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PAPER

Hypervalent iodine mediated synthesis of carbamate protected *p*-quinone monoimine ketals and *p*-benzoquinone monoketals†‡

Naganjaneyulu Bodipati and Rama Krishna Peddinti*

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A simple and efficient method for the synthesis of *p*-quinone monoimide ketals and *p*-benzoquinone monoketals by using a hypervalent iodine reagent, diacetoxyiodobenzene, has been developed. These two types of ketals are achieved from a single starting material by varying the reaction conditions.

Introduction

Quinone imines and bisimines are remarkably versatile starting materials in the synthesis of natural products[1,2] and in the synthesis of 5-methoxyindoles,[3] benzofused heterocycles[4] and tropone ring systems.[5] The major applications of these entities are in nucleophilic additions promoted by both acids and bases.[6–8] The stability of these reactive species is a function of the nature of the substitution on the nitrogen atom. Simple *p*-benzoquinone imines and *N*-alkyl-*p*-benzoquinone imines are highly unstable compounds and are prone to rapid hydrolysis. As a result, an electron-withdrawing group on the nitrogen atom of the *p*-benzoquinone imine is necessary to prevent decomposition. The methods most commonly used today to generate such synthons mostly rely on electrochemical oxidation of *p*-methoxyanilides or *p*-phenylenediamides.[9–12] The reported methods involve the use of *N*-arylsulfonyl and *N*-benzoyl groups as amide linkage.[13] The necessity for strongly acidic conditions for the removal of these groups during synthetic manipulation of the quinone imides limits their use.

On the contrary, the carbamate protected quinone imine ketals can be more easily hydrolysed than other imides and are stable enough under the hydrolysis conditions. Swenton *et al.* reported[14] an electrochemical method for the generation of carbamate protected quinone imine ketals, and later it was improved by Carreño and Ribagorda.[15] However, only a few chemical methods[16,17] for the generation of *p*-quinone imine ketals are reported in literature. No reports for the chemical generation of carbamate protected quinone imine ketals are available. Barret and Daudon[18] described a method for the generation of *p*-quinone monoimide ketals by using a hypervalent iodine reagent, iodosylbenzene. However, their procedure was used for *N*-arylsulfonyl and *N*-benzoyl-*p*-methoxyanilides and suffers from moderate yields. Herein we report for first time the chemical generation of carbamate protected *p*-quinone monoimide ketals by the diacetoxyiodobenzene (DIB) mediated oxidation of *N*-*tert*-butoxycarbonyl-*p*-methoxyanilides. We also extended this protocol for the oxidation of *N*-acyl-*p*-methoxyanilides, *N*-*tert*-butoxycarbonylanilides and *N*-acetylanilides into the corresponding *N*-protected *p*-benzoquinone imine ketals.

Results and discussion

Inspired by the protocols for obtaining the reactive orthobenzoquinone monoketals[19] and orthobenzoquinone monoimines[20] generated by the oxidation of 2-methoxyphenols and 2-aminophenols with hypervalent iodine reagents,[19b,c,20–22] we became interested to employ this strategy for the generation of *N*-*tert*-butoxycarbonyl-*p*-quinone imine ketals by oxidative dearomatization of *N*-*tert*-butoxycarbonyl-*p*-methoxyanilides. In our initial experiments, 1 mmol of *p*-methoxyanilide **1a** was treated with 1.2 mmol of DIB in methanol (5 mL) at room temperature to obtain the desired product, *p*-quinone imide ketal **4a** in low yield. This low yield of **4a** may be attributed to the presence of acetic acid, which was released during the progress of the reaction. To neutralize the acetic acid, we performed the reaction in the presence of the base $KHCO_3$. Indeed, as can be seen from entry 2, Table 1, the chemical yield was considerably improved with the introduction of $KHCO_3$. To gauge the effect of the base, the reaction was performed in the presence of different bases, the results of which are summarized in Table 1.

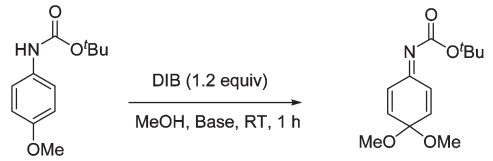
A complex mixture was formed when pyridine was used as the base (entry 3, Table 1). Among the bases tested, triethylamine was found to produce *p*-quinone imide ketal **4a** in optimal yield (entry 4, Table 1). When the reaction was carried out at 50 °C in the presence of triethylamine, the product was obtained in 81% yield (entry 7, Table 1). Since the products are sensitive towards silica gel, they were isolated on silica gel column

Department of Chemistry, Indian Institute of Technology, Roorkee-247 667, Uttarakhand, India. E-mail: rkpedfcy@iitr.ernet.in, ramakpeddinti@gmail.com; Fax: (+) 91 13 3227 3560; Tel: (+) 91 13 3228 5438

† Dedicated to our esteemed colleague Professor Gurudas Bhattacharjee on the occasion of his retirement.

‡ Electronic supplementary information (ESI) available: Copies of ^1H NMR and ^{13}C NMR spectra are provided. See DOI: 10.1039/c2ob25089f

Table 1 Optimization of the oxidation of *N-tert*-butoxycarbonyl-*p*-methoxyanilide (**1a**) by using DIB[a]

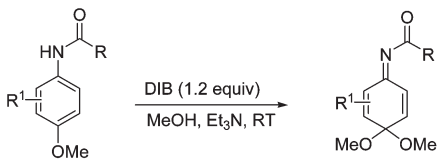


1a **4a**

Entry	Base[b]	Yield[c] (%)
1	—	21
2	$KHCO_3$	46
3	Pyridine	Trace
4	Et_3N	92
5	DBU	54
6	DABCO	62
7	Et_3N	81[d]

[a] All reactions were carried out under aerobic conditions. [b] 3 equiv of base used. [c] Yield of isolated products. [d] Reactions were carried out at 50 °C.

Table 2 DIB Mediated oxidation of differently substituted *p*-methoxyanilides



1 **4**

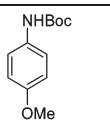
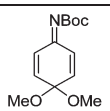
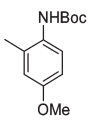
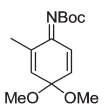
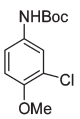
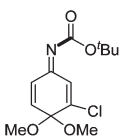
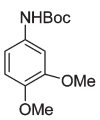
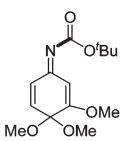
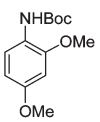
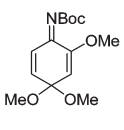
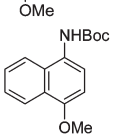
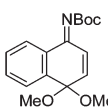
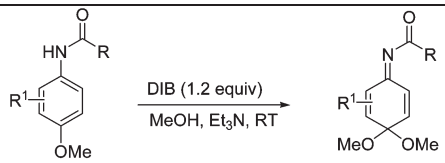
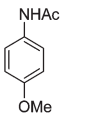
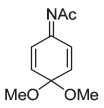
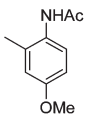
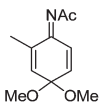
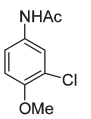
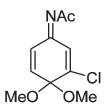
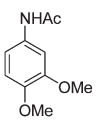
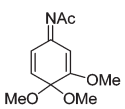
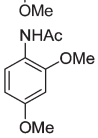
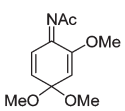
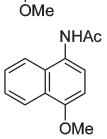
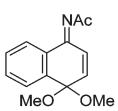
Entry	Substrate		Time (h)	Product		Yield[a] (%)
1		**1a**	1		**4a**	92
2		**1b**	1		**4b**	95
3		**1c**	2		**4c**	91[b]
4		**1d**	2		**4d**	92[b]
5		**1e**	3		**4e**	96
6		**1f**	2		**4f**	83

Table 2 *(Contd.)*



1 **4**

Entry	Substrate		Time (h)	Product		Yield[a] (%)
7		**1g**	1		**4g**	94
8		**1h**	1		**4h**	96
9		**1i**	2.5		**4i**	82
10		**1j**	2		**4j**	79
11		**1k**	2		**4k**	93
12		**1l**	2.5		**4l**	89

[a] Yield of pure and isolated products. [b] *cis*/*trans* mixture.

neutralized with triethylamine and stored in a freezer below 0 °C. With a consistent set of conditions in hand, we extended this procedure to differently substituted *N-tert*-butoxycarbonyl-*p*-methoxyanilides **1b–1f** (Table 2). The 2-substituted *p*-methoxyanilides **1b** and **1e** upon oxidation provided the products **4b** and **4e** as single isomers in 95 and 96% yield, respectively. On the other hand, the *p*-methoxyanilides **1c** and **1d** under the same conditions, as a result of steric reasons, gave mixtures of *cis* and *trans* imides **4c** and **4d** in 91 and 92% yield, respectively. The naphthalene amide **1f** underwent smooth oxidation to provide the corresponding imide **4f** in 83% yield.

Since there is much interest in the oxidation products of acylated aromatic amines,[23] we adopted the above protocol to oxidize *N*-acetyl-*p*-methoxyanilides **1g–1l**. When we attempted to purify the reaction mixture on silica gel, it led to a complex mixture of decomposed products in which noticeable amount of *p*-benzoquinone monoketal was present. Consequently, we purified *p*-benzoquinone monoimide ketals **4g–4l** in good yields (Table 2) on a silica gel column neutralized with triethylamine. It occurred to us that if we developed a method for the synthesis of *p*-benzoquinone monoketals from the same starting material, it would be a valuable addition to *p*-benzoquinone chemistry

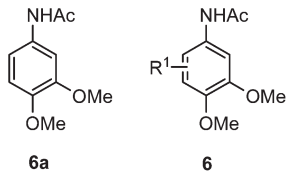
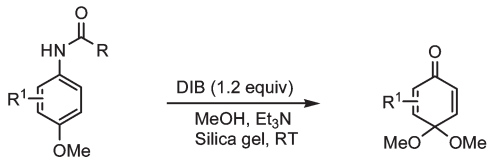


Fig. 1 *p*-Methoxyanilides.

Table 3 Synthesis of *p*-benzoquinone monoketals from *p*-methoxyanilides

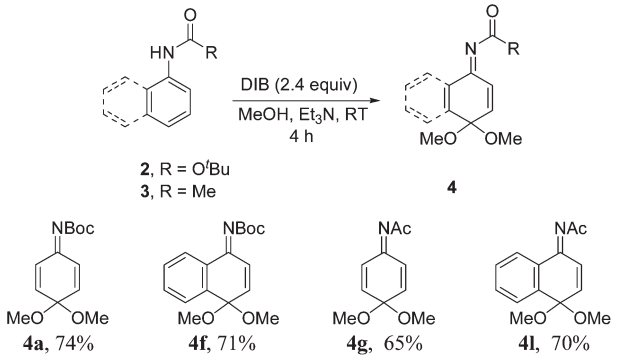


Entry	Substrate	Time (h)	Product	Yield[a] (%)
1	**1a**	5	**5a**	74
2	**1b**	4	**5b**	81
3	**1c**	6	**5c**	60
4	**1d**	6	**5d**	59
5	**1e**	5	**5e**	61
6	**1f**	4	**5f**	75[b]
7	**1g**	4	**5a**	84
8	**1h**	4	**5b**	89
9	**1i**	5	**5c**	71
10	**1j**	5	**5d**	76
11	**1k**	5	**5e**	74
12	**1l**	4	**5f**	82[b]

[a] Yield of pure and isolated products. [b] Yield of 1,4-naphthoquinone.

since these molecular entities are extremely valuable building blocks in natural product synthesis, particularly halogen substituted ketals.[24] Thus we carried out the reaction of **1g** in the absence of triethylamine, expecting that the released acetic acid would help to hydrolyze the imide ketal into quinone monoketal, but obtained *N*-acetyl-3,4-dimethoxyaniline (**6a**) in 81% yield instead of quinone ketal **5a**. This transformation took place due to the migration of one of the methoxy groups of *p*-quinone monoimide ketal **4g**. When we extended this protocol to anilides **1h–1k**, surprisingly we recovered only starting compounds instead of methoxy substituted *p*-methoxyanilides such as **6** (Fig. 1).

In subsequent studies we performed the oxidation of **1a** in the presence of silica gel and triethylamine. To our delight, *p*-quinone monoketal **5a** was obtained in good yield. Here triethylamine assisted the neutralization of acetic acid and silica gel facilitated the hydrolysis of imide ketal **3a** affording the quinone monoketal **5a** in a controlled manner. Under these conditions various *p*-methoxyanilides **1a–1l** were oxidized to the corresponding *p*-quinone monoketals **5a–5f** (Table 3). The reaction procedure worked better with acetylated *p*-methoxyanilides **1g–1l** than with the carbamate protected anilides. In general, the synthesis of *p*-quinone monoimide ketals and *p*-benzoquinone monoketals was achieved from the oxidation of the corresponding 4-methoxy substituted anilides and phenols. The main



Scheme 1 Double oxidation of anilides.

limitation of this procedure is non-availability of variously substituted 4-methoxyanilides/phenols.[24] In an effort to increase the library of precursors for *p*-quinone monoimide ketals and *p*-quinone monoketals, we attempted the reaction of simple anilides **2** and **3** with 2.4 equiv. of DIB in methanol at room temperature; the reaction went smoothly to furnish the corresponding ketals **4a**, **4f**, **4g**, **4l** in good yields (Scheme 1).

Conclusion

In summary, we have developed a new and facile chemical method for the synthesis of carbamate and acetyl protected quinone imine ketals and *p*-benzoquinone monoketals from various *p*-methoxyanilides and from simple anilides. The method is operationally simple and high yielding at room temperature and circumvents purification problems.

Experimental section

General information

Unless otherwise noted, chemicals were purchased at the highest purity grade available and were used without further purification. Methanol was distilled by using magnesium cake. Column chromatography was carried out using silica gel (100–200 mesh). Analytical thin layer chromatography was performed on 0.25 mm silica gel plates (60F-254) using UV light as visualizing agent. ^{1}H NMR spectra were recorded at 500 MHz and were recorded relative to the peak for $CDCl_3$ (δ 7.26) or TMS (δ 0.00). High-resolution mass spectra (HRMS) were recorded on Jeol JMS600H spectrometer. ^{1}H NMR coupling constants (*J*) are reported in Hertz, and multiplicities are indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet).

General procedure for *p*-quinone monoimide ketals

A solution of DIB (1.2 mmol) in methanol (2 mL) was added drop-wise to a solution of *p*-methoxyanilide (**1**, 1 mmol) and triethylamine (3 mmol) in methanol (3 mL) at room temperature. The reaction mixture was stirred at the same temperature for the time indicated in Table 2. After completion of the reaction the solvent was removed under reduced pressure and the crude reaction mixture was loaded directly onto a silica gel column

(100–200 mesh) neutralized with triethylamine. The product was eluted by using ethyl acetate in hexanes. The known products were characterized by comparison of their spectral data (^{1}H and ^{13}C NMR) with those of authentic samples.[11,14,15]

General procedure for *p*-benzoquinone monoketals 5

A solution of DIB (1.2 mmol) in methanol (2 mL) was added drop-wise to a mixture of *p*-methoxyanilide (**1**, 1 mmol), triethylamine (2.4 mmol) and silica gel (0.5 g, 100–200 mesh) in methanol (3 mL) at room temperature. The reaction mixture was stirred at the same temperature for the time indicated in Table 3. After completion of the reaction, the contents were filtered and the solvent was removed under reduced pressure and the crude reaction mixture was loaded directly onto a silica gel column (100–200 mesh). The product was eluted by using ethyl acetate in hexanes.

General procedure for double oxidation

A solution of DIB (2.4 mmol) in methanol (4 mL) was added drop-wise to a solution of anilides (**2** or **3**, 1 mmol) and triethylamine (5 mmol) in methanol (4 mL) at room temperature. The reaction mixture was stirred at the same temperature for 4 h. After completion of the reaction, the solvent was removed under reduced pressure and the crude reaction mixture was loaded directly onto a silica gel column (100–200 mesh) neutralized with triethylamine. The product **4** was eluted by using ethyl acetate in hexanes.

***N*-(*tert*-Butoxycarbonyl)-*p*-benzoquinone imine dimethyl acetal (4a).** Colorless oil; IR (film): 3062, 2926, 1694, 1606, 951, 835 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 6.53 (br, 2H), 6.41 (d, J = 10.5 Hz, 2H), 3.25 (s, 6H), 1.55 (s, 9H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz): δ 160.9, 156.1, 137.2, 130.0, 127.2, 113.8, 92.8, 82.5, 49.9 (2C), 27.8 (3C) ppm; HRMS (FAB+, *m*/*z*), calcd for $C_{13}H_{19}NO_4Na^+$ [M + Na]$^+$: 276.1212, found 276.1219.

***N*-(*tert*-Butoxycarbonyl)-2-methyl-*p*-benzoquinone imine dimethyl acetal (4b).** Colorless oil; IR (film): 3062, 1664, 976, 848 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.27 (br, 1H), 6.71 (s, 1H), 6.12 (s, 1H), 3.76 (s, 6H), 2.22 (s, 3H), 1.51 (s, 9H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz): δ 161.7, 153.6, 138.7, 136.7, 134.9, 115.5, 93.1, 82.4, 55.0 (2C), 28.1 (3C), 17.7 ppm; HRMS (FAB+, *m*/*z*), calcd for $C_{14}H_{21}NO_4Na^+$ [M + Na]$^+$: 290.1368, found 290.1374.

***N*-(*tert*-Butoxycarbonyl)-3-chloro-*p*-benzoquinone imine dimethyl acetal (4c).** Colorless oil; IR (film): 3065, 1665, 1249, 967, 865 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 6.70–6.69 (m, 1H), 6.59–6.55 (m, 1H), 6.44–6.42 (m, 1H), 3.24 (s, 6H), 1.55 (s, 9H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz): δ 158.7, 148.7, 136.8, 132.0, 131.9, 96.0, 94.2, 81.8, 51.1 (2C), 27.7 (3C) ppm; HRMS (FAB+, *m*/*z*), calcd for $C_{13}H_{18}{}^{35}ClNO_4Na^+$ [M + Na]$^+$: 310.0822, found 310.0818; calcd for $C_{13}H_{18}{}^{37}ClNO_4Na^+$ [M + Na]$^+$: 312.0793 found 312.0794.

***N*-(*tert*-Butoxycarbonyl)-3-methoxy-*p*-benzoquinone imine dimethyl acetal (4d).** Colorless oil; IR (film): 3046, 1685, 1080, 968, 847 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 6.39 (brd, J = 12.0 Hz, 2H), 5.74 (s, 1H), 3.80 (s, 3H), 3.29 (s, 6H), 1.57 (s, 9H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz): δ 152.8, 150.5, 132.0, 122.0, 120.9, 118.0, 95.0, 83.2, 56.0, 51.1 (2C), 27.7 (3C) ppm; HRMS (FAB+, *m*/*z*), calcd for $C_{14}H_{21}NO_5Na^+$ [M + Na]$^+$: 306.1317, found 306.1315.

***N*-(*tert*-Butoxycarbonyl)-2-methoxy-*p*-benzoquinone imine dimethyl acetal (4e).** Colorless oil; IR (film): 3050, 1689, 955, 918 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 6.48–6.43 (m, 1H), 6.33–6.29 (m, 1H), 5.48 (s, 1H), 3.71 (s, 3H), 3.30 (s, 6H), 1.52 (s, 9H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz): δ 186.1, 153.1, 139.3, 134.0, 129.5, 103.9, 99.9, 80.1, 56.1, 50.3 (2C), 28.0 (3C) ppm; HRMS (FAB+, *m*/*z*), calcd for $C_{14}H_{21}NO_5Na^+$ [M + Na]$^+$: 306.1317, found 306.1309.

***N*-(*tert*-Butoxycarbonyl)-1,4-naphthoquinone imine dimethyl acetal (4f).** Colorless oil; IR (film): 3056, 1680, 1209, 1193, 1095 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.27 (dd, J = 1.0, 9.0 Hz, 1H), 8.21 (dd, J = 1.0, 8.0 Hz, 1H), 7.84 (d, J = 8.5 Hz, 1H), 6.75 (d, J = 8.0 Hz, 1H), 6.71 (d, J = 10.5 Hz, 1H), 6.59 (d, J = 10.5 Hz, 1H), 3.13 (s, 6H), 1.60 (s, 9H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz): δ 162.0, 155.7, 139.9, 137.7, 132.2, 129.0, 126.6, 125.7, 125.2, 122.5, 95.4, 82.7, 55.5, 51.2, 28.1 (3C) ppm; HRMS (FAB+, *m*/*z*), calcd for $C_{17}H_{21}NO_4Na^+$ [M + Na]$^+$: 326.1368, found 326.1362.

***N*-Acetyl-*p*-benzoquinone imine dimethyl acetal (4g).** Colorless oil; IR (film): 3050, 2944, 1695, 1461, 963, 827 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 6.62 (d, J = 10.0 Hz, 2H), 6.33 (d, J = 10.0 Hz, 2H), 3.31 (s, 6H), 2.21 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz): δ 185.9, 151.7, 143.2, 139.1, 129.9, 126.4, 92.9, 50.1 (2C), 25.4 ppm; HRMS (FAB+, *m*/*z*), calcd for $C_{10}H_{13}NO_3H^+$ [M + H]$^+$: 196.0974, found 196.0978.

***N*-Acetyl-2-methyl-*p*-benzoquinone imine dimethyl acetal (4h).** Colorless oil; IR (film): 3060, 1675, 1465, 1071, 909 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 6.50 (dd, J = 2.5, 10.0 Hz, 1H), 6.39 (q, J = 1.5 Hz, 1H), 6.29 (d, J = 10.0 Hz, 1H), 3.37 (s, 6H), 2.23 (s, 3H), 2.04 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz): δ 186.1, 152.1, 139.1, 135.9, 134.9, 123.1, 93.2, 49.9 (2C), 25.4, 17.1 ppm; HRMS (FAB+, *m*/*z*), calcd for $C_{11}H_{15}NO_3Na^+$ [M + Na]$^+$: 232.0950, found 232.0959.

***N*-Acetyl-3-chloro-*p*-benzoquinone imine dimethyl acetal (4i).** Colorless oil; IR (film): 3054, 1694, 1080, 958 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 6.51 (dd, J = 3.0, 10.0 Hz, 1H), 6.41 (q, J = 1.5 Hz, 1H), 6.34 (d, J = 10.0 Hz, 1H), 3.37 (s, 6H), 2.28 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz): δ 186.1, 152.1, 139.1, 135.9, 134.9, 123.1, 93.2, 49.9 (2C), 25.4 ppm; HRMS (FAB+, *m*/*z*), calcd for $C_{10}H_{12}{}^{35}ClNO_3H^+$ [M + H]$^+$: 230.0584, found 230.0589; calcd for $C_{10}H_{12}{}^{37}ClNO_3H^+$ [M + H]$^+$: 232.0555 found 232.0561.

***N*-Acetyl-3-methoxy-*p*-benzoquinone imine dimethyl acetal (4j).** Colorless oil; IR (film): 3046, 1689, 959, 818, 744 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 6.35 (dd, J = 1.5, 10.0 Hz, 1H), 6.31 (d, J = 10.0 Hz, 1H), 5.52 (d, J = 1.5 Hz, 1H), 3.73 (s, 3H), 3.21 (s, 6H), 2.17 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz): δ 185.8, 164.3, 153.4, 156.8, 128.4, 98.0, 93.9, 55.4, 50.9 (2C),

25.1 ppm; HRMS (FAB+, *m*/*z*), calcd for $C_{11}H_{15}NO_4H^+$ [M + H]$^+$: 226.1079, found 226.1071.

***N*-Acetyl-2-methoxy-*p*-benzoquinone imine dimethyl acetal (4k).** Colorless oil; IR (film): 3062, 1694, 951, 881, 752 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 6.44 (dd, J = 2.5, 10.0 Hz, 1H), 6.22 (d, J = 10.0 Hz, 1H), 5.40 (d, J = 2.5 Hz, 1H), 3.63 (s, 3H), 3.25 (s, 6H), 2.19 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz): δ 184.4, 149.5, 146.3, 138.4, 126.6, 106.9, 96.3, 55.1, 50.0 (2C), 24.8 ppm; HRMS (FAB+, *m*/*z*), calcd for $C_{11}H_{15}NO_4Na^+$ [M + Na]$^+$: 248.0899, found 248.0892.

***N*-Acetyl-1,4-naphthoquinone imine dimethyl acetal (4l).** Colorless oil; IR (film): 3070, 1698, 1652, 1594, 972, 810 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.05 (d, J = 8.0 Hz, 1H), 7.63 (d, J = 8.0 Hz, 1H), 7.50 (t, J = 8.0 Hz, 1H), 7.36 (t, J = 8.0 Hz, 1H), 6.56 (s, 2H), 3.07 (s, 6H), 2.23 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz): δ 186.2, 150.7, 139.9, 137.7, 131.8, 130.6, 128.8, 126.4, 125.4 (2C), 95.0, 50.9 (2C), 25.6 ppm; HRMS (FAB+, *m*/*z*), calcd for $C_{14}H_{15}NO_3H^+$ [M + H]$^+$: 246.1130, found 246.1135.

***p*-Benzoquinone dimethyl acetal (5a).** Colorless oil; IR (film): 3062, 1682, 1461, 1072, 964 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 6.80 (dd, J = 1.5, 10.0 Hz, 2H), 6.25 (dd, J = 1.5, 10.0 Hz, 2H), 3.35 (s, 6H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz): δ 185.0, 143.2, 129.9, 92.4, 50.3 (2C) ppm; HRMS (FAB+, *m*/*z*), calcd for $C_8H_{10}O_3$ [M] $^+$: 154.0630, found 154.0637.

2-Methyl-*p*-benzoquinone dimethyl acetal (5b). Colorless oil; IR (film): 3066, 1694, 964, 810 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 6.73 (dd, J = 3.0, 10.0 Hz, 1H), 6.54 (dd, J = 1.5, 3.0 Hz, 1H), 6.19 (d, J = 10.0 Hz, 1H), 3.29 (s, 6H), 1.84 (d, J = 1.5 Hz, 3H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz): δ 185.7, 143.0, 138.5, 136.8, 129.9, 92.9, 50.2 (2C), 15.7 ppm; HRMS (FAB+, *m*/*z*), calcd for $C_9H_{12}O_3Na^+$ [M + Na]$^+$: 191.0684, found 191.0678.

3-Chloro-*p*-benzoquinone dimethyl acetal (5c). Colorless oil; IR (film): 3058, 1689, 955, 723 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 6.73 (dd, J = 1.0, 10.5 Hz, 1H), 6.55–6.54 (m, 1H), 6.40 (dd, J = 2.0, 10.0 Hz, 1H), 3.24 (s, 6H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz): δ 182.2, 151.7, 142.8, 130.7, 130.5, 93.9, 50.5 (2C) ppm; HRMS (FAB+, *m*/*z*), calcd for $C_8H_9{}^{35}ClO_3H^+$ [M + H]$^+$: 189.0318, found 189.0314; calcd for $C_8H_9{}^{37}ClO_3H^+$ [M + H]$^+$: 191.0289 found 191.0296.

3-Methoxy-*p*-benzoquinone dimethyl acetal (5d). Colorless oil; IR (film): 3047, 1692, 1463, 1295 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 6.49 (d, J = 10.0 Hz, 1H), 6.19 (d, J = 9.0 Hz, 1H), 5.52 (s, 1H), 3.68 (s, 3H), 3.17 (s, 6H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz): δ 186.1, 164.4, 153.6, 140.1, 130.9, 98.2, 55.6, 51.1 (2C) ppm; HRMS (FAB+, *m*/*z*), calcd for $C_9H_{12}O_4Na^+$ [M + Na]$^+$: 207.0633, found 207.0632.

2-Methoxy-*p*-benzoquinone dimethyl acetal (5e). Colorless oil; IR (film): 3058, 1689, 955, 723 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 6.51 (d, J = 10.0 Hz, 1H), 6.21 (d, J = 9.0 Hz, 1H), 5.54 (s, 1H), 3.67 (s, 3H), 3.15 (s, 6H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz): δ 186.2, 164.6, 153.7, 137.0, 131.0, 98.3, 55.9, 51.2 (2C) ppm; HRMS (FAB+, *m*/*z*), calcd for $C_9H_{12}O_4Na^+$ [M + Na]$^+$: 207.0633, found 207.0638.

1,4-Naphthoquinone (5f). Colorless oil; IR (film): 3056, 1675, 946, 731 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.11–8.07 (m, 2H), 7.79–7.75 (m, 2H), 6.69 (s, 2H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz): δ 185.1, 138.7, 134.1, 131.9, 126.5 ppm; HRMS (FAB+, *m*/*z*), calcd for $C_{10}H_6O_2H^+$ [M + H]$^+$: 159.0446, found 159.0441.

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Notes and references

1 S. K. Jackson, S. C. Banfield and M. A. Kerr, *Org. Lett.*, 2005, **7**, 1215–1218.
2 D. B. England, J. Magolan and M. A. Kerr, *Org. Lett.*, 2006, **8**, 2209–2212.
3 S. C. Banfield, D. B. England and M. A. Kerr, *Org. Lett.*, 2001, **3**, 3325–3327.
4 (*a*) V. Nair, C. Rajesh, R. Dhanya and N. P. Rath, *Org. Lett.*, 2002, **4**, 953–955; (*b*) V. Nair, R. Dhanya, C. Rajesh and S. Devipriya, *Synlett*, 2005, 2407–2419; and references therein.
5 M. C. Carreño, M. J. Sanz-Cuesta and M. Ribagorda, *Chem. Commun.*, 2005, 1007–1009.
6 T. A. Engler, S. P. Meduna, K. O. LaTessa and W. Chai, *J. Org. Chem.*, 1996, **61**, 8598–8506.
7 T. A. Engler, K. O. Lynch, Jr., W. Chai and S. P. Meduna, *Tetrahedron Lett.*, 1995, **36**, 2713–2716.
8 J. S. Swenton, B. R. Bonke, W. M. Clark, C.-P. Chen and K. V. Martin, *J. Org. Chem.*, 1990, **55**, 2027–2034.
9 T. E. Young and W. T. Beidler, *J. Org. Chem.*, 1984, **49**, 4833–4838.
10 J. S. Swenton, C. Shih, C.-P. Chen and C.-T. Chou, *J. Org. Chem.*, 1990, **55**, 2019–2026.
11 J. S. Swenton, T. N. Biggs and W. M. Clark, *J. Org. Chem.*, 1993, **58**, 5607–5614; and references therein.
12 M. Novak, J. S. Helmick, N. Oberlies and K. S. Rangappa, *J. Org. Chem.*, 1993, **58**, 867–878.
13 T. J. Holmes, Jr. and R. G. Lawton, *J. Org. Chem.*, 1983, **48**, 3146–3150.
14 J. S. Swenton, B. R. Bonke, C.-P. Chen and C.-T. Chou, *J. Org. Chem.*, 1989, **54**, 51–58.
15 M. C. Carreño and M. Ribagorda, *J. Org. Chem.*, 2000, **65**, 1231–1234.
16 T. A. Engler, W. Chai and K. O. Lynch, Jr., *Tetrahedron Lett.*, 1995, **36**, 7003–7006.
17 R. Adams and J. H. Looker, *J. Am. Chem. Soc.*, 1951, **73**, 1145–1149; and references therein.
18 R. Barret and M. Daudon, *Tetrahedron Lett.*, 1991, **32**, 2133–2134.
19 (*a*) C.-C. Liao and R. K. Peddinti, *Acc. Chem. Res.*, 2002, **35**, 856–866; (*b*) S. R. Surasani, V. S. Rajora, N. Bodipati and R. K. Peddinti, *Tetrahedron Lett.*, 2009, **50**, 773–775; (*c*) S. R. Surasani and R. K. Peddinti, *Tetrahedron Lett.*, 2011, **52**, 4615–4618.
20 N. Bodipati and R. K. Peddinti, *Org. Biomol. Chem.*, 2012, **10**, 1958–1961.
21 For reviews on hypervalent iodine reagents, see: (*a*) S. F. Kirsch and A. Duschek, *Angew. Chem., Int. Ed.*, 2011, **50**, 1524–1552; (*b*) V. V. Zhdankin, *Chem. Rev.*, 2008, **108**, 5299–5358; (*c*) L. Pouysegu, D. Deffieux and S. Quideau, *Tetrahedron*, 2010, **66**, 2235–2261; (*d*) V. Satam, A. Harad, R. Rajule and H. Pati, *Tetrahedron*, 2010, **66**, 7659–7706.
22 For the applications of DIB, see: (*a*) W. Liu, C. Chen and Q. Zhang, *Org. Biomol. Chem.*, 2011, **9**, 6484–6486; (*b*) P.-H. Lu, C.-S. Yang, B. Devendar and C.-C. Liao, *Org. Lett.*, 2010, **12**, 2642–2645; (*c*) Y. Zhao and Y.-Y. Yeung, *Org. Lett.*, 2010, **12**, 2128–2131; (*d*) R. Akula, M. Galligan and H. Ibrahim, *Chem. Commun.*, 2009, 6991–6993.
23 C.-P. Chen, C.-T. Chou and J. S. Swenton, *J. Am. Chem. Soc.*, 1987, **109**, 946–948; and references therein.
24 D. R. Hookins and R. J. K. Taylor, *Tetrahedron Lett.*, 2010, **51**, 6619–6621; and references therein.