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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", ethyl acetate is abbreviated with EtOAc. 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. 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, 500 MHz spectrometer. $^1$H NMR spectra are referenced to the residue solvent signals (δ$^1$H = 7.26 ppm for CDCl₃ and δ$^1$H = 7.16 ppm for benzene-đ₆). $^{13}$C NMR spectra are referenced to the central line of the residue solvent (δ$^{13}$C($^1$H) = 77.16 ppm for CDCl₃ and δ$^{13}$C($^1$H) = 128.06 for benzene-đ₆). 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. Selectivities of catalytic reactions were determined by GC analyses prior to chromatography and refer to the ratio of the GC areas of the corresponding isomers.
2. Optimization of Catalyst and Reaction Conditions

For all experiments related to optimization studies, \( p \)-cymene was used as an internal standard. The catalyst screening was performed in 1 mL ampoules (length = 270 mm, outer diameter = 5 mm, inner diameter = 3 mm, wall thickness = 1 mm) and all substrates were dried and degassed prior to use. Typical procedure: In a glovebox under \( N_2 \)-atmosphere, the catalyst (usually 0.01 mmol, 10 mol%) was weight in a 10 mL vial. Subsequently, \( N \)-benzylaniline (1, 183 mg, 1.0 mmol, 1.0 equiv), diphenylacetylene (2, 214 mg, 1.2 mmol, 1.2 equiv) and \( p \)-cymene (3 mg, 0.2 equiv) were weight in a different 10 mL vial to produce a stock solution in toluene (1 mL). A part of the stock solution was transferred into the vial with the catalyst and then the mixture was transferred into the ampoule which was quickly sealed with a natural gas/O\(_2\) torch. In cases, in which the amount of catalyst was below 6 mg, 1.0 mmol \( N \)-benzylaniline, 1.2 mmol diphenylacetylene, \( p \)-cymene 0.2 mmol and 0.1 mmol of the catalyst were weight into a vial. Toluene (1 mL) was added and then only a tenth of this solution was used for the catalytic reaction.

![Catalysts and ligands used for the screening.](image)

**Figure S1.** Catalysts and ligands used for the screening.
Table S1. Catalyst screening\[a\]

| Entry | Catalyst       | Ratio p-cymene/product\[b\] |
|-------|----------------|----------------------------|
| 1     | I              | 1:1                        |
| 2     | II             | 3:10                       |
| 3     | III            | -                          |
| 4     | IV             | -                          |
| 5     | Ti(NMe\(_2\))\(_4\) | -                         |
| 6     | TiBn\(_4\)     | -                          |
| 7     | Nb(NMe\(_2\))\(_5\) | -                       |
| 8     | Ta(NMe\(_2\))\(_5\) | -                       |
| 9     | Zr(NMe\(_2\))\(_4\) | -                       |

[a] Reaction conditions: \(N\)-benzylaniline (1, 18 mg, 0.10 mmol, 1.0 equiv), diphenylacetylene (2, 21 mg, 0.12 mmol, 1.2 equiv.), catalyst (0.01 mmol, 10 mol\%), toluene (0.1 mL), 140 °C, 2 h. [b] The ratio was determined by GC analysis. It refers to the ratio of the GC areas obtained for \(p\)-cymene and the product \((E)\)-\(N\)-(1,2,3-triphenylallyl)aniline (\(E\)-3).
Table S2. Optimization of the reaction conditions\(^{[a]}\)

![Reaction scheme]

| Entry | \(t\) [min] | \(T\) [°C] | Catalyst loading [mol\%] | Solvent [mL] | Ratio \(p\)-cymene/product\(^{[b]}\) |
|-------|-------------|------------|---------------------------|-------------|-------------------------------|
| 1     | 120         | 25         | 10                        | 0.1         | -                             |
| 2     | 120         | 80         | 10                        | 0.1         | -                             |
| 3     | 120         | 100        | 10                        | 0.1         | 7:10                          |
| 4     | 120         | 120        | 10                        | 0.1         | 6:10                          |
| 5     | 120         | 140        | 10                        | 0.1         | 3:10                          |
| 6     | 120         | 160        | 10                        | 0.1         | 6:10                          |
| 7     | 120         | 140        | 0                         | 0.1         | -                             |
| 8     | 120         | 140        | 2.5                       | 0.1         | 11:10                         |
| 9     | 120         | 140        | 5                         | 0.1         | 6:10                          |
| 10    | 120         | 140        | 7.5                       | 0.1         | 5:10                          |
| 11    | 120         | 140        | 10                        | 0.1         | 3:10                          |
| 13    | 240         | 140        | 10                        | 0.1         | 2:10                          |
| 14    | 360         | 140        | 10                        | 0.1         | 2:10                          |

\(^{[a]}\) Reaction conditions: \(N\)-benzylaniline (1, 18 mg, 0.1 mmol, 1 equiv), diphenylavetylene (2, 21 mg, 0.12 mmol, 1.2 equiv), catalyst II, toluene, \(T, t\). \(^{[b]}\) The ratio was determined by GC analysis. It refers to the ratio of the GC areas obtained for \(p\)-cymene and the product \((E)-N\)-(1,2,3-triphenylallyl)aniline (\(E\)-3).
3. Sensitivity Assessment

The optimized reaction conditions for the hydroaminoalkylation of diphenylacetylene (2, 21 mg, 0.1 mmol, 1.2 equiv) with N-benzylaniline (18 mg, 0.1 mmol, 1.0 equiv) with catalyst II (11 mg, 0.01 mmol, 10 mol%), at 140 °C for 4 h (Table S3, entry 14) were used for a sensitivity assessment, which is described in ref.\[3\]

Investigation of the influence of water, oxygen, temperature, light, concentration, and the possibility of upscaling was carried out. It was performed 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). In this sensitivity evaluation, all parameters were kept constant and only one changed. All results are displayed in Table S3 and Figure S2. The reaction is not influenced by light and concentration and the reaction also worked well on a larger scale. Furthermore, temperature has only a minor influence on the reaction. In contrast, water and oxygen have a major influence as titanium dioxide is formed from the catalyst in these cases. In summary, we recommend a performance under inert atmosphere and the reaction temperature is also important and should be kept at 140 °C.

Table S3. Results of the sensitivity assessment

| Parameter          | Variation          | Deviation from controlled yield |
|--------------------|--------------------|---------------------------------|
| Water              | + H₂O, V(H₂O) = 1% Vₓₓₓ | − 100%                           |
| Concentration      | Low                | Vₓₓₓ + 50% Vₓₓₓ                   | − 3%                             |
|                    | High               | Vₓₓₓ - 50% Vₓₓₓ                  | 0%                              |
| Oxygen             | Low                | inert Atmosphere                | 0%                              |
|                    | High               | + air                           | − 100%                          |
| Temperature        | High               | T + 20 °C                       | − 12%                           |
|                    | Low                | T − 20 °C                       | − 16%                           |
| Light Intensity    | High               | l × 16                          | 0%                              |
|                    | Low                | l/16                            | 0%                              |
| Large scale        |                    | n × 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 II (111 mg, 0.10 mmol, 10 mol%), the amine (1.0 mmol, 1.0 equiv), and the alkyne (1.2 mmol, 1.2 equiv). Afterwards, everything was dissolved in toluene (1 mL) 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, 16 h or 20 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. Prior to chromatography, the ratio of the E and the Z product was determined by GC analysis. In all reaction the Z stereoisomere was not observed.

**{(E)-N-(1,2,3-Triphenylallyl)aniline (E-3)}**

The general procedure was used to react N-benzenylaniline (1, 183 mg, 1.0 mmol) with diphenylacetylene (2, 214 mg, 1.2 mmol). Purification by chromatography (PE/EtOAc = 30:1, Rᵣ = 0.31) gave product E-3 (296 mg, 0.82 mmol, 82 %) as a colorless solid. The solid was dissolved in CH₂Cl₂ and the solution was transferred into an NMR tube. Afterwards, n-hexane was carefully added on top of the CH₂Cl₂ and the mixture was allowed to stand at room temperature until crystals suitable for X-ray analysis were formed (Table S4, Figure S76-78).

**¹H NMR** (500 MHz, CDCl₃): δ = 4.06 (br. s, 1 H), 5.09 (s, 1 H), 6.57 (d, J = 7.8 Hz, 2 H), 6.61 (t, J = 7.3 Hz, 1 H), 6.76 (s, 1 H), 6.81-6.83 (m, 2 H), 6.87-6.89 (m, 2 H), 6.94-6.95 (m, 3 H), 7.04-7.07 (m, 2 H), 7.10-7.12 (m, 3 H), 7.14-7.17 (m, 1 H) ppm.

**¹³C{¹H} NMR** (125 MHz, DEPT, CDCl₃): δ = 66.2 (CH), 113.8 (CH), 117.9 (CH), 126.9 (CH), 127.5 (CH), 127.7 (CH), 128.0 (CH), 128.3 (CH), 128.7 (CH), 129.2 (CH), 129.3 (CH), 129.4 (CH), 136.7 (C), 139.4 (C), 141.2 (C), 141.9 (C), 147.3 (C) ppm.

**IR** (neat): λ⁻¹ = 3402 (NH), 3077, 3052, 3020, 2837, 1599, 15074, 1500, 1491, 1447, 1426, 1313, 1262, 1232, 1180, 1154, 1124, 1074, 1027, 1004, 1001, 991, 972, 954, 926, 870, 846, 813, 776, 744, 699, 691, 627, 619, 607, 551, 537, 514 cm⁻¹.

**MS** (El, 70 eV): m/z (%) = 361 (7) [M]+, 269 (27) [M – C₆H₅N]+, 182 (100) [M – C₁₄H₁₁]+, 104 (22), 91 (20) [M – C₆H₅N]+, 77 (44) [M – C₂₁H₁₈N]+.

**HRMS** (El, 70 eV): m/z [M]+ calcd for C₂₇H₂₃N: 361.1825; found 361.1824.
(E)-4-Methyl-N-(1,2,3-triphenylallyl)aniline (E-6)

The general procedure was used to react N-benzyl-4-methylaniline (197 mg, 1.0 mmol) with diphenylacetylene (2, 214 mg, 1.2 mmol). Purification by chromatography (PE/EtOAc/NEt$_3$H = 100:2:1, $R_f = 0.38$) gave product E-6 (324 mg, 0.86 mmol, 86 %, GC purity > 99 %) as a colorless solid.

$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ = 2.13 (s, 3 H), 3.94 (br. s, 1 H), 5.07 (s, 1 H), 6.50-6.51 (m, 2 H), 6.76 (s, 1 H), 6.82-6.83 (m, 2 H), 6.87-6.89 (m, 4 H), 6.95-6.97 (m, 3 H), 7.10-7.12 (m, 3 H), 7.20-7.23 (m, 2 H), 7.28-7.30 (m, 2 H) ppm.

$^{13}$C{$^1$H} NMR (125 MHz, DEPT, CDCl$_3$): $\delta$ = 20.4 (CH$_3$), 66.4 (CH), 113.7 (CH), 126.7 (CH), 126.8 (CH), 127.3 (CH), 127.5 (C), 127.8 (CH) 128.1 (CH), 128.5 (CH), 128.6 (CH), 129.1 (CH), 129.3 (CH), 136.7 (C), 139.3 (C), 141.2 (C), 142.0 (C), 145.0 (C) ppm.

IR (neat): $\tilde{$\nu$}$ = 3412 (NH), 3050, 3021, 2854, 1600, 1500, 1446, 1426, 1310, 1263, 1220, 1156, 1114, 1070, 1014, 921, 867, 830, 780, 746, 690, 620, 599, 567, 549, 506 cm$^{-1}$.

MS (El, 70 eV): $m/z$ (%) = 375 (9) [M]$^+$, 269 (36), 196 (100) [M – C$_{14}$H$_{11}$]$^+$, 191 (76), 91 (49), 77 (18) [M – C$_{22}$H$_{20}$N]$^+$.

HRMS (El, 70 eV): $m/z$ [M]$^+$ calcd for C$_{28}$H$_{25}$N: 375.1982; found 375.1973.
(E)-3-Methyl-N-(1,2,3-triphenylallyl)aniline (E-7)

The general procedure was used to react N-benzyl-3-methylaniline (197 mg, 1.0 mmol) with diphenylacetylene (2, 214 mg, 1.2 mmol). Purification by chromatography (PE/EtOAc = 30:1, Rf = 0.31) gave product E-7 (328 mg, 0.87 mmol, 87%) as a colorless solid.

$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ = 2.15 (s, 3 H), 4.00 (br. s, 1 H), 5.08 (s, 1 H), 6.37-6.39 (m, 2 H), 6.43-6.45 (m, 1 H), 6.76 (s, 1 H), 6.81-6.83 (m, 2 H), 6.87-6.89 (m, 2 H), 6.93-6.96 (m, 4 H), 7.09-7.11 (m, 3 H), 7.13-7.21 (m, 3 H), 7.27-7.29 (m, 2 H) ppm.

$^{13}$C($^1$H) NMR (125 MHz, DEPT, CDCl$_3$): $\delta$ = 21.8 (CH$_3$), 66.2 (CH), 110.7 (CH), 114.6 (CH), 118.8 (C), 126.8 (CH), 127.7 (CH), 128.0 (CH) 128.3 (CH), 128.6 (CH), 128.7 (CH), 129.18 (CH), 129.22 (CH), 129.4 (CH), 136.8 (C), 138.9 (C), 139.5 (C), 141.3 (C), 142.0 (C), 147.4 (C) ppm.

IR (neat): $\tilde{\nu}$ = 3409 (NH), 3053, 3024, 1604, 1589, 1504, 1488, 1446, 1419, 1319, 1266, 1177, 1123, 1073, 1029, 993, 923, 863, 844, 766, 736, 691, 610, 551, 537 cm$^{-1}$.

MS (EI, 70 eV): m/z (%) = 375 (9) [M]$^+$, 269 (24), 196 (100) [M – C$_{14}$H$_{11}$]$^+$, 191 (56), 91 (45), 77 (11) [M – C$_{22}$H$_{20}$N]$^+$.

HRMS (EI, 70 eV): m/z [M]$^+$ calcd for C$_{28}$H$_{25}$N: 375.1982; found 375.1977.
(E)-4-Bromo-N-(1,2,3-triphenylallyl)aniline (E-8)

The general procedure was used to react N-benzyl-4-bromoaniline (262 mg, 1.0 mmol) with diphenylacetylene (2, 214 mg, 1.2 mmol). Purification by chromatography (PE/EtOAc = 30:1, 
$R_f$ = 0.23) gave product E-8 (135 mg, 0.31 mmol, 31 %) as a colorless solid.

$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ = 4.09 (br. s, 1 H), 5.05 (s, 1 H), 6.42-6.45 (m, 2 H), 6.72 (s, 1 H), 6.81-6.83 (m, 2 H), 6.85-6.87 (m, 2 H), 6.96-6.98 (m, 3 H), 7.11-7.15 (m, 5 H), 7.18-7.25 (m, 3 H), 7.27-7.29 (m, 2 H) ppm.

$^{13}$C($^1$H) NMR (125 MHz, DEPT, CDCl$_3$): $\delta$ = 65.9 (CH), 109.4 (C), 115.2 (CH), 126.9 (CH), 127.5 (CH), 127.7 (CH), 127.9 (CH) 128.5 (CH), 128.5 (CH), 128.6 (CH), 128.7 (CH), 129.0 (CH), 129.3 (CH), 131.9 (CH), 136.4 (C), 139.6 (C), 140.5 (C), 141.2 (C), 146.0 (C), 146.1 (C) ppm.

IR (neat): $\tilde{\nu}$ = 3416 (NH), 3018, 3054, 3024, 2962, 1592, 1490, 1446, 1393, 1310, 1293, 1263, 1237, 1179, 1156, 1126, 1110, 1073, 1029, 10000, 969, 921, 894, 867, 844, 810, 756, 736, 694, 641, 617, 599, 566, 541, 521, 503 cm$^{-1}$.

MS (El, 70 eV): $m/z$ (%) = 439 (6) [M]$^+$, 269 (62) [M – C$_6$H$_5$BrN]$^+$, 260 (40) [M – C$_{14}$H$_{11}$]$^+$, 191 (100), 91 (44), 77 (13) [M – C$_{21}$H$_{17}$BrN]$^+$.

HRMS (El, 70 eV): $m/z$ [M]$^+$ calcd for C$_{27}$H$_{22}$BrN: 439.0936; found 439.0930.
**(E)-3-Bromo-N(1,2,3-triphenylallyl)aniline (E-9)**

![Chemical Structure](image)

The general procedure was used to react \( N \)-benzyl-3-bromoaniline (262 mg, 1.0 mmol) with diphenylacetylene (2, 214 mg, 1.2 mmol). Purification by chromatography (PE/EtOAc = 30:1, \( R_f = 0.24 \)) gave product **E-9** (181 mg, 0.41 mmol, 41%) as a yellow solid.

\(^1\)H NMR (500 MHz, CDCl\(_3\)): \( \delta = 4.12 \) (br. s, 1 H), 5.07 (s, 1 H), 6.46 (dd, \( J = 1.8, 8.4 \text{ Hz} \), 2 H), 6.71-6.74 (m, 3 H), 6.82-6.84 (m, 2 H), 6.86-6.90 (m, 3 H), 6.97-6.98 (m, 3 H), 7.11-7.14 (m, 3 H), 7.24-7.29 (m, 5 H) ppm.

\(^1^3\)C\(^{1}\)H NMR (125 MHz, DEPT, CDCl\(_3\)): \( \delta = 65.7 \) (CH), 112.1 (CH), 116.4 (CH), 120.5 (CH), 123.1 (C), 126.9 (CH), 127.5 (CH) 127.76 (CH), 127.79 (CH), 127.9 (CH), 128.4 (CH), 128.6 (CH), 128.7 (CH), 129.0 (CH), 129.1 (CH), 130.4 (CH), 136.4 (C), 139.0 (C), 140.4 (C), 141.2 (C), 148.3 (C) ppm.

IR (neat): \( \lambda^{-1} = 3416 \) (NH), 3079, 3054, 3024, 2962, 1592, 1574, 1490, 1478, 1447, 1442, 1413, 1316, 1279, 1264, 1231, 1182, 1167, 1156, 1123, 1087, 1069, 1029, 1006, 986, 921, 884, 839, 757, 736, 696, 680, 609, 589, 564, 550, 535 cm\(^{-1}\).

**MS (El, 70 eV):** \( m/z (%) = \)

- 439 (3) [M]+, 269 (56) [M – C\(_6\)H\(_5\)BrN]+,
- 260 (60) [M – C\(_{14}\)H\(_{11}\)]+,
- 191 (100), 91 (49), 77 (20) [M – C\(_{21}\)H\(_{17}\)BrN]+.

**HRMS (El, 70 eV):** \( m/z [M]+ \) calcd for C\(_{27}\)H\(_{22}\)BrN: 439.0936; found 439.0930.
(E)-4-Chloro-N-(1,2,3-triphenylallyl)aniline (E-10)

The general procedure was used to react N-benzyl-4-chloroaniline (218 mg, 1.0 mmol) with diphenylacetylene (2, 214 mg, 1.2 mmol). Purification by chromatography (PE/EtOAc = 30:1, \( R_f = 0.33 \)) gave product \( \text{E-10} \) (315 mg, 0.80 mmol, 80 \%) as a colorless solid.

\(^1\)H NMR (500 MHz, CDCl\(_3\)): \( \delta = 4.08 \) (br. s, 1 H), 5.05 (s, 1 H), 6.47 (d, \( J = 8.7 \) Hz, 2 H), 6.72 (s, 1 H), 6.81-6.83 (m, 2 H), 6.85-6.87 (m, 2 H), 6.96-6.97 (m, 3 H), 6.99-7.02 (m, 3 H), 7.10-7.13 (m, 3 H), 7.17-7.24 (m, 3 H), 7.27-7.29 (m, 2 H) ppm.

\(^{13}\)C\(^{(1)}\)H NMR (125 MHz, DEPT, CDCl\(_3\)): \( \delta = 66.1 \) (CH), 114.7 (CH), 122.4 (C), 126.9 (CH), 127.4 (CH), 127.8 (CH) 127.9 (CH), 128.6 (CH), 128.98 (CH), 129.03 (CH), 129.3 (CH), 136.4 (C), 139.0 (C), 140.5 (C), 141.3 (C), 145.6 (C) ppm.

IR (neat): \( \lambda^{-1} = 3415 \) (NH), 3080, 3024, 1597, 1492, 1445, 1310, 1293, 1260, 1240, 1176, 1092, 1073, 1029, 813, 756, 693 cm\(^{-1}\).

MS (EI, 70 eV): \( m/z \) (%): 395 (7) [M\(^+\)], 269 (62) [M – C\(_{21}\)H\(_{17}\)]\(^+\), 191 (100), 91 (33), 77 (18) [M – C\(_{21}\)H\(_{17}\)ClN]\(^+\).

HRMS (EI, 70 eV): \( m/z \) [M\(^+\)] calcd for C\(_{27}\)H\(_{22}\)ClN: 395.1435; found 395.1440.
(E)-4-(Trifluoromethoxy)-N-(1,2,3-triphenylallyl)aniline (E-11)

The general procedure was used to react N-benzyl-4-(trifluoromethoxy)aniline (267 mg, 1.0 mmol) with diphenylacetylene (2, 214 mg, 1.2 mmol). Purification by chromatography (PE/EtOAc = 30:1, Rf = 0.31) gave product E-11 (331 mg, 0.74 mmol, 74 %) as a colorless solid.

1H NMR (500 MHz, CDCl3): δ = 4.14 (br. s, 1 H), 5.06-5.07 (s, 1 H), 6.52 (m, 2 H), 6.74-6.76 (m, 1 H), 6.84-6.97 (m, 9 H), 7.13-7.29 (m, 9 H) ppm.

13C{1H} NMR (125 MHz, DEPT, CDCl3): δ = 66.3 (CH), 113.9 (CH), 120.8 (q, J =256, CF3), 126.9 (CH), 127.5 (CH), 127.8 (CH), 127.9 (CH), 128.4 (CH) 128.6 (CH), 128.7 (CH), 129.0 (CH), 129.3 (CH), 136.4 (C), 139.0 (C), 140.6 (C), 141.3 (C), 145.9 (C) ppm.

19F{1H} NMR (470 MHz, CDCl3): δ = - 58.3 ppm.

IR (neat): λ−1 = 3420 (NH), 3059, 3027, 1612, 1509, 1492, 1447, 1250, 1220, 1201, 1153, 1127, 1073, 1046, 1029, 917, 830, 773, 756, 696, 669, 527 cm−1.

MS (El, 70 eV): m/z (%) = 445 (3) [M]+, 266 (100) [M – C14H11]+, 191 (84), 91 (27), 77 () [M – C22H17F3NO]+.

HRMS (El, 70 eV): m/z [M]+ calcd for C28H23F3NO: 445.1653; found 445.1637.
(E)-4-(Trifluoromethyl)-N-(1,2,3-triphenylallyl)aniline (E-12)

The general procedure was used to react N-benzyl-4-(trifluoromethyl)aniline (251 mg, 1.0 mmol) with diphenylacetylene (2, 214 mg, 1.2 mmol). Purification by chromatography (PE/EtOAc = 30:1, \( R_f = 0.22 \)) gave product E-12 (278 mg, 0.65 mmol, 65 %) as a yellow solid.

\(^1\)H NMR (500 MHz, CDCl\(_3\)): \( \delta = 4.38 \) (br. s, 1 H), 5.15 (s, 1 H), 6.57-6.59 (m, 2 H), 6.71 (s, 1 H), 6.82-6.88 (m, 4 H), 6.98 (s, 1 H), 7.15-7.16 (m, 3 H), 7.21-7.32 (m, 7 H) ppm.

\(^{13}\)C\(\{^1\)H\}\) NMR (125 MHz, DEPT, CDCl\(_3\)): \( \delta = 65.6 \) (CH), 112.8 (CH), 119.4 (q, \( J = 33 \) Hz, C), 125.0 (q, \( J = 270 \) Hz, CF\(_3\)), 126.6 (q, \( J = 4 \) Hz, CH), 127.0 (CH), 127.6 (CH) 127.8 (CH), 128.0 (CH), 128.6 (CH), 128.7 (CH), 128.8 (CH), 129.1 (CH), 129.3 (CH), 136.3 (C), 138.9 (C), 140.2 (C), 140.9 (C), 149.5 (C) ppm.

\(^{19}\)F\(\{^1\)H\}\) NMR (470 MHz, CDCl\(_3\)): \( \delta = -60.1 \) ppm.

IR (neat): \( \lambda^\circ \) = 3420 (NH), 3058, 3027, 1614, 1527, 1492, 1447, 1316, 1270, 1246, 1186, 1160, 1104, 1063, 1029, 1006, 921, 823, 756, 696 cm\(^{-1}\).

MS (El, 70 eV): \( m/z \) (%) = 429 (3) [M]+, 269 (21) [M – C\(_7\)H\(_5\)F\(_3\)N]+, 250 (100) [M – C\(_{14}\)H\(_{11}\)]+, 191 (51), 91 (18), 77 [M – C\(_{22}\)H\(_{17}\)F\(_3\)N]+.

HRMS (El, 70 eV): \( m/z \) [M]+ calcd for C\(_{28}\)H\(_{22}\)F\(_3\)N: 429.1704; found 429.1694.
(E)-4-(((Trifluoromethyl)thio)-N-(1,2,3-triphenylallyl)aniline (E-13)

The general procedure was used to react N-benzyl-4-(((trifluoromethyl)thio)aniline (229 mg, 1.0 mmol) with diphenylacetylene (2, 214 mg, 1.2 mmol). Purification by chromatography (PE/EtOAc = 30:1, Rf = 0.22) gave product E-13 (275 mg, 0.60 mmol, 60%) as a yellow solid.

\(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta = 4.37\) (br. s, 1 H), 5.13 (s, 1 H), 6.55-6.57 (m, 2 H), 6.72 (s, 1 H), 6.82-6.84 (m, 2 H), 6.87-6.89 (m, 2 H), 6.97-6.99 (m, 3 H), 7.13-7.16 (m, 3 H), 7.21-7.30 (m, 5 H), 7.31-7.35 (m, 2 H) ppm.

\(^{13}\)C\(^{1}\)H NMR (125 MHz, DEPT, CDCl\(_3\)): \(\delta = 65.7\) (CH), 110.4 (CH), 114.0 (CH), 127.0 (CH), 127.6 (CH), 127.8 (CH), 127.9 (CH) 128.6 (CH), 128.7 (CH), 128.8 (CH), 129.0 (CH), 129.3 (CH), 129.9 (q, J = 308, CF\(_3\)), 136.3 (C), 138.1 (CH), 140.2 (C), 140.9 (C), 149.2 (C) ppm.

\(^{19}\)F\(^{1}\)H NMR (470 MHz, CDCl\(_3\)): \(\delta = -44.4\) ppm.

IR (neat): \(\lambda^{-1} = 3422\) (NH), 3057, 3026, 1593, 1500, 1472, 1447, 1320, 1296, 1264, 1184, 1147, 1112, 1087, 1029, 1004, 923, 819, 753, 737, 696, 637, 619, 599, 579, 560, 543, 520 cm\(^{-1}\).

MS (El, 70 eV): \(m/z\) (%) = 461 (5) [M]\(^+\), 282 (75) [M – C\(_{14}\)H\(_{11}\)]\(^+\), 269 (65) [M – C\(_7\)H\(_5\)F\(_3\)NS]\(^+\), 191 (100), 91 (29), 77 (4) [M – C\(_{22}\)H\(_{17}\)F\(_3\)NS]\(^+\).

HRMS (El, 70 eV): \(m/z\) [M]\(^+\) calcd for C\(_{28}\)H\(_{22}\)F\(_3\)NS: 461.1425; found 461.1411.
(E)-N-(1-(4-Bromophenyl)-2,3-diphenylallyl)aniline (E-14)

![Structure of (E)-N-(1-(4-Bromophenyl)-2,3-diphenylallyl)aniline (E-14)](image)

The general procedure was used to react N-(4-bromobenzyl)aniline (262 mg, 1.0 mmol) with diphenylacetylene (2, 214 mg, 1.2 mmol). Purification by chromatography (PE/EtOAc = 30:1, Rf = 0.27) gave product E-14 (335 mg, 0.76 mmol, 76%) as a colorless solid.

**1H NMR** (500 MHz, CDCl₃): δ = 4.01 (br. s, 1 H), 5.08 (s, 1 H), 6.54 (d, J = 7.7 Hz, 2 H), 6.63 (t, J = 7.3 Hz, 1 H), 6.70 (s, 1 H), 6.80-6.82 (m, 2 H), 6.87-6.89 (m, 2 H), 6.96-6.97 (m, 3 H), 7.04-7.07 (m, 2 H), 7.13-7.18 (m, 5 H), 7.33-7.36 (m, 2 H) ppm.

**13C{1H} NMR** (125 MHz, DEPT, CDCl₃): δ = 65.5 (CH), 113.6 (CH), 118.0 (CH), 121.4 (C), 126.9 (CH), 127.5 (CH), 127.9 (CH) 128.7 (CH), 128.8 (CH), 129.0 (CH), 129.2 (CH), 129.3 (CH), 129.4 (CH), 131.7 (CH), 136.3 (C), 138.8 (C), 140.2 (C), 141.4 (C), 146.8 (C) ppm.

**IR** (neat): \( \tilde{\nu} \) = 3419 (NH), 3052, 3023, 1602, 1500, 1484, 1427, 1312, 1264, 1180, 1072, 1010, 870, 834, 734, 691 cm⁻¹.

**MS** (El, 70 eV): \( m/z \) (%) = 439 (2) [M⁺], 347 (15) [M - C₆H₆N⁺], 268 (100), 262 (67) [M - C₁₄H₁₁⁺], 191 (14), 178 (17) [M - C₁₃H₁₁BrN⁺], 91 (8), 77 (51) [M - C₂₁H₁₇BrN⁺].

**HRMS** (El, 70 eV): \( m/z \) [M⁺] calcd for C₂₇H₂₂BrN: 439.0936; found 439.0921.
(E)-N-(1-(4-Chlorophenyl)-2,3-diphenylallyl)aniline (E-15)

The general procedure was used to react N-(4-chlorobenzyl)aniline (218 mg, 1.0 mmol) with diphenylacetylene (2, 214 mg, 1.2 mmol). Purification by chromatography (PE/EtOAc = 30:1, Rf = 0.32) gave product E-15 (253 mg, 0.64 mmol, 64 %) as a colorless solid. The solid was dissolved in CH₂Cl₂ and the solution was transferred into an NMR tube. Afterwards, n-hexane was carefully added on top of the CH₂Cl₂ and the mixture was allowed to stand at room temperature until crystals suitable for X-ray analysis were formed (Table S4, Figure S79-81).

¹H NMR (500 MHz, CDCl₃): δ = 4.01 (br. s, 1 H), 5.09 (s, 1 H), 6.54 (d, J = 7.8 Hz, 2 H), 6.62 (t, J = 7.3 Hz, 1 H), 6.71 (s, 1 H), 6.80-6.82 (m, 2 H), 6.87-6.89 (m, 2 H), 6.95-6.96 (m, 3 H), 7.05-7.08 (m, 2 H), 7.13-7.17 (m, 3 H), 7.21-7.23 (m, 4 H) ppm.

¹³C{¹H} NMR (125 MHz, DEPT, CDCl₃): δ = 65.6 (CH), 113.8 (CH), 118.2 (CH), 127.1 (CH), 127.7 (CH), 128.0, 128.8 (CH), 128.90 (CH), 128.93 (CH), 129.2 (CH), 129.26 (CH), 129.34 (CH), 129.4 (CH), 129.4 (CH), 133.5 (C), 136.5 (C), 139.0 (C), 139.8 (C), 141.6 (C), 147.0 (C) ppm.

IR (neat): λ⁻¹ = 3393 (NH), 3077, 3054, 3019, 2837, 1600, 1573, 1500, 1492, 1484, 1446, 1442, 1427, 1401, 1304, 1283, 1260, 1230, 1183, 1174, 1156, 1123, 1103, 1087, 1074, 1029, 1011, 1003, 990, 930, 917, 878, 870, 834, 816, 807, 776, 766, 756, 746, 723, 719, 693, 639, 609, 581, 544, 533, 517 cm⁻¹.

MS (EI, 70 eV): m/z (%) = 395 (7) [M]+, 303 (33) [M – C₆H₆N]+, 225 (36), 216 (100) [M – C₁₄H₁₁]+, 91 (16), 77 (29) [M – C₂₁H₁₇ClN]+.

HRMS (EI, 70 eV): m/z [M]+ calcd for C₂₇H₂₂ClN: 395.1435; found 395.1435.
(E)-N-(1-(3-Bromophenyl)-2,3-diphenylallyl)aniline (E-16)

The general procedure was used to react N-(3-bromobenzyl)aniline (262 mg, 1.0 mmol) with diphenylacetylene (2, 214 mg, 1.2 mmol). Purification by chromatography (PE/EtOAc = 30:1, $R_f = 0.24$) gave product E-16 (149 mg, 0.34 mmol, 34 %) as a colorless solid.

$^1$H NMR (500 MHz, CDCl$_3$): $\delta = 4.02$ (br. s, 1 H), 5.09 (s, 1 H), 6.55 (d, $J = 7.8$ Hz, 2 H), 6.63 (t, $J = 7.3$ Hz, 1 H), 6.70 (s, 1 H), 6.81-6.83 (m, 2 H), 6.88-6.90 (m, 2 H), 6.96-6.97 (m, 3 H), 7.05-7.08 (m, 3 H), 7.13-7.15 (m, 3 H), 7.20-7.22 (m, 1 H), 7.29-7.31 (m, 1 H), 7.47 (t, $J = 1.7$ Hz, 1 H) ppm.

$^{13}$C{H} NMR (125 MHz, DEPT, CDCl$_3$): $\delta = 64.6$ (CH), 112.7 (CH), 117.1 (CH), 121.8 (C), 125.4 (CH), 125.9 (CH), 126.5 (CH) 126.9 (CH), 127.7 (CH), 128.0 (CH), 128.2 (CH), 128.3 (CH), 129.1 (CH), 129.7 (CH), 135.2 (CH), 137.7 (C), 140.2 (C), 142.5 (C), 145.8 (C) ppm.

IR (neat): $\lambda^{-1} = 3413$ (NH), 3079, 3051, 3022, 1732, 1600, 1569, 1500, 1472, 1446, 1442, 1427, 1310, 1263, 1243, 1180, 1126, 1072, 1027, 996, 926, 870, 787, 776, 747, 737, 717, 690, 610 cm$^{-1}$.

MS (EI, 70 eV): $m/z$ (%) = 439 (7) [M$^+$], 347 (16) [M – C$_6$H$_5$N$^+$], 268 (100), 260 (91) [M – C$_{14}$H$_{11}$]$^+$, 191 (27), 178 (30) [M – C$_{13}$H$_{11}$BrN$^+$], 91 (10), 77 (64) [M – C$_{21}$H$_{17}$BrN$^+$].

HRMS (EI, 70 eV): $m/z$ [M$^+$] calcd for C$_{27}$H$_{22}$BrN: 439.0936; found 439.0916.
(E)-N-(2,3-Diphenyl-1-(4-(trifluoromethyl)phenyl)allyl)aniline (E-17)

The general procedure was used to react N-(4-(trifluoromethyl)benzyl)aniline (201 mg, 1.0 mmol) with diphenylacetylene (2, 214 mg, 1.2 mmol). Purification by chromatography (PE/EtOAc = 30:1, $R_f = 0.23$) gave product E-17 (296 mg, 0.69 mmol, 69%) as a colorless solid.

$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ = 4.04 (br. s, 1 H), 5.19 (s, 1 H), 6.52 (d, $J = 7.7$ Hz, 2 H), 6.61 (t, $J = 7.3$ Hz, 1 H), 6.69 (s, 1 H), 6.79-6.81 (m, 2 H), 6.87-6.88 (m, 2 H), 6.94-6.95 (m, 3 H), 7.03-7.06 (m, 2 H), 7.11-7.13 (m, 3 H), 7.40 (d, $J = 8.2$ Hz, 1 H), 7.47 (d, $J = 8.2$ Hz, 1 H) ppm.

$^{13}$C($^1$H) NMR (125 MHz, DEPT, CDCl$_3$): $\delta$ = 65.5 (CH), 113.7 (CH), 120.9 (CH), 122.0 (q, $J = 272$ Hz, CF$_3$), 125.6 (q, $J = 4$ Hz, CH), 127.0 (CH), 127.7 (CH) 127.9 (CH), 128.0 (CH), 128.7 (CH), 129.0 (CH), 129.2 (CH), 129.29 (CH), 129.34 (CH), 129.8 (q, $J = 32$ Hz, C), 136.2 (C), 138.6 (C), 141.3 (C), 145.3 (C) 146.7 (C) ppm.

$^{19}$F($^1$H) NMR (470 MHz, CDCl$_3$): $\delta$ = -62.2 ppm.

IR (neat): $\lambda$$^{-1}$ = 3414 (NH), 3053, 3023, 1734, 1617, 1602, 1500, 1427, 1414, 1322, 1263, 1243, 1164, 1122, 1109, 1066, 1029, 1017, 993, 924, 871, 844, 777, 749, 690, 637, 629, 613, 597, 561, 543, 507 cm$^{-1}$.

MS (El, 70 eV): $m/z$ (%) = 429 (11) [M]$^+$, 337 (27) [M – C$_6$H$_6$N]$^+$, 259 (49), 250 (100) [M – C$_{14}$H$_{11}$]$^+$, 91 (16), 77 (62) [M – C$_{22}$H$_{17}$F$_3$N]$^+$.

HRMS (El, 70 eV): $m/z$ [M]$^+$ calcd for C$_{29}$H$_{22}$F$_3$N: 429.1704; found 429.1703.
The general procedure was used to react \( N \)-\( (3\text{-}(\text{trifluoromethyl})\text{benzyl})\text{aniline} \) (201 mg, 1.0 mmol) with diphenylacetylene (2, 214 mg, 1.2 mmol). Purification by chromatography (PE/EtOAc = 30:1, \( R_f = 0.20 \)) gave product \( \text{E-18} \) (278 mg, 0.65 mmol, 65 %) as a colorless solid.

\( ^1\text{H NMR} \) (500 MHz, CDCl\(_3\)): \( \delta = 4.29 \) (br. s, 1 H), 5.44 (s, 1 H), 6.80 (d, \( J = 8.4 \) Hz, 2 H), 6.87 (t, \( J = 7.3 \) Hz, 1 H), 6.96 (s, 1 H), 7.05-7.07 (m, 2 H), 7.19-7.20 (m, 2 H), 7.31 (t, \( J = 7.5 \) Hz, 2 H), 7.36-7.37 (m, 3 H), 7.55 (t, \( J = 7.7 \) Hz, 1 H), 7.67 (d, \( J = 7.7 \) Hz, 1 H), 7.72 (d, \( J = 7.7 \) Hz, 1 H), 7.81 (s, 1 H) ppm.

\( ^{13}\text{C}^{\text{1H}} \text{NMR} \) (125 MHz, DEPT, CDCl\(_3\)): \( \delta = 65.9 \) (CH), 113.9 (CH), 118.3 (CH), 124.2 (q, \( J = 272 \) Hz, CF\(_3\)), 124.6 (q, \( J = 4 \) Hz, CH), 127.2 (CH), 127.8 (CH) 128.1 (CH), 128.9 (CH), 129.2 (CH), 129.37 (CH), 129.40 (CH), 129.43 (CH) 131.1 (q, \( J = 32 \) Hz, C), 131.2 (CH), 136.3 (C), 136.3 (C), 138.7 (C), 141.4 (C) 142.4 (C), 146.9 (C) ppm.

\( ^{19}\text{F}^{\text{1H}} \text{NMR} \) (470 MHz, CDCl\(_3\)): \( \delta = -62.3 \) ppm.

\( \text{IR} \) (neat): \( \lambda^{-1} = 3415 \) (NH), 3053, 3023, 1602, 1500, 1447, 1426, 1326, 1313, 1264, 1163, 1122, 1094, 1072, 804, 747, 690 cm\(^{-1} \).

\( \text{MS} \) (El, 70 eV): \( m/z \% = 429 \) (9) [M]+, 337 (31) [M – C\(_6\)H\(_5\)N]+, 259 (33), 250 (100) [M – C\(_{14}\)H\(_{11}\)]+; 91 (16), 77 (36) [M – C\(_{22}\)H\(_{17}\)F\(_3\)N]+.

\( \text{HRMS} \) (El, 70 eV): \( m/z \) [M]+ calcd for C\(_{28}\)H\(_{22}\)F\(_3\)N: 429.1704; found 429.1694.
(E)-N-(1-(3-Chlorophenyl)-2,3-diphenylallyl)aniline (E-19)

The general procedure was used to react N-(3-chlorobenzyl)aniline (217 mg, 1.0 mmol) with diphenylacetylene (2, 214 mg, 1.2 mmol). Purification by chromatography (PE/EtOAc = 30:1, Rf = 0.20) gave product E-19 (276 mg, 0.70 mmol, 70%) as a colorless solid.

\(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta = 4.01\) (br. s, 1 H), 5.10 (s, 1 H), 6.53 (d, \(J = 8.8\) Hz, 2 H), 6.62 (t, \(J = 7.3\) Hz, 1 H), 6.70 (s, 1 H), 6.80-6.82 (m, 2 H), 6.87-6.89 (m, 2 H), 6.95-6.96 (m, 3 H), 7.04-7.07 (m, 2 H), 7.11-7.16 (m, 5 H), 7.31 (s, 1 H) ppm.

\(^1\)\(^3\)C{\(^1\)H} NMR (125 MHz, DEPT, CDCl\(_3\)): \(\delta = 65.7\) (CH), 113.8 (CH), 118.2 (CH), 126.1 (CH), 127.1 (CH), 127.7 (CH), 127.9 (CH) 128.0 (CH), 128.8 (CH), 129.2 (CH), 129.3 (CH), 129.4 (CH), 130.0 (CH), 134.7 (C), 136.4 (C), 138.9 (C), 141.4 (C), 143.4 (C), 147.0 (C) ppm.

IR (neat): \(\lambda^{-1} = 3413\) (NH), 3052, 3022, 2962, 1600, 1574, 1500, 1474, 1424, 1310, 1263, 1180, 1076, 789, 776, 747, 690 cm\(^{-1}\).

MS (El, 70 eV): \(m/z\) (%) = 395 (9) [M]+, 303 (23) [M – C\(_6\)H\(_6\)N]+, 225 (33), 216 (100) [M – C\(_{14}\)H\(_{11}\)]+, 91 (18), 77 (20) [M – C\(_{22}\)H\(_{17}\)F\(_3\)N]+.

HRMS (El, 70 eV): \(m/z\) [M]+ calcd for C\(_{27}\)H\(_{22}\)ClN: 395.1435; found 395.1435.
(E)-N-(2,3-Diphenyl-1-(trimethylsilyl)allyl)aniline (E-21)

The general procedure was used to react N-((trimethylsilyl)methyl)aniline (79 mg, 1.0 mmol) with diphenylacetylene (2, 214 mg, 1.2 mmol). Purification by chromatography (PE/EtOAc = 30:1, Rf = 0.35) gave product E-21 (181 mg, 0.51 mmol, 51%) as a colorless solid. Prior to chromatography, the ratio of the E and the Z product was determined by GC analysis to be 99:1.

\[ \text{H NMR} \text{ (500 MHz, CDCl}_3\text{): } \delta = 0.00 \text{ (s, 9 H), } 3.94 \text{ (s, 1 H), } 3.97 \text{ (br. s, 1 H), } 6.54 \text{ (s, 1 H), } 6.69-6.72 \text{ (m, 1 H), } 6.79-6.81 \text{ (m, 2 H), } 6.99-7.07 \text{ (m, 3 H), } 7.19-7.23 \text{ (m, 4 H), } 7.25-7.28 \text{ (m, 3 H) ppm.} \]

\[ \text{C\{H\}} \text{ NMR (125 MHz, DEPT, CDCl}_3\text{): } \delta = -2.6 \text{ (CH}_3\text{), } 54.0 \text{ (CH), } 113.4 \text{ (CH), } 117.4 \text{ (CH), } 125.2 \text{ (CH), } 126.0 \text{ (CH), } 127.4 \text{ (CH), } 127.9 \text{ (CH), } 128.5 \text{ (CH), } 129.1 \text{ (CH), } 129.4 \text{ (CH), } 129.6 \text{ (CH), } 137.8 \text{ (C), } 140.1 \text{ (C), } 142.3 \text{ (C), } 148.9 \text{ (C) ppm.} \]

\[ \text{Si\{H\}} \text{ INEPT NMR (99 MHz, 305.0 K, CDCl}_3\text{, D3 = 0.0068 s, D4 = 0.0313 s): } \delta = 4.6 \text{ ppm} \]

\[ \text{IR (neat): } \lambda_{\text{max}}(\text{cm}^{-1}) = 3396 \text{ (NH), } 3054, 3018, 2952, 2858, 1602, 1573, 1494, 1439, 1429, 1309, 1262, 1249, 1180, 1154, 1074, 1021, 924, 894, 870, 834, 816, 790, 776, 751, 721, 703, 691, 649, 619, 609, 560 \text{ cm}^{-1}. \]

\[ \text{MS (EI, 70 eV): } m/z(\%) = 357 \text{ (29)[M]}; 284 \text{ (100)[M - C}_3\text{H}_9\text{Si]; 191 (38), 91 (49), 73 (34)[M - C}_{21}\text{H}_{18}\text{N].} \]

\[ \text{HRMS (EI, 70 eV): } m/z[M]^+ \text{ calcd for C}_{24}\text{H}_{27}\text{NSi: } 357.1907; \text{ found } 357.1904. \]
(E)-N-(1,2-Diphenylpent-1-en-3-yl)aniline (E-22)

The general procedure was used to react N-propylaniline (135 mg, 1.0 mmol) with diphenylacetylene (2, 214 mg, 1.2 mmol) for 20 h. Purification by chromatography (PE/EtOAc = 60:1, \( R_f = 0.23 \)) and subsequent bulb-to-bulb distillation (250 °C, 8 \times 10^{-2} \text{ mbar}) gave product E-22 (30 mg, 0.10 mmol, 10%) as a yellow oil.

\(^1\text{H} \text{NMR} \ (500 \text{ MHz, C}_6\text{D}_6): \ \delta = 0.88 \ (t, J = 7.4 \text{ Hz, } 3 \text{ H}), 1.29 \ (dqd, J = 7.4, 7.4, 13.7 \text{ Hz, } 1 \text{ H}), 1.50 \ (dqd, J = 7.4, 7.4, 13.7 \text{ Hz, } 1 \text{ H}), 3.37 \ (br. s, 1 \text{ H}), 3.94 \ (t, J = 6.8 \text{ Hz, } 1 \text{ H}), 6.61 \ (s, 1 \text{ H}), 6.64-6.66 \ (m, 2 \text{ H}), 6.75 \ (tt, J = 1.1, 7.4 \text{ Hz, } 1 \text{ H}), 6.86-6.95 \ (m, 5 \text{ H}), 7.03-7.10 \ (m, 5 \text{ H}) \ 7.17-7.23 \ (m, 2 \text{ H}) \text{ ppm.}

\(^{13}\text{C}\{^1\text{H}\} \text{NMR} \ (125 \text{ MHz, DEPT, C}_6\text{D}_6): \ \delta = 11.1 \ (\text{CH}_3), 27.8 \ (\text{CH}_2), 63.3 \ (\text{CH}), 113.9 \ (\text{CH}), 117.7 \ (\text{CH}), 126.9 \ (\text{CH}), 127.4 \ (\text{CH}), 128.8 \ (\text{CH}), 129.1 \ (\text{CH}), 129.6 \ (\text{CH}), 129.6 \ (\text{CH}), 129.7 \ (\text{CH}), 137.1 \ (\text{C}), 139.2 \ (\text{C}), 143.0 \ (\text{C}), 148.1 \ (\text{C}) \text{ ppm.}

\text{IR (neat): } \lambda^{-1} = 3412 \ (\text{NH}), 3052, 3022, 2962, 2929, 1602, 1503, 1427, 1380, 1317, 1287, 1179, 1154, 1106, 1076, 1030, 917, 867, 812, 773, 747, 690, 613, 599, 537, 507 \text{ cm}^{-1}.

\text{MS (EI, } 70 \text{ eV): } m/z \% = 313 \ (7) \ [\text{M}]^+, 284 \ (100) \ [\text{M} - \text{C}_2\text{H}_5]^+, 206 \ (13), 191 \ (18), 178 \ (20), 165 \ (9), 134 \ (58) \ [\text{M} - \text{C}_14\text{H}_{11}]^+, 91 \ (49), 77 \ (29) \ [\text{C}_6\text{H}_5]^+, 65 \ (9), 51 \ (9).

\text{HRMS (EI, } 70 \text{ eV): } m/z \ [\text{M}]^+ \text{ calcd for C}_{27}\text{H}_{23}\text{N: } 313.1825; \text{ found } 313.1826.
(E)-N-Isopropyl-1,2,3-triphenylprop-2-en-1-amine (E-23)

The general procedure was used to react N-benzylpropan-2-amine (149 mg, 1.0 mmol) with diphenylacetylene (2, 214 mg, 1.2 mmol) for 20 h. Purification by chromatography (PE/EtOAc = 15:1, Rf = 0.21) gave product E-23 (79 mg, 0.24 mmol, 24 %) as a yellow oil.

The yellow oil was transferred into a small flask and HCl (2 M in Diethylether) was added to from the corresponding hydrochloride. The resulting solid was dissolved in CH₂Cl₂ and the solution was transferred into an NMR tube. Afterwards, n-hexane was carefully added on top of the CH₂Cl₂ and the mixture was allowed to stand at room temperature until crystals suitable for X-ray analysis were formed (Table S4, Figure S82-84).

**1H NMR** (500 MHz, C₆D₆): δ = 1.02 (d, J = 6.4 Hz, 3 H), 1.03 (d, J = 6.4 Hz, 3 H), 1.33 (br. s, 1 H), 2.95 (sept, J = 6.3 Hz, 1 H), 4.73 (s, 1 H), 6.88-6.92 (m, 1 H), 6.94-7.05 (m, 8 H), 7.06-7.12 (m, 3 H), 7.17-7.21 (m, 2 H), 7.42 (d, J = 7.3 Hz, 2 H) ppm.

**13C{¹H} NMR** (125 MHz, JMOD, C₆D₆): δ = 23.1 (CH₃), 23.6 (CH₃), 46.3 (CH), 67.9 (CH), 126.9 (CH), 127.3 (CH), 127.3 (CH), 128.5 (CH), 128.7 (CH), 129.7 (CH), 129.8 (CH), 137.5 (C), 140.3 (C), 143.1 (C), 145.0 (C) ppm.

**IR** (neat): λ⁻¹ = 3080, 3056, 3023, 2959, 2927, 2865, 1599, 1574, 1492, 1467, 1446, 1379, 1366, 1340, 1167, 1070, 1029, 920, 843, 820, 754, 693, 622, 600, 566, 544, 514 cm⁻¹.

**MS** (EI, 70 eV): m/z (%) = 327 (2) [M]+, 191 (11), 178 (9), 165 (7), 148 (100) [M – C₁₄H₁₁]+, 106 (31), 91 (7), 79 (16).

**HRMS** (EI, 70 eV): m/z [M]+ calcd for C₂₄H₂₅N: 327.1982; found 327.1973.
(E)-N-(2-Ethyl-1-phenylpent-2-en-1-yl)aniline (E-24)

The general procedure was used to react N-benzylaniline (1, 183 mg, 1.0 mmol) with hex-3-yne (20, 99 mg, 1.2 mmol) for 20 h. Purification by chromatography (PE/EtOAc = 30:1, Rf = 0.36) gave product E-24 (224 mg, 0.84 mmol, 84 %) as a colorless oil.

$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ = 1.02 (t, $J$ = 7.4 Hz, 3 H), 1.05 (t, $J$ = 7.4 Hz, 3 H), 1.99-2.25 (m, 4 H), 3.90 (br. s, 1 H), 4.98 (d, $J$ = 4.5 Hz, 1 H), 5.66 (dt, $J$ = 1.2, 7.3 Hz, 1 H), 6.64-6.69 (m, 2 H), 6.85-6.90 (m, 1 H), 7.22-7.26 (m, 1 H), 7.27-7.35 (m, 4 H), 7.43-7.47 (m, 2 H) ppm.

$^{13}$C($^1$H) NMR (125 MHz, JMOD, CDCl$_3$): $\delta$ = 14.1 (CH$_3$), 14.5 (CH$_3$), 21.2 (CH$_2$), 22.6 (CH$_2$), 63.9 (CH), 113.9 (CH), 117.8 (CH), 127.5 (CH), 128.8 (CH), 129.3 (CH), 129.4 (CH), 140.3 (C), 142.6 (C), 148.1 (C) ppm.

IR (neat): $\tilde{\nu}$ =3413 (NH), 3052, 3026, 2962, 2932, 2872, 1600, 1500, 1464, 1452, 1424, 1374, 1337, 1313, 1260, 1242, 1179, 1154, 1120, 1074, 1064, 1029, 993, 917, 866, 746, 699, 690, 619, 587, 559, 509 cm$^{-1}$.

MS (EI, 70 eV): $m/z$ (%) = 265 (27) [M]$^+$, 236 (33) [M – C$_2$H$_5$]$^+$, 182 (60) [M – C$_6$H$_{11}$]$^+$, 173 (42) [M – C$_5$H$_5$N]$^+$, 131 (100), 117 (62), 104 (27), 91 (42), 77 (50) [C$_6$H$_5$]$^+$, 65 (9).

HRMS (EI, 70 eV): $m/z$ [M]$^+$ calcd for C$_{27}$H$_{23}$N: 265.1825; found 265.1826.
**N-(3,3-Dimethyl-2-methylenbutyl)aniline (27)**

In a glovebox under N\textsubscript{2}-atmosphere, a schlenk tube with magnetic stir bar (6 mm) was charged with catalyst IV (54 mg, 0.10 mmol, 10 mol%), the N-methylaniline (25, 107 mg, 1.0 mmol, 1.0 equiv), and the tert-butylacetylene (26, 164 mg, 2 mmol, 2 equiv). Afterwards, everything was dissolved in toluene (1 mL). The tube was heated in an oil bath to 145 °C for 10 h. The Schlenk tube was then cooled to room temperature and opened. The crude reaction mixture was transferred into a flask with CH\textsubscript{2}Cl\textsubscript{2} (10 mL). After the solvent had been evaporated, purification by chromatography (PE/MTBE/Et\textsubscript{2}O = 200:1:1, RF = 0.1) gave product 27 (45 mg, 0.24 mmol, 24 %) as a yellow oil.

The yellow oil was transferred into a flask and HCl (2 M in Diethylether) was added to from the corresponding hydrochloride. Afterwards petroleum ether was carefully added on top of the diethylether and the mixture was allowed to stand at −20 °C until crystals suitable for X-ray analysis were formed (Table S4, Figure S85-87).

\[^{1}H\] NMR (500 MHz, CDCl\textsubscript{3}): \(\delta = 1.16\) (s, 9 H), 3.80 (s, 2 H), 5.00 (d, \(J = 1.2\) Hz, 1 H), 5.04 (d, \(J = 1.3\) Hz, 1 H), 6.61-6.63 (m, 2 H), 6.69-6.72 (m, 1 H), 7.16-7.29 (m, 2 H) ppm.

\[^{13}C\]\[^{1}H\] NMR (125 MHz, DEPT, CDCl\textsubscript{3}): \(\delta = 29.3\) (CH\textsubscript{3}), 35.3 (C), 45.2 (CH\textsubscript{2}), 107.6 (CH\textsubscript{2}), 113.0 (CH), 117.4 (CH), 129.2 (CH), 148.0 (C), 154.2(C) ppm.

IR (neat): \(\tilde{\nu} = 3420\) (NH), 3052, 3021,2963, 2870, 1736, 1637, 1602, 1505, 1479, 1464, 1429, 1385, 1362, 1329, 1268, 1202, 1154,1098, 900, 796,747 cm\(^{-1}\).

MS (EI, 70 eV): \(m/z\) (%) = 189 (20) [M]\(^+\), 132 (20), 106 (100).

HRMS (EI, 70 eV): \(m/z\) [M]\(^+\) calcd for C\textsubscript{13}H\textsubscript{19}N: 189.1512; found 189.1514.
5. Poor Substrates

No reaction was observed with the following N-benzylaniline derivatives:

Substrates which showed side reactions in reactions catalyzed by II and/or poor regioselectivity.
6. Synthesis of Ligand Precursor for Catalyst II

In comparison to the literature procedure,[4] the synthesis of catalyst II, was slightly optimized (optimized parameters are highlighted in *italics*). All other steps are similar to the literature.[4]

1-Bromo-3,5-di-tert-butylbenzene

![Chemical structure](image)

A two necked round bottom flask was charged with 1,3,5-tri-tert-butylbenzene (10.00 g, 40.6 mmol), iron powder (2.79 g, 49.9 mmol), chloroform (30 mL), and a magnetic stir bar. Over the course of 1 h a solution of bromine (13.63 g, 85.3 mmol) in chloroform (10 mL) was added dropwise under vigorous stirring. The solution was stirred at room temperature for 16 h before being poured into ice-water (100 mL). The organic layer was separated and washed with concentrated sodium bisulfite solution (3 × 50 mL), dried with MgSO\textsubscript{4} and the solvent was removed under reduced pressure. The crude product was purified by bulb-to-bulb distillation (180 °C, 30 mbar) to give the product (7.78 g, 28.9 mmol, 71 %) as a colorless solid.

\textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}): \(\delta = 1.31 (s, 18 H), 7.33 (s, 3 H)\) ppm.

\textsuperscript{13}C{\textsuperscript{1}H} NMR (125 MHz, DEPT, CDCl\textsubscript{3}): \(\delta = 31.5 (CH\textsubscript{3}), 35.2 (C), 121.2 (CH), 122.4 (C), 125.9 (CH), 153.2 (C)\) ppm.

\(N^2,N^6\)-Bis(3,5-di-tert-butylphenyl)pyridine-2,6-diamine

In a glovebox under nitrogen atmosphere, a dried Schlenk flask was charged with NaO\textsuperscript{Bu} (8.07 g, 84.0 mmol), DPEphos (1.29 g, 2.4 mmol), Pd\textsubscript{2}(dba)\textsubscript{3} (1.10 g, 1.2 mmol), and a magnetic stir bar. Subsequently, under argon counterflow, 1-bromo-3,5-di-tert-butylbenzene (19.39 g, 72.0 mmol), 2,6-diaminopyridine (3.27 g, 30.0 mmol), and toluene (150 mL) was added and an oven-dried reflux condenser was attached to the flask. The mixture was heated to 110 °C for 19.5 h and after cooling to room temperature, wet Et\textsubscript{2}O (100 mL) was added. The resulting slurry was filtered through Celite\textsuperscript{®}, washed with brine (3 × 80 mL), and dried with MgSO\textsubscript{4}. After thoroughly removing all solvent under reduced pressure, the residue was recrystallized from ethanol (250 mL) to give the product (5.47 g, 11.3 mmol, 37 %) as a colorless solid.

\textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}): \(\delta = 1.34 (s, 36 H), 6.30 (d, J = 8.0 Hz, 2 H), 6.68 (br.s, 2 H), 7.13-7.18 (m, 6 H), 7.34 (t, J = 8.0 Hz, 1 H)\) ppm.

\textsuperscript{13}C{\textsuperscript{1}H} NMR (125 MHz, JMOD, CDCl\textsubscript{3}): \(\delta = 31.6 (CH\textsubscript{3}), 35.1 (C), 97.6 (CH), 116.4 (CH), 117.8 (CH), 139.4 (C), 140.2 (CH), 152.0 (C), 155.3 (C)\) ppm.
7. Mechanistic Studies

Titanaaziridine 4 (30 mg, 0.048 mmol) and diphenylacetylene (2, 9 mg, 0.048 mmol) were dissolved in 0.6 mL of C_6D_6. The reaction mixture was allowed to stand for 24 h at room temperature which revealed a slow reaction progress. Subsequent heating of the reaction mixture to 80 °C for 48 h revealed nearly complete consumption of both starting materials. The solution was transferred into a vial and all volatile components were removed under vacuum. The residue was washed with small amounts of n-pentane (2×1 mL) and dried under vacuum to give 5 (23 mg, 0.029 mmol, 60 %) as a red brown solid.

^1H NMR (300 MHz, C_6D_6, 298 K): δ = 1.51-1.84 (m, 18H, CH_Ad/CH_2,Ad), 2.03-2.05 (m, 8H, CH_exo, CH_Ad/CH_2,Ad), 2.32-2.35 (m, 4H, CH_Ad/CH_2,Ad), 5.75-5.77 (m, 4H, C_5H_4), 6.40-6.41 (m, 4H, C_5H_4), 6.66-6.86 (m, 4H, CH_Aryl), 6.90-7.20 (m, 12H, CH_Aryl)*, 7.80-7.83 (m, 3H, CH_Aryl), 8.13 (m, 1H, CH_Aryl) ppm.

^13C{^1H} NMR (75 MHz, C_6D_6, 298 K): δ = 28.3 (CH_Ad), 28.5 (CH_Ad), 32.3 (CH_Ad), 33.1 (CH_2,Ad), 38.3 (CH_2,Ad), 38.7 (CH_2,Ad), 45.1 (CH_exo), 111.5 (C_5H_4), 113.2 (C_5H_4), 125.7 (C_5), 126.1 (CH_Aryl), 127.6 (CH_Aryl), 128.7 (CH_Aryl), 128.9 (CH_Aryl), 129.2 (CH_Aryl), 129.4 (CH_Aryl), 131.3 (CH_Aryl), 132.0 (CH_Aryl), 138.4 (C_5), 142.4 (C_5), 152.9 (C_5), 160.0 (CH_Aryl), 196.5 (Ti=C=Ti) ppm.

Note: The other signals overlap with the C_6D_6 signal.

HRMS (LIFDI): m/z [M]^+ calcd for C_57H_59NTi: 805.97; found 805.41.
8. NMR Spectra

(E)-N-(1,2,3-Triphenylallyl)aniline (E-3)

**Figure S3**: $^1$H NMR spectrum (500 MHz, 305 K, CDCl$_3$).

**Figure S4**: $^{13}$C($^1$H) NMR spectrum (125 MHz, 305 K, CDCl$_3$).
Figure S5: $^{13}$C/$^1$H HMQC NMR spectrum (125 MHz, 305 K, CDCl$_3$).

Figure S6: $^{13}$C/$^1$H HMBC NMR spectrum (125 MHz, 305 K, CDCl$_3$).
Figure S7: NOE spectrum (500 MHz, 305 K, CDCl₃).
(E)-4-Methyl-N-(1,2,3-triphenylallyl)aniline (E-6)

Figure S8: $^1$H NMR spectrum (500 MHz, 305 K, CDCl$_3$).

Figure S9: $^{13}$C($^1$H) NMR spectrum (125 MHz, 305 K, CDCl$_3$).
(E)-3-Methyl-N-(1,2,3-triphenylallyl)aniline (E-7)

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

**Figure S11:** $^{13}$C($^1$H) NMR spectrum (125 MHz, 305 K, CDCl$_3$).
(E)-4-Bromo-N-(1,2,3-triphenylallyl)aniline (E-8)

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$_3$).
(E)-3-Bromo-N-(1,2,3-triphenylallyl)aniline (E-9)

Figure S14: $^1$H NMR spectrum (500 MHz, 305 K, CDCl$_3$).

Figure S15: $^{13}$C($^1$H) NMR spectrum (125 MHz, 305 K, CDCl$_3$).
(E)-4-Chloro-N-(1,2,3-triphenylallyl)aniline (E-10)

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$_3$).
(E)-4-(Trifluoromethoxy)-N-(1,2,3-triphenylallyl)aniline (E-11)

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**: $^{19}$F($^1$H) NMR spectrum (470 MHz, 305 K, CDCl$_3$).
(E)-4-(Trifluoromethyl)-N-(1,2,3-triphenylallyl)aniline (E-12)

Figure S21: $^1$H NMR spectrum (500 MHz, 305 K, CDCl$_3$).

Figure S22: $^{13}$C($^1$H) NMR spectrum (125 MHz, 305 K, CDCl$_3$).
Figure S23: $^{19}$F($^1$H) NMR spectrum (470 MHz, 305 K, CDCl$_3$).
(E)-4-((Trifluoromethyl)thio)-N-(1,2,3-triphenylallyl)aniline (E-13)

Figure S24: $^1$H NMR spectrum (500 MHz, 305 K, CDCl$_3$).

Figure S25: $^{13}$C($^1$H) NMR spectrum (125 MHz, 305 K, CDCl$_3$).
Figure S26: $^{19}$F{H} NMR spectrum (470 MHz, 305 K, CDCl$_3$).
(E)-N-(1-(4-Bromophenyl)-2,3-diphenylallyl)aniline (E-14)

Figure S27: $^1$H NMR spectrum (500 MHz, 305 K, CDCl$_3$).

Figure S28: $^{13}$C($^1$H) NMR spectrum (125 MHz, 305 K, CDCl$_3$).
**(E)-N-(1-(4-Chlorophenyl)-2,3-diphenylallyl)aniline (E-15)**

**Figure S29:** $^1$H NMR spectrum (500 MHz, 305 K, CDCl$_3$).

**Figure S30:** $^{13}$C($^1$H) NMR spectrum (125 MHz, 305 K, CDCl$_3$).
\((E)-N-(1-(3\text{-Bromophenyl})-2,3\text{-diphenylylallyl})\text{aniline (E-16)}\)

\[\ \]

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

**Figure S32**: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (125 MHz, 305 K, CDCl$_3$).
(E)-N-(2,3-Diphenyl-1-(4-(trifluoromethyl)phenyl)allyl)aniline (E-17)

Figure S33: $^{13}$C($^1$H) NMR spectrum (500 MHz, 305 K, CDCl$_3$).

Figure S34: $^{13}$C($^1$H) spectrum (125 MHz, 305 K, CDCl$_3$).
Figure S35: $^{19}$F-{H} NMR spectrum (470 MHz, 305 K, CDCl$_3$).
(E)-N-(2,3-Diphenyl-1-(3-(trifluoromethyl)phenyl)allyl)aniline (E-18)

**Figure S36:** $^1$H NMR spectrum (500 MHz, 305 K, CDCl$_3$).

**Figure S37:** $^{13}$C($^1$H) NMR spectrum (125 MHz, 305 K, CDCl$_3$).
Figure S38: $^{19}$F($^1$H) NMR spectrum (470 MHz, 305 K, CDCl$_3$).
(E)-N-(1-(3-Chlorophenyl)-2,3-diphenylallyl)aniline (E-19)

Figure S39: $^1$H NMR spectrum (500 MHz, 305 K, CDCl$_3$).

Figure S40: $^{13}$C($^1$H) NMR spectrum (125 MHz, 305 K, CDCl$_3$).
(E)-N-(2,3-Diphenyl-1-(trimethylsilyl)allyl)aniline (E-21)

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: $^{29}$Si($^1$H) INEPT NMR (99 MHz, 305.0 K, CDCl$_3$, $D_3 = 0.0068$ s, $D_4 = 0.0313$ s).
Figure S44: $^1$H NMR spectrum (500 MHz, 305 K, C$_6$D$_6$).

Figure S45: $^{13}$C($^1$H) NMR spectrum (125 MHz, 305 K, C$_6$D$_6$).
(E)-N-Isopropyl-1,2,3-triphenylprop-2-en-1-amine (E-23)

Figure S46: $^1$H NMR spectrum (500 MHz, 305 K, C$_6$D$_6$).

Figure S47: $^{13}$C($^1$H) NMR spectrum (125 MHz, 305 K, C$_6$D$_6$).
(E)-N-(2-Ethyl-1-phenylpent-2-en-1-yl)aniline (E-24)

Figure S48: $^1$H NMR spectrum (500 MHz, 305 K, CDCl$_3$).

Figure S49: $^{13}$C($^1$H) NMR spectrum (125 MHz, 305 K, CDCl$_3$).
N-(3,3-Dimethyl-2-methylenbutyl)aniline (27)

Figure S50: $^1$H NMR spectrum (500 MHz, 305 K, CDCl$_3$).

Figure S51: $^{13}$C($^1$H) NMR spectrum (125 MHz, 305 K, CDCl$_3$).
1-Bromo-3,5-di-tert-butylbenzene

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$_3$).
$N,N'$-bis(3,5-Di-$tert$-butylphenyl)pyridine-2,6-diamine

**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$_3$).
Compound 5

Additional 24 h, 80 °C

Additional 24 h, 80 °C

24 h, rt

Figures S56. Excerpt of the $^1$H NMR spectra verifying the reaction of 4 and diphenylacetylene 2 to give 5.

Figure S57: $^1$H NMR spectrum of 5 (300 MHz, C$_6$D$_6$, rt).
Figure S58: $^{13}$C($^1$H) NMR spectrum of 5 (75 MHz, CsD$_6$, rt).
9. GC Analyses

Figure S59: GC analysis of the hydroaminoalkylation of diphenylacetylene (2) with $N$-benzylaniline (1) in the presence of catalyst I (Table S1, entry 1).

Figure S60: GC analysis of the hydroaminoalkylation of diphenylacetylene (1) with $N$-benzylaniline (1) in the presence of catalyst II (Table S1, entry 2).
Figure S61: GC analysis of the hydroaminoalkylation of diphenylacetylene (2) with N-benzylniline (1) in the presence of catalyst III (Table S1, entry 3).

Figure S62: GC analysis of the hydroaminoalkylation of diphenylacetylene (2) with N-benzylniline (1) in the presence of catalyst IV (Table S1, entry 4).
Figure S63: GC analysis of the hydroaminoalkylation of diphenylacetylene (2) with N-benzylaniline (1) in the presence of catalyst II (optimized conditions, Table S2, entry 14).
**Figure S64**: GC analysis of the purified product \textit{E-3} (optimized conditions).

**Figure S65**: GC analysis of the purified product \textit{E-3} (optimized conditions).
Figure S66: GC analysis of the hydroaminoalkylation of diphenylacetylene (2) with N-benzyl-4-bromoaniline in the presence of catalyst II (optimized conditions).

Figure S67: GC analysis of the hydroaminoalkylation of diphenylacetylene (2) with N-benzyl-3-bromoaniline in the presence of catalyst II (optimized conditions).
Figure S68: GC analysis of the hydroaminoalkylation of diphenylacetylene (2) with N-benzyl-4-methoxyaniline in the presence of catalyst II (optimized conditions).

Figure S69: GC analysis of the hydroaminoalkylation of diphenylacetylene (2) with N-((trimethylsilyl)methyl)aniline in the presence of catalyst II (optimized conditions).
Figure S70: GC analysis of the hydroaminoalkylation of diphenylacetylene (2) with N-propylaniline in the presence of catalyst II (optimized conditions).

Figure S71: GC analysis of the hydroaminoalkylation of diphenylacetylene (2) with N-benzylpropan-2-amine in the presence of catalyst II (optimized conditions).
Figure S72: GC analysis of the hydroaminoalkylation of 3-hexyne (20) with N-benzylaniline (1) in the presence of catalyst II (optimized conditions).
Figure S73: GC analysis of the hydroaminoalkylation of 1-Phenyl-1-butene with N-benzylaniline (1) in the presence of catalyst II.

Figure S74: GC analysis of the hydroaminoalkylation of 1-phenyl-1-hexyne with N-benzylaniline (1) in the presence of catalyst II.
Figure S75: GC analysis of the hydroaminoalkylation of tert-butylacetylene (26) with N-methylaniline (25) in the presence of catalyst IV.
10. Crystallographic Data

Single crystal X-ray data for **E-3, E-15, E-23, and 27** were measured on a Bruker AXS D8 Venture diffractometer (multilayer optics, Mo-Kα radiation with λ = 0.71073 Å, Kappa 4-circle goniometer, Photon III C14 CPAD detector). **II** was measured on a Bruker AXS Kappa Apex II Duo (Cu-Kα radiation with λ = 1.54178 Å, Kappa 4-circle goniometer, Apex II CCD detector). Empirical absorption corrections using equivalent reflections were performed with the program SADABS.\(^5\) The structures were solved with the program SHELXS\(^6\) and refined with SHELXL\(^7\) using the OLEX2\(^8\) GUI. All non H atoms were refined using anisotropic atomic displacement parameters, H atoms bonded to C were located in the difference Fourier maps and placed on idealized geometric positions with idealized atomic displacement parameters using the riding model, H atoms bonded to N were refined freely.

The crystallographic data can be obtained free of charge from https://www.ccdc.cam.ac.uk/structures/ quoting the CCDC numbers 2047601-2047605.
|                | E-3          | E-15         | E-23         | 27            |
|----------------|--------------|--------------|--------------|--------------|
| CCDC           | 2047602      | 2047605      | 2047603      | 2047601      |
| empirical formula | C_{27}H_{23}N | C_{27}H_{22}ClN | C_{24}H_{26}ClN | C_{13}H_{20}ClN |
| fw             | 361.46       | 395.90       | 363.91       | 225.75       |
| colour         | colorless    | colorless    | colorless    | colorless    |
| habit          | block        | block        | block        | block        |
| cryst. dimens., mm | 0.13 x 0.11 x 0.04 | 0.16 x 0.10 x 0.09 | 0.13 x 0.12 x 0.04 | 0.12 x 0.08 x 0.045 |
| cryst. system  | triclinic    | monoclinic   | monoclinic   | monoclinic   |
| space group    | P-1          | P2\text{/}c   | P2\text{/}c   | P2\text{/}n   |
| a, Å           | 10.0488(3)   | 10.8080(3)   | 11.9072(4)   | 11.5199(8)   |
| b, Å           | 10.3523(3)   | 9.9557(3)    | 9.5286(4)    | 7.6687(5)    |
| c, Å           | 10.4989(3)   | 19.5724(6)   | 18.5279(6)   | 15.1800(11)  |
| \(\alpha\), deg | 109.4141(11) | 90           | 90           | 90           |
| \(\beta\), deg | 100.6208(12) | 100.1844(12) | 93.6535(13)  | 107.982(3)   |
| \(\gamma\), deg | 92.3682(11)  | 90           | 90           | 90           |
| \(V\), Å\(^3\) | 1006.22(5)   | 2072.83(11)  | 2097.88(13)  | 1275.53(15)  |
| Z              | 2            | 4            | 4            | 4            |
| \(\rho\) calc, g cm\(^{-3}\) | 1.193        | 1.269        | 1.152        | 1.176        |
| \(\mu\), mm\(^{-1}\) | 0.068        | 0.197        | 0.189        | 0.270        |
| \(T\), K       | 100(2)       | 100(2)       | 100(2)       | 100(2)       |
| \(\theta\) range, deg | 2.075 – 36.316 | 1.914 – 36.318 | 1.714 – 34.971 | 2.658 – 34.963 |
| no. of rflns collected | 82760        | 156901       | 130973       | 70168        |
| no. of indep rflns (R(int)) | 9766         | 10055        | 9229         | 5606         |
| no. of rflns with \(I>2\sigma(I)\) | 8256         | 9003         | 8271         | 4723         |
| absorption correction | semi-empirical | semi-empirical | semi-empirical | semi-empirical |
| max, min transmission | 1.0000 and 0.9639 | 1.0000 and 0.9456 | 1.0000 and 0.9551 | 1.0000 and 0.9371 |
| final \(R\) indices \([I>2\sigma(I)]\) | \(R_1 = 0.0454\), \(wR_2 = 0.1187\) | \(R_1 = 0.0472\), \(wR_2 = 0.1286\) | \(R_1 = 0.0405\), \(wR_2 = 0.1083\) | \(R_1 = 0.0342\), \(wR_2 = 0.0854\) |
| \(R\) indices (all data) | \(R_1 = 0.0552\) | \(R_1 = 0.0528\) | \(R_1 = 0.0459\) | \(R_1 = 0.0437\) |
|                      | \( wR^2 = 0.1250 \) | \( wR^2 = 0.1325 \) | \( wR^2 = 0.1118 \) | \( wR^2 = 0.0913 \) |
|----------------------|----------------------|----------------------|----------------------|----------------------|
| **GOF on \( F^2 \)** | 1.015                | 1.094                | 1.075                | 1.083                |
| largest diff peak /  | 0.494 / -0.206       | 0.633 / -0.459       | 0.547 / -0.438       | 0.475 / -0.185       |
| hole (e.Å\(^3\))    |                      |                      |                      |                      |
Table 5: Crystal Structure Data for Compounds II.

|                              | II               |
|------------------------------|------------------|
| CCDC                        | 2047604          |
| empirical formula            | C₈₀H₁₂₈N₈Ti      |
| fw                          | 1249.80          |
| colour                      | brown            |
| habit                       | part             |
| cryst. dimens., mm          | 0.24 x 0.10 x 0.07 |
| cryst. system               | monoclinic       |
| space group                 | C2/c             |
| a, Å                        | 35.9076(9)       |
| b, Å                        | 12.2909(3)       |
| c, Å                        | 18.5103(5)       |
| α, deg                      | 90               |
| β, deg                      | 101.4213(12)     |
| γ, deg                      | 90               |
| V, Å³                       | 8007.5(4)        |
| Z                           | 4                |
| ρ calc., g cm⁻³             | 1.037            |
| μ, mm⁻¹                     | 1.227            |
| T, K                        | 150(2)           |
| θ range, deg               | 2.511 – 66.589   |
| no. of rflns collected      | 51161            |
| no. of indep rflns          | 7085             |
| (R(int))                    | 0.0395           |
| no. of rflns with l>2σ(l)   | 6523             |
| absorption correction       | semi-empirical   |
| max, min transmission       | 1.0000 and 0.9117 |
| final R indices [l>2σ(l)]   | R1 = 0.0510      |
| wR2 = 0.1472                |
| R indices (all data)        | R1 = 0.0545      |
| wR2 = 0.1522                |
| GOF on F²                   | 1.034            |
| largest diff peak / hole (eÅ³) | 0.457 / -0.490 |
Figure S76: Molecular structure of \textit{E-3}. Most hydrogen atoms have been omitted for clarity.

Figure S77: View along the \textit{a} axis showing the packing of molecules in the crystal structure of complex \textit{E-3}. Hydrogen atoms have been omitted for clarity.
Figure S78: Molecular structure of *E*-3. Hydrogen atoms (except H1, H1A, and H3) have been omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and angles (deg): N1–C1 1.4566(9), C1–C2 1.5308(9), C2–C3 1.3438(9), \( \sum \text{(angles)} \) (C2) 359.9, \( \sum \text{(angles)} \) (C3) 360.0.
**Figure S79:** Molecular structure of *E*-15. Most hydrogen atoms have been omitted for clarity.

**Figure S80:** View along the *b* axis showing the packing of molecules in the crystal structure of complex *E*-15. Hydrogen atoms have been omitted for clarity.
Figure S8: Molecular structure of **E-15**. Hydrogen atoms (except H1, H1A, and H3) have been omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and angles (deg): N1–C1 1.4629(10), C1–C2 1.5275(11), C2–C3 1.3420(10), ∑(angles)(C2) 360.0, ∑(angles)(C3) 360.0.
Figure S82: Molecular structure of \textit{E-23}. Most hydrogen atoms have been omitted for clarity.

Figure S83: View along the \textit{b} axis showing the packing of molecules in the crystal structure of complex \textit{E-23}. Hydrogen atoms have been omitted for clarity.
Figure S84: Molecular structure of \textit{E}-23. Hydrogen atoms (except H1, H1A, H1B, and H3) have been omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and angles (deg): N1–C1 1.5020(10), C1–C2 1.5197(11), C2–C3 1.3420(11), $\Sigma$\textsubscript{\text{angles}}(C2) 359.9, $\Sigma$\textsubscript{\text{angles}}(C3) 360.0.
Figure S85: Molecular structure of 27. Most hydrogen atoms have been omitted for clarity.

Figure S86: View along the b axis showing the packing of molecules in the crystal structure of complex 27. Hydrogen atoms have been omitted for clarity.
Figure S87: Molecular structure of 27. Hydrogen atoms (except H1, H1A, and H3) have been omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and angles (deg): N1–C7 1.5079(10), C7–C8 1.5199(11), C8–C13 1.3331(11), ∑(angles)(C8) 359.9, ∑(angles)(C13) 360.0.
Figure S88: Molecular structure of II. Most hydrogen atoms have been omitted for clarity.

Figure S89: View along the b axis showing the packing of molecules in the crystal structure of complex II. Hydrogen atoms have been omitted for clarity.
Figure S90: Molecular structure of II. Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and angles (deg): Ti1–N1 2.0958(13), Ti1–N2 2.2229(14), Ti1–N4 2.0958(13), N1–C2 1.368(2), N1–C7 1.411(2), N2–C2 1.363(2), N2–C6 1.338(2), N3–C6 1.376(2).
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