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DDQ-Mediated Formation of Carbon-Carbon Bonds: Oxidation of Imines

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Abstract: The reaction of imines with alkynes and alkenes, in the presence of 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ), to give quinoline derivatives is described. The mechanism of the annulation is discussed, and evidence supporting a non-concerted pathway, at least when the alkene is butyl vinyl ether, is reported. Preliminary information is also given about solid adducts of imines with DDQ, which do not seem to be involved in the reaction path leading to quinolines, and should account for the dependence of product yields on the position of substituents on the starting imines.

INTRODUCTION

Our group has been studying for several years the employment of imines in cyclization and annulation reactions leading to heterocyclic rings. At first, we explored the reactivity of imidoyl radicals, generated by hydrogen abstraction from aromatic Schiff bases in the presence of peroxides, and we achieved the synthesis of such N-heterocycles as phenanthridines,[1] quinolines,[2] benzo-1,2,4-triazines,[3a] and benzo-1,3-thiazoles.[3b] Cyclizations were also performed by other authors starting from suitably *ortho*-substituted imidoyl radicals arising from selenoimidates.[4]

The construction of quinoline derivatives was accomplished by cycloaddition between imines (pre-formed or generated *in situ* by condensation of aromatic amines and formaldehyde), and such electron-rich alkenes as dienes,[5] styrenes,[6] acetylenes,[7] enol ethers,[8] and enamines.[9] In these reactions it has not been well established the nature of the mechanism yet, namely whether it is multi-step or a synchronous inverse-electron-demand Diels-Alder cycloaddition.

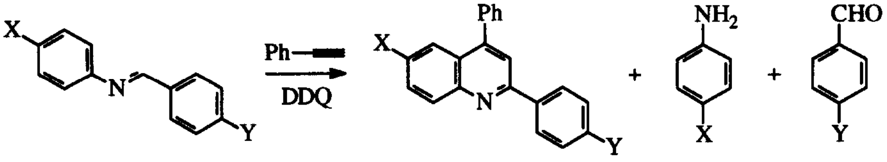
Recently, some papers on an EPR study of imine radical cations[10] suggested the possibility of employing electrophilic species, derived by one-electron oxidation of Schiff bases, in the synthesis of N-heterocycles. We showed that oxidation of a series of N-arylidenebenzenamines, by means of an acetonitrile solution of iron (III) chloride, in the presence of phenylacetylene or styrene led to quinolines and/or 1,2,3,4-tetrahydroquinoline derivatives in good yields;[11] this reaction was proved to involve reduction of Fe (III) ions and formation of imine radical cations. During this research we realised that the annulation could be accomplished in the presence of such an organic oxidant as tetrachloro-*p*-benzoquinone (chloranil); under these conditions we were able to use butyl vinyl ether as well.

Even better results were obtained with 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ), which has a higher reduction potential with respect to chloranil.[12] The dehydrogenating and oxidative properties of quinones and their charge-transfer complexes with aromatics or molecules containing heteroatoms are wellknown;[13] furthermore, in these last years, DDQ has been widely used in the functionalisation of organic compounds[14] and regioselective formation of carbon-carbon bonds.[15]

In the present paper we report the reaction between aromatic imines and alkynes or alkenes (including phenylacetylene, styrene, vinyl acetate, and butyl vinyl ether) in the presence of DDQ.

RESULTS AND DISCUSSION

Imines **1** (3 mmol) were allowed to react with phenylacetylene (30 mmol) in a boiling solution of DDQ (3.3 mmol) in anhydrous acetonitrile (20 mL)[16] until disappearance of the starting material (3-24 h).[17] Ammonia was bubbled into the solution,[18] the solvent was evaporated and the residue chromatographed on a silica gel column to give quinolines **2**, amines **3**, and aldehydes **4** (Scheme 1 and Table 1).



1 **2** **3** **4**

Scheme n. 1. Reaction of imines **1** with phenylacetylene and DDQ.

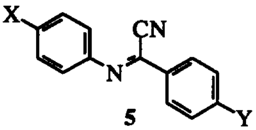
Table 1. Products Yields for the Reactions of Imines **1** with Phenylacetylene and DDQ.

1	X	Y	t (h)	**2** (%)^a	**3** (%)^a	**4** (%)^a
a	H	H	9	30	-	trace am.
b	MeO	H	3	55	-	trace am.
c	NC	H	7	43	25	trace am.
d	Cl	H	24	60	trace am.	trace am.
e	O_2N	H	9	44	25	2
f	H	OMe	24	26	-	15
g	H	CN	5	15	-	10
h	H	Cl	5	10	-	14
i	H	NO_2	24	10	-	17

[a] All yields are for isolated pure products and are based on the starting imine

In the reactions of **1a**, **1d**, **1f**, and **1i** trace amounts of the α-(phenylimino)benzeneacetonitrile **5** were found as well.

The amounts of annulation products **2** are strongly dependent on the position of the substituent: imines **1b-e** (X ≠ H, Y = H) led to good yields in quinoline, whereas derivatives **1a** and **1f-i** (X = H) gave much worse results. On the contrary, the character of the substituent did not seem to affect the yields of **2** and the reaction times.



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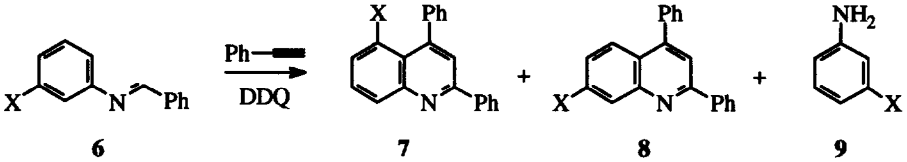
With imines **6**, bearing a *meta* substituent on the ring linked to the nitrogen atom, the reaction was not regioselective, as it afforded mixtures of quinolines **7** and **8**, with a slight preference for the **7** isomer (Scheme 2 and Table 2).



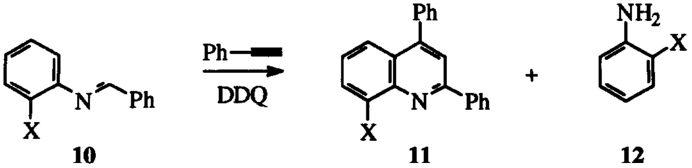
Scheme n. 2. Reaction of imines **6** with phenylacetylene and DDQ.

Table 2. Products Yields for the Reactions of Imines **6** with Phenylacetylene and DDQ.

6	X	t (h)	**7** (%)[a]	**8** (%)[a]	**9** (%)[a]
a	Me	240	-	-	-
b	MeO	240	-	-	-
c	NC	24	37	20	20
d	Cl	24	29	23	5
e	O_2N	4	24	17	17

[a] All yields are for isolated pure products and are based on the starting imine.

Imines **6a** and **6b** did not give any quinolines even after 10 days of reflux: this completely unexpected behaviour has not been rationalised yet, and it was also observed with imine **10a** , bearing the methyl group in the *ortho* position of the benzenamine ring. With the other imines of this kind (**10b-e**) the annulation proceeded according to the forecasts (Scheme 3 and Table 3).



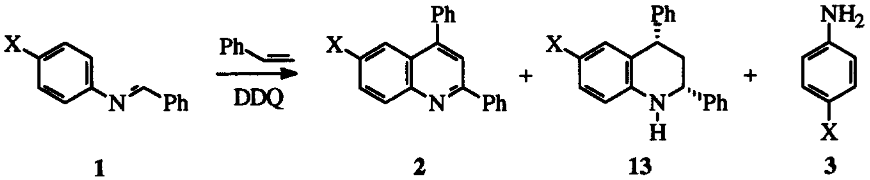
Scheme n. 3. Reaction of imines **10** with phenylacetylene and DDQ.

Table 3. Products Yields for the Reactions of Imines **10** with Phenylacetylene and DDQ.

10	X	t (h)	**11** (%)[a]	**12** (%)[a]
a	Me	240	-	-
b	MeO	4	20	-
c	NC	480	25	22
d	Cl	96	40	-
e	O_2N	5	23	50

[a] All yields are for isolated pure products and are based on the starting imine.

Reaction of imines **1** (Y = H) with styrene in the presence of 2 equiv of DDQ gave mixtures of quinolines **2** (Y = H), tetrahydro derivatives **13**, and amines **3** (Scheme 4 and Table 4).



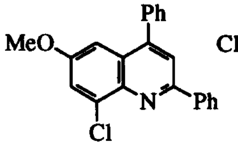
Scheme n. 4. Reaction of imines **1** with styrene and DDQ.

Table 4. Products Yields for the Reactions of Imines **1** with Styrene and DDQ.

1	X	t (h)	**2** (%)[a]	**13** (%)[a]	**3** (%)[a]
a	H	3	10	-	-
b	MeO	0.5	65	-	-
c	NC	9	50	19	trace am.
d	Cl	5	50	-	trace am.
e	O_2N	7	51	20	12
j	Me	0.75	25	-	-

[a] All yields are for isolated pure products and are based on the starting imine.

It is also worth pointing out that imine **1b** yielded an additional 10% of quinoline **14** and imine **1j** afforded the chloromethyl derivative **15** (14%) as well: the mechanism of formation of these products was not investigated.



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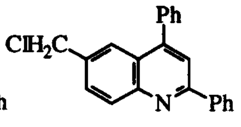

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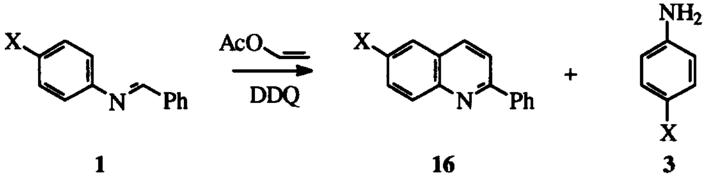
Also in the reactions with styrene, the change of the X-substituent did not significantly affect the yields of annulation products **2** and **13**, with the exception of imine **1a** (X = H), which was seen to react very poorly. On the contrary, reaction times were fairly correlated to the character of X, since the imines bearing an electron-withdrawing substituent (**1c**, **1e**) required longer reflux. The presence of a cyano or nitro group on the starting imine seems to be essential in order to isolate the tetrahydro derivatives **13**.

With vinyl acetate, the final reaction mixtures contained quinolines **16** (loss of the acetate group occurred) and amines **3** (Scheme 5 and Table 5).



Scheme n. 5. Reaction of imines 1 with vinyl acetate and DDQ.

Table 5. Products Yields for the Reactions of Imines 1 with Vinyl Acetate and DDQ.

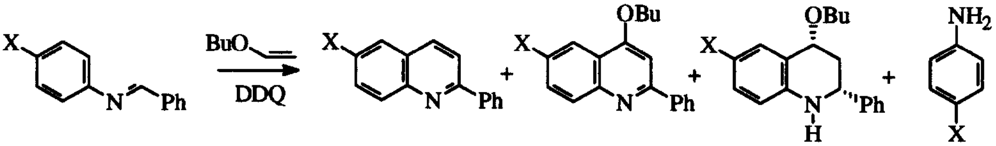
1	X	t (days)	**16** (%)^a	**3** (%)^a
a	H	2	16	-
b	MeO	1	26	-
c	NC	3	16	10
d	Cl	4	21	trace am.
e	O_2N	4	20	14

[a] All yields are for isolated pure products and are based on the starting imine
In all reactions trace amounts of nitrile **5** (Y = H) were found as well.

In spite of quite low yields of **16**, vinyl acetate allowed the synthesis of quinolines with no substituent in the 4-position, derivatives not accessible by previously reported synthetic procedures.[2, 11] In these reactions this alkene can be considered as a synthone for acetylene.

Finally, imines **1** were allowed to react with butyl vinyl ether and they afforded quinolines **16** and **17**, tetrahydroquinolines **18**, and amines **3** (Scheme 6 and Table 6). In each reaction we used 1 equiv of DDQ but variable amounts of alkene and different temperatures: the composition of the final mixtures strongly depended on the experimental conditions.

The stereochemistry of **18**, together with that of **13**, was investigated on the basis of ^{1}H-NMR data, and the substituents in the 2- and 4-positions were both found to be equatorial: in fact, coupling constants typical of axial-axial (10.5, 12.0 Hz) and axial-equatorial (2.6, 5.1 Hz) interactions were found between the methylenic protons in the 3-position and their two vicinal protons (see Experimental Section).



1 **16** **17** **18** **3**

Scheme n. 6. Reaction of imines **1** with butyl vinyl ether and DDQ.

Table 6. Products Yields for the Reactions of Imines **1** with Butyl Vinyl Ether and DDQ.

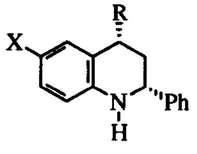
1	X	Alkene[a]	T (°C)	t (h)	**16** (%)[b]	**17** (%)[b]	**18** (%)[b]	**3** (%)[b]
a[c]	H	1	0	0.5	20	5	-	-
b	MeO	1	0	5	6	4	-	-
b	MeO	10	25	0.2	31	9	-	-
c	NC	1	80	24	16	-	-	23
c	NC	2	80	0.5	15	-	11	23
c	NC	2	25	1.5	7	-	-	-
c	NC	10	25	0.3	22	-	-	-
d	Cl	1	80	5	25	3	-	trace am.
d	Cl	2	80	0.2	33	2	-	-
d	Cl	10	25	0.2	35	3	-	-
e[d]	O_2N	1	80	15	11	-	-	17
e	O_2N	2	80	0.5	5	-	16	12
e	O_2N	10	25	0.3	-	-	10	-
k[d]	HO	2	80	0.4	20	-	-	-

[a] Equiv of butyl vinyl ether with respect to the starting imine. [b] All yields are for isolated pure products and are based on the starting imine. [c] In the presence of higher amounts of alkene, both at 0 °C and at room temperature, polymers of butyl vinyl ether were formed, from which annulation products could not be easily separated [d] This reaction afforded small amounts of a solid compound (molecular weight 301), probably an adduct between alkene and DDQ (see Experimental Section).

With imines **1a**, **1b**, and **1d**, quinolines **16** and small amounts of 4-butoxy derivatives **17** were obtained. The recovering of **17**, together with the formation of tetrahydroquinolines **13** in the reactions with styrene, let us assume that **19** or, more probably, an adduct of **19** with DDQ could be the initially-formed product in annulations with alkenes (we must remember that, in the absence of work-up, no product can be isolated).

When R = Ph (reactions with styrene) **19** can easily aromatize by loss of H_2; if R = OBu (reactions with butyl vinyl ether) the loss of butanol from positions 3 and 4 is competitive with dehydrogenation and a mixture of **16** and **17** was obtained; finally, if R = OAc (reactions with vinyl acetate) the elimination of acetic acid seems to be strongly favoured with respect to dehydrogenation, and 4-H derivatives **16** were exclusively formed. The finding of **19c** and **19e** in a few reactions with styrene and butyl vinyl ether might be ascribed to a particular stability of these compounds with X = CN or NO_2: in these cases, the adduct **19 / DDQ** could partially survive until the end of the reaction, giving **19** after work-up of the final mixtures.[19]

When imine **1c** was allowed to react at room temperature with 2 or 10 equiv of alkene, besides quinoline **16c**, compound **20c** was obtained in 16-18% yield. **20c** remained unchanged if kept for 1 h in a refluxing acetonitrile solution, but it afforded **16c** quantitatively in the presence of DDQ: this conversion was quite slow at room temperature (about 50% in 1 h) and very fast at 80 °C (complete in 30 min). Imine **1e** yielded the analogous compound **20e** (7%), whose behaviour completely resembled the one observed in the case of **20c**.



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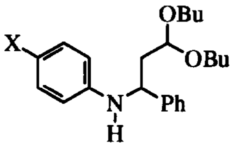


20c (X = NC), **20e** (X = O_2N)

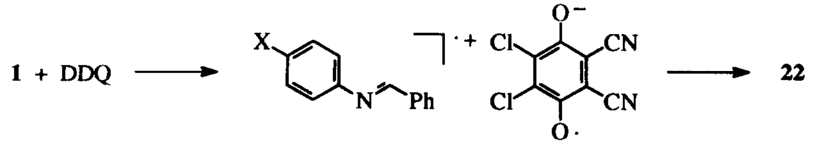
On the light of these results, the following mechanistic considerations can be outlined.

The initial electron transfer step from imine to DDQ (Scheme 7) seems to be a reasonable process: the formation of the imine radical cation has been demonstrated in iron (III) mediated annulations,[11] and EPR studies of charge-transfer complexes between benzylidenaniline (**1a**) and chloranil have also been reported in the literature.[20]

On the other hand, the intervention of imidoyl radicals or cations must be ruled out: the imidoyl radical obtained by hydrogen atom abstraction from **1b**, in the presence of phenylacetylene, should give two isomeric quinolines,[2b] and the imidoyl cation of **1a** was seen to attack benzonitrile to afford a quinazoline,[2c] whereas no product was obtained from the reaction of **1a** with benzonitrile and DDQ.

We could assume that the initially-formed ion-pair **21** might collapse to give an electrophilic species **22**, which is the responsible for the attack to the alkene or alkyne. The formation of an electrophilic intermediate was also proved by the reaction of imine **1a** with allyltributyltin, yielding the allylic compound **23a** (X = H) (Scheme 8); the same reaction carried out on imines **1l** (X = Br) and **10f** (X = I) gave derivatives **23l** (X = 4-Br) and **23f** (X = 2-I): the unobserved loss of bromine or iodine atom let us rule out the intervention of stannyl radicals and, consequently, the intermediacy of free-radicals deriving from the imine.

In the presence of phenylacetylene, **22** affords quinolines **2**: with this alkyne, at the moment, we cannot say whether the mechanism is a multi-step or a concerted one.



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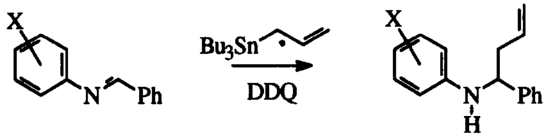
Scheme n. 7. Electron-transfer step in the reaction of imines with alkynes or alkenes in the presence of DDQ.



1a, 1l, 10f **23a, 23l, 23f**

Scheme n. 8. Reaction of imines **1a**, **1l**, and **10f** with allyltributyltin.

With alkenes, **22** gives rise to an intermediate which can cyclize on the phenyl ring linked to the nitrogen atom to yield quinoline derivatives, or, in the presence of an excess of butyl vinyl ether, it can attack another molecule of the alkene to afford **20** after work-up.[21]

The step leading from **20** to **16** is strongly dependent on the temperature, as discussed above, therefore **21** was isolated only in the reactions performed at room temperature.

The finding of **20** let us conclude that, at least with butyl vinyl ether, the mechanism of annulation between imines and alkenes is stepwise.

As far as the adducts of imines with DDQ are concerned, it is worth pointing out that acetonitrile solutions of the reactants, kept at room temperature in the absence of alkyne or alkene, afforded brown-greenish solid compounds, which were analysed by infrared spectroscopy and mass spectrometry.[22]

Mass spectra and high resolution mass spectra of solids yielded by imines **1a**, **1f**, **1g**, and **1h** are consistent with an adduct of imine and DDQ in a 1:1 ratio. On the contrary, compounds derived from **1b-e** have mass spectra which exhibit peaks corresponding to the starting imines.[23].

The IR spectra of solids from Schiff bases **1a**, **1d**, and **1h** are characterised by the absence of the strong absorption (1676 cm^{-1}) of quinone carbonyls. Compounds from **1a** and **1h** show a broad band near 3200 cm^{-1} and two absorptions of the cyano-group (2234 and 2254 cm^{-1}), features very close to that reported in the literature for $DDQH_2$.[24] Derivative from **1d** show a completely different spectrum, whose main characteristics are a single cyano-group absorption at 2218 cm^{-1} (identical to that observed for DDQ radical anion[24]) and a series of absorptions above 3000 cm^{-1}, among which a C-H stretching (3053 cm^{-1}) could be probably identified.[25]

Even if these data are not sufficient to established unambiguously the structure of the adducts between imines and DDQ, and studies are still in progress in order to obtain some more information, we could tentatively suggest that when X ≠ H and Y = H (imines **1b-e**) the precipitate might be the ion pair $\mathbf{1}^{\cdot+}$ / $\mathbf{DDQ}^{\cdot-}$; on the contrary, when X = H (imines **1a** and **1f-i**) the spin distribution on the imine radical cation could give rise to proton transfer from $\mathbf{1}^{\cdot+}$ to $\mathbf{DDQ}^{\cdot-}$, yielding a different solid adduct. This step appears to be irreversible, as adducts from **1f** and **1h**, refluxed for several days in acetonitrile in the presence of 10 equiv of phenylacetylene, did not react at all, whereas compounds from **1b** and **1d**, under the same conditions, afforded quinolines **2b** and **2d**, but with much longer reaction times with respect to entries **b** and **d** of Table 1.

This result let us suppose that solid adducts do not lay on the annulation pathway and this hypothesis might justify the dependence of the yields of quinolines on the position of substituents in the starting imines.

EXPERIMENTAL SECTION

General Procedures.

Melting points were determined on an Electrothermal capillary apparatus and are uncorrected. ^1H-NMR spectra were recorded in deuteriochloroform on Varian EM 360L (60 MHz) or Varian Gemini 200 (200 MHz) instruments, using tetramethylsilane as an internal standard. Mass spectra and high resolution mass spectra (HRMS) were performed with a VG 7070E spectrometer by electron impact with a beam energy of 70 eV. IR spectra were recorded in KBr on a Perkin-Elmer 983 spectrophotometer. GC-MS analyses were carried out on a Carlo Erba AUTO/HRGC/MS-QMD 1000 instrument equipped with a capillary column (Quadrex 007, 25 m x 0.25 mm I.D.) and a NIST/NBS library. Column chromatography was performed on silica gel (ICN Silica, 63-200, 60A), using light petroleum (40-70 °C) and a light petroleum/diethyl ether gradient (from 0 up to 100% diethyl ether) as eluant. Previously reported reaction products were identified by spectral comparison and mixed mp determination with authentic specimens.

Starting materials.

All reactions were carried out in anhydrous acetonitrile (Aldrich Chemie, $H_2O < 0.005\%$), using commercially available phenylacetylene, styrene (Aldrich Chemie), vinyl acetate, butyl vinyl ether, and DDQ (Janssen Chimica). Products **1a**,[26] **1b**,[27] **1c**,[28] **1d**,[29] **1e**,[30] **1f**,[31] **1g**,[32] **1h**,[33] **1i**,[34] **1j**,[31] **1k**,[35] **6a**,[31] **6b**,[36] **6c**,[37] **6d**,[38] **6e**,[39] **10a**,[39] **10b**,[40] **10d**,[31] and **10e**[41] were prepared according to the literature.

N-Phenylmethylene-2-aminobenzonitrile (10c).[42] A benzenic (100 mL) solution of 2-aminobenzonitrile (5.90 g, 50 mmol), benzaldehyde (5.30 g, 50 mmol), and *p*-toluenesulfonic acid (0.1 g) was refluxed for 4 h with azeotropic removal of water. The solvent was evaporated and the residue crystallised to give **10c** (8.75 g, 84%), mp = 109-111 °C (from light petroleum / benzene 30:70 v/v); 60 MHz ^{1}H-NMR δ 6.93-8.07 (9 H, m, Ar-*H*), 8.42 (1 H, s, -N=C*H*-); MS *m/e* 206 (M^+, 100), 205 (66), 179 (6), 104 (12), 103 (18), 102 (18), 89 (3), 77 (15); HRMS calcd for $C_{14}H_{10}N_2$ 206.08440, found 206.08498. Anal. calcd for $C_{14}H_{10}N_2$: C, 81.53; H, 4.89; N, 13.58. Found: C, 81.60; H, 4.87; N, 13.55.

Reactions of imines with phenylacetylene and DDQ.

General procedure. To a solution of imine (3 mmol) and DDQ (3.3 mmol) in acetonitrile (20 mL) phenylacetylene (30 mmol) was added, and the resulting mixture refluxed until complete disappearance of starting material (for reaction times see Table 1). The flask was cooled in an ice-bath, and ammonia was bubbled into the mixture for about 2 min. The solvent was removed under reduced pressure and the residue chromatographed to give quinolines **2**, amines **3**, and aldehydes **4**. The following reactions were performed according to this general procedure.

Reaction of 1a with phenylacetylene and DDQ. **1a** (0.54 g) gave, after 9 h of reflux, α-(phenylimino)-benzeneacetonitrile (**5a**),[43] and 2,4-diphenylquinoline (**2a**) (0.25 g, 30%), mp = 111-113 °C (from light petroleum / benzene 95:5 v/v) (lit.[2a] mp = 112-113 °C).

Reaction of 1b with phenylacetylene and DDQ. **1b** (0.63 g) yielded, after 3 h of reflux, 6-methoxy-2,4-diphenylquinoline (**2b**) (0.51 g, 55%), mp = 121-122 °C (from light petroleum / benzene 90:10 v/v) (lit.[2b] mp = 119-121 °C).

Reaction of 1c with phenylacetylene and DDQ. **1c** (0.62 g) afforded, after 7 h of reflux, 2,4-diphenyl-6-quinolinecarbonitrile (**2c**) (0.39 g, 43%), mp = 190-192 °C (from light petroleum / benzene 50:50 v/v) [200 MHz ^{1}H-NMR δ 7.43-7.68 (8 H, m, Ar-*H*), 7.85 (1 H, dd, *J* = 8.2, 1.2 Hz, Ar-*H*), 7.93 (1 H, s, Ar-*H*), 8.15-8.35 (4 H, m, Ar-*H*); MS *m/e* 306 (M^+, 96), 305 (100), 280 (5), 229 (9), 227 (14), 153 (11); HRMS calcd for $C_{22}H_{14}N_2$ 306.11570, found 306.11602. Anal. calcd for $C_{22}H_{14}N_2$: C, 86.25; H, 4.61; N, 9.14. Found: C, 86.32; H, 4.58; N, 9.10), and 4-aminobenzonitrile (**3c**) (0.15 g, 25%), mp = 82-85 °C (from light petroleum / benzene 60:40 v/v).[44]

Reaction of 1d with phenylacetylene and DDQ. **1d** (0.65 g) gave, after 24 h of reflux, α-(4-chlorophenylimino)benzeneacetonitrile (**5d**) (0.01 g, 2%), mp = 91-93 °C (from ethanol) (lit.[45] mp = 93.5-94.5 °C), 6-chloro-2,4-diphenylquinoline (**2d**) (0.57 g, 60%), mp = 130-131 °C (from light petroleum / benzene 60:40 v/v) (lit.[2b] mp = 127-129 °C), and 4-chlorobenzenamine (**3d**).[43]

Reaction of **1e** *with phenylacetylene and DDQ.* **1e** (0.68 g) afforded, after 9 h of reflux, 6-nitro-2,4-diphenylquinoline (**2e**) (0.43 g, 44%), mp = 208-210 °C (from ethanol / benzene 80:20 v/v) (lit.[11] mp = 208-210 °C), and 4-nitrobenzenamine (**3e**) (0.07 g, 25%), mp = 142-144 °C (from light petroleum / benzene 50:50 v/v).[44]

Reaction of **1f** *with phenylacetylene and DDQ.* **1f** (0.63 g) yielded, after 24 h of reflux, α-(phenylimino)-4-methoxybenzeneacetonitrile (**5f**) (0.02 g, 3%), mp = 116-118 °C (without recrystallisation) (lit.[45] mp = 118-119 °C), 2-(4-methoxyphenyl)-4-phenylquinoline (**2f**) (0.24 g, 26%), mp = 83-84 °C (from light petroleum / benzene 95:5 v/v) (lit.[2a] mp = 83-84 °C), and 4-methoxybenzaldehyde (**4f**) (0.06 g, 15%).[44]

Reaction of **1g** *with phenylacetylene and DDQ.* **1g** (0.62 g) gave, after 5 h of reflux, 4-(4-phenyl-2-quinolinyl)benzonitrile (**2g**) (0.15 g, 15%), mp = 176-178 °C (from light petroleum / benzene 60:40 v/v) [200 MHz ^{1}H-NMR δ 7.45-7.65 (6 H, m, Ar-*H*), 7.72-7.97 (5 H, m, Ar-*H*), 8.20-8.37 (3 H, m, Ar-*H*); MS *m/e* 306 (M$^+$, 100), 305 (97), 229 (3), 202 (12), 153 (9); HRMS calcd for $C_{22}H_{14}N_2$ 306.11570, found 306.11623. Anal. calcd for $C_{22}H_{14}N_2$: C, 86.25; H, 4.61; N, 9.14. Found: C, 86.32; H, 4.59; N, 9.09], and 4-cyanobenzaldehyde (**4g**) (0.06 g, 10%), mp = 91-92 °C (from ethanol).[44]

Reaction of **1h** *with phenylacetylene and DDQ.* **1h** (0.65 g) afforded, after 5 h of reflux, 2-(4-chlorophenyl)-4-phenylquinoline (**2h**) (0.10 g, 10%), mp = 106-107 °C (from light petroleum / benzene 95:5 v/v) (lit.[46] mp = 104 °C), and 4-chlorobenzaldehyde (**4h**) (0.06 g, 14%), mp = 47-50 °C (from ethanol).[44]

Reaction of **1i** *with phenylacetylene and DDQ.* **1i** (0.68 g) yielded, after 24 h of reflux, α-(phenylimino)-4-nitrobenzeneacetonitrile (**5i**),[43] 2-(4-nitrophenyl)-4-phenylquinoline (**2i**) (0.09 g, 10%), mp = 163-164 °C (from light petroleum / benzene 70:30 v/v) (lit.[46] mp = 160 °C), and 4-nitrobenzaldehyde (**4i**) (0.07 g, 17%), mp = 93-95 °C (from diethyl ether).[44]

Reaction of **6c** *with phenylacetylene and DDQ.* **6c** (0.62 g) gave, after 24 h of reflux, 2,4-diphenyl-7-quinolinecarbonitrile (**8c**) (0.18 g, 20%), mp = 173-174 °C (from light petroleum / benzene 50:50 v/v) [200 MHz ^{1}H-NMR δ 7.48-7.64 (9 H, m, Ar-*H*), 7.94 (1 H, s, Ar-*H*), 7.99 (1 H, d, *J* = 8.8 Hz, Ar-*H*), 8.17-8.24 (2 H, m, Ar-*H*), 8.58 (1 H, d, *J* = 1.6 Hz, Ar-*H*); MS *m/e* 306 (M$^+$, 87), 305 (100), 280 (3), 229 (9), 227 (13), 153 (9); HRMS calcd for $C_{22}H_{14}N_2$ 306.11570, found 306.11630. Anal. calcd for $C_{22}H_{14}N_2$: C, 86.25; H, 4.61; N, 9.14. Found: C, 86.33; H, 4.59; N, 9.08], 2,4-diphenyl-5-quinolinecarbonitrile (**7c**) (0.34 g, 37%), mp = 209-210 °C (from light petroleum / benzene 50:50 v/v) [200 MHz ^{1}H-NMR δ 7.43-7.62 (8 H, m, Ar-*H*), 7.76 (1 H, dd, *J* = 8.1, 7.3 Hz, Ar-*H*), 7.90 (1 H, s, Ar-*H*), 7.94 (1 H, dd, *J* = 7.3, 1.2 Hz, Ar-*H*), 8.17-8.24 (2 H, m, Ar-*H*), 8.47 (1 H, dd, *J* = 8.1, 1.2 Hz, Ar-*H*); MS *m/e* 306 (M$^+$, 100), 305 (90), 280 (8), 229 (13), 227 (11), 153 (11) 78 (16); HRMS calcd for $C_{22}H_{14}N_2$ 306.11570, found 306.11592. Anal. calcd for $C_{22}H_{14}N_2$: C, 86.25; H, 4.61; N, 9.14. Found: C, 86.30; H, 4.60; N, 9.10], and 3-aminobenzonitrile (**9c**) (0.07 g, 20%), mp = 47-51 °C (from light petroleum / benzene 70:30 v/v).[44]

Reaction of **6d** *with phenylacetylene and DDQ.* **6d** (0.65 g) yielded, after 24 h of reflux, 7-chloro-2,4-diphenylquinoline (**8d**) (0.22 g, 23%), mp = 96-98 °C (from light petroleum / benzene 60:40 v/v) (lit.[2b] mp = 94-95 °C), 5-chloro-2,4-diphenylquinoline (**7d**) (0.27 g, 29%), mp = 110-111 °C (from light petroleum / benzene 70:30 v/v) (lit.[11] mp = 111-112 °C), and 3-chlorobenzenamine (**9d**) (0.02 g, 5%).[44]

Reaction of **6e** *with phenylacetylene and DDQ.* **6e** (0.68 g) afforded, after 4 h of reflux, 7-nitro-2,4-diphenylquinoline (**8e**) (0.17 g, 17%), mp = 181-182 °C (from 2-propanol / benzene 50:50 v/v) (lit.[11] mp = 180-182 °C), 5-nitro-2,4-diphenylquinoline (**7e**) (0.23 g, 24%), mp = 142-143 °C (from 2-propanol / benzene 80:20 v/v) (lit.[11] mp = 141-143 °C), and 3-nitrobenzenamine (**9e**) (0.07 g, 17%), mp = 106-109 °C (from light petroleum / benzene 60:40 v/v).[44]

*Reaction of **10b** with phenylacetylene and DDQ.* **10b** (0.63 g) yielded, after 4 h of reflux, 8-methoxy-2,4-diphenylquinoline (**11b**) (0.19 g, 20%), mp = 126-127 °C (from light petroleum / benzene 90:10 v/v) (lit.[2b] mp = 122-124 °C).

*Reaction of **10c** with phenylacetylene and DDQ.* **10c** (0.62 g) gave, after 20 days of reflux, 2,4-diphenyl-8-quinolinecarbonitrile (**11c**) (0.23 g, 25%), mp = 169-170 °C (from light petroleum / benzene 60:40 v/v) [60 MHz ^{1}H-NMR δ 7.37-7.62 (9 H, m, Ar-*H*), 7.90-8.47 (5 H, m, Ar-*H*); MS *m/e* 306 (M$^+$, 91), 305 (100), 280 (3), 277 (5), 229 (8), 227 (11), 153 (11); HRMS calcd for $C_{22}H_{14}N_2$ 306.11570, found 306.11612. Anal. calcd for $C_{22}H_{14}N_2$: C, 86.25; H, 4.61; N, 9.14. Found: C, 86.31; H, 4.59; N, 9.10], and 2-aminobenzonitrile (**12c**) (0.08 g, 22%), mp = 45-48 °C (from light petroleum / benzene 90:10 v/v).[44]

*Reaction of **10d** with phenylacetylene and DDQ.* **10d** (0.65 g) afforded, after 4 days of reflux, 8-chloro-2,4-diphenylquinoline (**11d**) (0.38 g, 40%), mp = 117-118 °C (from light petroleum / benzene 70:30 v/v), 60 MHz ^{1}H-NMR δ 6.87-7.93 (12 H, m, Ar-*H*), 8.08-8.38 (2 H, m, Ar-*H*); MS *m/e* 317 (M$^+$ + 2, 31), 316 (M$^+$ + 1, 49), 315 (M$^+$, 87), 314 (100), 280 (21), 278 (11), 277 (12), 238 (7), 140 (19); HRMS calcd for $C_{21}H_{14}ClN$ 315.08148, found 315.08175. Anal. calcd for $C_{21}H_{14}ClN$: C, 79.87; H, 4.47; Cl, 11.22; N, 4.44. Found: C, 79.96; H, 4.45; Cl, 11.17; N, 4.42].

*Reaction of **10e** with phenylacetylene and DDQ.* **10e** (0.68 g) gave, after 5 h of reflux, 8-nitro-2,4-diphenylquinoline (**11e**) (0.22 g, 23%), mp = 194-196 °C (from light petroleum / benzene 60:40 v/v) [60 MHz ^{1}H-NMR δ 7.15-7.60 (9 H, m, Ar-*H*), 7.82-8.37 (4 H, m, Ar-*H*); MS *m/e* 326 (M$^+$, 100), 325 (80), 308 (7), 296 (5), 294 (4), 280 (19), 279 (36), 278 (31), 252 (14); HRMS calcd for $C_{21}H_{14}N_2O_2$ 326.10553, found 326.10628. Anal. calcd for $C_{21}H_{14}N_2O_2$: C, 77.29; H, 4.32; N, 8.58. Found: C, 77.38; H, 4.30; N, 8.55], and 2-nitrobenzenamine (**12e**) (0.22 g, 50%), mp = 69-71 °C (from light petroleum / benzene 50:50 v/v).[44]

Reactions of imines with styrene and DDQ.

General procedure. These reactions were carried out according to the general procedure previously described for phenylacetylene, but in the presence of 2.2 equiv of DDQ (6.6 mmol).

*Reaction of **1a** with styrene and DDQ.* **1a** (0.54 g) gave, after 3 h of reflux, **2a** (0.08 g, 10%), mp = 112-114 °C (from light petroleum / benzene 95:5 v/v) (lit.[2a] mp = 112-113 °C).

*Reaction of **1b** with styrene and DDQ.* **1b** (0.63 g) yielded, after 0.5 h of reflux, 8-chloro-6-methoxy-2,4-diphenylquinoline (**14**) (0.10 g, 10%), mp = 132-134 °C (from light petroleum / benzene 80:20 v/v) [200 MHz ^{1}H-NMR δ 3.80 (3 H, s, -OC*H*$_3$), 7.12 (1 H, d, *J* = 2.7 Hz, Ar-*H*), 7.45-7.64 (9 H, m, Ar-*H*), 7.68 (1 H, s, Ar-*H*), 8.24-8.33 (2 H, m, Ar-*H*); MS *m/e* 347 (M$^+$ + 2, 32), 346 (M$^+$ + 1, 29), 345 (M$^+$, 100), 332 (7), 330 (22), 316 (3), 314 (6), 295 (6), 294 (5), 267 (8), 266 (7); HRMS calcd for $C_{22}H_{16}ClNO$ 345.09204, found 345.09169. Anal. calcd for $C_{22}H_{16}ClNO$: C, 76.41; H, 4.66; Cl, 10.25; N, 4.05. Found: C, 76.50; H, 4.64; Cl, 10.23; N, 4.03], and **2b** (0.61 g, 65%), mp = 121-122 °C (from light petroleum / benzene 70:30 v/v) (lit.[2b] mp = 119-121 °C).

*Reaction of **1c** with styrene and DDQ.* **1c** (0.62 g) afforded, after 9 h of reflux, **2c** (0.46 g, 50%), mp = 190-192 °C (from light petroleum / benzene 50:50 v/v) (spectroscopic data are identical to those reported for compound **2c** obtained in the above reaction of **1c** with phenylacetylene), 1,2,3,4-tetrahydro-2,4-diphenyl-6-quinolinecarbonitrile (**13c**) (0.18 g, 19%), mp = 186-188 °C (from light petroleum / benzene 50:50 v/v) (lit.[11] mp = 188-190 °C) [200 MHz ^{1}H-NMR δ 2.18 (1 H, ddd, $J_1 = J_2 = J_3$ = 11.9 Hz, -CH-C*H*$_2$-CH-), 2.30 (1 H, m, -CH-C*H*$_2$-CH-), 4.20 (1 H, dd, *J* = 11.9, 4.7 Hz, -NH-C*H*-), 4.60-4.75 (2 H, m, -N*H*-CH- + -CH$_2$-C*H*-Ph), 6.52 (1 H, d, *J* = 8.1 Hz, Ar-*H*), 6.87 (1 H, bs, Ar-*H*), 7.17-7.50 (11 H, m, Ar-*H*)], and **3c**.[43]

Reaction of **1d** *with styrene and DDQ.* **1d** (0.65 g) gave, after 5 h of reflux, **2d** (0.47 g, 50%), mp = 130-131 °C (from light petroleum / benzene 60:40 v/v) (lit.[2a] mp = 127-129 °C), and **3d**.[43]

Reaction of **1e** *with styrene and DDQ.* **1e** (0.68 g) yielded, after 7 h of reflux, **2e** (0.50 g, 51%), mp = 206-208 °C (from ethanol / benzene 80:20 v/v) (lit.[11] mp = 208-210 °C), 1,2,3,4-tetrahydro-6-nitro-2,4-diphenylquinoline (**13e**) (0.20 g, 20%), mp = 178-179 °C (from 2-propanol / benzene 80:20 v/v) (lit.[11] mp = 177-179 °C) [200 MHz ^{1}H-NMR δ 2.18 (1 H, ddd, $J_1 = J_2 = J_3$ = 12.0 Hz, -CH-CH_2-CH-), 2.32 (1 H, m, -CH-CH_2-CH-), 4.21 (1 H, dd, J = 12.0, 5.1 Hz, -NH-C*H*-), 4.71 (1 H, dd, J = 12.0, 3.6 Hz, -CH_2-C*H*-Ph), 5.00 (1 H, bs, -N*H*-CH-), 6.48 (1 H, d, J = 8.8 Hz, Ar-*H*), 7.20-7.58 (11 H, m, Ar-*H*), 7.88 (1 H, dd, J = 9.0, 2.4 Hz, Ar-*H*)], and **3e** (0.05 g, 12%), mp = 141-144 °C (from light petroleum / benzene 50:50 v/v).[44]

Reaction of **1j** *with styrene and DDQ.* **1j** (0.59 g) gave, after 45 min of reflux, 6-methyl-2,4-diphenylquinoline (**2j**) (0.22 g, 25%), mp = 129-130 °C (from light petroleum / benzene 95:5 v/v) (lit.[2b] mp = 129-131 °C), and 6-(chloromethyl)-2,4-diphenylquinoline (**15**) (0.14 g, 14%), mp = 144-145 °C (from light petroleum / benzene 90:10 v/v) [200 MHz ^{1}H-NMR δ 4.71 (2 H, s, Cl-CH_2-), 7.48-7.63 (8 H, m, Ar-*H*), 7.79 (1 H, dd, J = 8.3, 1.8 Hz, Ar-*H*), 7.86 (1 H, s, Ar-*H*), 7.89 (1 H, d, J = 1.8 Hz, Ar-*H*), 8.16-8.30 (3 H, m, Ar-*H*); MS *m/e* 331 (M^+ + 2, 20), 329 (M^+, 57), 294 (100), 293 (11), 292 (7), 280 (5), 216 (5), 147 (16); HRMS calcd for $C_{22}H_{16}ClN$ 329.09713, found 329.09784. Anal. calcd for $C_{22}H_{16}ClN$: C, 80.11; H, 4.89; Cl, 10.75; N, 4.25. Found: C, 80.23; H, 4.85; Cl, 10.69; N, 4.23].

Reactions of imines with vinyl acetate and DDQ.

General procedure. These reactions were carried out and worked-up according to the general procedure described above for phenylacetylene.

Reaction of **1a** *with vinyl acetate and DDQ.* **1a** (0.54 g) gave, after 2 days of reflux, **5a**,[43] and 2-phenylquinoline (**16a**) (0.10 g, 16%), mp = 83-84 °C (from light petroleum / benzene 95:5 v/v) (lit.[47] mp = 85 °C).

Reaction of **1b** *with vinyl acetate and DDQ.* **1b** (0.63 g) yielded, after 24 h of reflux, α-(4-methoxyphenylimino)benzeneacetonitrile (**5b**) (0.02 g, 3%), mp = 78-81 °C (from light petroleum / benzene 70:30 v/v) (lit.[45] mp = 80.5-81.5 °C), and 6-methoxy-2-phenylquinoline (**16b**) (0.18 g, 26%), mp = 132-133 °C (from light petroleum / benzene 70:30 v/v) (lit.[47] mp = 132 °C).

Reaction of **1c** *with vinyl acetate and DDQ.* **1c** (0.62 g) afforded, after 3 days of reflux, α-(4-cyanophenylimino)benzeneacetonitrile (**5c**) (0.02 g, 3%), mp = 168-170 °C (from light petroleum / benzene 50:50 v/v) (lit.[45] mp = 171-172 °C), 2-phenyl-6-quinolinecarbonitrile (**16c**) (0.11 g, 16%), mp = 142-143 °C (from light petroleum / benzene 60:40 v/v) (lit.[48] mp = 142-143 °C), and **3c** (0.06 g, 10%), mp = 81-84 °C (from light petroleum / benzene 70:30 v/v).[44]

Reaction of **1d** *with vinyl acetate and DDQ.* **1d** (0.65 g) gave, after 4 days of reflux, **5d** (0.02 g, 3%), mp = 93-95 °C (from ethanol) (lit.[45] mp = 93.5-94.5 °C), 6-chloro-2-phenylquinoline (**16d**) (0.15 g, 21%), mp = 110-111 °C (from light petroleum / benzene 60:40 v/v) (lit.[49] mp =110-111 °C), and **3d**.[43]

Reaction of **1e** *with vinyl acetate and DDQ.* **1e** (0.68 g) yielded, after 4 days of reflux, α-(4-nitrophenylimino)benzeneacetonitrile (**5e**) (0.02 g, 3%), mp = 138-140 °C (from light petroleum / benzene 90:10 v/v) (lit.[50] mp = 140 °C), 6-nitro-2-phenylquinoline (**16e**) (0.15 g, 20%), mp = 184-185 °C (from light petroleum / benzene 60:40 v/v) [200 MHz ^{1}H-NMR δ 7.51-7.63 (3 H, m, Ar-*H*), 8.06 (1 H, d, J = 8.2 Hz, Ar-*H*), 8.20-8.32 (3 H, m, Ar-*H*), 8.41 (1 H, d, J = 8.2 Hz, Ar-*H*), 8.50 (1 H, dd, J = 8.9, 2.3 Hz, Ar-*H*), 8.81 (1 H, d, J = 2.3 Hz, Ar-*H*); MS *m/e* 250 (M^+, 100), 234 (2), 220 (6), 204 (30), 203 (23), 194 (14); HRMS calcd for $C_{15}H_{10}N_2O_2$ 250.07423, found 250.07404. Anal. calcd for $C_{15}H_{10}N_2O_2$: C, 71.99; H, 4.03; N, 11.19. Found: C, 72.10; H, 4.02; N, 11.16], and **3e** (0.06 g, 14%), mp = 140-143 °C (from light petroleum / benzene 50:50 v/v).[44]

Reactions of imines with butyl vinyl ether and DDQ.

General procedure. These reactions were performed and worked-up according to the general procedure previously described for phenylacetylene, except for temperatures and amounts of the alkene, which will be pointed out in each case (see also Table 6).

Reaction of 1a with butyl vinyl ether (1 equiv) and DDQ at 0 °C. **1a** (0.54 g) gave, after 30 min, **16a** (0.12 g, 20%), mp = 81-82 °C (from light petroleum / benzene 95:5 v/v) (lit.[47] mp = 85 °C), and 4-butoxy-2-phenylquinoline (**17a**) (0.04 g, 5%), mp = 70-73 °C (from light petroleum) [200 MHz ^{1}H-NMR δ 1.05 (3 H, t, J = 7.1 Hz, -CH_3), 1.55-1.75 (2 H, m, -CH_2CH$_3$), 1.90-2.05 (2 H, m, -OCH$_2$CH_2-), 4.30 (2 H, t, J = 6.3 Hz, -OCH_2-), 7.18 (1 H, s, Ar-H), 7.42-7.60 (4 H, m, Ar-H), 7.67-7.77 (1 H, m, Ar-H), 8.07-8.17 (3 H, m, Ar-H), 8.23 (1 H, dd, J = 8.3, 1.0 Hz, Ar-H); MS *m/e* 277 (M$^+$, 65), 234 (7), 221 (100), 220 (32), 204 (19), 193 (10), 57 (11); HRMS calcd for $C_{19}H_{19}NO$ 277.14666, found 277.14683. Anal. calcd for $C_{19}H_{19}NO$: C, 82.28; H, 6.90; N, 5.05. Found: C, 82.30; H, 6.87; N, 5.04].

Reaction of 1b with butyl vinyl ether (1 equiv) and DDQ at 0 °C. **1b** (0.63 g) yielded, after 5 h, **16b** (0.04 g, 6%), mp = 129-132 °C (from light petroleum / benzene 70:30 v/v) (lit.[47] mp = 132 °C), and 4-butoxy-6-methoxy-2-phenylquinoline (**17b**) (0.04 g, 4%), mp = 99-101 °C (from light petroleum / benzene 70:30 v/v) [200 MHz ^{1}H-NMR δ 1.07 (3 H, t, J = 6.7 Hz, -CH_3), 1.55-1.75 (2 H, m, -CH_2CH$_3$), 1.90-2.08 (2 H, m, -OCH$_2$CH_2-), 3.97 (3 H, s, -OCH_3), 4.30 (2 H, t, J = 5.3 Hz, -OCH_2-), 7.17 (1 H, s, Ar-H), 7.33-7.58 (5 H, m, Ar-H), 8.00-8.12 (3 H, m, Ar-H); MS *m/e* 307 (M$^+$, 100), 264 (5), 252 (85), 250 (16), 236 (50), 222 (7), 208 (29); HRMS calcd for $C_{20}H_{21}NO_2$ 307.15723, found 307.15784. Anal. calcd for $C_{20}H_{21}NO_2$: C, 78.15; H, 6.89; N, 4.56. Found: C, 78.21; H, 6.86; N, 4.54].

Reaction of 1b with butyl vinyl ether (10 equiv) and DDQ at 25 °C. **1b** (0.63 g) afforded, after 10 min, **16b** (0.22 g, 31%), mp = 131-133 °C (from light petroleum / benzene 70:30 v/v) (lit.[47] mp = 132 °C), and **17b** (0.08 g, 9%), mp = 100-101 °C (from light petroleum / benzene 70:30 v/v) (spectroscopic data are identical to those reported for compound **17b** obtained in the above reaction of **1b** with 1 equiv of butyl vinyl ether and DDQ at 0°C).

Reaction of 1c with butyl vinyl ether (1 equiv) and DDQ at 80 °C. **1c** (0.62 g) yielded, after 24 h of reflux, **5c** (0.02 g, 3%), mp = 169-170 °C (from light petroleum / benzene 50:50 v/v) (lit.[45] mp = 171-172 °C), **16c** (0.11 g, 16%), mp = 139-142 °C (from light petroleum / benzene 70:30 v/v) (lit.[48] mp = 142-143 °C), and **3c** (0.08 g, 23%), mp = 75-78 °C (from light petroleum / benzene 70:30 v/v).[44]

Reaction of 1c with butyl vinyl ether (2 equiv) and DDQ at 80 °C. **1c** (0.62 g) gave, after 30 min of reflux, **16c** (0.10 g, 15%), mp = 140-142 °C (from light petroleum / benzene 70:30 v/v) (lit.[48] mp = 142-143 °C), 4-butoxy-1,2,3,4-tetrahydro-2-phenyl-6-quinolinecarbonitrile (**18c**) (0.10 g, 11%), oil [200 MHz ^{1}H-NMR δ 0.95 (3 H, t, J = 7.2 Hz, -CH_3), 1.33-1.70 (4 H, m, -CH_2CH_2CH$_3$), 1.95 (1 H, ddd, $J_1 = J_2 = J_3$ = 11.6 Hz, -CHCH_2CH-), 2.47 (1 H, ddd, J = 11.6, 4.4, 3.2 Hz, -CHCH_2CH-), 3.45-3.73 (2 H, m, -OCH_2-), 4.52 (1 H, bs, -NHCH-), 4.59 (1 H, dd, J = 11.6, 3.2 Hz, -CHOBu), 4.65 (1 H, dd, J = 11.6, 4.4 Hz, -NHCH-), 6.46 (1 H, d, J = 8.0 Hz, Ar-H), 7.22-7.45 (6 H, m, Ar-H), 7.62-7.69 (1 H, m, Ar-H); MS *m/e* 306 (M$^+$, 100), 249 (13), 233 (92), 232 (34), 231 (92), 207 (16), 206 (24), 155 (67), 91 (52); HRMS calcd for $C_{20}H_{22}N_2O$ 306.17321, found 306.17352. Anal. calcd for $C_{20}H_{22}N_2O$: C, 78.40; H, 7.24; N, 9.14. Found: C, 78.51; H, 7.21; N, 9.10], and **3c** (0.08 g, 23%), mp = 74-77 °C (from light petroleum / benzene 70:30 v/v).[44]

Reaction of **1c** *with butyl vinyl ether (2 equiv) and DDQ at 25 °C.* **1c** (0.62 g) yielded, after 1.5 h, **16c** (0.05 g, 7%), mp = 143-144 °C (from light petroleum / benzene 70:30 v/v) (lit.[48] mp = 142-143 °C), and 3-(4-cyanophenylamino)-3-phenylpropanal dibutyl acetal (**20c**) (0.18 g, 16%), oil [200 MHz ^{1}H-NMR δ 0.85-1.00 (6 H, m, -CH_3), 1.30-2.20 (10 H, m, -CH_2CH_2CH$_3$ + -CHCH_2CH-), 3.30-3.70 (4 H, m, -OCH_2-), 4.48 (1 H, t, J = 5.2 Hz, -OCHO-), 4.52-4.71 (1 H, m, -NHCH-), 5.72 (1 H, bd, J = 3.5 Hz, -NHCH-), 6.42 (2 H, A part of AA'BB', J = 7.8 Hz, Ar-H), 7.25-7.45 (7 H, m, Ar-H); MS *m/e* 380 (M$^+$, 9), 306 (19), 249 (5), 233 (9), 231 (8), 207 (54), 206 (100), 57 (18); HRMS calcd for $C_{24}H_{32}N_2O_2$ 380.24638, found 380.24730. Anal. calcd for $C_{24}H_{32}N_2O_2$: C, 75.75; H, 8.48; N, 7.36. Found: C, 75.90; H, 8.45; N, 7.33].

Reaction of **1c** *with butyl vinyl ether (10 equiv) and DDQ at 25 °C.* **1c** (0.62 g) gave, after 20 min, **16c** (0.15 g, 22%), mp = 140-142 °C (from light petroleum / benzene 70:30 v/v) (lit.[48] mp = 142-143 °C), and **20c** (0.20 g, 18%), oil (spectroscopic data are identical to those reported for compound **20c** obtained in the above reaction of **1c** with 2 equiv of butyl vinyl ether and DDQ at 25 °C).

Reaction of **1d** *with butyl vinyl ether (1 equiv) and DDQ at 80 °C.* **1d** (0.65 g) afforded, after 5 h of reflux, **5d**,[43] **16d** (0.18 g, 25%), mp = 109-110 °C (from light petroleum / benzene 60:40 v/v) (lit.[49] mp = 110-111 °C), 4-butoxy-6-chloro-2-phenylquinoline (**17d**) (0.03 g, 3%), mp = 91-92 °C (from light petroleum / benzene 50:50 v/v) [200 MHz ^{1}H-NMR δ 0.90 (3 H, t, J = 7.3 Hz, -CH_3), 1.22-1.70 (4 H, m, -CH_2CH_2CH$_3$), 4.27 (2 H, t, J = 4.9 Hz, -OCH_2-), 7.17 (1 H, s, Ar-H), 7.22-7.30 (2 H, m, Ar-H), 7.43-7.57 (2 H, m, Ar-H), 7.63 (1 H, dd, J = 8.6, 2.0 Hz, Ar-H), 8.02-8.13 (2 H, m, Ar-H), 8.18 (1 H, d, J = 2.0 Hz, Ar-H); MS *m/e* 313 (M$^+$ + 2, 21), 311 (M$^+$, 68), 257 (34), 255 (100), 254 (22), 240 (5), 238 (12), 227 (5), 226 (3), 191 (8), 190 (7), 57 (9), 41 (16); HRMS calcd for $C_{19}H_{18}ClNO$ 311.10769, found 311.10795. Anal. calcd for $C_{19}H_{18}ClNO$: C, 73.19; H, 5.82; Cl, 11.37; N, 4.49. Found: C, 73.26; H, 5.80; Cl, 11.35; N, 4.48], and **3d**.[43]

Reaction of **1d** *with butyl vinyl ether (2 equiv) and DDQ at 80 °C.* **1d** (0.65 g) gave, after 10 min of reflux, **16d** (0.24 g, 33%), mp = 110-111 °C (from light petroleum / benzene 60:40 v/v) (lit.[49] mp = 110-111 °C), and **17d** (0.02 g, 2%), mp = 92-93 °C (from light petroleum / benzene 50:50 v/v) (spectroscopic data are identical to those reported for compound **17d** obtained in the above reaction of **1d** with 1 equiv of butyl vinyl ether and DDQ at 80 °C).

Reaction of **1d** *with butyl vinyl ether (10 equiv) and DDQ at 25 °C.* **1d** (0.65 g) afforded, after 10 min, **16d** (0.25 g, 35%), mp = 110-111 °C (from light petroleum / benzene 60:40 v/v) (lit.[49] mp = 110-111 °C), and **17d** (0.03 g, 3%), mp = 90-92 °C (from light petroleum / benzene 50:50 v/v) (spectroscopic data are identical to those reported for compound **17d** obtained in the above reaction of **1d** with 1 equiv of butyl vinyl ether and DDQ at 80 °C).

Reaction of **1e** *with butyl vinyl ether (1 equiv) and DDQ at 80 °C.* **1e** (0.68 g) gave, after 15 h of reflux, **5e** (0.02 g, 3%), mp = 140-141 °C (from light petroleum / benzene 90:10 v/v) (lit.[50] mp = 140 °C), **16e** (0.08 g, 11%), mp = 183-184 °C (from light petroleum / benzene 50:50 v/v) (spectroscopic data are identical to those reported for compound **16e** obtained in the above reaction of **1e** with vinyl acetate), adduct between butyl vinyl ether and DDQ (0.05 g), mp = 110-111 °C (from light petroleum / benzene 50:50 v/v) [200 MHz ^{1}H-NMR δ 0.90 (3 H, t, J = 6.8 Hz), 1.25-1.67 (4 H, m), 3.23 (1 H, dd, J = 17.3, 1.9 Hz), 3.52 (1 H, dd, J = 17.3, 6.0 Hz), 3.63 (1 H, dt, J = 8.8, 5.5 Hz), 3.90 (1 H, dt, J = 8.8, 5.5 Hz), 5.65-5.95 (2 H, bs + dd, J = 6.0, 1.9 Hz); MS *m/e* 305 (M$^+$ + 4, 5), 303 (M$^+$ + 2, 23), 301 (M$^+$, 37), 249 (13), 247 (57), 245 (100), 221 (3), 220 (4), 219 (15), 218 (17), 217 (26), 216 (25), 57 (41), 41 (44); HRMS calcd for $C_{13}H_{13}Cl_2NO_3$ 301.02725, found 301.02861. Anal. calcd for $C_{13}H_{13}Cl_2NO_3$: C, 51.68; H, 4.34; Cl, 23.47; N, 4.64. Found: C, 51.73; H, 4.33; Cl, 23.55; N, 4.62], and **3e** (0.07 g, 17%), mp = 138-141 °C (from light petroleum / benzene 50:50 v/v).[44] The structure of the adduct between butyl vinyl ether and DDQ was not fully investigated.

Reaction of **1e** *with butyl vinyl ether (2 equiv) and DDQ at 80 °C.* **1e** (0.68 g) yielded, after 30 min of reflux, **16e** (0.04 g, 5%), mp = 183-184 °C (from light petroleum / benzene 50:50 v/v) (spectroscopic data are identical to those reported for compound **16e** obtained in the above reaction of **1e** with vinyl acetate), 4-butoxy-1,2,3,4-tetrahydro-6-nitro-2-phenylquinoline (**18e**) (0.16 g, 16%), mp = 163-164 °C (from light petroleum / benzene 50:50 v/v) [200 MHz ^{1}H-NMR δ 0.95 (3 H, t, J = 6.3 Hz, -CH_3), 1.33-1.73 (4 H, m, -CH_2CH_2CH$_3$), 1.99 (1 H, ddd, J_1 = 11.8, J_2 = J_3 = 10.5 Hz, -CHCH_2CH-), 2.51 (1 H, ddd, J = 11.8, 4.2, 2.6 Hz, -CHCH_2CH-), 3.52-3.75 (2 H, m, -OCH_2-), 4.60-4.78 (3 H, m, -NHCH- + -NHCH- + -CHOBu), 6.45 (1 H, d, J = 8.4, Ar-H), 7.30-7.50 (5 H, m, Ar-H), 7.97 (1 H, dd, J = 8.4, 2.5 Hz, Ar-H), 8.30-8.35 (1 H, m, Ar-H) ; MS *m/e* 326 (M$^+$, 100), 269 (12), 253 (70), 251 (72), 207 (24), 206 (18), 205 (13), 175 (46), 91 (42); HRMS calcd for $C_{19}H_{22}N_2O_3$ 326.16304, found 326.16274. Anal. calcd for $C_{19}H_{22}N_2O_3$: C, 69.92; H, 6.79; N, 8.58. Found: C, 70.05; H, 6.76; N, 8.55], and **3e** (0.05 g, 12%), mp = 144-147 °C (from light petroleum / benzene 50:50 v/v).[44]

Reaction of **1e** *with butyl vinyl ether (10 equiv) and DDQ at 25 °C.* **1e** (0.68 g) afforded, after 20 min, 3-(4-nitrophenylamino)-3-phenylpropanal dibutyl acetal (**20e**) (0.13 g, 7%), oil [200 MHz ^{1}H-NMR δ 0.78-0.92 (6 H, m, -CH_3), 1.10-2.15 (10 H, m, -CH_2CH_2CH$_3$ + -CHCH_2CH-), 3.28-3.62 (4 H, m, -OCH_2-), 4.42 (1 H, t, J = 4.9 Hz, -OCHO-), 4.50-4.63 (1 H, m, -NHCH-), 6.00 (1 H, bd, J = 3.7 Hz, -NHCH-), 6.43 (2 H, A part of AA'BB', J = 8.2, Ar-H), 7.20-7.39 (5 H, m, Ar-H), 7.93 (2 H, B part of AA'BB', J = 8.2 Hz, Ar-H); MS *m/e* 400 (M$^+$, 7), 326 (50), 253 (30), 252 (12), 251 (27), 227 (52), 226 (100), 91 (13), 57 (29); HRMS calcd for $C_{23}H_{32}N_2O_4$ 400.23621, found 400.23694. Anal. calcd for $C_{23}H_{32}N_2O_4$: C, 68.97; H, 8.05; N, 6.99. Found: C, 69.09; H, 8.02; N, 6.95], and **18e** (0.16 g, 10%), mp = 161-163 °C (from light petroleum / benzene 50:50 v/v) (spectroscopic data are identical to those reported for compound **18e** obtained in the above reaction of **1e** with 2 equiv of butyl vinyl ether at 80 °C).

Reaction of **1k** *with butyl vinyl ether (2 equiv) and DDQ at 80 °C.* **1k** (0.59 g) gave, after 25 min of reflux, **16k** (0.13 g, 20%), mp = 216-218 °C (from 2-propanol / benzene 50:50 v/v) (lit.[51] mp = 218 °C), and adduct between butyl vinyl ether and DDQ (0.05 g), mp = 99-100 °C (from light petroleum / benzene 50:50 v/v) (spectroscopic data are identical to those previously reported for this compound in the above reaction of **1e** with 1 equiv of butyl vinyl ether and DDQ at 80 °C).

Reactions of **1a**, **1l**, *and* **10f** *with allyltributyltin and DDQ.*

Following the procedures previously described for the other alkenes, a solution of **1a** (0.54 g, 3 mmol), allyltributyltin (1.99 g, 6 mmol), and DDQ (0.76 g, 3.3 mmol) in acetonitrile (20 mL) was refluxed for 3 days. After usual work-up, starting material was obtained (~ 40%) together with N-(4-phenyl-1-buten-4-yl)benzenamine (**23a**) (0.18 g, 27%), oil [60 MHz ^{1}H-NMR δ 2.30-2.63 (2 H, m, CH$_2$=CH-CH_2-), 4.00 (1 H, bs, -NH-), 4.28 (1 H, dd, J = 6.0, 7.0 Hz, -NHCHCH$_2$-), 4.83-5.25 (2 H, m, CH_2=CH-CH$_2$-), 5.35-6.03 (1 H, m, CH$_2$=CH-CH$_2$-), 6.23-6.68 (3 H, m, Ar-H), 6.78-7.40 (7 H, m, Ar-H); MS *m/e* 223 (M$^+$, 4), 182 (100), 104 (14), 91 (6), 77 (28); HRMS calcd for $C_{16}H_{17}N$ 223.13610, found 223.13625. Anal. calcd for $C_{16}H_{17}N$: C, 86.06; H, 7.67; N, 6.27. Found: C, 86.12; H, 7.64; N, 6.24].

Reaction mixtures of **1l** and **10f** were refluxed for 5 days; after work-up, GC-MS analyses showed starting material (~ 50% and 70%, respectively), N-(4-phenyl-1-buten-4-yl)-4-bromobenzenamine (**23l**) (from **1l**) [MS *m/e* 303 (M$^+$ + 2, 5), 301 (M$^+$, 5), 262 (98), 260 (100), 184 (15), 182 (15), 157(12), 155 (11), 91 (8), 77 (19)], and N-(4-phenyl-1-buten-4-yl)-2-iodobenzenamine (**23f**) (from **10f**) [MS *m/e* 349 (M$^+$, 5), 308 (100), 230 (8), 180 (25), 104 (15), 91 (17), 77 (8)]. In both examples, compounds arising by loss of halogen from starting material or/and from reaction products were not detected at all.

Spectral data and melting points[52] *of solid adducts deriving from imines* **1a-i** *and DDQ.*

1a: mp = 241-243 °C; MS *m/e* 411 (M$^+$ + 4, 13), 410 (M$^+$ + 3, 18), 409 (M$^+$ + 2, 68), 408 (M$^+$ + 1, 43), 407 (M$^+$, 100), 406 (29), 196 (25),[53] 179 (8), 167 (5), 77 (8), 76 (8); HRMS calcd for $C_{21}H_{11}Cl_2N_3O_2$

407.02283, found 407.02388; IR υ_{max} (KBr) 3215 (b), 2254, 2234, 1624, 1497, 1441, 1427, 1345, 1200, and 1186 cm^{-1}. Anal. calcd for $C_{21}H_{11}Cl_2N_3O_2$: C, 61.78; H, 2.72; Cl, 17.37; N, 10.29. Found: C, 60.90; H, 2.76; Cl, 17.45; N, 10.36.

1b: mp = 152-155 °C (dec. at T > 180 °C); MS (scan 75) *m/e* 211 (100),[54] 210 (12), 196 (93), 167 (22), 77 (11), 64 (9), 63 (10); MS (scan 98) (spectrum of $DDQH_2$) *m/e* 232 (7), 230 (66), 228 (100), 204 (9), 202 (35), 200 (55), 110 (33), 87 (51), 77 (24). Anal. calcd for $C_{22}H_{13}Cl_2N_3O_3$: C, 60.29; H, 2.99; Cl, 16.18; N, 9.59. Found: C, 59.97; H, 3.06; Cl, 16.23; N, 9.66.

1c: MS (scan 23) *m/e* 206 (100),[54] 205 (88), 129 (10), 102 (33), 77 (8); scan 35 corresponded to the mass spectrum of $DDQH_2$. Anal. calcd for $C_{22}H_{10}Cl_2N_4O_2$: C, 60.99; H, 2.33; Cl, 16.37; N, 12.93. Found: C, 60.10; H, 2.40; Cl, 16.46; N, 13.01.

1d: mp = 180-190 °C (dec. at T > 210 °C); MS (scan 25) *m/e* 217 (32), 216 (35), 215 (100),[54] 214 (71), 140 (4), 138 (12), 113 (10), 111 (29), 75 (20); MS (scan 40) *m/e* 421 (38), 419 (25), 417 (100), 386 (6), 384 (38), 382 (63), 203 (18), 174 (54), 111 (38), 75 (28); IR υ_{max} (KBr) 3437 (b), 3217, 3053, 2218, 1663, 1542, and 1484 cm^{-1}. Anal. calcd for $C_{21}H_{10}Cl_3N_3O_2$: C, 56.98; H, 2.28; Cl, 24.03; N, 9.49. Found: C, 56.25; H, 2.31; Cl, 24.15; N, 9.57.

1e: MS (scan 34) *m/e* 226 (100),[54] 225 (31), 196 (16), 180 (11), 179 (18), 152 (13), 76 (27); scan 50 corresponded to the mass spectrum of $DDQH_2$. Anal. calcd for $C_{21}H_{10}Cl_2N_4O_4$: C, 55.65; H, 2.22; Cl, 15.64; N, 12.36. Found: C, 54.97; H, 2.24; Cl, 15.70; N, 12.43.

1f: mp > 350 °C; MS *m/e* 441 (M^+ + 4, 1), 439 (M^+ + 2, 4), 437 (M^+, 6), 227 (6), 226 (7), 136 (12), 135 (13), 133 (12), 92 (7), 90 (9), 64 (18), 51 (13), 36 (100); HRMS calcd for $C_{22}H_{13}Cl_2N_3O_3$ 437.03340, found 437.03397. Anal. calcd for $C_{22}H_{13}Cl_2N_3O_3$: C, 60.29; H, 2.99; Cl, 16.18; N, 9.59. Found: C, 59.92; H, 3.03; Cl, 16.24; N, 9.67.

1g: mp = 225-229 °C; MS *m/e* 436 (M^+ + 4, 8), 434 (M^+ + 2, 42), 432 (M^+, 54), 321 (6), 319 (12), 221 (15), 36 (100); HRMS calcd for $C_{22}H_{10}Cl_2N_4O_2$ 432.01808, found 432.01843. Anal. calcd for $C_{22}H_{10}Cl_2N_4O_2$: C, 60.99; H, 2.33; Cl, 16.37; N, 12.93. Found: C, 60.15; H, 2.39; Cl, 16.48; N, 13.02.

1h: mp > 350 °C; MS *m/e* 445 (M^+ + 4, 19), 443 (M^+ + 2, 46), 441 (M^+, 57), 321 (52), 319 (68), 230 (14), 108 (80), 36 (100); HRMS calcd for $C_{21}H_{10}Cl_3N_3O_2$ 440.98386, found 440.98412; IR υ_{max} (KBr) 3237, 2257, 2235, 1622, 1498, 1441, 1428, 1340, 1202, and 1186 cm^{-1}. Anal. calcd for $C_{21}H_{10}Cl_3N_3O_2$: C, 56.98; H, 2.28; Cl, 24.03; N, 9.49. Found: C, 56.20; H, 2.35; Cl, 24.18; N, 9.60.

1i: mp = 203-206 °C; no reliable mass spectrum was recorded. Anal. calcd for $C_{21}H_{10}Cl_2N_4O_4$: C, 55.65; H, 2.22; Cl, 15.64; N, 12.36. Found: C, 54.92; H, 2.26; Cl, 15.72; N, 12.45.

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16. Commercial anhydrous acetonitrile (Aldrich Chemie, H_2O < 0.005%) was used without further purification. Solvents containing higher amounts of water significantly lowered the yields of products because of partial hydrolysis of the starting imine; this behaviour was also observed with electrochemically-generated imine radical cations (see ref. 12b).
17. Mixing of imines and DDQ in acetonitrile produced immediately a brown-red solution, which turned to greenish in a few minutes.
18. In the absence of this work-up no product could be isolated by chromatography; bubbling of ammonia can be replaced by treatment with an aqueous solution of sodium hydroxide and extraction with diethyl ether: anyhow, the first procedure is faster and simpler.
19. DDQ is responsible for the loss of butanol from positions 3 and 4, as **18c** is rapidly converted to **16c** (30 min) when refluxed in acetonitrile in the presence of 2 equiv of quinone; in the absence of DDQ, **18c** remained unchanged.
20. a) Batyaev, I. M.; Gertman, G. A. *Deposited Doc.* **1977**, VINITI, 4488 (*Chem. Abs.* **1979**, *91*, 139920x). b) Al-Ghabsha, T. S.; Azzouz, A. S.; Hassan, Y. I. *Microchem. J.* **1986**, *33*, 389-391 (charge-transfer complexes between chloranil and aromatic aldoximes). c) It is also worth pointing out that a preliminary EPR experiment performed on an acetonitrile solution of **1a** and DDQ showed the strong and clear 5-lines signal of DDQ radical anion.
21. A carbocation can attack the oxygen atom of enol ethers, as proved by the reaction of N-phenylbenzimidoyl cation, obtained from Ph-N=C(Cl)Ph and $SnCl_4$, with butyl vinyl ether, affording Ph-N=C(OBu)Ph. This result gives also additional support to the non-intervention of imidoyl cations in DDQ-mediated annulations. The comparison between the reactions of the imine-DDQ complexes (attacking the C=C double bond of butyl vinyl ether) and the corresponding imidoyl cations (reacting to the oxygen atom of the same alkene) can be considered a further example of *umpolung*.

22. These compounds have very high melting points and are insoluble in the most common organic solvents. In acetone they dissolve to give products arising from hydrolysis of the starting imine. X-ray analyses were not successful because of their amorphous or unsuitable crystalline structures. With the solid from imine **1i**, we were also unable to record a reliable mass spectrum.
23. These spectra depended on the temperature of the ion source and, above 300 °C, peaks due to $DDQH_2$ were detected as well. The peak corresponding to molecular ion of the starting imine was the most important and persistent feature of the spectrum of all these compounds. It is worth pointing out that elemental analyses of all compounds derived from imines **1a-i** are consistent with adducts of imine and DDQ in a 1:1 ratio.
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52. Melting points refer to the solid compounds precipitated from the acetonitrile solution of imine and DDQ and not recrystallized. For some products, we were unable to record their melting points because the interval of fusion was not clearly defined.
53. Loss of 211 (2,3-dichloro-5,6-dicyano-4-hydroxyphenyl) from molecular ion (B/E analysis).
54. Molecular weight of the starting imine.