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A Thermal Cascade Route to Pyrroloisoindolone and Pyrroloimidazolones

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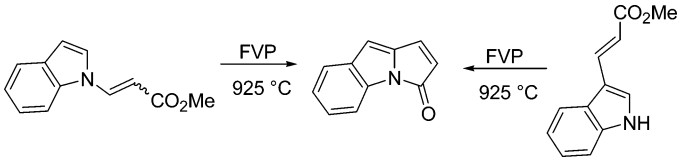

Flash vacuum pyrolysis (FVP) of indol-1-ylacrylate derivatives **11** and **15** or the isomeric indol-3-ylacrylates **21**, **22**, and **24** at 925 °C (0.05 Torr) provides pyrrolo[1,2-*a*]indol-3-ones **2**, **18**, **28**, and **29** in 53−90% yield by a cascade mechanism that involves a sigmatropic migration, elimination, electrocyclization sequence. Pyrrolo[1,2-*a*]imidazol-5-ones **3** and pyrrolo[1,2-*c*]imidazol-5-ones **4** were similarly obtained by FVP of corresponding 2,5-unsubstituted imidazol-1-ylacrylates (e.g., **33**), with the former isomer predominating in ca. 80:20 ratio. Migration to the 2-position is therefore favored in the initial sigmatropic shift. FVP of 2-substituted imidazol-1-ylacrylates **35**, **37**, and **51** (825−875 °C) instead give pyrrolo[1,2-*c*]imidazol-5-ones **56**−**58** only (88−91%), and that of 4,5-disubstituted imidazol-1-ylacrylates **39** and **41** (825−850 °C) provide pyrrolo[1,2-*a*]imidazol-5-ones **59** and **60** exclusively (93−95%), and thus the selectivity of the initial shift can be controlled by the presence of substituents on the imidazole 2- and 5-positions. FVP of the benzimidazole analogues **61** and **62** at 950 °C gave the pyrrolo[1,2-*a*]-benzimidazol-1-ones **6** (71%) and **63** (36%), respectively.

Introduction

The pyrrolizin-3-one ring system **1**[1] and its analogues are of interest because of their formally antiaromatic[2] nature and because of the biological activity of their derivatives. Thus, reduced pyrrolizines (pyrrolizidines) form the carbon skeleton of the necine bases of pyrrolizidine alkaloids,[3] and the skeleton of pyrrolo[1,2-*a*]indol-3-one **2** (a benzopyrrolizinone) is related to that of the mitomycin series of antibiotics.[4] Azapyrrolizinone systems **3** and **4** are highly reactive cyclic *N*-acylimidazoles, and the pyrrolo[1,2-*c*]imidazol-5-one system **4** is essentially a dehydrated form of *Z*-urocanic acid which is implicated in immunosuppressive activity in the skin.[5]

Conventional synthetic routes to these ring systems are scarce. However, we have shown that pyrrolizin-3-ones **1** and related ring systems can be conveniently made in the gas phase by flash vacuum pyrolysis (FVP) of Meldrum's acid derivatives[6,7] ("the Meldrum's route") and by FVP of pyrrol-2-ylacrylate derivatives ("the C-acrylate route").[7] The Meldrum's route has been extended to give pyrrolo[1,2-*a*]indol-3-one[8] **2** (a benzopyrrolizinone), and both methods can be used to make pyrrolo[1,2-*a*]-imidazol-5-one and pyrrolo[1,2-*c*]imidazol-5-one (azapyrrolizinone) systems[9,10] (**3** and **4**, respectively). However, both these routes can suffer from practical disadvantages. Certain substitution patterns are not available by the Meldrum's route,[6,7] or require inconvenient precursor syntheses, or may be prone to low yields as a consequence of poor precursor volatility. The C-acrylate route[7] is usually better in this latter regard but suffers from the availability of specifically substituted starting materials.

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(9) McNab, H. *J. Chem. Soc., Perkin Trans. 1* **1987**, 653−656 and references therein.
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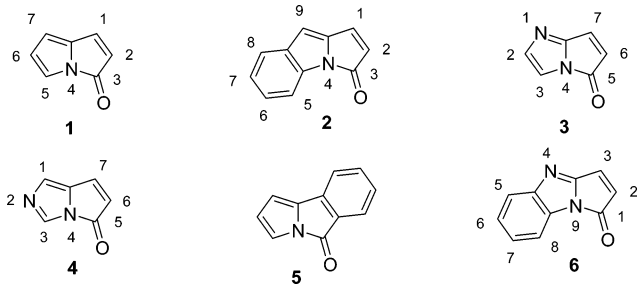
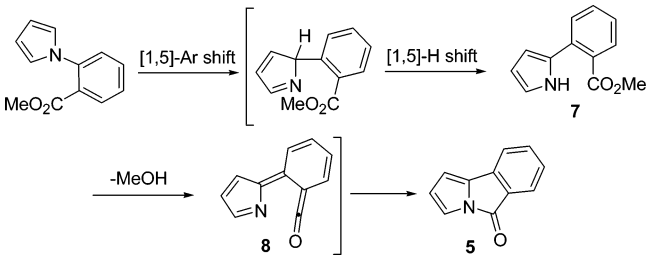


In work reported here, we have therefore extended our sigmatropic shift−elimination−cyclization cascade (Scheme 1), developed primarily[11] for the isomeric benzopyrrolizinone **5**, to syntheses of the benzopyrrolizinone **2** and azapyrrolizinone (**3** and **4**) systems. The key steps in the cascade are (i) a 1,5-sigmatropic shift of the N-substituent in the azole system, well recognized for alkyl and aryl groups[12−14] but also known for vinyl groups[14] to provide the intermediate **7**, (ii) elimination of methanol to generate ketene[11] **8**, and (iii) electrocyclization of the ketene in a pseudopericyclic process.[15] Steps (ii) and (iii) are common to the C-acrylate route.[7] The results of this study have provided optimum synthetic routes to the benzopyrrolizinone **2** (in two steps from simple indoles), given regiocontrolled routes to substituted azapyrrolizinones **3** and **4**, and provided a new route to the pyrrolo[1,2-*a*]benzimidazol-1-one (benzazapyrrolizinone) system **6**.

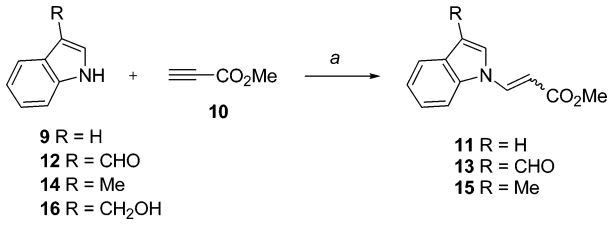
Results and Discussion

To explore the thermal cascade mechanism in the indole series, we used the key precursor, indol-1-ylacrylate **11**. Compounds of this type are known,[16] and the palladium-catalyzed conjugate addition of indole **9** to methyl propynoate **10** in triethylamine was carried out using the reported method to give **11** in 25−31% yield (see Supporting information). Although this provided enough material to establish the viability of the pyrolysis step (see below), it has proved to be too inefficient for routine use. However, other heavily substituted indol-1-ylacrylates have been made by reaction of the indole with propynoic esters in THF at room temperature, in the presence of 1 equiv of tetrabutylammonium fluoride (TBAF).[17] This method proved to be general for our purposes and was used to synthesize **11** and the 3-substituted precursors **13** and **15**, in >80% yield (Scheme 2). Some limitations of the procedure were identified. Thus, reduced yields were obtained if less than 1 equiv of TBAF was employed. Reaction of the alcohol **16** with methyl propynoate **10** gave a number of products that were not identified. Finally, indole **9** did not react with methyl phenylpropynoate in the presence of TBAF even after extended reaction times at reflux temperatures, and thus the method is best for the formation of indol-1-ylpropenoates that are unsubstituted in the 2- and 3-positions of the acrylate chain.

SCHEME 1

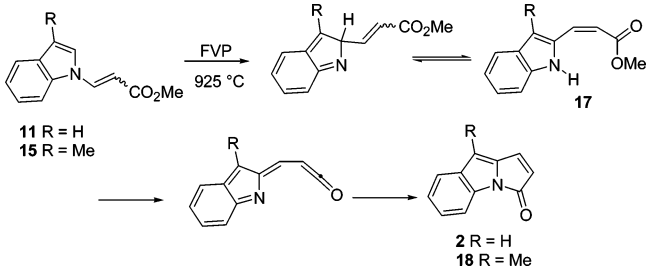


SCHEME 2 [a]



[a] Reagents: (a) TBAF, THF.

SCHEME 3



The parent compound **11** was obtained as a mixture of *E*- and *Z*-isomers, whereas the 3-substituted compounds **13** and **15** were exclusively *E*-isomers. No attempt was made to separate the isomers, which in any case would be subject to *E*/*Z* equilibration under the pyrolysis conditions.[18]

FVP of the indol-1-ylacrylate **11** required a furnace temperature of 925 °C for complete consumption of starting material, and pyrrolo[1,2-*a*]indol-3-one **2**, a yellow solid, was the sole product in 78% yield after purification (Scheme 3). The furnace temperature required for this transformation is significantly higher than those required for the Meldrum's route (typically 600−650 °C in our apparatus) or the C-acrylate route (typically 700 °C for *Z*-acrylate isomers and 800−850 °C for *E*-acrylate isomers). This suggests that the rate-determining step of the cascade route is the initial sigmatropic shift to **17** (R = H). However, the yield and purity of the product are not compromised by the high temperatures involved; this procedure gives the benzopyrrolizinone **2** in two steps from indole, in 75% (nonoptimized) overall yield. By comparison, the original synthesis of **2** required a potentially capricious photooxygenation step[19] and our previous FVP route[8] required the time-consuming preparation of indole-2-carbaldehyde.

The yield of the 1-methyl compound **18** was low (53%), owing to the coformation of carbazol-3-ol **19** (47%), which was not obtained by the Meldrum's route[8] (furnace temperature 600 °C) (Scheme 4). Repyrolysis of the benzopyrrolizinone **18**

(11) McNab, H.; Parsons, S.; Stevenson, E. *J. Chem. Soc., Perkin Trans. 1* **1999**, 2047−2048.
(12) Patterson, J. M. *Synthesis* **1976**, 281−304.
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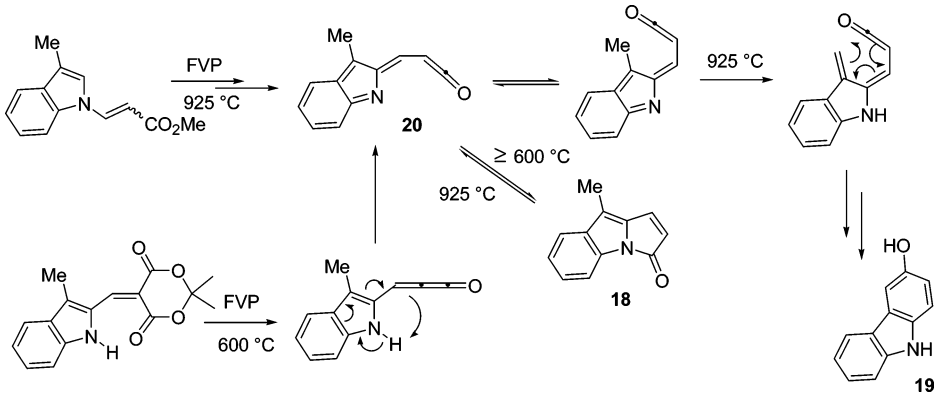
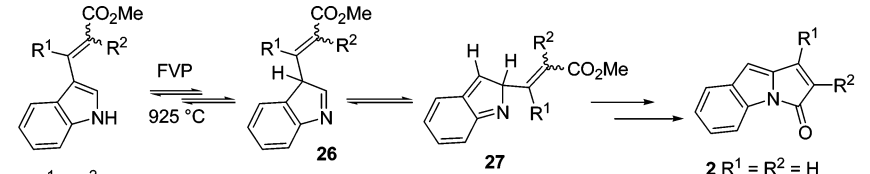
SCHEME 4



SCHEME 5

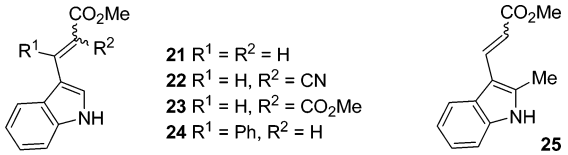


21 $R^1 = R^2 = H$
22 $R^1 = H$, $R^2 = CN$
23 $R^1 = H$, $R^2 = CO_2Me$
24 $R^1 = Ph$, $R^2 = H$

at 925 °C also provided a 1:1 mixture of **18** and **19**. These results suggest that the benzopyrrolizinone **18** is the kinetic product that can revert to the ketene **20** at high temperatures; the route to the thermodynamic product **19** is then initiated by 1,5-hydrogen shift from the methyl group (Scheme 4). This mechanism is consistent with the known electrocyclization of dienylketenes to phenol derivatives, first discovered by Brown and McMullen.[20]

FVP of the aldehyde precursor **13** at 925 °C led only to the parent pyrrolo[1,2-*a*]indol-3-one **2** (94%), and thus efficient thermal deformylation[21] takes place at such high temperatures.

Because the sigmatropic migration of groups is likely to be reversible between the 2- and 3-positions of indole,[13] some readily available indole-3-ylacrylate derivatives were also synthesized as potential pyrrolo[1,2-*a*]indol-3-one precursors. Compound **21** was made from indole-3-carbaldehyde by standard Wittig method (cf. ref 22), and Knoevenagel reaction provided compounds **22** and **23**.[23,24] The phenylacrylate **24** was made in 89% yield by application of a Pd(II)-catalyzed addition process, originally developed for the pyrrole series,[25] and here applied to indole chemistry for the first time. The product **24** was obtained as a 90:10 mixture of *E*- and *Z*-isomers, respectively; the regiochemistry of the reaction was established by a NOESY experiment. The known 2-methyl compound **25** was made[26] to study whether multiple sigmatropic shifts leading to cyclized products are possible in this series (cf. refs 11 and 12).



The feasibility of the route was established by the successful formation of **2** (70%) by FVP of the indol-3-ylacrylate **21** at 925 °C. The mechanism therefore involves an initial sequence of 1,5-hydrogen shifts to provide the intermediate **26** ($R^1 = R^2 = H$) which can then undergo a (slower) 1,5-acrylate shift to **27**, thus setting up the required connectivity (Scheme 5); elimination and cyclization then follow (cf. Scheme 3). In practice, this route proved more difficult to scale up than the indol-1-ylacrylate method, because of the higher inlet temperatures required, and thus the latter precursor is preferred as a synthetic route to pyrrolo[1,2-*a*]indol-3-one **2**.

The indol-3-ylacrylate route nevertheless provided a satisfactory method for the synthesis of the 2-cyano compound **28** (65% after chromatography), by FVP of **22** at 925 °C, but these conditions proved too severe for the malonate **23** and only decomposition products were obtained. The 1-phenyl compound **29** was also obtained in reasonable yield (57%) by FVP of **24**, but a second, isomeric product (6%) was isolated by chromatography. This material was unstable in solution, and thus its precise constitution could not be established. ^{1}H NMR spectroscopy showed that it had an NH and that the indole 2- and

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(24) Berestovitskaya, V. M.; Vasil'eva, O. S.; Aleksandrova, S. M.; Kobzareva, V. N.; Usik, N. V.; Novikov, B. M. *Russ. J. Gen. Chem.* (*Zh. Obshch. Khim.*) **2000**, *70*, 1154−1155.
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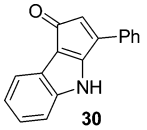
(26) Inhoffen, H. H.; Nordsiek, K.-H.; Schäfer, H. *Liebigs Ann. Chem.* **1963**, *668*, 104−121.

3-positions were both substituted. ^{13}C NMR spectroscopy showed the presence of a ketone carbonyl signal and that the phenyl group was still intact, which suggests that a ketene is able to cyclize onto carbon, in competition with the pseudopericyclic formation of **29**. The most likely structure is 3-phenyl-4*H*-cyclopenta[*b*]indol-1-one **30**, but the isomeric 1-phenyl-4*H*-cyclopenta[*b*]indol-3-one **31** cannot be ruled out, in which the sigmatropic shift step has been circumvented by prior cyclization. The influence of the phenyl substituent on this very minor mode of cyclization is unclear at this stage.



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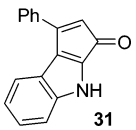


31

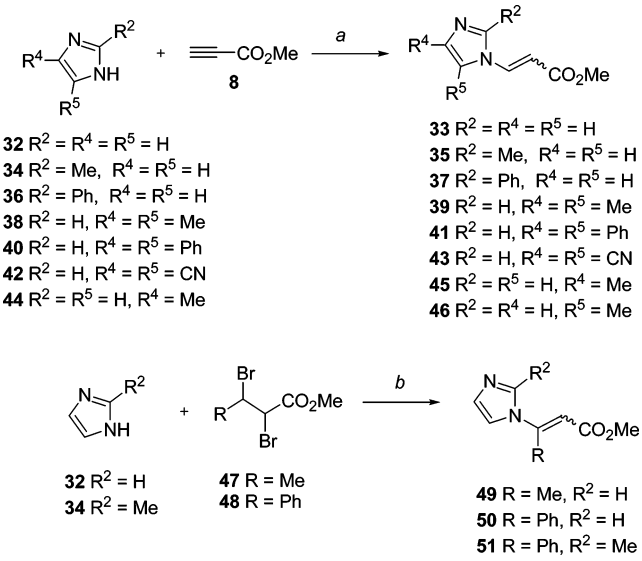
FVP of the disubstituted indole **25** at 925 °C gave only very small amounts of 9-methylpyrrolo[1,2-*a*]indol-3-one **18**, which could be identified by NMR spectroscopy of the crude pyrolysate.[8] The thermal interchange of the 2- and 3-substituents of **25** has been shown to be feasible but not synthetically useful in this case (cf. refs 27 and 28).

Application of the cascade strategy in the imidazole series introduces complications compared with the indole series. First, the N-substituents must undergo highly selective sigmatropic shifts for the method to be synthetically useful, and this is exacerbated by the properties of azapyrrolizinone systems, which are often unstable to crystallization and to chromatography. The main questions therefore concern the regiochemistry of the migration and whether any regioselectivity can be controlled by substituents on the imidazole periphery. Literature precedent is encouraging: Grimmett and co-workers have shown that flow pyrolysis of 1-phenylimidazole provides 2- and 4-phenylimidazoles in 94:6 ratio,[14] and, in preliminary work, we observed some selectivity in migrations of substituted acrylate and of aryl moieties en route to azapyrrolizinone analogues.[11]

Imidazol-1-ylacrylates, unsubstituted in the propenoate chain,[29,30] were made by treatment of the appropriate imidazole with methyl propynoate in refluxing toluene solution (Scheme 6) (cf. ref 30). Reactions of the diphenyl and dicyano compounds **40** and **42**, respectively, were carried out in chloroform solution for solubility reasons and required catalysis by triethylamine. The yield in the latter case was vanishingly low with insufficient material obtained for pyrolysis.

The imidazol-1-ylacrylates were generally obtained as mixtures of *E*- and *Z*-isomers (*E*-isomer $^3J_{HH}$ ca. 14 Hz, *Z*-isomer $^3J_{HH}$ ca. 10 Hz). The nature of the isomer was expected to be irrelevant for azapyrrolizinone formation (see below), and no attempt was made to separate them. Reaction of 4-methylimidazole **44** with methyl propynoate gave an inseparable 1:1 mixture of the acrylate isomers **45** and **46**, and therefore this route to methyl-substituted azapyrrolizinones was not pursued further.

SCHEME 6 [a]



[a] Reagents: (a) Toluene, reflux. (b) Et_3N, toluene, reflux.

N-Alkenylimidazoles with substituents in the alkenyl chain **49**−**51** were made by treatment of an excess of the imidazole with the dibromo compounds **47** or **48** in the presence of triethylamine, as previously reported.[29,30] Mixtures of *E*- and *Z*-isomers were again obtained; these were not unambiguously characterized, but as a general rule the α-methine signal of the propenoate side chain (at δ_H 5.7−6.5) was found to resonate at higher frequency for the *E*-isomer than that of the *Z*-isomer.

FVP of the parent compound **33**, fortuitously available as both *E*- and *Z*-isomers (Experimental Section), was chosen for preliminary studies. Separate FVP of *E*-**33** and *Z*-**33** at 900 °C (ca. 0.05 Torr) gave a crude pyrolysate that consisted of a 73:27 mixture of the known[9,10] pyrrolo[1,2-*a*]imidazol-5-one **3** as the major product and pyrrolo[1,2-*c*]imidazol-5-one **4** as the minor product, in ca. 80% overall yield. As expected, the configuration of the acrylate isomer had no effect on the cyclization, at the high temperatures involved. FVP of isomer mixtures of **49** and **50** similarly gave 7-substituted isomers **52**−**55** in excellent overall yield, with the pyrrolo[1,2-*a*]imidazol-5-ones **52** and **53** again the major products (80:20 ratio in both cases). Because of the poor stability of many azapyrrolizinones in solution, the NMR spectra were recorded immediately after the pyrolyses and analyses of the mixtures were made by analogy with the well-characterized NMR spectra of the parent azapyrrolizinones.[31] The thermal sigmatropic shift of the 1-alkenyl group to the imidazole 2-position is therefore favored over that to the 5-position before the cyclization. Unfortunately, the level of regioselectivity is much less than that previously observed for phenylimidazoles,[14] and it is essentially independent of substituents on the acrylate chain. Further work is required to probe the reasons for these differences. Because of the sensitivity of pyrroloimidazolones to chromatography and other purification techniques, this cascade approach does not supersede the C-acrylate route[10] as the method of choice for **3** and **4**, and it is not suitable for making pure 7-substituted isomers of either ring system.

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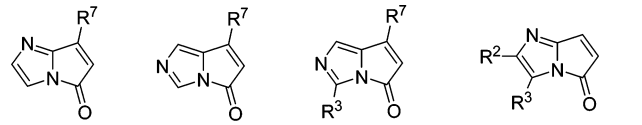
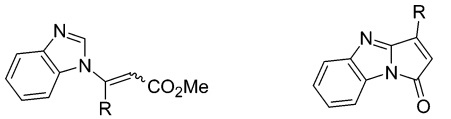


52 R^7 = Me
53 R^7 = Ph
54 R^7 = Me
55 R^7 = Ph
56 R^3 = Me, R^7 = H
57 R^3 = Ph, R^7 = H
58 R^3 = Me, R^7 = Ph
59 R^2 = R^3 = Me
60 R^2 = R^3 = Ph

On the other hand, we have found that blocking one of the possible migration sites of the *N*-propenoate by substituting either the 2-position (precursors **35**, **37**, and **51**) or the 4- and 5-positions of the imidazole ring (precursors **39** and **41**) leads to single azapyrrolizinone isomers. FVP of the 2-substituted derivatives **35**, **37**, and **51** (825−875 °C) caused clean cyclization to the pyrrolo[1,2-*c*]imidazol-5-ones **56**−**58**, respectively, in 88−91% yield. This is the method of choice for the synthesis of 3-substituted pyrrolo[1,2-*c*]imidazol-5-ones. In similar fashion, FVP of the 4,5-disubstituted precursors **39** and **41** at 825−850 °C gave the 2,3-disubstituted pyrrolo[1,2-*a*]imidazol-5-ones **59** and **60** in 93−95% yields. This is the method of choice for the synthesis of 2,3-disubstituted pyrrolo[1,2-*a*]imidazol-5-ones. In all of these cases, the migrating alkenyl group is forced in the direction opposite to the substituent at the adjacent position. This always overrides the "natural" direction of migration in the unsubstituted ring system. The nature of the interaction that causes this effect may be simply steric and is under investigation.

Finally, examples of the pyrrolo[1,2-*a*]benzimidazol-1-one (benzazapyrrolizinone) system **6** are rare, and the parent compound is known only in the patent literature.[32] Precursors **61** (as a 44:56 *E*/*Z* mixture; 95%) and **62** (exclusively as the *E*-isomer) were made by the methods of Scheme 6 (the latter only in low yield; see Experimental Section). FVP of **61** and **62** at 950 °C gave the pyrrolo[1,2-*a*]benzimidazol-1-ones **6** (71%) and **63** (36%), respectively, after some optimization of sublimation rate and trapping method. In both cases, rapid chromatography (<5 min on the column) was essential to obtain pure products.



61 R = H
62 R = Ph
6 R = H
63 R = Ph

It is noteworthy that the furnace temperatures required for the benzannelated examples (derived from indoles and benzimidazoles) are ca. 100 °C higher than those for the imidazole analogues, owing to the quinonoid intermediates involved in the former processes.

In conclusion, the work reported in this article has significantly extended the synthetic versatility of the high-temperature FVP cascade route (involving a sigmatropic migration, elimination, and cyclization) to a number of pyrrolizin-3-one analogues. In the pyrrolo[1,2-*a*]indol-3-one and pyrrolo[1,2-*a*]benzimidazol-1-one series, we believe that the routes to the unsubstituted compounds **2** and **6** are the best currently available, requiring just two simple steps from indoles or benzimidazoles, respectively. Regiocontrolled routes to substituted azapyrrolizinones **56**−**60** have made these among the easiest azapyrrolizinones to obtain. However, the very high furnace temperatures required for the initial sigmatropic shift stage of the cascade limit the available substituents, and often care is required in the workup. The chemical properties of these new ring systems will be reported in future articles.

Experimental Section

Methyl 3-(Indol-1-yl)-acrylate Derivatives. General Method.[17] A solution of TBAF (1 M in tetrahydrofuran, 1.0 cm^3, 1.0 mmol) was added dropwise to a solution of indole (1.0 mmol) and methyl propynoate **10** (84 mg, 1.0 mmol) in tetrahydrofuran (6 cm^3). The reaction mixture was stirred at room temperature for 30 min. Water (20 cm^3) was added, the organic components were extracted into ethyl acetate (3 × 40 cm^3), and the organic extracts were washed with water (10 cm^3) and dried ($MgSO_4$). Removal of the solvent under reduced pressure afforded an *E*/*Z* isomer mixture of the methyl 3-(indol-1-yl)-acrylate that was purified as described. The following derivatives were made by this method:

Methyl 3-(Indol-1-yl)-acrylate 11. Application of the general method using indole **9** (117 mg, 1.0 mmol) gave a 67:33 *E*/*Z* isomer mixture of methyl 3-(indol-1-yl)-acrylate **11** that was purified by distillation (192 mg, 96%); mp 81−83 °C, bp 170 °C (0.9 Torr); (Found: M^+ 201.0787. $C_{12}H_{11}NO_2$ requires *M* 201.0790); δ_H (*E*-isomer) 8.21 (1H, d, ^3J = 14.1), 7.59−7.47 (2H, m), 7.30 (1H, d, ^3J = 3.4), 7.29−7.11 (2H, m), 6.64 (1H, d, ^3J = 3.4), 5.88 (1H, d, ^3J = 14.1), and 3.74 (3H, s); δ_H (*Z*-isomer) 8.46 (1H, d, ^3J = 3.7), 6.58 (1H, d, ^3J = 3.7), 5.31 (1H, d, ^3J = 11.0), and 3.69 (3H, s) (other signals indistinguishable); δ_C (*E*-isomer) 167.7 (quat), 137.2, 135.9 (quat), 129.7 (quat), 123.8, 123.4, 122.3, 121.4, 109.9, 108.7, 100.0, and 51.5; *m*/*z* 201 (M^+, 100%), 171 (14), 170 (87), 143 (11), 142 (11), 117 (12), 115 (15), and 85 (10). (Data comparable with reported values for the ethyl ester;[16] see also Supporting information.)

Methyl 3-(3-Formylindol-1-yl)-acrylate 13. Application of the general method using indole 3-carbaldehyde **12** (145 mg, 1.0 mmol) gave an immediate change from colorless to dark brown, and thus the reaction was stirred at room temperature for only 10 min. Tetrahydrofuran was removed in vacuo, and the crude product was purified by dry flash chromatography on silica (8% DCM, 20% ethyl acetate in hexane) to give methyl *E*-3-(3-formylindol-1-yl)-acrylate **13** as a white solid (195 mg, 86%); mp 176−178 °C; (Found: M^+ 229.0737. $C_{13}H_{11}N_2O_3$ requires *M* 229.0739); δ_H 10.04 (1H, s), 8.21 (1H, d, ^3J = 7.8), 8.16 (1H, d, ^3J = 14.4), 8.00 (1H, s), 7.54 (1H, d, ^3J = 7.8), 7.33 (2H, dq, ^3J = 14.4 and 7.3), 6.17 (1H, d, ^3J = 14.4), and 3.77 (3H, s); δ_C 184.5, 165.9 (quat), 136.1 (quat), 135.6, 132.7, 125.0, 123.8, 121.8, 121.5 (quat), 109.5, 104.2, and 51.1 (CH_3) (one quaternary overlapping); *m*/*z* 229 (M^+, 100%), 228 (70), 198 (25), 185 (17), 170 (58), 140 (13), 116 (16), 115 (31), and 98 (14).

Methyl 3-(3-Methylindol-1-yl)-acrylate 15. Application of the general method using 3-methylindole **14** (131 mg, 1.0 mmol) gave a crude product that was absorbed onto silica and purified by dry flash chromatography (20% DCM, 2% ethyl acetate in hexane) to give methyl 3-(3-methylindol-1-yl)-acrylate **15** as a white solid (186 mg, 87%); mp 81−82 °C (from hexane); bp 169 °C (1.2 Torr); (Found: M^+ 215.0946. $C_{13}H_{13}NO_2$ requires *M* 215.0946); δ_H 8.14 (1H, d, ^3J = 13.9), 7.43 (1H, d, ^3J = 7.8), 7.26−7.10 (3H, m), 7.03 (1H, s), 5.73 (1H, dd, ^3J = 13.9 and ^5J = 0.9), 3.71 (3H, s), and 2.22 (3H, s); δ_C 167.5 (quat), 136.4, 135.8 (quat), 130.0 (quat), 123.3, 121.5, 119.9, 118.8, 118.0 (quat), 109.2, 97.9, 50.8 (CH_3), and 9.1 (CH_3); *m*/*z* 215 (M^+, 57%), 184 (47), 154 (17), 131 (81), 130 (100), 103 (23), and 77 (34).

Methyl 3-(1*H*-Indol-3-yl)-acrylate 21 (cf. ref 22). Methyl-(triphenylphosphoranylidene)acetate (0.67 g, 2 mmol) was added

(32) (a) Minami, M.; Kitamura, K. JP 45032716; *Chem. Abstr.* **1971**, *74*, 43051. (b) Minami, M. JP 45032715; *Chem. Abstr.* **1971**, *74*, 43057. (c) JP 59185349; *Chem. Abstr.* **1985**, *102*, 176456.

to a solution of indole 3-carboxaldehyde **12** (0.29 g, 2 mmol) in toluene (25 cm^3) and stirred overnight. The crude product was purified by dry flash chromatography on silica using a 15−50% ethyl acetate in hexane eluent gradient and afforded *E*- and *Z*-isomers of methyl 3-(1*H*-indol-3-yl)-acrylate **21** (0.35 g, 88%, 0.31 g of *E*-isomer, 0.04 g of *Z*-isomer); mp (*E*-isomer) 152−153 °C (lit.,[26] 153−154 °C); mp (*Z*-isomer) 162−164 °C (lit.,[26] 163−164 °C); δ_H (*E*-isomer) 8.46 (1H broad, NH), 7.89−7.79 (2H, m), 7.39 (1H, m), 7.32 (1H, d, ^3J = 15.7), 7.17−7.10 (2H, m), 6.34 (1H, d, ^3J = 15.7), and 3.81 (3H, s); δ_H (*Z*-isomer) 8.82 (1H, d, ^3J = 2.9), 8.57 (1H broad, NH), 7.67 (1H, m), 7.37−7.12 (3H, m), 7.23 (1H, d, ^3J = 12.4), 5.77 (1H, d, ^3J = 12.4), and 3.71 (3H, s); δ_C (*E*-isomer) 168.4 (quat), 138.6, 137.2 (quat), 129.6, 124.9 (quat), 122.4, 120.7, 119.8, 112.3 (quat), 111.8, 111.4, and 50.9 (CH_3); δ_C (*Z*-isomer) 168.8 (quat), 138.6, 137.0 (quat), 129.0, 125.1 (quat), 123.2, 121.4, 120.3, 113.3 (quat), 112.6, 111.7, and 51.4 (CH_3); *m*/*z* (*E*-isomer) 201 (M^+, 97%), 171 (32), 170 (100), 143 (40), 142 (24), 141 (39), 115 (71), and 114 (30); *m*/*z* (*Z*-isomer) 201 (M^+, 96%), 171 (34), 170 (100), 143 (37), 142 (28), 141 (43), 115 (66), and 114 (32).

Methyl 2-Cyano-3-(1*H*-indol-3-yl)-acrylate 22. A solution of indole 3-carboxaldehyde **12** (0.72 g, 5 mmol) and methyl cyanoacetate (0.495 g, 5 mmol) in toluene (15 cm^3) was treated with glacial acetic acid (15 drops) and piperidine (15 drops). The reaction was stirred for 2 h, after which a yellow precipitate formed. Toluene was removed in vacuo, and the crude solid was dissolved in DCM. Water (75 cm^3) was added, and the organic layer was separated. The aqueous layer was then extracted with DCM (3 × 25 cm^3), and the combined organic extracts were washed with water (50 cm^3) and then dried ($MgSO_4$). The solvent was removed to give methyl 2-cyano-3-(1*H*-indol-3-yl)-acrylate **22** (1.10 g, 97%); mp 183−185 °C (lit.,[23] 187−188 °C); δ_H 9.34 (1H, broad, NH), 8.57 (1H, m) 8.55 (1H, s), 7.77 (1H, m), 7.42 (1H, m), 7.31−7.12 (2H, m), and 3.86 (3H, s); δ_C 164.9 (quat), 147.2, 136.7 (quat), 132.4, 127.9 (quat), 124.0, 122.6, 118.7 (quat), 118.3, 113.1, 110.9 (quat), 92.9 (quat), and 53.0 (CH_3); *m*/*z* 226 (M^+, 38%), 195 (25), 145 (90), 144 (100), 116 (40), and 89 (45).

Dimethyl 2-(1*H*-Indol-3-ylmethylene)malonate 23. A solution of indole 3-carboxaldehyde **12** (0.72 g, 5 mmol) and dimethyl malonate (0.66 g, 5 mmol) in toluene (15 cm^3) with glacial acetic acid (15 drops) and piperidine (15 drops) was stirred for 45 min, after which the reaction was fitted with a Dean/Stark trap and briefly heated under reflux until red in color. Upon cooling, water (50 cm^3) was added to the mixture, and the organic layer was separated. The aqueous phase was then extracted with ether (3 × 25 cm^3), and the combined extracts were washed with water (50 cm^3) and dried ($MgSO_4$), after which the solvents were removed to give dimethyl 2-(1*H*-indol-3-ylmethylene)malonate **23** (0.62 g, 48%); mp 195−197 °C (from methanol) (lit.,[24] 117−119 °C). This compound was characterized as follows in view of the mp discrepancy with the literature: (Found: C, 64.8; H, 5.0; N, 4.9. $C_{14}H_{13}NO_4$ requires C, 64.85; H, 5.0; N, 5.4); (Found: M^+ 259.0841. $C_{14}H_{13}NO_4$ requires *M* 259.0845); δ_H 8.85 (1H, broad, NH), 8.16 (1H, s), 7.79−7.76 (2H, m), 7.35 (1H, m), 7.29−7.21 (2H, m), and 3.86 (6H, s); δ_C 168.8 (quat), 166.2 (quat), 136.3, 136.1 (quat), 128.3, 127.9 (quat), 123.8, 122.0, 119.2 (quat), 118.9, 112.1, 110.9 (quat), 53.0, and 52.8; *m*/*z* 259 (M^+, 100%), 228 (38), 199 (38), 196 (29), 170 (26), 145 (30), 144 (40), 141 (50), and 114 (27).

Methyl 3-(1*H*-Indol-3-yl)-3-phenylacrylate 24 (cf. ref 25). A solution of indole **9** (0.234 g, 2 mmol) and methyl phenylpropynoate (0.320 g, 2 mmol) in glacial acetic acid (25 cm^3) containing palladium(II) acetate (9 mg, 2% cat) was stirred at room temperature for 30 h. The crude product was absorbed onto silica and purified by dry flash chromatography (10−40% ethyl acetate in hexane eluent gradient) and then crystallized by evaporation of DCM at atmospheric pressure to give a 15:85 isomer mixture of methyl 3-(1*H*-indol-3-yl)-3-phenylacrylate **24** (0.477 g, 89%). The isomers were not separated, and neither isomer was assigned specific geometry; mp 159−161 °C; (Found: M^+ 277.1099. $C_{18}H_{15}NO_2$ requires *M* 277.1103); δ_H (major isomer) 8.58 (1H, broad, NH), 7.73 (1H, m), 7.31−7.24 (6H, m), 7.19−7.14 (2H, m), 6.70 (1H, d, ^3J = 2.9), 6.52 (1H, s), and 3.57 (3H, s); δ_H (minor isomer) 8.52 (1H, broad, NH), 7.07 (1H, m), 6.92−6.89 (2H, m), 6.19 (1H, s), and 3.65 (3H, s) (other signals indistinguishable); δ_C (major isomer) 167.6 (quat), 153.3 (quat), 140.2 (quat), 137.3 (quat), 129.8, 128.9 (2CH), 128.0, 127.8 (2CH), 125.1 (quat), 123.1, 121.4, 120.8, 118.6 (quat), 112.0, 111.4, and 51.1 (CH_3); *m*/*z* 277 (M^+, 100%), 246 (80), 219 (25), 218 (27), 217 (42), 216 (23), 204 (13), 191 (18), 189 (21), 165 (5), 144 (18), and 109 (20).

Methyl 3-(2-Methyl-1*H*-indol-3-yl)-acrylate 25. 2-Methyl-1*H*-indole-3-carboxaldehyde[33] (0.5 g, 3 mmol) and methyl(triphenylphosphoranylidene)acetate (1.05 g, 3 mmol) were dissolved in toluene (15 cm^3) and heated under reflux for 24 h. The solvent was removed in vacuo, and the product was purified by dry flash chromatography on silica (20% ethyl acetate in hexane) to give methyl *E*-3-(2-methyl-1*H*-indol-3-yl)-acrylate **25** (0.62 g, 93%); mp 153−154 °C (lit.,[26] 154−155 °C); δ_H 8.64 (1H, broad, NH), 8.05 (1H, d, ^3J = 15.8), 7.93 (1H, m), 7.42−7.26 (3H, m), 6.52 (1H, d, ^3J = 15.8), 3.92 (3H, s), and 2.60 (3H, s); δ_C 169.1 (quat), 140.2 (quat), 137.8, 135.6 (quat), 126.2 (quat), 122.3, 121.3, 119.8, 111.3, 110.8, 109.4 (quat), 51.3 (CH_3), and 12.2 (CH_3); *m*/*z* 215 (M^+, 100%), 184 (80), 183 (22), 156 (44), 155 (33), 154 (37), 128 (18), 129 (18), 78 (30), and 77 (41).

Flash Vacuum Pyrolysis Reactions. FVP reactions were carried out by sublimation of the precursor under reduced pressure through an empty silica tube (35 × 2.5 cm) heated by an electrical tube furnace. The products were usually collected in a U-tube cooled by liquid nitrogen situated at the exit point of the furnace, but in some cases a dry ice acetone cooled "cold finger" trap was used to minimize product degradation (see specific examples later in this section). Upon completion of the pyrolysis, the U-tube trap was allowed to warm to room temperature under an atmosphere of dry nitrogen. The product was dissolved in chloroform and removed from the trap. Evaporation of the solvent under reduced pressure gave the product. Products that were collected on the cold finger were washed from the cold surface with acetone under a dry nitrogen atmosphere, and the solution was worked up in the usual way. Pyrolysis conditions are reported in the form: precursor (quantity), furnace temperature (T_f), inlet temperature (T_i), pressure (P_{range}), and pyrolysis time (*t*).

3*H*-Pyrrolo[1,2-*a*]indol-3-one 2 [from Methyl 3-(Indol-1-yl)-acrylate 11]. FVP of **11** (300 mg, 1.5 mmol, T_i = 90 °C, T_f = 925 °C, *P* = 0.01−0.08 Torr, *t* = 40 min) afforded a solid yellow pyrolysate (230 mg, 90%), and subsequent purification by dry flash chromatography on silica (40% DCM in hexane) gave 3*H*-pyrrolo-[1,2-*a*]indol-3-one **2** (200 mg, 78%); mp 86−88 °C (lit.,[19] 86−89 °C); δ_H 7.58 (1H, ddd, ^3J = 7.7, 1.7 and ^4J = 0.9), 7.27 (1H, dt, ^3J = 7.7 and ^4J = 0.9), 7.15 (1H, td, ^3J = 7.7 and ^4J = 1.1), 7.02 (1H, d, ^3J = 5.8), 6.96 (1H, td, ^3J = 7.7 and ^4J = 1.1), 6.27 (1H, s), and 5.86 (1H, d, ^3J = 5.8); δ_C 164.8 (quat), 141.2 (quat), 134.9, 134.4 (quat), 133.7 (quat), 127.3 (2CH), 123.1, 122.7, 112.1, and 108.2; *m*/*z* 169 (M^+, 100%), 141 (47), 140 (37), 114 (26), 113 (16), 88 (12), 70 (13), and 63 (20).

FVP of Methyl 3-(3-Formylindol-1-yl)-acrylate 13. FVP of **13** (40 mg, 0.17 mmol, T_f = 925 °C, T_i = 205 °C, *P* = 0.02−0.12 Torr, *t* = 10 min) using a dry ice/acetone cold finger trap gave a solid yellow pyrolysate that was removed from the cold finger by dissolving in acetone. The solvent was removed in vacuo to provide exclusively 3*H*-pyrrolo[1,2-*a*]indol-3-one **2** (32 mg, 94%) after decarbonylation of the formyl group; mp 86−88 °C (lit.,[19] 86−89 °C); δ_H 7.59 (1H, ddd, ^3J = 7.7, 1.7 and ^4J = 0.9), 7.29 (1H, dt, ^3J = 7.7 and ^4J = 0.9), 7.15 (1H, td, ^3J = 7.7 and ^4J = 1.2),

(33) Downie, I. M.; Earle, M. J.; Heaney, H.; Shuhaiber, K. F. *Tetrahedron* **1993**, *49*, 71−79.

7.01 (1H, d, ^3J = 5.8), 6.96 (1H, td, ^3J = 7.7 and ^4J = 1.2), 6.28 (1H, s), and 5.86 (1H, d, ^3J = 5.8).

FVP of Methyl 3-(3-Methylindol-1-yl)-acrylate 15. FVP of **15** (95 mg, 4.4 mmol, T_f = 925 °C, T_i = 160 °C, P = 0.02−0.10 Torr, t = 13 min) using a dry ice/acetone cold finger trap gave a solid yellow pyrolysate (74 mg) that contained two major products. Separation by dry flash chromatography (5−30% ethyl acetate in hexane gradient) gave, in order of elution: 9-methyl-3*H*-pyrrolo-[1,2-*a*]indol-3-one **18** (36 mg, 53%); mp 92−93 °C (lit.,[8] 94−95 °C); δ_H 7.58 (1H, d, ^3J = 7.8), 7.24−7.20 (2H, m), 7.08 (1H, d, ^3J = 5.9), 7.02 (1H, d, ^3J = 7.8), 5.81 (1H, d, ^3J = 5.9), and 2.19 (3H, s) (compatible with literature data[8]); and 9*H*-carbazol-3-ol **19** (32 mg, 47%); mp 260−261 °C (lit.,[34] 259−260 °C); δ_H 10.80 (1H, br, s), 8.85 (1H, br, s), 7.90 (1H, d, ^3J = 7.8), 7.36−7.31 (2H, m), 7.24 (1H, dt, ^3J = 7.4, ^4J = 1.1), 7.22 (1H, d, ^3J = 8.4), 6.99 (1H, dt, ^3J = 7.4, ^4J = 1.1), and 6.83 (1H, dd, ^3J = 8.6 and 2.4); *m*/*z* 183 (M^+, 14%), 170 (7), 154 (8), 143 (28), 130 (14), 129 (100), 128 (21), 115 (8), and 102 (24).

Repyrolysis of 9-methyl-3*H*-pyrrolo[1,2-*a*]indol-3-one **18** at 925 °C (20 mg, 0.11 mmol, T_f = 925 °C, T_i = 160 °C, P = 0.02−0.05 Torr, t = 9 min) gave a 50:50 mixture of 9-methyl-3*H*-pyrrolo-[1,2-*a*]indol-3-one **18** and 9*H*-carbazol-3-ol **19** shown by ^{1}H NMR spectroscopy.

3*H*-Pyrrolo[1,2-*a*]indol-3-one 2 (from Methyl 3-(Indol-3-yl)-acrylate 21). FVP of methyl 3-(3*H*-indol-3-yl)-acrylate **21** (100 mg, 0.5 mmol, T_i = 210 °C, T_f = 925 °C, P = 0.01−0.09 Torr, t = 25 min) afforded a solid yellow pyrolysate (71 mg, 85%), and subsequent purification by dry flash chromatography on silica (40% DCM in hexane) gave 3*H*-pyrrolo[1,2-*a*]indol-3-one **2** (59 mg, 70%); mp 86−88 °C (lit.,[19] 86−89 °C); δ_H 7.60 (1H, ddd, ^3J = 7.7, 1.7 and ^4J = 0.9), 7.26 (1H, dt, ^3J = 7.7 and ^4J = 0.9), 7.15 (1H, td, ^3J = 7.7 and ^4J = 1.1), 7.02 (1H, d, ^3J = 5.8), 6.94 (1H, td, ^3J = 7.7 and ^4J = 1.1), 6.27 (1H, s), and 5.88 (1H, d, ^3J = 5.8). However, larger-scale pyrolysis (ca. 500 mg) was impractical because of the relative involatility of the precursor. Variation of inlet temperature (210−270 °C), throughput rate, and the use of a "cold finger" trap did not significantly increase yields. In practice, methyl 3-(3*H*-indol-1-yl)-acrylate **11** is a better precursor for 3*H*-pyrrolo[1,2-*a*]indol-3-one **2** on a preparative scale.

2-Cyano-3*H*-pyrrolo[1,2-*a*]indol-3-one 28. FVP of methyl 2-cyano-3-(1*H*-indol-3-yl)-acrylate **22** (302 mg, 1.3 mmol, T_f = 925 °C, T_i = 240 °C, P = 0.02−0.10 Torr, t = 20 min) using a dry ice/acetone cold finger trap gave a solid orange pyrolysate of 2-cyano-3*H*-pyrrolo[1,2-*a*]indol-3-one **28** (170 mg, 65%) that was purified by dry flash chromatography on silica (45% DCM and 1% ethyl acetate in hexane); mp 165−167 °C; (Found: M^+ 194.0478. $C_{12}H_6N_2O$ requires M 194.0480); δ_H 7.71 (1H, dt, ^3J = 7.9 and ^4J = 0.9), 7.70 (1H, s), 7.46 (1H, dt, ^3J = 7.9 and ^4J = 0.9), 7.39 (1H, td, ^3J = 7.8 and ^4J = 1.1), 7.16 (1H, td, ^3J = 7.8 and ^4J = 1.1), and 6.79 (1H, s); δ_C 158.7 (quat), 142.9, 137.4 (quat), 135.3 (quat), 133.5 (quat), 130.0, 124.5, 124.1, 115.3, 113.0, 111.6 (quat), and 111.2 (quat); *m*/*z* 194 (M^+, 100%), 166 (21), 165 (11), 140 (8), and 139 (26).

FVP of Methyl 3-(1*H*-Indol-3-yl)-3-phenylacrylate 24. FVP of **24** (120 mg, 0.14 mmol, T_f = 925 °C, T_i = 210 °C, P = 0.02−0.10 Torr, t = 8 min) using a dry ice/acetone cold finger trap gave a solid yellow pyrolysate that was washed into acetone and analyzed by TLC, indicating two products (99 mg, 94%). Separation by dry flash chromatography (30% DCM and 1% ethyl acetate in hexane for the first band and 80% ethyl acetate for the second band) gave, in order of elution: 1-phenyl-3*H*-pyrrolo[1,2-*a*]indol-3one **29** (60 mg, 57%); mp 111−113 °C; (Found: M^+ 245.0841. $C_{17}H_{11}NO$ requires M 245.0847); δ_H 7.68−7.62 (3H, m), 7.43−7.41 (3H, m), 7.37 (1H, dt, ^3J = 7.8 and ^4J = 0.8), 7.22 (1H, td, ^3J = 7.6 and ^4J = 1.1), 7.03 (1H, td, ^3J = 7.6 and ^4J = 1.1), 6.64 (1H, s), and 6.08 (1H, s); δ_C 164.8 (quat), 149.2 (quat), 140.3 (quat), 134.3 (quat), 130.8, 129.0 (2CH), 127.4, 127.0 (2CH), 123.1, 122.7, 119.9, 112.4, and 108.8 (two pairs of quaternary signals overlapping); *m*/*z* 245 (M^+, 100%), 217 (85), 216 (31), 204 (15), 189 (16), 149 (16), 123 (16), 109 (24), 95 (32), and 87 (94); and a product thought to be either 3-phenyl-4*H*-cyclopenta[*b*]indol-1-one **30** or 1-phenyl-4*H*-cyclopenta[*b*]indol-3-one **31** (6 mg, 6%) (decomposes in chloroform solution); mp 253−255 °C (dec); (Found: M^+ 245.0837. $C_{17}H_{11}NO$ requires M 245.0841); δ_H 11.44 (1H, br, s, NH), 8.02 (1H, dd, ^3J = 7.6 and ^4J = 0.6), 7.70−7.64 (4H, m), 7.47−7.41 (4H, m), and 6.59 (1H, s); δ_C 185.3 (quat), 147.9 (quat), 136.8 (quat), 135.4 (quat), 126.2 (quat), 111.0 (quat), 130.3, 128.8, 128.6 (2CH), 127.7 (2CH), 125.0, 124.2, 120.3, and 116.6 (one quaternary signal overlapping); *m*/*z* 245 (M^+, 100%), 244 (26), 217 (32), 216 (16), 189 (20), 169 (6), and 123 (9).

Methyl 3-(2*H*-Imidazol-1-yl)-acrylate 33. A solution of methyl propynoate **10** (4.20 g, 0.05 mol) and imidazole **32** (3.63 g, 0.05 mol) in toluene (15 cm^3) was heated under reflux for 2 h. The *E*-isomer of methyl 3-(2*H*-imidazol-1-yl)-acrylate **33** crystallized on cooling the solution. The product was filtered and recrystallized from the minimum volume of toluene. The filtrate from the original reaction was concentrated under reduced pressure. The product that crystallized was filtered and dissolved in ethyl acetate, and hexane was added to precipitate unreacted imidazole that was removed by filtration. This filtrate was then concentrated under reduced pressure to give *Z*-isomer **33**, which was recrystallized from toluene (6.42 g, 82%; 3.11 g, *E*-isomer, 3.31 g, *Z*-isomer); mp (*E*-isomer) 117−119 °C (lit.,[29] 121−122 °C); mp (*Z*-isomer) 46−48 °C; δ_H (*E*-isomer) 7.86 (1H, d, ^3J = 14.3), 7.74 (1H, s), 7.19 (1H, s), 7.10 (1H, s), 6.01 (1H, d, ^3J = 14.3), and 3.74 (3H, s); δ_H (*Z*-isomer) 8.02 (1H, s), 7.79 (1H, s), 7.02 (1H, s), 6.85 (1H, d, ^3J = 10.6), 5.44 (1H, d, ^3J = 10.6), and 3.69 (3H, s); δ_C (*E*-isomer) 166.1 (quat), 137.7, 136.4, 131.6, 115.9, 106.2, and 51.7 (CH_3); δ_C (*Z*-isomer) 166.9 (quat), 136.1 (2CH), 130.2, 115.5, 106.2, and 52.1 (CH_3).

Methyl 3-(2-Methylimidazol-1-yl)-acrylate 35. 2-Methylimidazole **34** (1.23 g, 15 mmol) and methyl propynoate **10** (1.26 g, 15 mmol) were added to toluene (15 cm^3) and heated under reflux for 2 h during which time the reaction darkened to deep yellow. Methyl 3-(2-methylimidazol-1-yl)-acrylate **35** crystallized upon removal of the solvent as the *E*-isomer exclusively (1.36 g, 55%); mp 92−93 °C (from toluene) (lit.,[30] 91−92 °C); δ_H 7.84 (1H, d, ^3J = 14.1), 7.15 (1H, s), 6.97 (1H, s), 5.93 (1H, d, ^3J = 14.1), 3.88 (3H, s), and 2.50 (3H, s); *m*/*z* 166 (M^+, 100%), 135 (82), 107 (81), 81 (28), and 67 (38).

Methyl 3-(2-Phenylimidazol-1-yl)-acrylate 37. A solution of 2-phenylimidazole **36** (0.43 g, 3 mmol) and methyl propynoate **10** (0.25 g, 3 mmol) in toluene was heated under reflux for 4 h. The solvent was then removed under reduced pressure, and the crude product was purified by Kugelrohr distillation to give methyl 3-(2-phenylimidazol-1-yl)-acrylate **37** (0.42 g, 61%) as a 34:66 mixture of *Z*- and *E*-isomers, respectively; bp 179 °C (3.8 Torr); (Found: C, 68.4; H, 5.4; N, 12.05. $C_{13}H_{12}N_2O_2$ requires C, 68.4; H, 5.25; N, 12.3); (Found: M^+ 228.0891. $C_{13}H_{12}N_2O_2$ requires M 228.0898); δ_H (*E*-isomer) 8.02 (1H, d, ^3J = 14.1), 7.59−7.52 (5H, m), 7.40 (1H, s), 7.18 (1H, s), 6.09 (1H, d, ^3J = 14.1), and 3.81 (3H, s); δ_H (*Z*-isomer) 7.99 (1H, s), 7.59−7.39 (5H, m), 7.20 (1H, s), 6.93 (1H, d, ^3J = 10.3), 5.61 (1H, d, ^3J = 10.3), and 3.82 (3H, s); δ_C (*E*-isomer) 166.9 (quat), 150.0 (quat), 137.8, 131.4, 130.3, 130.03 (2CH), 129.37 (2CH), 117.0, 107.5, and 52.4 (CH_3) (one quaternary overlapping); δ_C (*Z*-isomer) 165.1 (quat), 134.9, 129.96 (2CH), 129.44 (2CH), 129.1 (2CH), 122.4, 107.8, and 52.3 (CH_3) (two quaternaries overlapping); *m*/*z* 228 (M^+, 85%), 197 (48), 169 (100), 157 (49), and 128 (36).

Methyl 3-(4,5-Dimethylimidazol-1-yl)-acrylate 39. Methyl propynoate **10** (0.27 g, 3.2 mmol) was added to a solution of 4,5-dimethylimidazole **38** (0.26 g, 2.7 mmol) in toluene (25 cm^3), and the solution was heated under reflux, with stirring, for 30 min. Removal of the solvent under reduced pressure gave the crude

(34) Bisagni, E.; Ducrocq, C.; Hung, N. C. *Tetrahedron* **1980**, *36*, 1327−1330.

product, which was filtered and recrystallized from toluene (8 cm^3) to give methyl 3-(4,5-dimethylimidazol-1-yl)-acrylate **39** (0.39 g, 79%) as a 67:33 *E*/*Z* isomer mixture; mp 172−174 °C; (Found: M^+ 180.0890. $C_9H_{12}N_2O_2$ requires *M* 180.0899); δ_H (*E*-isomer) 7.70 (1H, s), 7.68 (1H, d, $^3J = 14.3$), 6.00 (1H, d, $^3J = 14.3$), 3.73 (3H, s), 2.16 (3H, s), and 2.10 (3H, s); δ_H (*Z*-isomer) 8.53 (1H, s), 6.79 (1H, d, $^3J = 10.5$), 5.67 (1H, d, $^3J = 10.5$), 3.66 (3H, s), 2.16 (3H, s), and 2.10 (3H, s); δ_C (*E*-isomer) 167.1 (quat), 136.3 (quat), 136.0, 133.8, 122.6 (quat), 105.8, 52.16 (CH_3), 12.7 (CH_3), and 9.1 (CH_3); δ_C (*Z*-isomer) 165.2 (quat), 137.8, 134.4 (quat), 131.9, 122.3, 106.8, 52.10 (CH_3), 12.7 (CH_3), and 9.1 (CH_3); *m*/*z* 180 (M^+, 100%), 179 (17), 165 (14), 164 (15), 149 (27), 121 (38), 93 (22), 80 (23), and 70 (45).

Methyl 3-(4,5-Diphenylimidazol-1-yl)-acrylate 41. Methyl propynoate **10** (0.21 g, 2.5 mmol) was added to a solution of 4,5-diphenylimidazole **40** (0.55 g, 2.5 mmol) in chloroform (25 cm^3) in the presence of triethylamine (1 cm^3), and the solution was heated under reflux, with stirring, for 72 h. The solvent was removed under reduced pressure, and the crude product was purified by dry flash chromatography (10−40% ethyl acetate in hexane as eluent) to give methyl 3-(4,5-diphenylimidazol-1-yl)-acrylate **41** (0.45 g, 59%) as a 88:12 *E*/*Z* isomer mixture; mp 208−210 °C (from toluene); (Found: C, 74.9; H, 5.25; N, 8.95. $C_{19}H_{16}N_2O_2$ requires C, 75.0; H, 5.25; N, 9.2); (Found: M^+ 304.1211. $C_{19}H_{16}N_2O_2$ requires *M* 304.1211); δ_H (*E*-isomer) 8.06 (1H, s), 7.54 (1H, d, $^3J = 14.5$), 7.51−7.42 (5H, m), 7.43−7.29 (2H, m), 7.24−7.16 (3H, m), 6.07 (1H, d, $^3J = 14.5$), and 3.70 (3H, s); δ_H (*Z*-isomer) 8.73 (1H, s), 6.53 (1H, d, $^3J = 10.3$), 5.54 (1H, d, $^3J = 10.3$), and 3.75 (3H, s) (with other signals overlapping); δ_C (*E*-isomer) 166.8 (quat), 140.3 (quat), 136.2, 135.0, 133.6 (quat), 131.5 (2CH), 130.0, 129.9 (2CH), 129.1 (quat), 128.7 (2CH), 128.3 (quat), 127.7, 127.4 (2CH), 107.6, and 52.4 (CH_3); δ_C (*Z*-isomer) 139.4, 132.5, and 108.2 (all other signals were indistinguishable); *m*/*z* 304 (M^+, 93%), 273 (14), 245 (100), 219 (97), 190 (32), 165 (85), 142 (30), 115 (49), and 89 (54).

Methyl 3-(4,5-Dicyanoimidazol-1-yl)-acrylate 43. Methyl propynoate **10** (0.29 g, 3.5 mmol) was added to a solution of 4,5-dicyanoimidazole **42** (0.41 g, 3.5 mmol) in chloroform (25 cm^3) in the presence of triethylamine (1 cm^3), and the solution was heated under reflux, with stirring, for 72 h. The crude product was purified by dry flash chromatography (10−20% ethyl acetate in hexane as eluent) to give methyl 3-(4,5-dicyanoimidazol-1-yl)-acrylate **43** as a 90:10 *E*/*Z* isomer mixture (0.04 g total, 6%); mp 140−142 °C; (Found: M^+ 202.0494. $C_9H_6N_4O_2$ requires *M* 202.0491); δ_H (*E*-isomer) ([$^2H_6$]acetone) 8.76 (1H, s), 8.08 (1H, d, $^3J = 14.4$), 6.83 (1H, d, $^3J = 14.4$), and 3.83 (3H, s); δ_H (*Z*-isomer) 7.90 (1H, d, $^3J = 12.1$), 5.67 (1H, d, $^3J = 12.1$), and 3.69 (3H, s) (imidazole singlet indistinguishable); δ_C (*E*-isomer) ([$^2H_6$]acetone) 163.8 (quat), 140.9, 133.1, 123.0 (quat), 112.8, 110.9 (CN), 110.6 (CN), 107.1 (quat), and 50.9; *m*/*z* 202 (M^+, 8%), 171 (17), 156 (53), 155 (98), 154 (100), 153 (99), 152 (76), 146 (36), 118 (53), and 113 (72).

Reaction of 4(5)-Methylimidazole with Methyl Propynoate. 4-Methylimidazole **44** (0.41 g, 5 mmol) and methyl propynoate **10** (0.42 g, 5 mmol) were heated under reflux in toluene (15 cm^3) for 2 h, during which time the reaction darkened to deep yellow. The solvent was removed under reduced pressure to afford a deep yellow crude liquid that was distilled [136 °C (5.0 Torr)], yielding a yellow oil (0.67 g, 80%). A ^1H NMR spectrum showed four characteristic doublets due to the α-methine proton of a propenoate carbon−carbon double bond in each case and hence indicating that the oil contained *E*- and *Z*-isomers of both methyl 3-(4-methylimidazol-1-yl)-acrylate **45** and methyl 3-(5-methylimidazol-1-yl)-acrylate **46**. Separation of the 4-methyl and 5-methyl isomers could not be achieved by distillation or by dry flash chromatography (very similar R_f values for all eluents).

Methyl 3-(2*H*-Imidazol-1-yl)-3-phenylacrylate 50. Methyl 2,3-dibromo-3-phenylpropanoate **48** (3.19 g, 10 mmol) was added to a solution of imidazole **32** (1.00 g, 15 mmol) and triethylamine (5.00 g, 50 mmol) in toluene (100 cm^3) and heated under reflux overnight. Water (60 cm^3) was added to the cooled reaction to dissolve the solids present. The solution was extracted with dichloromethane (3 × 50 cm^3), and the organic extracts were washed with water (60 cm^3) and dried ($MgSO_4$). The crude product was purified by dry flash chromatography on silica (50% ethyl acetate in hexane) to give a 17:83 isomer mixture of methyl 3-(2*H*-imidazol-1-yl)-3-phenylacrylate **50** (1.74 g, 78%); mp 102−103 °C (lit.,[29] 102−103 °C), which was not further analyzed; δ_H (major isomer) 7.51 (1H, s), 7.46−7.14 (5H, m), 7.06 (1H, d, $^4J = 1.1$), 6.84 (1H, d, $^4J = 1.1$), 6.16 (1H, s), and 3.59 (3H, s); δ_H (minor isomer) 7.00 (2H, dd, $^3J = 6.6$, $^4J = 1.1$), 6.06 (1H, s), and 3.52 (3H, s), other signals overlapping.

Methyl 3-(2-Methylimidazol-1-yl)-3-phenylacrylate 51. A solution of 2-methylimidazole **34** (0.68 g, 8.2 mmol) and methyl 2,3-dibromo-3-phenylpropanoate **48** (1.34 g, 4.1 mmol) in a mixture of toluene (35 cm^3) and triethylamine (5 cm^3) was heated under reflux overnight. The solvent was removed under reduced pressure, and the crude product was purified by dry flash chromatography (40% ethyl acetate in hexane as eluent) followed by Kugelrohr distillation to give methyl 3-(2-methylimidazol-1-yl)-3-phenylacrylate **51** as a 86:14 isomer mixture (0.70 g, 70%); bp 168 °C (3.0 Torr); (Found: M^+ 242.1052. $C_{14}H_{14}N_2O_2$ requires *M* 242.1053); δ_H (major isomer) 7.42−7.27 (3H, m), 7.17−7.13 (2H, m), 6.98 (1H, d, $^3J = 1.5$), 6.73 (1H, d, $^3J = 1.5$), 6.47 (1H, s), 3.58 (3H, s), and 2.09 (3H, s); δ_H (minor isomer) 6.86 (1H, d, $^3J = 1.5$), 6.77 (1H, d, $^3J = 1.5$), 5.95 (1H, s), and 2.04 (3H, s) (other signals indistinguishable); δ_C (major isomer) 163.7 (quat), 146.9 (quat), 145.1 (quat), 134.7 (quat), 131.1, 129.0 (2CH), 127.6, 126.4 (2CH), 120.0, 114.7, 51.6 (CH_3), and 12.7 (CH_3); δ_C (minor isomer) 165.1 (quat), 149.1 (quat), 145.4 (quat), 133.4 (quat), 130.5, 128.0, 120.6, 113.8, 51.5 (CH_3), and 14.3 (CH_3) (other signals indistinguishable); *m*/*z* 242 (M^+, 90%), 211 (59), 183 (88), 161 (47), 129 (36), 115 (60), 102 (76), and 56 (100).

FVP of Methyl 3-(2*H*-Imidazol-1-yl)-acrylate 33. Separate pyrolysis of *E*- and *Z*-isomers of methyl 3-(2*H*-imidazol-1-yl)-acrylate **33** under the same conditions (130 mg, $T_f = 900$ °C, $T_i = 120$ °C, $P = 0.017-0.065$ Torr, $t = 15$ min) gave solid yellow pyrolysates containing pyrrolo[1,2-*a*]imidazol-5-one **3** as the major product and pyrrolo[1,2-*c*]imidazol-5-one **4** as the minor product in a 73:27 ratio in each case (80 mg, 78%). Products were identified by comparison of their ^1H NMR spectra with those previously reported.[31] *Z*-Isomer pyrolysis δ_H (**3**) 7.17 (1H, d, $^3J = 6.2$), 6.95 (1H, s), 6.90 (1H, s), and 5.96 (1H, d, $^3J = 6.2$); δ_H (**4**) 7.70 (1H, s), 7.26 (1H, d, $^3J = 5.9$), 6.74 (1H, s), and 5.79 (1H, d, $^3J = 5.9$); *E*-isomer pyrolysis δ_H (**3**) 7.18 (1H, d, $^3J = 6.2$), 6.97 (1H, d, $J = 1.8$), 6.92 (1H, s), and 5.96 (1H, d, $^3J = 6.2$); δ_H (**4**) 7.69 (1H, s), 7.25 (1H, d, $^3J = 5.9$), 6.75 (1H, s), and 5.79 (1H, d, $^3J = 5.9$).

FVP of Methyl 3-(2*H*-Imidazol-1-yl)but-2-enoate 49. Pyrolysis of the isomer mixture of **49**[29] (see Supporting Information) (41 mg, $T_f = 850$ °C, $T_i = 110$ °C, $P = 0.020-0.038$ Torr, $t = 10$ min) gave a solid yellow pyrolysate of 7-methylpyrrolo[1,2-*a*]imidazol-5-one **52** as the major product and 7-methylpyrrolo[1,2-*c*]imidazol-5-one **54** as the minor product in a 80:20 ratio (with products identified by comparison with the ^1H NMR spectra of pyrrolo[1,2-*a*]imidazol-5-one and pyrrolo[1,2-*c*]imidazol-5-one[31] (25 mg, 76%); δ_H (**52**) 6.97 (1H, d, $^nJ = 1.5$), 6.89 (1H, s), 5.67 (1H, m), and 2.16 (3H, s); δ_H (**54**) 7.67 (1H, s), 6.76 (1H, s), 5.53 (1H, m), and 2.13 (3H, s).

FVP of Methyl 3-(2*H*-Imidazol-1-yl)-3-phenylacrylate 50. Pyrolysis of the isomer mixture of **50** (43 mg, $T_f = 850$ °C, $T_i = 140$ °C, $P = 0.012-0.026$ Torr, $t = 15$ min) gave a solid dark yellow pyrolysate of 7-phenylpyrrolo[1,2-*a*]imidazol-5-one **53** and 7-phenylpyrrolo[1,2-*c*]imidazol-5-one **55** in a 80:20 ratio, respectively (33 mg, 90%); (Found: M^+ 196.0621. $C_{12}H_8N_2O$ requires *M* 196.0636); δ_H (**53**) 8.11−8.05 (2H, m), 7.47−7.38 (3H, m), 7.07 (1H, m), 7.02 (1H, m), and 6.15 (1H, s); δ_C 162.7 (quat), 154.8 (quat),

149.0 (quat), 134.1, 134.0 (quat), 131.9, 128.8 (2CH), 128.4 (2CH), 116.6, and 113.8; δ_H (**55**) 7.80 (1H, s), 7.65−7.61 (2H, m), and 6.01 (1H, s), other signals overlapping.

3-Methylpyrrolo[1,2-*c*]imidazol-5-one 56. FVP of methyl 3-(2-methylimidazol-1-yl)-acrylate **35** (65 mg, T_f = 875 °C, T_i = 120 °C, P = 0.020−0.065 Torr, t = 7 min) gave a solid yellow pyrolysate of 3-methylpyrrolo[1,2-*c*]imidazol-5-one **56** (47 mg, 88%), mp > 195 °C (dec); (Found: M^+ 134.0479. $C_7H_6N_2O$ requires *M* 134.0480); δ_H 7.21 (1H, d, ^3J = 5.7), 6.60 (1H, s), 5.75 (1H, d, ^3J = 5.7), and 2.44 (3H, s); δ_C 163.5 (quat), 148.0 (quat), 137.1, 134.9 (quat), 126.2, 122.6, and 13.9; *m*/*z* 134 (M^+, 100%), 105 (19), 79 (38), and 42 (100).

3-Phenylpyrrolo[1,2-*c*]imidazol-5-one 57. FVP of methyl 3-(2-phenylimidazol-1-yl)-acrylate **37** (48 mg, T_f = 850 °C, T_i = 180 °C, P = 0.019−0.085 Torr, t = 9 min) gave 3-phenylpyrrolo-[1,2-*c*]imidazol-5-one **57** (36 mg, 88%) as a yellow oil; (Found: M^+ 196.0635. $C_{12}H_8N_2O$ requires *M* 196.0636); δ_H 8.37−8.30 (2H, m), 7.49−7.41 (3H, m), 7.31 (1H, d, ^3J = 5.9), 6.88 (1H, s), and 5.87 (1H, d, ^3J = 5.9); δ_C 163.3 (quat), 150.3 (quat), 136.8, 131.2, 128.3 (2CH), 128.2 (2CH), 127.6 (quat), 127.1, and 122.6 (one quaternary overlapping); *m*/*z* 196 (M^+, 65%), 168 (100), 141 (35), and 114 (39).

2,3-Dimethylpyrrolo[1,2-*a*]imidazol-5-one 59. FVP of methyl 3-(4,5-dimethylimidazol-1-yl)-acrylate **39** (40 mg, T_f = 850 °C, T_i = 80 °C, P = 0.020−0.075 Torr, t = 9 min) gave 2,3-dimethylpyrrolo[1,2-*a*]imidazol-5-one **59** (38 mg, 95%) as a red solid; mp > 205 °C (dec); (Found: M^+ 148.0634. $C_8H_8N_2O$ requires *M* 148.0636); δ_H 7.08 (1H, d, ^3J = 6.0), 5.88 (1H, d, ^3J = 6.0), 2.21 (3H, s), and 2.06 (3H, s); δ_C 164.1 (quat), 153.3 (quat), 139.9 (quat), 136.4, 126.6, 123.1 (quat), 12.0 (CH_3), and 8.5 (CH_3); *m*/*z* 180 (M^+, 78%), 133 (18), 107 (13), and 79 (49).

2,3-Diphenylpyrrolo[1,2-*a*]imidazol-5-one 60. FVP of methyl 3-(4,5-diphenylimidazol-1-yl)-acrylate **41** (76 mg, T_f = 825 °C, T_i = 230 °C, P = 0.010−0.100 Torr, t = 14 min) gave 2,3-diphenylpyrrolo[1,2-*a*]imidazol-5-one **60** (63 mg, 93%) as a red oil; (Found: M^+ 272.0944. $C_{18}H_{12}N_2O$ requires *M* 272.0949); δ_H 7.55−7.46 (5H, m), 7.40−7.36 (2H, m), 7.29−7.23 (4H, m), and 6.02 (1H, d, ^3J = 6.1); δ_C 163.3 (quat), 154.6 (quat), 143.6 (quat), 132.9 (quat), 129.2 (2CH), 128.6 (quat), 128.40, 128.35 (2CH), 128.2 (2CH), 127.9, 127.7, 127.6, 127.4 (2CH), and 127.2 (quat); *m*/*z* 272 (M^+, 15%), 244 (15), 165 (6), 121 (10), and 84 (100).

3-Methyl-7-phenylpyrrolo[1,2-*c*]imidazol-5-one 58. FVP of methyl 3-(2-methylimidazol-1-yl)-3-phenylacrylate **51** (42 mg, T_f = 875 °C, T_i = 160 °C, P = 0.010−0.060 Torr, t = 10 min) gave 3-methyl-7-phenylpyrrolo[1,2-*c*]imidazol-5-one **58** (33 mg, 91%) as a yellow solid; mp > 200 °C (dec); (Found: M^+ 210.0793. $C_{13}H_{10}N_2O$ requires *M* 210.0793); δ_H 7.72−7.67 (2H, m), 7.57−7.48 (3H, m), 7.02 (1H, s), 6.06 (1H, s), and 2.59 (3H, s); δ_C 163.4 (quat), 151.3 (quat), 147.6 (quat), 133.9 (quat), 131.7, 130.0 (quat), 129.1 (2CH), 127.3 (2CH), 126.6, 114.3, and 13.9 (CH_3); *m*/*z* 210 (M^+, 21%), 182 (14), 169 (29), 154 (10), 140 (49), 128 (28), 114 (62), 102 (78), and 42 (100).

Methyl 3-(Benzimidazol-1-yl)-acrylate 61. Methyl propynoate **10** (4.20 g, 50 mmol) was added dropwise to a stirred solution of benzimidazole (5.90 g, 50 mmol) in tetrahydrofuran (40 cm^3) and heated under reflux for 4 h. The solution was stirred overnight. The solvent was removed under reduced pressure, and the crude product was recrystallized from toluene (15 cm^3) to afford methyl 3-(benzimidazol-1-yl)-acrylate **61** as a 44:56 *E*/*Z* isomer mixture (9.58 g, 95%); mp 102−104 °C (lit.,[35] *Z*-isomer 95.5−96.5 °C, *E*-isomer 111.0−112.0 °C); δ_H (*E*-isomer) 8.06 (1H, s), 7.96 (1H, d, ^3J = 14.5), 7.72 (1H, m), 7.31−7.21 (3H, m), 6.14 (1H, d, ^3J = 14.5), and 3.70 (3H, s); δ_H (*Z*-isomer) 9.09 (1H, s), 7.72 (1H, m), 7.31−7.21 (3H, m), 6.94 (1H, d, ^3J = 10.4), 5.52 (1H, d, ^3J = 10.4), and 3.67 (3H, s); δ_C (*E*- and *Z*-isomers) 166.5 (quat), 164.9 (quat), 144.2 (quat), 143.9, 142.6 (quat), 141.3, 135.3, 133.1 (quat), 131.8 (quat), 130.3, 124.7, 124.02, 123.97, 123.6, 120.8, 120.4, 110.8, 109.2, 105.8, 105.0, 51.69 (CH_3), and 51.58 (CH_3); *m*/*z* 202 (M^+, 82%), 187 (35), 172 (43), 171 (100), 170 (40), 159 (37), 145 (73), 144 (57), 143 (60), 142 (67), 129 (48), and 118 (51).

Methyl 3-(Benzimidazol-1-yl)-3-phenylacrylate 62. Methyl 2,3-dibromo-3-phenylpropanoate **48** (3.19 g, 10 mmol) was added to a solution of benzimidazole (1.24 g 10 mmol) and triethylamine (5.0 g) in toluene (100 cm^3) and heated under reflux for 1.5 h. The solution was concentrated to afford a crude reaction mixture that was added to ether. Unreacted benzimidazole was filtered, and the filtrate was washed with water (2 × 40 cm^3), dried ($MgSO_4$), and concentrated under reduced pressure to give methyl α-bromocinnamate (2.13 g, quantitative); δ_H 8.22 (1H, s), 7.87−7.83 (2H, m), 7.44−7.40 (3H, m), and 3.90 (3H, s); *m*/*z* 242 and 240 (M^+, 36 and 38%), 211 (22), 209 (22), 183 (20), 181 (21), 162 (40), 161 (100) 129 (71), and 102 (98) (cf ref 36). This product was dissolved in toluene (100 cm^3), benzimidazole (1.24 g, 10 mmol) was added, and the solution was heated under reflux for 24 h. The solvent was removed, water (50 cm^3) was added, and the mixture was extracted with dichloromethane (3 × 30 cm^3). The organic extracts were washed with water (50 cm^3) and dried ($MgSO_4$). Removal of the magnesium sulfate and concentration of the filtrate under reduced pressure gave the crude product, which was recrystallized from toluene (20 cm^3) to give methyl 3-(benzimidazol-1-yl)-3-phenylacrylate **62** (0.49 g, 21%); mp 127−129 °C; (Found: M^+ 278.1051. $C_{17}H_{14}N_2O_2$ requires *M* 278.1055); δ_H 8.00 (1H, s), 7.83 (1H, dt, ^3J = 8.0, ^4J = 0.9), 7.51−7.41 (2H, m), 7.40−7.34 (2H, m), 7.31−7.22 (2H, m), 7.13 (1H, td, ^3J = 7.7, ^4J = 1.2), 6.80 (1H, dt, ^3J = 8.0, ^4J = 0.9), 6.43 (1H, s), and 3.59 (3H, s); δ_C 164.1 (quat), 146.0 (quat), 143.9, 143.5 (quat), 134.6 (quat), 133.5 (quat), 131.4, 129.0 (2CH), 127.5 (2CH), 123.5, 122.7, 120.4, 113.1, 111.3, and 51.7 (CH_3); *m*/*z* 278 (M^+, 51%), 263 (24), 247 (23), 219 (31), 161 (21), 118 (27), and 91 (100).

Pyrrolo[1,2-*a*]benzimidazol-1-one 6. Pyrolysis conditions for methyl 3-(benzimidazol-1-yl)-acrylate **61** required optimization of sublimation temperature by small-scale reactions (50 mg, T_f = 950 °C, T_i = 50−200 °C, P_{range} = 0.01−0.05 Torr, t = 12 min) leading to pyrrolo[1,2-*a*]benzimidazol-1-one **6**. However, pyrolysis on a larger scale was complicated by poor volatility (resulting in degradation of substrate) and degradation of products at the furnace exit/trap due to the high furnace temperature. Optimum conditions utilized a dry ice/acetone cold finger trap and slow sublimation of the substrate at an inlet temperature of 115 °C (0.50 g, 2.5 mmol, T_i = 115 °C, P_{range} = 0.01−0.10 Torr, t = 105 min) after which the pyrolysate was rinsed with dry ether from the cold trap surface under a dry nitrogen atmosphere. The crude product was absorbed onto silica and rapidly purified by dry flash chromatography (70% ethyl acetate in hexane) to give pyrrolo[1,2-*a*]benzimidazol-1-one **6**[32] (0.30 g, 71%); mp 106−108 °C (from cyclohexane); (Found: M^+ 170.0481. $C_{10}H_6N_2O$ requires *M* 170.0480); δ_H 7.62 (2H, dd, ^3J = 7.8 and 4.2), 7.35−7.12 (2H, m), 7.24 (1H, d, ^3J = 6.1), and 6.27 (1H, d, ^3J = 6.1); δ_C 162.4 (quat), 159.2 (quat), 148.9 (quat), 135.0, 132.6, 129.9 (quat), 127.2, 124.4, 121.8, and 111.7; *m*/*z* 170 (M^+, 31%), 143 (15), 142 (100), 118 (25), 115 (32), 114 (13), 102 (15), 91 (11), and 88 (11).

3-Phenylpyrrolo[1,2-*a*]benzimidazol-1-one 63. Pyrolyses of methyl 3-(benzimidazol-1-yl)-3-phenylacrylate **62** (92 mg, 0.33 mmol, T_f = 950 °C, T_i = 50−180 °C, P_{range} = 0.03−0.12 Torr, t = 23 min) using a dry ice/acetone cold finger trap were also complicated by thermal degradation of the product at the exit point of the furnace. The pyrolysate was rinsed from the trap in dry ether, absorbed onto silica, and purified by dry flash chromatography (50% ethyl acetate in hexane) to give 3-phenylpyrrolo[1,2-*a*]benzimidazol-1-one **63** (29 mg, 36%); mp 120−122 °C; (Found: M^+ 246.0790.

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$C_{16}H_{10}N_2O$ requires *M* 246.0793); δ_H 8.20−8.15 (2H, m), 7.73 (1H, ddd, $^3J = 7.9$, $^4J = 1.1$, and $^nJ = 0.7$), 7.66 (1H, ddd, $^3J = 7.9$, $^4J = 1.1$, and $^nJ = 0.7$), 7.55−7.46 (3H, m), 7.34 (1H, td, $^3J = 7.6$ and $^4J = 1.2$), 7.24 (1H, td, $^3J = 7.6$ and $^4J = 1.2$), and 6.44 (1H, s); δ_C 162.6 (quat), 148.7 (quat), 147.2 (quat), 131.8, 129.8 (quat), 129.0 (2CH), 128.6 (quat), 128.2 (2CH), 127.1, 125.4 (quat), 124.2, 121.8, 121.7, and 111.8; *m*/*z* 246 (M^+, 34%), 219 (23), 218 (62), 194 (9), 147 (10), 109 (23), and 86 (100).

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Supporting Information Available: Full experimental details for the synthesis of **9**, **47**, **48**, and **49** and FVP of **23** and **25**; NOESY spectrum of **24**. This material is available free of charge via the Internet at http://pubs.acs.org.

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