Supplementary Material for

Products, Mechanism, and Kinetics of OH Radical-initiated Oxidation Degradation of 2,4,4′-trichlorobiphenyl in the Atmosphere

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Keywords

PCB28, OH radicals, Reaction mechanism, Kinetic parameters

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Eighteen pages

Contains twelve Figures

Fig. S1(a). Optimized structures of pre-reactive complexes and product complexes at the MPWB1K/6-31+G(d,p) level of theory. Distances are in angstrom.

Fig. S1(b). Initial reaction schemes of OH radicals with PCB28.

Fig. S1(c). TST, CVT and CVT/SCT rate constants for PCB28+OH→IM16+H_2O.

Fig. S1(d). The frontier molecular orbital analyses of IM5b-IM5g.

Fig. S2(a). Secondary reaction scheme of IM12 with the potential barriers $\triangle E$ (kcal/mol) and reaction heats $\triangle H$ (kcal/mol).

Fig. S2(b). Secondary reaction scheme of IM12b-IM12e with the potential barriers $\triangle E$ (kcal/mol) and reaction heats $\triangle H$ (kcal/mol).

Fig. S2(c). Secondary reaction scheme of IM12b-1 and IM12c-1 with the potential barriers $\triangle E$ (kcal/mol) and reaction heats $\triangle H$ (kcal/mol).

Fig. S3. OH radical-initiated reaction scheme of PCB1 with the potential barriers $\triangle E$ (kcal/mol) and reaction heats $\triangle H$ (kcal/mol).

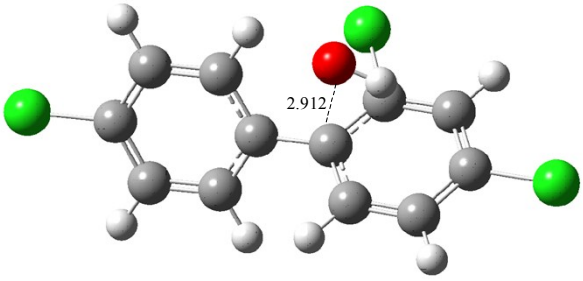
Fig. S4. OH radical-initiated reaction scheme of PCB4 with the potential barriers $\triangle E$ (kcal/mol) and reaction heats $\triangle H$ (kcal/mol).

Fig. S5. OH radical-initiated reaction scheme of PCB44 with the potential barriers $\triangle E$ (kcal/mol) and reaction heats $\triangle H$ (kcal/mol).

Fig. S6. OH radical-initiated reaction scheme of PCB110 with the potential barriers $\triangle E$ (kcal/mol) and reaction heats $\triangle H$ (kcal/mol).

Fig. S7. OH radical-initiated reaction scheme of PCB153 with the potential barriers

$\triangle E$ (kcal/mol) and reaction heats $\triangle H$ (kcal/mol).



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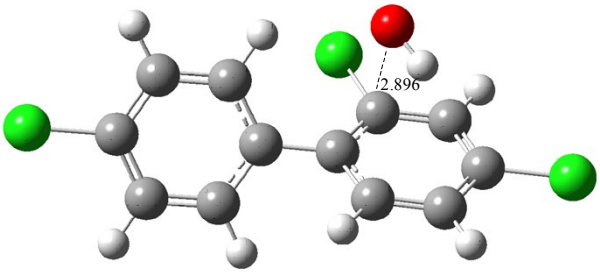

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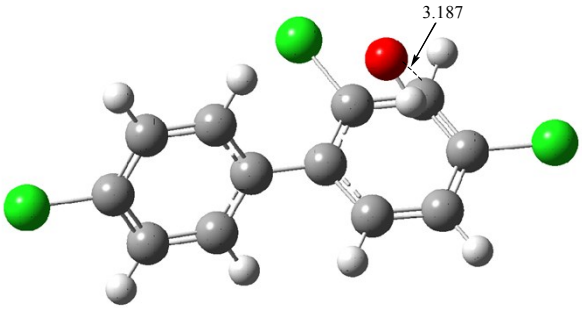

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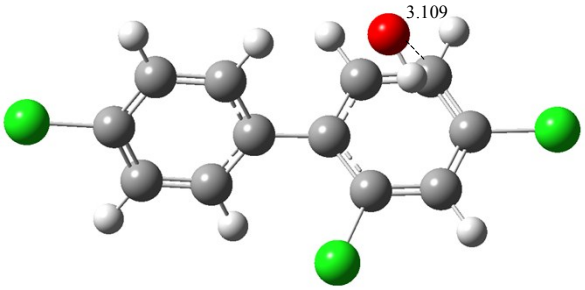

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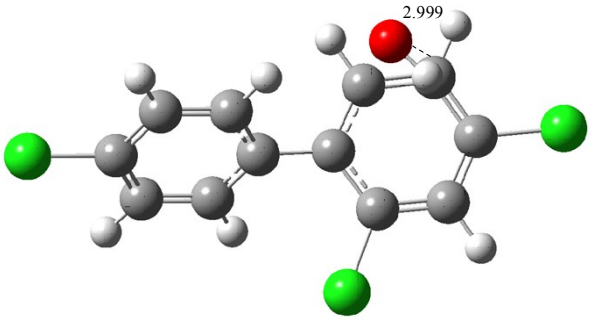

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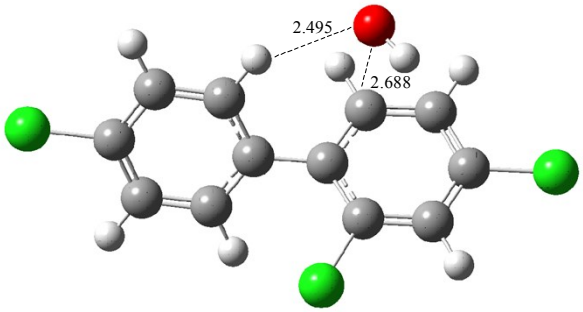

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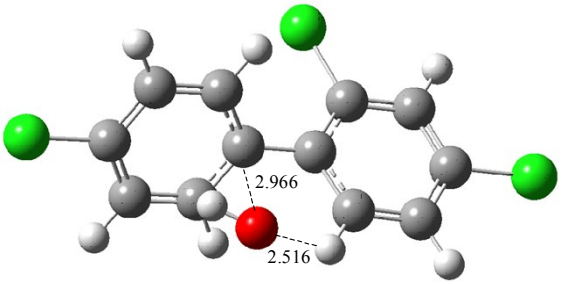

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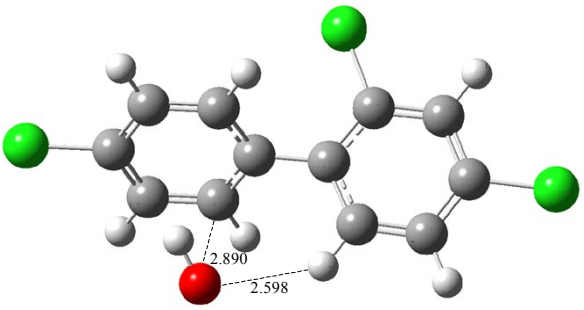

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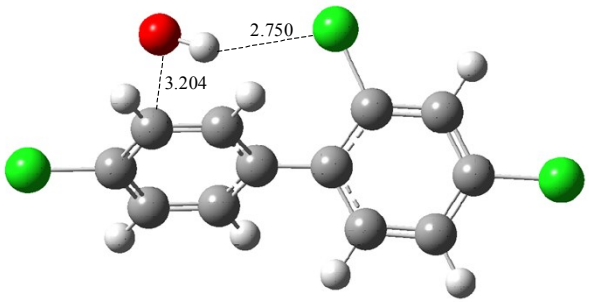

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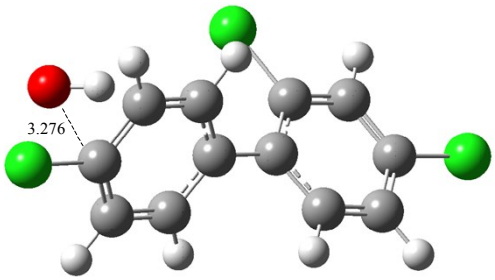

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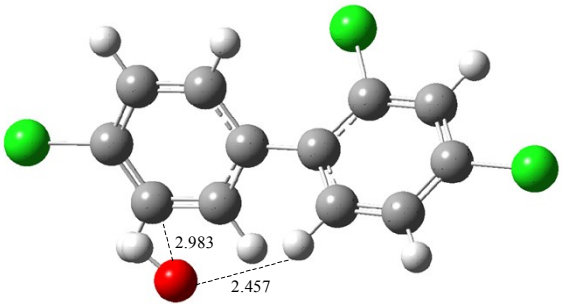

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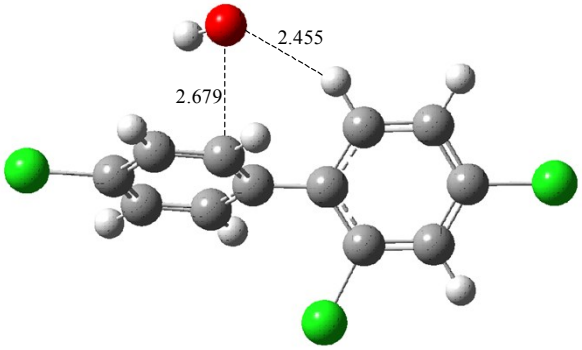

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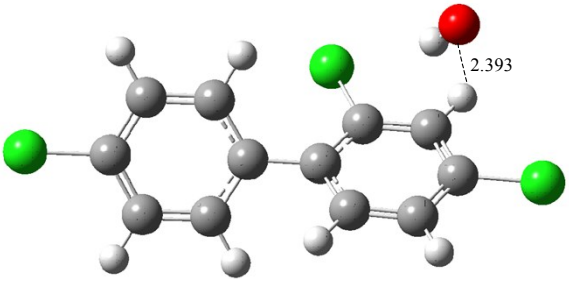

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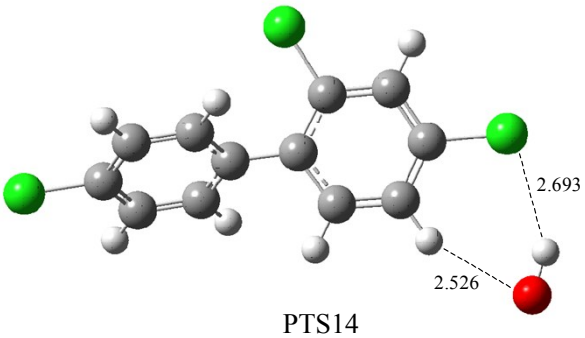

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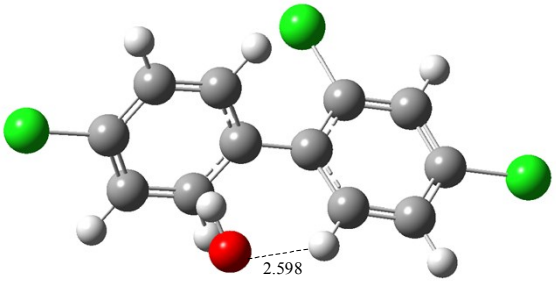

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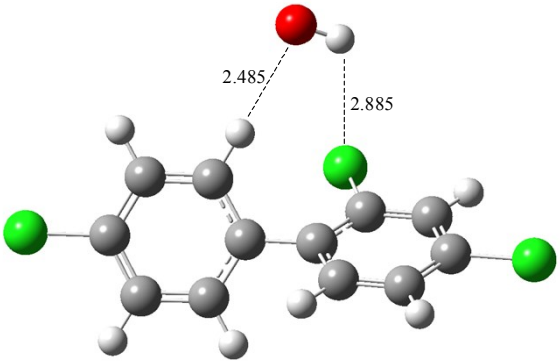

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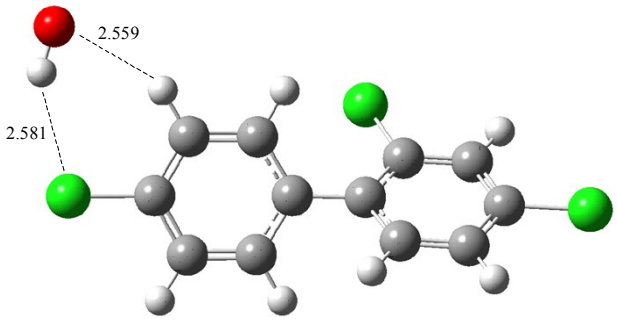

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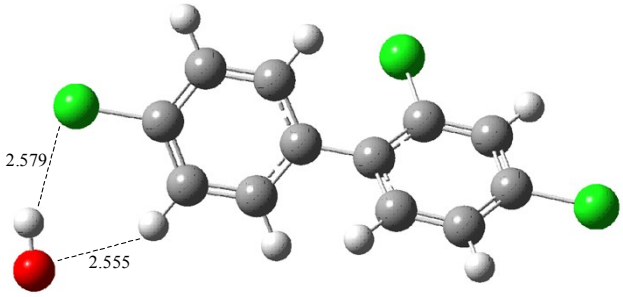

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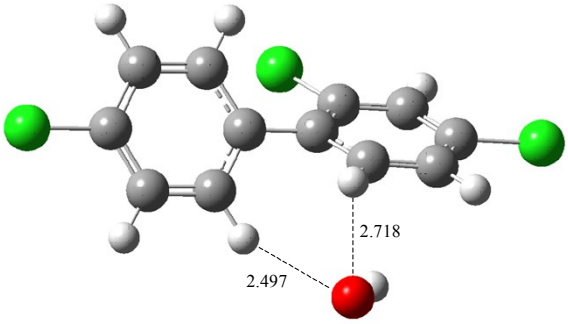

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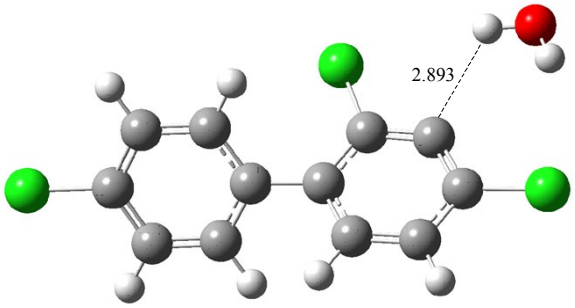

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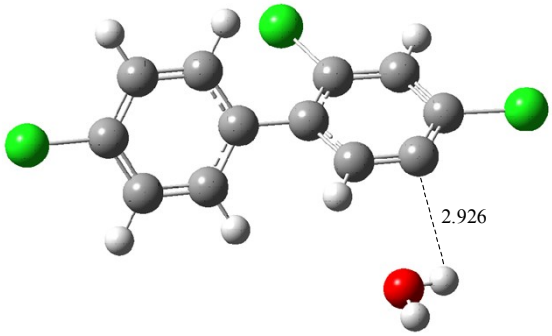

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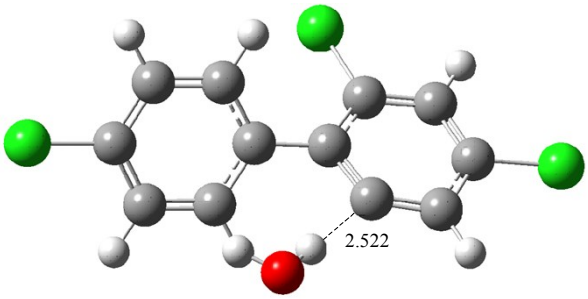

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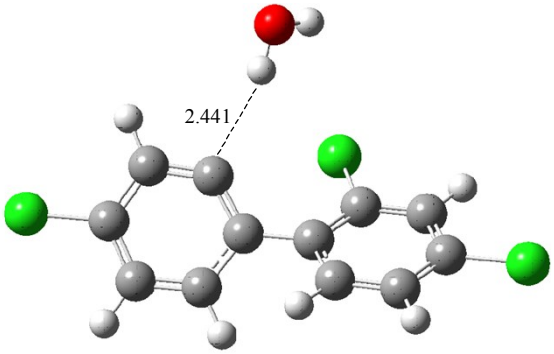

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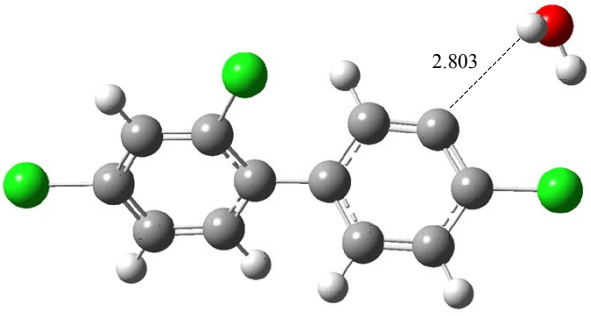

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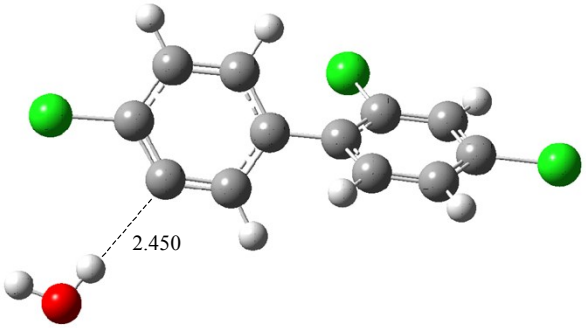

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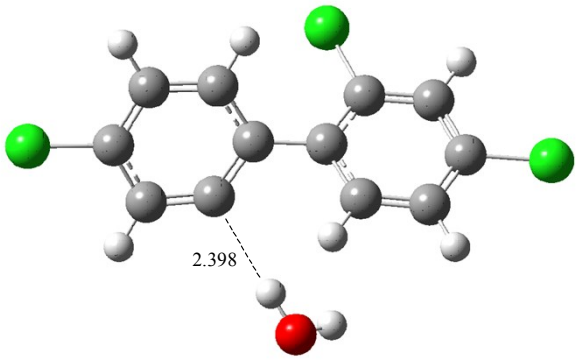


PIM19

Fig. S1(a)

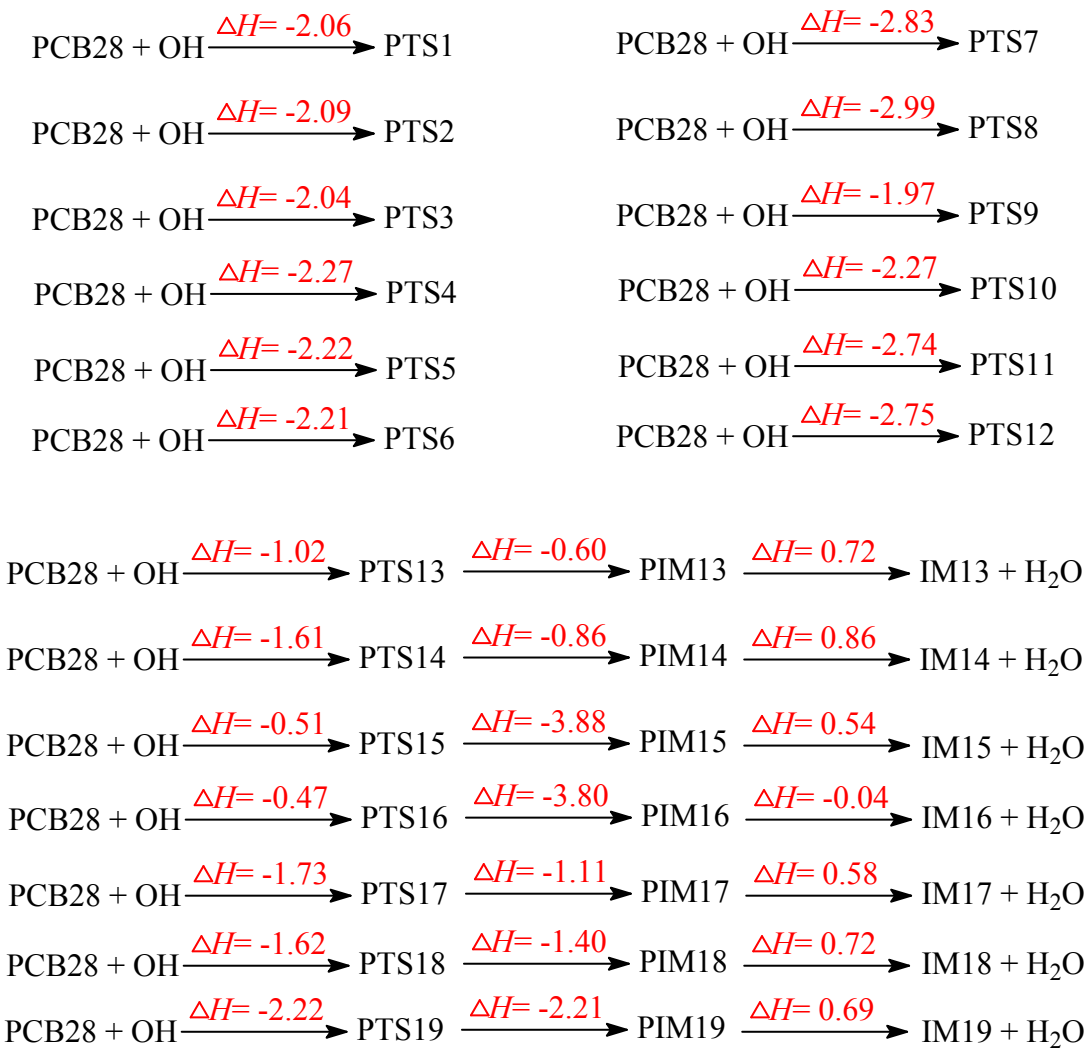

PCB28 + OH ΔH= -2.06 PTS1
PCB28 + OH ΔH= -2.09 PTS2
PCB28 + OH ΔH= -2.04 PTS3
PCB28 + OH ΔH= -2.27 PTS4
PCB28 + OH ΔH= -2.22 PTS5
PCB28 + OH ΔH= -2.21 PTS6
PCB28 + OH ΔH= -2.83 PTS7
PCB28 + OH ΔH= -2.99 PTS8
PCB28 + OH ΔH= -1.97 PTS9
PCB28 + OH ΔH= -2.27 PTS10
PCB28 + OH ΔH= -2.74 PTS11
PCB28 + OH ΔH= -2.75 PTS12
PCB28 + OH ΔH= -1.02 PTS13 ΔH= -0.60 PIM13 ΔH= 0.72 IM13 + H2O
PCB28 + OH ΔH= -1.61 PTS14 ΔH= -0.86 PIM14 ΔH= 0.86 IM14 + H2O
PCB28 + OH ΔH= -0.51 PTS15 ΔH= -3.88 PIM15 ΔH= 0.54 IM15 + H2O
PCB28 + OH ΔH= -0.47 PTS16 ΔH= -3.80 PIM16 ΔH= -0.04 IM16 + H2O
PCB28 + OH ΔH= -1.73 PTS17 ΔH= -1.11 PIM17 ΔH= 0.58 IM17 + H2O
PCB28 + OH ΔH= -1.62 PTS18 ΔH= -1.40 PIM18 ΔH= 0.72 IM18 + H2O
PCB28 + OH ΔH= -2.22 PTS19 ΔH= -2.21 PIM19 ΔH= 0.69 IM19 + H2O

Fig. S1(b)

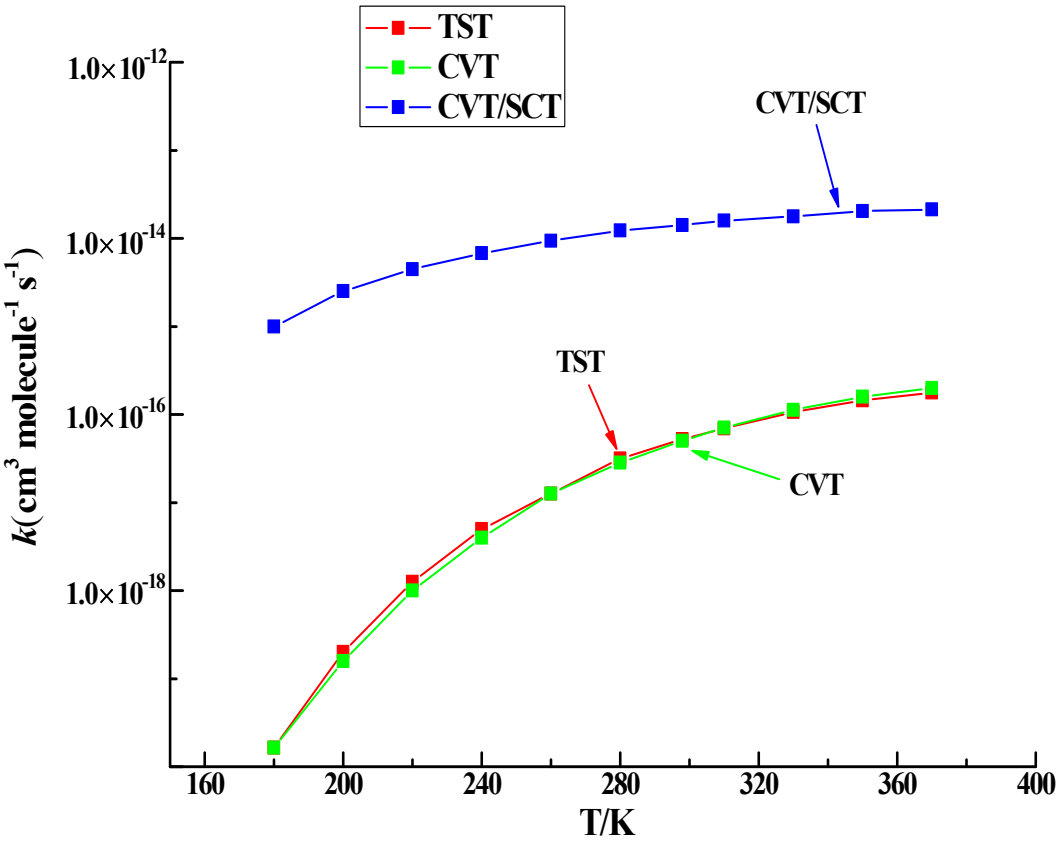
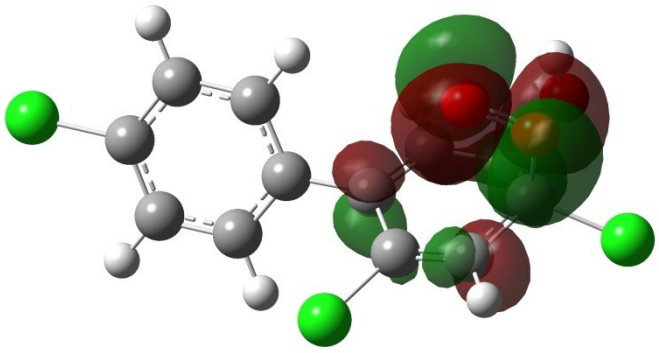
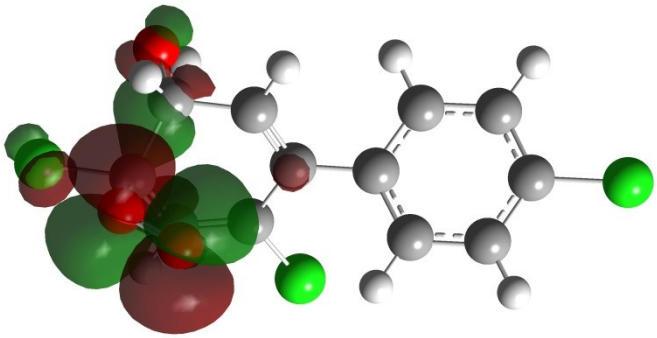

TST
CVT
CVT/SCT
1.0×10-12
1.0×10-14
1.0×10-16
1.0×10-18
k(cm3 molecule-1 s-1)
160
200
240
280
320
360
400
T/K

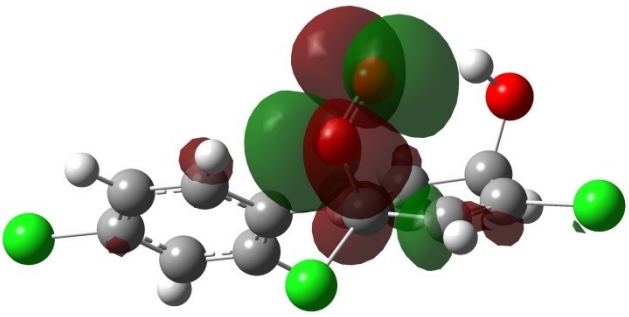
Fig. S1(c)



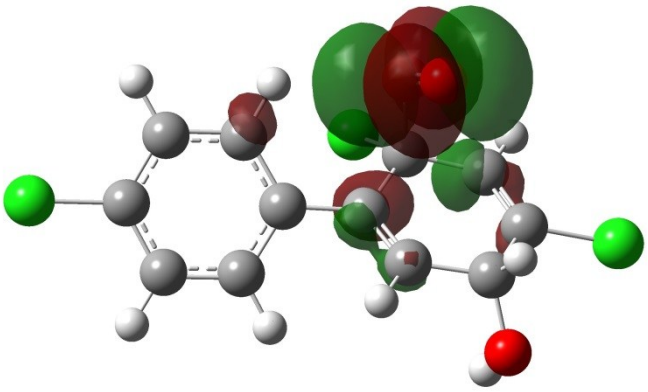
IM5b



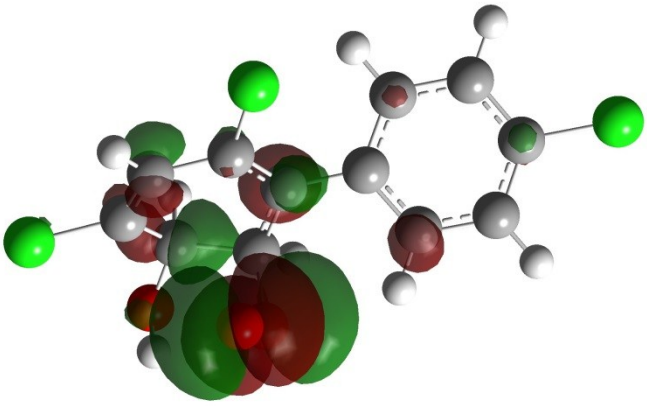
IM5c



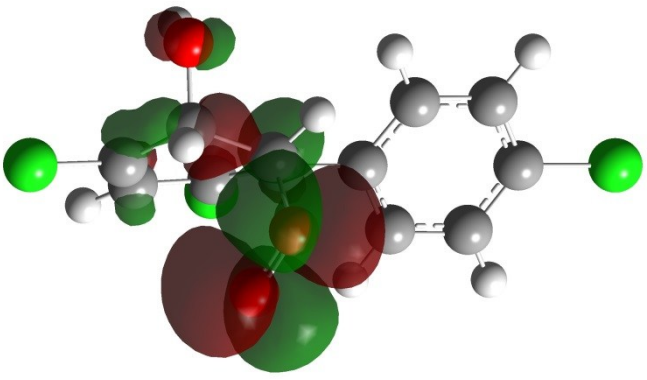
IM5d



IM5e



IM5f



IM5g

Fig. S1(d)

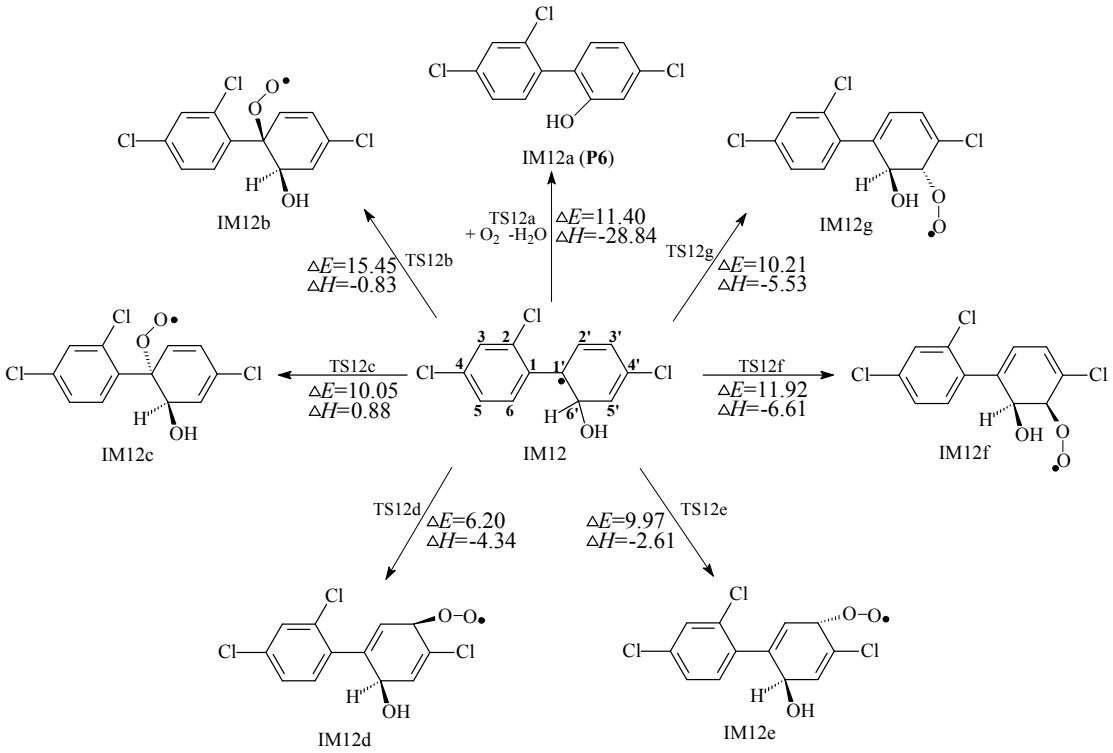

IM12a (P6)
TS12a
+ O2 -H2O
ΔE=11.40
ΔH=-28.84
IM12b
TS12b
ΔE=15.45
ΔH=-0.83
IM12g
TS12g
ΔE=10.21
ΔH=-5.53
IM12c
TS12c
ΔE=10.05
ΔH=0.88
IM12
IM12f
TS12f
ΔE=11.92
ΔH=-6.61
IM12d
TS12d
ΔE=6.20
ΔH=-4.34
IM12e
TS12e
ΔE=9.97
ΔH=-2.61

Fig. S2(a)

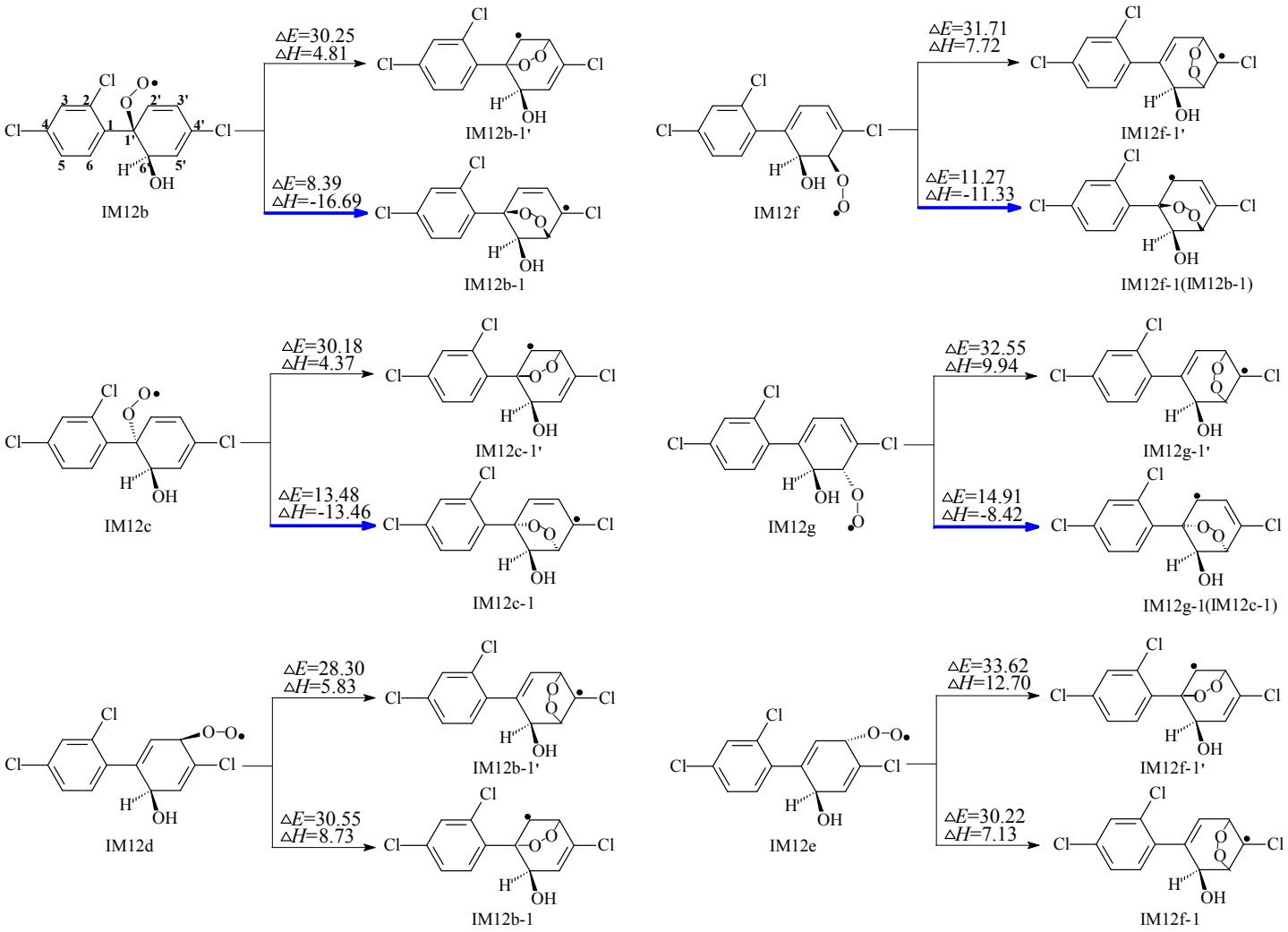

IM12b
△E=30.25
△H=4.81
IM12b-1'
△E=8.39
△H=-16.69
IM12b-1
IM12f
△E=31.71
△H=7.72
IM12f-1'
△E=11.27
△H=-11.33
IM12f-1(IM12b-1)
IM12c
△E=30.18
△H=4.37
IM12c-1'
△E=13.48
△H=-13.46
IM12c-1
IM12g
△E=32.55
△H=9.94
IM12g-1'
△E=14.91
△H=-8.42
IM12g-1(IM12c-1)
IM12d
△E=28.30
△H=5.83
IM12b-1'
△E=30.55
△H=8.73
IM12b-1
IM12e
△E=33.62
△H=12.70
IM12f-1'
△E=30.22
△H=7.13
IM12f-1

Fig. S2(b)

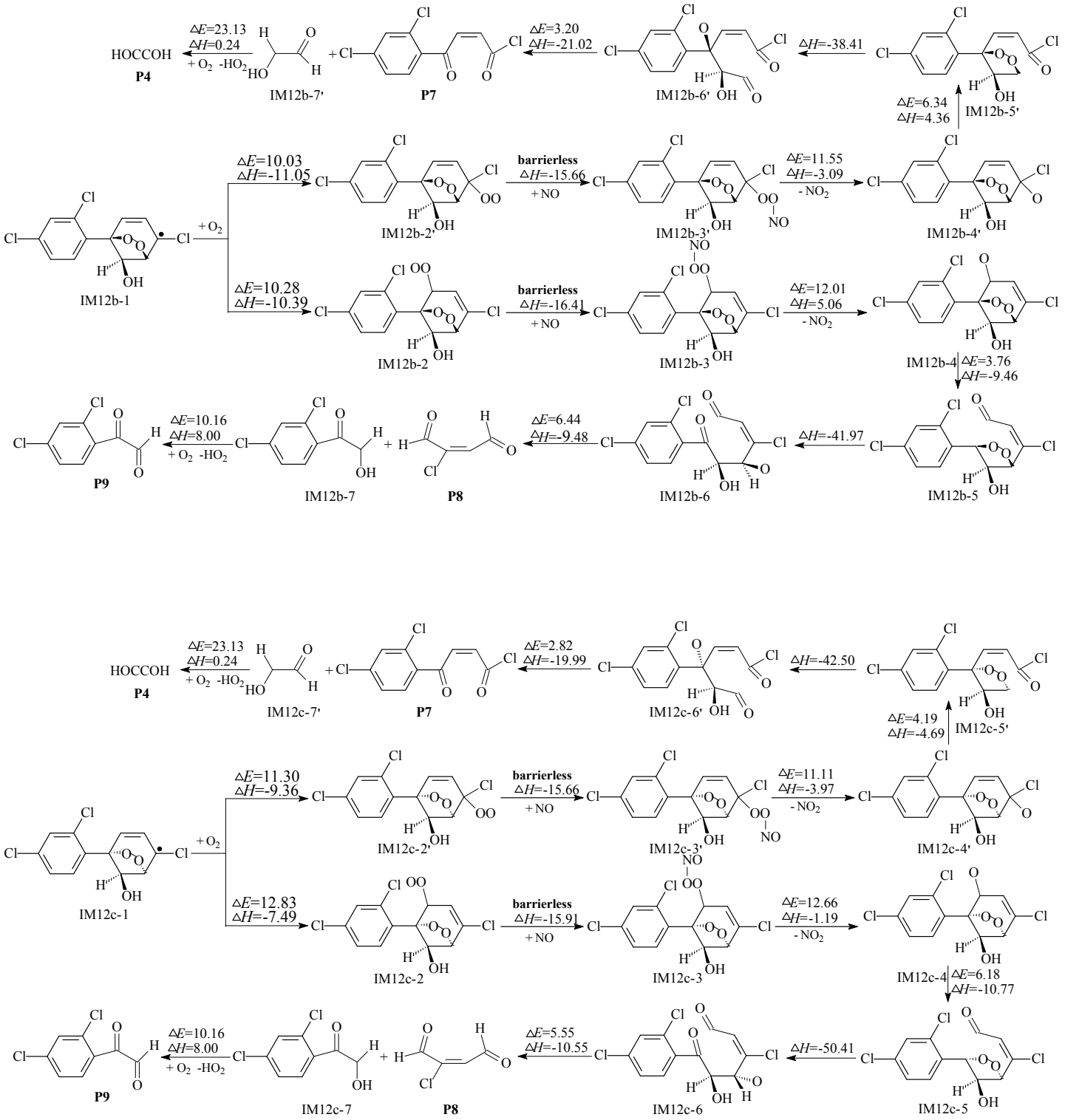

HOCCOH
P4
ΔE=23.13
ΔH=0.24
+ O2 -HO2
IM12b-7'
P7
ΔE=3.20
ΔH=-21.02
IM12b-6'
ΔH=-38.41
IM12b-5'
ΔE=6.34
ΔH=4.36
IM12b-1
+ O2
ΔE=10.03
ΔH=-11.05
IM12b-2'
barrierless
ΔH=-15.66
+ NO
IM12b-3'
ΔE=11.55
ΔH=-3.09
- NO2
IM12b-4'
ΔE=10.28
ΔH=-10.39
IM12b-2
barrierless
ΔH=-16.41
+ NO
IM12b-3
ΔE=12.01
ΔH=5.06
- NO2
IM12b-4
ΔE=3.76
ΔH=-9.46
P9
ΔE=10.16
ΔH=8.00
+ O2 -HO2
IM12b-7
P8
ΔE=6.44
ΔH=-9.48
IM12b-6
ΔH=-41.97
IM12b-5
HOCCOH
P4
ΔE=23.13
ΔH=0.24
+ O2 -HO2
IM12c-7'
P7
ΔE=2.82
ΔH=-19.99
IM12c-6'
ΔH=-42.50
IM12c-5'
ΔE=4.19
ΔH=-4.69
IM12c-1
+ O2
ΔE=11.30
ΔH=-9.36
IM12c-2'
barrierless
ΔH=-15.66
+ NO
IM12c-3'
ΔE=11.11
ΔH=-3.97
- NO2
IM12c-4'
ΔE=12.83
ΔH=-7.49
IM12c-2
barrierless
ΔH=-15.91
+ NO
IM12c-3
ΔE=12.66
ΔH=-1.19
- NO2
IM12c-4
ΔE=6.18
ΔH=-10.77
P9
ΔE=10.16
ΔH=8.00
+ O2 -HO2
IM12c-7
P8
ΔE=5.55
ΔH=-10.55
IM12c-6
ΔH=-50.41
IM12c-5

Fig. S2(c)

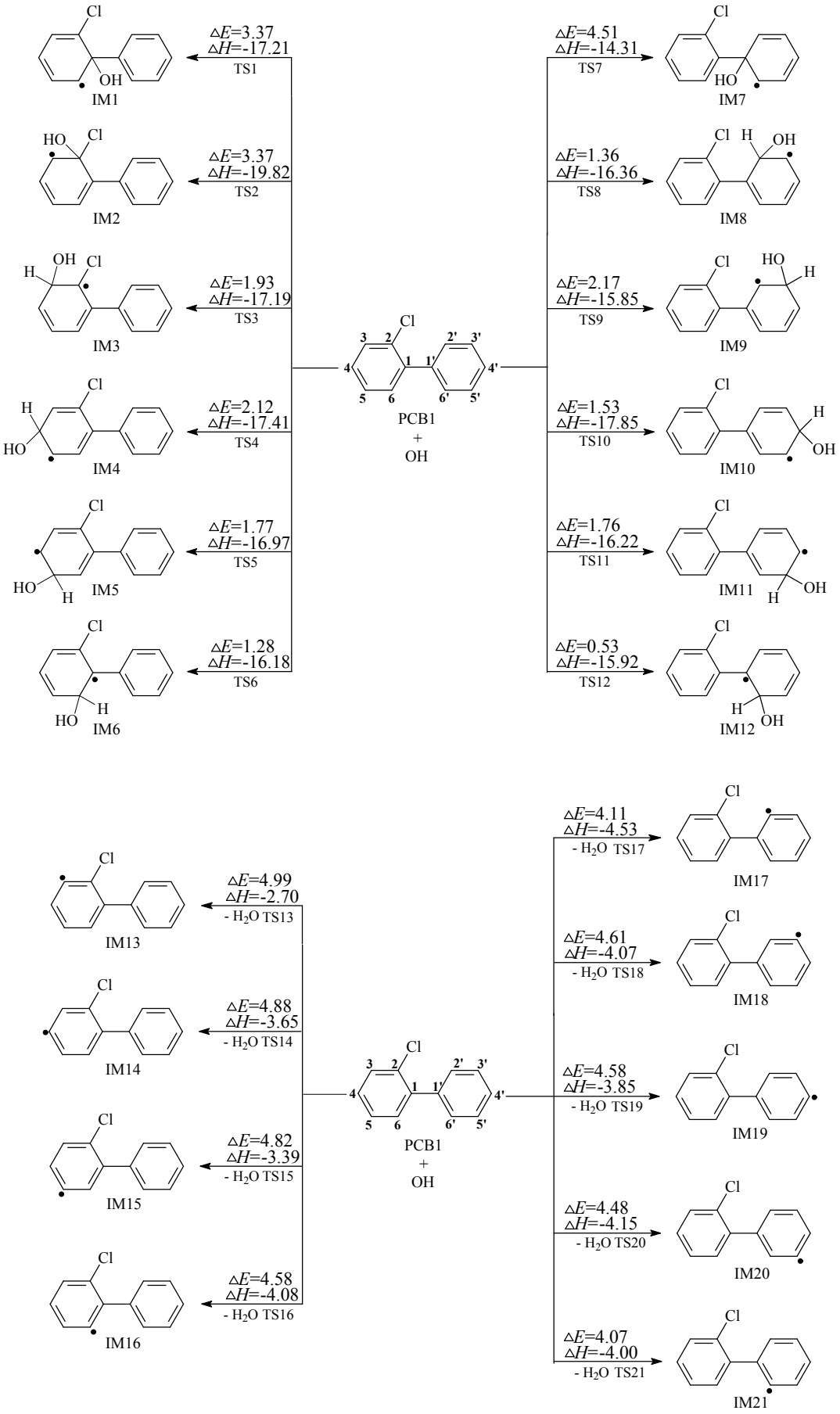

PCB1
+
OH
△E=3.37
△H=-17.21
TS1
IM1
△E=3.37
△H=-19.82
TS2
IM2
△E=1.93
△H=-17.19
TS3
IM3
△E=2.12
△H=-17.41
TS4
IM4
△E=1.77
△H=-16.97
TS5
IM5
△E=1.28
△H=-16.18
TS6
IM6
△E=4.51
△H=-14.31
TS7
IM7
△E=1.36
△H=-16.36
TS8
IM8
△E=2.17
△H=-15.85
TS9
IM9
△E=1.53
△H=-17.85
TS10
IM10
△E=1.76
△H=-16.22
TS11
IM11
△E=0.53
△H=-15.92
TS12
IM12
PCB1
+
OH
△E=4.99
△H=-2.70
- H2O TS13
IM13
△E=4.88
△H=-3.65
- H2O TS14
IM14
△E=4.82
△H=-3.39
- H2O TS15
IM15
△E=4.58
△H=-4.08
- H2O TS16
IM16
△E=4.11
△H=-4.53
- H2O TS17
IM17
△E=4.61
△H=-4.07
- H2O TS18
IM18
△E=4.58
△H=-3.85
- H2O TS19
IM19
△E=4.48
△H=-4.15
- H2O TS20
IM20
△E=4.07
△H=-4.00
- H2O TS21
IM21

Fig. S3

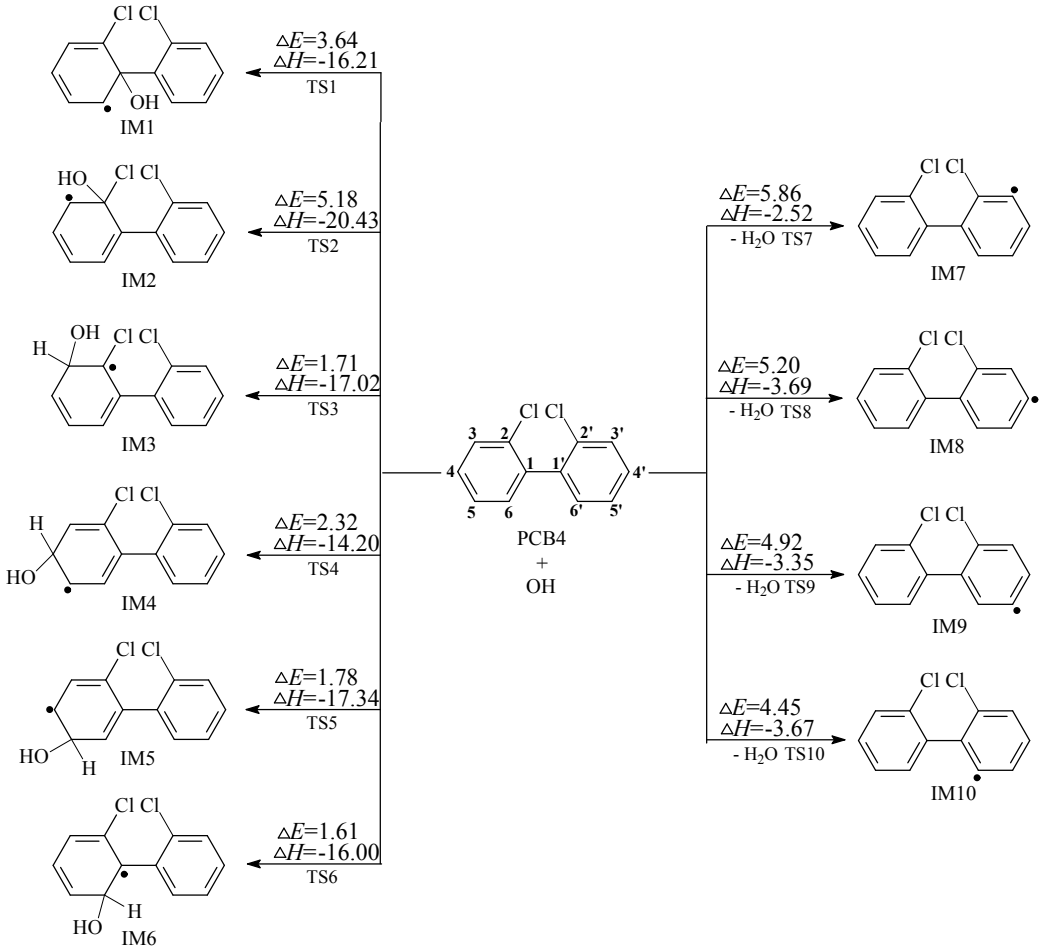

Cl Cl
OH
IM1
△E=3.64
△H=-16.21
TS1
HO
IM2
△E=5.18
△H=-20.43
TS2
H
IM3
△E=1.71
△H=-17.02
TS3
IM4
△E=2.32
△H=-14.20
TS4
IM5
△E=1.78
△H=-17.34
TS5
IM6
△E=1.61
△H=-16.00
TS6
PCB4
+
OH
IM7
△E=5.86
△H=-2.52
- H2O TS7
IM8
△E=5.20
△H=-3.69
- H2O TS8
IM9
△E=4.92
△H=-3.35
- H2O TS9
IM10
△E=4.45
△H=-3.67
- H2O TS10

Fig. S4

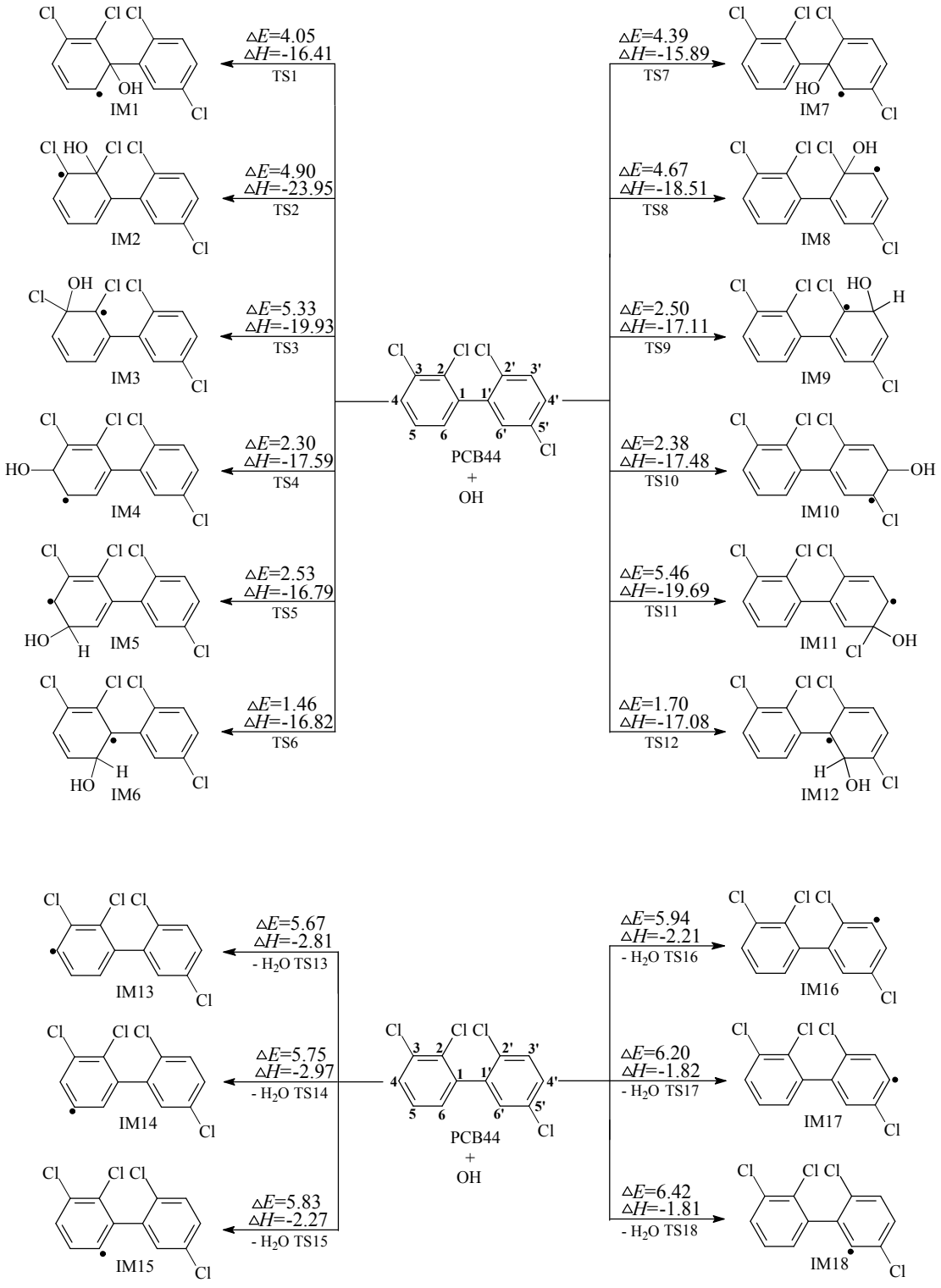

△E=4.05
△H=-16.41
TS1
IM1
△E=4.90
△H=-23.95
TS2
IM2
△E=5.33
△H=-19.93
TS3
IM3
△E=2.30
△H=-17.59
TS4
IM4
△E=2.53
△H=-16.79
TS5
IM5
△E=1.46
△H=-16.82
TS6
IM6
PCB44
+
OH
△E=4.39
△H=-15.89
TS7
IM7
△E=4.67
△H=-18.51
TS8
IM8
△E=2.50
△H=-17.11
TS9
IM9
△E=2.38
△H=-17.48
TS10
IM10
△E=5.46
△H=-19.69
TS11
IM11
△E=1.70
△H=-17.08
TS12
IM12
△E=5.67
△H=-2.81
- H2O TS13
IM13
△E=5.75
△H=-2.97
- H2O TS14
IM14
△E=5.83
△H=-2.27
- H2O TS15
IM15
PCB44
+
OH
△E=5.94
△H=-2.21
- H2O TS16
IM16
△E=6.20
△H=-1.82
- H2O TS17
IM17
△E=6.42
△H=-1.81
- H2O TS18
IM18

Fig. S5

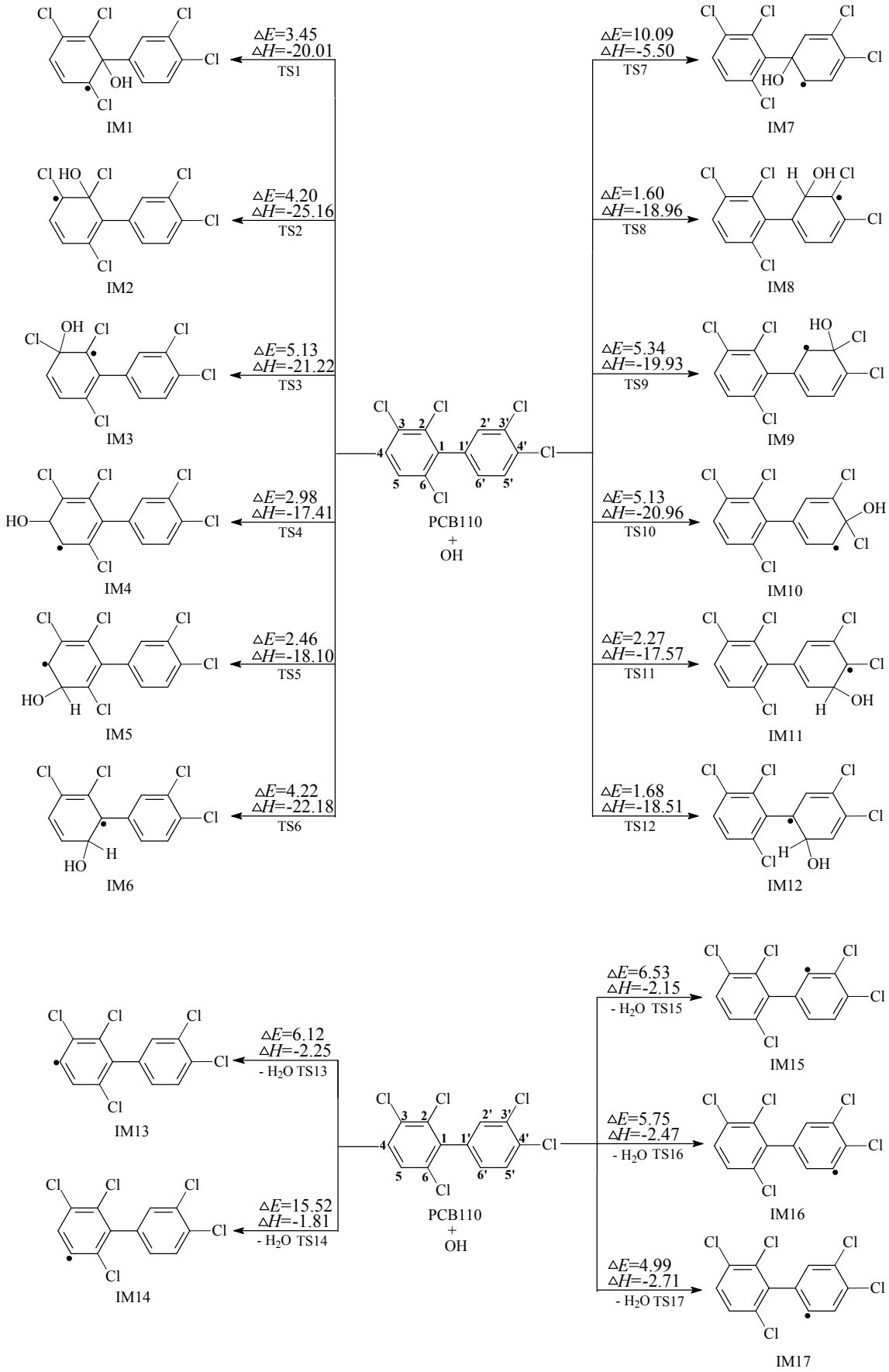

△E=3.45
△H=-20.01
TS1
IM1
△E=4.20
△H=-25.16
TS2
IM2
△E=5.13
△H=-21.22
TS3
IM3
△E=2.98
△H=-17.41
TS4
IM4
△E=2.46
△H=-18.10
TS5
IM5
△E=4.22
△H=-22.18
TS6
IM6
PCB110
+
OH
△E=10.09
△H=-5.50
TS7
IM7
△E=1.60
△H=-18.96
TS8
IM8
△E=5.34
△H=-19.93
TS9
IM9
△E=5.13
△H=-20.96
TS10
IM10
△E=2.27
△H=-17.57
TS11
IM11
△E=1.68
△H=-18.51
TS12
IM12
△E=6.12
△H=-2.25
- H2O TS13
IM13
△E=15.52
△H=-1.81
- H2O TS14
IM14
PCB110
+
OH
△E=6.53
△H=-2.15
- H2O TS15
IM15
△E=5.75
△H=-2.47
- H2O TS16
IM16
△E=4.99
△H=-2.71
- H2O TS17
IM17

Fig. S6

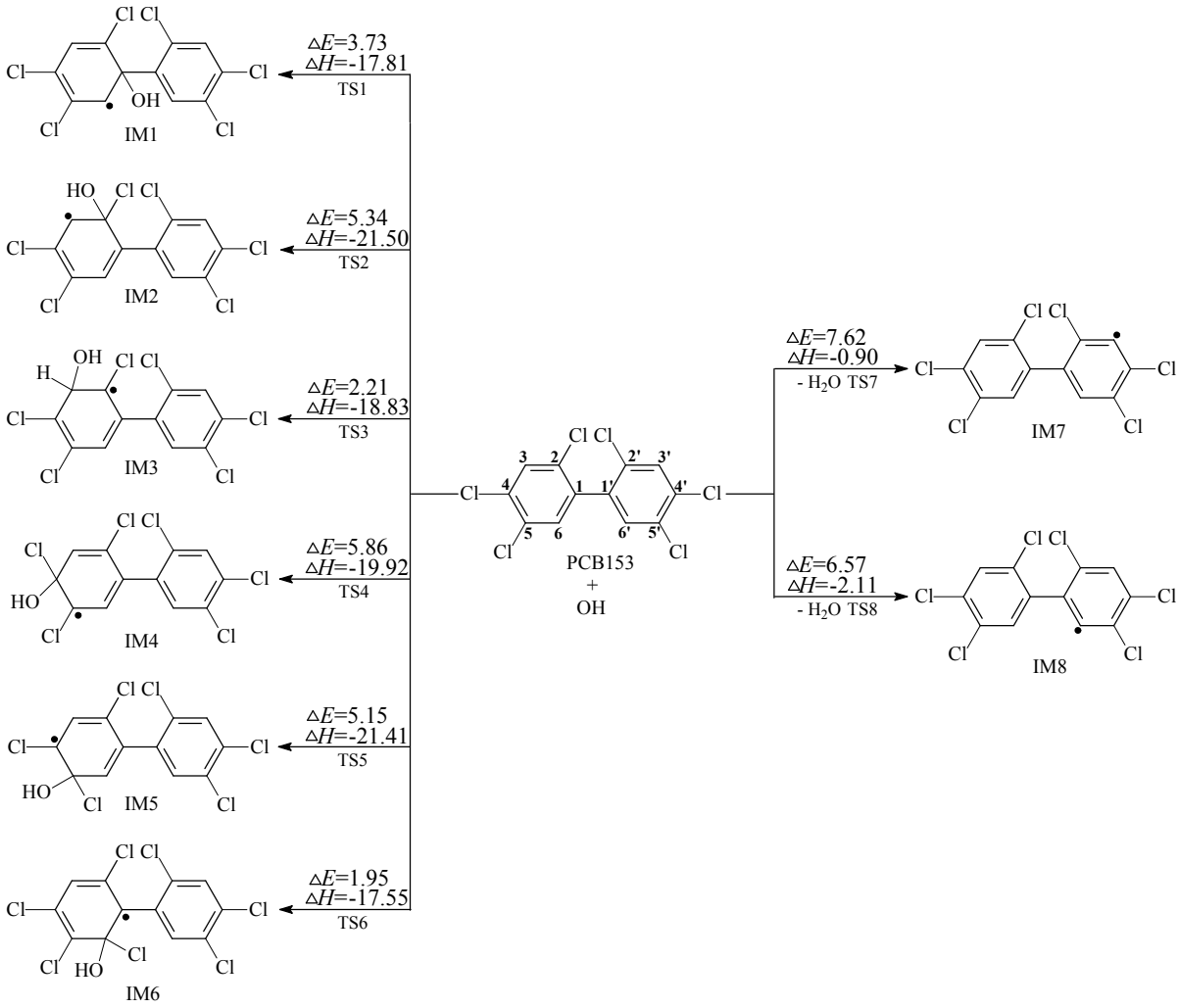

IM1
△E=3.73
△H=-17.81
TS1
IM2
△E=5.34
△H=-21.50
TS2
IM3
△E=2.21
△H=-18.83
TS3
IM4
△E=5.86
△H=-19.92
TS4
IM5
△E=5.15
△H=-21.41
TS5
IM6
△E=1.95
△H=-17.55
TS6
PCB153
+
OH
△E=7.62
△H=-0.90
- H2O TS7
IM7
△E=6.57
△H=-2.11
- H2O TS8
IM8

Fig. S7