Supporting Information

Fast Titanium-Catalyzed Hydroaminomethylation of Alkenes and the Formal Conversion of Methylamine

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1. General information

Unless otherwise noted, reactions were performed under air. All solvents were distilled prior to use. Petroleum ether (boiling range 40-60 °C) is abbreviated with "PE". All chemicals whose synthesis is not described on pages 3-26 were purchased from commercial sources and, unless otherwise noted, used without further purification. Silica gel from Grace (particle size = 40-63 µm) was used for chromatography. Silica gel 60 sheets with fluorescent indicator (254 nm) from Merck were used for thin layer chromatography; substances were detected with UV light, iodine or ninhydrin. Products that have already been reported in the literature were identified by $^1$H NMR spectroscopy and $^{13}$C NMR spectroscopy; all analytical data was found to be consistent with the literature. New substances were additionally characterized by infrared spectroscopy (IR), mass spectrometry (MS) and high resolution mass spectrometry (HRMS). NMR spectra were recorded on a Bruker Fourier 300, Bruker Avance DRX 500 or Bruker Avance III 500 MHz. $^1$H NMR spectra are referenced to the solvent (7.26 ppm for CDCl$_3$ or 7.16 ppm for benzene-d$_6$). $^{13}$C NMR spectra are referenced to the solvent (77.16 ppm for CDCl$_3$ or 128.06 ppm for benzene-d$_6$). $^{29}$Si NMR spectra are referenced to the external standard Me$_2$SiHCl (11.1 ppm). $^{19}$F NMR spectra are referenced to the internal standard C$_6$F$_6$ (−164.9 ppm). Infrared spectra were recorded on a Bruker Tensor 27, Bruker Vector 22 or Shimadzu IRSpirit QATR-S spectrometer. MS analyses were performed on a Thermo Scientific DFS (EI, 70 eV) or Shimadzu GCMS-QP2020 (EI, 70 eV). GC analyses were performed on a Shimadzu GC-2010 gas chromatograph (column: FS-SE-54-CB-0.25, length = 30 m, inner diameter = 0.32 mm, film thickness = 0.25 µm, (94%-methyl)-(5%-phenyl)-(1%-vinyl)polysiloxane) with a flame ionization detector. Selectivities were determined by the ratio of the corresponding GC areas.

4-Fluoro-N-methylaniline,[1,2] 4-chloro-N-methylaniline,[1,2] 4-bromo-N-methylaniline,[1,2] 4-methoxy-N-methylaniline,[3,2] 4-methylthio-N-methylaniline,[1,2] 4-trifluormethoxy-N-methylaniline,[3] N,N-diethyl-1-aminopent-5-ene,[4,5] 5-propoxypent-1-ene[2] and 5-trisopropylsiloxypent-1-ene[5,6,7] were synthesized according to literature procedures.
2. Synthesis of the catalyst

To emphasize the low price and availability of the used catalyst, as well as to encourage other work groups to reproduce and improve on the results, the following syntheses include a calculation of the total cost. Chemicals were purchased from TCI or Acros.

Ignoring the possibility of recovering the formamidine ligand, the total cost of the catalytic system (TiBn$_4$ and ligand) in our laboratory scale was determined to be 1.12 € per 1 mmol of catalyst (1.05 € per 1 g). The cost of catalyst in each reaction presented in the manuscript (2 mmol of substrate, 5 mol% catalyst loading) was 0.11 €.

Tetrabenzyltitanium (6)

Tetrabenzyltitanium is notorious for its very high price when purchased (540€, 5 g, MCAT) and tetraalkyltitanium species are avoided in general due to their thermal lability and laborious syntheses. However, the synthesis suggested here is very inexpensive, requires only standard glassware and very common equipment, and can be performed easily within only a few hours of work. We found that the additional effort of using dried, degassed solvents, Schlenk techniques and cooling below −18 °C (ice/NaCl) is mostly unnecessary, because the additional work time will affect the overall yield and especially the purity of the product far worse than short exposure to slight amounts of air, moisture and room temperature. Unless otherwise noted, the reaction was carried out under air in undried solvents as quickly as possible.

In a 500 mL-flask with magnetic stir bar, reflux condenser, CaCl$_2$-tube (0.77 €) and dropping funnel, magnesium turnings (25.6 g, 1.05 mol, 1.48 €) were suspended in Et$_2$O (200 mL, 1.51 €). BnCl (65.8 g, 520 mmol, 1.95 €) was added dropwise, fast enough to keep the solution boiling. A second 500 mL-flask with magnetic stir bar, septum, dropping funnel and CaCl$_2$-tube (0.77 €) was charged with Et$_2$O (200 mL, 1.51 €) and cooled to −15 °C with an ice/NaCl-bath (0.10 €), TiCl$_4$ (22.8 g, 120 mmol, 5.09 €) was slowly added via syringe through the septum at −15 °C; note that the addition cannot be done through the dropping funnel as the titanium source will immediately precipitate in contact with the ether atmosphere. The Grignard solution was decanted from excess magnesium into the dropping funnel of the second setup. The solid residue of magnesium was extracted with Et$_2$O (50 mL, 0.38 €) and the extract added to the dropping funnel. The Grignard solution was added to the suspension at −15 °C and then stirred for 30 min at room temperature (note that solidification can occur after addition of the Grignard solution, mechanical breakup of large solid deposits is advised before the stirring step at room temperature). The solvent was removed under reduced pressure at 0 °C. Remaining Et$_2$O was then removed under high vacuum at room temperature for 30 min, while shaking the flask to break up the solid into a powder (note that this step is of utmost importance, as even small amounts of ether will carry severe impurities of salts into the final product). Hexane (200 mL, 0.59 €) was added to the residue. A 500 mL flask with Schlenk frit, the opposite side of the Schlenk frit being filled with a pad of Na$_2$SO$_4$ (5 cm thickness, 1.57 €), was attached to the flask with the solid residue and crude product in hexane and the solution was filtered through the Na$_2$SO$_4$ pad. The remaining solid residue was extracted with further hexane (100 mL, 50 mL, 0.42 €). The solvent was removed under reduced pressure and traces of remaining solvents were removed under high vacuum. From this point onward, inert atmosphere (Ar) and baked out glassware were used. The crude product was dissolved in hexane (50 mL, 0.14 €) and filtered through a new Schlenk frit with a pad of dry Na$_2$SO$_4$ (0.79 €) into a 100 mL-Schlenk flask. The frit and Na$_2$SO$_4$ were flushed with hexane (20 mL, 0.06 €). The crude product solution was stored at −30 °C overnight to crystallize the product. The product was separated at −30 °C by filtration, washed with hexane (2×5 mL, 0.03 €) and dried under vacuum (note that after storing the solution at −30 °C for several days or from more concentrated solutions an orange to red solid will additionally start to precipitate - this is not the product!). The product was obtained as dry, very dark violet, almost black crystals that were ground into a dark violet powder (16.2 g, 39.3 mmol, 33 %, total cost 17.16 €). The product should not appear sticky, otherwise it is most certainly impure and inactive (due to either impurities being carried over through filtrations by residual ether or diphenylethane from faulty crystallization). The product needs to be stored under inert atmosphere at −30 °C or below. Decomposition will occur overnight at room temperature. We were able to use a batch of TiBn$_4$ in catalysis that was stored at −30 °C for a year, we did not observe a significant decrease in catalytic activity.

$^1$H NMR (C$_6$D$_6$, 300 MHz): $\delta = 2.81$ (s, 8 H), 6.62 (d, $J = 7.3$ Hz, 8 H), 6.94 (t, $J = 7.4$ Hz, 4 H), 7.08 (t, $J = 7.4$ Hz, 8 H) ppm.

$^{13}$C NMR (C$_6$D$_6$, DEPT, 125 MHz): $\delta = 98.3$ (CH$_2$), 124.7 (CH), 129.3 (CH), 129.7 (CH), 142.4 (C) ppm.
A 500 mL-flask with magnetic stir bar and boiling stones, large Vigreux column, Claisen bridge and receiving flask was charged with dicyclopentadiene (250 g, 1.89 mol, 10.50 €). The flask was heated to 200 °C and cyclopentadiene was collected. Cyclopentadiene (140 g, 2.12 mol) was then transferred into the drawn apparatus and stirred at 0 °C. Gaseous HCl was generated by slowly adding concentrated H$_2$SO$_4$ (600 mL, 11.3 mol, 9.79 €) into the 2 L-flask containing NaCl (620 g, 10.6 mol, 0.12 €) over 2.5 h. The reaction progress was monitored by weighting the reaction flask; the addition of HCl was aborted when the weight of the flask had increased by 66 g. The product was purified by distillation (65 mbar, 46 °C) and was obtained as colorless liquid (165.1 g, 1.61 mol, 76 % referenced to cyclopentadiene, total cost 20.41 €). Distillation at a atmospheric pressure is not advised due to low thermal stability of the product. The product was stored at −30 °C in a closed flask; it will decompose rapidly at room temperature, especially in the presence of impurities. The pure product can be stored at −30 °C over several weeks. Care must be taken when quenching residues and cleaning glassware, as the product aggressively reacts with water and some solvents.

$^1$H NMR (CDCl$_3$, 300 MHz): $\delta$ = 2.14-2.25 (m, 1 H), 2.31-2.44 (m, 2 H), 2.55-2.71 (m, 1 H), 5.02-5.07 (m, 1 H), 5.88-5.92 (m, 1 H), 6.03-6.07 (m, 1 H) ppm.

$^{13}$C NMR (CDCl$_3$, DEPT, 125 MHz): $\delta$ = 31.2 (CH$_2$), 34.6 (CH$_2$), 65.8 (CH), 132.3 (CH), 136.3 (CH) ppm.

IR (ATR): $\tilde{\nu}$ = 2939, 2847, 1607, 1499, 1429, 1276, 1213, 1159, 1042, 808 cm$^{-1}$.

MS (EI, 70 eV): $m/z$ (%) = 189 (100) [M$^+$], 174 (50), 158 (24), 146 (15), 129 (10), 117 (8).

HRMS (EI, 70 eV): calc. (C$_{12}$H$_{13}$NO) 189.1148, found 189.1144 [M$^+$].
2,6-Di(cyclopent-2-en-1-yl)-4-methoxyaniline (9)

A 250 mL flask with magnetic stir bar and reflux condenser was charged with 2-(cyclopent-2-en-1-yl)-4-methoxyaniline (138.3 g, 731 mmol, 74.48 €). 3-Chlorocyclopent-1-ene (37.5 g, 366 mmol, 4.64 €) was added quickly and the mixture was shaken to mix the substrates immediately (note that the mixture will heat up and solidify within less than a minute; any 3-chlorocyclopent-1-ene that is not mixed in at this point will decompose). The mixture was heated to 140 °C for 4 h. The mixture was dissolved in NaOH solution (2 M, 0.7 L, 0.93 €) and Et$_2$O (300 mL, 2.26 €). The layers were separated and the aqueous solution was extracted with further Et$_2$O (2×300 mL, 4.52 €). The combined organic layers were dried with MgSO$_4$ (1.06 €) and the ether was removed under reduced pressure. A distillation afforded the excess 2-(cyclopent-2-en-1-yl)-4-methoxyaniline (80.7 g, 427 mmol, −43.50 €) and the product (0.1 mbar, 178 °C), which was obtained as slightly green oil (64.5 g, 253 mmol, 69 %, total cost 44.39 €).

$^1$H NMR (CDCl$_3$, 300 MHz): δ = 1.70-1.86 (m, 2 H), 2.37-2.58 (m, 6 H), 3.73 (s, 3 H), 3.91-3.99 (m, 2 H), 5.81-5.86 (m, 2 H), 5.98-6.03 (m, 2 H), 6.55-6.58 (m, 2 H) ppm. The NH$_2$ protons appear as a very broad singlet with a not clearly identifiable maximum between 3.67-3.78 ppm.

$^{13}$C NMR (CDCl$_3$, DEPT, 125 MHz): δ = 30.8 (CH$_2$), 31.0 (CH$_2$), 32.5 (CH$_2$), 32.6 (CH$_2$), 47.0 (CH), 47.2 (CH), 55.7 (CH$_2$), 111.2 (CH), 111.4 (CH), 131.9 (C), 132.1 (C), 132.79 (CH), 132.83 (CH), 133.3 (CH), 133.5 (CH), 135.1 (C), 135.3 (C), 152.5 (C), 152.6 (C) ppm.

IR (ATR): $\bar{\nu}$ = 2938, 2847, 1597, 1463, 1314, 1123, 1143, 1060, 725 cm$^{-1}$.

MS (EI, 70 eV): $m/z$ (%) = 255 (100) [M]$^+$, 240 (42), 226 (16), 188 (14), 67 (14).

HRMS (EI, 70 eV): calc. (C$_{11}$H$_{12}$NO) 255.1618, found 255.1613 [M]$^+$.

2,6-Dicyclopentyl-4-methoxyaniline (10)

A 1 L flask with magnetic stir bar (7 cm) and reflux condenser was charged with 2,6-di(cyclopent-2-en-1-yl)-4-methoxyaniline (121.5 g, 476 mmol, 83.52 €), EtOAc (1 L, 14.03 €) and dry Pd/C$^{10}$ (9.98 g, 9.38 mmol, 2 %, 131.29 €). All joints were well greased and tightly secured with fork clamps. The apparatus was evacuated until the solvent started boiling and then vented with H$_2$. A 20 L-balloon with H$_2$ was attached (50-100 mbar of overpressure). The mixture was heated in a 100 °C oil bath for 165 h; the balloon was refilled during that time whenever the pressure was visibly reduced (total worth of H$_2$ ~1 €). The mixture was filtered, the Pd/C$^{10}$ washed with EtOAc (2.81 €), dried under vacuum (9.7 g, 9.1 mmol, −127.61 €) and successfully reused in other syntheses; no loss of catalytic activity was observed. The solvent was removed from the solution of crude product at reduced pressure. The product was isolated by distillation (0.027 mbar, 163 °C) and was obtained as slightly yellow, viscous oil (106.2 g, 409 mmol, 86 %, total cost 104.04 €).

$^1$H NMR (CDCl$_3$, 500 MHz): δ = 1.59-1.74 (m, 8 H), 1.78-1.86 (m, 4 H), 2.03-2.09 (m, 4 H), 3.04 (pent., J = 8.3 Hz, 2 H), 3.69 (br. s, 2 H), 3.77 (s, 3 H), 6.65 (s, 2 H) ppm.

$^{13}$C NMR (CDCl$_3$, JMOD, 125 MHz): δ = 25.3 (CH$_3$), 32.6 (CH$_3$), 40.6 (CH), 55.8 (CH$_2$), 109.5 (CH), 132.1 (C), 135.6 (C), 152.7 (C) ppm.

IR (ATR): $\bar{\nu}$ = 2947, 2867, 1598, 1461, 1355, 1306, 1219, 1141, 1051, 861 cm$^{-1}$.

MS (EI, 70 eV): $m/z$ (%) = 259 (100) [M]$^+$, 244 (68).

HRMS (EI, 70 eV): calc. (C$_{17}$H$_{16}$NO) 259.1931, found 259.1923 [M]$^+$.
A 250 mL-flask with magnetic stir bar, Vigreux column and Claisen bridge was charged with 2,6-dicyclopentyl-4-methoxyaniline (90.15 g, 348 mmol, 88.52 €), HC(OEt)$_3$ (25.75 g, 174 mmol, 1.19 €) and glacial AcOH (100 mg, 1.67 mmol, 0.01 €). The solution was stirred at 145 °C for 20 h. The solidified mixture was suspended in hexane (200 mL, 0.56 €) and filtrated. The solid was washed with hexane (300 mL, 0.84 €) and dissolved in boiling toluene (1.1 L, 4.54 €). The product precipitated from the solution at 4 °C overnight as a colorless solid (74.37 g, 141 mmol, 81 %, total cost 95.66 €). The product was ground into a very fine powder in a ball mill. This is of utmost importance for the use in any catalysis with short reaction times, since the extremely low solubility of the formamidine can render it useless otherwise.

$^1$H NMR (CDCl$_3$, 500 MHz): $\delta = 1.48$-1.56 (m, 7.1 H), 1.59-1.69 (m, 8.7 H)

$^{13}$C NMR (CDCl$_3$, DEPT, 125 MHz): $\delta = 25.7$ (CH$_2$), 25.8 (CH$_2$), 25.9 (CH$_2$), 26.1 (CH$_2$), 33.5 (CH$_3$), 34.6 (CH$_3$), 35.1 (CH$_3$), 35.2 (CH$_2$), 40.5 (CH), 40.78 (CH), 40.81 (CH), 55.38 (CH$_3$), 55.41 (CH$_3$), 55.5 (CH$_3$), 109.2 (CH), 109.57 (CH), 125.4 (CH), 128.3 (CH), 128.5 (C), 129.1 (CH), 137.6 (C), 138.0 (C), 142.7 (C), 145.2 (C), 148.8 (CH), 154.7 (C), 156.0 (C), 157.2 (C), 158.6 (C) ppm.

IR (ATR): $\lambda_{\text{max}}$ = 2949, 2864, 1656, 1600, 1556, 1458, 1341, 1298, 1196, 1055, 968, 885, 821 cm$^{-1}$.

MS (El, 70 eV): $m/z$ (%) = 503 (19), 415 (21), 399 (11), 341 (14), 327 (27), 281 (91), 221 (12), 147 (51), 73 (100).

HRMS (El, 70 eV): calc. (C$_{35}$H$_{48}$N$_2$O$_2$) 528.3710, found 528.3712 [M$^+$].

**Recovery of $N,N$-bis(2,6-dicyclopentyl-4-methoxyphenyl)formamidine (1)**

The very low solubility of this formamidine can be utilized to recover it from otherwise discarded reaction mixtures. The solutions are collected and solvents are distilled off. The residue is suspended in hexane and filtrated. The residue can then be washed with Et$_2$O, ETOAC, EtOH and hexane at will, the product will not dissolve. The residue is then extracted with CHCl$_3$ (100 mL per 1 g of formamidine) and filtrated to separate from insoluble impurities (TiO$_2$). The solvent is then removed from the solution of product in CHCl$_3$ under reduced pressure. The crude product is then dissolved in boiling toluene (15 mL per 1 g of formamidine) and stored at 4 °C overnight. The precipitated product is isolated by filtration and vacuum drying.
3. Hydroaminoalkylation reactions

General procedure A for the hydroaminoalkylation of alkenes

All substrates were dried and degassed prior to use. In a glovebox under N₂-atmosphere, a 5 mL ampoule (length = 130 mm, outer diameter = 10 mm, inner diameter = 7 mm, wall thickness = 1.5 mm) was charged with TiBr₄ (42 mg, 0.10 mmol, 5 mol%) and the amine (2 mmol). The mixture was stirred for 30 s. Finely ground N,N-bis(2,6-dicyclopentyl-4-methoxyphenyl)formamidine (53 mg, 0.10 mmol, 5 mol%) was added and the mixture was stirred for 20 min. [Note: This is done to counter the very low solubility of the formamidine. After stirring for 20 min at room temperature, most of the formamidine is in solution and the remaining solid dissolves within seconds at 155 °C. This pre-stirring step can be skipped entirely without sacrificing product yield, but the reaction time at 155 °C then needs to be increased by one minute to account for solvation of the ligand precursor.] The alkene (5 mmol) was added and the ampoule was sealed with a natural gas/O₂ torch. The ampoule was dipped into a 155 °C oil bath for the specified heating time. [Note: The reaction time over which the solution is at >140 °C is circa one minute shorter than the heating time.] The ampoule was then opened, the solution transferred into a flask with CH₂Cl₂ (30 mL) and quenched with EtOH (3 mL). The product was isolated by chromatography.

N-(2-Methylocty)aniline (2b_a)[10]

General procedure A was applied to N-methylaniline and 1-octene with a heating time of 2 min. The product was purified by chromatography (150 g SiO₂, PE/EtOAc = 20/1, Rf = 0.45) and isolated as colorless oil (411 mg, 1.87 mmol, 94 %).

¹H NMR (CDCl₃, 500 MHz): δ = 0.92 (t, J = 7.0 Hz, 3 H), 1.00 (d, J = 6.7 Hz, 3 H), 1.18-1.24 (m, 1 H), 1.28-1.50 (m, 9 H), 1.76 (oct, J = 6.6 Hz, 1 H), 2.91 (dd, J = 12.2 Hz, 7.2 Hz, 1 H), 3.08 (dd, J = 12.2 Hz, 5.9 Hz, 1 H), 3.82 (br. s, 1 H), 5.66 (d, J = 7.7 Hz, 2 H), 6.70 (t, J = 7.3 Hz, 1 H), 7.19 (t, J = 7.9 Hz, 2 H) ppm.

¹³C NMR (CDCl₃, DEPT, 125 MHz): δ = 14.1 (CH₃), 18.1 (CH₃), 22.7 (CH₂), 27.0 (CH₂), 29.6 (CH₂), 31.9 (CH₂), 33.0 (CH), 34.9 (CH₂), 50.5 (CH₂), 112.8 (CH), 117.1 (CH), 129.2 (CH), 148.6 (C) ppm.

2-Methyl-N-(2-methylocty)aniline (2b_b)

General procedure A was applied to N₂,2-dimethylaniline and 1-octene with a heating time of 1 h. The product was purified by chromatography (150 g SiO₂, PE/EtOAc = 60/1, Rf = 0.30) and isolated as yellow oil (37 mg, 0.16 mmol, 8 %).

¹H NMR (CDCl₃, 500 MHz): δ = 0.90 (t, J = 7.0 Hz, 3 H), 1.01 (d, J = 6.7 Hz, 3 H), 1.18-1.50 (m, 10 H), 1.81 (oct, J = 6.5 Hz, 1 H), 2.16 (s, 3 H), 2.94 (dd, J = 12.1 Hz, 7.4 Hz, 1 H), 3.11 (dd, J = 12.1 Hz, 5.8 Hz, 1 H), 3.66 (br. s, 1 H), 6.62-6.68 (m, 2 H), 7.06 (d, J = 7.3 Hz, 1 H), 7.14 (t, J = 7.6 Hz, 1 H) ppm.

¹³C NMR (CDCl₃, DEPT, 125 MHz): δ = 14.2 (CH₃), 17.6 (CH₃), 18.3 (CH₂), 22.8 (CH₂), 27.1 (CH₂), 29.7 (CH₂), 32.0 (CH₂), 32.9 (CH), 35.1 (CH₂), 50.7 (CH₂), 110.1 (CH), 117.0 (CH), 122.1 (C), 127.3 (CH), 130.2 (CH), 146.3 (C) ppm.

IR (ATR): λ [cm⁻¹] = 2955, 2925, 2853, 1606, 1587, 1513, 1468, 1317, 1260, 744, 632 cm⁻¹.

MS (EI): m/z (%) = 232.2 (2) [M⁺], 120.0 (30), 83.9 (50), 48.9 (100).

HRMS (EI): calc. (C₁₈H₂₅N) 233.2138, found 233.2137 [M⁺].
3-Methyl-N-(2-methyloctyl)aniline (2b_c)

General procedure A was applied to N,3-dimethylaniline and 1-octene with a heating time of 7 min. The product was purified by chromatography (150 g SiO₂, PE/EtOAc = 60/1, Rf = 0.14) and isolated as slightly yellow oil (437 mg, 1.87 mmol, 94 %).

\(^1\)H NMR (CDCl₃, 500 MHz): \(\delta = 0.92 \text{ (t, } J = 7.0 \text{ Hz, } 3 \text{ H}), 0.99 \text{ (d, } J = 6.7 \text{ Hz, } 3 \text{ H}), 1.17-1.24 \text{ (m, } 1 \text{ H}), 1.28-1.49 \text{ (m, } 9 \text{ H}), 1.76 \text{ (oct, } J = 6.6 \text{ Hz, } 1 \text{ H}), 2.30 \text{ (s, } 3 \text{ H}), 3.00 \text{ (dd, } J = 12.2 \text{ Hz, } 7.3 \text{ Hz, } 1 \text{ H}), 3.07 \text{ (dd, } J = 12.1 \text{ Hz, } 5.9 \text{ Hz, } 1 \text{ H}), 3.80 \text{ (br. s, } 1 \text{ H}), 6.43-6.47 \text{ (m, } 2 \text{ H}), 6.54 \text{ (d, } J = 7.4 \text{ Hz, } 1 \text{ H}), 7.08 \text{ (t, } J = 7.6 \text{ Hz, } 1 \text{ H}) \text{ ppm.}

\(^{13}\)C NMR (CDCl₃, DEPT, 125 MHz): \(\delta = 14.2 \text{ (CH₃), 18.2 (CH₃), 21.7 (CH₃), 22.8 (CH₂), 27.1 (CH₂), 29.8 (CH₂), 32.0 (CH₃), 33.1 (CH), 35.0 (CH₂), 50.6 (CH₂), 110.1 (CH), 113.7 (CH), 118.2 (CH), 129.2 (CH), 139.1 (C), 148.7 (C) ppm.}

4-Methyl-N-(2-methyloctyl)aniline (2b_d)

General procedure A was applied to N,4-dimethylaniline and 1-octene with a heating time of 10 min. The product was purified by chromatography (150 g SiO₂, PE/EtOAc = 60/1, Rf = 0.14) and isolated as colorless oil (444 mg, 1.90 mmol, 95 %).

\(^1\)H NMR (CDCl₃, 500 MHz): \(\delta = 0.92 \text{ (t, } J = 7.0 \text{ Hz, } 3 \text{ H}), 0.99 \text{ (d, } J = 6.7 \text{ Hz, } 3 \text{ H}), 1.16-1.23 \text{ (m, } 1 \text{ H}), 1.28-1.49 \text{ (m, } 9 \text{ H}), 1.76 \text{ (oct, } J = 6.5 \text{ Hz, } 1 \text{ H}), 2.26 \text{ (s, } 3 \text{ H}), 2.89 \text{ (dd, } J = 12.1 \text{ Hz, } 6.3 \text{ Hz, } 1 \text{ H}), 3.06 \text{ (dd, } J = 12.2 \text{ Hz, } 5.9 \text{ Hz, } 1 \text{ H}), 3.62 \text{ (br. s, } 1 \text{ H}), 6.57 \text{ (d, } J = 8.3 \text{ Hz, } 2 \text{ H}), 7.01 \text{ (d, } J = 8.3 \text{ Hz, } 2 \text{ H}) \text{ ppm.}

\(^{13}\)C NMR (CDCl₃, JMOD, 125 MHz): \(\delta = 14.2 \text{ (CH₃), 18.2 (CH₃), 20.5 (CH₂), 22.8 (CH₂), 27.1 (CH₂), 29.8 (CH₂), 32.0 (CH₃), 33.0 (CH), 34.9 (CH₂), 50.9 (CH₂), 113.0 (CH), 126.3 (C), 129.8 (CH), 146.4 (C) ppm.}

4-Fluoro-N-(2-methyloctyl)aniline (2b_e)

General procedure A was applied to 4-fluoro-N-methylaniline and 1-octene with a heating time of 15 min. The product was purified by chromatography (150 g SiO₂, PE/EtOAc = 60/1, Rf = 0.18) and isolated as colorless oil (432 mg, 1.82 mmol, 91 %).

\(^1\)H NMR (CDCl₃, 500 MHz): \(\delta = 0.90 \text{ (t, } J = 7.0 \text{ Hz, } 3 \text{ H}), 0.98 \text{ (d, } J = 6.7 \text{ Hz, } 3 \text{ H}), 1.15-1.22 \text{ (m, } 1 \text{ H}), 1.26-1.47 \text{ (m, } 9 \text{ H}), 1.73 \text{ (oct, } J = 6.4 \text{ Hz, } 1 \text{ H}), 2.85 \text{ (dd, } J = 12.0 \text{ Hz, } 7.3 \text{ Hz, } 1 \text{ H}), 3.02 \text{ (dd, } J = 12.0 \text{ Hz, } 5.9 \text{ Hz, } 1 \text{ H}), 3.57 \text{ (br. s, } 1 \text{ H}), 6.52-6.57 \text{ (m, } 2 \text{ H}), 6.86-6.91 \text{ (m, } 2 \text{ H}) \text{ ppm.}

\(^{13}\)C NMR (CDCl₃, JMOD, 125 MHz): \(\delta = 14.2 \text{ (CH₃), 18.2 (CH₃), 22.8 (CH₂), 27.1 (CH₂), 29.7 (CH₂), 32.0 (CH₃), 33.0 (CH), 34.9 (CH₂), 51.2 (CH₂), 113.6 (d, } J = 7.3 \text{ Hz, CH), 115.7 \text{ (d, } J = 22.2 \text{ Hz, CH), 145.1 (C), 155.8 (d, } J = 234.4 \text{ Hz, C) ppm.}
4-Chloro-N-(2-methyloctyl)aniline (2b_f)\textsuperscript{[10]}

General procedure A was applied to 4-chloro-N-methylaniline and 1-octene with a heating time of 6 min. The product was purified by chromatography (150 g SiO\textsubscript{2}, PE/EtOAc = 60/1, R\textsubscript{f} = 0.25) and isolated as colorless oil (459 mg, 1.81 mmol, 90%).

\textsuperscript{1}H NMR (CDCl\textsubscript{3}, 500 MHz): \( \delta = 0.89 \) (t, \( J = 7.1 \) Hz, 3 H), 0.96 (d, \( J = 6.7 \) Hz, 3 H), 1.14-1.20 (m, 1 H), 1.24-1.45 (m, 9 H), 1.72 (oct, \( J = 6.5 \) Hz, 1 H), 2.86 (dd, \( J = 12.2 \) Hz, 7.3 H, 1 H), 3.01 (dd, \( J = 12.2 \) Hz, 5.9 Hz, 1 H), 4.06 (br. s, 1 H), 6.52-6.55 (m, 2 H), 7.09-7.12 (m, 2 H) ppm.

\textsuperscript{13}C NMR (CDCl\textsubscript{3}, JMOD, 125 MHz): \( \delta = 14.2 \) (CH\textsubscript{3}), 18.2 (CH\textsubscript{3}), 22.8 (CH\textsubscript{2}), 27.0 (CH\textsubscript{2}), 29.7 (CH\textsubscript{2}), 32.0 (CH\textsubscript{2}), 32.9 (CH), 34.9 (CH\textsubscript{2}), 50.8 (CH\textsubscript{2}), 114.1 (CH), 121.9 (C), 129.2 (CH), 147.0 (C) ppm.

4-Bromo-N-(2-methyloctyl)aniline (2b_g)\textsuperscript{[11]}

General procedure A was applied to 4-bromo-N-methylaniline and 1-octene with a heating time of 15 min. The product was purified by chromatography (150 g SiO\textsubscript{2}, PE/EtOAc = 60/1, R\textsubscript{f} = 0.30) and isolated as colorless oil (551 mg, 1.85 mmol, 92%).

\textsuperscript{1}H NMR (CDCl\textsubscript{3}, 500 MHz): \( \delta = 0.89 \) (t, \( J = 7.0 \) Hz, 3 H), 0.96 (d, \( J = 6.7 \) Hz, 3 H), 1.13-1.20 (m, 1 H), 1.23-1.44 (m, 9 H), 1.72 (oct, \( J = 6.4 \) Hz, 1 H), 2.85 (dd, \( J = 12.2 \) Hz, 7.3 H, 1 H), 3.01 (dd, \( J = 12.2 \) Hz, 5.9 Hz, 1 H), 3.98 (br. s, 1 H), 6.47-6.50 (m, 2 H), 7.22-7.25 (m, 2 H) ppm.

\textsuperscript{13}C NMR (CDCl\textsubscript{3}, JMOD, 125 MHz): \( \delta = 14.2 \) (CH\textsubscript{3}), 18.1 (CH\textsubscript{3}), 22.8 (CH\textsubscript{2}), 27.0 (CH\textsubscript{2}), 29.7 (CH\textsubscript{2}), 32.0 (CH\textsubscript{2}), 32.9 (CH), 34.9 (CH\textsubscript{2}), 50.6 (CH\textsubscript{2}), 108.7 (C), 114.5 (CH), 132.0 (CH), 147.5 (C) ppm.

4-Methoxy-N-(2-methyloctyl)aniline (2b_h)\textsuperscript{[11]}

General procedure A was applied to 4-methoxy-N-methylaniline and 1-octene with a heating time of 15 min. The product was purified by chromatography (150 g SiO\textsubscript{2}, PE/EtOAc = 40/1, R\textsubscript{f} = 0.12) and isolated as colorless oil (407 mg, 1.63 mmol, 82%).

\textsuperscript{1}H NMR (CDCl\textsubscript{3}, 500 MHz): \( \delta = 0.91 \) (t, \( J = 7.0 \) Hz, 3 H), 0.98 (d, \( J = 6.7 \) Hz, 3 H), 1.15-1.23 (m, 1 H), 1.27-1.48 (m, 9 H), 1.74 (oct, \( J = 6.5 \) Hz, 1 H), 2.86 (dd, \( J = 12.0 \) Hz, 7.3 H, 1 H), 3.03 (dd, \( J = 12.0 \) Hz, 6.2 Hz, 1 H), 3.41 (br. s, 1 H), 3.76 (s, 3 H), 6.60 (d, \( J = 9.2 \) Hz, 2 H), 6.90 (d, \( J = 8.9 \) Hz, 2 H) ppm.

\textsuperscript{13}C NMR (CDCl\textsubscript{3}, JMOD, 125 MHz): \( \delta = 14.2 \) (CH\textsubscript{3}), 18.2 (CH\textsubscript{3}), 22.8 (CH\textsubscript{2}), 27.1 (CH\textsubscript{2}), 29.7 (CH\textsubscript{2}), 32.0 (CH\textsubscript{2}), 33.0 (CH), 34.9 (CH\textsubscript{2}), 51.5 (CH\textsubscript{2}), 55.9 (CH\textsubscript{3}), 114.1 (CH), 115.0 (CH), 143.0 (C), 152.0 (C) ppm.
4-Trifluormethoxy-N-(2-methyloctyl)aniline (2b_i)[11]

General procedure A was applied to 4-trifluormethoxy-N-methylaniline and 1-octene with a heating time of 2 min. The product was purified by chromatography (150 g SiO₂, PE/EtOAc = 80/1, Rf = 0.17) and isolated as colorless oil (550 mg, 1.81 mmol, 91 %).

\[\text{H NMR (CDCl}_3, 500 MHz): \delta = 0.89 (t, J = 7.0 Hz, 3 H), 0.98 (d, J = 6.7 Hz, 3 H), 1.15-1.22 (m, 1 H), 1.25-1.46 (m, 9 H), 1.73 (oct, J = 6.5 Hz, 1 H), 2.87 (dd, J = 12.2 Hz, 7.3 Hz, 1 H), 3.03 (dd, J = 12.2 Hz, 5.9 Hz, 1 H), 3.96 (br. s, 1 H), 6.56 (d, J = 8.9 Hz, 2 H), 7.03 (d, J = 8.5 Hz, 2 H) ppm.\]

\[\text{C NMR (CDCl}_3, JMOD, 125 MHz): \delta = 14.1 (CH₃), 18.2 (CH₃), 22.8 (CH₂), 27.1 (CH₂), 29.7 (CH₂), 32.0 (CH₂), 33.0 (CH), 34.9 (CH₂), 50.8 (CH₂), 113.0 (CH), 120.9 (q, J = 255.0 Hz, C), 122.5 (CH), 140.3 (C), 147.4 (C) ppm.\]

IR (ATR): \(\lambda_{max} = 2955, 2922, 2853, 1599, 1501, 1468, 1313, 1289, 1252, 1182, 966, 812\) cm\(^{-1}\).

MS (EI): \(m/z\) (%): 265.1 (47) [M]\\(^+\), 152.0 (100), 137.0 (15).

HRMS (ESI): calc. (C\(_{18}\)H\(_{27}\)NS) 265.1859, found 265.1859 [M]\\(^+\).

4-Methylthio-N-(2-methyloctyl)aniline (2b_j)

General procedure A was applied to 4-methylthio-N-methylaniline and 1-octene with a heating time of 10 min. The product was purified by chromatography (150 g SiO₂, PE/EtOAc = 60/1, Rf = 0.24) and isolated as colorless oil (480 mg, 1.81 mmol, 90 %).

\[\text{H NMR (CDCl}_3, 500 MHz): \delta = 0.90 (t, J = 7.0 Hz, 3 H), 0.97 (d, J = 6.7 Hz, 3 H), 1.15-1.20 (m, 1 H), 1.25-1.44 (m, 9 H), 1.73 (oct, J = 6.5 Hz, 1 H), 2.41 (s, 3 H), 2.87 (dd, J = 12.2 Hz, 7.3 Hz, 1 H), 3.04 (dd, J = 12.2 Hz, 5.9 Hz, 1 H), 3.98 (br.s, 1 H), 6.56 (d, J = 8.5 Hz, 2 H), 7.22 (d, J = 8.6 Hz, 2 H) ppm.\]

\[\text{C NMR (CDCl}_3, JMOD, 125 MHz): \delta = 14.2 (CH₃), 18.2 (CH₃), 19.5 (CH₃), 22.8 (CH₂), 27.0 (CH₂), 29.7 (CH₂), 32.0 (CH₂), 33.0 (CH), 34.9 (CH₂), 50.6 (CH₂), 113.5 (CH), 123.9 (C), 131.8 (CH), 147.5 (C) ppm.\]

IR (ATR): \(\lambda_{max} = 2955, 2922, 2853, 1599, 1501, 1468, 1313, 1289, 1252, 1182, 966, 812\) cm\(^{-1}\).

MS (EI): \(m/z\) (%): 265.1 (47) [M]\\(^+\), 152.0 (100), 137.0 (15).

HRMS (ESI): calc. (C\(_{18}\)H\(_{27}\)NS) 265.1859, found 265.1859 [M]\\(^+\).

\(\text{N-}(2\text{-Methyloctyl)cyclohexylamine (2b_k)[12]}\)

General procedure A was applied to N-methylcyclohexylamine and 1-octene with a heating time of 5 h. The product was purified by chromatography (150 g SiO₂, PE/EtOAc/EtOH/NEt₃ = 50/25/1/1, Rf = 0.18) and isolated as colorless oil (221 mg, 0.98 mmol, 49 %).

\[\text{H NMR (CDCl}_3, 500 MHz): \delta = 0.85-0.88 (m, 6 H), 1.01-1.35 (m, 16 H), 1.52-1.61 (m, 2 H), 1.68-1.74 (m, 2 H), 1.83-1.89 (m, 2 H), 2.33-2.39 (m, 2 H), 2.54 (dd, J = 11.4 Hz, 5.8 Hz, 1 H) ppm.\]

\[\text{C NMR (CDCl}_3, JMOD, 125 MHz): \delta = 14.2 (CH₃), 18.4 (CH₃), 22.8 (CH₂), 25.3 (CH₂), 26.3 (CH₂), 27.1 (CH₂), 29.8 (CH₂), 32.0 (CH₂), 33.5 (CH), 33.7 (CH₂), 33.8 (CH₂), 35.3 (CH₂), 53.7 (CH₂), 57.1 (CH) ppm.\]
N-(2-Methyloctyl)isobutylamine (2b_l)

General procedure A was applied to N-methylisobutylamine and 1-octene with a heating time of 2 h. The product was purified by removing volatiles under vacuum followed by capillary distillation. The product was obtained as colorless liquid (285 mg, 1.43 mmol, 71 %).

1H NMR (CDCl3, 500 MHz): δ = 0.84-0.89 (m, 12 H), 1.03-1.35 (m, 11 H), 1.54-1.62 (m, 1 H), 1.73 (nn, J = 6.7 Hz, 1 H), 2.31-2.41 (m, 3 H), 2.48 (dd, J = 11.6 Hz, 5.9 Hz, 1 H) ppm.

13C NMR (CDCl3, JMOD, 125 MHz): δ = 14.2 (CH3), 18.2 (CH3), 20.8 (CH3), 22.8 (CH3), 27.1 (CH3), 28.3 (CH3), 29.8 (CH2), 32.0 (CH3), 33.3 (CH3), 35.2 (CH2), 56.8 (CH2), 58.4 (CH2) ppm.

IR (ATR): λ= 2954, 2925, 2869, 1461, 1379, 1125, 723 cm⁻¹.

MS (EI): m/z (%) = 199.2 (11) [M]+, 156.1 (71), 86.0 (100).

HRMS (EI): calc. (C13H29N) 199.2295, found 199.2287 [M]+.

N5,N5-Diethyl-2-methyl-N1-phenylpentane-1,5-diamine (2b_m)

General procedure A was applied to N-methylaniline and N,N-diethyl-1-aminopent-4-ene with a heating time of 10 min. The product was purified by chromatography (100 g SiO2 PE/Et2O/NEt3 = 10/10/1, Rf = 0.31) and isolated as colorless oil (484 mg, 1.95 mmol, 97 %).

1H NMR (CDCl3, 500 MHz): δ = 0.95-1.05 (m, 9 H), 1.13-1.21 (m, 1 H), 1.40-1.59 (m, 3 H), 1.72-1.79 (m, 1 H), 2.37-2.43 (m, 2 H), 2.48-2.57 (m, 4 H), 2.86 (m, 1 H), 3.01-3.07 (m, 1 H), 3.72 (br.s, 1 H), 6.56-6.61 (m, 2 H), 6.64-6.69 (m, 1 H), 7.13-7.18 (m, 2 H) ppm.

13C NMR (CDCl3, JMOD, 125 MHz): δ = 11.7 (CH3), 18.2 (CH3), 24.6 (CH2), 32.7 (CH3), 33.0 (CH), 47.0 (CH2), 50.4 (CH2), 53.3 (CH3), 112.7 (CH), 117.0 (CH), 129.3 (CH), 148.7 (C) ppm.

IR (ATR): λ= 2962, 2927, 2868, 2794, 1602, 1505, 1469, 1320, 1259, 1070, 746, 692 cm⁻¹.

MS (EI): m/z (%) = 248.2 (44) [M]+, 174.1 (35), 156.1 (35), 106.0 (48), 86.0 (100).

HRMS (EI): calc. (C13H20N2) 248.2247, found 248.2244 [M]+.

N-(2-Methyl-5-propoxypentyl)aniline (2b_n)

General procedure A was applied to N-methylaniline and 5-propoxypent-1-ene with a heating time of 7 min. The product was purified by chromatography (150 g SiO2 PE/EtOAc = 20/1, Rf = 0.14) and isolated as colorless oil (427 mg, 1.81 mmol, 91 %).

1H NMR (CDCl3, 500 MHz): δ = 0.94 (t, J = 7.4 Hz, 3 H), 1.01 (d, J = 6.7 Hz, 3 H), 1.22-1.29 (m, 1 H), 1.50-1.73 (m, 5 H), 1.79 (oct, J = 6.4 Hz, 1 H), 2.93 (dd, J = 12.3 Hz, 7.2 Hz, 1 H), 3.08 (dd, J = 12.3 Hz, 6.0 Hz, 1 H), 3.39 (t, J = 6.8 Hz, 2 H), 3.43 (t, J = 6.5 Hz, 2 H), 3.70 (br.s, 1 H), 6.62 (d, J = 7.8 Hz, 2 H), 6.70 (t, J = 7.3 Hz, 1 H), 7.18 (t, J = 7.4 Hz, 2 H) ppm.

13C NMR (CDCl3, JMOD, 125 MHz): δ = 10.7 (CH3), 18.1 (CH3), 23.0 (CH3), 27.3 (CH3), 31.3 (CH3), 32.8 (CH3), 50.4 (CH2), 71.1 (CH2), 72.7 (CH2), 112.8 (CH), 117.1 (CH), 129.3 (CH), 148.6 (C) ppm.

IR (ATR): λ= 2929, 2854, 1604, 1507, 1321, 1260, 1115, 748, 693 cm⁻¹.

MS (EI): m/z (%) = 235.1 (5) [M]+, 106.0 (100), 83.9 (10), 77.0 (9).

HRMS (EI): calc. (C15H23NO) 235.1931, found 235.1931 [M]+.
**N-(2-Methyl-5-(trisopropylsilyl)oxy)pentyl)aniline (2b_o)**

![Chemical structure of N-(2-Methyl-5-(trisopropylsilyl)oxy)pentyl)aniline (2b_o)](image)

General procedure A was applied to N-methylaniline and 5-trisopropylsiloxypent-1-ene with a heating time of 5 min. The product was purified by chromatography (150 g SiO₂, PE/EtOAc = 60/1, Rᵣ = 0.14) and isolated as colorless oil (656 mg, 1.88 mmol, 94%).

**1H NMR** (CDCl₃, 500 MHz): δ = 1.00 (d, J = 6.7 Hz, 3 H), 1.03-1.13 (m, 21 H), 1.21-1.29 (m, 1 H), 1.50-1.69 (m, 3 H), 1.79 (oct, J = 6.3 Hz, 1 H), 2.92 (dd, J = 12.2 Hz, 7.2 Hz, 1 H), 3.07 (dd, J = 12.2 Hz, 6.0 Hz, 1 H), 3.69 (t, J = 6.3 Hz, 2 H), 4.06 (br. s, 1 H), 6.63 (d, J = 7.9 Hz, 2 H), 6.70 (t, J = 7.3 Hz, 1 H), 7.15-7.20 (m, 2 H) ppm.

**13C NMR** (CDCl₃, JMOD, 125 MHz): δ = 12.1 (CH₃), 18.2 (CH₃), 30.5 (CH₂), 31.0 (CH₂), 32.8 (CH), 50.6 (CH₂), 63.7 (CH₂), 113.0 (CH), 117.4 (CH), 129.4 (CH), 148.4 (C) ppm.

**29Si NMR** (CDCl₃, INEPT, 99 MHz): δ = 12.2 ppm.

**IR (ATR):** λ⁻¹ = 2940, 2865, 1603, 1505, 1462, 1319, 1256, 1100, 1012, 994, 882, 788, 746, 689 cm⁻¹.

**MS (El):** m/z (%): 349.2 (97) [M⁺; 306.0 (100), 263.0 (35), 174.1 (97), 146.1 (28), 129.0 (32), 106.0 (97), 74.9 (85), 60.1 (55).

**HRMS (El):** calc. (C₂₁H₃₃NOSi) 349.2795, found 349.2792 [M⁺].

**N-(2-(Trimethylsilyl)propyl)aniline (2b_p)**[^15]

![Chemical structure of N-(2-(Trimethylsilyl)propyl)aniline (2b_p)](image)

General procedure A was applied to N-methylaniline and trimethylvinylsilane with a heating time of 25 min. The product was purified by chromatography (150 g SiO₂, PE/EtOAc = 60/1, Rᵣ = 0.21) and isolated as colorless oil (total 380 mg, 1.83 mmol, 92 %) as a mixture of the desired product and the linear co-product (branched/linear = 82/18, determined by GC). The products could not be separated further, the yield of branched product was calculated to be 75 % based on the ratio shown by GC.

**1H NMR** (CDCl₃, 500 MHz): δ = 0.09 (s, 9 H), 1.07-1.10 (m, 4 H), 2.93-3.01 (m, 1 H), 3.31-3.36 (m, 1 H), 3.69 (br. s, 1 H), 6.65 (d, J = 7.7 Hz, 2 H), 6.74 (t, J = 7.3 Hz, 1 H), 7.22 (t, J = 7.4 Hz, 2 H) ppm.

**13C NMR** (CDCl₃, JMOD, 125 MHz): δ = -3.0 (CH₃), 12.9 (CH₃), 20.6 (CH), 46.7 (CH₂), 112.9 (CH), 117.1 (CH), 129.3 (CH), 148.6 (C) ppm.

**N-(Cyclopentylmethyl)aniline (2b_q)**[^14]

![Chemical structure of N-(Cyclopentylmethyl)aniline (2b_q)](image)

General procedure A was applied to N-methylaniline and cyclopentene with a heating time of 1 h. The product was purified by chromatography (160 g SiO₂, PE/EtOAc = 60/1, Rᵣ = 0.19) and isolated as colorless oil (337 mg, 1.92 mmol, 96 %).

**1H NMR** (CDCl₃, 500 MHz): δ = 1.32 (hex, J = 5.3 Hz, 2 H), 1.58-1.73 (m, 4 H), 1.84-1.90 (m, 2 H), 2.20 (sep, J = 7.6 Hz, 1 H), 3.07 (d, J = 7.3 Hz, 3 H), 3.67 (br. s, 1 H), 6.66 (d, J = 8.2 Hz, 2 H), 6.73 (t, J = 7.2 Hz, 1 H), 7.22 (t, J = 8.2 Hz, 2 H) ppm.

**13C NMR** (CDCl₃, JMOD, 125 MHz): δ = 25.4 (CH₂), 30.8 (CH₂), 39.6 (CH), 49.6 (CH₂), 112.8 (CH), 117.2 (CH), 129.3 (CH), 148.7 (C) ppm.
General procedure A was applied to N-methylaniline and methylenecyclohexane with a heating time of 2 h. The product was purified by chromatography (150 g SiO₂, PE/EtOAc = 60/1, Rᵋ = 0.22) and isolated as colorless oil (364 mg, 1.79 mmol, 90 %).

¹H NMR (CDCl₃, 500 MHz): δ = 1.00 (s, 3 H), 1.31-1.42 (m, 5 H), 1.45-1.56 (m, 5 H), 2.95 (s, 3 H), 3.76 (br. s, 1 H), 6.64-6.70 (m, 3 H), 7.18 (t, J = 8.3 Hz, 2 H) ppm.

¹³C NMR (CDCl₃, JMOD, 125 MHz): δ = 22.0 (CH₂), 23.5 (CH₃), 26.5 (CH₂), 34.4 (C), 36.0 (CH₂), 55.0 (CH₂), 112.9 (CH), 117.1 (CH), 129.3 (CH), 149.2 (C) ppm.

General procedure A was applied to N-methylaniline and 3-vinylcyclohexene with a heating time of 20 min. The product was purified by chromatography (160 g SiO₂, PE/EtOAc = 60/1, Rᵋ = 0.17) and isolated as colorless oil (341 mg, 1.58 mmol, 79 %). The product was obtained as a mixture of both diastereomers.

¹H NMR (CDCl₃, 500 MHz): δ = 0.99-1.04 (m, 3 H), 1.31-1.47 (m, 1 H), 1.67-1.82 (m, 3 H), 1.88-2.18 (m, 4 H), 2.94-3.00 (m, 1 H), 3.19-3.26 (m, 1 H), 3.71 (br. s, 1 H), 5.71-5.75 (m, 2 H), 6.65 (d, J = 7.9 Hz, 2 H), 6.71-6.76 (m, 1 H), 7.20-7.24 (m, 2 H) ppm.

¹³C NMR (CDCl₃, JMOD, 125 MHz): δ = 14.5 (CH₃), 14.9 (CH₂), 25.0 (CH₂), 25.9 (CH₂), 26.1 (CH₂), 27.0 (CH₃), 27.3 (CH₂), 29.7 (CH₂), 36.5 (CH), 36.8 (CH), 37.3 (CH), 37.5 (CH), 47.9 (CH₂), 48.0 (CH₂), 112.7 (CH), 117.1 (CH), 126.7 (CH), 126.9 (CH), 127.2 (CH), 129.3 (CH), 148.6 (C) ppm.

General procedure A was applied to N-methylaniline and 4-phenylbut-1-ene with a heating time of 20 min. The product was purified by chromatography (150 g SiO₂, PE/EtOAc = 60/1, Rᵋ = 0.27) and isolated as colorless oil (393 mg, 1.64 mmol, 82 %).

¹H NMR (CDCl₃, 500 MHz): δ = 1.07 (d, J = 6.4 Hz, 3 H), 1.50-1.58 (m, 1 H), 1.78-1.85 (m, 2 H), 2.60-2.67 (m, 1 H), 2.71-2.78 (m, 1 H), 2.97 (dd, J = 12.1 Hz, 6.7 Hz, 1 H), 3.11 (dd, J = 12.2 Hz, 5.6 Hz) ¹³C NMR (CDCl₃, JMOD, 125 MHz): δ = 18.1 (CH₃), 32.7 (CH), 33.4 (CH₂), 36.7 (CH₂), 50.5 (CH₂), 112.9 (CH), 117.3 (CH), 125.9 (CH), 128.5 (CH), 128.5 (CH), 129.4 (CH), 142.6 (C), 148.5 (C) ppm.
**N-(2-Methyl-3-phenylpropyl)aniline (2b_u)**

General procedure A was applied to N-methylaniline and 3-phenylprop-1-ene with a heating time of 6 min. The product was purified by chromatography (150 g SiO₂, PE/EtOAc = 20/1; Rᵣ = 0.19) and isolated as slightly yellow oil (384 mg, 1.70 mmol, 85 %).

**¹H NMR** (CDCl₃, 500 MHz): δ = 1.00 (d, J = 6.7 Hz, 3 H), 2.11 (oct, J = 6.9 Hz, 1 H), 2.53 (dd, J = 13.5 Hz, 7.8 Hz, 1 H), 2.78 (dd, J = 13.5 Hz, 6.4 Hz, 1 H), 2.98 (dd, J = 12.4 Hz, 7.0 Hz, 1 H), 3.12 (dd, J = 12.4 Hz, 6.0 Hz, 1 H), 3.86 (br. s, 1 H), 6.58 (d, J = 7.7 Hz, 2 H), 6.71 (t, J = 7.3 Hz, 1 H), 7.16-7.25 (m, 5 H), 7.31 (t, J = 7.6 Hz, 2 H) ppm.

**¹³C NMR** (CDCl₃, JMOD, 125 MHz): δ = 18.2 (CH₃), 35.1 (CH), 41.5 (CH₂), 50.1 (CH₂), 113.0 (CH), 117.4 (CH), 126.1 (CH), 128.4 (CH), 129.3 (CH), 129.4 (CH), 140.6 (C), 148.4 (C) ppm.

**N-(2-Phenylpropyl)aniline**

**¹H NMR** (CDCl₃, 500 MHz): δ = 1.25 (d, J = 7.0 Hz, 3 H), 2.97 (hex, J = 7.4 Hz, 1 H), 3.16 (dd, J = 12.4 Hz, 8.2 Hz, 1 H), 3.25 (dd, J = 12.4 Hz, 6.3 Hz, 1 H), 3.58 (br. s, 1 H), 6.49 (d, J = 7.7 Hz, 2 H), 6.60 (t, J = 7.3 Hz, 1 H), 7.07 (t, J = 7.5 Hz, 2 H), 7.13-7.17 (m, 3 H), 7.24 (t, J = 7.2 Hz, 2 H) ppm.

**¹³C NMR** (CDCl₃, DEPT, 125 MHz): δ = 19.8 (CH₃), 39.4 (CH), 51.1 (CH₂), 113.2 (CH), 117.6 (CH), 126.8 (CH), 127.4 (CH), 128.8 (CH), 129.4 (CH), 144.7 (C), 148.2 (C) ppm.

**N-(3-Phenylpropyl)aniline**

**¹H NMR** (CDCl₃, 500 MHz): δ = 1.98 (quint, J = 7.2 Hz, 2 H), 2.76 (t, J = 7.7 Hz, 2 H), 3.17 (t, J = 7.1 Hz, 2 H), 3.87 (br. s, 1 H), 6.62 (d, J = 7.7 Hz, 2 H), 6.73 (t, J = 7.3 Hz, 1 H), 7.16-7.25 (m, 5 H), 7.31 (t, J = 7.4 Hz, 2 H) ppm.

**¹³C NMR** (CDCl₃, DEPT, 125 MHz): δ = 31.1 (CH₂), 33.5 (CH₂), 43.8 (CH₂), 113.1 (CH), 117.6 (CH), 126.1 (CH), 128.5 (CH), 128.6 (CH), 129.4 (CH), 141.8 (C), 148.2 (C) ppm.

**N-(2-(o-Tolyl)propyl)aniline (2b_w) and N-(3-(o-tolyl)propyl)aniline (2l_w)**

General procedure A was applied to N-methylaniline and 2-methylstyrene with a heating time of 1 h. The products were purified by chromatography (150 g SiO₂, PE/EtOAc = 20/1) and isolated as colorless oils (branched: Rᵣ = 0.43, 32 mg, 0.14 mmol, 7 % / linear: Rᵣ = 0.29, 11 mg, 0.05 mmol, 2 %).

**¹H NMR** (CDCl₃, 500 MHz): δ = 1.32 (d, J = 6.4 Hz, 3 H), 2.31 (s, 3 H), 3.29-3.41 (m, 3 H), 4.07 (br. s, 1 H), 6.63 (d, J = 7.7 Hz, 2 H), 6.72 (t, J = 7.3 Hz, 1 H), 7.13-7.25 (m, 6 H) ppm.

**¹³C NMR** (CDCl₃, DEPT, 125 MHz): δ = 19.7 (CH₃), 19.7 (CH₃), 34.3 (CH), 50.7 (CH₂), 113.5 (CH), 117.9 (CH), 125.5 (CH), 126.4 (CH), 126.6 (CH), 129.4 (CH), 130.7 (CH), 136.3 (C), 142.7 (C), 147.9 (C) ppm.

**N-(3-(o-Tolyl)propyl)aniline**

**¹H NMR** (CDCl₃, 500 MHz): δ = 1.55 (br. s, 1 H), 1.96 (quint, J = 7.4 Hz, 2 H), 2.29 (s, 3 H), 2.71 (t, J = 7.9 Hz, 2 H), 3.21 (t, J = 7.1 Hz, 2 H), 6.77-6.84 (m, 3 H), 7.10-7.14 (m, 4 H), 7.21 (t, J = 7.5 Hz, 2 H) ppm.

**¹³C NMR** (CDCl₃, DEPT, 125 MHz): δ = 19.4 (CH₃), 29.2 (CH₂), 30.8 (CH₂), 45.6 (CH₂), 115.0 (CH), 119.9 (CH), 126.2 (CH), 126.3 (CH), 128.9 (CH), 129.5 (CH), 130.5 (CH), 136.0 (C), 139.6 (C), 146.0 (C) ppm.
General procedure A was applied to N-methylaniline and 3-methylstyrene with a heating time of 13 min. The products were purified by chromatography (150 g SiO2, PE/EtOAc = 60/1) and isolated as colorless oils (branched: Ri = 0.15, 297 mg, 1.32 mmol, 66 % / linear: Ri = 0.14, 115 mg, 0.51 mmol, 26 %).

**N-(2-(m-Tolyl)propyl)aniline**

1H NMR (CDCl3, 500 MHz): δ = 1.34 (d, J = 7.0 Hz, 3 H), 2.36 (s, 3 H), 3.04 (hex, J = 7.7 Hz, 1 H), 3.25 (dd, J = 12.3 Hz, 8.2 Hz, 1 H), 3.35 (dd, J = 12.3 Hz, 6.3 Hz, 1 H), 4.00 (br. s, 1 H), 6.62 (d, J = 7.7 Hz, 2 H), 6.72 (t, J = 7.3 Hz, 1 H), 7.02-7.08 (m, 3 H), 7.16-7.20 (m, 2 H), 7.23 (t, J = 7.5 Hz, 1 H) ppm.

13C NMR (CDCl3, JMOD, 125 MHz): δ = 20.0 (CH2), 21.6 (CH2), 39.2 (CH), 51.3 (CH2), 113.4 (CH), 117.8 (CH), 124.4 (CH), 127.6 (CH), 128.1 (CH), 128.7 (CH), 129.4 (CH), 138.4 (C), 144.5 (C), 147.9 (C) ppm.

**N-(3-(m-Tolyl)propyl)aniline**

1H NMR (CDCl3, 500 MHz): δ = 1.99 (quint, J = 7.2 Hz), 2.39 (s, 3 H), 2.75 (t, J = 7.7 Hz, J = 7.0 Hz, J = 7.3 Hz)

13C NMR (CDCl3, JMOD, 125 MHz): δ = 21.5 (CH2), 31.1 (CH2), 33.4 (CH2), 43.6 (CH2), 112.9 (CH), 117.4 (CH), 125.5 (CH), 126.8 (CH), 128.4 (CH), 129.5 (CH), 138.1 (C), 141.7 (C), 148.4 (C) ppm.

IR (ATR): λ−1 = 2927, 2860, 1603, 1507, 1322, 1259, 1181, 783, 748, 693 cm−1.

MS (EI): m/z (%) = 225.1 (53) [M]+, 106.0 (100), 77.0 (10).

HRMS (EI): calc. (C15H14N) 225.1512, found 255.1510 [M]+.

**N-(2-(p-Tolyl)propyl)aniline (2b_y) and N-(3-(p-tolyl)propyl)aniline (2l_y)**

General procedure A was applied to N-methylaniline and 4-methylstyrene with a heating time of 2 min. The products were purified by chromatography (150 g SiO2, PE/EtOAc = 60/1) and isolated as colorless oils (branched: Ri = 0.14, 296 mg, 1.31 mmol, 66 % / linear: Ri = 0.11, 106 mg, 0.47 mmol, 24 %).

**N-(2-(p-Tolyl)propyl)aniline**

1H NMR (CDCl3, 500 MHz): δ = 1.35 (d, J = 7.0 Hz, 3 H), 2.37 (s, 3 H), 3.06 (hex, J = 7.1 Hz, 1 H), 3.25 (dd, J = 12.2 Hz, 8.3 Hz, 1 H), 3.36 (dd, J = 12.3 Hz, 6.2 Hz, 1 H), 3.73 (br. s, 1 H), 6.61 (d, J = 8.2 Hz, 2 H), 6.73 (t, J = 7.3 Hz, 1 H), 7.14-7.21 (m, 6 H) ppm.13C NMR (CDCl3, JMOD, 125 MHz): δ = 20.0 (CH2), 21.2 (CH2), 38.9 (CH), 51.2 (CH2), 113.2 (CH), 117.5 (CH), 127.2 (CH), 129.4 (CH), 129.5 (CH), 136.3 (C), 141.5 (C), 148.1 (C) ppm.

**N-(3-(p-Tolyl)propyl)aniline**

1H NMR (CDCl3, 500 MHz): δ = 1.96 (quint, J = 7.4 Hz, 2 H), 2.36 (s, 3 H), 2.73 (t, J = 7.7 Hz, 2 H), 3.17 (t, J = 7.0 Hz, 2 H), 3.70 (br. s, 1 H), 6.63 (d, J = 8.3 Hz, 2 H), 6.73 (t, J = 7.2 Hz, 1 H), 7.11-7.22 (m, 6 H) ppm.

13C NMR (CDCl3, JMOD, 125 MHz): δ = 21.1 (CH2), 31.2 (CH2), 33.0 (CH2), 43.6 (CH2), 113.0 (CH), 117.5 (CH), 128.4 (CH), 129.2 (CH), 129.4 (CH), 135.5 (C), 138.7 (C), 148.3 (C) ppm.
4. Synthesis of silyl-protected amines

Method for preparing methyamine[5]

Liquid methyamine can be obtained easily and quickly from inexpensive bulk chemicals using only commonly available glassware. We encourage the use of the following procedure, but also want to emphasize the importance of proper safety measures. Loose joints, KOH waste, disassembly of the apparatus and contact of liquid methyamine with room temperature objects can discharge considerable amounts of methyamine gas, which poses a serious threat to eyes and respiratory tract. All glassware containing undiluted liquid methyamine must be cooled to −15 °C or lower! A full-face gas mask is mandatory for disassembly of the apparatus and handling of undiluted liquid methyamine!

A 1 L-Schlenk flask with dropping funnel was charged with KOH pellets (200 g) and kept at 50 °C with a water bath. The flask was connected to a chromatography column filled with KOH pellets (300 g); the column was connected to a reflux condenser (−20 °C) with 100 mL-Schlenk flask. The 100 mL-Schlenk flask was cooled to −18 °C with a cooling bath (NaCl/ice) and the outlet was connected to a gas bubbler. All glass joints were tightly secured with fork clamps. Methyamine solution (40 % in water, 70 mL, 0.90 mol) was slowly added through the dropping funnel. Liquid methyamine (25 g, 0.80 mmol, 89 %) was collected in the 100 mL-Schlenk flask and used for the synthesis of silylated methyamine without further purification or drying. It can be transferred into a different reaction apparatus with a Teflon cannula or decantation (We strongly advise wearing a full-face gas mask during decantation!).
**N,1,1,1-Tetramethylsilanamine (1)**[19]

![N,1,1,1-Tetramethylsilanamine](image)

A 500 mL-flask with reflux condenser (−20 °C) and magnetic stirring bar was charged with n-pentane (200 mL) and MeNH₂ (36.4 g, 1.17 mol) at −20 °C (Utmost care must be taken to ensure the reflux condenser stays below −15 °C at all times! A gas mask should be within reach!). At −20 °C, trimethylchlorosilane (21.2 g, 195 mmol) was carefully added. The mixture was refluxed for 1 h using a 20 °C water bath, two liquid layers formed. A −196 °C cooling trap was connected instead of the reflux condenser and excess MeNH₂ was removed until the second layer solidified. Solids were removed by filtration and the solvent was removed under reduced pressure. Under Ar atmosphere, the product was isolated by distillation (50 mbar overpressure, 72 °C) and was obtained as colorless liquid (8.02 g, 77.7 mmol, 40 %). The product needs to be stored under inert atmosphere, it will react violently with water and alcohols.

**1H NMR (C₆D₆, 300 MHz):** δ = -0.16 (br. s, 1 H), 0.05 (s, 9 H), 2.35 (d, J = 6.6 Hz, 3 H) ppm.

**13C NMR (C₆D₆, DEPT, 125 MHz):** δ = -0.4 (CH₃), 27.9 (CH₃) ppm. The ¹³C NMR shows additional signals at 14.3 ppm, 22.7 ppm and 34.5 ppm; these don’t originate from impurities in the product but from decomposition that occurred during the NMR measurement.

**1-tert-Butyl-N,1,1-trimethylsilanamine (3)**[20]

![1-tert-Butyl-N,1,1-trimethylsilanamine](image)

A 500 mL-flask with reflux condenser (−20 °C) and magnetic stirring bar was charged with petroleum ether (150 mL) and MeNH₂ (50 g, 1.6 mol) at −18 °C (Utmost care must be taken to ensure the reflux condenser stays below −15 °C at all times! A gas mask should be within reach!). At −18 °C, tert-butyldimethylchlorosilane (47 % in toluene, 165 g, 515 mmol) was added. The mixture was refluxed for 20 min using a 20 °C water bath, a solid formed. The solid was removed by filtration and the solvent and remaining MeNH₂ were removed under reduced pressure. The product was purified by distillation under Ar (141 °C) and was obtained as colorless liquid (30.91 g, 213 mmol, 41 %). The product is relatively stable and will decompose very slowly in contact with moisture or when diluted in alcohols. Note that this substance has an extremely high tendency to degrease glass joints, distillations need to be monitored very carefully and bottles with screw cap should be used for storage!

**1H NMR (C₆D₆, 300 MHz):** δ = -0.17 (br. s, 1 H), 0.00 (s, 6 H), 0.92 (s, 9 H), 2.39 (d, J = 6.6 Hz, 3 H) ppm.

**13C NMR (C₆D₆, DEPT, 125 MHz):** δ = -5.3 (CH₃), 18.8 (C), 26.7 (CH₃), 29.0 (CH₃) ppm.
5. Hydroaminoalkylation reactions with silyl-protected amines

General procedure A for the hydroaminoalkylation of alkenes (isolation of free primary amines) (5b)

All substrates were dried and degassed prior to use. In a glovebox under N₂-atmosphere, a 5 mL ampoule (length = 130 mm, outer diameter = 10 mm, inner diameter = 7 mm, wall thickness = 1.5 mm) with magnetic stir bar (6 mm) was charged with Ti(But)₂ (42 mg, 0.10 mmol, 5 mol%) and 1-tert-butyl-N,1,1-trimethylsilanamine (291 mg, 2 mmol). The mixture was stirred for 30 s and finely ground N,N-bis(2,6-dicyclopentyl-4-methoxyphenyl)formamide (53 mg, 0.10 mmol, 5 mol%) was added. The alkene (5 mmol) was added and the ampoule was sealed with a natural gas/O₂ torch. The ampoule was heated to 155 °C in an oil bath for 12 h. The solution was then transferred into a 20 mL-flask with CH₂Cl₂ (15 mL) and quenched with MeOH/H₂O (5 mL / 0.2 mL), the solution was left at room temperature overnight (deprotection of the amine takes 8-12 h). Alternatively, the product can be deprotected by boiling in EtOH/H₂O (40 mL / 10 mL) for 1 min. The product was then isolated by chromatography.

General procedure B for the hydroaminoalkylation of alkenes (isolation of tosylated amines) (5b)

Some volatile products could not be quantified as primary amines, because the removal of solvents after chromatography would reduce the isolated yield. These products were tosylated after the deprotection step. All substrates were dried and degassed prior to use. In a glovebox under N₂-atmosphere, a 5 mL ampoule (length = 130 mm, outer diameter = 10 mm, inner diameter = 7 mm, wall thickness = 1.5 mm) with magnetic stir bar (6 mm) was charged with Ti(But)₂ (42 mg, 0.10 mmol, 5 mol%) and 1-tert-butyl-N,1,1-trimethylsilanamine (291 mg, 2 mmol). The mixture was stirred for 30 s and finely ground N,N-bis(2,6-dicyclopentyl-4-methoxyphenyl)formamide (53 mg, 0.10 mmol, 5 mol%) was added. The alkene (5 mmol) was added and the ampoule was sealed with a natural gas/O₂ torch. The ampoule was heated to 155 °C in an oil bath for 12 h. The solution was then transferred into a 20 mL-flask with CH₂Cl₂ (15 mL) and quenched with MeOH/H₂O (5 mL / 0.2 mL), the solution was left at room temperature overnight. CH₂Cl₂ (30 mL), TосCl (762 mg, 4.0 mmol) and aqueous NaOH solution (2 M, 6 mL, 12 mmol) were added and the mixture was stirred at room temperature overnight. The mixture was diluted with H₂O (50 mL) and extracted with CH₂Cl₂ (3 × 50 mL). The combined organic layers were dried with MgSO₄ and the solvent was removed under reduced pressure. The product was isolated by chromatography.

1-tert-Butyl-1,1-dimethyl-N-(2-phenylpropyl)silanamine (isolation of silylated amine) (4b_I)

All substrates were dried and degassed prior to use. In a glovebox under N₂-atmosphere, a 25 mL ampoule (length = 150 mm, outer diameter = 18 mm, inner diameter = 15 mm, wall thickness = 1.5 mm) with magnetic stir bar (15 mm) was charged with Ti(But)₂ (510 mg, 1.24 mmol, 5 mol%) and 1-tert-butyl-N,1,1-trimethylsilanamine (3.63 g, 25.0 mmol). The mixture was stirred for 30 s and finely ground N,N-bis(2,6-dicyclopentyl-4-methoxyphenyl)formamide (661 mg, 1.25 mmol, 5 mol%) was added. Styrene (6.51 g, 62.5 mmol) was added and the ampoule was sealed with a natural gas/O₂ torch. The ampoule was heated at 155 °C in an oil bath for 12 h. The ampoule was opened under air and the content was transferred into a distillation setup with toluene (4 mL). The catalyst was quenched with 2-propanol (225 mL / 3.74 mmol) and the mixture was stirred at 90 °C for 5 min. All solvents and excess substrates were removed under vacuum at room temperature. The product was isolated by distillation (0.1 mbar, 82 °C) and obtained as colorless liquid (3.503 g, 14.0 mmol, 56 %, mixture of 95 % branched product and 5 % linear side product). After distillation, the product was stored under inert atmosphere (N₂). All attempts to isolate the product by chromatography (SiO₂) failed due to partial deprotection.

¹H NMR (CDCl₃, 500 MHz): δ = -0.554 (s, 3 H), -0.051 (s, 3 H), 0.18 (br. s, 1 H), 0.87 (s, 9 H), 1.13 (d, J = 7.0 Hz, 3 H), 2.54 (hex, J = 6.9 Hz, 1 H), 2.76-2.89 (m, 2 H), 7.05-7.10 (m, 3 H), 7.14-7.19 (m, 2 H) ppm.

¹³C NMR (CDCl₃, DEPT, 125 MHz): δ = -4.84 (CH₃), -4.76 (CH₂), 18.6 (C), 18.9 (CH₂), 26.7 (CH₃), 44.6 (CH), 50.6 (CH₂), 126.5 (CH), 127.8 (CH), 128.7 (CH), 145.9 (C) ppm.

²⁹Si NMR (CDCl₃, INEPT, 99 MHz): δ = 7.3 ppm.

IR (ATR): ν (cm⁻¹) = 2927, 2854, 1494, 1463, 1403, 1360, 1250, 1117, 1006, 827, 760, 697, 660 cm⁻¹.

MS (El, 70 eV): m/z (%): 192 (24), 144 (100), 135 (10), 88 (26), 73 (78), 59 (29).

Elemental composition: calc. (C₁₉H₂₂NSi) C 72.22, H 10.91, N 5.61, Si 11.26; found C 70.35, H 9.07, N 5.11.
4-Methyl-\(N\)-(2-methyloctyl)benzenesulfonamide (5b\_a)

General procedure B was applied to 1-octene. The product was purified by chromatography (50 g SiO\(_2\), PE/CH\(_2\)Cl\(_2\) = 1/1, R\(_f\) = 0.16) and isolated as highly viscous, colorless oil (481 mg, 1.62 mmol, 81%).

\(^1\)H NMR (CDCl\(_3\), 500 MHz): \(\delta = 8.33-0.88\) (m, 6 H), 1.01-1.07 (m, 1 H), 1.11-1.30 (m, 9 H), 1.54 (oct, \(J = 5.9\) Hz, 1 H), 2.42 (s, 3 H), 2.69-2.75 (m, 1 H); 2.81-2.86 (m, 1 H), 4.64 (br. s, 1 H), 7.30 (d, \(J = 8.2\) Hz, 2 H), 7.75 (d, \(J = 8.3\) Hz, 2 H) ppm.

\(^13\)C NMR (CDCl\(_3\), DEPT, 125 MHz): \(\delta = 14.2\) (CH\(_3\)), 17.6 (CH\(_3\)), 21.6 (CH\(_3\)), 22.7 (CH\(_2\)), 26.8 (CH\(_2\)), 29.5 (CH\(_2\)), 31.9 (CH\(_2\)), 33.3 (CH), 34.1 (CH\(_2\)), 49.2 (CH\(_2\)), 127.2 (CH), 129.8 (CH), 137.3 (C), 143.4 (C) ppm.

IR (ATR): \(\lambda^- = 3286, 2926, 2856, 1599, 1457, 1323, 1157, 1094, 813, 660, 550\) cm\(^{-1}\).

MS (EI): \(m/z\) (%) = 297 (1) [M]+, 184 (100), 155 (92), 142 (9), 126 (10), 91 (66).

HRMS (EI): calc. (C\(_{16}H_{23}NOS)\) 297.1757, found 297.1758 [M]+.

\(N\)-(2-Ethylheptyl)-4-methylbenzenesulfonamide (5b\_b)

General procedure B was applied to 2-octene. The products were purified twice by chromatography (50 g SiO\(_2\), PE/EtOAc = 4/1, R\(_f\) = 0.38) and isolated as colorless oil (5 mg, 0.02 mmol, 1%). The products were isolated as a mixture of 5b\_a and 5b\_b (71/29 according to \(^1\)H NMR) and could not be separated further.

\(^1\)H NMR (CDCl\(_3\), 500 MHz): \(\delta = 0.79\) (t, \(J = 7.4\) Hz, 3 H), 0.84-0.89 (m, 3 H), 1.12-1.37 (m, 8 H), 1.50-1.56 (m, 3 H), 2.44 (s, 3 H), 2.74 (dt, \(J = 12.4\) Hz, 6.6 Hz, 1 H); 2.83-2.88 (m, 1 H), 4.25 (br. t, \(J = 5.4\) Hz, 1 H), 7.33 (d, \(J = 8.0\) Hz, 2 H), 7.67 (d, \(J = 8.2\) Hz, 2 H) ppm.

\(^13\)C NMR (CDCl\(_3\), JMOD, 125 MHz): \(\delta = 10.8\) (CH\(_3\)), 17.6 (CH\(_3\)), 21.7 (CH\(_3\)), 22.7 (CH\(_2\)), 24.1 (CH\(_3\)), 26.3 (CH\(_3\)), 31.1 (CH\(_2\)), 32.2 (CH\(_2\)), 38.1 (CH), 45.9 (CH\(_2\)), 128.0 (CH), 129.8 (CH), 132.7 (C), 143.6 (C) ppm.

MS (EI, 70 eV): \(m/z\) (%) = 297 (<0.1%) [M]+; 207 (10), 184 (96), 155 (100), 91 (63).

4-Methyl-\(N\)-(2-methylhex-5-en-1-yl)benzenesulfonamide (5b\_c)

General procedure B was applied to 1,5-hexadiene. The product was purified by chromatography (50 g SiO\(_2\), CH\(_2\)Cl\(_2\), R\(_f\) = 0.18) and isolated as colorless oil (304 mg, 1.14 mmol, 57%).

\(^1\)H NMR (CDCl\(_3\), 500 MHz): \(\delta = 0.77-0.92\) (m, 4 H), 1.12-1.21 (m, 1 H), 1.37-1.44 (m, 1 H), 1.58 (oct, \(J = 6.8\) Hz, 1 H), 1.90-1.98 (m, 1 H), 1.99-2.07 (m, 1 H); 2.42 (s, 3 H), 2.74 (dt, \(J = 12.5\) Hz, 6.3 Hz, 1 H); 2.84 (dt, \(J = 12.5\) Hz, 6.2 Hz, 1 H), 4.67 (br. t, \(J = 5.0\) Hz, 1 H), 4.89-4.97 (m, 2 H), 5.71 (ddt, \(J = 17.0\) Hz, 10.3 Hz, 6.6 Hz, 1 H), 7.30 (d, \(J = 8.1\) Hz, 2 H), 7.75 (d, \(J = 8.2\) Hz, 2 H) ppm.

\(^13\)C NMR (CDCl\(_3\), JMOD, 125 MHz): \(\delta = 17.4\) (CH\(_2\)), 21.6 (CH\(_2\)), 31.0 (CH\(_2\)), 32.7 (CH), 33.2 (CH\(_2\)), 49.0 (CH\(_2\)), 114.8 (CH\(_2\)), 127.2 (CH), 129.8 (CH), 137.2 (C), 138.5 (CH), 143.4 (C) ppm.
4-Methyl-N-(2,3,3-trimethylbutyl)benzenesulfonamide (5b_d)\(^{[22]}\)

![Chemical structure](image)

General procedure B was applied to 3,3-dimethylbutene. The product was purified by chromatography (50 g SiO\(_2\), CH\(_2\)Cl\(_2\), R\(_f\) = 0.23) and isolated as slightly yellow oil (105 mg, 0.39 mmol, 19%).

\(^1\)H NMR (CDCl\(_3\), 500 MHz): \(\delta = 0.81\) (s, 9 H), \(0.85\) (d, \(J = 6.8\) Hz, 3 H), \(1.30\) (ddq, \(J = 10.1\) Hz, 3.5 Hz, 1 H), \(2.43\) (s, 3 H), \(2.54-2.59\) (m, 1 H), \(3.09-3.14\) (m, 1 H), \(4.37\) (br. s, 1 H), \(7.31\) (d, \(J = 8.0\) Hz, 2 H), \(7.75\) (d, \(J = 8.3\) Hz, 2 H) ppm.

\(^13\)C NMR (CDCl\(_3\), JMOD, 125 MHz): \(\delta = 13.1\) (CH\(_3\)), \(21.7\) (CH\(_3\)), \(27.4\) (CH\(_3\)), \(32.5\) (C), \(43.3\) (CH\(_2\)), \(45.9\) (CH\(_2\)), \(127.2\) (CH), \(129.8\) (CH), \(137.2\) (C), \(143.5\) (C) ppm.

IR (ATR): \(\lambda^\text{\text{\text{-1}}} = 3283, 2953, 2870, 1599, 1419, 1324, 1249, 1156, 1093, 1043, 833, 813, 750, 659, 549\) cm\(^{-1}\).

MS (EI): \(m/z\) (%) = 285 (0.1) [M]+, 270 (5), 228 (84), 155 (20), 149 (14), 138 (27), 119 (28), 105 (15), 91 (60), 74 (100), 65 (24).

HRMS (EI): calc. (C\(_{13}\)H\(_{23}\)NO\(_2\)SSi) 285.1213, found 285.1218 [M]+.

4-Methyl-N-(2-(trimethylsilyl)propyl)benzenesulfonamide (5b_e)

![Chemical structure](image)

General procedure B was applied to trimethylvinylsilane. The product was purified by chromatography (50 g SiO\(_2\), CH\(_2\)Cl\(_2\), R\(_f\) = 0.22) and isolated as colorless, very viscous oil (397 mg, 1.39 mmol, 70%). The product was obtained as a mixture of branched (82%) and linear product (18%) according to the \(^1\)H NMR. The products could not be separated.

\(^1\)H NMR (CDCl\(_3\), 500 MHz): \(\delta = 0.00\) (s, 9 H), \(0.84-0.91\) (m, 1 H), \(0.98\) (d, \(J = 7.2\) Hz, 3 H), \(2.48\) (s, 3 H), \(2.80\) (br. t, \(J = 11.1\) Hz, 1 H), \(3.14\) (br. d, \(J = 12.2\) Hz, 1 H), \(5.06\) (br. s, 1 H), \(7.36\) (d, \(J = 8.2\) Hz, 2 H), \(7.83\) (d, \(J = 8.3\) Hz, 2 H) ppm.

\(^13\)C NMR (CDCl\(_3\), DEPT, 125 MHz): \(\delta = -3.3\) (CH\(_3\)), \(12.3\) (CH\(_3\)), \(21.1\) (CH), \(21.5\) (CH\(_3\)), \(46.3\) (CH\(_2\)), \(127.1\) (CH), \(129.7\) (CH), \(129.8\) (CH), \(137.2\) (C), \(143.2\) (C) ppm.

\(^{29}\)Si NMR (CDCl\(_3\), INEPT, 99 MHz): \(\delta = 3.9\) ppm.

IR (ATR): \(\lambda^\text{\text{\text{-1}}} = 3283, 2953, 2870, 1599, 1419, 1324, 1249, 1156, 1093, 1043, 833, 813, 750, 659, 549\) cm\(^{-1}\).

MS (EI): \(m/z\) (%) = 285 (0.1) [M]+, 270 (5), 228 (84), 155 (20), 149 (14), 138 (27), 119 (28), 105 (15), 91 (60), 74 (100), 65 (24).

HRMS (EI): calc. (C\(_{13}\)H\(_{23}\)NO\(_2\)SSi) 285.1213, found 285.1218 [M]+.

4-Methyl-N-(2-methyl-3-(trimethylsilyl)propyl)benzenesulfonamide (5b_f)\(^{[23]}\)

![Chemical structure](image)

General procedure B was applied to trimethylallylsilane. The product was purified by chromatography (50 g SiO\(_2\), CH\(_2\)Cl\(_2\), R\(_f\) = 0.28) and isolated as colorless oil (484 mg, 1.62 mmol, 81%).

\(^1\)H NMR (CDCl\(_3\), 500 MHz): \(\delta = -0.04\) (s, 9 H), \(0.29\) (dd, \(J = 14.6\) Hz, 9.7 Hz, 1 H), \(0.56\) (dd, \(J = 14.6\) Hz, 4.2 Hz, 1 H), \(0.88\) (d, \(J = 6.6\) Hz, 3 H), \(1.63-1.73\) (m, 1 H), \(2.42\) (s, 3 H), \(2.68-2.73\) (m, 1 H), \(2.76-2.81\) (m, 1 H), \(4.60\) (br. t, \(J = 5.8\) Hz, 1 H), \(7.30\) (d, \(J = 8.0\) Hz, 2 H), \(7.75\) (d, \(J = 8.2\) Hz, 2 H) ppm.

\(^13\)C NMR (CDCl\(_3\), DEPT, 125 MHz): \(\delta = -0.7\) (CH\(_3\)), \(20.3\) (CH\(_3\)), \(21.6\) (CH\(_3\)), \(22.2\) (CH\(_2\)), \(30.2\) (CH), \(52.2\) (CH\(_2\)), \(127.2\) (CH), \(129.8\) (CH), \(137.5\) (C), \(143.4\) (C) ppm.
2-Methyl-5-((triisopropylsilyloxy)pentane-1-amine (5b_g)

![Chemical structure of 5b_g]

General procedure A was applied to 5-triisopropylsilyloxypent-1-ene. The product was purified by chromatography (25 g SiO₂, Et₂O/EtOH = 10/1, Rf = 0.11) and isolated as colorless oil (241 mg, 0.88 mmol, 44%).

³¹H NMR (CDCl₃, 500 MHz): δ = 0.89 (d, J = 6.6 Hz, 3 H), 0.99-1.17 (m, 22 H), 1.36-1.64 (m, 6 H), 2.47 (dd, J = 12.5 Hz, 6.7 Hz, 1 H), 2.61 (dd, J = 12.5 Hz, 5.3 Hz, 1 H), 3.65 (t, J = 6.6 Hz, 2 H) ppm.

¹³C NMR (CDCl₃, JMOD, 125 MHz): δ = 12.1 (CH), 17.6 (CH₃), 18.1 (CH₃), 30.4 (CH₂), 30.5 (CH₃), 36.2 (CH), 48.4 (CH₂), 63.8 (CH₂) ppm.

²⁹Si NMR (CDCl₃, INEPT, 99 MHz): δ = 12.1 ppm.

IR (ATR): λ⁻¹ = 2942, 2866, 2360, 2342, 1457, 1113, 753, 669 cm⁻¹.

MS (EI): m/z (%) = 273 (1) [M⁺], 230 (100), 171 (10), 130 (19), 98 (29), 75 (33), 61 (25) 55 (33).

HRMS (EI): calc. (C₁₃H₅₅NO₅Si) 273.2482, found 273.2487 [M⁺].

2-Methyl-5-propoxypentane-1-amine (5b_h)

![Chemical structure of 5b_h]

General procedure A was applied to 5-propoxypent-1-ene. The product was purified by chromatography (50 g SiO₂, Et₂O/MeOH/HNEt₂ = 40/2/1, Rf = 0.30) and isolated as colorless oil (245 mg, 1.54 mmol, 77%).

³¹H NMR (CDCl₃, 500 MHz): δ = 0.86-0.91 (m, 6 H), 1.09-1.16 (m, 1 H), 1.36-1.65 (m, 8 H), 2.47 (dd, J =12.5 Hz, 6.6 Hz, 1 H), 2.60 (dd, J = 12.5 Hz, 5.4 Hz, 1 H), 3.34 (t, J = 6.7 Hz, 2 H), 3.37 (t, J = 6.7 Hz, 2 H) ppm.

¹³C NMR (CDCl₃, DEPT, 125 MHz): δ = 10.7 (CH₃), 17.5 (CH₃), 23.0 (CH₂), 27.4 (CH₂), 30.8 (CH₂), 36.3 (CH), 48.4 (CH₃), 71.2 (CH₂), 72.7 (CH₂) ppm.

IR (ATR): λ⁻¹ = 2936, 2854, 2360, 2342, 1457, 1113, 753, 669 cm⁻¹.

MS (EI): m/z (%) = 159 (0.1) [M⁺], 116 (39), 100 (100), 70 (39), 55 (75).

HRMS (EI): calc. (C₉H₁₅NO) 159.1618, found 159.1617 [M⁺].

N-(Cyclopentylmethyl)-4-methylbenzenesulfonamide (5b_i)

![Chemical structure of 5b_i]

General procedure B was applied to cyclopentene. The product was purified by chromatography (50 g SiO₂, CH₂Cl₂, Rf = 0.14) and isolated as colorless oil (97 mg, 0.38 mmol, 19%).

³¹H NMR (CDCl₃, 500 MHz): δ = 1.07-1.15 (m, 2 H), 1.46-1.59 (m, 4 H), 1.66-1.73 (m, 2 H), 1.96 (hep, J = 7.2 Hz, 1 H), 2.43 (s, 3 H), 2.86 (t, J = 6.6 Hz, 2 H), 4.47 (br. s, 1 H), 7.30 (d, J = 8.2 Hz, 2 H), 7.75 (d, J = 8.3 Hz, 2 H) ppm.

¹³C NMR (CDCl₃, DEPT, 125 MHz): δ = 21.6 (CH₃), 25.3 (CH₃), 30.3 (CH₂), 39.6 (CH), 48.3 (CH₃), 127.2 (CH), 129.8 (CH), 137.1 (C), 143.4 (C) ppm.

IR (ATR): λ⁻¹ = 3283, 2952, 2867, 1599, 1426, 1322, 1154, 1092, 813, 660, 550 cm⁻¹.

MS (EI): m/z (%) = 253 (4) [M⁺], 184 (92), 172 (18), 155(100), 91 (98), 65 (28).

HRMS (EI): calc. (C₁₉H₁₉NO₂S) 253.1131, found 253.1128 [M⁺].
4-Methyl-N-((1-methylcyclohexyl)methyl)benzenesulfonamide (5b_j)

General procedure B was applied to methylenecyclohexane. The product was purified by chromatography (50 g SiO2, CH2Cl2, Rf = 0.25) and isolated as colorless oil (355 mg, 1.26 mmol, 63 %).

$^1$H NMR (CDCl3, 500 MHz): $\delta$ = 0.85 (s, 3 H), 1.20-1.28 (m, 5 H), 1.36-1.46 (m, 5 H), 2.42 (s, 3 H), 2.71 (d, $J$ = 6.7 Hz, 2 H), 4.57 (br. t, $J$ = 6.5 Hz, 1 H), 7.30 (d, $J$ = 8.1 Hz, 2 H), 7.75 (d, $J$ = 8.2 Hz, 2 H) ppm.

$^{13}$C NMR (CDCl3, DEPT, 125 MHz): $\delta$ = 21.6 (CH3), 21.7 (CH3), 23.2 (CH3), 26.2 (CH3), 33.8 (C), 35.3 (CH2), 53.5 (CH2), 127.2 (CH), 129.8 (CH), 137.4 (C), 143.3 (C) ppm.

IR (ATR): $\lambda$ = 3270, 2924, 2860, 2360, 2332, 1599, 1459, 1426, 1322, 1159, 1094, 1060, 870, 809, 659, 599, 546 cm$^{-1}$.

MS (EI): $m/z$ (%) = 281 (2) [M]+, 186 (72), 155 (61), 97 (100), 81 (18), 65 (26), 55 (99).

HRMS (EI): calc. (C16H17NO3S) 281.1444, found 281.1446 [M]+.

N-(2-(Cyclohex-3-en-1-yl)propyl)-4-methylbenzenesulfonamide (5b_k)

General procedure B was applied to 3-vinylcyclohexene. The product was purified by chromatography (50 g SiO2, CH2Cl2, Rf = 0.30) and isolated as colorless oil (497 mg, 1.69 mmol, 85 %). The diastereoisomers were not separated.

$^1$H NMR (CDCl3, 500 MHz): $\delta$ = 0.82-0.88 (m, 3 H), 1.11-2.05 (m, 8 H), 2.43 (s, 3 H), 2.76-2.82 (m, 1 H), 2.91-2.97 (m, 1 H), 4.55 (br. s, 1 H), 5.58-5.64 (m, 2 H), 7.31 (d, $J$ = 8.3 Hz, 2 H), 7.75 (d, $J$ = 8.3 Hz, 2 H) ppm.

$^{13}$C NMR (CDCl3, JMOD, 125 MHz): $\delta$ = 14.0 (CH3), 14.4 (CH3), 21.7 (CH3), 24.8 (CH2), 25.7 (CH2), 25.9 (CH2), 26.8 (CH2), 27.2 (CH2), 29.5 (CH2), 35.8 (CH), 36.0 (CH), 37.6 (CH), 37.8 (CH), 47.0 (CH2), 47.1 (CH2), 126.4 (CH), 126.5 (CH), 127.2 (CH), 129.8 (CH), 137.1 (C), 143.5 (C) ppm.

IR (ATR): $\lambda$ = 3283, 2923, 1599, 1320, 1154, 1092, 813, 730, 660, 549 cm$^{-1}$.

MS (EI): $m/z$ (%) = 293 (4) [M]+, 184 (36), 155 (80), 138 (54), 122 (36), 91 (100), 79 (37), 65 (28), 55 (13).

HRMS (EI): calc. (C16H16NO3S) 293.1453 [M]+.

4-Methyl-N-(2-phenylpropyl)benzenesulfonamide (5b_l)[24]

General procedure B was applied to styrene. The product was purified by chromatography (50 g SiO2, CH2Cl2, Rf = 0.20) and isolated as colorless oil (434 mg, 1.50 mmol, 75 %).

$^1$H NMR (CDCl3, 500 MHz): $\delta$ = 1.13 (d, $J$ = 7.0 Hz, 3 H), 2.32 (s, 3 H), 2.77 (br. s, $J$ = 7.4 Hz, 1 H), 2.92 (ddd, $J$ = 12.8 Hz, 8.1 Hz, 4.9 Hz, 1 H), 3.03-3.09 (m, 1 H), 4.51 (br. t, $J$ = 6.7 Hz, 1 H), 6.98 (d, $J$ = 8.2 Hz, 2 H), 7.10 (t, $J$ = 7.3 Hz, 1 H), 7.14-7.19 (m, 4 H), 7.58 (d, $J$ = 8.2 Hz, 2 H) ppm.

$^{13}$C NMR (CDCl3, DEPT, 125 MHz): $\delta$ = 19.2 (CH3), 21.5 (CH3), 39.8 (CH), 49.7 (CH2), 127.0 (CH), 127.1 (CH), 127.2 (CH), 128.8 (CH), 129.7 (CH), 137.1 (C), 143.1 (C), 143.3 (C) ppm.

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4-Methyl-N-(2-<o-tolyl>propyl)benzenesulfonamide (5b_m)\textsuperscript{[25]}

General procedure B was applied to 2-methylstyrene. The product was purified by chromatography (50 g SiO\textsubscript{2}, CH\textsubscript{2}Cl\textsubscript{2}, R\textsubscript{f} = 0.25) and subsequent thin layer chromatography (SiO\textsubscript{2}, PE/EtOAc = 4/1, R\textsubscript{f} = 0.48) and was isolated as colorless oil (4 mg, 0.01 mmol, 1 %).

\textsuperscript{1}HNMR (CDCl\textsubscript{3}, 500 MHz): \(\delta = 1.18 \text{ (d, } J = 6.6 \text{ Hz, } 3 \text{ H}), 2.26 \text{ (s, } 3 \text{ H}), 2.43 \text{ (s, } 3 \text{ H}), 3.02-3.07 \text{ (m, } 1 \text{ H}), 3.14-3.24 \text{ (m, } 2 \text{ H}), 4.19 \text{ (br. s, } 1 \text{ H}), 6.97-6.99 \text{ (m, } 1 \text{ H}), 7.09-7.15 \text{ (m, } 3 \text{ H}), 7.29 \text{ (d, } J = 8.0 \text{ Hz, } 2 \text{ H}), 7.67 \text{ (d, } J = 8.1 \text{ Hz, } 2 \text{ H}) \text{ ppm.}

\textsuperscript{13}CNMR (CDCl\textsubscript{3}, JMOD, 125 MHz): \(\delta = 19.1 \text{ (CH\textsubscript{3}}), 19.6 \text{ (CH\textsubscript{3}}), 21.7 \text{ (CH\textsubscript{3}}), 34.8 \text{ (CH)), 48.9 \text{ (CH\textsubscript{2}}), 125.0 \text{ (CH)), 126.7 \text{ (CH), 126.8 \text{ (CH), 129.9 \text{ (CH), 131.0 \text{ (CH), 136.4 \text{ (C), 137.0 \text{ (C), 141.0 \text{ (C), 143.5 \text{ (C) ppm.}}}

4-Methyl-N-(2-<m-tolyl>propyl)benzenesulfonamide (5b_n)

General procedure B was applied to 3-methylstyrene. The product was purified by chromatography (100 g SiO\textsubscript{2}, CH\textsubscript{2}Cl\textsubscript{2}, R\textsubscript{f} = 0.24) and isolated as slightly yellow, very viscous oil (238 mg, 0.78 mmol, 39 %).

\textsuperscript{1}HNMR (CDCl\textsubscript{3}, 500 MHz): \(\delta = 1.21 \text{ (d, } J = 7.0 \text{ Hz, } 3 \text{ H}), 2.30 \text{ (s, } 3 \text{ H}), 2.43 \text{ (s, } 3 \text{ H}), 2.82 \text{ (hex, } J = 6.9 \text{ Hz, } 1 \text{ H}), 2.99 \text{ (ddd, } J = 12.6 \text{ Hz, 8.6 Hz, 4.2 Hz, } 1 \text{ H}), 3.15-3.21 \text{ (m, } 1 \text{ H}), 3.34-4.39 \text{ (m, } 1 \text{ H}), 6.84-6.87 \text{ (m, } 2 \text{ H}), 7.03 \text{ (d, } J = 7.5 \text{ Hz, } 1 \text{ H}), 7.16 \text{ (t, } J = 7.5 \text{ Hz, } 1 \text{ H}), 7.28 \text{ (d, } J = 8.1 \text{ Hz, } 2 \text{ H}), 7.66 \text{ (d, } J = 8.3 \text{ Hz, } 2 \text{ H}) \text{ ppm.}

\textsuperscript{13}CNMR (CDCl\textsubscript{3}, JMOD, 125 MHz): \(\delta = 19.4 \text{ (CH\textsubscript{3}}, 21.5 \text{ (CH\textsubscript{2}}), 21.6 \text{ (CH\textsubscript{2}}), 39.7 \text{ (CH), 49.7 \text{ (CH\textsubscript{2}}), 124.2 \text{ (CH), 127.2 \text{ (CH), 127.9 \text{ (CH), 128.0 \text{ (CH), 128.8 \text{ (CH), 129.8 \text{ (CH), 137.0 \text{ (C), 138.5 \text{ (C), 142.9 \text{ (C), 143.4 \text{ (C) ppm.}}}

IR (ATR): \(\lambda^\text{\textdegree} = 3283, 2966, 2924, 2872, 1599, 1456, 1323, 1154, 1092, 1064, 813, 784, 704, 549 \text{ cm}^{-1}.

MS (EI): \(m/z \% = 303 \text{ (0.1) [M]^{-}}, 184 \text{ (85), 155 \text{ (100), 132 \text{ (41), 119 \text{ (47), 91 \text{ (86), 65 \text{ (20).}}}

HRMS (EI): calc. \text{(C_{17}H_{21}NO_2S)} 303.1288, found 303.1290 [M]^{+}.

2-(<p-Tolyl>)propan-1-amine (5b_o)\textsuperscript{[26]}

General procedure B was applied to 4-methylstyrene. The product was purified by chromatography (50 g SiO\textsubscript{2}, Et\textsubscript{2}O/MeOH/HNEt\textsubscript{2} = 40/2/1, R\textsubscript{f} = 0.38) and isolated as colorless oil (200 mg, 1.34 mmol, 67 %).

\textsuperscript{1}HNMR (CDCl\textsubscript{3}, 500 MHz): \(\delta = 1.24 \text{ (d, } J = 6.9 \text{ Hz, } 3 \text{ H}), 1.47 \text{ (br. s, } 2 \text{ H}), 2.33 \text{ (s, } 3 \text{ H}), 2.73 \text{ (hex, } J = 6.9 \text{ Hz, } 1 \text{ H}), 2.79-2.86 \text{ (m, } 2 \text{ H}), 7.09-7.14 \text{ (m, } 4 \text{ H)) ppm.}

\textsuperscript{13}CNMR (CDCl\textsubscript{3}, JMOD, 125 MHz): \(\delta = 19.5 \text{ (CH\textsubscript{3}}), 21.1 \text{ (CH\textsubscript{3}}), 43.1 \text{ (CH), 49.6 \text{ (CH\textsubscript{2}}), 127.3 \text{ (CH), 129.3 \text{ (CH), 136.0 \text{ (C), 142.0 \text{ (C) ppm.}}

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4-Methyl-N-(2-methyl-2-phenylpropyl)benzenesulfonamide (5b_p)\(^{[27]}\)

![Chemical Structure]

General procedure B was applied to \(\alpha\)-methylstyrene. The product was purified twice by chromatography (50 g SiO\(_2\), CH\(_2\)Cl\(_2\), \(R_t = 0.32\); 50 g SiO\(_2\), PE/EtOAc = 4/1, \(R_t = 0.33\)) and isolated as colorless oil (18 mg, 0.06 mmol, 3%).

\(^1\)H NMR (CDCl\(_3\), 500 MHz): \(\delta = 1.24\) (s, 6 H), 2.35 (s, 3 H), 2.97 (d, \(J = 6.5\) Hz, 2 H), 3.96 (br. t, \(J = 6.2\) Hz, 1 H), 7.11-7.24 (m, 7 H), 7.56 (d, \(J = 7.9\) Hz, 2 H) ppm.

\(^{13}\)C NMR (CDCl\(_3\), JMOD, 125 MHz): \(\delta = 21.7\) (CH\(_3\)), 26.7 (CH\(_3\)), 38.4 (C), 54.8 (CH\(_2\)), 126.0 (CH), 126.7 (CH), 127.2 (CH), 128.8 (CH), 129.8 (CH), 136.9 (C), 143.4 (C), 145.5 (C) ppm.

IR (ATR): \(\lambda_{\text{max}} = 3286, 2927, 2360, 1496, 1453, 1323, 1266, 1159, 1093, 1064, 909, 814, 730, 700, 660, 550\) cm\(^{-1}\).

MS (EI): \(m/z\) (%) = 303 (0.5) [M]+, 184 (19), 155 (57), 132 (64), 117 (22), 91 (100), 65 (22).

HRMS (EI): calc. (C\(_{17}\)H\(_{21}\)NO\(_2\)S) 303.1288, found 303.1281 [M]+.

4-Methyl-N-(2-methyl-3-phenylpropyl)benzenesulfonamide (5b_q)

![Chemical Structure]

General procedure B was applied to allylbenzene. The product was purified by chromatography (50 g SiO\(_2\), CH\(_2\)Cl\(_2\), \(R_f = 0.39\)) and isolated as colorless solid (518 mg, 1.71 mmol, 85%).

\(^1\)H NMR (CDCl\(_3\), 500 MHz): \(\delta = 0.75\) (d, \(J = 6.7\) Hz, 3 H), 1.78 (oct, \(J = 6.5\) Hz, 1 H), 2.24 (dd, \(J = 15.5\) Hz, 8.3 Hz, 1 H), 2.31 (s, 3 H), 2.57 (dd, \(J = 13.5\) Hz, 7.5 Hz, 1 H), 2.68 (dt, \(J = 12.6\) Hz, 6.5 Hz, 1 H), 2.76 (dt, \(J = 12.6\) Hz, 6.4 Hz, 1 H), 5.04 (br. t, \(J = 6.4\) Hz, 1 H), 6.95 (d, \(J = 7.1\) Hz, 2 H), 7.07 (t, \(J = 7.3\) Hz, 1 H), 7.13 (t, \(J = 7.6\) Hz, 2 H), 7.19 (d, \(J = 8.1\) Hz, 2 H), 7.65 (d, \(J = 8.3\) Hz, 2 H) ppm.

\(^{13}\)C NMR (CDCl\(_3\), JMOD, 125 MHz): \(\delta = 17.4\) (CH\(_3\)), 21.6 (CH\(_3\)), 35.3 (CH), 40.5 (CH\(_2\)), 48.7 (CH\(_2\)), 126.1 (CH), 127.1 (CH), 128.3 (CH), 129.1 (CH), 129.8 (CH), 137.0 (C), 139.9 (C), 143.4 (C) ppm.

IR (ATR): \(\lambda_{\text{max}} = 3286, 2927, 2360, 1496, 1453, 1323, 1266, 1159, 1093, 1064, 909, 814, 730, 700, 660, 550\) cm\(^{-1}\).

MS (EI): \(m/z\) (%) = 303 (0.5) [M]+, 184 (19), 155 (57), 132 (64), 117 (22), 91 (100), 65 (22).

HRMS (EI): calc. (C\(_{17}\)H\(_{22}\)NO\(_2\)S) 303.1288, found 303.1281 [M]+.

2-Methyl-4-phenylbutan-1-amine (5b_r)\(^{[28]}\)

![Chemical Structure]

General procedure A was applied to 4-phenylbutene. The product was purified by chromatography (50 g SiO\(_2\), Et\(_2\)O/MeOH/HNEt\(_2\) = 40/2/1, \(R_t = 0.30\)) and isolated as colorless oil (249 mg, 1.53 mmol, 76%).

\(^1\)H NMR (CDCl\(_3\), 500 MHz): \(\delta = 0.90\) (d, \(J = 6.6\) Hz, 3 H), 1.31-1.39 (m, 1 H), 1.46 (oct, \(J = 6.6\) Hz, 1 H), 1.60-1.67 (m, 1 H), 2.17 (br. s, 2 H), 2.44-2.53 (m, 2 H), 2.57-2.64 (m, 2 H), 7.08-7.12 (m, 3 H), 7.17-7.21 (m, 2 H) ppm.

\(^{13}\)C NMR (CDCl\(_3\), DEPT, 125 MHz): \(\delta = 17.4\) (CH\(_3\)), 33.5 (CH\(_2\)), 35.8 (CH), 36.3 (CH\(_3\)), 48.2 (CH\(_2\)), 125.8 (CH), 128.4 (CH), 142.8 (C) ppm.

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**N-(2-(4-Fluorophenyl)propyl)-4-methylbenzenesulfonamide (5b_s)**

General procedure B was applied to 4-fluorostyrene. The product was purified by chromatography (50 g SiO₂, CH₂Cl₂, Rᵣ = 0.20) and isolated as colorless oil (206 mg, 0.67 mmol, 34 %).

**¹H NMR** (CDCl₃, 500 MHz): δ = 1.20 (d, J = 7.0 Hz, 2 H), 2.43 (s, 3 H), 2.86 (hex, J = 6.7 Hz, 1 H), 3.13-3.19 (m, 1 H), 4.32 (br. t, J = 5.4 Hz, 1 H), 6.95 (t, J = 8.7 Hz, 2 H), 7.01-7.04 (m, 2 H), 7.28 (d, J = 8.0 Hz, 2 H), 7.65 (d, J = 8.3 Hz, 2 H) ppm.

**¹³C NMR** (CDCl₃, JMOD, 125 MHz): δ = 19.4 (CH₃), 21.7 (CH₃), 39.3 (CH), 49.8 (CH₂), 115.8 (d, J = 21.2 Hz, CH), 127.2 (CH), 128.7 (d, J = 7.9 Hz, CH), 129.8 (CH), 137.0 (C), 138.7 (C), 143.6 (C), 161.9 (d, J = 245.1 Hz, C) ppm.

**¹⁹F NMR** (CDCl₃, 470 MHz): −118.9 ppm.

**IR** (ATR): λ⁻¹ = 3284, 2965, 2927, 2876, 2360, 1600, 1510, 1457, 1419, 1324, 1222, 1156, 1092, 1014, 833, 813, 660, 547 cm⁻¹.

**MS** (EI): m/z (%) = 307 (0.1) [M⁺], 184 (100), 155 (100), 123 (32), 103 (22), 91 (82), 77 (10), 65 (22).

**HRMS** (EI): calc. (C₁₆H₁₈FNO₂S) 307.1037, found 307.1035 [M⁺].

**4-Methyl-N-(2-(perfluorophenyl)propyl)benzenesulfonamide (5b_t)**

General procedure B was applied to 1,2,3,4,5-pentafluorostyrene. The product was purified by chromatography (50 g SiO₂, CH₂Cl₂, Rᵣ = 0.19) and isolated as colorless oil (44 mg, 0.12 mmol, 6 %).

**¹H NMR** (CDCl₃, 500 MHz): δ = 1.28 (d, J = 6.9 Hz, 3 H), 2.43 (s, 3 H), 3.21-3.37 (m, 3 H), 4.76 (br. t, J = 6.5 Hz, 1 H), 7.27 (d, J = 8.0 Hz, 2 H), 7.64 (d, J = 8.2 Hz, 2 H) ppm.

**¹³C NMR** (CDCl₃, JMOD, 125 MHz): δ = 17.1 (CH₃), 21.9 (CH₃), 31.6 (CH), 47.2 (CH₂), 116.2 (C), 127.3 (CH), 130.1 (CH), 137.3 (C), 144.1 (C) ppm. The signals of fluorinated carbon seem to be between 135-150 ppm but are not identifiable with reasonable certainty.

**¹⁹F NMR** (CDCl₃, 470 MHz): δ = −165.1 - −165.0 (m), −159.4 (t, J = 20.8 Hz), −145.7 - −145.6 (m) ppm.

**IR** (ATR): λ⁻¹ = 3277, 2980, 2934, 2887, 2360, 1563, 1599, 1522, 1497, 1324, 1556, 1093, 1050, 967, 934, 836, 813, 661, 550 cm⁻¹.

**MS** (EI): m/z (%) = 196 (3), 184 (22), 155 (90), 91 (100), 65 (26).

**HRMS** (EI): calc. (C₁₆H₁₄F₅NO₂S) 379.0660, found 379.0651 [M⁺].
N-(2-(4-Chlorophenyl)propyl)-4-methylbenzenesulfonamide (5b_u)

General procedure B was applied to 4-chlorostyrene. The product was purified by chromatography (50 g SiO₂, CH₂Cl₂, Rₚ = 0.29) and isolated as colorless oil (88 mg, 0.27 mmol, 14%).

¹H NMR (CDCl₃, 500 MHz): δ = 1.13 (d, J = 7.0 Hz, 3 H), 2.35 (s, 3 H), 2.78 (hex, J = 6.9 Hz, 1 H), 2.91 (ddd, J = 12.7 Hz, 8.4 Hz, 5.2 Hz, 1 H), 3.04-3.10 (m, 1 H), 4.35 (br. t, J = 6.0 Hz, 1 H), 6.91-6.93 (m, 2 H), 7.12-7.15 (m, 2 H), 7.19 (d, J = 8.7 Hz, 2 H), 7.55-7.58 (m, 2 H) ppm.

¹³C NMR (CDCl₃, DEPT, 125 MHz): δ = 19.2 (CH₃), 21.6 (CH₃), 39.5 (CH), 49.7 (CH₂), 127.2 (CH), 128.6 (CH), 129.0 (CH), 129.8 (CH), 132.8 (C), 137.1 (C), 141.6 (C), 143.6 (C) ppm.

IR (ATR): λ⁻¹ = 3284, 2966, 2927, 2876, 1599, 1493, 1412, 1323, 1556, 1090, 1013, 909, 813, 729, 661, 550 cm⁻¹.

MS (EI): m/z (%) = 323 (0.3) [M⁺], 184 (100), 155 (99), 139 (20), 103 (25), 91 (75), 77 (15), 65 (19).

HRMS (EI): calc. (C₁₆H₁₈ClNO₂S) 323.0741, found 323.0754 [M⁺].

2-(4-Methoxyphenyl)propan-1-amine (5b_v)

General procedure A was applied to 4-methoxystyrene. The product was purified by chromatography (50 g SiO₂, Et₂O/MeOH/HNEt₂ = 40/2/1, Rₚ = 0.30) and isolated as colorless oil (220 mg, 1.33 mmol, 67%).

¹H NMR (CDCl₃, 500 MHz): δ = 1.23 (d, J = 6.9 Hz, 3 H), 1.43 (br. s, 2 H), 2.70 (hex, J = 6.8 Hz, 1 H), 2.76-2.85 (m, 2 H), 3.79 (s, 3 H), 6.84-6.87 (m, 2 H), 7.11-7.13 (m, 2 H) ppm.

¹³C NMR (CDCl₃, DEPT, 125 MHz): δ = 19.5 (CH₃), 42.8 (CH), 49.7 (CH₂), 55.4 (CH₃), 114.1 (CH), 128.3 (CH), 137.2 (C), 158.3 (C) ppm.
6. NMR spectra

Tetrabenzyltitanium (6)

\[ \text{1}^1\text{H NMR (C}_6\text{D}_6, 300 MHz)} \]

\[ \text{13}^1\text{C NMR (C}_6\text{D}_6, 125 MHz)} \]
3-Chlorocyclopent-1-ene (7)

![Chemical structure of 3-Chlorocyclopent-1-ene (7)]

**$^1$H NMR (CDCl$_3$, 300 MHz)**

- 1.01 (1H, d, J = 7 Hz)
- 1.02 (1H, d, J = 7 Hz)
- 1.03 (1H, d, J = 7 Hz)

**$^{13}$C NMR (CDCl$_3$, 125 MHz)**

- 138.3
- 132.3
- 65.8
- 34.6
- 31.2
2-(Cyclopent-2-en-1-yl)-4-methoxyaniline (8)

$^1$H NMR (CDCl$_3$, 300 MHz)

$^{13}$C NMR (CDCl$_3$, 125 MHz)
2,6-Di(cyclopent-2-en-1-yl)-4-methoxyaniline (9)

$^1$H NMR (CDCl$_3$, 300 MHz)

$^{13}$C NMR (CDCl$_3$, 125 MHz)
2,6-Dicyclopentyl-4-methoxyaniline (10)

\begin{align*}
\text{\H NMR (CDCl}_3, 500 \text{ MHz)} \quad & \\text{\C NMR (CDCl}_3, 125 \text{ MHz)} \\
\end{align*}
N,N-Bis(2,6-dicyclopentyl-4-methoxyphenyl)formamidine (1)

\[ \text{H NMR (CDCl}_3, 500 \text{ MHz)} \]

\[ \text{C NMR (CDCl}_3, 125 \text{ MHz)} \]

1H NMR (CDCl3, 500 MHz)

13C NMR (CDCl3, 125 MHz)
N-(2-Methyloctyl)aniline (2b_a)

$^{1}H$ NMR (CDCl$_3$, 500 MHz)

$^{13}C$ NMR (CDCl$_3$, 125 MHz)
2-Methyl-N-(2-methloctyl)aniline (2b_b)

\[
\begin{align*}
\text{H NMR (CDCl}_3\text{, 500 MHz)} & \\
\text{C NMR (CDCl}_3\text{, 125 MHz)} & 
\end{align*}
\]
3-Methyl-N-(2-methyloctyl)aniline (2b_c)

\[
\text{H NMR} \ (\text{CDCl}_3, \ 500 \text{ MHz})
\]

\[
\text{C NMR} \ (\text{CDCl}_3, \ 125 \text{ MHz})
\]

\[
\text{H NMR} \ (\text{CDCl}_3, \ 500 \text{ MHz})
\]

\[
\text{C NMR} \ (\text{CDCl}_3, \ 125 \text{ MHz})
\]
4-Methyl-N-(2-methyloctyl)aniline (2b_d)
4-Fluoro-N-(2-methyloctyl)aniline (2b_e)
4-Chloro-N-(2-methyloctyl)aniline (2b_f)

$\text{H NMR (CDCl}_3, 500 \text{ MHz)}$

$\text{C NMR (CDCl}_3, 125 \text{ MHz)}$

$\text{^13C NMR (CDCl}_3, 125 \text{ MHz)}$
4-Bromo-N-(2-methyloctyl)aniline (2b_g)

$^1$H NMR (CDCl$_3$, 500 MHz)

$^{13}$C NMR (CDCl$_3$, 125 MHz)
4-Methoxy-N-(2-methloctyl)aniline (2b_h)

$\text{H NMR (CDCl}_3, 500 \text{ MHz)}$

$\text{C NMR (CDCl}_3, 125 \text{ MHz)}$

$\text{H NMR (CDCl}_3, 500 \text{ MHz)}$

$\text{C NMR (CDCl}_3, 125 \text{ MHz)}$
4-Methylthio-N-(2-methyloctyl)aniline (2b_j)
$N$-(2-Methyloctyl)cyclohexylamine (2b_k)

$^1$H NMR (CDCl$_3$, 500 MHz)

$^13$C NMR (CDCl$_3$, 125 MHz)
$N$-(2-Methyloctyl)isobutylamine (2b_l)

$^1$H NMR (CDCl$_3$, 500 MHz)

$^13$C NMR (CDCl$_3$, 125 MHz)
$N_5N_5$-Diethyl-2-methyl-$N_1$-phenylpentane-1,5-diamine (2b_m)

$^1$H NMR (CDCl$_3$, 500 MHz)

$^13$C NMR (CDCl$_3$, 125 MHz)
N-(2-Methyl-5-propoxypentyl)aniline (2b_n)

$^1$H NMR (CDCl$_3$, 500 MHz)

$^13$C NMR (CDCl$_3$, 125 MHz)
$N$-(2-Methyl-5-((triisopropylsilyl)oxy)pentyl)aniline (2b_o)

$^1$H NMR (CDCl$_3$, 500 MHz)

$^{13}$C NMR (CDCl$_3$, 125 MHz)
$N$-(2-Methyl-5-((triisopropylsilyl)oxy)penty)aniline (2b_o)

$^{29}$Si NMR (CDCl$_3$, INEPT, 99 MHz)
$N$-(2-(Trimethylsilyl)propyl)aniline (2b_p)

$^1$H NMR (CDCl$_3$, 500 MHz)

$^13$C NMR (CDCl$_3$, 125 MHz)
$N$-(Cyclopentylmethyl)aniline (2b_q)

$^1$H NMR (CDCl$_3$, 500 MHz)

$^1$H NMR (CDCl$_3$, 500 MHz)

$^13$C NMR (CDCl$_3$, 125 MHz)
$N$-((1-Methylcyclohexyl)methyl)aniline (2b_r)

$^1$H NMR (CDCl$_3$, 500 MHz)

$^{13}$C NMR (CDCl$_3$, 125 MHz)
N-(2-(Cyclohex-3-en-1-yl)propyl)aniline (2b_s)

$^1$H NMR (CDCl$_3$, 500 MHz)

$^13$C NMR (CDCl$_3$, 125 MHz)
$N$-(2-Methyl-4-phenylbutyl)aniline (2b_t)

$^1$H NMR (CDCl$_3$, 500 MHz)

$^13$C NMR (CDCl$_3$, 125 MHz)
$N$-(2-Methyl-3-phenylpropyl)aniline (2b_u)

$\text{H NMR (CDCl}_3$, 500 MHz$)$

$\text{C NMR (CDCl}_3$, 125 MHz$)$

$^{13}$C NMR (CDCl$_3$, 125 MHz)
$N$-(2-Phenylpropyl)aniline (2b_v)

$^1$H NMR (CDCl$_3$, 500 MHz)

$^{13}$C NMR (CDCl$_3$, 125 MHz)

$^{13}$C NMR (CDCl$_3$, 125 MHz)
N-(3-Phenylpropyl)aniline (2I_v)

$\text{H NMR (CDCl}_3, 500 \text{ MHz)}$

$\text{C NMR (CDCl}_3, 125 \text{ MHz)}$
N-(2-(o-Tolyl)propyl)aniline (2b_w)

\[
\begin{align*}
\text{H NMR (CDCl}_3, 500 MHz) \\
\text{C NMR (CDCl}_3, 125 MHz)
\end{align*}
\]
$N$-(3-(o-Tolyl)propyl)aniline (2l_w)

$^1$H NMR (CDCl$_3$, 500 MHz)

$^1$C NMR (CDCl$_3$, 125 MHz)

$^{13}$C NMR (CDCl$_3$, 125 MHz)
$N$-(2-(m-Tolyl)propyl)aniline (2b_\text{x})

$^1$H NMR (CDCl$_3$, 500 MHz)

$^{13}$C NMR (CDCl$_3$, 125 MHz)
$N$-(3-(m-Tolyl)propyl)aniline ($2\_x$)

\[
\begin{align*}
\text{H NMR (CDCl}_3, 500 MHz) \\
\text{C NMR (CDCl}_3, 125 MHz)
\end{align*}
\]

$^1$H NMR (CDCl$_3$, 500 MHz)

$^{13}$C NMR (CDCl$_3$, 125 MHz)
N-(2-(p-Tolyl)propyl)aniline (2b_y)

$\text{H NMR (CDCl}_3$, 500 MHz)

$\text{C NMR (CDCl}_3$, 125 MHz)
$N$-(3-(p-Tolyl)propyl)aniline (2L_y)

$^1$H NMR (CDCl$_3$, 500 MHz)

$^{13}$C NMR (CDCl$_3$, 125 MHz)
N,1,1,1-Tetramethylsilanamine (11)

$\text{H NMR (C}_6\text{D}_6, 300 MHz)$

$\text{C NMR (C}_6\text{D}_6, 125 MHz)$
$1$-$tert$-Butyl-$N,1,1$-trimethylsilanamine (3)

$^1$H NMR ($\text{C}_6\text{D}_6$, 300 MHz)

$^13$C NMR ($\text{C}_6\text{D}_6$, 125 MHz)
1-tert-Butyl-1,1-dimethyl-N-(2-phenylpropyl)silanamine (4b_l)

$\text{H NMR (C}_6\text{D}_6, 500 MHz)$

$\text{C NMR (C}_6\text{D}_6, 125 MHz)$
1-tert-Butyl-1,1-dimethyl-N-(2-phenylpropyl)silanamine (4b_I)

$^{29}\text{Si NMR (C}_6\text{D}_6, 99 \text{ MHz)}$
4-Methyl-N-(2-methyloctyl)benzenesulfonamide (5b_a)

\[\text{H NMR (CDCl}_3, 500 \text{ MHz)}\]

\[\text{C NMR (CDCl}_3, 125 \text{ MHz)}\]

\[^{13}\text{C NMR (CDCl}_3, 125 \text{ MHz)}\]
$N$-(2-Ethylheptyl)-4-methylbenzenesulfonamide (5b\_b)
4-Methyl-N-(2-methylhex-5-en-1-yl)benzenesulfonamide (5b_c)

\[ \text{NMR (CDCl}_3\text{, 500 MHz)} \]

\[ \text{C NMR (CDCl}_3\text{, 125 MHz)} \]

\[ ^{1}H \text{ NMR (CDCl}_3\text{, 500 MHz)} \]

\[ ^{13}C \text{ NMR (CDCl}_3\text{, 125 MHz)} \]
4-Methyl-N-(2,3,3-trimethylbutyl)benzenesulfonamide (5b_d)

$^1$H NMR (CDCl$_3$, 500 MHz)

$^{13}$C NMR (CDCl$_3$, 125 MHz)
4-Methyl-N-(2-(trimethylsilyl)propyl)benzenesulfonamide (5b_e)

$\text{Si} \quad \text{N} \quad \text{SO}_2$ 

$\text{H} \text{NMR (CDCl}_3, 500 \text{ MHz)}$

$\text{C NMR (CDCl}_3, 125 \text{ MHz)}$

$\text{1H NMR (CDCl}_3, 500 \text{ MHz)}$

$\text{13C NMR (CDCl}_3, 125 \text{ MHz)}$

$\delta 143.2$, $\delta 137.2$, $\delta 127.1$, $\delta 46.3$, $\delta 21.1$, $\delta -12.3$, $\delta -3.3$
4-Methyl-N-(2-(trimethylsilyl)propyl)benzenesulfonamide (5b_e)

$^{29}$Si NMR (CDCl$_3$, 99 MHz)
4-Methyl-N-(2-methyl-3-(trimethylsilyl)propyl)benzenesulfonamide (5b-f)

$^1$H NMR (CDCl$_3$, 500 MHz)

$^{13}$C NMR (CDCl$_3$, 125 MHz)
2-Methyl-5-((triisopropylsilyl)oxy)pentan-1-amine (Sb_g)

\[
\text{H NMR (CDCl}_3, 500 \text{ MHz)}
\]

\[
\text{C NMR (CDCl}_3, 125 \text{ MHz)}
\]
2-Methyl-5-((triisopropylsilyl)oxy)pentan-1-amine (5b_g)

$^{29}\text{Si NMR (CDCl}_3, \text{ 99 MHz)}$
2-Methyl-5-propoxypentan-1-amine (5b_h)

\[
\begin{align*}
&\text{O} \quad \text{NH}_2 \\
&\text{H NMR (CDCl}_3, 500 \text{ MHz}) \\
&\text{C NMR (CDCl}_3, 125 \text{ MHz)}
\end{align*}
\]
$N$-(Cyclopentylmethyl)-4-methylbenzenesulfonamide (5b_i)

$^1$H NMR (CDCl$_3$, 500 MHz)

$^13$C NMR (CDCl$_3$, 125 MHz)
4-Methyl-N-((1-methylcyclohexyl)methyl)benzenesulfonamide (5b_j)

$\text{H NMR (CDCl}_3$, 500 MHz$)$

$\text{C NMR (CDCl}_3$, 125 MHz$)$
$N$-(2-(Cyclohex-3-en-1-yl)propyl)-4-methylbenzenesulfonamide (5b_k)

$^1$H NMR (CDCl$_3$, 500 MHz)

$^13$C NMR (CDCl$_3$, 125 MHz)
4-Methyl-N-(2-phenylpropyl)benzenesulfonamide (Sb_I)

$\text{H NMR (CDCl}_3, 500 \text{ MHz)}$

$\text{C NMR (CDCl}_3, 125 \text{ MHz)}$

$^1\text{H NMR (CDCl}_3, 500 \text{ MHz)}$

$^13\text{C NMR (CDCl}_3, 125 \text{ MHz)}$
4-Methyl-N-(2-(α-tolyl)propyl)benzenesulfonamide (5b_m)
4-Methyl-N-(2-(m-tolyl)propyl)benzenesulfonamide (5b\_n)

1H NMR (CDCl₃, 500 MHz)

13C NMR (CDCl₃, 125 MHz)
2-(p-Tolyl)propan-1-amine (Sb_o)

H NMR (CDCl₃, 500 MHz)

13C NMR (CDCl₃, 125 MHz)
4-Methyl-N-(2-methyl-2-phenylpropyl)benzenesulfonamide (5b_p)

\[ \text{Structure Image} \]

\[ \text{H NMR (CDCl}_3, 500 MHz) \]

\[ \text{Carbon NMR (CDCl}_3, 125 MHz) \]

\[ ^{13} \text{C NMR (CDCl}_3, 125 MHz) \]
4-Methyl-N-(2-methyl-3-phenylpropyl)benzenesulfonamide (5b_q)

$\text{H NMR (CDCl}_3, \text{ 500 MHz)}$

$\text{C NMR (CDCl}_3, \text{ 125 MHz)}$
2-Methyl-4-phenylbutan-1-amine (5b_r)

$\begin{align*}
\text{Ar} & \text{CHCH}_2\text{NH}_2
\end{align*}$

$^1$H NMR (CDCl$_3$, 500 MHz)

$^1^3$C NMR (CDCl$_3$, 125 MHz)

$\begin{align*}
\text{ppm} & \quad 8.0 & 7.5 & 7.0 & 6.5 & 6.0 & 5.5 & 5.0 & 4.5 & 4.0 & 3.5 & 3.0 & 2.5 & 2.0 & 1.5 & 1.0 & 0.5 & 0.0 \\
2.79 & \text{peak} & \text{peak} & \text{peak} & \text{peak} & \text{peak} & \text{peak} & \text{peak} & \text{peak} & \text{peak} & \text{peak} & \text{peak} & \text{peak} & \text{peak} & \text{peak} & \text{peak} & \text{peak} & \text{peak} \\
1.98 & \text{peak} & \text{peak} & \text{peak} & \text{peak} & \text{peak} & \text{peak} & \text{peak} & \text{peak} & \text{peak} & \text{peak} & \text{peak} & \text{peak} & \text{peak} & \text{peak} & \text{peak} & \text{peak} & \text{peak} \\
2.28 & \text{peak} & \text{peak} & \text{peak} & \text{peak} & \text{peak} & \text{peak} & \text{peak} & \text{peak} & \text{peak} & \text{peak} & \text{peak} & \text{peak} & \text{peak} & \text{peak} & \text{peak} & \text{peak} & \text{peak} \\
2.93 & \text{peak} & \text{peak} & \text{peak} & \text{peak} & \text{peak} & \text{peak} & \text{peak} & \text{peak} & \text{peak} & \text{peak} & \text{peak} & \text{peak} & \text{peak} & \text{peak} & \text{peak} & \text{peak} & \text{peak} \\
8.0 & \text{peak} & \text{peak} & \text{peak} & \text{peak} & \text{peak} & \text{peak} & \text{peak} & \text{peak} & \text{peak} & \text{peak} & \text{peak} & \text{peak} & \text{peak} & \text{peak} & \text{peak} & \text{peak} & \text{peak} \\
-
\end{align*}$
$N$-(2-(4-Fluorophenyl)propyl)-4-methylbenzenesulfonamide (5b_s)

$^1$H NMR (CDCl$_3$, 500 MHz)

$^13$C NMR (CDCl$_3$, 125 MHz)

$^13$C NMR (CDCl$_3$, 125 MHz)
N-(2-(4-Fluorophenyl)propyl)-4-methylbenzenesulfonamide (5b_s)

$^1\text{H}$ NMR (CDCl$_3$, 470 MHz)
4-Methyl-N-(2-(perfluorophenyl)propyl)benzenesulfonamide (5b_t)

$^{1}$H NMR (CDCl$_3$, 500 MHz)

$^{13}$C NMR (CDCl$_3$, 125 MHz)
4-Methyl-N-(2-(perfluorophenyl)propyl)benzenesulfonamide (5b_t)

$^{19}$F NMR (CDCl$_3$, 470 MHz)
$N$-(2-(4-Chlorophenyl)propyl)-4-methylbenzenesulfonamide (5b_u)
2-(4-Methoxyphenyl)propan-1-amine (5b_v)

\[
\begin{align*}
\text{H NMR (CDCl}_3, 500 \text{ MHz)} & \quad \text{ppm} \\
1.94 & \quad 1.84 & \quad 3.04 & \quad 1.87 & \quad 2.54 & \quad 2.96 \\
\end{align*}
\]

\[
\begin{align*}
\text{C NMR (CDCl}_3, 125 \text{ MHz)} & \quad \text{ppm} \\
-158.3 & \quad -137.2 & \quad -128.3 & \quad -114.1 & \quad -55.4 & \quad -49.7 & \quad -42.8 & \quad -19.5 \\
\end{align*}
\]
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8. Author contributions

| Author       | Role    | Contributions                                                                 |
|--------------|---------|-------------------------------------------------------------------------------|
| Jens Bielefeld | Lead    | project administration, investigation, data curation, writing of original draft |
| Sven Doye     | Support | validation, proofreading                                                       |