Supporting Information for

Heavier Alkaline Earth Catalysts for the Intermolecular Hydroamination of Vinylarenes, Dienes and Alkynes

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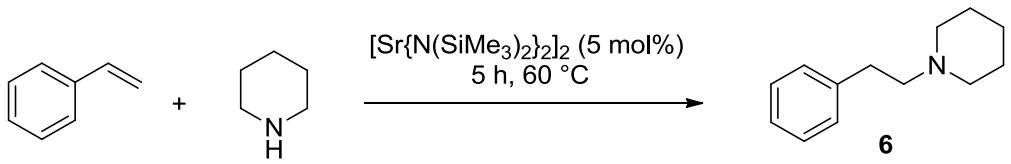
General Experimental Procedures

All manipulations were carried out using standard Schlenk line and glovebox techniques under an inert atmosphere of either nitrogen or argon. NMR experiments were conducted in Youngs tap NMR tubes made up and sealed in a Glovebox. All NMR spectra were obtained at +25 °C unless otherwise stated. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker DRX 400 (400 MHz for ^{1}H and 100 MHz for ^{13}C). Kinetic studies were carried out in cooperation with the NMR service staff of Imperial College London and measured by Peter Haycock. Chemical shifts are stated in *parts per million* (ppm) and referenced to the residual solvent peak ($CDCl_3$: ^{1}H: δ = 7.26 ppm, ^{13}C: δ = 77.16 ppm; d_6-benzene: ^{1}H: δ = 7.15 ppm, ^{13}C: δ = 128.06 ppm) or to tetramethylsilane (^{1}H: δ = 0.00 ppm). Coupling constants (*J*) are quoted in Hertz (Hz). The EI- and ESI-MS spectra were measured with a Micromass Platform II spectrometer (low resolution) and a Micromass Autospec Q spectrometer (low and high resolution) in methanol or ether. The measurements were conducted by the Mass Spectrometry Service of Imperial College London and run by Jonathan Barton. Thin layer chromatography (TLC) was conducted with E. Merck silica gel 60 F254 pre-coated plates (0.25 mm) and visualized initially by UV light (254 nm) and then by a potassium permanganate staining for permanent visualization. Column chromatography was performed on Merck silica gel 60, particle size 20-63 μm or BDH silica gel, particle size 33-70 μm. All chromatography eluents were BDH GPR grade and used without further purification. Petrol refers to BDH AnalaR GPR petroleum spirit 40-60 ºC. Elemental analyses were determined by the department of Health and Human Sciences at London Metropolitan University and conducted by Stephan Boyer. Results are quoted in weight percent of a particular element. Solvents were purchased from BDH laboratory supplies or the Aldrich Chemical Company. Solvents for flash chromatography were reagent or GPR grade and were used as received. Petrol refers to BDH AnalaR GPR petroleum spirit 40 - 60 ºC. Reaction solvents were distilled as specified: CH_2Cl_2, MeOH, pyridine and Et_3N were distilled from calcium hydride under a nitrogen atmosphere. Diethyl ether and THF were distilled from sodium and benzophenone under nitrogen atmosphere. Toluene was distilled from sodium under nitrogen atmosphere. If not specified otherwise all reagents were purchased from Aldrich Chemical Company. NMR solvents for catalytic reactions were of spectroscopic grade. D_6-benzene (99.5 atom%) and d_8-THF were freeze-pumped-thawed and refluxed over potassium overnight in a sealed ampule. After cooling down to room temperature the solution was

vacuum transferred to a pre-dried ampule and stored over molecular sieves (4 Å). For the hydroamination catalysis, all liquid amines and olefins were dried over CaH_2, distilled under inert atmosphere and freeze-pump-thawed three times to eliminate oxygen. The liquids for the hydroalkoxylation were dried twice over molecular sieves (4 Å) for at least three days and freeze-pump-thaw three times to eliminate oxygen. Solid substrates were dried for several hours *in vacuo* or sublimed. The amide precatalysts $[Ca\{N(SiMe_3)_2\}_2]_2$ **1**, $[Sr\{N(SiMe_3)_2\}_2]_2$ **2** and $[Ba\{N(SiMe_3)_2\}_2]_2$ **5**,[1,2] and tha alkyl precatlysts $[M\{CH(SiMe_3)_2\}_2(THF)_2]$ (M = Ca **3**, Sr **4**) aziridine[3] and but-3-en-1-ynylbenzene[4] were synthesized by literature procedures.

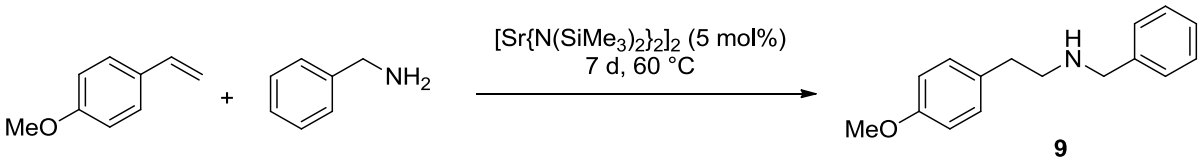
General experimental procedure for the catalytic hydroamination reaction of styrene derivatives: In a glovebox, a Youngs tap NMR tube was filled with the appropriate precatalyst (0.05 g, 0.13 mmol), the relevant amine (2.50 mmol) and the styrene derivative (2.50 mmol). To monitor the reaction by ^{1}H NMR spectroscopy a sealed tube filled with d_6-benzene was added. The NMR tube was sealed, removed from the glovebox and heated to 60 °C in a pre-heated oil bath. ^{1}H NMR spectra were measured in regular intervals until full conversion was observed. The products were exposed to air, diluted with Et_2O and the suspension was filtered through Celite. After evaporating to dryness, an oil was isolated, which was purified by column chromatography or vacuum distillation.

Synthesis of 1-phenethylpiperidine **6**[5]



The reaction was complete after 5 h at 60 °C. Purification by column chromatography (silica gel, $CHCl_3$: NH_3 in MeOH (7 M) = 20 : 0.5) yielded **6** as a colorless oil in 79% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ/ppm = 7.28 – 7.35 (m, 2H, H_{ar}), 7.20 – 7.26 (m, 3H, H_{ar}), 2.81 – 2.90 (m, 2H, NCH_2CH_2Ph), 2.56 – 2.65 (m, 2H, NCH_2CH_2Ph), 2.51 (bs, 4H, N(CH_2CH$_2$)$_2$CH$_2$), 1.67 (td, 4H, J = 5.6 Hz, J = 11.1 Hz, N(CH$_2$CH_2)$_2$CH$_2$), 1.45 – 1.55 (m, 2H, N(CH$_2$CH$_2$)$_2$CH_2). ^{13}C NMR (101 MHz, $CDCl_3$): δ/ppm = 140.6 (C_q), 128.7 (C_{ar}), 128.3 (C_{ar}), 126.0 (C_{ar}), 61.4 (NCH$_2$CH$_2$Ph), 54.5 (N(CH$_2$CH$_2$)$_2$CH$_2$), 33.6 (NCH$_2$$CH_2$Ph), 25.9 (N(CH$_2$$CH_2$)$_2CH_2$), 24.4 (N(CH$_2CH_2$)$_2$$CH_2$). HRMS (ESI) *m/z*: calc. for $C_{13}H_{20}N$: 190.1596 [M^+]; found 190.1595.

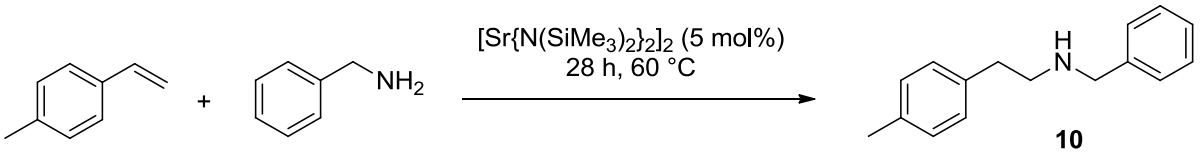
Synthesis of *N*-benzyl-2-(4-methoxyphenyl)ethanamine **9**[5]



9

The reaction was complete after 144 h at 60 °C. Purification by column chromatography (silica gel, $CHCl_3$: NH_3 in MeOH (7 M) = 100 : 0.4) yielded **9** as a colorless oil in 63% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ/ppm = 7.21 – 7.35 (m, 5H, H_{ar}), 7.12 (d, 2H, J = 8.6 Hz, H_{ar}), 6.83 (d, 2H, J = 8.7 Hz, H_{ar}), 3.80 (s, 2H, NHCH_2Ph), 3.79 (s, 3H, OCH_3), 2.83 – 2.91 (m, 2H, NHCH_2CH$_2$), 2.78 (t, 2H, J = 6.8 Hz, NHCH$_2$CH_2), 1.66 (bs, 1H, NH). ^{13}C NMR (101 MHz, $CDCl_3$): δ/ppm = 158.0 (C_q), 140.1 (C_q), 132.0 (C_q), 129.6 (C_{ar}), 128.4 (C_{ar}), 128.1 (C_{ar}), 126.9 (C_{ar}), 113.9 (C_{ar}), 55.3 (OCH$_3$), 53.8 (NHCH$_2$Ph), 50.7 (NHCH$_2$CH$_2$), 35.3 (NHCH$_2$$CH_2$). HRMS (ESI) *m/z*: calc. for $C_{16}H_{20}NO$: 242.1545 [M^+]; found 242.1553.

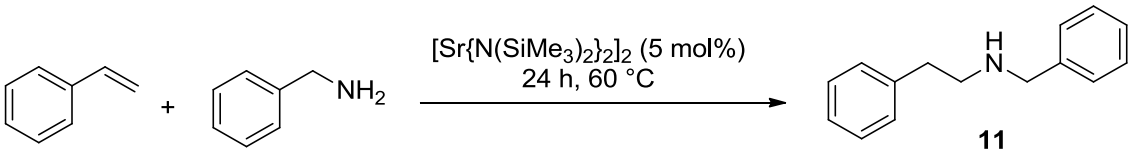
Synthesis of *N*-benzyl-2-*p*-tolylethanamine **10**[5]



10

The reaction was complete after 28 h at 60 °C. Purification by Kugelrohr distillation (0.04 mbar, T = 120 °C) yielded **10** as a colorless oil in 84% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ/ppm = 7.21 – 7.36 (m, 5H, H_{ar}), 7.10 (bs, 4H, H_{ar}), 3.81 (s, 2H, NHCH_2Ph), 2.86 – 2.93 (m, 2H, NHCH_2CH$_2$), 2.77 – 2.83 (m, 2H, NHCH$_2$CH_2), 2.32 (s, 3H, OCH_3), 1.88 (bs, 1H, NH). ^{13}C NMR (101 MHz, $CDCl_3$): δ/ppm = 139.9 (C_q), 136.8 (C_q), 135.6 (C_q), 129.1 (C_{ar}), 128.6 (C_{ar}), 128.4 (C_{ar}), 128.2 (C_{ar}), 127.0 (C_{ar}), 53.8 (NHCH$_2$Ph), 50.6 (NHCH$_2$CH$_2$), 35.7 (NHCH$_2$$CH_2$), 21.0 (O$CH_3$). HRMS (ESI) *m/z*: calc. for $C_{16}H_{20}N$: 226.1596 [M^+]; found 226.1602.

Synthesis of *N*-benzyl-2-phenylethanamine **11**[5]

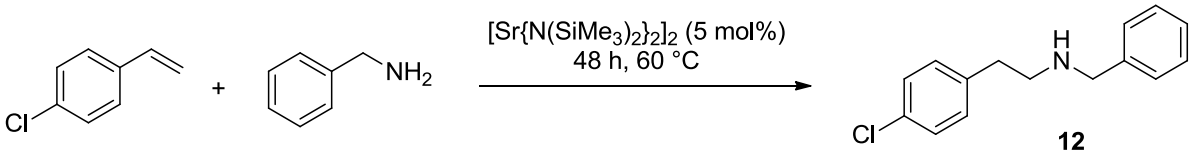


11

Reaction was complete after 24 h at 60 °C. Purification by column chromatography (silica gel, $CHCl_3$: NH_3 in MeOH (7 M) = 10 : 2.2) yielded **11** as a colorless oil in 78% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ/ppm = 7.16 – 7.36 (m, 10H, H_{ar}), 3.82 (s, 2H, NHCH_2Ph), 2.89 – 2.95 (m, 2H, NHCH_2CH$_2$), 2.82 – 2.88 (m, 2H, NHCH$_2$CH_2), 1.71 (bs, 1H, NH). ^{13}C NMR (101 MHz, $CDCl_3$): δ/ppm = 140.0 (C_q), 139.9 (C_q), 128.7 (C_{ar}), 128.4 (C_{ar}), 128.4

(C_{ar}), 128.1 (C_{ar}), 127.0 (C_{ar}), 126.1 (C_{ar}), 53.8 (NH*C*H_2Ph), 50.5 (NH*C*H_2CH_2), 36.2 (NHCH$_2$*C*H$_2$). HRMS (ESI) *m/z*: calc. for $C_{15}H_{18}N$: 212.1439 [M^+]; found 212.1445.

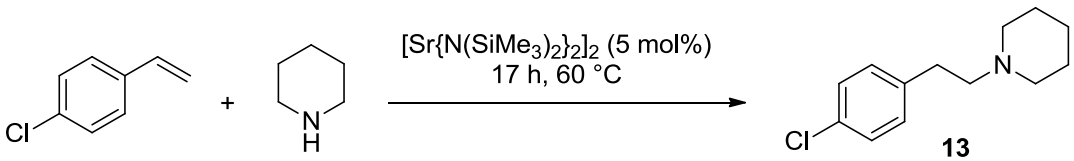
Synthesis of *N*-benzyl-2-(4-chlorophenyl)ethanamine **12**[5]



12

The reaction was complete after 48 h at 60 °C. Purification by column chromatography (silica gel, $CHCl_3$: NH_3 in MeOH (7 M) = 100 : 1) yielded **12** as a colorless oil in 65% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ/ppm = 7.21 – 7.36 (m, 7H, H_{ar}), 7.13 (d, 2H, J = 8.4 Hz, H_{ar}), 3.80 (s, 2H, NHCH_2Ph), 2.85 – 2.91 (m, 2H, NHCH_2CH$_2$), 2.77 – 2.83 (m, 2H, NHCH$_2$CH_2), 1.71 (bs, 1H, N*H*). ^{13}C NMR (101 MHz, $CDCl_3$): δ/ppm = 139.8 (C_q), 138.4 (C_q), 131.9 (C_q), 130.0 (C_{ar}), 128.5 (C_{ar}), 128.4 (C_{ar}), 128.1 (C_{ar}), 127.0 (C_{ar}), 53.8 (NH*C*H$_2$Ph), 50.2 (NH*C*H$_2$CH$_2$), 35.6 (NHCH$_2$*C*H$_2$). HRMS (ESI) *m/z*: calc. for $C_{15}H_{17}ClN$: 246.1031 [M^+]; found 246.1039.

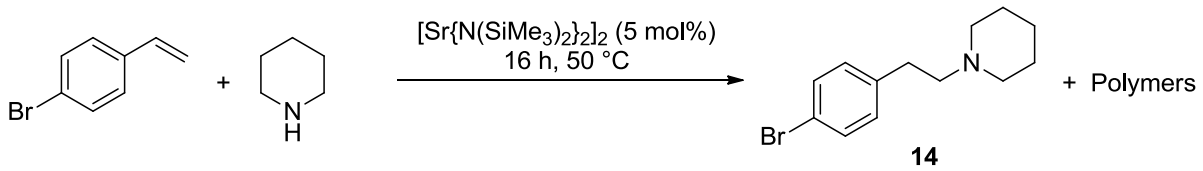
Synthesis of 1-(4-chlorophenethyl)piperidine **13**[5]



13

The reaction was complete after 17 h at 60 °C. Purification by column chromatography (silica gel, $CHCl_3$: NH_3 in MeOH (7 M = 100 : 1) yielded **13** as a colorless oil in 69% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ/ppm = 7.24 (d, 2H, J = 8.3 Hz, H_{ar}), 7.13 (d, 2H, J = 8.3 Hz, H_{ar}), 2.78 (dd, 2H, J = 6.5 Hz, J = 10.0 Hz, NCH_2CH_2Ph), 2.50 – 2.56 (m, 2H, NCH_2CH_2Ph), 2.47 (bs, 4H, N(CH_2CH$_2$)$_2$CH$_2$), 1.57 – 1.60 (m, 4H, N(CH$_2$CH_2)$_2$CH$_2$), 1.40 – 1.50 (m, 2H, N(CH$_2$CH$_2$)$_2$CH_2). ^{13}C NMR (101 MHz, $CDCl_3$): δ/ppm = 139.0 (C_q), 131.7 (C_q), 130.0 (C_{ar}), 128.4 (C_{ar}), 61.0 (N*C*H$_2$CH$_2$Ph), 54.5 {N(*C*H$_2$CH$_2$)$_2$CH$_2$}, 32.9 (NCH$_2$*C*H$_2$Ph), 25.9 {N(CH$_2$*C*H$_2$)$_2$CH$_2$}, 24.3 {N(CH$_2$CH$_2$)$_2$*C*H$_2$}. HRMS (ESI) *m/z*: calc. for $C_{13}H_{19}NCl$: 224.1206 [M^+]; found 224.1213.

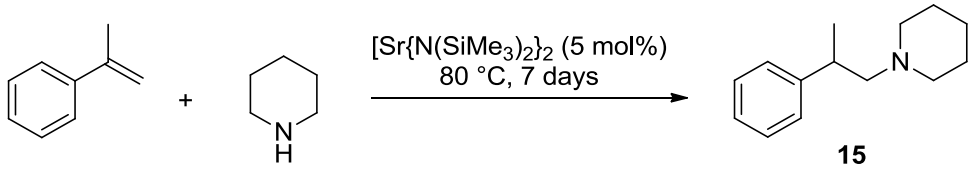
Synthesis of 1-(4-bromophenethyl)piperidine **14**[6]



14

No further conversion took place after 18 h at 60 °C (ca. 10% styrene left). Purification by Kugelrohr distillation (p = 0.2 mbar, 160 °C) yielded **14** as a colorless oil in 48% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ/ppm = 7.36 (d, 2H, *J* = 8.3 Hz, H_{Ar}), 7.05 (d, 2H, *J* = 8.3 Hz, H_{Ar}), 2.73 (dd, 2H, *J* = 6.5 Hz, *J* = 9.9 Hz, $NHCH_2CH_2$), 2.51 (dd, 2H, *J* = 6.5 Hz, *J* = 9.9 Hz, $NHCH_2CH_2$), 2.30 – 2.47 (m, 4H, $N(CH_2CH_2)_2CH_2$), 1.59 (td, 4H, *J* = 5.6 Hz, *J* = 11.0 Hz, $N(CH_2CH_2)_2CH_2$), 1.34 – 1.48 (m, 2H, $N(CH_2CH_2)_2CH_2$). ^{13}C NMR (101 MHz, $CDCl_3$): δ/ppm = 139.5 (C_q), 131.2 (C_{ar}), 130.3 (C_{ar}), 119.6 (C_q), 60.5 ($NHCH_2CH_2$), 54.4 ($N(CH_2CH_2)_2CH_2$), 33.0 ($NHCH_2CH_2$), 25.9 ($N(CH_2CH_2)_2CH_2$), 24.3 ($N(CH_2CH_2)_2CH_2$). HRMS (ESI) *m/z*: calc. for $C_{13}H_{19}BrN$: 268.0701 [M^+]; found 268.0693.

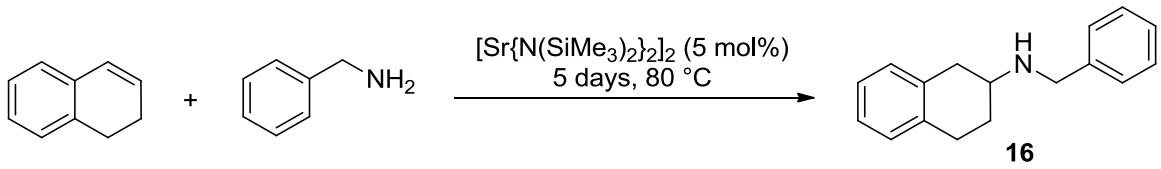
Synthesis of *N*-(2-phenylpropyl)piperidine **15**[5]



15

The reaction was worked up after 7 days at 80 °C. Purification by column chromatography (silica gel, CH_2Cl_2 : MeOH (10 : 0.3→10:1 and a few drops of aqueous ammonia) yielded **15** as a colorless oil in 66% yield (ca. 15% starting material left). ^{1}H NMR (400 MHz, $CDCl_3$): δ/ppm = 7.27 – 7.33 (m, 2H, H_{ar}), 7.16 – 7.24 (m, 2H, H_{ar}), 2.96 (sext., 1H, *J* = 7.0 Hz, PhC*H*), 2.38 – 2.50 (m, 2H, $N(CH_2CH_2)_2CH_2$), 2.24 – 2.36 (m, 2H, $PhCH(CH_3)CH_2N$), 1.47 – 1.64 (m, 4H, $N(CH_2CH_2)_2CH_2$), 1.35 – 1.46 (m, 2H, $N(CH_2CH_2)_2CH_2$), 1.28 (d, 3H, *J* = 6.9 Hz, $PhCH(CH_3)CH_2N$). ^{13}C NMR (101 MHz, $CDCl_3$): δ/ppm = 146.8 (C_q), 128.4 (C_{ar}), 127.4 (C_{ar}), 126.1 (C_{ar}), 67.2 ($PhCH(CH_3)CH_2N$), 55.1 ($N(CH_2CH_2)_2CH_2$), 37.6 (PhCH), 26.2 ($N(CH_2CH_2)_2CH_2$), 24.7 ($N(CH_2CH_2)_2CH_2$), 20.2 ($PhCH(CH_3)CH_2N$). HRMS (ESI) *m/z*: calc. for $C_{14}H_{22}N$: 204.1752 [M^+]; found 204.1749.

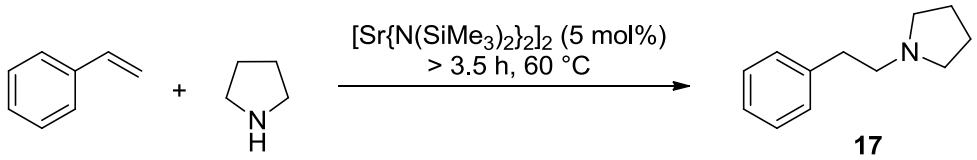
Synthesis of *N*-benzyl-1,2,3,4-tetrahydronaphthalen-2-amine **16**



16

The reaction was stopped after 5 days at 80 °C (^{1}H NMR: 76% product and 24% remaining diehydronaphtalene). Purification by Kugelrohr distillation (200 °C, 0.1 mbar) to yield **16** as a colorless oil (0.32 g, 1.34 mmol, 67%). ^{1}H NMR (400 MHz, d_6-benzene): δ/ppm = 7.31 (d, 2H, J = 7.4 Hz, H_{ar}), 7.20 (t, 2H, J = 7.4 Hz, H_{ar}), 7.11 (t, 1H, J = 7.3 Hz, H_{ar}), 7.01 – 7.07 (m, 2H, H_{ar}), 6.92 – 6.99 (m, 2H, H_{ar}), 3.64 (s, 2H, NHCH_2Ph), 2.80 (dd, 1H, J = 4.7 Hz, J = 15.8 Hz, CCH_{ab}CH), 2.68 – 2.75 (m, 1H, CCH$_{ab}$CH), 2.65 (t, 1H, J = 5.2 Hz, CCH$_{ab}$CH_{ab}), 2.48 – 2.58 (m, 1H, CCH$_{ab}$CH_{ab}), 2.45 (dd, 1H, J = 8.6 Hz, J = 15.8 Hz, CCH_{ab}CH), 1.69 – 1.80 (m, 1H, CCH_{ab}CH$_{ab}$), 1.41 (dtd, 1H, J = 5.6 Hz, J = 9.8 Hz, J = 12.7 Hz, CCH_{ab}CH$_{ab}$), 0.85 (bs, 1H, NHCH$_2$Ph). ^{13}C NMR (101 MHz, $CDCl_3$): δ/ppm = 141.7 (C_q), 136.6 (C_q), 135.7 (C_q), 129.7 (C_{ar}), 129.0 (C_{ar}), 128.5 (C_{ar}), 128.3 (C_{ar}), 127.0 (C_{ar}), 126.0 (C_{ar}), 126.0 (C_{ar}), 53.1 (CCH$_{ab}$CH), 51.4 (NHCH$_2$Ph), 37.1 (CCH$_{ab}$CH), 29.8 (CCH$_{ab}$CH$_{ab}$, 28.1 (CCH$_{ab}$CH$_{ab}$). HRMS (ESI) *m/z*: calc. for $C_{17}H_{20}N$: 238.1596 [M^+]; found 238.1595. IR (neat) $\tilde{\nu}$ / cm^{-1}: 3060, 3022, 2919, 2837, 1603, 1581, 1493, 1452, 1357, 1123, 1027. Anal. Calc. for $C_{17}H_{19}N$: C, 86.03; H, 8.07; N, 5.90; found: C, 85.98; H, 8.02; N, 5.86.

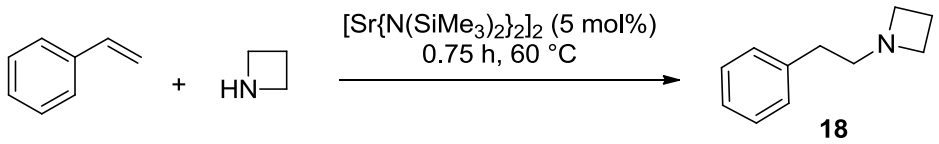
Synthesis of 1-phenethylpyrrolidine **17**[5]



17

The reaction was complete after less than 3.5 h at 60 °C. Purification by Kugelrohr distillation yielded **17** as a colorless oil in 90% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ/ppm = 7.19 – 7.35 (m, 5H, H_{ar}), 2.88 (dd, 2H, J = 5.9 Hz, J = 10.5 Hz, NCH_2CH_2Ph), 2.74 (dd, 2H, J = 5.8 Hz, J = 10.3 Hz, NCH_2CH_2Ph), 2.58 – 2.66 (m, 4H, N(CH_2CH$_2$)$_2$), 1.80 – 1.90 (m, 4H, N(CH$_2$CH_2)$_2$). ^{13}C NMR (101 MHz, $CDCl_3$): δ/ppm = 140.3 (C_{ar}), 128.4 (C_{ar}), 126.0 (C_{ar}), 58.3 (NCH$_2$CH$_2$Ph), 54.2 {N(CH$_2$CH$_2$)$_2$}, 35.7 (NCH$_2$CH$_2$Ph), 23.4 {N(CH$_2$CH$_2$)$_2$}. HRMS (ESI) *m/z*: calc. for $C_{12}H_{18}N$: 176.1439 [M^+]; found 176.1436.

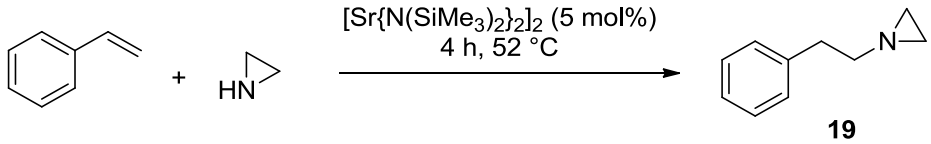
Synthesis of 1-phenethylazetidine **18**



18

The reaction was complete after 45 min at 60 °C. Purification by column chromatography (silica gel, $CHCl_3$: NH_3 in MeOH (7 M) = 10 : 0.4) yielded **18** as colorless oil in 81% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ/ppm = 7.15 – 7.21 (m, 3H, H_{ar}), 7.25 – 7.31 (m, 2H, H_{ar}), 3.19 (t, 4H, J = 7.0 Hz, N(CH_2)$_2$CH_2), 2.64 (bs, 4H, NCH_2CH_2Ph), 2.07 (q, 2H, J = 6.9 Hz, N(CH_2)$_2$CH_2). ^{13}C NMR (101 MHz, $CDCl_3$): δ/ppm = 140.2 (C_q), 128.6 (C_{ar}), 128.3 (C_{ar}), 126.0 (C_{ar}), 61.6 (NCH$_2$CH$_2$Ph), 55.3 {N(CH$_2$)$_2$CH$_2$}, 34.5 (NCH$_2$$CH_2$Ph), 17.8 {N(CH$_2$)$_2$$CH_2$}. HRMS (ESI) *m/z*: calc. for $C_{11}H_{16}N$: 162.1283 [M^+]; found 162.1282. Anal. Calc. for $C_{11}H_{15}N$: C, 81.94; H, 9.38; N, 8.69; found: C, 81.87; H, 9.27; N, 8.63.

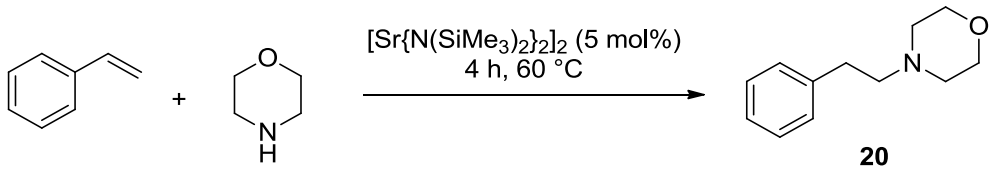
Synthesis of 1-phenethylaziridine **19**



19

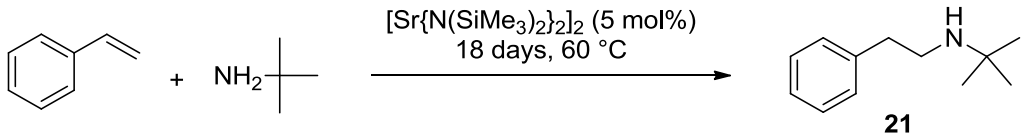
The reaction was complete after 4 h at 52 °C. Purification by vacuum distillation (bp = 55 °C at = 0.3 mbar) yielded **19** as a colorless oil 72% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ/ppm = 7.17 – 7.35 (m, 5H, H_{ar}), 2.90 (t, 2H, J = 7.6 Hz, NCH$_2$CH_2Ph), 2.43 – 2.50 (m, 2H, NCH_2CH$_2$Ph), 1.71 – 1.76 (m, 2H, N(C$H_a$$H_b$)$_2$), 1.06 – 1.12 (m, 2H, N(C$H_a$$H_b$)$_2$). ^{13}C NMR (101 MHz, $CDCl_3$): δ/ppm = 140.1 (C_q), 128.7 (C_{ar}), 128.3 (C_{ar}), 126.0 (C_{ar}), 63.6 (NCH$_2$CH$_2$Ph), 36.4 (NCH$_2$$CH_2$Ph), 27.3 {N($CH_aH_b$)$_2$}. HRMS (ESI) *m/z*: calc. for $C_{10}H_{14}N$: 148.1126 [M^+]; found 148.1131.

Synthesis of 4-phenethylmorpholine **20**[5]



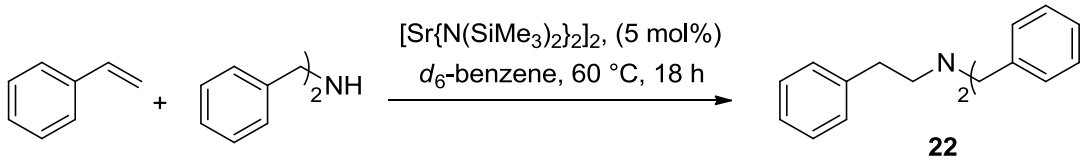
The reaction was finished after 4 h at 60 °C. Purification by column chromatography (silica gel, $CHCl_3$: NH_3 in MeOH (7 M = 100 : 1) yielded **20** as a colorless oil in 93% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ/ppm = 7.17 – 7.33 (m, 5H, H_{ar}), 3.76 (t, 4H, J = 4.6 Hz, O-CH_2), 2.82 (dd, 2H, J = 6.4 Hz, J = 10.0 Hz, NCH_2CH_2Ph), 2.62 (dd, 2H, J = 6.4 Hz, J = 10.0 Hz, NCH_2CH_2Ph), 2.55 (s, 4H, N(CH_2CH$_2$)$_2$O). ^{13}C NMR (101 MHz, $CDCl_3$): δ/ppm = 134.0 (C_q), 128.7 (C_{ar}), 128.4 (C_{ar}), 126.1 (C_{ar}), 66.9 (O-CH$_2$), 60.8 (NCH$_2$CH$_2$Ph), 53.6 (N(CH$_2$CH$_2$)$_2$O, 33.2 (NCH$_2$$CH_2$Ph). HRMS (ESI) *m/z*: calc. for $C_{12}H_{18}NO$: 192.1388 $[M]^+$; found 192.1390.

Synthesis of 2-methyl-*N*-phenethylpropan-2-amine **21**[7]



The reaction was stopped after 18 days at 60 °C (NMR: 58% product **21**, 17% remaining styrene). Purification by Kugelrohr distillation yielded **21** as a colorless oil in 57% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ/ppm = 7.20 – 7.35 (m, 5H, H_{ar}), 2.78 -2.89 (m, 4H, NCH_2CH_2Ph), 1.11 (s, 9H, C(CH_3)$_3$). ^{13}C NMR (101 MHz, $CDCl_3$): δ/ppm = 140.2 (C_q), 128.7 (C_{ar}), 128.4 (C_{ar}), 126.1 (C_{ar}), 50.4 (C(CH$_3$)$_3$), 44.1 (NCH$_2$CH$_2$Ph), 37.1 (NCH$_2$$CH_2$Ph), 28.9 (C($CH_3$)$_3$).

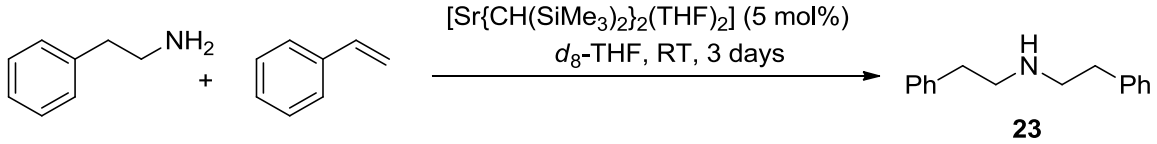
Synthesis of *N*,*N*-dibenzyl-2-phenylethanamine **22**[5]



A Youngs tap NMR tube was filled with $[Sr\{N(SiMe_3)_2\}_2]_2$ (0.02 g, 0.04 mmol), dibenzylamine (167.9 µL, 0.87 mmol) and d_6-benzene (177.5 µL). After the reactants were mixed, styrene was added (100.0 µL, 0.87 mmol). The tube was sealed, removed from the glovebox and placed in a pre-heated oil bath (60 °C). The reaction was monitored by

^{1}H NMR, which showed full conversion after 18 h. The reaction was treated with Et_2O, filtered over Celite and concentrated to a yellow oil. The crude was purified by column chromatography (CH_2Cl_2 → CH_2Cl_2 : MeOH = 10 : 0.04, R_f = 0.53 in CH_2Cl_2) to yield a colorless oil (0.21 g, 0.68 mmol, 78%). ^{1}H NMR (400 MHz, $CDCl_3$) δ/ppm: 7.13 – 7.40 (m, 13H, H_{ar}), 7.08 (d, 2H, J = 6.9 Hz, H_{ar}), 3.65 (s, 4H, {Ph-CH_2}$_2$N), 2.76 – 2.89 (m, 2H, NCH_2CH$_2$Ph), 2.64 – 2.73 (m, 2H, NCH$_2$CH_2Ph). ^{13}C NMR (101 MHz, $CDCl_3$) δ/ppm: 140.7 (C_q), 139.8 (C_q), 129.0 (C_{ar}), 128.8 (C_{ar}), 128.3 (C_{ar}), 126.9 (C_{ar}), 126.0 (C_{ar}), 58.3 (Ph-CH$_2$N), 55.2 (NCH$_2$CH$_2$Ph), 33.6 (NCH$_2$$CH_2$Ph). HRMS (ESI) *m/z* calc. for $C_{22}H_{24}N$ 302.1909; found 302.1911.

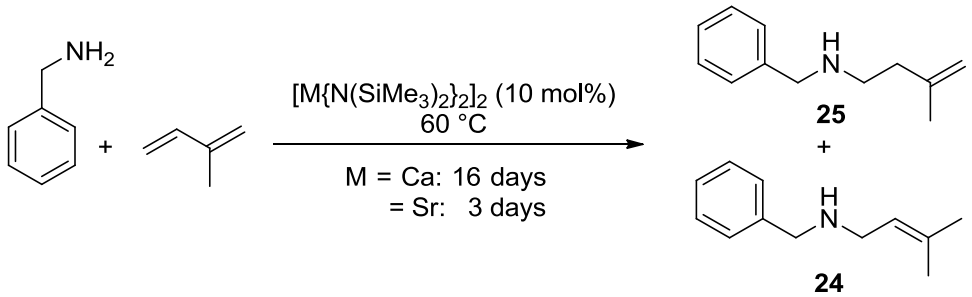
Synthesis of diphenylethylamine **23**



23

In a Young's tap NMR tube [Sr{CH(SiMe$_3$)$_2$}$_2$(THF)$_2$] (0.01 g, 0.01 mmol) was dissolved in d_8-THF (239.0 µL) and phenylethylamine (27.7 µL, 0.22 mmol) was added. After mixing the amine with the catalyst solution the light pink solution was treated with styrene (23.3 µL, 0.22 mmol). The tube was sealed, removed from the glovebox and monitored by ^{1}H NMR spectroscopy. After 3 days 70% of the styrene was cleanly converted into diphenylethylamine **23**. However, even after heating the reaction 3 h to 60 °C no further conversion could be initiated. The reaction was diluted with MeOH, filtered over Celite and purified by Kugelrohr distillation to yield a colorless oil (0.04 g, 0.15 mmol, 70%). ^{1}H NMR (400 MHz, $CDCl_3$) δ/ppm: 7.04 – 7.28(m, 10H, H_{ar}), 2.81 (t, 1H, J = 6.7 Hz, NCH_2CH$_2$), 2.70 (t, 1H, J = 6.7 Hz, NCH$_2$CH_2), 1.26 (bs, 1H, NH). ^{13}C NMR (101 MHz, $CDCl_3$) δ/ppm: 139.9 (C_q), 128.6 (C_{ortho}), 128.4 (C_{meta}), 126.0 (C_{para}), 51.0 (NCH$_2$CH$_2$), 36.3 (NCH$_2$$CH_2$).

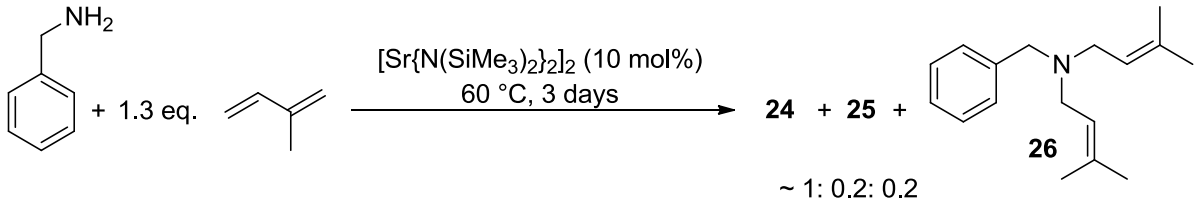
Synthesis of *N*-benzyl-3-methylbut-2-en-1-amine **24**[8]



A solution of [Sr{N(SiMe$_3$)$_2$}$_2$]$_2$ (0.05 g, 0.13 mmol) or [Ca{N(SiMe$_3$)$_2$}$_2$]$_2$ (0.05 g, 0.13 mmol), isopropene (0.17 g, 2.50 mmol) and benzylamine (0.27 g, 2.50 mol) was heated to 60 °C for 3 days (strontium catalyst) or 16 days (calcium catalyst). The resulting yellow

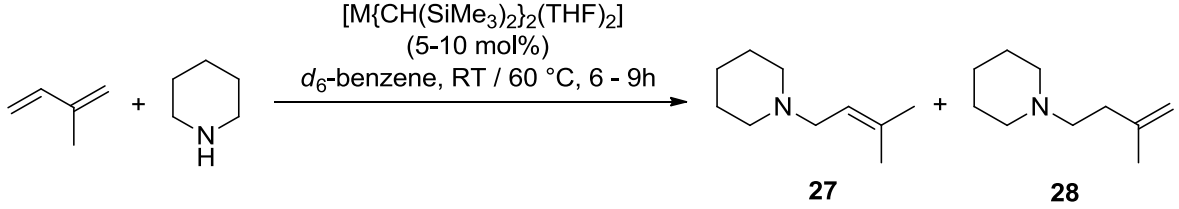
suspension was cooled to RT and exposed to air (intense red colour). After treatment with a water-Et_2O mixture (1:1) the suspension was filtered through Celite and the solids washed with Et_2O. The phases were separated, the organic phase was dried over $MgSO_4$ and evaporated to dryness yielding a yellow oil of a 5:1-mixture of **24** and **25** (0.39 g, 2.25 mmol, 90%). ^{1}H NMR (400 MHz, $CDCl_3$): δ/ppm = 7.20 – 7.35 (m, 8H, H_{ar}), 5.29 (t, 1H, J = 6.9 Hz, $CH_2C(H)=C(CH_3)_{ab}$, **24**), 4.78 (s, 1H, C=CH_{ab}, **25**), 4.73 (s, 1H, C=CH_{ab}, **25**), 3.81 (s, 2H, Bz-CH_2NH, **25**), 3.79 (s, 2H, Bz-CH_2NH, **24**), 3.23 (d, 2H, J = 6.9 Hz, NHCH_2, **24**), 2.75 (t, 2H, J = 6.9 Hz, NHCH_2CH$_2$, **25**), 2.25 (t, 2H, J = 6.9 Hz, NHCH$_2$CH_2, **25**), 1.73 (s, 3H, $CH_2C(H)=C(CH_3)_{ab}$, **24**), 1.71 (s, 3H, CH_3, **25**), 1.62 (s, 3H, $CH_2C(H)=C(CH_3)_{ab}$, **24**). ^{13}C NMR (101 MHz, $CDCl_3$): δ/ppm = 143.3 (C=CH$_{ab}$, **25**), 140.4 (C_q, **24**), 139.8 (C_q, **25**), 134.0 ($CH_2C(H)=C(CH_3)_{ab}$), 128.3 (C_{ar}, **25**), 128.1 (C_{ar}, **24**), 128.0 (C_{ar}, **24**), 127.9 (C_{ar}, **25**), 126.7 (C_{ar}), 123.0 (C_{ar}, **25**), 126.5 ($CH_2C(H)=C(CH_3)_{ab}$), 111.4 (C=CH_2), 53.8 (Bz-CH_2NH, **25**), 53.3 (Bz-CH_2NH, **24**), 46.7 (NHCH_2CH$_2$, **25**), 46.6 ($CH_2C(H)=C(CH_3)_{ab}$, **24**), 37.9 (NHCH$_2$CH$_2$, **25**), 25.6 ($CH_2C(H)=C(CH_3)_{ab}$, **24**), 22.1 (CH_3, **25**), 17.7 ($CH_2C(H)=C(CH_3)_{ab}$, **24**). HRMS (ESI) *m/z*: calc. for $C_{12}H_{18}N$ 176.1439; found 176.1429.

Synthesis of *N*,*N*-bis(3-methyl-2-buten-1-yl)-benzenemethanamine **26**[9]



Same reaction procedure as above, except 1.3 equ. of isopropene were used. Characterisation for **26**. ^{1}H NMR (400 MHz, $CDCl_3$): δ/ppm = 7.20 – 7.40 (m, 5H, H_{Ar}), 5.32 – 5.38 (m, 2H, $CH_2C(H)=C(CH_3)_{ab}$), 3.56 (s, 2H, Bz-CH_2NH), 3.05 (d, 4H, J = 6.8 Hz, NHCH_2), 1.76 (s, 6H, $CH_2C(H)=C(CH_3)_{ab}$), 1.64 (s, 6H, $CH_2C(H)=C(CH_3)_{ab}$). ^{13}C NMR (101 MHz, $CDCl_3$): δ/ppm = 134.2, 128.8, 128.3, 126.9, 122.1, 57.9, 51.1, 25.8, 17.8. HRMS (ESI) *m/z*: calc. for $C_{17}H_{26}N$ 244.2065; found 244.1979.

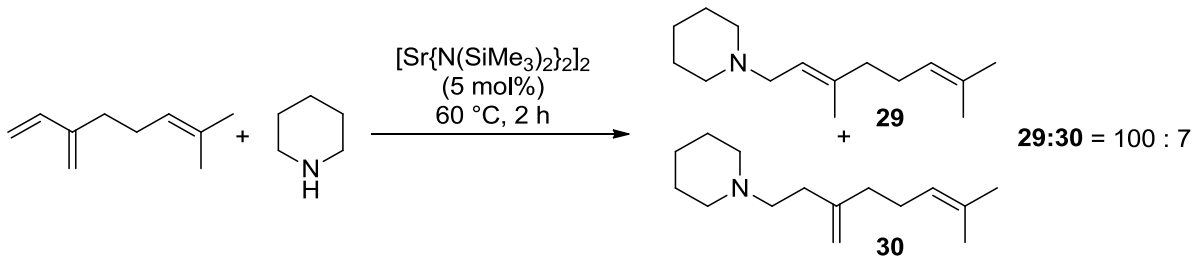
Synthesis of 1-(3-methylbut-2-enyl)piperidine **27**[9]



A Youngs tap NMR tube was filled with isopropene (10.0 µL, 0.10 mmol), piperidine (10.0 µL, 0.10 mmol), [Ca{CH(SiMe$_3$)$_2$}$_2$(THF)$_2$] or [Sr{CH(SiMe$_3$)$_2$}$_2$(THF)$_2$] (100 g/L,

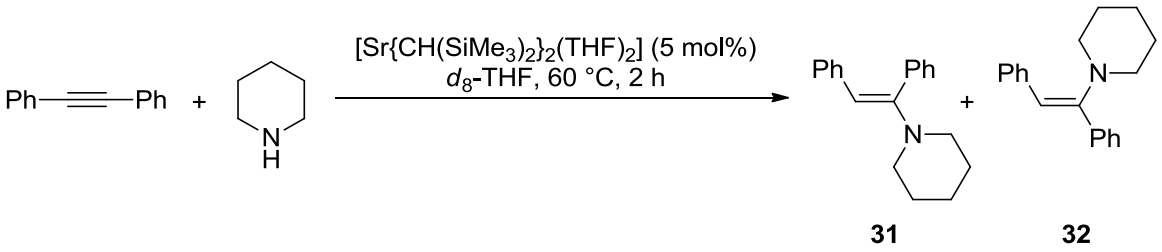
0.01 mmol or 0.01 mmol) and d_6-benzene (V_{total} = 440.0 µL). The tube was removed from the glovebox and heated in an oil bath to 60 °C in case of the calcium system and left at RT for the strontium catalysis. The reactions were monitored by ^{1}H NMR spectroscopy and after 9 h (**27** : **28** = 10 : 1) and 6 h (**27** : **28** = 38 : 1) full conversion was observed for calcium and strontium, respectively. The yields have been determined by NMR-integrations with 83% and 15% for the calcium and strontium, respectively. Characterisation of **27**: ^{1}H NMR (400 MHz, d_6-benzene) δ/ppm = 5.36 – 5.48 (m, 2H, $CH_2C(H)$=$C(CH_3)_{ab}$), 2.90 (d, 1H, J = 6.9 Hz, $CH_2C(H)$=$C(CH_3)_{ab}$), 2.25 – 2.45 (m, 4H, $N(CH_2CH_2)_2CH_2$), 1.63 (d, 3H, J = 0.9 Hz, $CH_2C(H)$=$C(CH_3)_{ab}$), 1.47 – 1.58 (m, 7H, $N(CH_2CH_2)_2CH_2$/$CH_2C(H)$=$C(CH_3)_{ab}$), 1.27 – 1.42 (m, 2H, $N(CH_2CH_2)CH_2$). ^{13}C NMR (101 MHz, $CDCl_3$): δ/ppm = 133.8 ($CH_2C(H)$=$C(CH_3)_{ab}$), 123.2 ($CH_2C(H)$=$C(CH_3)_{ab}$, 57.3 ($CH_2C(H)C(CH_3)_{ab}$), 54.8 ($N(CH_2CH_2)_2CH_2$), 26.6 ($N(CH_2CH_2)_2CH_2$), 25.9 ($CH_2C(H)$=$C(CH_3)_{ab}$, 25.0 ($N(CH_2CH_2)_2CH_2$), 18.0 ($CH_2C(H)$=$C(CH_3)_{ab}$). HRMS (ESI) *m/z*: calc. for $C_{10}H_{20}N$ 154.1596; found 154.1593.

Synthesis of (*Z*)-1-(3,7-dimethylocta-2,6-dienyl)piperidine **29**



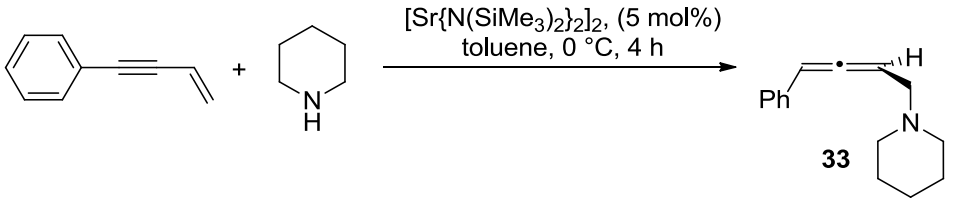
A Young's tap NMR tube was filled with $[Sr\{N(SiMe_3)_2\}_2]_2$ (0.04 g, 0.09 mmol), piperidine (177.8 µL, 1.80 mmol) and myrcene (310.0 µL, 1.80 mmol). After a homogenous solution was obtained, a sealed capillary filled with d_6-benzene was added, the tube sealed, removed from the glovebox and heated to 60 °C in an oil bath for 12 h. The reaction was diluted with wet Et_2O, filtered over a pad of Celite and the solvent was removed in *vacuo*. The colourless oil was purified by column chromatography (CH_2Cl_2 : MeOH/NH_3 = 10 : 0.4) to yield **29** and **30** as a colorless oil (0.29 g, 1.30 mmol, 72%). Characterisation of **29**: ^{1}H NMR (400 MHz, d_6-benzene) δ/ppm = 5.44 (dt, 1H, J = 1.2 Hz, J = 6.8 Hz, NCH_2CH), 5.10 - 5.20 (m, 1H, $CHCH_2CH_2$), 2.92 (d, 2H, J = 6.8 Hz, NCH_2CH), 2.22 – 2.52 (m, 4H, $N(CH_2CH_2)_2CH_2$), 2.08 – 2.16 (m, 2H, $CHCH_2CH_2$), 2.00 – 2.08 (m, 2H, $CHCH_2CH_2$), 1.64 (2, 3H, CH_3), 1.57 (2, 3H, CH_3), 1.48 – 1.53 (m, 7H, CH_3/$N(CH_2CH_2)_2CH_2$), 1.25 - 1.40 (m, 2H, $N(CH_2CH_2)_2CH_2$). ^{13}C NMR (101 MHz, $CDCl_3$): δ/ppm = 137.7 (C_q), 131.2 (C_q), 124.8 ($CHCH_2CH_2$), 122.9 (NCH_2CH), 57.2 (NCH_2CH), 54.8 ($N(CH_2CH_2)_2CH_2$), 40.2 ($CHCH_2CH_2$), 26.9 ($CHCH_2CH_2$), 26.5 ($N(CH_2CH_2)_2CH_2$), 25.9 (CH_3), 25.0 ($N(CH_2CH_2)CH_2$), 17.7 (CH_3), 16.4 (CH_3). IR (neat) $\tilde{\nu}$ / cm^{-1}: 2930, 2853, 2756, 1442, 1276, 1296, 1153, 1106, 1038, 990, 860, 775, 506. HRMS (ESI) *m/z*: calc. for $C_{15}H_{28}N$ 222.2222; found 222.2222.

Synthesis of 1-(1,2-diphenylvinyl)piperidine **31**



In a glovebox, a Young's tap NMR tube was filled with $[Sr\{CH(SiMe_3)_2\}_2(THF)_2]$ (0.01 g, 0.02 mmol) and dissolved in d_8-THF (220.0 µL). Piperidine (31.6 µL, 0.32 mmol) and diphenylacetylene (0.04 g, 0.22 mmol) in d_8-THF (220.0 µL) were added and the NMR tube was shaken upside down. The tube was removed from the glovebox and placed in a 60 °C oil bath. After 2 h full conversion was observed by ^{1}H NMR spectroscopy and GS/MS. The intense violet solution was diluted with Et_2O, filtered and purified by Kugelrohr distillation to yield **31** and **32** as a colorless oil (0.04 g, 0.15 mmol, 67%). **31**:**32** = 10:1. Compounds **31** and **32** are not stable on silica gel or alumina. The oxidised product is isolated. Characterisation for **31**: ^{1}H NMR (400 MHz, d_6-benzene) δ/ppm: 6.75 – 7.56 (m, 10H, H_{ar}), 5.70 (s, 1H, C=C*H*), 2.60 – 3.00 (m, 4H, N(CH_2CH$_2$)$_2$CH$_2$) , 1.24 – 1.65 (m, 6H, N(CH$_2$CH_2)$_2$CH_2). ^{13}C NMR (101 MHz, d_6-benzene) δ/ppm: 152.2 (C=*C*-N), 139.9 (C_q), 138.5 (C_q), 130.8 (C_{ar}), 129.0 (C_{ar}), 128.7 (C_{ar}), 128.3 (C_{ar}), 128.1 (C_{ar}), 124.4 (C_{ar}), 106.4 (C=*C*H), 50.3 (N(*C*H$_2$CH$_2$)$_2$CH$_2$), 26.4 (N(CH$_2$*C*H$_2$)$_2$CH$_2$), 24.8 (N(CH$_2$CH$_2$)$_2$*C*H$_2$). HRMS (ESI) *m/z*: calc. for $C_{19}H_{22}N$: 264.1752 [M^+]; found 264.1759.

Synthesis of *rac*-1-(4-phenylbuta-2,3-dienyl)piperidine **33**



In a glovebox, a Schlenk tube fitted with a Youngs tap was filled with $[Sr\{N(SiMe_3)_2\}_2]_2$ (0.02 g, 0.04 mmol), piperidine (77.1 µL, 0.78 mmol) and toluene (1.2 mL). The tube was sealed, removed from the glovebox and cooled to 0 °C. 3-Buten-1-yn-1-yl-benzene (100.0 µL, 0.78 mmol) was added and the reaction was stirred for 4 h at 0 °C. The reaction was quenched with 1.0 mL methanol and the solution was evaporated to dryness. The crude oil was purified by column chromatography (aluminium oxide, petrol ether : EtOAc = 10 : 0.1, then more polar) to yield **33** as a colorless oil (0.120 g, 0.560, 72%). ^{1}H NMR (400 MHz, d_6-benzene) δ/ppm: 7.27 (d, 2H, J = 7.5 Hz, H_{ar}), 7.06 – 7-15 (m, 2H, H_{ar}), 7.00 (dd, 1H, J = 7.3 Hz, J = 7.3, H_{ar}), 6.11 (td, 1H, J = 2.4 Hz, J = 6.2 Hz, Ph-C*H*) 5.58 (q, 1H, J = 6.9 Hz, C=C*H*CH$_2$), 3.03 (dd, 2H, J = 2.5 Hz, J = 7.0 Hz, C=CCHCH_2), 2.25 – 2.44 (m, 4H, N(CH_2CH$_2$)$_2$CH$_2$), 1.51 (td, 4H, J = 5.6 Hz, J = 11.0 Hz, N(CH$_2$CH_2)$_2$CH$_2$), 1.22 – 1.32

(m, 2H, $N(CH_2CH_2)_2CH_2$). ^{13}C NMR (101 MHz, $CDCl_3$): δ/ppm = 206.1 (C=$CHCH_2$), 134.6 (C_q), 128.7 (C_{ar}), 126.9 (C_{ar}), 126.8 (C_{ar}), 94.6 (Ph-CH), 91.8 (C=CHCH_2), 58.3 (C=CHCH_2), 54.1 ($N(CH_2CH_2)_2CH_2$), 26.1 ($N(CH_2CH_2)_2CH_2$, 24.3 ($N(CH_2CH_2)_2CH_2$). IR (neat) λ / cm^{-1}: 2933, 2853, 2797, 2748, 1948, 1495, 1458, 1338, 1299, 1153, 1108, 1038, 991. HRMS (ESI) *m/z*: calc. for $C_{15}H_{20}N$ 214.1596; found 214.1595.

Kinetic studies

In a typical experiment, an NMR sample was prepared as described above (see catalytic NMR experiments), but stored at -78 °C or 0 °C until kinetic measurements were initiated. For all kinetic measurements regarding the intermolecular hydroamination the alkene : amine ratio was 10 : 1 to maintain *pseudo* first-order conditions. The NMR sample was then inserted into a Bruker DRX 400 NMR spectrometer, which had been pre-heated to a chosen temperature. Data were acquired using four scans per time interval with a long pulse delay (8 s) to avoid signal saturation. The reaction kinetics were usually monitored using the intensity changes in the substrate resonances over three or more half-lives on the basis of amine consumption. The substrate concentration was determined by using an internal standard such as ferrocene, $(SiMe_3)_4Si$ or liberated $CH_2(SiMe_3)_2$ or $HN(SiMe_3)_2$. All data collected could be fit by least squares to Eq. S1.

$$Ln\frac{[Subs.]_{t=0}}{[Subs.]} = mt + A \qquad \text{Eq. S1}$$

where $[Subs.]_{t=0}$ is the initial substrate concentration and [*Subs.*] the substrate concentration at the specific reaction time. *T* is the time, *m* the slope of the graph and *A* the y-axis intercept.

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