Biradicals from Thermolysis of *N*-[2-(1-Alkynyl)phenyl]-*N*′-phenylcarbodiimides and Their Subsequent Transformations to 6*H*-Indolo[2,3-*b*]quinolines†

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Thermolysis of the carbodiimide **9a** in γ-terpinene at 138 °C produced 2-(phenylamino)quinoline (**11a**, 49%) and the parent 6*H*-indolo[2,3-*b*]quinoline (**14a**, 16%). Apparently, **11a** was produced via the biradical **10a** followed by hydrogen-atom abstraction from γ-terpinene. A two-step biradical pathway through **12a** or a one-step intramolecular Diels−Alder reaction could furnish **13a**, which then underwent tautomerization to give **14a**. With the carbodiimide **9b** having a trimethylsilyl substituent at the acetylenic terminus, thermolysis in refluxing *p*-xylene at 138 °C produced the 6*H*-indolo[2,3-*b*]quinoline **14b** (86%) exclusively. Treatment of **14b** with 6 N NaOH in refluxing ethanol then furnished **14a** in 92% yield. Similarly, the 6*H*-indolo[2,3-*b*]quinolines **14c**−**f** were obtained from thermolysis of the carbodiimides **9c**−**f**. The use of the aza-Wittig reaction between 4-methoxyphenyl isocyanate and the iminophosphoranes **2d** and **2f** to produce the corresponding carbodiimides followed by thermolysis furnished the 6*H*-indolo[2,3-*b*]quinolines **16d** and **16f** having a methoxy substituent at the C-2 position. Thermolysis of the carbodiimides **25a** and **25b** produced **26a** and **26b** having two indoloquinoline units connected at the 11 and 11′ positions with either a three-carbon or a five-carbon tether. Using 1,4-phenylene diisocyanate for the aza-Wittig reaction with 2 equiv of the iminophosphorane **2g** followed by thermolysis furnished **31** (66%) having two indoloquinoline units incorporated in the seven fused rings.

Introduction

We recently reported the use of iminophosphoranes **2**, readily prepared from treatment of 2-(1-alkynyl)anilines **1** with dibromotriphenylphosphorane (Ph_3PBr_2), for the aza-Wittig reaction with diphenylketene to produce *N*-[2-(1-alkynyl)phenyl]ketenimines **3** (Scheme 1).[1] The ketenimines **3** then were converted to the quinolines **5** and/or the 5*H*-benzo[*b*]carbazoles **8** depending on the nature of the substituent at the acetylenic terminus under mild thermal conditions. A similar study was also reported by Schmittel, Engels, and co-workers recently.[2] In the presence of an excess of 1,4-cyclohexadiene (1,4-CHD) as a hydrogen-atom donor, **3a** (R = H) was converted to the quinoline **5a** ($t_{1/2}$ = 0.37 h at 22 °C) in 49% yield. Apparently, the reaction proceeds through an initial cycloaromatization reaction to form the biradical **4a** followed by hydrogen-atom abstraction from 1,4-CHD. The transformation from **3a** to **4a** represents a new example of a growing list of the thermally induced biradical-forming cycloaromatization reactions. While the Bergman cyclization of (*Z*)-3-hexene-1,5-diynes (enediynes),[3] the Myers cyclization of (*Z*)-1,2,4-heptatrien-6-ynes (enyne-allenes),[4] and the Moore cyclization of enyne-ketenes[5] to biradical species have been extensively studied, the biradical-forming reactions involving other heteroatoms in the conjugated systems are rare.[6] The ability to produce **4a** from **3a** demonstrates the feasibility of placing a nitrogen atom in the conjugated system for the generation of biradicals under mild thermal conditions and provides a new avenue for the design of novel DNA-cleaving agents.[7]

Interestingly, when **3b** (R = $SiMe_3$) was heated under refluxing benzene, the benzocarbazole **8b** was produced exclusively ($t_{1/2}$ = 0.89 h at 72 °C). Presumably, the reaction proceeded through a different cascade sequence involving an initial formation of a five-membered ring to produce biradical **6b** followed by an intramolecular radical−radical combination to form **7b** and a subsequent tautomerization to furnish **8b**. While a one-step intramolecular Diels−Alder reaction of **3b** could also produce **7b** as reported previously in several analogous systems,[8] the presence of a sterically demanding trimethylsilyl group

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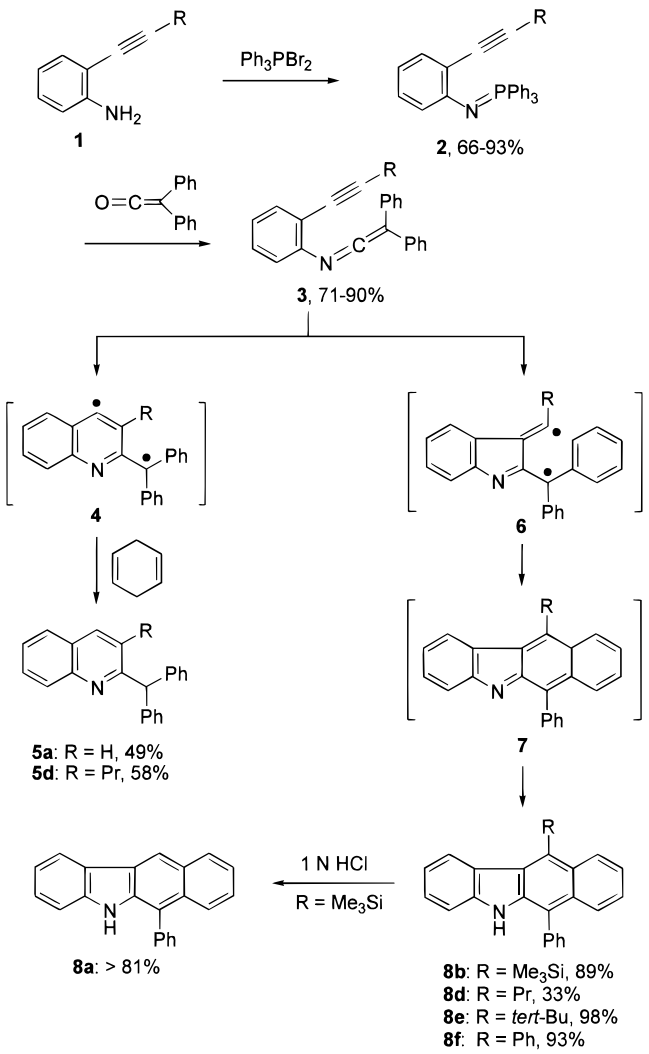
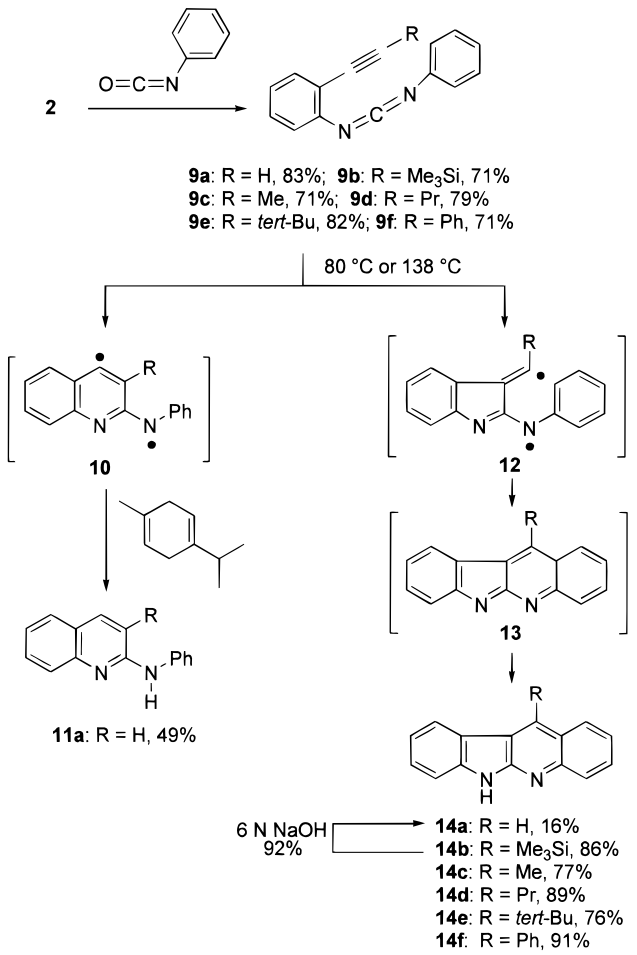
Scheme 1



Scheme 2



at the acetylenic terminus makes the concerted process unlikely to occur under mild thermal conditions. The reaction was directed toward **8b** presumably because of the emergence of a severe nonbonded steric interaction in **4b** (R = $SiMe_3$)[9] and the ability of the trimethylsilyl group in stabilizing an adjacent radical site in **6b**.[10] Such a change of the reaction pathway was also observed in a similar study[2] and in several analogous cases of ring closures of enyne-allenes[9,11] and enyne-ketenes.[12] Treatment of **8b** with 1 N HCl at 40 °C for 1 h produced the desilylated adduct **8a** (>81% yield). It is worth noting that **8a** could not be obtained from **3a** directly. With the ketenimine **3d** (R = Pr), both the quinoline **5d** (58%) and the benzocarbazole **8d** (33%) were produced. In the cases of **3e** (R = *t*-Bu) and **3f** (R = Ph), the benzocarbazoles **8e** and **8f** were produced exclusively. The presence of a sterically demanding *tert*-butyl group at the acetylenic terminus of **3e** makes the formation of **7e** via the concerted intramolecular Diels–Alder reaction unlikely.

A logical extension of this work involves replacing the ketenimine moiety in **3** with other heterocumulenes. Carbodiimide appears to be an excellent candidate for such a substitution. We now report our findings of using *N*-[2-(1-alkynyl)phenyl]-*N*′-phenylcarbodiimides **9** to produce biradicals and their subsequent transformations to 2-(phenylamino)quinoline (**11a**) and 6*H*-indolo[2,3-*b*]-quinolines **14** (Scheme 2).[13] Recently, there has been a surge of interest in developing new synthetic pathways to 6*H*-indolo[2,3-*b*]quinolines[8b,14] because several members of this group of compounds have been found to possess interesting biological activities.[15]

Results and Discussion

It was interesting to learn that carbodiimide **9a** had already been prepared previously by treatment of imi-

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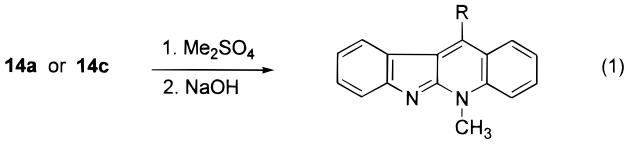
nophosphorane **2a** (R = H) with phenyl isocyanate.[16] Thermolysis of **9a** in toluene at 160 °C in a sealed tube furnished 2-(phenylamino)quinoline (**11a**, 40%) and the parent 6*H*-indolo[2,3-*b*]quinoline (**14a**, 19%).[16] We were able to reproduce similar results by heating **9a**, isolated in 83% yield from treatment of **2a** with phenyl isocyanate, in γ-terpinene at 138 °C to afford **11a** (49%) and **14a** (16%). Apparently, **11a** was produced via the biradical **10a** followed by hydrogen-atom abstraction from γ-terpinene. A two-step biradical pathway through **12a** or a one-step intramolecular Diels−Alder reaction could furnish **13a**, which then underwent tautomerization to give **14a**. Several analogous examples in which a carbon−carbon double bond replaces the triple bond in **9** for the intramolecular Diels−Alder reaction have been reported.[8b,14] The indoloquinoline **14a** was used as an immediate precursor for the synthesis of a naturally occurring alkaloid, 5-methyl-5*H*-indolo[2,3-*b*]quinoline (**15a**) (eq 1),[15,16] which was isolated from the roots of the West African plant *Cryptolepis sanguinolenta*[17] and was found to possess interesting biological activities.[15]



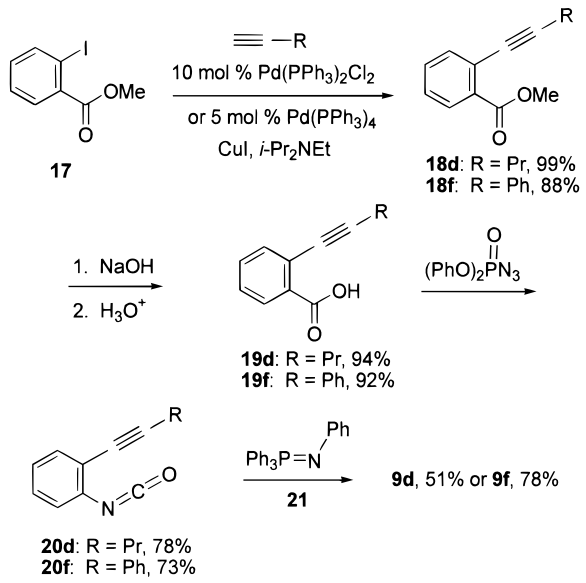
15a: R = H, 42%
15c: R = Me, 65%

The reaction sequence outlined in Scheme 2 could provide an efficient route to the indoloquinoline **14a** if the competing pathway toward the quinoline **11a** could be suppressed. The result with **3b** suggests that a trimethylsilyl group at the acetylenic terminus could serve as a surrogate for the hydrogen atom in directing the reaction toward the indoloquinoline **14b**. A subsequent protodesilylation reaction could lead to **14a**. It was gratifying to observe that thermolysis of **9b**, obtained in 71% from **2b** and phenyl isocyanate, in refluxing *p*-xylene at 138 °C produced **14b** in 86% yield. Similarly, heating the reaction mixture of **2b** and phenyl isocyanate in refluxing *p*-xylene without isolation of **9b** also gave **14b** (61%) in a single operation. Treatment of **14b** with 6 N NaOH in refluxing ethanol for 12 h then furnished **14a** in 92% yield.

When **9c** was subjected to thermolysis in *p*-xylene at 138 °C for 4 h, the indoloquinoline **14c** (77%) was produced exclusively, indicating a preferential formation of **13c** for subsequent tautomerization to **14c**. The corresponding quinoline **11c** (R = Me) was not detected. Direct thermolysis of the reaction mixture of **2c** and phenyl isocyanate in refluxing *p*-xylene without isolation of **9c** also afforded **14c** (59%) in a single operation. It was reported that **14c** could serve as the immediate precursor of 5,11-dimethyl-5*H*-indolo[2,3-*b*]quinoline (**15c**) (eq 1), which was found to display a strong antibacterial, antimycotic, and cytotoxic activity in vitro, as well as significant antitumor properties in vivo.[15]

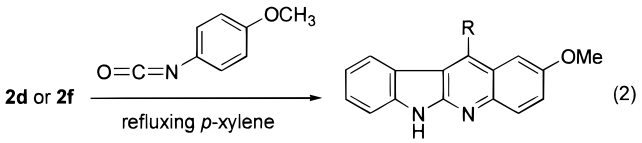
Similarly, when **9d** having a propyl group at the acetylenic terminus was heated either in refluxing *p*-xylene or in γ-terpinene at 138 °C, the indoloquinoline **14d** (89%) was produced exclusively, in sharp contrast

Scheme 3



to the ketenimine **3d** (R = Pr), which furnished the quinoline **5d** preferentially. In addition, the carbodiimide **9d** is thermally less labile than the ketenimine **3d**, and a higher temperature is needed to promote the reaction. Treatment of **2d** with phenyl isocyanate in refluxing *p*-xylene without isolation of **9d** also afforded **14d** directly in a one-step operation in 72% yield. With **9e** having a sterically very demanding *tert*-butyl group, thermolysis in refluxing *p*-xylene for 14 h produced the indoloquinoline **14e** (76%). Again, the presence of a *tert*-butyl group at the acetylenic terminus of **9e** makes the formation of **13e** via the concerted intramolecular Diels−Alder reaction unlikely. With a phenyl substituent at the acetylenic terminus of **9f**, thermolysis under refluxing benzene (80 °C) for 4 h was sufficient to induce the transformation to **14f**[18] in 91% yield. Direct thermolysis of the reaction mixture of **2f** and phenyl isocyanate in refluxing benzene without isolation of **9f** also afforded **14f** in 67% yield.

4-Methoxyphenyl isocyanate was also used for the aza-Wittig reaction with **2d** and **2f**. Thermolysis of the reaction mixtures furnished the indoloquinolines **16d** and **16f**[8b] having a methoxy substituent at the C-2 position (eq 2).



16d: R = Pr, 47%
16f: R = Ph, 55%

An alternative pathway to the carbodiimides **9** was also developed (Scheme 3). The Pd-catalyzed cross-coupling reaction between **17** and 1-alkynes furnished methyl 2-(1-alkynyl)benzoates **18**, which were hydrolyzed to afford **19**. Treatment of **19** with diphenyl phosphorazidate

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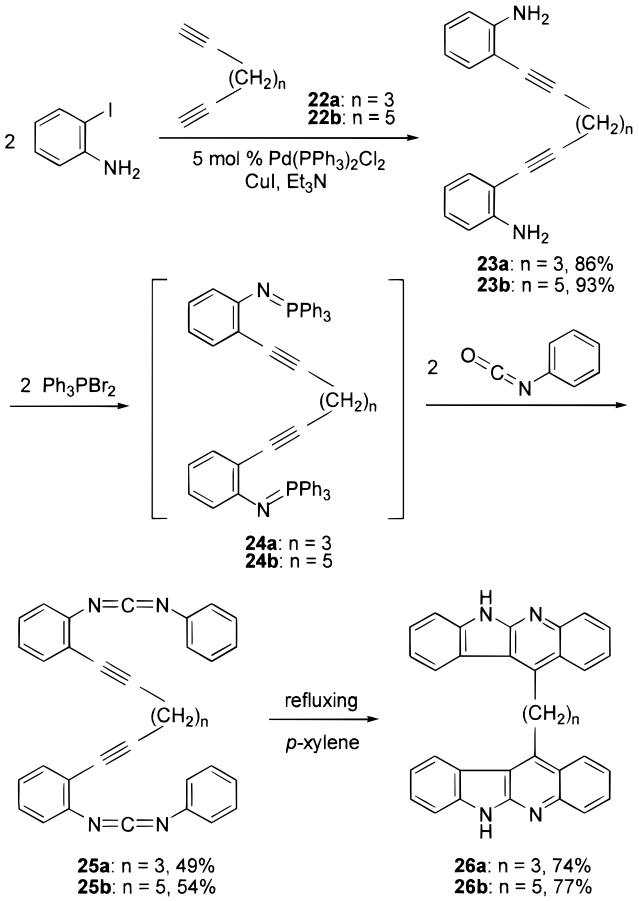
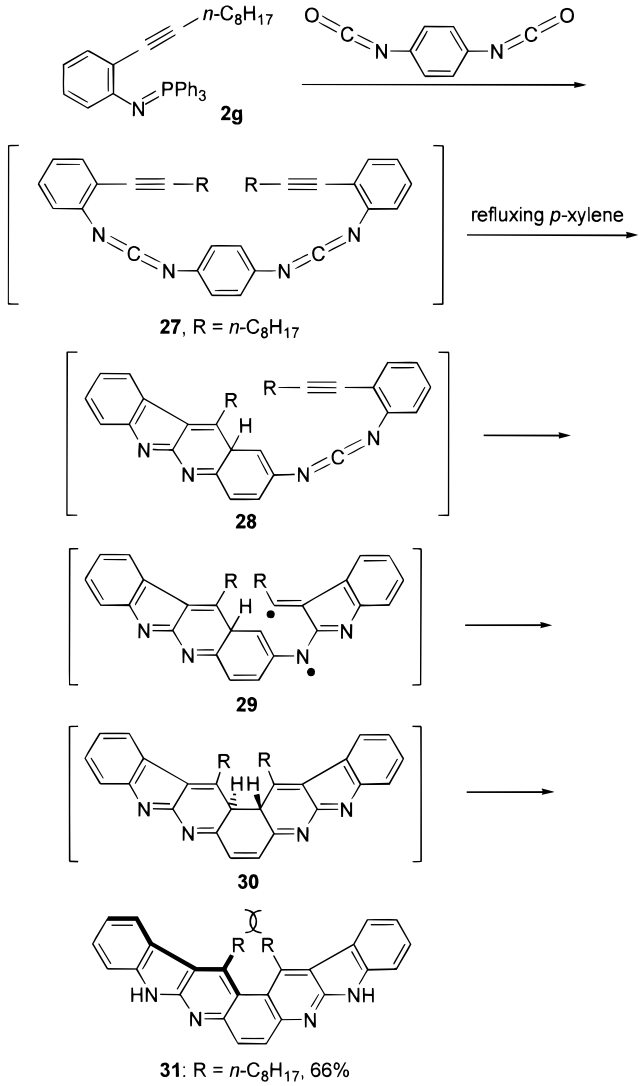
Scheme 4



(DPPA)[19] produced 2-(1-alkynyl)phenyl isocyanates **20**. The subsequent aza-Wittig reactions with the iminophosphorane **21**[20] then gave **9d** and **9f**. Thermolysis of the reaction mixtures of **20d** and **20f** with **21** in refluxing *p*-xylene also produced the indoloquinolines **14d** (50%) and **14f** (55%), respectively.

It is straightforward to adopt the synthetic sequence outlined in Scheme 2 for the preparation of **26a** and **26b** (Scheme 4) as potential bifunctional DNA intercalating agents.[21] The use of the diacetylenes **22a** and **22b** for cross coupling with 2 equiv of 2-iodoaniline eventually allowed the connection of the two indoloquinoline units in **26a** and **26b** with either a three-carbon or a five-carbon tether at the 11 and 11′ positions. The iminophosphoranes **24a** and **24b** were generated in situ from treatment of **23a** and **23b** with 2 equiv of Ph_3PBr_2 for the subsequent aza-Wittig reaction with 2 equiv of phenyl isocyanate, producing the carbodiimides **25a** and **25b** in 49% and 54% overall yield, respectively. It was possible to isolate the iminophosphoranes **24a** (20%) and **24b** (29%) by column chromatography (silica gel) albeit significant decomposition on the column. Treatment of the isolated **24a** with 2 equiv of phenyl isocyanate produced **25a** in 72% yield. Thermolysis of **25a** and **25b** in refluxing *p*-xylene then furnished **26a** (74%) and **26b** (77%), respectively.

Scheme 5



Treatment of 1,4-phenylene diisocyanate with 2 equiv of **2g** for the aza-Wittig reaction produced **27** in situ, which on thermolysis in refluxing *p*-xylene furnished **31** (66%) having two indoloquinoline units incorporated in the seven fused rings (Scheme 5). It was also possible to isolate **27** by column chromatography (silica gel) in 44% yield. The presence of the two *n*-octyl groups in **31** greatly enhances its solubility in organic solvents.

The structure assignment of **31** is based on high-resolution mass spectra, the ^{1}H and ^{13}C NMR spectra, and the NOE studies. The molecular ion was detected on a high-resolution mass spectrometer (m/z = 582.3698). The ^{1}H and ^{13}C NMR spectra showed the right number of signals and pattern of multiplicity consistent with the structure of **31**. Interestingly, the ^{1}H NMR spectrum (Figure 1) exhibited two sets of signals with equal intensity at δ 4.00 (2 H, ddd, J = 12.9, 8.7, 4.2 Hz) and 3.74 (2 H, dt, J = 13.4, 8.0 Hz), indicating that the benzylic hydrogens are diastereotopic. The benzylic hydrogens are diastereotopic because the fused ring structure in **31** is helical due to nonbonded steric interactions of the two *n*-octyl groups. This is reminiscent of the structures of the 4,5-dimethylphenanthrenes, which have been shown to possess a helical twist.[22] The signals of the benzylic hydrogens in DMSO-d_6 remained well separated and exhibited no line broadening even at 110

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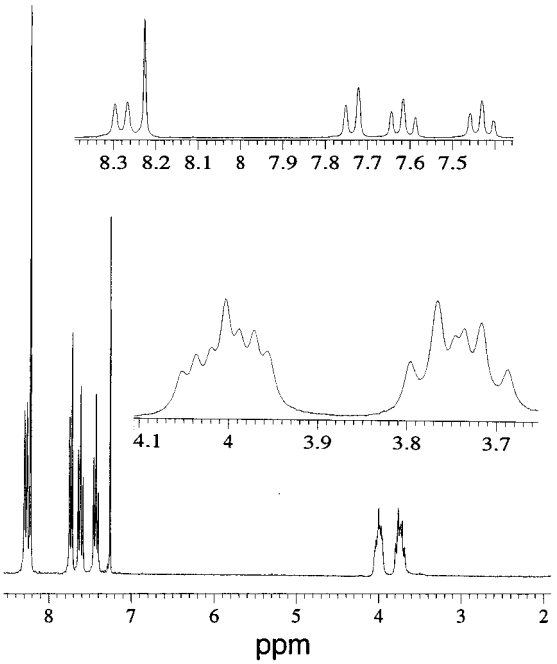
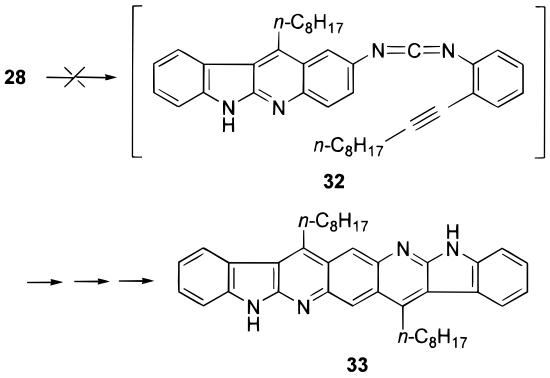


Figure 1. Partial ^{1}H NMR spectrum of the indoloquinoline **31** in $CDCl_3$.

Scheme 6



°C, indicating that the rate of the helix inversion is relatively slow on the NMR time scale even at 110 °C. A significant nuclear Overhauser effect was observed between the doublet aromatic signal at δ 8.28 and the benzylic signal at δ 4.00. However, the nuclear Overhauser effect was negligible with the benzylic signal at δ 3.74. In addition, no NOE interaction between the singlet aromatic signal at δ 8.23 and the two benzylic signals was observed.

The observation of two sets of benzylic signals and the lack of the NOE interaction with the singlet aromatic signal at δ 8.23 preclude the cycloaromatized isomer **33** depicted in Scheme 6 as the reaction product. Because **33** has essentially a planar ring structure, one would expect the ^{1}H NMR signal of the benzylic hydrogens of **33** to be a simple triplet as in the case of **14d**. Furthermore, one would also expect a strong NOE interaction between the benzylic hydrogens and the singlet aromatic hydrogens.

The preferential formation of **31** is presumably because the rate of transformation from **28** to **30** (Scheme 5) is faster than that of tautomerization of **28** to **32** (Scheme 6). Without a prior tautomerization, the biradical **29** has no choice but to cyclize to form **30**, producing **31** after two subsequent tautomerization reactions. Had the intermediate **28** underwent a tautomerization reaction to form **32** prior to the second indoloquinoline formation, one could have expected a preferential ring closure leading to **33** without nonbonded steric interactions between the two *n*-octyl groups. It is worth noting that the indoloquinoline **31** having an extended aromatic ring structure is potentially capable of intercalating DNA.[23]

Conclusions

Thermolysis of the carbodiimides **9** represents a new way of generating biradicals from unsaturated molecules having two nitrogen atoms in the conjugated system. The cascade sequence outlined in Scheme 2 also provides an efficient pathway to 6*H*-indolo[2,3-*b*]quinolines. The possibility of placing a wide variety of substituents at various positions of the 6*H*-indolo[2,3-*b*]quinoline structure by selecting suitable fragments for assembly is an especially attractive feature of this synthetic route.

Experimental Section

Diethyl ether (Et_2O) was distilled from benzophenone ketyl prior to use. Triethylamine was distilled from CaH_2. The 2-(1-alkynyl)anilines **1** (83−100% yield) were prepared from 2-iodoaniline according to the reported procedures.[1,24] 2-Iodoaniline was purchased from Oakwood Products, Inc., and was used as received. 1-Alkynes were obtained from Farchan Laboratories, Inc., and were used without further purification. Iminophosphoranes **2** were prepared according to the reported procedure.[1,14a] Dibromotriphenylphosphorane (Ph_3PBr_2), phenyl isocyanate, 4-methoxyphenyl isocyanate, 1,4-phenylene diisocyanate, diphenyl phosphorazidate (DPPA), $Pd(PPh_3)_2Cl_2$, $Pd(PPh_3)_4$, *p*-xylene (anhydrous), *N*,*N*-dimethylformamide (DMF), *N*,*N*-diisopropylethylamine, and γ-terpinene were purchased from Aldrich and were used as received. Methyl 2-iodobenzoate was purchased from Lancaster. Melting points are uncorrected. ^{1}H (270 MHz) and ^{13}C (67.9 MHz) NMR spectra were recorded in $CDCl_3$ using $CHCl_3$ (^{1}H δ 7.26) or $CDCl_3$ (^{13}C δ 77.00) as internal standard unless otherwise indicated.

2-(1-Propynyl)aniline (1c). A suspension of 2.190 g of 2-iodoaniline (10.0 mmol), 0.190 g of copper(I) iodide (1.00 mmol), and 0.562 g of $Pd(PPh_3)_2Cl_2$ (0.800 mmol) in 50 mL of triethylamine was cooled to −78 °C under a nitrogen atmosphere and degassed by freeze−pump−thaw. After the reaction mixture was allowed to warm to room temperature, 672 mL of gaseous propyne (27 mmol) was introduced with a gastight syringe, and the resulting mixture was stirred at room temperature for 27 h. The reaction mixture was then concentrated, and 200 mL of diethyl ether was added. The solid suspension was removed by filtration, and the filtrate was washed with water, dried over $MgSO_4$, and concentrated. The residue was purified by column chromatography (silica gel/10% diethyl ether in hexanes) to furnish 1.310 g of **1c** (10.0 mmol, 100%) as a yellow oil: IR (neat) 3469, 3374, 2044, 1614, 749 cm^{-1}; ^{1}H δ 7.25 (1 H, dd, J = 8.2, 1.5 Hz), 7.08 (1 H, td, J = 7.7, 1.5 Hz), 6.69−6.64 (2 H, m), 4.18 (2 H, br s), 2.11 (3 H, s); ^{13}C δ 147.61, 131.92, 128.74, 117.76, 114.10, 108.85, 90.96, 76.13, 4.51; MS *m*/*z* 131 (M^+), 130, 103, 77.

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2-(1-Propynyl)-*N*-(triphenylphosphoranylidene)benzenamine (2c). To 4.220 g of Ph_3PBr_2 (10.0 mmol) were added 1.310 g of **1c** (10.0 mmol), 2.78 mL of anhydrous triethylamine, and 100 mL of anhydrous benzene under a nitrogen atmosphere. The reaction mixture was heated under reflux for 4 h. The white triethylammonium bromide precipitate was removed by filtration, and the filtrate was concentrated. The residue was purified by column chromatography (silica gel/40−60% diethyl ether in hexanes) to furnish 2.776 g (7.10 mmol, 71%) of **2c** as colorless crystals: IR (KBr) 3088, 1605, 734 cm^{-1}; ^1H δ 7.9−7.77 (6 H, m), 7.6−7.4 (9 H, m), 7.30 (1 H, dt, J = 7.4, 2.0 Hz), 6.82 (1 H, td, J = 7.7, 1.6 Hz), 6.58 (1 H, t, J = 7.4 Hz), 6.49 (1 H, d, J = 8.2 Hz), 2.16 (3 H, s); ^{13}C δ 152.48, 132.68 (d, J = 9.8 Hz), 132.65, 131.54 (d, J = 2.6 Hz), 131.38 (d, J = 100.5 Hz), 128.43 (d, J = 11.9 Hz), 127.68, 121.58 (d, J = 9.3 Hz), 119.32 (d, J = 21.2 Hz), 117.08, 87.70, 80.76, 4.95.

***N*-(2-Ethynylphenyl)-*N′*-phenylcarbodiimide (9a).**[16] The following procedure for the preparation of **9a** is representative. To 0.377 g of **2a** (1.00 mmol) was introduced a solution of 0.119 g of phenyl isocyanate (1.00 mmol) in 15 mL of anhydrous benzene via cannula under a nitrogen atmosphere at room temperature. After 1 h, the reaction mixture was concentrated in vacuo, and the residue was purified by column chromatography (silica gel/5% diethyl ether in hexanes) to furnish 0.181 g (0.83 mmol, 83%) of **9a** as a yellow oil: IR (neat) 3285, 2258, 2139, 2103, 1592, 754, 689 cm^{-1}; ^1H δ 7.49 (1 H, dd, J = 7.6, 1.4 Hz), 7.37−7.28 (3 H, m), 7.25−7.10 (5 H, m), 3.26 (1 H, s); ^{13}C δ 140.58, 138.34, 133.60, 129.90, 129.37, 125.50, 125.14, 124.47, 124.40, 118.30, 83.88, 80.19; MS m/z 218 (M^+), 190, 114, 89, 77; HRMS calcd for $C_{15}H_{10}N_2$ 218.0844, found 218.0837.

***N*-[2-(1-Pentynyl)phenyl]-*N′*-phenylcarbodiimide (9d).** The same procedure was repeated as described for **9a** except that 0.871 g of **2d** (2.08 mmol) was treated with 0.248 g of phenyl isocyanate (2.08 mmol) in 30 mL of anhydrous benzene to afford 0.427 g (1.64 mmol, 79%) of **9d** as a yellow oil: IR (neat) 2247, 2143, 2107, 1592, 756, 689 cm^{-1}; ^1H δ 7.44 (1H, dd, J = 7.9, 1.5 Hz), 7.4−7.08 (8 H, m), 2.10 (2 H, t, J = 7.2 Hz), 1.46 (2 H, sextet, J = 7.3 Hz), 0.93 (3 H, t, J = 7.3 Hz); ^{13}C δ 139.16, 138.72, 133.65, 133.01, 129.25, 128.39, 125.12, 125.05, 124.25, 124.19, 120.78, 98.70, 76.87, 21.69, 21.53, 13.40; MS m/z 260 (M^+), 245, 231, 218; HRMS calcd for $C_{18}H_{16}N_2$ 260.1314, found 260.1312.

Alternatively, **9d** was also synthesized by treatment of **20d** with **21**. To 0.247 g of the iminophosphorane **21**[20] (0.700 mmol) in 10 mL of anhydrous benzene was introduced via cannula a solution of 0.13 g of 2-(1-pentynyl)phenyl isocyanate **20d** (0.70 mmol) in 10 mL of dry benzene under a nitrogen atmosphere at room temperature. After 1 h, the reaction mixture was concentrated in vacuo, and the residue was purified by flash column chromatography (silica gel/7% benzene in hexanes) to afford 0.093 g (0.358 mmol, 51%) of **9d**.

2-(Phenylamino)quinoline (11a)[8b,16] **and 6*H*-Indolo[2,3-*b*]quinoline (14a).**[15,16] A solution of 0.182 g (0.835 mmol) of **9a** in 2.0 mL of γ-terpinene was heated under a nitrogen atmosphere at 138 °C for 14 h. After the reaction mixture was cooled to room temperature, a pale yellow solid precipitated out of the solution and coated the inside wall of the flask. The γ-terpinene solution was removed with a pipet, and the remaining solid was washed with benzene and dried in vacuo to give 0.029 g (0.13 mmol, 16%) of **14a** (mp 338−340 °C (lit.[16] mp 342−346 °C)) as a pale yellow solid. The combined solution of benzene and γ-terpinene was concentrated in vacuo, and the residue was purified by preparative thin-layer chromatography (silica gel/40% diethyl ether in hexanes) to furnish 0.090 g (0.41 mmol, 49%) of **11a** (mp 101−103 °C (lit.[8b] 103−104 °C)) as a yellow solid.

The indoloquinoline **14a** was also obtained by heating a suspension of 0.076 g of **14b** (0.26 mmol) over 0.5 mL of a 6 N sodium hydroxide solution and 0.5 mL of ethanol under reflux for 12 h. Then, the reaction mixture was cooled to room temperature, and 0.5 mL of water was added. The supernatant liquid was removed with a pipet, and the residue was washed with water and dichloromethane to give 0.053 g of **14a** (0.24 mmol, 92%).

11-(Trimethylsilyl)-6*H*-indolo[2,3-*b*]quinoline (14b). A solution of 0.216 g of **9b** (0.745 mmol) in 3.0 mL of *p*-xylene was heated under reflux for 5 h. The reaction mixture was then concentrated, and the residue was purified by flash chromatography (silica gel/20−50% diethyl ether in hexanes) to afford 0.186 g (0.641 mmol, 86%) of **14b** as bright pale yellow crystals: mp 247−248 °C; IR (KBr) 3060, 1252, 864, 842, 743 cm^{-1}; ^1H δ 11.79 (1 H, br s, NH), 8.53 (1 H, d, J = 8.4 Hz), 8.26 (1 H, d, J = 7.9 Hz), 8.24 (1 H, dd, J = 7.9, 1.1 Hz), 7.78 (1 H, ddd, J = 8.2, 6.8, 1.3 Hz), 7.60−7.46 (3 H, m), 7.28 (1 H, ddd, J = 8.2, 6.9, 1.6 Hz), 0.80 (9 H, s); ^{13}C δ 152.14, 145.15, 144.57, 141.81, 129.21, 128.46, 128.38, 127.81, 127.12, 126.44, 125.18, 122.21, 121.54, 119.17, 110.87, 2.57; MS m/z 290 (M^+), 275, 259, 245, 231, 218, 73; HRMS calcd for $C_{18}H_{18}N_2Si$ 290.1239, found 290.1242.

The indoloquinoline **14b** (61% yield) was also synthesized in a one-pot operation from **2b** and phenyl isocyanate without isolation of **9b**.

11-Propyl-6*H*-indolo[2,3-*b*]quinoline (14d). A solution of 0.368 g of **9d** (1.42 mmol) in 4.0 mL of *p*-xylene was heated under reflux for 5 h. The reaction mixture was then concentrated, and the residue was purified by flash chromatography (silica gel/20−50% diethyl ether in hexanes) to afford 0.329 g (1.27 mmol, 89%) of **14d** as golden yellow crystals: mp 245−246 °C; IR (KBr) 3455, 1611, 739 cm^{-1}; ^1H δ 12.23 (1 H, br s, NH), 8.30 (1 H, d, J = 8.4 Hz), 8.22 (1 H, d, J = 8.2 Hz), 8.17 (1 H, d, J = 7.9 Hz), 7.77 (1 H, d, J = 7.6 Hz), 7.6−7.48 (3 H, m), 7.31 (1 H, t, J = 7.6 Hz), 3.65 (2 H, t, J = 8.0 Hz), 1.98 (2 H, sextet, J = 7.6 Hz), 1.24 (3 H, t, J = 7.4 Hz); ^{13}C δ 153.44, 146.26, 144.31, 141.38, 128.71, 127.45, 127.04, 124.17, 123.41, 122.67, 121.39, 119.99, 116.63, 110.93, 30.93, 22.92, 14.70; MS m/z 260 (M^+), 231. Anal. Calcd for $C_{18}H_{16}N_2$: C, 83.05; H, 6.19; N, 10.76. Found: C, 82.86; H, 6.16; N, 10.67.

The indoloquinoline **14d** (72% yield) was also synthesized in a one-pot operation from **2d** and phenyl isocyanate without isolation of **9d**.

Alternatively, **14d** was also synthesized by treatment of **20d** with **21**. To 0.247 g of the iminophosphorane **21**[20] (0.700 mmol) in 10 mL of *p*-xylene was introduced via cannula a solution of 0.13 g of 2-(1-pentynyl)phenyl isocyanate (**20d**, 0.70 mmol) in 10 mL of *p*-xylene under a nitrogen atmosphere. After 2 h at room temperature, the reaction mixture was heated under reflux for 12 h. The reaction mixture was then concentrated, and the residue was purified by flash chromatography (silica gel/30% diethyl ether in hexanes) to afford 0.091 g (0.35 mmol, 50%) of **14d**.

2-Methoxy-11-propyl-6*H*-indolo[2,3-*b*]quinoline (16d). To a solution of 0.650 g of **2d** (1.55 mmol) in 10 mL of anhydrous *p*-xylene was added via cannula a solution of 0.231 g of 4-methoxyphenyl isocyanate (1.55 mmol) in 10 mL of anhydrous *p*-xylene under a nitrogen atmosphere. The reaction mixture was heated under reflux for 5 h and then concentrated. The residue was purified by flash chromatography (silica gel/20−50% diethyl ether in hexanes) to afford 0.212 g (0.731 mmol, 47%) of **16d** as a pale yellow solid: mp 236−238 °C; IR (KBr) 3417, 1633, 1613, 1232, 823, 724 cm^{-1}; ^1H δ 9.66 (1 H, br s, NH), 8.18 (1 H, d, J = 7.9 Hz), 8.04 (1 H, d, J = 9.2 Hz), 7.56−7.49 (3 H, m), 7.45 (1 H, dd, J = 9.2, 2.6 Hz), 7.34−7.28 (1 H, m), 4.01 (3 H, s), 3.62 (2 H, t, J = 8.0 Hz), 1.98 (2 H, sextet, J = 7.6 Hz), 1.23 (3 H, d, J = 7.4 Hz); ^{13}C (DMSO-d_6) δ 154.70, 151.30, 142.14, 141.53, 141.34, 128.97, 127.31, 123.25, 120.56, 120.27, 119.44, 115.43, 110.68, 102.60, 55.37, 29.95, 22.27, 14.21; MS m/z 290 (M^+), 275, 261, 246, 218; HRMS calcd for $C_{19}H_{18}N_2O$ 290.1419, found 290.1420.

Methyl 2-(1-Pentynyl)benzoate (18d). To a degassed solution containing 1.755 g of $Pd(PPh_3)_2Cl_2$ (2.50 mmol), 0.488 g of CuI (2.56 mmol), 6.55 g of methyl 2-iodobenzoate (**17**, 25.0 mmol), and 14.0 mL of *N*,*N*-diisopropylethylamine (80.4 mmol) in 80 mL of DMF was added via cannula a degassed solution of 3.4 g (4.9 mL) of 1-pentyne (50 mmol) in 25 mL of DMF. After 24 h at room temperature, the reaction mixture was poured into a flask containing 200 mL of a saturated NH_4Cl solution and 200 mL of pentane. After filtration, the organic layer was separated, washed with water, dried over $MgSO_4$, and concentrated. The residue was distilled in vacuo to afford

5.00 g (24.8 mmol, 99%) of **18d** as a light yellow oil: IR (neat) 2234, 1731, 757, 702 cm^{-1}; ^1H δ 7.84 (1 H, dd, J = 7.9, 1.5 Hz), 7.47 (1 H, dd, J = 7.8, 1.4 Hz), 7.36 (1 H, td, J = 7.7, 1.5 Hz), 7.25 (1 H, td, J = 7.4, 1.5 Hz), 3.86 (3 H, s), 2.41 (2 H, t, J = 7.1 Hz), 1.62 (2 H, sextet, J = 7.2 Hz), 1.03 (3 H, t, J = 7.4 Hz); ^{13}C δ 166.74, 133.99, 131.74, 131.26, 129.92, 126.92, 124.28, 95.61, 79.21, 51.80, 21.97, 21.57, 13.36; MS *m*/*z* 202 (M^+), 174, 159, 143.

2-(1-Pentynyl)benzoic Acid (19d). A solution of 5.000 g (24.75 mmol) of **18d** in 30 mL of THF and 140 mL of 1 N NaOH was heated at 50 °C for 12 h. The reaction mixture was cooled in an ice−water bath and was acidified with dilute HCl. The organic layer was separated, washed with water, dried over $MgSO_4$, and concentrated. The residue was purified by recrystallization from 50% of diethyl ether in hexanes to afford 4.354 g (23.16 mmol, 94%) of **19d** as pale yellow needles: IR 2962, 2234, 1692, 757 cm^{-1}; ^1H δ 11.4 (1 H, br), 8.06 (1 H, dd, J = 7.9, 1.1 Hz), 7.55 (1 H, dd, J = 7.7, 1.2 Hz), 7.48 (1 H, td, J = 7.4, 1.5 Hz), 7.35 (1 H, td, J = 7.4, 1.5 Hz), 2.47 (2 H, t, J = 7.0 Hz), 1.68 (2 H, sextet, J = 7.4 Hz), 1.09 (3 H, t, J = 7.4 Hz); ^{13}C δ 171.53, 134.31, 132.34, 131.06, 130.64, 127.27, 124.91, 97.24, 79.00, 21.95, 21.77, 13.50; MS *m*/*z* 188 (M^+), 160, 159, 131, 118; HRMS calcd for $C_{12}H_{12}O_2$ 188.0837, found 188.0829.

2-(1-Pentynyl)phenyl Isocyanate (20d). To a solution of 3.22 g (17.1 mmol) of **19d** in 30 mL of anhydrous benzene were added 2.4 mL of triethylamine and 3.83 mL (17.8 mmol) of DPPA. After 3 h at room temperature, the reaction mixture was heated at reflux for 2 h until the nitrogen gas evolution had ceased. The reaction mixture was then washed with a saturated NH_4Cl solution, water, dried over $MgSO_4$, and concentrated. The residue was purified by flash chromatography (silica gel/3% diethyl ether in hexanes) to afford 2.48 g (13.41 mmol, 78%) of **20d** as a colorless oil: IR (neat) 2244, 1599, 1506, 755 cm^{-1}; ^1H δ 7.40 (1 H, dd, J = 7.7, 1.7 Hz), 7.20 (1 H, td, J = 7.2, 1.7 Hz), 7.10 (1 H, td, J = 7.5, 1.5 Hz), 7.00 (1 H, dd, J = 7.9, 1.2 Hz), 2.50 (2 H, t, J = 7.1 Hz), 1.72 (2 H, sextet, J = 7.2 Hz), 1.10 (3 H, t, J = 7.4 Hz); ^{13}C δ 135.10, 131.95, 128.38, 127.38, 125.10, 123.19, 121.52, 99.38, 76.36, 21.62, 21.49, 13.46; MS *m*/*z* 185 (M^+), 170, 156, 130, 128; HRMS calcd for $C_{12}H_{11}NO$ 185.0841, found 185.0849.

Aniline 23a. To a degassed solution containing 0.702 g of $Pd(PPh_3)_2Cl_2$ (1.00 mmol), 0.19 g of CuI (1.00 mmol), 4.60 g of 2-iodoaniline (21.0 mmol), and 80 mL of Et_3N was added 1.17 mL of 1,6-heptadiyne (**22a**, 10.2 mmol). After 16 h at room temperature, the reaction mixture was heated at 45 °C for 8 h. Then the reaction mixture was poured into a flask containing 200 mL of a saturated NH_4Cl solution and 100 mL of Et_2O. After filtration, the organic layer was separated, washed with water, dried over $MgSO_4$, and concentrated. The residue was purified by flash column chromatography (silica gel/50% diethyl ether in hexanes) to furnish 2.415 g (8.814 mmol, 86%) of **23a** as a yellow oil: IR (neat) 3467, 3371, 1612, 748 cm^{-1}; ^1H δ 7.30 (2 H, dd, J = 8.0, 1.4 Hz), 7.13 (2 H, td, J = 8.5, 1.5 Hz), 6.74−6.69 (4 H, m), 4.21 (4 H, br s, NH), 2.69 (4 H, t, J = 6.9 Hz), 1.94 (2 H, quintet, J = 7.0 Hz), ^{13}C δ 147.61, 131.92, 128.88, 117.66, 114.06, 108.37, 94.22, 77.77, 27.82, 18.70; MS *m*/*z* 274 (M^+), 207, 191, 144, 131.

Iminophosphorane 24a. The reaction mixture of 0.965 g (3.52 mmol) of **23a**, 3.12 g (7.39 mmol) of Ph_3PBr_2, 2.0 mL of anhydrous triethylamine, and 30 mL of anhydrous benzene was heated under reflux for 5 h. Triethylammonium bromide was removed by filtration, and the filtrate was concentrated. The residue was purified through a short column (silica gel/40% diethyl ether and 5% ethanol in hexanes) to afford 0.565 g (0.711 mmol, 20%) of **24a** as colorless crystals: IR 1583, 1477, 1435, 694 cm^{-1}; ^1H δ 7.81 (12 H, m), 7.44 (18 H, m), 7.32 (2 H, dt, J = 7.7, 2.1 Hz), 6.84 (2 H, td, J = 7.7, 1.6 Hz), 6.59 (2 H, t, J = 7.2 Hz), 6.52 (2 H, d, J = 7.9 Hz), 2.72 (4 H, t, J = 7.2 Hz), 2.07 (2 H, quintet, J = 7.2 Hz); ^{13}C δ 152.27, 133.94, 132.64 (d, J = 9.8 Hz), 131.56 (d, J = 2.6 Hz), 131.15 (d, J = 99.9 Hz), 128.44 (d, J = 11.9 Hz), 127.68, 121.63 (d, J = 9.3 Hz), 119.39 (d, J = 22.3 Hz), 117.13, 91.67, 81.97, 29.05, 19.68.

Carbodiimide 25a. A mixture of 1.096 g (4.00 mmol) of **23a**, 3.518 g (8.33 mmol) of Ph_3PBr_2, 2.2 mL of anhydrous triethylamine, and 40 mL of anhydrous benzene was heated under reflux for 5 h. Triethylammonium bromide was removed by filtration, and the filtrate was concentrated. The crude **24a** was used directly without further purification. To the crude **24a** in 20 mL of anhydrous benzene was introduced via cannula a solution of 0.953 g (8.01 mmol) of phenyl isocyanate in 60 mL of anhydrous benzene under a nitrogen atmosphere at room temperature. After 4 h, the reaction mixture was concentrated in vacuo, and the residue was purified by column chromatography (silica gel/5% diethyl ether in hexanes) to afford 0.941 g (1.98 mmol, 49% overall yield from **23a**) of **25a** as a yellow oil: IR (neat) 2136, 2102, 1590, 1482, 754 cm^{-1}; ^1H δ 7.37 (2 H, dd, J = 7.7, 1.7 Hz), 7.3−7.18 (10 H, m), 7.13−7.06 (6 H, m), 2.11 (4 H, t, J = 7.2 Hz), 1.48 (2 H, quintet, J = 7.2 Hz); ^{13}C δ 139.05, 138.78, 133.69, 133.11, 129.34, 128.64, 125.20, 124.33, 124.22, 120.54, 97.51, 77.35, 26.94, 18.93; MS *m*/*z* 476 (M^+), 359, 277, 194; HRMS calcd for $C_{33}H_{24}N_4$ 476.2001, found 476.2012.

The carbodiimide **25a** was also obtained by treatment of the purified **24a** with phenyl isocyanate. To 0.156 g of **24a** (0.196 mmol) in 10 mL of anhydrous benzene was introduced via cannula a solution of 0.047 g of phenyl isocyanate (0.39 mmol) in 5 mL of anhydrous benzene under a nitrogen atmosphere at room temperature. After 4 h, the reaction mixture was concentrated in vacuo, and the residue was purified by flash chromatography (silica gel/2% diethyl ether in hexanes) to afford 0.067 g (0.141 mmol, 72%) of **25a**.

Indoloquinoline 26a. A solution of 0.246 g (0.52 mmol) of **25a** in 80 mL of *p*-xylene was heated under reflux for 5 h. After the reaction mixture was cooled to room temperature, the yellow precipitate was separated by centrifugation. After two cycles of heating the precipitate in 20 mL of *p*-xylene at 60 °C followed by centrifugation and decanting the supernatant liquid, the remaining solid was pumped to dryness in vacuo to afford 0.183 g (0.384 mmol, 74%) of **26a** as a yellow solid: IR 1699, 870, 755 cm^{-1}; ^1H (DMSO-d_6) δ 11.69 (2 H, br s, NH), 8.56 (2 H, d, J = 8.3 Hz), 7.99 (2 H, d, J = 8.4 Hz), 7.75−7.68 (4 H, m), 7.51 (2 H, t, J = 7.6 Hz), 7.40 (4 H, d, J = 3.9 Hz), 6.95 (2 H, m, J = 4.2 Hz), 3.96 (4 H, t, J = 7.3 Hz), 2.33 (2 H, m); ^{13}C (DMSO-d_6) δ 153.02, 147.01, 143.06, 141.86, 129.11, 128.23, 128.03, 124.90, 123.72, 123.45, 123.26, 120.70, 119.95, 116.00, 111.28, 30.16, 28.28; MS *m*/*z* 476 (M^+), 401, 375, 277, 245, 232; HRMS calcd for $C_{33}H_{24}N_4$ 476.2001, found 476.2025.

Carbodiimide 27. To 2.876 g (5.88 mmol) of **2g** in 10 mL of anhydrous benzene was introduced via cannula a solution of 0.471 g (2.94 mmol) of 1,4-phenylene diisocyanate in 60 mL of anhydrous benzene under a nitrogen atmosphere at room temperature. After 2 h, the reaction mixture was concentrated in vacuo, and the residue was purified by column chromatography (silica gel/2% diethyl ether in hexanes) to afford 0.75 g (1.29 mmol, 44%) of **27** as a colorless liquid: IR 2103, 836, 755 cm^{-1}; ^1H δ 7.39 (2 H, dm, J = 7.7, 2 Hz), 7.22 (2 H, td, J = 6.9, 1.7 Hz), 7.17 (4 H, s), 7.10 (4 H, t, J = 7.2 Hz), 2.13 (4 H, t, J = 6.9 Hz), 1.43 (4 H, quintet, J = 7.2 Hz), 1.24 (20 H, br), 0.87 (6 H, t, J = 6.6 Hz); ^{13}C δ 138.56, 136.28, 133.70, 133.10, 128.48, 125.33, 125.12, 124.36, 120.91, 99.10, 76.79, 31.83, 29.19, 29.12, 28.99, 28.36, 22.66, 19.80, 14.11.

Indoloquinoline 31. To a solution of 0.14 g (0.286 mmol) of **2g** in 10 mL of anhydrous *p*-xylene was added via cannula a solution of 0.023 g (0.144 mmol) of 1,4-phenylene diisocyanate in 50 mL of anhydrous *p*-xylene under a nitrogen atmosphere at room temperature. After 1 h, the reaction mixture was heated under reflux for 6 h. The reaction mixture was then concentrated, and the residue was purified by column chromatography (silica gel/20% diethyl ether and 5% ethanol in hexanes) to afford 0.055 g (0.094 mmol, 66%) of **31** as a yellow solid: IR 1600, 818, 735 cm^{-1}; ^1H δ 11.08 (2 H, s), 8.28 (2 H, d, J = 7.9 Hz), 8.23 (2 H, s), 7.74 (2 H, d, J = 8.1 Hz), 7.62 (2 H, t, J = 7.4 Hz), 7.43 (2 H, t, J = 7.3 Hz), 4.00 (2 H, ddd, J = 12.9, 8.7, 4.2 Hz), 3.74 (2 H, dt, J = 13.4, 8.0 Hz), 1.79 (2 H, br), 1.62 (2 H, br), 1.15−0.82 (20 H, m), 0.67 (6 H, t, J = 7.0 Hz); ^1H (DMSO-d_6) δ 11.96 (2 H, s), 8.23 (2 H, d, J = 8.1 Hz), 7.90 (2 H, s), 7.58 (2 H, d, J = 7.3 Hz), 7.53 (2 H, t, J = 8.1 Hz), 7.32 (2 H, t, J = 6.9 Hz), 3.96 (2 H, m), 3.59 (2 H, m), 1.48 (2 H, br), 1.22 (2 H, br), 1.05−0.56 (26 H, m); ^{13}C δ

152.01, 145.65, 140.35, 130.17, 126.97, 123.39, 121.49, 120.40, 119.74, 115.05, 111.28, 33.89, 31.58, 29.90, 29.18, 28.87, 22.41, 13.94; ^{13}C (DMSO-d_6) δ 151.98, 146.07, 144.40, 140.96, 130.85, 127.20, 123.61, 120.94, 120.37, 119.43, 113.94, 111.59, 32.70, 31.47, 29.48, 28.66, 28.38, 28.24, 22.33, 14.31; MS *m*/*z* 582 (M^+), 469, 384, 371, 272; HRMS calcd for $C_{40}H_{46}N_4$ 582.3722, found 582.3698.

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Supporting Information Available: Experimental procedures, spectroscopic and analytical data for **2g**, **9b**,**c**,**e**,**f**, **14c**,**e**,**f**, **16f**, **18f**, **19f**, **20f**, **23b**, **24b**, **25b**, and **26b**, and ^{1}H and ^{13}C NMR spectra for compounds **1c**,**g**, **2c**,**g**, **9a**−**f**, **14b**−**f**, **16d**,**f**, **18d**,**f**, **19d**,**f**, **20d**,**f**, **23a**,**b**, **24a**,**b**, **25a**,**b**, **26a**,**b**, **27**, and **31** (76 pages). See any current masthead page for ordering and Internet access information.

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