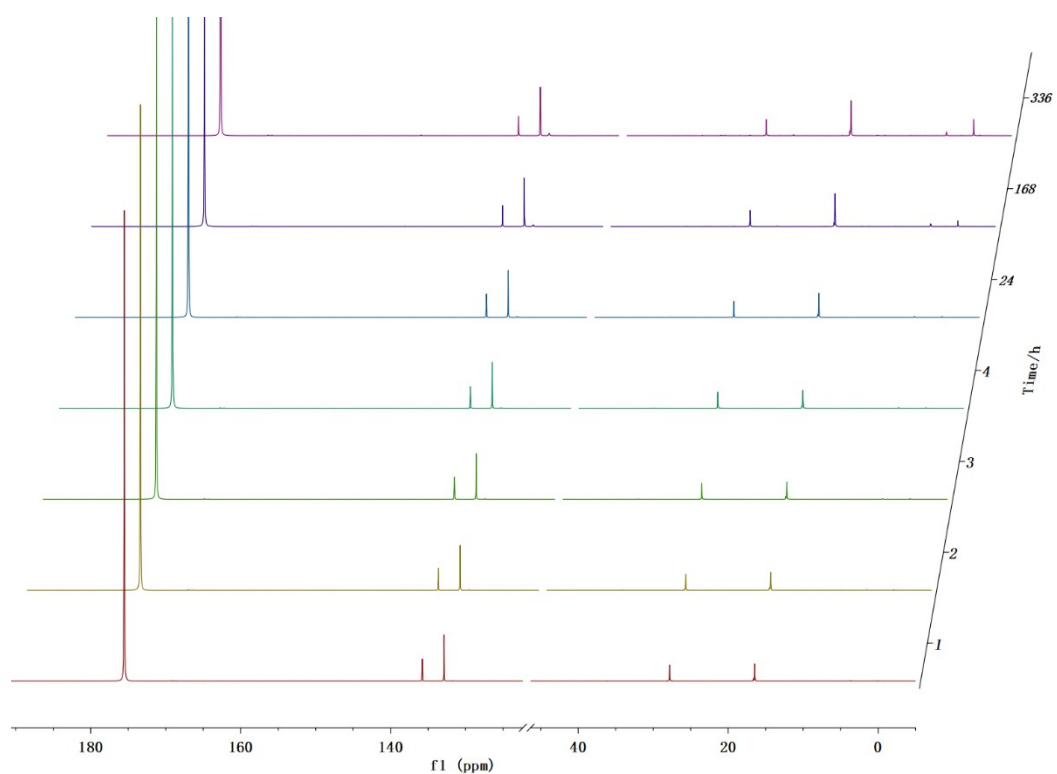


Fig. S11 The growing peak during the in situ monitoring of acetic acid in ^1H NMR with TPPO as internal standard.

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ig. S12 In situ and ex situ monitoring for the stability of benzoic acid during ^{31}P NMR with TPPO as internal standard.

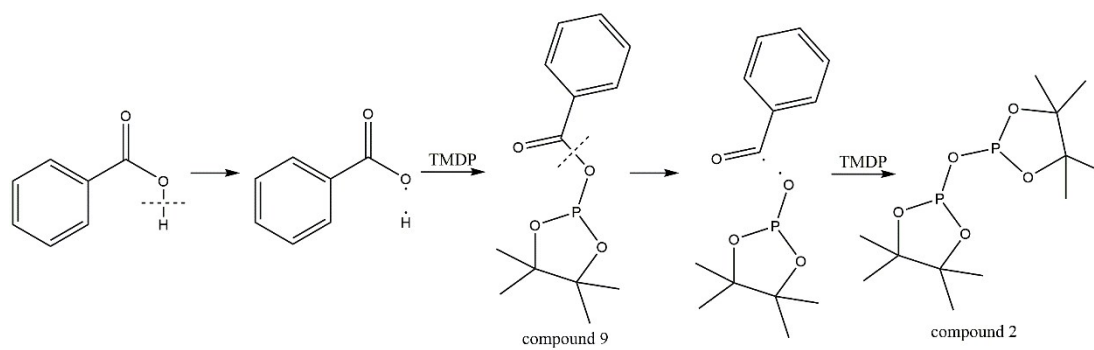
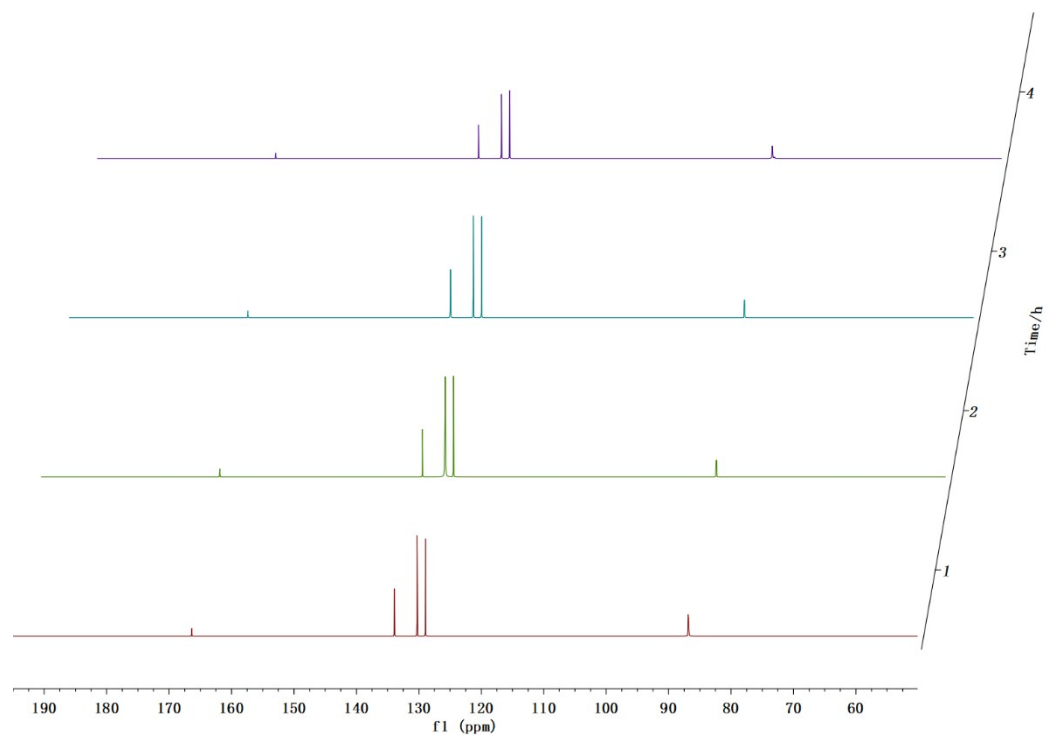


Fig. S13 One possible decomposition pathway for benzoic acid in ^{31}P NMR.



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ig. S14 The peaks of benzoic acid during the in situ monitoring in ^{13}C NMR with TPPO as internal standard.

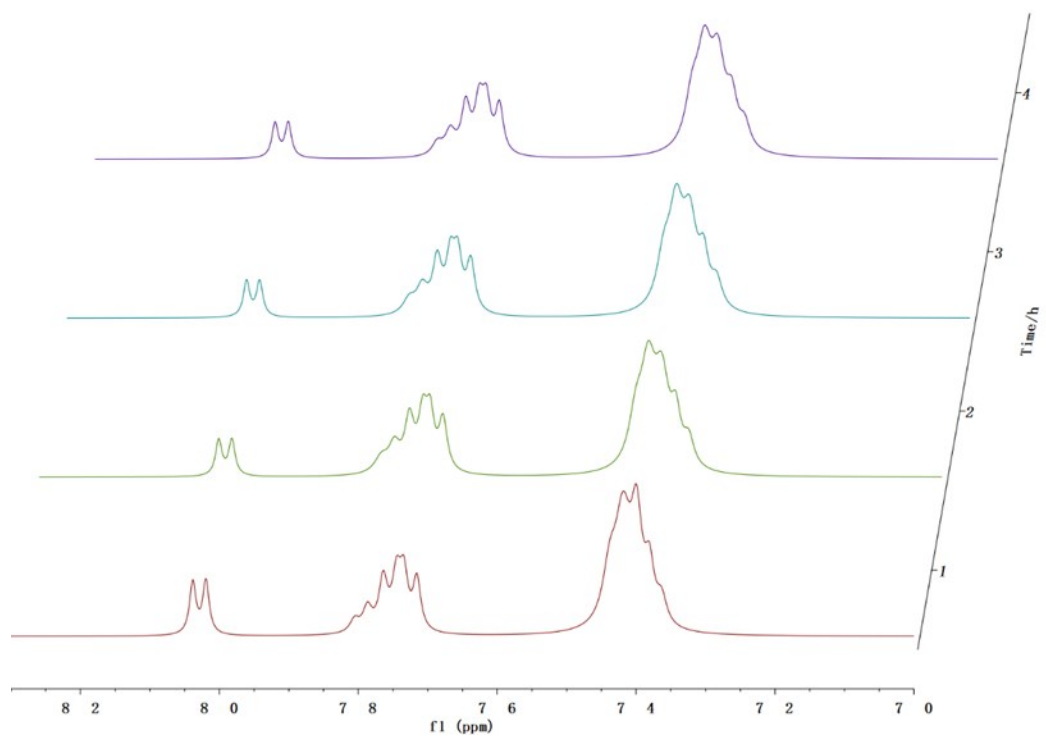


Fig. S15 The peaks of benzoic acid during the in situ monitoring in ^1H NMR with TPPO as internal standard.

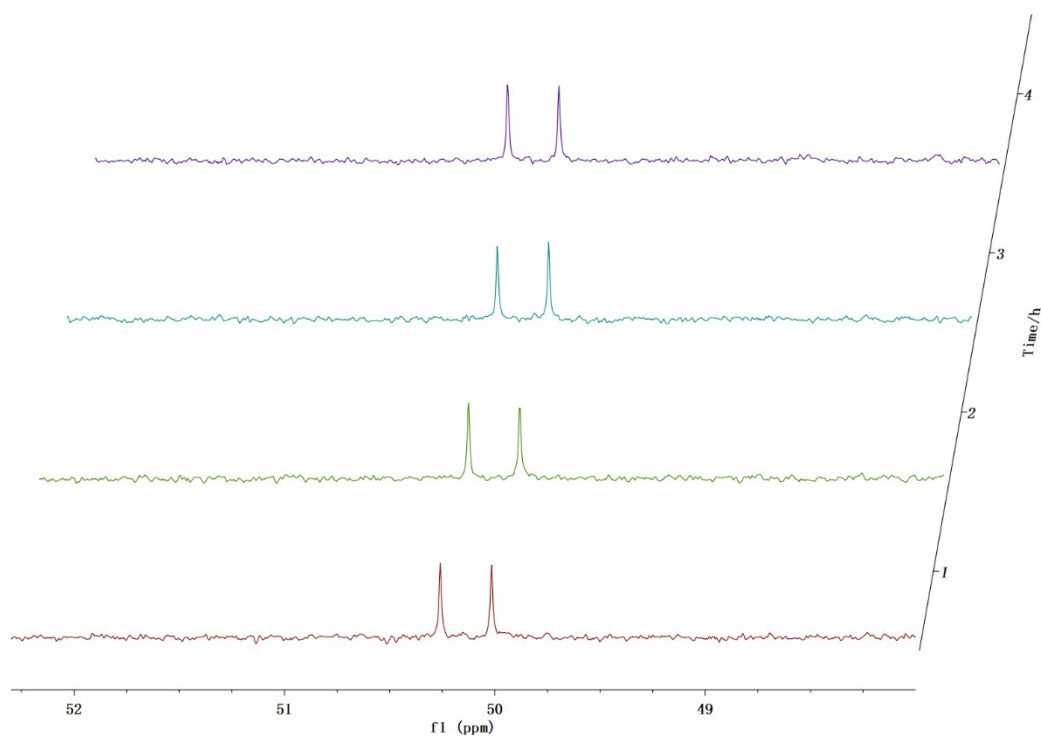


Fig. S16 The peak of methanol during the in situ monitoring in ^{13}C NMR with TPPO as internal standard.

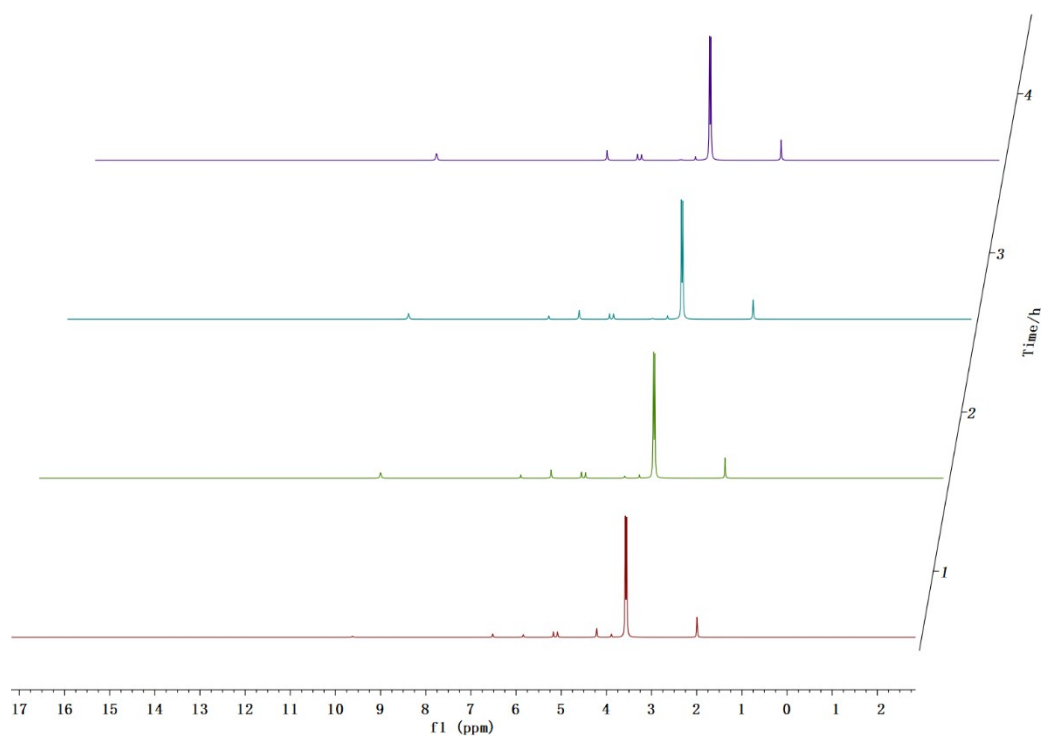


Fig. S17 The peak of methanol during the in situ monitoring in ^1H NMR with TPPO as internal standard.

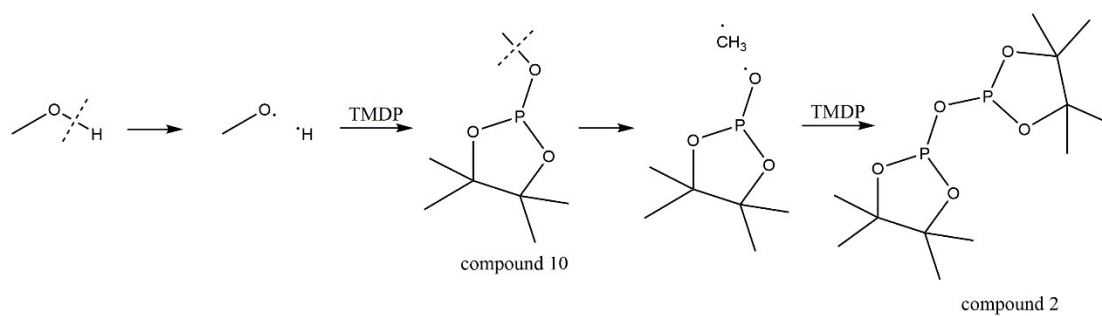


Fig S18. The major decomposition pathway for methanol in ^{31}P NMR.

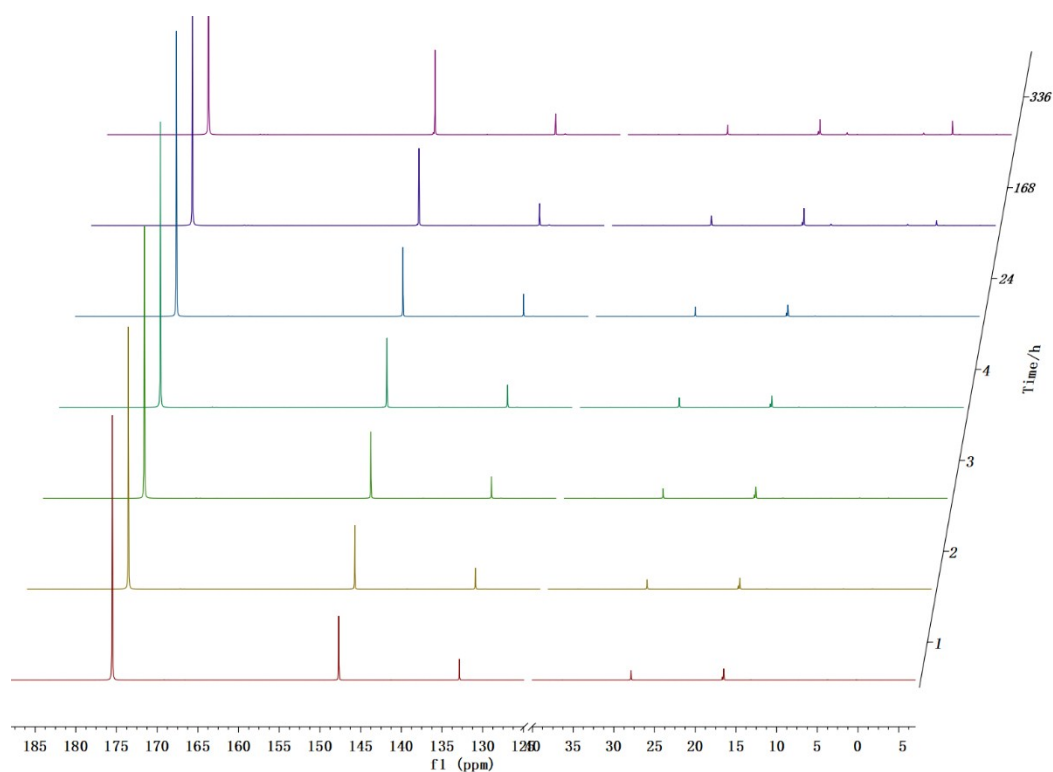


Fig. S19 In situ and ex situ monitoring for the stability of ethylene glycol during ^{31}P NMR with TPPO as internal standard.

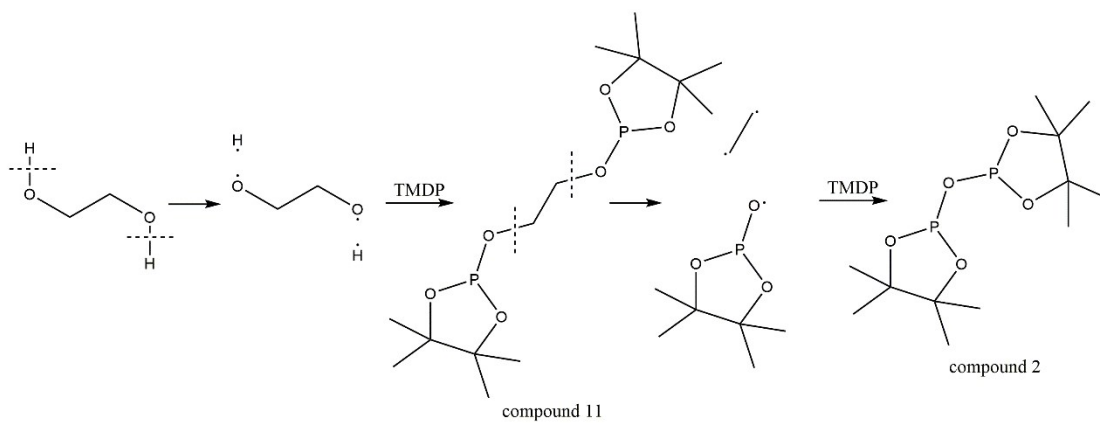


Fig. S20 The major decomposition pathway for ethylene glycol in ^{31}P NMR.

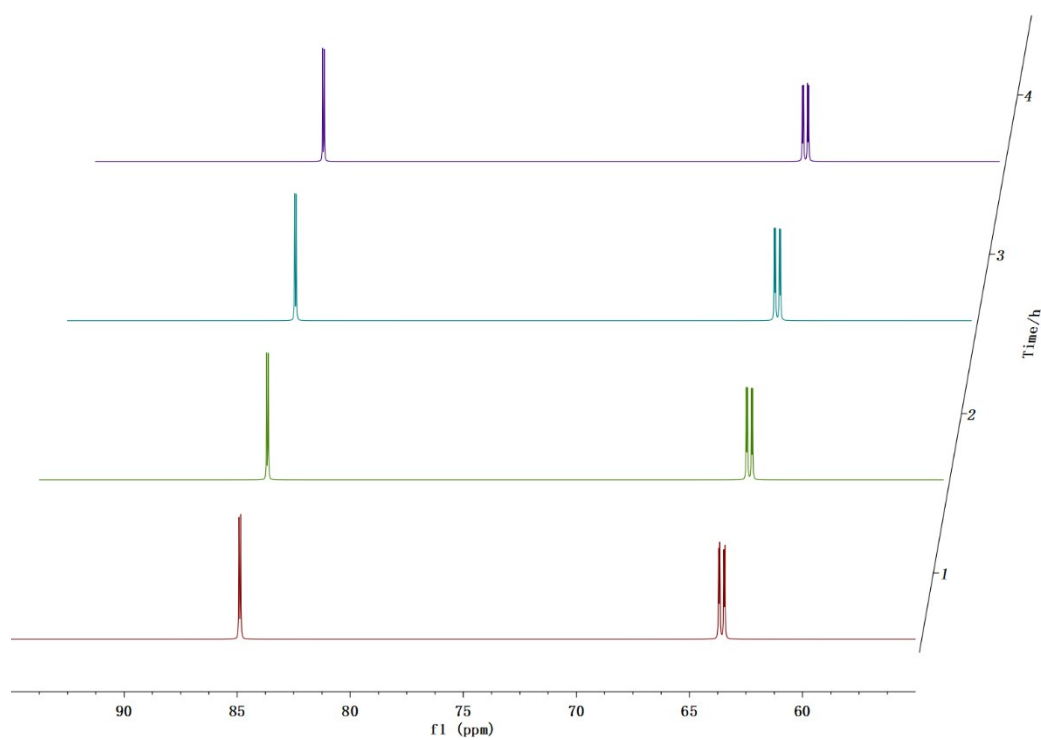


Fig. S21 The peaks of ethylene glycol during the in situ monitoring in ^{13}C NMR with TPPO as internal standard.

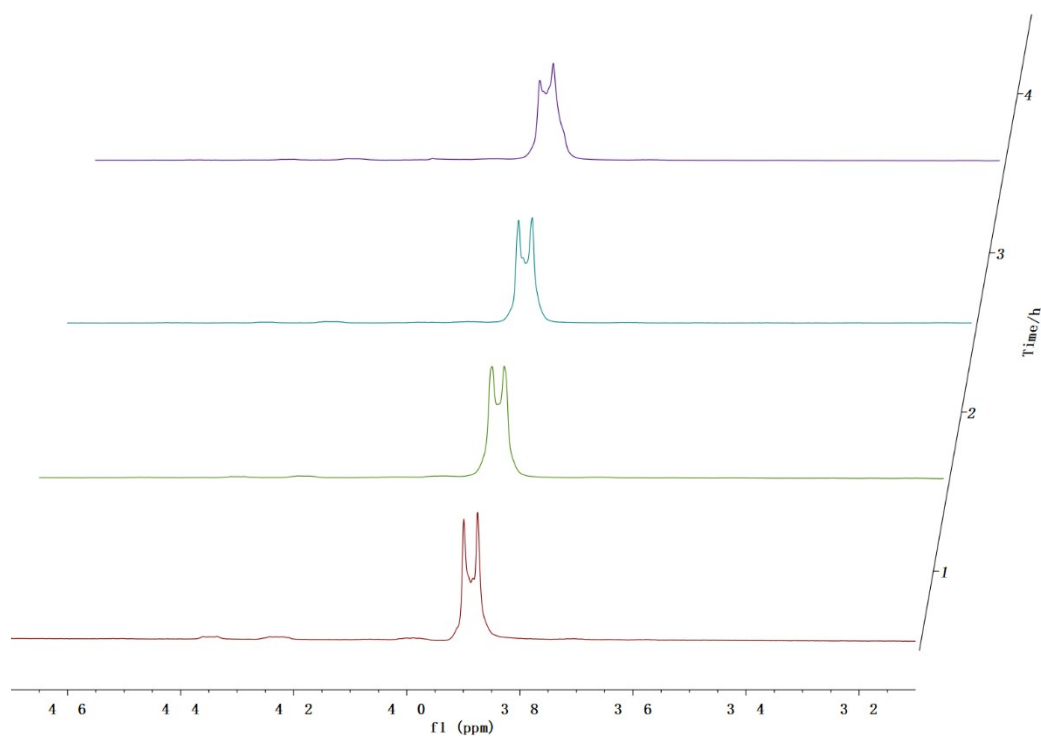


Fig. S22 The peak of ethylene glycol during the in situ monitoring in ^1H NMR with TPPO as internal standard.

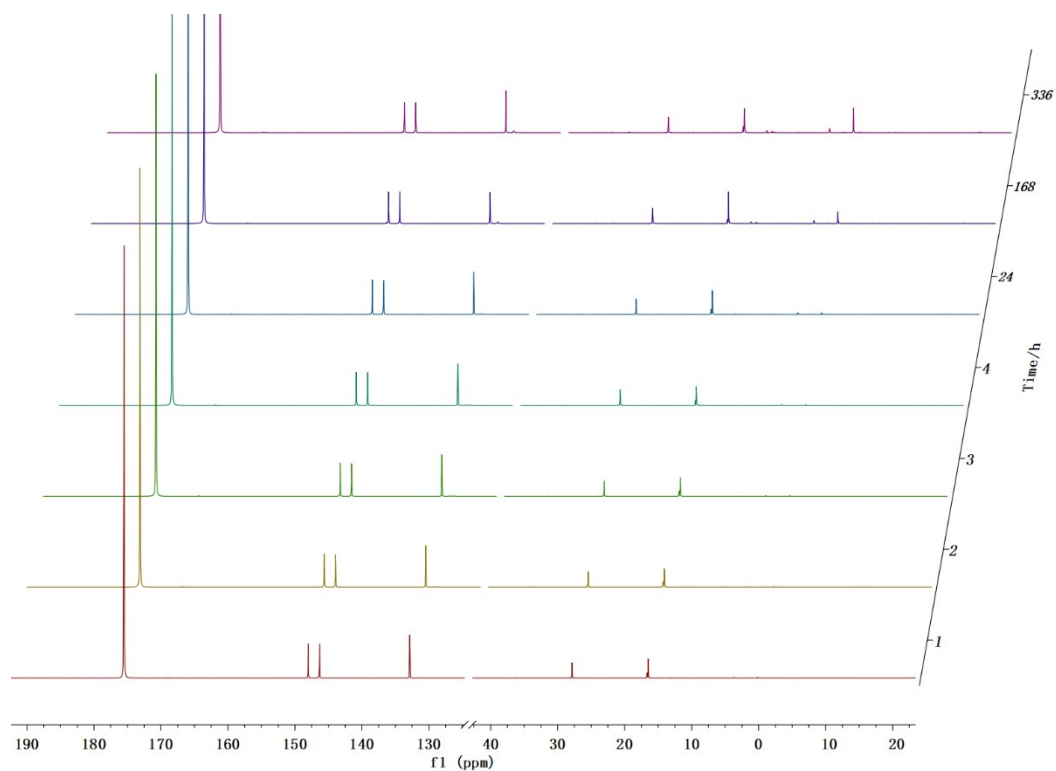


Fig. S23 In situ and ex situ monitoring for the stability of 1,2 propanediol during ^{31}P NMR with TPPO as internal standard.

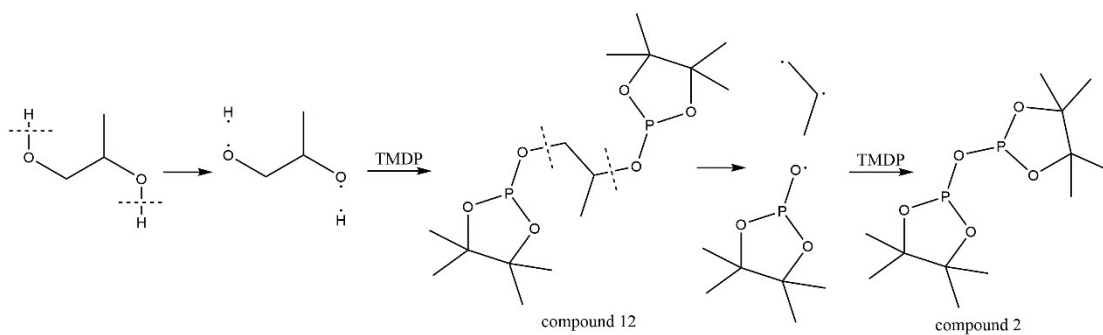


Fig. S24 The major decomposition pathway for 1,2-propanediol in ^{31}P NMR.

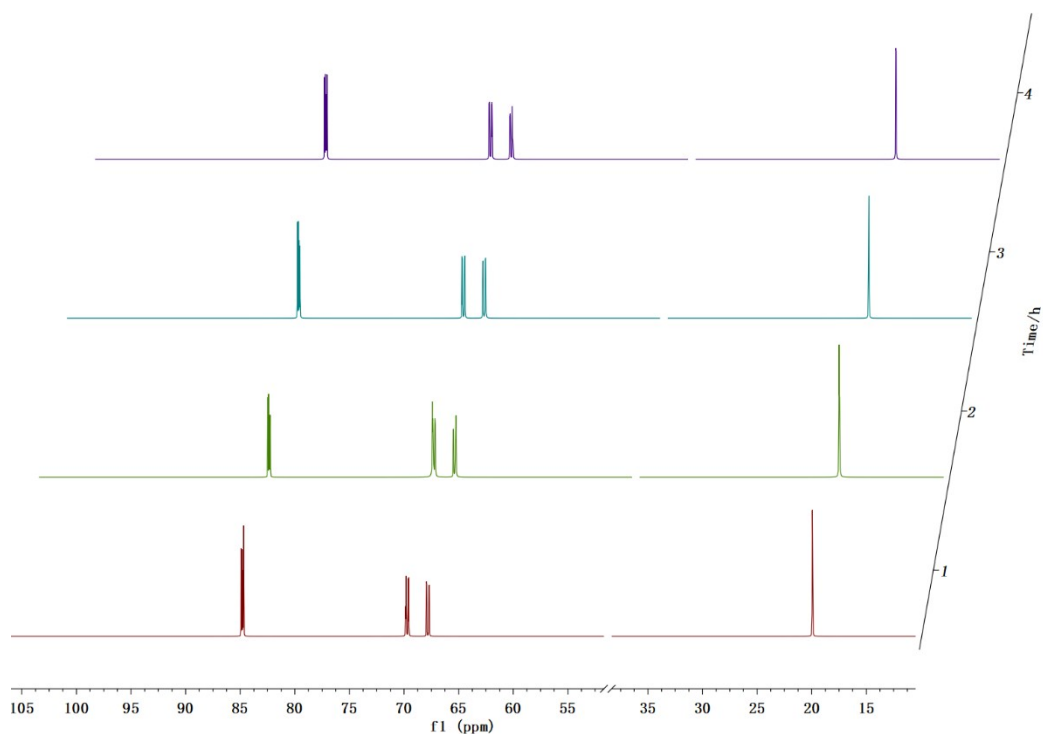


Fig. S25 The peaks of 1,2-propanediol during the in situ monitoring in ^{13}C NMR with TPPO as internal standard.

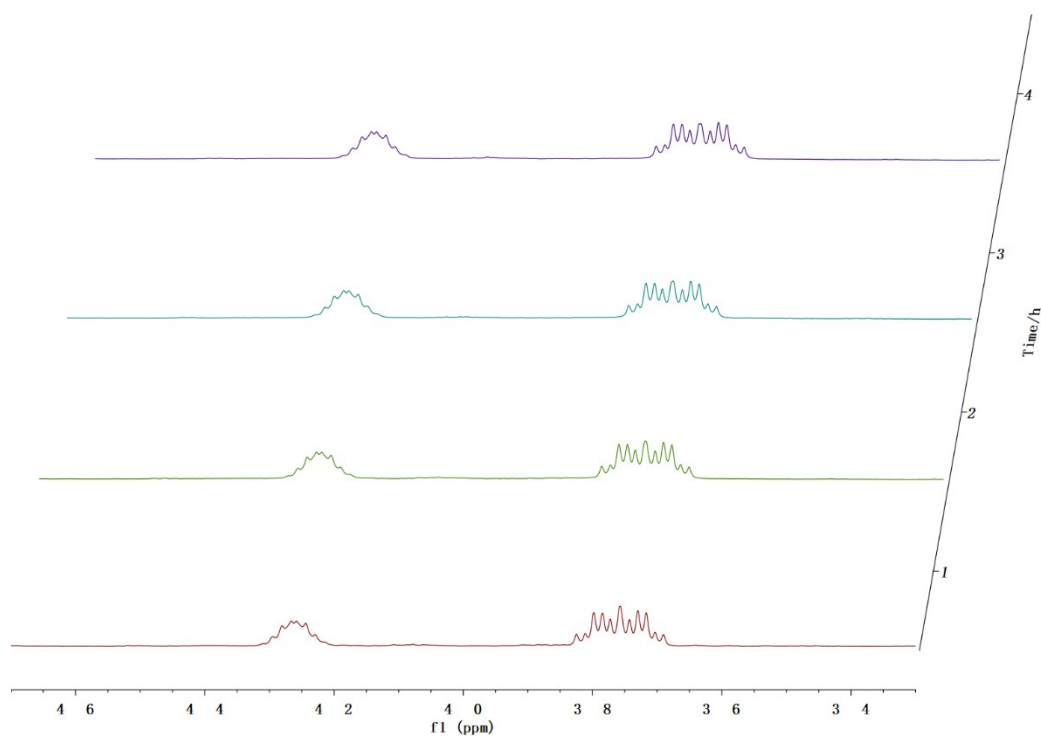


Fig. S26 The peaks of 1,2-propanediol during the in situ monitoring in ^1H NMR with TPPO as internal standard.

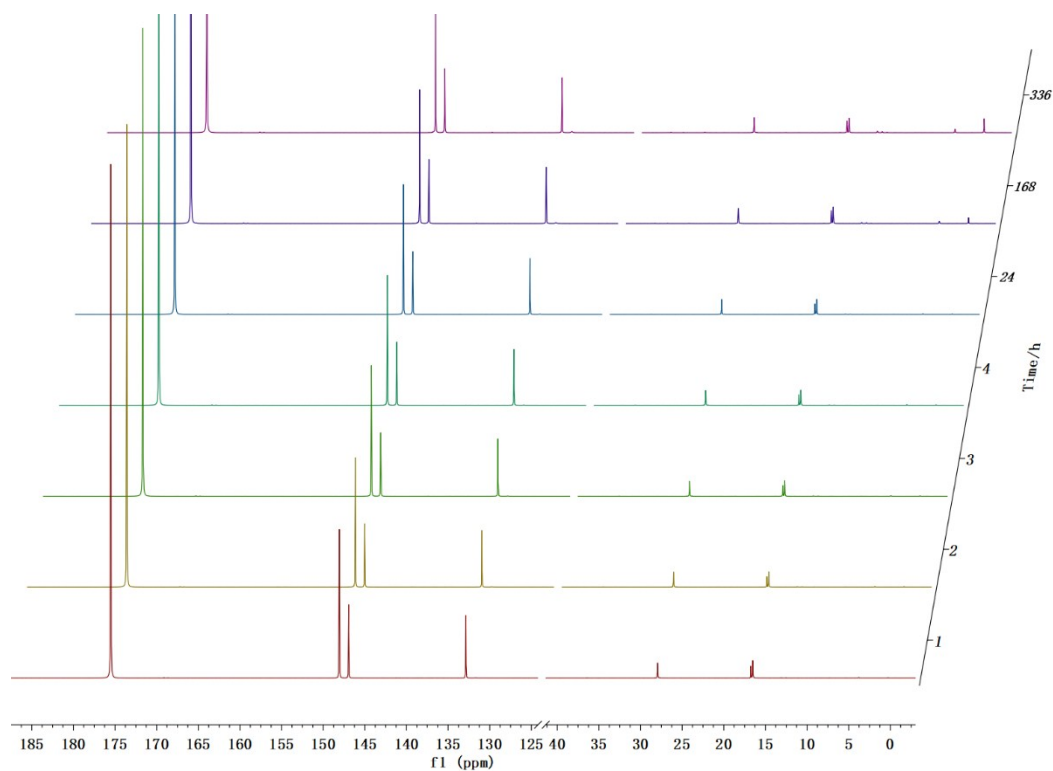


Fig. S27 In situ and ex situ monitoring for the stability of glycerin during ^{31}P NMR with TPPO as internal standard.

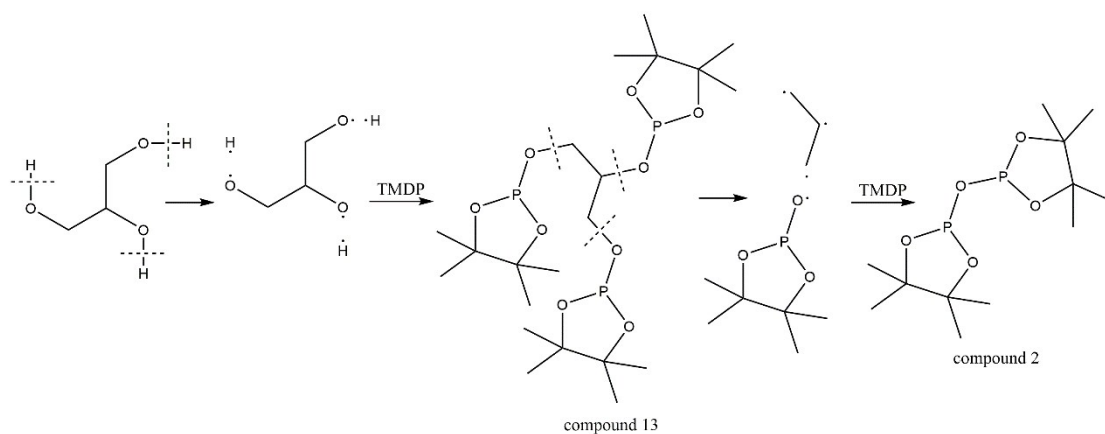


Fig. S28 The major decomposition pathway for glycerin in ^{31}P NMR.

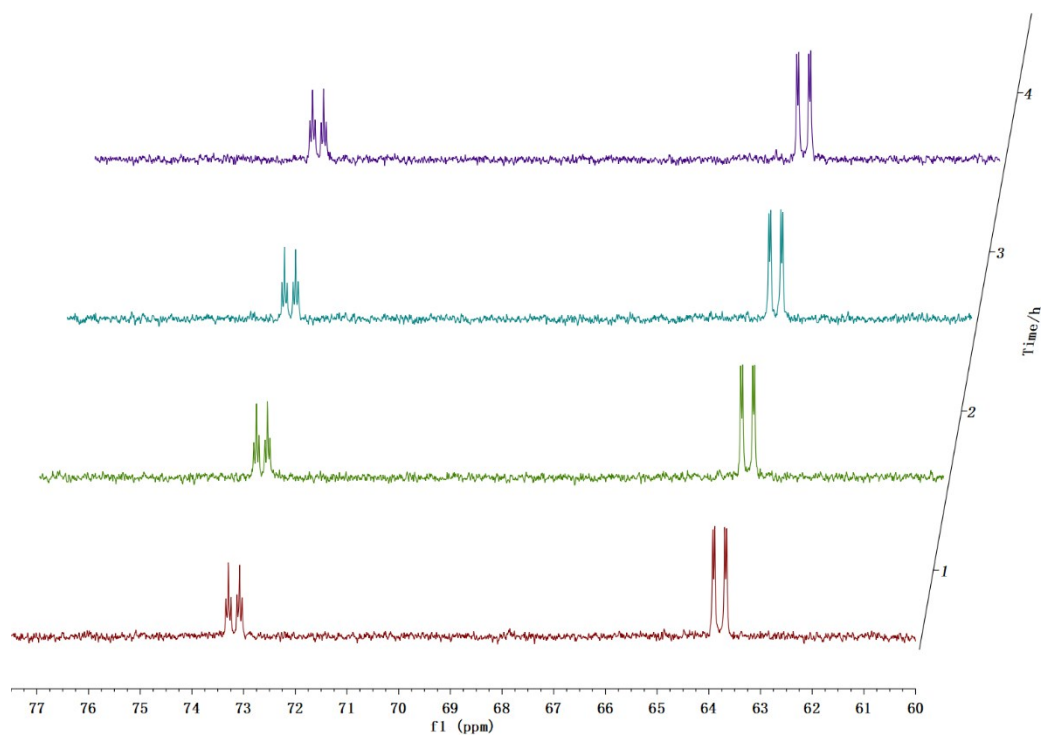


Fig. S29 The peaks of glycerin during the in situ monitoring in ^{13}C NMR with TPPO as internal standard.

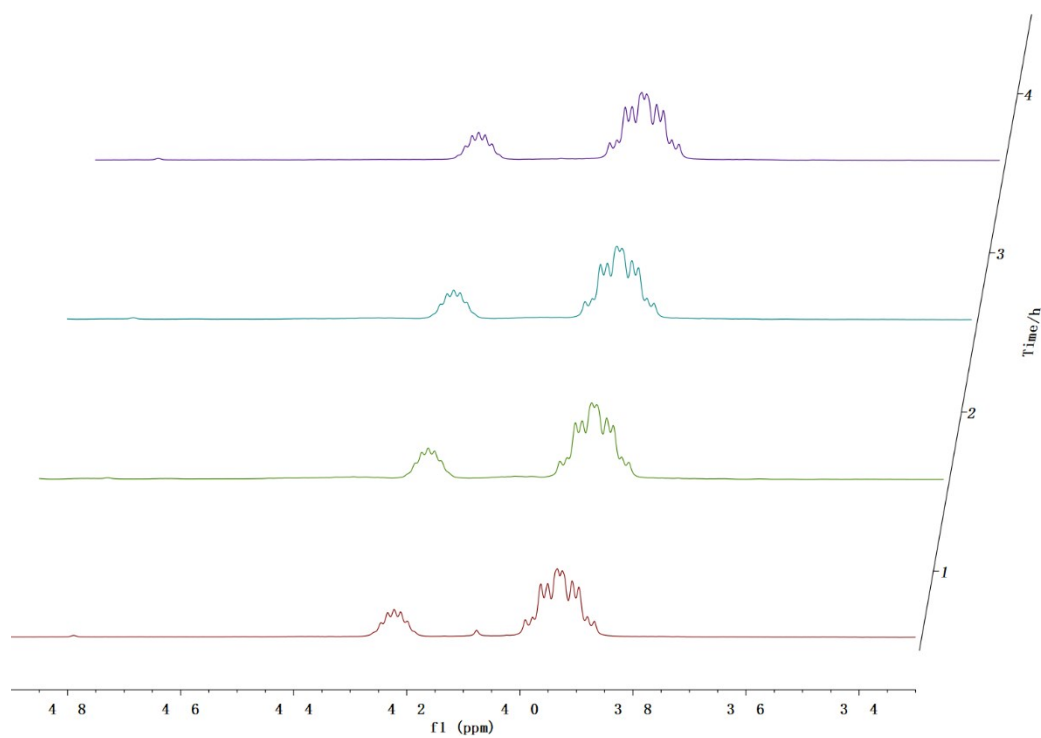


Fig. S30 The peaks of glycerin during the in situ monitoring in ^1H NMR with TPPO as internal standard.

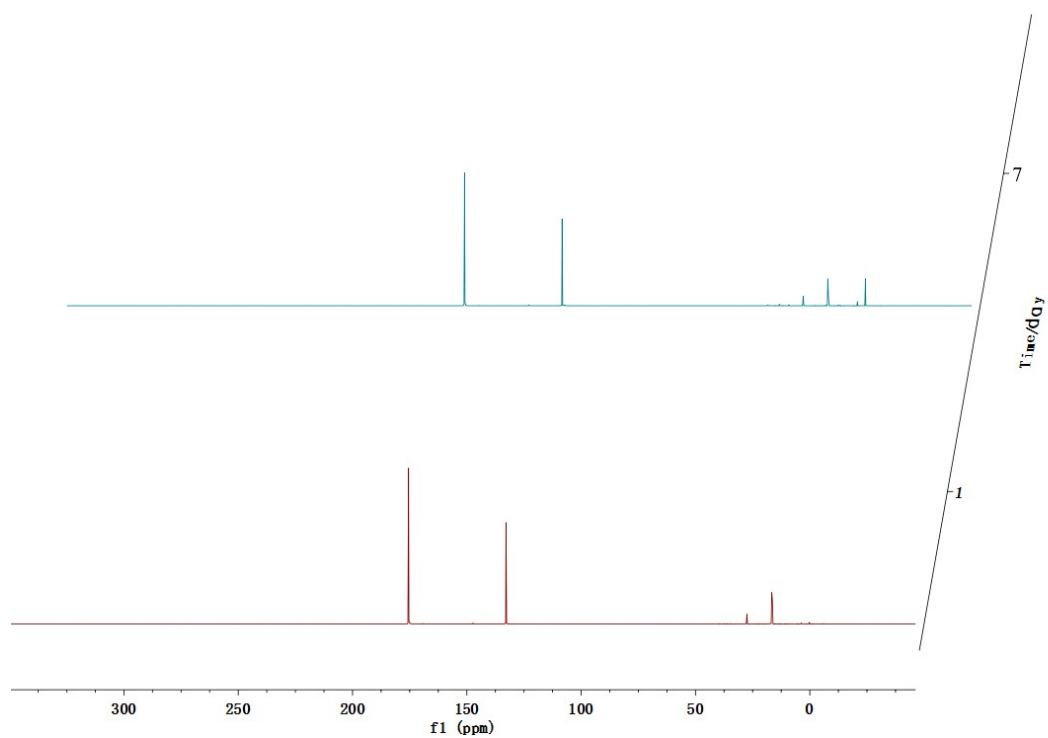


Fig. S31 Ex situ ^{31}P NMR monitoring for the sample added no model compound with TPPO as internal standard.

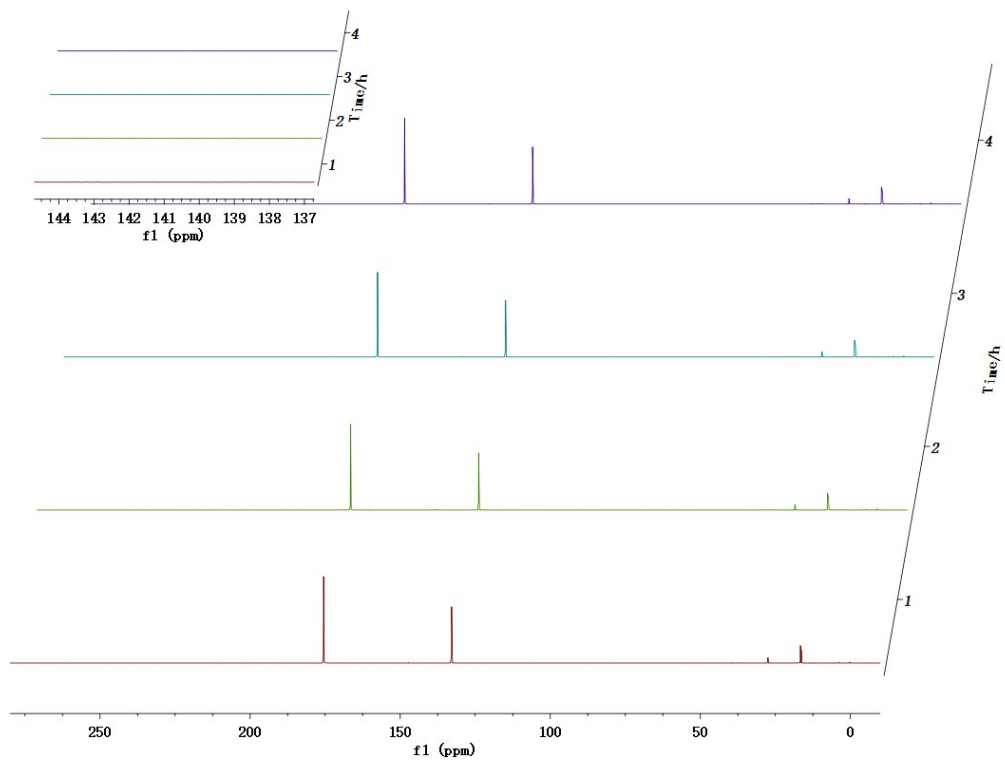


Fig. S32 In situ ^{31}P NMR monitoring for the sample added no model compound with TPPO as internal standard.

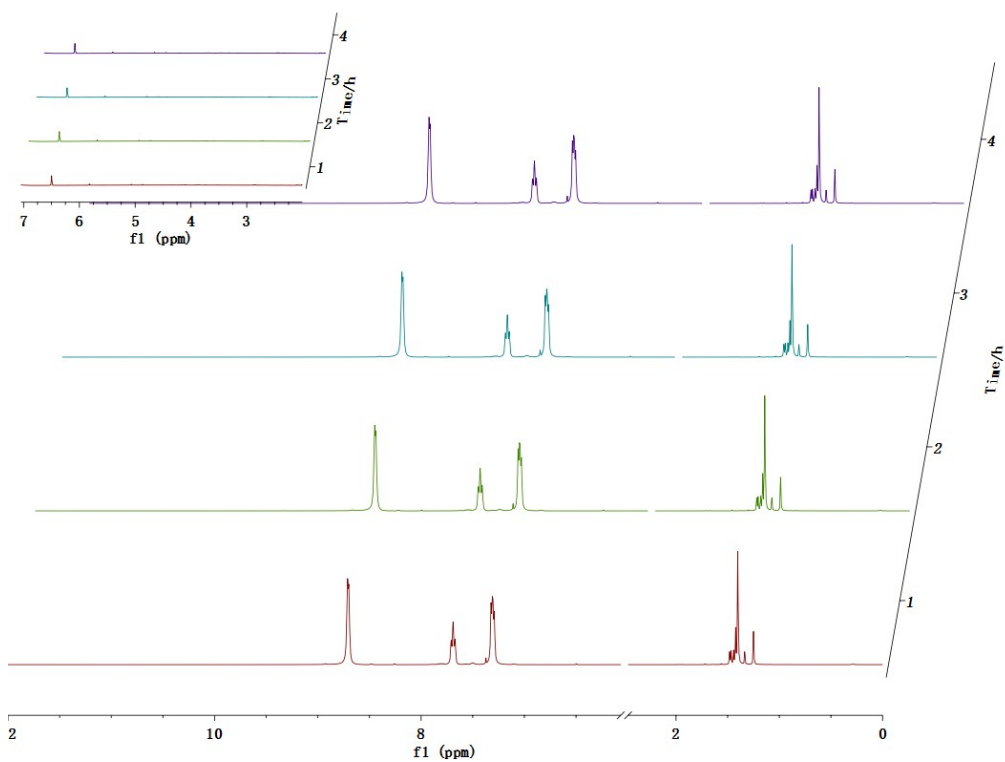


Fig. S33 In situ ^1H NMR monitoring for the sample added no model compound with TPPO as internal standard.

Table S1 Chemical shifts and integration regions for internal standards and functional groups for different hydroxyl groups (Reproduced from Ref. 32 with permission from the Royal Society of Chemistry. ^a

| Functional group | Integration region (ppm) |
|---------------------------------|--------------------------|
| Triphenylphosphine oxide (TPPO) | ~27.5ppm |
| Aliphatic OH | 150.0-145.5 |
| Phenolic OH | 144.7-137.3 |
| Acid OH | 136.6-133.6 |
| Water peak | 133.1-131.3 16.9-15.1 |

^a chemical shift provided is for the corresponding hydroxyl group after derivatization with TMDP.

Table S2 The weights of different model compounds, ISTP solutions, anhydrous pyridine, and TMDP.

| Sample | weight (mg) | weight of original solution and anhydrous pyridine (g) | weight of TMDP (g) |
|----------------------|-------------|--|--------------------|
| acetic acid | 6.0 | 0.5891 | 0.1113 |
| formic acid | 1.0 | 0.5947 | 0.1148 |
| benzoic acid | 2.6 | 0.5962 | 0.1142 |
| oxalic acid | 2.7 | 0.5996 | 0.1152 |
| methanol | 1.1 | 0.5901 | 0.1145 |
| 1,2-Propylene glycol | 2.4 | 0.5909 | 0.1129 |
| glycerin | 4.0 | 0.5933 | 0.1146 |
| Ethylene glycol | 5.5 | 0.5926 | 0.1144 |

Table S3 The test parameters of ^{31}P , ^1H and ^{13}C NMR.

| Parameter | ^{31}P NMR | ^1H NMR | ^{13}C NMR |
|---------------|---------------------|------------------|---------------------|
| TD | 65536 | 65536 | 65536 |
| SWH (Hz, ppm) | 64102.6, 395.656 | 8012.82, 20.0234 | 26041.67, 258.779 |
| AQ (s) | 0.5111808 | 4.0894465 | 1.2582912 |
| D1 (s) | 25.000000000 | 8.000000000 | 1.500000000 |
| NS | 64 | 16 | 1500 |
| RT | 25.511180800 | 12.089446500 | 2.758291200 |

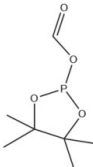
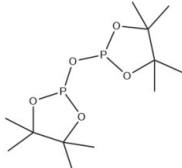
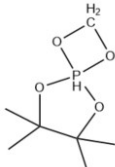
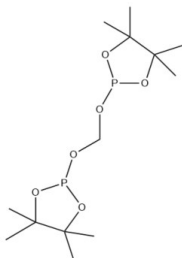
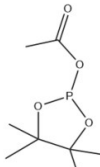
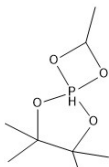
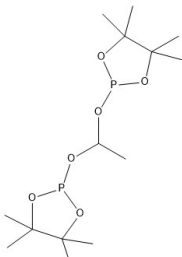
Table S4 The content of TMDP and aliphatic OH and water wt% for the methanol during 4 hours of in situ stability tests with different D1.

| Time | TMDP (mmol/g ^a) | | Aliphatic OH (mmol/g ^a) | | H ₂ O wt% ^b | |
|------|-----------------------------|---------|-------------------------------------|---------|-----------------------------------|---------|
| | D1=25s | D1=100s | D1=25s | D1=100s | D1=25s | D1=100s |
| 1h | 0.4346 | 0.4346 | 0.0351 | 0.0350 | 2.49 | 2.49 |
| 2h | 0.4324 | 0.4325 | 0.0348 | 0.0348 | 2.55 | 2.54 |
| 3h | 0.4319 | 0.4318 | 0.0346 | 0.0347 | 2.57 | 2.56 |
| 4h | 0.4302 | 0.4302 | 0.0345 | 0.0345 | 2.58 | 2.58 |

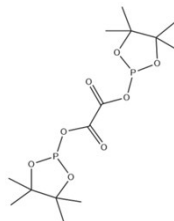
^a The calculation method: (Integration of spectral region of interest \times mmol TPPO) / (Integration of TPPO region \times total mass(g) of NMR sample)

^b The percentage calculation method: (Integration of water region \times mmol TPPO \times 278.29g/mol TPPO \times 100) / (1000 \times TPPO purity \times Integration of TPPO region \times total mass(g) of NMR sample)

Table S5 Naming of compounds mentioned in study.

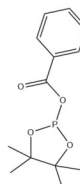
| Source of Compound | Chemical structure | Naming |
|---|--|------------|
| Product derived from TMDP and formic acid |  | compound 1 |
| Product derived from TMDP and water |  | compound 2 |
| One possible decomposition intermediate of compound 1 |  | compound 3 |
| One possible decomposition product of compound 1 |  | compound 4 |
| Product derived from TMDP and acetic acid |  | compound 5 |
| One possible decomposition intermediate of compound 5 |  | compound 6 |
| One possible decomposition product of compound 5 |  | compound 7 |

Product derived from TMDP and oxalic acid



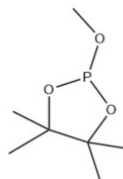
compound 8

Product derived from TMDP and benzoic acid



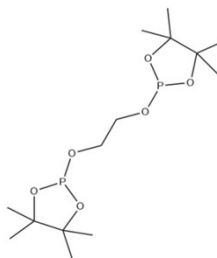
compound 9

Product derived from TMDP and methanol



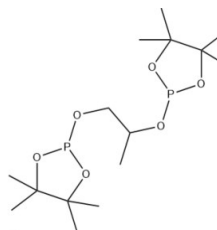
compound 10

Product derived from TMDP and ethylene glycol



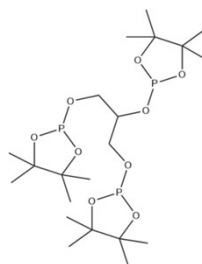
compound 11

Product derived from TMDP and 1,2-propanediol



compound 12

Product derived from TMDP and glycerin



compound 13

Table S6 Different hydroxyl group contents and water wt% for the acetic acid during 4 hours of in situ and 14 days of ex situ stability tests with TPPO as internal standard.

| Time | Aliphatic OH mmol/g ^a | Phenolic OH mmol/g ^a | Carboxylic OH mmol/g ^a | H ₂ O wt% ^b |
|------|-------------------------------------|------------------------------------|--------------------------------------|-----------------------------------|
| 1h | 0.0007 | 0.0000 | 0.2415 | 3.95 |
| 2h | 0.0005 | 0.0010 | 0.2395 | 4.00 |
| 3h | 0.0015 | 0.0010 | 0.2376 | 3.99 |
| 4h | 0.0027 | 0.0007 | 0.2361 | 4.03 |
| 1d | 0.0079 | 0.0000 | 0.2177 | 4.17 |
| 7d | 0.0241 | 0.0025 | 0.1767 | 2.39 |
| 14d | 0.0345 | 0.0032 | 0.1474 | 1.53 |

^a The calculation method: (Integration of spectral region of interest × mmol TPPO)/(Integration of TPPO region × total mass(g) of NMR sample)

^b The percentage calculation method: (Integration of water region × mmol TPPO × 278.29g/mol TPPO × 100)/(1000 × TPPO purity × Integration of TPPO region × total mass(g) of NMR sample)

Table S7 Different hydroxyl group contents and water wt% for the benzoic acid during 4 hours of in situ and 14 days of ex situ stability tests with TPPO as internal standard.

| Time | Aliphatic OH mmol/g ^a | Phenolic OH mmol/g ^a | Carboxylic OH mmol/g ^a | H ₂ O wt% ^b |
|------|-------------------------------------|------------------------------------|--------------------------------------|-----------------------------------|
| 1h | 0.0000 | 0.0000 | 0.0220 | 1.95 |
| 2h | 0.0002 | 0.0008 | 0.0216 | 1.94 |
| 3h | 0.0005 | 0.0002 | 0.0213 | 1.98 |
| 4h | 0.0000 | 0.0004 | 0.0209 | 1.99 |
| 1d | 0.0005 | 0.0006 | 0.0204 | 2.10 |
| 7d | 0.0005 | 0.0004 | 0.0200 | 2.73 |
| 14d | 0.0014 | 0.0004 | 0.0184 | 2.84 |

^a The calculation method: (Integration of spectral region of interest × mmol TPPO)/(Integration of TPPO region × total mass(g) of NMR sample)

^b The percentage calculation method: (Integration of water region × mmol TPPO × 278.29g/mol TPPO × 100)/(1000 × TPPO purity × Integration of TPPO region × total mass(g) of NMR sample)

Table S8 Different hydroxyl group contents and water wt% for the methanol during 4 hours of in situ and 14 days of ex situ stability tests with TPPO as internal standard.

| Time | Aliphatic OH mmol/g ^a | Phenolic OH mmol/g ^a | Carboxylic OH mmol/g ^a | H ₂ O wt% ^b |
|------|-------------------------------------|------------------------------------|--------------------------------------|-----------------------------------|
| 1h | 0.0511 | 0.0000 | 0.0000 | 2.05 |
| 2h | 0.0509 | 0.0004 | 0.0002 | 2.05 |
| 3h | 0.0507 | 0.0004 | 0.0005 | 2.06 |
| 4h | 0.0505 | 0.0004 | 0.0002 | 2.10 |
| 1d | 0.0495 | 0.0000 | 0.0002 | 2.21 |
| 7d | 0.0484 | 0.0000 | 0.0007 | 2.31 |
| 14d | 0.0482 | 0.0006 | 0.0009 | 2.56 |

^a The calculation method: (Integration of spectral region of interest × mmol TPPO)/(Integration of TPPO region × total mass(g) of NMR sample)

^b The percentage calculation method: (Integration of water region × mmol TPPO × 278.29g/mol TPPO × 100)/(1000 × TPPO purity × Integration of TPPO region × total mass(g) of NMR sample)

Table S9 Different hydroxyl group contents and water wt% for the ethylene glycol glycol during 4 hours of in situ and 14 days of ex situ stability tests with TPPO as internal standard.

| Time | Aliphatic OH mmol/g ^a | Phenolic OH mmol/g ^a | Carboxylic OH mmol/g ^a | H ₂ O wt% ^b |
|------|-------------------------------------|------------------------------------|--------------------------------------|-----------------------------------|
| 1h | 0.1283 | 0.0000 | 0.0000 | 1.81 |
| 2h | 0.1280 | 0.0009 | 0.0014 | 1.82 |
| 3h | 0.1274 | 0.0013 | 0.0007 | 1.82 |
| 4h | 0.1271 | 0.0008 | 0.0002 | 1.83 |
| 1d | 0.1264 | 0.0007 | 0.0000 | 1.86 |
| 7d | 0.1237 | 0.0007 | 0.0000 | 2.17 |
| 14d | 0.1230 | 0.0007 | 0.0007 | 1.91 |

^a The calculation method: (Integration of spectral region of interest × mmol TPPO)/(Integration of TPPO region × total mass(g) of NMR sample)

^b The percentage calculation method: (Integration of water region × mmol TPPO × 278.29g/mol

$\text{TPPO} \times 100) / (1000 \times \text{TPPO purity} \times \text{Integration of TPPO region} \times \text{total mass(g) of NMR sample})$

Table S10 Different hydroxyl group contents and water wt% for the 1,2 propanediol during 4 hours of in situ and 14 days of ex situ stability tests with TPPO as internal standard.

| Time | Aliphatic OH mmol/g ^a | Phenolic OH mmol/g ^a | Carboxylic OH mmol/g ^a | H ₂ O wt% ^b |
|------|-------------------------------------|------------------------------------|--------------------------------------|-----------------------------------|
| 1h | 0.0859 | 0.0000 | 0.0000 | 2.08 |
| 2h | 0.0854 | 0.0000 | 0.0005 | 2.11 |
| 3h | 0.0850 | 0.0000 | 0.0002 | 2.10 |
| 4h | 0.0847 | 0.0004 | 0.0005 | 2.12 |
| 1d | 0.0843 | 0.0004 | 0.0002 | 2.24 |
| 7d | 0.0824 | 0.0007 | 0.0002 | 2.37 |
| 14d | 0.0813 | 0.0004 | 0.0009 | 2.45 |

^a The calculation method: $(\text{Integration of spectral region of interest} \times \text{mmol TPPO}) / (\text{Integration of TPPO region} \times \text{total mass(g) of NMR sample})$

^b The percentage calculation method: $(\text{Integration of water region} \times \text{mmol TPPO} \times 278.29\text{g/mol TPPO} \times 100) / (1000 \times \text{TPPO purity} \times \text{Integration of TPPO region} \times \text{total mass(g) of NMR sample})$

Table S11 Different hydroxyl group contents and water wt% for the glycerin during 4 hours of in situ and 14 days of ex situ stability tests with TPPO as internal standard.

| Time | Aliphatic OH mmol/g ^a | Phenolic OH mmol/g ^a | Carboxylic OH mmol/g ^a | H ₂ O wt% ^b |
|------|-------------------------------------|------------------------------------|--------------------------------------|-----------------------------------|
| 1h | 0.1770 | 0.0000 | 0.0000 | 2.02 |
| 2h | 0.1754 | 0.0009 | 0.0007 | 2.04 |
| 3h | 0.1746 | 0.0008 | 0.0008 | 2.05 |
| 4h | 0.1737 | 0.0002 | 0.0005 | 2.07 |
| 1d | 0.1714 | 0.0006 | 0.0008 | 2.11 |
| 7d | 0.1703 | 0.0005 | 0.0002 | 2.13 |
| 14d | 0.1696 | 0.0007 | 0.0003 | 2.12 |

^a The calculation method: $(\text{Integration of spectral region of interest} \times \text{mmol TPPO}) / (\text{Integration of TPPO region} \times \text{total mass(g) of NMR sample})$

TPPO region \times total mass(g) of NMR sample)

^b The percentage calculation method: (Integration of water region \times mmol TPPO \times 278.29g/mol TPPO \times 100)/(1000 \times TPPO purity \times Integration of TPPO region \times total mass(g) of NMR sample)

Table S12 The result of changes in the amount of phenolic OH in the sample added no model compound during in situ monitoring process.

| Time/h | 1 | 2 | 3 | 4 |
|-----------------------|--------|--------|--------|--------|
| Phenolic OH mmol/g | 0.0001 | 0.0003 | 0.0005 | 0.0001 |