# A sustainable iron-catalyzed aerobic oxidative C-C and C-O bond cleavage of lignin model to phenol and methyl benzoate

Shaoyuan Guo [a], Xinli Tong *[,a], Lingwu Meng [a], and Guobao Yang [a]

[a] *Tianjin Key Laboratory of Organic Solar Cells and Photochemical Conversion, School of Chemistry and Chemical Engineering, Tianjin University of Technology, Tianjin 300384, P. R. China.*

** E-mail address: tongxinli@tju.edu.cn or tongxli@sohu.com.*

## Supporting Information

### 1. The aerobic oxidative cleavage processes of lignin model with iron catalysts

The results of the oxidative cleavage of lignin model with several iron-based catalysts are provided in the Table S1. It can be seen that 47.1% conversion of **1** was attained with the $Fe_3C$ + C as catalyst system, in which the yields of **2** and **3** were 42.8% and 4.3%, repectively. Both the conversion and product yields are near to those with the single $Fe_3C$ as catalyst. It showed that the synergy effect in the used Fe-N-C-850 catalyst is greatly siginificant to the oxidation reaction. Moreover, when the Fe-glu-800, Fe-xylan-800 and Fe-phen-glu-800 were used as catalysts for the oxidative cleavage processes of **1**, the conversion of substrate was respectively 22.9%, 19.7% and 39.7%, which showed that the preparation methods are closely related to the activities of iron-based catalysts.

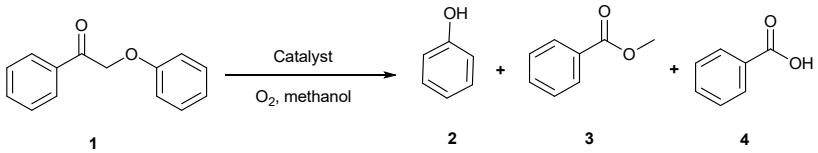



**Table S1**. The oxidative transformation of **1** with different iron catalysts [a]

| Entry | Catalysts | Conv. (%) [b] | The yield of product (%) [b] | | |
|---|---|---|---|---|---|
| | | | **2** | **3** | **4** + others |
| 1 | $Fe_3C$ + C | 47.1 | 42.8 | 4.3 | - |
| 2 | Fe-glu-800 | 22.9 | 9.0 | 3.8 | - |
| 3 | Fe-xylan-800 | 19.7 | 8.8 | 3.2 | - |
| 4 | Fe-phen-glu-800 | 39.7 | 13.3 | 3.3 | - |

[a] Reaction conditions: 0.1 g of **1**, 0.025 g catalyst, in 17 mL methanol solvent, with 0.3 Mpa of $O_2$ pressure, at 120 °C, for 2 h;

[b] The conversion and selectivity of product were attained by GC using the internal standard method.

## 2. The effects of additives on oxidative transformation of 2-phenoxy-1-phenyl ethanone

The effects of amine derivatives as additives on the oxidative transformation of **1** were investigated and the obtained results are given in the Table S2.

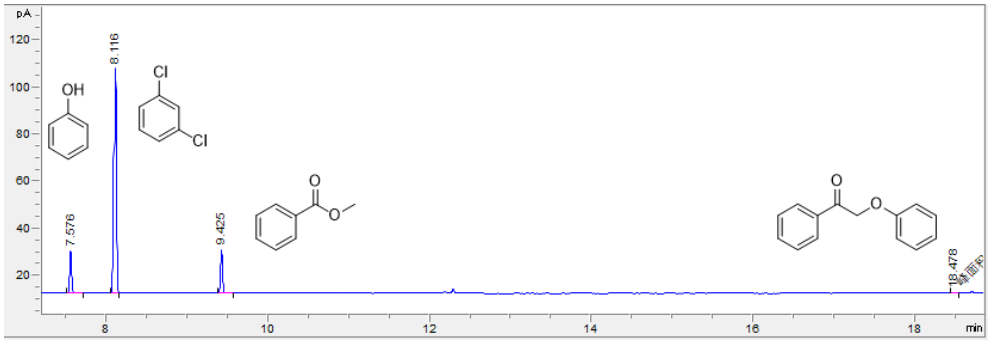
**Table S2**. The oxidative transformation of **1** with different additives [a]

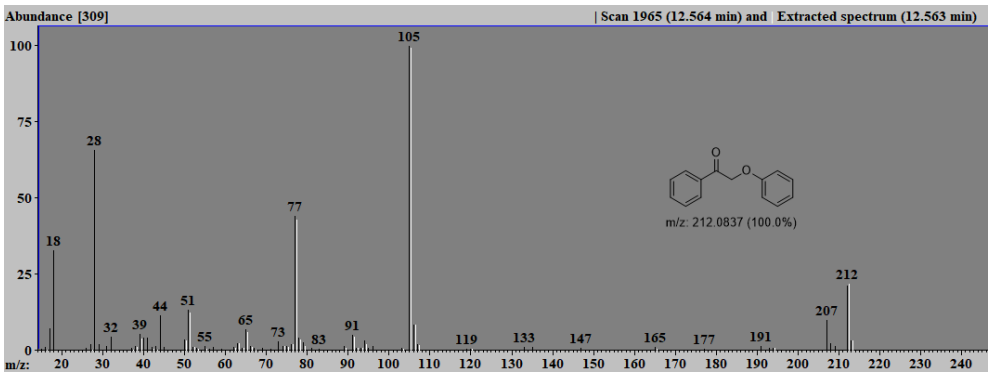
| Entry | Additive | Conv. (%) [b] | The yield of product (%)[b] | | |
|---|---|---|---|---|---|
| | | | **2** | **3** | **4** |
| 1 | aniline | 85.3 | 85.2 | 11.7 | - |
| 2 | ammonium acetate | 98.2 | 71.5 | 22.7 | - |
| 3 | ammonia | 98.2 | 97.9 | 31.9 | - |

[a] Reaction conditions: 0.1 g of **1**, 0.025 g of Fe-N-C-850 catalyst, in 17 mL methanol, under 0.3 Mpa of $O_2$ pressure, at 120 °C, for 2 h;

[b] The conversion and selectivity of product were attained by GC using the internal standard method.

## 3. The GC and GC-MS spectra of obtained products



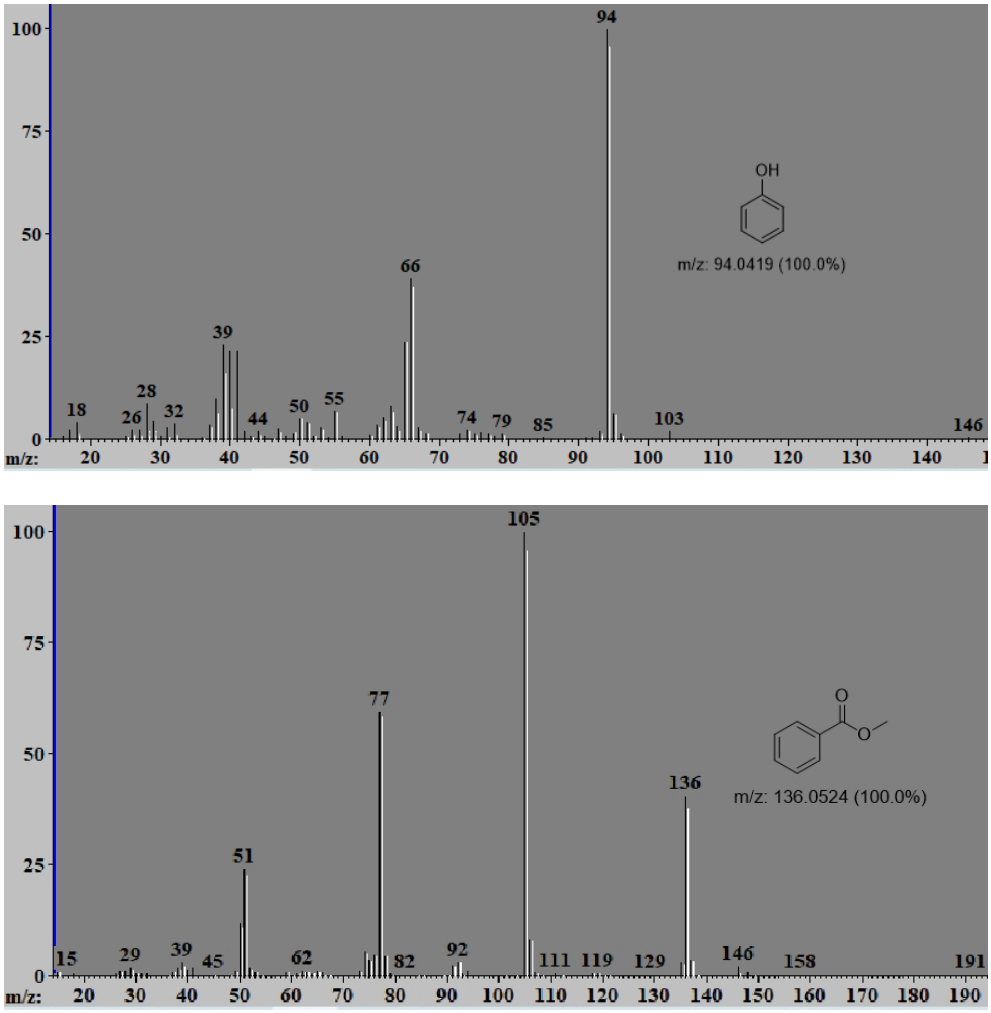
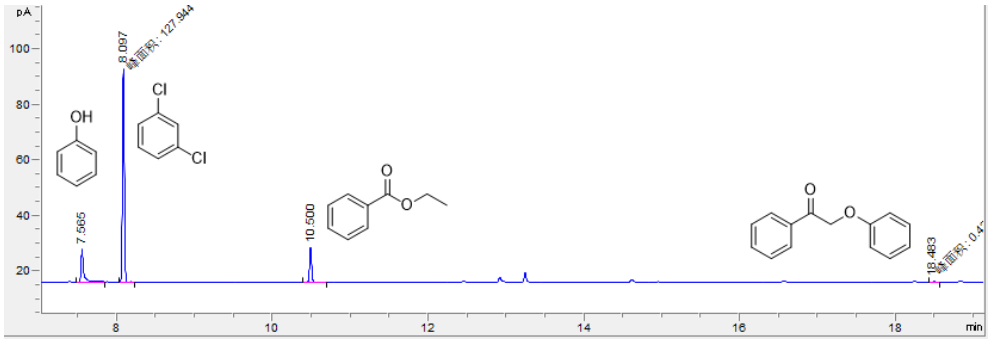



**Figure S1**. The GC and GC-MS spectra for the reaction of 2-phenoxy-1-phenyl ethanone in the methanol solvent



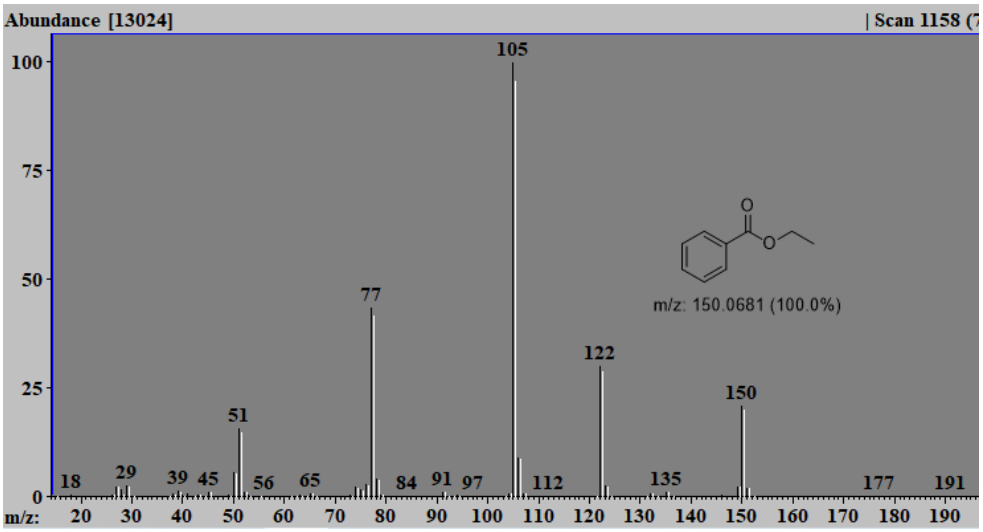



**Figure S2**. The GC and GC-MS spectra of the reaction of 2-phenoxy-1-phenyl ethanone in the ethanol solvent

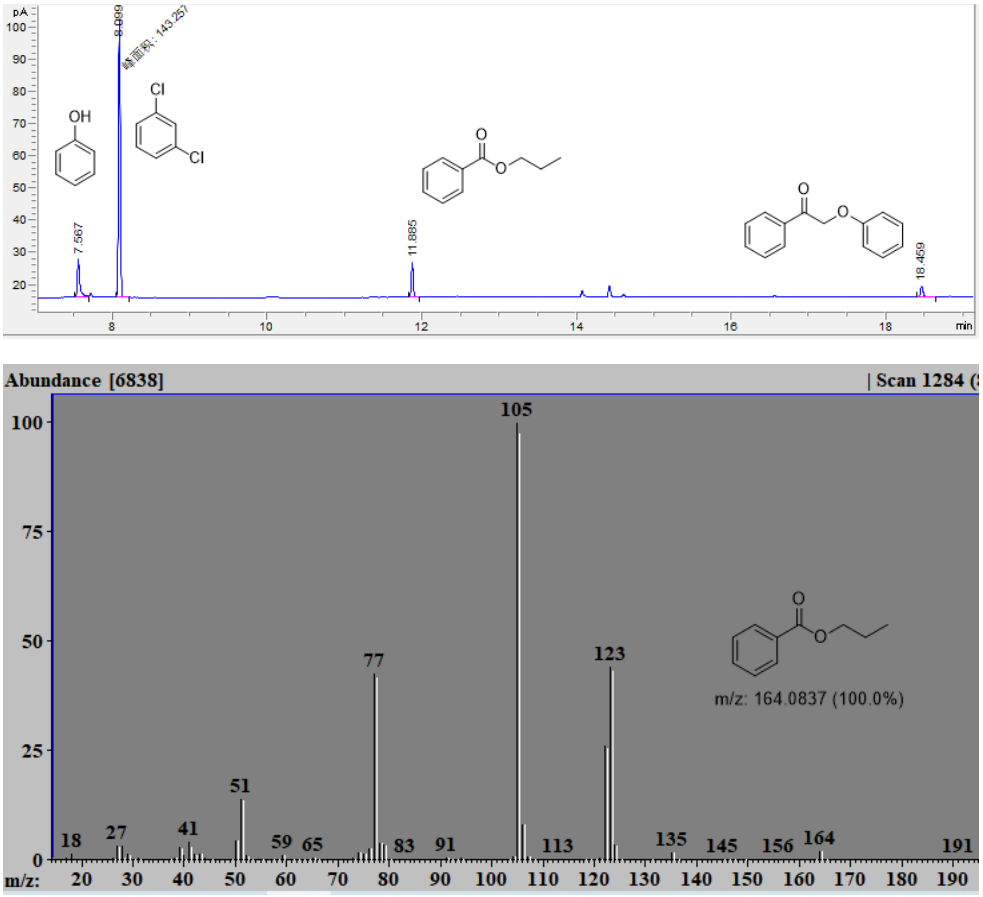



**Figure S3**. The GC and GC-MS spectra for the reaction of 2-phenoxy-1-phenyl ethanone in the n-propanol

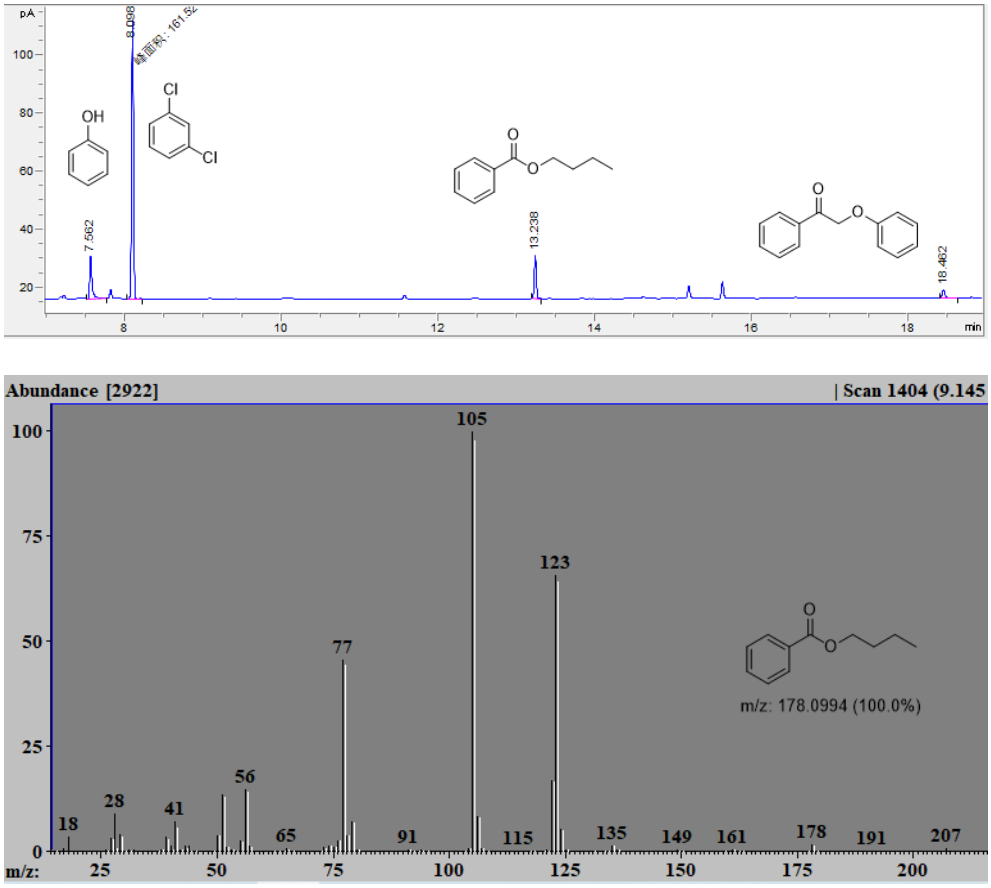
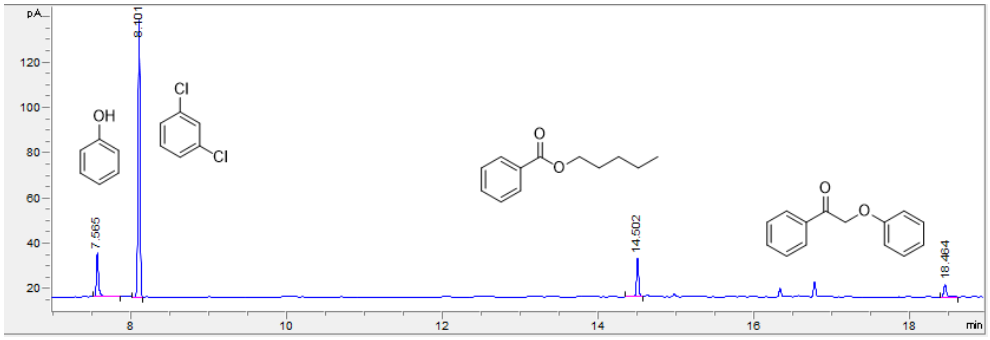



**Figure S4**. The GC and GC-MS spectra for the reaction of 2-phenoxy-1-phenyl ethanone in the n-butanol



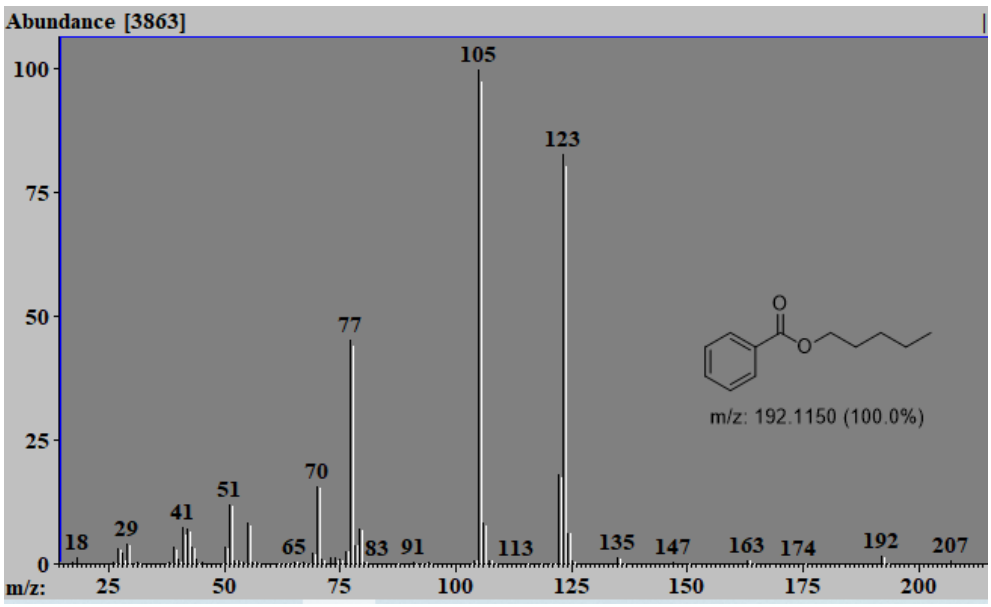
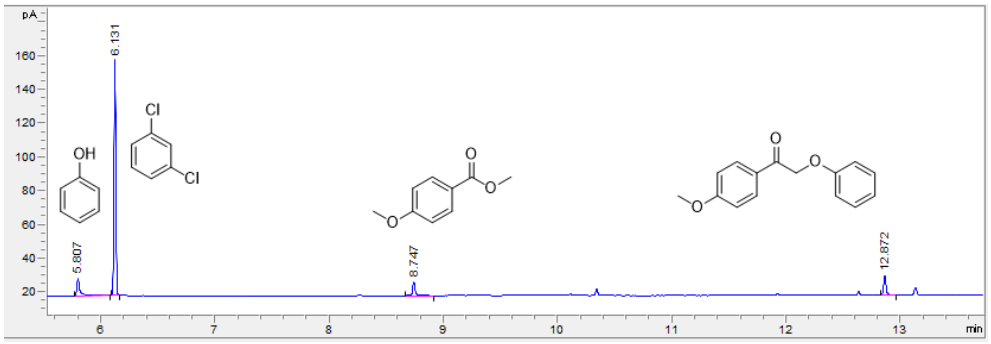
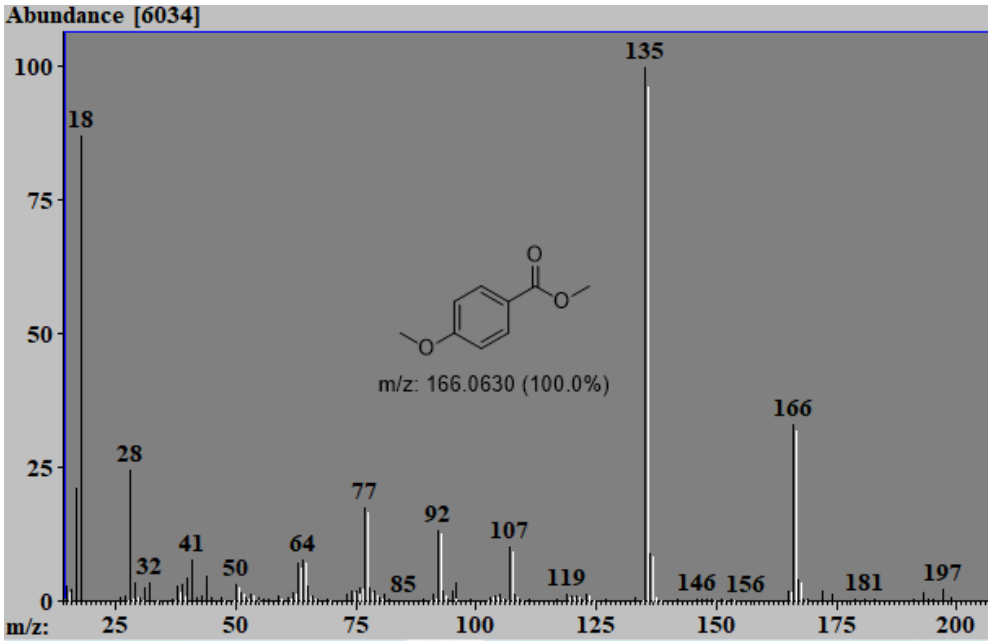



**Figure S5**. The GC and GC-MS spectra for the reaction of 2-phenoxy-1-phenyl ethanone in the n-pentanol



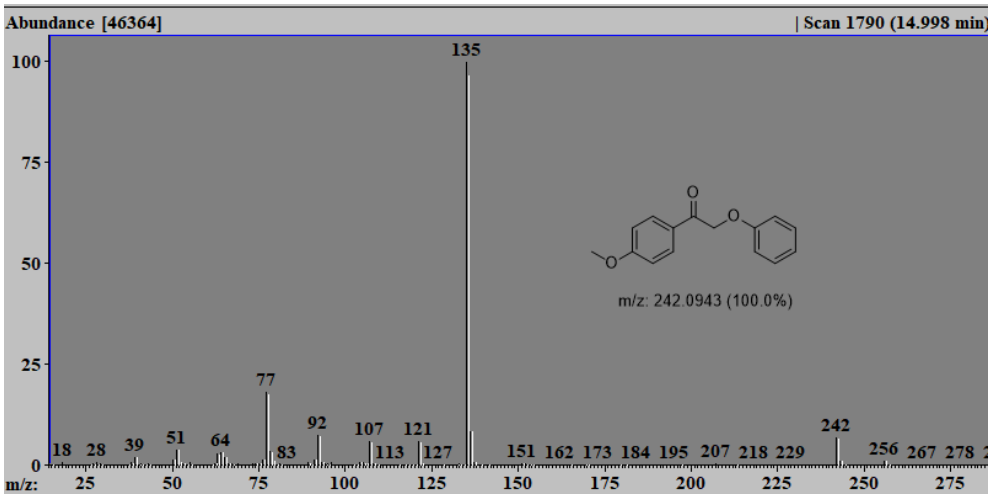
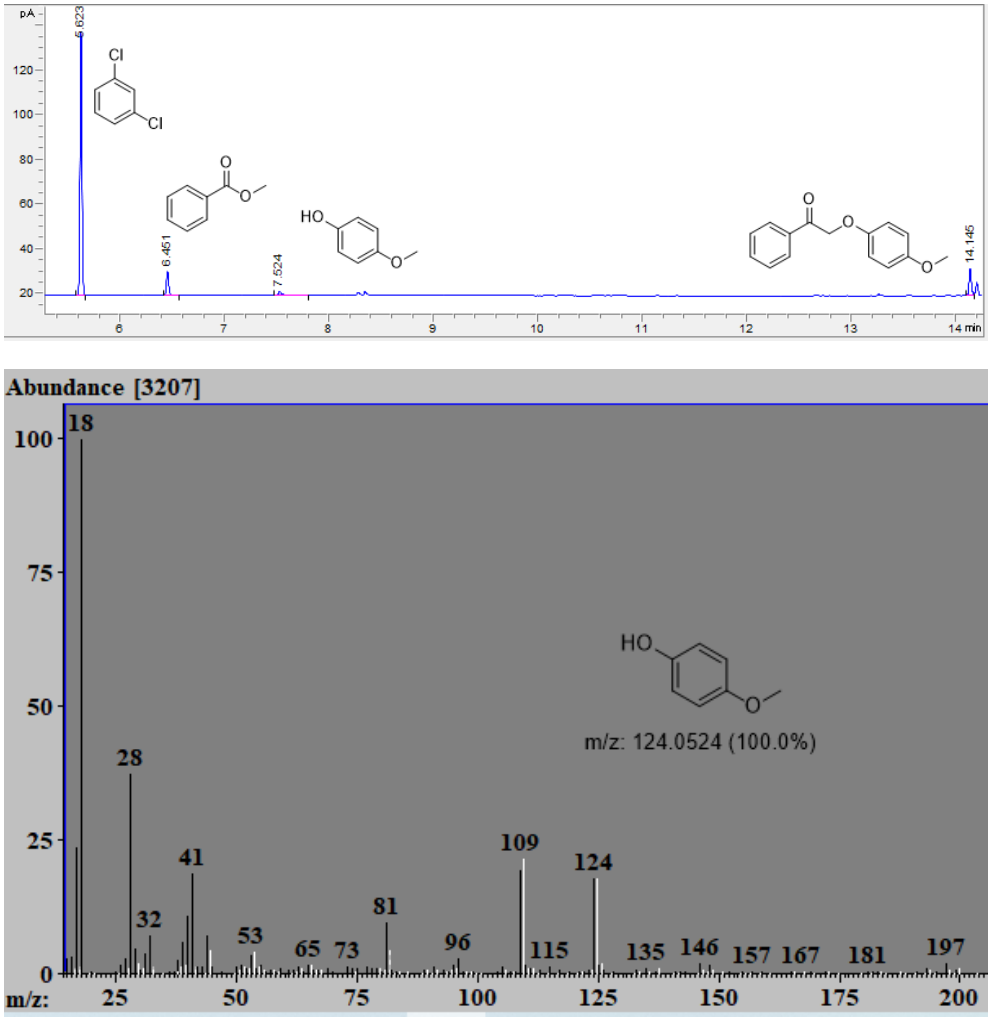



**Figure S6**. The GC and GC-MS spectra for the reaction of 2-phenoxy-1-(4-methoxyphenyl)ethanone in the methanol



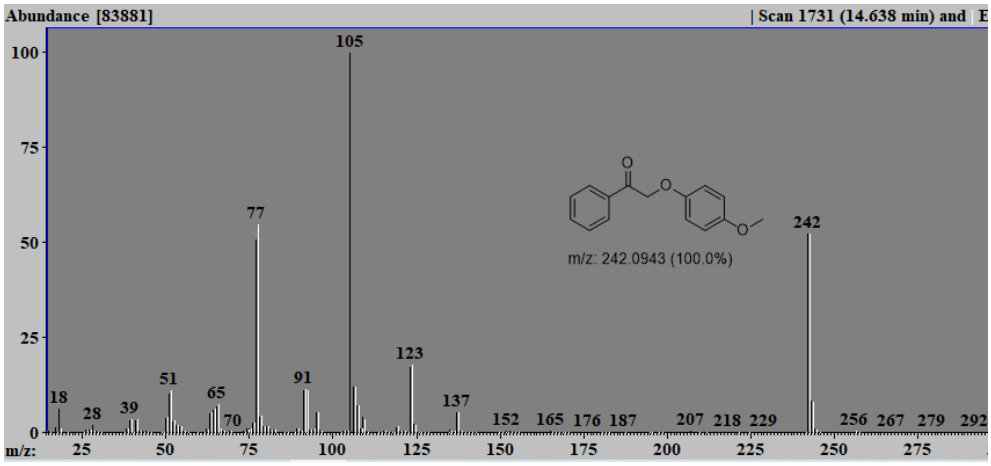
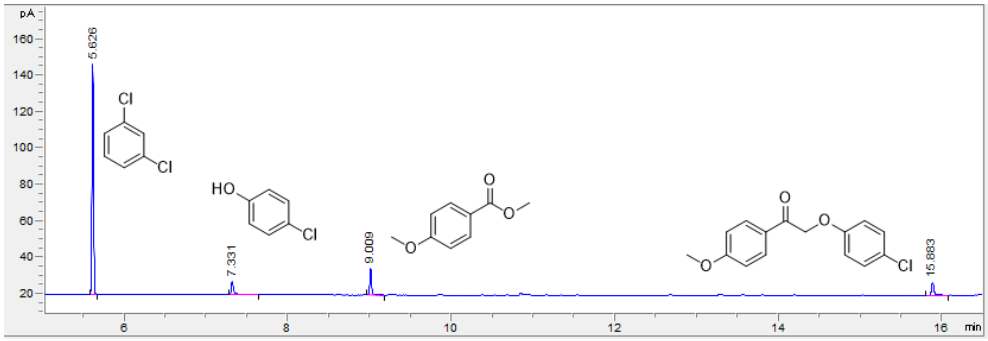
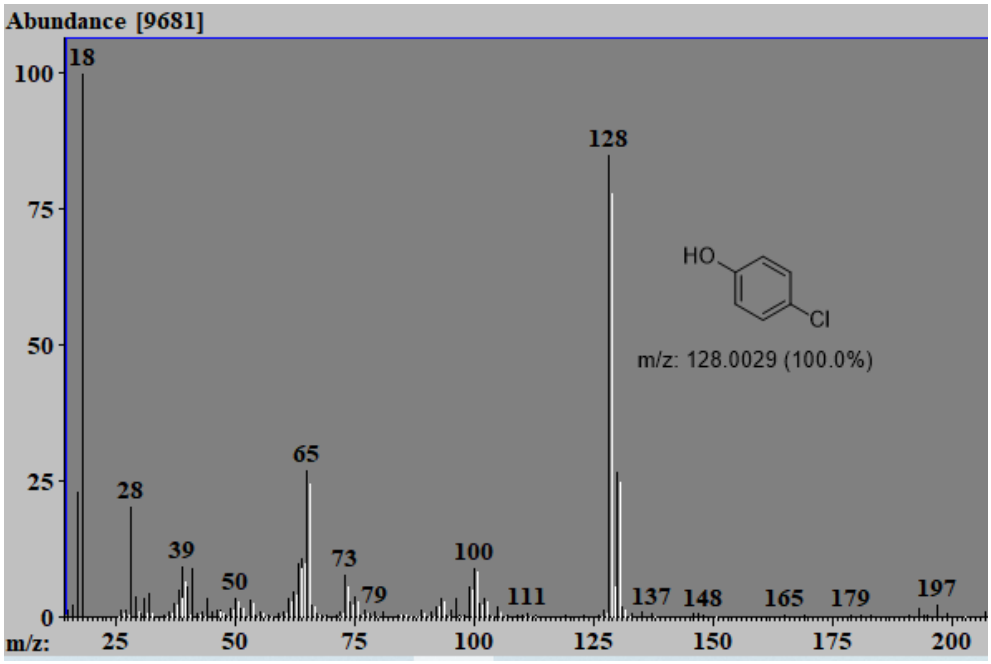



**Figure S7**. The GC and GC-MS spectra for the reaction of 2-(4-methoxyphenoxy)-1-phenylethanone in the methanol



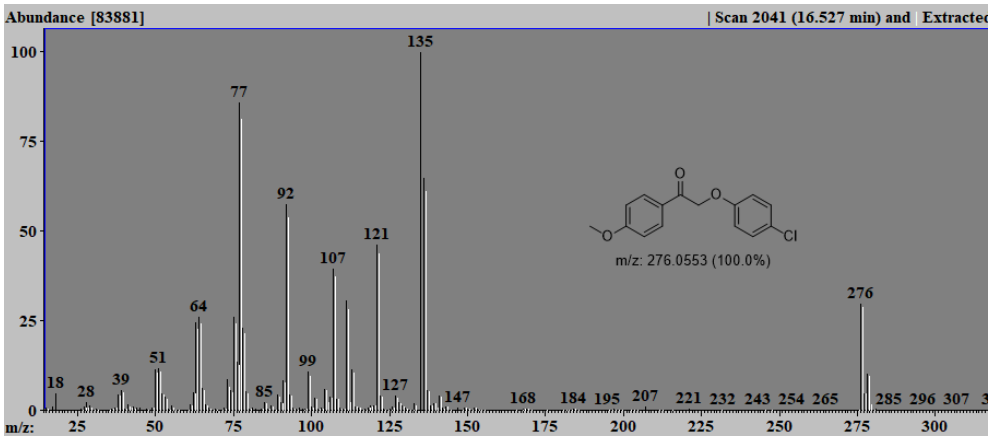
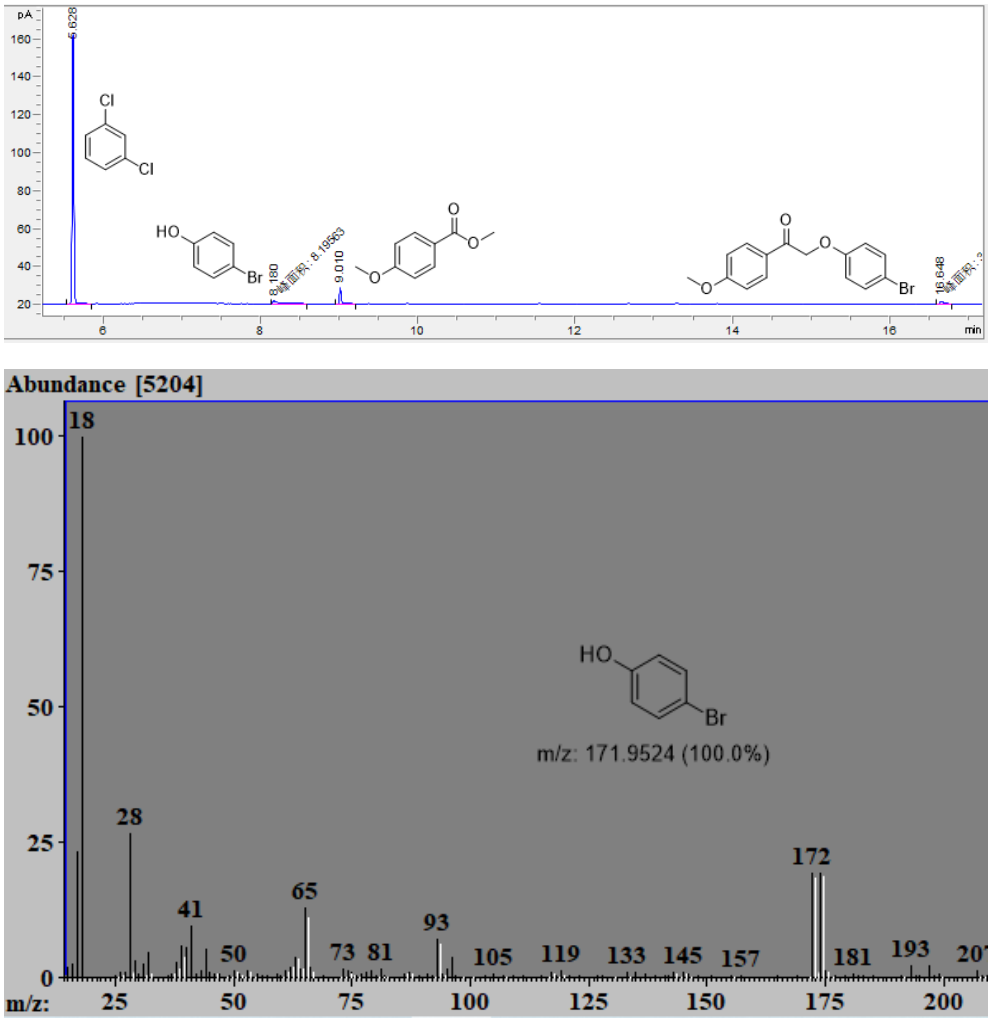



**Figure S8**. The GC and GC-MS spectra for the reaction of 2-(4-methoxyphenoxy)-1-(4-chlorophenyl)ethanone in the methanol



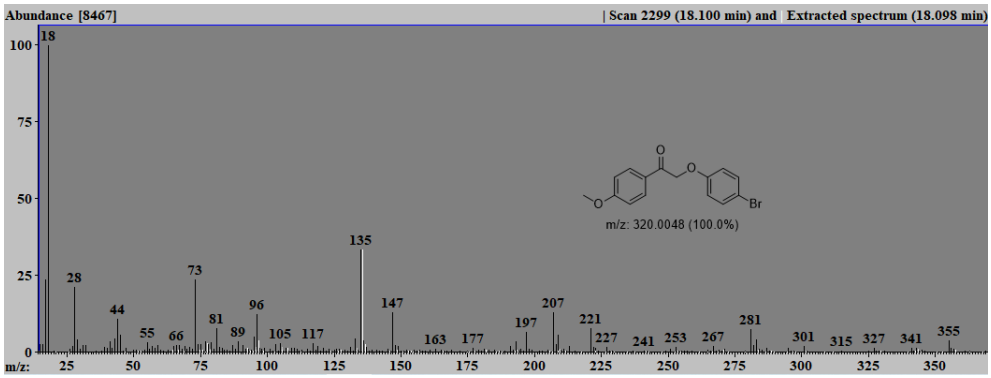



**Figure S9**. The GC and GC-MS spectra for the reaction of 2-(4-methoxyphenoxy)-1-(4-bromophenyl)ethanone in the methanol

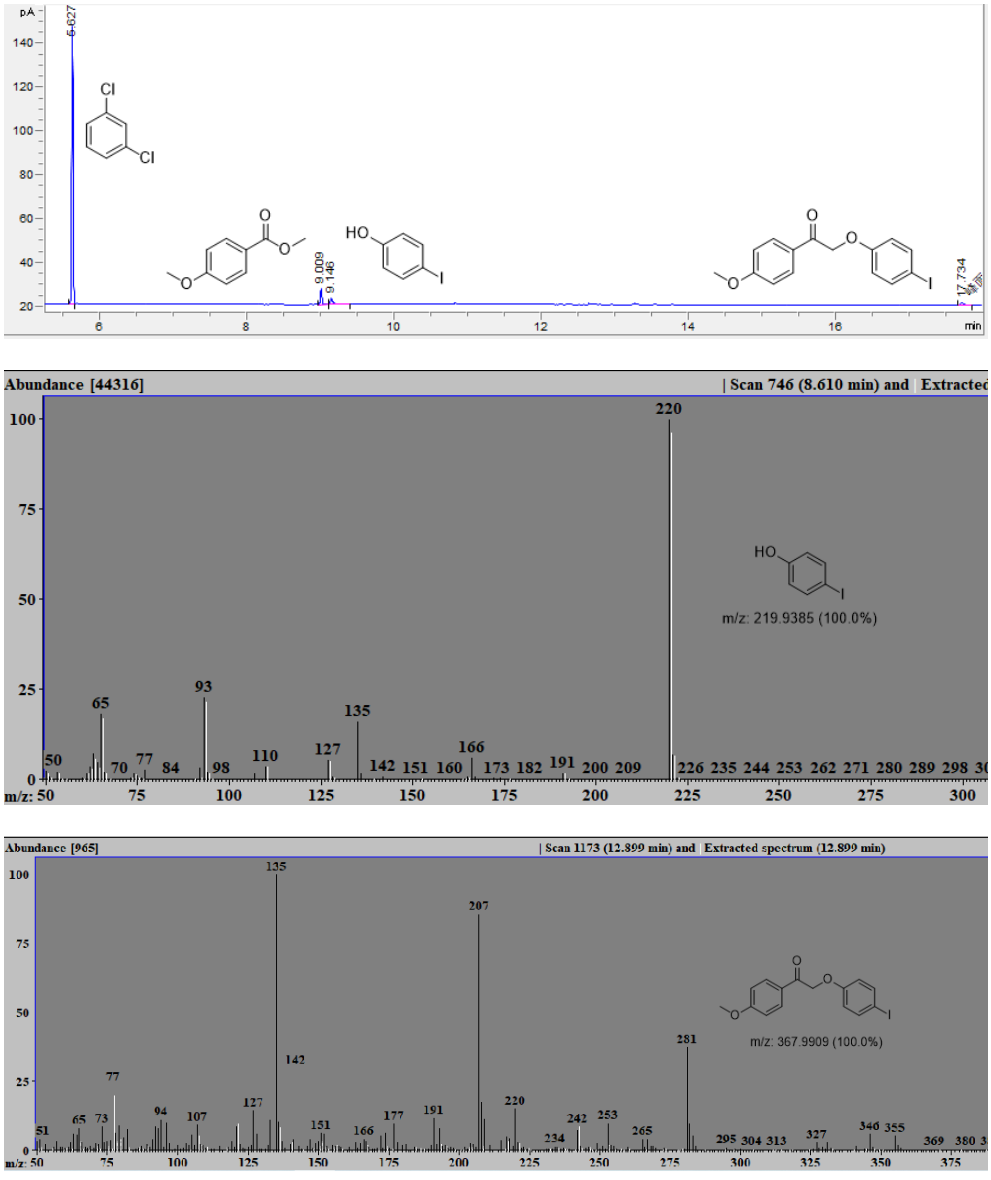



**Figure S10**. The GC and GC-MS spectra for the reaction of 2-(4-methoxyphenoxy)-1-(4-iodophenyl)ethanone in the methanol