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Facile addition reactions of allylsilanes to quinolines and isoquinolines activated by chloroformate ester and a catalytic amount of triflate ion

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Abstract—Addition reactions of allylsilanes to quinolines acylated by chloroformate esters are promoted by a catalytic amount of triflate ion to give 2-allyl-1,2-dihydroquinoline derivatives in good yields. A variety of functional groups on quinoline ring are tolerated in the reaction. The similar reactions of allylsilanes with isoquinolines afford cyclized benzoisoquinuclidine derivatives in good yields, along with 1-allyl-1,2-dihydroisoquinoline derivatives, depending on the reaction conditions. In addition, 2-substituted allylic silanes can be utilized in the present addition reactions to afford the 2-substituted and 1-substituted 1,2-dihydro-quinolines and -isoquinolines, respectively.

Addition reactions of organometallic reagents with quaternary aza-aromatic ions acylated by chloroformates or acyl chlorides have been of great importance for synthesizing a variety of physiologically active nitrogen compounds, including alkaloids.[1] Rather reactive organometallics such as organolithium, Grignard, organocopper, and metal enolate reagents have been used in the most of the reactions. On the other hand, nucleophilic reactions of allylic metal reagents have been extensively studied to introduce allylic groups as versatile carbon functionality.[2] Meanwhile, we have reported that allylic tin reagents readily react with aza-aromatic ions acylated by chloroformates and acyl chlorides in a chemo- and/or regioselective manner, providing a simple and effective method for introducing allylic substituents into nitrogen heterocycles.[3] Although allylic silicon reagents have been widely utilized as useful carbon nucleophiles, it has been proven that allyltrimethylsilane is not sufficiently nucleophilic to react with pyridine acylated by methyl chloroformate.[3a] Considering that the organosilicon reagents are generally less toxic and more easily handled than organotin reagents,[4] it would be highly advantageous that such organosilicon reagents could be utilized in the above reactions. Thus, we thought that an exchange of chloride ion to less nucleophilic counter ion could enhance the electrophilicity of *N*-acylated aza-aromatic ions. We now wish to report here that the addition reactions of allylsilanes with quinolinium and isoquinolinium ions acylated by chloroformates can be promoted by a catalytic amount of a triflate ion to afford allylated heterocyclic products in good yields.[5]

1. Results and Discussion

1.1. Reactions of quinolines

When quinoline (**1a**) was treated with allyltrimethylsilane (**2a**) in the presence of phenyl chloroformate in dry dichloromethane at rt for 24 h, the addition reaction took place only slightly. Since the similar reaction with allyltributyltin gives the 2-allyl-1,2-dihydroquinoline derivative, it is apparent that allylsilane is less reactive than allyltin.[6] Then, we added silver salts to the reaction mixture, because it could be anticipated that pulling off the chloride ion by silver ion would enhance the electrophilicity of the *N*-phenoxycarbonylquinolinium ion. When silver triflate (1.5 equiv.) was added to the reaction mixture, the addition proceeded smoothly at rt (2 h) to afford *N*-phenoxycarbonyl-2-allyl-1,2-dihydroquinoline (**3a**) in 98% yield (Scheme 1). We also examined the effect of a couple of other silver salts. The results are summarized in Table 1 (Entries 1–4).

The results shown in Table 1 clearly indicate that replacement of the chloride ion with the less nucleophilic counter ion should enhance the electrophilicity of the

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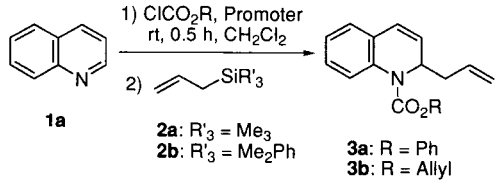


Scheme 1.

N-acylquinolinium ion. Among the silver salts used, silver triflate gave the best result.

We next pursued the possibility that *a catalytic amount* of silver triflates and other triflates can promote the addition reactions in dichloromethane or acetonitrile (Entries 5–15, Table 1). The results summarized in Table 1 demonstrate that silver triflates as well as other triflates can work well even in a catalytic amount, although a longer reaction time is required. Thus, it is evident that triflate ion promotes the reaction. It has been also found that silver triflate gave better results for the reactions in acetonitrile than other triflates (Entries 6, 8, 11 and 13).

A plausible reaction pathway for catalytic reaction is shown in Scheme 2. Exchange of the chloride ion of *N*-acylquinolinium chloride **4** with triflate ion should generate the more nucleophilic *N*-acylquinolinium triflate **5**, which would react with allyltrimethylsilane to give the adduct **3a** as well as trimethylsilyl triflate. Then, trimethylsilyl triflate should replace the chloride ion of **4** with the triflate ion to regenerate **5**. Indeed, trimethylsilyl triflate can promote the reaction (Entries 10, 11, Table 1).[7] We traced the reaction by ^{1}H NMR. When phenyl chloroformate was added to a solution of **1a** in $CDCl_3$, ^{1}H NMR demonstrated almost no signal shifted to more down-field, indicating that **4** was formed in only a slight amount in the equilibrium.[8] After silver triflate was added to this solution, ^{1}H NMR showed new signals shifted to more down-field at 10.02 and 9.34 due to the assumed **5**, which disappeared by addition of **2a** to the mixture, giving the adduct **3a**.

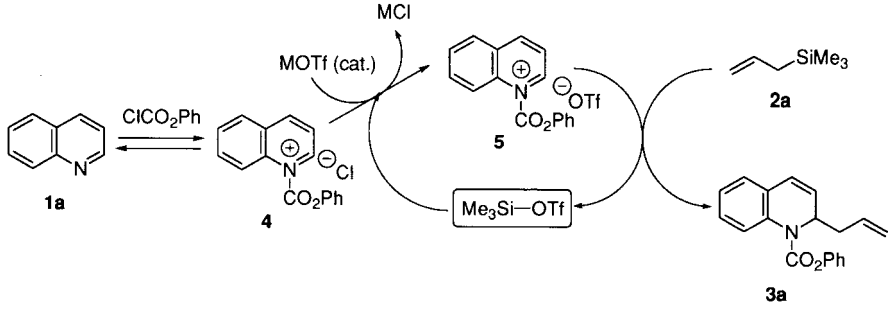
Furthermore, we tried to isolate **5** in order to clarify that **5** is the active species in the present reaction. To solution of an equimolar amount of phenyl chloroformate and silver triflate in dry acetonitrile in ice bath was added 1 equiv. of quinoline and the reaction mixture was stirred for 1 h.[9] The supernatant was collected and evaporation of the solvent followed by washing with dry dichloromethane gave air-sensitive colorless solid. ^{1}H NMR of the solid in CD_3CN showed signals at δ=9.89 (dd, 1H) due to H2 and δ=9.48 (d, 1H) due to H4, as well as signals at δ=7.63 (m, 4H), 7.53 (m, 1H) due to the phenyl group, supporting the structure of *N*-phenoxycarbonylquinolinium ion (**5**). Addition of allyltrimethylsilane to **5** in acetonitrile solution afford **3a** in 95% yield. These results clearly indicated that the active species of the present addition reaction is **5**.

We have also examined the catalytic reactions of other quinoline derivatives having substituents in dichloromethane as well as acetonitrile (Scheme 3). The results

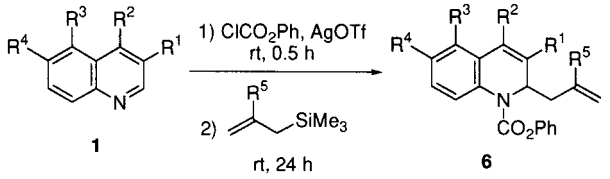
Table 1. Reactions of **2** with **1a** activated by chloroformate ester and promoter

Entry	R	Promoter (eq)	SiR'_3	Solvent	Time (h)	Product	Yield (%)[a]
1	Ph	None	$SiMe_3$	CH_2Cl_2	24	**3a**	<8
2	Ph	AgOTf (1.5)	$SiMe_3$	CH_2Cl_2	2	**3a**	98
3	Ph	AgBF4 (1.0)	$SiMe_3$	CH_2Cl_2	3	**3a**	47
4	Ph	$AgClO_4$(2,4,6-Coll)$_2$ (1.0)	$SiMe_3$	CH_2Cl_2	3	**3a**	93
5	Ph	AgOTf (0.1)	$SiMe_3$	CH_2Cl_2	24	**3a**	84
6	Ph	AgOTf (0.1)	$SiMe_3$	CH_3CN	24	**3a**	87
7	Ph	LiOTf (0.1)	$SiMe_3$	CH_2Cl_2	24	**3a**	87
8	Ph	LiOTf (0.1)	$SiMe_3$	CH_3CN	24	**3a**	79
9	Ph	NaOTf (0.1)	$SiMe_3$	CH_2Cl_2	24	**3a**	76
10	Ph	Me_3SiOTf (0.1)	$SiMe_3$	CH_2Cl_2	24	**3a**	85
11	Ph	Me_3SiOTf (0.1)	$SiMe_3$	CH_3CN	24	**3a**	71
12	Ph	AgOTf (0.1)	$SiMe_2Ph$	CH_2Cl_2	24	**3a**	79
13	Ph	AgOTf (0.1)	$SiMe_2Ph$	CH_3CN	24	**3a**	85
14	Allyl	AgOTf (0.1)	$SiMe_3$	CH_2Cl_2	24	**3b**	82
15	Allyl	LiOTf (0.1)	$SiMe_3$	CH_2Cl_2	24	**3b**	43

[a] Isolated yield.



Scheme 2.



Scheme 3.

are summarized in Table 2. As shown in Table 2, various functional group including nitro group can be tolerated in the present reaction. The addition reactions take place at the 2-position of quinolines selectively, showing high regioselectivity. It should be also noted that acetonitrile is generally a better solvent than dichloromethane, indicating the ionic nature of the reaction. Similar reactions of quinoline with a couple of 2-substituted allyltrimethylsilanes to the above also proceed smoothly in acetonitrile (Entries 9–11, Table 2). As shown in Table 2, 1,2-adducts were obtained in good to moderate yields. Thus, functionalized allylic substituents can be introduced into quinoline system regioselectively.

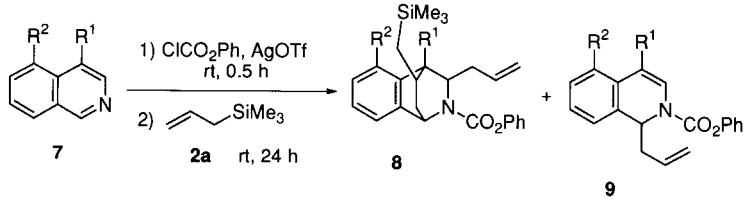
1.2. Reactions of isoquinolines

We next turned our attention to isoquinoline systems, which are one of the most important basic skeleton of many physiologically active compounds. When allyltrimethylsilane (**2a**) was allowed to react with isoquinoline (**7a**) activated by phenyl chloroformate and silver triflate (1.5 equiv.) in dry dichloromethane, the addition of 2 equiv. of **2a** to **7a** took place, affording an unexpected benzoisoquinuclidine derivative **8a** as a 1:1 mixture of rotamers in 83% yield (Scheme 4, Table 3). The mono-allylated

Table 2. Reactions of allylic silanes with substituted quinolines activated by $ClCO_2Ph$ and a catalytic amount of AgOTf (0.1 equiv.)

Entry	R^1	R^2	R^3	R^4	R^5	Product	Yield (%)[a]	Yield (%)[b]
1	Br	H	H	H	H	**6a**	86	Quant.
2	Me	H	H	H	H	**6b**	79	90
3	CN	H	H	H	H	**6c**	79[c,d]	93[e]
4	CO_2Me	H	H	H	H	**6d**	53[f]	92[g]
5	H	CHO	H	H	H	**6e**	59	75
6	H	H	NO_2	H	H	**6f**	92	Quant.
7	H	H	H	NO_2	H	**6g**	91	Quant.
8	H	H	H	OMe	H	**6h**	56	84
9	H	H	H	H	CH_3	**6i**	–	93
10	H	H	H	H	CH_2Cl	**6j**	–	64
11	H	H	H	H	CH_2OSiMe_3	**6k** (R=CH_2OH)	–	67

[a] Isolated yield for the reaction in CH_2Cl_2.
[b] Isolated yield for the reaction in CH_3CN.
[c] The reaction was conducted at 70°C in $ClCH_2CH_2Cl$.
[d] The 1,4-adduct (**6c′**) was formed in 9% yield.
[e] **6c′** was formed in 7% yield.
[f] The 1,4-adduct (**6d′**) was formed in 11% yield.
[g] **6d′** was formed in 7% yield.



Scheme 4.

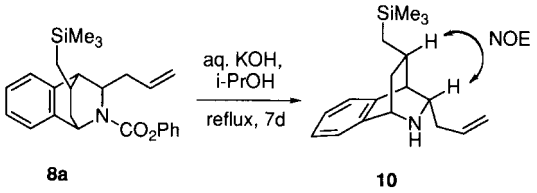
Table 3. Reactions of **2a** with isoquinolines activated $ClCO_2Ph$ and a catalytic amount of AgOTf (0.1 equiv.)

Entry	R^1	R^2	Solvent	Products	Yield (%)[a]	Ratio of **8**/**9**
1[b]	H	H	CH_2Cl_2	**8a**, **9a**	83	>95/<5[c]
2	H	H	CH_2Cl_2	**8a**, **9a**	77	>95/<5[c]
3	Br	H	CH_2Cl_2	**8b**, **9b**	90	95/5[c]
4	H	NO_2	CH_2Cl_2	**8c**, **9c**	82	>95/<5[c]
5	H	H	CH_3CN	**8a**, **9a**	94	69/31[d]
6	Br	H	CH_3CN	**8b**, **9b**	95	42/58[c]
7	H	NO_2	CH_3CN	**8c**, **9c**	90	41/59[c]
8	H	H	CH_3NO_2	**8a**, **9a**	83	>95/<5[c]

[a] Isolated yield.
[b] 1.5 equiv. of AgOTf was used.
[c] Determined by ^1H NMR.
[d] Determined by the isolated yields.

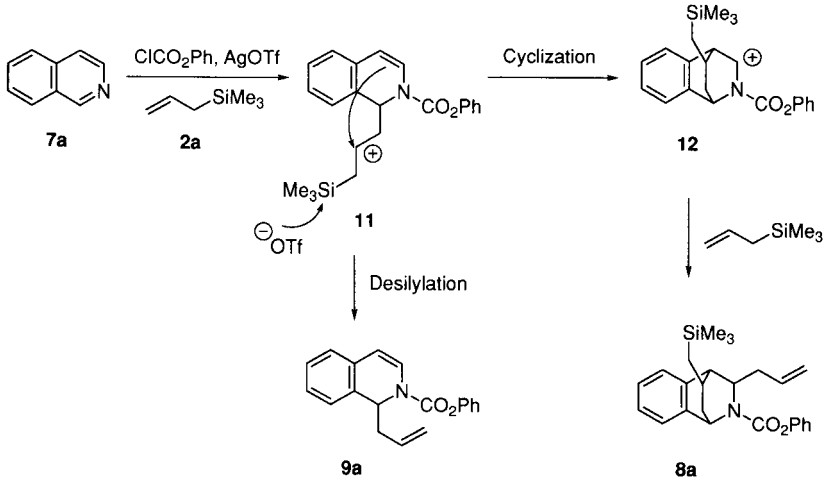
product **9a** was not detected by ^1H NMR. The structure of **8a** was elucidated by 2D NMR analyses. The catalytic amount (0.1 equiv.) of silver triflate also promoted the reaction to give **8a** selectively. Similarly, the reactions of substituted isoquinolines to the above afforded benzoisoquinuclidine derivatives as well (Entries 2–4). It has been found that the reactions of isoquinolines in acetonitrile gave the cyclized products **8** as well as uncyclized 1-allyl-1,2-dihydroisoquinoline derivatives **9** (Entries 5–7). It should be noted, however, that the similar reaction of **2a** with **7a** in nitromethane resulted in the selective formation of the cyclized product **8a** (Entry 8).

In order to determine the stereochemistry of the cyclized product **8a**, the phenoxycarbonyl group was removed[10] to



Scheme 5.

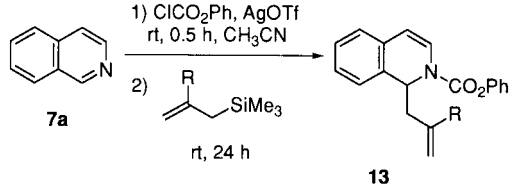
mediate **11**, which could undergo the intramolecular electrophilic addition to the enamide moiety to produce the cyclized iminium ion **12**. The second addition of **2a** to **12** would eventually afford the cyclized products **8a**. On the other hand, desilylation of **11** could give the 1,2-adduct **9a**. In acetonitrile solution, the cationic intermediates **11** might be stabilized by the solvent and, therefore, the removal of the trimethylsilyl group leading to the 1,2-adduct **9a** would compete with the cyclization pathway. Since the cyclized



Scheme 6.

give a single compound **10** (Scheme 5), indicating that **8a** is a mixture of rotamers at the carbamoyl groups. The NOESY spectrum of **10** showed NOE between the protons attached to the carbons bearing the allyl and trimethylsilylmethyl substituents, suggesting that the two substituents on the isoquinuclidine skeleton direct to the benzene ring.

The above results are in a marked contrast to the reaction of allyltin in which the 1,2-adduct **9** is obtained in high yield. A possible reaction pathway is shown in Scheme 6. The first addition of allyltrimethylsilane (**2a**) to the *N*-phenoxycarbonylisoquinolinium ion would produce the cationic inter-



Scheme 7.

Table 4. Reactions of 2-substituted allylsilanes with isoquinoline activated by $ClCO_2Ph$ and a catalytic amount of AgOTf (0.1 equiv.)

Entry	R	Product	Yield (%)[a]
1	CH_3	**13a**	Quant.
2	CH_2Cl	**13b**	77
3	CH_2OSiMe_3	**13c** (R=CH_2OH)	59

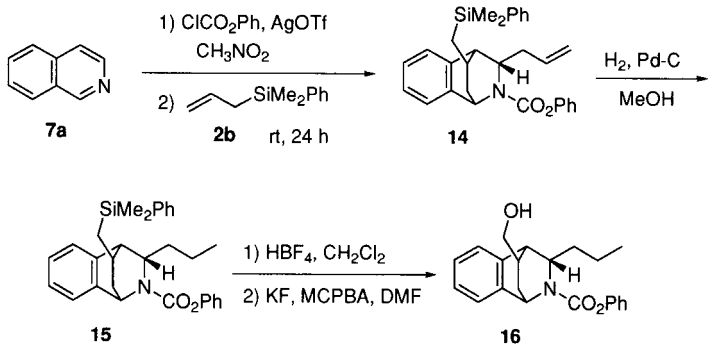
[a] Isolated yield.

product **8a** is produced selectively in nitromethane, it can be said that polarity of the solvent alone could not be responsible for the selectivity.

The reactions of isoquinoline with 2-substituted allylsilanes were also conducted in the usual way and the 1,2-adducts **13** were obtained selectively (Scheme 7, Table 4). Thus, steric hindrance as well as stability of the cationic intermediates would be critical in these cases.

Finally, we examined functionalization of the silyl group of the cyclized product **8** by the Tamao–Fleming oxidation method.[11] In order to oxidize silyl group, we tried to introduce dimethylphenylsilyl group in the isoquinuclidine system. When allydimethylphenylsilane (**2b**) was allowed to react with isoquinoline activated by phenyl chloroformate and silver triflate in dichloromethane, the cyclized product **14** was obtained in only 12% yield. We have found, however, that a similar reaction in nitromethane to the above greatly increased the yield of **14** up to 89%. Hydrogenation of the allyl group followed by oxidation of the dimethylphenylsilyl group afforded the alcohol **16** in good yield (Scheme 8).

In summary, we have found an effective method for introduction of allylic groups into quinoline and isoquinoline systems by means of allylic silicone reagents. The promoter, silver triflate, is required in only a catalytic amount. The reactions are highly chemo- and regioselective. In the reactions of isoquinolines, benzoisoquinuclidine derivatives are obtained unexpectedly, providing a new synthetic way for the bicyclic aza-system.



Scheme 8.

2. Experimental

2.1. General

All manipulation of oxygen and moisture-sensitive materials were conducted under argon atmosphere. All the temperatures are uncorrected. IR spectra were taken on a HORIBA FT-300 spectrometer. ^{1}H NMR spectra were measured with JEOL EX-270 and JEOL A-500 spectrometers using TMS as the internal standard. ^{13}C NMR spectra were obtained on JEOL A-500 spectrometer using $CDCl_3$ as the internal standard. Additional NMR spectra were recorded by DEPT, H–H COSY, and C–H COSY methods on JEOL A-500 spectrometer. Column chromatography was carried out by using Wako-gel C-200. TLC analysis was carried out by using DC-Alufolien Kieselgel 60 F254 (MERCK). Microanalyses were performed by the Kyoto University Elemental Analysis Center. Dichloromethane, 1,2-dichloroethane and acetonitrile were distilled over P_2O_5 under argon gas before use. Nitromethane, DMF and toluene were distilled over calcium hydride under argon gas before use. Most of reagents were purchased from Aldrich Chemical Company, Wako Pure Chemical Industries, Nakarai Tesque, Tokyo Kasei Kogyo Co. and Shin-etsu Chemical Industry.

2.2. General procedures for reactions of allylic silanes with quinolines activated by a chloroformate ester and a catalytic amount of a triflate

To a solution of quinoline **1** (1.0 mmol) in CH_2Cl_2 or CH_3CN (2 mL) was added $ClCO_2Ph$ or $ClCO_2Allyl$ (1.5 mmol) and a trifluoromethanesulfonate (0.1 mmol) at rt. Then the reaction mixture was stirred for 0.5 h. To the reaction mixture was added an allylic silane (1.5 mmol) under ice-cooling and the mixture was stirred at rt for 24 h. Ether (5 mL) and saturated aqueous $NaHCO_3$ (3 mL) were added, and the organic layer was separated. The aqueous layer was extracted with ether (5 mL×5). The combined organic layer was dried (Na_2SO_4) and the solvent was evaporated. The residue was purified by chromatography on silica gel (hexane–AcOEt as the eluent) to give the product **3** or **6**.

2.2.1. 2-Allyl-1-phenoxycarbonyl-1,2-dihydroquinoline (3a). IR (neat) 1726, 1489, 1329, 1119, 748 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.75 (br s, 1H), 7.42 (t, 2H, J=8 Hz), 7.13–7.29 (m, 6H), 6.58 (d, 1H, J=9 Hz), 6.14 (dd, 1H, J=9, 6 Hz), 5.89 (m, 1H), 5.25 (dd, 1H, J=6, 14 Hz), 5.13 (d, 1H, J=10 Hz), 5.07 (d, 1H, J=17 Hz), 2.33 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 152.7 (C), 151.0 (C), 133.9 (C), 133.5 (CH), 129.2 (CH), 127.6 (CH), 127.3 (C), 126.2 (CH), 125.4 (CH), 125.1 (CH), 124.6 (CH), 121.5 (CH), 117.9 (CH_2), 52.6 (CH), 37.4 (CH_2); Anal. Calcd for $C_{19}H_{17}NO_2$: C, 78.33; H, 5.88; N, 4.81. Found: C, 78.27; H, 5.77; N, 4.69.

2.2.2. 2-Allyl-1-allyloxycarbonyl-1,2-dihydroquinoline (3b). IR (neat) 1707, 1489, 1392, 1315, 1250 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.59 (br s, 1H), 7.21 (m, 1H), 7.09 (m, 2H), 6.48 (d, 1H, J=10 Hz), 6.04 (dd, 1H, J=7, 10 Hz), 5.97 (m, 1H), 5.77 (m, 1H), 5.33 (d, 1H, J=17 Hz), 5.23 (d, 1H, J=11 Hz), 5.10 (m, 1H), 5.02 (d, 1H, J=10 Hz), 4.97 (d, 1H, J=17 Hz), 4.72 (m, 2H), 2.19 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 153.9 (C), 134.2 (C), 133.5 (CH), 132.4 (CH), 129.1 (CH), 127.3 (CH), 127.2 (C), 126.1 (CH), 124.9 (CH), 124.7 (CH), 124.1 (CH), 117.6 (CH_2), 66.4 (CH_2), 52.1 (CH), 37.5 (CH_2); Anal. Calcd for $C_{16}H_{17}NO_2$: C, 75.57; H, 6.34; N, 5.49. Found: C, 75.50; H, 6.47, N, 5.43.

2.2.3. 2-Allyl-3-bromo-1-phenoxycarbonyl-1,2-dihydroquinoline (6a). IR (neat) 1722, 1487, 1385, 1319, 1201, 739 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.50–7.85 (br 1H), 7.38 (t, 2H, J=8 Hz), 7.08–7.29 (m, 6H), 6.86 (s, 1H), 5.82 (m, 1H), 5.32 (dd, 1H, J=4, 10 Hz), 5.10 (d, 1H, J=9 Hz), 5.02 (d, 1H, J=17 Hz), 2.53 (m, 1H), 2.22 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 152.4 (C), 150.9 (C), 132.9 (CH), 132.4 (C), 129.4 (CH), 128.1 (CH), 127.4 (C), 127.1 (CH), 125.7 (CH), 125.1 (CH), 121.5 (CH), 118.7 (CH_2), 59.5 (CH), 34.9 (CH_2); Anal. Calcd for $C_{19}H_{16}BrNO_2$: C, 61.64; H, 4.36; N, 3.78. Found: C, 61.58; H, 4.43; N, 3.73.

2.2.4. 2-Allyl-3-methyl-1-phenoxycarbonyl-1,2-dihydroquinoline (6b). IR (neat) 1720, 1489, 1390, 1325, 1246, 1203, 750 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.54–7.78 (br, 1H), 7.35 (t, 2H, J=8 Hz), 7.04–7.20 (m, 6H), 6.25 (d, 1H, J=1 Hz), 5.83 (m, 1H), 5.06 (d, 1H, J=9 Hz), 4.98 (m, 2H), 2.30 (m, 1H), 2.13 (m, 1H), 1.96 (d, 3H, J=1 Hz); ^{13}C NMR ($CDCl_3$) δ 152.7 (C), 151.1 (C), 139.3 (C), 137.8 (C), 134.0 (CH), 132.5 (C), 129.2 (CH), 128.3 (C), 126.6 (CH), 125.4 (CH), 125.3 (CH), 124.6 (CH), 121.5 (CH), 120.8 (CH), 117.7 (CH_2), 56.7 (CH), 35.4 (CH_2), 20.8 (CH_3); Anal. Calcd for $C_{20}H_{19}NO_2$: C, 78.66; H, 6.27; N, 4.59. Found: C, 78.37; H, 6.19; N, 4.29.

2.2.5. 2-Allyl-3-cyano-1-phenoxycarbonyl-1,2-dihydroquinoline (6c). Mp 134–135°C; IR (neat) 2214, 1726,

1487, 1390, 1321, 1246, 1200, 754 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.75 (br s, 1H), 7.39 (s, 1H), 7.37 (t, 2H, J=7 Hz), 7.14–7.23 (m, 6H), 5.81 (m, 1H), 5.38 (dd, 1H, J=5, 9 Hz), 5.14 (d, 1H, J=10 Hz), 5.03 (d, 1H, J=17 Hz), 2.44 (m, 1H), 2.27 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 152.0 (C), 150.5 (C), 138.4 (CH), 134.4 (C), 131.7 (CH), 130.9 (CH), 129.2 (CH), 127.9 (CH), 125.7 (CH), 125.0 (CH), 124.8 (CH), 124.5 (C), 121.2 (CH), 119.3 (CH_2), 116.9 (C), 110.9 (C), 52.9 (CH), 36.3 (CH_2); Anal. Calcd for $C_{20}H_{16}N_2O_2$: C, 75.93; H, 5.10; N, 8.86. Found: C, 75.86; H, 5.18; N, 8.76.

2.2.6. 4-Allyl-3-cyano-1-phenoxycarbonyl-1,4-dihydroquinoline (6c′). IR (neat) 2210, 1747, 1489, 1317, 1200, 754 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.05 (d, 1H, J=7 Hz), 7.96 (s, 1H), 7.45 (t, 2H, J=8 Hz), 7.16–7.33 (m, 6H), 5.71 (m, 1H), 5.11 (d, 1H, J=10 Hz), 5.08 (d, 1H, J =17 Hz), 3.70 (t, 1H, J=6 Hz), 2.52 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 150.2 (C), 149.8 (C), 138.6 (CH), 134.2 (C), 132.6 (CH), 129.7 (CH), 128.6 (CH), 128.1 (C), 127.6 (CH), 126.6 (CH), 126.5 (CH), 121.4 (CH), 121.2 (CH), 119.3 (CH_2), 118.0 (C), 97.3 (C), 41.4 (CH_2), 39.9 (CH); Anal. Calcd for $C_{20}H_{16}N_2O_2$: C, 75.93; H, 5.10. Found: C, 76.15; H, 5.18.

2.2.7. 2-Allyl-3-methoxycarbonyl-1-phenoxycarbonyl-1,2-dihydroquinoline (6d). IR (neat) 1720, 1487, 1325, 1200, 758 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.82 (br s, 1H), 7.56 (s, 1H), 7.13–7.38 (m, 8H), 5.88 (m, 1H), 5.73 (dd, 1H, J=4, 10 Hz), 5.08 (d, 1H, J=10 Hz), 4.95 (d, 1H, J=17 Hz), 3.83 (s, 3H), 2.36 (m, 1H), 2.17 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 165.1 (C), 152.4 (C), 150.8 (C), 135.2 (C), 133.7 (CH), 133.4 (CH), 130.3 (CH), 129.2 (CH), 128.4 (CH), 125.9 (C), 125.6 (CH), 124.7 (CH), 121.5 (CH), 118.1 (CH_2), 52.0 (CH_3), 51.7 (CH), 36.6 (CH_2). Anal. Calcd for $C_{21}H_{19}NO_4$: C, 72.19; H, 5.48; N, 4.01. Found: C, 72.27; H, 5.59; N, 3.95.

2.2.8. 4-Allyl-3-methoxycarbonyl-1-phenoxycarbonyl-1,4-dihydroquinoline (6d′). IR (neat) 1749, 1711, 1655, 1489, 1350, 1192, 754 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.31 (s, 1H), 8.04 (d, 1H, J=8 Hz), 7.44 (t, 2H, J=8 Hz), 7.18–7.31 (m, 6H), 5.68 (m, 1H), 4.98 (d, 1H, J=10 Hz), 4.91 (d, 1H, J=17 Hz), 3.99 (t, 1H, J=6 Hz), 3.82 (s, 3H), 2.40 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 166.4 (C), 150.5 (C), 150.4 (C), 135.8 (CH), 135.1 (C), 134.0 (CH), 130.6 (C), 129.6 (CH), 128.9 (CH), 126.8 (CH), 126.3 (CH), 125.9 (CH), 121.6 (CH), 121.0 (CH), 117.8 (CH_2), 115.9 (C), 51.8 (CH_3), 41.5 (CH), 37.9 (CH_2). Anal. Calcd for $C_{21}H_{19}NO_4$: C, 72.19; H, 5.48. Found: C, 72.06; H, 5.55.

2.2.9. 2-Allyl-4-formyl-1-phenoxycarbonyl-1,2-dihydroquinoline (6e). IR (neat) 1722, 1697, 1491, 1390, 1325, 1250, 1201, 756 cm^{-1}; ^1H NMR ($CDCl_3$) δ 9.71 (s, 1H), 8.25 (dd, 1H, J=2, 8 Hz), 7.69 (br, 1H), 7.32–7.38 (m, 3H), 7.14–7.22 (m, 3H), 6.94 (d, 1H, J=6 Hz), 5.81 (m, 1H), 5.47 (m, 1H), 5.12 (d, 1H, J=10 Hz), 5.02 (d, 1H, J=17 Hz), 2.33 (m, 1H), 2.22 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 190.8 (CH), 152.3 (C), 150.8 (C), 148.9 (C), 134.2 (CH), 133.6 (C), 132.2 (CH), 129.3 (CH), 128.8 (CH), 125.7 (C), 125.6 (CH), 125.0 (CH), 122.9 (C), 121.4 (CH), 118.8 (CH_2), 52.4 (CH), 35.5 (CH_2); Anal. Calcd for $C_{20}H_{17}NO_3$: C, 75.22; H, 5.73; N, 4.39. Found: C, 75.00; H, 5.45; N, 4.36.

2.2.10. 2-Allyl-5-nitro-1-phenoxycarbonyl-1,2-dihydroquinoline (6f). IR (neat) 1724, 1527, 1467, 1388, 1317, 1201, 736 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.98 (br s, 1H), 7.73 (d, 1H, J=8 Hz), 7.18–7.42 (m, 6H), 7.14 (d, 1H, J=10 Hz), 6.40 (dd, 1H, J=6, 10 Hz), 5.86 (m, 1H), 5.29 (m, 1H), 5.14 (d, 1H, J=10 Hz), 5.04 (d, 1H, J=17 Hz), 2.36 (m, 1H), 2.23 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 152.3 (C), 150.6 (C), 146.1 (C), 135.5 (C), 133.3 (CH), 132.8 (CH), 129.7 (CH), 129.3 (CH), 127.0 (CH), 125.7 (CH), 121.8 (C), 121.3 (CH), 120.6 (CH), 119.7 (CH), 118.3 (CH_2), 51.8 (CH), 36.8 (CH_2); Anal. Calcd for $C_{19}H_{16}N_2O_4$: C, 67.85; H, 4.79; N, 8.33. Found: C, 68.13; H, 4.76; N, 8.36.

2.2.11. 2-Allyl-6-nitro-1-phenoxycarbonyl-1,2-dihydroquinoline (6g). IR (neat) 1726, 1579, 1520, 1487, 1304, 1200, 1120, 744 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.06 (dd, 1H, J=2, 9 Hz), 7.98 (d, 1H, J=2 Hz), 7.90 (d, 1H, J=9 Hz), 7.16–7.41 (m, 5H), 6.58 (d, 1H, J=10 Hz), 6.22 (dd, 1H, J=6, 10 Hz), 5.81 (m, 1H), 5.28 (m, 1H), 5.09 (d, 1H, J=10 Hz), 5.02 (d, 1H, J=17 Hz), 2.36 (m, 1H), 2.23 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 152.2 (C), 150.5 (C), 143.8 (C), 140.0 (C), 132.5 (CH), 131.0 (CH), 129.4 (CH), 127.7 (C), 125.9 (CH), 124.5 (CH), 123.9 (CH), 122.7 (CH), 121.4 (CH), 121.3 (CH), 118.6 (CH_2), 53.1 (CH), 38.1 (CH_2); Anal. Calcd for $C_{19}H_{16}N_2O_4$: C, 67.85; H, 4.79; N, 8.33. Found: C, 68.11; H, 4.74; N, 8.29.

2.2.12. 2-Allyl-6-methoxy-1-phenoxycarbonyl-1,2-dihydroquinoline (6h). IR (neat) 1718, 1495, 1394, 1327, 1311, 1269, 1203, 1163, 741 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.50–7.77 (br, 1H), 7.17–7.41 (m, 5H), 6.81 (dd, 1H, J=2, 9 Hz), 6.69 (d, 1H, J=2 Hz), 6.52 (d, 1H, J=9 Hz), 6.14 (br, 1H), 5.03–5.21 (m, 3H), 3.82 (s, 3H), 2.29 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 156.5 (C), 152.8 (C), 151.1 (C), 133.6 (CH), 130.5 (C), 129.2 (CH), 128.4 (C), 126.9 (C), 126.1 (C), 125.4 (CH), 125.1 (CH), 121.6 (CH), 117.8 (CH_2), 113.1 (CH), 111.0 (CH), 55.4 (CH_3), 52.6 (CH), 37.0 (CH_2); Anal. Calcd for $C_{20}H_{19}NO_3$: C, 74.75; H, 5.96; N, 4.36. Found: C, 74.59; H, 5.99; N, 4.49.

2.2.13. 2-Methallyl-1-phenoxycarbonyl-1,2-dihydroquinoline (6i). IR (neat) 1720, 1489, 1390, 1323, 1234, 1203, 754 cm^{-1}; ^1H NMR ($CDCl_3$, 55°C) δ 7.69 (br s, 1H), 7.34 (t, 2H, J=8 Hz), 7.06–7.23 (m, 6H), 6.51 (d, 1H, J=9 Hz), 6.09 (dd, 1H, J=6, 9 Hz), 5.27 (m, 1H), 4.85 (s, 1H), 4.65 (s, 1H), 2.22 (dd, 1H, J=9, 13 Hz), 2.10 (dd, 1H. J=6, 13 Hz), 1.83 (s, 3H); ^{13}C NMR ($CDCl_3$, 55°C) δ 152.7 (C), 151.3 (C), 141.1 (C), 133.9 (C), 129.6 (CH), 129.2 (CH), 127.6 (CH), 127.5 (C), 126.2 (CH), 125.4 (CH), 125.0 (CH), 124.6 (CH), 121.5 (CH), 113.7 (CH_2), 51.5 (CH), 41.0 (CH_2), 22.3 (CH_3); Anal. Calcd for $C_{20}H_{19}NO_2$: C, 78.66; H, 6.27; N, 4.59. Found: C, 78.38; H, 6.22; N, 4.59.

2.2.14. 2-(2-Chloromethyl-2-propenyl)-1-phenoxycarbonyl-1,2-dihydroquinoline (6j). IR (neat) 1720, 1489, 1327, 746 cm^{-1}; ^1H NMR ($CDCl_3$, 55°C) δ 7.64 (br s, 1H), 7.34 (t, 2H, J=7 Hz), 7.09–7.24 (m, 6H), 6.54 (d, 1H, J=10 Hz), 6.11 (dd, 1H, J=6, 10 Hz), 5.28 (m, 1H), 5.24 (s, 1H), 4.93 (s, 1H), 4.24 (d, 1H, J=12 Hz), 4.08 (d, 1H, J=12 Hz), 2.42 (dd, 1H, J=5, 14 Hz), 2.26 (dd, 1H, J=10 and 14 Hz); ^{13}C NMR ($CDCl_3$, 55°C) δ 152.8 (C), 151.2 (C), 141.0 (C), 133.6 (C), 129.3 (CH), 129.1 (CH),

127.8 (CH), 127.4 (C), 126.4 (CH), 125.5 (CH), 125.4 (CH), 125.1 (CH), 124.8 (CH), 121.4 (CH), 117.8 (CH_2), 51.2 (CH), 47.5 (CH_2), 36.2 (CH_2); Anal. Calcd for $C_{20}H_{18}ClNO_2$: C, 70.69; H, 5.34; N, 4.12. Found: C, 70.89; H, 5.40; N, 4.12.

2.2.15. 2-(2-Hydroxymethyl-2-propenyl)-1-phenoxycarbonyl-1,2-dihydroquinoline (6k). IR (neat) 3444, 1718, 1489, 1392, 1329, 1205, 739 cm^{-1}; ^1H NMR ($CDCl_3$, 55°C) δ 7.57 (br s, 1H), 7.33 (t, 2H, J=7 Hz), 7.08–7.24 (m, 6H), 6.52 (d, 1H, J=9 Hz), 6.11 (dd, 1H, J=6, 9 Hz), 5.26 (m, 1H), 5.15 (s, 1H), 4.81 (s, 1H), 4.15 (d, 1H, J=13 Hz), 4.10 (d, 1H, J=4 Hz), 2.30 (br, 1H), 2.22 (m, 2H); ^{13}C NMR ($CDCl_3$, 55°C) δ 153.2 (C), 151.2 (C), 144.6 (C), 133.5 (C), 129.5 (CH), 129.3 (CH), 127.7 (CH), 127.4 (C), 126.4 (CH), 125.5 (CH), 125.0 (CH), 124.9 (CH), 124.8 (CH), 121.4 (CH), 114.0 (CH_2), 66.2 (CH_2), 52.2 (CH), 36.6 (CH_2); Anal. Calcd for $C_{20}H_{19}NO_3$: C, 74.75; H, 5.96; N, 4.36. Found: C, 74.53; H, 6.11, N, 4.40.

2.2.16. 1-Phenoxycarbonylquinolinium trifluoromethanesulfonate (5). To a solution of $ClCO_2Ph$ (644 mg, 4.1 mmol) and AgOTf (1054 mg, 4.1 mmol) in dry CH_3CN (10 mL) was added quinoline (**1a**, 516 mg, 4.0 mmol) under ice-cooling. The reaction mixture was stirred for 1 h. Stirring was stopped and AgCl was allowed to settle. The clear yellow supernatant was transformed using a cannula. The solvent was evaporated and the residual solid was washed with dry CH_2Cl_2 (4 mL) twice to give air-sensitive **5** (619 mg, 1.6 mmol): ^1H NMR (CD_3CN) δ 9.89 (dd, 1H, J=1, 6 Hz), 9.48 (d, 1H, J=8 Hz), 8.88 (d, 1H, J=9 Hz), 8.51 (dd, 1H, J=1, 9 Hz), 8.38 (t, 1H, J=8 Hz), 8.24 (dd, 1H, J=6, 8 Hz), 8.13 (t, 1H, J=8 Hz), 7.59–7.66 (m, 4H), 7.53 (m, 1H); ^{13}C NMR (CD_3CN) δ 156.0 (CH), 151.5 (C), 149.6 (CH), 148.8 (C), 139.3 (CH), 138.0 (C), 132.5 (CH), 131.9 (CH), 131.5 (C), 131.4 (CH), 129.3 (CH), 122.3 (CH), 121.7 (CH), 121.5 (CH).

2.3. General procedures for reactions of allylic silanes with isoquinolines activated by phenyl chloroformate and a catalytic amount of silver triflate

To a solution of isoquinoline **7** (1.0 mmol) in CH_2Cl_2 or CH_3CN or CH_3NO_2 (2 mL) was added $ClCO_2Ph$ (1.5 mmol) and AgOTf (0.1 mmol) at rt. Then the reaction mixture was stirred for 0.5 h. To the reaction mixture was added an allylic silane (2.5 mmol) under ice-cooling and the mixture was stirred at rt for 24 h. Ether (5 mL) and saturated aqueous $NaHCO_3$ (3 mL) were added, and the organic layer was separated. The aqueous layer was extracted with ether (5 mL×5). The combined organic layer was dried (Na_2SO_4) and the solvent was evaporated. The residue was purified by chromatography on silica gel (hexane–AcOEt as the eluent) to give the cyclized product 8 and/or the 1,2-adduct **9** or **13**.

2.3.1. (3S^*,9S^*)-3-Allyl-9-trimethylsilylmethyl-2-phenoxycarbonyl-1,2,3,4-tetrahydro-1,4-ethanoisoquinoline (8a). IR (neat) 1714, 1390, 1205, 850, 746 cm^{-1}; ^1H NMR ($CDCl_3$, 55°C, a mixture of rotamers) δ 7.28–7.52 (m, 9H), 5.83 (m, 1H), 5.37 5.34 (s, 1H), 5.19 (d, 1H, J=10 Hz), 5.08 (d, 1H, J=17 Hz), 4.10 4.05 (d, 1H, J=10 Hz), 3.13 (s, 1H), 2.63 (br, 2H), 2.28 (br, 1H), 1.61 1.49 (m, 1H), 1.07 1.00 (m, 1H), 0.66 0.63 (d, 1H, J=6 Hz), 0.26 (m, 1H), 0.12 (s, 9H); ^{13}C NMR ($CDCl_3$, 55°C, a mixture of rotamers) δ 154.0 153.4 (C), 151.6 151.5 (C), 139.2 139.1 (C), 137.1 136.8 (C), 134.4 134.3 (CH), 129.1 (CH), 127.6 127.5 (CH), 127.4 127.3 (CH), 126.8 126.7 (CH), 125.0 (CH), 123.0 122.8 (CH), 121.7 121.5 (CH), 117.4 117.2 (CH_2), 59.6 59.2 (CH), 52.2 51.4 (CH), 46.3 45.8 (CH), 38.6 37.9 (CH_2), 37.7 36.4 (CH_2), 31.1 31.2 (CH_2), 25.5 (CH_2), −0.8 (CH_3); Anal. Calcd for $C_{25}H_{31}NO_2Si$: C, 74.03; H, 7.70; N, 3.45. Found: C, 74.08; H, 7.80; N, 3.50.

2.3.2. (3S^*,9S^*)-3-Allyl-4-bromo-9-trimethylsilylmethyl-2-phenoxycarbonyl-1,2,3,4-tetrahydro-1,4-ethanoisoquinoline (8b). IR (neat) 1716, 1387, 1205, 841, 742 cm^{-1}; ^1H NMR ($CDCl_3$, a mixture of rotamers) δ 7.58 (d, 1H, J=7 Hz), 7.14–7.42 (m, 8H), 5.43 (m, 1H), 5.28 5.23 (d, 1H, J=2 Hz), 4.74 (m, 2H), 4.41 4.36 (t, 1H, J=5 Hz), 2.63 (m, 2H), 2.45 (m, 1H), 1.90 (m, 1H), 1.37 (d, 1H, J=14 Hz), 1.20 1.12 (dd, 1H, J=4, 12 Hz), −0.02 (s, 9H), −0.23 (m, 1H); ^{13}C NMR ($CDCl_3$, a mixture of rotamers) δ 153.3 153.2 (C), 151.1(C), 136.6 136.5 (C), 136.4 136.3 (C), 135.3, 135.1 (CH), 129.3 129.2 (CH), 128.2 128.0 (CH), 128.1 (CH), 128.0 127.9 (CH), 125.3 125.2 (CH), 123.1 122.9 (CH), 121.6 121.4 (CH), 116.1, 115.8 (CH_2), 76.5 75.8 (C), 65.1 64.8 (CH), 52.1 51.1 (CH), 40.1 40.0 (CH), 39.6 39.1 (CH_2), 38.7 38.0 (CH_2), 23.5 23.4 (CH_2), −0.9 (CH_3); Anal. Calcd for $C_{25}H_{30}BrNO_2Si$: C, 61.98; H, 6.24; N, 2.89. Found: C, 61.87; H, 6.09; N, 2.90.

2.3.3. (3S^*,9S^*)-3-Allyl-9-trimethylsilylmethyl-5-nitro-2-phenoxycarbonyl-1,2,3,4-tetrahydro-1,4-ethanoisoquinoline (8c). IR (neat) 1714, 1529, 1394, 1358, 1205, 856, 735 cm^{-1}; ^1H NMR ($CDCl_3$, a mixture of rotamers) δ 8.05 (d, 1H, J=9 Hz), 7.57–7.13 (m, 7H), 5.68 (m, 1H), 5.39 5.33 (d, 1H, J=2 Hz), 4.98 (d, 1H, J=10 Hz), 4.86 (d, 1H, J=17 Hz), 4.24 (s, 1H), 4.08 4.01 (m, 1H), 2.56 (m, 2H), 2.32 (br, 1H), 1.47 1.36 (m, 1H), 0.89–1.01 (m, 2H), 0.02 (m, 1H), 0.00 (s, 9H); ^{13}C NMR ($CDCl_3$, a mixture of rotamers) δ 153.9 153.1 (C), 151.0 (C), 148.7 148.6 (C), 141.9 141.8 (C), 133.4 133.2 (CH), 133.2 132.9 (C), 129.2 (CH), 128.4 128.2 (CH), 127.3 127.2 (CH), 125.3 125.2 (CH), 123.6, 123.5 (CH), 121.6 121.4 (CH), 117.7, 117.5 (CH_2), 59.1 58.6 (CH), 51.6 50.8 (CH), 42.6 42.1 (CH), 38.2 37.2 (CH_2), 36.9 36.3 (CH_2), 31.0 30.9 (CH), 24.7 24.6 (CH_2), −1.0 (CH_3); Anal. Calcd for $C_{25}H_{30}N_2O_4Si$: C, 66.64; H, 6.71; N, 6.22. Found: C, 66.37; H, 6.74; N, 6.19.

2.3.4. 1-Allyl-2-phenoxycarbonyl-1,2-dihydroisoquinoline (9a). IR (neat) 1726, 1358, 1329, 1236, 1201, 746 cm^{-1}; ^1H NMR ($CDCl_3$, a mixture of rotamers) δ 7.39 (m, 2H), 7.09–7.26 (m, 7H), 7.01 6.98 (dd, 1H, J=1, 8 Hz), 6.02 5.95 (d, 1H, J=8 Hz), 5.85 (m, 1H), 5.51 5.45 (t, 1H, J=7 Hz), 5.00–5.11 (m, 2H), 2.39–2.62 (m, 2H); ^{13}C NMR ($CDCl_3$, a mixture of rotamers) δ 152.1 151.5 (C), 151.0 150.8 (C), 134.0 133.7 (CH), 132.4 132.3 (C), 130.2 129.9 (C), 129.4 (CH), 127.9 127.8 (CH), 127.1 126.9 (CH), 126.4 126.2 (CH), 125.8 125.7 (CH), 125.0 124.9 (CH), 124.8 124.1 (CH), 121.5 (CH), 118.5 117.9 (CH_2), 110.1 109.7 (CH), 55.4 55.6 (CH), 40.3 39.9 (CH_2); Anal. Calcd for $C_{19}H_{17}NO_2$: C, 78.33; H, 5.88; N, 4.18. Found: C, 78.12; H, 5.71; N, 4.47.

2.3.5. 1-Allyl-4-bromo-2-phenoxycarbonyl-1,2-dihydroisoquinoline (9b). IR (neat) 1729 1396, 1321, 1197 cm^{-1}; ^1H NMR ($CDCl_3$, a mixture of rotamers) δ 7.53 7.52 (d, 1H, J=7 Hz), 7.08–7.42 (m, 9H), 5.81 (m, 1H), 5.50 5.46 (t, 1H, J=7 Hz), 5.02–5.14 (m, 2H), 2.40–2.63 (m, 2H); ^{13}C NMR ($CDCl_3$, a mixture of rotamers) δ 151.3, 150.8 (C), 150.7, 150.6 (C), 133.4, 133.1 (CH), 132.5, 132.4 (C), 129.5 (CH), 129.4 129.1 (C), 128.5, 128.1 (CH), 128.3, 128.1 (CH), 126.2, 126.0 (CH), 125.9 (CH), 125.5, 125.0 (CH), 125.1, 124.9 (CH), 121.4 121.3 (CH), 119.0, 118.4 (CH_2), 105.4, 105.0 (C), 56.8, 55.9 (CH), 40.4, 40.0 (CH_2); Anal. Calcd for $C_{19}H_{16}BrNO_2$: C, 61.64; H, 4.36; N, 3.78. Found: C, 61.53; H, 4.28; N, 3.66.

2.3.6. 1-Allyl-5-nitro-2-phenoxycarbonyl-1,2-dihydroisoquinoline (9c). Mp 111°C; IR (Nujol) 1724 1527, 1279, 1200, 746 cm^{-1}; ^1H NMR ($CDCl_3$, a mixture of rotamers) δ 7.91 (m, 1H), 7.13–7.43 (m, 8H), 6.77 6.71 (d, 1H, J=9 Hz), 5.79 (m, 1H), 5.57 5.52 (t, 1H, J=7 Hz), 5.14 5.10 (d, 1H, J=10 Hz), 5.07 5.02 (d, 1H, J=17 Hz), 2.42–2.66 (m, 2H); ^{13}C NMR ($CDCl_3$, a mixture of rotamers) δ 151.5, 151.0 (C), 150.7, 150.5 (C), 144.7 (C), 134.5 134.4 (CH), 132.9, 132.6 (CH), 131.5 131.2 (CH), 129.5 129.4 (CH), 129.3, 128.5 (CH), 126.7, 126.6 (CH), 126.1, 126.0 (CH), 125.3 125.0 (C), 124.5, 124.3 (CH), 121.4, 121.3 (CH), 119.6, 119.0 (CH_2), 103.9, 103.7 (CH), 56.3, 55.4 (CH), 39.7, 39.3 (CH_2); Anal. Calcd for $C_{19}H_{16}N_2O_4$: C, 67.85; H, 4.79; N, 8.33. Found: C, 67.73; H, 4.66; N, 8.27.

2.3.7. (3S^*,9S^*)-3-Allyl-5-trimethylsilylmethyl-1,2,3,4-tetrahydro-1,4-ethanoisoquinoline (10). To a solution of **8a** (1160 mg, 2.9 mmol) in 2-propanol (55 mL) was added 28.2 mL of 7.5 M aqueous KOH (212 mmol) at rt. The reaction mixture was heated at reflux for 6 days, cooled to rt, and concentrated under vaccuo. The aqueous layer was extracted with ether (55 mL) four times. The combined organic layer was washed with brine and dried (K_2CO_3) and the solvent was evaporated. The crude product was purified by Kugel–Rohr distillation to afford **10** (596 mg, 73%): bp 140°C/0.5 mmHg; IR (neat) 2951, 1250, 856, 835, 756 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.05–7.21 (m, 4H), 5.66 (m, 1H), 4.96 (d, 1H, J=10 Hz), 4.88 (d, 1H, J=17 Hz), 3.86 (s, 1H), 3.20 (t, 1H, J=7 Hz), 2.69 (s, 1H), 2.34 (m, 1H), 2.10 (m, 1H), 1.63 (m, 1H), 1.52 (m, 1H), 1.47 (br, 1H), 0.90 (m, 1H), 0.38 (dd, 1H, J=5, 15 Hz), 0.01 (d, 1H, J=15 Hz), −0.03 (s, 9H); ^{13}C NMR ($CDCl_3$) δ 143.0 (C), 136.5 (C), 134.9 (CH), 127.5 (CH), 126.1 (CH), 126.0 (CH), 121.0 (CH), 116.8 (CH_2), 56.4 (CH), 51.1 (CH), 46.8 (CH), 40.8 (CH_2), 37.3 (CH_2), 32.3 (CH), 25.4 (CH_2), −0.8 (CH_3); Anal. Calcd for $C_{18}H_{27}NSi$: C, 75.73; H, 9.53; N, 4.91. Found: C, 75.97; H, 9.52; N, 4.83.

2.3.8. 1-Methallyl-2-phenoxycarbonyl-1,2-dihydroisoquinoline (13a). IR (neat) 1727, 1356, 1329, 1201, 777, 746 cm^{-1}; ^1H NMR ($CDCl_3$, a mixture of rotamers) δ 7.43 (m, 2H), 7.14–7.31 (m, 7H), 7.07 (d, 1H, J=8 Hz), 6.12 6.04 (d, 1H, J=8 Hz), 5.62 (m, 1H), 4.98 4.90 (s, 1H), 4.77 4.71 (s, 1H), 2.73 2.62 (dd, 1H, J=9, 13 Hz), 2.24 2.17 (dd, 1H, J=5, 13 Hz), 1.92 1.91 (s, 3H); ^{13}C NMR ($CDCl_3$, a mixture of rotamers) δ 152.1 151.4 (C), 151.2 151.0 (C), 141.6 140.8 (C), 132.9 132.8 (C), 130.2 129.8 (C), 129.3 129.2 (CH), 127.8 127.6 (CH), 127.0 126.9 (CH), 126.2 126.0 (CH), 125.6 125.5 (CH), 125.0 124.8 (CH), 124.6 123.9 (CH), 121.5 121.3 (CH), 114.9 114.1 (CH_2), 110.2 109.8 (CH), 55.3 54.6 (CH), 43.7 43.3 (CH_2), 22.5 22.4 (CH_3); Anal. Calcd for $C_{20}H_{19}NO_2$: C, 78.66; H, 6.27; N, 4.59. Found: C, 78.45; H, 6.22; N, 4.32.

2.3.9. 1-(2-Chloromethyl-2-propenyl)-2-phenoxycarbonyl-1,2-dihydroisoquinoline (13b). IR (neat) 1728, 1360, 1331, 1236, 1203, 748 cm^{-1}; ^1H NMR ($CDCl_3$, a mixture of rotamers) δ 7.13–7.47 (m, 9H), 7.05 (d, 1H, J=8 Hz), 6.14 6.06 (d, 1H, J=8 Hz), 5.61 (m, 1H), 5.35 5.28 (s, 1H), 5.03 5.00 (s, 1H), 4.36 4.19 (d, 1H, J=12 Hz), 4.11 (d, 1H, J=12 Hz), 2.72 (m, 1H), 2.53 (m, 1H); ^{13}C NMR ($CDCl_3$, a mixture of rotamers) δ 151.9 151.6 (C), 150.8 150.6 (C), 141.5 140.3 (C), 132.3 132.1 (C), 129.9 129.6 (C), 129.5 129.4 (CH), 129.3 (CH), 128.0 127.9 (CH), 127.3 127.0 (CH), 126.2 126.1 (CH), 125.8 125.7 (CH), 125.1, 124.9 (CH), 124.2, 123.6 (CH), 121.4 (CH), 121.3 120.8 (CH), 119.0 118.1 (CH_2), 110.4 110.1 (CH), 55.0 54.1 (CH), 47.6 (CH_2), 38.6 38.5 (CH_2); Anal. Calcd for $C_{20}H_{18}ClNO_2$: C, 70.69; H, 5.34; N, 4.12. Found: C, 70.68; H, 5.33; N, 4.07.

2.3.10. 1-(2-Hydroxymethyl-2-propenyl)-2-phenoxycarbonyl-1, 2-dihydroisoquinoline (13c). Mp 118–120°C; IR (neat) 3446, 1691, 1394, 1205, 734 cm^{-1}; ^1H NMR ($CDCl_3$, a mixture of rotamers) δ 7.06–7.38 (m, 9H), 7.00 (d, 1H, J=7 Hz), 6.06 6.03(d, 1H, J=8 Hz), 5.58 5.52 (dd, 1H, J=5, 10 Hz), 5.20 5.15 (s, 1H), 4.87 (s, 1H), 4.14 (m, 2H), 2.94 (br, 1H), 2.59 (m, 1H), 2.23 (m, 1H); ^{13}C NMR ($CDCl_3$, a mixture of rotamers) δ 152.3 152.1 (C), 150.8 150.7 (C), 145.1 144.0 (C), 132.9 132.6 (C), 129.9 129.3 (C), 129.4 129.3 (CH), 127.9 127.8 (CH), 127.4 127.0 (CH), 126.1 126.0 (CH), 125.8 (CH), 125.1 125.0 (CH), 124.3 123.3 (CH), 121.4 121.3 (CH), 114.5, 114.2 (CH_2), 110.3 (CH), 67.0 65.4 (CH_2), 55.4 (CH), 39.7 38.5 (CH_2); Anal. Calcd for $C_{20}H_{19}NO_3$: C, 74.75; H, 5.96; N, 4.36. Found: C, 74.59; H, 5.99; N, 4.12.

2.3.11. (3S^*,9S^*)-3-Allyl-5-dimethylphenylsilylmethyl-2-phenoxycarbonyl-1,2,3,4-tetrahydro-1,4-ethanoisoquinoline (14). To a solution of isoquinoline (**7a**, 129 mg, 1.0 mmol) in dry CH_3NO_2 (2 mL) were added $ClCO_2Ph$ (236 mg, 1.5 mmol) and AgOTf (26 mg, 0.1 mmol) at rt. The reaction mixture was stirred at rt for 30 min. To the reaction mixture was added allyldimethylphenylsilane (**2b**, 440 mg, 2.5 mmol) under ice-cooling and the mixture was stirred at rt for 24 h. Ether (5 mL) and sat. aqueous $NaHCO_3$ (3 mL) were added, and the organic layer was separated. The aqueous layer was extracted with ether (5 mL×5). The combined organic layer was dried (Na_2SO_4) and the solvent was evaporated. The crude product was purified by chromatography on silica gel (hexane–AcOEt as the eluent) to afford **14** (417 mg, 89%): IR (neat) 1712, 1392, 1205, 733 cm^{-1}; ^1H NMR ($CDCl_3$, a mixture of rotamers) δ 7.11–7.58 (m, 14H), 5.74 (m, 1H), 5.31 5.28 (d, 1H, J=3 Hz), 5.13 (d, 1H, J=10 Hz), 5.02 (dd, 1H, J=6, 17 Hz), 3.99 3.94 (td, 1H, J=3, 10 Hz), 3.06 (m, 1H), 2.57 (m, 2H), 2.26 (m, 1H), 1.48 1.38 (m, 1H), 1.01 0.95 (dd, 1H, J=5, 12 Hz), 0.83 (m, 1H), 0.48 (dd, 1H, J=9, 14 Hz), 0.41 (s, 3H), 0.37 0.36 (s, 3H); ^{13}C NMR ($CDCl_3$, a mixture of rotamers) δ 153.9 153.3 (C), 151.3 151.2 (C), 139.0 138.9 (C), 138.9 138.8 (C), 136.8 136.5 (C), 134.2 134.0 (CH), 133.4 (CH), 129.1 (CH), 128.9 (CH), 127.8

127.7 (CH), 127.6 127.4 (CH), 127.4 127.2 (CH), 126.7 126.6 (CH), 125.1 125.0 (CH), 122.9 122.7 (CH), 121.7 121.5 (CH), 117.5, 117.4 (CH_2), 59.3 58.8 (CH), 51.9 51.2 (CH), 45.4 44.9 (CH), 38.6 37.7 (CH_2), 37.6 36.2 (CH_2), 30.9 (CH), 24.7 24.6 (CH2), −2.0, −2.10 (CH_3), −2.7 (CH_3); Anal. Calcd for $C_{30}H_{33}NO_2Si$: C, 77.05; H, 7.11; N, 2.99. Found: C, 77.01; H, 7.07; N, 2.77.

2.3.12. (3*S,9*S**)-5-Dimethylphenylsilylmethyl-2-phenoxycarbonyl-3-propyl-1,2,3,4-tetrahydro-1,4-ethanoisoquinoline (15).** To a solution of **14** (4627 mg, 9.9 mmol) in MeOH (120 mL) was added 5% Pd–C (361 mg) at rt. The reaction mixture was stirred vigorously under an atmosphere of H_2 at rt for 4 h. The catalyst was removed by filtration and the filtrate was dried (Na_2SO_4) and the solvent was evaporated. The residue was purified by chromatography on silica gel (CH_2Cl_2 as the eluent) to afford **15** (4636 mg, 100%): IR (neat) 1714, 1390, 1207, 737 cm^{-1}; ^1H NMR ($CDCl_3$, a mixture of rotamers) δ 7.01–7.49 (m, 14H), 5.19 5.14 (d, 1H, J=3 Hz), 3.79 (m, 1H), 2.88 (s, 1H), 2.43 (m, 1H), 2.15 (m, 1H), 1.53 (m, 1H), 1.20 (m, 2H), 0.89 0.83 (dd, 1H, J=5, 13 Hz), 0.79–0.67 (m, 3H), 0.62, 0.52 (m, 1H), 0.38 (m, 1H), 0.32 0.31 (s, 3H), 0.27 0.26 (s, 3H); ^{13}C NMR ($CDCl_3$, a mixture of rotamers) δ 154.1 153.5 (C), 151.4 151.3 (C), 139.2 139.1 (C), 139.1 138.9 (C), 137.2 136.9 (C), 133.5 (CH), 129.2 (CH), 129.0 (CH), 127.9 127.8 (CH), 127.4,127.3 (CH), 127.3 127.2 (CH), 126.7 126.6 (CH), 125.1 125.0 (CH), 123.0 122.8 (CH), 121.8 121.6 (CH), 59.8 59.3 (CH), 52.0 51.2 (CH), 45.7 45.3 (CH), 38.8 37.9 (CH_2), 35.2 33.8 (CH_2), 31.0 (CH), 24.9 24.8 (CH_2), 18.6 (CH_2), 13.9 13.8 (CH_3), −2.0 (CH_3), −2.6 (CH_3); Anal. Calcd for $C_{30}H_{35}NO_2Si$: C, 76.72; H, 7.51; N, 2.98. Found: C, 76.95; H, 7.58; N, 2.98.

2.3.13. (3*S,9*S**)-5-Hydroxymethyl-2-phenoxycarbonyl-3-propyl-1,2,3,4-tetrahydro-1,4-ethanoisoquinoline (16).** To a solution of **15** (1564 mg, 3.3 mmol) in CH_2Cl_2 (10 mL) was added HBF_4-Et_2O (0.866 mL, 5.0 mmol) at 0°C. The reaction mixture was stirred at rt for 24 h, quenched with H_2O (10 mL), and diluted with CH_2Cl_2 (30 mL) and the organic layer was separated. The aqueous layer was extracted with CH_2Cl_2. The combined organic layer was dried (Na_2SO_4) and the solvent was evaporated to afford the fluorosilane derivative which was used without purification. To a solution of the fluorosilane derivative (1338 mg, 3.3 mmol) and anhydrous KF (415 mg, 7.2 mmol) in DMF (12.5 mL) was added MCPBA (2564 mg, 70%, 10.4 mmol) in DMF (10.5 mL) at rt. The reaction mixture was stirred at rt for 24 h, diluted with CH_2Cl_2, and washed successively with sat. aqueous $Na_2S_2O_3$, sat. aqueous Na_2CO_3, and brine. The organic layer was separated and dried (Na_2SO_4), and the solvent was evaporated. The residue was purified by chromatography on silica gel (hexane–AcOEt as the eluent) to afford **16** (675 mg, 58%): IR (neat) 3440, 1697, 1396, 1205, 1041, 737 cm^{-1}; ^1H NMR ($CDCl_3$, a mixture of rotamers) δ 7.10–7.35 (m, 9H), 5.28 5.21 (d, 1H, J=3 Hz), 3.90 3.83 (m, 1H), 3.40 3.34 (s, 1H), 3.06 (m, 1H), 2.97 (br, 1H), 2.80 (m, 1H), 2.33 (m, 1H), 2.18 (m, 1H), 1.58 (m, 1H), 1.35 (m, 1H), 1.24 (m, 1H), 0.80 (m, 3H), 0.73 (m, 1H), 0.64 (m, 1H); ^{13}C NMR ($CDCl_3$, a mixture of rotamers) δ 154.0 153.3 (C), 151.1 151.0 (C), 138.5 138.4 (C), 136.8 136.5 (C), 129.0 (CH), 127.5, 127.4 (CH), 126.9, 126.8 (CH), 126.7, 126.6 (CH), 125.0 (CH), 122.9 122.8 (CH), 121.6 121.4 (CH), 65.1 65.0 (CH_2), 59.4 59.0 (CH), 51.5 50.8 (CH), 38.9 38.7 (CH), 37.0 (CH), 35.1 33.8 (CH_2), 31.7 30.8 (CH_2), 18.5 18.4 (CH_2), 13.7 (CH_3); Anal. Calcd for $C_{22}H_{25}NO_3$: C, 75.19; H, 7.17; N, 3.99. Found: C, 74.96; H, 7.24; N, 4.00.

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