

## Supporting Information

### Catalytic Dehalogenation with Activated Borane, a Porous Borane Cluster Polymer

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## Experimental section

### Materials

*Nido*-B<sub>10</sub>H<sub>14</sub> (Katchem, Czech Republic) was purified by column chromatography (Silicagel, *n*-hexane) followed by recrystallization from *n*-hexane before transferring to a Ar-filled glovebox. Benzene, *cy*-hexane, *n*-hexane and toluene were dried over Na/benzophenone and freshly distilled before use. CH<sub>2</sub>Cl<sub>2</sub> (VWR, HPLC grade) was dried by a solvent purification system SP1 (LC Technology Solution, USA). Trifluorotoluene, trichlorotoluene, 1-fluorooctane, 1-chlorooctane, fluorocyclohexane, chlorocyclohexane, and triethylsilane were used as received from commercial vendors. The synthesis of **ActB** was done under Ar using a standard Schlenk technique and Ar-filled glovebox (PureLab, Inert corp.). The catalytic reactions were carried out in a Microwave synthesizer – CEM Discover SP. The catalytic mixtures were prepared in the glovebox, closed with a cap and removed from the glovebox just before the start of the reaction.

### Instrumental methods

<sup>1</sup>H and <sup>19</sup>F NMR spectra were measured on a JEOL 600 MHz or Bruker Avance NEO 500 MHz NMR spectrometers. The <sup>1</sup>H chemical shifts were referenced to the residual signal of the deuterated solvents, <sup>19</sup>F spectra were measured with reference to the PhCF<sub>3</sub> signal at –63.72 ppm.

GC-MS analyses were performed with a Thermo Focus DSQ instrument using a capillary column Thermo TR-5MS (15 m, ID 0.25 mm). GC-FID measurements were performed on an Agilent 6890 with a DB-5 column (length: 50 m, ID 0.32 mm, stationary phase thickness: 1 μm) with *n*-decane as an internal standard. Standard calibration procedures were performed for all compounds available in pure form (0.5–0.03125 mmol/mL concentration range).

Adsorption isotherms of Ar at 87 K were recorded using a 3P micro 300 Instrument (3P Instruments) using a CryoTune 87K. Prior to adsorption experiments, the samples were evacuated at 100 °C for at least 24 h using the measuring port of the adsorption instrument.

FT-IR was recorded on a Nicolet Avatar spectrometer using an ATR technique with a Si crystal on samples enclosed in a cuvette under inert atmosphere.

SEM images were recorded using a HR-SEM FEI NanoSEM 450 equipped with a circular backscatter and EDX detector, operating at an accelerating voltage of 5 kV. The samples were deposited onto a silicon wafer chip.

### **Synthesis of Activated Borane (ActB)**

**ActB** was prepared analogously to a previously established method using dried toluene and Ar-filled glovebox, briefly, 2.0 g *nido*-B<sub>10</sub>H<sub>14</sub> was dissolved in 50 mL of toluene, transferred to a stainless-steel autoclave (Berghof BR-300) and heated at 250 °C for 24 h. The obtained dark solid was subsequently Soxhlet extracted with toluene, to remove all soluble impurities. The extraction was done until the washings were colourless, at least for 24 h. The resulting black solid was then dried in vacuum at 100°C for 4 h.

### **General procedure for the dehalogenation reactions**

20 mg of the **ActB** catalyst was placed into a 10 mL CEM Corp. Pressure Vessels (Pyrex), followed by the stirrer, substrate (1 mmol), toluene (2 mL), Et<sub>3</sub>SiH (1.5 or 4.5 mmol) and in the case of fluorinated substrates fluorobenzene (1 mmol) which was used as an internal standard. The pressure vessel was closed by silicone/TPFE cap and placed into a microwave synthesizer – CEM Discover SP. The microwave heating with a continuous stirring was allowed to run for the predefined time, after which the sample was taken, centrifuged to remove the solid catalyst and analysed by <sup>19</sup>F NMR (trifluorotoluene and 1-fluorooctane) or GC (fluorocyclohexane, trichlorotoluene, 1-chlorooctane and chlorocyclohexane).

### **Blank tests**

Control experiments were done in a similar way either without **ActB** or separately without Et<sub>3</sub>SiH. The reactions were done at 140°C for 1 h for all substrates. Additionally, for trifluoro- and trichlorotoluene the experiments were done without catalyst at 200 °C for 1 h. In all cases no conversion was observed, except for reaction with fluorocyclohexane without Et<sub>3</sub>SiH, which case is discussed in detail.

### **Catalyst reuse**

The reaction mixture was prepared as for a standard catalytic test using PhCF<sub>3</sub> (see above). The reaction was performed at 140°C for 8 h. After the completion of the reaction the vessel was transferred to the glovebox, left for sedimentation and then a 0.5mL sample was taken for NMR analysis. Consequently, fresh substrate and silane were added – 4.5 mmol of Et<sub>3</sub>SiH

(0.72 mL) and 1 mmol of PhCF<sub>3</sub> (0.14 mL) and then the reaction was run for 8 h as the original experiment. This procedure was repeated seven times.

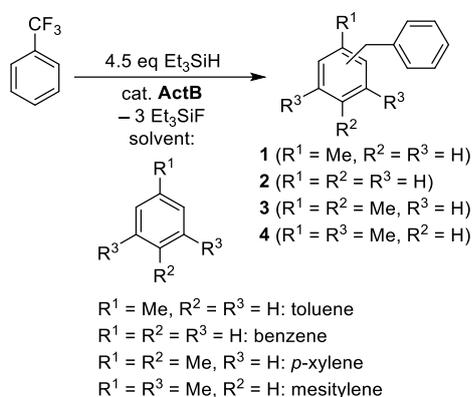
### Determination of concentration of catalytic centres

The reaction mixture was prepared as for a standard catalytic test using PhCF<sub>3</sub> (see above). To each of the reaction mixtures TEPO was added, so that a set of reactions with TEPO amounts between 0.01 to 0.19 mmol of TEPO per 1 g of **ActB** catalyst were prepared. The reaction mixtures were then heated for 2 h at 140°C and analyzed as described above.

### Recovering the catalyst after reaction

To analyse the catalyst after the reaction, a standard catalytic test using PhCF<sub>3</sub> run at 140°C for 8 h was performed, however, in 5 times larger quantity using a 35 mL microwave reaction tube. After the reaction was completed the reaction vessel was transferred to the glovebox, filtered through a fritted glass funnel, washed 6 times with toluene and dried under vacuum at 100 °C for 4 h.

### Isolation of the Friedel-Crafts products from the PhCF<sub>3</sub> reaction



The reaction of PhCF<sub>3</sub> in toluene was performed as described above at 140 °C, 8 h. The products of Friedel–Crafts reaction were separated by filtration, evaporation of the solvent, followed by column chromatography using hexane/dichloromethane in 4:1 ratio as a mobile phase. The isolated yield was 122 mg (67 %). Identity of the product **1** was confirmed by NMR (the two isomers observed were assigned as 2-benzyltoluene and 4-benzyltoluene in a ratio ca. 2:3 according to the literature<sup>1</sup>) and GC-MS. **1**: <sup>1</sup>H NMR (CDCl<sub>3</sub>) 2-benzyltoluene: δ 2.26 (s, 3H, *Me*), 4.00 (s, 2H, CH<sub>2</sub>), 7,10-7.30 (m, 9H, *Ph* and C<sub>6</sub>H<sub>4</sub>) ppm; 4-benzyltoluene: δ 2.33 (s, 3H, *Me*), 3.96 (s, 2H, CH<sub>2</sub>), 7,10-7.30 (m, 9H, *Ph* and C<sub>6</sub>H<sub>4</sub>) ppm. MS (*m/z*/rel. int.): 182(M<sup>+</sup>)/44; 167/100; 165/49; 152/19; 139/5; 128/5; 115/4; 104/4; 91/7; 77/2; 65/15; 51/9; 39/9; 28/2.

In an analogous manner, reactions were performed using PhCF<sub>3</sub> and the following aromatic substrates as solvents and the corresponding products were isolated:

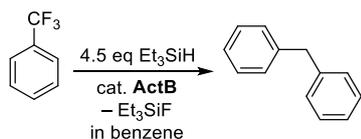
Benzene gave diphenylmethane **2** as the major product (45 mg, 27% yield). **2**: <sup>1</sup>H NMR (CDCl<sub>3</sub>): <sup>1</sup>H: δ 3.97 (s, 2 H, CH<sub>2</sub>), 7.13-7.32 (m, 10 H, Ph); <sup>13</sup>C{<sup>1</sup>H}: δ 42.1 (CH<sub>2</sub>), 126.2 (CH<sub>p</sub> of Ph), 128.6, 129.1 (2x CH of Ph), 141.3 (C<sub>ipso</sub> of Ph) ppm.

*p*-Xylene gave 2-benzyl-1,4-dimethylbenzene **3** (81 mg, 41% yield). **3**: <sup>1</sup>H NMR (CDCl<sub>3</sub>): <sup>1</sup>H: δ 2.19, 2.28 (2x s, 3 H, Me), 3.94 (s, 2 H, CH<sub>2</sub>), 6.90-7.28 (m, 8 H, Ph and C<sub>6</sub>H<sub>3</sub>) ppm.

Mesitylene gave 2-benzyl-1,3,5-trimethylbenzene **4** (131 mg, 62% yield). **4**: <sup>1</sup>H NMR (CDCl<sub>3</sub>): <sup>1</sup>H: δ 2.20 (s, 6 H, 2 Me), 2.28 (s, 3 H, Me), 4.01 (s, 2 H, CH<sub>2</sub>), 6.87-7.25 (m, 7 H, Ph and C<sub>6</sub>H<sub>2</sub>) ppm.

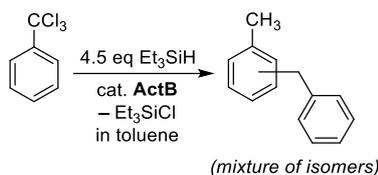
### GC-MS identification of selected products

*The reaction of PhCF<sub>3</sub> in benzene at 140°C:*



Diphenylmethane (**2**): MS (m/z/rel. int.): 168(M<sup>+</sup>)/80; 167/100; 165/42; 153/35; 139/13; 128/9; 115/9; 102/2; 82/2; 77/2; 65/25; 63/31; 51/58; 50/29; 39/43; 28/5.

*The reaction of PhCCl<sub>3</sub> at 140 °C, 8 h:*



Benzyltoluene (**1**, mixture of isomers): MS (m/z/rel. int.): 182(M<sup>+</sup>)/44; 167/100; 165/49; 152/19; 139/5; 128/5; 115/4; 104/4; 91/7; 77/2; 65/15; 51/9; 39/9; 28/2.

*The reaction of PhCCl<sub>3</sub> at 140 °C, 1 h – intermediate product detected:*

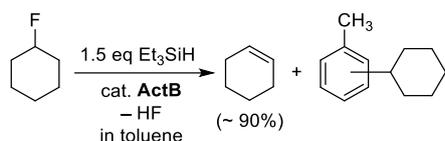
HCCl<sub>2</sub>Ph: 162/4, 160/7; 127/36, 125/100; 99/2; 63/23; 62/13, 61/6; 51/9; 50/8; 39/11; 38/7; 32/3; 28/7.

The reaction of 1-fluorooctane or 1-chlorooctane at 140 °C:



Friedel-Crafts products (mixture of isomers) octyltoluene: MS (m/z/rel. int.): 204(M<sup>+</sup>)/41; 175/19; 133/59; 117/22; 105/100; 91/12; 65/2; 55/4; 41/17; 29/13; 28/3.

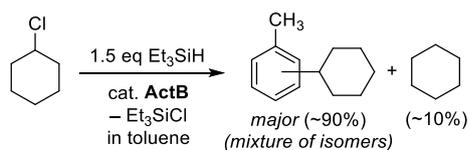
The reaction of 1-fluorocyclohexane at 140°C:



Cyclohexene: MS (m/z/rel. int.): 82(M<sup>+</sup>)/16; 67/55; 54/100; 41/31; 39/62; 28/35; 27/15.

Friedel-Crafts products (mixture of isomers) cyclohexyltoluene: MS (m/z/rel. int.): 174(M<sup>+</sup>)/58; 159/6; 131/100; 129/25; 118/62; 117/48; 115/27; 105/22; 91/20; 65/3; 56/4; 51/5, 41/5; 39/7; 28/9; dicyclohexyltoluene: MS (m/z/rel. int.): 256(M<sup>+</sup>)/100; 227/4; 200/21; 187/20; 173/44; 153/8; 143/22; 131/51; 128/32; 127/14; 119/12; 115/15; 105/20, 91/4; 83/3; 55/15; 41/10; 32/3; 28/19.

The reaction of chlorocyclohexane at 140 °C:



Cyclohexene: MS (m/z/rel. int.): 84(M<sup>+</sup>)/15; 69/4; 56/100; 55/43, 41/78; 39/53; 32/27; 28/55.

## NMR spectra of selected reaction products

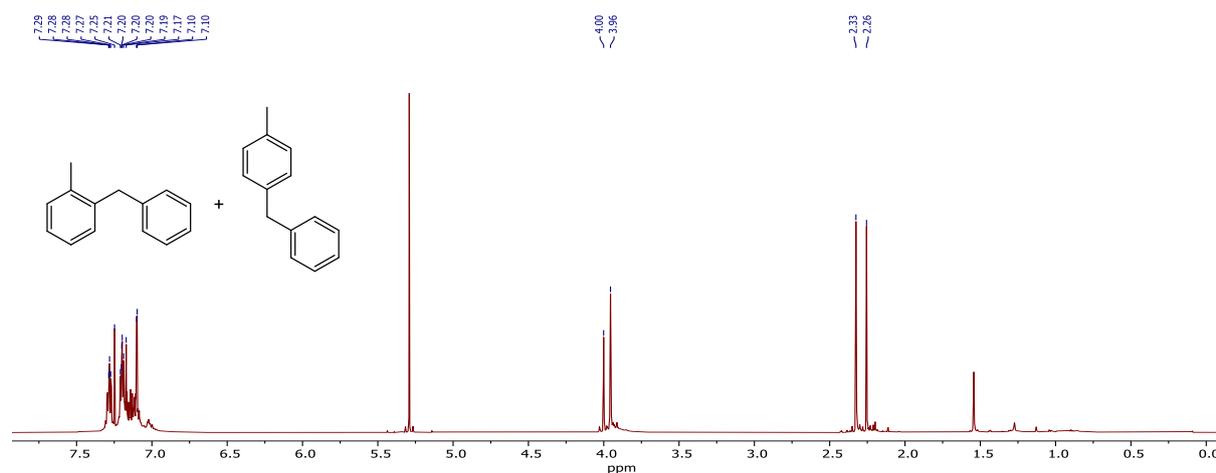


Figure S1: <sup>1</sup>H NMR (CDCl<sub>3</sub>, 600MHz) spectrum of **1** (2-benzyltoluene and 4-benzyltoluene), isolated Friedel-Crafts products from the reaction of PhCF<sub>3</sub> in toluene at 140 °C, 8 h.

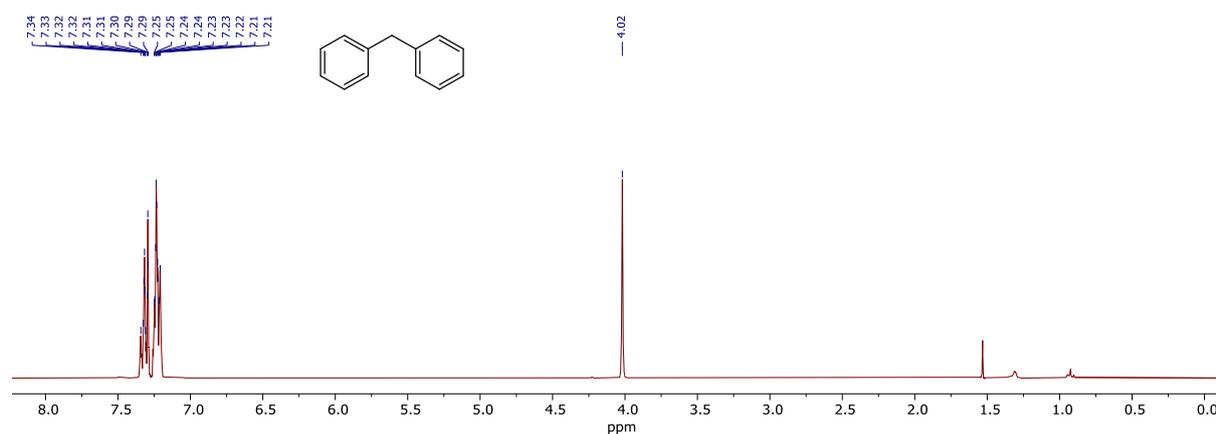


Figure S2: <sup>1</sup>H NMR (CDCl<sub>3</sub>, 600MHz) spectrum of **2**, isolated Friedel-Crafts product from the reaction of PhCF<sub>3</sub> in benzene at 140 °C, 8 h.

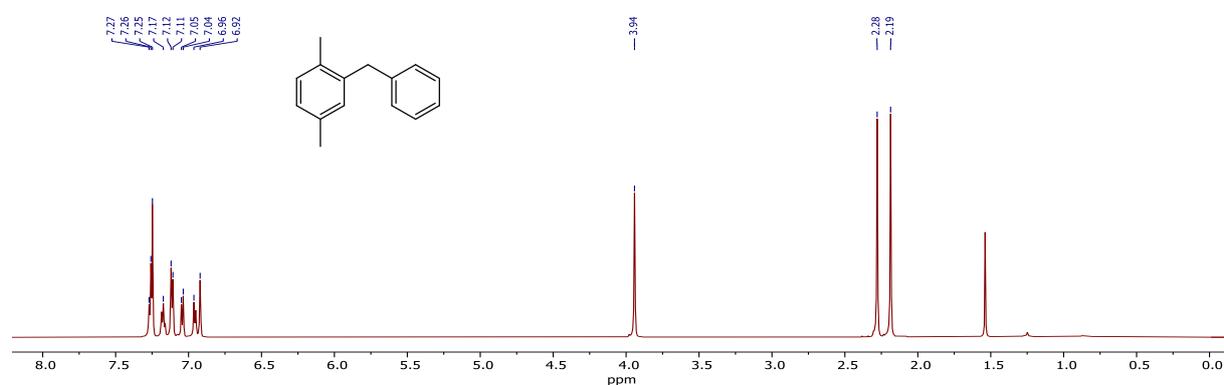


Figure S3: <sup>1</sup>H NMR (CDCl<sub>3</sub>, 600MHz) spectrum of **3**, isolated Friedel-Crafts product from the reaction of PhCF<sub>3</sub> in *p*-xylene at 140 °C, 8 h.

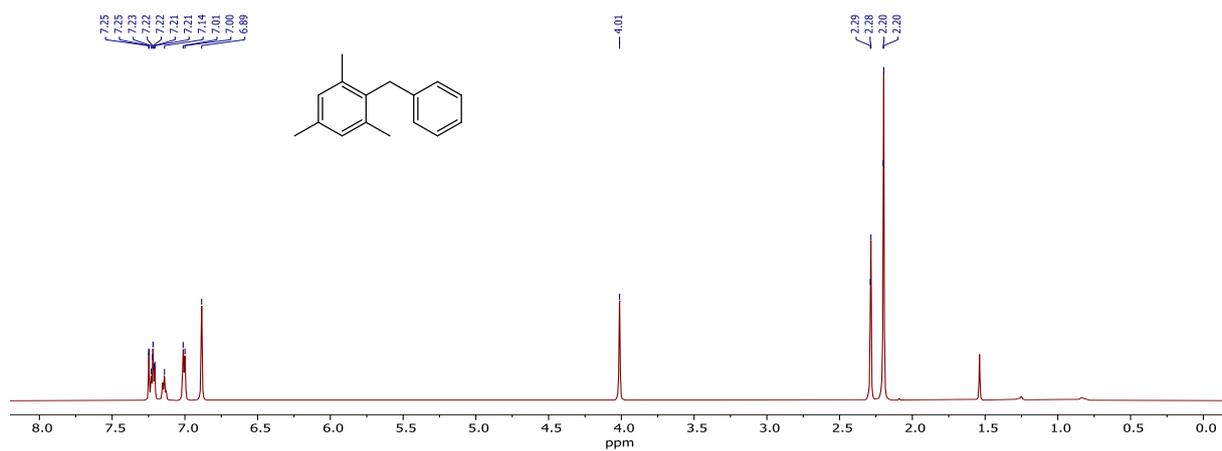


Figure S4:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 600MHz) spectrum of **4**, isolated Friedel-Crafts product from the reaction of  $\text{PhCF}_3$  in mesitylene at 140 °C, 8 h.

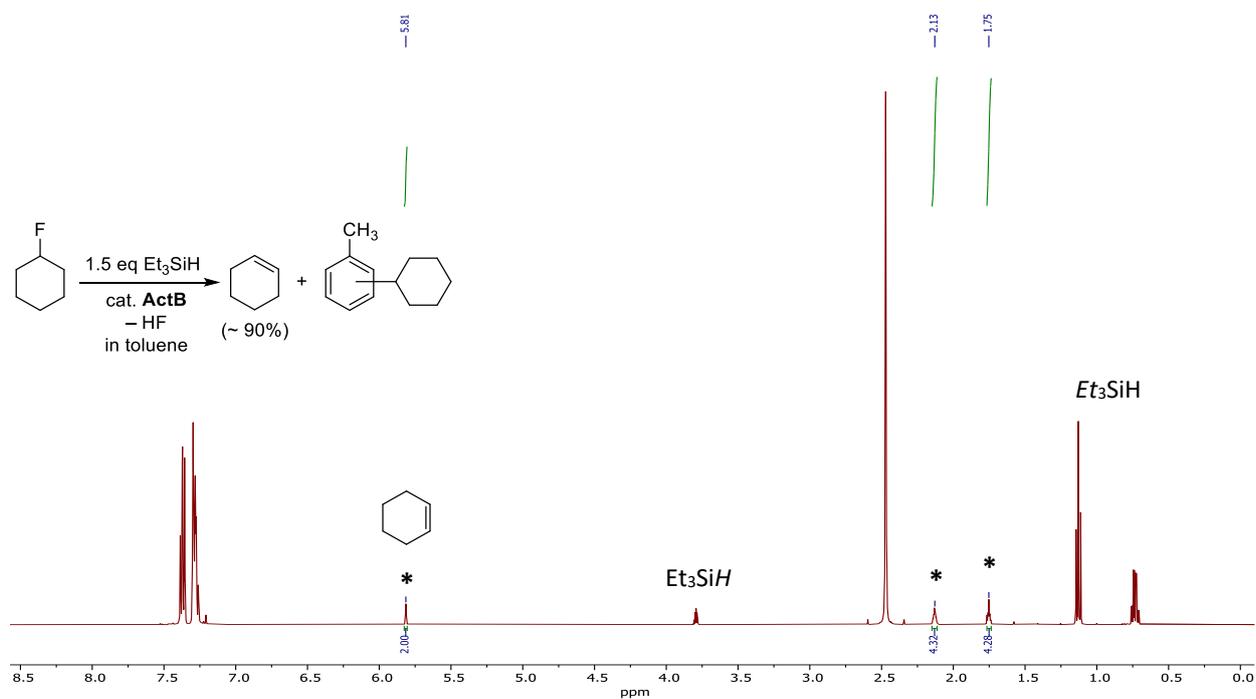


Figure S5:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500MHz) spectrum of crude reaction mixture of fluorocyclohexane in toluene at 100 °C, 1 h, signals of cyclohexene indicated by asterisk.

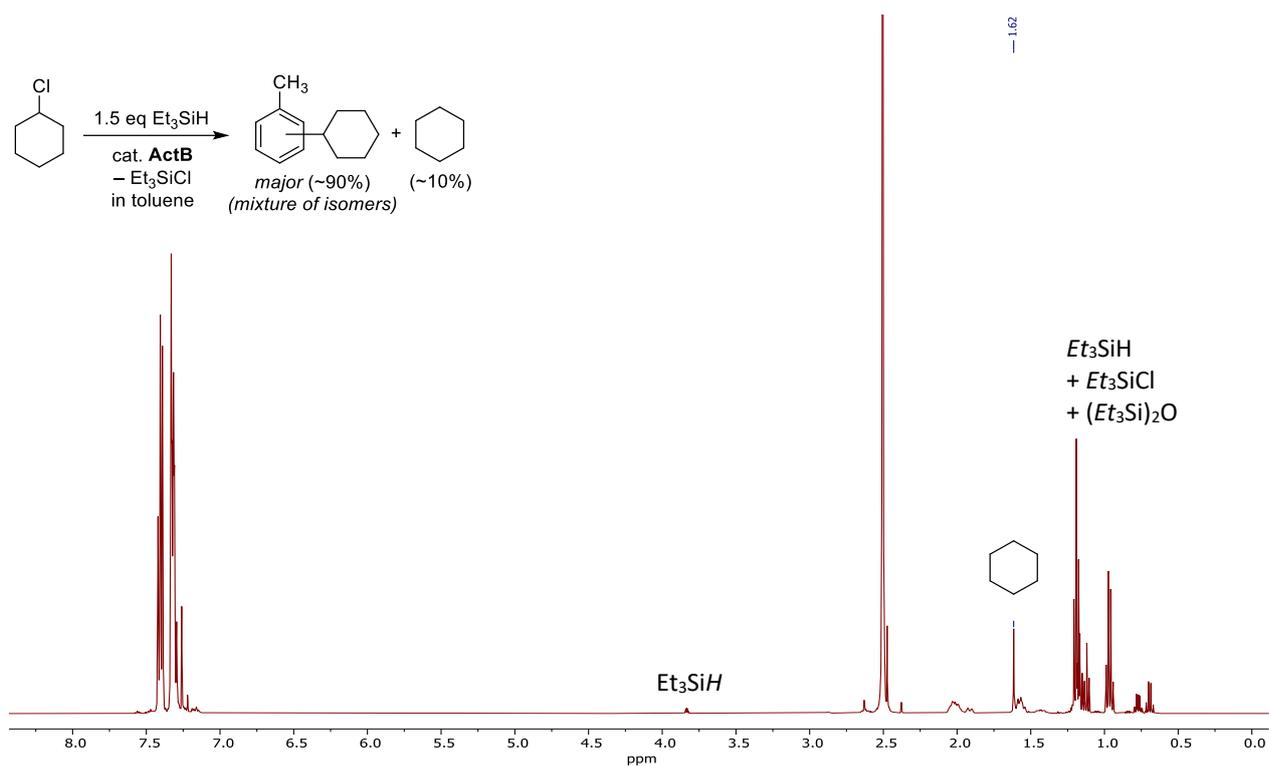


Figure S6:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500MHz) spectrum of crude reaction mixture of chlorocyclohexane in toluene at  $140^\circ\text{C}$ , 8 h.

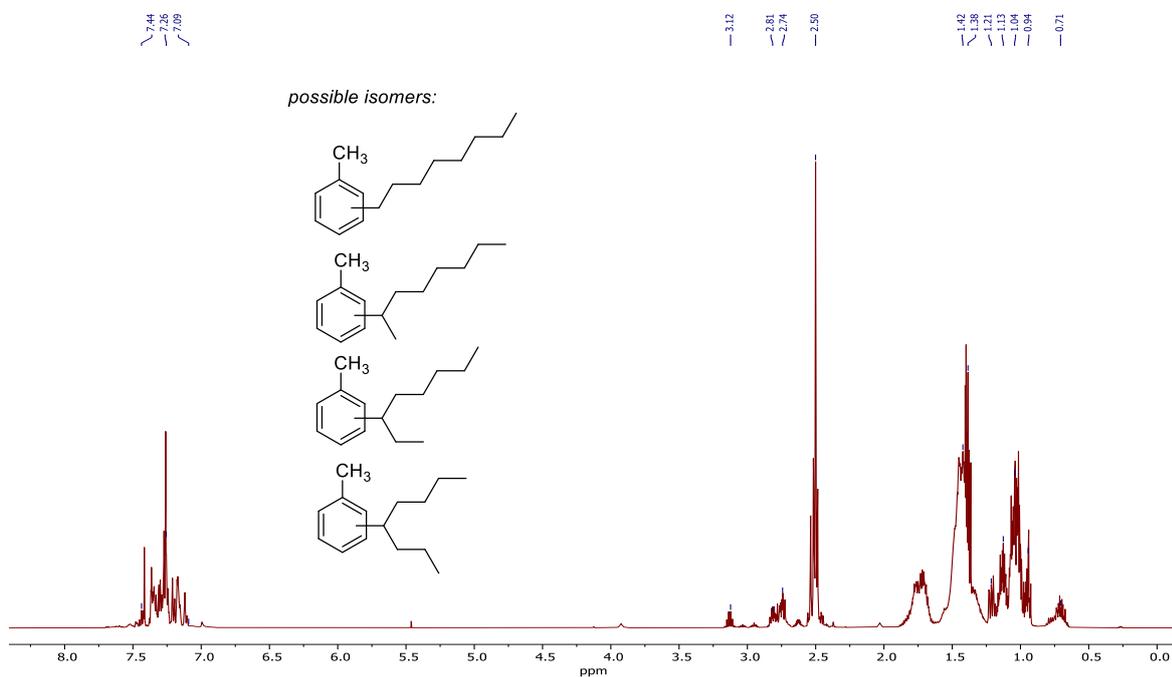


Figure S7:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500MHz) spectrum of the reaction mixture of 1-fluorooctane at  $140^\circ\text{C}$ , 1 h, volatiles removed.

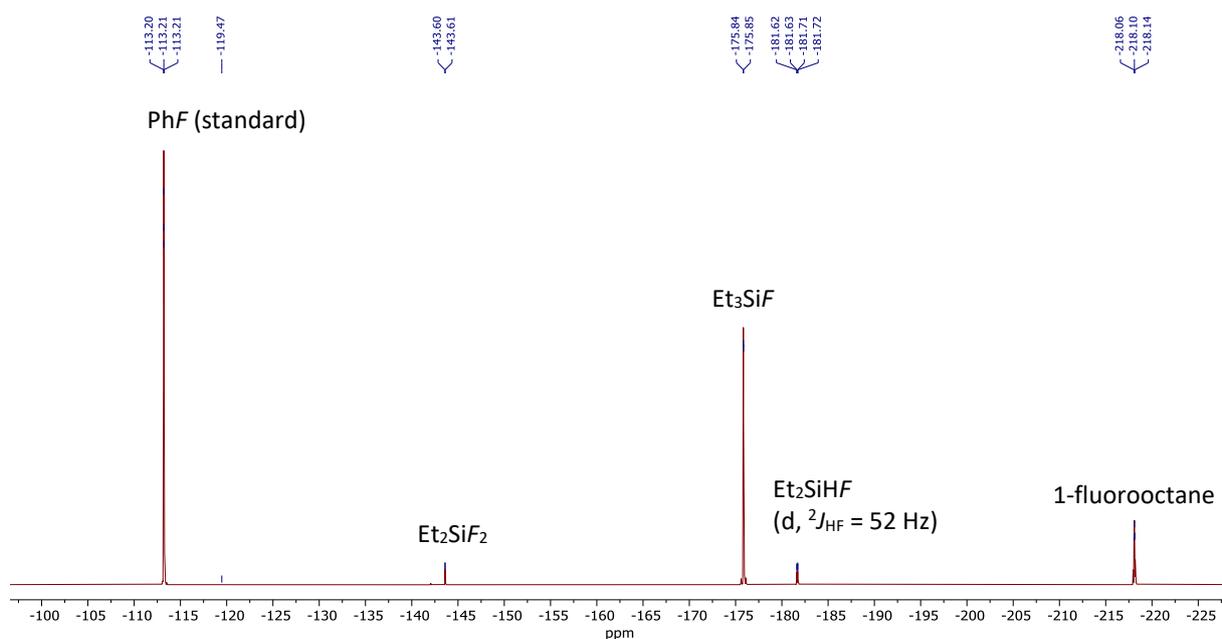


Figure S8:  $^{19}\text{F}$  NMR ( $\text{CDCl}_3$ , 500MHz) spectrum of the crude reaction mixture of 1-fluorooctane in toluene at 140 °C, 1 h.

#### Adsorption measurements (Ar at 87 K):

Catalyst as prepared and after use in the HDF of  $\text{PhCF}_3$  (standard conditions as described above).

	$S_{\text{BET}}$ ( $\text{m}^2\text{g}^{-1}$ )	Pore size (nm)	$V_{\text{pore}}$ ( $\text{cm}^3\text{g}^{-1}$ )
<b>As prepared</b>	827	2.3	0.5
<b>After use</b>	90	7.0	0.16

<b>Catalyst as prepared</b>			
<b>Adsorption</b>		<b>Desorption</b>	
P/P <sub>0</sub>	$V_{\text{ads}}$ ( $\text{cm}^3\text{g}^{-1}$ STP)	P/P <sub>0</sub>	$V_{\text{ads}}$ ( $\text{cm}^3\text{g}^{-1}$ STP)
$4.06 \cdot 10^{-5}$	27.78143	0.96353	388.47419
$8.75 \cdot 10^{-5}$	37.03771	0.93329	386.86468
$1.6191 \cdot 10^{-4}$	46.27839	0.90287	384.6987
$2.7424 \cdot 10^{-4}$	55.4777	0.87564	382.37859
$4.3025 \cdot 10^{-4}$	64.604	0.84838	379.92048
$6.4798 \cdot 10^{-4}$	73.66106	0.82137	377.3539

9.4541.10 <sup>-4</sup>	82.63931	0.79332	374.58059
0.00134	91.49793	0.76615	371.63102
0.00183	100.24932	0.7383	368.62578
0.00245	108.84204	0.71278	365.77937
0.00323	117.29087	0.68613	362.72174
0.00422	125.55561	0.66077	359.76665
0.00542	133.66568	0.63559	356.67047
0.00686	141.51926	0.60977	353.29896
0.00853	149.04481	0.58475	350.03228
0.01057	156.27524	0.56011	346.68428
0.01685	168.38112	0.53601	342.87551
0.02321	180.27003	0.51152	339.20991
0.0309	190.86928	0.48758	334.92448
0.03972	199.85163	0.46354	330.94799
0.04922	207.76778	0.44061	326.28153
0.0595	214.47372	0.41648	322.37025
0.0709	220.90394	0.39276	317.38147
0.08271	226.19381	0.36885	312.89709
0.0946	231.02037	0.34578	308.21672
0.10693	235.11312	0.31758	301.85396
0.12861	240.94872	0.2927	295.74749
0.1505	246.73443	0.26586	289.58081
0.17291	251.75433	0.24126	282.805
0.19566	256.17936	0.21809	276.26891
0.21877	260.32474	0.19596	270.10787
0.24232	263.73852	0.17463	263.04328
0.26275	268.96766	0.15349	255.79351
0.28287	272.86719	0.13307	248.0094
0.30359	275.88593	0.11381	239.60732
0.32282	279.78204	0.0951	231.18701
0.34208	282.63853		

0.36447	285.91136
0.38363	289.70415
0.40383	292.27576
0.42318	295.6101
0.44142	298.83156
0.4613	301.71646
0.48071	304.75665
0.49999	307.52762
0.5175	310.54661
0.53505	313.46379
0.55356	316.0522
0.57061	318.63987
0.58796	320.65158
0.60388	323.80078
0.62866	328.49163
0.65422	332.57172
0.68017	336.51752
0.70603	340.47748
0.73203	344.83792
0.75729	349.73236
0.77075	351.80577
0.78434	353.96694
0.81087	357.45636
0.83699	361.89125
0.86117	367.42931
0.88637	372.60615
0.91299	376.84868
0.93821	383.1774
0.96353	388.47419

<b>Catalyst after use</b>			
<b>Adsorption</b>		<b>Desorption</b>	
P/P <sub>0</sub>	V <sub>ads</sub> (cm <sup>3</sup> g <sup>-1</sup> STP)	P/P <sub>0</sub>	V <sub>ads</sub> (cm <sup>3</sup> g <sup>-1</sup> STP)
0.03323224	3.12986	0.9827908	44.36505
0.0501596	3.71731	0.93357496	41.0735
0.06596248	3.7779	0.88538319	38.54053
0.08112281	4.18387	0.83936005	36.11117
0.09606226	4.66367	0.79526458	34.17449
0.10449582	4.86543	0.75325742	32.21443
0.14216572	5.94132	0.71092899	30.17214
0.17961474	7.15626	0.67068886	28.28268
0.2173248	8.04109	0.63137241	26.52862
0.25443246	9.9626	0.58820061	24.43177
0.29023493	11.62244	0.54567138	22.63097
0.32439084	13.03091	0.50667621	21.01093
0.35977163	14.26453	0.46663688	19.13878
0.39501186	16.07984	0.42701923	17.46665
0.4293485	17.42038	0.38916861	15.95208
0.45995027	18.7695	0.35117743	14.34887
0.48824285	20.01224	0.29210236	12.36114
0.51770007	21.38607	0.24728401	10.24439
0.5491452	22.62668	0.20387126	8.59752
0.58085137	24.20107	0.16592024	6.89479
0.61044915	25.13018	0.12806962	5.71626
0.63705502	26.46307	0.09086156	4.49664
0.66516688	27.73158		
0.69438314	29.38166		
0.71916175	30.56546		
0.74679169	31.87207		
0.78759406	33.69481		

0.80926027	34.41587		
0.8528939	36.49766		
0.89825441	38.89114		
0.94259083	41.31388		
0.9827908	44.36505		

## EDX analysis

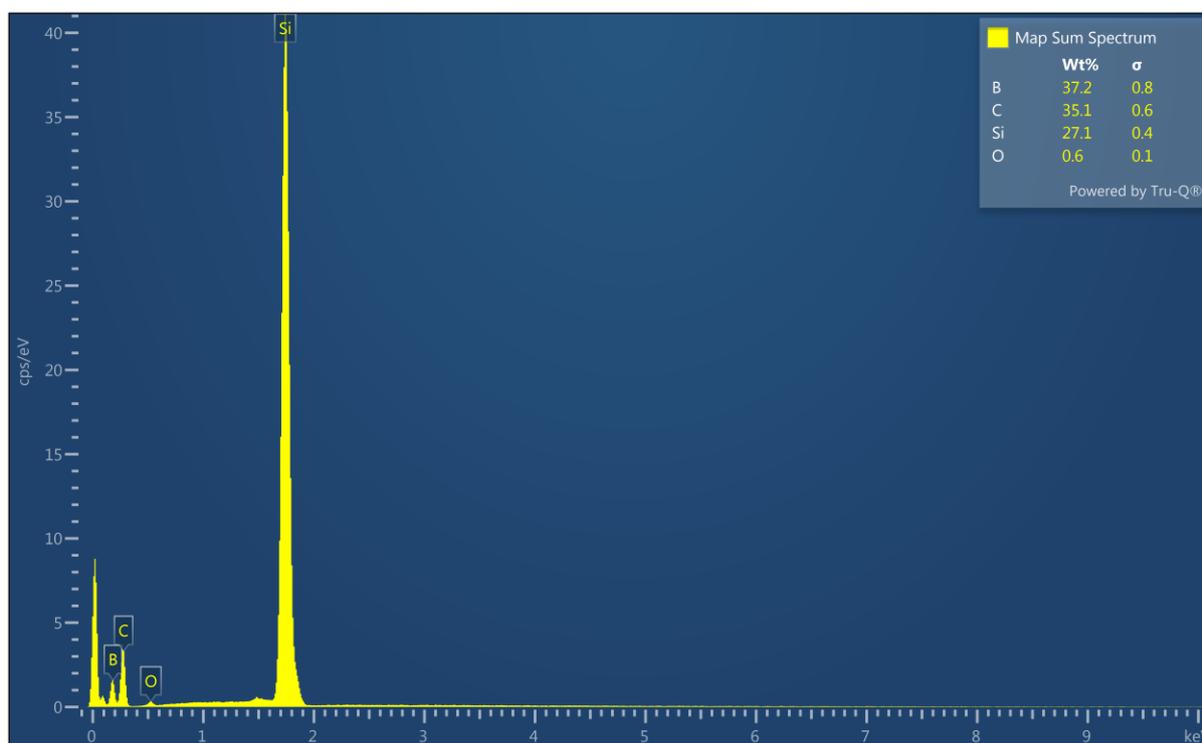


Figure S9: Energy-dispersive X-ray spectrum of the as prepared **ActB**. The silicon signal comes from the sample holder.

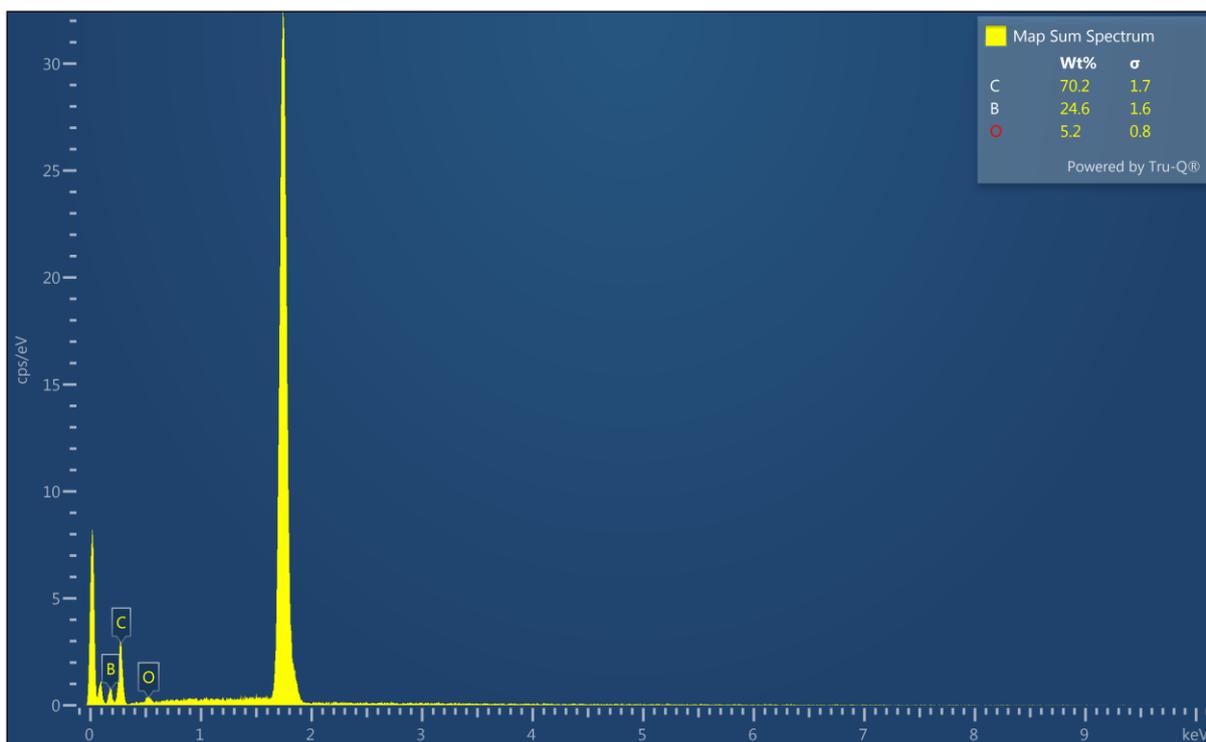


Figure S10: Energy-dispersive X-ray spectrum of **ActB** after catalytic reaction. The silicon signal comes from the sample holder.

#### References:

- 1 (a) J. D. St. Denis, C. C. G. Scully, C. F. Lee and A. K. Yudin, *Org. Lett.*, 2014, **16**, 1338; (b) R. B. Bedford, M. Huwe and M. C. Wilkinson, *Chem. Commun.*, 2009, 600.