Supporting Information

Alkene Hydrogenations by Soluble Iron Nanocluster Catalysts

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General

Analytical Thin-Layer Chromatography: TLC was performed using aluminium plates with silica gel and fluorescent indicator (Merck, 60, F254). Thin layer chromatography plates were visualized by exposure to ultraviolet light (366 or 254 nm) or by immersion in a staining solution of molybdophosphoric acid in ethanol or potassium permanganate in water.

Column Chromatography: Flash column chromatography with silica gel 60 from KMF (0.040-0.063 mm). Mixtures of solvents used are noted in brackets.

Chemicals and Solvents: Commercially available olefins were distilled under reduced pressure prior use. Solvents (THF, Et₂O, n-hexane, toluene) were distilled over sodium and benzophenone and stored over molecular sieves (4 Å). LiN(SiMe₃)₂ (SigmaAldrich, 97%) was sublimated and stored under argon. HN(SiMe₃)₂, HNEt₂, HN(iPr)₂, HNPhMe and 2,2,6,6-tetramethylpiperidine were distilled over CaH₂ and stored under argon prior use. HNPh₂ was recrystallized in n-pentane. Solvents used for column chromatography were distilled under reduced pressure prior use (ethyl acetate), DiBAIH (1 M in toluene), AlMe₃ (2 M in toluene), Al(Bu)₃ were used as received from SigmaAldrich or diluted before use.

High Pressure Reactor: Hydrogenation reactions were carried out in 160 and 300 mL high pressure reactors (Parr™) in 4 mL glass vials. The reactors were loaded under argon, purged with H₂ (1 min), sealed and the internal pressure was adjusted. Hydrogen (99.9992%) was purchased from Linde.

¹H- und ¹³C-NMR-Spectroscopy: Nuclear magnetic resonance spectra were recorded on a Bruker Avance 300 (300 MHz) and Bruker Avance 400 (400 MHz). ¹H-NMR: The following abbreviations are used to indicate multiplicities: s = singlet; d = doublet; t = triplet, q = quartet; m = multiplet, dd = doublet of doublet, dt = doublet of triplet, dq = doublet of quartet, ddt = doublet of doublet of quartet. Chemical shift δ is given in ppm to tetramethylsilane.

Fourier-Transformations-Infrared-Spectroscopy (FT-IR): Spectra were recorded on a Varian Scimitar 1000 FT-IR with ATR-device. All spectra were recorded at room temperature. Wave number is given in cm⁻¹. Bands are marked as s = strong, m = medium, w = weak and b = broad.

Gas chromatography with FID (GC-FID): HP6890 GC-System with injector 7683B and Agilent 7820A System. Column: HP-5, 19091J-413 (30 m × 0.32 mm × 0.25 µm), carrier gas: N₂. GC-FID was used for reaction control and catalyst screening (Calibration with internal standard n-pentadecane and analytically pure samples).

Gas chromatography with mass-selective detector (GC-MS): Agilent 6890N Network GC-System, mass detector 5975 MS. Column: HP-5MS (30m × 0.25 mm × 0.25 µm, 5% phenylmethylsiloxane, carrier gas: H₂. Standard heating procedure: 50 °C (2 min), 25 °C/min -> 300 °C (5 min)

Chiral gas chromatography with FID (chiral GC-FID): Fisons GC 8000. Column: CP-Chirasil-Dex CB (25 m x 0.25 mm ID, 0.25 µm film), carrier gas: Ar. Injection 0.1 µL. Inlet: 200 °C, Detector: 200 °C, Culum 50-200 °C with 3 to 10 °C per minute.

Headspace gas chromatography with TCD (HS-GC-TCD): Infinicon 3000 Micro GC. Column: 5 Å molecular sieves, carrier gas: argon. Standard heating procedure: 120 °C (3 min). Headspace GC-TCD was used for quantification of H₂, CH₄ and C₂H₆ in the reduction of FeX₂ salts (X = N(SiMe₃)₂, Cl) with aluminium organyls (DiBAIH, Al(Bu)₃, AlMe₃). Calibrations of examined gases were conducted by hydridation of LiAlH₄ (H₂), MeMgCl (CH₄) and EtMgCl (C₂H₆).

Headspace gas chromatography with mass-selective detector (HS-GC-MS): Agilent 7890 B GC-system, mass detector AccuTOF GCX from Jeol. Column: HP 5 (30 m x 0.25 mm x 0.25 µm) from Agilent, carrier gas: helium. Standard heating procedure: 22.2 °C (2 min). 1 °C/min (17.8 min) → 40 °C (3 min) with a flow of 0.6 mL/min. Split 50:1. Injection: 1 µL at 120 °C.
**High resolution mass spectrometry (HRMS):** The spectra were recorded by the Central Analytics Lab at the Department of Chemistry, University of Regensburg, on a MAT SSQ 710 A from Finnigan.

**Gas-uptake reaction monitoring:** Gas-uptake was monitored with a *Man On the Moon X201* kinetic system to maintain a constant reaction pressure. The system was purged with hydrogen prior use. Reservoir pressure was set to about 9 bar H₂. Calibration of the reservoir pressure drop in relation to H₂ consumption was performed by quantitative hydrogenation of various amounts of α-methylstyrene with a Pd/C catalyst in 1 mL of THF.

**Dynamic Light Scattering:** Dynamic light scattering experiments were performed with the help of a goniometer CGS-II from *ALV* (Germany). The goniometer is equipped with an ALV-7004/Fast Multiple Tau digital correlator and a vertical-polarized 22 mW HeNe-laser (wavelength = 632.8 nm). All measurements were done at a scattering angle of 90° after thermostating to 25 °C. The measurement time was 300 s. The obtained correlation functions were fitted with the software TableCurve 2d v5.01 by a monomodal equation.
General procedures

General method for catalyst preparation

In an argon-filled glovebox a flame-dried flask was charged with a solution of Fe[N(SiMe$_3$)$_2$]$_2$ in toluene (50 mM, 1 mL, 50 µmol). A solution of DiBAIH in toluene (100 mM, 1 mL, 100 µmol) was added via syringe. The solution turned black immediately and was stirred at room temperature for 5 minutes prior to use.

General method for in situ catalyst preparation with LiN(SiMe$_3$)$_2$

In an argon-filled glovebox a flame-dried flask was charged with LiN(SiMe$_3$)$_2$ (16.7 mg; 100 µmol) and suspended in toluene (1 mL). FeCl$_2$(thf)$_{1.5}$ (11.7 mg, 50 µmol) was added and the resulting suspension was stirred at room temperature. After 60 minutes a solution of DiBAIH in toluene (100 mM, 1 mL, 100 µmol) was added via syringe. The solution turned black immediately and was stirred at room temperature for 5 minutes prior to use.

General method for in situ catalyst preparation with various amines

In an argon-filled glovebox a flame-dried flask was charged with an amine (110 µmol) and toluene (0.8 mL). A solution of tBuLi in toluene (50 mM, 0.2 mL, 100 µmol) was added at room temperature. After 30 minutes of stirring, FeCl$_2$(thf)$_{1.5}$ (11.7 mg, 50 µmol) was added and the resulting suspension was stirred for 60 minutes. After that, a solution of DiBAIH in toluene (100 mM, 1 mL, 100 µmol) was added via syringe. The solution turned black immediately and was stirred at room temperature for 5 minutes prior to use.

General method for catalytic hydrogenation

In an argon-filled glovebox a flame-dried 4 mL reaction vial was charged with the substrate (0.2 mmol) and n-pentadecane as internal reference for GC-FID quantification (0.2 mmol). After addition of freshly prepared catalyst suspension (400 µL; 5 mol% [Fe]), the reaction vial was transferred to a high pressure reactor which was sealed and removed from the glovebox. The reactor was purged with H$_2$ (3 × 3 bar) and the reaction pressure and temperature were set. After the indicated reaction time, the vial was retrieved and hydrolized with a saturated aqueous solution of sodium hydrogen carbonate (0.5 mL). The reaction mixture was extracted with ethyl acetate (1 × 0.5 mL) and analyzed by GC-FID and GC-MS.

For product isolation, 0.5 to 1 mmol of the starting material was used. After quenching, the product was extracted with ethyl acetate (3 × 3 mL), washed with brine (10 mL), dried over sodium sulfate and filtered over a pad of silica. Removal of the solvent at reduced pressure afforded the product in high purity.

General method for kinetic examination in catalytic hydrogenation

A flame-dried 10 mL 2-neck flask was connected to a *Man on the Moon X201* gas-uptake system and kept at 23 °C with the help of a water bath. After purging with H$_2$, the system was set to a reaction pressure of 1.9 bar. Freshly prepared catalyst mixture (1 mL) was added via syringe and stirred for 2 minutes. Monitoring of the hydrogen uptake started with the addition of the substrate (0.5 mmol).
Optimization experiments

Stability of the catalyst

The catalyst stability was determined by comparison of the hydrogenation rate of 1-phenylcyclohexene after several catalyst treatments. Turnover frequencies were calculated upon the yield after 7 minutes.

Table S1. Comparison of TOF after various catalyst pretreatments.

| Entry | Reductant | Catalyst pretreatment | TOF \(a\) / h\(^{-1}\) |
|-------|-----------|-----------------------|---------------------|
| 1     | DiBAIH    | freshly prepared      | 41                  |
| 2     | DiBAIH    | storage for 5 d in solution | 37          |
| 3     | DiBAIH    | removal of solvent and resolution | 30          |
| 4     | DiBAIH    | removal of solvent, storage for 5 d under argon and resolution | 27          |
| 5     | AlMe\(_3\) | freshly prepared      | 13                  |
| 6     | AlMe\(_3\) | storage for 20 h in solution | <1          |
| 7     | DiBAIH    | \textit{in situ} synthesis of Fe[\(\text{N(SiMe}_3\text{)}_2\)]\(_2\) | 27          |

\(a\) determined with yield after 7 minutes.

Figure S1. Catalyst in solution after 20 h storage under argon: a) Fe[\(\text{N(SiMe}_3\text{)}_2\)]\(_2\)-DiBAIH; b) FeCl\(_2\)(thf)\(_{1.5}\)-LiN(SiMe\(_3\))\(_2\)-DiBAIH; c) Fe[\(\text{N(SiMe}_3\text{)}_2\)]\(_2\)-AlMe\(_3\).
Synthesis of catalysts, reagents, and starting materials

General procedure for styrene synthesis in a Wittig reaction

A 50 mL flask was charged with a suspension of methyltriphenylphosphonium bromide (1 equiv.) in THF (0.7 M). Then, NaH-suspension in paraffine (60%, 1 equiv.) was added in small portions. The reaction mixture was stirred at room temperature for 20 h followed by a dropwise addition of a solution of a ketone/aldehyde derivative (1 equiv.) in THF (0.7 M). The reaction mixture was stirred for 2 d at room temperature, quenched with H₂O (15 mL) and extracted with Et₂O (3 × 15 mL). The combined organic layers were dried (Na₂SO₄), concentrated and subjected to silica gel flash chromatography (n-pentane).

Synthesis of \{Fe[N(SiMe₃)₂]₂\}

Synthesis according to R. A. Andersen, K. Faegri, J. C. Green, A. Haaland, M. F. Lappert, W. P. Leung, K. Rypdal, *Inorg. Chem.* 1988, 27, 1782–1786 with slight modifications.

A flame-dried Schlenk-flask under argon was charged with LiN(SiMe₃)₂ (6.37 g, 2.2 equiv., 38.1 mmol) in diethyl ether (60 mL). At 0 °C FeCl₂ (2.24 g, 1.0 equiv., 17.1 mmol, 97%) was added in portions. The resulting reaction mixture was allowed to warm to room temperature and stirred for 24 h. The solid residue was suspended in n-hexane (25 mL) filtered over a glass frit and washed with n-hexane (5 × 3 mL). After removing the solvent under reduced pressure, the crude product was purified by distillation under reduced pressure (90 °C, 10⁻³ mbar) to obtain a dark green oil which crystallizes upon standing at room temperature.

\( \text{C}_{24}\text{H}_{72}\text{Fe}_2\text{N}_4\text{Si}_8 \)
753.24 g/mol

Yield 4.71 g, 12.5 mmol (73%)

\(^1\text{H}-\text{NMR}\)
(400 MHz, C₆D₆) \(\delta = 64.10\) (bs).

Analytical data were in full agreement with R. A. Andersen, K. Faegri, J. C. Green, A. Haaland, M. F. Lappert, W. P. Leung, K. Rypdal, *Inorg. Chem.* 1988, 27, 1782–1786.

2,3-Dimethyl-1H-indene

Synthesis following the procedure described by M. V. Troutman, D. H. Appella, S. L. Buchwald, *J. Am. Chem. Soc.* 1999, 121, 4916–4917.

\( \text{C}_{11}\text{H}_{12} \)
144.22 g/mol

Appearance colorless liquid

Yield 1.49 g, 10.3 mmol (69%)

TLC \(R_t = 0.66\) (SiO₂, n-pentane)
\(^{1}\)H-NMR (300 MHz, CDCl\(_3\)) \(\delta 7.37\) (dp, \(J = 7.3, 0.9 \text{ Hz}, 1H\)), \(7.31 - 7.21\) (m, 2H), \(7.12\) (td, \(J = 7.2, 1.5 \text{ Hz}, 1H\)), \(3.31 - 3.21\) (m, 2H), \(2.07\) (q, \(J = 1.0 \text{ Hz}, 3H\)), \(2.04\) (tq, \(J = 2.1, 1.1 \text{ Hz}, 3H\)).

\(^{13}\)C-NMR (75 MHz, CDCl\(_3\)) \(\delta 126.05, 123.55, 122.97, 117.91, 42.46, 13.95, 10.17\).

GC-MS \(t_R = 6.77\) min, (EI, 70 eV): \(m/z = 144\) [M\(^+\)], 129, 115, 89, 77, 63, 51.

Analytical data were in full agreement with M. G. Schrems, E. Neumann, A. Pfaltz, *Angew. Chem. Int. Ed.* 2007, 46, 8274–8276.

**Dibenzo[\(a,e\)]cyclooctatetraene (dct)**

Synthesis following the procedure described by G. Franck, M. Brill, G. Helmchen, *J. Org. Chem.* 2012, 89, 55-65.

\[
\begin{array}{c}
\text{C}_{16}\text{H}_{12}
\end{array}
\]

204.27 g/mol

**Appearance**
colorless solid

**Yield**
912 mg, 4.46 mmol (47%)

**TLC**
\(R_f = 0.46\) (SiO\(_2\), hexanes)

\(^{1}\)H-NMR (300 MHz, CDCl\(_3\)): \(\delta 7.19 - 7.13\) (m, 4H), \(7.10 - 7.02\) (m, 4H), \(6.76\) (s, 4H).

\(^{13}\)C-NMR (75 MHz, CDCl\(_3\)): \(\delta 137.1, 133.3, 129.1, 126.8\).

**GC-MS**
\(t_R = 9.35\) min, (EI, 70 eV): \(m/z = 204\) [M\(^+\)].

Analytical data were in full agreement with G. Franck, M. Brill, G. Helmchen, *J. Org. Chem.* 2012, 89, 55-65.

**4-Phenyl-1,2-dihydronaphthalene**

Synthesis was performed by Schachtner, Josef, *Dissertation 2016*, Regensburg.

\[
\begin{array}{c}
\text{C}_{16}\text{H}_{14}
\end{array}
\]

206.29 g/mol

**Appearance**
colorless liquid

**Yield**
912 mg, 4.46 mmol (47%)

**TLC**
\(R_f = 0.41\) (SiO\(_2\), hexanes)
**1H-NMR**

(300 MHz, CDCl$_3$) $\delta$ 7.43 – 7.27 (m, 5H), 7.24 – 7.05 (m, 3H), 7.01 (dd, $J = 7.4$, 1.6 Hz, 1H), 6.09 (t, $J = 4.7$ Hz, 1H), 2.86 (t, $J = 7.9$ Hz, 2H), 2.42 (ddd, $J = 9.1$, 7.2, 4.7 Hz, 2H).

**13C-NMR**

(75 MHz, CDCl$_3$) $\delta$ 128.9, 128.3, 127.8, 127.7, 127.2, 126.3, 125.6, 28.4, 23.7.

**GC-MS**

$t_R = 9.37$ min, (EI, 70 eV): $m/z = 206$ [M]$^+$, 178, 165, 152, 128, 102, 78, 51.

Analytical data were in full agreement with P. Peach, D. J. Cross, J. A. Kenny, I. Houston, L. Campbell, T. Walsgrove, M. Wills, *Tetrahedron*, 2006, 62, 1864-1876.

1-Phenyl-1-cyclopentene

Synthesis was performed by Schachtner, Josef, *Dissertation 2016*, Regensburg.

![1-Phenyl-1-cyclopentene](image)

*C$_{11}$H$_{12}$*

144.22 g/mol

**Appearance**

colorless liquid

**Yield**

1.99 g, 13.8 mmol (69%)

**TLC**

$R_f = 0.66$ (SiO$_2$, hexanes)

**1H-NMR**

(300 MHz, CDCl$_3$) $\delta$ 7.48 – 7.42 (m, 2H), 7.36 – 7.27 (m, 2H), 7.25 – 7.18 (m, 1H), 6.19 (h, $J = 2.1$ Hz, 1H), 2.82 – 2.61 (m, 2H), 2.54 (tq, $J = 7.6$, 2.5 Hz, 2H), 2.15 – 1.93 (m, 2H).

**13C-NMR**

(75 MHz, CDCl$_3$) $\delta$ 128.29, 128.27, 127.60, 126.82, 126.12, 125.91, 125.54, 66.45, 33.37, 33.18, 28.91, 28.08, 23.37, 19.35.

**GC-MS**

$t_R = 6.94$ min, (EI, 70 eV): $m/z = 144$ [M]$^+$, 129, 115, 103, 91, 77, 63, 51.

Analytical data were in full agreement with W. Su, S. Urgaonkar, P. A. McLaughlin, J. G. Verkade, *J. Am. Chem. Soc.* 2004, 126, 16433–16439.

1-Phenyl-1-cycloheptene

Synthesis was performed by Schachtner, Josef, *Dissertation 2016*, Regensburg.

![1-Phenyl-1-cycloheptene](image)

*C$_{13}$H$_{16}$*

172.27 g/mol

**Appearance**

colorless liquid

**Yield**

2.89 g, 16.8 mmol (84%)
TLC  \( R_f = 0.69 \) (SiO\(_2\), hexanes)

\(^1\)H-NMR  
(300 MHz, CDCl\(_3\)) \( \delta \) 7.42 – 7.16 (m, 5H), 6.13 (td, \( J = 6.8, 1.3 \) Hz, 1H), 2.75 – 2.52 (m, 2H), 2.43 – 2.25 (m, 2H), 1.94 – 1.80 (m, 2H), 1.74 – 1.50 (m, 4H).

\(^{13}\)C-NMR  
(75 MHz, CDCl\(_3\)) \( \delta \) 144.99, 130.45, 128.13, 126.26, 125.67, 32.86, 32.82, 28.92, 26.98, 26.85.

GC-MS  
\( t_R = 7.97 \) min, (EI, 70 eV): \( m/z \) = 172 \([M^+]\), 157, 144, 129, 115, 104, 91, 77, 63, 51.

Analytical data were in full agreement with G. Baddeley, J. Chadwick, H. T. Taylor, *J. Chem. Soc.* **1956**, 451.

(1-cyclopropylvinyl)benzene

Synthesis following the general procedure for styrene synthesis in a Wittig reaction.

\[
\text{C}_{11}\text{H}_{12}
\]

144.22 g/mol

Appearance  colorless liquid

Yield  1.27 g, 8.8 mmol (80%)

TLC  \( R_f = 0.53 \) (SiO\(_2\), hexanes)

\(^1\)H-NMR  
(300 MHz, CDCl\(_3\)) \( \delta \) 7.67 – 7.57 (m, 2H), 7.42 – 7.26 (m, 3H), 5.30 (d, \( J =1.0, 1 \)H), 4.95 (t, \( J =1.2, 1 \)H), 1.67 (td, \( J =8.3, 5.4, 1.2, 1 \)H), 0.92 – 0.79 (m, 2H), 0.61 (ddd, \( J =6.4, 5.4, 4.1, 2 \)H).

\(^{13}\)C-NMR  
(75 MHz, CDCl\(_3\)) \( \delta \) 149.47, 141.75, 128.28, 127.58, 126.25, 109.15, 77.58, 77.16, 77.16, 76.74, 15.78, 6.83.

GC-MS  
\( t_R = 6.31 \) min, (EI, 70 eV): \( m/z = 144 \) \([M^+]\), 129, 115, 103, 91, 77, 63, 51.

Analytical data were in full agreement with C. Chatalova-Sazepin, Q. Wang, G. M. Sammis, J. Zhu, *Angew. Chem. Int. Ed.* **2015**, 54, 5443–5446.

4-(Cyclohex-1-enyl)-N,N-dimethylaniline

Synthesis was performed by Schachtner, Josef, *Dissertation 2016*, Regensburg.

\[
\text{C}_{14}\text{H}_{19}\text{N}
\]

201.31 g/mol
**Appearance**  
colorless liquid

**Yield**  
1.65 g, 8.20 mmol (82%)

**TLC**  
$R_f = 0.82$ (SiO<sub>2</sub>, hexanes)

**<sup>1</sup>H-NMR**  
(300 MHz, CDCl<sub>3</sub>) $\delta$ 7.41 – 7.19 (m, 2H), 6.76 (ddd, $J = 13.1, 6.8, 2.8$ Hz, 2H), 6.06 – 6.00 (m, 1H), 2.96 (d, $J = 2.8$ Hz, 6H), 2.35 – 2.49 (m, 2H), 2.27 – 2.14 (m, 2H), 1.87 – 1.73 (m, 2H), 1.61 – 1.72 (m, 2H).

**<sup>13</sup>C-NMR**  
(75 MHz, CDCl<sub>3</sub>) $\delta$ 149.4, 136.0, 129.1, 125.6, 121.7, 116.7, 112.7, 112.6, 40.8, 40.7, 27.4, 25.9, 23.2, 22.4.

**GC-MS**  
$t_R = 9.59$ min, (EI, 70 eV); $m/z = 202$ [M]<sup>+</sup>, 180, 157, 129, 101, 77, 51.

Analytical data were in full agreement with K. Ishiuka, H. Seike, T. Hatakeyama, M. Nakamura, *J. Am. Chem. Soc.* **2010**, 132, 13117-13119.

### 4-Bromo-α-methylstyrene

Synthesis following the general procedure for styrene synthesis in a Wittig reaction.

![C9H9Br](image)

197.08 g/mol

**Appearance**  
colorless oil

**Yield**  
1.06 g, 5.39 mmol (77%)

**TLC**  
$R_f = 0.59$ (SiO<sub>2</sub>, n-pentane)

**<sup>1</sup>H-NMR**  
(400 MHz, CDCl<sub>3</sub>) $\delta$ 7.50-7.35 (m, 2H), 7.42-7.29 (m, 2H), 5.36 (s, 1H), 5.10 (s, 1H), 2.12 (s, 3H).

**<sup>13</sup>C-NMR**  
(101 MHz, CDCl<sub>3</sub>) $\delta$ 142.2, 140.1, 131.3, 127.2, 121.4, 113.1, 21.7.

**GC-MS**  
$t_R = 6.51$ min, (EI, 70 eV); $m/z = 197$ [M]<sup>+</sup>, 183, 171, 156, 115, 102, 91, 75, 63, 51.

Analytical data were in full agreement with T. Taniguchi, A. Yajima, H. Ishibashi, *Adv. Synth. Catal.* **2011**, 353, 2643–2647.

### 4-Iodo-α-methylstyrene

Synthesis following the general procedure for styrene synthesis in a Wittig reaction.

![C9H9I](image)

244.08 g/mol
Appearance: colorless solid
Yield: 1.21 g, 4.96 mmol (71%)

TLC: $R_f = 0.84$ (SiO$_2$, n-pentane)

$^1$H-NMR: (300 MHz, CDCl$_3$) $\delta$ 7.70 – 7.59 (m, 2H), 7.24 – 7.15 (m, 2H), 5.40 – 5.33 (m, 1H), 5.12 – 5.07 (m, 1H), 2.14 – 2.09 (m, 3H).

$^{13}$C-NMR: (75 MHz, CDCl$_3$) $\delta$ 142.28, 140.70, 137.27, 134.97, 127.41, 113.15, 92.88, 21.62.

GC-MS: $t_R = 7.14$ min, (EI, 70 eV): $m/z = 244$ [M$^+$], 127, 115, 102, 91, 75, 63, 50.

Analytical data were in full agreement with G. B. Bachman, C. L. Carlson, M. Robinson, *J. Am. Chem. Soc.* 1951, 73, 1964–1965.

4-Methoxy-α-methylstyrene

Synthesis following the general procedure for styrene synthesis in a Wittig reaction.

$\text{C}_{18}\text{H}_{12}\text{O}$
148.20 g/mol

Appearance: colorless liquid
Yield: 1.04 g, 7.02 mmol (35%)

TLC: $R_f = 0.25$ (SiO$_2$, n-pentane)

$^1$H-NMR: (300 MHz, CDCl$_3$) $\delta$ 7.42 (d, $J = 8.9$ Hz, 2H), 6.87 (d, $J = 8.9$ Hz, 2H), 5.29 (s, 1H), 4.99 (s, 1H), 3.82 (s, 3H), 2.13 (s, 3H).

$^{13}$C-NMR: (75 MHz, CDCl$_3$) $\delta$ 159.05, 142.56, 133.74, 126.60, 113.54, 110.68, 55.30, 21.94.

GC-MS: $t_R = 6.39$ min, (EI, 70 eV): $m/z = 148$ [M$^+$], 127, 133, 115, 105, 89, 77, 75, 63, 51.

Analytical data were in full agreement with A. Fryszkowska, K. Fisher, J. M. Gardiner, G. M. Stephens, *J. Org. Chem.* 2008, 73, 4295–4298.

Methyl(4-(prop-1-en-2-yl)phenyl)sulfane

Synthesis following the general procedure for styrene synthesis in a Wittig reaction.

$\text{C}_{10}\text{H}_{12}\text{S}$
164.27 g/mol

Appearance: colorless solid
Yield 1.09 g, 6.63 mmol (33%)

TLC $R_t = 0.44$ (SiO$_2$, n-pentane)

$^1$H-NMR (300 MHz, CDCl$_3$) $\delta$ 7.45 – 7.35 (m, 2H), 7.25 – 7.18 (m, 2H), 5.36 (dq, $J$=1.6, 0.8, 1H), 5.06 (dq, $J$=1.5, 1.5, 1H), 2.49 (s, 3H), 2.14 (dd, $J$=1.5, 0.8, 3H).

$^{13}$C-NMR (75 MHz, CDCl$_3$) $\delta$ 142.51, 138.01, 137.49, 126.37, 125.90, 111.96, 21.75, 15.91.

GC-MS $t_R = 7.38$ min, (EI, 70 eV): $m/z$ = 164 [M$^+$], 149, 134, 115, 102, 91, 77, 69, 51.

Analytical data were in full agreement with G. Fraenkel, J. M. Geckle, *J. Am. Chem. Soc.* 1980, 102, 2869–2880.

1-(Benzyloxy)-4-vinylbenzene

Synthesis following the general procedure for styrene synthesis in a Wittig reaction.

$$\text{C}_{15}\text{H}_{14}\text{O}$$

210.27 g/mol

Appearance colorless solid

Yield 1.25 g, 5.97 mmol (74%)

TLC $R_t = 0.28$ (SiO$_2$, n-pentane)

$^1$H-NMR (300 MHz, CDCl$_3$) $\delta$ 7.49 – 7.29 (m, 7H), 6.99 – 6.90 (m, 2H), 6.67 (dd, $J$ = 17.6, 10.9 Hz, 1H), 5.63 (dd, $J$ = 17.6, 0.9 Hz, 1H), 5.14 (dd, $J$ = 10.9, 0.9 Hz, 1H), 5.08 (s, 2H).

$^{13}$C-NMR (75 MHz, CDCl$_3$) $\delta$ 158.57, 136.94, 136.21, 130.69, 128.63, 128.02, 127.50, 127.43, 114.88, 111.75, 70.03.

GC-MS $t_R = 9.40$ min, (EI, 70 eV): $m/z$ = 197 [M$^+$], 183, 171, 156, 115, 102, 91, 75, 63, 51.

Analytical data were in full agreement with N. Kakusawa, K. Yamaguchi, J. Kouchichiro, *J. Organomet. Chem.* 2005, 12, 2956-2966.

4-(Benzyloxy)benzaldehyde

Synthesis following the procedure by S. K. Das, G. Panda, *Tetrahedron* 2008, 19, 4162-4173.

$$\text{C}_{14}\text{H}_{12}\text{O}_2$$

212.24 g/mol

Appearance colorless solid
Yield  
1.72 g, 8.12 mmol (81%)

TLC  
$R_t = 0.20$ (SiO$_2$, hexanes/ethyl acetate = 9/1)

$^1$H-NMR  
(300 MHz, CDCl$_3$) $\delta$ 9.89 (s, 1H), 7.84 (d, $J = 8.7$ Hz, 2H), 7.48 – 7.33 (m, 5H), 7.08 (d, $J = 8.7$ Hz, 2H), 5.16 (s, 2H).

$^{13}$C-NMR  
(75 MHz, CDCl$_3$) $\delta$ 190.82, 163.72, 135.93, 132.02, 130.11, 128.75, 128.36, 127.51, 115.15, 70.28.

GC-MS  
$t_R = 9.96$ min, (EI, 70 eV); $m/z = 212$ [M$^+$], 152, 121, 91, 77, 65, 51.

Analytical data were in full agreement with T. Shintou, T. Mukaiyama, *J. Am. Chem. Soc.*, 2004, 23, 7359-7367.

1-(but-3-en-1-yloxy)-4-fluorobenzene

Synthesis following the procedure by J. A. Murphy, F. Schoenebeck, N. J. Findlay, D. W. Thomson, S. Zhou, J. Garnier; *J. Am. Chem. Soc.*, 2009, 131, 6475-6479.

\[
\begin{align*}
&\text{C}_{10}\text{H}_{11}\text{FO} \\
&166.20 \text{ g/mol}
\end{align*}
\]

**Appearance**  
colorless liquid

Yield  
1.89 g, 11.38 mmol (76%)

TLC  
$R_t = 0.80$ (SiO$_2$, hexanes/ethyl acetate = 99/1)

$^1$H-NMR  
(300 MHz, CDCl$_3$) $\delta$ 7.03 – 6.91 (m, 2H), 6.88 – 6.78 (m, 2H), 5.90 (ddt, $J = 17.0$, 10.2, 6.7 Hz, 1H), 5.14 (qdd, $J = 3.0$, 2.6, 1.4 Hz, 2H), 3.97 (t, $J = 6.7$ Hz, 2H), 2.53 (qt, $J = 6.7$, 1.3 Hz, 2H).

$^{13}$C-NMR  
(75 MHz, CDCl$_3$) $\delta$ 158.81, 155.66, 155.00, 134.37, 117.11, 115.92, 115.62, 115.59, 115.49, 67.86, 33.67.

GC-MS  
$t_R = 5.96$ min, (EI, 70 eV); $m/z = 166$ [M$^+$], 138, 125, 112, 95, 83, 75, 55.

HRMS  
(EI, $m/z$): found 166.0798 [M$^+$] (calculated 166.0794).

FT-IR  
(ATR-film) in [cm$^{-1}$] 2872 (w), 1642 (w), 1504 (s), 1472 (m), 1431 (w), 1388 (w), 1294 (w), 1247 (m), 1202 (s), 1096 (m), 1036 (m), 988 (m), 916 (s), 825 (s), 744 (s), 513 (s).

*N*-Methyl-1,2,3,6-tetrahydrophthalimide

Synthesis was performed by Schachtner, Josef, *Dissertation 2016*, Regensburg.
\[ \text{C}_9\text{H}_{11}\text{NO}_2 \]

165.19 g/mol

**Appearance**  
colorless solid

**Yield**  
5.7 g, 34.5 mmol (70%)

**TLC**  
\( R_f = 0.42 \) (SiO\(_2\), hexanes/ethyl acetate 2/1)

**\(^1\)H-NMR**  
(400 MHz, CDCl\(_3\)) \( \delta \) 5.92-5.85 (m, 2H), 3.12-3.05 (m, 2H), 2.96 (s, 3H), 2.64-2.58 (m, 2H), 2.27-2.19 (m, 2H).

**GC-MS**  
\( t_R = 7.58 \) min (EI, 70 eV): \( m/z = 165 \ [M^+] \), 150, 136, 107, 80, 65, 57, 51.

Analytical data were in full agreement with E. Schefczik, *Chem. Ber.* 1965, 98, 1270–1281.

---

(3-methylbut-2-en-2-yl)benzene

Synthesis following the procedure by W. Adam, M. A. Arnold, M. Grüne, W. M. Nau, U. Pischel, C. R. Saha-Möller, *Organic Letters* 2002, 4, 537-540.

\[ \text{C}_{11}\text{H}_{14} \]

146.23 g/mol

**Appearance**  
colorless liquid

**Yield**  
850 mg, 5.8 mmol (39%)

**\(^1\)H-NMR**  
(300 MHz, CDCl\(_3\)) \( \delta \) 7.36 – 7.13 (m, 5H), 1.99 (s, 3H), 1.84 (s, 3H), 1.62 (s, 3H).

**\(^{13}\)C-NMR**  
(75 MHz, CDCl\(_3\)) \( \delta \) 145.35, 130.00, 128.44, 127.94, 127.23, 125.73, 22.11, 20.85, 20.59.

**GC-MS**  
\( t_R = 5.62 \) min, (EI, 70 eV): \( m/z = 146 \ [M^+] \), 131, 115, 103, 91, 77, 65, 51.

Analytical data were in full agreement with W. Adam, M. A. Arnold, M. Grüne, W. M. Nau, U. Pischel, C. R. Saha-Möller, *Org. Lett.* 2002, 4, 537-540.
Hydrogenation products

Propane-1,2-diyl dibenzene

\[
\text{C}_{16}\text{H}_{16} \\
196.29 \text{ g/mol}
\]

\text{H-NMR} \\
(300 MHz, CDCl\textsubscript{3}) \(\delta\) 7.44 – 7.10 (m, 10H), 3.17 – 2.95 (m, 2H), 2.91 – 2.78 (m, 1H), 1.31 (d, \(J = 6.8\) Hz, 3H).

\text{C-NMR} \\
(75 MHz, CDCl\textsubscript{3}) \(\delta\) 147.05, 140.88, 129.23, 128.37, 128.17, 127.11, 126.09, 125.91, 45.13, 41.96, 21.23.

\text{GC-MS} \\
\(t_R = 8.24\) min, (EI, 70 eV): \(m/z = 196\) [M\textsuperscript{+}], 178, 165, 152, 139, 128, 115, 105, 91, 77, 65, 51.

Analytical data were in full agreement with C. Metallinos, J. Zaifman, L. Van Belle, L. Dodge, M. Pilkington, \textit{Organometallics} 2009, 28, 4534-4543.

2,3,4-trimethylpentane

\[
\text{C}_{10}\text{H}_{18} \\
114.23 \text{ g/mol}
\]

\text{H-NMR} \\
(300 MHz, CDCl\textsubscript{3}) \(\delta\) 1.73 – 1.54 (m, \(J = 6.7\) Hz, 2H), 1.00 – 0.92 (m, 1H), 0.87 (d, \(J = 6.8\) Hz, 6H), 0.79 (d, \(J = 6.7\) Hz, 6H), 0.73 (d, \(J = 6.8\) Hz, 3H).

\text{C-NMR} \\
(75 MHz, CDCl\textsubscript{3}) \(\delta\) 45.12, 29.65, 21.73, 18.31, 10.81.

\text{GC-MS} \\
\(t_R = 2.24\) min, (EI, 70 eV): \(m/z = 114\) [M\textsuperscript{+}], 83, 71, 55.

Analytical data were in full agreement with the data available on vendor website (Sigma-Aldrich product number 257508, CAS Number 565-75-3)

(3-methylbutan-2-yl)benzene

\[
\text{C}_{11}\text{H}_{16} \\
148.28 \text{ g/mol}
\]

\text{H-NMR} \\
(300 MHz, CDCl\textsubscript{3}) \(\delta\) 7.35 – 7.14 (m, 5H), 2.42 (p, \(J = 7.2\) Hz, 1H), 1.77 (dp, \(J = 7.7, 6.6\) Hz, 1H), 1.24 (d, \(J = 7.0\) Hz, 3H), 0.94 (d, \(J = 6.7\) Hz, 3H), 0.76 (d, \(J = 6.7\) Hz, 3H).

\text{C-NMR} \\
(75 MHz, CDCl\textsubscript{3}) \(\delta\) 147.10, 128.02, 127.65, 125.68, 125.10, 46.88, 34.45, 21.20, 20.20, 18.78.

\text{GC-MS} \\
\(t_R = 5.41\) min, (EI, 70 eV): \(m/z = 148\) [M\textsuperscript{+}], 131, 115, 105, 77, 65, 51.

Analytical data were in full agreement with V. Jurčík, S. P. Nolan, C. S. J. Cazin, \textit{Chemistry – A European Journal} 2009, 15, 2509-2511.

1,2-dimethyl-2,3-dihydro-1\textit{H}-indene

\[
\text{C}_{10}\text{H}_{14} \\
146.23 \text{ g/mol}
\]
\( ^1H\text{-NMR} \quad (400 \text{ MHz, CDCl}_3) \delta 7.23 - 7.10 (m, 4H), 3.17 (p, J = 7.1 \text{ Hz, 1H}), 3.04 - 2.92 (m, 1H), 2.63 - 2.53 (m, 2H), 1.15 (d, J = 7.2 \text{ Hz, 3H}), 0.99 (d, J = 6.8 \text{ Hz, 3H}). \)

\( ^{13}C\text{-NMR} \quad (75 \text{ MHz, CDCl}_3) \delta 148.81, 142.95, 126.10, 126.04, 124.48, 123.59, 42.39, 39.39, 37.84, 15.20, 14.67. \)

\( \text{GC-MS} \quad t_R = 6.03 \text{ min, (EI, 70 eV): } m/z = 146 [M^+] , 131, 115, 103, 91, 77, 63, 51. \)

Analytical data were in full agreement with R. P. Yu, J. M. Darmon, J. M. Hoyt, G. W. Margulieux, Z. R. Turner, P. J. Chirik, ACS Catal. 2012, 2, 1760–1764.

5,6,11,12-tetrahydrodibenzo[a,e][8]annulene

\[
\begin{array}{c}
\text{C}_{16}\text{H}_{16} \\
\text{208.30 g/mol}
\end{array}
\]

\( ^1H\text{-NMR} \quad (300 \text{ MHz, CDCl}_3) \delta 7.06 - 6.93 (m, 8H), 3.07 (s, 8H). \)

\( ^{13}C\text{-NMR} \quad (75 \text{ MHz, CDCl}_3) \delta 140.60, 129.67, 126.10, 35.16. \)

\( \text{GC-MS} \quad t_R = 9.45 \text{ min, (EI, 70 eV): } m/z = 208 [M^+] , 193, 178, 165, 115, 104, 91, 78, 63, 51. \)

Analytical data were in full agreement with D. Guijarro, B. Mancheño, M. Yus, Tetrahedron 1992, 48, 4593–4600.

Phenylcyclohexane

\[
\begin{array}{c}
\text{C}_{12}\text{H}_{16} \\
\text{160.26 g/mol}
\end{array}
\]

\( ^1H\text{-NMR} \quad (300 \text{ MHz, CDCl}_3) \delta 7.34 - 7.25 (m, 2H), 7.24 - 7.14 (m, 3H), 2.60 - 2.39 (m, 1H), 2.00 - 1.79 (m, 4H), 1.80 - 1.73 (m, 1H), 1.51 - 1.19 (m, 5H). \)

\( ^{13}C\text{-NMR} \quad (75 \text{ MHz, CDCl}_3) \delta 148.1, 128.3, 126.5, 125.8, 44.7, 34.52, 27.0, 26.2. \)

\( \text{GC-MS} \quad t_R = 7.30 \text{ min, (EI, 70 eV): } m/z = 160 [M^+] , 143, 129, 115, 102, 91, 77, 63, 51. \)

Analytical data were in full agreement with W. M. Czaplik, M. Mayer, A. Jacobi von Wangelin, Angew. Chem. Int. Ed. 2009, 48, 607–610.
1-Phenyl-1,2,3,4-tetrahydronaphthalene

![C16H16](image)

\[ \text{C}_{16}\text{H}_{16} \]

208.30 g/mol

\( ^1\text{H-NMR} \) (300 MHz, CDCl\textsubscript{3}) \( \delta \) 7.37 – 7.10 (m, 7H), 7.09 – 7.01 (m, 1H), 6.86 (d, \( J = 7.8 \) Hz, 1H), 4.14 (t, \( J = 6.6 \) Hz, 1H), 3.04 – 2.76 (m, 2H), 2.31 – 2.10 (m, 1H), 2.03 – 1.68 (m, 3H).

\( ^{13}\text{C-NMR} \) (75 MHz, CDCl\textsubscript{3}) \( \delta \) 147.55, 139.40, 137.61, 130.21, 128.99, 128.88, 128.25, 125.96, 125.92, 125.66, 45.65, 33.30, 29.82, 21.00.

\( \text{GC-MS} \) \( t_R = 9.33 \) min, (EI, 70 eV): \( m/\ell = 208 \) [M\textsuperscript{+}], 179, 165, 152, 130, 115, 104, 91, 78, 63, 51.

Analytical data were in full agreement with S. T. Bright, J. M. Coxon, P. J. Steel, \textit{J. Org. Chem.} \textbf{1990}, \textit{55}, 1338–1344.

Phenylcycloheptane

![C13H18](image)

\[ \text{C}_{13}\text{H}_{18} \]

174.29 g/mol

\( ^1\text{H-NMR} \) (300 MHz, CDCl\textsubscript{3}) \( \delta \) 7.35 – 7.11 (m, 5H), 2.76 – 2.56 (m, 1H), 2.00 – 1.75 (m, 4H), 1.74 – 1.49 (m, 8H).

\( ^{13}\text{C-NMR} \) (75 MHz, CDCl\textsubscript{3}) \( \delta \) 150.05, 128.31, 126.70, 125.52, 47.10, 36.86, 27.99, 27.27.

\( \text{GC-MS} \) \( t_R = 7.80 \) min, (EI, 70 eV): \( m/\ell = 174 \) [M\textsuperscript{+}], 117, 104, 91, 78, 65, 55.

Analytical data were in full agreement with S. Kawamura, K. Ishizuka, H. Takaya, M. Nakamura, \textit{Chem. Commun.} \textbf{2010}, \textit{46}, 6054–6056.

1,1-Diphenylethane

![C14H14](image)

\[ \text{C}_{14}\text{H}_{14} \]

182.27 g/mol

\( ^1\text{H-NMR} \) (300 MHz, CDCl\textsubscript{3}) \( \delta \) 7.35 – 7.11 (m, 10H), 4.15 (q, \( J = 7.1 \) Hz, 1H), 1.63 (d, \( J = 7.2 \) Hz, 3H).

\( \text{GC-MS} \) \( t_R = 7.97 \) min, (EI, 70 eV): \( m/\ell = 182 \) [M\textsuperscript{+}], 167, 152, 139, 128, 115, 103, 89, 77, 63, 51.

Analytical data were in full agreement with F. Schoenebeck, J. A. Murphy, S.-z. Zhou, Y. Uenoyama, Y. Miclo, T. Tuttle, \textit{J. Am. Chem. Soc.} \textbf{2007}, \textit{129}, 13368–13369.
1-Cyclopropyl-1-phenylethane

\[
\text{C}_{11}\text{H}_{14}
\]

146.23 g/mol

\textsuperscript{1}H-NMR (300 MHz, CDCl\textsubscript{3}) \(\delta\) 7.41 – 7.26 (m, 4H), 7.25 – 7.17 (m, 1H), 1.99 (dq, \(J = 9.2, 7.0\) Hz, 1H), 1.35 (d, \(J = 7.0\) Hz, 3H), 0.96 (qt, \(J = 9.1, 8.0, 5.0\) Hz, 1H), 0.65 – 0.36 (m, 2H), 0.27 – 0.09 (m, 2H).

\textsuperscript{13}C-NMR (75 MHz, CDCl\textsubscript{3}) \(\delta\) 147.38, 128.23, 127.00, 125.89, 44.67, 21.62, 18.56, 4.64, 4.34.

GC-MS \(t_R = 5.87\) min, (EI, 70 eV): \(m/z = 146\) [M\(^+\)], 131, 117, 105, 91, 77, 65, 51.

Analytical data were in full agreement with T. N. Gieshoff, M. Villa, A. Welther, M. Plois, U. Chakraborty, R. Wolf, A. Jacobi von Wangelin, Green Chem 2015, 17, 1408–1413.

2,6,10-Trimethyldodecane

\[
\text{C}_{18}\text{H}_{32}
\]

212.42 g/mol

\textsuperscript{1}H-NMR (300 MHz, CDCl\textsubscript{3}) \(\delta\) 1.77 – 1.44 (m, 4H), 1.42 – 0.98 (m, 14H), 0.93 – 0.75 (m, 14H).

\textsuperscript{13}C-NMR (75 MHz, CDCl\textsubscript{3}) \(\delta\) 42.41, 39.43, 39.39, 37.88, 37.48, 37.43, 37.41, 37.32, 37.01, 36.97, 35.76, 35.64, 34.47, 34.44, 34.42, 33.07, 32.83, 32.80, 30.56, 29.59, 29.49, 28.47, 28.00, 25.31, 24.84, 24.53, 22.78, 22.74, 22.64, 19.76, 19.70, 19.28, 19.22, 16.22, 11.46, 11.43.

GC-MS \(t_R = 7.18\) min, (EI, 70 eV): \(m/z = 212\) [M\(^+\)], 183, 127, 113, 85, 71, 57.

Analytical data were in full agreement with D. K. Dalling, R. J. Pugmire, D. M. Grant, W. E. Hull, Magn. Reson. Chem. 1986, 24, 191–198.

Ethane-1,1,2-triyltribenzene

\[
\text{C}_{20}\text{H}_{18}
\]

258.36 g/mol
$^1$H-NMR (300 MHz, CDCl$_3$) δ 7.30 – 7.09 (m, 13H), 7.05 – 6.95 (m, 2H), 4.24 (t, $J = 7.8$ Hz, 1H), 3.37 (d, $J = 7.8$ Hz, 2H).

$^{13}$C-NMR (75 MHz, CDCl$_3$) δ 144.45, 140.26, 129.08, 128.34, 128.05, 126.19, 125.88, 53.11, 42.11.

GC-MS $t_R = 10.67$ min, (EI, 70 eV): $m/z = 258$ [M$^+$], 167, 152, 139, 128, 115, 102, 91, 77, 65, 51.

Analytical data were in full agreement with T. C. Fessard, H. Motoyoshi, E. M. Carreira, *Angew. Chem. Int. Ed.* 2007, 46, 2078–2081.

**Pinane**

Mixture of diastereomers.

$\text{C}_{10}\text{H}_{18}$

138.25 g/mol

$^1$H-NMR mixture of isomers

$^{13}$C-NMR (75 MHz, CDCl$_3$) δ 67.98, 65.88, 48.07, 47.62, 41.35, 40.88, 39.49, 38.82, 35.95, 33.96, 29.35, 28.30, 26.84, 26.54, 25.63, 24.61, 23.93, 23.83, 23.22, 23.04, 22.90, 21.61, 20.09, 15.29.

GC-MS $t_R = 4.67$ min, (EI, 70 eV): $m/z = 138$ [M$^+$], 123, 95, 81, 67, 55.

Analytical data were in full agreement with A. Stolle, B. Ondruschka, W. Bonrath, T. Netscher, M. Findeisen, M. M. Hoffmann, *Chemistry* 2008, 14, 6805–6814.

**1,2,3,4-Tetrahydroquinoline**

$\text{C}_9\text{H}_{11}\text{N}$

133.19 g/mol

$^1$H-NMR (300 MHz, CDCl$_3$) δ 7.03 – 6.92 (m, 2H), 6.62 (td, $J = 7.4$, 1.2 Hz, 1H), 6.50 (d, $J = 7.8$ Hz, 1H), 3.98 (s, 1H), 3.37 – 3.25 (m, 2H), 2.78 (t, $J = 6.4$ Hz, 2H), 2.03 – 1.88 (m, 2H).

$^{13}$C-NMR (75 MHz, CDCl$_3$) δ 144.82, 129.56, 126.76, 121.48, 116.97, 114.23, 42.03, 27.02, 22.22.

GC-MS $t_R = 7.17$ min, (EI, 70 eV): $m/z = 133$ [M$^+$], 118, 104, 91, 77, 63, 51.
Analytical data were in full agreement with M. Ortiz-Marciales, L. D. Rivera, M. de Jesus, S. Espinosa, J. A. Benjamin, O. E. Casanova, I. G. Figueroa, S. Rodríguez, W. Correa, J. Org. Chem. 2005, 70, 10132–10134.

10,11-Dihydro-5H-dibenzo[b,f]azepine

![10,11-Dihydro-5H-dibenzo[b,f]azepine](image)

$\text{C}_{14}\text{H}_{13}\text{N}$

195.27 g/mol

$^1\text{H-NMR}$

(300 MHz, CDCl$_3$) $\delta$ 7.18 – 7.04 (m, 4H), 6.89 – 6.66 (m, 4H), 6.02 (s, 1H), 3.12 (s, 4H).

$^{13}\text{C-NMR}$

(75 MHz, CDCl$_3$) $\delta$ 141.38, 129.62, 127.57, 125.76, 118.38, 116.86, 33.87.

GC-MS

$t_R = 10.16 \text{ min}, \text{ (EI, 70 eV)}: m/z = 195 [\text{M}^+]$, 180, 167, 152, 118, 97, 89, 77, 63, 51.

Analytical data were in full agreement with J. A. Profitt, H. H. Ong, J. Org. Chem. 1979, 44, 3972–3974.

4-Cyclohexyl-N,N-dimethylaniline

![4-Cyclohexyl-N,N-dimethylaniline](image)

$\text{C}_{14}\text{H}_{21}\text{N}$

203.33 g/mol

$^1\text{H-NMR}$

(300 MHz, CDCl$_3$) $\delta$ 7.15 – 7.07 (m, 2H), 6.77 – 6.72 (m, 2H), 2.93 (s, 6H), 2.52 – 2.38 (m, 1H), 1.94 – 1.80 (m, 4H), 1.78 – 1.70 (m, 1H), 1.48 – 1.34 (m, 4H), 1.34 – 1.25 (m, 1H).

$^{13}\text{C-NMR}$

(75 MHz, CDCl$_3$) $\delta$ 127.34, 113.11, 43.53, 41.06, 34.75, 27.05, 26.26.

GC-MS

$t_R = 9.30 \text{ min}, \text{ (EI, 70 eV)}: m/z = 203, 160, 146, 134, 118, 103, 91, 77, 65, 55.$

Analytical data were in full agreement with Z. Li, H.-M. Sun, Q. Shen, Org. Biomol. Chem. 2016, 14, 3314–3321.

1-Chloro-4-isopropylbenzene

![1-Chloro-4-isopropylbenzene](image)

$\text{C}_9\text{H}_{11}\text{Cl}$

154.64 g/mol

$^1\text{H-NMR}$

(300 MHz, CDCl$_3$) $\delta$ 7.25 (m, 2H), 7.21–7.09 (m, 2H), 2.89 (m, 1H), 1.23 (d, $J = 6.9 \text{ Hz}$, 6H).
\[ \text{C-NMR} \quad (75 \text{ MHz}, \text{CDCl}_3) \delta 142.3, 131.3, 128.4, 127.8, 33.6, 23.9. \]

\[ \text{GC-MS} \quad t_R = 5.37 \text{ min, (EI, 70 eV): } m/z = 154 \ [\text{M}^+], 139, 125, 119, 105, 89, 77, 63, 51. \]

Analytical data were in full agreement with S. S. Kim, C. S. Kim, J. Org. Chem. 1999, 64, 9261–9264.

1-Bromo-4-isopropylbenzene

\[ \text{C}_9\text{H}_{11}\text{Br} \quad 199.09 \text{ g/mol} \]

\[ \text{H-NMR} \quad (300 \text{ MHz}, \text{CDCl}_3) \delta 7.47 – 7.36 (\text{m, 2H}), 7.15 – 7.04 (\text{m, 2H}), 2.87 (\text{hept, } J = 6.9 \text{ Hz, 1H}), 1.23 (\text{d, } J = 6.9 \text{ Hz, 6H}). \]

\[ \text{C-NMR} \quad (101 \text{ MHz}, \text{CDCl}_3) \delta 147.8, 131.3, 128.2, 119.3, 33.7, 30.9, 23.8. \]

\[ \text{GC-MS} \quad t_R = 6.16 \text{ min, (EI, 70 eV): } m/z = 198 \ [\text{M}^+], 185, 169, 158, 143, 119, 104, 91, 77, 63, 51. \]

Analytical data were in full agreement with M. A. Hall, J. Xi, C. Lor, S. Dai, R. Pearce, W. P. Dailey, R. G. Eckenhoff, J. Med. Chem. 2010, 53, 5667–5675.

1-Isopropyl-4-methoxybenzene

\[ \text{C}_{10}\text{H}_{14}\text{O} \quad 180.24 \text{ g/mol} \]

\[ \text{H-NMR} \quad (300 \text{ MHz}, \text{CDCl}_3) \delta 7.15 (\text{d, } J = 8.8 \text{ Hz, 2H}), 6.84 (\text{d, } J = 8.7 \text{ Hz, 2H}), 3.79 (\text{s, 3H}), 2.95 – 2.78 (\text{m, 1H}), 1.24 (\text{s, 3H}), 1.21 (\text{s, 3H}). \]

\[ \text{C-NMR} \quad (75 \text{ MHz}, \text{CDCl}_3) \delta 156.86, 141.06, 127.26, 113.77, 55.27, 33.28, 24.24. \]

\[ \text{GC-MS} \quad t_R = 5.93 \text{ min, (EI, 70 eV): } m/z = 150 \ [\text{M}^+], 120, 105, 91, 77, 65, 51. \]

Analytical data were in full agreement with Cahiez, G.; Foulgoc, L.; Moyeux, A. Angew. Chem. Int. Ed. 2009, 48, 2969–2972.

Methyl(4-(prop-2-yl)phenyl)sulfane

\[ \text{C}_{10}\text{H}_{14}\text{S} \quad 166.28 \text{ g/mol} \]
$^1$H-NMR (300 MHz, CDCl$_3$) δ 7.26 – 7.19 (m, 2H), 7.19 – 7.13 (m, 2H), 2.88 (p, $J = 6.9$ Hz, 1H), 2.48 (s, 3H), 1.24 (d, $J = 6.9$ Hz, 6H).

$^{13}$C-NMR (75 MHz, CDCl$_3$) δ 146.11, 135.05, 127.20, 127.01, 77.47, 77.04, 76.62, 33.65, 24.00, 16.42.

GC-MS $t_R = 7.20$ min, (EI, 70 eV): $m/z = 166$ [M$^+$], 151, 136, 104, 91, 77, 51.

Analytical data were in full agreement with X.-m. Wu, J.-m. Lou, G.-b. Yan, *Synlett* 2016, 27, 2269–2273.

**4-Ethylaniline**

![Chemical structure of 4-Ethylaniline](image)

$C_8H_{11}N$

121.18 g/mol

$^1$H-NMR (300 MHz, CDCl$_3$) δ 7.01 (d, $J = 8.5$ Hz, 2H), 6.68 (d, $J = 8.3$ Hz, 2H), 3.78 (s, 2H), 2.56 (q, $J = 7.6$ Hz, 2H), 1.20 (t, $J = 7.6$ Hz, 3H).

$^{13}$C-NMR (101 MHz, CDCl$_3$) δ 143.23, 134.98, 128.64, 115.64, 28.03, 15.98.

GC-MS $t_R = 6.11$ min, (EI, 70 eV): $m/z = 121$ [M$^+$], 106, 93, 77, 65, 51.

Analytical data were in full agreement with B. Wang, H.-X. Sun, G.-Q. Lin, Z.-H. Sun, *Adv. Synth. Catal.* 2009, 351, 415-422.

**1-Benzzyloxy-4-ethylbenzene**

![Chemical structure of 1-Benzzyloxy-4-ethylbenzene](image)

$C_{15}H_{16}O$

212.29 g/mol

$^1$H-NMR (300 MHz, CDCl$_3$) δ 7.51 – 7.30 (m, 5H), 7.18 – 7.11 (m, 2H), 6.97 – 6.89 (m, 2H), 5.07 (s, 2H), 2.62 (q, $J = 7.6$ Hz, 2H), 1.24 (t, $J = 7.6$ Hz, 3H).

$^{13}$C-NMR (75 MHz, CDCl$_3$) δ 156.89, 137.30, 136.72, 128.78, 128.60, 127.92, 127.52, 114.72, 70.08, 28.03, 15.93.

GC-MS $t_R = 9.17$ min, (EI, 70 eV): $m/z = 212$ [M$^+$], 122, 107, 91, 77, 65, 51.

Analytical data were in full agreement with C. Zhu, N. Yukimura, M. Yamane, *Organometallics* 2010, 29, 2098–2103.

**Trimethyl-(1-phenylethoxy)silane**
C_{11}H_{18}OSi

194.35 g/mol

^1H-NMR (300 MHz, CDCl\textsubscript{3}) δ 7.36 – 7.18 (m, 5H), 4.86 (q, J = 6.4 Hz, 1H), 1.43 (d, J = 6.3 Hz, 3H), 0.07 (s, 9H).

^13C-NMR (75 MHz, CDCl\textsubscript{3}) δ 146.33, 128.02, 126.73, 125.24, 70.48, 26.78, 0.00.

GC-MS \( t_R = 5.74 \text{ min}, \) (EI, 70 eV): \( m/z = 179 \) [M-CH\textsubscript{3}], 105, 75, 51.

Analytical data were in full agreement with Y. Onishi, Y. Nishimoto, M. Yasuda, A. Baba, Org. Lett. 2011, 13, 2762–2765.

4-Fluorobenzyl-\textit{n}-butylether

C_{10}H_{13}FO

168.21 g/mol

^1H-NMR (300 MHz, CDCl\textsubscript{3}) δ 7.02 – 6.91 (m, 2H), 6.87 – 6.78 (m, 2H), 3.92 (t, J = 6.5 Hz, 2H), 1.75 (m, 2H), 1.56 – 1.41 (m, 2H), 0.97 (t, J = 7.4 Hz, 3H).

^13C-NMR (75 MHz, CDCl\textsubscript{3}) δ 158.68, 155.53, 155.28, 115.87, 115.56, 115.44, 115.33, 77.46, 77.24, 77.04, 76.62, 68.31, 31.35, 19.24, 13.87.

GC-MS \( t_R = 6.04 \text{ min}, \) (EI, 70 eV): \( m/z = 168 \) [M\textsuperscript{+}], 112, 95, 83, 75, 57, 50.

HRMS (EI, \( m/z \)): found 168.0954 [M\textsuperscript{+}] (calculated 168.0950).

FT-IR (ATR-film) in [cm\textsuperscript{-1}] 2961 (m), 2937 (m), 2874 (w), 1504 (s), 1472 (m), 1390 (w), 1292 (w), 1247 (m), 1206 (s), 1096 (w), 1069 (w), 1028 (w), 974 (w), 825 (s), 755 (s), 723 (m), 512 (m).

2-Methylhexahydro-1\textit{H}-isoindole-1,3(2\textit{H})-dione

C_{9}H_{13}NO\textsubscript{2}

167.21 g/mol

^1H-NMR (300 MHz, CDCl\textsubscript{3}) δ 2.97 (s, 3H), 2.85 (td, J = 4.5, 2.2 Hz, 2H), 1.98 – 1.80 (m, 2H), 1.80 – 1.68 (m, 2H), 1.53 – 1.35 (m, 4H).
$^{13}$C-NMR (75 MHz, CDCl$_3$) $\delta$ 179.95, 77.46, 77.04, 76.62, 39.77, 24.67, 23.71, 21.61.

GC-MS $t_R = 7.77$ min, (EI, 70 eV): $m/z = 167$ [M$^+$], 138, 113, 82, 67, 54.

Analytical data were in full agreement with B. Bailey, R. D. Haworth, J. McKenna, *J. Chem. Soc.* 1954, 967.

$n$-Butylbenzene

$\text{C}_{10}\text{H}_{14}$

$\rho_p$ = 134.22 g/mol

$^1$H-NMR (300 MHz, CDCl$_3$) $\delta$ 7.38 – 7.27 (m, 2H), 7.20 (m, 3H), 2.68 – 2.57 (m, 2H), 1.71 – 1.54 (m, 2H), 1.37 (dq, $J = 14.5$, 7.3 Hz, 2H), 0.94 (t, $J = 7.3$ Hz, 3H).

$^{13}$C-NMR (75 MHz, CDCl$_3$) $\delta$ 142.95, 128.44, 128.24, 125.57, 35.71, 33.73, 22.42, 14.01.

GC-MS $t_R = 5.09$ min, (EI, 70 eV): $m/z = 134$ [M$^+$], 128, 115, 105, 92, 77, 65, 51.

Analytical data were in full agreement with L. Ackermann, A. R. Kapdi, C. Schulzke, *Org. Lett.* 2010, 12, 2298–2301.
Synthesis and characterization of [FeN(SiMe$_3$)$_2$]$_4$(toluene)

General

Chemicals and Solvents: Solvents (THF, Et$_2$O, n-hexane, toluene) were distilled over sodium and benzophenone and stored over molecular sieves (4 Å). All manipulations were performed under purified argon inside a glovebox or using Schlenk techniques. Fe[N(SiMe$_3$)$_2$]$_2$ was synthesized as described in chapter Fehler! Verweisquelle konnte nicht gefunden werden. DiBAlH was used as received from SigmaAldrich (1 M in toluene).

$^1$H- und $^{13}$C-NMR-Spectroscopy: Nuclear magnetic resonance spectra were recorded on a Bruker Avance 300 (300 MHz) and Bruker Avance 400 (400 MHz). $^1$H-NMR: The following abbreviations are used to indicate multiplicities: s = singlet; d = doublet; t = triplet, q = quartet; m = multiplet, dd = doublet of doublet, dt = doublet of triplet, dq = doublet of quartet, ddt = doublet of doublet of quartet. Chemical shift $\delta$ is given in ppm to tetramethylsilane.

Scheme. Synthesis of [Fe$_4$]-cluster [FeN(SiMe$_3$)$_2$]$_4$(toluene)

A 10 mL flame-dried Schlenk flask was charged with Fe[N(SiMe$_3$)$_2$]$_2$ (190 mg, 0.50 mmol) in a mixture of n-hexane/toluene (4 mL, 3/1). A solution of DiBAlH in toluene (0.50 mmol, 1 M, 0.50 mL) was added at room temperature via syringe with immediate color change from green to brown-black. The reaction mixture was stirred at room temperature for 30 minutes, filtered through a P4 frit after which the solvent was removed completely under reduced pressure. The dark brown oily residue was powderized by 3 cycles freeze-pump-thaw and crystallized in n-hexane (0.3 mL) at -30 °C. After 24 h, a dark crystalline compound was obtained in 38% yield (46 mg, 0.048 mmol).

$^1$H-NMR (400 MHz, C$_6$D$_6$) $\delta$ 52.84 (bs), -1.83 (bs), -5.31 (bs), -12.06 (bs), -20.57 (bs), -22.73 (bs); effective magnetic moment (C$_6$D$_6$): $\mu_{\text{eff}} = 2.0 \mu_B$; melting point = 123 °C; elemental analysis calcd for Fe$_4$N$_4$Si$_8$C$_{31}$H$_{80}$ (957.07): C 38.90, H 8.43, N 5.85; found: C 38.05, H 8.19, N 5.87.
Figure. $^1$H-NMR of [FeN(SiMe$_3$)$_2$]$_4$(toluene) in C$_6$D$_6$. Peak assignments: SiMe$_3$ (●), toluene (○).

For X-Ray structure determination, a suitable crystal (0.19×0.16×0.11) mm$^3$ was selected and mounted on a MITIGEN holder with inert oil on a SuperNova, Single source at offset, Atlas diffractometer. The crystal was kept at $T = 123.00(10)$ K during data collection. Using Olex2 (Dolomanov et al., 2009)$^1$, the structure was solved in the space group P2$_1$/c (# 14) by Direct Methods using the ShelXT (Sheldrick, 2015)$^2$ structure solution program and refined by Least Squares using version 2014/7 of ShelXL (Sheldrick, 2015)$^3$. All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and refined using the riding model. Data were measured using $w$ scans scans of 1.0° per frame for 6.0 s using CuKa radiation (micro-focus sealed X-ray tube, n/a kV, n/a mA). The total number of runs and images was based on the strategy calculation from the program CrysAlisPro (Agilent). The maximum resolution achieved was $Q = 76.438$.°

Cell parameters were retrieved using the CrysAlisPro (Agilent) software and refined using CrysAlisPro (Agilent) on 23809 reflections, 55% of the observed reflections. Data reduction was performed using the CrysAlisPro (Agilent) software which corrects for Lorentz polarisation. The final completeness is 99.90 out to 76.438 in $\Theta$. The absorption coefficient $\mu$ of this material is 11.172 at this wavelength ($\lambda = 1.54184$) and the minimum and maximum transmissions are 0.70913 and 1.00000.

Crystal Data. C$_{31}$H$_{80}$Fe$_4$N$_4$Si$_8$, $M_r =$ 957.11, monoclinic, P2$_1$/c (No. 14), $a = 18.59832(16)$ Å, $b =$ 14.75827(12) Å, $c = 18.28580(17)$ Å, $\beta = 96.4495(8)^\circ$, $\alpha = \gamma = 90^\circ$, $V =$ 4987.31(7) Å$^3$, $T =$ 123.00(10) K, $Z =$ 4, $Z' =$ 1, $\mu$(CuK$\alpha$) = 11.172, 43076 reflections measured, 10425 unique ($R_{int} =$

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2 Sheldrick, G.M., Crystal structure refinement with ShelXL, Acta Cryst., (2015), C27, 3-8.

3 Sheldrick, G.M., ShelXT-Integrated space-group and crystal-structure determination, Acta Cryst., (2015), A71, 3-8.
0.0307) which were used in all calculations. The final \( wR^2 \) was 0.0650 (all data) and \( R_f \) was 0.0262 (I > 2(I)).

**Figure.** X-Ray structure of \([\text{FeN(SiMe}_3\text{)}_2]_4(\text{toluene})\) visualized with software *Mercury*. Hydrogen atoms are omitted for clarity.

**Synthesis of \([\text{Fe}_6\{\text{N(SiMe}_3\text{)}_2\}_6\text{H}_5\}] \text{ and } [\text{Fe}_7\{\text{N(SiMe}_3\text{)}_2\}_7\text{H}_6]:**

A light green solution of \(\text{Fe}\{\text{N(SiMe}_3\text{)}_2\}_2\) (190 mg, 0.50 mmol) in \(n\)-hexane (2 mL) was treated with 0.5 mL of 1(M) DiBAlH solution (0.50 mmol) in \(n\)-hexane at ambient temperature. The color of the solution immediately turned to dark red-brown and it was stirred for three hour. The solution was evaporated completely to a dark red-brown sticky solid, which was treated with 0.5 mL of \(n\)-hexane and the obtained suspension was stored at room temperature overnight. The dark brown solid was isolated by filtration through glass pipette embedded with glass-filter. Dark red-brown single crystals were obtained by slow evaporation of the \(n\)-hexane solution at room temperature. Composition of the product to \([\text{Fe}_6\{\text{N(SiMe}_3\text{)}_2\}_6\text{H}_5\}] \text{ and } [\text{Fe}_7\{\text{N(SiMe}_3\text{)}_2\}_7\text{H}_6]\) in 4 :1 ratio was verified by X-ray analysis, elemental analysis and LIFDI-MS. Yield: 37 mg (0.028 mmol, 35 %). Elemental analysis calculated for \(\text{C}_{36}\text{H}_{113}\text{Fe}_6\text{N}_6\text{Si}_{12}\): C 32.91, H 8.69, N 6.40; found: C 33.4, H 8.51, N 6.3. \(^1\text{H NMR (CD}_6\text{D, 400.13 MHz, 300K): –16.34 (SiMe}_3\text{), –3.29 (SiMe}_3\text{), 29.72 (SiMe}_3\text{).} \)
Figure: $^1$H NMR spectrum of Fe6/Fe7 cluster mixture (C$_6$D$_6$, 400.13 MHz, 300K).
**Figure:** LIFDI-MS spectrum of Fe6/Fe7 cluster mixture in toluene.
**Figure:** Diamond plot of the Fe6 Cluster.

**Figure:** Diamond plot of the Fe7 Cluster.