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1. General procedures

Reagents were supplied by Aldrich and were used without further purification (octanal was distilled before being used).³¹H NMR experiments were obtained using a Varian INOVA 500 (¹H, 500 MHz) spectrometer. The chemical shifts are given in delta (δ) values (ppm). Samples were analyzed by GC VARIAN 3900.

2. Characterization.

All the products here synthesized were previously reported and purified by medium pressure column chromatography (Combi-Flash Teledyne ISCO) with n-Hexane-Ethylacetate. According to bibliography data the compounds were characterized as following:

Compound (13) and compounds entries 1, 3 and 5, Table 2, were analyzed by the following GC method (VARIAN 3900). Analysis time: 60 min., Column Cyclodex B Pressure: 15.00 Psi Oven Temperature: To= 60°C, Tf=130°C. Rate: 1.2ºC/min Detector: T: 300ºC, Injector: T: 230ºC, Helium flow: 25mL/min, Nitrogen flow: 30mL/min, Air flow: 300mL/min.

Compound entry 2, Table 2 was analyzed by GC VARIAN 3900. Analysis time: 30 min., Column CyclodexB Pressure: 15.00 Psi Oven Temperature: To= 60ºC, Tf=130ºC. Rate: 10ºC/min Detector: T: 300ºC, Injector: T: 230ºC, Helium flow: 25mL/min, Nitrogen flow: 30mL/min, Air flow: 300mL/min.

Compounds entry 4, 6 and 7, Table 2 were analyzed by using a Varian INOVA 500 (¹H, 500 MHz) spectrometer.

2-phenyl-2-((trimethylsilyl)oxy)propanenitrile (13)

\[ \begin{align*}
\text{Si} & \quad \text{O} \\
\text{N} & \quad \text{CH}_3 \\
\text{Ph} & \quad \text{Ph}
\end{align*} \]

³¹H-RMN (CDCl₃, 500 MHz): δ 0.181 (s, 9H, 3xCH₃), 1.868 (s, 3H, CH₃), 7.515-7.403 (m, 5H, Ph).
1-((trimethylsilyl)oxy)cyclohexanecarbonitrile (Table 2 entry 1).

\[ \text{H-RMN (CDCl}_3, \text{ 500 MHz): } \delta \ 0.230 \ (s, \ 9H, \ 3xCH}_3), \ 1.519-2.027 \ (m, \ 10H, \ \text{cyclohexyl}). \]

2-phenyl-2-((trimethylsilyl)oxy)acetonitrile (Table 2 entry 2).

\[ \text{H-RMN (CDCl}_3, \text{ 500 MHz): } \delta \ 0.181 \ (s, \ 9H, \ 3xCH}_3), \ 5.503 \ (s, \ 1H, \ CH), \ 7.400-7.499 \ (m, \ 5H, \ Ph). \]

2-(furan-2-yl)-2-((trimethylsilyl)oxy)acetonitrile (Table 2 entry 3).

\[ \text{H-RMN (CDCl}_3, \text{ 500 MHz): } \delta \ 0.226 \ (s, \ 9H, \ 3xCH}_3), \ 5.559 \ (s, \ 1H, \ CH), \ 6.427-6.539 \ (m, \ 1H, \ 2xfuran), \ 7.445-7.454 \ (m, \ 1H, \ furan). \]

2-(4-fluorophenyl)-2-((trimethylsilyl)oxy)acetonitrile (Table 2 entry 4).

\[ \text{H-RMN (CDCl}_3, \text{ 500 MHz): } \delta \ 0.246 \ (s, \ 9H, \ 3xCH}_3), \ 5.478 \ (s, \ 1H, \ CH), \ 7.056-7.126 \ (m, \ 2H, \ Ph), \ 7.433-7.480 \ (m, \ 2H, \ Ph). \]

(E)-4-phenyl-2-((trimethylsilyl)oxy)but-3-enenitrile (Table 2 entry 5).

\[ \text{H-RMN (CDCl}_3, \text{ 500 MHz): } \delta \ 0.275 \ (s, \ 9H, \ 3xCH}_3), \ 5.117-5.132 \ (m, \ 1H, \ CH), \ 6.172-6.216 \ (m, \ 1H, \ CH), \ 6.800-6.834 \ (m, \ 1H, \ CH), \ 7.239-7.419 \ (m, \ 5H, \ Ph). \]
2-(p-tolyl)-2-((trimethylsilyl)oxy)acetonitrile (Table 2 entry 6).

\[
\text{Si} \quad \text{N} \\
\text{C} \quad \text{H} \\
\text{O} \\
\text{Si} \quad \text{C} \quad \text{N}
\]

\(^1\)H-RMN (CDCl\(_3\), 500 MHz): \(\delta\) 0.221 (s, 9H, 3xCH\(_3\)), 2.372 (s, 3H, CH\(_3\)), 5.458 (s, 1H, CH), 7.226-7.380 (m, 4H, Ph).

2-((trimethylsilyl)oxy)nonanenitrile (Table 2 entry 7).

\[
\text{Si} \quad \text{N} \\
\text{C} \quad \text{H} \\
\text{O} \\
\text{Si} \quad \text{C} \quad \text{N}
\]

\(^1\)H-RMN (CDCl\(_3\), 500 MHz): \(\delta\) 0.180 (s, 9H, 3xCH\(_3\)), 0.892 (s, 3H, CH\(_3\)), 1.270-1.538 (m, 10H, CH\(_2\)), 1.756-1.801 (m, 2H, CH\(_2\)), 4.369-4.395 (m, 1H, CH).
4. Productivity calculation

Productivity = (mol product/mol cat.) x (1/time(h))

REF. 6:
Mol product = mol benzaldehyde x Yield = 0.001mol x 99% = 0.00099 mol
Mol cat. = V x ρ/Fw = (0.5mL x 1.231g/mL) / (340.29g/mol) = 0.0018087 mol
Time = 24h
Productivity = (0.00099mol/0.0018087mol) x (1/24h) = 0.023

REF. 7:
Mol product = mol benzaldehyde x Yield = 0.005mol x >99% = 0.005 mol
Mol cat. = 0.01% Mol product = 0.005mol x (0.01/100) = 0.0000005 mol
Time = 30min = 0.5h
Productivity = (0.005mol/0.0000005mol) x (1/0.5h) = 20000

REF. 26:
Mol product = mol acetophenone x Yield = 0.200mol x 99% = 0.198 mol
Mol cat. = 0.125g x 3.2mmol/g = 0.4mmol = 0.0004mol
Time = 20h
Productivity = (0.198mol/0.0004mol) x (1/20h) = 25

E factor calculation

E factor = kg waste/kg product

E factor = [ (mol benzaldehyde x Fw benzaldehyde) + (mol TMSCN x Fw TMSCN) + (mL solvent x ρ solvent) - (mol benzaldehyde x Yield x Fw product) ] / [mol benzaldehyde x Yield x Fw product]

REF. 6:
Solvent = 3x15mL diethyl ether
ρ diethyl ether = 0.7134 g/mL
\[ E \text{ factor} = \frac{[(0.001 \text{ mol} \times 106 \text{ g/mol}) + (0.002 \text{ mol} \times 99.21 \text{ g/mol}) + (3 \times 15 \text{ mL} \times 0.7134 \text{ g/mL})] - (0.001 \text{ mol} \times (99 \%/100) \times 205.09 \text{ g/mol})}{0.001 \text{ mol} \times (99 \%/100) \times 205.09 \text{ g/mol}} = 158.6 \]

**REF. 7:**
Solvent= 3x50mL hexane
ρ hexane= 0.6548 g/mL

\[ E \text{ factor}= \frac{[(0.005 \text{ mol} \times 106 \text{ g/mol}) + (0.006 \text{ mol} \times 99.21 \text{ g/mol}) + (3 \times 50 \text{ mL} \times 0.6548 \text{ g/mL})] - (0.005 \text{ mol} \times >99\% \times 205.09 \text{ g/mol})}{0.005 \text{ mol} \times >99\% \times 205.09 \text{ g/mol}} = 95.8 \approx 96 \]
<table>
<thead>
<tr>
<th>SOLVENT</th>
<th>CAT.</th>
<th>CONDITIONS</th>
<th>YIELD</th>
<th>TIME</th>
<th>TEMP.</th>
<th>TYPE OF REACTOR</th>
</tr>
</thead>
<tbody>
<tr>
<td>REF. 6</td>
<td>[OMIM]PF₆</td>
<td>0,5 mL 1mmol benzaldehyde/2mmol TMSCN</td>
<td>99%</td>
<td>24 h</td>
<td>r.t.</td>
<td>batch</td>
</tr>
<tr>
<td></td>
<td>[OMIM]PF₆</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>[OMIM]PF₆</td>
<td>0,01% 5 mmol benzaldehyde/6mmol TMSCN</td>
<td>&gt;99%</td>
<td>30 min</td>
<td>r.t.</td>
<td>batch</td>
</tr>
<tr>
<td>REF. 7</td>
<td>[BMIM]SBF₆</td>
<td>Sc(OTf)₃ 0,125g 200 mmol acetophenone/220 mmol TMSCN</td>
<td>99%</td>
<td>20 h</td>
<td>60°C</td>
<td>flow</td>
</tr>
<tr>
<td>OUR</td>
<td>SolFC</td>
<td>600 mg 114 mmol acetophenone/125 mmol TMSCN</td>
<td>99%</td>
<td>4 min&lt;sup&gt;a&lt;/sup&gt;</td>
<td>r.t.</td>
<td>flow</td>
</tr>
</tbody>
</table>

<sup>a</sup> Residence time for a flow rate of 0.1 mL/min
5. Swelling of the supported catalyst.

a) Dry volume = 1 ml

b) Wet volume at 25.5h = 2mL

Swelling (v_f-v_i/v_i x 100).
3. NMR Spectra (corresponding with the reaction crude).

(13)
(Table 2 Entry 1)
(Table 2 Entry 2)
(Table 2 Entry 3)
(Table 2 Entry 4)
(Table 2 Entry 5)
(Table 2 Entry 6)
(Table 2 Entry 7)