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Supplementary Information for

Mechanism and Kinetic Study on the Reaction of Benzoic acid with OH Radicals, NO_3 and SO_4^- Radicals in Atmosphere

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Captions

Fig. S1 The reactants, transition states, intermediates, complex and products for the abstraction and addition reaction of 2-hydroxybenzoic acid, 6-hydroxybenzoic acid with OH radical.

Fig. S2 The reactants, transition states, intermediates, complex and products for the abstraction and addition reaction of 3-hydroxybenzoic acid, 5-hydroxybenzoic acid with OH radical.

Fig. S3 The reactants, transition states, intermediates, complex and products for the abstraction and addition reaction of 4-hydroxybenzoic acid with OH radical.

Fig. S4 The reactants, transition states, intermediates, complex and products for the addition and abstraction reaction of 2-hydroxybenzoic acid, 6-hydroxybenzoic acid with OH radical.

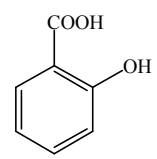
Fig. S5 The reactants, transition states, intermediates, complex and products for the addition and abstraction reaction of 3-hydroxybenzoic acid, 5-hydroxybenzoic acid with OH radical.

Fig. S6 The reactants, transition states, intermediates, complex and products for the addition and abstraction reaction of 4-hydroxybenzoic acid with OH radical.

Table S1 The reaction potential barriers (ΔE_b) and reaction energy (ΔE_r) in water droplets

Table S2 The Enthalpy change (ΔH), entropy change (ΔS) and free energy change (ΔG) at 1 atm and 298 K

Description of the product DHBA



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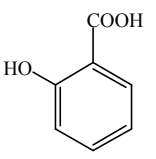
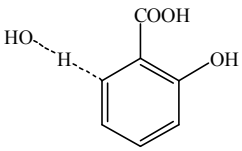


6-HBA

OH

H_2O



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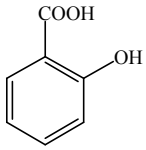

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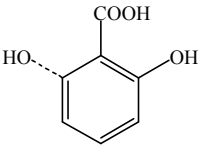

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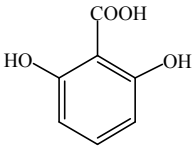

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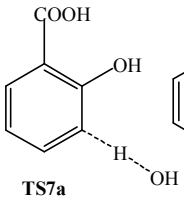

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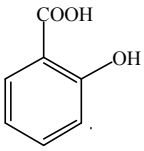

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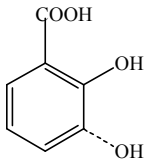

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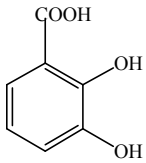

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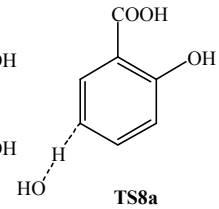

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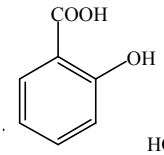

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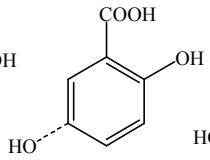

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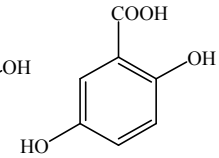

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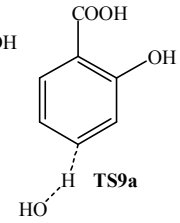

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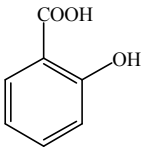

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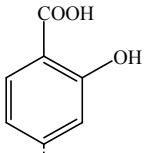

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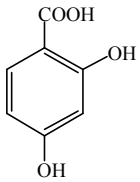

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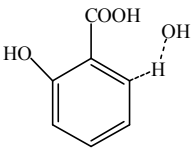

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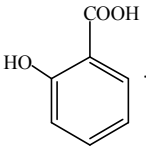

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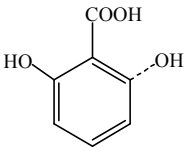

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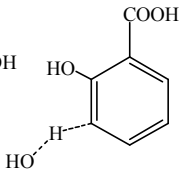

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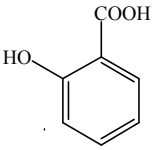

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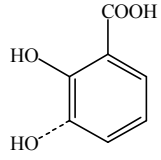

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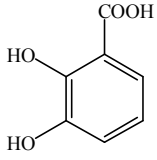

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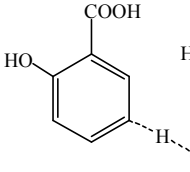

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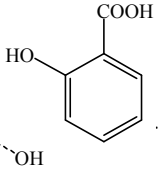

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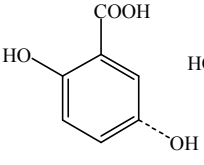

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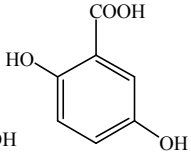

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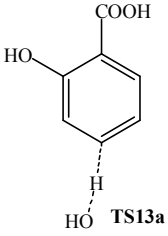

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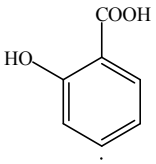

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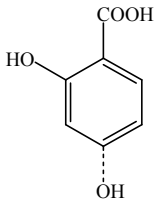

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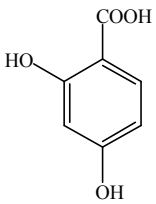

4,6-DHBA

Fig. S1 The reactants, transition states, intermediates, complex and products for the abstraction and addition reaction of 2-hydroxybenzoic acid, 6-hydroxybenzoic acid with OH radical.

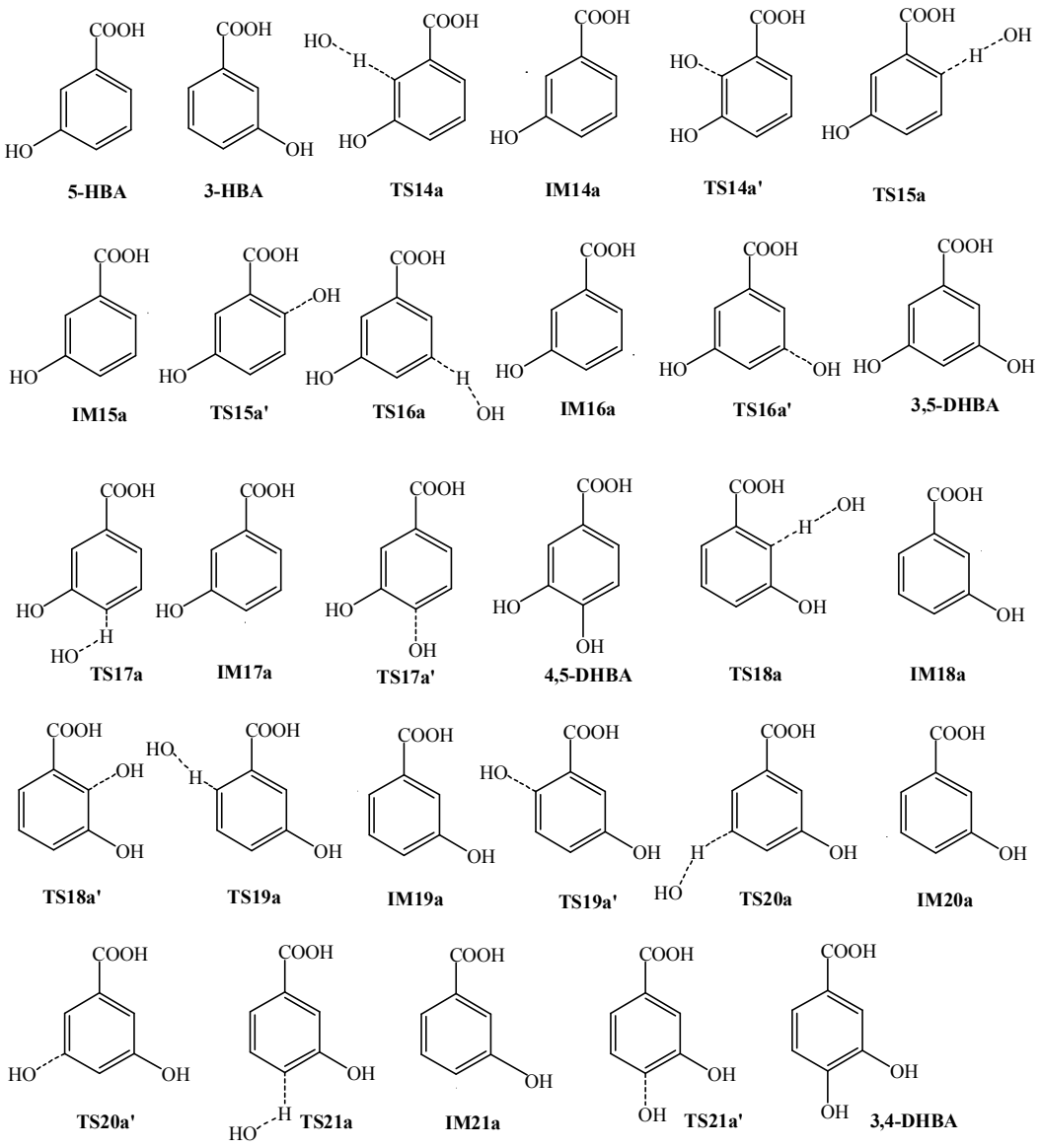

Fig. S2 The reactants, transition states, intermediates, complex and products for the abstraction and addition reaction of 3-hydroxybenzoic acid, 5-hydroxybenzoic acid with OH radical.

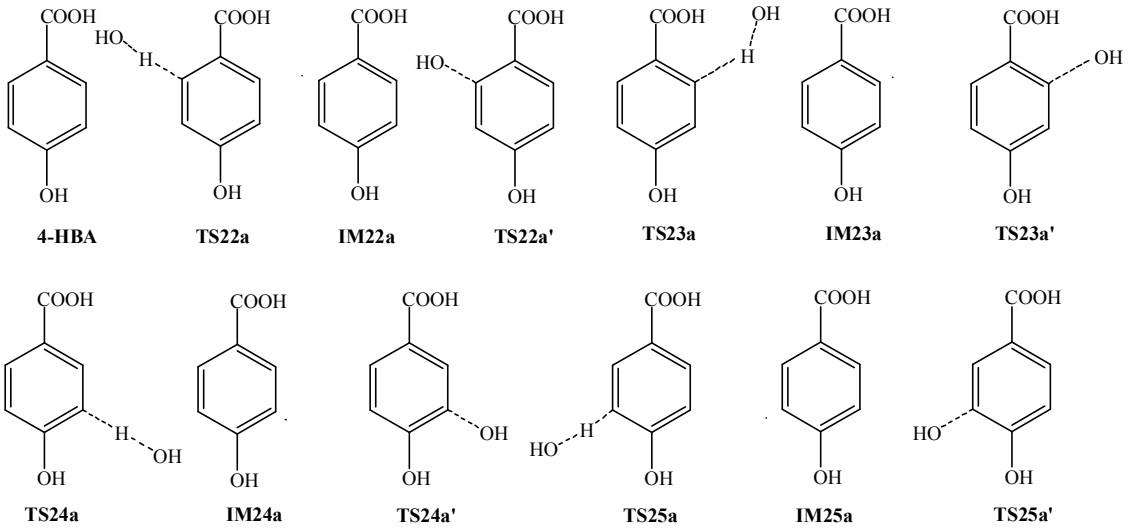

Fig. S3 The reactants, transition states, intermediates, complex and products for the abstraction and addition reaction of 4-hydroxybenzoic acid with OH radical.

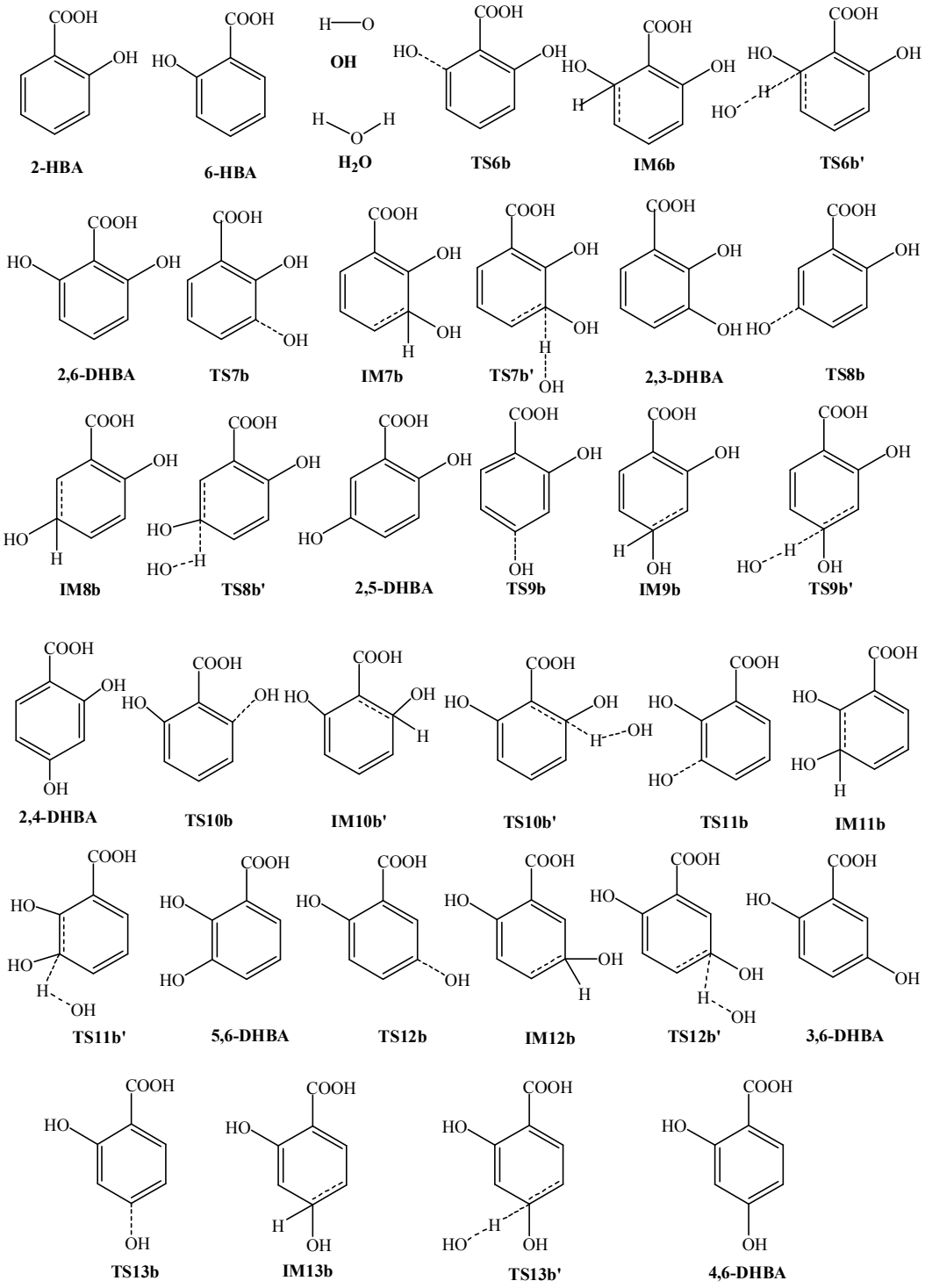

Fig. S4 The reactants, transition states, intermediates, complex and products for the addition and abstraction reaction of 2-hydroxybenzoic acid, 6-hydroxybenzoic acid with OH radical.

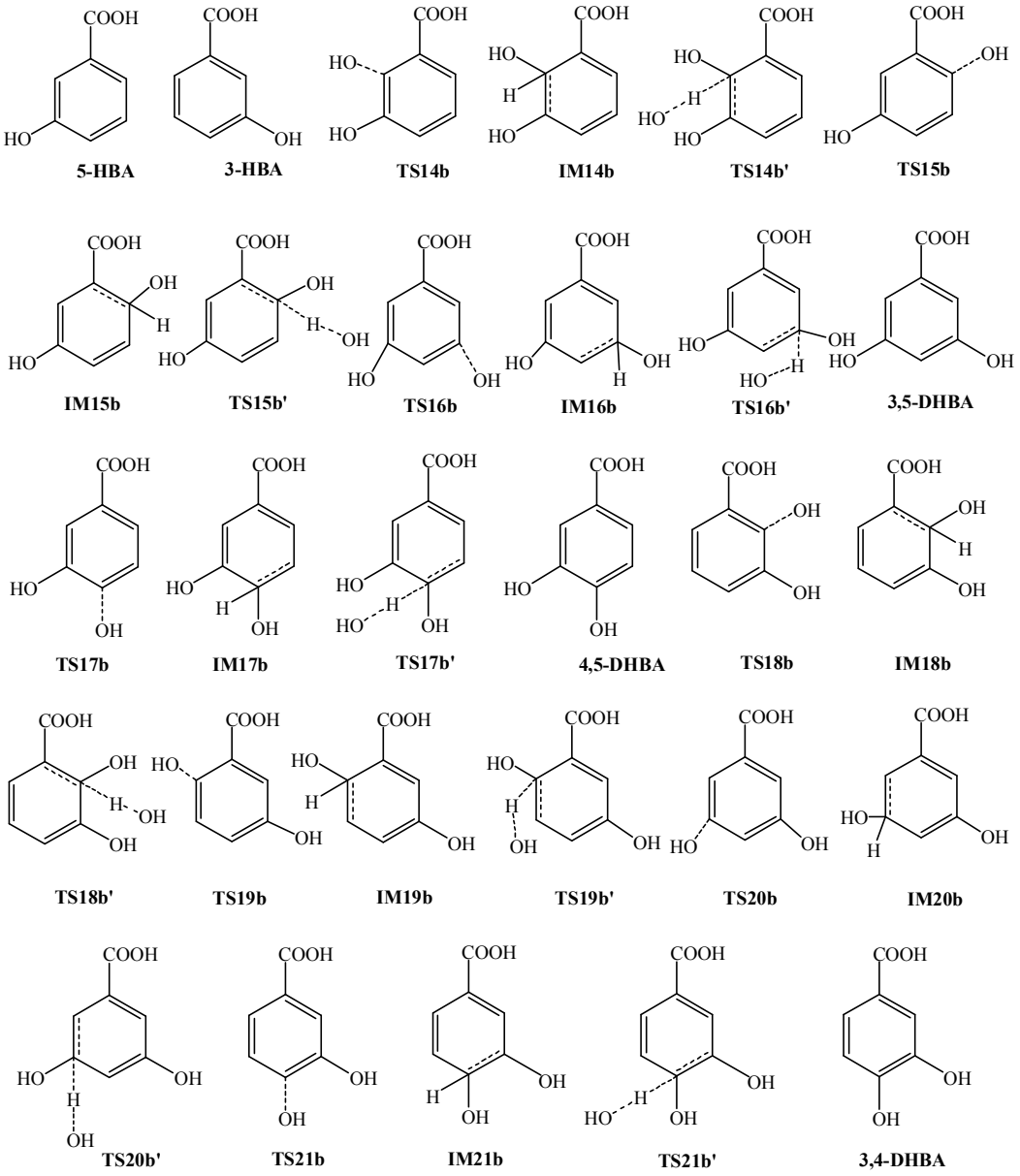

Fig. S5 The reactants, transition states, intermediates, complex and products for the addition and abstraction reaction of 3-hydroxybenzoic acid, 5-hydroxybenzoic acid with OH radical.

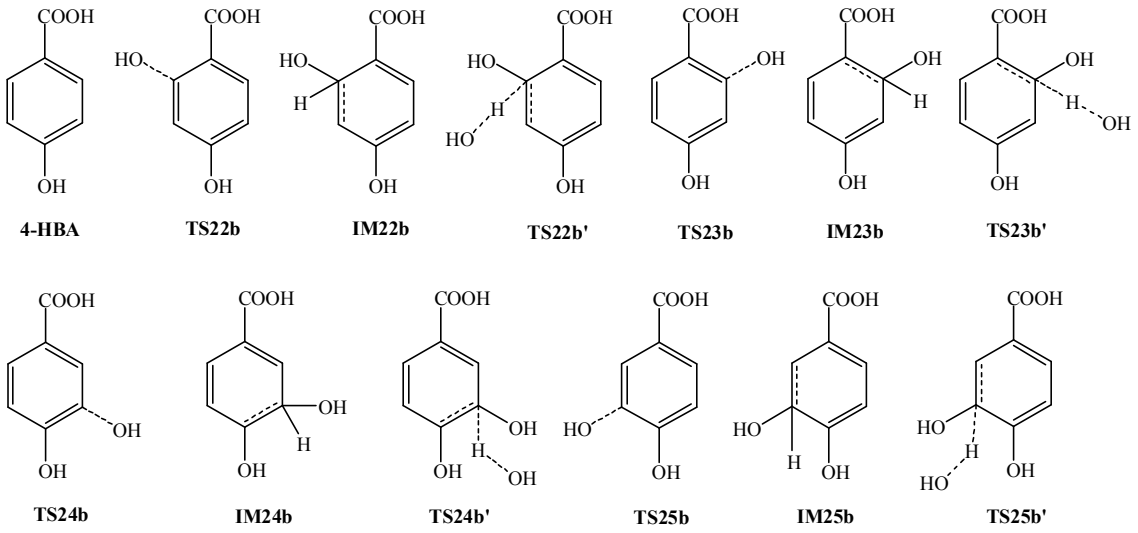

Fig. S6 The reactants, transition states, intermediates, complex and products for the addition and abstraction reaction of 4-hydroxybenzoic acid with OH radical.

Table S1 The reaction potential barriers (ΔE_b) and reaction energy (ΔE_r) in water droplets

Reaction	ΔE_b	ΔE_r
	kcal/mol	**kcal/mol**
BA+OH→TS1g→IM1g+H_2O	8.15	-4.72
IM1g+O_2→IM2g		-89.01
IM2g+NO→IM3g		-17.83
IM3g→TS2g→IM4g+NO_2	16.21	-16.58
IM4g+H_2O→TS3g→3-HBA+OH	34.40	28.72
BA+OH→TS4g→IM5g+H_2O	8.16	-4.65
IM5g+O_2→IM6g		-89.17
IM6g+NO→IM7g		-17.83
IM7g→TS5g→IM8g+NO_2	16.39	-16.37
IM8g+H_2O→TS6g→5-HBA+OH	33.3	28.53
BA+OH→TS1g'→IM1g'	1.83	-16.87
IM1g'+O_2→IM2g'		-50.26
IM2g'+NO→IM3g'		-18.70
IM3g'→TS2g'→IM4g'+NO_2	38.54	5.62
IM4g'+H_2O→TS3g'→IM5g'+OH	22.17	12.42
IM5g'+OH→TS4g'→IM6g'+H_2O	1.99	-54.27
IM6g'+OH→TS5g'→2,5-DHBA+H_2O	1.38	-96.54
IM1g'+O_2→IM7g'		-0.44
IM7g'+NO→IM8g'		-62.86
IM8g'→TS6g'→IM9g'+NO_2	13.86	-26.28
IM1g'+O_2→IM10g'		-50.60
IM10g'+NO→IM11g'		-19.53
IM11g'→TS7g'→IM12g'+NO_2	21.86	-7.75
IM1g'+O_2→IM13g'		-53.36
IM13g'+NO→IM14g'		-18.79
IM14g'→TS8g'→IM15g'+NO_2	24.84	-3.98

Table S1 The reaction potential barriers (ΔE_b), reaction energy (ΔE_r), Enthalpy change (ΔH), entropy change (ΔS) and free energy change (ΔG) at 1 atm and 298 K in water droplets

Reaction	ΔH	ΔS	ΔG
	kcal/mol	**cal/(mol•K)**	**kcal/mol**
BA+OH→TS1a→IM1a+H_2O	-6.74	4.11	-7.96
BA+OH→TS2a→IM2a+H_2O	-8.32	4.73	-9.73
BA+OH→TS3a→IM3a+H_2O	-8.92	3.75	-10.04
BA+OH→TS4a→IM4a+H_2O	-8.62	3.56	-9.68
BA+OH→TS5a→IM5a+H_2O	-8.77	3.61	-9.85
BA+OH→TS1b→IM1b	-23.29	-37.16	-12.21
BA+OH→TS2b→IM2b	-23.64	-37.49	-12.46
BA+OH→TS3b→IM3b	-21.73	-37.49	-10.55
BA+OH→TS4b→IM4b	-21.60	-37.40	-10.45
BA+OH→TS5b→IM5b	-24.96	-37.47	-13.79
BA+NO_3→TS1-NO_3→IM1a+HNO_3	22.49	2.82	21.66
BA+NO_3→TS2-NO_3→IM2a+HNO_3	20.91	3.44	19.89
BA+NO_3→TS3-NO_3→IM3a+HNO_3	20.31	2.46	19.58
BA+NO_3→TS4-NO_3→IM4a+HNO_3	20.61	2.27	19.93
BA+NO_3→TS5-NO_3→IM5a+HNO_3	20.46	2.32	19.77
BA+SO_4^-→TS1-SO_4^-→IM1a+HSO_4^-	23.18	2.24	22.51
BA+SO_4^-→TS2-SO_4^-→IM2a+HSO_4^-	21.60	2.86	20.74
BA+SO_4^-→TS3-SO_4^-→IM3a+HSO_4^-	20.99	1.88	20.43
BA+SO_4^-→TS4-SO_4^-→IM4a+HSO_4^-	21.29	1.69	20.79
BA+SO_4^-→TS5-SO_4^-→IM5a+HSO_4^-	21.15	1.75	20.63
BA+OH→TS1g→IM1g+H_2O	-8.85	3.98	-10.03
IM1g+O_2→IM2g	-46.85	-41.11	-34.59
IM2g+NO→IM3g	-27.04	-45.98	-13.33
IM3g→TS2g→IM4g+NO_2	-12.35	53.83	-28.40
IM4g+H_2O→TS3g→3-HBA+OH	34.31	-6.01	36.10
BA+OH→TS4g→IM5g+H_2O	-8.58	3.83	-9.73
IM5g+O_2→IM6g	-47.05	-41.07	-34.81
IM6g+NO→IM7g	-27.06	-45.95	-13.36

IM7g→TS5g→IM8g+NO_2	-11.96	53.53	-27.92
IM8g+H_2O→TS6g→5-HBA+OH	33.96	-5.69	35.65
BA+OH→TS1g'→IM1g'	-21.45	-37.10	-10.39
IM1g'+O_2→IM2g'	-4.81	-44.14	8.35
IM2g'+NO→IM3g'	-29.14	-43.92	-16.04
IM3g'→TS2g'→IM4g'+NO_2	9.94	52.45	-5.70
IM4g'+H_2O→TS3g'→IM5g'+OH	16.95	-2.88	17.81
IM5g'+OH→TS4g'→IM6g'+H_2O	-59.78	1.91	-60.35
IM6g'+OH→TS5g'→2,5-DHBA+H_2O	-97.38	6.97	-99.45
IM1g'+O_2→IM7g'	38.05	-42.67	50.78
IM7g'+NO→IM8g'	-65.31	-47.48	-51.16
IM8g'→TS6g'→IM9g'+NO_2	-23.45	55.07	-39.87
IM1g'+O_2→IM10g'	-6.73	-44.91	6.66
IM10g'+NO→IM11g'	-29.56	-43.84	-16.49
IM11g'→TS7g'→IM12g'+NO_2	-1.54	51.50	-16.90
IM1g'+O_2→IM13g'	-8.71	-44.31	4.50
IM13g'+NO→IM14g'	-29.12	-43.73	-16.08
IM14g'→TS8g'→IM15g'+NO_2	2.13	50.17	-12.83

Production of DHBA

After the structure of monohydroxybenzoic acids are optimized, the ortho-, meta- and para-addition products are obtained according to the different positions that OH radicals added in the benzene ring. By comparing the energy of the products, five kinds of reaction products with the lowest energy are selected, and then the OH radicals are added to obtain DHBA, resulting in four types of DHBAs. The reaction processes of the DHBA generation are similar to produce of MHBA.

The meaning of each symbol in following figures are similar to that of **Fig. 1**, as well as the atom labels of carbon sites. ΔE_b represents the reaction potential barrier and ΔE_r represents the reaction energy. The reaction channels are shown as following formulas and the unit of energy is kcal/mol. After optimization of the products and energy comparison, the products with lowest energy in two pathways are consistent. There are 10 kinds of the dihydroxy addition reaction products and they are shown in **Fig. 3**. In the reactions, the two pathways to form intermediate IM and the product DHBA are exothermic reactions.

In both pathways of the elementary reactions to product intermediates, The potential barriers of addition elementary reactions are smaller than the abstraction elementary reactions, and the releasing heat of the additon initiated reactions are also less than the abstraction initiated reactions. Besides, in the abstraction initiated reactions, the potential barrier to finally get the 4,6-DHBA is smallest for 7.30 kcal/mol, while to finally product the 3,4-DHBA is biggest for 9.08 kcal/mol. In the additon initiated reactions, the potential barrier to finally get the 3,4-DHBA is smallest for 0.06 kcal/mol, while to finally product the 4,5-DHBA is biggest for 4.68 kcal/mol.

In the abstraction and addition reaction of monohydroxybenzoic acid with OH radicals, firstly, the OH radical abstracts the hydrogen atom in the benzene ring of the monohydroxybenzoic acid which means that the OH radical is close to the remaining carbon sites, the OH radical and hydrogen atom remove in the form of H_2O and the rest is the intermediate IM after a transition state. Then another OH radical and IM are combined to product dihydroxybenzoic acid.

(1) The abstraction and addition reaction of ortho-hydroxybenzoic acid (ortho-HBA)

For the addition reactions of 2-hydroxybenzoic acid (2-HBA) with OH radicals, the reaction potential barrier of the initiated reaction and get the final product 2,6-DHBA of 7.71 kcal/mol is

lowest and that of the 2,5-DHBA with 8.86 kcal/mol is highest. As for the 6-HBA, the reaction potential barriers to generate intermediates, 8.58 kcal/mol for the product 4,6-DHBA is minimum, while 8.96 kcal/mol for the product 5,6-DHBA is maximum. The following formulas show the reaction processes of the abstraction and addition reaction of 2-HBA and 6-HBA with OH radicals, as well as reaction potential barriers and reaction energy.

2-HBA+OH→TS6a→IM6a+H_2O	ΔE_b=7.71 kcal/mol	ΔE_r=-3.23 kcal/mol	(6a)
IM6a+OH→TS6a′→2,6-DHBA	ΔE_b=1.83 kcal/mol	ΔE_r=-117.07 kcal/mol	(6a′)
2-HBA+OH→TS7a→IM7a+H_2O	ΔE_b=8.83 kcal/mol	ΔE_r=-1.88 kcal/mol	(7a)
IM7a+OH→TS7a′→2,3-DHBA	ΔE_b=0.08 kcal/mol	ΔE_r=-114.55 kcal/mol	(7a′)
2-HBA+OH→TS8a→IM8a+H_2O	ΔE_b=8.86 kcal/mol	ΔE_r=-2.41 kcal/mol	(8a)
IM8a+OH→TS8a′→2,5-DHBA	ΔE_b=0.59 kcal/mol	ΔE_r=-112.34 kcal/mol	(8a′)
2-HBA+OH→TS9a→IM9a+H_2O	ΔE_b=8.64 kcal/mol	ΔE_r=-4.12 kcal/mol	(9a)
IM9a+OH→TS9a′→2,4-DHBA	ΔE_b=4.29 kcal/mol	ΔE_r=-114.72 kcal/mol	(9a′)
6-HBA+OH→TS10a→IM10a+H_2O	ΔE_b=8.92 kcal/mol	ΔE_r=-3.64 kcal/mol	(10a)
IM10a+OH→TS10a′→2,6-DHBA	ΔE_b=1.75 kcal/mol	ΔE_r=-113.68 kcal/mol	(10a′)
6-HBA+OH→TS11a→IM11a+H_2O	ΔE_b=8.96 kcal/mol	ΔE_r=-1.73 kcal/mol	(11a)
IM11a+OH→TS11a′→5,6-DHBA	ΔE_b=0.08 kcal/mol	ΔE_r=-114.52 kcal/mol	(11a′)
6-HBA+OH→TS12a→IM12a+H_2O	ΔE_b=8.85 kcal/mol	ΔE_r=-2.54 kcal/mol	(12a)
IM12a+OH→TS12a′→3,6-DHBA	ΔE_b=0.55 kcal/mol	ΔE_r=-112.04 kcal/mol	(12a′)
6-HBA+OH→TS13a→IM13a+H_2O	ΔE_b=8.58 kcal/mol	ΔE_r=-4.27 kcal/mol	(13a)
IM13a+OH→TS13a′→4,6-DHBA	ΔE_b=4.88 kcal/mol	ΔE_r=-114.70 kcal/mol	(13a′)

(2) The abstraction and addition reaction of meta-hydroxybenzoic acid (meta-HBA)

The potential barriers of meta-HBA and OH radicals are different. The addition initiated reaction of 5-HBA to form the 5,6-DHBA has the least potential barrier of 8.36 kcal/mol, and the

reaction to form the 4,5-DHBA has the largest potential barrier of 9.06 kcal/mol. In the hydrogen atom abstraction initiated reactions for 3-HBA, the potential barriers to generate the final product 3,6-DHBA (7.89 kcal/mol) is smallest, however the biggest that of the 3,4-DHBA is 9.08 kcal/mol. The reaction of the meta-reactions, reaction potential barriers and reaction energy are shown below, in addition, a part of the reactants and products are shown in before formulas, therefore there are no longer repeat numbers.

5-HBA+OH→TS14a→IM14a+H_2O ΔE_b=8.36 kcal/mol ΔE_r=-1.43kcal/mol (14a)

IM14a+OH→TS14a′→5,6-DHBA ΔE_b=0.17 kcal/mol ΔE_r=-119.25 kcal/mol (14a′)

5-HBA+OH→TS15a→IM15a+H_2O ΔE_b=9.03 kcal/mol ΔE_r=-2.29 kcal/mol (15a)

IM15a+OH→TS15a′→2,5-DHBA ΔE_b=0.53 kcal/mol ΔE_r=-113.91 kcal/mol (15a′)

5-HBA+OH→TS16a→IM16a+H_2O ΔE_b=8.67 kcal/mol ΔE_r=-3.53 kcal/mol (16a)

IM16a+OH→TS16a′→3,5-DHBA ΔE_b=3.41 kcal/mol ΔE_r=-113.17 kcal/mol (16a′)

5-HBA+OH→TS17a→IM17a+H_2O ΔE_b=9.06 kcal/mol ΔE_r=-2.03 kcal/mol (17a)

IM17a+OH→TS17a′→4,5-DHBA ΔE_b=0.29 kcal/mol ΔE_r=-115.81 kcal/mol (17a′)

3-HBA+OH→TS18a→IM18a+H_2O ΔE_b=8.23 kcal/mol ΔE_r=-2.06 kcal/mol (18a)

IM18a+OH→TS18a′→2,3-DHBA ΔE_b=0.19 kcal/mol ΔE_r=-115.88 kcal/mol (18a′)

3-HBA+OH→TS19a→IM19a+H_2O ΔE_b=7.89 kcal/mol ΔE_r=-1.69 kcal/mol (19a)

IM19a+OH→TS19a′→3,6-DHBA ΔE_b=0.38 kcal/mol ΔE_r=-117.37 kcal/mol (19a′)

3-HBA+OH→TS20a→IM20a+H_2O ΔE_b=8.83 kcal/mol ΔE_r=-3.56 kcal/mol (20a)

IM20a+OH→TS20a′→3,5-DHBA ΔE_b=3.50 kcal/mol ΔE_r=-113.18 kcal/mol (20a′)

3-HBA+OH→TS21a→IM21a+H_2O ΔE_b=9.08 kcal/mol ΔE_r=-2.08 kcal/mol (21a)

IM21a+OH→TS21a′→3,4-DHBA ΔE_b=0.31 kcal/mol ΔE_r=-115.64kcal/mol (21a′)

(3) The abstraction and addition reaction of para-hydroxybenzoic acid (para-HBA)

In the reaction processes of para-HBA with OH radicals to generate the intermediates IMa, the

potential barriers from the 4-HBA to product 4,6-DHBA is smallest for 7.30 kcal/mol and 3,4-DHBA for 9.05 kcal/mol is largest. The reaction processes are as follows in the following formulas, moreover, some of the reactants and products have been shown before.

4-HBA+OH→TS22a→IM22a+H_2O ΔE_b=7.30 kcal/mol ΔE_r=-2.94 kcal/mol (22a)

IM22a+OH→TS22a′→4,6-DHBA ΔE_b=2.73 kcal/mol ΔE_r=-118.75 kcal/mol (22a′)

4-HBA+OH→TS23a→IM23a+H_2O ΔE_b=8.69 kcal/mol ΔE_r=-3.45 kcal/mol (23a)

IM23a+OH→TS23a′→2,4-DHBA ΔE_b=4.37 kcal/mol ΔE_r=-115.13 kcal/mol (23a′)

4-HBA+OH→TS24a→IM24a+H_2O ΔE_b=9.05 kcal/mol ΔE_r=-1.72 kcal/mol (24a)

IM24a+OH→TS24a′→3,4-DHBA ΔE_b=0.02 kcal/mol ΔE_r=-114.23 kcal/mol (24a′)

4-HBA+OH→TS25a→IM25a+H_2O ΔE_b=7.42 kcal/mol ΔE_r=-2.31 kcal/mol (25a)

IM25a+OH→TS25a′→4,5-DHBA ΔE_b=1.01 kcal/mol ΔE_r=-113.82 kcal/mol (25a′)

When the OH radicals have the addition and abstraction reactions with MHBA, in the first place, the OH radical is close to the remaining carbon atoms in the benzene ring of monohydroxybenzoic acid and get the transition states TS which the OH radical vibrates to the carbon atom in the benzene ring. After the OH radical is attached to the carbon atom, the intermediate is generated. Then another OH radical abstracts the hydrogen atom in the benzene ring, where the carbon site has been added with OH radicals, and form a molecular of H_2O and the final product.

(4) The addition and abstraction reaction of ortho-HBA

The addition and abstraction reactions of ortho-HBA with OH radicals may produce intermediate IMb. The potential barriers of the 2-HBA for the final product 2,5-DHBA is 0.12 kcal/mol which is lowest and that of the 2,4-DHBA is 3.14 kcal/mol which is highest. The lowest and highest potential barriers for the 6-hydroxybenzoic acid to produce the final product 5,6-DHBA and the 4,6-DHBA are 0.51 and 3.27 kcal/mol, respectively. The reaction processes, reaction potential barriers and reaction energy are as following text.

2-HBA+OH→TS6b→IM6b ΔE_b=1.05 kcal/mol ΔE_r=-20.02 kcal/mol (6b)

IM6b+OH→TS6b′→2,6-DHBA+H_2O ΔE_b=3.86 kcal/mol ΔE_r=-100.27 kcal/mol (6b′)

2-HBA+OH→TS7b→IM7b ΔE_b=0.65 kcal/mol ΔE_r=-19.54 kcal/mol (7b)

IM7b+OH→TS7b′→2,3-DHBA+H_2O ΔE_b=3.36 kcal/mol ΔE_r=-96.89 kcal/mol (7b′)

2-HBA+OH→TS8b→IM8b ΔE_b=0.12 kcal/mol ΔE_r=-16.52 kcal/mol (8b)

IM8b+OH→TS8b′→2,5-DHBA+H_2O ΔE_b=3.53 kcal/mol ΔE_r=-98.23 kcal/mol (8b′)

2-HBA+OH→TS9b→IM9b ΔE_b=3.14 kcal/mol ΔE_r=-17.32 kcal/mol (9b)

IM9b+OH→TS9b′→2,4-DHBA+H_2O ΔE_b=4.17 kcal/mol ΔE_r=-101.52 kcal/mol (9b′)

6-HBA+OH→TS10b→IM10b ΔE_b=1.04 kcal/mol ΔE_r=-20.44 kcal/mol (10b)

IM10b+OH→TS10b′→2,6-DHBA+H_2O ΔE_b=1.43 kcal/mol ΔE_r=-96.89 kcal/mol (10b′)

6-HBA+OH→TS11b→IM11b ΔE_b=0.51 kcal/mol ΔE_r=-19.81 kcal/mol (11b)

IM11b+OH→TS11b′→5,6-DHBA+H_2O ΔE_b=3.60 kcal/mol ΔE_r=-96.44 kcal/mol (11b′)

6-HBA+OH→TS12b→IM12b ΔE_b=0.83 kcal/mol ΔE_r=-16.53 kcal/mol (12b)

IM12b+OH→TS12b′→3,6-DHBA+H_2O ΔE_b=3.81 kcal/mol ΔE_r=-98.05 kcal/mol (13b′)

6-HBA+OH→TS13b→IM13b ΔE_b=3.27 kcal/mol ΔE_r=-17.21 kcal/mol (13b)

IM13b+OH→TS13b′→4,6-DHBA+H_2O ΔE_b=4.17 kcal/mol ΔE_r=-101.77 kcal/mol (13b′)

(5) The addition and abstraction reaction of meta-HBA

In the addition reaction processes of meta-HBA with OH radicals may generate the intermediates IMa. The potential barriers of the 5-HBA to produce the final product 2,5-DHBA is 0.16 kcal/mol while that of the 5,6-DHBA is 3.22 kcal/mol. For the 3-HBA, the potential barrier for initiated reaction and to form the 3,4-DHBA is 0.84 kcal/mol, to form 3,6-DHBA is 4.17 kcal/mol.

The reaction potential barriers and reaction energy are depicted below, and some of the reactants and products are shown before.

5-HBA+OH→TS14b→IM14b ΔE_b=3.22 kcal/mol ΔE_r=-23.19 kcal/mol (14b)

IM14b+OH→TS14b′→5,6-DHBA+H_2O ΔE_b=0.66 kcal/mol ΔE_r=-97.49 kcal/mol (14b′)

5-HBA+OH→TS15b→IM15b ΔE_b=0.16 kcal/mol ΔE_r=-21.55 kcal/mol (15b)

IM15b+OH→TS15b′→2,5-DHBA+H_2O ΔE_b=0.99 kcal/mol ΔE_r=-94.66 kcal/mol (15b′)

5-HBA+OH→TS16b→IM16b ΔE_b=2.59 kcal/mol ΔE_r=-15.55 kcal/mol (16b)

IM16b+OH→TS16b′→3,5-DHBA+H_2O ΔE_b=4.01 kcal/mol ΔE_r=-101.13 kcal/mol (16b′)

5-HBA+OH→TS17b→IM17b ΔE_b=0.89 kcal/mol ΔE_r=-22.85 kcal/mol (17b)

IM17b+OH→TS17b′→4,5-DHBA+H_2O ΔE_b=3.77 kcal/mol ΔE_r=-95.00 kcal/mol (17b′)

3-HBA+OH→TS18b→IM18b ΔE_b=2.70 kcal/mol ΔE_r=-23.07 kcal/mol (18b)

IM18b+OH→TS18b′→2,3-DHBA+H_2O ΔE_b=2.16 kcal/mol ΔE_r=-94.86 kcal/mol (18b′)

3-HBA+OH→TS19b→IM19b ΔE_b=4.17 kcal/mol ΔE_r=-21.71 kcal/mol (19b)

IM19b+OH→TS19b′→3,6-DHBA+H_2O ΔE_b=1.31 kcal/mol ΔE_r=-97.35 kcal/mol (19b′)

3-HBA+OH→TS20b→IM20b ΔE_b=2.71 kcal/mol ΔE_r=-15.29 kcal/mol (20b)

IM20b+OH→TS20b′→3,5-DHBA+H_2O ΔE_b=4.01 kcal/mol ΔE_r=-101.45 kcal/mol (20b′)

3-HBA+OH→TS21b→IM21b ΔE_b=0.84 kcal/mol ΔE_r=-23.01 kcal/mol (21b)

IM21b+OH→TS21b′→3,4-DHBA+H_2O ΔE_b=3.73 kcal/mol ΔE_r=-94.71 kcal/mol (21b′)

(6) The addition and abstraction reaction of para-HBA

In the para-HBA and OH radicals addition reactions, the potential barriers to form the final product 3,4-DHBA is 0.06 kcal/mol while that of the 4,5-DHBA is 4.68 kcal/mol. The reaction potential barriers and reaction energy are shown below, part of the reactants and products are shown in before text.

4-HBA+OH→TS22b→IM22b ΔE_b=2.57 kcal/mol ΔE_r=-17.21 kcal/mol (22b)

IM22b+OH→TS22b′→4,6-DHBA+H_2O ΔE_b=1.72 kcal/mol ΔE_r=-104.47 kcal/mol (22b′)

4-HBA+OH→TS23b→IM23b ΔE_b=2.80 kcal/mol ΔE_r=-16.35 kcal/mol (23b)

IM23b+OH→TS23b′→2,4-DHBA+H_2O ΔE_b=2.82 kcal/mol ΔE_r=-102.23 kcal/mol (23b′)

4-HBA+OH→TS24b→IM24b ΔE_b=0.06 kcal/mol ΔE_r=-17.65 kcal/mol (24b)

IM24b+OH→TS24b′→3,4-DHBA+H_2O	ΔE_b=3.82 kcal/mol	ΔE_r=-98.30 kcal/mol	(24b′)
4-HBA+OH→TS25b→IM25b	ΔE_b=4.68 kcal/mol	ΔE_r=-18.61 kcal/mol	(25b)
IM25b+OH→TS25b′→4,5-DHBA+H_2O	ΔE_b=5.64 kcal/mol	ΔE_r=-97.52 kcal/mol	(25b′)