Intermolecular Hydroaminoalkylation of Propadiene

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1. General Information

All reactions were performed under an inert atmosphere of nitrogen or argon. All solvents were distilled prior to use. Petroleum ether (boiling range 40-60 °C) is abbreviated with “PE”, tert-butyl methyl ether is abbreviated with MTBE. All chemicals whose synthesis is not described on the following pages were purchased from commercial sources and, unless otherwise noted, used without further purification. N-Benzylaniline derivatives were synthesized according to a literature procedure\[1\] and degassed prior to use. A solution of propadiene in toluene (c = 0.4 molL\(^{-1}\)) was generated according to literature procedures.\[2,3\] 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. Products that have already been reported in the literature were identified by \(^1\)H NMR, \(^13\)C NMR and \(^19\)F 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\(_2\) 500 MHz spectrometer. \(^1\)H NMR spectra are referenced to the residue solvent signals (δ\(^1\)H = 7.26 ppm for CDCl\(_3\) and δ\(^1\)H = 7.16 ppm for benzene-\(\text{d}_6\)). \(^13\)C NMR spectra are referenced to the central line of the residue solvent (δ\(^{13}\)C\(\{\text{\(^1\)H}\}\) = 77.16 ppm for CDCl\(_3\) and δ\(^{13}\)C\(\{\text{\(^1\)H}\}\) = 128.06 for benzene-\(\text{d}_6\)). 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). HRMS analyses were performed on a Thermo Scientific DFS (EI, 70 eV). GC analyses were performed on a Shimadzu GC-2010 gas chromatograph (column: FS-SE-54-CB-0.25, length = 30m, inner diameter = 0.32mm, film thickness = 0.25μm, (94%-methyl)-(5%-phenyl)-(1%-vinyl)polysiloxane) with a flame ionization detector. Regioselectivities of catalytic reactions were determined by GC analyses prior to chromatography and refer to the ratio of the GC areas of the corresponding regioisomers.
2. Optimization of Catalyst and Reaction Conditions

For all experiments related to optimization studies, \( p \)-cymene was added to the solution of propadiene in toluene as an internal standard \([c(p\text{-cymene}) = 0.026 \text{ molL}^{-1}]\). The catalyst screening was performed in 5 mL ampoules (length = 240 mm, outer diameter = 10 mm, inner diameter = 7 mm, wall thickness = 1.5 mm) equipped with a magnetic stir bar and all substrates were dried and degassed prior to use. Typical procedure: In a glovebox under \( \text{N}_2 \)-atmosphere, the catalyst (usually 0.01 mmol, 10 mol\%) and \( N \)-methylaniline or \( N \)-benzylaniline (0.1 mmol, 1.0 equiv) were weight in a 10 mL vial. Subsequently, a solution of propadiene in toluene \((c = 0.4 \text{ molL}^{-1}, 0.75 \text{ mL}, 0.3 \text{ mmol}, 3.0 \text{ equiv})\) was added to the vial via syringe and then the mixture was transferred into the ampoule which was quickly sealed with a natural gas/O\(_2\) torch. It should be mentioned that the mix-and-seal-process must be performed as quickly as possible. Studies showed that a slow mix-and-seal-process strongly reduces the conversion of \( N \)-methylaniline or \( N \)-benzylaniline. In cases, in which the amount of catalyst was below 6 mg, 1.0 mmol \( N \)-benzylaniline and 0.1 mmol of the catalyst were weight into a vial. The propadiene solution \((c = 0.4 \text{ molL}^{-1}, 7.5 \text{ mL})\) was added and then only a tenth of this solution was used for the catalytic reaction. If the volume of the propadiene solution was less than 0.75 mL, the reaction mixture was filled up with a toluene solution mixed with \( p \)-cymene \((c = 0.026 \text{ molL}^{-1})\). This was done in order to always have the same concentration of the internal standard \( p \)-cymene in the reaction mixture and thus to allow for exact comparisons.

![Figure S1. Catalysts and ligands used for the screening.](image-url)
Table S1. Catalyst screening\(^{[a]}\)

| Entry | Catalyst       | Equivalents propadiene | Ratio \(\rho\)-cymene/product\(^{[b]}\) |
|-------|----------------|------------------------|----------------------------------------|
| 1     | IVa            | 3                      | -                                      |
| 2     | IVb            | 3                      | -                                      |
| 3     | V              | 3                      | -                                      |
| 4     | \(\text{Ti(NMe}_2)_4\) | 3                  | -                                      |
| 5     | TiBn\(_4\)        | 3                      | -                                      |
| 6     | VI             | 3                      | -                                      |
| 7     | Nb(NMe\(_2\))_5\) | 3                  | -                                      |
| 8     | Ta(NMe\(_2\))_5\) | 3                  | -                                      |
| 9     | Zr(NMe\(_2\))_4\) | 3                  | -                                      |
| 10    | V              | 2                      | -                                      |
| 11    | V              | 1                      | -                                      |

[a] Reaction conditions: \(N\)-methylaniline (11 mg, 0.1 mmol, 1 equiv), propadiene in toluene (\(c = 0.4 \text{ moL}^{-1}\), 0.75 mL, 0.3 mmol, 3 equiv), catalyst (0.01 mmol, 10 mol\%), 140 °C, 30 min. [b] The ratio was determined by GC analysis. It refers to the ratio of the GC areas obtained for \(\rho\)-cymene and the branched product \(N\)-(2-methylallyl)aniline (3b).
Table S2. Catalyst screening[a]

![Reaction Diagram](image)

| Entry | Catalyst         | Ratio p-cymene/product[b] |
|-------|------------------|---------------------------|
| 1     | IVa              | 4:10                      |
| 2     | IVb              | -                         |
| 3     | V                | 8:10                      |
| 4     | Ti(NMe₂)₄       | -                         |
| 5     | TiBn₄           | -                         |
| 6     | VI               | -                         |
| 7     | Nb(NMe₂)₅       | -                         |
| 8     | Ta(NMe₂)₅       | -                         |
| 9     | Zr(NMe₂)₄       | -                         |

[a] Reaction conditions: N-benzylaniline (18 mg, 0.1 mmol, 1 equiv), propadiene in toluene (c = 0.4 molL⁻¹, 0.75 mL, 0.3 mmol, 3 equiv), catalyst (0.01 mmol, 10 mol%), 140 °C, 30 min. [b] The ratio was determined by GC analysis. It refers to the ratio of the GC areas obtained for p-cymene and the branched product N-(2-methyl-1-phenylallyl)aniline (4b).
Table S3. Optimization of the reaction conditions\[^a\]

| Entry | t [min] | T [°C] | Catalyst loading [mol%] | Equivalents propadiene | Ratio p-cymene/product\[^a\] |
|-------|--------|--------|--------------------------|------------------------|-----------------------------|
| 1     | 30     | 25     | 10                       | 3.0                    | -                           |
| 2     | 30     | 100    | 10                       | 3.0                    | 16:10                       |
| 3     | 30     | 120    | 10                       | 3.0                    | 10:10                       |
| 4     | 30     | 140    | 10                       | 3.0                    | 4:10                        |
| 5     | 30     | 160    | 10                       | 3.0                    | 8:10                        |
| 6     | 30     | 140    | 0                        | 3.0                    | -                           |
| 7     | 30     | 140    | 2.5                      | 3.0                    | 14:10                       |
| 8     | 30     | 140    | 5                        | 3.0                    | 9:10                        |
| 9     | 30     | 140    | 7.5                      | 3.0                    | 8:10                        |
| 10    | 30     | 140    | 10                       | 1.0                    | 10:10                       |
| 11    | 30     | 140    | 10                       | 1.2                    | 4:10                        |
| 12    | 30     | 140    | 10                       | 2.0                    | 4:10                        |
| 13    | 60     | 140    | 10                       | 1.2                    | 3:10                        |
| 14    | 120    | 140    | 10                       | 1.2                    | 2:10                        |
| 15    | 240    | 140    | 10                       | 1.2                    | 2:10                        |

\[^a\] Reaction conditions: N-benzylniline (18 mg, 0.1 mmol, 1 equiv), propadiene in toluene (c = 0.4 molL\(^{-1}\)), catalyst IVa. T, t. [b] The ratio was determined by GC analysis. It refers to the ratio of the GC areas obtained for p-cymene and the branched product N-(2-methyl-1-phenylallyl)aniline (4b).
3. Sensitivity Assessment

![Chemical structure](image)

The optimized reaction conditions for the hydroaminoalkylation of propadiene with \( N \)-benzylaniline (18 mg, 0.1 mmol, 1.0 equiv), propadiene in toluene (\( c = 0.4 \text{ molL}^{-1}, 0.3 \text{ mL}, 0.12 \text{ mmol}, 1.2 \text{ equiv} \)), catalyst IVa (7 mg, 0.01 mmol, 10 mol\%), 140 °C, 4 h, Table S3, entry 15] were used for a sensitivity assessment, which is described in ref.[5]

The influence of water, oxygen, temperature, light, concentration, and the possibility of upscaling was investigated. This investigation was carried out in ampoules (length = 240 mm, outer diameter = 10 mm, inner diameter = 7 mm, wall thickness = 1.5 mm) and \( p \)-cymene was used as internal standard for the calculation of GC yields (100% conversion of \( N \)-benzylaniline measured by GC-FID on a 0.1 mmol scale refers to an isolated yield of the branched product of 92%). For the sensitivity evaluation, in each experiment, only one parameter was changed, while all others were kept constant. The results are shown in Table S4 and Figure S2. Water and oxygen totally inhibit the reaction, as titanium dioxide is formed in these cases. On the other hand, light and concentration have no influence on the reaction and the reaction also worked well on a larger scale. The temperature has only a minor influence on the reaction. An elevated reaction temperature causes the formation of unwanted by-products while at lower temperature, the reaction proceeds slower. In conclusion, performance of the reaction under inert atmosphere is essential and the reaction temperature should be kept at 140 °C.

Table S4. Results of the sensitivity assessment

| Parameter      | Variation                        | Deviation from controlled yield |
|----------------|----------------------------------|---------------------------------|
| Water          | \(+ H_2O, V(H_2O) = 1\% V_{rxn}\) | \(- 100\%\)                     |
| Concentration  | Low \( V_{rxn} + 30\% V_{rxn} \) | \(0\%)                          |
|                | High \( c(\text{propadiene}) = 0.4 \text{ molL}^{-1}\) | \(0\%)                          |
| Oxygen         | Low \(+ \text{air}\)             | \(- 100\%\)                     |
|                | High \(T + 20 \text{ °C}\)       | \(- 15\%)                       |
| Temperature    | Low \(T - 20 \text{ °C}\)       | \(- 34\%)                       |
| Light Intensity| High \(I \times 16\)             | \(0\%)                          |
|                | Low \(I/16\)                     | \(0\%)                          |
| Large scale    | \(n \times 10\)                 | \(0\%)                          |
Figure S2. Result of the sensitivity assessment.
4. Catalytic Reactions

**General Procedure:** In a glovebox under N₂-atmosphere, a 5 mL ampoule (length = 240 mm, outer diameter = 10 mm, inner diameter = 7 mm, wall thickness = 1.5 mm) with magnetic stir bar (6 mm) was charged with catalyst IVa (66 mg, 0.10 mmol, 10 mol%) and the amine (1.0 mmol, 1.0 equiv). A solution of propadiene (c = 0.4 molL⁻¹, 3.0 mL, 1.20 mmol, 1.2 equiv) was added and the ampoule was sealed with a natural gas/O₂ torch. The ampoule was heated in an oil bath to 140 °C for 4 h. The ampoule was then cooled to room temperature and opened. The crude reaction mixture was transferred into a flask with CH₂Cl₂ (10 mL). After the solvent had been evaporated, the desired hydroaminoalkylation product was isolated by column chromatography or bulb-to-bulb distillation.

**N-(2-Methyl-1-phenylallyl)aniline (4b)**

The general procedure was used to react N-benzylaniline (1b, 183 mg, 1.0 mmol) with propadiene. Purification by chromatography (170 g SiO₂, PE/MTBE = 40:1, Rf = 0.35), gave product 4b (197 mg, 0.87 mmol, 87%) as a yellow oil. Prior to chromatography, the ratio of the branched and the linear product was determined by GC analysis to be 92:8. According to GC analysis, the purity of the product was found to be >99%.

**¹H NMR** (500 MHz, CDCl₃): \( \delta = 1.71 \) (s, 3 H), 4.10 (br. s, 1 H), 4.77 (s, 1 H), 5.01 (s, 1 H), 5.18 (s, 1 H), 6.58 (d, \( J = 7.0 \) Hz, 2 H), 6.70 (t, \( J = 7.1 \) Hz, 1 H), 7.13-7.16 (m, 2 H), 7.28-7.29 (m, 1 H), 7.33-7.35 (m, 2 H), 7.38-7.40 (m, 2 H) ppm.

**¹³C{¹H} NMR** (125 MHz, JMOD, CDCl₃): \( \delta = 19.8 \) (CH₃), 64.5 (CH), 112.6 (CH₂), 113.5 (CH), 117.6 (CH), 127.5 (CH), 128.8 (CH), 129.2 (CH), 141.4 (C), 144.7 (C), 147.6 (C) ppm.

**IR** (neat): \( \tilde{\nu} = 3412 \) (NH), 3083, 3052, 2972, 2850, 1652, 1599, 1500, 1452, 1426, 1374, 1312, 1267, 1239, 1179, 1154, 1119, 1076, 1029, 993, 953, 901, 870, 829, 746, 699, 690, 617, 579, 507 cm⁻¹.

**MS** (El, 70 eV): \( m/z \) (%) = 223 (53) [M⁺], 208 (9) [M – CH₃⁺], 182 (68) [M – C₃H₅⁺], 146 (6) [M – C₆H₅⁺], 131 (100) [M – C₁₀H₁₂N⁺], 115 (20), 104 (19), 91 (50), 77 (44) [M – C₁₀H₁₂N⁺], 65 (9), 51 (18).

**HRMS** (El, 70 eV): \( m/z \) [M⁺] calcd for C₁₆H₁₇N: 223.1356; found 223.1352.

**4-Methyl-N-(2-methyl-1-phenylallyl)aniline (5b)**

The general procedure was used to react N-benzyl-4-methylaniline (197 mg, 1.0 mmol) with propadiene. Purification by chromatography (200 g SiO₂, PE/EtOAc = 50:1, \( R_f = 0.19 \)), gave product 5b (185 mg, 0.78 mmol, 78%) as a yellow oil. Prior to chromatography, the ratio of the branched and the linear product
was determined by GC analysis to be 97:3. According to GC analysis, the purity of the product was found to be >99%.

$^1$H NMR (500 MHz, CDCl$_3$): $\delta = 1.71$ (s, 3 H), 2.23 (s, 3 H), 3.98 (br. s, 1 H), 4.75 (s, 1 H), 5.00 (s, 1 H), 5.18 (s, 1 H), 6.52 (d, $J = 8.2$ Hz, 2 H), 6.97 (d, $J = 8.0$ Hz, 2 H), 7.28-7.30 (m, 1 H), 7.33-7.36 (m, 2 H), 7.39-7.40 (m, 2 H) ppm.

$^{13}$C($^1$H) NMR (125 MHz, DEPT, CDCl$_3$): $\delta = 19.8$ (CH$_3$), 20.5 (CH$_3$), 64.7 (CH), 112.5 (CH$_2$), 113.7 (CH), 126.8 (C), 127.5 (CH), 127.6 (CH), 128.7 (CH), 129.7 (CH), 141.6 (C), 144.9 (C), 145.3 (C) ppm.

IR (neat): $\lambda_{\text{max}}$ = 3410 (NH), 3062, 3026, 2972, 2917, 2863, 1617, 1516, 1492, 1452, 1403, 1373, 1314, 1300, 1264, 1182, 1127, 1069, 1029, 901, 804, 774, 743, 699, 631, 550, 510 cm$^{-1}$.

MS (El, 70 eV): $m/z$ (%) = 237 (73) [M$^+$], 222 (13) [M – CH$_3$]$^+$, 196 (91) [M – C$_3$H$_5$]$^+$, 131 (100) [M – C$_7$H$_9$N]$^+$, 91 (34) [M – C$_{10}$H$_{12}$N]$^+$.

HRMS (El, 70 eV): $m/z$ [M$^+$] calcd for C$_{17}$H$_{19}$N: 237.1517; found 237.1510.

3-Methyl-N-(2-methyl-1-phenylallyl)aniline (6b)

The general procedure was used to react N-benzyl-3-methylaniline (197 mg, 1.0 mmol) with propadiene. Purification by chromatography (150 g SiO$_2$, PE/EtOAc = 50/1, $R_f = 0.20$), gave product 6b (198 mg, 0.83 mmol, 83%) as a yellow oil. Prior to chromatography, the ratio of the branched and the linear product was determined by GC analysis to be 97:3. According to GC analysis, the purity of the product was found to be >99%.

$^1$H NMR (500 MHz, CDCl$_3$): $\delta = 1.71$ (s, 3 H), 2.25 (s, 3 H), 4.07 (br. s, 1 H), 4.76 (s, 1 H), 5.01 (s, 1 H), 5.18 (s, 1 H), 6.40 (m, 2 H), 6.55 (d, $J = 7.4$ Hz, 1 H), 7.04 (t, $J = 7.7$ Hz, 1 H), 7.27-7.30 (m, 1 H), 7.32-7.35 (m, 2 H), 7.38-7.39 (m, 2 H) ppm.

$^{13}$C($^1$H) NMR (125 MHz, JMODE, CDCl$_3$): $\delta = 19.9$ (CH$_3$), 21.8 (CH$_3$), 64.4 (CH), 110.6 (CH), 112.6 (CH$_2$), 114.4 (CH), 118.6 (CH), 127.5 (CH), 127.6 (CH), 128.8 (CH), 129.1 (CH), 138.9 (C), 141.6 (C), 144.8 (C), 147.4 (C) ppm.

IR (neat): $\lambda_{\text{max}}$ = 3410 (NH), 3083, 3025, 2972, 2916, 2863, 1617, 1516, 1506, 1486, 1452, 1374, 1320, 1303, 1272, 1177, 1114, 1072, 1029, 993, 901, 844, 767, 740, 699, 690, 586 cm$^{-1}$.

MS (El, 70 eV): $m/z$ (%) = 237 (54) [M$^+$], 222 (8) [M – CH$_3$]$^+$, 196 (98) [M – C$_3$H$_5$]$^+$, 131 (100) [M – C$_7$H$_9$N]$^+$, 91 (65) [M – C$_{10}$H$_{12}$N]$^+$, 77 (9), 65 (10).

HRMS (El, 70 eV): $m/z$ [M$^+$] calcd for C$_{17}$H$_{19}$N: 237.1517; found 237.1510.
4-Bromo-\(N\)-(2-methyl-1-phenylallyl)aniline (7b)

The general procedure was used to react \(N\)-benzyl-4-bromoaniline (262 mg, 1.0 mmol) with propadiene. Purification by chromatography (170 g SiO\(_2\), PE/EtOAc = 50/1, \(R_f = 0.24\)), gave product 7b (248 mg, 0.82 mmol, 82%) as a yellow oil. Prior to chromatography, the ratio of the branched and the linear product was determined by GC analysis to be 96:4. According to GC analysis, the purity of the product was found to be >98%.

\(\text{\^H NMR} (500 \text{ MHz}, \text{CDCl}_3): \delta = 1.70 \text{ (s, 3 H), 4.71 \text{ (s, 1 H), 5.02 \text{ (s, 1 H), 5.15 \text{ (s, 1 H)}, 6.46 \text{ (d, J = 8.6 Hz, 2 H), 7.20-7.24 \text{ (m, 2 H), 7.28-7.33 \text{ (m, 1 H)}, 7.35-7.37 \text{ (m, 4 H ppm)}}.}

\(\text{\^{13}C}\{\text{\^H} \} \text{ NMR} (125 \text{ MHz, JMOD, CDCl}_3): \delta = 19.8 \text{ (CH\(_3\)), 64.4 \text{ (CH), 109.3 \text{ (C), 112.8 \text{ (CH\(_2\)}, 115.2 \text{ (CH), 127.5 \text{ (CH), 128.9 \text{ (CH), 131.9 \text{ (CH), 140.9 \text{ (C), 144.2 \text{ (C), 146.4 \text{ (C ppm.}}}

\(\text{IR (neat): } \hat{\nu} = 3413 \text{ (NH), 3083, 3027, 2972, 2934, 2850, 1652, 1592, 1489, 1452, 1394, 1374, 1312, 1292, 1266, 1234, 1177, 1124, 1072, 1029, 1000, 903, 810, 699, 659, 527 \text{ cm}^{-1}.\)

\(\text{MS (EI, 70 eV): } m/z (=) = 301 \text{ (29) [M]+}, 260 \text{ (33) [M – C\(_3\)H\(_5\)]+}, 131 \text{ (100) [M – C\(_6\)H\(_6\)BrN]+}, 91 \text{ (33), 77 (9).}

\(\text{HRMS (EI, 70 eV): } m/z [\text{M}]+ \text{ calcd for C\(_{16}\)H\(_{16}\)BrN: 301.0466; found 301.0454.}

3-Bromo-\(N\)-(2-methyl-1-phenylallyl)aniline (8b)

The general procedure was used to react \(N\)-benzyl-3-bromoaniline (262 mg, 1.0 mmol) with propadiene. Purification by chromatography (170 g SiO\(_2\), PE/EtOAc = 50/1, \(R_f = 0.23\)), gave product 8b (251 mg, 0.83 mmol, 83%) as a yellow oil. Prior to chromatography, the ratio of the branched and the linear product was determined by GC analysis to be 92:8. According to GC analysis, the purity of the product was found to be >99%.

\(\text{\^H NMR} (500 \text{ MHz, CDCl}_3): \delta = 1.70 \text{ (s, 3 H), 4.73 \text{ (s, 1 H), 5.03 \text{ (s, 1 H), 5.16 \text{ (s, 1 H), 6.49 \text{ (d, J = 7.5 Hz, 1 H), 6.73 \text{ (s, 1 H), 6.82 \text{ (d, J = 7.7 Hz, 1 H)}, 6.99 \text{ (t, J = 8.0 Hz, 1 H), 7.28-7.34 \text{ (m, 1 H), 7.35-7.36 \text{ (m, 4 H ppm.}}}

\(\text{\^{13}C}\{\text{\^H} \} \text{ NMR} (125 \text{ MHz, JMOD, CDCl}_3): \delta = 20.2 \text{ (CH\(_3\)), 64.6 \text{ (CH), 112.5 \text{ (CH), 113.2 \text{ (CH\(_2\)}, 116.5 \text{ (CH), 120.8 \text{ (CH), 123.5 \text{ (C), 127.8 \text{ (CH), 128.2 \text{ (CH), 129.2 \text{ (CH), 130.8 \text{ (CH), 141.1 \text{ (C), 144.3 \text{ (C), 149.0 \text{ (C ppm.}}}

\(\text{IR (neat): } \hat{\nu} = 3413 \text{ (NH), 3062, 2972, 2912, 2852, 1593, 1490, 1479, 1452, 1412, 1374, 1319, 1279, 1230, 1167, 1114, 1086, 1067, 1030, 986, 901, 841, 759, 699, 679, 641, 580, 517 \text{ cm}^{-1}.\)
**MS** (El, 70 eV): \( m/z \) (%) = 301 (6) [M]\(^+\), 260 (15) [M − C\(_3\)H\(_5\)]\(^+\), 131 (100) [M − C\(_6\)H\(_6\)BrN]\(^+\), 91 (33), 77 (10).

**HRMS** (El, 70 eV): \( m/z \) [M]\(^+\) calcd for C\(_{16}\)H\(_{16}\)BrN: 301.0466; found 301.0453.

4-Methoxy-N-(2-methyl-1-phenylallyl)aniline (9b)

The general procedure was used to react N-benzyl-4-methoxyaniline (213 mg, 1.0 mmol) with propadiene. Purification by chromatography (170 g SiO\(_2\), PE/EtOAc = 40/1, \( R_f = 0.15\)), gave product 9b (161 mg, 0.64 mmol, 64%) as a yellow oil. Prior to chromatography, the ratio of the branched and the linear product was determined by GC analysis to be 99:1. According to GC analysis, the purity of the product was found to be >99%.

\( ^1\)H NMR (500 MHz, CDCl\(_3\)): \( \delta = 1.70 \) (s, 3 H), 3.73 (s, 3 H), 4.70 (s, 1 H), 4.99 (s, 1 H), 5.19 (s, 1 H), 6.56 (d, \( J = 8.7 \) Hz), 6.73-6.76 (m, 2 H), 7.27-7.29 (m, 1 H), 7.32-7.35 (m, 2 H), 7.38-7.40 (m, 2 H) ppm.

\( ^{13}\)C\({ }^{[1]}\)H NMR (125 MHz, DEPT, CDCl\(_3\)): \( \delta = 19.7 \) (CH\(_3\)), 55.8 (CH\(_3\)), 65.3 (CH), 112.5 (CH\(_3\)), 114.7 (CH), 114.8 (CH), 127.4 (CH), 128.7 (CH), 141.7 (C), 145.1 (C), 152.2 (C) ppm.

**IR** (neat): \( \tilde{\nu} = 3406 \) (NH), 3060, 2933, 2907, 2832, 1509, 1450, 1404, 1373, 1177, 1122, 1097, 1069, 1034, 900, 816, 764, 741, 699, 557, 521 cm\(^{-1}\).

**MS** (El, 70 eV): \( m/z \) (%) = 253 (97) [M]\(^+\), 212 (56) [M − CH\(_3\)]\(^+\), 131 (100) [M − C\(_7\)H\(_8\)NO]\(^+\), 121 (33) [M − C\(_{10}\)H\(_{11}\)]\(^+\), 116 (14), 91 (30), 77 (9).

**HRMS** (El, 70 eV): \( m/z \) [M]\(^+\) calcd for C\(_{17}\)H\(_{19}\)NO: 253.1467; found 253.1455.

3-Methoxy-N-(2-methyl-1-phenylallyl)aniline (10b)

The general procedure was used to react N-benzyl-3-methoxyaniline (213 mg, 1.0 mmol) with propadiene. Purification by chromatography (170 g SiO\(_2\), PE/EtOAc = 50/1, \( R_f = 0.11\)), gave product 10b (157 mg, 0.62 mmol, 62%) as a yellow oil. Prior to chromatography, the ratio of the branched and the linear product was determined by GC analysis to be 90:10. According to GC analysis, the purity of the product was found to be >99%.

\( ^1\)H NMR (500 MHz, CDCl\(_3\)): \( \delta = 1.71 \) (s, 3 H), 3.74 (s, 3 H), 4.77 (s, 1 H), 5.02 (s, 1 H), 5.18 (s, 1 H), 6.16 (s, 1 H), 6.23 (d, \( J = 7.7 \) Hz, 1 H), 6.29 (dd, \( J = 8.1, 1.1 \) Hz, 1 H), 7.05 (t, \( J = 8.1 \) Hz, 1 H), 7.28-7.30 (m, 1 H), 7.33-7.40 (m, 4 H) ppm.
\[^{13}\text{C}\{^1\text{H}\}]\text{NMR}\ (125 \text{ MHz, DEPT, CDCl}_3): \, \delta = 19.8 \ (\text{CH}_3), \, 55.1 \ (\text{CH}_3), \, 64.6 \ (\text{CH}), \, 99.8 \ (\text{CH}), \, 102.9 \ (\text{CH}), \, 106.8 \ (\text{CH}), \, 112.7 \ (\text{CH}_2), \, 127.5 \ (\text{CH}), \, 127.7 \ (\text{CH}), \, 128.8 \ (\text{CH}), \, 129.9 \ (\text{CH}), \, 141.4 \ (\text{C}), \, 144.7 \ (\text{C}), \, 148.9 \ (\text{C}), \, 160.8 \ (\text{C}) \text{ ppm.}\n
\[\text{IR (neat): } \lambda^{-1} = 3400 \ (\text{NH}), \, 3083, \, 3027, \, 2969, \, 2934, \, 2909, \, 2834, \, 1612, \, 1504, \, 1492, \, 1450, \, 1373, \, 1340, \, 1303, \, 1243, \, 1207, \, 1174, \, 1159, \, 1116, \, 991, \, 900, \, 826, \, 754, \, 741, \, 699, \, 686, \, 584 \text{ cm}^{-1}.
\]

\[\text{MS (EI, 70 eV): } m/z \, (\%) = 253 \ (50) \ [\text{M}]^+, \, 212 \ (61) \ [\text{M} – \text{CH}_3]^+, \, 131 \ (100) \ [\text{M} – \text{C}_7\text{H}_9\text{NO}]^+, \, 116 \ (18), \, 91 \ (63), \, 77 \ (24).
\]

\[\text{HRMS (EI, 70 eV): } m/z \ [\text{M}]^+ \text{ calcd for } C_{17}\text{H}_{19}\text{NO}: 253.1467; \text{ found } 253.1457.
\]

**N-(2-Methyl-1-phenylallyl)-4-(trifluoromethoxy)aniline (11b)**

The general procedure was used to react \(N\)-benzyl-4-(trifluoromethoxy)aniline (267 mg, 1.0 mmol) with propadiene. Purification by chromatography (170 g SiO\(_2\), PE/EtOAc = 50/1, \(R_f = 0.23\)), gave product 11b (230 mg, 0.75 mmol, 75%) as a yellow oil. Prior to chromatography, the ratio of the branched and the linear product was determined by GC analysis to be 99:1. According to GC analysis, the purity of the product was found to be >99%.

\[^1\text{H} \text{NMR (500 MHz, CDCl}_3): \, \delta = 1.71 \ (s, 3 \text{ H}), \, 4.13 \ (\text{br. s, 1 H}), \, 4.72 \ (s, 1 \text{ H}), \, 5.03 \ (s, 1 \text{ H}), \, 5.16 \ (s, 1 \text{ H}), \, 6.54 \ (d, \, J = 8.6 \text{ Hz, 2 H}), \, 7.00 \ (d, \, J = 8.3 \text{ Hz, 2 H}), \, 7.29-7.33 \ (m, 1 \text{ H}), \, 7.34-7.39 \ (m, 4 \text{ H}) \text{ ppm.}\n\]

\[^{13}\text{C}\{^1\text{H}\}]\text{NMR (125 MHz, DEPT, CDCl}_3): \, \delta = 19.8 \ (\text{CH}_3), \, 64.8 \ (\text{CH}), \, 112.8 \ (\text{CH}_2), \, 113.9 \ (\text{CH}), \, 120.9 \ (q, \, J = 255 \text{ Hz, C}), \, 122.3 \ (\text{CH}), \, 127.5 \ (\text{CH}), \, 127.9 \ (\text{CH}), \, 128.9 \ (\text{CH}), \, 140.8 \ (\text{C}), \, 141.0 \ (\text{C}), \, 144.3 \ (\text{C}), \, 146.3 \ (\text{C}) \text{ ppm.}\n\]

\[^{19}\text{F}\{^1\text{H}\}]\text{NMR (470 MHz, CDCl}_3): \, \delta = -58.4 \text{ ppm.}\n\]

\[\text{IR (neat): } \lambda^{-1} = 3422 \ (\text{NH}), \, 3058, \, 3032, \, 2976, \, 2916, \, 2854, \, 1611, \, 1510, \, 1453, \, 1406, \, 1376, \, 1250, \, 1222, \, 1200, \, 1150, \, 1120, \, 1067, \, 1029, \, 1011, \, 904, \, 824, \, 793, \, 699, \, 670, \, 641, \, 521 \text{ cm}^{-1}.
\]

\[\text{MS (EI, 70 eV): } m/z \, (\%) = 307 \ (54) \ [\text{M}]^+, \, 266 \ (8) \ [\text{M} – \text{C}_3\text{H}_5]^+, \, 131 \ (100) \ [\text{M} – \text{C}_7\text{H}_6\text{F}_3\text{NO}]^+, \, 116 \ (11), \, 91 \ (24), \, 77 \ (3).
\]

\[\text{HRMS (EI, 70 eV): } m/z \ [\text{M}]^+ \text{ calcd for } C_{17}\text{H}_{16}\text{F}_3\text{NO}: 307.1184; \text{ found } 307.1183\]
N-(2-Methyl-1-phenylallyl)-4-(trifluoromethyl)aniline (12b)

The general procedure was used to react N-benzyl-4-(trifluoromethyl)aniline (251 mg, 1.0 mmol) with propadiene. Purification by chromatography (170 g SiO$_2$, PE/EtOAc = 50/1, $R_f = 0.23$), gave product 12b (226 mg, 0.78 mmol, 78%) as a yellow oil. Prior to chromatography, the ratio of the branched and the linear product was determined by GC analysis to be 99:1. According to GC analysis, the purity of the product was found to be >99%.

$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ = 1.72 (s, 3 H), 4.36 (br. s, 1 H), 4.80 (s, 1 H), 5.04 (s, 1 H), 5.14 (s, 1 H), 6.58 (d, $J = 8.5$ Hz, 2 H), 7.30-7.34 (m, 1 H), 7.37-7.39 (m, 6 H) ppm.

$^{13}$C{^1}H NMR (125 MHz, DEPT, CDCl$_3$): $\delta$ = 19.9 (CH$_3$), 64.5 (CH), 112.8 (CH), 113.0 (CH$_2$), 119.3 (q, $J = 33$ Hz, C), 125.0 (q, $J = 270$ Hz, C), 126.6 (q, $J = 4$ Hz, CH), 127.5 (CH), 128.0 (CH), 129.0 (CH), 140.6 (C), 143.9 (C), 149.9 (C) ppm.

$^{19}$F{^1}H NMR (470 MHz, CDCl$_3$): $\delta$ = -61.0 ppm.

IR (neat): $\vec{\nu}$ = 3423 (NH), 3086, 3032, 2976, 2919, 2856, 1616, 1529, 1484, 1453, 1413, 1376, 1317, 1274, 1186, 1159, 1104, 1061, 1030, 1007, 939, 904, 821, 746, 699, 653, 590, 529, 507 cm$^{-1}$.

MS (EI, 70 eV): m/z (%) = 291 (48) [M]$^+$, 250 (83) [M – C$_3$H$_5$]$^+$, 145 (33), 131 (100) [M – C$_2$H$_6$F$_3$N]$^+$, 116 (11), 91 (29), 77 (9).

HRMS (EI, 70 eV): m/z [M]$^+$ calcd for C$_{17}$H$_{16}$F$_3$N: 291.1229; found 291.1226.

4-Chloro-N-(2-methyl-1-phenylallyl)aniline (13b)

The general procedure was used to react N-benzyl-4-chloroaniline (218 mg, 1.0 mmol) with propadiene. Purification by chromatography (170 g SiO$_2$, PE/EtOAc = 50/1, $R_f = 0.14$), gave product 13b (203 mg, 0.79 mmol, 79%) as a yellow oil. Prior to chromatography, the ratio of the branched and the linear product was determined by GC analysis to be 96:4. According to GC analysis, the purity of the product was found to be >99%.

$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ = 1.70 (s, 3 H), 4.50 (br. S, 1 H), 4.71 (s, 1 H), 5.02 (s, 1 H), 5.15 (s, 1 H), 6.51 (d, $J = 7.4$ Hz, 1 H), 7.07-7.10 (m, 2 H), 7.28-7.37 (m, 5 H) ppm.

$^{13}$C{^1}H NMR (125 MHz, DEPT, CDCl$_3$): $\delta$ = 20.2 (CH$_3$), 64.9 (CH), 113.1 (CH$_2$), 115.0 (CH) 122.6 (C), 127.8 (CH), 129.2 (CH), 129.3 (CH), 141.3 (C), 144.6 (C), 146.3 (C) ppm.
IR (neat): $\tilde{\nu} = 3416$ (NH), 3062, 3027, 2972, 2937, 2850, 1651, 1597, 1493, 1452, 1397, 1374, 1310, 1293, 1266, 1234, 1176, 1124, 1090, 1029, 1003, 903, 811, 699, 676, 533 cm$^{-1}$.

MS (EI, 70 eV): $m/z$ (%) = 257 (41) [M]$^+$; 215 (55) [M – C$_3$H$_5$]$^+$, 131 (100) [M – C$_7$H$_6$ClN]$^+$, 116 (15), 91 (36), 77 (4).

HRMS (EI, 70 eV): $m/z$ [M]$^+$ calcd for C$_{16}$H$_{16}$ClN: 257.0966; found 257.0960.

N-(2-Methyl-1-(3-(trifluoromethyl)phenyl)allyl)aniline (14b)

The general procedure was used to react N-(3-(trifluoromethyl)benzyl)aniline (251 mg, 1.0 mmol) with propadiene. Purification by bulb-to-bulb distillation (144 °C, 8 × 10$^{-3}$ mbar), gave product 14b (269 mg, 0.92 mmol, 92%) as a slightly yellow oil. Prior to bulb-to-bulb distillation, the ratio of the branched and the linear product was determined by GC analysis to be 94:6. According to GC analysis, the purity of the product was found to be 95% (+ 5% 14l).

$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ = 1.73 (s, 3 H), 4.87 (s, 1 H), 5.06 (s, 1 H), 5.16 (s, 1 H), 6.56-6.61 (m, 2 H), 6.74 (tt, $J$ = 7.4, 1.0 Hz, 1 H), 7.14-7.20 (m, 2 H), 7.47 (t, $J$ = 7.7 Hz, 1 H), 7.56 (d, $J$ = 7.8 Hz, 1 H), 7.60 (d, $J$ = 8.2 Hz, 1 H), 7.66-7.68 (m, 1 H) ppm.

$^{13}$C($^1$H) NMR (125 MHz, DEPT, CDCl$_3$): $\delta$ = 19.7 (CH$_3$), 64.2 (CH), 113.8 (CH), 113.9 (CH$_2$), 118.2 (CH), 124.3 (q, $J$ = 272 Hz, C), 124.3 (q, $J$ = 4 Hz, CH), 124.6 (q, $J$ = 4 Hz, CH), 129.3 (CH), 129.3 (CH), 130.9 (CH), 131.2 (q, $J$ = 32 Hz, C), 142.6 (C), 144.3 (C), 147.2 (C) ppm.

$^{19}$F($^1$H) NMR (470 MHz, CDCl$_3$): $\delta$ = -62.5 ppm.

IR (neat): $\tilde{\nu} = 3415$ (NH), 3053, 3022, 2976, 2940, 2916, 2854, 1652, 1602, 1502, 1447, 1429, 1377, 1326, 1267, 1240, 1163, 1119, 1094, 1072, 1029, 993, 906, 871, 799, 747, 703, 690, 667, 584, 571, 507 cm$^{-1}$.

MS (EI, 70 eV): $m/z$ (%) = 291 (44) [M]$^+$; 276 (13) [M – CH$_3$]$^+$, 250 (100) [M – C$_3$H$_5$]$^+$, 199 (48) [M – C$_6$H$_6$N]$^+$, 179 (19), 159 (26), 146 (11) [M – C$_7$H$_4$F$_3$]$^+$, 130 (16), 115 (12), 104 (14), 93 (7), 77 (47) [M – C$_{17}$H$_{15}$F$_3$N]$^+$, 65 (9), 51 (18).

HRMS (EI, 70 eV): $m/z$ [M]$^+$ calcd for C$_{17}$H$_{15}$F$_3$N: 291.1229; found 291.1223.
The general procedure was used to react \(N\)-(3-bromobenzyl)aniline (262 mg, 1.0 mmol) with propadiene. Purification by chromatography (170 g SiO\(_2\), PE/EtOAc = 30:1, \(R_t = 0.29\)), gave product 15b (252 mg, 0.83 mmol, 83%) as a yellow oil. Prior to chromatography, the ratio of the branched and the linear product was determined by GC analysis to be 91:9. According to GC analysis, the purity of the product was found to be 94% (+ 6% 15l).

\(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta = 1.73\) (s, 3 H), 4.77 (s, 1 H), 5.04 (s, 1 H), 5.16 (s, 1 H), 6.58 (d, \(J = 7.9\) Hz, 2 H), 6.74 (t, \(J = 7.3\) Hz, 1 H), 7.15-7.19 (m, 2 H), 7.22 (t, \(J = 7.8\) Hz, 1 H), 7.34 (d, \(J = 7.7\) Hz, 1 H), 7.43 (d, \(J = 7.9\) Hz, 1 H), 7.56 (t, \(J = 1.5\) Hz, 1 H) ppm.

\(^{13}\)C\{\(^1\)H\} NMR (125 MHz, JMOD, CDCl\(_3\)): \(\delta = 19.8\) (CH\(_3\)), 64.1 (CH), 113.6 (CH\(_2\)), 113.7 (CH), 118.1 (CH), 122.9 (C), 126.2 (CH), 129.3 (CH), 130.3 (CH), 130.5 (CH), 130.8 (CH), 143.8 (C), 144.2 (C), 147.1 (C) ppm.

IR (neat): \(\tilde{\nu} = 3407\) (NH), 3080, 3052, 3019, 2972, 2936, 2912, 2850, 1652, 1600, 1569, 1500, 1472, 1427, 1374, 1313, 1264, 1179, 1154, 1119, 1072, 1029, 996, 903, 871, 779, 747, 690, 619, 590, 506 cm\(^{-1}\).

MS (EI, 70 eV): \(m/z\) (%) = 301 (16) [M]\(^+\), 286 (4) [M – CH\(_3\)]\(^+\), 260 (30) [M – C\(_3\)H\(_5\)]\(^+\), 209 (2) [M – C\(_6\)H\(_4\)N]\(^+\), 180 (8), 146 (9) [M – C\(_6\)H\(_4\)Br]\(^+\), 130 (100), 115 (25), 104 (11), 93 (5), 77 (34) [M – C\(_{10}\)H\(_{11}\)BrN]\(^+\), 65 (8), 51 (14).

HRMS (EI, 70 eV): \(m/z\) [M]\(^+\) calcd for C\(_{16}\)H\(_{16}\)BrN: 301.0461; found 301.0455.

The general procedure was used to react \(N\)-(3-chlorobenzyl)aniline (218 mg, 1.0 mmol) with propadiene. Purification by chromatography (170 g SiO\(_2\), PE/EtOAc = 30:1, \(R_t = 0.24\)), gave product 16b (210 mg, 0.81 mmol, 81%) as a yellow oil. Prior to chromatography, the ratio of the branched and the linear product was determined by GC analysis to be 93:7. According to GC analysis, the purity of the product was found to be 94% (+ 6% 16l).

\(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta = 1.74\) (s, 3 H), 4.79 (s, 1 H), 5.05 (s, 1 H), 5.17 (s, 1 H), 6.59 (d, \(J = 8.0\) Hz, 2 H), 6.75 (t, \(J = 7.3\) Hz, 1 H), 7.15-7.20 (m, 2 H), 7.27-7.32 (m, 3 H), 7.41 (s, 1 H) ppm.
$^{13}$C{[1H]} NMR (125 MHz, JMOD, CDCl₃): $\delta$ = 19.8 (CH₃), 64.2 (CH), 113.5 (CH₂), 113.7 (CH), 118.1 (CH), 125.7 (CH), 127.6 (CH), 127.8 (CH), 129.3 (CH), 130 (CH), 134.7 (C), 143.6 (C), 144.2 (C), 147.1 (C) ppm.

IR (neat): $\lambda^{-1}$ = 3412 (NH), 3082, 3052, 3020, 2973, 2937, 2913, 2852, 1684, 1652, 1600, 1573, 1500, 1473, 1427, 1376, 1313, 1264, 1250, 1180, 1154, 1119, 1077, 993, 903, 871, 841, 781, 746, 689, 619, 591 cm⁻¹.

MS (El, 70 eV): $m/z$ (%) = 257 (55) [M]+, 242 (13) [M – CH₃]+, 216 (100) [M – C₆H₅]+, 180 (7) [M – C₆H₅]+, 165 (52) [M – C₆H₅N]+, 146 (14) [M – C₆H₅Cl]+, 130 (69), 115 (25), 104 (21), 93 (9), 77 (65) [M – C₁₀H₁₁ClN]+, 65 (12), 51 (27).

HRMS (EI, 70 eV): $m/z$ [M]+ calcd for C₁₁H₁₅ClN: 257.0966; found 257.0958.

**N-(1-(4-Methoxyphenyl)-2-methylallyl)aniline (17b)**

![Structure](image)

The general procedure was used to react $N$-(4-methoxybenzyl)aniline (213 mg, 1.0 mmol) with propadiene. Purification by chromatography (170 g SiO₂, PE/MTBE = 30:1, $Rf$ = 0.22), gave product 17b (205 mg, 0.81 mmol, 81%) as a yellow oil. Prior to chromatography, the ratio of the branched and the linear product was determined by GC analysis to be 94:6. According to GC analysis, the purity of the product was found to be 94% (+ 6% 17l).

$^1$H NMR (500 MHz, CDCl₃): $\delta$ = 1.77 (s, 3 H), 3.85 (s, 3 H), 4.06 (br. s, 1 H), 4.78 (s, 1 H), 5.06 (s, 1 H), 5.23 (s, 1 H), 6.63 (d, $J$ = 7.9 Hz, 2 H), 6.76 (t, $J$ = 7.3 Hz, 1 H), 6.95 (d, $J$ = 8.7 Hz, 2 H), 7.18-7.24 (m, 2 H), 7.36 (d, $J$ = 8.7 Hz, 2 H) ppm.

$^{13}$C{[1H]} NMR (125 MHz, JMOD, CDCl₃): $\delta$ = 19.9 (CH₃), 55.3 (CH₃), 63.8 (CH₃), 112.2 (CH₂), 113.5 (CH), 114.1 (CH), 117.5 (CH), 128.6 (CH), 129.1 (CH), 133.5 (C), 144.8 (C), 147.6 (C), 159.1 (C) ppm.

IR (neat): $\lambda^{-1}$ = 3405 (NH), 3050, 3002, 2934, 2910, 2834, 1652, 1597, 1586, 1500, 1463, 1442, 1427, 1373, 1312, 1303, 1270, 1244, 1173, 1154, 1119, 1107, 1072, 1031, 993, 953, 896, 869, 840, 826, 807, 781, 747, 690, 621, 606, 570, 527, 504 cm⁻¹.

MS (El, 70 eV): $m/z$ (%) = 253 (15) [M]+, 212 (12) [M – C₆H₅]+, 168 (5), 161 (100) [M – C₆H₅N]+, 146 (12) [M – C₆H₅O]+, 131 (7), 115 (6), 104 (8), 91 (12), 77 (16) [M – C₁₂H₁₄NO]+, 65 (6), 51 (6).

HRMS (El, 70 eV): $m/z$ [M]+ calcd for C₁₇H₁₉NO: 253.1461; found 253.1461.
N-(2-Methyl-1-(4-(trifluoromethyl)phenyl)allyl)aniline (18b)

![Chemical structure](image)

The general procedure was used to react N-(4-(trifluoromethyl)benzyl)aniline (251 mg, 1.0 mmol) with propadiene. Purification by chromatography (170 g SiO₂, PE/MTBE = 40:1, Rf = 0.27), gave product 18b (239 mg, 0.82 mmol, 82%) as a yellow oil. Prior to chromatography, the ratio of the branched and the linear product was determined by GC analysis to be 94:6. According to GC analysis, the purity of the product was found to be >99%.

1H NMR (500 MHz, CDCl₃): δ = 1.74 (s, 3 H), 4.10 (br. s, 1 H), 4.88 (s, 1 H), 5.06 (s, 1 H), 5.15 (s, 1 H), 6.59 (d, J = 8.0 Hz, 2 H), 6.75 (t, J = 7.3 Hz, 1 H), 7.14-7.20 (m, 2 H), 7.53 (d, J = 8.1 Hz, 2 H), 7.62 (d, J = 8.2 Hz, 2 H) ppm.

13C{1H} NMR (125 MHz, JMOD, CDCl₃): δ = 19.7 (CH₃), 64.3 (CH), 113.8 (CH), 113.9 (CH₂), 118.3 (CH), 124.3 (q, J = 272 Hz, C), 125.7 (q, J = 4 Hz, CH), 127.8 (CH), 129.3 (CH), 129.9 (q, J = 32 Hz, C), 144.4 (C), 145.5 (C), 147.0 (C) ppm.

19F{1H} NMR (470 MHz, CDCl₃): δ = -62.5 ppm.

IR (neat): λ⁻¹ = 3415 (NH), 3053, 3022, 2977, 2940, 2917, 1652, 1617, 1602, 1502, 1449, 1429, 1416, 1376, 1322, 1267, 1163, 1119, 1109, 1066, 1017, 993, 954, 904, 870, 847, 809, 769, 747, 690, 666, 620, 604, 523, 507 cm⁻¹.

MS (El, 70 eV): m/z (%) = 291 (44) [M]+, 276 (12) [M – CH₃]+, 250 (100) [M – C₃H₅]+, 199 (40) [M – C₆H₄N]+, 179 (15), 159 (21), 146 (10) [M – C₆H₃F]⁺, 130 (15), 115 (11), 104 (12), 93 (7), 77 (38) [M – C₁₇H₁₁F₃N]+, 65 (7), 51 (14).

HRMS (El, 70 eV): m/z [M]+ calcd for C₁₇H₁₆F₃N: 291.1229; found 291.1223.

N-(1-(4-Bromophenyl)-2-methylallyl)aniline (19b)

![Chemical structure](image)

The general procedure was used to react N-(4-bromobenzyl)aniline (262 mg, 1.0 mmol) with propadiene. Purification by bulb-to-bulb distillation (171 °C, 3 × 10⁻³ mbar), gave product 19b (273 mg, 0.90 mmol, 90%) as a slightly yellow oil. Prior to bulb-to-bulb distillation, the ratio of the branched and the linear product was determined by GC analysis to be 93:7. According to GC analysis, the purity of the product was found to be 95% (+ 5% 19l).
$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ = 1.72 (s, 3 H), 4.76 (s, 1 H), 5.02 (s, 1 H), 5.14 (s, 1 H), 6.57 (d, $J$ = 7.9 Hz, 2 H), 6.73 (t, $J$ = 7.3 Hz, 1 H), 7.13-7.18 (m, 2 H), 7.28 (d, $J$ = 8.4 Hz, 2 H), 7.48 (d, $J$ = 8.4 Hz, 2 H) ppm.

$^{13}$C($^1$H) NMR (125 MHz, JMOD, CDCl$_3$): $\delta$ = 19.8 (CH$_3$), 64.0 (CH), 113.4 (CH$_2$), 113.8 (CH), 118.1 (CH), 121.5 (C), 129.2 (CH), 129.2 (CH), 131.9 (CH), 140.4 (C), 144.4 (O), 147.1 (C) ppm.

IR (neat): $\lambda_{\text{max}}$ = 3412 (NH), 3082, 3050, 3022, 2972, 2939, 2913, 2852, 1683, 1652, 1600, 1500, 1489, 1427, 1406, 1374, 1310, 1266, 1179, 1154, 1119, 1092, 1014, 993, 980, 870, 840, 799, 747, 690, 620, 591, 537 cm$^{-1}$.

MS (EI, 70 eV): $m/z$ (%) = 257 (54) [M$^+$], 242 (13) [M – CH$_3$]$^+$, 216 (69) [M – C$_3$H$_5$]$^+$, 180 (6) [M – C$_6$H$_5$]$^+$, 165 (100) [M – C$_6$H$_5$N]$^+$, 146 (5) [M – C$_6$H$_4$Cl]$^+$, 130 (77), 115 (25), 104 (21), 89 (8), 77 (58) [M – C$_{10}$H$_{11}$ClN]$^+$, 65 (9), 51 (22).

HRMS (EI, 70 eV): $m/z$ [M$^+$] calcd for C$_{16}$H$_{16}$BrN: 301.0461; found 301.0449.

**N-(1-(4-Chlorophenyl)-2-methylallyl)aniline (20b)**

The general procedure was used to react N-(4-chlorobenzyl)aniline (218 mg, 1.0 mmol) with propadiene. Purification by bulb-to-bulb distillation (161 °C, 2 × 10$^{-3}$ mbar), gave product 20b (250 mg, 0.97 mmol, 97%) as a slightly yellow oil. Prior to bulb-to-bulb distillation, the ratio of the branched and the linear product was determined by GC analysis to be 94:6. According to GC analysis, the purity of the product was found to be 94% (+ 6% 20l).

$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ = 1.72 (s, 3 H), 4.78 (s, 1 H), 5.03 (s, 1 H), 5.15 (s, 1 H), 6.58 (d, $J$ = 7.9 Hz, 2 H), 6.74 (t, $J$ = 7.3 Hz, 1 H), 7.14-7.19 (m, 2 H), 7.31-7.36 (m, 4 H) ppm.

$^{13}$C($^1$H) NMR (125 MHz, JMOD, CDCl$_3$): $\delta$ = 19.8 (CH$_3$), 64.0 (CH), 113.4 (CH$_2$), 113.9 (CH), 118.2 (CH), 128.9 (CH), 128.9 (CH), 129.3 (CH), 133.4 (C), 139.8 (C), 144.4 (O), 147.0 (C) ppm.

IR (neat): $\lambda_{\text{max}}$ = 3412 (NH), 3082, 3050, 3022, 2972, 2939, 2913, 2852, 1683, 1652, 1600, 1500, 1489, 1427, 1406, 1374, 1310, 1266, 1179, 1154, 1119, 1092, 1014, 993, 980, 870, 840, 799, 747, 690, 620, 591, 537 cm$^{-1}$.

MS (EI, 70 eV): $m/z$ (%) = 257 (54) [M$^+$], 242 (13) [M – CH$_3$]$^+$, 216 (69) [M – C$_3$H$_5$]$^+$, 180 (6) [M – C$_6$H$_5$]$^+$, 165 (100) [M – C$_6$H$_5$N]$^+$, 146 (5) [M – C$_6$H$_4$Cl]$^+$, 130 (77), 115 (25), 104 (21), 89 (8), 77 (58) [M – C$_{10}$H$_{11}$ClN]$^+$, 65 (9), 51 (22).

HRMS (EI, 70 eV): $m/z$ [M$^+$] calcd for C$_{16}$H$_{16}$ClN: 257.0966; found 257.0960.


\textit{N}-1-(4-Fluorophenyl)-2-methylallylaniline (21b)

The general procedure was used to react \textit{N}-\textit{(4-fluorobenzyl)}aniline (201 mg, 1.0 mmol) with propadiene. Purification by chromatography (170 g SiO\textsubscript{2}, PE/EtOAc = 30:1, \(R_f = 0.40\)), gave product 21b (221 mg, 0.92 mmol, 92\%) as a yellow oil. Prior to chromatography, the ratio of the branched and the linear product was determined by GC analysis to be 93:7. According to GC analysis, the purity of the product was found to be 94\% (+ 6\% 21l). The product 21b decomposes relatively fast in CDCl\textsubscript{3} and therefore, NMR spectra should be recorded immediately after 21b had been dissolved in CDCl\textsubscript{3}.

\textbf{1H NMR} (500 MHz, CDCl\textsubscript{3}): \(\delta = 1.72\) (s, 3 H), 4.77 (s, 1 H), 5.02 (s, 1 H), 5.16 (s, 1 H), 6.59 (d, \(J = 7.9\) Hz, 2 H), 6.73 (t, \(J = 7.3\) Hz, 1 H), 7.02-7.07 (m, 2 H), 7.14-7.19 (m, 2 H), 7.34-7.39 (m, 2 H) ppm.

\textbf{13C\{1H\} NMR} (125 MHz, JMOD, CDCl\textsubscript{3}): \(\delta = 19.8\) (CH\textsubscript{3}), 63.8 (CH), 113.0 (CH\textsubscript{2}), 113.7 (CH), 115.6 (d, \(J = 21\) Hz, CH), 117.9 (CH), 129.1 (d, \(J = 8\) Hz, CH), 129.2 (CH), 137.1 (C), 144.6 (C), 147.3 (C), 162.3 (d, \(J = 246\) Hz, C) ppm.

\textbf{19F\{1H\} NMR} (470 MHz, CDCl\textsubscript{3}): \(\delta = -115.1\) ppm.

\textbf{IR} (neat): \(\lambda_{\text{max}}\) cm\textsuperscript{-1} = 3413 (NH), 3083, 3052, 2973, 2937, 2914, 2853, 1683, 1652, 1601, 1500, 1446, 1429, 1374, 1310, 1267, 1220, 1180, 1156, 1117, 1092, 1072, 1014, 993, 899, 870, 843, 816, 794, 747, 690, 604, 566, 507.

\textbf{MS} (EI, 70 eV): \(m/z\) (%) = 241 (40) [M]\textsuperscript{+}, 226 (9) [M – CH\textsubscript{3}]\textsuperscript{+}, 200 (46) [M – C\textsubscript{6}H\textsubscript{5}]\textsuperscript{+}, 149 (100) [M – C\textsubscript{6}H\textsubscript{5}N]\textsuperscript{+}, 133 (13), 109 (51), 95 (5), 77 (37) [M – C\textsubscript{10}H\textsubscript{11}FN]\textsuperscript{+}, 65 (6), 51 (15).

\textbf{HRMS} (EI, 70 eV): \(m/z\) [M]\textsuperscript{+} calcd for C\textsubscript{16}H\textsubscript{16}FN: 241.1261; found 241.1254.

\textit{N},2-Dimethyl-1-phenylprop-2-en-1-amine (22b)

The general procedure was used to react \textit{N}-methyl-1-phenylmethanamine (121 mg, 1.0 mmol) with propadiene. Purification by bulb-to-bulb distillation (47 °C, 3.0 \times 10\textsuperscript{-1} mbar), gave product 22b (109 mg, 0.68 mmol, 68\%) as a colorless liquid. Prior to bulb-to-bulb distillation, the ratio of the branched and the linear product was determined by GC analysis to be 97:3. According to GC analysis, the purity of the product was found to be >98\%.

\textbf{1H NMR} (500 MHz, CDCl\textsubscript{3}): \(\delta = 1.58\) (s, 3 H), 2.37 (s, 3 H), 4.03 (s, 1 H), 4.90 (s, 1 H), 5.15 (s, 1 H), 7.22-7.26 (m, 1 H) 7.30-7.35 (m, 4 H) ppm.
$^{13}$C$\{^1$H$\}$ NMR (125 MHz, DEPT, CDCl$_3$): $\delta = 19.1$ (CH$_3$), 20.1 (CH$_3$), 70.9 (CH), 111.4 (CH$_2$), 127.3 (CH), 127.4 (CH), 128.4 (CH), 141.9 (C), 146.4 (C) ppm.

IR (neat): $\tilde{\lambda}^{-1} = 3333$ (NH), 3063, 3026, 2969, 2872, 2846, 2789, 1646, 1600, 1492, 1474, 1452, 1372, 1234, 1130, 1106, 1074, 1030, 980, 896, 852, 746, 699, 619, 550, 535 cm$^{-1}$.

MS (El, 70 eV): $m/z$ (%) = 161 (2) [M]$^+$, 146 (2) [M – CH$_3$]$^+$, 131 (3) [M – C$_{10}$H$_{11}$]$^+$ 120 (100) [M – C$_8$H$_{10}$N]$^+$, 115 (5) [M – C$_3$H$_8$]$^+$, 91 (8), 84 (10).

HRMS (ESI, +): $m/z$ [M+H]$^+$ calcd for C$_{11}$H$_{16}$N$: 162.1283; found 162.1288.

$N$-Ethyl-2-methyl-1-phenylprop-2-en-1-amine (23b)

The general procedure was used to react $N$-benzylethanamine (135 mg, 1.0 mmol) with propadiene. Purification by bulb-to-bulb distillation (53 °C, 2.7 $\times$ 10$^{-1}$ mbar), gave product 23b (133 mg, 0.76 mmol, 76%) as a colorless liquid. Prior to bulb-to-bulb distillation, the ratio of the branched and the linear product was determined by GC analysis to be 95:5. According to GC analysis, the purity of the product was found to be >98%.

$^1$H NMR (300 MHz, CDCl$_3$): $\delta = 0.99$ (t, $J = 6.2$ Hz, 3 H), 1.44 (s, 3 H), 2.37-2.43 (m, 1 H), 2.44-2.51 (m, 1 H), 4.03 (s, 1 H), 4.75 (s, 1 H), 5.02 (s, 1 H), 7.08-7.11 (m, 1 H), 7.16-7.23 (m, 1 H) ppm.

$^{13}$C$\{^1$H$\}$ NMR (125 MHz, DEPT, CDCl$_3$): $\delta = 15.4$ (CH$_3$), 19.1 (CH$_3$), 42.2 (CH$_2$), 68.8 (CH), 111.1 (CH$_2$), 127.2 (CH), 127.4 (CH), 128.4 (CH) ppm.

IR (neat): $\tilde{\lambda}^{-1} = 3064, 2967, 2811, 2809, 1647, 1601, 1492, 1452, 1372, 1260, 1122, 1104, 1073, 1027, 1014, 896, 804, 757, 744, 699, 633, 573, 530.

MS (El, 70 eV): $m/z$ (%) = 174 (2) [M]$^+$, 160 (2) [M – CH$_3$]$^+$, 146 (3) [M – C$_2$H$_5$]$^+$ 134 (100) [M – C$_3$H$_5$]$^+$, 115 (6), 98 (8) [M – C$_8$H$_{10}$N]$^+$, 84 (10).

HRMS (ESI, +): $m/z$ [M+H]$^+$ calcd for C$_{12}$H$_{18}$N$: 176.1439; found 176.1442.
**N-Isopropyl-2-methyl-1-phenylprop-2-en-1-amine (24b)**

![Chemical structure]

The general procedure was used to react N-benzylpropan-2-amine (149 mg, 1.0 mmol) with propadiene. Purification by bulb-to-bulb distillation (67 °C, 2.7 × 10⁻¹ mbar), gave product 24b (127 mg, 0.67 mmol, 67%) as a colorless liquid. Prior to bulb-to-bulb distillation, the ratio of the branched and the linear product was determined by GC analysis to be 94:6. According to GC analysis, the purity of the product was found to be >99%.

^1H NMR (300 MHz, CDCl₃): δ = 1.04 (d, J = 6.2 Hz, 3 H), 1.08 (d, J = 6.3 Hz, 3 H), 1.57 (s, 3 H), 2.74 (sept, J = 6.3 Hz, 1 H), 4.29 (s, 1 H), 4.89 (s, 1 H), 5.12 (s, 1 H), 7.20 - 7.36 (m, 5 H) ppm.

^13C{¹H} NMR (125 MHz, DEPT, CDCl₃): δ = 19.0 (CH₃), 23.0 (CH₃), 23.2 (CH₃), 45.7 (CH), 65.4 (CH), 111.1 (CH₂), 126.9 (CH), 127.2 (CH), 128.2 (CH), 142.7 (C), 146.9 ppm.

IR (neat): λ⁻¹ = 3083, 3025, 2962, 2932, 2867, 1645, 1493, 1470, 1452, 1379, 1367, 1340, 1169, 1123, 1067, 1030, 896, 856, 760, 746, 732, 699, 627, 571, 532 cm⁻¹.

MS (EI, 70 eV): m/z (%) = 189 (2) [M]⁺, 146 (100) [M – C₃H₅]⁺, 130 (11), 106 (73), 91 (23), 79 (25).

HRMS (ESI, +): m/z [M+H]⁺ calcd for C₁₃H₂₀N⁺: 190.1596; found 190.1597.

**N-(3-methylbut-3-en-2-yl)aniline (25b)**

![Chemical structure]

The general procedure was used to react N-ethylaniline (121 mg, 1.0 mmol) with propadiene. Instead of 4 h, the reaction mixture was stirred for 16 h. Purification by chromatography (150 g SiO₂, PE/EtOAc = 30:1, Rf = 0.38) gave product 25b (29 mg, 0.18 mmol, 18%) as a brown oil. Prior to chromatography, the ratio of the branched and the linear product was determined by GC analysis to be 96:4. According to GC analysis, the purity of the product was found to be >98%.

^1H NMR (500 MHz, CDCl₃): δ = 1.35 (d, J = 6.7 Hz, 3 H), 1.75 (s, 3 H), 3.96 (br. s, 1 H), 3.91 (q, J = 6.7 Hz, 1 H), 4.87 (m, 1 H), 5.01 (m, 1 H), 6.58-6.61 (m, 2 H), 6.67-6.71 (m, 1 H), 7.15-7.18 (m, 2 H) ppm.

^13C{¹H} NMR (125 MHz, JMOD, CDCl₃): δ = 18.3 (CH₃), 21.4 (CH₃), 54.7 (CH), 110.7 (CH₂), 113.4 (CH), 117.3 (CH), 129.2 (CH), 147.5 (C) 147.7 (C) ppm.

IR (neat): λ⁻¹ = 3411 (NH), 3080, 3053, 2965, 2928, 2870, 1648, 1600, 1503, 1451, 1428, 1371, 1315, 1254, 1178, 1154, 1088, 1075, 1047, 1030, 992, 894, 867, 804, 745, 690, 540, 505 cm⁻¹.

MS (El, 70 eV): m/z (%) = 161 (45) [M]⁺, 146 (100) [M – CH₃]⁺, 131 (19), 120 (100) [M – C₃H₅]⁺, 118 (28), 104 (10), 93 (33) [M – C₅H₉]⁺, 77 (38) [M – C₆H₆]⁺, 65 (17).
HRMS (ESI, +): m/z [M+H]^+ calcld for C_{11}H_{16}N^+: 162.1283; found 162.1281.

N-(2-methylpent-1-en-3-yl)aniline (26b)

The general procedure was used to react N-propylaniline (135 mg, 1.0 mmol) with propadiene. Instead of 4 h, the reaction mixture was stirred for 16 h. Purification by chromatography (570 g SiO₂, PE/EE = 30:1, Rf = 0.41) gave product 26b (40 mg, 0.23 mmol, 23%) as a brown oil. Prior to chromatography, the ratio of the branched and the linear product was determined by GC analysis to be 94:6. According to GC analysis, the purity of the product was found to be >98%.

^1H NMR (500 MHz, CDCl₃): δ = 0.96 (t, J = 7.4, 3 H), 1.62-1.67 (m, 2 H), 1.67 (s, 3 H), 3.66 (t, J = 6.8, 1 H), 4.92 (s, 1 H), 4.96 (s, 1 H), 6.61 (d, J = 7.8, 2 H), 6.68 (t, J = 7.3, 1 H), 7.13-7.16 (m, 2 H) ppm.

^13C{^1H} NMR (125 MHz, JMOD, CDCl₃): δ = 10.9 (CH₃), 17.9 (CH₃), 27.3 (CH₂), 61.4 (CH), 112.5 (CH₂), 113.6 (CH), 117.3 (CH), 129.2 (CH), 145.5 (C), 147.6 (C) ppm.

IR (neat): λ = 3408 (NH), 3053, 2963, 2924, 2873, 2854, 1732, 1601, 1502, 1455, 1428, 1371, 1315, 1274, 1255, 1180, 1152, 1142, 1078, 892, 867, 745, 690, 594, 532, 505 cm⁻¹.

MS (EI, 70 eV): m/z (%) = 175 (18) [M]^+, 146 (100) [M – C₂H₅]^+, 134 (15) [M – C₃H₅]^+, 131 (20), 118 (20), 114 (7), 93 (9), 77 (20) [M – C₆H₅]^+, 65 (6), 51 (9).

HRMS (ESI, +): m/z [M+H]^+ calcld for C_{12}H_{18}N^+: 176.1439; found 176.1436.

2-Allyl-1,2,3,4-tetrahydroquinoline (28b) and 2-(prop-1-en-2-yl)-1,2,3,4-tetrahydroquinoline (28l)

The general procedure was used to react 1,2,3,4-tetrahydroquinoline (133 mg, 1.0 mmol) with propadiene. Instead of 4 h, the reaction mixture was stirred for 16 h. After purification by flash chromatography (120 g SiO₂, PE/EtOAc = 30:1, Rf = 0.30), 28b (19 mg, 0.11 mmol, 11%) was isolated as a brown oil. In addition, a second fraction (Rf = 0.25) containing 28l (18 mg, 0.10 mmol, 10%) as a brown oil was isolated. Prior to chromatography, the ratio of the branched and the linear product was determined by GC analysis to be 59:41. According to GC analysis, the product 28b contained traces of 28l and 28l contained traces of 28b.

2-Allyl-1,2,3,4-tetrahydroquinoline (28b):

^1H NMR (500 MHz, CDCl₃): δ = 1.80 (s, 3 H), 182-1.88 (m, 1 H), 1.97-2.02 (m, 1 H), 2.70 (m, 1 H), 2.70-2.75 (m, 1 H), 2.80-2.87 (m, 1 H), 3.82 (dd, J = 9.0, 3.2 Hz, 1 H), 4.89 (s, 1 H), 5.02 (s, 1 H), 6.53 (d, J = 7.9 Hz, 1 H), 6.62 (d, J = 7.3 Hz, 1 H), 6.97 (t, J = 7.7 Hz, 2 H) ppm.

^13C{^1H} NMR (125 MHz, JMOD, CDCl₃): δ = 18.9 (CH₃), 26.2 (CH₂), 26.9 (CH₂), 57.3 (CH), 111.1 (C), 114.0 (CH), 117.0 (CH), 121.1 (CH), 126.9 (CH), 129.3 (CH), 144.8 (C), 147.6 (C) ppm.
IR (neat): $\nu$ = 3400 (NH), 3074, 3053, 3014, 2974, 2842, 1640, 1606, 1586, 1482, 1446, 1434, 1349, 1309, 1274, 1252, 1206, 1176, 1154, 1120, 1061, 1036, 1021, 994, 913, 841, 810, 743, 716, 620, 537 cm$^{-1}$.

MS (EI, 70 eV): $m/z$ (%) = 173 (34) [M$^+$], 158 (8) [M – CH$_3$]$^+$, 143 (4), 132 (100) [M – C$_3$H$_5$]$^+$, 117 (16), 103 (5), 91 (4), 77 (12).

HRMS (ESI, +): $m/z$ [M+H]$^+$ calcd for C$_{12}$H$_{16}$N$: 174.1283; found 174.1276.

2-(Prop-1-en-2-yl)-1,2,3,4-tetrahydroquinoline (28I):

$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ = 1.62-1.69 (m, 1 H), 1.96-2.01 (m, 1 H), 2.17-2.23 (m, 1 H), 2.33-2.38 (m, 1 H), 2.72-2.78 (m, 1 H), 3.29-3.34 (m, 1 H), 3.88 (s, 1 H), 5.16-5.18 (m, 1 H), 5.18-5.20 (m, 1 H), 6.47-6.49 (m, 1 H), 6.60-6.63 (m, 1 H), 6.95-6.98 (m, 1 H) ppm.

$^{13}$C($^1$H) NMR (125 MHz, DEPT, CDCl$_3$): $\delta$ = 26.4 (CH$_2$), 28.3 (CH$_2$), 41.8 (CH$_2$), 50.7 (CH), 114.2 (C), 117.2 (CH), 118.1 (CH), 126.9 (CH), 129.4 (CH), 135.1 (CH), 149.6 (C) ppm.

IR (neat): $\nu$ = 3403 (NH), 3053, 3016, 2927, 2842, 1648, 1607, 1585, 1500, 1482, 1447, 1436, 1373, 1310, 1273, 1253, 1236, 1167, 1154, 1116, 1034, 1022, 897, 851, 827, 743, 713, 700, 537 cm$^{-1}$.

MS (EI, 70 eV): $m/z$ (%) = 173 (10) [M$^+$], 158 (8), 132 (100) [M – C$_3$H$_5$]$^+$, 117 (16), 103 (4), 91 (2), 77 (9).

HRMS (ESI, +): $m/z$ [M+H]$^+$ calcd for C$_{12}$H$_{16}$N$: 174.1283; found 174.1281.
5. Unreactive Substrates

No reaction was observed with the following \( N \)-benzylaniline derivatives:
6. Mechanism Studies

Complex 29⁶ (0.250 g, 0.453 mmol) was suspended in 10 mL of n-hexane. propadiene (2) (1.1 mL, 0.453 mmol; 0.4 molL⁻¹ in toluene) was added. A color change from yellow to yellow-green is observed after a few minutes of vigorous stirring. The reaction mixture was stirred for 4 h at room temperature. All volatile components were removed under vacuum to yield 30 and 31 in a 10:1 ratio as a yellow-green sticky solid. No further purification steps are required. Only the signals of the major product 30 are given below.

**Combined yield:** 0.196 g (0.331 mmol, 73%).

**¹H NMR** (500 MHz, C₆D₆, 305 K): δ = 1.40-1.44 (m, 2H, CH₂Ad/CH₂Ad), 1.49-1.52 (m, 2H, CH₂Ad/CH₂Ad), 1.52-1.68 (m, 22H, CH₄Ad), 2.26-2.27 (m, 2H, CH₂Ad/CH₂Ad), 2.74 (s, 2H, CH₄exo), 2.98-3.00 (m, 2H, NCH₂CH₂), 3.30 (t, 3JH,H = 6.6 Hz, 2H, NCH₂CH₂), 4.20-4.21 (m, 1H, TiC=CH₂), 5.44-5.46 (m, 2H, C₅H₄), 5.65-5.66 (m, 1H, TiC=CH₂), 5.78-5.79 (m, 2H, o-CH₃PhN), 5.90-5.92 (m, 2H, C₅H₄), 6.14-6.15 (m, 2H, C₅H₄), 6.30-6.31 (m, 2H, C₅H₄), 6.72-6.75 (m, 1H, p-CH₃PhN), 7.08-7.12 (m, 2H, m-CH₃PhN) ppm.

**¹³C{¹H} NMR** (126 MHz, C₆D₆, 305 K): δ = 28.2 (CH₂Ad), 28.3 (CH₂Ad), 32.2 (CH₂Ad), 32.4 (CH₂Ad), 38.2 (CH₂Ad), 38.6 (CH₂Ad), 39.0 (CH₂Ad), 44.0 (CH₄exo), 46.1 (NCH₂CH₂), 52.8 (NCH₂CH₂), 110.9 (C₅H₄), 113.0 (C₅H₄), 113.2 (C₅H₄), 114.40 (TiC₅=CH₂), 114.43 (o-CH₃PhN), 117.1 (p-CH₃PhN), 118.1 (C₅H₄), 128.2 (m-CH₃PhN)**, 136.6 (C₅q=ipso), 156.6 (C₅q), 207.6 (TiC₅=CH₂) ppm.

* = overlap with signals of 7
** = overlap with C₆D₆ signal

**¹⁵N NMR** (51 MHz, C₆D₆, 305 K): δ = 196.2 ppm.
7. NMR Spectra

Figure S3: $^1$H NMR of the crude mixture of compounds 4b and 4l (500 MHz, 305 K, CDCl$_3$).

Figure S4: $^1$H NMR of the crude mixture of compounds 4b and 4l (500 MHz, 305 K, CDCl$_3$).
Figure S5: $^1$H NMR of the crude mixture of compounds 4b and 4l (500 MHz, 305 K, CDCl$_3$).
Figure S6: $^1$H NMR spectrum (500 MHz, 305 K, CDCl$_3$).

Figure S7: $^{13}$C($^1$H) spectrum (125 MHz, 305 K, CDCl$_3$).
4-Methyl-\(N\)-(2-methyl-1-phenylallyl)aniline (5b)

Figure S8: \(^1\text{H} \)NMR spectrum (500 MHz, 305 K, CDCl\(_3\)).

Figure S9: \(^{13}\text{C}\{^1\text{H}\} \) spectrum (125 MHz, 305 K, CDCl\(_3\)).
3-Methyl-\(N\)-(2-methyl-1-phenylallyl)aniline (6b)

Figure S10: \(^1\)H NMR spectrum (500 MHz, 305 K, CDCl\(_3\)).

Figure S11: \(^{13}\text{C}\{^1\text{H}\}\) NMR spectrum (125 MHz, 305 K, CDCl\(_3\)).
4-Bromo-\(N\)-(2-methyl-1-phenylallyl)aniline (7b)

Figure S12: \(^1\)H NMR spectrum (500 MHz, 305 K, CDCl\(_3\)).

Figure S13: \(^{13}\)C\(^\{1\}H\) NMR spectrum (125 MHz, 305 K, CDCl\(_3\)).
3-Bromo-\(N\)-\(\text{methyl}-\text{1-phenylallyl}\)aniline (8b)

\[
\begin{align*}
\text{Br} & \quad \text{H} \\
\text{N} & \quad \text{M} \quad \text{H} \\
\text{Br} & \quad \text{H}
\end{align*}
\]

**Figure S14**: \(^1\text{H}\) NMR spectrum (500 MHz, 305 K, CDCl\(_3\)).

**Figure S15**: \(^1\text{C}(^1\text{H})\) NMR spectrum (125 MHz, 305 K, CDCl\(_3\)).
4-Methoxy-N-(2-methyl-1-phenylallyl)aniline (9b)

Figure S16: $^1$H NMR spectrum (500 MHz, 305 K, CDCl$_3$).

Figure S17: $^{13}$C($^1$H) NMR spectrum (125 MHz, 305 K, CDCl$_3$).
3-Methoxy-N-(2-methyl-1-phenylallyl)aniline (10b)

Figure S18: $^1$H NMR spectrum (500 MHz, 305 K, CDCl$_3$).

Figure S19: $^{13}$C($^1$H) NMR spectrum (125 MHz, 305 K, CDCl$_3$).
Figure S20. $^1$H NMR spectrum (500 MHz, 305 K, CDCl$_3$).

Figure S21. $^{13}$C($^1$H) NMR spectrum (125 MHz, 305 K, CDCl$_3$).
Figure S22: $^{19}$F($^1$H) NMR spectrum (139 MHz, 305 K, CDCl$_3$).
$N$-(2-Methyl-1-phenylallyl)-4-(trifluoromethyl)aniline (12b)

**Figure S23**: $^1$H NMR spectrum (500 MHz, 305 K, CDCl$_3$).

**Figure S24**: $^{13}$C($^1$H) NMR spectrum (125 MHz, 305 K, CDCl$_3$).
Figure S25: $^{19}$F($^1$H) NMR spectrum (139 MHz, 305 K, CDCl$_3$).
4-Chloro-N-(2-methyl-1-phenylallyl)aniline (13b)

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\text{Figure S26: } ^1\text{H NMR spectrum (500 MHz, 305 K, CDCl}_3\text{).}
\]

\[
\text{Figure S27: } ^{13}\text{C} (^1\text{H}) \text{ NMR spectrum (125 MHz, 305 K, CDCl}_3\text{).}
\]
*N*(2-Methyl-1-(3-(trifluoromethyl)phenyl)allyl)aniline (14b)

![Chemical structure](image)

**Figure S28**: $^1$H NMR spectrum (500 MHz, 305 K, CDCl$_3$).

**Figure S29**: $^{13}$C($^1$H) NMR spectrum (125 MHz, 305 K, CDCl$_3$).
Figure S30: $^{19}$F (1H) NMR spectrum (139 MHz, 305 K, CDCl₃).
N-(1-(3-Bromophenyl)-2-methylallyl)aniline (15b)

**Figure S31**: $^1$H NMR spectrum (500 MHz, 305 K, CDCl$_3$).

**Figure S32**: $^{13}$C($^1$H) NMR spectrum (125 MHz, 305 K, CDCl$_3$).
$N$-(1-(3-Chlorophenyl)-2-methylallyl)aniline (16b)

Figure S33: $^1$H NMR spectrum (500 MHz, 305 K, CDCl$_3$).

Figure S34: $^{13}$C($^1$H) NMR spectrum (125 MHz, 305 K, CDCl$_3$).
\textit{N}(1-(4-Methoxyphenyl)-2-methylallyl)aniline (17b)

\textbf{Figure S35}: $^1$H NMR spectrum (500 MHz, 305 K, CDCl$_3$).

\textbf{Figure S36}: $^{13}$C($^1$H) NMR spectrum (125 MHz, 305 K, CDCl$_3$).
N-(2-Methyl-1-(4-(trifluoromethyl)phenyl)allyl)aniline (18b)

Figure S37: $^1$H NMR spectrum (500 MHz, 305 K, CDCl$_3$).

Figure S38: $^{13}$C($^1$H) NMR spectrum (125 MHz, 305 K, CDCl$_3$).
Figure S39: $^{19}$F($^1$H) NMR spectrum (139 MHz, 305 K, CDCl$_3$).
Figure S38: $^{13}$C($^1$H) NMR spectrum (125 MHz, 305 K, CDCl$_3$).

Figure S40: $^1$H NMR spectrum (500 MHz, 305 K, CDCl$_3$).
Figure S41: $^1$H NMR spectrum (500 MHz, 305 K, CDCl$_3$).

Figure S42: $^{13}$C($^1$H) NMR spectrum (125 MHz, 305 K, CDCl$_3$).
**Figure S43**: $^1$H NMR spectrum (500 MHz, 305 K, CDCl$_3$).

**Figure S44**: $^{13}$C($^1$H) NMR spectrum (125 MHz, 305 K, CDCl$_3$).
Figure S45. $^{19}F(1H)$ NMR spectrum (139 MHz, 305 K, CDCl$_3$).
N$_2$-Dimethyl-1-phenylprop-2-en-1-amine (22b)

Figure S46: $^1$H NMR spectrum (500 MHz, 305 K, CDCl$_3$).

Figure S47: $^{13}$C($^1$H) NMR spectrum (125 MHz, 305 K, CDCl$_3$).
N-Ethyl-2-methyl-1-phenylprop-2-en-1-amine (23b)

Figure S48: $^1$H NMR spectrum (300 MHz, 305 K, CDCl$_3$).

Figure S49: $^{13}$C($^1$H) NMR spectrum (125 MHz, 305 K, CDCl$_3$).
**N*-Isopropyl-2-methyl-1-phenylprop-2-en-1-amine (24b)**

![Chemical Structure Image]

**Figure S50:** $^1$H NMR spectrum (300 MHz, 305 K, CDCl$_3$).

**Figure S51:** $^{13}$C($^1$H) NMR spectrum (125 MHz, 305 K, CDCl$_3$).
$N$-(3-Methylbut-3-en-2-yl)aniline (25b)

Figure S52: $^1$H NMR spectrum (500 MHz, 305 K, CDCl$_3$).

Figure S53: $^{13}$C($^1$H) NMR spectrum (125 MHz, 305 K, CDCl$_3$).
Figure S54: $^1$H NMR spectrum (500 MHz, 305 K, CDCl$_3$).

Figure S55: $^{13}$C($^1$H) NMR spectrum (125 MHz, 305 K, CDCl$_3$).
2-Allyl-1,2,3,4-tetrahydroquinoline (28l)

Figure S56: $^1\text{H}$ NMR spectrum (500 MHz, 305 K, CDCl$_3$).

Figure S57: $^{13}\text{C}[^1\text{H}]$ NMR spectrum (125 MHz, 305 K, CDCl$_3$).
2-(Prop-1-en-2-yl)-1,2,3,4-tetrahydroquinoline (28b)

Figure S58: $^1$H NMR spectrum (500 MHz, 305 K, CDCl₃).

Figure S59: $^{13}$C($^1$H) NMR spectrum (125 MHz, 305 K, CDCl₃).
Titanium Complexes 30 and 31

Figure S60: $^1$H NMR spectrum of 30 and 31 (500 MHz, C$_6$D$_6$, 305 K); 0.89, 1.24 ppm: $n$-hexane.

Figure S61: $^{13}$C($^1$H) NMR spectrum of 30 and 31 (126 MHz, C$_6$D$_6$, 305 K).
Figure S62: $^{15}$N/$^1$H HMBC NMR spectrum of 30 and 31 (51 MHz, C$_6$D$_6$, 305 K).

Figure S63: Excerpt of the $^1$H NMR spectrum of 30 and 31 (500 MHz, C$_6$D$_6$, 305 K).
8. GC Analyses

**Figure S64**: GC analysis of the hydroaminoalkylation of propadiene (2) with N-benzylaniline (1b) in the presence of catalyst IVa (Table S2, entry 1).

**Figure S65**: GC analysis to show the ratio of 4b and 4l (Table S2, entry 1).
Figure S66: GC analysis of the hydroaminoalkylation of propadiene (2) with N-benzylaniline (1b) in the presence of catalyst IVb (Table S2, entry 2).

Figure S67: GC analysis of the hydroaminoalkylation of propadiene (2) with N-benzylaniline (1b) in the presence of the catalyst V (Table S2, entry 3).
Figure S68: GC analysis of the hydroaminoalkylation of propadiene (2) with N-benzylaniline (1b) in the presence of catalyst VI (Table S2, entry 6).

Figure S69: GC analysis of the hydroaminoalkylation of propadiene (2) with N-benzylaniline (1b) in the presence of catalyst IVa (optimized conditions, Table S3, entry 15).
Figure S70: GC analysis of the purified product 4b (optimized conditions, Table S3, entry 15).

Figure S71: GC analysis of the hydroaminoalkylation of propadiene (2) with N-ethylaniline in the presence of catalyst IVa and a reaction time of 4 h.
Figure S72: GC analysis of the hydroaminoalkylation of propadiene (2) with N-propylaniline in the presence of catalyst IVa and a reaction time of 4 h.

Figure S73: GC analysis of the hydroaminoalkylation of propadiene (2) with N-isobutylaniline in the presence of catalyst IVa and a reaction time of 4 h.
Figure S74: GC analysis of the hydroaminoalkylation of propadiene (2) with N-ethylaniline in the presence of catalyst IVa and a reaction time of 16 h.

Figure S75: GC analysis of the hydroaminoalkylation of propadiene (2) with N-propylaniline in the presence of catalyst IVa and a reaction time of 16 h.
Figure S76: GC analysis of the hydroaminoalkylation of propadiene (2) with N-isobutylaniline in the presence of catalyst IVa and a reaction time of 16 h.
9. References

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