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Supporting Information

Alkene Hydrogenations by Soluble Iron Nanocluster Catalysts

*Tim N. Gieshoff, Uttam Chakraborty, Matteo Villa, and Axel Jacobi von Wangelin**

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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 molybdatophosphoric 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, Et_2O, *n*-hexane, toluene) were distilled over sodium and benzophenone and stored over molecular sieves (4 Å). $LiN(SiMe_3)_2$ (*SigmaAldrich*, 97%) was sublimated and stored under argon. $HN(SiMe_3)_2$, $HNEt_2$, HN(*i*Pr)$_2$, HNPhMe and 2,2,6,6-tetramethylpiperidine were distilled over CaH_2 and stored under argon prior use. $HNPh_2$ was recrystallized in *n*-pentane. Solvents used for column chromatography were distilled under reduced pressure prior use (ethyl acetate). DiBAlH (1 M in toluene), $AlMe_3$ (2 M in toluene), $Al(^iBu)_3$ 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 H_2 (1 min), sealed and the internal pressure was adjusted. Hydrogen (99.9992%) was purchased from *Linde*.

^{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 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: N_2. 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: H_2. 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, Colum 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 H_2, CH_4 and C_2H_6 in the reduction of FeX_2 salts (X = $N(SiMe_3)_2$, Cl) with aluminium organyls (DiBAlH, $Al(^iBu)_3$, $AlMe_3$). Calibrations of examined gases were conducted by hydrolization of $LiAlH_4$ (H_2), MeMgCl (CH_4) and EtMgCl (C_2H_6).

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 × 0.25 mm × 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 H_2. Calibration of the reservoir pressure drop in relation to H_2 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 = 623.8 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 DiBAlH 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 DiBAlH 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 ^{n}BuLi 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 DiBAlH 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

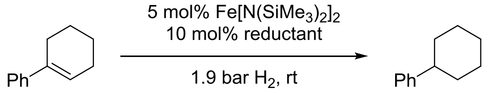
A flame-dried 10 mL 2-neck flask was connected to a *Man on the Moon X201* gas-uptake system and kept at 23 °C with the help of a water bath. After purging with H_2, the system was set to a reaction pressure of 1.9 bar. Freshly prepared catalyst mixture (1 mL) was added via syringe and stirred for 2 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	DiBAlH	freshly prepared	41
2	DiBAlH	storage for 5 d in solution	37
3	DiBAlH	removal of solvent and resolvation	30
4	DiBAlH	removal of solvent, storage for 5 d under argon and resolvation	27
5	$AlMe_3$	freshly prepared	13
6	$AlMe_3$	storage for 20 h in solution	<1
7	DiBAlH	*in situ* synthesis of $Fe[N(SiMe_3)_2]_2$	27

[a] determined with yield after 7 minutes.

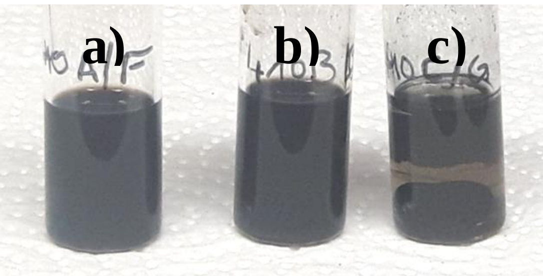


Figure S1. Catalyst in solution after 20 h storage under argon; a) $Fe[N(SiMe_3)_2]_2$-DiBAlH; b) $FeCl_2(thf)_{1.5}$-$LiN(SiMe_3)_2$-DiBAlH; c) $Fe[N(SiMe_3)_2]_2$-$AlMe_3$.

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 H_2O (15 mL) and extracted with Et_2O (3 × 15 mL). The combined organic layers were dried (Na_2SO_4), concentrated and subjected to silica gel flash chromatography (*n*-pentane).

Synthesis of $\{Fe[N(SiMe_3]_2\}_2$

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.

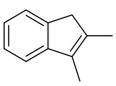
A flame-dried *Schlenk*-flask under argon was charged with $LiN(SiMe_3)_2$ (6.37 g, 2.2 equiv., 38.1 mmol) in diethyl ether (60 mL). At 0 °C $FeCl_2$ (2.24 g, 1.0 equiv., 17.1 mmol, 97%) was added in portions. The resulting reaction mixture was allowed to warm to room temperature and stirred for 24 h. 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.

$\{Fe[N(SiMe_3)_2]_2\}_2$	**$C_{24}H_{72}Fe_2N_4Si_8$** 753.24 g/mol
Yield	4.71 g, 12.5 mmol (73%)
^{1}H-NMR	(400 MHz, C_6D_6) $\delta = 64.10$ (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-1*H*-indene

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

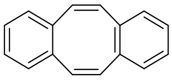
	**$C_{11}H_{12}$** 144.22 g/mol
Appearance	colorless liquid
Yield	1.49 g, 10.3 mmol (69%)
TLC	$R_f = 0.66$ (SiO_2, *n*-pentane)

^{1}H-NMR	(300 MHz, $CDCl_3$) δ 7.37 (dp, *J* = 7.3, 0.9 Hz, 1H), 7.31 – 7.21 (m, 2H), 7.12 (td, *J* = 7.2, 1.5 Hz, 1H), 3.31 – 3.21 (m, 2H), 2.07 (q, *J* = 1.0 Hz, 3H), 2.04 (tq, *J* = 2.1, 1.1 Hz, 3H).
^{13}C-NMR	(75 MHz, $CDCl_3$) δ 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)

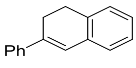
Synthesis following the procedure described by G. Franck, M. Brill, G. Helmchen, *J. Org. Chem.* **2012**, *89*, 55-65.

	**$C_{16}H_{12}$** 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, $CDCl_3$): δ 7.19–7.13 (m, 4H), 7.10–7.02 (m, 4H), 6.76 (s, 4H).
^{13}C-NMR	(75 MHz, $CDCl_3$): δ 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.

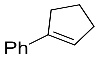
	**$C_{16}H_{14}$** 206.29 g/mol
Appearance	colorless liquid
Yield	912 mg, 4.46 mmol (47%)
TLC	R_f = 0.41 (SiO_2, hexanes)

^{1}H-NMR	(300 MHz, $CDCl_3$) δ 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).
^{13}C-NMR	(75 MHz, $CDCl_3$) δ 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. Houson, L. Campbell, T. Walsgrove, M. Wills, *Tetrahedron*, **2006**, *62*, 1864-1876.

1-Phenyl-1-cyclopentene

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



$C_{11}H_{12}$

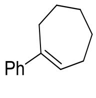
144.22 g/mol

Appearance	colorless liquid
Yield	1.99 g, 13.8 mmol (69%)
TLC	R_f = 0.66 (SiO_2, hexanes)
^{1}H-NMR	(300 MHz, $CDCl_3$) δ 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).
^{13}C-NMR	(75 MHz, $CDCl_3$) δ 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.



$C_{13}H_{16}$

172.27 g/mol

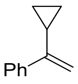
Appearance	colorless liquid
Yield	2.89 g, 16.8 mmol (84%)

TLC	R_f = 0.69 (SiO_2, hexanes)
^{1}H-NMR	(300 MHz, $CDCl_3$) δ 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, $CDCl_3$) δ 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.



$C_{11}H_{12}$

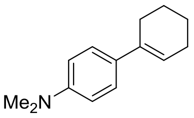
144.22 g/mol

Appearance	colorless liquid
Yield	1.27 g, 8.8 mmol (80%)
TLC	R_f = 0.53 (SiO_2, hexanes)
^{1}H-NMR	(300 MHz, $CDCl_3$) δ 7.67 – 7.57 (m, 2H), 7.42 – 7.26 (m, 3H), 5.30 (d, *J*=1.0, 1H), 4.95 (t, *J*=1.2, 1H), 1.67 (ttd, *J*=8.3, 5.4, 1.2, 1H), 0.92 – 0.79 (m, 2H), 0.61 (ddd, *J*=6.4, 5.4, 4.1, 2H).
^{13}C-NMR	(75 MHz, $CDCl_3$) δ 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.



$C_{14}H_{19}N$

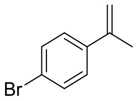
201.31 g/mol

Appearance	colorless liquid
Yield	1.65 g, 8.20 mmol (82%)
TLC	$R_f = 0.82$ (SiO_2, hexanes)
^{1}H-NMR	(300 MHz, $CDCl_3$) δ 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).
^{13}C-NMR	(75 MHz, $CDCl_3$) δ 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): $m/z = 202$ $[M]^+$, 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.



C_9H_9Br

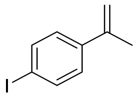
197.08 g/mol

Appearance	colorless oil
Yield	1.06 g, 5.39 mmol (77%)
TLC	$R_f = 0.59$ (SiO_2, *n*-pentane)
^{1}H-NMR	(400 MHz, $CDCl_3$) δ 7.50-7.35 (m, 2H), 7.42-7.29 (m, 2H), 5.36 (s, 1H), 5.10 (s, 1H), 2.12 (s, 3H).
^{13}C-NMR	(101 MHz, $CDCl_3$) δ 142.2, 140.1, 131.3, 127.2, 121.4, 113.1, 21.7.
GC-MS	$t_R = 6.51$ min, (EI, 70 eV): $m/z = 197$ $[M^+]$, 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.



C_9H_9I

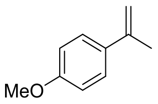
244.08 g/mol

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, $CDCl_3$) δ 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, $CDCl_3$) δ 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.



$C_{10}H_{12}O$

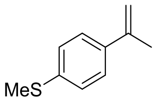
148.20 g/mol

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, $CDCl_3$) δ 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, $CDCl_3$) δ 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, 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.



$C_{10}H_{12}S$

164.27 g/mol

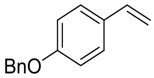
Appearance	colorless solid

Yield	1.09 g, 6.63 mmol (33%)
TLC	R_f = 0.44 (SiO_2, *n*-pentane)
^{1}H-NMR	(300 MHz, $CDCl_3$) δ 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, $CDCl_3$) δ 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

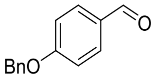
Synthesis following the general procedure for styrene synthesis in a Wittig reaction.

	**$C_{15}H_{14}O$**
	210.27 g/mol
Appearance	colorless solid
Yield	1.25 g, 5.97 mmol (74%)
TLC	R_f = 0.28 (SiO_2, *n*-pentane)
^{1}H-NMR	(300 MHz, $CDCl_3$) δ 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, $CDCl_3$) δ 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.

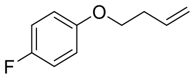
	**$C_{14}H_{12}O_2$**
	212.24 g/mol
Appearance	colorless solid

Yield	1.72 g, 8.12 mmol (81%)
TLC	R_f = 0.20 (SiO_2, hexanes/ethyl acetate = 9/1)
^{1}H-NMR	(300 MHz, $CDCl_3$) δ 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, $CDCl_3$) δ 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.

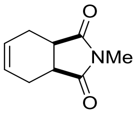
1-(but-3-en-1-yloxy)-4-fluorobenzene

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.

	**$C_{10}H_{11}FO$** 166.20 g/mol
Appearance	colorless liquid
Yield	1.89 g, 11.38 mmol (76%)
TLC	R_f = 0.80 (SiO_2, hexanes/ethyl acetate = 99/1)
^{1}H-NMR	(300 MHz, $CDCl_3$) δ 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, $CDCl_3$) δ 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 [$M^{+\bullet}$] (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.



$C_9H_{11}NO_2$

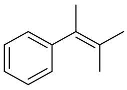
165.19 g/mol

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, $CDCl_3$): δ 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.



$C_{11}H_{14}$

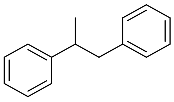
146,23 g/mol

Appearence	colorless liquid
Yield	850 mg, 5.8 mmol (39%)
^{1}H-NMR	(300 MHz, $CDCl_3$) δ 7.36 – 7.13 (m, 5H), 1.99 (s, 3H), 1.84 (s, 3H), 1.62 (s, 3H).
^{13}C-NMR	(75 MHz, $CDCl_3$) δ 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-diyldibenzene



$C_{15}H_{16}$

196,29 g/mol

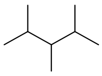
^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.44 – 7.10 (m, 10H), 3.17 – 2.95 (m, 2H), 2.91 – 2.78 (m, 1H), 1.31 (d, J = 6.8 Hz, 3H).

^{13}C-NMR (75 MHz, CDCl3) δ 147.05, 140.88, 129.23, 128.37, 128.17, 127.11, 126.09, 125.91, 45.13, 41.96, 21.23.

GC-MS t_R = 8,24 min, (EI, 70 eV): *m/z* = 196 [M^+], 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, *Organometallics* **2009**, *28*, 4534-4543.

2,3,4-trimethylpentane



C_8H_{18}

114,23 g/mol

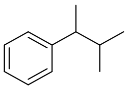
^{1}H-NMR (300 MHz, $CDCl_3$) δ 1.73 – 1.54 (m, *J* = 6.7 Hz, 2H), 1.00 – 0.92 (m, 1H), 0.87 (d, *J* = 6.8 Hz, 6H), 0.79 (d, *J* = 6.7 Hz, 6H), 0.73 (d, *J* = 6.8 Hz, 3H).

^{13}C-NMR (75 MHz, $CDCl_3$) δ 45.12, 29.65, 21.73, 18.31, 10.81.

GC-MS t_R = 2,24 min, (EI, 70 eV): *m/z* = 114 [M^+], 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



$C_{11}H_{16}$

148,28 g/mol

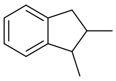
^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.35 – 7.14 (m, 5H), 2.42 (p, *J* = 7.2 Hz, 1H), 1.77 (dp, *J* = 7.7, 6.6 Hz, 1H), 1.24 (d, *J* = 7.0 Hz, 3H), 0.94 (d, *J* = 6.7 Hz, 3H), 0.76 (d, *J* = 6.7 Hz, 3H).

^{13}C-NMR (75 MHz, $CDCl_3$) δ 147.10, 128.02, 127.65, 125.68, 46.88, 34.45, 21.20, 20.20, 18.78.

GC-MS t_R = 5,41 min, (EI, 70 eV): *m/z* = 148 [M^+], 131, 115, 105, 77, 65, 51.

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

1,2-dimethyl-2,3-dihydro-1*H*-indene



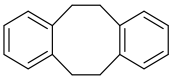
$C_{11}H_{14}$

146.23 g/mol

^{1}H-NMR	(400 MHz, $CDCl_3$) δ 7.23 – 7.10 (m, 4H), 3.17 (p, J = 7.1 Hz, 1H), 3.04 – 2.92 (m, 1H), 2.63 – 2.53 (m, 2H), 1.15 (d, J = 7.2 Hz, 3H), 0.99 (d, J = 6.8 Hz, 3H).
^{13}C-NMR	(75 MHz, $CDCl_3$) δ 148.81, 142.95, 126.10, 126.04, 124.48, 123.59, 42.39, 39.39, 37.84, 15.20, 14.67.
GC-MS	t_R = 6.03 min, (EI, 70 eV): *m/z* = 146 [M^+], 131, 115, 103, 91, 77, 63, 51.

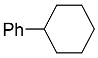
Analytical data were in full agreement with R. P. Yu, J. M. Darmon, J. M. Hoyt, G. W. Margulieux, Z. R. Turner, P. J. Chirik, *ACS Catal.* **2012**, *2*, 1760–1764.

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

	**$C_{16}H_{16}$** 208.30 g/mol
^{1}H-NMR	(300 MHz, $CDCl_3$) δ 7.06 – 6.93 (m, 8H), 3.07 (s, 8H).
^{13}C-NMR	(75 MHz, $CDCl_3$) δ 140.60, 129.67, 126.10, 35.16.
GC-MS	t_R = 9.45 min, (EI, 70 eV): *m/z* = 208 [M^+], 193, 178, 165, 115, 104, 91, 78, 63, 51.

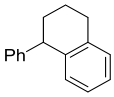
Analytical data were in full agreement with D. Guijarro, B. Mancheño, M. Yus, *Tetrahedron* **1992**, *48*, 4593–4600.

Phenylcyclohexane

	**$C_{12}H_{16}$** 160.26 g/mol
^{1}H-NMR	(300 MHz, $CDCl_3$) δ 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-NMR	(75 MHz, $CDCl_3$) δ 148.1, 128.3, 126.5, 125.8, 44.7, 34.52, 27.0, 26.2.
GC-MS	t_R = 7.30 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



$C_{16}H_{16}$

208.30 g/mol

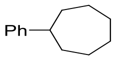
^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.37 – 7.10 (m, 7H), 7.09 – 7.01 (m, 1H), 6.86 (d, *J* = 7.8 Hz, 1H), 4.14 (t, *J* = 6.6 Hz, 1H), 3.04 – 2.76 (m, 2H), 2.31 – 2.10 (m, 1H), 2.03 – 1.68 (m, 3H).

^{13}C-NMR (75 MHz, $CDCl_3$) δ 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.

GC-MS t_R = 9.33 min, (EI, 70 eV): *m/z* = 208 [M^+], 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, *J. Org. Chem.* **1990**, *55*, 1338–1344.

Phenylcycloheptane



$C_{13}H_{18}$

174.29 g/mol

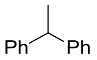
^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.35 – 7.11 (m, 5H), 2.76 – 2.56 (m, 1H), 2.00 – 1.75 (m, 4H), 1.74 – 1.49 (m, 8H).

^{13}C-NMR (75 MHz, $CDCl_3$) δ 150.05, 128.31, 126.70, 125.52, 47.10, 36.86, 27.99, 27.27.

GC-MS t_R = 7.80 min, (EI, 70 eV): *m/z* = 174 [M^+], 117, 104, 91, 78, 65, 55.

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

1,1-Diphenylethane



$C_{14}H_{14}$

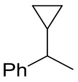
182.27 g/mol

^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.35 – 7.11 (m, 10H), 4.15 (q, *J*=7.1, 1H), 1.63 (d, *J*=7.2, 3H).

GC-MS t_R = 7.97 min, (EI, 70 eV): *m/z* = 182 [M^+], 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, *J. Am. Chem. Soc.* **2007**, *129*, 13368–13369.

1-Cyclopropyl-1-phenylethane



$C_{11}H_{14}$

146.23 g/mol

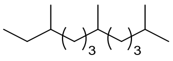
^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.41 – 7.26 (m, 4H), 7.25 – 7.17 (m, 1H), 1.99 (dq, *J* = 9.2, 7.0 Hz, 1H), 1.35 (d, *J* = 7.0 Hz, 3H), 0.96 (qt, *J* = 9.1, 8.0, 5.0 Hz, 1H), 0.65 – 0.36 (m, 2H), 0.27 – 0.09 (m, 2H).

^{13}C-NMR (75 MHz, $CDCl_3$) δ 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



$C_{15}H_{32}$

212.42 g/mol

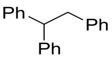
^{1}H-NMR (300 MHz, $CDCl_3$) δ 1.77 – 1.44 (m, 4H), 1.42 – 0.98 (m, 14H), 0.93 – 0.75 (m, 14H).

^{13}C-NMR (75 MHz, $CDCl_3$) δ 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



$C_{20}H_{18}$

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).

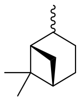
^{13}C-NMR (75 MHz, $CDCl_3$) δ 144.45, 140.26, 129.08, 128.34, 128.05, 126.19, 125.88, 53.11, 42.11.

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.



$C_{10}H_{18}$

138.25 g/mol

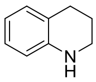
^{1}H-NMR mixture of isomers

^{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



$C_9H_{11}N$

133.19 g/mol

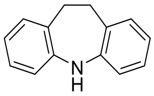
^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.03 – 6.92 (m, 2H), 6.62 (td, *J* = 7.4, 1.2 Hz, 1H), 6.50 (d, *J* = 7.8 Hz, 1H), 3.98 (s, 1H), 3.37 – 3.25 (m, 2H), 2.78 (t, *J* = 6.4 Hz, 2H), 2.03 – 1.88 (m, 2H).

^{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. Rodriguez, W. Correa, *J. Org. Chem.* **2005**, *70*, 10132–10134.

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



$C_{14}H_{13}N$

195.27 g/mol

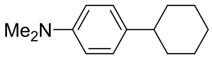
^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.18 – 7.04 (m, 4H), 6.89 – 6.66 (m, 4H), 6.02 (s, 1H), 3.12 (s, 4H).

^{13}C-NMR (75 MHz, $CDCl_3$) δ 141.38, 129.62, 127.57, 125.76, 118.38, 116.86, 33.87.

GC-MS t_R = 10.16 min, (EI, 70 eV): m/z = 195 [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



$C_{14}H_{21}N$

203.33 g/mol

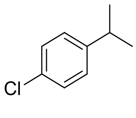
^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.15 – 7.07 (m, 2H), 6.77 – 6.72 (m, 2H), 2.93 (s, 6H), 2.52 – 2.38 (m, 1H), 1.94 – 1.80 (m, 4H), 1.78 – 1.70 (m, 1H), 1.48 – 1.34 (m, 4H), 1.34 – 1.25 (m, 1H).

^{13}C-NMR (75 MHz, $CDCl_3$) δ 127.34, 113.11, 43.53, 41.06, 34.75, 27.05, 26.26.

GC-MS t_R = 9.30 min, (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



$C_9H_{11}Cl$

154.64 g/mol

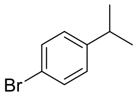
^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.25 (m, 2H), 7.21–7.09 (m, 2H), 2.89 (m, 1H), 1.23 (d, *J* = 6.9 Hz, 6H).

^{13}C-NMR (75 MHz, $CDCl_3$) δ 142.3, 131.3, 128.4, 127.8, 33.6, 23.9.

GC-MS t_R = 5.37 min, (EI, 70 eV): *m/z* = 154 [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



$C_9H_{11}Br$

199.09 g/mol

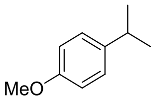
^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.47 – 7.36 (m, 2H), 7.15 – 7.04 (m, 2H), 2.87 (hept, *J* = 6.9 Hz, 1H), 1.23 (d, *J* = 6.9 Hz, 6H).

^{13}C-NMR (101 MHz, $CDCl_3$) δ 147.8, 131.3, 128.2, 119.3, 33.7, 30.9, 23.8.

GC-MS t_R = 6.16 min, (EI, 70 eV): *m/z* = 198 [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



$C_{10}H_{14}O$

180.24 g/mol

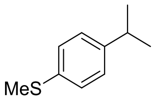
^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.15 (d, *J* = 8.8 Hz, 2H), 6.84 (d, *J* = 8.7 Hz, 2H), 3.79 (s, 3H), 2.95 – 2.78 (m, 1H), 1.24 (s, 3H), 1.21 (s, 3H).

^{13}C-NMR (75 MHz, $CDCl_3$) δ 156.86, 141.06, 127.26, 113.77, 55.27, 33.28, 24.24.

GC-MS t_R = 5.93 min, (EI, 70 eV): m/z = 150 [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



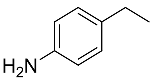
$C_{10}H_{14}S$

166.28 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.

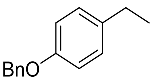
Analytical data were in full agreement with X.-m. Wu, J.-m. Lou, G.-b. Yan, *Synlett* **2016**, *27*, 2269–2273.

4-Ethylaniline

	**$C_8H_{11}N$** 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.

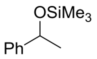
Analytical data were in full agreement with B. Wang, H.-X. Sun, G.-Q. Lin, Z.-H. Sun, *Adv. Synth. Catal.* **2009**, *351*, 415-422.

1-Benzyloxy-4-ethylbenzene

	**$C_{15}H_{16}O$** 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

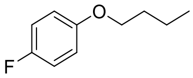
^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.36 – 7.18 (m, 5H), 4.86 (q, *J* = 6.4 Hz, 1H), 1.43 (d, *J* = 6.3 Hz, 3H), 0.07 (s, 9H).

^{13}C-NMR (75 MHz, $CDCl_3$) δ 146.33, 128.02, 126.73, 125.24, 70.48, 26.78, 0.00.

GC-MS t_R = 5.74 min, (EI, 70 eV): *m/z* = 179 [M-CH_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-*n*-butylether



$C_{10}H_{13}FO$

168.21 g/mol

^{1}H-NMR (300 MHz, $CDCl_3$) 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).

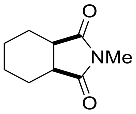
^{13}C-NMR (75 MHz, $CDCl_3$) δ 158.68, 155.53, 155.28, 115.87, 115.56, 115.44, 115.33, 77.46, 77.24, 77.04, 76.62, 68.31, 31.35, 19.24, 13.87.

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

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

FT-IR (ATR-film) in [cm^{-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*H*-isoindole-1,3(2*H*)-dione



$C_9H_{13}NO_2$

167.21 g/mol

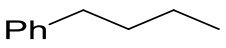
^{1}H-NMR (300 MHz, $CDCl_3$) δ 2.97 (s, 3H), 2.85 (td, *J* = 4.5, 2.2 Hz, 2H), 1.98 – 1.80 (m, 2H), 1.80 – 1.68 (m, 2H), 1.53 – 1.35 (m, 4H).

^{13}C-NMR (75 MHz, $CDCl_3$) δ 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



$C_{10}H_{14}$

134.22 g/mol

^{1}H-NMR (300 MHz, $CDCl_3$) δ 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, $CDCl_3$) δ 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.

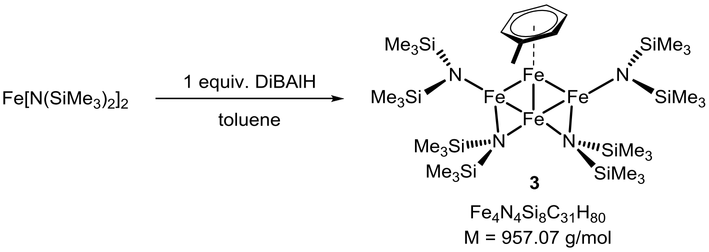
Analytical data were in full agreement with L. Ackermann, A. R. Kapdi, C. Schulzke, *Org. Lett.* **2010**, *12*, 2298–2301.

Synthesis and characterization of $[FeN(SiMe_3)_2]_4$(toluene)

General

Chemicals and Solvents: Solvents (THF, Et_2O, *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 δ 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_6D_6) δ 52.84 (bs), -1.83 (bs), -5.31 (bs), -12.06 (bs), -20.57 (bs), -22.73 (bs); effective magnetic moment (C_6D_6): $\mu_{\mathrm{eff}} = 2.0\ \mu_B$; melting point = 123 °C; elemental analysis calcd for $Fe_4N_4Si_8C_{31}H_{80}$ (957.07): C 38.90, H 8.43, N 5.85; found: C 38.05, H 8.19, N 5.87.

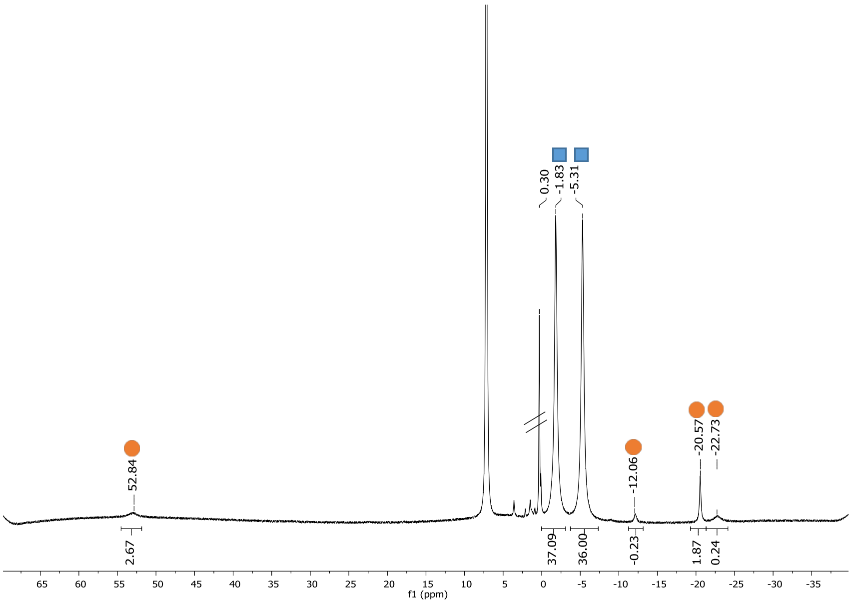


Figure. ^{1}H-NMR of [FeN(SiMe$_3$)$_2$]$_4$(toluene) in C$_6$D$_6$. Peak assignments: SiMe$_3$ (🟦), toluene (🟠).

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 Θ. The absorption coefficient μ of this material is 11.172 at this wavelength (λ = 1.54184) and the minimum and maximum transmissions are 0.70913 and 1.00000.

Crystal Data. $C_{31}H_{80}Fe_4N_4Si_8$, 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, β = 96.4495(8)°, α = γ = 90°, V = 4987.31(7) Å^3, T = 123.00(10) K, Z = 4, Z' = 1, μ(CuK$_\alpha$) = 11.172, 43076 reflections measured, 10425 unique (R_{int} =

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[1] O.V. Dolomanov and L.J. Bourhis and R.J. Gildea and J.A.K. Howard and H. Puschmann, Olex2: A complete structure solution, refinement and analysis program, *J. Appl. Cryst.*, (2009), **42**, 339-341.

[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_1 was 0.0262 (I > 2(I)).

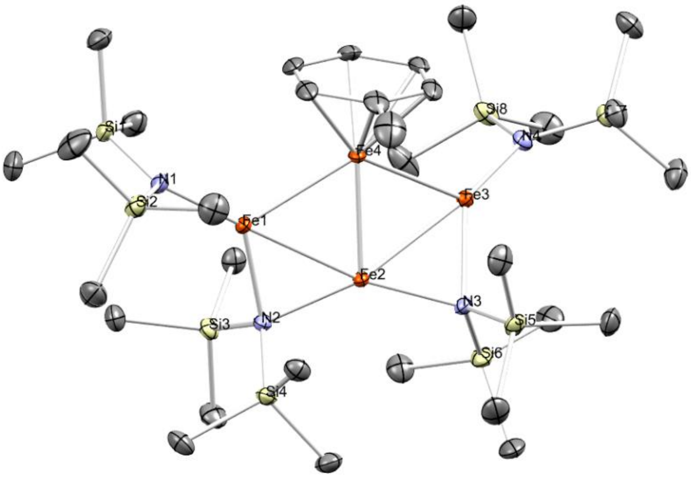

Figure. X-Ray structure of **$[FeN(SiMe_3)_2]_4$(toluene)** visualized with software *Mercury*. Hydrogen atoms are omitted for clarity.

Synthesis of $[Fe_6\{N(SiMe_3)_2\}_6H_5]$ and $[Fe_7\{N(SiMe_3)_2\}_7H_6]$:

A light green solution of $Fe\{N(SiMe_3)_2\}_2$ (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 $[Fe_6\{N(SiMe_3)_2\}_6H_5]$ and $[Fe_7\{N(SiMe_3)_2\}_7H_6]$ 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 $C_{36}H_{113.2}Fe_{6.2}N_6Si_{12}$: C 32.91, H 8.69, N 6,40; found: C 33.4, H 8.51, N 6.3. ^1H NMR (C_6D_6, 400.13 MHz, 300K): −16.34 ($SiMe_3$), −3.29 ($SiMe_3$), 29.72 ($SiMe_3$).

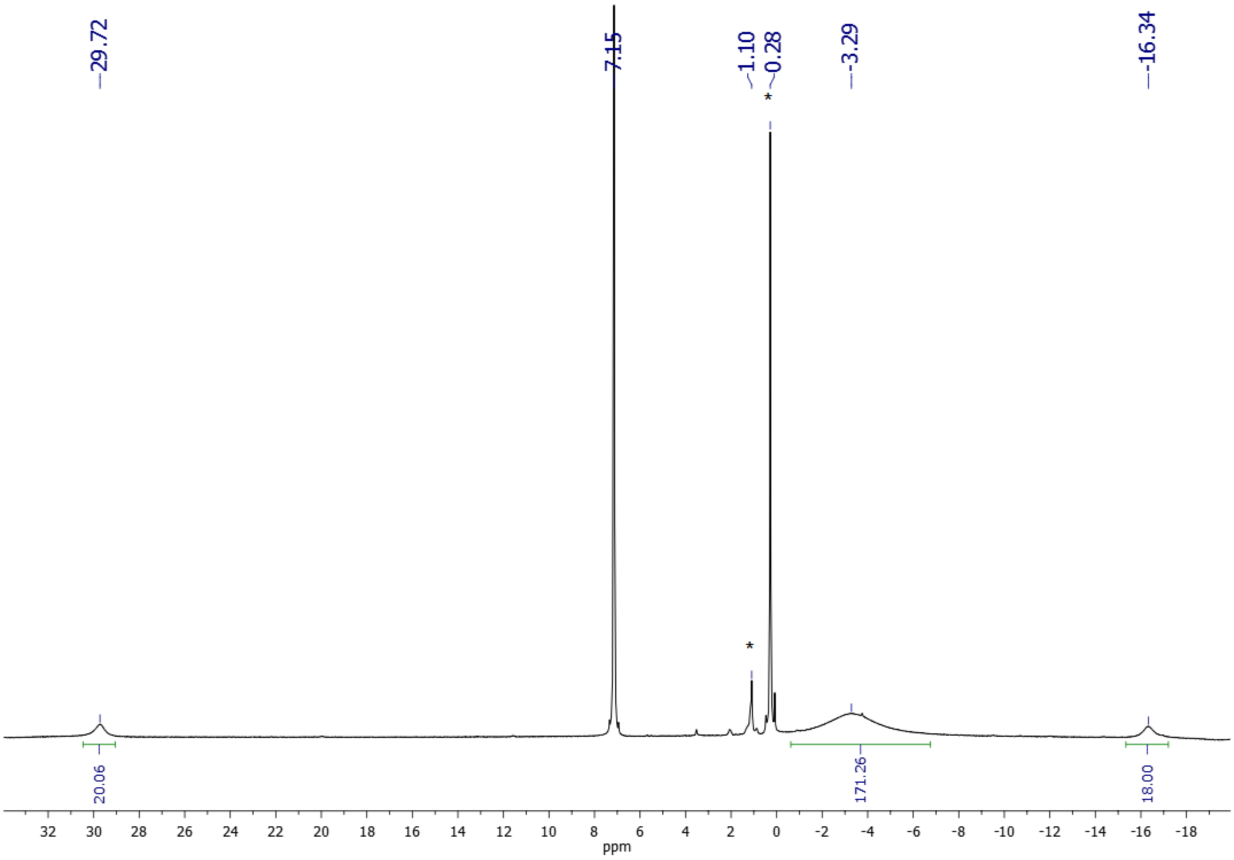

Figure: ^{1}H NMR spectrum of Fe6/Fe7 cluster mixture (C_6D_6, 400.13 MHz, 300K).

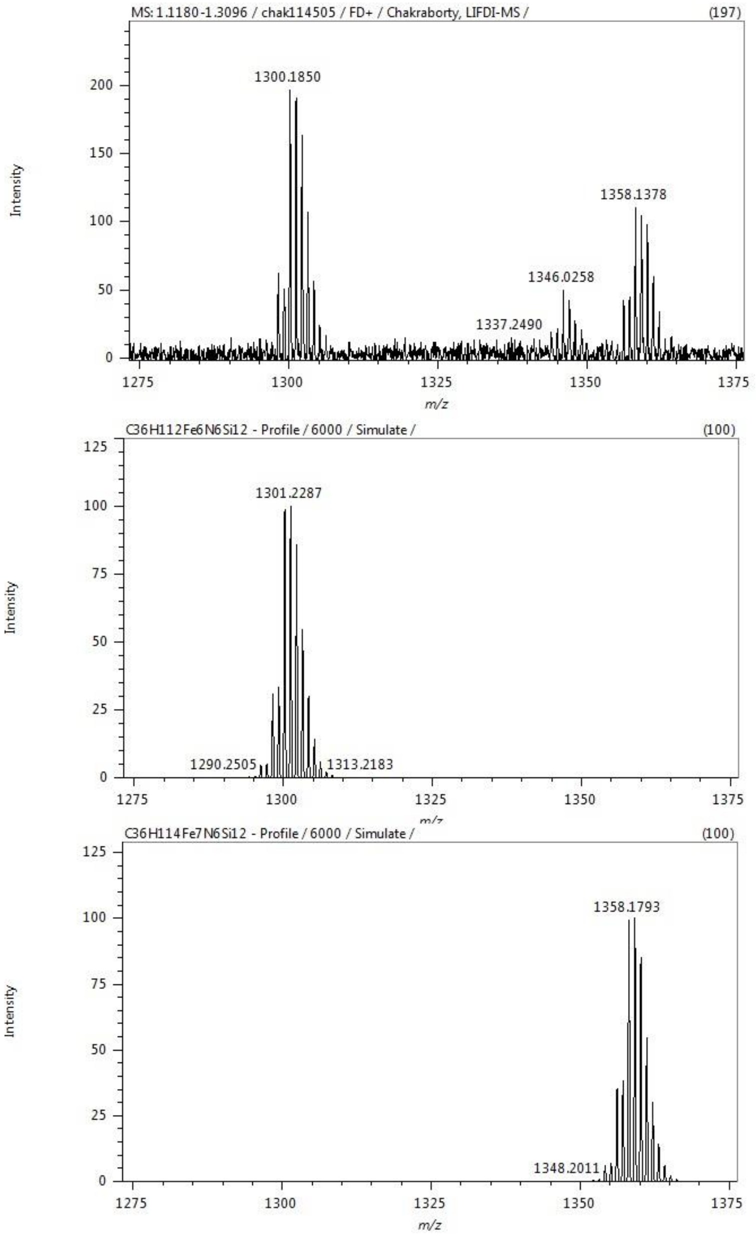

Figure: LIFDI-MS spectrum of Fe6/Fe7 cluster mixture in toluene.

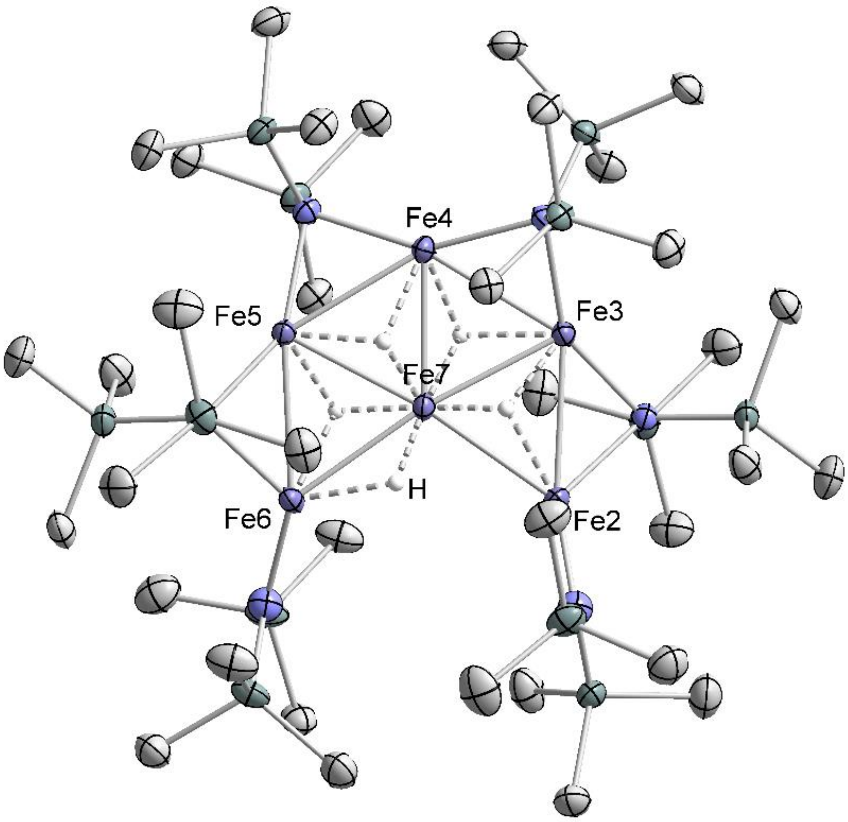

Figure: Diamond plot of the Fe6 Cluster.

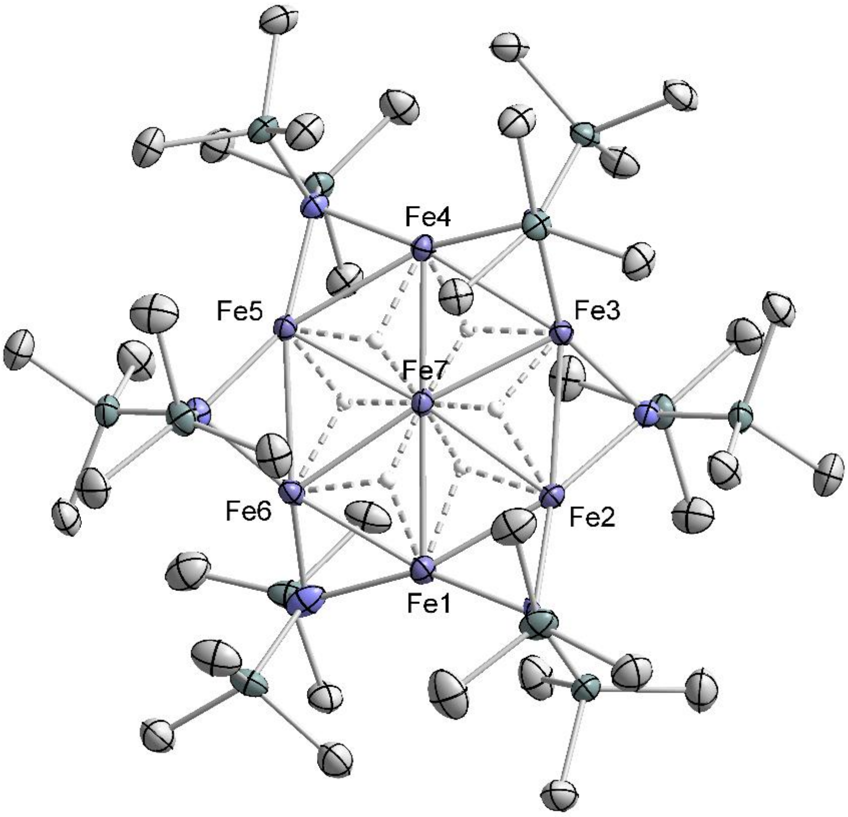

Figure: Diamond plot of the Fe7 Cluster.