# Anodic Oxidation of *N*-Protected 4-Methoxy Anilines: Improved Synthesis of Quinone Imine Acetals

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Recent synthetic applications of quinone imines[1] and bisimines[2] have focused on nucleophilic additions promoted by both acids and bases.[3] These reactions require the use of stable *N*-arylsulfonyl derivatives of quinone imines to avoid decomposition, which occurs with more labile protecting groups. However, the strongly acidic conditions necessary to remove the sulfonyl group,[4] after transformation of the quinone imine, limit their synthetic potential. Although *N*-acyl derivatives are also available,[2c] similar problems arise upon amide hydrolysis. Simple *p*-benzoquinone imines are extremely unstable compounds and are subject to rapid hydrolysis. With the exception of *N*-aryl quinone imine acetals,[5] they should be generated in situ for further studies or synthetic manipulation.[6] The difficulties found in the synthesis and isolation of such derivatives could be the origin of their limited synthetic use.[7] The most general method for the preparation of both quinone derivatives stems on the chemical oxidation of *p*-methoxy anilides or *p*-phenylene diamides,[2a,b] mainly effected with Ce(IV) salts[8] or Pb(AcO)$_4$.[4,9] In all cases the presence of an imide (*N*-acyl or *N*-arylsulfonyl group) is required to prevent decomposition of the resulting imine in the conditions where these chemical oxidations are performed. Although electrochemical oxidation of *p*-amino phenols[6] has served for the in situ preparation of simple quinone imines, their isolation was subjected to the same limitations as chemical methods. *N*-Acylated quinone imine acetals,[10] as well as *N*-acyl-*p*-quinol imine ethers,[11] are easily available through anodic oxidation of *p*-methoxy or *p*-alkyl substituted anilides.[12] The former could be considered as masked quinone imines.

In connection with a program directed toward the synthesis and applications of chiral sulfinyl *p*-quinol derivatives,[13] we were interested in carbamate-protected quinone imine ketals, which could be the precursors of amino *p*-quinol analogues. Among the carbamate groups,[14] we chose the *tert*-butylcarbamoyl because it is stable enough to allow synthetic manipulation and is more easily hydrolizable than other. Despite the general accessibility of *N*-acylated quinone imine acetals, few examples of carbamate-protected ones have been reported. Swenton[10a] described the anodic oxidation of *N*-BOC and *N*-methoxycarbonyl-*p*-methoxy anilines using both platinum anode and cathode. Apparently, the use of a copper cathode did not allow oxidation to be completed. Although good yields of isolated products were obtained, reaction conditions appear critical, and the use of the platinum cathode introduced a serious limitation due to the cost of this material. We report herein the anodic oxidation of differently *N*-substituted *p*-methoxy anilines **1** based on the use of a copper cathode and show that *N*-*tert*-butylcarbamoyl-protected quinone imine acetals can be prepared in good yields using a very simple experimental procedure. This electrochemical oxidation has been also checked in other *N*-substituted derivatives such as acetanilides, *p*-toluenesulfonamides, and phenylhydrazines, as well as *N*-alkyl and *N*-sulfinyl anilines.

## Result and Discussion

Starting *N*-*tert*-butoxycarbonyl-*p*-methoxy anilines **1a**−**f** were obtained by direct treatment of adequately substituted commercially available anilines with (BOC)$_2$O following the reported procedure for aliphatic amines.[15] Sulfonamide **1g**, acetanilide **1h**, and propynylaniline **1i** were prepared by conventional procedures involving reaction of *p*-methoxy aniline with *p*-toluenesulfonyl chloride, acetic anhydride, and propargyl bromide, respectively. Synthesis of **1j** was achieved by hydrogenation (Al/Hg) of the 4-methoxy azobenzene precursor, and preparation of **1k** (63% yield) was carried out by sequential treatment of *p*-methoxy aniline with *n*-BuLi and menthyl *p*-toluene sulfinate.[16] This procedure gives acces to enantiopure (*S*)-*N*-(*p*-tolyl sulfinyl)-4-methoxy aniline **1k** (Scheme 1).

(1) For applications of *p*-quinone monoimines, see (a) Engler, T. A.; Chai, W.; Lynch, K. O., Jr.; Meduna, S. P. *Tetrahedron Lett.* **1995**, *36*, 7003. (b) Engler, T. A.; Chai, W.; LaTessa, K. O. *J. Org. Chem.* **1996**, *61*, 9297 and references therein. (c) Engler, T. A.; Chai, W. *Tetrahedron Lett.* **1996**, *37*, 6969.

(2) For applications of *p*-quinone bisimines, see: (a) Engler, T. A.; Wanner, J. *Tetrahedron Lett.* **1997**, *38*, 6135. (b) Engler, T. A.; Meduna, S. P.; LaTessa, K. O.; Chai, W. *J. Org. Chem.* **1996**, *61*, 8598. (c) Boger, D. L.; Zarrinmayeh, H. *J. Org. Chem.* **1990**, *55*, 1379. (d). Boger, D. L.; Coleman, R. S. *J. Am. Chem. Soc.* **1988**, *110*, 4796. (e) Holmes, T. J., Jr.; Lawton, R. G. *J. Org. Chem.* **1983**, *48*, 3146.

(3) For Lewis acid promoted cycloadditions with styrenyl systems, see: (a) Engler, T. A.; Scheibe, C. M.; Iyengar, R. *J. Org. Chem.* **1997**, *62*, 8274. (b) Engler, T. A.; Lynch, K. O., Jr.; Chai, W.; Meduna, S. P. *Tetrahedron Lett.* **1995**, *36*, 2713.

(4) (a) Adams R.; Looker, J. H. *J. Am. Chem. Soc.* **1951**, *73*, 1145. (b) Adams, R.; Whitaker, L. *J. Am. Chem. Soc.* **1956**, *78*, 658.

(5) (a) Carreño, M. C.; Cuerva, J. M.; Echavarren, A.; Ribagorda, M. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 1449. (b) Coutts, I. G. C.; Southcott, M. R. *J. Chem. Res.* **1988** (S) 241; (M) 1921.

(6) (a) Harmalker, S. P.; Sawyer, D. T. *J. Org. Chem.* **1984**, *49*, 3579−85. (b) Young, T. E.; Beidler, W. T. *J. Org. Chem.* **1984**, 49, 4833. (c) Young, T. E.; Babbit, B. W. *J. Org. Chem.* **1983**, *48*, 562.

(7) Reviews: (a) *The Chemistry of the Carbon*−*Nitrogen Double Bond*; Patai, S., Ed. Interscience Publishers: New York, 1970; pp 633−729. (b) *The Chemistry of Quinonoid Compounds*; Patai, S., Rappoport, Z., Eds.; John Wiley & Sons: New York, 1988; Vol. II, Parts 1 and 2. (c) Grundmann, C. *Methoden der Organischen Chemie* (Houben-Weyl); Thieme: Stuttgart, 1977: Vol. 7/3b, Chapter V.

(8) Engler, T. A.; Chai, W.; Lynch, K. O., Jr. *Tetrahedron Lett.* **1995**, *36*, 7003.

(9) Adams, R.; Reifschneider, W. *Bull. Soc. Chim. Fr.* **1958**, 23.

(10) (a) Swenton, J. S.; Bonke, B. R.; Chen, C.-P.; Chou, C.-T. *J. Org. Chem.* **1989**, *54*, 51. (b) Swenton, J. S.; Bonke, B. R.; Clark, W. M.; Chen, C.-P.; Martin, K. V. *J. Org. Chem.* **1990**, *55*, 2027.

(11) (a) Novak, M.; Helmick, J. S.; Oberlies, N.; Rangappa, K.; Clark, W. M.; Swenton, J. S. *J. Org. Chem.* **1993**, *58*, 867. (b) Swenton, J. S.; Biggs, T. N.; Clark, W. M. *J. Org. Chem.* **1993**, *58*, 5607.

(12) Chen, C.-P.; Chou, C.-T.; Swenton, J. S. *J. Am. Chem. Soc.* **1987**, *109*, 946.

(13) (a) Carreño, M. C.; Pérez González, M.; Fischer, J. *Tetrahedron Lett.* **1995**, *36*, 4893. (b) Carreño, M. C.; Pérez González, M.; Ribagorda, M.; Fischer, J. *J. Org. Chem.* **1996**, *61*, 6758. (c) Carreño, M. C.; Pérez González, M.; Houk, K. N. *J. Org. Chem.* **1997**, *62*, 9128. (d) Carreño, M. C.; Pérez González, M.; Ribagorda, M.; Houk, K. N. *J. Org. Chem.* **1998**, *63*, 3687.

(14) Greene, T. W.; Wuts, P. G. *Protective Groups in Organic Synthesis*, 3rd ed.; Wiley-Interscience: New York, 1999.

(15) (a) Stahl, G. L.; Walter, R.; Smith, C. W. *J. Org. Chem.* **1978**, *43*, 2285.

(16) Solladié, G.; Hutt, J.; Girardin, A. *Synthesis* **1987**, 173.

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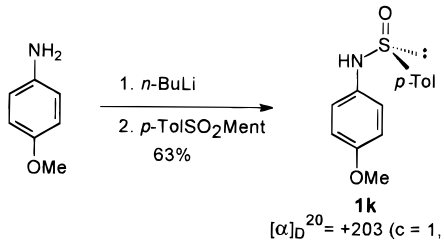
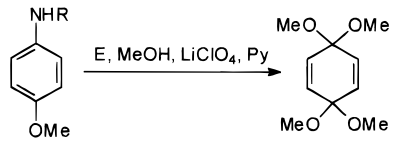
**Scheme 1**




Anodic oxidation of compounds **1** was effected in a single cell apparatus with a 5 cm diameter × 5 cm 45-mesh Pt anode and a copper wire (1.5 mm × 10 cm) situated inside as a cathode, using a methanol solution of **1** in the presence of lithium perchlorate as electrolyte and an added base, which is necessary to avoid decomposition of the final product. As previously observed for anilides,[10a] reaction products and yields were dependent on an array of experimental variables, namely, current density, added base and workup of the reaction, as well as the nature of the substituent existent on the nitrogen. The best results were obtained when a methanolic solution of **1** (0.1−1 equiv), $LiClO_4$, and pyridine (1 equiv) was subjected to a constant current of 0.1 A (2 V) at 0 °C. Although pyridine was reported to promote the formation of pyridinium derivatives in the electrochemical oxidation of *p*-methoxy-benzanilide,[17] in our case, analogous pyridinium salts were not detected. The amount of $LiClO_4$ necessary in each case was different. The electrolyte was added to the methanol solution until the current rose to 0.1 A. Addition of $NaHCO_3$ instead of pyridine as a base did not allow completion of the reaction, probably as a consequence of its low solubility in methanol. Although 2,6-lutidine was soluble enough and gave yields similar to those obtained with pyridine, further removal of the former was inconvenient, which made the isolation process difficult. Workup was carried out by removal of the solvent at reduced pressure, extraction of the product with ethyl acetate, and washing with brine. Although the resulting quinone imine acetals **2** were stable enough to be purified by flash chromatography (with the exception of **2e**), they must be stored in a freezer below 0 °C. The results of these reactions are indicated in Table 1.

*N*-BOC-*p*-methoxy aniline **1a** reacted in 6 h to give derivative **2a** after removal of the methanol and pyridine under vacuum in quantitative yield. Although the crude product **2a** was >97% pure by $^1$H NMR, flash column chromatography allowed its isolation pure in 70% yield (Table 1, entry 1). The oxidation of 2- and 3-methoxy-substituted derivatives **1b** and **1c** (entries 2 and 3), as well as that of *N*-BOC-4-methoxy-2-methyl aniline **1d**, gave rise to the formation of quinone imine acetals **2b**, **2c**, and **2d**, respectively, in good isolated yields. Compound **2c** was characterized as a mixture of the syn and anti imines. As expected, substrates **1b**−**d** bearing electron-donating substituents at the aromatic ring (OMe and Me) were also easily oxidized as a consequence of the effect of the substituents on the oxidation potential[18]

**Scheme 2**




**1** **4**

**i**: R= $CH_2$—≡—H (77 %)

**j**: R= NHPh (95 %)

**k**: R= (*S*) SO*p*-Tol (62 %)

and in accordance with the proposed mechanism for similar anodic oxidations.[19] *N*-BOC-4-methoxynaphthylamine **1e** behaved similarly, affording pure quinone imine acetal **2e** in 97% crude yield (entry 5). In this case chromatographic purification gave a complex mixture of decomposition products. When a Cl subtituent is present in the starting anilide **1f**, quinone imine acetal **2f** could be obtained in 68% yield and characterized as a syn/anti mixture if the crude reaction mixture was directly purified by flash chromatography. If the usual workup was followed (washing with brine), 3-chloro-*p*-benzoquinone dimethyl monoacetal **3** was the isolated product. The higher electrophilicity of the imine carbon in the initial oxidation product **2f**, due to the electron-withdrawing effect of the Cl, should facilitate the formation of **3**, even in the presence of pyridine.

*N*-*p*-Toluenesulfonyl-*p*-methoxyaniline **1g** and *p*-methoxyacetanilide **1h** also gave the quinone imine acetals **2g** ad **2h** in good yields (Table 1, entries 7 and 8) following this oxidation procedure.

Finally, under similar conditions (E, MeOH, $LiClO_4$, Py), compounds **1i**, **1j**, and **1k**, lacking an amide or carbamate *N*-protecting group, evolved into *p*-benzoquinone dimethyl bisacetal **4**[20] in good yields. The unstability of the *p*-benzoquinone imine acetals that should result in these reactions would explain their further evolution to **4** (Scheme 2)

It is important to note that this electrochemical oxidation allows the synthesis of *N*-BOC-protected quinone imine acetals **2** following an experimentally simple procedure that avoids the consumption of an expensive Pt cathode. The use of pyridine as an added base prevents the experimental complication arising when $NaHCO_3$ was the base of choice, which forces the periodical washing of the electrodes during the electrolysis.[10a]

In summary, a simple synthesis of *N*-protected quinone imine acetals that improves the method previously reported has been developed. Transformation of **2** into different interesting amino derivatives will be described in future papers.

## Experimental Section

**General.** All reactions were monitored by TLC, which was performed on precoated silicagel 60 $F_{254}$ plates. Flash column chromatography was effected with silicagel 60 (230−240 mesh). $^1$H NMR spectra were recorded at 200 or 300 MHz. $^{13}$C NMR were recorded at 50 or 75 MHz. Chemical shifts are reported in ppm relative to TMS in $CDCl_3$. All NMR spectra were obtained in $CDCl_3$ at room temperature. HRMS were measured at 70 eV.

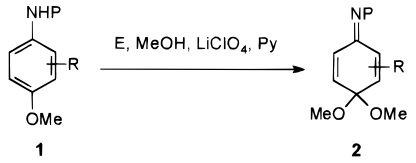
(17) Ikenoya, S.; Masui, M.; Ohmori, H.; Sayo, H. *J. Chem. Soc., Perkin Trans.* 2 **1974**, 571. (b) Masui, M.; Ohmori, H.; Sayo, H.; Ueda, A. *J. Chem. Soc., Perkin Trans. 2* **1976**, 1180.

(18) Electron-donating substituents decrease the oxidation potential of aromatic derivatives (see: Weingberg, H. L. *Technique of Electroorganic Synthesis Part II*; John Wiley: New York, 1975.)

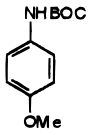
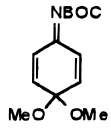
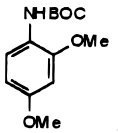
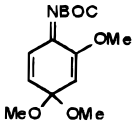
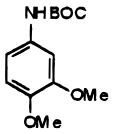
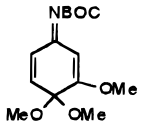
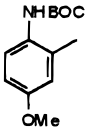
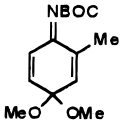
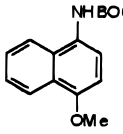
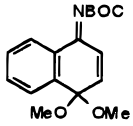
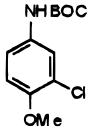
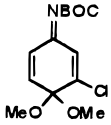
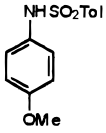
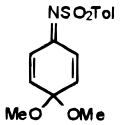
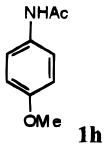
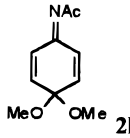
(19) (a) Dolson, M. G.; Swenton, J. S. *J. Am. Chem. Soc.* **1981**, *103*, 2361. (b) Swenton, J. S. *Acc. Chem. Res.* **1983**, *16*, 74.

(20) (a) Belleau, B.; Weinberg, N. L. *J. Am. Chem. Soc.* **1963**, *85*, 2525. (b) Weinberg, N. L.; Belleau, B. *Tetrahedron* **1973**, *29*, 279.

**Table 1. Anodic Oxidation of *N*-Protected *p*-Methoxy Anilines 1**




1 2

| Entry | Compound | g | $LiClO_4$ (eq.) | Time (h) | Product | Yield (%) |
|---|---|---|---|---|---|---|
| 1 |  1a | 3 | 1 | 6 |  2a | 70 |
| 2 |  1b | 1.06 | 0.4 | 7 |  2b | 62 |
| 3 |  1c | 0.2 | 0.6 | 4 |  2c | 70 |
| 4 |  1d | 2.1 | 0.3 | 7 |  2d | 71 |
| 5 |  1e | 1 | 1 | 4 |  2e[a] | 97[b] |
| 6 |  1f | 0.32 | 0.6 | 3 |  2f[a] | 68 |
| 7 |  1g | 0.67 | 0.6 | 5 |  2g | 77 |
| 8 |  1h | 0.2 | 1 | 4 |  2h | 69 |

[a] Syn/anti mixture. [b] Crude yield

All reagents were purchased from Aldrich and were used without further purification.

**(*S*)-*N*-(*p*-Tolylsulfinyl)-4-methoxyaniline (1k).** A 2.5 M solution of *n*-BuLi in hexane (3.25 mL, 8.12 mmol, 2 equiv) was slowly added to a mixture of 4-methoxyaniline (500 mg, 4.06 mmol, 1 equiv) and 10 mL of THF at −78 °C. After 15 min of stirring at this temperature, the resulting mixture was added to a solution of (−)-menthyl *p*-toluene sulfinate (1.49 g, 5.07 mmol, 1.25 equiv) in 3 mL of THF at room temperature. After 30 min of stirring, 5 mL of a saturated solution of $NH_4Cl$ was added, and the organic phase was washed (NaCl saturated solution, 2 × 10 mL), dried ($Na_2SO_4$), and evaporated to dryness. The resulting oil crystallized on addition of an ether/hexane mixture (671 mg, 63% yield). White solid. Mp: 98−101 °C (hexane); $[\alpha]^{20}_D = +203$ ($c = 1$, $CHCl_3$). $^1H$ NMR: $\delta$ 7.62−7.28 (AA′BB′ system, 4H), 7.03 (d, 1H, $J = 6.6$ Hz), 6.69 (d, 1H, $J = 6.6$ Hz), 6.10 (bs, 1H), 3.75 (s, 3H), 2.41 (s, 3H). $^{13}C$ NMR: 156, 141, 133, 129 (2C), 125 (2C), 122.4, 122.2 (2C), 114 (2C), 55, 21

(3C). Anal. Calcd for $C_{14}H_{15}NO_2S$: C, 64.34; H, 5.79; N, 5.36; S, 12.27. Found: C, 64.60; H, 5.52; N, 5.15; S, 12.06.

**General Procedure for Anodic Oxidation.** Electrolysis was carried out in a single cell apparatus in reagent grade methanol, using a circular platinum gauze anode (5 cm × 5 cm in diameter) 45-mesh, a copper wire cathode (1.5 mm × 10 cm), and a AMEL (model 549) power supply. A solution of the corresponding aniline derivative **1** (1 equiv), pyridine (1 equiv), and $LiClO_4$ (0.3−1 equiv) in MeOH was anodically oxidized at 0 °C, under constant current (0.1 A, 2 V). The reaction was monitored by TLC. The methanolic solution was evaporated in a vacuum, extracted with AcOEt, washed with brine solution, dried over $Na_2SO_4$, filtered, and concentrated in a vacuum. Flash column chromatography afforded compounds **2**.

***N*-(*tert*-Butoxycarbonyl)-*p*-benzoquinone Imine Dimethyl Acetal (2a).** Compound **2a** was obtained from *N*-(*tert*-butoxycarbonyl)-4-methoxyaniline **1a** (3 g, 0.01 mol, 1 equiv) using 1 mL (0.01 mol, 1equiv) of pyridine, 1.4 g of $LiClO_4$ (0.01 mol, 1 equiv), and 250 mL of MeOH as a colorless oil (hexanes/ethyl acetate 10:1, 1.7 g, 70%). $^1$H NMR: $\delta$ 6.46 (brd, 2H, $J$ = 10.2 Hz), 6.33 (d, 2H, $J$ = 10.2 Hz), 3.26 (s, 6H), 1.48 (s, 9H). $^{13}$C NMR: 160.4, 155.6, 139.9, 138.5, 129.0, 121.8, 92.2, 81.7, 49.1 (2C), 27.8 (3C). HRMS: *m*/*z* calcd for $M^+$ 253.1314, found 253.1319.

***N*-(*tert*-Butoxycarbonyl)-2-methoxy-*p*-benzoquinone Imine Dimethyl Acetal (2b).** Compound **2b** was obtained from *N*-(*tert*-butoxycarbonyl)-2,4-dimethoxyaniline **1b** (1 g, 3.9 mmol, 1 equiv) using 337 $\mu$L (3.9 mmol, 1 equiv) of pyridine, 200 mg of $LiClO_4$ (1.58 mmol, 0.4 equiv), and 250 mL of MeOH. After removal of MeOH and extraction with AcOEt, the crude product was directly purified by flash column chromatography (hexanes/ethyl acetate 4:1, 62%) as a light yellow oil. $^1$H NMR: $\delta$ 7.0 (brd, $J$ = 10.2 Hz, 1H), 6.15 (dd, $J$ = 10.2 and 1.7 Hz, 1H), 5.54 (d, $J$ = 1.7 Hz, 1H), 3.69 (s, 3H), 3.02 (6H, s), 1.28 (s, 9H). $^{13}$C NMR: 167.8, 152.9, 140.6, 129.2 (2C), 103.6 (2C), 80.79, 79.9, 59.9, 55.8, 51.0, 27.8 (3C). HRMS: *m*/*z* calcd. for $M^+$ 283.1419, found 283.1421.

***N*-(*tert*-Butoxycarbonyl)-3-methoxy-*p*-benzoquinone Imine Dimethyl Acetal (2c).** Compound **2c** was obtained from *N*-(*tert*-butoxycarbonyl)-3,4-dimethoxyaniline **1c** (300 mg, 1.2 mmol) using 100 $\mu$L (1.2 mmol) of pyridine, 76 mg of $LiClO_4$ (0.72 mmol, 0.6 equiv), and 100 mL of MeOH as a light yellow oil (AcOEt/hexane 2:1, 235 mg, 70% yield). $^1$H NMR (syn and anti): $\delta$ 6.45 (brd, $J$ = 10.2 Hz, 1H), 6.31 (brd, $J$ = 10.2 Hz, 1H), 5.68 (brs, 1H), 3.75 (s, 3H), 3.23 (6H, s), 1.51 (s, 9H). $^{13}$C NMR: $\delta$ 164.2 (br), 161.9 (br), 158.6, 148.7, 137.2 (br), 136.9 (br) 124(br), 94.2, 82.6, 55.5, 51.1 and 49.8 (2C), 27.8 and 27.7 1 and 27.6 (3C). HRMS: *m*/*z* calcd for $M^+$ 283.1419, found 283.1415.

***N*-(*tert*-Butoxycarbonyl)-2-methyl-*p*-benzoquinone Imine Dimethyl Acetal (2d).** Compound **2d** was obtained from *N*-(*tert*-butoxycarbonyl)-4-methoxy-2-methylaniline **1d** (2.1 g, 8.8 mmol, 1 equiv), using 714 $\mu$L of pyridine (8.8 mmol, 1 equiv), 336 mg of $LiClO_4$ (3.1 mmol, 0.3 equiv), and 250 mL of MeOH as a light red oil (hexanes/ethyl acetate 6:1, 1.7 g, 71%). $^1$H NMR: $\delta$ 6.48 (dd, 1H, $J$ = 2.3 and 10.3 Hz), 6.33 (dq, 1H, $J$ = 1.4 and 2.3 Hz), 6.32 (d, 1H, $J$ = 10.3 Hz), 3.29 (s, 6H), 1.97 (d, 3H, $J$ = 1.4 Hz), 1.53 (s, 9H). $^{13}$C NMR: 161.6, 156.4, 138.7, 136.2, 134.8, 122.8, 93.1, 82.2, 49.7 (2C), 27.8 (3C), 16.9. HRMS: *m*/*z* calcd for $M^+$ 267.1470, found 267.1470.

***N*-(*tert*-Butoxycarbonyl)-1,4-naphthoquinone Imine Dimethyl Acetal (2e).** Compound **2e** was obtained from *N*-(*tert*-butoxycarbonyl)-4-methoxynaphthylamine **1e** (1 g, 3.6 mmol, 1 equiv) using 295 $\mu$L of pyridine (3.6 mmol, 1 equiv), 383 mg of $LiClO_4$ (3.6 mmol, 1 equiv), and 250 mL of MeOH as a light yellow oil after removal of the methanol and pyridine under vacuum and extraction with AcOEt (97% crude yield). Compound **2e** decomposes to a black oil if the organic phase was washed with brine and upon standing at room temperature or even at 0 °C after 24 h. It could not be purified by flash chromatography. $^1$H NMR (syn and anti): $\delta$ 8.6 (brs, 1H), 8.21 (dd, 1H, $J$ = 1.4 and 7.9 Hz), 7.71 (dd, 1H, $J$ = 1.6 and 8 Hz), 7.59 (dt, 1H, $J$ = 1.3 and 7.6 Hz), 7.43 (dt, 1H, $J$ = 1.6 and 8 Hz), 6.73 (d, 1H, $J$ = 10.2 Hz), 6.59 (d, 1H, $J$ = 10.2 Hz), 3.13 (6H, s), 1.6 (s, 9H). $^{13}$C NMR: 162.2, 155.3, 148.8, 139.9, 137.3, and 136.6, 132.0 and 130.9, 128.7, 126.2, 125.5, 125.2 and 123.8, 95.2, 82.9, 50.8 and 49.8 (2C), 27.7 (3C).

***N*-(*tert*-Butoxycarbonyl)-3-chloro-*p*-benzoquinone Imine Dimethyl Acetal (2f).** Compound **2f** was obtained from *N*-(*tert*-butoxycarbonyl)-3-chloro-4-methoxylaniline **1f** (317 mg 1.23 mmol, 1 equiv), using 100 $\mu$L of pyridine (1.23 mmol, 1 equiv), 83 mg of $LiClO_4$ (0.6 mmol, 0.4 equiv), and 100 mL of MeOH. After removal of MeOH and extraction with AcOEt, the crude product was directly purified by flash column chromatography (hexanes/ethyl acetate 6:1, 240 mg, 68% yield, colorless oil). $^1$H NMR (syn and anti): $\delta$ 6.67 (d, 1H, $J$ = 2.1 Hz), 6.55 (dd, 1H, $J$ = 2.1 and 10.2 Hz), 6.0 and 5.89 (2d, 1H, $J$ = 10.2 Hz), 3.22 and 3.18 (2s, 6H), 1.53 and 1.42 (2s, 9H). $^{13}$C NMR: 160.4, 156.2 and 156**,** 148.5, 146, 139.7and 139.0, 132.4 and 132.1, 124.9 and 123.9, 95.1, 83.1, 51.2 and 51.0 and 50.1 (2C), 27.8 and 27.5 (3C). HRMS: (EI) *m*/*z* calcd for $M^+$ 287.0924, found 287.0929.

When washed with brine and extracted with ethyl acetate the crude mixture resulting from **1f** was quantitatively transformed into 3-chloro-*p*-benzoquinone dimethyl acetal **3**. $^1$H NMR: $\delta$ 6.79 (d, 1H, $J$ = 10.2 Hz), 6.61 (d, 1H, $J$ = 2.1 Hz), 6.45 (dd, 1H, $J$ = 2.1 and 10.2 Hz), 3.31 (s, 6H). $^{13}$C NMR: 183, 152.6, 143.7, 131.8, 131.4, 94.8, 51.4 (2C).$^{13}$C NMR: 184.1, 152.2, 144, 132.8, 132, 94.2, 52.1 (2C).

***N*-(*p*-Toluenesulfonyl)-*p*-benzoquinone Imine Dimethylacetal (2g).** Compound **2g** was obtained from *N*-(*p*-toluenesulfonyl)-4-methoxyanilide **1g** (670 mg, 2.41 mmol) using 194 $\mu$L (2.41 mmol) of pyridine, 256 mg of $LiClO_4$ (1.4 mmol, 0.6 equiv), and 100 mL of MeOH. Compound **2g** was isolated pure as a purple solid after crystallization with ether (573 mg, 77%). Mp 111.4−111.9. $^1$H NMR: $\delta$ 7.85 and 7.32 (AA′BB′ system, 4H), 7.62 (dd, 1H, $J$ = 2 and 12.8 Hz), 6.76 (dd, 1H, $J$ = 2.7 and 12.8 Hz), 6.69 (dd, 1H, $J$ = 2.7 and 10.2 Hz), 6.34 (dd, 1H, $J$ = 2 and 10.2 Hz), 3.34 (s, 6H), 2.48 (s, 3H). $^{13}$C NMR: 162.9, 143.9, 143.3, 142.0, 137.2, 130.2, 129.3 (2C), 127.0 (2C), 122.8, 91.8, 50.0 (2C), 21.3. HRMS: *m*/*z* calcd for $M^+$ 307.0878, found 307.0875.

***N*-Acetyl *p*-Benzoquinone Imine Dimethylacetal (2h).**[10a] Compound **2h** was obtained from 4-methoxyacetanilide **1h** (200 mg, 1.2 mmol) using 180 $\mu$L (1.2 mmol) of pyridine, 127 mg of $LiClO_4$ (1.2 mmol, 1 equiv) and 100 mL of MeOH. Compound **2h** was isolated pure as a yellow oil (195 mg, 69%). $^1$H NMR: $\delta$ 6.54 (d, $J$ = 10.8 Hz, 1H), 6.38 (d, $J$ = 10.8 Hz, 1H), 3.35 (s, 6H), 2.20 (s, 3H).

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**Supporting Information Available:** $^1$H and $^{13}$C NMR spectra of compounds **2a**−**g** and **3** and $^1$H NMR spectrum of **2h**. This material is available free of charge via the Internet at http://pubs.acs.org.

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