

EPR/MS combination: Mechanism elucidation applied to thiol compounds

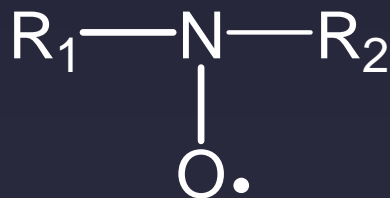


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à la Chimie Structurale, Campus de St Jérôme, 13397 Marseille cedex 20.

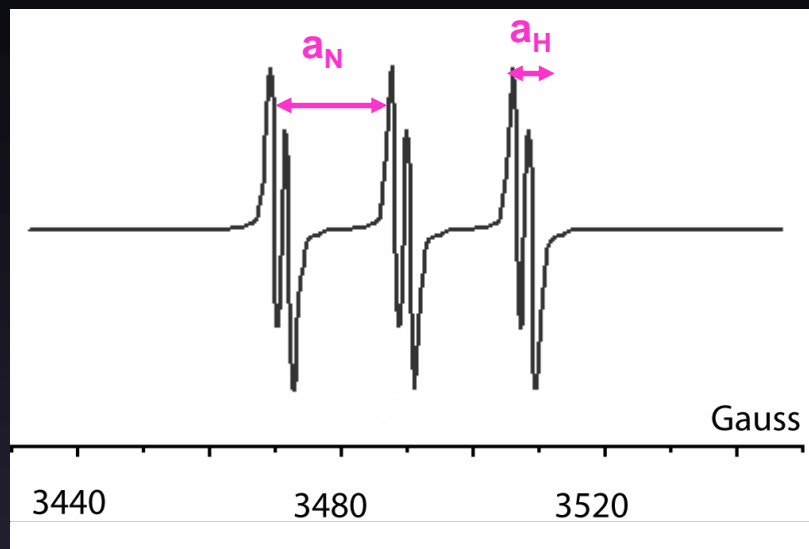
Electronic Paramagnetic Resonance

- Specificity → paramagnetic species only
- Sensitivity → concentration 10^{-7} - 10^{-8} mol/L
- Structure → g factor, hyperfine coupling constants...



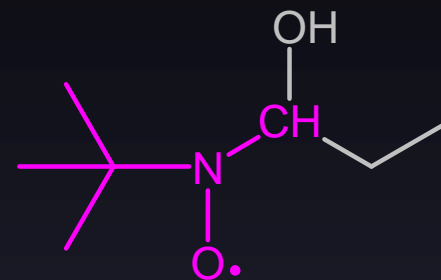
Nitroxide

EPR/MS Combination



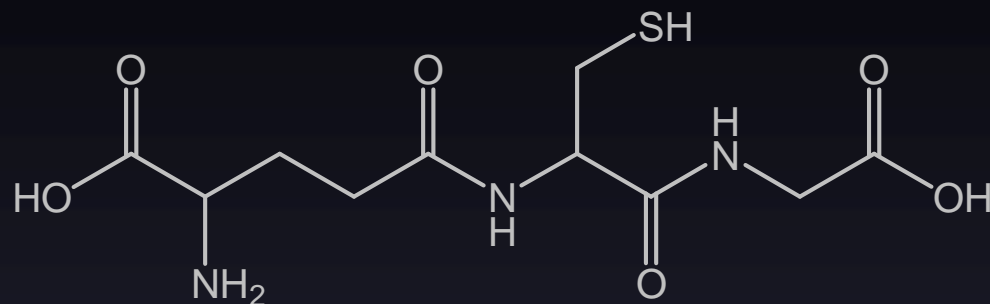
$a_N \sim 15.5 \text{ G}$

$a_H \sim 1.8 \text{ G}$

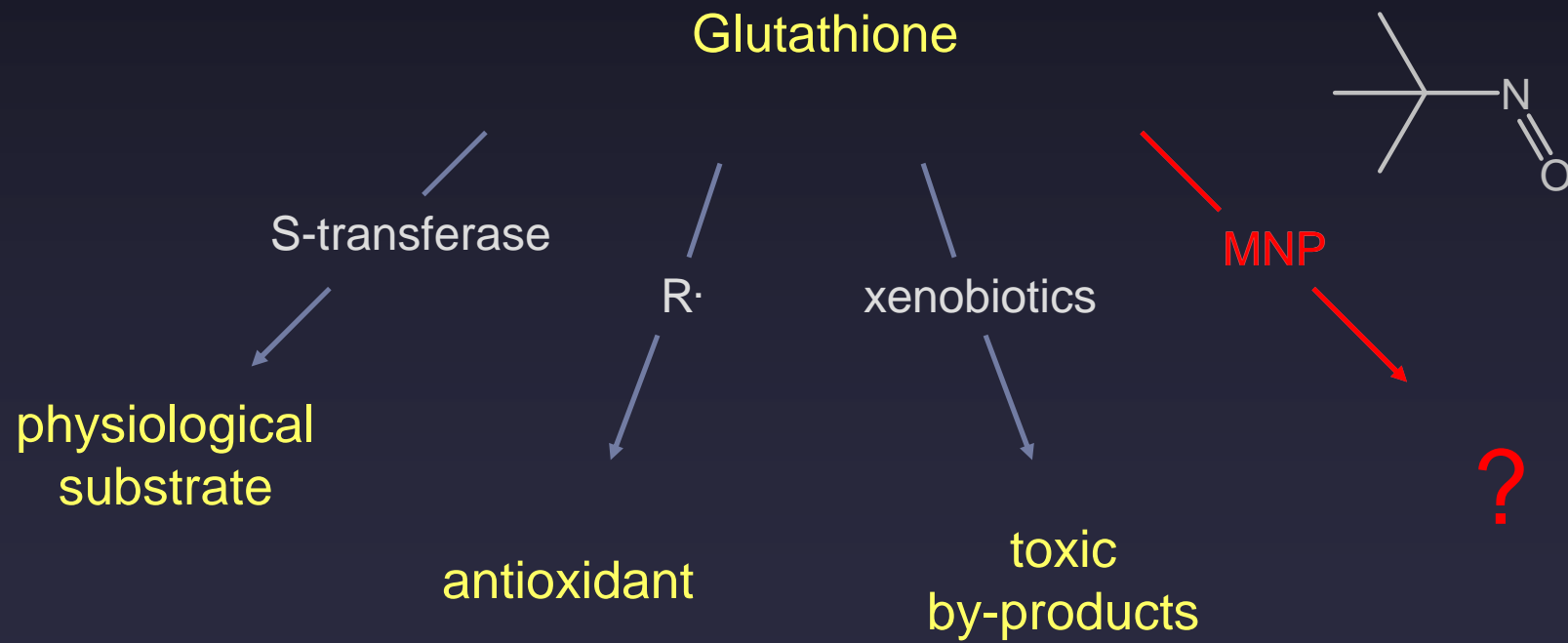


How to access the global structure of nitroxide ?

Aim of the study: reactivity of glutathione toward MNP



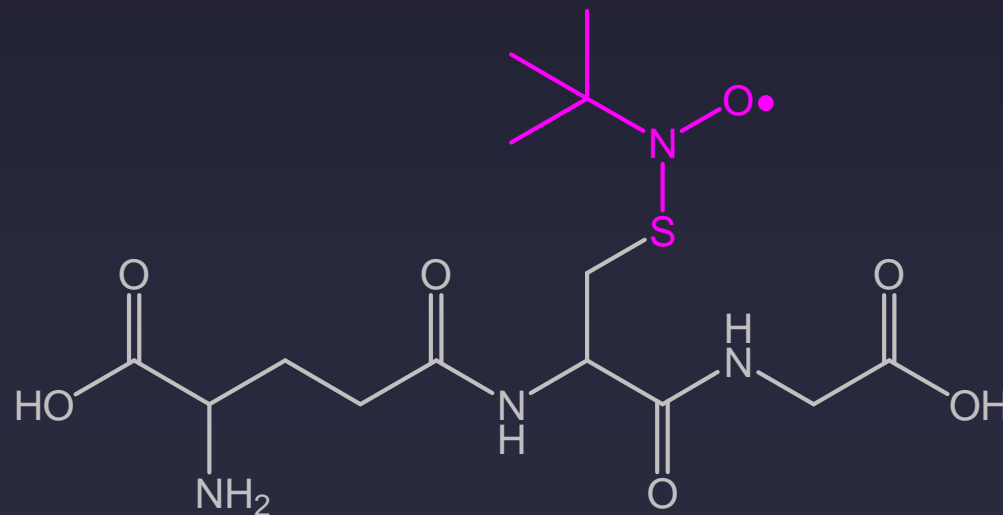
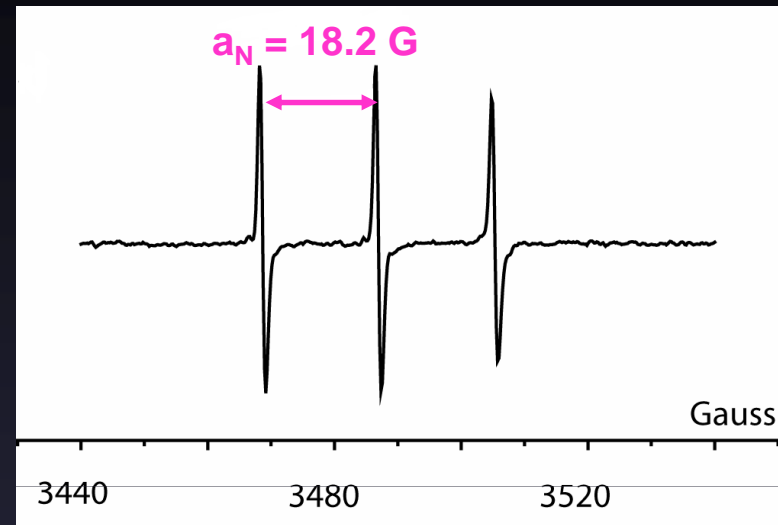
Glutathione



S-adduct

Experimental conditions

- 1) Glutathione
MNP
- 2) Oxidant



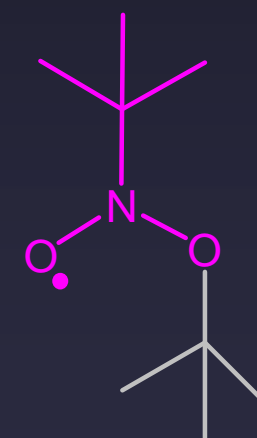
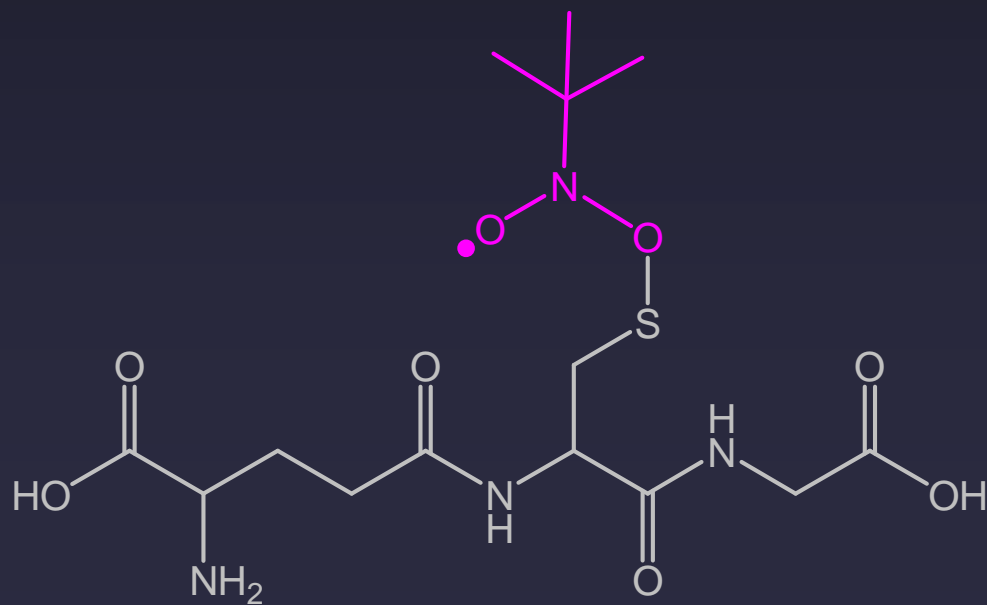
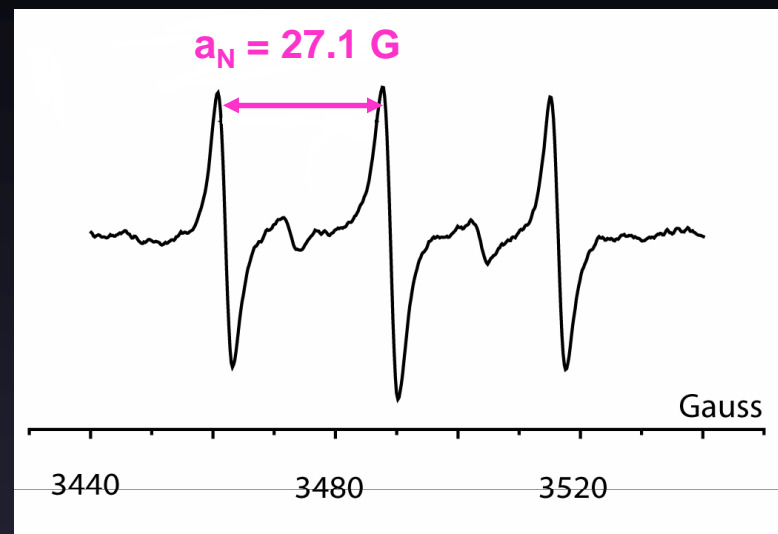
EPR Study

O-adduct

Experimental conditions

1) Glutathione
MNP
Oxidant

2) Photo-irradiation

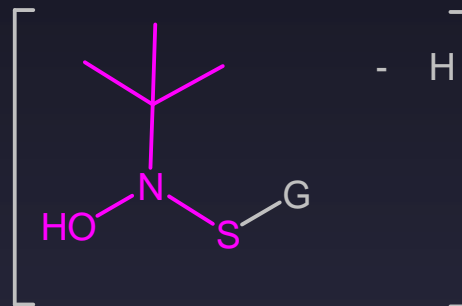


MS Study

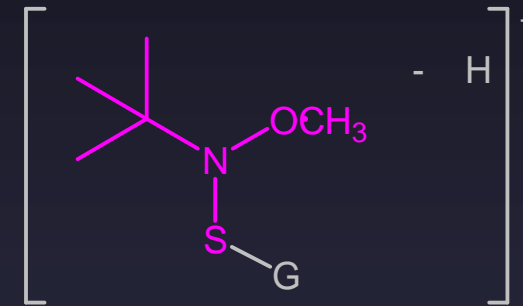
ESI-MS in negative mode

- No Detection of S- and O-adducts as nitroxides
- Detection of derived redox species

S-adduct

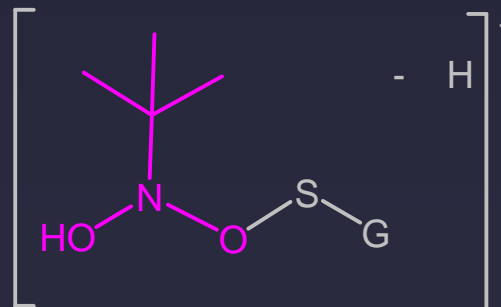


m/z 393.1



m/z 407.1

O-adduct

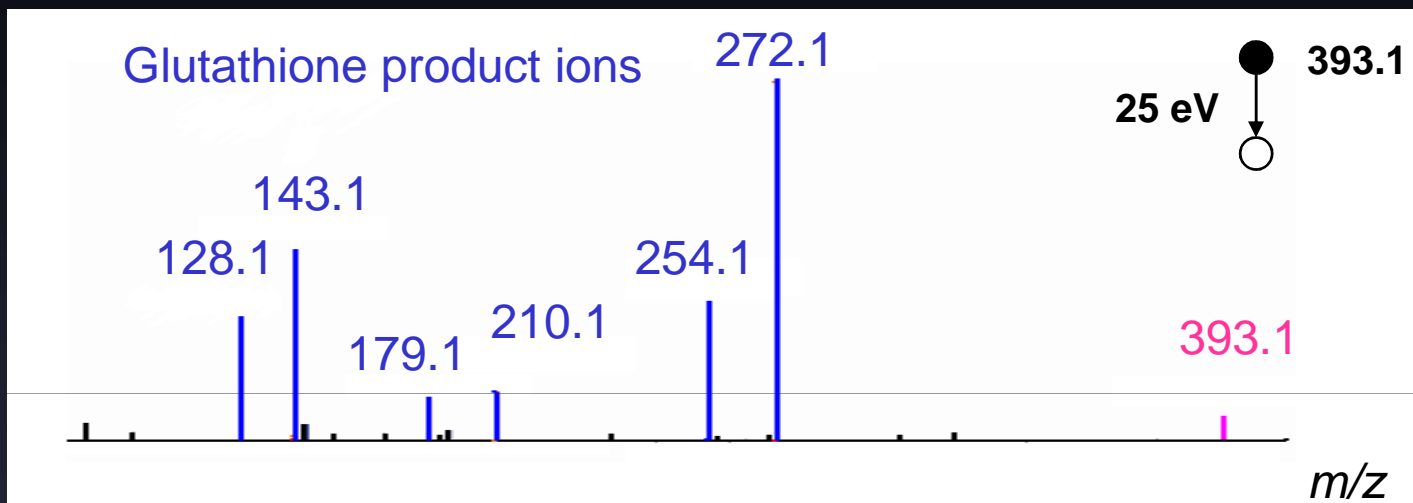


m/z 409.1

MS/MS Study

S-adduct

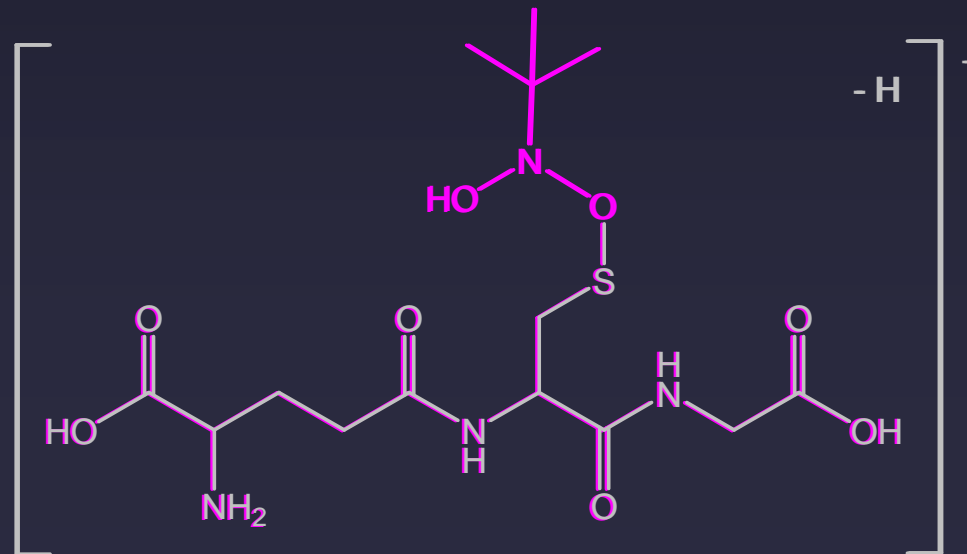
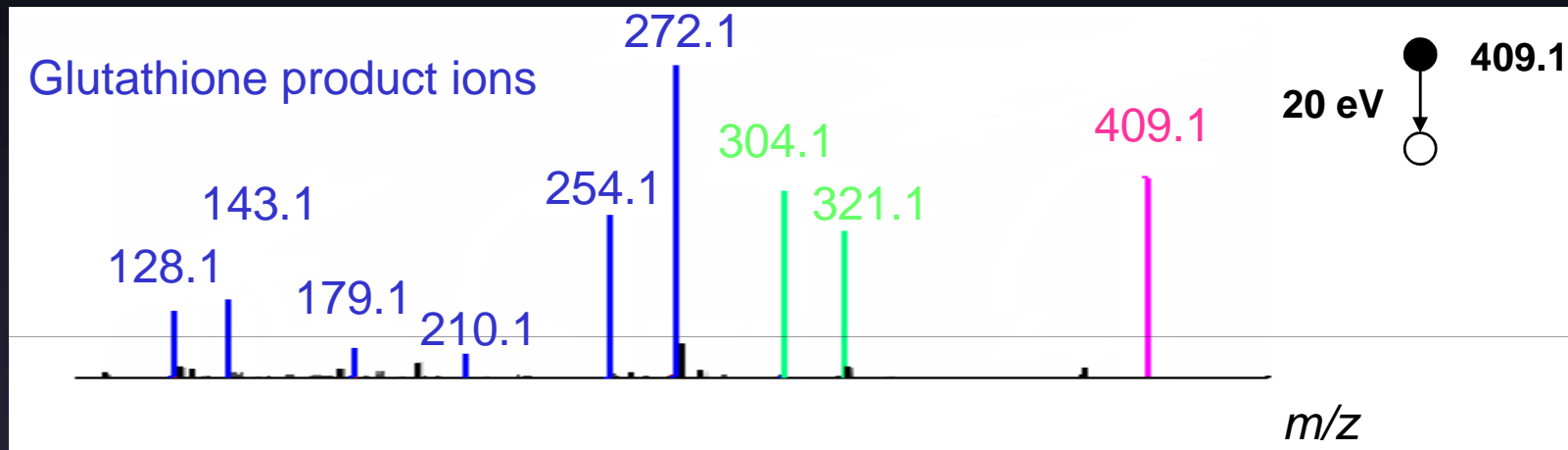
ESI-MS/MS in negative mode



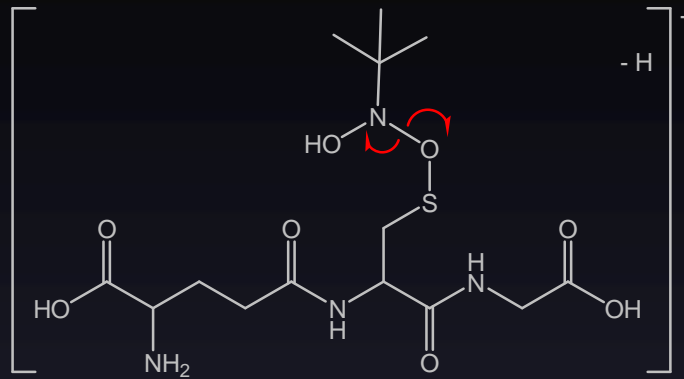
MS/MS Study

O-adduct

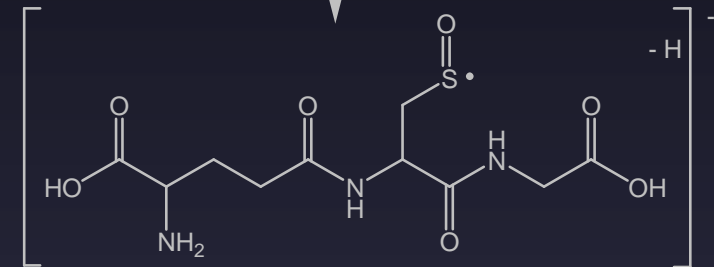
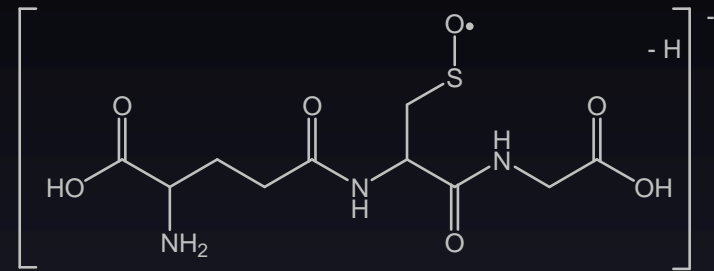
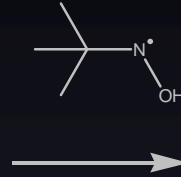
ESI-MS/MS in negative mode



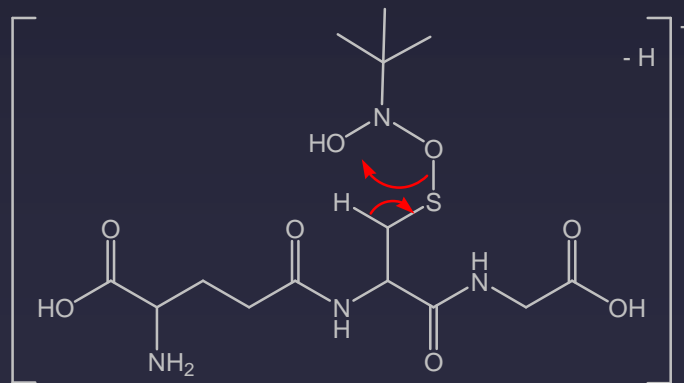
MS/MS Study



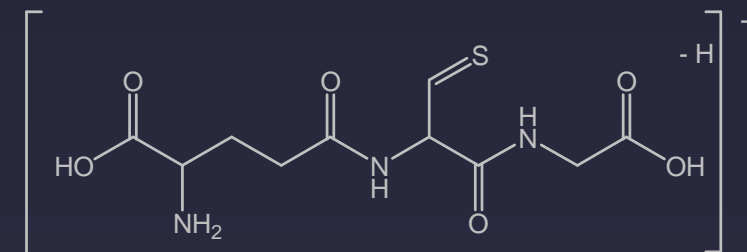
m/z 409.1



m/z 321.1



m/z 409.1



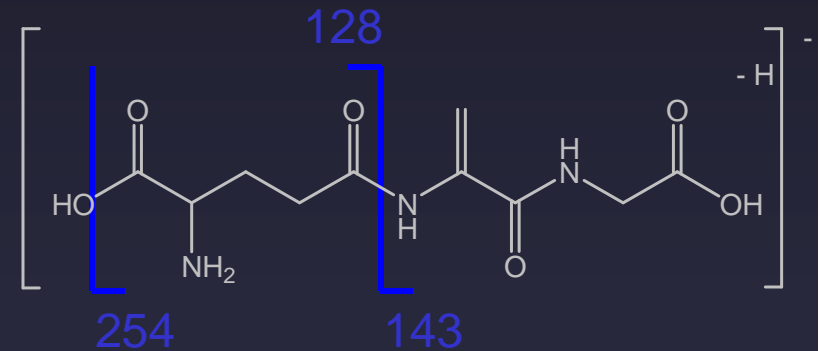
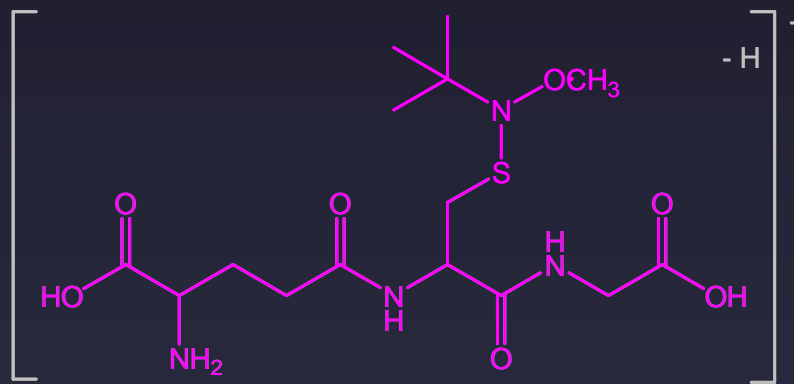
m/z 304.1

MS/MS Study

Methylated product of S-adduct

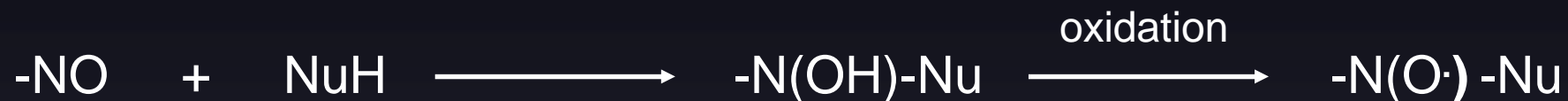
ESI-MS/MS in negative mode

Glutathione product ions



Mechanism elucidation

Forrester-Hepburn



Inverted spin trapping

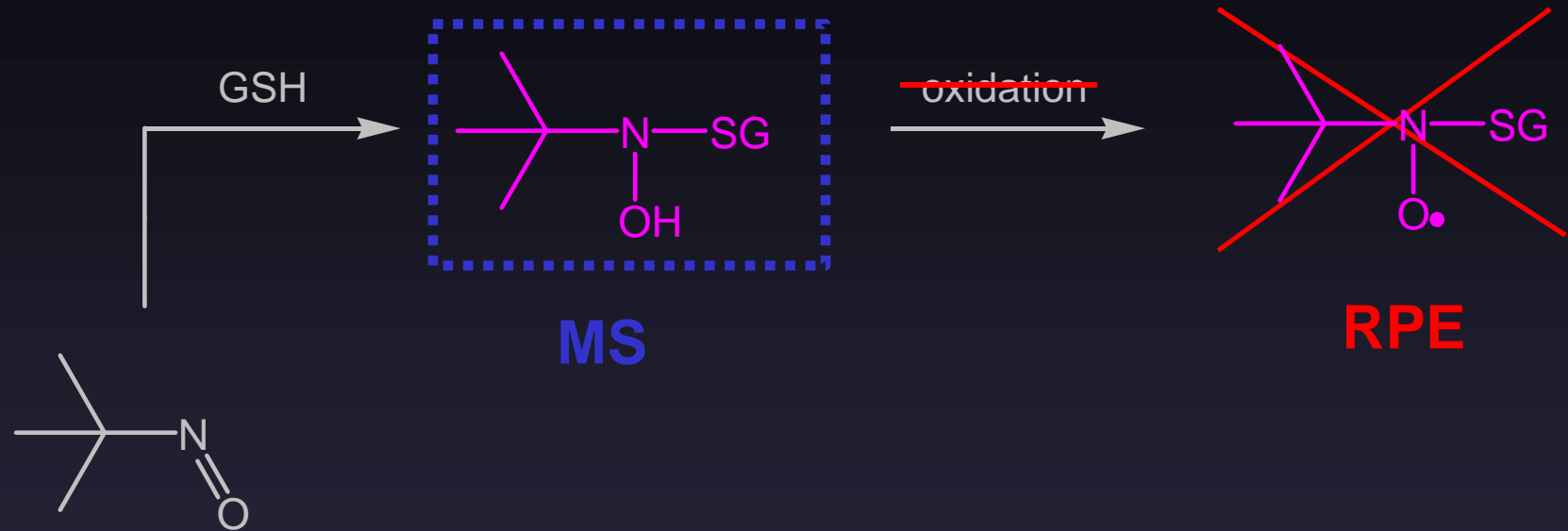


Detection of reaction intermediates
Distinct experimental conditions

Mechanism elucidation

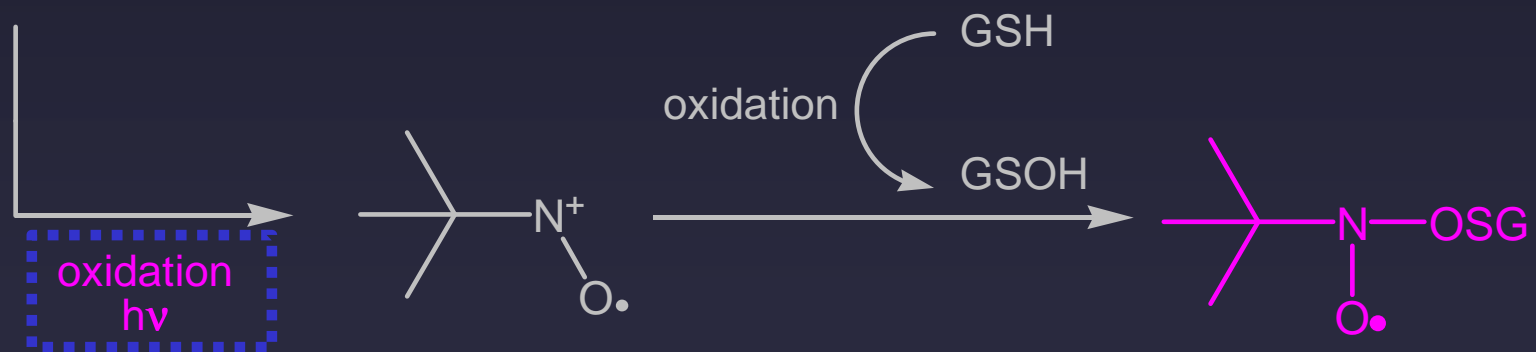
S-adduct

Forrester-Hepburn



O-adduct

Inverted spin trapping



Conclusion

MNP/GSH/oxidant

Stable S-adduct

New O-adduct

Derivatization methylated product



Detailed reactivity of glutathione toward MNP

EPR/MS

Structural characterization

Mechanism elucidation



Efficient method for radical study

Acknowledgments

Organization committee

SMAP 2009

SACS team

Provence University,
Laboratory LCP,
Marseille

Spectropole

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