Supporting Information:

Theory and Practice of Alkyl Phenol Synthesis. Tert-octylphenols

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Abbreviations

Diisobutylene (DIB) *tert*-butylphenol (TBPh); *sec*-butylphenol (SBPh); *tert*-octylphenol (TOPh); *sec*-octylphenol (SOPh).

Analysis and Identification. GC analyses of reaction mixtures were carried out with Chromatec-Crystal 2000 M gas chromatograph equipped with a flame ionization detector (FID) and a SE-30 (stationary phase is cross-linked 100% dimethylpolysiloxane) capillary column of 60 m × 250 µm × 0.25 µm (column length × internal diameter × film thickness). The carrier gas is helium. The temperature of injection is 543 K, and the temperature of the FID is 573 K. The temperature of a column oven was chosen separately.

Identification of all components was performed by means of the chemical experiment and gas chromatography-mass spectrometry (GC-MS). GC-MS analyses were carried out with Agilent 6850 equipped with a mass-selective detector Agilent 5975C VL (MSD) and a HP-5MS capillary column of 30 m × 250 µm × 0.25 µm (column length × internal diameter × film thickness). The electron ionization (EI) is 70 eV.

Alkyl phenyl ethers. It was found that C8-alkylphenyl ethers are not formed at the conditions that were described in the manuscript. The products of TOPh destruction did not contain C4-alkyl phenyl ethers in addition. All obtained mass-spectra do not characterize the products as alkyl phenyl ethers.

The process of phenol alkylation with isobutylene to obtain 4-TBPh is the closest analog of the phenol alkylation with DIB. Study results[1] and long-term experience in the 4-TBPh manufacture show that reaction mixtures do not contain C4-alkyl phenyl ethers.

2-*Tert*-octylphenol and 4-*tert*-octylphenol. The structure of 4-TOPh (component 13 in Figure 1) was confirmed by means of mass spectrometry. Obtained spectrum (Figure S1) shows 100% match of the NIST database.

Under kinetic and thermodynamic control of alkylation, 2-TOPh (component 12 in Figure 1) demonstrates the characteristic behavior. Although the retention time of 2-TOPh is less than 4-TOPh (Figure 1), the 2-TOPh spectrum (Figure S1) shows the set of ions corresponding 4-TOPh (m/z 206, m/z 135).

3-Tert-octylphenol. To detect the presence or absence of 3-TOPh in a reaction system, we used the following procedures. Alkylation products, which were preliminary obtained by alkylation over A-36, were isomerized over A-36 at 409 K for 60 min. The further increase in isomerization time was accompanied by the destruction processes of TOPhs to form tert-butylphenols. The ratio of 4-tert-butylphenol to 4-tert-octylphenol attained 97.5/2.5 for 150 min. The composition of reactive mixtures was obtained by means of GC. It is extremely difficult to separate meta- and para-alkylphenols by GC; hence we have analyzed mixtures of alkylphenols and their silyl ethers.

As a result, it was found that 3-TOPh and 3-TBPh were not formed under conditions of alkylation, which were considered in this manuscript, and isomerization. After alkylphenols were quantitatively converted into their silyl ethers, the reaction mixture was solely presented by 2- and 4-substituted structures. The method of silylation for alkylphenols and analysis conditions were given in work.[2]

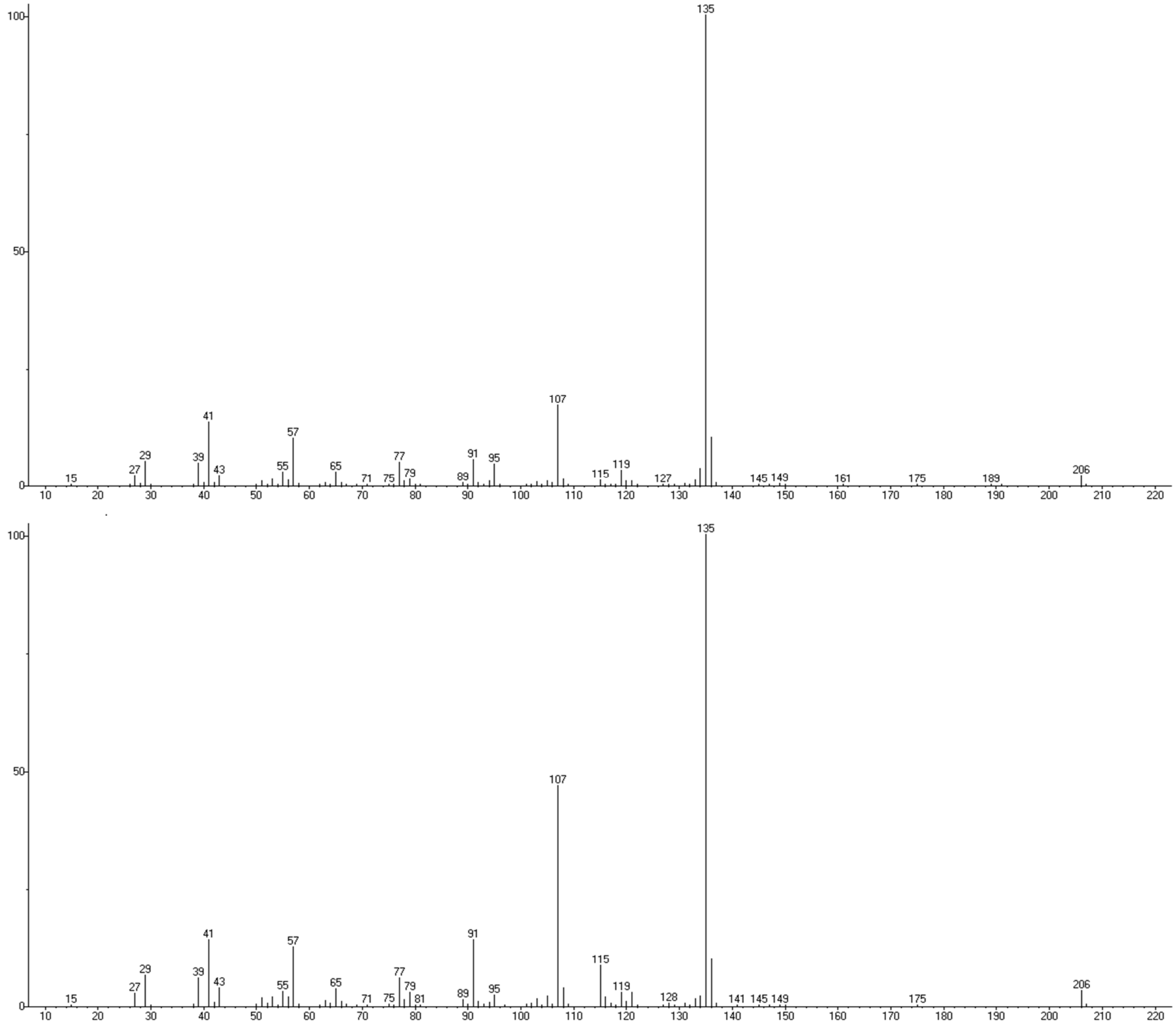


Figure S1. EI mass-spectra of 4-TOPh (at the top) and 2-TOPh (at the bottom).

The mass-spectra of silyl ethers are shown on Figure S2. The following ions unambiguously identify the structure of silyl ethers: m/z 278 (low abundance); m/z 207 (100% abundance); m/z 73. The quantitative conversion of TOPhs into their silyl ethers allow to avoid mistake in identification of each isomer on chromatograms (Figures S3 and S4). Thus the reaction mixtures did not contain meta-substituted structures.

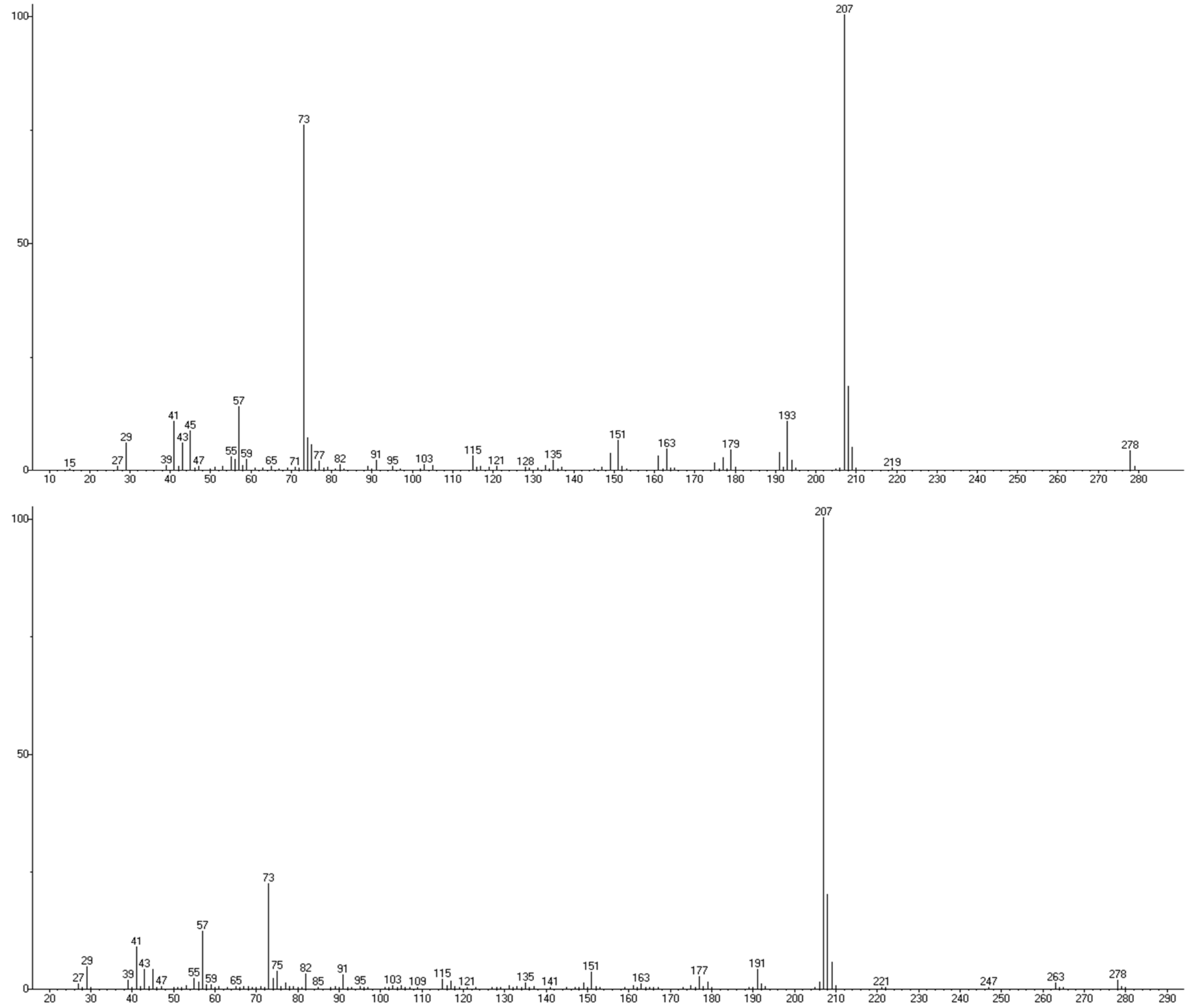


Figure S2. EI mass-spectrum of silyl ethers of 2-TOPh (at the top) and silyl ether of 4-TOPh (at the bottom).

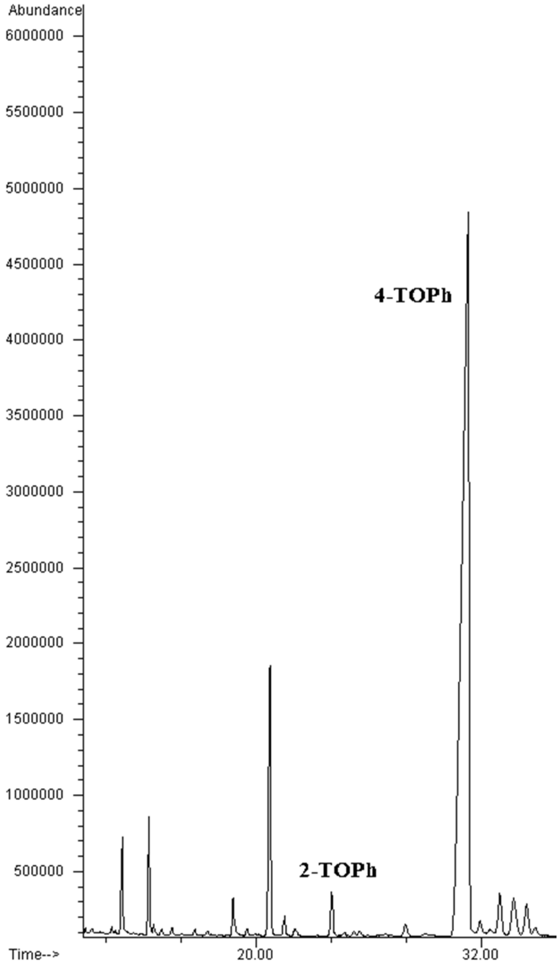


Figure S3. Chromatogram of TOPhs.

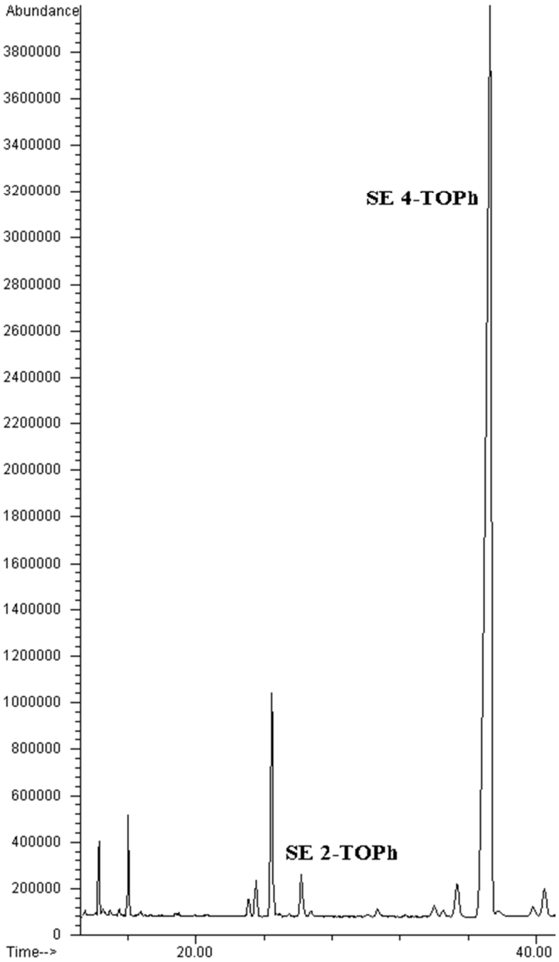


Figure S4. Chromatogram of silyl ether of TOPhs.

Moreover, 3-TBPh was not detected after phenol alkylation and isomerization of alkylate. This fact also confirmed the absence of 3-TOPh in reaction products. All positional isomers of TBPh were synthesized by us, so we clearly found the position of 3-TOPh on the chromatograms (Figures S5 and S6). Mass-spectra of silyl ethers of mono-*tert*-butylphenols are shown on Figures S7.

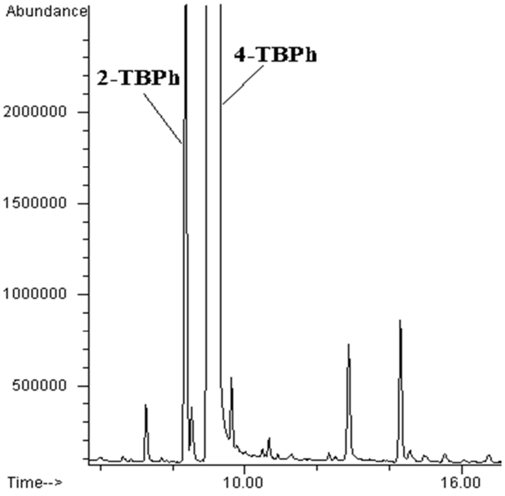


Figure S5. Chromatogram of TBPh.

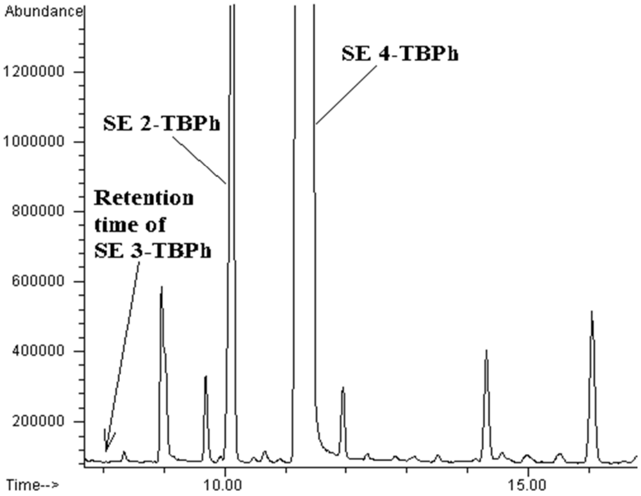


Figure S6. Chromatogram of silyl ether of TBPh.

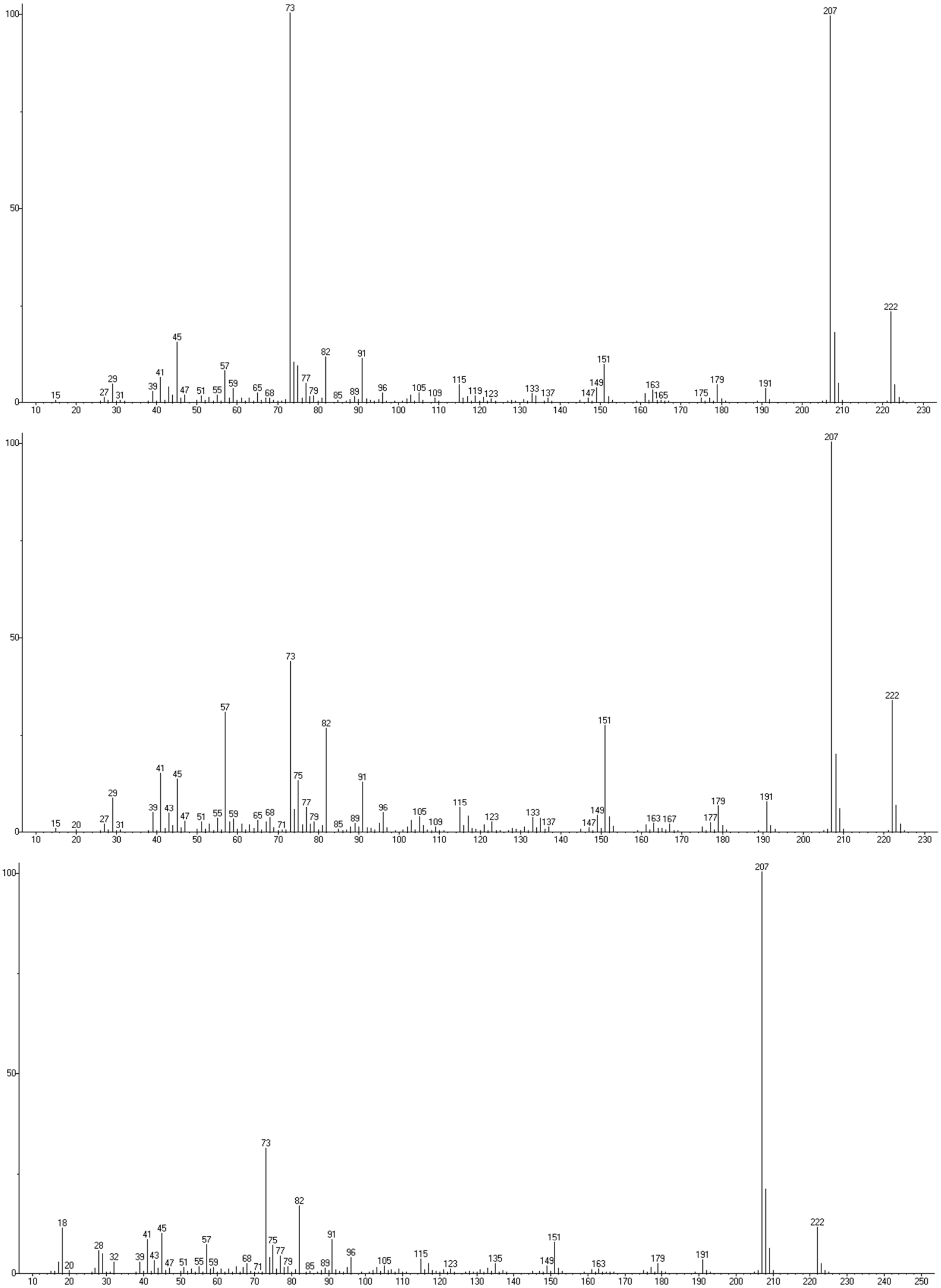


Figure S7. EI mass-spectrum of silyl ethers of 2-tert-butylphenol (at the top), silyl ether of 3-tert-butylphenol (at the middle), silyl ether of 4-tert-butylphenol (at the bottom).

Skeletal rearrangement of TOPhs. TOPhs skeletal rearrangement is the essential issue of acid catalysis. In this work, we purposefully chose conditions for phenol alkylation with DIB, the structural isomerization of *tert*-octyl substituent was significantly decreased as a result. It was experimentally found that the skeletal rearrangement weakly occurs at high temperatures.

However, this does not mean that the structural isomerization does not generally occur. The increase in temperature, a catalyst concentration, reaction time and an activity of catalyst (a moisture content) leads to the noticeable increase in an amount of the structural isomers. The redistribution of concentrations also occurs in the group of TOPhs isomers, hence the structures that have thermodynamic stability prevail in the reaction mixture and destructive transformations are intensified. These observed processes are shown in Figure S8.

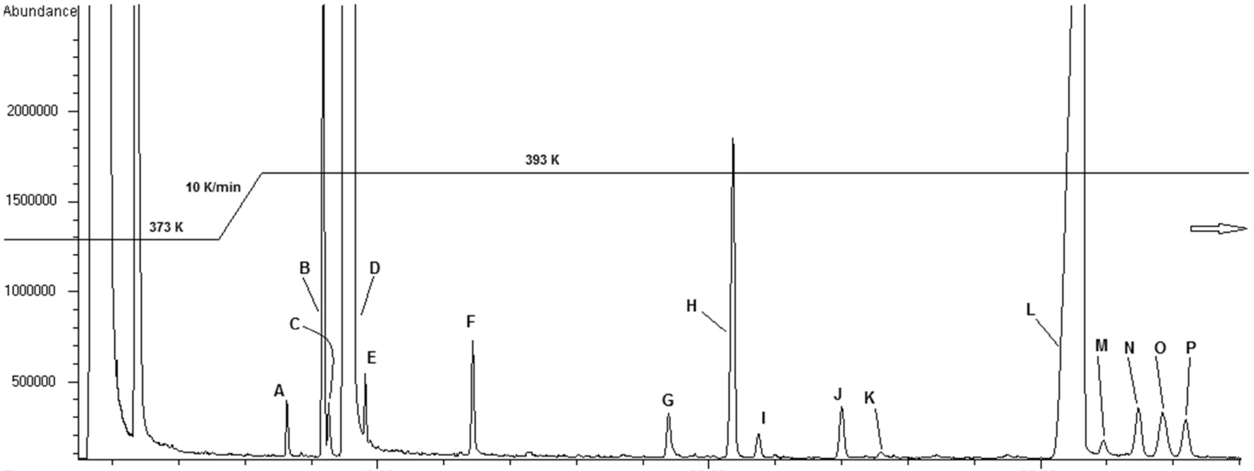
To identify tertiary and secondary octylphenols, the approach described by Campbell et al.[3] was used in this work. The main indicators are the ion at m/z 206 of low abundance, the fragment ion at m/z 135 (100% relative abundance in the spectra of tertiary structures), the fragment ion at m/z 121 (100% relative abundance in the spectra of secondary structures).[3,4]

Almost all isomers of octylphenol were separated by GS analysis (Figure S8). The obtained spectra on Figure S9H-S9T correctly identify the structure of isomers. It was found that sec-octylphenols were not prevailed at all experimental conditions (alkylation and isomerization). At first glance, this fact contradicts the results obtained by Campbell C. B. et al.[3,5] Moreover, it also is contradicts the study where secondary branched alkylaromatic hydrocarbons 5 times dominates over the tertiary isomers at the equilibrium condition.[6]

However, we carefully analyzed the structures, which were discussed in the mentioned above works, and found that the isomerization of tertiary isomers into unstrained secondary structures was studied (isomerization of products of alkylation phenol or catechol with 2-butyl-1-octene;[3] isopentenylbenzenes isomerization;[6] isomerization of products of phenol alkylation with decene-1[5]).

In the reviewed manuscript, the isomerization of sterically hindered structures has been discussed. We think that tertiary structures are the main reason why the low concentrations of sec-octylphenols were obtained. These tertiary compounds have structures different than 1,1,3,3-tetramethylphenols and represent a major group of isomers during the phenol alkylation with DIB and the further isomerization.

The isomeric transformations into secondary and tertiary structures hardly proceeded under chosen experimental conditions; hence the structural isomerization was excluded from the kinetic model.



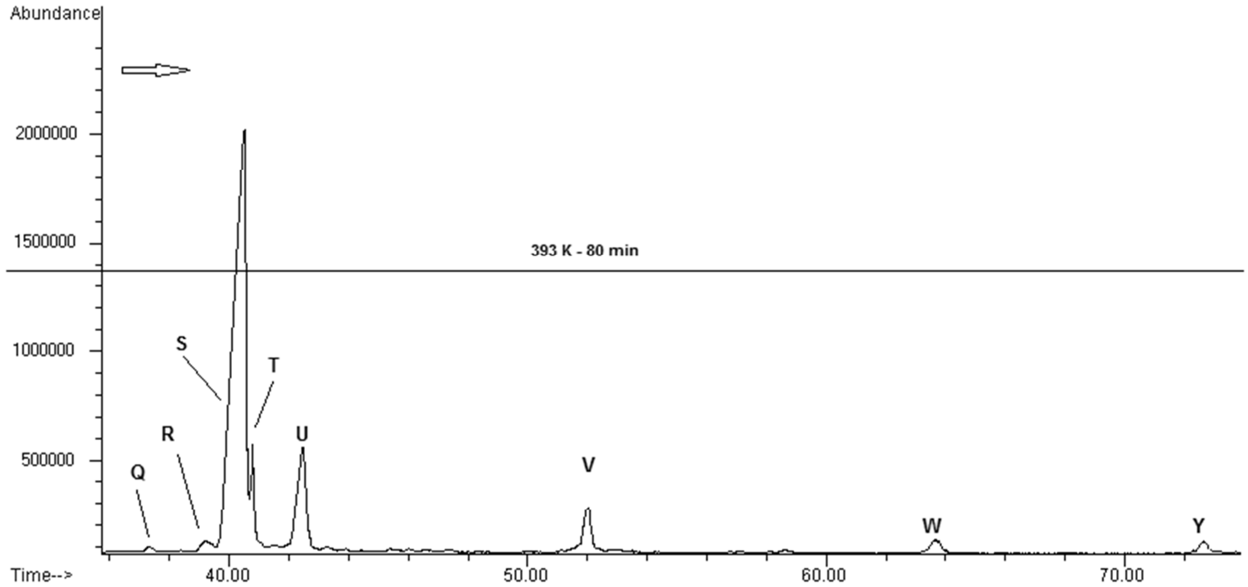


Figure S8. Typical chromatogram for phenol alkylation with DIB for 60 min at 409 K: **(A)** – 4-isopropylphenol; **(B)** – 2-TBPh; **(C)** – 2-*sec*-butylPh; **(D)** – 4-TBPh; **(E)** – 4-*sec*-butylPh; **(F) –** 4-*tert*-pentylphenol; **(G) –** 4-*tert*-hexylphenol; **(H)** 2,4-di-*tert*-butylphenol; **(I) –** 2-isopropyl-4-pentylphenol (possibly); **(J) –** 2-TOPh (2-(1,1,3,3-tetramethylbutyl)phenol); **(K) –** 2-SOPh-K**; (L) –** 4-TOPh (4-(1,1,3,3-tetramethylbutyl)phenol)**; (M)** – 4-TOPh-M; **(N)** – 4-SOPh-N; **(O)** – 4-TOPh-O; **(P)**– 4-TOPh-P**; (Q) –** 4-SOPh-Q**; (R) –** the mixed peak containing *sec*-OPh; **(S)** – 4-TOPh-S**; (T)** – 4-TOPh-T; **(U) –** the mixed peak containing *sec*-OPh; **(V) –** 4-TOPh-V**; (W)** - 2-*tert*-octyl-4-*tert*-butylphenol; **(Y)** - 2-*tert*-butyl-4-*tert*-octylphenol.

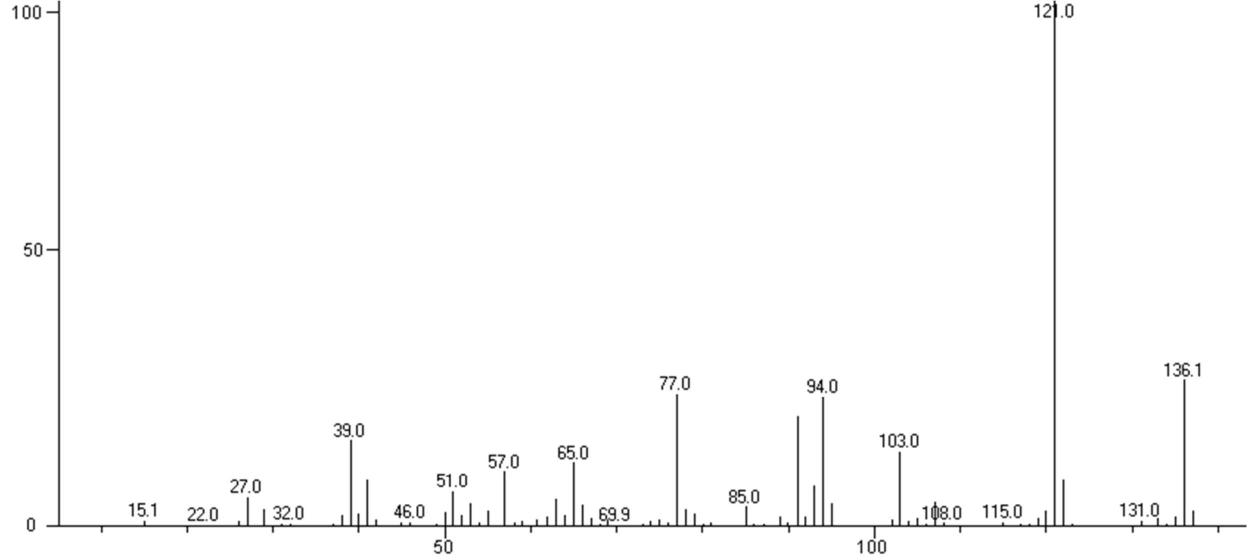


Figure S9A. EI mass-spectrum of 4-isopropylphenol (component A on Figure S8)

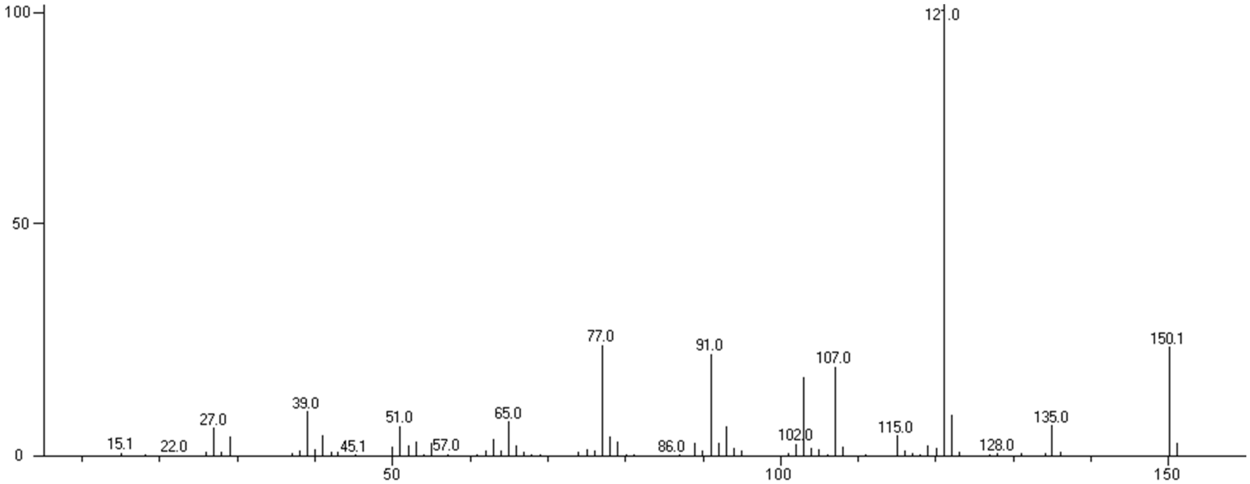


Figure S9B. EI mass-spectrum of 2-SBPh (component C on Figure S8)

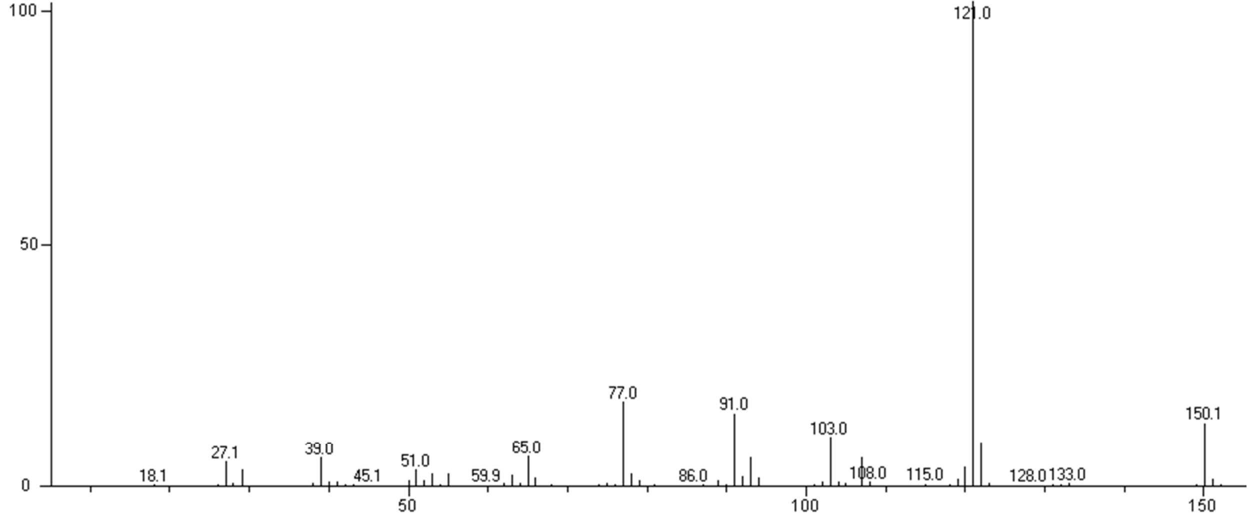


Figure S9C. EI mass-spectrum of 4-SBPh (component E on Figure S8)

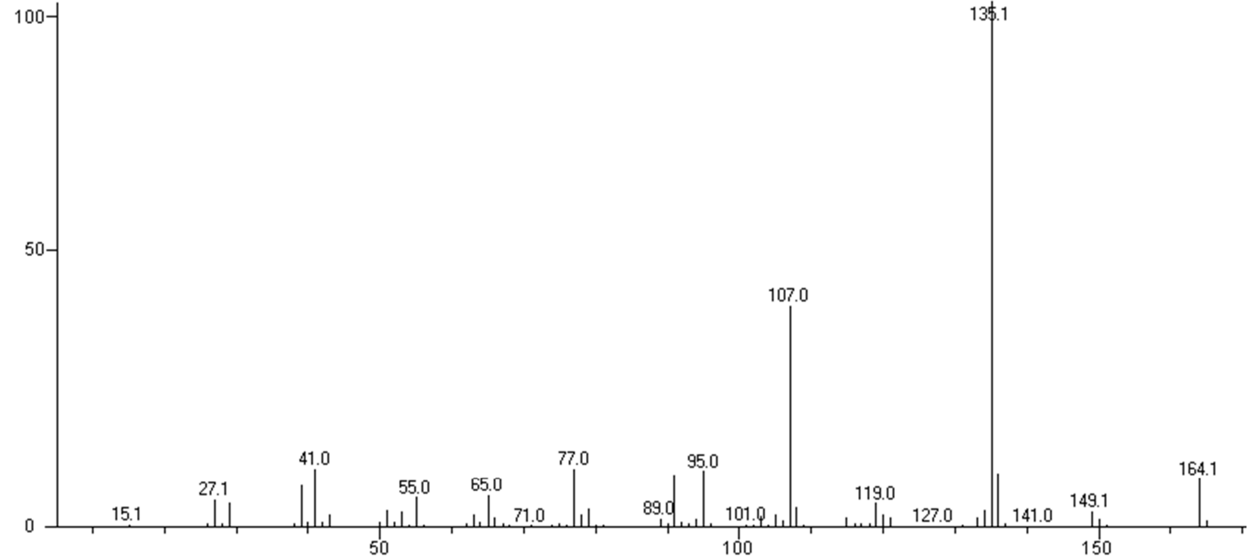


Figure S9D. EI mass-spectrum of 4-*tert*-pentylphenol (component F on Figure S8)

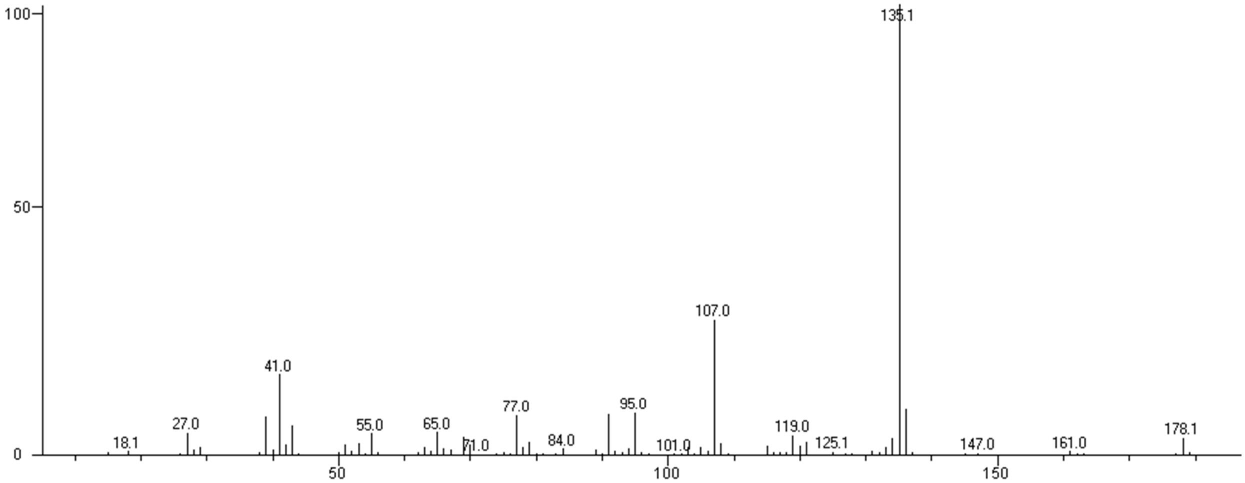


Figure S9E. EI mass-spectrum of 4-*tert*-hexylphenol (component G on Figure S8)

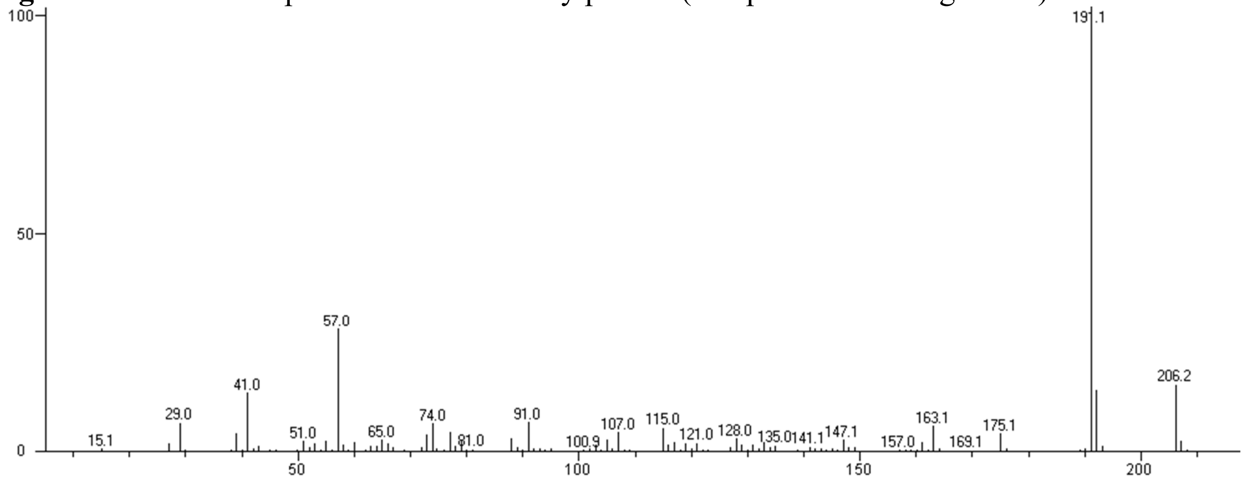


Figure S9F. EI mass-spectrum of 2,4-di-*tert*-butylphenol (component H on Figure S8)

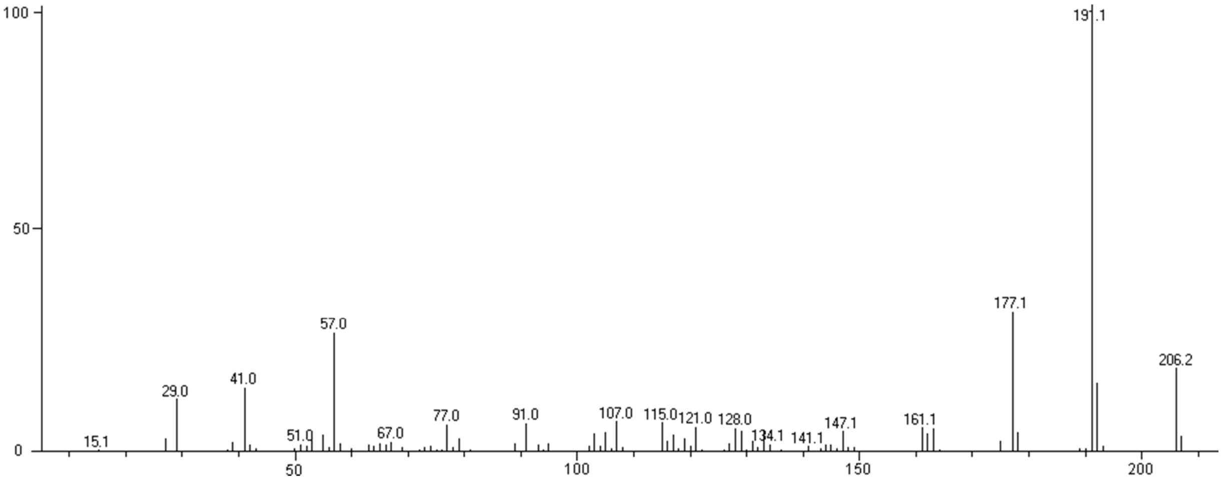


Figure S9G. EI mass-spectrum of 2-isoropyl-4-pentylphenol (component I on Figure S8)

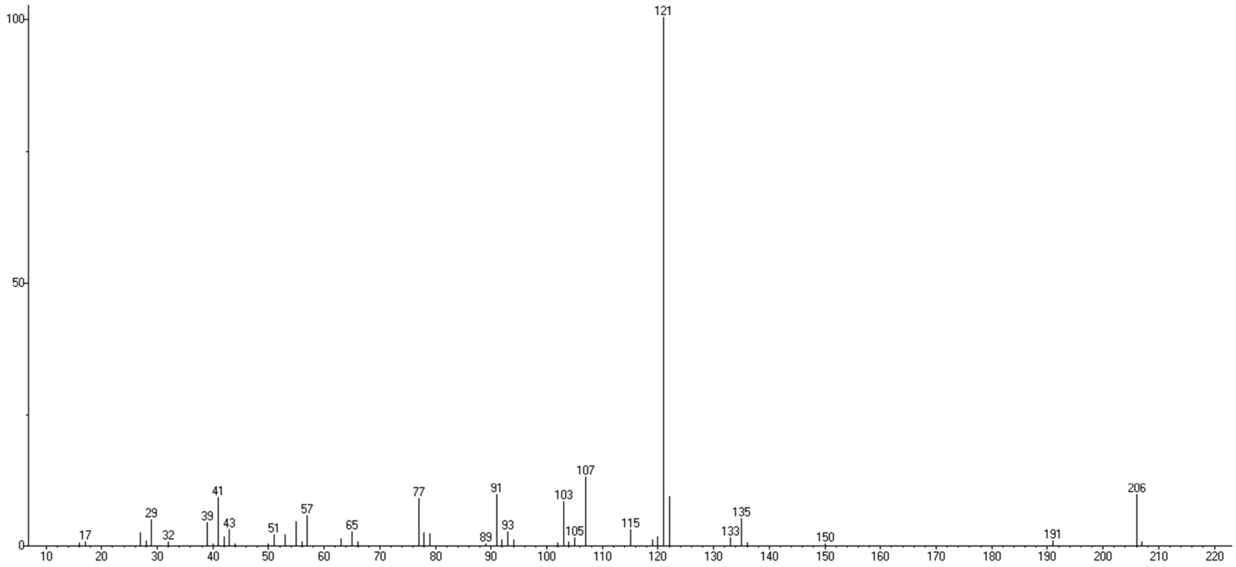


Figure S9H. EI mass-spectrum of 2-SOPh (component K on Figure S8)

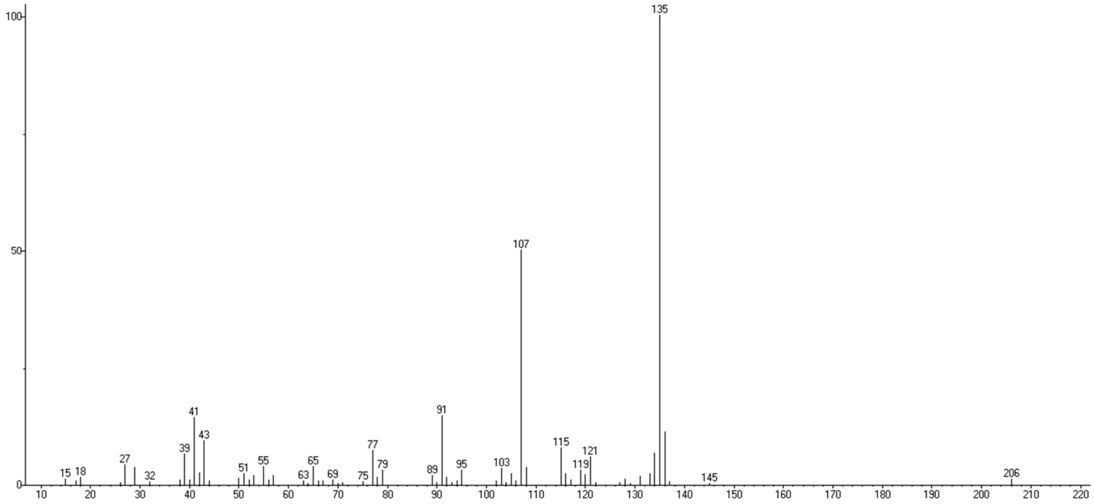


Figure S9I. EI mass-spectrum of 4-TOPh (component M on Figure S8)

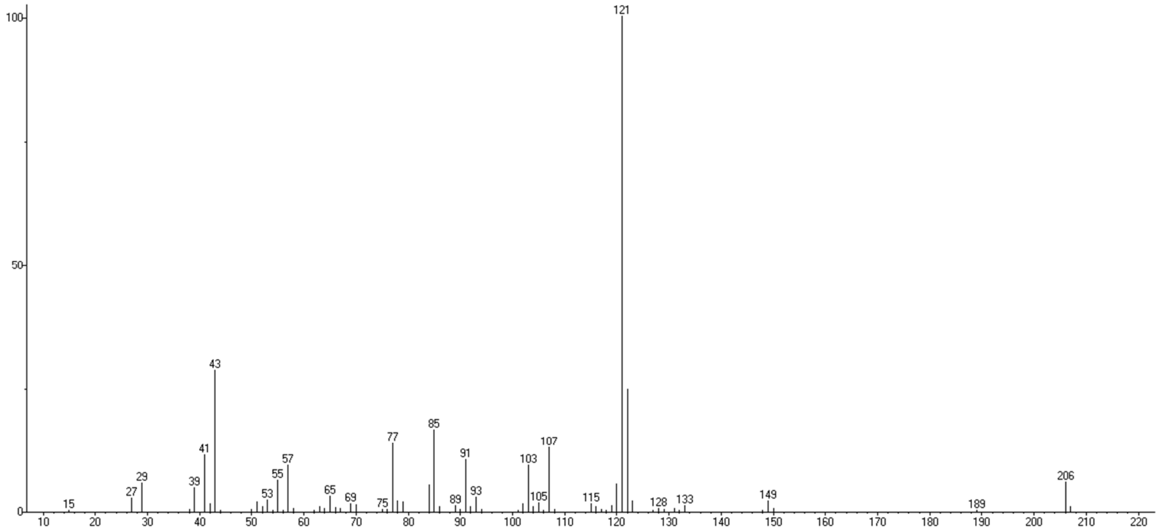


Figure S9J. EI mass-spectrum of 4-SOPh (component N on Figure S8)

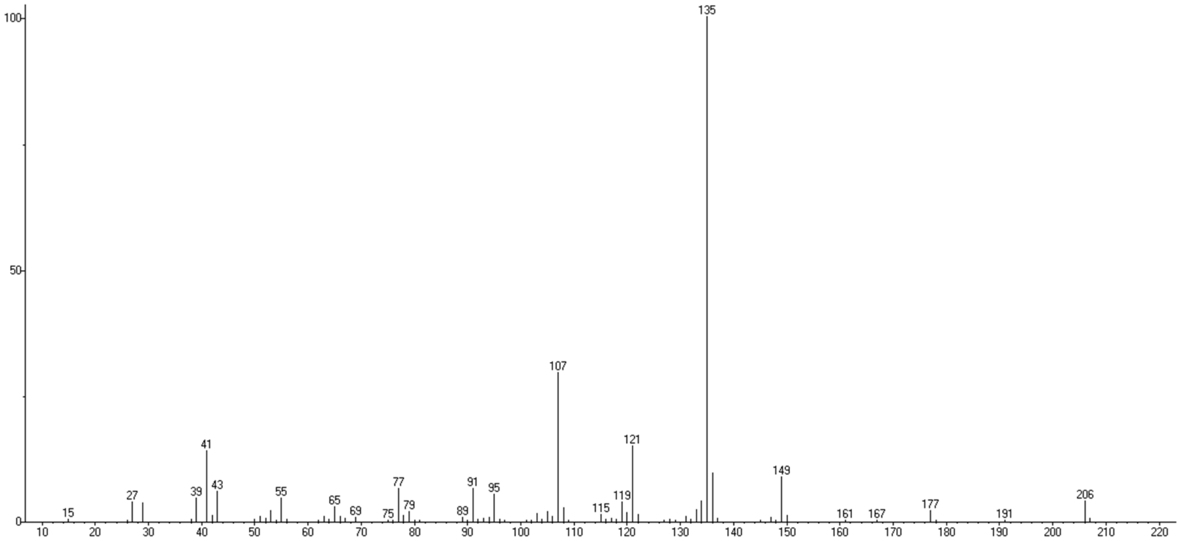


Figure S9K. EI mass-spectrum of 4-TOPh (component O on Figure S8)

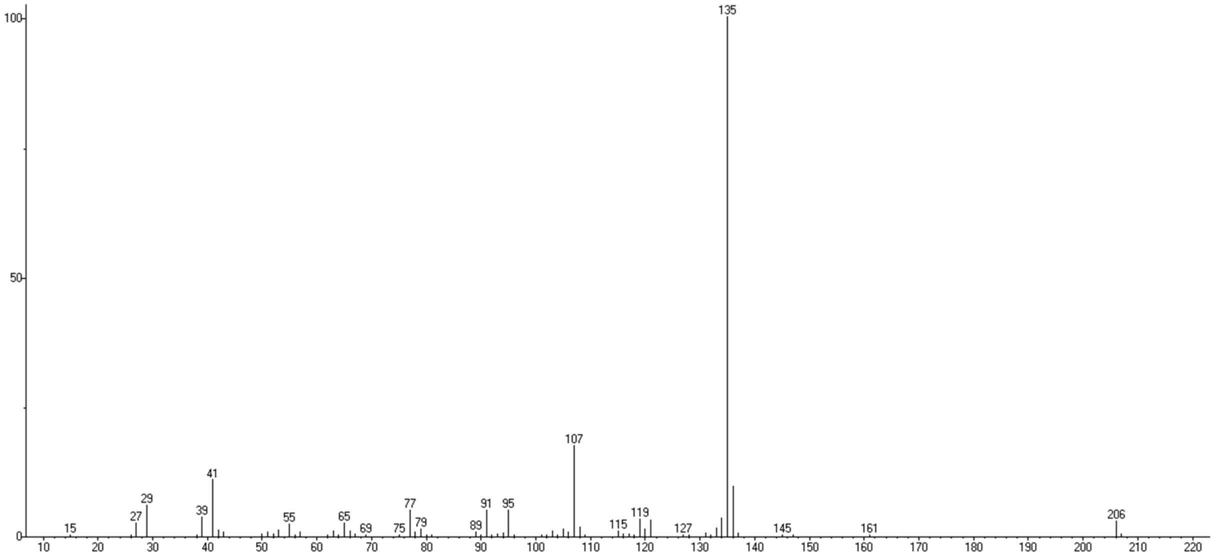


Figure S9L. EI mass-spectrum of 4-TOPh (component P on Figure S8)

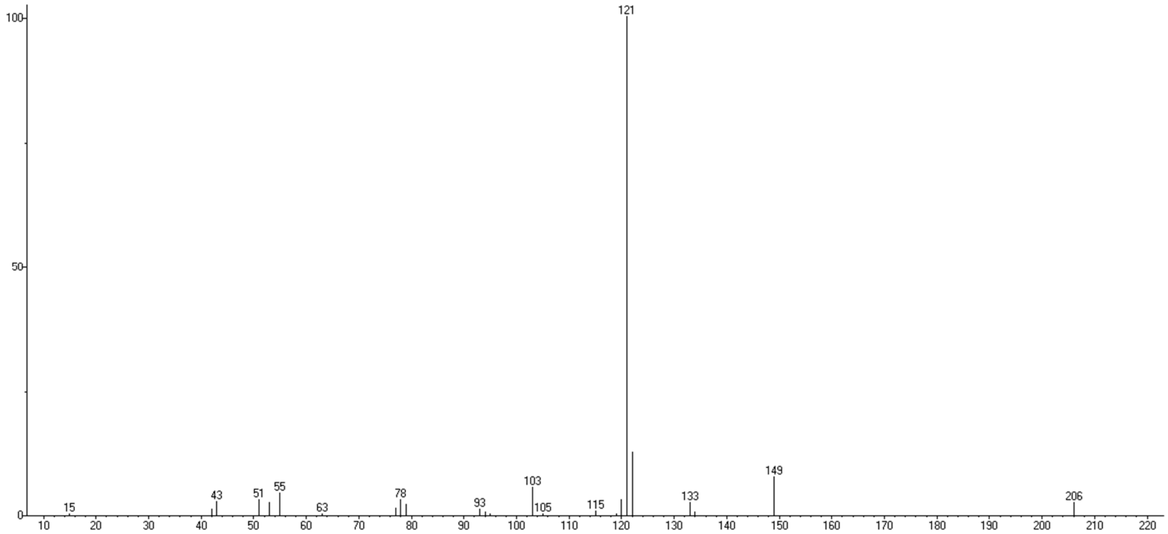


Figure S9M. EI mass-spectrum of 4-SOPh (component Q on Figure S8)

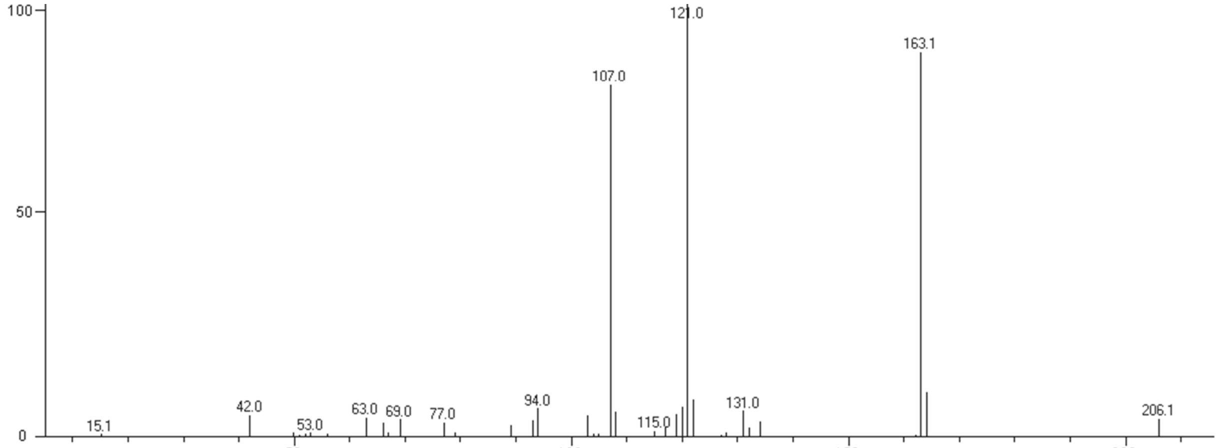


Figure S9N. EI mass-spectrum of 4-SOPh (component R on Figure S8 - the mixed peak containing *sec*-OPh)

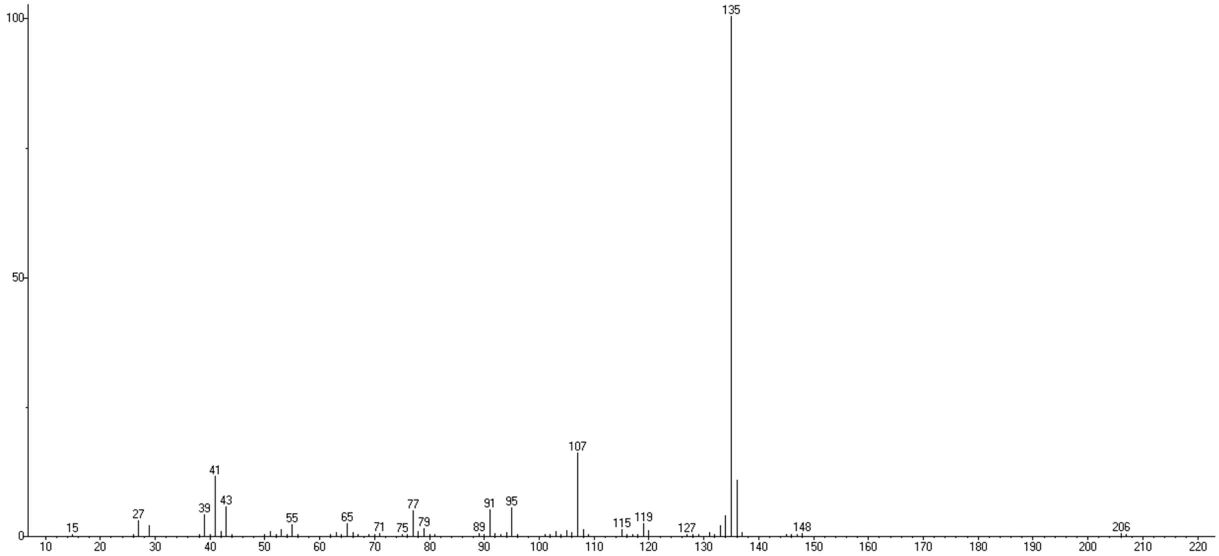


Figure S9O. EI mass-spectrum of 4-TOPh (component S on Figure S8)

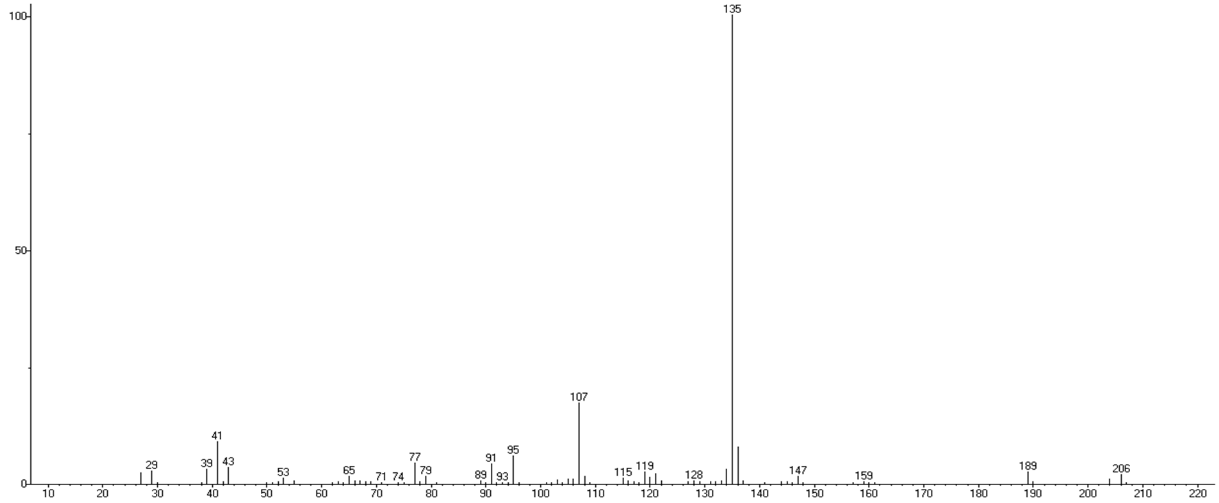


Figure S9P. EI mass-spectrum of 4-TOPh (component T on Figure S8)

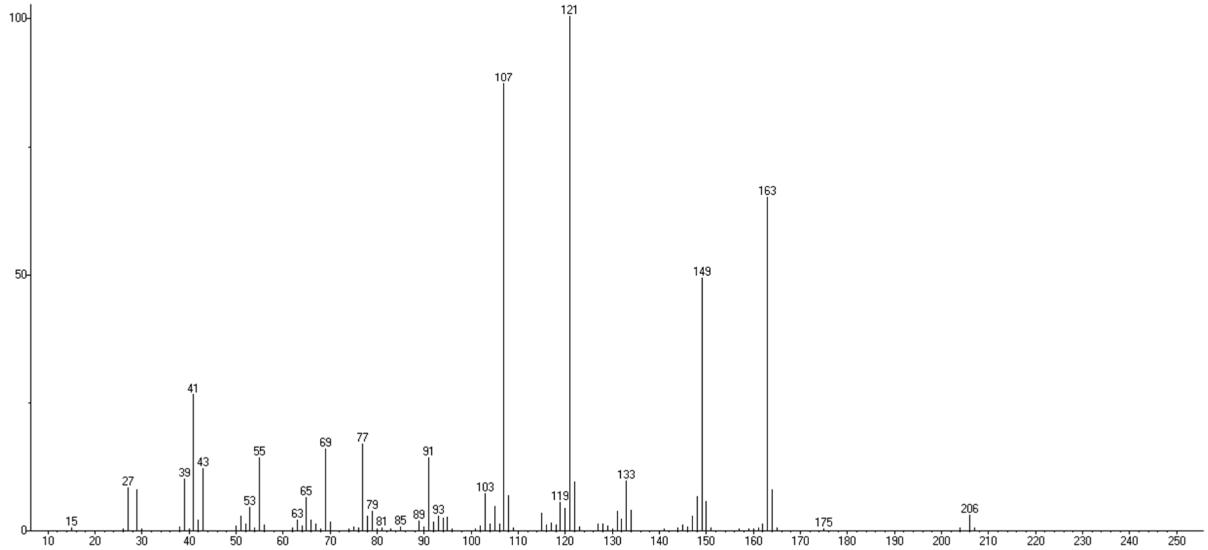


Figure S9Q. EI mass-spectrum of 4-SOPh (component U on Figure S8)

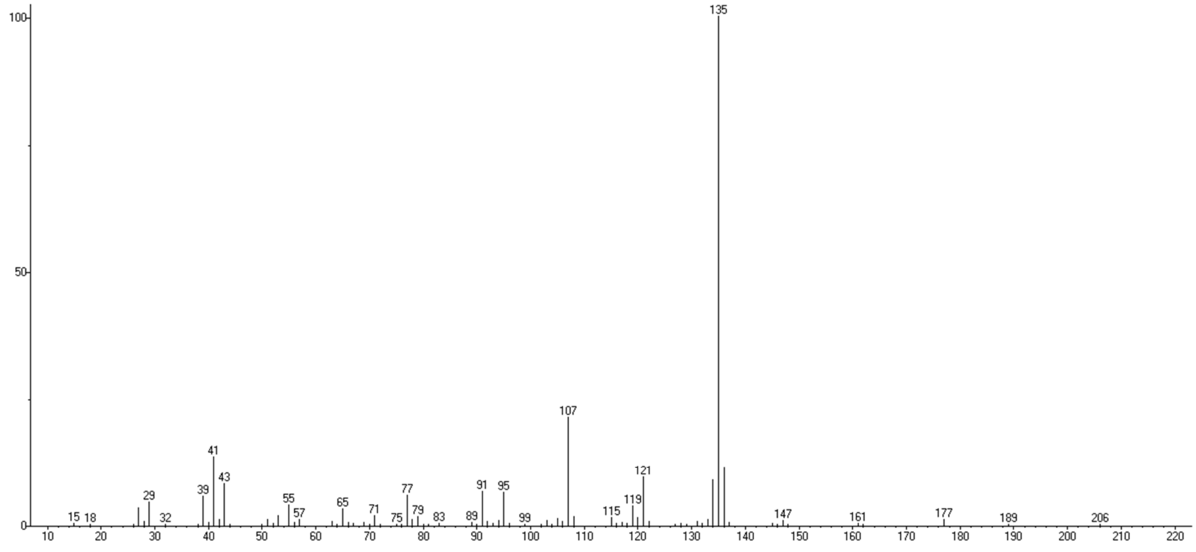


Figure S9R. EI mass-spectrum of 4-TOPh (component V on Figure S8)

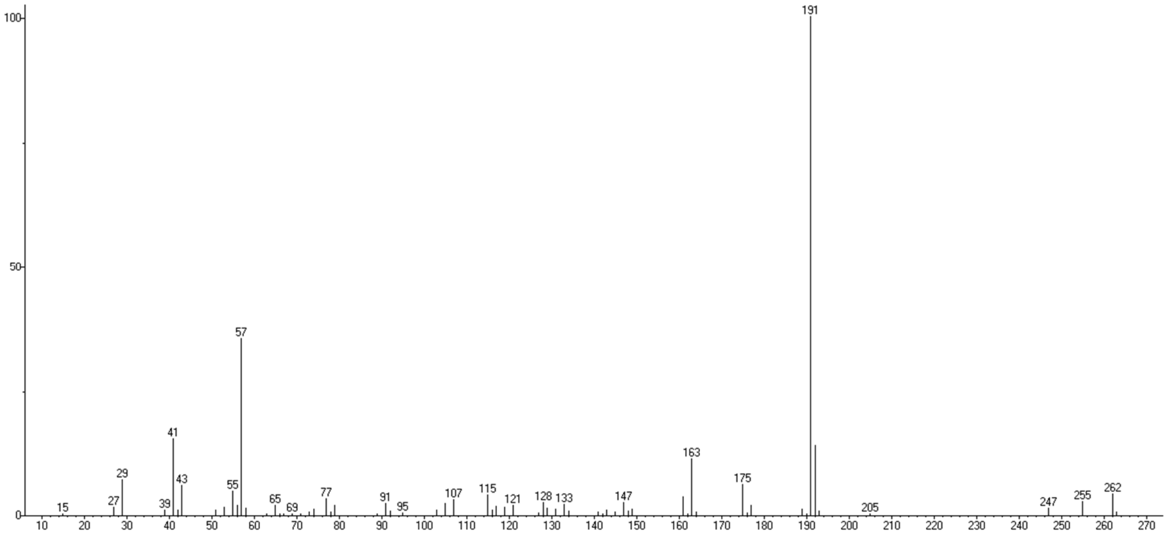


Figure S9S. EI mass-spectrum of 2-*tert*-octyl-4-*tert*-butylphenol (component W on Figure S8)

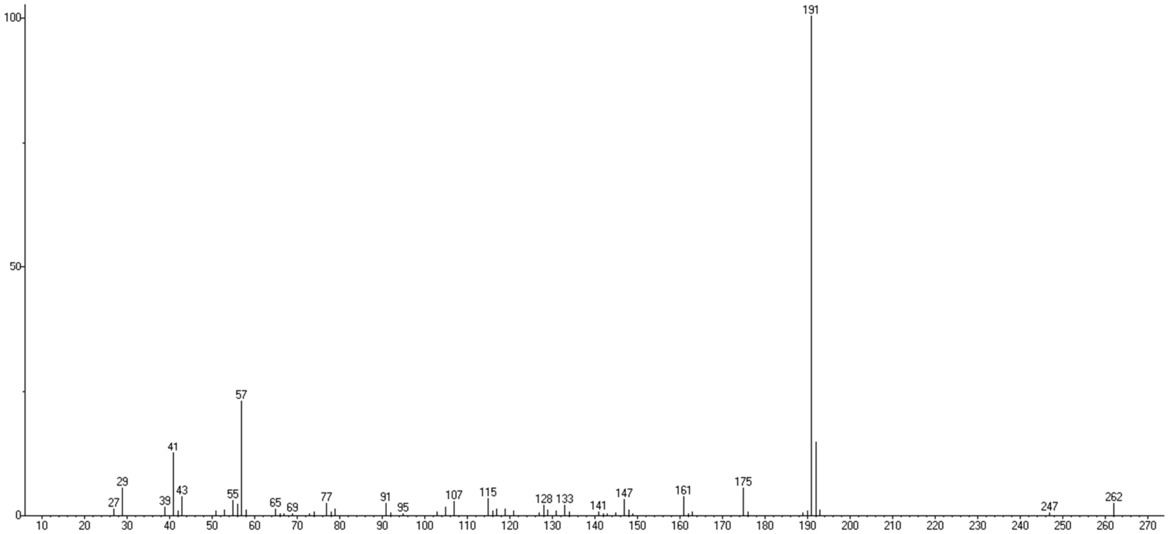


Figure S9T. EI mass-spectrum of 2-*tert*-butyl-4-*tert*-octylphenol (component Y on Figure S8)

Catalyst properties. The properties of industrial-grade Amberlyst 36 Dry is given on Table S1.

Table S1. The properties of industrial-grade A-36 according to a product data sheet[7]

Physical form Ionic form as shipped	Opaque beads
Ionic form as shipped	Hydrogen
Concentration of acid sites	≥ 5.40 eq/kg
Water content	≤ 1.65%
Shipping weight	770 g/L
Particle size	
Fines content	< 0.300 mm: 5.0% max
Coarse beads	> 1.180 mm: 5.0% max
Nitrogen BET	0.550 to 0.700 mm
Surface area	33 m^2/g
Average pore diameter	240 Å
Total pore volume	0.20 cc/g
Swelling	Dry to phenol: 20%

References

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(7) Amberlyst 36 Dry. Product data sheet. http://msdssearch.dow.com/PublishedLiteratureDOWCOM/dh_08d3/0901b803808d308c.pdf?filepath=liquidseps/pdfs/noreg/177-03092.pdf&fromPage=GetDoc (accessed Jul 20, 2016).

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