

**A NEW CONVENIENT METHOD FOR SYNTHESIS OF 3-(2-
OXOETHYLIDENE)ISOINDOLIN-1-ONES EMPLOYING
PALLADIUM(II) ACETATE AND DDQ[†]**

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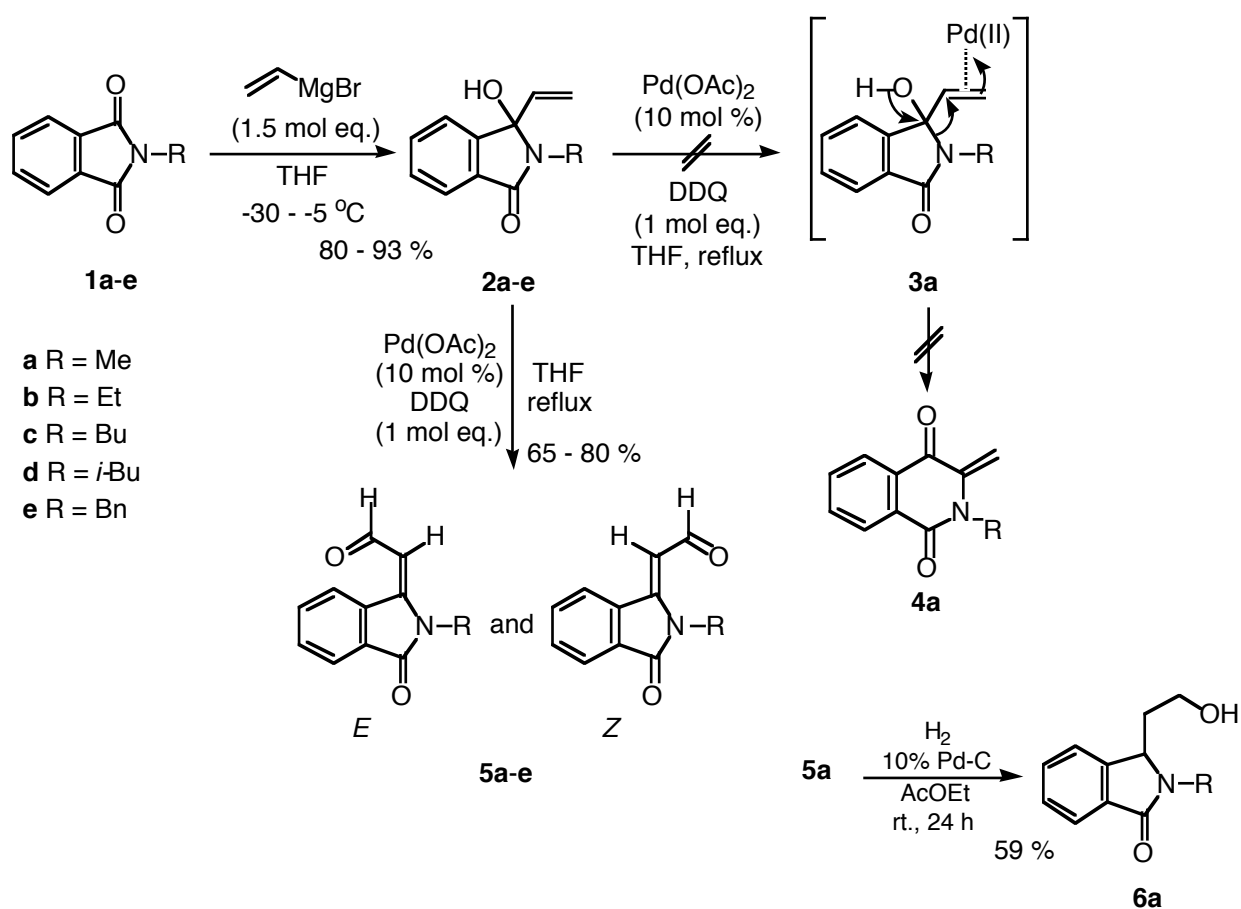
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Abstract – Treatment of 2-alkyl-3-hydroxy-3-vinylisoindolin-1-ones with 10 mol % of Pd(OAc)₂ and 1 mol eq. of DDQ in THF under reflux gave 3-(2-oxoethylidene)isoindolin-1-ones in 65-80% yields.

Since the success of a ring-expansion reaction of 1-vinyl-1-cyclobutanols with PdCl₂(PhCN)₂ and *p*-benzoquinone by Clark and Thiensathit in 1985,¹ there have been many interesting reports of the Pd(II)-catalyzed ring expansion reactions of 4-alkynyl-4-hydroxycyclobutenones with Pd(OCOCF₃)₂,² 1-vinyl-1-trimethylsilyloxycyclobutanes with PdCl₂(PhCN)₂,³ 1-vinyl-1-triethylsilyloxycyclobutanes with PdCl₂(MeCN)₂ in the presence of *p*-benzoquinone (BQ) or Pd(OAc)₂ in the presence of AsPh₃,⁴ and 1-vinyl-1-cyclobutanols with Pd(OAc)₂ in the presence of 2,3-dichloro-5,6-dicyanoquinone (DDQ).⁵

In a series of studies of the palladium-catalyzed ring-expansion reactions by our group,⁶ we attempted at some reactions of 3-hydroxy-2-methyl-3-vinylisoindolin-1-one (**2a**) using Pd(OAc)₂ and an oxidizing reagent in order to obtain an isoquinolone (**4a**) via **3a**. 2-Alkyl-3-hydroxy-3-vinylisoindolin-1-ones (**2a-e**) were synthesized in 80-93% yields by treatment of the corresponding *N*-alkylphthalimides (**1a-e**)⁷ with 1.5 mol eq. of vinylmagnesium bromide in THF at -30 - -5 °C (Scheme 1). Thus, compound (**2a**) was allowed to react with 10 mol % of Pd(OAc)₂ in the presence of 1 mol eq. of oxidizing reagent such as DDQ, *N*-methylmorpholine *N*-oxide (NMO), cerium(IV) ammonium nitrate (CAN), and BQ in THF under reflux. Although the reactions using NMO, CAN, and BQ resulted in 96%, 8%, and 99% recoveries of **2a**, respectively, the use of DDQ afforded 3-(2-oxoethylidene)isoindolin-1-one (**5a**) as an *E* and *Z* (94 : 6) mixture in 78% yield in place of the desirable ring-expanded product (**4a**), as shown in Scheme 1.

[†] On the occasion of the 30th Anniversary of Heterocycles.



Scheme 1.

The structure of pure *E*-**5a** (mp 184-185 °C), obtained by recrystallization of the *E* and *Z* mixture from EtOH, was assigned by its characteristic spectroscopic data and the selected HMBC correlations depicted in Figure 1, and then identical with the reported data (¹H-NMR, IR, and mp 183-184 °C) of the known compound⁸ which was prepared by Pandit *et al.* Hydrogenation product of **5a** was also determined to be the known compound (**6a**)⁸ in comparison with its physical data.

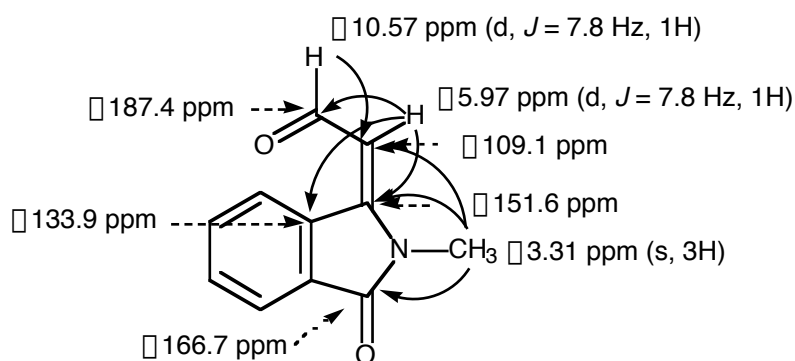


Figure 1. Important HMBC correlations of compound (**5a**)

Similar treatment of compounds (**2b-e**) with 10 mol % of Pd(OAc)₂ in the presence of 1 mol eq. of DDQ in THF under reflux furnished the corresponding 3-(2-oxoethylidene)isoindolin-1-ones (**5b-e**) (65-80% yields) as each *E* and *Z* mixture in a highly *E*-selective manner (*E* : *Z* = 96 : 4), as shown in Table 1. Pure compound (*E*-**5b**) (mp 131-132 °C) was obtained by recrystallization of the *E* and *Z* mixture from EtOH.

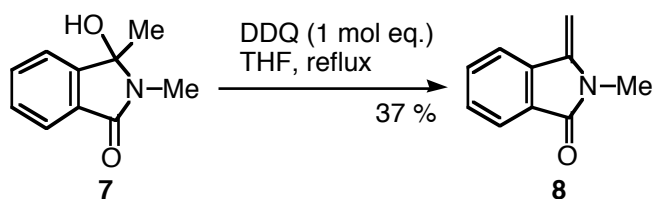
Table 1. Conversion of 2-Alkyl-3-hydroxy-3-vinylisoindolin-1-ones (**2a-e**) to 2-Alkyl-3-(2-oxoethylidene)isoindolin-1-ones (**5a-e**) Employing Pd(OAc)₂ and DDQ

Compound	Time / h	Product	Yield ^{a)} / %	<i>E</i> : <i>Z</i> ^{b)}
2a	6	5a	78	94 : 6
2b	4	5b	79	96 : 4
2c	5	5c	70	96 : 4
2d	5	5d	65	96 : 4
2e	4	5e	80	96 : 4

a) Total yield of an *E* and *Z* mixture.

b) Determined by ¹H-NMR (400 MHz, CDCl₃) spectral analysis of the crude product.

In order to realize the reaction mechanism (**2** → **5**), several reactions were tentatively taken place as follows. Treatment of **2a** with 10 mol % of Pd(OAc)₂ alone in THF under reflux for 24 h turned out to be recovery (37%) of **2a**. 2,3-Dimethyl-3-hydroxyisoindolin-1-one (**7**) was treated with 1 mol eq. of DDQ in THF under reflux for 6 h to give a dehydrated product (**8**)⁹ in 37% yield, as shown in Scheme 2.



Scheme 2.

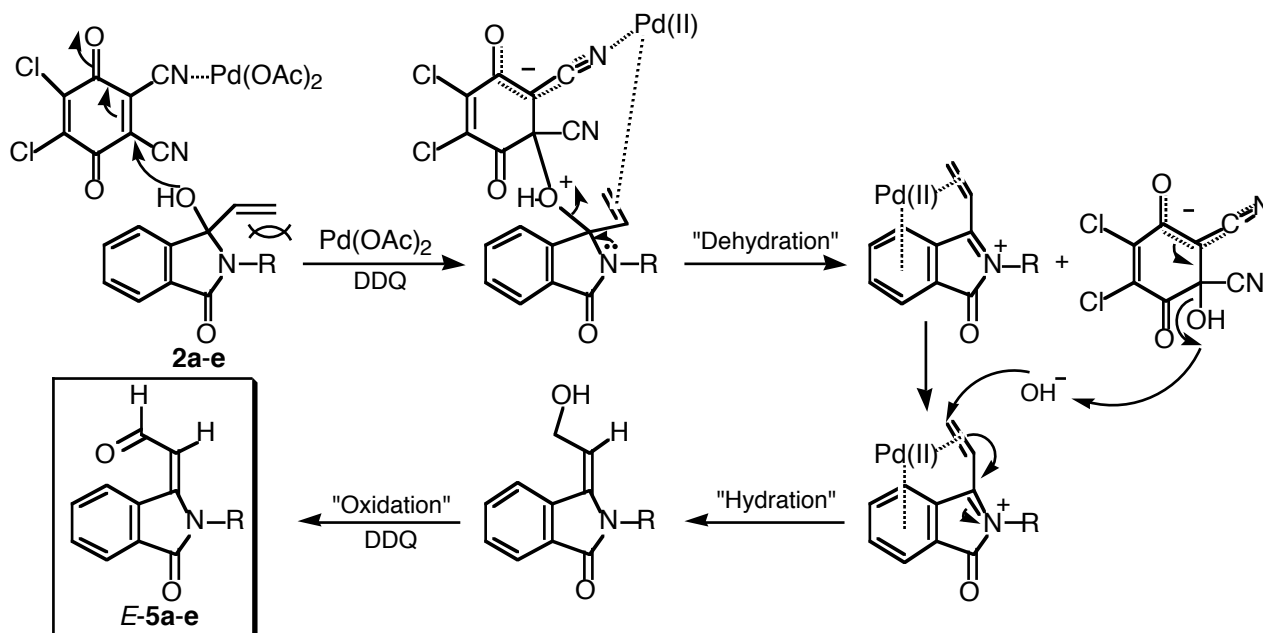
Similar reactions of **2a-e** with 1 mol eq. of DDQ under reflux without the use of Pd(OAc)₂ afforded the corresponding compounds (**5a-d**) as each *E* and *Z* mixture with various ratios and in lower yields (30-51%) than the cases together with Pd(OAc)₂. All results are summarized in Table 2. Formation of **5** in a high or good *E*-selective manner can be explained in terms of the steric repulsion between the vinyl group and the RN group in the course of hydration to the conjugated α,β -unsaturated iminium moiety with concerted double bond migration. However, the difference of each *E* : *Z* ratio of the products is unclear. On the basis of the experimental results described above, we propose a plausible reaction mechanism (Scheme 3) involving possibly Lewis-acidic activation by Pd(OAc)₂ to DDQ (CN group) for easy dehydration and coordination of both vinyl and phenyl groups to Pd(II) in order to provide the high *E*-selectivity toward **5**.

Table 2. Conversion of 2-Alkyl-3-hydroxy-3-vinylisoindolin-1-ones (**2a-e**) to 2-Alkyl-3-(2-oxoethylidene)isoindolin-1-ones (**5a-e**) Employing DDQ

Compound	Time / h	Product	Yield ^{a)} / %	<i>E</i> : <i>Z</i> ^{b)}
2a	10	5a	30	94 : 6
2b	24	5b	38	82 : 18
2c	27	5c	46	87 : 13
2d	25	5d	51	96 : 4
2e	44	5e	39	91 : 9

a) Total yield of an *E* and *Z* mixture.

b) Determined by ¹H-NMR (400 MHz, CDCl₃) spectral analysis of the crude product.



Scheme 3.

Although three kinds of synthetic methods for 3-(2-oxoethylidene)isoindolin-1-ones have been reported by Müller and Seefeldler,¹⁰ Soetens and Pandit,⁸ and Omar *et al.*,¹¹ respectively, the present new method seems to be simple and mechanistically interesting.

EXPERIMENTAL

All melting points were determined on a Yanaco micro melting point apparatus and are uncorrected. IR spectra were obtained using a Perkin-Elmer 1720 or JASCO FT/IR-420 IR Fourier transform spectrophotometer. ¹H NMR (400 MHz) and ¹³C NMR (100 MHz) spectra were recorded on a JEOL JNM-AL400 spectrometer. Chemical shifts are given in δ values (ppm) using tetramethylsilane (TMS) as an internal standard. EI-MS were recorded on a JEOL JMS SX-102A spectrometer. Elementary combustion analyses were performed using a Yanaco CHN CORDER MT-5. All reactions were monitored by TLC employing 0.25 mm silica gel plates (Merck 5715; 60 F₂₅₄). Preparative TLC (PTLC)

was performed on 0.5 mm silica gel plates (Merck 5744; 60 F₂₅₄). Column chromatography was carried out on silica gel (Kanto Chemical N60 (spherical, neutral); 63-210 μ m). Anhydrous THF was used as purchased from Kanto Chemical. All other reagents were used as purchased.

Typical Procedure for Preparation of 2-Alkyl-3-hydroxy-3-vinylisoindolin-1-ones (2a-e)

To a solution of *N*-ethylphthalimide (**1b**) (1.05 g, 6.00 mmol) in anhydrous THF (30 mL) was added vinylmagnesium bromide (0.97 mol/L in hexane, 9.28 mL, 9.00 mmol) at -30 °C and the temperature was then raised to -5 °C over 2 h under argon. The reaction mixture was treated with an aqueous solution saturated with NH₄Cl and extracted with CHCl₃. The combined extracts were washed with brine, dried over MgSO₄, and filtered. The filtrate was evaporated *in vacuo* to afford a crude product, which was purified by column chromatography on silica gel with *n*-hexane-AcOEt (2 : 1) to give 2,3-dihydro-2-ethyl-3-hydroxy-3-vinylisoindolin-1-one (**2b**) (1.10 g, 90%) as colorless prisms. mp 128.5-129.5 °C (AcOEt); IR (KBr) 3278, 1671 cm⁻¹; ¹H-NMR (400 MHz, CDCl₃) δ 1.17 (t, *J* = 7.2 Hz, 3 H), 3.17 (dq, *J* = 14.2, 7.1 Hz, 1 H), 3.37 (dq, *J* = 14.2, 7.1 Hz, 1 H), 3.91 (s, 1 H), 5.41 (dd, *J* = 10.5, 1.0 Hz, 1 H), 5.64 (ddd, *J* = 17.0, 10.4, 1.2 Hz, 1 H), 5.82 (dd, *J* = 16.8, 1.0 Hz, 1 H), 7.36-7.42 (m, 2 H), 7.49-7.52 (d, 2 H); HREI-MS calcd for C₁₂H₁₃NO₂ MW 203.0946, found *m/z* 203.0968 (M⁺); Anal. Calcd for C₁₂H₁₃NO₂: C, 70.92; H, 6.45; N, 6.89. Found: C, 70.71; H, 6.46; N, 6.86.

3-Hydroxy-2-methyl-3-vinylisoindolin-1-one (2a) colorless needles, 80% yield. mp 141-142 °C (AcOEt); IR (KBr) 3313, 1686 cm⁻¹; ¹H-NMR (400 MHz, CDCl₃) δ 2.76 (s, 3 H), 3.82 (s, 1 H), 5.43 (dd, *J* = 10.3, 1.0 Hz, 1 H), 5.62 (dd, *J* = 17.1, 10.3 Hz, 1 H), 5.74 (d, *J* = 17.1 Hz, 1 H), 7.38 (t, *J* = 7.3 Hz, 1 H), 7.42-7.56 (m, 3 H); HREI-MS calcd for C₁₁H₁₁NO₂ MW 189.0790, found *m/z* 189.0772 (M⁺); Anal. Calcd for C₁₁H₁₁NO₂: C, 69.83; H, 5.86; N, 7.40. Found: C, 69.70; H, 5.92; N, 7.26.

2-Butyl-3-hydroxy-3-vinylisoindolin-1-one (2c) colorless needles, 95% yield. mp 90-91 °C (AcOEt); IR (KBr) 3294, 1687 cm⁻¹; ¹H-NMR (400 MHz, CDCl₃) δ 0.88 (t, *J* = 7.4 Hz, 3 H), 1.28 (sext, *J* = 7.4 Hz, 2 H), 1.45-1.67 (m, 2 H), 3.02 (ddd, *J* = 14.6, 9.0, 5.0 Hz, 1 H), 3.27 (ddd, *J* = 14.6, 9.3, 5.0 Hz, 1 H), 3.98 (s, 1H), 5.40 (dd, *J* = 10.5, 1.0 Hz, 1 H), 5.62 (ddd, *J* = 17.0, 10.4, 0.9 Hz, 1 H), 5.81 (dd, *J* = 17.0, 0.9 Hz, 1 H), 7.37 (d, *J* = 7.6 Hz, 1 H), 7.41 (d, *J* = 8.1 Hz, 1 H), 7.51 (t, *J* = 8.5 Hz, 2 H); HREI-MS calcd for C₁₄H₁₇NO₂ MW 231.1259, found *m/z* 231.1297 (M⁺); Anal. Calcd for C₁₄H₁₇NO₂: C, 72.70; H, 7.41; N, 6.06. Found: C, 72.59; H, 7.40; N, 6.06.

3-Hydroxy-2-isobutyl-3-vinylisoindolin-1-one (2d) colorless plates, 92% yield. mp 111-112 °C (AcOEt); IR (KBr) 3232, 1671 cm⁻¹; ¹H-NMR (400 MHz, CDCl₃) δ 0.89 (t, *J* = 7.0 Hz, 6 H), 2.09-2.20 (m, 1 H), 2.99 (dd, *J* = 13.9, 8.1 Hz, 1 H), 3.19 (s, 1 H), 3.28 (dd, *J* = 13.8, 7.4 Hz, 1 H), 5.42 (dd, *J* =

10.4, 1.1 Hz, 1 H), 5.65 (dd, $J = 17.1, 10.0$ Hz, 1 H), 5.81 (dd, $J = 17.1, 1.2$ Hz, 1 H), 7.43 (d, $J = 7.3$ Hz, 1 H), 7.43 (t, $J = 7.2$ Hz, 1 H), 7.54 (t, $J = 7.1$ Hz, 1 H), 7.65 (d, $J = 7.1$ Hz, 1 H); HREI-MS calcd for $C_{14}H_{17}NO_2$ MW 231.1259, found m/z 231.1276 (M^+); Anal. Calcd for $C_{14}H_{17}NO_2$: C, 72.70; H, 7.41; N, 6.06. Found: C, 72.47; H, 7.34; N, 6.01.

2-Benzyl-3-hydroxy-3-vinylisoindolin-1-one (2e) white powder, 92% yield. mp 125-126 °C (AcOEt); IR (KBr) 3295, 1694 cm^{-1} ; 1H -NMR (400 MHz, $CDCl_3$) δ 3.81 (s, 1 H), 4.31 (d, $J = 15.1$ Hz, 1 H), 4.48 (d, $J = 15.1$ Hz, 1 H), 5.29 (d, $J = 11.0$ Hz, 1 H), 5.46 (dd, $J = 17.0, 10.4$ Hz, 1 H), 5.77 (d, $J = 17.1$ Hz, 1 H), 7.14-7.48 (m, 7 H), 7.52 (t, $J = 7.3$ Hz, 1 H), 7.63 (d, $J = 7.6$ Hz, 1 H); HREI-MS calcd for $C_{17}H_{15}NO_2$ MW 265.1103, found m/z 265.1092 (M^+); Anal. Calcd for $C_{17}H_{15}NO_2$: C, 76.96; H, 5.70; N, 5.28. Found: C, 76.72; H, 5.72; N, 5.27.

Typical Procedure for the Conversion of 2-Alkyl-3-hydroxy-3-vinylisoindolin-1-ones (2a-e) to 2-Alkyl-3-(2-oxoethylidene)isoindolin-1-ones (5a-e) Employing $Pd(OAc)_2$ and DDQ

A solution of **2b** (40.6 mg, 0.2 mmol), $Pd(OAc)_2$ (4.5 mg, 10 mol %) and DDQ (45.4 mg, 0.2 mmol) in anhydrous THF (4.0 mL) was refluxed under argon for 6 h. The reaction mixture was evaporated *in vacuo* and then $CHCl_3$ was added to the residue. The resultant suspension was filtered and the filtrate was evaporated *in vacuo* to afford a crude product, which was purified by column chromatography on silica gel with *n*-hexane-AcOEt (4 : 1) to give **5b** (31.7 mg, 79%) as a pale yellow powder and as an *E* and *Z* mixture.

2-Ethyl-3-(2-oxoethylidene)isoindolin-1-one (5b) (as a mixture of *E* : *Z* = 96 : 4, 1H -NMR spectral analysis), pale yellow powder. Repeated recrystallization of the *E* and *Z* mixture from EtOH gave the pure *E*-isomer as colorless needles. mp 131-132 °C; IR (KBr) 1720, 1659 cm^{-1} ; 1H -NMR (400 MHz, $CDCl_3$) δ 1.28 (t, $J = 7.3$ Hz, 3 H), 3.87 (q, $J = 7.1$ Hz, 2 H), 6.00 (d, $J = 7.8$ Hz, 1 H), 7.64-7.72 (m, 2 H), 7.91-7.95 (m, 1 H), 8.10-8.14 (m, 1 H), 10.60 (d, $J = 7.8$ Hz, 1 H); HREI-MS calcd for $C_{12}H_{11}NO_2$ MW 201.0790, found m/z 201.0809 (M^+); Anal. Calcd for $C_{12}H_{11}NO_2$: C, 71.63; H, 5.51; N, 6.96. Found: C, 71.46; H, 5.65; N, 6.78.

2-Methyl-3-(2-oxoethylidene)isoindolin-1-one (5a) (as a mixture of *E* : *Z* = 94 : 6, 1H -NMR spectral analysis), pale yellow powder, 78% total yield. Repeated recrystallization of the *E* and *Z* mixture from EtOH gave the pure *E*-isomer as colorless needles. mp 184-185 °C (lit.,¹¹ 183-184 °C); IR (KBr) 1724, 1655 cm^{-1} ; 1H -NMR (400 MHz, $CDCl_3$) δ 3.31 (s, 3 H), 5.97 (d, $J = 7.8$ Hz, 1 H), 7.63-7.73 (m, 2 H), 7.87-7.97 (m, 1 H), 8.13 (d, $J = 7.1$ Hz, 1 H), 10.57 (d, $J = 7.8$ Hz, 1 H); ^{13}C -NMR (100 MHz, $CDCl_3$)

□26.3, 109.0, 123.9, 125.5, 130.1, 131.5, 133.0, 133.7, 151.5, 166.6, 187.2; HREI-MS calcd for $C_{11}H_9NO_2$ MW 187.0633, found m/z 187.0630 (M^+); Anal. Calcd for $C_{11}H_9NO_2$: C, 70.58; H, 4.85; N, 7.48. Found: C, 70.36; H, 4.94; N, 7.34.

2-Butyl-3-(2-oxoethylidene)isoindolin-1-one (5c) (as a mixture of $E : Z = 96 : 4$, 1H -NMR spectral analysis), pale yellow oil, 70% total yield. IR (neat) (E, Z -mixture) 1729, 1652 cm^{-1} ; 1H -NMR (400 MHz, $CDCl_3$) (E -isomer of E, Z -mixture) □0.96 (t, $J = 7.3$ Hz, 3H), 1.33-1.49 (m, 2 H), 1.59-1.79 (m, 2 H), 3.80 (t, $J = 7.5$ Hz, 2 H), 5.99 (d, $J = 7.8$ Hz, 1 H), 7.60-7.77 (m, 2 H), 7.89-8.00 (m, 1 H), 8.08-8.16 (m, 1 H), 10.60 (d, $J = 7.8$ Hz, 1 H); HREI-MS calcd for $C_{14}H_{15}NO_2$ MW 229.1103, found m/z 229.1098 (M^+).

2-Isobutyl-3-(2-oxoethylidene)isoindolin-1-one (5d) (as a mixture of $E : Z = 96 : 4$, 1H -NMR spectral analysis), pale yellow powder, 65% total yield. mp 119.5-123 °C (EtOH) (E, Z -mixture). IR (KBr) (E, Z -mixture) 1722, 1644 cm^{-1} ; 1H -NMR (400 MHz, $CDCl_3$) (E -isomer of E, Z -mixture) □0.94-1.24 (m, 6 H), 2.06-2.21 (m, 1 H), 3.63 (d, $J = 7.6$ Hz, 2 H), 5.98 (d, $J = 7.8$ Hz, 1 H), 7.60-8.15 (m, 4 H), 10.60 (d, $J = 7.8$ Hz, 1 H); HREI-MS calcd for $C_{14}H_{15}NO_2$ MW 229.1103, found m/z 229.1119 (M^+); Anal. Calcd for $C_{14}H_{15}NO_2$: C, 73.34; H, 6.59; N, 6.11. Found: C, 73.33; H, 6.67; N, 6.09.

2-Benzyl-3-(2-oxoethylidene)isoindolin-1-one (5e) (as a mixture of $E : Z = 96 : 4$, 1H -NMR spectral analysis), pale yellow prisms, 80% total yield. mp 136.5-138.5 °C (EtOH) (E, Z -mixture). IR (KBr) (E, Z -mixture) 1725, 1648 cm^{-1} ; 1H -NMR (400 MHz, $CDCl_3$) (E -isomer of E, Z -mixture) □5.03 (s, 2 H), 5.94 (d, $J = 7.6$ Hz, 1 H), 7.21-7.39 (m, 5 H), 7.66-7.77 (m, 2 H), 7.96-8.02 (m, 1 H), 8.11-8.14 (m, 1 H), 10.49 (d, $J = 7.8$ Hz, 1 H); HREI-MS calcd for $C_{17}H_{13}NO_2$ MW 263.0946, found m/z 263.0941 (M^+).

3-(2-Hydroxyethyl)-2-methylisoindolin-1-one (6a)

A mixture of **5a** (34.1 mg, 0.182 mmol) and 10% Pd/C (11 mg) in AcOEt (3 mL) was subjected to hydrogenation at 1 atm for 24 h. The solution was filtered and the filtrate was evaporated *in vacuo*. The residue was purified by PTLC with *n*-hexane-AcOEt (1 : 4) to give the known compound (**6a**) (20.4 mg, 59%)⁸ as a colorless oil. IR (neat) 3393, 1668 cm^{-1} ; 1H -NMR (400 MHz, $CDCl_3$) □1.96 (s, 1 H), 2.14-2.38 (m, 2 H), 3.14 (s, 3 H), 3.48-3.63 (m, 2 H), 4.61 (dd, $J = 5.1, 4.6$ Hz, 1 H), 7.42-7.58 (m, 3 H), 7.82 (d, $J = 7.3$ Hz, 1 H); HREI-MS calcd for $C_{11}H_{13}NO_2$ MW 191.0946, found m/z 191.0969 (M^+).

2,3-Dimethyl-3-hydroxyisoindolin-1-one (7)

To a solution of *N*-methylphthalimide (**1a**) (1.61 g, 10.0 mmol) in anhydrous THF (50 mL) was added methylmagnesium bromide (3.0 mol/L in Et_2O , 5.0 mL, 15.0 mmol) at -30 °C and the temperature was

then raised to -5 °C over 2 h under argon. The reaction mixture was treated with an aqueous solution saturated with NH₄Cl and extracted with CHCl₃. The combined extracts were washed with brine, dried over MgSO₄, and filtered. The filtrate was evaporated *in vacuo* to afford a crude product, which was purified by column chromatography on silica gel with *n*-hexane-AcOEt (1 : 3) to give the known compound (**7**) (1.70 g, 96%)⁹ as colorless prisms. mp 128.0-128.5 °C (*n*-hexane-AcOEt) (lit.,⁹ mp 134-136 °C); IR (KBr) 3255, 1680 cm⁻¹; ¹H-NMR (400 MHz, CDCl₃) δ 1.56 (d, *J* = 0.49 Hz, 3 H), 2.87 (s, 3 H), 6.22 (d, *J* = 0.49 Hz, 1 H), 7.48-7.52 (m, 1 H), 7.59-7.66 (m, 3 H); HREI-MS calcd for C₁₀H₁₁NO₂ MW 177.0790, found *m/z* 177.0779 (M⁺); Anal. Calcd for C₁₀H₁₁NO₂: C, 67.78; H, 6.26; N, 7.90. Found: C, 67.55; H, 6.30; N, 7.80.

1-Methylene-2-methylisoindolin-1-one (**8**)

A solution of **7** (177.2 mg, 1.0 mmol) and DDQ (227.0 mg, 1.0 mmol) in anhydrous THF (10.0 mL) was refluxed under argon for 6 h. The reaction mixture was evaporated *in vacuo* to afford a crude product, which was purified by column chromatography on silica gel with *n*-hexane-AcOEt (2 : 1) to give the known compound (**8**) (58.5 mg, 37%)⁹ as a pale yellow gum. IR (KBr) 1710, 1643, 1433 cm⁻¹; ¹H-NMR (400 MHz, CDCl₃) δ 3.28 (s, 3 H), 4.84 (d, *J* = 2.2 Hz, 1 H), 5.17 (d, *J* = 2.2 Hz, 1 H), 7.46-7.50 (m, 1 H), 7.54-7.58 (m, 1 H), 7.66-7.69 (m, 1 H), 7.81-7.83 (m, 1 H); HREI-MS calcd for C₁₀H₉NO MW 159.0684, found *m/z* 159.0676 (M⁺).

Typical Procedure for the Conversion of 2-Alkyl-3-hydroxy-3-vinylisoindolin-1-ones (**2a-e**) to 2-Alkyl-3-(2-oxoethylidene)isoindolin-1-ones (**5a-e**) Employing DDQ

A solution of **2b** (40.6 mg, 0.2 mmol) and DDQ (45.4 mg, 0.2 mmol) in anhydrous THF (4.0 mL) was refluxed under argon for 24 h. The reaction mixture was evaporated *in vacuo* and then CHCl₃ was added to the residue. The resultant suspension was filtered and the filtrate was evaporated *in vacuo* to afford a crude product, which was purified by column chromatography on silica gel with *n*-hexane-AcOEt (4 : 1) to give **5b** [a *E* : *Z* (82 : 18) mixture, (15.4 mg, 38%)] as a pale yellow powder.

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