Supporting Information

Ru-catalyzed repetitive batch borylative coupling of olefins in ionic liquids or ionic liquids/scCO₂ systems

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1. General information:

1.1. NMR analyses

\(^1\)H and \(^{13}\)C NMR, spectra were recorded at 25 °C on Bruker UltraShield 300 MHz. Chemical shifts were reported in ppm with the reference to the residue portion solvent peak. Chloroform-d\(_1\) or acetone-d\(_6\) were used as solvents and for internal deuterium lock. The multiplicities were reported as follows: singlet (s), doublet (d), a doublet of triplets (dt), multiplet (m), triplet (t) and broad resonances (br).

1.2. GC-MS analysis

The mass spectra of the products were obtained by GC-MS analysis on a Bruker Scion 436-GC with a 30m Varian DB-5 0.25mm capillary column and a Scion SQ-MS mass spectrometry detector. Two temperature programs were used a) 60 °C (3 min), 10°C/min, 250 °C (30 min), b) 100 °C (3 min), 10°C/min, 280 °C (44.5 min).

1.3. ICP-MS analysis

Caution: All manipulation should be carried out under the fume hood. Serious risk of chemical burns. 50 mg of product from the extraction was placed into 100 mL Teflon beaker equipped with a magnetic stirring bar and 30 mL of concentrated HNO\(_3\) was added. The mixture was heated up to complete evaporation of the solvent. In the same manner, the mixture was treated with aqua regia and 20% solution of HF. Subsequently, 20 mL of concentrated sulphuric acid was added and the solution was heated up to partial evaporation of H\(_2\)SO\(_4\). Then, the mixture was diluted with deionized water, filtered (if necessary) and analyzed by inductively coupled plasma-mass spectroscopy (ICP-MS). The analysis was performed on a quadrupole mass spectrometer with excitation in an inductively coupled plasma (Perkin-Elmer Nexion 300D), which was optimized prior to measurements using the appropriate SETUP SOLUTION from Perkin-Elmer. Samples were analyzed in liquid form using an injection system consisting of an concentric nebulizer and cyclonic spray. Data were processed by NexION\textsuperscript{TM} v. 1.0 software.

2. Catalyst leaching in selected catalytic runs

Table S1. Ruthenium content in selected extracts.

<table>
<thead>
<tr>
<th>Olefin</th>
<th>Ru content in extract [ppm]</th>
<th>cat@[BMIm][TfO]</th>
<th>cat@[EMPyr][Tf2N]</th>
<th>cat@[BMIm][TfO]/scCO(_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>(2a)</td>
<td>(2b)</td>
<td>(2a)</td>
<td>(2b)</td>
</tr>
<tr>
<td>Run 1</td>
<td>7.1\textsuperscript{a}, 0.77\textsuperscript{b}</td>
<td>6.8, 0.64\textsuperscript{b}</td>
<td>7.0\textsuperscript{a}, 0.69\textsuperscript{b}</td>
<td>6.9, 0.75\textsuperscript{b}</td>
</tr>
<tr>
<td>2</td>
<td>6.8\textsuperscript{a}</td>
<td>-</td>
<td>6.5\textsuperscript{a}</td>
<td>-</td>
</tr>
<tr>
<td>5</td>
<td>6.4\textsuperscript{a}</td>
<td>-</td>
<td>6.7\textsuperscript{a}</td>
<td>-</td>
</tr>
<tr>
<td>8</td>
<td>4.6\textsuperscript{a}, 0.68\textsuperscript{b}</td>
<td>5.1</td>
<td>4.7\textsuperscript{a}, 0.71\textsuperscript{b}</td>
<td>5.1\textsuperscript{a}</td>
</tr>
</tbody>
</table>

\textsuperscript{a}) n-Heptane extraction, \textsuperscript{b}) ScCO\(_2\) extraction
3. Spectra of isolated products

Figure S1. $^1$H NMR spectrum of 3a

Figure S2. $^{13}$C NMR spectrum of 3a
Figure S3. \(^1\)H NMR spectrum of 3b

Figure S4. \(^{13}\)C NMR spectrum of 3b
Figure S5. $^1$H NMR spectrum of 3c

Figure S6. $^{13}$C NMR spectrum of 3c
Figure S7. $^1$H NMR spectrum of 3d

Figure S8. $^{13}$C NMR spectrum of 3d
Figure S9. $^1$H NMR spectrum of 3e

Figure S10. $^{13}$C NMR spectrum of 3e
Figure S11. $^1$H NMR spectrum of 3f

Figure S12. $^{13}$C NMR spectrum of 3f
Figure S13. $^1$H NMR spectrum of 3g

Figure S14. $^{13}$C NMR spectrum of 3g
Figure S15. $^1$H NMR spectrum of 3h

Figure S16. $^{13}$C NMR spectrum of 3h
Figure S17. $^1$H NMR spectrum of 3i

Figure S18. $^{13}$C NMR spectrum of 3i
Figure S19. $^1$H NMR spectrum of 3j

Figure S20. $^{13}$C NMR spectrum of 3j
Figure S21. $^1$H NMR spectrum of 4

Figure S22. $^{13}$C NMR spectrum of 4
Figure S23. $^1$H NMR spectrum of 5

Figure S24. $^{13}$C NMR spectrum of 5