Supplementary Information for

**Highly efficient and practical hydrogenation of olefins catalyzed by in situ generated iron complex catalysts**

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1. General Information

a. Materials
All manipulations were carried out using standard Schlenk, high-vacuum and glovebox techniques. THF, Et₂O, DME, 1,4-dioxane, and toluene was distilled from sodium benzophenone ketyl prior to use. FeCl₂ (99.99%) and LiAlH₄ were purchased from Alfa Aesar and Admas, respectively, and used as received. Styrene, 4-methoxystyrene, 1-hexene, 1-octene, vinylcyclohexane, allylbenzene, 2-phenyl-1-propene, 1,1-diphenylethylene, 2-methyl-3-phenyl-1-propene, cyclohexene, 2-octene (Z/E = 1:4), N,N-dimethylallylamine were purchased from Acros, Alfa Aesar, TCI, or Strem. Other alkenes were prepared by Wittig olefination from corresponding ketone. All alkenes were distilled over LiAlH₄ or CaH₂ before use. THF-d₈ was purchased from Aldrich under an atmosphere of argon and stored in glovebox. FeCl₂-L₁,¹ Fe(bipy)Cl₂,² Fe(phen)Cl₂,³ FeCl₂-L₄,³ FeCl₂-L₇,⁴ FeCl₂-L₈⁵ and FeCl₂-phosphines⁶ were prepared according to the reported procedures.

b. Analytical Methods
NMR spectra were recorded with a Bruker AV 400 spectrometer at 400 MHz (¹H NMR) and 101 MHz (¹³C NMR). Chemical shifts (δ values) were reported in ppm down field from internal Me₄Si (¹H NMR and ¹³C NMR). ³¹P NMR chemical shifts were referenced to an external H₃PO₄ standard. Data for ¹H NMR are recorded as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, quint = quintuplet, m = multiplet or unresolved, br = broad, coupling constant (s) in Hz, integration). Conversions were assayed by gas-chromatography (GC) by comparison to authentic samples or by ¹H NMR analyses. The GC analyses were performed on an Agilent 7890A instrument equipped with an interCap-1 capillary column (30 × 0.25 × 0.25 cm).
2. Preparation and Analyses of Fe-L8 Complexes

**FeCl₂-L8**: FeCl₂ (63 mg, 0.5 mmol, 1 equiv), 6-di-tert-butylphosphinomethyl-2, 2’-bipyridine (L8) (157 mg, 0.55 mmol, 1.1 equiv) and THF (5 mL) were added to a 10 mL Schlenk tube filled with N₂. The reaction mixture was stirred for 24 h and then the solvent was removed under vacuum. The residue was redissolved in CH₂Cl₂ (2 mL), then Et₂O (10 mL) was added to the solution and solids precipitated. After filtered, the residue was washed with Et₂O and dried under vacuum to afford the red solids (175 mg, 79% yield). 

1H NMR (400 MHz, CDCl₃) δ -14.82 (s, 1H), 0.87 (s, 1H), 9.29 (s, 1H), 14.05 (s, 18H), 24.51 (s, 2H), 52.65 (s, 1H), 53.01 (s, 1H), 77.25 (s, 1H), 80.75 (s, 1H).

**Fe-L8-(H)₂**: In an argon filled glovebox, to the mixture of FeCl₂-L8 (0.005 mmol) and LiAlH₄ (0.025 mmol), 1 mL THF-d₈ was introduced and the resulting mixture was stirred for 1 min. Then the resulting dark red solution was detected through NMR. 1H NMR (400 MHz, THF-d₈) δ -18.92 (d, Jₘ⁻ = 20 Hz, 2H), 1.08 (d, Jₘ⁻ = 8.0 Hz, 18H), 3.29 (br, 2H), 6.0 (br, 1H), 6.23 (br, 1H), 6.41 (br, 1H), 6.72 (br, 1H), 6.88 (m, 2H), 9.73 (br, 1H). 31P NMR (162 MHz, THF-d₈) δ 134.06. 27Al NMR(104 MHz, THF-d₈) δ 99.32 (br).
$^{31}$P NMR of Fe-L8-(H)$_2$

$^{27}$Al NMR of Fe-L8-(H)$_2$
3. Typical Procedure of Olefins Hydrogenation

To a high-pressure autoclave charged with FeCl₂-L8 (0.005 mmol), LiAlH₄ (0.025 mmol) and a stir bar, 1 mL of the THF was introduced. The mixture was stirred under an argon atmosphere at ambient temperature for 1 min to generate a black-red solution. Alkene (5 mmol) was then added into the resulted solution. The autoclave was purged four times with hydrogen and finally pressurized to 30 atm. The reaction mixture was stirred at room temperature until the consumption of hydrogen stopped (judged by the pressure reduction). The autoclave was depressurized. The residue was dissolved in Et₂O and filtered through a short plug of celite. All hydrogenation products are known, identified by GC-MS and ¹H NMR, and the conversions were determined by ¹H NMR and GC analysis. For the hydrogenation of styrene, the quantitative yield was observed by GC method with dodecane as an internal standard. For other substrates, the reactions are very clean, and only desired products are determined through GC and ¹H NMR analyses of crude reaction mixtures.

Table S1 The TOFs of the hydrogenation of styrene at various conversion states

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<th>Time (min)</th>
<th>Conv. (%)</th>
<th>TOF (h⁻¹)</th>
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<tr>
<td>3</td>
<td>3</td>
<td>99.96</td>
<td>19,992</td>
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4. $^1$H NMR Spectra and GC Charts of Hydrogenation Products

Ethylbenzene (from styrene)

\[ \text{Reaction conditions: general procedure, FeCl}_2\cdot L8 (0.005 mmol), \text{LiAlH}_4 (0.025 mmol), \text{styrene (5 mmol), 1 mL THF, 30 atm H}_2, \text{rt, 5 min, 100\% conversion to ethylbenzene.} \]

The quantitative yield was observed by GC method with dodecane as an internal standard. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 1.24 (t, $J = 8.0$ Hz, 3H, CH$_3$), 2.65 (q, $J = 8.0$ Hz, 2H, CH$_2$), 7.14-7.23 (m, 3H, Ar-H), 7.25-7.30 (m, 2H, Ar-H).

\[ \text{GC conditions: interCap-1 column, injector temp. 230 \degree C, detector temp. 250 \degree C,} \]

50 \degree C ramps 10 \degree C/min to 100 \degree C, ramps 3 \degree C/min to 120 \degree C, ramps 10 \degree C/min to 300 \degree C, N$_2$ fluency 1.0 mL/min. $t = 5.545$ min for styrene and $t = 5.174$ min for ethylbenzene.
| Peak RetTime Type Width Area Height Area |
|---|---|---|---|---|
| # | [min] | [min] | [pA*s] | [pA] | % |
| 1 | 5.174 | BV | 0.0341 | 9192.59473 | 3961.34009 | 1.000e2 |
1-Ethyl-4-methylbenzene (from 4-methylstyrene)

**Reaction conditions:** general procedure, FeCl₂-L8 (0.005 mmol), LiAlH₄ (0.025 mmol), 4-methylstyrene (5 mmol), 1 mL THF, 30 atm H₂, rt, 10 min, 100% conversion to 1-ethyl-4-methylbenzene. ¹H NMR (400 MHz, CDCl₃) δ 1.22 (t, J = 8.0 Hz, 3H; CH₃), 2.32 (s, 3H; CH₃), 2.62 (q, J = 8.0 Hz, 2H; CH₂), 7.07-7.11 (m, 4H; Ar-H).

**GC conditions:** interCap-1 column, injector temp. 230 °C, detector temp. 250 °C, 50 °C ramps 10 °C/min to 100 °C, ramps 3 °C/min to 120 °C, ramps 10 °C/min to 300 °C, N₂ fluency 1.0 mL/min. ́t = 11.505 min for 4-methylstyrene and ́t = 10.430 min for 1-ethyl-4-methylbenzene.
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1-Ethyl-3-methylbenzene (from 3-methylstyrene)

**Reaction conditions:** general procedure, FeCl$_2$-L8 (0.005 mmol), LiAlH$_4$ (0.025 mmol), 3-methylstyrene (5 mmol), 1 mL THF, 30 atm H$_2$, rt, 15 min, 100% conversion to 1-ethyl-3-methylbenzene. $^1$H NMR (400 MHz, CDCl$_3$) δ 1.23 (t, $J$ = 8.0 Hz, 3H; CH$_3$), 2.33 (s, 3H; CH$_3$), 2.62 (q, $J$ = 8.0 Hz, 2H; CH$_2$), 7.01-7.15 (m, 3H; Ar-H), 7.18 (t, $J$ = 8.0 Hz, 1H; Ar-H).

**GC conditions:** interCap-1 column, injector temp. 230 °C, detector temp. 250 °C, 50 °C ramps 10 °C/min to 100 °C, ramps 3 °C/min to 120 °C, ramps 10 °C/min to 300 °C, N$_2$ fluency 1.0 mL/min. $t$ = 7.206 min for 3-methylstyrene and $t$ = 6.701 min for 1-ethyl-3-methylbenzene.
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1-Ethyl-2-methylbenzene (from 2-methylstyrene)

Reaction conditions: general procedure, FeCl₂-L8 (0.005 mmol), LiAlH₄ (0.025 mmol), 2-methylstyrene (5 mmol), 1 mL THF, 30 atm H₂, rt, 15 min, 100% conversion to 1-ethyl-2-methylbenzene. ¹H NMR (400 MHz, CDCl₃) δ 1.21 (t, J = 8.0 Hz, 3H; CH₃), 2.30 (s, 3H; CH₃), 2.63 (q, J = 8.0 Hz, 2H; CH₂), 7.05-7.15 (m, 4H; Ar-H).

GC conditions: interCap-1 column, injector temp. 230 °C, detector temp. 250 °C, 50 °C ramps 10 °C/min to 100 °C, ramps 3 °C/min to 120 °C, ramps 10 °C/min to 300 °C, N₂ fluency 1.0 mL/min. t = 7.555 min for 2-methylstyrene and t = 7.340 min for 1-ethyl-2-methylbenzene.
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1-tert-Butyl-4-ethylbenzene (from 4-tert-butylstyrene)

![Chemical Structure](image)

**Reaction conditions:** general procedure, FeCl$_2$-L8 (0.005 mmol), LiAlH$_4$ (0.025 mmol), 4-tert-butylstyrene (5 mmol), 1 mL THF, 30 atm H$_2$, rt, 5 min, 100% conversion to 1-tert-butyl-4-ethylbenzene. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 1.24 (t, $J = 8.0$ Hz, 3H; CH$_3$), 1.31 (s, 9H; CH$_3$), 2.63 (q, $J = 8.0$ Hz, 2H; CH$_2$), 7.14 (d, $J = 8.0$ Hz, 2H; Ar-H), 7.32 (d, $J = 8.0$ Hz, 2H; Ar-H).

**GC conditions:** interCap-1 column, injector temp. 230 °C, detector temp. 250 °C, 50 °C ramps 10 °C/min to 100 °C, ramps 3 °C/min to 120 °C, ramps 10 °C/min to 300 °C, N$_2$ fluency 1.0 mL/min. $t =$16.343 min for 4-tert-butylstyrene and $t =$ 15.581 min for 1-tert-butyl-4-ethylbenzene.
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1-Ethyl-4-methoxybenzene (from 4-methoxystyrene)

**Reaction conditions:** general procedure, FeCl$_2$-L8 (0.005 mmol), LiAlH$_4$ (0.025 mmol), 4-methoxystyrene (5 mmol), 1 mL THF, 30 atm H$_2$, rt, 3 min, 100% conversion to 1-ethyl-4-methoxybenzene. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 1.21 (t, $J = 8.0$ Hz, 3H; CH$_3$), 2.60 (q, $J = 8.0$ Hz, 2H; CH$_2$), 3.78 (s, 3H; CH$_3$), 6.83 (d, $J = 8.0$ Hz, 2H; Ar-H), 7.11 (d, $J = 8.0$ Hz, 2H; Ar-H).

**GC conditions:** interCap-1 column, injector temp. 230 °C, detector temp. 250 °C, 50 °C ramps 10 °C/min to 300 °C, N$_2$ fluency 1.0 mL/min. $t = 12.153$ min for 4-methoxystyrene and $t = 11.652$ min for 1-ethyl-4-methoxybenzene.
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1-Chloro-4-ethylbenzene (from 4-chlorostyrene)

Reaction conditions: general procedure, FeCl₂-L8 (0.005 mmol), LiAlH₄ (0.025 mmol), 4-chlorostyrene (5 mmol), 1 mL THF, 30 atm H₂, rt, 6 h, 98% conversion to 1-chloro-4-ethylbenzene. ¹H NMR (400 MHz, CDCl₃) δ 1.21 (t, J = 8.0 Hz, 3H; CH₃), 2.62 (q, J = 8.0 Hz, 2H; CH₂), 7.11-7.22 (m, 2H; Ar), 7.23-7.25 (m, 2H; Ar).

GC conditions: interCap-1 column, injector temp. 230 °C, detector temp. 250 °C, 50 °C ramps 10 °C/min to 100 °C, ramps 3 °C/min to 120 °C, ramps 10 °C/min to 300 °C, N₂ fluency 1.0 mL/min. t = 9.264 min for 4-chlorostyrene and t = 8.658 min for 1-chloro-4-ethylbenzene.
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**n-Hexane (from 1-hexene)**

**Reaction conditions:** general procedure, FeCl₂-L8 (0.005 mmol), LiAlH₄ (0.025 mmol), 1-hexene (5 mmol), 1 mL THF, 30 atm H₂, rt, 20 min, 100% conversion to n-hexane. \(^1\)H NMR (400 MHz, CDCl₃) δ 0.87 (t, J = 8.0 Hz, 6H; CH₃), 1.23-1.30 (m, 8H; CH₂).

**GC conditions:** interCap-1 column, injector temp. 230 °C, detector temp. 250 °C, 45 °C holds for 10 min, ramps 10 °C/min to 300 °C, N₂ fluency 1.0 mL/min. \(t = 6.974\) min for 1-hexene and \(t = 7.262\) min for n-hexane.
Peak RetTime Type Width Area Height Area %
# [min] [min] [pA*s] [pA]     %
 1 7.262 BV 0.0670 2.60615e4 6338.10889 1.000e2
n-Octane (from 1-octene)

**Reaction conditions:** general procedure, FeCl₂-L8 (0.005 mmol), LiAlH₄ (0.025 mmol), 1-octene (5 mmol), 1 mL THF, 30 atm H₂, rt, 30 min, 96% conversion to n-octane. 

¹H NMR (400 MHz, CDCl₃) δ 0.88 (t, J = 8.0 Hz, 6H; CH₃), 1.24-1.30 (m, 12H; CH₂).

**GC conditions:** interCap-1 column, injector temp. 230 °C, detector temp. 250 °C, 50 °C ramps 10 °C/min to 100 °C, ramps 3 °C/min to 120 °C, ramps 10 °C/min to 300 °C, N₂ fluency 1.0 mL/min. t = 7.392 min for 1-octene, t = 7.547 min for n-octane and t = 7.680 min for isomer of 1-octene.
Peak RetTime Type Width Area Height Area %
# [min] [min] [pA*s] [pA] %
1 7.547 VV 0.0674 2.38796e4 4856.62402 95.78315
2 7.680 VB 0.0313 1051.29907 526.50568 4.21685
Ethylcyclohexane (from vinylcyclohexane)

**Reaction conditions**: general procedure, FeCl$_2$-L8 (0.005 mmol), LiAlH$_4$ (0.025 mmol), vinylcyclohexane (5 mmol), 1 mL THF, 30 atm H$_2$, rt, 20 min, 100% conversion to ethylcyclohexane. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 0.83-0.89 (m, 5H; CH$_3$, CH$_2$), 1.13-1.22 (m, 6H; CH$_2$), 1.65-1.73 (m, 5H; CH$_2$, CH).

**GC conditions**: interCap-1 column, injector temp. 230 °C, detector temp. 250 °C, 50 °C ramps 10 °C/min to 100 °C, ramps 3 °C/min to 120 °C, ramps 10 °C/min to 300 °C, N$_2$ fluency 1.0 mL/min. $t = 7.889$ min for vinylcyclohexane and $t = 8.024$ min for ethylcyclohexane.
Peak RetTime Type Width Area Height Area %
1 8.024 BB 0.0382 2054.60449 850.40735 1.000e2
Propylbenzene (from allylbenzene)

**Reaction conditions:** general procedure, FeCl₂-L8 (0.005 mmol), LiAlH₄ (0.025 mmol), allylbenzene (5 mmol), 1 mL THF, 30 atm H₂, 15 min, 100% conversion to propylbenzene. ¹H NMR (400 MHz, CDCl₃) δ 0.94 (t, J = 8.0 Hz, 3H; CH₃), 1.62-1.68 (m, 2H; CH₂), 2.58 (t, J = 8.0 Hz, 2H; CH₂), 7.15-7.18 (m, 3H; Ar-H), 7.25-7.29 (m, 2H; Ar-H).

**GC conditions:** interCap-1 column, injector temp. 230 °C, detector temp. 250 °C, 50 °C ramps 10 °C/min to 100 °C, ramps 3 °C/min to 120 °C, ramps 10 °C/min to 300 °C, N₂ fluency 1.0 mL/min. t = 6.580 min for allylbenzene and t = 6.825 min for propylbenzene.
Peak RetTime Type Width Area Height Area %
1 6.825 BB  0.0654 3.54163e4  6734.84131  1.000e2
Isopropylbenzene (from 2-phenyl-1-propene)

\[
\text{Reaction conditions: general procedure, } \text{FeCl}_2 \text{-L8 (0.005 mmol), LiAlH}_4 (0.025 \text{ mmol),}
\]
2-phenyl-1-propene (5 mmol), 1 mL THF, 30 atm H\textsubscript{2}, 50 °C, 1 h, 100% conversion to isopropylbenzene. \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) δ 1.25 (d, \( J = 8.0 \) Hz, 6H; CH\textsubscript{3}), 2.86-2.95 (m, 1 H; CH), 7.14-7.32 (m, 5 H; Ar-H).

\[
\text{GC conditions: interCap-1 column, injector temp. 230 °C, detector temp. 250 °C,}
\]
50 °C ramps 10 °C/min to 100 °C, ramps 3 °C/min to 120 °C, ramps 10 °C/min to 300 °C, N\textsubscript{2} fluency 1.0 mL/min. \( t = 10.814 \) min for 2-phenyl-1-propene and \( t = 8.879 \) min for isopropylbenzene.
Isobutylbenzene (from 2-methyl-3-phenyl-1-propene)

\[
\text{\begin{tikzpicture}
\draw[thick,red,-latex] (0,0) -- (1,0);
\end{tikzpicture}}
\]

**Reaction conditions:** general procedure, FeCl$_2$-L8 (0.005 mmol), LiAlH$_4$ (0.025 mmol), 2-methyl-3-phenyl-1-propene (5 mmol), 1 mL THF, 30 atm H$_2$, rt, 1.5 h, 100% conversion to isobutylbenzene. $^1$H NMR (400 MHz, CDCl$_3$) δ 0.90 (d, $J = 8.0$ Hz, 6H; CH$_3$), 1.81-1.89 (m, 1H; CH), 2.47 (d, $J = 8.0$ Hz, 2H; CH$_2$), 7.13-7.19 (m, 3H; Ar-H), 7.23-7.29 (m, 2H; Ar-H).

**GC conditions:** interCap-1 column, injector temp. 230 °C, detector temp. 250 °C, 50 °C ramps 10 °C/min to 100 °C, ramps 3 °C/min to 120 °C, ramps 10 °C/min to 300 °C, N$_2$ fluency 1.0 mL/min. $t = 10.390$ min for 2-methyl-3-phenyl-1-propene and $t = 10.219$ min for isobutylbenzene.
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Ethane-1,1-diyl dibenzene (from 1,1-diphenylethylene)

![Chemical structure of ethane-1,1-diyl dibenzene](image)

**Reaction conditions:** general procedure, FeCl$_2$-L8 (0.005 mmol), LiAlH$_4$ (0.025 mmol), 1,1-diphenylethylene (5 mmol), 1 mL THF, 30 atm H$_2$, 2 h, 50 °C, rt, 78% conversion to ethane-1,1-diyl dibenzene. $^1$H NMR (400 MHz, CDCl$_3$) δ 1.64 (d, $J$ = 4.0 Hz, 3H; CH$_3$), 4.15 (q, $J$ = 8.0 Hz, 1H; CH), 7.17-7.33 (m, 10H; Ar-H)

![NMR spectrum](image)

**GC conditions:** interCap-1 column, injector temp. 230 °C, detector temp. 250 °C, 50 °C ramps 10 °C/min to 300 °C, N$_2$ fluency 1.0 mL/min. $t$ = 16.838 min for 1,1-diphenylethylene and $t$ = 16.542 min for ethane-1,1-diyl dibenzene.
Peak RetTime Type Width Area Height Area %
# [min] [min] [pA*s] [pA] [pA] [pA] [pA]
1 16.542 BB 0.0577 8778.71875 2059.73315 78.12795
2 16.791 BB 0.0399 2457.61743 929.24011 21.87205

THF
Cyclohexane (from cyclohexene)

Reaction conditions: general procedure, FeCl₂-L8 (0.005 mmol), LiAlH₄ (0.025 mmol), cyclohexene (5 mmol), 1 mL THF, 30 atm H₂, 50 °C, 1 h, 40% conversion to cyclohexane. ¹H NMR (400 MHz, CDCl₃) δ 1.43 (s, 12 H).

GC conditions: interCap-1 column, injector temp. 230 °C, detector temp. 250 °C, 50 °C holds for 10 min, ramps 10 °C/min to 300 °C, N₂ fluency 1.0 mL/min. t = 9.182 min for cyclohexene and t = 8.700 min for cyclohexane.
FID1 A, Front Signal (GNIGN4-CYCLOPENTENE0000.D)

Peak RetTime Type Width Area Height Area %
--- | -------- | ------ | ------ | ------ | ------ | ------ |
1  8.700  BB   0.0683  992.41956  230.28899  40.21303
2  9.236  BB   0.0699  1475.48608  331.78387  59.78697
n-Octene (from 2-octene)

Reactions:

**Reaction conditions:** general procedure, FeCl$_2$-L8 (0.005 mmol), LiAlH$_4$ (0.025 mmol), 2-octene ($Z/E = 1:4$, 5 mmol), 1 mL THF, 30 atm H$_2$, 50 °C, 5 h, 80% conversion to n-octane. $^1$H NMR (400 MHz, CDCl$_3$) δ 0.88 (t, $J = 8.0$ Hz, 6H; CH$_3$), 1.24-1.32 (m, 12 H; CH$_2$).

**GC conditions:** interCap-1 column, injector temp. 230 °C, detector temp. 250 °C, 50 °C ramps 10 °C/min to 100 °C, ramps 3 °C/min to 120 °C, ramps 10 °C/min to 300 °C, N$_2$ fluency 1.0 mL/min. $t = 7.504$ min and $t = 7.666$ min for 2-octene ($Z/E$ mixture) and $t = 7.448$ min for n-octane and isomers of the substrate.
Z/E mixture

THF

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**N,N-dimethyl-\(n\)-propylamine (from N,N-dimethylallylamine)**

**Reaction conditions:** general procedure, FeCl\(_2\)-L8 (0.005 mmol), LiAlH\(_4\) (0.025 mmol), N,N-dimethylallylamine (5 mmol), 1 mL THF, 30 atm H\(_2\), rt, 6 h, 100% conversion to N,N-dimethyl-\(n\)-propylamine. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 0.90 (t, \(J = 8.0\) Hz, 3H; CH\(_3\)), 1.42-1.54 (m, 2H; CH\(_2\)), 2.19-2.23 (m, 8H; CH\(_3\)+CH\(_2\)).

**GC conditions:** interCap-1 column, injector temp. 230 \(^\circ\)C, detector temp. 250 \(^\circ\)C, 50 \(^\circ\)C holds for 10 min, ramps 10 \(^\circ\)C/min to 300 \(^\circ\)C, N\(_2\) fluency 1.0 mL/min. \(t = 7.948\) min for N,N-dimethylallylamine and \(t = 8.195\) min for N,N-dimethyl-\(n\)-propylamine.
Peak RetTime Type Width Area Height Area %
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5. References: