

Electronic Supplementary Information

The Baeyer—Villiger Rearrangement With Metal Triflates: New Developments Toward Mechanism

Piotr Latos, Agnieszka Siewniak, Magdalena Sitko, Anna Chrobok*

Department of Chemical Organic Technology and Petrochemistry, Silesian University of Technology, Krzywoustego 4, 44-100 Gliwice, Poland

Correspondence to: Anna.Chrobok@polsl.pl

MS spectra

Experimental procedures

MS spectra

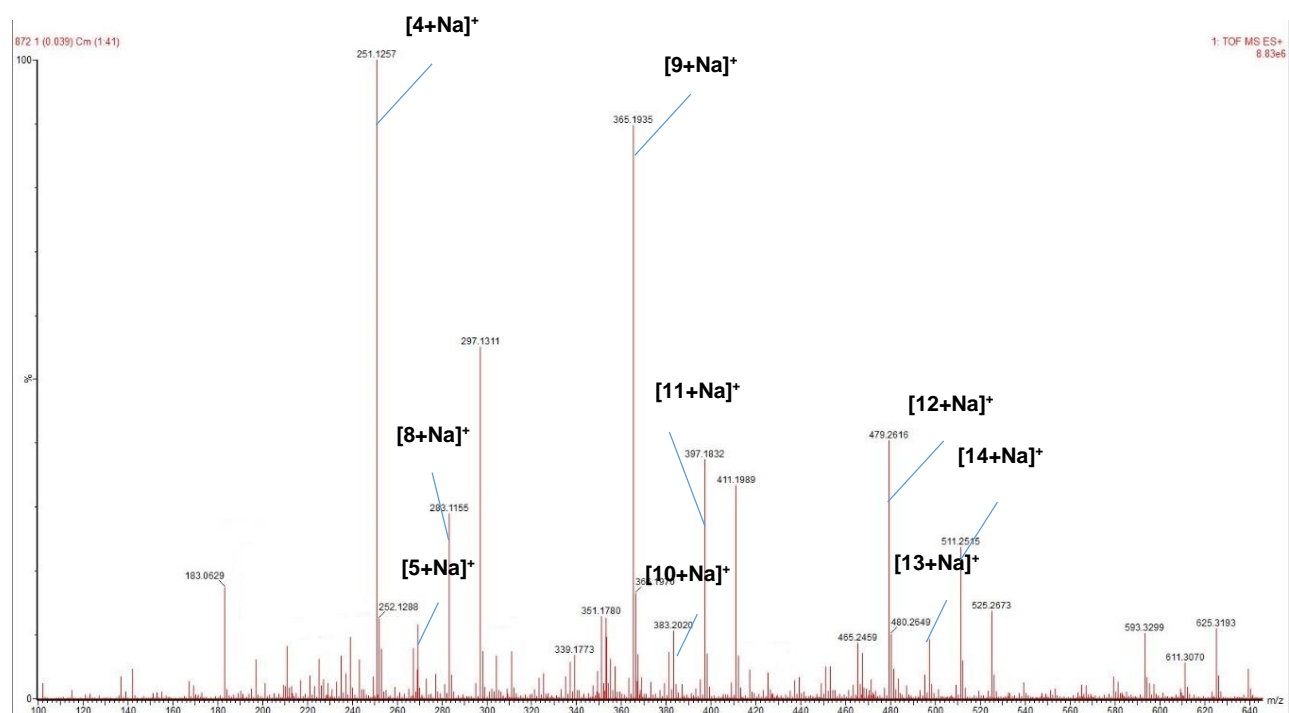


Fig. S1 MS spectrum of the post reaction mixture after the BV oxidation of cyclohexanone with 60 wt.% aq. H₂O₂, in the presence of Ga(OTf)₃. The spectrum was recorded for the solution with NaI addition (for explanation of the descriptions, see Fig. 5)

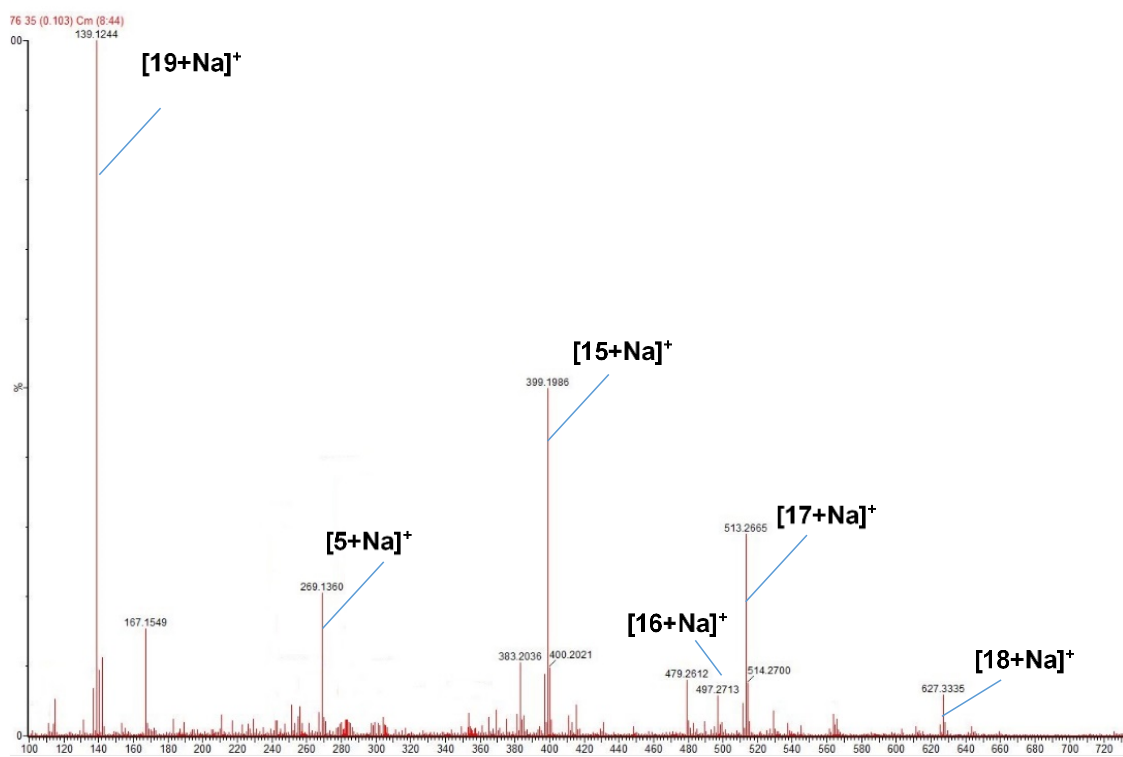


Fig. S2 MS spectrum of the post reaction mixture after the BV oxidation of cyclohexanone with 60 wt.% aq. H₂O₂, in the presence of Er(OTf)₃. The spectrum was recorded for the solution with NaI addition (for explanation of the descriptions, see Fig. 7)

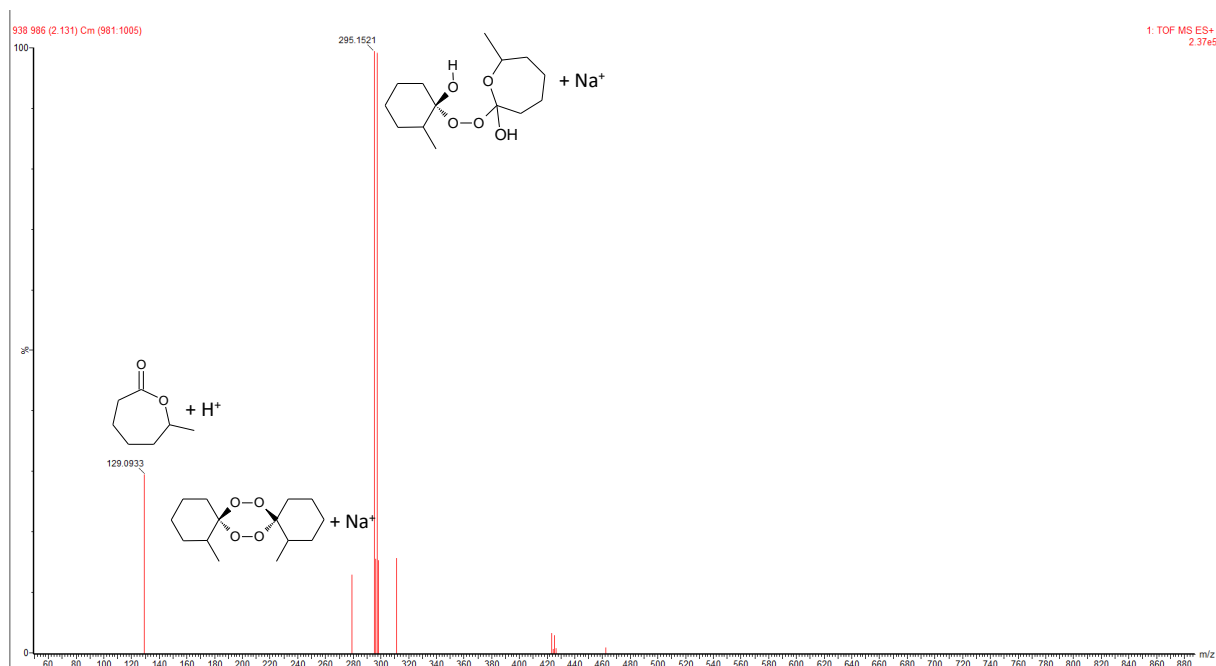


Fig. S3 MS spectrum of the post reaction mixture after the BV oxidation of 2-methylcyclohexanone with 60 wt.% aq. H_2O_2 , in the presence of $\text{Ga}(\text{OTf})_3$.

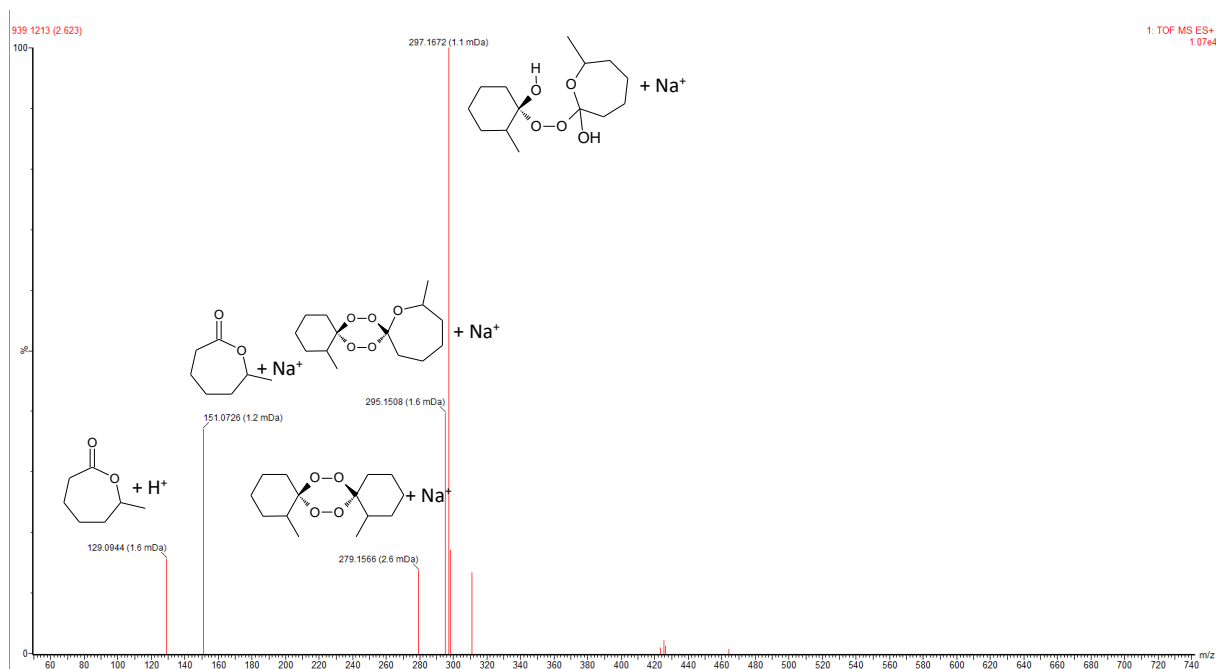


Fig. S4 MS spectrum of the post reaction mixture after the BV oxidation of 2-methylcyclohexanone with 60 wt.% aq. H_2O_2 , in the presence of $\text{Er}(\text{OTf})_3$.

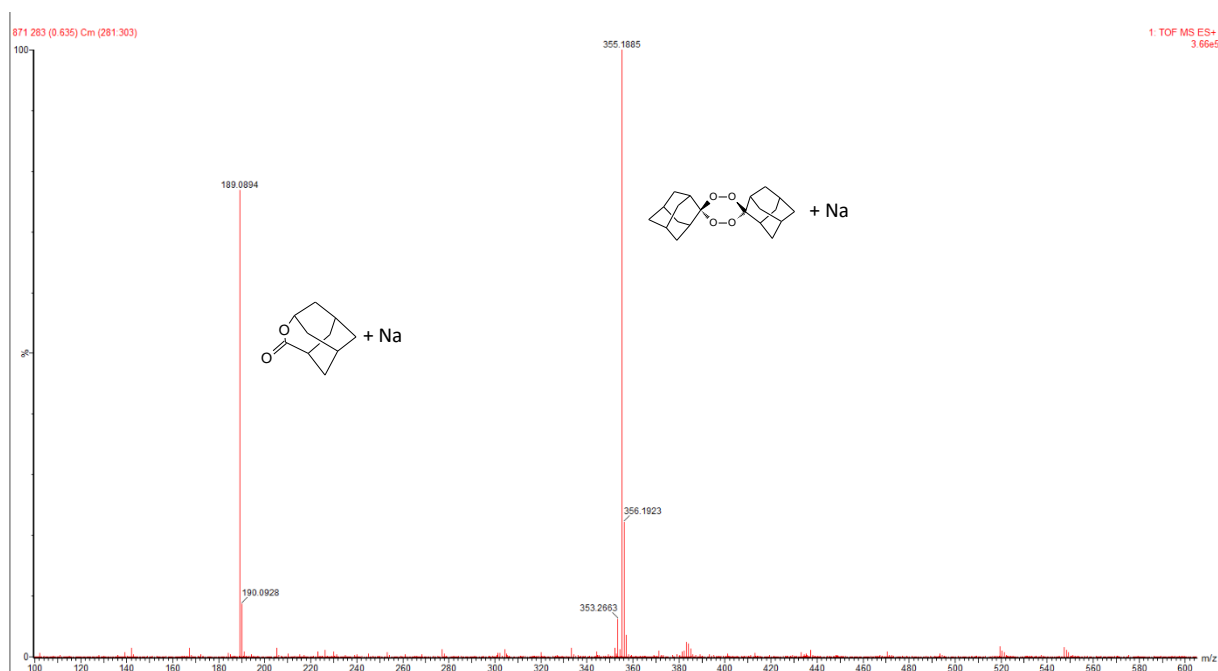


Fig. S5 MS spectrum of the post reaction mixture after the BV oxidation of 2-adamantanone with 60 wt.% aq. H_2O_2 , in the presence of $\text{Ga}(\text{OTf})_3$.

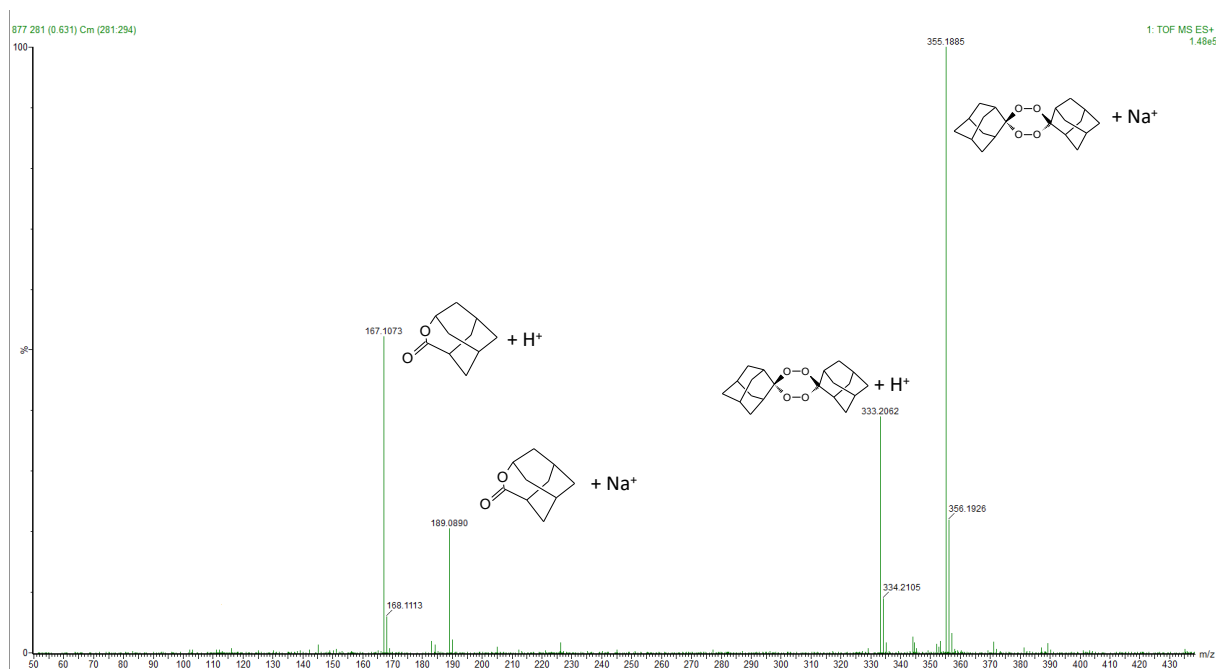


Fig. S6 MS spectrum of the post reaction mixture after the BV oxidation of 2-adamantanone with 60 wt.% aq. H_2O_2 , in the presence of $\text{Er}(\text{OTf})_3$.

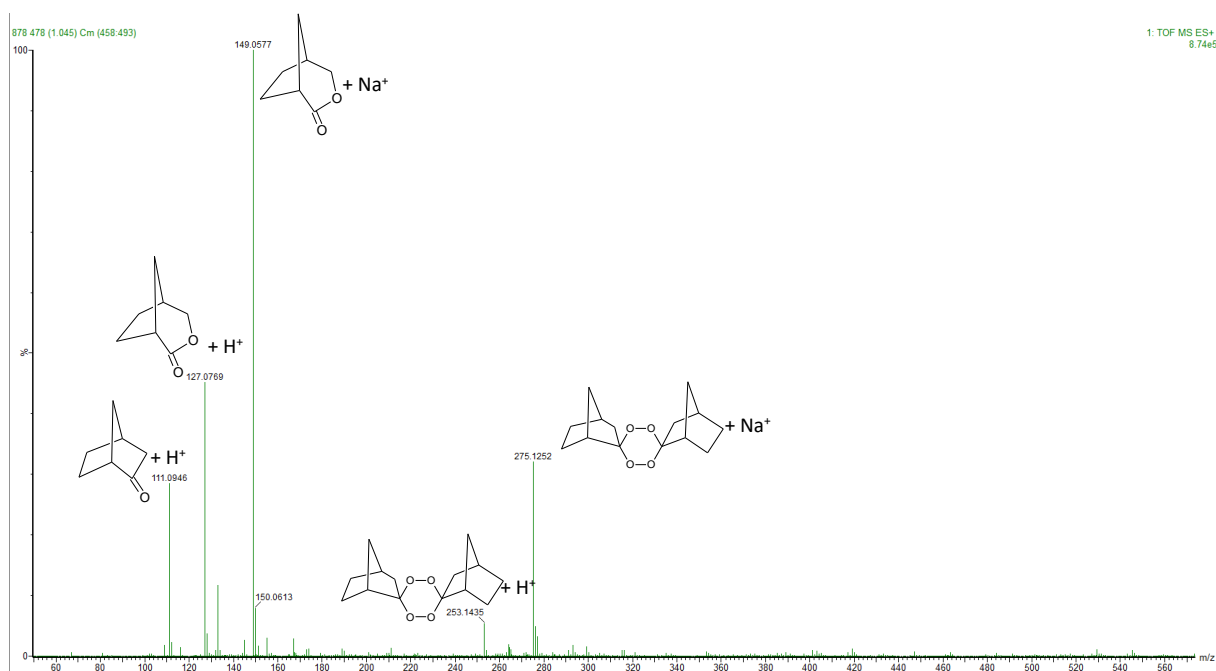


Fig. S7 MS spectrum of the post reaction mixture after the BV oxidation of norcamphor with 60 wt.% aq. H_2O_2 , in the presence of $\text{Ga}(\text{OTf})_3$.

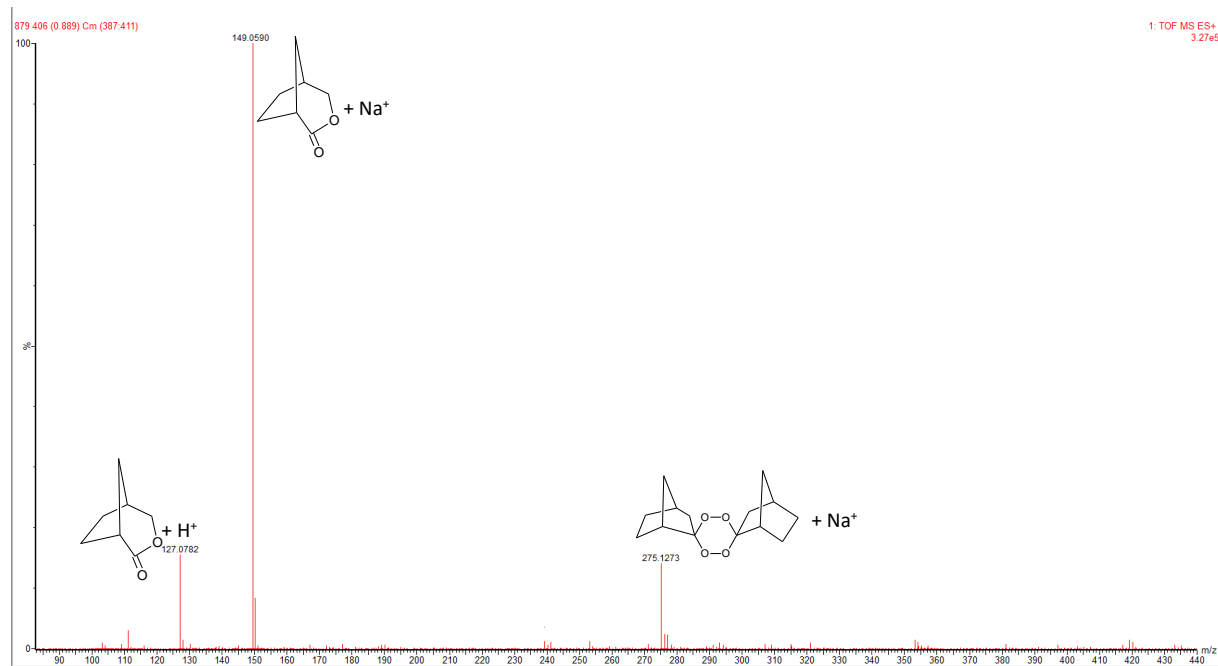


Fig. S8 MS spectrum of the post reaction mixture after the BV oxidation of norcamphor with 60 wt.% aq. H_2O_2 , in the presence of $\text{Er}(\text{OTf})_3$.

Experimental procedures

Materials and apparatus

Erbium(III) triflate, norcamphor, 2-adamantanone, cyclohexanone, decane, hydrogen peroxide, trifluoromethanesulfonic acid, retinyl acetate were purchased from Sigma-Aldrich (Merck, Germany); gallium(III) triflate was purchased from ABCR (Germany); nitric acid were purchased from Avantor Performance Materials (Poland).

GC analyses were performed on a Shimadzu GC-2010 Plus equipped with a flame ionization detector (FID) and a Zebron ZB-5MSi column (30 m × 0.32 mm 0.25 μm film).

High resolution mass spectrometry analyses were performed on a Waters Xevo G2 Q-TOF mass spectrometer (Waters Corporation) equipped with an ESI source operating in positive-ion modes. Full-scan MS data were collected from 100 to 1000 Da in positive ion mode with scan time of 0.1 s. Data were collected in centroid mode and mass was corrected during acquisition using leucine enkephalin solution as an external reference (Lock-Spray TM; m/z 556.2771 Da ($[M+H]^+$) in positive ESI mode. The accurate mass and composition for the molecular ion adducts were calculated using the MassLynx software (Waters).

Experimental procedure for the Baeyer-Villiger oxidation

Typical reaction was carried out in a two-neck 25 mL round-bottom flask equipped with a reflux condenser, sealed with a septum and placed on a magnetic stirrer. A ketone (0.069 – 0.100 g, 0.67 mmol), metal triflate (10 mol%), toluene (5 mL) and n-decane (0.10 mmol, an internal GC standard) were added to the flask. The reaction was carried out at 70 °C and at 1000 rpm. Then, an aqueous solution of H₂O₂ (2.01 mmol) was added, and the content of the flask was mixed for 3 h. Periodically, during the reaction, 10 mL of the samples diluted with methylene chloride were collected to monitor the progress of the reaction using GC and LC-MS.

Experimental procedure for retinyl carbocation formation

Solutions of retinyl acetate, Ga(OTf)₃, Er(OTf)₃ (0.0003 M) and TfOH (0.0001 M) in an anhydrous nitrobenzene were prepared. The retinyl acetate solution (1.5 mL) and the acid solution (1.5 mL) were added into a quartz cuvette. Then, the UV/VIS spectra of the mixtures were recorded using a Jasco V-650 spectrophotometer. The yellow color of the solution is responsible for the presence of retinyl acetate, which shows maximum absorption at a wavelength about 430 nm. The blue color is responsible for the occurrence of retinyl carbocation, and the maximum absorption occurs at 590 - 630 nm.