Electronic Supplementary Material (ESI) for RSC Advances.

Supporting information

Selective Wacker type oxidation of a macrocyclic diene to the corresponding monounsaturated ketone used as fragrance

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I. GC chromatogram for the Wacker type oxidation of 1,9-cyclohexadecadiene (1)

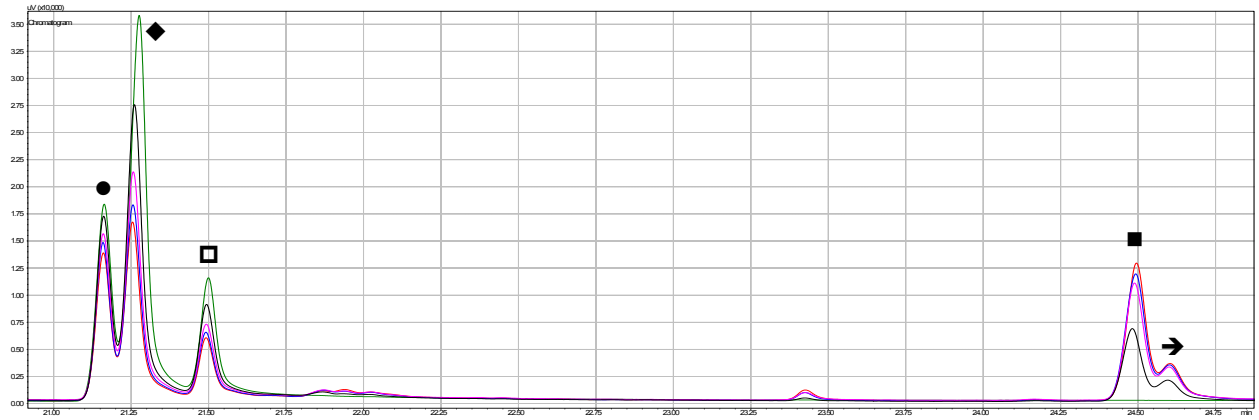

Figure S1 Chromatogram for the oxidation of the isomeric mixture of 1,9-CHDD to 8-CHD at different reaction times: ● *trans*/*trans*-1,9-CHDD, ◆ *cis*/*trans*-1,9-CHDD, ◘ *cis*/*cis*-1,9-CHDD, ■ *trans*-8-CHD, ➔ *cis*-8-CHD, – t = 0 h, – t = 1 h, – t = 3 h, – t = 5 h, – t = 8 h.

II. NMR spectra of the isomeric mixture of 1,9-cyclohexadecadiene (1)

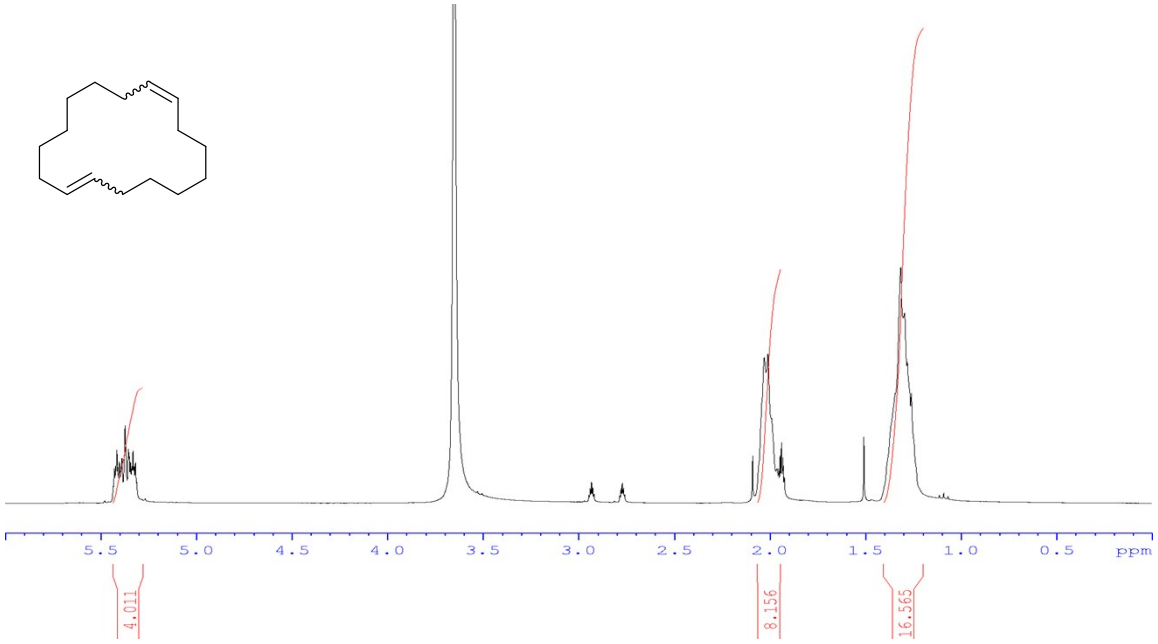

Figure S2 ^{1}H-NMR spectrum of the isomeric mixture of 1,9-cyclohexadecadiene (**1**) in a solvent mixture consisting of DMA-d_9, MeCN-d_3 and H_2O. Spectrum is calibrated to the methyl group of the deuterated acetonitrile (1.94 ppm).

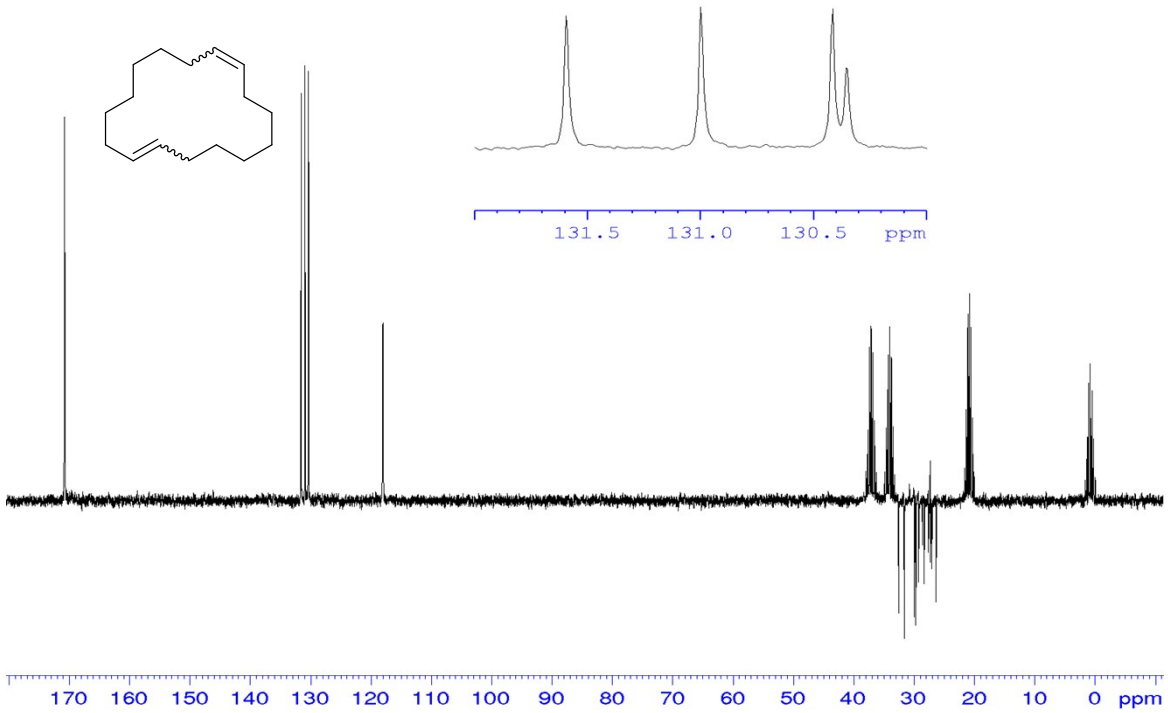

Figure S3 ^{13}C DEPT 135 NMR spectrum of the isomeric mixture of 1,9-cyclohexadecadiene (**1**) in a solvent mixture consisting of DMA-d_9, MeCN-d_3 and H_2O. Spectrum is calibrated to the acetyl group of the deuterated dimethylacetamide in the solvent mixture (20.738 ppm).

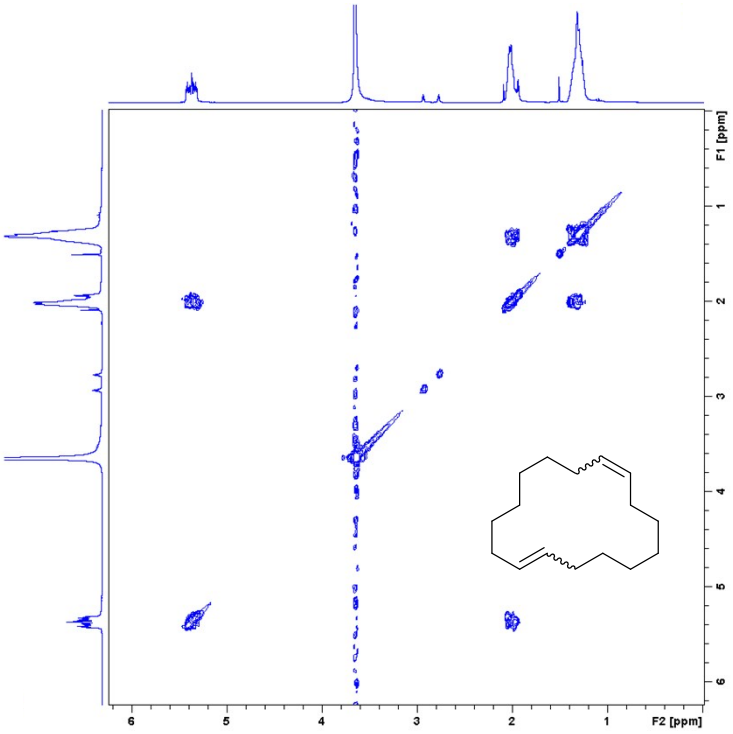

Figure S4 $^{1}H,^{1}H$-COSY spectrum of the isomeric mixture of 1,9-cyclohexadecadiene (**1**) in a solvent mixture consisting of DMA-d_9, MeCN-d_3 and H_2O. Spectrum is calibrated to the methyl group of the deuterated acetonitrile (1.94 ppm).

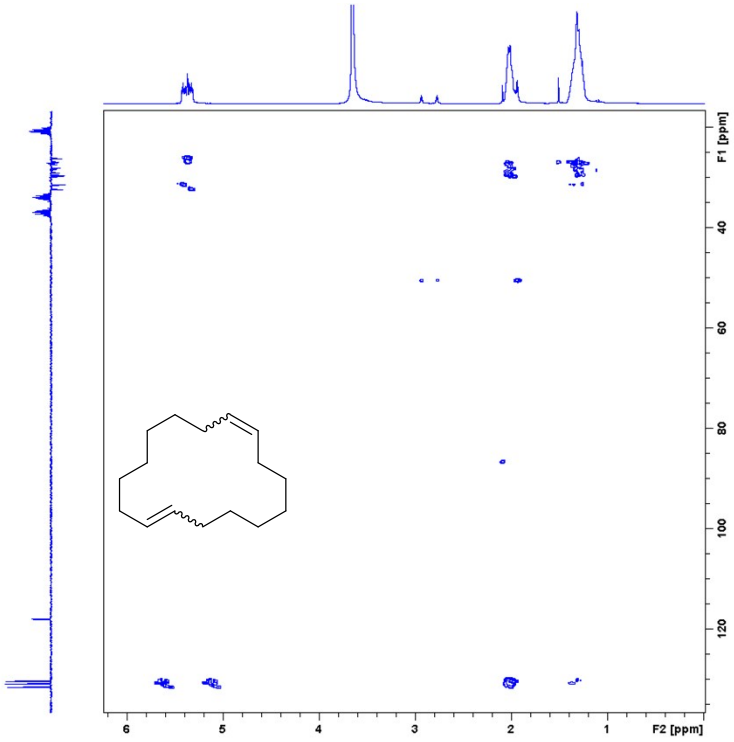

Figure S5 $^{1}H,^{13}C$-HMBC spectrum of the isomeric mixture of 1,9-cyclohexadecadiene (**1**) in a solvent mixture consisting of DMA-d_9, MeCN-d_3 and H_2O. Spectrum is calibrated to the methyl group of the deuterated acetonitrile (1.94 ppm) and to the acetyl group of the deuterated dimethylacetamide in the solvent mixture (20.738 ppm).

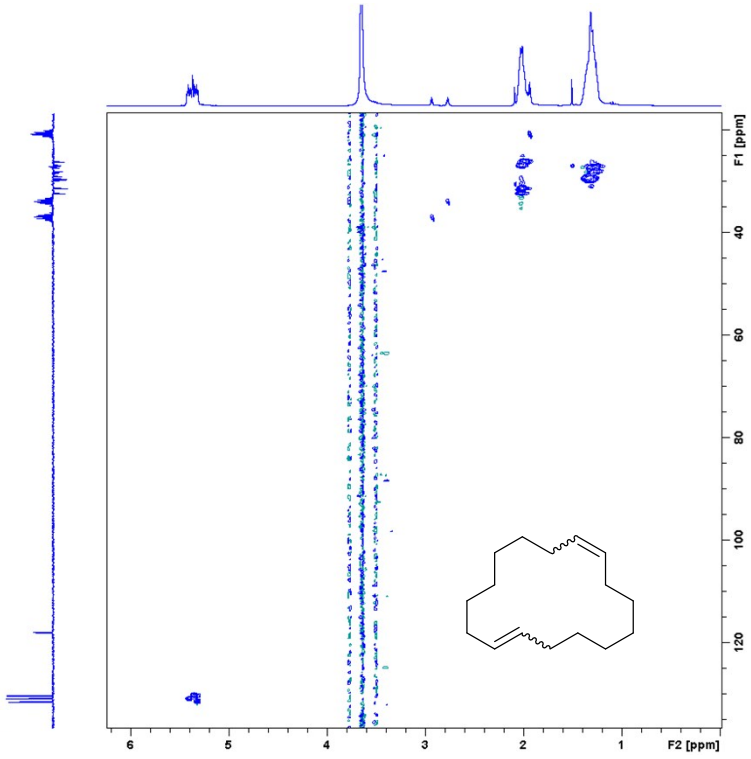

Figure S6 $^{1}H,^{13}C$-HSQC spectrum of the isomeric mixture of 1,9-cyclohexadecadiene (**1**) in a solvent mixture consisting of DMA-d_9, MeCN-d_3 and H_2O. Spectrum is calibrated to the methyl group of the deuterated acetonitrile (1.94 ppm) and to the acetyl group of the deuterated dimethylacetamide in the solvent mixture (20.738 ppm).

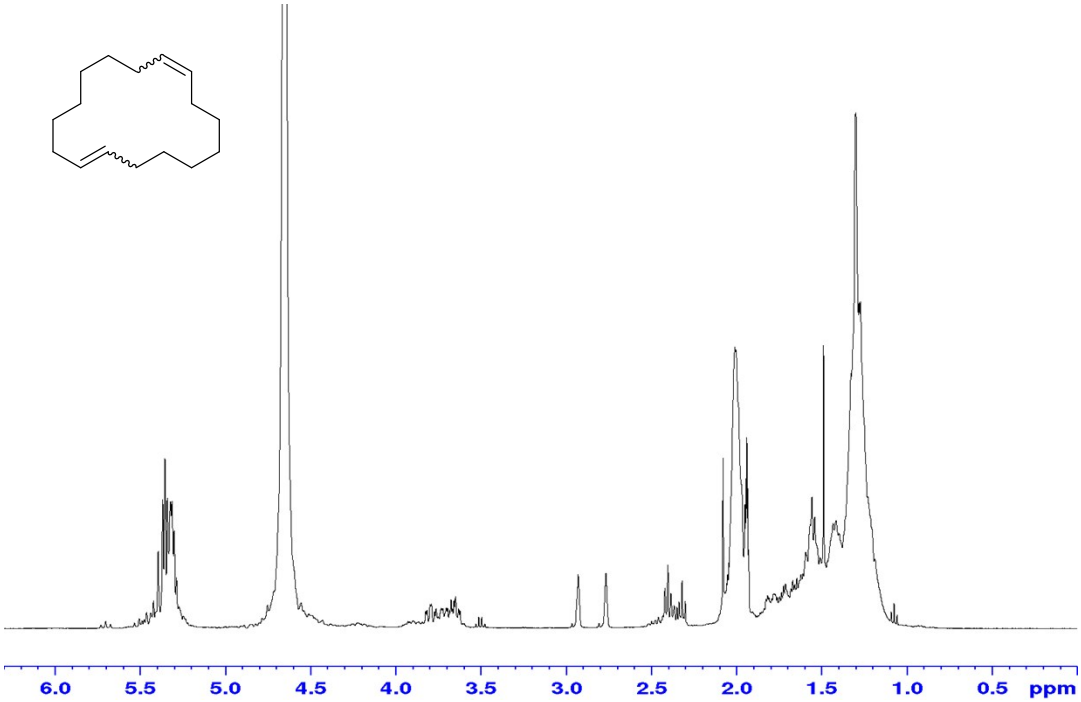

Figure S7 ^{1}H-NMR spectrum of the isomeric mixture of 1,9-cyclohexadecadiene (**1**) after addition of $Pd(NO_3)_2 \cdot 2\ H_2O$ in a solvent mixture consisting of DMA-d_9, MeCN-d_3 and H_2O. Spectrum is calibrated to the methyl group of the deuterated acetonitrile (1.94 ppm).

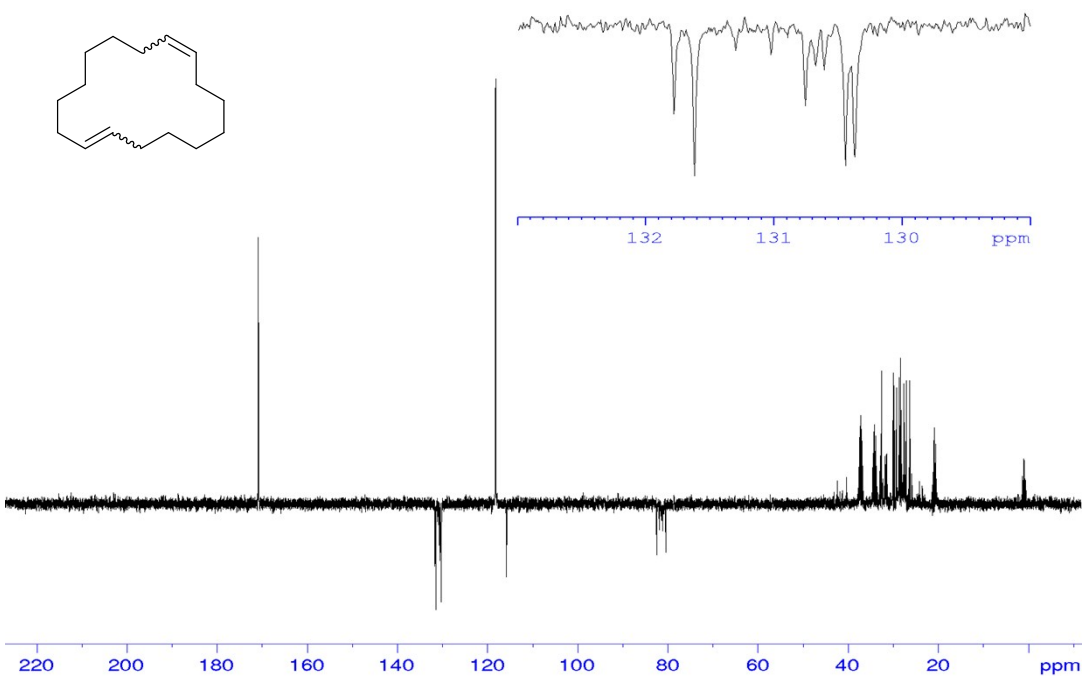

Figure S8 ^{13}C APT NMR spectrum of the isomeric mixture of 1,9-cyclohexadecadiene (**1**) after addition of $Pd(NO_3)_2 \cdot 2\ H_2O$ in a solvent mixture consisting of DMA-d_9, MeCN-d_3 and H_2O. Spectrum is calibrated to the acetyl group of the deuterated dimethylacetamide in the solvent mixture (20.738 ppm).

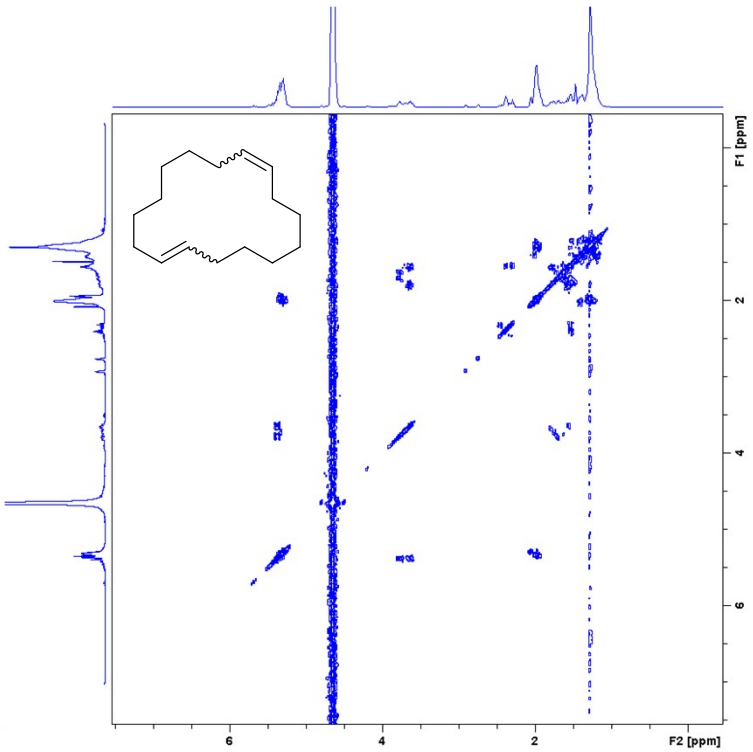

Figure S9 $^{1}H,^{1}H$-COSY spectrum of the isomeric mixture of 1,9-cyclohexadecadiene (**1**) after addition of $Pd(NO_3)_2 \cdot 2\ H_2O$ in a solvent mixture consisting of DMA-d_9, MeCN-d_3 and H_2O. Spectrum is calibrated to the methyl group of the deuterated acetonitrile (1.94 ppm).

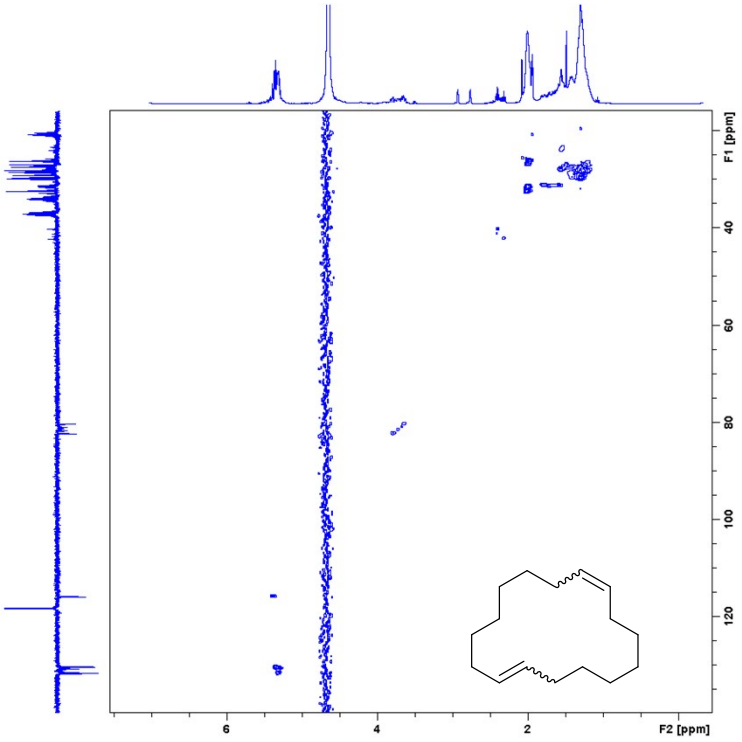

Figure S10 $^{1}H,^{13}C$-HSQC spectrum of the isomeric mixture of 1,9-cyclohexadecadiene (**1**) after addition of $Pd(NO_3)_2 \cdot 2\ H_2O$ in a solvent mixture consisting of DMA-d_9, MeCN-d_3 and H_2O. Spectrum is calibrated to the methyl group of the deuterated acetonitrile (1.94 ppm) and to the acetyl group of the deuterated dimethylacetamide in the solvent mixture (20.738 ppm).

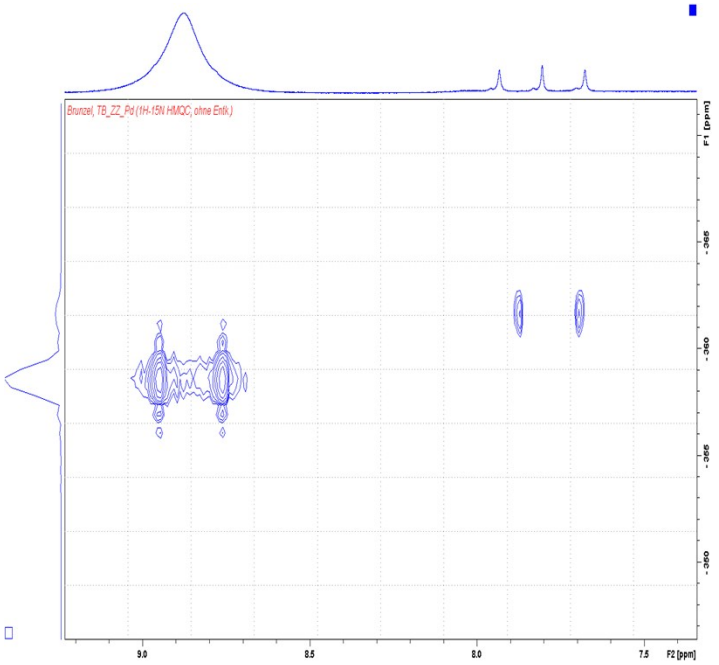

Figure S11 $^{1}H,^{15}N$-HMBC spectrum of (Z/Z)-1,9-cyclohexadecadiene (**1**) after addition of $Pd(NO_3)_2 \cdot 2\ H_2O$ and $Fe(NO_3)_3 \cdot 9\ H_2O$ in a solvent mixture consisting of DMA-d_9, MeCN-d_3 and H_2O. The sample was aged for three days.

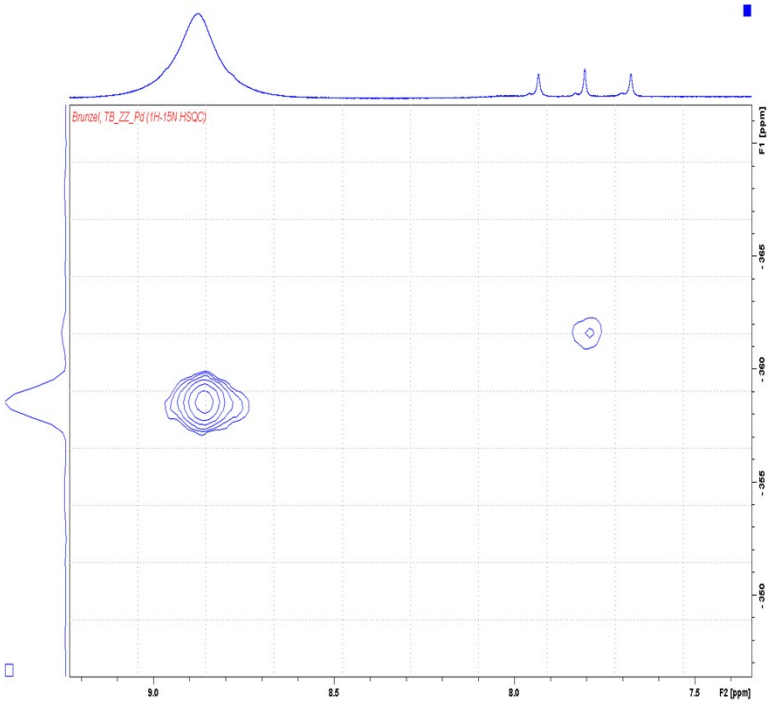

Figure S12 $^{1}H,^{15}N$-HSQC spectrum of (Z/Z)-1,9-cyclohexadecadiene (**1**) after addition of $Pd(NO_3)_2 \cdot 2\ H_2O$ and $Fe(NO_3)_3 \cdot 9\ H_2O$ in a solvent mixture consisting of DMA-d_9, MeCN-d_3 and H_2O. The sample was aged for three days.

III. Analytical data for the isomeric diketone mixture (3)

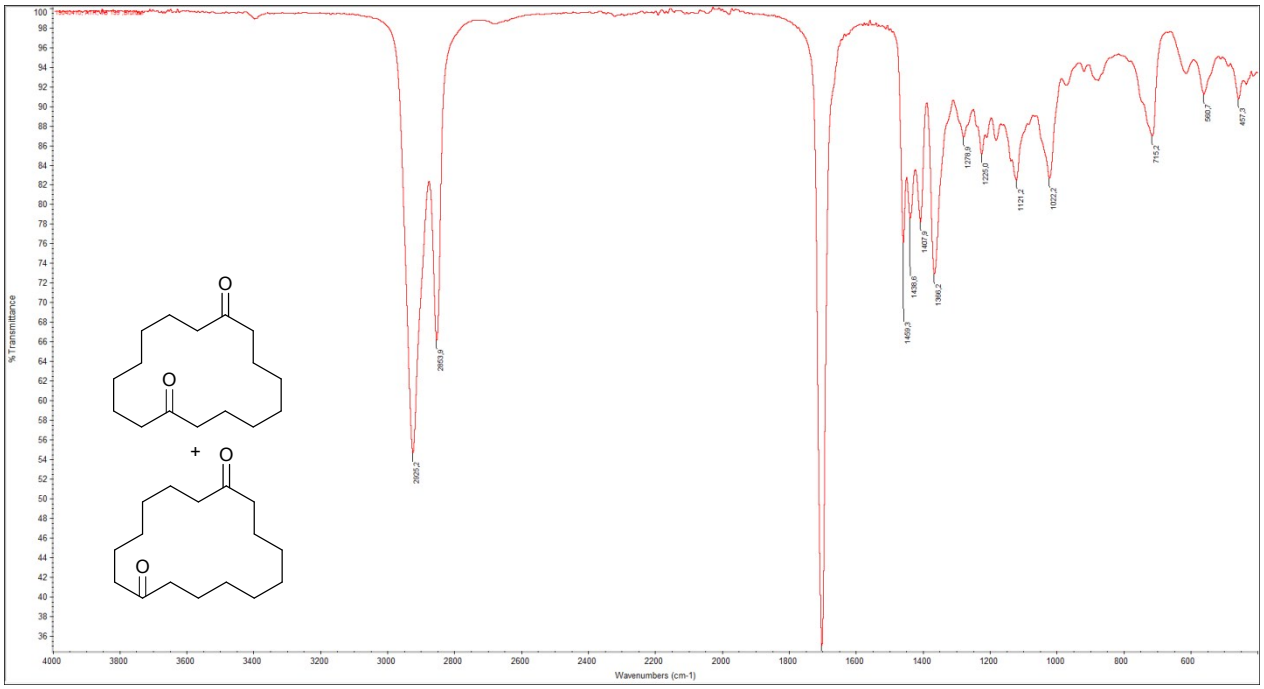

Figure S13 ATR-IR spectrum of the isomeric diketone mixture (**3**) consisting of cyclohexadecane-1,8-dione and cyclohexadecane-1,9-dione.

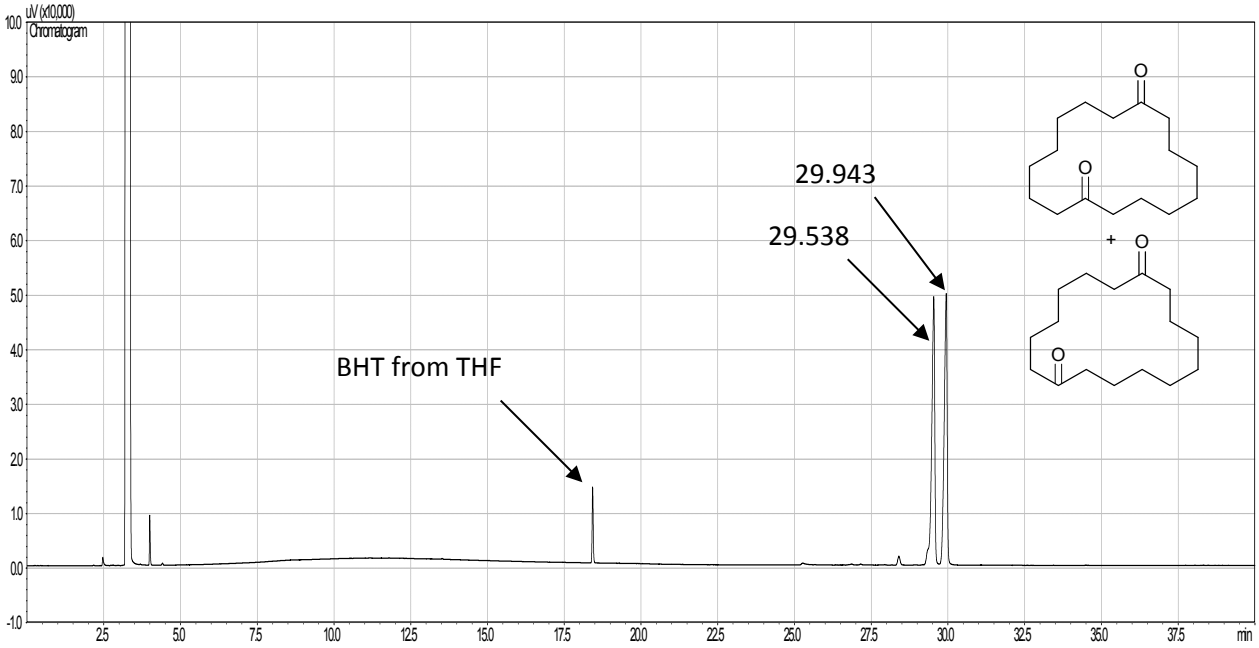

Figure S14 GC from the isolated diketone mixture (**3**) consisting of cyclohexadecane-1,8-dione and cyclohexadecane-1,9-dione.

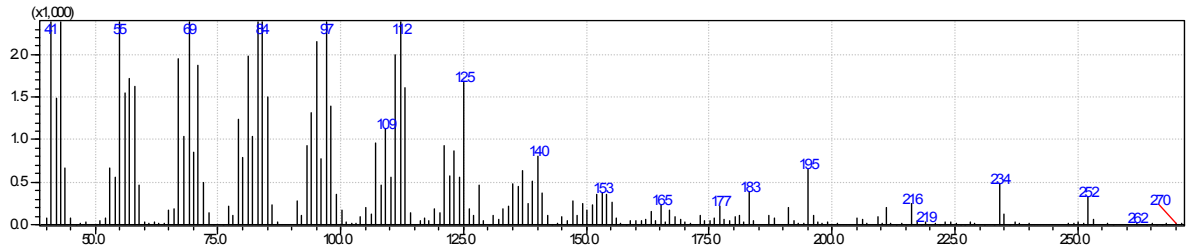

Figure S15 Mass spectrum of the GC signal with the retention time of 29.538 min

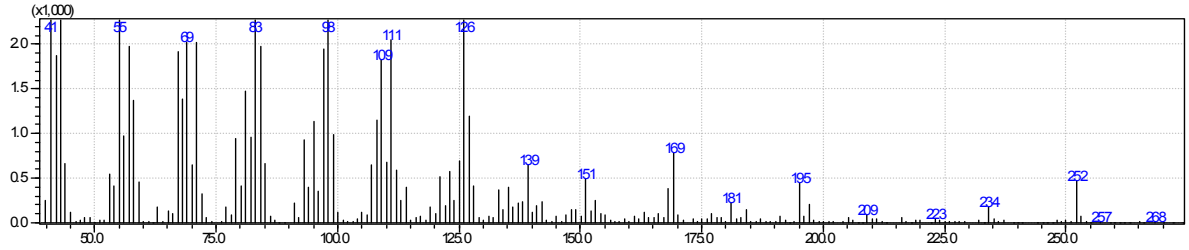

Figure S16 Mass spectrum of the GC signal with the retention time of 29.943 min

target	**252.20838**	found mass	**252.20869**

Table S1 HR-MS (EI) of the diketone (**3**)

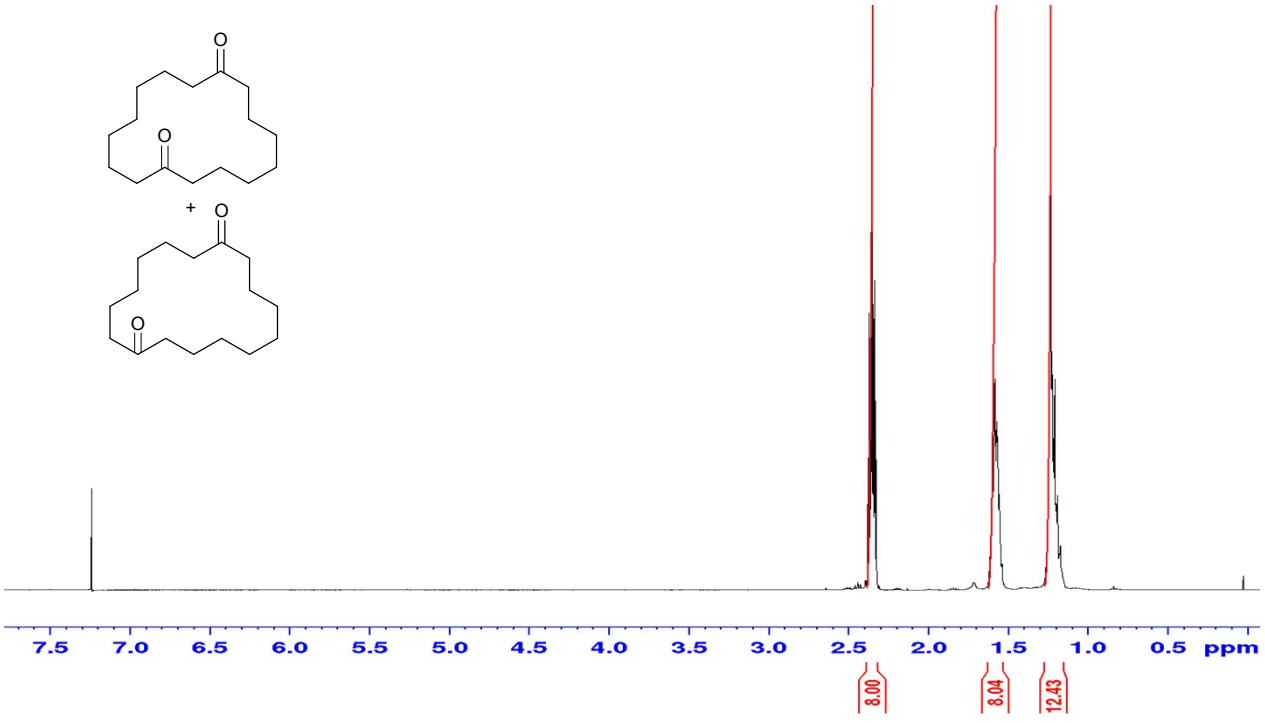

Figure S17 ^{1}H-NMR s of the isomeric mixture of the diketone (**3**) consisting of cyclohexadecane-1,8-dione and cyclohexadecane-1,9-dione in $CDCl_3$.

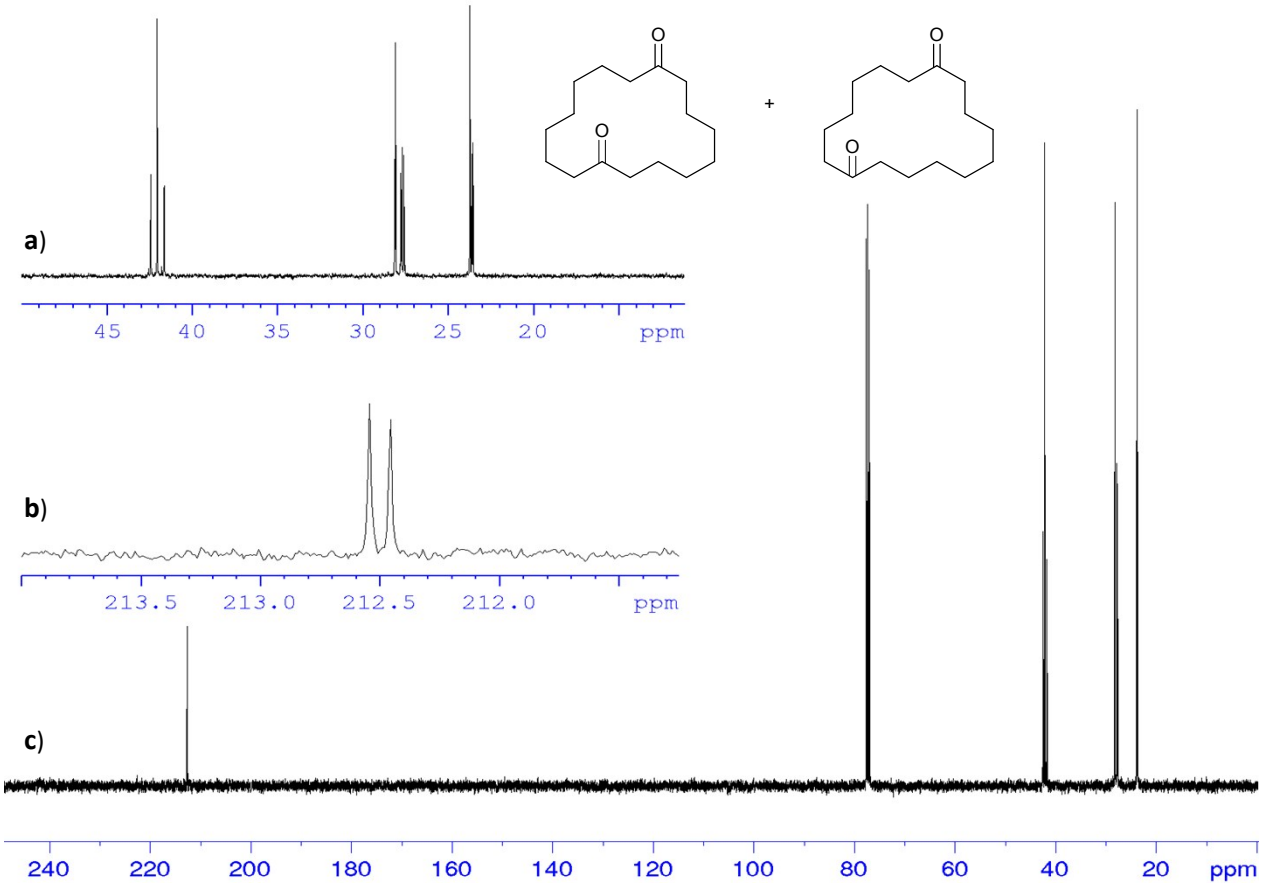

Figure S18 ^{13}C-NMR spectrum of the isomeric mixture of the diketone (**3**) consisting of cyclohexadecane-1,8-dione and cyclohexadecane-1,9-dione in $CDCl_3$. **a**) High field aliphatic signal range. **b**) Low field olefinic signal range. **c**) Whole spectrum.

atom	calculated for $C_{16}H_{28}O_2$	found for $C_{16}H_{28}O_2$
C	**76.14** wt.%	**76.08** wt.%
H	**11.18** wt.%	**10.67** wt.%

Table S2 Elemental analysis of the isomeric mixture with the molecular mass M($C_{16}H_{28}O_2$) = 252.3971 g/mol.

IV. Equations for the conversion, selectivity, yield and recovery rate

Conversion

$$X_S = \frac{n_{S,0} - n_S}{n_{S,0}} \cdot 100 = 1 - \frac{n_S}{n_{S,0}} \cdot 100$$

X_S	Conversion of the substrate
$n_{S,0}$	Initial moles of the substrate
n_S	Moles of the substrate found after reaction

Selectivity

$$S_P = \frac{n_P}{n_{S,0} - n_S} \cdot 100$$

S_P	Selectivity of the product
$n_{S,0}$	Initial moles of substrate
n_S	Moles of substrate found after reaction
n_P	Moles of product found after reaction

Yield

$$Y_P = \frac{n_P}{n_{S,0}} \cdot 100$$

Y_P	Yield of the product
$n_{S,0}$	Initial moles of substrate
n_P	Moles of product found after reaction

Recovery rate

$$rr = \frac{\sum n_S + n_P}{n_{S,0}} \cdot 100$$

rr	Recovery rate of the reaction
$n_{S,0}$	Initial moles of substrate
n_S	Moles of substrate found after reaction
n_P	Moles of product found after reaction