

## Supporting Information

### A novel method to synthesize diphenyl carbonate from carbon dioxide and phenol in the presence of methanol

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#### 1 General information

Toluene and ethanol was purified using magnesium, and stored under a nitrogen atmosphere. Ethylenediamine was distilled and o-diaminobenzene was recrystallized prior to use. Carbon dioxide with a purity of 99.99% was commercially available. Other chemical reagents were analytical grade and used without further purification. The conversion of phenol, yield and selectivity towards diphenyl carbonate (DPC) and methyl phenyl (MPC) in the liquid product were analyzed using GC-122 gas chromatograph with HP-5 capillary column (30 m × 0.32 mm × 0.25 μm, 5% phenyl methyl-siloxane) and FID detector. GC-MS analyses were performed using Agilent 7890A/5975C GC equipped with HP-5 capillary column and EI source. The detection was performed in the scan mode from m/z 50 to 550. 1.0 ml/min helium was used as the carrier gas. The ionization voltage and source temperature was 70 eV and 230 °C, respectively. DFT calculations using the Becke3LYP(B3LYP) hybrid functional. Frequency calculations at the same level of theory have also been performed to identify all of the stationary points as minima (zero imaginary frequencies) or transition states (one imaginary frequency), and to provide free energies at 298.15 K, which include entropic contributions by taking into account the vibrational, rotational, and translational motions of the species under consideration. Transition states were located using the Berny algorithm.

#### 2 Experimental

##### 2.1 Investigation of dehydrating agent

Although the direct synthesis of DPC from CO<sub>2</sub> and phenol catalyzed by AlBr<sub>3</sub> in the presence of CH<sub>3</sub>OH is feasible, the yield of DPC is very low compared to the previous works

(Table 1).<sup>1</sup> This may be ascribed to the thermodynamic limitations. Since the synthesis of DPC accompanied by the formation of H<sub>2</sub>O, the reaction is possibly promoted by the removal of H<sub>2</sub>O from the system. A series of dehydrating agent such as 3Å molecular sieve (MS) were employed to remove water. Results in Table S1 showed that almost no increase in the yield of DPC was observed.

**Table S1** Results of the synthesis of DPC from CO<sub>2</sub> and phenol with various dehydrating agent<sup>a</sup>

Entry	Dehydrating agent	Yield of DPC (%) <sup>b</sup>	Yield of MPC (%) <sup>b</sup>
1	-	6.0	1.3
2	3Å	6.2	1.4
3	Anhydrous Na <sub>2</sub> SO <sub>4</sub>	5.8	1.4
4	Silica gel	5.5	1.0
5	NaA zeolite	6.1	0.8

<sup>a</sup> Reaction conditions: 10 mmol phenol, 30 mmol CH<sub>3</sub>OH, 3 mmol AlBr<sub>3</sub> and dehydrating/phenol=3wt% at 100 °C and 9 MPa for 2 h. <sup>b</sup> Determined by GC, based on the charged phenol.

## 2.2 General procedure for the preparation of salen complex

The salen ligands and complexes were prepared according to our previous work.<sup>2</sup>

### 2.2.1 Preparation of 5-[(chlorotriphenylphosphoranyl)methyl]-2-hydroxybenzaldehyde

Salicylaldehyde (125 mmol), paraformaldehyde (225 mmol), and conc. HCl (100 ml) were stirred in a flask for 3 days under nitrogen at room temperature. The resulting solids were washed with 0.5% NaHCO<sub>3</sub> and dried under vacuum. White needle-like crystals were obtained by recrystallization with petroleum ether. The chloromethylated product (10 mmol) was then reacted further with triphenylphosphine (10 mmol) or tri-n-butylphosphine (10 mmol) at 100 °C in toluene for 7 h to give 5-[(chlorotriphenylphosphoranyl)methyl]-2-hydroxybenzaldehyde.

### 2.2.2 Preparation of salen ligands

Salicylaldehyde (20 mmol) was dissolved in absolute ethanol (1 ml/100 mg salicylaldehyde). A few drops of CH<sub>2</sub>Cl<sub>2</sub> were added if the salicylaldehyde was still not completely dissolved after heating. The ethylamine (10 mmol) was then added and the solution was stirred at reflux for 2 h. Ethanol and water were then removed in vacuo, the salen was obtained as solid and recrystallized from ethanol.

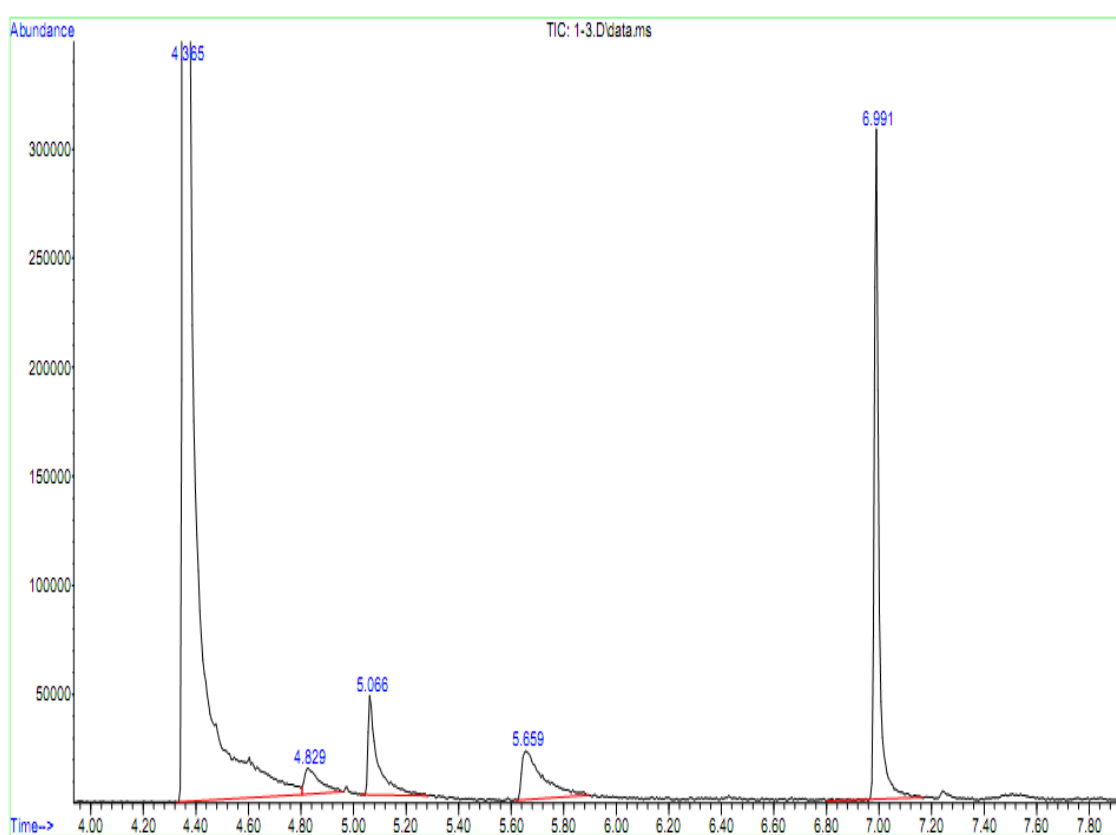
### 2.2.3 Preparation of salen complex

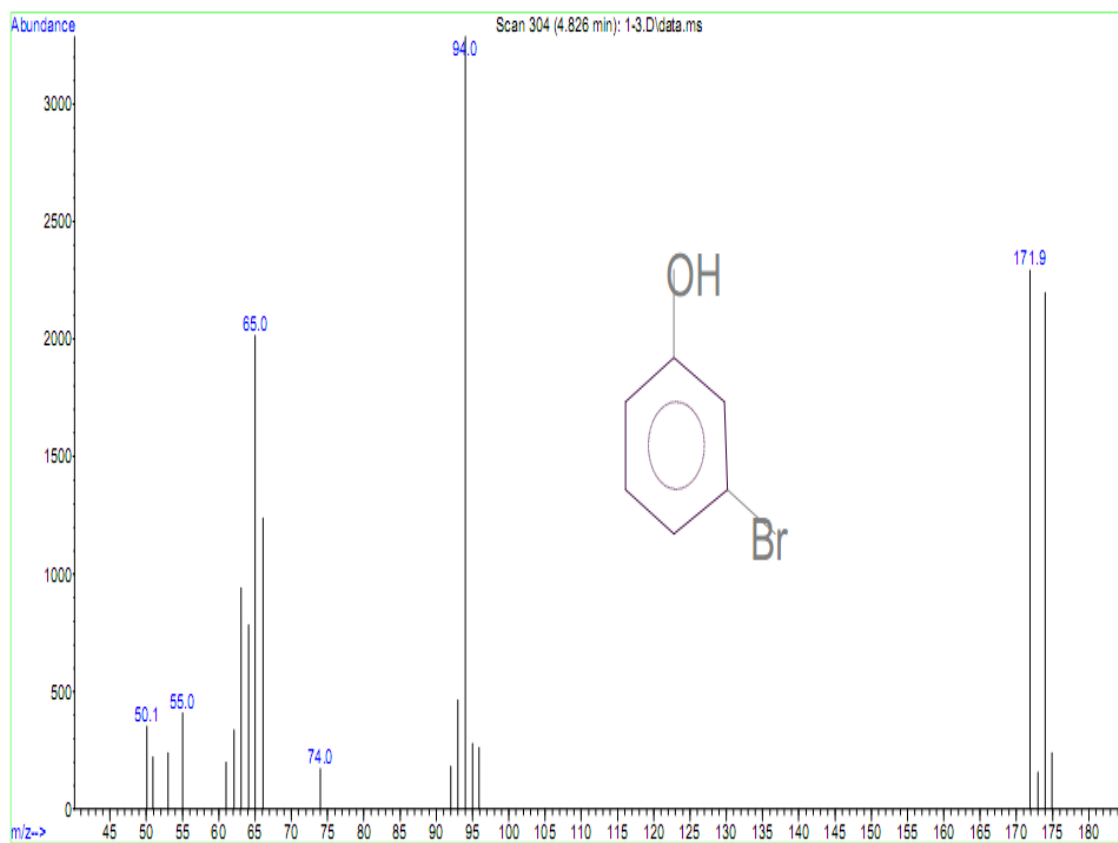
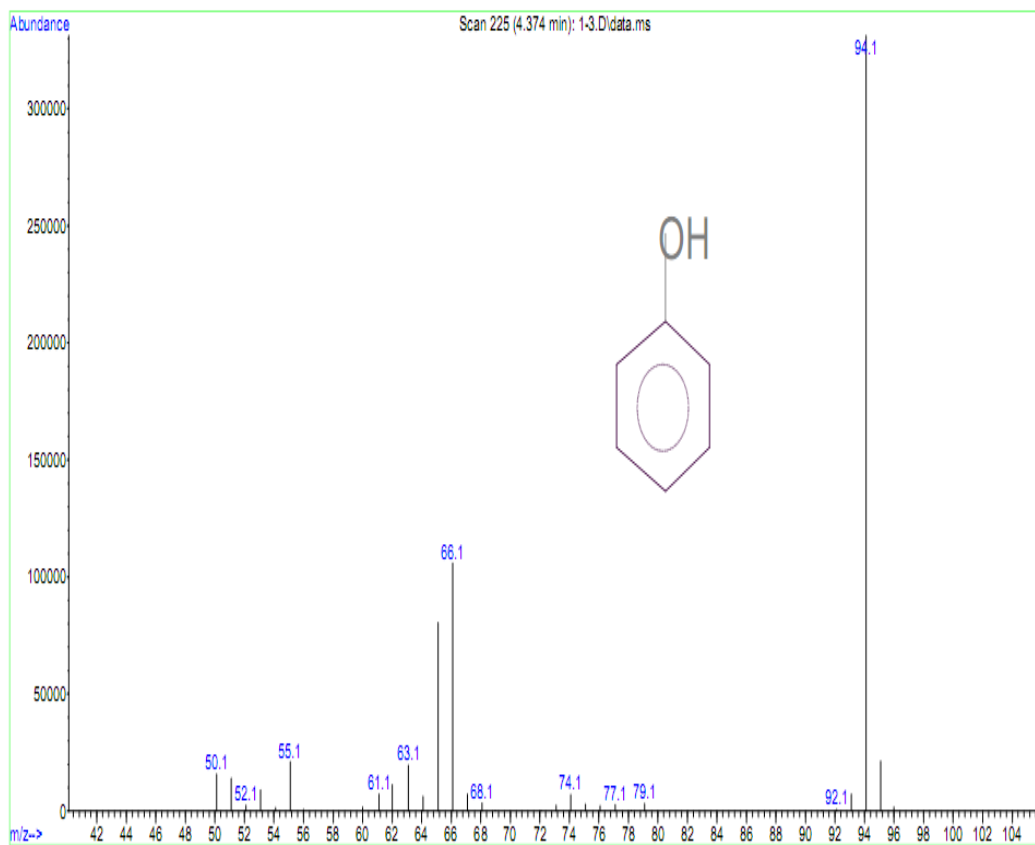
Inorganic metallic salt (5 mmol) was added to the ethanol (50 ml) solution of salen (5 mmol) at rt. The resulting mixture was refluxed under N<sub>2</sub> for 2 h. The resulting solution was cooled to rt and the volatiles were then removed. The residue was dried under vacuum for 12 h to give complex, which was used as the catalyst without further purification.

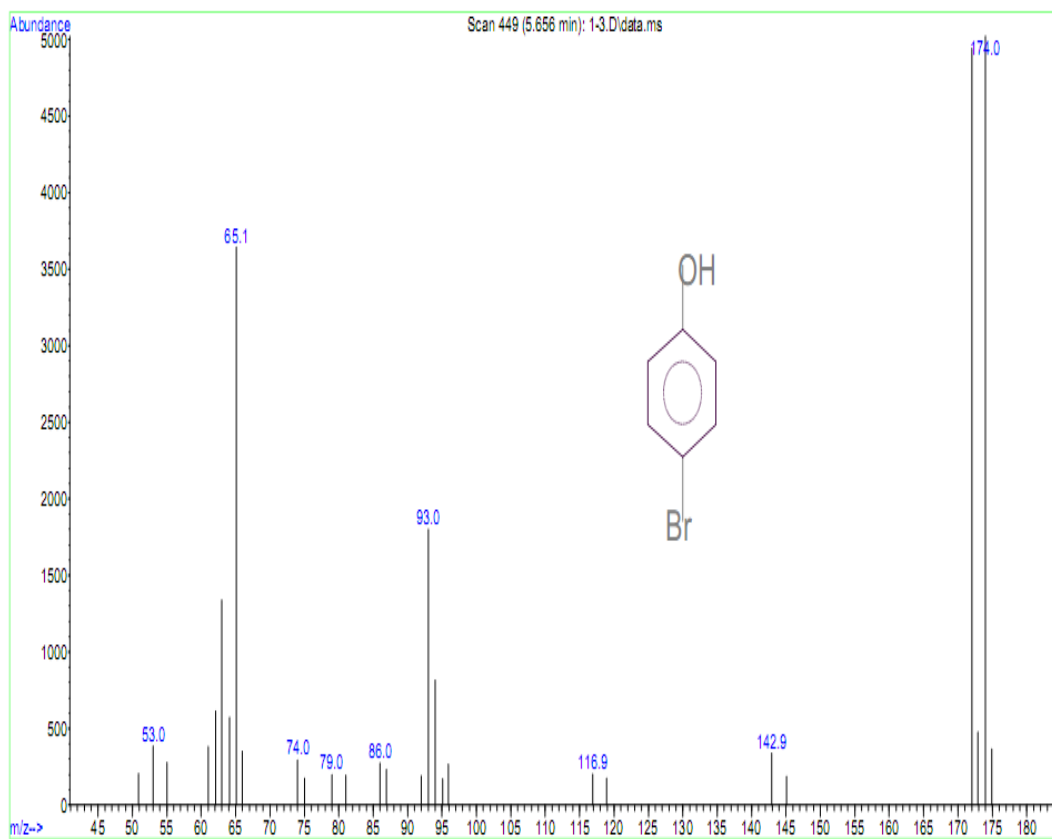
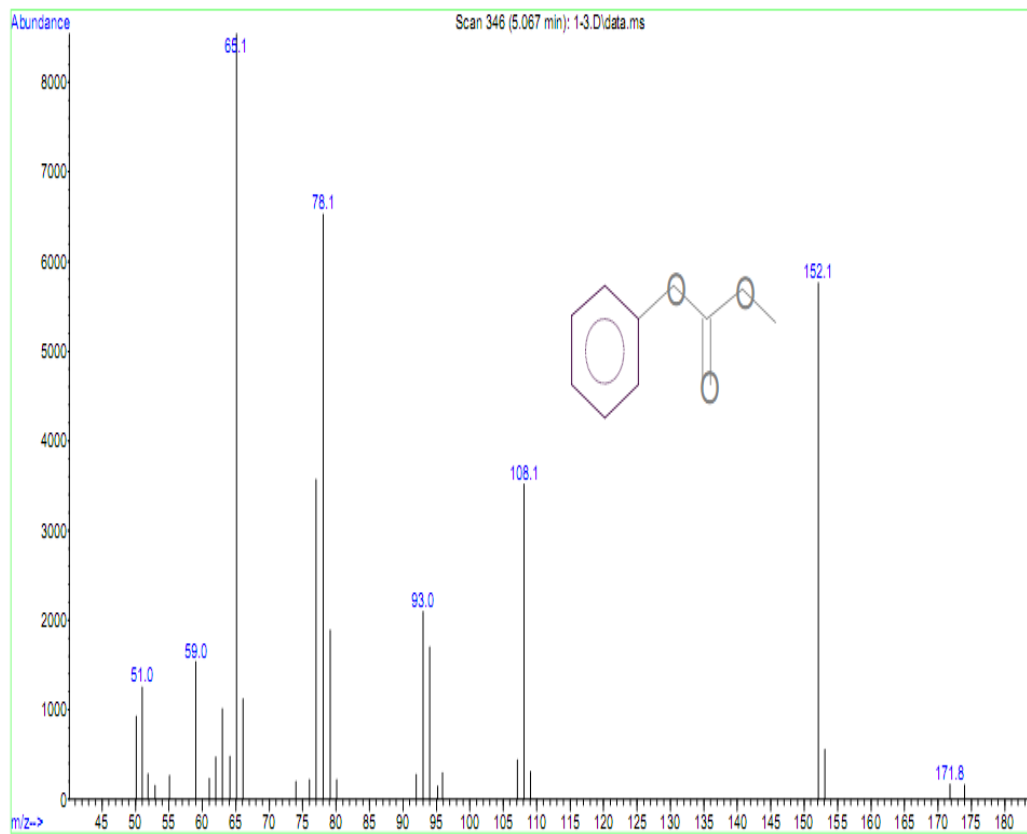
## 3 Results

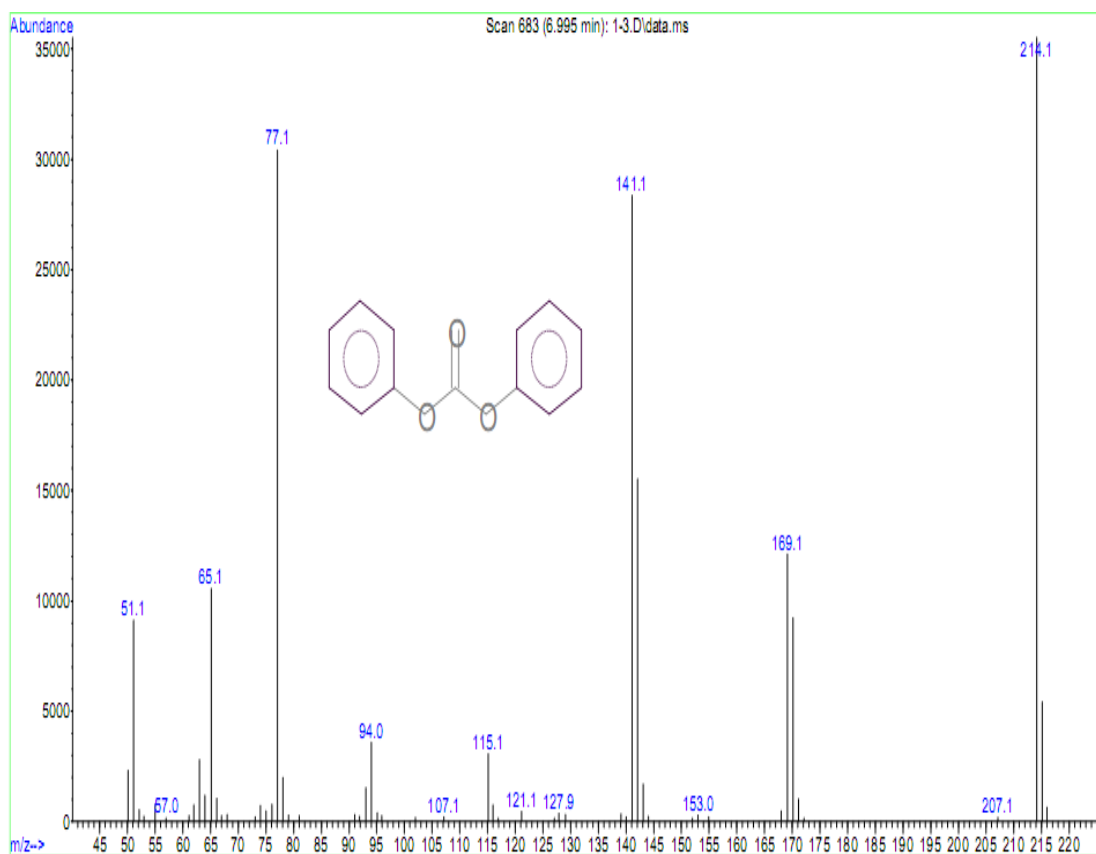
### 3.1 Results of GC-MS

#### 3.1.1 Using AlBr<sub>3</sub> as catalyst

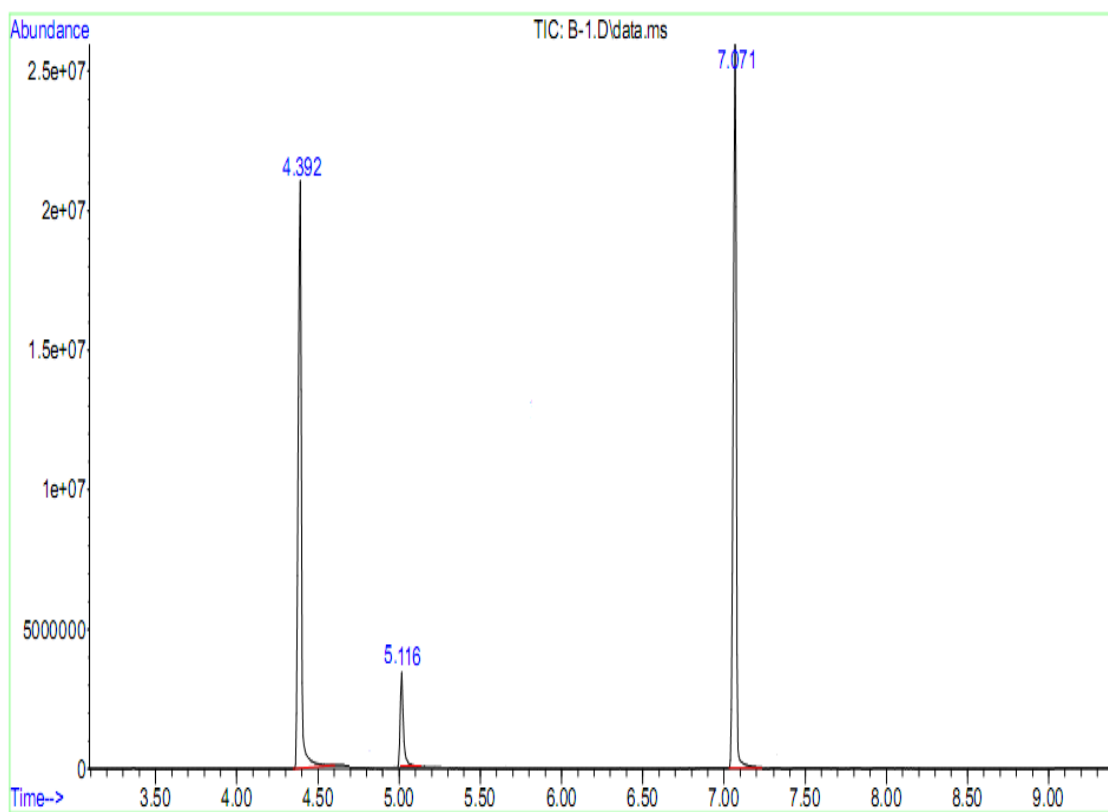


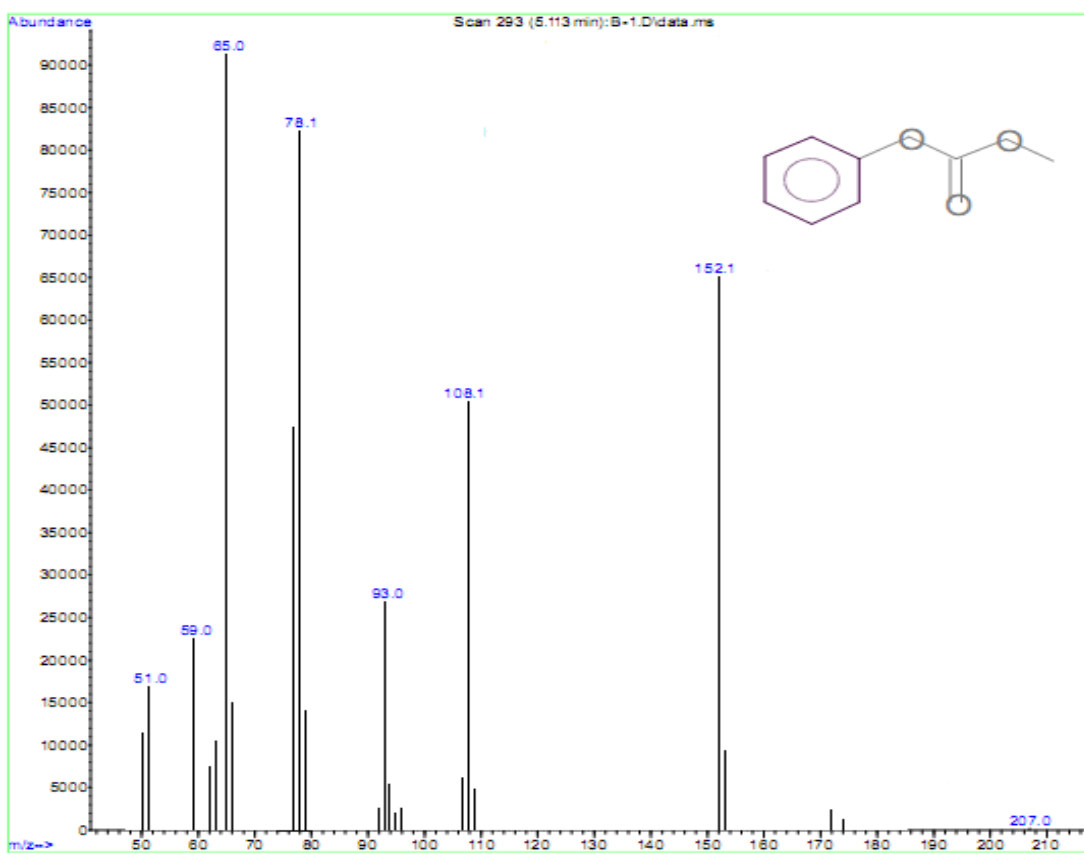
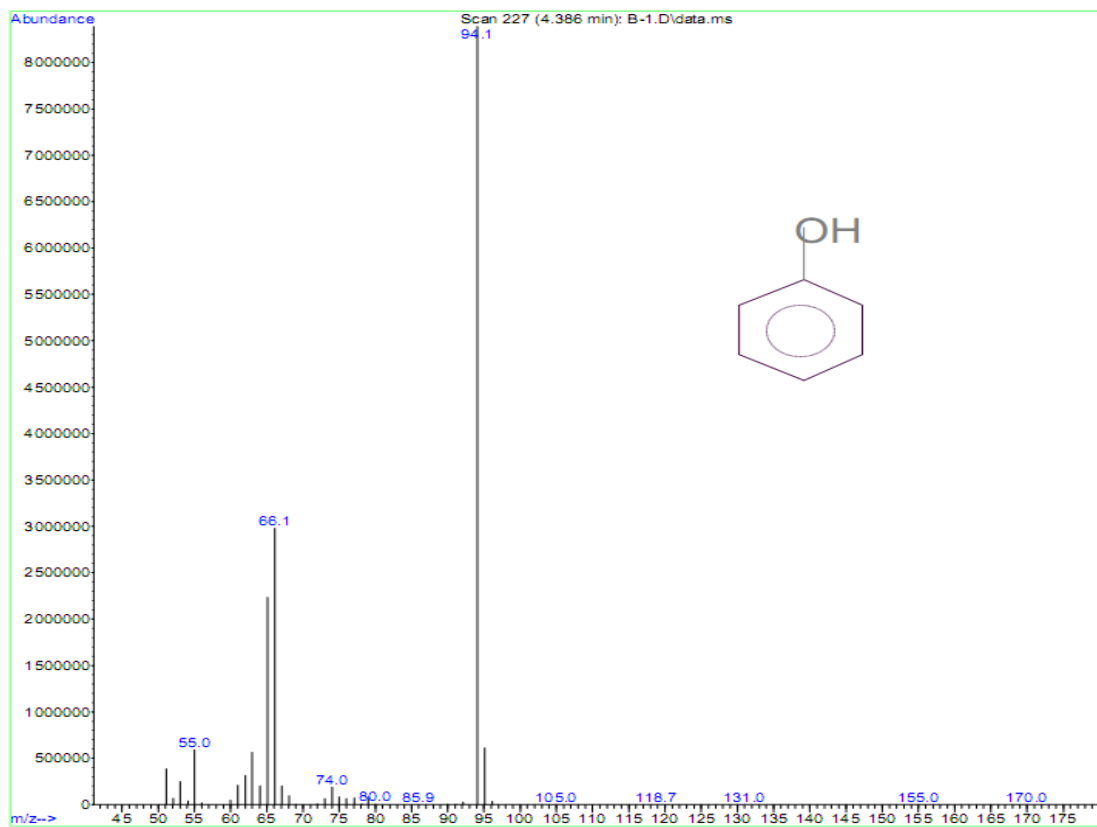


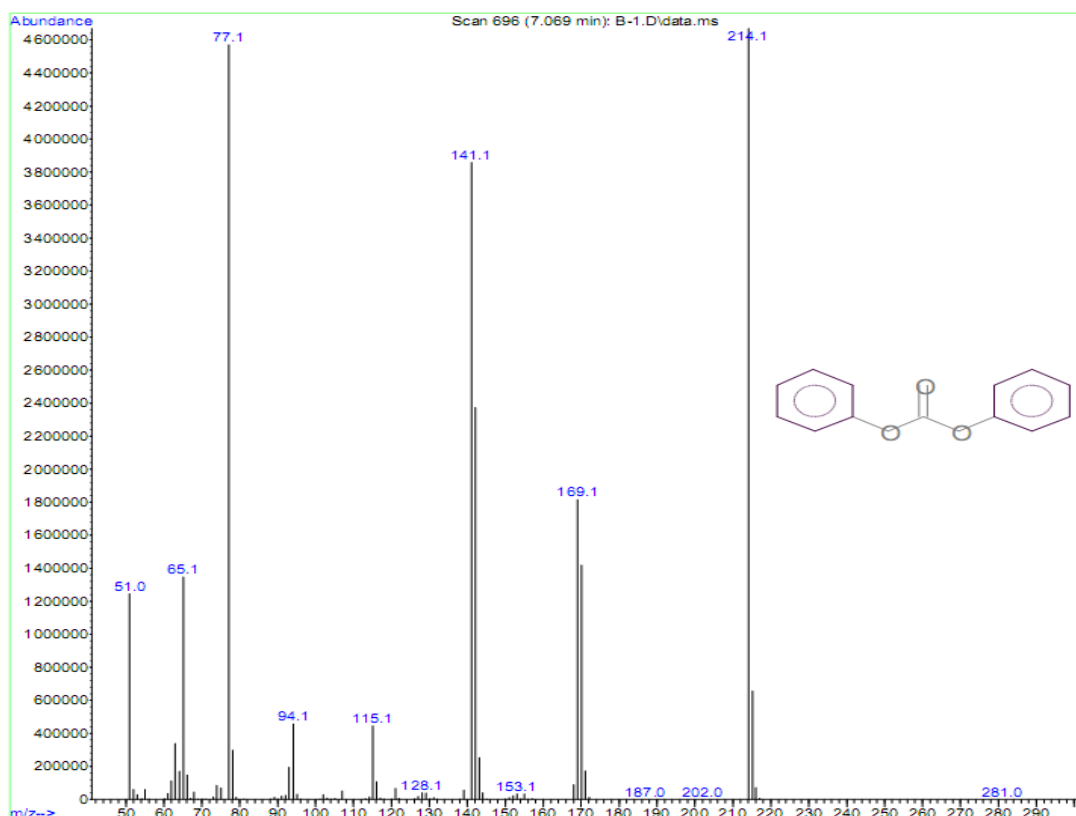




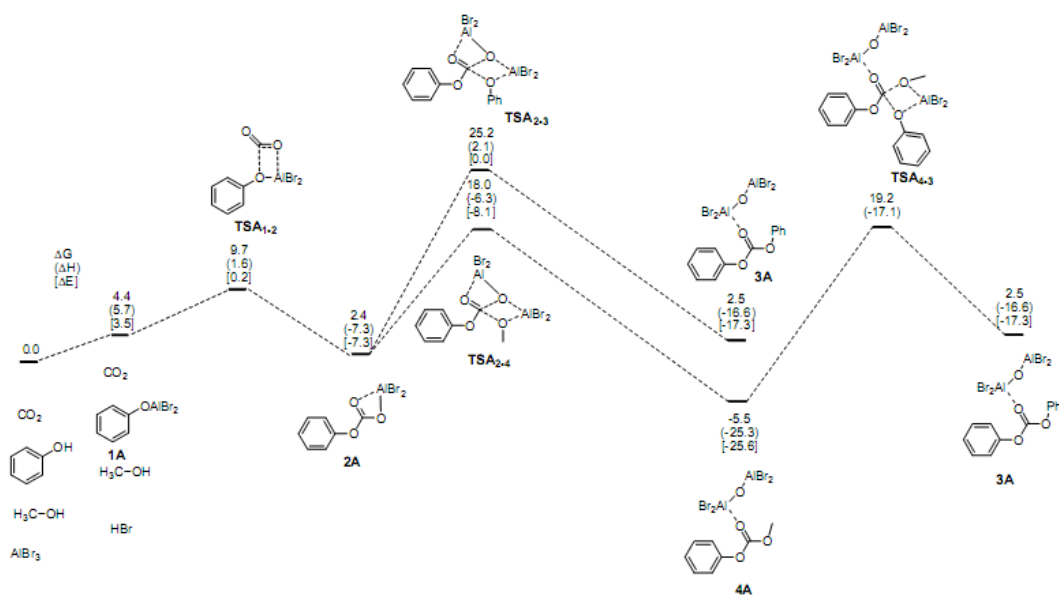
### 3.1.2 Using salen(Co)(OAc) as catalyst







### 3.2 Results of DFT calculation



### References

- (a) G. Z. Fan, S. I. Fujita, B. Zou, N. Masahiro, X. C. Meng and M. Arai, *Catal. Lett.*, 2009, **133**, 280-287; (b) G. Z. Fan, Z. G. Wang, B. Zou and M. Wang, *Fuel Process. Tech.*, 2011, **92**, 1052-1055.
- X. Miao, J. Q. Wang, W. Ying, Y. Du and L. N. He, *ChemSusChem*, 2008, **1**, 236-241.