Supplementary Information (SI) for Chemical Science.

Supplementary Information

Palladium-catalyzed aerobic homocoupling of aliphatic olefins to dienes: evidence for rate-limiting concerted metalation-deprotonation

Sam Van Minnebruggen†, Harry Poels-Ryckeboer†, Hendrik Van Dessel†, Frederick Martens†, Wouter Stuyck†, Tom Nelis†, Igor Beckers†, Aram Bugaev‡, Dirk De Vos†*

†Centre for Membrane Separations, Adsorption, Catalysis and Spectroscopy for Sustainable Solutions

(cMACS) , KU Leuven, 3001 Leuven, Belgium

‡SuperXAS beamline, Paul Scherrer Institute, 5232 Villigen, Switzerland

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1. Experimental details

A. Chemicals

All chemicals were used as received: palladium acetate (Acros, 99.9%), 2-hydroxypyridine (Sigma-Aldrich, 97%), 5-CF_3-2-pyridinone (J&K scientific, 98%), 2-hydroxy-5-nitropyridine (Fisher scientific, 99%), 2-hydroxy-4-methylpyridine (J&K scientific, 98%), 2-hydroxy-5-methylpyridine (J&K scientific, 97%), 5-bromo-2-hydroxypyridine (Ambeed, 98%), 2,4-dihydroxypyridine (Merck, 97%), 6-hydroxynicotinic acid methyl ester (Fluorochem, 97%), 1-octene (Fisher scientific, 99%), *trans*-2-octene (Fisher scientific, 97%), 2-methyl-1-heptene (TCI, 98%), cyclooctene (Fisher scientific, 95%), 4-methyl-1-hexene (TCI, 99%), vinylcyclohexane (Fisher scientific, 97%), *t*-butylethylene (Fisher scientific, 95%), allylcyclohexane (Fisher scientific, 97%), 1,7-octadiene (TCI, 97%), allylbenzene (Acros, 98%), *N,N*-dimethylacetamide (VWR, 99.8%), *N,N*-dimethylformamide (Sigma Aldrich, 99.8%), *N*-butyl-2-pyrrolidone (Carl Roth, >99.5%), dimethyl sulfoxide (Fisher scientific, 99%), valeronitrile (Sigma-Aldrich, 99.5%), 2,4-dichlorotoluene (Sigma-Aldrich, 99%), *N*-methyl-2-pyrrolidone (VWR, 99%), styrene (Fisher scientific, 99%), styrene-d_8 (Merck, 98% D), 4-methoxystyrene (Fisher scientific, 98%), 4-chlorostyrene (Fisher scientific, 99%), 4-*t*-butylstyrene (Fisher scientific, 94%), 4-methylstyrene (TCI, 98%), acetic acid (Fisher scientific, 99.9985%), pivalic acid (TCI, 99%), dichloroacetic acid (Merck, 99%), benzoic acid (Merck, 99%), 4-methoxybenzoic acid (Merck, 99%), chloroacetic acid (Aldrich, 99%), trifluoroacetic acid (Fisher scientific, 99%), tetradecane (TCI, 99%), *t*-butyl acrylate (J&K scientific, 99.5%)

B. Catalytic reaction

In a typical reaction, 15 µmol $Pd(OAc)_2$ and 45 µmol 2-hydroxypyridine were added to a glass vial. Next, 1.4 mL dimethylacetamide (dry), 1.5 mmol acetic acid, 1.6 mL 1-octene, tetradecane (internal standard) and a magnetic stirring bar were added. Ensure that the solution is fully homogeneous (especially with 5-NO_2-2-OH-pyridine and $PdCl_2$). Subsequently, O_2 was continuously supplied during reaction by a balloon on the vial, sparging the reaction mixture with a second needle. Then the reaction mixture was heated to reaction temperature and magnetically stirred at 500 rpm. For the screening of different O_2 partial pressures, a gas mixture was prepared in a 50 ml Premex pressure vessel by admixing the right quantities of O_2 and N_2. The contents of the pressure vessel were subsequently used to fill the balloon. Note that working under O_2 atmosphere in combination with organic vapors poses an explosion risk.

Product identification was done by gas chromatography coupled to mass spectrometry (GC-MS) with an Agilent 6890 GC, equipped with a HP-5ms column and a 5973 MSD mass spectrometer. Product quantification was done using a GC equipped with a CP Sil 8 CB column, based on effective carbon numbers and tetradecane as an internal standard. Activity is typically expressed in turnover frequency (TOF) as $TOF = \frac{mol_{product}}{mol_{palladium} * h}$ which simplifies to h^{-1}. In some occasions, activity is also expressed as turnover number (TON): $TON = \frac{mol_{product}}{mol_{palladium}}$.

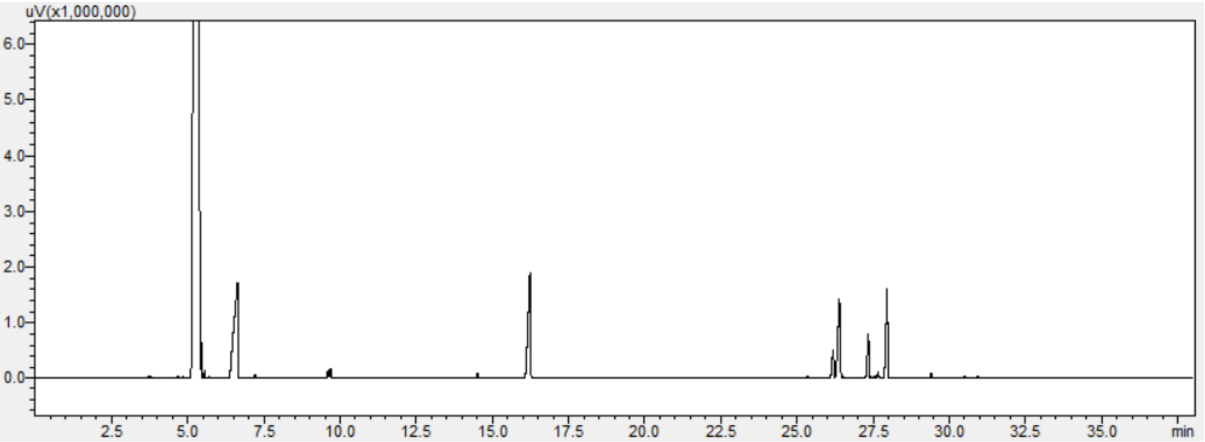
C. Product isolation

For the product isolation, a scaled up reaction was performed in which O_2 was bubbled through the solution, open under reflux. Cooling down the reaction mixture (+ adding water) led to a phase separation. The upper layer contained mainly 1-octene and hexadecadiene isomers. The bottom layer was then washed with hexane to further remove product. The 1-octene or other reactant was removed under vacuum. As such, we obtained an isolated yield of 123 mg product for the reaction depicted in Figure 4 (3.9 M olefin), corresponding to a TOF of 37 h^{-1} (40 h^{-1} using GC analysis). The bottom layer comprised the Pd-catalyst in the polar dimethylacetamide. The product was analyzed by NMR (^{1}H, COSY) on a 600 MHz Bruker Avance II+600 and GC-MS. In case of product crystallization (e.g. 4-methoxystyrene), crystals were dissolved in $CDCl_3$ and ^{1}H-NMR was measured at elevated temperatures to keep the product in solution (50°C).

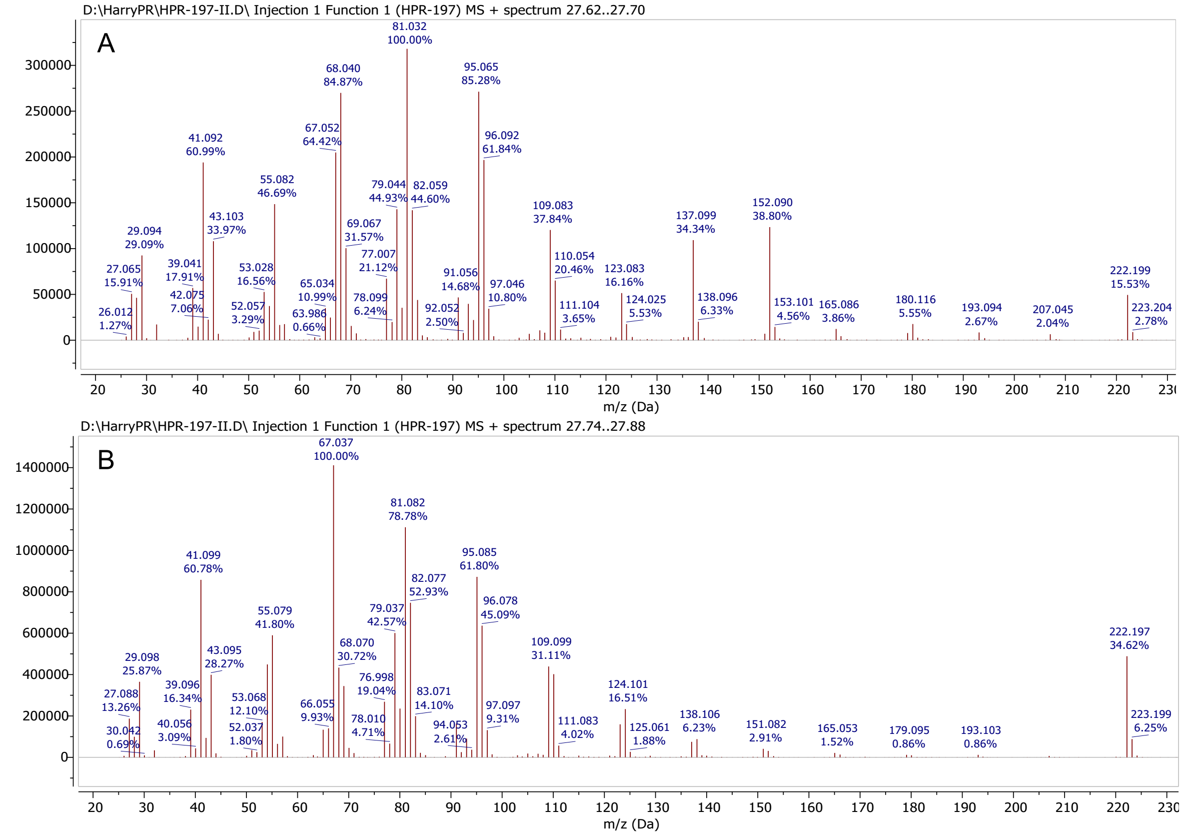
In case no phase separation happened, the volatile substrate was evaporated and the product mixture analysis was done on the crude mixture.

2. Product identification

2.1 Product mixture obtained from 1-octene

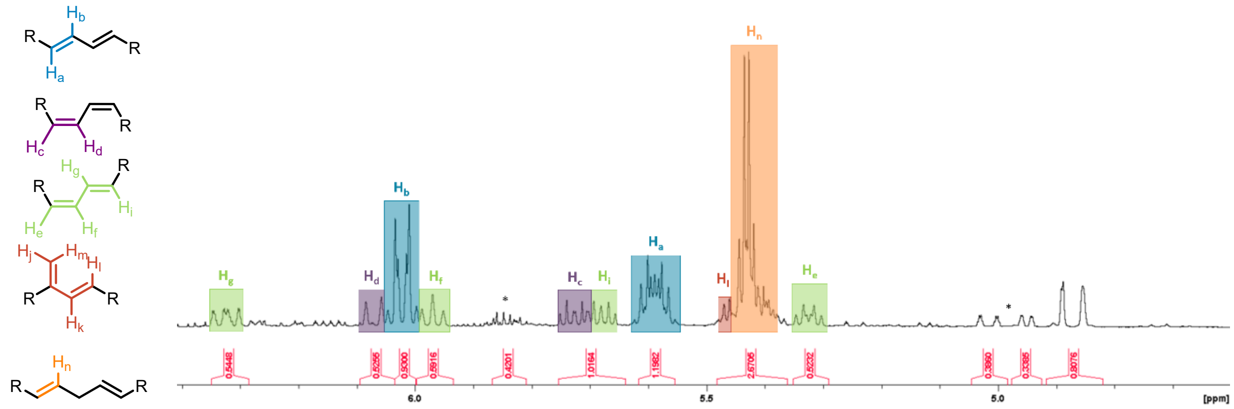


(a) GC

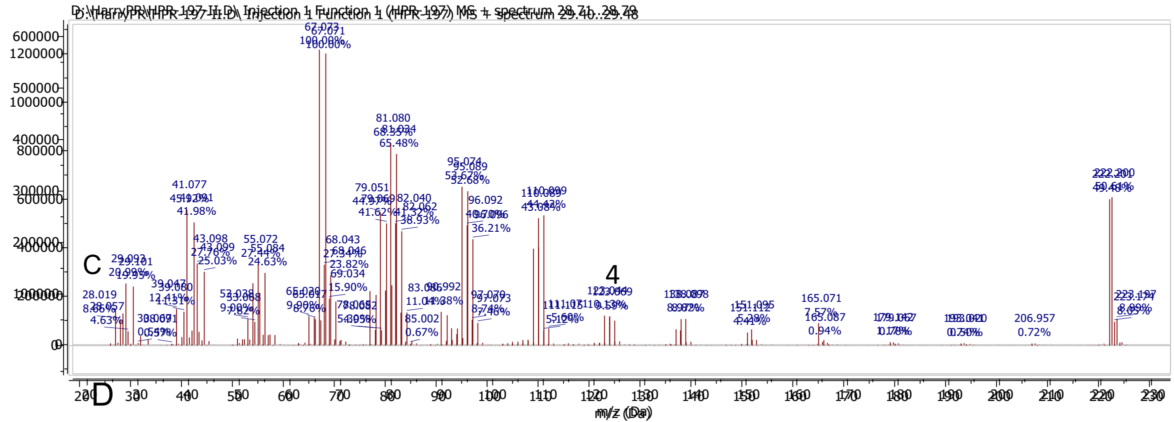


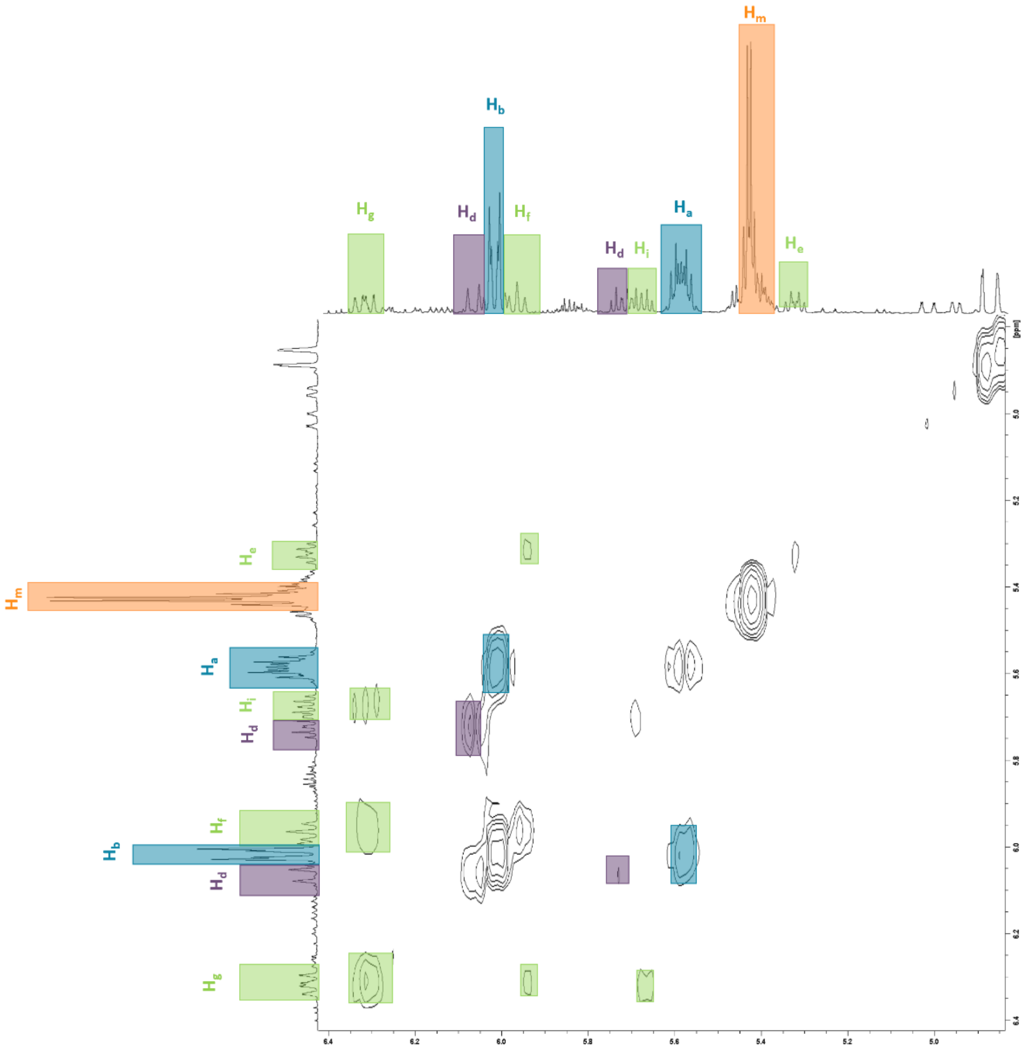
(b) GC-MS

(c) ^{1}H-NMR

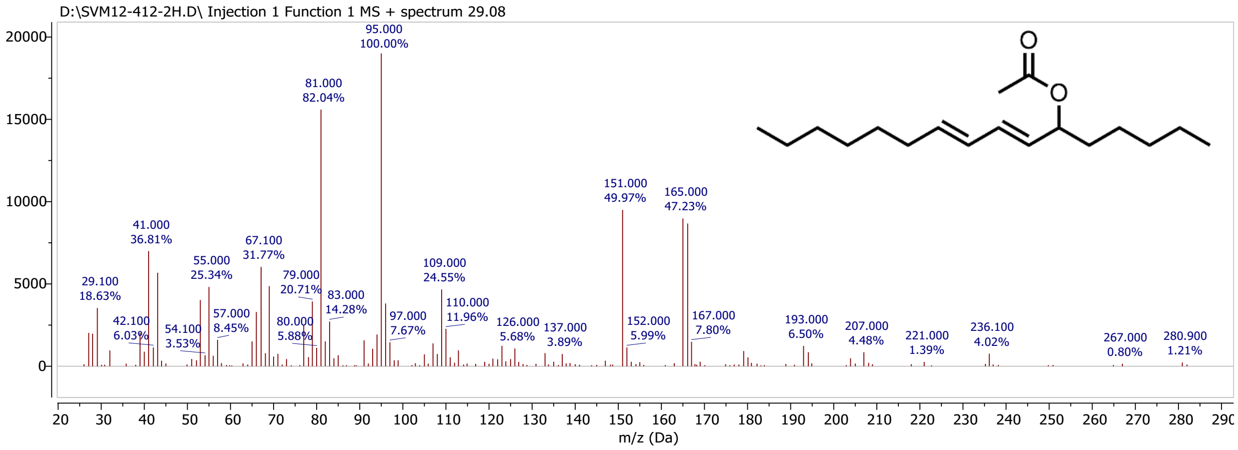


(d) COSY





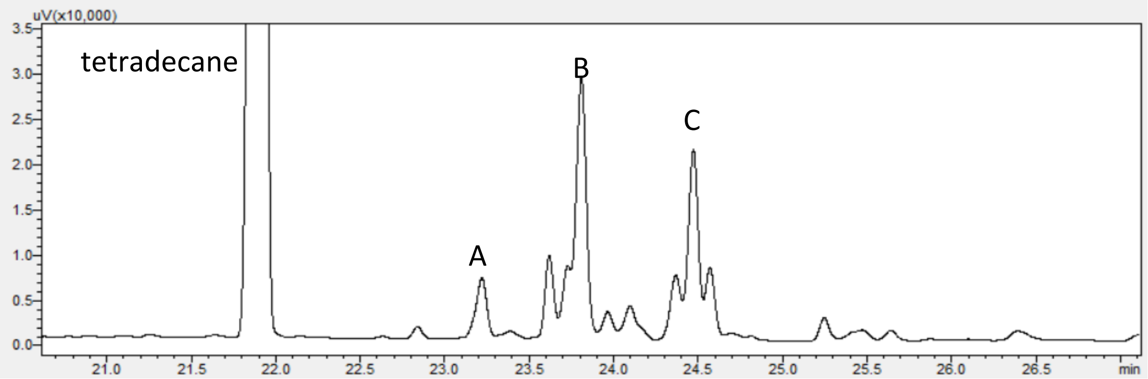
The product mixture comprised 4 major C_{16}-diene products, labeled A-D in the GC chromatogram, which had a relative abundance of respectively 13, 29, 26 and 32%. These products were further identified by ^{1}H-NMR. Here, we used simulated ^{1}H-NMR spectra as obtained from Chemdraw for comparison. Based on H_a (*t,t*; I = 1.1982, 2 H), H_d (*c,c*; I = 0.5255, 2 H), H_g (*c,t*; I = 0.5448, 1 H) and H_n (non-conjugated; I = 2.6705, 4 H), products A-D were identified as respectively *cis,cis*-7,9-hexadecadiene; *trans,trans*-7,9-hexadecadiene; *cis,trans*-7-9-hexadecadiene and *trans,trans*-6,9-hexadecadiene. * points out residual 1-octene in the sample.



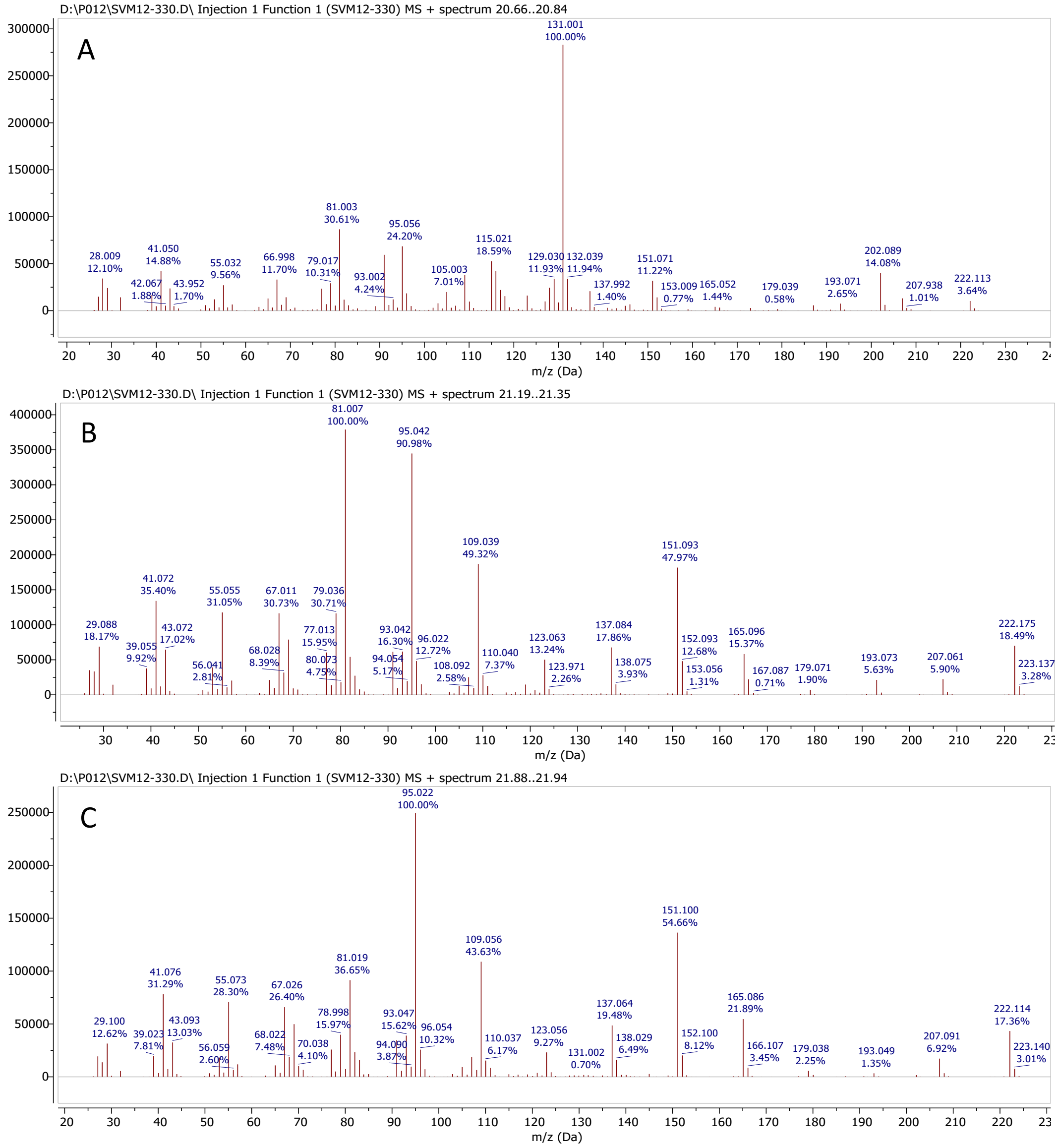
(e) Side-product

Figure S1a. (**a**) Gas chromatogram of a reference reaction with 1-octene. Reaction conditions: 15 µmol Pd(OAc)$_2$, 7 eq 2-OH-pyridine, 100 eq AcOH, 1 mL 1-octene, 1.4 mL *N,N*-dimethylacetamide and 50 µL dodecane (internal standard) at 100°C under O$_2$ atmosphere (sparged) after 30 min. (**b**) GC-MS spectra (EI, 70 eV) of relevant molecules shown in (a). (**c**) and (**d**) give respectively the ^{1}H-NMR and COSY of the purified product mixture (+ peak assignment). (**e**) gives the GC-MS spectrum of one of the side products formed at long reaction times (EI, 70 eV).

2.2 Product mixture obtained from 2-octene



(a) GC

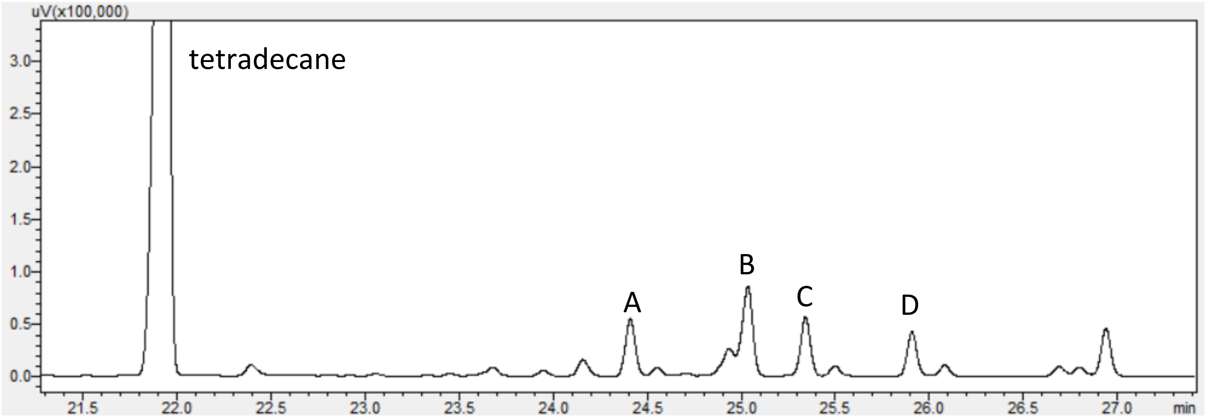


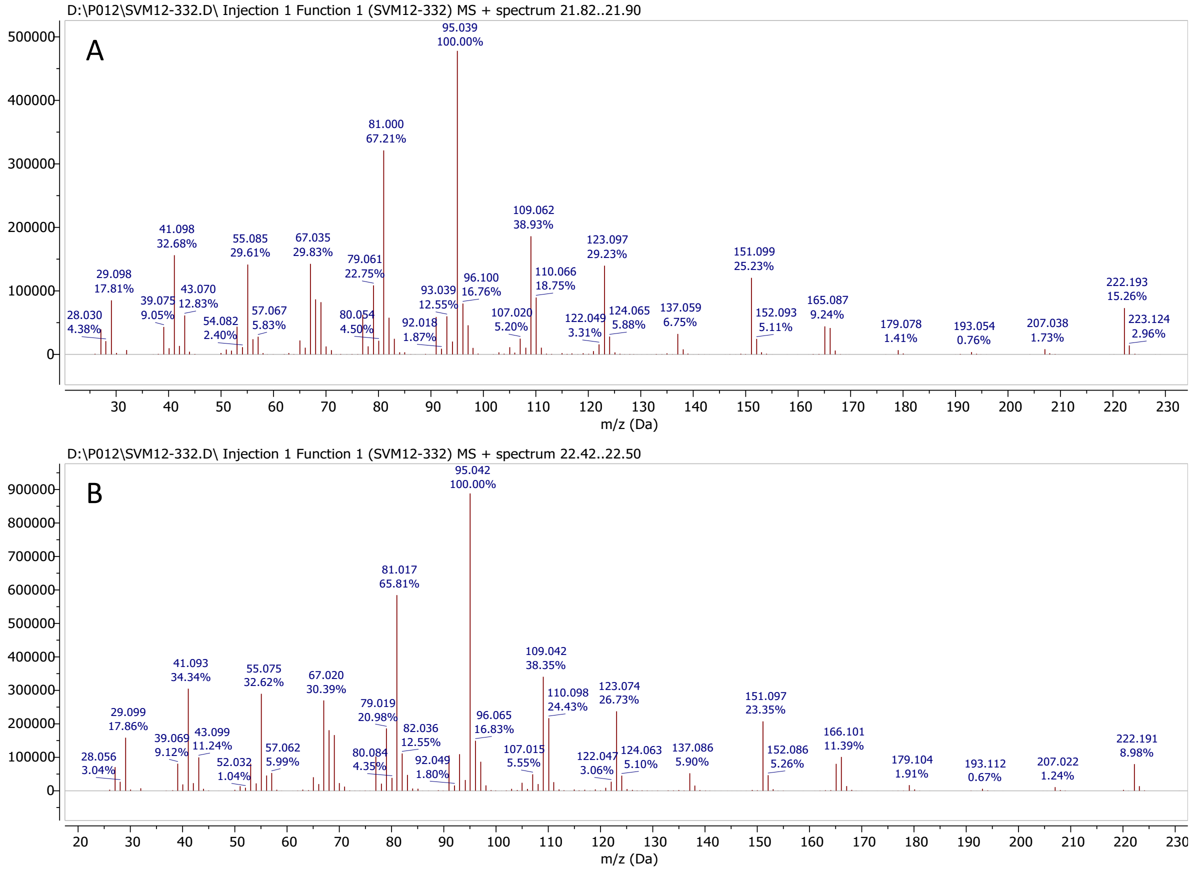
(b) GC-MS

Figure S1b. (**a**) Gas chromatogram of a reference reaction with 2-octene. Reaction conditions: 15 µmol $Pd(OAc)_2$, 7 eq 2-OH-pyridine, 100 eq AcOH, 1 mL 2-octene, 1.4 mL DMA and 50 µL tetradecane at 100°C under O_2 atmosphere (sparged) after 30 min. (**b**) GC-MS spectra (EI, 70 eV) of relevant molecules shown in (a).

2.3 Product mixture obtained from 2-methyl-1-heptene

(a) GC





(b) GC-MS

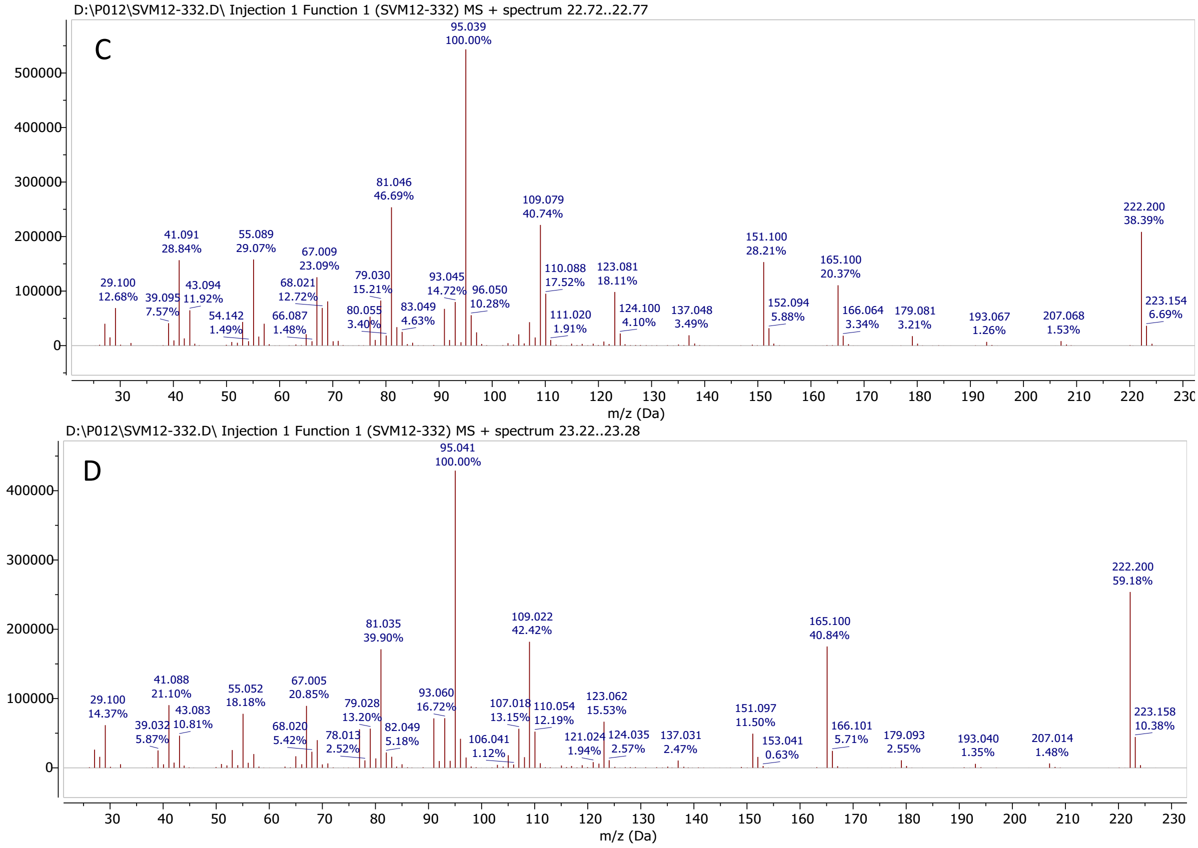
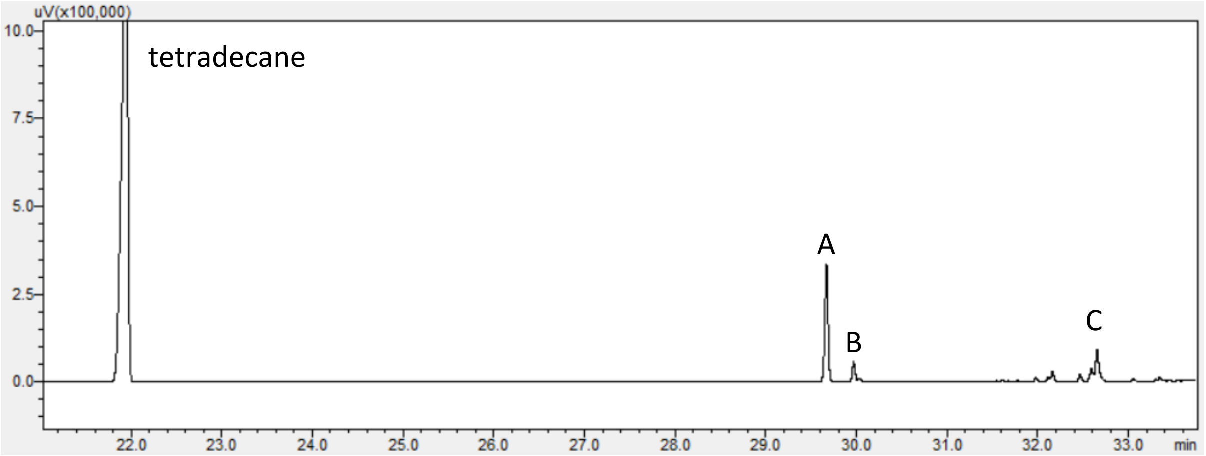


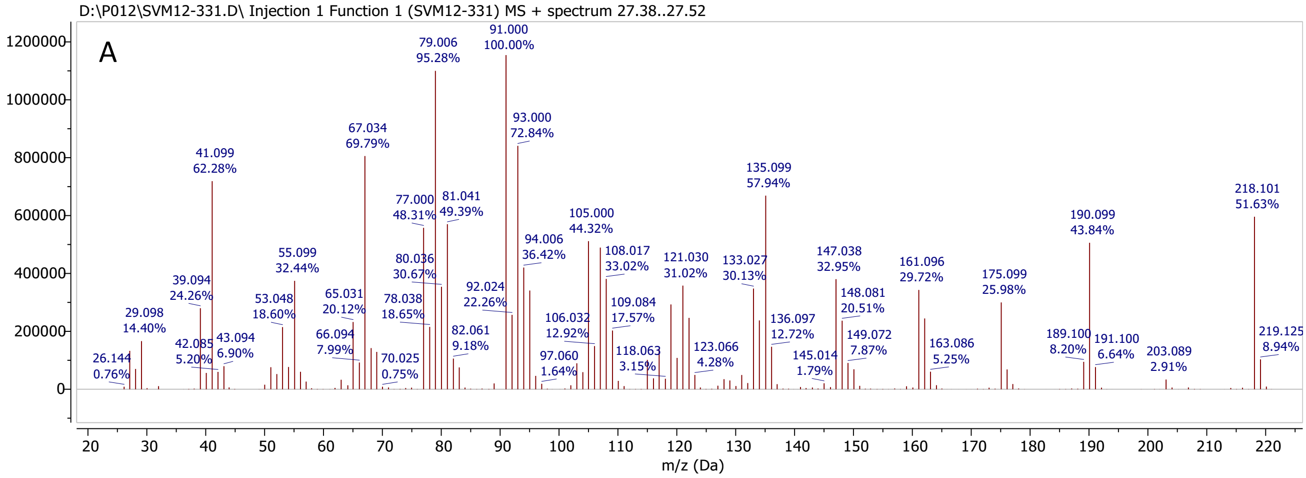
Figure S1c. (**a**) Gas chromatogram of a reference reaction with 2-methyl-1-heptene. Reaction conditions: 15 µmol Pd(OAc)$_2$, 7 eq 2-OH-pyridine, 100 eq AcOH, 1 mL 2-methyl-1-heptene, 1.4 mL DMA and 50 µL tetradecane at 100°C under O$_2$ atmosphere (sparged) after 30 min. (**b**) GC-MS spectra (EI, 70 eV) of relevant molecules shown in (a).

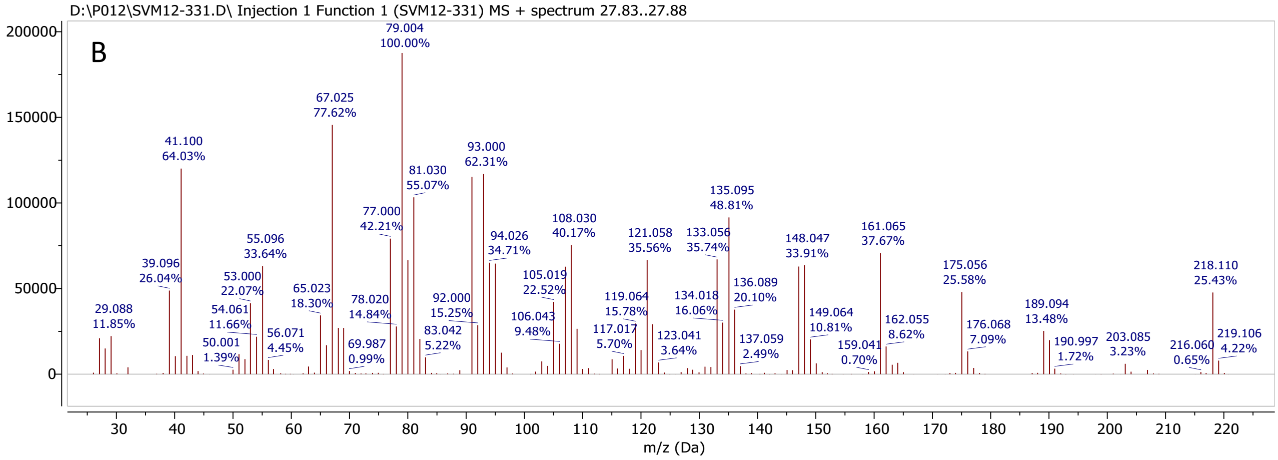
2.4 Product mixture obtained from cyclooctene

(a) GC



(b) GC-MS





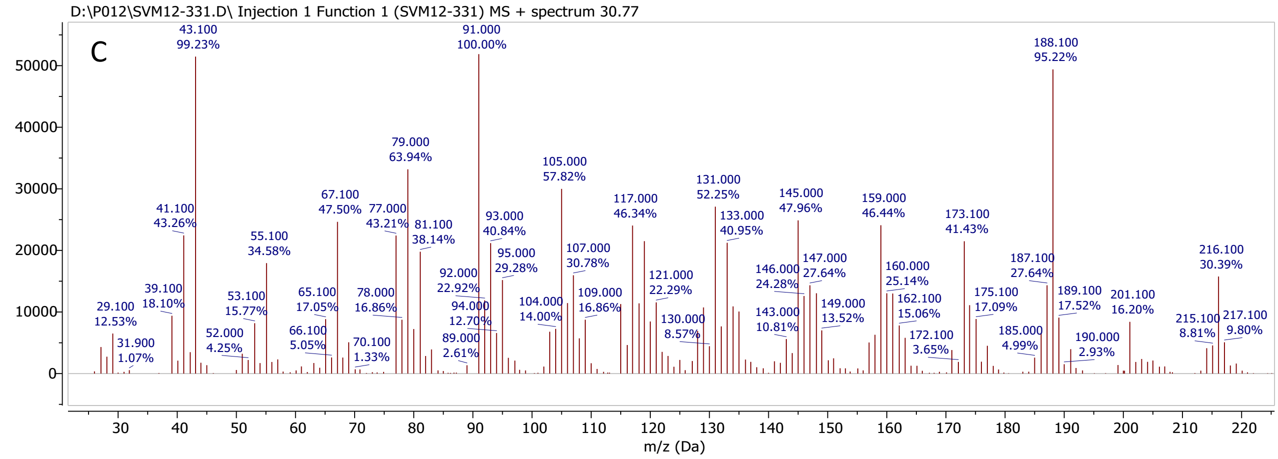
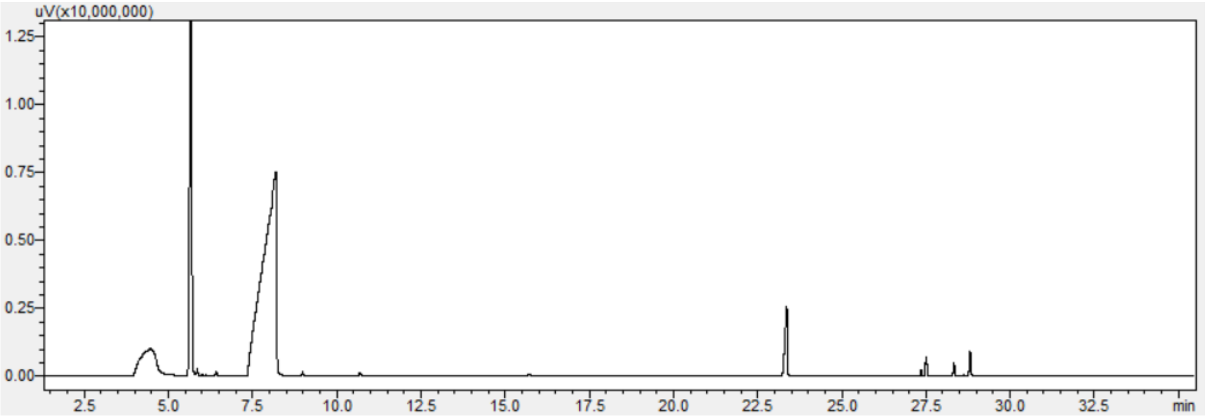
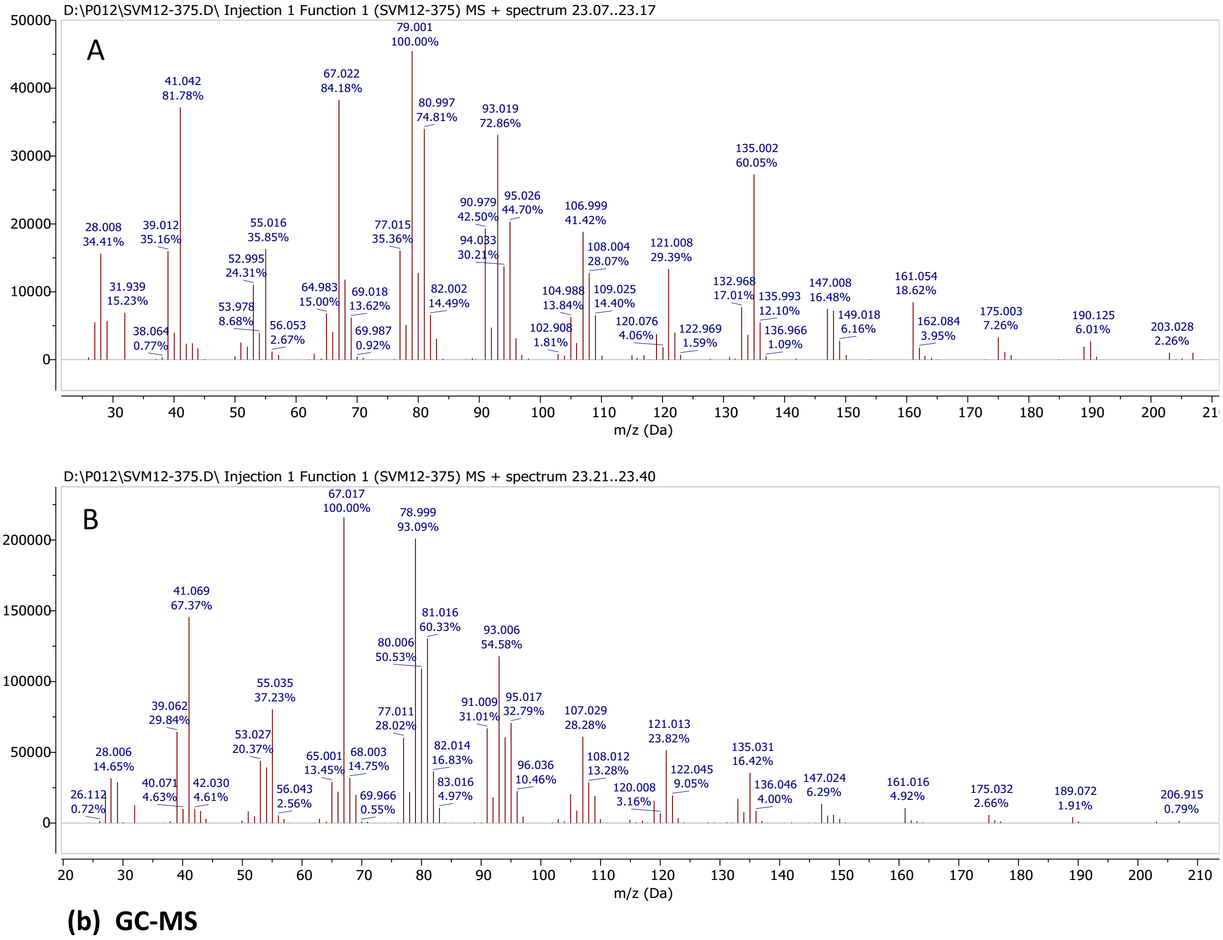


Figure S1d. (**a**) Gas chromatogram of a reference reaction with cyclooctene. Reaction conditions: 15 µmol Pd(OAc)$_2$, 7 eq 2-OH-pyridine, 100 eq AcOH, 1 mL cyclooctene, 1.4 mL DMA and 50 µL tetradecane at 100°C under O$_2$ atmosphere (sparged) after 30 min. (**b**) GC-MS spectra (EI, 70 eV) of relevant molecules shown in (a).

2.5 Product mixture obtained from 1,7-octadiene



(a) GC



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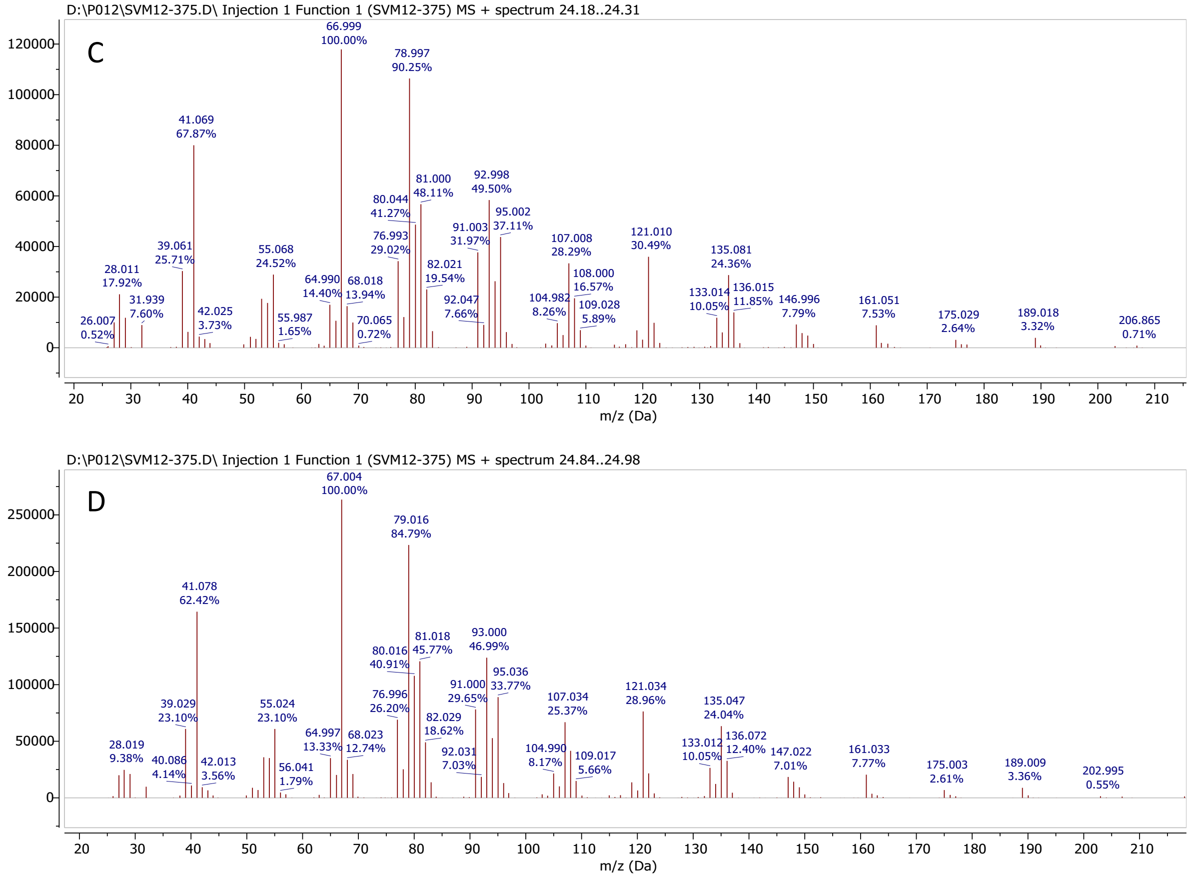
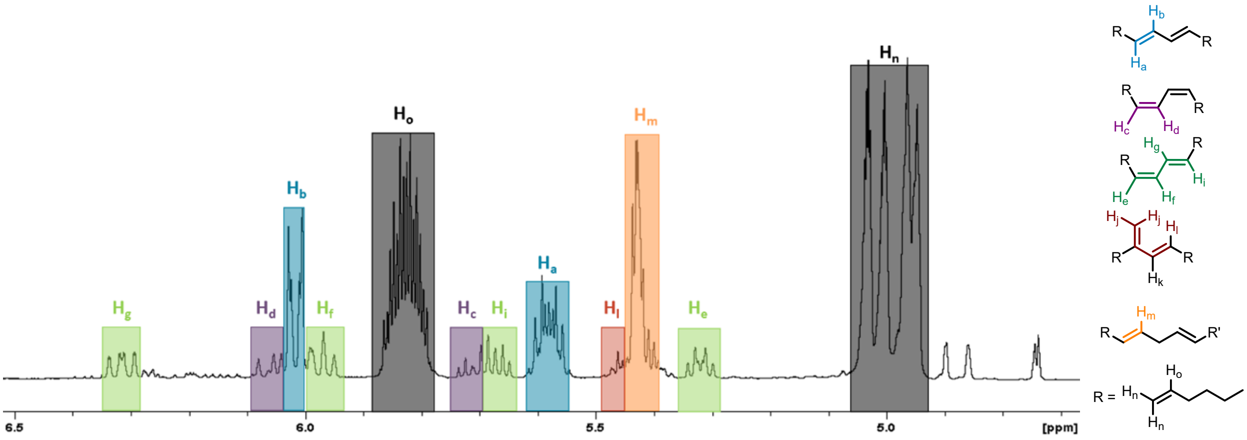
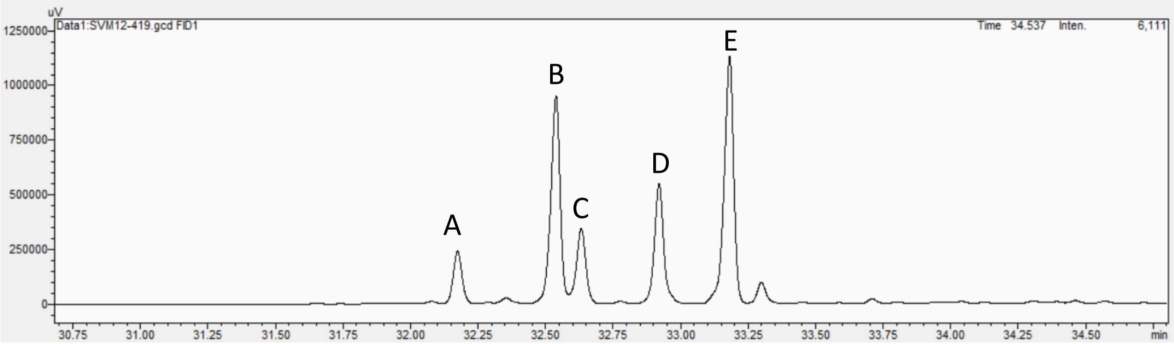




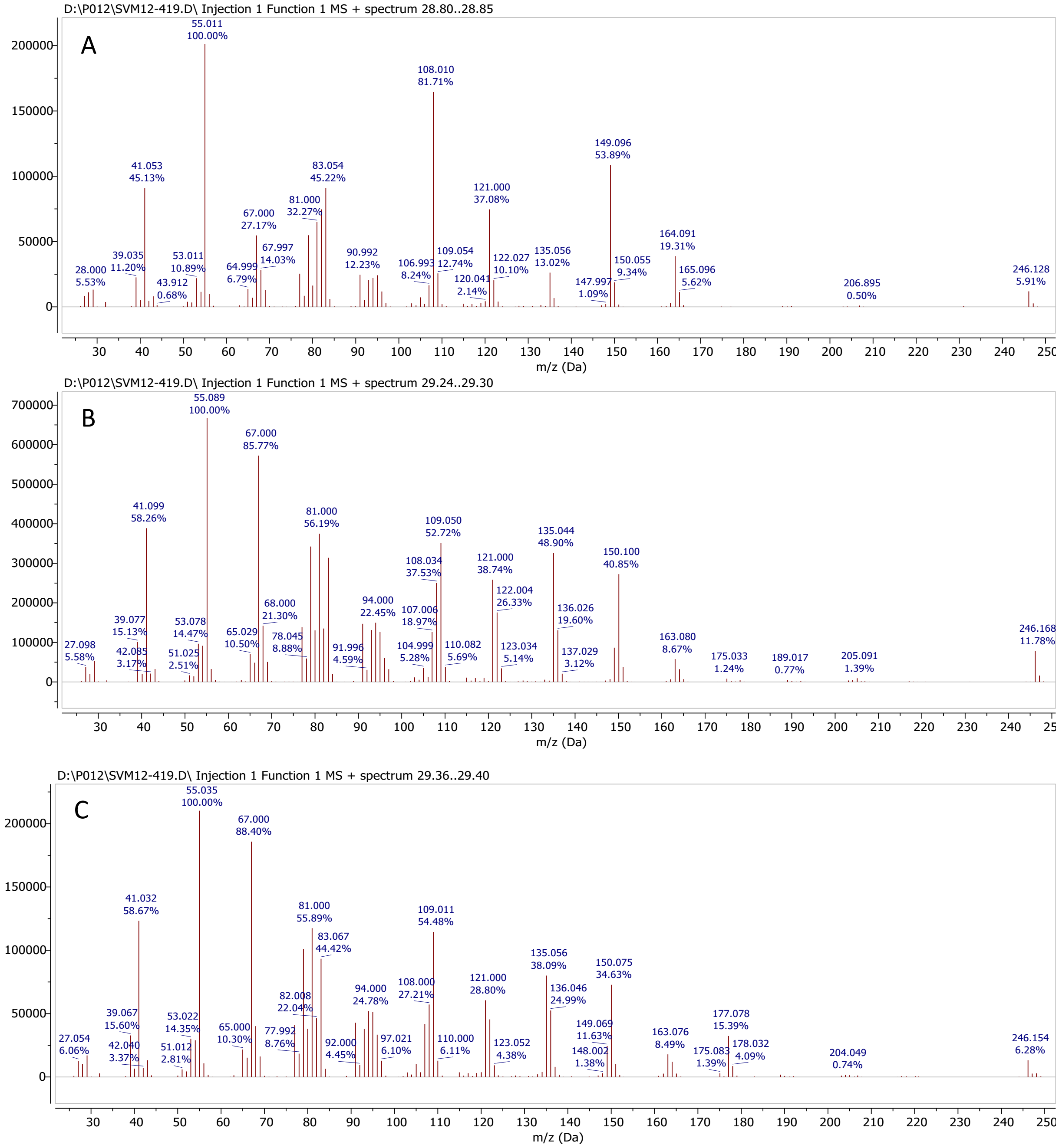
(c) ^{1}**H-NMR**

Figure S1e. (**a**) Gas chromatogram of a reference reaction with 1,7-octadiene. Reaction conditions: 15 µmol Pd(OAc)$_2$, 7 eq 2-OH-pyridine, 100 eq AcOH, 1 mL 1,7-octadiene, 1.4 mL DMA and 50 µL tetradecane at 100°C under O$_2$ atmosphere (sparged) after 30 min. (**b**) GC-MS spectra (EI, 70 eV) of relevant molecules shown in (a). (**c**) ^{1}H-NMR of the isolated product mixture (+ peak assignment).

2.6 Products obtained from allylcyclohexane



(a) GC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83.054
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67.000
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67.997
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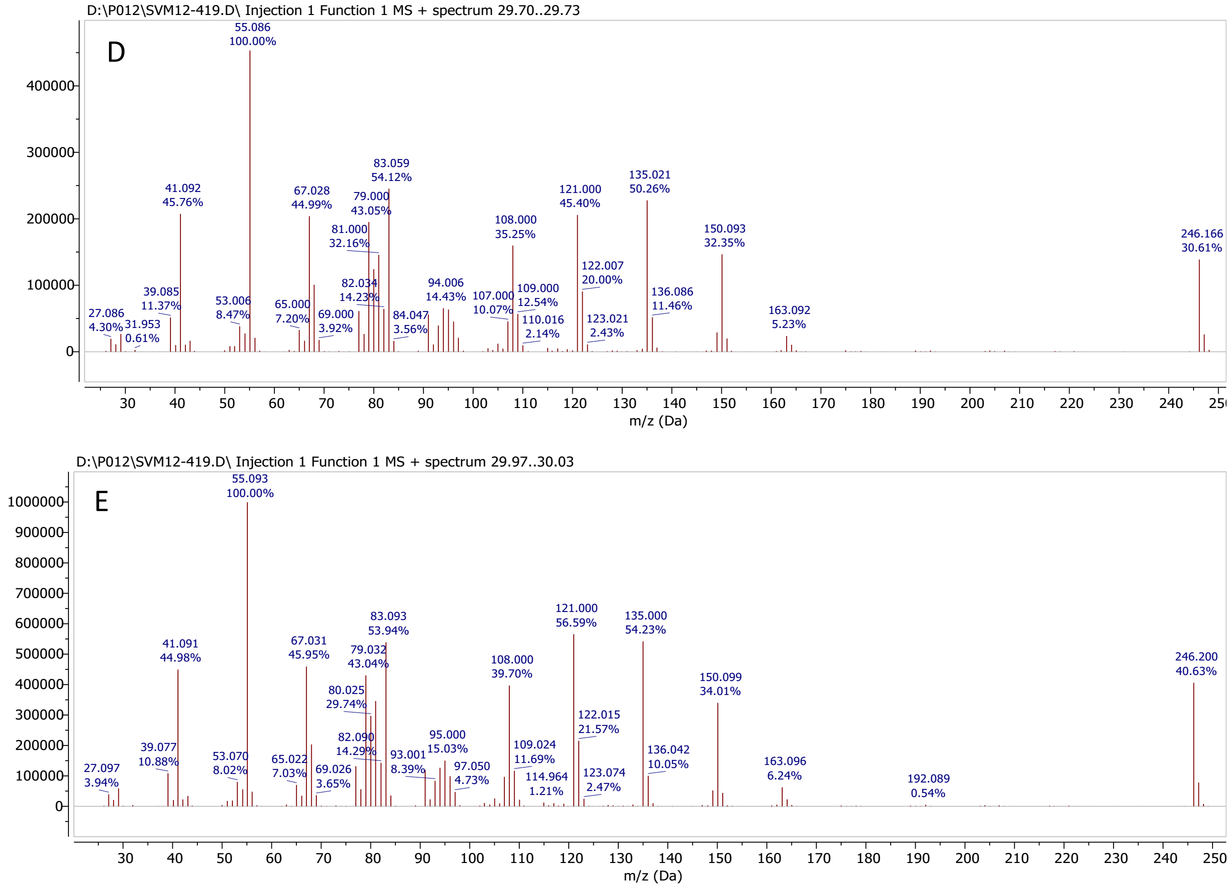
m/z (Da)

(b) GC-MS



(c) ^{1}H-NMR

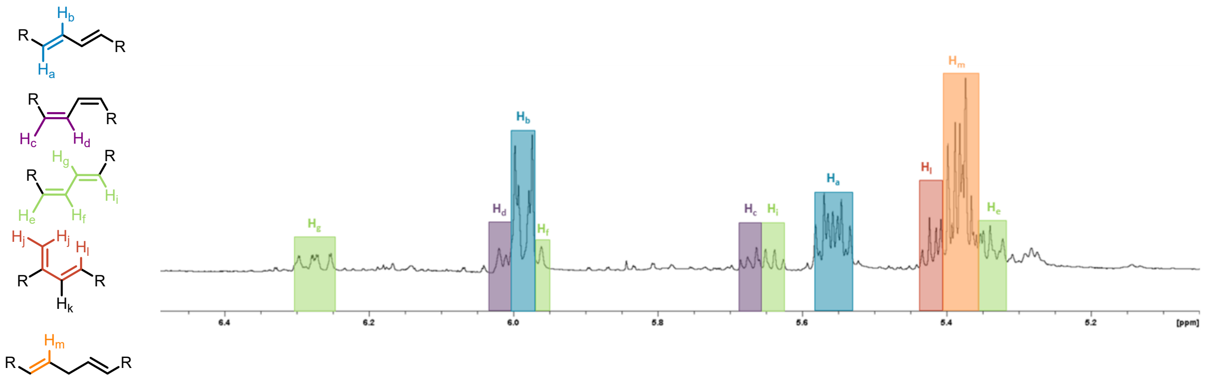
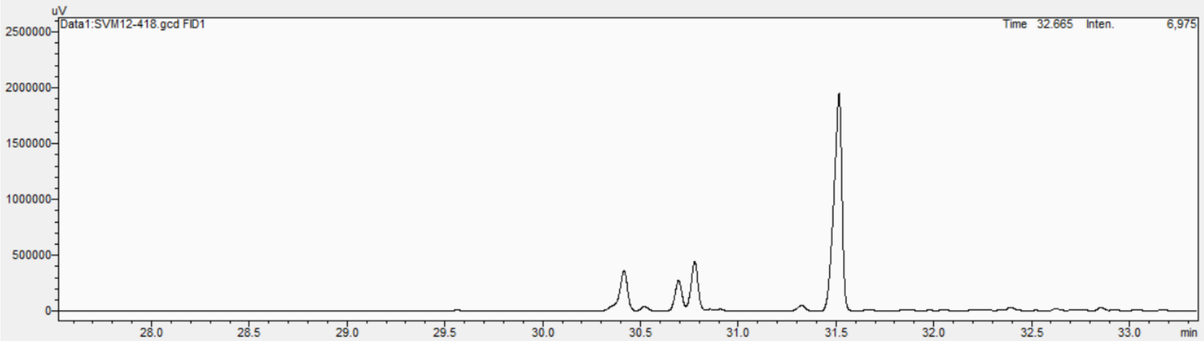
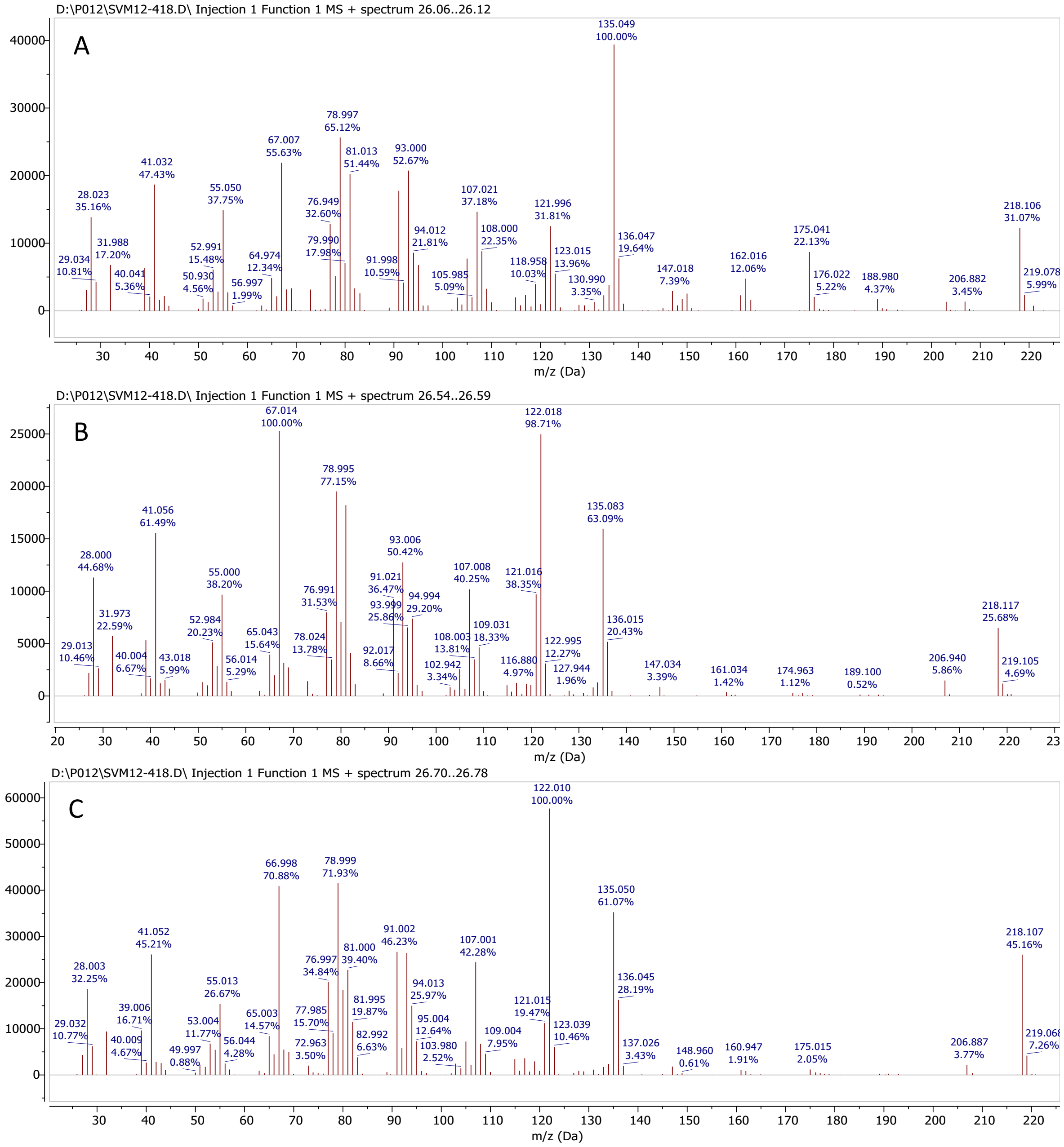


Figure S1f. (**a**) Gas chromatogram of a typical reaction with allylcyclohexane. Reaction conditions: 15 µmol $Pd(OAc)_2$, 7 eq 2-OH-pyridine, 100 eq AcOH, 1 mL allylcyclohexane, 1.4 mL DMA and 50 µL tetradecane at 100°C under O_2 atmosphere (sparged) after 30 min. (**b**) GC-MS spectra (EI, 70 eV) of relevant molecules shown in (a). (**c**) ^{1}H-NMR of the isolated product mixture (+ peak assignment).

2.7 Products obtained from vinylcyclohexane



(a) GC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107.021 37.18%
28.023 35.16%
76.949 32.60%
121.996 31.81%
218.106 31.07%
108.000 22.35%
175.041 22.13%
94.012 21.81%
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91.998 10.59%
118.958 10.03%
147.018 7.39%
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176.022 5.22%
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130.990 3.35%
56.997 1.99%
B
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135.083 63.09%
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93.006 50.42%
28.000 44.68%
107.008 40.25%
121.016 38.35%
55.000 38.20%
91.021 36.47%
76.991 31.53%
94.994 29.20%
93.999 25.86%
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136.015 20.43%
52.984 20.23%
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65.043 15.64%
108.003 13.81%
78.024 13.78%
122.995 12.27%
29.013 10.46%
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40.004 6.67%
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121.015 19.47%
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77.985 15.70%
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137.026 3.43%
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160.947 1.91%
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148.960 0.61%
m/z (Da)
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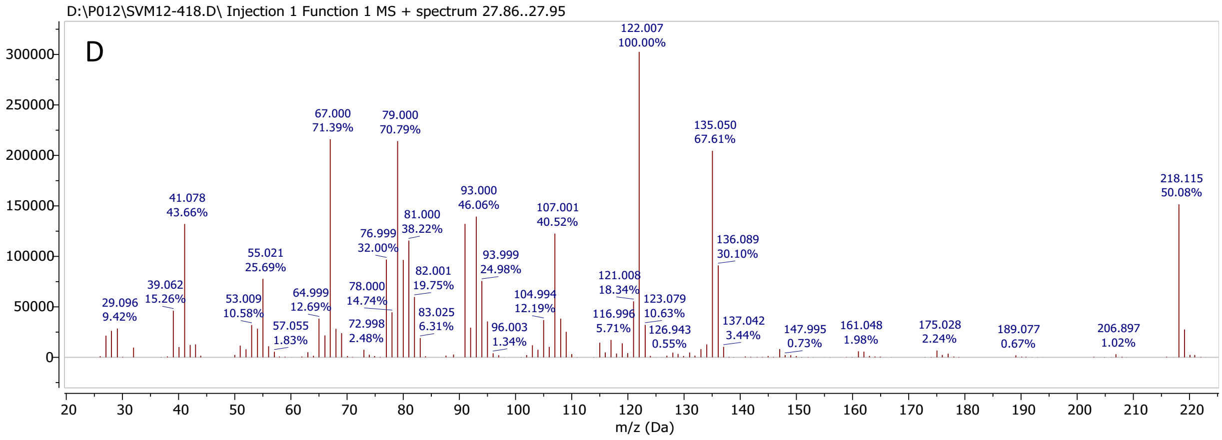
(b) GC-MS



(c) ^{1}H-NMR

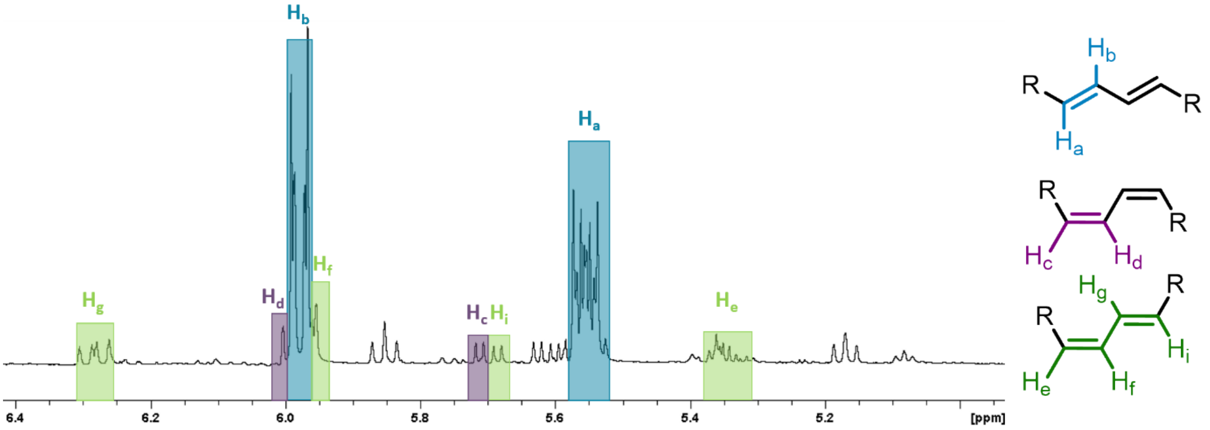
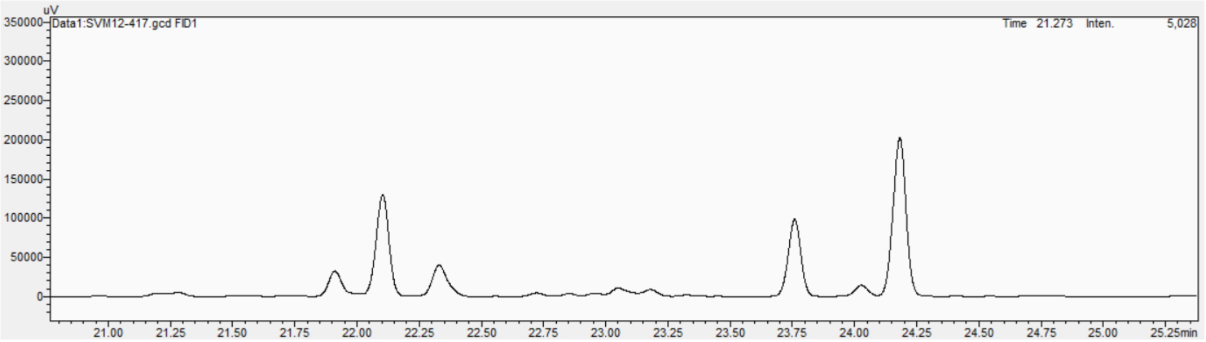


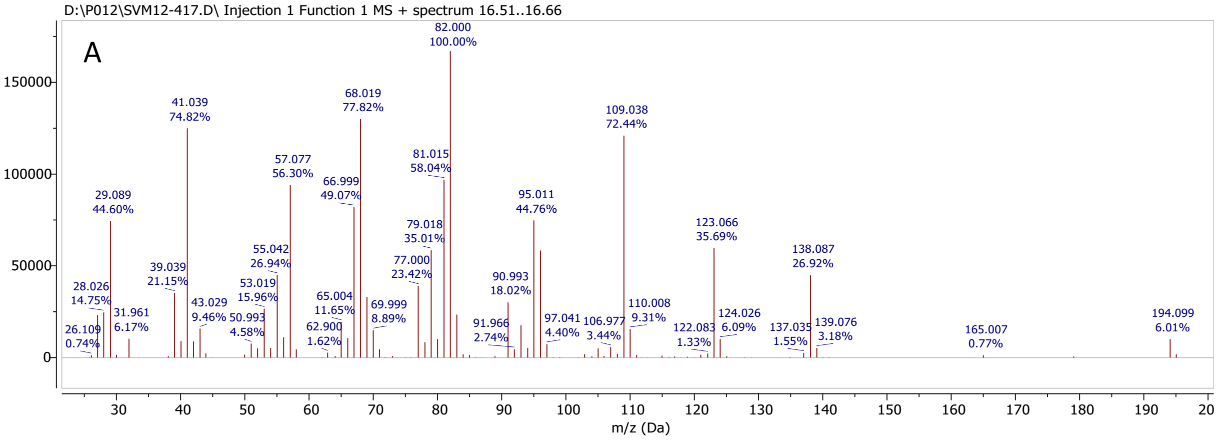
Figure S1g. (**a**) Gas chromatogram of a reference reaction with vinylcyclohexane. Reaction conditions: 15 µmol Pd(OAc)$_2$, 7 eq 2-OH-pyridine, 100 eq AcOH, 1 mL vinylcyclohexane, 1.4 mL DMA and 50 µL tetradecane at 100°C under O$_2$ atmosphere (sparged) after 30 min. (**b**) GC-MS spectra (EI, 70 eV) of relevant molecules shown in (a). (**c**) ^{1}H-NMR of the isolated product mixture (+ peak assignment). Some traces of vinylcyclohexane might still be present (5.85 ppm).

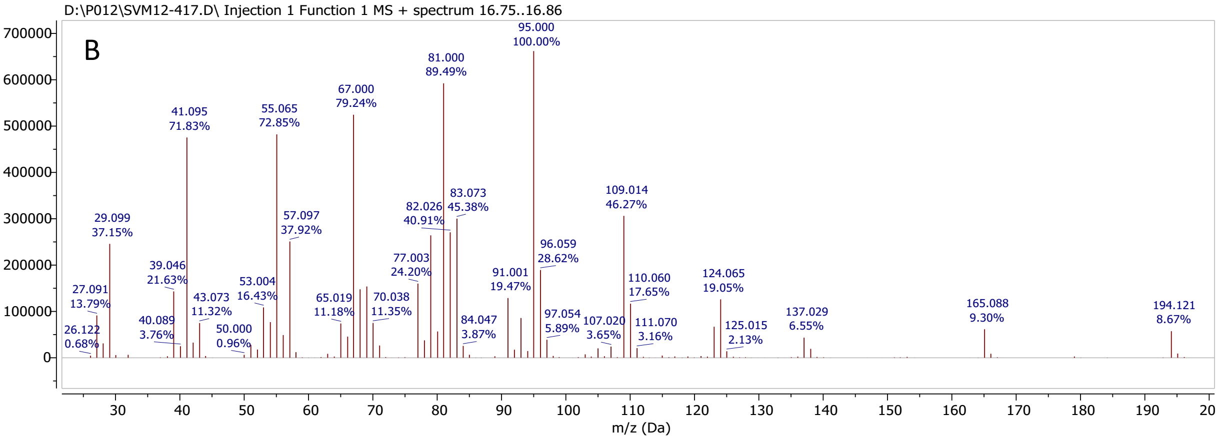
2.8 Products obtained from 4-methyl-1-hexene

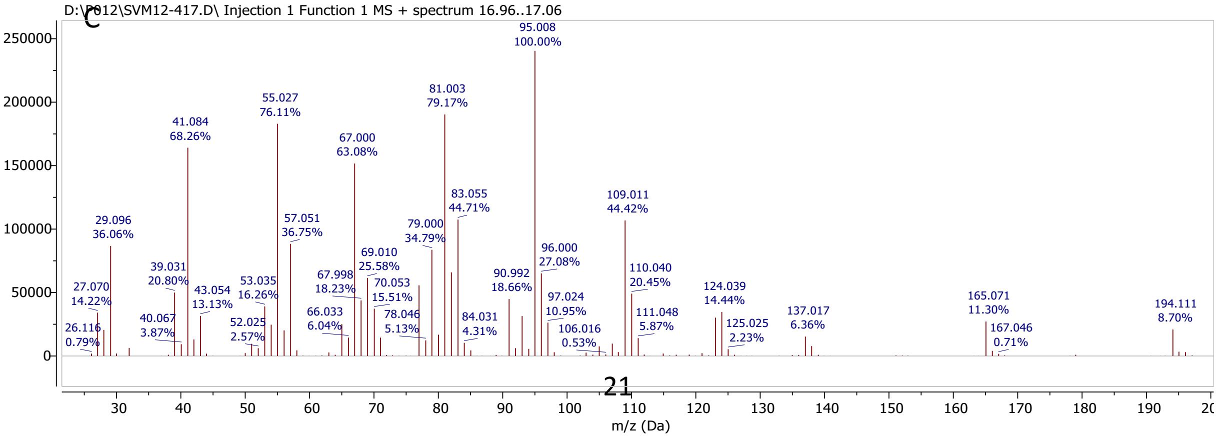


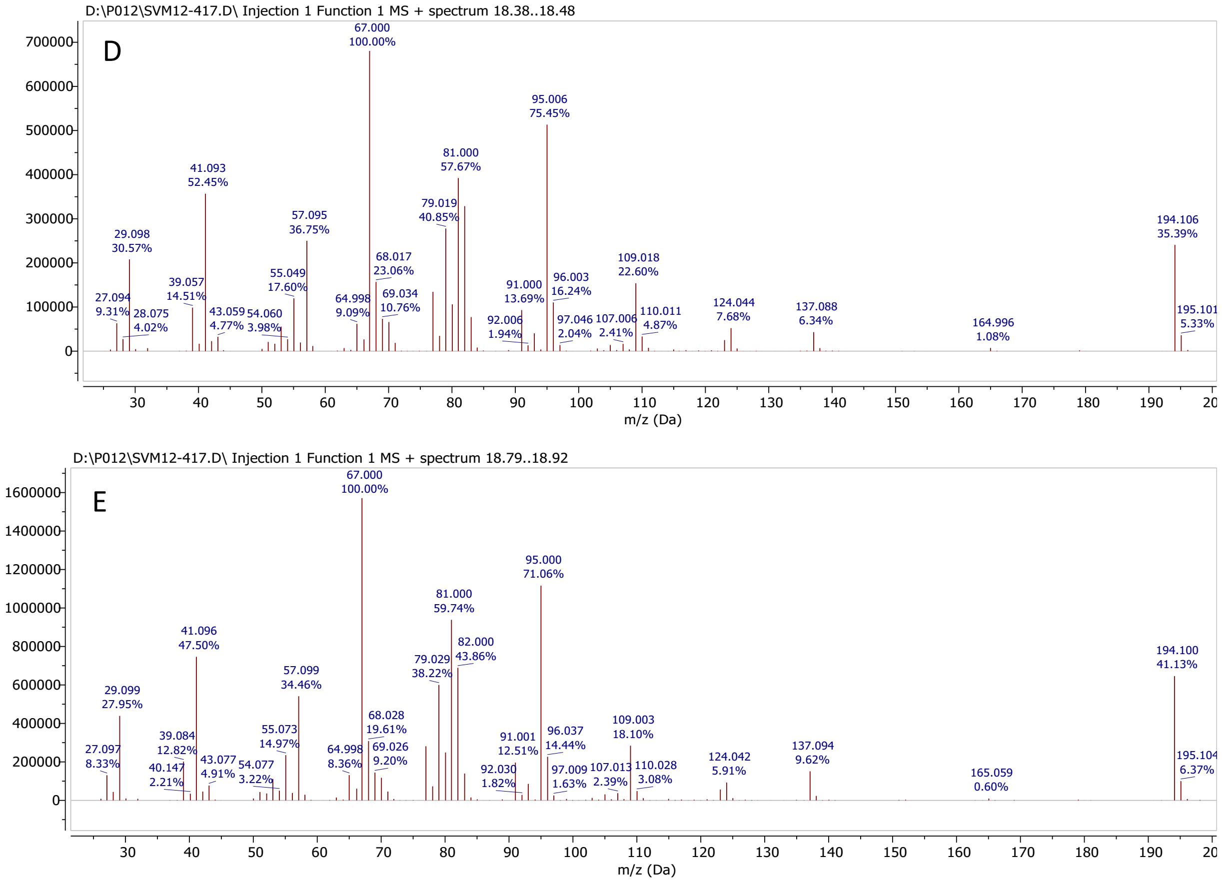
(a) GC

(b) GC-MS









(c) ^{1}H-NMR

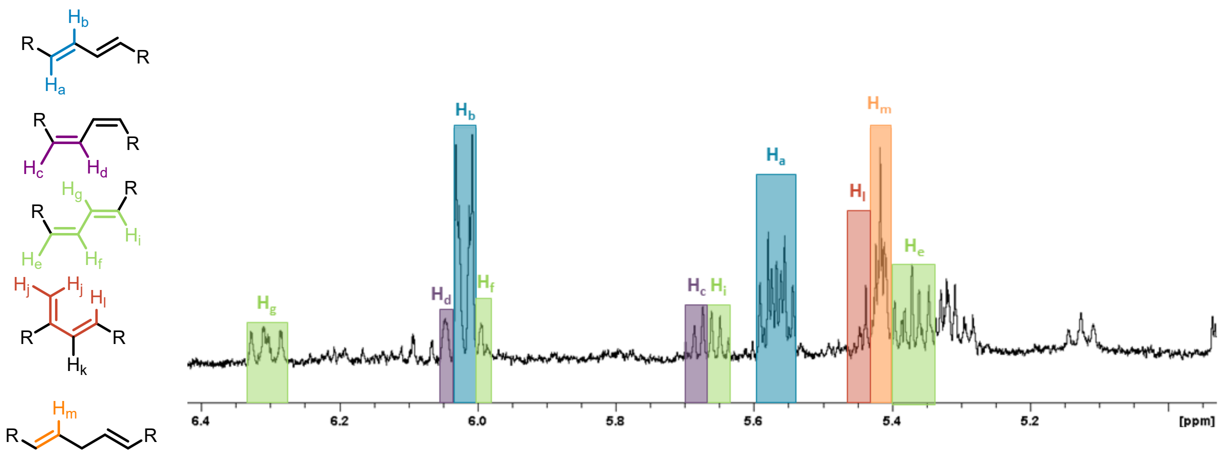
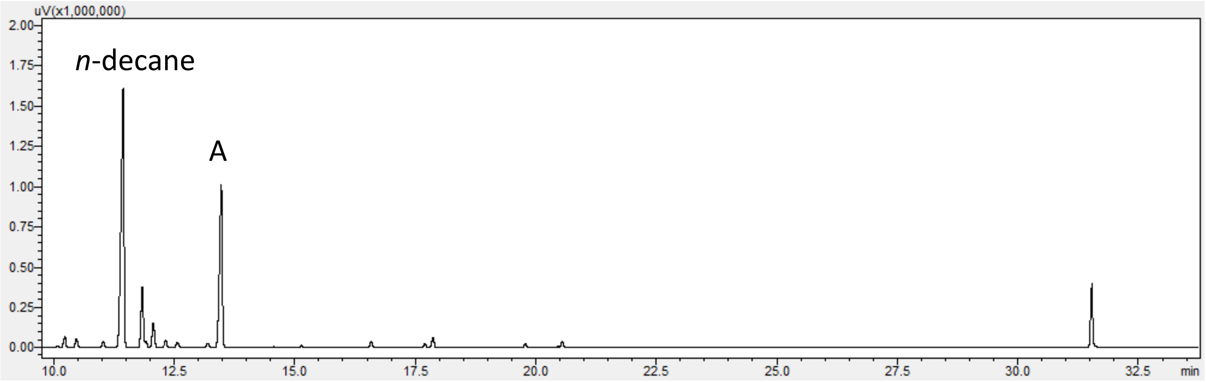
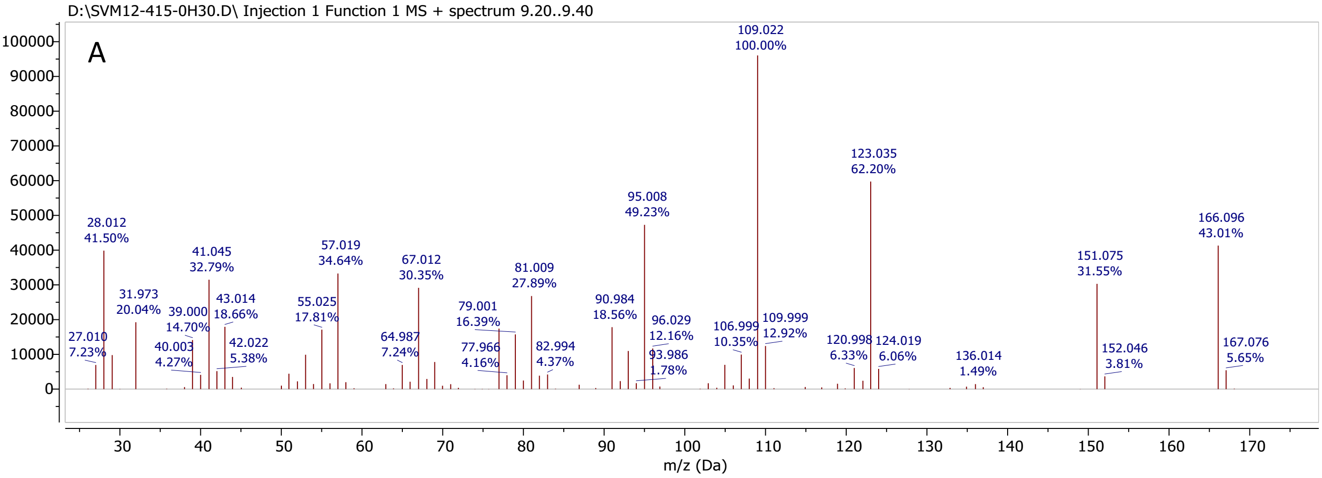


Figure S1h. (**a**) Gas chromatogram of a reference reaction with 4-methyl-1-hexane. Reaction conditions: 15 µmol Pd(OAc)$_2$, 7 eq 2-OH-pyridine, 100 eq AcOH, 1 mL 4-methyl-1-hexane, 1.4 mL DMA and 50 µL tetradecane at 100°C under O$_2$ atmosphere (sparged) after 30 min. (**b**) GC-MS spectra (EI, 70 eV) of relevant molecules shown in (a). (**c**) ^{1}H-NMR of the isolated product mixture (+ peak assignment).

2.9 Products obtained from *t*-butylethylene

(a) GC





(b) GC-MS

(c) ^{1}H-NMR

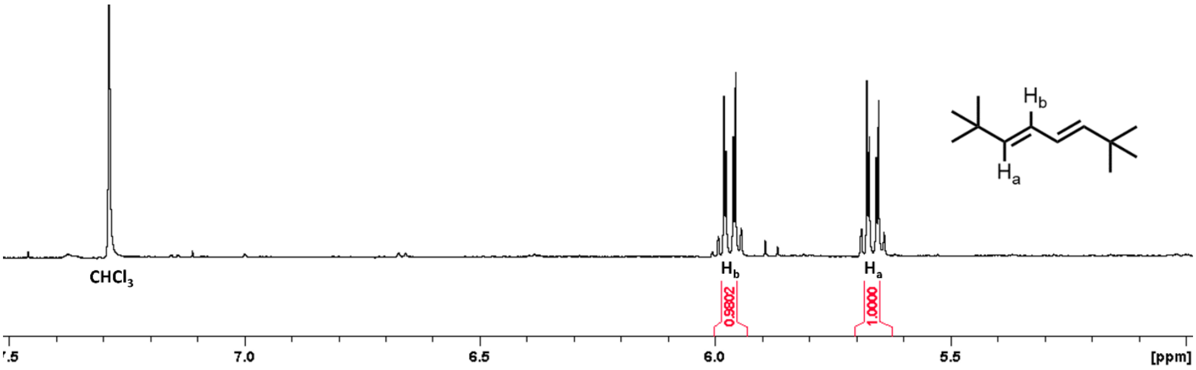
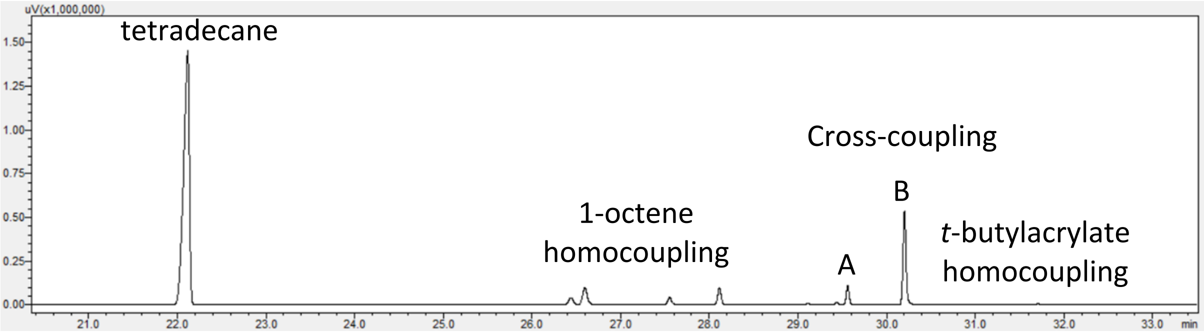
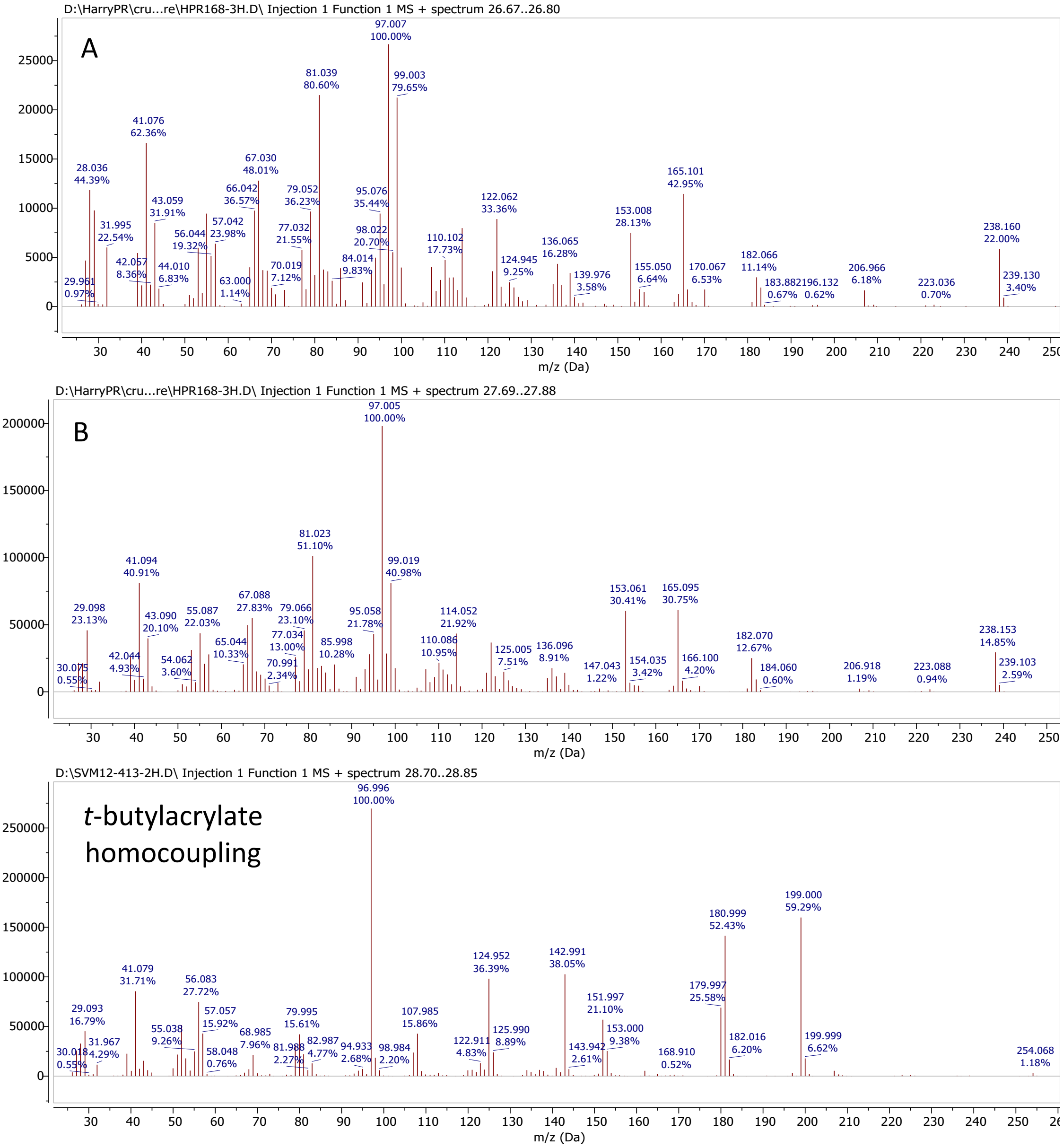


Figure S1i. (**a**) Gas chromatogram of a reference reaction with *t*-butylethylene. Reaction conditions: 15 µmol Pd(OAc)$_2$, 7 eq 2-OH-pyridine, 100 eq AcOH, 1 mL *t*-butylethylene, 1.4 mL DMA and 50 µL tetradecane at 100°C under O$_2$ atmosphere (sparged) after 30 min. (**b**) GC-MS spectra (EI, 70 eV) of relevant molecules shown in (a). (**c**) ^{1}H-NMR of the isolated product mixture (+ peak assignment).

2.10 *t*-Butylacrylate/1-octene: competition experiment

(a) GC



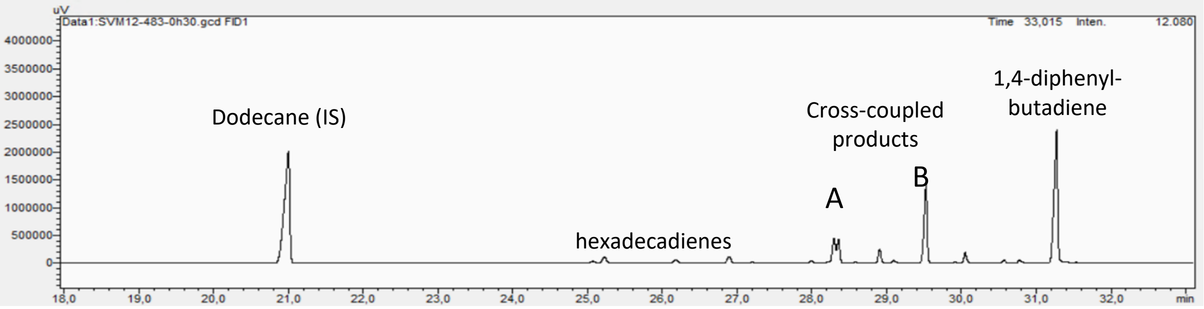


(b) GC-MS

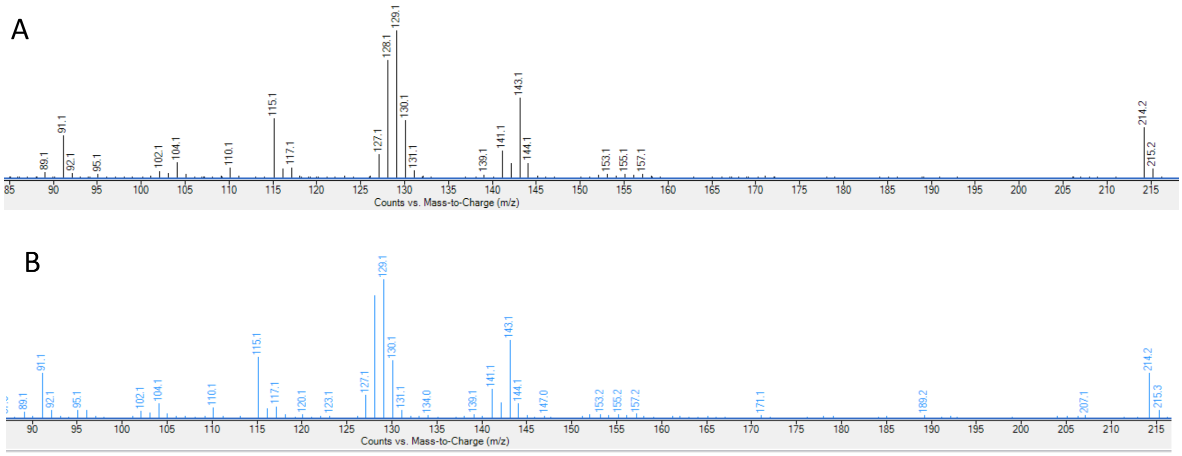
Figure S1j. (**a**) Gas chromatogram of the cross-coupling reaction of 1-octene and *t*-butylacrylate. Reaction conditions: 15 µmol $Pd(OAc)_2$, 7 eq 2-OH-pyridine, 500 eq AcOH, 1.4 mL DMA, 2.5 mL 1-octene, 1 mL *t*-butylacrylate and 50 µL tetradecane at 100°C under O_2 atmosphere (sparged) after 45 min. (**b**) GC-MS spectra (EI, 70 eV) of relevant molecules shown in (a).

2.11 Styrene/1-octene: competition experiment

(a) GC



(b) GC-MS



1,4-diphenylbutadiene

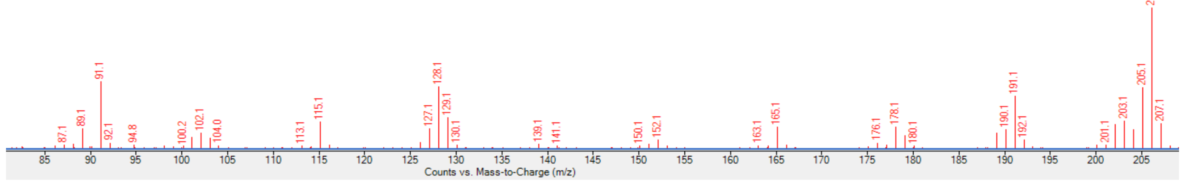
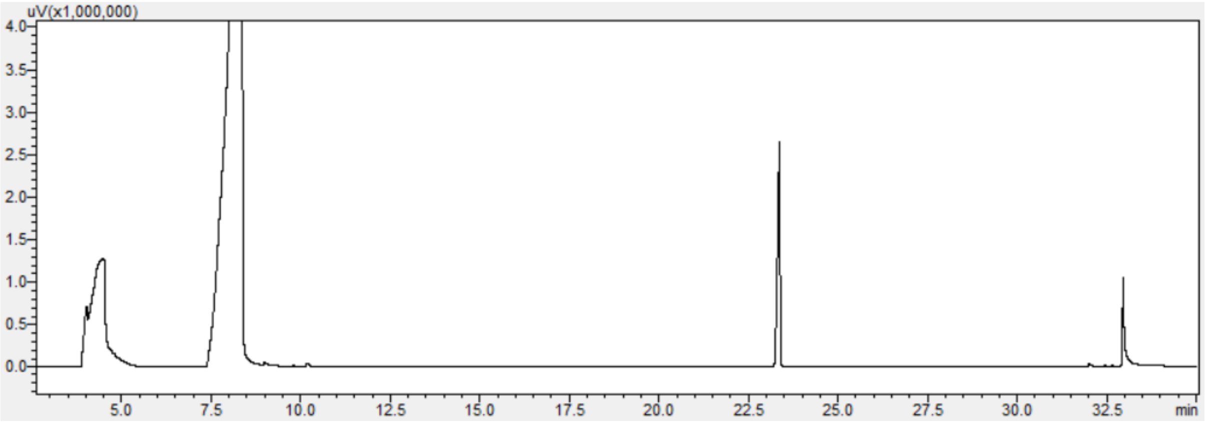


Figure S1k. (**a**) Gas chromatogram of the cross-coupling reaction of 1-octene and styrene. Reaction conditions: 15 µmol Pd(OAc)$_2$, 3 eq 2-OH-pyridine, 100 eq AcOH, 1.4 mL DMA, 2 mL 1-octene, 1.5 mL styrene and 50 µL dodecane at 80°C under O$_2$ atmosphere (sparged) after 30 min. (**b**) GC-MS spectra (EI, 70 eV) of relevant molecules shown in (a).

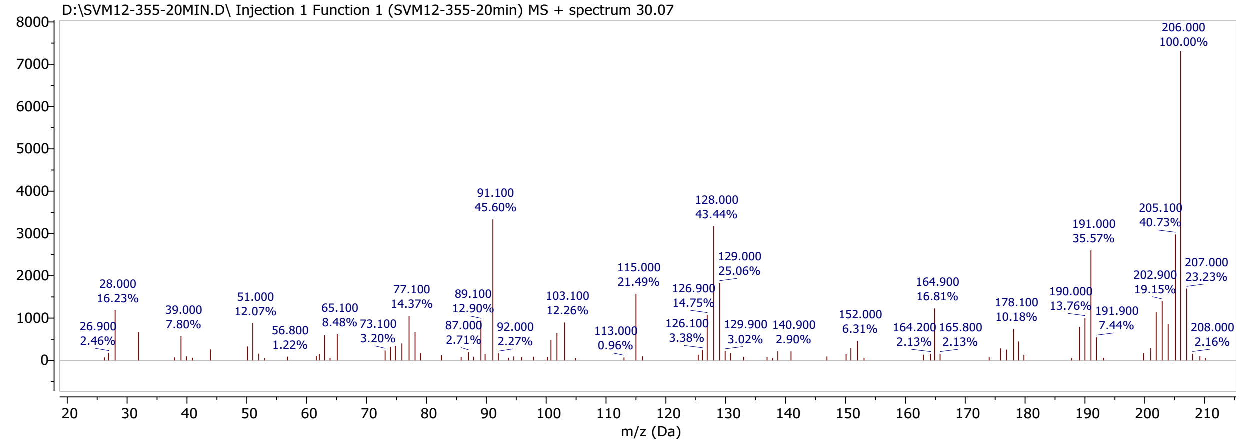
2.12 Styrene product mixture



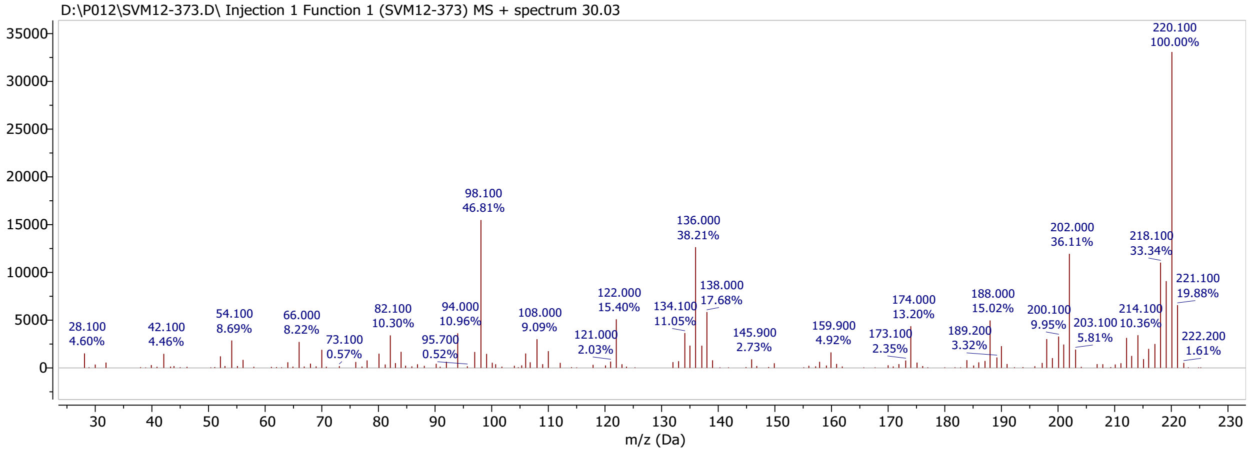
(a) GC

(b) GC-MS

Styrene



Styrene-d_8



(c) ^{1}H-NMR

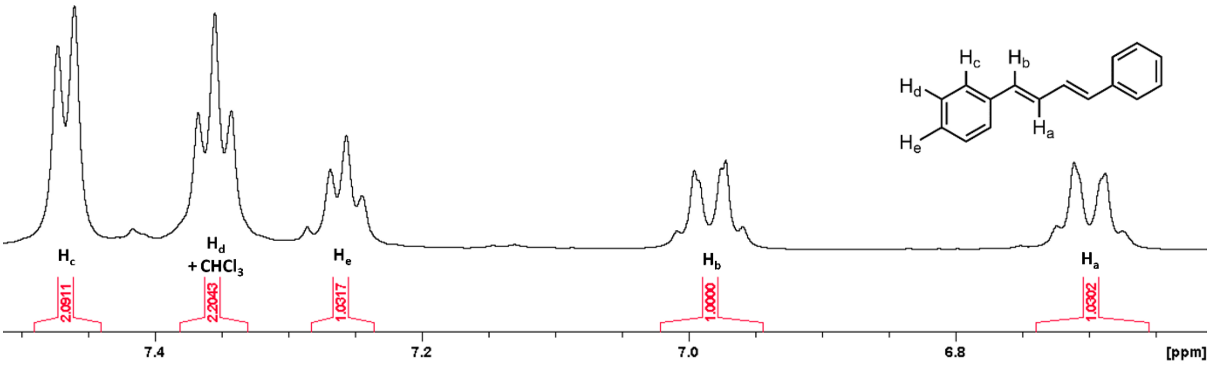
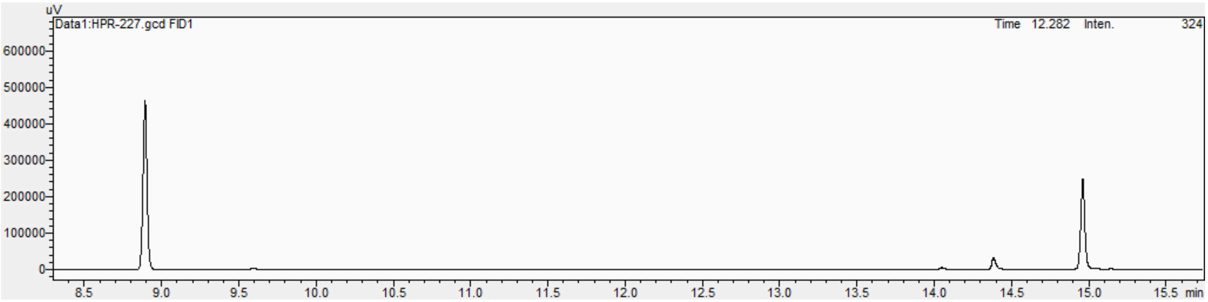
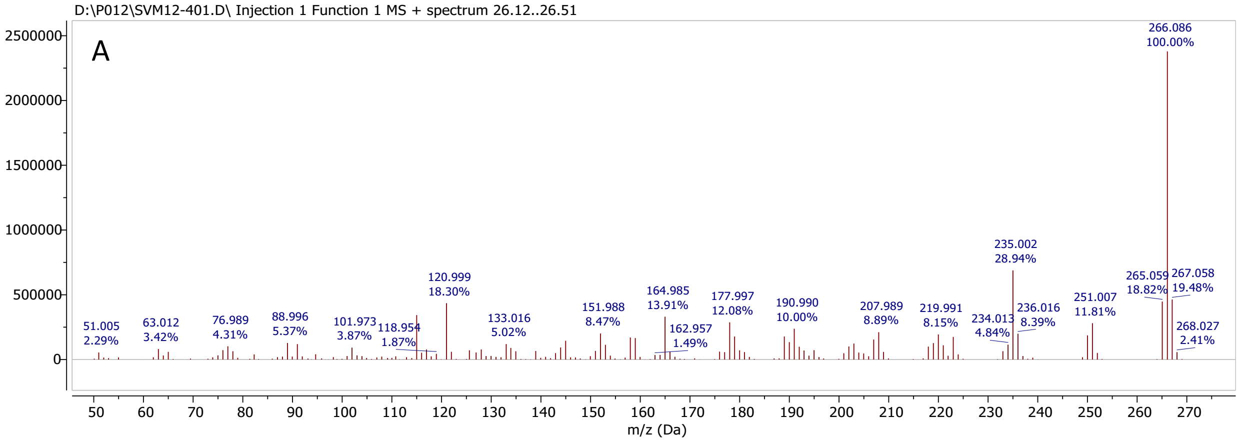


Figure S1l. (**a**) Gas chromatogram of a reference reaction with styrene. Reaction conditions: 15 µmol Pd(OAc)$_2$, 3 eq 2-OH-pyridine, 100 eq AcOH, 1 mL styrene, 1.4 mL DMA and 50 µL tetradecane at 80°C under O$_2$ atmosphere (sparged) after 10 min. (**b**) GC-MS spectra (EI, 70 eV) of relevant molecules shown in (a). (**c**) ^{1}H-NMR of the purified product mixture (+ peak assignment).

2.13 4-methoxystyrene



(a) GC



(b) GC-MS

(c) ^{1}H-NMR

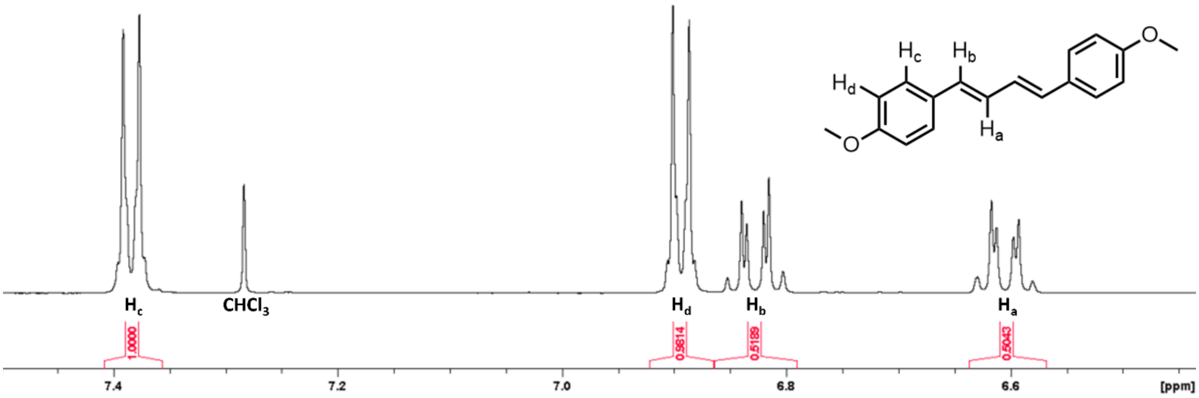
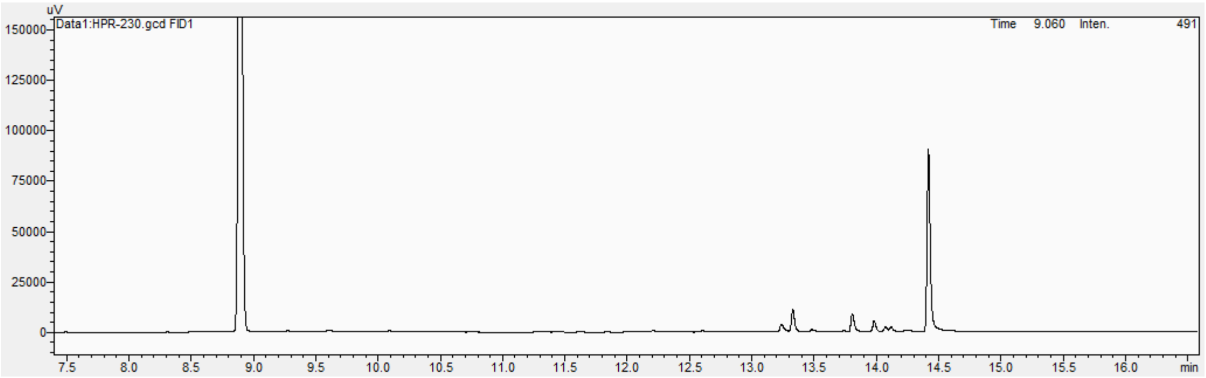
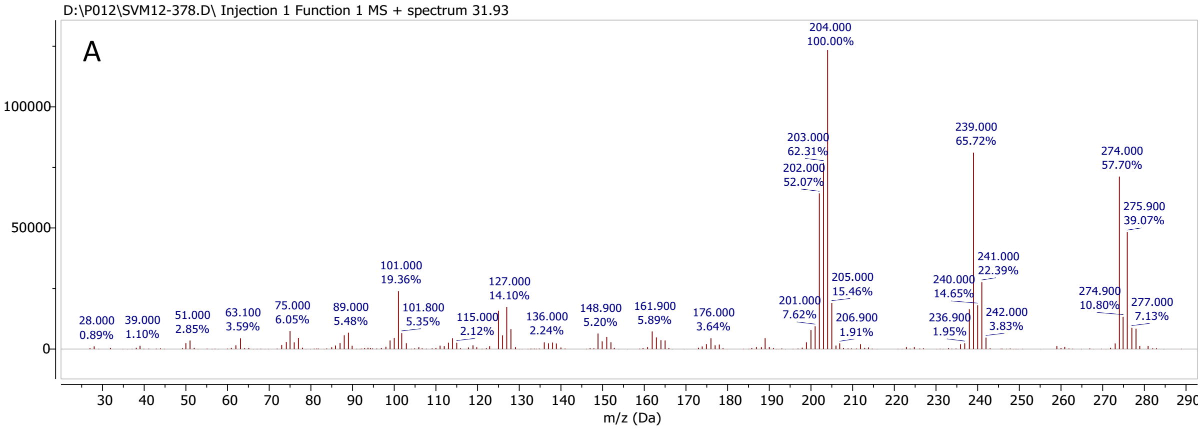


Figure S1m. (**a**) Gas chromatogram of a reference reaction with 4-methoxystyrene. Reaction conditions: 15 µmol Pd(OAc)$_2$, 3 eq 2-OH-pyridine, 100 eq AcOH, 1 mL 4-methoxystyrene, 1.4 mL DMA and 50 µL tetradecane at 80°C under O$_2$ atmosphere (sparged) after 10 min. (**b**) GC-MS spectra (EI, 70 eV) of relevant molecules shown in (a). (**c**) ^{1}H-NMR of the crystallized product mixture (+ peak assignment).

2.14 4-chlorostyrene

(a) GC





(b) GC-MS

(c) ^{1}H-NMR

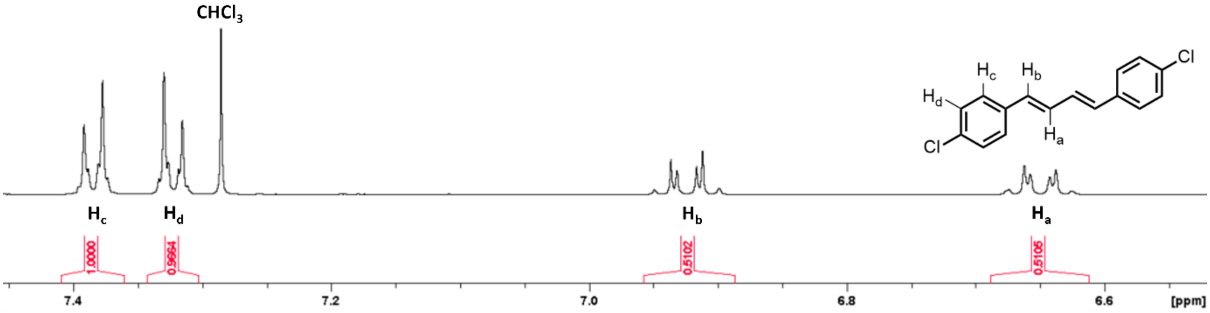
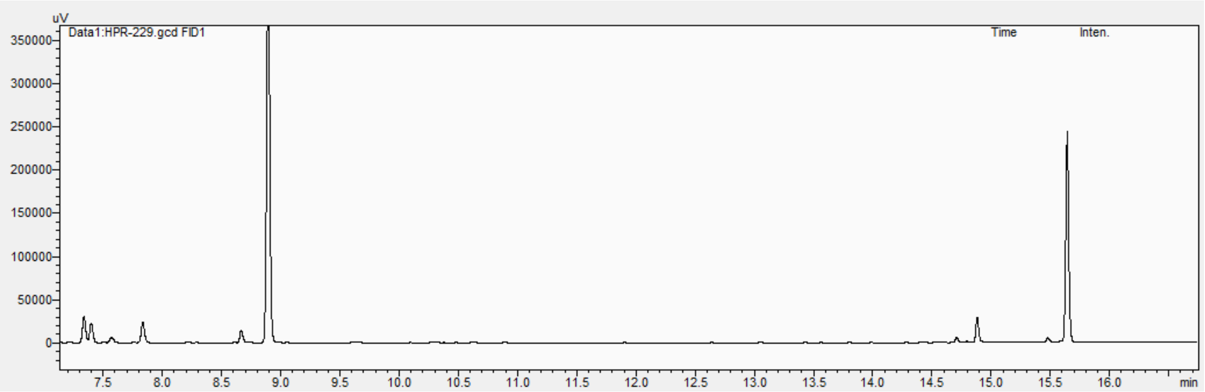


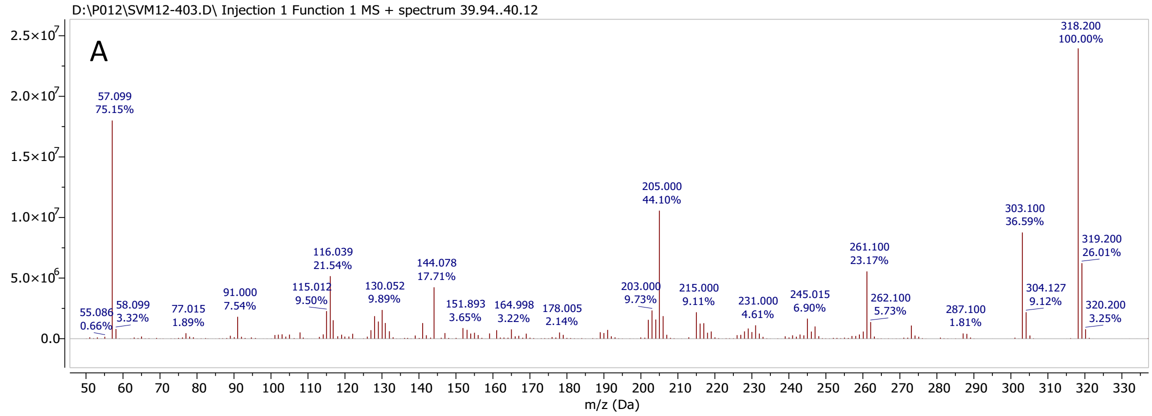
Figure S1n. (**a**) Gas chromatogram of a reference reaction with 4-chlorostyrene. Reaction conditions: 15 µmol Pd(OAc)$_2$, 3 eq 2-OH-pyridine, 100 eq AcOH, 1 mL 4-chlorostyrene, 1.4 mL DMA and 50 µL tetradecane at 80°C under O$_2$ atmosphere (sparged) after 10 min. (**b**) GC-MS spectra (EI, 70 eV) of relevant molecules shown in (a). (**c**) ^{1}H-NMR of the crystallized product mixture (+ peak assignment).

2.15 4-*t*-butylstyrene



(a) GC

(b) GC-MS



(c) ^{1}H-NMR

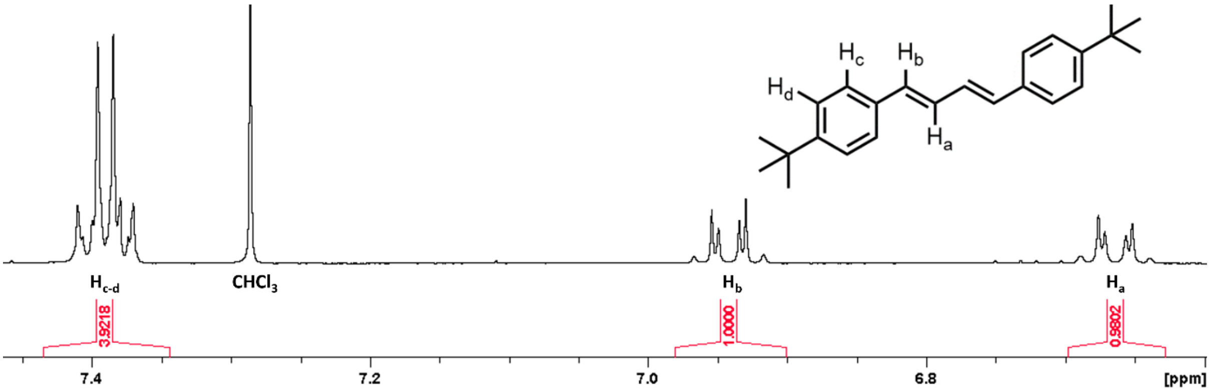
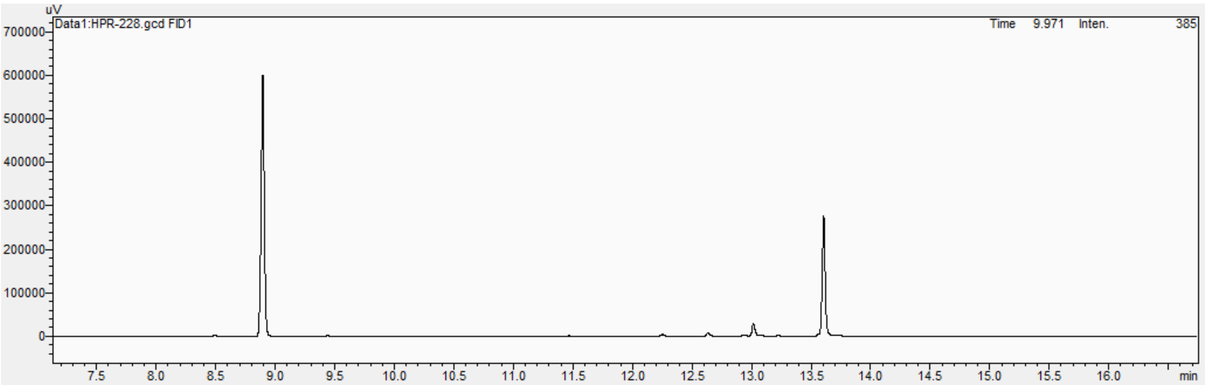
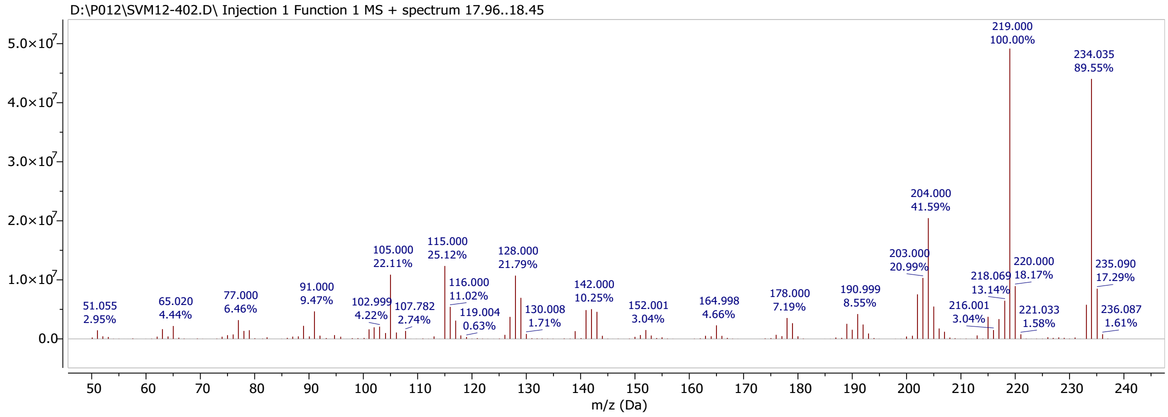


Figure S1o. (**a**) Gas chromatogram of a reference reaction with 4-*t*-butylstyrene. Reaction conditions: 15 µmol Pd(OAc)$_2$, 3 eq 2-OH-pyridine, 100 eq AcOH, 1 mL 4-*t*-butylstyrene, 1.4 mL DMA and 50 µL tetradecane at 80°C under O$_2$ atmosphere (sparged) after 10 min. (**b**) GC-MS spectra (EI, 70 eV) of relevant molecules shown in (a). (**c**) ^{1}H-NMR of the crystallized product mixture (+ peak assignment).

2.16 4-methylstyrene



(a) GC



(b) GC-MS

(c) ^{1}H-NMR

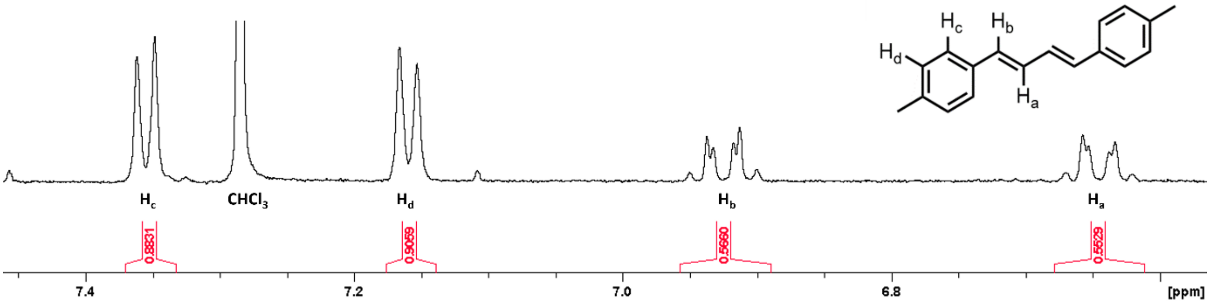


Figure S1p. (**a**) Gas chromatogram of a reference reaction with 4-methylstyrene. Reaction conditions: 15 µmol Pd(OAc)$_2$, 3 eq 2-OH-pyridine, 100 eq AcOH, 1 mL 4-methylstyrene, 1.4 mL DMA and 50 µL tetradecane at 80°C under O$_2$ atmosphere (sparged) after 10 min. (**b**) GC-MS spectra (EI, 70 eV) of relevant molecules shown in (a). (**c**) ^{1}H-NMR of the crystallized product mixture (+ peak assignment).

3. Optimization of reaction conditions

Table S1. Ligand screening. Reaction conditions: 15 µmol $Pd(OAc)_2$, 7 eq ligand, 100 eq acetic acid, 1.4 mL DMA, 0.2 mL 1-octene and 50 µL tetradecane at 80°C under O_2 atmosphere (sparged) after 1 h.

Entry	Ligand	TOF ($mol_{prod}/(mol_{Pd}*h)$)
1	2,2'-bipyridine-5,5'-dicarboxylic acid	0
2	1,10-phen-5,6-dione	0
3	phenanthroline	0
4	2,2'-bipyridine	0
5	4,5-diazafluoren-9-one	0
6	pyridine	0
7	2-OH-pyridine	2.04
8	2,4-$(OH)_2$-pyridine	1.52
9	2-OH-4-NH_3-pyridine	0.27
10	2-OH-5-NO_2-pyridine	1.33
11	2-OH-5-CF_3-pyridine	1.17
12	2-OH-4-CH_3-pyridine	1.25
13	2-OH-5-CH_3-pyridine	1.03
14	2-OH-6-CH_3-pyridine	0.65
15	2-OH-6-CF_3-pyridine	0.45
16	2-OH-5-Br-pyridine	1.67
17	2-OH-3,5-$(CF_3)_2$-pyridine	2.50
18	4,5-diazafluoren-9-one	0.38
19	*N*-acetyl-L-phenylalanine	0.32
20	proline	0
21	2,5-$(COOH)_2$-pyridine	0
22	3,5-$(COOH)_2$-pyridine	0
23	4-OCH_3-pyridine	0

Table S2. Structure-activity relationship between functionalized hydroxypyridine and catalytic activity. Hammett parameters for pyridine screening shown in Figure 1 and S2. Herein, the values were taken as such that its effect on the OH-group was considered. For 4-OH, a mesomeric withdrawing effect was assumed on the pyridinone group, justifying the choice for negative σ- parameter.[1]

Functional group	Hammett parameter
Reference	0
4-OH-	-0.38 (=σ_{para})
5-CH_3-	-0.14 (=σ_{para})
5-Br	0.26 (=σ_{para})
5-COOMe-	0.47 (=σ_{para})
5-CF_3-	0.53 (=σ_{para})
5-NO_2-	0.81 (=σ_{para})

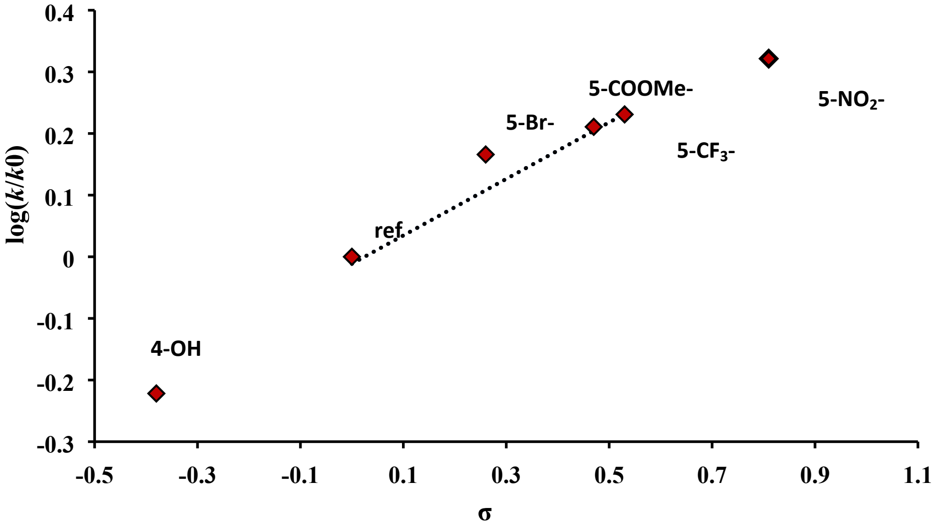


Figure S2. Linear free-energy relationship between rate constant and σ-parameter of substituted 2-OH-pyridine ligand in presence of carboxylic acid. Reaction conditions: 15 µmol $Pd(OAc)_2$, 3 eq ligand, 200 eq pivalic acid, 1 mL 1-octene, 1.4 mL DMA and 50 µL tetradecane at 90°C under O_2 atmosphere (sparged) after 1h. The ligands used in this screening and their corresponding σ-values are shown in Table S2.

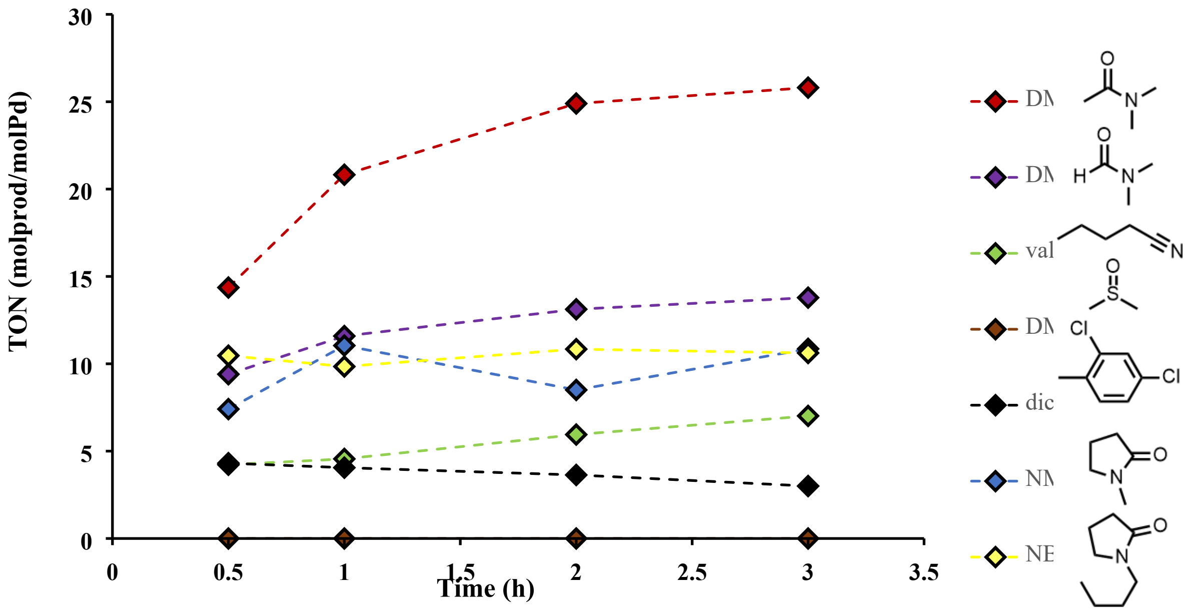


Figure S3. Solvent screening. Reaction conditions: 15 µmol Pd(OAc)$_2$, 7 eq 2-OH-pyridine, 500 eq AcOH, 1.4 mL solvent, 1 mL 1-octene and 50 µL tetradecane at 100°C under O$_2$ atmosphere (sparged).

Table S3. Carboxylic acid screening (Figure 2). Reaction conditions: 15 µmol Pd(OAc)$_2$, 7 eq 2-OH-pyridine, 100 eq carboxylic acid, 1.4 mL dimethylacetamide, 0.6 mL 1-octene and 50 µL tetradecane at 100°C under O$_2$ atmosphere (sparged) after 60 min.

Entry	Carboxylic acid	pKa
1	pivalic acid^3	5.0
2	acetic acid^2	4.8
3	4-methoxy benzoic acid^3	4.5
4	benzoic acid^3	4.2
5	chloroacetic acid^2	2.8
6	dichloroacetic acid^2	1.4

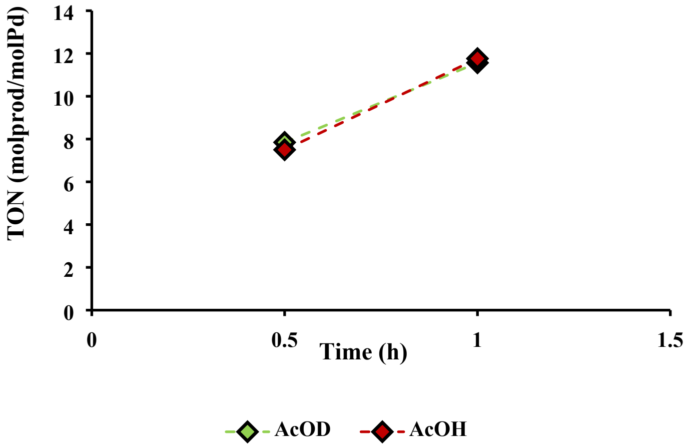


Figure S4. Role of acetic acid deuteration on the reaction rate: kinetic isotope effect. Reaction conditions: 15 µmol Pd(OAc)$_2$, 7 eq 2-OH-pyridine, 100 eq carboxylic acid, 1.4 mL DMA, 0.6 mL 1-octene and 50 µL tetradecane at 100°C under O$_2$ atmosphere (sparged) after 60 min.

4. Catalyst recycling

In the experiments aiming to recycle the catalyst, a reaction was run for 1 h. Subsequently, the reaction was cooled down, leading to phase separation. The apolar top layer (containing the 1-octene and the product) was removed and fresh 1-octene was added to the polar bottom layer containing the Pd-catalyst. This was repeated for 5 runs.

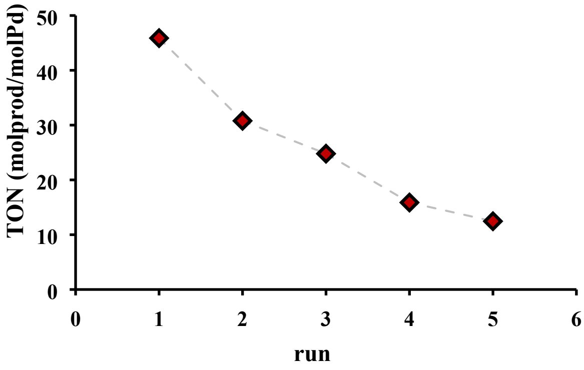


Figure S5. Recycling of catalyst solution over multiple runs. Reaction conditions: 15 µmol $Pd(OAc)_2$, 3 eq 2-OH-pyridine, 100 eq AcOH, 1.4 mL DMA, 2 mL 1-octene and 50 µL tetradecane at 100°C under O_2 atmosphere (sparged) after 60 min.

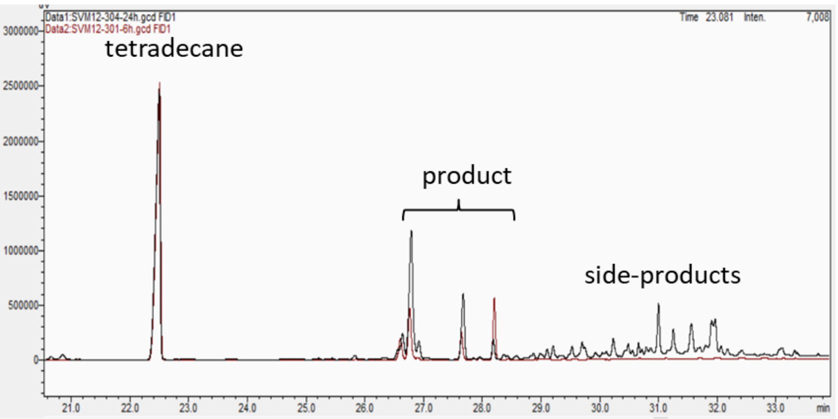


Figure S6. Degradation of conjugated hexadecadiene product at long reaction times. Reaction conditions: 15 µmol $Pd(OAc)_2$, 7 eq 2-OH-pyridine, 100 eq AcOH, 1.4 mL DMA, 0.6 mL 1-octene and 50 µL tetradecane at 100°C under O_2 atmosphere (sparged). GC-MS of the side-products is given in Figure S1 (**a**).

5. X-ray absorption spectroscopy

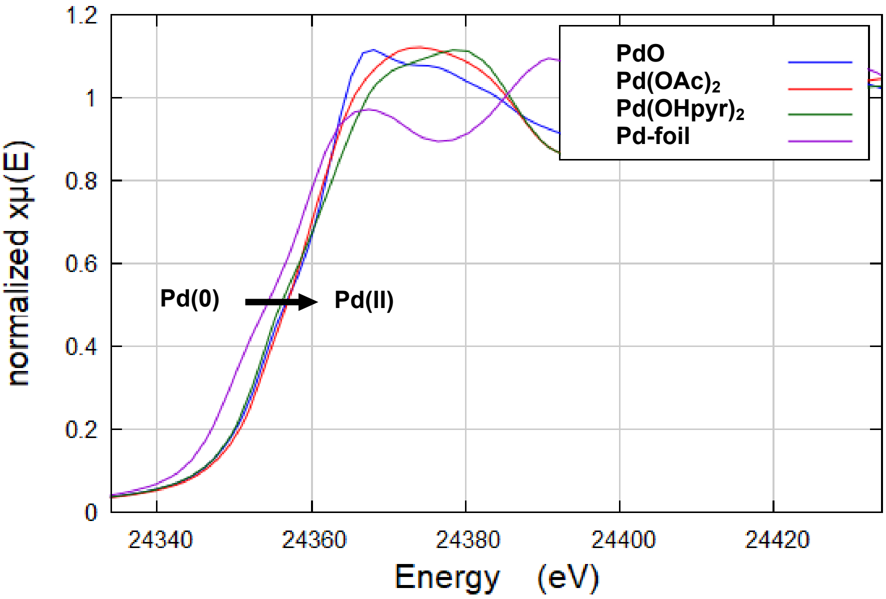


Figure S7. XANES spectra for $Pd(OAc)_2$ dissolved in DMA (with and without 2-OH-pyridine) benchmarked with reference Pd-precursors (PdO and metallic Pd foil).

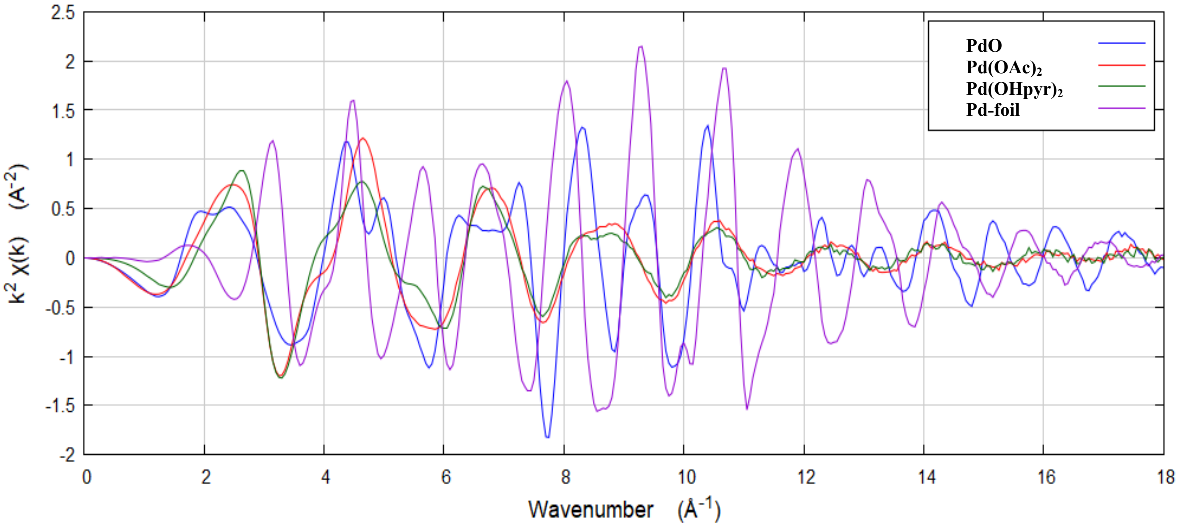


Figure S8. Experimental κ²-weighted EXAFS for the $Pd(OAc)_2$ complexes compared to some reference Pd-precursors.

On top of the ex situ samples (Figure 9 and S8), also some in situ samples were measured (during reaction, O_2 balloon). Upon heating the sample to reaction temperature, the maximum at 24380 eV started lowering, similarly to $Pd(NH_3)_4(NO_3)_2$ (dashed blue line in Figure S9 (c)). These observations suggest that the number of oxygen neighbours diminishes. At the same time, a slight reduction is observed by a shift of the edge towards lower energies (Figure S9 (a)). This can be explained by a small shift in average oxidation state of the Pd-species from Pd(II) → Pd(0), indicating reaction occurring. Notably, no Pd-Pd signal was detected in FT-EXAFS (Figure S9 (d) and (e)).

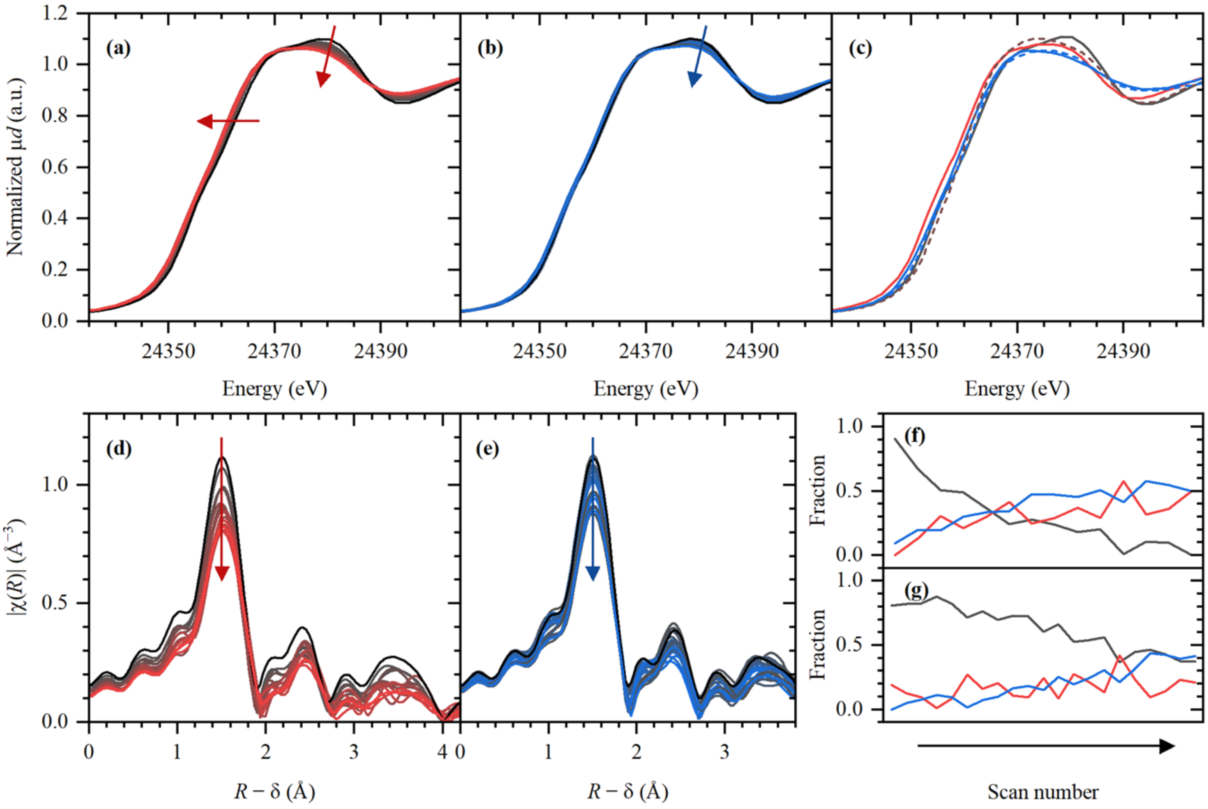


Figure S9. XANES spectra of (a) reaction mixture ($Pd(OAc)_2$ + ligand) upon heating (from black to red), (b) Reaction mixture without ligand upon heating (from black to blue) and (c) 3 components (solid lines) extracted from the whole dataset (red, blue and black from dataset (a) and (b), using MCR-procedure together with the spectra of reference $Pd(OAc)_2$ (dashed brown) and $Pd(NH_3)_4(NO_3)_2$ (dashed blue). Parts (d) and (e) show the FT-EXAFS data of the reaction mixture with and without ligand, respectively. Parts (f) and (g) show the evolution of the MCR components upon heating of respectively the reaction mixture with and without ligand, respectively.

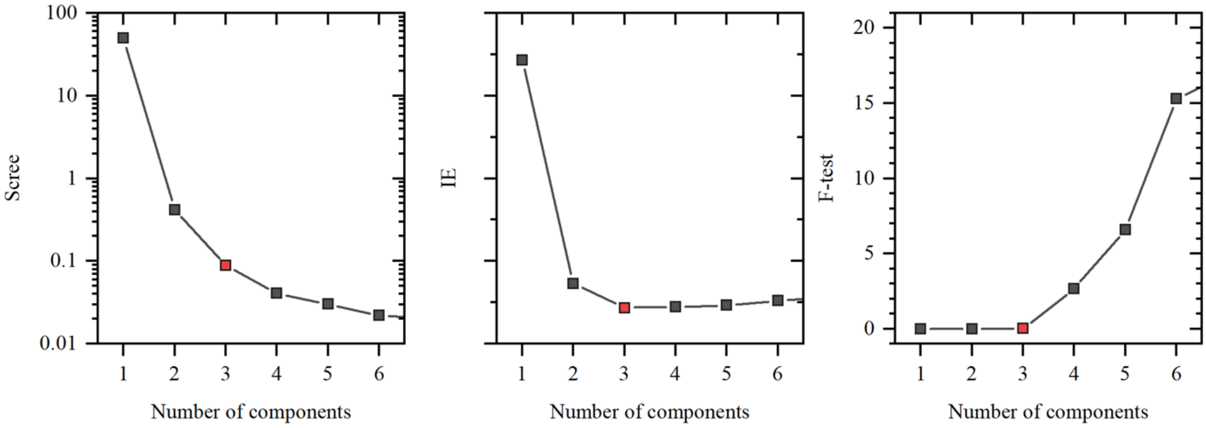


Figure S10. Statistical analysis of the dataset comprising of the reaction mixture with and without ligand heated *in situ*. The analysis was performed in PyFitIt code.

PCA analysis (Figure S10) revealed the presence of 3 different components, and an MCR procedure was then applied to deconvolute the whole dataset into 3 spectra of pure species (Figure S10 (c)) and their concentrations. The analysis also shows the higher stability of the initial state (black component) for the mixture without 2-OH-pyridine. In absence of the ligand, the Pd-O interactions are more likely to persist, on top of Pd-N interactions with the dimethylacetamide solvent. In the case of the mixture heated with ligand, more Pd-N interactions were observed as the contribution of $Pd(NH_3)_4(NO_3)_2$ (blue line in (f)) increased faster. This corresponds to a more strongly interacting ligand.

References

1 M. Smith and J. March, in March's Advanced Organic Chemistry, Wiley, 2007, 395-417.

2 J. Vana, J. Bartacek, J. Hanusek, J. Roithova and M. Sedlak, *J. Org. Chem.*, 2019, **84** (20), 12746-12754.

3 J. A. Dean, in Handbook of Organic Chemistry, McGraw-Hill Book, 1987, 7-456