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# 1. Materials and Methods

 $H_2$  (purity 99.9999%) was purchased from Air Liquide (China). Difluorobenzene (Aladdin) was dried by reflux under N<sub>2</sub> over sodium and freshly distilled. Bromobenzene (Sinopharm) and benzene (Sinopharm) were dried by reflux under N<sub>2</sub> over CaH<sub>2</sub>. Toluene (Sinopharm) was purified by an MBraun solvent purification system (MB-SPS-800). Cumene (TCI), ethylbenzene (Innochem) and *m*-xylene (Sigma Aldrich) were dried over 4Å molecular sieves. Naphthalene (Aladdin), anthracene (J&K), phenanthrene (Sinopharm), biphenyl (Adamas), mesitylene (Adamas, safedry with molecular sieves), *o*-xylene (Innochem, extra dry), *p*-xylene (Innochem, extra dry), *n*-octane (Sinopharm) and trimethyl(phenyl)silane (Innochem) were used as received. Borenium complexes 1 and 2 were synthesized according the literature. <sup>1,2</sup>

High pressure autoclaves were purchased from Shanghai LABE Instrument Co. Ltd (Model DCS-30N). NMR spectra were recorded on Bruker SPECT NMR (400 MHz for <sup>1</sup>H, 100 MHz for <sup>13</sup>C) spectrometer with CDCl<sub>3</sub> (from J&K) as solvent. Chemical shifts ( $\delta$ ) are reported in ppm relative to CDCl<sub>3</sub>  $\delta$  = 7.26 for <sup>1</sup>H NMR spectra and  $\delta$  = 77.16 for <sup>13</sup>C NMR spectra. GC-MS analyses were obtained on a Thermo Scientific Focus GC Gas Chromatograph system equipped with a TG-SQC-15 m × 0.25 mm × 0.25 µm capillary column (Thermo Scientific) and FID detector or a Shimadzu GC-2010 Pro Gas Chromatograph system equipped with a Rtx-5 30 m × 0.25 µm capillary column and FID detector.

#### 2. General procedure for borenium-catalyzed hydrodealkylation of alkylarenes

Inside of a N<sub>2</sub>-filled glovebox, **1** and arene were dissolved in o-C<sub>6</sub>H<sub>4</sub>F<sub>2</sub> (0.5 mL) and transferred into the well of an autoclave. After the head of the autoclave was assembled, the autoclave was taken out of the glovebox and connected to a H<sub>2</sub> gas cylinder. The connection line was flushed with H<sub>2</sub> three times. Then the autoclave was pressurized to 60 bars of H<sub>2</sub> and placed in a 80 °C oil bath for 24 hours. The autoclave was then cooled in a liquid nitrogen bath for 5 min, followed by releasing the H<sub>2</sub> pressure. Afterwards, the autoclave was moved out of the liquid nitrogen bath and warmed to room temperature in about 30 min. Octane or mesitylene was added into the well of an autoclave as internal standard. The resulting reaction mixture was then subjected to GC/MS analysis. The identities of products were confirmed by comparison of the mass spectra and retention times of the products with those of authentic compounds as well as results in literatures.

# Hydrogenation of toluene

The reaction was conducted according to the general procedure with toluene (40.2 mg, 0.436 mmol) and 1 (51.4 mg, 0.040 mmol) in o-C<sub>6</sub>H<sub>4</sub>F<sub>2</sub> (0.5 mL) under H<sub>2</sub> atmosphere (60 bar) at 80 °C for 24 h. GC/MS analysis of the reaction mixture showed formation of methylcyclohexane (98 m/z) in 88% yield with octane (41.3 mg, 0.362 mmol) as internal standard.



Fig S1. GC data for hydrogenation of toluene

### Hydrogenation of o-xylene

The reaction was conducted according to the general procedure with *o*-xylene (46.7 mg, 0.440 mmol) and **1** (51.2 mg, 0.040 mmol) in o-C<sub>6</sub>H<sub>4</sub>F<sub>2</sub> (0.5 mL) under H<sub>2</sub> atmosphere (60 bar) at 80 °C for 24 h. GC/MS analysis of the reaction mixture showed formation of 1,2-dimethylcyclohexane (112 m/z) in 86% yield with mesitylene (51.3 mg, 0.427 mmol) as internal standard. The ratio of cis and trans isomer of 1,2-dimethylcyclohexane is 90:10 according to GC/MS analysis.<sup>3</sup>



Fig S2. GC data for hydrogenation of o-xylene

### Hydrogenation of *m*-xylene

The reaction was conducted according to the general procedure with *m*-xylene (42.6 mg, 0.401 mmol) and **1** (51.0 mg, 0.040 mmol) in o-C<sub>6</sub>H<sub>4</sub>F<sub>2</sub> (0.5 mL) under H<sub>2</sub> atmosphere (60 bar) at 80 °C for 24 h. GC/MS analysis of the reaction mixture showed formation of 1,3-dimethylcyclohexane (112 m/z) in 99% yield with mesitylene (42.4 mg, 0.353 mmol) as internal standard. The ratio of cis and trans isomer of 1,3-dimethylcyclohexane is 60:40 according to GC/MS analysis.<sup>3</sup>



Fig S3. GC data for hydrogenation of *m*-xylene

### Hydrogenation of *p*-xylene

The reaction was conducted according to the general procedure with *p*-xylene (41.9 mg, 0.395 mmol) and **1** (51.1 mg, 0.040 mmol) in o-C<sub>6</sub>H<sub>4</sub>F<sub>2</sub> (0.5 mL) under H<sub>2</sub> atmosphere (60 bar) at 80 °C for 24 h. GC/MS analysis of the reaction mixture showed formation of 1,4-dimethylcyclohexane (112 m/z) in 99% yield with mesitylene (43.7 mg, 0.364 mmol) as internal standard. The ratio of cis and trans isomer of 1,4-dimethylcyclohexane is 47:53 according to GC/MS analysis.<sup>3</sup>



Fig S4. GC data for hydrogenation of p-xylene

### Hydrogenation of ethylbenzene

The reaction was conducted according to the general procedure with ethylbenzene (41.4 mg, 0.390 mmol) and **1** (50.9 mg, 0.040 mmol) in o-C<sub>6</sub>H<sub>4</sub>F<sub>2</sub> (0.5 mL) under H<sub>2</sub> atmosphere (60 bar) at 80 °C for 24 h. GC/MS analysis of the reaction mixture showed formation of ethylcyclohexane (112 m/z) in 88% yield with octane (40.5 mg, 0.355 mmol) as internal standard.



Fig S5. GC data for hydrogenation of ethylbenzene

### Hydrogenation of cumene

The reaction was conducted according to the general procedure with cumene (48.5 mg, 0.403 mmol) and 1 (51.3 mg, 0.040 mmol) in o-C<sub>6</sub>H<sub>4</sub>F<sub>2</sub> (0.5 mL) under H<sub>2</sub> atmosphere (60 bar) at 80 °C for 24 h. GC/MS analysis of the reaction mixture showed formation of isopropylcyclohexane (126 m/z) in 28% yield with octane (42.8 mg, 0.375 mmol) as internal standard.



Fig S6. GC data for hydrogenation of cumene

### Hydrogenation of mesitylene

The reaction was conducted according to the general procedure with mesitylene (49.8 mg, 0.414 mmol) and 1 (51.6 mg, 0.040 mmol) in o-C<sub>6</sub>H<sub>4</sub>F<sub>2</sub> (0.5 mL) under H<sub>2</sub> atmosphere (60 bar) at 80 °C for 24 h. GC/MS analysis of the reaction mixture showed formation of 1,3,5-trimethylcyclohexane (126 m/z) in 69% yield with octane (54.3 mg, 0.475 mmol) as internal standard. The ratio of  $\alpha\alpha\alpha$  and  $\alpha\alpha\beta$  isomer of 1,3,5-trimethylcyclohexane is 87/13 according to GC/MS analysis.<sup>3</sup>



Fig S7. GC data for hydrogenation of mesitylene

### Hydrogenation of biphenyl

The reaction was conducted according to the general procedure with biphenyl (61.6 mg, 0.399 mmol) and **1** (51.1 mg, 0.040 mmol) in o-C<sub>6</sub>H<sub>4</sub>F<sub>2</sub> (0.5 mL) under H<sub>2</sub> atmosphere (60 bar) at 80 °C for 24 h. GC/MS analysis of the reaction mixture showed formation of bicyclohexyl (166 m/z) in 33% yield with octane (48.1 mg, 0.421 mmol) as internal standard.



Fig S8. GC data for hydrogenation of biphenyl

### Complete hydrogenation of naphthalene

The reaction was conducted according to the general procedure with naphthalene (51.7 mg, 0.403 mmol) and **1** (51.3 mg, 0.040 mmol) in o-C<sub>6</sub>H<sub>4</sub>F<sub>2</sub> (0.5 mL) under H<sub>2</sub> atmosphere (60 bar) at 25 °C for 24 h. GC/MS analysis of the reaction mixture showed formation of decalin (138 m/z) in 95% yield with octane (43.5 mg, 0.381 mmol) as internal standard. The ratio of *cis* and *trans* isomer of decalin is 93:7 according to GC/MS analysis.<sup>3</sup>



Fig S9. GC data for hydrogenation of naphthalene

### Partial hydrogenation of naphthalene

The reaction was conducted according to the general procedure with naphthalene (51.8 mg, 0.404 mmol) and **1** (10.3 mg, 0.008 mmol) in o-C<sub>6</sub>H<sub>4</sub>F<sub>2</sub> (0.5 mL) under H<sub>2</sub> atmosphere (5 bar) at 25 °C for 6 h. 200 mg of silica gel was added to the reaction mixture and the volatile was removed under vacuum. The resulting mixture was transferred to a column prefilled with 900 mg of silica gel. Petroleum ether was used to rinse the product out of the column. After removal of solvent under vacuum, tetralin was obtained as colorless liquid (43.0 mg, 0.325 mmol) in 81% yield.

<sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>, 298 K):  $\delta$  [ppm] = 7.05-7.26 (m, 4H), 2.78 (t, <sup>2</sup>*J*<sub>H-H</sub> = 6.4 Hz, 4H), 1.79-1.83 (m 4H).

<sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>, 298 K): δ [ppm] = 23.36, 29.52, 125.52, 129.25, 137.24.









#### **Complete hydrogenation of anthracene**

The reaction was conducted according to the general procedure with anthracene (175.3 mg, 0.984 mmol) and **1** (122.3 mg, 0.096 mmol) in o-C<sub>6</sub>H<sub>4</sub>F<sub>2</sub> (1.3 mL) under H<sub>2</sub> atmosphere (60 bar) at 25 °C for 24 h. GC/MS analysis of the reaction mixture showed formation of two isomers of perhydroanthracene in a 1:5 ratio. 200 mg of silica gel was added to the reaction mixture and the volatile was removed under vacuum. The resulting mixture was transferred to a column prefilled with 900 mg of silica gel. Petroleum ether was used to rinse the product out of the column. After removal of solvent under vacuum, perhydroanthracene was obtained as colorless liquid (180 mg, 0.936 mmol) in 95% yield. Based on the NMR analysis, the two isomers are *trans-syn-trans*-perhydroanthracene and *cis-trans*-perhydroanthracene.<sup>4</sup>



Fig S12. GC data for complete hydrogenation of anthracene



Fig S13. <sup>1</sup>H NMR spectrum of mixture of two perhydroanthracene isomers in CDCl<sub>3</sub>



Fig S14.  ${}^{13}C{}^{1}H$  NMR spectrum of mixture of two perhydroanthracene isomers in CDCl<sub>3</sub>



Fig S15. <sup>13</sup>C{<sup>1</sup>H} DEPT ( $\theta$  = 135°) NMR spectrum of mixture of two perhydroanthracene isomers in CDCl<sub>3</sub>

# Partial hydrogenation of anthracene

The reaction was conducted according to the general procedure with anthracene (71.2 mg, 0.400 mmol) and **1** (10.2 mg, 0.008 mmol) in o-C<sub>6</sub>H<sub>4</sub>F<sub>2</sub> (1.0 mL) under H<sub>2</sub> atmosphere (5 bar) at 25 °C for 6 h. 200 mg of silica gel was added to the reaction mixture and the volatile was removed under vacuum. The resulting mixture was transferred to a column prefilled with 900 mg of silica gel. Petroleum ether was used to rinse the product out of the column. After removal of solvent under vacuum, 9,10-dihydroanthracene was obtained as white solid (65.1 mg, 0.361 mmol) in 90% yield.

<sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>, 298 K):  $\delta$  [ppm] = 7.21-7.33 (m, 8H), 3.97 (s, 4H).

<sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>, 298 K): δ [ppm] = 36.32, 126.23, 127.53, 136.83.



Fig S16. <sup>1</sup>H NMR spectrum of 9,10-dihydroanthracene in CDCl<sub>3</sub>



Fig S17.  $^{13}C\{^{1}H\}$  NMR spectrum of 9,10-dihydroanthracene in CDCl3

#### Hydrogenation of phenanthrene

The reaction was conducted according to the general procedure with phenanthrene (71.3 mg, 0.400 mmol) and **1** (51.5 mg, 0.040 mmol) in o-C<sub>6</sub>H<sub>4</sub>F<sub>2</sub> (0.5 mL) under H<sub>2</sub> atmosphere (60 bar) at 80 °C for 24 h. 200 mg of silica gel was added to the reaction mixture and the volatile was removed under vacuum. The resulting mixture was transferred to a column prefilled with 900 mg of silica gel. Petroleum ether was used to rinse the product out of the column. After removal of solvent under vacuum, 9,10-dihydrophenanthrene was obtained as white solid (65.3 mg, 0.362 mmol) in 91% yield.

<sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>, 298 K): δ [ppm] = 7.76 (d,  ${}^{2}J_{H-H}$  = 7.8 Hz, 2H), 7.29-7.33 (m, 2H), 7.21-7.24 (m, 4H), 2.89 (s, 4H).

<sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>, 298 K): δ [ppm] = 29.21, 123.85, 127.09, 127.52, 128.27, 134.64, 137.54.



Fig S18. <sup>1</sup>H NMR spectrum of 9,10- dihydrophenanthrene in CDCl<sub>3</sub>



Fig S19.  ${}^{13}C{}^{1}H$  NMR spectrum of 9,10-dihydrophenanthrene in CDCl<sub>3</sub>

### Hydrogenation of benzene

Inside of a N<sub>2</sub>-filled glovebox, **1** (207 mg, 0.162 mmol) and benzene (62.4 mg, 0.799 mmol) were dissolved in o-C<sub>6</sub>H<sub>4</sub>F<sub>2</sub> (0.5 mL) and transferred into the well of an autoclave. After the head of the autoclave was assembled, the autoclave was taken out of the glovebox and connected to a H<sub>2</sub> gas cylinder. The connection line was flushed with H<sub>2</sub> three times. Then the autoclave was pressurized to 60 bars of H<sub>2</sub> in a 80 °C oil bath for 72 hours. The autoclave was then cooled in a liquid nitrogen bath for 5 min, followed by releasing the H<sub>2</sub> pressure. Afterwards, the autoclave was moved out of the liquid nitrogen bath and warmed to room temperature in about 30 min. Trimethyl(phenyl)silane (120.2 mg, 0.800 mmol) was added into the well of an autoclave as internal standard. The resulting reaction mixture was then subjected to quantitative  ${}^{13}C{}^{1}H$  NMR analysis. Based on the integration ratio of cyclohexane and trimethyl(phenyl)silane, cyclohexane was formed in 53% yield.



Fig S20. Quantitative  ${}^{13}C{}^{1}H$  NMR spectrum of reaction mixture of benzene hydrogenation

### 3. Mechanism Study

#### 3.1 Kinetic study of toluene hydrogenation

### 3.1.1 Determination of the reaction order of H<sub>2</sub>

Inside of a N<sub>2</sub>-filled glovebox, **1** (25.5 mg, 0.020 mmol) and toluene (36.8 mg, 0.400 mmol) were dissolved in 1.5 mL o-C<sub>6</sub>H<sub>4</sub>F<sub>2</sub> and transferred into the well of an autoclave. After the head of the autoclave was assembled, the autoclave was taken out of the glovebox and connected to a H<sub>2</sub> gas cylinder. The connection line was flushed with H<sub>2</sub> three times. Then the autoclave was pressurized to designated pressure of H<sub>2</sub>. After that, the autoclave was heated to the 80 °C in an oil bath and stirred for 1 h. The autoclave was then cooled in a liquid nitrogen bath for 5 min, followed by releasing the H<sub>2</sub> pressure. Afterwards, the autoclave was moved out of the liquid nitrogen bath and warmed to room temperature in about 30 min. Octane was added into the well of an autoclave as internal standard. The resulting reaction mixture was then subjected to GC/MS analysis. The initial rate of the reaction was deduced from the amount of methylcyclohexane present in the solution. This procedure was repeated with various pressures of H<sub>2</sub>.

**Table S1.** initial rates under various H<sub>2</sub> pressures

_	p(H <sub>2</sub> )/Pa	n(methylcyclohexane)/mmol	initial rate/ $M \cdot s^{-1}$
-	3.0×10 <sup>6</sup>	0.0496	9.18×10 <sup>-6</sup>
	$4.0 \times 10^{6}$	0.0567	1.05×10 <sup>-5</sup>
	5.0×10 <sup>6</sup>	0.0714	1.32×10 <sup>-5</sup>
	$5.9 \times 10^{6}$	0.0784	1.45×10 <sup>-5</sup>



Figure S21. Plot of ln(initial rate) against ln[p(H<sub>2</sub>)] at 80 °C

### 3.1.2 Determination of the reaction order of toluene

Inside of a N<sub>2</sub>-filled glovebox, **1** (25.5 mg, 0.020 mmol) and toluene were dissolved in 1.5 mL o-C<sub>6</sub>H<sub>4</sub>F<sub>2</sub> and transferred into the well of an autoclave. After the head of the autoclave was assembled, the autoclave was taken out of the glovebox and connected to a H<sub>2</sub> gas cylinder. The connection line was flushed with H<sub>2</sub> three times. Then the autoclave was pressurized to 60 bar of H<sub>2</sub>. After that, the autoclave was heated to 80 °C in an oil bath and stirred for 1 h. The autoclave was then cooled in a liquid nitrogen bath for 5 min, followed by releasing the H<sub>2</sub> pressure. Afterwards, the autoclave was moved out of the liquid nitrogen bath and warmed to room temperature in about 30 min. Octane was added into the well of an autoclave as internal standard. The resulting reaction mixture was then subjected to GC/MS analysis. The initial rate of the reaction was deduced from the amount of methylcyclohexane present in the solution. This procedure was repeated with various amounts of toluene.

Table S2. initial rates with various concentrations of toluene								
m(toluene)/mg	n(toluene)/mmol	[toluene]/M	n(methylcyclohexane)/mmol	initial rate/ $M \cdot s^{-1}$				
18.3	0.199	0.133	0.0457	8.46×10 <sup>-6</sup>				
36.9	0.400	0.267	0.0784	1.45×10 <sup>-5</sup>				
55.3	0.600	0.400	0.0952	1.76×10 <sup>-5</sup>				
73.9	0.802	0.535	0.1300	2.41×10 <sup>-5</sup>				
92.1	1.000	0.677	0.1399	2.59×10 <sup>-5</sup>				

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Figure S22. Plot of ln(initial rate) against ln[toluene] at 80 °C

#### 3.1.3 Determination of the reaction order of 1

Inside of a N<sub>2</sub>-filled glovebox, **1** and toluene (36.8 mg, 0.400 mmol) were dissolved in 6 mL o-C<sub>6</sub>H<sub>4</sub>F<sub>2</sub> and transferred into the well of an autoclave. After the head of the autoclave was assembled, the autoclave was taken out of the glovebox and connected to a H<sub>2</sub> gas cylinder. The connection line was flushed with H<sub>2</sub> three times. Then the autoclave was pressurized to 60 bar of H<sub>2</sub>. After that, the autoclave was heated to 80 °C in an oil bath and stirred for 30 min. The autoclave was then cooled in a liquid nitrogen bath for 5 min, followed by releasing the H<sub>2</sub> pressure. Afterwards, the autoclave was moved out of the liquid nitrogen bath and warmed to room temperature in about 30 min. Octane was added into the well of an autoclave as internal standard. The resulting reaction mixture was then subjected to GC/MS analysis. The initial rate of the reaction was deduced from the amount of methylcyclohexane present in the solution. This procedure was repeated with various amounts of **1**.

Table S3. initial rates with various concentrations of I							
m( <b>1</b> )/mg	n(1)/mmol	[ <b>1</b> ]/M	n(methylcyclohexane)/mmol	initial rate/ $M \cdot s^{-1}$			
25.5	0.020	3.33×10 <sup>-3</sup>	0.0318	2.95×10 <sup>-6</sup>			
38.3	0.040	5.00×10 <sup>-3</sup>	0.0507	4.69×10 <sup>-6</sup>			
51.0	0.060	6.67×10 <sup>-3</sup>	0.0664	6.15×10 <sup>-6</sup>			
63.8	0.080	8.33×10 <sup>-3</sup>	0.0816	7.55×10 <sup>-6</sup>			

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Figure S23. Plot of ln(initial rate) against ln[1] at 80 °C

### 3.2 Benzene hydrogenation under D<sub>2</sub> at room temperature

The reaction was conducted according to the general procedure with benzene (31.0 mg, 0.397 mmol) and 1 (51.3 mg, 0.040 mmol) in o-C<sub>6</sub>H<sub>4</sub>F<sub>2</sub> (0.5 mL) under D<sub>2</sub> atmosphere (60 bar) at room temperature for 24 h. GC/MS analysis of the reaction mixture showed deuteration of benzene.



Figure S24. a) MS data for benzene in reaction mixture after the reaction; b) MS data for  $C_6H_6$ ; c) MS data for  $C_6D_6$ 

# 4. Reference

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