Multistep Reversible Redox Systems, LXIII[◇]

2,5-Disubstituted *N,N′*-Dicyanoquinone Diimines (DCNQIs) – Syntheses, and Redox Properties

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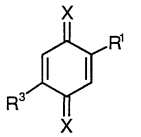
Quinones **1a**–**q** and DCNQIs **2a**–**g** have been synthesized in order to investigate substituent effects. It was necessary to employ novel synthetic routes for the introduction of iodine into **1f** (**7**), the trifluoromethyl group into **1g**–**i**, deuterium into **1m**–**p**, and especially for the chloride/fluoride exchange of **1j** to **1k**, and **1l**. With few exceptions both **1** and **2** undergo reversible electron transfer in two steps including thermodynamically very stable radical cations (lg K_{SEM} > 10, cyclic voltammetry). Linear correlations have been found between E_2 (OX/SEM) data of **1** and **2** with $(\sigma_m + \sigma_p)/2$ and between E_2 of **1** and **2**. Correlations have also been found between E_2 and the LUMO energies of **1** and **2**. The crystal structure of quinone **1i** shows some special interactions due to the two CF_3 groups, whereas the structures of DCNQIs **2d** and **2g** link up with those evaluated earlier.

Within the series of new quinoid derivatives[5] 2,5-disubstituted *N,N′*-dicyano-1,4-benzoquinone diimines **2** (DCNQIs) have gained special importance due to the exceptional conducting properties of their radical anion salts[6]. In addition to the derivatives already reported[5] we now describe syntheses and properties of DCNQIs **2**, together with, where necessary, their precursors, quinones **1** (Scheme 1). The charge-transfer (CT) complexes and radical anion salts derived from these DCNQIs will also be presented.

Scheme 1

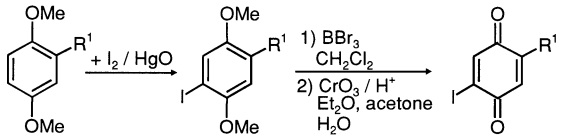


1 : X = O
2 : X = N–CN

	R^1	R^3
a	Cl	I
b	Br	I
c	I	I
d	Cl	OMe
e	Br	OMe
f	I	OMe
g	CH_3	CF_3
h	OMe	CF_3
i	CF_3	CF_3

	R^1	R^3
j	CH_2Cl	CH_2Cl
k	CH_2Cl	CH_2F
l	CH_2F	CH_2F
m	CH_3 2D	CH_3
n	CH_3	CD_3
o	CD_3	CD_3
p	CD_3 2D	CD_3
q	CH_3 $=N^{13}CN$	CH_3

Scheme 2



	R^1	%	%
a	Cl	52	83
b	Br	29	91
c	I	48	79

Syntheses of Haloquinones 1a–f

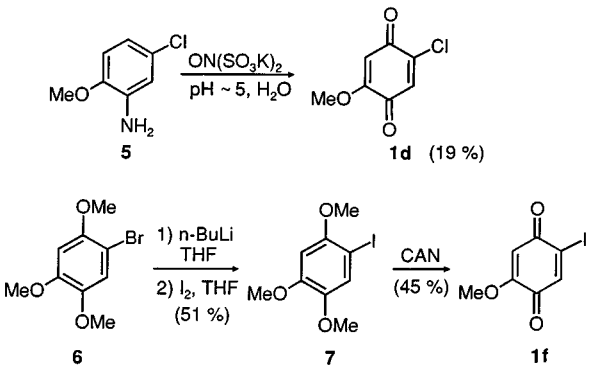
Iodonation of the substituted 1,4-dimethoxybenzenes **3a**–**c**, using the well-established reagent iodine/mercury oxide[7] yielded the expected dihalogenated derivatives **4a**–**c** in reasonable yields. Quantitative demethylation of **4a**–**c** with subsequent oxidation then afforded the expected quinones **1a**–**c** in high purity and yield (Scheme 2). The use of a superior iodination reagent, benzyltriethylammonium dichloroiodate (BTMA-ICl_2), has recently been reported[8]. Although a yield of 90% of **1c** from 1,4-dimethoxybenzene in acetic acid was originally reported, we were unable to reproduce these results (ca. 59% yield) , however, isolated 79% of **1c** using dichloromethane as the solvent.

The halogen/methoxy-substituted quinones **1d**[9] and **1e**[10] have already been described. However, we replaced the cumbersome route to **1d**[9] by a simple one-step approach from the inexpensive amine **5**. The yield was rather low, but this was compensated by the high purity of **1d** (no isomers, Scheme 3).

[◇] Part LXII: Ref.[1].

  1434–193X/98/0202–0335 $ 17.50+.50/0

Scheme 3



Direct iodination of 1,2,4-trimethoxybenzene by both of the methods discussed above was not successful. It is already known[11] that consecutive formation of the corresponding biphenyl derivative prevails. A convenient alternative is based on halogen exchange **6** → **7** and direct oxidative demethylation[12] of **7** to quinone **1f** (Scheme 3).

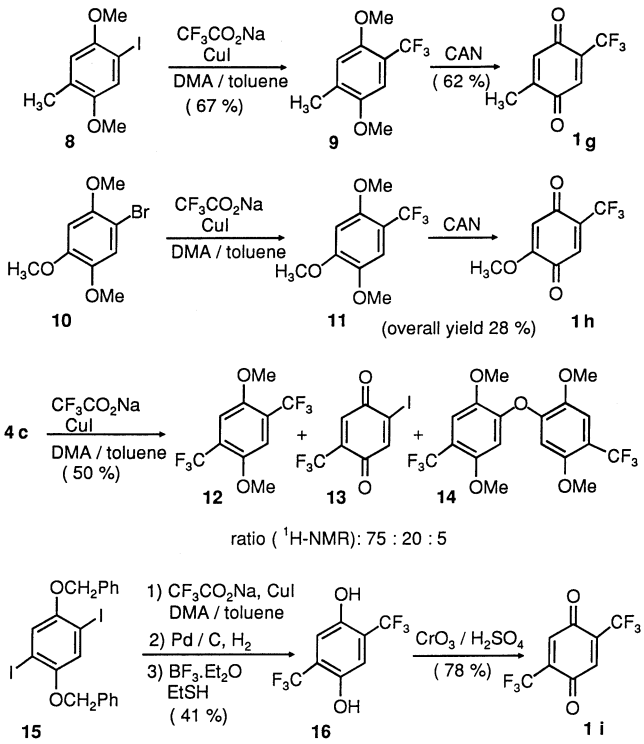
Syntheses of Trifluoromethyl-Substituted Quinones 1g−i

The synthesis of quinones **1g−i** requires appropriate aromatic precursors carrying one or two trifluoromethyl groups. For these precursors two general routes[13] have to be considered: (a) Transformation of a CX_3 (X = Cl, SMe) group into CF_3 by e.g. SF_4 or ET_2NSF_3 (DAST). Since this approach requires rather unusual starting materials this route was excluded. (b) Introduction of the CF_3 group into the aromatic ring by *ipso* substitution of haloaromatics using (trifluoromethyl)copper. This short-lived intermediate may be produced either from gaseous CF_3I (using an autoclave) and copper, or more conveniently[14] from CF_3CO_2Na/CuI by decarboxylation. We found the latter procedure to be suited for our purpose (Scheme 4).

Starting from **8**, substitution to **9** occurs rather smoothly, as does oxidation of **9** to **1g**. The complications associated with **7** (vide supra) mean that use of the bromoderivative **10** is advisable for the introduction of the trifluoromethyl group. The expected product **11** could indeed be isolated and easily oxidized to **1h**. However, in the first step (**10** → **11**) a complex reaction mixture (57%) was formed which contained besides **11** (65%), the starting material (16%), the halogen exchange product **8** (10%) and the corresponding diphenyl derivative (5%). From these results it is not surprising that trifluoromethylation of 2,5-diodo-1,4-dimethoxybenzene (**4c**) affords a mixture of **12**, **13**, and **14**.

Unfortunately, demethylation of **12** either using boron tribromide or by oxidative cleavage with Ce^{IV} is not possible. Substituting **4c** by the corresponding dibenzyl ether **15** paves the way to hydroquinone **16** and quinone **1i**. However, debenzylation does not proceed by catalytic hydrogenation although this procedure does remove impurities (dehalogenation) of the crude product. Instead, the benzylic protecting groups **15** are smoothly cleaved to hydroquinone **16** by the established reagent $EtSH/Et_2OBF_3$[15].

Scheme 4

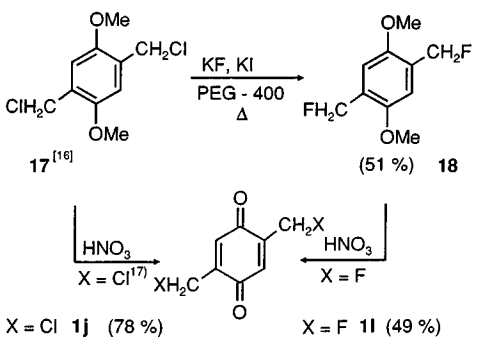


Synthesis of Halomethyl Quinones 1j and 1l

The methoxy group in **1** and **2** is the only substituent without rotational symmetry that fits into the general crystal lattice $I_{4a/a}$ of the radical anion salts of **2**[6]. However, a $-CH_2F$ group, which may be introduced via $-CH_2Cl$, may also yield radical anion salts of **2** with the same crystal structure.

The easily accessible bis(chloromethylated) 1,4-dimethoxybenzene **17**[16] is smoothly oxidized to quinone **1j**[17]. For the preparation of **1l** we therefore chose to synthesise **18** by exchange of the chlorine in **17** by fluorine. Of the several reported methods for this halogen exchange treatment of **17** potassium fluoride in polyethylene glycol in the presence of potassium iodide[18] worked best (Scheme 5). Oxidation of **18** affords the expected quinone **1l** in an equivalent process to **17**.

Scheme 5

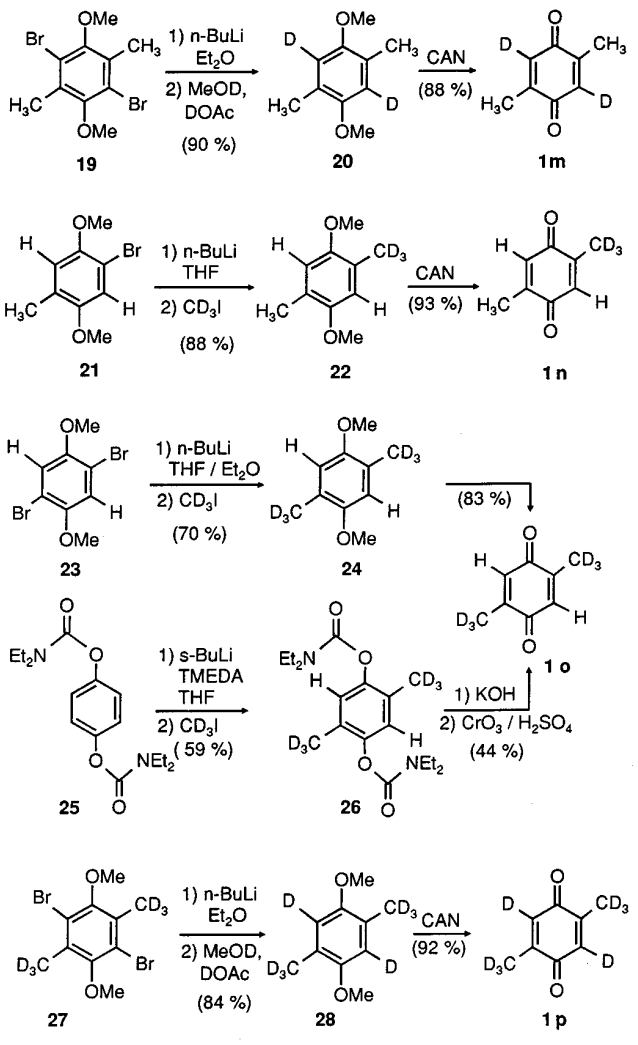


Syntheses of Quinones 1m−q Labelled with Isotopes

Deuterated quinones **1m−p** are important precursors for the production of DCNQI copper salts which have unique properties[6][19]. Inspired by these results, all possible isomers of deuterated 2,5-dimethylbenzoquinone-1,4 have recently been prepared, albeit by a different approach[20].

According to Scheme 6 the most reliable method for introducing either deuterium (> 95%) or CD_3 groups (via ICD_3) into aromatic rings is halogen/lithium exchange which works smoothly not only for **21** and **23** but also for the persubstituted derivatives **19** and **27**[21]. Dilithiation of e.g. **25**[22] is less rapid and resulted only in 85% deuteration of **26**. Hydrolysis of e.g. **26** is also rather difficult to achieve (cf. ref.[23]).

Scheme 6

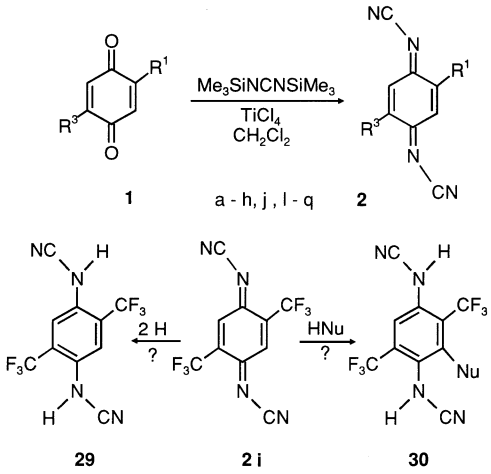


Oxidative cleavage of the hydroquinone dimethyl ethers **20**, **22**, **24**, and **28** afforded the corresponding quinones **1j−m** in high yield. The amount of deuterium in the reagent CD_3I (> 99.5%) is fully transferred to the products (MS). The dideuterated quinone **1m** has already been prepared from perdeuterated *p*-xylene using deuterated reagents in all steps[24].

Syntheses of DCNQIs 2a−q

According to our general procedure[5] outlined in Scheme 7 quinones **1a−h**, **1j** and **1l−q** are smoothly transformed into the corresponding DCNQIs **2**.

Scheme 7



Difficulties are only observed with the rather sensitive **2i** [ν(C≡N) = 2180 cm^{-1}, ν(C=N) = 1555 cm^{-1}] which is contaminated with either the reduction product *N,N′*-dicyano-1,4-diaminobenzene **29** or the 1,4-addition product **30** [ν(C≡N) = 2255 cm^{-1}, ν(C=N) = 1525 cm^{-1}, cf. ref.[25]]. Even after careful recrystallization, **2i** (16%) still contains some of these impurities. The very low energy LUMO of **2i** (vide infra) points to both the strong reducibility and nucleophilicity of **2i**.

DCNQI **2q** was prepared from 2,5-dimethyl-1,4-benzoquinone by the same route (70%) except that ^{13}C-enriched bis(trimethylsilyl)carbodiimide was employed. The latter is easily accessible by the established route[26] from ^{13}C-cyanamide. Although the published preparation for this reagent[27] could not be reproduced[28], reaction of ^{13}C-bromocyan with ammonia in ethanol starting from −78 °C afforded a nearly quantitative yield of ^{13}C-cyanamide.

Redox Properties of Quinones 1 and DCNQI 2

In an extension of earlier work[6] both quinones **1** and DCNQIs **2** were studied using cyclic voltammetry under the same conditions. According to Scheme 8, two reversible one-electron transfers at E_2 and E_1 are expected. This ideal behavior is followed by nearly all quinones **1** and DCNQIs **2**, including the highly sensitive **2i** (R^1, R^3 = CF_3) as exemplified by Figure 1.

However, in accordance with earlier results[5], the second reduction step of quinones **1** is not fully reversible, probably due to aggregational effects. Therefore, in Table 1, where all relevant data are collected, only approximated semiquinone formation constants K_{SEM} are given.

Obviously, R^1/R^3 = CH_2Cl and CH_2F cause decomposition on introduction of the second electron into $\mathbf{2j}_{SEM}$. This is especially true for semiquinone radical anions of **1j** and **1l** where the working electrode (Pt) is already blocked

Scheme 8

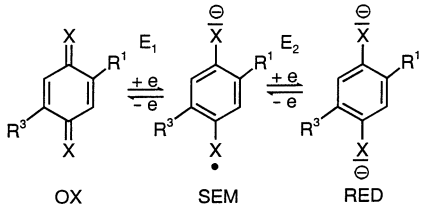
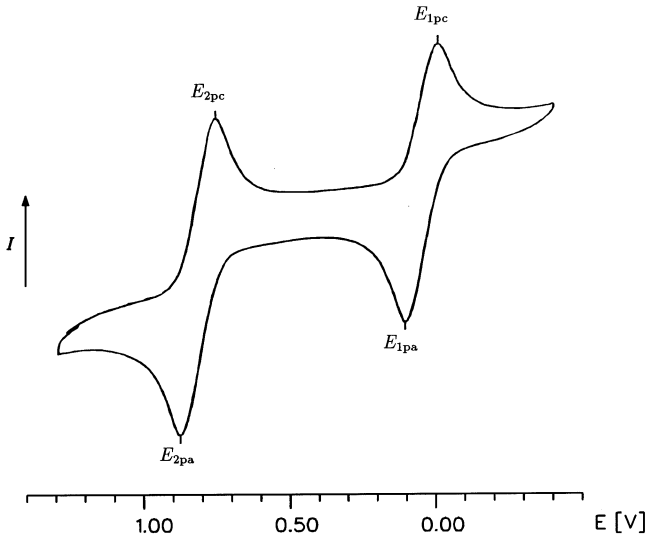
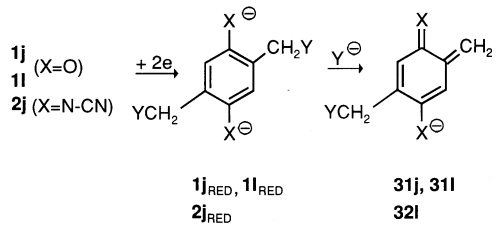


Figure 1. Cyclovoltammogram of DCNQI **2i** (R^1, R^3 = CF_3) in CH_2Cl_2 versus Ag/AgCl/CH_3CN; $nBu_4N^+BF_4^-$, scan rate 100 mV/s (ferrocene = 539 mV)



after only one scan. It seems probable from Scheme 9 that a halide ion is expelled from $\mathbf{1j}_{RED}$, $\mathbf{1l}_{RED}$ and $\mathbf{2j}_{RED}$.

Scheme 9



1,2-Quinonemethides **31j** and **31l** or the 1,2-quinoneimines **32l** are formed in this way. Both classes of compounds are highly reactive (dimerization, polymerization etc.[29]). In $\mathbf{1}_{RED}$ with X = $-O^-$ the negative charge is better available for the extraction of Y^- than with X = $-N-CN^-$. Therefore quinones **1j** and **1l** are expected to decompose more readily than DCNQIs **2j** (or **2l**) on reduction. Furthermore, fluoride is a much worse leaving group than chloride, especially in aprotic solvents. This is consistent with the relative decomposition rates $\mathbf{1}_{RED}$ > $\mathbf{1l}_{RED}$ and $\mathbf{2j}_{RED}$ >> **2l**, although even the latter shows strongly diminished concentration in the second reduction wave.

In full accord with earlier observations[5][6], K_{SEM} values of the DCNQIs **2** are smaller by a factor of approximately

Table 1. Potentials E_1 and E_2 from cyclovoltammograms of quinones **1** and DCNQIs **2** in CH_2Cl_2 versus Ag/AgCl/MeCN, $nBu_4N^+BF_4^-$; n = number of formally transferred electrons, log K_{SEM} = semiquinone formation constant (ferrocene = 539 mV)

1	R^1/R^2	E_2 [V]	n	E_1 [V][a]	n	lg K_{SEM}
a	Cl/I	+0.01	0.56	−0.74	0.45	≈13
b	Br/I	+0.03	0.37	−0.77	0.30	≈14
c	I/I	+0.02	0.43	−0.77	0.25	≈13
d	Cl/MeO	−0.25	0.9	−1.01	0.21	≈13
e	Br/MeO	−0.22	0.33	−1.06	0.16	≈14
f	I/OCH_3	−0.25	0.59	−1.01	0.27	≈14
g	CF_3/CH_3	−0.13	0.47	−0.97	0.19	≈15
h	CF_3/OCH_3	−0.13	0.66	−1.00	0.30	≈15
i	CF_3/CF_3	+0.23	0.35	−0.68	0.18	≈15
j[b]	CH_2Cl/CH_2Cl	−0.36[c]	0.42	irr.	–	–
l[b]	CH_2F/CH_2F	−0.31	0.50	irr.	–	–

2	R^1/R^3	E_2 [V]	n	E_1 [V]	n	lg K_{SEM}
a	Cl/I	+0.64	0.59	+0.01	0.59	10.7
b	Br/I	+0.65	0.54	+0.02	0.56	10.7
c	I/I	+0.63	0.74	±0.00	0.84	10.7
d	Cl/MeO	+0.43	0.74	−0.19	0.84	10.5
e	Br/MeO	+0.44	0.33	−0.20	0.54	10.9
f	I/OCH_3	+0.40	0.74	−0.20	0.74	10.2
g	CF_3/CH_3	+0.55	0.74	−0.14	0.74	11.6
h	CF_3/OCH_3	+0.53	0.74	−0.15	0.74	11.4
i	CF_3/CF_3	+0.83	0.79	+0.06	0.79	13.1
j[b]	CH_2Cl/Cl_2Cl	+0.35	0.91	irr.	–	–
l[b]	CH_2F/CH_2F	+0.33	0.98	+0.35	0.42	11.5

[a] Quasi reversible. – [b] In MeCN. – [c] Not fully reversible.

10^3 compared to the K_{SEM} values of the corresponding quinones **1**. These differences are probably mainly due to smaller Coulomb repulsions in the more extended DCNQI π-systems. It has already beeen demonstrated[30] that the Coulomb integral J_{mm} of the two electrons in the HOMO of the reduced form is basically responsible for ΔH_R of the equilibrium OX + RED ⇌ 2 SEM. A quantitative correlation between J_{mm} from SCF calculations and log K_{SEM} from CV data has already been derived for other two-step redox systems[31].

Figure 2 demonstrates an excellent linear correlation (r = 0.993) between E_2 (quinone) and E_2 (DCNQI) for **1a–o** and **2a–o** together with all corresponding derivatives published so far.

The gradient a = 0.82 indicates that the differences for the first reduction potentials (E_2) become smaller with increasing acceptor strength of the substrates. This substituent effect may either originate from differing solvation energies of OX and SEM ($\Delta\Delta G_{solv}$) or from the differing electron affinities. Since experimental data are not available for the latter, Koopman's electron affinities ($-\varepsilon_{LUMO}$ [eV]) were calculated. In Figure 3 these data are correlated with the corresponding E_2 potentials.

The two linear correlations shown in Figure 3 are both very good. The gradients differ by 0.08 mV/eV and demonstrate again the weaker substituent effect with increasing electron affinities. In the region where the two curves nearly meet (at 2.2–2.3 eV) their difference amounts to only 0.05 V, well within the limits of error for these semiempirical

Figure 2. Correlation of the potentials E_2 (quinone) and E_2 (DCNQI) for **1a**−**o** and **2a**−**o** (□) together with those of all other 2,5-disubstituted derivatives (O) published

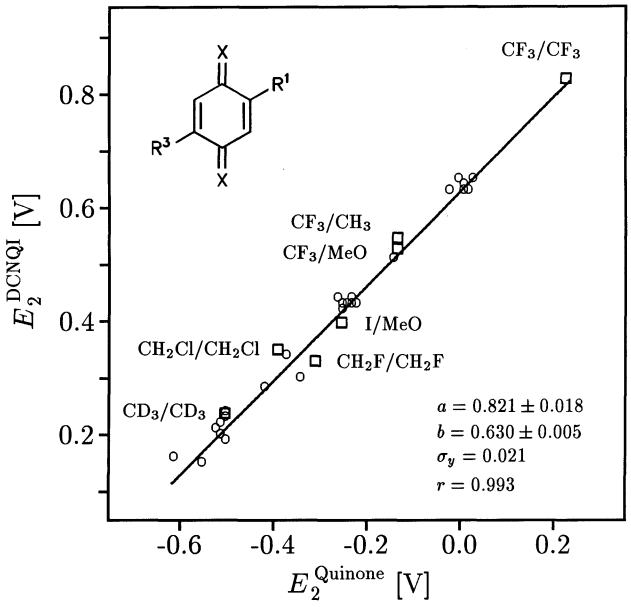
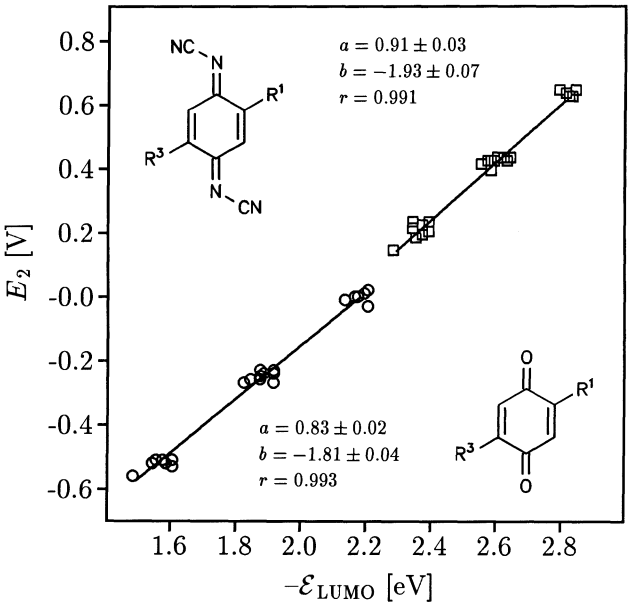


Figure 3. Correlation of the potentials E_2 (23 quinones and DCNQIs) with Koopman's electron affinities (negative LUMO energies) calculated with the AM1 program



correlations. From these results different solvation energies for the systems under discussion become very improbable, leaving intrinsic (electronic) factors as the most plausible reason for the observed effects. As already demonstrated there exists a linear correlation between the first reduction potentials E_2 of disubstituted quinones together with their DCNQI derivatives and $(\sigma_m + \sigma_p)/2$[32]. The results presented in this paper are collected in Figure 4 and 5 and complement this previously published data.

An excellent correlation is obtained again even for such extreme electron attracting substituents as CF_3/CF_3.

Figure 4. Plot of the first reduction potentials E_2 of 2,5-disubstituted quinones versus the Hammett parameter $(\sigma_m + \sigma_p)/2$; (○) former data[6], (□) data from this paper, (◇) excluded from the calculated correlation

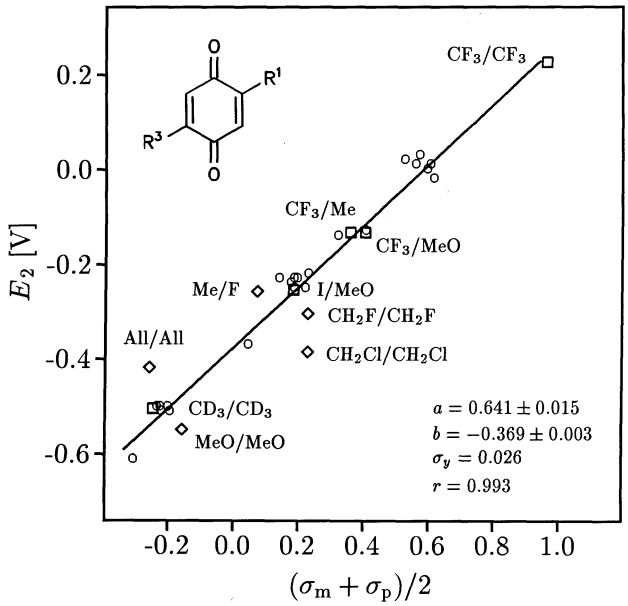
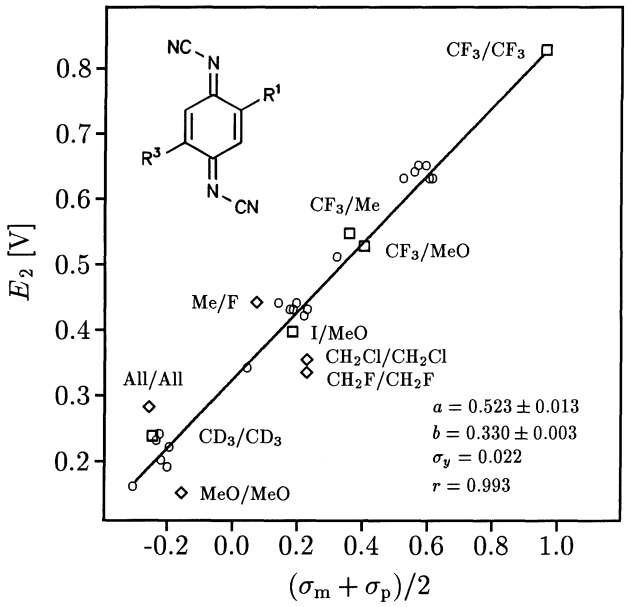
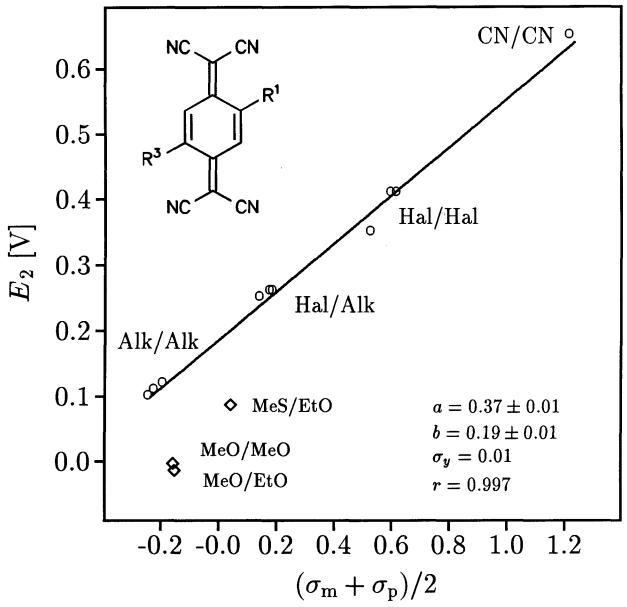


Figure 5. Plot of the first reduction potentials E_2 of the corresponding DCNQIs versus the Hammett parameter $(\sigma_m + \sigma_p)/2$; (○) former data[6], (□) data from this paper, (◇) excluded from the calculated correlation



On the other hand stronger deviations are observed for the combinations CH_3/F, allyl/allyl, MeS/MeS, MeO/MeO which had to be excluded from the correlation $E_2 = a\,(\sigma_m + \sigma_p)/2 + b$ to obtain $r = 0.993$. With the exception of CH_3/F, the deviating substituents are bent and may prefer to adopt different conformations in OX and SEM as suggested by AM1 calculations[3]. The dependence upon the

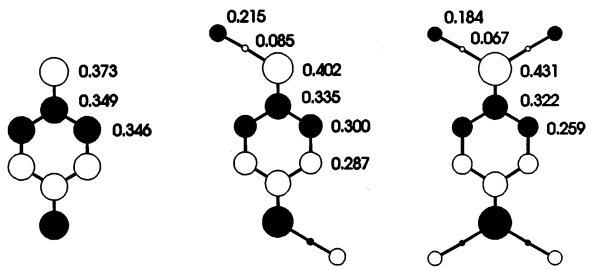
Figure 6. Plot of the first reduction potentials E_2 of TCNQs[32] versus the Hammett parameter $(\sigma_m + \sigma_p)/2$; (◇) excluded from the calculated correlation



parameter $(\sigma_m + \sigma_p)/2$ implies that σ_m and σ_p affect the potentials with the same weight, independent of the nature of the substituents. This will, however, obviously not be the case if the differences of σ_m and σ_p become large (e.g. OMe).

In general the substituent effects are stronger in quinones than in the corresponding DCNQIs as can be derived from the steeper gradient in Figure 4. In 2,5-disubstituted TCNQs[32] the substituent effects are definitely even smaller (a = 0.37, Figure 6). The order of this sensitivity to substituent effects can be derived from the LUMO orbital coefficients in positions 2(5) of 1,4-benzoquinone, DCNQI and TCNQ (Figure 7). In connection with the extension of the π-system these coefficients decrease appreciably in the above mentioned order.

Figure 7. Orbital coefficients of the LUMOs of 1,4-benzoquinone (left), DCNQI (center) and TCNQ (right) according to AM1 calculations



Semiempirical Calculations for Some DQNQIs

In connection with earlier MO calculations for 2,5-disubstituted DCNQIs[33], AM1 calculations were performed for five of the newly snythesized DCNQIs. The newly implemented program package MOPAC 6.0 now contains AM1 parameters for halogens as well as a localization algorithm by which the canonical molecular orbitals can be transformed into a set of localized orbitals. In this way, the σ-orbitals of the nitrile nitrogen atoms may be safely identified. Two orbitals, σ n^1 and σ n^2, are found which are nearly colinear with the two nitrile groups in a DCNQI molecule. The relevant data are collected in Table 2.

Table 2. Data from AM1 calculations of 2,5-disubstituted DCNQIs (R^1, R^3) for OX and SEM (radical anion). Orbital energies for LUMO, HOMO, σ-n [eV]; charge densities at the nitrile and imino nitrogen atoms (q_N)

	R^1/R^3	CD_3/CD_3	I/OCH_3	CF_3/OCH_3	CF_3/CH_3	CF_3/CF_3
OX	ε_{LUMO}	−2.40	−2.59	−2.83	−2.88	−3.31
	$\varepsilon_{\sigma n1}$	−22.03	−22.02	−22.46	−22.41	−22.62
	$\varepsilon_{\sigma n2}$	−22.03	−22.28	−22.15	−22.24	−22.62
	q_N (C≡N) × 10^3 [a]	−29.5	−21.1	−10.0	−7.4	+14.4
	q_N (=N<) × 10^3 [a]	−70.2	−44.5	−30.9	−45.4	−20.7
SEM	ε_{HSOMO}	−0.89	−1.15	−1.36	−1.36	−1.78
	$\varepsilon_{\sigma n1}$	−17.92	−18.12	−18.28	−18.28	−18.57
	$\varepsilon_{\sigma n2}$	−17.92	−18.13	−18.27	−18.25	−18.57
	q_N (C≡N) × 10^3 [a]	−209	−194	−183	−184	−160
	q_N (=N<) × 10^3 [a]	−235	−206	−200	−213	−193

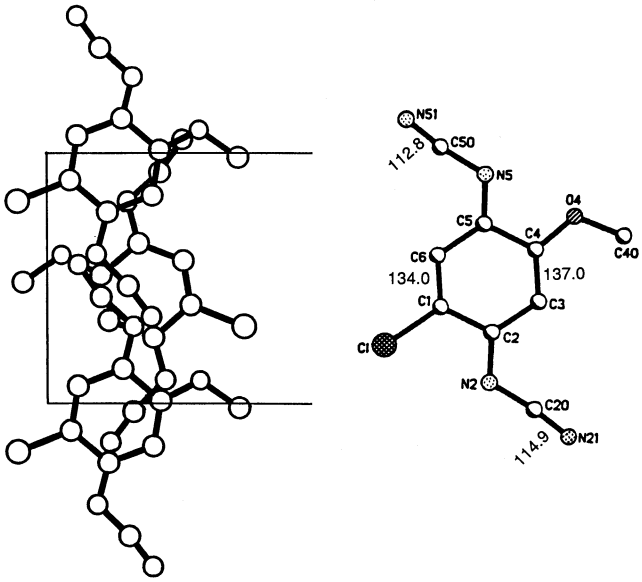
As expected, the data for **2o** (CD_3/CD_3) coincide with those for **2m** (CH_3/CH_3)[33]. The electron-withdrawing effect of the other substituents is reflected in lower HOMO, SOMO and σ-n energies for both OX and SEM. With two CF_3 groups (**2i**) the partial charge q_N at the nitrile groups even becomes positive. From these calculations the first reduction potentials E_2 were estimated to be 0.63 V (**2h**; OCH_3/CF_3), the highest potential so far observed for 2,5-disubstituted DCNQIs. These potentials are in very good agreement with the experimental ones given in Table 1.

Some Crystal Structures of Quinoid Compounds

We concentrated on the X-ray analysis of **2d**, **1c** and **2g** because of our interest in the arrangement of the bent methoxy group and the structural effect of the rather bulky trifluoromethyl group.

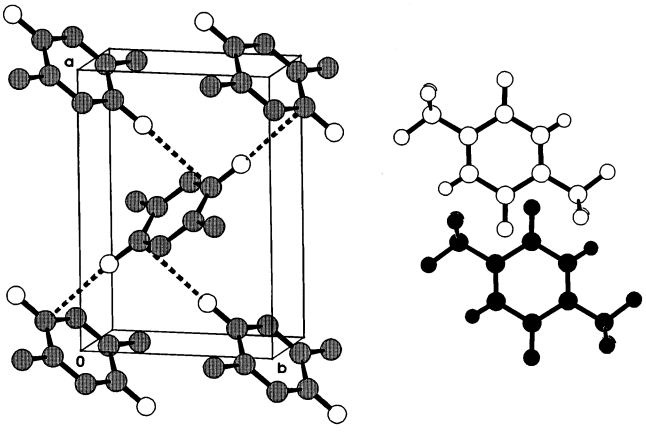
(a) *2-Chloro-N,N′-dicyano-5-methoxy-1,4-benzoquinone Diimine* (**2d**): The crystals of DCNQI **2d** belong to the space group *Cc* in which the molecules are arranged parallel to the *b,c* plane of the unit cell, the next higher molecule thereby always being placed with its cyano group above the ring of the lower one (Figure 8, left). The molecular geometry of **2d** is presented in Figure 8, right. Bond lengths and angles compare well with those of the unsubstituted DCNQI[34] and its 2,5-dimethyl derivative[28]. However, in **2d** the C3−C4 bond is elongated by 3 pm due to the 5-methoxy group which even stretches the nitrile bond (C20−N21) by 2 pm. The deviation of the two N−CN groups from linearity by 8° corresponds to those in other DCNQIs[28][34] and indicates slight deviations from the ideal sp^3 and sp^2 hybridizations, respectively.

Figure 8. Left: 2-Cl,5-MeO-DCNQI (**2b**): *b,c* projection of the unit cell (space group *Cc*); right: geometry of 2-Cl,5-MeO-DCNQI (**2b**) from X-ray data and some bond lengths



(b) *2,5-Bis(trifluoromethyl)-1,4-benzoquinone* (**1i**): Crystals of quinone **1i** belong to the space group $P2_1/a$. The unit cell contains two molecules of **1i** which can be transformed into one another by a twofold helical twist parallel to the *x* axis. Quinone **1i** forms layers along the *a*/*b* plane. As demonstrated by Figure 9 the shortest distances are found between the carbonyl oxygen atom of one molecule and the carbonyl carbon atom of the next, being even shorter (3.1−3.2 Å) than the sum of the van der Waals radii of the two atoms.

Figure 9. Left: view onto the *b* plane of the unit cell of 2,5-bis(trifluoromethyl)-1,4-benzoquinone, demonstrating the shortest distances between two molecules within one layer; fluoro and hydrogen atoms are not shown for clarity; right: view on the plane of two neighboring molecules along the shortest cell axis *b*



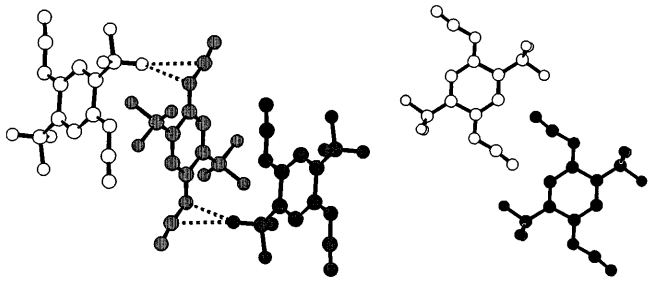
The same type of packing is found for chloranil which also adopts the space group $P2_1/a$[35]. Although the sum of the van der Waals volumes of the substituents from two molecules of **1i** (4 × CF_3, 4 × H: 164.4 Å^3[36]) is only slightly larger [$\Delta(\Sigma V_S)$ = 5.2 Å^3] than for chloranil (8 × Cl: 159. Å^3[36]) the volume of the unit cell of **1i** exceeds that of chloranil by ΔV_C = 14.6 Å^3. The coefficient $\Delta(\Sigma V_S)/\Delta V_C$ = 0.36 is smaller than the average packing coefficients C_K = 0.65−0.77[37] for organic compounds. The less dense packing of **1i** is also reflected in the larger intermolecular distances in crystals of **1i** [*d*(C=O···C=O) = 2.95 Å, d_{TC} = 3.67 Å] compared to chloranil with 2.85 Å and 3.13 Å, respectively.

The C−F bond lengths (1.32−1.33 Å) coincide with relevant data from the literature[38]. However, the intermolecular C−C distances of neighboring CF_3 groups (4.26−4.77 Å) are well below the "rotational diameter" (5.2−5.6 Å) of a CF_3 group. This means that the two CF_3 groups are interlocked like cogwheels. Therefore, rotation of these CF_3 groups is expected either to be coupled or to pass an energy barrier when jumping into the next low energy position after rotation by 120°.

(c) *2-Methyl-5-trifluoromethyl-DCNQI* (**2g**): The unsymmetrically substituted DCNQI **2g** forms crystals from the space group *R*3. Its unit cell contains nine molecules of **2g**. Due to disorder the data for a DCNQI molecule **2g** are taken from the data containing two CF_3 groups which occupy the crystal position only by 50% (center of inversion in **2g**). For similar reasons the positions of the hydrogen atoms at the methyl group and at C3/C6 could not be evaluated.

Within the crystal lattices no distances are shorter than the usual van der Waals data. The shortest distances are found between a CF_3 group and the NCN moiety of the next molecule as demonstrated in Figure 10.

Figure 10. Left: shortest distances between neighboring molecules of 2-methyl-5-trifluoromethyl-DCNQI (**2g**) in the crystal lattice (*R*3); right: view onto the planes of two molecules of **2g** along the stacking axis *c*



The crystal structure of **2g** (*R*3) represents a third packing type for DCNQIs and related acceptors which until now has not been observed. Both the unsubstituted DCNQI[34] and the 2,5-bis(cyanimino)-2,5-dihydrothieno[3,2-*b*]thiophene (2,5-Br_2DCNTT)[39] crystallize in the monoclinic space group $P2_1/c$. Both 2,5-Me_2DCNQI[40] and the aforementioned 2-Cl-5-MeO-DCNQI (**2d**) (space groups *Pnma* and *Cc* respectively) are found with similar arranged molecular layers. Obviously the crystal lattices of these donors are not determined by a common electronic interaction in contrast to DCNQI CT complexes and radical cation salts.

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Experimental Section

General: M.p.: corrected. − IR, ^{1}H NMR, ^{13}C NMR, UV, CV, cf. ref.[1].

Table 3. X-ray data for **2d**[49], **2g**[49], and **1l**[50]

compound	**2d**	**2g**	**1l**
empirical formula	$C_9H_5N_4OCl$	$C_{10}H_5N_4F_3$	$C_8H_2F_6O_2$
molecular mass	220.62	238.17	244.09
a [pm]	1283.7(5)	1859.3(5)	953.5(5)
b [pm]	998.7(4)		589.6(5)
c [pm]	975.5(4)	813.9(4)	813.6(5)
β [deg]	130.02(3)		69.82(2)
V [pm^3]	957.9(7)×10^6	2452(2)×10^6	429.3(5)×10^6
Z	4	9	2
d(calcd) [g×cm^{-3}]	1.530	1.451	1.887
crystal system	monoclinic	rhombohedral	monoclinic
space group	*Cc*	*R*3	$P2_1/a$
diffractometer	Siemens R3m/V	Siemens R3m/V	Syntex $P2_1$
radiation		Mo *Kα*	
monochromator		graphite	
crystal size [mm]	0.15 x 1.15 x 0.05	0.05 x 0.05 x 1.75	1.0 x 0.7 x 0.7
data collection mode	Wyckoff - scan	Wyckoff - scan	ω - scan
theta range [deg]	1.75 - 27.5	1.75 - 27.5	1.75 - 22.5
recip. latt. segment	h = 0 → 16	0 → 24	-10 → 10
	k = 0 → 12	0 → 24	0 → 6
	l = -12 → 9	-31 → 31	-9 → 9
no. refl. measd.	1216	1369	2034
no. unique refl.	1112	1053	1095
no. refl. $F > 3\sigma(F)$	1035	457	771
lin. abs. coeff. [mm^{-1}]	0.37	0.12	0.24
abs. correction	ψ-scan	ψ-scan	none
solution by		direct phase determination	
method of refinement		Full-Matrix LSQ. Hydrogen positions of riding model with fixed isotropic *U*	
data-to-parameter ratio	7.72	5.02	9.02
R, R_w	0.049, 0.045	0.116, 0.083	0.047, unit weights
weighting scheme		$w = 1/\sigma^2(F)$	
largest difference peak	0.25 eÅ^{-3}	0.20 eÅ^{-3}	0.11 eÅ^{-3}
largest difference hole	0.32 eÅ^{-3}	0.18 eÅ^{-3}	0.10 eÅ^{-3}
program used		Siemens SHELXTL PLUS	

Iodinated 1,4-Dimethoxybenzene Derivatives. − General Procedure 1 (GP1): Equivalent amounts of the appropriate 1,4-dimethoxybenzene, iodine (I_2) and yellow mercury oxide[7] were treated with ultrasound (10 min) and heated for 30 min to 90°C. The brown mixture was continuously extracted with refluxing toluene (3−4 h) and then decolorized by washing with solutions of NaI and $NaHSO_3$. After drying with $MgSO_4$, the solvent was removed by distillation under reduced pressure and the brown residue recrystallized from methanol.

1-Chloro-4-iodo-2,5-dimethoxybenzene (**4a**): GP1 with 2-chloro-1,4-dimethoxybenzene (17.3 g, 100 mmol), iodine (25.4 g, 100 mmol), and HgO (23.8 g, 110 mmol). Colorless needles of **1a** (13.7 g, 52%), m.p. 114°C. − IR (KBr): $\tilde{\nu}$ = 2820 cm^{-1} (C−H), 1480 (C=C), 1450, 1425, 1350, 1270, 1205 (C−O), 1065, 1020, 845, 835, 760. − ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 3.89, 3.94 (2 s, 3 H, 1-, 4-OCH_3), 6.95 (s, 1 H, 3-H), 7.39 (s, 1 H, 6-H). − ^{13}C NMR ($CDCl_3$, 100.6 MHz,): δ = 7.28, 57.44 (2 q, 1-, 4-OCH_3), 83.42 (s, C-5), 113.34 (d, C-2), 114.76 (s, C-3), 123.26 (d, C-6), 150.06 (s, C-1), 152.96 (s, C-4). − MS (70 eV); *m/z* (%): 300 (32) [M$^+$(^{37}Cl)], 298 (100) [M$^+$(^{35}Cl) − CH_3), 283 (74) [M$^+$(^{35}Cl) − CH_3]. − $C_8H_8O_2ClI$ (298.5): calcd. C 32.19, H 2.71, found C 31.87, H 2.71.

1-Bromo-4-iodo-2,5-dimethoxybenzene (**4b**): GP1 with 5-bromo-1,4-dimethoxybenzene (10.5 g, 50.0 mmol), iodine (12.7 g, 50.0 mmol) and HgO (13.0 g, 60.0 mmol). From methanol (2 ×) **1a** (4.81 g, 29%) colorless needles, m.p. 138°C. − IR (KBr): $\tilde{\nu}$ = 2800 cm^{-1} (C−H), 1470 (C=C), 1440, 1415, 1337, 1260, 1195 (C−O), 1050, 1010, 838, 823, 741. − ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 3.98, 4.04 (2 s, 3 H, 1-, 4-OCH_3), 7.18 (s, 1 H, 3-H), s, 1 H, 6-H). − ^{13}C NMR ($CDCl_3$, 100.6 MHz,): δ = 57.44, 57.55 (2 q, 1-, 4-OCH_3), 84.41 (s, C-5), 112.19 (s, C-2), 116.26 (d, C-3), 123.14 (d, C-6), 151.17 (s, C-1), 153.33 (s, C-4). − MS (70 eV); *m/z* (%): 344 (95) [M$^+$ (^{81}Br)], 342 (100) [M$^+$ (^{79}Br)], 329 (54) [M$^+$ (^{81}Br) − CH_3], 327 (56) [M$^+$ (^{79}Br) − CH_3]. − $C_8H_8O_2BrI$ (343.0): calcd. C 28.01, H 2.36; found C 28.87, H 2.20.

1,4-Diiodo-2,5-dimethoxybenzene (**4c**): GP1 with 2-iodo-1,4-dimethoxybenzene (5.00 g, 18.9 mmol), iodine (4.79 g, 18.9 mmol), HgO (4.33 g, 20.0 mmol). Colorless crystals of **1c**, m.p. 169°C. − IR (KBr): $\tilde{\nu}$ = 2810 cm^{-1} (C−H), 1475 C=C), 1438, 1425, 1340, 1265, 1210 (C−O), 1058, 1015, 847, 835, 745. − ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 3.82 (s, 6-H, 2 × OCH_3), 7.22 (s, 2 H, 3-, 6-H). − ^{13}C NMR ($CDCl_3$, 50.3 MHz,): δ = 57.06 (q, 2 × OCH_3), 85.33 (s, C-2, -5), 121.46 (d, C-3, -6), 153.18 (s, C-1, -4). − MS (70 eV); *m/z* (%): 390 (100) [M$^+$], 375 (44) [M$^+$ − CH_3]. − $C_8H_8I_2O_2$ (390.0); calcd. C 24.69, H 2.07; found C 24.36, H 2.11.

1-Iodo-2,4,5-trimethoxybenzene (**7**): To 2-bromo-1,4,5-trimethoxybenzene (**6**, 21.3g, 86.2 mmol) in THF (50 ml) was added *n*-butyllithium (131 mmol; 2.5 M in hexane) at −70°C. After stirring for 1 h at −70°C, a solution of iodine (16.7 g, 131 mmol) in THF (50 ml) was slowly added. After 2 h at room temp. and addition of 2 N HCl (30 ml) and H_2O (100 ml), the mixture was extracted with diethyl ether (3 × 100 ml). The organic phase was extracted with water (3 × 30 ml) and dried with Na_2SO_4. After evaporation of the solvent, the residue was crystallized from ethanol (70 ml) yield to **7** (12.9 g, 51%), m.p. 70°C (m.p. ref.[11]: 70°C). − ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 3.78, 3.80, 3.88 (3 s, 9 H, OCH_3), 6.50 (s, 1 H, 6-H), 7.20 (s, 1 H, 3-H): − ^{13}C NMR ($CDCl_3$, 63 MHz): δ = 56.13, 56.65, 57.25 (3 q, OCH_3), 72.95 (s, C-2), 97.79 d, C-6), 121.89 (d, C-3), 144.18 (s, C-5), 150.17, 152.96 (2 s, C-1, -4). − $C_9H_{11}IO_3$ (294.1): calcd. C 36.76 H 3.77; found C 36.96, H 3.83.

Trifluoromethylated 1,4-Dimethoxybenzene Derivatives. − General Procedure 2 (GP2): GP2 was based on a patent[14]. The bromo- or iodo-substituted hydroquinone ether, the corresponding amounts of sodium trifluoroacetate and copper(I) iodide were suspended under argon in dry toluene in a three-necked round-bottom flask equipped with a stirrer and a Claisen bridge. About half of it was distilled off to remove traces of water. After addition of dry dimethyl acetamide, the solvent was distilled until the temperature of the mixture increased to 152−153°C. After stirring for 6−8 h at this temperature, the mixture was cooled to 70°C and the solvent removed in vacuo until 30−50 ml remained. MTB or DE (50 ml) was added to the cooled mixture which was then filtered through a Buchner funnel (diameter 7 cm) covered with silica gel (2−3 cm). The filter cake of CuI was removed in portions which were suspended in MTB or DE (100 ml) and filtered again. This procedure was repeated 2 or 3 times. The organic phases were extraced with water (3 × 50 ml) and dried with Na_2SO_4. The crude product remained after removal of the solvent under reduced pressure.

1,4-Dimethoxy2-methyl-5-trifluoromethylbenzene (**9**): GP2 with 5-chloro-2-methyl-1,4-dimethoxybenzene (**8**, obtained according to ref.[8] in 72% yield; 16.7 g, 60.0 mmol), CF_3CO_2Na (24.5 g, 180 mmol), CuI (22.8 g, 120 mmol), toluene (100 ml), dimethyl acetamide (300 ml). The brown crude product (12.1 g) yielded **9** (8.80 g, 67%) as colorless crystals, m.p. 72−73°C from methanol (40 ml). − IR (KBr): $\tilde{\nu}$ = 3000 cm^{-1}, 2970, 2940, 2880, 2885 (CH), 1630, 1600, 1510 (C=C). − ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 2.26 (s, 3

H, CH_3), 3.81, 3.85 (2 s, 6 H, OCH_3), 6.83 (s, 1 H, 3-H), 7.00 (s, 1-, 6-H). – ^{13}C NMR ($CDCl_3$, 63 MHz): δ = 16.48 (q, CH_3), 55.92, 56.82 (2 q, OCH_3), 108.71 (dq, $J_{^{13}C-^{19}F}$ = 5.3 Hz, C-6), 115.60 (d, C-3), 116.24 (q, $J_{^{13}C-^{19}F}$ = 30.9 Hz, C-5), 123.80 (q, $J_{^{13}C-^{19}F}$ = 272 Hz, CF_3), 132.16 (s, C-2), 151.14 (s, C-1,-4). – MS (70 eV); *m/z* (%): 220 (62) [M^+], 205 (100) [$M^+ - CH_3$]. – $C_{10}H_{11}F_3O_2$ (220.2): calcd. C 54.55, H 5.04; found C 54.35, H 5.05.

1,2,4-Trimethoxy-5-trifluoromethylbenzene (**11**): GP2 with 2-bromo-1,4,5-trimethoxybenzene (**10**, 24.7 g, 100 mmol), CF_3CO_2Na (40.8 g, 300mmol) CuI (38.1 g, 200 mmol), toluene (150 ml), dimethyl acetamide (500 ml). Recrystallization of the crude product from ethanol (50ml) afforded a colorless mixture (13.8 g, 58%), which contained (^1H NMR) **10** (16%), **11** (65%), **8** (10%) and probably 2,2′,4,4′,5,5′-hexamethoxydiphenyl ether (5%). Flash chromatography (PE/CH_2Cl, 9:1) of 0.81 g yielded **11** (0.43 g) as colorless crystals, m.p. 73–74°C. – IR (KBr): $\tilde{\nu}$ = 3000 cm^{-1}, 2960, 2935, 2830 (CH), 1610, 1590, 1510 (C=C). – ^1H NMR ($CDCl_3$, 250 MHz): δ = 3.83, 3.85, 3.90 (3 s, 9 H, OCH_3), 6.56 (s, 1 H, 3-H), 7.02 (s, 1 H, 6-H). – ^{13}C NMR ($CDCl_3$, 63 MHz): δ = 56.00, 56.55, 56.69 (3 q, OCH_3), 97.94 (d, C-3), 109.89 (q, $J_{^{13}C-^{19}F}$ = 31.5 Hz, C-5), 110.34 (dq, $J_{^{13}C-^{19}F}$ = 5.3 Hz, C-6), 123.80 (q, J^{13}_{C-19F} = 272 Hz, CF_3), 142.35 (s, C-2), 152.58 (s, C-1, -4). – MS (70 eV); *m/z* (%): 236 (100) [M^+], 221 (75) [$M^+ - CH_3$]. – $C_{10}H_{11}F_3O_3$ (236.2): calcd. C 50.85, H 4.69; found C 51.07, H 4.82.

1,4-Dimethoxy-2,5-bis(trifluoromethyl)benzene (**12**): GP2 with **4c** (19.5 g, 50.0 mmol), CF_3CO_2Na (54.4 g, 400 mmol), CuI (38.1 g, 200 mmol), toluene (100 ml), dimethyl acetamide (300 ml). 8 h reaction time. The crude product (7.38 g, 50%) contained (^1H NMR) **12** (75%), 2-iodo-1,4-dimethoxy-5-trifluoromethylbenzene (**13**, 20%), and probably 2,2′,5,5′-tetramethoxy-4,4′-bis(trifluoromethyl)diphenyl ether (**14**, 5%). Flash chromatography (PE/CH_2Cl_2, 8:1) yielded **12** (3.54 g, 26%) as colorless crystals, m.p. 130–131°C (131–132°C[41]). – IR (KBr): $\tilde{\nu}$ = 3080 cm^{-1}, 2975, 2945, 2875, 2840 (CH), 1510 (C=C). – ^1H NMR ($CDCl_3$, 250 MHz): δ = 3.90 (s, 6 H, OCH_3), 7.22 (s, 2 H, 3-, 6-H). – ^{13}C NMR ($CDCl_3$, 63 MHz): δ = 56.53 (q, OCH_3), 111.46 (dq, $J_{^{13}C-^{19}F}$ = 5.7 Hz, C-3, -6), 122.39 (q, $J_{^{13}C-^{19}F}$ = 31.3 Hz, C-2, -5), 122.55 (q, $J_{^{13}C-^{19}F}$ = 31.3 Hz, C-2, -5), 122.55 (q, $J_{^{13}C-^{19}F}$ = 273 Hz, CF_3), 150.62 (s, C-1, -4). – MS (70 eV); *m/z* (%): 274 (97) [$M^+ - CH_3$]. – $C_{10}H_8F_6O_2$ (274.2): calcd. C 43.81, H 2.94; found C 43.53, H 3.23.

Deuterated Hydroquinone Derivatives. – 1,4-Dideuterio-2,5-dimethoxy-3,6-dimethylbenzene (**20**): By analogy to ref.[21] *n*-butyllithium (57.2 mmol, 2.5 M in hexane) was added at –55°C to 3,6-dibromo-1,4-dimethoxy-2,5-dimethylbenzene (**19**, 8.43 g, 26.0 mmol) in diethyl ether (DE) (230 ml). The colorless suspension was warmed to room temp. and then refluxed (30 min). After cooling to –70°C, [D_4]methanol (> 99%, 5.5 ml) was added. After warming the mixture to room temperature, [carboxy-D]acetic acid (98% D, 6.6 ml) was added, the organic phase was washed with water (3 × 50 ml) and dried with Na_2SO_4. The solvent was evaporated and the residue recrystallized from ethanol (30ml) to yield **20** (3.96 g,. 90%) as colorless needles, m.p. 109°C. – ^1H NMR ($CDCl_3$, 250 MHz): δ = 2.28 (s, 6 H, CH_3), 3.84 (s, 6 H, OCH_3), 6.73 (s, < 0.09 H, 3-, 6-H). Deuteration of positions 3 and 6 > 95% – ^{13}C NMR ($CDCl_3$, 63 MHz): δ = 15.95 (q, CH_3), 55.91 (q, OCH_3), 113.18 (t, $J_{^{13}C-D}$ = 23.7 Hz, C-3, -6), 124.00 (s, C-2, -5), 151.26 (s, C-1, -4). – MS (70 eV); *m/z* (%): 168 (49.48) [M^+], 167 (5.38 [$M^+ - 1$], 166 (1.04) [$M^+ - 2$], 153 (100) [$M^+ - CH_3$]. Deuterations of positions 3 and 6 > 93%. – $C_{10}H_{12}D_2O_2$ (168.2):[51] calcd. C 71.41, H 8.52; found C 71.36, H 8.59.

1,4-Dimethoxy-2-methyl-5-trideuteriomethylbenzene (**22**): At –78°C *n*-butyllithium (22.0 ml, 55.0 mmol, 2.5 M in hexane) was added to a solution of 2-bromo-5-methyl-1,4-dimethoxybenzene (**21**, 11.6 g, 50.0 mmol) in THF (100 ml). The suspension was warmed to –50°C and cooled again to –70°C before trideuteriomethyl iodide (> 99.5% D, 10.9 g, 75.0 mmol) in THF (20 ml) was added. After stirring at room temp. (2 h), the mixture was acidified with 2 N HCl (30 ml) and water (100 ml). Extraction of the organic phase with DE (3 × 100 ml), washing with water, drying with Na_2SO_4 and evaporation of the solvent afforded the crude product. From ethanol (70 ml) colorless crystals of **22** (7.42 g, 88%), m.p. 110–111°C, were obtained. – IR (KBr): $\tilde{\nu}$ = 3020 cm^{-1}, 2980, 2930, 2890, 2835, 2825 (CH), 2220, 2200, 2220, 2055 (CD), 1500 (C=C), 1455, 1390, 1365, 1290, 1205, 1035, 890, 785, 635. – ^1H NMR ($CDCl_3$, 250 MHz): δ = 2.24 (s, 3 H, CH_3), 3.81 (s, 6 H, OCH_3), 6.69 (s, 2 H, 3-, 6-H). – ^{13}C NMR ($CDCl_3$, 63 MHz): δ = 16.05 (q, CH_3), 56.05 (q, OCH_3), 113.64 (d, C-3, -6), 124.11, 124.25 (2 s, C-2, -5), 151.40 (s, C-1, -4). – MS (70 eV); *m/z* (%): 169 (51.79) [M+], 168 (0.39) [$M^+ - 1$], 154 (100) [$M^+ - CH_3$]. Deuteration of CD_3 > 99.7%. – $C_{10}H_{11}D_3O_2$ (169.2): calcd. C 70.99, H 8.54;[51] found C 71.37, H 8.13.

1,4-Dimethoxy-2,5-bis(trideuteriomethyl)benzene (**24**): By adaption of ref.[42][43] *n*-butyllithium (2.5 M in hexane, 70 ml, 175 mmol) and hexane (100 ml) were cooled to –90°C before 2,5-dibromo-1,4-dimethoxybenzene (**23**), dissolved in DE (100 ml) and THF (100 ml), was added. The jelly-like mixture was stirred at –40°C (30 min) and trideuteriomethyl iodide (29.0 g, 200 mmol) in THF (30 ml) was added. The mixture was slowly warmed to room temp. and then stirred for 3 h. Work up according to **22** yielded **24** (8.32 g, 69%) from ethanol (80 ml), m.p. 109°C. – IR (KBr): $\tilde{\nu}$ = 3020 cm^{-1}, 2980, 2930, 2885, 2835, 2810 (CH), 2220, 2200, 2110, 2050 (CD), 1500 (C=C), 1455, 1390, 1280, 1200, 1050, 1030, 890, 830, 615. – ^1H NMR ($CDCl_3$, 250 MHz): δ = 3.78 (s, 6 H, OCH_3), 6.66 (s, 2 H, 3-, 6-H). – ^{13}C NMR ($CDCl_3$, 63 MHz): δ = 56.04 (q, OCH_3), 113.62 (d, C-3, -6), 124.09 (s, C-2, -5), 151.40 (s, C-1, -4). – MS (70 eV); *m/z* (%): 172 (52.01) [M^+], 171 (0.66) [$M^+ - 1$], 157 (100) [$M^+ - CH_3$]. Deuteration of 2 CD_3 > 99%. – $C_{10}H_8D_6O_2$ (172.2):[51] calcd. 69.76, H 8.58; found C 69.48, H 8.26.

1,4-Dideuterio-2,5-dimethoxy-3,6-bis(trideuteriomethyl)benzene (**28**): By analogy to the undeuterated compound[44] bromination of **24** (5.13 g, 29.8 mmol) afforded **28** (8.01 g, 81%) of 3,6-dibromo-1,4-dimethoxy-2,5-bis(trideuteriomethyl)benzene (**27**), m.p. 125–126°C (undeuterated: 85%, m.p. 125–126°C[44]). By adapting ref.[21] *n*-butyllithium (2.5 M in hexane, 20.7 ml, 51.7 mmol) was added at –55°C to **27** (7.75 g, 23.5 mmol) in DE (230 ml). The suspension was warmed to room temp., refluxed (30 min) and cooled to –70°C before [D_4]methanol (> 99% D, 5 ml) was added. When room temp. was regained [carboxy-D]acetic acid (98% D, 6 ml) was added and the reaction mixture washed with water and dried with Na_2SO_4. After removal of the solvent and recrystallization from ethanol (20 ml), **28** (3.44 g, 84%), m.p. 110–111°C, was obtained. – IR (KBr): $\tilde{\nu}$ = 2980 cm^{-1}, 2935, 2880, 2800 (CH), 2220, 2200, 2100, 2060, 2040 (CD), 1505 (C=C), 1430, 1370, 1280, 1195, 1180, 1085, 1030, 935, 800, 720, 610. – ^1H NMR ($CDCl_3$, 250 MHz): δ = 3.81 (s, 6 H, OCH_3), 6.69 (s, < 0.06 H, 3-, 6-H). Deuterations of positions 3 and 6 > 97%. – ^{13}C NMR ($CDCl_3$, 63 MHz): δ = 56.00 (q, OCH_3), 113.24 (t, $J_{^{13}C-D}$ = 24 Hz, C-3, -6), 123.86 (s, C-2, -5), 151.34 (s, C-1, -4). MS (70 eV); *m/z* (%): 174 (54.06) [M^+], 173 (2.16) [$M^+ - 1$], 172 (0.63) [$M^+ - 2$], 159 (100) [$M^+ - CH_3$]. Deuterations of 2 CD_3 > 97%. – $C_{10}H_6D_8O_2$ (174.2):[51] calcd. C 68.97, H 8.62; found C 68.73, H 8.40.

2,5-Bis(trideuteriomethyl)hydroquinone-O,O′-bis(N,N′-diethylcarbamate) (**26**): In an adaption to ref.[22], TMEDA (12.8 g, 110 mmol) was added at –78°C to *n*-butyllithium (1.3 M in cyclo-

hexane/hexane 98:2, 85 ml, 0.11 mol) in THF (80 ml). After stirring (30 min), hydroquinone-O,O′-bis(*N,N′*-diethylcarbamate) (**25**, 12.6 g, 48.4 mmol) in THF (120 ml) was slowly added and after stirring (1 h, −78°C) trideuteriomethyl iodide (12.8 g, 125 mmol). The stirred mixture was slowly warmed to room temp. and then acidified with 2 N HCl (50 ml). Washing the organic phase with water, drying with Na_2SO_4 and evaporation of the solvent afforded crude **26** (8.9 g) from petroleum ether (PE) (50−70°C) 8.37 g (59%), m.p. 85°C, which was directly transformed into **1l** by GP3(b) (vide infra). − IR (KBr): $\tilde{\nu}$ = 2960 cm^{-1}, 2920, 2890, 2860 (CH), 1695 (C=O). − ^1H NMR ($CDCl_3$, 60 MHz): δ = 1.18 (t, *J* = 7.4 Hz, 12 H, CH_2CH_3), 3.53 (q, *J* = 7.4 Hz, 8 H, CH_2CH_3), 7.20 (s, 2 H, 3-, 6-H).

1,4-Benzoquinones by Oxidation of Aromatic Precursors. − General Procedure 3 (GP3): (a) To 2.1 equiv. of BBr_3 in dichloromethane was added at −78°C a concentrated solution of the 1,4-dimethoxybenzene, whereby a colorless precipitate was formed (cf. ref.[45]). After stirring for 15 h at room temp., the clear solution was poured onto ice (200 g) and extracted with DE. After washing with water, the organic phase was dried with Na_sSO_4. On evaporation of the solvent the crude hydroquinones remained which were directly oxidized. (b) The hydroquinones were dissolved in an acetone/water (5:1) mixture. At 0°C a 2 M solution (0.7 equiv.) of chromium(IV) oxide in H_2SO_4 (33%) was then slowly added. After stirring (30 min), the mixture was extracted with dichloromethane. The organic phase was washed with water and dried with $MgSO_4$. Evaporation of the solvent yielded the crude quinone.

General Procedure 4 (GP4): According to ref.[12] an aqueous solution of 2.2−2.5 equiv. of cerium(IV) ammonium nitrate was added to a solution of the hydroquinone dimethyl ether in acetonitrile. After stirring (30 min), the mixture was extracted with dichloromethane. The organic phase was washed with water and dried with $MgSO_4$. Evaporation of the solvent yielded the crude quinone.

2-Chloro-5-iodo-1,4-benzoquinone (**1a**): GP3(a) with **4a** (10.0 g, 33.5 mmol), CH_2Cl_2 (50ml), BBr_3 (18.8 g, 75.0 mmol) in CH_2Cl_2 (80 ml). GP3(b) with the crude hydroquinone (9.06 g, 33.5 mmol, 100%), 200 ml acetone/water, CrO_3/H_2SO_4 (2 M, 11.5 ml, 22.3 mmol, 1 h, 0°C). The crude quinone was crystallized from ethanol (150 ml) to afford **1a** (7.47 g, 83%), orange crystals, m.p. 154°C. − IR (KBr): $\tilde{\nu}$ = 3050 cm^{-1} (C−H), 1645 (C=O), 1570, 1540 (C=C). − UV (CH_3CN): λ_{max} (lg ε) = 243 nm (3.76), 287 (3.85), 370 (3.07). − ^1H NMR ($CDCl_3$/TMS, 250 MHz): δ = 7.16 (s, 1 H, 3-H), 7.80 (s, 1 H, 6-H). − ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 119.96 (s, C-5), 131.59 (d, C-3), 144.41 (s, C-2), 144.99 (d, C-6), 176.43 (s, C-1), 178.29 (s, C-4). − MS (70 eV); *m/z* (%): 270 (35) [M^+ (^{37}Cl)], 268 (100) [M^+ (^{35}Cl)]. − $C_6H_2O_2ClI$ (270.4): calcd. C 26.84, H 0.75; found C 26.42, H 0.41.

2-Bromo-5-iodo-1,4-benzoquinone (**1b**): GP3(a): With **4b** (6.00 g, 17.5 mmol) in CH_2Cl_2 (80 ml), BBr_3 (1.17 M in CH_2Cl_2, 30 ml, 35.1 mmol). GP3(b): With the crude hydroquinone (5.51 g, 17.5 mmol, 100%), acetone/water (200 ml), CrO_3/H_2SO_4 (2 M, 3.90ml, 7.80 mmol). The red residue was crystallized from ethanol (50 ml) to afford **1b** (4.97 g, 91%), brick-red crystals, m.p. 177°C. − IR (KBr): $\tilde{\nu}$ = 3065 cm^{-1} (=C−H), 1660, 1645 (C=O), 1575, 1540 (C=C). − UV (CH_3CN): λ_{max} (lg ε) = 240 nm (3.71), 295 (3.89), 370 (2.86). − ^1H NMR ($CDCl_3$, 200 MHz): δ = 7.47 (s, 1 H, 3-H), 7.80 (s, 1 H, 6-H). − ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 119.71 (s, C-5), 135.92 (d, C-3), 137.75 (s, C-2), 144.81 (d, C-6), 176.51 (s, C-1), 177.50 (s, C-4). − MS (70 eV); *m/z* (%): 314 (59) [M^+(^{81}Br)], 312 (55) [M^+(^{79}Br)]. − $C_6H_2O_2BrI$ (312.9): calcd. C 23.03, H 0.65; found C 22.85, H 0.77.

2,5-Diiodo-1,4-benzoquinone (**1c**): GP3(a) **4c** (2.50 g, 6.41 mmol), in CH_2Cl_2 (100 ml), BBr_3 (3.76 g, 15.0 mmol) in CH_2Cl_2 (50 ml). − GP3(b) with the crude hydroquinone (2.32 g, 100%) in acetone/water (100 ml), CrO_3/H_2SO_4 (2 M, 2.20 ml, 4.40 mmol). Brown crude **1c** (1.85 g) was crystallized from ethanol (200 ml, −25°C) to yield yellow plates of **1c** (1.65 g, 72%). − IR (KBr): $\tilde{\nu}$ = 3050 cm^{-1} (=C−H), 1665 (C=O), 1575 (C=C). − UV (CH_3CN): λ_{max} (lg ε) = 238 nm (3.88), 308 (3.77), 353 (3.60). − ^1H NMR ($CDCl_3$, 200 MHz): δ = 7.90 (s, 2 H, 3-, 6-H). − ^{13}C NMR ($CDCl_3$, 50.3 MHz): δ = 119.57 (s, C-2, -5), 143.62 (d, C-3, -6), 177.51 (s, C-1, -4). − MS (70 eV); *m/z* (%): 361 (7) [M^+ + 1 H], 360 (100) [M^+]. − $C_6H_2O_2I_2$ (359.9): calcd. C 20.02, H 0.56; found C 20.29, H 0.55.

2-Chloro-5-methoxy-1,4-benzoquinone (**1d**): A solution of potassium nitrosodisulfonate (13.4 g, 50.0 mmol) and potassium hydrogen phosphate in water (200 ml) was added to 5-chloro-2-methoxyaniline (3.15 g, 20.0 mmol) in acetonitrile (100 ml). On stirring (1.5 h, 20°C) the violet solution turned red. The mixture was extracted with $CHCl_3$ (2 × 100 ml), the solvent removed on washing with cold DE (2 × 10 ml) the red residue became yellow. After crystallization from methanol (40 ml) flash chromatography (silica gel, CH_2Cl_2) yielded a yellow microcrystalline powder of **1d** (660 mg, 10%), m.p. 173−174°C (ref.[9], m.p. 173−174°C).

2-Iodo-5-methoxy-1,4-benzoquinone (**1f**): GP4 with **7** (13.0 g, 44.3 mmol) in acetonitrile (100 ml), Ce^{IV} reagent (53.5 g, 98.5 mmol) in water (100 ml). Flash chromatography (SiO_2, CH_2Cl_2) of the crude product yielded **1f** (5.31 g, 45%), orange crystals, m.p. 191°C. − IR (KBr): $\tilde{\nu}$ = 3050 cm^{-1}, 3020, 2970, 2925 (CH), 1650 (C=O), 1600, 1560 (C=C), 1450, 1430, 1365, 1350, 1310, 1260, 1190, 1160, 990, 910, 900, 850, 810. − UV (CH_3CN): λ_{max} (lg ε) = 237 nm (3.76), 294 (3.99), 322 (sh, 3.58). − ^1H NMR ($CDCl_3$, 250 MHz): δ = 3.86 (s, 3 H, OCH_3), 6.20 (s, 1 H, 6-H), 7.62 (s, 1 H, 3-H). − ^{13}C NMR ($CDCl_3$, 63 MHz): δ = 56.50 (q, OCH_3), 105.76 (d, C-6), 122.20 (s, C-2), 143.72 (d, C-3), 159.00 (s, C-5), 178.61, 180.23 (2 s, C-1, -4). − MS (70 eV); *m/z* (%): 264 (M) [M^+], 236 (49) [M^+ − CO]. − $C_7H_5IO_3$ (264.0): calcd. C 31.85, H 1.90; found C 32.00, H 1.88.

2-Methyl-5-trifluoromethyl-1,4-benzoquinone (**1g**): GP4 with **9** (10.6 g, 48.0 mmol) in acetonitrile (100 ml), Ce^{IV} reagent (55.3 g, 101 mmol) in water (100 ml). Flash chromatography (SiO_2,PE/CH_2Cl_2, 1:1) of the crude product afforded **1g** (5.62 g, 62%) after crystallization from hexane (30ml), yellow plates, m.p. 37°C. − IR (CCl_4): $\tilde{\nu}$ = 3055 cm^{-1}, 2970, 2940, 2910 (CH), 1660 (C=O), 1610 (C=C), 1435, 1420, 1380, 1360, 1340, 1270, 1230, 1165, 1120, 1000, 970, 925. − UV (CH_3CN): λ_{max} (lg ε) = 241 nm (4.22), 314 (3.08). − ^1H NMR ($CDCl_3$, 250 MHz): δ = 2.10 (d, ^4J = 1.6 Hz, 3 H, CH_3), 6.70 (q, ^4J = 1.6 Hz, 1 H, 3-H), 7.08 (q, $^4J^1{}_{H\text{-}}{}^{19}{}_{F}$ = 1.1 Hz, 1 H, 6-H). − ^{13}C NMR ($CDCl_3$, 63 MHz): δ = 15.36 (q, CH_3), 120.47 (q, $J_{^{13}C\text{-}^{19}F}$ = 275 Hz, CF_3), 133.76 (d, C-3), 134.61 (q, $J_{^{13}C\text{-}^{19}F}$ = 32.1 Hz, C-5), 134.72 (dq, $J_{^{13}C\text{-}^{19}F}$ = 5.0 Hz, C-6), 146.39 (s, C-2), 181.59 (s, C-4), 186.28 (s, C-1). − MS (70 eV); *m/z* (%): 190 (86) [M^+], 162 (100) [M^+ − CO], 122 (96), 68 (25). − $C_8H_5F_3O_2$ (190.1): calcd. C 50.54, H 2.65; found C 50.30, H 2.72.

2-Methoxy-5-trifluoromethyl-1,4-benzoquinone (**1h**): GP4 with **11** contaminated by products **10** and **8** (vide supra, 13.0 g, ca. 55 mmol) in acetonitrile (110 ml), Ce^{IV} reagent (63.6 g, 116 mmol) in water (100 ml). Flash chromatography (SiO_2, PE/CH_2Cl_2, 1:4, yielded **1h** (5.51 g, 28% based on **10**), yellow crystals, m.p. 103°C (subl., ref.[46] m.p. 101−102°C). − IR (CCl_4): $\tilde{\nu}$ = 3060 cm^{-1}, 3005, 2960, 2920, 2835 (CH), 1680, 1660 (C=O), 1595 (C=C), 1450, 1430, 1370, 1350, 1265, 1210, 1190, 1160, 1015, 960, 850. − UV (CH_3CN): λ_{max} (lg ε) = 250 nm (4.04), 363 (3.09). − ^1H NMR ($CDCl_3$, 250 MHz): δ = s, 3 H, OCH_3), 6.01 (s, 1 H, 3-H), 7.01 (q,

$^4J^1_{H\text{-}^{19}F}$ = 1.1 Hz, 1 H, 6-H). − ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 56.61 (q, OCH_3), 108.29 (d, C-3), 122.79 (q, $J_{^{13}C\text{-}^{19}F}$ = 175 Hz, CF_3), 133.05 (dq, $J_{^{13}C\text{-}^{19}F}$ = 5.4 Hz, C-6), 134.80 (q, $J_{^{13}C\text{-}^{19}F}$ = 31.4 Hz, C-5), 158.60 (s, C-2), 180.39, 181.40 (2 s, C-1, -4). − MS (70 eV); *m/z* (%): 206 (26) [M^+], 178 (23) [M^+ − CO], 176 (27) [M^+ − OCH_2], 122 (20) [M*l*2 + CF_3], 69 (100) [CF_3^+]. − $C_8H_5F_3O_3$ (206.1): calcd. C 46.62, H 2.45; found C 47.08, H 2.34.

2,5-Bis(trifluoromethyl)-1,4-benzoquinone (**1i**): GP3(a) with **4c** (24.7 g, 63.3 mmol) in CH_2Cl_2 (100ml), BBr_3 (33.1 g, 132 mmol) in CH_2Cl_2 (50 ml). The crude hydroquinone was dissolved in 2 N NaOH (79 ml, 158 mmol) and ethanol (200 ml) and treated with benzyl bromide (32.3 g, 189 mmol) in ethanol (100 ml) by refluxing for 1 h. From the cooled reaction mixture the precipitate was isolated and recrystallized from toluene to yield 2,5-diiodohydroquinonedibenzyl ether (**15**, 20.9 g, 61%) as colorless needles, m.p. 186−187°C. − ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 5.06 (s, 2 H, OCH_2Ph), 7.25−7.55 (m, 12 H, arom. H). − ^{13}C NMR ($CDCl_3$, 63 MHz): δ = 72.05 (t, OCH_2Ph), 86.51 (s, C-2, -5), 123.59 (d, C-3, -6), 127.24, 128.05, 128.57 (3 d, $OCH_2C_6H_5$), 136.18 (s, $OCH_2C_6H_5$), 152.81 (s, C-1, -4). − GP2 with **15** (17.9 g, 33.0 mmol), CF_2CO_2Na (35.9 g, 264 mmol), CuI (25.1 g, 132 mmol) in toluene (75 ml). Dimethylacetamide (150 ml) was added and the mixture distilled until it reached 152−153°C and stirred (8 h) at this temperature. Work up (GP3) yielded an oker-colored solid (12.5 g). By catalytic hydrogenation in ethanol the crude product (12.5 g) was only purified [150ml, 75°C, 0.5 g Pd/C (10% Pd), 4 bar H_2, 12 h). By analogy to ref.[15] the colorless solid (9.41 g) was suspended in ethanethiol (85 ml) and treated at 0°C with $BF_3{\cdot}Et_2O$ (49.7 g, 350 mmol). After stirring (2 h, 20°C), the mixture was hydrolyzed with ice-cold water. Extraction with DE, drying with Na_2SO_4 and removal of the solvent and reagents at 1 Torr yielded a yellowish solid (5.40 g). Flash chromatography (SiO_2, PE/EA, 2:1) yielded 2,5-bis(trifluoromethyl)hydroquinone [3.31 g (41%), m.p. 160°C (subl.)]. − ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 4.90 (s, 2 H, OH), 7.07 (s, 2 H, 3-, 6-H). − ^{13}C NMR (CD_3OD, 63 MHz): δ = 115.92 (dq, $J_{^{13}C\text{-}^{19}F}$ = 3.7 Hz, C-3, -6), 121.93 (q, $J_{^{13}C\text{-}^{19}F}$ = 31.3 Hz, C-2, -5), 124.01 (q, $J_{^{13}C\text{-}^{19}F}$ = 272 Hz, CF_3) 149.07 (s, C-1, -4). − GP3 with the hydroquinone **16** (3.01 g, 12.2 mmol) in acetone/water (40 ml), CrO_3/H_2SO_4 (2 M, 4.28 ml, 8.56 mmol). From ethanol (40 ml) the crude product afforded (2.33 g, 78%) yellow plates, m.p. 154°C (subl.). − IR (KBr): $\tilde{\nu}$ = 3060 cm^{-1} (CH), 1670 (C=O), 1350, 1275, 1225, 1170, 1160, 1020, 930. − UV (CH_3CN): λ_{max} (lg ε) = 238 nm (4.18), 305 (2.75). − ^{1}H NMR ([D_6]acetone, 250 MHz): δ = 7.27 (q, $^4J_{^1H\text{-}^{19}F}$ = 1.0 Hz, 2 H, 3-, 6-H). − ^{13}C NMR ([D_6]acetone, 63 MHz): δ = 120.59 (q, $J_{^{13}C\text{-}^{19}F}$ = 275 Hz, CF_3), 134.22 (q, $J_{^{13}C\text{-}^{19}F}$ = 31.5 Hz, C-2, -5), 135.94 (dq, $J_{^{13}C\text{-}^{19}F}$ = 5.0 Hz, C-3, -6), 180.59 (s, C-1, -4). − MS (70 eV); *m/z* (%): 244 (89) [M^+], 216 (52) [M^+ − CO], 122 (100) [M^+/2]. − $C_8H_2F_6O_2$ (244.1): calcd. C 39.37, H 0.83; found C 39.83, H 1.14.

2,5-Bis(fluormethyl)-1,4-dimethoxybenzene (**18**): By adaption of ref.[18] 2,5-bis(chloromethyl)-1,4-dimethoxybenzene[16] (**17**, 9.40 g, 40.0 mmol), KF (9.31 g, 160 mmol), KI (1.11 g, 9 mmol, polyethylene glycol 400 (16.0 g, 40 mmol) and acetonitrile (10ml) were heated in an inert atmosphere for 10 h to 80°C. The reaction was monitored by TLC (SiO_2, toluene, R_f = 0.58). After removing the acetonitrile under reduced pressure and addition of water (150 ml), the mixture was continuously extracted with DE (500ml, 4 h). The organic phase was dried with $MgSO_4$ and the solvent evaporated. The residue (6.2 g) was recrystallized from methanol to yield **18** (4.10 g, 51%) as colorless crystal, m.p. 115−116°C. − IR (KBr): $\tilde{\nu}$ = 3054 cm^{-1}, 2999−2837 (C−H), 1513 (C=C), 1237, 1211 (OMe). − ^{1}H NMR ($CDCl_3$/TMS): δ = 3.83 (s, 6 H, OCH_3), 5.46 (d, 4 H, CH_2F, $^2J_{H\text{-}F}$ = 49.4 Hz), 6.95 (s, 2 H, arom. H). − ^{13}C NMR ($CDCl_3$/TMS): δ = 56.1 (OCH_3), 81.1 (d, CH_2F, $J_{C\text{-}F}$ = 17.6 Hz), 111.2 (s, 3,6 arom. C), 125.7 (d, 2,5 arom. C, $^2J_{C\text{-}F}$ = 17.6 Hz), 150.4 (s, 1,4 arom. C). − $C_{10}H_{12}F_2O_2$ (202.20): calcd. C 59.40, H 5.98, found C 59.18, H 5.69.

2,5-Bis(fluoromethyl)-1,4-benzoquinone (**1l**): By analogy to ref.[16][17] conc. HNO_3 was slowly added to **18** (2.00 g, 10 mmol) in acetic acid (40 ml) at 0−10°C. After 1 h, the mixture was diluted with ice-cold water (150 ml) and extracted with DE (3 × 50 ml). The organic phase was extracted with water (2 × 100 ml) and dried with $MgSO_4$ and the solution concentrated until precipitation occurred (30−50 ml) which was completed by addition of PE. The remaining solid was recrystallized from methanol to afford **1l** (0.84 g, 49%), m.p. 123−124°C. − IR (KBr): $\tilde{\nu}$ = 3061 cm^{-1}, 2942 (CH), 1649 (C=C, C=O). − ^{1}H NMR ($CDCl_3$/TMS): δ = 5.32 (q, 4 H, $^2J_{H\text{-}F}$ = 46.1 Hz, $^4J_{H\text{-}F}$ = 2.1 Hz), 6.81 (m, 2 H, 3-, 6-H). − ^{13}C NMR ($CDCl_3$/TMS): δ = 78.3 (d, CH_2F, $^1J_{C\text{-}F}$ = 173.9 Hz), 144.1 (d, 3,6-C, $^3J_{C\text{-}F}$ = 17.1 Hz), 185.7 (d, C=O, $^3J_{C\text{-}F}$ = 7.6 Hz). − $C_8H_6F_2O_2$ (172.13): calcd. C 55.82, H 3.51; found C 55.82, H 3.58.

2,5-Dideuterio-3,6-dimethyl-1,4-benzoquinone (**1m**): GP4 with **20** (3.84 g, 22.8 mmol) in acetonitrile (50ml), Ce^{IV} reagent (31.3 g, 57.1 mmol) in water (50 ml). From ethanol the crude product yielded **1m** (2.78 g, 88%) as yellow needles, m.p. 123−124°C. − IR (KBr): $\tilde{\nu}$ = 2960 cm^{-1} (CH), 2270 (CD), 1650 (C=O), 1595 (C=C), 1430, 1375, 1300, 1200, 1045, 960, 910, 790, 690, 630. − ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 1.95 (s, 6 H, CH_3), 6.52 (q, ^4J = 1.6 Hz, < 0.09 H, 3-, 6-H). Deuteration of positions 3 and 6 > 95%. − ^{13}C NMR ($CDCl_3$, 63 MHz): δ = 15.26 (q, CH_3), 132.85 (t, $J_{^{13}C\text{-}D}$ = 25.3 Hz, C-3, -6), 145.50 (s, C-2, -5), 187.89 (s, C-1, -4). − MS (70 eV); *m/z* (%): 138 (83.57) [M^+], 137 (6.90) [M^+ − 1], 136 (0.47) [M^+ − 2], 110 (29) [M^+/2]. Deuteration in positions 3,6 = 95%. − $C_8H_6D_2O_2$ (138.1):[51] calcd. C 69.56, H 6.00; found C 70.11, H 5.92.

2-Methyl-5-trideuteriomethyl-1,4-benzoquinone (**1n**): GP4 **22** (5.08 g, 30.0 mmol) in acetonitrile (70 ml) Ce^{IV} reagent (36.2 g, 66.0 mmol) in water (70 ml). From ethanol (60 ml) the crude product afforded **1n** (3.88 g, 93%) as yellow crystals, m.p. 125°C. − IR (KBr): $\tilde{\nu}$ = 3030 cm^{-1}, 2950, 2920 (CH), 1650 (C=O), 1600 (C=C), 1430, 14109, 1375, 1360, 1350, 1260, 1240, 1160, 1035, 1010, 930, 910, 865, 820, 760, 690, 635. − ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 1.96 (d, ^4J = 1.6 Hz, 3 H, CH_3), 6.53 (q, ^4J = 1.6 Hz, 1 H, 3-H), 6.53 (s, 1 H, 6-H). − ^{13}C NMR ($CDCl_3$, 63 MHz): δ = 15.42 (q, CH_3), 133.30, 133.45 (2 d, C-3, -6), 145.72 (s, C-2, -5), 187.96 (s, C-1, -4). − MS (70 eV); *m/z* (%): 139 (100) [M^+], 138 (1.20) [M^+ − 1], 137 (0.44) [M^+ − 2], 111 (56) [M^+ − CO], 114 (33) [M^+ − CO], 71 (72) [M^+/2 + CD_3], 68 (68) [M^+/2 + CH_3]. Deuteration of CD_3 = 99.3%. − $C_8H_5D_3O_2$ (139.1):[51] calcd. C 69.06, H 6.04; found C 69.48, H 5.92.

2,5-Bis(trideuteriomethyl)-1,4-benzoquinone (**1o**): (a) GP4 with **24** (1.80 g, 10.5 mmol) in acetonitrile (30 ml), Ce^{IV} reagent (12.1 g, 22.1 mmol) in water (30ml). From ethanol (20 ml) the crude product yielded **10** (1.24 g, 83%) as yellow needles, m.p. 124−125°C. − IR (KBr): $\tilde{\nu}$ = 3030 cm^{-1} (CH), 1640 (C=O), 1590 (C=C), 1345, 1250, 1165, 1030, 930, 865, 725, 660, 610. − ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 6.60 (s, 2 H, 3-, 6-H). − ^{13}C NMR ($CDCl_3$, 63 MHz): δ = 133.23 (d, C-3, -6), 145.49 (s, C-2, -5), 187.83 (s, C-1, -4). − MS (70 eV); *m/z* (%): 142 (72.73) [M^+], 141 (0.52) [M^+ − 1], 140 (0.18) [M^+ − 2], 71 (100) [M^+/2]. Deuteration of both CD_3 = 99.7%. − $C_8H_2D_6O_2$ (142.1):[51] calcd. C 67.62, H 6.14; found C 67.33, H 5.89. − (b) NaOH (4.0 g, 0.10 mol) in water (30 ml) was added to **26** (8.10 g, 27.5 mmol) in methanol (200 ml). After refluxing for 4 d, the mixture was poured into ice-cold water,

neutralized (pH = 4−5) with conc. HCl and extracted with CH_2Cl_2. The organic phase was washed with water, the solvent evaporated. The crude hydroquinone was oxidized according to GP3(b) in acetone/water (120 ml) with CrO_3/H_2SO_4 (2 M, 9.05 ml, 18.1 mmol). Flash chromatography (SiO_2, CH_2Cl/PE, 1:1) yielded **10** (1.69 g, 43%) yellow crystals, m.p. 124°C, mixed m.p. with the product from procedure (a), no depression.

2,5-Dideuterio-3,6-bis(trideuteriomethyl)-1,4-benzoquinone (**1p**): GP4 with **28** (3.05 g, 17.5 mmol) in acetonitrile (50 ml) Ce^{IV} reagent (24.0 g, 43.8 mmol) in water (50 ml). From ethanol (15 ml) the crude quinone yielded **1p** (2.31 g, 92%), yellow crystals, m.p. 125−126°C. − IR (KBr): $\tilde{\nu}$ = 2260 cm^{-1} (CD), 1630 (C=O), 1580 (C=C), 1320, 1295, 1235, 1175, 1105, 1045, 1030, 975, 810, 780, 685, 660. − UV (CH_3CN): λ_{max} (lg ε) = 250 nm (4.28), 256 sh (4.22). − ^{13}C NMR ($CDCl_3$, 63 MHz): δ = 133.00 (t, $J_{^{13}C\text{-}D}$ = 24.8 Hz, C-3, -6), 145.49 (s, C-2, -5), 188.03 (s, C-1, -4). − MS (70 eV); *m/z* (%): 144 (100.00) [M^+], 143 (5.60) [M^+ − 1], 142 (0.38) [M^+ − 2], 72 (82) [$M^+/2$]. Overall deuteration = 97%. − $C_8D_8O_2$ (144.1):[51] calcd. C 66.69, H 6.22; found C 66.84, H 5.76.

2,5-Disubstituted N,N′-Dicyano-1,4-benzoquinone Diimines. − General Procedure 5 (GP5): Bis(trimethylsilyl)carbodiimide (5 equiv.) were added at 0°C to titanium tetrachloride (5 equiv.) in dry dichloromethane, whereby an orange color develops. Subsequently, a solution of the 1,4-benzoquinone (1 equiv.) in dichloromethane was slowly added. The reaction mixture was stirred for 4−20 h at 20°C, while monitoring by DC (SiO_2, CH_2Cl_2). After hydrolysis with ice-cold water, the mixture was immediately extracted with dichloromethane. The organic phase was washed with water until pH ≈ 5 was attained, dried with $MgSO_4$ and the solvent evaporated. In most cases the pure DCNQI derivative was obtained after one crystallization.

2-Chloro-N,N′-dicyano-5-iodo-1,4-benzoquinone Diimine (**2a**): GP5 with **1a** (3.50 g, 13.1 mmol) in CH_2Cl_2 (50 ml, 8 h). From toluene (150 ml)/methylcyclohexane (300 ml) deep red crystals of **2a** (2.50 g, 61%), m.p. 210°C (dec.) were obtained. − IR (KBr): $\tilde{\nu}$ = 3040 cm^{-1} (=C−H), 2175 (C≡N), 1555 (C=C), 1540 (C=N), 1240, 1090, 1040, 890, 805, 805, 645. − UV (CH_3CN): λ_{max} (lg ε) = 210 (4.04), 340 (4.32), 350 (4.39), 3.68 sh (4.28). − ^1H NMR ($CDCl_3$, 250 MHz): δ = 7.83 (s, 1 H, 3-H), 8.38 (s, 1 H, 6-H). − ^{13}C NMR: Solubility too low. − MS (70 eV); *m/z* (%): 318 (36) [M^+ (^{37}Cl)], 316 (100) [M^+ (^{35}Cl)], 281 (8) [M^+ (^{35}Cl) − ^{35}Cl], 189 (36) [M^+(^{35}Cl) − I]. − $C_8H_2N_4ClI$ (316.5): calcd. C 30.36, H 0.64, N 17.71; found C 30.23, H 0.89, N 18.18.

2-Bromo-N,N′-dicyano-5-iodo-1,4-benzoquinone Diimine (**2b**): GP5 with **1b** (4.00 g, 12.0 mmol) in CH_2Cl_2 (120 ml) 16 h. The crude product (3.50 g) yielded from toluene (100ml)/methylcyclohexane (400 ml) red-brown crystals of **2b** (3.13 g, 72%), m.p. 226°C (dec.). − IR (KBr): $\tilde{\nu}$ = 3040 cm^{-1} (=C−H), 2175 (C≡N), 1560 (C=C), 1540 (C=N), 1325, 1010, 890, 795. − UV (CH_3CN): λ_{max} (lg ε) = 355 (4.32), 370 sh (4.24). Due to the very low solubility NMR spectra of **2b** could not be recorded. − MS (70 eV); *m/z* (%): 362 (83) [M^+ (^{81}Br)], 360 (76) [M^+(^{81}Br)], 254 (76)[M^+(^{81}Br) − ^{81}Br − CN], 127 (78) [I], 77 (100) [C_4HN_2]. − $C_8H_2N_4BrI$ (360.9): calcd. C 26.62, H 0.56, N 15.53; found C 26.66, H 0.65, N 15.21.

N,N′-Dicyano-2,5-diiodo-1,4-benzoquinone Diimine (**2c**): GP5 with **1c** (1.00 g, 2.78 mmol) in CH_2Cl_2 (20 ml), 14 h. From toluene (60 ml)/methylcyclohexane (100 ml) deep red needles of **2c** (476 mg, 42%), m.p. 233°C (dec.) were isolated. − IR (KBr): $\tilde{\nu}$ = 3020 cm^{-1} (=C−H), 2165 (C≡N), 1545 (C=C), 1555 (C=N), 1225, 1000,740. − UV (CH_3CN): λ_{max} (lg ε) = 335 sh (4.17), 3.57 (4.26), 399 sh (3.86). Due to low solubility, signals of lower intensity could not be recorded. − MS (70 eV); *m/z* (%): 408 (100) [M^+], 281 (32) [M^+ − I], 154 (19) [M^+ − 2 I], 127 (54) [I], 77 (60) [C_3HN_2]. − $C_8H_2N_4I_2$ (408.0): calcd. C 23.55, H 0.50, N 13.74; found C 23.55, H 0.48, N 13.45.

2-Chloro-N,N′-dicyano-5-methoxy-1,4-benzoquinone Diimine (**2d**): GP5 with **1d** (660 mg, 3.80 mmol) in CH_2Cl_2 (60 ml), 7 h. From toluene (50ml)/methylcyclohexane (100 ml) red-brown needles of **2d** (615 mg, 73%), m.p. 185°C (dec.) were obtained. − IR (KBr): $\tilde{\nu}$ = 3020 cm^{-1} (=C−H), 2165 (C≡N), 1555 (C=C), 1535 (C=N), 1220. − UV (CH_3CN): λ_{max} (lg ε) = 260 nm (3.49), 350 (4.60), 370 sh (4.19), 430 (3.31). − ^1H NMR ($CDCl_3$, 250 MHz): *anti*: δ = 4.04 (s, 3 H, OCH_3), 6.74 (s, 1 H, 6-H), 7.66 (s, 1 H, 3-H); *syn*: δ = 4.10 (s, 3 H, OCH_3), 6.62 (s, 1 H, 6-H), 7.32 (s, 1 H, 3-H). − ^{13}C NMR ($CDCl_3$, 200 MHz): δ = 112.39, 113.03 (C≡N), 134.73 (C-2), 178.25 (C-1, -4); *syn*: δ = 57.92 (OCH_3), 103.47 (C-6), 132.12 (C-2); *anti*: δ = 57.47 (OCH_3), 102.74 (C-6), 126.93 (C-3). Due to low solubility signals of lower intensity could not be recorded. − MS (70 eV); *m/z* (%): 222 (25) [M^+ (^{35}Cl) − ^{35}Cl − OCH_3], 130 (100) [M^+ (^{37}Cl) − ^{35}Cl − OCH_3CN). − $C_9H_5ClIN_4O$ (220.6): calcd. C 48.99, H 2.29, N 25.40; found C 49.17, H 2.21, N 25.19.

2-Bromo-N,N′-dicyano-5-methoxy-1,4-benzoquinone Diimine (**2e**): GP5 with 2-bromo-5-methoxy-1,4-benzoquinone[10] (**1e**, 1.00 g, 4.61 mmol) in CH_2Cl_2 (50 ml), 20 h. The crude product (1.08 g) was crystallized from toluene (150 ml)/methylcyclohexane (220 ml) to afford brown needles of **2e** (840 mg, 69%), m.p. 180°C (dec.). − IR (KBr): $\tilde{\nu}$ = 3035 cm^{-1} (=C−H), 2170 (C≡N), 1560 (C=C), 1555 (C=N), 1230. − UV (CH_3CN): λ_{max} (lg ε) = 293 nm (3.56), 340 sh (4.39), 355 (4.44), 365 sh (4.29), 440 (2.94). − ^1H NMR ($CDCl_3$, 250 MHz): *anti*: δ = 4.04 (s, 3 H, OCH_3), 6.74 (s, 1 H, 6-H), 7.92 (s, 1 H, 3-H); *syn*: δ = 4.06 (s, 3 H, OCH_3), 6.64 (s, 1 H, 6-H), 7.58 (s, 1 H, 3-H). − ^{13}C NMR ($CDCl_3$, 200 MHz): δ = 112.46, 113.22 (C≡N), 168.74 (C-1), 171.41 (C-4); *syn*: δ = 62.22 (OCH_3), 105.10 (C-6), 132.87 (C-3), 137.53 (C-2); *anti*: δ = 59.33 (OCH_3), 101.77 (C-6), 129.40 (C-3), 137.19 (C-2). Due to low solubility signals of lower intensity could not be recorded. − MS (70 eV); *m/z* (%): 266 (46) [M^+ (^{81}Br)], 264 (32) [M^+ (^{79}Br)], 211 (37) [M^+ (^{81}Br) − ^{81}Br − OCH_3], 155 (72) [M^+ (^{79}Br) − OCH_3], 130 (100) [M^+ (^{81}Br) − ^{79}Br − OCH_3 − CN]. − $C_9H_5N_4BrO$ (265.1): calcd. C 40.78, H 1.91, N 21.14; found C 40.68, H 1.64, N 20.93.

N,N′-Dicyano-2-iodo-5-methoxy-1,4-benzoquinone Diimine (**2f**): GP5 with **1f** (2.50 g, 9.47 mmol) in CH_2Cl_2 (100 ml), 16 h. From toluene (50 ml)/methylcyclohexane (160 ml) red-violet crystals of **2f** (1.67 g, 56%), m.p. 209°C (dec.) were isolated. − IR (KBr): $\tilde{\nu}$ = 3020 cm^{-1} (CH), 2170 (C≡N), 1600 (C=C), 1545 (C=N), 1445, 1395, 1285, 1220, 1175, 1030, 990, 935, 890, 850, 820. − UV (CH_3CN): λ_{max} (lg ε) = 304 nm sh (3.81), 364 (4.25), 379 sh (4.21). − ^1H NMR ($CDCl_3$, 250 MHz): δ = 4.04 (s, 3 H, OCH_3), 6.79 (s, 1 H, 6-H), 8.26 (s, 1 H, 3-H) [*anti*-**2f**, 77%]; 4.07 (s, 3 H, OCH_3), 6.67 (s, 1 H, 6-H), 7.93 (s, 1 H, 3-H) [*syn*-**2f**, 23%]. − MS (70 eV); *m/z* (%): 314 (100) [M^+ − 2 H], 312 (49) [M^+], 299 (30) [M^+ + 2 H − CH_3]. − $C_9H_5IN_4O$ (312.1): calcd. C 34.64, H 1.62, N 17.95; found C 34.84, H 1.62, N 18.28.

N,N′-Dicyano-2-methyl-5-trifluoromethyl-1,4-benzoquinone Diimine (**2g**): GP5 with **1g** (4.75 g, 25.0 mmol) in CH_2Cl_2 (100 ml), 16 h. Crystallization of the crude product (3.40 g) from methylcyclohexane yielded orange crystals of **2g** (2.35 g, 39%), m.p. 154°C (dec.). − IR (KBr): $\tilde{\nu}$ = 3040 cm^{-1} (CH), 2180 (C≡N), 1640, 1590 (C=C), 1430, 1290, 1175, 1160, 1040, 910. − UV (CH_3CN): λ_{max} (lg ε) = 327 nm (4.38), 340 sh (4.34). − ^1H NMR ($CDCl_3$, 250 MHz): δ = 2.38 (s, 3 H, CH_3), 7.46 (s, 1 H, 3-H), 7.83 (s, 1 H, 6-H). − ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 16.02 (q, CH_3), 127.39

(d, C-3), 127.90 (d, C-6), 146.06 (s, C-2), 169.62 (s, C-4), 172.91 (s, C-1). − MS (70 eV); *m/z* (%): 240 (20) [M^+ + 2 H], 238 (77) [M^+], 186 (100) [M^+ − 2 CN]. − $C_{10}H_5F_3N_4$ (238.2): calcd. C 50.43, H 2.12, N 23.52; found C 50.41, H 2.17, N 23.04.

N,N′-Dicyano-2-methoxy-5-trifluoromethyl-1,4-benzoquinone Diimine (**2h**): GP5 with **1h** (5.15 g, 25.0 mmol) in CH_2Cl_2 (100 ml), 16 h. The crude product (5.45 g) afforded from toluene (90 ml)/methylcyclohexane (280 ml) orange-red, microcrystalline **2h** (4.01 g, 63%), m.p. 136°C. − IR (KBr): $\tilde{\nu}$ = 3060 cm^{-1}, 3040, 3020, 2940 (CH), 2170 (C≡N), 1630, 1580 (C=C), 1555 (C=N), 1410, 1275, 1240, 1165, 1030, 1000, 945, 915, 860, 670, 650. − UV (CH_3CN): λ_{max} (lg ε) = 330 nm (4.30), 344 sh (4.24), 425 (3.72). − ^1H NMR ($CDCl_3$, 250 MHz): δ = 4.08 (s, 3 H, OCH_3), 6.74 (s, 1 H, 3-H), 7.78 (s, 1 H, 6-H) [*anti*-**2g**, 497%]; 4.11 (s, 3 H, OCH_3), 6.64 (s, 1 H, 3-H), 7.53 (s, 1 H, 6-H) [*syn*-**2g**, 51%]. − MS (70 eV); *m/z* (%): 256 (55) [M^+ + 2 H], 254 (100) [M^+]. − $C_{10}H_5F_3N_4O$ (254.2): calcd. C 47.26, H 1.98, N 22.04; found C 48.54, H 1.91, N 22.08.

N,N′-Dicyano-2,5-bis(trifluoromethyl)-1,4-benzoquinone Diimine (**2i**): GP5 with **1i** (1.46 g, 5.00mmol) in CH_2Cl_2 (70 ml), 16 h. The crude product (0.86 g) was just dissolved in boiling toluene. Addition of hot methylcyclohexane until the solution turned slightly turbid and cooling of the mixture yielded a violet powder of **2i** (228 mg, 16%), m.p. 180°C (dec.). The main crystal fraction contained a mixture of **2i** and its dihydro derivative [ν(C≡N): 2255 cm^{-1}; ν(C=C): 1525 cm^{-1} (cf. ref.[25])]. − IR (KBr): $\tilde{\nu}$ = 3055 cm^{-1} (CH). 2180 (C≡N), 1555 (C=N), 1395, 1290, 1160, 1035, 910, 835, 740. − UV (CH_3CN): λ_{max} (lg ε) = 316 nm sh (4−19). 330 (4.26), 346 (4.24). − MS (70 eV); *m/z* (%): 294 (28) [M^+ + 2 H], 292 (100) [M^+]. − $C_{10}H_2F_6N_4$ (292.1): calcd. C 41.11, H 0.69, N 19.18; found C 41.21, H 1.12, N 19.46.

2,5-Bis(chloromethyl)-N,N′-dicyano-1,4-benzoquinone Diimine (**2j**): GP5 with 2,5-bis(chloromethyl)-1,4-benzoquinone[16][17] **1j** (2.48 g, 12 mmol) in CH_2Cl_2 (50 ml), 4 h. Crystallization from toluene yielded yellow crystals of **2j** (2.37 g, 78%), m.p. 137−139°C. − IR (KBr): $\tilde{\nu}$ = 3052, 3022, 2970 (C−H), 2175 (C≡N), 1603 (C=C), 1571 (C=N), 1298, 1152, 918, 728. − ^1H NMR ($CDCl_3$/TMS): δ = 4.62 (d, 4 H, CH_2Cl, $^4J_{H-H}$ = 1.6 Hz), 7.70 (t, 2 H, 3,6-quinoid, $^4J_{H-H}$ = 1.5 Hz. − ^{13}C NMR ($CDCl_3$/TMS): δ = 39.1 (s, CH_2Cl), 112.5 (C≡N), 128.3 (3-, 6-C), 144.7 (2-, 5-C), 173.4 (1-, 4-C). − $C_{10}H_6Cl_2N_4$ (253.1): calcd. C 47.46, H 2.39, N 22.14; found: C 47.17, H 2.37, N 21.80.

N,N′-Dicyano-2,5-bis(fluoromethyl)-1,4-benzoquinone Diimine (**2l**): At 0°C $Et_3N{\cdot}3$ HF in CH_2Cl_2 (5 ml) was slowly added to titanium tetrachloride (2.28 g, 16.0 mmol) in dry CH_2Cl_2 (10 ml). After stirring for 2 h at room temp., bis(trimethylsilyl)carbodiimide (2.44 g, 15.0 mmol) was added to the yellow solution in an ultrasonic bath. A deep red precipitate formed. After 30 min, **1l** (0.69 g, 4.0 mmol) in CH_2Cl_2 (3 ml) was added at 0°C and the reaction monitored by TLC (SiO_2, toluene) until **1l** was consumed (20−40 min). Work up acccording to GP5. Flash chromatography (SiO_2, toluene/acetic acid, 200:1). Fraction 1: **2l** (170 mg, 19%) yellow powder, m.p. 176−178°C. − IR (KBr): $\tilde{\nu}$ = 3034, 2945 (C−H), 2180 (C≡N), 1602 (C=C), 1568 (C=N). − ^1H NMR ($CDCl_3$/TMS): δ = 5.50 (q, 4 H, CH_2F, $^2J_{H-F}$ = 46 Hz, $^4J_{H-F}$ = 1.7 Hz), 7.55 (m, 2 H, quinoid H). − ^{13}C NMR ($CDCl_3$/TMS): δ = 78.4 (d, CH_2F, J'_{C-F} = 177.5 Hz), 112.3 (C≡N), 124.8 (d, 3-, 6-C, $^3J_{C-F}$ = 12.6 Hz), 144.9 (d, 2-, 5-C, $^2J_{C-F}$ = 18.2 Hz), 172.6 (s, 1-, 4-C). − $C_{10}H_6F_2N_4$ (220.2): calcd. C 54.55, H 2.75, N 25.45; found: C 54.30, H 2.76, N 25.16. − Fraction 2: Mixture of 4-chloromethyl-*N,N′*-dicyano-2-fluoromethyl-1,4-benzoquinone diimine (**2k**) and the dichloro derivative **2j** (190 mg) which could not be separated without decomposition.

N,N′-Dicyano-2,5-dideuterio3,6-dimethyl-1,4-benzoquinone Diimine (**2m**): GP5 with **1m** (2.50 g, 18.1 mmol) in CH_2Cl_2 (100 ml), 16 h. From acetonitrile (250ml) bronze-colored plates of **2m** (2.23 g, 80%), m.p. 180°C (dec.). − IR (KBr): $\tilde{\nu}$ = 2255 cm^{-1} (C−D), 2170 (C≡N), 1578 (C=C), 1530 (C=N), 1425, 1380, 1340, 1223, 1113, 1085, 1030, 1000, 920, 800, 770, 680, 623. − MS (70 eV); *m/z* (%): 188 (73) [M^+ + 2 H], 186 (100) [M^+], 159 (95) [M^+ − HCN], 158 (43) [M^+ − DCN]. − $C_{10}H_6D_2N_4$ (186.2): calcd. C 64.51, H 4.45, N 30.09; found C 64.99, H 4.45, N 30.11.

N,N′-Dicyano-2-methyl-5-trideuteriomethyl-1,4-benzoquinone Diimine (**2n**)[47]: GP5 with **1n** (2.78 g, 20.0 mmol) in CH_2Cl_2 (100 ml), 16 h. From acetonitrile (300 ml) bronze-colored scales of **2n** (3.01 g, 80%), m.p. 176°C, were isolated. − IR (KBr): $\tilde{\nu}$ = 2160 cm^{-1} (C≡N), 1573 (C=C), 1523 (C=N), 1360, 1287, 1175, 1030, 1003, 923, 890, 825, 787, 633, 620. − MS (70 eV); *m/z* (%): 189 (63) [M^+ + 2 H], 187 (100) [M^+], 160 (50) [M^+ − HCN], 159 (58) [M^+ − DCN]. − $C_{10}H_5D_3N_4$ (187.2): calcd. C 64.17, H 4.49, N 29.93; found C 63.75, H 4.31, N 29.97.

N,N′-Dicyano-2,5-bis(trideuteriomethyl)-1,4-benzoquinone Diimine (**2o**)[47]: GP5 with **1o** (6.25 g, 35.0 mmol) in CH_2Cl_2 (100 ml), 16 h. Crystallization from acetonitrile (150 ml) yielded bronze-colored plates of **2o** (1.39 g, 84%), m.p. 201°C (dec.). − IR (KBr): $\tilde{\nu}$ = 3010 cm^{-1} (C−H), 2165 (C≡N), 1573 (C=C), 1525, (C=N), 1278, 1183, 1028, 925, 873, 850, 760, 650, 603. − MS (70 eV); *m/z* (%): 192 (84) [M^+ + 2 H], 190 (100) [M^+], 162 (71) [M^+ − DCN]. − $C_{10}H_2D_6N_4$ (190.2): calcd. C 63.17, H 4.59, N 29.47; found C 63.57, H 4.17, N 30.30.

N,N′-Dicyano-2,5-dideuterio-3,6-bis(trideuteriomethyl)-1,4-benzoquinone Diimine (**2p**): GP5 with **1p** (2.02 g, 14.0 mmol) in CH_2Cl_2 (100 ml), 16 h. From acetonitrile orange scales of **2p** (2.11 g, 78%) were isolated. − IR (KBr): $\tilde{\nu}$ = 2250 cm^{-1} (C−D), 2160 (C≡N), 1558 (C=C), 1530, 1520 (C=N), 1410, 1345, 1330. 1200, 1130, 1028, 765, 735, 643. − UV (CH_3CN): λ_{max} (lg ε) = 343 nm (4.46), 358 sh (4.30). − MS (70 eV); *m/z* (%): 194 (17) [M^+ + 2 H], 192 (100) [M^+], 164 (74) [M^+ − DCN]. − $C_{10}D_8N_4$ (192.1): calcd. C 62.51, H 4.66, N 29.16; found C 62.25, H 4.21, N 29.28.

N,N′-[^{13}C]Dicyano-2,5-dimethyl-1,4-benzoquinone Diimine (**2q**): (a) $Br^{13}CN$ was obtained from $K^{13}CN$ (15% ^{13}C) and bromine by adapting ref.[48]. Yield 75%, m.p. 28°C (75−85%, m.p. 28°C for BrCN[47]). In a variation of ref.[27] $Br^{13}CN$ (13.9 g, 131 mmol) in DE (50 ml) was added to ammonia (4.60 g, 270 mol) in ethanol (70 ml) at −78°C in a pressure vessel and stirred for 16 h at 20°C. Precipitated NH_4Br was filtered off and washed with DE (3 × 50 ml). From the concentrated solution (40 ml) further NH_4Br was removed and the solvent evaporated to yield [^{13}C]cyanamide (5.40 g, 98%) which was dissolved in DE (50 ml) and added within 1 h at 0°C to trimethylsilyl chloride (34.1 ml, 270 mmol) in DE (140ml)[26]. After stirring at 20°C (2 h), the precipitate was filtered off and washed with DE. From the organic phase bis(trimethylsilyl)-[^{13}C]carbodiimide (17.6 g, 74%), b.p. 58−61°C/20 Torr, was isolated.− (b) GP5 with a different ratio of reagents: 2,5-Dimethyl-1,4-benzoquinone (1.36 g, 10.0mmol) in CH_2Cl_2 (50 ml), $TiCl_4$ (7.60 g, 40.0mmol), bis(trimethylsilyl)-[^{13}C]carbodiimide (4.66 g, 25.0 mmol), 4.5 h. From acetonitrile (100ml) umber-colored plates of **2g** (1.30 g, 70%), m.p. 189°C (dec.), were isolated (unlabelled: m.p. 189°C[28]). − IR (KBr): $\tilde{\nu}$ = 3020 cm^{-1} (=C−H), 2980 (C−H), 2177, 2167 (C≡N), 2127, 2112 (^{13}C≡N), 1580 (C=C), 1535, 1525 (C=N). − $C_{10}H_8N_4$ (184.4): calcd. C 65.10, H 4.37, N 30.51; found C 65.21, H 4.41, N 30.48.

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[50] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-100695 (**1l**). Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: int. code + 44(1223)336-033, E-mail: deposit@chemcrys.cam.ac.uk].
[51] Deuterium was calculated as hydrogen (20/18 per D) since H and D were determined as H_2O. The actual content of deuterium was determined by MS.

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