Supporting Information

Radiation- and Photo-induced Oxidation Pathways of Methionine in Model Peptide Backbone Under Anoxic Conditions

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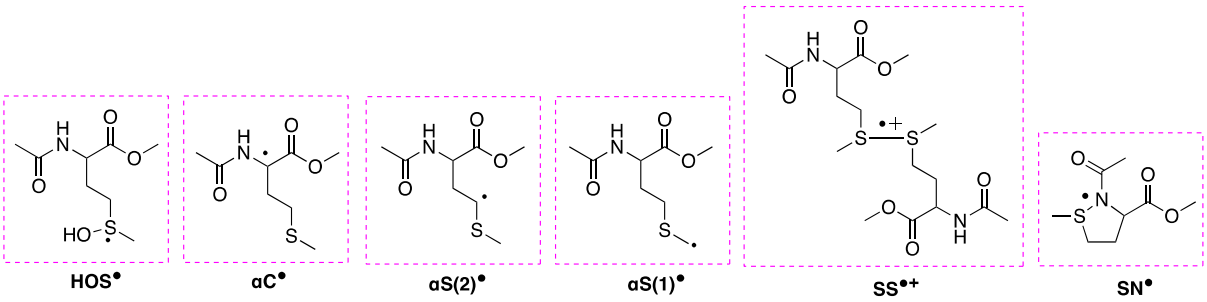


Figure S1. The structures of six reactive intermediates identified in the pulse radiolysis experiments.

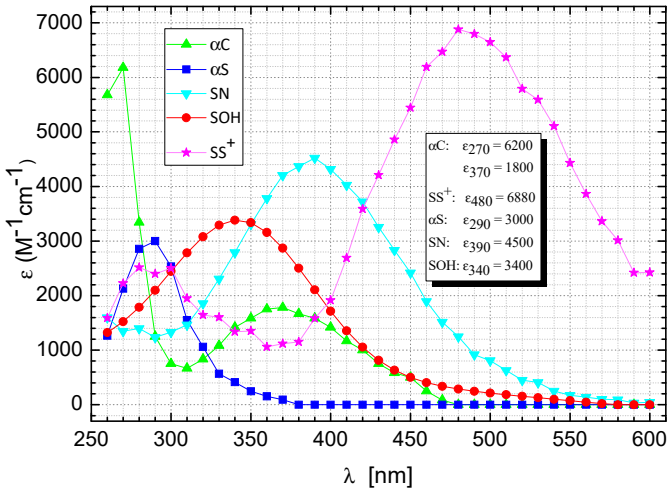


Figure S2. Reference spectra used in the resolutions of the transient absorption spectra following •OH-induced oxidation of $CH_3C(O)N$-Met-OCH_3.

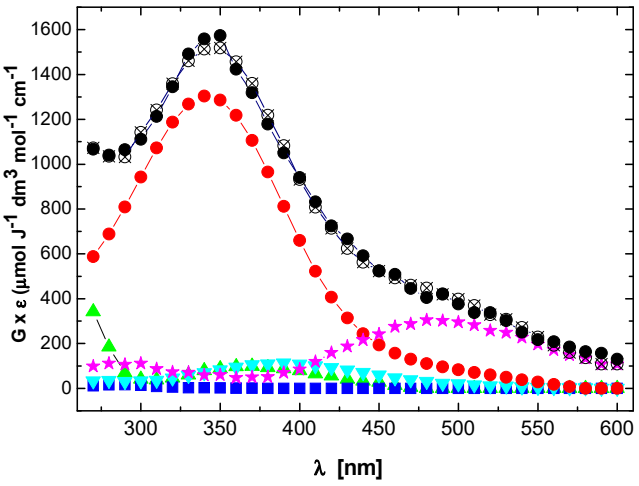


Figure S3. Resolution of the spectral components: HOS• (●), αC• (▲), αS(1)• and αS(2)• (■), SS•+ (★), SN• (▼) in the transient absorption spectrum recorded 1.1 μs (●– experimental; ⊗– fit) after the electron pulse in N_2O-saturated aqueous solution containing 0.2 mM AcN-Met-OMe at pH 7.0.

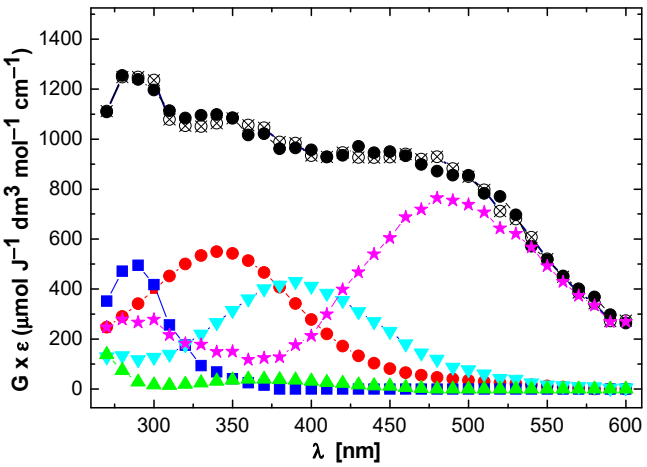


Figure S4. Resolution of the spectral components: HOS$^{\bullet}$ (●), αC$^{\bullet}$ (▲), αS(1)$^{\bullet}$ and αS(2)$^{\bullet}$ (■), SS$^{\bullet+}$ (★), SN$^{\bullet}$ (▼) in the transient absorption spectrum recorded 3 μs (●– experimental; ⊗– fit) after the electron pulse in N_2O-saturated aqueous solution containing 0.2 mM AcN-Met-OMe at pH 7.0

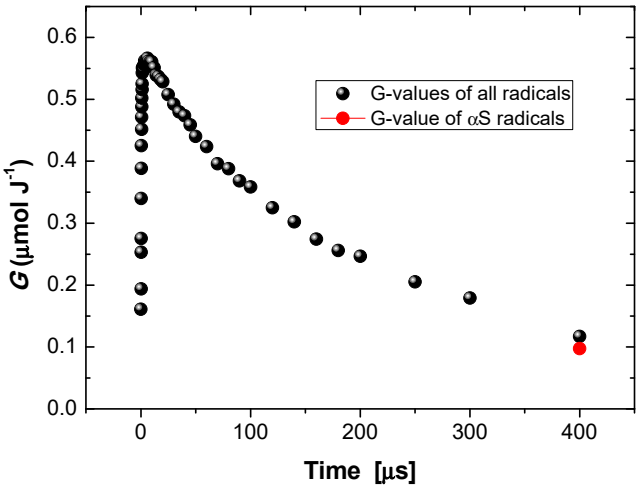


Figure S5. The sum of all radicals (HOS$^{\bullet}$, αC$^{\bullet}$, SS$^{\bullet+}$, SN$^{\bullet}$, αS$^{\bullet}$) taken in spectral resolution as a function of time.

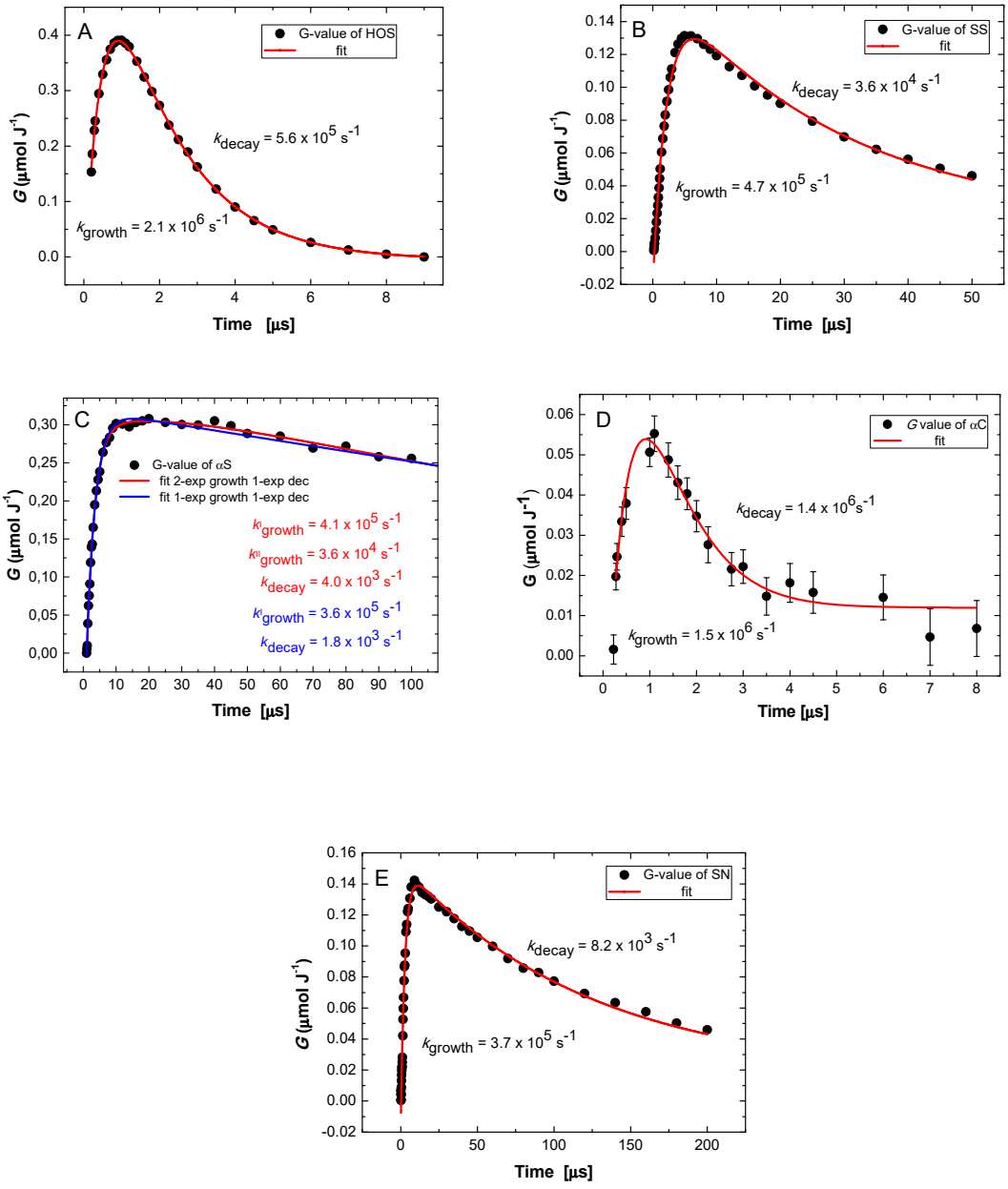
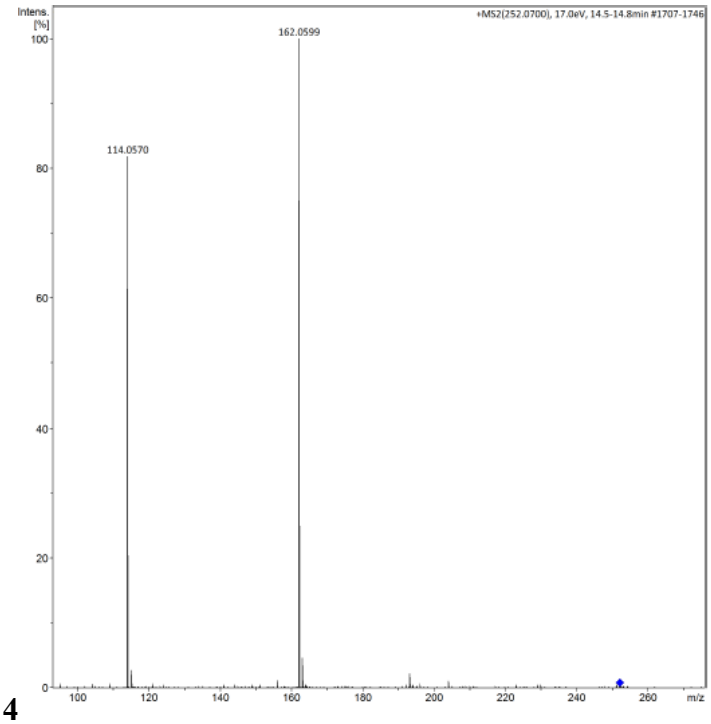
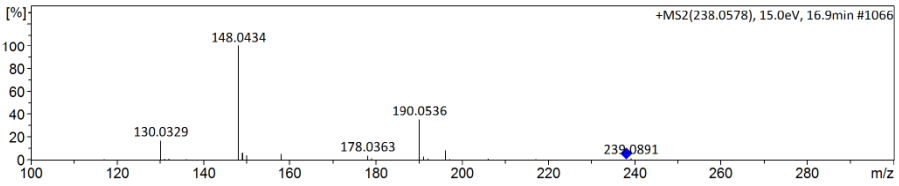


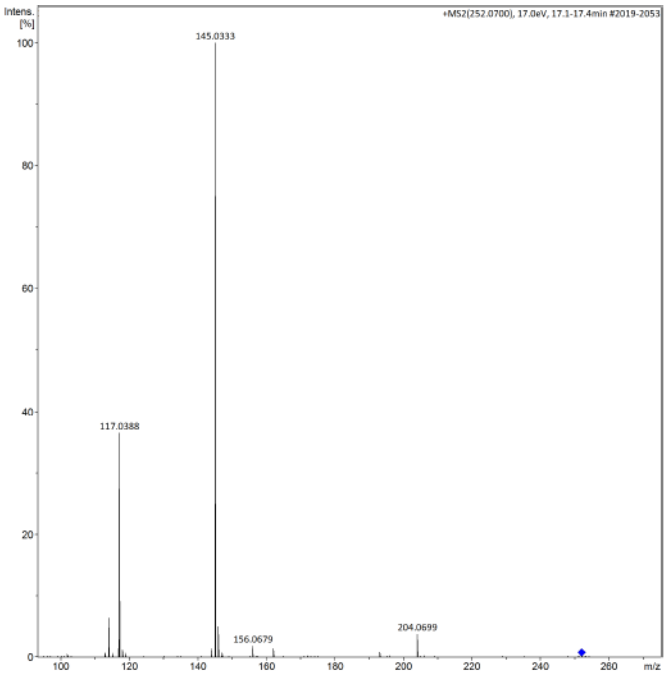
Figure S6. First-order kinetic fits of the growth and decay of radicals HOS$^{\bullet}$ (panel A), SS$^{\bullet+}$ (panel B), αS$^{\bullet}$ (panel C), αC$^{\bullet}$ (panel D), and SN$^{\bullet}$ (panel E).



Compound **4**



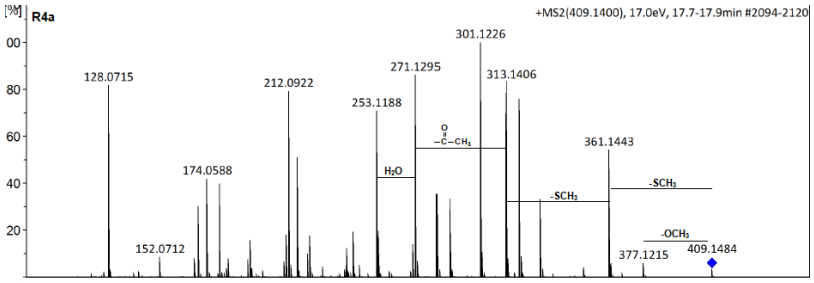
Compound **5**



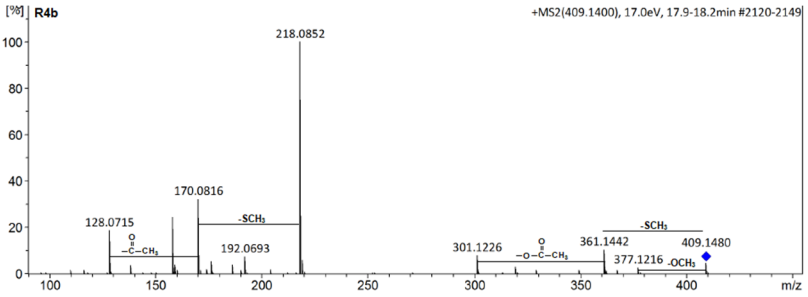
Compound **6**

Figure S7. High-resolution MS/MS spectra of the products **4** (*m/z* 252.0731) and **6** (*m/z 252.0732*) derived from the cross-termination of **αS (1)**• and **αS(2)**• with CH_3S• and product **5** (m/z 238.0578) – a disulfide.

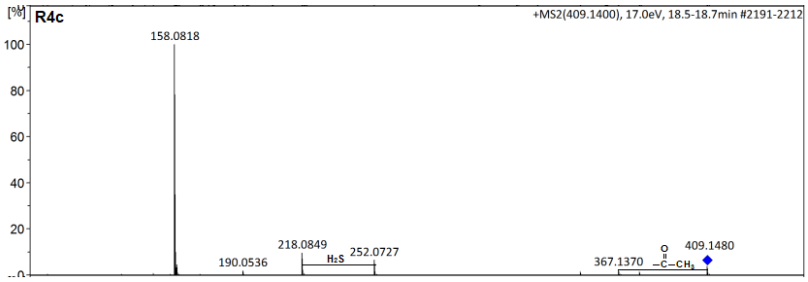
Compound **7**



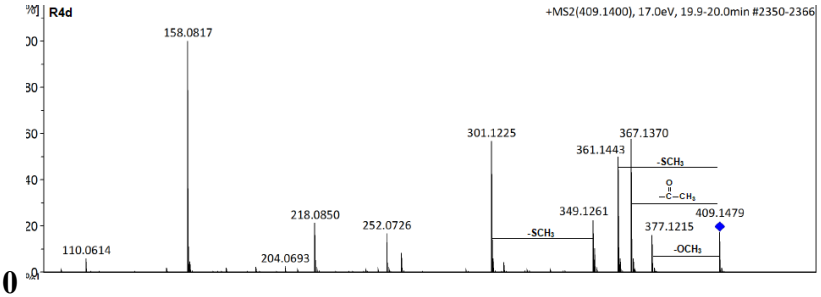
Compound **8**



Compound **9**



Compound **10**



Compound **11**

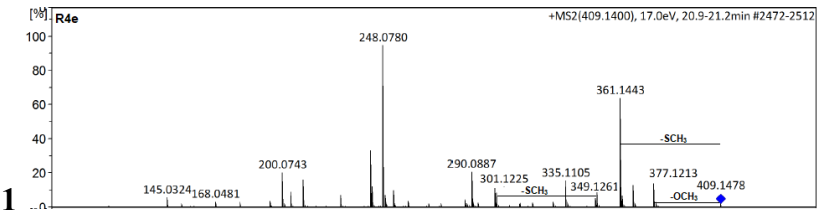


Figure S8. High-resolution MS/MS spectra of the five dimeric products **7** (*m/z* 409.1484), **8** (*m/z* 409.1480), **9** (*m/z* 409.1480), **10** (*m/z* 409.1479) and **11** (*m/z* 409.1478) derived from the combination of two **αS•** radicals.

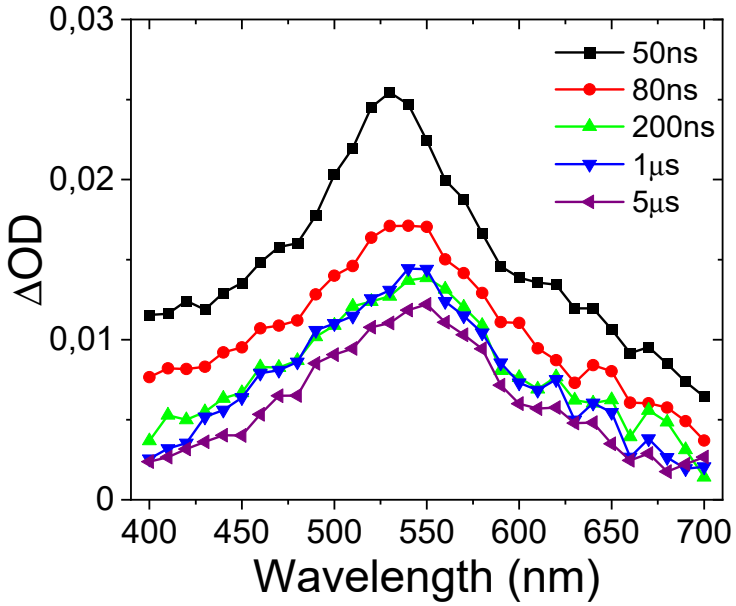
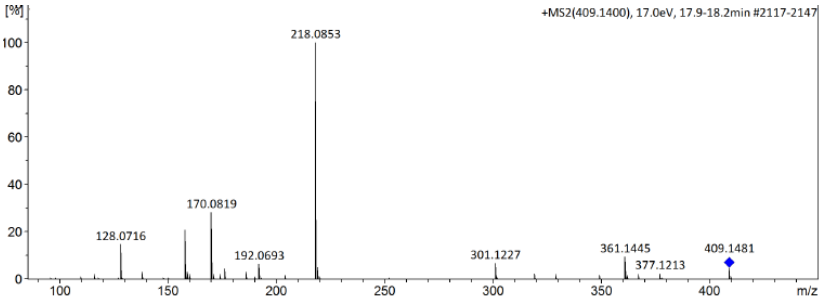
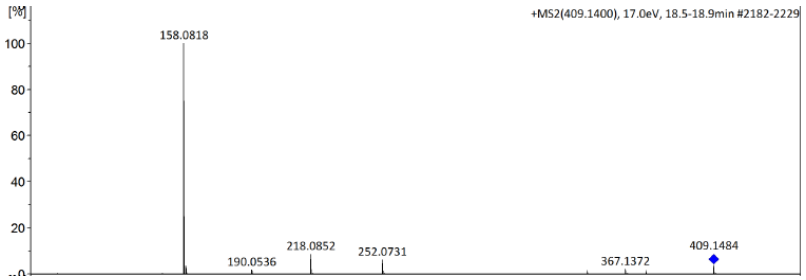


Figure S9. Transient absorption spectra following LFP of CB (4mM) and *N*-AcMetOCH$_3$ (20mM) for different delay times at pH 7. The initially formed CB excited triplet with a transient absorption maximum at 520 nm (50 ns delay time) yields ketyl radical CBH$^\bullet$ with a maximum at 550 nm (observed at 1-5 μs timescale).

Photolysis 8



Photolysis 9



Photolysis 10

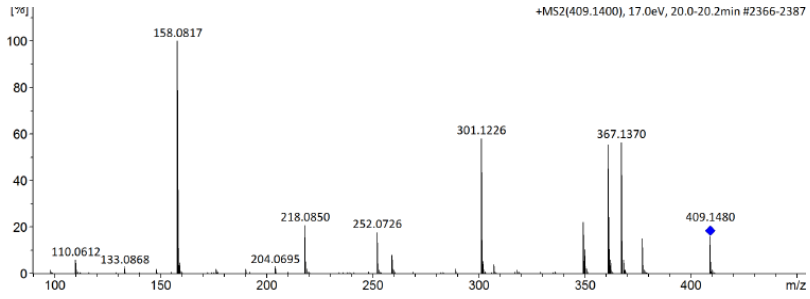
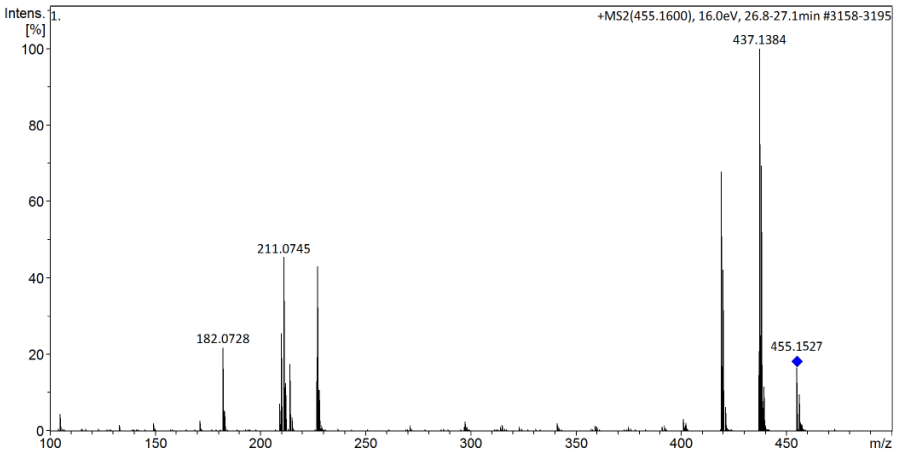


Figure S10. High-resolution MS/MS spectra of the dimeric products **8** (*m/z* 409.1481), **9** (*m/z* 409.1484) and **10** (*m/z* 409.1480) derived from the combination of two **αS(2)•** radicals.

Photolysis 18



Photolysis 19

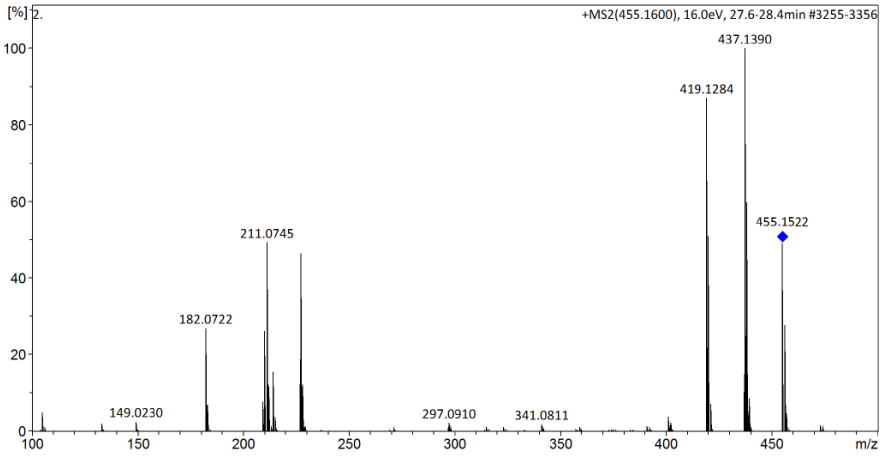
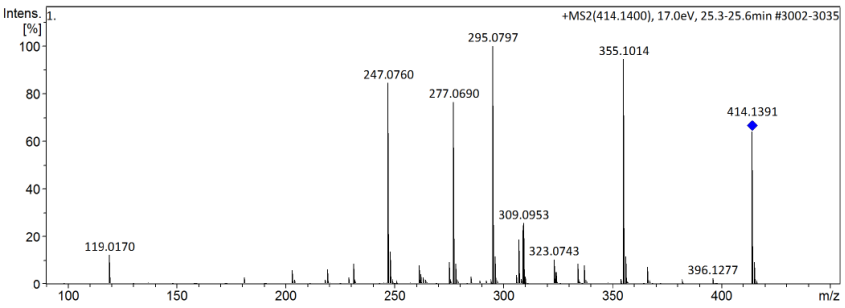
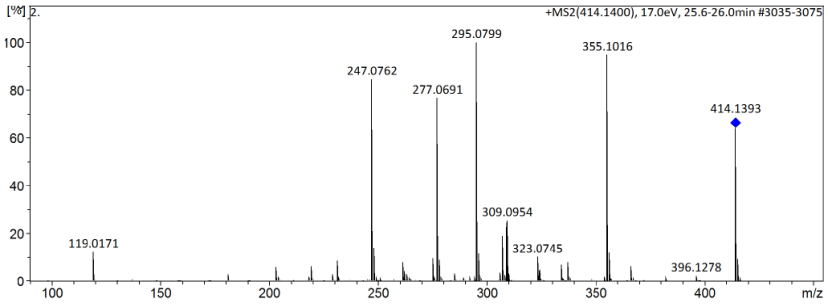


Figure S11. High-resolution MS/MS spectra of the two dimeric products **18** (*m/z* 455.1527) and **19** (*m/z* 455.1522) derived from of the combination of two **CBH**• radicals.

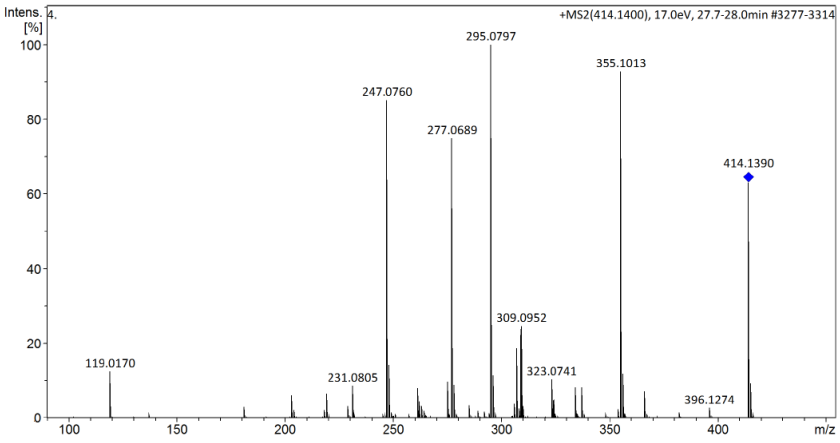
Photolysis 12



Photolysis 13



Photolysis 16



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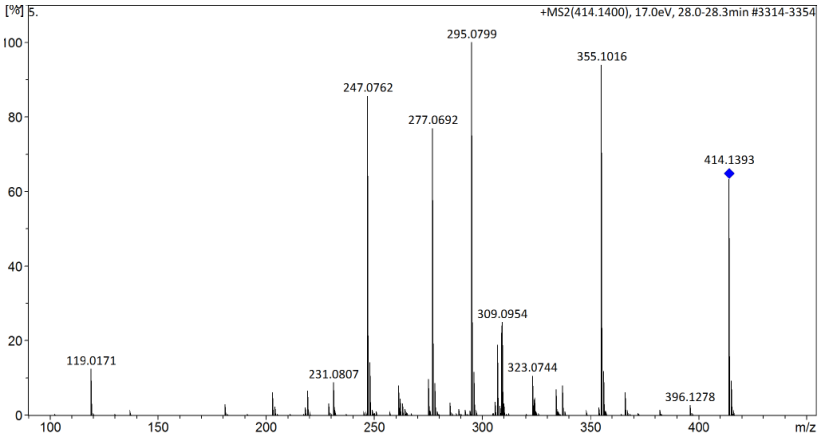

Figure S12. High-resolution MS/MS spectra of the products **12** (*m/z* 414.1391, **13** (*m/z* 414.1393), **16** (*m/z* 414.1390) and **17** (m/z 414.1393) derived from the cross-termination of **αS•** and **CBH•** radicals.

Photolysis 14

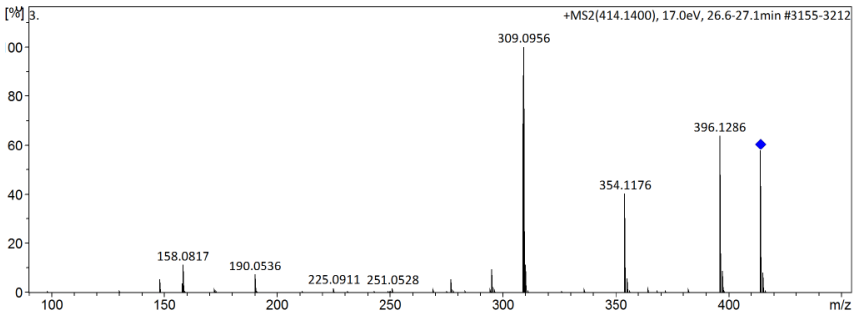

Figure S13. High-resolution MS/MS spectra of the product **14** (m/z 414.1392) derived from the cross-termination of **αS•** and **CBH•** radicals.