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NOVEL METHODS OF SYNTHESIZING NAPHTHO[1,2-*c*]FURAN-1,3-DIONE AND BENZO[*e*]ISOINDOLE-1,3-DIONE

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Dedicated to Professor Barry M. Trost on the occasion of his 65th birthday

Abstract – Convenient methods of synthesizing naphtho[1,2-*c*]furan-1,3-dione and benzo[*e*]isoindole-1,3-dione from phenylbutyric acid derivatives have been established. Naphtho[1,2-*c*]furan-1,3-dione and benzo[*e*]isoindole-1,3-dione were obtained respectively from 4,5-dihydronaphtho[1,2-*c*]furan-1,3-dione and 4,5-dihydrobenzo[*e*]isoindole-1,3-dione by aromatization with 10% Pd-C in AcOH under mild conditions. In addition, benzo[*e*]isoindole-1,3-dione derivatives were obtained from 4,5-dihydronaphtho[1,2-*c*]furan-1,3-dione by imidation and simultaneous aromatization with primary amine in AcOH in one pot.

INTRODUCTION

Naphtho[1,2-*c*]furan-1,3-dione and benzo[*e*]isoindole-1,3-dione are useful intermediates for medicines, agrochemicals and chemicals, e.g. 6-methacryloxyethyl 1,2,6-naphthalenetricarboxylic cyclic anhydride, which is used as a dental adhesive, [1] and 2-[1-(3-ethoxy-4-methoxyphenyl)-2-methylsulfonylethyl]-benzo[*e*]isoindoline-1,3-dione, which reduces levels of TNF α and inhibits PDE IV in mammals. [2]

Conventionaly, several methods have been reported for the synthesis of naphtho[1,2-*c*]furan-1,3-dione. For example, ethyl 3-carboethoxy-2-oxo-5-phenylpentanate, derived from phenylbutyric acid, was cyclized to obtain 4,5-dihydronaphtho[1,2-*c*]furan-1,3-dione, then aromatized by heating at 250°C with sulfur to obtain naphtho[1,2-*c*]furan-1,3-dione. [3] α-Bromostylene was cyclized with maleic anhydride to afford 1,2-dihydronaphtho[1,2-*c*]furan-1,3-dione, then aromatized by heating at 250°C with sulfur to give naphtho[1,2-*c*]furan-1,3-dione. [4] 1-Chloromethyl-2-methylnaphthalene, derived from 2-methylnaphthalene, was heated at 240°C under elevated pressure with sodium bichromate to yield

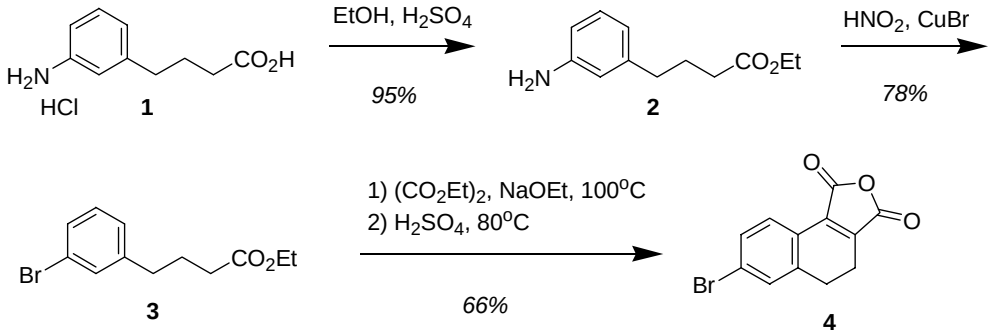
1,2-naphthalenedicarboxylic acid, [5] then reacted with acetic anhydride to give naphtho[1,2-*c*]furan-1,3-dione. However, all of these methods require extremely high temperatures (*ca.* 240-250 °C), so they are difficult to use in the case of unstable compounds.

Several methods have been developed for aromatization by dehydrogenation, [6] e.g. using sulfur, selenium, platinum, palladium, aluminum chloride, ammonium ceric nitrate (CAN), chloranil, 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ), trityl tetrafluoroborate, diphenylpicrylhydrazyl, etc. Hence, we planned the development of novel methods to obtain naphtho[1,2-*c*]furan-1,3-dione and benzo[*e*]isoindole-1,3-dione, which in normally produced by amidation, under mild and convenient conditions.

RESULTS AND DISCUSSION

1. Synthesis of 4,5-dihydronaphtho[1,2-*c*]furan-1,3-dione

Among several methods of synthesizing naphtho[1,2-*c*]furan-1,3-dione, we focused on that *via* 4,5-dihydronaphtho[1,2-*c*]furan-1,3-dione, because of its inexpensive starting material and reagents. 7-Bromo-4,5-dihydronaphtho[1,2-*c*]furan-1,3-dione (**4**), a new compound, was prepared from 4-(3-aminophenyl)butanoic acid hydrochloride (**1**) as shown in Scheme 1. Ethyl 4-(3-bromophenyl)butanoate (**3**) was reacted with diethyl oxalate and base, then acid was added to the reaction mixture to give **4**.

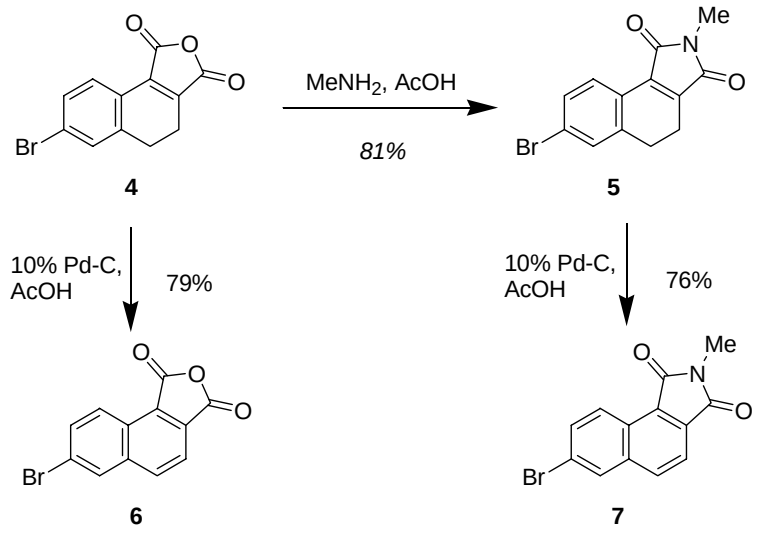


Scheme 1. Synthesis of 7-bromo-4,5-dihydronaphtho[1,2-*c*]furan-1,3-dione

2. Aromatization to naphtho[1,2-*c*]furan-1,3-dione and benzo[*e*]isoindole-1,3-dione using 10% Pd-C

To avoid the extremely high temperature needed for aromatization using sulfur, we studied DDQ and 10% Pd-C to obtain 7-bromonaphtho[1,2-*c*]furan-1,3-dione (**6**) from **4**. In the case of DDQ, the products were complex mixtures. In the case of 10% Pd-C, the reaction proceeded under mild conditions. Consequently, we determined the conditions for the reaction of **4** with 10% Pd-C (50%wet) (4 times the weight of **4**) in AcOH at 120°C, and obtained **6** in 79% yield as shown in Scheme 2.

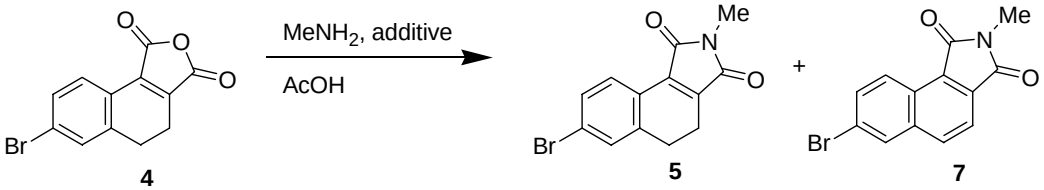
Similarly, 7-bromo-2-methyl-1*H*-benzo[*e*]isoindole-1,3(2*H*)-dione (**7**) was obtained in 76% yield from 7-bromo-2-methyl-4,5-dihydro-1*H*-benzo[*e*]isoindole-1,3(2*H*)-dione (**5**), which was obtained in 81% yield by the reaction of **4** with 2eq. of 40% methylamine (MeOH solution) in AcOH, by the same reaction as **4** to **6**.



Scheme 2. Aromatization using 10% Pd-C

This method of aromatization using 10% Pd-C is a mild and convenient way of synthesizing naphtho[1,2-*c*]furan-1,3-dione and benzo[*e*]isoindole-1,3-dione derivatives.

Table 1. Reaction from **4** to **5** and/or **7**



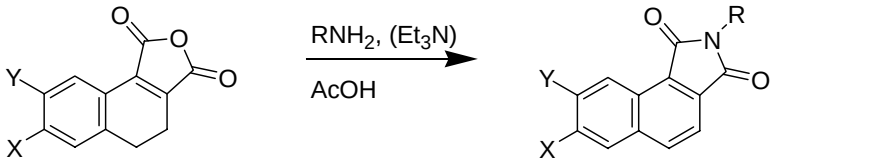
Entry	$MeNH_2$ (eq.)	Additive (eq.)	Conditions	Ratio by HPLC [b]	
				5	**7**
1	2	none	120°C – 4 h	95	5
2	10	none	120°C – 4 h	77	23
			24 h	53	48
3	25	none	120°C – 4 h	36	64
			24 h	4	96
4	50	none	120°C – 4 h	23	77
			24 h	**0.1**	**99.9**
5	2	Et_3N (8)	120°C – 4 h	20	80
			24 h	2	98
6	2	Et_3N (23)	120°C – 4 h	2	98
			24 h	**ND** [c]	**100**
7	10	Et_3N (15)	120°C – 4 h	10	90
			24 h	**ND**	**100**
8	10	AcONa (15)	120°C – 4 h	45	55
			24 h	6	94

a 300 eq. of AcOH was used as solvent. b Determined at 220nm. c ND = Not detected.

3. One-pot imidation and aromatization to benzo[*e*]isoindole-1,3-dione using primary amine

In the course of our studies of the conversion of **4** to **5**, we noticed that the ratio of the aromatized compound (**7**) increased depending on the equivalent of methylamine as shown in Table 1. (Entries 1-4) Furthermore, this reaction was accelerated by addition of triethylamine. (Entries 5-7)

Consequently, using only methylamine and base in refluxing AcOH, **7** was obtained in 81% yield by imidation and simultaneous aromatization by oxidation in one-pot starting from **4** as shown in Scheme 3. Using the same procedure, several benzo[*e*]isoindole-1,3-dione derivatives (**9, 11, 12, 13**) were obtained in good yield by imidation and simultaneous aromatization by oxidation in one pot from 4,5-dihydronaphtho[1,2-*c*]furan-1,3-dione derivatives (**4, 8, 10**).



4 (X=Br, Y=H)
8 (X=H, Y=H)
10 (X=H, Y=OMe)

7 (R=Me, X=Br, Y=H); *81%* [a]
9 (R=Me, X=H, Y=H); *71%* [a]
11 (R=Me, X=H, Y=OMe); *49%* [a]
12 (R=Bn, X=Br, Y=H); *56%* [a]
13 (R=Ph, X=Br, Y=H); *87%* [a]
[a] *isolated yield*

Scheme 3. One pot imidation and aromatization using primary amine

CONCLUSION

In conclusion, we achieved the synthesis of naphtho[1,2-*c*]furan-1,3-dione and benzo[*e*]isoindole-1,3-dione in acetic acid with 10% Pd-C under mild conditions. Unexpectedly, benzo[*e*]isoindole-1,3-dione was obtained by imidation and simultaneous aromatization by oxidation in refluxing acetic acid with primary amine in two steps, one pot.

EXPERIMENTAL

Melting points were determined based on differential scanning calorimetry (DSC). IR spectra were recorded on a Thermo Electron Nicolet 4700 spectrophotometer. NMR spectra were recorded on a Bruker DPX300 spectrometer. ^{1}H and ^{13}C NMR chemical shifts were referenced to the internal deuterated solvent or tetramethylsilane. HPLC was performed with a Hitachi L-6200, Hitachi L-4000 UV spectrophotometric detector at 220 nm, and YMC ODS-Pack A-302 150 mm×4.6 mm i.d. column. DSC, MS spectra and elemental analyses were performed at Takeda Analytical Research Laboratories, Ltd.. All commercial chemicals and solvents were of reagent grade and used without further purification.

Ethyl 4-(3-aminophenyl)butanoate (2). To a suspension of 4-(3-aminophenyl)butanoic acid hydrochloride (**1**; 4.31 g, 20 mmol) in EtOH (10 mL) was added conc. H_2SO_4 (0.4 mL), and the resulting

mixture was refluxed for 1 h. After cooling, AcOEt (20 mL) and 1N-NaOH (40 mL) were added to the reaction mixture and separated. The organic extract was washed with 1N-NaOH (30 mL) and H_2O (30 mL x 2) and concentrated in vacuo to give **2** (3.93 g, 94.7%) as a pale brown liquid; HPLC(50 mM KH_2PO_4-MeCN= 50:50) t_R: 2.1(**1**), 5.4(**2**); ^{1}H-NMR(300 MHz, $CDCl_3$): δ 1.24(t, *J*=7.1 Hz, 3H), 1.92(quint, *J*=7.4 Hz, 2H), 2.30(t, *J*=7.4 Hz, 2H), 2.55(t, *J*=7.4 Hz, 2H), 3.62(br, 2H), 4.12(q, *J*=7.1 Hz, 2H), 6.49-6.58(m, 3H), 7.02-7.08(m, 1H); ^{13}C-NMR(75 MHz, $CDCl_3$): δ 14.2, 26.3, 33.6, 35.0, 60.1, 112.7, 115.2, 118.7, 129.2, 142.6, 146.4, 173.5.

Ethyl 4-(3-bromophenyl)butanoate (3). To a solution of **2** (207 mg, 1 mmol) and 48% HBr (1 mL) was added an H_2O (0.5 mL) solution of sodium nitrite (69 mg, 1 mmol), and the resulting mixture was added to a solution of copper(I) bromide (143 mg, 1 mmol) and 48% HBr (0.2 mL) in acetone (2 mL). After the resulting mixture was stirred for 1 h, AcOEt (6 mL) and H_2O (4 mL) were added to the reaction mixture and separated. The organic extract was washed with 1N-NaOH (4 mL x 2) and H_2O (4 mL x 2) and concentrated in vacuo to give **3** (210 mg, 77.5%) as an orange liquid; HPLC(50 mM KH_2PO_4-MeCN= 30:70) t_R: 2.8(**2**), 7.4(**3**); ^{1}H-NMR(300 MHz, $CDCl_3$): δ 1.26(t, *J*=7.1 Hz, 3H), 1.94(quint, *J*=7.4 Hz, 2H), 2.31(t, *J*=7.4 Hz, 2H), 2.62(t, *J*=7.4 Hz, 2H), 4.13(q, *J*=7.1 Hz, 2H), 7.10-7.19(m, 2H), 7.30-7.33(m, 2H); ^{13}C-NMR(75 MHz, $CDCl_3$): δ 14.2, 26.2, 33.5, 34.7, 60.3, 122.4, 127.1, 129.1, 129.9, 131.5, 143.7, 173.2.

7-Bromo-4,5-dihydronaphtho[1,2-*c*]furan-1,3-dione (4). To a suspension of sodium ethoxide (61 mg, 0.9 mmol) in THF (1 mL) were added diethyl oxalate (105 mg, 0.72 mmol) and **3** (163 mg, 0.6 mmol), and the resulting mixture was stirred at 100°C for 1 h. After cooling, 80% H_2SO_4 (4 mL) was added to the mixture at 0°C, and the resulting mixture was stirred at 80°C for 30 min. After cooling, the resulting precipitates were collected by filtration, washed with H_2O (2 mL x 3) and dried in vacuo to give **4** (110 mg, 65.9%) as a pale yellow crystalline powder; HPLC(50 mM KH_2PO_4-MeCN= 30:70) t_R: 7.4(**3**), 4.9(**4**); mp 181.9°C (AcOH); IR(KBr): 1833.9, 1755.0, 1262.3, 876.6 cm^{-1}; ^{1}H-NMR(300 MHz, $CDCl_3$): δ 2.79(t, *J*=8.5 Hz, 2H), 3.09(t, *J*=8.5 Hz, 2H), 7.46(s, 1H), 7.49(dd, *J*=8.1 Hz, 1.9 Hz, 1H), 7.91(d, *J*=8.1 Hz, 1H); ^{13}C-NMR(75 MHz, $CDCl_3$): δ 18.5, 26.7, 124.0, 126.7, 127.7, 130.8, 131.8, 138.7, 138.8, 139.8, 162.8, 163.9; MS(EI): m/z 278[M]$^+$; Anal. Calcd for $C_{12}H_7O_3Br$: C, 51.64; H, 2.53. Found: C, 51.96; H, 2.74.

7-Bromo-2-methyl-4,5-dihydro-1*H*-benzo[e]isoindole-1,3(2*H*)-dione (5). To a suspension of **4** (279 mg, 1 mmol) in AcOH (17 mL) was added 40% methylamine (methanol solution) (0.16 mL, 2 mmol) at 0°C, and the resulting mixture was stirred at 120°C for 4 h. After cooling, the resulting precipitates were collected by filtration, washed with MeOH (4 mL x 3) and dried in vacuo to give **5** (235 mg, 80.5%) as a yellow crystalline powder; HPLC(50 mM KH_2PO_4-MeCN= 30:70) t_R: 4.8(**4**), 5.9(**5**); mp 169.1°C

(AcOH); IR(KBr): 1759.7, 1696.0, 1435.4, 1382.9 cm^{-1}; ^{1}H-NMR(300 MHz, $CDCl_3$): δ 2.67(t, *J*=8.4 Hz, 2H), 2.99(t, *J*=8.4 Hz, 2H), 3.05(s, 3H), 7.38(s, 1H), 7.42(dd, *J*=8.2 Hz, 1.9 Hz, 1H), 7.96(d, *J*=8.2 Hz, 1H); ^{13}C-NMR(75 MHz, $CDCl_3$): δ 17.9, 23.6, 27.0, 124.6, 125.6, 127.1, 130.3, 131.4, 135.4, 138.1, 138.7, 169.4, 170.1; MS(EI): m/z 291$[M]^+$; Anal. Calcd for $C_{13}H_{10}NO_2Br$: C, 53.45; H, 3.45; N, 4.79. Found: C, 53.71; H, 3.43; N, 4.89.

7-Bromonaphtho[1,2-*c*]furan-1,3-dione (6). To a suspension of **4** (28 mg, 0.1 mmol) in AcOH (1 mL) was added 10% Pd-C (50% wet) (112 mg), and the resulting mixture was stirred at 120°C for 6 h. After cooling, Pd-C was filtered off and washed with AcOEt, and the mother solution was concentrated in vacuo to give **6** (22 mg, 78.6%) as a white crystalline powder; HPLC(50 mM KH_2PO_4-MeCN= 30:70) t_R: 4.9(**4**), 5.0(**6**); mp 211.6°C (AcOH); IR(KBr): 1840.4, 1759.2, 1281.6, 882.1 cm^{-1}; ^{1}H-NMR(300 MHz, DMSO-d_6): δ 8.04(dd, *J*=8.8 Hz, 2.0 Hz, 1H), 8.07(d, *J*=8.6 Hz, 1H), 8.48(d, *J*=8.4 Hz, 1H), 8.55(d, *J*=9.0 Hz, 1H), 8.58(d, *J*=1.8 Hz, 1H); ^{13}C-NMR(75 MHz, DMSO-d_6): δ 120.8, 123.7, 125.6, 125.8, 127.8, 131.4, 131.5, 133.6, 136.4, 137.4, 163.2(2C); MS(EI): m/z 276$[M]^+$; Anal. Calcd for $C_{12}H_5O_3Br$: C, 52.02; H, 1.82. Found: C, 52.14; H, 2.07.

7-Bromo-2-methyl-1*H*-benzo[*e*]isoindole-1,3(2*H*)-dione (7) from 5 using 10% Pd-C. To a suspension of **5** (29 mg, 0.1 mmol) in AcOH (1 mL) was added 10% Pd-C (50% wet) (116 mg), and the resulting mixture was stirred at 120°C for 10 h. After cooling, Pd-C was filtered off and washed with AcOEt, and the mother solution was concentrated in vacuo to give **7** (22 mg, 75.9%) as a white crystalline powder; HPLC(50 mM KH_2PO_4-MeCN= 30:70) t_R: 5.9(**5**), 6.2(**7**); mp 238.7 °C (AcOH); IR(KBr): 1758.0, 1707.5, 1697.9, 1379.8cm^{-1}; ^{1}H-NMR(300 MHz, $CDCl_3$): δ 3.22(s, 3H), 7.78(dd, *J*=9.0 Hz, 1.9 Hz, 1H), 7.88(d, *J*=8.3 Hz, 1H), 8.05(d, *J*=8.3 Hz, 1H), 8.12(d, *J*=1.8 Hz, 1H), 8.80(d, *J*=9.0 Hz, 1H); ^{13}C-NMR(75 MHz, $CDCl_3$): δ 23.9, 119.6, 123.4, 126.3, 126.5, 127.9, 130.7, 131.6, 132.9, 133.7, 137.5, 168.7, 169.3; MS(EI): m/z 289$[M]^+$; Anal. Calcd for $C_{13}H_8NO_2Br.0.4H_2O$: C, 52.52; H, 2.98; N, 4.71. Found: C, 52.60; H, 2.94; N, 4.67.

7 from 4 using methylamine and triethylamine. To a suspension of **4** (70 mg, 0.25 mmol) in AcOH (4.3 mL) were added 40% methylamine (methanol solution) (0.04 mL, 0.5 mmol) and triethylamine (582 mg, 5.75 mmol) at 0°C, and the resulting mixture was stirred at 120°C for 24 h. After cooling, the resulting precipitates were collected by filtration, washed with MeOH (1 mL x 3) and dried in vacuo to give **7** (59 mg, 80.8%) as a yellow crystalline powder; HPLC(50 mM KH_2PO_4-MeCN= 30:70) t_R: 4.8(**4**), 5.9(**5**), 6.2(**7**).

2-Methyl-1*H*-benzo[*e*]isoindole-1,3(2*H*)-dione (9). To a suspension of 4,5-dihydronaphtho[1,2-*c*]-furan-1,3-dione (**8**; 60 mg, 0.3 mmol) in AcOH (3 mL) was added 40% methylamine (methanol solution) (1.2 mL, 15 mmol) at 0°C, and the resulting mixture was stirred at 120°C for 48 h. After cooling, the resulting precipitates were collected by filtration, washed with MeOH (1 mL x 3) and dried in vacuo to

give **9** (45 mg, 71.4%) as a pale yellow crystalline powder; HPLC(50 mM KH_2PO_4-MeCN= 65:35) t_R: 31.4(**8**), 30.3(**9**); mp 167.4°C (AcOH); IR(KBr): 1706.7, 1694.6, 1437.1, 1378.8 cm^{-1}; ^{1}H-NMR(300 MHz, $CDCl_3$): δ 3.19(s, 3H), 7.59-7.71(m, 2H), 7.79(d, *J*=8.2 Hz, 1H), 7.90(d, *J*=8.1 Hz, 1H), 8.09(d, *J*=8.2 Hz, 1H), 8.87(d, *J*=8.3 Hz, 0.8 Hz, 1H); ^{13}C-NMR(75 MHz, $CDCl_3$): δ 23.7, 118.3, 124.8, 127.4, 127.8, 128.6(2C), 129.3, 131.3, 134.7, 136.4, 168.9, 169.6; MS(ESI): m/z 212$[M+H]^+$; Anal. Calcd for $C_{13}H_9NO_2$: C, 73.92; H, 4.29; N, 6.63. Found: C, 73.80; H, 4.19; N, 6.64.

8-Methoxy-2-methylbenzo[*e*]isoindole-1,3-dione (11). To a suspension of 8-methoxy-4,5-dihydro-naphtho[1,2-*c*]furan-1,3-dione (**10**; 115 mg, 0.5 mmol) in AcOH (8.5 mL) were added 40% methylamine (methanol solution) (0.08 mL, 1 mmol) and triethylamine (1.16 g, 11.5 mmol) at 0°C, and the resulting mixture was stirred at 120°C for 24 h. After cooling, the resulting precipitates were collected by filtration, washed with MeOH (2 mL x 3) and dried in vacuo to give **11** (59 mg, 48.8%) as a pale yellow crystalline powder; HPLC(50 mM KH_2PO_4-MeCN= 30:70) t_R: 3.7(**10**), 4.3(**11**); mp 173.8 °C (AcOH); IR(KBr): 1753.3, 1708.5, 1695.9, 1377.8 cm^{-1}; ^{1}H-NMR(300 MHz, $CDCl_3$): δ 3.19(s, 3H), 3.99(s, 3H), 7.23(dd, *J*=9.1 Hz, 2.6 Hz, 1H), 7.64(d, *J*=8.1 Hz, 1H), 7.76(d, *J*=9.1 Hz, 1H), 7.98(d, *J*=8.1 Hz, 1H), 8.14(d, *J*=2.4 Hz, 1H); ^{13}C-NMR(75 MHz, $CDCl_3$): δ 23.6, 55.6, 102.0, 116.1, 122.1, 125.5, 129.6, 130.0, 131.7, 132.3, 134.3, 160.5, 169.1, 170.0; MS(ESI): m/z 242$[M+H]^+$; Anal. Calcd for $C_{14}H_{11}NO_3.0.1H_2O$: C, 68.73; H, 4.61; N, 5.73. Found: C, 68.74; H, 4.50; N, 5.77.

2-Benzyl-7-bromobenzo[*e*]isoindole-1,3-dione (12). To a suspension of **4** (84 mg, 0.3 mmol) in AcOH (5.1 mL) were added benzylamine (64 mg, 0.6 mmol) and triethylamine (698 mg, 6.9 mmol) at 0°C, and the resulting mixture was stirred at 120°C for 24 h. After cooling, the resulting precipitates were collected by filtration, washed with MeOH (1.5 mL x 3) and dried in vacuo to give **12** (61 mg, 55.5%) as an orange crystalline powder; HPLC(50 mM KH_2PO_4-MeCN= 30:70) t_R: 4.8(**4**), 13.0(**12**); mp 157.9 °C (AcOH); IR(KBr): 1697.7, 1397.3, 1387.9, 1352.8 cm^{-1}; ^{1}H-NMR(300 MHz, $CDCl_3$): δ 4.88(s, 2H), 7.24-7.35(m, 3H), 7.45-7.48(m, 2H), 7.75(dd, *J*=9.0 Hz, 1.9 Hz, 1H), 7.85(d, *J*=8.3 Hz, 1H), 8.01(d, *J*=8.3 Hz, 1H), 8.08(d, *J*=1.7 Hz, 1H), 8.77(d, *J*=9.0 Hz, 1H); ^{13}C-NMR(75 MHz, $CDCl_3$): δ 41.6, 119.7, 123.5, 126.3, 126.5, 127.7, 127.8, 128.6(2C), 128.7(2C), 130.7, 131.4, 132.9, 133.8, 136.4, 137.5, 168.2, 168.8; MS(ESI): m/z 366$[M+H]^+$; Anal. Calcd for $C_{19}H_{12}NO_2Br$: C, 62.32; H, 3.30; N, 3.82. Found: C, 62.24; H, 3.36; N, 3.96.

7-Bromo-2-phenylbenzo[*e*]isoindole-1,3-dione (13). To a suspension of **4** (84 mg, 0.3 mmol) in AcOH (5.1 mL) were added phenylamine (56 mg, 0.6 mmol) and triethylamine (698 mg, 6.9 mmol) at 0°C, and the resulting mixture was stirred at 120°C for 24 h. After cooling, the resulting precipitates were collected by filtration, washed with MeOH (1.5 mL x 3) and dried in vacuo to give **13** (92 mg, 86.8%) as a yellow crystalline powder; HPLC(50 mM KH_2PO_4-MeCN= 30:70) t_R: 4.8(**4**), 9.2(**13**); mp 292.2 °C (AcOH);

IR(KBr): 1716.1, 1502.2, 1384.9, 749.8 cm^{-1}; ^{1}H-NMR(300 MHz, $CDCl_3$): δ 7.37-7.56(m, 5H), 7.84(dd, *J*=9.0 Hz, 1.9 Hz, 1H), 7.99(d, *J*=8.3 Hz, 1H), 8.15(d, *J*=8.3 Hz, 1H), 8.18(d, *J*=1.9 Hz, 1H), 8.89(d, *J*=9.0 Hz, 1H); ^{13}C-NMR(75 MHz, $CDCl_3$): δ 120.0, 123.8, 126.57, 126.61(2C), 126.7, 128.1, 129.1, 129.2(2C), 130.9, 131.2, 131.6, 133.2, 134.3, 137.8, 167.5, 168.1; MS(ESI): m/z 352$[M+H]^+$; Anal. Calcd for $C_{18}H_{10}NO_2Br$: C, 61.39; H, 2.86; N, 3.98. Found: C, 61.39; H, 2.92; N, 4.07.

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