

Supporting information for

Complete Hydrodehalogenation of Polyfluorinated and other Polyhalogenated Benzenes under Mild Catalytic Conditions

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SI-1 TEM images

Transmission electron microscope images of the Rh/Al₂O₃ catalyst are shown in Figure SI-1. Transmission electron microscope (TEM) analysis was performed on a CM12 microscope (Philips) with 100 kV acceleration voltage. The Rh particle size distribution was estimated by statistical analysis on ca. 270 Rh particles; Rh particles on the Al₂O₃ support had an average diameter of 2.7 nm. Rhodium dispersion was estimated from TEM particle size distribution and was approx. 45 %. The variation of volume of rhodium particles due to a change of oxidation during catalysis was neglected and the particles were considered as truncated cubic octahedrons.

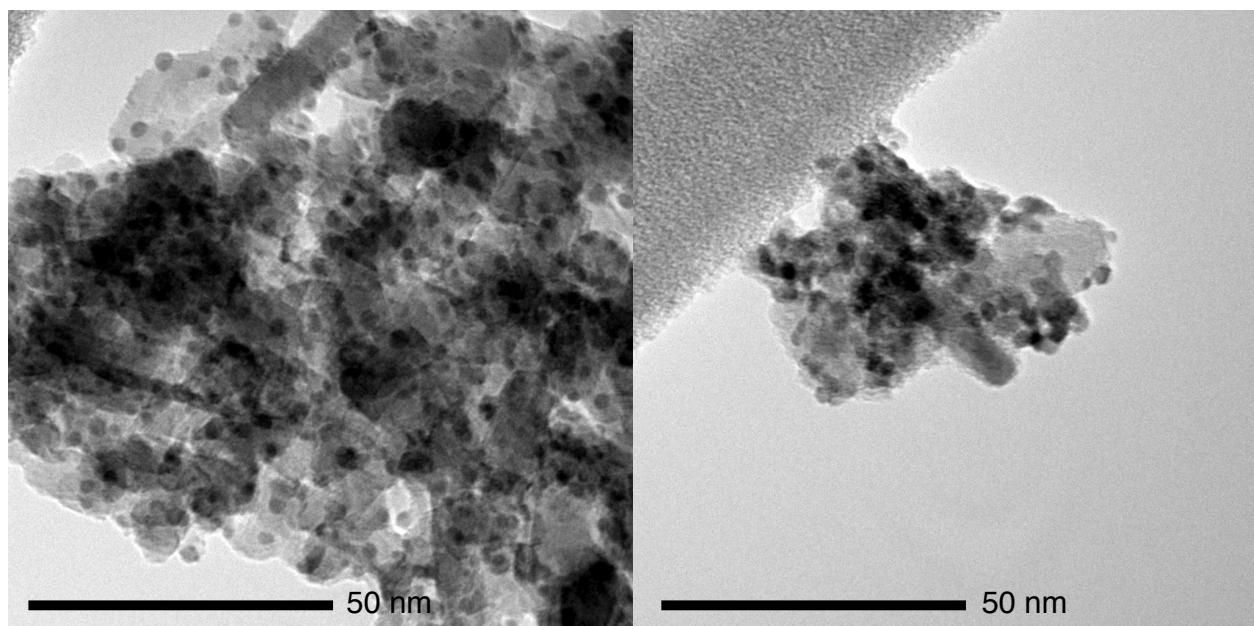


Figure SI-1: TEM images of two Rh/Al₂O₃ catalyst grains with small (average diameter 2.7 nm) Rh particles on them.

SI-2 Reagents and analytical methods

Reagents

Hydrogen (99.999 %), N2 (99.999 %), and He (99.999 %) were purchased from Carbegas (Switzerland). Penta- and hexafluorobenzene, 1,2-, 1,3-, 1,4-difluorobenzene, 1,2,3-, 1,2,4-, 1,3,5-trifluorobenzene, 1,2,3,4-, 1,2,3,5- and 1,2,4,5-tetrafluorobenzene were purchased from TCI Europe (Belgium). 1,2-Dichloroethane was purchased from Merck (Switzerland). All other authentic standards were purchased from Sigma-Aldrich (Switzerland). Milli-Q water (18.2 MΩ cm-1), generated from NANOpure Diamond purifying system (Barnstead), was used for all experiments.

Analytical methods

Headspace samples. The headspace aliquots were analyzed by gas chromatography coupled to mass spectrometry (GC-MS) using a Thermo Scientific Trace GC Ultra and a Thermo Scientific DSQ Quadrupole MS. Benzene, cyclohexane, all fluorinated benzenes, mixed halogenated benzenes, unhalogenated benzenes, chlorobenzene and 4-chlorotoluene were analyzed by GC-MS. The column used was a Restek Rtx-1 Crossbond 100% dimethyl polysiloxane (30 m × 0.32 mm × 4 μm film thickness). Temperature profiles applied were different for fluorinated benzenes, the mixed halogenated benzenes and for the headspace samples of the chlorinated benzenes batch experiments:

- 1) Fluorinated benzenes: 70 °C (9 min)
- 2) Mixed halogenated benzenes: 70 °C (2 min), ramp 30 °C/min to 140 °C (3.7 min), ramp 30 °C/min to 200 °C (2.5 min) - the program was shorted depending on the retention time of the starting material or the internal standard

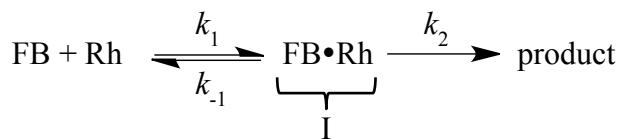
3) Headspace samples of the chlorinated benzenes batch experiments: 90 °C (2 min), ramp 30 °C/min to 150 °C (6 min)

Headspace standard calibration curves were derived from 20 mL crimp cap headspace vials with the same water-to-headspace ratio as in the bottles used for the batch experiments and were based on the total amount added to the bottle.

Bulk phase samples. The bulk water samples were analyzed by a Thermo Scientific Trace GC Ultra equipped with an electron capture detector (GC-ECD), injection was performed by a PAL autosampler system. The needle of the autosampler was calibrated to draw only from the hexane phase in the HPLC vial. Complete separation of all chlorinated benzenes and 1,2-dichloroethane was achieved with a Restek Rxi-5ms Crossbond 5% diphenyl / 95% dimethylpolysiloxane column (30 m × 0.25 mm × 0.25 µm film thickness). The oven temperature profile was 50°C (3.5 min), ramp 20 °C min-1 to 80 °C (8 min), ramp 10 °C min-1 to 100 °C (25 min), ramp 40 °C min-1 to 200 °C (7 min) for hexachlorobenzene and was shortened according to the retention time of the starting material. Calibration standards were prepared with the same procedure as used for the bulk phase samples in the batch experiments; the 100 µL aliquots were taken from standards prepared in 20 mL crimp cap headspace vials with the same water-to-headspace ratio as in the bottles used for the batch experiments.

SI-3 Langmuir-Hinshelwood calculations

The surface-mediated reaction can be described by the mechanism:



The fluorobenzenes (FB) have to bind to the Rh in a reversible first step and then undergo transformation. A pseudo-first order kinetic law can be derived (Equations SI-1 to SI-9) from the above shown reaction steps by doing a quasi-steady-state approximation for the FB•RH intermediate (Equation SI-5) and assuming that the sum of the loss rates of the intermediate are higher than the formation rate (Equation SI-7). The observed rate constant, k_{obs} , is an amalgam of the surface binding (k_1 , k_{-1}) and substance transformation kinetics (k_2) (Equation SI-9).

$$\frac{d[\text{prod}]}{dt} = k_2[I] \quad (\text{SI-1})$$

$$[\text{Rh}] = [\text{Rh}]_T - [I] \quad (\text{SI-2})$$

$$\frac{d[I]}{dt} = 0 = k_1[\text{FB}][\text{Rh}] - k_{-1}[I] - k_2[I] \quad (\text{SI-3})$$

$$0 = k_1[\text{FB}][\text{Rh}]_T - k_1[\text{FB}][I] - k_{-1}[I] - k_2[I] \quad (\text{SI-4})$$

$$[I]_{ss} = \frac{k_1[\text{FB}][\text{Rh}]_T}{k_1[\text{FB}] + k_{-1} + k_2} \quad (\text{SI-5})$$

$$\frac{d[\text{prod}]}{dt} = \frac{k_1 k_2 [\text{FB}][\text{Rh}]_T}{k_1[\text{FB}] + k_{-1} + k_2} \quad (\text{SI-6})$$

$$\text{When } k_1[\text{FB}] \ll k_{-1} + k_2 \quad (\text{SI-7})$$

$$\frac{d[\text{prod}]}{dt} = \frac{k_1 k_2 [\text{Rh}]_T [\text{FB}]}{k_{-1} + k_2} \quad (\text{SI-8})$$

$$k_{\text{obs}} = \frac{k_1 k_2 [\text{Rh}]_T}{k_{-1} + k_2} \quad (\text{SI-9})$$

SI-4 Reactive standard normalization and rate variability

Table 1 is divided into four series of experiments: fluorobenzenes, chlorobenzenes, mixed halogenated benzenes, and benzene derivatives. The experiments within each series were performed within approximately two weeks. From the experiments of one series to the experiments of another series, several months passed. The catalyst shows a significant variability in performance, which is illustrated both by the errors on single rate constants (duplicate experiments performed within two weeks) and by the differences in the rate constants derived from experiments in different series. For example, the rate constant derived for chlorobenzene was $3.0 \pm 0.7 \text{ h}^{-1}$ in the chlorobenzenes series and $4.7 \pm 1.0 \text{ h}^{-1}$ in mixed halogenated benzenes series. In this case, the errors given in Table 1 do not capture the whole variability of the catalyst performance over a time period of several months. The use of a reactive standard can correct for these differences, the k_{rel} of chlorobenzene are 1.2 ± 0.2 and 1.1 ± 0.3 in the two series, respectively. For the fluorinated benzenes, the comparison to the mixed halogenated benzenes section is omitted, as a different reactive standard was used. Nevertheless, for this work, we were mainly interested in comparing the rate constants of experiments conducted within each experiment series. For this comparison, the errors given in Table 1 are applicable.

SI-5 Hexafluorobenzene intermediates and models for fitting

Figure SI-2 shows the individual traces of the minor intermediates for which only the fits were shown in Figure 1b.

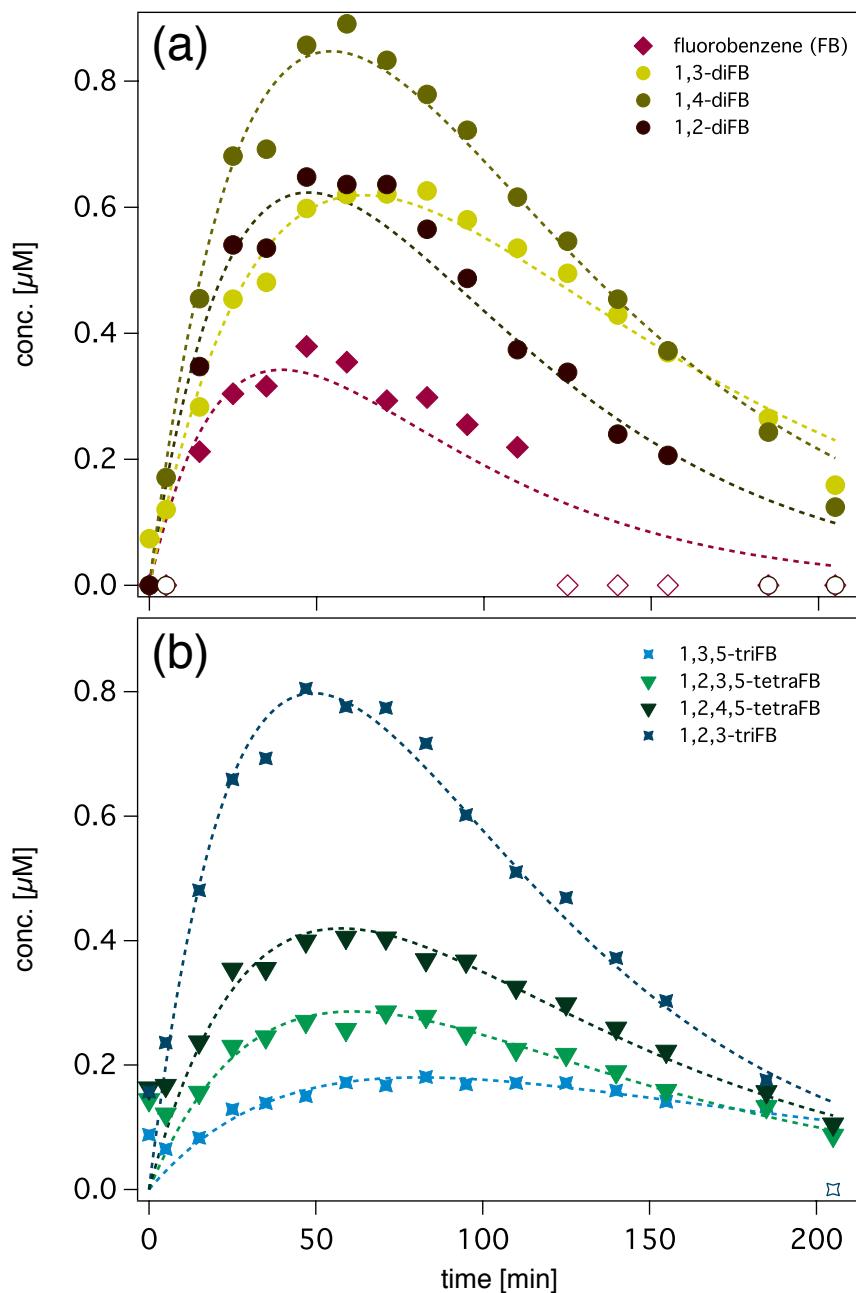


Figure SI-2: Details of intermediate growth and decay traces during the degradation of hexafluorobenzene: (a) fluorobenzene (FB), 1,2-diFB, 1,3-diFB and 1,4-diFB and (b) 1,2,3-triFB, 1,3,5-triFB, 1,2,4,5-tetraFB and 1,2,4,5-tetraFB. They are individually fit to the growth and decay model shown in Figure SI-3b. Empty markers indicate values below the limit of detection.

Hexafluorobenzene degradation, sum of intermediate formation and degradation and cyclohexane formation in Figure 2a were fitted to the model given in Figure 2c and Figure SI-3a. The model was developed for and applied to fluorobenzene degradation by Baumgartner and McNeill.² In the model, hexafluorobenzene is degraded to an unknown/unobserved intermediate (I). From the unknown intermediate (I) both a two-step pathway (through the sum of intermediates $\sum C_6 H_n F_{6-n}$, $n = 1 - 6$) and a direct pathway leads to cyclohexane. Equations SI-10 to SI-13 are the differential equations representing the model.

$$\frac{d[C_6 F_6]}{dt} = -k_{\text{obs}} [C_6 F_6] \quad (\text{SI-10})$$

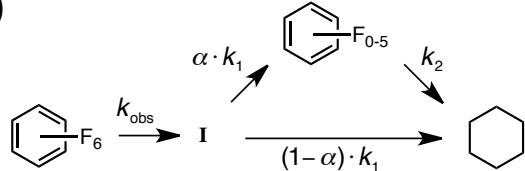
$$\frac{d[I]}{dt} = k_{\text{obs}} [C_6 F_6] - k_1 [I] \quad (\text{SI-11})$$

$$\frac{d[\sum C_6 H_n F_{6-n}]}{dt} = \alpha k_1 [I] - k_2 \left[\sum C_6 H_n F_{6-n} \right] \quad (\text{SI-12})$$

$$\frac{d[C_6 H_{12}]}{dt} = (1-\alpha) k_1 [I] + k_2 \left[\sum C_6 H_n F_{6-n} \right] \quad (\text{SI-13})$$

The formation and degradation of the individual intermediates in Figure 1b and Figure SI-2 were fitted to the growth and decay model shown in Figure SI-3b using IGOR Pro.³

(a)



(b)

$$[C_6H_nF_{6-n}] = \frac{k_{\text{obs}} \cdot f \cdot A_0}{k - k_{\text{obs}}} \cdot (e^{-k_{\text{obs}} \cdot t} - e^{-k \cdot t})$$

Figure SI-3: (a) Kinetic model for the degradation of hexafluorobenzene to cyclohexane through the sum of all intermediates. Arrows correspond to pseudo-first order degradation. (b) The growth and decay model used for fitting the data for the individual intermediates $C_6H_nF_{6-n}$ ($n=1-6$) of hexafluorobenzene. The parameters k_{obs} (pseudo-first order degradation rate constant of hexaFB) and A_0 (initial concentration of hexaFB) were derived from the hexafluorobenzene degradation pseudo-first order kinetic fit and kept constant for the fitting of the intermediates, f (fraction of hexafluorobenzene that is going to the fitted intermediate) and k (pseudo-first order degradation constant of the intermediate) were fitted for each individual intermediate.

SI-6 Model Fits FB and CB congener degradation rate constants

Graphical representation of the model fits that were used to compare FB and CB congener degradation is shown in Figure SI-4. Two different models were applied.

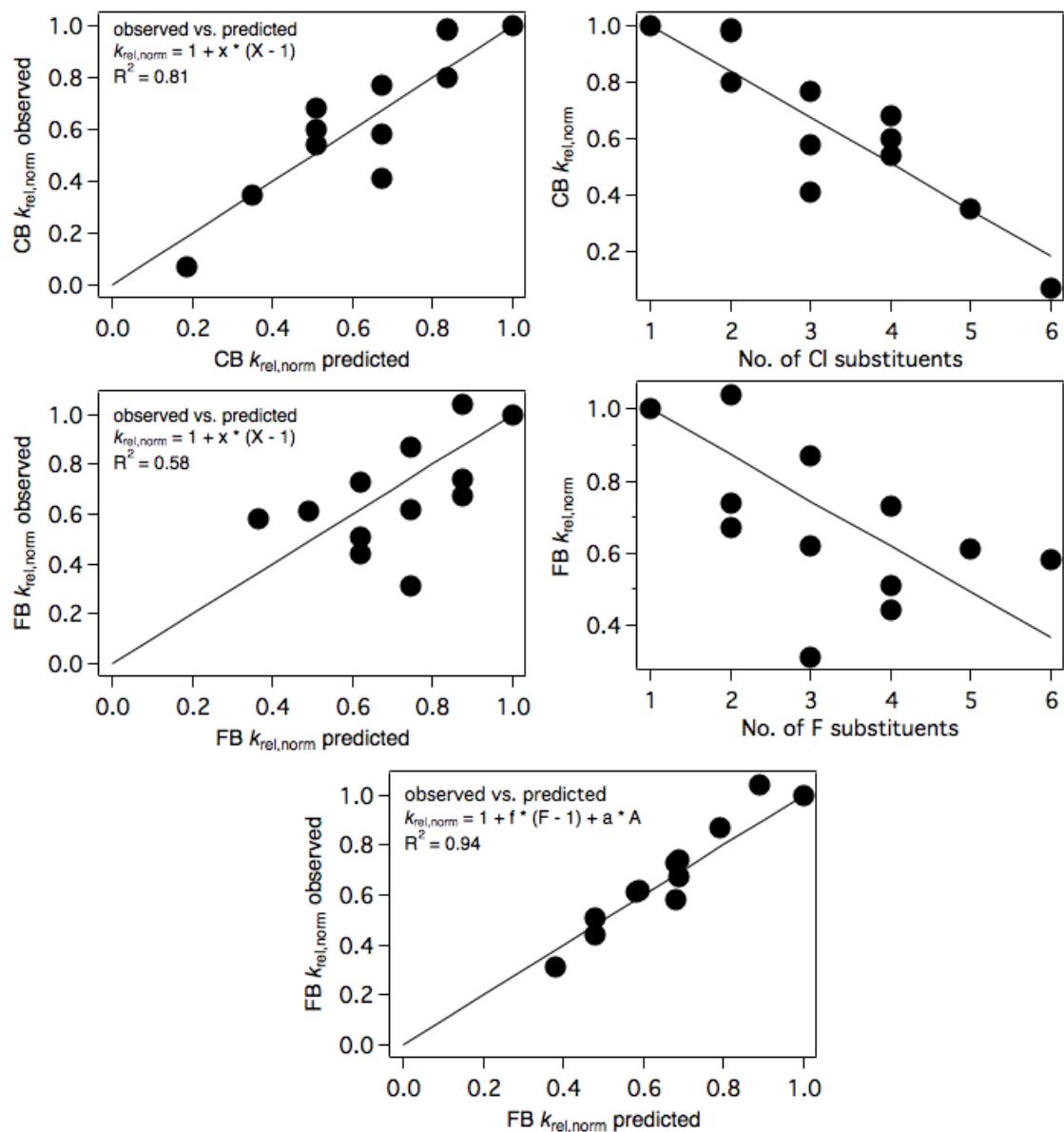


Figure SI-4: Model fits for the comparison of CB and FB congener degradation. The first four graphs show the fit for the CB rate constants (first row) and the FB rate constants (second row) to the model $k_{\text{rel},\text{norm}} = 1 + x(X - 1)$ (Equation 1). The graph on the bottom shows the fit of the FB degradation rate constants to the model $k_{\text{rel},\text{norm}} = 1 + f(F - 1) + aA$ (Equation 2).

SI-7 Limits of detection and quantification

Limits of detection and limits of quantification for all compounds measured with GC-MS and GC-ECD are given in Table SI-1.

Table SI-1: Limits of detection (LOD) and limits of quantification (LOQ) for all measured compounds.

Compound name	LOD [μ M]	LOQ [μ M]
analytical method: GC-MS		
fluorobenzene (FB)	0.15	0.5
1,2-diFB	0.1	0.3
1,3-diFB	0.1	0.3
1,4-diFB	0.1	0.3
1,2,3-triFB	0.1	0.3
1,2,4-triFB	0.1	0.3
1,3,5-triFB	0.07	0.2
1,2,3,4-tetraFB	0.1	0.3
1,2,3,5-tetraFB	0.07	0.2
1,2,4,5-tetraFB	0.07	0.2
pentaFB	0.07	0.2
hexaFB	0.07	0.2
chlorobenzene (CB)	0.2	0.6
bromobenzene	0.4	1.2
iodobenzene	0.6	1.8
1-fluoro-4-chlorobenzene	0.15	0.5
1-fluoro-4-bromobenzene	0.3	1
1-chloro-4-bromobenzene	1.0	3
1-chloro-4-iodobenzene	1.2	3.5
benzene	0.2	0.6
cyclohexane	0.07	0.2
methylcyclohexane	0.07	0.2
4-chlorotoluene	0.1	0.3

toluene	0.1	0.3
α,α,α -trifluorotoluene	0.1	0.3
analytical method: GC-ECD		
12-diCB	0.03	0.1
13-diCB	0.03	0.1
14-diCB	0.03	0.1
123-triCB	0.007	0.02
124-triCB	0.01	0.03
135-triCB	0.007	0.02
1234-tetraCB	0.003	0.01
1235-tetraCB	0.007	0.02
1245-tetraCB	0.01	0.03
pentaCB	0.002	0.005
hexaCB	0.002	0.005

SI-8 Scope of catalytic system – Structures

Apart from performing dehalogenation and hydrogenation of benzene, the Rh/Al₂O₃ and H₂ catalytic system hydrogenates benzenes with a variety of substituents. For this study, several substituted benzenes were tested (end product in parenthesis): Toluene (methylcyclohexane), fluorotoluene (all isomers, methylcyclohexane), anisole (methoxycyclohexane), ethylbenzene (ethylcyclohexane), benzoic acid (cyclohexanecarboxylic acid), phenol (cyclohexanol). Hydrogenation is generally slightly slower than dehalogenation but on the same order of magnitude, half-lives varied between 10 and 50 min. Rates constants are shown in Table SI-2.

Table SI-2: Pseudo-first order rate constants (k_{obs}), rate constants normalized to the reactive standard (k_{rel}), rate constants normalized to the reactive standard and to the respective

monohalogenated benzene ($k_{\text{rel,norm}}$) and half-lives ($t_{1/2}$, based on k_{obs}) for substituted benzenes.

Only one batch experiment was conducted per compound, errors are the errors of the fit.

	$k_{\text{obs}} [\text{h}^{-1}]$	$k_{\text{rel}} [-]$	$k_{\text{rel,norm}} [-]$	$t_{1/2} [\text{min}]$
substituted benzenes	Rh: $2.44 \text{ mg}_{\text{Rh}} \text{ L}^{-1}$	IS: α,α,α -trifluorotoluene		
tolune	2.6 ± 0.03	1.8 ± 0.1		16 ± 0.2
4-fluorotoluene	3.6 ± 0.5	2.2 ± 0.3		12 ± 1.6
ethylbenzene	2.7 ± 0.3	1.6 ± 0.3		15 ± 1.8
anisole	2.1 ± 0.3	1.6 ± 0.2		19 ± 2.6
phenol	3.9 ± 0.3	3.7 ± 0.4		11 ± 0.9
benzoic acid	0.8 ± 0.1	0.5 ± 0.1		52 ± 4.0

Structures of all compounds tested in the catalytic system with Rh/Al₂O₃ and H₂ and the end products of the catalytic reactions are shown in Figure SI-5.

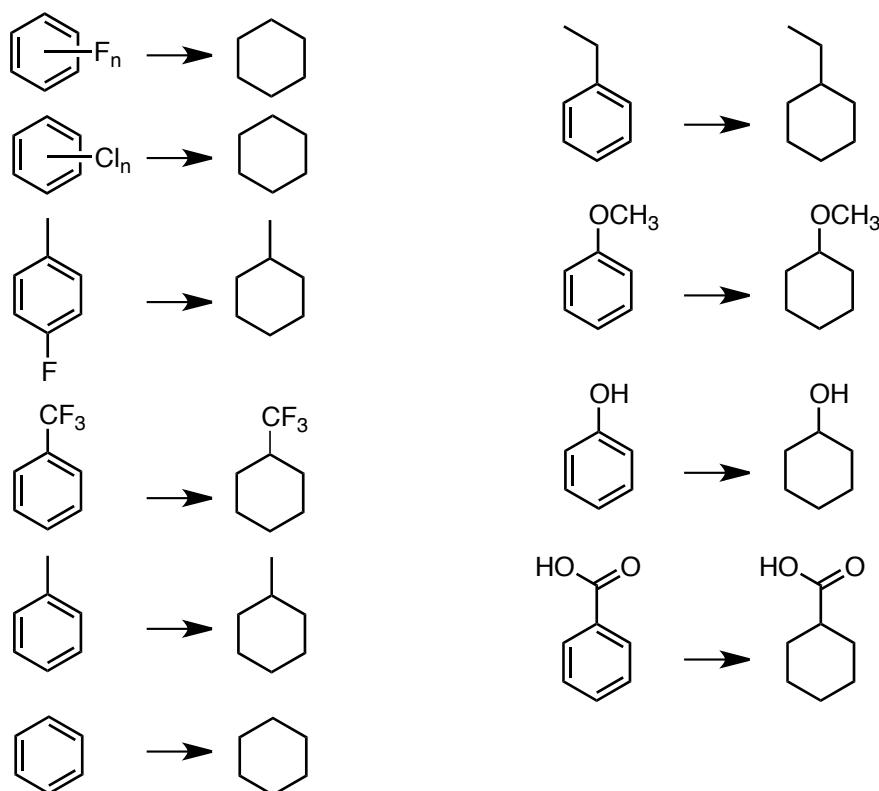


Figure SI-5: Starting materials and end products for all tested substances.

References

- (1) Reichert, P., Concepts underlying a computer program for the identification and simulation of aquatic systems, **1994**. CH-8600 Dübendorf, Switzerland.
- (2) Baumgartner, R.; McNeill, K. Hydrodefluorination and Hydrogenation of Fluorobenzene under Mild Aqueous Conditions. *Environ. Sci. Technol.* **2012**, *46*, 10199.
- (3) WaveMetrics, IGOR Pro Version 6.22A, **1988-2011**.