Access to Indoles *via* Diels-Alder Reactions of 2-Vinylpyrroles with Maleimides

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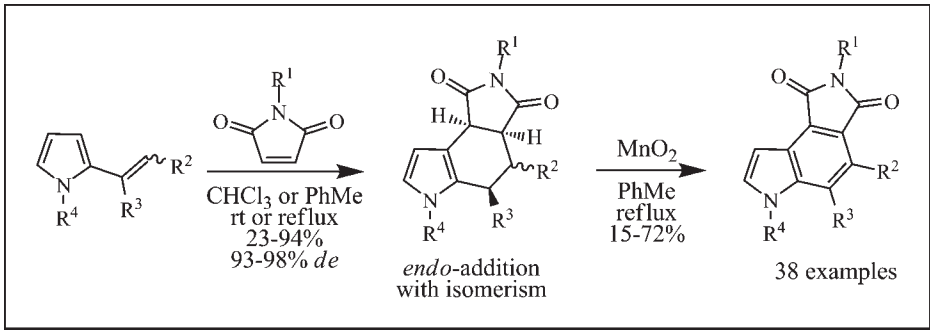

Variously substituted 2-vinylpyrroles underwent an *endo*-addition [4+2] cycloaddition reaction with maleimides followed by a spontaneous highly diastereoselective (93–98% *de*) isomerization to give tetrahydroindoles in moderate to excellent yield. Treatment with activated MnO_2 in refluxing toluene provided the corresponding indoles in moderate to good yield. This highly convergent methodology for formation of indoles is versatile and the starting materials are conveniently prepared.

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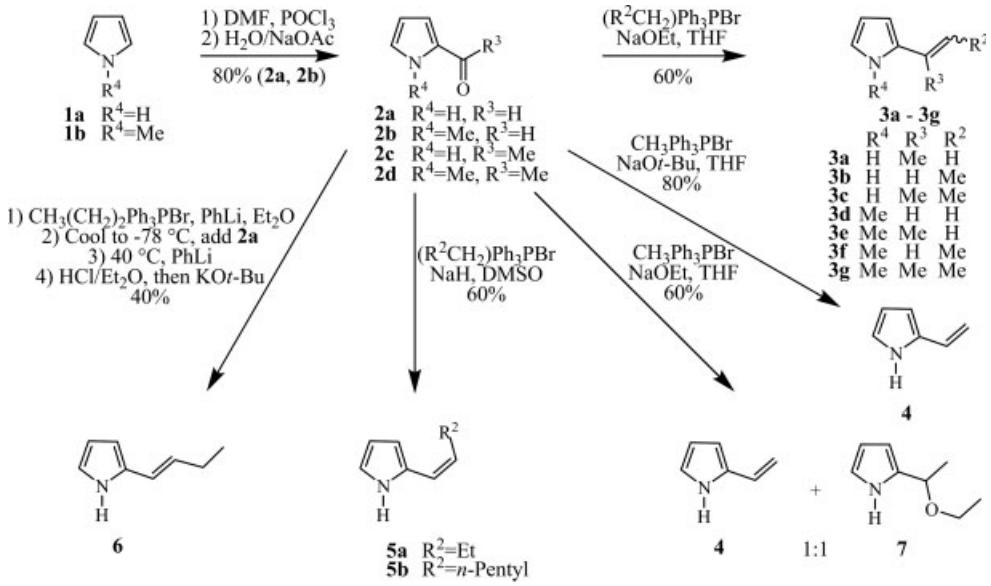
INTRODUCTION

The formation of indole continues to attract much study [1] because of its frequent occurrence in nature and its biological activity in both natural [2] and synthetic [3] products. We have reported that 3-vinylindoles are generated from condensation of indole and ketones, which then undergo an *in situ* Diels-Alder reaction with maleimides to form tetrahydrocarbazoles [4]. We recently reported the analogous work in which pyrroles are condensed with cyclic ketones to give 2-vinylpyrroles that also undergo *in situ* Diels-Alder reactions with maleimides to give the corresponding tetrahydroindoles, many of which exhibited high levels of *in vitro* activity against a variety of human cancer cell lines [5]. Although the *in situ* Diels-Alder approach toward indoles is advantageous with its one-pot method, it is somewhat limited in that acidic conditions are required to catalyze the condensation, and pyrroles are well known to form polymers under acidic conditions [6]. Indeed, we battled with the formation of polymeric material when using vinylpyrroles for *in situ* Diels-Alder reactions and found that to circumvent the problem, the use of 5-alkyl-substituted pyrroles was essential.

These results inspired us to explore the Diels-Alder chemistry of separately prepared 2-vinylpyrroles. Preparing the vinylpyrrole in a separate step *via* methods not using acidic conditions has the advantage of allowing the use of 5-unsubstituted 2-vinylpyrroles in Diels-Alder reactions. In addition, we were interested in effecting aromatization of the resulting tetrahydroindoles to give indoles. Some studies have been conducted on this route toward indoles using as the dienophiles carboxyl-substituted acetylenes [7,8], several acyclic electron-deficient alkenes [8,9], maleic anhydride and/or *N*-phenylmaleimide with *N*-benzenesulfonyl-2-vinylpyrrole [9,10] and methyl 3-nitroacrylate with *N*-*p*-toluenesulfonyl-2-vinylpyrroles [11] (neither of which was taken through to the aromatic indole), tetrachloro- or tetrabromocyclopropene with *N*-*p*-toluenesulfonyl-2-vinylpyrrole [12], *N*-phenylmaleimide with *N*-methyl- and *N*-propanoyloxy-2-vinylpyrrole [9], *N*-H-maleimide with 3-(*N*-alkyl-2-pyrrolyl) acrylates [13] and *N*-alkyl-2-styrylpyrroles [13,14], and one report using various maleimides with both *N*-H and *N*-alkyl-2-vinylpyrroles [15]. Several of these studies report biological activity from this class of compounds, particularly anticancer activity [13–15]. To our knowledge, no prior broad study of the efficacy of the synthesis of indoles *via* Diels-Alder reactions of 5-unsubstituted 2-vinylpyrroles with *N*-substituted maleimides has been reported. In most of the earlier studies, only *N*-alkyl-substituted pyrroles were studied, presumably due to both the higher reactivity of *N*-H pyrroles and the formation of Michael-addition products between the adduct

Scheme 1. Synthesis of 2-vinylpyrroles.



and dienophile when certain *N*-H-2-vinylpyrroles are used in Diels-Alder reactions, reported here for the first time. None of the earlier studies has characterized the diastereoselective isomerism of the adduct, potentially valuable for synthetic applications. We report here the first demonstration of the use of chiral maleimides in Diels-Alder reactions with 2-vinylpyrroles.

Herein, we report 38 examples where indoles are conveniently available from oxidation of the corresponding tetrahydroindoles, formed *via* Diels-Alder reactions of both *N*-H and *N*-alkyl-2-vinylpyrroles with a wide range of *N*-substituted maleimides. We also report a highly diastereoselective isomerism of the Diels-Alder adduct, and isolation of Michael-addition products between the adduct and the dienophile with the major product being the more sterically congested diastereomer. Additionally, we report an improved synthesis of *N*-H-2-vinylpyrrole.

RESULTS AND DISCUSSION

Synthesis of starting materials. A Vilsmeier-Haack formylation [16] was performed on the appropriate pyrrole (**1a** and **1b**, Scheme 1) to give pyrrole-2-carboxaldehydes **2a** and **2b**. Next, a Wittig reaction was conducted on **2a** and **2b** or on commercially available **2c** and **2d** to form the appropriate vinylpyrrole **3–6** [7a,8,17,18]. Various procedures for the Wittig reaction were used to synthesize the vinylpyrroles. The common procedure for the synthesis of 2-vinylpyrroles [18,19] using sodium ethoxide as the base for formation of the ylide was used to make methyl-substituted vinylpyrroles **3a–3g**. For vinylpyrroles **3b**, **3c**, **3f**, and **3g**, this procedure gave ~1:3.9, 2.8:1, 1:1.8, and 1:1.5 *E*:*Z* molar mixtures, respectively, as determined by ^{1}H NMR, which were used without further purification for formation of the Diels-Alder adducts. Vinylpyrrole **3a** decomposed or polymerized [20] rapidly at room temperature (rt) to a dark viscous liquid before it could be used in any Diels-Alder reaction.

Although the sodium ethoxide procedure produced the desired *N*-H-2-vinylpyrrole **4**, it also consistently gave a 1:1 molar ratio of the unwanted and not easily separated byproduct 2-(1-ethoxyethyl)-pyrrole **7**. X-ray crystallography proved the structure of **7** (Fig. 1). The isolation of **7** was surprising, considering the lack of mention of this compound in any literature procedure for synthesis of **4**. Although the mixture of **4** and **7** was used as is for

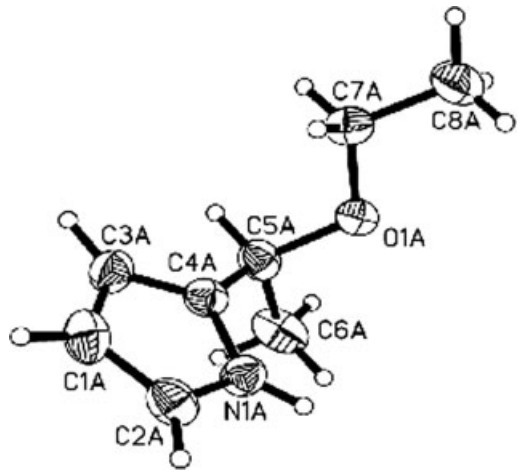
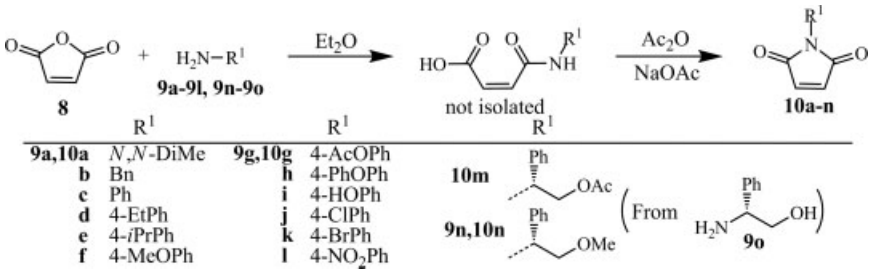


Figure 1. ORTEP representation of the X-ray structure of 2-(1-ethoxyethyl)pyrrole (**7**).

Scheme 2. Synthesis of maleimides.



formation of the Diels-Alder adducts, a search for a way to avoid contamination with this impurity was sought, which probably comes from an acid-catalyzed addition of ethoxide to the vinyl group in the expected Markovnikov orientation. Eliminating the acidic aqueous sodium bisulfite wash from the workup had no effect on the proportion of **7** formed. Heating the mixture of **4** and **7** in DMSO was attempted with the hope of effecting deethanolysis, which did occur, but with the destruction of a large amount of the desired **4**, probably from polymerization. It was found that using sodium *t*-butoxide in place of sodium ethoxide completely eliminated the byproduct and gave a higher efficiency than the sodium ethoxide procedure, with a consistent yield of ~80%, and less need for excess methyltriphenylphosphonium bromide and base (1.25 equiv) than was required for complete conversion using the sodium ethoxide procedure (2 equiv).

To determine whether the Diels-Alder reactions of 2-vinylpyroles with maleimides took place with the predicted *endo*-addition, vinylpyrroles with predominantly *E* or *Z* stereochemistry were desired. Ethyl- and pentyl-substituted vinylpyrroles **5a** and **5b** were made from aldehyde **2a** with the Corey procedure for the Wittig reaction [21], using methylsulfinyl carbanion as the base, formed from the reaction of DMSO with sodium hydride. ^{1}H NMR analysis showed that this procedure gave **5a** [18a] exclusively as the *Z* isomer and **5b** in a 1:9 *E*:*Z* mixture. For comparison of the stereochemistry in the resulting Diels-Alder adducts, (*E*)-2-(2-ethylvinyl)pyrrole **6** [18a] was synthesized using the Schlosser modification of the Wittig reaction [22], giving a 40% yield of an ~12:1 *E*:*Z* molar mixture.

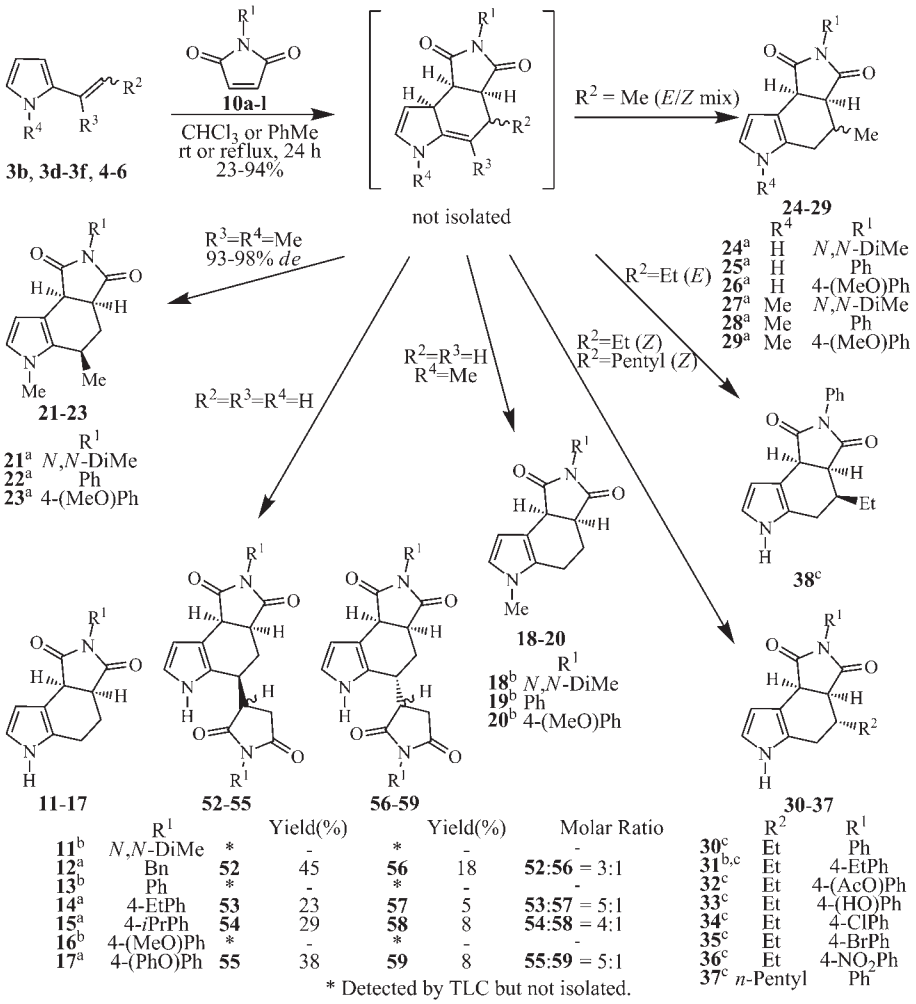
Maleimides were synthesized by the typical procedure [23], by reaction of maleic anhydride **8** with the appropriate primary amine **9a–9l** and **9n–9o**, and then heating the resulting amide-acid in an excess of acetic anhydride (10 equiv) with sodium acetate (0.5 equiv), giving the corresponding *N*-substituted maleimide (**10a–10n**, Scheme 2). When the acid from reaction of **8** with (*R*)-(−)-phenylglycinol (**9o**) was cyclized, the primary alcohol group was acetylated, giving acetate **10m**. To make the chiral methyl ether **10n**, (*R*)-2-methoxy-1-phenylethanamine (**9n**) was synthesized by methylation of **9o** by reaction of sodium hydride followed by addition of methyl iodide [24].

Diels-Alder reactions. Diels-Alder reactions of 2-vinylpyrroles **3b–3g**, **4**, and **5a** with maleimides **10a–10f**, **10h**, **10m**, and **10n** in chloroform gave adducts **11–29**, **31**, and **39–51** (Scheme 3, Table 1). The chiral adducts **39–51** were not isolated but were taken directly through to the aromatic indoles **85–97** (Scheme 4). The reaction solution was refluxed, if necessary, and stopped when complete, as indicated by TLC. Alternatively, the Diels-Alder reactions of 2-vinylpyrroles **5** and **6** with maleimides **10c**, **10d**, **10g**, and **10i–10l** were run in refluxing toluene, giving adducts **30–38**. In both procedures, vinylpyrroles **3–6** were used in slight excess (1.1 equiv) to simplify the required chromatographic purification procedure, because, while the vinylpyrroles were always eluted first, unreacted maleimides generally were eluted very near to the adducts. The unrearranged adducts were not isolated in any case; instead, the rearomatized form of the adducts was obtained. Although an extensive case-by-case comparison of the efficiency of the two procedures was not undertaken, adduct **31** was produced in both chloroform (70% yield) and toluene (41%). Further, comparing the average yield of the toluene-procedure-derived products **30–38** (38%) to the average yield of the chloroform-procedure-derived products **12**, **14**, **15**, **17–29**, and **31** (73%), the chloroform procedure gave better yields.

To determine whether *endo*- or *exo*-addition was predominant, the orientation of a terminal substituent on the vinyl group of the pyrrole was studied in the resulting isomerized adducts using nuclear Overhauser effect (NOE) experiments (Fig. 2). For description of the orientation, the diastereomer with the *syn* 3a-H and 8b-H protons (Fig. 3) protruding from the α-face and the fused maleimide protruding from the β-face will always be used, corresponding to the structures at the top of Figure 2, this convention is also used throughout the Experimental.

2-(2-Methylvinyl)-pyrroles **3b** and **3f** gave the expected mixture of 4α-Me and 4β-Me in rearranged adducts **24–29**, expected for either *endo*- or *exo*-

Scheme 3. Diels-Alder reactions of 2-vinylpyrroles.



Reaction conditions: [a] $CHCl_3$, rt, 24 h [b] $CHCl_3$, reflux, 24 h [c] PhMe, reflux, 24 h

addition. (*Z*)-2-Vinylpyrroles **5a** and **5b** gave adducts **30–37** with exclusively 4α-Et and 4α-*n*-pentyl substituents, as shown by ^{1}H NMR analysis. Correspondingly, adduct **38** from the *E*-vinylpyrrole **6** had mainly 4β-Me with ~12:1 ratio of 4β-Et to 4α-Et product. To the extent of ^{1}H NMR sensitivity, this is strong evidence of predominantly *endo*-addition Diels-Alder reactions.

The spontaneous rearrangement of Diels-Alder adducts to their aromatic counterparts was also observed in our previous work with *in situ* Diels-Alder reactions of 2-vinylpyrrole with maleimides [5]. As noted in that work, because orbital symmetry considerations forbid suprafacial 1,3-hydride shifts and antarafacial 1,3-hydride shifts are geometrically difficult [25], the isomerism probably takes place *via* acid catalysis, a ''formal 1,3-hydride shift'' [26]. A proton should approach from the least sterically hindered face of the adduct, the opposite face from which the maleimide protrudes and the same face from which the 8b-H and 3a-H protons protrude (the α-face); thus, the 5-H proton of the rearranged adduct would have the predominant orientation of α. The predominance of a particular diastereomer was observed in our earlier work [4,5], and to verify it occurred here as well, NOE experiments were performed on the rearranged adducts **22** and **23**, which had a methyl substituent at the 5-postion; compound **21** had overlapping ^{1}H NMR peaks which prevented accurate measurement of NOE interactions. The assignment of the two peaks corresponding to the 4α-H and 4β-H protons was confirmed by a weak NOE interaction between the 8bα-H and 4α-H protons, whereas no interaction between the 8bα-H and 4β-H protons was observed. Additionally, a much stronger interaction was observed between the 3aα-H and 4α-H protons than between the 3aα-H and 4β-H protons. A strong NOE interaction between the 4α-H and 5-H protons occurred, with no

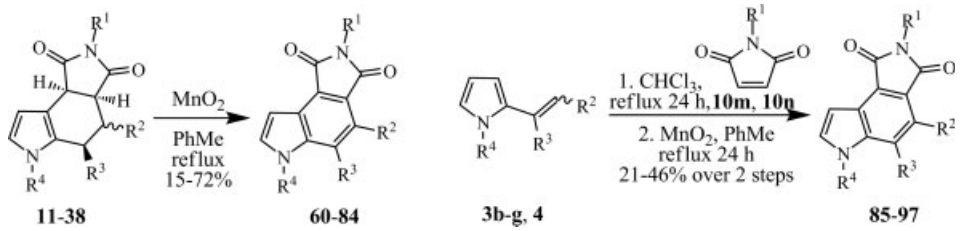
Table 1

Diels-Alder reactions of 2-vinylpyrroles.

Vinylpyrrole	Maleimide	R^1	R^2	R^3	R^4	Conditions	Adduct	Yield %	PhMe reflux t	Indole	Yield %[a]
4	**10a**	*N,N*-DiMe	H	H	H	$CHCl_3$, reflux 24 h	**11**	–[b]	24 h	**60**	64
4	**10b**	Bn	H	H	H	$CHCl_3$, rt 24 h	**12**	23	3 h	**61**	45
4	**10c**	Ph	H	H	H	$CHCl_3$, reflux 24 h	**13**	–[b]	24 h	**62**	67
4	**10d**	4-EtPh	H	H	H	$CHCl_3$, rt 24 h	**14**	49	3 h	**63**	47
4	**10e**	4-*i*PrPh	H	H	H	$CHCl_3$, rt 24 h	**15**	32	3 h	**64**	61
4	**10f**	4-(MeO)Ph	H	H	H	$CHCl_3$, reflux 24 h	**16**	–[b]	24 h	**65**	64
4	**10h**	4-(PhO)Ph	H	H	H	$CHCl_3$, rt 24 h	**17**	33	3 h	**66**	38
3d	**10a**	*N,N*-DiMe	H	H	Me	$CHCl_3$, reflux 24 h	**18**	89	24 h	**67**	66
3d	**10c**	Ph	H	H	Me	$CHCl_3$, reflux 24 h	**19**	94	24 h	**68**	71
3d	**10f**	4-(MeO)Ph	H	H	Me	$CHCl_3$, reflux 24 h	**20**	93	24 h	**69**	66
3e	**10a**	*N,N*-DiMe	H	Me	Me	$CHCl_3$, rt 24 h	**21**	86	24 h	**70**	70
3e	**10c**	Ph	H	Me	Me	$CHCl_3$, rt 24 h	**22**	91	24 h	**71**	72
3e	**10f**	4-(MeO)Ph	H	Me	Me	$CHCl_3$, rt 24 h	**23**	93	24 h	**72**	66
3b	**10a**	*N,N*-DiMe	Me	H	H	$CHCl_3$, rt 24 h	**24**	57	24 h	**73**	57
3b	**10c**	Ph	Me	H	H	$CHCl_3$, rt 24 h	**25**	93	24 h	**74**	61
3b	**10f**	4-(MeO)Ph	Me	H	H	$CHCl_3$, rt 24 h	**26**	90	24 h	**75**	59
3f	**10a**	*N,N*-DiMe	Me	H	Me	$CHCl_3$, rt 24 h	**27**	67	24 h	**76**	56
3f	**10c**	Ph	Me	H	Me	$CHCl_3$, rt 24 h	**28**	89	24 h	**77**	62
3f	**10f**	4-(MeO)Ph	Me	H	Me	$CHCl_3$, rt 24 h	**29**	84	24 h	**78**	61
5a	**10c**	Ph	Et	H	H	PhMe, reflux 24 h	**30**	36	24 h	**79**	44
5a	**10d**	4-EtPh	Et	H	H	PhMe, reflux 24 h	**31**	41	3 h	**80**	53
5a	**10d**	4-EtPh	Et	H	H	$CHCl_3$, reflux 24 h	**31**	70	–	–	–
5a	**10g**	4-(AcO)Ph	Et	H	H	PhMe, reflux 24 h	**32**[c]	31	24 h	**81**[c]	15
5a	**10i**	4-(HO)Ph	Et	H	H	PhMe, reflux 24 h	**33**	54	–	–[d]	–[d]
5a	**10j**	4-ClPh	Et	H	H	PhMe, reflux 24 h	**34**	32	24 h	**82**	33
5a	**10k**	4-BrPh	Et	H	H	PhMe, reflux 24 h	**35**	35	24 h	**83**	36
5a	**10l**	4-NO_2Ph	Et	H	H	PhMe, reflux 24 h	**36**	45	24 h	**84**	28
5b	**10c**	Ph	Pentyl	H	H	PhMe, reflux 24 h	**37**	30	–	–	–
6	**10c**	Ph	Et	H	H	PhMe, reflux 24 h	**38**	41	–	–	–
4	**10m**	$AcOCH_2CHPh$	H	H	H	$CHCl_3$, reflux 24 h	**39**	–	24 h	**85**	46
3b	**10m**	$AcOCH_2CHPh$	Me	H	H	$CHCl_3$, reflux 24 h	**40**	–	24 h	**86**	27
3d	**10m**	$AcOCH_2CHPh$	H	H	Me	$CHCl_3$, reflux 24 h	**41**	–	24 h	**87**	44
3c	**10m**	$AcOCH_2CHPh$	Me	Me	H	$CHCl_3$, reflux 24 h	**42**	–	24 h	**88**	29
3f	**10m**	$AcOCH_2CHPh$	Me	H	Me	$CHCl_3$, reflux 24 h	**43**	–	24 h	**89**	26
3g	**10m**	$AcOCH_2CHPh$	Me	Me	Me	$CHCl_3$, reflux 24 h	**44**	–	24 h	**90**	21
4	**10n**	$MeOCH_2CHPh$	H	H	H	$CHCl_3$, reflux 24 h	**45**	–	24 h	**91**	39
3b	**10n**	$MeOCH_2CHPh$	Me	H	H	$CHCl_3$, reflux 24 h	**46**	–	24 h	**92**	30
3e	**10n**	$MeOCH_2CHPh$	H	Me	Me	$CHCl_3$, reflux 24 h	**47**	–	24 h	**93**	26
3d	**10n**	$MeOCH_2CHPh$	H	H	Me	$CHCl_3$, reflux 24 h	**48**	–	24 h	**94**	40
3c	**10n**	$MeOCH_2CHPh$	Me	Me	H	$CHCl_3$, reflux 24 h	**49**	–	24 h	**95**	32
3f	**10n**	$MeOCH_2CHPh$	Me	H	Me	$CHCl_3$, reflux 24 h	**50**	–	24 h	**96**	29
3g	**10n**	$MeOCH_2CHPh$	Me	Me	Me	$CHCl_3$, reflux 24 h	**51**	–	24 h	**97**	23

[a] Yields for chiral indoles are over two steps.
[b] Crude yields for adducts **11** (64%), **13** (92%), and **16** (90%) include double-addition type products detected by TLC but not isolated.
[c] Product was deacetylated to **81** during the reaction or workup.
[d] Only starting material **33** was recovered, but see note c above.

Scheme 4. Aromatization of Diels-Alder adducts.



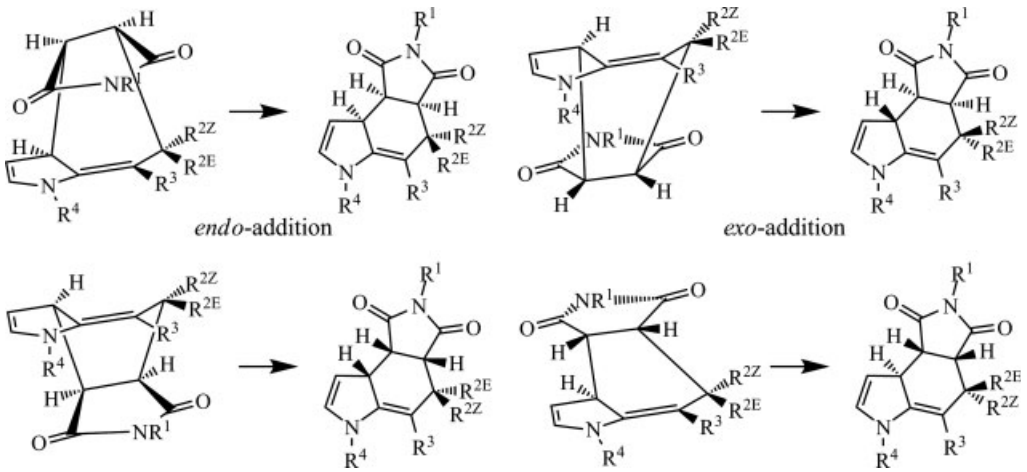


Figure 2. Effect of *endo*- or *exo*-addition on the stereochemistry of Diels-Alder adducts.

detectable interaction between the 4α-H proton and the 5-methyl group. Correspondingly, a strong NOE interaction was seen between the 4β-H proton and the 5-methyl group, whereas no detectable response was observed between the 4β-H and 5-H protons, showing the 5-methyl group to be in the β-orientation. The ^{1}H NMR integrations of **21–23** showed between a 13:1 and 54:1 molar ratio of major to minor product, a 93–98% diastereomeric excess. The predominant diastereomers had the sterically more congested configuration, with the 5-methyl group protruding from the same face as the maleimide.

The high diastereoselectivity of the formal 1,3-hydride shift is further evidenced from products **52–59**. These types of products were detected whenever unsubstituted vinylpyrrole **4** was used in Diels-Alder reactions with maleimides, where they were isolated and characterized in four reactions. Compound **56** was not completely separated from **52**, although sufficient purity was obtained to accurately report ^{1}H NMR data. In several cases, these products were detected by TLC but not isolated, although their masses were included in determining the percent yield; hence, yields for products **11**, **13**, and **16** do not reflect the actual isolated yield. NOE studies of **55** and **59** verified the structure of products **52–59**, giving evidence of the same kind of stereochemistry as described earlier for the 5β-Me adducts **22** and **23** (Fig. 4).

For minor product **59**, an NOE interaction was observed between the 8bα-H proton and a geminal proton of the succinimide substituent, an interaction absent in major product **55**. In **55**, an interaction between the 8bα-H and 4α-H protons showed a *syn*-relationship. Multiple strong interactions were observed in compound **55** between the 4β-H proton and the succinimide protons, whereas no such interactions were observed with the 4α-H proton, giving evidence that the succinimide is attached to the β-face in the major product. In compounds **52–59**, the stereochemistry of the succinimidyl proton at the point of attachment was not determined. However, coupling constants and NOE interactions between the geminal protons of the succinimide and the succinimidyl proton at the point of attachment did allow determination of a probable *syn*- or *anti*-relationship. In compound **55**, the ^{1}H NMR peaks of the 5α-H proton

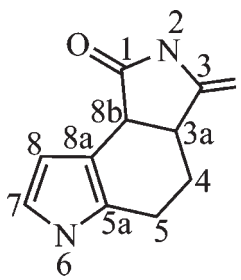


Figure 3. Numbering scheme.

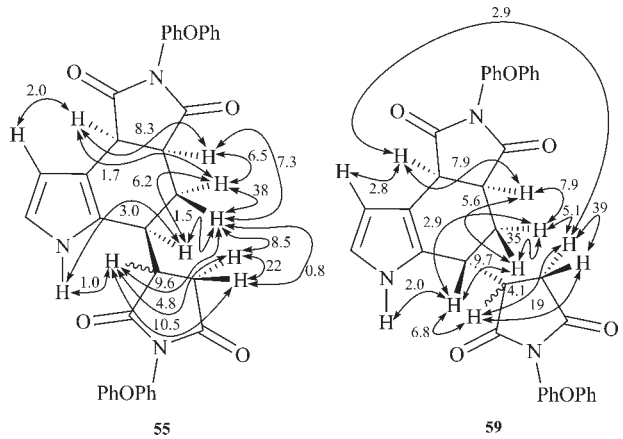


Figure 4. NOE experiments. *Numbers indicate % enhancement.

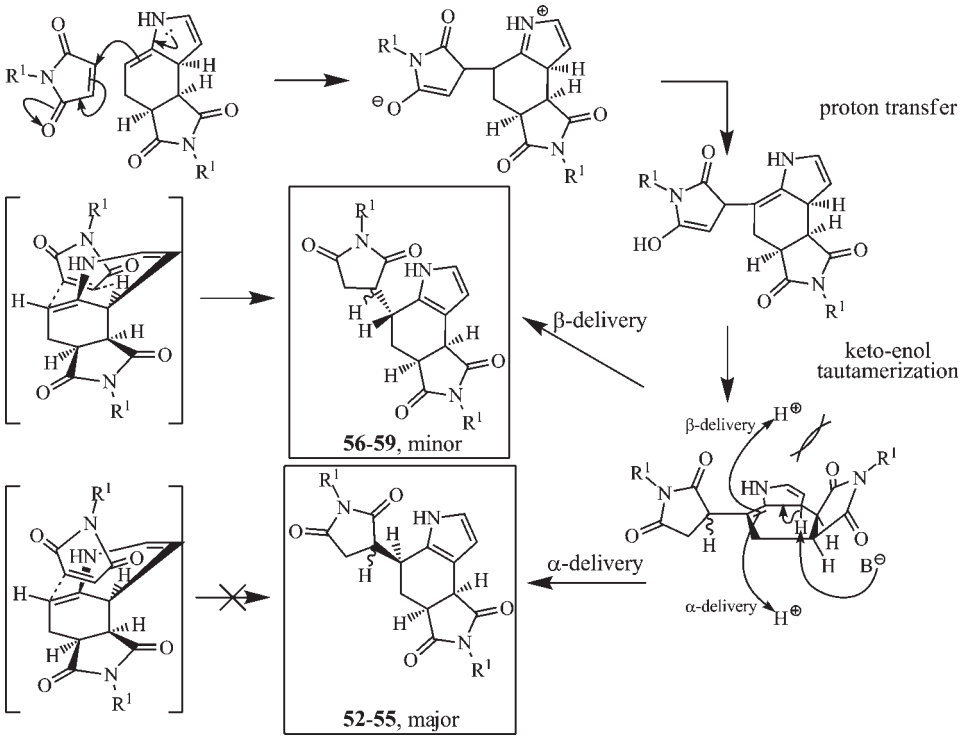


Figure 5. Proposed mechanism for the formation of **52–59**.

and the proton at the point of succinimide attachment overlapped too greatly to allow accurate measurement of NOE interactions.

When first detected, products **52–59** were assumed to be the result of ene-reactions between the Diels-Alder adduct and the maleimide, as there are several reports of ene-products formed between Diels-Alder adducts and their corresponding dienophiles [27]. However, after determining the stereochemistry at C5, it was realized that an ene reaction could not adequately explain the formation of both epimers. Although an ene reaction could justify the formation of minor products **56–59**, the tight transition state required [28] makes the ene reaction an impossible route toward major products **52–55** (Fig. 5). Because the more sterically congested epimers **52–55** were the predominant products, thermodynamic equilibration of the feasibly ene-reaction-formed **56–59** is also highly unlikely.

In light of the diastereoselective rearrangement at C5 noted in this work and in our earlier *in situ* Diels-Alder reaction work [4,5], it was realized that our mechanistic explanation for formation of the rearranged adducts could also explain the formation of **52–59**. A Michael-addition of the unrearranged adduct to the maleimide would result in 5-succinimide-substituted adducts. When a proton approaches the molecule to cause the formal 1,3-hydride shift, an addition from the least sterically congested face (the α-face in the Figures) would predominate and would result in products **52–55**, with a smaller amount of hydrogen delivery occurring from the more sterically occluded face to give minor products **56–59**. The presence of the succinimide substituent at C5 may cause the steric environment of the α-face to be more similar to the β-face than does a 5-methyl group; this would explain the 3:1–5:1 ratios of products **52–59** (75–83% *de*) as contrasted with the higher diastereomeric excess observed in 5-methyl products **21–23** (93–98% *de*).

Aromatization of Diels-Alder adducts. Diels-Alder adducts **11–32**, **34–36**, and **39–51** were dehydrogenated using activated MnO_2, giving the corresponding indoles **60–84** in 15–72% yield and giving chiral indoles **85–97** with 21–46% yield over two steps (Scheme 4, Table 1). Using manganese sulfate with potassium permanganate [29] to make the activated MnO_2 gave consistent and moderate-yielding aromatizations. Some restrictions to this technique apply, as when aromatization of hydroxyl-adduct **33** was attempted, only starting material was obtained. Competition for adsorption on the oxide surface of the activated MnO_2 from the phenol group of **33** may have partially deactivated the reagent. When MnO_2 treatment of acetoxy-adduct **32** was conducted, the hydroxy-indole **81** was the exclusive product isolated. When oxidation occurs, water can be produced, but deacetylation appears to be unprecedented under these oxidative conditions; therefore, the aromatized

product was more likely deacetylated on silica gel during chromatography, giving **81**. Aromatization and purification of chiral adducts **39–44** gave indoles **85–90** with no deacetylation.

Biological activity. While participating in the Developmental Therapeutics Program at the National Cancer Institute (NCI), we submitted 11 compounds to the NCI for a one-dose 60 human tumor cell line prescreen: compounds **12**, **14**, **17**, **30**, **32**, **33**, **61**, **63**, **66**, and **79**. Of these, two compounds, **63** and **66**, were judged by the NCI to have sufficient activity to justify screening with 60 human tumor cell lines at five concentrations with 10-fold dilutions, from 1×10^{-4} to 1×10^{-8} M. Both of these compounds were found to have high levels of activity against many of the 60 different cell lines tested. Compound **63** was most active against non–small-cell lung cancer HOP-92 and melanoma cell lines SK-MEL-5 and LOX IMVI with an IC_{50} of 322, 412, and 462 ng/mL, respectively. Compound **66** was most active against breast cancer HS 578T, melanoma UACC-257, and leukemia RPMI-8226, with an IC_{50} of 3.5, 34, and 230 ng/mL, respectively.

CONCLUSIONS

Variously substituted 2-vinylpyrroles undergo *endo*-addition Diels-Alder additions with maleimides, followed by a highly diastereoselective (93–98% *de*) rearrangement to tetrahydroindoles in moderate to excellent yield. Treatment with activated MnO_2 in refluxing toluene gives the corresponding indole aromatized products in moderate to good yield. This highly convergent methodology for formation of indoles is flexible and the starting materials are conveniently prepared.

EXPERIMENTAL

General. Solvents and reagents were purchased and used as received. Flash chromatography was performed using 230–450 mesh silica gel. TLC analyses were performed on plastic-backed plates precoated with 0.2-mm silica with F_{254} indicator. Infrared spectra were recorded on a 4000 FTIR spectrometer; only the most intense and/or diagnostic peaks are reported. High-resolution mass spectra were recorded with a time-of-flight instrument using electrospray ionization with PEG as an internal calibrant. For NMR spectra, chemical shifts (δ) were referenced to the solvent. ^{13}C NMR spectra were proton decoupled. Melting points are uncalibrated. Elemental analyses were performed by M-H-W Laboratories, Phoenix, AZ. Petroleum ether refers to the fraction boiling at 35–60°C.

^{1}H NMR analysis. In the ^{1}H NMR spectra of adducts **11–38**, the 8bα-H proton often appears as a doublet of doublet of doublets in 5-unsubstituted adducts; COSY experiments indicate that the 8bα-H proton is coupled not only to the 3aα-H proton but also to the 5-bond-distant 5-H protons with a coupling constant of about 1.5 Hz [10,30]. In 5-methyl adducts, the 3aα-H proton was sometimes observed to couple to the 5α-H proton at 0.6–0.9 Hz. Additionally, in 4-alkyl adducts, the 3aα-H proton was coupled to the 5α-H proton at ~1.0 Hz. For indoles **60–97**, the 8-H proton and the 5-H proton were consistently coupled at about 1.0 Hz [31].

General methods for the preparation of vinylpyrroles. ***Method I.*** Sodium ethoxide (0.125 mol, 2.5 equiv, made freshly from sodium (2.87 g, 0.125 mol, 2.5 equiv) and EtOH followed by evaporation using a rotating evaporator) was suspended with the appropriate alkyltriphenylphosphonium bromide (0.1 mol, 2 equiv) in THF (50 mL) [18,19]. The mixture was stirred at rt under nitrogen for 3 h. Then, a solution of the appropriate pyrrole-2-carboxaldehyde **2a** or **2b** or 2-acetylpyrrole **2c** or **2d** (0.05 mol) in THF (20 mL) was added over 1 min, and the mixture was stirred under reflux for 15 h. The solvent was removed using a rotating evaporator, the residue was suspended in dichloromethane and filtered, and the filter cake was washed with dichloromethane (3 × 50 mL). The filtrate was washed with saturated $NaHSO_3$ (50 mL), saturated Na_2CO_3 (50 mL), and brine (50 mL), and dried over Na_2SO_4. The solvent was removed using a rotating evaporator and the crude product was vacuum-distilled, giving the appropriate pure 2-vinylpyrrole (with the exception of **4**, see later) at comparable 60% yield [18,19]. When method I was used to generate vinylpyrrole **4**, **7** was found to be an unwanted byproduct in an ~1:1 molar ratio to the desired product. This mixture was used without further purification in subsequent Diels-Alder reactions.

Method II. Potassium *t*-butoxide (14.76 g, 0.132 mol, 1.25 equiv) was added slowly to methyltriphenylphosphonium bromide (46.98 g, 0.132 mol, 1.25 equiv) in THF (100 mL) at 0°C. Formation of the bright yellow color characteristic of the ylide was observed immediately. The mixture was stirred at rt under nitrogen for 30 min and then cooled to 0°C. A solution of the pyrrole **2a** (10.00 g, 0.105 mmol) in THF (20 mL) was added over 5 min, with stirring, and refluxed for 30 min until TLC analysis indicated the reaction was complete. The mixture was allowed to cool to rt and filtered. The filter cake was washed with diethyl ether (4 × 25 mL). The filtrate was washed with saturated $NaHSO_3$ (50 mL), saturated Na_2CO_3 (50 mL), and brine (50 mL), and dried over anhydrous Na_2SO_4. The solvents were removed using a rotating evaporator and the residue was vacuum-distilled, giving **4** as a colorless liquid (7.66 g, 78%). The ^{1}H and ^{13}C NMR data matched the values in the literature [18,19].

For Diels-Alder reactions, vinylpyrroles **5a** and **5b** were synthesized using Corey's procedure for the Wittig reaction [21], and method I was used to synthesize vinylpyrroles **3a–g**. However, for purposes of characterization **3a–c**, **3e–f**, and **5b** were synthesized using method II.

2-(2-Propenyl)-1H-pyrrole (3a). Method II with **2c** (3.16 g, 0.029 mol) and distillation at 37°C/0.04 mm Hg gave **3a** (436 mg, 14%) as a white waxy solid [17a]: mp 71–73°C; ^{1}H NMR (300 MHz, $CDCl_3$, δ) 8.32 (bs, 1H, 1-H), 6.82 (ddd, J = 2.8, 2.8, 1.4 Hz, 1H, 5-H), 6.37 (dddd, J = 3.1, 3.1, 1.7, 1.3 Hz, 1H, 3-H), 6.32 (dddd, J = 3.3, 2.6, 2.6, 0.9 Hz, 1H, 4-H), 5.09–5.11 (m, 1H, 1′-H *cis* to pyrrole), 4.91–4.93 (m, 1H, 1′-H *trans* to pyrrole), 2.17 (ddd, J = 1.6, 0.8, 0.8 Hz, 3H, 3′-H); ^{13}C NMR (75 MHz, $CDCl_3$, δ) 135.1, 133.2, 118.8, 109.5, 107.0, 105.7, 20.8; IR (thin film, cm^{-1}) 3450(bs), 3400(s),

2969(s), 2925(m), 2840(w), 1634(m), 1597(m), 1557(w), 1499(w), 1470(m), 1403(m), 1235(m), 1110(w), 1035(m); HRMS *m/z* (M + H^+) calcd. for C_7H_9N: 108.0808, found 108.0815.

2-(1-Propenyl)-1H-pyrrole (3b). Method II with **2a** (2.66 g, 0.028 mol) and distillation at 35.5°C/0.05 mm Hg gave **3b** (2.32 g, 77%) as a white solid [17b,18a]: 1.0:3.9 *E*:*Z*; mp 27–28°C; ^{1}H NMR (300 MHz, $CDCl_3$, δ) 8.10 (bs, 1H, 1-H), 6.82 (ddd, *J* = 2.6, 2.6, 1.4 Hz, 1H, 5maj-H), 6.74 (ddd, *J* = 2.7, 2.7, 1.4 Hz, 1H, 5min-H), 6.22–6.42 (m, 3H, 3-H, 4-H, 1′-H), 5.80–5.93 (m, 1H, 2′min-H), 5.61–5.74 (m, 1H, 2′maj-H), 2.03–2.07 (m, 3H, 3′maj-H), 1.93–1.97 (m, 3H, 3′min-H); ^{13}C NMR (75 MHz, $CDCl_3$, δ) 130.4, 122.2, 121.8, 120.9, 120.4, 118.0, 117.8, 109.6, 109.4, 109.0, 106.6, 18.5, 15.2; IR (thin film, cm^{-1}) 3469(s), 3396(bs), 3107(w), 3024(m), 2963(m), 2950(m), 2935(m), 2857(w), 1642(m), 1603(w), 1546(w), 1459(m), 1409(w), 1366(m), 1294(w), 1278(w), 1216(w), 1118(m), 1098(m), 1032(m), 957(w), 800(s); HRMS *m/z* (M + H^+) calcd. 108.0808, found 108.0802. Anal. Calcd. for C_7H_9N: C, 78.46; H, 8.47; N, 13.07. Found: C, 78.28; H, 8.66; N, 12.94.

2-(2-But-2-enyl)-1H-pyrrole (3c). Method II with **2c** (3.16 g, 0.029 mol) and distillation at 43°C/0.04 mm Hg gave **3c** (922 mg, 26%) as a colorless liquid: 2.8:1.0 *E*:*Z*; ^{1}H NMR (300 MHz, $CDCl_3$, δ) 8.32 (bs, 1H, 1-H), 6.87 (ddd, *J* = 2.4, 2.4, 2.4 Hz, 1H, 5maj-H), 6.77 (ddd, *J* = 2.2, 2.2, 2.2 Hz, 1H, 5min-H), 6.36–6.40 (m, 2H, 3maj-H, 4maj-H), 6.27–6.31 (m, 2H, 3min-H, 4min-H), 5.67–5.76 (m, 1H, 3′min-H), 5.50–5.59 (m, 1H, 3′maj-H), 2.12–2.15 (m, 3H, 1′maj-H), 2.05–2.07 (m, 3H, 1′min-H), 1.97–2.01 (m, 3H, 4′maj-H), 1.86–1.90 (m, 3H, 4′min-H); ^{13}C NMR (75 MHz, $CDCl_3$, δ) 134.9, 132.4, 127.6, 126.9, 119.5, 117.8, 117.5, 116.0, 109.1, 109.0, 108.4, 105.2, 23.1, 15.4, 14.4, 13.7; IR (thin film, cm^{-1}) 3481(s), 3419(bm), 2973(m), 2922(m), 2862(m), 1643(w), 1551(w), 1452(m), 1403(m), 1378(m), 1353(w), 1119(m), 1090(m), 1068(w), 1036(m), 806(m), 791(m); HRMS *m/z* (M + H^+) calcd. 122.0964, found 122.0965. Anal. Calcd. for $C_8H_{11}N$: C, 79.29; H, 9.15; N, 11.56. Found: C, 79.22; H, 8.96; N, 11.33.

N-Methyl-2-(2-propenyl)-1H-pyrrole (3e). Method II with **2d** (3.57 g, 0.029 mol) and distillation at 31.5°C/0.04 mm Hg gave **3e** (1.62 g, 46%) as a colorless liquid [7a,17c,17e,17f]: ^{1}H NMR (300 MHz, $CDCl_3$, δ) 6.77 (ddd, *J* = 2.7, 1.4, 1.4 Hz, 1H, 5-H), 6.37 (ddd, *J* = 3.7, 1.9, 1.9 Hz, 1H, 3-H), 6.30 (ddd, *J* = 3.8, 2.7, 1.8 Hz, 1H, 4-H), 5.26 (dq, *J* = 3.0, 1.5 Hz, 1H, 1′-H *cis* to pyrrole), 5.17 (dq, *J* = 3.0, 1.5 Hz, 1H, 1′-H *trans* to pyrrole), 3.85 (d, *J* = 1.2 Hz, 3H, 1-CH_3), 2.28 (dddd, *J* = 1.7, 1.7, 1.0, 0.9 Hz, 3H, 3′-H); ^{13}C NMR (75 MHz, $CDCl_3$, δ) 135.9, 134.7, 124.7, 111.6, 108.8, 107.3, 36.3, 24.1; IR (thin film, cm^{-1}) 3104(m), 2974(s), 2952(s), 2921(s), 2881(m), 2806(w), 2726(w), 1794(w), 1701(w), 1626(s), 1478(s), 1449(m), 1434(s), 1413(m), 1374(m), 1363(m), 1313(s), 1260(m), 1224(w), 1094(m), 1062(w), 997(w), 789(m), 605(m); HRMS *m/z* (M + H^+) calcd. 122.0964, found 122.0959. Anal. Calcd. for $C_8H_{11}N$: C, 79.29; H, 9.15; N, 11.56. Found: C, 79.54; H, 8.92; N, 11.54.

N-Methyl-2-(1-propenyl)-1H-pyrrole (3f). Method II with **2b** (3.50 g, 0.032 mol) and distillation at 32.5°C/0.04 mm Hg gave **3f** (2.66 g, 68%) as a colorless liquid [17d,17g,17i]: 1.0:1.8 *E*:*Z*; ^{1}H NMR (300 MHz, $CDCl_3$, δ) 6.72 (ddd, *J* = 2.9, 1.5, 1.5 Hz, 1H, 5maj-H), 6.66 (ddd, *J* = 2.4, 2.0, 2.0 Hz, 1H, 5min-H), 6.36–6.44 (m, 2H, 3-H, 4-H), 6.29–6.32 (m, 1H, 1′maj-H), 6.20–6.23 (m, 1H, 5′min-H), 6.06–6.19 (m, 1H, 2′min-H), 5.76–5.88 (m, 1H, 2′maj-H), 3.69 (s, 3H, 1min-CH_3), 3.69 (s, 3H, 1maj-CH_3), 2.04–2.08 (m, 3H, 3′maj-H), 1.98–2.02 (m, 3H, 2′maj-H); ^{13}C NMR (75 MHz, $CDCl_3$, δ) 132.4, 130.4, 124.3, 124.1, 122.24, 122.16, 120.1, 118.6, 109.6, 107.8, 107.6, 105.3, 34.1, 18.9, 15.3; IR (thin film, cm^{-1}) 3103(m), 3018(m), 2967(s), 2937(s), 2917(s), 2860(m), 1698(w), 1640(w), 1479(s), 1450(m), 1412(m), 1376(m), 1356(w), 1342(w), 1302(m), 1292(s), 1241(w), 1228(w), 1089(m), 1064(w), 1033(w), 998(w), 832(w), 781(m), 649(s), 608(s); HRMS *m/z* (M + H^+) calcd. 122.0964, found 122.0956. Anal. Calcd. for $C_8H_{11}N$: C, 79.29; H, 9.15; N, 11.56. Found: C, 79.50; H, 8.93; N, 11.80.

2-(2-But-2-enyl)-N-methyl-1H-pyrrole (3g). Method II with **2d** (3.50 g, 0.032 mol) and distillation at 31.5°C/0.04 mm Hg gave **3g** (1.01 g, 23%) as a colorless liquid: 1.0:1.5 *E*:*Z*; ^{1}H NMR (300 MHz, $CDCl_3$, δ) 6.70 (ddd, *J* = 2.7, 1.8, 1.8 Hz, 1H, 5maj-H), 6.64 (ddd, *J* = 2.7, 2.0, 2.0 Hz, 1H, 5min-H), 6.24 (ddd, *J* = 3.5, 2.4, 2.4 Hz, 1H, 3maj-H), 6.18 (ddd, *J* = 3.6, 2.4, 2.4 Hz, 1H, 3min-H), 6.10 (dddd, *J* = 3.9, 3.9, 2.0, 2.0 Hz, 1H, 4min-H), 6.02 (dddd, *J* = 3.8, 3.8, 2.0, 2.0 Hz, 1H, 4maj-H), 5.74–5.84 (m, 1H, 3′maj-H), 5.60–5.69 (m, 1H, 3′min-H), 3.68 (d, *J* = 2.1 Hz, 3H, 1min-CH_3), 3.57 (d, *J* = 1.8 Hz, 3H, 1maj-CH_3), 2.04–2.06 (m, 3H, 1′-H), 1.85–1.90 (m, 3H, 4′min-H), 1.59–1.64 (m, 3H, 4′maj-H); ^{13}C NMR (75 MHz, $CDCl_3$, δ) 137.7, 133.6, 129.1, 128.1, 126.3, 124.1, 122.7, 121.4, 107.4, 107.1, 106.8, 33.3, 34.0, 25.5, 17.3, 15.5, 14.2; IR (thin film, cm^{-1}) 3106(m), 3026(m), 2943(m), 2918(m), 2884(m), 2857(w), 2810(w), 1703(w), 1638(m), 1484(s), 1451(m), 1367(w), 1305(s), 1261(w), 1228(w), 1091(m), 1058(w), 1009(w), 954(m), 789(m), 648(s), 605(m); HRMS *m/z* (M + H^+) calcd. for $C_9H_{13}N$: 136.1121, found 136.1124.

2-Ethenyl-1H-pyrrole (4). Method II with **2a** (10.00 g, 0.105 mol) and distillation at 30°C/0.04 mm Hg gave **4** (7.66 g, 78%) as a colorless liquid [18,19]; the ^{1}H and ^{13}C NMR data matched the literature values [18,19]. Anal. Calcd. for C_6H_7N: C, 77.38; H, 7.58; N, 15.04. Found: C, 77.17; H, 7.67; N, 14.83.

2-(1-Heptenyl)-1H-pyrrole (5b). Method II with **2a** (2.91 g, 0.031 mol) and distillation at 68°C/0.04 mm Hg gave **5b** (4.40 g, 81%) as a colorless liquid: 1.0:9.0 *E*:*Z*; ^{1}H NMR (300 MHz, $CDCl_3$, δ) 8.10 (bs, 1H, 1-H), 6.81 (ddd, *J* = 2.3, 2.3, 1.7 Hz, 1H, 5maj-H), 6.74 (ddd, *J* = 2.6, 2.6, 1.4 Hz, 1H, 5min-H), 6.21–6.37 (m, 3H, 3-H, 4-H, 1′-H), 5.85 (ddd, *J* = 16.1, 7.0, 7.0 Hz, 1H, 2′min-H), 5.53 (ddd, *J* = 12.8, 6.8, 5.8 Hz, 1H, 2′maj-H), 2.45 (ddt, *J* = 7.3, 7.2, 1.8 Hz, 2H, 3′maj-H), 2.25 (dt, *J* = 7.2, 7.1, 1.5 Hz, 2H, 3′min-H), 1.34–1.65 (m, 6H, 4′-H, 5′-H, 6′-H), 1.01 (t, *J* = 7.2 Hz, 3H, 7′-H); ^{13}C NMR (75 MHz, $CDCl_3$, δ) 134.0, 133.7, 130.3, 128.9, 128.8, 128.7, 128.6, 126.3, 120.5, 119.0, 117.8, 117.7, 109.6, 109.4, 108.9, 106.7, 32.9, 31.8, 31.5, 29.4, 29.4, 22.7, 14.2; IR (thin film, cm^{-1}) 3469(s), 3392(bs), 3105(m), 3014(m), 2957(s), 2926(s), 2857(s), 1712(w), 1639(m), 1545(w), 1460(m), 1434(m), 1412(m), 1379(m), 1293(w), 1280(w), 1212(w), 1182(w), 1118(m), 1095(m), 1033(m), 955(m), 799(m), 949(m); HRMS *m/z* (M + H^+) calcd. 164.1434, found 164.1434. Anal. Calcd. for $C_{11}H_{17}N$: C, 80.93; H, 10.50; N, 8.58. Found: C, 81.07; H, 10.32; N, 8.74.

2-(1-Ethoxyethyl)-N-methyl-1H-pyrrole (7). A 1:1 molar mixture of **4** and **7**, prepared using method I, was left in a

refrigerator for 6 months, giving large colorless crystals of **7**. The crystals were removed and the liquid **4** was washed off using ice-cold petroleum ether, giving colorless crystals: mp 26.5–28.5°C; ^{1}H NMR (300 MHz, $CDCl_3$, δ) 8.39 (bs, 1H, 1-H), 6.78 (ddd, J = 2.6, 2.6, 1.6 Hz, 1H, 5-H), 6.16 (ddd, J = 3.3, 2.7, 2.5 Hz, 1H, 4-H), 6.08 (ddd, J = 3.5, 2.6, 1.5 Hz, 1H, 3-H), 4.55 (q, J = 6.6 Hz, 1H, 1′-H), 3.44 (dq, J = 12.0, 7.0 Hz, 1H, OCH_2CH_3), 3.40 (dq, overlapped, J = 11.7, 7.0 Hz, 1H, OCH_2CH_3), 1.51 (d, J = 6.6 Hz, 3H, 2′-H), 1.19 (dd, J = 6.9, 7.2 Hz, 3H, OCH_2CH_3); ^{13}C NMR (75 MHz, $CDCl_3$, δ) 133.7 (C2), 117.5 (C5), 107.9 (C4), 106.0 (C3), 71.1 (C1′), 63.4 (OCH_2CH_3), 21.7 (C2′), 15.5 (OCH_2CH_3); IR (film, cm^{-1}) 3464(m), 3322(w), 3054(m), 2980(m), 2933(w), 2873(w), 1446(w), 1422(w), 1373(w), 1325(w), 1266(s), 1151(w), 1086(m), 1028(w), 1006(w), 896(w), 796(w), 739(s), 707(s). X-ray data for **7** in CIF format are available in the Supporting Information.

General method for the synthesis of chiral maleimides. The primary amine (0.070 mol) dissolved in a large excess of diethyl ether (100 mL) was added over 20 min using a dropping funnel to a 2-L flask containing maleic anhydride (6.85 g, 0.070 mol, 1 equiv) dissolved in diethyl ether (500 mL) [23]. Throughout the addition, the mixture turned into a thick off-white suspension. The suspension was concentrated to half-volume, cooled in the freezer, and vacuum-filtered, giving the crude acid as a thick paste. Acetic anhydride (300 mL) and sodium acetate (2.87 g, 0.035 mol, 0.5 equiv) were added to the crude acid and the mixture was heated to 100°C in a boiling water bath for 2 h. The mixture was then cooled to rt, diluted with water (200 mL), and portions of $NaHCO_3$ were added slowly with vigorous stirring until the acetic acid was nearly neutralized. The solution was extracted with ether (3 × 200 mL), and the organic extracts were washed with saturated $NaHCO_3$ until neutral, then washed with water (100 mL) and brine (100 mL), and dried over anhydrous Na_2SO_4. The solvent was removed using a rotating evaporator and the product was purified using flash chromatography on silica gel using ethyl acetate/hexanes to give the pure chiral maleimide in moderate yield (∼50%).

(+)-(R)-2-(2,5-Dioxo-1H-pyrrol-1-yl)-2-phenylethyl acetate (10m). The general method gave **10m** (8.167 g, 45%) as a light-red oil: $[\alpha]^{23}_D$ +1.7 (*c* 10.0, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$, δ) 7.43–7.46 (m, 2H, Ph), 7.33–7.40 (m, 3H, Ph), 6.71 (s, 2H, vinyl-H), 5.43 (dd, J = 10.5, 5.4 Hz, 1H, 2′-H), 4.99 (dd, J = 11.1, 10.5 Hz, 1H, 1′-H), 4.71 (dd, J = 11.1, 5.4 Hz, 1H, 1′-H), 2.04 (s, 3H, OAc); ^{13}C NMR (75 MHz, $CDCl_3$, δ) 170.7, 170.6, 135.9, 134.3, 128.9, 128.6, 128.0, 62.4, 53.6, 20.8; IR (film, cm^{-1}) 3465(m), 3101(m), 2950(w), 1743(s), 1713(s), 1399(s), 1370(s), 1232(s), 1163(m), 1043(m), 828(m), 696(s); HRMS *m*/*z* (M + Na^+) calcd. for $C_{14}H_{13}NO_4$: 282.0738, found 282.0740.

(+)-(R)-1-(2-Methoxy-1-phenylethyl)-1H-pyrrole-2,5-dione (10n). The general method gave **10n** (7.608 g, 47%) as white crystals: mp 55–56°C; $[\alpha]^{23}_D$ +22.5 (*c* 1.0, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$, δ) 7.41–7.45 (m, 2H, Ph), 7.30–7.38 (m, 3H, Ph), 6.68 (s, 2H, vinyl-H), 5.38 (dd, J = 10.5, 5.4 Hz, 1H, 1′-H), 4.46 (dd, J = 11.2, 11.2 Hz, 1H, 2′-H), 3.82 (dd, J = 10.9, 5.4 Hz, 1H, 2′-H), 3.39 (s, 3H, OCH_3); ^{13}C NMR (75 MHz, $CDCl_3$, δ) 171.0, 137.0, 134.2, 128.8, 128.3, 128.0, 70.8, 58.8, 54.3; IR (film, cm^{-1}) 3460(bm), 3095(m), 2915(m), 2810(w), 1706(s), 1400(m), 1368(m), 1154(w), 1110(m), 826(m), 696(s); HRMS *m*/*z* (M + Na^+) calcd. for $C_{13}H_{13}NO_3$: 254.0783, found 254.0783.

General method for Diels-Alder reactions. A mixture of the vinylpyrrole (0.0050 mol, 1.1 equiv) and the maleimide (0.0045 mol) (1) in chloroform (20 mL) was stirred at rt for 24 h and, if TLC analysis indicated maleimide remaining, the mixture was also refluxed for 24 h (method A) or (2) in toluene (20 mL) was refluxed for 24 h (method B). The solvent was removed using a rotating evaporator. The crude adduct was purified with flash chromatography or MPLC with ethyl acetate/hexanes as eluent, except in the case of chiral adducts, which were used without further purification in the next step.

General method for the dehydrogenation of Diels-Alder adducts. A mixture of the adduct (3.76 mmol) and activated MnO_2 [29] (18.8 mmol, 5 equiv) in toluene (30 mL) was refluxed for 2–3 h until the reaction was complete, as indicated by TLC (method C), or refluxed for 24 h (method D). For dehydrogenation of chiral adducts, the crude Diels-Alder reaction product was placed in toluene (30 mL) along with activated MnO_2 (5 equiv) and refluxed for 24 h (method E). The mixture was cooled to rt and filtered through a fine glass frit. The insoluble manganese salts were washed with several portions of dichloromethane until the washings ran clear (5 × 20 mL), and the combined organic filtrate and washings were evaporated to dryness using a rotating evaporator. Flash chromatography or MPLC with ethyl acetate/hexanes as eluent provided the desired product in good yields.

2-Dimethylamino-3aα,4,5,8bα-tetrahydro-2H,6H-pyrrolo[3,4-e]indole-1,3-dione (11). Method A with vinylpyrrole **4** and maleimide **10a** gave **11** (597 mg, 64% crude yield, including contamination from double-addition type products, detected by TLC; the crude adduct was recrystallized from methylene chloride/petroleum ether, giving the pure compound, but the isolated yield is not available) as a light-brown powder: mp 56–57°C; ^{1}H NMR (300 MHz, $CDCl_3$, δ) 8.02 (bs, 1H, 6-H), 6.68 (dd, J = 2.7, 2.7 Hz, 1H, 7-H), 6.37 (dd, J = 2.9, 2.9 Hz, 1H, 8-H), 3.89 (ddd, J = 8.1, 1.4, 1.4 Hz, 1H, 8bα-H), 3.18 (ddd, J = 7.8, 5.4, 5.4 Hz, 1H, 3aα-H), 2.84 (s, 6H, $N(CH_3)_2$), 2.57–2.65 (m, 2H, 5α-H and 5β-H), 2.34 (dddd, J = 13.6, 5.1, 5.1, 5.1 Hz, 1H, 4β-H), 2.00 (dddd, J = 13.7, 8.6, 6.3, 5.1 Hz, 1H, 4α-H); ^{13}C NMR (75 MHz, $CDCl_3$, δ) 177.6, 176.7, 127.1, 117.2, 109.9, 107.7, 44.0, 38.8, 38.7, 22.2, 19.5; IR (film, cm^{-1}) 3361(bs), 2930(m), 1777(w), 1711(s), 1448(w), 1369(m), 1200(m), 1147(m), 719(w); HRMS *m*/*z* (M + Na^+) calcd. 256.1057, found 256.1057. Anal. Calcd. for $C_{12}H_{15}N_3O_2$: C, 61.79; H, 6.48; N, 18.01. Found: C, 61.59; H, 6.32; N, 17.90.

2-Benzyl-3aα,4,5,8bα-tetrahydro-2H,6H-pyrrolo[3,4-e]indole-1,3-dione (12). Method A with vinylpyrrole **4** and maleimide **10b** gave **12** (258 mg, 23%) as a colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$, δ) 7.98 (bs, 1H, 6-H), 7.24–7.29 (m, 5H, Ph), 6.68 (dd, J = 2.7, 2.7 Hz, 1H, 7-H), 6.37 (dd, J = 2.7, 2.7 Hz, 1H, 8-H), 4.64 (AA′ d, J = 14.4 Hz, 1H, Bn), 4.58 (AA′ d, J = 14.1 Hz, 1H, Bn), 3.98 (ddd, J = 8.1, 1.2, 1.2 Hz, 1H, 8bα-H), 3.24 (ddd, J = 7.8, 5.1, 5.1 Hz, 1H, 3aα-H), 2.61 (dddd, J = 16.0, 5.3, 5.3, 0.9 Hz, 1H, 5β-H), 2.51 (dddd, J = 15.4, 9.9, 5.4, 0.9 Hz, 1H, 5α-H), 2.37 (dddd, J = 13.5, 4.8, 4.8, 4.8, 1H, 4β-H), 1.99 (dddd, J = 13.7, 9.8, 5.5, 5.3 Hz, 1H, 4α-H); ^{13}C NMR (75 MHz, $CDCl_3$, δ) 179.0, 178.0, 136.0, 128.7, 128.4, 127.8, 127.2, 117.2, 110.4, 107.6, 42.3, 40.4, 40.1, 22.2, 19.6; IR (KBr, cm^{-1}) 3450s, 3100w, 2924m,

2980w, 1701s; HRMS *m/z* (M + Na^+) calcd. 303.1105, found 303.1093. Anal. Calcd. for $C_{17}H_{16}N_2O_2$: C, 72.84; H, 5.75; N, 9.99. Found: C, 72.92; H, 5.75; N, 9.43.

2-Phenyl-3aα,4,5,8bα-tetrahydro-2H,6H-pyrrolo[3,4-e]indole-1,3-dione (13). Method A with vinylpyrrole **4** and maleimide **10c** gave **13** (980 mg, 92% crude yield, including contamination from double-addition type products, detected by TLC; the crude adduct was recrystallized from methylene chloride/petroleum ether, giving the pure compound, but the isolated yield is not available) as a light-brown powder: mp 155–156°C; ^{1}H NMR (300 MHz, $CDCl_3$, δ) 7.95 (bs, 1H, 6-H), 7.41–7.47 (m, 2H, Ph), 7.33–7.39 (m, 1H, Ph), 7.23–7.28 (m, 2H, Ph), 6.70 (dd, *J* = 2.9, 2.9 Hz, 1H, 7-H), 6.41 (dd, *J* = 2.6, 2.6 Hz, 1H, 8-H), 4.15 (ddd, *J* = 8.1, 1.4, 1.4 Hz, 1H, 8bα-H), 3.45 (ddd, *J* = 8.1, 5.0, 5.0 Hz, 1H, 3aα-H), 2.63–2.67 (m, 2H, 5α-H and 5β-H), 2.53 (dddd, *J* = 13.6, 4.5, 4.5, 4.5 Hz, 1H, 4β-H), 2.06 (dddd, *J* = 13.4, 8.3, 7.6, 5.2 Hz, 1H, 4α-H); ^{13}C NMR (75 MHz, $CDCl_3$, δ) 178.3, 177.3, 132.1, 129.1, 128.4, 127.3, 126.4, 117.3, 110.2, 107.7, 40.5, 40.4, 22.0, 19.4; IR (film, cm^{-1}) 3374(bs), 2857(m), 1775(w), 1707(s), 1596(w), 1498(m), 1383(m), 1177(m), 1064(m), 793(m), 723(m); HRMS *m/z* (M + Na^+) calcd. 289.0948, found 289.0947. Anal. Calcd. for $C_{16}H_{14}N_2O_2$: C, 72.16; H, 5.30; N, 10.52. Found: C, 71.96; H, 5.43; N, 10.57.

2-(4-Ethylphenyl)-3aα,4,5,8bα-tetrahydro-2H,6H-pyrrolo[3,4-e]indole-1,3-dione (14). Method A with vinylpyrrole **4** and maleimide **10d** gave **14** (577 mg, 49%) as a white powder: mp 144–146°C; ^{1}H NMR (300 MHz, $CDCl_3$, δ) 7.93 (bs, 1H, 6-H), 7.26 (d, *J* = 8.9, 2H, Ph), 7.15 (d, *J* = 8.4 Hz, 2H, Ph), 6.70 (dd, *J* = 2.6, 2.6 Hz, 1H, 7-H), 6.41 (dd, *J* = 2.7, 2.7 Hz, 1H, 8-H), 4.13 (ddd, *J* = 7.8, 1.4, 1.4 Hz, 1H, 8bα-H), 3.43 (ddd, *J* = 8.1, 5.0, 5.0 Hz, 1H, 3aα-H), 2.63–2.71 (m, 2H, 5α-H and 5β-H), 2.66 (q, overlapped, *J* = 7.6 Hz, 2H, CH_2CH_3), 2.52 (dddd, *J* = 13.7, 4.6, 4.6, 4.6 Hz, 1H, 4β-H), 2.06 (dddd, *J* = 13.4, 8.4, 7.3, 5.1 Hz, 1H, 4α-H), 1.23 (t, *J* = 7.7 Hz, 3H, CH_2CH_3); ^{13}C NMR (75 MHz, $CDCl_3$, δ) 178.7, 177.7, 144.7, 129.6, 128.6, 127.3, 126.4, 117.3, 110.1, 107.4, 40.6, 40.4, 28.7, 22.1, 19.4, 15.6; IR (KBr, cm^{-1}) 3340(bs), 3030(w), 2970(m), 2940(m), 2860(w), 1780(m), 1700(s), 1600(w), 1510(m), 1445(w), 1395(s), 1360(w), 1310(w), 1295(w), 1205(m), 1195(m), 1170(m), 850(w), 815(w), 785(m), 720(m), 695(m); HRMS *m/z* (M + Na^+) calcd. 317.1261, found 317.1262. Anal. Calcd. for $C_{18}H_{18}N_2O_2$: C, 73.45; H, 6.16; N, 9.52. Found: C, 73.60; H, 6.26; N, 9.36.

2-(4-Isopropylphenyl)-3aα,4,5,8bα-tetrahydro-2H,6H-pyrrolo[3,4-e]indole-1,3-dione (15). Method A with vinylpyrrole **4** and maleimide **10e** gave **15** (395 mg, 32%) as a light-orange powder: mp 188–190°C; ^{1}H NMR (300 MHz, $CDCl_3$, δ) 7.93 (bs, 1H, 6-H), 7.29 (d, *J* = 8.4 Hz, 2H, Ph), 7.16 (d, *J* = 8.7 Hz, 2H, Ph), 6.70 (dd, *J* = 2.6, 2.6 Hz, 1H, 7-H), 6.41 (dd, *J* = 2.6, 2.6 Hz, 1H, 8-H), 4.13 (ddd, *J* = 8.1, 1.4, 1.4 Hz, 1H, 8bα-H), 3.44 (ddd, *J* = 8.1, 5.0, 5.0 Hz, 1H, 3aα-H), 2.92 (septet, *J* = 6.9 Hz, 1H, $CH(CH_3)_2$), 2.65 (m, 2H, 5α-H and 5β-H), 2.52 (dddd, *J* = 13.7, 4.6, 4.6, 4.6 Hz, 1H, 4β-H), 2.06 (dddd, *J* = 13.5, 8.3, 7.4, 5.1 Hz, 1H, 4α-H), 1.24 (d, *J* = 6.9 Hz, 6H, $CH(CH_3)_2$); ^{13}C NMR (75 MHz, $CDCl_3$, δ) 178.6, 177.5, 149.2, 129.6, 127.2 (two peaks overlapped), 117.2, 110.2, 107.6, 40.5, 40.4, 34.0, 24.0, 22.0, 19.4; ^{13}C NMR (75 MHz, DMSO-d_6, δ) 179.0, 177.8, 148.9, 130.7, 127.2 (three peaks overlapped), 117.1, 110.0, 106.8, ~40 (two peaks obscured by DMSO), 33.7, 24.3, 22.5, 19.5; IR (KBr, cm^{-1}) 3444(m), 3353(bs), 3105(w), 2959(m), 2931(m), 2863(w), 1773(w), 1704(s), 1513(m), 1463(w), 1428(w), 1381(m), 1347(w), 1280(w), 1194(m), 1177(m), 1152(m), 1093(w), 1067(w), 1051(w), 721(m); HRMS *m/z* (M + Na^+) calcd. 331.1418, found 331.1410. Anal. Calcd. for $C_{19}H_{20}N_2O_3$: C, 74.00; H, 6.54; N, 9.08. Found: C, 74.00; H, 6.51; N, 9.16.

2-(4-Methoxyphenyl)-3aα,4,5,8bα-tetrahydro-2H,6H-pyrrolo[3,4-e]indole-1,3-dione (16). Method A with vinylpyrrole **4** and maleimide **10f** gave **16** (1.067 g, 90% crude yield, including contamination from double-addition type products, detected by TLC; the crude adduct was recrystallized from methylene chloride/petroleum ether, giving the pure compound, but the isolated yield is not available) as a white powder: mp 187–188°C; ^{1}H NMR (300 MHz, $CDCl_3$, δ) 7.94 (bs, 1H, 6-H), 7.17 (d, *J* = 9.0 Hz, 2H, Ph), 6.94 (d, *J* = 9.0 Hz, 2H, Ph), 6.70 (dd, *J* = 2.7, 2.7 Hz, 1H, 7-H), 6.41 (dd, *J* = 2.9, 2.9 Hz, 1H, 8-H), 4.15 (ddd, *J* = 8.1, 1.4, 1.4 Hz, 1H, 8bα-H), 3.82 (s, 3H, OCH_3), 3.45 (ddd, *J* = 7.8, 5.0, 5.0 Hz, 1H, 3aα-H), 2.63–2.67 (m, 2H, 5α-H and 5β-H), 2.53 (dddd, *J* = 13.5, 4.5, 4.5, 4.5 Hz, 1H, 4β-H), 2.06 (dddd, *J* = 13.7, 8.0, 7.7, 5.2 Hz, 1H, 4α-H); ^{13}C NMR (75 MHz, $CDCl_3$, δ) 178.5, 177.5, 159.3, 127.7, 127.2, 124.8, 117.2, 114.4, 110.4, 107.7, 55.6, 40.5, 40.3, 22.0, 19.4; IR (film, cm^{-1}) 3378(bm), 2931(w), 2842(w), 1776(w), 1704(s), 1608(w), 1513(s), 1466(w), 1441(w), 1389(m), 1300(w), 1251(m), 1168(m), 1030(w), 729(w); HRMS *m/z* (M + Na^+) calcd. 319.1054, found 319.1056. Anal. Calcd. for $C_{17}H_{16}N_2O_3$: C, 68.91; H, 5.44; N, 9.45. Found: C, 68.86; H, 5.61; N, 9.28.

2-(4-Phenoxyphenyl)-3aα,4,5,8bα-tetrahydro-2H,6H-pyrrolo[3,4-e]indole-1,3-dione (17). Method A with vinylpyrrole **4** and maleimide **10h** gave **17** (473 mg, 33%) as a light-yellow powder: mp 200–202°C; ^{1}H NMR (300 MHz, $CDCl_3$, δ) 7.93 (bs, 1H, 6-H), 7.33–7.39 (m, 2H, Ph), 7.21 (d, *J* = 9.0 Hz, 2H, Ph), 7.12–7.17 (m, 1H, Ph), 7.01–7.06 (m, 2H, Ph), 7.03 (d, overlapped, *J* = 9.0 Hz, 2H, Ph), 6.70 (dd, *J* = 2.7, 2.7 Hz, 1H, 7-H), 6.41 (dd, *J* = 2.7, 2.7 Hz, 1H, 8-H), 4.14 (ddd, *J* = 8.1, 1.4, 1.4 Hz, 1H, 8bα-H), 3.44 (ddd, *J* = 7.8, 4.9, 4.9 Hz, 1H, 3aα-H), 2.63–2.67 (m, 2H, 5α-H and 5β-H), 2.53 (dddd, *J* = 13.4, 4.6, 4.6, 4.6 Hz, 1H, 4β-H), 2.06 (dddd, *J* = 13.6, 8.5, 7.3, 5.1 Hz, 1H, 4α-H); ^{1}H NMR (300 MHz, DMSO-d_6) 10.60 (bs, 1H, 6-H), 7.39–7.44 (m, 2H, Ph), 7.15–7.20 (m, 1H, Ph), 7.19 (d, overlapped, *J* = 8.7 Hz, 2H, Ph), 7.03–7.07 (m, 2H, Ph), 7.05 (d, overlapped, *J* = 8.7 Hz, 2H, Ph), 6.59 (dd, *J* = 2.6, 2.6 Hz, 1H, 7-H), 6.04 (dd, *J* = 2.4, 2.4 Hz, 1H, 8-H), 4.02 (d, *J* = 8.1 Hz, 1H, 8bα-H), 3.51 (ddd, *J* = 8.1, 5.2, 5.2 Hz, 1H, 3aα-H), 2.58 (ddd, *J* = 15.5, 4.7, 4.7 Hz, 1H, 5β-H), 2.43 (ddd, 15.2, 10.0, 4.9 Hz, 1H, 5α-H), 2.23 (dddd, *J* = 13.5, 4.8, 4.8, 4.8 Hz, 1H, 4β-H), 1.88 (dddd, *J* = 13.6, 10.1, 5.2, 5.2 Hz, 1H, 4α-H); ^{13}C NMR (75 MHz, DMSO-d_6, δ) 178.9, 177.8, 156.9, 156.6, 130.8, 129.1, 127.9, 127.3, 124.5, 119.7, 118.9, 117.1, 110.0, 106.8, 22.5, 21.3, 19.5, 18.2; IR (KBr, cm^{-1}) 3387(bs), 3104(w), 2960(w), 2934(w), 2854(w), 1771(w), 1702(s), 1588(m), 1506(m), 1487(m), 1430(w), 1390(m), 1352(w), 1285(w), 1244(s), 1199(m), 1179(m), 1155(m), 1093(w), 1069(w), 876(w), 723(m); HRMS *m/z* (M + Na^+) calcd. 381.1210, found 381.1202. Anal. Calcd. for $C_{22}H_{18}N_2O_3$: C, 73.73; H, 5.06; N, 7.82. Found: C, 73.95; H, 5.03; N, 7.71.

2-Dimethylamino-6-methyl-3aα,4,5,8bα-tetrahydro-2H,6H-pyrrolo[3,4-e]indole-1,3-dione (18). Method A with vinylpyrrole **3d** and maleimide **10a** gave **18** (880 mg, 89%) as a dark-

brown oil: ^{1}H NMR (300 MHz, $CDCl_3$, δ) 6.54 (d, J = 2.7 Hz, 1H, 7-H), 6.28 (d, J = 2.7 Hz, 1H, 8-H), 3.87 (ddd, J = 8.1, 1.4, 1.4 Hz, 1H, 8bα-H), 3.50 (s, 3H, 6-CH_3), 3.15 (ddd, J = 8.1, 5.3, 5.3 Hz, 1H, 3aα-H), 2.85 (s, 6H, $N(CH_3)_2$), 2.58 (dddd, J = 16.1, 5.6, 5.6, 1.2 Hz, 1H, 5β-H), 2.48 (dddd, J = 15.5, 9.5, 5.6, 1.2 Hz, 1H, 5α-H), 2.34 (dddd, J = 13.4, 5.3, 5.3, 5.3 Hz, 1H, 4β-H), 1.99 (dddd, J = 13.5, 9.1, 5.5, 5.5 Hz, 1H, 4α-H); ^{13}C NMR (75 MHz, $CDCl_3$, δ) 177.5, 176.6, 128.1, 121.5, 110.1, 106.5, 44.0, 38.9, 38.6, 33.2, 22.1, 18.2; IR (film, cm^{-1}) 3105(w), 3054(w), 2931(m), 2891(m), 1777(m), 1716(s), 1497(m), 1446(m), 1364(s), 1270(w), 1248(w), 1181(m), 1145(m), 1053(w), 714(m); HRMS m/z (M + Na^+) calcd. 270.1214, found 270.1221. Anal. Calcd. for $C_{13}H_{17}N_3O_2$: C, 63.14; H, 6.93; N, 16.99. Found: C, 62.94; H, 7.07; N, 16.76.

6-Methyl-2-phenyl-3aα,4,5,8bα-tetrahydro-2H,6H-pyrrolo[3,4-e]indole-1,3-dione (19). Method A with vinylpyrrole **3d** and maleimide **10c** gave **19** (1.054 g, 94%) as a light-brown powder: mp 169–170°C; ^{1}H NMR (300 MHz, $CDCl_3$, δ) 7.38–7.47 (m, 2H, Ph), 7.32–7.38 (m, 1H, Ph), 7.24–7.29 (m, 2H, Ph), 6.57 (d, J = 2.7, 2.7 Hz, 1H, 7-H), 6.33 (d, J = 2.7, 2.7 Hz, 1H, 8-H), 4.13 (ddd, J = 8.4, 1.4, 1.4 Hz, 1H, 8bα-H), 3.52 (s, 3H, 6-CH_3), 3.43 (ddd, J = 8.1, 4.5, 4.4 Hz, 1H, 3aα-H), 2.50–2.68 (m, 3H, 4β-H, 5α-H and 5β-H), 2.05 (dddd, J = 15.4, 12.5, 6.2, 5.0 Hz, 1H, 4α-H); ^{13}C NMR (75 MHz, $CDCl_3$, δ) 178.2, 177.2, 132.2, 129.0, 128.3, 128.2, 126.4, 121.6, 110.6, 106.5, 40.6, 40.4, 33.2, 21.7, 18.2; IR (film, cm^{-1}) 3060(w), 2931(m), 2849(w), 1777(w), 1711(s), 1596(w), 1498(m), 1455(w), 1380(m), 1290(w), 1269(w), 1173(m), 1150(m), 718(m), 692(m); HRMS m/z (M + Na^+) calcd. 303.1105, found 303.1109. Anal. Calcd. for $C_{17}H_{16}N_2O_2$: C, 72.84; H, 5.75; N, 9.99. Found: C, 72.60; H, 5.67; N, 9.81.

2-(4-Methoxyphenyl)-6-methyl-3aα,4,5,8bα-tetrahydro-2H,6H-pyrrolo[3,4-e]indole-1,3-dione (20). Method A with vinylpyrrole **3d** and maleimide **10f** gave **20** (1.154 g, 93%) as a cream-colored powder: mp 161–162°C; ^{1}H NMR (300 MHz, $CDCl_3$, δ) 7.17 (d, J = 9.0 Hz, 2H, Ph), 6.94 (d, J = 9.0 Hz, 2H, Ph), 6.57 (d, J = 2.7 Hz, 1H, 7-H), 6.33 (d, J = 2.7 Hz, 1H, 8-H), 4.11 (ddd, J = 8.4, 2.0, 2.0 Hz, 1H, 8bα-H), 3.82 (s, 3H, OCH_3), 3.52 (s, 3H, 6-CH_3), 3.40 (ddd, J = 7.8, 4.7, 4.7 Hz, 1H, 3aα-H), 2.49–2.68 (m, 3H, 4β-H, 5α-H and 5β-H), 2.05 (dddd, J = 16.5, 7.6, 6.0, 4.5 Hz, 1H, 4α-H); ^{13}C NMR (75 MHz, $CDCl_3$, δ) 178.5, 177.5, 159.3, 128.2, 127.6, 124.9, 121.5, 114.3, 110.6, 106.5, 55.6, 40.5, 40.4, 33.2, 21.8, 18.2; IR (film, cm^{-1}) 2934(w), 2841(w), 1776(w), 1709(s), 1609(w), 1513(s), 1442(w), 1386(m), 1300(w), 1250(m), 1171(m), 1151(w), 1030(w); HRMS m/z (M + Na^+) calcd. 333.1210, found 333.1222. Anal. Calcd. for $C_{18}H_{18}N_2O_3$: C, 69.66; H, 5.85; N, 9.03. Found: C, 69.89; H, 6.00; N, 8.90.

2-Dimethylamino-5β,6-dimethyl-3aα,4,5α,8bα-tetrahydro-2H,6H-pyrrolo[3,4-e]indole-1,3-dione (21). Method A with vinylpyrrole **3e** and maleimide **10a** with reflux gave **21** (899 mg, 86%) as a light-orange powder: mp 100–101°C; maj/min = 13:1; ^{1}H NMR (300 MHz, $CDCl_3$, δ) 6.55 (d, J = 2.7 Hz, 1H, 7-H), 6.28 (d, J = 2.7 Hz, 1H, 8-H), 3.92 (dd, J = 9.0, 0.6 Hz, 1H, 8bα-H), 3.53 (s, 3H, 6-CH_3), 3.14 (ddd, J = 8.9, 7.0, 2.3 Hz, 1H, 3aα-H), 3.02 (dddq, J = 7.2, 5.7, 2.1, 0.6 Hz, 1H, 5α-H), 2.87 (s, 6H, $N(CH_3)_2$), 2.50 (ddd, J = 14.1, 2.1, 2.1 Hz, 1H, 4β-H), 2.04 (ddd, J = 14.1, 7.2, 5.7 Hz, 1H, 4α-H), 1.11 (d, J = 7.2 Hz, 3H, 5β-CH_3); ^{13}C NMR (75 MHz, $CDCl_3$, δ) 178.7, 176.6, 132.5, 121.9, 109.2, 106.5, 43.7, 38.3, 36.8, 33.0, 28.8, 25.3, 22.0; IR (film, cm^{-1}) 2962(s), 1777(m), 1711(s), 1500(w), 1446(w), 1369(m), 1293(w), 1189(m), 1149(m), 1046(w); HRMS m/z (M + Na^+) calcd. 284.1370, found 284.1373. Anal. Calcd. for $C_{14}H_{19}N_3O_2$: C, 64.35; H, 7.33; N, 16.08. Found: C, 64.15; H, 7.12; N, 16.18.

5β,6-Dimethyl-2-phenyl-3aα,4,5α,8bα-tetrahydro-2H,6H-pyrrolo[3,4-e]indole-1,3-dione (22). Method A with vinylpyrrole **3e** and maleimide **10c** with reflux gave **22** (1.071 g, 91%) as a light-yellow cream-colored powder: mp 239–240°C; maj/min = 54:1; ^{1}H NMR (300 MHz, $CDCl_3$, δ) 7.42–7.48 (m, 2H, Ph), 7.33–7.39 (m, 1H, Ph), 7.25–7.29 (m, 2H, Ph), 6.58 (d, J = 3.0 Hz, 1H, 7-H), 6.32 (d, J = 2.7 Hz, 1H, 8-H), 4.16 (d, J = 8.7 Hz, 1H, 8bα-H), 3.55 (s, 3H, 6-CH_3), 3.39 (ddd, J = 8.8, 6.7, 2.2 Hz, 1H, 3aα-H), 3.08 (ddq, J = 6.6, 6.6, 2.4 Hz, 1H, 5α-H), 2.62 (ddd, J = 14.1, 2.1, 2.1 Hz, 1H, 4β-H), 2.16 (ddd, J = 14.0, 6.3, 6.3 Hz, 1H, 4α-H), 1.19 (d, J = 6.9 Hz, 3H, 5β-CH_3); ^{13}C NMR (75 MHz, $CDCl_3$, δ) 179.5, 177.3, 132.6, 132.3, 129.1, 128.4, 126.4, 122.0, 109.5, 106.5, 40.0, 38.6, 33.1, 29.0, 25.4, 22.2; IR (film, cm^{-1}) 2960(m), 2956(m), 1775(w), 1711(s), 1595(w), 1499(m), 1453(w), 1380(m), 1348(m), 1293(w), 1270(w), 1175(m), 1157(m), 1062(w), 741(w), 728(w), 717(w), 691(m); HRMS m/z (M + Na^+) calcd. 317.1261, found 317.1253. Anal. Calcd. for $C_{18}H_{18}N_2O_2$: C, 73.45; H, 6.16; N, 9.52. Found: C, 73.55; H, 6.31; N, 9.51.

2-(4-Methoxyphenyl)-5β,6-dimethyl-3aα,4,5α,8bα-tetrahydro-2H,6H-pyrrolo[3,4-e]indole-1,3-dione (23). Method A with vinylpyrrole **3e** and maleimide **10f** with reflux gave **23** (1.207 g, 93%) as a white powder: mp 190–191°C; maj/min = 37:1; ^{1}H NMR (300 MHz, $CDCl_3$, δ) 7.18 (d, J = 9.3 Hz, 2H, Ph), 6.95 (d, J = 9.3 Hz, 2H, Ph), 6.57 (d, J = 3.0 Hz, 1H, 7-H), 6.32 (d, J = 2.7 Hz, 1H, 8-H), 4.15 (dd, J = 8.7, 0.6 Hz, 1H, 8bα-H), 3.82 (s, 3H, OCH_3), 3.55 (s, 3H, 6-CH_3), 3.37 (ddd, J = 8.9, 6.8, 2.3 Hz, 1H, 3aα-H), 3.07 (dddq, J = 6.9, 5.7, 2.1, 0.6 Hz, 1H, 5α-H), 2.61 (ddd, J = 14.1, 2.1, 2.1 Hz, 1H, 4β-H), 2.15 (ddd, J = 14.1, 6.9, 5.7 Hz, 1H, 4α-H), 1.17 (d, J = 6.9 Hz, 3H, 5β-CH_3); ^{13}C NMR (75 MHz, $CDCl_3$, δ) 179.7, 177.5, 159.4, 132.6, 127.7, 125.0, 122.0, 114.5, 109.6, 106.5, 55.6, 39.9, 38.5, 33.1, 29.0, 25.4, 22.2; IR (film, cm^{-1}) 2964(m), 1777(w), 1709(s), 1610(w), 1513(s), 1386(m), 1299(w), 1250(m), 1196(m), 1030(w); HRMS m/z (M + Na^+) calcd. 347.1367, found 347.1367. Anal. Calcd. for $C_{19}H_{20}N_2O_3$: C, 70.35; H, 6.21; N, 8.64. Found: C, 70.20; H, 6.37; N, 8.44.

2-Dimethylamino-4-methyl-3aα,4,5,8bα-tetrahydro-2H,6H-pyrrolo[3,4-e]indole-1,3-dione (24). Method A with vinylpyrrole **3b** and maleimide **10a** with reflux gave **24** (564 mg, 57%) as a brown powder: mp 117–118°C; maj/min = 1.4:1.0; ^{1}H NMR (300 MHz, $CDCl_3$, δ) 7.94 (bs, 1H, 6-H), 6.66–6.69 (m, 1H, 7-H), 6.35–6.66 (m, 1H, 8-H), 3.83–3.87 (m, 1H, 8bα-H), 3.12 (ddd, J = 7.8, 4.4, 0.9 Hz, 1H, 3aαmin-H), 2.83–2.88 (m, 1H, 3aαmaj-H), 2.85 (s, overlapped by 3aαmaj-H, 6H, $N(CH_3)_2$maj), 2.84 (s, overlapped by 3aαmaj-H, 6H, $N(CH_3)_2$min), 2.32–2.78 (m, 3H, 4-H and 5-H × 2), 1.34 (d, J = 6.9 Hz, 3H, 4βmin-CH_3), 1.56 (d, J = 6.9 Hz, 3H, 4αmaj-CH_3); ^{13}C NMR (75 MHz, $CDCl_3$, δ) 177.2, 176.6, 125.7, 117.2, 109.0, 107.5, 45.1, 44.0, 37.9, 28.2, 27.4, 19.5; IR (film, cm^{-1}) 3321(bm), 2960(m), 1776(w), 1710(s), 1448(w), 1367(m), 1199(m), 1145(m), 1063(w), 719(w); HRMS m/z (M + Na^+) calcd. 270.1214, found 270.1217. Anal. Calcd. for $C_{13}H_{17}N_3O_2$: C, 63.14; H, 6.93; N, 16.99. Found: C, 63.40; H, 7.10; N, 16.88.

4-Methyl-2-phenyl-3aα,4,5,8bα-tetrahydro-2H,6H-pyrrolo[3,4-e]indole-1,3-dione (25). Method A with vinylpyrrole **3b** and maleimide **10c** with reflux gave **25** (1.043 g, 93%) as a cream-colored powder: mp 208–209°C; maj/min = 2.0:1.0; ^{1}H NMR (300 MHz, $CDCl_3$, δ) 7.90 (bs, 1H, 6-H), 7.21–7.46 (m, 5H, Ph), 6.68–6.71 (m, 1H, 7-H), 6.39–6.41 (m, 1H, 8-H), 4.11 (d, J = 7.8 Hz, 1H, 8bαmin-H), 4.10 (d, overlapped by 8bαmin-H, J = 7.5 Hz, 1H, 8bαmaj-H), 3.38 (dd, J = 7.7, 4.1 Hz, 1H, 3aαmin-H), 3.14 (ddd, J = 8.0, 5.0, 0.9 Hz, 1H, 3aαmaj-H), 2.39–2.86 (m, 3H, 4-H and 5-H × 2), 1.47 (d, J = 6.9 Hz, 3H, 4βmin-CH_3), 1.21 (d, J = 6.9 Hz, 3H, 4αmaj-CH_3); ^{13}C NMR (75 MHz, DMSO-d_6, δ) 178.3, 177.5, 133.0, 129.4, 128.6, 127.4, 125.8, 117.2, 109.0, 106.8, 46.7, 41.3, 28.6, 27.5, 19.9; IR (film, cm^{-1}) 3367(bs), 3050(m), 2990(m), 2900(m), 1776(w), 1693(s), 1591(w), 1495(w), 1453(w), 1386(m), 1177(m), 1164(m), 1065(w), 786(w), 769(w), 741(w); HRMS m/z (M + Na^+) calcd. 303.1105, found 303.1103. Anal. Calcd. for $C_{17}H_{16}N_2O_2$: C, 72.84; H, 5.75; N, 9.99. Found: C, 72.61; H, 5.59; N, 9.96.

2-(4-Methoxyphenyl)-4-methyl-3aα,4,5,8bα-tetrahydro-2H,6H-pyrrolo[3,4-e]indole-1,3-dione (26). Method A with vinylpyrrole **3b** and maleimide **10f** with reflux gave **26** (1.117 g, 90%) as a cream-colored powder: mp 163–164°C; maj/min = 1.3:1.0; ^{1}H NMR (300 MHz, $CDCl_3$, δ) 7.91 (bs, 1H, 6-H), 7.10–7.19 (m, 4H, Ph), 6.68–6.71 (m, 1H, 7-H), 6.38–6.41 (m, 1H, 8-H), 4.05–4.11 (m, 1H, 8bα-H), 3.82 (s, 3H, OCH_3), 3.36 (ddd, J = 7.5, 4.2, 0.6 Hz, 1H, 3aαmin-H), 3.11 (ddd, J = 8.0, 4.5, 0.9 Hz, 1H, 3aαmaj-H), 2.37–2.86 (m, 3H, 4-H and 5-H × 2), 1.45 (d, J = 6.9 Hz, 1H, 4βmin-CH_3), 1.21 (d, J = 7.2 Hz, 1H, 4αmaj-CH_3); ^{13}C NMR (75 MHz, $CDCl_3$, δ) 178.1, 177.5, 159.3, 127.7, 125.7, 124.7, 117.3, 114.4, 109.3, 107.5, 55.6, 46.8, 39.4, 28.0, 27.2, 19.6; IR (film, cm^{-1}) 3370(bs), 2930(m), 2870(m), 1767(w), 1703(s), 1609(w), 1513(s), 1442(w), 1389(m), 1300(w), 1251(m), 1192(m), 1166(m), 1028(w), 721(w); HRMS m/z (M + Na^+) calcd. 333.1210, found 333.1216. Anal. Calcd. for $C_{18}H_{18}N_2O_3$: C, 69.66; H, 5.85; N, 9.03. Found: C, 69.45; H, 6.00; N, 8.83.

2-Dimethylamino-4,6-dimethyl-3aα,4,5,8bα-tetrahydro-2H,6H-pyrrolo[3,4-e]indole-1,3-dione (27). Method A with vinylpyrrole **3f** and maleimide **10a** with reflux gave **27** (700 mg, 67%) as a cream-colored powder: mp 85–86°C; maj/min = 1.2:1.0; ^{1}H NMR (300 MHz, $CDCl_3$, δ) 6.55 (d, J = 2.7 Hz, 1H, 7min-H), 6.52 (d, J = 2.7 Hz, 1H, 7maj-H), 6.28 (d, J = 2.7 Hz, 1H, 8min-H), 6.26 (d, J = 2.7 Hz, 1H, 8maj-H), 3.85 (ddd, J = 7.5, 1.4, 1.4 Hz, 1H, 8bαmaj-H), 3.80–3.84 (m, overlapped by 8bαmaj-H, 1H, 8bαmin-H), 3.09 (ddd, J = 7.6, 4.1, 0.6 Hz, 1H, 3aαmaj-H), 2.81–2.86 (m, 1H, 3aαmin-H), 2.85 (s, overlapped by 3aαmin-H, 6H, $N(CH_3)_2$min), 2.83 (s, overlapped by 3aαmin-H, 6H, $N(CH_3)_2$maj), 2.27–2.70 (m, 3H, 4-H and 5-H × 2), 1.40 (d, J = 6.6 Hz, 3H, 4βmaj-CH_3), 1.18 (d, J = 6.6 Hz, 4αmaj-CH_3); ^{13}C NMR (75 MHz, $CDCl_3$, δ) 176.8, 176.5, 128.0, 121.4, 110.2, 106.3, 44.0, 43.5, 39.9, 33.1, 29.9, 26.5, 18.2; IR (film, cm^{-1}) 2956(m), 2893(m), 1776(m), 1713(s), 1500(w), 1448(m), 1365(m), 1196(m), 1181(m), 1144(m), 706(w), 662(w); HRMS m/z (M + Na^+) calcd. 284.1370, found 284.1370. Anal. Calcd. for $C_{14}H_{19}N_3O_2$: C, 64.35; H, 7.33; N, 16.08. Found: C, 64.30; H, 7.51; N, 16.11.

4,6-Dimethyl-2-phenyl-3aα,4,5,8bα-tetrahydro-2H,6H-pyrrolo[3,4-e]indole-1,3-dione (28). Method A with vinylpyrrole **3f** and maleimide **10c** with reflux gave **28** (1.048 g, 89%) as a light-brown powder: mp 178–179°C; maj/min = 2.4:1.0; ^{1}H NMR (300 MHz, $CDCl_3$, δ) 7.20–7.46 (m, 5H, Ph), 6.57 (d, J = 2.7 Hz, 1H, 7min-H), 6.55 (d, J = 2.7 Hz, 1H, 7maj-H), 6.32 (d, J = 2.7 Hz, 1H, 8min-H), 6.30 (d, J = 2.7 Hz, 1H, 8maj-H), 4.07–4.13 (m, 1H, 8bα-H), 3.51 (s, 3H, 6-CH_3), 3.36 (ddd, J = 7.4, 3.8, 1.0 Hz, 1H, 3αmaj-H), 3.12 (ddd, J = 8.0, 4.8, 0.9 Hz, 1H, 3αmin-H), 2.32–2.83 (m, 3H, 4-H and 5-H × 2), 1.52 (d, J = 6.9 Hz, 3H, 4αmaj-CH_3), 1.23 (d, J = 6.9 Hz, 3H, 4βmin-CH_3); ^{13}C NMR (75 MHz, $CDCl_3$, δ) 177.3, 177.0, 132.1, 129.0, 128.4, 128.2, 126.4, 121.6, 110.7, 106.4, 45.5, 42.0, 33.2, 30.0, 26.4, 18.7; IR (film, cm^{-1}) 3060(m), 3030(m), 2929(m), 1775(w), 1710(s), 1597(w), 1498(m), 1453(w), 1377(m), 1174(m), 1142(m), 691(w); HRMS m/z (M + Na^+) calcd. 317.1261, found 317.1268. Anal. Calcd. for $C_{18}H_{18}N_2O_2$: C, 73.45; H, 6.16; N, 9.52. Found: C, 73.51; H, 5.98; N, 9.54.

2-(4-Methoxyphenyl)-4,6-dimethyl-3aα,4,5,8bα-tetrahydro-2H,6H-pyrrolo[3,4-e]indole-1,3-dione (29). Method A with vinylpyrrole **3f** and maleimide **10f** with reflux gave **29** (1.090 g, 84%) as a light-brown powder: mp 126–127°C; maj/min = 2.4:1.0; ^{1}H NMR (300 MHz, $CDCl_3$, δ) 7.10–7.19 (m, 2H, Ph), 6.90–7.00 (m, 2H, Ph), 6.57 (d, J = 2.7 Hz, 1H, 7min-H), 6.55 (d, J = 3.0, 1H, 7maj-H), 6.32 (d, J = 3.0 Hz, 1H, 8min-H), 6.30 (d, J = 3.0 Hz, 1H, 8maj-H), 4.05–4.10 (m, 1H, 8bα-H), 3.82 (s, 3H, OCH_3), 3.51 (s, 3H 6-CH_3), 3.33 (ddd, J = 7.6, 3.8, 1.1 Hz, 1H, 3αmaj-H), 3.09 (ddd, J = 7.9, 4.6, 0.8, 1H, 3aαmin-H), 2.32–2.81 (m, 3H, 4-H and 5-H × 2), 1.51 (d, J = 6.9 Hz, 3H, 4αmaj-CH_3), 1.22 (d, J = 7.2 Hz, 1H, 4βmin-CH_3); ^{13}C NMR (75 MHz, $CDCl_3$, δ) 177.6, 177.3, 159.2, 128.4, 127.7, 124.8, 121.5, 114.3, 110.8, 106.4, 55.6, 45.4, 41.8, 33.2, 30.0, 26.5, 18.6; IR (film, cm^{-1}) 2950(m), 2931(m), 2839(m), 1770(w), 1708(s), 1610(w), 1513(s), 1442(w), 1384(m), 1300(w), 1250(m), 1168(m), 1143(w), 1031(w), 704(w); HRMS m/z (M + Na^+) calcd. 347.1367, found 347.1362. Anal. Calcd. for $C_{19}H_{20}N_2O_3$: C, 70.35; H, 6.21; N, 8.64. Found: C, 70.51; H, 6.40; N, 8.79.

4α-Ethyl-2-phenyl-3aα,4β,5,8bα-tetrahydro-2H,6H-pyrrolo[3,4-e]indole-1,3-dione (30). Method B with vinylpyrrole **5a** and maleimide **10c** gave **30** (424 mg, 36%) as a white powder: mp 203–204°C; ^{1}H NMR (500 MHz, $CDCl_3$, δ) 7.93 (bs, 1H, 6-H), 7.40–7.44 (m, 2H, Ph), 7.32–7.36 (m, 1H, Ph), 7.22–7.27 (m, 2H, Ph), 6.66 (dd, J = 2.8, 2.8 Hz, 1H, 7-H), 6.35 (dd, J = 2.5, 2.5 Hz, 1H, 8-H), 4.05 (ddd, J = 7.5, 1.4, 1.4 Hz, 1H, 8bα-H), 3.28 (ddd, J = 7.5, 4.0, 0.9 Hz, 1H, 3aα-H), 2.77 (ddd, J = 15.8, 5.3, 1.7 Hz, 1H, 5β-H), 2.61 (m, 1H, 4β-H), 2.51 (dd, J = 15.8, 2.5 Hz, 1H, 5α-H, see 3aα-H and 8bα-H), 1.56 (ddq, J = 14.1, 8.0, 7.3 Hz, 1H, 4α-CH_2CH$_3$), 1.44 (ddq, J = 14.4, 7.5, 7.3 Hz, 1H, 4α-CH_2CH$_3$), 1.00 (dd, J = 7.3, 7.3 Hz, 3H, 4α-CH$_2$CH_3); ^{1}H NMR (300 MHz, DMSO-d_6, δ) 10.57 (bs, 1H, 6-H), 7.35–7.48 (m, 3H, Ph), 7.17–7.18 (m, 2H, Ph), 6.59 (dd, J = 2.6, 2.6 Hz, 1H, 7-H), 6.02 (dd, J = 2.6, 2.6 Hz, 1H, 8-H), 3.98 (d, J = 7.8 Hz, 1H, 8bα-H), 3.41 (ddd, J = 8.1, 4.2, 0.9 Hz, 1H, 3aα-H), 2.60 (dd, J = 15.9, 5.1 Hz, 1H, 5β-H), 2.45 (dd, J = 15.6, 3.6 Hz, 1H, 5α-H), 2.32–2.40 (m, 1H, 4β-H), 1.47 (ddq, J = 14.2, 7.5, 6.8 Hz, 1H, 4α-CH_2CH$_3$), 1.32 (ddq, J = 14.3, 7.7, 7.5 Hz, 1H, 4α-CH_2CH$_3$), 0.93 (dd, J = 7.5, 7.5 Hz, 3H, 4α-CH$_2$CH_3); ^{13}C NMR (75 MHz, $CDCl_3$, δ) 178.1, 177.3, 132.1, 129.0, 128.3, 126.4, 125.6, 117.2, 109.6, 107.6, 45.2, 39.3, 33.9, 25.6, 23.8, 12.1; ^{13}C NMR (75 MHz, DMSO-d_6, δ) 178.6, 177.7, 132.9, 129.4, 128.6, 127.3, 125.5, 117.2, 109.2, 106.7, 44.8, ~40 (obscured by DMSO), 34.4, 25.6, 24.1, 12.3; IR (KBr, cm^{-1}) 3346(bs),

3064(w), 2962(m), 2962(m), 2925(m), 2875(m), 2859(m), 1771(m), 1699(s), 1599(w), 1499(m), 1459(w), 1390(m), 1308(w), 1287(w), 1187(s), 1150(m), 1083(w), 1065(w), 743(m), 731(m), 689(m); HRMS *m/z* (M + Na^+) calcd. 317.1261, found 317.1263. Anal. Calcd. for $C_{18}H_{18}N_2O_2$: C, 73.45; H, 6.16; N, 9.52. Found: C, 73.60; H, 6.08; N, 9.71.

4α-Ethyl-2-(4-ethylphenyl)-3aα,4β,5,8bα-tetrahydro-2H,6H-pyrrolo[3,4-e]indole-1,3-dione (31). Method A with vinylpyrrole **5a** and maleimide **10d** gave **31** (903 mg, 70%), method B with vinylpyrrole **5a** and maleimide **10d** gave **31** (529 mg, 41%), as a light-orange powder: mp 247–248°C; ^{1}H NMR (300 MHz, $CDCl_3$, δ) 7.93 (bs, 1H, 6-H), 7.25 (d, *J* = 8.1 Hz, 2H, Ph), 7.14 (d, *J* = 8.4 Hz, 2H, Ph), 6.67 (dd, *J* = 2.6, 2.6 Hz, 1H, 7-H), 6.36 (dd, *J* = 2.7, 2.7, 1H, 8-H), 4.05 (ddd, *J* = 7.8, 1.2, 1.2 Hz, 1H, 8bα-H), 3.28 (ddd, *J* = 7.8, 3.9, 0.9 Hz, 1H, 3aα-H), 2.78 (ddd, *J* = 15.3, 5.4, 0.9 Hz, 1H, 5β-H), 2.66 (q, *J* = 7.6 Hz, 2H, PhCH_2CH$_3$), 2.58–2.64 (m, overlapped by PhCH_2CH$_3$, 1H, 4β-H), 2.52 (dd, *J* = 15.6, 3.0 Hz, 1H, 5α-H, see 3aα-H and 8bα-H), 1.56 (ddq, *J* = 13.8, 7.5, 6.9 Hz, 1H, 4α-CH_2CH$_3$), 1.44 (ddq, *J* = 14.3, 7.4, 7.2 Hz, 1H, 4α-CH_2CH$_3$), 1.23 (t, *J* = 7.7 Hz, 3H, PhCH$_2$CH_3), 1.00 (dd, *J* = 7.7 Hz, 3H, 4α-CH$_2$CH_3); ^{13}C NMR (75 MHz, $CDCl_3$, δ) 178.3, 177.5, 144.6, 129.6, 128.5, 126.3, 125.6, 117.1, 109.7, 107.6, 45.2, 39.3, 34.0, 28.6, 25.6, 23.8, 15.5, 12.1; IR (KBr, cm^{-1}) 3342(bs), 2960(m), 2929(w), 2872(w), 1768(m), 1697(s), 1514(m), 1461(w), 1444(w), 1392(m), 1306(w), 1289(w), 1190(s), 1151(m), 834(w), 772(m), 723(m), 702(m); HRMS *m/z* (M + Na^+) calcd. 345.1574, found 345.1575. Anal. Calcd. for $C_{20}H_{22}N_2O_2$: C, 74.51; H, 6.88; N, 8.69. Found: C, 74.48; H, 6.96; N, 8.68.

4-(4α-Ethyl-1,3-dioxo-3aα,4β,5,8bα-tetrahydro-2H,6H-pyrrolo[3,4-e]indol-2-yl)phenyl acetate (32). Method B with vinylpyrrole **5a** and maleimide **10g** gave **32** (437 mg, 31%) as a cream-colored powder: mp 218–219°C; ^{1}H NMR (300 MHz, $CDCl_3$, δ) 7.93 (bs, 1H, 6-H), 7.29 (d, *J* = 9.3 Hz, 2H, Ph), 7.16 (d, *J* = 9.0 Hz, 2H, Ph), 6.67 (dd, *J* = 2.7, 2.7 Hz, 1H, 7-H), 6.35 (dd, *J* = 2.7, 2.7 Hz, 1H, 8-H), 4.06 (ddd, *J* = 7.8, 1.4, 1.4 Hz, 1H, 8bα-H), 3.29 (ddd, *J* = 7.7, 3.9, 0.9 Hz, 1H, 3aα-H), 2.78 (ddd, *J* = 14.4, 5.4, 1.2 Hz, 1H, 5β-H), 2.58–2.65 (m, 1H, 4β-H), 2.52 (dd, *J* = 15.8, 3.2 Hz, 1H, 5α-H, see 3aα-H and 8bα-H), 2.29 (s, 3H, Ac), 1.56 (ddq, *J* = 14.4, 7.5, 7.4 Hz, 1H, 4α-CH_2CH$_3$), 1.47 (ddq, *J* = 14.7, 7.4, 7.2 Hz, 1H, 4α-CH_2CH$_3$), 1.01 (dd, *J* = 7.4, 7.4 Hz, 3H, 4α-CH$_2$CH_3); ^{13}C NMR (75 MHz, $CDCl_3$, δ) 177.9, 177.1, 169.2, 150.1, 129.5, 127.4, 125.6, 122.2, 117.2, 109.5, 107.5, 45.1, 39.3, 33.9, 25.6, 23.8, 21.2, 12.1; IR (KBr, cm^{-1}) 3359(bs), 3114(w), 3081(w), 2964(m), 2926(m), 2876(m), 2855(w), 1767(m), 1699(s), 1601(w), 1510(m), 1464(w), 1441(w), 1392(s), 1372(m), 1199(s), 1150(m), 1105(w), 1084(w), 1016(w), 938(w), 911(w), 849(w), 773(m), 719(m), 706(m); HRMS *m/z* (M + Na^+) calcd. 375.1316, found 375.1317. Anal. Calcd. for $C_{20}H_{20}N_2O_4$: C, 68.17; H, 5.72; N, 7.95. Found: C, 67.89; H, 5.53; N, 7.90.

4α-Ethyl-2-(4-hydroxyphenyl)-3aα,4β,5,8bα-tetrahydro-2H,6H-pyrrolo[3,4-e]indole-1,3-dione (33). Method B with vinylpyrrole **5a** and maleimide **10i** gave **33** (670 mg, 54%) as a cream-colored powder: mp 238–239°C; ^{1}H NMR (300 MHz, DMSO-d_6, δ) 10.54 (bs, 1H, 6-H), 9.70 (s, 1H, OH), 6.92 (d, *J* = 9.0 Hz, 2H, Ph), 6.78 (d, *J* = 8.7 Hz, 2H, Ph), 6.57 (dd, *J* = 2.6, 2.6 Hz, 1H, 7-H), 6.01 (dd, *J* = 2.4, 2.4 Hz, 1H, 8-H), 3.93 (d, *J* = 7.8 Hz, 1H, 8bα-H), 3.35 (dd, overlapped by H_2O, *J* = 4.2, 7.8 Hz, 1H, 3aα-H), 2.57 (dd, *J* = 16.2, 4.8 Hz, 1H, 5β-H), 2.44 (dd, *J* = 15.6, 3.3 Hz, 1H, 5α-H), 2.33–2.39 (m, 1H, 4β-H), 1.45 (ddq, *J* = 13.8, 7.5, 7.2 Hz, 1H, 4α-CH_2CH$_3$), 1.27 (ddq, *J* = 14.1, 7.7, 7.5 Hz, 1H, 4α-CH_2CH$_3$), 0.91 (dd, *J* = 7.5, 7.5 Hz, 3H, 4α-CH$_2$CH_3); ^{13}C NMR (75 MHz, DMSO-d_6, δ) 178.9, 178.0, 157.6, 128.6, 125.5, 124.0, 117.1, 115.8, 109.4, 106.7, 44.6, ~40 (obscured by DMSO), 34.4, 25.6, 24.1, 12.3; IR (KBr, cm^{-1}) 3467(m), 3374(bm), 2965(w), 2927(w), 2877(w), 1767(w), 1696(s), 1601(w), 1518(m), 1447(w), 1398(m), 1274(w), 1198(m), 1165(m), 1105(w), 1065(w), 1021(w), 837(w), 776(w), 725(m), 708(m); HRMS *m/z* (M + Na^+) calcd. 333.1210, found 333.1205. Anal. Calcd. for $C_{18}H_{18}N_2O_3$: C, 69.66; H, 5.85; N, 9.03. Found: C, 69.49; H, 6.05; N, 9.20.

2-(4-Chlorophenyl)-4α-ethyl-3aα,4β,5,8bα-tetrahydro-2H,6H-pyrrolo[3,4-e]indole-1,3-dione (34). Method B with vinylpyrrole **5a** and maleimide **10j** gave **34** (421 mg, 32%) as a white powder: mp 197–198°C; ^{1}H NMR (300 MHz, $CDCl_3$, δ) 7.88 (bs, 1H, 6-H), 7.40 (d, *J* = 9.0 Hz, 2H, Ph), 7.22 (d, *J* = 9.0 Hz, 2H, Ph), 6.69 (dd, *J* = 2.9, 2.9 Hz, 1H, 7-H), 6.36 (d, *J* = 2.7, 2.7 Hz, 1H, 8-H), 4.06 (ddd, *J* = 8.1, 1.4, 1.4 Hz, 1H, 8bα-H), 3.29 (ddd, *J* = 7.8, 3.6, 1.0 Hz, 1H, 3aα-H), 2.78 (ddd, *J* = 15.3, 5.4, 1.5 Hz, 1H, 5β-H), 2.58–2.65 (m, 1H, 4β-H), 2.53 (dd, *J* = 16.0, 2.6 Hz, 1H, 5α-H, see 3aα-H and 8bα-H), 1.54 (ddq, overlapped by H_2O, *J* = 14.5, 1.2, 7.2 Hz, 1H, 4α-CH_2CH$_3$), 1.44 (ddq, *J* = 14.5, 7.2, 7.2 Hz, 1H, 4α-CH_2CH$_3$), 1.28 (dd, *J* = 7.2, 7.2 Hz, 3H, 4α-CH$_2$CH_3); ^{13}C NMR (75 MHz, $CDCl_3$, δ) 177.8, 177.0, 134.0, 130.6, 129.2, 127.6, 125.6, 117.3, 109.4, 107.6, 45.1, 39.3, 33.9, 25.6, 23.8, 12.1; IR (KBr, cm^{-1}) 3370(s), 3342(s), 3095(w), 2969(m), 2925(m), 2877(m), 2856(m), 1769(m), 1698(s), 1600(w), 1495(m), 1463(w), 1445(w), 1390(m), 1358(m), 1308(w), 1274(w), 1183(s), 1149(m), 1090(m), 1066(w), 1017(w), 768(m), 715(m); HRMS *m/z* (M + Na^+) calcd. 351.0872, found 351.0871. Anal. Calcd. for $C_{18}H_{17}ClN_2O_2$: C, 65.75; H, 5.21; N, 8.52. Found: C, 65.58; H, 5.09; N, 8.69.

2-(4-Bromophenyl)-4α-ethyl-3aα,4β,5,8bα-tetrahydro-2H,6H-pyrrolo[3,4-e]indole-1,3-dione (35). Method B with vinylpyrrole **5a** and maleimide **10k** gave **35** (523 mg, 35%) as a cream-colored powder: mp 193–194°C; ^{1}H NMR (300 MHz, $CDCl_3$, δ) 7.88 (bs, 1H, 6-H), 7.55 (d, *J* = 8.7 Hz, 2H, Ph), 7.16 (d, *J* = 8.7 Hz, 2H, Ph), 6.69 (dd, *J* = 2.6, 2.6 Hz, 1H, 7-H), 6.35 (dd, *J* = 2.7, 2.7 Hz, 1H, 8-H), 4.06 (ddd, *J* = 7.5, 1.2, 1.2 Hz, 1H, 8bα-H), 3.29 (ddd, *J* = 7.8, 3.6, 0.9 Hz, 1H, 3aα-H), 2.78 (ddd, *J* = 15.6, 5.4, 1.8 Hz, 1H, 5β-H), 2.59–2.65 (m, 1H, 4β-H), 2.53 (dd, *J* = 16.5, 2.1 Hz, 1H, 5α-H, see 3aα-H and 8bα-H), 1.53 (ddq, overlapped by H_2O, *J* = 14.0, 7.5, 7.5 Hz, 1H, 4α-CH_2CH$_3$), 1.44 (ddq, *J* = 14.0, 7.5, 7.5 Hz, 1H, 4α-CH_2CH$_3$), 1.01 (dd, *J* = 7.4, 7.4 Hz, 3H, 4α-CH$_2$CH_3); ^{13}C NMR (75 MHz, $CDCl_3$, δ) 177.8, 176.9, 132.2, 131.1, 127.9, 125.6, 122.0, 117.3, 109.4, 107.6, 45.2, 39.3, 33.9, 25.6, 23.8, 12.1; IR (KBr, cm^{-1}) 3364(s), 3341(s), 3092(w), 2963(m), 2924(m), 2875(m), 2860(m), 1771(w), 1699(s), 1599(w), 1492(m), 1463(w), 1444(w), 1389(m), 1358(w), 1307(w), 1274(w), 1184(s), 1148(m), 1069(m), 1015(m), 935(w), 829(w), 783(w), 767(m), 714(m); HRMS *m/z* (M + Na^+) calcd. 395.0366, found 395.0363. Anal. Calcd. for $C_{18}H_{17}BrN_2O_2$: C, 57.92; H, 4.59; N, 7.51. Found: C, 57.71; H, 4.54; N, 7.59.

4α-Ethyl-2-(4-nitrophenyl)-3aα,4β,5,8bα-tetrahydro-2H,6H-pyrrolo[3,4-e]indole-1,3-dione (36). Method B with vinylpyrrole

5a and maleimide **10l** gave **36** (611 mg, 45%) as a cream-colored powder: mp 145–146°C; ^{1}H NMR (300 MHz, $CDCl_3$, δ) 8.29 (d, J = 9.0 Hz, 2H, Ph), 7.92 (bs, 1H, 6-H), 7.57 (d, J = 9.3 Hz, 2H, Ph), 6.71 (dd, J = 2.9, 2.9 Hz, 1H, 7-H), 6.35 (dd, J = 2.7, 2.7 Hz, 1H, 8-H), 4.11 (ddd, J = 7.9, 1.4, 1.4 Hz, 1H, 8bα-H), 3.34 (ddd, J = 7.7, 3.8, 0.9 Hz, 1H, 3aα-H), 2.80 (ddd, J = 15.6, 5.3, 1.7 Hz, 1H, 5β-H), 2.61–2.70 (m, 1H, 4β-H), 2.56 (dd, J = 15.8, 2.9 Hz, 1H, 5α-H, see 3aα-H and 8bα-H), 1.39–1.63 (m, 2H, 4-CH_2CH$_3$), 1.02 (dd, J = 7.2, 7.2 Hz, 3H, 4-CH$_2$CH_3); ^{13}C NMR (75 MHz, $CDCl_3$, δ) 177.3, 176.4, 146.7, 137.8, 126.7, 125.6, 124.3, 117.5, 109.1, 107.5, 45.2, 39.3, 33.8, 25.5, 23.8, 12.1; IR (KBr, cm^{-1}) 3375(bm), 3115(w), 2960(m), 2929(w), 2873(w), 1771(w), 1704(s), 1611(w), 1598(w), 1519(m), 1499(m), 1460(w), 1384(m), 1348(m), 1297(w), 1193(m), 1170(m), 1147(m), 1105(w), 1067(w), 1019(w), 851(w), 782(w), 743(m), 717(m); HRMS m/z (M + Na$^+$) calcd. for $C_{18}H_{17}N_3O_4$: 362.1112, found 362.1114.

4α-n-Pentyl-2-phenyl-3aα,4β,5,8bα-tetrahydro-2H,6H-pyrrolo[3,4-e]indole-1,3-dione (37). Method B with vinylpyrrole **5b** and maleimide **10c** gave **37** (404 mg, 30%) as a light-brown powder: mp 208–209°C; ^{1}H NMR (300 MHz, $CDCl_3$, δ) 7.90 (bs, 1H, 6-H), 7.40–7.46 (m, 2H, Ph), 7.32–7.37 (m, 1H, Ph), 7.22–7.27 (m, 2H, Ph), 6.68 (dd, J = 2.7, 2.7 Hz, 1H, 7-H), 6.37 (dd, J = 2.7, 2.7 Hz, 1H, 8-H), 4.07 (d, J = 7.8 Hz, 1H, 8bα-H), 3.28 (ddd, J = 8.0, 3.0, 0.9 Hz, 1H, 3aα-H), 2.79 (ddd, J = 15.5, 5.2, 1.1 Hz, 1H, 5β-H), 2.67–2.75 (m, 1H, 4β-H), 2.50 (dd, J = 15.3, 2.0 Hz, 1H, 5α-H, see 3aα-H), 1.25–1.52 (m, 8H, 4α-(CH_2)$_4$CH$_3$), 0.90 (t, J = 6.9 Hz, 3H, 4α-(CH$_2$)$_4$CH_3); ^{13}C NMR (75 MHz, $CDCl_3$, δ) 178.0, 177.3, 132.1, 129.0, 128.3, 126.4, 125.6, 117.2, 109.6, 107.6, 45.4, 39.3, 32.7, 32.2, 31.8, 27.3, 24.3, 22.7, 14.1; IR (KBr, cm^{-1}) 3361(bs), 3066(w), 2953(m), 2926(s), 2855(m), 1766(w), 1708(s), 1598(w), 1497(m), 1457(w), 1380(s), 1291(w), 1187(m), 1150(w), 1090(w), 1072(w), 742(w); HRMS m/z (M + Na$^+$) calcd. 359.1731, found 359.1734. Anal. Calcd. for $C_{21}H_{24}N_2O_2$: C, 74.97; H, 7.19; N, 8.33. Found: C, 74.72; H, 6.93; N, 8.22.

4β-Ethyl-2-phenyl-3aα,4α,5,8bα-tetrahydro-2H,6H-pyrrolo[3,4-e]indole-1,3-dione (38). Method B with vinylpyrrole **6** and maleimide **10c** gave **38** (483 mg, 41%) as a cream-colored powder: mp 182–183°C; maj/min = 12:1; ^{1}H NMR (300 MHz, $CDCl_3$, δ) 7.89 (bs, 1H, 6-H), 7.41 (dd, J = 7.8, 7.8 Hz, 2H, Ph), 7.32–7.38 (m, 1H, Ph), 7.20 (d, J = 7.5 Hz, 2H, Ph), 6.67 (dd, J = 2.5, 2.5 Hz, 1H, 7-H), 6.36 (dd, J = 2.8, 2.8 Hz, 1H, 8-H), 4.11 (ddd, J = 7.5, 1.3, 1.3 Hz, 1H, 8bα-H), 3.46 (ddd, J = 7.3, 3.8, 0.9 Hz, 1H, 3aα-H), 2.74 (dd, J = 15.8, 4.3 Hz, 1H, 5α-H, see 3aα-H and 8bα-H), 2.51 (ddd, J = 15.0, 11.0, 1.5 Hz, 1H, 5β-H), 2.08–2.15 (m, 1H, 4α-H), 2.05 (ddq, overlapped by 4α-H, J = 13.1, 7.5, 7.5 Hz, 1H, 4β-CH_2CH$_3$), 1.95 (ddq, J = 13.1, 7.5, 7.5 Hz, 1H, 4β-CH_2CH$_3$), 1.07 (dd, J = 7.5, 7.5 Hz, 3H, 4β-CH$_2$CH_3); ^{13}C NMR (75 MHz, $CDCl_3$, δ) 177.25, 177.20, 132.0, 129.0, 128.3, 127.5, 126.5, 117.4, 111.0, 107.4, 44.1, 42.0, 37.3, 25.5, 25.2, 12.6; IR (KBr, cm^{-1}) 3369(bs), 3112(w), 3053(m), 2958(m), 2925(m), 2895(m), 2871(m), 2840(w), 1768(m), 1706(w), 1595(m), 1553(w), 1497(m), 1455(m), 1384(s), 1316(w), 1294(m), 1268(w), 1194(s), 1153(m), 1137(m), 1089(w), 1059(m), 1026(w), 994(w), 910(w), 817(w), 719(s); HRMS m/z (M + Na$^+$) calcd. 317.1261, found 317.1262. Anal. Calcd. for $C_{18}H_{18}N_2O_2$: C, 73.45; H, 6.16; N, 9.52. Found: C, 73.21; H, 6.13; N, 9.72.

2-Benzyl-5β-(1-benzyl-2,5-dioxopyrrolidin-3-yl)-3aα,4,5α,8bα-tetrahydro-2H,6H-pyrrolo[3,4-e]indole-1,3-dione (52). Method A with vinylpyrrole **4** and maleimide **10b** gave **52** (421 mg, 45%) as a light-brown powder: mp 212–213°C; ^{1}H NMR (300 MHz, $CDCl_3$, δ) 10.58 (bs, 1H, 6-H), 7.32–7.42 (m, 5H, Ph), 7.18–7.26 (m, 5H, Ph), 6.76 (dd, J = 2.6, 2.6 Hz, 1H, 7-H), 6.34 (dd, J = 2.7, 2.7 Hz, 1H, 8-H), 4.74 (AA′ d, J = 14.1 Hz, 1H, Bn), 4.69 (AA′ d, J = 13.8 Hz, 1H, Bn), 4.59 (AA′ d, J = 14.4 Hz, 1H, Bn), 4.52 (AA′ d, J = 14.4 Hz, 1H, Bn), 4.02 (dd, J = 7.8, 1.2 Hz, 1H, 8bα-H), 3.32 (ddd, J = 7.9, 4.7, 3.5 Hz, 1H, 3aα-H), 3.01 (ddd, J = 9.4, 9.4, 6.1 Hz, 1H, 1′-H), 2.93 (dd, overlapped by 1′-H, J = 17.3, 9.6 Hz, 1H, 2′-H), 2.83–2.95 (m, overlapped by 2′-H, 1H, 5α-H), 2.77 (dd, overlapped by 5α-H, J = 17.0, 5.6 Hz, 1H, 2′-H), 2.54 (ddd, J = 13.3, 3.8, 3.8 Hz, 1H, 4β-H), 1.58 (ddd, J = 13.3, 11.5, 4.9 Hz, 1H, 4α-H); ^{13}C NMR (75 MHz, $CDCl_3$, δ) 180.0, 178.2, 177.7, 174.7, 135.8, 135.3, 129.0, 128.9, 128.7, 128.4, 128.3, 127.9, 127.3, 118.3, 111.8, 107.2, 44.6, 42.9, 42.3, 40.1, 40.0, 33.0, 31.5, 26.6; IR (KBr, cm^{-1}) 3446(w), 3329(bs), 3062(w), 3033(w), 2924(m), 2854(w), 1772(m), 1702(s), 1586(w), 1495(w), 1453(w), 1433(m), 1398(s), 1341(m), 1314(m), 1292(w), 1167(s), 1119(w), 1083(w), 714(m), 696(m); HRMS m/z (M + Na$^+$) calcd. 490.1738, found 490.1745. Anal. Calcd. for $C_{28}H_{25}N_3O_4$: C, 71.93; H, 5.39; N, 8.99. Found: C, 71.97; H, 5.44; N, 8.70.

2-(4-Ethylphenyl)-5β-(1-(4-ethylphenyl)-2,5-dioxopyrrolidin-3-yl)-3aα,4,5α,8bα-tetrahydro-2H,6H-pyrrolo[3,4-e]indole-1,3-dione (53). Method A with vinylpyrrole **4** and maleimide **10d** gave **53** (228 mg, 23%) as a light-brown powder: mp 173–174°C; ^{1}H NMR (300 MHz, $CDCl_3$, δ) 10.52 (bs, 1H, 6-H), 7.35 (d, J = 8.4 Hz, 2H, Ph), 7.25 (d, J = 8.4 Hz, 2H, Ph), 7.20 (d, J = 8.4 Hz, 2H, Ph), 7.12 (d, J = 8.4 Hz, 2H, Ph), 6.75 (dd, J = 2.9, 2.9 Hz, 1H, 7-H), 6.39 (dd, J = 2.7, 2.7 Hz, 1H, 8-H), 4.19 (dd, J = 8.1, 1.2 Hz, 1H, 8bα-H), 3.57 (ddd, J = 8.0, 4.7, 3.4 Hz, 1H, 3aα-H), 3.24 (ddd, J = 9.1, 9.1, 6.2 Hz, 1H, 1′-H), 3.13–3.23 (m, overlapped by 1′-H, 1H, 5α-H), 3.11 (dd, overlapped by 5α-H, J = 17.7, 8.7 Hz, 1H, 2′-H), 2.98 (dd, J = 17.7, 6.6 Hz, 1H, 2′-H), 2.73 (ddd, J = 12.9, 3.6, 3.6 Hz, 1H, 4β-H), 2.72 (q, overlapped by 4β-H, J =7.6 Hz, 2H, CH_2CH$_3$), 2.66 (q, overlapped by CH_2CH$_3$, J = 7.7 Hz, 2H, CH_2CH$_3$), 1.75 (ddd, J = 13.2, 10.8, 4.8 Hz, 1H, 4α-H), 1.28 (t, J = 7.1 Hz, 3H, CH$_2$CH_3), 1.23 (t, J = 7.2 Hz, 3H, CH$_2$CH_3); ^{13}C NMR (75 MHz, $CDCl_3$, δ) 179.7, 177.7, 177.1, 174.2, 145.6, 144.8, 129.4, 129.0, 128.9, 128.6, 127.3, 126.4, 126.2, 118.4, 111.8, 107.3, 44.8, 40.4, 40.2, 33.2, 31.6, 28.7, 28.6, 26.6, 15.5, 15.4; IR (KBr, cm^{-1}) 3353(bs), 3122(w), 3103(w), 3038(w), 2964(m), 2930(m), 2872(w), 1777(m), 1711(s), 1580(w), 1514(m), 1485(w), 1459(w), 1440(w), 1390(s), 1294(w), 1282(w), 1179(s), 1117(m), 1064(w), 832(m), 797(w), 768(w), 731(m); HRMS m/z (M + Na$^+$) calcd. 518.2051, found 518.2069. Anal. Calcd. for $C_{30}H_{29}N_3O_4$: C, 72.71; H, 5.90; N, 8.48. Found: C, 73.00; H, 6.19; N, 8.34.

2-(4-Isopropylphenyl)-5β-(1-(4-isopropylphenyl)-2,5-dioxopyrrolidin-3-yl)-3aα,4,5α,8bα-tetrahydro-2H,6H-pyrrolo[3,4-e]indole-1,3-dione (54). Method A with vinylpyrrole **4** and maleimide **10e** gave **54** (304 mg, 29%) as a light-brown powder: mp 148–150°C; ^{1}H NMR (300 MHz, $CDCl_3$, δ) 10.45 (bs, 1H, 6-H), 7.37 (d, J = 8.4 Hz, 2H, Ph), 7.27 (d, J = 8.7 Hz, 2H, Ph), 7.20 (d, J = 8.4 Hz, 2H, Ph), 7.13 (d, J = 8.4 Hz, 2H, Ph), 6.70 (dd, J = 2.4, 2.4 Hz, 1H, 7-H), 6.38 (dd, J = 2.7,

2.7 Hz, 1H, 8-H), 4.17 (d, J = 7.8 Hz, 1H, 8bα), 3.56 (ddd, J = 7.7, 4.0, 4.0 Hz, 1H, 3aα), 3.24 (ddd, J = 8.8, 8.8, 6.1 Hz, 1H, 1′-H), 2.85–3.25 (m, overlapped by 1′-H, 5H, 2′-H × 2 and 5α-H and C*H*$(CH_3)_2$ × 2), 2.69 (ddd, J = 13.4, 3.8, 3.8 Hz, 1H, 4β-H), 1.72 (ddd, J = 13.0, 10.7, 4.3 Hz, 1H, 4α-H), 1.29 (d, J = 6.9 Hz, 6H, CH(C*H*$_3$)$_2$), 1.24 (d, J = 6.9 Hz, 6H, CH(C*H*$_3$)$_2$); ^{13}C NMR (75 MHz, $CDCl_3$, δ) 179.7, 177.8, 177.2, 174.4, 150.1, 149.3, 129.4, 129.0, 127.6, 127.3, 127.2, 126.4, 126.1, 118.4, 111.8, 107.3, 44.6, 40.4, 40.2, 35.04, 34.97, 33.1, 31.5, 26.4, 24.0; IR (KBr, cm^{-1}) 3354(bs), 3039(w), 2960(s), 2928(m), 2871(m), 1779(m), 1708(s), 1574(w), 1514(m), 1461(m), 1385(s), 1281(w), 1168(s), 1114(m), 1059(m), 831(m), 732(m), 693(m), 659(m); HRMS m/z (M + Na$^+$) calcd. 546.2364, found 546.2377. Anal. Calcd. for $C_{32}H_{33}N_3O_4$: C, 73.40; H, 6.35; N, 8.02. Found: C, 73.18; H, 6.52; N, 8.04.

2-(4-Phenoxyphenyl)-5β-(1-(4-phenoxyphenyl)-2,5-dioxopyrrolidin-3-yl)-3aα,4,5α,8bα-tetrahydro-2H,6H-pyrrolo[3,4-e]indole-1,3-dione (55). Method A with vinylpyrrole **4** and maleimide **10h** gave **55** (474 mg, 38%) as a cream-colored powder: mp 133–135°C; ^{1}H NMR (300 MHz, $CDCl_3$, δ) 10.51 (bs, 1H, 6-H), 7.33–7.42 (m, 4H, Ph), 7.01–7.26 (m, 14H, Ph), 6.76 (dd, J = 2.6, 2.6 Hz, 1H, 7-H), 6.39 (dd, J = 2.6, 2.6 Hz, 1H, 8-H), 4.20 (dd, J = 7.8, 1.4 Hz, 1H, 8bα-H), 3.58 (ddd, J = 8.0, 4.7, 3.3 Hz, 1H, 3aα-H), 3.13–3.26 (m, 1H, 5α-H), 3.25 (ddd, overlapped by 5α-H, J = 9.2, 9.2, 6.2 Hz, 1H, 1′-H), 3.14 (dd, overlapped by 5α-H, J = 17.7, 8.7 Hz, 1H, 2′-H), 3.00 (dd, J = 17.9, 6.5 Hz, 1H, 2′-H), 2.74 (ddd, J = 13.3, 4.3, 3.5 Hz, 1H, 4β-H), 1.76 (ddd, J = 13.1, 11.0, 4.9 Hz, 1H, 4α-H); ^{13}C NMR (75 MHz, $CDCl_3$, δ) 179.7, 177.7, 177.1, 174.2, 158.2, 157.3, 156.5, 156.2, 130.1, 130.0, 128.0, 127.8, 127.3, 126.6, 125.9, 124.3, 124.0, 119.9, 119.5, 118.8, 118.5, 111.8, 107.4, 44.7, 40.4, 40.2, 33.2, 31.6, 26.5; IR (KBr, cm^{-1}) 3346(bs), 3061(m), 2922(m), 1778(m), 1718(s), 1588(m), 1506(s), 1487(s), 1388(m), 1286(m), 1244(s), 1196(m), 1113(m), 1067(m), 1017(w), 875(m), 845(m), 770(m), 695(m); HRMS m/z (M + Na$^+$) calcd. 646.1949, found 646.1951. Anal. Calcd. for $C_{38}H_{29}N_3O_6$: C, 73.18; H, 4.69; N, 6.74. Found: C, 73.40; H, 4.87; N, 6.61.

2-Benzyl-5α-(1-benzyl-2,5-dioxopyrrolidin-3-yl)-3aα,4,5β,8bα-tetrahydro-2H,6H-pyrrolo[3,4-e]indole-1,3-dione (56) and 2-benzyl-5β-(1-benzyl-2,5-dioxopyrrolidin-3-yl)-3aα,4,5α,8bα-tetrahydro-2H,6H-pyrrolo[3,4-e]indole-1,3-dione (52). Method A with vinylpyrrole **4** and maleimide **10b** followed by fractional recrystallizations from CH_2Cl_2/petroleum ether gave **56** (168 mg, 18%) as a light-brown powder, with a maximum purity of **56**:**52** in a 5:1 molar ratio, mass calculated from ^{1}H NMR, spectroscopic data for **56** only reported: mp 86–91°C; ^{1}H NMR (300 MHz, $CDCl_3$, δ) 7.36–7.41 (m, 4H, Ph), 7.27–7.28 (m, 6H, Ph), 7.02 (bs, 1H, 6-H), 6.24 (dd, J = 2.6, 2.6 Hz, 1H, 7-H), 6.15 (dd, J = 2.7, 2.7 Hz, 1H, 8-H), 4.79 (AA′ d, J = 13.8 Hz, 1H, Bn), 4.62 (AA′ d, J = 13.8 Hz, 1H, Bn), 4.61 (AA′ d, overlapped, J = 14.1 Hz, 1H, Bn), 4.54 (AA′ d, J = 14.1 Hz, 1H, Bn), 3.89 (dd, J = 7.8, 0.6 Hz, 1H, 8bα-H), 3.63 (dddd, J = 7.5, 5.4, 3.3, 0.8 Hz, 1H, 5β-H), 3.17 (ddd, J = 8.0, 8.0, 5.6 Hz, 1H, 3aα-H), 3.13 (ddd, overlapped by 5β-H, J = 8.9, 5.8, 3.1 Hz, 1H, 1′-H), 2.74 (dd, J = 18.0, 9.3 Hz, 1H, 2′-H *syn* to 1′-H), 2.26 (ddd, J = 13.5, 7.8, 5.7 Hz, 1H, 4β-H), 2.22 (dd, overlapped by 4β-H, J = 18.0, 5.7 Hz, 1H, 2′-H *anti* to 1′-H), 1.88 (ddd, J = 13.6, 7.7, 5.8 Hz, 1H, 4α-H); IR (KBr, cm^{-1}) 3382(bm), 3063(w), 3033(m), 2922(s), 2853(m), 1773(m), 1702(s), 1585(w), 1495(w), 1455(w), 1432(m), 1397(m), 1341(m), 1314(w), 1166(m), 1083(w), 1065(w), 723(w), 699(m); HRMS m/z (M + Na$^+$) calcd. 490.1738, found 490.1739. Anal. Calcd. for $C_{28}H_{25}N_3O_4$: C, 71.93; H, 5.39; N, 8.99. Found: C, 71.87; H, 5.52; N, 8.73.

2-(4-Ethylphenyl)-5α-(1-(4-ethylphenyl)-2,5-dioxopyrrolidin-3-yl)-3aα,4,5β,8bα-tetrahydro-2H,6H-pyrrolo[3,4-e]indole-1,3-dione (57). Method A with vinylpyrrole **4** and maleimide **10d** gave **57** (50 mg, 5%) as a cream-colored powder: mp 252–254°C; ^{1}H NMR (300 MHz, $CDCl_3$, δ) 7.96 (bs, 1H, 6-H), 7.34 (d, J = 8.4 Hz, 2H, Ph), 7.29 (d, J = 8.7 Hz, 2H, Ph), 7.16 (d, J = 8.4 Hz, 2H, Ph), 7.15 (d, overlapped, J = 8.4 Hz, 2H, Ph), 6.71 (dd, J = 2.7, 2.7 Hz, 1H, 7-H), 6.48 (dd, J = 2.7, 2.7 Hz, 1H, 8-H), 4.14 (d, J = 8.1 Hz, 1H, 8bα-H), 3.92 (ddd, J = 5.9, 5.9, 3.3 Hz, 1H, 5β-H), 3.40 (ddd, J = 9.2, 6.8, 3.3 Hz, 1H, 1′-H), 3.39 (ddd, overlapped by 1′-H, J = 9.6, 7.9, 5.3 Hz, 1H, 3aα-H), 2.95 (dd, J = 17.6, 9.2 Hz, 1H, 2′-H *syn* to 1′-H), 2.71 (q, J = 7.7 Hz, 2H, C*H*$_2$CH$_3$), 2.68 (q, overlapped by C*H*$_2$CH$_3$, J = 7.5 Hz, 2H, C*H*$_2$CH$_3$), 2.52 (dd, J = 17.6, 6.8 Hz, 1H, 2′-H *anti* to 1′-H), 2.42 (ddd, J = 13.9, 9.2, 5.9 Hz, 1H, 4β-H), 2.21 (ddd, J = 13.7, 5.7, 5.7 Hz, 1H, 4α-H), 1.27 (t, J = 7.6 Hz, 3H, CH$_2$C*H*$_3$), 1.25 (t, overlapped by CH$_2$C*H*$_3$, J = 7.6 Hz, 3H, CH$_2$C*H*$_3$); ^{13}C NMR (75 MHz, $CDCl_3$, δ) 179.1, 177.9, 176.1, 174.9, 145.5, 144.9, 129.3, 129.1, 129.0, 128.7, 126.23, 126.18, 124.6, 119.4, 113.5, 108.4, 45.4, 39.8, 38.9, 31.3, 30.3, 28.7, 28.4, 15.5; IR (KBr, cm^{-1}) 3462(w), 3364(bs), 3037(w), 2965(m), 2929(m), 2871(w), 1776(m), 1705(s), 1514(m), 1488(w), 1458(w), 1386(s), 1354(m), 1313(w), 1301(w), 1223(w), 1163(s), 1190(s), 1110(w), 1100(w), 1083(w), 770(m), 720(m); HRMS m/z (M + Na$^+$) calcd. 518.2051, found 518.2059. Anal. Calcd. for $C_{30}H_{29}N_3O_4$: C, 72.71; H, 5.90; N, 8.48. Found: C, 72.99; H, 5.93; N, 8.70.

2-(4-Isopropylphenyl)-5α-(1-(4-isopropylphenyl)-2,5-dioxopyrrolidin-3-yl)-3aα,4,5β,8bα-tetrahydro-2H,6H-pyrrolo[3,4-e]indole-1,3-dione (58). Method A with vinylpyrrole **4** and maleimide **10e** gave **58** (84 mg, 8%) as a cream-colored powder: mp 280–282°C; ^{1}H NMR (300 MHz, $CDCl_3$, δ) 7.94 (bs, 1H, 6-H), 7.37 (d, J = 8.1 Hz, 2H, Ph), 7.31 (d, J = 8.4 Hz, 2H, Ph), 7.17 (d, J = 8.7 Hz, 2H, Ph), 7.16 (d, J = 8.4 Hz, 2H, Ph), 6.71 (dd, J = 2.9, 2.9 Hz, 1H, 7-H), 6.48 (dd, J = 2.6, 2.6 Hz, 1H, 8-H), 4.14 (d, J = 8.4 Hz, 1H, 8bα-H), 3.93 (ddd, J = 5.6, 5.6, 3.2 Hz, 1H, 5β-H), 3.40 (ddd, J = 9.2, 6.6, 3.3 Hz, 1H, 1′-H), 3.40 (ddd, overlapped, J = 9.3, 8.0, 5.6 Hz, 1H, 3α-H), 2.97 (septet, J = 7.0 Hz, 1H, C*H*$(CH_3)_2$), 2.95 (dd, overlapped by C*H*$(CH_3)_2$ × 2, J = 17.6, 9.2 Hz, 1H, 2′-H *syn* to 1′-H), 2.94 (dd, overlapped by C*H*$(CH_3)_2$ and 2′-H, J = 6.9 Hz, 1H, C*H*$(CH_3)_2$), 2.53 (dd, J = 17.9, 6.8 Hz, 1H, 2′-H *anti* to 1′-H), 2.43 (ddd, J = 14.0, 9.0, 5.9 Hz, 1H, 4β-H), 2.21 (ddd, J = 14.0, 5.8, 5.8 Hz, 1H, 4α-H), 1.28 (d, J = 7.2 Hz, 6H, CH(C*H*$_3$)$_2$), 1.26 (d, overlapped by CH(C*H*$_3$)$_2$, J = 7.2 Hz, 6H, CH(C*H*$_3$)$_2$); ^{13}C NMR (75 MHz, $CDCl_3$, δ) 179.1, 177.9, 176.1, 175.0, 150.0, 149.5, 129.3, 129.1, 127.6, 127.3, 126.2, 126.1, 124.6, 119.4, 113.5, 108.4, 45.4, 39.8, 38.9, 34.0, 31.3, 30.3, 28.4, 24.0; IR (KBr, cm^{-1}) 3365(bs), 3038(w), 2961(s), 2927(m), 2899(m), 1776(m), 1708(s), 1514(m), 1460(w), 1387(s), 1355(m), 1306(w), 1187(s), 1160(s), 1105(m), 1085(w), 1055(m), 832(m), 727(m); HRMS m/z (M + Na$^+$) calcd. 546.2364, found 546.2373. Anal. Calcd. for $C_{32}H_{33}N_3O_4$: C, 73.40; H, 6.35; N, 8.02. Found: C, 73.22; H, 6.51; N, 7.96.

2-(4-Phenoxyphenyl)-5α-(1-(4-phenoxyphenyl)-2,5-dioxopyrrolidin-3-yl)-3aα,4,5β,8bα-tetrahydro-2H,6H-pyrrolo[3,4-e]indole-1,3-dione (59). Method A with vinylpyrrole **4** and maleimide **10h** gave **59** (100 mg, 8%) as a white powder: mp 267–268°C; ^{1}H NMR (300 MHz, $CDCl_3$, δ) 7.94 (bs, 1H, 6-H), 7.34–7.43 (m, 4H, Ph), 7.03–7.24 (m, 14H, Ph), 6.72 (dd, J = 2.9, 2.9 Hz, 1H, 7-H), 6.48 (dd, J = 2.7, 2.7 Hz, 1H, 8-H), 4.15 (d, J = 8.1 Hz, 1H, 8bα-H), 3.93 (ddd, J = 5.6, 5.6, 3.4 Hz, 1H, 5β-H), 3.41 (ddd, J = 9.0, 6.6, 3.3 Hz, 1H, 1′-H), 3.41 (ddd, overlapped by 1′-H, J = 9.1, 7.8, 5.9 Hz, 1H, 3aα-H), 2.96 (dd, J = 17.7, 9.0 Hz, 1H, 2′-H *syn* to 1′-H), 2.53 (dd, 17.7, 6.6 Hz, 1H, 2′-H *anti* to 1′-H), 2.43 (ddd, J = 14.2, 8.6, 5.6 Hz, 1H, 4β-H), 2.21 (ddd, J = 14.0, 5.9, 5.9 Hz, 1H, 4α-H); ^{13}C NMR (75 MHz, DMSO-d_6, δ) 179.0, 178.2, 177.2, 176.1, 157.1, 156.60, 156.59, 130.8, 129.4, 128.0, 127.9, 127.2, 124.6, 119.75, 119.69, 118.9, 118.4, 111.5, 107.2, 43.4, ~40 (obscured by DMSO), 38.4, 33.2, 32.7, 28.5; ^{13}C NMR (75 MHz, $CDCl_3$, δ) 179.01, 178.95, 177.8, 174.8, 157.6, 154.6, 152.8, 130.1, 130.0, 127.82, 127.78, 126.2, 126.0, 124.6, 124.3, 124.0, 119.8, 119.6, 119.4, 118.8, 113.5, 108.4, 45.4, 39.7, 38.9, 31.3, 30.3, 28.3; IR (KBr, cm^{-1}) 3358(bs), 3053(w), 2994(W), 2950(w), 2915(m), 2856(w), 1770(m), 1711(s), 1589(m), 1506(m), 1489(m), 1456(w), 1386(m), 1350(w), 1294(w), 1244(s), 1193(m), 1155(m), 1102(m), 1072(m), 1019(w), 880(w), 800(w), 760(m), 730(m), 699(m); HRMS m/z (M + Na$^+$) calcd. 646.1949, found 646.1958. Anal. Calcd. for $C_{38}H_{29}N_3O_6$: C, 73.18; H, 4.69; N, 6.74. Found: C, 72.96; H, 4.80; N, 6.58.

2-Dimethylamino-2H,6H-pyrrolo[3,4-e]indole-1,3-dione (60). Method D with adduct **11** gave **60** (55 mg, 64%) as orange crystals: mp 237–238°C; ^{1}H NMR (300 MHz, DMSO-d_6, δ) 11.89 (bs, 1H, 6-H), 7.79 (m, 2H, 4-H and 5-H), 7.49 (dd, J = 8.1, 1.2 Hz, 1H, 7-H), 6.79 (ddd, J = 2.1, 2.1, 0.9 Hz, 1H, 8-H), 2.89 (s, 6H, N(CH_3)$_2$); ^{13}C NMR (75 MHz, DMSO-d_6, δ) 168.6, 168.4, 141.3, 132.5, 122.8, 122.5, 121.3, 117.3, 115.4, 100.2, 45.0; IR (film, cm^{-1}) 3251(bs), 2940(m), 2870(m), 1756(m), 1704(s), 1448(m), 1440(w), 1357(m), 1274(w), 1142(w), 1104(m), 740(m); HRMS m/z (M + Na$^+$) calcd. 252.0744, found 252.0748. Anal. Calcd. for $C_{12}H_{11}N_3O_2$: C, 62.87; H, 4.84; N, 18.33. Found: C, 62.68; H, 4.81; N, 18.17.

2-Benzyl-2H,6H-pyrrolo[3,4-e]indole-1,3-dione (61). Method C with adduct **12** gave **61** (47 mg, 45%) as a yellow powder: mp 195–196°C; ^{1}H NMR (300 MHz, DMSO-d_6, δ) 11.99 (bs, 1H, 6-H), 7.81 (dd, J = 8.1, 1.1 Hz, 1H, 5-H), 7.79–7.81 (m, overlapped by 4-H, 1H, 7-H), 7.56 (d, J = 8.1 Hz, 1H, 4-H), 7.23–7.37 (m, 5H, Ph), 6.81 (ddd, J = 3.0, 2.0, 0.9 Hz, 1H, 8-H), 4.76 (s, 2H, Bn); ^{13}C NMR (75 MHz, $CDCl_3$, δ) 169.7, 169.4, 140.4, 137.2, 129.7, 128.7, 128.6, 127.7, 125.2, 124.0, 123.2, 116.4, 115.8, 102.1, 41.4; ^{13}C NMR (75 MHz, DMSO-d_6, δ) 169.7, 169.4, 141.3, 137.8, 132.6, 129.1, 127.8 (two peaks overlapped), 124.3, 123.0, 115.2, 113.8, 100.3, ~40 (obscured by DMSO); IR (KBr, cm^{-1}) 3275(bs), 3108(w), 3057(w), 3035(w), 2941(w), 1756(m), 1687(s), 1590(w), 1508(w), 1492(w), 1455(w), 1433(m), 1398(m), 1368(m), 1340(m), 1272(w), 1062(m), 764(w), 745(m), 675(m); HRMS m/z (M + Na$^+$) calcd. 299.0792, found 299.0794. Anal. Calcd. for $C_{17}H_{12}N_2O_2$: C, 73.90; H, 4.38; N, 10.14. Found: C, 73.63; H, 4.28; N, 9.90.

2-Phenyl-2H,6H-pyrrolo[3,4-e]indole-1,3-dione (62). Method D with adduct **13** gave **62** (66 mg, 67%) as bright-yellow crystals: mp 265–266°C; ^{1}H NMR (300 MHz, acetone-d_6, δ) 11.16 (bs, 1H, 6-H), 7.94 (dd, J = 8.4, 0.9 Hz, 1H, 5-H), 7.82 (dd, J = 2.9, 2.9 Hz, 1H, 7-H), 7.68 (d, J = 8.4 Hz, 1H, 4-H), 7.55–7.60 (m, 4H, Ph), 7.40–7.44 (m, 1H, Ph), 7.01 (ddd, J = 3.2, 2.1, 0.9 Hz, 1H, 8-H); ^{13}C NMR (75 MHz, DMSO-d_6, δ) 168.9, 168.6, 141.3, 132.9, 132.5, 129.3, 128.1, 127.8, 124.1, 123.1, 123.0, 117.5, 115.8, 100.5; IR (film, cm^{-1}) 3288(bs), 2953(m), 2870(m), 1753(m), 1696(s), 1620(w), 1590(w), 1495(w), 1490(w), 1365(m), 1265(w), 1227(w), 1153(w), 1061(w), 753(m); HRMS m/z (M + Na$^+$) calcd. 285.0635, found 285.0641. Anal. Calcd. for $C_{16}H_{10}N_2O_2$: C, 73.27; H, 3.84; N, 10.68. Found: C, 73.00; H, 3.73; N, 10.82.

2-(4-Ethylphenyl)-2H,6H-pyrrolo[3,4-e]indole-1,3-dione (63). Method C with adduct **14** gave **63** (51 mg, 47%) as a yellow powder: mp 172–173°C; ^{1}H NMR (300 MHz, $CDCl_3$, δ) 8.82 (bs, 1H, 6-H), 7.76 (d, J = 8.4 Hz, 1H, 4-H), 7.71 (dd, J = 8.1, 0.9 Hz, 1H, 5-H), 7.52 (dd, J = 3.3, 2.4 Hz, 1H, 7-H), 7.40 (d, J = 8.7 Hz, 2H, Ph), 7.34 (d, J = 8.7 Hz, 2H, Ph), 7.13 (ddd, J = 3.1, 2.0, 0.8 Hz, 1H, 8-H), 2.72 (q, J = 7.7 Hz, 2H, CH_2CH$_3$), 1.29 (t, J = 7.7 Hz, 3H, CH$_2$CH_3); ^{13}C NMR (75 MHz, DMSO-d_6, δ) 169.1, 168.7, 143.9, 141.3, 132.6, 130.4, 128.7, 127.8, 124.2, 123.1, 123.0, 117.5, 115.8, 100.4, 28.4, 16.2; IR (KBr, cm^{-1}) 3417(bs), 3319(w), 2963(w), 2929(w), 1760(m), 1706(s), 1629(w), 1592(w), 1517(m), 1460(w), 1426(w), 1380(s), 1366(s), 1274(w), 1228(w), 1088(m), 1068(w), 823(w), 800(w), 759(m), 745(m); HRMS m/z (M + Na$^+$) calcd. 313.0948, found 313.0942. Anal. Calcd. for $C_{18}H_{14}N_2O_2$: C, 74.47; H, 4.86; N, 9.65. Found: C, 74.35; H, 4.94; N, 9.51.

2-(4-Isopropylphenyl)-2H,6H-pyrrolo[3,4-e]indole-1,3-dione (64). Method C with adduct **15** gave **64** (70 mg, 61%) as yellow needle-like crystals: mp 178–179°C; ^{1}H NMR (300 MHz, $CDCl_3$, δ) 8.68 (bs, 1H, 6-H), 7.78 (d, J = 8.4 Hz, 1H, 4-H), 7.73 (dd, J = 8.1, 0.9 Hz, 1H, 5-H), 7.55 (dd, J = 2.4, 0.9 Hz, 1H, 7-H), 7.41 (d, J = 8.4 Hz, 2H, Ph), 7.37 (d, J = 8.4 Hz, 2H, Ph), 7.15 (ddd, J = 3.1, 2.0, 1.0 Hz, 1H, 8-H), 2.98 (septet, J = 6.9 Hz, 1H, CH(CH$_3$)$_2$), 1.30 (d, J = 6.9 Hz, 6H, CH(CH_3)$_2$); ^{13}C NMR (75 MHz, DMSO-d_6, δ) 169.1, 168.7, 148.4, 141.3, 132.6, 130.5, 127.8, 127.2, 124.2, 123.1, 123.0, 117.6, 115.8, 108.5, 100.5, 39.2, 24.4; IR (KBr, cm^{-1}) 3419(s), 2960(m), 2925(s), 2855(m), 1758(m), 1711(s), 1516(w), 1457(w), 1427(w), 1378(m), 1367(m), 1315(w), 1274(m), 1227(w), 1155(w), 1120(m), 1070(w), 714(w); HRMS m/z (M + Na$^+$) calcd. 327.1105, found 327.1113. Anal. Calcd. for $C_{19}H_{16}N_2O_2$: C, 74.98; H, 5.30; N, 9.20. Found: C, 74.71; H, 5.12; N, 9.07.

2-(4-Methoxyphenyl)-2H,6H-pyrrolo[3,4-e]indole-1,3-dione (65). Method D with adduct **16** gave **65** (70 mg, 64%) as brown crystals: mp 220–221°C; ^{1}H NMR (300 MHz, acetone-d_6, δ) 11.12 (bs, 1H, 6-H), 7.93 (dd, J = 8.1, 0.9 Hz, 1H, 5-H), 7.81 (dd, J = 2.9, 2.9 Hz, 1H, 7-H), 7.66 (d, J = 8.1 Hz, 1H, 4-H), 7.44 (d, J = 9.0 Hz, 2H, Ph), 7.09 (d, J = 9.0 Hz, 2H, Ph), 6.98–7.02 (m, 1H, 8-H), 3.89 (s, 3H, OCH$_3$); ^{13}C NMR (75 MHz, acetone-d_6, δ) 168.7, 168.4, 159.0, 141.2, 131.2, 128.5, 125.6, 124.6, 123.4, 123.2, 116.8, 115.4, 114.0, 100.7, 55.0; IR (film, cm^{-1}) 3300(bs), 2920(m), 2810(m), 1758(w), 1706(s), 1517(m), 1441(w), 1369(m), 1250(m), 1155(w), 1117(w), 743(m); HRMS m/z (M + Na$^+$) calcd. 315.0741, found 315.0743. Anal. Calcd. for $C_{17}H_{12}N_2O_3$: C, 69.86; H, 4.14; N, 9.58. Found: C, 69.67; H, 4.10; N, 9.39.

2-(4-Phenoxyphenyl)-2H,6H-pyrrolo[3,4-e]indole-1,3-dione (66). Method C with adduct **17** gave **66** (51 mg, 38%) as

bright yellow crystals: mp 193–194°C; ^{1}H NMR (300 MHz, $CDCl_3$, δ) 8.72 (bs, 1H, 6-H), 7.78 (d, J = 8.4 Hz, 1H, 4-H), 7.73 (dd, J = 8.4, 0.8 Hz, 1H, 5-H), 7.56 (dd, J = 3.2, 2.6 Hz, 1H, 7-H), 7.36–7.48 (m, 4H, Ph), 7.08–7.19 (m, 6H, 8-H, Ph); ^{13}C NMR (75 MHz, DMSO-d_6, δ) 169.0, 168.7, 156.8, 156.6, 141.3, 132.6, 130.7, 129.6, 127.9, 124.4, 124.2, 123.1, 123.0, 119.6, 119.0, 117.6, 115.8, 100.5; IR (KBr, cm^{-1}) 3316(bm), 3065(w), 1764(m), 1703(s), 1629(w), 1588(w), 1506(m), 1487(m), 1460(w), 1433(w), 1383(m), 1370(m), 1241(s), 1151(m), 1105(m), 1089(m), 1070(m), 1005(w), 870(w), 822(w), 744(m), 691(m); HRMS *m/z* (M + Na$^+$) calcd. 377.0897, found 377.0883. Anal. Calcd. for $C_{22}H_{14}N_2O_3$: C, 74.57; H, 3.98; N, 7.91. Found: C, 74.44; H, 3.93; N, 7.54.

2-Dimethylamino-6-methyl-2H,6H-pyrrolo[3,4-e]indole-1,3-dione (67). Method D with adduct **18** gave **67** (60 mg, 66%) as yellow crystals: mp 201–202°C; ^{1}H NMR (300 MHz, acetone-d_6, δ) 7.84 (d, J = 8.4 Hz, 1H, 4-H), 7.67 (d, J = 3.3 Hz, 1H, 7-H), 7.57 (dd, J = 8.1, 0.6 Hz, 1H, 5-H), 6.88 (dd, J = 3.0, 0.6 Hz, 1H, 8-H), 3.99 (s, 3H, 6-CH_3), 2.99 (s, 6H, N(CH_3)$_2$); ^{13}C NMR (75 MHz, $CDCl_3$, δ) 168.8, 168.5, 141.2, 134.6, 123.5, 122.7, 122.0, 115.8, 114.2, 100.7, 45.2, 33.4; IR (film, cm^{-1}) 3102(m), 2969(m), 2877(m), 2854(w), 1763(m), 1706(s), 1509(w), 1498(w), 1375(w), 1357(m), 1296(w), 1168(w), 1092(w), 1023(w); HRMS *m/z* (M + Na$^+$) calcd. 266.0901, found 266.0892. Anal. Calcd. for $C_{13}H_{13}N_3O_2$: C, 64.19; H, 5.39; N, 17.27. Found: C, 64.46; H, 5.30; N, 17.27.

6-Methyl-2-phenyl-2H,6H-pyrrolo[3,4-e]indole-1,3-dione (68). Method D with adduct **19** gave **68** (74 mg, 71%) as bright orange-yellow crystals: mp 214–215°C; ^{1}H NMR (300 MHz, CD_2Cl_2, δ) 7.76 (d, J = 8.4 Hz, 1H, 4-H), 7.71 (dd, J = 8.4, 0.6 Hz, 1H, 5-H), 7.41–7.58 (m, 6H, 7-H and Ph), 7.03 (dd, J = 3.9, 0.7 Hz, 1H, 8-H), 3.93 (s, 3H, 6-CH_3); ^{13}C NMR (75 MHz, CD_2Cl_2, δ) 168.8, 168.3, 141.3, 134.9, 132.6, 129.0, 127.8, 127.6, 126.9, 124.3, 123.6, 115.7, 114.6, 100.4, 33.5; IR (film, cm^{-1}) 3125(m), 2900(w), 1759(m), 1710(s), 1595(m), 1512(m), 1490(m), 1453(w), 1377(s), 1361(s), 1294(m), 1223(w), 1171(w), 1094(w), 1063(w), 744(m); HRMS *m/z* (M + Na$^+$) calcd. 299.0792, found 299.0792. Anal. Calcd. for $C_{17}H_{12}N_2O_2$: C, 73.90; H, 4.38; N, 10.14. Found: C, 73.71; H, 4.28; N, 10.14.

2-(4-Methoxyphenyl)-6-methyl-2H,6H-pyrrolo[3,4-e]indole-1,3-dione (69). Method D with adduct **20** gave **69** (76 mg, 66%) as bright-yellow crystals: mp 236–237°C; ^{1}H NMR (300 MHz, CD_2Cl_2, δ) 7.75 (d, J = 8.4 Hz, 1H, 4-H), 7.70 (dd, J = 8.4, 0.6 Hz, 1H, 5-H), 7.44 (d, J = 3.3 Hz, 1H, 7-H), 7.38 (d, J = 9.0 Hz, 2H, Ph), 7.06 (d, J = 9.0 Hz, 2H, Ph), 7.01 (dd, J = 3.3, 0.7 Hz, 1H, 8-H), 3.93 (s, 3H, OCH_3), 3.89 (s, 3H, 6-CH_3); ^{13}C NMR (75 MHz, DMSO-d_6, δ) 169.1, 168.7, 159.1, 141.4, 136.6, 129.2, 125.4, 124.2, 123.3, 123.2, 115.9, 115.6, 114.6, 99.8, 55.9, 33.6; IR (film, cm^{-1}) 3125(w), 2988(m), 2870(w), 1753(m), 1709(s), 1509(s), 1388(m), 1366(w), 1352(w), 1299(m), 1249(s), 1170(w), 1092(w), 806(w), 704(m); HRMS *m/z* (M + Na$^+$) calcd. 329.0897, found 329.0908. Anal. Calcd. for $C_{18}H_{14}N_2O_3$: C, 70.58; H, 4.61; N, 9.15. Found: C, 70.40; H, 4.59; N, 9.01.

2-Dimethylamino-5,6-dimethyl-2H,6H-pyrrolo[3,4-e]indole-1,3-dione (70). Method D with adduct **21** gave **70** (68 mg, 70%) as bright-yellow crystals: mp 226–227°C; ^{1}H NMR (300 MHz, $CDCl_3$, δ) 7.33 (s, 1H, 4-H), 7.21 (d, J = 3.3 Hz, 1H, 7-H), 6.95 (d, J = 3.0 Hz, 1H, 8-H), 4.13 (s, 3H, 6-CH_3), 3.05 (s, 6H, N(CH_3)$_2$), 2.87 (s, 3H, 5-CH_3); ^{13}C NMR (75 MHz, DMSO-d_6, δ) 168.5, 168.3, 139.6, 137.8, 129.0, 124.1, 122.8, 119.6, 117.4, 99.2, 45.0, 37.3, 20.1; IR (film, cm^{-1}) 3120(m), 2998(m), 2963(m), 2875(m), 2815(m), 1757(s), 1709(s), 1596(w), 1517(m), 1477(w), 1448(m), 1348(s), 1321(m), 1188(w), 1172(m), 1105(w), 1015(w), 760(m), 740(m); HRMS *m/z* (M + Na$^+$) calcd. 280.1057, found 280.1055. Anal. Calcd. for $C_{14}H_{15}N_3O_2$: C, 65.35; H, 5.88; N, 16.33. Found: C, 65.55; H, 5.99; N, 16.50.

5,6-Dimethyl-2-phenyl-2H,6H-pyrrolo[3,4-e]indole-1,3-dione (71). Method D with adduct **22** gave **71** (79 mg, 72%) as bright orange-yellow crystals: mp 225–226°C; ^{1}H NMR (300 MHz, $CDCl_3$, δ) 7.48–7.53 (m, 4H, Ph), 7.45 (s, 1H, 4-H), 7.38–7.41 (m, 1H, Ph), 7.24 (d, J = 3.0 Hz, 1H, 7-H), 7.01 (d, J = 3.0 Hz, 1H, 8-H), 4.16 (s, 3H, 6-CH_3), 2.91 (s, 3H, 5-CH_3); ^{13}C NMR (75 MHz, DMSO-d_6, δ) 168.8, 168.4, 139.7, 138.0, 132.9, 129.4, 129.3, 128.0, 127.7, 124.6, 124.4, 121.3, 117.9, 99.5, 37.3, 20.1; IR (film, cm^{-1}) 3120(m), 2940(m), 1752(m), 1706(s), 1596(w), 1517(w), 1501(m), 1453(w), 1405(w), 1376(m), 1356(m), 1321(w), 1226(w), 1102(w), 753(m); HRMS *m/z* (M + Na$^+$) calcd. 313.0948, found 313.0945. Anal. Calcd. for $C_{18}H_{14}N_2O_2$: C, 74.47; H, 4.86; N, 9.65. Found: C, 74.70; H, 4.63; N, 9.80.

2-(4-Methoxyphenyl)-5,6-dimethyl-2H,6H-pyrrolo[3,4-e]indole-1,3-dione (72). Method D with adduct **23** gave **72** (79 mg, 66%) as bright-red crystals: mp 229-230°C; ^{1}H NMR (300 MHz, CD_2Cl_2, δ) 7.43 (s, 1H, 4-H), 7.36 (d, J = 9.0 Hz, 2H, Ph), 7.31 (d, J = 3.0 Hz, 1H, 7-H), 7.05 (d, J = 9.0 Hz, 2H, Ph), 6.97 (d, J = 3.0 Hz, 1H, 8-H), 4.17 (s, 3H, 6-CH_3), 3.88 (s, 3H, OCH_3), 2.94 (s, 3H, 5-CH_3); ^{13}C NMR (75 MHz, DMSO-d_6, δ) 169.1, 168.7, 159.0, 139.6, 137.92, 137.87, 129.2, 125.4, 124.6, 124.4, 121.1, 117.8, 114.6, 99.5, 55.9, 37.3, 20.1; IR (film, cm^{-1}) 3104(m), 2938(m), 2844(m), 1751(m), 1698(s), 1512(s), 1461(m), 1384(m), 1356(m), 1327(w), 1299(w), 1249(m), 1171(m), 1090(w), 1074(w), 1031(w), 802(w); HRMS *m/z* (M + Na$^+$) calcd. 343.1054, found 343.1069. Anal. Calcd. for $C_{19}H_{16}N_2O_3$: C, 71.24; H, 5.03; N, 8.74. Found: C, 71.62; H, 5.10; N, 8.55.

2-Dimethylamino-4-methyl-2H,6H-pyrrolo[3,4-e]indole-1,3-dione (73). Method D with adduct **24** gave **73** (52 mg, 57%) as yellow crystals: mp 255–256°C; ^{1}H NMR (300 MHz, $CDCl_3$, δ) 8.70 (bs, 1H, 6-H), 7.41–7.45 (m, 2H, 5-H and 7-H), 7.03 (ddd, J = 3.2, 2.0, 1.1 Hz, 1H, 8-H), 3.07 (s, 6H, N(CH_3)$_2$), 2.77 (d, J = 0.9 Hz, 3H, 4-CH_3); ^{13}C NMR (75 MHz, DMSO-d_6, δ) 169.2, 168.1, 141.3, 131.8, 129.3, 121.6, 121.5, 119.5, 118.3, 100.0, 44.9, 18.2; IR (film, cm^{-1}) 3250(bs), 2995(m), 2880(m), 2871(m), 1748(m), 1697(s), 1446(m), 1402(w), 1390(w), 1350(m), 1101(w), 762(m); HRMS *m/z* (M + Na$^+$) calcd. 266.0901, found 266.0907. Anal. Calcd. for $C_{13}H_{13}N_3O_2$: C, 64.19; H, 5.39; N, 17.27. Found: C, 63.96; H, 5.34; N, 17.08.

4-Methyl-2-phenyl-2H,6H-pyrrolo[3,4-e]indole-1,3-dione (74). Method D with adduct **25** gave **74** (63 mg, 61%) as yellow crystals: mp 305-306°C; ^{1}H NMR (300 MHz, acetone-d_6, δ) 10.93 (bs, 1H, 6-H), 7.72 (dd, J = 2.9, 2.9 Hz, 1H, 7-H), 7.67 (dq, J = 0.9, 0.9 Hz, 1H, 5-H), 7.50–7.60 (m, 4H, Ph), 7.40–7.50 (m, 1H, Ph), 6.94 (ddd, J = 3.6, 2.1, 0.9 Hz, 1H, 8-H), 2.77 (d, J = 0.6 Hz, 3H, 4-CH_3); ^{13}C NMR (75 MHz, DMSO-d_6, δ) 169.0, 168.4, 141.4, 132.9, 131.9, 129.7, 129.3, 128.0, 127.9, 123.2, 121.9, 121.2, 118.5, 100.3, 18.4; IR (film, cm^{-1}) 3288(bs), 2900(m), 2880(m), 1764(w), 1752(m), 1693(s), 1640(w), 1496(m), 1392(m), 1368(m), 1167(w), 763(m);

HRMS *m/z* (M + Na^+) calcd. 299.0792, found 299.0785. Anal. Calcd. for $C_{17}H_{12}N_2O_2$: C, 73.90; H, 4.38; N, 10.14. Found: C, 73.71; H, 4.54; N, 9.86.

2-(4-Methoxyphenyl)-4-methyl-2H,6H-pyrrolo[3,4-e]indole-1,3-dione (75). Method D with adduct **26** gave **75** (68 mg, 59%) as yellow crystals: mp 207–208°C; ^{1}H NMR (300 MHz, acetone-d_6, δ) 10.91 (bs, 1H, 6-H), 7.71 (dd, *J* = 3.0, 2.6 Hz, 1H, 7-H), 7.66 (dq, *J* = 0.9, 0.9 Hz, 1H, 5-H), 7.43 (d, *J* = 9.3 Hz, 2H, Ph), 7.08 (d, *J* = 9.0 Hz, 2H, Ph), 6.94 (ddd, *J* = 3.2, 2.0, 0.9 Hz, 1H, 8-H), 3.89 (s, 3H, OCH_3), 2.76 (d, *J* = 0.9 Hz, 3H, 4-CH_3); ^{13}C NMR (75 MHz, DMSO-d_6, δ) 169.6, 168.6, 159.0, 141.4, 131.7, 129.6, 129.3, 125.5, 123.2, 121.9, 121.2, 118.4, 114.5, 100.3, 55.8, 18.4; IR (film, cm^{-1}) 3331(bs), 2989(m), 2810(m), 1756(m), 1702(s), 1518(m), 1400(m), 1301(w), 1256(m), 1168(w), 1117(w), 760(m); HRMS *m/z* (M + Na^+) calcd. 329.0897, found 329.0905. Anal. Calcd. for $C_{18}H_{14}N_2O_3$: C, 70.58; H, 4.86; N, 8.98. Found: C, 70.77; H, 4.86; N, 8.98.

2-Dimethylamino-4,6-dimethyl-2H,6H-pyrrolo[3,4-e]indole-1,3-dione (76). Method D with adduct **27** gave **76** (54 mg, 56%) as light-yellow crystals: mp 179–180°C; ^{1}H NMR (300 MHz, $CDCl_3$, δ) 7.31 (dq, *J* = 1.0, 0.9 Hz, 1H, 5-H), 7.25 (d, *J* = 3.3 Hz, 1H, 7-H), 6.95 (dd, *J* = 3.3, 0.9 Hz, 1H, 8-H), 3.84 (s, 3H, 6-CH_3), 3.07 (s, 6H, $N(CH_3)_2$), 2.78 (d, *J* = 0.9 Hz, 3H, 4-CH_3); ^{13}C NMR (75 MHz, $CDCl_3$, δ) 169.4, 168.3, 141.3, 134.0, 130.3, 122.3, 122.2, 119.8, 115.6, 100.5, 45.1, 33.3, 18.5; IR (film, cm^{-1}) 3125(m), 3100(m), 2945(m), 3877(m), 3851(m), 1759(m), 1704(s), 1632(w), 1513(m), 1470(w), 1446(w), 1403(w), 1375(m), 1353(m), 1294(w), 1099(m), 758(w); HRMS *m/z* (M + Na^+) calcd. 280.1057, found 280.1057. Anal. Calcd. for $C_{14}H_{15}N_3O_2$: C, 65.35; H, 5.88; N, 16.33. Found: C, 65.11; H, 5.71; N, 16.38.

4,6-Dimethyl-2-phenyl-2H,6H-pyrrolo[3,4-e]indole-1,3-dione (77). Method D with adduct **28** gave **77** (68 mg, 62%) as bright orange-yellow crystals: mp 181–182°C; ^{1}H NMR (300 MHz, $CDCl_3$, δ) 7.45–7.55 (m, 4H, Ph), 7.35–7.41 (m, 2H, 5-H and Ph), 7.28 (d, *J* = 3.0 Hz, 1H, 7-H), 6.99 (d, *J* = 2.7, 0.9 Hz, 1H, 8-H), 3.85 (s, 3H, 6-CH_3), 2.84 (d, *J* = 0.9 Hz, 3H, 4-CH_3); ^{13}C NMR (75 MHz, $CDCl_3$, δ) 169.3, 168.3, 141.4, 134.1, 132.4, 130.6, 129.0, 127.5, 126.7, 123.9, 122.5, 121.4, 115.8, 100.7, 33.3, 18.6; IR (film, cm^{-1}) 3120(m), 2900(m), 2860(m), 1754(m), 1710(S), 1595(w), 1492(m), 1375(s), 1357(s), 1294(w), 1168(w); HRMS *m/z* (M + Na^+) calcd. 313.0948, found 313.0951. Anal. Calcd. for $C_{18}H_{14}N_2O_2$: C, 74.47; H, 4.86; N, 9.65. Found: C, 74.28; H, 4.61; N, 9.60.

2-(4-Methoxyphenyl)-4,6-dimethyl-2H,6H-pyrrolo[3,4-e]indole-1,3-dione (78). Method D with adduct **29** gave **78** (73 mg, 61%) as bright-yellow crystals: mp 243–244°C; ^{1}H NMR (300 MHz, CD_2Cl_2, δ) 7.43 (dq, *J* = 0.9, 0.9 Hz, 1H, 5-H), 7.37–7.40 (m, 3H, 7-H and Ph), 7.06 (d, *J* = 9.0 Hz, 2H, Ph), 6.95 (dd, *J* = 3.0, 0.9 Hz, 1H, 8-H), 3.89 (s, 3H, 6-CH_3 or OCH_3), 3.87 (s, 3H, 6-CH_3 or OCH_3), 2.83 (d, *J* = 0.9 Hz, 3H, 4-CH_3); ^{13}C NMR (75 MHz, DMSO-d_6, δ) 169.6, 168.5, 159.1, 141.5, 136.0, 129.6, 129.3, 125.4, 123.5, 122.1, 121.3, 117.0, 114.6, 99.6, 55.9, 33.5, 18.5; IR (film, cm^{-1}) 3120(m), 2999(m), 2940(w), 2860(w), 1751(m), 1706(s), 1632(w), 1612(w), 1510(s), 1480(w), 1438(w), 1402(m), 1382(m), 1362(w), 1345(m), 1290(m), 1244(s), 1167(m), 1113(w), 1089(w), 1028(w); HRMS *m/z* (M + Na^+) calcd. 343.1054, found 343.1064. Anal. Calcd. for $C_{19}H_{16}N_2O_3$: C, 71.24; H, 5.03; N, 8.74. Found: C, 71.41; H, 4.87; N, 8.54.

4-Ethyl-2-phenyl-2H,6H-pyrrolo[3,4-e]indole-1,3-dione (79). Method D with adduct **30** gave **79** (48 mg, 44%) as light-brown crystals: mp 261–262°C; ^{1}H NMR (300 MHz, DMSO-d_6, δ) 11.85 (bs, 1H, 6-H), 7.81 (ddd, *J* = 2.0, 1.0, 1.0 Hz, 1H, 8-H), 7.75 (dd, *J* = 3.0, 3.0 Hz, 1H, 7-H), 7.64 (d, *J* = 0.9 Hz, 1H, 5-H), 7.39–7.55 (m, 5H, Ph), 3.15 (q, *J* = 7.5 Hz, 2H, 4-CH_2CH_3), 1.28 (t, *J* = 7.4 Hz, 3H, 4-CH_2CH_3); ^{13}C NMR (75 MHz, DMSO-d_6, δ) 169.1, 168.4, 141.6, 136.5, 132.9, 132.1, 129.3, 128.1, 128.0, 123.5, 122.0, 120.7, 117.2, 100.3, 24.9, 16.1; IR (KBr, cm^{-1}) 3300(bs), 2970(m), 1763(m), 1683(s), 1637(m), 1592(w), 1496(m), 1456(w), 1368(s), 1163(w), 1101(w), 1062(w), 848(w), 760(m); HRMS *m/z* (M + Na^+) calcd. 313.0948, found 313.0945. Anal. Calcd. for $C_{18}H_{14}N_2O_2$: C, 74.47; H, 4.86; N, 9.65. Found: C, 74.61; H, 4.88; N, 9.48.

4-Ethyl-2-(4-ethylphenyl)-2H,6H-pyrrolo[3,4-e]indole-1,3-dione (80). Method C with adduct **31** gave **80** (63 mg, 53%) as orange crystals: mp 238–239°C; ^{1}H NMR (300 MHz, DMSO-d_6, δ) 11.83 (bs, 1H, 6-H), 7.73 (dd, *J* = 2.4, 0.9 Hz, 1H, 7-H), 7.63 (d, *J* = 0.6 Hz, 1H, 5-H), 7.36–7.39 (m, 4H, Ph), 6.80 (ddd, *J* = 2.9, 1.7, 1.0 Hz, 1H, 8-H), 3.14 (q, *J* = 7.4 Hz, 2H, 4-CH_2CH_3), 2.67 (q, *J* = 7.6 Hz, 2H, PhCH_2CH_3), 1.27 (t, *J* = 7.5 Hz, 3H, 4-CH_2CH_3), 1.23 (t, *J* = 7.7, 3H, $PhCH_2CH_3$); ^{13}C NMR (75 MHz, DMSO-d_6, δ) 169.3, 168.5, 143.7, 141.5, 136.4, 132.1, 130.4, 128.6, 127.9, 123.5, 121.9, 120.7, 117.1, 100.3, 28.4, 24.9, 16.2, 16.1; IR (KBr, cm^{-1}) 3307(bs), 2964(m), 2929(w), 2871(w), 1757(m), 1696(s), 1633(w), 1514(m), 1458(m), 1368(s), 1294(m), 1167(m), 1117(w), 1095(m), 1066(w), 832(w), 764(m), 726(w); HRMS *m/z* (M + Na^+) calcd. 341.1261, found 341.1260. Anal. Calcd. for $C_{20}H_{18}N_2O_2$: C, 75.45; H, 5.70; N, 8.80. Found: C, 75.70; H, 5.58; N, 8.20.

4-Ethyl-2-(4-hydroxyphenyl)-2H,6H-pyrrolo[3,4-e]indole-1,3-dione (81). Method D with adduct **32** gave **81** (17 mg, 15%) as yellow crystals: mp 265–267°C; ^{1}H NMR (500 MHz, DMSO-d_6, δ) 11.80 (bs, 1H, 6-H), 9.69 (bs, 1H, Ph-O*H*), 7.69–7.74 (m, 1H, 5-H), 7.58–7.62 (m, 1H, 7-H), 7.18 (d, *J* = 7.5 Hz, 2H, Ph), 6.85 (d, *J* = 8.0 Hz, 2H, Ph), 6.75–6.79 (m, 1H, 8-H), 3.11 (q, *J* = 7.3 Hz, 2H, 4-CH_2CH_3), 1.25 (t, *J* = 7.3 Hz, 3H, 4-CH_2CH_3); ^{13}C NMR (75 MHz, DMSO-d_6, δ) 169.6, 168.8, 157.4, 141.5, 136.3, 132.0, 129.5, 123.8, 123.5, 121.9, 120.7, 117.0, 115.8, 100.2, 24.9, 16.1; IR (KBr, cm^{-1}) 3464(m), 3311(bs), 3115(w), 2966(m), 2926(m), 1751(m), 1683(s), 1636(w), 1597(w), 1515(s), 1455(w), 1379(s), 1295(w), 1269(m), 1206(m), 1162(m), 1114(m), 1087(w), 834(w), 765(w); HRMS *m/z* (M + Na^+) calcd. for $C_{18}H_{14}N_2O_3$: 329.0897, found 329.0906.

2-(4-Chlorophenyl)-4-ethyl-2H,6H-pyrrolo[3,4-e]indole-1,3-dione (82). Method D with adduct **34** gave **82** (40 mg, 33%) as yellow crystals: mp 219–220°C; ^{1}H NMR (300 MHz, $CDCl_3$, δ) 8.56 (bs, 1H, 6-H), 7.53 (app. s, 1H, 5-H), 7.47–7.49 (m, 5H, 7-H and Ph), 7.09 (app. dd, *J* = 2.3, 2.3 Hz, 1H, 8-H), 3.25 (q, *J* = 7.6 Hz, 2H, 4-CH_2CH_3), 1.36 (t, *J* = 7.7 Hz, 3H, 4-CH_2CH_3); ^{1}H NMR (300 MHz, DMSO-d_6, δ) 11.86 (bs, 1H, 6-H), 7.64 (d, *J* = 0.9 Hz, 1H, 5-H), 7.59 (d, *J* = 9.0 Hz, 2H, Ph), 7.50 (d, *J* = 9.0 Hz, 2H, Ph), 7.49 (dd, *J* = 3.1, 2.6 Hz, 1H, 7-H), 6.80 (ddd, *J* = 3.0, 1.8, 1.1 Hz, 1H, 8-H), 3.14 (q, *J* = 7.4 Hz, 2H, 4-CH_2CH_3), 1.27 (t, *J* = 7.5 Hz, 3H, 4-CH_2CH_3); ^{13}C NMR (75 MHz, DMSO-d_6, δ) 168.9, 168.1, 141.6, 136.5, 132.4, 132.2, 131.8, 129.6, 129.3, 123.4, 122.0, 120.7, 117.2, 100.3, 24.9, 16.0; IR (KBr, cm^{-1}) 3308(bs),

3105(w), 2968(m), 2933(w), 2880(w), 1762(m), 1707(s), 1635(w), 1495(m), 1459(w), 1409(m), 1376(s), 1313(w), 1295(m), 1241(w), 1209(w), 1167(w), 1109(w), 1092(m), 1066(w), 1016(w), 852(w), 830(m), 807(m), 781(m), 753(m), 717(w); HRMS *m/z* (M + Na^+) calcd. for $C_{18}H_{13}ClN_2O_2$: 347.0559, found 347.0557.

2-(4-Bromophenyl)-4-ethyl-2H,6H-pyrrolo[3,4-e]indole-1,3-dione (83). Method D with adduct **35** gave **83** (50 mg, 36%) as yellow crystals: mp 246–247°C; ^{1}H NMR (300 MHz, $CDCl_3$, δ) 8.53 (bs, 1H, 6-H), 7.63 (d, *J* = 9.0 Hz, 2H, Ph), 7.53 (d, *J* = 0.9 Hz, 1H, 5-H), 7.48 (dd, *J* = 3.3, 2.4 Hz, 1H, 7-H), 7.42 (d, *J* = 9.0 Hz, 2H, Ph), 7.10 (ddd, *J* = 3.2, 2.2, 0.9 Hz, 1H, 8-H), 3.25 (q, *J* = 7.4 Hz, 2H, 4-C*H*$_2$CH$_3$), 1.37 (t, *J* = 7.7 Hz, 3H, 4-CH$_2$C*H*$_3$); ^{1}H NMR (300 MHz, DMSO-d_6, δ) 11.86 (bs, 1H, 6-H), 7.75 (dd, *J* = 2.7 Hz, 1H, 7-H), 7.72 (d, *J* = 8.7 Hz, 2H, Ph), 7.65 (d, *J* = 0.9 Hz, 1H, 5-H), 7.44 (d, *J* = 8.7 Hz, 2H, Ph), 6.80 (ddd, *J* = 3.0, 2.0, 0.9 Hz, 1H, 8-H), 3.14 (q, *J* = 7.5 Hz, 2H, 4-C*H*$_2$CH$_3$), 1.27 (t, *J* = 7.5 Hz, 3H, 4-CH$_2$C*H*$_3$); ^{13}C NMR (75 MHz, DMSO-d_6, δ) 168.8, 168.1, 141.6, 136.5, 132.2, 129.9, 123.4, 122.0, 120.9, 120.69, 120.65, 117.2, 105.0, 100.3, 24.9, 16.1; IR (KBr, cm^{-1}) 3307(bs), 3100(w), 3082(w), 2966(m), 2878(w), 1763(m), 1707(s), 1637(m), 1493(m), 1460(w), 1367(s), 1314(w), 1298(w), 1243(w), 1209(w), 1167(w), 1122(w), 1108(w), 1090(w), 1074(m), 1012(w), 980(w), 820(m), 790(m), 740(m); HRMS *m/z* (M + Na^+) calcd. 391.0053, found 391.0044. Anal. Calcd. for $C_{18}H_{13}BrN_2O_2$: C, 58.56; H, 3.55; N, 7.59. Found: C, 58.59; H, 3.41; N, 7.46.

4-Ethyl-2-(4-nitrophenyl)-2H,6H-pyrrolo[3,4-e]indole-1,3-dione (84). Method D with adduct **36** gave **84** (35 mg, 28%) as light-orange crystals: mp 296–297°C; ^{1}H NMR (300 MHz, DMSO-d_6, δ) 11.90 (bs, 1H, 6-H), 8.39 (d, *J* = 9.3 Hz, 1H, Ph), 7.83 (d, *J* = 9.3 Hz, 2H, Ph), 7.77 (dd, *J* = 2.9, 2.9 Hz, 1H, 7-H), 7.68 (d, *J* = 0.6 Hz, 1H, 5-H), 6.84 (ddd, *J* = 3.2, 2.0, 1.1 Hz, 1H, 8-H), 3.16 (q, *J* = 7.4 Hz, 2H, 4-C*H*$_2$CH$_3$), 1.29 (t, *J* = 7.5 Hz, 3H, 4-CH$_2$C*H*$_3$); ^{13}C NMR (75 MHz, DMSO-*d*6, δ) 168.4, 167.7, 146.1, 141.7, 138.9, 136.7, 132.4, 127.9, 124.6, 123.4, 122.1, 120.6, 117.6, 100.4, 25.0, 16.1; IR (KBr, cm^{-1}) 3378(bs), 3120(w), 2970(w), 2933(w), 2879(w), 1765(m), 1718(s), 1631(w), 1591(m), 1516(m), 1498(m), 1471(w), 1411(w), 1376(m), 1318(s), 1213(m), 1185(m), 1165(w), 1718(s), 1631(w), 1591(m), 1516(m), 1498(m), 1471(m), 1411(w), 1376(m), 1318(s), 1213(m), 1185(m), 1165(m), 1110(m), 1086(m), 1051(m), 851(m), 781(m), 750(m); HRMS *m/z* (M + Na^+) calcd. 358.0799, found 358.0800. Anal. Calcd. for $C_{18}H_{13}N_3O_4$: C, 64.47; H, 3.91; N, 12.53. Found: C, 64.10; H, 4.25; N, 12.16.

(+)-(R)-2-(1,3-Dioxo-2H,6H-pyrrolo[3,4-e]indol-2-yl)-2-phenylethyl acetate (85). Method A with vinylpyrrole **4** and maleimide **10m** gave adduct **39**, which with method E gave **85** (641 mg, 46%) as dark-yellow crystals: mp 62–63°C; $[\alpha]^{23}_D$ +2.1 (*c* 1.0, $CHCl_3$); ^{1}H NMR (300 MHz, CD_2Cl_2, δ) 8.88 (bs, 1H, 6-H), 7.74 (dd, *J* = 8.1, 0.9 Hz, 1H, 5-H), 7.64 (d, *J* = 8.1 Hz, 1H, 4-H), 7.56–7.61 (m, 3H, 7-H and Ph), 7.31–7.42 (m, 3H, Ph), 7.04 (ddd, *J* = 3.2, 2.0, 1.1 Hz, 1H, 8-H), 5.63 (dd, *J* = 9.9, 5.7 Hz, 1H, 2′-H), 5.13 (dd, *J* = 11.1, 9.9 Hz, 1H, 1′-H), 4.83 (dd, *J* = 11.1, 5.7 Hz, 1H, 1′-H), 2.02 (s, 3H, Ac); ^{13}C NMR (75 MHz, $CDCl_3$, δ) 171.2, 170.2, 169.8, 140.9, 136.7, 130.5, 128.9, 128.5, 128.1, 124.5, 123.4, 123.2, 116.4, 116.1, 101.5, 63.0, 53.2, 21.0; IR (film, cm^{-1}) 3360(bs), 1749(m), 1698(s), 1629(w), 1458(w), 1350(s), 1236(m), 1041(w), 750(m), 699(m); HRMS *m/z* (M + Na^+) calcd. 371.1003, found 371.1009. Anal. Calcd. for $C_{20}H_{16}N_2O_4$: C, 68.96; H, 4.63; N, 8.04. Found: C, 68.80; H, 4.62; N, 8.00.

(R)-2-(4-Methyl-1,3-dioxo-2H,6H-pyrrolo[3,4-e]indol-2-yl)-2-phenylethyl acetate (86). Method A with vinylpyrrole **3b** and maleimide **10m** gave adduct **40**, which with method E gave **86** (391 mg, 27%) as light-yellow crystals: mp 158–159°C; ^{1}H NMR (300 MHz, CD_2Cl_2, δ) 8.85 (bs, 1H, 6-H), 7.55–7.59 (m, 2H, Ph), 7.33–7.46 (m, 5H, 5-H, 7-H and Ph), 6.95 (ddd, *J* = 3.1, 2.1, 1.0 Hz, 1H, 8-H), 5.65 (dd, *J* = 9.6, 6.0 Hz, 1H, 2′-H), 5.16 (dd, *J* = 11.1, 9.6 Hz, 1H, 1′-H), 4.86 (dd, *J* = 6.0, 11.1 Hz, 1H, 1′-H), 2.73 (d, *J* = 0.9 Hz, 3H, 4-CH_3), 2.01 (s, 3H, Ac); ^{13}C NMR (75 MHz, $CDCl_3$, δ) 171.2, 170.4, 169.6, 140.8, 137.0, 130.7, 129.7, 128.9, 128.4, 128.2, 123.6, 121.9, 121.7, 117.6, 101.5, 63.1, 53.0, 21.0, 18.3; IR (film, cm^{-1}) 3370(bs), 1747(m), 1696(s), 1637(m), 1457(w), 1391(m), 1350(m), 1238(m), 1043(w), 767(m), 738(w), 700(m); HRMS *m/z* (M + Na^+) calcd. 385.1160, found 385.1161. Anal. Calcd. for $C_{21}H_{18}N_2O_4$: C, 69.60; H, 5.01; N, 7.73. Found: C, 69.51; H, 4.98; N, 7.52.

(+)-(R)-2-(6-Methyl-1,3-dioxo-2H,6H-pyrrolo[3,4-e]indol-2-yl)-2-phenylethyl acetate (87). Method A with vinylpyrrole **3d** and maleimide **10m** gave adduct **41**, which with method E gave **87** (638 mg, 44%) as light-brown crystals: mp 52–53°C; $[\alpha]^{23}_D$ +3.6 (*c* 2.0, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$, δ) 7.66 (dd, *J* = 8.4, 0.6 Hz, 1H, 5-H), 7.57–7.61 (m, 2H, Ph), 7.58 (d, overlapped, *J* = 8.4 Hz, 1H, 4-H), 7.28–7.40 (m, 4H, 7-H, Ph), 6.98 (d, *J* = 3.0 Hz, 1H, 8-H), 5.65 (dd, *J* = 10.2, 5.7 Hz, 1H, 2′-H), 5.16 (dd, *J* = 10.5, 10.5 Hz, 1H, 1′-H), 4.87 (dd, *J* = 10.7, 5.7 Hz, 1H, 1′-H), 3.89 (s, 3H, 6-CH_3), 2.01 (s, 3H, Ac); ^{13}C NMR (75 MHz, $CDCl_3$, δ) 170.8, 169.9, 169.5, 141.1, 136.8, 134.6, 128.8, 128.4, 128.2, 124.2, 123.6, 123.5, 115.7, 114.1, 100.1, 62.8, 53.3, 33.4, 20.9; IR (film, cm^{-1}) 3447(bs), 3108(w), 3063(w), 2950(w), 1741(s), 1703(s), 1626(w), 1511(m), 1457(m), 1352(s), 1295(m), 1232(s), 1042(m), 749(s), 701(s); HRMS *m/z* (M + Na^+) calcd. 385.1160, found 385.1166. Anal. Calcd. for $C_{21}H_{18}N_2O_4$: C, 69.60; H, 5.01; N, 7.93. Found: C, 69.75; H, 4.89; N, 7.93.

(+)-(R)-2-(5,6-Dimethyl-1,3-dioxo-2H,6H-pyrrolo[3,4-e]indol-2-yl)-2-phenylethyl acetate (88). Method A with vinylpyrrole **3c** and maleimide **10m** gave adduct **42**, which with method E gave **88** (437 mg, 29%) as yellow crystals: mp 125–126°C; $[\alpha]^{23}_D$ +3.9 (*c* 2.0, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$, δ) 7.56–7.59 (m, 2H, Ph), 7.27–7.41 (m, 4H, 4-H and Ph), 7.20 (d, *J* = 3.3 Hz, 1H, 7-H), 6.94 (d, *J* = 3.0 Hz, 1H, 8-H), 5.60 (dd, *J* = 9.9, 5.4 Hz, 1H, 2′-H), 5.14 (dd, *J* = 11.1, 10.2 Hz, 1H, 1′-H), 4.85 (dd, *J* = 11.1, 5.4 Hz, 1H, 1′-H), 4.13 (s, 3H, 6-CH_3), 2.87 (s, 3H, 5-CH_3), 2.00 (s, 3H, Ac); ^{13}C NMR (75 MHz, $CDCl_3$, δ) 170.8, 169.9, 169.6, 139.6, 136.9, 136.0, 128.8, 128.3, 128.2, 127.6, 124.8, 124.7, 121.9, 118.2, 100.5, 62.9, 53.2, 37.3, 20.9, 20.4; IR (film, cm^{-1}) 3440(bs), 1742(m), 1701(s), 1518(w), 1496(w), 1367(m), 1347(s), 1232(m), 1089(w), 762(w), 750(w), 731(w), 701(w); HRMS *m/z* (M + Na^+) calcd. 399.1316, found 399.1328. Anal. Calcd. for $C_{22}H_{20}N_2O_4$: C, 70.20; H, 5.36; N, 7.44. Found: C, 70.08; H, 5.39; N, 7.29.

(+)-(R)-2-(4,6-Dimethyl-1,3-dioxo-2H,6H-pyrrolo[3,4-e]indol-2-yl)-2-phenylethyl acetate (89). Method A with vinylpyrrole **3f** and maleimide **10m** gave adduct **43**, which with method E gave **89** (391 mg, 26%) as brownish-orange crystals: mp 163–164°C; $[\alpha]^{23}_D$ +5.9 (*c* 5.0, $CHCl_3$); ^{1}H NMR (300 MHz,

$CDCl_3$, δ) 7.57–7.60 (m, 2H, Ph), 7.27–7.40 (m, 4H, 5-H and Ph), 7.25 (d, J = 3.0 Hz, 1H, 7-H), 6.98 (d, J = 3.0 Hz, 1H, 8-H), 5.63 (dd, J = 10.2, 5.7 Hz, 1H, 2′-H), 5.15 (dd, J = 11.1, 10.2 Hz, 1H, 1′-H), 4.88 (dd, J = 11.1, 5.7 Hz, 1H, 1′-H), 3.81 (s, 3H, 6-CH_3), 2.77 (s, 3H, 4-CH_3), 2.02 (s, 3H, Ac); ^{13}C NMR (75 MHz, $CDCl_3$, δ) 170.8, 170.4, 169.4, 141.2, 137.0, 134.0, 130.2, 128.8, 128.6, 128.3, 123.8, 122.2, 121.4, 115.5, 100.3, 62.9, 53.0, 33.2, 21.0, 18.4; IR (film, cm^{-1}) 3440(bm), 2925(w), 1746(s), 1698(s), 1510(w), 1381(m), 1350(s), 1291(w), 1233(m), 1041(w), 763(w), 701(w); HRMS m/z (M + Na^+) calcd. 399.1316, found 399.1301. Anal. Calcd. for $C_{22}H_{20}N_2O_4$: C, 70.20; H, 5.36; N, 7.44. Found: C, 70.31; H, 5.49; N, 7.36.

(+)-(R)-2-(4,5,6-Trimethyl-1,3-dioxo-2H,6H-pyrrolo[3,4-e]indol-2-yl)-2-phenylethyl acetate (90). Method A with vinylpyrrole **3g** and maleimide **10m** gave adduct **44**, which with method E gave **90** (328 mg, 21%) as yellow crystals: mp 197–198°C; $[\alpha]^{23}_D$ +4.1 (*c* 2.5, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$, δ) 7.55–7.59 (m, 2H, Ph), 7.28–7.40 (m, 3H, Ph), 7.14 (d, J = 2.7 Hz, 1H, 7-H), 6.92 (d, J = 3.0 Hz, 1H, 8-H), 5.62 (dd, J = 9.9, 5.7 Hz, 1H, 2′-H), 5.14 (dd, J = 10.7, 9.9 Hz, 1H, 1′-H), 4.88 (dd, J = 11.1, 5.7 Hz, 1H, 1′-H), 4.12 (s, 3H, 6-CH_3), 2.75 (s, 3H, 4-CH_3 or 5-CH_3), 2.74 (s, 3H, 4-CH_3 or 5-CH_3), 2.01 (s, 3H, Ac); ^{13}C NMR (75 MHz, $CDCl_3$, δ) 170.8, 169.3, 140.0, 137.1, 136.4, 129.4, 128.8, 128.3, 128.2, 126.8, 123.4, 122.0, 121.3, 116.5, 100.0, 62.9, 53.2, 38.0, 25.8, 14.5, 13.8; IR (film, cm^{-1}) 3451(bs), 1746(m), 1697(s), 1498(w), 1455(w), 1387(m), 1344(m), 1309(w), 1231(m), 1039(w), 806(w), 766(m), 730(w); HRMS m/z (M + Na^+) calcd. 413.1473, found 413.1456. Anal. Calcd. for $C_{23}H_{22}N_2O_4$: C, 70.75; H, 5.68; N, 7.17. Found: C, 70.82; H, 5.65; N, 6.96.

(+)-(R)-2-(2-Methoxy-1-phenylethyl)-2H,6H-pyrrolo[3,4-e]indole-1,3-dione (91). Method A with vinylpyrrole **4** and maleimide **10n** gave adduct **45**, which with method E gave **91** (500 mg, 39%) as light-yellow crystals: mp 63–64°C; $[\alpha]^{23}_D$ +27.0 (*c* 5.0, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$, δ) 8.75 (bs, 1H, 6-H), 7.55–7.60 (m, 4H, 4-H and 5-H and Ph), 7.28–7.43 (m, 4H, 7-H and Ph), 6.98 (dd, J = 3.3, 1.8 Hz, 1H, 8-H), 5.63 (dd, J = 10.2, 5.7 Hz, 1H, 1′-H), 4.69 (dd, J = 10.2, 10.2 Hz, 1H, 2′-H), 4.01 (dd, J = 10.2, 5.7 Hz, 1H, 2′-H), 3.47 (s, 3H, OCH_3); ^{13}C NMR (75 MHz, $CDCl_3$, δ) 170.4, 169.9, 140.6, 137.5, 130.3, 128.9, 128.4, 128.2, 124.0, 123.1, 122.8, 115.9, 115.8, 101.5, 71.4, 58.9, 53.8; IR (film, cm^{-1}) 3402(bs), 1754(m), 1699(s), 1610(m), 1458(w), 1393(w), 1353(s), 1109(w), 750(m), 700(m); HRMS m/z (M + Na^+) calcd. 343.1054, found 343.1045. Anal. Calcd. for $C_{19}H_{16}N_2O_3$: C, 71.24; H, 5.03; N, 8.74. Found: C, 71.46; H, 5.14; N, 8.82.

(+)-(R)-2-(2-Methoxy-1-phenylethyl)-4-methyl-2H,6H-pyrrolo[3,4-e]indole-1,3-dione (92). Method A with vinylpyrrole **3b** and maleimide **10n** gave adduct **46**, which with method E gave **92** (401 mg, 30%) as dark-yellow crystals: mp 139–140°C; $[\alpha]^{23}_D$ +14.9 (*c* 2.3, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$, δ) 8.68 (bs, 1H, 6-H), 7.57–7.60 (m, 2H, Ph), 7.28–7.40 (m, 5H, 5-H and 7-H and Ph), 6.79–6.81 (m, 1H, 8-H), 5.62 (dd, J = 10.2, 5.7 Hz, 1H, 1′-H), 4.77 (dd, J = 10.2, 10.2 Hz, 1H, 2′-H), 4.00 (dd, J = 10.2, 5.4 Hz, 1H, 2′-H), 3.52 (s, 3H, OCH_3), 2.65 (d, J = 0.9 Hz, 3H, 4-CH_3); ^{13}C NMR (75 MHz, CD_2Cl_2, δ) 170.4, 169.6, 140.5, 137.9, 130.3, 129.5, 128.7, 128.6, 128.2, 128.1, 123.3, 121.3, 117.2, 101.1, 71.4, 58.7, 53.3, 18.0; IR (film, cm^{-1}) 3413(bs), 1749(w), 1694(s), 1636(m), 1456(w), 1394(w), 1350(m), 766(w), 699(w); HRMS m/z (M + Na^+) calcd. for $C_{20}H_{18}N_2O_3$: 357.1210, found 357.1211.

(+)-(R)-2-(2-Methoxy-1-phenylethyl)-4,5-dimethyl-2H,6H-pyrrolo[3,4-e]indole-1,3-dione (93). Method A with vinylpyrrole **3e** and maleimide **10n** gave adduct **47**, which with method E gave **93** (362 mg, 26%) as light-yellow crystals: mp 177–178°C; $[\alpha]^{23}_D$ +17.6 (*c* 0.8, $CHCl_3$); ^{1}H NMR (300 MHz, CD_2Cl_2 δ) 8.67 (bs, 1H, 6-H), 7.53–7.60 (m, 2H, Ph), 7.28–7.41 (m, 4H, 7-H, Ph), 6.87 (d, J = 3.0, 1.8 Hz, 1H, 8-H), 5.59 (dd, J = 9.9, 5.7 Hz, 1H, 1′-H), 4.60 (dd, J = 9.9, 9.9 Hz, 1H, 2′-H), 4.02 (dd, 9.9, 5.5 Hz, 1H, 2′-H), 3.47 (s, 3H, OCH_3), 2.67 (s, 3H, 4-CH_3), 2.45 (s, 3H, 5-CH_3); ^{13}C NMR (75 MHz, CD_2Cl_2, δ) 170.9, 169.3, 139.9, 138.0, 129.0, 128.6, 128.1, 128.0, 127.9, 125.4, 121.9, 120.9, 120.5, 101.6, 71.5, 58.8, 53.9, 13.2, 13.1; IR (film, cm^{-1}) 3430(bs), 2900(w), 1747(m), 1693(s), 1650(m), 1394(m), 1352(m), 1092(w), 767(m), 732(m), 699(m); HRMS m/z (M + Na^+) calcd. 371.1367, found 371.1351. Anal. Calcd. for $C_{21}H_{20}N_2O_3$: C, 72.40; H, 5.79; N, 8.04. Found: C, 72.22; H, 5.74; N, 7.88.

(+)-(R)-2-(2-Methoxy-1-phenylethyl)-6-methyl-2H,6H-pyrrolo[3,4-e]indole-1,3-dione (94). Method A with vinylpyrrole **3d** and maleimide **10n** gave adduct **48**, which with method E gave **94** (535 mg, 40%) as light-yellow crystals: mp 123–124°C; $[\alpha]^{23}_D$ +30.4 (*c* 5.0, $CHCl_3$); ^{1}H NMR (300 MHz, CD_2Cl_2, δ) 7.59–7.62 (m, 2H, 4-H, 5-H), 7.54–7.58 (m, 2H, Ph), 7.28–7.52 (m, 4H, 7-H and Ph), 6.94 (dd, J = 3.3, 0.9 Hz, 1H, 8-H), 5.58 (dd, J = 9.9, 6.3 Hz, 1H, 1′-H), 4.52 (dd, J = 9.6, 9.6 Hz, 1H, 2′-H), 4.02 (dd, J = 9.9, 6.0 Hz, 1H, 2′-H), 3.89 (s, 3H, 6-CH_3), 3.41 (s, 3H, OCH_3); ^{13}C NMR (75 MHz, $CDCl_3$, δ) 170.2, 169.8, 141.0, 137.7, 134.4, 128.7, 128.3, 128.1, 124.5, 123.9, 123.5, 115.7, 113.9, 100.6, 71.4, 58.9, 53.9, 33.4; IR (film, cm^{-1}) 3443(bs), 2905(m), 2800(w), 1755(m), 1702(s), 1511(m), 1458(w), 1385(m), 1353(s), 1295(w), 1114(m), 1090(w), 748(s), 700(m); HRMS m/z (M + Na^+) calcd. 357.1210, found 357.1200. Anal. Calcd. for $C_{20}H_{18}N_2O_3$: C, 71.84; H, 5.43; N, 8.38. Found: C, 71.61; H, 5.32; N, 8.41.

(+)-(R)-2-(2-Methoxy-1-phenylethyl)-5,6-dimethyl-2H,6H-pyrrolo[3,4-e]indole-1,3-dione (95). Method A with vinylpyrrole **3c** and maleimide **10n** gave adduct **49**, which with method E gave **95** (446 mg, 32%) as orangish-yellow crystals: mp 157–158°C; $[\alpha]^{23}_D$ +30.2 (*c* 5.0, $CHCl_3$); ^{1}H NMR (300 MHz, CD_2Cl_2, δ) 7.53–7.58 (m, 2H, Ph), 7.27–7.39 (m, 4H, 4-H, Ph), 7.25 (d, J = 3.3 Hz, 1H, 7-H), 6.89 (d, J = 3.3 Hz, 1H, 8-H), 5.54 (dd, J = 9.6, 5.7 Hz, 1H, 1′-H), 4.49 (dd, J = 9.6, 9.6 Hz, 1H, 2′-H), 4.12 (s, 3H, 6-CH_3), 4.02 (dd, J = 9.6, 6.0 Hz, 1H, 2′-H), 3.40 (s, 3H, OCH_3), 2.88 (s, 3H, 5-CH_3); ^{13}C NMR (75 MHz, CD_2Cl_2, δ) 170.0, 169.6, 139.4, 138.1, 136.0, 128.6, 128.2, 127.9, 127.7, 124.8, 124.4, 121.8, 117.6, 99.9, 71.3, 58.6, 53.6, 37.1, 20.0; IR (film, cm^{-1}) 3440(bs), 2999(w), 2933(w), 2805(w), 1750(m), 1696(s), 1518(w), 1495(w), 1404(w), 1347(s), 1116(m), 1092(w), 760(w), 750(w), 730(w), 701(m), 661(m); HRMS m/z (M + Na^+) calcd. 371.1367, found 371.1372. Anal. Calcd. for $C_{21}H_{20}N_2O_3$: C, 72.40; H, 5.79; N, 8.04. Found: C, 72.56; H, 5.93; N, 7.96.

(+)-(R)-2-(2-Methoxy-1-phenylethyl)-4,6-dimethyl-2H,6H-pyrrolo[3,4-e]indole-1,3-dione (96). Method A with vinylpyrrole **3f** and maleimide **10n** gave adduct **50**, which with method

E gave **96** (404 mg, 29%) as yellow crystals: mp 132–133°C; $[\alpha]^{23}_D$ +30.2 (*c* 5.0, $CHCl_3$); ^{1}H NMR (300 MHz, CD_2Cl_2, δ) 7.54–7.58 (m, 2H, Ph), 7.30–7.40 (m, 5H, 5-H and 7-H and Ph), 6.88 (dd, J = 3.0, 0.9 Hz, 1H, 8-H), 5.57 (dd, J = 9.3, 6.0 Hz, 1H, 1′-H), 4.53 (dd, J = 9.9, 9.9 Hz, 1H, 2′-H), 4.04 (dd, J = 9.9, 6.3 Hz, 1H, 2′-H), 3.82 (s, 3H, 6-CH_3), 3.42 (s, 3H, OCH_3), 2.77 (d, J = 0.9 Hz, 3H, 4-CH_3); ^{13}C NMR (75 MHz, $CDCl_3$, δ) 170.6, 169.6, 141.0, 138.0, 133.7, 129.8, 128.8, 128.4, 128.1, 123.7, 122.0, 121.3, 115.2, 100.1, 71.4, 58.9, 53.7, 33.0, 18.3; IR (film, cm^{-1}) 3442(bs), 2915(w), 2790(w), 1749(m), 1697(s), 1636(m), 1508(w), 1350(m), 1291(w), 1104(w), 762(m), 700(m); HRMS *m/z* (M + Na^+) calcd. 371.1367, found 371.1381. Anal. Calcd. for $C_{21}H_{20}N_2O_3$: C, 72.40; H, 5.79; N, 8.04. Found: C, 72.30; H, 5.81; N, 7.84.

(+)-(R)-2-(2-Methoxy-1-phenylethyl)-4,5,6-trimethyl-2H,6H-pyrrolo[3,4-e]indole-1,3-dione (97). Method A with vinylpyrrole **3g** and maleimide **10n** gave adduct **51**, which with method E gave **97** (333 mg, 23%) as dark-orange crystals: mp 164–165°C; $[\alpha]^{23}_D$ +26.5 (*c* 0.4, $CHCl_3$); ^{1}H NMR (300 MHz, CD_2Cl_2, δ) 7.52–7.58 (m, 2H, Ph), 7.28–7.40 (m, 3H, Ph), 7.17 (d, J = 3.0 Hz, 1H, 7-H), 6.86 (d, J = 3.3 Hz, 1H, 8-H), 5.56 (dd, J = 9.6, 6.0 Hz, 1H, 1′-H), 4.50 (dd, J = 9.6, 9.6 Hz, 1H, 2′-H), 4.10 (s, 3H, 6-CH_3), 4.04 (dd, J = 9.9, 6.0 Hz, 1H, 2′-H), 3.42 (s, 3H, OCH_3), 2.73 (s, 3H, 4-CH_3 or 5-CH_3), 2.72 (s, 3H, 4-CH_3 or 5-CH_3); ^{13}C NMR (75 MHz, CD_2Cl_2, δ) 170.9, 169.4, 139.9, 138.2, 136.4, 129.2, 128.5, 128.1, 127.8, 126.9, 123.2, 122.0, 121.3, 99.5, 71.4, 58.6, 53.3, 37.9, 14.3, 13.4; IR (film, cm^{-1}) 3450(bs), 2932(w), 1748(m), 1695(s), 1519(w), 1496(w), 1395(m), 1345(m), 1309(w), 1112(w), 765(m), 731(m), 700(m); HRMS *m/z* (M + Na^+) calcd. for $C_{22}H_{22}N_2O_3$: 385.1523, found 385.1518.

^{1}H and ^{13}C NMR spectra for compounds **3a-3c**, **3e-3g**, **5b**, **7**, **10m**, **10n**, **11-38**, **53-97**, the ^{1}H NMR spectrum for compound **52**, biological activity data for compounds **63** and **66**, and X-ray data for 7 in CIF format. This material is available online free of charge (see Supporting Information).

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