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TOTAL SYNTHESIS OF CARBAZOLE-1,4-QUINONE ALKALOID KOENIGINEQUINONES A AND B BASED ON A ONE-POT CYCLOCARBONYLATION PROCEDURE FROM 2-ALKENYL-3-IODOINDOLE

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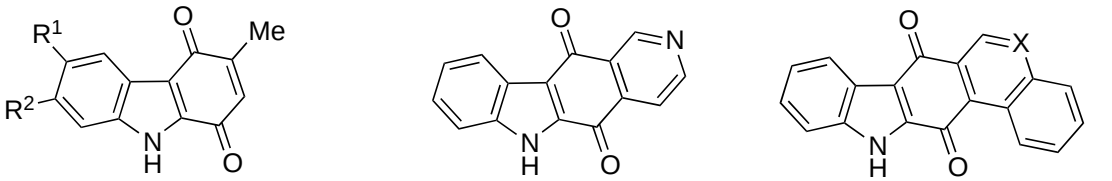
We dedicate this paper to Professor Dr. Lutz F. Tietze, University of Göttingen, on the celebration of his 75th birthday

Abstract – Total syntheses of koeniginequinones A and B, isolated from *Murraya koenigii*, were newly achieved by constructing of carbazole-1,4-quinone using a one-pot Pd-catalyzed cyclocarbonylation method with 2-(but-2-en-1-yl)-3-iodoindoles derived from known methyl 6-methoxyindole-2-carboxylate and methyl 5,6-dimethoxyindole-2-carboxylate, followed by desilylation, and an oxidation sequence.

INTRODUCTION

The quinone framework is an important core structure in many chemotherapeutic agents, such as mitomycins and anthracyclines.[1] Carbazole quinone alkaloids exhibit antitumor,[2] neuronal cell-protecting,[3] and antimalarial activities[4] (Figure 1), and are therefore attractive targets for synthetic and medicinal chemists.[5] Murrayaquinone A (**1**) was isolated by Furukawa *et al*. from *Murraya euchrestifolia* in 1983,[6] and exhibits cardiotonic and antitumor activities. Total synthesis of **1**, including a formal synthesis, was reported by 14 groups using original synthetic approaches.[7-10] Fifteen years later, koeniginequinones A (**2a**) and B (**2b**) were isolated by Chowdhury from *Murraya koenigii*,[8] and their first total synthesis was completed by a Japp-Klingemann reaction of aryldiazonium salts and



murrayaquinone A (**1**) : R^1=R^2=H
koeniginequinone A (**2a**) : R^1=H, R^2=OMe
koeniginequinone B (**2b**) : R^1=R^2=OMe

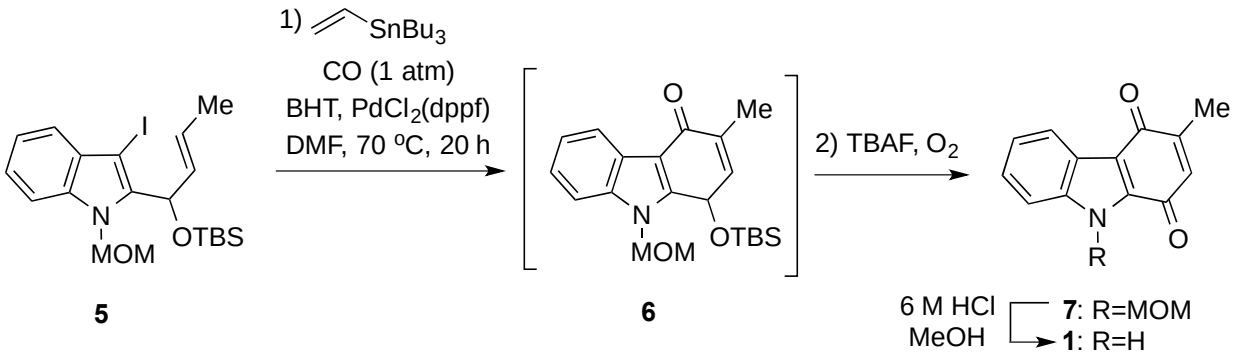
ellipticine quinone (**3**)

calothrixin A (**4a**) : X=N→O
calothrixin B (**4b**) : X=N

Figure 1

cyclohexane-1,2-dione, followed by cyclization of the obtained arylhydrazone. Furthermore, the Knölker group reported the total synthesis of **2a** and **2b** based on regioselective addition of arylamines to 2-methyl-1,4-benzoquinone, followed by a palladium(II)-catalyzed oxidative cyclization.[12b] To date, the total synthesis of koeniginequinones A (**2a**) and B (**2b**) has been achieved by four[11,12] and two[11,12b] groups, respectively.

We are interested in the unique structure and pharmacologic action of poly-substituted carbazole and carbazolequinone alkaloids. To date, we have constructed the carbazole framework by an allene-mediated electrocyclic reaction of the 6π-electron system as a key step. Based on this method, the total synthesis of murrayaquinone A (**1**),[8] carbazomycin G,[13] carquinostatin A,[14] carbazoquinocins,[15] carbazomadurins,[16] and calothrixins (**4**)[17] has been established. We also recently reported the construction of carbazole-1,4-quinone using a tandem ring-closing metathesis (RCM) and dehydrogenation reaction, and developed the total synthesis of murrayaquinone A (**1**) from *N*-MOM-3-iodoindole-2-carbaldehyde in four steps.[9] In addition, we achieved a new, efficient one-pot synthesis of carbazole-1,4-quinone **7** by a cyclocarbonylation reaction between 3-iodo-2-propenylindole **5** and CO (1 atm) in the presence of a tributyl(vinyl)tin and Pd-catalyst, followed by desilylation and oxidation reactions through an intermediate **6** (Scheme 1).[10]

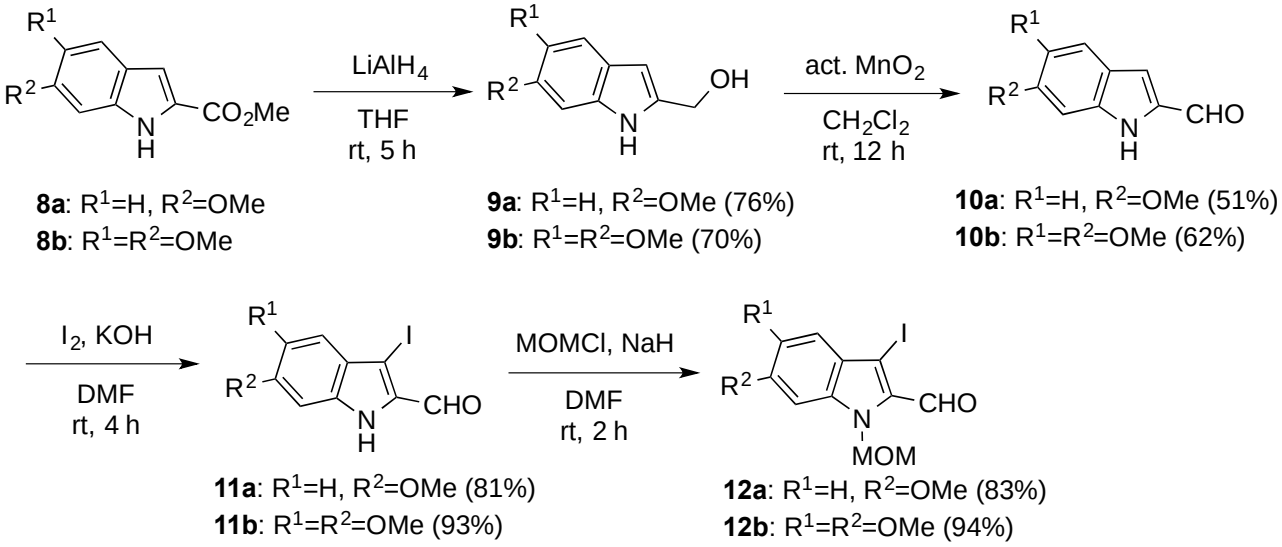


Scheme 1

Herein we describe a new total synthesis of koeniginequinones A (**2a**) and B (**2b**) based on the construction of a carbazole-1,4-quinone framework using a one-pot cyclocarbonylation method with the appropriate 3-iodo-2-propenylindoles.

RESULTS AND DISCUSSION

As depicted in Scheme 2, indole-2-carbaldehydes **12a** and **12b** were prepared from the methyl indole-2-carboxylates **8a** and **8b** according to Dierk's procedure.[18] Reduction of methyl indole-2-carboxylates **8a** and **8b** with $LiAlH_4$ gave the alcohols **9a** (76%) and **9b** (70%), which were oxidized with active MnO_2 to give the indole-2-carbaldehydes **10a** (51%) and **10b** (62%), respectively. Subsequent treatment of **10a** and **10b** with I_2 in the presence KOH afforded 3-iodoindole **11a** (81%) and **11b** (93%), respectively, which were treated with chloromethyl methyl ether to produce the *N*-MOM-indoles **12a** (83%) and **12b** (94%), respectively.



8a: R^1=H, R^2=OMe
8b: R^1=R^2=OMe

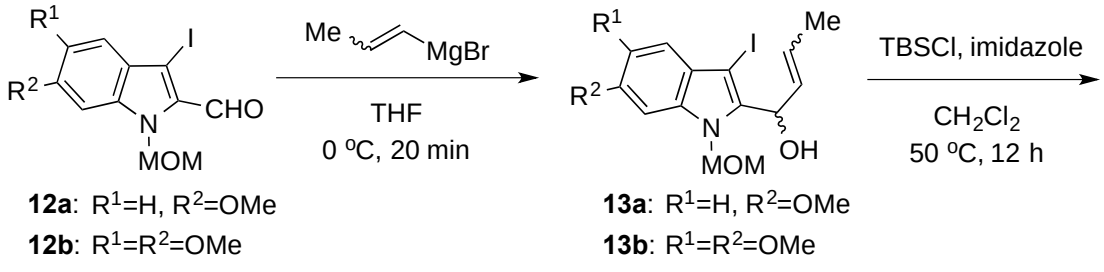
9a: R^1=H, R^2=OMe (76%)
9b: R^1=R^2=OMe (70%)

10a: R^1=H, R^2=OMe (51%)
10b: R^1=R^2=OMe (62%)

11a: R^1=H, R^2=OMe (81%)
11b: R^1=R^2=OMe (93%)

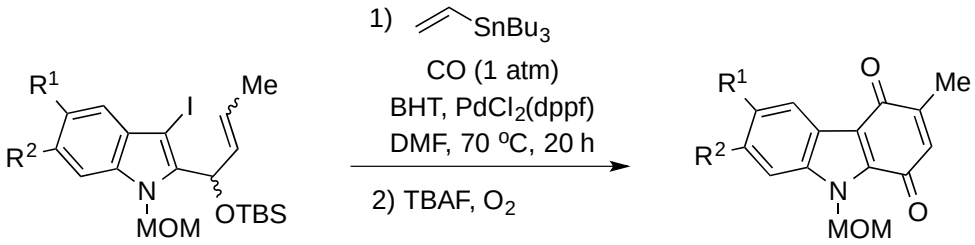
12a: R^1=H, R^2=OMe (83%)
12b: R^1=R^2=OMe (94%)

Scheme 2



12a: R^1=H, R^2=OMe
12b: R^1=R^2=OMe

13a: R^1=H, R^2=OMe
13b: R^1=R^2=OMe



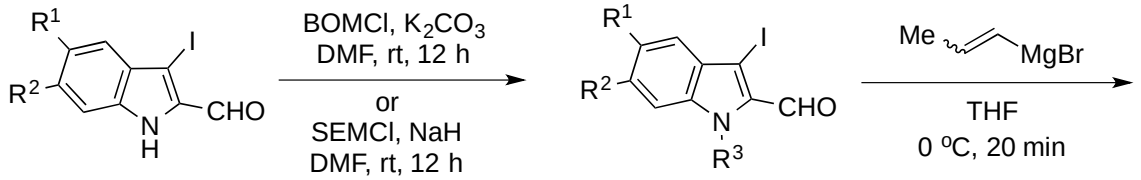
14a: R^1=H, R^2=OMe (97%)
14b: R^1=R^2=OMe (87%)

15a: R^1=H, R^2=OMe (30%)
15b: R^1=R^2=OMe (41%)

Scheme 3

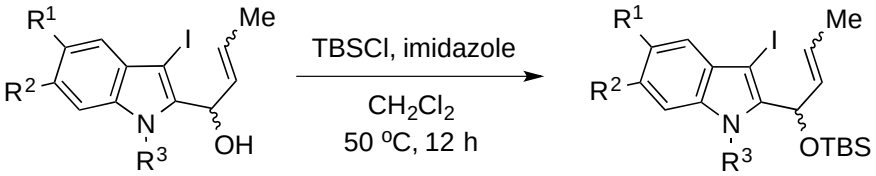
For the synthesis of carbazole-1,4-quinones **15a** and **15b**, we prepared important substrates **14a** and **14b** (Scheme 3). The Grignard reaction of 3-iodoindole-2-carbaldehydes **12a** and **12b** with

propenylmagnesium bromide gave unstable alcohols **13a** and **13b**, which were immediately treated with TBSCl in the presence of imidazole to yield *O*-TBS ethers **14a** (97%) and **14b** (87%), respectively, in two steps. The *O*-TBS ethers **14** were subjected to a one-pot cyclocarbonylation reaction under CO (1 atm) atmosphere in the presence of a tributyl(vinyl)tin and Pd-catalyst, followed by desilylation and oxidation reactions to provide the corresponding carbazole-1,4-quinones **15a** (30%) and **15b** (41%), respectively, as expected. Finally, cleavage of the *N*-MOM group of **15a** and **15b** was examined under several acid conditions, but koeniginequinones A (**2a**) and B (**2b**) were not obtained at all, contrary to our expectation. This result indicated that the MOM group was not a suitable protecting group for carbazolequinones.



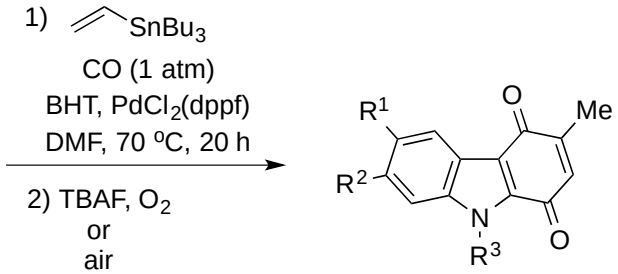
11a: R^1=H, R^2=OMe
11b: R^1=R^2=OMe

16a: R^1=H, R^2=OMe, R^3=BOM (92%)
17a: R^1=H, R^2=OMe, R^3=SEM (94%)
16b: R^1=R^2=OMe, R^3=BOM (91%)
17b: R^1=R^2=OMe, R^3=SEM (98%)



18a : R^1=H, R^2=OMe, R^3=BOM
19a : R^1=H, R^2=OMe, R^3=SEM
18b : R^1=R^2=OMe, R^3=BOM
19b : R^1=R^2=OMe, R^3=SEM

20a : R^1=H, R^2=OMe, R^3=BOM (80% from **16a**)
21a : R^1=H, R^2=OMe, R^3=SEM (85% from **17a**)
20b : R^1=R^2=OMe, R^3=BOM (92% from **16b**)
21b : R^1=R^2=OMe, R^3=SEM (61% from **17b**)



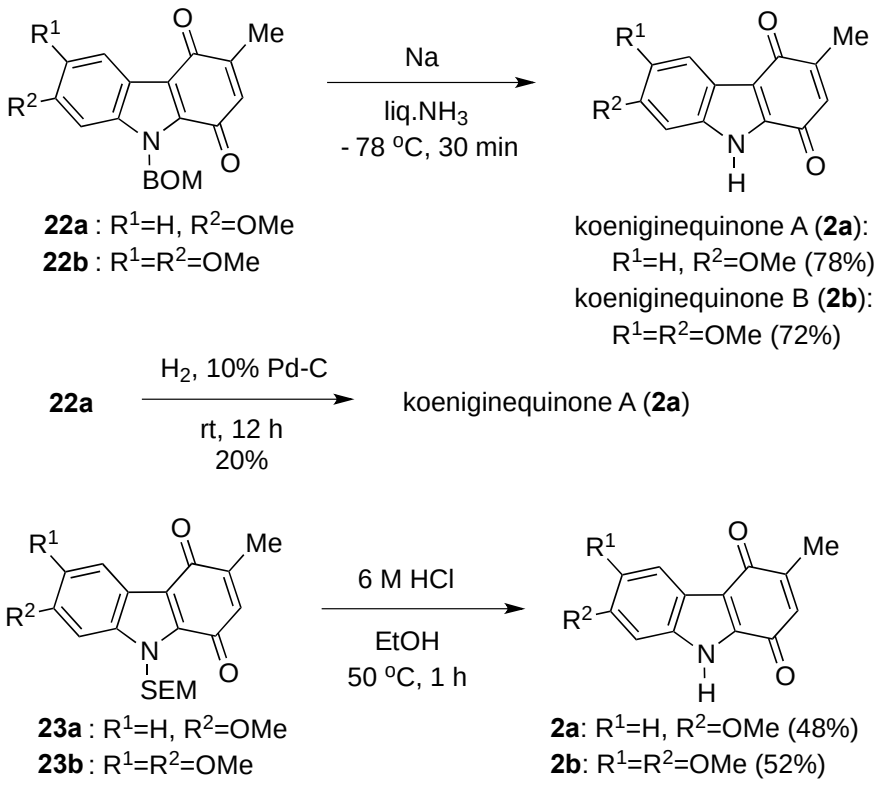
22a : R^1=H, R^2=OMe, R^3=BOM (69%)
23a : R^1=H, R^2=OMe, R^3=SEM (59%)
22b : R^1=R^2=OMe, R^3=BOM (39%)
23b : R^1=R^2=OMe, R^3=SEM (37%)

Scheme 4

For the total synthesis of koeniginequinones A (**2a**) and B (**2b**), we selected benzyloxymethyl (BOM) and trimethylsilylethoxymethyl (SEM) groups as protecting groups (Scheme 4). Treatment of **11a** and **11b** with chloromethyl benzyl ether gave *N*-BOM-indoles **16a** and **16b** in excellent yields. Treatment of **11a** and **11b** with trimethylsilylethoxymethyl chloride also afforded *N*-SEM-indoles **17a** and **17b**,

respectively. The Grignard reaction of indole-2-carbaldehydes **16a**, **16b**, **17a**, and **17b** with propenylmagnesium bromide gave unstable alcohols **18a**, **18b**, **19a**, and **19b**, which were immediately treated with TBSCl and imidazole to produce *O*-TBS ethers **20a** (80%), **20b** (92%), **21a** (85%), and **21b** (61%), respectively, in two steps. Four *O*-TBS ethers **20a**, **20b**, **21a**, and **21b** were subjected to a similar one-pot cyclocarbonylation reaction under CO (1 atm) atmosphere in the presence of a tributyl(vinyl)tin and Pd-catalyst, followed by desilylation and oxidation to give *N*-protected carbazole-1,4-quinones **22a** (69%), **22b** (39%), **23a** (59%), and **23b** (37%).

Finally, to complete the total synthesis of koeniginequinones A (**2a**) and B (**2b**), we attempted to deprotect the BOM and SEM groups of **22** and **23** (Scheme 5). Treatment of *N*-BOM-carbazolequinones **22a** and **22b** with Na in liquid NH_3 gave the desired koeniginequinones A (**2a**) (78%) and B (**2b**) (72%), respectively, in good yields. Reduction of **22a** with H_2 in the presence of 10% Pd-C afforded koeniginequinone A (**2a**) in a low yield. On the other hand, treatment of *N*-SEM-koeniginequinones **23a** and **23b** with 6 M HCl in EtOH provided koeniginequinones A (**2a**) (48%) and B (**2b**) (52%) in moderate yields. The BOM group was a better protecting group than the SEM and MOM groups in carbazolequinone compounds. The physical and spectroscopic data of our synthetic koeniginequinones A (**2a**) and B (**2b**) were consistent with natural and synthetic koeniginequinones A (**2a**) and B (**2b**) in all respects.



Scheme 5

CONCLUSION

Total synthesis of the carbazole-1,4-quinone alkaloid koeniginequinones A (**2a**) and B (**2b**) was newly achieved by applying of our one-pot cyclocarbonylation procedure to indole-2-carboxylates **8a** and **8b** in eight steps. Novel carbazole-1,4-quinone synthesis was realized. The BOM group was a better protecting group than the SEM and the MOM groups for the synthesis of carbazole-1,4-quinone natural products. The biologic activity of koeniginequinones A (**2a**) and B (**2b**) and their derivatives is under evaluation.

EXPERIMENTAL

General Methods: All non-aqueous reactions were carried out under an atmosphere of nitrogen in dried glassware unless otherwise noted. Solvents were dried and distilled according to standard protocols. Analytical thin-layer chromatography was performed with Silica gel $60PF_{254}$ (Merck). Silica gel column chromatography was performed with Silica gel 60 (70-230 mesh, Canto Co. Lit.). All melting points were determined on Yanagimoto micro melting point apparatus and are uncorrected. Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded on a JEOL AL-300 at 300 MHz. Chemical shifts are reported relative to Me_4Si (δ 0.00). NMR spectra were measured with $CDCl_3$ unless otherwise noted. Multiplicity is indicated by one or more of the following: s (singlet); d (doublet); t (triplet); q (quartet); m (multiplet); br (broad). Carbon nuclear magnetic resonance (^{13}C NMR) spectra were recorded on a JEOL AL-300 at 75 MHz. Chemical shifts are reported relative to $CDCl_3$ (δ 77.0) and DMSO-d_6 (δ 39.7). Infrared spectra were recorded with ATR method using a Shimadzu FTIR-8000 spectrophotometer and Technologies DuraScop. Low and High-resolution mass spectra were recorded on JEOL JMS-700 spectrometers by direct inlet system.

6-Methoxyindol-2-ylmethanol 9a

A solution of methyl indole-2-carboxylate **8a** (500 mg, 2.44 mmol) in THF (10 mL) was added dropwise to a solution of $LiAlH_4$ (139 mg, 3.66 mmol) in THF (10 mL) under cooling with ice-water. After stirring at rt for 5 h, the reaction mixture was quenched with water, and filtered through Celite pad. The filtrate was extracted with EtOAc. The organic layer was washed with brine, dried over Na_2SO_4, and evaporated *in vacuo*. The residue was purified by column chromatography using EtOAc-hexane (3:7, v/v) as an eluent to give the alcohol **9a** (330 mg, 76%). mp 104-105 °C (EtOAc); ^{1}H-NMR ($CDCl_3$) δ: 8.21 (1H, br s), 7.44 (1H, d, *J*=8.6 Hz), 6.81 (1H, d, *J*=2.1 Hz), 6.77 (1H, dd, *J*=8.6, 2.1 Hz), 6.33 (1H, s), 4.77 (2H, s), 3.83 (3H, s), 1.85 (1H, br s); ^{13}C-NMR ($CDCl_3$) δ: 156.5, 137.2, 136.4, 122.2, 121.2, 109.9, 100.6, 94.5, 58.7, 55.6. MS *m/z*: 177 (M^+); HR-MS (EI) Calcd for $C_{10}H_{11}NO_2$: 177.0790. Found: 177.0810.

5,6-Dimethoxyindol-2-ylmethanol 9b

The same procedure as above was carried out using methyl indole-2-carboxylate **8b** (600 mg, 2.55 mmol) to give the alcohol **9b** (370 mg, 70%). mp 134-135 ºC (EtOAc); ^{1}H-NMR ($CDCl_3$) δ: 8.22 (1H, br s), 7.02 (1H, s), 6.81 (1H, s), 6.30 (1H, s), 4.76 (2H, d, *J*=4.2 Hz), 3.90 (3H, s), 3.89 (3H, s), 2.00 (1H, br s); ^{13}C-NMR ($CDCl_3$) δ: 147.1, 145.1, 136.1, 130.8, 120.6, 102.3, 100.6, 94.4, 58.6, 56.3, 56.1. MS *m/z*: 207 (M^+); HR-MS (EI) Calcd for $C_{11}H_{13}NO_3$: 207.0895. Found: 207. 0879.

6-Methoxyindole-2-carbaldehyde 10a

A solution of alcohol **9a** (500 mg, 2.82 mmol) in CH_2Cl_2 (10 mL) was added dropwise to a solution of activated MnO_2 (486 mg, 28.2 mmol) in CH_2Cl_2 (20 mL). After stirring at 50 ºC for 12 h, the reaction mixture was filtered through Celite pad. The organic layer was evaporated *in vacuo*. The residue was purified by column chromatography using EtOAc-hexane (3:7, v/v) as an eluent to give the aldehyde **10a** (252 mg, 51%). mp 123-124 ºC (EtOAc); IR (ATR) ν: 1612 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 9.72 (1H, s), 9.06 (1H, br s), 7.60 (1H, dd, *J*=8.6, 2.1 Hz), 7.21 (1H, d, *J*=2.1 Hz), 6.84 (1H, dd, *J*=8.6, 2.2 Hz), 6.83 (1H, s), 3.88 (3H, s); ^{13}C-NMR ($CDCl_3$) δ: 181.0, 160.4, 139.5, 135.5, 124.3, 121.8, 115.6, 113.3, 93.6, 55.5. MS *m/z*: 175 (M^+); HR-MS (EI) Calcd for $C_{10}H_9NO_2$: 175.0633. Found: 175.0617.

5,6-Dimethoxyindole-2-carbaldehyde 10b

The same procedure as above was carried out using the alcohol **9b** (500 mg, 2.42 mmol) to give the aldehyde **10b** (307 mg, 62%). mp 162-164 ºC (EtOAc); IR (ATR) ν: 1619 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 9.69 (1H, s), 9.43 (1H, br s), 7.17 (1H, m), 7.07 (1H, s), 6.87 (1H, s), 3.96 (3H, s), 3.93 (3H, s); ^{13}C-NMR ($CDCl_3$) δ: 180.7, 151.7, 146.5, 135.0, 134.6, 120.4, 115.6, 102.5, 93.9, 56.0, 55.9. MS *m/z*: 205 (M^+); HR-MS (EI) Calcd for $C_{11}H_{11}NO_3$: 205.0739. Found: 205.0769.

3-Iodo-6-methoxyindole-2-carbaldehyde 11a

A solution of I_2 (1.67 g, 6.6 mmol) in DMF (30 mL) was added to a solution of the aldehyde **10a** (0.96 g, 6.6 mmol) and powdered KOH (1.3 g, 23.8 mmol) under cooling with ice-water. After stirring at rt for 4 h, the mixture was poured into a solution of NH_3 (50 mL) and $NaHSO_3$ (500 mg, 4.8 mmol) in water (500 mL). The precipitates were separated by filtration to give the 3-iodoindole **11a** (1.45 g, 81%) mp 166-168 ºC (EtOAc); IR (ATR) ν: 1620 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 9.70 (1H, s), 9.27 (1H, br s), 7.46 (1H, d, *J*=8.8 Hz), 6.90 (1H, dd, *J*=8.8, 2.1 Hz), 6.79 (1H, d, *J*=2.1 Hz), 3.88 (3H, s); ^{13}C-NMR ($CDCl_3$) δ: 181.9, 161.3, 138.6, 133.1, 125.3, 124.4, 114.3, 93.6, 73.6, 55.7. MS *m/z*: 300 (M^+); HR-MS (EI) Calcd for $C_{10}H_8INO_2$: 300.9600. Found: 300.9575.

3-Iodo-5,6-dimethoxyindole-2-carbaldehyde 11b

The same procedure as above was carried out using the aldehyde **10b** (800 mg, 3.90 mmol) to give the 3-iodoindole **11b** (1.20 g, 93%). mp 187-188 ºC (EtOAc); IR (ATR) ν: 1628 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 9.67 (1H, s), 9.65 (1H, br s), 6.87 (1H, s), 6.83 (1H, s), 3.98 (3H, s), 3.97 (3H, s); ^{13}C-NMR ($CDCl_3$) δ: 181.6, 152.7, 147.5, 133.1, 132.7, 124.2, 102.4, 93.8, 72.9, 56.3, 56.2. MS *m/z*: 330 (M^+); HR-MS (EI) Calcd for $C_{11}H_{10}INO_3$: 330.9705. Found: 330.9705.

3-Iodo-6-methoxy-*N*-(methoxymethyl)indole-2-carbaldehyde 12a

A solution of 3-iodoindole **11a** (500 mg, 1.84 mmol) in DMF (15 mL) was added to a suspension of 60% NaH (89 mg, 2.21 mmol) in DMF (5 mL) under cooling with ice-water. After stirring at the same temperature for 30 min, chloromethyl methyl ether (0.28 mL, 2.21 mmol) was added to the above mixture. The reaction mixture was stirred at the rt for 2 h, which was treated with water (30 mL). The mixture was extracted with EtOAc. The organic layer was washed with water and brine and dried over Na_2SO_4. The solvent was removed, and the residue was purified by column chromatography (silica gel, 30 g) using EtOAc-hexane (3:7, v/v) as an eluent to give the *N*-MOM-indole **12a** (632 mg, 83%). mp 96-97 ºC (EtOAc); IR (ATR) ν: 1651 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 9.87 (1H, s), 7.47 (1H, d, *J*=9.0 Hz), 6.94 (1H, dd, *J*=9.0, 2.2 Hz), 6.88 (1H, d, *J*=2.2 Hz), 5.95 (2H, s), 3.91 (3H, s), 3.31 (3H, s); ^{13}C-NMR ($CDCl_3$) δ: 183.5, 161.5, 141.8, 131.0, 124.8, 124.6, 114.7, 92.8, 79.8, 74.5, 56.0, 55.7. MS *m/z*: 344 (M^+); HR-MS (EI) Calcd for $C_{12}H_{12}INO_3$: 344.9862. Found: 344.9879.

3-Iodo-5,6-dimethoxy-*N*-(methoxymethyl)indole-2-carbaldehyde 12b

The same procedure as above was carried out using 3-iodoindole **11b** (900 mg, 2.72 mmol) to give the *N*-MOM-indole **12b** (966 mg, 94%). mp 156-157 ºC (EtOAc); IR (ATR) ν: 1651 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 9.84 (1H, s), 6.90 (1H, s), 6.89 (1H, s), 5.97 (2H, s), 4.00 (3H, s), 3.99 (3H, s), 3.31 (3H, s); ^{13}C-NMR ($CDCl_3$) δ: 183.0, 152.8, 147.9, 135.8, 130.5, 123.7, 102.8, 92.9, 78.8, 74.6, 56.4, 56.3, 55.9. MS *m/z*: 374 (M^+); HR-MS (EI) Calcd for $C_{13}H_{14}INO_4$: 374.9968. Found: 374.9983.

2-[1-(*tert*-Butyldimethylsilyloxy)but-2-en-1-yl]-3-iodo-6-methoxy-*N*-methoxymethylindole 14a

A solution of propenylmagnesium bromide (0.5 M in THF, 0.92 mL, 0.46 mmol) was added dropwise to a solution of *N*-MOM-indole **12a** (105 mg, 0.3 mmol) in THF (5 mL) under cooling with ice-water. After stirring at rt for 1 h, the reaction mixture was quenched with aqueous NH_4Cl solution (saturated), and then was extracted with EtOAc. The organic layer was washed with brine, dried over Na_2SO_4, and evaporated *in vacuo*. The alcohol **13a** was used then without purification, because it was unstable. A solution of *tert*-butyldimethylsilyl chloride (137 mg, 0.91 mmol) in CH_2Cl_2 (5 mL) was added to a solution of the alcohol **13a** and imidazole (228 mg, 1.52 mmol) under cooling with ice-water. After stirring at 50 ºC for

12 h, the reaction mixture was quenched with water, and then the mixture was extracted with EtOAc. The organic layer was washed with brine, dried over Na_2SO_4, and evaporated *in vacuo*. The residue was purified by column chromatography using EtOAc-hexane (1:9, v/v) as an eluent to give the silyl ether **14a** (148 mg, 97%). ^{1}H-NMR ($CDCl_3$) δ: 7.12 (1H, d, *J*=8.7 Hz), 6.82 (1H, d, *J*=2.4 Hz), 6.71 (1H, dd, *J*=8.7, 2.4 Hz), 5.32-5.79 (5H, m), 3.72 (3H, s), 3.19 (9H/5, s), 3.13 (6H/5, s), 1.61 (9H/5, dd, *J*=6.7, 0.7 Hz), 1.55 (6H/5, dd, *J*=5.3, 1.4 Hz), 0.75 (27H/5, s), 0.73 (18H/5, s), 0.02 (9H/5, s), 0.01 (6H/5, s), -0.18 (9H/5, s), -0.22 (6H/5, s). MS *m/z*: 501 (M^+); HR-MS (EI) Calcd for $C_{21}H_{32}INO_3Si$: 501.1196. Found: 501.1187.

2-[1-(*tert*-Butyldimethylsilyloxy)but-2-en-1-yl]-3-iodo-5,6-dimethoxy-*N*-methoxymethylindole 14b

The same procedure as above was carried out using *N*-MOM-indole **12b** (100 mg, 0.27 mmol) to give the silyl ether **14b** (125 mg, 87%). ^{1}H-NMR ($CDCl_3$) δ: 7.00 (2H/5, s), 6.99 (3H/5, s), 6.82 (1H, s), 5.48-5.92 (5H, m), 3.96 (3H, s), 3.94 (3H, s), 3.32 (9H/5, s), 3.27 (6H/5, s), 1.75 (9H/5, dd, *J*=6.8, 1.2 Hz), 1.70 (6H/5, dd, *J*=5.0, 1.0 Hz), 0.90 (27H/5, s), 0.88 (18H/5, s), 0.17 (9H/5, s), 0.15 (6H/5, s), -0.03 (9H/5, s), -0.07(6H/5, s). MS *m/z*: 531 (M^+); HR-MS (EI) Calcd for $C_{22}H_{34}INO_4Si$: 531.1302. Found: 531.1277.

6-Methoxy-3-methyl-*N*-(methoxymethyl)carbazole-1,4-quinone 15a

Carbon monoxide was bubbled for 5 min to a mixture of the silyl ether **14a** (100 mg, 0.20 mmol), tributyl(vinyl)tin (190 mg, 0.60 mmol), BHT (54 mg, 0.24 mmol), and $PdCl_2$(dppf) (33 mg, 0.040 mmol) in DMF (20 mL) at rt. The resulting mixture was stirred at 70 ºC for 20 h under a CO atmosphere. After cooling to an ambient temperature, TBAF (1 M in THF, 0.3 mL, 0.30 mmol) was added to the mixture and then the mixture was stirred at the same temperature for 1 h under O_2 atmosphere. The mixture was quenched with water and then the mixture was extracted with EtOAc. The organic layer was washed with brine, dried over Na_2SO_4, and evaporated *in vacuo*. The residue was purified by column chromatography using EtOAc-hexane (1:9, v/v) as an eluent to give the carbazole-1,4-quinone **15a** (17 mg, 30%). mp 145-146 ºC (EtOAc); IR (ATR) ν: 1647, 1654 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 8.15 (1H, d, *J*=8.8 Hz), 7.02 (1H, dd, *J*=8.8, 2.2 Hz), 6.96 (1H, d, *J*=2.2 Hz), 6.43 (1H, q, *J*=1.6 Hz), 5.98 (2H, s), 3.90 (3H, s), 3.44 (3H, s), 2.13 (3H, d, *J*=1.6 Hz); ^{13}C-NMR ($CDCl_3$) δ: 184.3, 180.6, 160.1, 146.4, 140.5, 133.1, 133.1, 123.9, 118.5, 118.0, 116.1, 93.8, 75.0, 56.3, 55.6, 15.5 MS *m/z*: 285 (M^+); HR-MS (EI) Calcd for $C_{16}H_{15}NO_4$: 285.1001. Found: 285.1002.

5,6-Dimethoxy-3-methyl-*N*-(methoxymethyl)carbazole-1,4-quinone 15b

The same procedure as above was carried out using the silyl ether **14b** (100 mg, 0.17 mmol) to give the carbazole-1,4-quinone **15b** (22 mg, 41%). mp 228-230 ºC (EtOAc); IR (ATR) ν: 1635, 1624 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 7.65 (1H, s), 6.96 (1H, s), 6.42 (1H, q, *J*=1.6 Hz), 5.99 (2H, s), 3.99 (3H, s), 3.98

(3H, s), 3.33 (3H, s), 2.13 (3H, d, *J*=1.6 Hz); ^{13}C-NMR ($CDCl_3$) δ: 184.5, 180.1, 151.2, 149.4, 146.2, 134.5, 133.4, 132.3, 118.1, 117.5, 102.3, 93.5, 75.2, 56.3, 56.2, 56.2, 15.5. MS *m/z*: 315 (M^+); HR-MS (EI) Calcd for $C_{17}H_{17}NO_5$: 315.1107. Found: 315.1123.

_N_-(Benzyloxymethyl)-3-iodo-6-methoxyindole-2-carbaldehyde 16a

A solution of 3-iodoindole **11a** (350 mg, 1.15 mmol) in DMF (10 mL) was added to a suspension of K_2CO_3 (794 mg, 5.75 mmol) in DMF (5 mL) under cooling with ice-water. After stirring at the same temperature for 30 min, benzyl chloromethyl ether (0.79 mL, 5.75 mmol) was added to the above mixture. The reaction mixture was stirred at rt for 12 h, which was treated with water (30 mL). The mixture was extracted with EtOAc. The organic layer was washed with water and brine and dried over Na_2SO_4. The solvent was removed, and the residue was purified by column chromatography (silica gel, 30 g) using EtOAc-hexane (1:9, v/v) as an eluent to give the *N*-BOM-indole **16a** (445 mg, 92%). mp 88-89 ºC (EtOAc); IR (ATR) ν: 1662 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 9.85 (1H, s), 7.45 (1H, d, *J*=8.8 Hz), 7.21-7.38 (5H, m), 6.93 (1H, dd, *J*=8.8, 2.2 Hz), 6.86 (1H, d, *J*=2.2 Hz), 6.08 (2H, s), 4.54 (2H, s), 3.87 (3H, s); ^{13}C-NMR ($CDCl_3$) δ: 183.5, 161.5, 141.8, 128.4, 128.3, 127.9, 127.8, 127.7 124.8, 124.7, 114.8, 92.9, 73.1, 70.4, 69.5, 55.8. MS *m/z*: 421 (M^+); HR-MS (EI) Calcd for $C_{18}H_{16}NO_3$: 421.0175. Found: 421.0171.

_N_-(Benzyloxymethyl)-3-iodo-5,6-dimethoxyindole-2-carbaldehyde 16b

The same procedure as above was carried out using 3-iodoindole **11b** (200 mg, 0.60 mmol) to give the *N*-BOM-indole **16b** (246 mg, 91%). mp 109-111 ºC (EtOAc); IR (ATR) ν: 1651 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 9.82 (1H, s), 7.19-7.38 (5H, m), 6.87 (2H, s), 6.08 (2H, s), 4.52 (2H, s), 3.99 (3H, s), 3.95 (3H, s); ^{13}C-NMR ($CDCl_3$) δ: 183.0, 152.7, 147.8, 137.3, 135.8, 130.3, 128.3, 127.8, 127.7, 123.6, 102.7, 93.1, 78.9, 73.1, 70.3, 56.4, 56.2. MS *m/z*: 451 (M^+); HR-MS (EI) Calcd for $C_{19}H_{18}NO_4$: 451.0281. Found: 451.0281.

3-Iodo-6-methoxy-_N_-(trimethylsilylethoxymethyl)indole-2-carbaldehyde 17a

A solution of 3-iodoindole **11a** (200 mg, 0.66 mmol) in DMF (5 mL) was added to a suspension of 60% NaH (32 mg, 0.80 mmol) in DMF (5 mL) under cooling with ice-water. After stirring at the same temperature for 30 min, trimethylsilylethoxymethyl chloride (0.14 mL, 0.80 mmol) was added to the above mixture. The reaction mixture was stirred at rt for 2 h, which was treated with water (15 mL). The mixture was extracted with EtOAc. The organic layer was washed with water and brine and dried over Na_2SO_4. The solvent was removed, and the residue was purified by column chromatography (silica gel, 30 g) using EtOAc-hexane (3:7, v/v) as an eluent to give the *N*-SEM-indole **17a** (269 mg, 94%). mp 52-54 ºC (EtOAc); IR (ATR) ν: 1616 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 9.86 (1H, s), 7.45 (1H, d, *J*=8.6 Hz), 6.93

(1H, dd, *J*=8.6, 2.2 Hz), 6.89 (1H, d, *J*=2.2 Hz), 5.97 (2H, s), 3.90 (3H, s), 3.57 (2H, t, *J*=8.1 Hz), 0.89 (2H, t, *J*=8.1 Hz), -0.07 (9H, s); ^{13}C-NMR ($CDCl_3$) δ: 183.4, 161.3, 141.8, 130.9, 124.7, 124.6, 114.6, 93.0, 79.5, 72.9, 65.8, 55.7, 17.8, -1.4. MS *m/z*: 431 (M^+); HR-MS (EI) Calcd for $C_{16}H_{22}INO_3Si$: 431.0414. Found: 431.0444.

3-Iodo-5,6-dimethoxy-*N*-(trimethylsilylethoxymethyl)indole-2-carbaldehyde 17b

The same procedure as above was carried out using 3-iodoindole **11b** (200 mg, 0.60 mmol) to give the *N*-SEM-indole **17b** (246 mg, 98%). mp 63-65 ºC (EtOAc); IR (ATR) ν: 1651 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 9.83 (1H, s), 6.92 (1H, s), 6.88 (1H, s), 5.98 (2H, s), 3.99 (6H, s), 3.56 (2H, t, *J*=7.9 Hz), 0.88 (2H, t, *J*=7.9 Hz), -0.07 (9H, s); ^{13}C-NMR ($CDCl_3$) δ: 183.0, 152.6, 147.8, 135.9, 130.3, 123.7, 102.7, 93.2, 78.9, 73.0, 65.8, 56.4, 56.2, 17.8, -1.4. MS *m/z*: 461 (M^+); HR-MS (EI) Calcd for $C_{17}H_{24}INO_4Si$: 461.0519. Found: 461.0523.

***N*-Benzyloxymethyl-2-[1-(*tert*-butyldimethylsilyloxy)but-2-en-1-yl]-3-iodo-6-methoxyindole 20a**

A solution of propenylmagnesium bromide (0.5 M in THF, 1.71 mL, 0.86 mmol) was added dropwise to a solution of *N*-BOM-indole **16a** (238 mg, 0.57 mmol) in THF (5 mL) under cooling with ice-water. After stirring at rt for 1 h, the reaction mixture was quenched with aqueous NH_4Cl solution (saturated), which was extracted with EtOAc. The organic layer was washed with brine, dried over Na_2SO_4, and evaporated *in vacuo*. The alcohol **18a** was then used without purification, because it was unstable. A solution of *tert*-butyldimethylsilyl chloride (258 mg, 1.71 mmol) in CH_2Cl_2 (10 mL) was added to a solution of the alcohol **18a** and imidazole (194 mg, 2.85 mmol) under cooling with ice-water. After stirring at 50 ºC for 12 h, the reaction mixture was quenched with water, and then the mixture was extracted with EtOAc. The organic layer was washed with brine, dried over Na_2SO_4, and evaporated *in vacuo*. The residue was purified by column chromatography using EtOAc-hexane (1:9, v/v) as an eluent to give the silyl ether **20a** (264 mg, 80%). ^{1}H-NMR ($CDCl_3$) δ: 7.25-7.34 (6H, m), 6.83-6.95 (2H, m), 5.49-5.99 (5H, m), 4.57 (3H/5, d, *J*=11.7 Hz), 4.51 (3H/5, d, *J*=11.7 Hz), 4.49 (2H/5, d, *J*=11.7 Hz), 4.44 (2H/5, d, *J*=11.7 Hz), 3.81 (3H, s), 1.77 (9H/5, dd, *J*=7.1, 1.5 Hz), 1.69 (6H/5, dd, *J*=4.8, 1.8 Hz), 0.89 (27H/5, s), 0.87 (18H/5, s), 0.16 (9H/5, s), 0.15 (6H/5, s), -0.03 (9H/5, s), -0.06 (6H/5, s). MS *m/z*: 577 (M^+); HR-MS (EI) Calcd for $C_{27}H_{36}INO_3Si$: 577.1509. Found: 577.1495.

***N*-Benzyloxymethyl-2-[1-(*tert*-butyldimethylsilyloxy)but-2-en-1-yl]-3-iodo-5,6-dimethoxyindole 20b**

The same procedure as above was carried out using *N*-BOM-indole **16b** (248 mg, 0.55 mmol) to give the silyl ether **20b** (307 mg, 92%). ^{1}H-NMR ($CDCl_3$) δ: 7.26-7.34 (5H, m), 6.97 (3H/5, s), 6.92 (2H/5, s), 6.83 (1H, s), 5.47-5.96 (5H, m), 4.54 (3H/5, d, *J*=11.7 Hz), 4.48 (3H/5, d, *J*=11.7 Hz), 4.46 (2H/5, d,

J=11.3 Hz), 4.41 (2H/5, d, *J*=11.3 Hz), 3.97 (3H, s), 3.86 (3H, s), 1.77 (9H/5, dd, *J*=7.1, 1.5 Hz), 1.70 (6H/5, dd, *J*=5.3, 1.7 Hz), 0.90 (27H/5, s), 0.88 (18H/5, s), 0.17 (9H/5, s), 0.16 (6H/5, s), -0.02 (9H/5, s), -0.06 (6H/5, s). MS *m/z*: 607 (M^+); HR-MS (EI) Calcd for $C_{28}H_{38}INO_4Si$: 607.1615. Found: 607.1590.

2-[1-(*tert*-Butyldimethylsilyloxy)but-2-en-1-yl]-3-iodo-6-methoxy-*N*-(trimethylsilylethoxymethyl)-indole 21a

The same procedure as above was carried out using *N*-SEM-indole **17a** (190 mg, 0.44 mmol) to give the silyl ether **21a** (85 mg, 85%). ^{1}H-NMR ($CDCl_3$) δ: 7.26 (1H, d, *J*=8.8 Hz), 7.01 (3H/5, d, *J*=2.2 Hz), 6.99 (2H/5, *J*=2.2 Hz), 6.84 (1H, dd, *J*=8.8, 2.3 Hz), 5.46-5.92 (5H, m), 3.86 (3H, s), 3.48-3.67 (2H, m), 1.76 (9H/5, dd, *J*=7.1, 1.5 Hz), 1.70 (6H/5, *J*=4.8, 1.5 Hz), 0.88-0.98 (11H, m), 0.15 (9H/5, s), 0.14 (6H/5, s), 0.08 (27H/5, s), -0.03 (18H/5, s), -0.05 (9H/5, s), -0.08 (6H/5, s). MS *m/z*: 587 (M^+); HR-MS (EI) Calcd for $C_{25}H_{42}INO_3Si_2$: 587.1748. Found: 587.1755.

2-[1-(*tert*-Butyldimethylsilyloxy)but-2-en-1-yl]-3-iodo-5,6-methoxy-*N*-(trimethylsilylethoxymethyl)-indole 21b

The same procedure as above was carried out using *N*-SEM-indole **17b** (169 mg, 0.37 mmol) to give the silyl ether **21b** (60 mg, 61%). ^{1}H-NMR ($CDCl_3$) δ: 7.04 (3H/5, s), 7.03 (2H/5, s), 6.83 (1H, s), 5.47-5.90 (5H, m), 3.96 (3H, s), 3.93 (3H, s), 3.47-3.67 (2H, m), 1.75 (9H/5, dd, *J*=7.2, 1.0 Hz), 1.70 (6H/5, dd, *J*=5.1, 1.2 Hz), 0.88-0.98 (11H, m), 0.16 (9H/5, s), 0.14 (6H/5, s), 0.02 (27H/5, s), 0.00 (18H/5, s), -0.05 (9H/5, s), -0.09 (6H/5, s). MS *m/z*: 617 (M^+); HR-MS (EI) Calcd for $C_{26}H_{44}INO_4Si_2$: 617.1854. Found: 617.1853.

***N*-(Benzyloxymethyl)-6-methoxy-3-methylcarbazole-1,4-quinone 22a**

Carbon monoxide was bubbled for 5 min to a mixture of the silyl ether **20a** (100 mg, 0.17 mmol), tributyl(vinyl)tin (169 mg, 0.51 mmol), BHT (57 mg, 0.26 mmol), and $PdCl_2$(dppf) (28 mg, 0.034 mmol) in DMF (20 mL) at rt. The resulting mixture was stirred at 70 ºC for 20 h under a CO atmosphere. After cooling to an ambient temperature, TBAF (1 M in THF, 0.17 mL, 0.17 mmol) was added to the mixture and then the mixture was stirred at the same temperature for 1 h under O_2 atmosphere. The mixture was quenched with water and then the mixture was extracted with EtOAc. The organic layer was washed with brine, dried over Na_2SO_4, and evaporated *in vacuo*. The residue was purified by column chromatography using EtOAc-hexane (1:9, v/v) as an eluent to give the carbazole-1,4-quinone **22a** (43 mg, 69%).

The same procedure as above was carried out using the silyl ether **20a** (100 mg, 0.17 mmol) to give the carbazole-1,4-quinone **22a** (43 mg, 69%). mp 117-118 ºC (EtOAc); IR (ATR) ν: 1639, 1624 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 8.13 (1H, d, *J*=8.8 Hz), 7.20-7.28 (5H, m), 7.02 (1H, dd, *J*=8.8, 2.2 Hz), 6.96 (1H, d,

J=2.2 Hz), 6.42 (1H, q, *J*=1.6 Hz), 6.11 (2H, s), 4.57 (2H, s), 3.87 (3H, s), 2.13 (3H, d, *J*=1.6 Hz); ^{13}C-NMR ($CDCl_3$) δ: 184.3, 180.6, 160.1, 146.4, 140.6, 137.1, 133.0, 132.9, 128.4, 127.9, 127.7, 123.9, 118.6, 118.0, 116.1, 93.8, 73.6, 70.8, 55.7, 15.5. MS *m/z*: 361 (M^+); HR-MS (EI) Calcd for $C_{22}H_{19}NO_4$: 361.1314. Found: 361.1299.

_N_-(Benzyloxymethyl)-5,6-dimethoxy-3-methylcarbazole-1,4-quinone 22b

The same procedure as above was carried out using the silyl ether **20b** (100 mg, 0.17 mmol) to give the carbazole-1,4-quinone **22b** (26 mg, 39%). mp 143-145 ºC (EtOAc); IR (ATR) ν: 1635, 1612 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 7.64 (1H, s), 7.30-7.20 (5H, m), 6.95 (1H, s), 6.42 (1H, q, *J*=1.6 Hz), 6.12 (2H, s), 4.55 (2H, s), 4.00 (3H, s), 3.94 (3H, s), 2.13 (3H, d, *J*=1.6 Hz); ^{13}C-NMR ($CDCl_3$) δ: 184.5, 180.1, 151.1, 149.4, 146.2, 137.0, 134.5, 133.4, 132.1, 128.4, 128.0, 127.9, 127.8, 118.2, 117.5, 102.3, 93.7, 73.8, 70.8, 56.3, 15.5. MS *m/z*: 391 (M^+); HR-MS (EI) Calcd for $C_{23}H_{21}NO_5$: 391.1420. Found: 371.1546.

6-Methoxy-3-methyl-_N_-(trimethylsilylethoxymethyl)carbazole-1,4-quinone 23a

Carbon monoxide was bubbled for 5 min to a mixture of the silyl ether **21a** (50 mg, 0.09 mmol), tributyl(vinyl)tin (86 mg, 0.27 mmol), BHT (30 mg, 0.135 mmol), and $PdCl_2$(dppf) (15 mg, 0.02 mmol) in DMF (10 mL) at rt. The resulting mixture was stirred at 70 ºC for 20 h under a CO atmosphere. After cooling to an ambient temperature, the mixture was stirred at the same temperature for 1 h under O_2 atmosphere. The mixture was quenched with water and then the mixture was extracted with EtOAc. The organic layer was washed with brine, dried over Na_2SO_4, and evaporated *in vacuo*. The residue was purified by column chromatography using EtOAc-hexane (1:9, v/v) as an eluent to give the carbazole-1,4-quinone **23a** (20 mg, 59%). mp 95-96 ºC (EtOAc); IR (ATR) ν: 1635, 1612 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 8.15 (1H, d, *J*=8.8 Hz), 7.01 (1H, dd, *J*=8.8, 2.2 Hz), 6.97 (1H, d, *J*=2.2 Hz), 6.41 (1H, q, *J*=1.6 Hz), 6.00 (2H, s), 3.90 (3H, s) 3.58 (2H, t, *J*=8.0 Hz), 2.12 (3H, d, *J*=1.6 Hz), 0.91 (2H, t, *J*=8.0 Hz), -0.06 (9H, s); ^{13}C-NMR ($CDCl_3$) δ:184.3, 180.6, 160.0, 146.4, 140.6, 133.0, 133.0, 123.8, 118.4, 118.0, 116.1, 93.9, 73.3, 66.2, 55.6, 17.8, 15.6, -1.4. MS *m/z*: 371 (M^+); HR-MS (EI) Calcd for $C_{20}H_{25}NO_4Si$: 371.1553. Found: 371.1546.

5,6-Dimethoxy-3-methyl-_N_-(trimethylsilylethoxymethyl)carbazole-1,4-quinone 23b

The same procedure as above was carried out using the silyl ether **24b** (50 mg, 0.08 mmol) to give the carbazole-1,4-quinone **23b** (12 mg, 37%). mp 139-141 ºC (EtOAc); IR (ATR) ν: 1639, 1616 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 7.65 (1H, s), 6.98 (1H, s), 6.41 (1H, q, *J*=1.6 Hz), 6.01 (2H, s), 3.99 (3H, s), 3.98 (3H, s), 3.58 (2H, t, *J*=8.1 Hz), 2.13 (3H, d, *J*=1.6 Hz), 0.90 (2H, t, *J*=8.1 Hz), -0.07 (9H, s); ^{13}C-NMR

($CDCl_3$) δ:184.5, 180.1, 151.0, 149.3, 146.2, 134.5, 133.3, 132.1, 117.9, 117.5, 102.2, 93.8, 73.5, 66.2, 56.2, 56.1, 17.7, 15.5, -1.4. MS *m/z*: 401 (M^+); HR-MS (EI) Calcd for $C_{21}H_{27}NO_5Si$: 401.1658. Found: 401.1632.

Koeniginequinone A 2a from 22a by the Birch conditions

A solution of *N*-BOM-carbazole-1,4-quinone **22a** (10 mg, 0.028 mmol) in THF (3 mL) was added to a liq. NH_3 under -78 ºC. After stirring at the same temperature for 10 min, Na (6.4 mg, 0.28 mmol) was added to the above mixture. The mixture was stirred for 30 min, which was quenched with NH_4Cl, and then the mixture was extracted with EtOAc. The organic layer was washed with brine, dried over Na_2SO_4, and evaporated in *vacuo*. The residue was purified by column chromatography using EtOAc-hexane (1:9, v/v) as an eluent to give koeniginequinone A **2a** (5 mg, 78%). mp 241-242 ºC (EtOAc) (mp 241 ºC, Lit.[11]); IR (ATR) ν: 3221, 1651, 1631 cm^{-1}. ^{1}H-NMR (DMSO-d_6) δ: 12.63 (1H, br s), 7.90 (1H, d, *J*=8.9 Hz), 6.96 (1H, dd, *J*=8.9, 2.2 Hz), 6.92 (1H, d, *J*=2.2 Hz), 6.56 (1H, q, *J*=1.6 Hz), 3.82 (3H, s), 2.04 (3H, d, *J*=1.6 Hz); ^{13}C-NMR (DMSO-d_6) δ: 183.3, 179.4, 158.7, 147.1, 138.8, 135.0, 131.6, 122.4, 117.7, 115.9, 115.1, 95.0, 55.3, 15.5. MS *m/z*: 241 (M^+); HR-MS (EI) Calcd for $C_{14}H_{11}NO_3$: 241.0739. Found: 241.0721.

Koeniginequinone B 2b from 22b by the Birch conditions

The same procedure as above was carried out using *N*-BOM-carbazole-1,4-quinone **22b** (50 mg, 0.13 mmol) to give koeniginequinone B **2b** (25mg, 72%). mp 245-246 ºC (EtOAc) (mp 246-247 ºC, Lit.[11]); IR (ATR) ν: 3286, 1631, 1619 cm^{-1}. ^{1}H-NMR (DMSO-d_6) δ: 12.60 (1H, br s), 7.40 (1H, s), 6.92 (1H, s), 6.54 (1H, q, *J*=1.6 Hz), 3.83 (6H, s), 2.04 (3H, d, *J*=1.6 Hz); ^{13}C-NMR (DMSO-d_6) δ:183.3, 178.8, 150.2, 148.5, 147.0, 134.0, 132.8, 131.9, 117.1, 115.8, 101.3, 95.2, 79.1, 55.6, 15.4. MS *m/z*: 241 (M^+); HR-MS (EI) Calcd for $C_{15}H_{13}NO_4$: 271.0845. Found: 271.0873.

Koeniginequinone A 2a from 22a by Pd-C catalyzed hydrogenation

A solution of *N*-BOM-carbazole-1,4-quinone **22a** (15 mg, 0.042 mmol) was added dropwise to a solution of 10% Pd-C (10 mg, 0.042 mmol) in MeOH (20 mL) under H_2 atmosphere. After stirring at rt for 12 h, the reaction mixture was filtered through Celite pad. The organic layer was evaporated *in vacuo*. The residue was purified by column chromatography using EtOAc-hexane (3:7, v/v) as an eluent to give koeniginequinone A **2a** (2 mg, 20%). Physical and spectral data were consistent with the synthetic or natural **2a** in all respects

Koeniginequinone A 2a from 23a

A mixture of *N*-SEM-carbazole-1,4-quinone **23a** (60 mg, 0.16 mmol) and 6 M HCl (5 mL) in EtOH (5

mL) was heated at 50 ºC for 1 h. After cooling to an ambient temperature, the mixture was basified with an aqueous Na_2CO_3 (saturated) solution, and then the resulting mixture was extracted with EtOAc. The organic layer was washed with brine, dried over Na_2SO_4 and concentrated *in vacuo*. The residue was purified by column chromatography (silica gel, 30 g) using EtOAc-hexane (3:7, v/v) as an eluent to give the koeniginequinone A **2a** (22 mg, 48%). Physical and spectral data were consistent with the synthetic or natural **2a** in all respects.

Koeniginequinone B 2b from 23b

The same procedure as above was carried out using *N*-SEM-carbazole-1,4-quinone **23b** (20 mg, 0.05 mmol) to give koeniginequinone B **2b** (7 mg, 52%). Physical and spectral data were consistent with the synthetic or natural **2b** in all respects.

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