

HETEROCYCLES, Vol. 80, No. 2, 2010, pp. 1479 - 1488. © The Japan Institute of Heterocyclic Chemistry
Received, 6th August, 2009, Accepted, 11th September, 2009, Published online, 15th September, 2009
DOI: 10.3987/COM-09-S(S)107

OXIDATIVE DIMERIZATION OF 4-METHOXYNAPHTHYLAMINES IN THE PRESENCE OF SEMICONDUCTORS[§]

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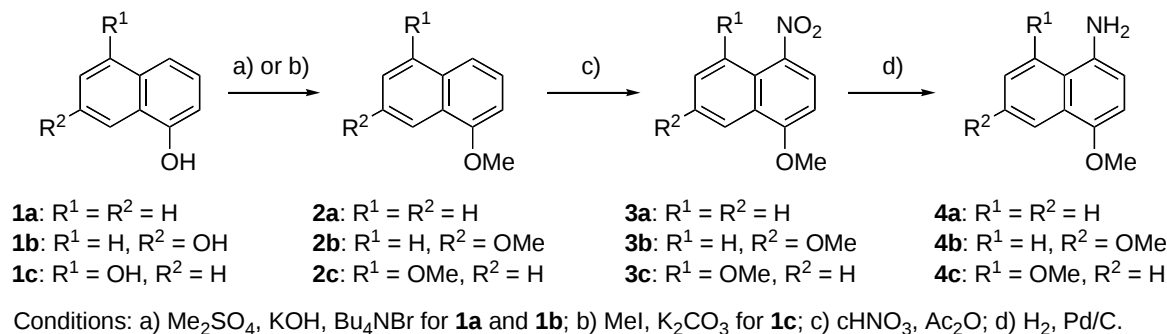
Abstract – Three types of 4-methoxynaphthylamines **4a-c** were oxidized by treatment with metal oxides under molecular oxygen (O₂). 4-Methoxy-1-naphthylamine **4a** and 4,6-dimethoxy-1-naphthylamine **4b**, on treatment with TiO₂ under O₂, gave mainly 2-amino-1,4-naphthoquinone derivatives **5a** and **5b**, respectively whereas 4,8-dimethoxy-1-naphthylamine **4c** afforded an unique carbazole **6c** as the major product.

Most of semiconductor-mediated transformation of organic molecules are initiated by photo-irradiation,¹⁻¹⁰ namely photo-catalytic reaction as well as electrochemistry using semiconductors as electrodes.^{11,12} In stark contrast, we recently reported that oxidative dimerization of naphthols and phenols mediated by semiconductors and molecular oxygen (O₂).¹³⁻¹⁵ In this context, we would like to report herein reactions of 4-methoxynaphthylamines by treatment with semiconductor and O₂.

Preparation of the starting 4-methoxynaphthylamines is outlined in Scheme 1. *O*-Methylation of 1-naphthols **1a-c** by Me₂SO₄ or MeI gave 1-methoxynaphthalenes **2a-c**, which were treated with nitric acid and acetic anhydride to provide 4-methoxy-1-nitronaphthalenes **3a-c**. Finally, reduction of nitro groups in **3a-c** by hydrogenation afforded 4-methoxynaphthylamines **4a-c**.

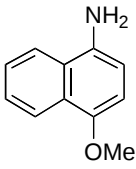
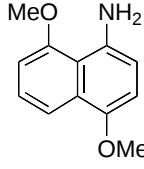
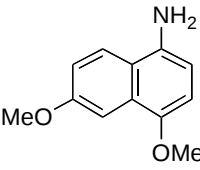
[§] This paper is dedicated to Professor Emeritus Akira Suzuki, with respect and admiration, on the occasion of his 80th birthday.

Scheme 1



Before synthetic experiments, we measured cyclic voltammetry of **4a-c** to examine their oxidation potentials (E^{ox} s) (Table 1). The measurements showed low oxidation potentials, ca. 0.5 V for **4a** and **4b** and 0.33 V for **4c** in CH_2Cl_2 . The oxidation potentials (0.37 V and 0.23 V for **4a** and **4c**, respectively) in MeCN were further lower. These experiments implied that 4-methoxy-1-naphthylamines **4a-c** readily underwent single electron transfer (SET) reaction to give radical cation species.

Table 1. Oxidative Potentials of 1-Naphthylamines^{a)}

1-Naphthylamine	CH_2Cl_2 E^{ox} b)	MeCN E^{ox} b)	1-Naphthylamine	CH_2Cl_2 E^{ox} b)	MeCN E^{ox} b)
 4a	0.49 V	0.37 V	 4c	0.33 V	0.23 V
 4b	0.5 V	not measured			

a) Potentials (V) are versus Ag/AgCl; all substrates were measured in the range of about 0.0-2.0 V. The oxidation potentials of anodic current (E) were obtained by cyclic voltammetry of 0.1 mM solutions of the substrates in an argon-saturated solvent containing 0.1 M $n-Bu_4NClO_4$ as a supporting electrolyte at a Pt electrode. The voltage scan rate in cyclic voltammetry was 100 $mV\ s^{-1}$ at 23 °C. b) E^{ox} = the first halfwave oxidation potential.¹⁶

Oxidation of 4-methoxynaphthylamine **4a** was first examined with various metal oxides, SnO_2 , ZrO_2 , NbO_5 , and TiO_2 in oxygen-saturated solvents (Table 2, entries 1-8). As a result, it was found that use of TiO_2 shortened reaction time both in CH_2Cl_2 and in MeCN to give oxidative dimerized product, aminoquinone **5a**, as the major product along with small amount of another dimerized product, carbazole **6a** (entries 7 and 8). Next, oxidative dimerization of **4a** with TiO_2 in various solvents was conducted at

room temperature (entries 9-14). The reaction did not proceed at room temperature in MeNO₂, DMF, and dioxane probably due to reduced reactivity of TiO₂ by coordination with the solvent (entries 10-12). Use of aromatic solvents improved the reaction (entries 13-15). Thus, the reaction in benzene completed even at room temperature within 3 h to afford **5a** in 50% yield and a small amount (4%) of **6a** (entry 13). Considering toxicity of benzene, toluene was examined as the solvent (entries 14 and 15). Although the reaction in toluene seemed to be slightly less efficient than that in benzene (entry 14), mild heating at 60°C accelerated the reaction to give **5a** and **6a** in comparable yield to that of entry 13 (entry 15).

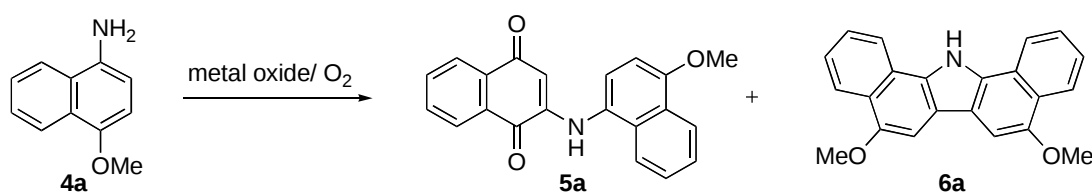
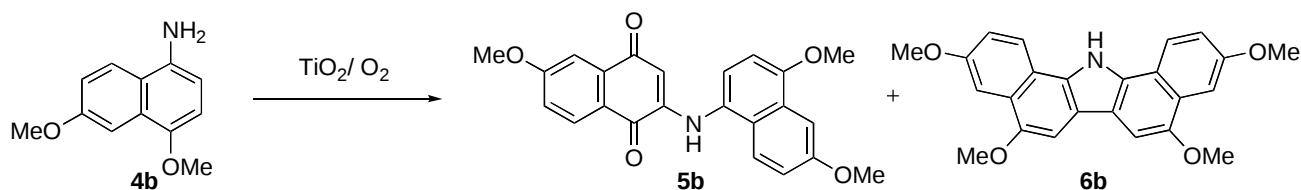


Table 2. Oxidative dimerization of **4a** with various metal oxides

Entry	Catalyst	Solvent	Temp. (°C)	Time (h)	Product (%) ^{a)}		Recovered 4a (%)
					5a	6a	
1	SnO ₂	CH ₂ Cl ₂	rt	96	trace	—	36
2	SnO ₂	MeCN	70	53		complex mixture	
3	ZrO ₂	CH ₂ Cl ₂	rt	96	17	trace	12
4	ZrO ₂	MeCN	70	48		complex mixture	
5	Nb ₂ O ₅	CH ₂ Cl ₂	rt	96	34	trace	12
6	Nb ₂ O ₅	MeCN	70	30		complex mixture	
7	TiO ₂	CH ₂ Cl ₂	rt	3	34	8	—
8	TiO ₂	MeCN	70	3	55	trace	—
9	TiO ₂	MeCN	rt	3	43	trace	
10	TiO ₂	MeNO ₂	rt	3		no reaction	—
11	TiO ₂	DMF	rt	3		no reaction	—
12	TiO ₂	dioxane	rt	3		no reaction	—
13	TiO ₂	benzene	rt	3	50	4	—
14	TiO ₂	toluene	rt	3	19	2	—
15	TiO ₂	toluene	60	0.5	48	6	—

^{a)} Isolated yield.

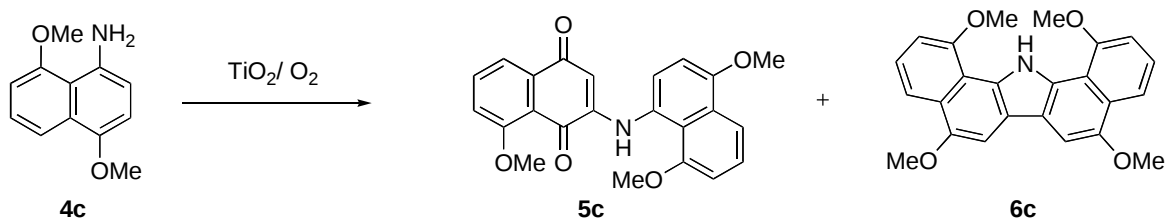
We next examined oxidation reaction of **4b** by using TiO₂ and O₂ (Table 3). In the case of **4b**, both MeCN and toluene could be used for oxidation reaction. Thus, mild heating **4b** with TiO₂ in oxygen-saturated solvents, MeCN and toluene afforded aminoquinone **5b** in 36% and 38% yields, respectively along with small amount of carbazole **6b** (entries 2 and 4).

Table 3. Oxidative dimerization of **4b** with TiO_2

Entry	Solvent	Temp. (°C)	Time (h)	Product (%) ^{a)}	
				5b	6b
1	MeCN	rt	3	33	6
2	MeCN	70	0.5	36	6
3	toluene	rt	2.5	25	6
4	toluene	60	0.5	38	2
5	toluene	100	0.5	17	-

a) Isolated yield.

4,8-Dimethoxynaphthyl-1-amine (**4c**) having the lowest oxidation potential indicated different distribution of the products (Table 4). Naphthylamine **4c** reacted with TiO_2 in oxygen-saturated MeCN at room temperature to give equal amount (23% yield, each) of aminoquinone **5c** and carbazole **6c** (entry 1). Use of higher reaction temperature led to increase of aminoquinone **5c** (entry 2). Oxidation reaction of **4c** in toluene showed reversal of distribution of product (entry 3). Thus, reaction of **4c** at room temperature in toluene for 1.5 h provided carbazole **6c** in 63% yield accompanied by aminoquinone **5c** in 27% yield.

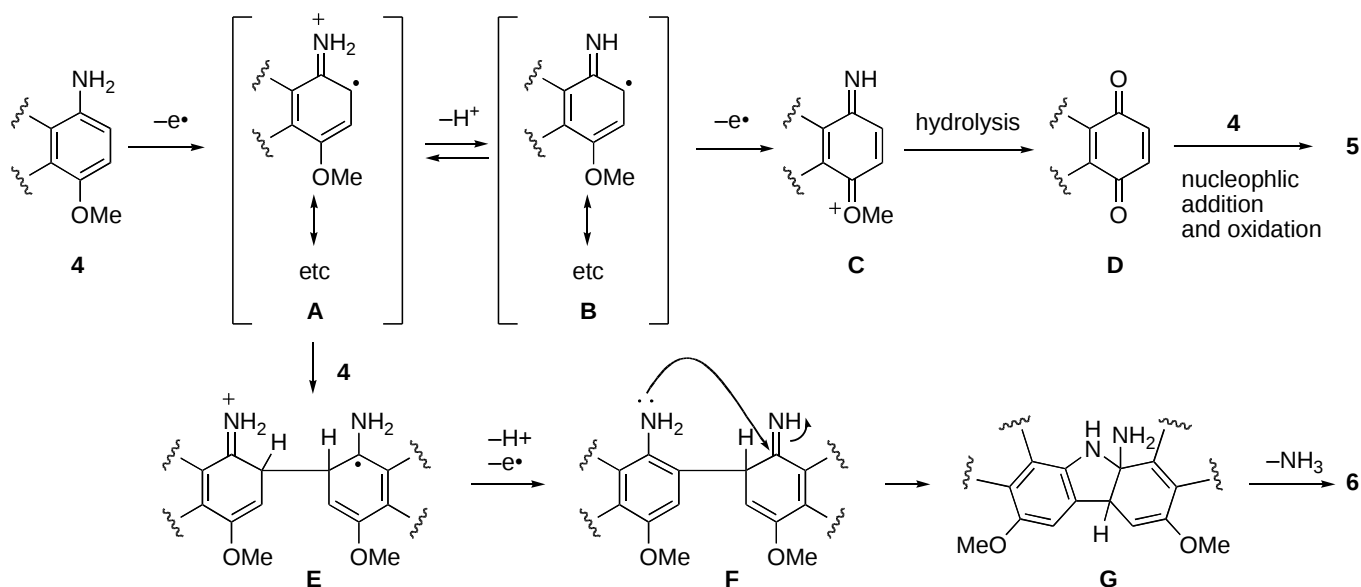
Table 4. Oxidative dimerization of **4c** with TiO_2

Entry	Solvent	Temp. (°C)	Time (h)	Product (%) ^{a)}	
				5c	6c
1	MeCN	rt	3	23	23
2	MeCN	70	4	40	17
3	toluene	rt	1.5	27	63

a) Isolated yield.

Although the detailed mechanism for the formation of **5** and **6** remains unclear, it may involve radical cation **A** (Scheme 2). Thus, the electron-rich 1-naphthylamine **4** causes SET reaction to generate radical cation **A**, which subsequently loses a proton to lead radical **B**. SET reaction of radical **B** gives cation **C**, which undergoes hydrolysis to provide quinone **D**. Finally, nucleophilic addition of **4** to quinone **D** followed by oxidation affords aminoquinone **5**. On the other hand, long-lived radical cation **A** can react with another **4** to give intermediate **E**, which causes cyclization to yield **6** via intermediates **F** and **G**. Accordingly, electron-rich **4c** tends to afford carbazole **6c**. Use of toluene, a non-polar solvent, might stabilize **A** by suppressing SET reaction of **B** into **C** leading to quinone **5**, and hence carbazole **6c** became the main product (Table 4, entry 3).

Scheme 2



EXPERIMENTAL

All melting points are uncorrected. Infrared (IR) spectra were recorded with a JASCO IR-700 spectrometer, and ^1H - and ^{13}C -NMR spectra with JEOL JNM-AL300 with tetramethylsilane as an internal standard. Mass spectra were recorded on a JEOL JMS-D300 or Shimadzu QP-5000 spectrometer. Merck Kieselgel 60 (230–400 mesh), Wako silica gel C-200 were used for column chromatography. Although compounds **3a** and **3c** are known,¹⁷ their preparation and characterization are presented here.

1-Methoxynaphthalene (2a)

Dimethyl sulfate (420 mL, 4.5 mol) was added dropwise to a stirred mixture of 1-naphthol (**1a**, 400 g, 2.8 mol), tetra-*n*-butylammonium bromide (116 g, 0.36 mol) in THF (760 mL) and a solution of KOH (500 g, 8.9 mol) in water (300 mL) at 0 °C, and the mixture was further stirred for 1.5 h at the same temperature.

To the mixture was added a 10% aqueous solution of NaOH (500 mL). The whole was extracted with AcOEt (1.5 L x 3), and organic layer was washed with water and brine, dried (MgSO₄), and concentrated in vacuo. The crude product was purified by column chromatography on silica gel (CH₂Cl₂) to give **2a** (420 g, 95%) as an oil. IR (KBr) cm⁻¹: 1580. ¹H-NMR (300 MHz, CDCl₃) δ: 4.00 (3H, s), 6.81 (1H, dd, *J* = 1.5, 7.0 Hz), 7.35-7.51 (4H, m), 7.79 (1H, m), 8.26 (1H). ¹³C-NMR (75 MHz, CDCl₃) δ: 55.2, 103.7, 120.1, 121.9, 125.1, 125.5, 125.8, 126.3, 127.4, 134.4, 155.3. LR-MS *m/z*: 158 (M⁺). HR-MS *m/z*: 158.0734 (Calcd for C₁₁H₁₀O: 158.0732).

1-Methoxy-4-nitronaphthalene (3a)

A mixture of nitric acid (51 mL, 0.56 mol) in acetic anhydride (100 mL, 0.98 mol) was added dropwise to a solution of **2a** (92 g, 0.63 mol) in acetic anhydride (280 mL, 2.7 mol) at 0 °C, and the resulting mixture was stirred at the same temperature for 4 h. To the mixture was added ice-cold water, and the mixture was stirred for 5 h. The precipitates were collected by filtration and purified by column chromatography on silica gel (*n*-hexane-AcOEt, 1:20) to give **3a** (64 g, 50%) as yellow needles. mp 85.0-87.0 °C (CH₂Cl₂-hexane). IR (KBr) cm⁻¹: 1625. ¹H-NMR (300 MHz, CDCl₃) δ: 4.11 (3H, s), 6.83 (1H, d, *J* = 8.8 Hz), 7.60 (1H, m, 6 or 7-H), 7.74 (1H, m, 6 or 7-H), 8.38 (1H, dd, *J* = 0.7, 1.0, 8.5 Hz, 5 or 8-H), 8.41 (1H, d, *J* = 8.6 Hz, 3-H), 8.79 (1H, dd, *J* = 0.7, 0.9, 8.7 Hz). ¹³C NMR (75 MHz, CDCl₃) δ: 56.0, 101.6, 122.5, 123.0, 125.1, 126.2, 126.4, 127.0, 129.7, 138.6, 160.3. LR-MS *m/z*: 203 (M⁺). HR-MS *m/z*: 203.0599 (Calcd for C₁₁H₉NO₃: 203.0582).

4-Methoxy-1-naphthylamine (4a)

A mixture of **3a** (1.00 g, 4.9 mmol) and 10% Pd-C (200 mg) in THF was stirred at room temperature for 3 h under an atmosphere of hydrogen. The mixture was filtered through a pad of Celite, and the filtrate was concentrated in vacuo. The crude product was purified by column chromatography on silica gel (*n*-hexane-AcOEt, 2:1) to give **4a** (721 mg, 85%) as crystals. mp 38.0-40.0 °C (Et₂O-*n*-hexane). IR (KBr) cm⁻¹: 3360, 3185. ¹H NMR (300 MHz, CDCl₃) δ: 3.94 (3H, s), 6.67 (1H, d, *J* = 8.1 Hz), 6.72 (1H, d, *J* = 8.1 Hz), 7.49 (2H, m), 7.82 (1H, m), 8.24 (1H, m). ¹³C-NMR (75 MHz, CDCl₃) δ: 55.8, 104.4, 109.6, 120.9, 122.5, 125.2, 125.2, 125.6, 126.1, 135.2, 149.2. LR-MS *m/z*: 173 (M⁺). HR-MS *m/z*: 173.0855 (Calcd for C₁₁H₁₁NO: 173.0841).

1,7-Dimethoxynaphthalene (2b)

Using a procedure similar to that for the preparation of **2a**, treatment of 1,7-naphthalenediol **1b** (15.0 g, 94 mmol) with dimethyl sulfate (97 mL, 1.0 mol), tetra-*n*-butylammonium bromide (3.90 g, 12 mmol), and KOH (116 g, 2.1 mol) in THF-water (1:2, 150 mL) gave crude product, which was purified by

column chromatography on silica gel (*n*-hexane-AcOEt, 1:10) to afford **2b** (17 g, 95%) as an oil. IR (KBr) cm^{-1} : 1630, 1605, 1510. ^1H -NMR (300 MHz, CDCl_3) δ : 3.75 (3H, s), 3.85 (3H, s), 6.76 (1H, d, $J = 7.7$ Hz), 7.00 (1H, dd, $J = 2.6, 9.5$ Hz), 7.10 (1H, br t, $J = 7.9$ Hz), 7.24 (1H, d, $J = 8.1$ Hz), 7.40 (1H, d, $J = 2.6$ Hz), 7.60 (1H, d, $J = 8.9$ Hz). ^{13}C -NMR (75 MHz, CDCl_3) δ : 55.7, 55.9, 101.3, 105.4, 119.8, 120.9, 124.5, 127.5, 130.1, 130.9, 155.5, 158.5. LR-MS m/z : 188 (M^+). HR-MS m/z : 188.0813 (Calcd for $\text{C}_{12}\text{H}_{12}\text{O}_2$: 188.0837).

1,7-Dimethoxy-4-nitronaphthalene (3b)

Using a procedure similar to that for the preparation of **3a**, treatment of **2b** (5.00 g, 27 mmol) with nitric acid (2.1 mL, 24 mmol) in acetic anhydride (16 mL) gave crude product, which was purified by column chromatography on silica gel (*n*-hexane-AcOEt, 1:20) to afford **3b** (2.1 g, 35%). IR (KBr) cm^{-1} : 1605. ^1H -NMR (300 MHz, CDCl_3) δ : 3.95 (3H, s), 4.09 (3H, s), 6.77 (1H, d, $J = 8.6$ Hz), 7.35 (1H, dd, $J = 2.7, 9.5$ Hz), 7.60 (1H, d, $J = 2.8$ Hz), 8.24 (1H, d, $J = 8.8$ Hz), 8.68 (1H, d, $J = 9.5$ Hz). ^{13}C -NMR (75 MHz, CDCl_3) δ : 55.4, 56.3, 101.1, 102.3, 122.0, 122.2, 124.5, 125.3, 127.1, 139.3, 158.0, 159.3. LR-MS m/z : 233 (M^+). HR-MS m/z : 233.0684 (Calcd for $\text{C}_{12}\text{H}_{11}\text{NO}_4$: 233.0688).

4,6-Dimethoxy-1-naphthylamine (4b)

Using a procedure similar to that for the preparation of **4a**, treatment of **3b** (1.50 g, 6.4 mmol) with 10% Pd-C (300 mg) in THF (10 mL) under hydrogen gave crude product, which was purified by column chromatography on silica gel (*n*-hexane-AcOEt, 1:10) to afford **4b** (1.10 g, 88%). mp 77.0-79.0 °C (Et_2O -*n*-hexane). IR (KBr) cm^{-1} : 3385, 3215. ^1H -NMR (300 MHz, CDCl_3) δ : 3.94 (6H, br s), 6.57 (1H, d, $J = 8.1$ Hz), 6.66 (1H, d, $J = 8.1$ Hz), 7.15 (1H, dd, $J = 2.8, 9.2$ Hz), 7.54 (1H, d, $J = 2.6$ Hz), 7.73 (1H, d, $J = 9.2$ Hz). ^{13}C -NMR (75 MHz, CDCl_3) δ : 55.3, 55.8, 100.9, 105.3, 107.6, 117.9, 120.4, 122.8, 127.2, 135.4, 148.3, 157.4. LR-MS m/z : 203 (M^+). HR-MS m/z : 203.0947 (Calcd for $\text{C}_{12}\text{H}_{13}\text{NO}_2$: 203.0946).

4,8-Dimethoxy-1-naphthylamine (2c)

A mixture of 1,5-naphthalenediol (**1c**, 5.00 g, 31 mmol), methyl iodide (9.7 mL, 0.16 mol), and K_2CO_3 in DMF (50 mL) was stirred at room temperature for 2 h. The mixture was poured into ice-cold water (50 mL), and the resulting precipitates were collected by filtration to give sufficiently pure **2c** (4.7 g, 80%) as granules. mp 181.0-183.0 °C (CH_2Cl_2 -*n*-hexane). IR (KBr) cm^{-1} : 1595. ^1H -NMR (300 MHz, CDCl_3) δ : 3.99 (6H, s), 6.84 (2H, d, $J = 7.7$ Hz), 7.37 (2H, br t, $J = 8.3$ Hz), 7.83 (2H, d, $J = 8.8$ Hz). ^{13}C -NMR (75 MHz, CDCl_3) δ : 55.5, 104.5, 114.2, 125.1, 126.6, 155.2. LR-MS m/z : 188 (M^+). HR-MS m/z : 188.0826 (Calcd for $\text{C}_{12}\text{H}_{12}\text{O}_2$: 188.0837).

1,5-Dimethoxy-4-nitronaphthalene (3c)

Using a procedure similar to that for the preparation of **3a**, treatment of **2c** (1.00 g, 5.3 mmol) with nitric acid (0.4 mL, 4.7 mol) in acetic anhydride (8 mL) gave crude product, which was purified by column chromatography on silica gel (*n*-hexane-AcOEt, 1:20) to afford **3c** (540 mg, 43%) as granules. mp 166.0-168.0 °C (CH₂Cl₂-hexane). IR (KBr) cm⁻¹: 1595, 1530, 1515. ¹H-NMR (300 MHz, CDCl₃) δ: 3.92 (3H, s), 4.04 (3H, s), 6.75 (1H, d, *J* = 8.3 Hz, 2-H), 7.02 (1H, dd, *J* = 0.7, 7.8 Hz), 7.50 (1H, br t, *J* = 8.2 Hz), 7.50 (1H, d, *J* = 8.3 Hz, 3-H), 7.91 (1H, dd, *J* = 0.9, 8.6 Hz). ¹³C-NMR (75 MHz, CDCl₃) δ: 56.0, 56.1, 102.3, 108.4, 114.7, 117.2, 127.2, 132.4, 141.0, 153.7, 157.1. LR-MS *m/z*: 233 (M⁺). HR-MS *m/z*: 233.0701 (Calcd for C₁₂H₁₁NO₄: 233.0688).

4,8-Dimethoxy-1-naphthylamine (4c)

Using a procedure similar to that for the preparation of **4a**, treatment of **3c** (1.00 g, 4.3 mmol) with 10% Pd-C (200 mg) in THF (60 mL) under hydrogen gave crude product, which was purified by column chromatography on silica gel (*n*-hexane-CH₂Cl₂, 1:1) to afford **4c** (742 mg, 85%) as granules. mp 158.0-160.0 °C (CH₂Cl₂-*n*-hexane). IR (KBr) cm⁻¹: 3495, 3380. ¹H-NMR (300 MHz, CDCl₃) δ: 3.91 (3H, s), 3.96 (3H, s), 6.52 (1H, d, *J* = 8.3 Hz), 6.70 (1H, d, *J* = 8.3 Hz), 6.77 (1H, dd, *J* = 0.9, 7.7 Hz), 7.30 (1H, br t, *J* = 8.1 Hz), 7.80 (1H, dd, *J* = 1.0, 8.5 Hz). ¹³C-NMR (75 MHz, CDCl₃) δ: 55.7, 55.1, 104.8, 106.5, 109.1, 115.0, 116.1, 125.2, 128.4, 138.1, 147.3, 157.4. LR-MS *m/z*: 203 (M⁺). HR-MS *m/z*: 203.0978 (Calcd for C₁₂H₁₃NO₂: 203.0946).

2-(4-Methoxynaphthalen-1-ylamino)-1,4-naphthoquinone (5a) and 5,8-dimethoxy-13H-dibenzo[a,i]-carbazole (6a)

Oxygen was sufficiently bubbled through a mixture of **4a** (50 mg, 0.29 mmol) and TiO₂ (1.00 g, 0.63 mmol) in toluene (15 mL). The mixture was heated under oxygen in a sealed tube at 60 °C for 0.5 h. The mixture was filtered through a pad of Celite, and the filtrate was concentrated in vacuo. The crude product was chromatographed on silica gel (*n*-hexane-CH₂Cl₂, 5:1) to give **5a** (23.0 mg, 48%), **6a** (2.8 mg, 6%).

5a: Red granules, mp 199.0-201.0 °C (CH₂Cl₂-*n*-hexane). IR (KBr) cm⁻¹: 3375, 1630, 1600. ¹H-NMR (300 MHz, CDCl₃) δ: 4.05 (3H, s), 6.83 (1H, d, *J* = 8.3 Hz), 7.38 (1H, t, *J* = 8.1 Hz), 7.54 (2H, m), 7.58 (1H, s), 7.67 (1H, dt, *J* = 1.5, 7.5 Hz), 7.75 (1H, dd, *J* = 1.5, 7.5 Hz), 7.80 (1H, m), 8.08 (1H, dd, *J* = 1.5, 7.5 Hz), 8.12 (1H, dd, *J* = 1.5, 7.5 Hz), 8.33 (1H, m). ¹³C-NMR (75 MHz, CDCl₃) δ: 55.8, 103.2, 103.4, 121.8, 122.9, 123.9, 125.3, 126.0, 126.2, 126.3, 126.4, 127.5, 130.0, 130.6, 132.2, 133.5, 134.9, 147.5, 155.0, 182.3, 183.7. LR-MS *m/z*: 329 (M⁺). HR-MS *m/z*: 329.1029 (Calcd for C₂₁H₁₅NO₃: 329.1052).

6a: Colorless syp. IR (KBr) cm⁻¹: 3315. ¹H-NMR (DMSO-*d*₆) δ: 4.16 (6H, s), 7.60 (2H, t, *J* = 7.3 Hz),

7.76 (2H, t, $J = 7.3$ Hz), 7.81 (2H, s), 8.34 (2H, d, $J = 7.3$ Hz), 8.71 (2H, d, $J = 7.3$ Hz), 12.40 (1H, s). LR-MS m/z : 327 (M^+).

7-Methoxy-2-(4,6-dimethoxynaphthalen-1-ylamino)-1,4-naphthoquinone (5b) and 3,5,8,10-tetramethoxy-13H-dibenzo[a,i]carbazole (6b)

(a) Using a procedure similar to that for the preparation of **5a** and **6a**, treatment of **4b** (50 mg, 0.25 mmol) with TiO_2 (1.00 g, 0.63 mmol) in MeCN (15 mL) at 70 °C under oxygen gave crude product, which was purified by column chromatography on silica gel (*n*-hexane- CH_2Cl_2 , 2:1) to afford **5b** (17.5 mg, 36%) and **6b** (2.9 mg, 6%).

(b) The same reaction in toluene at 60 °C afforded **5b** (18.5 mg, 38%) and **6b** (1.0 mg, 2%).

5b: IR (KBr) cm^{-1} : 3330, 1665, 1630. ^1H -NMR (300 MHz, CDCl_3) δ : 3.950 (3H, s), 3.954 (3H, s), 4.04 (3H, s), 5.78 (1H, s), 6.81 (1H, d, $J = 8.2$ Hz), 7.11 (1H, dd, $J = 2.6, 8.6$ Hz), 7.19 (1H, dd, $J = 2.6, 9.3$ Hz), 7.22 (1H, d, $J = 8.4$ Hz), 7.55 (1H, d, $J = 2.6$ Hz), 7.60 (1H, d, $J = 2.6$ Hz), 7.65 (1H, s), 7.71 (1H, d, $J = 9.3$ Hz), 8.10 (1H, d, $J = 8.4$ Hz). ^{13}C -NMR (75 MHz, CDCl_3) δ : 55.4, 55.7, 55.9, 101.2, 102.7, 103.9, 109.8, 118.6, 119.9, 121.1, 123.6, 123.8, 125.1, 125.5, 127.4, 129.0, 136.2, 147.8, 153.8, 157.9, 165.1, 180.8, 183.3. LR-MS m/z : 389 (M^+). HR-MS m/z : 389.1286 (Calcd for $\text{C}_{23}\text{H}_{19}\text{NO}_5$: 389.1263).

6b: Blue purple powder, mp 257.0-261.0 °C (CH_2Cl_2 -*n*-hexane). IR (KBr) cm^{-1} : 3400. ^1H -NMR (300 MHz, CDCl_3) δ : 3.82 (6H, s), 4.00 (6H, s), 7.14 (2H, dd, $J = 2.6, 9.0$ Hz), 7.55 (2H, s), 7.61 (2H, d, $J = 2.6$ Hz), 8.30 (2H, d, $J = 9.0$ Hz), 11.21 (1H, s). ^{13}C -NMR (75 MHz, CD_2Cl_2) δ : 55.5, 55.9, 97.1, 103.0, 117.1, 117.3, 118.0, 121.8, 125.7, 128.7, 149.5, 157.0. LR-MS m/z : 387 (M^+). HR-MS m/z : 387.1502 (Calcd for $\text{C}_{24}\text{H}_{21}\text{NO}_4$: 387.1470).

8-Methoxy-2-(4,8-dimethoxynaphthalen-1-ylamino)-1,4-naphthoquinone (5c) and 1,5,8,12-tetramethoxy-13H-dibenzo[a,i]carbazole (6c)

Using a procedure similar to that for the preparation of **5a** and **6a**, treatment of **4c** (50 mg, 0.25 mmol) with TiO_2 (1.00 g, 0.63 mmol) in toluene (15 mL) at room temperature under oxygen gave crude product, which was purified by column chromatography on silica gel (CH_2Cl_2) to afford **5c** (13.1 mg, 27%) and **6c** (30.5 mg, 63%).

5c: Purple granules, mp 209.0-211.0 °C (CH_2Cl_2 -*n*-hexane). IR (KBr) cm^{-1} : 3450, 1670, 1625. ^1H -NMR (300 MHz, CDCl_3) δ : 4.01 (3H, s), 4.06 (3H, s), 4.09 (3H, s), 6.54 (1H, s), 6.83 (1H, d, $J = 8.6$ Hz), 6.94 (1H, d, $J = 7.7$ Hz), 7.22 (1H, d, $J = 8.3$ Hz, 7-H), 7.407 (1H, t, $J = 8.2$), 7.409 (1H, d, $J = 8.4$ Hz), 7.68 (1H, t, $J = 8.1$ Hz), 7.80 (1H, d, $J = 8.1$ Hz), 7.92 (1H, d, $J = 8.4$ Hz), 10.14 (1H, s). ^{13}C -NMR (75 MHz, CDCl_3) δ : 55.8, 56.2, 56.5, 100.0, 104.0, 107.0, 115.3, 115.9, 118.5, 118.8, 119.6, 119.7, 125.9, 127.4, 128.3, 135.9, 136.0, 146.0, 152.5, 156.1, 160.1, 180.9, 183.6. LR-MS m/z : 389 (M^+). HR-MS m/z :

389.1270 (Calcd for C₂₃H₁₉NO₅: 389.1263).

6c: Colorless crystals, mp over 300 °C (CH₂Cl₂-*n*-hexane). IR (KBr) cm⁻¹: 3490. ¹H-NMR (300 MHz, DMSO-*d*₆) δ: 4.10 (6H, s), 4.26 (6H, s), 7.25 (2H, d, *J* = 7.7 Hz), 7.49 (2H, t, *J* = 8.1 Hz), 7.85 (2H, s), 7.90 (2H, d, *J* = 8.1 Hz), 11.27 (1H, s). ¹³C-NMR (75 MHz, DMSO-*d*₆) δ: 55.9, 56.2, 98.0, 106.0, 113.2, 115.0, 116.7, 124.6, 125.4, 126.1, 148.6, 155.1. LR-MS *m/z*: 387 (M⁺). HR-MS *m/z*: 387.1463 (Calcd for C₂₄H₂₁NO₄: 387.1470).

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