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SYNTHESIS OF *N*-METHYLPHENANTHRIDINONE DERIVATIVES FUSED WITH A SILACYCLOHEXANE RING BY RADICAL REACTION USING TRIBUTYLTIN HYDRIDE‡

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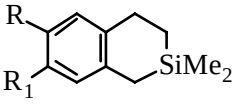
Abstract - Radical reaction of (*N*-methyl-7-bromo-2,2-dimethyl-2-silatetralin-6-ylamino)veratramide (**8a**) and -piperonamides (**8b**) in boiling benzene using tributyltin hydride and AIBN gave two kinds of *N*-methylphenanthridinone derivatives (**15** and **16**), which were cyclized at 6- and 2-positions of aroylic acid moiety. On the other hand, similar reaction of *N*-methyl-*N*-(2-bromoveratryl and 2-bromopiperonyl)-2,2-dimethyl-2-silatetralin-6-carboxamides (**14**) produced *N*-methylphenanthridinone deivatives (**17**) as each sole product, in which cyclization occurred at 5-position of 2-silatetralin moiety.

For the purpose of exploring biologically active organosilicon compounds,[2] we have reported synthesis of 2-silatetralin derivatives[3,4] (**Figure**). As a part of the aim, synthesis of *N*-methylphenanthridinone derivatives containing a silicon atom was examined. The present paper is concerned with synthesis of *N*-methylphenanthridinone derivatives (**15-17**) fused with a silacyclohexane ring starting from 2-silatetralin (9).



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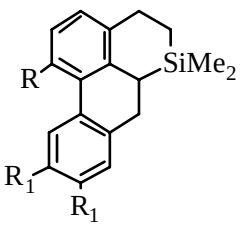
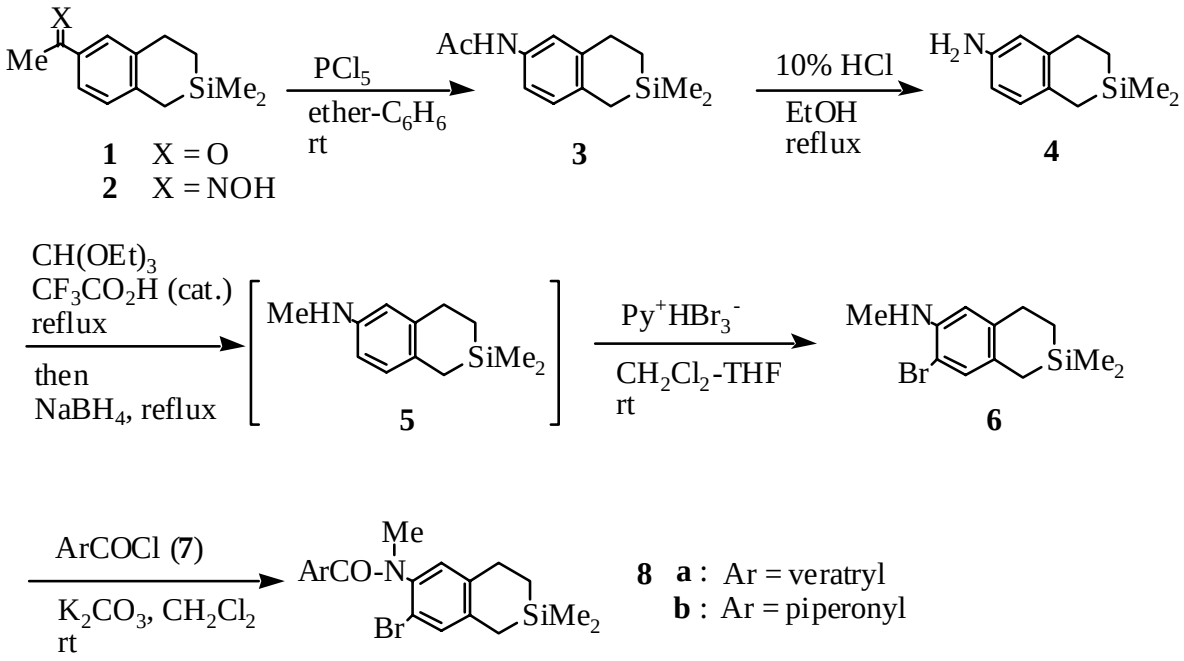


R = R_1 = H
R = H, R_1 = OMe
R = H, R_1 + R_1 = OCH_2O
R = R_1 = OMe
R = OMe, R_1 + R_1 = OCH_2O etc.

Figure

‡ Dedicated in the memory of Dr. Kenji Koga.

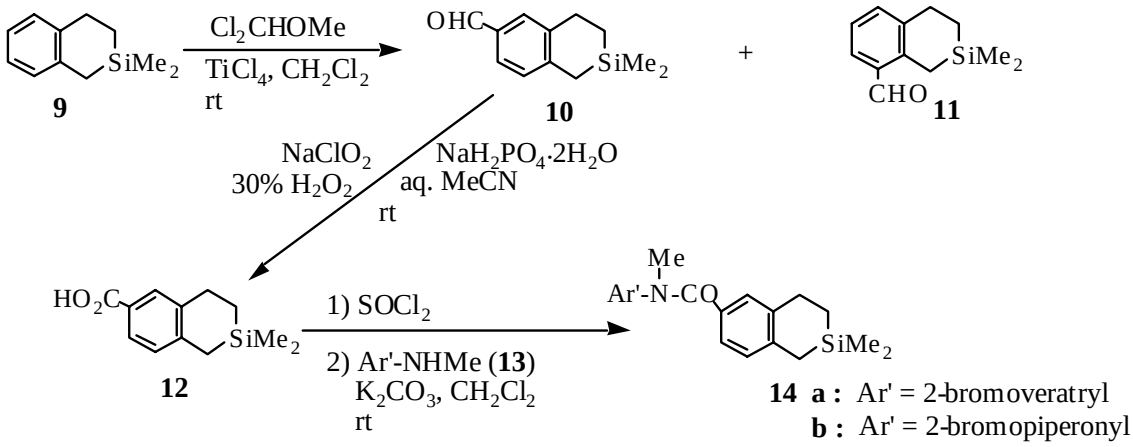
Starting materials for radical reaction were obtained as follows. Namely, *N*-(7-bromo-2-silatetralin-6-yl)aroylamides (**8**) were prepared from 6-acetyl-2-silatetralin (**1**)[5] in 7 steps (**Scheme 1**). Beckmann



Scheme 1

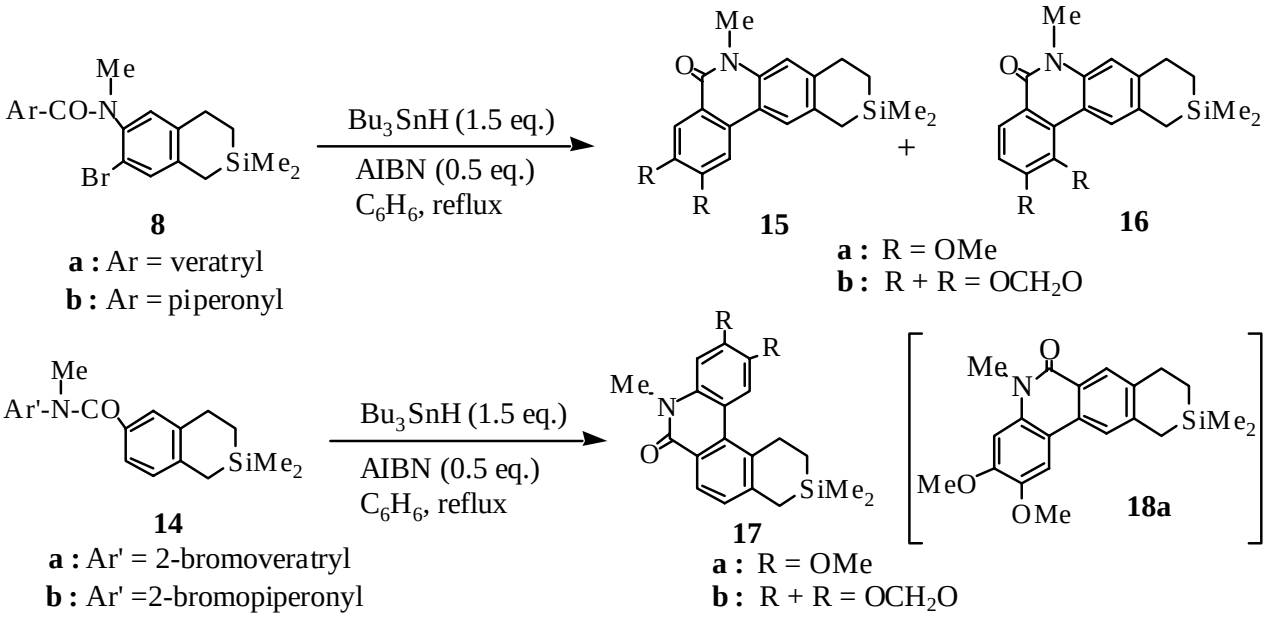
rearrangement of oxime (**2**) of **1** with PCl_5 in ether and benzene at room temperature gave 6-acetylamino-2-silatetralin (**3**), acidic hydrolysis of which afforded 6-amino-2-silatetralin (**4**) in 75 % yield. *N*-Methylation[6] of **4** followed by bromination with pyridinium tribromide in CH_2Cl_2 at room temperature produced 7-bromo-6-methylamino-2-silatetralin (**6**) in 50 % yield (3 steps). The structure was determined by its ^{1}H NMR spectrum, showing two singlets (each 1H) at δ 7.14 and 6.44. Amidation of **6** with veratric and piperonic acid chlorides (**7**) in CH_2Cl_2 containing K_2CO_3 at room temperature afforded *N*-methyl-(7-bromo-2-silatetralin-6-yl)aroylamides (**8**) in good yields.

On the other hand, *N*-bromoaryl-2-silatetralin-6-carboxamides (**14**) were prepared from 2-silatetralin (**9**) in 3 steps (**Scheme 2**). Friedel-Crafts type reaction of **9** using dichloromethoxymethane[7] in the presence of titanium chloride in CH_2Cl_2 at room temperature gave 6- (**10**) and 8-formyl- (**11**) 2-silatetralins in 39 and 20 % yields, respectively. The structures were confirmed by their ^{1}H NMR spectra [δ 7.62, 7.22 (each 1H, d, *J* = 7.6 Hz) for **10** and δ 7.64 (1H, d, *J* = 7.6 Hz), 7.31 (1H, d *J* = 7.3 Hz), 7.18 (1H, dd, *J* = 7.6, 7.3 Hz) for **11**]. Oxidation of **10** in a usual way was unfruitful. However, **10** was oxidized smoothly with sodium chlorite[8] and 35 % hydrogen peroxide in aqueous acetonitrile containing sodium dihydrogenphosphate at room temperature to produce 2-silatetralin-6-carboxylic acid (**12**) in 93 % yield. Amidation of **12** through the acid chloride with 2-bromo-*N*-methylveratrylamine (**13a**)[9] and 2-bromo-*N*-methylpiperonylamine (**13b**)[9] gave *N*-methyl-*N*-bromoaryl-2-silatetralin-6-carboxamides (**14**) in good yields.



Scheme 2

With starting materials (**8**, **14**) in hand, radical reaction was run (**Scheme 3**). A mixture of **8a**, Bu_3SnH and AIBN in benzene was refluxed for 5 h. After usual work-up, separation of the products by preparative thin-layer chromatography (TLC) on silica gel gave two kinds of cyclized products (**15a** and **16a**) in 39 and 10 % yields, respectively. The structure of **15a** was determined by the presence of four singltes (each 1H) at δ 7.93, 7.80, 7.58, and 7.16, while that of **16b** was proved by the presence of two pairs of doublet (each 1H, *J* = 8.9 Hz) at δ 8.01 and 7.35 and two singlets (each 1H) at δ 7.83 and 7.09



Scheme 3

in the respective ^{1}H NMR spectrum. Similarly, reaction of **8b** afforded **15b** and **16b** in 36 and 10 % yields. On the other hand, analogous reaction of **14a** gave a cyclized product (**17a**) in 25 % yield, the structure of which was confirmed on thebasis of the ^{1}H NMR spectrum, showing two pairs of doublet (each 1H, *J* = 8.3 Hz) at δ 7.89 and 7.41 and two singlets (each 1H) at δ 7.62 and 6.80. Thus, this evidence supported the cyclization to take place at 5-positon of 2-silatetralin moiety. *N*-Methylphenanthridinone isomer

(**18a**), which was cyclized at 7-position of 2-silatetralin moiety, was not detected. With **14b**, cyclized product (**17b**) was also obtained in 22 % yield.

In conclusion, synthesis of *N*-methylphenanthridinone derivatives (**15-17**) fused with a silacyclohexane ring by radical reaction was accomplished, though improvement of yield remained.

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The authors are grateful to Mrs. F. Hasegawa of this faculty for MS spectral measurements.

EXPERIMENTAL

General. All melting points were measured on a Yanagimoto melting point apparatus and are uncorrected. IR spectra were obtained with a JASCO FT/IR-400 on KBr disk, unless otherwise noted. ^{1}H and ^{13}C NMR spectra were taken with a JEOL JNM AL-300 (300 MHz for ^{1}H NMR and 75 MHz for ^{13}C NMR) spectrometer in $CDCl_3$ solution with CH_2Cl_2 as the internal standard. MS spectra were measured on a Hitachi M-80 or a JOEL JMS D-300 spectrometer. Column chromatography was run over silica gel (Merck Kieselgel 60). Preparative TLCs were performed on a Merck 5744 plate. Organic extracts were dried over $MgSO_4$ and the solvent was removed under reduced pressure.

6-Amino-2,2-dimethyl-2-silatetralin (4)— A solution of oxime (**2**) (7.20 g, 0.031 mol) [prepared by oximylation of 6-acetyl-2-silatetralin (**1**) in a usual way] in benzene (120 mL)-ether (40 mL) was stirred with PCl_5 (10.3 g, 0.050 mol) at rt for 1 h. After the reaction was quenched with water, the product was taken up in ether. Usual work-up of the ether extract followed by purification on column chromatography (hexane : EtOAc = 5 : 1 ~ 1 : 2) gave 6-acetylamino-2-silatetralin (**3**) (6.37 g, 88 %, mp 88-89°C) [^{1}H NMR δ 2.13 (3H, s), 0.02 (6H, s); ^{13}C NMR δ 168.3, 142.2, 134.8, 134.4, 129, 119.7, 118.0, 29.6, 24.3, 20.1, 11.4, -2.0, -2.1 ; IR 3214, 1647 cm^{-1}; MS *m/z* 233 (M^+)].

A solution of 6-acetylamino-2-silatetralin (**3**) (1.50 g, 6.43 mmol) in EtOH (20 mL) was refluxed with 10 % HCl (20 mL) for 5 h. Work-up as usual gave an oily product, which was chromatographed (hexane : EtOAc = 20 : 1) to leave 6-amino-2-silatetralin (**4**) (0.93 g, 75 %) as a pale yellow oil. ^{1}H NMR δ 6.87, 6.48 (each 1H, d, *J* = 7.3 Hz), 6.50, 6.48 (each 1H, s), 3.41 (2H, br), 0.03 (6H, s): ^{13}C NMR δ 143.4, 142.6, 130.2, 127.9, 115.5, 113.1, 29.7, 19.3, 11.7, -2.1; IR (film) 3431 cm^{-1}; MS *m/z* 191 (M^+); HRMS *m/z* calcld for $C_{11}H_{17}NSi$ (M^+) 191.1129, found 191.1127.

7-Bromo-6-methylamino-2,2-dimethyl-2-silatetralin (6) – A solution of 6-amino compound (**4**) (1.13 g, 5.93 mmol) in $CH(OEt)_3$ (20 mL) containing CF_3CO_2H (few drops) was refluxed for 7 h. Removal of the solvent produced an oily product, which was refluxed with $NaBH_4$ (0.45 g, 11.9 mmol) in EtOH (30 mL) for 3 h. Usual work-up followed by extraction with $CHCl_3$ and removal of the solvent gave an oily

product, which was chromatographed (hexane : EtOAc = 20 : 1) to leave 6-methylamino-2,2-dimethyl-2-silatetralin (**5**) (0.88 g, 72 %) as a pale yellow oil [^{1}H NMR δ 6.91, 6.43 (each 1H, d, *J* = 7.3 Hz), 6.45 (1H, s), 2.81 (3H, s), 3.38 (1H, br), 0.03 (6H, s): ^{13}C NMR δ 143.3, 138.9, 126.7, 123.1, 109.3, 106.7, 27.5, 26.4, 15.6, 8.3, -0.20; IR (film) 3407 cm^{-1}].

A solution of the 6-methylamino compound (**5**) (0.89 g, 4.32 mmol) in CH_2Cl_2 (43 mL)-THF (20 mL) was stirred with pyridinium tribromide (2.76 g, 8.64 mmol) at rt for 2 h. Usual work-up gave an oily product, which was chromatographed (hexane : EtOAc = 20 : 1) to produce the title compound (**6**) (0.86 g, 70 %) as an oil. ^{1}H NMR δ 7.14, 6.44 (each 1H, s), 2.87 (3H, s), 0.03 (6H, s); ^{13}C NMR δ 142.8, 141.8, 132.4, 127.1, 110.9, 106.5, 30.6, 29.4, 18.7, 11.3, -2.4; IR (film) 3421 cm^{-1}; MS *m/z* 283 (M^+), 285 (M^++ 2); HRMS *m/z* calcld for $C_{12}H_{18}NBrSi$ (M^+) 283.0392, found 283.0396.

***N*-(7-Bromo-2,2-dimethyl-2-silatetralin-6-yl)-*N*-methylveratramide and -piperonamide (8):** a) A mixture of **6** (341 mg, 1.20 mmol), acid chloride (**7a**) [prepared from veratric acid (182 mg, 1.00 mmol) and $SOCl_2$ (0.29 mL, 4.0 mmol) in a usual manner], and K_2CO_3 (209 mg, 1.50 mmol) in CH_2Cl_2 (5 mL) was stirred at rt for 24 h. Work-up as usual followed by chromatography (hexane : EtOAc = 20 : 1 ~ 3 : 1) produced bromo-amide (**8a**) (429 mg, 96 %, mp 51-52°C). ^{1}H NMR δ 7.23, 6.92, 6.78 (each 1H, s), 6.96, 6.61 (each 1H, *J* = 8.3 Hz), 3.79, 3.69, 3.44 (each 3H, s), 0.03, -0.04 (each 3H, s); ^{13}C NMR δ 170.5, 150.1, 147.6, 142.3, 140.8, 140.1, 133.5, 129.4, 128.2, 121.9, 119.5, 111.7, 109.8, 55.7, 55.6, 37.4, 28.9, 20.5, 11.1, -2.2, -2.3; IR 1635 cm^{-1}; MS *m/z* 447 (M^+), 449 (M^++ 2).

b) 6-Methylamino-2-silatetralin (**6**) (375 mg, 1.32 mmol), acid chloride (**7b**) [prepared from piperonic acid (183 mg, 1.10 mmol) and $SOCl_2$ (0.32 mL, 4.40 mmol) in a usual manner], K_2CO_3 (228 mg, 1.65 mmol), and CH_2Cl_2 (7.5 mL) were used. After reaction similar to that noted for **8a**, chromatography (hexane : EtOAc = 20 : 1 ~ 5 : 1) produced bromo-amide (**8b**) (453 mg, 95 %, mp 124-125°C). ^{1}H NMR δ 7.22 (1H, s), 5.86 (2H, s), 3.33 (3H, s), 0.05, -0.06 (each 3H, s); ^{13}C NMR δ 170.2, 148.9, 146.9, 142.2, 140.2, 133.5, 129.8, 129.3, 123.2, 119.5, 109.0, 107.2, 101.1, 37.4, 28.9, 20.6, 11.1, -2.2, -2.4; IR 1638 cm^{-1}; MS *m/z* 431 (M^+), 433 (M^++2).

Formylation of 2,2-dimethyl-2-silatetralin (9) – To an ice-cooled, stirred solution of **9** (4.00 g, 22.7 mmol) and $TiCl_4$ (8.69 g, 45.4 mmol) in CH_2Cl_2 (20 mL) was rapidly added Cl_2CHOMe (5.22 g, 45.4 mmol) in CH_2Cl_2 (10 mL) and stirring was continued at rt for 15 min. The mixture was carefully quenched with water under ice-cooling and the product was taken up in CH_2Cl_2. Work-up as usual followed by chromatography (hexane : EtOAc = 20 : 1) gave 6- (**10**) (1.81 g, 39 %) and 8-formyl-2-silatetalins (**11**) (0.94 g, 20 %) as each oil, respectively.

*6-Formyl-2,2-dimethyl-2-silatetralin (**10**)*: ^{1}H NMR δ 9.82, 7.60 (each 1H, s), 7.62, 7.22 (each 1H, d, *J* = 7.6 Hz), 0.05 (6H, s); ^{13}C NMR δ 192.2, 147.0, 142.3, 133.8, 129.8, 128.7, 128.5, 29.4, 22.3, 11.1, -2.1:

IR (film) 1694 cm^{-1}; MS *m/z* 204 (M^+).

*8-Formyl-2,2-dimethyl-2-silatetralin (**11**)* : ^{1}H NMR δ 10.32 (1H, s), 7.64, (1H, d, *J* = 7.6 Hz), 7.31 (1H, d, *J* = 7.3 Hz), 7.18 (1H, dd, *J* = 7.6, 7.3 Hz), 0.04 (6H, s); ^{13}C NMR δ 193.1, 143.5, 142.1, 133.5, 133.4, 130.2, 124.6, 29.4, 15.1, 10.9, -2.3: IR (film) 1697 cm^{-1}; MS *m/z* 204 (M^+).

6-Carboxy-2,2-dimethyl-2-silatetralin (12) – A mixture of 6-formyl-2-silatetralin (**10**) (1.14 g, 5.60 mmol) in 35 % H_2O_2 (0.60 g, 6.1 mmol), $NaH_2PO_2 \cdot 2H_2O$ (0.20 g, 1.68 mmol), MeCN (5.6 mL), and water (1.7 mL) was stirred with $NaClO_2$ (0.71 g, 7.84 mmol) at rt for 24 h. After filtration, the organic layer was evaporated and water was added to the residue. The product was taken up in CH_2Cl_2. Usual work-up of the CH_2Cl_2 extract gave the title compound (**12**) (1.25 g, 93 %, mp 156-157°C). ^{1}H NMR δ 7.86, 7.16 (each 1H, d, *J* = 7.6 Hz), 7.86 (1H, s), 0.05 (6H, s); ^{13}C NMR δ 172.3, 145.5, 141.4, 129.1, 129.0, 128.1, 125.4, 29.1, 21.7, 10.8, -2.5; IR 2886-2561, 1688 cm^{-1}; MS *m/z* 220 (M^+).

***N*-(2-Bromoveratryl and 2-bromopiperonyl)-*N*-Methyl-2,2-dimethyl-2-silatetralin-6-carboxamides (14)**: a) Acid chloride [prepared from **12** (165 mg, 0.75 mmol) and $SOCl_2$ (0.21 mL, 3.00 mmol)], *N*-methyl-2-bromoveratrylamine (**13a**) (222 mg, 0.90 mmol), and K_2CO_3 (156 mg, 1.13 mmol) in CH_2Cl_2 (5 mL) were used. After reaction similar to that noted for **8a**, chromatography (hexane : EtOAc = 20 : 1 ~ 4 : 1) afforded bromo-amide (**14a**) (341 mg, 98 %, mp 101-102°C). ^{1}H NMR δ 7.11 (1H, s), 3.82, 3.67, 3.45 (each 3H, s), -0.04, -0.05 (each 3H, s); ^{13}C NMR δ 171.7, 148.7, 140.9, 140.7, 136.7, 132.3, 129.3, 128.4, 127.7, 125.9, 115.2, 113.2, 112.7, 56.2, 56.1, 37.1, 29.4, 21.1, 11.3, -2.2; IR 1633 cm^{-1}; MS *m/z* 447 (M^+), 449 (M^++2).

b) Acid chloride [prepared from **12** (286 mg, 1.30 mmol) and $SOCl_2$ (0.38 mL, 5.20 mmol)], *N*-methyl-2-bromopiperonylamine (**13b**) (359 mg, 1.60 mmol), K_2CO_3 (216 mg, 1.60 mmol), and CH_2Cl_2 (10 mL) were used. After reaction similar to that noted for **8a**, chromatography (hexane : EtOAc = 20 : 1 ~ 3 : 1) afforded bromo-amide (**14b**) (512 mg, 91 %. 119-121°C). ^{1}H NMR δ 7.17, 6.55 (each 1H, s), 5.93, 5.91 (each 1H, s), 3.30 (3H, s), -0.04, -0.05 (each 3H, s); ^{13}C NMR δ 171.2, 147.6, 141.0, 137.6, 132.1, 131.3, 128.4, 127.8, 125.9, 113.9, 112.5, 110.3, 102.2, 37.1, 29.4, 21.2, 11.3, -2.2; IR 1637 cm^{-1}; MS *m/z* 431 (M^+), 433 (M^++2).

General procedure for Radical Reaction of Bromo-Amides (8, 14) --- A solution of bromo-amides (**8**, **14**), Bu_3SnH (1.5 eq.), and AIBN (0.5 eq.) in benzene was refluxed for 5 h. After removal of the solvent, water was added to the residue and the product was taken up in ether. The ether extract was washed with brine and dried. A residue obtained on removal of the solvent was dissolved in MeCN. The MeCN solution was washed with hexane. Evaporation of MeCN gave oily products, which were purified by preparative TLC.

From bromo-amides (8) a) Bromo-amide (**8a**) (58.8 mg, 0.13 mmol), Bu_3SnH (59.3 mg, 0.195 mmol), AIBN (10.7 mg, 0.065 mmol), and benzene (6.5 mL) were used. Preparative TLC (developing solvent:

benzene : EtOAc = 7 : 1, three time developments) afforded afforded cyclized product (**15a**) (20.1 mg, 39 %, mp 151-153°C) and cyclized product (**16a**) (5.2 mg, 10 %) as oil.

*N-Methylphenanthridinone (**15a**)* : ^{1}H NMR δ 7.93, 7.80, 7.58, 7.16 (each 1H, s), 4.11, 4.03, 3.80 (each 3H, s), 0.09 (6H, s); ^{13}C NMR δ 161.2, 153.1, 149.3, 143.0, 135.1, 132.5, 128.5, 122.8, 119.3, 117.4, 114.5, 109.1, 102.4, 56.1, 30.2, 29.9, 20.2, 11.6, -2.0; IR 1633 cm^{-1}; MS *m/z* 367 (M^+).

*N-Methylphenanthridinone (**16a**)* : ^{1}H NMR δ 8.01, 7.35 (each 1H, d, *J* = 8.9 Hz), 7.83, 7.09 (each 1H, s), 4.00, 3.96, 3.73 (each 3H, s), 0.07 (6H, s); IR (film) 1651 cm^{-1}; MS *m/z* 367 (M^+).

b) Bromo-amide (**8b**) (60.4 mg, 0.14 mmol), Bu_3SnH (61.8 mg, 0.21 mmol), AIBN (12.0 mg, 0.07 mmol), and benzene (7 mL) were used. Preparative TLC (developing solvent: benzene : EtOAc = 12 : 1, three time developments) afforded cyclized product (**15b**) (17.9 mg, 36 %, mp 181-184°C) and a cyclized product (**16b**) (5.0 mg, 10 %, mp 131-132°C).

*N-Methylphenanthridinone (**15b**)* : ^{1}H NMR δ 7.88, 7.75, 7.59, 7.13 (each 1H, s), 6.09 (2H, s), 3.77 (3H, s), 0.08 (6H, s); ^{13}C NMR δ 161.0, 152.0, 147.9, 143.3, 135.0, 132.5, 130.6, 123.2, 120.8, 117.4, 106.9, 101.8, 100.2, 30.2, 29.9, 20.3, 11.6, -2.0; IR 1643 cm^{-1}; MS *m/z* 351 (M^+); HRMS *m/z* calcd for $C_{20}H_{21}NO_3Si$ 351.1291 (M^+), found 351.1284.

*N-Methylphenanthridinone (**16b**)* : ^{1}H NMR δ 7.81, 7.10 (each 1H, s), 7.76, 7.20 (each 1H, d, *J* = 8.3 Hz), 6.22 (2H, s), 3.7 (3H, s), 0.07 (6H, s); ^{13}C NMR δ 159.3, 147.7, 147.3, 143.1, 134.9, 132.7, 129.1, 128.5, 123.4, 117.6, 114.8, 112.8, 102.6, 30.1, 29.3, 20.6, 11.6, -2.0; IR 1653 cm^{-1}; MS *m/z* 351 (M^+); HRMS *m/z* calcd for $C_{20}H_{21}NO_3Si$ 351.1291 (M^+), found 351.1289.

From bromo-amides (14) : a) Bromo-amide (**14a**) (58.8 mg, 0.13 mmol), Bu_3SnH (59.3 mg, 0. 195 mmol), AIBN (10.7 mg, 0.065 mmol), and benzene (6.5 mL) were used. Preparative TLC (developing solvent: benzene : EtOAc = 7 : 1, three time developments) afforded *N*-methylphenanthridinone (**17a**) (12.2 mg, 25 %) as an oil. ^{1}H NMR δ 7.89, 7.41 (each 1H, d, *J* = 8.3 Hz), 7.62, 6.80 (each 1H, s), 4.00 (6H, s), 3.76 (3H, s), 0.02 (6H, s); ^{13}C NMR δ 159.1, 146.5, 141.5, 141.2, 136.1, 129.7, 128.8, 128.2, 118.6, 115.1, 108.9, 102.0, 94.6, 52.7, 52.4, 26.6, 20.6, 18.6, 7.0, -2.0; IR (film) 1640 cm^{-1}; MS *m/z* 367 (M^+).

b) Bromo-amide (**14b**) (60.4 mg, 0.14 mmol), Bu_3SnH (61.5 mg, 0.21 mmol), AIBN (12.6 mg, 0.07 mmol), and benzene (7 mL) were used. Preparative TLC (developing solvent: benzene : EtOAc = 15 : 1, three time developments) afforded *N*-methylphenanthridinone (**17b**) (11.0 mg, 22 %, mp 155-156°C). ^{1}H NMR δ 7.83, 7.40 (each 1H, d, *J* = 8.3 Hz), 7.62, 6.86 (each 1H, s), 6.03 (2H, s), 3.71 (3H, s), 0.02 (6H, s); ^{13}C NMR δ 162.7, 148.7, 145.1, 143.6, 140.0, 133.6, 133.5, 132.1, 118.9, 113.8, 108.9, 102.0, 101.6, 95.7, 30.7, 24.2, 22.3, 10.6, -2.3; IR 1647 cm^{-1}; MS *m/z* 351 (M^+); HRMS *m/z* calcd for $C_{20}H_{21}NO_3Si$ 351.1291 (M^+), found 351.1289.

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9. 2-Bromo-*N*-methylveratrylamine (**13a**) was prepared from veratric acid in 4 steps (azidation; Crutius rearrangement; reduction; bromination). Also 2-bromo-*N*-methylpiperonylamine (**13b**) was obtained from piperonic acid in a manner similar to that noted for **13a**.