Radical Alkylation of Heteroaromatic Bases with Polysilane Compounds

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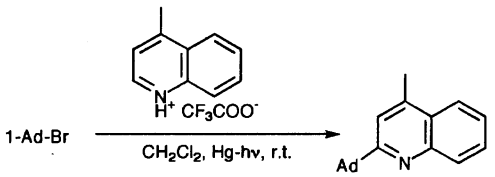
Alkyl halides were treated with protonated heteroaromatic bases in the presence of 1,1,1,3,3,3-hexamethyl-2,2-bis(trimethylsilyl)trisilane under photochemical conditions to give the corresponding alkylated heteroaromatic bases easily. The alkylation of protonated heteroaromatic bases with 1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilane proceeded effectively under photochemical conditions or thermal conditions. The present method is the first report on the alkylation of heteroaromatic bases under non-oxidative conditions.

Recently, free radical reactions in organic synthesis have become increasingly important.[1] Especially, the carbon–carbon bond forming reactions via intramolecular or intermolecular radical pathways are one of the superior methods in organic synthesis.[2] Among these reactions, the alkylation reactions of heteroaromatic bases are useful and interesting, because alkylated heteroaromatic bases are important fragments in organic synthesis and in potent biological active compounds; furthermore, the radical alkylation of heteroaromatic bases shows the opposite reactivity and selectivity to ionic substitution like the Friedel–Crafts reaction.[3] Therefore, the radical substitution reactions onto heteroaromatic bases have been extensively studied, especially by Minisci.[3—6] However, most of the reactions have been carried out under oxidative conditions using peroxide. To our knowledge, only a few methods such as the Barton (-type) reactions are known for the alkylation of heteroaromatic bases under non-oxidative conditions though the starting materials are carboxylic acids.[5,6] Tributylstannane and hexabutyldistannane have been most frequently used as radical mediators in synthetic chemistry.[7] However, organotin compounds are toxic, and generally function as a reducing agent; moreover, complete removal of the tin species from the reaction mixture is difficult. Thus, there have been few studies on the alkylation of heteroaromatic bases by tin radical mediators.[8] Here, as a part of our study on the non-oxidative alkylation of aromatic bases,[9] we report full details on the alkylation of heteroaromatic bases using polysilane compounds.

Results and Discussion

Photochemical Reactions. Organotin compounds such as hexabutyldistannane and tributylstannane have been utilized extensively as radical mediators.[7] Although silicon and tin atoms are the same 14 group elements, there has been little research on organosilane compounds as radical mediators.[10] 1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilane was recently reported as a valuable reagent for radical-mediated organic synthesis, i.e., reduction and carbon–carbon bond forming reactions,[10] however, it has never been used as a radical alkylation reagent onto heteroaromatic bases with alkyl halides. The physical properties of 1,1,1,3,3,3-hexamethyl-2,2-bis(trimethylsilyl)trisilane, which was first synthesized in 1967,[11] have been studied in detail.[12] However, there has been little study on its use as a reagent in organic synthesis. Against this backgrounds, we carried out the alkylation of 4-methylquinoline with adamantyl halides in the presence of these polysilane compounds under irradiation with a high-pressure mercury lamp, and the reactivities of these organosilane compounds and organotin compounds in the alkylation of 4-methylquinoline with adamantyl halides under the same irradiation conditions were compared (Table 1). The results showed that polysilane compounds, such as 1,1,1,3,3,3-hexamethyl-2,2-bis(trimethylsilyl)trisilane and 1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilane, were excellent reagents for the alkylation of heteroaromatic bases. Here, it is very

Table 1. Relative Reactivities with Non-Oxidative Reagents[a)]



Entry	Reagent[b)]	Yield/%
1	$(TMS)_4Si$	83(88)[c)]
2	$(TMS)_3SiH$	73(89)[c)]
3	$(TMS)_3SiBr$	28
4	$(PhMe_2Si)_2$	13[d)]
5	$(Me_3Si)_2$	2
6	$(Bu_3Sn)_2$	16[e)](74)[c,e)]
7	Bu_3SnH-AIBN	9[e)](51)[c,e)]
8	Ph_2SiH_2-AIBN	4

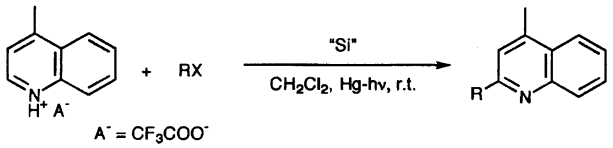
a) Hg-$h\nu$: High pressure mercury lamp (400 W). Entries 1—6: Reaction was carried out with 1-Ad-Br (0.5 mmol), salt (2.5 mmol), and reagent (1.0 mmol) in dichloromethane (6 ml). Entries 7 and 8: Reaction was carried out with 1-Ad-Br (0.5 mmol), salt (2.5 mmol), reagent (1.0 mmol), and AIBN (1.0 mmol) in dichloromethane (6 ml). b) Based on alkyl halide, 2.0 molar amounts of reagent were used. c) Adamantyl iodide was used instead of adamantyl bromide. d) 2,4-Dimethylquinoline was obtained in 8% yield as a by-product. e) 2-Butyl-4-methylquinoline was obtained in 5—7% yield as a by-product.

important to note that the above two polysilane compounds gave the alkylated products in good yields in both alkyl iodide and alkyl bromide as a starting material, since the starting material in the oxidative alkylation of heteroaromatic bases was alkyl iodides alone[3] among alkyl halides.

Initially, in the reaction with 1,1,1,3,3,3-hexamethyl-2,2-bis(trimethylsilyl)trisilane, we thought that 2-halo-1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilane or 1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilane should be formed as a by-product, and as expected, formation of small amounts of 2-halo-1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilane (10—20%) and 1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilane (trace) was identified by gas chromatography, though the former silane compound was easily hydrolyzed on silica gel by column chromatography. However, the amount of 1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilane was small. This results suggested that 1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilane formed from 1,1,1,3,3,3-hexamethyl-2,2-bis(trimethylsilyl)trisilane, might function as an alkylation reagent again in the reaction of adamantyl bromide with heteroaromatic bases under photochemical conditions. In practice, 1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilane showed equal reactivity with 1,1,1,3,3,3-hexamethyl-2,2-bis(trimethylsilyl)trisilane as shown in Table 1, and further, even 2-bromo-1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilane also played a minor role as a radical initiator. Other reagents such as diphenyltetramethyldisilane, hexamethyldisilane, hexabutyldistannane, tributylstannane, and diphenylsilane did not work as effective alkylation reagents with adamantyl bromide, though some of them functioned as moderate alkylation reagents with adamantyl iodide. Other alkyl groups were introduced into 4-methylquinoline in the presence of 1,1,1,3,3,3-hexamethyl-2,2-bis(trimethylsilyl)trisilane or 1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilane under the same irradiation conditions, and the results are summarized in Table 2. The reactivities of alkyl halides increased in the following orders; primary<secondary<tertiary alkyl groups and alkyl chloride≪alkyl bromide<alkyl iodide (Entries 1—6 in Table 2; Alkyl chloride did not react at all). Menthyl, cholestanyl, benzyl, and hydroxyethyl groups could be also introduced into 2-position of 4-methylquinoline as shown in Table 2 (Entries 7—10). Moreover, other heteroaromatic bases such as benzothiazole, methyl isonicotinate, 4-cyanopyridine, and 5-(2-acetoxyethyl)-4-methylthiazole, could be alkylated with adamantyl bromide in moderate yields (Table 3). The present reactions are applicable to other substrates and their utilization for the synthesis of *C*-nucleoside by the coupling of anomeric sugar radicals and heteroaromatic bases can be expected.

The following experiments were carried out to elucidate the reaction mechanism. In the reaction with cyclopropylmethyl bromide in the presence of polysilane compounds under photochemical conditions, only the ring-opened compound was obtained as shown in Scheme 1. This could be explained as follows: The cyclopropylmethyl radical formed underwent rapid ring-opening[13] followed by the trapping of the formed 3-butenyl radical with protonated 4-methylquinoline to give 2-(3-butenyl)-4-methylquinoline as a sole product.

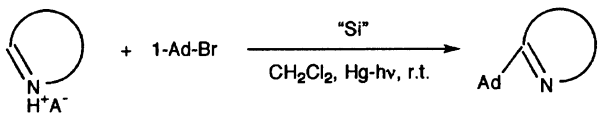
Table 2. Photostimulated Alkylation of 4-Methylquinoline[a]

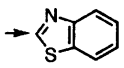
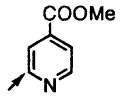
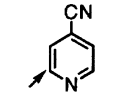
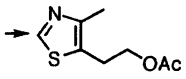


Entry	RX	Yields/%	
		$(TMS)_4Si$	$(TMS)_3SiH$
1	1-Ad-I	88	89
2	1-Ad-Br	83	73
3	*c*-$C_6H_{11}I$	63	76
4	*c*-$C_6H_{11}Br$	61	44
5	*n*-$C_8H_{17}I$	40	63
6	*n*-$C_8H_{17}Br$	48	33
7	$PhCH_2Br$	48	50
8	$HOCH_2CH_2Br$	32	30
9	Menthyl Bromide	60	56
10	Cholestanyl Bromide	22	58

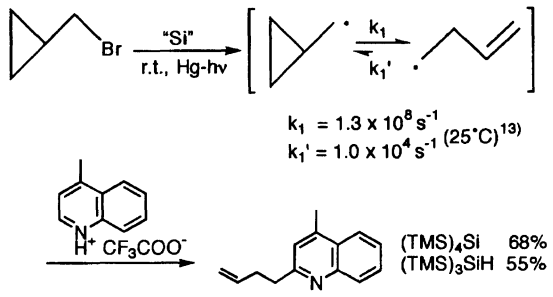
a) Reaction was carried out with RX (0.5 mmol), salt (2.5 mmol), and silane compound (1.0 mmol) in dichloromethane (6 ml).

Table 3. Photostimulated Alkylation of Other Heteroaromatic Bases[a]



Entry	Base	Yields/%	
		$(TMS)_4Si$	$(TMS)_3SiH$
1		78	35
2		23	35
3		27	26
4		20	30

→: C–C Bond forming position. a) Reaction was carried out with 1-Ad-Br (0.5 mmol), salt (2.5 mmol), silane compound (1.0 mmol) in dichloromethane (6 ml).



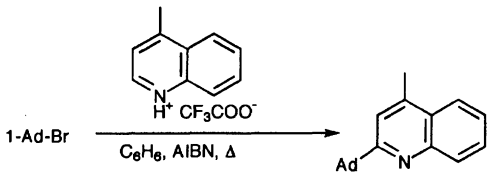
Scheme 1.

The reduction of adamantyl bromide was attempted in the presence of 1,1,1,3,3,3-hexamethyl-2,2-bis(trimethylsilyl)trisilane and a hydrogen donor such as 1,4-cyclohexadiene under the same irradiation conditions with a high-pressure mercury lamp. However, the reaction did not occur and the starting silane compound was recovered quantitatively. This result suggested that a heteroaromatic base was necessary for the generation of silyl radical.

Previously, the addition of allyl group to 2-phenylpyrrolium with allylsilane[14] and the ipso substitution of cyanobenzene with tetraalkylsilanes[15] under photochemical conditions, which proceeded via a single electron transfer from silane compounds to 2-phenylpyrrolium and cyanobenzene, respectively were reported. Thus we deduced that this reaction would proceed via a single electron transfer (SET) pathway from polysilanes to protonated heteroaromatic bases. Actually, the alkylation of 4-methylquinoline with adamantyl bromide and 1,1,1,3,3,3-hexamethyl-2,2-bis(trimethylsilyl)trisilane in the presence of an electron transfer inhibitor such as *m*-dinitrobenzene under the same conditions, was retarded markedly, and only a trace amount of product was obtained. Based on these results, the reaction mechanism is postulated as shown in Scheme 2. First, one electron transfer from the polysilane compound to the heteroaromatic base excited by irradiation to form 2,2,2-trimethyl-1,1-bis(trimethylsilyl)disilanyl radical or trimethylsilyl radical. Then halogen atom abstraction by the silyl radical[10] gives the corresponding alkyl radicals which further react with the protonated heteroaromatic base resulting in the formation of the alkylated heteroaromatic base, via the oxidation of an amine intermediate by silyl cation or the oxidation of an aminium radical intermediate by silyl radical species. Two silyl species, 1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilane and 2-halo-1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilane, are formed as by-products in this reaction.

Reactions under Thermal Conditions. In the presence of 1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilane and α,α'-azobisisobutyronitrile (AIBN), a mixture of heteroaromatic base and alkyl halide was heated in benzene or toluene at refluxing temperature to give the corresponding alkylated heteroaromatic bases as shown in Table 4. This result is very surprising, because 1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilane has been believed to be, like tributylstannane, a reducing agent.[10] 1,1,1,3,3,3-hexamethyl-2,2-bis(trimethylsilyl)trisilane did not react under these thermal conditions because of its high thermal stability. When the reaction was carried out in the presence of tributylstannane or other silane compounds instead of 1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilane, the yield of the alkylated product was poor. Other alkyl groups were also introduced into 2-position of 4-methylquinoline in the presence of 1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilane under the thermal conditions and the results are shown in Table 5. Tertiary alkyl groups are the most reactive, and primary groups are less reactive (Entries 1—6 in Table 5). There was very little difference in the reactivities between alkyl iodides and alkyl bromides (Entries 1—6 in Table 5), while alkyl chloride did not react at all. Menthyl, cholestanyl, and

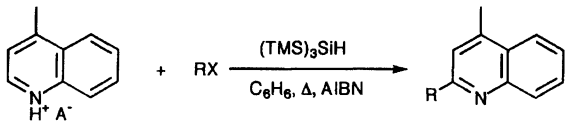
Table 4. Relative Reactivities under Thermal Conditions[a]



Entry	Reagent	Yield/%
1	(TMS)$_3$SiH	90
2	(TMS)$_3$SiBr	11
3	Bu$_3$SnH	4[b]
4	Ph$_2$SiH$_2$	9

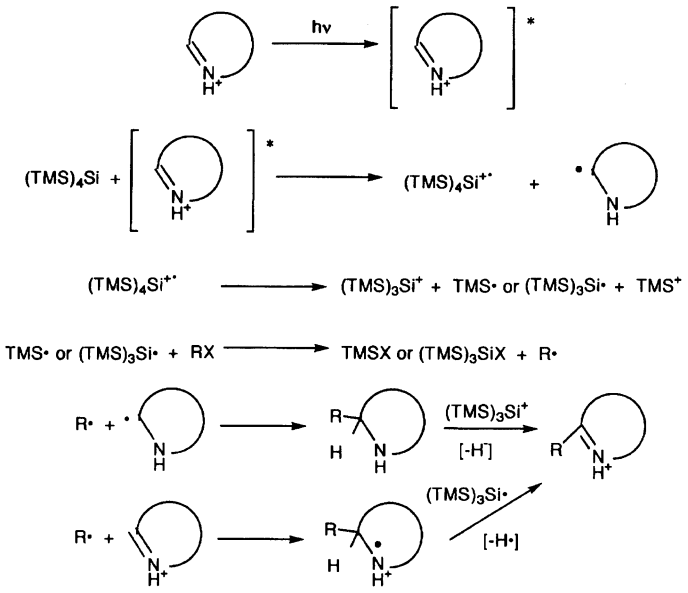
a) Reaction was carried out with 1-Ad-Br (0.5 mmol), salt (2.5 mmol), AIBN (1.0 mmol), and reagent (1.0 mmol) in benzene (6 ml). b) 2-Butyl-4-methylquinoline was obtained in 8% yield as a by-product.

Table 5. Alkylation of 4-Methylquinoline[a]



Entry	RX	Yield/%
1	1-Ad-I	86
2	1-Ad-Br	90
3	*c*-C$_6$H$_{11}$I	76
4	*c*-C$_6$H$_{11}$Br	79
5	*n*-C$_8$H$_{17}$I	44
6	*n*-C$_8$H$_{17}$Br	43
7	PhCH$_2$Br	45
8	Menthyl bromide	30
9	Cholestanyl bromide	59

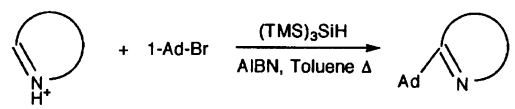
a) Reaction was carried out with RX (0.5 mmol), salt (2.5 mmol), AIBN (1.0 mmol), and silane compound (1.0 mmol) in benzene (6 ml).

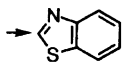
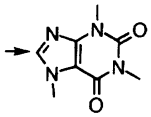
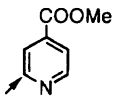
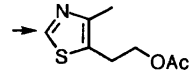


Scheme 2. Reaction pathway.

benzyl bromides also reacted with 4-methylquinoline to give the corresponding products in moderated yields. Other heteroaromatic bases such as benzothiazole, caffeine, methyl isonicotinate, 4-cyanopyridine, and 5-(2-acetoxyethyl)-4-methylthiazole could be alkylated with adamantyl bromide in moderated yields as shown in Table 6. In the thermal reaction there was less difference in the reactivities among heteroaromatic bases as compared with the photochemical reaction.

Table 6. Alkylation of Other Heteroaromatic Bases[a)]

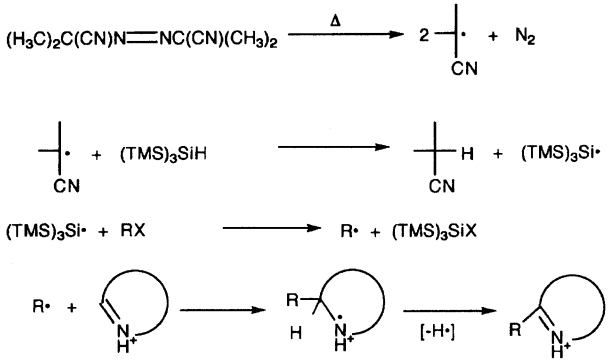


Entry	Base	Yield/%
1		83
2		47
3		62
4		57
5		45

→: C–C Bond forming position. a) Reaction was carried out with 1-Ad-Br (0.5 mmol), salt (2.5 mmol), AIBN (1.0 mmol), and silane compound (1.0 mmol) in toluene (6 ml).

The reaction mechanism is deduced as shown in Scheme 3. During this reaction, 2-halo-1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilane was also obtained together with the alkylation product. However, the present alkylation reaction of protonated heteroaromatic bases with 1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilane did not occur without AIBN, and the addition of a catalytic amount of AIBN gave only a trace amount of alkylated heteroaromatic bases. Thus, this reaction requires one or two molar amounts of AIBN based on alkyl halides to get the product in moderate yields. This means that the isobutyronitrile radical formed abstracts not only a hydrogen atom from 1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trislane to give the corresponding 2,2,2-trimethyl-1,1-bis(trimethylsilyl)disilanyl radical but also a hydrogen atom from the aminium radical intermediate to give the alkylated product.

In conclusion, 1,1,1,3,3,3-hexamethyl-2,2-bis(trimethylsilyl)trisilane and 1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilane are useful reagents for the alkylation of heteroaromatic bases under thermal or photochemical



Scheme 3.

conditions in view of their availability, non-toxicity, and non-oxidant properties, and both alkyl iodides and bromides can be used as the alkylation sources.

Experimental

Microanalyses were performed with a Perkin–Elmer 240 elemental analyser at the Chemical Analysis Center of Chiba University. IR and ^{1}H NMR spectra were measured with Hitachi 215, JEOL-MH-100, and JEOL-JNM-FX 270 spectrometers, respectively. Mass spectra were measured with Hitachi M-60 and JEOL-HX-110. Wako gel C-200 was used for column chromatography, Kieselgel 60 F_{254} (Merck) was used for TLC, and Wakogel B-5F was used for preparative (pTLC).

Materials. Most of the alkyl halides, tin compounds, heteroaromatic bases, and simple organic chemicals were commercially available. Menthyl bromide and cholestanyl bromide were prepared by the reaction of the corresponding alcohols with phosphorus tribromide. Adamantyl iodide was prepared from the corresponding alcohol by hydriodic acid. The following compounds were prepared according to the procedures described in the literature: 1,1,1,3,3,3-hexamethyl-2,2-bis(trimethylsilyl)trisilane,[16] 1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilane,[17] and 2-bromo-1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilane.[17]

General Procedure for the Alkylation of Heteroaromatic Bases under Photochemical Conditions. All reactions were carried out in pyrex tubes. To a solution of salt (2.5 mmol) of trifluoroacetic acid and heteroaromatic base, and alkyl halide (0.5 mmol) in dry dichloromethane (6 ml) was added 1,1,1,3,3,3-hexamethyl-2,2-bis(trimethylsilyl)trisilane (1 mmol) under argon atmosphere. The solution was irradiated with a high-pressure mercury lamp (400 W, Shigemi AHH400S) for 14 h at 30 °C. The resulting solution was quenched with saturated aqueous sodium hydrogen carbonate. Then the organic layer was extracted with dichloromethane and dried over Na_2SO_4. After removal of the solvent under reduced pressure, the residual oil was purified by pTLC on silica gel.

2-(1-Adamantyl)-4-methylquinoline: Mp 120.0—122.0 °C; IR (KBr) 3040, 2880, 2840, 1590, 1440, 760 cm^{-1}; ^{1}H NMR (100 MHz, CCl_4) δ=1.80 (6H, s, adamantyl), 2.07 (9H, s, adamantyl), 2.60 (3H, s, CH_3), 7.15 (1H, s, H-3), 7.30—7.60 (2H, m, H-6 and 7), 7.80 (1H, d, J=9.0 Hz, H-5), 7.90 (1H, d, J=9.0 Hz, H-8); Anal. ($C_{20}H_{23}N$) C, H, N.

2-Cyclohexyl-4-methylquinoline: Oil; IR (neat) 3050, 2910, 2845, 1600, 1450, 770 cm^{-1}; ^{1}H NMR (100 MHz, CCl_4) δ=1.10—2.00 (10H, m, cyclohexyl), 2.47 (3H, s, CH_3), 2.30—2.88 (1H, m, aromatic-CH–), 6.75 (1H, s, H-3), 7.00—7.40 (2H, m, H-6 and 7), 7.50 (1H, d, J=9.0 Hz, H-5), 7.75 (1H, d, J=9.0 Hz, H-8); Anal. ($C_{16}H_{19}N$) C, H, N.

4-Methyl-2-octylquinoline: Oil; IR (neat) 2890, 2810, 1595, 760 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ=0.88 (3H, t, J=6.6 Hz, octyl-CH_3), 1.26—1.81 (12H, m, –$(CH_2)_6$–), 2.70 (3H, s, CH_3), 2.92 (2H, t, J=4.0 Hz, aromatic-CH_2–), 7.17 (1H, s, H-3), 7.52 (1H, ddd, J=8.9, 7.5, and 1.4 Hz, H-6), 7.68 (1H, ddd, J=9.0, 7.5, and 1.1 Hz, H-7), 7.96 (1H, dd, J=8.9 and 1.1 Hz, H-5), 8.06 (1H, dd, J=9.0 and 1.4 Hz, H-8); Anal. ($C_{18}H_{25}N$) C, H, N.

(–)-2-(*p*-Menth-3-yl)-4-methylquinoline: Oil; $[\alpha]_D^{24}$ –53.13 (c 0.096, $CHCl_3$); IR (neat) 2900, 1595, 1440, 760 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ=0.67 (3H, d, J=6.6 Hz, CH_3), 0.81 (3H, d, J=7.0 Hz, CH_3), 0.86 (3H, d, J=6.6 Hz, CH_3), 1.02—1.98 (10H, m, cyclohexyl), 2.7 (3H, s, CH_3), 7.16 (1H, s, H-3), 7.53 (1H, ddd, J=8.7, 6.8, and 1.4 Hz, H-6), 7.68 (1H, ddd, J=8.7, 6.8, and 1.4 Hz, H-7), 7.96 (1H, dd, J=8.7 and 1.4 Hz, H-5), 8.12 (1H, dd, J=8.7 and 1.4 Hz, H-8). HRMS (FAB): Found: $(M+H)^+$=282.2227. Calcd for $C_{20}H_{27}N$: (M+H)=282.2220. Anal. ($C_{20}H_{27}N$) C, H, N.

2-(3-Cholestanyl)-4-methylquinoline: Mp 182—184 °C; $[\alpha]_D^{24}$ 24.41 (c 0.12, $CHCl_3$); IR (KBr) 2900, 1590, 760 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ=0.67 (3H, s, CH_3), 0.85 (3H, d, J=1.4 Hz, CH_3), 0.88 (3H, d, J=1.4 Hz, CH_3), 0.90 (3H, s, CH_3), 0.93 (3H, s, CH_3), 0.99—2.15 (31H, m), 2.67 (3H, d, J=1.1 Hz, CH_3), 2.91 (1H, m, CH), 7.16 (1H, s, H-3), 7.47 (1H, ddd, J=8.0, 6.8, and 0.8 Hz, H-6), 7.64 (1H, ddd, J=8.0, 6.8 and 0.8 Hz, H-7), 7.92 (1H, dd, J=8.0 and 0.8 Hz, H-5), 8.05 (1H, dd, J=8.0 and 0.8 Hz, H-8); Anal. ($C_{37}H_{55}N$) C, H, N.

2-(2-Hydroxyethyl)-4-methylquinoline: Mp 97.3—97.8 °C (lit,[18] mp 97—98 °C). HRMS (FAB): Found: $(M+H)^+$=188.1079. Calcd for $C_{12}H_{13}ON$: (M+H)=188.1075.

2-(3-Butenyl)-4-methylquinoline: Oil; IR (neat) 2890, 1595, 920, 760 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ=2.52—2.63 (2H, m, CH_2=CHC$\underline{H}_2CH_2$), 2.67 (3H, d, J=0.8 Hz, CH_3), 3.01 (2H, dd, J=8.5 and 7.1 Hz, CH_2=$CHCH_2C\underline{H}_2$), 4.98 (1H, dq, J=10.0 and 2.1 Hz, C$\underline{H}_2$=$CHCH_2CH_2$), 5.08 (1H, dq, J=17.1 and 2.1 Hz, C$\underline{H}_2$=$CHCH_2CH_2$), 5.91 (1H, ddt, J=17.1, 10.0, and 7.1 Hz, CH_2=C$\underline{H}CH_2CH_2$), 7.12 (1H, d, J=0.8 Hz, H-3), 7.49 (1H, ddd, J=5.9, 4.9, and 1.0 Hz, H-6), 7.67 (1H, ddd, J=6.0, 4.9, and 0.9 Hz, H-7), 7.94 (1H, dd, J=5.9 and 0.9 Hz, H-5), 8.05 (1H, dd, J=6.0 and 1.0 Hz, H-8). HRMS (FAB): Found: $(M+H)^+$=198.1281. Calcd for $C_{14}H_{15}N$: (M+H)=198.1283.

2-Benzyl-4-methylquinoline: Mp 74.6—76.2 °C; IR (KBr) 3200, 2950, 1715, 1180 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ=2.60 (3H, s, CH_3), 4.29 (2H, s, –CH_2–), 7.07 (1H, s, H-3), 7.22—7.37 (5H, m, phenyl), 7.52 (1H, ddd, J=8.8, 7.5, and 1.6 Hz, H-6), 7.69 (1H, ddd, J=8.8, 7.5, and 1.1 Hz, H-7), 7.93 (1H, dd, J=8.8 and 1.1 Hz, H-5), 8.11 (1H, d, J=8.8 Hz, H-8). HRMS (FAB): Found: $(M+H)^+$=234.1285. Calcd for $C_{17}H_{15}N$: (M+H)=234.1283.

2-(1-Adamantyl)benzothiazole: Mp 102.3—104.2 °C; IR (KBr) 2900, 2850, 1450, 1370; ^{1}H NMR (100 MHz, CCl_4) δ=1.75 (6H, s, adamantyl), 2.05 (9H, s, adamantyl), 7.10—7.40 (2H, m, H-5 and 6), 7.60—7.90 (2H, m, H-4 and 7); Anal. ($C_{17}H_{19}NS$) C, H, N.

Methyl 2-(1-Adamantyl)isonicotinate: Mp 36.5—38.0 °C; IR (KBr) 2890, 2840, 1725, 1295, 1220, 770 cm^{-1}; ^{1}H NMR (100 MHz, CCl_4) δ=1.60—2.30 (15H, m, adamantyl), 3.90 (3H, s, CH_3), 7.55 (1H, d, J=6.0 Hz, H-5), 7.75 (1H, s, H-3), 8.68 (1H, d, J=6.0 Hz, H-6); Anal. ($C_{17}H_{21}NO_2$) C, H, N.

2-(1-Adamantyl)-4-cyanopyridine: Mp 134.5—136.1 °C; IR (KBr) 2870, 2825, 1580, 1540, 1450, 845 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ=1.60—2.20 (15H, m, adamantyl), 7.25 (1H, d, J=6.0 Hz, H-5), 7.40 (1H, s, H-3), 8.67 (1H, d, J=6.0 Hz, H-6); Anal. ($C_{16}H_{18}N_2$) C, H, N.

5-(2-Acetoxyethyl)-2-(1-adamantyl)-4-methylthiazole: Oil; IR (neat) 2875, 1735, 1445, 1360, 1240, 1050 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ=1.61—2.13 (18H, m, adamantyl and CH_3COO–), 2.33 (3H, s, CH_3), 3.01 (2H, t,

J=3.5 Hz, CH_2), 4.22 (2H, t, J=3.5 Hz, OCH_2). HRMS (FAB): Found: $(M+H)^+$=320.1684. Calcd for $C_{18}H_{25}NO_2S$: (M+H)=320.1684.

1,1,1,3,3,3-Hexamethyl-2-(trimethylsilyl)-2-trisilanol: Oil; IR (neat) 3310, 2900, 1595, 1055, 845, 760 cm^{-1}; ^1H NMR (100 MHz, $CDCl_3$) δ=0.09 (36H, s, CH_3); MS (EI): M^+=264.

General Procedure for the Alkylation of Heteroaromatic Bases under Thermal Conditions. To a solution of salt (2.5 mmol) of trifluoroacetic acid and heteroaromatic base, and alkyl halide (0.5 mmol) in dry benzene (6 ml) were added 1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilane (1.0 mmol) and AIBN (1.0 mmol) under argon atmosphere. The mixture was heated to refluxing temperature for 14 h. After the reaction, the residue was worked up in the usual way.

2-(1-Adamantyl)caffeine: Mp 249—250 °C; IR (KBr) 2850, 1690, 1650, 1415, 640 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ=1.80 (6H, bs, adamantyl), 2.15 (9H, bs, adamantyl), 3.39 (3H, s, CH_3), 3.56 (3H, s, CH_3), 4.16 (3H, s, CH_3); MS (FAB): $(M+H)^+$=329.

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