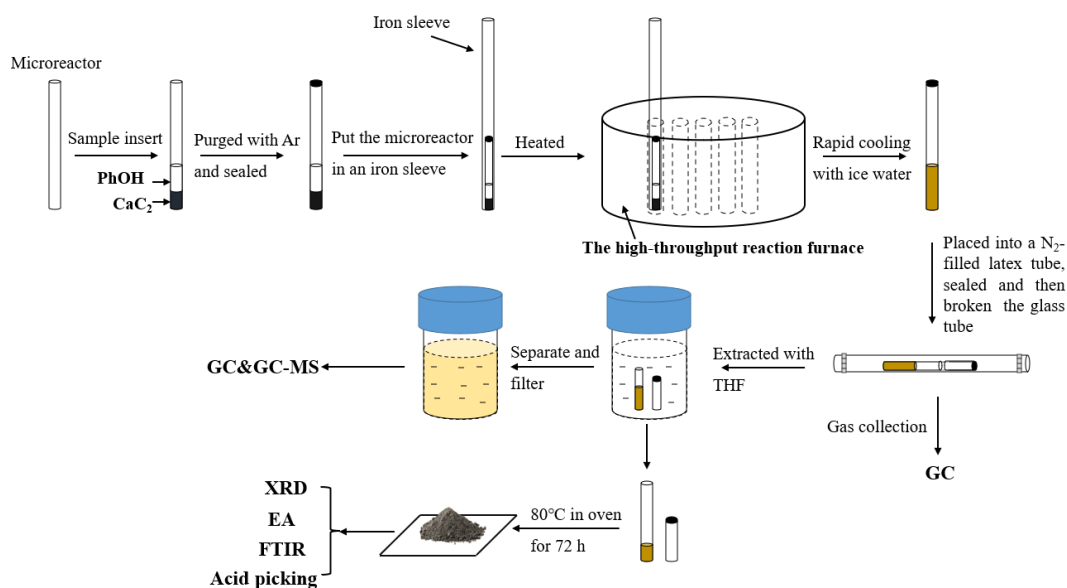


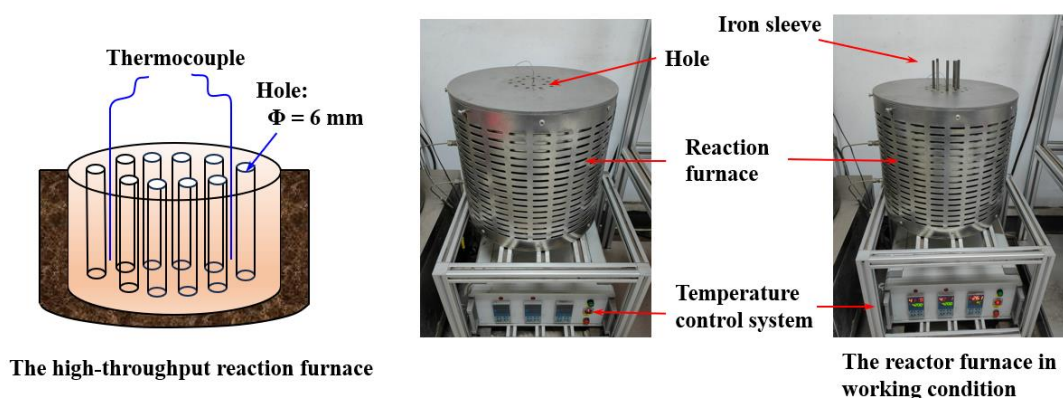
## **Supplementary Information**

### **Synthesis of ethylphenols and xanthenes via reaction of calcium carbide and phenol: Experimental and theoretical studies**

X. Liu, Y. Yan, Z. Liu and Q. Liu\*



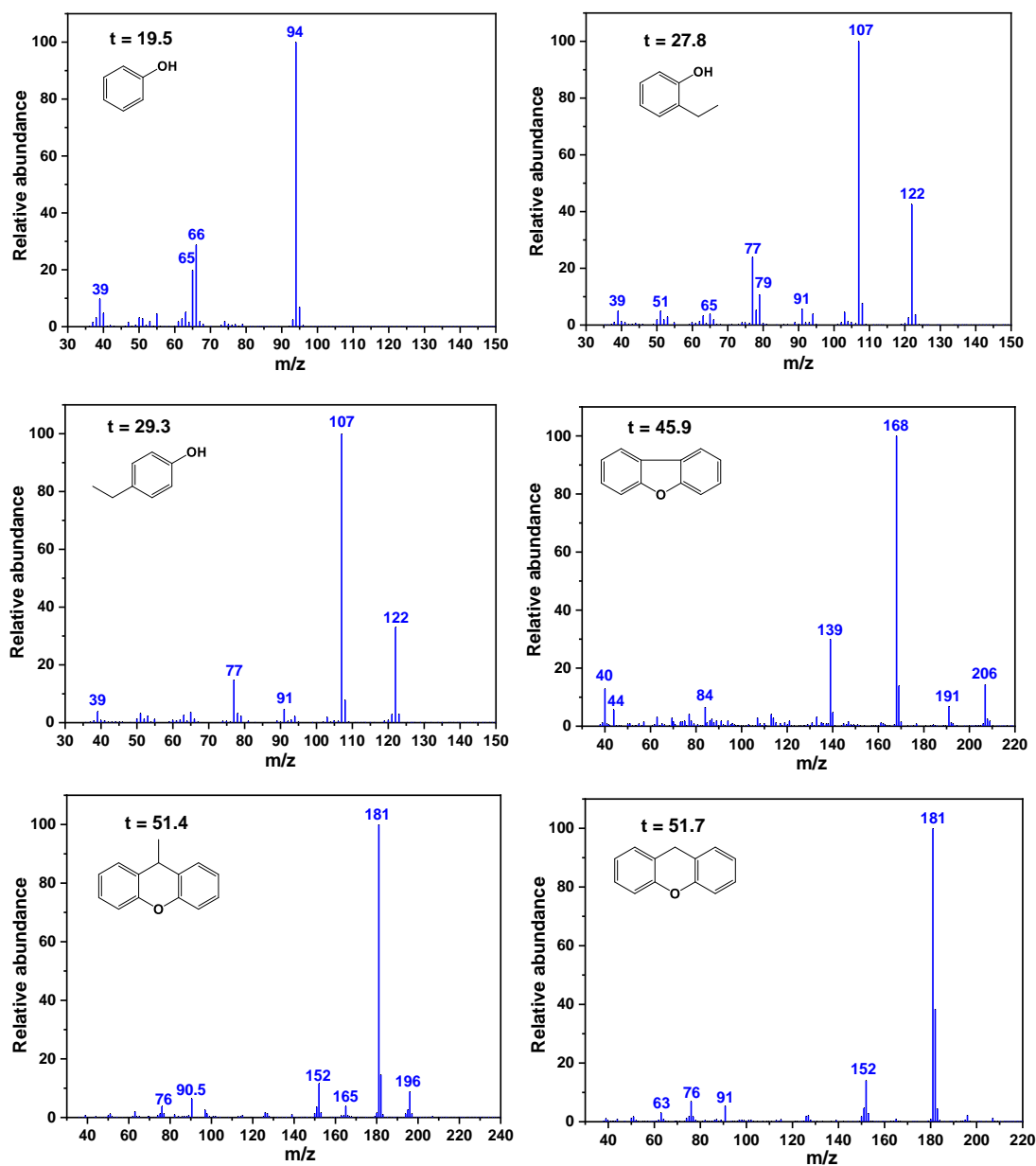
**Figure S1.** Experimental process diagram.



**Figure S2.** Schematic diagram and photograph of the high-throughput reactor furnace.

Advantages of this reaction unit over the autoclave include:

- (1) By introducing the microreactors into the preheated furnace at the target temperature, the reactants' temperature can be elevated to the desired level within 2 min without overshooting, thereby minimizing side reactions that may occur at lower temperatures during the heating-up period;
- (2) In this experiment, milligram-scale reaction materials are employed to simulate the reactions occurring within a finite element of an industrial reactor. This approach mitigates issues related to uneven mass and heat transfer in the reaction unit, thereby facilitating a more accurate analysis of the reaction mechanism.



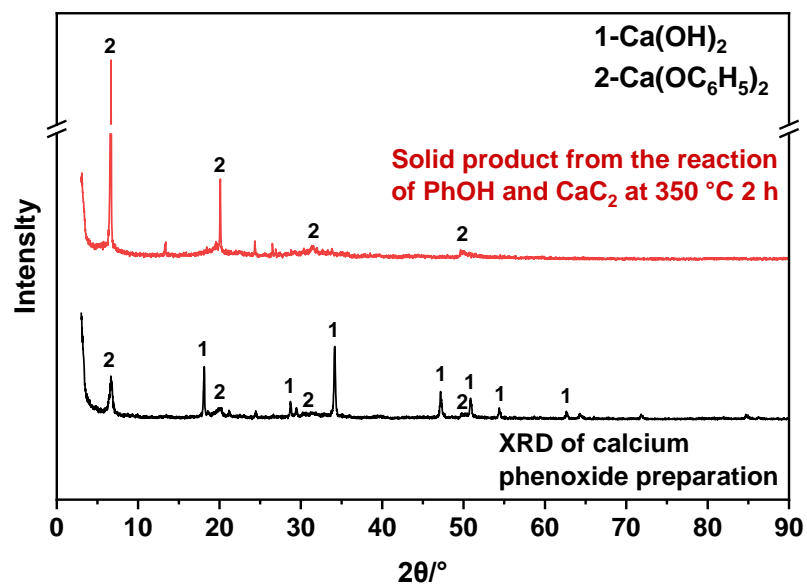
**Figure S3.** Mass spectra of the liquid products.

Reaction conditions:  $\text{CaC}_2$  (2.5 mg, 0.036 mmol):PhOH = 1:8 (molar ratio). T = 350 °C, t = 2 h.

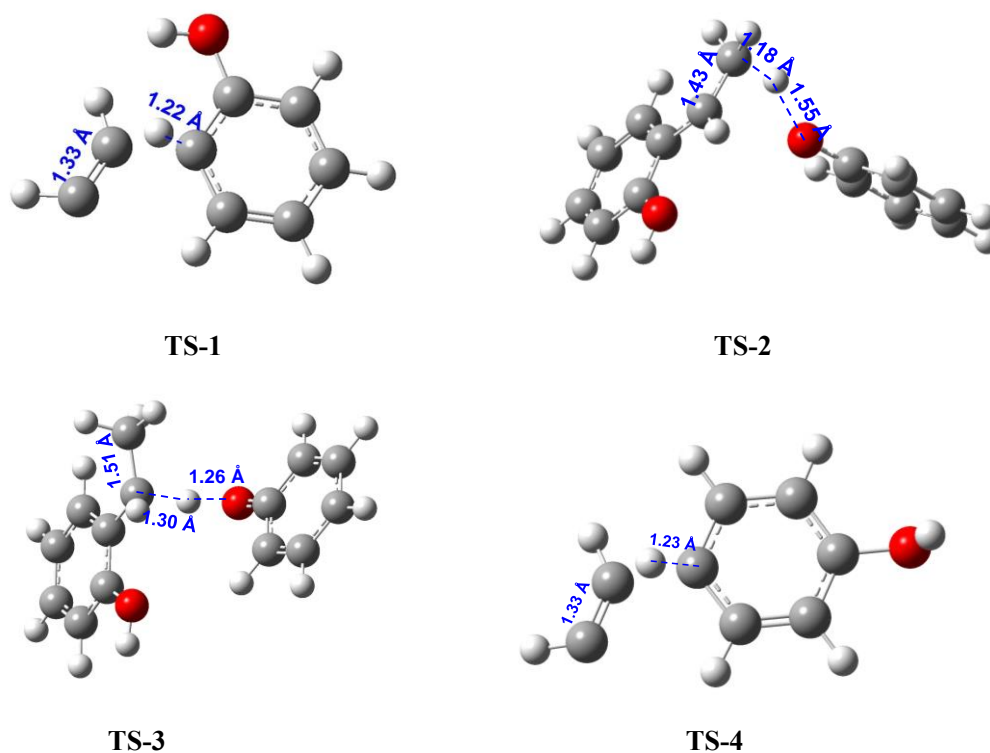
#### The preparation method of calcium phenoxide:

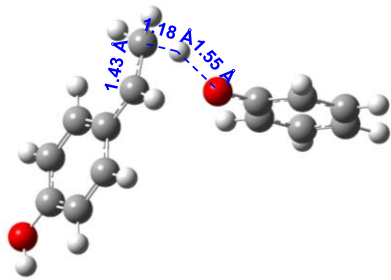
$\text{Ca}(\text{OH})_2$  and PhOH were added in the 1:2 molar ratio and heated at 60 °C for 3 h to obtain calcium phenoxide;

In order to remove the water and unreacted PhOH, it was dried in a drying oven at 105 °C for 1 h.

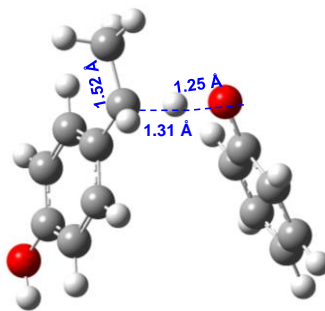


**Figure S4.** XRD of calcium phenoxide preparation and the solid product from the reaction of PhOH and CaC<sub>2</sub>.

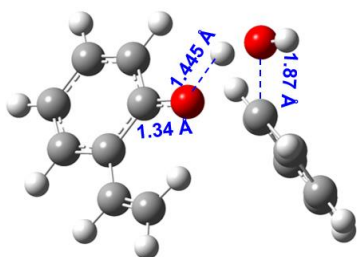




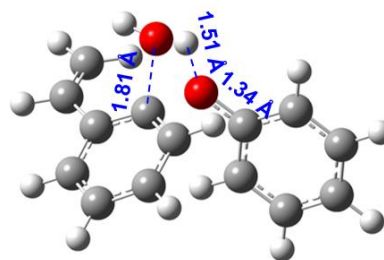
TS-5



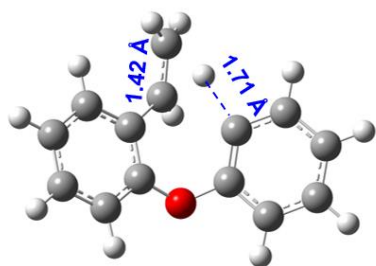
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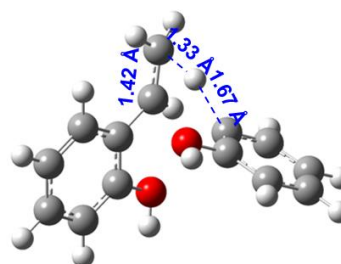
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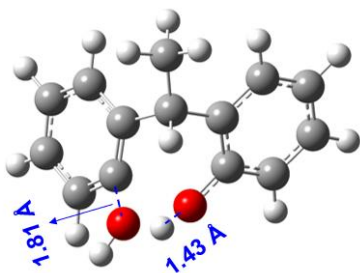
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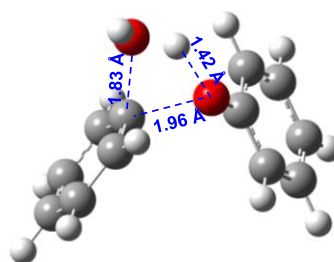
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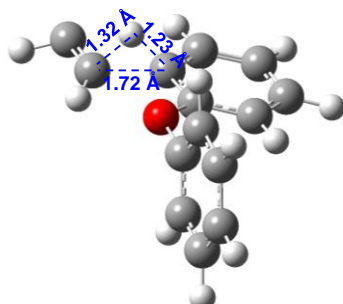
TS-10



TS-11

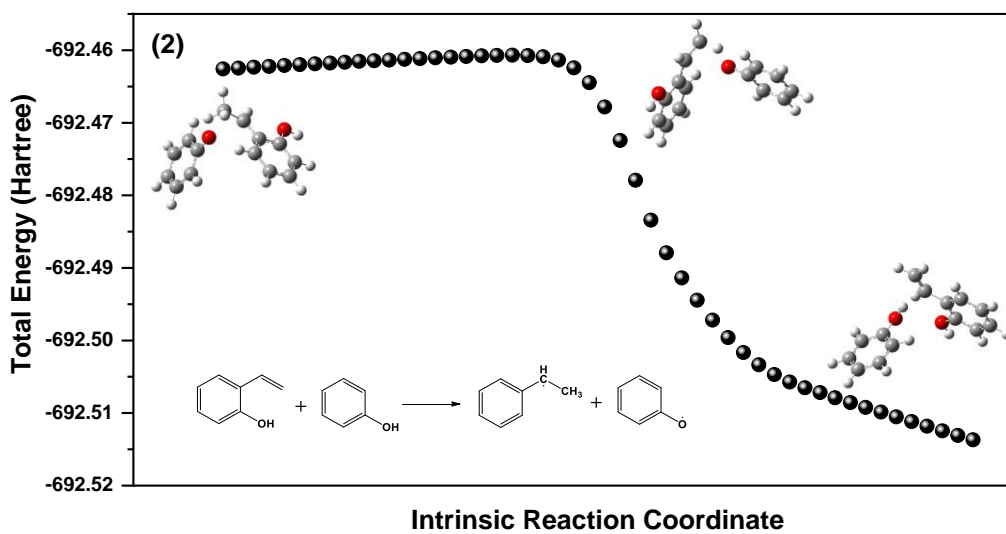
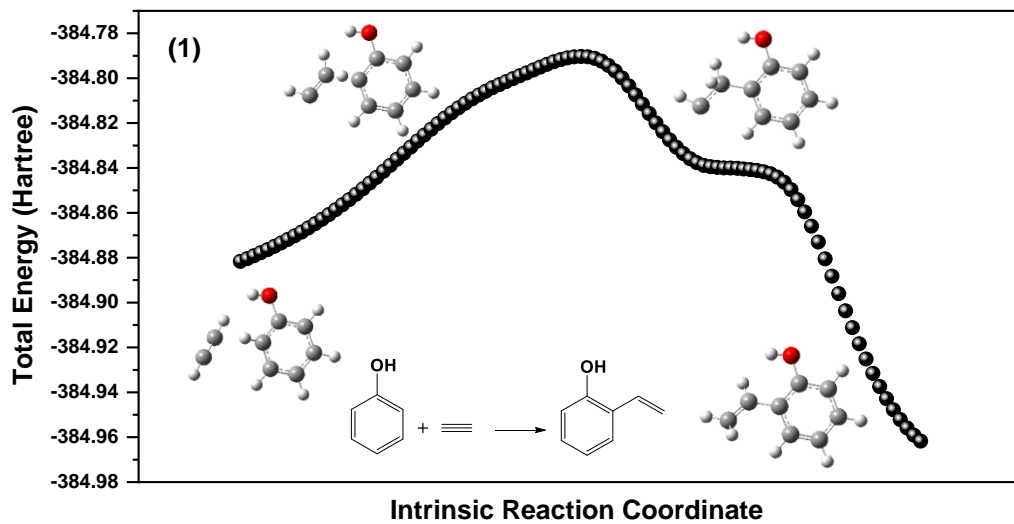


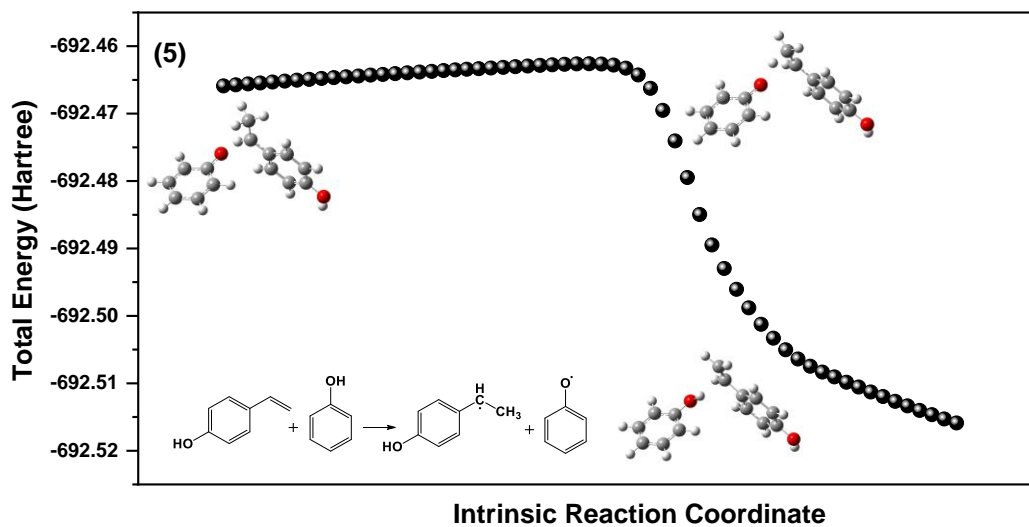
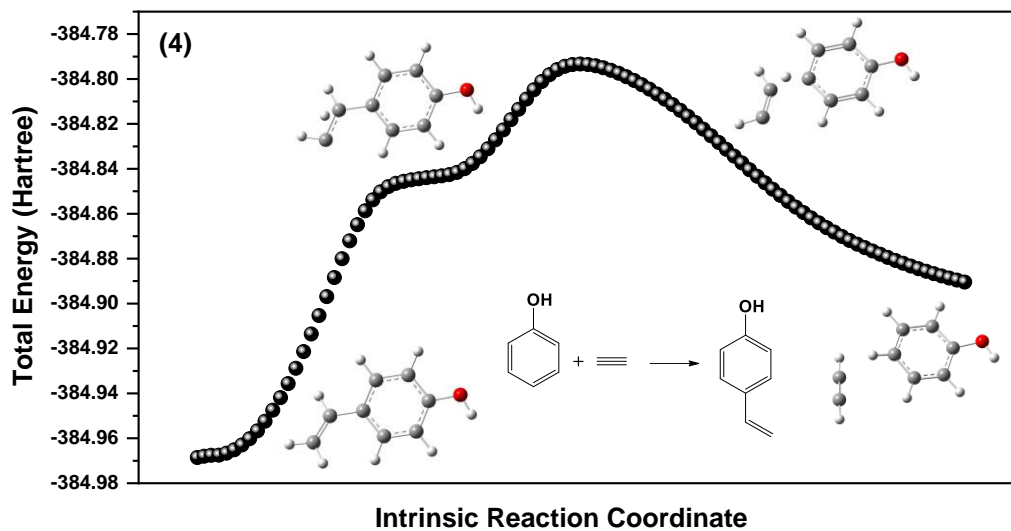
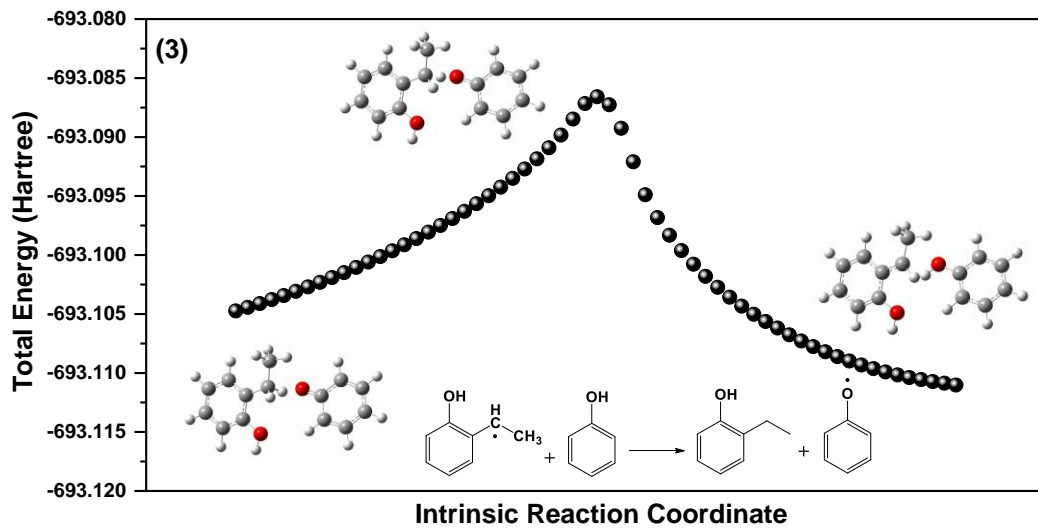
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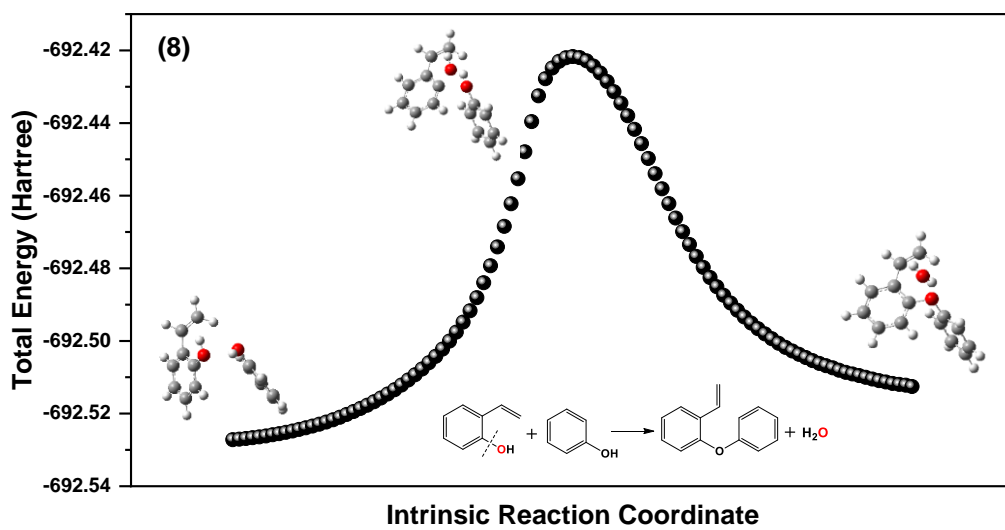
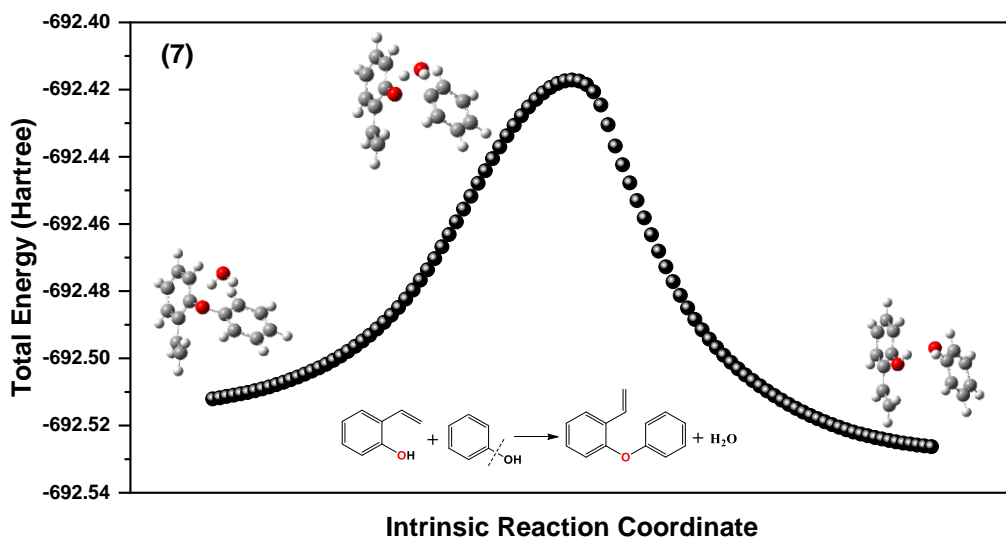
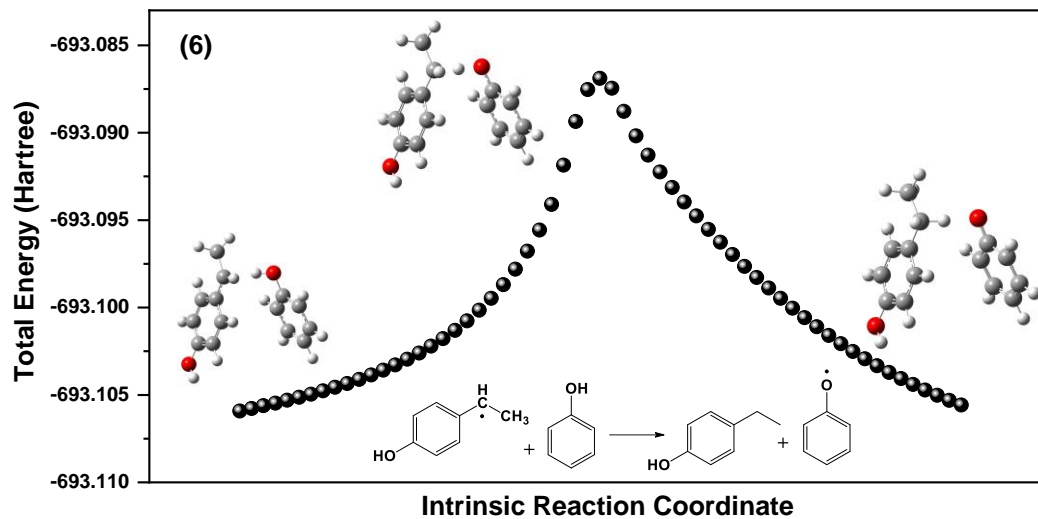


TS-13

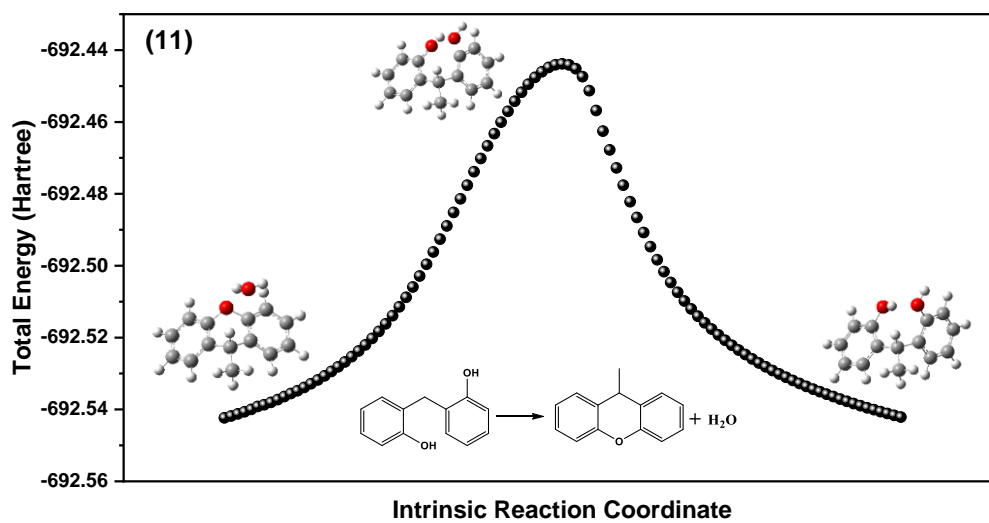
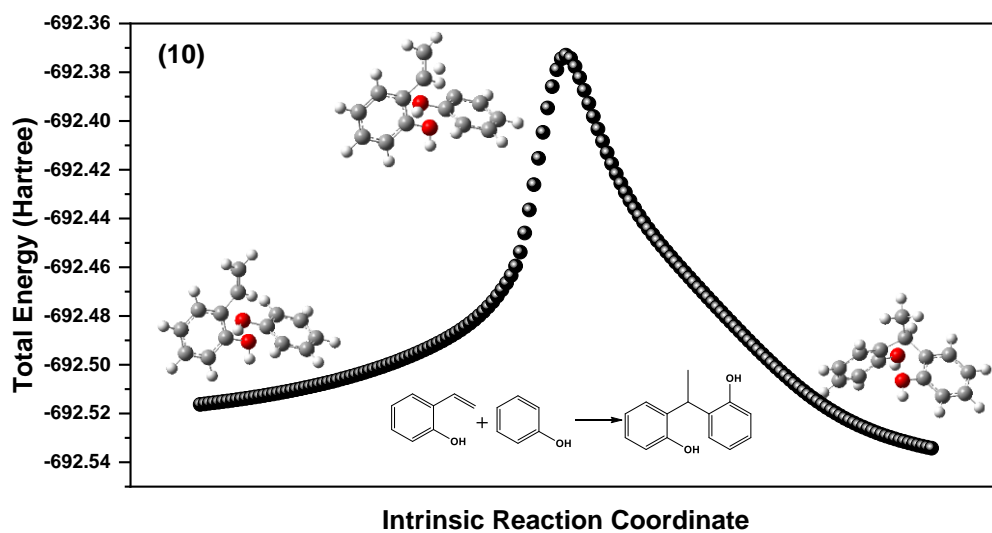
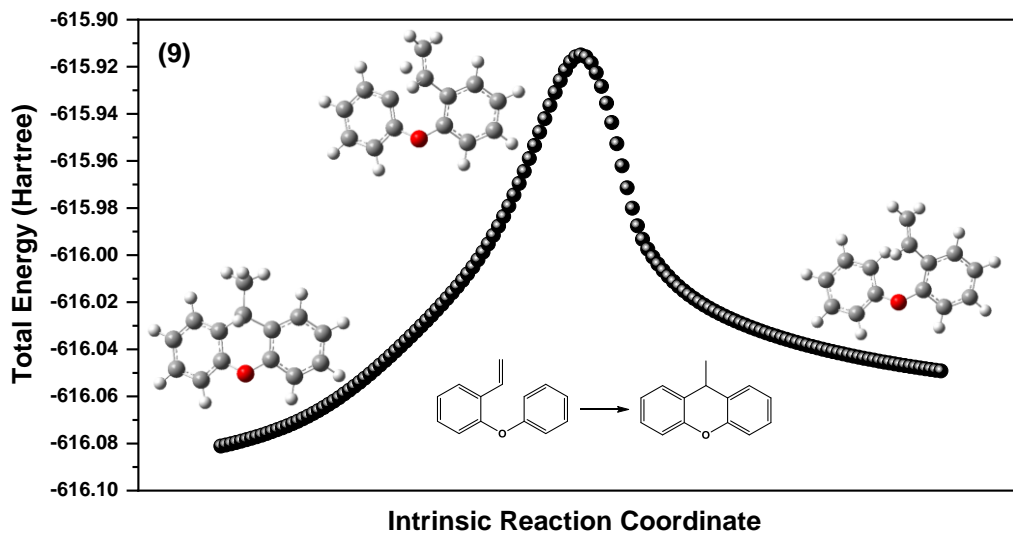
Figure S5. The bond length parameter of transition state.











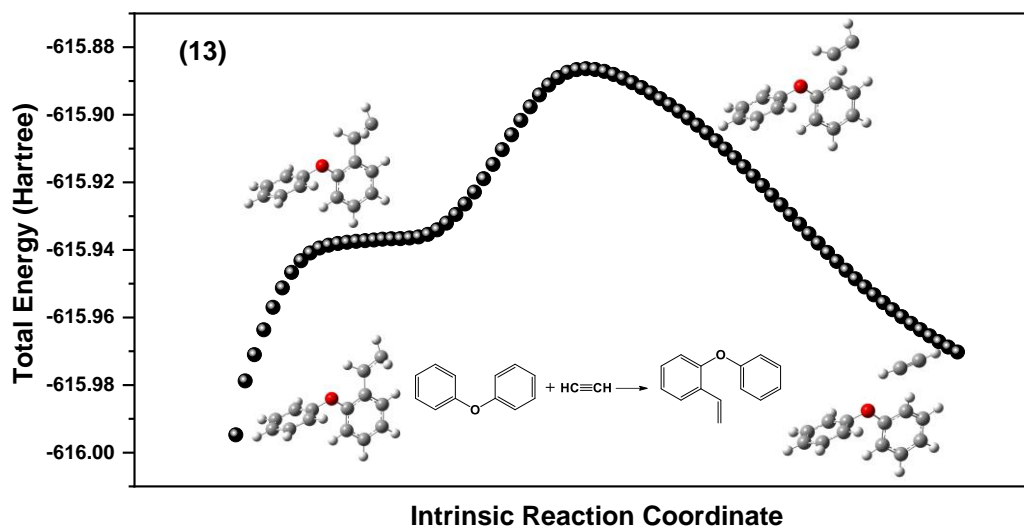
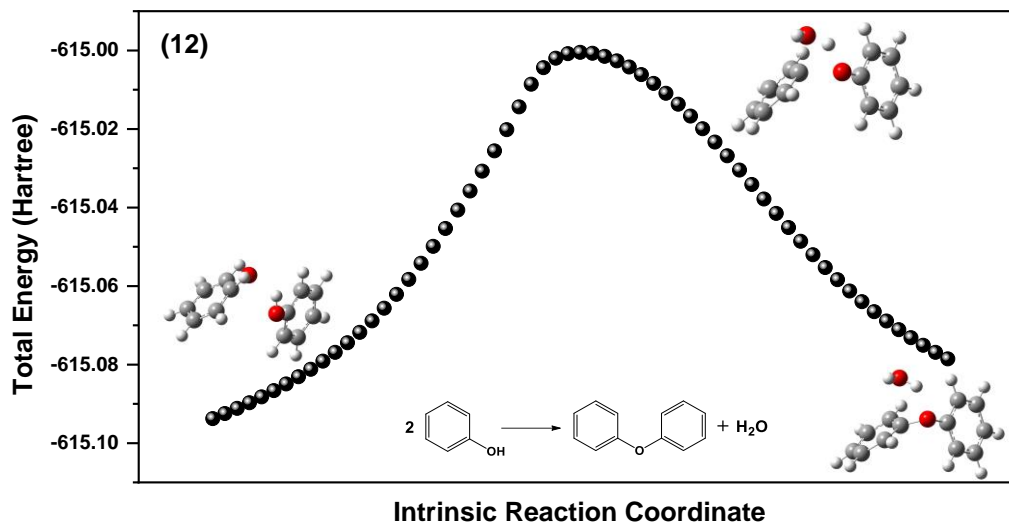
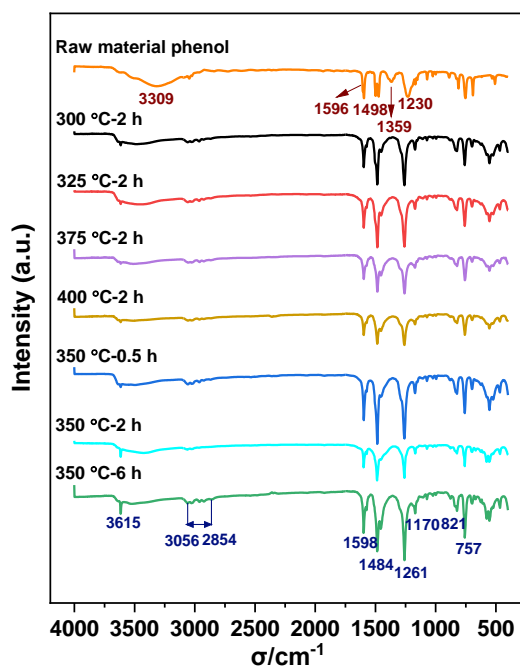


Figure S6. Intrinsic reaction coordinates (IRC) for each stage of the reaction.

Table S1. Elemental analysis and carbon yield calculation of solids

| Entry | Temp./°C | Time/h | C/wt.% | H/wt.% | mSolid/mg | Y <sub>C</sub> Solid/% |
|-------|----------|--------|--------|--------|-----------|------------------------|
| 1     | 350      | 0.5    | 53.21  | 4.65   | 10.47     | 25.8                   |
| 2     | 350      | 2      | 57.55  | 4.68   | 10.32     | 27.5                   |
| 3     | 350      | 6      | 59.5   | 4.54   | 13.03     | 35.9                   |
| 4     | 300      | 2      | 55.29  | 4.75   | 9.61      | 24.6                   |
| 5     | 400      | 2      | 61.44  | 4.6    | 13.64     | 38.8                   |



**Figure S7.** IR spectra of solid products at different reaction conditions.

The infrared diffraction peaks of organic components in the solid products obtained under different reaction conditions are also basically the same. Taking the solid product at 350 °C for 6 h as an example, the skeleton vibration peaks of the benzene ring (1484  $\text{cm}^{-1}$ , 1598  $\text{cm}^{-1}$ ), the stretching vibration peak of the hydroxyl group (3615  $\text{cm}^{-1}$ ), and the C-O bond stretching vibration peak of the hydroxyl group (1261  $\text{cm}^{-1}$ ) indicates that the organic components of the solid product are mostly phenolic substances. The appearance of methyl and methylene absorption peaks (2854-3056  $\text{cm}^{-1}$ ) and ether bond stretching vibration peak (1170  $\text{cm}^{-1}$ ) indicates that alkyl side chains and ether bonds may also be present in the solid product. Comparing the infrared spectrum of the raw material PhOH, it was found that the C-O bond stretching vibration peak of the phenolic hydroxyl group increased from 1230  $\text{cm}^{-1}$  to 1261  $\text{cm}^{-1}$ , and the stretching vibration peak of the phenolic hydroxyl group (3309  $\text{cm}^{-1}$ ) moved to the high band, accompanied by the disappearance of the in-plane bending vibration peak of the hydroxyl group (1359  $\text{cm}^{-1}$ ), indicating that the phenolic compounds in the solid product may be adsorbed on  $\text{CaC}_2$ /calcium phenoxide.

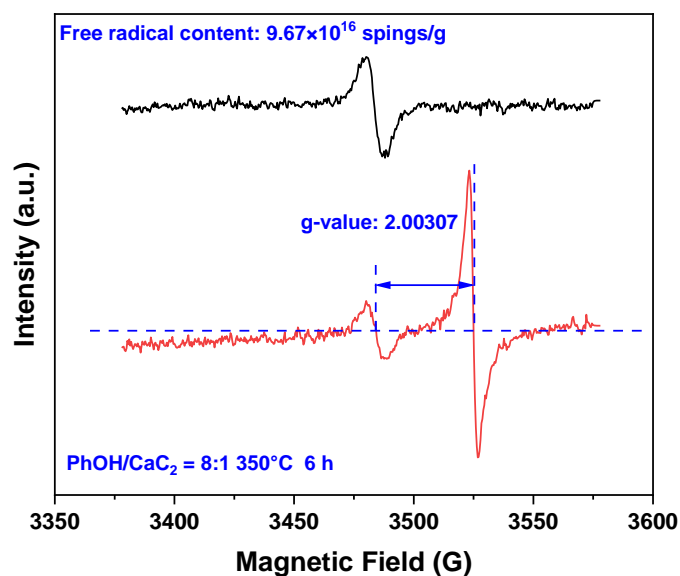
**Table S2.** Changes in the product after adding dihydrophenanthrene(DHP)

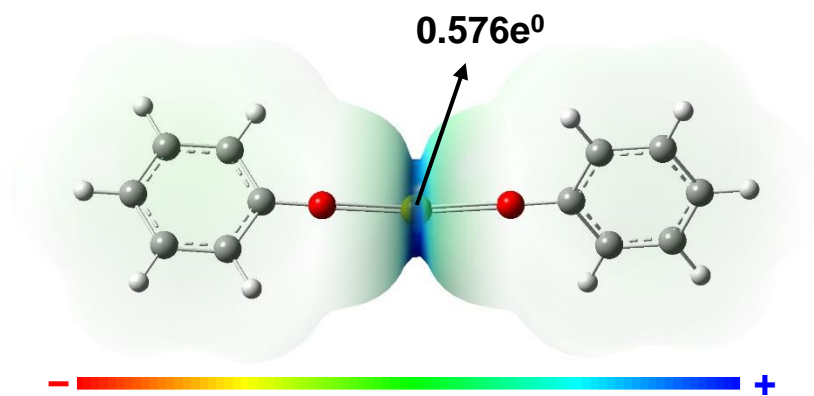
| Entry | PhOH/<br>CaC <sub>2</sub> /<br>DHP | PhOH<br>Conv./% | DHP<br>Conv./% | Product yield/% |                   |                   |                          |
|-------|------------------------------------|-----------------|----------------|-----------------|-------------------|-------------------|--------------------------|
|       |                                    |                 |                | Xanthene        | 2-Ethyl<br>phenol | 4-Ethyl<br>phenol | Total of<br>ethylphenols |
| 1     | 8:1:0                              | 45.8            | -              | 21.8            | 15.2              | 9.2               | 24.4                     |
| 2     | 8:1:1                              | 34.8            | 88.3           | 9.1             | 23.5              | 34.6              | 58.1                     |
| 3     | 8:1:2                              | 33.1            | 43.9           | 7.1             | 21.9              | 38.5              | 60.4                     |
| 4     | 8:1:4                              | 31.1            | 25.8           | 6.3             | 18.6              | 37.7              | 56.3                     |

Reaction conditions: T = 350 °C, t = 4 h.

### ESR Measurements:

The free radical concentration of a sample was measured by installing the reactor directly in the ESR spectrometer (EMXplus-10/12 from Bruker) that was operated at 9.85 GHz and 0.1 mW. The central magnetic field was 348 mT, the modulation amplitude was 1.0 G, the sweep width was 5 mT, the sweep time was 50 s, and the time constant was 0.01 s. The measurements were obtained at 18 °C, and the signals were calibrated by 2,2-diphenyl-1-picrylhydrazyl (DPPH). The ESR signal intensity and radical concentration showed excellent linearity, and the reactor itself showed no influence on the ESR data.

**Figure S8.** The free radical concentration and g-value in the system.



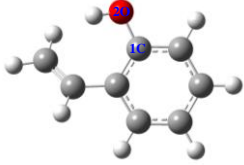
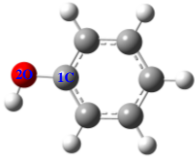
**Figure S9.** Electrostatic potential energy surface of calcium phenoxide.

**Table S3.** The proportional relationship between 9-methylxanthene and xanthene

| Entry | Temp./°C | Time/h | Xanthenes yield/% | The proportion of <i>i</i> in xanthenes |          |
|-------|----------|--------|-------------------|---|----------|
|       |          |        |                   | 9-methylxanthene                        | xanthene |
| 1     | 300      | 2      | 6.35              | 71.72                                   | 28.28    |
| 2     | 325      | 2      | 15.89             | 57.96                                   | 42.04    |
| 3     | 350      | 2      | 17.56             | 51.93                                   | 48.07    |
| 4     | 375      | 2      | 17.09             | 43.87                                   | 56.13    |
| 5     | 400      | 2      | 17.63             | 35.79                                   | 64.21    |
| 6     | 350      | 0.5    | 7.10              | 55.56                                   | 44.35    |
| 7     | 350      | 6      | 24.25             | 54.95                                   | 45.05    |

From **Table S3**, it can be seen that temperature is an important factor affecting the transformation of 9-methylxanthene to xanthene.

**Table S4.** Bond dissociation energies of different substances

|               | Molecular Model   | Bond-breaking position | Bond dissociation energy $\Delta G$ (kJ/mol) |
|---------------|---|------------------------|--|
| 2-Vinylphenol |  | 1C-2O                  | 365.6  |
| Phenol        |  | 1C-2O                  | 376.1  |

### Cycle experiment:

Take the dry solid product after the reaction between PhOH and CaC<sub>2</sub>, added 0.5 mL of 25% dilute sulfuric acid solution, shaken and added 1 mL of carbon disulfide solution, let it stand for a few minutes, and after the solution was separated, removed the supernatant and conducted GC analysis. The results were shown **Table S5**.

**Table S5.** Cycle experiments of calcium phenoxide

| Entry | Temperature/°C | Time/h | The recovery rate of PhOH/% |
|-------|----------------|--------|-----------------------------|
| 1     | 300            | 2      | 4.59                        |
| 2     | 325            | 2      | 5.01                        |
| 3     | 375            | 2      | 6.77                        |
| 4     | 400            | 2      | 4.95                        |
| 5     | 350            | 6      | 4.85                        |
| 6     | 350            | 2      | 5.94                        |
| 7     | 350            | 0.5    | 3.82                        |

As can be seen from the table, the recovery rate of PhOH is less than the theoretical amount of PhOH generated by calcium phenoxide. This discrepancy may arise from conducting only a single extraction process, whereas PhOH is soluble in water and typically necessitates multiple extractions for complete removal. This experiment underscores the potential of calcium phenoxide to engage in the reaction cycle via acidification, thereby enhancing PhOH utilization.

### Calculation formulas for Table 5

$$Y_{PhOH \text{ liquid product}} = \frac{3 \times Y_{Ethylphenol} + 2 \times Y_{Xanthene}}{8} \times 100\%$$

$$S_{PhOH \text{ liquid product}} = \frac{Y_{PhOH \text{ liquid product}}}{X_{PhOH}} \times 100\%$$

$$Y_{PhOH \text{ Calcium phenoxide}} = \frac{2 \times Y_{calcium phenoxide}}{8} \times 100\%$$

$$S_{PhOH \text{ calcium phenoxide}} = \frac{Y_{PhOH \text{ calcium phenoxide}}}{X_{PhOH}} \times 100\%$$

$$S_{PhOH \text{ unidentified}} = 100\% - S_{PhOH \text{ liquid product}} - S_{PhOH \text{ calcium phenoxide}}$$

When calculating the selectivity of the product based on CaC<sub>2</sub>, since the conversion rate of CaC<sub>2</sub> is 100%, the selectivity of the product is equal to the yield.

$$S_{CaC2 \text{ unidentified}} = 100\% - S_{CaC2 \text{ liquid product}} - S_{CaC2 \text{ acetylene}}$$

### Experimental steps for g-level

Typically, PhOH (10.5 g, 113.6 mmol) and CaC<sub>2</sub> (0.5 g, 7.1 mmol) were added into a quartz tube in a stirred autoclave reactor (Parr 4597, 50 mL). Then, the reactor was sealed, purged with Ar of 2.0 MPa for 5 times to remove air and heated to a specified temperature under stirring at a speed of 200 rpm. After the indicated reaction time, the reactor was cooled to room temperature with ice water. The gas product was collected carefully with a gas collecting bag, and the solid and liquid products were quantitatively transferred to a centrifuge tube under nitrogen atmosphere for separation, and the liquid product yields were shown in **Table S6**.

**Table S6.** Comparison of results of amplification experiments

| m <sub>CaC<sub>2</sub></sub><br>(mg) | Reactor      | Heating-<br>up time | Cooling<br>time | X <sub>PhOH</sub><br>(%) | Y <sub>i</sub> (%) |                       |                       | Experi-<br>mental<br>error <sup>a</sup><br>(%) |     |
|--------------------------------------|--------------|---------------------|-----------------|--------------------------|--------------------|-----------------------|-----------------------|--|-----|
|                                      |              |                     |                 |                          | Xant<br>henes      | 2-<br>ethylph<br>enol | 4-<br>ethylph<br>enol |  |     |
| 2.5                                  | Microreactor | <2 min              | <15 s           | 29.0                     | 26.0               | 21.2                  | 17.1                  | 5.1  | 0.4 |
| 500                                  | Autoclave    | 38 min              | 1.5 h           | 36.7                     | 21.4               | 16.5                  | 12.7                  | 10.7   | 4.3 |

Reaction condition: T = 350 °C, t = 6 h, PhOH/CaC<sub>2</sub> = 16:1.

a: Errors arising from inherent equipment issues and the intermediate operational procedures.