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Anionic Indole *N*-Carbamoyl N → C Translocation. A Directed remote Metalation Route to 2-Aryl- and 2-Heteroarylindoles. Synthesis of Benz[*a*]carbazoles and Indeno[1,2-*b*]indoles

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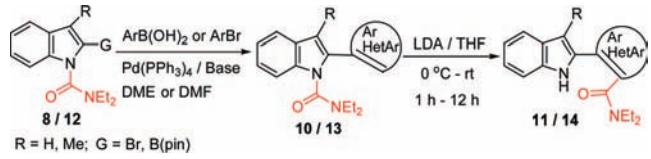
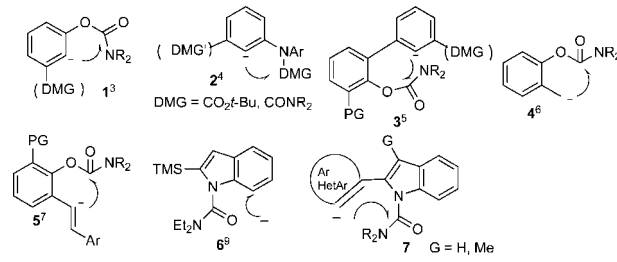
ABSTRACT



A new LDA-induced anionic N−C carbamoyl migration of 2-arylindoles (7) is reported. Treatment of *N*-carbamoylindoles 10 and 13, readily available by direct and *ipso*-borodesilylative Suzuki−Miyaura cross-coupling routes from 8 and 12, respectively, provides a general route to functionalized 2-arylindoles 11 and 14, respectively (Tables 1 and 2). The reaction has been applied to the synthesis of benzo[*a*]carbazoles 16 and indeno[1,2-*b*]indoles 18, and its intramolecularity has been established by a crossover experiment (Scheme 4).

Carbanion chemistry[1] continues to noticeably impact synthetic method development for the construction of aromatics and heteroaromatics.[1c–d] In context of contributions from our laboratories which aim to enhance links to the directed ortho metalation (DoM) reaction,[2] the anionic *O*- (**1**)[3] and *N*-*ortho* (**2**) Fries,[4] its remote (**3**)[5] and homologous (**4**)[6] counterparts, and most recently, *O*- to *C*-carbamoyl transfer (**5**)[7] have constituted key steps in establishing unusual substitution patterns and facilitating efficient total synthesis (Scheme 1).[8]

Scheme 1[a]



[a]DMG = directed metalation group.

The recent finding that the indole N-CONEt$_2$ serves, after 2-TMS protection, as an excellent DMG for C-7 deprotonation (**6**)[9] and the availability of 2-arylindoles by Suzuki−Miyaura cross-coupling chemistry[10] have provided, in combination, the opportunity for the discovery of a new directed remote metalation (DreM) concept (**7**). Herein, we report preliminary studies on this reaction which piggy-backs the carbamoyl DMG to the 2-aryl substituent for further DoM.

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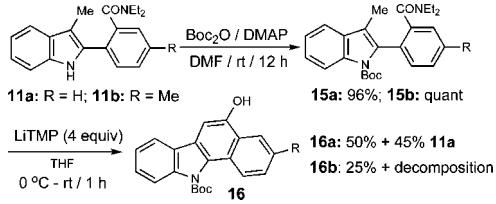
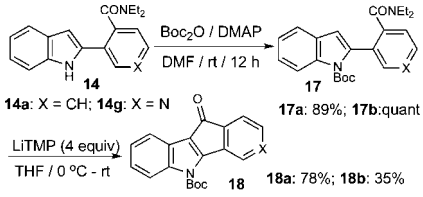
It also facilitates formation of derivatives **11** which, due to steric encumbrance, are obtained less efficiently or may be unavailable by direct cross-coupling[11] and allows the construction of benzocarbazoles and indeno[1,2-*b*]indoles (Schemes 2 and 3), compounds of considerable current interest in the areas of antitumor,[12] estrogen deficiency,[13] melatoninergic disorder,[14] and protein kinase inhibition.[15]

Scheme 2

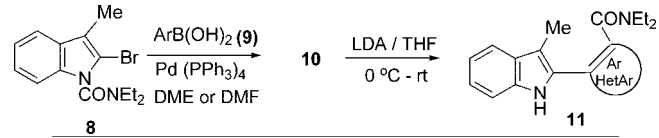


Scheme 3



The results of our preliminary investigations comprise two series of 2-aryl- and 2-heteroarylindoles and are summarized in Tables 1 and 2. In the first series with a view toward remote anionic cyclization chemistry to fused carbazoles,[11] *N*-carbamoyl-2-aryl-3-methylindoles **10a**−**i**[16] were prepared by generally efficient Suzuki−Miyaura cross-coupling of the *N*-carbamoyl-2-bromoskatole **8**[17] with a variety of aryl- and heteroarylboronic acids **9a**−**i**, respectively (Table 1).[18] In the prototype reaction (Table 1, entry 1), treatment of **10a** with 2 equiv of LDA[19] led to the formation of the *N*-carbamoyl migration product **11a** in 80% yield. Table 1 illustrates selected cases which deserve brief

Table 1. Synthesis of 2-(Carbamoyl)arylindoles **11a**−**i**: The Direct Suzuki−Miyaura Cross-Coupling Route from **8**



	Aryboronic acid (**9**)	Xcoupl product (**10**)	yield, %[a]	Migration product (**11**)	yield, %[a]
1	**9a** R = H	**10a**	92	**11a**	80
2	**9b** R = Me	**10b**	90	**11b**	92
3	**9c**	**10c**	80	**11c**	55
4	**9d**	**10d**	89	**11d**	55
5	**9e**	**10e**	95	**11e**	94
6	**9f**	**10f**	72	**11f**	65[c]
7	**9g** X = O	**10g**	65[b]	**11g**	75[d]
8	**9h** X = S	**10h**	85	**11h**	56[e]
9	**9i**	**10i**	89	**11i**	50

[a] Isolated yields. [b] $Pd_2(dba)_3$/SPhos/K_3PO_4/MeOH/50 h. [c] −40°C/1 h. [d] −40°C/2 equiv of LDA/1 h. [e] 0 °C/2 equiv/40 min.

(3) Sibi, M. P.; Snieckus, V. *J. Org. Chem.* **1983**, *48*, 1935.
(4) MacNeil, S. L.; Wilson, B. J.; Snieckus, V. *Org. Lett.* **2006**, *8*, 1133.
(5) Wang, W.; Snieckus, V. *J. Org. Chem.* **1992**, *57*, 424.
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(7) Reed, M. A.; Chang, M.; Snieckus, V. *Org. Lett.* **2004**, *6*, 2297.
(8) (a) For an outstanding review, see: Clayden, J. In *Chemistry of Oganolithium Compounds*; Rappoport, Z., Marek, I., Eds.; John Wiley & Sons, Ltd.: Chichester, 2004; p 495. (b) For discussion regarding the mechanistic and synthetic aspects of the complex-induced proximity effect (CIPE) on organolithium chemistry, including DreM, see: Whisler, M. C.; MacNeil, S.; Snieckus, V.; Beak, P. *Angew. Chem., Int. Ed.* **2004**, *43*, 2206.
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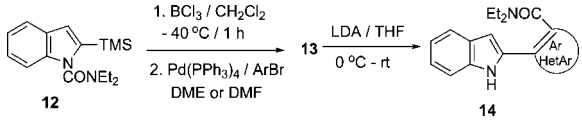
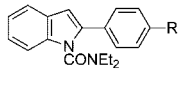
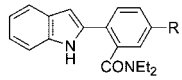
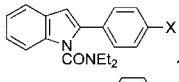
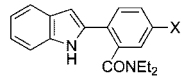
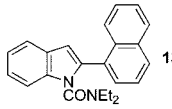
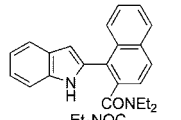
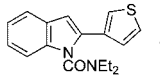
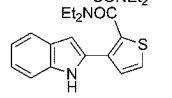
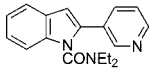
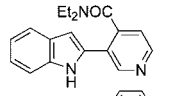
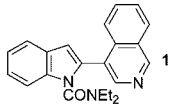
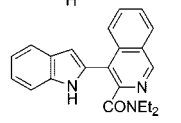
(13) (a) Miller, C. P.; Collini, M. D.; Tran, B. D. *PCT Int. Appl.* **1999**, 59 pp. (b) Wang, J. B.; Ji, Q. G.; Xu, J.; Wu, X. H.; Xie, Y. Y. *Synth. Commun.* **2005**, *35*, 581.
(14) (a) Wierzbicki, M.; Boussard, M. F.; Rousseau, A.; Boutin, J. A.; Delagrange, P. *Eur. Pat. Appl.* **2002**, 15 pp. (b) Boussard, M. F.; Truche, S.; Rousseau-Rojas, A.; Briss, S.; Descamps, S.; Droual, M.; Wierzbicki, M.; Ferry, G.; Audinot, V.; Delagrange, P.; Boutin, J. A. *Eur. J. Med. Chem.* **2006**, *41*, 306.
(15) (a) Gribble, G. W. In *The Alkaloids*; Brossi, A., Ed.; Academic Press: New York, 1990; Vol. 39, p 239. (b) Sanchez-Martinez, C.; Shih, C.; Faul, M. M.; Zhu, G.; Paal, M. *Bioorg. Med. Chem. Lett.* **2003**, *13*, 3835.
(16) For methods of 2-arylindole synthesis, see: (a) Fischer indole synthesis: Robinson, B. *Chem. Rev* **1969**, *69*, 227; Slätt, J.; Bergman, J. *Tetrahedron* **2002**, *58*, 9187. (b) Transition-metal-catalyzed coupling−cyclization: Hong, K. B.; Lee, C. W.; Yum, E. K. *Tetrahedron Lett.* **2004**, *45*, 693; Cacchi, S.; Fabrizi, G.; Parisi, L. M. *Org. Lett.* **2003**, *5*, 3843. (c) C−H arylation: Wang, X.; Gribkov, D. V.; Sames, D. *J. Org. Chem.* **2007**, *72*, 146, and references cited therein. (d) From acyclic phosphoryloxy ene carbamates: Fuwa, H.; Sasaki, M. *Org. Lett.* **2007**, *9*, 3347. For their bioactivity studies, see: (e) Harper, S.; Pacini, B.; Avolio, S.; Di Filippo, M.; Migliaccio, G.; Laufer, R.; De Francesco, R.; Rowley, M.; Narjes, F. *J. Med. Chem.* **2005**, *48*, 1314 (Inhibitors of Hepatitis C Virus NS5B Polymerase). (f) Meng, C. Q.; Ni, L.; Worsencrott, K. J.; Ye, Z.; Weingarten, M. D.; Simpson, J. E.; Skudlarek, J. W.; Marino, E. M.; Suen, K.; Kunsch, C.; Howard, R. B.; Sundell, C. L. 229th ACS National Meeting, San Diego, CA, March 13−17, 2005; American Chemical Society: Washington, DC, 2005; Abstract No. 587 (antiasthmatic). (g) Kaufmann, D.; Pojarova, M.; Vogel, S.; Liebl, R.; Gastpar, R.; Gross, D.; Nishino, T.; Pfaller, T.; von Angerer, E. *Bioorg. Med. Chem.* **2007**, *15*, 5122 (antimitotic).
(17) Prepared in 92% yield by *ipso*-bromodesilylation of *N*,*N*-diethyl-3-methyl-2-(trimethylsilyl)-1*H*-indole-1-carboxamide; see the Supporting Information.
(18) With the exception of **9i**, which was prepared by hydroboration (see: Kalinin, A. V.; Scherer, S.; Snieckus, V. *Angew. Chem., Int. Ed.* **2003**, *42*, 3399), all other arylboronic acids were obtained from commercial sources.
(19) For a typical experimental procedure, see the Supporting Information.

Table 2. Synthesis of 2-(Carbamoyl)arylindoles **14a**−**g**: The *ipso*-Borodesilyation−Suzuki−Miyaura Cross-Coupling Route from **12**



Entry	Xcouple product (**13**)	yield (%)[a]	Migration product (**14**)	yield (%)[a]
1		**13a** 85[b] R = H		**14a** quant
2		**13b** 67 R = OMe		**14b** quant
3		**13c** 71 X = Cl		**14c** 45
4		**13d** 75 X = Br		**14d** 36
5		**13e** 77		**14e** 60
6		**13f** 89[c]		**14f** 73[d]
7		**13g** 70[c]		**14g** 75
8		**13h** 80[b]		**14h** 67

[a] Isolated yields. [b] For preparation, see ref 10. [c] Boropinacolates were used. [d] 0 °C for 40 min.

comment. In simple cases, 2 equiv of LDA was sufficient for smooth rearrangement while in substituted derivatives, e.g., **10c**,**d**, up to 4 equiv of LDA was necessary for optimum yields. Weak (entry 2) and strong (entry 5) electron-donating groups provide excellent yields of products and a synergistic DMG effect, analogous to that observed in *m*-di-DMG-substituted benzenes, is demonstrated by the regioselective migration result (entry 4) albeit in lower yield. A fluoro substituent is tolerated (entry 6), carbamoyl transfer to furan and thiophene rings is observed to the expected, more acidic site[20] (entries 7 and 8) and a styryl case (entry 9)[21] demonstrating an interesting migration to a vinyl anion analogous to that observed generally for *O*-carbamate series,[7] may be noted. The present methodology for the synthesis of *N*-substituted skatole derivatives **10** circumvents the direct Suzuki−Miyaura coupling route,[11] whose inefficiency is presumably due to a tri-*ortho*-substitution hindrance effect.[22]

As an alternative route to 2-arylindoles, with the aim of making 3-unsubstituted systems in order to leave the option for further well-established electrophilic substitution chemistry,[23] the recently disclosed method[10] was adapted. Thus, using the common starting *N*-carbamoyl-2-TMS indole **12**,[9] *ipso*-borodesilylation followed by in situ Suzuki−Miyaura cross coupling of the presumed dichloroborane[24,25] with selected aryl bromides led to a variety of 2-aryl (Table 2, entries 1−5) and heteroaryl (entries 6−8) indole derivatives. For the cross coupling, expected halogen chemoselectivity[26] (entries 3 and 4) was observed (see the Supporting Information). In this series, the remote metalation−*N*-carbamoyl migration reaction also proceeded smoothly and, in some cases (entries 1 and 6, Table 2), in higher yields than the corresponding skatole derivatives (entries 1 and 8, Table 1). In the heteroaryl series, the thienyl product **13f**, obtained by an inverted partner route, is unexceptional in terms of greater C-2 over C-3 acidity,[20] the pyridyl case **13g** follows previous observations on deprotonation site selectivity,[27] and the isoquinoline derivative **13h** shows presumably the result of great heteroring C−H acidity and/or CIPE alignment over the alternate *peri*-position.

To further advance synthetic utility, the application of the directed remote metalation (DreM) concept[5,8b] was tested on several carbamoyl-translocated skatole products **11a** and **11b** (Scheme 2). After a not unexpected failure at an attempt to affect a one-pot procedure by subjection of a solution of the initially formed anion corresponding to the migration product **11a** to treatment with additional LDA,[28] this reaction solution was treated with Boc anhydride, and product **15a** was subjected to reaction with LiTMP to give the benzo[*a*]carbazole **16a** in 88% yield (based on recovered **11a**).[29,30] The corresponding *m*-tolyl series, **11b** → **15b** → **16b**, gave, not surprisingly, a less synthetically useful result.

In a further enhancement of synthetic utility (Scheme 3), the 2-arylindoles **14a** and **14g** were protected as the corresponding Boc derivatives **17a** and **17b**, and the isolated products were subjected to LDA conditions as above to

(20) (a) Reutov, O. A.; Beletskaya, I. P.; Butin, K. P. *CH-Acids*; Pergamon Press: Oxford, 1978; pp 67–119. (b) Katritzky, A. R.; Ress, C. W. *Comprehensive Heterocyclic Chemistry*; Pergamon Press: Oxford, 1984; pp 238, 650–771.

(21) The structure of **11i** was confirmed by 2D NMR, see the Supporting Information.

(22) For developments in overcoming steric effects in the Suzuki−Miyaura reaction, see: Barder, T. E.; Walker, S. D.; Martinelli, S. R.; Buchwald, S. L. *J. Am. Chem. Soc.* **2005**, *127*, 4685.

(23) (a) Sundberg, R. J. *Indoles*; 2nd ed.; Academic Press: London, San Diego, 1996. (b) Joule, J. A.; Mills, K. *Heterocyclic Chemistry*; 4th ed.; Blackwell Science: Oxford, 2000; p 325. (c) Joule, J. A. *Science of Synthesis*; Thomas, E. J., Ed.; Thieme: Stuttgart, 2000; Vol. 10, p 361.

(24) Known but sensitive compounds, see: (a) Haubold, W.; Herdtle, J.; Gollinger, W.; Einholz, W. *J. Organomet. Chem.* **1986**, *315*, 1. (b) Kaufmann, D. *Chem. Ber.* **1987**, *120*, 853.

(25) In some cases (entries 6 and 7), the corresponding boropinacolates were isolated and gave, upon cross coupling, better yields of products. This may be due to the more robust nature and easier handling of the boropinacolates; see: Abaraca, B.; Ballesteros, R.; Blanco, F.; Bouillon, A.; Collot, V.; Dominguez, J.-R.; Lancelot, J.-C.; Rault, S. *Tetrahedron* **2004**, *60*, 4887.

(26) (a) *Metal-Catalyzed Cross-Coupling Reactions*; de Meijere, A., Diederich, F., Eds.; Wiley-VCH: New York, 2004; Chapter 2. (b) Grushin, V. V.; Alper, H. *Chem. Rev.* **1994**, *94*, 1047.

(27) (a) Mongin, F.; Quéguiner, G. *Tetrahedron* **2001**, *57*, 4059. (b) Quéguiner, G.; Marsais, F.; Snieckus, V.; Epsztajn, J. *Adv. Heterocycl. Chem.* **1991**, *52*, 187.

(28) The resulting N-anion is expected to deacidify the already weakly acidic 3-methyl hydrogens. The indole C-3 methyl hydrogen acidity is expected to be lower than the corresponding C-2 acidity on the basis of previous results (Naruse, Y.; Ito, Y.; Inagaki, S. *J. Org. Chem.* **1991**, *56*, 2256), and our observation that deprotonation of 1,2,3-trimethylindole followed by methyl iodide quench affords 1,3-dimethyl-2-ethylindole (95% yield: Zhao, Y.; Snieckus, V. Unpublished results).

(29) For recent syntheses of carbazoles, see: (a) Tsuchimoto, T.; Matsubayashi, H.; Kaneko, M.; Shirakawa, E.; Kawakami, Y. *Angew. Chem., Int. Ed.* **2005**, *44*, 1336. (b) Liu, C.-Y.; Knochel, P. *Org. Lett.* **2005**, *7*, 2543. (c) Martínez-Esperón, M. F.; Rodríguez, D.; Castedo, L.; Saá, C. *Org. Lett.* **2005**, *7*, 2213. (d) Campeau, L.-C.; Parisien, M.; Jean, A.; Fagnou, K. J. *Am. Chem. Soc.* **2006**, *128*, 581.

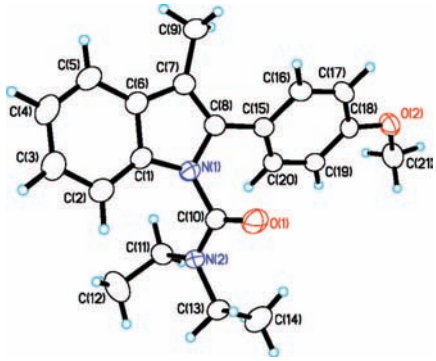


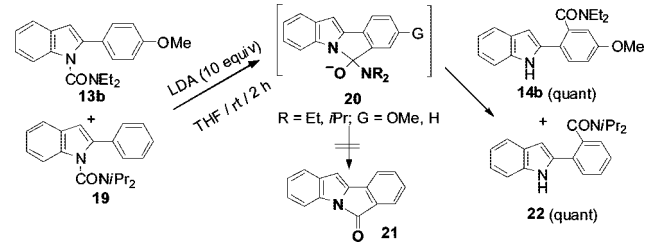
Figure 1. ORTEP view of compound **10e** with atomic numbering scheme.

afford the indeno[1,2-*b*]indoles **18a** and the corresponding aza derivative **18b** in 78% and 35% yields, respectively. Interestingly, since, to the best of our knowledge, direct Friedel−Crafts reaction of the carboxylic acids corresponding to **17a**,**b**-type compounds has not been reported, the above DreM route may serve as a useful method for the preparation of these somewhat unexplored ring systems.[13,14]

Based on considerable precedent,[8b] a carbamoyl-LDA coordination (CIPE) is suggested to play a role in the deprotonation−migration reaction.[31] Examination of models and the X-ray crystal structure of **10e** (Figure 1), although with the normal caveat of inadequate argument based on solid-state analysis and lack of knowledge of the structure of the derived lithiated species,[32] one may expect a reasonable Burgi−Dunitz angle[33] trajectory approach of an incipient 2-aryl anion toward the carbamoyl carbonyl.[1]

The carbamoyl translocation reaction of **13a** was conveniently followed by React IR and showed smooth disappearance of the N-CONEt$_2$ band at ν 1684 cm^{-1} over 1 h and the concomitant appearance of the CONEt$_2$ band at ν 1601 cm^{-1}. This suggests that the migration proceeds via the tetrahedral intermediate **20**, whose conversion to product rather than 6-oxo-6*H*-isoindolo[2,1-*a*]indole **21** (ν 1720 cm^{-1})[34] is driven by strain and indole N-anion leaving group propensity.[35,36] As a test of intramolecularity of the migration, a crossover experiment was executed (Scheme 4). Thus, treatment of a 1:1 mixture of **13b** and **19** under the standard LDA conditions afforded **14b**and **22** in quantitative conversions. Although the expected

Scheme 4



rate differences in the migration of **13b** and **19** were qualitatively observed, this result nevertheless supports an intramolecular pathway for the *N*-carbamoyl translocation reaction.

In conclusion, a new and general anionic *N*-carbamoyl migration, **10**, **13** → **11**, **14** has been added to the tool box of synthetic carbanionic aromatic chemistry (Scheme 1).[37] This reaction offers an alternative to direct cross-coupling approaches to 2-arylindoles[16]which may be undermined by steric hindrance effects[16] and provides products **11** and **14**, useful for further DoM and DreM reactions as well as additional anionic technology for the synthesis of benzocarbazoles (**16a**,**b**)[38] and an anionic route to indeno[1,2-*b*]indole (**18a**) and azaindeno[1,2-*b*]indole (**18b**).

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Note Added in Proof. For a more direct approach to *N*-carbamoyl-2,3-diphenylindoles, see: Leogane, O.; Lebel, H. *Angew. Chem., Int. Ed.* **2008**, *47*, 350.

Supporting Information Available: Experimental procedures and characterization of new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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(30) Since compounds **16a**,**b** were found to be unstable, they were transformed into their triflate **16c** and acetate **16d** derivatives, respectively, for characterization; see the Supporting Information.

(31) For a metal−halogen exchange driven DreM reaction, see: Ruiz, J.; Ardeo, A.; Ignacio, R.; Sotomayor, N.; Lete, E. *Tetrahedron* **2005**, *61*, 3311.

(32) For enlightening work on DMG-based *ortho*-lithiated aromatics, see: (a) Singh, K. J.; Collum, D. B. *J. Am. Chem. Soc.* **2006**, *128*, 13753. (b) Ma, Y.; Collum, D. B. *J. Am. Chem. Soc.* **2007**, *129*, 14818. (c) Clayden, J.; Davies, R. P.; Hendy, M. A.; Snaith, R.; Wheatley, A. E. H. *Angew. Chem., Int. Ed.* **2001**, *40*, 1238. For synthetic chemists, an essential tutorial and review on LDA-mediated reactions has appeared: (d) Collum, D. B.; McNeil, A. J.; Ramirez, A. *Angew. Chem., Int. Ed.* **2007**, *46*, 2007.

(33) (a) Burgi, H. B.; Dunitz, J. D.; Lehn, J.-M.; Wipff, G. *Tetrahedron* **1974**, *30*, 1563. (b) Burgi, H. B.; Dunitz, J. D. J. *Am. Chem. Soc.* **1987**, *109*, 2924.

(34) (a) Itahara, T. *Synthesis* **1979**, *2*, 151. (b) For an intramolecular aerobic oxidative coupling synthesis, see: Dwight, T. A.; Rue, N. R.; Charyk, D.; Josselyn, R.; DeBof, B. *Org. Lett.* **2007**, *9*, 3137.

(35) For React IR evidence of DreM paths to fluorenones, see: Alessi, M.; Larkin, A. L.; Ogilvie, K. A.; Green, L. A.; Lai, S.; Lopez, S.; Snieckus, V. *J. Org. Chem.* **2007**, *75*, 1588.

(36) Interestingly, in a recent report, LDA treatment of *N*-pivaloyl 2-phenylindole has been shown not lead to the analogous migration but loss of the pivaloyl group. Although a rationale was not given, this result may be due to its less favorable equilibrium to the alkoxide tetrahedral intermediate and poorer coordinating and hence metalating properties of the pivaloyl compared to carbamoyl and perhaps Boc groups; see: Avendaño, C.; Sánchez; J, D.; Menéndez, J. C *Synlett* **2005**, *1*, 107.

(37) Attempts to effect the analogous migration using the indole *N*-phosphodiamidate (*N*-P(O)(NR$_2$)$_2$) derivative corresponding to **13a** under the same LDA conditions failed: Zhao, Z.; Snieckus, V. Unpublished results.

(38) Although yields of products from the present and previous route[11] are comparable, different phenolic benzocarbazole isomers (C-4 vs C-3) are obtained.

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