Novel Anionic Annelation Tactics for Construction of Fused Heteroaromatic Frameworks. 1. Synthesis of 4-Substituted Pyrazolo[4,3-*c*]quinolines, 9-Substituted Pyrazolo[3,4-*c*]quinolines, and 1,4-Dihydrochromeno[4,3-*c*]pyrazoles

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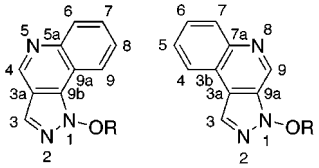
4-Substituted pyrazolo[4,3-*c*]quinolines **4a**−**i** and **6a**−**b** were prepared from pyrazole **3** whereas 9-substituted pyrazolo[3,4-*c*]quinolines **9a**−**d** and **17** were prepared from pyrazole **13** utilizing anionic annelation techniques. 1,4-Dihydrochromeno[4,3-*c*]pyrazoles **7a**−**c** were accessed from pyrazole **3**, extending the method for the synthesis of **4a**−**i**.

Introduction

We recently described the synthesis of 1-hydroxypyrazolo[4,3-*c*]quinoline **1b** and 1-hydroxypyrazolo[3,4-*c*]-quinoline **2b** starting from C-4 or C-5 substituted 1-(benzyloxy)pyrazoles.[1] A range of biological activities has been



reported for the parent ring systems,[2] though syntheses starting from pyrazoles remain unexplored. We undertook the development of routes to access the functionalized derivatives of **1b** and **2b**. Introduction of substituents in the benzene C-ring should be straightforward, expanding the previously developed protocols,[1,3,4] as outlined in Figure 1 for **1a** (steps a and b). Functionalization of the pyrazole ring was described in a subsequent paper.[5] Herein, we report the functionalization of the pyridine ring of **1a** and **2a**[6] as shown in Figure 1 (steps

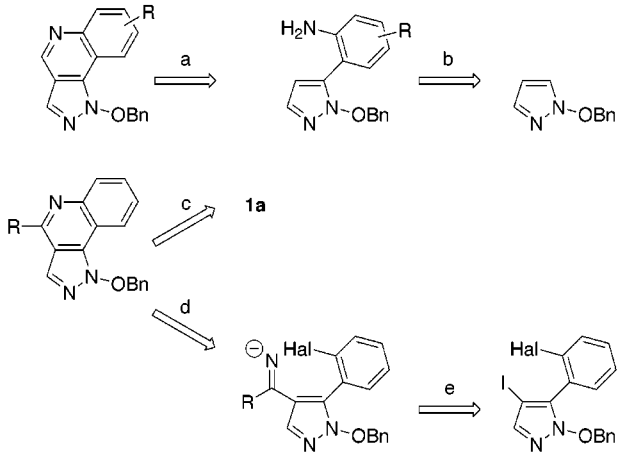


Figure 1. Possible retrosynthetic approaches to functionalized derivatives of pyrazoloquinolines **1a** and **2a** (**1a** as an example): (a) annelation as in ref 1; (b) Pd-catalyzed C−C bond formation as in ref 3; (c) functionalization of **1a** via α-metalation of the pyridine ring; (d) annelation via nucleophilic aromatic displacement of halogen by imine anion; (e) halogen−metal exchange followed by addition to nitriles.

d and e for **1a**) through a novel anionic annelation strategy. The method developed was extended to the synthesis of 1,4-dihydrochromeno[4,3-*c*]pyrazoles **7a**−**c**.

Results and Discussion

Initially, α-metalation of Bn-protected **1a** and **2a** (Figure 1, step c) appeared to be the easiest method for introduction of α-substituents.[7] However, attempts to metalate **2a** with LTMP suffered from migration of the

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(1) Pawlas, J.; Vedsø, P.; Jakobsen, P.; Huusfeldt, P. O.; Begtrup, M. *J. Org. Chem.* **2000**, *65*, 9001.

(2) (a) Benzodiazepine antagonists: Cecchi, L.; Colotta, V.; Melani, F.; Palazzino, G.; Filacchioni, G.; Martini, C.; Giannaccini, G.; Lucacchini, A. *J. Pharm. Sci.* **1989**, *78*, 437. (b) Acetylcholinesterase inhibitors: Gatta, F.; Del Giudice, M. R.; Pomponi, M.; Marta, M. *Heterocycles* **1992**, *34*, 991. (c) Antiinflammatory agents: Katner, S. A. U.S. Patent 3890324, 17 Jun 1975; *Chem. Abstr.* **1975**, *83*, 1641169b. (d) Antimalarial and antiviral agents: Mekheimer, R. *Pharm.* **1994**, *49*, 486. Hassan, A. A.; Mekheimer, R.; Mohamed, N. K. *Pharm.* **1997**, *8*, 589. (e) Interleukin 1 antagonists: Skotnicki, J.; Gilman, S. C.; Steinbaugh, B. A.; Musser, J. H. U.S. Patent 4748246, 31 May 1988; *Chem. Abstr.* **1988**, *109*, 110425u.

(3) Kristensen, J.; Begtrup, M.; Vedsø, P. *Synthesis* **1998**, 1604.

(4) Felding, J.; Kristensen, J.; Bjerregaard, T.; Sander, L.; Vedsø, P.; Begtrup, M. *J. Org. Chem.* **1999**, *64*, 4196.

(5) Pawlas, J.; Greenwood, J. R.; Vedsø, P.; Liljefors, T.; Jakobsen, P.; Huusfeldt, P. O.; Begtrup, M. *J. Chem. Soc., Perkin Trans.* **2001**, 861.

(6) The relationship between the biological activity and the α-substitution pattern has been investigated; see refs 2a and 2e.

(7) For reviews on α-metalation of π-deficient aza-heteroaromatics, see: (a) Comins, D. L.; O'Connor, S. *Adv. Heterocycl. Chem.* **1988**, *44*, 199. (b) Quéguiner, G.; Marsais, F.; Snieckus, V.; Epsztajn, J. *Adv. Heterocycl. Chem.* **1991**, *52*, 187. (c) Rewcastle, G. W.; Katritzky, A. *Adv. Heterocycl. Chem.* **1993**, *56*, 155.

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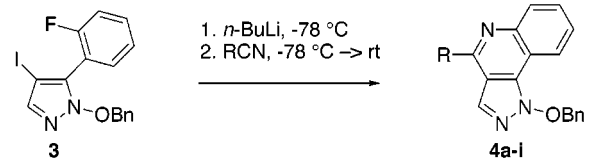
BnO group and formation of dimers.[8] Other bases that we examined[9,10] were also problematic. Thus, we considered introduction of substituents in the ring-closing step, starting from a substituted 1-(benzyloxy)pyrazole. We envisaged that addition to arylnitriles by a C-4 lithiated pyrazole followed by nucleophilic fluorine displacement from a 2-fluorophenyl substituent pre-installed at C-5 might give access to 4-substituted derivatives of **1a** as depicted in Figure 1 (steps d and e). To the best of our knowledge. such an annelation strategy for preparation of fused quinolines has not previously been reported.[11] Thus, 5-(2-fluorophenyl)-4-iodopyrazole **3** (Table 1) was prepared from 1-(benzyloxy)pyrazole[12] in 75% yield.[13] A control experiment in which **3** was subjected to iodine−lithium exchange using 1.1 equiv of *n*-BuLi at −78 °C followed by quenching with MeOD gave good deuterium incorporation at C-4,[14] and these conditions were then employed for iodine−lithiation exchange of **3** throughout. Thus, **3** was treated with *n*-BuLi and benzonitrile was added. After 5 min, the reaction was brought to room temperature. A new, highly fluorescent product arose, which was isolated as the expected 4-phenylpyrazolo[4,3-*c*]quinoline **4a** in 69% yield[15] (Table 1, entry 1). The scope of this ring-closing process was then examined by employing a series of nitriles. As presented in Table 1, neutral (entries 2, 5, 7), electron-withdrawing (entries 3, 4, 6, 9), and electron-donating (entry 8) substituents are tolerated. Sterically congested nitriles (entries 7−9) also participated, though with considerably lower yields. However, 2-cyanobiphenyl and 2-bromobenzonitrile did not give the cyclized product, most likely for steric reasons. Instead of addition, only protonation of C-4 took place. Attempts to use acetonitrile in this reaction gave only protonation at C-4, also due to the high acidity of the α-protons (pK_a ca. 25). To access 4-alkyl-substituted derivatives, a cyano group was introduced at C-4 by lithiation of **3** followed by reaction with tosyl cyanide, to give the 4-cyanopyrazole **5** in 70% yield (Scheme 1). Treatment of cyanopyrazole **5** with MeLi or *n*-BuLi at −78 °C followed by warming to room temperature gave the cyclized products **6a** and **6b**, respectively. PhLi and *t*-BuLi failed to react in this manner, presumably due to insufficient nucleophilicity.

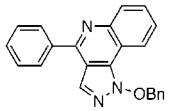
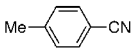
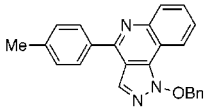
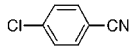
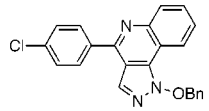
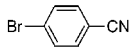
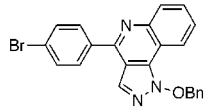
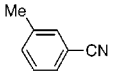
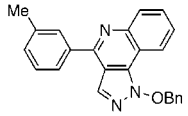
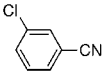
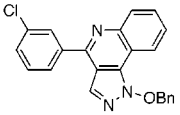
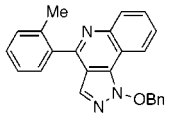
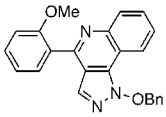
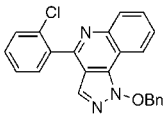
The scope of the method for synthesis of **4a**−**i** could be extended to the preparation of chromeno[4,3-*c*]pyrazoles using aldehydes as electrophiles instead of nitriles. Thus, iodine−lithium exchange of pyrazole **3** was followed by addition of aldehydes. The lithium alkoxides that resulted from this addition did not cyclize spontaneously as the lithio-imines obtained from the addition of nitriles did. The ring closure had to be promoted by NaH in refluxing THF to produce chromeno[4,3-*c*]pyrazoles **7a**−**c** in 60−78% yields (from **3**), giving easy access to this structural class, for which a range of biological activities have been reported (Scheme 2).[16]

Pyrazole **8** (eq 1) was prepared by the known procedure,[4] to examine the possibility of applying the protocol

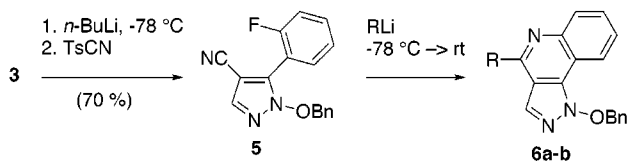
Table 1. Synthesis of 4-Substituted Pyrazolo[4,3-*c*]quinolines 4a−i



3 **4a-i**

Entry	Nitrile	Product	Yield (%)
1		 **4a**	69
2		 **4b**	57
3		 **4c**	59
4		 **4d**	27
5		 **4e**	56
6		 **4f**	54
7		 **4g**	40
8		 **4h**	27
9		 **4i**	35

Scheme 1



6a-b

RLi	Product	Yield (%)
MeLi	**6a**	70
n-BuLi	**6b**	56

(8) Quinoline metalation with lithium bases leads to dimerization: Clarke, A. C.; McNamara, S.; Meth-Cohn, O. *Tetrahedron Lett.* **1974**, 2373.

(9) $(TMP)_2Mg$: Eaton, P. E.; Lee, C.-H.; Xiong, Y. *J. Am. Chem. Soc.* **1989**, *111*, 8016.

(10) $TMPZn^tBu_2Li$: Kondo, Y.; Shilai, M.; Uchiyama, M.; Sakamoto, T. *J. Am. Chem. Soc.* **1999**, *121*, 3539.

(11) Srivastava and Bhaduri have reported a related strategy for preparation of benzo[1,8-*c*]naphthyridines: Srivastava, R. P.; Bhaduri, N. A. P. *Synthesis* **1987**, 512.

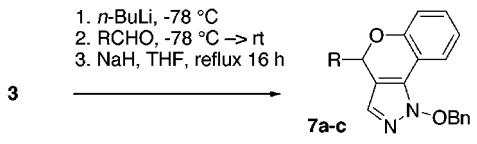
(12) Vedsø, P.; Begtrup, M. *J. Org. Chem.* **1995**, *60*, 4995.

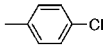
(13) Synthesized using the known metalation/transmetalation/cross-coupling procedure (ref 3) followed by iodination with ICl.

(14) D/H ratio was ca. 9/1 according to ^1H NMR spectrum of the crude product.

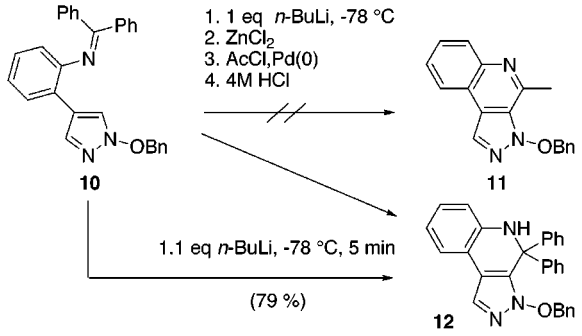
(15) The less than quantitative yield of **4a**−**i** can be ascribed to competitive abstraction of the ortho proton from benzonitriles, as the C-4 protonated side product was always detected in the reaction mixture.

Scheme 2

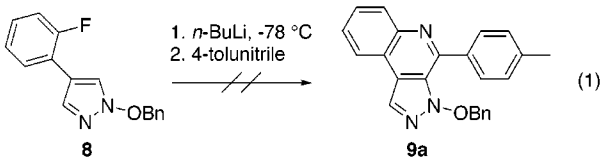


RCHO	Product	Yield (%)
	**7a**	78
	**7b**	60
CH_2O	**7c**	63

Scheme 3



used for synthesis of **4a**−**i** (Table 1) for preparation of 9-substituted analogues of pyrazoloquinoline **2b**. Com-

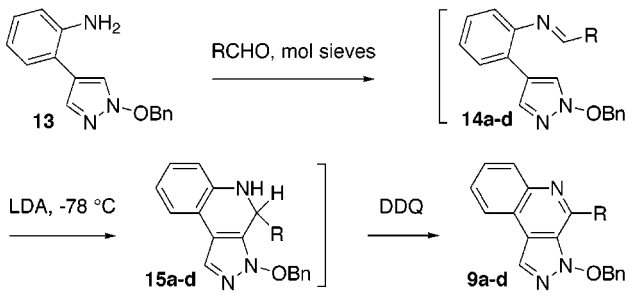


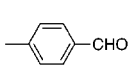
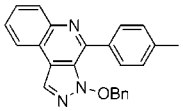
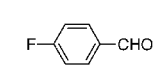
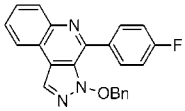
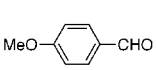
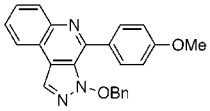
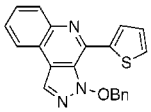
(1)

pound **8** was treated with *n*-BuLi at −78 °C and quenched with MeI; the H-5 proton signal of **8** at 7.66 ppm disappeared completely, and a methyl group signal (3H intense) arose at 1.92 ppm, confirming the preferential C-5 lithiation[12] of **8**. However, lithiation of **8** followed by addition of 4-tolunitrile or benzonitrile did not afford even trace amounts of the expected cyclized products such as **9a**. Starting material was recovered despite quenching the reaction mixture with MeOD, suggesting that C-5-lithiated **8** abstracts a proton from the 2-position of 4-tolunitrile or benzonitrile[17] instead of adding to the cyano group.

In an alternative approach to the 9-substituted derivatives of **2b**, we attempted C-5 acylation[3] of benzophenone imine-protected **10**,[18] followed by hydrolysis of the benzophenone imine moiety (Scheme 3). However, the cyclized product **11** was not formed, and hydropyridine **12** was isolated instead. Treatment of **10** only with *n*-BuLi followed by warming to room temperature (Scheme 3) also gave **12**. Apparently, intramolecular attack of the

Table 2. Synthesis of 9-Substituted Pyrazolo[4,3-*c*]quinolines 9a−d



Entry	Aldehyde	Product		Yield (%)
1			**9a**	71
2			**9b**	66
3			**9c**	53
4			**9d**	63

C-5 lithio-anion at the azomethine carbon is kinetically favored over addition of external electrophiles such as $ZnCl_2$. This rules out C-5 acylation of **10**. However, replacing the benzophenone imine moiety in **10** for an aldimine function allowed the formation of the desired 9-substituted derivatives of **2b**. Thus, the Schiff base **14a** (Table 2) was treated with LDA[19] to form the dihydropyridine **15a**. Subsequent DDQ-induced aromatization[20] of **15a** gave pyrazoloquinoline **9a** in 71% yield from **13** (Table 2, entry 1). As depicted in Table 2, this process is compatible with electron-withdrawing (entry 2), electron-donating (entry 3), and heteroaromatic (entry 4) substrates. However, the Schiff bases **14** of both 2-tolualdehyde and 1-naphthaldehyde failed to cyclize under these conditions, suggesting that the greater steric bulk prevented the LDA-promoted C-5 lithiation.[21]

It was also shown to be possible to prepare 9-(4-methylphenylamino)pyrazolo[3,4-*c*]quinoline **17** from pyrazole **13** (Scheme 4). The intermediate carbodiimide **16**[22] was treated with LDA to effect intramolecular attack in the same manner as found for **14a**−**d**, producing **17** in 45% yield (from **13**), demonstrating good opportunities for further applications of this annelation method toward other substrates derived from **13**.

In conclusion, representative 4-substituted pyrazolo-[4,3-*c*]quinolines **4a**−**i** and **6a**−**b**, 9-substituted pyrazolo-[3,4-*c*]quinolines **9a**−**d** and **17**, and 1,4-dihydrochromeno-

(16) For biologically active chromeno[4,3-*c*]pyrazoles, see: (a) Antialergetics: Di Parsia, M. T.; Suárez, C.; Vítolo, M. V.; Márquez, V. E. *J. Med. Chem.* **1981**, *24*, 117. (b) Antimicrobial agents: Muthusubramanian, L.; Misra, G. S. *Eur. J. Med. Chem. Chim. Ther.* **1986**, *21*, 163. (c) Antiinflamatory agents: Bertenshaw, S. R.; Talley, J. J.; Rogier, D. J.; Graneto, M. J.; Koboldt, C. M.; Zhang, Y. *Bioorg. Med. Chem. Lett.* **1996**, *6*, 2827.

(17) Ortho-protons from benzonitrile were removed using LTMP: Krizan, T. D.; Martin, J. C. *J. Am. Chem. Soc.* **1983**, *105*, 6155.

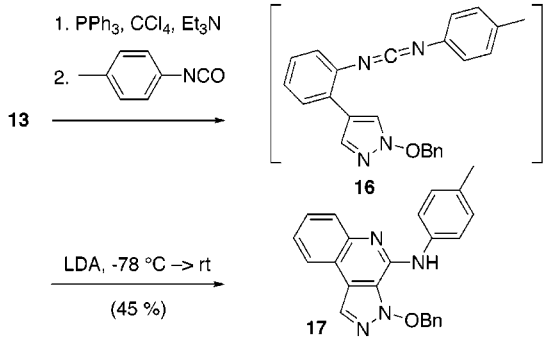
(18) The originally employed Boc protected **13** was abandoned due to problems with the acidity of the N-H proton.

(19) *n*-BuLi and *t*-BuLi added to the C=N bond of **14a**, whereas LTMP was much less reactive than LDA.

(20) MnO_2 and aerial oxidation gave substantial amounts of the debenzyloxylated **9a** as the side product.

(21) The Schiff bases were recovered with H-5 present despite MeOD quenching.

Scheme 4



[4,3-*c*]pyrazoles **7a**−**c** were synthesized in a straightforward manner starting from C-4 and C-5 aryl-substituted 1-(benzyloxy)pyrazoles. The synthetic tactics, introduced herein for the synthesis of substituted tricyclic pyrazoles, constitute a novel means of constructing functionalized fused heteroaromatic frameworks from readily available monocyclic precursors and as such could be implemented to synthesize a variety of aromatic and heteroaromatic structures. Further studies along these lines are in progress.

Experimental Section

General Comments. See ref 1.

1-Benzyloxy-4-iodo-5-(2-fluorophenyl)pyrazole (3). To a solution of 1-benzyloxypyrazole[12] (1.00 g, 5.8 mmol) in THF (20 mL) was added dropwise 1.6 M *n*-BuLi in hexanes (4.0 mL, 6.3 mmol) at −78 °C. After 5 min, 1 M $ZnCl_2$ in THF (8.7 mL, 8.7 mmol) was added. The solution was allowed to warm to room temperature, and 2-fluoroiodobenzene (1.90 g, 8.7 mmol) and $Pd(PPh_3)_4$ (0.25 g, 0.23 mmol) in DMF (30 mL) were added. The mixture was heated to 80 °C, quenched with saturated aquesous NH_4Cl (50 mL), and extracted with ether (3 × 100 mL). The crude 1-(benzyloxy)-5-(2-fluorophenyl)pyrazole[3] was concentrated and redissolved in CH_2Cl_2 (20 mL), and K_2CO_3 (4.00 g, 29.0 mmol) and ICl (2.80 g, 17.4 mmol) were added. After 1 h at room temperature, the reaction was quenched with Na_2SO_3 (1 M, 100 mL), extracted with CH_2Cl_2 (3 × 100 mL), concentrated in vacuo, and filtered through a pad of silica gel (10 g) using EtOAc/heptane, 1:3, to give the crude product. The coeluting 1-(benzyloxy)-4-iodopyrazole[4] was distilled off using a Kugelrohr apparatus (1.0 mBar/201 °C) to give 1.70 g (75%) of **3** as a thick dark-yellow oil. R_f (EtOAc/heptane, 1:4) 0.44. δ_H ($CDCl_3$): 7.47 (s, 1H), 7.46−6.96 (m, 9H), 5.17 (s, 2H). δ_C ($CDCl_3$): 159.70 (s(d), J = 246.9 Hz), 138.51 (d), 132.95 (s), 132.64 (s(d), J = 0.6 Hz), 132.28 (d(d), J = 2.3 Hz), 131.50 (d(d), J = 8.3 Hz), 129.74 (d), 129.23 (d), 128.55 (d), 123.94 (d(d), J = 3.7 Hz), 115.93 (d(d), J = 21.4 Hz), 115.42 (s(d), J = 15.1 Hz), 80.52 (t), 57.87 (s). Anal. Calcd for $C_{16}H_{12}FIN_2O$: C, 48.75; H, 3.07; N, 7.11. Found: C, 48.54; H, 2.93; N, 7.17.

Preparation of Pyrazoloquinolines 4a−i. General Procedure. To a stirred solution of **3** (197 mg, 0.5 mmol) in 4 mL of THF at −78 °C was added dropwise 1.6 M *n*-BuLi in hexanes (0.34 mL, 0.55 mmol) at −78 °C. After 5 min, arylnitrile (0.65 mmol) was added, the solution was allowed to warm to room temperature, and 5 mL of heptane was added. The crude mixture was adsorbed on a silica gel plug (5 g) and purified by vacuum filtration using EtOAc/heptane, 1:8.

1-Benzyloxy-4-phenylpyrazolo[4,3-*c*]quinoline (4a). Following the general procedure using benzonitrile gave 121 mg (69%) of **4a** as colorless crystals, mp 133−134 °C (EtOAc/heptane). R_f (EtOAc/heptane, 1:2) 0.40. δ_H ($CDCl_3$): 8.55 (dd, J = 8.1, 1.5 Hz, 1H), 8.27 (d, J = 8.3 Hz, 1H), 8.13 (s, 1H), 8.12−8.08 (m, 2H), 7.78−7.35 (m, 10H), 5.55 (s, 2H). δ_C ($CDCl_3$): 154.25 (s), 145.71 (s), 138.77 (s), 133.66 (s), 133.00 (s), 130.08 (d), 130.03 (d), 129.87 (d), 129.65 (d), 129.40 (d), 129.33 (d), 129.01 (d), 128.92 (d), 128.87 (d), 126.56 (d), 122.14 (d), 114.22 (s), 113.25 (s), 80.94 (t). Anal. Calcd for $C_{23}H_{17}N_3O$: C, 78.61; H, 4.88; N, 11.79. Found: C, 78.34; H, 4.92; N, 11.79.

1-Benzyloxy-4-(4-methylphenyl)pyrazolo[4,3-*c*]quinoline (4b). Following the general procedure using 4-tolunitrile gave 102 mg (57%) of **4b** as colorless crystals, mp 133−134 °C (EtOAc/heptane). R_f (EtOAc/heptane, 1:4) 0.27. δ_H ($CDCl_3$): 8.54 (dd, J = 8.1, 1.3 Hz, 1H), 8.24 (d, J = 8.1 Hz, 1H), 8.12 (s, 1H), 8.00 (d, J = 8.1 Hz, 2H), 7.73 (dt, J = 8.1, 1.4 Hz, 1H), 7.57 (dt, J = 7.6, 1.1 Hz, 1H), 7.54−7.34 (m, 7H), 5.54 (s, 2H), 2.48 (s, 3H). δ_C ($CDCl_3$): 154.14, 145.69, 139.95, 135.95, 133.60, 132.98, 129.95, 129.64, 129.57, 129.33, 129.27, 128.81, 128.77, 126.32, 122.07, 114.15, 113.23, 80.94, 21.46, one carbon signal overlapped. Anal. Calcd for $C_{24}H_{19}N_3O$: C, 78.88; H, 5.24; N, 11.50. Found: C, 79.05; H, 5.40; N, 11.36.

1-Benzyloxy-4-(4-chlorophenyl)pyrazolo[4,3-*c*]quinoline (4c). Following the general procedure using 4-chlorobenzonitrile gave 111 mg (59%) of **4c** as yellow crystals, mp 155−157 °C (EtOAc/heptane). R_f (EtOAc/heptane, 1:2) 0.46. δ_H ($CDCl_3$): 8.56 (dd, J = 8.6, 0.9 Hz, 1H), 8.24 (d, J = 8.2 Hz, 1H), 8.09 (s, 1H), 8.06 (d, J = 8.7 Hz, 2H), 7.75 (dt, J = 8.5, 1.5 Hz, 1H), 7.64−7.35 (m, 8H), 5.55 (s, 2H). δ_C ($CDCl_3$): 160.73 (s), 145.58 (s), 137.19 (s), 136.07 (s), 133.70 (s), 132.93 (s), 130.17 (d), 130.04 (d), 130.00 (d), 129.67 (d), 129.51 (d), 129.22 (d), 128.97 (d), 128.87 (d), 126.77 (d), 122.16 (d), 114.23 (s), 112.99 (s), 80.98 (t).

1-Benzyloxy-4-(4-bromophenyl)pyrazolo[4,3-*c*]quinoline (4d). Following the general procedure using 4-bromobenzonitrile gave 58 mg (27%) of **4d** as yellow crystals, mp 162−163 °C (heptane). R_f (EtOAc/heptane, 1:2) 0.38. δ_H ($CDCl_3$): 8.56 (dd, J = 8.6, 1.5 Hz, 1H), 7.61 (d, J = 8.3 Hz, 1H), 8.10 (s, 1H), 8.00 (d, J = 8.3 Hz, 2H), 7.80−7.35 (m, 9H), 5.56 (s, 2H). δ_C ($CDCl_3$): 161.41 (s), 152.89 (s), 133.72 (s), 132.85 (s), 132.25 (d), 130.55 (d), 130.03 (d), 129.73 (d), 129.25 (d), 128.90 (d), 128.86 (s), 126.97 (d), 124.70 (s), 122.20 (d), 114.15 (s), 112.84 (s), 81.04 (t), two carbon signals overlapped. Anal. Calcd for $C_{23}H_{16}BrN_3O$·25 mol % H_2O: C, 63.53; H, 3.82; N 9.66. Found: C, 63.22; H, 3.91; N, 9.49.

1-Benzyloxy-4-(3-methylphenyl)pyrazolo[4,3-*c*]quinoline (4e). Following the general procedure using 3-tolunitrile gave 103 mg (56%) of **4e** as off-white crystals, mp 97−98 °C (EtOAc/heptane). R_f (EtOAc/heptane, 1:4) 0.42. δ_H ($CDCl_3$): 8.54 (d, J = 8.5 Hz, 1H), 8.29 (d, J = 8.3 Hz, 1H), 8.12 (s, 1H), 7.93 (s, 1H), 7.73 (t, J = 8.4 Hz, 1H), 7.57 (t, J = 8.1 Hz, 1H), 7.53−7.32 (m, 7H), 5.54 (s, 2H), 2.51 (s, 3H). δ_C ($CDCl_3$): 154.46 (s), 145.57 (s), 138.85 (s), 138.55 (s), 133.62 (s), 133.01 (s), 130.73 (d), 130.01 (d), 129.95 (d), 129.64 (d), 129.52 (d), 129.50 (d), 129.41 (d), 128.87 (d), 128.83 (d), 126.53 (d), 126.12 (d), 122.13 (d), 114.20 (s), 113.28 (s), 80.92 (t), 21.49 (q). Anal. Calcd for $C_{24}H_{19}N_3O$: C, 78.88; H, 5.24; N, 11.50. Found: C, 78.88; H, 5.17; N, 11.42.

1-Benzyloxy-4-(3-chlorophenyl)pyrazolo[4,3-*c*]quinoline (4f). Following the general procedure using 3-chlorobenzonitrile gave 104 mg (54%) of **4f** as yellow crystals, mp 113−114 °C (EtOAc/heptane). R_f (EtOAc/heptane, 1:2) 0.40. δ_H ($CDCl_3$): 8.56 (dd, J = 9.1, 1.0 Hz, 1H), 8.27 (d, J = 8.3 Hz, 1H), 8.12 (s, 1H), 8.11−8.10 (m, 1H), 8.01−7.94 (m, 1H), 7.76 (dt, J = 8.5, 1.5 Hz, 1H), 7.61 (dt, J = 8.2, 1.3 Hz, 1H), 7.55−7.34 (m, 7H), 5.56 (s, 2H). δ_C ($CDCl_3$): 160.41 (s), 152.57 (s), 135.11 (s), 133.72 (s), 132.88 (s), 130.21 (d), 130.02 (d), 129.95 (d), 129.70 (d), 129.60 (d), 129.00 (d), 128.88 (d), 127.06 (d), 126.96 (d), 122.18 (d), 114.26 (s), 112.96 (s), 112.95 (s), 81.01 (t), two carbon signals overlapped. Anal. Calcd for $C_{23}H_{16}ClN_3O$: C, 71.60; H, 4.18; N 10.89. Found: C, 71.86; H, 4.47; N, 10.69.

1-Benzyloxy-4-(2-methylphenyl)pyrazolo[4,3-*c*]quinoline (4 g). Following the general procedure using 2-tolunitrile gave 71 mg (40%) of **4g** as off-white crystals, mp 88−90 °C (EtOAc/heptane). R_f (EtOAc/heptane, 1:2) 0.38. δ_H ($CDCl_3$): 8.58 (dd, J = 9.1, 1.5 Hz, 1H), 8.26 (d, J = 8.7 Hz, 1H), 7.76 (dt, J = 8.5, 1.5 Hz, 1H), 7.75 (s, 1H), 7.63 (dt, J = 8.2, 1.3 Hz, 1H), 7.56−7.28 (m, 9H), 5.55 (s, 2H), 2.36 (s, 3H). δ_C ($CDCl_3$): 155.88 (s), 145.43 (s), 143.01 (s), 137.70 (s), 136.58 (s), 133.16 (s), 132.96 (s), 131.26 (d), 130.02 (d), 129.66 (d), 129.51 (d), 129.44 (d), 129.42 (d), 129.15 (d), 128.85 (d), 126.70 (d), 125.91

(d), 122.19 (d), 114.55 (s), 114.16 (s), 81.02 (t), 19.94 (q). Anal. Calcd for $C_{24}H_{19}N_3O$: C, 78.88; H, 5.24; N, 11.50. Found: C, 78.59; H, 5.25; N, 11.29.

1-Benzyloxy-4-(2-methoxyphenyl)pyrazolo[4,3-*c*]quinoline (4h). Following the general procedure using 2-methoxybenzonitrile gave 51 mg (27%) of **4h** as colorless crystals, mp 119−120 °C (EtOAc/heptane). R_f (EtOAc/heptane, 1:4) 0.30. δ_H ($CDCl_3$): 8.56 (dd, J = 9.1, 1.5 Hz, 1H), 8.30 (d, J = 7.7 Hz, 1H), 7.80 (s, 1H), 7.74 (dt, J = 8.5, 1.5 Hz, 1H), 7.66 (dt, J = 7.5, 1.3 Hz, 1H), 7.66−6.92 (m, 9H), 5.53 (s, 2H), 3.82 (s, 3H). δ_C ($CDCl_3$): 157.16 (s), 133.21 (s), 132.82 (s), 131.50 (d), 131.01 (d), 129.96 (d), 129.60 (d), 129.21 (d), 128.87 (d), 126.65 (d), 122.14 (d), 121.26 (d), 114.69 (s), 114.45 (s), 111.40 (d) 80.93 (t), 55.41 (q), five carbon signals overlapped. Anal. Calcd for $C_{24}H_{19}N_3O_2$: C, 75.57; H, 5.02; N, 11.02. Found: C, 76.10; H, 5.14; N, 10.76.

1-Benzyloxy-4-(2-chlorophenyl)pyrazolo[4,3-*c*]quinoline (4i). Following the general procedure using 2-chlorobenzonitrile gave 66 mg (35%) of **4i** as colorless crystals, mp 130−131 °C (EtOAc/heptane). R_f (EtOAc/heptane, 1:2) 0.31. δ_H ($CDCl_3$): 8.57 (dd, J = 7.1, 1.0 Hz, 1H), 8.27 (d, J = 8.3 Hz, 1H), 7.80−7.34 (m, 11H), 7.78 (s, 1H), 5.55 (s, 2H). δ_C ($CDCl_3$): 153.19 (s), 145.44 (s), 137.42 (s), 133.05 (s), 132.95 (s), 132.70 (s), 131.36 (d), 130.48 (d), 130.32 (d), 130.12 (d), 130.03 (d), 129.66 (d), 129.64 (d), 129.45 (d), 128.86 (d), 127.19 (d), 127.03 (d), 122.24 (d), 114.48 (s), 114.20 (s), 81.06 (t).

1-(Benzyloxy)-4-cyano-5-(2-fluorophenyl)pyrazole (5). To a solution of **3** (1.05 g, 2.7 mmol) in THF (10 mL) was added dropwise 1.6 M *n*-BuLi in hexanes (1.8 mL, 2.9 mmol) at −78 °C. After 5 min, 4-toluenesulfonyl cyanide (0.63 g, 3.4 mmol) was added and the reaction mixture was allowed to warm to room temperature. The crude mixture was concentrated in vacuo, adsorbed on a silica gel plug (5 g), and purified by vacuum filtration using EtOAc/heptane, 1:8, to give 547 mg (70%) of **5** as colorless oil. R_f (EtOAc/heptane, 1:2) 0.46. δ_H ($CDCl_3$): 7.74 (s, 1H), 7.49−6.92 (m, 9H), 5.24 (s, 2H). δ_C ($CDCl_3$): 159.41 (d, J = 253.9 Hz), 137.10 (d, J = 1.3 Hz), 136.14 (d, J = 0.7 Hz), 132.45 (d, J = 8.4 Hz), 132.05, 131.29 (d, J = 1.8 Hz), 129.75 (d, J = 15.1 Hz), 128.64, 124.31, (d, J = 3.8 Hz), 116.38, 116.10, 112.97 (d, J = 0.6 Hz), 112.95 (d, J = 14.6 Hz), 90.94 (d, J = 1.1 Hz), 80.89. Anal. Calcd for $C_{17}H_{12}FN_3O$: C, 69.62; H, 4.12; N, 14.33. Found: C, 69.31; H, 4.29; N, 14.10.

1-Benzyloxy-4-methylpyrazolo[4,3-*c*]quinoline (6a). To a solution of **5** (45 mg, 0.15 mmol) in THF (3 mL) was added dropwise 1.6 M MeLi in ether (0.10 mL, 0.17 mmol) at −78 °C. After 5 min, the reaction mixture was allowed to warm to room temperature, quenched with saturated aqueous NH_4Cl (20 mL), taken up with CH_2Cl_2 (3 × 20 mL) and dried with $MgSO_4$, and concentrated in vacuo. Preparative TLC purification (EtOAc/heptane, 1:2) gave 31 mg (70%) of **6a** as yellow crystals, mp 129−131 °C (ether/heptane). R_f (EtOAc/heptane, 1:2) 0.34. δ_H ($CDCl_3$): 8.47 (ddd, J = 9.1, 1.5, 0.6 Hz, 1H), 8.09 (d, J = 8.1 Hz, 1H), 7.98 (s, 1H), 7.69 (dt, J = 8.5, 1.5 Hz, 1H), 7.54 (dt, J = 8.3, 1.3 Hz, 1H), 7.50−7.32 (m, 5H), 5.51 (s, 2H), 2.88 (s, 3H). δ_C ($CDCl_3$): 154.36, 145.48, 132.98, 132.56, 129.98, 129.62, 129.23, 129.02, 128.84, 128.35, 126.03, 122.17, 114.77, 114.15, 80.90, 22.15. Anal. Calcd for $C_{18}H_{15}N_3O$: C, 74.72; H, 5.23; N, 14.52. Found: C, 74.51; H, 5.29; N, 14.38.

1-Benzyloxy-4-*n*-butylpyrazolo[4,3-*c*]quinoline (6b). Likewise, *n*-BuLi (0.12 mL, 0.19 mmol) was added to a solution of **5** (50 mg, 0.17 mmol) in THF (4 mL), and the protocol described for **6a** was followed to give 32 mg (56%) of **6b** as off-white crystals, mp 84−85 °C (EtOAc/heptane). R_f (EtOAc/heptane, 1:2) 0.41 δ_H ($CDCl_3$): 8.48 (dd, J = 9.1, 1.5 Hz, 1H), 8.12 (d, J = 9.0 Hz, 1H), 7.98 (s, 1H), 7.69 (dt, J = 8.6, 1.5 Hz, 1H), 7.54 (dt, J = 8.3, 1.3 Hz, 1H), 7.50−7.35 (m, 5H), 5.51 (s, 2H), 3.16 (t, J = 7.8 Hz, 3H), 1.96−1.84 (m, 2H), 1.56−1.44 (m, 2H), 0.99 (t, J = 7.3 Hz, 3H). δ_C ($CDCl_3$): 158.52, 145.55, 133.02, 132.78, 129.98, 129.61, 129.21, 129.16, 128.84, 128.25, 125.99, 122.15, 114.34, 114.17, 80.91, 36.18, 31.48, 22.78, 13.84.

Preparation of Dihydrochromenopyrazoles 7a−c. General Procedure. To a stirred solution of **3** (100 mg, 0.25 mmol) in 4 mL of THF at −78 °C was added dropwise 1.6 M *n*-BuLi in hexanes (0.18 mL, 0.28 mmol) at −78 °C. After 5 min, the aldehyde (0.30 mmol) was added, the solution was allowed to warm to room temperature, and 5 mL of heptane was added. Filtration through a pad of silica gel (EtOAc/heptane, 1:3) was followed by concentration in vacuo and treatment with NaH (60 mg, 2.5 mmol) in THF (3 mL) at 70 °C for 16 h. The reaction was quenched with EtOAc (5 mL) and water (10 mL) was added. Extraction with EtOAc (3 × 10 mL), $MgSO_4$ drying, and concentration in vacuo gave the crude product, which was purified by using the procedure used for **4a**−**i**.

1-Benzyloxy-4-(4-methylphenyl)-1,4-dihydrochromeno-[4,3-*c*]pyrazole (7a). Following the general procedure using 4-tolualdehyde gave 73 mg (78%) of **7a** as yellow crystals, mp 123−124 °C (EtOAc/heptane). R_f (EtOAc/heptane, 1:2) 0.49. δ_H ($CDCl_3$): 7.73 (dd, J = 7.6, 1.7 Hz, 1H), 7.50−6.92 (m, 13H), 6.29 (s, 1H), 5.39 (d, J = 10.2 Hz, 1H), 5.35 (d, J = 10.2 Hz, 1H), 2.37 (s, 3H). δ_C ($CDCl_3$): 153.20, 138.98, 137.60, 136.82, 133.27, 130.19, 130.16, 129.65, 129.58, 128.87, 127.84, 122.91, 121.75, 117.64, 114.29, 113.21, 99.15, 80.84, 21.28, one carbon signal overlapped.

1-Benzyloxy-4-(2-thienyl)-1,4-dihydrochromeno[4,3-*c*]-pyrazole (7b). Following the general procedure using 2-thiophenecarboxaldehyde gave 54 mg (60%) of **7b** as off-white crystals, mp 88−89 °C (EtOAc/heptane). R_f (EtOAc/heptane, 1:2) 0.45. δ_H ($CDCl_3$): 7.75 (dd, J = 9.1, 1.7 Hz, 1H), 7.46−6.93 (m, 11H), 6.60 (s, 1H), 5.38 (s, 2H). δ_C ($CDCl_3$): 152.35, 143.25, 133.05, 130.10, 130.05, 129.53, 128.76, 128.68, 127.06, 127.03, 126.95, 126.78, 122.82, 121.90, 117.71, 114.02, 112.50, 80.76, 71.85. Anal. Calcd for $C_{21}H_{16}N_2O_2S$·40 mol % H_2O: C, 68.61; H, 4.61; N 7.62. Found: C, 68.75; H, 4.43; N, 7.61.

1-Benzyloxy-1,4-dihydrochromeno[4,3-*c*]pyrazole (7c). Following the general procedure using gaseous formaldehyde[23] gave 51 mg (63%) of **7c** as yellow crystals, mp 111−113 °C (EtOAc/heptane). R_f (EtOAc/heptane, 1:2) 0.50. δ_H ($CDCl_3$): 7.69 (dd, J = 7.3, 1.8 Hz, 1H), 7.42−6.92 (m, 8H), 7.12 (s, 1H), 5.32 (s, 2H), 5.24 (s, 2H). δ_C ($CDCl_3$): 153.39 (s), 133.10 (s), 129.93 (d), 129.85 (d), 129.42 (d), 128.70 (d), 127.49 (d), 126.77 (s), 122.84 (d), 121.70 (d), 117.16 (d), 114.47 (s), 109.74 (s), 80.66 (t), 64.18 (t).

1-Benzyloxy-4-(2-fluorophenyl)pyrazole (8). Following the known procedure[4] starting with 1-(benzyloxy)-4-iodopyrazole (2.6 g, 8.7 mmol) and using 2-iodofluorobenzene as aryl halide gave 1.79 g (77%) of **8** as colorless crystals, mp 74−75 °C (EtOAc/heptane). R_f (EtOAc/heptane, 1:2) 0.45. δ_H ($CDCl_3$): 7.66 (t, J = 1.1 Hz, 1H), 7.50−7.03 (m, 10H), 5.34 (s, 2H). δ_C ($CDCl_3$): 159.70 (s(d), J = 248.4 Hz), 133.70 (s), 131.66 (d(d), J = 3.5 Hz), 129.74 (d), 129.39 (d), 128.77 (d), 127.79 (d(d), J = 8.4 Hz), 127.25 (d(d), J = 4.3 Hz), 124.36 (d(d), J = 3.4 Hz), 121.87 (d(d), J = 8.8 Hz), 119.87 (s(d), J = 13.9 Hz), 116.08 (d(d), J = 21.5 Hz), 113.70 (s(d), J = 1.6 Hz), 80.66 (t). Anal. Calcd for $C_{16}H_{13}FN_2O$: C, 71.63; H, 4.88; N 10.44. Found: C, 71.84; H, 5.02; N, 10.34.

***N*-[2-(1-Benzyloxypyrazol-4-yl)phenyl]benzophenoneimine (10).** A mixture of benzophenone (3.7 mmol), 4-(2-aminophenyl)-1-(benzyloxy)pyrazole (**13**)[4] (3.4 mmol), $Si(OEt)_4$ (4.4 mmol), and one drop of concentrated H_2SO_4 was placed in a flask equipped with a still head. The solution was heated at 160 °C under nitrogen overnight. The distillate (EtOH) was discarded, and the residue was dissolved in Et_2O (20 mL), washed with a saturated $NaHCO_3$ solution and H_2O (10 mL each), and dried with $MgSO_4$, and the solvents were removed. FC (heptane/EtOAc 10:1) gave 1.1 g (75%) of **10** as a thick yellow oil. R_f (EtOAc/heptane, 1:2) 0.42. δ_H ($CDCl_3$): 7.80−7.74 (m, 2H), 7.63 (d, J = 1.1 Hz, 1H), 7.57−7.38 (m, 4H), 7.31 (d, J = 1.1 Hz, 1H), 7.28−6.83 (m, 12H), 6.42−6.36 (m, 1H), 5.25 (s, 2H). δ_C ($CDCl_3$): 167.82, 148.14, 138.86, 136.07, 133.83, 131.86, 131.06, 129.60, 129.49, 129.25, 128.76, 128.69, 128.64, 128.41, 127.91, 126.63, 126.34, 123.54, 123.41, 122.00, 120.50, 117.71, 80.32.

(22) Prepared according to: Molina, P.; Alajarin, M.; Vidal, A.; Sanchez-Andrada, P. *J. Org. Chem.* **1992**, *57*, 929.

(23) Lüning, U.; Baumgartner, H.; Manthey, C.; Meynhardt, B. *J. Org. Chem.* **1996**, *61*, 7922.

1-Benzyloxy-9,9-diphenyl-8,9-dihydropyrazolo[3,4-*c*]-quinoline (12). To a solution of **10** (154 mg, 0.36 mmol) in THF (3 mL) was added 1.6 M *n*-BuLi in hexanes (0.27 mL, 0.43 mmol) at −78 °C. After 5 min, the reaction mixture was allowed to warm to room temperature, quenched with saturated aqueous NH_4Cl (20 mL), taken up with CH_2Cl_2 (3 × 20 mL), dried with $MgSO_4$, and concentrated in vacuo. FC (heptane/EtOAc, 6:1) gave 121 mg (79%) of **12** as colorless crystals, mp 178−180 °C (EtOAc/heptane). R_f (EtOAc/heptane, 1:2) 0.45. δ_H ($CDCl_3$): 7.60 (s, 1H), 7.40−6.65 (m, 19H), 4.68 (s, 1H), 4.59 (s, 2H). δ_C ($CDCl_3$): 144.61, 140.19, 133.78, 132.68, 129.66, 129.13, 128.67, 128.63, 128.59, 128.18, 127.63, 127.22, 122.70, 119.26, 116.57, 114.30, 114.03, 79.46, 65.54. Anal. Calcd for $C_{29}H_{23}N_3O$: C, 81.09; H, 5.40; N, 9.78. Found: C, 80.87; H, 5.47; N, 9.80.

Preparation of Pyrazoloquinolines 9a−d. General Procedure. Compound **13** (0.5 mmol), the aryl aldehyde (0.5 mmol), and 3 Å molecular sieves (2 g) were stirred at 50 °C for 24 h in dry toluene (5 mL). The reaction mixture was adsorbed onto a silica gel plug (5 g), vacuum-filtered (heptane/EtOAc, 4:1), and concentrated to give the crude Schiff base **14a−d**, which was in turn redissolved in THF (1 mL) and added to a solution of premade LDA (0.5 mmol) in THF (5 mL) at −78 °C. After 5 min, the reaction was allowed to warm to room temperature, DDQ (1.5 mmol) was added, and the mixture was stirred for 10 min. The solvents were removed, and the residue was redissolved in ether (20 mL) and washed successively with 1 M $NaHCO_3$ (3 × 15 mL) and brine (1 × 15 mL). The combined organic layers were dried with $MgSO_4$ and concentrated to give the crude product, which was purified by vacuum filtration (silica gel) using EtOAc/heptane, 1:10.

1-Benzyloxy-9-(4-methylphenyl)pyrazolo[3,4-*c*]quinoline (9a). Following the general procedure using 4-tolualdehyde gave 131 mg (71%) of **9a** as colorless crystals, mp 131−132 °C (EtOAc/heptane). R_f (EtOAc/heptane, 1:2) 0.53. δ_H ($CDCl_3$): 8.27 (s, 1H), 8.26−8.16 (m, 2H), 7.75 (d, J = 8.1 Hz, 2H), 7.70−7.61 (m, 2H), 7.35−7.12 (m, 5H), 6.76 (d, J = 7.1 Hz, 2H), 4.87 (s, 2H), 2.48 (s, 3H). δ_C ($CDCl_3$): 146.82 (s), 142.90 (s), 139.54 (s), 134.32 (s), 132.42 (s), 130.11 (d), 130.03 (d), 129.21 (d), 128.86 (d), 128.28 (d), 127.70 (d), 127.38 (d), 126.58 (s), 126.12 (d), 122.47 (s), 122.25 (d), 120.84 (s), 81.54 (t), 21.35 (q), one carbon signal overlapped. Anal. Calcd for $C_{24}H_{19}N_3O$: C, 78.88; H, 5.24; N, 11.50. Found: C, 78.81; H, 5.46; N, 11.51.

1-Benzyloxy-9-(4-fluorophenyl)pyrazolo[3,4-*c*]quinoline (9b). Following the general procedure using 4-fluorobenzaldehyde gave 122 mg (66%) of **9b** as brown crystals, mp 203−206 °C (EtOAc/heptane). R_f (EtOAc/heptane, 1:2) 0.56. δ_H ($CDCl_3$): 8.30 (s, 1H), 8.27−8.18 (m, 2H), 7.86−7.65 (m, 4H), 7.32−7.12 (m, 5H), 6.76 (d, J = 7.6 Hz, 2H), 4.96 (s, 2H). δ_C ($CDCl_3$): 162.04 (s), 156.37 (s), 145.47 (s), 142.80 (s), 132.30 (s), 132.18 (d(d), J = 8.5 Hz), 130.10 (d), 129.95 (d), 129.36 (d), 128.45 (d), 127.94 (d), 127.50 (d), 126.25 (d), 122.48 (s), 122.28 (d), 120.84 (s), 115.08 (d(d), J = 21.8 Hz), 81.53 (t), one carbon signal overlapped.

1-Benzyloxy-9-(4-methoxyphenyl)pyrazolo[3,4-*c*]quinoline (9c). Following the general procedure using 4-methoxybenzaldehyde gave 101 mg (53%) of **9c** as bright yellow crystals, mp 62−64 °C (heptane). R_f (EtOAc/heptane, 1:2) 0.44. δ_H ($CDCl_3$): 8.28 (s, 1H), 8.26−8.18 (m, 2H), 7.83 (d, J = 8.9 Hz, 2H), 7.70−7.63 (m, 2H), 7.30−6.99 (m, 5H), 6.80 (d, J = 8.1 Hz, 2H), 4.90 (s, 2H), 3.90 (s, 3H). δ_C ($CDCl_3$): 160.97, 146.42, 142.95, 132.44, 131.64, 130.11, 130.01, 129.59, 129.24, 128.32, 127.56, 127.36, 126.60, 126.14, 122.49, 122.21, 120.72, 113.56, 81.58, 55.37.

1-Benzyloxy-9-(2-thienyl)pyrazolo[3,4-*c*]quinoline (9d). Following the general procedure using 2-thiophenecarboxaldehyde gave 113 mg (63%) of **9d** as yellow crystals, mp 110−112 °C (EtOAc/heptane). R_f (EtOAc/heptane, 1:2) 0.42. δ_H ($CDCl_3$): 8.30 (s, 1H), 8.22−8.14 (m, 2H), 7.96 (dd, J = 3.8, 1.1 Hz, 1H), 7.70−7.54 (m, 3H), 7.32−6.98 (m, 6H), 5.12 (s, 2H). δ_C ($CDCl_3$): 160.29 (s), 142.49 (s), 140.14 (s), 132.34 (s), 131.18 (d), 130.24 (d), 129.77 (d), 129.42 (d), 129.17 (d), 128.49 (d), 127.81 (d), 127.72 (d), 127.51 (d), 126.54 (d), 125.87 (s), 122.94 (s), 122.11 (d), 120.72 (s), 81.98 (t).

1-Benzyloxy-9-(4-methylphenylamino)pyrazolo[3,4-*c*]-quinoline (17). To a solution of **13**[4] (133 mg, 0.5 mmol) in dry acetonitrile (2.5 mL) were added triphenylphosphine (262 mg, 1 mmol), triethylamine (2.5 mL), and CCl_4 (1.0 mL). The reaction mixture was stirred at room temperature for 16 h and filtered. The filtrate was passed through a silica gel (5 g) plug (EtOAc/heptane, 1:3) and concentrated. The resulting iminophosphorane was in turn dissolved in dry toluene (4 mL), and 4-tolyl isocyanate (67 mg, 0.5 mmol) was added. The reaction mixture was stirred at room temperature for 1 h and filtered through a silica gel (5 g) plug (EtOAc/heptane, 1:5), and solvents were removed in vacuo to give carbodiimide **16** which was dissolved in THF (1 mL) and added to a solution of premade LDA (0.5 mmol) in THF (5 mL) at −78 °C. After 5 min, the reaction was allowed to warm to room temperature and quenched with saturated aqueous NH_4Cl (10 mL). Extraction with EtOAc (3 × 10 mL), $MgSO_4$ drying, and concentration in vacuo gave the crude product, which was purified by vacuum filtration (silica gel) using EtOAc/heptane, 1:6, to give 86 mg (45%) of **17** as slightly yellow crystals, mp 122−123 °C (EtOAc/heptane). R_f (EtOAc/heptane, 1:2) 0.46. δ_H ($CDCl_3$): 8.09 (s, 1H), 7.96 (dd, J = 7.9, 1.3 Hz, 1H), 7.86 (dd, J = 8.3, 0.8 Hz, 1H), 7.66 (d, J = 8.3 Hz, 2H), 7.65 (s, 1H), 7.53−7.30 (m, 7H), 7.16 (d, J = 8.3 Hz, 2H), 5.54 (s, 2H), 2.34 (s, 3H). δ_C ($CDCl_3$): 143.15, 140.77, 136.83, 132.27, 132.16, 130.16, 129.38, 129.15, 127.40, 127.20, 126.31, 123.93, 121.99, 121.80, 120.41, 119.34, 118.44, 82.29, 20.86, one carbon signal overlapped. Anal. Calcd for $C_{24}H_{20}N_4O$: C, 75.77; H, 5.30; N, 14.73. Found: C, 75.47; H, 5.39; N, 14.58.

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Supporting Information Available: Spectral data for all compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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