A Manganese Nanosheet: New Cluster Topology and Catalysis

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1 General

All experiments for air-sensitive compounds were performed under an atmosphere of dry argon, by using standard Schlenk and glovebox techniques. Elemental analyses were determined by the analytical department of Regensburg University.

Analytical Thin-Layer Chromatography: TLC was performed using aluminum 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, Et2O, n-hexane, toluene) were distilled over sodium and benzophenone and stored over molecular sieves (4 Å).

Crystalline LiN(SiMe3)2 (Sigma-Aldrich, 97%) was used as received. Solvents used for column chromatography were distilled under reduced pressure prior use (ethyl acetate). DiBAlH (1 M in n-hexane), DiBAlH (1 M in toluene), AlMe3 (2 M in toluene), Al(iBu)3 were used as received from Sigma Aldrich 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), then three times with 2 bar H2, sealed and the internal pressure was adjusted. Hydrogen (99.9992%) was purchased from Linde.

1H- and 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 Agilent Cary 630 FTIR 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 (30 m × 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)

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.
2 General procedures

General method for catalytic hydrogenation

In an argon-filled glove box an oven-dried 4 mL reaction vial was charged with the substrate (0.2 mmol). 10 mL catalyst solution in hexane or heptane was prepared from Mn(hmds)₂ (37.6 mg, 0.1 mmol) and Dibal-H (0.2 mL of 1(M) Dibal-H in hexane) during overnight. After addition of prepared catalyst solution (1 mL; 5 mol% [Mn]), the reaction vial was transferred to a high pressure reactor which was sealed and removed from the glovebox. The reactor was purged with H₂ (3 × 2 bar) and the reaction pressure and temperature were set. After the indicated reaction time, the vial was retrieved and hydrolyzed with a saturated aqueous solution of sodium hydrogen carbonate (0.5 mL). The reaction mixture was extracted with ethyl acetate (3 × 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), dried over sodium sulfate and filtered over a pad of silica. Removal of the solvent at reduced pressure afforded the product in high purity.

For amine isolation as a free base, the product was filtered through a pad of aluminium oxide, eluted with ethyl acetate (3 × 2mL) and dried under vacuum to remove all the volatiles to obtain the product. Product was further purified, where it is necessary, by chromatography using silica gel neutralized with Et₃N (10%) and pentane/ethyl acetate (10/1) as eluent.

For amine isolation as a chloride salt, the product was filtered through a pad of silica, eluted with ether and converted into the hydrochloride salt using a 1 M solution of HCl in ether (1 mL). The precipitate was collected via filtration or – if no precipitate formed – the solvent removed under reduced pressure.

General method for in situ catalyst preparation with LiN(SiMe₃)₂

In an argon-filled glovebox an oven-dried 4 mL glass vial was charged with LiN(SiMe₃)₂ (16.7 mg; 100 µmol) and dissolved in THF (1 mL). MnBr₂ (2.1 mg, 10 µmol). A solution of DiBAIH in n-hexane (20 mM, 1 mL, 20 µmol) was added via syringe. The solution turned brown immediately and was stirred at room temperature for 5 minutes prior to use.

General method for kinetic examination in catalytic hydrogenation

A flame-dried 10 mL two-neck flask was connected to a Man on the Moon X20I gas-uptake system. After purging with H₂, the system was set to a reaction pressure of 1.9 bar. A catalyst mixture was prepared by treatment of Mn(hmds)₂ (9.4 mg, 25 µmol in 2 mL n-hexane) with DiBAIH (1 M, 50 µL, 50 µmol) and stirring for ca. 5 minutes. Monitoring of the hydrogen uptake started with the addition of the substrate (0.5 mmol).

3 Synthesis and characterization of [Mn₆(µ⁻H)₄(µ-H)₂{µ-N(SiMe₃)₂}] (2)

Method 1: A solution of HBPin (0.39 mL in 5 mL of n-hexane, 2.69 mmol) was portionwise added to a light pinkish solution of Mn[N(SiMe₃)₂]₂ (1.00 g, 2.66 mmol) in n-hexane (5 mL) during 5h. The obtained dark brown suspension was stirred further 1h and filtered. The dark filtrate was stored at −35 °C for 2 days and the obtained crystalline solid was isolated by decanting the mother liquor and dried in vacuo affording complex [Mn₆(µ⁻H)₄(µ-H)₂{µ-N(SiMe₃)₂}]₄[N(SiMe₃)₂] as a very air-sensitive brown solid. Yield: 102 mg (0.079 mmol, 18 %). Elemental analysis calculated for C₃₆H₁₄₈Mn₆N₂Si₁₂ (1298.00 g/mol): C 33.31, H 8.85, N 6.47; found: C 33.54, H 8.62, N 6.43.
Method 2: A light pinkish solution of Mn\{N(SiMe\_3)\_2\}_\_2 (188 mg, 0.50 mmol) in n-hexane (2 mL) was treated with 0.5 mL of 1(M) DiBAIH 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 ca. 10 minutes. The slightly turbid mixture was filtered and the filtrate was stored at −35 °C. A small amount of dark brown colored crystals suitable for X-ray crystallography were obtained. Formation of \[\text{Mn}_6(\mu_3-\text{H})_4(\mu-\text{H})_2(\mu-\text{N(SiMe}_3)_2)_4(\text{N(SiMe}_3)_2)_2\] was determined by single crystal X-ray crystallography.

\[\text{Mn}_6\text{H}_6(\text{hmds})_6\]
**Figure S1.** UV-vis spectrum of 2 in n-hexane.

**Figure S2.** Solid IR (ATR) spectrum of 2.
Cyclotrimerization reactions of phenyl acetylene

A mixture of phenylacetylene (44 µL, 40.92 mg, 0.4 mmol) and Mn₆H₆(hmds)₆ (4.3 mg, 3.3 µmol, 0.83 mol%) in 2 mL of hexane was stirred for three days at room temperature giving a black reaction mixture with some amount of black particles. Reaction mixture was filtered over a plug of silica and the plug was eluted further with 3×2 mL of ethyl acetate. Solvent was removed under vacuum and the product was isolated by chromatography using pentane and ethyl acetate mixture (95:5).

1,3,5-Triphenylbenzene and 1,2,4-triphenylbenzene (1:1)

C₂₄H₁₈
306.41 g/mol

Appearance Yellow oil
Yield 19 mg, 0.06 mmol (47%)

¹H-NMR (300 MHz, CDCl₃) δ 7.81 (s, 3H), 7.75 – 7.65 (m, 10H), 7.56 – 7.35 (m, 15H), 7.28 – 7.17 (m, 5H).

¹³C-NMR (75 MHz, CDCl₃) δ 142.48, 141.61, 141.27, 141.24, 141.11, 140.72, 140.50, 139.67, 131.25, 130.05, 130.01, 129.56, 128.99, 128.07, 128.04, 127.69, 127.58, 127.50, 127.28, 126.74, 126.66, 126.27, 125.32.

GC-MS tᵣ = 12.59 min, (EI, 70 eV): m/z = 306 [M⁺], 291, 276, 265, 252, 239, 226, 215, 145, 113, 91, 77, 63, 52.

tᵣ = 13.71 min, (EI, 70 eV): m/z = 306 [M⁺], 302, 289, 276, 228, 207, 189, 151, 113, 102, 91, 77, 63, 51.

Analytical data were in full agreement with A. Geny, N. Agenet, L. Iannazzo, M. Malacria, C. Aubert, V. Gandon, Angewandte Chemie International Edition 2009, 48, 1810–1813.
5 Reaction of 2 with 4-Me-Pyridine

\[ \text{Mn}_6\text{H}_6(\text{hmds})_6 \xrightarrow{\text{6 equiv. } \text{MePy}} \text{Mn}_6(\text{MePy})_6\text{H}_x(\text{hmds})_y \]

\[ \text{MePy} = \begin{array}{c}
\text{N} \\
\end{array} \]
Hydroboration of pyridine

A screw-cap NMR tube was charged with 2 (2.2 mg, 1.7 µmol, 0.83 mol% compared to MePy) in 0.6 mL C₆D₆ and treated with HBpin (58 µL, 0.4 mmol) followed by addition of MePy (19.5 µL, 0.2 mmol). NMR tube was heated at 50 °C and the conversion of MePy was monitored by ¹H NMR spectroscopy.
**1,2-addition product:** $^1$H NMR (400 MHz, C$_6$D$_6$) δ 6.70 (d, $J = 7.4$ Hz, 1H), 4.96 (dd, $J = 7.4$, 1.6 Hz, 1H), 4.89 – 4.82 (m, 1H), 4.16 (dd, $J = 4.0$, 1.7 Hz, 2H), 1.58 (dd, $J = 7.3$, 2.9 Hz, 3H), 1.01 (s, 12H).

**1,4-addition product:** $^1$H NMR (400 MHz, C$_6$D$_6$) δ 6.51 (d, $J = 8.0$ Hz, 2H, signals overlapped with 1,4-product), 4.60 – 4.53 (m, 2H), 3.02 (m, 2H), 1.01 (s, 12H, overlapped with the signal of 1,4-product), Me-Py protons are overlapped with the Bpin signals.

Data are in accordance with the reported values: M. Arrowsmith, M. S. Hill, T. Hadlington, G. Kociok-Köhn, C. Weetman, *Organometallics* 2011, 30, 5556–5559.

**After 16h**
After 64h

A screw-cap NMR tube was charged with Mn(hmds)$_2$ (3.8 mg, 0.01 mmol, 5 mol% compared to Py), Py (19.5 µL, 0.2 mmol) and HBpin (58 µL, 0.4 mmol). The NMR tube was heated at 50 °C and the conversion of Py was monitored by $^1$H NMR spectroscopy.

1,2-addition product: $^1$H NMR (400 MHz, C$_6$D$_6$) δ 6.69 (d, $J = 7.4$ Hz, 1H), 5.78 (dd, $J = 9.0$, 5.4 Hz, 1H), 5.17 – 5.03 (m, 2H), 4.14 (d, $J = 2.9$ Hz, 2H), 1.00 (s, 12H).

1,4-addition product: $^1$H NMR (400 MHz, C$_6$D$_6$) δ 6.51 (d, $J = 8.0$ Hz, 2H), 4.60 – 4.53 (m, 2H), 2.81 (m, 2H), 0.97 (s, 12H).

Data are in accordance with the reported values: M. Arrowsmith, M. S. Hill, T. Hadlington, G. Kociok-Köhn, C. Weetman, Organometallics 2011, 30, 5556–5559.
After 16h

After 32h
After 72h
7 X-ray structure

$[\text{Mn}_6(\mu_3-H)_4(\mu-H)_2][\mu-N(\text{SiMe}_3)_2]_4[N(\text{SiMe}_3)_2]_2]$ crystallizes as $n$-hexane monosolvate. For X-Ray structure determination, a suitable crystal 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 $P2_1/n$ 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). The total number of runs and images was based on the strategy calculation from the program CrysAlisPro (Agilent).

Cell parameters were retrieved using the CrysAlisPro (Agilent) software and refined using CrysAlisPro (Agilent). Data reduction was performed using the CrysAlisPro (Agilent) software which corrects for Lorentz polarization.

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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.
Crystal Data for \([\text{Mn}_6(\mu_3-H)_{4}(\mu_2-H)_{2}(\mu-N(\text{SiMe}_3)_{2})_{4}(N(\text{SiMe}_3)_{2})_{2}]}\), n-hexane

| Property                                      | Value                        |
|-----------------------------------------------|------------------------------|
| Identification code                           | UCJ65_red                    |
| Empirical formula                             | \(\text{C}_{42}\text{H}_{128}\text{Mn}_6\text{N}_6\text{Si}_{12}\) |
| Formula weight                                 | 1384.22                      |
| Temperature/K                                  | 123.0                        |
| Crystal system                                 | monoclinic                   |
| Space group                                    | \(\text{P}2_1/n\)            |
| \(a/\text{Å}\)                                | 9.16670(10)                  |
| \(b/\text{Å}\)                                | 23.2172(3)                   |
| \(c/\text{Å}\)                                | 17.4631(3)                   |
| \(\alpha/°\)                                  | 90                           |
| \(\beta/°\)                                   | 90.2310(10)                  |
| \(\gamma/°\)                                  | 90                           |
| Volume/\(\text{Å}^3\)                         | 3716.56(9)                   |
| \(Z\)                                         | 2                            |
| \(\rho_{\text{calc}}/\text{g/cm}^3\)         | 1.237                        |
| \(\mu/\text{mm}^{-1}\)                        | 10.124                       |
| \(F(000)\)                                    | 1480.0                       |
| Crystal size/mm\(^3\)                         | 0.2 \times 0.1 \times 0.07  |
| Radiation                                      | \(\text{CuK}\alpha (\lambda = 1.54184)\) |
| 2\(\Theta\) range for data collection/°       | 7.616 to 147.71              |
| Index ranges                                   | -11 \leq h \leq 11, -28 \leq k \leq 28, -21 \leq l \leq 21 |
| Reflections collected                          | 30226                        |
| Independent reflections                        | 7438 \([R_{\text{int}} = 0.0354, R_{\text{sigma}} = 0.0282]\) |
| Data/restraints/parameters                     | 7438/72/357                  |
| Goodness-of-fit on \(F^2\)                    | 1.019                        |
| Final R indexes [\(I\geq2\sigma(I)\)]        | \(R_1 = 0.0272, wR_2 = 0.0681\) |
| Final R indexes [all data]                     | \(R_1 = 0.0315, wR_2 = 0.0707\) |
| Largest diff. peak/hole / e \(\text{Å}^{-3}\) | 0.44/-0.36                  |
8 Magnetic measurements

Temperature-dependent magnetic susceptibility measurements were carried out with a Quantum-Design MPMS-XL-5 SQUID magnetometer equipped with a 5 Tesla magnet in the range from 2 to 295 K in a magnetic field of 0.5 T. The polycrystalline sample was contained in a Teflon bucket and fixed in a non-magnetic sample holder. Each raw data file for the measured magnetic moment was corrected for the diamagnetic contribution of the Teflon bucket according to $M^{\text{dia}} = \chi_g \cdot m \cdot H$, with experimentally obtained gram susceptibility of Teflon bucket ($\chi_g = -3.80 \cdot 10^{-7}$ emu/(g\cdot Oe)). The molar susceptibility data were corrected for the diamagnetic contribution according to $\chi^{\text{mag}}_{M}(\text{sample}) = -0.5 \cdot M \cdot 10^{-6}$ cm$^3$mol$^{-1}$.

Literature: O. Kahn Molecular Magnetism, VCH Publishers Inc., New York, 1993.

Experimental $\chi_M T$ vs. $T$ data were modelled using a fitting procedure to the spin Hamiltonian for six manganese (II) $S = 5/2$ ions with two coupling constants and additional term for Zeeman splitting:

$$\dot{H} = -2J_{\parallel}(\hat{S}_1 \hat{S}_2 + \hat{S}_2 \hat{S}_3 + \hat{S}_3 \hat{S}_4 + \hat{S}_4 \hat{S}_5 + \hat{S}_5 \hat{S}_6) - 2J_{\perp}(\hat{S}_1 \hat{S}_6 + \hat{S}_2 \hat{S}_5 + \hat{S}_3 \hat{S}_4 + \hat{S}_4 \hat{S}_3 + \hat{S}_5 \hat{S}_2 + \hat{S}_6 \hat{S}_1) + g\mu_B \sum_{i=1}^{6} \hat{S}_i \quad \text{(Eq. 1)}$$
Poisoning studies

Scheme S1. Poisoning studies with trimethylphosphine (PMe₃) and dibenzo[a,e]cyclooctatetraene (dct).
10 Synthesis of 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).

(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%)

\[ ^1\text{H}-\text{NMR} \] (300 MHz, CDCl3) 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).

\[ ^{13}\text{C}-\text{NMR} \] (75 MHz, CDCl3) 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.

\[ \text{GC-MS} \] \( t_R = 6.31 \text{ min}, \) (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%)

\[ ^1\text{H}-\text{NMR} \] (300 MHz, CDCl3) 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).

\[ ^{13}\text{C}-\text{NMR} \] (75 MHz, CDCl3) 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.

\[ \text{GC-MS} \] \( t_R = 9.59 \text{ min}, \) (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.

\[
\text{C}_9\text{H}_9\text{Br}
\]

197.08 g/mol

**Appearance** colorless oil

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

\[^1^H\text{-NMR}\] (400 MHz, CDCl\(_3\)) \(\delta\) 7.50-7.35 (m, 2H), 7.42-7.29 (m, 2H), 5.36 (s, 1H), 5.10 (s, 1H), 2.12 (s, 3H).

\[^{13}\text{C-NMR}\] (101 MHz, CDCl\(_3\)) \(\delta\) 142.2, 140.1, 131.3, 127.2, 121.4, 113.1, 21.7.

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

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

4-Methoxy-α-methylstyrene

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

\[
\text{C}_{10}\text{H}_{12}\text{O}
\]

148.20 g/mol

**Appearance** colorless liquid

**Yield** 1.04 g, 7.02 mmol (35%)

**TLC** \(R_f = 0.25\) (SiO\(_2\), n-pentane)

\[^1^H\text{-NMR}\] (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).

\[^{13}\text{C-NMR}\] (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): \(m/z = 148 [M^+], 127, 133, 115, 105, 89, 77, 63, 51.\)

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.
Dibenzo[a,e]cyclooctatetraene (dct)

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

C₁₆H₁₂

204.27 g/mol

Appearance

colorless solid

Yield

912 mg, 4.46 mmol (47%)

TLC

R₁ = 0.46 (SiO₂, hexanes)

¹H-NMR

(300 MHz, CDCl₃): δ 7.19–7.13 (m, 4H), 7.10–7.02 (m, 4H), 6.76 (s, 4H).

¹³C-NMR

(75 MHz, CDCl₃): δ 137.1, 133.3, 129.1, 126.8.

GC-MS

tᵣ = 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.

1-Phenyl-1-cyclopentene

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

C₁₁H₁₂

144.22 g/mol

Appearance

colorless liquid

Yield

1.99 g, 13.8 mmol (69%)
\( ^1\text{H-NMR} \) (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).

\( ^{13}\text{C-NMR} \) (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.

\( \text{GC-MS} \) \( t_R = 6.94 \) 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, \textit{J. Am. Chem. Soc.} \textbf{2004}, \textit{126}, 16433–16439.

\textit{1-Phenyl-1-cycloheptene}

Synthesis was performed by Schachtner, Josef, \textit{Dissertation} \textbf{2016}, Regensburg.

\[\text{C}_{13}\text{H}_{16}\]

172.27 g/mol

\textbf{Appearance} colorless liquid

\textbf{Yield} 2.89 g, 16.8 mmol (84%)  

\( ^1\text{H-NMR} \) (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).

\( ^{13}\text{C-NMR} \) (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.

\( \text{GC-MS} \) \( t_R = 7.97 \) 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, \textit{J. Chem. Soc.} \textbf{1956}, 451.
11 Hydrogenation products

Propane-1,2-diyldibenzene

\[
\text{C}_{15}\text{H}_{16}
\]

196.29 g/mol

\({}^1\text{H-NMR}\)

(300 MHz, CDCl\(_3\)) \(\delta\) 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).

\({}^{13}\text{C-NMR}\)

(75 MHz, CDCl\(_3\)) \(\delta\) 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\(^+\)], 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.

Phenylcyclohexane

\[
\text{C}_{12}\text{H}_{16}
\]

160.26 g/mol

\({}^1\text{H-NMR}\)

(300 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).

\({}^{13}\text{C-NMR}\)

(75 MHz, CDCl\(_3\)) \(\delta\) 148.1, 128.3, 126.5, 125.8, 44.7, 34.52, 27.0, 26.2.

\({}\text{GC-MS}\)

\(t_R = 7.30\) 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.

1,1-Diphenylethane

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

182.27 g/mol

\({}^1\text{H-NMR}\)

(300 MHz, CDCl\(_3\)) \(\delta\) 7.35 – 7.11 (m, 10H), 4.15 (q, \(J = 7.1\), 1H), 1.63 (d, \(J = 7.2\), 3H).

\({}\text{GC-MS}\)

\(t_R = 7.97\) 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

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

146.23 g/mol
Ethane-1,1,2-triyltribenzene

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

- \( M = 258.36 \) g/mol

\[ \Delta 7.30 – 7.09 \text{ (m, 13H)}, 7.05 – 6.95 \text{ (m, 2H)}, 4.24 \text{ (t, } J = 7.8 \text{ Hz, 1H), 3.37 (d, } J = 7.8 \text{ Hz, 2H).} \]

\[ \Delta 144.45, 140.26, 129.08, 128.34, 128.05, 126.19, 125.88, 53.11, 42.11. \]

- \( t_R = 5.87 \) min, (EI, 70 eV): \( m/z = 258 \text{ [M] }^+, 167, 152, 139, 128, 115, 102, 91, 77, 65, 51. \)

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

1-Chloro-4-isopropylbenzene

\[ \text{C}_{9}\text{H}_{11}\text{Cl} \]

- \( M = 154.64 \) g/mol

\[ \Delta 7.25 \text{ (m, 2H)}, 7.21 – 7.09 \text{ (m, 2H)}, 2.89 \text{ (m, 1H), 1.23 (d, } J = 6.9 \text{ Hz, 6H).} \]

\[ \Delta 142.3, 131.3, 128.4, 127.8, 33.6, 23.9. \]

- \( t_R = 5.37 \) 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-Isopropyl-4-methoxybenzene

\[ \text{C}_{10}\text{H}_{14}\text{O} \]

- \( M = 180.24 \) g/mol

\[ \Delta 7.15 \text{ (d, } J = 8.8 \text{ Hz, 2H)}, 6.84 \text{ (d, } J = 8.7 \text{ Hz, 2H), 3.79 (s, 3H), 2.95 – 2.78 \text{ (m, 1H), 1.24 (s, 3H), 1.21 (s, 3H).} \]

- Analytical data were in full agreement with S. S. Kim, C. S. Kim, *J. Org. Chem.* 1999, 64, 9261–9264.
Methyl(4-(prop-2-yl)phenyl)sulfane

C_{10}H_{14}S

166.28 g/mol

^1H-NMR

(300 MHz, CDCl\textsubscript{3}) \(\delta 7.26 – 7.19 \) (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).

^13C-NMR

(75 MHz, CDCl\textsubscript{3}) \(\delta 146.11, 135.05, 127.20, 127.01, 77.47, 77.04, 76.62, 33.65, 24.00, 16.42\).

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.

(4R)-\(p\)-menthene

C\textsubscript{10}H\textsubscript{18}

138.25 g/mol

Appearance

colorless liquid

Yield

81 mg, 0.59 mmol (73%)

^1H-NMR

(300 MHz, CDCl\textsubscript{3}) \(\delta 5.39 – 5.25 \) (m, 1H), 2.01 – 1.88 (m, 2H), 1.77 – 1.69 (m, 2H), 1.64 (brs, 3H), 1.50-1.40 (m, 2H), 1.26-1.17 (m, 2H), 0.89 (d, \(J = 4.3 \) Hz), 0.87 (d, \(J = 4.3 \) Hz).

^13C-NMR

(75 MHz, CDCl\textsubscript{3}) \(\delta 133.99, 121.03, 40.00, 32.30, 28.97, 26.49, 23.51, 20.02, 19.71\).

GC-MS

\(t_R = 4.92\) min, (EI, 70 eV): \(m/z = 138 \) [M^+] , 123, 95, 81, 67, 55.

Analytical data were in full agreement with D. F. Schneider, M. S. Viljoen, Tetrahedron 2002, 58, 5307–5315.

N-Cinnamylaniline hydrochloride

C\textsubscript{15}H\textsubscript{16}ClN

245.75 g/mol

Yield

119.1 mg, 0.48 mmol (96%)

^1H-NMR

(300 MHz, CDCl\textsubscript{3}) \(\delta 7.61 – 7.51 \) (m, 5H), 7.44 (ddt, \(J = 5.5, 2.6, 1.6 \) Hz, 2H), 7.38 – 7.29 (m, 3H), 6.84 (d, \(J = 16.2 \) Hz, 1H), 6.35 (dt, \(J = 15.9, 7.3 \) Hz, 1H), 4.20 (dd, \(J = 7.3, 1.2 \) Hz, 2H).
C-NMR (75 MHz, CDCl$_3$) $\delta$ 140.74, 136.76, 136.25, 131.48, 131.09, 129.97, 129.82, 127.91, 124.16, 118.74, 55.34.

GC-MS (freebase) $t_R = 10.29$ min, (EI, 70 eV): $m/z = 209$ [M$^+$], 192, 132, 117, 106, 91, 77, 65, 51.

HRMS Calcd. for C$_{15}$H$_{16}$N$^+$ 210.1277; found: 210.1274.

IR 3380 (b), 3060 (w), 2915 (m), 2661 (m), 2423 (m), 1588 (m), 1491 (m), 1446 (m), 969 (m), 738 (s), 690 (s) cm$^{-1}$.

N-Benzylaniline hydrochloride

![C$_{13}$H$_{14}$ClN](image)

$219.71$ g/mol

Yield 106.9 mg, 0.49 mmol (98%)

$^1$H-NMR (300 MHz, MeOD) $\delta$ 7.58 – 7.49 (m, 3H), 7.46 – 7.38 (m, 7H), 4.61 (s, 2H).

$^{13}$C-NMR (75 MHz, MeOD) $\delta$ 136.36, 131.98, 131.47, 131.34, 130.83, 130.15, 124.15, 56.92.

GC-MS (freebase) $t_R = 9.04$ min, (EI, 70 eV): $m/z = 183$ [M$^+$], 154, 106, 91, 77, 65, 51.

Analytical data were in full agreement with T. Li, X. Cui, L. Sun, C. Li, RSC Adv. 2014, 4, 33599.

N-Benzyl-2-tert-butylamine hydrochloride

![C$_{11}$H$_{18}$ClN](image)

$199.72$ g/mol

Yield 35.4 mg, 0.18 mmol (89%)

$^1$H-NMR (300 MHz, MeOD) $\delta$ 7.59 – 7.41 (m, 5H), 4.19 (s, 2H), 1.47 (s, 9H).

$^{13}$C-NMR (75 MHz, MeOD) $\delta$ 133.15, 131.09, 130.59, 130.35, 58.71, 46.69, 27.93, 25.89.

GC-MS (freebase) $t_R = 6.25$ min, (EI, 70 eV): $m/z = 163$ [M$^+$], 148, 106, 91, 77, 65, 51.

HRMS Calcd. for C$_{11}$H$_{18}$N$^+$ 164.1434; found: 164.1432.

IR 3370 (b), 3038 (w), 2974 (m), 2192 (m), 2109 (m), 2050 (m), 1375 (s), 1204 (m), 1118 (m), 760 (s), 693 (s) cm$^{-1}$.

N-(4-Methoxybenzyl)aniline hydrochloride
**C_{14}H_{15}CINO**

249.74 g/mol

**Yield**

47.9 mg, 0.19 mmol (96%)

**^1H-NMR**

(300 MHz, MeOD) δ 7.61 – 7.49 (m, 3H), 7.44 – 7.37 (m, 2H), 7.36 – 7.29 (m, 2H), 7.03 – 6.89 (m, 2H), 4.54 (s, 2H), 3.80 (s, 3H).

**^13C-NMR**

(75 MHz, MeOD) δ 162.34, 136.10, 133.12, 131.40, 131.07, 124.33, 123.54, 115.45, 56.85, 55.86.

**GC-MS (freebase)**

$t_R = 10.13$ min, (EI, 70 eV): $m/z = 213 [M^+]$, 168, 121, 106, 91, 77, 65, 51.

**Elemental Analysis**

Calcd. for C_{14}H_{15}NO: 214.1226; found: 214.1226.

**IR**

3060 (w), 2896 (m), 2840 (m), 2669 (s), 2550 (s), 2423 (s), 1595 (s), 1513 (s), 1305 (m), 1249 (s), 1033 (s), 815 (s), 795 (s) cm$^{-1}$.

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**N-Benzyl-4-(methylthio)aniline**

C_{14}H_{15}NS

229.34 g/mol

**Yield**

42.8 mg, 0.19 mmol (93%)

**^1H-NMR**

(300 MHz, CDCl$_3$) δ 7.39 – 7.33 (m, 4H), 7.25 – 7.19 (m, 2H), 6.63 – 6.56 (m, 2H), 4.32 (s, 2H), 2.41 (s, 3H).

**^13C-NMR**

(75 MHz, CDCl$_3$) δ 146.87, 139.08, 131.45, 128.69, 127.48, 127.34, 124.56, 113.53, 48.35, 19.13.

**GC-MS**

$t_R = 10.91$ min, (EI, 70 eV): $m/z = 229 [M^+]$, 214, 180, 152, 138, 91, 77, 65, 51.

Analytical data were in full agreement with W. Zhou, M. Fan, J. Yin, Y. Jiang, D. Ma, *J. Am. Chem. Soc.* 2015, 137, 11942.

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**N-Cinnamylaniline**

C_{15}H_{15}N

209.29 g/mol

**Yield**

49.2 mg, 0.24 mmol (51%)
\(^{1}\text{H-NMR}\) (300 MHz, CDCl\(_3\)) \(\delta\) 7.33 – 7.20 (m, 3H), 7.19 – 7.08 (m, 4H), 6.66 (tt, \(J = 7.3, 1.1\) Hz, 1H), 6.63 – 6.51 (m, 3H), 6.26 (dt, \(J = 15.9, 5.7\) Hz, 1H), 3.87 (dd, \(J = 5.7, 1.6\) Hz, 2H), 3.78 (s, 1H).

\(^{13}\text{C-NMR}\) (75 MHz, CDCl\(_3\)) \(\delta\) 148.2, 137.0, 131.6, 129.4, 128.7, 127.7, 127.2, 126.5, 117.8, 113.2, 46.4.

\(\text{GC-MS}\) \(t_R = 10.13\) min, (EI, 70 eV): \(m/z = 209\ [\text{M}^+]\), 192, 178, 165, 152, 132, 117, 106, 91, 77, 65, 51.

Analytical data were in full agreement with S. Karnakanti, Z.-L. Zang, S. Zhao, P.-L. Shao, P. Hu, Y. He, \textit{Chem. Commun.} \textbf{2017}, \textit{53}, 11205.

\textit{N-(4-Methoxycinnamyl)aniline}

\(\text{C}_{16}\text{H}_{17}\text{NO}\)

239.32 g/mol

\textbf{Yield} 40.8 mg, 0.17 mmol (crude 89\%, isolated 49\%)

\(^{1}\text{H-NMR}\) (300 MHz, CDCl\(_3\)) \(\delta\) 7.35 – 7.28 (m, 2H), 7.24 – 7.16 (m, 2H), 6.92 – 6.80 (m, 2H), 6.73 (tt, \(J = 7.4, 1.1\) Hz, 1H), 6.70 – 6.65 (m, 2H), 6.58 (dt, \(J = 15.8, 1.6\) Hz, 1H), 6.20 (dt, \(J = 15.8, 5.9\) Hz, 1H), 3.92 (dd, \(J = 5.9, 1.6\) Hz, 2H), 3.81 (s, 3H).

\(^{13}\text{C-NMR}\) (75 MHz, CDCl\(_3\)) \(\delta\) 159.3, 148.2, 131.2, 129.7, 129.4, 127.6, 124.8, 117.7, 114.1, 113.2, 55.4, 46.4.

\(\text{GC-MS}\) \(t_R = 11.19\) min, (EI, 70 eV): \(m/z = 239\ [\text{M}^+]\), 222, 207, 190, 178, 165, 147, 133, 115, 103, 91, 77, 65, 51.

Analytical data were in full agreement with N. Nishina, Y. Yamamoto, \textit{Tetrahedron} \textbf{2009}, \textit{65}, 1799.

\textit{N-(4-Fluorocinnamyl)aniline}

\(\text{C}_{15}\text{H}_{14}\text{FN}\)

227.28 g/mol

\textbf{Yield} 45.4 mg, 0.20 mmol (crude 83\%, isolated 50\%)
$^1$H-NMR (300 MHz, CDCl$_3$) δ 7.40 – 7.27 (m, 2H), 7.24 – 7.16 (m, 2H), 7.08 – 6.93 (m, 2H), 6.74 (tt, J = 7.3, 1.1 Hz, 1H), 6.70 – 6.65 (m, 2H), 6.59 (dt, J = 15.8, 1.6 Hz, 1H), 6.25 (dt, J = 15.9, 5.7 Hz, 1H), 3.94 (dd, J = 5.8, 1.6 Hz, 2H), 3.87 (brs, 1H).

$^{13}$C-NMR (75 MHz, CDCl$_3$) δ 162.4 (d, J = 246.7 Hz), 148.1, 133.1 (d, J = 3.2 Hz), 130.4, 129.4, 127.9 (d, J = 8.0 Hz), 126.9 (d, J = 2.3 Hz), 117.8, 115.6 (d, J = 21.5 Hz), 113.2, 46.3.

GC-MS $t_R$ = 10.10 min, (EI, 70 eV): $m/z$ = 227 [M$^+$], 210, 196, 183, 165, 150, 135, 115, 109, 93, 77, 65, 51.

Analytical data were in full agreement with N. Nishina, Y. Yamamoto, Tetrahedron 2009, 65, 1799.

$N$-(4-$N'$,$N'$-Dimethylaminocinnamyl)aniline

\[
\begin{align*}
\text{C}_{17}\text{H}_{20}\text{N}_2 & \\
& 252.36 \text{ g/mol}
\end{align*}
\]

Yield 34.1 mg, 0.14 mmol (crude 74 %, isolated 34%)

$^1$H-NMR (300 MHz, CDCl$_3$) δ 7.29 (dd, J = 9.2, 2.4 Hz, 2H), 7.23 – 7.16 (m, 2H), 6.79 – 6.65 (m, 5H), 6.55 (d, J = 15.8 Hz, 1H), 6.14 (dt, J = 15.6, 6.0 Hz, 1H), 3.90 (dd, J = 6.0, 1.5 Hz, 2H), 3.70 (brs, 1H), 2.96 (s, 6H).

$^{13}$C-NMR (75 MHz, CDCl$_3$) δ 150.2, 148.4, 131.9, 129.4, 127.4, 125.4, 122.5, 117.6, 113.2, 112.5, 46.7, 40.7.

GC-MS $t_R$ = 11.97 min, (EI, 70 eV): $m/z$ = 252 [M$^+$], 234, 221, 207, 192, 173, 160, 146, 134, 115, 105, 93, 79, 66, 51.

$N$-butylcyclohexanamine

\[
\begin{align*}
\text{C}_{10}\text{H}_{11}\text{N} & \\
& 155.29 \text{ g/mol}
\end{align*}
\]

Yield 34.7 mg, 0.22 mmol (54%)
1H-NMR (300 MHz, CDCl₃) δ 2.63 – 2.56 (m, 1H), 2.38 (ddd, J = 10.4, 7.0, 3.8 Hz, 1H), 1.88 – 1.84 (m, 2H), 1.72 – 1.68 (m, 2H), 1.50 – 0.99 (m, 10H), 0.89 (t, J = 7.2 Hz, 3H).

13C-NMR (75 MHz, CDCl₃) δ 57.05, 46.84, 33.76, 32.72, 26.31, 25.25, 20.70, 14.14.

GC-MS tᵣ = 5.94 min, (EI, 70 eV): m/z = 155 [M⁺], 126, 112, 98, 84, 70, 56.

Analytical data were in agreement with V. R. Jumde, E. Petricci, C. Petrucci, N. Santillo, M. Taddei, L. Vaccaro, Org. Lett. 2015, 17, 3990–3993.

N-(3-phenylpropyl)aniline

C₁₅H₁₇N 211.31 g/mol

Yield 27 mg, 0.13 mmol (89%)

1H-NMR (300 MHz, CDCl₃) δ 7.36 – 7.31 (m, 2H), 7.26 – 7.17 (m, 6H), 6.75 – 6.70 (m, 1H), 6.65 – 6.59 (m, 2H), 3.63 (s br, 1H), 3.18 (t, J = 7.0 Hz, 1H), 2.82 – 2.70 (m, 2H), 2.03 – 1.93 (m, 2H).

13C-NMR (75 MHz, CDCl₃) δ 148.46, 141.79, 129.35, 128.56, 128.53, 126.08, 117.33, 112.85, 43.51, 33.52, 31.19.

GC-MS tᵣ = 9.74 min, (EI, 70 eV): m/z = 211 [M⁺], 118, 106, 91, 77, 65, 51.

Analytical data were in agreement with Adam, J. R. Cabrero-Antonino, K. Junge, R. Jackstell, M. Beller, Angew. Chem. Int. Ed. 2016, 55, 11049–11053.

8-methyl-1,2,3,4-tetrahydroquinoline

C₁₀H₁₃N 147.22 g/mol

Yield 16 mg, 0.11 mmol (55%)

1H-NMR (300 MHz, CDCl₃) δ 6.87 (t, J = 6.9 Hz, 2H), 6.57 (t, J = 7.0 Hz, 1H), 3.66 (s br, 1H), 3.38 (m, 2H), 2.80 (m, 2H), 2.09 (s, 3H), 1.95 (s, 2H).
$^{13}$C-NMR (75 MHz, CDCl$_3$) $\delta$ 142.82, 127.96, 127.50, 121.31, 120.99, 116.52, 42.46, 27.40, 22.27, 17.30.

GC-MS $t_R =$ 7.36 min, (EI, 70 eV): $m/z = 147$ [M$^+$], 144, 132, 117, 103, 91, 77, 65, 51.

Analytical data were in agreement with J.-F. Zhang, R. Zhong, Q. Zhou, X. Hong, S. Huang, H.-Z. Cui, X.-F. Hou, ChemCatChem 2017, 9, 2496–2505.
12 Selected NMR-Spectra

[Image of NMR spectra with annotations]

# corresponds to the signal used for calculating the relative ratio of products

[Further annotations and data points on the spectra]
