A New Method for the Synthesis of Iminoquinones via DMP-Mediated Oxidative Reaction

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Abstract: Iminoquinones were synthesized by oxidation of primary and secondary amines with hypervalent iodine reagent Dess–Martin periodinane in average to good yields, and possible mechanisms were postulated. This methodology is convenient to establish a library of diversified iminoquinone compounds and has great significance for their potential application in the field of pharmaceuticals.

Key words: iodine, amines, oxidation, electron transfer, quinones, quinone monoimines

Hypervalent iodine compounds have proved to be mild and selective oxidizing agents in an impressive array of synthetic methodologies and have received much attention in recent years. 2-Iodoxybenzoic acid [IBX, 1-hydroxy-1,2-benziodoxol-3(1*H*)-one 1-oxide] was first synthesized in 1893;[1] however, it was rarely used in organic synthesis until 1983 when Dess and Martin transformed IBX into the highly soluble Dess–Martin periodinane.[2]

Dess–Martin periodinane [DMP, 1,1,1-triacetoxy-1,1-dihydro-1,2-benziodoxol-3(1*H*)-one] has emerged as the reagent of choice for the oxidation of primary and secondary alcohols to aldehydes and ketones. The synthetic applications of DMP have been highlighted in a number of reviews.[3] Its unique oxidizing properties and convenience of use have ensured the advance DMP to a widely employed reagent in the synthesis of biologically important natural products. Recently DMP was used in the key oxidation steps in the total syntheses of cyclotheonamide B,[4] (±)-deoxypreussomerin A,[5] racemic brevioxime,[6] erythromycin B,[7] (+)-discodermolide,[8] (+)-cephalostatin 7,[9] (+)-cephalostatin 12,[9] (+)-ritterazine K,[9] 3-*O*-galloyl-(2*R*,3*R*)-epicatechin-4β,8-[3-*O*-galloyl-(2*R*,3*R*)-epicatechin],[10] fredericamycin A,[11] indolizidine alkaloids (–)-205A, (–)-207A, and (–)-235B,[12] 1,19-aza-1,19-desoxy-avermectin B1a,[13] angucytcline antibiotics,[14] tricyclic β-lactam antibiotics,[15] and the platelet aggregation-inhibiting γ-lactam PI-091.[16]

The iminoquinone moiety is important in a large number of antineoplastic drugs and plays a significant role in the nucleus of actinomycins, which are powerful, highly toxic, natural antibiotics that target DNA as intercalating agents.[17] Recently, we reported an efficient synthetic approach to iminoquinone compounds via hypervalent iodine oxidation of primary amines. A variety of substituted primary amines were tested, and series of 2-amino-1,4-benzoquinone 4-phenylimines were obtained in excellent yields under mild conditions.[18,19] In particular cases, two useful compounds 4,4′-diazenediyldianiline and 1-amino-5-aza-10,11-dithiadibenza[*a*,*d*]cyclohepten-2-one were obtained, which are of great potential application in the fields of chemosensors and photochemical switches as well as pharmaceuticals.

Our first attempts to establish the generality of DMP oxidized primary amine systems were inspiring. In ongoing research programs, we discerned that tetrabutylammonium bromide (TBAB) is useful in some cases of IBX- or DMP-involved oxidation transformations; it can be used as an activator for hypervalent iodine reagents. Initially, we applied tetrabutylammonium bromide as an additive in the 4-chloroaniline (**1a**)/DMP reaction system; thin-layer chromatography (TLC) indicated that the starting material had been consumed within two hours. Much to our interest, a different transformation had occurred. After isolation and characterization, the new compound was identified as brominated benzoquinone **2a** (Scheme 1). Encouraged by this result, we next explored the scope of our newly developed process using various primary amines **1**; the results are summarized in Figure 1. It was demonstrated that several *p*-substituted anilines **1a–f** were smoothly converted into the corresponding brominated benzoquinones **2a–f** in average to good yields. In particular, in the case of *p*-halo-substituted anilines **1a**,**d–f**, the one-step of oxidation and bromination was of excellent chemoselectivity. However, the limitation of our methodology was obvious. The position of substitution has a decisive impact on the transformation. With the exception of *p*-substituted anilines, other substituted anilines gave exclusively nonbrominated benzoquinone products or a mixture of both products.

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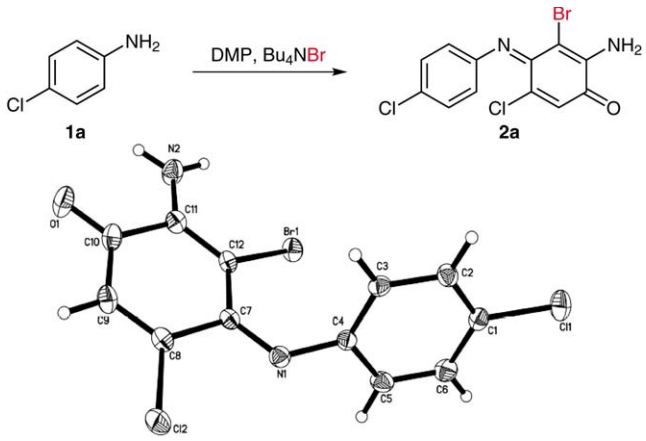


Scheme 1 Synthesis and X-ray crystal structure of **2a**[20]

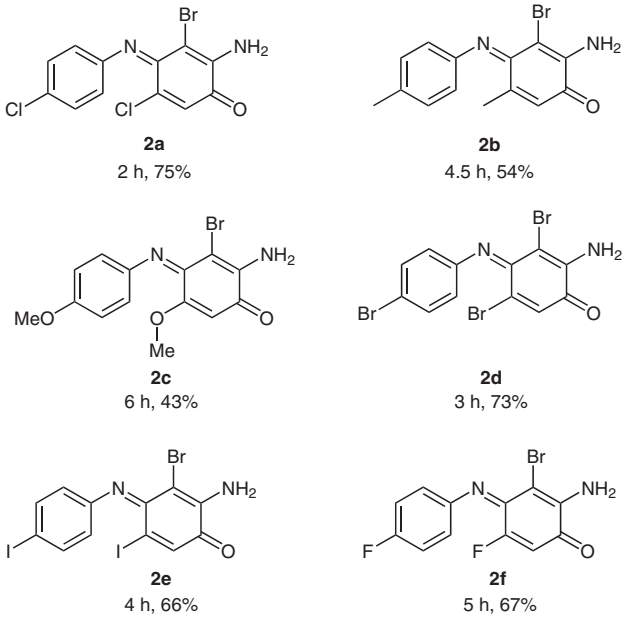
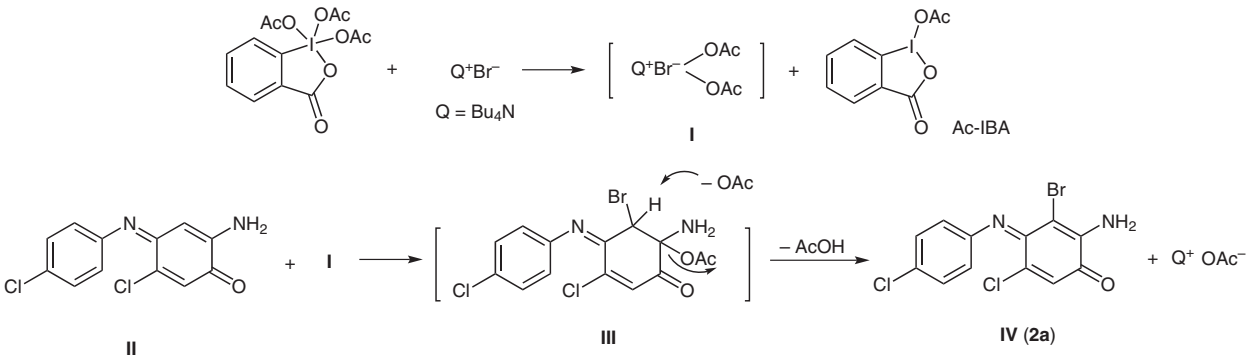


Figure 1

Akamanchi and co-workers reported a one-step procedure for preparation of brominated unsaturated carbonyl compounds.[21] In this case, the acetate ligand of DMP is probably transferred to tetrabutylammonium bromide forming an orange-yellow solution, which may be attributed to the formation of tetrabutylammonium diacetoxybromate **I**. Similarly, in our reaction system, it is envisaged that the bromate **I**[22] is formed in the first instance and it undergoes addition to the double bond in **II** to form bromoacetoxylated intermediate **III**. The acetate ion formed in the reaction acts as a base to abstract hydrogen, which is acidic due as a result of C=N conjugation and the electronegativity of bromine atom, to furnish the final product brominated benzoquinone **IV** (Scheme 2).

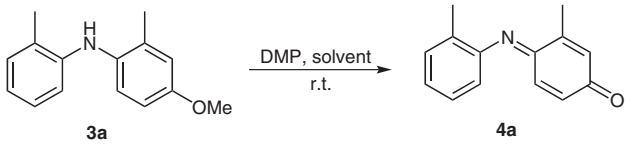
Recognizing that the scope and versatility of the reaction could be enhanced if the library of starting materials was expanded to other available compounds, our further explorations focused on the reaction of diphenylamines in the presence of DMP. Despite great efforts, the most highly substituted diphenylamine gave very complicated results under a variety of reaction conditions. Attempts to further improve the yield of the major products were thwarted by the increased production of side products. Conversely, in special cases, iminoquinones could be formed predominately by correct choice of the designated position and the nature of the specific functional group. When the diphenylamine contains a *p*-methoxy group, the reaction could be carried out successfully. Apart from this particular case, other alkoxy-substituted diphenylamines gave poor results, for instance, ethoxy, phenoxy, and vinyloxy. As a result, the remarkable collaboration of both NH and OMe groups renders this methodology to be one with unique chemoselectivity.

Our initial screening experiments chose 4-methoxy-2-methyl-*N*-(2-tolyl)aniline (**3a**) as a model substrate (Table 1). Investigations on a variety of reaction conditions established that in the presence of a small amount of water (20% mol), **3a** (1 mmol) and DMP (1.8 mmol) dissolved in dichloromethane (2 mL) and stirred at room temperature for five hours gave the desired product **4a** in 87% yield (entry 10). We reasoned that the DMP partially hydrolyzed by small amount water is of stronger nucleophilicity. However, in aqueous media formation of compound **4a** was suppressed, resulting in a more complicated product mixture. It also should be noted that when tetrabutylammonium bromide was applied as an additive, no brominated compound was observed, and also no apparent promotion effect was detected.



Scheme 2 The postulated mechanism

Table 1 Optimization of the Reaction Conditions[a]



3a **4a**

Entry	DMP (mmol)	Solvent	Additive (mmol)	Yield (%)
1	1.0	CH_2Cl_2	–	27
2	1.0	$CHCl_3$	–	15
3	1.0	acetone	–	20
4	1.0	CH_2Cl_2	H_2O (0.2)	35
5	1.0	H_2O	–	–[b]
6	1.0	CH_2Cl_2	TBAB (1.0)	26
7	1.2	CH_2Cl_2	H_2O (0.2)	64
8	1.4	CH_2Cl_2	H_2O (0.2)	74
9	1.6	CH_2Cl_2	H_2O (0.2)	70
10	1.8	CH_2Cl_2	H_2O (0.2)	87

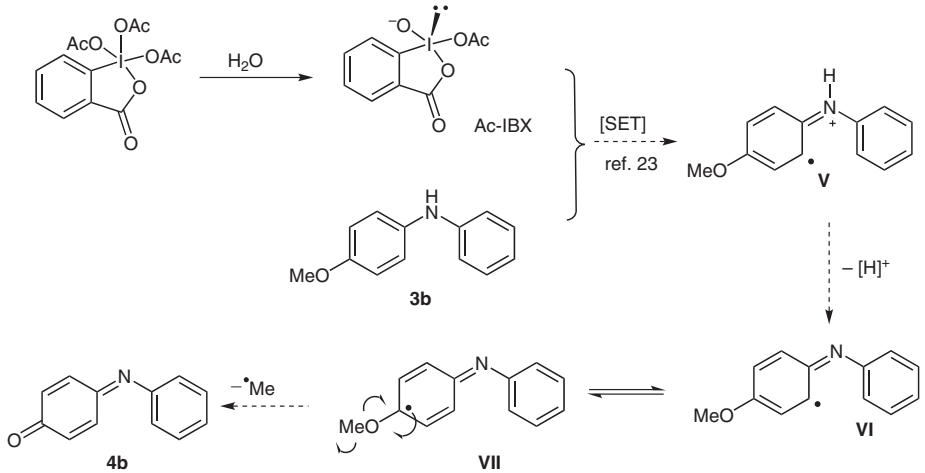
[a] **3a** (1.0 mmol), solvent (2 mL), air atmosphere, r.t., 5 h.
[b] No reaction.

Having established suitable reaction conditions for the oxidation of diphenylamines with DMP, we proceeded to investigate the scope and limitation of this new methodology. A variety of *p*-methoxy-substituted diphenylamines **3** were employed, a selection of pertinent examples is displayed in Table 2. All diphenylamines **3a–i** employed were converted into the corresponding iminoquinones **4a–i** in good yields. In general, yields were higher for the multiply substituted diphenylamines than those for less-substituted diphenylamines. For instance, 4-methoxy-*N*-phenylaniline (**3a**), 4-methoxy-2-methyl-*N*-phenylaniline (**3d**), and *N*-(2-chlorophenyl)-4-methoxyaniline (**3h**) as well as 4-methoxy-*N*-(biphenyl-4-yl)aniline (**3i**) gave the corresponding products **4** with average yields. Notably, the reactions were also significantly affected by the electronic properties of the substituents on the benzene ring. Electron-donating groups have evident positive effects. Methyl-substituted substrate **3c** was converted into iminoquinone **4c** in 65% yield (entry 3); however, for the chlorinated substrate **3h**, the reaction was not only relatively sluggish (12 h), but also the isolated yield of **4h** was less than 50% (entry 8). For the multiply substituted *p*-methoxy-substituted diphenylamines, high steric hindrance around the NH group demonstrated no negative effect and compounds **3a**,**e–g** reacted to give the corresponding products **4a**,**e–g** in high isolated yields in less than five hours.

Based on a previous report,[23] we proposed a pathway based on single electron transfer (SET) mechanism (Scheme 3). The hydrolyzed DMP reagent Ac-IBX acts as an extraordinary oxidant which then initiates the single electron transfer from substrate **3b** to give intermediate **V**. After releasing the hydrogen proton, **V** should rapidly lead to species **VI**, the resultant free radical **VI** was probably less stable than its resonance form **VII**, with the single electron located at the methoxy-attached carbon. Consequently, because of the potential urgency to form a larger conjugative effect, the methyl radical was freed from intermediate **VII**, and the final product **4b** was achieved.

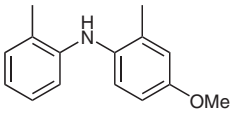
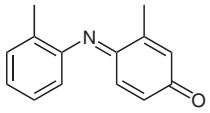
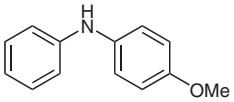
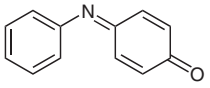
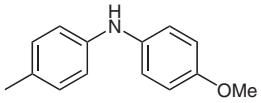
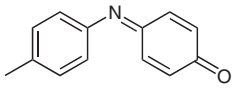
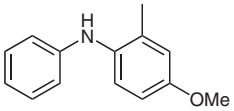
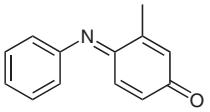
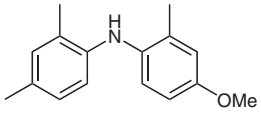
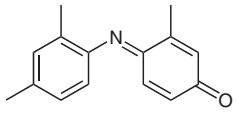
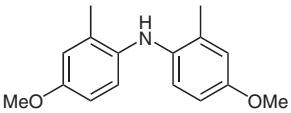
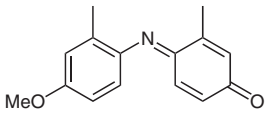
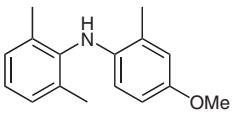
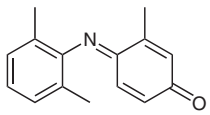
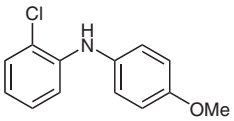
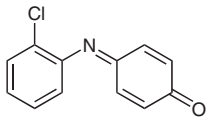
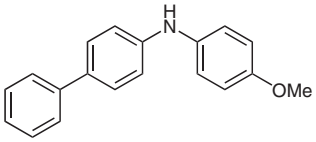
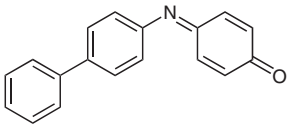
In conclusion, from the transformation of two classes of amines, iminoquinones were obtained; in particular the brominated products lend themselves to establish easily a library of diversified iminoquinones. The significance of this reaction gives iminoquinones a more important place in the field of potential pharmaceuticals applications. Meanwhile, the apparent collaboration of the specific structure and designated position of functional groups in the aromatic rings gives this methodology unique chemoselectivity.

All NMR spectra were recorded on a Brüker Avance Digital spectrometer [400 MHz (^{1}H), 100 MHz (^{13}C)]; TMS as the internal reference in $CDCl_3$. IR spectra were recorded on a Shimadzu IR-408 spectrometer. Mass spectra were recorded on a HP5989B mass spectrometer. Melting points were uncorrected. Room temperature = 15–25°C.



Scheme 3 The postulated mechanism

Table 2 Scope of the Substrates **3** for the Formation of Iminoquinones **4**[a]

Entry	Substrate[b]	Time (h)	Product	Yield[c] (%)
1	 **3a**	5	 **4a**	87
2	 **3b**	8	 **4b**	56
3	 **3c**	5	 **4c**	65
4	 **3d**	4	 **4d**	54
5	 **3e**	3	 **4e**	78
6	 **3f**	3	 **4f**	80
7	 **3g**	3	 **4g**	84
8	 **3h**	12	 **4h**	47
9	 **3i**	12	 **4i**	54

[a] Substrates are commercially available and used without further purification.
[b] Conditions: substrate **3** (1.0 mmol), DMP (1.8 mmol), CH_2Cl_2 (2 mL), H_2O (0.2 mmol), r.t.
[c] Yields indicate product obtained after column chromatography.

Brominated Benzoquinones 2; General Procedure

To a soln of DMP (1.3 g, 2.64 mmol) in CH_2Cl_2 (5 mL) was added TBAB (0.64 g, 2.0 mmol) and aniline **1** (1.5 mmol). The mixture was stirred at r.t. until complete consumption of the aniline (TLC). The soln was washed with H_2O (3 × 5 mL) and the organic phase was dried (anhyd Na_2SO_4). After filtration, the solvent was removed and the residue was purified by column chromatography (silica gel) to afford a soln **2**, which was volatilized at r.t. for period during which time crystallized compounds were formed.

Benzoquinones 4; General Procedure

To a soln of DMP (0.89 g, 1.8 mmol) in CH_2Cl_2 (5 mL) was added aniline **3** (1.0 mmol) and H_2O (0.2 mmol) was added dropwise. The mixture was stirred at r.t. until complete consumption of the aniline

(TLC), and purified by column chromatography (silica gel) to afford **4**.

2-Amino-3-bromo-5-chloro-4-(4-chlorophenylimino)cyclohexa-2,5-dienone (2a)
Red solid; mp 150–152 °C.

IR (KBr): 3477, 3385, 1650, 1618, 1575, 1460, 1200, 1055, 1021, 975, 868 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.32–7.27 (m, 2 H), 6.89 (s, 1 H), 6.76–6.72 (m, 2 H), 5.21 (s, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 181.2, 157.3, 150.8, 147.2, 132.8, 130.2, 123.7, 119.6, 117.6, 110.5.

MS (FAB): *m*/*z* = 345.9 $[M + H]^+$.

Anal. Calcd for $C_{12}H_7BrCl_2N_2O$: C, 41.65; H, 2.04; N, 8.10. Found: C, 41.68; H, 2.08; N, 7.93.

2-Amino-3-bromo-5-methyl-4-(4-tolylimino)cyclohexa-2,5-dienone (2b)
Red solid; mp 138–140 °C.

IR (KBr): 3485, 3364, 1650, 1612, 1545, 1460, 1210, 1165, 1080, 865, 838 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.14–7.12 (d, *J* = 8.0 Hz, 2 H), 6.68–6.66 (d, *J* = 8.0 Hz, 2 H), 6.48 (s, 1 H), 5.10 (s, 2 H), 2.34 (s, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 179.8, 150.8, 143.9, 133.4, 129.1, 126.2, 118.8, 118.6, 117.7, 117.6, 29.6, 20.9.

MS (FAB): *m*/*z* = 304.0 $[M + H]^+$.

2-Amino-3,5-dibromo-4-(4-bromophenylimino)cyclohexa-2,5-dienone (2d)
Red solid; mp 147–149 °C.

IR (KBr): 3476, 3380, 1662, 1620, 1580, 1460, 1210, 1010, 1000, 985, 856 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.35–7.29 (m, 2 H), 6.87 (s, 1 H), 6.74–6.70 (m, 2 H), 5.24 (s, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 182.2, 156.4, 155.8, 143.2, 130.8, 130.2, 124.8, 119.2, 116.6, 110.4.

MS (FAB): *m*/*z* = 433.8 $[M + H]^+$.

2-Amino-3-bromo-5-iodo-4-(4-iodophenylimino)cyclohexa-2,5-dienone (2e)
Red solid; mp 155–157 °C.

IR (KBr): 3480, 3370, 1650, 1600, 1575, 1458, 1232, 1000, 975, 862 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.42–7.32 (m, 2 H), 6.77 (s, 1 H), 6.75–6.72 (m, 2 H), 5.35 (s, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 182.2, 156.4, 155.8, 143.2, 130.8, 130.2, 124.8, 119.2, 116.6, 110.4.

MS (FAB): *m*/*z* = 527.8 $[M + H]^+$.

3-Methyl-4-(2-tolylimino)cyclohexa-2,5-dienone (4a)
Red oil.

IR (KBr): 3356, 1650, 1612, 1570, 1480, 1356, 1034, 766, 654 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.11 (s, 1 H), 7.01–6.98 (d, *J* = 9.6 Hz, 2 H), 6.57 (s, 1 H), 6.49–6.42 (m, 3 H), 2.33 (s, 3 H), 2.16 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 178.0, 156.1, 148.6, 145.5, 135.3, 133.3, 131.4, 130.4, 129.4, 128.7, 123.6, 118.8, 20.9, 17.9.

MS (FAB): *m*/*z* = 211.1 $[M + H]^+$.

4-(Phenylimino)cyclohexa-2,5-dienone (4b)
Red oil.

IR (KBr): 3358, 1650, 1600, 1580, 1453, 1432, 875, 863 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.40–7.39 (t, *J* = 8.0, 7.6 Hz, 2 H), 7.32–7.22 (m, 2 H), 7.10–7.07 (dd, *J* = 2.4 Hz 1 H), 6.89–6.87 (d, *J* = 8.0 Hz, 2 H), 6.71–6.68 (dd, *J* = 2.0 Hz 1 H), 6.55–6.52 (m, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 187.5, 157.3, 149.3, 141.8, 133.4, 128.9, 126.1, 120.6.

MS (FAB): *m*/*z* = 183.1 $[M + H]^+$.

4-(4-Tolylimino)cyclohexa-2,5-dienone (4c)
Red oil.

IR (KBr): 3346, 1648, 1612, 1580, 1467, 1438, 981, 865, 821 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.50 (s, 1 H), 7.39–7.37 (m, 1 H), 7.24–7.22 (d, *J* = 8.0 Hz, 1 H), 7.16–7.13 (m, 1 H), 6.96–6.93 (dd, *J* = 2.4 Hz, 1 H), 6.83–6.81 (d, *J* = 8.0 Hz, 1 H), 6.73–6.67 (m, 1 H), 6.55–6.52 (m, 1 H), 2.37 (S, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 187.7, 158.4, 145.3, 133.4, 129.6, 128.2, 121.0, 120.5, 20.5.

MS (FAB): *m*/*z* = 197.1 $[M + H]^+$.

3-Methyl-4-(phenylimino)cyclohexa-2,5-dienone (4d)
Red oil.

IR (KBr): 3346, 1648, 1612, 1580, 1467, 1438, 981, 865, 821 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.40–7.36 (t, *J* = 7.6 Hz, 2 H), 7.22–7.18 (t, *J* = 8.0 Hz, 1 H), 7.08–6.94 (m, 1 H), 6.84–6.82 (d, *J* = 7.6 Hz, 2 H), 6.55 (s, 1 H), 6.44–6.41 (m, 1 H), 2.27 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 187.7, 157.7, 149.5, 149.4, 132.6, 130.8, 128.8, 128.5, 125.6, 119.9, 18.0.

MS (FAB): *m*/*z* = 197.1 $[M + H]^+$.

4-(2,4-Dimethylphenylimino)-3-methylcyclohexa-2,5-dienone (4e)
Red oil.

IR (KBr): 3348, 1658, 1600, 1580, 1478, 1369, 1002, 756, 654 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.09 (s, 1 H), 7.02–6.99 (d, *J* = 9.6 Hz, 2 H), 6.57 (s, 1 H), 6.49–6.42 (m, 2 H), 2.35 (s, 3 H), 2.33 (s, 3 H), 2.15 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 188.0, 157.1, 149.6, 145.9, 135.8, 132.3, 131.4, 130.6, 129.6, 128.7, 126.6, 118.8, 20.9, 18.1, 17.9.

MS (FAB): *m*/*z* = 225.1 $[M + H]^+$.

4-(4-Methoxy-2-methylphenylimino)-3-methylcyclohexa-2,5-dienone (4f)
Red oil.

IR (KBr): 3356, 1660, 1612, 1585, 1450, 1365, 1012, 778, 754 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.07 (s, 1 H), 7.02–6.99 (d, *J* = 9.6 Hz, 2 H), 6.57 (s, 1 H), 6.48–6.42 (m, 2 H), 3.73 (s, 3 H), 2.36 (s, 3 H), 2.13 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 187.0, 156.1, 148.6, 145.5, 136.8, 134.3, 131.4, 130.4, 129.2, 128.4, 126.6, 116.8, 54.9, 18.1, 17.9.

MS (FAB): *m*/*z* = 241.1 $[M + H]^+$.

4-(2,6-Dimethylphenylimino)-3-methylcyclohexa-2,5-dienone (4g)
Red oil.

IR (KBr): 3350, 1648, 1600, 1570, 1488, 1374, 1012, 764, 664 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.07–7.05 (d, *J* = 8.0 Hz, 2 H), 6.99–6.97 (m, 1 H), 6.63–6.60 (d, *J* = 10.0 Hz, 1 H), 6.56 (s, 1 H), 6.37–6.34 (m, 1 H), 2.36 (s, 3 H), 1.96 (s, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 187.6, 158.8, 149.0, 147.8, 132.6, 130.9, 128.3, 127.8, 124.8, 124.3, 18.1, 17.9.

MS (FAB): *m*/*z* = 225.1 $[M + H]^+$.

4-(2-Chlorophenylimino)cyclohexa-2,5-dienone (4h)
Red oil.

IR (KBr): 3358, 1652, 1600, 1589, 1478, 1465, 1121, 876, 769, 664 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.49–7.47 (m, 1 H), 7.39–7.36 (m, 1 H), 7.32–7.28 (m, 1 H), 7.20–7.15 (m, 1 H), 6.91–6.88 (m, 1 H), 6.79–6.77 (m, 1 H), 6.74–6.71 (m, 1 H), 6.55–6.52 (m, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 187.2, 158.8, 146.5, 141.2, 133.6, 133.2, 130.1, 128.3, 127.1, 126.6, 124.6, 120.7.

MS (FAB): *m*/*z* = 217.0 $[M + H]^+$.

4-(Biphenyl-4-ylimino)cyclohexa-2,5-dienone (4i)
Red oil.

IR (KBr): 3358, 1650, 1610, 1586, 1478, 1454, 1006, 965, 875 cm^{-1}.

^1H NMR (400 MHz, CDCl3): δ = 7.67–7.62 (m, 4 H), 7.49–7.45 (t, *J* = 7.6 Hz, 2 H), 7.40–7.32 (m, 2 H), 7.21–7.18 (m, 1 H), 7.01–6.99 (d, *J* = 8.4 Hz, 2 H), 6.74–6.71 (dd, *J* = 2.0 Hz, 1 H), 6.59–6.56 (dd, *J* = 2.4 Hz, 1 H).

^{13}C NMR (100 MHz, CDCl3): δ = 187.6, 157.4, 148.5, 141.8, 140.0, 139.3, 133.4, 132.8, 128.9, 127.7, 126.9, 121.5.

MS (FAB): *m*/*z* = 259.1 $[M + H]^+$.

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