Synthesis of β-amino ketones containing organosilicon groups: catalytic enantioselective three-component Mannich-type reaction

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Aldimines, generated *in situ* from 4-[2,2-bis(trimethylsilyl)ethenyl]benzaldehyde and aromatic amines, undergo Mannich-type reactions with cyclic and acyclic ketones. The one-pot reaction is efficiently catalysed by zirconium oxychloride ($ZrOCl_2.8H_2O$) at room temperature. β-Amino carbonyl compounds containing bis(trimethylsilyl)ethenyl groups are obtained in acceptable to good yields with moderate to high stereoselectivity under solvent-free conditions.

Keywords: vinylbis(silanes), Mannich-type reaction, β-amino ketones, zirconium oxychloride

Despite many publications describing applications of organosilicon chemistry in synthesis, few involve vinylsilanes.[1–3] We have, however, shown that readily available compounds of this type may be used to develop ways of making new carbon–carbon bonds in a range of organosilicon compounds containing a wide range of functional groups.[4–7]

Previously, we described the synthesis of bis(trimethylsilyl)-ethenyl derivatives containing imine and amine groups.[7] We have now used Mannich-type reactions of aldehydes containing bis(trimethylsilyl)ethenyl groups to synthesise new β-aminoketones. These are attractive targets for chemical synthesis because of their possible biological activity and potential applications in the synthesis of pharmaceutical agents and natural products.[8–16]

As $ZrOCl_2.8H_2O$ is reported to be an efficient Lewis acid catalyst for the one-pot synthesis of β-aminoketones[8,17,18] we chose it for our study of Mannich-type reactions between 4-[2,2-bis(trimethylsilyl)ethenyl]benzaldehyde (**1**), aromatic amines, and ketones.

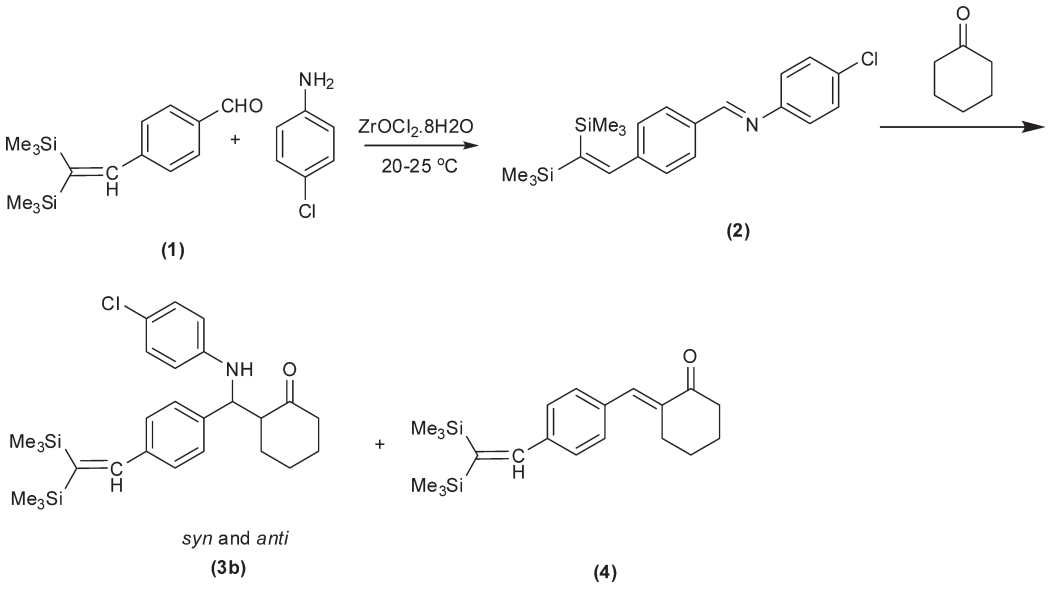
Results and discussion

Reactions were studied in various solvents and under solvent-free conditions in the presence of 15 mol% $ZrOCl_2.8H_2O$ at room temperature with a very simple work-up procedure. To find the optimal conditions for the reaction of 4-[2,2-bis (trimethylsilyl)ethenyl]benzaldehyde[7] with 4-chloroaniline and cyclohexanone (Scheme 1) we carried out experiments described in Table 1. These indicated that highest yields and shortest reaction times were achieved under solvent-free conditions (yield 90% in 15 minutes). Reactions in aqueous or organic solvents gave lower yields together with the side-product **4**. The reaction in EtOH gave a high yield (70% in 1 h) but in MeCN and EtOAc the imine **2** was isolated as sole product after 15 minutes. Increasing the reaction time to 1 h led to formation of compound **3b**, together with a few percent of **4**. In water, the imine **2** was isolated as the main product even after 1 day.

Table 1 Mannich reactions of 4-[2,2-bis(trimethylsilyl)ethenyl] benzaldehyde (1 mmol), aniline (1 mmol), and cyclohexanone (3 equiv.) in various solvents

Solvent	Time	Yield/% [a]	
		(3b)	**(4)**
MeCN	1 h	60	20
EtOAC	1 h	40	20
EtOH	15 min	50	–
EtOH	1 h	70	10
H_2O	8 h	20	–
Solvent-free	15 min	90	–

[a]Yields obtained by PTLC.



Scheme 1 Mannich reaction of 4-[2,2-bis(trimethylsilyl)ethenyl]benzaldehyde with 4-chloroaniline and cyclohexanone.

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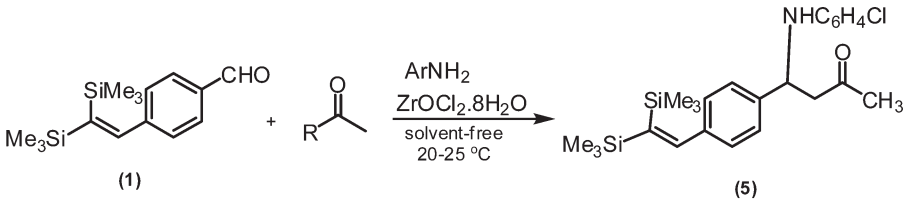


5a R=Me, Ar=C_6H_5, 20min, 80%

5b R=Me, Ar=4-ClC_6H_4, 30min, 75%

5c R=Ph, Ar=4-ClC_6H_4, 60min, 70%

Scheme 2 Mannich-type reaction of aldehyde **1** with aromatic amines and cyclic ketones.

In order to explore the generality and scope of the new procedure, three-component one-pot Mannich type reactions of aldehyde **1** with various aromatic amines and cyclic ketones were tested under the conditions found to be optimal for 4-chloroaniline (Scheme 2). The results are summarised in Table 2. All the reactions proceeded rapidly without solvent in the presence of 15 mol% $ZrOCl_2.8H_2O$ at room temperature to give the corresponding *β*-aminoketones containing the [2,2-bis(trimethylsilyl)ethenyl] group; yields were achieved good to high *anti* stereoselectivity (Table 2). The *anti* and *syn* isomers were identified by the coupling constants (*J*) of the vicinal protons adjacent to C=O and NH in their ^{1}H NMR spectra, as described in the literature.[8,16] The value of *J* of the *anti* isomer is higher than of the *syn* one.

Similarly, Mannich reactions of aldehyde **1**, anilines, and acyclic ketones such as acetone and acetophenone were investigated. The overall reaction is best formulated in Scheme 3. The time required for completion of reactions with acetophenone was longer than that for reactions with acetone.

Table 2 Yields and selectivity of direct Mannich-type reaction of aldehyde **1** with various aromatic amines and cyclic ketones without solvent

Ketone	Amine	Product	Time/ min	Yield[a] /%	*Anti*/ *Syn*[b]
n =1	$C_6H_5NH_2$	**3a**	10	65	62:38
n =1	4-$ClC_6H_4NH_2$	**3b**	15	90	68:32
n =1	3-$ClC_6H_4NH_2$	**3c**	15	80	70:30
n =1	3,4-$Cl_2C_6H_3NH_2$	**3d**	20	86	70:30
n =1	4-$FC_6H_4NH_2$	**3e**	20	82	75:25
n =1	4-$NO_2C_6H_4NH_2$	**3f**	20	89	61:39
n =1	4-$MeC_6H_4NH_2$	**3g**	15	85	80:20
n =1	4-n$BuC_6H_4NH_2$	**3h**	20	80	90:10
n =1	*α*-$C_{10}H_7NH_2$	**3i**	120	60	83:17
n =2	$C_6H_5NH_2$	**3j**	40	70	66:34
n =2	4-$ClC_6H_4NH_2$	**3k**	45	75	80:20

[a] Yields obtained by PTLC.
[b] *anti/syn* ratio determined from ^{1}H NMR spectra.

Conclusion

Three-component Mannich reactions of 4-[2,2-bis(trimethylsilyl) ethenyl]benzaldehyde (1), anilines and ketones are efficiently catalysed by $ZrOCl_2.8H_2O$ under solvent-free conditions. The present catalytic system provides an attractive protocol for the synthesis of *β*-aminoketones containing bis(trimethylsilyl)ethenyl groups summarised in the following points: (1) high yields; (2) good stereoselectivities; (3) facile operations; (4) environmentally benign reaction conditions; (5) highly efficient catalyst activity; and (6) avoidance of the troublesome preparation of enol derivatives and pre-formed imines.

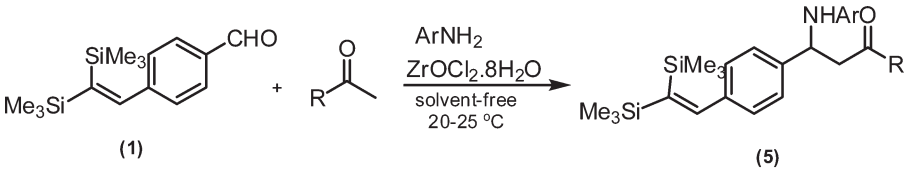
Experimental

All chemicals were used as purchased. 4-[2,2-Bis(trimethylsilyl)-ethenyl]benzaldehyde (1) was synthesised as described in the literature.[7] NMR spectra were recorded with a Bruker FT-400 MHz spectrometer at 400.13 (^{1}H) and 100.61 (^{13}C) MHz at room temperature. Except where indicated, $CDCl_3$ was used as solvent. The FTIR spectra from KBr discs were recorded on a Bruker-Tensor 270 spectrometer. Elemental analyses were obtained with a Vario EL III instrument. The products were purified by PTLC on silica gel with hexane/ethyl acetate as eluent. All compounds were characterised by spectroscopic data and elemental analysis.

General reaction procedure

4-[2,2-Bis(trimethylsilyl)ethenyl]benzaldehyde (1 mmol), cyclohexanone (3 mmol), and $ZrOCl_2.8H_2O$ (15 mol%) were added successively to aniline (1 mmol) at room temp. (20–25 °C) and the mixture was stirred for 10 min. Then CH_2Cl_2 (10 mL) was added, and the catalyst removed by filtration. The filtrate was washed with saturated aqueous $NaHCO_3$ solution and brine, dried with anhydrous Na_2SO_4, and solvent removed. The crude residue was purified by PTLC on silica gel using hexane/ethyl acetate (10:2) to afford the product. Details are given for each compound below.

2-[(4-(2,2-Bis(trimethylsilyl)ethenyl)phenyl)(phenylamino)methyl] cyclohexanone (**3a**): Yellow viscous oil; yield 65% (*anti/syn* 62:38), (silica gel, hexane/ethyl acetate 10:2, R_f = 0.72); FTIR (KBr, cm^{-1}): 836, 1251 ($SiCH_3$), 1494, 1603 (Ar), 1720 (CO), 2856, 2953, 3032 (CH), 3432 (NH); ^{1}H NMR (DMSO): *δ* –0.12 (s, 9 H, $SiMe_3$), 0.14 (s, 9 H, $SiMe_3$), 1.17–2.35 (m, 8 H, CH_2), 2.73 (s, br, 1 H, COC*H*, *anti*+*syn*), 4.73 (s, br, C*H*N, *anti*), 4.80 (s, br, C*H*N, *syn*), 6.42–6.50



5a R=Me, Ar=C_6H_5, 20min, 80%

5b R=Me, Ar=4-ClC_6H_4, 30min, 75%

5c R=Ph, Ar=4-ClC_6H_4, 60min, 70%

Scheme 3 Mannich reaction of aldehyde **1**, anilines and acyclic ketones.

(m, 3 H, Ar), 6.92 (s, 2 H, Ar), 7.06 (s, 2 H, Ar), 7.27–7.43 (m, 2 H, Ar), 7.69 (s, 1 H, HC=, *anti+syn*); ^{13}C NMR (DMSO): δ 0.6, 1.9 ($SiMe_3$), 23.1–55.6 (CH_2), 56.5 (CN), 113.1–155.0 (Ar), 209.6, 210.9 (CO). Anal. Calcd for $C_{27}H_{39}NOSi_2$: C, 72.10; H, 8.74; N, 3.11. Found: C, 72.53; H, 8.93; N, 2.76%.

2-[(4-(2,2-Bis(trimethylsilyl)ethenyl)phenyl)(4-chlorophenylamino) methyl]cyclohexanone (**3b**): Brown viscous oil; yield 90% (*anti/syn* 69:31), (silica gel, hexane/ethyl acetate 10:3, R_f = 0.5), FTIR (KBr, cm^{-1}): 838, 1250 ($SiCH_3$), 1499, 1603 (Ar), 1706 (CO), 2945 (CH), 3422 (NH); ^{1}H NMR: δ –0.11 (s, 9 H, $SiMe_3$), 0.16 (s, 9 H, $SiMe_3$), 1.57–2.40 (m, 8 H, CH_2), 2.42–2.47 (m, 1 H, COC*H*, *syn+anti*), 4.52 (d, *J* = 7.6 Hz, 0.68 H, C*H*N, *anti*), 4.69 (d, *J* = 4.0 Hz, 0.32 H, C*H*N, *syn*), [6.44 (d, *J* = 8.8 Hz), 6.52 (d, *J* = 8.4 Hz,), 2 H, Ar, *anti+syn*], 6.97-7.28 (m, 7 H, Ar), 7.68 (s, 1 H, HC=, *anti+syn*); ^{13}C NMR: δ –0.5, 0.9 ($SiCH_3$), 21.8-56.7 (C), 58.0 (CN), 114.5-153.3 (Ar), 210.4 and 211.9 (CO). Anal. Calcd for $C_{27}H_{38}ClNOSi_2$: C, 66.97; H, 7.91; N, 2.89. Found: C, 66.65; H, 8.13; N, 2.53%.

2-[(4-(2,2-Bis(trimethylsilyl)ethenyl)phenyl)(3-chlorophenylamino) methyl]cyclohexanone (**3c**): Yellow viscous oil; yield 80% (*anti/syn* 70:30), (silica gel, hexane/ethyl acetate 10:2, R_f = 0.86), FTIR (KBr, cm^{-1}): 839, 1250 ($SiMe_3$), 1498, 1599 (Ar), 1707 (CO), 2858, 2923 (CH), 3425 (NH); ^{1}H NMR: δ –0.19 (s, 9 H, $SiMe_3$), 0.08 (s, 9 H, $SiMe_3$), 1.48–2.37 (m, 8 H, CH_2), 2.63–2.67 (m, 1 H, COC*H*, *anti+ syn*), 4.48 (d, *J* = 7.2 Hz, 0.7 H, C*H*N, *anti*), 4.65 (s, 0.3 H, C*H*N, *syn*), 6.29–6.49 (m, 3 H, Ar), 6.82–7.20 (m, 5 H, Ar), 7.60 (s, 1 H, HC=, *anti+syn*); ^{13}C NMR: δ –0.72, 0.68 ($SiMe_3$), 22.5–56.0 (CH_2) 56.4 (CN), 110.8–153.2 (Ar), 209.9, 211.2 (CO). Anal. Calcd for $C_{27}H_{38}ClNOSi_2$: C, 66.97; H, 7.91; N, 2.89. Found: C, 66.35; H, 8.20; N, 2.76%.

2-[(4-(2,2-Bis(trimethylsilyl)ethenyl)phenyl)(3,4-dichlorophenyl-amino)methyl]cyclohexanone (**3d**): White solid; yield 86% (*anti/syn* 70:30), (silica gel, hexane/ethyl acetate 10:2, R_f = 0.58), m.p. 105–107 °C; FTIR (KBr, cm^{-1}): 840, 1249 ($SiMe_3$), 1495, 1598 (Ar), 1704 (CO), 2861, 2943 (CH), 3407 (NH); ^{1}H NMR: δ –0.10 (s, 9 H, $SiMe_3$), 0.16 (s, 9 H, $SiMe_3$), 1.53–2.00 (m, 6 H, CH_2), 2.25–2.45 (m, 2 H, CH_2CO), 2.68–2.78 (m, 1 H, COC*H*, *anti+syn*), 4.49 (d, *J* = 7.2 Hz, 0.7 H, C*H*N, *anti*), 4.66 (d, *J* = 3.2 Hz, 0.3 H, C*H*N, *syn*), 4.80 (s, br, 1 H, NH), 6.33–6.36 (m, 1 H, Ar), [6.56 (d, *J* = 2.8 Hz, *anti*) and 6.57 (d, *J* = 2.7 Hz, *syn*), 1 H, Ar], 7.02–7.25 (m, 5 H, Ar), 7.69 (s, 1 H, HC=, *anti+syn*); ^{13}C NMR: δ –0.6, 0.9 ($SiMe_3$), 22.7–56.4 (CH_2), 57.1 (CN), 112.6–153.2 (Ar), 210.3, 211.6 (CO). Anal. Calcd for $C_{27}H_{37}Cl_2NOSi_2$: C, 62.52; H, 7.19; N, 2.70. Found: C, 62.55; H, 7.40; N, 2.56%.

2-[(4-(2,2-Bis(trimethylsilyl)ethenyl)phenyl)(4-fluorophenylamino) methyl]cyclohexanone (**3e**): Brown viscous oil; yield 82% (*anti/syn* 75:25), (silica gel, hexane/ethyl acetate 10:3, R_f = 0.65), FTIR (KBr, cm^{-1}): 837, 1252 ($SiMe_3$), 1510, 1629 (Ar), 1706 (CO), 2858, 2928 (CH), 3419 (NH); ^{1}H NMR: δ –0.08 (s, 9 H, $SiMe_3$), 0.19 (s, 9 H, $SiMe_3$), 1.61–2.49 (m, 8 H, CH_2), 2.70–2.80 (m, 1 H, COC*H*, *anti+syn*), 4.56 (d, *J* = 7.6 Hz, 0.75 H, C*H*N, *anti*), 4.7 (d, *J* = 3.7 Hz, 0.25 H, C*H*N, *syn*), 6.44–6.49 (m, 2 H, Ar), 6.72–6.78 (m, 2 H, Ar), 7.13 (d, *J* = 7.6 Hz, 2 H, Ar), 7.27 (d, *J* = 7.2 Hz, 2 H, Ar), 7.72 (s, 1 H, HC=, *syn+anti*); ^{13}C NMR: δ –0.57, 0.8 ($SiMe_3$), 22.5–57.0 (CH_2), 57.6 (CN), 114.0–156.0 (Ar), 210.4, 211.7 (CO). Anal. Calcd for $C_{27}H_{38}FNOSi_2$: C, 69.33; H, 8.19; N, 2.99. Found: C, 69.37; H, 8.40; N, 2.58%.

2-[(4-(2,2-Bis(trimethylsilyl)ethenyl)phenyl)(4-nitrophenylamino) methyl]cyclohexanone (**3f**): Yellow solid; yield 89% (*anti/syn* 61:39) (silica gel, hexane/ethyl acetate 10:4, R_f = 0.85), m.p. 157–160 °C; FTIR (KBr, cm^{-1}): 838, 1254 ($SiMe_3$), 1531, 1599 (Ar), 1708 (CO), 2859, 2932 (CH), 3391 (NH); ^{1}H NMR: δ –0.11 (s, 9 H, $SiMe_3$), 0.16 (s, 9 H, $SiMe_3$), 1.59–2.00 (m, 6 H, CH_2), 2.32–2.43 (m, 2 H, CH_2CO), 2.83–2.85 (m, 1 H, COCH, *anti+syn*), 4.66 (t, 0.61 H, C*H*N, *anti*), 4.81 (t, 0.39 H, C*H*N,*syn*), [5.60 (d, *J* = 6.0 Hz, *syn*) and 5.63 (d, *J* = 6.4 Hz, *anti*), 1 H, NH], 6.46 (d, *J* = 8.8 Hz, 2 H, Ar), 7.12–7.14 (m, 2 H, Ar), 7.23 (d, *J* = 6.9 Hz, 2 H, Ar), 7.69 (s, 1 H, HC=, *anti+syn*), 7.96 (d, *J* = 9.2 Hz, 2 H, Ar); ^{13}C NMR: δ –0.0, 0.8 ($SiMe_3$), 16.9–55.9 (CH_2), 56.9 (CN), 111.2–153.0 (Ar), 210.2, 211.3 (CO);Anal. Calcd for $C_{27}H_{38}N_2O_3Si_2$: C, 65.54; H, 7.74; N, 5.66. Found: C, 65.83; H, 7.93; N, 5.39%.

2-[(4-(2,2-Bis(trimethylsilyl)ethenyl)phenyl)(p-tolylamino)methyl] cyclohexanone (**3g**): Yellow solid; yield 85% (*anti/syn* 80:20), (silica gel, hexane/ethyl acetate 10:2, R_f = 0.6), m.p. 109–111°C. FTIR (KBr, cm^{-1}): 840, 1250 ($SiMe_3$), 1556, 1618 (Ar), 1707 (CO), 2860, 2933 (CH), 3408 (NH); ^{1}H NMR: δ 0.05 (s, 9 H, $SiMe_3$), 0.32 (s, 9 H, $SiMe_3$), 1.69–2.62 (m, 8 H, CH_2), 2.30 (s, 3 H, Me), 2.83–2.93 (m, 1 H, COCH, *anti+syn*), 4.60 (s, br, 1 H, NH), 4.74 (d, *J* = 7.6 Hz, 0.8 H, C*H*N, *anti*), 4.87 (d, *J* = 4.0 Hz, 0.2 H, C*H*N, *syn*), 6.57 (d, *J* = 8.0 Hz, 2 H, Ar), 6.98 (d, *J* = 8.4 Hz, 2 H, Ar), 7.25 (d, *J* = 7.6 Hz, 2 H, Ar), 7.42 (d, *J* =8.0 Hz, 2 H, Ar), 7.84 (s, 1 H, HC= *anti+syn*); ^{13}C NMR: δ –0.5, 0.6 ($SiMe_3$), 19.3–56.4 (CH_2), 57.0 (CN), 113.0–153.6 (Ar), 210.4, 211.8 (CO). Anal. Calcd for $C_{28}H_{41}NOSi_2$: C, 72.51; H, 8.91; N, 3.02. Found: C, 72.21; H, 8.93; N, 2.69%.

2-[(4-(2,2-Bis(trimethylsilyl)ethenyl)phenyl)(4-butylphenylamino) methyl]cyclohexanone (**3h**): Yellow solid; yield 80% (*anti/syn* 90:10), (silica gel, hexane/ethyl acetate 10:2, R_f = 0.65), m.p. 90–93°C. FTIR (KBr, cm^{-1}): 838, 1248 ($SiMe_3$), 1517, 1616 (Ar), 1707 (CO), 2859, 2931, 2953, 3019 (CH), 3405 (NH); ^{1}H NMR: δ 0.05 (s, 9 H, $SiMe_3$), 0.31 (s, 9 H, $SiMe_3$), 1.02 (t, *J* = 6.4 Hz, 3 H, Bu), 1.40–1.47 (m, 2 H, Bu), 1.58–1.65 (m, 2 H, Bu), 1.75–2.04 (m, 6 H, CH_2), 2.47–2.57 (m, 4 H, CH_2CO + Bu), 2.83–3.01 (m, 1 H, COCH, *anti+syn*), 4.59 (s, br, 1 H, NH), 4.74 (d, *J* = 6.8 Hz, 0.9 H, C*H*N, *anti*), 4.88 (d, *J* = 4.0 Hz, 0.1 H, C*H*N, *syn*), 6.58 (d, *J* = 7.2 Hz, 2 H, Ar), 6.99 (d, *J* = 6.8 Hz, 2 H, Ar), 7.25 (d, *J* = 6.8 Hz, 2 H, Ar), 7.4 (d, *J* = 7.2 Hz, 2 H, Ar), 7.85 (s, 1 H, HC=, *syn+anti*); ^{13}C NMR: δ –0.5, 0.9 ($SiMe_3$), 12.9–57.0 (CH_2), 112.9–153.6 (Ar), 210.4, 211.8 (CO). Anal. Calcd for $C_{31}H_{47}NOSi_2$: C, 73.60; H, 9.36; N, 2.77. Found: C, 73.31; H, 9.29; N, 2.32%.

2-[(4-(2,2-Bis(trimethylsilyl)ethenyl)phenyl)(naphth-1-ylamino) methyl]cyclohexanone (**3i**): Brown viscous oil; yield 60% (*anti/syn* 83:17), (silica gel, hexane/ethyl acetate 10:2, R_f = 0.75), FTIR (KBr, cm^{-1}): 840, 1250 ($SiMe_3$), 1527, 1580, 1630 (Ar), 1703 (CO), 2860, 2943, 3056 (CH), 3430 (NH); ^{1}H NMR: δ –0.11 (s, 9 H, $SiMe_3$), 0.15 (s, 9 H, $SiMe_3$), 1.66–2.06 (m, 6 H, CH_2), 2.34–2.45 (m, 2 H, CH_2CO), 2.86–2.91 (m, 1 H, COCH, *anti+syn*), 4.76 (d, *J* = 6.8 Hz, 0.83 H, C*H*N, *anti*), 4.90 (s, 0.17 H, C*H*N, *syn*), 5.60 (s, br, 1 H, NH), 6.34 (d, *J* = 7.2 Hz, 1 H, Ar), 7.06–7.15 (m, 4 H, Ar), 7.34 (d, *J* = 8.0 Hz, 2 H, Ar), 7.42–7.49 (m, 4 H, Ar), 7.69 (s, 1 H, HC=, *syn+anti*); ^{13}C NMR: δ –0.3, 0.9 ($SiMe_3$), 22.3–57.1 (CH_2), 105.1–153.4 (Ar), 200.6, 212.4 (CO). Anal. Calcd for $C_{31}H_{41}NOSi_2$: C, 74.49; H, 8.27; N, 2.80. Found: C, 74.68; H, 8.56; N, 2.46%.

2-[(4-(2,2-Bis(trimethylsilyl)ethenyl)phenyl)(phenylamino)methyl] cycloheptanone (**3j**): Yellow viscous oil; yield 70% (*anti/syn* 66:34), (silica gel, hexane/ethyl acetate, 10:2, R_f = 0.65); FTIR (KBr, cm^{-1}): 838, 1251 ($SiMe_3$), 1503, 1555, 1603 (Ar), 1694 (CO), 2857, 2928, 3052 (CH), 3411 (NH); ^{1}H NMR: δ –0.05 (d, *J* = 8 Hz, 9 H, $SiMe_3$), 0.21 (s, 9 H, $SiMe_3$), 1.72–2.77 (m, 10 H, CH_2), 2.88–2.95 (m, 1 H, COC*H*, *anti+syn*), 4.53 (d, *J* = 7.2 Hz, 0.66 H, C*H*N, *anti*), 4.59 (d, *J* = 4.4 Hz, 0.34 H, C*H*N, *syn*), 5.00 (s, br, 1 H, NH), 6.55 (d, *J* = 8.4 Hz, 2 H, Ar), 7.09–7.34 (m, 7 H, Ar), 7.74 (s, 1 H, HC=, *anti+syn*); ^{13}C NMR: δ –0.25, 0.9 ($SiMe_3$), 23.3–59.2 (CH_2) 112.5–153.4 (Ar), 214.7, 215.4 (CO). Anal. Calcd for $C_{28}H_{41}NOSi_2$: C, 72.51; H, 8.91; N, 3.02. Found: C, 72.34; H, 9.24; N, 2.66%.

2-[(4-(2,2-Bis(trimethylsilyl)ethenyl)phenyl)(4-chlorophenylamino) methyl]cycloheptanone (**3k**): Yellow solid; yield 75% (*anti/syn* 80:20), (silica gel, hexane/ethyl acetate, 10:2, R_f = 0.83); m.p. 107–109 °C; FTIR (KBr, cm^{-1}): 839, 1254 ($SiMe_3$), 1645, 1696, (Ar), 2856, 2926 (CH), 1736 (CO), 3444 (NH); ^{1}H NMR: δ –0.11 (s, 9 H, $SiMe_3$), 0.16 (s, 9 H, $SiMe_3$), 1.70–2.50 (m, 10 H, CH_2), 2.81–2.91 (m, 1 H, COC*H*, *anti+syn*), 4.41(d, *J* = 6.8 Hz, 0.8 H, C*H*N, *anti*), 4.47 (s, 0.2 H, C*H*N, *syn*), 5.02 (s, 1 H, NH), 6.40 (d, *J* = 8.8 Hz, 2 H, Ar), 6.95 (d, *J* = 8.4 Hz, 2 H, Ar), 7.08 (d, *J* = 7.8 Hz, 2 H, Ar), 7.19 (d, *J* = 7.6 Hz, 2 H, Ar), 7.68 (s, 1 H, HC=, *syn+anti*); ^{13}C NMR: δ –0.56, 0.9 ($SiMe_3$), 23.29–59.20 (CH_2), 113.69–153.20 (Ar), 214.7 (CO). Anal. Calcd for $C_{28}H_{40}ClNOSi_2$: C, 67.50; H, 8.09; N, 2.81. Found: C, 67.83; H, 8.33; N, 2.93%.

2-[4-(2,2-Bis(trimethylsilyl)ethenyl)benzylidene]cycloheptanone (**4**): Yellow viscous oil. (silica gel, hexane/ethyl acetate 10:3, R_f = 0.8); FTIR (KBr, cm^{-1}): 838, 1252 ($SiCH_3$), 1490, 1693 (Ar), 1703 (CO), 2857, 2928, 3052 (CH), ^{1}H NMR (400 MHz, $CDCl_3$, ppm): –0.03 (s, 9 H, $SiMe_3$), 0.17 (s, 9 H, $SiMe_3$), 1.77–1.94 (m, 4 H, CH_2), 2.54 (t, *J* = 6.4 Hz, 2 H, CH_2), 2.85 (t, *J* = 5.6 Hz, 2 H, CH_2CO), 7.19 (d, *J* = 7.6 Hz, 2 H, Ar), 7.34 (d, *J* =7.6 Hz, 2 H, Ar), 7.5 (s, 1 H, HC=), 7.71 (s, 1 H, HC=). ^{13}C NMR: δ –0.5, 0.9 ($SiCH_3$), 21.7–57.7 (CH_2), 112.5–156.3 (Ar and C_{vinyl}), 211.9 (CO).

4-*[4-(2,2-Bis(trimethylsilyl)ethenyl)phenyl]-4-(phenylamino)butan-2-one* (**5a**): Brown viscous oil; yield 80% (silica gel, hexane/ethyl acetate, 10:2, R_f = 0.5); FTIR (KBr, cm^{-1}): 839, 1254 ($SiMe_3$), 1425, 1460, 1612 (Ar), 1709 (CO), 2856, 2925 (CH), 3448 (NH), ^{1}H NMR: δ –0.08 (s, 9 H, $SiMe_3$), 0.18 (s, 9 H, $SiMe_3$), 2.10 (s, 3 H, CH_3CO), 2.92 (d, *J* = 6.4 Hz, 2 H, CH_2), 4.82 (t, *J* = 6.4 Hz, 1 H, CHN), 6.52 (d,

J = 7.6 Hz, 2 H, Ar), 6.66–7.15 (m, 5H, Ar), 7.27 (d, J = 8.0 Hz, 2 H, Ar), 7.70 (s, 1 H, HC=); ^{13}C NMR: δ –0.5, 0.9 ($SiMe_3$), 21.7–53.4 (CH_2COCH_3), 112.9–153.3 (Ar), 206.2 (CO). Anal. Calcd for $C_{24}H_{35}NOSi_2$: C, 70.36; H, 8.61; N, 3.42. Found: C, 70.65; H, 8.95; N, 3.16%.

4-[4-(2,2-Bis(trimethylsilyl)ethenyl)phenyl]-4-(4-chlorophenylamino) butan-2-one (**5b**): Pale yellow solid; yield 75% (silica gel, hexane/ethyl acetate, 10:2, R_f = 0.56); m.p. 107–110˚C FTIR (KBr, cm^{-1}): 839, 1254 ($SiMe_3$), 1501, 1604, 1647 (Ar), 1710 (CO), 2656, 2926 (CH), 3410 (NH); ^{1}H NMR: δ –0.04 (s, 9 H, $SiMe_3$), 0.22 (s, 9 H, $SiMe_3$), 2.13 (s, 3 H, CH_3CO), 2.95 (d, J = 6.4 Hz, 2 H, CH_2CO), 4.59 (s, 1 H, NH), 4.79 (t, J = 6.4 Hz, 1 H, CHN), 6.47 (d, J = 8.8 Hz, 2 H, Ar), 7.04 (d, J = 8.8 Hz, 2 H, Ar), 7.16 (d, J = 8.0 Hz, 2 H, Ar), 7.28 (d, J = 8.0 Hz, 2 H, Ar), 7.74 (s, 1 H, HC=); ^{13}C NMR: δ –0.5, 0.9 ($SiMe_3$), 21.7–53.5 (CH_2CO), 114.0–153.2 (Ar), 206.1 (CO). Anal. Calcd for $C_{24}H_{34}ClNOSi_2$: C, 64.90; H, 7.72; N, 3.15. Found: C, 65.12; H, 7.94; N, 2.86%.

3-[(4-(2,2-Bis(trimethylsilyl)ethenyl)phenyl]-3-(4-chlorophenyl-amino)-1-phenylpropan-1-one (**5c**): Yellow solid; yield 70% (silica gel, hexane/ethyl acetate, 10:2, R_f = 0.92); m.p. 105–107 °C FTIR (KBr, cm^{-1}): 836, 1255 ($SiMe_3$), 1670 (CO), 2859, 2926, 3097 (CH), 3391 (NH); ^{1}H NMR: δ –0.11 (s, 9 H, $SiMe_3$), 0.16 (s, 9 H, $SiMe_3$), 3.37–3.51 [2×dd: 3.40 (dd, J = 8.0 Hz, J = 16.0 Hz 1 H, CH_2), 3.48 (dd, J = 4.8 Hz, J = 16.0 Hz, 1 H, CH_2), CH_2 Diastereotopic protons], 4.64 (s, br, 1 H, NH), 4.90–4.93 (m, 1 H, CHN), 6.44 (d, J = 8.8 Hz, 2H, Ar), 6.99-758 (m, 9 H, Ar), 7.69 (s, 1 H, HC=), 7.69 (d, J = 7.2 Hz, 2 H, Ar), ^{13}C NMR: δ –0.51, 0.93 ($SiMe_3$), 28.7–54.0 (CH_2), 114.1–153.2 (Ar), 197.3 (CO). Anal. Calcd for $C_{29}H_{36}ClNOSi_2$: C, 68.81; H, 7.17; N, 2.77. Found: C, 68.55; H, 7.42; N, 2.40%.

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References

1 P. Pawluc, G. Hreczycho and B. Marciniec, *J. Org. Chem.*, 2006, **71**, 8676.
2 D.M. Hodgson and P. Comina, *J. Chem. Commun.*, 1996, 755.
3 D.M. Hodgson, P.J. Comina and M.G.B. Drew, *J. Chem. Soc., Perkin Trans. 1*, 1997, 2279.
4 K.D. Safa, K. Ghorbanpour, A. Hassanpour and S. Tofangdarzade, *J. Organomet. Chem*., 2009, **694**, 1907.
5 K.D. Safa, M. Namvari, A. Hassanpour and S. Tofangdarzade, *J. Organomet. Chem.*, 2009, **694**, 2448.
6 K.D. Safa, F. Behmagham and K. Ghorbanpour, *J. Organomet. Chem.*, 2011, **696**, 1840.
7 K.D. Safa, J.V. Mardipour and Y.O. Mosaei, *J. Organomet. Chem*., 2011, **696**, 802.
8 A. Shahrisa and M. Zirak, *J. Heterocycl Chem.*, 2010, **47**, 594.
9 M. Wang, Z.G. Song and X. Wan, *Monatsh Chem.*, 2009, **140**, 1205.
10 H. Wu, Y. Shen, L.Y. Fan, Y. Wan, P. Zhang, C. Chen and W.X. Wang, *Tetrahedron*, 2007, **63**, 2404.
11 H. Mao, J. Wan and Y. Pan, *Tetrahedron*, 2009, **65**, 1026.
12 M. Arend, B. Westermann and N. Risch, *Angew. Chem. Int. Ed.*, 1998, **37**, 1044.
13 K. Manabe and S. Kobayashi, *Org. Lett.*, 1999, **1**, 1965.
14 T. Ollevier and E. Nadeau, *J. Org. Chem.*, 2004, **69**, 9292.
15 W.G. Shou, Y.Y. Yang and Y.G. Wang, *Tetrahedron Lett.*, 2006, **47**, 1845.
16 N. Azizi, L. Torkiyan and M.R. Saidi, *Org. Lett.*, 2006, **8**, 2079.
17 B. Eftekhari-Sis, A. Abdollahifar, M.M. Hashemi and Zirak, M., *Eur. J. Org. Chem.*, 2006, **22**, 5152.
18 R. Ghosh, S. Maiti, A. Chakraborty, S. Chakraborty and A.K. Mukherjee, *Tettrahedron*, 2006, **62**, 4059.