TWO-DIMENSIONAL ION MOBILITY FOR CHARACTERIZATION OF PCB METABOLITES

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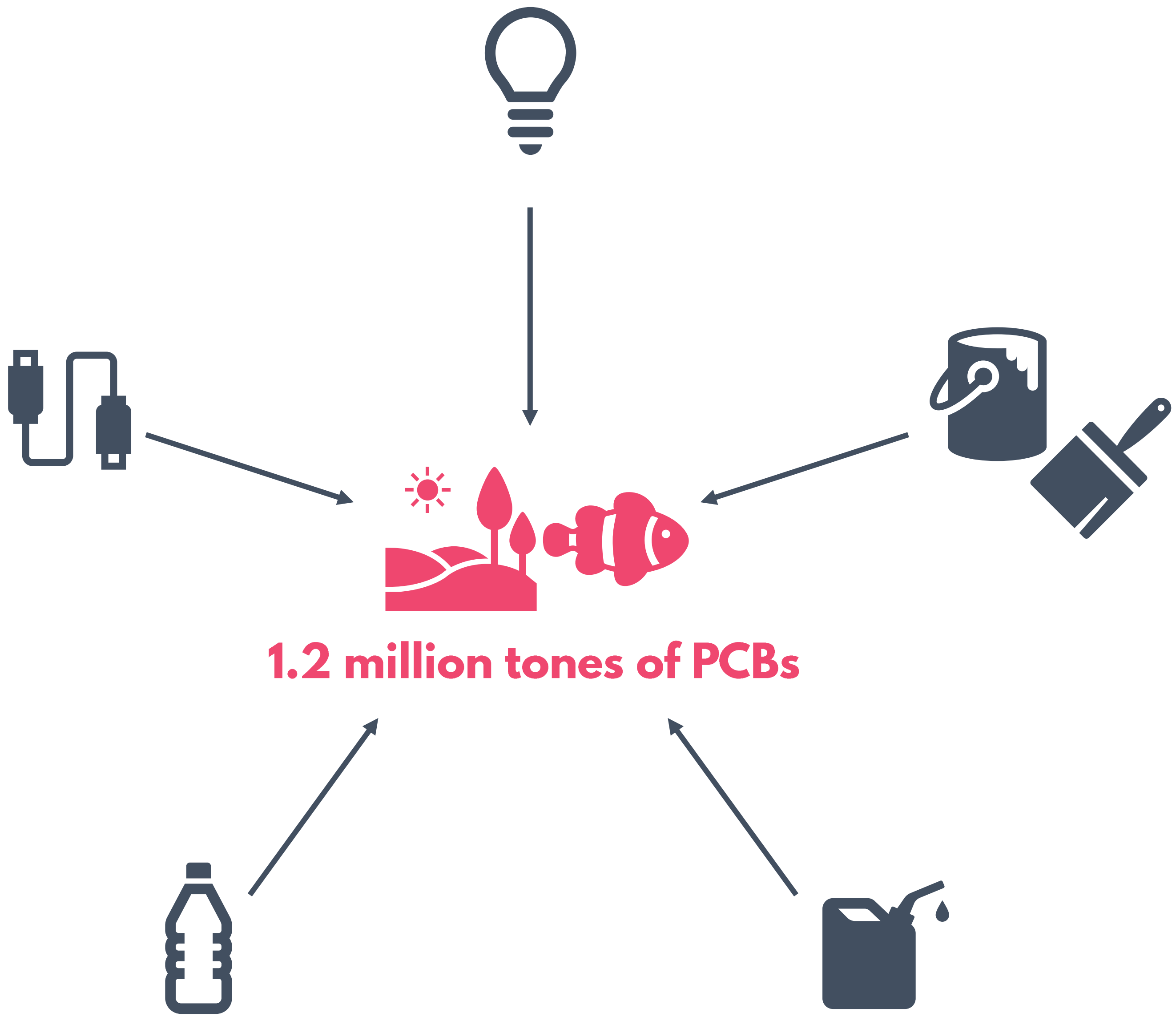
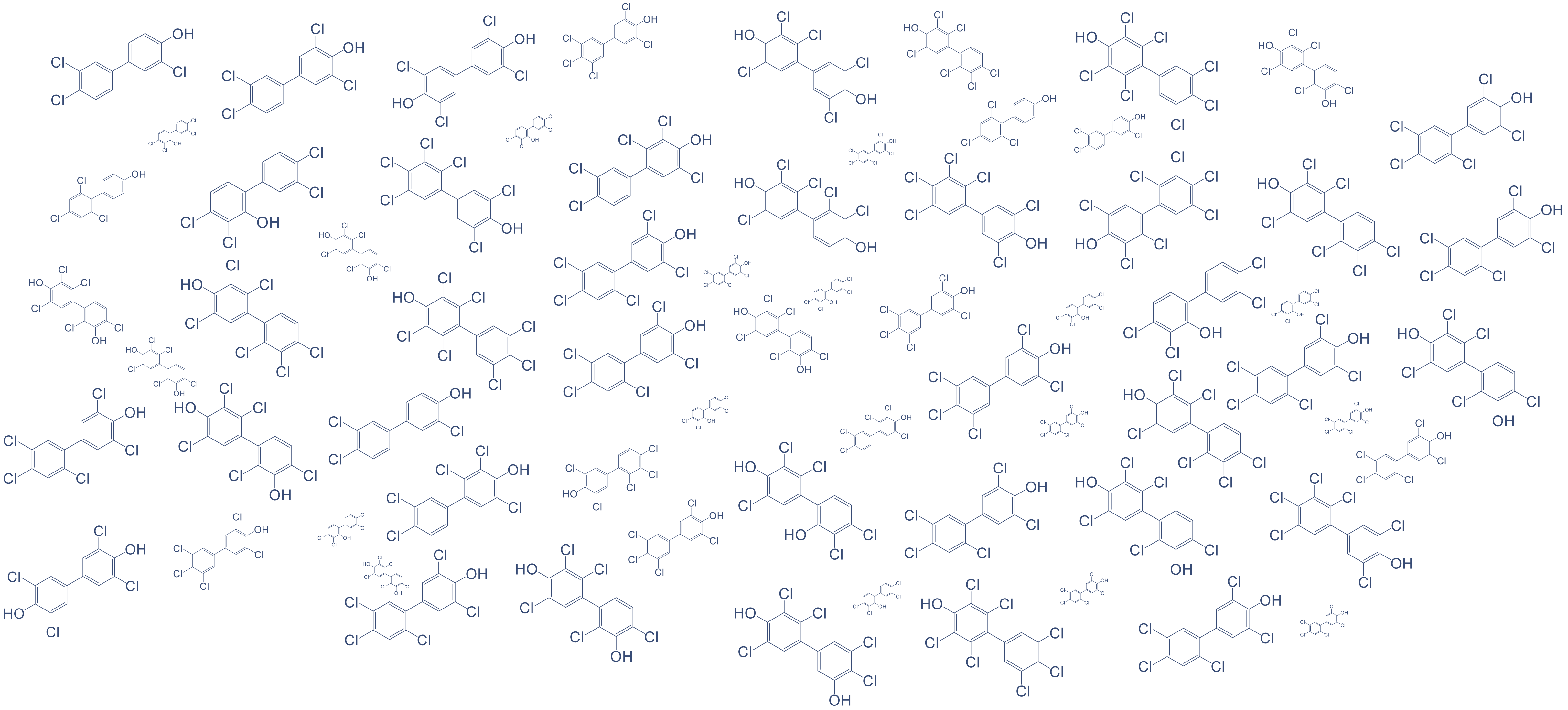
Kruvelab.com

PCBs



OH-PCBs



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OH-PCBs

Over 800 structures

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OH-PCBs

Over 800 structures

- Environmental fates
- Toxicity
- Quantification

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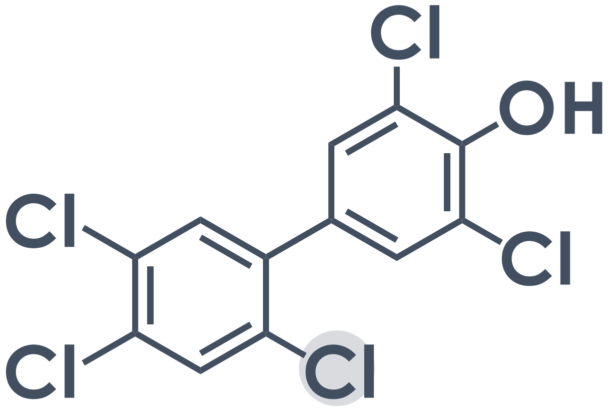
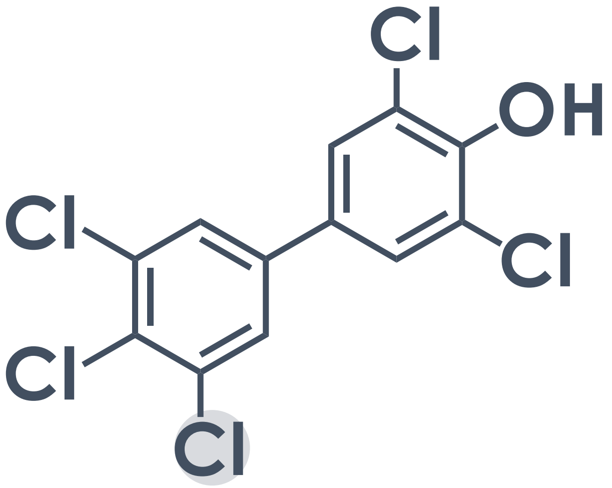
HOW TO TELL THEM APART?

Similar MS^2, retention time and CCS





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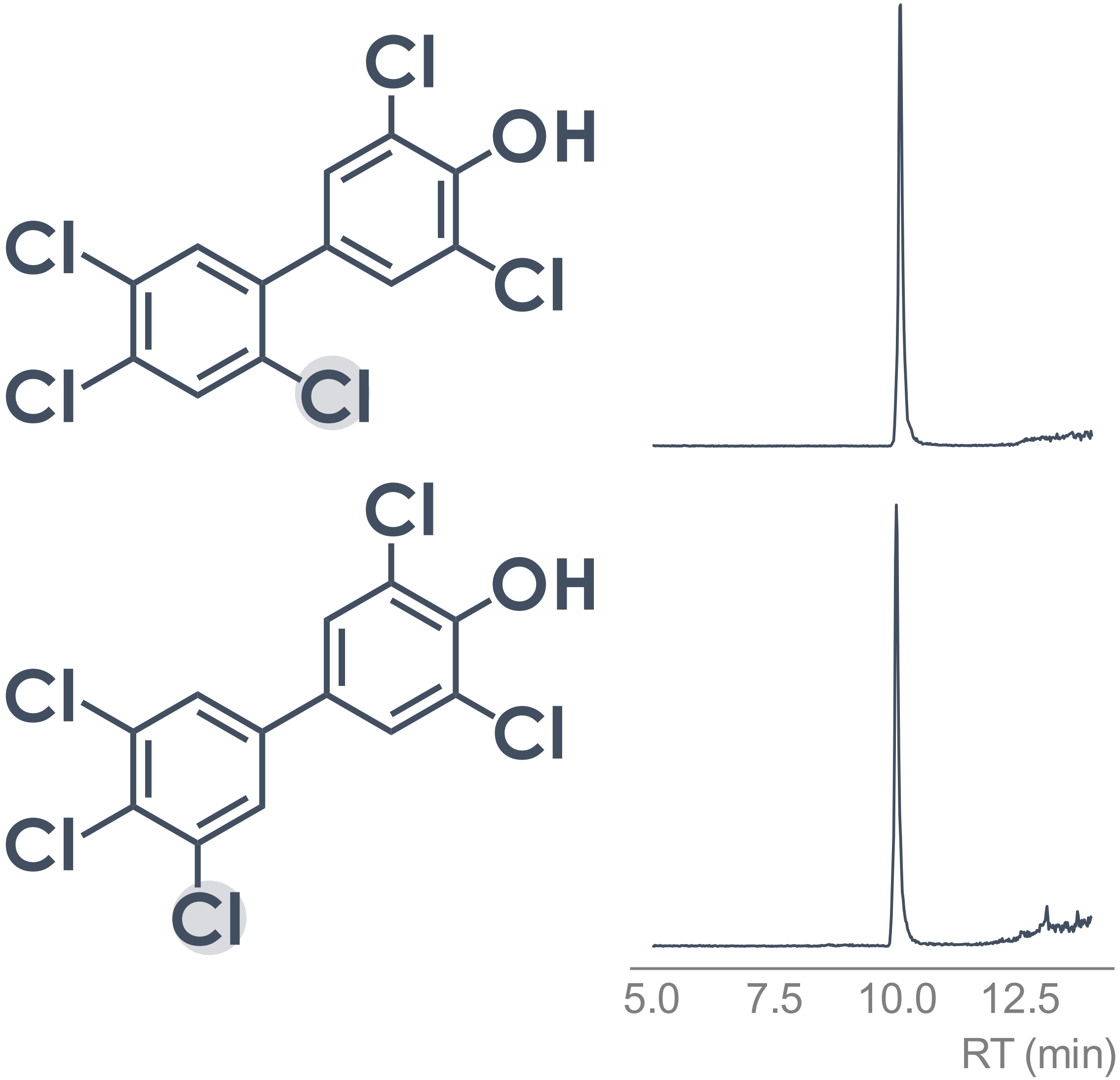
HOW TO TELL THEM APART?

Similar MS², retention time and CCS



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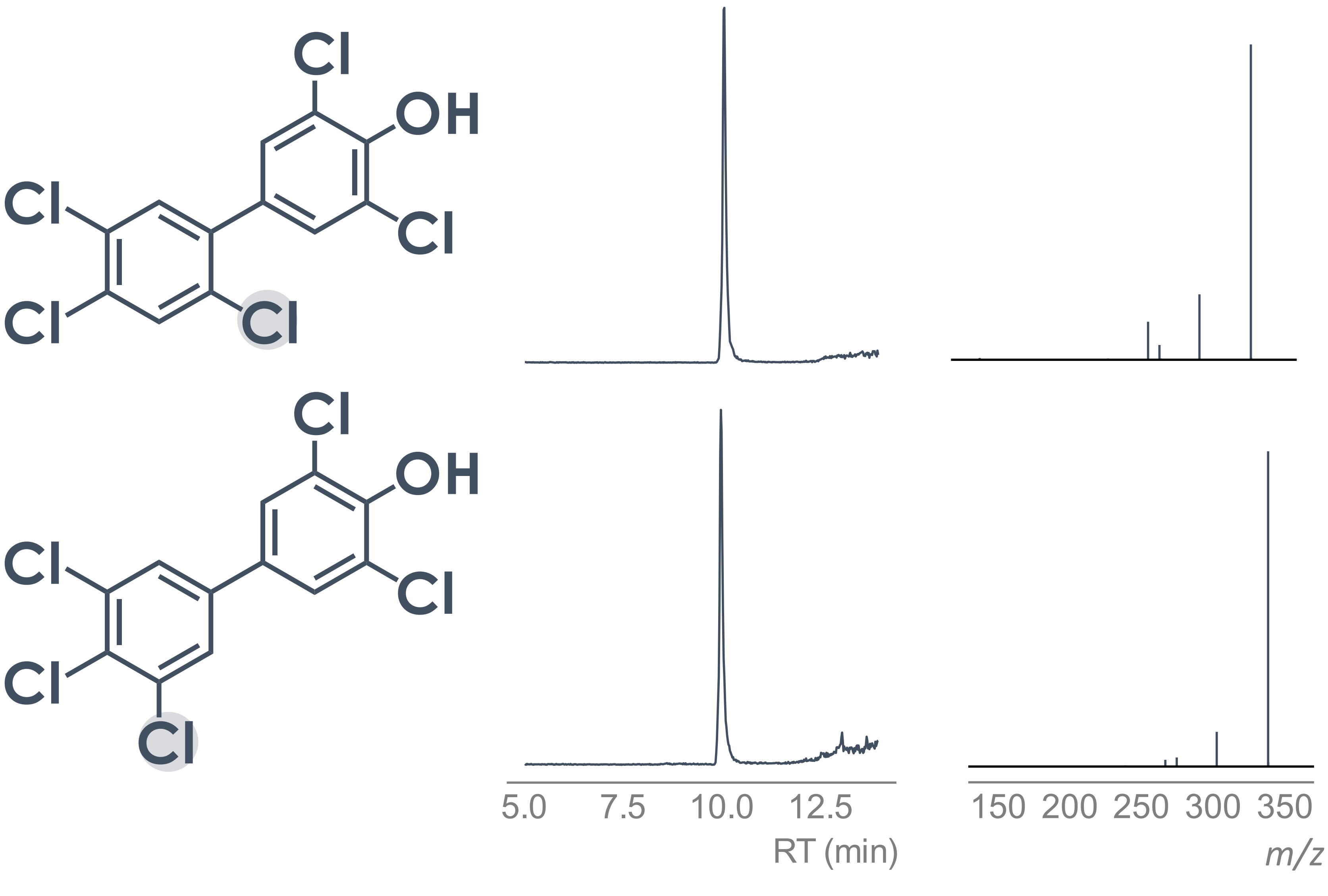
HOW TO TELL THEM APART?

Similar MS^2, retention time and CCS



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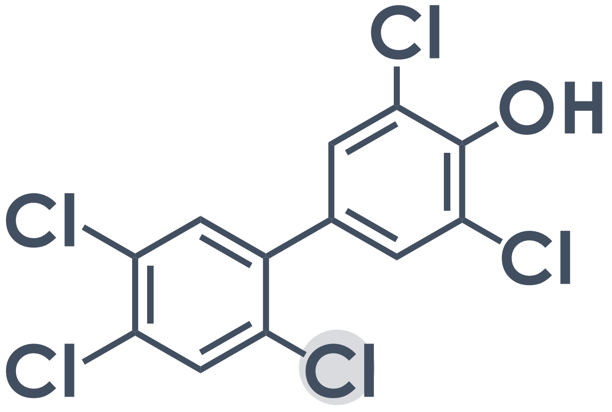
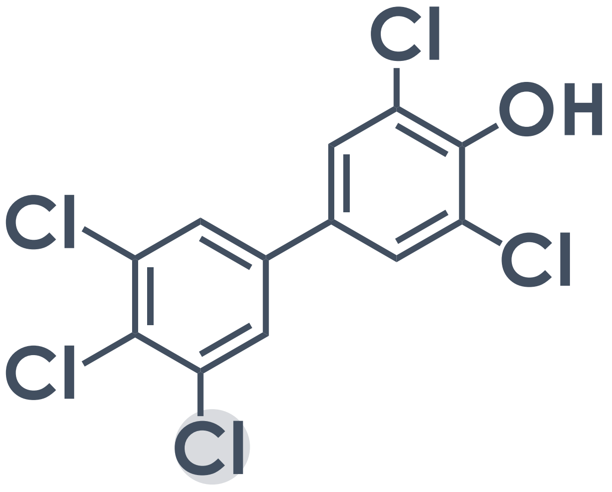
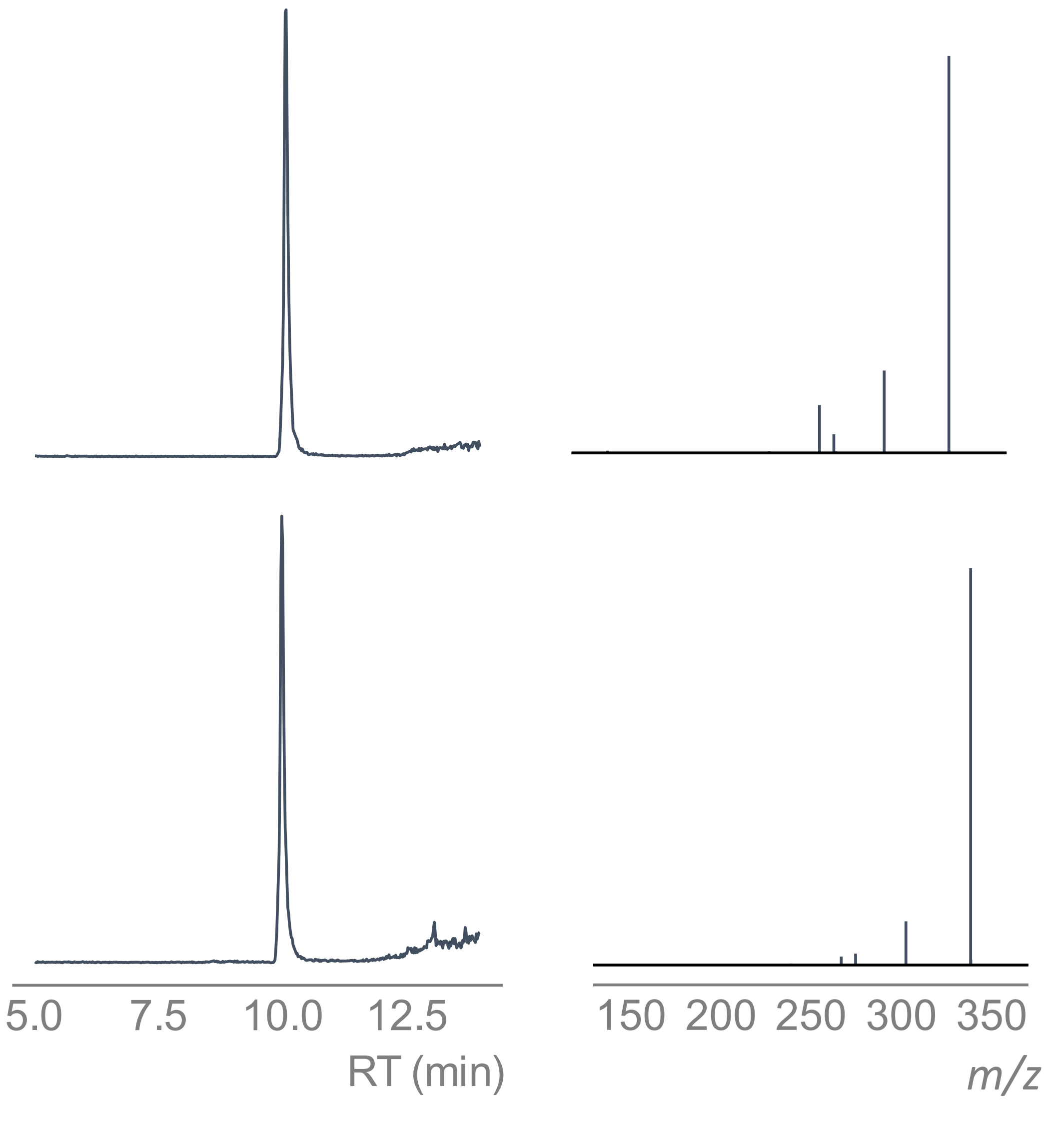
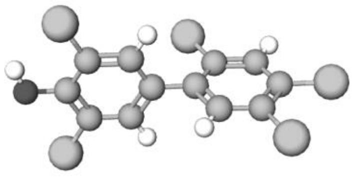
HOW TO TELL THEM APART?

Similar MS², retention time and CCS

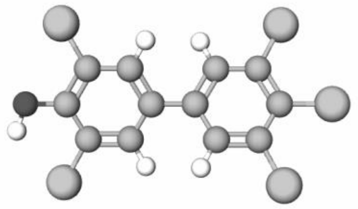








CCS = 166.6 A²



CCS = 165.8 A²

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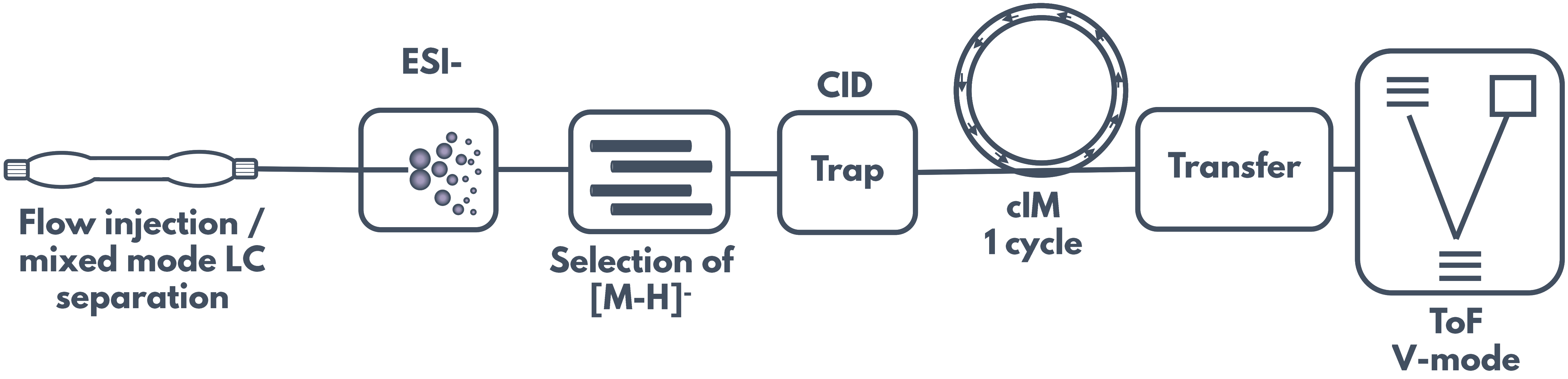
CYCLIC ION MOBILITY

Obtaining fragment-ion CCS

18 OH-PCB standards



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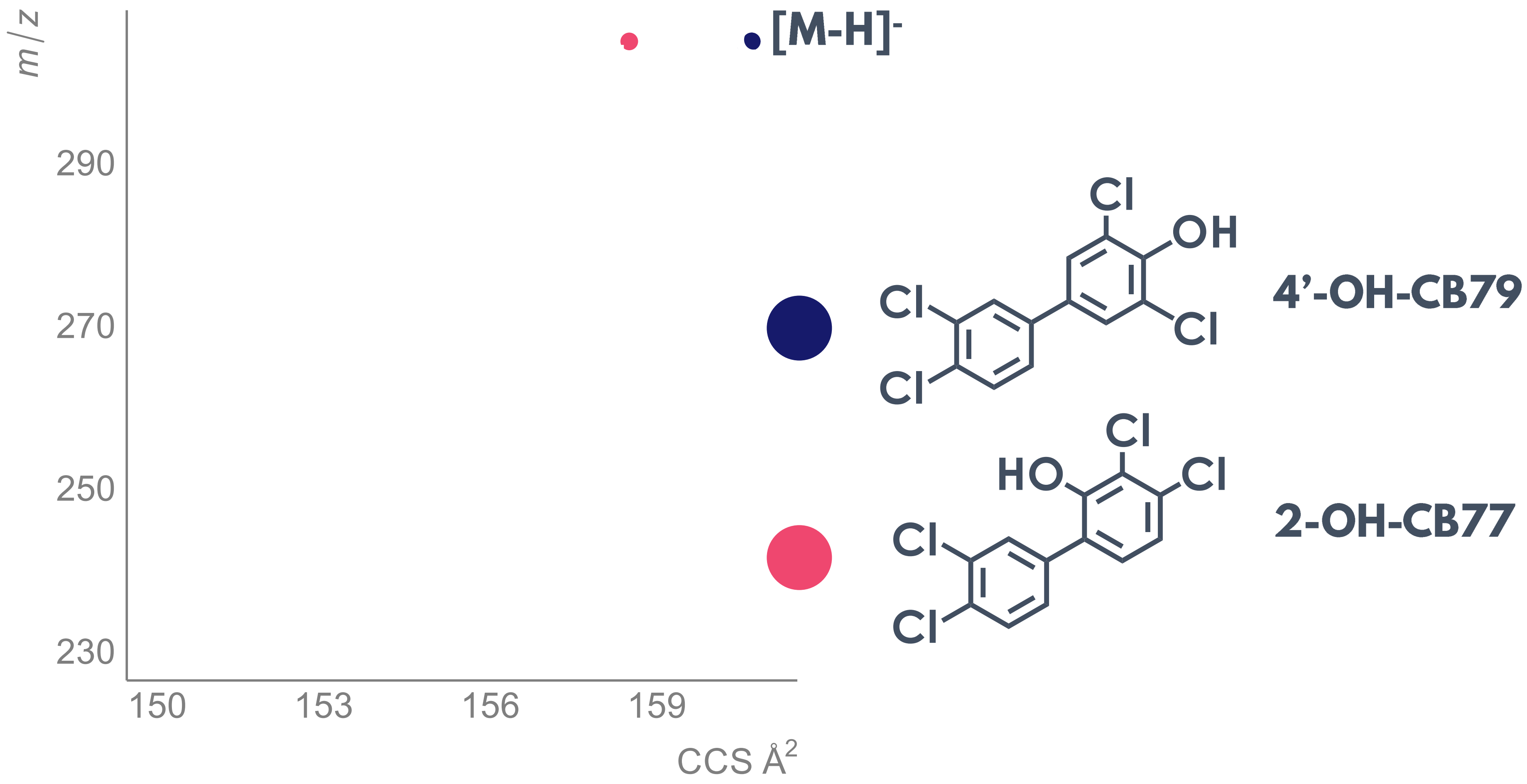
FRAGMENT ION CCS

Larger parent ion, smaller fragment ion



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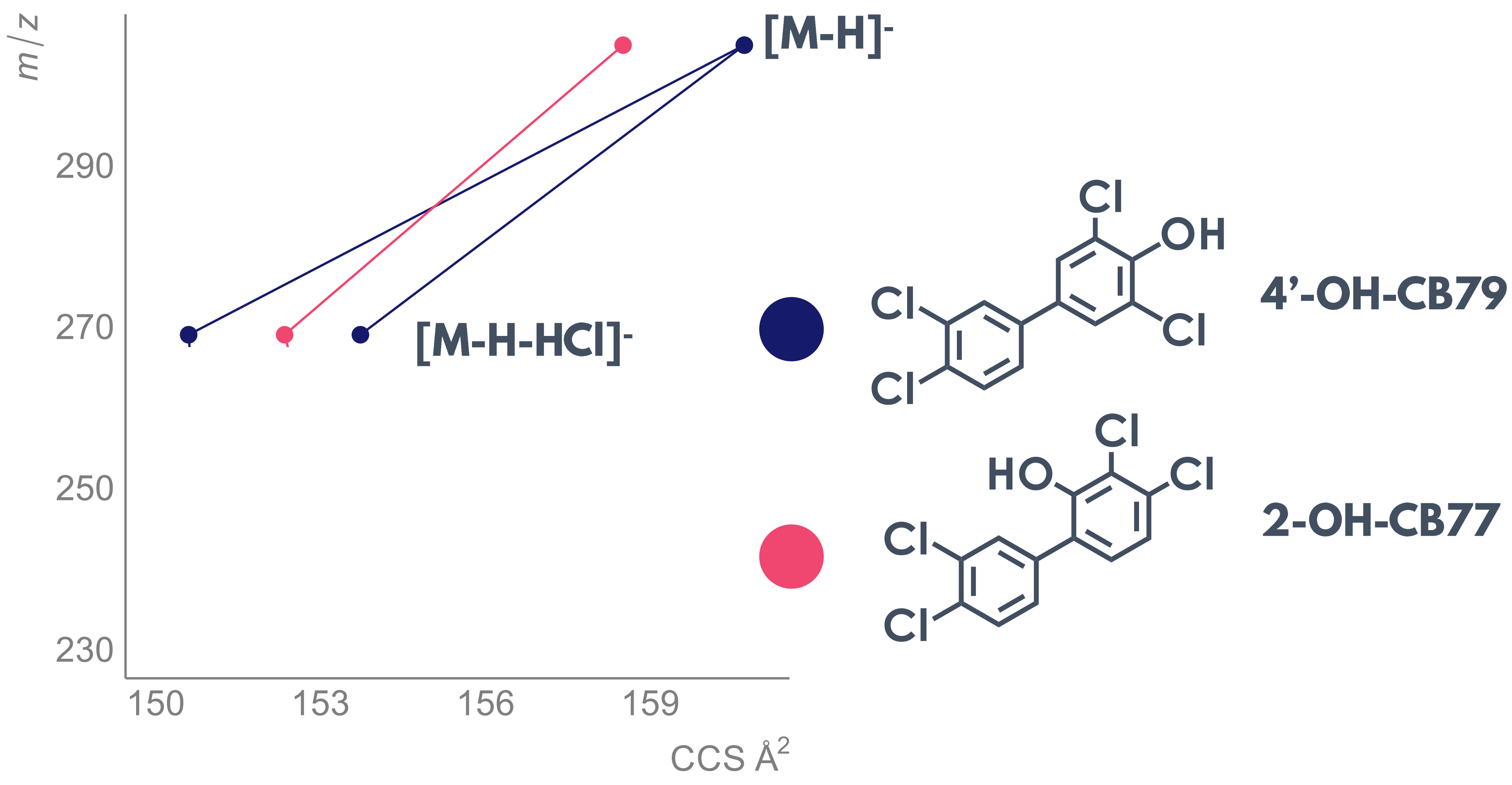
FRAGMENT ION CCS

Larger parent ion, smaller fragment ion



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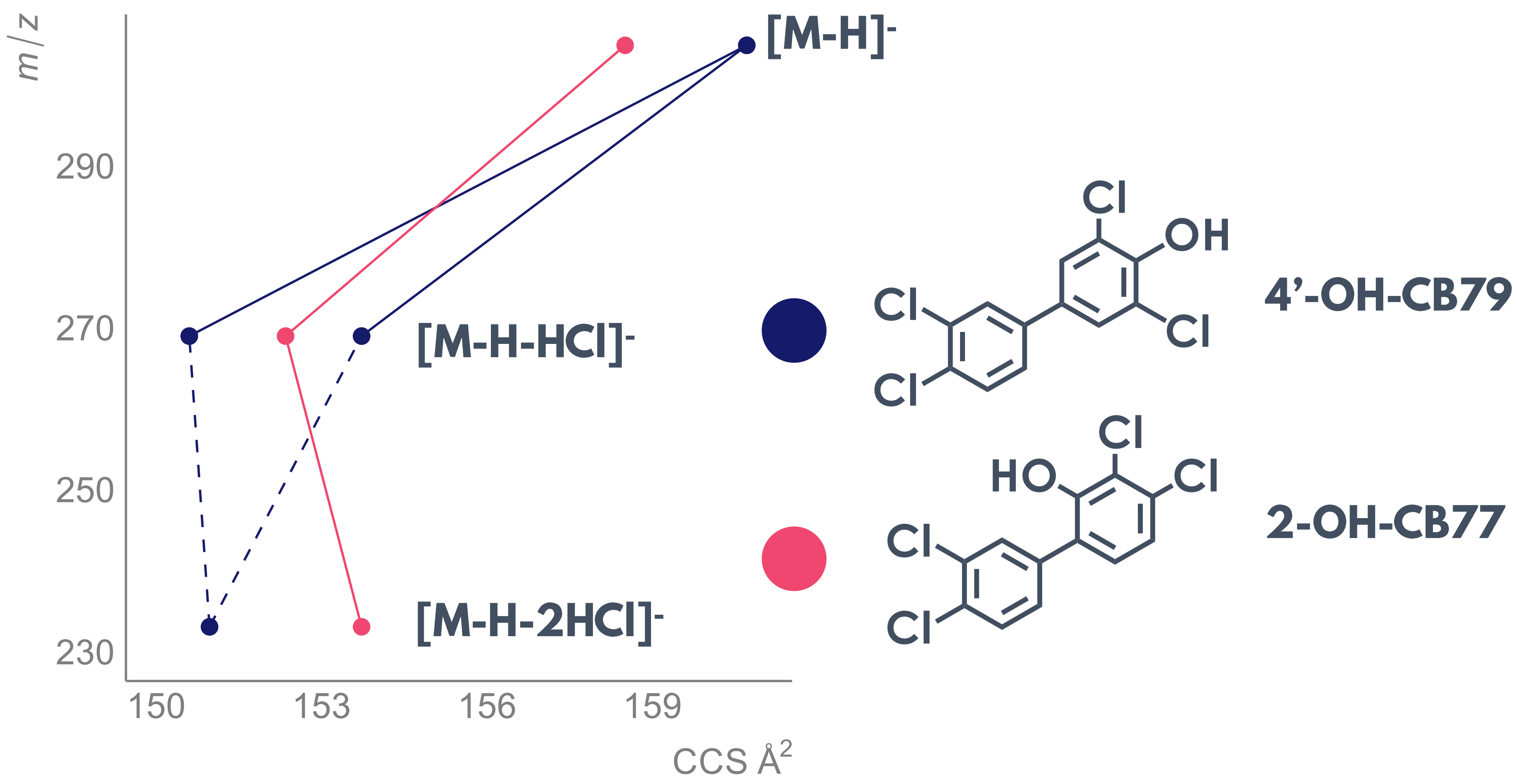
FRAGMENT ION CCS

Larger parent ion, smaller fragment ion



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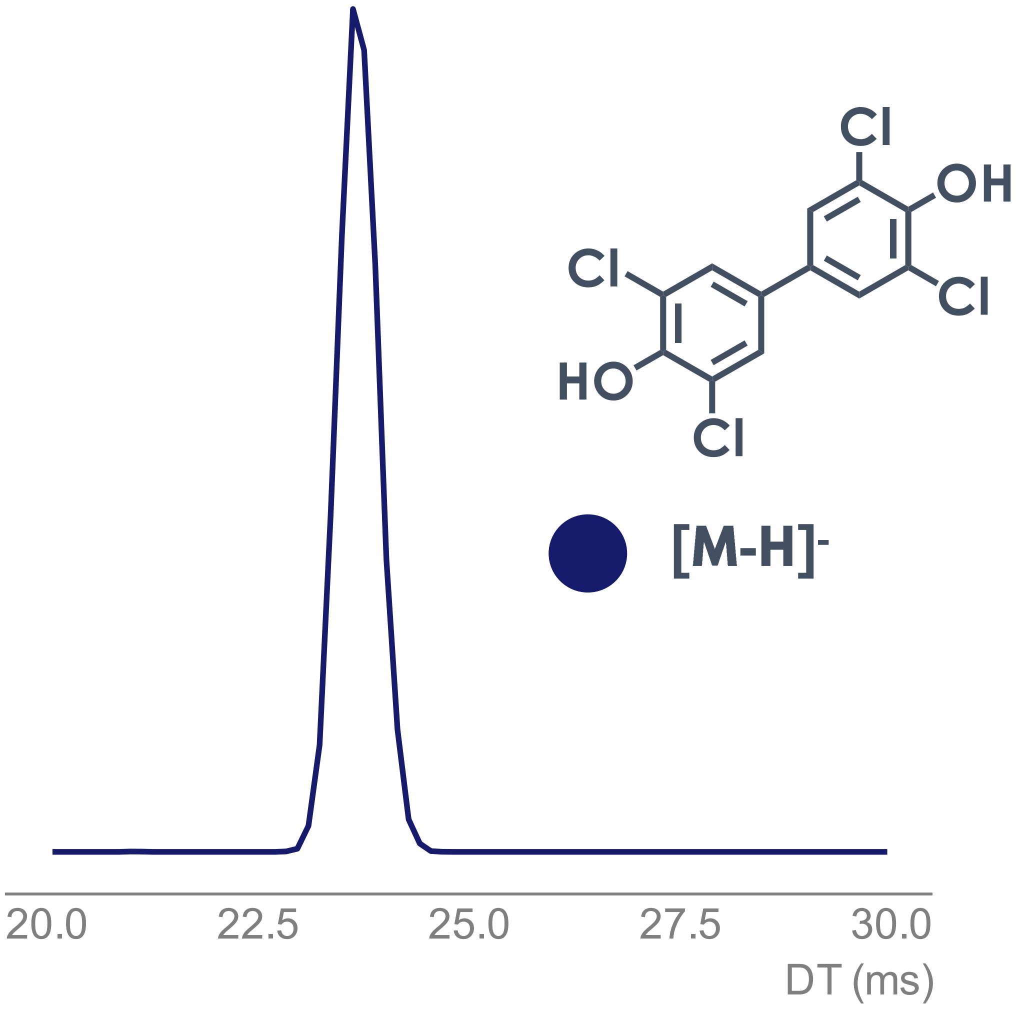
MULTIPLE FRAGMENT ION PEAKS



4,4'-diOH-CB80

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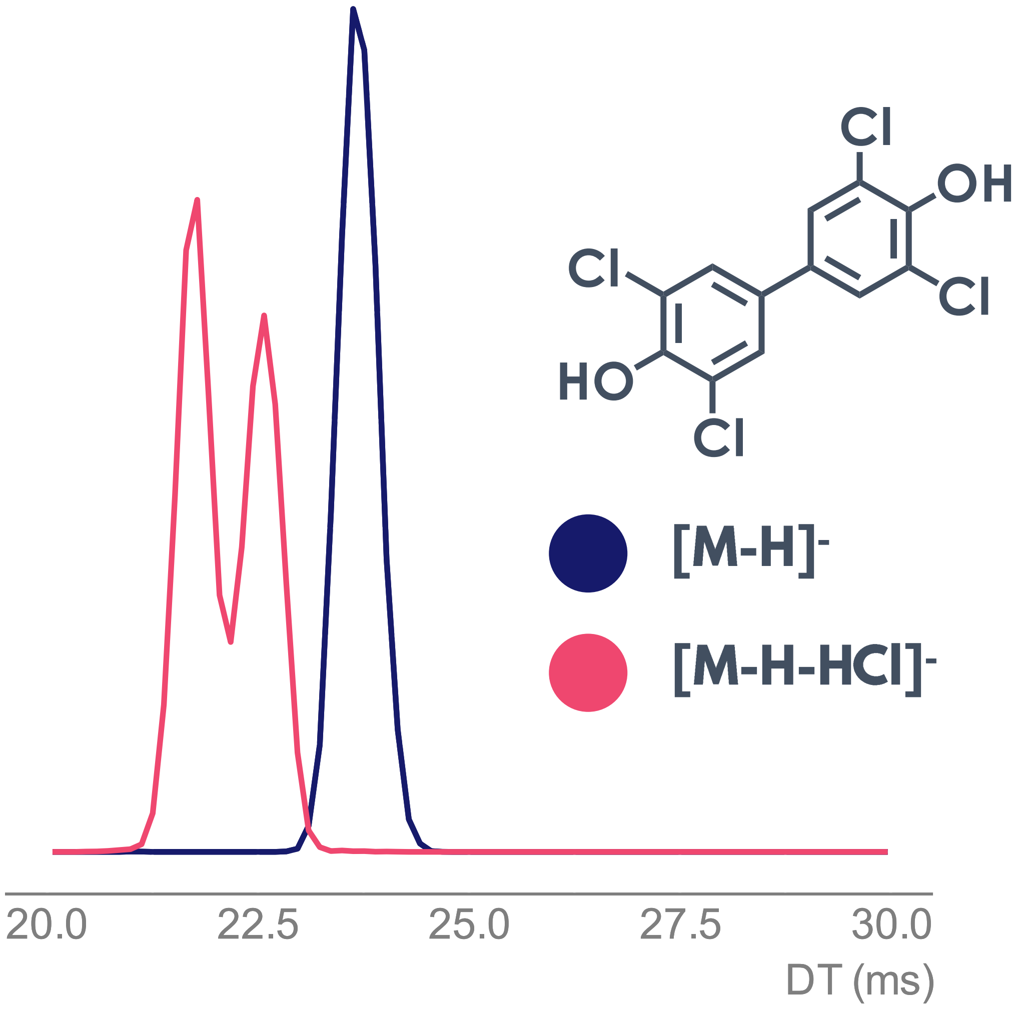
MULTIPLE FRAGMENT ION PEAKS



4,4’-diOH-CB80

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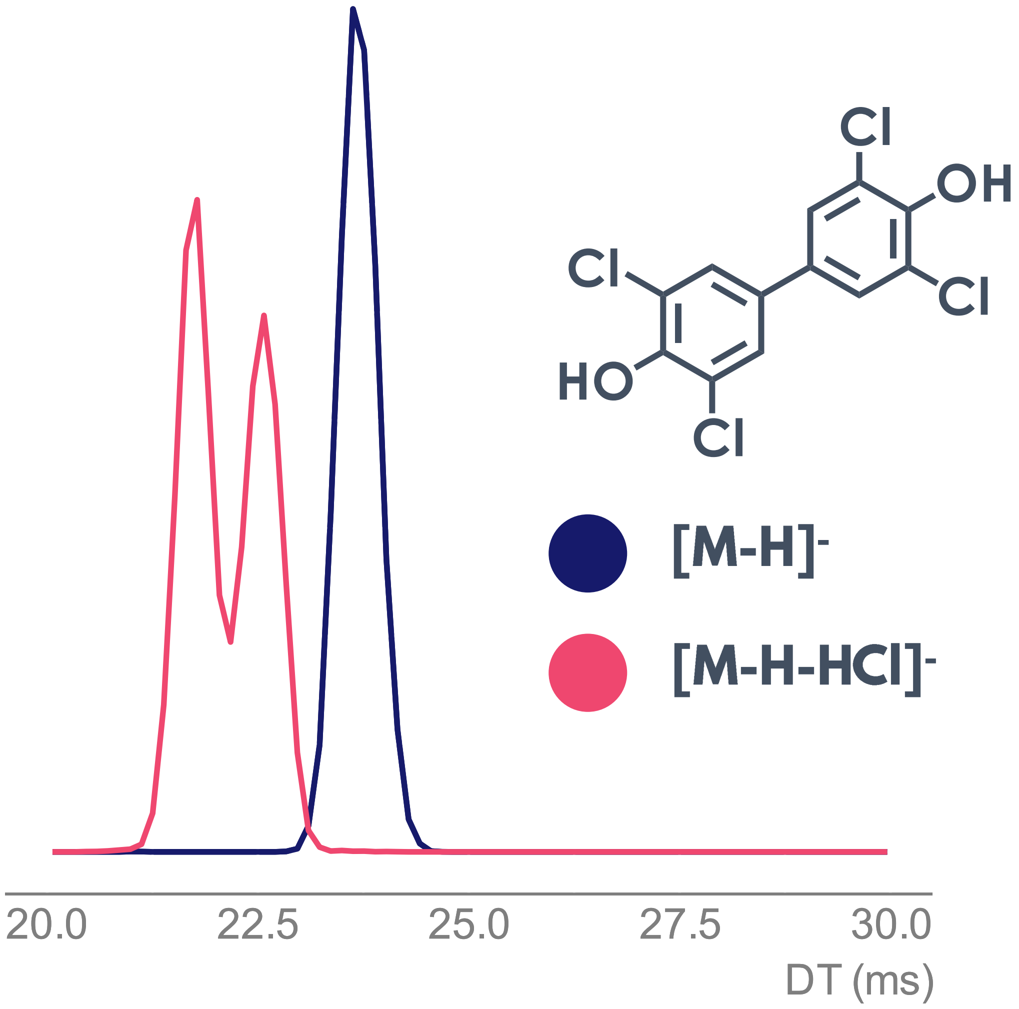
MULTIPLE FRAGMENT ION PEAKS



4,4'-diOH-CB80

Isomeric fragments?

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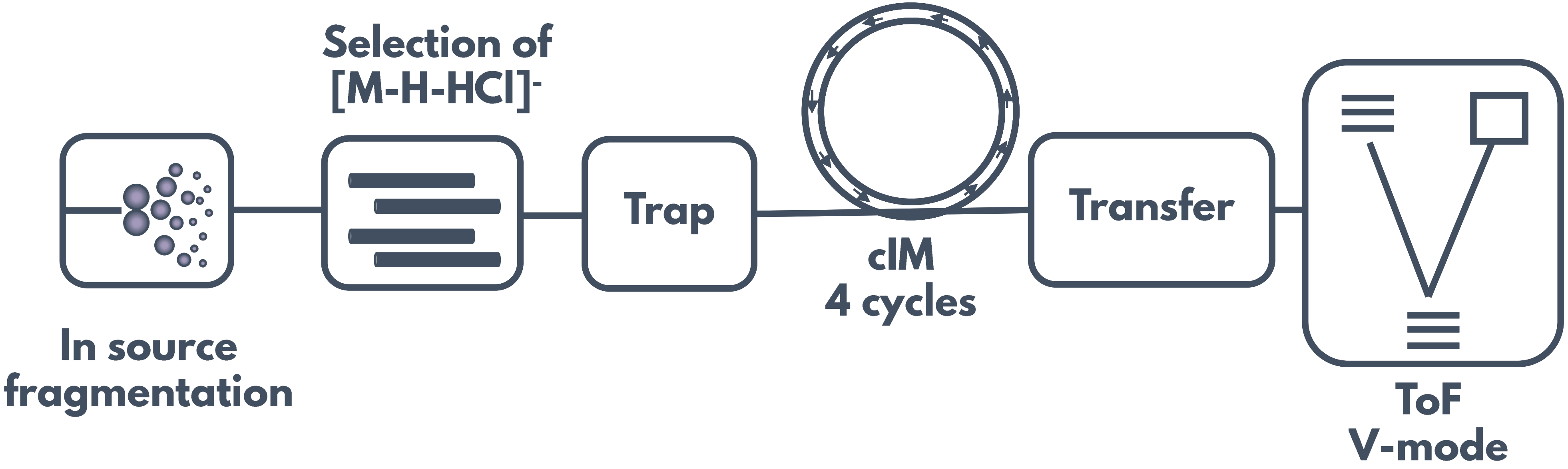
SEPARATING THE FRAGMENTS



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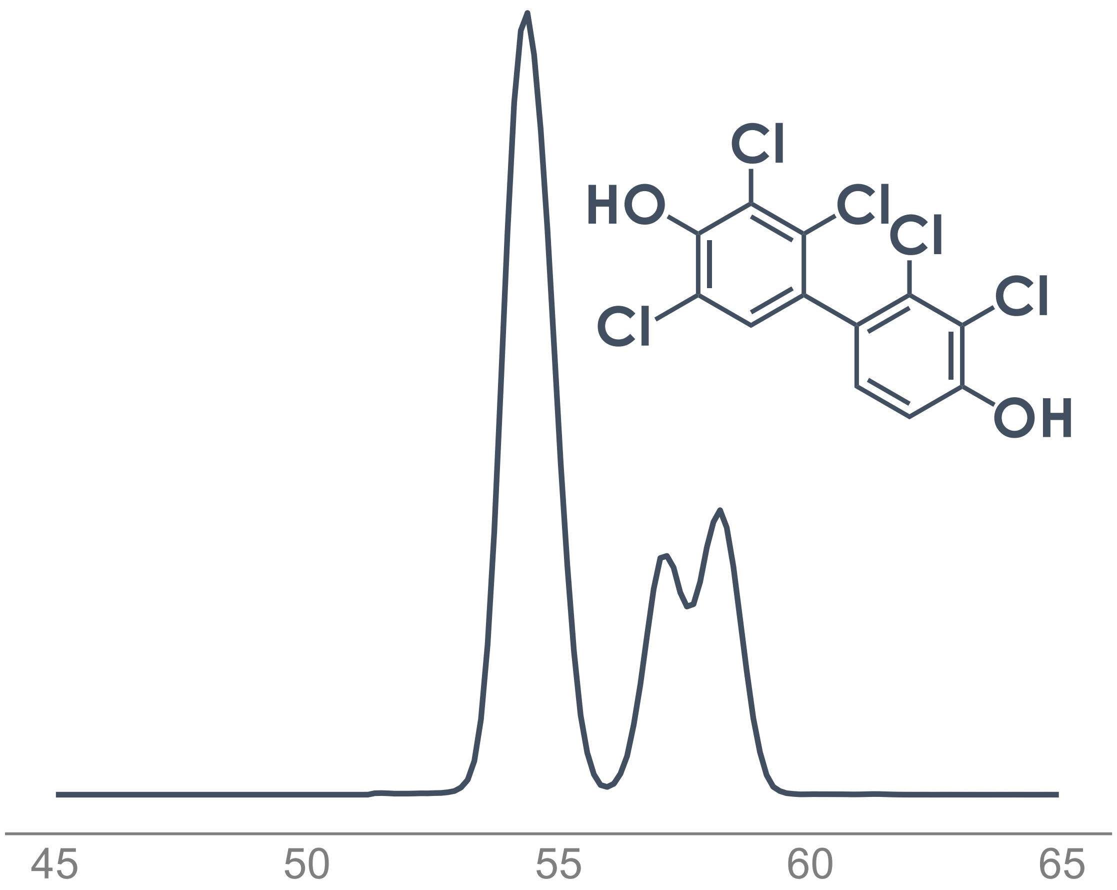
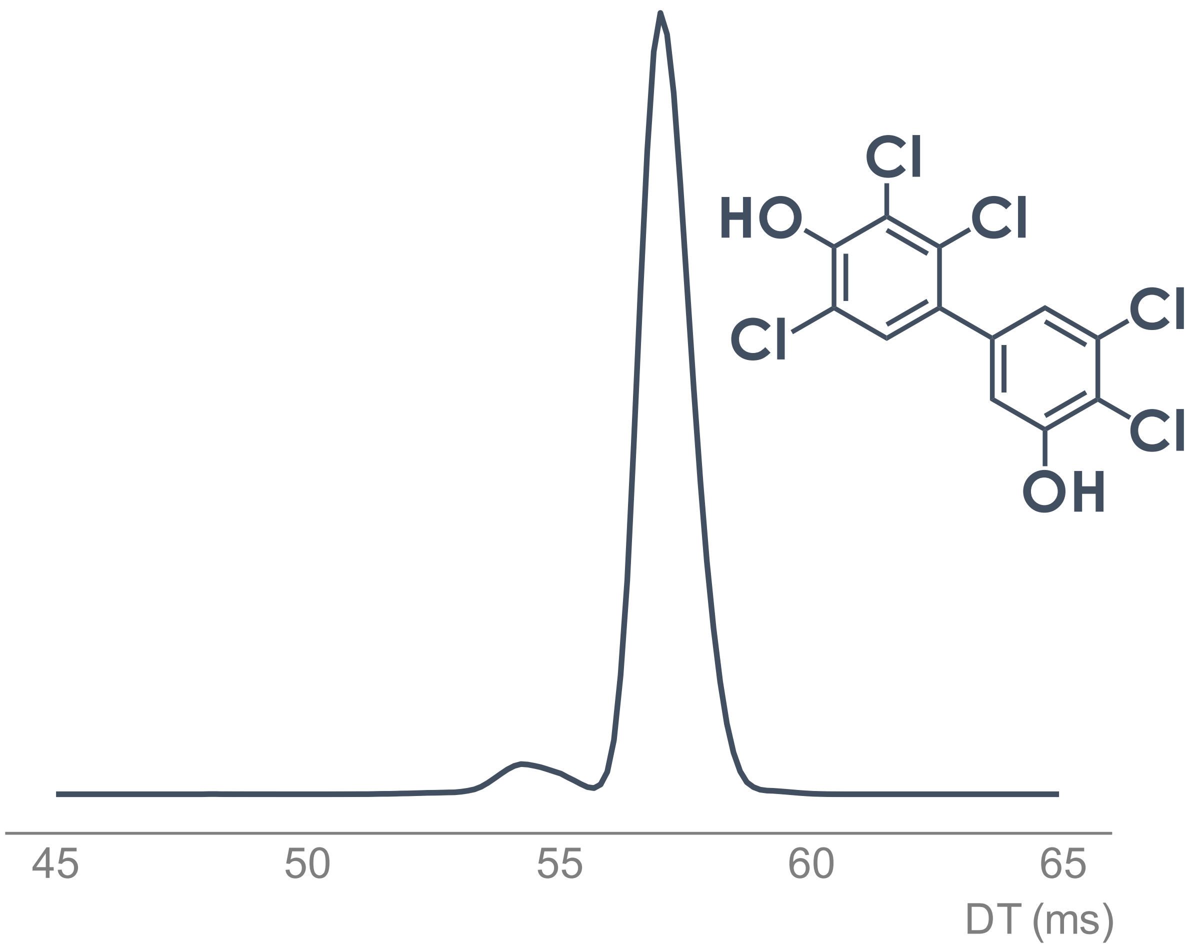
ISOMERIC FRAGMENT IONS

The number of peaks varies between isomers

$[M\text{-}H\text{-}HCl]^-$



$[M\text{-}H\text{-}HCl]^-$



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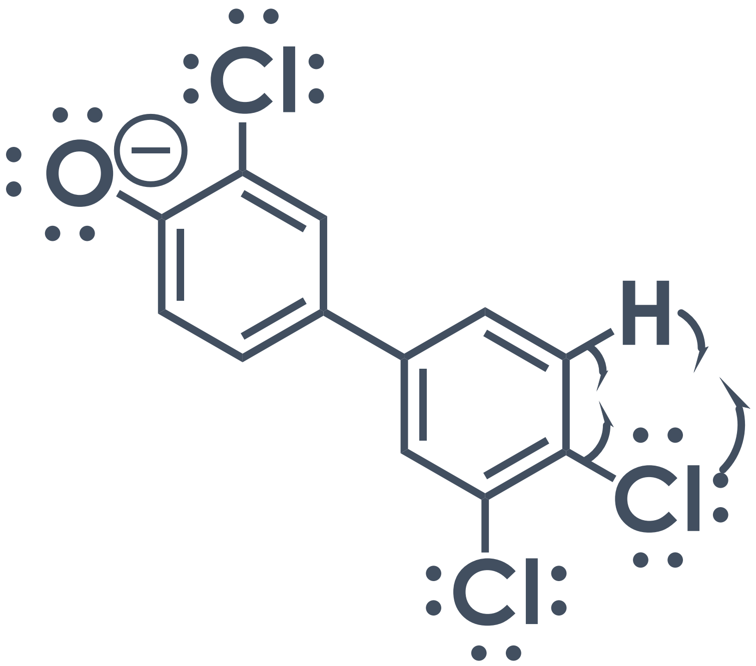
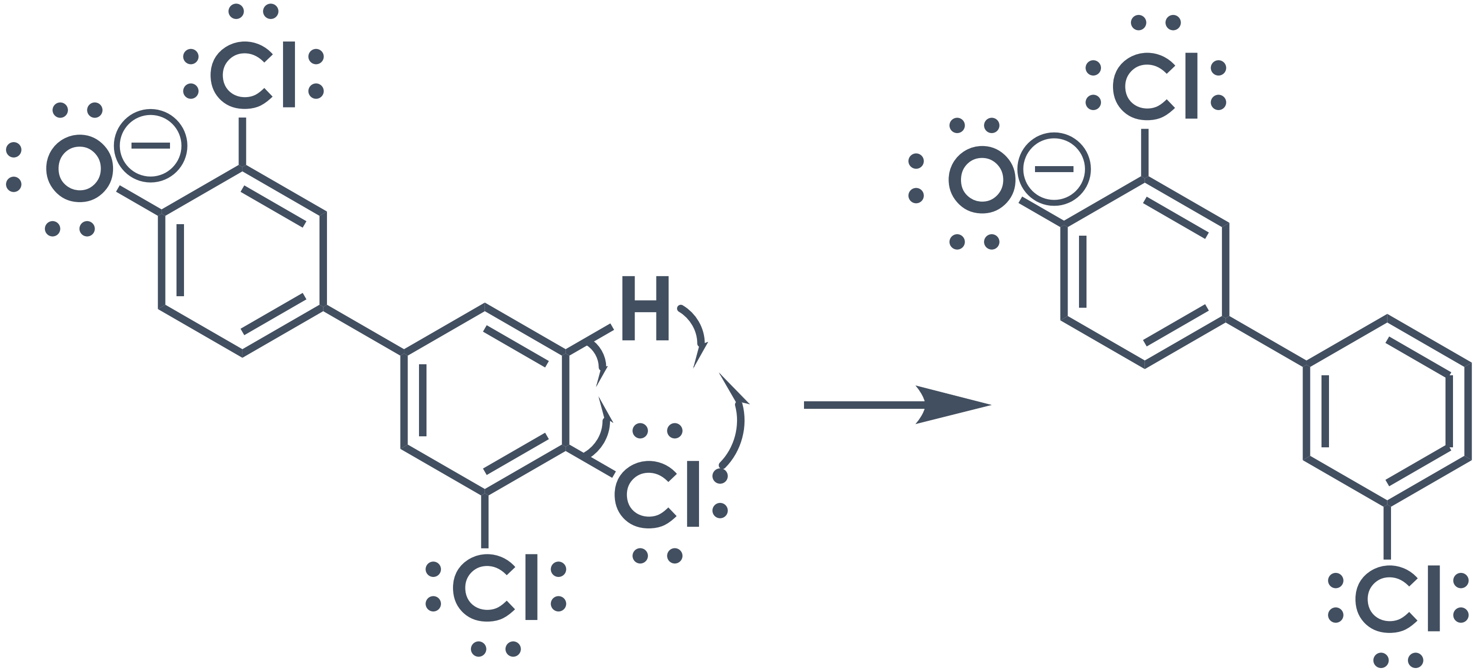
FRAGMENTATION MECHANISM

What are the structures?



FRAGMENTATION MECHANISM

What are the structures?



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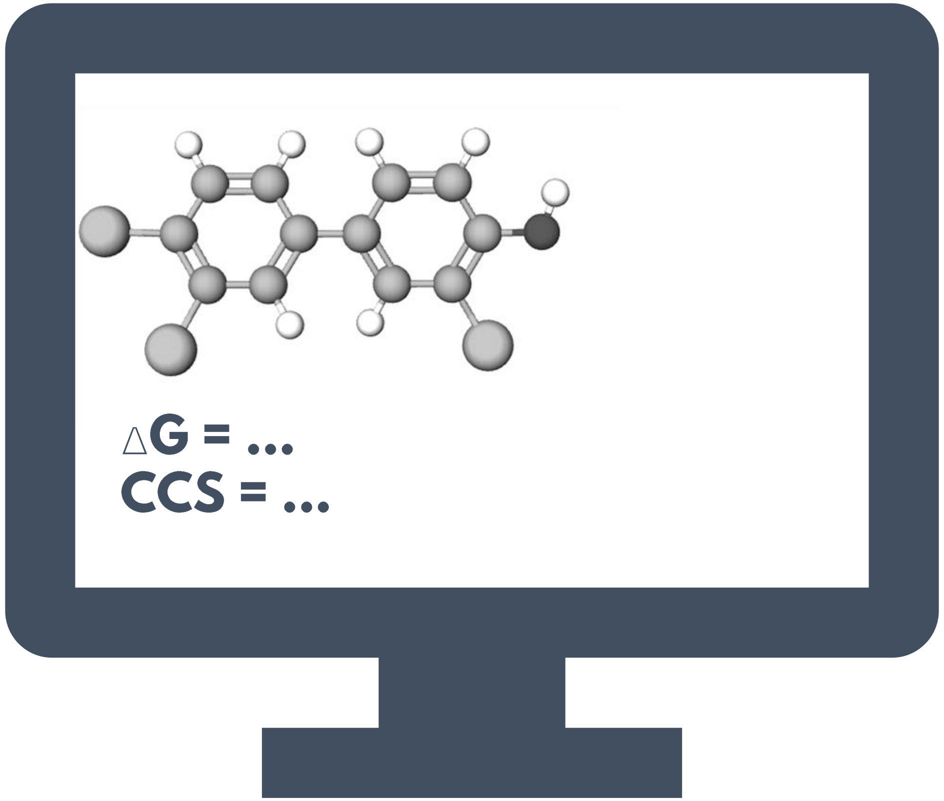
CALCULATING ∆G AND CCS



Gibbs free energy of DFT structures calculated in Gaussian 16 by Sofja Tšepelevitš

CCS calculated using IMoS Trajectory model

Gaussian 16, Frisch et al. 2016; IMoS v1.10 Larriba 2020

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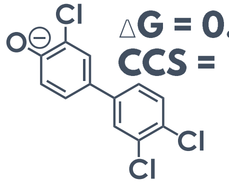
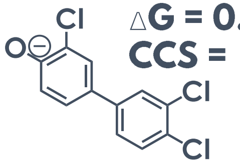
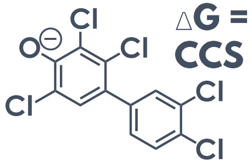
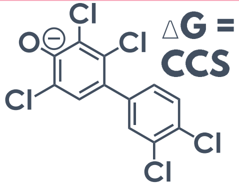
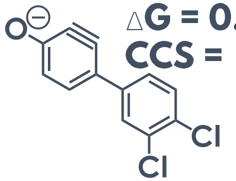
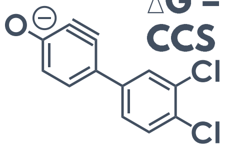
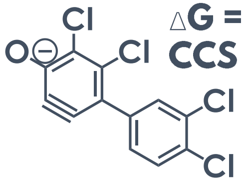
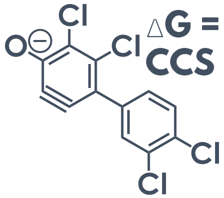
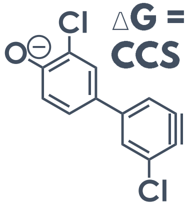
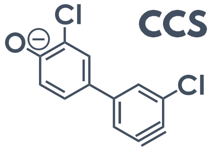
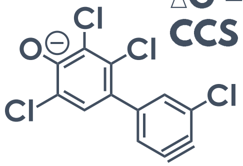
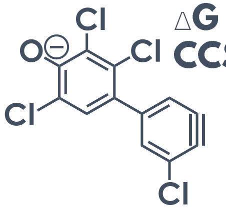
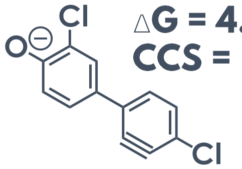
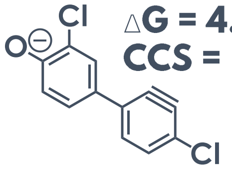
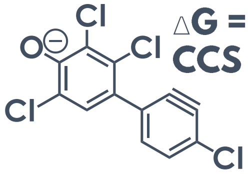
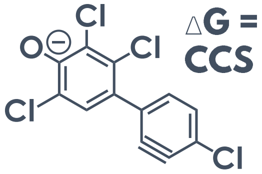
ΔG AND CCS

Gibbs free energies (kcal/mol) and CCS (A²)

4'-OH-CB35		4-OH-CB107	
$[M-H]^-$		$[M-H]^-$	
 ΔG = 0.00 CCS = 156.6	 ΔG = 0.17 CCS = 158.2	 ΔG = 0.03 CCS = 162.9	 ΔG = 0.00 CCS = 163.7
$[M-H-HCl]^-$		$[M-H-HCl]^-$	
 ΔG = 0.00 CCS = 152.0	 ΔG = 0.24 CCS = 150.9	 ΔG = 0.00 CCS = 157.4	 ΔG = 0.17 CCS = 156.8
 ΔG = 8.95 CCS = 148.9	 ΔG = 9.08 CCS = 157.3	 ΔG = 5.86 CCS = 157.2	 ΔG = 5.74 CCS = 156.6
 ΔG = 4.03 CCS = 149.8	 ΔG = 4.23 CCS = 149.9	 ΔG = 0.00 CCS = 153.4	 ΔG = 3.22 CCS = 154.3

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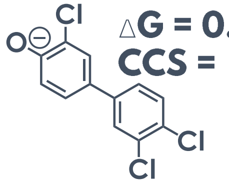
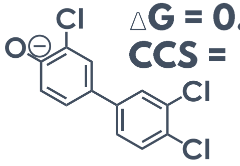
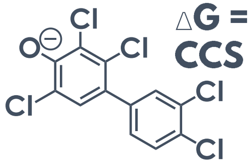
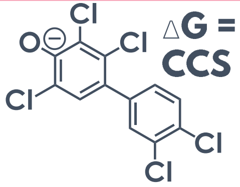
ΔG AND CCS

Gibbs free energies (kcal/mol) and CCS (A^2)

4'-OH-CB35		4-OH-CB107	
$[M-H]^-$		$[M-H]^-$	
 ΔG = 0.00 CCS = 156.6	 ΔG = 0.17 CCS = 158.2	 ΔG = 0.03 CCS = 162.9	 ΔG = 0.00 CCS = 163.7
$[M-H-HCl]^-$		$[M-H-HCl]^-$	
 ΔG = 0.00 CCS = 152.0	 ΔG = 0.24 CCS = 150.9	 ΔG = 0.00 CCS = 157.4	 ΔG = 0.17 CCS = 156.8
 ΔG = 8.95 CCS = 148.9	 ΔG = 9.08 CCS = 157.3	 ΔG = 5.86 CCS = 157.2	 ΔG = 5.74 CCS = 156.6
 ΔG = 4.03 CCS = 149.8	 ΔG = 4.23 CCS = 149.9	 ΔG = 0.00 CCS = 153.4	 ΔG = 3.22 CCS = 154.3

ΔG AND CCS

Gibbs free energies (kcal/mol) and CCS (A²)

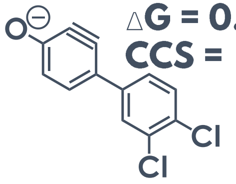
4'-OH-CB35

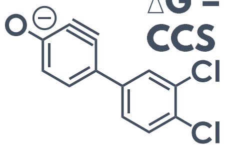
[M-H]⁻

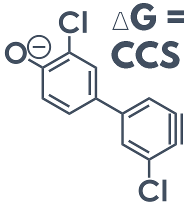
ΔG = 0.00
CCS = 156.6

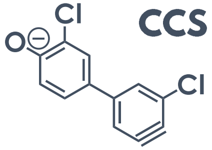
ΔG = 0.17
CCS = 158.2

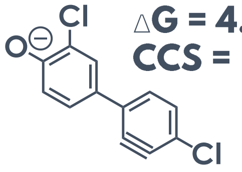
[M-H-HCl]⁻

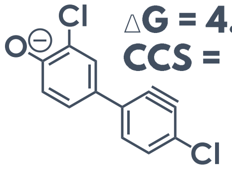

ΔG = 0.00
CCS = 152.0


ΔG = 0.24
CCS = 150.9


ΔG = 8.95
CCS = 148.9


ΔG = 9.08
CCS = 157.3


ΔG = 4.03
CCS = 149.8


ΔG = 4.23
CCS = 149.9

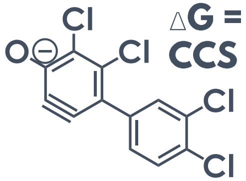
4-OH-CB107

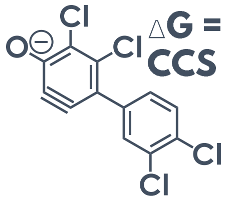
[M-H]⁻

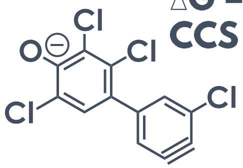
ΔG = 0.03
CCS = 162.9

ΔG = 0.00
CCS = 163.7

[M-H-HCl]⁻


ΔG = 0.00
CCS = 157.4


ΔG = 0.17
CCS = 156.8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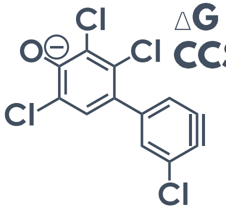
ΔG = 5.74
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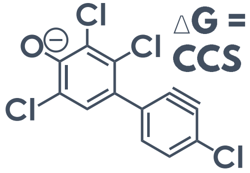
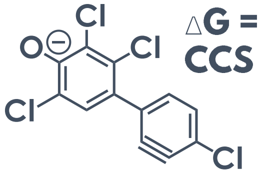

ΔG = 0.00
CCS = 153.4


ΔG = 3.22
CCS = 154.3

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ΔG AND CCS

Gibbs free energies (kcal/mol) and CCS (A^2)

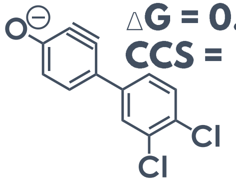
4’-OH-CB35

[M-H]$^-$

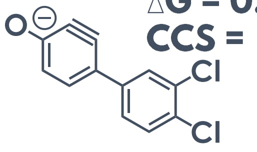
ΔG = 0.00
CCS = 156.6

ΔG = 0.17
CCS = 158.2

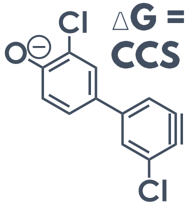
[M-H-HCl]$^-$



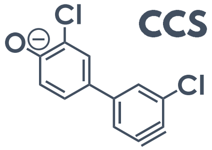
ΔG = 0.00
CCS = 152.0



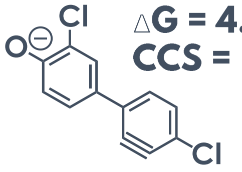
ΔG = 0.24
CCS = 150.9



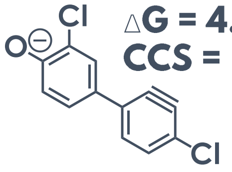
ΔG = 8.95
CCS = 148.9



ΔG = 9.08
CCS = 157.3



ΔG = 4.03
CCS = 149.8



ΔG = 4.23
CCS = 149.9

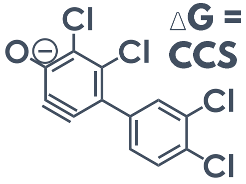
4-OH-CB107

[M-H]$^-$

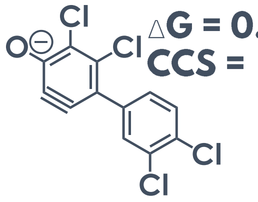
ΔG = 0.03
CCS = 162.9

ΔG = 0.00
CCS = 163.7

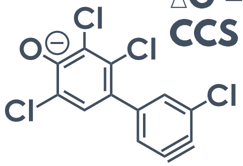
[M-H-HCl]$^-$



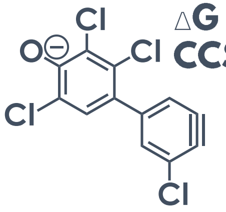
ΔG = 0.00
CCS = 157.4



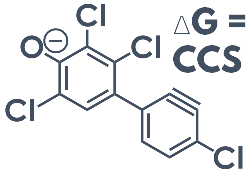
ΔG = 0.17
CCS = 156.8



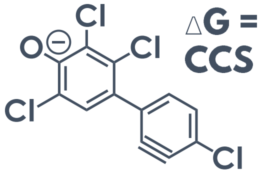
ΔG = 5.86
CCS = 157.2



ΔG = 5.74
CCS = 156.6



ΔG = 0.00
CCS = 153.4



ΔG = 3.22
CCS = 154.3

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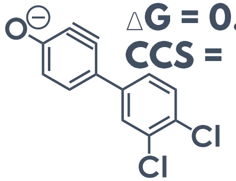
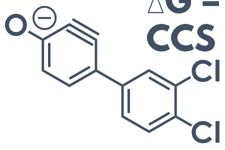
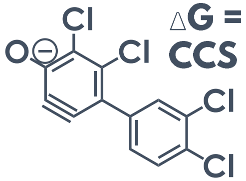
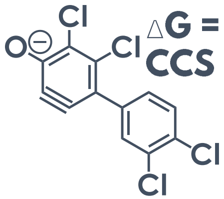
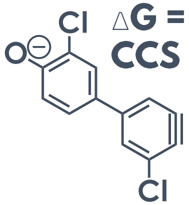
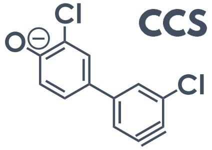
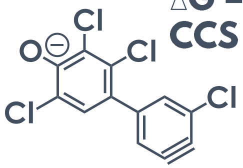
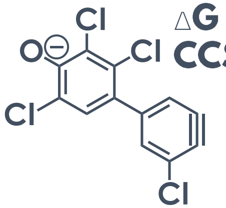
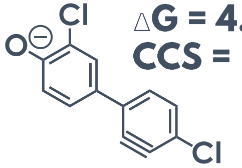
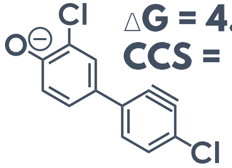
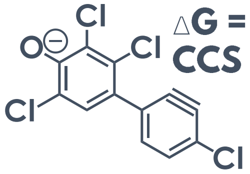
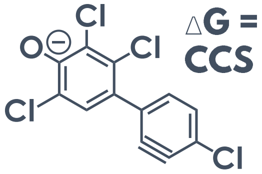
ΔG AND CCS

Gibbs free energies (kcal/mol) and CCS ($Å^2$)

4'-OH-CB35		4-OH-CB107	
$[M-H]^-$		$[M-H]^-$	
ΔG = 0.00 CCS = 156.6	ΔG = 0.17 CCS = 158.2	ΔG = 0.03 CCS = 162.9	ΔG = 0.00 CCS = 163.7
$[M-H-HCl]^-$		$[M-H-HCl]^-$	
 ΔG = 0.00 CCS = 152.0	 ΔG = 0.24 CCS = 150.9	 ΔG = 0.00 CCS = 157.4	 ΔG = 0.17 CCS = 156.8
 ΔG = 8.95 CCS = 148.9	 ΔG = 9.08 CCS = 157.3	 ΔG = 5.86 CCS = 157.2	 ΔG = 5.74 CCS = 156.6
 ΔG = 4.03 CCS = 149.8	 ΔG = 4.23 CCS = 149.9	 ΔG = 0.00 CCS = 153.4	 ΔG = 3.22 CCS = 154.3

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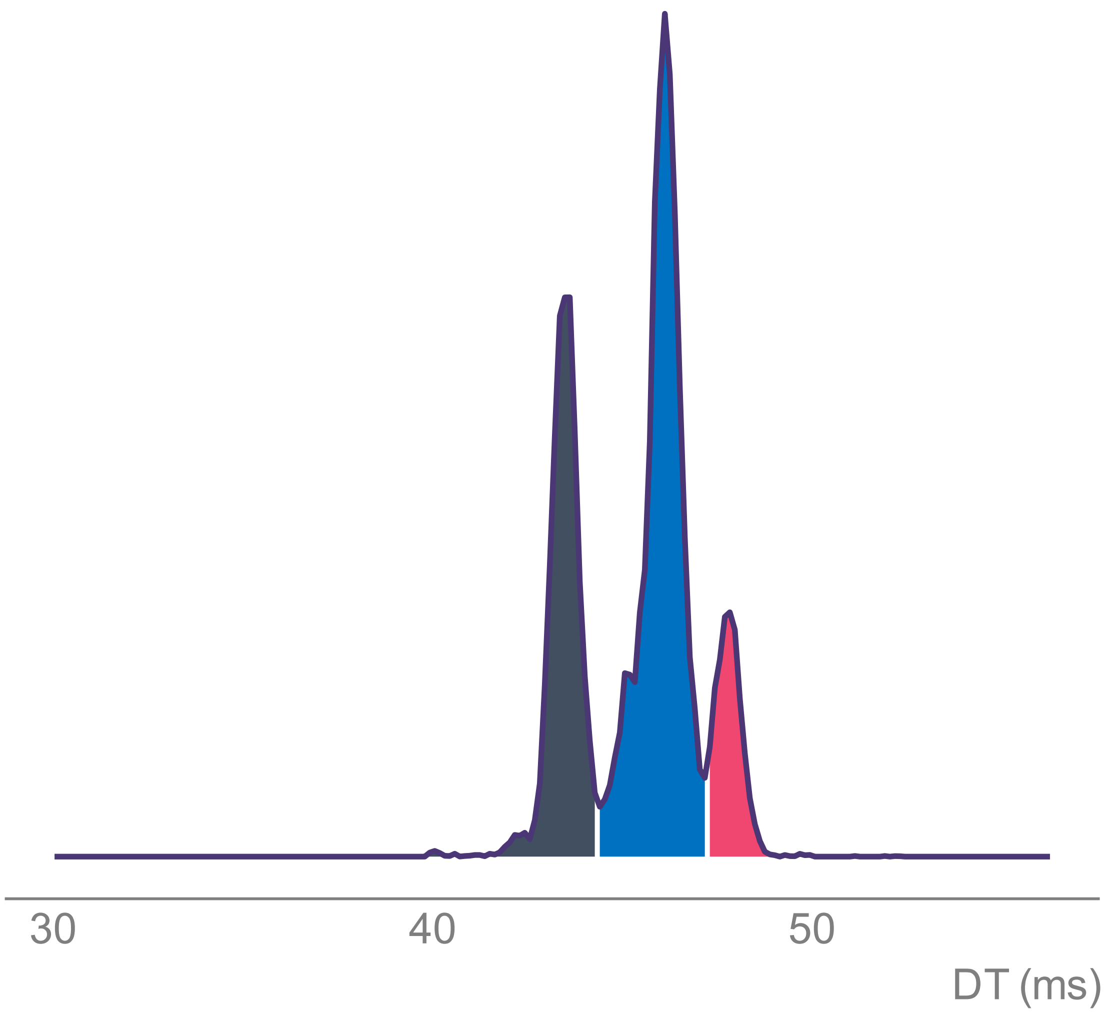
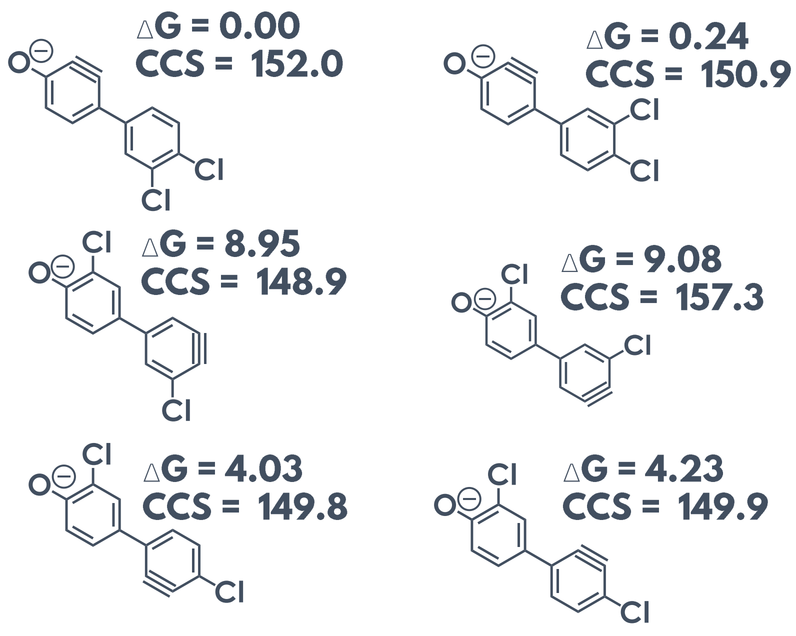
ASSIGNING THE FRAGMENT STRUCTURES





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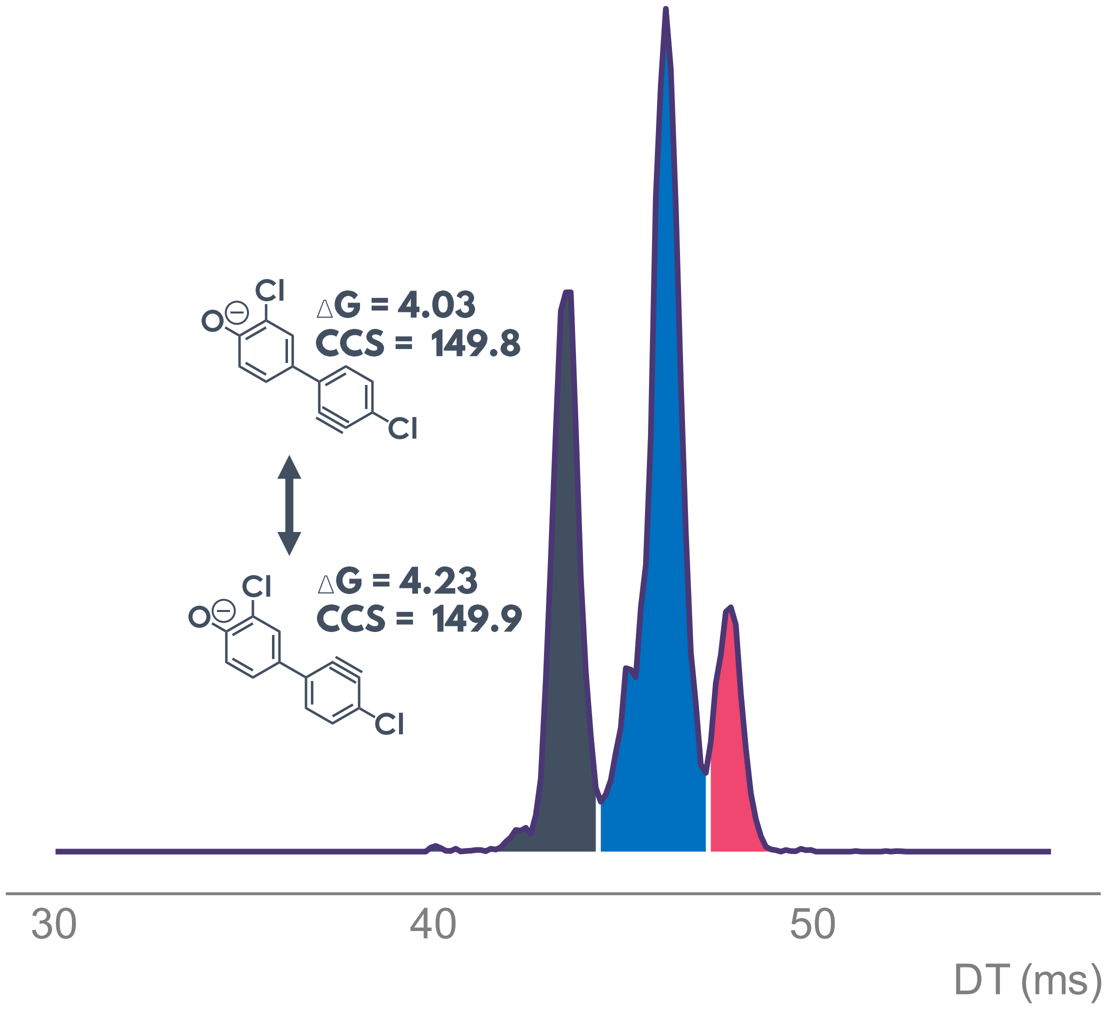
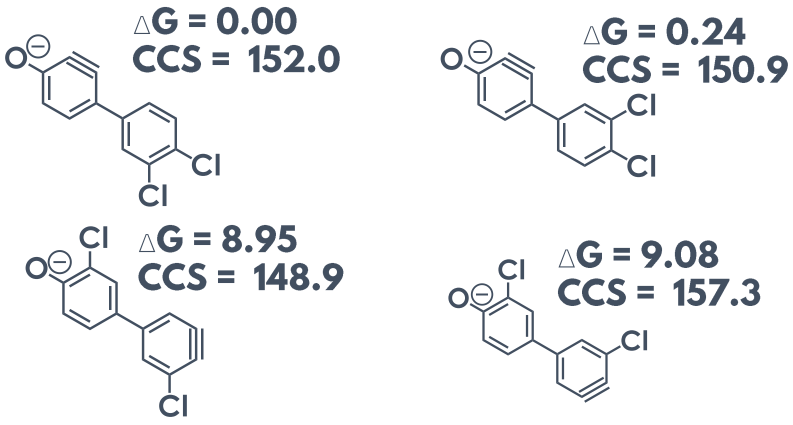
ASSIGNING THE FRAGMENT STRUCTURES





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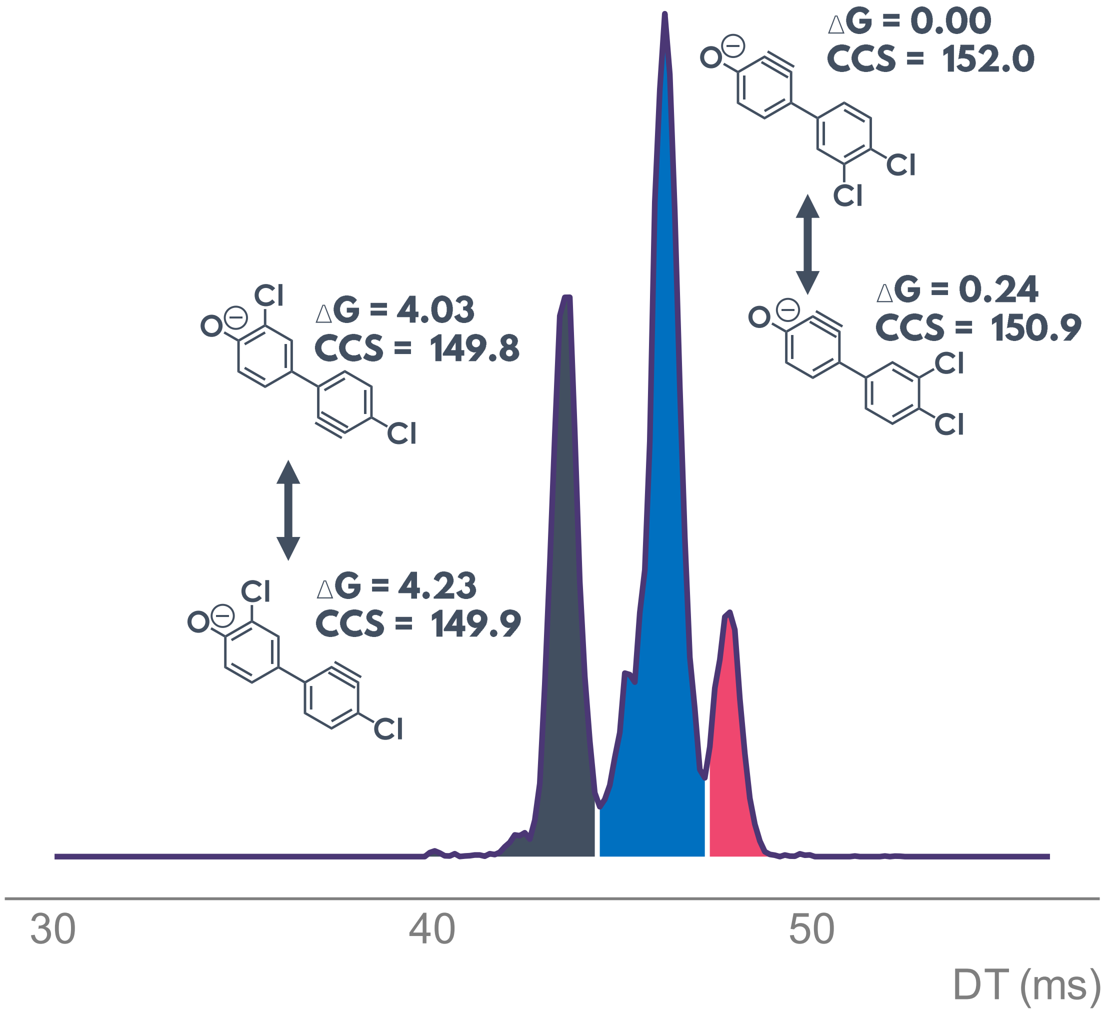
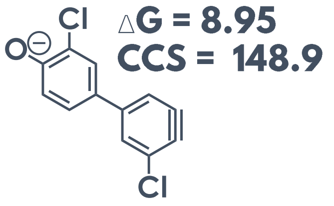
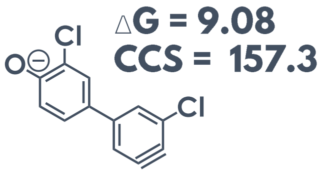
ASSIGNING THE FRAGMENT STRUCTURES







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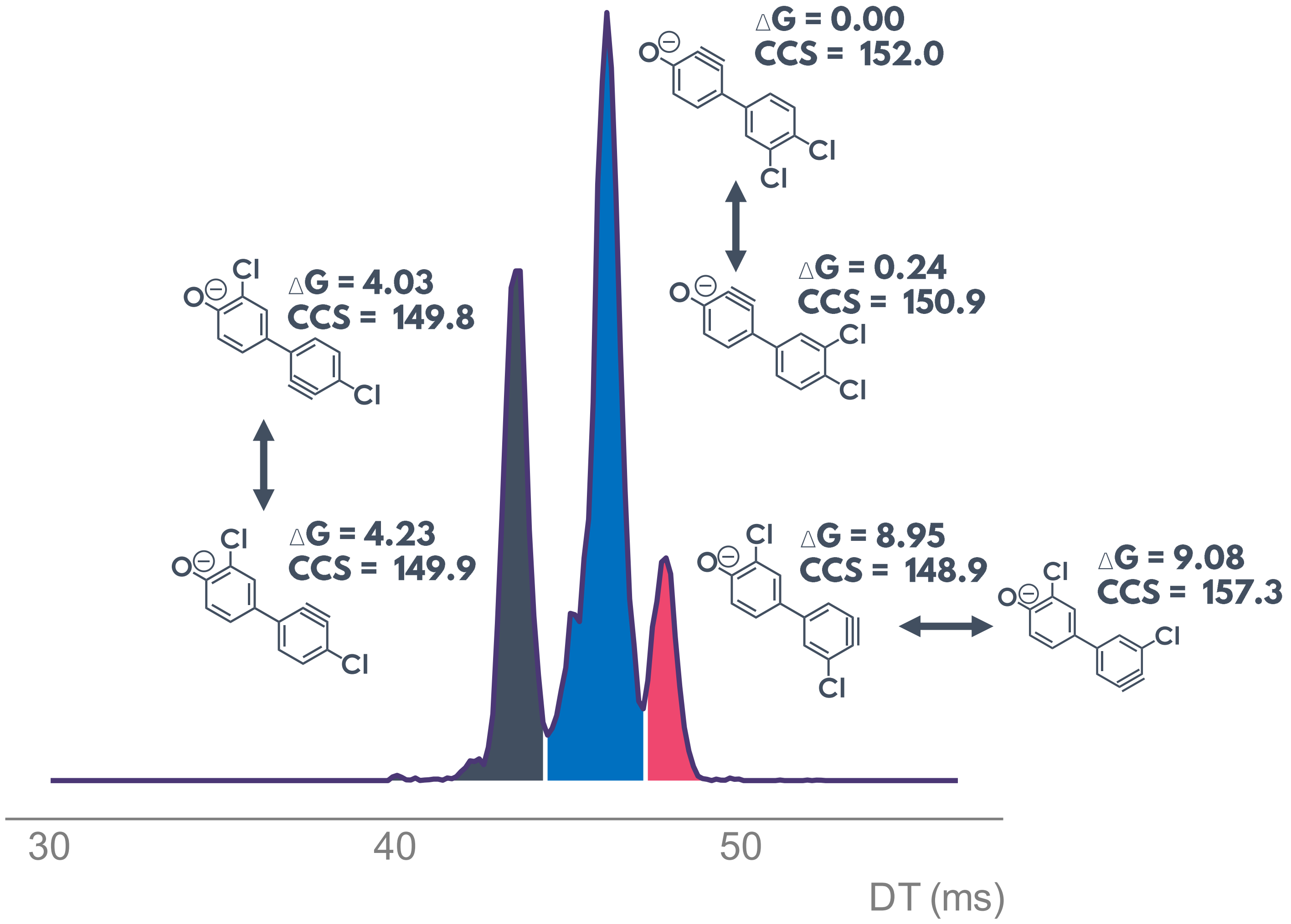
ASSIGNING THE FRAGMENT STRUCTURES



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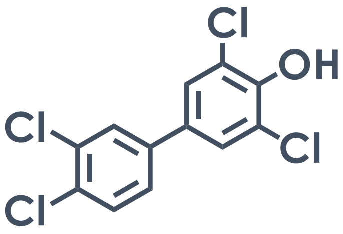
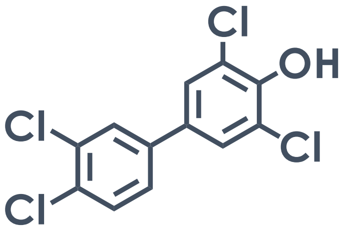
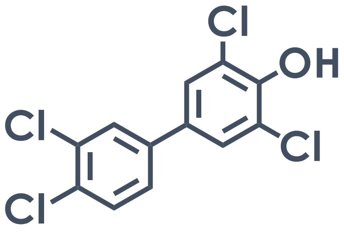
CONCLUSIONS



Analysing CCS of parent and fragment ions together can be more informative



The OH-PCBs form isomeric fragments which may be useful for identification



Combining IMS^n with CCS and DFT calculations can aid the determination of fragment structures

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Sofja Tšepelevitš, Henrik Hupatz

Kruve lab group

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