JOC Article

SmI_2-Promoted Radical Addition Reactions with *N*-(2-Indolylacyl)oxazolidinones: Synthesis of Bisindole Compounds

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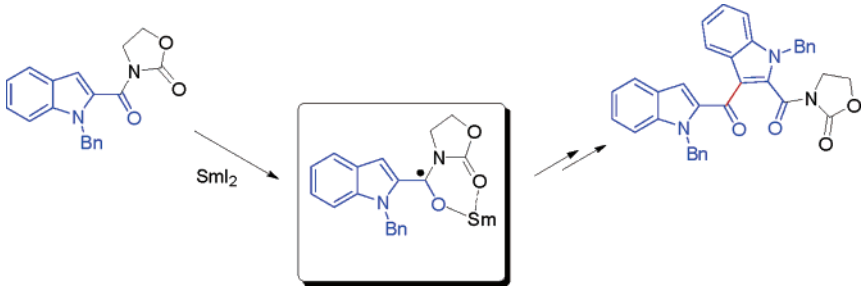

The treatment of *N*-acyl oxazolidinones of *N*-benzyl 2-indolecarboxylic acids varying in the substitution pattern of the indole ring with samarium diiodide at −78 °C led to the formation of two indole dimer products. The major product isolated in yields from 55 to 59% represents an unsymmetrical dimer arising from 1,4-addition to the 2-indolecarboxylic acid derivative of a possible ketyl-type radical anion intermediate originating from the reduction of the exocyclic carbonyl group of the *N*-acyl oxazolidinone. The minor dimer, represented by a symmetrical diketone, was produced in yields ranging from 11 to 23%. Even in the presence of an α,β-unsaturated amide, dimerization was the preferred pathway rather than the formation of a γ-keto amide. Upon treatment with acid, the unsymmetrical indole dimer cyclized to form a diindolequinone. Finally, the *N*-acyl oxazolidinones of pyrrole-2-carboxylic acid and 3-indolecarboxylic acid preferred in both cases to undergo C−C bond formation with an acrylamide in the presence of SmI_2 rather than dimerization.

Introduction

The 2-acylindole alkaloids represent a diverse collection of natural products possessing a variety of remarkable biological activities.[1] In the past few years, the Barcelona group has successfully been synthesizing several 2-acylindole compounds, including ellipticine quinones and the alkaloid calothrixin B, exploiting as the key step either intermolecular additions[2] or intramolecular cyclization reactions[3] of 2-indolylacyl radicals with alkene and aromatic acceptors. These reactive intermediates can be effectively generated from their corresponding selenoesters using either reductive conditions, such as tributyltin hydride (or in some instances tris(trimethylsilyl)silane) in the presence of a radical initiator as exemplified in Scheme 1,[2,3a] or nonreductive conditions with hexabutylditin and *hν*.[3b] The replacement of selenoesters with alternative functionality would nevertheless be attractive due to stability issues encompassing the acyl radical precursors, as well as their preparation from unstable selenol intermediates.[4] Likewise, the substitution of tin-mediated radical conditions with other radical-generating

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(1) (a) Sundberg, R. J. *Indoles*; Academic Press: New York, 1996. (b) Joule, J. A. *Science of Synthesis* (*Houben-Weyl, Methods of Molecular Transformations*); Georg Thieme Verlag: Stuttgart, 2000; Vol. 10, pp 361−652. (c) Somei, M.; Yamada, F. *Nat. Prod. Rep.* **2005**, *22*, 73 and 761.

(2) Bennasar, M.-L.; Roca, T.; Griera, R.; Bosch, J. *Org. Lett.* **2001**, *3*, 1697.

(3) (a) Bennasar, M.-L.; Roca, T.; Ferrando, F. *Org. Lett.* **2004**, *6*, 759. (b) Bennasar, M.-L.; Roca, T.; Ferrando, F. *J. Org. Chem.* **2005**, *70*, 9077. (c) Bennasar, M.-L.; Roca, T.; Ferrando, F. *Org. Lett.* **2006**, *8*, 561.

(4) For a comprehensive review on acyl radical chemistry, see: Chatgilialoglu, C.; Crich, D.; Komatsu, M.; Ryu, I. *Chem. Rev.* **1999**, *99*, 1991.

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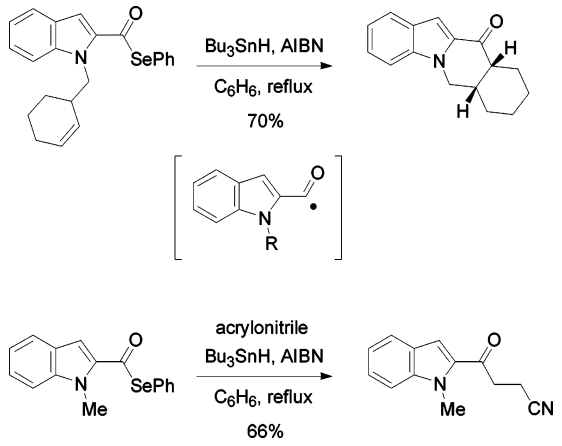
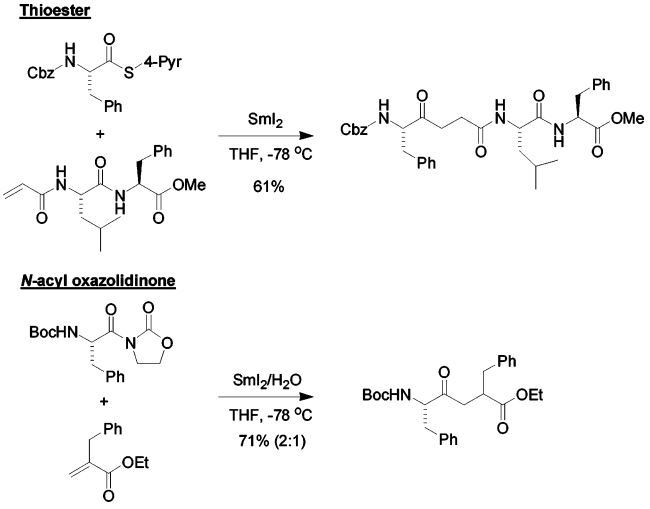
SCHEME 1. Examples of *n*-Bu_3SnH-Mediated 2-Indolylacyl Radical Additions to Alkenes



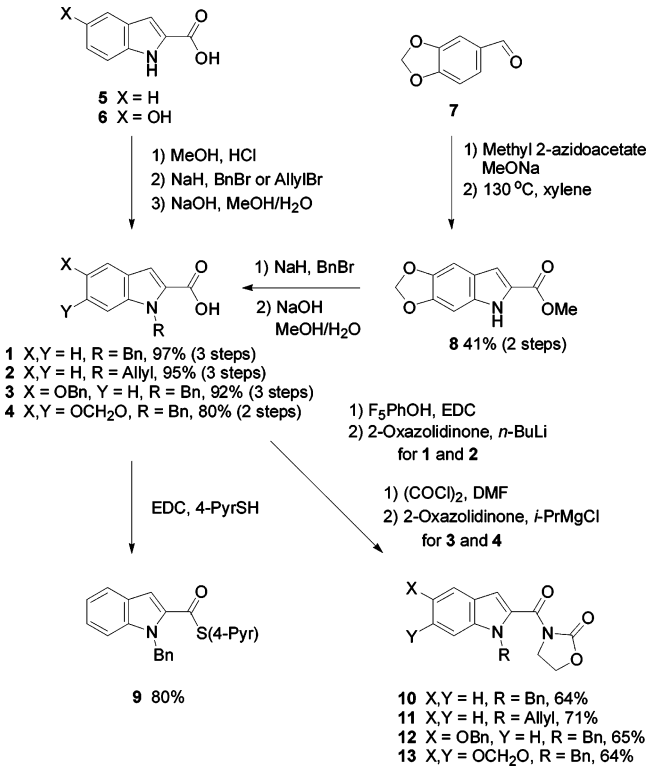
SCHEME 2. Examples of Radical Addition Reactions with 4-Pyridylthioesters and *N*-Acyl Oxazolidinones



conditions would be advantageous owing to purification problems and concerns regarding disposal of toxic tin wastes.

We have recently reported a convenient synthesis of γ-keto ester/amides from a SmI_2-promoted radical addition of thiopyridyl esters of amino acids to acrylamides and acrylates.[5,6] Although the ketones formed were identical to the products from a formal acyl radical addition reaction, we proposed the intermediacy of a ketyl-type radical anion as the reacting partner with the electrophilic olefin, due to the lack of decarbonylation products typically observed for acyl radical intermediates generated from amino acid precursors.[7] In addition, we have demonstrated the aptitude of *N*-acyl oxazolidinones in the presence of acrylates or amides and SmI_2 and excess water to provide the same class of compounds in a more reliable manner (Scheme 2).[8] For these reactions, an alternative mechanism was proposed encompassing a chemoselective reduction of the α,β-unsaturated amide or ester to a C3 radical species which ultimately adds to the imide carbonyl of the *N*-acyl oxazolidinone.[9]

SCHEME 3



We therefore set out to investigate the possibility of promoting similar C−C bond forming reactions with either the thiopyridyl esters of 2-indolecarboxylic acids or their corresponding *N*-acyl oxazolidinones, potentially providing a suitable alternative to the tin-hydride-mediated reactions with selenoesters. In this paper, we report our efforts directed at promoting these radical addition reactions. Contrary to our initial expectations, we disclose a novel SmI_2-mediated dimerization process of indole derivatives providing a rapid access to bisindole compounds that possess structural entities resembling a series of biologically active products.

Results and Discussion

Synthesis of Precursors. The synthesis of the appropriately functionalized 2-indolecarboxylic acids required for this study is outlined in Scheme 3. Four different 2-indolecarboxylic acids **1**−**4** with variations in the substitution pattern of the aryl ring and at the nitrogen atom were first prepared. Starting from the commercially available carboxylic acids **5** and **6**, a three-step sequence involving methyl ester formation, N-benzylation (including O-benzylation for **6**), or N-allylation, followed by ester cleavage, led to the known functionalized indole derivatives

(5) Blakskjær, P.; Høj, B.; Riber, D.; Skrydstrup, T. *J. Am. Chem. Soc.* **2003**, *125*, 4030.

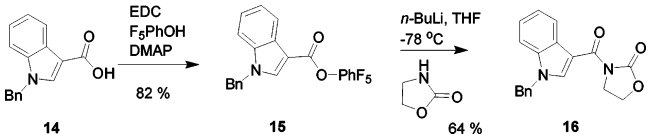
(6) See also: (a) Mikkelsen, L. M.; Jensen, C. M.; Høj, B.; Blakskjær, P.; Skrydstrup, T. *Tetrahedron* **2003**, *59*, 10541. (b) Jensen, C. M.; Lindsay, K. B.; Andreasen, P.; Skrydstrup, T. *J. Org. Chem.* **2005**, *70*, 7512. (c) Lindsay, K. B.; Skrydstrup, T. *J. Org Chem.* **2006**, *71*, 4766.

(7) For representative examples where decarbonylation precedes acyl radical addition, see: (a) Crich, D.; Eustace, K. A.; Ritchie, T. J. *Heterocycles* **1989**, *111*, 7558. (b) Boger, D. L.; Mathvink, R. J. *J. Org. Chem.* **1992**, *57*, 1429. (c) Stojanovic, A.; Renaud, P. *Synlett* **1997**, 181. (d) Quirante, J.; Vila, X.; Escolano, C.; Bonjoch, J. *J. Org. Chem.* **2002**, *67*, 2323.

(8) (a) Jensen, C. M.; Lindsay, K. B.; Taaning, R. H.; Karaffa, J.; Hansen, A. M.; Skrydstrup, T. *J. Am. Chem. Soc.* **2005**, *127*, 6544. (b) Karaffa, J.; Lindsay, K. B.; Skrydstrup, T. *J. Org Chem.* **2006**, *71*, 8219.

(9) Hansen, A. M.; Lindsay, K. B.; Sudhadevi Antharjanam, P. K.; Karaffa, J.; Daasbjerg, K.; Flowers, R. A., II; Skrydstrup, T. *J. Am. Chem. Soc.* **2006**, *128*, 9616.

SCHEME 4



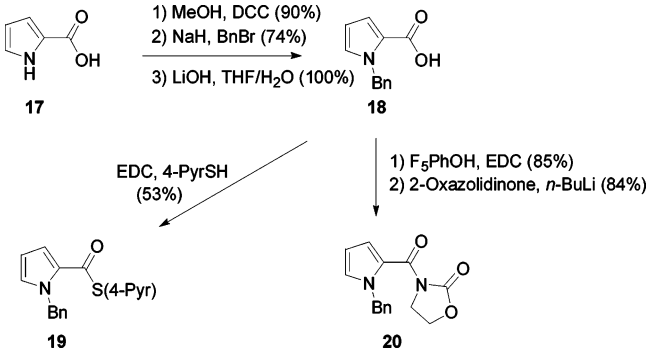
1−**3** in good yields.[10] Synthesis of the methylenedioxyindolecarboxylic acid **4** required an initial indole synthesis exploiting the Hemetsberger reaction according to the work of Rebelo and co-workers.[11] Hence, condensation of aldehyde **7** with the methyl 2-azidoacetate provided the corresponding vinyl azide in 41% yield, which was quantitatively cyclized to the methyl 2-indolecarboxylate **8** upon heating in xylene. Further elaboration as before supplied the *N*-benzyl compound **4**.

Preparation of the thioester **9** was achieved in an unoptimized yield of 80% using an EDC-promoted coupling of the acid **1** with 4-mercaptopyridine.[5] On the other hand, two approaches were adapted for the introduction of the oxazolidinone group. In the first approach, the 2-oxazolidinone is deprotonated in THF with *n*-BuLi under low temperature and then added to the corresponding pentafluorophenyl ester of **1** or **2**. Although this procedure provided the *N*-acyl oxazolidinones **10** and **11** in good yields, the protocol is nevertheless inconvenient due to the low solubility of the lithiated oxazolidinone in THF. Later, we found that adaptation of the Merck procedure for the preparation of Weinreb's amides proved also worthy and more reliable.[12] Hence, THF solutions of the acid chlorides generated from **3** and **4** were subjected to a solution of the 2-oxazolidinone pretreated with isopropyl magnesium chloride leading to the *N*-(2-indolyl)oxazolidinones **12** and **13** in an approximate yield of 65% for both cases.

To investigate the effect of the carboxylate position on the indole ring for these SmI_2-promoted radical additions, we also prepared the corresponding oxazolidinone derivative **16** of the 3-indolecarboxylic acid as illustrated in Scheme 4. Indole 3-carboxylic acid **14** was prepared from indole in three steps as outlined by Hopkins et al. in an 81% overall yield.[13] Transformation of acid **14** into the oxazolidinone **16** proved to be less compliant when compared to the 2-indole acid systems, and other methods tried were wholly ineffective. For example, activating the 2-oxazolidinone with either $Al(CH_3)_3$ or *i*-PrMgCl prior to addition to PFP ester **15** gave little or no reaction, whereas using the corresponding acid chloride of **14** in a similar manner gave unexpected side products. We eventually settled on transforming the acid into its pentafluorophenyl ester **15**, followed by reaction with 2-oxazolidinone that had been deprotonated via a very slow addition to a diluted solution of *n*-BuLi in THF at −78 °C. At best, it was found that an approximate 9:1 mixture of products was formed using this method, where the minor byproduct corresponded to a ring-opened oxazolidinone adding to the activated ester, and this impurity was only successfully removed by recrystallization.

Finally, the importance of the indole ring for the subsequent radical addition studies was examined with the 4-thiopyridine

SCHEME 5



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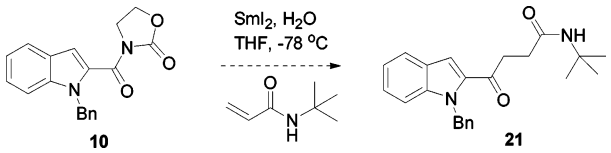
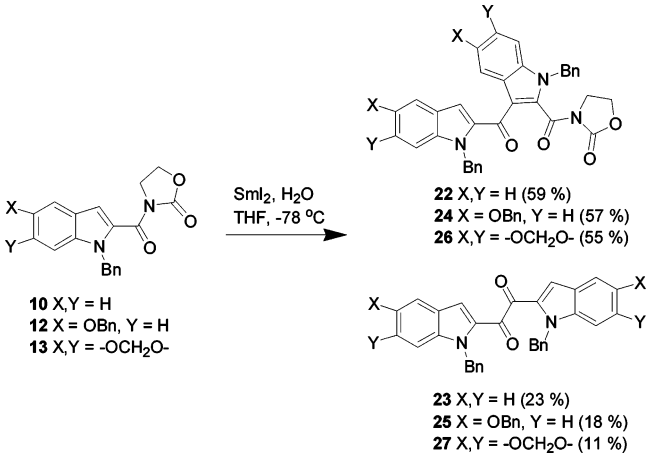


SCHEME 7



ester and the *N*-acyl oxazolidinone derivative of pyrrole-2-carboxylic acid. The synthesis of these compounds is depicted in Scheme 5 starting from the acid **17**. As before, a three-step sequence was applied for converting **17** to the *N*-benzyl pyrrole derivative **18**.[14,15] Subsequent transformation to the two potential radical addition precursors **19** and **20** proceeded without incident.

SmI_2-Promoted Addition Studies. Initial studies regarding the SmI_2-promoted coupling of thioesters **9** and **19** with activated alkenes revealed that these substrates were unreactive using standard conditions,[5] invariably only unreacted thioester could be recovered, albeit in diminished amounts due to losses upon workup. This was unsurprising as we have previously only been able to achieve success with thioesters of amino acids.[5,6]

We had initially intended to react the oxazolidinone derivatized indole **10** with activated alkenes and SmI_2 as depicted in Scheme 6.[8] To our surprise, none of the desired coupling product **21** was obtained, instead two new compounds were isolated.

Conducting the same reaction in the absence of activated alkene allowed isolation of pure products which revealed that

(10) Olgen, S.; Akaho, E.; Nebioglu, D. *Eur. J. Med. Chem.* **2001**, *36*, 747.

(11) da Rosa, F. A. F.; Rebelo, R. A.; Nascimento, M. G. *J. Braz. Chem. Soc.* **2003**, *14*, 11.

(12) Williams, J. M.; Jobson, R. B.; Yasuda, N.; Marchesini, G.; Dolling, U. H.; Grabowski, E. J. J. *Tetrahedron Lett.* **1995**, *36*, 5461.

(13) Hopkins, C. R.; Czekaj, M.; Kaye, S. S.; Gao, Z.; Pribish, J.; Pauls, H.; Liang, G.; Sides, K.; Cramer, D.; Cairns, J.; Luo, Y.; Lim, H.-K.; Vaz, R.; Rebello, S.; Maignan, S.; Dupuy, A.; Mathieu, M.; Levell, J. *Bioorg. Med. Chem. Lett.* **2005**, *15*, 2734.

(14) Ruest, L.; Menard, H.; Moreau, V.; Laplante, F. *Can. J. Chem.* **2002**, *80*, 1662.

(15) Anderson, H. J.; Griffiths, S. J. *Can. J. Chem.* **1967**, *45*, 2227.

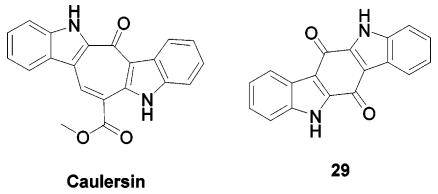
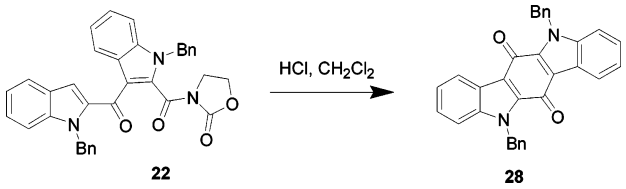


FIGURE 1. Biologically active indole dimers.

SCHEME 8



these two compounds were in fact indole dimers **22** and **23** (Scheme 7). Further optimization of the conditions allowed isolation of these two derivatives in a 59 and 23% yield, respectively.

Compound **22** was not stable, decomposing over time to give a deep red, highly insoluble solid. This decomposition was accelerated by treatment with dilute HCl. Treatment of a CH_2Cl_2 solution of **22** with one drop of 0.1 M HCl gave a slow enough reaction to allow formation of crystals which then revealed the decomposition product to be **28** (Scheme 8), the structure of which was identified via X-ray crystallography (see Supporting Information). We have not been able to characterize this material further due to its poor solubility in all organic solvents examined. Compound **23** was crystalline, and its structural assignment was ultimately confirmed by X-ray crystallography (see Supporting Information).

Of particular interest is the structural similarity of compounds **22** and **28** to biologically active indole dimers (Figure 1). For example, **22** possesses the carbonyl bridged bisindole framework seen in the marine alkaloid, caulersin.[16,17] Compound **28** is simply the *N*-benzyl-protected version of indolocarbazole **29**, a compound which represents a potent agonist for the aryl hydrocarbon receptor.[18,19]

We briefly experimented with using an *N*-allyl protecting group for the indole substrates, by reaction of oxazolidinone **11**, but it soon became apparent that this was an inferior choice. While the dimerization products could be obtained, as evidenced by mass spectrometry, the products were always obtained in lower yield and in poor purity due to several additional unidentified byproducts.

Scheme 9 depicts a possible mechanistic scenario for the formation of the indole dimers **22** and **23** from the oxazolidinone **10**. SmI_2-mediated reduction of the exocyclic carbonyl group of the *N*-acyl oxazolidinone generates a ketyl-type radical anion intermediate **30**. 1,4-Addition of this radical to the C−C double bond in **10** leads to the formation of a new C2-centered carbon radical which eventually undergoes reduction to an enolate species followed by protonation from the solvent or upon workup.

Subsequent oxidation in air provides the unsymmetrical dimer **22**. On the other hand, ketyl radical **30** can also undergo a homodimerization or a 1,2-addition to the carbonyl group of **10**, which in both cases ultimately leads to the diketone **23**. Although we cannot exclude the presence of the C3-centered carbon radical **31**, the dimer product **32** was not detected.

In view of the biological relevance of derivatized indoles, two further indoles were examined (Scheme 7). The *N*,*O*-dibenzyl-5-hydroxy indole **12** was also subjected to treatment with SmI_2. The novel dimers **24** and **25** were obtained in 57 and 18% yield, respectively, and as before, the asymmetrical dimer **24** was poorly stable. The indole **13** was also examined, and once again, the reaction proceeded smoothly giving the two dimers **26** and **27** in 38 and 10% yield, respectively. Interestingly, this dimerization gave better results when water was omitted from the reaction, affording the two dimers in a yield of 55 and 11%, respectively. Fortuitously, both crystallinity and stability of compounds **26** and **27** appeared to be improved by the additional oxygen substitution of the indole. This allowed X-ray crystal structures to be obtained for both products (see Supporting Information), confirming our proposed structural assignment. Once again, decomposition was easily promoted, and treating a sample of **26** in CH_2Cl_2 with a single drop of 0.1 M HCl gave the familiar deep red insoluble solid. While we presume this compound to possess a similar structure to that presented for compound **28** above, no suitable crystals could be grown for X-ray crystallography, and thus no structural assignment has been included here.

For all three of the above dimerization reactions, it is expected that the yield of the asymmetrical dimer would be higher than that reported due to its low stability causing some losses upon workup and isolation. This was highlighted experimentally by a significant variation in yields between what were essentially repeat experiments.

Finally, to satisfy our own curiosity, the indole-3-oxazolidinone **16** was also prepared and examined (Scheme 10). Treatment of **16** with SmI_2 and H_2O as before gave a reaction that proceeded at a much slower rate (significant recovered starting material after 18 h) when compared with its 2-substituted counterpart, giving a complicated mixture of products, none of which could be assigned to the expected products **33** and **34**.[20] For this reason, we elected to examine its addition to an activated alkene. The coupling reaction with *tert*-butyl acrylamide using standard conditions[8] afforded the product **35** in 55% yield (74% based on recovered **16**). Such a difference in the reactivity of the 2- and 3-substituted indoles was not surprising when considering the significant steric and electronic difference between the two systems.

The pyrrole oxazolidinone **20** also underwent coupling with an activated alkene. In this case, *n*-butyl acrylate was used, which afforded γ-keto ester **36** with a coupling yield of 52% under standard conditions (Scheme 11). Taken together, these two results indicate that the dimerization process is unique to the 2-substituted indole oxazolidinones.

In conclusion, we have presented a new indole dimerization reaction which is promoted by SmI_2. The products obtained in

(16) Su, J.-Y.; Zhu, Y.; Zeng, L.-M.; Xu, X.-H. *J. Nat. Prod.* **1997**, *60*, 1043.

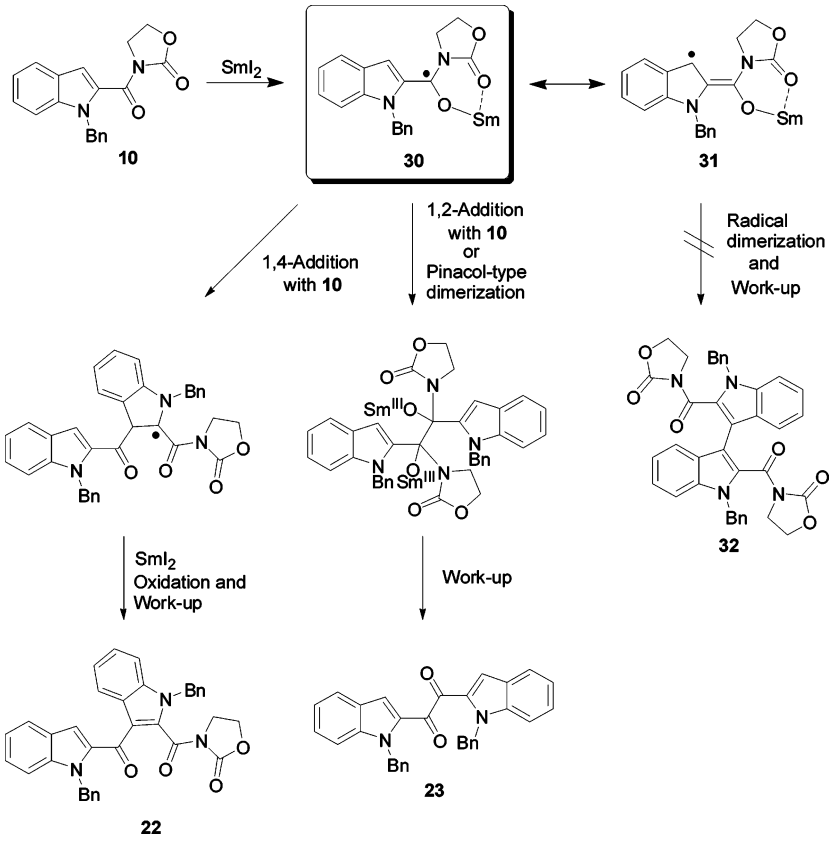
(17) For previous syntheses of caulersin, see: (a) Fresneda, P. M.; Molina, P.; Saez, M. A. *Synlett* **1999**, 1651. (b) Wahlström, N.; Stensland, B.; Bergman, J. *Tetrahedron* **2004**, *60*, 2147. (c) Miki, Y.; Aoki, Y.; Miyatake, H.; Minematsu, T.; Hibino, H. *Tetrahedron Lett.* **2006**, *47*, 5215.

(18) (a) Whitlock, J. P., Jr. *Annu. Rev. Pharmacol. Toxicol.* **1999**, *39*, 103. (b) Nebert, D. W.; Roe, A. L.; Dieter, M. Z.; Solis, W. A.; Yang, Y.; Dalton, T. P. *Biochem. Pharmacol.* **2000**, *59*, 65.

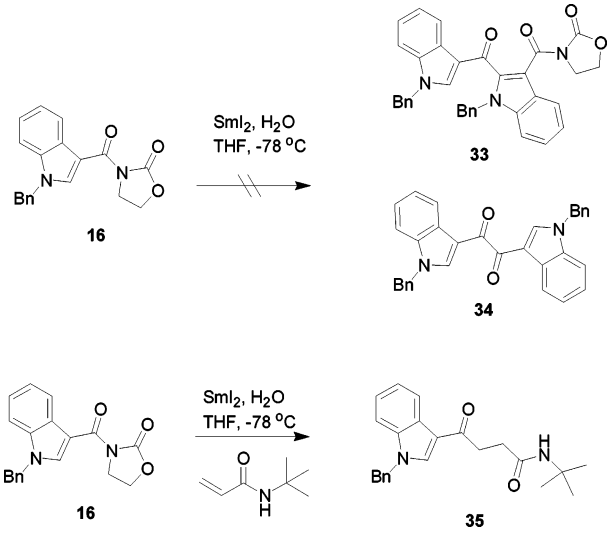
(19) Bergman, J.; Wahlström, N.; Yudina, L. N.; Tholander, J.; Lidgren, G. *Tetrahedron* **2002**, *58*, 1443.

(20) Interestingly, dimerization reactions involving the C2-position have previously been observed in SmI_2-promoted coupling reactions of indole-3-carbonyl compounds. Lin, S.-C; Yang, F.-D.; Shiue, J.-S.; Yang, S.-M.; Fang, J.-M. *J. Org. Chem.* **1998**, *63*, 2909.

SCHEME 9



SCHEME 10

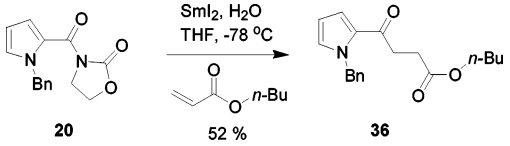


this process are both novel and exotic, and in view of the prominence of indoles within biologically relevant compounds, we expect considerable further interest in this class of compounds.

Experimental Section

***S*-Pyridin-4-yl 1-Benzyl-1*H*-indole-2-carbothioate (9).** The indole acid **1** (100 mg, 0.398 mmol) was dissolved in CH_2Cl_2 (10 mL) before 4-mercaptopyridine (88 mg, 0.792 mmol) and EDC·HCl (172 mg, 0.897 mmol) were added. The mixture was stirred at 20 °C for 3 h, then poured into 5% $NaHCO_3$ (40 mL) and extracted with CH_2Cl_2 (3 × 20 mL). The combined organic portions were dried ($MgSO_4$), filtered, and evaporated in vacuo. The pure product was obtained by column chromatography (increasing polarity from 20 to 40% EtOAc in pentane as eluant), which gave the title compound (115 mg, 0.319 mmol, 80%): ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.65 (dd, J = 4.8, 1.6 Hz, 2H), 7.77 (d, J = 7.6 Hz, 1H), 7.67 (s, 1H), 7.45 (dd, J = 4.0, 1.2 Hz, 2H), 7.33−7.38 (m, 2H), 7.18−7.27 (m, 4H), 7.02 (d, J = 6.4 Hz, 2H), 5.74 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 179.7, 150.0 (2C), 140.1, 138.4, 137.4, 132.4, 128.5 (2C), 128.2 (2C), 127.2, 126.7, 126.1 (2C), 126.0, 123.0, 121.5, 112.3, 111.0, 48.1.

SCHEME 11



3-(1-Benzyl-1*H*-indole-2-carbonyl)oxazolidin-2-one (10). Method A: *n*-BuLi (2.8 mL, 4.48 mmol, 1.60 M in THF) was dissolved in THF (3 mL), then the solution was cooled to −78 °C. A solution of 2-oxazolidinone (396 mg, 4.549 mmol) in THF (5 mL) was then added dropwise over 10 min, and the solution was stirred for a further 30 min. A solution of PFP ester **38** (2.08 g, 4.98 mmol) in THF (7 mL) was then added dropwise over 5 min, and the mixture was stirred at −78 °C for 1 h before it was poured into water (50 mL) and extracted with EtOAc (3 × 50 mL). The combined organic portions were dried ($MgSO_4$), filtered, and evaporated in vacuo. The pure product was obtained by column chromatography (increasing polarity from 10 to 60% EtOAc in pentane as eluant), which gave the title compound (1.00 g, 3.12 mmol, 70%) as a colorless solid. **Method B:** The indole acid **1** (1.50 g, 5.97 mmol) was dissolved in CH_2Cl_2 (25 mL), then DMF (three drops) and oxalyl chloride (1.30 mL, 14.93 mmol) were added. The mixture was stirred at 20 °C for 1 h, by which time gas evolution had ceased. All volatiles were removed in vacuo, giving the crude acid chloride

which was used immediately without further purification. In a separate flask, 2-oxazolidinone (779 mg, 8.95 mmol) was dissolved in THF (20 mL), and then the solution was cooled to 0 °C before *n*-BuLi (1.60 M in hexanes, 5.60 mL, 8.96 mmol) was added. This mixture was stirred at 0 °C for 1 h, then a solution of the acid chloride (5.97 mmol) in THF (10 mL) was added dropwise over 5 min. The mixture was stirred at 0 °C for 1 h, then poured into water (50 mL) and extracted with EtOAc (3 × 20 mL). The combined organic portions were dried ($MgSO_4$), filtered, and evaporated to dryness. The pure product was obtained by column chromatography (increasing polarity from 20 to 60% EtOAc in pentane as eluant), which gave the title compound (1.32 g, 4.11 mmol, 69%) as a colorless solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.71 (d, J = 8.0 Hz, 1H), 7.12−7.32 (m, 7H), 7.04−7.08 (m, 2H), 5.67 (s, 2H), 4.42 (t, J = 8.0 Hz, 2H), 4.08 (t, J = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 162.2, 153.2, 139.5, 137.9, 128.6 (3C), 127.2, 126.2 (2C), 126.0, 125.7, 123.0, 120.9, 112.9, 110.7, 62.1, 48.0, 43.8. HRMS $C_{19}H_{16}N_2O_3$ [M + Na^+]: calcd 343.1059, found 343.1049.

3-(1-Allyl-1*H*-indole-2-carbonyl)oxazolidin-2-one (11). Method A: *n*-BuLi (1.2 mL, 1.92 mmol, 1.60 M in THF) was dissolved in THF (3 mL), and then the solution was cooled to −78 °C. To this was added dropwise a solution of 2-oxazolidinone (170 mg, 1.95 mmol) in THF (3 mL) over 10 min, then the solution was stirred for a further 30 min. A solution of PFP ester **39** (900 mg, 2.45 mmol) in THF (3 mL) was then added dropwise over 5 min, and the mixture was stirred at −78 °C for 2 h before it was poured into water (50 mL) and extracted with EtOAc (3 × 50 mL). The combined organic portions were dried ($MgSO_4$), filtered, and evaporated in vacuo. The pure product was obtained by column chromatography (30% EtOAc in pentane as eluant), which gave the title compound (410 mg, 1.52 mmol, 79%) as a colorless solid. **Method B:** The indole acid **2** (3.66 g, 11.42 mmol) was dissolved in CH_2Cl_2 (50 mL), then DMF (five drops) and oxalyl chloride (2.50 mL, 28.5 mmol) were added. The mixture was stirred at 20 °C for 1 h, by which time gas evolution had ceased, then all volatiles were removed in vacuo, giving the crude acid chloride, which was used immediately without further purification. In a separate flask, 2-oxazolidinone (1.49 g, 17.12 mmol) was dissolved in THF (30 mL), then the solution was cooled to 0 °C before *n*-BuLi (1.60 M in hexanes, 10.7 mL, 17.12 mmol) was added. This mixture was stirred at 0 °C for 1 h, after which a solution of the acid chloride (11.4 mmol) in THF (12 mL) was added dropwise over 5 min. The mixture was stirred at 0 °C for 1 h, then poured into water (50 mL) and extracted with EtOAc (3 × 30 mL). The combined organic portions were dried ($MgSO_4$), filtered, and evaporated to dryness. The pure product was obtained by column chromatography (increasing polarity from 20 to 60% EtOAc in pentane as eluant), which gave the title compound (1.94 g, 7.18 mmol, 63%) as a colorless solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.68 (d, J = 8.0 Hz, 1H), 7.30−7.38 (m, 2H), 7.23 (s, 1H), 7.15 (ddd, J = 8.4, 6.4, 2.0 Hz, 1H), 6.01 (ddt, J = 17.2, 10.0, 5.2 Hz, 1H), 5.13 (dd, J = 10.0, 1.2 Hz, 1H), 5.02−5.06 (m, 2H), 4.98 (dd, J = 17.2, 1.2 Hz, 1H), 4.49 (t, J = 8.0 Hz, 2H), 4.17 (t, J = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 161.9, 153.1, 138.9, 133.5, 128.2, 125.6, 125.3, 122.7, 120.6, 116.2, 112.3, 110.4, 62.0, 46.7, 43.7. HRMS $C_{15}H_{14}N_2O_3$ [M + Na^+]: calcd 293.0902, found 293.0905.

3-(1-Benzyl-5-(benzyloxy)-1*H*-indole-2-carbonyl)oxazolidin-2-one (12). The indole acid **3** (456 mg, 1.28 mmol) was dissolved in CH_2Cl_2 (20 mL), and DMF (3 drops) and oxalyl chloride (0.35 mL, 4.00 mmol) were added. The mixture was stirred at 20 °C for 1 h, by which time gas evolution had ceased. All volatiles were removed in vacuo, giving the crude acid chloride, which was used immediately without further purification. In a separate flask, 2-oxazolidinone (278 mg, 3.19 mmol) was dissolved in THF (10 mL), then the solution was cooled to 0 °C before *i*-PrMgCl (2 M in THF, 1.55 mL, 3.10 mmol) was added. This mixture was stirred at 0 °C for 30 min, after which a solution of the acid chloride (1.28 mmol) in THF (10 mL) was added dropwise over 5 min. The mixture was stirred at 0 °C for 2 h, then at 20 °C for 2 h, before it was poured into water (50 mL) and extracted with $CHCl_3$ (4 × 25 mL). The combined organic portions were dried ($MgSO_4$), filtered, and evaporated to dryness. The pure product was obtained by column chromatography (applied in 2 mL of DMF, increasing polarity from 20 to 100% EtOAc in pentane as eluant), which gave the title compound (354 mg, 0.830 mmol, 65%) as a colorless solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.14−7.48 (m, 11H), 7.02−7.08 (m, 3H), 5.63 (s, 2H), 5.09 (s, 2H), 4.43 (t, J = 7.6 Hz, 2H), 4.08 (t, J = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 162.0, 154.0, 153.2, 137.9, 137.5, 128.8, 128.6 (3C), 128.5 (3C), 127.9, 127.5 (2C), 127.2, 126.1 (2C), 118.1, 112.4, 111.7, 104.4, 70.6, 62.1, 48.2, 43.9. HRMS $C_{26}H_{22}N_2O_4$ [M + Na^+]: calcd 449.1477, found 449.1471.

3-(5-Benzyl-5*H*-[1,3]dioxolo[4,5-*f*]indole-6-carbonyl)oxazolidin-2-one (13). The indole acid **4** (1.72 g, 5.82 mmol) was dissolved in CH_2Cl_2 (30 mL), and DMF (four drops) and oxalyl chloride (1.27 mL, 14.50 mmol) were added. The mixture was stirred at 20 °C for 1 h, by which time gas evolution had ceased, then all volatiles were removed in vacuo, giving the crude acid chloride, which was used immediately without further purification. In a separate flask, 2-oxazolidinone (1.013 g, 11.636 mmol) was dissolved in THF (30 mL), then the solution was cooled to 0 °C before *i*-PrMgCl (2 M in THF, 5.82 mL, 11.69 mmol) was added. This mixture was stirred at 0 °C for 30 min, then a solution of the acid chloride (5.82 mmol) in THF (15 mL) was added dropwise over 5 min. The mixture was stirred at 0 °C for 2 h, then at 20 °C for 2 h, before it was poured into water (100 mL) and extracted with EtOAc (3 × 30 mL). The combined organic portions were dried ($MgSO_4$), filtered, and evaporated to dryness. The pure product was obtained by column chromatography (increasing polarity from 10 to 60% EtOAc in pentane, then 30 to 50% EtOAc in CH_2Cl_2 as eluant), which gave the title compound (1.35 g, 3.70 mmol, 64%) as a colorless solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.15−7.30 (m, 4H), 7.05 (d, J = 7.6 Hz, 2H), 6.99 (s, 1H), 6.65 (s, 1H), 5.93 (s, 2H), 5.60 (s, 2H), 4.44 (t, J = 7.6 Hz, 2H), 4.09 (t, J = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 161.4, 153.6, 148.5, 144.4, 137.7, 136.4, 128.6 (3C), 127.2, 126.1 (2C), 120.2, 114.2, 101.1, 100.1, 90.9, 62.2, 48.4, 44.0. HRMS $C_{20}H_{16}N_2O_5$ [M + Na^+]: calcd 387.0957, found 387.0950.

Perfluorophenyl 1-Benzyl-1*H*-indole-3-carboxylate (15). The indole-3-carboxylic acid **14** (500 mg, 1.99 mmol) was dissolved in CH_2Cl_2 (16 mL) then pentafluorophenol (521 mg, 2.83 mmol), EDC·HCl (664 mg, 3.46 mmol), and DMAP (12 mg, 0.098 mmol) were added. The mixture was stirred at 20 °C for 18 h, then poured into water (50 mL) and extracted with CH_2Cl_2 (3 × 20 mL). The combined organic portions were dried ($MgSO_4$), filtered, and evaporated in vacuo. The pure product was obtained by column chromatography (increasing polarity from 2 to 10% EtOAc in pentane as eluant), which gave the title compound (682 mg, 1.63 mmol, 82%) as a colorless solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.20 (d, J = 7.6 Hz, 1H), 8.07 (s, 1H), 7.20−7.41 (m, 8H), 5.40 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 160.1, 143.2 (br), 140.7 (br, 2C), 139.4 (br, 2C), 138.2 (br), 137.2, 136.7, 135.4, 129.4 (2C), 128.7, 127.4 (2C), 127.1, 124.0, 123.2, 121.9, 111.0, 104.3, 51.4. HRMS $C_{22}H_{12}F_5NO_2$ [M + Na^+]: calcd 440.0686, found 440.0680.

3-(1-Benzyl-1*H*-indole-3-carbonyl)oxazolidin-2-one (16). *n*-BuLi (5.2 mL, 8.32 mmol, 1.60 M in THF) was dissolved in THF (33 mL), then the solution was cooled to −78 °C. To this was added dropwise a solution of 2-oxazolidinone (1.014 g, 11.65 mmol) in THF (33 mL) over 20 min, after which the solution was stirred for a further 60 min. A solution of PFP ester **15** (1.67 g, 4.16 mmol) in THF (33 mL) was added dropwise over 5 min. The mixture was stirred at −78 °C for 30 min, then at 20 °C for 2 h, by which time TLC indicated complete consumption of **15**. The mixture was poured into water (50 mL) and saturated NaCl (50 mL) and extracted with EtOAc (3 × 50 mL), then the combined organic portions were dried ($MgSO_4$), filtered, and evaporated in vacuo.

The pure product was obtained by column chromatography (increasing polarity from 10 to 60% EtOAc in pentane as eluant), which gave 1.01 g of product approximately 95% pure, followed by recrystallization from CH_2Cl_2/pentane which gave 856 mg (2.68 mmol, 64%) as a colorless solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.25 (d, J = 8.0 Hz, 1H), 8.16 (s, 1H), 7.17−7.32 (m, 8H), 5.36 (s, 2H), 4.48 (t, J = 8.0 Hz, 2H), 4.22 (t, J = 7.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 163.7, 154.4, 137.6, 136.4, 136.0, 129.2 (2C), 128.6, 128.4, 127.3 (2C), 123.5, 122.8, 122.3, 110.6, 107.4, 62.5, 51.2, 44.4. HRMS $C_{19}H_{16}N_2O_3$ [M + Na^+]: calcd 343.1059, found 343.1048.

***S*-Pyridin-4-yl 1-Benzyl-1*H*-pyrrole-2-carbothioate (19).** *N*-Benzyl pyrrole-2-carboxylic acid **18** (150 mg, 0.745 mmol) was dissolved in CH_2Cl_2 (9 mL), after which the solution was cooled to 0 °C before 4-mercaptopyridine (88 mg, 0.792 mmol) and EDC·HCl (172 mg, 0.897 mmol) were added. The mixture was stirred at 0 °C for 10 min, then at 20 °C for 4 h, before it was diluted with CH_2Cl_2 (30 mL), washed with 5% $NaHCO_3$ (30 mL) and water (30 mL), dried over $MgSO_4$, filtered, and evaporated in vacuo. The pure product was obtained by column chromatography (30% EtOAc in pentane as eluant), which gave the title compound (116 mg, 0.394 mmol, 53%) as a colorless solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.61 (d, J = 6.4 Hz, 2H), 7.42 (d, J = 6.4 Hz, 2H), 7.23−7.34 (m, 4H), 7.08 (d, J = 8.0 Hz, 2H), 6.99 (dd, J = 2.4, 1.6 Hz, 1H), 6.26 (dd, J = 4.0, 2.8 Hz, 1H), 5.48 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 176.6, 149.7 (2C), 139.0, 137.1, 131.1, 128.6 (2C), 128.2 (3C), 127.6, 126.9 (2C), 119.9, 109.6, 52.3.

3-(1-Benzyl-1*H*-pyrrole-5-carbonyl)oxazolidin-2-one (20). A solution of *n*-BuLi (2.2 mL, 3.52 mmol, 1.6 M in THF) in THF (4 mL) was cooled to −78 °C, then 2-oxazolidinone (307 mg, 3.53 mmol) in THF (7 mL) was added dropwise over 10 min. The mixture was stirred at −78 °C for 30 min, then the PFP ester **37** (1.43 g, 3.89 mmol) dissolved in THF (5 mL) was added via syringe and the mixture stirred for a further 3 h. The mixture was poured into saturated NH_4Cl (40 mL) and extracted with EtOAc (3 × 25 mL), then the combined organic portions were dried ($MgSO_4$), filtered, and evaporated in vacuo. The pure product was obtained by column chromatography (40% CH_2Cl_2 in pentane as eluant), which gave the title compound (800 mg, 2.96 mmol, 84%) as a colorless solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.22−7.34 (m, 3H), 7.11 (d, J = 7.2 Hz, 2H), 7.01−7.03 (m, 1H), 6.91−6.94 (m, 1H), 6.23 (dd, J = 4.8, 3.2 Hz, 1H), 5.48 (s, 2H), 4.41 (t, J = 7.6 Hz, 2H), 4.04 (t, J = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 160.5, 153.6, 137.9, 130.4, 128.6 (2C), 127.5, 126.8 (2C), 123.2, 121.6, 108.7, 62.1, 52.1, 43.9. HRMS $C_{15}H_{14}N_2O_3$ [M + Na^+]: calcd 293.0902, found 293.0906.

Perfluorophenyl 1-Benzyl-1*H*-pyrrole-2-carboxylate (37). *N*-Benzyl pyrrole-2-carboxylic acid **18** (150 mg, 0.746 mmol) was dissolved in CH_2Cl_2 (9 mL), after which pentafluorophenol (143 mg, 0.777 mmol) and EDC·HCl (172 mg, 0.897 mmol) were added. The mixture was stirred at 20 °C for 18 h, then poured into 5% $NaHCO_3$ (40 mL) and extracted with CH_2Cl_2 (3 × 20 mL). The combined organic portions were dried ($MgSO_4$), filtered, and evaporated in vacuo. The pure product was obtained by column chromatography (5% EtOAc in pentane as eluant), which gave the title compound (233 mg, 0.624 mmol, 85%) as a colorless solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.27−7.38 (m, 4H), 7.17 (d, J = 1.6 Hz, 1H), 7.15 (d, J = 0.8 Hz, 1H), 7.08 (t, J = 1.6 Hz, 1H), 6.33 (dd, J = 4.4, 2.8 Hz, 1H), 5.55 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 156.2, 142.8 (br), 140.3 (br, 2C), 139.0 (br, 2C), 137.1, 136.6 (br), 131.6, 128.7 (2C), 127.8, 127.0 (2C), 121.1, 118.7, 109.6, 52.3.

Perfluorophenyl 1-Benzyl-1*H*-indole-2-carboxylate (38). The indole acid **1** (1.50 g, 5.97 mmol) was dissolved in CH_2Cl_2 (22 mL), and the solution was cooled to 0 °C before pentafluorophenol (1.15 g, 6.25 mmol), EDC·HCl (1.37 g, 7.15 mmol), and DMAP (145 mg, 1.19 mmol) were added. The mixture was stirred at 0 °C for 10 min, then at 20 °C for 3 h, before it was diluted with CH_2Cl_2 (40 mL), washed with saturated $NaHCO_3$ (3 × 30 mL) and water (30 mL), dried over $MgSO_4$, filtered, and evaporated in vacuo to give the crude title compound (2.08 g, 4.98 mmol, 83%), which was used without further purification or analysis. HRMS $C_{22}H_{12}F_5NO_2$ [M + Na^+]: calcd 440.0686, found 440.0662.

Perfluorophenyl 1-Allyl-1*H*-indole-2-carboxylate (39). The indole acid **2** (1.20 g, 5.96 mmol) was dissolved in CH_2Cl_2 (22 mL), after which the solution was cooled to 0 °C before pentafluorophenol (1.15 g, 6.25 mmol), EDC·HCl (1.37 g, 7.15 mmol), and DMAP (145 mg, 1.19 mmol) were added. The mixture was stirred at 0 °C for 10 min, then at 20 °C for 3 h, before it was diluted with CH_2Cl_2 (50 mL), washed with saturated $NaHCO_3$ (3 × 30 mL) and then water (30 mL), dried over $MgSO_4$, filtered, and evaporated in vacuo to give the crude title compound (1.98 g, 5.39 mmol, 90%), which was used without further purification or analysis.

General Procedure for Dimerization. The starting indole oxazolidinone (0.45 mmol) was dissolved in THF (7.5 mL), and any additives were added before the solution was cooled to −78 °C under an atmosphere of argon. To this was added dropwise a solution of SmI_2 (0.1 M solution in THF, 15 mL, 1.50 mmol) over 5−10 min. The mixture was stirred at −78 °C for 18 h, then the flask was flushed with O_2 to quench excess SmI_2. The mixture was poured into saturated aqueous $Na_2S_2O_3$ and extracted with EtOAc (3 × 20 mL), then the combined organic portions were dried ($MgSO_4$), filtered, and evaporated in vacuo. The pure products were obtained from the crude orange oil by column chromatography using the stated solvent system.

3-(1-Benzyl-3-(1-benzyl-1*H*-indole-2-carbonyl)-1*H*-indole-2-carbonyl)oxazolidin-2-one (22) and 1,2-Bis(1-benzyl-1*H*-indol-2-yl)ethane-1,2-dione (23). The indole oxazolidinone **10** (144 mg, 0.450 mmol) was reacted according to the general procedure for dimerization except that water (54 μL, 3.00 mmol) was added. Increasing polarity from 5 to 50% EtOAc in pentane was used as the eluant for column chromatography, which gave the asymmetrical dimer **22** (89 mg, 0.161 mmol, 71%) as an oil and the symmetrical dimer **23** (24 mg, 0.051 mmol, 23%) as a yellow solid. For compound **22**: ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.00 (d, J = 8.0 Hz, 1H), 7.69 (d, J = 8.0 Hz, 1H), 7.12−7.38 (m, 17H), 5.74 (br s, 2H), 5.48 (br s, 2H), 3.50−4.00 (br m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 182.4, 161.9, 151.5, 139.2, 138.1, 137.0, 136.8, 135.8, 135.4, 128.6 (2C), 128.4 (2C), 127.8, 127.0, 126.9 (2C), 126.6 (2C), 126.3, 125.5, 125.4, 124.6, 122.8, 122.7, 122.6, 120.8, 119.3, 112.9, 110.9, 110.7, 62.0, 48.4, 47.9, 42.5. HRMS $C_{35}H_{27}N_3O_4$ [M + Na^+]: calcd 576.1899, found 576.1907. For compound **23**: ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.61 (d, J = 8.4 Hz, 2H), 7.36−7.45 (m, 4H), 7.25−7.34 (m, 6H), 7.10−7.18 (m, 6H), 7.03 (s, 2H), 5.96 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 185.5 (2C), 141.0 (2C), 137.9 (2C), 130.8 (2C), 128.7 (4C), 127.6 (2C), 127.4 (2C), 126.6 (4C), 126.4 (2C), 123.7 (2C), 121.4 (2C), 118.1 (2C), 110.9 (2C), 48.3 (2C). HRMS $C_{32}H_{24}N_2O_2$ [M + Na^+]: calcd 491.1735, found 491.1750.

3-(1-Benzyl-3-(1-benzyl-5-(benzyloxy)-1*H*-indole-2-carbonyl)-5-(benzyloxy)-1*H*-indole-2-carbonyl)oxazolidin-2-one (24) and 1,2-Bis(1-benzyl-5-(benzyloxy)-1*H*-indol-2-yl)ethane-1,2-dione (25). The indole oxazolidinone **12** (191 mg, 0.450 mmol) was reacted according to the general procedure for dimerization, except that water (54 μL, 3.00 mmol) was added. Increasing polarity from 10 to 75% EtOAc in pentane was used as the eluant for column chromatography, which gave the asymmetrical dimer **24** (85 mg, 0.111 mmol, 49%) as an oil and the symmetrical dimer **25** (27 mg, 0.040 mmol, 18%) as a yellow solid. For compound **24**: ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.68 (d, J = 2.0 Hz, 1H), 7.47 (d, J = 7.2 Hz, 2H), 7.03−7.42 (m, 24H), 5.50−5.80 (br s, 2H), 5.44 (s, 2H), 5.10 (s, 2H), 5.01 (s, 2H), 3.15−3.85 (br m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 182.3, 161.7, 155.6, 153.8, 151.4, 138.1, 137.7, 137.1, 137.0, 135.9, 135.4, 134.5, 132.4, 128.7 (2C), 128.5 (4C), 128.4 (2C), 127.8 (2C), 127.8, 127.5 (2C), 127.5 (2C), 127.1, 126.8 (2C), 126.6 (2C), 126.6, 126.5,119.0, 117.3, 116.5, 111.9, 111.6, 111.1, 104.7, 104.3, 70.5, 70.5, 61.9, 48.6, 48.1, 42.5. HRMS $C_{49}H_{39}N_3O_6$ [M + Na^+]: calcd 788.2737, found 788.2737.

For compound **25**: ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.00−7.48 (m, 26H), 6.92 (s, 2H) 5.91 (s, 4H), 5.08 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 185.4 (2C), 154.1 (2C), 138.0 (2C), 137.0 (2C), 136.8 (2C), 131.1 (2C), 128.7 (4C), 128.6 (4C), 128.4 (2C), 127.9 (2C), 127.4 (4C), 127.3 (2C), 126.5 (4C), 120.3 (2C), 117.3 (2C), 111.9 (2C), 104.4 (2C), 70.6 (2C), 48.4 (2C). HRMS $C_{46}H_{36}N_2O_4$ [M + Na^+]: calcd 703.2573, found 703.2578.

3-(5-Benzyl-7-(5-benzyl-5*H*-[1,3]dioxolo[4,5-*f*]indole-6-carbonyl)-5*H*-[1,3]dioxolo[4,5-*f*]indole-6-carbonyl)oxazolidin-2-one (26) and 1,2-Bis(5-benzyl-5*H*-[1,3]dioxolo[4,5-*f*]indol-6-yl)ethane-1,2-dione (27). The indole oxazolidinone **13** (164 mg, 0.450 mmol) was reacted according to the general procedure for dimerization. Increasing polarity from 10 to 75% EtOAc in pentane was used as the eluant for column chromatography, which gave the asymmetrical dimer **26** (79 mg, 0.123 mmol, 55%) as an amber gum and the symmetrical dimer **27** (14 mg, 0.025 mmol, 11%) as a yellow solid. For compound **26**: ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.34 (s, 1H), 7.10−7.32 (m, 10H), 7.06 (s, 1H), 6.98 (s, 1H), 6.71 (s, 2H), 5.94 (s, 4H), 5.50−5.75 (br m, 2H), 5.41 (br s, 2H), 3.50−4.05 (br m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 181.2, 161.8, 151.8, 148.2, 147.2, 145.2, 144.2, 138.0, 136.5, 135.9, 135.8, 133.0, 132.5, 128.8 (2C), 128.5 (2C), 127.8, 127.1, 126.7 (2C), 126.6 (2C), 120.8, 120.4, 120.3, 113.9, 101.2, 101.1, 100.7, 100.1, 91.0, 90.9, 62.0, 48.6, 48.3, 42.9. HRMS $C_{37}H_{27}N_3O_8$ [M + Na^+]: calcd 664.1696, found 664.1694. For compound **27**: ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.24−7.34 (m, 6H), 7.11 (d, J = 7.2 Hz, 4H), 6.93 (s, 2H), 6.87 (s, 2H), 6.75 (s, 2H), 5.97 (s, 4H), 5.87 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 184.3 (2C), 149.9 (2C), 144.8 (2C), 138.1 (2C), 137.8 (2C), 130.2 (2C), 128.7 (4C), 127.3 (2C), 126.5 (4C), 120.9 (2C), 118.2 (2C), 101.4 (2C), 100.1 (2C), 90.5 (2C), 48.5 (2C). HRMS $C_{34}H_{24}N_2O_6$ [M + Na^+]: calcd 579.1532, found 579.1541.

4-(1-Benzyl-1*H*-indol-3-yl)-*N*-*tert*-butyl-4-oxobutanamide (35). The indole oxazolidinone **16** (107 mg, 0.333 mmol) and *tert*-butylacrylamide (60 mg, 0.500 mmol) were dissolved in THF (4 mL), then water (48 μL, 2.66 mmol) was added before the solution was cooled to −78 °C under an atmosphere of argon. To this was added dropwise a solution of SmI_2 (0.1 M solution in THF, 10 mL, 1.00 mmol) over 15−20 min. The mixture was stirred at −78 °C for 18 h, then the flask was flushed with O_2 to quench excess SmI_2. The mixture was poured into saturated aqueous $Na_2S_2O_3$ (30 mL) and extracted with EtOAc (3 × 20 mL), then the combined organic portions were dried ($MgSO_4$), filtered, and evaporated in vacuo. The pure product was obtained by column chromatography (increasing polarity from 5 to 40% Et_2O in 1:1 CH_2Cl_2/pentane as eluant), which gave the title compound (66 mg, 0.182 mmol, 55%) as a colorless solid and recovered **16** (20 mg, 0.062 mmol, 19%): ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.38 (d, J = 7.8 Hz, 1H), 7.85 (s, 1H), 7.14−7.33 (m, 8H), 5.79 (br s, 1H), 5.32 (s, 2H), 3.20 (t, J = 6.8 Hz, 2H), 2.56 (t, J = 6.8 Hz, 2H), 1.32 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 194.6, 172.2, 137.3, 135.9, 135.2, 129.3 (2C), 128.5, 127.3 (2C), 126.7, 123.7, 122.9, 122.8, 116.9, 110.4, 51.3, 51.0, 35.4, 32.0, 29.0 (3C). HRMS $C_{23}H_{26}N_2O_2$ [M + Na^+]: calcd 385.1892, found 385.1898.

***n*-Butyl 4-(1-Benzyl-1*H*-pyrrol-2-yl)-4-oxobutanoate (36).** The pyrrole oxazolidinone **20** (50 mg, 0.185 mmol) was dissolved in THF (3.5 mL), then water (20 μL, 1.110 mmol) and *n*-butylacrylate (80 μL, 0.55 mmol) were added before the solution was cooled to −78 °C under an atmosphere of argon. To this was added dropwise a solution of SmI_2 (0.1 M solution in THF, 10 mL, 1.00 mmol) over 15−20 min. The mixture was stirred at −78 °C for 18 h, then the flask was flushed with O_2 to quench excess SmI_2. The mixture was poured into saturated aqueous $Na_2S_2O_3$ (30 mL) and extracted with EtOAc (3 × 20 mL), then the combined organic portions were dried ($MgSO_4$), filtered, and evaporated in vacuo. The pure product was obtained by column chromatography (10% EtOAc in pentane as eluant), which gave the title compound (30 mg, 0.096 mmol, 52%) as a colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.20−7.31 (m, 3H), 7.05−7.10 (m, 3H), 6.89 (dd, J = 2.4, 1.6 Hz, 1H), 6.19 (dd, J = 4.0, 1.6 Hz, 1H), 5.58 (s, 2H), 4.06 (t, J = 6.8 Hz, 2H), 3.13 (t, J = 6.8 Hz, 2H), 2.66 (t, J = 6.8 Hz, 2H), 1.58 (pent, J = 7.2 Hz, 2H), 1.36 (sext, J = 7.6 Hz, 2H), 0.91 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 188.8, 173.3, 138.4, 130.6 (2C), 130.0, 128.8 (2C), 127.6, 127.3, 119.9, 108.9, 64.7, 52.7, 33.9, 30.8, 28.8, 19.3, 13.9. HRMS $C_{19}H_{23}NO_3$ [M + Na^+]: calcd 336.1576, found 336.1569.

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Supporting Information Available: Experimental details and copies of ^{1}H NMR and ^{13}C NMR spectra for compounds **9**−**13**, **15**, **16**, **19**, **20**, **22**−**27**, and **35**−**37**. CIF files for compounds **23** and **26**−**28**. This material is available free of charge via the Internet at http://pubs.acs.org.

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