Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supporting Information

Combined two steps transformations of (±)-citronellal to menthol over extrudated Ru-MCM-41 catalysts in a continuous reactor

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EXPERIMENTAL

Gel preparation

Table S1. Chemicals for gel solution preparation.

	Purity	Supplier
Fumed Silica	Scintran	BDH Laboratory
Sodium silicate solution	Water glass	Merck
Cetyltrimethylammonium Bromide	95%	Sigma-Aldrich
Aluminium Isopropoxide	98+%	Sigma-Aldrich
Tetramethylammonium Silicate	15-20% solution in water	Sigma-Aldrich

In order to prepare Na-MCM-41 mesoporous material, at first three different solution were prepared: Solution A: 16.6 g of fumed silica were dissolved in 102.8 g of distilled water and stirred for 15 min; Solution B: 22.8 g of sodium silicate solution were dissolved in 46.8 g of tetramethylammonium silicate and stirred for 25 min; Solution C: 51.8 g of cetyltrimethylammonium bromide were dissolved in 348 g of distilled water and stirred for 30 min. First, solution B was added to A and mixed; second the solution C was added to the previous mixture and finally 4 g of aluminium isopropoxide were added followed by stirring for 30 min.

Table S2. pH measurement of the gel prepared.

	A	B	C	A+B	A+B+C	A+B+C+ $C_9H_{21}O_3Al$	A+B+C+ $C_9H_{21}O_3Al$*
Gel solution	4.5	11.6	7.8	11.3	11.4	11.5	10.5

*after ultrasound treatment and synthesis in the oven.

Chemicals

Table S3. Reactants and solvent for catalytic tests.

	Purity	Supplier	Notes
Cyclohexane	≥ 99.9%	Alfa Aesar	
(+)-Isopulegol	≥ 99.9% (GC)	Fluka	
β-Citronellol	≥ 95.0%	Sigma-Aldrich	Racemic mixture
(±)-Citronellal	≥ 95.0% (GC)	Sigma-Aldrich	Racemic mixture

Definitions

Conversion of the reactant was calculated by using the following equation;[1-3]

$$X\,(\%) = \frac{C_0 - C_i}{C_0} * 100 \qquad (1)$$

where X is conversion of the reactant at time t, %, C_0 denotes the initial molar concentration of the reactant, mol/l, C_i - molar concentration of the reactant at time t, mol/l.

Yield was calculated according to:

$$Y_p\,(\%) = \frac{Cp}{C_0} * 100 \qquad (2)$$

where Y_p is yield to product *p*, C_p is molar concentration of the product *p*, mol/l. C_0 denotes the initial molar concentration of the reactant, mol/l.

The liquid phase mass balance closure is defined as a sum of the concentration of citronellal at a certain time and the concentrations of products visible in the GC chromatogram divided by the initial concentration of citronellal, denoted as MB:[1,2]

$$MB\,(\%) = \frac{\Sigma m_i}{\Sigma m_0} * 100 \qquad (3)$$

$\sum m_i$ = sum of mass concentration of all components at different sampling times

$\sum m_0$ = sum of mass concentration of all components at time = 0

The reaction rates (r) and turnover frequency (TOF) are calculated as follows:

$$r_{extrudates} = \frac{\Delta \dot{n}}{m_{cat}} \left[\frac{mol}{s.g}\right] \qquad (4)$$

$$r_{powder\ catalyst} = \frac{\Delta n}{\Delta t . m_{cat}} \left[\frac{mol}{s.g}\right] \qquad (5)$$

$$TOF_{extrudates} = \frac{\dot{n}_{in} - \dot{n}_{out}}{n_{metal}} \left[\frac{1}{s}\right] \qquad (6)$$

$$TOF_{powder\ catalyst} = \frac{\Delta n \cdot V_l}{\Delta t . n_{metal}} \left[\frac{1}{s}\right] \qquad (7)$$

where $_{extrudates}$ is obtained over extrudates in trickle-bed reactor and $_{powder\ catalyst}$ is obtained over powder catalyst in a batch reactor, $\Delta \dot{n}$ denotes the change in molar flow rate of the feed at time zero and time t in a trickle bed reactor, $\Delta n/\Delta t$ reacted moles per time interval Δt in a batch reactor, m_{cat} is catalyst mass, V_l is liquid volume and n_{metal} is moles of metal.[1-3]

RESULTS AND DISCUSSION

Catalyst characterization results

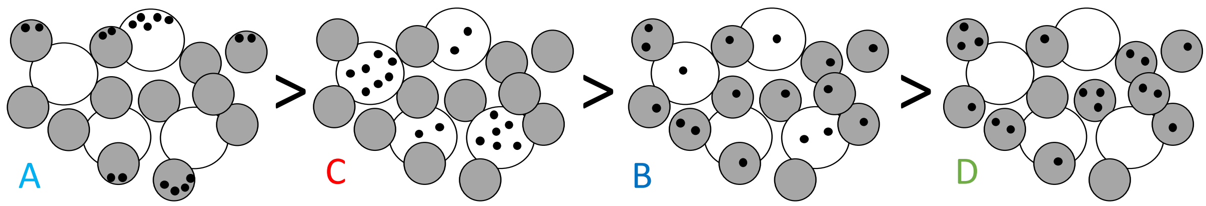

Figure S1. A schematic picture of the catalysts employed in this study, showing different distances between the metal and acid sites: a) A – Ru/(H-MCM-41+Bindizl-50/80), post synthesis; b) C – (Ru/Bindizl-50/80)+H-MCM-41, in-situ synthesis; c) B - Ru/(H-MCM-41+Bindizl-50/80), in-situ synthesis; d) D – (Ru/H-MCM-41)+Bindizl-50/80, in-situ synthesis. Legend: H-MCM-41 (grey circle), Bindizl-50/80 (white circle), Ru (black dots).[4]

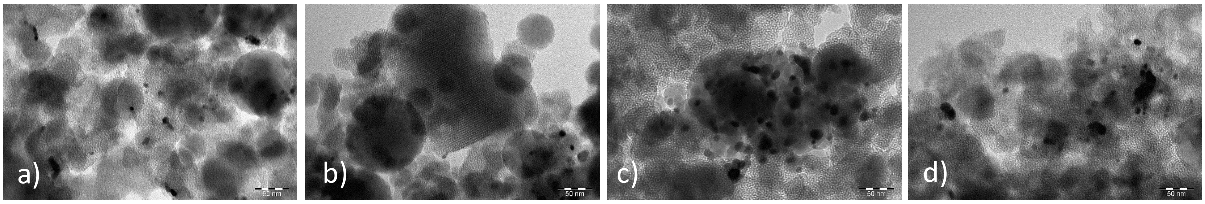

Figure S2. TEM images: a) A – Ru/(H-MCM-41+Bindizl-50/80), post synthesis; b) B - Ru/(H-MCM-41+Bindizl-50/80), in-situ synthesis; c) C – (Ru/Bindizl-50/80)+H-MCM-41, in-situ synthesis; d) D – (Ru/H-MCM-41)+Bindizl-50/80, in-situ synthesis.

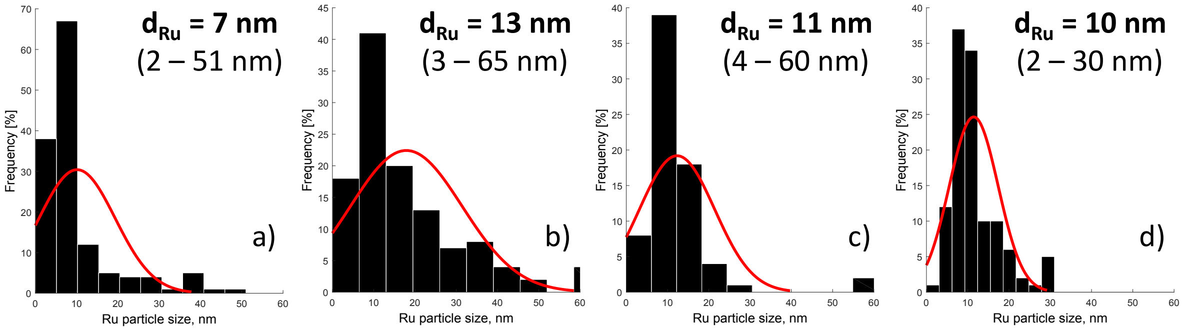

Figure S3. Ru particle size distribution: a) A – Ru/(H-MCM-41+Bindizl-50/80), post synthesis; b) B - Ru/(H-MCM-41+Bindizl-50/80), in-situ synthesis; c) C – (Ru/Bindizl-50/80)+H-MCM-41, in-situ synthesis; d) D – (Ru/H-MCM-41)+Bindizl-50/80, in-situ synthesis.

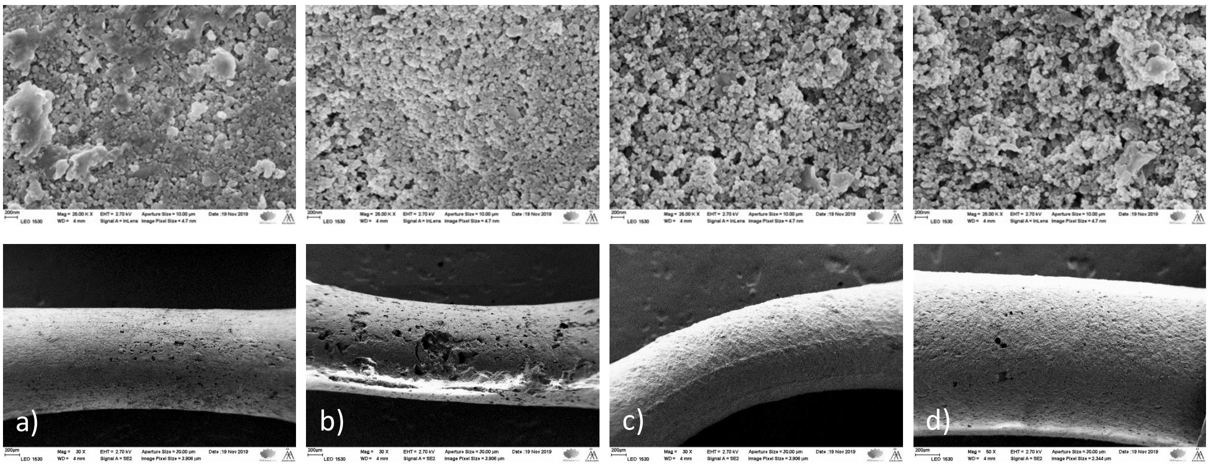

Figure S4. SEM images: a) A – Ru/(H-MCM-41+Bindizl-50/80), post synthesis; b) B - Ru/(H-MCM-41+Bindizl-50/80), in-situ synthesis; c) C – (Ru/Bindizl-50/80)+H-MCM-41, in-situ synthesis; d) D – (Ru/H-MCM-41)+Bindizl-50/80, in-situ synthesis.

Table S4. Brønsted and Lewis acid sites. Legend: P – H-MCM-41, powder catalyst; P - 70% H-MCM-41 + 30% Bindizl-50/80; A – Ru/(H-MCM-41+Bindizl-50/80), post synthesis; B - Ru/(H-MCM-41+Bindizl-50/80), in-situ synthesis; C – (Ru/Bindizl-50/80)+H-MCM-41, in-situ synthesis; D – (Ru/H-MCM-41)+Bindizl-50/80, in-situ synthesis.*

Type	**Brønsted acidity, µmol/g**				**Lewis acidity, µmol/g**				**Total acidity**
	weak	*medium*	*strong*	∑	*weak*	*medium*	*strong*	∑	*µmol/g*
P	41	19	24	84	20	14	21	56	140
P*	48	12	7	67	25	16	9	50	118
A	36	1	0	37	22	2	0	24	60
B	31	0	0	31	21	0	0	21	51

C	32	3	0	35	23	2	0	25	60
D	29	0	0	29	22	0	0	22	52

Catalytic results

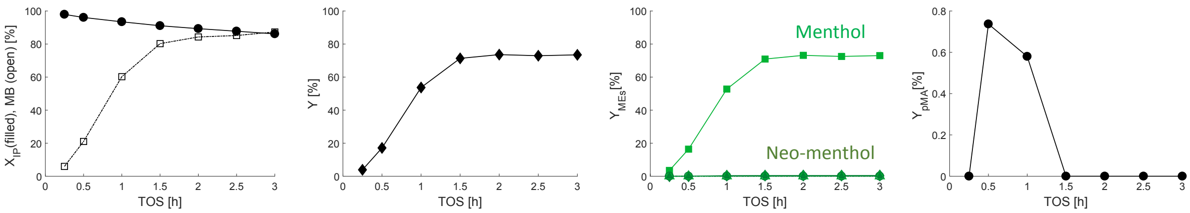

Figure S5. Menthol synthesis from isopulegol over B - Ru/(H-MCM-41+Bindizl-50/80), in-situ synthesis extrudates: a) conversion and mass balance, b) total yield, c) yield of menthols, d) yield of p-menthane on time-on-stream.

Table S5. Reaction rate (r) and turnover frequency (TOF) in menthol synthesis.

Reactant	Catalyst	r^0	TOF^0	X	r	TOF
-	-	*mol/s/g*	*1/s*	*%*	*mol/s/g*	*1/s*
Isopulegol	B	$5.66 \cdot 10^{-7}$	0.0049	86	$4.98 \cdot 10^{-7}$	0.0043
Citronellol	B	$4.91 \cdot 10^{-7}$	0.0043	96	$4.72 \cdot 10^{-7}$	0.0041
Citronellal	A	$6.42 \cdot 10^{-7}$	0.0052	87	$5.58 \cdot 10^{-7}$	0.0045
	B	$5.85 \cdot 10^{-7}$	0.0051	85	$4.96 \cdot 10^{-7}$	0.0043
	C	$6.64 \cdot 10^{-7}$	0.0072	94	$6.21 \cdot 10^{-7}$	0.0068
	D	$6.07 \cdot 10^{-7}$	0.0052	96	$5.88 \cdot 10^{-7}$	0.0050
Citronellal	B^{II}	$6.11 \cdot 10^{-7}$	0.0053	85	$5.58 \cdot 10^{-7}$	0.0049
	B^{III}	$5.86 \cdot 10^{-7}$	0.0051	83	$5.07 \cdot 10^{-7}$	0.0044

after 3 h of time-on-stream; Legend: A – Ru/(H-MCM-41+Bindizl), post synthesis (light blue square); B – Ru/(H-MCM-41+Bindizl), in-situ synthesis (dark blue diamond); C – (Ru/Bindizl)+H-MCM-41 (red triangle); D – (Ru/H-MCM-41)+Bindizl (green circle).

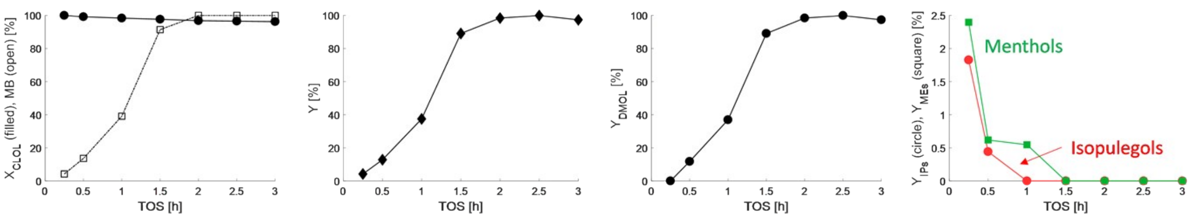

Figure S6. Menthol synthesis from β-citronellol over B - Ru/(H-MCM-41+Bindizl-50/80), in-situ synthesis extrudates: a) conversion and mass balance, b) total yield, c) yield of 3,7-dimethyloctan-1-ol, d) yield of menthols and isopulegols on time-on-stream.

Table S6. Menthol isomers in menthol synthesis from (±)-citronellal after 3 h of TOS over: A – Ru/(H-MCM-41+Bindizl-50/80), post synthesis; B - Ru/(H-MCM-41+Bindizl-50/80), in-situ synthesis; C – (Ru/Bindizl-50/80)+H-MCM-41, in-situ synthesis; D – (Ru/H-MCM-41)+Bindizl-50/80, in-situ synthesis.

	Y_{MEs}	Y_{ME}	Y_{NME}	Y_{IME}	Y_{NIME}	Y_{ME}/Y_{MEs}	Y_{NME}/Y_{MEs}	Y_{IME}/Y_{MEs}	Y_{NIME}/Y_{MEs}
A	37.9	25.8	9.4	0.5	2.2	68	25	1	6
B	38.4	26.5	9.1	0.5	2.3	69	24	1	6
C	31.3	21.8	7.4	0.3	1.8	70	24	1	6

D	46.6	32.1	11.1	0.6	2.7	69	24	1	6

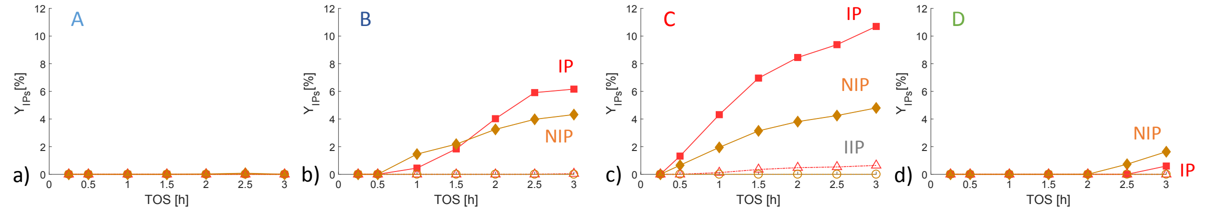

Figure S7. Isopulegol isomers as a function of time-on-stream in menthol synthesis from (±)-citronellal over: a) A – Ru/(H-MCM-41+Bindizl-50/80), post synthesis; b) B - Ru/(H-MCM-41+Bindizl-50/80), in-situ synthesis; c) C – (Ru/Bindizl-50/80)+H-MCM-41, in-situ synthesis; d) D – (Ru/H-MCM-41)+Bindizl-50/80, in-situ synthesis. Legend: isopulegol (IP, red, filled square), neoisopulegol (NIP, orange, filled diamond), isoisopulegol (IIP, red, empty triangle), neoisoisopulegol (NIIP, orange, empty circle).

Table S7. Isopulegol isomers in menthol synthesis from (±)-citronellal after 3 h of TOS over: A – Ru/(H-MCM-41+Bindizl-50/80), post synthesis; B - Ru/(H-MCM-41+Bindizl-50/80), in-situ synthesis; C – (Ru/Bindizl-50/80)+H-MCM-41, in-situ synthesis; D – (Ru/H-MCM-41)+Bindizl-50/80, in-situ synthesis.

	Y_{IPs}	Y_{IP}	Y_{NP}	Y_{IIP}	Y_{NIIP}	Y_{IP}/Y_{IPs}	Y_{NIP}/Y_{IPs}	Y_{IIP}/Y_{IPs}	Y_{NIIP}/Y_{IPs}
A	0.0	0.0	0.0	0.0	0.0	-	-	-	-
B	10.5	6.2	4.3	0.1	0.0	59	41	0	0
C	16.1	10.7	4.8	0.6	0.0	66	30	4	0
D	2.2	0.6	1.6	0.0	0.0	27	73	0	0

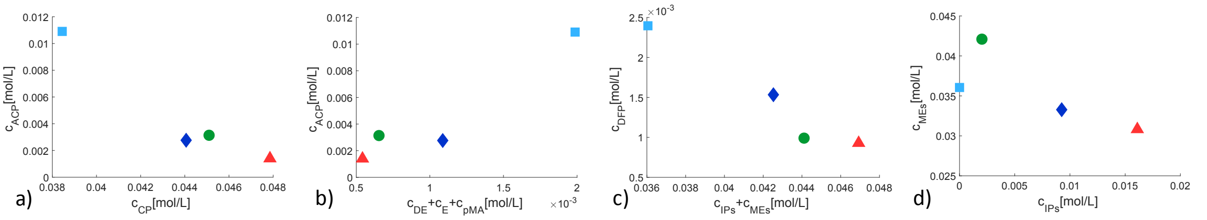

Figure S8. a, b) The concentration of acyclic hydrogenation products as a function of the concentration of cyclic products and the concentration of p-menthadiene, p-menthaene, and p-menthane; c) the concentration of defunctionalization products as a function of the concentration of isopulegols and menthols; d) the concentration of menthols as a function of the concentration of isopulegols. Legend: A – Ru/(H-MCM-41+Bindizl), post synthesis (light blue square); B – Ru/(H-MCM-41+Bindizl), in-situ synthesis (dark blue diamond); C – (Ru/Bindizl)+H-MCM-41 (red triangle); D – (Ru/H-MCM-41)+Bindizl (green circle).

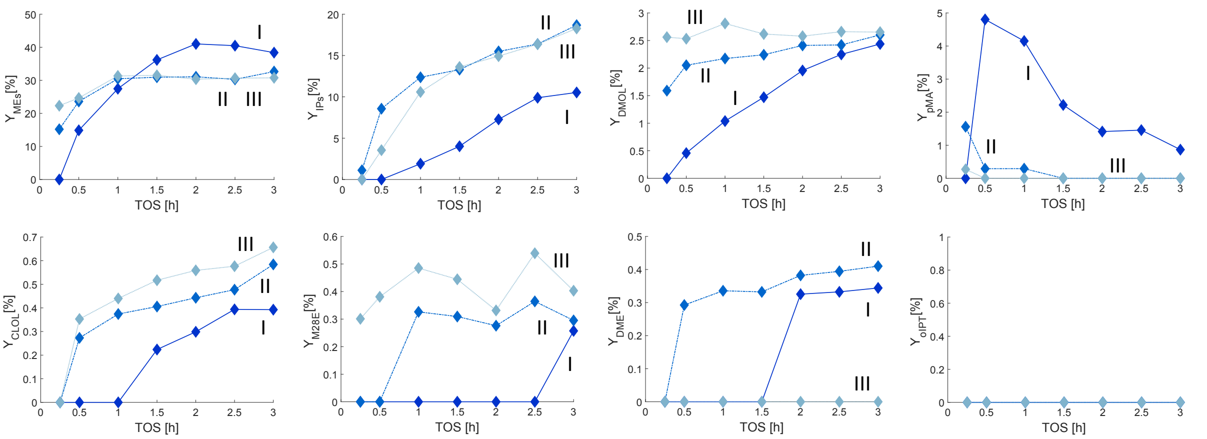

Figure S9. Product distribution in menthol synthesis from (±)-citronellal: a) menthols, b) isopulegols, c) 3,7-dimethyloctan-1-ol, d) p-menthane, e) citronellol, f) metha-2,8-diene, g) 2,6-dimethyloctane, h) o-

isopropenyltoluene. Legend: I - fresh B - Ru/(H-MCM-41+Bindizl-50/80), in-situ synthesis; II - reused II B - Ru/(H-MCM-41+Bindizl-50/80), in-situ synthesis; III - reused III B - Ru/(H-MCM-41+Bindizl-50/80), in-situ synthesis.

Table S8. Menthol isomers in menthol synthesis from (±)-citronellal after 3 h of TOS over: B - fresh B - Ru/(H-MCM-41+Bindizl-50/80), in-situ synthesis; B^{II} - reused II B - Ru/(H-MCM-41+Bindizl-50/80), in-situ synthesis; B^{III} - reused III B - Ru/(H-MCM-41+Bindizl-50/80), in-situ synthesis.

	Y_{MEs}	Y_{ME}	Y_{NME}	Y_{IME}	Y_{NIME}	Y_{ME}/Y_{MEs}	Y_{NME}/Y_{MEs}	Y_{IME}/Y_{MEs}	Y_{NIME}/Y_{MEs}
B	38.4	26.5	9.1	0.5	2.3	69	24	1	6
B^{II}	32.6	22.3	7.4	0.5	2.1	68	23	2	6
B^{III}	30.8	21.6	6.8	0.4	2.0	70	22	1	6

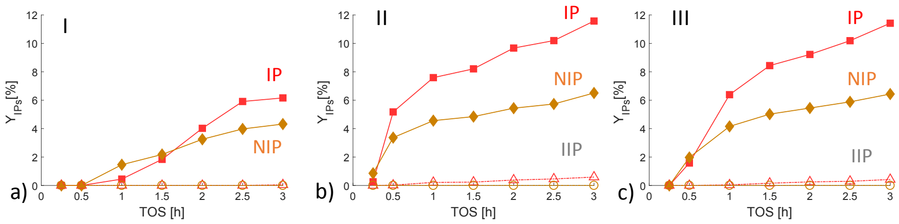

Figure S10. Isopulegol isomers as a function of time-on-stream in menthol synthesis from (±)-citronellal over: a) fresh B - Ru/(H-MCM-41+Bindizl-50/80), in-situ synthesis; b) reused II B - Ru/(H-MCM-41+Bindizl-50/80), in-situ synthesis; c) reused III B - Ru/(H-MCM-41+Bindizl-50/80), in-situ synthesis. Legend: isopulegol (IP, red, filled square), neoisopulegol (NIP, orange, filled diamond), isoisopulegol (IIP, red, empty triangle), neoisoisopulegol (NIIP, orange, empty circle).

Table S9. Isopulegol isomers in menthol synthesis from (±)-citronellal after 3 h of TOS over: B - fresh B - Ru/(H-MCM-41+Bindizl-50/80), in-situ synthesis; B^{II} - reused II B - Ru/(H-MCM-41+Bindizl-50/80), in-situ synthesis; B^{III} - reused III B - Ru/(H-MCM-41+Bindizl-50/80), in-situ synthesis.

	Y_{IPs}	Y_{IP}	Y_{NP}	Y_{IIP}	Y_{NIIP}	Y_{IP}/Y_{IPs}	Y_{NIP}/Y_{IPs}	Y_{IIP}/Y_{IPs}	Y_{NIIP}/Y_{IPs}
B	10.5	6.2	4.3	0.1	0.0	59	41	0	0
B^{II}	18.7	11.6	6.5	0.6	0.0	62	35	3	0
B^{III}	18.3	11.4	6.4	0.4	0.0	62	35	2	0

References

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