Supporting Information

Z-selective Alkyne Semi-Hydrogenation Catalysed by Piano-Stool N-Heterocyclic Carbene Iron Complexes

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Experimental.

**General comments.** The synthesis and analytical details of complexes 1\textsuperscript{S1}, 2\textsuperscript{S1} and 3\textsuperscript{S2} have been described previously. All manipulations were carried out under an inert nitrogen atmosphere using standard Schlenk techniques. Chloroform, 1,2-dichlorobenzene and 1,2-dichloroethane were dried over 4 Å molecular sieves and bubbled with argon before use. THF was dried by passage through solvent purification columns and stored over molecular sieves. All other reagents were commercially available and used as received. \textsuperscript{1}H-NMR spectra were measured at 25 °C on Bruker spectrometers operating at 300 or 400 MHz. GC analysis was performed using an Agilent 7820A GC with a HP-5 capillary column (30 m x 320 μm x ID 0.25 μm) between 45 and 250 °C with a heating rate of 30 °C and a hold time of 1 min at 250 °C. Anisole (GC) and hexamethylbenzene (NMR) were used as internal standards for catalysis.

**General procedure for semi-hydrogenation of alkynes.** To a 10 mL Schlenk tube was added the alkyne (0.2 mmol), silane (0.4 mmol), hexamethylbenzene (3.2 mg; 0.02 mmol; internal standard for NMR analysis) or anisole (22 μL; 0.2 mmol; internal standard for GC analysis) and solvent (1.25 mL). The mixture was equilibrated to 60 °C for 5 mins and the catalyst added as a solid (0.01 mmol; 5 mol%). Aliquots were taken at selected times and diluted with CDCl\textsubscript{3} and CHCl\textsubscript{3} for analysis by \textsuperscript{1}H NMR spectroscopy and GC respectively.

Time-dependent catalytic conversions and yields.

*Figure S1.* Time-conversion profiles using various silanes (left) and solvents (right) for the semi-hydrogenation of phenylacetylene using 1b as catalyst precursor.
**Figure S2.** Semi-reduction time-conversion profiles for 4-substituted alkynes using 1b as catalyst precursor.

**Table S1.** Comparison of catalytic conversions and yields after short (8 h) and prolonged (24 h) reaction times.

<table>
<thead>
<tr>
<th>R</th>
<th>Conversion(yield)/%a</th>
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<tbody>
<tr>
<td></td>
<td>8 h</td>
</tr>
<tr>
<td>Br</td>
<td>91(83)</td>
</tr>
<tr>
<td>CF₃</td>
<td>98(72)</td>
</tr>
<tr>
<td>CH₃</td>
<td>94(68)</td>
</tr>
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a Conversion and yields determined spectroscopically by ¹H NMR analysis.

**References.**