Pergamon

Tetrahedron 54 (1998) 4493–4506

TETRAHEDRON

# Rhodium(I)-catalysed Hydrocarbonylation and Silylcarbonylation Reactions of Alkynes in the Presence of Primary Amines Leading to 2-Pyrrolidinones and 4-Silylated 1-Aza-1,3-butadienes

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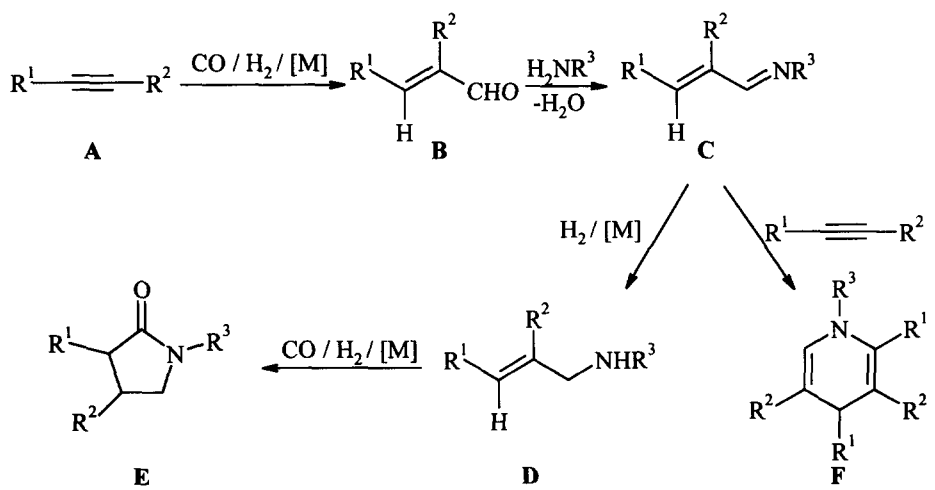
Received 24 December 1997; accepted 10 February 1998

**Abstract.** Rh(I)-catalysed hydrocarbonylation of alkynes **1** in the presence of primary amines gives substituted 2-pyrrolidinones **3** in a one-pot procedure. Replacement of hydrogen by hydrosilanes via silylcarbonylation leads to 4-silylated 1-aza-1,3-butadienes **5**. These azadienes are converted with dimethyl acetylenedicarboxylate to 1,4-dihydropyridines **8** via Diels-Alder reaction.


Transition metal catalysed hydroformylation of olefins in the presence of amines offers a convenient method for selective alkylation of primary and secondary amines.[1] This multi-step "hydroaminomethylation" procedure includes hydroformylation of the alkene, followed by condensation of the intermediate aldehyde with a primary or secondary amine to generate an imine or enamine, respectively, and final hydrogenation to give the saturated amine in a one-pot procedure. An analogous reaction sequence starting from alkynes, as outlined in scheme 1, has not yet been studied.




Scheme 1. Carbonylation of alkynes in the presence of primary amines

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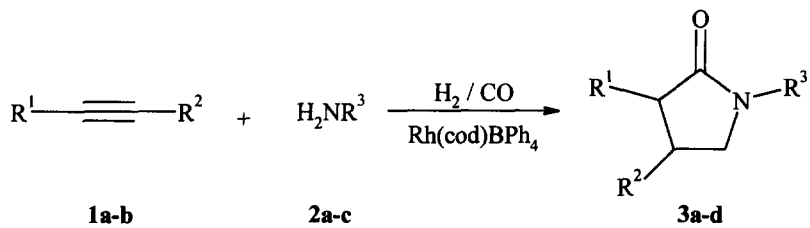
0040-4020/98/$19.00 
*PII:* S0040-4020(98)00160-4

Hydroformylation of alkynes **A** in the presence of primary amines should lead to condensation of the primarily generated $\alpha,\beta$-unsaturated aldehydes **B** to form the corresponding azadienes **C**. Selective hydrogenation of the imino double-bond gives allylic amines **D**. Allylic amines with one NH-bond are known to undergo carbonylative cyclisation to 2-pyrrolidinones **E**.[2] On the other hand azadienes **C** may undergo further conversions, e.g. via Diels-Alder reaction with a second alkyne unit to form dihydropyridins of type **F**.[3]

Complex reaction sequences leading to 2-pyrrolidinones **E** or to cycloadducts of type **F** in the presence of $H_2$ and CO can compete with alternative reaction pathways. Thus alkynes under hydroformylation conditions usually form saturated aldehydes or alcohols[4] and if azadienes of type **C** are obtainable at all, a selective hydrogenation of the imino group might pose severe problems for further one-pot conversions to pyrrolidinones **E**. The former problem has recently been solved. The selective hydroformylation of internal alkynes to $\alpha,\beta$-unsaturated aldehydes without further hydrogenation was described using specific catalyst systems. [5]

We here report the first examples of a one-pot synthesis of substituted 2-pyrrolidinones starting from alkynes and amines under hydroformylation conditions.




**1a-b** **2a-c** **3a-d**

Scheme 2. Synthesis of 2-pyrrolidinones via hydrocarbonylation of alkynes in the presence of primary amines

Table 1. Hydrocarbonylation of Alkynes **1** with $CO/H_2$ and Amines **2** Catalysed by $Rh(cod)BPh_4$

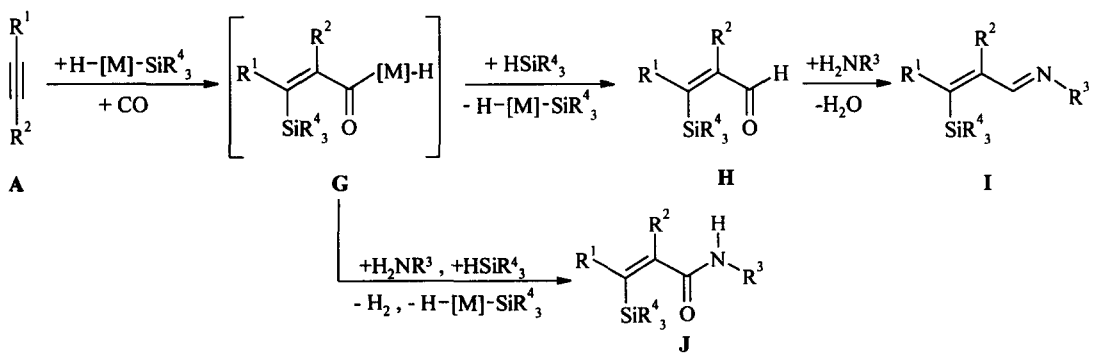
| entry | alkyne | $R^1$ | $R^2$ | amine | $R^3$ | product **3** | yield (%) |
|---|---|---|---|---|---|---|---|
| 1[a] | **1a** | H | Ph | **2a** | Bu | **3a** | 21 |
| 2 | **1a** | H | Ph | **2b** | Hex | **3b** | 37 |
| 3[b] | **1a** | H | Ph | **2b** | Hex | **3b** | 30 |
| 4 | **1a** | H | Ph | **2c** | Benzyl | **3c** | 25 |
| 5 | **1b** | Pr | Pr | **2c** | Benzyl | **3d** | 14 |

All reactions were carried out in dioxane at 100 °C, with 100 bar $CO/H_2$ (1:1) for 3 d following the general procedure A; [a] The reaction was run for 20 h; [b] The reaction was carried out with a $CO/H_2$-ratio of 1:3.

As summarized in table 1, hydrocarbonylation of alkynes **1a-b** in the presence of primary amines **2a-c** and $Rh(cod)BPh_4$ as catalyst precursor leads to pyrrolidinones **3a-d**. Noteworthy, with the unsymmetrical phenylacetylene **1a** (entries 1-4) only one of the two possible regioisomers is formed, indicating a high regioselectivity in this multi-step dicarbonylation procedure. However, moderate yields and selectivities up to now prevent a straightforward synthetic application of this method, e.g. towards the synthesis of pharmaceutically interesting γ-butyrolactams.[6]

In this sequence the alkyne, the amine and two molecules of carbon monoxide are connected to generate substituted 2-pyrrolidinones presumably via allylic amines of type **D** (scheme 1). A multi-step reaction of this type, however, allows various alternative pathways leading to several byproducts. Thus, without incorporation of the amine reductive carbonylation leads to 5*H*-furan-2-ones. Formation of these products is known to be promoted especially under high partial pressures of carbon monoxide.[7] On the other hand with increasing hydrogen pressure complete reduction of the intermediates leads to products, such as saturated amines. Moreover, the formation of amides is observed due to hydrocarboxylation reaction of the alkynes. All these side products are responsible for the moderate yields of the pyrrolidinones **3a-d** as described above.

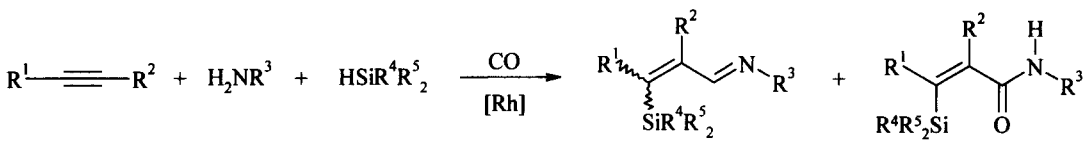
In order to suppress these side reactions alternative methods for the carbonylation of alkynes in the presence of amines have to be found. For this reason replacement of hydrogen by hydrosilanes offers a promising approach leading to β-silyl substituted α,β-unsaturated aldehydes. The transition metal catalysed silylformylation reaction of alkynes with $HSiR_3$/CO has been subject of intensive studies in various research groups over the past years.[8-13] Compared with hydrogen the use of $HSiR_3$ in carbonylation permits milder reaction conditions.[8-12] Furthermore, hydrogenation reactions of unsaturated compounds can not occur. A conversion of this type in the presence of amines has not yet been studied. Here in a consecutive reaction step amine condensation products might result (scheme 3).




Scheme 3. Formation of 4-silylated azadienes from alkynes by silylformylation in the presence of amines

Silylformylation of alkynes **A** in the presence of primary amines should lead to azabutadienes **I**, after amine condensation of the corresponding enals **H** (scheme 3). On the other hand, in an alternative pathway the intermediate acylrhodium species **G** might react with N-nucleophiles to form acrylamides **J**. In an intramolecular version a process similar to the latter was reported by Matsuda et al., who carried out a silylformylation reaction of propargylic amines leading to β-lactams.[9c]

With equimolar amounts of phenylacetylene **1a**, triethylsilane **4a** and hexylamine **2b** under silylformylation conditions the 4-silylsubstituted 1,3-azadiene **5a** is obtained only in moderate yields as a mixture of 1*E*,3*Z*- and 1*E*,3*E*-isomers. In addition, the 3-silylated *Z*-acrylamide derivative **6a** is generated in comparable amounts (scheme 4).




**1a,c** **2a-b,d-h** **4a-b** **5a-j** **6a-b**

Scheme 4. Silylformylation of acetylenes in the presence of primary amines

Table 2. Reactions of Triorganosilanes with Alkynes Catalysed by $Rh(cod)BPh_4$ or $[RhCl(cod)]_2$ in the Presence of Carbon Monoxide and Primary Amines

| entry | 1 | $R^1$ | $R^2$ | 2 | $R^3$ | 4 | $R^4$ | $R^5$ | products | yield 5 (%) | 3*Z*/3*E*-ratio 5 | yield 6 (%) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 6[a] | **1a** | H | Ph | **2b** | Hex | **4a** | Et | Et | **5a, 6a** | 75 | 1.4 / 1 | 21 |
| 7[a] | **1a** | H | Ph | **2a** | Bu | **4a** | Et | Et | **5b, 6b** | 74 | 1.9 / 1 | 23 |
| 8[a] | **1a** | H | Ph | **2d** | *t*-Bu | **4a** | Et | Et | **5c** | 86 | 1 / 1 | - |
| 9 | **1a** | H | Ph | **2e** | R(+)-PhEt | **4b** | Ph | Me | **5d** | 96 | 1.4 / 1 | - |
| 10 | **1a** | H | Ph | **2f** | *i*-Pr | **4b** | Ph | Me | **5e** | 89 | 1.4 / 1 | - |
| 11[b] | **1a** | H | Ph | **2f** | *i*-Pr | **4b** | Ph | Me | **5e** | 72 | 1.2 / 1 | - |
| 12[c] | **1c** | H | Bu | **2f** | *i*-Pr | **4a** | Et | Et | **5f** | 64 | > 20 / 1 | - |
| 13[c] | **1c** | H | Bu | **2e** | R(+)-PhEt | **4a** | Et | Et | **5g** | 82 | > 20 / 1 | - |
| 14 | **1c** | H | Bu | **2b** | Hex | **4a** | Et | Et | **5h** | 88 | > 20 / 1 | - |
| 15 | **1c** | H | Bu | **2g** | *p*-Ph(OMe) | **4a** | Et | Et | **5i** | 94 | > 20 / 1 | - |
| 16[a] | **1c** | H | Bu | **2h** | Allyl | **4a** | Et | Et | **5j** | 85 | > 20 / 1 | - |

All reactions were run with $Rh(cod)BPh_4$ (1 mol-%, based on the amount of silane) in toluene at 60°C and a pressure of 50 bar CO for 22 h following the general procedure B; [a] $CH_2Cl_2$ was used as solvent; [b] The reaction was carried out at a pressure of 1 atm CO and ambient temperature for 20 h and at 40 °C for 72 h in a Schlenk flask ; [c] $[RhCl(cod)]_2$ is used as catalyst precursor

Increasing the amount of silane leads to a prefered formation of the aldehyde **H** from the acyl rhodium species **G** (scheme 3). This way the selectivity of the reaction is improved only insignificantly. The best results for the formation of **5a** are achieved by replacement of toluene by a solvent of higher polarity. With $CH_2Cl_2$ used as solvent, **5a** is obtained in a yield of 75 % (entry 6, table 2), reducing the yield of the undesired side product **6a** to 21 %. The same conversion with *n*-butylamine under similar conditions gives comparable results (entry 7). The formation of amides of type **6** is only observed, if an amine with a small sterical demand is employed. With *t*-butylamine the *β*-silylated acrylic amide is not detected and the azadiene **5c** is obtained in good yields (entry 8).

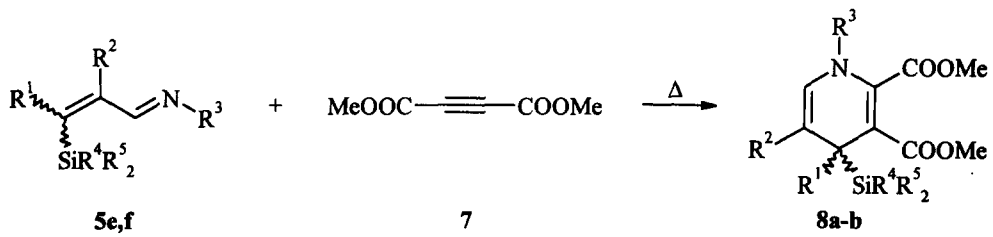
Similarly with dimethylphenylsilane **4b** instead of triethylsilane **4a** the azadienes **5d** and **5e** are obtained in good yields as well (entries 9+10). Under milder reaction conditions (ambient temperature, 1 atm CO) no conversion is observed. Whereas with rising the reaction temperature to 40 °C a 72 hours reaction time is required to get a moderate yield, however, with no significant change in the 3*E*/3*Z*-ratio (entry 11).

Further conversions using 1-hexyne **1c** and triethylsilane **4a** in the presence of a variety of primary amines are listed in table 2 (entries 12-16), with both aromatic and aliphatic amines giving satisfactory yields. The products **5f-j** are obtained as 1*E*/3*Z*-isomers (configuration determined by $^1$H NOESY in the case of **5j**). Thus the conjugation of the double bond with an aromatic substituent in case of azadienes of type **5** appears to be essential for rapid isomerisation.

In entries 12 and 13 the dimeric rhodium complex $[RhCl(cod)]_2$ is used with slighly lower efficiency than $Rh(cod)BPh_4$, as used by Alper and Zhou[12a] in silylformylations. Alper observed, that $[RhCl(cod)]_2$ as catalyst precursor contrary to zwitterionic or cationic complexes often leads to complex product mixtures. With $Rh(cod)BPh_4$ as catalyst precursor the formation of disilanes can be suppressed, while especially in the case of $HSiMe_2Ph$ in combination with $[RhCl(cod)]_2$ this side reaction causes selectivity problems. Secondary amines like morpholine do not react. In our hands only silylformylation product (ca. 70 %) and no incorporation of amine is observed.

Stereochemically the amides **6** are exclusively formed in the *Z*-configuration (as proven by $^1$H NOESY experiment in the case of **6b**). This gives evidence for a stereoselective *syn*-silylformylation leading to *Z*-configuration at the CC double bond. This is in agreement with earlier results describing silylformylation as regio- and *syn*-selective.[8d,10a] The thermodynamically more stable azadienes **5** with 3*E*-configuration are generated via isomerisation from the initially formed 3*Z*-isomer. Surnin and Stadnichuk[14] observed almost complete conversion of 4-silylated 1-aza-1,3-butadienes from 3*Z*- into the *E*-configuration over a two-day period. The 1-aza-1,3-butadienes of type **5** show higher stability. At room temperature a significant isomerisation takes place only after several weeks (determined by NMR spectroscopy, product **5f**).

Under the reaction conditions applied no detectable amounts of products of type **F** are formed, due to the low reactivity of the alkynes **1a-c** as dienophiles. With more reactive alkynes, such as dimethyl acetylene-dicarboxylate 4-silylated 1,4-dihydropyridines **8a-b** are obtained with moderate yields (table 3). Products of this type exhibit two non eqivalent allyl silane subunits offering various pathways for further conversions.




**5e,f** **7** **8a-b**

Scheme 5. Diels-Alder reaction of azadienes **5** with dimethyl acetylene dicarboxylate **7**

Table 3: Diels-Alder Reaction of 4-Silylsubstituted 1-Aza-1,3-dienes with Dimethyl Acetylene Dicarboxylate

| entry | solvent | **5** | $R^1$ | $R^2$ | $R^3$ | $R^4$ | $R^5$ | product **8** | yield (%) |
|---|---|---|---|---|---|---|---|---|---|
| 17[a] | xylene | **5e** | H | Ph | *i*-Pr | Ph | Me | **8a** | 38 |
| 18[a] | xylene | **5f** | H | Bu | *i*-Pr | Et | Et | **8b** | 33 |
| 19[b] | $CH_3CN$ | **5f** | H | Bu | *i*-Pr | Et | Et | **8b** | 51 |

The reaction was run following general procedure C; [a] The reactions were carried out with two equivalents of the dienophile; [b] The reaction was run with one equivalent of the dienophile.

## Conclusion

Hydrocarbonylation of acetylenes with $CO/H_2$ in the presence of primary amines leads to substituted 2-pyrrolidinones in a multi-step sequence. Under the reaction conditions used, however, low selectivities are observed due to hydrogenation and other side reactions depending on the chosen $H_2/CO$-ratio. Employing hydrosilanes instead of hydrogen the carbonylation reaction of alkynes with primary amines proceeds with a high chemo-, regio- and stereoselectivity leading to a variety of 4-silylated 1-aza-1,3-butadienes in good to excellent yields. This reaction represents a modified type of silylformylation and may serve as a convenient method for the synthesis of azadienes starting from alkynes. The products upon Hetero-Diels-Alder reaction gives 4-silylated 1,4-dihydro-pyridines. Products of this type may prove as precursors for various dihydro- or tetrahydropyridine systems, e. g. as NADH models[15] and calcium channel blockers[16].

## Experimental Section

All chemicals were purchased from commercial sources. The catalyst precursors $[RhCl(cod)]_2$[17] and $Rh(cod)BPh_4$[18] were prepared as described. Column chromatography was carried out on alumina N (act. I) from ICN Biomedicals, Eschwege, or with silica gel 60 from Merck, Darmstadt. $^1H$ and $^{13}C$ NMR spectra were recorded on a Bruker DPX 300 or DRX 400 spectrometer using $CDCl_3$ as the solvent and $CH_2Cl_2$ as the internal standard. IR spectra were performed on a Nicolet Impact 400 D, mass spectra on a Finnigan CA 5 and elemental analysis on a Leco, CHNS-932. Analytical gas chromatography was performed on a Fisons 8130 gas chromatograph with 30 m CP sil-5 capillaries. GC-MS spectra were obtained by using a comparable capillary and a Finnigan MAT 8320 (MS). Pressure reactions have been carried out in autoclaves (type A, 250 ml, PTFE-insert) from Berghof, Eningen.

General procedure A: Preparation of 2-pyrrolidinones **3a-d**

20 ml abs. dioxane, 5.0 mmol alkyne **1a-b**, 5.5 mmol amine **2a-c**, 1 mol-% (based to the amount of the alkyne) of $Rh(cod)BPh_4$ were placed in an autoclave. After flushing with argon the reactor was pressurized with 50 bar hydrogen and 50 bar carbon monoxide and heated to 100 °C for 3 d. After removing the solvent by rotary evaporation the catalyst was separated by column filtration. The products were separated and purified by column chromatography.

**1-Butyl-4-phenyl-pyrrolidin-2-one (3a)**

Obtained from **1a** and butyl amin **2a** in 21 % yield. $^1H$ NMR (400 MHz, $CDCl_3$, 20 °C): δ [ppm] = 0.96 (t, $^3J$ = 7.3 Hz, 3H), 1.36 (m, 2H), 1.55 (m, 2H), 2.59 (dd, $^2J$ = 16.7 Hz, $^3J$ = 8.4 Hz, 1H), 2.84 (dd, $^2J$ = 16.8 Hz, $^3J$ = 9.0 Hz, 1H), 3.36 (t*, $^3J$ = 7.3 Hz, 1H), 3.37 (t*, $^3J$ = 7.4 Hz, 1H), 3.41 (dd, $^2J$ = 9.6 Hz, $^3J$ = 7.2 Hz, 1H), 3.59 (m, 1H), 3.77 (dd, $^2J$ = 9.5 Hz, $^3J$ = 8.5 Hz, 1H), 7.26 (m, 3H), 7.37 (m, 2H). $^{13}C$ NMR (100 MHz, $CDCl_3$, 20 °C): δ [ppm] = 13.7 ($CH_3$), 20.0 ($CH_2$), 29.3 ($CH_2$), 37.3 (CH), 39.0 ($CH_2$), 42.2 ($CH_2$), 54.4 ($CH_2$), 126.7 (CH), 127.0 (CH), 128.8 (CH), 142.5 (Cq), 173.6 (Cq). IR (neat): $\tilde{\nu}$ [$cm^{-1}$] = 3062 w, 3029 m, 2960 s, 2930 s, 2872 s, 1688 s, 1494 m, 1454 m, 1430 m, 1260 m, 1083 m, 700 m. GC-MS (EI, 70 eV): m/z = 217 ($M^+$; 100%), 174 (10%), 117 (5%), 104 (9%), 91 (6%).

**1-Hexyl-4-phenyl-pyrrolidin-2-one (3b)**

Obtained from **1a** and hexyl amin **2b** in up to 37 %. The spectroscopical data are identical to those in the literature[19].

**1-Benzyl-4-phenyl-pyrrolidin-2-one (3c)**

Obtained from **1a** and benzyl amin **2c** in 25 % yield. The spectroscopical data are identical to those in the literature[20].

**1-Benzyl-3,4-dipropyl-pyrrolidin-2-one (3d)**

Obtained from **1b** and benzyl amin **2c** in 14 % yield. $^1$H NMR (400 MHz, $CDCl_3$, 20 °C): δ [ppm] = 0.91 (t, $^3$J = 6.8 Hz, 3H), 0.98 (t, $^3$J = 6.9 Hz, 3H), 1.29 (m, 4H), 1.55 (m, 3H), 1.76 (m, 1H), 2.00 (m, 1H), 2.15 (m, 1H), 2.81 (dd, $^2$J = 9.2 Hz, $^3$J = 6.8 Hz, 1H), 3.31 (t*, J = 8.8 Hz, 1H), 4.41 (d, $^2$J = 14.7 Hz, 1H), 4.51 (d, $^2$J = 14.7 Hz, 1H), 7.24 (m, 2H), 7.29 (m, 1H), 7.35 (m, 2H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ [ppm] = 13.9 ($CH_3$), 14.1 ($CH_3$), 20.0 ($CH_2$), 20.2 ($CH_2$), 32.7 ($CH_2$), 36.7 ($CH_2$), 37.0 (CH), 46.3 ($CH_2$), 47.8 (CH), 50.7 ($CH_2$), 127.2 (CH), 127.8 (CH), 128.4 (CH), 136.5 (Cq), 176.4 (Cq). IR (neat): $\tilde{\nu}$ [cm$^{-1}$] = 3087 w, 3064 w, 3030 w, 2958 vs, 2929 vs, 2872 s, 1694 vs, 1495 m, 1454 s, 1357 w, 1263 m, 740 m, 701 s. GC-MS (EI, 70 eV): m/z = 260 ($M^+$; 100%), 217 (9%), 174 (14%), 106 (4%), 91 (24%), 65 (8%), 55 (9%). Anal. calc. for $C_{17}H_{25}NO$: C, 78.7; H, 9.7; N, 5.4. Found: C, 78.6; H, 10.2; N, 5.4.

General procedure B: Preparation of 4-silylated 1-aza-1,3-butadienes **5a-j**

A mixture of alkyne (5.0 mmol), silane (5.2 mmol), primary amine (5.2 mmol) and Rh catalyst (1 mol-%, based to the amount of silane) in 10 ml of dry toluene was placed in an autoclave. After flushing the autoclave with argon the reactor was pressurized to 50 bar with CO and the reaction mixture was magnetically stirred at 60 °C for 22 h. Then the autoclave was allowed to cool to room temperature and the solvent was removed by rotary evaporation. The residue was dissolved in methyl *t*-butyl ether and filtered through neutral alumina. The isolation of the products was carried out via Kugelrohr distillation.

**1*E*-N-Hexyl-3-phenyl-4-triethylsilyl-1-aza-1,3-butadiene (5a) (1.4 : 1 mixture of the 3*Z*- and 3*E*-isomers)**

Obtained from **1a**, **2b** and **4a** in 75 % yield. Both, 1*E*, 3*Z*- and 1*E*, 3*E*-isomer: $^{13}$C NMR (100 MHz, $CDCl_3$, 20 °C): δ [ppm] = 13.9 (2x$CH_3$), 22.5 ($CH_2$), 22.6 ($CH_2$) 26.9 ($CH_2$), 27.0 ($CH_2$), 30.5 ($CH_2$), 30.7 ($CH_2$), 31.5 (2x$CH_2$), 127.4 (CH), 127.5 (CH), 127.7 (CH), 128.4 (CH), 129.1 (CH), 139.9 (Cq), 141.2 (Cq). IR (neat): $\tilde{\nu}$ [cm$^{-1}$] = 1632 m, 1580 m, 1015 s, 699 s. GC-MS (EI, 70 eV): m/z = 329 ($M^+$, 100%), 300 (52%), 258 (54%). Anal. Calcd. for $C_{21}H_{35}NSi$: C, 76.5; H, 10.7; N, 4.2. Found: C, 76.0; H, 10.6; N, 4.5. 1*E*, 3*Z*-isomer: $^1$H NMR (400 MHz, $CDCl_3$, 20 °C): δ [ppm] = 0.84 (q, 6H, $^3$J = 7.8 Hz), 0.97 (m, 3H), 1.09 (t, 9H, $^3$J = 7.8 Hz), 1.32-1.48 (6H), 1.75 (m, 2H), 3.64 (t, 2H, $^3$J = 6.7 Hz), 6.42 (s, 1H), 7.24-7.50 (5H), 8.39 (s, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$, 20 °C): δ [ppm] = 5.1 ($CH_2$, $^1J_{Si-C}$=53.5 Hz), 7.5 ($CH_3$), 62.1 ($CH_2$), 138.9 (CH), 154.9 (Cq), 161.5 (CH). 1*E*, 3*E*-isomer: $^1$H NMR (400 MHz, $CDCl_3$, 20 °C): δ [ppm] = 0.45 (q, 6H, $^3$J = 7.8 Hz), 0.92 (t, 9H, $^3$J = 7.9 Hz), 0.97 (m, 3H), 1.35-1.45 (6H), 1.66 (m, 2H), 3.56 (t, 2H, $^3$J = 7.0 Hz), 6.33 (s,

1H), 7.24-7.50 (5H), 8.13 (s, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$, 20 °C): δ [ppm] = 4.0 ($CH_2$, $^1J_{Si-C}$=53.5 Hz), 7.3 ($CH_3$), 61.6 ($CH_2$), 139.3 (CH), 156.4 (Cq), 165.5 (CH).

**_Z_-N-Hexyl-2-phenyl-3-triethylsilyl-acrylamide (6a)**

Obtained from **1a**, **2b** and **4a** in 21 % yield. $^1$H NMR (400 MHz, $CDCl_3$, 20 °C): δ [ppm] = 0.79 (q, 6H, $^3J$ = 7.9 Hz), 0.92 (m,3H), 1.03 (t, 9H, $^3J$ = 7.9 Hz), 1.30-1.34 (6H), 1.55 (m, 2H), 3.35 (m, 2H), 5.66 (sbr, 1H), 6.22 (s, 1H), 7.34-7.37 (5H). $^{13}$C NMR (100 MHz, $CDCl_3$, 20 °C): δ [ppm] = 4.0 ($CH_2$), 7.6 ($CH_3$), 13.8 ($CH_3$), 22.4 ($CH_2$), 26.5 ($CH_2$), 29.2 ($CH_2$), 31.3 ($CH_2$), 39.6 ($CH_2$), 126.9 (CH), 128.1 (CH), 128.3 (CH), 133.7 (CH), 139.3 (Cq), 152.7 (Cq), 168.8 (Cq). IR (neat): $\tilde{\nu}$ [$cm^{-1}$] = 3230vs, 1632 s, 1591 m, 755 m. GC-MS (EI, 70 eV): m/z = 346 ($M^+$, 4%), 316 (100%), 232 (20%). Anal. Calcd. for $C_{21}H_{35}NOSi$: C, 73.0; H, 10.2; N, 4.1. Found: C, 72.7; H, 9.8; N, 4.0.

**1_E_-N-Butyl-3-phenyl-4-triethylsilyl-1-aza-1,3-butadiene (5b) (1.9 : 1 mixture of the 3_Z_- and 3_E_-isomers)**

Obtained from **1a**, **2a** and **4a** in 75 % yield. Both, 1_E_,3_Z_- and 1_E_,3_E_ isomer: $^{13}$C NMR (100 MHz, $CDCl_3$, 20 °C): δ = 13.7 ($CH_3$), 13.8 ($CH_3$), 20.3 (2x$CH_2$), 32.7 ($CH_2$), 32.8 ($CH_2$), 127.3 (CH), 127.4 (CH), 127.7 (CH), 128.3 (CH), 129.0 (CH), 140.0 (Cq), 141.1 (Cq). IR (neat): $\tilde{\nu}$ [$cm^{-1}$] = 1632 m, 1565 m, 1015 s, 735 s. GC-MS (EI, 70 eV): m/z = 302 ($M^+$, 51%), 272 (100%), 258 (29%), 189 (30%), 115 (15%). 1_E_,3_Z_-isomer: $^1$H NMR (400 MHz, $CDCl_3$, 20 °C): δ [ppm] = 0.83 (q, 6H, $^3J$ = 7.8 Hz), 0.95-1.00 (3H), 1.10 (t, 9H, $^3J$ = 7.8 Hz), 1.32-1.78 (4H), 3.64 (t, 2H, $^3J$ = 7.0 Hz), 6.43 (s, 1H), 7.20-7.55 (5H), 8.41 (s, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$, 20 °C): δ [ppm] = 5.1 ($CH_2$), 7.4 ($CH_3$), 61.7 ($CH_2$), 138.9 (CH), 154.9 (Cq), 161.5 (CH). 1_E_,3_E_-isomer: $^1$H NMR (400 MHz, $CDCl_3$, 20 °C): δ [ppm] = 0.46 (q, 6H, $^3J$ = 7.8 Hz), 0.92 (t, 9H, $^3J$ = 7.8 Hz), 0.95-1.05 (3H), 1.32-1.78 (4H), 3.57 (t, 2H, $^3J$ = 7.0 Hz), 6.35 (s, 1H), 7.20-7.55 (5H), 8.13 (s, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$, 20 °C): δ [ppm] = 4.0 ($CH_2$,), 7.3 ($CH_3$), 61.2 ($CH_2$), 139.3 (CH), 156.3 (Cq), 165.5 (CH).

**_Z_-N-Butyl-2-phenyl-3-triethylsilyl-acrylamide (6b)**

Obtained from **1a**, **2a** and **4a** in 23 % yield. $^1$H NMR (400 MHz, $CDCl_3$, 20 °C): δ [ppm] = 0.75 (q, 6H, $^3J$ = 7.8 Hz), 0.93 (t,3H, $^3J$ = 7.3 Hz), 0.99 (t, 9H, $^3J$ = 7.8 Hz), 1.33 (m, 2H), 1.52 (m, 2H), 3.34 (m, 2H), 5.57 (sbr, 1H), 6.20 (s, 1H), 7.25-7.49 (5H). $^{13}$C NMR (100 MHz, $CDCl_3$, 20 °C): δ [ppm] = 4.1 ($CH_2$), 7.7 ($CH_3$), 13.7 ($CH_3$), 20.1 ($CH_2$), 31.4 ($CH_2$), 39.5 ($CH_2$), 127.0 (CH), 128.2 (CH), 128.4 (CH), 134.0 (CH), 139.4 (Cq), 152.7 (Cq), 168.9 (Cq). IR (neat): $\tilde{\nu}$ [$cm^{-1}$] = 3293 vs, 1639 s, 1589 m, 799 m. GC-MS (EI, 70 eV): m/z = 318 ($M^+$, 5%), 289 (100%), 232 (14%).

**1*E*-N-*t*-Butyl-3-phenyl-4-triethylsilyl-1-aza-1,3-butadiene (5c) (1 : 1 mixture of the 3*Z*- and 3*E*-isomers)**

Obtained from **1a**, **2d** and **4a** in 86 % yield. Both, 1*E*,3*Z*- and 1*E*,3*E*-isomer: $^{13}$C NMR (100 MHz, $CDCl_3$, 20 °C): δ [ppm] = 4.2 ($CH_2$), 5.1 ($CH_2$), 7.4 ($CH_3$), 7.5 ($CH_3$), 29.5 ($CH_3$), 29.6 ($CH_3$), 57.0 (Cq), 57.7 (Cq), 127.2 (CH), 127.4 (CH), 127.6 (CH), 128.5 (CH), 129.4 (CH), 137.3 (CH), 138.2 (CH), 139.8 (Cq), 141.2 (Cq), 155.2 (Cq), 156.0 (CH), 157.0 (Cq), 159.2 (CH). IR (neat): $\tilde{\nu}$ [$cm^{-1}$] = 1631 m, 1579 m, 1015 s, 734 s. GC-MS (EI, 70 eV): m/z = 302 ($M^+$, 75%), 272 (72%), 244 (38%), 216 (30%), 57 (100%). 1*E*,3*Z*-isomer: $^1$H NMR (400 MHz, $CDCl_3$, 20 °C): δ [ppm] = 0.86 (q, 6H, $^3J$ = 7.8 Hz), 1.13 (t, 9H, $^3J$ = 7.8 Hz), 1.37 (s, 9H), 6.45 (s, 1H), 7.20-7.59 (5H), 8.44 (s, 1H). 1*E*,3*E*-isomer: $^1$H NMR (400 MHz, $CDCl_3$, 20 °C): δ [ppm] = 0.49 (q, 6H, $^3J$ = 7.8 Hz), 0.96 (t, 9H, $^3J$ = 7.8 Hz), 1.29 (s, 9H), 6.35 (s, 1H), 7.20-7.59 (5H), 8.15 (s, 1H).

**1*E*-N-R-Phenylethyl-3-phenyl-4-dimethylphenylsilyl-1-aza-1,3-butadiene (5d) (1.4 : 1 mixture of the 3*Z*-and 3*E*-isomers)**

Obtained from **1a**, **2e** and **4b** in 96 % yield. Both, 1*E*,3*Z*- and 1*E*,3*E*-isomer: $^{13}$C NMR (100 MHz, $CDCl_3$, 20 °C): δ [ppm] = -1.9 ($CH_3$), -1.8 ($CH_3$), -0.5 (2x$CH_3$), 24.4 ($CH_3$), 25.0 ($CH_3$), 69,5 (CH), 69.7 (CH), 126.5-133.7 (16xCH+4xCq), 139.1 (CH), 140.6 (CH), 144.5 (Cq), 145.3 (Cq), 154.4 (Cq), 156.3 (Cq), 160.0 (CH), 163.7 (CH). IR (neat): $\tilde{\nu}$ [$cm^{-1}$] = 1631 m, 1579 m, 1492 m, 1113 s, 841 s, 818 s, 698 s. GC-MS (EI, 70 eV): m/z = 369 ($M^+$-1, 1%), 207 (22%), 117 (100%). 1*E*,3*Z*-isomer: $^1$H NMR (400 MHz, $CDCl_3$, 20 °C): δ [ppm] = 0.38 (s, 3H), 0.39 (s, 3H), 1.32 (d, 3H, $^3J$ = 6.7 Hz), 4.22 (q, 3H, $^3J$ = 6.7 Hz), 6.48 (s, 1H), 7.01-7.54 (15H), 8.22 (s, 1H). 1*E*,3*E*-isomer: $^1$H NMR (400 MHz, $CDCl_3$, 20 °C): δ [ppm] = 0.00 (s, 3H), 0.01 (s, 3H), 1.38 (d, 3H, $^3J$ = 6.7 Hz), 4.36 (q, 3H, $^3J$ = 6.6 Hz), 6.40 (s, 1H), 7.01-7.54 (15H), 8.06 (s, 1H).

**1*E*-N-Isopropyl-3-phenyl-4-dimethylphenylsilyl-1-aza-1,3-butadiene (5e) (≈1.4 : 1 mixture of the 3*Z*-and 3*E*-isomers)**

Obtained from **1a**, **2f** and **4b** in up to 89 % yield. Both, 1*E*,3*Z*- and 1*E*,3*E*-isomer: $^{13}$C NMR (100 MHz, $CDCl_3$, 20 °C): δ [ppm] = -1.9 ($CH_3$), -0.5 ($CH_3$), 23.7 ($CH_3$), 23.8 ($CH_3$), 61.3 (CH), 61.5 (CH), 125.8-133.7 (10 x CH + 2 x Cq), 137.6 (CH), 139.1 (CH), 139.4 (Cq), 140.8 (Cq), 154.3 (Cq), 156.3(Cq), 158.7 (CH), 162.3 (CH). IR (neat): $\tilde{\nu}$ [$cm^{-1}$] = 1630 m, 1581 m, 1428 m, 838 s, 698 s. GC-MS (EI, 70 eV): m/z = 308 ($M^+$,100%), 281 (14%), 266 (49%), 246 (29%), 74 (37%). 1*E*,3*Z*-isomer: $^1$H NMR (400 MHz, $CDCl_3$, 20 °C): δ [ppm] = 0.54 (s, 6H), 1.12 (d, 6H, $^3J$ = 6.3 Hz), 3.31 (sept, 1H; $^3J$ = 6.3 Hz), 6.54 (s, 1H), 7.13-7.79 (10H), 8.31 (s, 1H). 1*E*,3*E*-isomer: $^1$H NMR (400 MHz, $CDCl_3$, 20 °C): δ [ppm] = 0.11 (s, 6H), 1.18 (d, 6H, $^3J$ = 6.3 Hz), 3.45 (sept, 1H; $^3J$ = 6.3 Hz), 6.50 (s, 1H), 7.13-7.79 (10H), 8.11 (s, 1H).

**1*E*,3*Z*-N-Isopropyl-3-butyl-4-triethylsilyl-1-aza-1,3-butadiene (5f)**

Obtained from **1c**, **2f** and **4a** in 64 % yield. $^1$H NMR (400 MHz, $CDCl_3$, 20 °C): δ [ppm] = 0.62 (q, 6H, $^3$J = 7.8 Hz), 0.87 (t, 3H, $^3$J = 7.3 Hz), 0.92 (t, 9H, $^3$J = 7.8 Hz), 1.15 (d, 6H, $^3$J = 6.3 Hz), 1.20-1.42 (4H), 2.36 (t, 2H, $^3$J = 7.5 Hz), 3.34 (sept, 6H, $^3$J = 6.3 Hz), 5.92 (s, 1H), 8.04 (s, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$, 20 °C): δ [ppm] = 5.3 ($CH_2$), 7.5 ($CH_3$), 14.1 ($CH_3$), 22.4 ($CH_2$), 24.0 ($CH_3$), 30.8 ($CH_2$), 33.9 ($CH_2$), 61.5 (CH), 134.1 (CH), 156.7 (Cq), 159.9 (CH). IR (neat): $\tilde{\nu}$ [cm$^{-1}$] = 1628 s, 1581 s, 1465 s, 1458 s, 760 s. GC-MS (EI, 70 eV): m/z = 268 ($M^+$, 100%), 238 (80%), 224 (38%), 196 (30 %).

**1*E*,3*Z*-N-(R-Phenylethyl)-3-butyl-4-triethylsilyl-1-aza-1,3-butadiene (5g)**

Obtained from **1c**, **2e** and **4a** in 82 % yield. $^1$H NMR (400 MHz, $CDCl_3$, 20 °C): δ [ppm] = 0.52 (q, 6H, $^3$J = 7.8 Hz), 0.83 (t, 3H, $^3$J = 7.1 Hz), 0.84 (t, 9H, $^3$J = 7.9 Hz), 1.26 (m, 2H), 1.39 (m, 2H), 1.43 (d, 3H, $^3$J = 6.8 Hz), 2.41 (m, 2H), 4.34 (q, 1H, $^3$J = 6.8 Hz), 5.92 (s, 1H), 7.15-7.29 (5H), 8.00 (s, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$, 20 °C): δ [ppm] = 5.3 ($CH_2$), 7.5 ($CH_3$), 14.1 ($CH_3$), 22.5 ($CH_2$), 24.7 ($CH_3$), 31.0 ($CH_2$), 34.1 ($CH_2$), 69.0 (CH), 126.7 (2xCH), 128.3 (CH), 135.1 (CH), 145.1 (Cq), 156.8 (Cq), 161.0 (CH). IR (neat): $\tilde{\nu}$ [cm$^{-1}$] = 1629 s, 1581 s, 1014 s, 759 s. GC-MS (EI, 70 eV): 330 ($M^+$, 100%), 300 (25%), 224 (40%), 105 (80%). Anal. Calcd. for $C_{21}H_{35}NSi$: C, 76.5; H, 10.7; N, 4.2. Found: C, 76.2; H, 10.5; N, 4.4.

**1*E*,3*Z*-N-Hexyl-3-butyl-4-triethylsilyl-1-aza-1,3-butadiene (5h)**

Obtained from **1c**, **2b** and **4a** in 88 % yield. $^1$H NMR (400 MHz, $CDCl_3$, 20 °C): δ [ppm] = 0.68 (q, 6H, $^3$J = 7.8 Hz), 0.83-0.92 (6H), 0.95 (t, 9H, $^3$J = 7.8 Hz), 1.25-1.69 (12H), 2.45 (t, 2H, $^3$J = 7.8 Hz), 3.48 (t, 2H, $^3$J = 6.9 Hz), 6.00 (s, 1H), 8.04 (s, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$, 20 °C): δ [ppm] = 5.3 ($CH_2$), 7.4 ($CH_3$), 13.9 ($CH_3$), 14.0 ($CH_3$), 22.4 ($CH_2$), 22.6 ($CH_2$), 26.9 ($CH_2$), 30.7 ($CH_2$), 30.8 ($CH_2$), 31.6 ($CH_2$), 34.1 ($CH_2$), 61.2 ($CH_2$), 134.7 (CH), 156.4 (Cq), 162.4 (CH). IR (neat): $\tilde{\nu}$ [cm$^{-1}$] = 1631 m, 1582 m, 1014 m, 725 s. GC-MS (EI, 70 eV): m/z = 310 ($M^+$, 24%), 280 (65%), 238 (35%), 224 (100%), 194 (29 %) 140 (44%) 112 (50%).

**1*E*,3*Z*-N-(p-Methoxyphenyl)-3-butyl-4-triethylsilyl-1-aza-1,3-butadiene (5i)**

Obtained from **1c**, **2g** and **4a** in 94 % yield. $^1$H NMR (400 MHz, $CDCl_3$, 20 °C): δ [ppm] = 0.74 (q, 6H, $^3$J = 7.8 Hz), 0.96 (m, 3H), 0.99 (t, 9H, $^3$J = 7.8 Hz), 1.43 (m, 2H), 1.58 (m, 2H), 2.61 (t, 2H, $^3$J = 7.7 Hz), 3.83 (s, 3H), 6.22 (s, 1H), 6.94 (d, 2H, $^3$J = 8.8 Hz), 7.14 (d, 2H, $^3$J = 8.8 Hz), 8.30 (s, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$, 20 °C): δ [ppm] = 5.3 ($CH_2$), 7.5 ($CH_3$), 14.0 ($CH_3$), 22.5 ($CH_2$), 31.0 ($CH_2$), 33.8 ($CH_2$), 55.3 ($CH_3$), 114.3 (CH), 122.1 (CH), 137.9 (CH), 145.2 (Cq), 156.8 (Cq), 158.0 (Cq), 160.1 (CH). IR (neat): $\tilde{\nu}$ [cm$^{-1}$] = 1685 m, 1613 s, 1503 s, 1246 s, 721 s. GC-MS (EI, 70 eV): m/z = 331 ($M^+$-1, 29%), 301 (100%), 259 (44%), 59 (15%). Anal. Calcd. for $C_{20}H_{33}NOSi$: C, 72.4; H, 10.0 N, 4.2. Found: C, 71.9; H, 9.8; N, 4.4.

**1*E*,3*Z*-N-Allyl-3-butyl-4-triethylsilyl-1-aza-1,3-butadiene (5j)**

Obtained from **1c**, **2h** and **4a** in 85 % yield. $^1$H NMR (400 MHz, $CDCl_3$, 20 °C): δ [ppm] = 0.60 (q, 6H, $^3J$ = 7.8 Hz), 0.83 (m, 3H), 0.90 (t, 9H, $^3J$ = 7.8 Hz), 1.22-1.47 (4H), 2.39 (t, 2H, $^3J$ = 7.7 Hz), 4.08 (m, 2H), 5.06 (m, 1H), 5.09 (m, 1H), 5.94 (m, 1H), 5.99 (s, 1H), 8.01 (s, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$, 20 °C): δ [ppm] = 5.2 ($CH_2$), 7.4 ($CH_3$), 14.0 ($CH_3$), 22.4 ($CH_2$), 30.8 ($CH_2$), 33.9 ($CH_2$), 63.2 ($CH_2$), 115.8 ($CH_2$), 135.7 (CH), 135.8 (CH), 156.2 (Cq), 163.8 (CH). IR (neat): $\tilde{\nu}$ [$cm^{-1}$] = 1643 m, 1629 m, 1583 m, 1016 s, 726 s. GC-MS (EI, 70 eV): m/z = 266 ($M^+$, 63%), 236 (100%), 224 (37%), 194 (46%).

General procedure C: Preparation of 1,4-dihydropyridines **8a,b** via Diels-Alder reaction

The reactions were carried out with 2.6 mmol of the azadiene **5e,f** and 5.2 mmol (entry 19: 2.6 mmol) dimethyl acetylenedicarboxylate **7** in 10 ml of the dry solvent (table 3). After heating for 6 days at reflux temperature the solvent was removed by distillation under reduced pressure. The products were isolated by column chromatography on alumina (hexane : $Et_2O$ = 2 : 1).

**5-Phenyl-1-isopropyl-4-dimethylphenylsilyl-1,4-dihydropyridine-2,3-dicarbonic acid dimethylester (8a)**

Obtained from **5e** and **7** in 38 % yield. $^1$H NMR (400 MHz, $CDCl_3$, 20 °C): δ [ppm] = 0.19 (s, 3H), 0.24 (s, 3H), 1.07 (d, 3H, $^3J$ = 6.5 Hz), 1.19 (d, 3H, $^3J$ = 6.5 Hz), 3.43 (sept, 1H, $^3J$ = 6.5 Hz), 3.48 (s, 3H), 3.59 (s, 1H), 3.91 (s, 3H), 6.12 (s, 1H), 7.20-7.45 (10H). $^{13}$C NMR (100 MHz, $CDCl_3$, 20 °C): δ [ppm] = -3.9 ($CH_3$), 21.2 ($CH_3$), 21.7 ($CH_3$), 27.6 (CH), 50.7+51.0 (CH+$CH_3$), 52.8 ($CH_3$), 96.4 (Cq), 118.2 (Cq), 119.5 (CH), 125.0 (CH), 126.4 (CH), 127.3 (CH), 128.3 (CH), 128.8 (CH), 134.2 (CH), 137.6 (Cq), 139.4 (Cq), 144.8 (Cq), 166.0(Cq), 166.8 (Cq). IR (neat): $\tilde{\nu}$ [$cm^{-1}$] = 1736 s, 1686 s, 1581 m, 730 m. MS (EI, 70 eV): m/z = 449 ($M^+$-1, 42%), 434 (74%), 314 (97%), 272 (72%), 240 (100%), 154 (81%), 135 (98%), 105 (75%).

**5-Butyl-1-isopropyl-4-triethylsilyl-1,4-dihydropyridine-2,3-dicarbonic acid dimethyl-ester (8b)**

Obtained from **5f** and **7** in up to 51 % yield. $^1$H NMR (400 MHz, $CDCl_3$, 20 °C): δ [ppm] = 0.52 (m, 6H), 0.89 (m, 3H), 0.93 (t, 9H, $^3J$ = 7.8 Hz), 1.15 (d, 3H, $^3J$ = 6.6 Hz), 1.18 (d, 3H, $^3J$ = 6.6 Hz), 1.23-1.58 (4H), 1.82 (m, 1H), 1.95 (m, 1H), 2.77 (s, 1H), 3.42 (sept, 1H, $^3J$ = 6.7 Hz), 3.61 (s, 3H), 3.83 (s, 3H), 5.56 (s, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$, 20 °C): δ [ppm] = 2.8 ($CH_2$), 7.5 ($CH_3$), 13.9 ($CH_3$), 21.0+21.8+25.2 (2x$CH_3$+CH), 22.5 ($CH_2$), 29.6 ($CH_2$), 33.9 ($CH_2$), 50.5+51.0+52.6 (CH+2x$CH_3$), 95.2 (Cq), 116.2 (CH), 120.1 (Cq), 145.1 (Cq), 166.5 (Cq), 167.4 (Cq). IR (neat): $\tilde{\nu}$ [$cm^{-1}$] = 1742 s, 1692 s, 1572 m, 736 m. GC-MS (EI, 70 eV): m/z = 410 ($M^+$-1, 8%), 394 (29%), 378 (100%), 294 (89%), 252 (53%), 220 (94%). Anal. Calcd. for $C_{22}H_{39}NO_4Si$: C, 64.5; H, 9.6; N, 3.4. Found: C, 64.9; H, 9.8; N, 3.7.

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