Available online at www.sciencedirect.com
ScienceDirect
Tetrahedron
Tetrahedron 63 (2007) 1107–1115

Highly stereoselective synthesis of *para*-substituted (*E*)-*N*-styrylcarbazoles via sequential silylative coupling–Hiyama coupling reaction

Wiesław Prukała, Bogdan Marciniec,* Mariusz Majchrzak and Maciej Kubicki

Department of Organometallic Chemistry, Faculty of Chemistry, Adam Mickiewicz University, Grunwaldzka 6, 60-780 Poznań, Poland

Received 21 August 2006; revised 7 November 2006; accepted 23 November 2006

Abstract—A series of new *para*-substituted (*E*)-(*N*)-styrylcarbazoles, i.e., eight (*E*)-9-[2-(aryl)ethenyl]-9*H*-carbazoles (**5**–**12**) and 1,4-bis[(*E*)-2-(9*H*-carbazol-9-yl)vinyl]benzene (**13**), have been synthesized in high yield and stereoselectively by a sequential silylative coupling–Hiyama coupling reaction, i.e., coupling of commercially available 9-vinylcarbazole with vinyltriethoxysilane or divinyltetramethyldisiloxane in the presence of $[RuHCl(CO)(PCy_3)_2]$ (**I**), followed by Pd (**II**) catalyzed *cross*-coupling with *para*-substituted iodobenzenes. The tandem procedure has facilitated the synthesis of **13**. X-ray structures of the intermediate silylvinylcarbazole (**4**), as well as products **12** and **13** have been obtained.

1. Introduction

The synthesis of carbazole derivatives with various substituents has been well studied, particularly since this class of compounds is of great interest in pharmacological applications and in molecular electronics.

Some carbazole alkaloids have been isolated from *Murraya euchrestifolia*,[1a] *Murraya koenigii*,[1b–e] and *Micromelum minutum*.[1f] Muraya plants have been widely used as anti-dysenterics, astringents, analgesics, or febrifuges in folk medicine in China and other Asian countries.[2a] Isolated carbazole derivatives exhibit various biological activities such as anti-tumor,[1e,2b] anti-oxidative,[1d] anti-inflammatory, and anti-mutagenic activities.[1c,f]

On the other hand, carbazole-based compounds play a very important role in electroactive and photoactive materials and are also considered to be potential candidates for electronic devices, such as color displays, organic semiconductor laser, solar cells, etc.[3a]

A particular feature of the condensed aromatic rings in the carbazole is their ability to π-stack, which contributes to their binding affinity in macromolecules and gives rise to molecular ordering via self assembly in the solid-state. Compounds possessing a π-conjugated system are widely used as good hole-transporting materials in polymeric light-emitting diodes (PLEDs)[3b–e] as an organic light-emitting diode (OLED).[4a,b] Polymeric light-emitting diodes (PLEDs) can emit white,[3c] pure deep blue,[3d] green, or red light.[3e]

With regard to the applications of carbazole derivatives, a critical issue is the solubility in water or in organic solvents, which strongly depends on *N*-substituted hydrophilic or hydrophobic chain. Therefore, *N*-substituted carbazole derivatives are very attractive.[4a–c] However, so far, only a few methods for the synthesis of *N*-vinyl- [5a–e] (or *N*-styrylcarbazoles)[5e,f] have been described, mostly based on the reactions of carbazole occurring in the medium of a strong base either with acetylene (and phenylacetylene)[5a,f] or with β-bromostyrene catalyzed by palladium catalyst.[5e]

In the past two decades, we have developed two universal methods for the functionalization of vinylorganosilicon compounds. Both methods, i.e., silylative coupling (**SC**) and *cross*-metathesis (**CM**), are based on transition metal-catalyzed reactions of vinylsilicon compounds with olefins.[6] The **SC** reaction occurs via cleavage of the =C–H bond of the olefin and the =C–Si bond of vinylsilane in contrast to *cross*-metathesis, which starts with the same substrates and ends with the same products through cleavage of the C=C bonds.[6a] However, alkyl substituted vinylsilanes appear to be quite inactive in ruthenium-catalyzed *cross*-metathesis.[7] We have recently reported the highly stereoselective synthesis of (*E*)-9-[2-(silyl)ethenyl]-9*H*-carbazole via the silylative-coupling reaction.[8a]

Keywords: *Cross*-coupling; Hiyama coupling; Homogenous catalysis; 9-Vinylcarbazole.

* Corresponding author. Tel.: +48 61 8291 366; fax: +48 61 8291 508; e-mail: marcinb@amu.edu.pl

0040–4020/$ - see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tet.2006.11.065

The use of palladium-catalyzed *cross*-coupling protocol (Hiyama coupling) permits the further transformation of organic compounds with a vinylsilicon groups into the desired products[9] in high yield and with good stereoselectivity. The mild conditions of many transition metal-catalyzed reactions allow their use as tandem reactions (without isolation of intermediate products). Such tandem reactions of organosilicon compounds are well known, e.g., intermolecular hydrosilylation/*cross*-coupling,[10a] intramolecular hydrosilylation/*cross*-coupling,[10b,c] silylformylation/*cross*-coupling,[10d] Mirozouki–Heck reaction/*cross*-coupling,[10e,f] ring-closing metathesis/*cross*-coupling,[10g–i] or Alder-Ene/*cross*-coupling.[10j,k] We have further reported our preliminary sequential *cross*-metathesis/Hiyama coupling[8b] as well as silylative coupling/Hiyama coupling[8a,b] reactions.

Herein, we now report the sequential silylative coupling of *N*-vinylcarbazole with vinyl-substituted silanes and disiloxane, and further catalytic transformation via Hiyama coupling with *para*-substituted iodobenzenes to give π-conjugated *para*-substituted (*E*)-*N*-styrylcarbazoles.

2. Results and discussion

The starting *N*-silylvinylcarbazole derivatives (**3** and **4**) were prepared by the silylative-coupling reaction of commercially available 9-vinylcarbazole and vinyltriethoxysilane[8a] or divinyltetramethyldisiloxane in the presence of 1 mol % (calculated for one active vinylsilyl group) ruthenium complex $[RuH(Cl)(CO)(PCy_3)_3]$ (**I**) according to Scheme 1. The reaction permits the synthesis of **3** and **4** with very good final yield and high stereoselectivity (*E* products >99%) under optimum reaction conditions (see Section 4).

The progress in the catalytic transformation of the substrates and their complete consumption within 20 h were monitored by GC and GC–MS methods. But the *trans*-vinylene fragment between silicon atom (Si–*H*C=CH–) and suitable carbon atom (Si–HC=C*H*–) in the molecules unambiguously was confirmed by proton spectroscopic analysis (the coupling constants were as follows: J_{H-H}=17.3 Hz for **3** and 17.1 Hz for **4**). In contrast to the silylative-coupling reaction, the *cross*-metathesis on vinylcarbazole system affords the expected products in low yield.[8a]

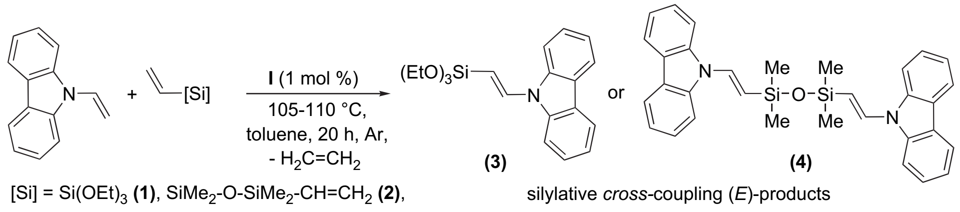
(*E*)-9-[2-(Triethoxysilyl)ethenyl]-9*H*-carbazole (**3**), obtained via silylative-coupling in the presence of Pd catalyst $[Pd_2(dba)_3]$ (**II**), undergoes *cross*-coupling (Hiyama coupling) reactions giving exclusively *para*-substituted *N*-styrylcarbazole derivatives (Scheme 2).

The reactions were performed in an open system under a gentle flow of argon at 30 °C for 72 h. The results obtained are collected in Table 1.

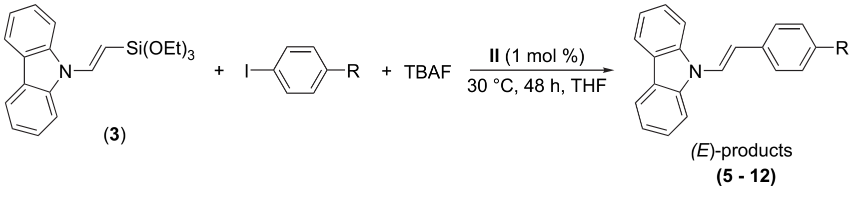
This Hiyama coupling of **3** with a number of iodoarenes containing *para*-substituted electron-withdrawing (or electron-donating) groups in the presence of $[Pd_2(dba)_3]$/TBAF system in THF (**II**) leads to the highly selective formation of trans-products (>99%). Formation of traces of the cis-isomer was confirmed only by GC–MS analysis. The reactions examined revealed that electron-withdrawing groups in the *para*-position of the phenyl ring of the aryl iodides tested accelerate the palladium-catalyzed *cross*-coupling of the alkenes investigated. Under the presented conditions, the catalytic transformation of substrates was almost complete after 24 h for nitro- or acetyl-substituent, and after 48 h for acetamido substituent. The yields of isolated products were above 86%. For *para*-substituted iodoarenes with electron-donating groups the use of longer reaction time was necessary to obtain satisfactory yields of products.

4-Iodoaniline did not undergo palladium-catalyzed *cross*-coupling reaction even at elevated temperature (Table 1). This compound probably reacts with the palladium complex, by nitrogen coordination, which inhibits further transformations.

Low catalyst loadings (1.5%) may be used in these reactions, which are advantageous from an economical point of view, but longer reaction times are necessary to obtain satisfactory yields. In the presence of a higher amount of the catalyst (3–5%) the *cross*-coupling reaction is complete after a few hours (Tables 2 and 3) or even after 10 min.[11] The



Scheme 1. *Cross*-coupling of 9-vinylcarbazole with vinyltriethoxysilane (**1**) and divinyltetramethyldisiloxane (**2**).



Scheme 2. Hiyama coupling reaction of (*E*)-9-[2-(triethoxysilyl)ethenyl]-9*H*-carbazole (**3**) with *para*-substituted iodobenzenes.

Table 1. Results of catalytic transformation of silylcarbazole derivatives with *para*-substituted iodobenzenes via Hiyama coupling reaction catalyzed by **II**

Entry	R	Time (h)	Conversion of iodoarene (%)	Yield (%) (product)
1	F	48	90	79 (**5**)
2	Cl	48	81	72 (**6**)
3	Br	48	93	71 (**7**)
4	$COCH_3$	24	99	86 (**8**)
5	NO_2	24	99	98 (**9**)
6	CH_3	48	90	81 (**10**)
7	NH_2	72	0	0
8	NH_2*	72	~10	0
9	$NHCOCH_3$	48	96	91 (**11**)
10	OCH_3	48	74	66 (**12**)

Reaction conditions: $[Si]/[IC_6H_4R]/[TBAF]=1:0.9:1.2$; $T=30$ °C; Ar (open system); *$T=45$ °C.

Table 2. Results of catalytic transformation of silylcarbazole derivatives with 1,4-diiodobenzene

Molar ratio ViSi/Pd	Time (h)	Conversion of diiodobenzene (%)	Selectivity (%) *E*	Selectivity (%) *Z*	Biphenyl (%)
(I) Carbazole–HC═CH–Si(OEt)$_3$ (**3**)					
1:0.015	24	98	>99	—	—
1:0.015	48	>99	>99	—	—
1:0.05	2	85	>99	Trace	~8
1:0.05	3	99	>99	Trace	~9
(II) Carbazole–HC═CH–Si–Me$_2$–O–Si–Me$_2$–HC═CH–carbazole (**4**)[a]					
1:0.03	3	94	>99	—	—
1:0.03	5	99	>99	—	—

Reaction conditions: $[Si]/[IC_6H_4I]/[TBAF]=1:0.4:1.2$; $T=30$ °C; Ar (open system); THF 0.3 M.

[a] $[Si]/[IPhI]/[TBAF]=0.5:0.4:1.2$; $T=30$ °C; Ar (open system); THF 0.3 M.

Table 3. Results of catalytic transformation of silylcarbazole derivatives with 1,4-diiodobenzene via Hiyama coupling tandem reaction catalyzed by Pd(0)

Molar ratio ViSi/IPhI	Time (h)	Conversion of diiodobenzene (%)	Selectivity (%) *E*	Selectivity (%) *Z*	Polymerization products
1:0.4	3	85	>99	—	—
1:0.4	5	99	>99	Trace	Trace
1:0.4	10	100	>99	Trace	Middle

Reaction conditions: $[II]/[Si]/[IC_6H_4I]/[TBAF]=0.03:1:0.4:1.2$; $T=30$ °C; Ar (open system); THF 0.3 M.

substituents on the styryl-group of the final products (**5–12**) are amenable to further modifications.

The high yield and stereoselectivity of the Hiyama coupling reaction in ═C–C$_{vinyl}$ formation are very attractive for the synthesis of nitrogen atom-containing π-conjugation. The use of 1,4-diiodobenzene in the catalytic transformation described above allows access to 1,4-bis[(*E*)-2-(9*H*-carbazol-9-yl)vinyl]benzene (**13**) in excellent yield (92%) (Scheme 3). The results obtained are collected in Table 2.

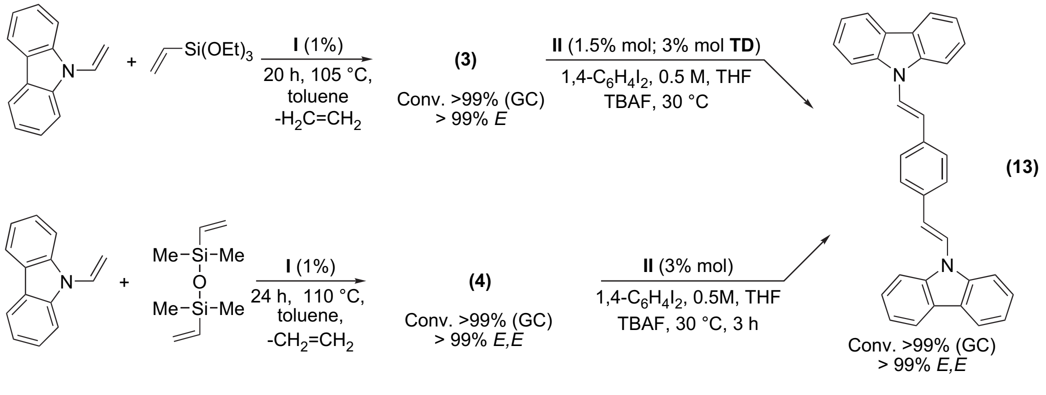
A higher amount (5%) of catalyst **II** increases the formation of biphenyl (<9%) in the *cross*-coupling reactions. Reduction of the catalyst loading to 1.5% requires longer reaction time (48 h).

On the basis of the catalytic results, additional experiments were carried out on the tandem reaction system (without isolation of compound **3**), according to Scheme 3. Product **3** synthesized in the first 'product–substrate' step undergoes catalytic transformation with 1,4-diiodobenzene to give the desired product **13**. Conversion of substrates (>99%) and selectivity (>99%) were determined by GC and GC–MS methods with an internal standard. The use of low catalyst loading of **II** (1.5%) in this tandem reaction requires longer reaction times, which sometimes results in *cross*-linking of by-products making it impossible to isolate the products. The next step in this study was to prepare and apply 1,3-bis[((*E*)-2-(9*H*-carbazol-9-yl)-vinyl)]-1,1,3,3-tetramethyldisiloxane (**4**) in forming the alkene bond (Scheme 3).

Compound **4**, obtained in a procedure similar to **3**, undergoes catalytic transformation with 1,4-diiodobenzene in the presence of the same catalyst **II** to give product **13** with a yield and stereoselectivity similar to that of the tandem reaction (Table 3).

Due to the structure of compound 1,3-bis[((*E*)-2-(9*H*-carbazol-9-yl)-vinyl)]-1,1,3,3-tetramethyldisiloxane (**4**) as a starting material, there was no observed *cross*-linking of by-products in the Hiyama coupling reaction.

Because *N*-vinylcarbazoles are widely used as building blocks in photosensitive and photoelectronic polymers and composites, the Pd-catalyzed *cross*-coupling following the silylative-coupling reaction of *N*-vinylcarbazole with



Scheme 3. Synthesis of 1,4-bis[(*E*)-2-(9*H*-carbazol-9-yl)vinyl]benzene (**13**) via tandem reaction.

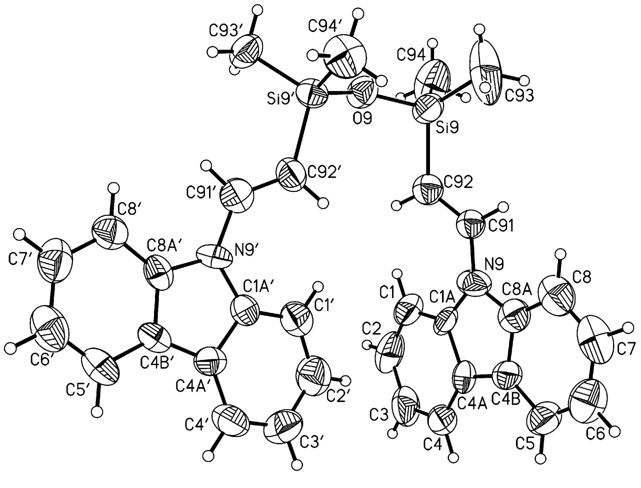


Figure 1. ORTEP representation of compound **4**. The ellipsoids are drawn at 50% probability level, and hydrogen atoms are depicted as spheres with arbitrary radii.

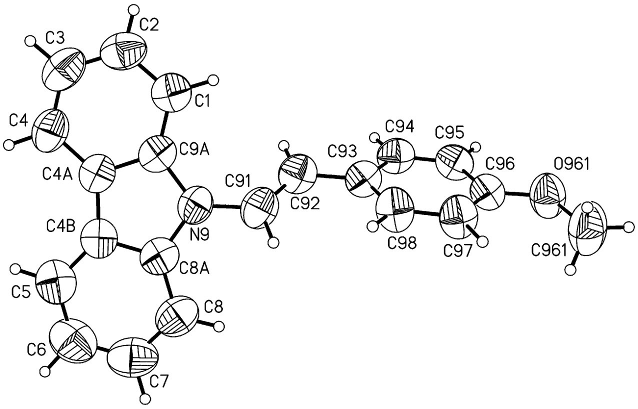


Figure 2. ORTEP representation of compound **12**. The ellipsoids are drawn at 50% probability level, and hydrogen atoms are depicted as spheres with arbitrary radii.

vinylsilanes is a versatile method suitable for industrial applications.

All compounds revealed an *E*-configuration, confirmed by spectroscopic methods (IR, ^{1}H NMR, ^{13}C NMR, and MS in Section 4).

The structures of 1,3-bis[((*E*)-2-(9*H*-carbazol-9-yl)-vinyl)]-1,1,3,3-tetramethyldisiloxane (**4**), (*E*)-9-(4-methoxystyryl)-9*H*-carbazole (**12**), and 1,4-bis[(*E*)-2-(9*H*-carbazol-9-yl) vinyl]benzene (**13**) were characterized by X-ray crystallography (Figs. 1–3).

The perspective views of molecules **4**, **12**, and **13** are shown in Figures 1–3, respectively. The bond lengths and angles are typical.[8a] Note the short length of the double bond in **13**, 1.237(3) Å, which can, however, be an effect of libration.

In all three compounds the carbazole ring systems are planar, even though some deviations from the least-squares planes calculated for **13** ring atoms are statistically significant: the maximum values are 0.075(2) Å and 0.071(2) Å in **4**, 0.015(2) Å in **12**, and 0.030(2) Å in **13**. In **4** the two carbazole moieties are almost perpendicular; the dihedral angle between their planes is 84.73(2)°; in **12** the phenyl ring is also significantly twisted with respect to the carbazole ring system (dihedral angle of 64.29(4)°), while in **13** both carbazole fragments are perfectly parallel, due to the symmetry of the molecule, and the angle between these planes and the plane of the central phenyl ring is relatively small, 12.8(2)°. In both **12** and **13** the phenyl rings are almost perfectly planar, all the deviations from the least-squares planes are within experimental errors.

The orientation of the vinyl group with respect to the carbazole rings can be described, e.g., by the torsion angle C–N–C=C. The values of these angles show that the vinyl groups are slightly but significantly deviated from coplanarity with the carbazole plane: the values of these angles are 20(2)° and −21.2(4)° in **4**, −44.4(2)° in **12**, and −16.8(4)° in **13**. These values are larger than in (*E*)-9-[2-(dimethylphenylsilyl)ethenyl]-9*H*-carbazole (5.9(3)°), but comparable to closely related (*E*)-9-[2-(trimethylsilyl)ethenyl]-9*H*-carbazole (−20.2(3)°).[8a]

3. Conclusions

The palladium-catalyzed *cross*-coupling reaction of (*E*)-9-[2-(triethoxysilyl)ethenyl]-9*H*-carbazole (**3**) with *para*-substituted iodoarenes affords eight new (*E*)-9-[2-(aryl) ethenyl]-9*H*-carbazoles (**5–12**). Similarly, the *cross*-coupling

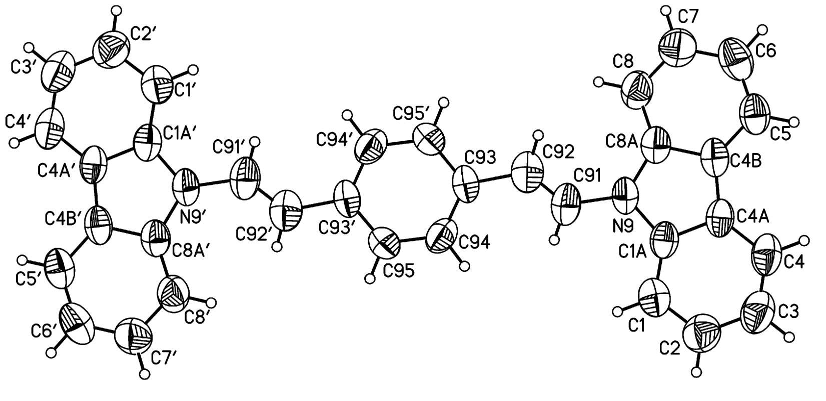


Figure 3. ORTEP representation of compound **13**. The ellipsoids are drawn at 50% probability level, and hydrogen atoms are depicted as spheres with arbitrary radii.

of **3** and 1,3-bis[((*E*)-2-(9*H*-carbazol-9-yl)-vinyl)]-1,1,3,3-tetramethyldisiloxane (**4**) with *para*-diiodobenzene leads to compound 1,4-bis[(*E*)-2-(9*H*-carbazol-9-yl)vinyl]benzene (**13**) with highly π-conjugated double bond system. The tandem silylative coupling–Hiyama coupling reaction has been finally worked out. The structures of **4**, **12**, and **13** have also been solved.

4. Experimental

4.1. General methods

^{1}H NMR (300 MHz), ^{13}C NMR (75 MHz), and ^{29}Si NMR (60 MHz) and DEPT spectra were recorded on Varian XL 300 MHz spectrometer in $CDCl_3$ (or CD_3COCD_3) solution. Chemical shifts are reported in δ (parts per million) with reference to tetramethylsilane as internal standard. IR spectra (KBr pellets) were recorded on a Brucker ITS 113v spectrometer. Analytical gas chromatographic (GC) analyses were performed on a Varian Star 3400CX with a DB-5 fused silica capillary column (30 m×0.15 mm) and TCD. Mass spectra of the monomers and products were obtained by GC–MS analysis (Varian Saturn 2100T, equipped with a BD-5 capillary column (30 m) and an ion trap detector). High-resolution mass spectroscopic (HRMS) analyses were performed on an AMD-402 mass spectrometer. Thin-layer chromatography (TLC) was performed on plates coated with 250 μm thick silica gel (Merck), and column chromatography was performed with silica gel 60 (70–230 mesh, Fluka). Benzene and hexane were dried by distillation from sodium hydride; similarly, toluene and diethyl ether were distilled from sodium and hexane from calcium hydride under argon. All liquid substrates were also dried and degassed by bulb-to-bulb distillation. All the reactions were carried out under dry argon atmosphere. Melting points are uncorrected and were determined by using Boetius melting-point apparatus.

4.2. Materials

The chemicals were obtained from the following sources: CH_2Cl_2, EtOAc, toluene, decane, diethyl ether, and hexane were purchased from Fluka; CD_3COCD_3 and $CDCl_3$ from Dr. Glaser A.G. Basel; 9-vinylcarbazole, vinyltriethoxysilane, iodobenzene, 1-bromo-4-iodobenzene, 4-iodotoluene, 1-chloro-4-iodobenzene, 1-fluoro-4-iodobenzene, 4-iodoacetophenone, 1-methoxy-4-idoiodobenzene, 1,4-diiodobenzene, 4-nitroiodobenzene, 4-aminoiodobenzene, and tetrabutylammonium fluoride (TBAF) were bought from Aldrich; 1,1,3,3-tetramethyldisiloxane from Gelest; 4-acetamidoiodobenzene has been synthesized from 4-aminoiodobenzene by following standard procedure.[12a] The ruthenium and palladium complexes—$[RuH(Cl)(CO)(PCy_3)_2]$ (**I**),[12b] $[Pd_2(dba)_3]$ (**II**),[12c] were prepared according to procedure described in literature.

4.3. Catalytic examinations of Hiyama coupling reaction

In a typical catalytic test, the reagents and decane as internal standard (5% by volume of all components) were dissolved in tetrahydrofuran and placed in a glass ampoule under argon (usually used at the molar ratio: $[ViSi]/[IC_6H_4R]/[TBAF]=1:0.9:1.2$). Then, the palladium catalyst (**II**) (1.5 mol %) was added and the ampoule was heated from 30 °C to 45 °C for 48 h. The progress of the reaction was monitored by gas chromatography.

4.4. Catalytic examinations of silylative coupling–Hiyama coupling tandem reaction

In a typical catalytic test, (*E*)-9-[2-(triethoxysilyl)ethenyl]-9*H*-carbazole (**3**) is not isolated after silylative-coupling reaction (5% decane as internal standard, amount calculated from GC analyses). Then, the solvent was gently evaporated under vacuum pump and the other reagents with an appropriate amount of THF were placed in a glass ampoule under argon (usually used at the molar ratio: $[ViSi]/[IC_6H_4I]/[TBAF]=1:0.4:1.2$). After that, the palladium catalyst (**II**) (3 mol %) was added and the ampoule was heated at 30 °C for 24 h.

During catalytic experimental parts the conversion of the substrates was calculated using the internal standard method. The composition of the reaction mixture was analyzed by GC and GC–MS.

4.5. Synthesis of silylcarbazole derivatives

The syntheses via silylative *cross*-coupling were performed under argon using $[RuH(Cl)(CO)(PCy_3)_3]$ (**I**) as the catalyst. Reagents and solvents were dried and deoxygenated. The details are presented below.

4.5.1. (*E*)-9-[2-(Triethoxysilyl)ethenyl]-9*H*-carbazole (3). The title compound was prepared in a manner similar to that reported in Ref. 8a with modifications, which facilitated an improvement in the yield of the reaction synthesis. $[RuH(Cl)(CO)(PCy_3)_3]$ (**I**) (47 mg, 0.065 mmol), toluene (4.87 mL), vinyltriethoxysilane (0.925 g, 4.87 mmol), and 9-vinylcarbazole (1.88 g, 9.47 mmol) were placed in a 20 mL mini-reactor with side neck closed with a silicon septum, equipped with a magnetic stirring bar and condenser connected to a bubbler. The reaction mixture was heated at 105 °C for 8 h under an argon flow. Then, vinylsilane (0.694 g, 3.65 mmol) was added and the reaction continued for 12 h. After that, the excess of solvent was removed under vacuum, and the reaction mixture was injected onto a short silica-gel column (mobile phase: hexane/EtOAc 40:1/ Et_3N-3% volume; $R_f=0.65$). In this way the final product was separated from the residues of catalyst and the remains of small amount of polymeric material derivative of vinylcarbazole (uncontrolled radical polymerization of vinylamine). The last step was the distillation under reduced pressure (135–137 °C/1 mmHg) to give 2.72 g (7.66 mmol) of **3** in 90% as a colorless liquid. ^{1}H NMR ($CDCl_3$, δ (ppm)): 1.36 (t, 9H, –CH_3), 3.99 (q, 6H, –CH_2–), 5.73 (d, 1H, $J_{H-H}=17.3$ Hz, Si–*H*C=CH–N), 7.33 (t, 1H, Ph), 7.51 (t, 1H, Ph), 7.78 (t, 1H, Ph), 7.79 (d, 1H, $J_{H-H}=17.3$ Hz, Si–HC=C*H*–N), 8.08 (d, 1H, Ph); ^{13}C NMR ($CDCl_3$, δ (ppm)): 18.6 (–CH_3), 31.1 (–CH_2–), 111.3 (Ph), 113.0 (Ph), 120.6 (Ph), 121.3 (Ph), 124.8 (C_i at C_4N), 126.6 (Si–HC=*C*H–N<), 134.2 (C_i at C_4N), 139.9 (Si–H*C*=CH–N<); ^{29}Si NMR ($CDCl_3$, δ (ppm)): −54.14. HRMS calcd for $C_{20}H_{25}NO_3Si$: 355.16037, found 355.16018. Anal. Calcd for $C_{20}H_{25}NO_3Si$: C 67.57, H 7.09, N 3.94. Found: C 67.69, H 7.11, N 3.93.

4.5.2. 1,3-Bis[((*E*)-2-(9*H*-carbazol-9-yl)-vinyl)]-1,1,3,3-tetramethyldisiloxane (4). [RuH(Cl)(CO)(PCy_3)$_3$] (**I**) (35 mg, 0.048 mmol), toluene (7.20 mL, 0.75 M), divinyl-1,1,3,3-tetramethyldisiloxane (0.449 g, 2.41 mmol), and 9-vinylcarbazole (1.39 g, 7.19 mmol) as a mixture were heated in a 20 mL glass mini-reactor with magnetic stirring bar and condenser connected to a bubbler at 105–110 °C under an argon flow for 20 h. The next steps were carried out in the same way as **I**. The mixture hexane/EtOAc (50:1) was applied as an eluant (R_f=0.55). The final product was obtained with 80% conversion (0.996 g, 1.93 mmol) as a white powdered crystal. Single crystals of **4** suitable for X-ray crystal structure were obtained by recrystallization from hexane at room temperature. ^{1}H NMR ($CDCl_3$, δ (ppm)): 0.42 (s, –Si(C*H*$_3$)$_2$–), 6.06 (d, 1H, $J_{H–H}$=17.1 Hz, Si–*H*C=CH–N), 7.32 (t, 1H, Ph), 7.38 (t, 1H, Ph), 7.54 (d, 1H, $J_{H–H}$=17.1 Hz, Si–HC=C*H*–N), 7.39 (d, 1H, Ph), 8.04 (d, 1H, Ph); ^{13}C NMR ($CDCl_3$, δ (ppm)): 1.6 (–*C*H$_3$), 110.7 (Ph), 111.3 (Ph), 120.1 (Ph), 120.8 (Ph), 124.2 (C_i at C_4N), 126.2 (Si–HC=*C*H–N<), 134.6 (C_i at C_4N), 139.1 (Si–H*C*=CH–N<); ^{29}Si NMR ($CDCl_3$, δ (ppm)): 0.64. HRMS calcd for $C_{32}H_{32}N_2OSi_2$: 516.20535, found: 516.20529. Anal. Calcd for $C_{32}H_{32}N_2OSi_2$: C 74.37, H 6.24, N 5.42. Found: C 74.33, H 6.23, N 5.41.

4.6. Syntheses of carbazole derivatives

The synthesis was performed under argon using [Pd_2(dba)$_3$] (**II**) as the catalyst, reagents, and solvent. The final product was isolated from the reaction mixture. The details are presented below.

4.6.1. Synthesis of (*E*)-9-(4-fluorostyryl)-9*H*-carbazole (5). [Pd_2(dba)$_3$] (**II**) (0.916 mg, 0.001 mmol), THF (0.2 mL), (*E*)-9-[2-(triethoxysilyl)ethenyl]-9*H*-carbazole (**3**) (35.4 mg, 0.1 mmol), tetrabutylammoniumfluoride (32.0 mg, 0.12 mmol), and 1-fluoro-4-iodobenzene (0.0104 mL, 0.09 mmol) were placed in 1.5 mL glass ampoule. The mixture was heated at 30 °C for 24 h under an argon atmosphere. The degree of conversion was calculated by GC and GC–MS analyses. The final product was separated from the reaction mixture using column with silica (TLC, R_f=0.38, hexane/EtOAc=30:1) to afford 20.4 mg (79% yield) of **5** as white crystals, mp 123–126 °C (dec). IR (KBr) 946.1 (trans –C=C–); ^{1}H NMR ($CDCl_3$, δ (ppm)): 7.62 (d, 1H, $J_{H–H}$=14.5 Hz, >N–C*H*=), 7.06–8.11 (m, 12H, H in carbazole and phenyl ring), 7.02 (d, 1H, $J_{H–H}$=14.3 Hz, Ph–C*H*=); ^{13}C NMR ($CDCl_3$, δ (ppm)): 110.4, 115.6, 115.9, 118.7, 120.3, 120.7, 123.0, 123.9, 126.2, 127.1, 127.2, 132.3, 139.4, 160.3, 163.6. EIMS *m*/*z* 287 (M$^+$, 100), 272 (4), 259 (3), 241 (1), 204 (0.5), 191 (3), 167 (14), 140 (7), 120 (5), 115 (2), 101 (8), 75 (9). HRMS calcd for $C_{20}H_{14}NF$ (EI): 287.11102, found: 287.10967.

4.6.2. Synthesis of (*E*)-9-(4-chlorostyryl)-9*H*-carbazole (6). The title compound was prepared in a similar manner as described above for **5** using siloxane (**3**) and 1-chloro-4-iodobenzene (21.5 mg, 0.09 mmol), and was purified via column chromatography (TLC, R_f=0.45, hexane/EtOAc=30:1) to provide 19.8 mg of **6** as white crystals (72%), mp 122–125 °C (dec). IR (KBr) 948.2 (trans –C=C–); ^{1}H NMR ($CDCl_3$, δ (ppm)): 7.00 (d, 1H, $J_{H–H}$=14.5 Hz, >N–C*H*=), 7.25–8.10 (m, 12H, H in carbazole and phenyl ring), 7.69 (d, 1H, $J_{H–H}$=14.5 Hz, Ph–C*H*=); ^{13}C NMR ($CDCl_3$, δ (ppm)): 110.5, 117.9, 120.3, 120.8, 123.7, 124.1, 126.3, 126.8, 128.9, 132.6, 134.7, 139.3. EIMS *m*/*z* 303 (M$^+$, 100), 288 (3), 267 (24), 241 (5), 228 (1), 204 (2), 191 (4), 167 (21), 151 (8), 140 (12), 133 (16), 120 (8), 115 (4), 102 (11), 75 (16). HRMS calcd for $C_{20}H_{14}N^{35}Cl$ (EI): 303.08148, found: 303.08097.

4.6.3. Synthesis of (*E*)-9-(4-bromostyryl)-9*H*-carbazole (7). The title compound was prepared in a similar manner as described above for **5** using siloxane (**3**) and *para*-bromo-4-iodobenzene (25.5 mg, 0.09 mmol), which was purified via column chromatography (TLC, R_f=0.35, hexane/EtOAc=30:1) to provide 22.2 mg of **7** as white crystals (71%), mp 126–129 °C (dec). IR (KBr) 947.5 (trans –C=C–); ^{1}H NMR ($CDCl_3$, δ (ppm)): 6.99 (d, 1H, $J_{H–H}$=14.5 Hz, >N–C*H*=), 7.25–8.10 (m, 12H, H in carbazole and phenyl ring), 7.71 (d, 1H, $J_{H–H}$=14.5 Hz, Ph–C*H*=); ^{13}C NMR ($CDCl_3$, δ (ppm)): 110.6, 117.9, 120.4, 120.7, 123.9, 124.2, 126.4, 127.2, 131.9, 135.3, 139.4. EIMS *m*/*z* 349 (M$^+$, 100), 347 (M$^+$, 100), 334 (3), 332 (3), 267 (38), 241 (12), 228 (3), 219 (7), 191 (6), 167 (27), 151 (4), 140 (15), 133 (18), 120 (6), 115 (5), 102 (15), 92 (4), 87 (4), 75 (9). HRMS calcd for $C_{20}H_{14}N^{79}Br$ (EI): 347.03098, found: 347.02999, and for $C_{20}H_{14}N^{81}Br$ (EI): 349.02890, found: 349.02655.

4.6.4. Synthesis of (*E*)-1-(4-(2-(9*H*-carbazol-9-yl)vinyl)-phenyl)ethanone (8). The title compound was prepared in a similar manner as described above for **5** using siloxane (**3**) and 4-iodoacetophenone (22.1 mg, 0.09 mmol), and was purified via column chromatography (TLC, R_f=0.63, hexane/EtOAc=3:1) to provide 24.0 mg (86% yield) of **8** as white crystals, mp 152–155 °C (dec). IR (KBr) 961.7 (trans –C=C–); ^{1}H NMR ($CDCl_3$, δ (ppm)): 2.63 (s, 3H, CO–C*H*$_3$), 7.06 (d, 1H, $J_{H–H}$=14.2 Hz, >N–C*H*=), 7.25–8.11 (m, 12H, H in carbazole and phenyl ring), 7.87 (d, 1H, $J_{H–H}$=14.2 Hz, Ph–C*H*=); ^{13}C NMR ($CDCl_3$, δ (ppm)): 26.5, 110.7, 116.8, 120.4, 121.3, 124.4, 125.5, 126.4, 129.1, 135.4, 139.3, 141.4, 197.4. EIMS *m*/*z* 311 (M$^+$, 100), 296 (26), 268 (26), 241 (13), 228 (3), 204 (2), 191 (2), 167 (6), 140 (5), 133 (6), 115 (3), 102 (6), 91 (1), 75 (3). HRMS calcd for $C_{22}H_{17}NO$ (EI): 311.13101, found: 311.12847.

4.6.5. Synthesis of (*E*)-9-(4-nitrostyryl)-9*H*-carbazole (9). The title compound was prepared in a similar manner as described above for **5** using siloxane (**3**) and 4-nitroiodobenzene (22.4 mg, 0.09 mmol), and was purified via column chromatography (TLC, R_f=0.12, hexane/EtOAc=30:1) to provide 27.7 mg (98% yield) of **9** as orange crystals, mp 182–185 °C (dec). IR (KBr) 930.6 (trans –C=C–); ^{1}H NMR ($CDCl_3$, δ (ppm)): 7.07 (d, 1H, $J_{H–H}$=14.5 Hz, >N–C*H*=), 7.20–8.30 (m, 12H, H in carbazole and phenyl ring), 7.93 (d, 1H, $J_{H–H}$=14.5 Hz, Ph–C*H*=); ^{13}C NMR ($CDCl_3$, δ (ppm)): 110.8, 114.6, 120.4, 121.6, 124.3, 124.6, 125.6, 126.5, 126.9, 139.0, 143.5, 146.1. EIMS *m*/*z* 314 (M$^+$, 100), 284 (14), 268 (26), 254 (9), 241 (18), 228 (5), 217 (4), 204 (6), 191 (4), 167 (27), 140 (10), 133 (5), 120 (4), 115 (3), 102 (8), 91 (2), 75 (4). HRMS calcd for $C_{20}H_{14}N_2O_2$ (EI): 314.10553, found: 314.10298.

4.6.6. Synthesis of (*E*)-9-(4-methylstyryl)-9*H*-carbazole (10). The title compound was prepared in a similar manner as described above for **5** using siloxane (**3**) and 4-iodotoluene (19.6 mg, 0.09 mmol), and was purified via column chromatography (TLC, R_f=0.46, hexane/EtOAc=30:1) to provide 20.6 mg (81% yield) of **10** as white crystals, mp 110–112 °C (dec). IR (KBr) 945.8 (trans –C=C–); ^{1}H NMR ($CDCl_3$, δ (ppm)): 2.39 (s, 3H, $-CH_3$), 7.04 (d, 1H, J_{H-H}=14.3 Hz, >N–C*H*=), 7.20–8.11 (m, 12H, H in carbazole and phenyl ring), 7.56 (d, 1H, J_{H-H}=14.3 Hz, Ph–C*H*=); ^{13}C NMR ($CDCl_3$, δ (ppm)): 21.3, 110.4, 120.1, 120.2, 120.5, 122.4, 123.9, 125.6, 126.1, 129.5, 133.2, 137.0, 139.5. EIMS *m/z* 283 (M^+, 100), 268 (10), 254 (3), 241 (2), 204 (2), 191 (2), 167 (9), 140 (5), 115 (11), 91 (5), 77 (3). HRMS calcd for $C_{21}H_{17}N$ (EI): 283.13611, found: 283.13811.

4.6.7. Synthesis of (*E*)-*N*-(4-(2-(9*H*-carbazol-9-yl)vinyl)-phenyl)acetamide (11). The title compound was prepared in a similar manner as described above for **5** using silane (**3**) and 4-acetamidoiodobenzene (23.5 mg, 0.09 mmol), and was purified via column chromatography (TLC, R_f=0.10, hexane/EtOAc=3:1) to provide 26.9 mg (91% yield) of white crystals, mp 155–159 °C (dec). IR (KBr) 967.5 (trans –C=C–); ^{1}H NMR ($CDCl_3$, δ (ppm)): 2.21 (s, 3H, $-COCH_3$), 7.02 (d, 1H, J_{H-H}=14.5 Hz, >N–C*H*=), 7.20–8.11 (m, 13H, H in carbazole, phenyl ring and =C*H*–Ph); ^{13}C NMR ($CDCl_3$, δ (ppm)): 110.5, 119.3, 120.1, 120.2, 120.6, 121.5, 122.6, 123.9, 125.7, 126.2, 126.3, 137.8, 139.4, 168.0. EIMS *m/z* 326 (M^+, 1), 284 (1), 261 (60), 219 (100), 191 (3), 167 (3), 133 (3), 128 (2), 105 (2), 92 (41), 75 (2), 65 (22). HRMS calcd for $C_{22}H_{18}N_2O$ (EI): 326.14191, found: 326.14068.

4.6.8. Synthesis of (*E*)-9-(4-methoxystyryl)-9*H*-carbazole (12). The title compound was prepared in a similar manner as described above for **5** using siloxane (**3**) and 1-methoxy-4-idoiodobenzene (21.5 mg, 0.09 mmol), and was purified via column chromatography (TLC, R_f=0.33, hexane/EtOAc=30:1) to provide 17.8 mg (66% yield) of white crystals, mp 116–120 °C (dec). IR (KBr) 944.3 (trans –C=C–); ^{1}H NMR ($CDCl_3$, δ (ppm)): 3.86 (s, 3H, $-OCH_3$), 7.01 (d, 1H, J_{H-H}=14.3 Hz, >N–C*H*=), 6.94–8.11 (m, 12H, H in carbazole and Ph), 7.56 (d, 1H, J_{H-H}=14.5 Hz, Ph–C*H*=); ^{13}C NMR ($CDCl_3$, δ (ppm)): 55.4, 110.4, 114.3, 120.3, 120.5, 121.5, 123.9, 126.2, 127.0, 128.7, 139.6, 159.1. EIMS *m/z* 299 (M^+, 8), 284 (3), 254 (2), 234 (3), 195 (3), 167 (100), 139 (12), 113 (4), 83 (7), 63 (7). HRMS calcd for $C_{21}H_{17}NO$ (EI): 299.13101, found: 299.13366.

4.6.9. Synthesis of 1,4-bis[(*E*)-2-(9*H*-carbazol-9-yl)vinyl]-benzene (13). [$Pd_2(dba)_3$] (1.4 mg, 0.0015 mmol), THF (0.2 mL), (*E*)-9-[2-(triethoxysilyl)ethenyl]-9*H*-carbazole (**3**) (35.6 mg, 0.1 mmol), tetrabutylammoniumfluoride (32.0 mg, 0.12 mmol), and 1,4-diiodobenzene (13.0 mg, 0.04 mmol) were placed in 1.5 mL glass ampoule. The mixture was heated at 30 °C for 24 h under an argon atmosphere. The degree of conversion was calculated by GC and GC–MS analyses. The final product was separated from reaction mixture using column with silica (TLC, R_f=0.18, hexane/EtOAc=30:1) to afford 34.0 mg (92% yield) of **13** as yellow crystals, mp 271–273 °C (dec). IR (KBr) 937.6 (trans –C=C–); ^{1}H NMR (CD_3COCD_3, δ (ppm)): 7.33 (t, J_{H-H}=7.5 Hz, 4H, 3,6,3′,6′-H in carbazole), 7.54 (t, J_{H-H}=7.8 Hz, 4H, 2,7,2′,7′-H in carbazole), 7.77 (s, 4H, Ph), 7.98 (d, J_{H-H}=8.3 Hz, 4H, 1,8,1′,8′-H in carbazole), 7.26 (d, J_{H-H}=14.6 Hz, 2H, N–CH=), 8.13 (d, J_{H-H}=14.6 Hz, 2H, Ph–CH=), 8.20 (d, J_{H-H}=7.7 Hz, 4H, 4,5,4′,5′-H in carbazole); ^{13}C NMR (CD_3COCD_3, δ (ppm)): 111.92, 119.56, 121.08, 121.73, 124.08, 124.92, 127.21, 127.30. EIMS *m/z* 460 (M^+, 100), 293 (6), 292 (7), 267 (2), 230 (13), 195 (1), 167 (9), 140 (2), 127 (1), 115 (1), 77 (1). HRMS calcd for $C_{34}H_{24}N_2$ (EI): 460.19394, found: 460.19121.

4.6.10. Synthesis of 1,4-bis[(*E*)-2-(9*H*-carbazol-9-yl) vinyl]benzene (13) via 1,3-bis[((*E*)-2-(9*H*-carbazol-9-yl)-vinyl)]-1,1,3,3-tetramethyldisiloxane (4). [$Pd_2(dba)_3$] (1.37 mg, 0.0015 mmol), THF (0.2 mL), 1,3-bis[((*E*)-2-(9*H*-carbazol-9-yl)vinyl)]-1,1,3,3-tetramethyldisiloxane (**4**) (25.8 mg, 0.05 mmol), tetrabutylammoniumfluoride (32.0 mg, 0.12 mmol), and 1,4-diiodobenzene (13.0 mg, 0.04 mmol) were placed in 1.5 mL glass ampoule. The mixture was heated at 30 °C for 24 h under an argon atmosphere. The degree of conversion was calculated by GC and GC–MS analyses. The final product was separated from reaction mixture using column with silica (TLC, R_f=0.18, hexane/EtOAc=30:1) to afford 17.2 mg (93.5% yield) of **13** as yellow crystals. The spectral data match with those reported above.

4.6.11. Synthesis of 1,4-bis[(*E*)-2-(9*H*-carbazol-9-yl) vinyl]benzene (13) via tandem reaction with (3). In a typical tandem reaction (*E*)-9-[2-(triethoxysilyl)ethenyl]-9*H*-carbazole (**3**) is not isolated after silylative-coupling reaction (see procedure above for **3**). The course of the reaction was followed by gas chromatography. After 20 h the yield of product has been checked by GC and suitable amount of (*E*)-9-[2-(triethoxysilyl)ethenyl]-9*H*-carbazole (**3**) (0.1 mmol) solution was transferred under argon into 1.5 mL glass ampoule. Then, the solvent was gently evaporated under vacuum pump and the [$Pd_2(dba)_3$] (2.74 mg, 0.003 mmol), THF (0.2 mL), tetrabutylammoniumfluoride (32.0 mg, 0.12 mmol), and 1,4-diiodobenzene (13.0 mg, 0.04 mmol) were placed in this glass ampoule. Next the mixture was heated at 30 °C for 10 h under an argon atmosphere. The final product was separated from reaction mixture using column with silica (TLC, R_f=0.18, hexane/EtOAc=30:1), to afford 16.6 mg (90% yield) of **13** as yellow crystals. The spectral data match with those reported above.

4.7. X-ray crystal structure analysis

For all compounds, the X-ray diffraction data were measured at room temperature, using graphite-monochromatized Mo K_α radiation (λ=0.71073 Å), by the ω-scan technique on a KUMA-KM4CCD diffractometer equipped with CCD camera.[13] The data were corrected for Lorentz-polarization effects.[14] Accurate unit-cell parameters were determined by a least-squares fit of 3657 for **4**, 3917 for **12**, and 3657 for **13** reflections chosen from the whole data sets. The structures were solved with SHELXS-97[15] and refined with the full-matrix least-squares procedure on F^2 by SHELXL-97.[16] Scattering factors incorporated in SHELXL-93 were used. The function $\sum w(|F_o|^2-|F_c|^2)^2$ was minimized with $w^{-1}=[\sigma^2(F_o)^2+(A\times P)^2]$, where $P=[\max(F_o^2, 0)+2F_c^2]/3$ and A=0.04 for **4**, 0.045 for **12**, and 0.04 for **13**. No empirical extinction corrections were applied for **4** and **13**, while for **12** the empirical extinction factor x was used to modify the structural factors according to the formula $F_c'=kF_c(1+0.001\times F_c^2\lambda^3/\sin(2\theta)]^{-1/4}$,[16] converged at 0.0062(10). All non-hydrogen atoms were refined anisotropically. In **12** the positional and isotropical displacement parameters of hydrogen atoms were refined, in **4** and **13** the hydrogen atoms were put in the idealized positions and refined as 'riding model'; in both these structures U_{iso} values of hydrogen atoms were set at 1.2 times U_{eq} of appropriate carrier atom. In the structure of **4** one of the C=C groups is disordered, and two alternative positions for this group were found with site occupation factors of 0.51(2) and 0.49(2). The disordered carbon atoms were successfully refined with anisotropical displacement parameters. The molecules of **13** are symmetrical, the middle point of the central phenyl ring lies at the center of symmetry. In the trigonal structure of this compound, **13**, there are voids along three-fold axis that might be filled with disordered linear molecules; there is some residual electron density (of ca. 0.4 eÅ^{-3}) in these voids.

4.7.1. Compound 4. $C_{32}H_{32}N_2OSi_2$, M_r=516.78, orthorhombic, *Pbca*, a=13.0736(10) Å, b=20.4927(16) Å, c=21.2292(17) Å, V=5687.6(8) Å^3, Z=8, d_x=1.21 g cm^{-3}, μ(Mo Kα)=0.152 mm^{-1}, F(000)=2192, 29327 reflections measured up to θ_{max}=25°, 5001 independent (R_{int}=0.112), 333 parameters, final $R(F)[I>2\sigma(I)]$=0.035, $wR(F^2)$=0.068, S=0.62, $\Delta\rho_{max}$=0.18 eÅ^{-3}, $\Delta\rho_{min}$=−0.16 eÅ^{-3}.

4.7.2. Compound 12. $C_{21}H_{17}NO$, M_r=299.36, monoclinic, $P2_1/c$, a=9.3544(12) Å, b=10.6160(13) Å, c=16.790(2) Å, β=100.619(11)°, V=1638.8(4) Å^3, Z=4, d_x=1.21 g cm^{-3}, μ(Mo Kα)=0.074 mm^{-1}, F(000)=2178, 9960 reflections measured to θ_{max}=25°, 2868 independent (R_{int}=0.022), 275 parameters, final $R(F)[I>2\sigma(I)]$=0.035, $wR(F^2)$=0.083, S=1.01, $\Delta\rho_{max}$=0.12 eÅ^{-3}, $\Delta\rho_{min}$=−0.12 eÅ^{-3}.

4.7.3. Compound 13. $C_{34}H_{24}N_2$, M_r=460.55, trigonal, *R*-3, a=b=33.649(2) Å, c=5.6110(5) Å, Z=9, d_x=1.25 g cm^{-3}, μ(Mo Kα)=0.073 mm^{-1}, F(000)=632, 14629 reflections measured to θ_{max}=25°, 2158 independent (R_{int}=0.037), 163 parameters, final $R(F)[I>2\sigma(I)]$=0.049, $wR(F^2)$=0.150, S=0.99, $\Delta\rho_{max}$=0.49 eÅ^{-3}, $\Delta\rho_{min}$=−0.16 eÅ^{-3}.

5. Supplementary data

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, Nos. CCDC-615171 (**4**), CCDC-615172 (**12**), and CCDC-615173 (**13**). Copies of the data may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK. Fax: +44 1223 336 033, e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk.

Acknowledgements

This work was supported by Grant No. PBZ-KBN 118/T09/2004/17 from the Ministry of Science and Higher Education (Poland).

References and notes

1. (a) Ito, C.; Nakagawa, M.; Wu, T.-S.; Furukawa, H. *Chem. Pharm. Bull.* **1991**, *39*, 1668; (b) Ito, C.; Thoyama, Y.; Omura, M.; Kajiura, I.; Furukawa, H. *Chem. Pharm. Bull.* **1993**, *41*, 2096; (c) Ramsewak, R. S.; Nair, M. G.; Strasburg, G. M.; DeWitt, D. L.; Nitiss, J. L. *J. Agric. Food Chem.* **1999**, *47*, 444; (d) Tachibana, Y.; Kikuzaki, H.; Lajis, N. H.; Nakatani, N. *J. Agric. Food Chem.* **2001**, *49*, 5589; (e) Ito, C.; Itoigawa, M.; Nakao, K.; Murata, T.; Tsuboi, M.; Kaneda, N.; Furukawa, H. *Phytomedicine* **2006**, *13*, 359; (f) Nakahara, K.; Trakoontivakorn, G.; Alzoreky, N. S.; Ono, H.; Onishi-Kameyama, M.; Yoshida, M. *J. Agric. Food Chem.* **2002**, *50*, 808.
2. (a) Kan, W. S. *Manual of Medicinal Plants in Taiwan*; National Research Institute of Chinese Medicine: Taiwan, 1972; Vol. 2, pp 377–378; (b) Itoigawa, M.; Kashiwada, Y.; Ito, C.; Furukawa, H.; Tachibana, Y.; Bastow, K. F.; Lee, K. H. *J. Nat. Prod.* **2000**, *63*, 893.
3. (a) Friend, R. H.; Gymer, R. W.; Holmes, A. B.; Burroughes, J. H.; Mark, R. N.; Taliani, C.; Bradley, D. D. C.; Dos Santos, D. A.; Bredas, J. L.; Logdlund, M.; Salaneck, W. R. *Nature* **1999**, *397*, 121 and literature cited therein; (b) Diaz-Garcia, M. A.; Wright, D.; Casperson, J. D.; Smith, B.; Glazer, E.; Moerner, W. E.; Sukhomlinova, L. I.; Twieg, R. J. *Chem. Mater.* **1999**, *11*, 1784; (c) Paik, K. L.; Baek, N. S.; Kim, H. K.; Lee, J.-H.; Lee, Y. *Macromolecules* **2002**, *35*, 6782; (d) Lu, J.; Tao, Y.; D'iorio, M.; Li, Y.; Ding, J.; Day, M. *Macromolecules* **2004**, *37*, 2442; (e) Zhang, X.; Chen, Z.; Yang, C.; Li, Z.; Zhang, K.; Yao, H.; Qin, J.; Chen, J.; Cao, Y. *Chem. Phys. Lett.* **2006**, *422*, 386.
4. (a) Shi, J.; Huang, M.; Xin, Y.; Chen, Z.; Gong, Q.; Xu, S.; Cao, S. *Mater. Lett.* **2003**, *59*, 2199; (b) Pan, J.-H.; Chiu, H.-L.; Wang, B.-C. *J. Mol. Struct.: THEOCHEM* **2005**, *725*, 89; (c) Hyun, A.-R.; Lee, J.-H.; Kang, I.-N.; Park, J.-W. *Thin Solid Films* **2006**, *209*, 127.
5. (a) Reppe, W. *Liebigs Ann. Chem.* **1956**, *601*, 81; (b) Tzalis, D.; Koradin, C.; Knochel, P. *Tetrahedron Lett.* **1999**, *40*, 6193; (c) Shostakovsky, M. F.; Skvortsova, G. G.; Domnina, E. S. *Russ. Chem. Rev.* **1969**, *38*, 892; (d) Brustolin, F.; Castelvetro, V.; Ciardelli, F.; Ruggeri, G.; Colligiani, A. *J. Polym. Sci., Part A: Polym. Chem.* **2001**, *39*, 253; (e) Lebedev, A. Y.; Izmer, V. V.; Kazyul'kin, D. N.; Beletskaya, I. P.; Voskoboynikov, A. Z. *Org. Lett.* **2002**, *4*, 623; (f) Filimonov, W. D. *Chem. Heterocycl. Compd. (Russ.)* **1981**, *2*, 207.
6. (a) Marciniec, B.; Pietraszuk, C. *Curr. Org. Chem.* **2003**, *7*, 691; (b) Marciniec, B.; Pietraszuk, C. *Handbook of Metathesis*; Grubbs, R., Ed.; Wiley-VCH: Weinheim, 2003; Chapter 2.13, p 455; (c) Marciniec, B.; Pietraszuk, C. *Top. Organomet. Chem.* **2004**, *11*, 197; (d) Marciniec, B.; Zaidlewicz, M.; Pietraszuk, C.; Kownacki, I. *Comprehensive Organic Functional Group Transformations II*; Katritzky, A. R., Taylor, R. J. K., Eds.; Elsevier Science: Amsterdam, 2005; Chapter 2.18; (e) Marciniec, B. *Coord. Chem. Rev.* **2005**, *249*, 2374.
7. Pietraszuk, C.; Marciniec, B.; Fischer, H. *Organometallics* **2000**, *19*, 913.
8. (a) Marciniec, B.; Majchrzak, M.; Prukała, W.; Kubicki, M.; Chadyniak, D. *J. Org. Chem.* **2005**, *70*, 8550; (b) Prukała, W.; Majchrzak, M.; Pietraszuk, C.; Marciniec, B. *J. Mol. Catal. A: Chem.* **2006**, *254*, 58.
9. (a) Hiyama, T.; Hatanaka, Y. *Pure Appl. Chem.* **1994**, *66*, 1471; (b) DeShong, P.; Handy, C. J.; Mowery, M. E. *Pure Appl. Chem.* **2000**, *72*, 1655; (c) Denmark, S. E.; Sweis, R. F. *Chem. Pharm.*

Bull. **2002**, *50*, 1531; (d) Hiyama, T.; Shirakawa, E. *Top. Curr. Chem.* **2002**, *219*, 61; (e) Denmark, S. E.; Sweis, R. F. *Acc. Chem. Res.* **2002**, *35*, 835; (f) Itami, Y.; Marciniec, B.; Kubicki, M. *Organometallics* **2003**, *22*, 3717; (g) Li, J. H.; Deng, C. L.; Liu, W. J.; Xie, Y. X. *Synthesis* **2005**, *18*, 3039; (h) Pierrat, P.; Gros, P.; Fort, Y. *Org. Lett.* **2005**, *7*, 697; (i) Denmark, S. E.; Baird, J. D. *Chem.—Eur. J.* **2006**, *12*, 4954.

10. (a) Denmark, S. E.; Wang, Z. *Org. Lett.* **2001**, *3*, 1073; (b) Denmark, S. E.; Pan, W. *Org. Lett.* **2001**, *3*, 61; (c) Denmark, S. E.; Pan, W. *Org. Lett.* **2003**, *5*, 1119; (d) Denmark, S. E.; Kobayashi, T. *J. Org. Chem.* **2003**, *68*, 5153; (e) Itami, K.; Nokami, T.; Ishimura, Y.; Mitsudo, K.; Kamei, T.; Yoshida, J.-i. *J. Am. Chem. Soc.* **2001**, *123*, 11577; (f) Itami, K.; Nokami, T.; Yoshida, J.-i. *J. Am. Chem. Soc.* **2001**, *123*, 5600; (g) Denmark, S. E.; Yang, S.-M. *Org. Lett.* **2001**, *3*, 1749; (h) Denmark, S. E.; Yang, S.-M. *J. Am. Chem. Soc.* **2002**, *124*, 2102; (i) Denmark, S. E.; Yang, S.-M. *J. Am. Chem. Soc.* **2002**, *124*, 15196; (j) Trost, B. M.; Machacek, M. R.; Ball, Z. T. *Org. Lett.* **2003**, *5*, 1895; (k) Trost, B. M.; Machacek, M. R.; Faulk, B. D. *J. Am. Chem. Soc.* **2006**, *128*, 6745.
11. (a) Denmark, S. E.; Choi, J. Y. *J. Am. Chem. Soc.* **1999**, *121*, 5821; (b) Seganish, W. M.; DeShong, P. *Org. Lett.* **2004**, *6*, 4379; (c) Denmark, S. E.; Butler, C. R. *Org. Lett.* **2006**, *8*, 63.
12. (a) *Vogel's Textbook of Practical Organic Chemistry*, 5th ed.; Longman Group UK Limited: Harlow, 1989; (b) Yi, C. S.; Lee, D. W.; Chen, Y. *Organometallics* **1999**, *18*, 2043; (c) Ukai, T.; Kawazura, H.; Ishii, Y. *J. Organomet. Chem.* **1974**, *65*, 253.
13. CrysAlisCCD. *User Guide v.171*; Oxford Diffraction Poland Sp.: Wrocław, Poland, 2003.
14. CrysAlisRed. *CCD Data Reduction GUI v.171*; Oxford Diffraction Poland Sp.: Wrocław, Poland, 2003.
15. Sheldrick, G. M. *Acta Crystallogr., Sect. A* **1990**, *46*, 467.
16. Sheldrick, G. M. *SHELXL-97, Program for the Refinement of Crystal Structures*; University of Gőttingen: Gőttingen, Germany, 1997.