

Novel Generation and Cycloaddition of *N*-Silylated Azomethine Ylides from α -Silylimidates and Trifluorosilane

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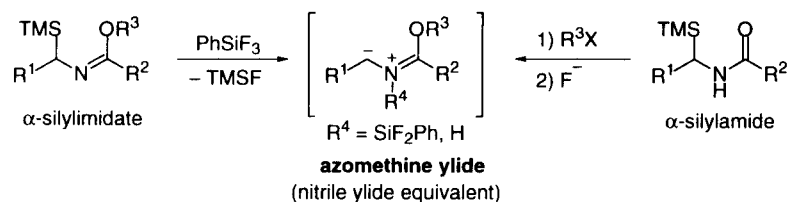
Abstract: The Generation of *N*-silylated azomethine ylides was achieved by the reaction of α -silylimidates and trifluorophenylsilane. The generated azomethine ylides can be regarded as synthetic equivalents of nitrile ylides since they have an alkoxy group which may serve as a leaving group. Cycloaddition with acetylenic or olefinic dipolarophiles proceeded smoothly to give pyrrole or pyrroline derivatives in good to excellent yields. For example, α -silylimidate **1** was treated with 1.2 equiv of trifluorophenylsilane in the presence of 1 equiv of dimethyl acetylenedicarboxylate to give pyrrole **2** in 97% yield. Furthermore, when starting with a secondary α -silylamide, the one-pot synthesis of *N*-unsubstituted azomethine ylides could be achieved by the successive treatment with alkylation and desilylation agents. © 1999 Elsevier Science Ltd. All rights reserved.

INTRODUCTION

1,3-Dipolar cycloaddition has been widely used for the synthesis of heterocyclic compounds because of its utility for creating two sets of bonds in a single operation and because stereoselectivity is easily predictable.¹ Among a number of 1,3-dipoles, the azomethine ylide² is one of the most important dipoles for the synthesis of various five-membered nitrogen heterocycles. A number of workers have developed practical and useful methods for the generation of azomethine ylides. One involves the ring opening of aziridines,³ which works well when the aziridine has an electron-withdrawing substituent on the carbon atom. Another important method involves generation from α -silylimine derivatives.² This enables the generation of less-stabilized azomethine ylides, which lack α -substituents to stabilize the negatively charged carbon, by taking advantage of the fact that carbon-silicon bonds are easily cleaved by nucleophiles. Thus, desilylation of α -silyliminium salts,⁴ treatment of α -silylimine derivatives with an acyl halide,⁵ trimethylsilyl triflate⁶ or trifluoroacetic acid,⁷ and the water-induced desilylation of α -silylimine derivatives⁸ have been developed. Recently, the generation of *N*-unsubstituted azomethine ylides by protodesilylation of (2-azaallyl)silanes has been reported by Pearson.⁹ On the other hand, in earlier papers, we reported that azomethine ylides can be generated from *N*-(silylmethyl)imines¹⁰ or *N*-(silylmethyl)amides¹¹ via an intramolecular silatropic shift which is based on the strong affinity between silicon and oxygen or nitrogen. It is noteworthy that this method does not require any additives and can be performed under completely neutral conditions.

The present article describes the novel generation of *N*-silylated azomethine ylides carrying an alkoxy group by simply treating α -silylimidates with trifluorophenylsilane. The thus generated azomethine ylides

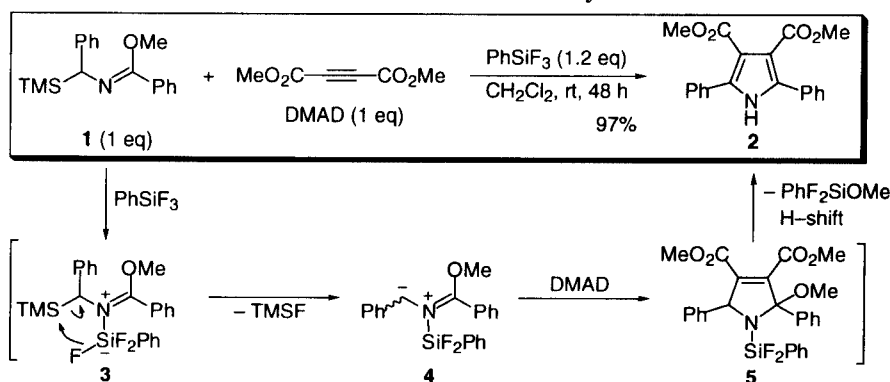
function as synthetic equivalents of *N*-unsubstituted azomethine ylides or nitrile ylides as the result of the elimination of alkoxy moiety after cycloadditions. A convenient one-pot synthesis for generating *N*-unsubstituted azomethine ylides from α -silylimide is also reported.



RESULTS AND DISCUSSION

A solution of methyl *N*-[α -(trimethylsilyl)benzyl]benzimidate (**1**) and dimethyl acetylenedicarboxylate (DMAD, 1 equiv) in dichloromethane was treated with trifluorophenylsilane¹² (1.2 equiv) at room temperature for 48 h to give 3,4-dimethoxycarbonyl-2,5-diphenylpyrrole (**2**) in 97% yield (Scheme 1). The product was isolated by silica gel chromatography and the structure was determined by spectral analysis. A proposed mechanism for the generation of an azomethine ylide intermediate and the subsequent cycloaddition is also illustrated in Scheme 1. Quaternization of the nitrogen of the α -silylimide **1** with trifluorophenylsilane gives intermediate **3**, in which the nitrogen atom is positively charged and the silicon atom is negatively charged. It seems likely that an intramolecular attack of a fluoride ion leaving from the anionic silicon to another silicon atom gives the *N*-silylated azomethine ylide **4**. The generated azomethine ylide undergoes 1,3-dipolar cycloaddition with DMAD to give pyrroline **5** which is smoothly converted to pyrrole **2** by the elimination of a silylether, followed by aromatization.

Scheme 1. Generation of Azomethine Imine from α -Silylimide with Fluorosilane



The effect of additives which are capable of acting as both quaternization and desilylation agents were also examined (Table 1). When difluoromethylphenylsilane was used, the reaction was rather sluggish and **2** was obtained in 30% yield after 192 h, with 68% of starting **1** remaining unchanged (entry 1). On the other hand, with trifluorophenylsilane, **2** was obtained in 83% after 20 h or 97% after 48 h (entries 2, 3). Trimethylsilyl trifluoromethanesulfonate (TMSOTf), which is known to be a strong silylation agent, did not

give **2**, indicating that triflate anion (OTf^-) could not act as a desilylation agent (entry 4). In this case, the addition of a desilylation agent such as cesium fluoride was effective to some extent, although two-step operations were required and the yield was moderate (entry 5). Ultimately, trifluorophenylsilane was found to be the most effective reagent.

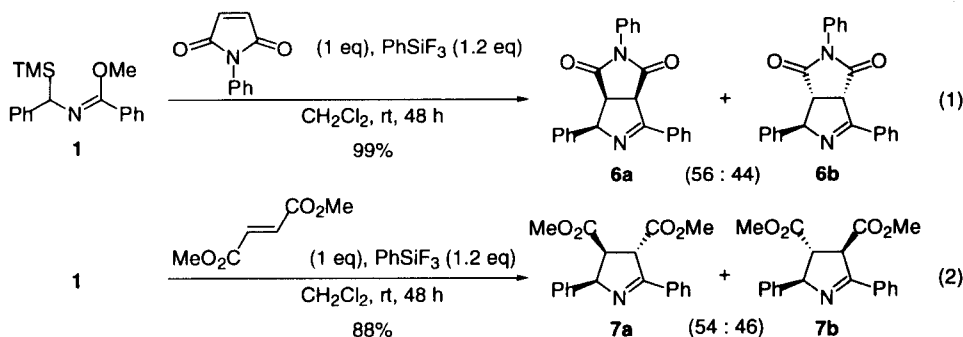
Table 1. Effect of Additives

	1	+	DMAD (1 eq)	$\xrightarrow[\text{CH}_2\text{Cl}_2, \text{rt}]{\text{additive}}$	2
entry	additive (eq)			time (h)	yield ^a (%)
1	PhMeSiF ₂ (1.2)			192	30 ^b
2	PhSiF ₃ (1.2)			20	83
3	PhSiF ₃ (1.2)			48	97
4	TMSOTf ^c (1.2)			20	0
5	TMSOTf (1), CsF (1)			20	41

^a Isolated yield after silica gel chromatography. ^b **1** was recovered in 68% yield.

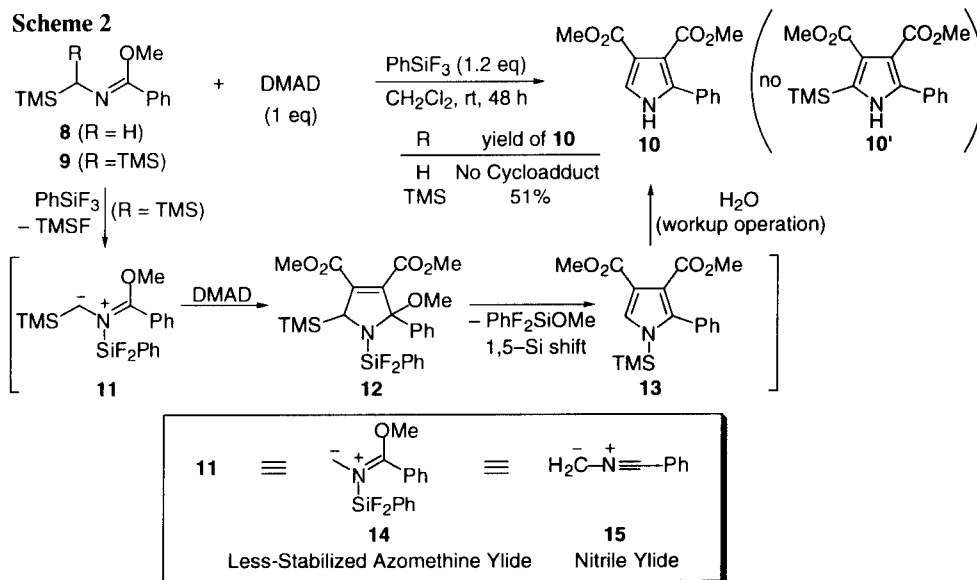
^c TMSOTf = $\text{Me}_3\text{SiOSO}_2\text{CF}_3$

The reactions of **1** with olefinic dipolarophiles and trifluorophenylsilane also proceeded smoothly to afford the corresponding cycloadducts. With *N*-phenylmaleimide as a dipolarophile, a mixture of bicyclic compounds (**6a** and **6b**) was obtained in nearly quantitative yield (eq 1). With dimethyl fumarate, a mixture of **7a** and **7b** was obtained in good yield (eq 2). It is noteworthy that the above two cycloadditions proceeded with complete stereospecificity with the olefins used.¹³ This fact is consistent with the stereospecificity which is observed for general 1,3-dipoles and olefins.¹

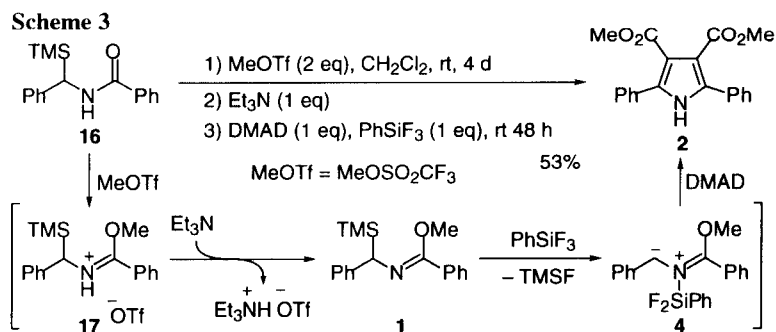


Also of interest was the possibility of generating a less-stabilized azomethine ylide which bears no stabilizing group on one of the α -carbons. The reaction of methyl *N*-(trimethylsilylmethyl)benzimidate (**8**) was initially examined, but the cycloadduct could not be obtained (Scheme 2). This problem was solved by introducing another trimethylsilyl group to **8**. Thus, methyl *N*-[bis(trimethylsilyl)methyl]benzimidate (**9**) was subsequently treated with DMAD and trifluorophenylsilane to give 3,4-dimethoxycarbonyl-2-phenylpyrrole (**10**) in moderate yield. It is interesting that the predicted 5-trimethylsilyl-substituted pyrrole **10'** was not

obtained at all. This may be explained as follows. The elimination of a silylether from the initially formed cycloadduct **12** followed by 1,5-silicon shift gave the *N*-silylated pyrrole **13**. The *N*-unsubstituted pyrrole **10** was probably obtained by hydrolysis during the work up operation. From a synthetic point of view, the azomethine ylide **11** can be taken as equivalent to the less-stabilized azomethine ylide **14** and, at the same time, a less-stabilized nitrile ylide **15** (Scheme 2).

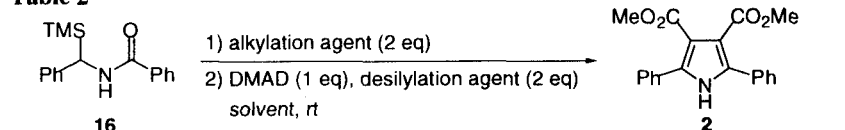


α -Silylimidate **1** can be easily prepared by *O*-alkylation of α -silylamide **16** followed by neutralization. Therefore, a one-pot synthesis of pyrrole **2** from **16** was examined (Scheme 3). The alkylation of **16** with methyl trifluoromethanesulfonate (MeOTf) gave an iminium salt **17**. This salt was subsequently treated with triethylamine, DMAD, and trifluorophenylsilane *in situ* to give **2** in moderate yield.



An alternative route to an azomethine ylide involved the direct desilylation of iminium salt **17**. Thus, **2** was also obtained by the sequential treatment of **16** with alkylation and desilylation agents in the presence of DMAD (Table 2). Regarding the choice of solvent, it was found that dichloromethane was optimal (entries 3–

5). The use of acetonitrile (entry 1) or dimethoxyethane (entry 2) as a more polar solvent or toluene (entry 6) as a less polar solvent resulted in moderate yields. Using dichloromethane as the solvent, an optimization of the time required for the alkylation reaction was performed. When alkylation was carried out for 10 h or 48 h, a small amount of unreacted **16** was detected (entries 3, 4). For 96 h, on the other hand, **16** was completely consumed and **2** was obtained in 87% yield (entry 5). The use of tetrabutylammonium fluoride (entry 7) as a desilylation agent or Meerwein's reagent (entry 8) as an alkylation agent also gave **2** in moderate yield.

Table 2


entry	alkylation		desilylation		solvent	yield ^a (%)	recovery of 16 ^a (%)
	reagent	time (h)	reagent	time (h)			
1	MeOTf	24	CsF	24	CH ₃ CN	32	0
2	MeOTf	72	CsF	15	DME	52	36
3	MeOTf	10	CsF	22	CH ₂ Cl ₂	62	17
4	MeOTf	48	CsF	15	CH ₂ Cl ₂	74	11
5	MeOTf	96	CsF	15	CH ₂ Cl ₂	87	0
6	MeOTf	96	CsF	15	toluene	41	30
7	MeOTf	96	Bu ₄ NF ^b	15	CH ₂ Cl ₂	51	0
8	Et ₃ O ⁺ BF ₄ ⁻	1	CsF	15	CH ₂ Cl ₂	48	13

^a Isolated yield after silica gel chromatography. ^b 1 equiv of Bu₄NF was used.

CONCLUSION

In summary, we demonstrated novel methods for the generation of azomethine ylides under relatively mild reaction conditions. Treatment of α -silylimidates with trifluorophenylsilane gave *N*-silylated azomethine ylides which carry a leaving group (OMe). The function of trifluorophenylsilane is very interesting, since it acts as both a quaternization and a desilylation agent. Cycloaddition of the thus generated azomethine ylides with acetylenic or olefinic dipolarophiles gave *N*-unsubstituted pyrroles or pyrrolines, showing that these azomethine ylides are the synthetic equivalents of *N*-unsubstituted azomethine ylides or nitrile ylides. Compared to the conventional methods which require both quaternization and desilylation steps, this method has great advantages in terms of operation and the use of an inexpensive reagent.¹² From a secondary α -silylamide as a starting material, successive treatment with alkylation and desilylation agents in the same solvent gave an *N*-unsubstituted azomethine ylide, which is, in practice, useful for the preparation of *N*-unsubstituted pyrroles. Further extension of the present methods to the generation of other 1,3-dipoles such as azomethine imines is now under way.

EXPERIMENTAL

General. Melting points were determined on a Yanaco melting point apparatus and are uncorrected. Infrared spectra were obtained on a HITACHI 270-30 spectrometer or JASCO FT/IR-410 spectrometer. ¹H and ¹³C NMR spectra were recorded with a JEOL FT-NMR JNM EX 270 spectrometer (¹H NMR, 270

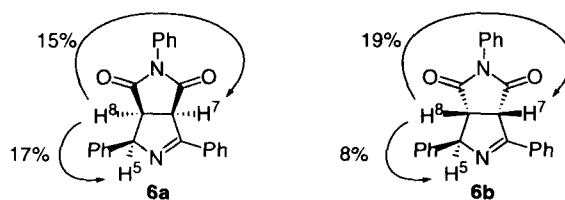
MHz; ^{13}C NMR, 68 MHz). Chemical shifts are reported in parts per million (δ), relative to internal TMS at 0.00 for ^1H NMR and chloroform at 77.0 for ^{13}C NMR. GC-MS analyses were measured on a Shimadzu GCMS QP-5000 mass spectrometer. High-resolution mass spectra (HRMS) were obtained on a JEOL JMS-DX303HF spectrometer. Elemental analyses were performed at the Analytical Center, Faculty of Engineering, Osaka University. The products were purified by chromatography on silica gel (Merck Kieselgel 60, 63–200 μm) and, if necessary, further purified by a Recycling Preparative HPLC (Japan Analytical Industry Co. Ltd., LC-908) equipped with a GPC columns (JAIGEL-1H, 2H). Analytical thin layer chromatography was performed using EM reagent 0.25 mm silica gel 60-F plates. Visualization was accomplished with UV light or treatment with an ethanol solution of phosphomolybdic acid (5%) followed by heating. All reactions were carried out under a nitrogen atmosphere. Organic solvents were dried and distilled prior to use.

Methyl *N*-[α -(trimethylsilyl)benzyl]benzimidate (1). To a solution of *N*-[α -(trimethylsilyl)benzyl]benzamide (283 mg, 1.00 mmol) in dichloromethane (10 mL) was added methyl trifluoromethanesulfonate (226 μL , 2.00 mmol) and the solution was stirred at room temperature for 96 h. The reaction mixture was washed with 1 N NaOH soln. (10 mL \times 1), dried (MgSO_4), filtered and evaporated to give **1** (309 mg, 100%) as a pale yellow oil: IR (neat) 2952, 1654 (C=N) cm^{-1} ; ^1H NMR (CDCl_3 , 270 MHz) δ -0.11 (s, 9 H, TMS), 3.90 (s, 3 H, OMe), 4.25 (s, 1 H, ArCHN), 7.11–7.16 (m, 1 H, ArH), 7.22–7.28 (m, 6 H, ArH), 7.35–7.40 (m, 3 H, ArH); ^{13}C NMR (CDCl_3 , 68 MHz) δ -3.7, 52.9, 57.9, 124.8, 125.9, 127.9, 128.0, 128.3, 129.2, 132.2, 143.7, 158.2; MS m/z 297 (M^+ , 1), 224 (M^+ - TMS, 9), 193 (M^+ - TMSOMe, 100); HRMS calcd for $\text{C}_{18}\text{H}_{23}\text{NOSi}$ 297.1549, found 297.1541.

Methyl *N*-[bis(trimethylsilyl)methyl]benzimidate (9). To a solution of *N*-[bis(trimethylsilyl)methyl]benzamide (200 mg, 0.715 mmol) in dichloromethane (7 mL) was added methyl trifluoromethanesulfonate (162 μL , 1.43 mmol) and the solution was stirred at room temperature for 160 h. The reaction mixture was washed with 1 N NaOH soln. (7 mL \times 1), dried (MgSO_4), filtered and evaporated to give **9** (210 mg, 100%) as a colorless oil: IR (neat) 2956, 1652 (C=N) cm^{-1} ; ^1H NMR (CDCl_3 , 270 MHz) δ -0.06 (s, 18 H, TMS), 2.69 (s, 1 H, SiCHSi), 3.68 (s, 3 H, OMe), 7.19–7.23 (m, 2 H, ArH), 7.31–7.33 (m, 3 H, ArH); MS m/z 293 (M^+ , 7), 189 (M^+ - TMSOMe, 56); HRMS calcd for $\text{C}_{15}\text{H}_{27}\text{NOSi}_2$ 293.1631, found 293.1628.

General Procedure for the Generation and Cycloaddition of Azomethine Ylides from α -Silylimidates and Fluorosilanes. A typical procedure is shown below: To a solution of **1** (100 mg, 0.336 mmol) in dichloromethane (3.4 mL) were successively added dimethyl acetylenedicarboxylate (DMAD, 47.7 mg, 0.336 mmol) and trifluorophenylsilane (65.4 mg, 0.403 mmol) at room temperature and the mixture was stirred at the same temperature for 48 h. The mixture was washed with water (3.4 mL \times 1), dried (MgSO_4), and concentrated to give a colorless oil (191 mg). The crude oil was chromatographed on 5.7 g of silica gel (eluent : hexane / AcOEt = 9 / 1 then 4 / 1) to give 3,4-dimethoxycarbonyl-2,5-diphenylpyrrole (**2**, 109 mg, 97%) as colorless needles: mp 151–153 $^\circ\text{C}$; IR (KBr) 3272 (NH), 1713 (C=O), 1486, 1459, 1245, 1135, 765, 694 cm^{-1} ; ^1H NMR (CDCl_3 , 270 MHz) δ 3.77 (s, 6 H, OMe), 7.34–7.57 (m, 10 H, ArH), 8.62 (brs, 1 H, NH); ^{13}C NMR (CDCl_3 , 68 MHz) δ 51.8, 114.0, 128.0, 128.4, 130.7, 134.5, 165.7; MS m/z 335 (M^+ , 100), 304 (M^+ - OMe, 81); Anal. Calcd for $\text{C}_{20}\text{H}_{17}\text{NO}_4$: C, 71.63; H, 5.11; N, 4.18. Found: C, 71.55; H, 5.16; N, 4.24.

1,3,5-Triphenyl-2,6-dioxo-1,4-diazabicyclo[3.3.0]oct-3-ene (6). According to the general procedure, **1** (80 mg, 0.269 mmol) was reacted with *N*-phenylmaleimide (46.6 mg, 0.269 mmol) and trifluorophenylsilane (52.4 mg, 0.323 mmol) in dichloromethane (2.7 mL) at room temperature for 48 h. The resulting diastereomers were separated by silica gel chromatography (SiO₂ 7.0 g, eluent: hexane / AcOEt = 9 / 1 then 4 / 1) to give **6a** (54.0 mg, 55%) as a white solid and **6b** (43.0 mg, 44%) as a white solid. Data for **6a**: mp 253–256 °C; IR (KBr) 1710 (C=O) cm⁻¹; ¹H NMR (CDCl₃, 270 MHz) δ 4.15 (dd, *J* = 8.9, 10.2 Hz, 1 H, ArCHCH), 4.84 (d, *J* = 8.9 Hz, 1 H, ArC(=N)CH), 6.07 (d, *J* = 10.2 Hz, 1 H, ArCH), 6.70–6.73 (m, 2 H, ArH), 7.17–7.53 (m, 11 H, ArH), 8.28–8.31 (m, 2 H, ArH); ¹³C NMR (CDCl₃, 68 MHz) δ 49.5, 56.7, 77.6, 126.0, 127.6, 128.3, 128.4, 128.5, 128.6, 128.9, 129.7, 131.3, 131.8, 131.9, 137.0, 167.6, 171.9, 173.3; MS *m/z* 366 (M⁺, 100); HRMS calcd for C₂₄H₁₈N₂O₂ 366.1368, found 366.1374. Data for **6b**: mp 188–189 °C; IR (KBr) 1710 (C=O) cm⁻¹; ¹H NMR (CDCl₃, 270 MHz) δ 3.79 (dd, *J* = 3.6, 8.6 Hz, 1 H, ArCHCH), 4.89 (dd, *J* = 2.6, 8.6 Hz, 1 H, ArC(=N)CH), 5.86 (dd, *J* = 2.6, 3.6 Hz, 1 H, ArCH), 7.26–7.56 (m, 13 H, ArH), 8.29–8.33 (m, 2 H, ArH); ¹³C NMR (CDCl₃, 68 MHz) δ 53.5, 56.3, 78.4, 126.3, 126.4, 127.8, 128.3, 128.5, 128.8, 128.9, 129.1, 129.7, 131.4, 131.8, 142.0, 166.5, 171.6, 176.0; MS *m/z* 366 (M⁺, 100); HRMS calcd for C₂₄H₁₈N₂O₂ 366.1368, found 366.1386. The stereochemistry was assigned based on differential NOE experiments. Irradiation of H⁸ of **6a** resulted in an NOE enhancement of 17% at H⁵ and 15% at H⁷. Similarly, irradiation of H⁸ of **6b** resulted in an NOE enhancement of 8% at H⁵ and 19% at H⁷.



3,4-Dimethoxycarbonyl-2,5-diphenyl-1-pyrroline (7). According to the general procedure, **1** (100 mg, 0.336 mmol) was reacted with dimethyl fumarate (46.6 mg, 0.336 mmol) and trifluorophenylsilane (65.4 mg, 0.403 mmol) in dichloromethane (3.4 mL) at room temperature for 48 h. The product was isolated as a mixture of diastereomers (**7a** and **7b**, 99.9 mg, 88%) after silica gel chromatography (SiO₂ 5.3 g, eluent : hexane / AcOEt = 9 / 1). The structures were confirmed by a comparison of the spectral data with those of the previously reported compounds.¹¹ The ratio between **7a** and **7b** was determined by ¹H NMR.

3,4-Dimethoxycarbonyl-2-phenylpyrrole (10). According to the general procedure, methyl *N*-[bis(trimethylsilyl)methyl]benzimidate (**9**, 40 mg, 0.136 mmol) was reacted with DMAD (19.3 mg, 0.136 mmol) and trifluorophenylsilane (26.5 mg, 0.163 mmol) in dichloromethane (1.4 mL) at room temperature for 48 h. Purification by silica gel chromatography (SiO₂ 3.0 g, eluent : hexane / AcOEt = 9 / 1 then 4 / 1) gave **10** (18.1 mg, 51%) as a pale yellow crystalline solid: mp 109–111 °C; IR (KBr) 3284 (NH), 1678 (C=O) cm⁻¹; ¹H NMR (CDCl₃, 270 MHz) δ 3.79 (s, 3 H, OMe), 3.80 (s, 3 H, OMe), 7.26–7.43 (m, 5 H, ArH), 9.32 (br, 1 H, NH); ¹³C NMR (CDCl₃, 68 MHz) δ 51.5, 52.2, 113.8, 116.3, 124.0, 127.3, 128.4, 128.8, 130.7, 134.0, 164.2, 167.0; MS *m/z* 259 (M⁺, 60), 228 (M⁺ – OMe, 100); HRMS calcd for C₁₄H₁₃NO₄ 259.0844, found 259.0847; Anal. Calcd for C₁₄H₁₃NO₄: C, 64.86; H, 5.05; N, 5.40. Found: C, 64.60; H, 5.08; N, 5.41.

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12. Trifluorophenylsilane can be readily prepared from trichlorophenylsilane and antimony (III) fluoride which are commercially available inexpensive reagents, see: Damrauer, R.; Danahey, E. *Organometallics* **1986**, *5*, 1490.
13. As we reported in reference 11, in the reaction of dimethyl maleate and the azomethine ylide generated from α -silylamide **16** by 1,4-silatropic shift, epimerization at 3-position of the cycloadduct occurred since the hydrogen at 3-position is highly acidic. From this result, in this work, we did not perform the cycloaddition with dimethyl maleate to avoid a complication of the stereochemistry.