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Synthesis of 2,5-Dihydroxy-3-(indol-3-yl)benzoquinones by Acid-Catalyzed Condensation of Indoles with 2,5-Dichlorobenzoquinone

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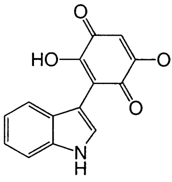
Three methods for the conjugate addition of indoles to 2,5-dichlorobenzoquinone have been developed. A wide variety of indoles substituted with halogen, alkyl, alkoxy, and aryl groups participate in anaerobic condensation reactions promoted by HCl, H_2SO_4, or CH_3CO_2H. The hydroquinone product is partially oxidized by excess dichlorobenzoquinone and fully converted to the 2,5-dichloro-3-(indol-3-yl)benzoquinone targets by DDQ or Ag_2CO_3 oxidation. 2,5-Dihydroxy-3-(indol-3-yl)benzoquinones can be obtained from the dichlorides by alkaline hydrolysis. The rotational characteristics of the biaryl bond created in these reactions have been examined by theoretical and spectroscopic methods.

Introduction

The indol-3-ylbenzoquinone substructure (**1**) is present in a wide range of natural products with diverse biological activity. Our interest in the synthesis of a bisindolylquinone member of this family, demethylasterriquinone B1, was based on its original report as an orally active nonpeptidyl mimic of insulin.[1] It has subsequently been shown to have activity as an agonist of the nerve growth factor receptor.[2] Demethylasterriquinone analogues also inhibit the interaction between the SH2 (*Src* homology 2) domains of receptor tyrosine kinases and their “adapter” protein Grb2, exhibiting anticancer activity as a consequence.[3] Bisindolylquinones containing substructure **1** have been isolated from a wide range of fungi, including *Aspergillus terreus, Chaetomium* sp., and *Pseudomassaria* sp.[4]

Synthetic approaches to the structural unit **1** based on the condensation of indole with a quinone are quite old. Historically, the reaction of indole with benzoquinone itself goes back to 1911, though these workers did not isolate their red product.[5] This reaction was reinvestigated by Bu’Lock in 1951, but the product was isolated only in low yield.[6] The efficiency of the condensation of 2-methylindole with excess benzoquinone was much improved (90%) by conducting it anaerobically (eq 2) or using an acidic clay as catalyst.[7] A second equivalent of quinone apparently serves to oxidize the initial hydroquinone addition product (vide infra). Under the same reaction conditions, indole provides the addition product in 70% yield.



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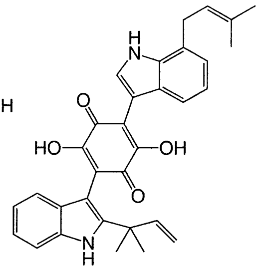

demethylasterriquinone B1

2

Our earlier study[8] concerning the HCl-catalyzed condensation of indoles with 2,5-dichlorobenzoquinone has been expanded to include many more indoles. The 2,5-substitution of the quinone with heteroatoms was needed to provide precursors to the 2,5-dihydroxybenzoquinones of the fungal natural products. Two other acid-catalyzed addition protocols have been introduced that enable the production from diverse indoles of indol-3-ylquinones that cannot be obtained using our original procedure.

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(1) Zhang, B.; Salituro, G.; Szalkowski, D.; Li, Z.; Zhang, Y.; Royo, I.; Vilella, D.; Diez, M. T.; Pelaez, F.; Ruby, C.; Kendall, R. L.; Mao, X.; Griffin, P.; Calaycay, J.; Zierath, J. R.; Heck, J. V.; Smith, R. G.; Moller, D. E. *Science* **1999**, *284*, 974−977.

(2) Wilkie, N.; Wingrove, P. B.; Bilsland, J. G.; Young, L.; Harper, S. J.; Hefti, F.; Ellis, S.; Pollack S. J. *J. Neurochem*. **2001**, *78*, 1135−45.

(3) Harris, G. D.; Nguyen, A.; Strawn, L.; Fong, A.; App, H.; Le, T.; Sutton, B.; Tang, P. C. *Abstracts of Papers*, 215th National Meeting of the American Chemical Society, St. Louis, MO, March 29 to April 3, 1998; American Chemical Society: Washington, DC, 1998; MEDI 163. Alvi, K. A.; Pu, H. Luche, M.; Rice, A.; App, H.; McMahon, G.; Dare, H.; Margolis, B. *J. Antibiot*. **1999**, *52*, 215−223.

(4) Arai, K.; Yamamoto, Y. *Chem. Pharm. Bull*. **1990,** *38*, 2929−32. Kaji, A.; Saito, R.; Hata, Y.; Kiriyama, N. *Chem. Pharm. Bull*. **1999**, *47*, 77−82.

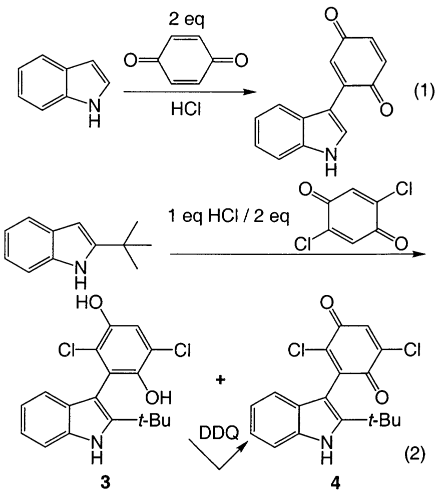
(5) Mohlau, R.; Redlich, R. *Ber. Dtsch. Chem. Ges*. **1911**, *44*, 3605.

(6) Bu’Lock, J. D.; Harley-Mason, J. *J. Chem. Soc*. **1951**, 703.

(7) Corradini, M. G.; Costantini, C.; Prota, G. Schultz, T. M. *Gazz. Chim. Ital*. **1989**, *119*, 153−4. Maiti, A. K.; Bhattacharya, P. *J. Chem. Res., Synop*. **1997**, 424−425.

(8) Pirrung, M. C.; Park, K.; Li, Z. *Org. Lett*. **2001**, *3*, 365−7.

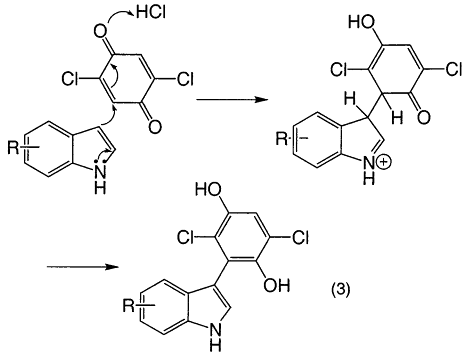
10.1021/jo0204597 CCC: $22.00



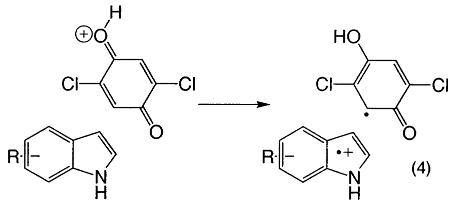
Results

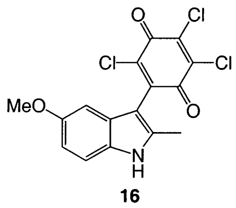
To begin this study, we examined the anaerobic condensation of 2-*tert*-butylindole (1 equiv) with a variety of quinones (2 equiv) promoted by HCl (1 equiv) in THF. The quinones studied included 2,5-dihydroxybenzoquinone, 2,5-diacetoxybenzoquinone, 2,5-dichloro-3,6-dimethoxy-benzoquinone, tetrabromobenzoquinone, 2,5-dibromobenzoquinone, and 2,5-dichlorobenzoquinone. Only in the latter case was any product obtained. In contrast to the reported[7] reaction of indole with benzoquinone, both the hydroquinone **3** and the desired quinone **4** were obtained, despite the fact that 2 equiv of dichlorobenzoquinone was used. Evidently, the oxidation of **3** by dichlorobenzoquinone is slow compared to the oxidation step in eq 1. This mixture of oxidation states was addressed by oxidation of **3** to **4** with excess dichlorodicyanobenzoquinone (DDQ).

A presumptive mechanism for the formation of indol-3-ylquinones in this reaction is shown in eq 3. The nucleophilic 3-position of the indole adds to the unsubstituted position of the quinone, which is activated by protonation. The initial addition product tautomerizes to the hydroquinone, which is partially oxidized by 2,5-dichlorobenzoquinone. A priori, one could propose nucleophilic attack at either quinone carbon. The vinylogous acid chloride character of the substituted carbon might suggest this site would be favored. Sterics might favor the unsubstituted carbon. Electronic effects can explain the observation of attack at the unsubstituted carbon. AM1 molecular orbital calculations show the Mulliken charge at the substituted carbon is −0.10 and that at the unsubstituted carbon is −0.18.



Reaction optimization and examination of the scope of this acid-catalyzed addition/DDQ oxidation process were then undertaken. In a number of cases where high yields of the condensation product are not obtained, a significant amount of 2,5-dichlorobenzoquinone is recovered after the reaction despite the fact that this starting material was depleted; this was explained by the formation of 2,5-dichlorohydroquinone (TLC) during the reaction. Unreacted indoles are generally not recovered in such cases. Products of substitution of one of the chlorides of DDQ by the indole are sometimes observed, but indole-derived products are not always found, suggesting that the indoles are somehow destroyed. One explanation for these observations is an alternative mechanism for the addition reaction (eq 4). An electron-transfer reaction between the indole and the protonated quinone would give a radical/radical cation pair. This pair could couple to produce the same intermediate proposed in the simple polar mechanism. Alternatively, if that coupling were slow due to electronic or steric factors in the indole, the indole radical cation could undergo side reactions, and the semiquinone radical could be further reduced. The chemisty of indole radical cations generated electrochemically is known;[9] they generally undergo oligomerization, with prevalent coupling at the 3- and 6-positions, as those are the sites of maximum spin density. Another side reaction occasionally observed was formation of trichloroindol-3-ylquinones. These byproducts could be formed by reaction of the product indol-3-ylquinone with HCl, leading to a trichlorohydroquinone that is further oxidized. This process can be eliminated by reducing the HCl to 0.3 equiv. The chlorination side products in the production of indolylquinones **8** and **9** were identified as **16** and **17**.

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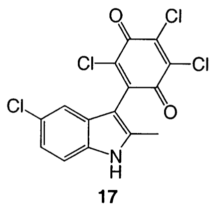
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For study of the reaction scope, a standard protocol was adopted using 1 equiv of indole and 2 equiv of quinone with 1 equiv of concentrated HCl in THF. After the mixture is stirred overnight (10 h) at room temperature, DDQ (2 equiv) is added and the reaction mixture is stirred for 2−4 h. Examples are collected in Table 1. The reactivity of indoles in the condensation reaction is a consequence of both steric and electronic factors. Indoles

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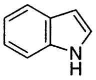
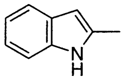
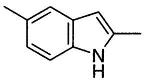
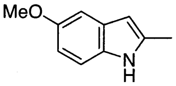
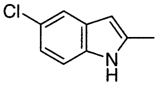
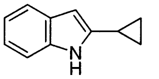
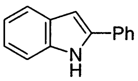
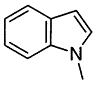
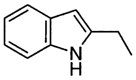
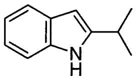
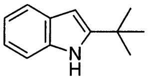
[9] Jensen, G. M.; Goodin, D. B.; Bunte, S. W. *J. Phys. Chem.* **1996**, *100*, 954. Walden, S. E.; Wheeler, R. A. *J. Chem. Soc., Perkin Trans. 2* **1996**, 2663. Mackintosh, J. G.; Wright, S. J.; Langridge-Smith, P. R. R.; Mount, A. R. *J. Chem. Soc., Faraday Trans.* **1996**, 4109. Naruto, S.; Yonemitsu, O. *Chem. Pharm. Bull.* **1980**, *28*, 900.

TABLE 1

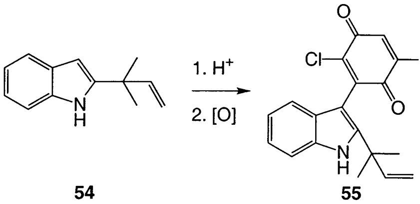
Indole	Indolylquinone	Yield
	**5**	70%
	**6**	97%
	**7**	91%
	**8**	89%
	**9**	75%
	**10**	95%
	**11**	89%
	**12**	87%
	**13**	95%
	**14**	70%
	**15**	54%

bearing electron-withdrawing groups do not participate. The most electron-rich indoles with a substituent at the 2-position are the best reactants. Indoles with no substitution on the heterocycle give a slightly lower yield. This reaction is limited by steric effects, and the limit is reached at 2-*tert*-butylindole. Indoles with any higher *tert*-alkyl substitution, such as 2-isoprenylindole or 2-(1,1-dimethylpropyl)indole, fail in this reaction.

This HCl-catalyzed process constituted an encouraging initial step toward general synthetic access to indol-3-ylquinones, but was still limited by the side reactions involving HCl. In addition, many of the desired indol-3-ylquinones (**18** and **19**) cannot be synthesized using this procedure. Improvements were therefore sought with other mineral acid promoters that would not offer nucleophilic counterions that could add to the product. A selection (H_3PO_4, HBF_4, $HClO_4$, H_2SO_4) was screened in pilot reactions, and sulfuric acid was found superior. A new reaction protocol was therefore developed using sulfuric acid in THF. Some of these reactions were inconveniently slow, so a solvent change was examined, and it was discovered that acetonitrile enhances the reaction rate. The results of the application of the sulfuric acid method to a large range of indoles are summarized in Table 2. These reactions were followed by TLC until all of the indole was consumed, and require from one week to half an hour. In cases where low yields are reported, we generally observe that the cause is instability of the indole to the acidic reaction conditions.

Because of the sensitivity of some indoles to acid, an even milder acid catalyst was sought. Several organic acids were screened, including acetic acid, *p*-toluenesulfonic acid, and trifluoroacetic acid. It was found that refluxing acetic acid is very effective in promoting the addition reaction. In addition, milder reagents for the oxidation of the hydroquinone to the quinone were sought. The potency of DDQ is clearly unnecessary for the oxidation phase of this transformation, as partial oxidation occurs even with dichlorobenzoquinone. Convenience was also a consideration, which led us to silver carbonate on Celite (Fetizon's reagent[10]), as this reagent can be removed at the end of the reaction by simple filtration.

We offer 2-isoprenylindole (**54**) as an example of the value of the improving technologies for the acid-promoted addition of indoles to quinones. We sought to perform this reaction as a key step in our total synthesis of demethylasterriquinone B1. Conversion of 2-isoprenylindole to **55** cannot be accomplished with the HCl protocol, but with the acetic acid method, the yield is 80% (M. C. Pirrung and Y. Liu, unpublished data).



(5)

54 **55**

These are clearly electrophilic addition reactions, as electron-donating groups accelerate the reaction (compare **23**/**24** vs **25**). Alkylindoles give good to excellent yields. Halogenated indoles give moderate to good yields. We have never been successful in adding indoles bearing any type of electron-withdrawing group (CHO, NO_2, CO_2R) using any of these protocols. Substitution at the 4-position of the indole affects the reaction negatively, which is readily attributed to a steric effect near the nucleophile. In some instances, it is possible to add indoles bearing unprotected alcohols. On a few occasions, products from the addition of a second equivalent of indole to the indolylquinone to form the bisindolylquinone were observed, but these never exceeded 5% of the products.

The final goal of this study was the production of 2,5-dihydroxybenzoquinones from the indol-3-yl-2,5-dichlorobenzoquinones (eq 5). In the work of Harris,[11] conversion of 1,4-bis(indol-3-yl)-2,5-dibromobenzoquinones to the 2,5-dihydroxybenzoquinone was performed with KOH in MeOH. A challenging aspect of preparing these compounds by the Harris method is their instability

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[10] Balogh, V.; Fetizon, M.; Golfier, M. *J. Org. Chem.* **1971**, *36*, 1339.

[11] Harris, G. D.; Nguyen, A.; App, H.; Hirth, P.; McMahon, G.; Tang, C. *Org. Lett.* **1999**, *1*, 431.

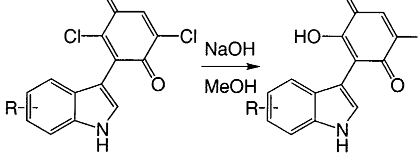
TABLE 2. Yield (%) and Reaction Time (h) in the Acid-Promoted Condensation of Indoles with 2,5-Dichlorobenzoquinone

		procedure A		procedure b		procedure C	
indole	product	yield	time^{a}	yield	time^{b}	yield	time^{b}
indole	**5**	70				75	8
2-methylindole	**6**	97				96	2
2,5-dimethylindole	**7**	91					
2-methyl-5-methoxyindole^{c}	**8**	89					
2-methyl-5-chloroindole^{c}	**9**	75					
2-cyclopropylindole	**10**	95					
2-phenylindole	**11**	89					
N-methylindole	**12**	87					
2-ethylindole	**13**	95					
2-isopropylindole	**14**	70					
2-*tert*-butylindole	**15**	54				90	2
2-(1-methylcyclopropyl)indole	**18**			46	1	90	2
2-(1-methylcyclohexyl)indole	**19**			50	24	91	10
4-fluoroindole	**20**	0	120	16	42	14	22
4-chloroindole	**21**	0	120	54	92		
4-bromoindole	**22**	0	120	50^{d}	24		
4-methoxyindole	**23**			2^{e}	0.5	66	3
4-benzyloxyindole	**24**			1^{e}	0.5	65	3
4-methylindole	**25**			39	21	76	20
5-fluoroindole	**26**			50	5	74	6
5-chloroindole	**27**			56	0.5	72	24
5-bromoindole	**28**			57	0.5	73	24
5-hydroxyindole	**29**			52^{e}	0.5	6	0.5
5-methoxyindole	**30**			96	0.5		
5-benzyloxyindole	**31**			92	0.5		
5-methylindole	**32**			82	6	72	2
6-fluoroindole	**33**			37	5	63	6
6-chloroindole	**34**			58	20	55	6
6-benzyloxyindole	**35**			14^{e}	2	22^{e}	22
6-methylindole	**36**			63	1	75	20
7-methylindole	**37**	81				83	22
7-propylindole	**38**			82	6	81	5
7-*tert*-butylindole	**39**			81	6	82	8
7-phenylindole	**40**			66	12	66	4
7-methoxyindole	**41**	13	20	62	9	50	68
7-benzyloxyindole	**42**			71	5	65	6
7-fluoroindole	**43**					43	48
7-chloroindole	**44**			17	96	63	72
7-bromoindole	**45**			34	72	41	48
7-benzylindole	**46**			89	1		
7-*o*-methylbenzylindole	**47**			88	1		
1*H*-benzo[*g*]indole	**48**			34	48		
2,6-dimethylindole	**49**					89	6
2,7-dimethylindole	**50**			59	2	94	1
6,7-dimethylindole	**51**			90	0.16	88	4
5,6-methylenedioxyindole	**52**			10^{e}	2	29^{d,e}	2
5,6-dimethoxyindole	**53**			9^{e}	24	33^{e}	0.5

[a] Variation from the standard reaction time (10 h). [b] Time for consumption of indole using THF as solvent. [c] Used 0.3 equiv of HCl. [d] Acetonitrile was substituted for THF. [e] Indole unstable under the reaction conditions.

to standard silica gel chromatography, requiring them to be purified by reversed-phase HPLC and limiting the preparative scale on which such reactions could be conducted. Oxalic acid-coated silica gel has been used for purification of the asterriquinones,[12] and it was successfully adopted here as our preparative purification method.

The deceptively simple transformation of 2,5-dichlorobenzoquinones to the dihydroxyquinones by hydrolysis can be problematic with the indol-3-yldichloroquinones. The KOH procedure of Harris provides *no* desired product, as the unsubstituted quinone carbon can be readily attacked by hydroxide, leading eventually to the hydroxylated indol-3-yldichloroquinones. Diligent experimentation provided a reliable protocol involving adding 10% aq NaOH to a warm solution of indol-3-yldichloroquinone in MeOH and heating at reflux for 20−30 min (0.02 M final concentration). The concentration is crucial, as a 2-fold increase causes a decrease in yield by half. Hydrolysis reactions using this method proceed in 52−90% isolated yield. The results of the hydrolysis of these compounds are summarized in Table 3. The indol-3-yldihydroxyquinone products are generally blue-green crystalline compounds.



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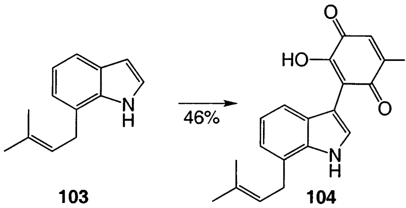
[12] Yamamoto, Y.; Nishimura, K.; Kiriyama, N. *Chem. Pharm. Bull.* **1976**, *24*, 1853−9.

TABLE 3. Yields (%) in the Hydrolysis of Indol-3-yl-2,5-dichlorobenzoquinones

indole	reactant	product	yield
indole	**5**	**56**	59
2-methylindole	**6**	**57**	62
2,5-dimethylindole	**7**	**58**	73
5-methoxy-2-methylindole	**8**	**59**	81
5-chloro-2-methylindole	**9**	**60**	87
2-cyclopropylindole	**10**	**61**	81
2-phenylindole	**11**	**62**	65
N-methylindole	**12**	**63**	62
2-ethylindole	**13**	**64**	77
2-isopropylindole	**14**	**65**	80
2-*tert*-butylindole	**15**	**66**	52
2-(1-methylcyclopropyl)indole	**18**	**67**	87
2-(1-methylcyclohexyl)indole	**19**	**68**	90
4-fluoroindole	**20**	**69**	65
4-chloroindole	**21**	**70**	74
4-bromoindole	**22**	**71**	86
4-methoxyindole	**23**	**72**	82
4-benzyloxyindole	**24**	**73**	81
4-methylindole	**25**	**74**	81
5-fluoroindole	**26**	**75**	72
5-chloroindole	**27**	**76**	62
5-bromoindole	**28**	**77**	56
5-hydroxyindole	**29**	**78**	70
5-methoxyindole	**30**	**79**	63
5-benzyloxyindole	**31**	**80**	63
5-methylindole	**32**	**81**	80
6-fluoroindole	**33**	**82**	80
6-chloroindole	**34**	**83**	71
6-benzyloxyindole	**35**	**84**	83
6-methylindole	**36**	**85**	82
7-methylindole	**37**	**86**	66
7-propylindole	**38**	**87**	73
7-*tert*-butylindole	**39**	**88**	83
7-phenylindole	**40**	**89**	76
7-methoxyindole	**41**	**90**	75
7-benzyloxyindole	**42**	**91**	84
7-fluoroindole	**43**	**92**	75
7-chloroindole	**44**	**93**	70
7-bromoindole	**45**	**94**	71
7-benzylindole	**46**	**95**	85
7-*o*-methylbenzylindole	**47**	**96**	96
1*H*-benzo[*g*]indole	**48**	**97**	70
2,6-dimethylindole	**49**	**98**	73
2,7-dimethylindole	**50**	**99**	84
6,7-dimethylindole	**51**	**100**	75
5,6-methylenedioxyindole	**52**	**101**	57
5,6-dimethoxyindole	**53**	**102**	65

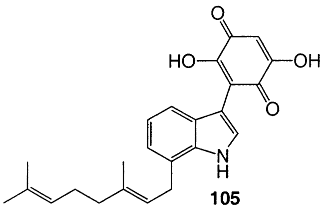
These methods can be applied to the synthesis of interesting natural product substructures. Previous results suggested that the addition of 7-substituted indoles should proceed without difficulty, so 7-prenylindole[13] (**103**) was investigated in the addition reaction. While the sulfuric acid protocol (2 h) is effective, the product is stable only in solution, so it was directly hydrolyzed to provide the asterriquinone "half-molecule" **104** in 46% overall yield. Likewise, 7-geranylindole[13] and 7-farnesylindole[13] can be converted by multistep processes without isolation of the intermediates to **105** (32%) and **106** (31%).

The basic structure of the indol-3-yl-benzoquinones is similar to a biaryl, so it was expected that their preferred conformations as a function of the indole 2-substituent would affect the conjugation length and therefore the UV properties of these compounds. The indole 2-substituent should also affect the barrier to rotation about the biaryl bond. Molecular mechanics minimization (MacSpartan MMFF) of demethylasterriquinone B1 suggests a dihedral angle for the biaryl bond to the 2-unsubstituted indole of 67°, with a rotational barrier of 9 kcal/mol. A dihedral angle of 90° is suggested for the biaryl bond to the 2-isoprenylindole, with a rotational barrier of 50 kcal/mol. Thus, rotation of this bond is effectively locked. For a homologous series of the simple monoindol-3-ylquinones prepared in this study, MMFF-calculated dihedral angles and rotational barriers are given in Table 4. These results suggest that tertiary indole 2-substituents will prevent rotation of the biaryl bond at room temperature. They also show a higher rotational barrier for the dichloroquinones than for the dihydroxyquinones.

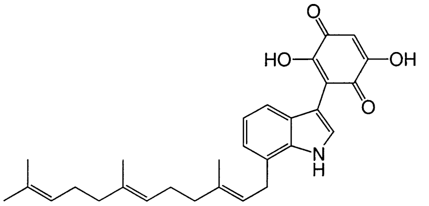


(7)

103 **104**



105



106

UV spectra were recorded for these dichloroquinones and dihydroxyquinones, with the data also summarized in Table 4. The dichloroquinones show two bands, while the dihydroxyquinones show three; this third band is a closely spaced pair of maxima whose relative intensity varies slightly (Figure 1). The absorption maxima of all of these compounds are relatively insensitive to the 2-position substituent, but the extinction coefficients increase modestly with increasing bulk.

Discussion and Summary

One concern in performing the addition of indoles to quinones was a possible secondary reaction of the indolylquinone product with another equivalent of indole, giving a bisindolylquinone. This would defeat our purpose of developing the first stage of a reaction sequence that would be selective in adding two different indoles sequentially. Two factors, stoichiometry and kinetics, impact the observed product composition in this reaction. Ideally, the nucleophilic addition of the indole to the quinone and the oxidation of the resulting hydroquinone would be temporally separated. Performing this reaction sequentially, rather than under equilibrium conditions, is analogous to a kinetic aldol condensation. In principle,

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[13] Pirrung, M. C.; Wedel, M.; Zhao, Y. *Synlett* **2002**, 143.

TABLE 4. Rotational (Molecular Mechanics) and UV−Vis Spectral Properties of Indol-3-yl-2,5-dichlorobenzoquinones and Indol-3-yl-2,5-dihydroxybenzoquinones

		MMFF		peak 1		peak 2		peak 3	
compd	substituent	θ_{min} (deg)	$\Delta G^{\ddagger}$	λ_1	log ϵ_1	λ_2	log ϵ_2	λ_3	log ϵ_3
5	H	73	14.8	214	4.5	270	4.2		
6	Me	78	21.9	220	4.5	270	4.3		
13	Et	79	23.4	219	4.6	270	4.4		
14	*i*-Pr	90	31.8	221	4.6	271	4.4		
15	*t*-Bu	90	31.0	219	4.7	273	4.3		
11	Ph	90	25.3	207	4.9	286	4.4		
56	H	57	9.7	208	4.6			284/290	4.2
57	Me	66	16.0	211	4.6	224	4.6	284/290	4.3
64	Et	74	18.6	209	4.7	224	4.6	283/290	4.4
65	*i*-Pr	72	21.6			225	4.6	284/290	4.4
66	*t*-Bu	90	34.0			222	4.6	283/289	4.4
62	Ph	75	18.2	209	4.6	240	4.5	296	4.5

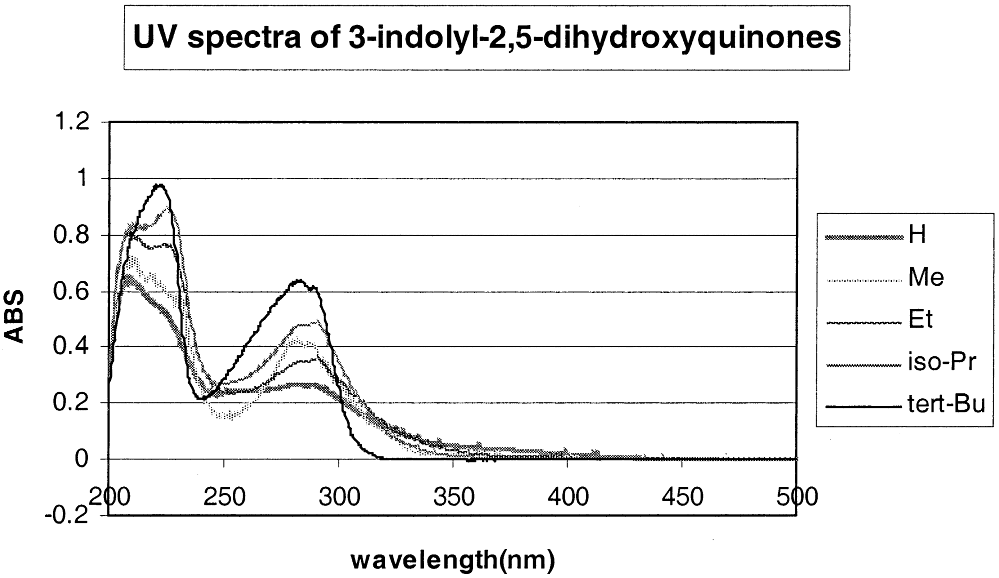
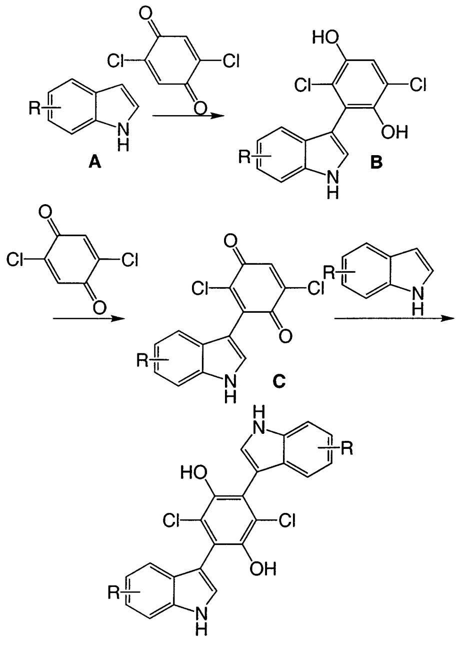


FIGURE 1. UV spectra of 3-indolyl-2,5-dihydroxybennzoquinones (30 μM in MeOH).

performing the reaction anaerobically and using only 1 equiv of quinone should produce hydroquinone **B** and prevent a second addition because no indolylquinone **C** would be present. Of course, if the oxidation of **B** by starting quinone were faster than the initial addition of **A**, limiting the quinone stoichiometry would not prevent production of bisindolylquinone. However, depletion of the starting quinone as the reaction proceeds would make this process slow. Inclusion of a second equivalent of quinone keeps the rate of the addition reaction high throughout consumption of the indole, but could also form some **C**. Kinetic factors make a selective monoaddition reaction possible even though **C** is formed in the presence of the indole. Two components of a reaction rate are the rate constant and the concentration. The rate constant effects that work in favor of the monoaddition reaction are the relatively slow oxidation of **B** to **C**, keeping the **C** concentration low, and the slow protic acid-catalyzed addition of indoles to **C**. The concentration effects are depletion of the indole limiting reagent that is needed for the addition to **C** and the low **C** concentration.

The issue of the reaction mechanism is not easily resolved. Indeed, there may be no single mechanism followed throughout all of the examples studied, with either polar or radical processes being favored by particular reactants and conditions, and with both potentially operating in a particular reaction. Probes for the radical mechanism include two 2-cyclopropylindoles, which did *not* exhibit the ring opening usually indicative



of radical processes. However, the cyclopropyl groups are not located at positions on the indoles that would have the largest spin density[9] if they were converted to their radical cations, so this negative result cannot determine much concerning mechanism. Alternatively, substitution at or near positions of high spin density in the indole radical cation could either aid the coupling by stabilizing the radical or sterically inhibiting indole−indole coupling, or could favor side reactions by inhibiting the radical cation/radical coupling. Examination of the results of coupling the methylated indoles **6**, **25**, **32**, **36**, and **37** under our mildest reaction conditions shows no significant difference in reaction efficiency that would support radical-based mechanisms. We still consider the radical pathway as a viable alternative to the polar mechanism because it provides the only explanation for the production of the reduced quinone in some reactions.

Other methods for the synthesis of bisindolylquinones from indole subunits have involved the condensation of tetrabromobenzoquinone with 2 equiv of a 2-substituted indole under basic conditions. This method was recently used in a synthesis of tetrahydroasterriquinone E.[11] A related method substitutes 2,5-dibromo-3,6-dimethoxybenzoquinone for bromanil, permitting regiochemical control in the base-promoted addition.[14] However, neither of these methods can link a quinone core to an *N*-alkylated indole. This capability proved valuable in a recent study of the effects on biological activity of methyl substitution at all nuclear positions, a “methyl scan”, in the natural product demethylasterriquinone B1.[15]

The synthetic methods described here have provided access to a diverse set of monoindolyldihydroxybenzoquinones. While biological studies are beyond the scope of this paper, members of our synthetic library have exhibited activities against a range of targets, including kinases and phosphatases. This work will be reported separately.

Experimental Section

General Methods. The oxalic acid-precoated silica gel was prepared by the literature procedure: suspension of silica gel in 0.1 N oxalic acid overnight, filtration, washing with H_2O, and drying in an oven at 100 °C overnight. Proton chemical shifts are reported in parts per million using tetramethylsilane (δ 0.00) or residual protons in d_6-acetone (δ 2.04) or d_4-methanol (δ 3.30) as an internal standard. Carbon chemical shifts are reported in parts per million using $CDCl_3$ (δ 77.0), d_6-acetone (δ 29.8), or d_4-methanol (δ 49.0) as an internal standard. Most of the indoles used in this study are commercially available. Those that are not commercially available but known were prepared using literature procedures as follows: 2-ethylindole;[16] 2-cyclopropylindole;[16] 2-*tert*-butylindole;[17] 2-isoprenylindole (**54**);[17] 2-isopropylindole.[18]

2,6-Dimethyl-1*H*-indole. *N*-(2,5-Dimethylphenyl)acetamide (3.00 g, 0.018 mol) was dissolved in anhydrous THF (50 mL) at 0 °C. *n*-BuLi (2.5 M in hexane, 30 mL) was added dropwise under a nitrogen atmosphere. The mixture was then allowed to reflux overnight, diluted with ethyl acetate (50 mL), and then quenched with saturated aqueous ammonium chloride solution (15 mL). The organic layer was separated, washed with brine, dried (Na_2SO_4), and evaporated under reduced pressure. The crude product was purified by flash column chromatography using ethyl acetate/hexane to give the title compound as a yellow solid (0.15 g, 6%). Mp: 87−88 °C (lit.[19] 88.5 °C). ^{1}H NMR ($CDCl_3$): δ 7.94 (1H, br s), 7.35 (1H, d, J = 8.4 Hz), 7.02 (1H, s), 6.86 (1H, d, J = 8.0 Hz), 6.11 (1H, m), 2.40 (3H, s), 2.36 (3H, s).

2,7-Dimethyl-1*H*-indole. *N*-(2,6-Dimethylphenyl)acetamide (5.0 g, 0.03 mol) was dissolved in anhydrous THF (75 mL) at 0 °C. *n*-BuLi (2.5 M in hexane, 42 mL) was added dropwise under a nitrogen atmosphere. The mixture was allowed to reflux overnight, diluted with ethyl acetate (100 mL), and then quenched with saturated aqueous ammonium chloride solution (20 mL). The organic layer was separated, washed with brine, dried (Na_2SO_4), and evaporated under reduced pressure. The crude product was purified by flash column chromatography using ethyl acetate/hexane to give the title compound as a yellow solid (2.6 g, 58%). Mp: 34−35 °C (lit.[19] 35−37 °C). ^{1}H NMR (d_6-acetone): δ 9.78 (1H, br s), 7.26 (1H, d, J = 7.2 Hz), 6.87 (1H, t, J = 7.2 Hz), 6.79 (1H, d, J = 7.2 Hz), 6.12 (1H, m), 2.42 (3H, s), 2.38 (3H, s).

A new indole was prepared using the following procedures.

1-Methylcyclopropanecarboxylic Acid *o*-Tolylamide. 1-Methylcyclopropanecarboxylic acid (2.0 g, 0.02 mol) in benzene (10 mL) was treated with oxalyl chloride (10 mL, 0.11 mol) and DMF (3 drops) at room temperature under stirring for 2 h. The reaction mixture was evaporated to dryness, redissolved in benzene (10 mL), and evaporated to dryness again. The crude acid chloride was dissolved in THF (10 mL) and treated with *o*-toluidine (3.2 mL, 0.03 mol) and triethylamine (2.8 mL). The mixture was allowed to reflux for 1 h and diluted with ethyl acetate. The organic layer was washed with satd aqueous NaCl and dried (Na_2SO_4). After flash column chromatography, the title compound (2.1 g, 56%) was obtained as a white solid. Mp: 142−143 °C. ^{1}H NMR (d_6-acetone): δ 8.15 (1H, br s), 7.55 (1H, dd, J = 8.1, 1.2 Hz), 7.20−7.11 (2H, m), 7.05 (1H, dt, J = 7.5, 1.5 Hz), 2.51 (3H, s), 1.16 (2H, q, J = 3.3 Hz), 0.63 (2H, q, J = 3.6 Hz). ^{13}C NMR (d_6-acetone): δ 172.6, 137.1, 130.3, 126.1, 125.1, 124.7, 20.0, 19.4, 17.4, 15.7. IR (KBr): 3287, 3018, 2979, 2924, 2859, 1761, 1652, 1540, 1291 cm^{-1}. HRMS (EI): m/z calcd for $C_{12}H_{15}NO$ [M$^+$] 189.1154, found 189.1154.

2-(1-Methylcyclopropyl)-1*H*-indole. 1-Methylcyclopropanecarboxylic acid *o*-tolylamide (0.246 g, 1.3 mmol) was dissolved in anhydrous THF (10 mL) at 0 °C. *n*-BuLi (2.65 M in hexane, 2 mL) was added dropwise under a nitrogen atmosphere. The mixture was stirred at 0 °C for 1 h and for 5 h at room temperature. The mixture was diluted with ethyl acetate (10 mL) and quenched with satd aqueous NH_4Cl solution (10 mL). The organic layer was separated, washed with brine, dried (Na_2SO_4), and evaporated under reduced pressure. The crude product was purified by flash column chromatography using ethyl acetate/hexane to give the title compound as a yellow solid (0.19 g, 86%). Mp: 61−62 °C. ^{1}H NMR ($CDCl_3$): δ 7.86 (1H, br s), 7.58 (1H, d, J = 7.5 Hz), 7.30 (1H, d, J = 7.5 Hz), 7.22−7.09 (2H, m), 6.27 (1H, d, J = 1.5 Hz), 1.54 (3H, s), 1.06−0.98 (2H, m), 0.89−0.81 (2H, m). ^{13}C NMR ($CDCl_3$): δ 145.1, 136.0, 129.0, 121.3, 120.04, 119.99, 110.6, 98.2, 31.2, 24.0, 15.9, 14.6. IR (KBr): 3423, 3048, 2959, 2931, 2873, 1583, 1550, 1463 cm^{-1}. HRMS (EI): m/z calcd for $C_{12}H_{13}N$ [M$^+$] 171.1048, found 171.1043.

General Procedure for the Addition of Indoles to 2,5-Dichlorobenzoquinone. Procedure A (HCl). Described

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[17] Sanz-Cerveral, J. F.; Glinka, T.; Williams, R. M. *Tetrahedron* **1993**, *49*, 8471.

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for 2,5-Dichloro-3-(2-methyl-1*H*-indol-3-yl)[1,4]benzoquinone (6). To a solution of 2-methylindole (0.500 g, 3.81 mmol) in THF (30 mL) was added 2,5-dichloro-1,4-benzoquinone (1.35 g, 7.62 mmol) at room temperature. To this mixture was added concentrated HCl (12 N, 0.38 mL, 4.57 mmol) dropwise. After the reaction mixture was stirred for 5 h (5−12 h) at room temperature, DDQ (1.73 g, 7.62 mmol) was added. After being stirred for 3 h (3−12 h) at room temperature, the mixture was diluted with EtOAc (100 mL). The organic solution was washed with satd aqueous $NaHCO_3$ (3 × 100 mL) and satd aqueous NaCl (100 mL) and dried over Na_2SO_4. The residue was concentrated and purified by flash column chromatography using 15% EtOAc in hexane as eluent to afford pure **6** (1.13 g, 97%) as a blue solid. Mp: 158−159 °C. $R_f = 0.35$ (3:7, EtOAc/hexane). ^1H NMR ($CDCl_3$): δ 8.40 (br s, NH), 7.24−7.11 (m, 5H), 2.26 (s, 3H). ^1H NMR (d_6-acetone): δ 10.60 (1H, br s), 7.39 (1H, s), 7.36 (1H, d, $J = 7.8$ Hz), 7.24 (1H, d, $J = 7.8$ Hz), 7.10 (1H, t, $J = 7.8$ Hz), 7.01 (1H, t, $J = 7.8$ Hz). ^{13}C NMR ($CDCl_3$) δ 177.7, 176.6, 144.3, 139.8, 139.3, 136.9, 135.1, 133.1, 126.6, 122.0, 120.5, 119.6, 110.8, 104.8, 13.9. IR (KBr): 3388, 3061, 1676, 1566, 1459, 1250, 1032, 749 cm^{-1}. HRMS (EI): *m/z* calcd for $C_{15}H_9Cl_2NO_2$ $[M^+]$ 305.0010, found 305.0002.

General Procedure for the Addition of Indoles to 2,5-Dichlorobenzoquinone. Procedure B (H_2SO_4). Described for 2,5-Dichloro-3-(5-methoxy-1*H*-indol-3-yl)[1,4]benzoquinone (30). To a solution of 2,5-dichloro-1,4-benzoquinone (0.242 g, 1.37 mmol) in THF (3 mL) was added H_2SO_4 (35 μL, 0.68 mmol) at room temperature. To this mixture was added 5-methoxyindole (0.100 g, 0.68 mmol). After the reaction mixture was stirred for 1 h at room temperature under nitrogen protection, DDQ (0.232 g, 1.02 mmol) was added. After being stirred for 2 h, the mixture was diluted with ethyl acetate (100 mL). The organic layer was washed with satd aqueous NaHCO3 (3 × 20 mL) and satd aqueous NaCl (20 mL) and dried over Na_2SO_4. The solution was concentrated and purified by flash column chromatography using 15% EtOAc in hexane as eluent to afford 2,5-dichloro-3-(5-methoxy-1*H*-indole-3-yl)[1,4]benzoquinone (0.211 g, 96%) as blue needles from benzene/hexane. Mp: 195−196 °C. ^1H NMR ($CDCl_3$): δ 6.78 (1H, d, $J = 2.4$ Hz), 6.93 (1H, dd, $J = 2.1$, 8.4 Hz), 7.23 (1H, s), 7.34 (1H, d, $J = 9.0$ Hz), 7.54 (1H, d, $J = 3.0$ Hz), 8.62 (1H, br s). ^{13}C NMR (d_6-acetone): δ 55.2, 103.8, 106.7, 112.4, 112.8, 126.5, 130.9, 131.0, 131.4, 133.4, 139.8, 143.7, 154.8, 177.8, 178.0. IR (KBr): 3328, 3043, 2924, 2855, 1675, 1638, 1543, 1484, 1260, 1227 cm^{-1}. Anal. Calcd. for $C_{15}H_9Cl_2NO_3$: C, 55.93; H, 2.82; N, 4.35. Found: C, 55.72; H, 2.99; N, 4.24.

General Procedure for the Addition of Indoles to 2,5-Dichlorobenzoquinone. Procedure C (AcOH). Described for 2,5-Dichloro-3-[2-(1-methylcyclopropyl)-1*H*-indol-3-yl][1,4]benzoquinone (18). To a solution of 2,5-dichloro-1,4-benzoquinone (0.177 g, 1.00 mmol) in AcOH (2 mL) was added 2-(1-methyl-cyclopropyl)indole (0.081 g, 0.47 mmol). After the reaction mixture was stirred for 2 h at 50 °C under nitrogen protection, Ag_2CO_3 on Celite (50%, 0.500 g, 0.90 mmol) was added. After being stirred for 4 h at room temperature, the solution was diluted with ethyl acetate (100 mL). The organic layer was washed with satd aqueous NaHCO3 (3 × 20 mL) and satd aqueous NaCl (20 mL) and dried over Na_2SO_4. The solution was concentrated and purified by flash column chromatography using 15% EtOAc in hexane as eluent to afford 2,5-dichloro-3-[2-(1-methylcyclopropyl)-1*H*-indol-3-yl]-[1,4]benzoquinone (0.148 g, 90%) as blue needles from benzene/hexane. Mp: 170−171 °C. ^1H NMR (d_6-acetone): δ 0.53−0.60 (1H, m), 0.64−0.70 (1H, m), 0.70−0.77 (1H, m), 0.92−0.98 (1H, m), 1.48 (3H, s), 7.01 (1H, dt, $J = 1.2$, 7.5 Hz), 7.10 (1H, dt, $J = 1.2$, 7.5 Hz), 7.24 (1H, dd, $J = 0.6$, 7.2 Hz), 7.37 (1H, d, $J = 7.8$ Hz), 7.39 (1H, s), 10.70 (1H, s). ^{13}C NMR (d_6-acetone): δ 13.3, 14.1, 15.1, 24.5, 103.6, 111.4, 119.7, 119.9, 121.9, 126.8, 133.8, 136.0, 140.4, 140.8, 143.9, 144.0, 177.1, 177.9. IR (KBr): 3409, 3059, 3004, 2966, 2927, 1662, 1620, 1567, 1435, 1270, 1241, 1028, 755 cm^{-1}. Anal. Calcd for $C_{18}H_{13}Cl_2NO_2$: C, 62.45; H, 3.78; N, 4.05. Found: C, 62.30; H, 3.77; N, 3.94.

General Procedure for the Hydrolysis of Indol-3-yl-2,5-dichlorobenzoquinones. Procedure D. Described for 2,5-Dihydroxy-3-[2-(1-methylcyclopropyl)-1*H*-indol-3-yl]-[1,4]benzoquinone (67). To a refluxing solution of 2,5-dichloro-3-[2-(1-methylcyclopropyl)][1,4]benzoquinone (0.056 g, 0.16 mmol) in MeOH (6 mL) was added 10% aqueous NaOH (3 mL) dropwise. After refluxing for a 1/2 h, the mixture was poured into cold water (20 mL). H_2SO_4 (10%) was added to acidify the mixture, which was extracted with EtOAc (3 × 10 mL). The organic layer was washed with satd aqueous NaCl (10 mL) and dried over Na_2SO_4. The solution was concentrated and purified by flash column chromatography (oxalic acid-coated silica gel) using 30% EtOAc in hexane as the eluent to afford 2,5-dihydroxy-3-[2-(1-methylcyclopropyl)-1*H*-indol-3-yl]-[1,4]benzoquinone (0.044 g, 87%) as dark blue needles from acetone/hexane. Mp: 103 °C dec. ^1H NMR (d_6-acetone): δ 0.55−0.62 (2H, m), 0.81−0.87 (2H, m), 1.45 (3H, s), 6.08 (1H, s), 6.93 (1H, dt, $J = 0.9$, 8.1 Hz), 7.04 (1H, dt, $J = 1.2$, 8.1 Hz), 7.22 (1H, d, $J = 7.8$ Hz), 7.31 (1H, dd, $J = 0.9$, 8.1 Hz), 9.0−10.1 (2H, br s), 10.34 (1H, br s). ^{13}C NMR (d_6-acetone): δ 13.3, 14.8, 24.4, 101.4, 103.6, 110.8, 112.3, 119.0, 119.5, 121.1, 128.4, 135.8, 142.2. IR (KBr): 3300, 3077, 2958, 2924, 1640, 1360, 1190, 746 cm^{-1}. HRMS (EI): *m/z* calcd for $C_{18}H_{15}NO_4$ 309.1001, found 309.0999.

2,5-Dichloro-3-(1*H*-indol-3-yl)[1,4]benzoquinone (5). Yield: 70%. Mp: 124−125 °C. IR (KBr): 3362, 3062, 2922, 1666,1645, 1559, 1248 cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.19 (1H, s), 7.20−7.28 (2H, m), 7.38 (1H, m), 7.41 (1H, m), 7.47 (1H, d, $J = 3$ Hz), 8.94 (1H, br s). ^{13}C NMR ($CDCl_3$): δ 107.2, 112.0, 121.3, 122.0, 123.3, 125.3, 129.8, 133.4, 135.8, 137.4, 138.5, 144.3, 177.5, 178.0. HRMS (EI): *m/z* calcd for $C_{14}H_7Cl_2NO_2$ $[M^+]$ 290.9854, found 290.9865.

2,5-Dichloro-3-(2,5-dimethyl-1*H*-indol-3-yl)[1,4]benzoquinone (7). Blue crystals from benzene/hexane. Mp: 185−186 °C. Yield: 91%. IR (KBr): 3346, 2922, 1671, 1656, 1559, 1259 cm^{-1}. ^1H NMR ($CDCl_3$): δ 2.32 (3H, s), 2.41 (3H, s), 6.94 (1H, m), 6.97 (1H, m), 7.18 (1H, dd, $J = 0.6$, 8.4 Hz), 7.21 (1H, s), 8.19 (1H, br s). ^{13}C NMR ($CDCl_3$): δ 14.3, 21.9, 104.8, 110.7, 119.8, 123.9, 127.2, 130.3, 133.4, 133.7, 137.1, 139.8, 140.1, 144.7, 177.0, 178.1. Anal. Calcd for $C_{16}H_{11}Cl_2NO_2$: C, 60.02; H, 3.46; N, 4.37. Found: C, 59.80; H, 3.58; N, 4.43.

2,5-Dichloro-3-(5-methoxy-2-methyl-1*H*-indol-3-yl)[1,4]-benzoquinone (8). Blue crystals from benzene/hexane. Mp: 199.2−199.5 °C. Yield: 89%. IR (KBr): 3357, 2938, 2895, 2820, 1672, 1645, 1565, 1275, 1253 cm^{-1}. ^1H NMR ($CDCl_3$): δ 2.28 (3H, s), 3.78 (3H, s), 6.58 (1H, d, $J = 2.4$ Hz), 6.80 (1H, dd, $J = 2.4$, 9 Hz), 7.17 (1H, d, $J = 9$ Hz), 7.22 (1H, s), 8.22 (1H, br s). ^{13}C NMR ($CDCl_3$): δ 14.4, 56.2, 102.5, 105.1, 111.8, 112.2, 127.5, 130.4, 133.4, 137.8, 139.7, 139.9, 144.7, 154.9, 176.9, 178.1. HRMS (EI): *m/z* calcd for $C_{16}H_{11}Cl_2NO_2$ $[M^+]$ 335.0116, found 335.0123.

2,5-Dichloro-3-(5-chloro-2-methyl-1*H*-indol-3-yl)[1,4]-benzoquinone (9). Blue crystals from benzene/hexane. Mp: 254−255 °C. Yield: 75%. IR (KBr): 3336, 3078, 1678, 1656, 1570, 1275 cm^{-1}. ^1H NMR (d_6-acetone): δ 2.36 (3H, s), 7.07 (1H, dd, $J = 2.1$, 8.7 Hz), 7.30 (1H, d, $J = 2.1$ Hz), 7.38 (1H, dd, $J = 0.6$, 8.7 Hz), 7.39 (1H, s), 10.9 (1H, br s). ^{13}C NMR (d_6-acetone): δ 13.0, 104.7, 112.4, 119.1, 121.4, 125.1, 128.7, 133.4, 134.5, 139.1, 139.3, 140.5, 144.2, 176.9, 178.1. Anal. Calcd for $C_{15}H_8Cl_3NO_2$: C, 52.90; H, 2.37; N, 4.11. Found: C, 52.79; H, 2.44; N, 3.97.

2,5-Dichloro-3-(2-cyclopropyl-1*H*-indol-3-yl)[1,4]-benzoquinone (10). This compound was synthesized according to general procedure A from 2-cyclopropyl-1*H*-indole (100 mg, 0.636 mmol) and 2,5-dichloro-1,4-benzoquinone (225 mg, 1.27 mmol) and obtained as a blue solid (200 mg, 95%). Mp: 181−182 °C. $R_f = 0.37$ (3:7, EtOAc/hexane). ^1H NMR ($CDCl_3$): δ 8.32 (1H, br s), 7.09−7.23 (5H, m), 1.87 (1H, m), 0.93 (2H, m), 0.70 (2H, m). ^{13}C NMR ($CDCl_3$) δ 177.8, 176.4, 144.3, 141.9, 139.6(2C), 134.7, 133.0, 126.6, 122.1, 120.5, 119.5, 110.9, 105.3, 9.4, 7.3. IR (KBr): 3450, 3386, 3061, 1676, 1650, 1561, 1448, 1273, 1241, 1032, 882, 745 cm^{-1}. Anal. Calcd for $C_{17}H_{11}Cl_2NO_2$: C, 61.47; H, 3.34; N, 4.22. Found: C, 61.71; H, 3.36; N, 4.20.

2,5-Dichloro-3-(2-phenyl-1*H*-indol-3-yl)[1,4]benzoquinone (11). Blue crystals from benzene/hexane. Mp: 170−171 °C. Yield: 89%. ^{1}H NMR ($CDCl_3$): δ 7.20 (1H, m), 7.21 (1H, s), 7.28−7.31 (2H, m), 7.36−7.43 (5H, m), 7.47 (1H, m), 8.61 (1H, br s). ^{13}C NMR ($CDCl_3$): δ 104.7, 111.9, 120.4, 121.3, 123.3, 127.3, 127.5, 129.1, 129.4, 132.4, 133.4, 136.2, 139.6, 140.5, 141.3, 144.7, 176.5, 177.8. IR (KBr): 3384, 3056, 1683, 1565, 1446, 1248 cm^{-1}. Anal. Calcd for $C_{20}H_{11}Cl_2NO_2$: C, 65.24; H, 3.01; N, 3.73. Found: C, 64.61; H, 3.14; N, 3.76.

2,5-Dichloro-3-(1-methyl-1*H*-indol-3-yl)[1,4]benzoquinone (12). Blue crystals from benzene/hexane. Yield: 85%. Mp: 156.1−156.2 °C. IR (KBr): 3142, 3057, 2911, 1683, 1656, 1559, 749 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 3.91 (3H, s), 7.21 (1H, s), 7.23 (1H, m), 7.31 (1H, m), 7.39 (1H, d, J = 9.3 Hz), 7.40 (1H, dd, J = 0.9, 6.9 Hz). ^{13}C NMR ($CDCl_3$): δ 33.9, 105.6, 110.3, 121.1, 122.3, 122.9, 126.0, 133.5, 134.4, 137.0, 138.4, 144.1, 178.0. Anal. Calcd for $C_{15}H_9Cl_2NO_2$: C, 58.85; H, 2.97; N, 4.58. Found: C, 58.69; H, 3.07; N, 4.57.

2,5-Dichloro-3-(2-ethyl-1*H*-indol-3-yl)[1,4]benzoquinone (13). This compound was synthesized according to general procedure A from 2-ethyl-1*H*-indole (100 mg, 0.689 mmol) and 2,5-dichloro-1,4-benzoquinone (244 mg, 1.38 mmol) and obtained as a blue solid (209 mg, 95%). Mp: 143−144 °C. R_f = 0.38 (3:7, EtOAc/hexane). ^{1}H NMR ($CDCl_3$): δ 8.48 (br s, NH), 7.29 (m, 1H), 7.20 (s, 1H), 7.19−7.08 (m, 3H), 2.61 (qd, J = 7.5, 3.0 Hz, 2H), 1.27 (t, J = 7.5 Hz, 3H); ^{1}H NMR (d_6-acetone): δ 10.62 (1H, br s), 7.40 (1H, s), 7.38 (1H, d, J = 8.1 Hz), 7.24 (1H, d, J = 8.1 Hz), 7.09 (1H, t, J = 8.1 Hz), 7.01 (1H, t, J = 8.1 Hz), 7.71 (2H, q, J = 7.8 Hz), 1.30 (3H, t, J = 7.8). ^{13}C NMR ($CDCl_3$): δ 177.7, 176.6, 144.3, 142.1, 140.2, 139.5, 135.2, 133.0, 126.4, 121.9, 120.5, 119.6, 110.9, 103.7, 21.2, 13.4. IR (KBr): 3394, 3050, 2973, 1677, 1646, 1563, 1447, 1241, 1038, 746 cm^{-1}. Anal. Calcd for $C_{16}H_{11}Cl_2NO_2$: C, 60.02; H, 3.46; Cl, 22.15; N, 4.37. Found: C, 59.99; H, 3.51; N, 4.18.

2,5-Dichloro-3-(2-isopropyl-1*H*-indol-3-yl)[1,4]benzoquinone (14). This compound was synthesized according to general procedure A from 2-isoprenyl-1*H*-indole (50 mg, 0.314 mmol) and 2,5-dichloro-1,4-benzoquinone (111 mg, 0.629 mmol) and obtained as a blue solid (74 mg, 70%). Mp: 187−188 °C. R_f = 0.26 (1:4, EtOAc/hexane). ^{1}H NMR ($CDCl_3$): δ 8.40 (br s, NH), 7.36 (m, 1H), 7.22 (s, 1H), 7.21−7.08 (m, 3H), 2.88 (septet, J = 6.9 Hz, 1H), 1.35 (d, J = 6.9 Hz, 3H), 1.27 (d, J = 6.9 Hz, 3H). ^{13}C NMR ($CDCl_3$): δ 177.7, 176.6, 145.8, 144.4, 140.9, 139.7, 135.1, 133.1, 126.1, 122.0, 120.4, 119.5, 111.0, 102.6, 27.4, 22.9, 22.3. IR (KBr): 3421, 3312, 3053, 2963, 1671, 1569, 1440, 1241, 1031, 759 cm^{-1}. HRMS (EI): m/z calcd for $C_{17}H_{13}Cl_2NO_2$ [M$^+$] 333.0323, found 333.0313.

2,5-Dichloro-3-(2-*tert*-butyl-1*H*-indol-3-yl)[1,4]benzoquinone (15). Mp: 235−236 °C. IR (KBr): 3419, 3317, 3059, 2965, 1673, 1585, 1462, 1245, 1029, 742 cm^{-1}. ^{1}H NMR (d_6-acetone): δ 10.40 (1H, br s), 7.47 (1H, s), 7.35 (1H, d, J = 7.8 Hz), 7.23(1H, d, J = 7.8 Hz), 7.08 (1H, t, J = 7.8 Hz), 6.95 (1H, t, J = 7.8 Hz), 1.38 (9H, s). ^{13}C NMR ($CDCl_3$): δ 178.0, 177.7, 145.3, 145.1, 143.2, 142.7, 134.9, 133.5, 127.1, 122.6, 120.6, 118.3, 111.1, 102.1, 33.6, 30.5. HRMS (EI): m/z calcd for $C_{18}H_{15}Cl_2NO_2$ [M$^+$] 347.0480, found 347.0491.

2,3,5-Trichloro-6-(5-methoxy-2-methyl-1*H*-indol-3-yl)-[1,4]benzoquinone (16). Mp: 203−204 °C. IR (KBr): 3351, 2937, 2833, 1673, 1557, 1482, 1205, 1085 cm^{-1}.^{1}H NMR ($CDCl_3$): δ 8.25 (1H, br s), 7.22 (1H, d, J = 8.7 Hz), 6.83 (1H, dd, J = 2.4, 8.7 Hz), 6.59 (1H, d, J = 2.4 Hz), 3.80 (3H, s), 2.32 (3H, s). ^{13}C NMR ($CDCl_3$): δ 175.3, 172.1, 155.1, 141.7, 140.9, 139.8, 139.0, 138.2, 130.4, 127.5, 122.4, 111.8, 105.1, 102.6, 56.1, 14.3. HRMS (EI): m/z calcd for $C_{16}H_{10}Cl_3NO_2$ [M$^+$] 368.9726, found 368.9726.

2,3,5-Trichloro-6-(5-chloro-2-methyl-1*H*-indol-3-yl)[1,4]-benzoquinone (17). Mp: 228−229 °C. IR (KBr): 3350, 1674, 1564, 1468, 1247, 1158, 1089 cm^{-1}.^{1}H NMR (d_6-acetone): δ 11.00 (1H, br s), 7.39 (1H, d, J = 8.4 Hz), 7.32 (1H, d, J = 1.8 Hz), 7.08 (1H, dd, J = 1.8, 8.4 Hz), 2.37 (3H, s). ^{13}C NMR (d_6-acetone): δ 175.3, 172.0, 141.2, 140.1, 139.8, 139.4, 134.5, 128.7, 125.3, 121.5, 119.2, 112.5, 104.5, 13.0. HRMS (EI): m/z calcd for $C_{15}H_7Cl_4NO_2$ [M$^+$] 372.9231, found 372.9232.

2,5-Dichloro-3-[2-(1-methylcyclohexyl)-1*H*-indol-3-yl]-[1,4]benzoquinone (19). Blue needles from benzene/hexane. Mp: 184−185 °C. ^{1}H NMR (d_6-acetone): δ 1.36 (3H, s), 1.38−1.66 (10H, m), 6.96 (1H, dt, J = 1.2, 7.2 Hz), 7.08 (1H, dt, J = 1.2, 7.2 Hz), 7.23 (1H, d, J = 7.8 Hz), 7.37 (1H, d, J = 8.1 Hz), 7.45 (1H, s), 10.39 (1H, br s). ^{13}C NMR (d_6-acetone): δ 22.6, 22.8, 26.2, 27.4, 37.5, 37.8, 38.2, 102.4, 111.2, 118.5, 119.5, 121.5, 127.4, 134.0, 135.6, 142.4, 142.8, 143.9, 145.0, 177.8. IR (KBr): 3421, 3320, 3054, 2936, 2863, 1672, 1618, 1573, 1515, 1457, 1205, 1024 cm^{-1}. Anal. Calcd for $C_{21}H_{19}Cl_2NO_2$: C, 64.96; H, 4.93; N, 3.61. Found: C, 65.04; H, 4.89; N, 3.63.

3-(4-Fluoro-1*H*-indol-3-yl)-2,5-dichloro[1,4]benzoquinone (20). Blue needles from benzene/hexane. Mp: 161−162 °C. ^{1}H NMR (d_6-acetone): δ 6.79 (1H, ddd, J = 0.7, 7.6, 11.2 Hz), 7.15 (1H, dt, J = 5.2, 7.6 Hz), 7.34 (1H, d, J = 8 Hz), 7.38 (1H, s), 7.66 (1H, d, J = 2.8 Hz), 11.15 (1H, s). ^{13}C NMR (d_6-acetone): δ 104.5, 105.7, 105.9, 108.6, 123.1, 123.2, 129.2, 133.6, 139.1, 143.6, 154.9, 157.2, 177.5 177.8. IR (KBr): 3386, 3067, 1671, 1577, 1505, 1422, 1318, 1265, 1226, 1019 cm^{-1}. Anal. Calcd for $C_{14}H_6Cl_2FNO_2$: C, 54.22; H, 1.95; N, 4.52. Found: C, 54.15; H, 1.89; N, 4.58.

3-(4-Chloro-1*H*-indol-3-yl)-2,5-dichloro[1,4]benzoquinone (21). Blue needles from benzene/hexane. Mp: 204−205 °C. ^{1}H NMR (d_6-acetone): δ 7.07 (1H, dd, J = 0.8, 7.6 Hz), 7.15 (1H, t, J = 7.6 Hz), 7.40 (1H, s), 7.49 (1H, dd, J = 0.8, 8.0 Hz), 7.60 (1H, d, J = 2.8 Hz), 11.17 (1H, br s). ^{13}C NMR (d_6-acetone): δ 106.3, 111.4, 121.0, 123.2, 124.4, 125.0, 128.4, 133.6, 137.9, 140.5, 140.9, 143.9, 177.7, 177.9. IR (KBr): 3350, 3115, 3068, 1673, 1659, 1572, 1416, 1274, 1196, 1023 cm^{-1}. Anal. Calcd for $C_{14}H_6Cl_3NO_2$: C, 51.49; H, 1.85. Found: C, 51.33; H, 2.00.

3-(4-Bromo-1*H*-indol-3-yl)-2,5-dichloro[1,4]benzoquinone (22). Blue needles from benzene/hexane. Mp: 247−248 °C. ^{1}H NMR (d_6-acetone): δ 7.09 (1H, t, J = 8.0 Hz), 7.25 (1H, dd, J = 0.8, 8.0 Hz), 7.41 (1H, s), 7.54 (1H, dd, J = 0.8, 8.0 Hz), 7.60 (1H, d, J = 3.2 Hz), 11.11 (1H, br s). ^{13}C NMR (d_6-acetone): δ 107.3, 111.2, 111.9, 113.1, 123.5, 124.3, 126.0, 128.2, 133.6, 137.7, 141.0, 144.1, 177.6, 177.9. IR (KBr): 3367, 3116, 3068, 1651, 1613, 1570, 1517, 1480, 1412, 1021, 875 cm^{-1}. Anal. Calcd for $C_{14}H_6BrCl_2NO_2$: C, 45.32; H, 1.63. Found: C, 45.38; H, 1.84.

2,5-Dichloro-3-(4-methoxy-1*H*-indol-3-yl)[1,4]benzoquinone (23). Blue needles from benzene/hexane. Mp: 195−196 °C. ^{1}H NMR (d_6-acetone): δ 3.76 (1H, s), 6.58 (1H, dd, J = 3.6, 5.1 Hz), 7.11 (1H, s), 7.12(1H, d, J = 1.5 Hz), 7.35 (1H, s), 7.56 (1H, d, J = 3 Hz), 10.86 (1H, br s). ^{13}C NMR (d_6-acetone): δ 55.0, 101.2, 105.4, 106.5, 123.6, 126.8, 127.0, 133.2, 136.4, 138.0, 141.9, 143.6, 153.3, 177.6, 177.8. IR (KBr): 3324, 3042, 2967, 1676, 1638, 1546, 1486, 1260, 1229, 1009 cm^{-1}. Anal. Calcd for $C_{15}H_9Cl_2NO_3$: C, 55.93; H, 2.82; N, 4.35. Found: C, 56.09; H, 2.87; N, 4.32.

3-(4-Benzyloxy-1*H*-indol-3-yl)-2,5-dichloro[1,4]benzoquinone (24). Blue needles from benzene/hexane. Mp: 193−194 °C. ^{1}H NMR (d_6-acetone): δ 5.01 (2H, s), 6.64 (1H, dd, J = 2.4, 6.4 Hz), 7.06 (1H, s), 7.4−7.7 (2H, m), 7.23−7.34 (5H, m), 7.45 (1H, d, J = 2.8 Hz), 10.79 (1H, br s). ^{13}C NMR (d_6-acetone): δ 70.3, 102.1, 105.6, 106.3, 117.8, 123.5, 126.3, 127.8, 128.0, 128.6, 132.9, 137.5, 138.1, 141.7, 143.8, 152.7, 177.2, 177.8. IR (KBr): 3346, 3116, 3063, 3034, 1673, 1656, 1572, 1508, 1453, 1423, 1270 cm^{-1}. Anal. Calcd for $C_{21}H_{13}Cl_2NO_3$: C, 63.34; H, 3.29. Found: C, 63.26; H, 3.40.

2,5-Dichloro-(4-methyl-1*H*-indol-3-yl)[1,4]benzoquinone (25). Blue needles from benzene/hexane. Mp: 192−193 °C. ^{1}H NMR (d_6-acetone): δ 2.28 (3H,s), 6.83 (1H, dt, J = 0.6, 5.4 Hz), 7.06 (1H, t, J = 5.7 Hz), 7.32 (1H, d, J = 6 Hz), 7.39 (1H d_6-acetone,s), 7.44 (1H, d, J = 2.1 Hz), 10.77 (1H, br s). ^{13}C NMR (d_6-acetone): δ 19.3, 107.1, 110.0, 122.0, 122.5, 126.1, 127.1, 129.8, 133.8, 136.9, 140.4, 142.0, 143.7, 177.9, 178.3. IR (KBr): 3369, 3114, 3068, 1669, 1553, 1511, 1267, 1182, 1019, 876, 753 cm^{-1}. Anal. Calcd for $C_{15}H_9Cl_2NO_2$: C, 58.85; H, 2.96. Found: C, 58.85; H, 2.91.

3-(5-Fluoro-1*H*-indol-3-yl)-2,5-dichloro[1,4]benzoquinone (26). Blue needles from benzene/hexane. Mp: 175−176 °C. ^{1}H NMR (d_6-acetone): δ 7.00 (1H,dt, $J = 2.1, 9.0$ Hz), 7.16 (1H, dd, $J = 1.2, 10.2$ Hz), 7.35 (1H, s), 7.53 (1H, dd, $J = 4.5, 8.7$ Hz), 7.79 (1H, d, $J = 2.7$ Hz), 11.1 (1H, br s). ^{13}C NMR (d_6-acetone): δ 106.4, 106.7, 110.3, 110.7, 113.2, 113.3, 132.2, 133.0, 133.3, 143.8, 156.5, 159.6, 177.4, 177.8. IR (KBr): 3394, 3131, 3063, 2956, 2925, 1678, 1656, 1570, 1423, 1258, 1011 cm^{-1}. Anal. Calcd for $C_{14}H_6Cl_2FNO_2$: C, 54.22; H, 1.95; N, 4.52. Found: C, 54.30; H, 2.01; N, 4.54.

3-(5-Chloro-1*H*-indol-3-yl)-2,5-dichloro[1,4]benzoquinone (27). Blue needles from benzene/hexane. Mp: 189−190 °C. ^{1}H NMR (CDCl$_3$): δ 7.24 (1H, s), 7.25 (1H, dd, $J = 0.9, 2.1$ Hz), 7.36 (1H, d, $J = 0.9$ Hz), 7.37−7.39 (1H, m), 7.58 (1H, d, $J = 3$ Hz), 8.60 (1H, s). ^{13}C NMR (d_6-acetone): δ 106.4, 113.6, 120.9, 122.4, 125.7, 127.2, 131.7, 133.4, 134.9, 137.5, 138.7, 143.9, 177.5, 177.9. IR (KBr): 3331, 3053, 1675, 1652, 1568, 1505, 1460, 1274, 1247, 803 cm^{-1}. Anal. Calcd for $C_{14}H_6Cl_3NO_2$: C, 51.49; H, 1.85; N, 4.29. Found: C, 51.51; H, 2.01; N, 4.26.

3-(5-Bromo-1*H*-indol-3-yl)-2,5-dichloro[1,4]benzoquinone (28). Blue needles from benzene/hexane. Mp: 205−206 °C. ^{1}H NMR (d_6-acetone): δ 7.31 (1H, dd, $J = 2.0, 8.8$ Hz), 7.37 (1H, s), 7.50 (1H, d, $J = 8.4$ Hz), 7.62 (1H, s), 7.76 (1H, d, $J = 2.8$ Hz), 11.14 (1H, s). ^{13}C NMR (d_6-acetone): δ 106.3, 113.3, 114.0, 123.9, 125.0, 127.8, 131.5, 133.4, 135.2, 137.5, 138.8, 143.9, 177.5, 177.9. IR (KBr): 3382, 3138, 3058, 1671, 1650, 1571, 1457, 1271, 1245, 1113, 1010 cm^{-1}. Anal. Calcd for $C_{14}H_6BrCl_2NO_2$: C, 45.32; H, 1.63; N, 3.78. Found: C, 45.56; H, 1.77; N, 3.70.

2,5-Dichloro-3-(5-hydroxy-1*H*-indol-3-yl)-[1,4]benzoquinone (29). Blue needles from benzene/hexane. Mp: 101 °C dec. ^{1}H NMR (d_6-acetone): δ 6.80 (2H, m), 7.33 (1H, s), 7.34 (1H, m), 7.65 (1H, d, $J = 3.3$ Hz), 7.92 (1H, br s), 10.86 (1H, br s). ^{13}C NMR (d_6-acetone): δ 103.7, 105.9, 106.2, 112.4, 112.6, 113.4, 113.8, 131.1, 131.1, 131.3, 133.4. IR (KBr): 3500, 3121, 1698, 1566, 1167, 1102, 851, 694, 617 cm^{-1}. Anal. Calcd for $C_{14}H_7Cl_2NO_3$: C, 54.57; H, 2.29. Found: C, 54.95; H, 2.62.

3-(5-Benzyloxy-1*H*-indol-3-yl)-2,5-dichloro[1,4]benzoquinone (31). Blue needles from benzene/hexane. Mp: 164−165 °C. ^{1}H NMR (CDCl$_3$): δ 5.08 (2H, s), 6.89 (1H, s, $J = 2.1$ Hz), 7.01 (1H, dd, $J = 2.4, 8.7$ Hz), 7.22 (1H,s), 7.26(1H, s), 7.30−7.50 (6H, m) 7.53 (1H, d, $J = 2.7$ Hz), 8.64 (1H, br s). ^{13}C NMR (d_6-acetone): δ 70.5, 105.6, 106.6, 112.8, 113.0, 126.3, 126.6, 127.8, 128.5, 131.0, 131.2, 131.7, 133.4, 138.1, 139.2, 143.8, 153.9, 177.7, 178.0. IR (KBr): 3342, 3065, 3037, 2907, 2874, 1674, 1564, 1480, 1426, 1258, 1009 cm^{-1}. Anal. Calcd for $C_{21}H_{13}Cl_2NO_3$: C, 63.34; H, 3.29; N, 3.52. Found: C, 63.24; H, 3.42; N, 3.49.

2,5-Dichloro-3-(5-methyl-1*H*-indol-3-yl)[1,4]benzoquinone (32). Blue needles from benzene/hexane. Mp: 176−177 °C. ^{1}H NMR (d_6-acetone): δ 2.40 (3H, s), 7.02 (1H, dd, $J = 1.8, 8.4$ Hz), 7.20 (1H, m), 7.33 (1H, s), 7.40 (1H, d, $J = 8.4$ Hz), 7.66 (1H, dd, $J = 3.0$ Hz), 10.89 (1H, br s). ^{13}C NMR (d_6-acetone): δ 21.27, 106.4, 111.9, 121.4, 123.9,126.2, 129.3, 130.6, 133.4, 134.8, 136.4, 139.3, 143.6, 177.8, 177.9. IR (KBr): 3367, 3069, 2919, 2859, 1657, 1654, 1561, 1507, 1423, 1248, 1111 cm^{-1}. Anal. Calcd for $C_{15}H_9Cl_2NO_2$: C, 58.85; H, 2.96. Found: C, 58.95; H, 3.14.

3-(6-Fluoro-1*H*-indol-3-yl)-2,5-dichloro[1,4]benzoquinone (33). Blue needles from benzene/hexane. Mp: 168−169 °C. ^{1}H NMR (d_6-acetone): δ 6.95 (1H, tt, $J = 1.8, 9$ Hz), 7.28 (1H, dt, $J = 1.8, 9.6$ Hz), 7.37 (1H, d, $J = 2.1$ Hz), 7.40 (1H, d, $J = 5.4, 8.7$ Hz), 7.72 (1H, d, $J = 2.4$ Hz), 11.12 (1H, br s). ^{13}C NMR (d_6-acetone): δ 98.1, 98.4, 106.8, 108.6, 108.9, 122.6, 122.7, 131.0, 133.4, 143.8, 158.2, 161.4, 177.4, 177.9. IR (KBr): 3380, 3079, 2920, 1650, 1559, 1453, 1409, 1235, 1140, 1010, 882 cm^{-1}. Anal. Calcd for $C_{14}H_6Cl_2FNO_2$: C, 54.22; H, 1.95. Found: C, 54.48; H, 2.06.

3-(6-Chloro-1*H*-indol-3-yl)-2,5-dichloro[1,4]benzoquinone (34). Blue needles from benzene/hexane. Mp: 182−183 °C. ^{1}H NMR (CDCl$_3$): δ 7.18 (1H, dd, $J = 1.8, 8.7$ Hz), 7.23 (1H, s), 7.26 (1H, s), 7.31 (1H, d, $J = 8.7$ Hz), 7.44 (1H, dd, $J = 0.6, 1.8$ Hz), 7.54 (1H, d, $J = 2.7$ Hz), 8.75 (1H, br s).^{13}C NMR (d_6-acetone): δ 106.9, 112.0, 117.9, 120.7, 122.8, 124.7, 127.7, 131.3, 133.4, 136.8, 138.6, 143.8, 177.4, 177.8. IR (KBr): 3325, 3122, 3071, 2962, 2926, 1673, 1564, 1517, 1449, 1401, 1020 cm^{-1}. Anal. Calcd for $C_{14}H_6Cl_3NO_2$: C, 51.49; H, 1.85; N, 4.29. Found: C, 51.77; H, 1.94; N, 4.21.

3-(6-Benzyloxy-1*H*-indol-3-yl)-2,5-dichloro[1,4]benzoquinone (35). Blue needles from benzene/hexane. Mp: 180 °C dec. ^{1}H NMR (d_6-acetone): δ 5.15 (2H, s), 6.90 (1H, dd, $J = 2.4, 9.0$ Hz), 7.14 (1H, d, $J = 2.1$ Hz), 7.26−7.36 (3H, m), 7.39 (2H, t, $J = 7.2$ Hz), 7.50 (2H, d, $J = 7.2$ Hz), 7.61 (1H, d, $J = 2.4$ Hz), 10.84 (1H, br s). ^{13}C NMR (d_6-acetone): δ 70.2, 96.6, 106.9, 111.1, 120.4, 122.4, 122.9, 127.6, 127.8, 128.6, 129.6, 129.8, 133.4, 137.2, 138.0, 143.7, 155.8, 177.4, 177.9. IR (KBr): 3396, 3127, 3064, 2946, 2815, 1672, 1651, 1560, 1237, 1011, 819 cm^{-1}. Anal. Calcd for $C_{21}H_{13}Cl_2NO_3$: C, 63.34; H, 3.29; N, 3.52. Found: C, 63.07; H, 3.43; N, 3.45.

2,5-Dichloro-3-(6-methyl-1*H*-indol-3-yl)[1,4]benzoquinone (36). Blue needles from benzene/hexane. Mp: 169−170 °C. ^{1}H NMR (d_6-acetone): δ 2.39 (3H, s), 6.92 (1H, dd, $J = 0.8, 4.4$ Hz), 7.25 (1H, d, $J = 8.4$ Hz), 7.24−7.26 (2H, m), 7.61 (1H, d, $J = 2.8$ Hz), 10.92 (1H, br s). ^{13}C NMR (d_6-acetone): δ 20.9, 106.6, 112.0, 121.5,122.1, 123.8, 130.3, 131.9, 133.4, 136.2, 136.9, 139.2, 143.7, 177.7, 178.0. IR (KBr): 3409, 3065, 2918, 1652, 1557, 1256, 1236, 1116, 1015, 878, 805 cm^{-1}. Anal. Calcd for $C_{15}H_9Cl_2NO_2$: C, 58.85; H, 2.96. Found: 58.94; H, 3.08.

2,5-Dichloro-3-(7-methyl-1*H*-indol-3-yl)[1,4]benzoquinone (37). This compound was synthesized according to general procedure A from 7-methyl-1*H*-indole (100 mg, 0.762 mmol) and 2,5-dichloro-1,4-benzoquinone (270 mg, 1.52 mmol) and obtained as a blue solid (188 mg, 81%). Mp: 187−188 °C. $R_f = 0.31$ (3:7, EtOAc/hexane). ^{1}H NMR (CDCl$_3$): δ 8.70 (br s, NH), 7.55 (d, $J = 3.0$ Hz, 1H), 7.32 (m, 1H), 7.21 (s, 1H), 7.11 (m, 2H), 2.53 (s, 3H). ^{1}H NMR (d_6-acetone): δ 10.95 (1H, br s), 7.68 (1H, m), 7.37 (1H, m), 7.25 (1H, m), 7.03 (2H, m), 2.55 (3H, s). ^{13}C NMR (d_6-acetone): δ 178.0, 177.7, 143.7, 139.3, 136.3, 135.9, 133.4, 130.0, 125.7, 122.9, 121.5, 120.5, 119.4, 107.2, 16.2. IR (KBr): 3403, 3072, 1670, 1563, 1431, 1236, 1037, 750 cm^{-1}. Anal. Calcd for $C_{15}H_9Cl_2NO_2$: C, 58.85; H, 2.97; N, 4.58. Found: C, 58.62; H, 2.78; N, 4.53.

2,5-Dichloro-3-(7-propyl-1*H*-indol-3-yl)[1,4]benzoquinone (38). Blue needles from benzene/hexane. Mp: 140−141 °C. ^{1}H NMR (d_6-acetone): δ 1.00 (3H, t, $J = 7.2$ Hz), 1.77 (2H, h, $J = 7.5$ Hz), 2.93 (2H, dd, $J = 9.0, 16.5$ Hz), 7.03 (1H, s), 7.06 (1H, t, $J = 7.2$ Hz), 7.24 (1H, dd, $J = 1.5, 6.9$ Hz), 7.34 (1H, s), 7.67 (1H, dd, $J = 1.2, 3.0$ Hz), 11.09 (1H, br s). ^{13}C NMR (d_6-acetone): δ 13.9, 23.6, 33.4, 107.2, 119.5,120.5, 122.1, 125.9, 126.3, 130.1, 133.4, 135.4, 136.5, 139.2, 143.7, 177.6, 177.9. IR (KBr): 3401, 3062, 2958, 2929, 2871, 2858, 1670, 1572, 1434, 1115, 1023 cm^{-1}. Anal. Calcd for $C_{17}H_{13}Cl_2NO_2$: C, 61.10; H, 3.92. Found: C, 60.94; H, 4.13.

3-(7-*tert*-Butyl-1*H*-indol-3-yl)-2,5-dichloro[1,4]benzoquinone (39). Blue needles from benzene/hexane. Mp: 189−190 °C. ^{1}H NMR (d_6-acetone): δ 1.54 (9H, s), 7.06 (1H, t, $J = 7.8$ Hz), 7.15 (1H, d, $J = 6.6$ Hz), 7.27 (1H, d, $J = 7.8$ Hz), 7.37 (1H, s), 7.64 (1H, d, $J = 3.3$ Hz), 10.77 (1H, br s). ^{13}C NMR (d_6-acetone): δ 34.5, 106.8, 118.9,119.3, 120.3, 127.0, 129.5, 133.4, 133.6, 134.4, 137.0, 139.3, 143.7, 177.6, 177.9. IR (KBr): 3438, 3064, 2963, 1659, 1565, 1422, 1269, 1113, 1026, 750 cm^{-1}. Anal. Calcd for $C_{18}H_{15}Cl_2NO_2$: C, 62.08; H, 4.34. Found: C, 62.32; H, 4.58.

2,5-Dichloro-3-(7-phenyl-1*H*-indol-3-yl)[1,4]benzoquinone (40). Blue needles from benzene/hexane. Mp: 185−186 °C. ^{1}H NMR (d_6-acetone): δ 7.21−7.25 (2H, m), 7.35 (1H, s), 7.38−7.44 (2H, m), 7.47−7.53 (2H, m), 7.66 (2H, dd, $J =$

1.2, 8.4 Hz), 7.70 (1H, d, J = 2.8 Hz), 10.94 (1H, br s). ^{13}C NMR (d_6-acetone): δ 118.0, 119.0, 120.5, 120.9, 121.1, 122.5, 126.7, 127.7,128.7, 129.2, 130.9, 132.6, 133.5, 133.9, 138.9, 139.1, 143.8, 143.8, 177.6, 178.0. IR (KBr): 3424, 3328, 3137, 3069, 3029, 1675, 1651, 1568, 1426, 755 cm^{-1}. Anal. Calcd for $C_{20}H_{11}Cl_2NO_2$: C, 65.24; H, 3.01; N, 3.80. Found: C, 65.44; H, 3.44; N, 3.60.

2,5-Dichloro-3-(7-methoxy-1*H*-indol-3-yl)[1,4]benzoquinone (41). Blue needles from benzene/hexane. Mp: 183−184 °C. ^{1}H NMR (CDCl$_3$): δ 3.94 (3H, s), 6.67 (1H, d, J = 7.6 Hz), 6.96 (1H, dd, J = 0.8, 8.0 Hz), 7.09 (1H, t, J = 8.0 Hz), 7.17 (1H, s), 7.50 (1H, d, J = 3.2 Hz), 8.94 (1H, br s). ^{13}C NMR (d_6-acetone): δ 55.1,102.5, 107.2, 114.4, 120.9, 126.7, 127.4, 129.8, 133.4, 136.7, 139.2, 143.8, 146.9, 177.6, 178.0. IR (KBr): 3391, 3152, 1667, 1626, 1499, 1419, 1114, 1013. Anal. Calcd for $C_{15}H_9Cl_2NO_3$: C, 55.93; H, 2.82; N, 4.35. Found: C, 56.16; H, 2.94; N, 4.23.

3-(7-Benzyloxy-1*H*-indol-3-yl)-2,5-dichloro[1,4]benzoquinone (42). Blue needles from benzene/hexane. Mp: 174−175 °C. ^{1}H NMR (d_6-acetone): δ 5.29 (2H, s), 6.85 (1H, dd, J = 1.6, 6.8 Hz), 6.99−7.07 (2H, m), 7.35 (1H, t, J = 7.2 Hz), 7.36 (1H, s), 7.42 (2H, dt, J = 1.2, 7.2 Hz), 7.57 (1H, d, J = 7.2 Hz), 7.66 (1H, d, J = 2.8 Hz), 11.25 (1H, br s). ^{13}C NMR (d_6-acetone): δ 70.0, 103.8, 107.2, 114.6, 120.8, 127.0, 127.6, 127.97, 128.0, 128.6, 129.7, 129.8, 133.4, 137.6, 139.2, 143.8, 146.0, 177.6, 178.0. IR (KBr): 3380, 3066, 2918, 2872, 1674, 1657, 1567, 1428, 1244, 1111 cm^{-1}. Anal. Calcd for $C_{21}H_{13}Cl_2NO_3$: C, 63.34; H, 3.29. Found: C, 63.50; H, 3.38.

3-(7-Fluoro-1*H*-indol-3-yl)-2,5-dichloro[1,4]benzoquinone (43). Blue needles from benzene/hexane. Mp: 177−178 °C. ^{1}H NMR (d_6-acetone): δ 6.98 (1H, dd, J = 8.0, 11.2 Hz), 7.09 (1H, dt, J = 4.8, 8.0 Hz), 7.24 (1H, d, J = 8.0 Hz), 7.40 (1H, s), 7.76 (1H, d, J = 2.8 Hz), 11.41 (1H, br s). ^{13}C NMR (d_6-acetone): δ 106.8, 107.0, 117.6, 120.5, 120.6, 130.6, 130.8, 131.1, 132.6, 133.4, 138.8, 143.9, 177.5, 177.9. IR (KBr): 3395, 3096, 1671, 1573, 1503, 1423, 1265, 1236, 1109, 1038 cm^{-1}. Anal. Calcd for $C_{14}H_6Cl_2FNO_2$: C, 54.22; H, 1.95. Found: C, 54.36; H, 2.09.

3-(7-Chloro-1*H*-indol-3-yl)-2,5-dichloro[1,4]benzoquinone (44). Blue needles from benzene/hexane. Mp: 213-214 °C. ^{1}H NMR (d_6-acetone): δ 7.14 (1H, t, J = 8.0 Hz), 7.27 (1H, dd, J = 0.8, 7.6 Hz), 7.40 (1H, s), 7.41 (1H, dd, J = 0.8, 8.0 Hz), 7.77 (1H, d, J = 3.2 Hz), 11.23 (1H, br s). ^{13}C NMR (d_6-acetone): δ 108.2, 120.8, 121.4, 122.0, 128.0, 130.9, 131.0, 133.7, 138.9, 144.1, 177.6, 178.1. IR (KBr): 3406, 3071, 2950, 1678, 1649, 1542, 1508, 1434, 1247, 1204 cm^{-1}. Anal. Calcd for $C_{14}H_6Cl_3NO_2$: C, 51.49; H, 1.85; N, 4.29. Found: C, 51.59; H, 2.01; N, 4.28.

3-(7-Bromo-1*H*-indol-3-yl)-2,5-dichloro[1,4]benzoquinone (45). Blue needles from benzene/hexane. Mp: 191−192 °C. ^{1}H NMR (d_6-acetone): δ 7.09 (1H, t, J = 8.0 Hz), 7.41 (1H, s), 7.44 (2H, dt, J = 0.8, 8.0 Hz), 7.77 (1H, d, J = 1.6 Hz), 11.14 (1H, br s). ^{13}C NMR (d_6-acetone): δ 104.8, 108.0, 121.0, 121.6, 124.9, 127.5, 130.6, 130.7, 133.4, 138.1, 138.7, 143.9, 177.4, 178.0. IR (KBr): 3368, 3160, 3060, 2972, 2866, 1662, 1561, 1262, 1098, 1012, 882 cm^{-1}. Anal. Calcd for $C_{14}H_6BrCl_2NO_2$: C, 45.32; H, 1.63; N, 3.78. Found: C, 45.47; H, 1.75; N, 3.81.

3-(7-Benzyl-1*H*-indol-3-yl)-2,5-dichloro[1,4]benzoquinone (46). Blue needles from benzene/hexane. Mp: 159−160 °C. ^{1}H NMR (d_6-acetone): δ 4.30 (2H, s), 7.01 (1H, d, J = 6.6 Hz), 7.08 (1H, t, J = 7.2 Hz), 7.14−7.22 (1H, m), 7.24−7.33 (4H, m), 7.35 (1H, s), 7.66 (1H, d, J = 3.0 Hz), 10.95 (1H, s). ^{13}C NMR (d_6-acetone): δ 37.0, 107.3, 117.8, 120.0, 120.6, 122.5, 122.9, 125.0, 126.3, 128.6, 129.0, 130.2, 132.5, 133.4, 135.3, 140.3, 143.7, 177.5, 177.9. IR (KBr): 3414, 3059, 1676, 1656, 1566, 1434, 1266, 1237, 1113, 1033 cm^{-1}. Anal. Calcd for $C_{21}H_{13}Cl_2NO_2$: C, 65.99; H, 3.43; N, 3.66. Found: C, 65.74; H, 3.49; N, 3.71.

2,5-Dichloro-3-[7-(2-methyl-benzyl)-1*H*-indol-3-yl][1,4]-benzoquinone (47). Blue needles from benzene/hexane. Mp: 101−102 °C. ^{1}H NMR (d_6-acetone): δ 2.27 (3H, s), 4.28 (2H, s), 6.75 (1H, d, J = 6.9 Hz), 7.00−7.23 (5, m), 7.30 (1H, d, J = 8.1 Hz), 7.33 (1H, s), 7.68 (1H, d, J = 3.3 Hz), 11.00 (1H, br s). ^{13}C NMR (d_6-acetone): δ 19.1, 34.5, 107.3, 119.9, 120.1, 120.6, 122.0, 122.4, 124.1, 126.0, 126.2, 126.4, 129.4, 130.3, 133.4, 135.5, 136.8, 138.0, 139.2, 143.7, 177.6, 177.9. IR (KBr): 3414, 3060, 2920, 2857, 1656, 1561, 1433, 1237, 1110, 1031 cm^{-1}. Anal. Calcd for $C_{22}H_{15}Cl_2NO_2$: C, 66.68; H, 3.82; N, 3.53. Found: C, 65.88; H, 3.85; N, 3.79.

3-(1*H*-Benzo[g]indol-3-yl)-2,5-dichloro[1,4]benzoquinone (48). Blue needles from benzene/hexane. Mp: 210−211 °C. ^{1}H NMR (d_6-acetone): δ 7.18−7.25 (1H, m), 7.38−7.62 (6H, m), 7.72−7.75 (1H, m), 7.97 (1H, d, J = 8.1 Hz), 8.49 (1H, d, J = 8.1 Hz), 11.85 (1H, br s). ^{13}C NMR (d_6-acetone): δ 111.0, 118.0, 119.8, 120.4, 120.9, 121.3, 124.0, 124.4, 125.9, 127.8, 128.7, 133.4. IR (KBr): 3340, 3063, 2922, 1675, 1651, 1558, 1272, 1224, 1021, 871 cm^{-1}. HRMS (FAB): m/z calcd for $C_{18}H_9Cl_2NO_2$ 341.0010, found 341.0013.

3-(2,6-Dimethyl-1*H*-indol-3-yl)-2,5-dichloro[1,4]-benzoquinone (49). Blue needles from benzene/hexane. Mp: 114−115 °C. ^{1}H NMR (d_6-acetone): δ 2.34 (3H, s), 2.39 (3H, s), 6.86 (1H, d, J = 8.7 Hz), 7.12 (1H, d, J = 8.1 Hz), 7.17 (1H, s), 7.37 (1H, s), 10.46 (1H, br s). ^{13}C NMR (d_6-acetone): δ 13.0, 21.1, 102.6, 111.0, 119.6, 121.5, 125.4, 130.9, 133.4, 136.4, 136.8, 140.1, 144.0, 176.9, 178.1. IR (KBr): 3266, 3064, 2958, 2921, 1677, 1654, 1568, 1466, 1258, 1033 cm^{-1}. Anal. Calcd for $C_{16}H_{11}Cl_2NO_2$: C, 60.02; H, 3.46; N, 4.37. Found: C, 59.76; H, 3.54; N, 4.32.

3-(2,7-Dimethyl-1*H*-indol-3-yl)-2,5-dichloro[1,4]benzoquinone (50). Blue needles from benzene/hexane. Mp: 95−96 °C. ^{1}H NMR (d_6-acetone): δ 2.35 (3H, s), 2.49 (3H, s), 6.86−6.96 (2H, m), 7.07(1H, d, J = 6.9 Hz), 7.36 (1H, s), 10.51 (1H, br s). ^{13}C NMR (d_6-acetone): δ 13.1, 16.4, 105.4, 117.6, 120.1, 120.4, 122.2, 127.2, 133.4, 135.4, 137.2, 139.8, 140.1, 144.0, 176.9, 178.1. IR (KBr): 3362, 3064, 2919, 2860, 1675, 1620, 1453, 1269, 1243, 884 cm^{-1}. Anal. Calcd for $C_{16}H_{11}Cl_2NO_2$: C, 60.02; H, 3.46; N, 4.37. Found: C, 60.19; H, 3.59; N, 4.31.

3-(6,7-Dimethyl-1*H*-indol-3-yl)-2,5-dichloro[1,4]benzoquinone (51). Blue needles from benzene/hexane. Mp: 184−185 °C. IR (KBr): 3387, 3071, 2920, 2860, 1675, 1551, 1506, 1433, 1263 cm^{-1}. ^{1}H NMR (d_6-acetone): δ 2.36 (3H, s), 2.46 (3H, s), 6.95 (1H, d, J = 8.4 Hz), 7.12 (1H, d, J = 8.0 Hz), 7.33 (1H, s), 7.61 (1H, d, J = 2.8 Hz), 10.84 (1H, s). ^{13}C NMR (d_6-acetone): δ 12.6, 18.6, 107.2, 118.9, 119.2, 123.1, 124.0, 129.6, 130.0, 133.4, 136.6, 139.1, 143.6, 177.7, 178.0. Anal. Calcd for $C_{16}H_{11}Cl_2NO_2$: C, 60.02; H, 3.46; N, 4.37. Found: C, 59.98; H, 3.59; N, 4.23.

3-(5,6-Methylenedioxy-1*H*-indol-3-yl)-2,5-dichloro[1,4]-benzoquinone (52). Blue needles from benzene/hexane. Mp: 170 °C dec. ^{1}H NMR (d_6-acetone): δ 5.95 (2H, s), 6.82 (1H, s), 6.99 (1H, s), 7.34 (1H, s), 7.54 (1H, d, J = 3.0 Hz), 10.82 (1H, br s).^{13}C NMR (d_6-acetone): δ 92.6, 100.3, 101.0, 107.1, 120.2, 128.9, 131.3, 133.3, 136.4, 139.2, 143.6, 143.7, 145.3, 177.6, 178.0. IR (KBr): 3337, 3066, 2971, 2874, 1668, 1566, 1426, 1042, 942 cm^{-1}. Anal. Calcd for $C_{15}H_7Cl_2NO_4$: C, 53.60; H, 2.10. Found: C, 53.61; H, 2.23.

3-(5,6-Dimethoxy-1*H*-indol-3-yl)-2,5-dichloro[1,4]-benzoquinone (53). Blue needles from benzene/hexane. Mp: 186−187 °C. IR (KBr): 3300, 3040, 2952, 2957, 2829, 1634, 1546, 1484, 1228, 1087 cm^{-1}. ^{1}H NMR (d_6-acetone): δ 3.78 (3H, s), 3.84 (3H, s), 6.93 (1H, s), 7.10 (1H, s), 7.36 (1H, s), 7.56 (1H, d, J = 2.7 Hz), 10.82 (1H, br s). ^{13}C NMR (d_6-acetone): δ 55.7, 56.0, 95.8, 104.7, 106.8, 117.6, 119.0, 120.6, 129.1, 130.8, 133.4, 143.6, 145.9, 147.9, 177.7, 177.9. Anal. Calcd for $C_{16}H_{11}Cl_2NO_4$: C, 54.57; H, 3.15. Found: C, 51.03; H, 3.32.

2,5-Dihydroxy-3-(1*H*-indol-3-yl)[1,4]benzoquinone (56). Yield: 59%. Mp: 219−220 °C. IR (KBr): 3421, 3301, 1666, 1293, 1235, 931 cm^{-1}. ^{1}H NMR (d_6-acetone): δ 10.6 (1H, br s), 9.0−10.0 (2H, br), 7.59 (1H, d, J = 2.4 Hz), 7.52 (1H, d, J = 8.1 Hz), 7.44 (1H, d, J = 8.1 Hz), 7.11 (1H, t, J = 8.1 Hz), 7.02 (1H, t, J = 8.1 Hz), 6.01 (1H, s). ^{13}C NMR (d_6-acetone): δ 136.4, 127.6, 126.9, 121.9, 121.5, 119.2, 112.1, 111.5, 104.7, 103.2. HRMS (FAB): *m/z* calcd for $C_{14}H_9NO_4$ [M$^+$] 255.0532, found 255.0529.

2,5-Dihydroxy-3-(2-methyl-1*H*-indol-3-yl)[1,4]benzoquinone (57). Yield: 62%. Mp: 222−223 °C. IR (KBr): 3392, 3313, 1630, 1359, 1294, 1186 cm^{-1}. ^{1}H NMR (d_6-acetone): δ 10.27 (1H, br s), 7.30 (1H, d, $J = 8.1$ Hz), 7.23 (1H, d, $J = 8.1$ Hz), 7.02 (1H, t, $J = 8.1$ Hz), 6.94 (1H, t, $J = 8.1$ Hz), 6.04 (1H, s), 2.32 (3H, s). ^{13}C NMR (d_6-acetone): δ136.0, 135.5, 128.6, 120.6, 119.8, 119.0, 111.9, 110.5, 103.4, 102.2, 12.8. Anal. Calcd for $C_{15}H_{11}NO_4$: C, 66.91, H, 4.12, N, 5.20. Found: C, 66.69, H, 4.26, N, 5.11. HRMS (FAB): *m/z* calcd for $C_{15}H_{11}NO_4$ [M$^+$] 269.0688, found 269.0691.

2,5-Dihydroxy-3-(2,5-dimethyl-1*H*-indol-3-yl)[1,4]benzoquinone (58). Green crystals from benzene/hexane. Yield: 73%. Mp: 231−232 °C. IR (KBr): 3416, 3287, 2917, 2858, 1619, 1355, 1184 cm^{-1}; ^{1}H NMR (d_6-acetone): δ 10.12 (1H, br s), 9.0−10.0 (2H, br), 7.18 (1H, d, $J = 8.1$ Hz), 7.01 (1H, s), 6.85 (1H, d, $J = 8.4$ Hz), 6.04 (1H, s), 2.33 (3H, s), 2.29 (3H, s).^{13}C NMR (d_6-acetone): δ 135.5, 134.4, 128.8, 127.6, 122.1, 119.6, 110.2, 103.4, 101.7, 21.1, 12.8. HRMS (FAB): *m/z* calcd for $C_{16}H_{13}NO_4$ [M$^+$] 283.0845, found 283.0846.

2,5-Dihydroxy-3-(5-methoxy-2-methyl-1*H*-indol-3-yl)-[1,4]benzoquinone (59). Yield: 81%. Mp: 212 °C dec. IR (KBr): 3389, 3080, 2925, 1612, 1484, 1358, 1329, 1198, 799 cm^{-1}. ^{1}H NMR (d_6-acetone): δ 10.10 (1H, br s), 9.0−9.8 (2H, br), 7.16 (1H, d, $J = 6.6$ Hz), 6.75 (1H, s), 6.65 (1H, $J = 6.6$ Hz), 6.00 (1H, s), 3.70 (3H, s), 2.26 (3H, s). ^{13}C NMR (d_6-acetone): δ 154.1, 136.2, 131.0, 129.1, 112.0, 111.0, 110.4, 103.3, 102.3, 102.1, 55.1, 12.7. HRMS (FAB): *m/z* calcd for $C_{16}H_{13}NO_5$ [M$^+$] 299.0794, found 299.0795.

3-(5-Chloro-2-methyl-1*H*-indol-3-yl)-2,5-dihydroxy[1,4]-benzoquinone (60). Yield: 87%. Mp: 230 °C dec. IR (KBr): 3440, 3315, 1632, 1470, 1358, 1184, 795 cm^{-1}. ^{1}H NMR (d_6-acetone): δ 10.43 (1H, br s), 9.0−10.0 (2H, br), 7.28 (1H, d, $J = 6.3$ Hz), 7.23 (1H, d, $J = 1.5$ Hz), 6.98 (1H, dd, $J = 6.3$, 1.5 Hz), 6.00 (1H, s), 2.29 (3H, s). ^{13}C NMR (d_6-acetone): δ 137.5, 134.5, 129.7, 124.3, 120.5, 119.2, 111.9, 111.0, 103.4, 12.6. HRMS (FAB): *m/z* calcd for $C_{17}H_{13}NO_4$ [M$^+$] 303.0298, found 303.0302.

3-(2-Cyclopropyl-1*H*-indol-3-yl)-2,5-dihydroxy[1,4]-benzoquinone (61). Yield: 81%. Mp: 179−180 °C. IR (KBr): 3358, 2921, 1632, 1461, 1364, 1187, 955, 741 cm^{-1}. ^{1}H NMR (d_6-acetone): δ 10.0 (1H, br s), 9.2−10.0 (2H, br), 7.27 (1H, d, $J = 7.8$ Hz), 7.21 (1H, d, $J = 7.8$ Hz), 7.01 (1H, t, $J = 7.8$ Hz), 6.93 (1H, t, $J = 7.8$ Hz), 6.05 (1H, s), 1.99 (1H, m), 0.89 (4H, m). ^{13}C NMR (d_6-acetone): δ 140.5, 135.7, 128.6, 120.7, 119.4, 119.1, 111.9, 110.7, 103.5, 102.6, 9.2, 7.1. HRMS (FAB): *m/z* calcd for $C_{17}H_{13}NO_4$ [M$^+$] 295.0845, found 295.0846.

2,5-Dihydroxy-3-(2-phenyl-1*H*-indol-3-yl)[1,4]benzoquinone (62). Green crystals from benzene/hexane. Yield: 65%. Mp: 227−228 °C. ^{1}H NMR (d_6-acetone): δ 10.8 (1H, br s), 9.0−10.0 (2H, br), 7.67 (2H, m), 7.45 (1H, m), 7.38 (3H, m), 7.29 (1H, m), 7.12 (1H, t, $J = 8.4$ Hz), 7.03 (1H, t, $J = 7.2$ Hz), 6.06 (1H, s). ^{13}C NMR (d_6-acetone): δ 137.0, 136.7, 133.7, 129.1, 128.8, 127.7, 127.2, 122.1, 120.3, 119.6, 112.1, 111.4, 103.8, 102.3. IR (KBr): 3422, 3303, 3051, 1629, 1355, 1296 cm^{-1}. HRMS (FAB): *m/z* calcd for $C_{20}H_{13}NO_4$ [M$^+$] 331.0845, found 331.0846.

2,5-Dihydroxy-3-(1-methyl-1*H*-indol-3-yl)[1,4]benzoquinone (63). Green crystals from benzene/hexane. Mp: 201−202 °C. Yield: 62%. IR (KBr): 3286, 1627, 1533, 1355, 1298, 1234, 1188, 935, 735 cm^{-1}. ^{1}H NMR (d_6-acetone): δ 9.0−10.0 (2H, br) 7.52 (1H, d, $J = 8.1$ Hz), 7.49 (1H, s), 7.41 (1H, d, $J = 8.4$ Hz), 7.19 (1H, t, $J = 7.5$ Hz), 7.05 (1H, t, $J = 7.5$ Hz), 6.01 (1H, s), 3.89 (3H, s). ^{13}C NMR (d_6-acetone): δ 137.0, 131.6, 127.4, 122.2, 121.5, 119.2, 111.8, 109.5, 103.6, 103.2, 32.4. HRMS (FAB): *m/z* calcd for $C_{15}H_{11}NO_4$ [M$^+$] 269.0688, found 269.0681.

2,5-Dihydroxy-3-(2-ethyl-1*H*-indol-3-yl)[1,4]benzoquinone (64). Green crystals from benzene/hexane. Yield: 77%. Mp: 157−158 °C. IR (KBr): 3395, 3320, 3062, 2976, 1629, 1361, 1291, 1173 cm^{-1}. ^{1}H NMR (d_6-acetone): δ 10.27 (1H, br s), 9.0−10.0 (2H, br), 7.31 (1H, d, $J = 7.8$ Hz), 7.22 (1H, d, $J = 7.8$ Hz), 6.94−7.08 (2H, m), 6.04 (1H, s), 2.68 (2H, q, $J = 7.8$ Hz), 1.28 (3H, t, $J = 6.9$ Hz). ^{13}C NMR (d_6-acetone): δ 140.8, 136.2, 128.4, 120.7, 119.8, 119.0, 111.8, 110.7, 103.5, 101,1, 20.9, 13.4. HRMS (FAB): *m/z* calcd for $C_{16}H_{13}NO_4$ [M$^+$] 283.0845, found 283.0846.

2,5-Dihydroxy-3-(2-isopropyl-1*H*-indol-3-yl)[1,4]benzoquinone (65). Yield: 80%. Mp: 140 °C dec. IR (KBr): 3352, 3290, 2926, 1627, 1363, 1306, 1189, 955, 744 cm^{-1}. ^{1}H NMR (d_6-acetone): δ 10.29 (1H, br s), 9.0−10.0 (2H, br), 7.31 (1H, d, $J = 7.8$ Hz), 7.21 (1H, d, $J = 7.8$ Hz), 7.02 (1H, t, $J = 7.8$ Hz), 6.93 (1H, t, $J = 7.8$ Hz), 6.05 (1H, s), 3.03 (1H, m), 1.32 (6H, d, $J = 6.9$ Hz). ^{13}C NMR (d_6-acetone): δ 144.7, 136.3, 128.3, 120.7, 119.7, 118.9, 111.9, 110.8, 103.5, 100.1, 27.3, 22.2. HRMS (FAB): *m/z* calcd for $C_{17}H_{15}NO_4$ [M$^+$] 297.1001, found 297.0997.

3-(2-*tert*-Butyl-1*H*-indol-3-yl)-2,5-dihydroxy[1,4]benzoquinone (66). Yield: 52%. Mp: 195 °C dec. IR (KBr): 3434, 3329, 2963, 1634, 1597, 1365, 1239, 944, 745 cm^{-1}. ^{1}H NMR (d_6-acetone): δ 10.13 (1H, br s), 8.8−9.8 (2H, br), 7.27 (1H, d, $J = 6.0$ Hz), 7.14 (1H, d, $J = 6.0$ Hz), 6.99 (1H, t, $J = 6.0$ Hz), 6.88 (1H, t, $J = 6.0$ Hz), 6.05 (1H, s), 1.34 (9H, s). ^{13}C NMR (d_6-acetone): δ 145.2, 135.6, 129.3, 121.0, 118.9, 118.5, 113.8, 110.7, 103.8, 99.5, 33.3, 29.7. HRMS (FAB): *m/z* calcd for $C_{17}H_{13}NO_4$ [M$^+$] 311.1158, found 311.1158

2,5-Dihydroxy-3-[2-(1-methylcyclohexyl)-1*H*-indol-3-yl]-[1,4]benzoquinon e (68). Dark blue needles from acetone/hexane. Mp: 191−192 °C. ^{1}H NMR (d_6-acetone): δ 1.34 (3H, s), 1.25−1.60 (10H, m), 6.08 (1H, s), 6.90 (1H, dt, $J = 1.2$, 6.9 Hz), 7.02 (1H, dt, $J = 1.2$, 7.2 Hz), 7.17 (1H, d, $J = 7.8$ Hz), 7.32 (1H, dt, $J = 0.9$, 8.1 Hz), 8.5−10.0 (2H, br s), 10.12 (1H, br s). ^{13}C NMR (d_6-acetone): δ 23.0, 26.3, 37.6, 37.8, 100.4, 103.8, 110.7, 113.8, 118.5, 118.8, 120.9, 129.4, 135.6, 143.8. IR (KBr): 3270, 2975, 2932, 2862, 1700, 1535, 1465, 938, 717 cm^{-1}. HRMS (EI): *m/z* calcd for $C_{21}H_{21}NO_4$ 351.1471, found 351.1471.

3-(4-Fluoro-1*H*-indol-3-yl)-2,5-dihydroxy[1,4]benzoquinone (69). Dark blue needles from acetone/hexane. Mp: 248 °C dec. ^{1}H NMR (d_6-acetone): δ 6.04 (1H, s), 6.70 (1H, dd, $J = 7.8$, 11.1 Hz), 7.09 (1H, dt, $J = 5.1$, 8.1 Hz), 7.28 (1H, dd, $J = 3.3$, 8.1 Hz), 7.43 (1H, d, $J = 2.4$ Hz), 8.0−10.4 (2H, br s), 10.76 (1H, br s). ^{13}C NMR (d_6-acetone): δ 103.5, 104.6, 104.9, 108.0, 122.2, 122.3, 126.8, 139.4, 155.0, 158.3. IR (KBr): 3452, 2954, 2852, 1661, 1639, 1359, 1232, 1192, 1035, 934 cm^{-1}. HRMS (EI): *m/z* calcd for $C_{14}H_8FNO_4$ 273.0437, found 273.0436.

3-(4-Chloro-1*H*-indol-3-yl)-2,5-dihydroxy[1,4]benzoquinone (70). Dark blue needles from acetone/hexane. Mp: 230 °C dec. ^{1}H NMR (d_6-acetone): δ 6.05 (1H, s), 7.01 (1H, dd, $J = 0.8$, 7.6 Hz), 7.10 (1H, t, $J = 8.0$ Hz), 7.40 (1H, d, $J = 2.4$ Hz), 7.44 (1H, dd, $J = 0.8$, 8.0 Hz), 8.6−10.1 (2H, br s), 10.77 (1H, br s). ^{13}C NMR (d_6-acetone): δ 103.6, 104.0, 110.9, 112.5, 120.4, 122.3, 124.9, 125.6, 127.2, 138.1. IR (KBr): 3324, 2953, 1628, 1536, 1484, 1424, 1353, 1187, 927 cm^{-1}. HRMS (FAB): *m/z* calcd for $C_{14}H_8ClNO_4$ 289.0142, found 289.0143.

3-(4-Bromo-1*H*-indol-3-yl)-2,5-dihydroxy[1,4]benzoquinone (71). Dark blue needles from acetone/hexane. Mp: 232 °C dec. ^{1}H NMR (d_6-acetone): δ 6.06 (1H, s), 7.04 (1H, t, $J = 8.0$ Hz), 7.20 (1H, dd, $J = 0.8$, 8.0 Hz), 7.41 (1H, d, $J = 2.8$ Hz), 7.50 (1H, dd, $J = 0.8$, 8.0 Hz), 9.0−10.0 (2H, br s), 10.77 (1H, br s).^{13}C NMR (d_6-acetone): δ 103.6, 104.9, 111.4, 113.7, 122.7, 123.7, 126.3, 127.2, 127.3, 137.8. IR (KBr): 3326, 2983, 2854, 1629, 1540, 1341, 1187, 934 cm^{-1}. HRMS (EI): *m/z* calcd for $C_{14}H_8BrNO_4$ 332.9637, found 332.9634.

2,5-Dihydroxy-3-(4-methoxy-1*H*-indol-3-yl)[1,4]benzoquinone (72). Dark green needles from acetone/hexane. Mp: 225 °C dec. ^{1}H NMR (d_6-acetone): δ 3.71 (3H, s), 6.00 (1H, s), 6.48 (1H, dd, $J = 3.2$, 5.6 Hz), 7.03 (1H, d, $J = 2.0$ Hz), 7.04 (1H, s), 7.23 (1H, d, $J = 2.8$ Hz), 8.5−9.8 (2H, br s), 10.42 (1H, br s). ^{13}C NMR (d_6-acetone): δ 54.9, 100.2, 103.2, 103.7, 105.0, 113.9, 118.2, 122.6, 124.6, 138.2, 154.3. IR (KBr): 3314, 2958, 2933, 1634, 1511, 1357, 1200, 1089, 936 cm^{-1}. HRMS (EI): *m*/*z* calcd for $C_{15}H_{11}NO_5$ 285.0637, found 285.0635.

3-(4-Benzyloxy-1*H*-indol-3-yl)-2,5-dihydroxy[1,4]benzoquinone (73). Dark green needles from acetone/hexane. Mp: 188−189 °C. ^{1}H NMR (d_6-acetone): δ 5.03 (2H, s), 5.88 (1H, s), 6.60 (1H, dd, J = 1.6, 7.2 Hz), 7.06 (1H, q, J = 8.4 Hz), 7.07 (1H, d, J = 2.8 Hz), 7.21 (1H, d, J = 2.4 Hz), 7.24−7.32 (3H, m), 7.34 (1H, d, J = 1.6 Hz), 7.36 (1H, d, J = 2.0 Hz), 8.8−9.8 (2H, br s), 10.44 (1H, br s).^{13}C NMR (d_6-acetone): δ 69.7, 101.1, 103.0, 103.7, 105.2, 113.8, 118.3, 122.6, 124.5, 127.2, 127.6, 128.4, 137.9, 138.3, 153.4. IR (KBr): 3396, 3308, 2918, 2869, 1628, 1506, 1443, 1318, 1075 cm^{-1}. HRMS (EI): *m*/*z* calcd for $C_{21}H_{15}NO_5$ 361.0950, found 361.0952.

2,5-Dihydroxy-3-(4-methyl-1*H*-indol-3-yl)[1,4]benzoquinone (74). Dark green needles from acetone/hexane. Mp: 220 °C dec. ^{1}H NMR (d_6-acetone): δ 2.36 (3H, s), 6.05 (1H, s), 6.76 (1H, dt, J = 0.9, 6.9 Hz), 7.00 (1H, t, J = 7.6 Hz), 7.23 (1H, d, J = 2.4 Hz), 7.27 (1H, d, J = 8.1 Hz), 8.5−10.2 (2H, br s), 10.41 (1H, br s). ^{13}C NMR (d_6-acetone): δ 18.7, 103.7, 104.4, 109.6, 114.1, 121.0, 121.7, 125.6, 126.8, 130.1, 136.9. IR (KBr): 3417, 3328, 3128, 2959, 2927, 2861, 1628, 1533, 1357, 934 cm^{-1}. HRMS (EI): *m*/*z* calcd for $C_{15}H_{11}NO_4$ 269.0688, found 269.0688.

3-(5-Fluoro-1*H*-indol-3-yl)-2,5-dihydroxy[1,4]benzoquinone (75). Dark blue needles from acetone/hexane. Mp: 225−226 °C. ^{1}H NMR (d_6-acetone): δ 6.03 (1H, s), 6.93 (1H, dt, J = 2.4, 9.2 Hz), 7.26 (1H, dd, J = 2.4, 6.4 Hz), 7.44 (1H, dd, J = 4.8, 8.8 Hz), 7.69 (1H, d, J = 2.4 Hz), 8.2−10.4 (2H, br s), 10.69 (1H, br s). ^{13}C NMR (d_6-acetone): δ 103.2, 106.6, 106.9, 109.5, 109.8, 112.3, 112.4, 129.6, 133.0, 156.5, 158.8. IR (KBr): 3449, 3294, 2956, 2855, 1627, 1486, 1335, 1230, 1184, 933 cm^{-1}. HRMS (EI): *m*/*z* calcd for $C_{14}H_8FNO_4$ 273.0437, found 273.0442.

3-(5-Chloro-1*H*-indol-3-yl)-2,5-dihydroxy[1,4]benzoquinone (76). Dark blue needles from acetone/hexane. Mp: 192−193 °C. ^{1}H NMR (d_6-acetone): δ 6.03 (1H, s), 7.12 (1H, dd, J = 2.1, 8.7 Hz), 7.46 (1H, d, J = 8.7 Hz), 7.56 (1H, d, J = 1.8 Hz), 7.67 (1H, d, J = 2.7 Hz), 8.5−10.0 (2H, br s), 10.78 (1H, br s). ^{13}C NMR (d_6-acetone): δ 103.2, 104.6, 111.3, 112.9, 121.3, 121.6, 124.6, 128.0, 129.3, 134.8. IR (KBr): 3409, 3302, 2917, 2879, 1631, 1529, 1354, 1231, 933 cm^{-1}. HRMS (EI): *m*/*z* calcd for $C_{14}H_8ClNO_4$ 289.0142, found 289.0144.

3-(5-Bromo-1*H*-indol-3-yl)-2,5-dihydroxy[1,4]benzoquinone (77). Dark blue needles from acetone/hexane. Mp: 210−211 °C. ^{1}H NMR (d_6-acetone): δ 6.02 (1H, s), 7.24 (1H, dd, J = 1.8, 8.7 Hz), 7.42 (1H, d, J = 8.7 Hz), 7.65 (1H, d, J = 2.7 Hz), 7.71 (1H, d, J = 2.1 Hz), 8.5−10.2 (2H, br s), 10.82 (1H, br s). ^{13}C NMR (d_6-acetone): δ 103.2, 104.5, 112.2, 113.3, 124.2, 124.4, 128.6, 129.0, 129.1, 135.1 IR (KBr): 3309, 3035, 1631, 1455, 1349, 1322, 1230, 930 cm^{-1}. HRMS (EI): *m*/*z* calcd for $C_{14}H_8BrNO_4$ 332.9637, found 332.9636.

2,5-Dihydroxy-3-(5-hydroxy-1*H*-indol-3-yl)[1,4]benzoquinone (78). Dark green needles from acetone/hexane. Mp: 235 °C dec. ^{1}H NMR (d_6-acetone): δ 6.00 (1H, s), 6.73 (1H, dd, J = 2.4, 8.7 Hz), 6.92 (1H, d, J = 2.4 Hz), 7.26 (1H, d, J = 8.7 Hz), 7.51 (1H, d, J = 3.0 Hz), 7.6−7.8 (1H, br s), 8.0−10.0 (2H, br s), 10.39 (1H, br s). ^{13}C NMR (d_6-acetone): δ 103.1, 104.0, 106.2, 111.7, 112.2, 127.8, 128.0, 128.2, 131.1, 151.0 IR (KBr): 3302, 1697, 1630, 1463, 1357, 1202, 935, 856, 802 cm^{-1}. HRMS (EI): *m*/*z* calcd for $C_{14}H_9NO_5$ 271.0481, found 271.0482.

2,5-Dihydroxy-3-(5-methoxy-1*H*-indol-3-yl)[1,4]benzoquinone (79). Dark green needles from acetone/hexane. Mp: 178 °C dec. ^{1}H NMR (d_6-acetone): δ 6.01 (1H, s), 6.79 (1H, dd, J = 2.4, 8.7 Hz), 7.06 (1H, d, J = 2.4 Hz), 7.33 (1H, d, J = 8.7 Hz), 7.56 (1H, d, J = 3.0 Hz), 8.5−10.0 (2H, br s), 10.47 (1H, br s). ^{13}C NMR (d_6-acetone): δ 55.1, 103.1, 104.0, 104.5, 111.8, 112.0, 127.4, 128.2, 131.5, 154.1. IR (KBr): 3324, 3124, 3070, 3004, 2959, 2924, 2838, 1629, 1481, 1354, 1208 cm^{-1}. HRMS (EI): *m*/*z* calcd for $C_{15}H_{11}NO_5$ 285.0637, found 285.0639.

3-(5-Benzyloxy-1*H*-indol-3-yl)-2,5-dihydroxy[1,4]benzoquinone (80). Dark green needles from acetone/hexane. Mp: 198 °C dec. ^{1}H NMR (d_6-acetone): δ 5.08 (2H, s), 6.01 (1H, s), 6.88 (1H, dd, J = 2.7, 8.7 Hz), 7.20 (1H, d, J = 2.4 Hz), 7.37 (1H, d, J = 1.8 Hz), 7.3−7.4 (3H, m), 7.48 (2H, d, J = 6.6 Hz), 7.58 (1H, d, J = 2.7 Hz), 8.0−10.2 (2H, br s), 10.50 (1H, br s).^{13}C NMR (d_6-acetone): δ 70.5, 103.1, 104.6, 105.8, 112.0, 112.4, 127.4, 127.7, 127.8, 128.4, 128.5, 131.7, 138.5, 158.3. IR (KBr): 3110, 3035, 2919, 2866, 1632, 1479, 1358, 1195, 1018, 930 cm^{-1}. HRMS (EI): *m*/*z* calcd for $C_{21}H_{15}NO_5$ 361.0950, found 361.0951.

2,5-Dihydroxy-3-(5-methyl-1*H*-indol-3-yl)[1,4]benzoquinone (81). Dark green needles from acetone/hexane. Mp: 190 °C dec. ^{1}H NMR (d_6-acetone): δ 2.09 (3H, s), 6.02 (1H, s), 6.96 (1H, dd, J = 1.6, 8.4 Hz), 7.31 (1H, s), 7.32 (1H, d, J = 8.4 Hz), 7.53 (1H, d, J = 2.8 Hz), 8.2−10.2 (2H, br s), 10.46 (1H, br s).^{13}C NMR (d_6-acetone): δ 21.1, 103.1, 104.2, 111.2, 112.2, 121.6, 123.1, 127.2, 127.7, 128.0, 134.8. IR (KBr): 3305, 3045, 1631, 1350, 1232, 1203, 932, 798 cm^{-1}. HRMS (EI): *m*/*z* calcd for $C_{15}H_{11}NO_4$ 269.0688, found 269.0683.

3-(6-Fluoro-1*H*-indol-3-yl)-2,5-dihydroxy[1,4]benzoquinone (82). Dark green needles from acetone/hexane. Mp: 130−131 °C. ^{1}H NMR (d_6-acetone): δ 6.03 (1H, s), 6.85 (1H, dt, J = 2.4, 9.6 Hz), 7.19 (1H, dd, J = 2.4, 9.9 Hz), 7.51 (1H, dd, J = 5.4, 9.0 Hz), 7.60 (1H, d, J = 2.7 Hz), 8.2−10.4 (2H, br s), 10.67 (1H, br s). ^{13}C NMR (d_6-acetone): δ 97.2, 97.6, 103.2, 107.5, 107.8, 122.9, 126.0, 123.6, 128.2, 136.2, 158.1, 161.2. IR (KBr): 3350, 1626, 1528, 1454, 1361, 1235 cm^{-1}. HRMS (EI): *m*/*z* calcd for $C_{14}H_8FNO_4$ 273.0437, found 273.0436.

3-(6-Chloro-1*H*-indol-3-yl)-2,5-dihydroxy[1,4]benzoquinone (83). Dark green needles from acetone/hexane. Mp: 229 °C dec. ^{1}H NMR (d_6-acetone): δ 6.03 (1H, s), 7.04 (1H, dd, J = 1.8, 8.7 Hz), 7.50 (1H, d, J = 1.8 Hz), 7.52 (1H, d, J = 8.7 Hz), 7.64 (1H, d, J = 2.4 Hz), 8.4−10.4 (2H, br s), 10.74 (1H, br s). ^{13}C NMR (d_6-acetone): δ 103.2, 105.0, 111.3, 111.4, 119.6, 123.2, 125.6, 127.0, 128.6, 136.8. IR (KBr): 3418, 3305, 2956, 1623, 1534, 1451, 1357, 936 cm^{-1}. HRMS (EI): *m*/*z* calcd for $C_{14}H_8ClNO_4$ 289.0142, found 289.0144.

3-(6-Benzyloxy-1*H*-indol-3-yl)-2,5-dihydroxy[1,4]benzoquinone (84). Dark green needles from acetone/hexane. Mp: 205 °C dec. ^{1}H NMR (d_6-acetone): δ 5.14 (2H, s), 6.01 (1H, s), 6.80 (1H, dd, J = 2.4, 8.7 Hz), 7.07 (1H, d, J = 2.1 Hz), 7.26−7.58 (9H, m), 8.4−10.2 (2H, br s), 10.44 (1H, br s). ^{13}C NMR (d_6-acetone): δ 70.2, 96.0, 103.1, 104.7, 110.1, 121.5, 122.7, 126.7, 127.6, 127.7, 128.5, 137.0, 138.2, 155.4. IR (KBr): 3414, 3314, 2925, 1631, 1353, 1299, 1239, 1023, 935 cm^{-1}. HRMS (EI): *m*/*z* calcd for $C_{21}H_{15}NO_5$ 361.0950, found 361.0951.

2,5-Dihydroxy-3-(6-methyl-1*H*-indol-3-yl)[1,4]benzoquinone (85). Dark green needles from acetone/hexane. Mp: 190 °C dec. ^{1}H NMR (d_6-acetone): δ 2.37 (3H, s), 5.97 (1H, s), 6.84 (1H, dd, J = 1.6, 8.4 Hz), 7.20 (1H, s), 7.38 (1H, d, J = 8.4 Hz), 7.48 (1H, d, J = 2.8 Hz), 8.0−10.0 (2H, br s), 10.45 (1H, br s). ^{13}C NMR (d_6-acetone): δ 21.0, 103.2, 104.6, 111.3, 112.3, 121.0, 121.7, 124.8, 127.1, 130.9, 136.8. IR (KBr): 3398, 2919, 2855, 1701, 1617, 1530, 1452, 932 cm^{-1}. HRMS (EI): *m*/*z* calcd for $C_{15}H_{11}NO_4$ 269.0688, found 269.0685.

2,5-Dihydroxy-3-(7-methyl-1*H*-indol-3-yl)[1,4]benzoquinone (86). Green crystals from benzene/hexane. Yield: 66%. Mp: 218−219 °C. IR (KBr): 3427, 3326, 1618, 1325, 1291, 1185 cm^{-1}. ^{1}H NMR (d_6-acetone): δ 10.58 (1H, br s), 9.0−10.0 (2H, br), 7.56 (1H, d, J = 2.7 Hz), 7.36 (1H, t, J = 4.5 Hz), 6.95 (1H, s), 6.93(1H, s), 6.02 (1H, s), 2.52 (3H, s). ^{13}C NMR (d_6-acetone): δ 135.8, 127.2, 126.6, 122.1, 120.6, 119.6, 119.5, 112.2, 105.2, 103.2, 16.4. HRMS (FAB): *m*/*z* calcd For $C_{15}H_{11}NO_4$ [M$^+$] 269.0688, found 269.0686.

2,5-Dihydroxy-3-(7-propyl-1*H*-indol-3-yl)[1,4]benzoquinone (87). Dark green needles from acetone/hexane. Mp: 207 °C dec. ^{1}H NMR (d_6-acetone): δ 0.98 (3H, t, J = 7.6 Hz), 1.76 (2H, h, J = 7.6 Hz), 2.89 (1H, t, J = 7.6 Hz), 6.02 (1H, s), 6.94−7.00 (2H, m), 7.39−7.39 (1H, m), 7.54 (1H, d, J = 2.8 Hz), 8.4−10.0 (2H, br s), 10.58 (1H, br s). ^{13}C NMR (d_6-acetone): δ 13.7, 23.3, 33.3, 103.2, 105.1, 112.2, 119.4, 119.7, 121.4, 125.4, 126.9, 127.2, 134.3. IR (KBr): 3421, 3330, 2955, 2868, 1615, 1534, 1354, 1297, 1230, 1195 cm^{-1}. HRMS (EI): *m*/*z* calcd for $C_{17}H_{15}NO_4$ 297.1001, found 297.1001.

3-(7-*tert*-Butyl-1*H*-indol-3-yl)-2,5-dihydroxy[1,4]benzoquinone (88). Dark green needles from acetone/hexane. Mp: 210−211 °C. ^{1}H NMR (d_6-acetone): δ 1.53 (9H, s), 6.03 (1H, s), 6.98 (1H, t, J = 8.0 Hz), 7.08 (1H, dd, J = 1.2, 7.6 Hz), 7.36 (1H, d, J = 8.0 Hz), 7.51 (1H, d, J = 2.8 Hz), 9.0−10.0 (2H, br s), 10.35 (1H, br s). ^{13}C NMR (d_6-acetone): δ 29.8, 34.2, 103.2, 104.6, 112.0, 118.1, 119.3, 120.1, 126.8, 128.0, 133.5, 133.6. IR (KBr): 3337, 2967, 2866, 1631, 1360, 1299, 1223, 931 cm^{-1}. HRMS (EI): m/z calcd for $C_{18}H_{17}NO_4$ 311.1158, found 311.1158.

2,5-Dihydroxy-3-(7-phenyl-1*H*-indol-3-yl)[1,4]benzoquinone (89). Dark green needles from acetone/hexane. Mp: 210−211 °C. ^{1}H NMR (d_6-acetone): δ 6.04 (1H, s), 7.1−7.2 (2H, m), 7.40 (1H, t, J = 7.4 Hz), 7.4−7.7 (7H, m), 9.0−10.2 (2H, br s), 10.58 (1H, br s). ^{13}C NMR (d_6-acetone): δ 103.3, 105.1, 119.9, 121.3, 121.4, 121.7, 125.9, 127.4, 127.9, 128.1, 128.6, 129.1, 133.8, 139.4. IR (KBr): 3402, 3325, 3029, 2950, 2923, 1633, 1524, 1428, 1343, 760 cm^{-1}. HRMS (EI): m/z calcd for $C_{20}H_{13}NO_4$ 331.0845, found 331.0844.

2,5-Dihydroxy-3-(7-methoxy-1*H*-indol-3-yl)[1,4]benzoquinone (90). Dark green needles from acetone/hexane. Mp: 202−203 °C. ^{1}H NMR (d_6-acetone): δ 3.91 (3H, s), 5.98 (1H, s), 6.64 (1H, d, J = 5.7 Hz), 6.91 (1H, t, J = 6.0 Hz), 7.09 (1H, d, J = 6.0 Hz), 7.51 (1H, d, J = 1.8 Hz), 7.8−10.2 (2H, br s), 10.63 (1H, br s). ^{13}C NMR (d_6-acetone): δ 55.0, 101.7, 103.2, 105.2, 112.1, 114.8, 119.7, 126.7, 127.1, 128.4, 146.6. IR (KBr): 3390, 3311, 2928, 1634, 1501, 1449, 1354, 1097, 933 cm^{-1}. HRMS (EI): m/z calcd for $C_{15}H_{11}NO_5$ 285.0637, found 285.0636.

3-(7-Benzyloxy-1*H*-indol-3-yl)-2,5-dihydroxy[1,4]benzoquinone (91). Dark green needles from acetone/hexane. Mp: 202 °C dec. ^{1}H NMR (d_6-DMSO): δ 5.23 (2H, s), 5.84 (1H, s), 6.38 (1H, d, J = 7.6 Hz), 6.81 (1H, d, J = 8.0 Hz), 6.87 (1H, d, J = 8.0 Hz), 7.26−7.32 (2H, m), 7.36 (2H, t, J = 7.2 Hz), 7.52 (2H, d, J = 7.6 Hz), 9.0−10.0 (2H, br s), 11.42 (1H, br s). ^{13}C NMR (d_6-DMSO): δ 69.8, 103.5, 104.4, 105.5, 112.7, 115.0, 119.6, 126.7, 127.5, 128.2, 128.4, 128.8, 129.1, 138.0, 145.6. IR (KBr): 3421, 2960, 2925, 2856, 1631, 1501 cm^{-1}. HRMS (EI): m/z calcd for $C_{21}H_{15}NO_5$ 361.0950, found 361.0950.

3-(7-Fluoro-1*H*-indol-3-yl)-2,5-dihydroxy[1,4]benzoquinone (92). Dark blue needles from acetone/hexane. Mp: 201 °C dec. IR (KBr): 3420, 3277, 3162, 2923, 2861, 1632, 1357, 1299, 1234 cm^{-1}. ^{1}H NMR (d_6-acetone): δ 6.03 (1H, s), 6.90 (1H, dd, J = 8.0, 11.6 Hz), 6.99 (1H, dt, J = 4.8, 8.0 Hz), 7.34 (1H, d, J = 8.0 Hz), 7.65 (1H, J = 2.8 Hz), 9.0−10.2 (2H, br s), 11.00 (1H, br s). ^{13}C NMR (d_6-acetone): δ 103.3, 106.0, 106.2, 111.3, 118.0, 119.3, 119.4, 128.1, 128.3, 130.7. HRMS (EI): m/z calcd for $C_{14}H_8FNO_4$ 273.0437, found 273.0440.

3-(7-Chloro-1*H*-indol-3-yl)-2,5-dihydroxy[1,4]benzoquinone (93). Dark blue needles from acetone/hexane. Mp: 207 °C dec. ^{1}H NMR (d_6-acetone): δ 6.04 (1H, s), 7.04 (1H, t, J = 10.4 Hz), 7.20 (1H, d, J = 10.0 Hz), 7.66 (1H, d, J = 4.0 Hz), 9.0−10.2 (2H, br s), 10.86 (1H, br s). ^{13}C NMR (d_6-acetone): δ 103.4, 106.1, 111.2, 116.4, 120.1, 120.9, 121.0, 128.4, 128.7, 133.3. IR (KBr): 3428, 3310, 3091, 1626, 1354, 1296, 1063, 930 cm^{-1}. HRMS (EI): m/z calcd for $C_{14}H_8ClNO_4$ 289.0142, found 289.0138.

3-(7-Bromo-1*H*-indol-3-yl)-2,5-dihydroxy[1,4]benzoquinone (94). Dark blue needles from acetone/hexane. Mp: 225−226 °C. ^{1}H NMR (d_6-acetone): δ 6.04 (1H, s), 6.99 (1H, t, J = 7.8 Hz), 7.35 (1H, dd, J = 0.6, 7.8 Hz), 7.54 (1H, d, J = 8.1 Hz), 7.66 (1H, d, J = 2.7 Hz), 8.4−10.0 (2H, br s), 10.76 (1H, br s). ^{13}C NMR (d_6-acetone): δ 103.4, 104.3, 106.2, 111.3, 120.6, 121.4, 124.1, 128.4, 130.8, 134.7. IR (KBr): 3330, 2959, 2929, 2854, 1617, 1531, 1433, 1354, 1292, 932 cm^{-1}. HRMS (EI): m/z calcd for $C_{14}H_8BrNO_4$ 332.9637, found 332.9637.

3-(7-Benzyl-1*H*-indol-3-yl)-2,5-dihydroxy[1,4]benzoquinone (95). Dark green needles from acetone/hexane. Mp: 206−207 °C. ^{1}H NMR (d_6-acetone): δ 4.28 (2H, s), 6.02 (1H, s), 6.92−7.03 (2H, m), 7.14−7.34 (5H, m), 7.41 (1H, d, J = 7.5 Hz), 7.54 (1H, d, J = 2.7 Hz), 8.6−10.3 (2H, br s), 10.49 (1H, br s). ^{13}C NMR (300 Hz, d_6-acetone): δ 37.1, 103.2, 105.2, 112.0, 119.6, 120.2, 122.2, 124.1, 126.1, 127.1, 127.4, 128.5, 128.9, 135.2, 140.7. IR (KBr): 3422, 3326, 3084, 3027, 1612, 1532, 1438, 1353 cm^{-1}. HRMS (EI): m/z calcd for $C_{21}H_{15}NO_4$ 345.1001, found 345.1001.

2,5-Dihydroxy-3-[7-(2-methylbenzyl)-1*H*-indol-3-yl][1,4]benzoquinone (96). Dark green needles from acetone/hexane. Mp: 220 °C dec. ^{1}H NMR (d_6-acetone): δ 2.27 (3H, s), 4.25 (2H, s), 6.02 (1H, s), 6.70 (1H, d, J = 7.2 Hz), 6.92−7.04 (2H, m), 7.05−7.15 (2H, m), 7.18 (1H, t, J = 7.2 Hz), 7.56 (1H, d, J = 2.4 Hz), 8.8−10.2 (2H, br s), 10.56 (1H, br s). ^{13}C NMR (d_6-acetone): δ 19.1, 34.6, 103.2, 105.2, 112.1, 119.5, 120.2, 121.6, 123.2, 126.1, 126.5, 126.9, 127.4, 129.4, 130.2, 135.4, 136.8, 138.3. IR (KBr): 3304, 2966, 1699, 1624, 1434, 1350, 1218 cm^{-1}. HRMS (EI): m/z calcd for $C_{22}H_{17}NO_4$ 359.1158, found 359.1157.

3-(1*H*-Benzo[*g*]indol-3-yl)-2,5-dihydroxy[1,4]benzoquinone (97). Dark green needles from acetone/hexane. Mp: 210 °C dec. ^{1}H NMR (d_6-acetone): δ 6.05 (1H, s), 7.42 (1H, dt, J = 1.5, 6.9 Hz), 7.45−7.56 (2H, m), 7.60−7.68 (2H, m), 7.93 (1H, d, J = 8.1 Hz), 8.36 (1H, d, J = 8.1 Hz), 8.8−10.5 (2H, br s), 11.51 (1H, br s). ^{13}C NMR (d_6-acetone): δ 103.2, 106.4, 111.9, 119.8, 120.3, 122.1, 122.4, 123.9, 125.4, 128.6, 130.5, 130.8. IR (KBr): 3318, 3158, 3060, 2923, 2855, 1612, 1353, 1291, 929, 814 cm^{-1}. HRMS (FAB): m/z calcd for $C_{18}H_{11}NO_4$ 305.0688, found 305.0686.

3-(2,6-Dimethyl-1*H*-indol-3-yl)-2,5-dihydroxy[1,4]benzoquinone (98). Dark green needles from acetone/hexane. Mp: 210 °C dec. ^{1}H NMR (d_6-acetone): δ 2.28 (3H, s), 2.37 (3H, s), 6.03 (1H, s), 6.78 (1H, d, J = 8.7 Hz), 7.07−7.14 (2H, m), 8.4−9.9 (2H, br s), 10.09 (1H, br s). ^{13}C NMR (d_6-acetone): δ 12.8, 21.2, 103.4, 110.5, 119.6, 120.7, 126.5, 129.9, 134.8, 136.4. IR (KBr): 3384, 3324, 2975, 2912, 2857, 1637, 1352, 1295, 1228, 1184 cm^{-1}. HRMS (EI): m/z calcd for $C_{16}H_{13}NO_4$ 283.0845, found 283.0849.

3-(2,7-Dimethyl-1*H*-indol-3-yl)-2,5-dihydroxy[1,4]benzoquinone (99). Dark green needles from acetone/hexane. Mp: 206 °C dec. ^{1}H NMR (d_6-acetone): δ 2.32 (3H, s), 2.47 (3H, s), 6.05 (1H, s), 6.85 (1H, s), 6.88 (1H, d, J = 7.2 Hz), 7.07 (1H, dd, J = 2.1, 7.2 Hz), 8.5−10.0 (2H, br s), 10.16 (1H, br s). ^{13}C NMR (d_6-acetone): δ 12.8, 16.4, 102.6, 103.4, 112.0, 117.6, 119.2, 119.7, 121.3, 128.2, 135.2, 135.4. IR (KBr): 3331, 2945, 2856, 1629, 1559, 1454, 1185, 932 cm^{-1}. HRMS (EI): m/z calcd for $C_{16}H_{13}NO_4$ 283.0845, found 283.0846.

3-(6,7-Dimethyl-1*H*-indol-3-yl)-2,5-dihydroxy[1,4]benzoquinone (100). Dark green needles from acetone/hexane. Mp: 220 °C dec. ^{1}H NMR (d_6-acetone): δ 2.35 (3H, s), 2.43 (3H, s), 6.01 (1H, s), 6.86 (1H, d, J = 8.1 Hz), 7.25 (1H, d, J = 7.8 Hz), 7.50 (1H, d, J = 2.7 Hz), 8.8−10.2 (2H, br s), 10.38 (1H, br s). ^{13}C NMR (d_6-acetone): δ 12.7, 18.8, 103.1, 118.2, 112.5, 119.1, 122.2, 123.1, 125.0, 126.9, 128.6, 129.9. IR (KBr): 3340, 3150, 2921, 2869, 1615, 1533, 1351 cm^{-1}. HRMS (EI): m/z calcd for $C_{16}H_{13}NO_4$ 283.0845, found 283.0850.

3-(5,6-Methylenedioxy-1*H*-indol-3-yl)-2,5-dihydroxy[1,4]benzoquinone (101). Dark green needles from acetone/hexane. Mp: 335 °C dec. ^{1}H NMR (d_6-acetone): δ 5.91 (2H, s), 6.00 (1H, s), 6.92 (1H, d, J = 0.8 Hz), 6.94 (1H, d, J = 0.4 Hz), 7.44 (1H, d, J = 2.8 Hz), 8.8−10.2 (2H, br s), 10.42 (1H, br s). ^{13}C NMR (d_6-acetone): δ 92.4, 100.6, 100.64, 100.8, 103.0, 109.8, 126.2, 126.3, 131.2, 142.8, 144.7. IR (KBr): 3420, 3077, 2937, 2844, 1624, 1470, 1330 cm^{-1}. HRMS (EI): m/z calcd for $C_{15}H_9NO_6$ 299.0430, found 299.0428.

3-(5,6-Dimethoxy-1*H*-indol-3-yl)-2,5-dihydroxy[1,4]benzoquinone (102). Dark green needles from acetone/hexane. Mp: 360 °C dec. ^{1}H NMR (d_6-acetone): δ 3.77 (3H, s), 3.81 (3H, s), 6.00 (1H, s), 7.02 (1H, s), 7.09 (1H, s), 7.46 (1H, d, J = 2.7 Hz), 8.2−10.0 (2H, br s), 10.38 (1H, br s). ^{13}C NMR (d_6-acetone): δ 55.7, 56.0, 95.3, 103.0, 104.6, 105.4, 120.0, 126.2, 130.9, 145.3, 147.6. IR (KBr): 3467, 3342, 2962, 2917, 1628, 1485, 1339 cm^{-1}. HRMS (FAB): m/z calcd for $C_{16}H_{13}NO_6$ 315.0743, found 315.0744.

2,5-Dihydroxy-3-[7-(3-methylbut-2-enyl)-1*H*-indol-3-yl][1,4]benzoquinone (104). Mp: 215−217 °C. IR (KBr): 3406, 3330, 1619, 1355, 1293, 1161, 930 cm^{-1}. ^{1}H NMR (d_6-

acetone): δ 10.40 (1H, br s), 9.2−9.8 (2H, br), 7.54 (1H, d, *J* = 3 Hz), 7.36 (1H, m), 6.95−7.00 (2H, m), 6.02 (1H, s), 5.46 (1H, m), 3.63 (2H, d, *J* = 7.2 Hz), 1,77 (3H, s), 1,75 (3H, s). ^{13}C NMR (d_6-acetone): δ 135.2, 132.7, 127.3, 126.9, 124.5, 122.4, 120.9, 119.8, 119.5, 112.1, 105.1, 103.2, 25.2, 17.3. HRMS (FAB): *m*/*z* calcd for $C_{17}H_{13}NO_4$ [M$^+$] 323.1158, found 323.1157.

2,5-Dihydroxy-3-(7-geranyl-1*H*-indol-3-yl)[1,4]benzoquinone (105). Dark green needles from acetone/hexane. Mp: 160−161 °C. ^{1}H NMR (d_6-acetone): δ 1.59 (3H, s), 1.66 (3H, s), 1.77 (3H, s), 2.10 (4H, m), 5.13 (1H, t, *J* = 6.5 Hz), 5.50 (1H, t, *J* = 7.5 Hz), 6.02 (1H, s), 6.97 (2H, m), 7.37 (1H, t, *J* = 4.5 Hz), 7.55 (1H, d, *J* = 3.0 Hz), 7.8−10.2 (2H, br s), 10.43 (1H, br s). ^{13}C NMR (d_6-acetone): δ 15.8, 17.2, 25.4, 26.8, 39.9, 103.2, 105.2, 112.1, 115.5, 119.5, 119.7, 120.8, 122.2, 124.4, 126.9, 127.2, 131.1, 135.2, 136.5. IR (KBr): 3324, 3169, 2967, 2920, 1614, 1531, 1438, 1354, 1292, 929 cm^{-1}. HRMS (FAB): *m*/*z* calcd for $C_{24}H_{25}NO_4$ 391.1784, found 391.1790.

2,5-Dihydroxy-3-(7-farnesyl-1*H*-indol-3-yl)[1,4]benzoquinone (106). Dark green needles from acetone/hexane. Mp: 165−166 °C. ^{1}H NMR (d_6-acetone): δ 1.58 (3H, s), 1.60 (3H, s), 1.64 (3H, s), 1.78 (3H, s), 1.92−2.22 (8H, m), 3.65 (2H, d, *J* = 7.2 Hz), 5.10 (1H, t, *J* = 6.9 Hz), 5.17 (1H, t, *J* = 6.9 Hz), 5.50 (1H, t, 7.2 Hz), 6.02 (1H, s), 6.94−7.00 (2H, m), 7.37 (1H, t, *J* = 4.8 Hz), 7.54 (1H, d, *J* = 2.7 Hz), 8.4−10.0 (2H, br s), 10.42 (1H, br s). ^{13}C NMR (d_6-acetone): δ 15.6, 15.8, 17.2, 25.3, 26.7, 26.9, 39.9, 103.2, 105.2, 112.1, 119.5, 119.8, 120.8, 122.2, 124.3, 124.4, 124.5, 126.9, 127.2, 130.9, 134.9, 135.2, 136.6. IR (KBr): 3419, 3326, 3164, 2967, 2918, 1611, 1531, 1439, 1353, 801 cm^{-1}. HRMS (FAB): *m*/*z* calcd for $C_{29}H_{33}NO_4$ 459.2410, found 459.2412.

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Supporting Information Available: ^{1}H NMR spectra of compounds characterized by high-resolution mass spectrometry (**5, 6, 8, 14−17, 48, 56, 58−102, 104−106,** 1-methylcyclopropanecarboxylic acid *o*-tolylamide, and 2-(1-methylcyclopropyl)indole). This material is available free of charge via the Internet at http://pubs.acs.org.

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