EurJOC European Journal of Organic Chemistry

FULL PAPER

DOI: 10.1002/ejoc.201301004

An (Aminopyrimidinato)titanium Catalyst for the Hydroamination of Alkynes and Alkenes

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Keywords: Synthetic methods / Hydroamination / Nitrogen heterocycles / Alkenes / Alkynes / Amines / Titanium

A new (aminopyrimidinato)titanium complex has been synthesised from inexpensive and easily accessible 2-(*tert*-butylamino)pyrimidine and $[Ti(NMe_2)_4]$ and used as a catalyst for the intermolecular hydroamination of alkynes as well as the cyclization of aminoalkenes. The hydroamination reactions of 1-phenylpropyne and terminal arylalkynes deliver the corresponding anti-Markovnikov addition products with excellent yields and regioselectivities.

Introduction

The direct addition of N–H across carbon–carbon multiple bonds represents a very promising synthetic approach towards waste-free production of various nitrogen-containing molecules. As a consequence, the so-called hydroamination of unactivated alkenes and alkynes has been extensively investigated in recent years[1] and it turned out that group 4 metal complexes are among the most promising catalysts for these highly desirable synthetic transformations.[2] Interestingly, a number of these group 4 metal complexes are also able to catalyze a closely related reaction, the so-called hydroaminoalkylation of alkenes, which involves the addition of the α-C–H bond of an amine across a C–C double bond.[3,4] During a recent study directed towards optimization of the latter transformation, we found that (2-aminopyridinato)titanium complexes,[5] generated in situ from $[Ti(NMe_2)_4]$ and 2-(methylamino)pyridine, are particularly efficient catalysts for the regioselective hydroaminoalkylation of styrenes.[4g] Inspired by this finding and by the surprising fact that, to the best of our knowledge, corresponding catalysts have never been used for alkyne hydroamination before, we decided to investigate the potential use of (aminopyridinato)titanium complexes as well as titanium complexes with other *N*,*N*-chelating ligands as hydroamination catalysts. In this context, it must be noted that in 2005 and 2007, Eisen et al. described the unusual hydroamination of methylenecyclopropanes in the presence of a titanium catalyst that contained two 2-[(diphenylphosphanyl)amino]pyridinato ancillary ligands[6] and, very recently, during the course of our sudy, Schafer and Kempe et al. presented the first examples of (2-aminopyridinato)-titanium catalysts for the intramolecular hydroamination of primary aminoalkenes.[7]

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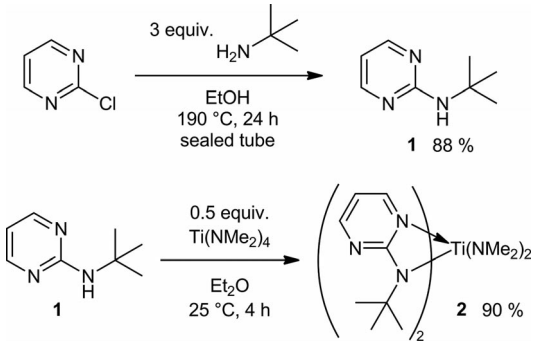
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejoc.201301004.

Results and Discussion

Initial hydroamination reactions of alkynes that were performed in the presence of the above mentioned (2-aminopyridinato)titanium catalysts generated in situ from $[Ti(NMe_2)_4]$ and one or two equivalents of 2-(methylamino)pyridine gave only disappointing results. However, based on the well-established fact that sterically hindered and electrophilic titanium complexes usually represent highly active hydroamination catalysts,[2] we chose 2-(*tert*-butylamino)pyrimidine (**1**; Scheme 1) as a promising alternative ligand precursor because it consists of a sterically demanding *tert*-butylamino group in combination with a more electron-deficient pyrimidine ring. Aminopyrimidine **1** is easily accessible in one step from commercially available and inexpensive 2-chloropyrimidine and *tert*-butylamine by nucleophilic aromatic substitution.[8] Treatment of $[Ti(NMe_2)_4]$ with two equivalents of ligand precursor **1** at room temperature in diethyl ether resulted in the clean formation of aminopyrimidinato complex **2** in excellent yield (Scheme 1). The obtained solid material could be recrystallized from hexanes to give red crystals that were suitable for X-ray crystallographic analysis (Figure 1).[9] The solid-state structure surprisingly reveals a highly unsymmetrical and strongly distorted octahedral geometry around the titanium centre. However, initial hydroamination reactions of 1-phenylpropyne (**3**) with *p*-toluidine (**4**) revealed that complex **2** is a competent catalyst for the intermolecular hydroamination of alkynes (Table 1). In the presence of 5 mol-% **2**, the reaction goes to completion within 24 h at 80 °C and, after subsequent reduction ($NaBH_3CN/ZnCl_2$), the product **5a** could be isolated in 97% yield (Table 1, entry 3). Particularly important is the fact that no formation of the Markovnikov regioisomer **5b** could be observed by GC analysis.

This finding is in sharp contrast to a comparable control experiment performed with $[Ti(NMe_2)_4]$ as the hydroamination catalyst,[10] which resulted in the formation of a 93:7 mixture of regioisomers **5a** and **5b** (91% yield).



Scheme 1. Synthesis of bis[2-(*tert*-butylamino)pyrimidine]bis(dimethylamino)titanium (**2**).[8]

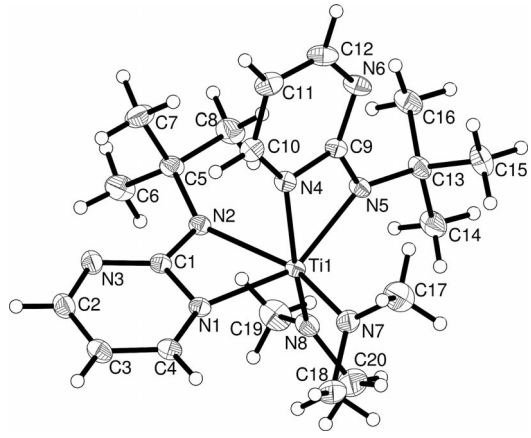
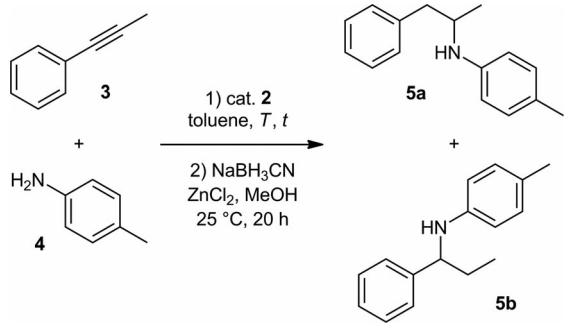


Figure 1. X-ray crystal structure of complex **2**.[9] Selected bond lengths [Å] and angles [°]: Ti1–N1 2.1875(9), Ti1–N2 2.2055(9), Ti1–N4 2.2548(8), Ti1–N5 2.0686(9), Ti1–N7 1.9234(8), Ti1–N8 1.9233(8), N1–Ti1–N2 60.79(3), N4–Ti1–N5 61.60(3), C1–N1–Ti1 94.08(6), C1–N2–Ti1 95.10(6), C9–N4–Ti1 90.11(6), C9–N5–Ti1 98.93(6).

Although the reaction sequence of 1-phenylpropyne (**3**) with *p*-toluidine (**4**) also gives satisfactory results with a lower catalyst loading (3 mol-%; Table 1, entry 9) or a reduced reaction time (12 h) of the hydroamination step (Table 1, entry 7), we performed additional hydroamination/reduction sequences with alkyne **3** and a variety of primary amines under the conditions detailed in Table 1, entry 3 (5 mol-% **2**, 80 °C, 24 h). The corresponding results shown in Table 2 (entries 1–10) clearly show that the aminopyrimidinato complex **2** is a very good catalyst for highly regioselective addition of many aryl- and alkylamines to 1-phenylpropyne (**3**). When methyl- or methoxy-substituted anilines were used as amine substrates (Table 2, entries 1–4) for the hydroamination/reduction sequence, the corresponding biologically interesting 2-phenylethylamine derivatives could be isolated in excellent yields (≥ 89%). In all cases, the regioselectivity of amine addition to 1-phenylpropyne (**3**) was ≥ 99:1 in favour of the anti-Markovnikov regioisomer. Although *ortho*,*ortho*-dimethyl-substituted substrates 2,6-dimethylaniline and 2,4,6-trimethylaniline clearly represent good substrates for the two-step process, the presence of one large *ortho*-bromo substituent on the aniline system leads to a significantly reduced rate of the hydroamination reaction (Table 2, entry 5). In this case, the reaction time of the hydroamination step had to be extended to 48 h to obtain the corresponding product **9a** in a moderate yield of only 59%. Interestingly, the *ortho*-bromo derivative also results in a slightly reduced regioselectivity (97:3) of the hydroamination reaction. On the other hand, various alkylamines (Table 2, entries 6–10) undergo the hydroamination/reduction sequence with much better yields (≥ 85%). However, as observed before,[11] the regioselectivity of the hydroamination significantly decreases with decreasing steric bulk of the amine substrate. As a result, the use of sterically less demanding *n*-octylamine or benzylamine led to regioselectivities of only 9:1 (Table 2, entries 6 and 7). Regarding these two substrates, it is also worth mentioning that the hydroamination does not require slow addition of the amine to the reaction mixture, which was essential for the corresponding $[Ind_2TiMe_2]$-catalysed (Ind = η^5-indenyl) hydroamination reactions.[11b] Among the sterically more demanding alkylamines, isobutylamine, cyclopentylamine and benzhydrylamine, the latter substrate clearly gave the most promising result (Table 2, entry 10) because the obtained product **14a** (90% yield) represents an N-protected amphetamine, which can easily be deprotected

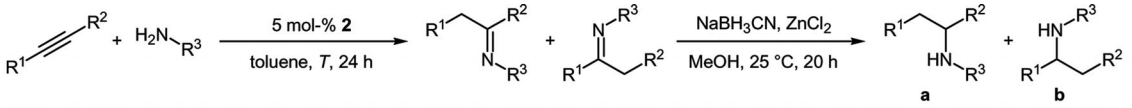
Table 1. Hydroamination of 1-phenylpropyne (**3**) with *p*-toluidine (**4**) catalysed by complex **2** and subsequent reduction.



Entry	Catalyst **2** [mol-%]	*T* [°C]	*t* [h]	Yield [%][a]	Ratio **5a/5b**[b]
1	5	105	24	97	>99:1
2	5	90	24	97	>99:1
3	5	80	24	97	>99:1
4	5	70	24	54	>99:1
5	5	60	24	10	>99:1
6	5	80	18	95	>99:1
7	5	80	12	90	>99:1
8	5	80	6	70	>99:1
9	3	80	24	90	>99:1
10	1	80	24	20	97:3

[a] Reaction conditions: (1) alkyne **3** (2.40 mmol), amine **4** (2.64 mmol), catalyst **2**, toluene (1 mL); (2) $NaBH_3CN$ (4.80 mmol), $ZnCl_2$ (2.40 mmol), MeOH (10 mL), 25 °C, 20 h, yields refer to isolated compounds. [b] The ratio of **5a/5b** was determined by GC analysis prior to flash chromatography.

Table 2. Hydroamination/reduction reaction sequences with alkynes and primary amines performed with catalyst **2**.



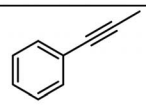
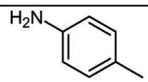
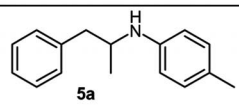
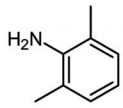
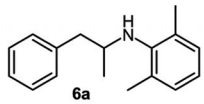
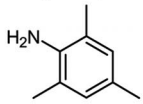
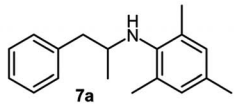
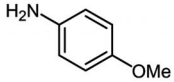
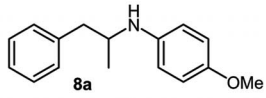
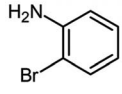
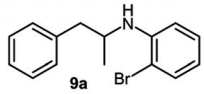
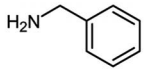
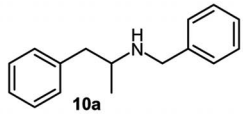
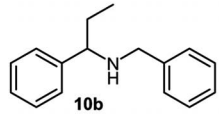
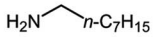
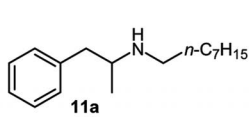
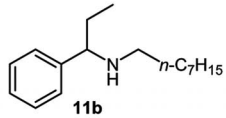
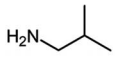
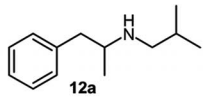
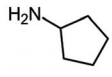
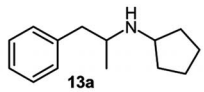
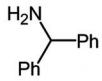
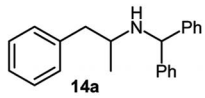
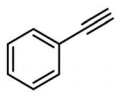
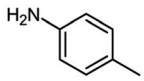
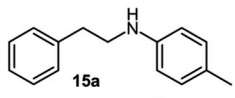
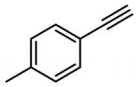
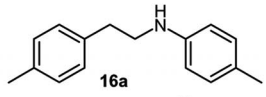
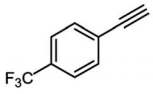
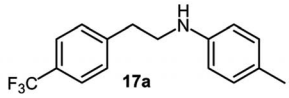
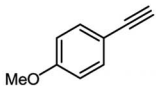
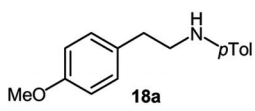
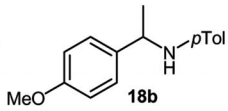
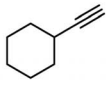
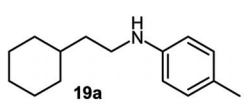
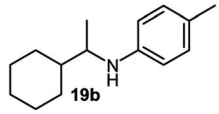
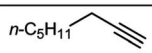
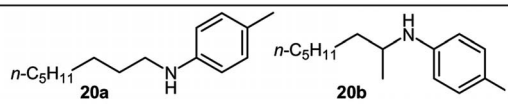
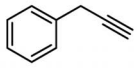
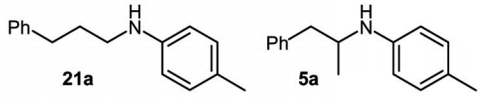
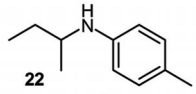
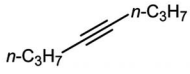
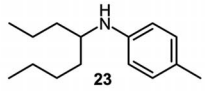
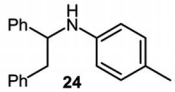
Entry	Alkyne	Amine	T [°C]	Products	Yield [%][a]	Ratio a/b[b]
1			80	 **5a**	97	>99:1
2			80	 **6a**	89	99:1
3			80	 **7a**	93	>99:1
4			80	 **8a**	96	>99:1
5			80	 **9a**	59[c]	97:3
6			80	 **10a**  **10b**	86	90:10
7			80	 **11a**  **11b**	92	89:11
8			80	 **12a**	85	96:4
9			80	 **13a**	93	96:4
10			80	 **14a**	90	99:1
11			50	 **15a**	87	99:1
12			50	 **16a**	79	98:2
13			50	 **17a**	87	99:1
14			80	 **18a**  **18b**	85	88:12
15			80	 **19a**  **19b**	92	33:67

Table 2. *(continued)*.

Entry	Alkyne	Amine	*T* [°C]	Products	Yield [%][a]	Ratio **a**/**b**[b]
16			80	 **20a** **20b**	85	8:92
17			80	 **21a** **5a**	88	16:84
18			80	 **22**	61	–
19			120	 **23**	71	–
20			120	 **24**	95	–

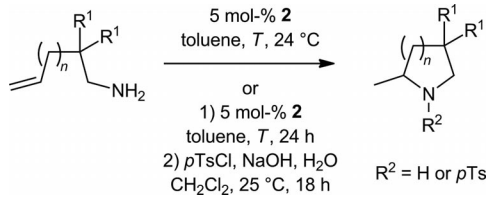
[a] Reaction conditions: (1) alkyne (2.40 mmol), amine (2.64 mmol), catalyst **2** (0.12 mmol, 5 mol-%), toluene (1 mL), 50–120 °C, 24 h; (2) $NaBH_3CN$ (4.80 mmol), $ZnCl_2$ (2.40 mmol), MeOH (10 mL), 25 °C, 20 h, yields refer to isolated compounds (**a** + **b**). [b] The ratio of **a**/**b** was determined by GC analysis prior to flash chromatography. [c] The reaction time was 48 h.

under reductive conditions.[12] The very good regioselectivity of the hydroamination (99:1) clearly proves that benzhydrylamine is a much better ammonia equivalent for the hydroamination of alkynes than benzylamine, which only gave a modest regioselectivity (90:10; Table 2, entry 6). In this context, it should be noted that product **8a** (Table 2, entry 4) also contains a protecting group on the nitrogen atom. The well-established *p*-methoxyphenyl group can easily be cleaved under oxidative conditions.[13] Probably as a result of the sterically very demanding aminopyrimidinato ligands of catalyst **2** so far, no successful reaction could be achieved with *tert*-butylamine.

To gain a preliminary impression of the behaviour of additional alkynes, we then focused on the corresponding transformations of terminal aryl- and alkylalkynes with *p*-toluidine (**4**; Table 2, entries 11–17). First, it must be mentioned that electron-neutral and electron-poor arylalkynes undergo facile hydroamination even at 50 °C with excellent regioselectivities of ≥ 98:2 in favour of the anti-Markovnikov addition products (Table 2, entries 11–13).[14] Although hydroamination of the electron-rich arylalkyne 4-methoxyphenylacetylene was slow at 50 °C, a good yield of the hydroamination/reduction sequence could be achieved when the hydroamination was performed at 80 °C. However, in this case a significantly reduced regioselectivity of only 88:12 was observed (Table 2, entry 14). Interestingly and in good agreement with reported results with other titanium catalysts,[11b] the regioselectivity of the hydroamination was reversed when alkylalkynes were used as substrates (Table 2, entries 15–17). In these cases, the Marovnikov addition products are formed preferentially, with modest to good selectivities. However, even in these cases the combined yields of both regioisomers obtained from the hydroamination/reduction sequences were good.

To complete the investigation of the behaviour of various alkynes, we also used aminopyrimidinato catalyst **2** for hydroamination/reduction sequences of less reactive dialkyl- or diaryl-substituted internal alkynes (Table 2, entries 18–20). Whereas the hydroamination of 2-butyne already takes place at 80 °C with a reasonable rate (Table 2, entry 18), high-yielding transformations of the sterically more demanding alkynes 4-octyne and diphenylacetylene re-

Table 3. Intramolecular hydroamination of aminoalkenes catalysed by complex **2**.[a]



Entry	*n*	R^1	*T* [°C]	R^2	Yield [%][b]
1	1	Ph (**25**)	95	H (**26**)	45
2	1	Ph (**25**)	105	H (**26**)	96
3	1	Ph (**25**)	120	H (**26**)	99
4	1	–$(CH_2)_5$– (**27**)	120	*p*Ts (**28**)	64
5	1	–$(CH_2)_5$– (**27**)	140	*p*Ts (**28**)	76
6	1	–$(CH_2)_5$– (**27**)	160	*p*Ts (**28**)	83
7	1	Me (**29**)	160	*p*Ts (**30**)	–
8	2	Ph (**31**)	140	H (**32**)	75
9	2	Ph (**31**)	160	H (**32**)	87
10	2	–$(CH_2)_5$– (**33**)	160	*p*Ts (**34**)	37
11	2	Me (**35**)	105–160	*p*Ts (**36**)	–
12	3	Ph (**37**)	105–200	H (**38**)	–

[a] Reaction conditions: (1) aminoalkene (2.00 mmol), catalyst **2** (0.10 mmol, 5 mol-%), toluene (1 mL), 95–200 °C, 24 h; if applicable (2) *p*-toluenesulfonyl chloride (3.00 mmol), NaOH (1 M, 6 mL), CH_2Cl_2 (20 mL), 25 °C, 18 h. [b] Isolated yield.

quired elevated temperatures (Table 2, entries 19 and 20). However, even in these cases, the products of the hydroamination/reduction sequences were obtained in good to very good yields.

Finally, we found that aminopyrimidinato complex **2** was also able to catalyze the intramolecular hydroamination of selected *gem*-disubstituted aminoalkenes (Table 3). A selection of corresponding pyrrolidines (**26**, **28**) and piperidine (**32**, **34**) derivatives could be isolated in good to very good yields from reaction mixtures that had been stirred for 24 h at elevated temperatures in the presence of 5 mol-% catalyst **2**. This finding, in combination with the results described for the hydroamination of alkynes, strongly underlines the impression that titanium complexes with aminopyridinato ligands[7] or other *N*,*N*-chelating ligands represent a very promising new class of hydroamination catalysts.

Conclusions

Our studies have shown that an (aminopyrimidinato)titanium complex can be used as an efficient catalyst for the intermolecular hydroamination of alkynes as well as the cyclization of selected *gem*-disubstituted aminoalkenes. Particularly important is the fact that corresponding reactions of 1-phenylpropyne and terminal arylalkynes deliver the corresponding anti-Markovnikov hydroamination products with excellent yields and regioselectivities. This finding, in combination with the good results obtained with the two ammonia equivalents benzhydrylamine and *p*-methoxyaniline, will offer a number of synthetic possibilities for future applications of the process. The new hydroamination catalyst is easily accessible from inexpensive and readily available starting materials {2-(*tert*-butylamino)pyrimidine and $[Ti(NMe_2)_4]$} and represents the first example of a catalyst for the hydroamination of alkynes that contains an aminoheteroaromatic ancillary ligand. Further studies dealing with early-transition-metal hydroamination catalysts obtainable from many other easily accessible aminoheteroaromatics will be reported in due course.

Experimental Section

General: All reactions were performed under an inert atmosphere of nitrogen in oven-dried Schlenk tubes (Duran glassware, 100 mL, ø = 30 mm) equipped with Teflon stopcocks and magnetic stirring bars (15 × 4.5 mm). Complex $[Ti(NMe_2)_4]$, *tert*-butylamine, 2-chloropyrimidine and toluene (toluene extra dry with molecular sieves) were purchased from Acros Organics. 2-(*tert*-Butylamino)-pyrimidine (**1**) was synthesised according to a literature procedure.[8] Prior to use, all alkynes, amines and aminoalkenes were purified by Kugelrohr distillation and degassed. Alkynes, amines, aminoalkenes, bis[2-(*tert*-butylamino)pyrimidine]bis(dimethylamino)titanium (**2**) and toluene were stored in a nitrogen-filled glovebox (M. Braun, Unilab). All other reagents were purchased from commercial sources and were used without further purification. Unless otherwise noted, yields refer to isolated yields of pure compounds as gauged by thin-layer chromatography (TLC), ^1H and ^{13}C NMR spectroscopy. The ratio of regioisomers was determined by gas chromatography prior to flash chromatography. For thin-layer chromatography, silica on aluminium foil with fluorescent indicator 254 nm from Fluka was used. The substances were detected with UV light and/or iodine. For flash chromatography, silica gel from Fluka (particle size 0.037–0.063 mm) was used. Prior to use, hexanes, ethyl acetate and *tert*-butylmethyl ether (MTBE) were distilled for flash chromatography. All products that have already been reported in the literature were characterized by ^1H NMR, ^{13}C NMR and ^{19}F NMR spectroscopic analysis if applicable and identified by comparison with the literature data. New products were additionally characterized by infrared (IR) spectroscopy and mass spectrometry (MS and HRMS). NMR spectra were recorded with Bruker Avance DRX 500 MHz or Bruker Avance III 500 MHz spectrometers. All ^1H NMR spectra are reported in δ units (ppm) relative to the signal of $CDCl_3$ (δ = 7.26 ppm), or the signal of ferrocene (δ = 4.00 ppm), or the signal of the methyl group of $[D_8]$toluene (δ = 2.08 ppm). All ^{13}C NMR spectra are reported in δ units (ppm) relative to the central line of the triplet for $CDCl_3$ (δ = 77.16 ppm) or to the methyl group of $[D_8]$toluene (δ = 20.43 ppm). ^{19}F NMR spectra are reported in δ units (ppm) relative to the signal of $CFCl_3$ (δ = 0.00 ppm). Mass spectra were recorded with a Finnigan MAT 95 spectrometer (EI) or a Waters Q-TOF Premier spectrometer (ESI). Infrared spectra were recorded with a Bruker Tensor 27 spectrometer equipped with a MKII Golden Single Reflection Diamond using an attenuated total reflection (ATR) method. GC analyses were performed with a Shimadzu GC-2010 plus gas chromatograph equipped with a flame-ionization detector. Melting points were determined in a capillary with a Schropp-Gerätetechnik melting point MPM-H2 apparatus.

Bis[2-(*tert*-butylamino)pyrimidine]bis(dimethylamino)titanium (2): $[Ti(NMe_2)_4]$ (0.673 g, 3.0 mmol) was slowly added to a solution of 2-(*tert*-butylamino)pyrimidine (**1**; 0.907 g, 6.0 mmol) in Et_2O (5 mL) at 25 °C. The reaction mixture was stirred for 4 h and then the solvent was removed under vacuum. The resulting solid was recrystallized from hexanes to give red crystals of complex **2** (1.178 g, 2.70 mmol, 90%). ^1H NMR (500 MHz, $[D_8]$toluene, 25 °C): δ = 7.89 (dd, J = 4.4, 2.9 Hz, 2 H, Ar-*H*), 7.43 (br. s, 2 H, Ar-*H*), 5.54 (t, J = 4.7 Hz, 2 H, Ar-*H*), 3.22 (s, 12 H, N-CH_3), 1.59 (s, 18 H, CH_3) ppm. ^{13}C NMR (125 MHz, $[D_8]$toluene, 25 °C): δ = 166.1 (C), 159.1 (CH), 151.3 (CH), 104.7 (CH), 55.1 (C), 48.5 (CH_3), 30.2 (CH_3) ppm. MS (ESI, CH_2Cl_2 + MeOH): *m*/*z* (%) = 436 (100) $[M]^+$.

Intermolecular Hydroamination of Alkynes. General Procedure A: An oven-dried Schlenk tube equipped with a Teflon stopcock and a magnetic stirring bar was transferred into a nitrogen-filled glovebox and charged with catalyst **2** (52 mg, 0.12 mmol, 5 mol-%), alkyne (2.40 mmol), amine (2.64 mmol) and toluene (1 mL). The tube was sealed and the resulting mixture was heated to 50–120 °C (Table 2) for 24 h, then the mixture was cooled to room temperature, and a mixture of $NaBH_3CN$ (302 mg, 4.80 mmol) and anhydrous $ZnCl_2$ (327 mg, 2.40 mmol) in anhydrous methanol (10 mL) was added. The mixture was stirred at 25 °C for 20 h, then CH_2Cl_2 (40 mL) and saturated aqueous Na_2CO_3 solution (50 mL) were added. After extraction, the organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (5 × 20 mL). The combined organic layers were dried with $MgSO_4$ and, after concentration under vacuum, the residue was purified by flash chromatography (SiO_2) to give the amine products.

Intramolecular Hydroamination of Alkenes. General Procedure B: An oven-dried Schlenk tube equipped with a Teflon stopcock and a magnetic stirring bar was transferred into a nitrogen-filled

glovebox and charged with catalyst **2** (44 mg, 0.10 mmol, 5 mol-%), aminoalkene (2.00 mmol) and toluene (1 mL). The tube was sealed and the resulting mixture was heated to 95–200 °C (Table 3) for 24 h, then the mixture was cooled to room temperature and hydrolysed with wet CH_2Cl_2 (20 mL). After concentration under vacuum, the residue was purified by flash chromatography (SiO_2) to give the amine product.

Intramolecular Hydroamination of Alkenes and Subsequent Formation of a *p*-Toluenesulfonamide. General Procedure C: An oven-dried Schlenk tube equipped with a Teflon stopcock and a magnetic stirring bar was transferred into a nitrogen-filled glovebox and charged with catalyst **2** (44 mg, 0.10 mmol, 5 mol-%), aminoalkene (2.00 mmol) and toluene (1 mL). The tube was sealed and the resulting mixture was heated to 120–160 °C (Table 3) for 24 h, then the mixture was cooled to room temperature and hydrolysed with wet CH_2Cl_2 (20 mL). The obtained mixture was transferred into a 50 mL round-bottom flask and *p*-toluenesulfonyl chloride (572 mg, 3.00 mmol) and aqueous sodium hydroxide (1 M, 6 mL) were added. The resulting two-phase mixture was stirred at 25 °C for 18 h, then the organic layer was separated and dried with $MgSO_4$. After concentration under vacuum, the residue was purified by flash chromatography (SiO_2) to give the *p*-toluenesulfonamide product.

4-Methyl-*N*-(1-methyl-2-phenylethyl)aniline (5a):[11a] General procedure A (80 °C) was used to synthesise the title compound from 1-phenylpropyne and *p*-toluidine. Purification by flash chromatography (SiO_2; hexanes/EtOAc, 20:1) gave product **5a** (525 mg, 2.33 mmol, 97%) as a colourless oil. R_f = 0.23 (hexanes/EtOAc, 20:1). ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 7.42 (t, J = 7.3 Hz, 2 H, Ar-*H*), 7.34 (t, J = 7.4 Hz, 1 H, Ar-*H*), 7.31 (d, J = 7.0 Hz, 2 H, Ar-*H*), 7.14 (d, J = 8.3 Hz, 2 H, Ar-*H*), 6.69 (d, J = 8.4 Hz, 2 H, Ar-*H*), 3.92–3.77 (m, 1 H, C*H*), 3.46 (br. s, 1 H, N-*H*), 3.06 (dd, J = 13.4, 4.7 Hz, 1 H, CH_2), 2.80 (dd, J = 13.4, 7.4 Hz, 1 H, CH_2), 2.39 (s, 3 H, CH_3), 1.26 (d, J = 6.4 Hz, 3 H, CH_3) ppm. ^{13}C NMR (125 MHz, DEPT, $CDCl_3$, 25 °C): δ = 145.0 (C), 138.7 (C), 129.9 (CH), 129.6 (CH), 128.4 (CH), 126.4 (C), 126.3 (CH), 113.7 (CH), 49.7 (CH), 42.3 (CH_2), 20.5 (CH_3), 20.3 (CH_3) ppm.

2,6-Dimethyl-*N*-(1-methyl-2-phenylethyl)aniline (6a):[11b] General procedure A (80 °C) was used to synthesise the title compound from 1-phenylpropyne and 2,6-dimethylaniline. Purification by flash chromatography (SiO_2; hexanes/EtOAc, 20:1) gave product **6a** (510 mg, 2.14 mmol, 89%) as a colourless oil. R_f = 0.28 (hexanes/EtOAc, 20:1). ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 7.35 (t, J = 7.4 Hz, 2 H, Ar-*H*), 7.27 (t, J = 7.4 Hz, 1 H, Ar-*H*), 7.24 (d, J = 7.0 Hz, 2 H, Ar-*H*), 7.06 (d, J = 7.5 Hz, 2 H, Ar-*H*), 6.88 (t, J = 7.5 Hz, 1 H, Ar-*H*), 3.62–3.54 (m, 1 H, C*H*), 3.01 (dd, J = 13.0, 4.8 Hz, 1 H, CH_2), 2.98 (br. s, 1 H, N-*H*), 2.63 (dd, J = 13.0, 8.5 Hz, 1 H, CH_2), 2.31 (s, 6 H, CH_3), 1.12 (d, J = 6.4 Hz, 3 H, CH_3) ppm. ^{13}C NMR (125 MHz, DEPT, $CDCl_3$, 25 °C): δ = 144.8 (C), 139.5 (C), 129.5 (CH), 129.3 (C), 129.0 (CH), 128.4 (CH), 126.2 (CH), 121.5 (CH), 54.2 (CH), 44.5 (CH_2), 20.9 (CH_3), 19.2 (CH_3) ppm.

2,4,6-Trimethyl-*N*-(1-methyl-2-phenylethyl)aniline (7a): General procedure A (80 °C) was used to synthesise the title compound from 1-phenylpropyne and 2,4,6-trimethylaniline. Purification by flash chromatography (SiO_2; hexanes/EtOAc, 20:1) gave product **7a** (563 mg, 2.22 mmol, 93%) as a colourless oil. R_f = 0.25 (hexanes/EtOAc, 20:1). ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 7.39 (t, J = 7.3 Hz, 2 H, Ar-*H*), 7.31 (t, J = 7.3 Hz, 1 H, Ar-*H*), 7.28 (d, J = 7.1 Hz, 2 H, Ar-*H*), 6.93 (s, 2 H, Ar-*H*), 3.59–3.51 (m, 1 H, C*H*), 3.06 (dd, J = 13.0, 4.8 Hz, 1 H, CH_2), 2.93 (br. s, 1 H, N-*H*), 2.65 (dd, J = 13.0, 8.5 Hz, 1 H, CH_2), 2.35 (s, 3 H, CH_3), 2.32 (s, 6 H, CH_3), 1.16 (d, J = 6.4 Hz, CH_3) ppm. ^{13}C NMR (125 MHz, DEPT, $CDCl_3$, 25 °C): δ = 142.2 (C), 139.6 (C), 130.8 (C), 129.6 (CH), 129.5 (C), 129.5 (CH), 128.3 (CH), 126.1 (CH), 54.4 (CH), 44.5 (CH_2), 20.8 (CH_3), 20.7 (CH_3), 19.0 (CH_3) ppm. MS (EI, 70 eV): m/z (%) = 253 (1) $[M]^+$, 162 (100) $[C_{11}H_{16}N]^+$, 91 (19) $[C_7H_7]^+$. HRMS (EI, 70 eV): calcd. for $C_{18}H_{23}N$ 253.1825; found 253.1826. IR (ATR): $\tilde{\nu}$ = 661, 698, 738, 761, 855, 920, 987, 1030, 1099, 1128, 1221, 1259, 1343, 1373, 1439, 1454, 1473, 1495, 1594, 2857, 2923, 2962, 3027, 3382 cm^{-1}.

4-Methoxy-*N*-(1-methyl-2-phenylethyl)aniline (8a):[15] General procedure A (80 °C) was used to synthesise the title compound from 1-phenylpropyne and *p*-methoxyaniline. Purification by flash chromatography (SiO_2; hexanes/EtOAc, 10:1) gave product **8a** (556 mg, 2.30 mmol, 96%) as a colourless oil. R_f = 0.23 (hexanes/EtOAc, 10:1). ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 7.35 (t, J = 7.4 Hz, 2 H, Ar-*H*), 7.27 (t, J = 7.4 Hz, 1 H, Ar-*H*), 7.24 (d, J = 7.0 Hz, 2 H, Ar-*H*), 6.86 (d, J = 8.9 Hz, 2 H, Ar-*H*), 6.67 (d, J = 8.9 Hz, 2 H, Ar-*H*), 3.80 (s, 3 H, O-CH_3), 3.77–3.70 (m, 1 H, C*H*), 3.27 (br. s, 1 H, N-*H*), 2.99 (dd, J = 13.4, 4.8 Hz, 1 H, CH_2), 2.72 (dd, J = 13.4, 7.4 Hz, 1 H, CH_2), 1.19 (d, J = 6.4 Hz, 3 H, CH_3) ppm. ^{13}C NMR (125 MHz, DEPT, $CDCl_3$, 25 °C): δ = 152.1 (C), 141.4 (C), 138.7 (C), 129.6 (CH), 128.4 (CH), 126.3 (CH), 115.1 (CH), 55.8 (CH_3), 50.5 (CH), 42.4 (CH_2), 20.3 (CH_3) ppm.

2-Bromo-*N*-(1-methyl-2-phenylethyl)aniline (9a): General procedure A (80 °C) was used to synthesise the title compound from 1-phenylpropyne and *o*-bromoaniline. The reaction time of the hydroamination was 48 h. Purification by flash chromatography (SiO_2; hexanes/MTBE, 200:1) gave product **9a** (410 mg, 1.41 mmol, 59%) as a colourless oil. R_f = 0.17 (hexanes/MTBE, 200:1). ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 7.47 (d, J = 7.9 Hz, 1 H, Ar-*H*), 7.35 (t, J = 7.5 Hz, 2 H, Ar-*H*), 7.31–7.19 (m, 4 H, Ar-*H*), 6.75 (d, J = 8.1 Hz, 1 H, Ar-*H*), 6.60 (t, J = 7.6 Hz, 1 H, Ar-*H*), 4.36 (br. s, 1 H, N-*H*), 3.87–3.79 (m, 1 H, C*H*), 2.99 (dd, J = 13.5, 5.0 Hz, 1 H, CH_2), 2.79 (dd, J = 13.5, 7.2 Hz, 1 H, CH_2), 1.24 (d, J = 6.5 Hz, 3 H, CH_3) ppm. ^{13}C NMR (125 MHz, DEPT, $CDCl_3$, 25 °C): δ = 144.0 (C), 138.2 (C), 132.7 (CH), 129.6 (CH), 128.6 (CH), 128.5 (CH), 126.5 (CH), 117.6 (CH), 112.0 (CH), 110.2 (C), 49.7 (CH), 42.3 (CH_2), 20.2 (CH_3) ppm. MS (EI, 70 eV): m/z (%) = 291 (1) [M, ^{81}Br]$^+$, 289 (2) [M, ^{79}Br]$^+$, 200 (80) $[C_8H_9BrN, ^{81}Br]^+$, 198 (100) $[C_8H_9BrN, ^{79}Br]^+$, 91 (43) $[C_7H_7]^+$. HRMS (ESI, +): calcd. for $C_{15}H_{16}N^{79}BrK$ 328.0103; found 328.0105. IR (ATR): $\tilde{\nu}$ = 638, 668, 699, 737, 793, 833, 923, 966, 1017, 1046, 1091, 1113, 1151, 1161, 1201, 1217, 1245, 1282, 1319, 1377, 1427, 1453, 1497, 1506, 1594, 2926, 2966, 3026, 3062, 3402 cm^{-1}.

1-Phenyl-2-benzylaminopropane (10a)[11a] **and 1-Phenyl-1-benzylaminopropane (10b):**[11a] General procedure A (80 °C) was used to synthesise the title compounds from 1-phenylpropyne and benzylamine. Purification by flash chromatography (SiO_2; hexanes/EtOAc/Et_3N, 100:20:1) gave products **10a** (416 mg, 1.85 mmol, 77%) and **10b** (49 mg, 0.22 mmol, 9%) as colourless oils.

Compound 10a: R_f = 0.16 (hexanes/EtOAc/Et_3N, 100:20:1). ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 7.33–7.28 (m, 4 H, Ar-*H*), 7.27–7.21 (m, 4 H, Ar-*H*), 7.19 (d, J = 7.1 Hz, 2 H, Ar-*H*), 3.88 (d, J = 13.3 Hz, 1 H, N-CH_2), 3.77 (d, J = 13.3 Hz, 1 H, N-CH_2), 3.01–2.94 (m, 1 H, C*H*), 2.81 (dd, J = 13.4, 7.0 Hz, 1 H, CH_2), 2.67 (dd, J = 13.4, 6.5 Hz, 1 H, CH_2), 1.66 (br. s, 1 H, N-*H*), 1.13 (d, J = 6.3 Hz, 3 H, CH_3) ppm. ^{13}C NMR (125 MHz, DEPT, $CDCl_3$, 25 °C): δ = 140.5 (C), 139.5 (C), 129.4 (CH), 128.4 (CH), 128.1 (CH), 126.9 (CH), 126.2 (CH), 53.8 (CH), 51.4 (CH_2), 43.6 (CH_2), 20.3 (CH_3) ppm.

Compound 10b: R_f = 0.34 (hexanes/EtOAc/Et_3N, 100:20:1). ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 7.32–7.11 (m, 10 H, Ar-*H*), 3.59 (d, J = 13.2 Hz, 1 H, N-CH_2), 3.50–3.43 (m, 1 H, C*H*), 3.47

(d, J = 13.4 Hz, 1 H, N-CH_2), 1.77–1.66 (m, 1 H, CH_2), 1.65–1.55 (m, 1 H, CH_2), 1.19 (s, 1 H, N-H), 0.72 (t, J = 7.4 Hz, 3 H, CH_3) ppm. ^{13}C NMR (125 MHz, DEPT, $CDCl_3$, 25 °C): δ = 143.7 (C), 140.4 (C), 128.5 (CH), 128.4 (CH), 127.6 (CH), 127.2 (CH), 127.0 (CH), 64.3 (CH), 51.5 (CH_2), 31.0 (CH_2), 10.9 (CH_3) ppm.

***N*-(1-Phenylpropan-2-yl)octane-1-amine (11a) and *N*-(1-Phenylpropan-1-yl)octane-1-amine (11b):** General procedure A (80 °C) was used to synthesise the title compounds from 1-phenylpropyne and *n*-octylamine. Purification by flash chromatography (SiO_2; hexanes/MTBE/Et_3N, 20:5:1) gave products **11a** (500 mg, 2.02 mmol, 84%) and **11b** (50 mg, 0.20 mmol, 8%) as colourless oils.

Compound 11a: R_f = 0.26 (hexanes/MTBE/Et_3N, 20:5:1). ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 7.33 (t, J = 7.4 Hz, 2 H, Ar-H), 7.25–7.21 (m, 3 H, Ar-H), 2.97–2.89 (m, 1 H, CH), 2.78 (dd, J = 13.3, 7.0 Hz, 1 H, CH_2), 2.74–2.68 (m, 1 H, N-CH_2), 2.65 (dd, J = 13.3, 6.5 Hz, 1 H, CH_2), 2.60–2.53 (m, 1 H, N-CH_2), 1.54–1.40 (m, 2 H, CH_2), 1.38–1.24 (m, 10 H, CH_2), 1.10 (d, J = 6.3 Hz, 3 H, CH_3), 0.93 (t, J = 7.0 Hz, 3 H, CH_3) ppm. ^{13}C NMR (125 MHz, DEPT, $CDCl_3$, 25 °C): δ = 139.6 (C), 129.3 (CH), 128.4 (CH), 126.1 (CH), 54.7 (CH), 47.4 (CH_2), 43.7 (CH_2), 31.9 (CH_2), 30.3 (CH_2), 29.5 (CH_2), 29.3 (CH_2), 27.4 (CH_2), 22.7 (CH_2), 20.3 (CH_3), 14.2 (CH_3) ppm. MS (EI, 70 eV): *m*/*z* (%) = 247 (1) $[M]^+$, 156 (100) $[C_{10}H_{22}N]^+$, 91 (19) $[C_7H_7]^+$. HRMS (ESI, +): calcd. for $C_{17}H_{30}N$ 248.2378; found 248.2376. IR (ATR): $\tilde{\nu}$ = 599, 625, 635, 698, 741, 845, 909, 1031, 1085, 1130, 1342, 1373, 1454, 1495, 1603, 2853, 2923, 2957, 3027 cm^{-1}.

Compound 11b: R_f = 0.33 (hexanes/MTBE/Et_3N, 20:5:1). ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 7.38–7.21 (m, 5 H, Ar-H), 3.49 (dd, J = 8.0, 5.7 Hz, 1 H, CH), 2.49–2.37 (m, 2 H, N-CH_2), 1.83–1.74 (m, 1 H, CH_2), 1.70–1.60 (m, 1 H, CH_2), 1.51–1.38 (m, 2 H, CH_2), 1.32–1.18 (m, 10 H, CH_2), 0.87 (t, J = 6.9 Hz, 3 H, CH_3), 0.80 (t, J = 7.4 Hz, 3 H, CH_3) ppm. ^{13}C NMR (125 MHz, DEPT, $CDCl_3$, 25 °C): δ = 144.2 (C), 128.4 (CH), 127.5 (CH), 127.0 (CH), 65.4 (CH), 48.0 (CH_2), 32.0 (CH_2), 31.0 (CH_2), 30.3 (CH_2), 29.6 (CH_2), 29.4 (CH_2), 27.5 (CH_2), 22.8 (CH_2), 14.2 (CH_3), 10.9 (CH_3) ppm. MS (EI, 70 eV): *m*/*z* (%) = 247 (1) $[M]^+$, 218 (100) $[C_{15}H_{24}N]^+$, 91 (48) $[C_7H_7]^+$. HRMS (ESI, +): calcd. for $C_{17}H_{30}N$ 248.2378; found 248.2373. IR (ATR): $\tilde{\nu}$ = 601, 701, 754, 839, 901, 922, 1030, 1126, 1200, 1303, 1360, 1380, 1456, 1494, 1604, 1734, 2806, 2855, 2926, 2959, 3029, 3064, 3085 cm^{-1}.

2-Isobutylamino-1-phenylpropane (12a): General procedure A (80 °C) was used to synthesise the title compound from 1-phenylpropyne and isobutylamine. Purification by flash chromatography (SiO_2; hexanes/EtOAc/Et_3N, 30:1:1) gave product **12a** (412 mg, 2.15 mmol, 90%) as a colourless oil. R_f = 0.23 (hexanes/EtOAc/Et_3N, 30:1:1). ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 7.28 (t, J = 7.4 Hz, 2 H, Ar-H), 7.22–7.16 (m, 3 H, Ar-H), 2.90–2.82 (m, 1 H, N-CH), 2.73 (dd, J = 13.3, 7.0 Hz, 1 H, N-CH_2), 2.61 (dd, J = 13.3, 6.5 Hz, 1 H, N-CH_2), 2.47 (dd, J = 11.4, 6.8 Hz, 1 H, CH_2), 2.35 (dd, J = 11.4, 6.8 Hz, 1 H, CH_2), 1.73–1.62 (m, 1 H, CH), 1.44 (br. s, 1 H, N-H), 1.05 (d, J = 6.3 Hz, 3 H, CH_3), 0.83 (d, J = 6.7 Hz, 3 H, CH_3), 0.82 (d, J = 6.7 Hz, 3 H, CH_3) ppm. ^{13}C NMR (125 MHz, DEPT, $CDCl_3$, 25 °C): δ = 139.7 (C), 139.3 (CH), 128.4 (CH), 126.2 (CH), 55.5 (CH_2), 54.7 (CH), 43.7 (CH_2), 28.4 (CH), 20.8 (CH_3), 20.7 (CH_3), 20.4 (CH_3) ppm. MS (EI, 70 eV): *m*/*z* (%) = 191 (1) $[M]^+$, 100 (100) $[C_6H_{14}N]^+$, 91 (36) $[C_7H_7]^+$. HRMS (ESI, +): calcd. for $C_{13}H_{22}N$ 192.1752; found 192.1750. IR (ATR): $\tilde{\nu}$ = 600, 700, 743, 826, 912, 964, 1032, 1091, 1126, 1214, 1246, 1292, 1345, 1373, 1456, 1471, 1497, 1604, 1739, 2812, 2871, 2928, 2957, 3029, 3065, 3086 cm^{-1}.

2-Cyclopentylamino-1-phenylpropane (13a):[11b] General procedure A (80 °C) was used to synthesise the title compound from 1-phenylpropyne and cyclopentylamine. Purification by flash chromatography (SiO_2; hexanes/EtOAc/Et_3N, 12:4:1) gave product **13a** (456 mg, 2.23 mmol, 93%) as a colourless oil. R_f = 0.42 (hexanes/EtOAc/Et_3N, 12:4:1). ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 7.31 (t, J = 7.3 Hz, 2 H, Ar-H), 7.25–7.18 (m, 3 H, Ar-H), 3.26–3.19 (m, 1 H, N-CH), 3.03–2.96 (m, 1 H, N-CH), 2.78 (dd, J = 13.3, 6.8 Hz, 1 H, CH_2), 2.62 (dd, J = 13.3, 6.8 Hz, 1 H, CH_2), 1.96–1.88 (m, 1 H, cyclopentyl-H), 1.87–1.80 (m, 1 H, cyclopentyl-H), 1.69–1.47 (m, 4 H, cyclopentyl-H), 1.32–1.23 (m, 1 H, cyclopentyl-H), 1.22–1.12 (m, 1 H, cyclopentyl-H), 1.09 (d, J = 6.3 Hz, 3 H, CH_3) ppm. ^{13}C NMR (125 MHz, DEPT, $CDCl_3$, 25 °C): δ = 139.7 (C), 129.3 (CH), 128.4 (CH), 126.2 (CH), 57.0 (CH), 53.0 (CH), 43.9 (CH_2), 33.9 (CH_2), 33.0 (CH_2), 23.8 (CH_2), 23.8 (CH_2), 20.6 (CH_3) ppm.

2-Benzhydrylamino-1-phenylpropane (14a): General procedure A (80 °C) was used to synthesise the title compound from 1-phenylpropyne and benzhydrylamine. Purification by flash chromatography (SiO_2; hexanes/EtOAc, 40:1) gave product **14a** (649 mg, 2.23 mmol, 93%) as a colourless oil. R_f = 0.13 (hexanes/EtOAc, 40:1). ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 7.46 (d, J = 7.5 Hz, 2 H, Ar-H), 7.41–7.26 (m, 11 H, Ar-H), 7.22 (d, J = 7.1 Hz, 2 H, Ar-H), 5.09 (s, 1 H, CH), 3.00–2.93 (m, 1 H, CH), 2.91 (dd, J = 13.0, 6.7 Hz, 1 H, CH_2), 2.75 (dd, J = 13.0, 6.2 Hz, 1 H, CH_2), 1.80 (br. s, 1 H, N-H), 1.20 (d, J = 6.2 Hz, 3 H, CH_3) ppm. ^{13}C NMR (125 MHz, DEPT, $CDCl_3$, 25 °C): δ = 144.7 (C), 144.0 (C), 139.6 (C), 129.5 (CH), 128.5 (CH), 128.4 (CH), 128.3 (CH), 127.4 (CH), 127.4 (CH), 126.9 (CH), 126.9 (CH), 126.1 (CH), 64.2 (CH), 51.8 (CH), 43.9 (CH_2), 20.6 (CH_3) ppm. MS (EI, 70 eV): *m*/*z* (%) = 301 (1) $[M]^+$, 210 (19) $[C_{15}H_{16}N]^+$, 167 (100) $[C_{13}H_{12}]^+$, 91 (10) $[C_7H_7]^+$. HRMS (ESI, +): calcd. for $C_{22}H_{24}N$ 302.1909; found 302.1905. IR (ATR): $\tilde{\nu}$ = 600, 621, 639, 695, 743, 832, 913, 1028, 1060, 1075, 1089, 1139, 1180, 1278, 1344, 1373, 1451, 1492, 1599, 1624, 1661, 2845, 2925, 2961, 3025, 3060 cm^{-1}.

4-Methyl-*N*-(2-phenylethyl)aniline (15a):[15] General procedure A (50 °C) was used to synthesise the title compound from phenylacetylene and *p*-toluidine. Purification by flash chromatography (SiO_2; hexanes/EtOAc, 40:1) gave product **15a** (440 mg, 2.09 mmol, 87%) as a colourless oil. R_f = 0.10 (hexanes/EtOAc, 40:1). ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 7.43 (t, J = 7.4 Hz, 2 H, Ar-H), 7.38–7.31 (m, 3 H, Ar-H), 7.12 (d, J = 8.3 Hz, 2 H, Ar-H), 6.66 (d, J = 8.4 Hz, 2 H, Ar-H), 3.59 (br. s, 1 H, N-H), 3.49 (t, J = 7.1 Hz, 2 H, N-CH_2), 3.01 (t, J = 7.1 Hz, 2 H, CH_2), 2.38 (s, 3 H, CH_3) ppm. ^{13}C NMR (125 MHz, DEPT, $CDCl_3$, 25 °C): δ = 145.8 (C), 139.5 (C), 129.8 (CH), 128.9 (CH), 128.6 (CH), 126.7 (C), 126.4 (CH), 113.3 (CH), 45.5 (CH_2), 35.6 (CH_2), 20.5 (CH_3) ppm.

4-Methyl-*N*-[2-(4-methylphenyl)ethyl]aniline (16a):[16] General procedure A (50 °C) was used to synthesise the title compound from *p*-methylphenylacetylene and *p*-toluidine. Purification by flash chromatography (SiO_2; hexanes/EtOAc, 40:1) gave product **16a** (427 mg, 1.89 mmol, 79%) as a colourless solid. The obtained solid material could be recrystallized from ethanol to give colourless crystals that were suitable for X-ray crystallographic analysis.[17] R_f = 0.21 (hexanes/EtOAc, 40:1). ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 7.22–7.12 (m, 4 H, Ar-H), 7.05 (d, J = 8.0 Hz, 2 H, Ar-H), 6.59 (d, J = 8.4 Hz, 2 H, Ar-H), 3.52 (br. s, 1 H, N-H), 3.40 (t, J = 7.1 Hz, 2 H, N-CH_2), 2.91 (t, J = 7.1 Hz, 2 H, CH_2), 2.39 (s, 3 H, CH_3), 2.31 (s, 3 H, CH_3) ppm. ^{13}C NMR (125 MHz, DEPT, $CDCl_3$, 25 °C): δ = 145.9 (C), 136.4 (C), 135.9 (C), 129.8 (CH), 129.3 (CH), 128.7 (CH), 126.7 (C), 113.3 (CH), 45.6 (CH_2), 35.1 (CH_2), 21.1 (CH_3), 20.5 (CH_3) ppm.

4-Methyl-*N*-{2-[4-(trifluoromethyl)phenyl]ethyl}aniline (17a): General procedure A (50 °C) was used to synthesise the title compound

from *p*-trifluoromethylphenylacetylene and *p*-toluidine. Purification by flash chromatography (SiO_2; hexanes/EtOAc, 40:1) gave product **17a** (583 mg, 2.09 mmol, 87%) as a yellow oil. R_f = 0.06 (hexanes/EtOAc, 40:1). ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 7.64 (d, J = 8.1 Hz, 2 H, Ar-*H*), 7.38 (d, J = 8.0 Hz, 2 H, Ar-*H*), 7.09 (d, J = 8.3 Hz, 2 H, Ar-*H*), 6.63 (d, J = 8.3 Hz, 2 H, Ar-*H*), 3.54 (br. s, 1 H, N-*H*), 3.47 (t, J = 7.0 Hz, 2 H, N-CH_2), 3.01 (t, J = 7.0 Hz, 2 H, CH_2), 2.33 (s, 3 H, CH_3) ppm. ^{13}C NMR (125 MHz, DEPT, $CDCl_3$, 25 °C): δ = 145.5 (C), 143.8 (C), 130.0 (CH), 129.2 (CH), 128.9 (q, $^2J_{C,F}$ = 32.4 Hz, C), 127.1 (C), 125.6 (q, $^3J_{C,F}$ = 3.7 Hz, CH), 124.4 (q, $^1J_{C,F}$ = 271.8 Hz, CF_3), 113.4 (CH), 45.2 (CH_2), 35.5 (CH_2), 20.5 (CH_3) ppm. ^{19}F NMR (470 MHz, $CDCl_3$, 25 °C): δ = –62.3 ppm. MS (EI, 70 eV): *m*/*z* (%) = 279 (12) $[M]^+$, 159 (5) $[C_8H_6F_3]^+$, 120 (100) $[C_8H_{10}N]^+$, 91 (12) $[C_7H_7]^+$. HRMS (ESI, +): calcd. for $C_{16}H_{17}NF_3$ 280.1313; found 280.1310. IR (ATR): $\tilde{\nu}$ = 596, 616, 707, 735, 809, 842, 955, 1020, 1068, 1111, 1163, 1260, 1323, 1419, 1482, 1521, 1586, 1618, 2868, 2924, 3022, 3405 cm^{-1}.

***N*-[2-(4-Methoxyphenyl)ethyl]-4-methylaniline (18a) and *N*-[1-(4-Methoxyphenyl)ethyl]-4-methylaniline (18b):**[18] General procedure A (80 °C) was used to synthesise the title compounds from *p*-methoxyphenylacetylene and *p*-toluidine. Purification by flash chromatography (SiO_2; hexanes/EtOAc, 20:1) gave products **18a** (460 mg, 1.80 mmol, 75%) and **18b** (61 mg, 0.24 mmol, 10%) as colourless oils.

Compound 18a: R_f = 0.07 (hexanes/EtOAc, 20:1). ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 7.18 (d, J = 8.5 Hz, 2 H, Ar-*H*), 7.05 (d, J = 8.1 Hz, 2 H, Ar-*H*), 6.91 (d, J = 8.6 Hz, 2 H, Ar-*H*), 6.60 (d, J = 8.3 Hz, 2 H, Ar-*H*), 3.84 (s, 3 H, O-CH_3), 3.52 (br. s, 1 H, N-*H*), 3.38 (t, J = 7.0 Hz, 2 H, N-CH_2), 2.89 (t, J = 7.0 Hz, 2 H, CH_2), 2.30 (s, 3 H, CH_3) ppm. ^{13}C NMR (125 MHz, DEPT, $CDCl_3$, 25 °C): δ = 158.3 (C), 145.7 (C), 131.4 (C), 129.9 (CH), 129.8 (CH), 126.9 (C), 114.1 (CH), 113.4 (CH), 55.3 (CH_3), 45.8 (CH_2), 34.6 (CH_2), 20.5 (CH_3) ppm. MS (EI, 70 eV): *m*/*z* (%) = 241 (6) $[M]^+$, 121 (17) $[C_8H_9O]^+$, 120 (100) $[C_8H_{10}N]^+$, 91 (15) $[C_7H_7]^+$, 77 (5) $[C_6H_5]^+$. HRMS (ESI, +): calcd. for $C_{16}H_{20}NO$ 242.1545; found 242.1540. IR (ATR): $\tilde{\nu}$ = 703, 806, 1034, 1090, 1111, 1125, 1177, 1242, 1300, 1318, 1441, 1463, 1477, 1510, 1583, 1613, 2834, 2859, 2917, 3001, 3398 cm^{-1}.

Compound 18b: R_f = 0.12 (hexanes/EtOAc, 20:1). ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 7.35 (d, J = 8.7 Hz, 2 H, Ar-*H*), 6.98 (d, J = 8.4 Hz, 2 H, Ar-*H*), 6.92 (d, J = 8.7 Hz, 2 H, Ar-*H*), 6.52 (d, J = 8.4 Hz, 2 H, Ar-*H*), 4.49 (q, J = 6.7 Hz, 1 H, C*H*), 3.83 (s, 3 H, O-CH_3), 2.26 (s, 3 H, CH_3), 1.54 (d, J = 6.7 Hz, 3 H, CH_3) ppm. ^{13}C NMR (125 MHz, DEPT, $CDCl_3$, 25 °C): δ = 158.5 (C), 145.1 (C), 137.5 (C), 129.7 (CH), 127.0 (CH), 126.4 (C), 114.1 (CH), 113.6 (CH), 55.3 (CH_3), 53.2 (CH), 25.1 (CH_3), 20.5 (CH_3) ppm.

***N*-[2-(Cyclohexyl)ethyl]-4-methylaniline (19a) and *N*-[1-(Cyclohexyl)ethyl]-4-methylaniline (19b):** General procedure A (80 °C) was used to synthesise the title compounds from cyclohexylacetylene and *p*-toluidine. Purification by flash chromatography (SiO_2; hexanes/MTBE, 30:1) gave products **19a** (160 mg, 0.74 mmol, 31%) and **19b** (317 mg, 1.46 mmol, 61%) as colourless oils.

Compound 19a: R_f = 0.18 (hexanes/MTBE, 30:1). ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 7.03 (d, J = 7.1 Hz, 2 H, Ar-*H*), 6.59 (d, J = 7.3 Hz, 2 H, Ar-*H*), 3.42 (br. s, 1 H, N-*H*), 3.15 (t, J = 7.3 Hz, 2 H, N-CH_2), 2.29 (s, 3 H, CH_3), 1.83–0.74 (m, 13 H) ppm. ^{13}C NMR (125 MHz, DEPT, $CDCl_3$, 25 °C): δ = 146.4 (C), 129.8 (CH), 126.5 (C), 113.1 (CH), 42.3 (CH_2), 37.3 (CH_2), 35.7 (CH), 33.5 (CH_2), 26.7 (CH_2), 26.4 (CH_2), 20.5 (CH_3) ppm. MS (EI, 70 eV): *m*/*z* (%) = 217 (9) $[M]^+$, 120 (100) $[C_8H_{10}N]^+$, 91 (8) $[C_7H_7]^+$. HRMS (ESI, +): calcd. for $C_{15}H_{24}N$ 218.1909; found 218.1906. IR (ATR): $\tilde{\nu}$ = 704, 805, 888, 1123, 1149, 1182, 1251, 1301, 1317, 1405, 1447, 1479, 1519, 1583, 1618, 2849, 2919, 3017, 3401 cm^{-1}.

Compound 19b: R_f = 0.25 (hexanes/MTBE, 30:1). ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 6.98 (d, J = 8.2 Hz, 2 H, Ar-*H*), 6.53 (d, J = 8.2 Hz, 2 H, Ar-*H*), 3.33–3.27 (m, 1 H, C*H*), 2.25 (s, 3 H, CH_3), 1.88–1.64 (m, 5 H, cyclohexyl-*H*), 1.51–1.41 (m, 1 H, cyclohexyl-*H*), 1.35–0.97 (m, 5 *H*, cyclohexyl-*H*), 1.12 (d, J = 6.5 Hz, 3 H, CH_3) ppm. ^{13}C NMR (125 MHz, DEPT, $CDCl_3$, 25 °C): δ = 145.6 (C), 129.9 (CH), 126.1 (C), 113.6 (CH), 53.8 (CH), 43.1 (CH), 30.0 (CH_2), 28.5 (CH_2), 26.8 (CH_2), 26.7 (CH_2), 26.5 (CH_2), 20.5 (CH_3), 17.5 (CH_3) ppm. MS (EI, 70 eV): *m*/*z* (%) = 217 (5) $[M]^+$, 134 (100) $[C_9H_{12}N]^+$, 91 (5) $[C_7H_7]^+$. HRMS (ESI, +): calcd. for $C_{15}H_{24}N$ 218.1909; found 218.1903. IR (ATR): $\tilde{\nu}$ = 703, 804, 841, 890, 954, 993, 1008, 1042, 1063, 1078, 1121, 1142, 1159, 1182, 1250, 1298, 1316, 1373, 1404, 1448, 1483, 1517, 1582, 1618, 2851, 2921, 2963, 3016, 3408 cm^{-1}.

4-Methyl-*N*-(1-methylheptyl)aniline (20b):[11b] General procedure A (80 °C) was used to synthesise the title compound from 1-octyne and *p*-toluidine. Purification by flash chromatography (SiO_2; hexanes/MTBE, 200:1) gave products **20a** (36 mg, 0.16 mmol, 7%) and **20b** (411 mg, 1.87 mmol, 78%) as colourless oils.

Compound 20b: R_f = 0.07 (hexanes/MTBE, 200:1). ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 6.88 (d, J = 8.3 Hz, 2 H, Ar-*H*), 6.42 (d, J = 8.4 Hz, 2 H, Ar-*H*), 3.36–3.28 (m, 1 H, C*H*), 3.19 (br. s, 1 H, N-*H*), 2.14 (s, 3 H, CH_3), 1.55–1.42 (m, 1 H, CH_2), 1.37–1.14 (m, 9 H, CH_2), 1.06 (d, J = 6.3 Hz, 3 H, CH_3), 0.80 (t, J = 6.9 Hz, 3 H, CH_3) ppm. ^{13}C NMR (125 MHz, DEPT, $CDCl_3$, 25 °C): δ = 145.5 (C), 129.9 (CH), 126.1 (C), 113.5 (CH), 49.0 (CH), 37.3 (CH_2), 32.0 (CH_2), 29.5 (CH_2), 26.3 (CH_2), 22.8 (CH_2), 20.9 (CH_3), 20.5 (CH_3), 14.2 (CH_3) ppm.

4-Methyl-*N*-(3-phenylpropyl)aniline (21a):[19] General procedure A (80 °C) was used to synthesise the title compound from 3-phenylpropyne and *p*-toluidine. Purification by flash chromatography (SiO_2; hexanes/EtOAc, 20:1) gave products **21a** (97 mg, 0.43 mmol, 18%) and **5a** (378 mg, 1.68 mmol, 70%) as colourless oils.

Compound 21a: R_f = 0.13 (hexanes/EtOAc, 40:1). ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 7.34–7.27 (m, 2 H, Ar-*H*), 7.24–7.16 (m, 3 H, Ar-*H*), 7.00 (d, J = 8.2 Hz, 2 H, Ar-*H*), 6.57 (d, J = 8.3 Hz, 2 H, Ar-*H*), 3.15 (t, J = 7.1 Hz, 2 H, N-CH_2), 2.74 (t, J = 7.6 Hz, 2 H, CH_2), 2.25 (s, 3 H, CH_3), 1.97 (pent, J = 7.3 Hz, 2 H, CH_2), 1.28 (br. s, 1 H, N-*H*) ppm. ^{13}C NMR (125 MHz, DEPT, $CDCl_3$, 25 °C): δ = 145.6 (C), 141.8 (C), 129.9 (CH), 128.6 (CH), 128.5 (CH), 127.3 (C), 126.1 (CH), 113.7 (CH), 44.4 (CH_2), 33.5 (CH_2), 31.1 (CH_2), 20.5 (CH_3) ppm.

4-Methyl-*N*-(1-methylpropyl)aniline (22):[20] General procedure A (80 °C) was used to synthesise the title compound from 2-butyne and *p*-toluidine. Purification by flash chromatography (SiO_2; hexanes/MTBE, 30:1) gave product **22** (239 mg, 1.46 mmol, 61%) as a colourless oil. R_f = 0.22 (hexanes/MTBE, 30:1). ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 7.06 (d, J = 8.4 Hz, 2 H, Ar-*H*), 6.59 (d, J = 8.4 Hz, 2 H, Ar-*H*), 3.48–3.41 (m, 1 H, C*H*), 3.33 (br. s, 1 H, N-*H*), 2.32 (s, 3 H, CH_3), 1.72–1.61 (m, 1 H, CH_2), 1.58–1.48 (m, 1 H, CH_2), 1.23 (d, J = 6.4 Hz, 3 H, CH_3), 1.03 (t, J = 7.5 Hz, 3 H, CH_3) ppm. ^{13}C NMR (125 MHz, DEPT, $CDCl_3$, 25 °C): δ = 145.5 (C), 129.8 (CH), 126.0 (C), 113.5 (CH), 50.2 (CH), 29.7 (CH_2), 20.4 (CH_3), 20.3 (CH_3), 10.5 (CH_3) ppm.

4-Methyl-*N*-(1-propylpentyl)aniline (23):[21] General procedure A (120 °C) was used to synthesise the title compound from 4-octyne and *p*-toluidine. Purification by flash chromatography (SiO_2; hex-

anes/MTBE, 30:1) gave product **23** (374 mg, 1.70 mmol, 71%) as a colourless oil. R_f = 0.33 (hexanes/MTBE, 30:1). ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 7.03 (d, J = 8.3 Hz, 2 H, Ar-*H*), 6.56 (d, J = 8.4 Hz, 2 H, Ar-*H*), 3.40–3.33 (m, 1 H, C*H*), 3.34 (br. s, 1 H, N-*H*), 2.29 (s, 3 H, CH_3), 1.63–1.33 (m, 10 H, CH_2), 0.98 (t, J = 7.2 Hz, 3 H, CH_3), 0.96 (t, J = 7.1 Hz, 3 H, CH_3) ppm. ^{13}C NMR (125 MHz, DEPT, $CDCl_3$, 25 °C): δ = 146.0 (C), 129.9 (CH), 125.7 (C), 113.1 (CH), 53.0 (CH), 37.4 (CH_2), 34.8 (CH_2), 28.2 (CH_2), 23.0 (CH_2), 20.4 (CH_3), 19.3 (CH_2), 14.4 (CH_3), 14.2 (CH_3) ppm.

***N*-(1,2-Diphenylethyl)-4-methylaniline (24):**[11b] General procedure A (120 °C) was used to synthesise the title compound from diphenylacetylene and *p*-toluidine. Purification by flash chromatography (SiO_2; hexanes/EtOAc, 20:1) gave product **24** (655 mg, 2.28 mmol, 95%) as a colourless oil. R_f = 0.31 (hexanes/EtOAc, 20:1). ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 7.45–7.29 (m, 8 H, Ar-*H*), 7.22 (d, J = 7.0 Hz, 2 H, Ar-*H*), 6.97 (d, J = 8.3 Hz, 2 H, Ar-*H*), 6.49 (d, J = 8.4 Hz, 2 H, Ar-*H*), 4.66 (dd, J = 8.3, 5.7 Hz, 1 H, C*H*), 4.13 (br. s, 1 H, N-*H*), 3.22 (dd, J = 14.0, 5.7 Hz, 1 H, CH_2), 3.10 (dd, J = 14.0, 8.3 Hz, 1 H, CH_2), 2.27 (s, 3 H, CH_3) ppm. ^{13}C NMR (125 MHz, DEPT, $CDCl_3$, 25 °C): δ = 145.1 (C), 143.7 (C), 137.9 (C), 129.6 (CH), 129.3 (CH), 128.6 (CH), 128.6 (CH), 127.1 (CH), 126.8 (C), 126.7 (CH), 126.6 (CH), 113.9 (CH), 59.6 (CH), 45.3 (CH_2), 20.4 (CH_3) ppm.

2-Methyl-4,4-diphenylpyrrolidine (26):[4a] General procedure B (120 °C) was used to synthesise the title compound from aminoalkene **25**. Purification by flash chromatography (SiO_2; MTBE/7N NH_3 in MeOH, 19:1) gave product **26** (470 mg, 1.98 mmol, 99%) as a colourless oil. R_f = 0.19 (MTBE/7N NH_3 in MeOH, 19:1). ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 7.18–7.04 (m, 8 H, Ar-*H*), 7.03–6.96 (m, 2 H, Ar-*H*), 3.52 (d, J = 11.4 Hz, 1 H, N-CH_2), 3.32 (d, J = 11.4 Hz, 1 H, N-CH_2), 3.25–3.17 (m, 1 H, C*H*), 2.58 (dd, J = 12.7, 6.6 Hz, 1 H, CH_2), 2.11 (br. s, 1 H, N-*H*), 1.88 (dd, J = 12.7, 9.1 Hz, 1 H, CH_2), 1.05 (d, J = 6.4 Hz, 3 H, CH_3) ppm. ^{13}C NMR (125 MHz, DEPT, $CDCl_3$, 25 °C): δ = 147.8 (C), 147.0 (C), 128.3 (CH), 128.3 (CH), 127.0 (CH), 127.0 (CH), 126.0 (CH), 126.0 (CH), 57.9 (CH_2), 57.3 (C), 53.1 (CH), 47.1 (CH_2), 22.3 (CH_3) ppm.

***N*-(*p*-Tolylsulfonyl)-3-methyl-2-azaspiro[4,5]decane (28):**[22] General procedure C (160 °C) was used to synthesise the title compound from aminoalkene **27**. Purification by flash chromatography (SiO_2; hexanes/EtOAc, 15:1) gave product **28** (511 mg, 1.66 mmol, 83%) as a colourless solid. R_f = 0.20 (hexanes/EtOAc, 15:1). ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 7.67 (d, J = 8.2 Hz, 2 H, Ar-*H*), 7.25 (d, J = 8.2 Hz, 2 H, Ar-*H*), 4.23–4.14 (m, 1 H, C*H*), 3.56 (d, J = 12.7 Hz, 1 H, N-CH_2), 2.57 (d, J = 12.8 Hz, 1 H, N-CH_2), 2.39 (s, 3 H, CH_3), 1.97–1.85 (m, 1 H, CH_2), 1.57–1.12 (m, 11 H, CH_2), 0.91 (d, J = 6.9 Hz, 3 H, CH_3) ppm. ^{13}C NMR (125 MHz, DEPT, $CDCl_3$, 25 °C): δ = 142.8 (C), 138.4 (C), 129.5 (CH), 127.1 (CH), 48.5 (CH), 48.0 (CH_2), 38.2 (CH_2), 33.0 (C), 30.9 (CH_2), 26.6 (CH_2), 26.5 (CH_2), 21.6 (CH_3), 21.5 (CH_2), 21.4 (CH_2), 14.3 (CH_3) ppm.

2-Methyl-5,5-diphenylpiperidine (32):[23] General procedure B (160 °C) was used to synthesise the title compound from aminoalkene **31**. Purification by flash chromatography (SiO_2; MTBE/7N NH_3 in MeOH, 19:1) gave product **32** (483 mg, 1.74 mmol, 87%) as a colourless oil. R_f = 0.18 (MTBE/7N NH_3 in MeOH, 19:1). ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 7.26 (d, J = 8.0 Hz, 2 H, Ar-*H*), 7.18 (t, J = 7.8 Hz, 2 H, Ar-*H*), 7.10–7.01 (m, 3 H, Ar-*H*), 6.99 (d, J = 7.3 Hz, 2 H, Ar-*H*), 6.96 (t, J = 7.2 Hz, 1 H, Ar-*H*), 3.76 (dd, J = 13.7, 3.1 Hz, 1 H, N-CH_2), 2.97 (d, J = 13.7 Hz, 1 H, N-CH_2), 2.68–2.59 (m, 1 H, C*H*), 2.59–2.50 (m, 1 H, CH_2), 2.10–2.01 (m, 1 H, CH_2), 1.70 (br. s, 1 H, N-*H*), 1.52–1.45 (m, 1 H, CH_2), 1.06–0.96 (m, 1 H, CH_2), 0.86 (d, J = 6.4 Hz, 3 H, CH_3) ppm. ^{13}C NMR (125 MHz, DEPT, $CDCl_3$, 25 °C): δ = 148.8 (C), 144.7 (C), 128.7 (CH), 128.3 (CH), 126.5 (CH), 125.9 (CH), 125.9 (CH), 55.8 (CH_2), 52.4 (CH), 45.3 (C), 35.5 (CH_2), 31.4 (CH_2), 22.5 (CH_3) ppm.

***N*-(*p*-Tolylsulfonyl)-3-methyl-2-azaspiro[5,5]undecane (34):** General procedure C (160 °C) was used to synthesise the title compound from aminoalkene **33**. Purification by flash chromatography (SiO_2; hexanes/EtOAc, 20:1) gave product **34** (240 mg, 0.75 mmol, 37%) as a colourless solid. R_f = 0.14 (hexanes/EtOAc, 20:1), m.p. 71.4–73.2 °C. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 7.69 (d, J = 8.0 Hz, 2 H, Ar-*H*), 7.26 (d, J = 7.8 Hz, 2 H, Ar-*H*), 4.24–4.17 (m, 1 H, C*H*), 3.57 (d, J = 12.7 Hz, 1 H, N-CH_2), 2.59 (d, J = 12.7 Hz, 1 H, N-CH_2), 2.41 (s, 3 H, CH_3), 1.98–1.86 (m, 1 H, CH_2), 1.59–1.16 (m, 13 H, CH_2), 0.94 (d, J = 6.8 Hz, 3 H, CH_3) ppm. ^{13}C NMR (125 MHz, DEPT, $CDCl_3$, 25 °C): δ = 142.8 (C), 138.6 (C), 129.6 (CH), 127.2 (CH), 48.5 (CH), 48.2 (CH_2), 38.3 (CH_2), 33.1 (C), 31.1 (CH_2), 30.2 (CH_2), 26.7 (CH_2), 26.6 (CH_2), 21.6 (CH_2), 21.6 (CH_3), 21.5 (CH_2), 14.4 (CH_3) ppm. MS (EI, 70 eV): *m*/*z* (%) = 321 (1) $[M]^+$, 306 (45) $[C_{17}H_{24}NO_2S]^+$, 212 (12), 155 (29) $[C_7H_7O_2S]^+$, 91 (100) $[C_7H_7]^+$. HRMS (ESI, +): calcd. for $C_{18}H_{27}NO_2NaS$ 344.1660; found 344.1664. IR (ATR): $\tilde{\nu}$ = 547, 604, 661, 707, 750, 817, 859, 902, 918, 932, 961, 985, 1008, 1034, 1093, 1132, 1146, 1168, 1220, 1249, 1285, 1301, 1318, 1382, 1450, 1493, 1596, 2849, 2923 cm^{-1}.

Supporting Information (see footnote on the first page of this article): Copies of the ^{1}H and ^{13}C NMR spectra of all products. X-ray crystal structure of product **16a**.

Acknowledgments

The authors thank the Deutsche Forschungsgemeinschaft (DFG) for financial support of the research.

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[9] Complex **2**: Red crystals, dimensions $0.43 \times 0.25 \times 0.23$ mm^3, monoclinic, space group *I*2/*a*, unit cell dimensions: a = 17.0232(3) Å, b = 15.7340(3) Å, c = 17.7778(5) Å, α = 90°, β = 104.8130(10)°, γ = 90°, V = 4603.41(18) Å^3, Z = 8, ρ = 1.260 Mg/m^3, Θ_{max} = 35.20°, radiation Mo K_α, λ = 0.71073 Å, ϕ and ω-scans with Bruker KAPPA APEX-II CCD at T = 120(2) K, 96014 reflections measured, 10158 unique [R_{int} = 0.0342], 7963 observed [$I > 2\sigma(I)$], intensities were corrected for Lorentz and polarization effects, an empirical absorption correction was applied using Bruker SAINT based on the Laue symmetry of the reciprocal space, μ = 0.394 mm^{-1}, T_{min} = 0.8484, T_{max} = 0.9148, structure solved by direct methods and refined against F^2 with a Full-matrix least-squares algorithm using the SHELXS-97 software package, 272 parameters refined, hydrogen atoms were treated using appropriate riding models, goodness of fit 1.058 for observed reflections, final residual values R_1 = 0.0369, wR_2 = 0.0962 for observed reflections, largest diff. peak, hole 0.680 and –0.328 e Å^{-3}. CCDC-925787 contains the supplementary crystallographic data for **2**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[17] Product **16a**: Colourless crystals, dimensions $0.63 \times 0.44 \times 0.12$ mm^3, monoclinic, space group *P*2(1)/*c*, unit cell dimensions: a = 261882(16) Å, b = 5.6083(4) Å, c = 8.9619(6) Å, α = 90°, β = 93.682(4)°, γ = 90°, V = 1313.53(15) Å^3, Z = 4, ρ = 1.139 Mg/m^3, Θ_{max} = 29.56°, radiation Mo K_α, λ = 0.71073 Å, ϕ and ω-scans with Bruker KAPPA APEX-II CCD at T = 120(2) K, 36777 reflections measured, 3669 unique [R_{int} = 0.0423], 2977 observed [$I > 2\sigma(I)$], intensities were corrected for Lorentz and polarization effects, an empirical absorption correction was applied using Bruker SAINT based on the Laue symmetry of the reciprocal space, μ = 0.066 mm^{-1}, T_{min} = 0.9601, T_{max} = 0.9919, structure solved by direct methods and refined against F^2 with a Full-matrix least-squares algorithm using the SHELXS-97 software package, 160 parameters refined, hydrogen atoms were treated using appropriate riding models, goodness of fit 1.091 for observed reflections, final residual values R_1 = 0.0589, wR_2 = 0.1560 for observed reflections, largest diff. peak, hole 0.363 and –0.193 e Å^{-3}. CCDC-953364 contains the supplementary crystallographic data for **16a**. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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Received: July 5, 2013
Published Online: October 2, 2013

