Directed Ortho Metalation of *N,N*-Diethylbenzamides. Silicon Protection of Ortho Sites and the *o*-Methyl Group

Robert J. Mills, Nicholas J. Taylor, and Victor Snieckus*

Guelph-Waterloo Centre for Graduate Work in Chemistry, University of Waterloo, Waterloo, Ontario, Canada N2L 3G1

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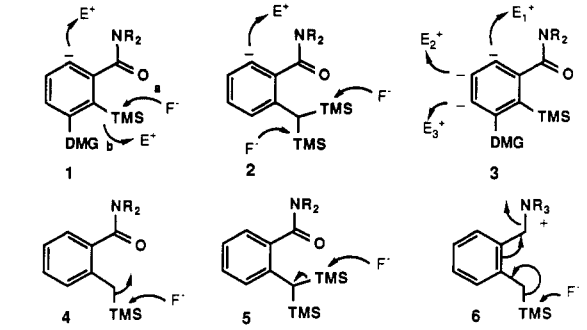
New general methodology of value in aromatic chemistry based on silicon protection of preferred ortho metalation sites in benzamides and *o*-methyl groups in *o*-toluamides (**1**, **2**, Scheme I) is described. According to these methodologies, routes (Schemes II and V) to 1,2,5-, 1,2,4,5-, and 1,2,3-substituted aromatics with a variety of functionalities and oxidation states have been developed (Tables I and II). These tactics are used for the synthesis of difficult to access halo (**10a-b**, Scheme III) and methyl (**21**, **25**, Scheme VI) heterocycles. Ipso bromodesilylation reactions with bromine lead regiospecifically to *o*-bromobenzamides (**12a,c**, **14**, Scheme IV). Walk-around-the-ring metalation processes provide highly substituted aromatics **27**, **28**, **29**, and **30** (Scheme VII); the X-ray structure of the hexasubstituted derivative **30** shows a significant puckering of the aromatic ring. Cesium fluoride induced carbodesilylation of *o*-silylbenzamides with benzaldehyde affords, after TsOH cyclization, phthalides (**31a-c**, Scheme VIII) and constitutes a neutral alternative to the directed ortho metalation approach. α- and α,α-silylated *o*-toluamides are used in fluoride-mediated carbodesilylation (**34a,d**, Scheme IX) and desilylative Peterson olefination (**35**, Scheme X) procedures, respectively. The utility of α-silylated *o*-toluamide for the synthesis of a tetralin (**38**, Scheme XI) via an *o*-quinodimethane species is given.

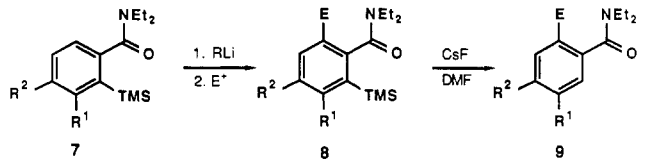
In spite of its early history[1] and definitive mechanistic base,[2] synthetic aromatic silicon chemistry, in contrast to its aliphatic counterpart, remains substantially underexplored.[3] Early reports of rate-enhanced electrophilic ipso desilylation[4] and mild base-induced carbodesilylation[5] of aromatic and benzlic silanes has stimulated recent activity to develop the synthetic potential of these two classes of reactions for aromatic and heteroaromatic systems.[6-9] The demonstration of fluoride catalysis for the carbodesilylation reaction[9d] has allowed the use of base-sensitive silanes (e.g. nitrotoluene-derived) for C–C bond forming processes.[10,11] The present work originated with the following observations: (a) *o*-silylbenzamides are easily prepared by directed ortho metalation,[12,13] (b) arylsilanes are stable to alkyllithium reagents,[1,14] (c) α-mono and α,α'-disilyl-*o*-toluamides should be readily derived by metalation,[15] (d) as demonstrated by Beak, *o*-isopropyl-*N,N*-diethylbenzamide undergoes metalation exclusively at C-6,[16] and (e) silyl groups are smoothly removed by fluoride. These facts led to a number of conceptual goals aimed at expanding the scope of the benzamide-directed metalation strategy[17] for the synthesis of polysubstituted aromatics (Scheme I): to

Scheme I[a]



[a] DMG = Directed metalation group.

Scheme II



(1) Eaborn, C. *Organosilicon Compounds*; Butterworths: New York, 1960.
(2) Eaborn, C. *J. Organomet. Chem.* **1975**, *100*, 43.
(3) Colvin, E. W. *Silicon in Organic Synthesis*; Butterworths: London, 1981; p 125. Weber, W. P. *Silicon Reagents for Organic Synthesis*; Springer-Verlag: Berlin, 1983; p 114.
(4) Perrin, C. L. *J. Org. Chem.* **1971**, *36*, 420. Hartshorn, S. R. *Chem. Soc. Rev.* **1974**, *3*, 167.
(5) Webb, A. F.; Sethi, D. S.; Gilman, H. *J. Organomet. Chem* **1970**, *21*, 61. Pinkerton, F. H.; Thames, S. F. *J. Heterocycl. Chem.* **1972**, *9*, 67 and references cited therein. Ogawa, M.; Yasui, M; Matsui, M. *Agr. Biol. Chem.* **1970**, *34*, 970.
(6) Electrophile-induced ipso desilylation: Felix, G.; Dunogues, J.; Calas, R. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 402. Felix, G.; Dunogues, J.; Pisciotti, F.; Calas, R. *Ibid.* **1977**, *16*, 488. Miller, R. B.; Tsang, T. *Tetrahedron Lett.* **1988**, 6715. Barrett, A. G. M.; O'Neil, I. A. *J. Org. Chem.* **1988**, *53*, 1815. For a review, see: Dunogues, J. *Chemtech* **1982**, *12*, 372.
(7) For recent applications: (a) Funk, R. L.; Vollhardt, K. P. C. *J. Am. Chem. Soc.* **1979**, *101*, 215. (b) Wilbur, D. S.; Stone, W. E.; Anderson, K. W. *J. Org. Chem.* **1983**, *48*, 1542.
(8) Ipso Friedel–Crafts carbodesilylations on heterocyclic systems with or without Lewis catalyst: Majchrzak, M. W.; Simchen, G. *Synthesis* **1986**, 956. Dondoni, A.; Fantin, G.; Fogagnolo, M.; Medici, A.; Pedrini, P. *J. Org. Chem.* **1989**, *54*, 693 and references cited therein. Barrett, A. G. M.; Dauzonne, D.; Williams, D. J. *J. Chem. Soc., Chem. Commun.* **1982**, 636.
(9) Base-induced carbodesilylations: (a) Effenberger, F.; Schollkopf, K. *Chem. Ber.* **1985**, *118*, 4377. (b) Effenberger, F.; Schollkopf, K. *Ibid.* **1985**, *118*, 4356. (c) Effenberger, F.; Spiegler, W. *Ibid.* **1985**, *118*, 3900. (d) Effenberger, F.; Spiegler, W. *Ibid.* **1985**, *118*, 3872. (e) Effenberger, F.; Krebs, A. *J. Org. Chem.* **1984**, *49*, 4687.
(10) Bartoli, G.; Bosco, M.; Caretti, D.; Dalpozzo, R.; Todesco, P. E. *J. Org. Chem.* **1987**, *52*, 4381 and references cited therein; Kessar, S. V.; Singh, P.; Venugopal, D. *J. Chem. Soc., Chem. Commun.* **1985**, 1258.
(11) For an interesting intramolecular case involving an imminium electrophile, see: Takano, S.; Numata, H.; Ogasawara, K. *J. Chem. Soc., Chem. Commun.* **1982**, 769.
(12) (a) Beak, P.; Brown, R. A. *J. Org. Chem.* **1982**, *42*, 1823. (b) de Silva, S. O.; Reed, J. N.; Snieckus, V. *Tetrahedron Lett.* **1978**, 5099.
(13) The first o-silylated benzamide appears to have been prepared by Sandifer, R. M.; Beam, C. F.; Perkins, M.; Hauser, C. R. *Chem. Ind.* **1977**, 231.
(14) Habich, D.; Effenberger, F. *Synthesis* **1979**, 841.
(15) Sibi, M. P.; Miah, M. A. J.; Snieckus, V. *J. Org. Chem.* **1984**, *49*, 737.
(16) Beak, P.; Tse, A.; Hawkins, J.; Chen, C.-W.; Mills, S. *Tetrahedron* **1983**, *39*, 1983.
(17) Snieckus, V. *Bull. Soc. Chim. Fr.* (II) **1988**, 67; Snieckus, V. *Lect. Heterocycl. Chem.* **1984**, 95. Beak, P.; Snieckus, V. *Acct. Chem. Res.* **1982**, *15*, 306.

0022-3263/89/1954-4372$01.50/0

Table I. Synthesis of Polysubstituted Benzamides 9

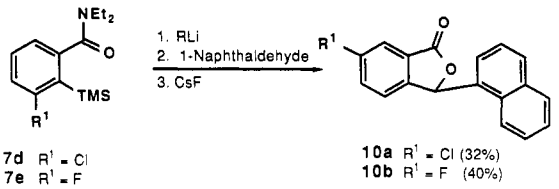
compd 7				compd 8					compd 9				
	R^1	R^2	E^+		E	R^1	R^2	yield,[a] %		E	R^1	R^2	yield,[a] %
7a	H	H	MeI	**8a**	Me	H	H	91	**9a**		*b*		
7b	OMe	H	MeI	**8b**	Me	OMe	H	74	**9b**	Me	OMe	H	85
7b			DMF	**8c**	CHO	OMe	H	88	**9c**	CHO	OMe	H	76
7b			$ClCONEt_2$	**8d**	$CONEt_2$	OMe	H	89	**9d**	$CONEt_2$	OMe	H	73
7b			PhNCS	**8e**	CSNHPh	OMe	H	89	**9e**	*c*			
7b			TMSCl	**8f**	TMS	OMe	H	89	**9f**	*b*			
7b			$(MeS)_2$	**8g**	SMe	OMe	H	89	**9g**	SMe	OMe	H	82
7b			I_2	**8h**	I	OMe	H	86	**9h**	I	OMe	H	93
7c	OMe	OMe	MeOD	**8i**	D	OMe	OMe	79	**9i**	D	OMe	OMe	65
7c			MeI	**8j**	Me	OMe	OMe	90	**9j**	Me	OMe	OMe	87
7c			DMF	**8k**	CHO	OMe	OMe	56	**9k**	*c*			
7d	Cl	H	MeOD	**8l**	D	Cl	H	89	**9l**	D	Cl	H	90
7d			MeI	**8m**	Me	Cl	H	89	**9m**	*c*			
7d			DMF	**8n**	CHO	Cl	H	76	**9n**	CHO	Cl	H	80
7e	F	H	MeOD	**8o**	D	F	H	*d*	**9o**	D	F	H	95
7e			MeI	**8p**	Me	F	H	80	**9p**	Me	F	H	90
7e			DMF	**8q**	CHO	F	H	58	**9q**	*c*			

[a] Yields are based on purified (chromatographed or distilled) material. [b] Desilylation not attempted. [c] Not obtained under the general desilylation conditions. [d] Not isolated.

silylate the more reactive metalation site common to the amide and other directed metalation groups (DMG) in order to test further metalation at C-6 (**1**) (assuming $CONEt_2$ > DMG as a metalation director); accepting Beak's rationale,[16] to similarly probe metalation at C-6 (**2**) (subsequent desilylation in **1**, path a and **2** would lead to useful aromatic substitution patterns); to effect regioselective ipso bromo desilylation in the presence of electron-donating groups (**1**, path b); to develop "walk-around-the-ring" metalations by sequential introduction of electrophiles which function as DMGs (**3**); to establish fluoride-mediated carbodesilylation **1**, path a and **4**)[9,10] and desilylative Peterson olefination (**5**);[18] to convert **4** into a useful synthon for *o*-quinodimethane generation (**6**).[19]

Herein we detail[20] the realization of these concepts. Our studies show that the liaison of the reliable benzamide-directed metalation tactic[17] with expedient silicon protection[21] provides new scope and versatility in synthetic aromatic chemistry.[22] In the accompanying paper in this issue,[23] we describe the value of the derived products for the synthesis of polycyclic aromatic hydrocarbons and naturally occurring anthraquinones.

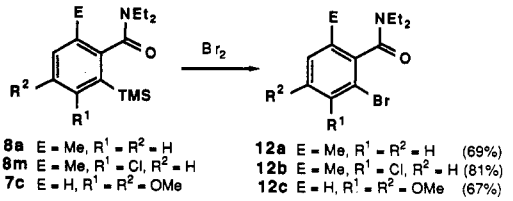
Scheme III



7d R^1 = Cl
7e R^1 = F

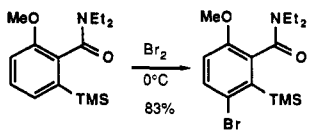
10a R^1 = Cl (32%)
10b R^1 = F (40%)

Scheme IV



8a E = Me, R^1 = R^2 = H
8m E = Me, R^1 = Cl, R^2 = H
7c E = H, R^1 = R^2 = OMe

12a E = Me, R^1 = R^2 = H (69%)
12b E = Me, R^1 = Cl, R^2 = H (81%)
12c E = H, R^1 = R^2 = OMe (67%)



13 **14**

Silicon Aromatic C–H Protection and Bromo Ipso Desilylation. In the prototype reaction, the known[24] *o*-silylbenzamide **7a** (Scheme II, Table I) was metalated under standard conditions (*s*-BuLi/TMEDA/THF/−78 °C) followed by MeI quench to give the trisubstituted benzamide **8a** in high yield. With this result in hand, the concept of silicon protection of the more reactive metalation site (**1**) was examined with a series of 3-substituted 2-(trimethylsilyl)benzamides **7b–e**, readily prepared by taking advantage of the previously demonstrated regiospecific metalation of 3-methoxy-,[12,24] 3-chloro-,[24] and 3-fluoro-*N,N*-diethylbenzamides.[25] With the preferred metalation site blocked, these were lithiated under the standard conditions and quenched with a variety of electrophiles to afford, in good to excellent yields, the contiguously tetra- and pentasubstituted benzamides **8b–q** (Table I). The tetrasubstituted aromatics showed diagnostic AB ^1H NMR aromatic proton patterns (see the Experimental Section). Attempts to use silicon protection

(18) For normal Peterson reactions on benzyl silanes, see: Bennetau, B.; Dunogues, J. *Tetrahedron Lett.* **1983**, *24*, 4217. Konakahara, T.; Takagi, Y. *Synthesis* **1979**, 192. See also: Konakahara, T.; Sato, K. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 1241.

(19) Reviews: (a) Wong, H. N. C.; Lau, K.-L.; Tam, K.-F. *Top. Curr. Chem.* **1986**, *133*, 83. (b) Ito, Y. In *Current Trends in Synthesis*; Nozaki, H., Ed.; Pergamon Press: London, 1981; pp 169–176. (c) For recent work, see: Trahanovsky, W. S.; Macias, J. R. *J. Am. Chem. Soc.* **1986**, *108*, 6820. (d) Ito, Y.; Nakajo, E.; Sho, K.; Saegusa, T. *Synthesis* **1985**, 698. (e) For a variation, see: Takano, S.; Otaki, S.; Owasawara, K. *Heterocycles* **1985**, *23*, 2811. (f) For a related 1,4-elimination from a benzylstannane, see: Sano, H.; Oktsuka, H.; Migita, T. *J. Am. Chem. Soc.* **1988**, *110*, 2014.

(20) Preliminary report: Mills, R. J.; Snieckus, V. *J. Org. Chem.* **1983**, *48*, 1565.

(21) According to Disraeli, "protection is not a principle, but an expedient"; see: Haslam, E. *Chem. Ind.* **1981**, 674.

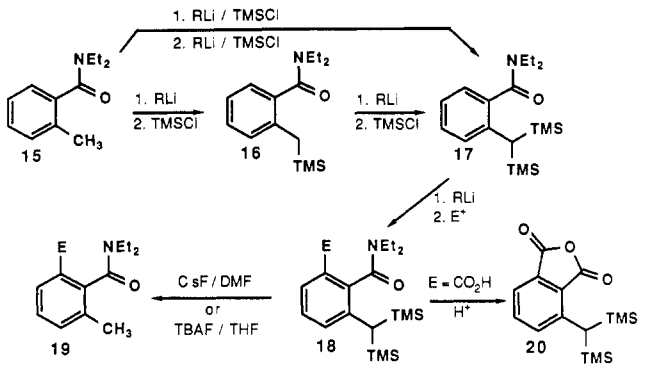
(22) To the best of our knowledge, the concept had been only briefly and unsuccessfully explored in a thiophene system: Slocum, D. W.; Gierer, P. L. *J. Org. Chem.* **1973**, *38*, 4189. Since our preliminary report,[20] it has been applied: Billedeau, R.; Sibi, M. P.; Snieckus, V. *Tetrahedron Lett.* **1983**, 4515. Reed, J. N.; Snieckus, V. *Ibid.* **1983**, 3795. Altintas, N. M.S. Thesis, University of Waterloo, 1984. Doadt, E. G.; Ph.D. Thesis, University of Waterloo, 1988. Ronald, R. C.; Wheeler, C. J. *J. Org. Chem.* **1984**, *49*, 1658. Kang, J.; Lim, K. J.; Kim, W.-J.; Lee, C. H. *Bull. Korean Chem. Soc.* **1984**, *5*, 87. Wood, R. D.; Ganem, B. *Tetrahedron Lett.* **1983**, 4391. Abarca, B.; Gomez, E.; Jones, G.; Mouat, D. J. Royal Society of Chemistry, Heterocyclic Group Meeting, Jan. 6, 1984, London; Abstr. p 15. Carpenter, A. J.; Chadwick, D. J. *Tetrahedron* **1986**, *42*, 2351. Dondoni, A.; Fantin, G.; Fogagnolo, M.; Medici, A.; Pedrini, P. *Synthesis* **1987**, 998 and references therein. Lipshutz, B. H.; Huff, B.; Hagen, W. *Tetrahedron Lett.* **1988**, *29*, 3411.

(23) Mills, R. J.; Snieckus, V. *J. Org. Chem.*, following paper in this issue.

(24) Beak, P.; Brown, R. A. *J. Org. Chem.* **1982**, *47*, 34.

(25) Reed, J. N. Ph.D. Thesis, University of Waterloo, 1985.

Scheme V



to effect metalation ortho to weaker DMGs such as in 2-chloro- and 2-methoxy-6-silylbenzamides were unsuccessful under a variety of alkyllithium conditions.[26]

Exploration of methods for desilylation led to the use of CsF in wet refluxing DMF as the conditions of choice. In this manner, most of the compounds **8b–q** were converted into a diverse series of 1,2,5- and 1,2,4,5-substituted derivatives **9b–q**. Although the overall yields of the transformations **7** → **8** → **9** are high, they might be further enhances by in situ formation of the silyl intermediates **7** and by direct desilylation of the crude compounds **8**.

Illustrative of more complex sequences achievable by the silicon protection concept are the conversions of **7d** and **7e** into the halophthalides **10a** and **10b**, respectively (Scheme III). In these cases, the intermediates were not purified but directly desilylated (under which conditions cyclization occurs) to give products which are not easily accessible by alternate methodology.

Although the mechanism of the electrophilic ipso desilylation is well understood,[3] its synthetic application in complex substituted aromatics has not been sufficiently explored.[6] Based on sparse information,[7b,27,28] arylsilanes bearing electron-donating groups (e.g. OMe) appear to strongly direct non-ipso reactions while electron-withdrawing functions (e.g. CO_2H) tolerate ipso desilylation processes. The high-yield accessibility of the silyl systems **7** and the requirement for *o*-bromobenzamide intermediates,[29,30] prompted a brief study of ipso bromodesilylation reactions (**1**, path b).

Treatment of silyl benzamides **8a** and **8m** (Scheme IV) with bromine in refluxing CCl_4 resulted in smooth ipso reaction to afford the bromo products **12a** and **12b**, respectively, in high yields. The bromination of the dimethoxy derivative **7c** at 0 °C gave the ipso product **12c** (67%) together with minor amounts of 2,6-dibromo and 2-silyl-6-bromo compounds (see the Experimental Section). Finally, similar low-temperature bromination of **13** provided the nonipso result **14**. This limted study shows that ipso bromodesilylations are dominant in the presence of carboxamide, methyl, and chloro functionality. In systems with appropriately located, strongly electron donating groups, normal electrophilic substitution effects are observed (**14**) although ipso reactions may predominate in a situation dictated by relief of steric congestion (**7c**).

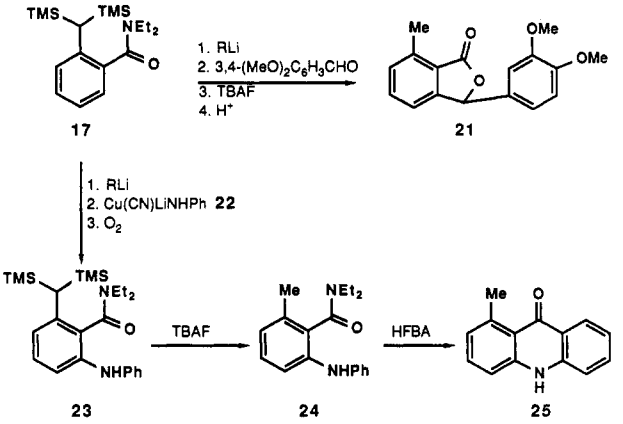
Silicon *o*-Methyl Protection. The observation of Beak and co-workers that 2-isopropylbenzamides undergo

Table II. Synthesis of 6-Substituted 2-Methylbenzamides 19

E^+	compd 18	yield,[a] %	compd 19	yield,[a] %
MeOD	**18a**, D	*b*	**19a**, D	94
MeI	**18b**, Me	91	**19b**, Me	81
DMF	**18c**, CHO	86	**19c**, CHO	78
CO_2	**18d**, CO_2H	*c*	**19d**, CO_2H	*d*
$(MeS)_2$	**18e**, SMe	76	**19e**, SMe	96
TMSCl	**18f**, TMS	86	**19f** (**8a**), TMS	83

[a] See footnote a, Table I. [b] Not isolated. [c] Not isolated but converted directly into the phthalic anhydride **20** by acid treatment (see Experimental Section). [d] Not obtained.

Scheme VI

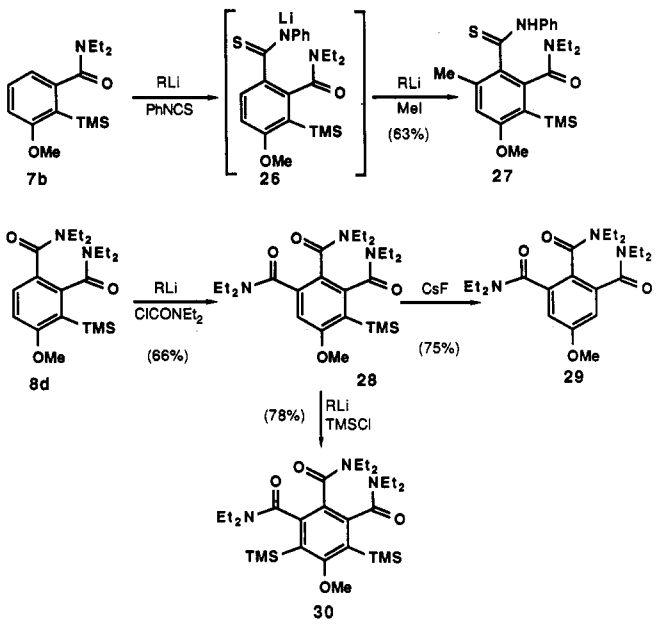


lithiation exclusively at C-6[16] and the well-established precedence for benzylic desilylation[31] prompted experiments on silicon protection of *o*-toluamides. Beak rationalized his results on the basis of a destabilizing steric interaction between the methyl and amide groups in the formation of the benzylic carbanion or the transition state leading to it. Consideration of the relative effective sizes of the two groups (A_{TMS} = 2.5–2.6 vs A_{Me} = 1.74)[32] suggested that an analogous result may be observed using α,α'-disilylated benzamides.

The requisite disilylated benzamide **17** (Scheme V) was prepared in high yield from the *o*-toluamide **15** either via the monosilylated derivative **16** or directly in a one-pot procedure.[33,34] Standard metalation followed by MeOD quench furnished the deuterated derivative **18a** (Table II), which was not isolated but transformed by desilylation into **19a**. The position of deuterium incorporation was evident from the characteristic ABC aromatic proton pattern in the ^1H NMR spectrum. A variety of electrophiles were introduced to give products **18b–f**, and these were desilylated, with one exception (**18d**), to afford the contiguously trisubstituted benzamides **19b–f**.[35] Whereas TBAF in THF was an ineffective desilylating agent for arylsilanes **8**, it was found to be the reagent of choice for the conversion of **18** into **19**. The carboxylated intermediate **18d** was converted under acidic conditions into the phthalic anhydride **20** with retention of bisilyl functionality. The

(26) Mills, R. J. Ph.D. Thesis, University of Waterloo, 1984.
(27) Hashimoto, T. *J. Pharm. Soc. Jpn.* **1960**, *80*, 1399.
(28) Eaborn, C.; Webster, D. E. J. *J. Chem. Soc.* **1960**, 179.
(29) Mills, R. J.; Horvath, R. F.; Sibi, M. P.; Snieckus, V. *Tetrahedron Lett.* **1985**, *26*, 1145.
(30) The general utility of functionalized bromobenzenes in metal–halogen exchange processes is inherent in the Parham reaction: Parham: W. E.; Bradsher, C. K. *Acct. Chem. Res.* **1982**, *15*, 300.
(31) Colvin, E. W. *Chem. Soc. Rev.* **1978**, *7*, 15. Chan, T. H.; Fleming, I. *Synthesis* **1979**, 761.
(32) Kitching, K.; Olszowy, H. A.; Drew, G. M.; Adcock, W. *J. Org. Chem.* **1982**, *47*, 5153. We thank Professor Kitching for a preprint.
(33) The useful in situ trapping procedure devised by Martin may be an alternate method for the preparation of such substances: Krizan, T. D.; Martin, J. C. *J. Am. Chem. Soc.* **1983**, *105*, 6155.
(34) The benzoic acid chlorides corresponding to **16** and **17** have been similarly prepared: Chenard, B. L.; Slapak, C.; Anderson, D. K.; Swenton, J. S. *J. Chem. Soc., Chem. Commun.* **1981**, 179. We thank Professor Swenton for calling our attention to this result.
(35) For related results involving amination of ortho lithiated benzamides, see: Reed, J. N.; Snieckus, V. *Tetrahedron Lett.* **1983**, 3795.

Scheme VII



isolation of **19f** in high yield demonostrates the comparably much more rapid benzylic over aryl desilylation process.

To demonstrate the utility of synthon **17** in somewhat more complex strategies, the synthesis of the *peri*-methylphthalide **21** and acridone **25** derivatives was executed (Scheme VI). The conversion of **17** into **21** was carried out without isolation of intermediates while its transformation into **25** involved intermediates **23** and **24** and followed recent work in our laboratories on *o*-N-arylation of ortho-lithiated benzamides using anilidocyano cuprate reagents (**22**).[36]

Although the synthetic procedure leading to functionalized trisubstituted aromatics **19** is of considerable synthetic value, ascribing the result to simple C-6 metalation[37] is precluded by lack of information concerning kinetic and thermodynamic acidities. The slow formation of a benzylic lithiated species of **17** and its rapid rearrangement to the ortho-lithiated intermediate cannot be ruled out.[16] Attempts to detect both species by allowing the initially *s*-BuLi/TMEDA treated solution of **17** to warm from −78 °C to −40 °C, maintaining it at that temperature (5 h), and quenching with MeOD afforded only the C-6 deuterated product **18a** with no evidence (400-MHz NMR) of benzylic deuteration.

Iterative Metalation. To further enhance the synthetic utility of *o*-silylbenzamides **7**, the concept of iterative metalation using introduced electrophiles which function as DMGs (**3**) was explored in two cases (Scheme VII). In the first sequence, benzamide **7b**, upon standard metalation followed by quench with phenyl isothiocyanate, led to the generation of the lithio thioamide intermediate **26**. In view of the previous demonstration of the DMG capabilities of secondary thioamides,[38] the intermediate was subjected to in situ metalation followed by MeI quench to afford, in one pot, the pentasubstituted benzamide **27**. In the second sequence, the silyl phthalamide **8d** was metalated and quenched with $ClCONEt_2$ to furnish, in good yield, the triamide **28**, which, incidentally, was desilylated to afford compound **29**. To complete a "walk-around-the-ring" sequence by directed metalation, **28** was deprotonated and quenched with excess of TMSCl to give the hexasubstituted benzene **30**. Crystals suitable for single-crystal X-ray structure determination were readily secured in order to examine this highly congested molecule.

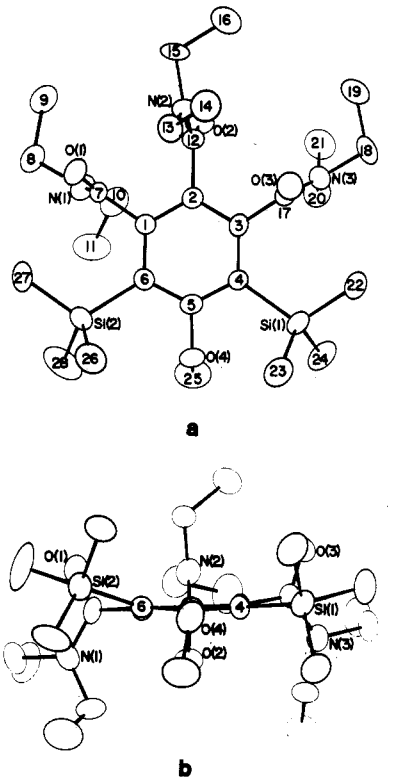


Figure 1. (a) ORTEP plot of **30** viewed from above the plane of the benzene ring. (b) ORTEP plot of **30** viewed from along the axis of the O–C(5) bond.

Figure 1, parts a and b, show ORTEP plots of the final structure in two perspectives. The six ring carbon atoms are not coplanar; two distinct planes exist, C(6), C(1), C(2), C(3), and C(3), C(4), C(5), C(6), showing average deviations from the least-square plane of ±0.001 Å and 0.001 Å, respectively; C(3) and C(5) lie above the plane by +0.009 and +0.020 Å, respectively, while C(4) and C(6) lie below by −0.019 and −0.010 Å, respectively. The extent of the ring puckering is indicated by the substantial dihedral angle of 5.3° between the two planes. The average bond distance between aromatic carbons, 1.399 Å, is typically that in benzene (1.395 Å). Since the three carboxamides are oriented nearly orthogonal to the C(6), C(1), C(2), C(3) plane, no overlap of the π-system with the three substituents is expected. This lack of π-participation is reflected in the rather longer than expected ring to carboxamide substituent C–C bond lengths (1.501–1.531 Å). Similar larger than expected C–C bond lengths linking the benzene rings in hexaphenylbenzene (1.473–1.531 Å) have been reported.[39] The internal benzene ring bond angles also reflect the distortion within the molecule due to the bulk of substituents and the size of the TMS groups at C(4) and C(6) are reflected in the abnormally large internal bond angle of 125.3° at C(5). In hexasubstituted benzenes, the ring substituent atoms often alternate above and below the least-squares plane of the benzene ring.[40] The out-of-plane deviations for the ring substituent atoms in **30** (0.014–0.570

(36) Iwao, M.; Reed, J. N.; Snieckus, V. *J. Am. Chem. Soc.* **1982**, *104*, 5531.

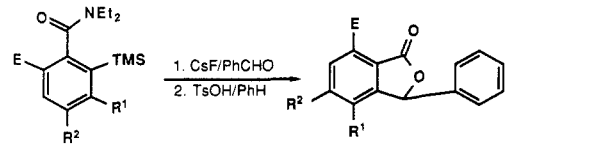
(37) Caution should be exercised in concluding that the site of electrophile incorporation is the site of deprotonation. Bey, A. E.; Weyenberg, D. R. *J. Org. Chem.* **1966**, *31*, 2036.

(38) Fitt, J. J.; Gschwend, H. W. *J. Org. Chem.* **1976**, *41*, 4029.

(39) Bart, J. C. J. *Acta Cryst.* **1968**, *B24*, 1277.

(40) Weissensteiner, W.; Schuster, I. I.; Blout, J. F.; Mislow, K. *J. Am. Chem. Soc.* **1986**, *108*, 6664 and references cited therein.

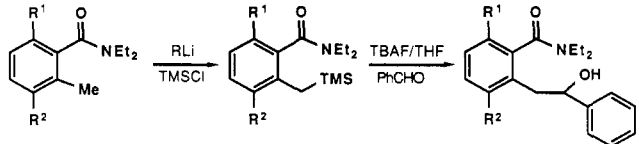
Scheme VIII



7a E = R¹ = R² = H
7c E = H; R¹ = R² = OMe
8m E = Me; R¹ = Cl; R² = H

31a E = R¹ = R² = H (48%)
31b E = H; R¹ = R² = OMe (49%)
31c E = Me; R¹ = Cl; R² = H (45%)

Scheme IX



	R¹	R²				
15	H	H	16	H	H	(84%)
32a	OMe	H	33a	OMe	H	(80%)
32b	H	Cl	33b	H	Cl	(83%)
32c	H	OMe	33c	H	OMe	(68%)

	R¹	R²	
34a	H	H	(79%)
34b	OMe	H	(46%)
34c	H	Cl	(82%)
34d	H	OMe	(82%)

Å), though not alternating, are of a magnitute greater than those reported for most hexasubstituted benzenes with bulky substituents.[40] These out-of-plane deviations undoubtedly also reflect the steric bulk of the substituents. A systematic study of highly substituted benzenes obtained by directed metalation may be of structural interest.

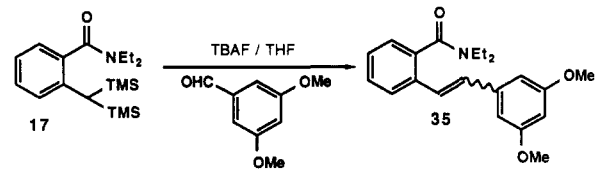
Carbodesilylations of Silylbenzamides. The ready availability of the various silylbenzamides and the reports by Effenberger on fluoride-induced carbodesilylations[9] prompted the exploration of these derivatives in useful C–C bond forming reactions (concepts **1a**, **2**, **4–6**, Scheme I).

The *o*-silylbenzamides **7a**, **7c**, and **8m** were treated with benzaldehyde in refluxing anhydrous DMF in the presence of CsF to give intermediate amide carbinols, which, without purification, were subjected to TsOH cyclization to give the phthalides **31a**, **31b**, and **31c**, respectively (Scheme VIII). Reference to Effenberger's detailed mechanistic studies[9] suggests that the modest yields obtained in these reactions may be due to competitive substituent effects: base-catalyzed carbodesilylation with benzaldehyde of 2-chloro(trimethylsilyl)benzene occurs in DMF at −60 °C whereas that of the corresponding 2-methoxy- and 2-ethoxycarbonyl systems requires 100 °C in HMPT.[9d] Competitive formylation by DMF[9c] was not observed. These reactions proceed under neutral conditions and therefore complement routes based on directed metalation.[41] They may find more general utility for particular situations in which the substituents are sensitive to alkyllithiums, thereby precluding an approach based on the metalation tactic.

Similarly, benzylic carbodesilylation[10] was realized (Scheme IX). Thus treatment of the benzylsilanes **16**, **33a–c**, readily obtained from the *o*-toluamides **15**, **32a–c**, with benzaldehyde in the presence of anhydrous TBAF led smoothly to the carbinols **34a–d**. As in the arylsilane carbodesilylations above, this methodology provides a neutral alternative to the directed metalation approach and should be adaptable to the synthesis of natural and unnatural isocoumarins.[42]

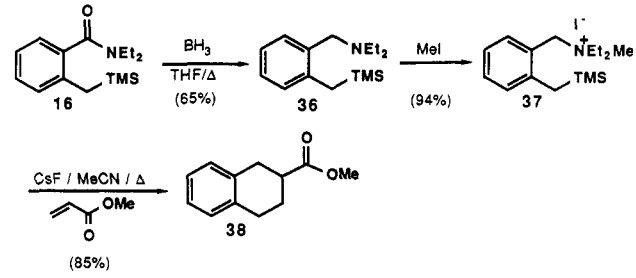
The use of the disilyl-*o*-toluamide **17** as an equivalent of **16** in a Peterson olefination process was also tested (Scheme X). Treatment of **17** with 3,5-dimethoxybenz-

Scheme X



(74%)

Scheme XI



(85%)

aldehyde in the presence of 1 equiv of TBAF gave a good yield of the stilbene **35** as a mixture of cis and trans isomers. This reaction may serve as a prototype and an alternate to the Wittig reaction for the preparation of unusual stilbenes.

The increasing synthetic significance of the Saegusa–Ito procedure for the generation of *o*-quinodimethanes[19] encouraged the establishment of a link between this reaction and the directed metalation methodology. Diborane reduction[43] of the monosilyl-*o*-toluamide **16** (Scheme XI) gave the benzyl amide **36**, which was converted into the quaternary ammonium salt **37**. Treatment of **37** under the Saegusa–Ito conditions gave the tetralin ester **38** in good yield. The application of more difficult to access tetralins appears feasible.[44]

Conclusions

Silicon protection of benzamide ortho sites **7** and *o*-toluamide methyl groups **17** to strongly basic alkyllithiums is a useful tactic for the regiospecific construction of a variety of new polysubstituted aromatics **9** (Table I) and **19** (Table II) with differential oxidation states and is conducive to the development of interesting new strategies (Schemes III, V, and VII). Silicon introduction is achieved under directed metalation control using mild conditions compared to the harsher conditions of Grignard and related procedures.[3] Ipso bromodesilylation leads to the regioselective preparation of valuable[23] bromobenzamides (Scheme IV). Fluoride-induced carbodesilylations of *o*-silylbenzamides and mono- and disilyl-*o*-toluamides provide new mild methodology for carbon chain extension (Schemes VIII–X) which, in contrast to directed metalation, can accommodate base-sensitive substituents and therefore show complementary and perhaps more general utility.

This work considerably expands the potential of the directed ortho metalation reaction in synthetic aromatic chemistry. Ortho metalation or carbodesilylation processes offer complementary and altenative regimens to classical Friedel–Crafts chemistry for aromatic C–C bond forma-

(41) de Silva, S. O.; Watanabe, M.; Snieckus, V. *J. Org. Chem.* **1979**, *44*, 4802.
(42) Watanabe, M.; Sahara, M.; Kubo, M.; Furukawa, S.; Billedeau, R.; Snieckus, V. *J. Org. Chem.* **1984**, *49*, 742.
(43) Sibi, M. P.; Shankaran, K.; Hahn, W. R.; Alo, B. I.; Snieckus, V. *Tetrahedron Lett.* **1987**, *28*, 2933.
(44) Wiseman has reported this annelation method on 2-((trimethylsilyl)methyl)-3-furancarboxamide: Wiseman, J. R.; Gregor, W. E., 188th ACS National Meeting, Philadelphia, PA, Aug 26–31, 1984; ORGN-137. We thank Dr. Wiseman for a long abstract of this paper.

tion. In view of the large number of available DMGs, the broader application of these methods may be anticipated.

Experimental Section

General Methods. Microanalyses were performed by Galbraith Laboratories Inc., Knoxville, TN. Melting points were recorded on a Büchi SMP-20 apparatus and are uncorrected. The temperatures given for Kugelrohr distillations are those of air bath temperatures and not necessarily an accurate measure of the boiling points. IR spectra were recorded on a Perkin-Elmer 983 spectrometer. ^{1}H NMR spectra were recorded on Bruker WH-400, AM-250, and WP-80 instruments in $CDCl_3$ with tetramethylsilane as an internal standard unless otherwise stated. ^{13}C NMR spectra were recorded on Bruker AM-250 and WP-80 instruments in $CDCl_3$ referenced to $CHCl_3$ at 77.11 ppm. Mass spectra (MS) were determined on a high-resolution Varian MAT-CH7 instrument at 70 eV unless stated otherwise. Preparative high-pressure liquid chromatography (HPLC) was performed on a Waters Prep-500 instrument using commercially available prepacked SiO_2 columns. Medium-pressure column chromatography (MPLC) was performed using silica gel 60 (0.04–0.063 and 0.063–0.20 mm) obtained from Brinkman (Canada) with hexane/EtOAc as eluent (1:1 to 9:1) unless otherwise specified.

n-BuLi as a solution in hexanes, *s*-BuLi as a solution in cyclohexane, and *t*-BuLi as a solution in pentane were purchased from Aldrich Chemical Co. Solutions of alkyllithiums were stored under argon in septum-capped bottles and desiccated at 0 °C. The titer of all alkyllithiums was determined prior to use with 2,5-dimethoxybenzyl alcohols[45] as the standard. *N,N,N',N'*-tetramethylethylenediamine (TMEDA) and TMSCl were also purchased from Aldrich Chemical Co. TMEDA was dried and distilled from CaH_2 and stored over 4-Å molecular sieves in septum capped bottle under argon. THF and Et_2O were freshly distilled from sodium-benzophenone ketyl prior to use. All lithiations were performed using syringe–septum cap techniques in oven-dried glassware under an atmosphere of dry high purity argon.

The phrase "workup in the usual manner" refers to treatment of the reaction mixture with saturated aqueous NH_4Cl, extraction with CH_2Cl_2, washing of the combined organic extracts with saturated brine solution, drying of the organic extract over Na_2SO_4, and evaporation to dryness in vacuo to afford the crude product. Subsequent chromatography and/or recrystallization and distillation of the crude material afforded pure products.

Preparation of N,N-Diethylbenzamides. The following benzamides were prepared by standard methods, purified by distillation or recrystallization, and stored in air-tight containers.

***N,N*-Diethylbenzamide**: bp 72 °C (0.05 mm) [lit.[46] bp 150–155 °C (15 mm)].

***N,N*-Diethyl-2-methoxybenzamide**: bp 89–90 °C (0.03 mm) [lit.[47] bp 100–104 °C (1 mm)].

***N,N*-Diethyl-3-methoxybenzamide**: bp 102–104 °C (0.03 mm) (lit.[48] mp 48 °C).

***N,N*-Diethyl-3,4-dimethoxybenzamide**: bp 130–132 °C (0.03 mm).[25]

***N,N*-Diethyl-3-chlorobenzamide**: bp 118–120 °C (0.1 mm) [lit.[49] bp 106–108 °C (0.6 mm)].

***N,N*-Diethyl-3-fluorobenzamide**: bp 80–82 °C (0.03 mm); IR (neat) ν(max) 1636 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.18 (br, 6 H), 3.40 (br, 4 H), 6.97–7.52 (m, 4 H); MS *m/e* 195 (M^+, 17), 194 (21), 123 (100), 95 (30).

Anal. Calcd for $C_{11}H_{14}FNO$: C, 67.67; H, 7.23; N, 7.17. Found: C, 67.50; H, 7.12; N, 7.07.

***N,N*-Diethyl-2-methylbenzamide**: bp 82–83 °C (0.01 mm) [lit.[47] bp 105 °C (1 mm)].

Standard Procedures. A. Lithiation of Benzamides. A solution of the benzamide, dissolved in anhydrous THF (5 mL), was added dropwise to a stirred solution of a 1:1 *s*-BuLi–TMEDA complex in anhydrous THF at −78 °C under argon. After 1 h at −78 °C, the mixture was treated with an excess of the appropriate electrophile. The resulting solution was then allowed to warm to ambient temperature overnight, after which 20 mL of saturated aqueous NH_4Cl was added and the THF removed in vacuo. Workup in the usual manner afforded the crude product.

B. Desilylation of Silylated Benzamides with CsF. The silylated benzamide (10 mmol), dissolved in of DMF (50 mL) containing water (5 mL), was treated with an excess of CsF. The resulting mixture was held at reflux for 1-20 h. After cooling, the mixture was evaporated to dryness in vacuo and the residue was dissolved in anhydrous Et_2O (150 mL). Remaining CsF was removed by filtration and the organic phase washed with saturated NaCl solution, dried over Na_2SO_4 and evaporated to dryness in vacuo to afford the crude product.

C. Desilylation of Silylated Benzamides with TBAF. The silylated benzamide (10 mmol), dissolved in THF (50 mL), was treated with an excess of TBAF (1 M solution in THF). The resulting solution was stirred at room temperature overnight. Removal of the solvent in vacuo followed by workup in the usual manner afforded the crude product.

Preparation of Silylbenzamides 7a–e. *N,N*-Diethyl-2-(trimethylsilyl)benzamide (7a). Standard procedure A was followed. To a solution of *s*-BuLi (14.7 mL, 18.9 mmol of a 1.29 M solution) and TMEDA (2.8 mL, 18.9 mmol) in anhydrous THF (5 mL) at −78 °C under argon was dropwise added a solution of *N,N*-diethylbenzamide (3.072 g, 17.2 mmol) in anhydrous THF (5 mL). The mixture was stirred for 1 h and treated witht TMSCl (6.7 mL, 51.6 mmol), and the resulting solution was allowed to warm to ambient temperature overnight (8 h). Saturated aqueous NH_4Cl (20 mL) was added, the THF was removed in vacuo, and the reaction mixture was processed in the usual manner to afford 3.01 g (70%) of **7a** as a colorless solid: mp 53–54 °C (hexane); IR ($CHCl_3$) ν(max) 1624 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.28 (s, 9 H), 1.18 (m, 6 H), 3.18 (q, J = 7 Hz, 2 H), 3.56 (q, J = 7 Hz, 2 H), 7.11–7.66 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ (rel intensity) −0.2 (100), 12.8 (24), 13.7 (22), 38.9 (24), 43.4 (23), 125.5 (48), 127.7 (48), 128.3 (45), 134.9 (46), 137.5 (17), 142.8 (17), 172.3 (13); ^{29}Si NMR ($CDCl_3$) δ −3.1; MS *m/e* (rel intensity) 249 (M^+, 2) 235 (40), 234 (100), 177 (69), 160 (20).

Anal. Calcd for $C_{14}H_{23}NOSi$: C, 67.42; H, 9.29; N, 5.62. Found: C, 67.71; H, 9.06; N, 5.39.

The following compounds were prepared according to the above general procedure.

***N,N*-Diethyl-3-methoxy-2-(trimethylsilyl)benzamide (7b).** According to procedure A, a mixture of *N,N*-diethyl-3-methoxybenzamide (3.247 15.7 mmol), *s*-BuLi (15.7 mL of a 1.1 M solution, 17.3 mmol), and TMEDA (2.6 mL, 17.3 mmol), was treated with TMSCl (6.1 mL, 47.1 mmol). Workup in the usual manner followed by MPLC afforded 4.12 g (94%) of **7b** as a colorless solid: mp 54–55 °C (hexane); IR ($CHCl_3$) ν(max) 1618 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.25 (s, 9 H), 1.16 (m, 6 H), 3.1–3.8 (m, 4 H), 3.81 (s, 3 H), 6.69–6.86 (m, 2 H), 7.23–7.42 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ (rel intensity) 0.4 (100), 12.6 (44), 13.5 (41), 38.8 (47), 43.2 (45), 54.9 (36), 109.6 (46), 118.7 (46), 124.2 (4), 130.2 (43), 144.5 (8), 164.7 (7), 171.6 (7); MS (30 eV) *m/e* (rel intensity) 279 (M^+, 1), 265 (27), 264 (100).

Anal. Calcd for $C_{15}H_{25}NO_2Si$: C, 64.47; H, 9.02; N, 5.01. Found: C, 64.55; H, 9.31; N, 5.03.

***N,N*-Diethyl-3,4-dimethoxy-2-(trimethylsilyl)benzamide (7c).** According to procedure A, to a mixture of *N,N*-diethyl-3,4-dimethoxybenzamide (10.29 g, 43.4 mmol), *s*-BuLi (36.7 mL of a 1.3 M solution, 47.7 mmol), and TMEDA (7.2 mL, 47.7 mmol) was added TMSCl (16.9 mL, 130.2 mmol). Workup in the usual manner followed by HPLC (hexane/EtOAc, 9:1) afforded 12.7 g (95%) of **7c** as an off-white solid: mp 57–58 °C (hexane); IR ($CDCl_3$) ν(max) 1617 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.28 (s, 9 H), 1.07 (t, J = 7 Hz, 3 H), 1.25 (t, J = 7 Hz, 3 H), 3.21 (q, J = 7 Hz, 2 H), 3.51 (q, J = 7 Hz, 2 H), 3.86 (s, 6 H), 6.88 (s, 2 H); ^{13}C NMR ($CDCl_3$) δ (rel intensity) 1.0 (100), 12.8 (32), 13.8 (33), 39.1 (31), 43.5 (30), 55.6 (30), 60.6 (27), 113.3 (34), 122.2 (39), 130.3 (10), 136.2 (18), 151.7 (13), 171.8 (17); MS *m/e* (rel intensity) 309 (M^+, 2), 295 (22), 294 (100).

Anal. Calcd for $C_{16}H_{27}NO_3Si$: C, 62.09; H, 8.79; N, 4.53. Found: C, 62.28; H, 9.17; N, 4.56.

(45) Winkle, M. R.; Lansinger, J. M.; Ronald, R. C. *J. Chem. Soc., Chem. Commun.* **1980**, 87.
(46) Hauser, C. R.; Walker, H. G. *J. Am. Chem. Soc.* **1969**, *91*, 295.
(47) McCabe, E. T.; Barthel, W. F.; Gertler, S. I.; Hall, S. A. *J. Org. Chem.* **1954**, *19*, 493.
(48) Grammaticakis, P. *Bull. Soc. Chim. Fr.* **1964**, 924.
(49) Johnson, H. L.; Skinner, W. A.; Skidmore, D.; Mailbach, H. I. *J. Med. Chem.* **1968**, *11*, 1265.

N,N-Diethyl-3-chloro-2-(trimethylsilyl)benzamide (7d). According to procedure A, to a mixture of *N,N*-diethyl-3-chlorobenzamide (5.715 g, 27 mol), *s*-BuLi (20.4 mL of a 1.5 M solution, 29.7 mmol), and TMEDA (4.5 mL, 29.7 mmol) was added TMSCl (8.6 mL, 66 mmol). Workup in the usual manner followed by MPLC afforded 5.29 g (67%) of **7d** as a colorless crystalline solid: bp 39–40 °C (CH_2Cl_2–hexane); IR ($CHCl_3$) ν(max) 1624 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.38 (s, 9 H), 1.07 (t, J = 7 Hz, 3 H), 1.25 (t, J = 7 Hz, 3 H), 3.06–3.57 (m, 4 H), 6.96–7.33 (m, 3 H); ^{13}C NMR ($CDCl_3$) δ (rel intensity) 0.8 (100), 12.6 (26), 13.4 (27), 38.9 (24), 43.3 (33), 124.2 (28), 129.4 (25), 129.7 (25), 134.7 (8), 141.8 (19), 145.1 (10), 170.5 (12); MS m/e (rel intensity) 284 (2), 283 (M^+, 1) 282 (3), 270 (36), 269 (20), 268 (100).

Anal. Calcd for $C_{14}H_{22}ClNOSi$: C, 59.24; H, 7.81; N, 4.93. Found: C, 59.01; H, 7.60; N, 5.00.

N,N-Diethyl-3-fluoro-2-(trimethylsilyl)benzamide (7e). According to procedure A, to a mixture of *N,N*-diethyl-3-fluorobenzamide (4.019 g, 20.6 mmol), *s*-BuLi (18.9 mL of a 1.2 M solution, 22.7 mmol), and TMEDA (3.4 mL, 22.7 mmol) was added TSMCl (6.5 mL, 51.5 mmol). Workup in the usual manner followed by short-path distillation afforded 4.833 g (88%) of **7e** as a colorless oil: bp 89–91 °C (0.05 mm); IR (neat) ν(max) 1638 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.30 (d, J = 2 Hz, 9 H), 1.09 (t, J = 7 Hz, 3 H), 1.27 (t, J = 7 Hz, 3 H), 3.20 (q, J = 7 Hz, 2 H), 3.62 (q, J = 7 Hz, 2 H), 6.85–7.42 (m, 3 H); ^{13}C NMR ($CDCl_3$) δ (rel intensity) 0.2 (100), 12.8 (64), 13.7 (66), 39.1 (68), 43.4 (67), 114.7 (33), 115.1 (28), 121.9 (49), 130.8 (34), 130.9 (30), 144.6 (6), 144.7 (5), 165.8 (6), 169.7 (8), 170.7 (6); MS m/e (rel intensity) 267 (M^+, 1), 253 (55), 252 (100), 195 (35).

Anal. Calcd for $C_{14}H_{22}FNOSi$: C, 62.88; H, 8.29; N, 5.24. Found: C, 62.64; H, 8.19; N, 5.24.

Preparation of Benzamides 8a–q. N,N-Diethyl-2-methyl-6-(trimethylsilyl)benzamide (8a). According to procedure A, to a solution of benzamide **7a** (1.098 g, 4.4 mmol), *s*-BuLi (4.4 mL of a 1.1 M solution, 4.8 mmol), and TMEDA (0.7 mL, 4.8 mmol) was added MeI (2.64 mL, 44 mmol). Workup in the usual manner followed by MPLC and short-path distillation afforded 1.05 g (91%) of **8a** as a colorless oil: bp 125 °C (0.05 mm); IR (neat) ν(max) 1632 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.26 (s, 9 H), 1.03 (t, J = 7 Hz, 3 H), 1.29 (t, J = 7 Hz, 3 H), 2.19 (s, 3 H), 2.97–4.01 (m, 4 H), 7.16–7.47 (m, 3 H); ^{13}C NMR ($CDCl_3$) δ (rel intensity) –0.1 (100), 12.5 (44), 13.2 (43), 18.9 (31), 38.4 (43), 42.8 (41), 127.3 (43), 130.5 (43), 132.2 (46), 132.6 (19), 136.1 (13), 141.9 (11), 170.9 (10); MS m/s (rel intensity) 263 (M^+, 6), 248 (100), 191 (87), 135 (31).

Anal. Calcd for $C_{15}H_{25}NOSi$: C, 68.38; H, 9.57; N, 5.32. Found: C, 68.09; H, 9.90; N, 5.21.

N,N-Diethyl-3-methoxy-6-methyl-2-(trimethylsilyl)benzamide (8b). According to procedure A, to a mixture of benzamide **7b** (910 mg, 3.3 mmol), *s*-BuLi (3.2 mL of a 1.2 M solution, 3.6 mmol), and TMEDA (0.5 mL, 3.6 mmol) was added MeI (0.4 mL, 6.6 mmol). Workup in the usual manner followed by MPLC afforded 700 mg (74%) of **8b** as a colorless solid: mp 68–68.5 °C (hexane); IR ($CHCl_3$) ν(max) 1619 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.24 (s, 9 H), 1.04 (t, J = 7 Hz, 3 H), 1.26 (t, J = 7 Hz, 3 H), 2.16 (s, 3 H), 2.98–4.16 (m, 4 H), 3.78 (s, 3 H), 6.72 (d, J = 8 Hz, 1 H, C_4-H), 7.14 (d, J = 8 Hz, 1 H, C_5-H); MS m/e (rel intensity) 293 (M^+, 7), 279 (21), 278 (100), 221 (20).

Anal. Calcd for $C_{16}H_{27}NO_2Si$: C, 65.48; H, 9.27; N, 4.77. Found: C, 65.72; H, 9.12; N, 4.76.

N,N-Diethyl-6-formyl-3-methoxy-2-(trimethylsilyl)benzamide (8c). According to procedure A, a solution of benzamide **7b** (660 mg, 2.4 mmol), *s*-BuLi (2 mL of a 1.3 M solution, 2.6 mmol), and TMEDA (0.4 mL, 2.6 mmol) was added DMF (1 mL, 12 mmol). Workup in the usual manner followed by MPLC afforded 726 mg (88%) of **8c** as a colorless solid: mp 87–87.5 °C (Et_2O); IR ($CHCl_3$) ν(max) 1677, 1630 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.28 (s, 9 H), 1.02 (t, J = 7 Hz, 3 H), 1.32 (t, J = 7 Hz, 3 H), 2.98–3.80 (m, 4 H), 3.90 (s, 3 H), 6.93 (d, J = 9 Hz, 1 H, C_4-H), 7.99 (d, J = 9 Hz, 1 H, C_5-H), 9.90 (s, 1 H, CHO); ^{13}C NMR ($CDCl_3$) δ (rel intensity) 0.3 (100), 12.5 (43), 13.3 (43), 39.3 (39), 43.3 (43), 55.3 (40), 109.7 (41), 125.1 (17), 125.9 (28), 132.6 (45), 147.3 (21), 168.2 (25), 168.9 (27), 189.5 (45); MS m/e (rel intensity) 307 (M^+, 5), 293 (22), 292 (100), 278 (52), 262 (58), 235 (46), 234 (25), 221 (20), 72 (56).

Anal. Calcd for $C_{16}H_{25}NO_3Si$: C, 62.50; H, 8.20; N, 4.56. Found: C, 62.88; H, 8.53; N, 4.55.

N,N-Diethyl-2-(diethylcarbamoyl)-4-methoxy-3-(trimethylsilyl)benzamide (8d). According to procedure A, to a solution of benzamide **7b** (1.75 g, 6.3 mmol), *s*-BuLi (6.3 mL of a 1.1 M solution, 6.9 mmol), and TMEDA (1 mL, 6.9 mmol) was added *N,N*-diethylcarbamoyl chloride (2.3 mL, 19 mmol). Workup in the usual manner followed by MPLC afforded 2.12 g (89%) of **8d** as a fine colorless powder: mp 76–76.5 °C (hexane); IR ($CHCl_3$) ν(max) 1628 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.26 (s, 9 H), 0.93–1.26 (m, 12 H), 2.91–3.74 (m, 8 H), 3.83 (s, 3 H), 6.81 (d, J = 8 Hz, 1 H, C_5-H), 7.22 (d, J = 8 Hz, 1 H, C_6-H); ^{13}C NMR ($CDCl_3$) δ (rel intensity) 0.6 (100), 12.5 (38), 12.9 (23), 13.1 (44), 13.9 (23), 38.7 (48), 39.1 (23), 43.4 (24), 43.6 (49), 55.2 (41), 109.2 (43), 124.6 (6), 127.7 (13), 128.5 (45), 140.7 (7), 164.6 (12), 169.1 (7), 170.0 (7); MS m/e (rel intensity) 378 (M^+, 5), 363 (38), 307 (21), 306 (87), 305 (100), 264 (70), 262 (43), 234 (23), 232 (64), 72 (100).

Anal. Calcd for $C_{20}H_{34}N_2O_3Si$: C, 63.45; H, 9.05; N, 7.40. Found: C, 63.72; H, 8.98; N, 7.42.

N,N-Diethyl-6-(phenylthiocarbamoyl)-3-methoxy-2-(trimethylsilyl)benzamide (8e). According to procedure A, to a solution of benzamide **7b** (1.0 g, 3.6 mmol), *s*-BuLi (3.6 mL of a 1.1 M solution, 3.6 mmol), and TMEDA (0.6 mL, 4 mmol) was added phenyl isothiocyanate (0.5 mL, 4.3 mmol). Workup in the usual manner followed by MPLC afforded 1.32 g (89%) of **8e** as yellow needles: mp 144–145 °C (Et_2O–hexane); IR ($CHCl_3$) ν(max) 3334, 1609 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.04 (s, 9 H), 0.98 (m, 6 H), 2.86–3.30 (m, 4 H), 3.86 (s, 3 H), 6.90 (d, AB, J = 8 Hz, 1 H, C_4-H), 7.19–7.46 (m, 3 H), 7.90–8.08 (m, 3 H), 9.85 (br, 1 H, exchanged with D_2O); MS m/e (rel intensity) 414 (M^+, 11), 381 (34), 342 (22), 341 (28), 328 (20), 327 (63), 326 (75), 223 (22), 72 (100).

Anal. Calcd for $C_{22}H_{30}N_2O_2SSi$: C, 63.73; H, 7.29; N, 6.76. Found: C, 63.80; H, 7.44; N, 6.74.

N,N-Diethyl-2,6-bis(trimethylsilyl)-3-methoxybenzamide (8f). According to procedure A, to a solution of benzamide **7b** (1.02 g, 3.6 mmol), *s*-BuLi (3.6 mL of a 1.1 M solution, 4 mmol), and TMEDA (0.6 mL, 4 mmol) was added TMSCl (1.4 mL, 10.8 mmol). Workup in the usual manner followed by MPLC afforded 1.14 g (89%) of **8f** as a colorless solid: mp 74–75 °C (hexane); IR ($CHCl_3$) ν(max) 1615 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.24 (s, 9 H), 0.26 (s, 9 H, $SiMe_3$), 1.0 (t, J = 7 Hz, 3 H), 1.26 (t, J = 7 Hz, 3 H), 3.1 (q, J = 7 Hz, 2 H), 3.3–4.2 (m, 2 H), 3.81 (s, 3 H), 6.81 (d, J = 8 Hz, 1 H, C_4-H), 7.57 (d, J = 8 Hz, 1 H, C_5-H); ^{13}C NMR ($CDCl_3$) δ (rel intensity) 0.8 (99), 1.2 (100), 12.8 (40), 13.2 (35), 38.6 (35), 43.0 (34), 55.0 (31), 108.9 (35), 124.1 (10), 127.6 (14), 138.1 (35), 149.5 (13), 165.3 (17), 171.6 (13); MS (30 eV) m/e (rel intensity) 351 (M^+, 1), 337 (28), 336 (100), 278 (43).

Anal. Calcd for $C_{18}H_{33}NO_2Si_2$: C, 61.48; H, 9.46; N, 3.98. Found: C, 61.45; H, 9.66; N, 3.83.

N,N-Diethyl-3-methoxy-6-(methylthio)-2-(trimethylsilyl)benzamide (8g). According to procedure A, to a solution of benzamide **7b** (2.20 g, 7.9 mmol), *s*-BuLi (6.7 mL of a 1.3 M solution, 8.7 mmol), and TMEDA (1.3 mL, 8.7 mmol) was added dimethyldisulfide (0.9 mL, 1.3 mmol). Workup in the usual manner followed by MPLC afforded 2.28 g (89%) of **8g** as colorless solid: mp 79–80.5 °C (hexane); IR ($CHCl_3$) ν(max) 1624 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.25 (s, 9 H), 1.07 (t, J = 7 Hz, 3 H), 1.29 (t, J = 7 Hz, 3 H), 2.40 (s, 3 H), 3.03–3.22 (m, 3 H), 3.80 (s, 3 H), 3.86–3.97 (m, 1 H), 6.79 (d, J = 8.5 Hz, 1 H, C_4-H), 7.41 (d, J = 8.5 Hz, 1 H, C_5-H); ^{13}C NMR ($CDCl_3$) (rel intensity) δ 0.4 (100), 12.1 (39), 13.2 (37), 19.1 (36), 38.6 (37), 42.8 (36), 55.2 (34), 110.3 (37), 125.1 (13), 125.4 (12), 134.1 (36), 146.2 (11), 163.9 (14), 168.9 (16); MS m/e (rel intensity) 325 (M^+, 25), 311 (22), 310 (100), 264 (35), 253 (20).

Anal. Calcd for $C_{16}H_{27}NO_2SSi$: C, 59.03; H, 8.36; N, 4.30. Found: C, 59.30; H, 8.40; N, 4.34.

N,N-Diethyl-6-iodo-3-methoxy-2-(trimethylsilyl)benzamide (8h). According to procedure A, to a solution of benzamide **7b** (2.09 g, 7.5 mmol), *s*-BuLi (5.8 mL of a 1.4 M solution, 8.3 mmol), and TMEDA (1.2 mL, 8.3 mmol) was added a solution of resublimed iodine (2.3 g, 9 mmol) in THF (5 mL). Workup in the usual manner followed by MPLC afforded 2.61 g (86%) of **8h** as a colorless solid: mp 100–101 °C (hexane); IR ($CHCl_3$) ν(max) 1625 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.24 (s, 9 H), 1.12 (t, J = 7 Hz, 3 H), 1.31 (t, J = 7 Hz, 3 H), 3.04–3.32 (m, 3 H), 3.78–3.91

(m, 1 H), 3.79 (s, 3 H), 6.56 (d, J = 9 Hz, 1 H, C_4-H), 7.74 (d, J = 9 Hz, 1 H, C_5-H); ^{13}C NMR ($CDCl_3$) δ (rel intensity) 0.4 (100), 12.0 (37), 13.1 (38), 38.8 (35), 42.9 (37), 55.2 (33), 84.2 (15), 111.7 (37), 127.2 (11), 140.9 (35), 147.3 (12), 164.5 (16), 169.8 (15); MS m/e (rel intensity) 405 (M^+, 7), 391 (21), 390 (100), 234 (44).

Anal. Calcd for $C_{15}H_{24}INO_2Si$: C, 44.45; H, 5.97; N, 3.46. Found: C, 44.79; H, 6.00; N, 3.57.

N,N-Diethyl-6-deuterio-3,4-dimethoxy-2-(trimethylsilyl)benzamide (8i). According to procedure A, to a solution of benzamide **7c** (1.6 g, 5.2 mmol), s-BuLi (4.1 mL of a 1.2 M solution, 5.7 mmol), and TMEDA (0.8 mL, 5.7 mmol) was added MeOD (2.1 mL, 52 mmol). Workup in the usual manner followed by MPLC afforded 1.31 g (79%) of **8i** (98% d_1 by MS) as colorless crystals: mp 59–60 °C (hexane); IR ($CHCl_3$) ν(max) 1617 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.28 (s, 9 H), 1.07 (t, J = 7 Hz, 3 H), 1.25 (t, J = 7 Hz, 3 H), 3.22 (q, J = 7 Hz, 2 H), 3.52 (q, J = 7 Hz, 2 H), 3.86 (s, 6 H), 6.89 (s, 1 H, C_5-H); ^{13}C NMR ($CDCl_3$) δ (rel intensity) 1.0 (100), 12.8 (37), 13.8 (36), 39.1 (38), 43.5 (37), 55.6 (36), 60.6 (34), 113.2 (42), 130.3 (13), 136.1 (15), 151.8 (17), 154.6 (13), 171.8 (17); MS m/e (rel intensity) 310 (M^+, 2), 296 (27), 295 (100).

N,N-Diethyl-3,4-dimethoxy-6-methyl-2-(trimethylsilyl)benzamide (8j). According to procedure A, to a solution of benzamide **7c** (6.62 g, 21.4 mmol), s-BuLi (18.0 mL of a 1.3 M solution, 23.5 mmol), and TMEDA (3.5 mL, 23.5 mmol) was added MeI (6.6 mL, 107 mmol). Workup in the usual manner followed by MPLC afforded 6.64 g (96%) of **8j**. Purification by recrystallization yielded 6.23 g (90%) of **8j** as colorless crystals: mp 86–87 °C (Et_2O–hexane); IR ($CHCl_3$) ν(max) 1616 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.25 (s, 9 H), 1.02 (t, J = 7 Hz, 3 H), 1.24 (t, J = 7 Hz, 3 H), 2.18 (s, 3 H), 2.86–3.3 (m, 4 H), 3.82 (s, 6 H), 6.73 (s, 1 H, C_5-H); ^{13}C NMR ($CDCl_3$) δ (rel intensity) 1.1 (100), 12.7 (38), 13.5 (39), 19.0 (30), 38.9 (42), 42.9 (41), 55.6 (38), 60.6 (31), 116.0 (37), 129.3 (23), 134.7 (17), 151.0 (18), 152.5 (13), 170.7 (16); MS m/e (rel intensity) 323 (M^+, 14), 309 (22), 308 (100), 251 (39).

Anal. Calcd for $C_{17}H_{29}NO_3Si$: C, 63.12; H, 9.04; N, 4.33. Found: C, 63.04; H, 8.86; N, 4.35.

N,N-Diethyl-3,4-dimethoxy-6-formyl-2-(trimethylsilyl)benzamide (8k). According to procedure A, to a solution of benzamide **7c** (2.57 g, 8.9 mmol), s-BuLi (7.8 mL of a 1.3 M solution, 9.8 mmol), and TMEDA (1.5 mL, 9.8 mmol) was added DMF (3.4 mL, 44.5 mmol). Workup in the usual manner followed by MPLC afforded 1.63 g (56%) of **8k** as colorless crystals: mp 98–99 °C (Et_2O–hexane); IR ($CHCl_3$) ν(max) 1680, 1624 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.29 (s, 9 H), 1.02 (t, J = 7 Hz, 3 H), 1.30 (t, J = 7 Hz, 3 H), 2.99–3.24 (m, 4 H), 3.92 (s, 3 H), 3.96 (s, 3 H), 7.53 (s, 1 H, C_5-H), 9.92 (s, 1H, CHO); ^{13}C NMR ($CDCl_3$) δ (rel intensity) 0.8 (100), 12.8 (40), 13.5 (39), 39.7 (36), 43.8 (40), 55.6 (37), 60.8 (32), 112.0 (41), 128.4 (23), 130.3 (15), 140.3 (20), 151.5 (21), 159.4 (13), 168.3 (22), 189.8 (35); MS m/e (rel intensity) 337 (M^+, 4), 323 (23), 322 (100), 308 (51), 294 (46), 292 (60), 265 (64), 236 (35).

Anal. Calcd for $C_{17}H_{27}NO_4Si$: C, 60.50; H, 8.06; N, 4.15. Found: C, 60.75; H, 8.40; N, 4.11.

N,N-Diethyl-3-chloro-6-deuterio-2-(trimethylsilyl)benzamide (8l). According to procedure A, to a solution of benzamide **7d** (2.18 g, 7.7 mmol), s-BuLi (7.0 mL of a 1.3 M solution, 8.5 mmol), and TMEDA (1.3 mL, 8.5 mmol) was added MeOD (1.6 mL, 38.5 mmol). Workup in the usual manner followed by MPLC afforded 1.94 g (89%) of **8l** (99% d_1 by MS) as a colorless solid: mp 60–61 °C (hexane); IR ($CHCl_3$) ν(max) 1624 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.39 (s, 9 H), 1.08 (t, J = 7 Hz, 3 H), 1.26 (t, J = 7 Hz, 3 H), 3.06–3.57 (m, 4 H), 7.27–7.31 (br, 2 H); ^{13}C NMR ($CDCl_3$) δ (rel intensity) 0.9 (100), 12.7 (36), 13.5 (35), 39.1 (40), 43.5 (35), 129.7 (53), 134.9 (10), 142.1 (13), 145.2 (14), 170.7 (14); MS m/e (rel intensity) 284 (M^+, 1), 271 (35), 269 (100).

N,N-Diethyl-3-chloro-6-methyl-2-(trimethylsilyl)benzamide (8m). According to procedure A, to a solution of benzamide **7d** (5.69 g, 20.6 mmol), s-BuLi (17.4 mL of a 1.3 M solution, 22.7 mmol), and TMEDA (2.4 mL, 22.7 mmol) was added MeI (6.2 mL, 103 mmol). Workup in the usual manner followed by short-path distillation afforded 5.31 g (89%) of **8m** as a colorless oil: bp 116–118 °C (0.02 mm); IR (neat) ν(max) 1633 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.38 (s, 9 H), 1.05 (t, J = 7 Hz, 3 H), 1.27 (t, J = 7 Hz, 3 H), 2.20 (s, 3 H), 2.96–3.27 (m, 3 H), 3.94–4.02 (m, 1 H), 7.14–7.29 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ (rel intensity) 1.1 (100), 12.3 (35), 13.1 (34), 18.6 (27), 38.7 (30), 42.7 (31), 129.3 (33), 131.7 (25), 132.1 (39), 133.7 (12), 139.1 (16), 143.9 (13), 169.5 (16); MS m/e (rel intensity) 298 (M^+, 2), 284 (48), 283 (27), 282 (100), 225 (51).

Anal. Calcd for $C_{15}H_{24}ClNOSi$: C, 60.48; H, 8.12; N, 4.70. Found: C, 60.25; H, 8.30; N, 4.51.

N,N-Diethyl-3-chloro-6-formyl-2-(trimethylsilyl)benzamide (8n). According to procedure A, to a solution of benzamide **7d** (2.34 g, 8.2 mmol), s-BuLi (7.3 mL of a 1.3 M solution, 9.0 mmol), and TMEDA (1.4 mL, 9.0 mmol) was added DMF (3.2 mL, 41 mmol). Workup in the usual manner followed by MPLC afforded 1.95 g (76%) of **8n** as a colorless solid: mp 81–82 °C (hexane); IR ($CHCl_3$) ν(max) 1691, 1630 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.43 (s, 9 H), 1.03 (t, J = 7 Hz, 3 H), 1.32 (t, J = 7 Hz, 3 H), 2.99–3.43 (m, 3 H), 3.74–3.92 (m, 1 H), 7.48 (d, J = 8 Hz, 1 H, C_4-H), 7.89 (dd, J = 8 Hz, 1 H, C_5-H), 9.98 (s, 1 H, CHO); MS m/s (rel intensity) 311 (M^+, 2), 298 (37), 297 (20), 296 (100), 284 (35), 282 (98), 268 (56), 266 (60).

Anal. Calcd for $C_{15}H_{22}ClNO_2Si$: C, 57.77; H, 7.11; N, 4.49. Found: C, 57.90; H, 7.47; N, 4.39.

N,N-Diethyl-3-fluoro-6-methyl-2-(trimethylsilyl)benzamide (8p). According to procedure A, to a solution of benzamide **7e** (2.74 g, 10.2 mmol), s-BuLi (9.0 mL of a 1.3 M solution, 11.2 mmol), and TMEDA (1.7 mL, 11.2 mmol) was added MeI (3.2 mL, 51 mmol). The crude product (homogeneous by TLC) was passed through a short column of silica followed by short-path distillation to afford 2.29 g (80%) of **8p** as a colorless viscous oil: bp 102–104 °C (0.05 mm); IR (neat) ν(max) 1632 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.30 (d, 9 H), 1.05 (t, J = 7 Hz, 3 H), 1.27 (t, J = 7 Hz, 3 H), 2.20 (s, 3 H), 3.07–3.98 (m, 4 H), 7.07–7.27 (m, 2 H); MS m/e (rel intensity) 281 (M^+, 3), 267 (29), 266 (100), 252 (20), 209 (42).

Anal. Calcd for $C_{15}H_{24}FNOSi$: C, 64.01; H, 8.60; N, 4.98. Found: C, 63.92; H, 8.54; N, 5.02.

N,N-Diethyl-3-fluoro-6-formyl-2-(trimethylsilyl)benzamide (8q). According to procedure A, to a solution of benzamide **7e** (1.76 g, 6.6 mmol), s-BuLi (5.8 mL of a 1.3 M solution, 7.3 mmol), and TMEDA (1.1 mL, 7.3 mmol) was added DMF (2.5 mL, 33 mmol). Workup in the usual manner followed by short-path distillation afforded 1.12 g (58%) of **8q** as a colorless viscous oil: bp 116–120 °C (0.05 mm); IR (neat) ν(max) 1700, 1635 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.34 (d, 9 H), 1.03 (t, J = 7 Hz, 3 H), 1.33 (t, J = 7 Hz, 3 H), 2.98–3.97 (m, 4 H), 7.12 (t, J = 8.5 Hz, 1 H, C_4-H), 7.99 (dd, J = 8.5, 6 Hz, 1 H, C_5-H), 9.97 (s, 1 H, CHO); MS m/e (rel intensity) 295 (M^+, 2), 281 (20), 280 (100), 266 (89), 252 (56), 250 (53), 224 (21), 223 (60), 222 (26), 209 (24), 194 (23), 151 (25), 79 (20), 77 (40).

Anal. Calcd for $C_{15}H_{22}FNO_2Si$: C, 60.98; H, 7.51; N, 4.74. Found: C, 61.26; H, 7.81; N, 4.58.

N,N-Diethyl-2-methoxy-6-(trimethylsilyl)benzamide (13). According to procedure A, to a solution of N,N-diethyl-2-methoxybenzamide (5.00 g, 24.1 mmol), s-BuLi (26.6 mL of a 1 M solution, 26.6 mmol), and TMEDA (4.0 mL, 26.6 mmol) was added TMSCl (9.4 mL, 72.3 mmol). Workup in the usual manner followed by MPLC gave 5.16 g (80%) of **13**: mp 50–51 °C (Et_2O–hexane); IR ($CHCl_3$) ν(max) 1625 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.26 (s, 9 H), 1.04 (t, J = 7.2 Hz, 3 H), 1.26 (t, J = 7.2 Hz, 3 H), 3.13 (m, 2 H, ABX), 3.57 (m, 2 H, ABX), 3.78 (s, 3 H), 6.90 (dd, J = 7.5, 1.7 Hz, 1 H), 7.16 (dd, J = 7.5, 1.7 Hz, 1 H), 7.31 (dd, J = 7.5 Hz, 1 H); MS m/e (rel intensity) 279 (M^+, 5), 265 (21), 264 (100), 207 (77).

Anal. Calcd for $C_{15}H_{25}NO_2Si$: C, 64.47; H, 9.02; N, 5.01. Found: C, 64.32; H, 8.97; N, 4.95.

Preparation of Desilylated Benzamides 9a–q. N,N-Diethyl-3-methoxy-6-methylbenzamide (9b). According to procedure B, benzamide **8b** (527 mg, 1.8 mmol) was treated with an excess of CsF for 12 h. Workup in the usual manner followed by MPLC afforded 338 mg (85%) of **9b** as a colorless oil: bp 76–80 °C (0.01 mm); IR (neat) ν(max) 1620 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.04 (t, J = 7 Hz, 3 H), 1.25 (t, J = 7 Hz, 3 H), 2.20 (s, 3 H), 3.14 (q, J = 7 Hz, 2 H), 3.6 (br, 2 H), 3.78 (s, 3 H), 6.69–7.16 (m, 3 H); MS m/e (rel intensity) 221 (M^+, 37), 220 (26), 206 (23), 149 (100), 148 (23), 121 (39).

Anal. Calcd for $C_{13}H_{19}NO_2$: C, 70.56; H, 8.65; N, 6.33. Found: C, 70.77; H, 9.01; N, 6.27.

N,N-Diethyl-2-formyl-5-methoxybenzamide (9c). According to procedure B, benzamide **8c** (450 mg, 1.5 mmol) was

treated with an excess of CsF for 15 h. Workup in the usual manner followed by MPLC afforded 260 mg (76%) of **9c** as a colorless oil: bp 98–104 °C (0.01 mm); IR (neat) ν(max) 1680, 1620 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.05 (t, J = 7 Hz, 3 H), 1.31 (t, J = 7 Hz, 3 H), 3.13 (q, J = 7 Hz, 2 H), 3.61 (q, J = 7 Hz, 2 H), 3.89 (s, 3 H), 6.82 (d, J = 2.3 Hz, 1 H, C_6-H), 7.00 (dd, J = 8.6, 2.3 Hz, 1 H, C_4-H), 7.90 (d, J = 8.6 Hz, 1 H, C_3-H), 9.91 (s, 1 H, CHO); ^{13}C NMR ($CDCl_3$) δ (rel intensity) 12.6 (86), 13.9 (82), 39.1 (78), 42.8 (87), 55.7 (76), 112.1 (92), 114.4 (91), 125.8 (39), 132.2 (100), 141.8 (34), 164.0 (41), 168.2 (33), 188.8 (83); MS m/e (rel intensity) 235 (M^+, 5), 207 (46), 206 (100), 163 (100), 136 (29), 135 (100), 107 (21), 77 (21), 72 (26); HRMS calcd for $C_{13}H_{17}NO_3$ 235.1209, found 235.1210.

***N,N*-Diethyl-2-(diethylcarbamoyl)-4-methoxybenzamide (9d).** According to procedure B, benzamide **8d** (1.25 g, 3.3 mmol) was treated with an excess of CsF for 12 h. Workup in the usual manner followed by MPLC afforded 740 mg (73%) of **9d** as a colorless oil: bp 106–110 °C (0.01 mm); IR (neat) ν(max) 1640, 1636 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.94–1.12 (m, 6 H), 1.14–1.22 (m, 6 H), 3.23–3.28 (m, 4 H), 3.45–3.50 (br, 4 H), 3.83 (s, 3 H), 6.79 (d, J = 2.6 Hz, 1 H, C_3-H), 6.89 (dd, J = 8.5, 2.6 Hz, 1 H, C_5-H), 7.20 (d, J = 8.5 Hz, 1 H, C_6-H); ^{13}C NMR ($CDCl_3$) δ (rel intensity) 12.5 (76), 13.8 (82), 38.9 (77), 43.4 (78), 55.2 (88), 111.4 (98), 113.6 (100), 127.4 (95), 136.6 (25), 159.2 (24), 169.1 (17), 169.4 (19); MS m/e (rel intensity) 306 (M^+, 26), 305 (21), 235 (24), 234 (100), 206 (54), 160 (38), 135 (29), 72 (98).

Anal. Calcd for $C_{17}H_{26}N_2O_3$: C, 66.64; H, 8.55; N, 9.14. Found: C, 66.46; H, 8.36; N, 9.31.

***N,N*-Diethyl-5-methoxy-2-(methylthio)benzamide (9g).** According to procedure B, benzamide **8g** (1.36 g, 4.2 mmol) was treated with an excess of CsF for 8 h. Workup in the usual manner followed by MPLC afforded 812 mg (82%) of **9g** as a colorless oil: bp 112–115 °C (0.05 mm); IR (neat) ν(max) 1624 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.06 (t, J = 7 Hz, 3 H), 1.28 (t, J = 7 Hz, 3 H), 2.42 (s, 3 H), 3.14 (q, J = 7 Hz, 2 H), 3.59 (q, J = 7 Hz, 2 H), 6.73–6.94 (m, 2 H, C_4-H and C_6-H), 7.35 (d, J = 8.6 Hz, 1 H, C_3-H); ^{13}C NMR ($CDCl_3$) δ (rel intensity) 12.3 (79), 13.7 (88), 18.4 (58), 38.5 (86), 42.5 (85), 55.2 (100), 111.5 (87), 114.8 (91), 124.3 (21), 132.2 (76), 140.5 (19), 158.3 (29), 168.7 (16); MS m/e (rel intensity) 253 (M^+, 52), 252 (21), 181 (100), 180 (29).

Anal. Calcd for $C_{13}H_{19}NO_2S$: C, 61.63; H, 7.56; N, 5.53. Found: C, 61.38; H, 7.84; N, 5.49.

***N,N*-Diethyl-2-iodo-5-methoxybenzamide (9h).** According to procedure B, benzamide **8h** (1.44 g, 3.6 mmol) was treated with an excess of CsF for 8 h. Workup in the usual manner followed by MPLC afforded 1.11 g (93%) of **9h** as a colorless viscous oil: bp 140–144 °C (0.05 mm); IR (neat) 1632 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.09 (t, J = 7 Hz, 3 H), 1.29 (t, J = 7 Hz, 3 H), 3.03–3.36 (m, 4 H), 3.78 (s, 3 H), 6.57–6.79 (m, 2 H, C_4-H and C_6-H), 7.66 (d, J = 8.6 Hz, 1 H, C_3-H); ^{13}C NMR ($CDCl_3$) δ (rel intensity) 12.3 (61), 13.7 (89), 38.6 (82), 42.5 (77), 55.2 (88), 80.8 (22), 112.5 (78), 116.0 (96), 139.5 (100), 143.3 (22), 159 (21), 169.3 (16); MS m/e (rel intensity) 333 (M^+, 56), 332 (53), 261 (100), 206 (23), 135 (21).

Anal. Calcd for $C_{12}H_{16}INO_2$: C, 43.26; H, 4.84; N, 4.20. Found: C, 42.83; H, 4.62; N, 4.57.

***N,N*-Diethyl-2-deuterio-4,5-dimethoxybenzamide (9i).** According to procedure B, benzamide **8i** (1.05 g, 3.8 mmol) was treated with an excess of CsF for 12 h. Workup in the usual manner followed by MPLC afforded 584 mg (65%) of **9i** (96% d_1 by MS) as a colorless oil: bp 135–140 °C (0.1 mm); IR (neat) ν(max) 1620 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.19 (t, J = 7 Hz, 6 H), 3.42 (q, J = 7 Hz, 4 H), 3.89 (s, 6 H), 6.86 (s, 1 H, C_3-H), 6.95 (s, 1 H, C_6-H); ^{13}C NMR ($CDCl_3$) δ (rel intensity) 13.2 (8), 39.5 (2), 42.3 (2), 55.5 (100), 109.8 (54), 110.1 (57), 129.1 (18), 148.4 (12), 149.3 (13), 170.5 (10); MS m/e (rel intensity) 238 (M^+, 22), 166 (100), 165 (29).

***N,N*-Diethyl-4,5-dimethoxy-2-methylbenzamide (9j).** According to procedure B, benzamide **8j** (1.47 g, 4.5 mmol) was treated with an excess of CsF for 20 h. Workup in the usual manner followed by MPLC afforded 990 mg (87%) of **9j** as a colorless oil: bp 126–128 °C (0.05 mm); IR (neat) ν(max) 1612 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.05 (t, J = 7 Hz, 3 H), 1.26 (t, J = 7 Hz, 3 H), 2.23 (s, 3 H), 3.12–3.62 (m, 4 H), 3.85 (s, 3 H), 3.87 (s, 3 H), 6.69 (s, 2 H); ^{13}C NMR ($CDCl_3$) δ (rel intensity) 12.8 (43), 13.9 (53), 18.2 (60), 38.7 (47), 42.5 (45), 55.8 (100), 55.9 (96), 109.1 (75), 113.3 (84), 126.2 (47), 128.9 (43), 146.8 (38), 148.8 (47), 170.5 (37); MS m/e (rel intensity) 251 (M^+, 46), 236 (23), 180 (25), 179 (100), 178 (24), 151 (32).

Anal. Calcd for $C_{14}H_{21}NO_3$: C, 66.91; H, 8.42; N, 5.57. Found: C, 66.49; H, 8.47; N, 5.66.

***N,N*-Diethyl-5-chloro-2-deuteriobenzamide (9l).** Benzamide **8l** (1.18 g, 4.0 mmol) was treated with an excess of CsF for 12 h according to procedure B. Workup in the usual manner followed by MPLC afforded 797 mg (90%) of **9l** (98% d_1 by MS) as a colorless oil: bp 110–114 °C (0.05 mm); IR (neat) ν(max) 1628 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.1 (br, 3 H), 1.24 (br, 3 H), 3.24 (br, 2 H), 3.54 (br, 2 H), 7.28–7.38 (m, 3 H); ^{13}C NMR ($CDCl_3$) δ (rel intensity) 12.5 (31), 13.8 (32), 39.0 (32), 42.9 (31), 126.1 (88), 128.8 (85), 129.4 (100), 133.9 (15), 138.6 (15), 169.1 (12); MS m/e (rel intensity) 212 (M^+, 21), 211 (22), 142 (31), 140 (100), 112 (27).

***N,N*-Diethyl-5-chloro-2-formylbenzamide (9n).** Benzamide **8n** (350 mg, 1.1 mmol) was treated with an excess of CsF for 8 h according to procedure B. Workup in the usual manner followed by MPLC afforded 215 mg (80%) of **9n** as a colorless oil: bp 105–108 °C (0.05 mm); IR (neat) ν(max) 1701, 1639 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.06 (t, J = 7 Hz, 3 H), 1.31 (t, J = 7 Hz, 3 H), 3.14 (q, J = 7 Hz, 2 H), 3.62 (q, J = 7 Hz, 2 H), 7.35 (d, J = 2.0 Hz, 1 H, C_6-H), 7.51 (dd, J = 8.3 and 2.0 Hz, 1 H, C_4-H), 7.89 (d, J = 8.3 Hz, 1 H, C_3-H), 10.00 (s, 1 H, CHO); ^{13}C NMR ($CDCl_3$) δ (rel intensity) 12.6 (84), 13.9 (71), 39.3 (92), 43.0 (85), 127.0 (100), 129.4 (83), 130.8 (17), 131.3 (65), 140.6 (18), 140.9 (15), 167.0 (12), 189.1 (88); MS m/e (rel intensity) 238 (M^+ – 1, 1), 212 (27), 210 (82), 169 (22), 167 (68), 141 (32), 139 (100), 110 (33).

Satisfactory elemental analysis for this compound could not be obtained.

***N,N*-Diethyl-6-deuterio-3-fluorobenzamide (9o).** According to procedure A, a solution of benzamide **7e** (1.01 g, 3.8 mmol), *s*-BuLi (3.8 mL of a 1.1 M solution, 4.2 mmol), and TMEDA (0.6 mL, 4.2 mmol) was treated with MeOD (0.8 mL, 19 mmol). Workup in the usual manner afforded a clear oil, which was directly treated with an excess of CsF for 1 h according to procedure B. Subsequent workup and Kugelrohr distillation afforded 706 mg (95%) of **9o** (95% d_1 by MS) as a colorless oil: bp 105–110 °C (0.1 mm); IR (neat) ν(max) 1631 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.18 (t, J = 7 Hz, 6 H), 3.38 (br, 4 H), 7.01–7.48 (m, 3 H); ^{13}C NMR ($CDCl_3$) δ (rel intensity) 12.3 (27), 13.6 (27), 38.8 (29), 42.7 (28), 112.8 (77), 113.2 (79), 115.3 (72), 115.6 (73), 129.5 (93), 129.7 (100), 138.7 (13), 138.8 (16), 159.9 (18), 163.8 (22), 168.9 (18); MS m/e (rel intensity) 196 (M^+, 47), 195 (41), 125 (20), 124 (100), 96 (65).

***N,N*-Diethyl-6-fluoro-2-methylbenzamide (9p).** According to procedure B, benzamide **8p** (1.34 g, 4.8 mmol) was treated with an excess of CsF for 1 h. Workup in the usual manner followed by MPLC afforded 885 mg (90%) of **9p** as a colorless oil: bp 105–108 °C (0.05 mm); IR (neat) ν(max) 1636 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.05 (t, J = 7 Hz, 3 H), 1.25 (t, J = 7 Hz, 3 H), 2.24 (s, 3 H), 3.13 (q, J = 7 Hz, 2 H), 3.53 (br, 2 H), 6.83–7.16 (m, 3 H); MS m/e (rel intensity) 209 (M^+, 29), 208 (27), 137 (100), 109 (40).

Anal. Calcd for $C_{12}H_{16}FNO$: C, 68.88; H, 7.71; N, 6.69 Found: C, 68.53; H, 7.78; N, 6.72.

Preparation of Phthalides 10a and 10b. 6-Chloro-3-(1-naphthyl)phthalide (10a). Accordig to procedure A, a solution of benzamide **7d** (2.99 g, 10.5 mmol), *s*-BuLi (9.3 mL of a 1.3 M solution, 11.6 mmol), and TMEDA (1.8 mL, 11.6 mmol) was treated with freshly distilled 1-naphthaldehyde (1.6 mL, 11.6 mmol). Workup in the usual manner afforded a viscous yellow oil, which was treated with an excess of CsF for 12 h according to procedure B. Subsequent workup and MPLC of the crude product afforded 982 mg (32%) of **10a** as a colorless powder: mp 121–123 °C (Et_2O–hexane); IR ($CHCl_3$) ν(max) 1771 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.24–8.27 (m, 11 H); MS m/e (rel intensity) 296 (32), 294 (M^+, 100), 215 (40), 213 (20).

Anal. Calcd for $C_{18}H_{11}ClO_2$: C, 73.35; H, 3.76. Found: C, 73.13; H, 3.87.

6-Fluoro-3-(1-naphthyl)phthalide (10b). According to procedure A, a solution of benzamide **7e** (2.05 g, 7.6 mmol), *s*-BuLi (6.7 mL of a 1.3 M solution, 8.4 mmol), and TMEDA (1.3 mL, 8.4 mmol) was treated with freshly distilled 1-naphthaldehyde (1.1 mL, 8.4 mmol). Workup in the usual manner afforded a viscous orange oil, which the was treated with an excess of CsF for 1 h according to procedure B. Subsequent workup and MPLC of the crude product afforded 853 mg (40%) of **10b** as a colorless

powder: mp 121–123 °C (Et_2O); IR ($CHCl_3$) ν(max) 1768 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.25–8.25 (m, 11 H); MS m/e (rel intensity) 279 (20), 278 (M^+, 100), 233 (36).

Anal. Calcd for $C_{18}H_{11}FO_2$: C, 77.69; H, 3.98. Found: C, 77.81; H, 3.96.

Preparation of Bromobenzamides 12a–c, 14. *N,N*-Diethyl-2-bromo-6-methylbenzamide (12a). Benzamide **8a** (1.04 g, 3.9 mmol) in CCl_4 (10 mL) was treated with Br_2 (2 mL 39.5 mmol). The resulting solution was held at reflux for 8 h, cooled, and treated carefully with saturated $NaHSO_3$ solution (10 mL). Subsequent workup in the usual manner followed by MPLC afforded 732 mg (69%) of **12a** as colorless crystals: mp 70–70.5 °C (Et_2O); IR ($CHCl_3$) ν(max) 1625 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.09 (t, J = 7 Hz, 3 H), 1.29 (t, J = 7 Hz, 3 H), 2.30 (s, 3 H), 3.16 (q, J = 7 Hz, 2 H), 3.47–3.77 (m, 2 H), 7.07–7.44 (m, 3 H); MS m/e (rel intensity) 271 (M^+ + 2, 26), 270 (3), 269 (M^+, 25), 256 (54), 254 (54), 199 (97), 197 (100), 190 (79).

Anal. Calcd for $C_{12}H_{16}BrNO$: C, 53.34; H, 5.97; N, 5.18. Found: C, 53.19; H, 5.83; N, 5.46.

***N,N*-Diethyl-2-bromo-3-chloro-6-methylbenzamide (12b).** Benzamide **8m** (223 mg, 0.8 mmol) in CCl_4 (15 mL) at 0 °C was treated with Br_2 (0.4 mL, 8 mmol). The resulting solution was stirred at 0 °C for 2 h and quenched with saturated $NaHSO_3$ solution (5 mL). Subsequent workup in the usual manner followed by MPLC afforded 184 mg (81%) of **12b** as a colorless oil: IR (neat) ν(max) 1640 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.10 (t, J = 7 Hz, 3 H), 1.29 (t, J = 7 Hz, 3 H), 2.28 (s, 3 H), 3.14 (q, 2 H, J = 7 Hz), 3.47–3.76 (m, 2 H), 7.09 (d, J = 8.1 Hz, 1 H, C_5-H), 7.34 (d, J = 8.1 Hz, 1 H, C_4-H); MS m/e (rel intensity) 305 (21), 303 (M^+, 16), 290 (30), 288 (22), 235 (25), 233 (100), 231 (80), 224 (41); HRMS calcd for $H_{12}H_{15}BrClNO$ 303.00265, found 303.0010.

***N,N*-Diethyl-2-bromo-3,5-dimethoxybenzamide (12c).** Benzamide **7c** (988 mg, 3.2 mmol) in CCl_4 (14 mL) at 0 °C was treated with Br_2 (2 mL, 39 mmol). The resulting solution was stirred at 0 °C for 30 min and quenched with saturated $NaHSO_3$ solution (20 mL). Subsequent workup in the usual manner followed by MPLC afforded three fractions.

Fraction 1: 335 mg (27%) of *N,N*-diethyl-6-bromo-3,4-dimethoxy-2-(trimethylsilyl)benzamide; colorless oil; IR (neat) ν(max) 1637 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.28 (s, 9 H), 1.11 (t, J = 7 Hz, 3 H), 1.27 (t, J = 7 Hz, 3 H), 3.05–3.79 (m, 4 H), 3.85 (s, 6 H), 7.09 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ (rel intensity) 0.8 (100), 12.1 (37), 13.2 (40), 38.9 (37), 43.0 (38), 60.5 (32), 114.2 (17), 117.9 (37), 132.0 (12), 135.4 (12), 151.7 (16), 153.6 (11), 168.4 (16); MS m/e (rel intensity) 389 (M^+ + 2, 8), 388 (3), 387 (M^+, 8), 374 (100), 372 (98); HRMS calcd for $C_{16}H_{26}BrNO_3Si$ 387.08658 and 389.08458, found 387.0843 and 389.0821.

Fraction 2: 66 mg (5%) of *N,N*-diethyl-2,6-dibromo-3,4-dimethoxybenzamide; colorless oil; IR (neat) ν(max) 1637 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.15 (t, J = 7 Hz, 3 H), 1.28 (t, J = 7 Hz, 3 H), 3.16 (q, J = 7 Hz, 2 H), 3.60 (q, J = 7 Hz, 2 H), 3.84 (s, 3 H), 3.88 (s, 3 H), 7.07 (s, 1 H, C_5-H); MS m/e (rel intensity) 395 (M^+ + 2, 4), 323 (25), 74 (100).

Fraction 3: 679 mg (67%) of *N,N*-diethyl-2-bromo-3,4-dimethoxybenzamide (**12c**); colorless oil; bp 134–140 °C (0.05 mm); IR (neat) ν(max) 1631 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.05 (t, J = 7 Hz, 3 H), 1.26 (t, J = 7 Hz, 3 H), 3.01–3.79 (m, 4 H), 3.86 (s, 3 H), 3.88 (s, 3 H), 6.92–7.00 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ (rel intensity) 12.3 (94), 13.7 (88), 38.8 (100), 42.6 (93), 55.9 (94), 60.3 (82), 111.6 (94), 114.8 (39), 122.2 (86), 131.9 (58), 146.4 (34), 153.3 (58), 167.9 (56); MS m/e (rel intensity) 316 (M^+ + 2, 24), 314 (M^+, 23), 245 (97), 243 (100), 236 (35), 85 (29).

Anal. Calcd for $C_{13}H_{18}BrNO_3$: C, 49.54; H, 5.76; N, 4.44. Found: C, 49.51; H, 5.60; N, 4.81.

***N,N*-Diethyl-3-bromo-6-methoxy-2-(trimethylsilyl)benzamide (14).** Benzamide **13** (1.01 g, 3.6 mmol) in CCl_4 (15 mL) at 0 °C was treated with Br_2 (2 mL, 39 mmol). The resulting solution was stirred at 0 °C for 1 h and quenched with saturated $NaHSO_3$ solution (10 mL). Subsequent workup in the usual manner followed by MPLC afforded 1.07 g (83%) of **14** as colorless crystals: mp 89–89.5 °C (hexane); IR ($CHCl_3$) ν(max) 1624 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.42 (s, 9 H), 1.05 (t, J = 7 Hz, 3 H), 1.24 (t, J = 7 Hz, 3 H), 3.02–3.72 (m, 4 H), 3.76 (s, 3 H), 6.83 (d, J = 8.8 Hz, 1 H, C_5-H), 7.49 (d, J = 8.8 Hz, 1 H, C_4-H); MS m/e (rel intensity) 358 (M^+, 4), 345 (20), 344 (100), 343 (20), 342 (98), 287 (30), 285 (30).

Anal. Calcd for $C_{15}H_{22}BrNO_2Si$: C, 50.56; H, 6.22; N, 3.93. Found: C, 50.17; H, 6.28; N, 4.00.

Preparation of Mono- and Disilylated *o*-Toluamides. *N,N*-Diethyl-2-[(trimethylsilyl)methyl]benzamide (16). According to procedure A, a solution of *N,N*-diethyl-2-methylbenzamide (5.79 g, 30.3 mmol), *s*-BuLi (22.4 mL of a 1.3 M solution, 30.3 mmol), and TMEDA (4.6 mL, 30.3 mmol) was treated with TMSCl (3.9 mL, 30.3 mmol). Workup in the usual manner followed by HPLC and short-path distillation afforded 6.95 g (87%) of benzamide **16** as a colorless oil: bp 88–89 °C (0.03 mm); IR (neat) ν(max) 1636 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.02 (s, 9 H), 1.04 (t, J = 7 Hz, 3 H), 1.25 (t, J = 7 Hz, 3 H), 2.08 (s, 2 H), 3.13 (q, J = 7 Hz, 2 H), 3.52 (br, 2 H), 7.0–7.22 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ (rel intensity) –1.2 (100), 12.8 (33), 13.9 (30), 23.3 (40), 38.7 (32), 42.8 (32), 123.9 (43), 126.0 (45), 128.1 (43), 135.6 (20), 137.2 (25), 170.7 (14); MS m/e (rel intensity 263 (M^+, 8), 262 (23), 249 (20), 248 (100), 119 (31), 74 (34).

Anal. Calcd for $C_{15}H_{25}NOSi$: C, 68.39; H, 9.57; N, 5.32. Found: C, 68.32; H, 9.65; N, 5.31.

***N,N*-Diethyl-2-[bis(trimethylsilyl)methyl]benzamide (17).** According to procedure A, a solution of benzamide **16** (1.79 g, 6.8 mmol), *s*-BuLi (5.8 mL of a 1.3 M solution, 7.5 mmol), and TMEDA (1.1 mL, 7.5 mmol) was treated with TMSCl (3.8 mL, 34 mmol). Workup in the usual manner followed by HPLC and short-path distillation afforded 2.29 g (94%) of benzamide **17** as a colorless oil: bp 110–112 °C (0.02 mm); IR (neat) ν(max) 1629 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.05 (s, 18 H), 1.11 (t, J = 7 Hz, 3 H), 1.32 (t, J = 7 Hz, 3 H), 1.82 (s, 1 H), 2.80–4.0 (br, 4 H), 6.91–7.20 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ (rel intensity) 0.5 (100), 12.7 (26), 13.9 (27), 24.6 (44), 38.2 (30), 43.0 (28), 122.6 (47), 126.0 (4), 128.0 (45), 128.8 (45), 135.5 (15), 141.2 (16), 170.6 (13); MS m/e (rel intensity) 335 (M^+, 25), 334 (55), 320 (43), 249 (21), 248 (100), 73 (90).

Anal. Calcd for $C_{18}H_{33}NOSi_2$: C, 64.41; H, 9.91; N, 4.17. Found: C, 64.21; H, 9.96; N, 4.19.

One-Pot Preparation of *N,N*-Diethyl-2-[bis(trimethylsilyl)methyl]benzamide (17). A solution of *N,N*-diethyl-2-methylbenzamide (**15**) (4.39 g, 22.9 mmol) in THF (20 mL) was added dropwise to a stirred solution of *s*-BuLi (18.7 mL of a 1.3 M solution, 23 mmol) and TMEDA (3.8 mL, 23 mmol) in THF (150 mL) at –78 °C under argon. The resulting burgundy solution was stirred at –78 °C for 1 h and treated with TMSCl (3.0 mL, 23 mmol). To this solution were added consecutively TMEDA (3.8 mL, 23 mmol) and *s*-BuLi (18.7 mL, 23 mmol), regenerating the burgundy color. After a further 45 min at –78 °C, TMSCl (4.4 mL, 34 mmol) was added. The resulting clear solution was allowed to warm to ambient temperature overnight. Workup in the usual manner followed by short-path distillation afforded 7.03 g (91%) of **17**, identical (IR, ^1H NMR, MS) with a sample as prepared above.

***N,N*-Diethyl-2-[bis(trimethylsilyl)methyl]-6-methylbenzamide (18b).** According to procedure A, a solution of benzamide **17** (847 mg, 2.5 mmol), *s*-BuLi (2.1 mL of a 1.3 M solution, 2.7 mmol), and TMEDA (0.4 mL, 2.7 mmol) was treated with MeI (0.8 mL, 12.5 mmol). Workup in the usual manner followed by MPLC and short-path distillation afforded 804 mg (91%) of **18b** as a colorless oil: bp 110–112 °C (0.03 mm); IR (neat) ν(max) 1630 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.03 (s, 9 H), 0.07 (s, 9 H), 1.08 (t, J = 7 Hz, 3 H), 1.25 (t, J = 7 hz, 3 H), 1.82 (s, 1 H), 2.23 (s, 3 H), 2.98–3.95 (m, 4 H), 6.76–7.19 (m, 3 H); ^{13}C NMR ($CDCl_3$) δ (rel intensity) 0.3 (96), 1.3 (100), 12.6 (41), 13.9 (37), 19.7 (23), 24.6 (41), 37.6 (39), 42.4 (37), 125.0 (42), 125.7 (45), 127.2 (43), 134.1 (15), 135.8 (11), 139.9 (14), 169.9 (15); MS m/e (rel intensity) 349 (M^+, 19), 335 (29), 334 (100), 262 (64), 73 (83).

Anal. Calcd for $C_{19}H_{35}NOSi_2$: C, 65.27; H, 10.09; N, 4.01. Found: C, 65.29; H, 9.83; N, 3.81.

***N,N*-Diethyl-2-formyl-6-[bis(trimethylsilyl)methyl]benzamide (18c).** According to procedure A, a solution of benzamide **17** (1.15 g, 3.4 mmol), *s*-BuLi (2.8 mL of a 1.4 M solution, 3.9 mmol), and TMEDA (0.6 mL, 3.9 mmol) was treated with DMF (3.3 mL, 42.5 mmol). Workup in the usual manner followed by MPLC and recrystallization afforded 1.07 g (86%) of **18c** as colorless cyrstals: mp 72.5–73.0 °C (hexane); IR ($CHCl_3$) ν(max) 1692, 1625 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.08 (s,, 9 H), 0.12 (s, 9 H), 0.99 (t, J = 7 Hz, 3 H), 1.27 (t, J = 7 Hz, 3 H), 1.67 (s, 1 H), 2.07–4.18 (m, 4 H), 7.14–7.52 (m, 2 H, C_4-H, C_5-H), 7.68 (dd,

J = 6.8, 2.2 Hz,, 1 H, C_3-H); MS m/e (rel intensity) 363 (M^+, 10), 348 (59), 335 (28), 334 (89), 293 (29), 292 (100), 248 (22), 73 (100).

Anal. Calcd for $C_{19}H_{33}NO_2Si_2$: C, 62.76; H, 9.15; N, 3.85. Found: C, 62.59; H, 9.56; N, 3.85.

4-[Bis(trimethylsilyl)methyl]phthalic Anhydride (20). According to procedure A, a solution of benzamide **17** (2.21 g, 6.6 mmol), *s*-BuLi (5.6 mL of a 1.3 M solution, 7.2 mmol), and TMEDA (1.1 mL, 7.2 mmol) was treated with dry CO_2 gas for 45 min. Workup in the usual manner afforded a yellow gum, which was dissolved in $CHCl_3$ (50 mL) containing SiO_2 (15 g) and 12 N HCl (20 drops). The resulting mixture was stirred at room temperature (96 h). The solution was filtered through Celite, and the cake was washed with CH_2Cl_2. The combined filtrate was dried (Na_2SO_4), and the solvent was removed in vacuo. MPLC followed by recrystallization afforded 1.57 g (78%) of **20** as a colorless solid: mp 57–58 °C (hexane); IR ($CHCl_3$) ν(max) 1769, 1702, 1613 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.06 (s, 9 H), 0.07 (s, 9 H), 3.23 (s, 1 H), 7.35–7.72 (m, 3 H); MS m/e (rel intensity) 306 (M^+, 56), 291 (62), 277 (58), 147 (100), 146 (31), 133 (24), 115 (37), 74 (27); HRMS calcd for $C_{15}H_{22}Si_2O_3$ 306.11076, found 306.1096.

***N,N*-Diethyl-2-(methylthio)-6-[bis(trimethylsilyl)methyl]benzamide (18e).** According to procedure A, a solution of benzamide **17** (1.58 g, 4.7 mmol), *s*-BuLi (4.1 mL of a 1.3 M solution, 5.3 mmol), and TMEDA (0.8 mL, 5.3 mmol) was treated with $(MeS)_2$ (0.6 mL, 7.1 mmol). Workup in the usual manner followed by MPLC and short-path distillation afforded 1.37 g (76%) of **18e** as a pale yellow oil: bp 136–138 °C (0.05 mm); IR (neat) ν(max) 1630 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.04 (s, 9 H), 0.07 (s, 9 H), 1.21 (q, J = 7 Hz, 6 H), 1.61 (s, 1 H), 2.41 (s, 3 H), 2.97–3.94 (m, 4 H), 6.83 (dd, J = 7.2, 1.7 Hz, 1 H, C_5-H), 6.95–7.32 (m, 2 H, C_3-H, C_4-H); ^{13}C NMR ($CDCl_3$) δ (rel intensity) 0.4 (100), 1.3 (100), 12.6 (39), 13.9 (40), 17.5 (32), 25.1 (34), 37.8 (36), 42.7 (38), 123.4 (37), 126.1 (38), 127.9 (37), 135.3 (12), 136.7 (12), 141.4 (15), 168.4 (15); MS m/e (rel intensity) 381 (M^+, 24), 366 (54), 335 (31), 334 (100), 294 (56), 246 (25), 73 (100).

Satisfactory analytical data could not be obtained.

***N,N*-Diethyl-2-(trimethylsilyl)-6-[bis(trimethylsilyl)methyl]benzamide (18f).** According to procedure A, a solution of benzamide **17** (1.79 g, 5.3 mmol), *s*-BuLi (4.3 mL of a 1.4 M solution, 6.0 mmol), and TMEDA (0.9 mL, 6.0 mmol) was treated with TMSCl (3.4 mL, 26.5 mmol). Workup in the usual manner followed by MPLC and recrystallization afforded 2.04 g (94%) of **18f** as colorless needles: mp 69.5–70.5 °C (CH_2Cl_2–hexane); IR ($CHCl_3$) ν(max) 1624 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.01 (s, 9 H), 0.12 (s, 9 H), 0.24 (s, 9 H), 1.03 (t, J = 7.1 Hz, 3 H), 1.25 (t, J = 7.0 Hz, 3 H), 1.59 (s, 1 H), 2.91–3.18 (m, 3 H), 4.08–4.11 (m, 1 H), 6.95 (d, J = 7.6 Hz, 1 H), 7.17–7.27 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ (rel intensity) 0.2 (100), 1.6 (61), 12.5 (25), 13.3 (25), 23.9 (24), 37.7 (24), 42.4 (25), 126.7 (24), 128.7 (23), 129.9 (25), 137.6 (10), 138.9 (13), 140.6 (11), 170.6 (12); MS m/e (rel intensity) 407 (M^+, 6), 335 (35), 334 (100), 73 (47).

Anal. Calcd for $C_{21}H_{41}NOSi_3$: C, 61.85; H, 10.13; N, 3.43. Found: C, 61.46; H, 10.07; N, 3.22.

Preparation of 1,2,3-Trisubstituted Benzamides 19a–e.

***N,N*-Diethyl-6-deuterio-2-methylbenzamide (19a).** According to procedure A, a solution of benzamide **17** (1.3 g, 3.9 mmol), *s*-BuLi (3.4 mL of a 1.3 M solution, 4.3 mmol), and TMEDA (0.7 mL, 4.3 mmol) was treated with MeOD (0.8 mL, 19 mmol). Workup in the usual manner afforded a clear oil, which was then treated with TBAF (9 mL, 9 mmol) in wet THF according to procedure C. Subsequent workup and MPLC afforded 705 mg (94%) of **19a** (95% d_1 by MS) as a colorless oil, bp 92–95 °C (0.01 mm); IR (neat) ν(max) 1628 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.03 (t, J = 7 Hz, 3 H), 1.26 (t, J = 7 Hz, 3 H), 2.29 (s, 3 H), 3.12 (q, J = 7 Hz, 2 H), 3.46–3.62 (br, 2 H), 7.22 (br, 3 H); ^{13}C NMR ($CDCl_3$) δ (rel intensity) 12.8 (88), 13.9 (80), 18.7 (34), 38.6 (98), 42.5 (100), 125.5 (78), 128.4 (83), 130.2 (87), 133.7 (11), 137.0 (8), 170.7 (8); MS m/e (rel intensity) 192 (M^+, 24), 177 (24), 121 (35), 120 (100), 119 (27), 92 (46).

***N,N*-Diethyl-2,6-dimethylbenzamide (19b).** Benzamide **18b** (900 mg, 2.6 mmol) was treated with TBAF (5.6 mL, 5.6 mmol) in wet THF (15 mL) according to procedure C. Workup in the usual manner followed by MPLC afforded 429 mg (81%) of **19b** as a colorless oil: bp 106–108 °C (0.02 mm); IR (neat) ν(max) 1622 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.03 (t, J = 7 Hz, 3 H), 1.28 (t, J = 7 Hz, 3 H), 2.25 (s, 6 H), 3.11 (q, J = 7 Hz, 2 H), 3.61 (q, J = 7 Hz, 2 H), 6.92–7.24 (m, 3 H); MS m/e (rel intensity) 205 (M^+, 16), 190 (23), 134 (21), 133 (100), 132 (20), 105 (28).

Anal. Calcd for $C_{13}H_{19}NO$: C, 76.06; H, 9.33; N, 6.82. Found: C, 76.26; H, 9.30; N, 6.59.

***N,N*-Diethyl-2-formyl-6-methylbenzamide (19c).** Benzamide **18c** (650 mg, 1.8 mmol) was treated with an excess of CsF for 3 h according to procedure B. Workup in the usual manner followed by MPLC aforded 305 mg (78%) of **19c** as a colorless oil: bp 86–88 °C (0.01 mm); IR (neat) ν(max) 1691, 1631 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.00 (t, J = 7 Hz, 3 H), 1.33 (t, J = 7 Hz, 3 H), 2.34 (s, 3 H), 3.08 (q, J = 7 Hz, 2 H), 3.55–3.82 (m, 2 H), 7.39–7.82 (m, 3 H), 10.01 (s, 1 H, CHO); MS m/e (rel intensity) 219 (M^+, 1), 189 (68), 147 (100).

Anal. Calcd for $C_{13}H_{17}NO_2$: C, 71.20; H, 7.81; N, 6.39. Found: C, 71.15; H, 7.82; N, 6.03.

***N,N*-Diethyl-2-(methylthio)-6-methylbenzamide (19e).** Benzamide **18e** (806 mg, 2.1 mmol) was treated with an excess of CsF for 1 h according to procedure B. Workup in the usual manner followed by MPLC afforded 482 mg (96%) of **19e** as a colorless oil: bp 86–90 °C (0.01 mm); IR (neat) ν(max) 1620 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.07 (t, J = 7 Hz, 3 H), 1.29 (t, J = 7 Hz, 3 H), 2.26 (s, 3 H), 2.45 (s, 3 H), 3.13 (q, J = 7 Hz), 3.62 (q, J = 7 Hz, 2 H), 7.03–7.23 (m, 3 H); ^{13}C NMR ($CDCl_3$) δ (rel intensity) 12.6 (94), 13.9 (81), 17.2 (78), 19.1 (54), 38.7 (89), 42.6 (93), 125.6 (91), 127.7 (100), 128.6 (99), 134.7 (59), 137.9 (22), 168.7 (26); MS m/e (rel intensity) 236 (M^+, 16), 165 (100).

Anal. Calcd for $C_{13}H_{19}NOS$: C, 65.78; H, 8.07; N, 5.90. Found: C, 65.61; H, 8.25; N, 5.62.

Preparation of *peri*-Methylphthalide 21 and -acridone 25.

7-Methyl-3-[(3,4-dimethoxy)phenyl]phthalide (21). According to procedure A, to a solution of benzamide **17** (1.63 g, 4.9 mmol), *s*-BuLi (4.5 mL of a 1.2 M solution, 5.3 mmol), and TMEDA (0.8 mL, 5.3 mmol) was added 3,4-dimethoxybenzaldehyde (869 mg, 5.2 mmol). Workup in the usual manner gave a red oil, which was treated directly with an excess of CsF for 12 h according to procedure B. Standard workup afforded a tar, which was treated with *p*-toluenesulfonic acid in toluene at reflux for 1 h. Removal of the solvent in vacuo, followed by MPLC and recrystallization of the red solid obtained, furnished 812 mg (65%) of **21** as colorless crystals: mp 99–100 °C (Et_2O); IR ($CHCl_3$) ν(max) 1754 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.75 (s, 3 H), 3.82 (s, 3 H), 3.88 (s, 3 H), 6.28 (s, 1 H), 6.69 (br, 1 H), 6.87 (d, J = 1 Hz, 1 H), 7.07–7.62 (m, 3 H); MS m/e (rel intensity) 284 (M^+, 100), 253 (53), 165 (45), 119 (21), 118 (32).

Anal. Calcd for $C_{17}H_{16}O_4$: C, 64.47; H, 9.02; N, 5.01. Found: C, 64.29; H, 9.27; N, 4.98.

***N,N*-Diethyl-2-(*N*-phenylamino)-6-[bis(trimethylsilyl)methyl]benzamide (23).** A solution of benzamide **17** (2.5 g, 7.4 mmol) in anhydrous THF (10 mL) was added dropwise to a cold stirred solution of *s*-BuLi (7.1 mL of a 1.2 M solution, 8.1 mmol) and TMEDA (1.2 mL, 8.1 mmol) in anhydrous THF (200 mL) at −78 °C under argon. The resulting orange solution of the lithiated benzamide was stirred at −78 °C for 1 h. In a separate reaction vessel, a solution of the lithioanilide, prepared from aniline (3.4 mL, 37 mmol) (freshly distilled from Zn powder) and *n*-BuLi (26.4 mL, 37 mmol, 1.4 M solution) in anhydrous THF (50 mL) at −10 °C under argon, was treated with anhydrous CuCN (3.0 g, 37 mmol). The resulting purple solution of the cuprate was stirred for 15 min at −10 °C and then slowly injected into the solution of the lithiated benzamide. After 2 h at −78 °C, oxygen was rapidly passed through the solution for 30 min, the cooling bath was removed, and the mixture was treated with a 10% solution of concentrated NH_4OH in saturated NH_4Cl solution (20 mL). Evaporation to dryness in vacuo gave a brown oil, which was dissolved in CH_2Cl_2 (500 mL). The mixture was filtered through Celite, and the cake was washed with CH_2Cl_2 until the filtrate was clear. The combined filtrate was washed successively with 100 mL of concentrated NH_4OH (10%) in saturated NH_4Cl solution and saturated NaCl solution and dried (Na_2SO_4). Removal of solvent in vacuo gave a tar, which, after MPLC, yielded a red solid. Recrystallization from CH_2Cl_2–hexane afforded 1.53 g (48%) of **23** as an off white solid: mp 169–170 °C; IR ($CHCl_3$) ν(max) 3407, 1613 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.06 (s, 9 H), 0.14 (s, 9 H), 0.98 (t, J = 7 Hz, 3 H), 1.24 (t, J = 7 Hz, 3 H), 1.59 (s, 1 H), 3.07–4.20 (m, 4 H), 5.90 (br, 1 H, exchanged with D_2O), 6.66–7.36 (m, 8 H); MS m/e (rel intensity) 427 (25), 426 (M^+, 71),

411 (58), 340 (31), 339 (100), 334 (31), 266 (21).

Anal. Calcd for $C_{24}H_{38}N_2OSi_2$: C, 67.55; H, 8.98; N, 6.56. Found: C, 67.68; H, 8.63; N, 6.55.

***N,N*-Diethyl-2-(*N*-phenylamino)-6-methylbenzamide (24).** According to procedure C, a solution of compound **23** (800 mg, 1.9 mmol) in wet THF (50 mL) was treated with TBAF (4.2 mL, 4.2 mmol, 1 M in THF). After 5 min, TLC indicated the absence of starting material. Workup in the usual manner followed by MPLC afforded 403 mg (95%) of **24** as a colorless solid: mp 97–98 °C (hexane); IR ($CHCl_3$) ν(max) 3408, 1611 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.99 (t, J = 7 Hz, 3 H), 1.25 (t, J = 7 Hz, 3 H), 2.24 (s, 3 H), 3.06–3.97 (m, 4 H), 5.92 (br, 1 H, exchanged with D_2O), 6.81–7.36 (m, 8 H); MS m/e (rel intensity) 282 (M^+, 30), 210 (28), 209 (100).

Anal. Calcd for $C_{18}H_{22}N_2O_2$: C, 76.56; H, 7.85; N, 9.92. Found: C, 76.16; H, 7.84; N, 9.92.

1-Methylacridone (25). A solution of **24** (100 mg, 0.4 mmol) in heptafluorobutyric acid (5 mL) was refluxed for 36 h. The turquoise solution was cooled and carefully neutralized with saturated Na_2CO_3 solution. The mixture was extracted with CH_2Cl_2, and the combined organics were washed (saturated NaCl solution) and dried (Na_2SO_4). Evaporation to dryness followed by MPLC afforded 37 mg (50%) of a tan solid, mp 302–304 °C (MeOH). Sublimation provided a sample of **25**: mp 310 °C dec (lit.[50] mp 315 °C); ^1H NMR (DMSO-d_6) δ 2.86 (s, 3 H), 7.33 (d, J = 7.2 Hz, 1 H, C_4-H or C_5-H), 7.43–7.54 (m, 2 H, C_4-H or C_5-H and C_6-H), 7.63–7.69 (m, 1 H, C_7-H), 8.15 (dd, J = 7.9 Hz and 0.8 Hz, 1 H, C_8-H), 11.55 (s, 1 H, exchanged with D_2O); MS m/e (rel intensity) 209 (M^+, 100). Compound **25** slowly decomposed under ambient conditions.

Iterative Metalations. Preparation of Compounds 27–30. *N,N*-Diethyl-5-methoxy-3-methyl-2-(phenylthiocarbamoyl)-6-(trimethylsilyl)benzamide (27). A solution of benzamide **7b** (948 mg, 3.4 mmol) in anhydrous THF (5 mL) was added dropwise to a stirred solution of *s*-BuLi (2.6 mL, 3.4 mmol, 1.3 M solution) and TMEDA (0.5 mL, 3.4 mmol) in anhydrous THF (60 mL) at −78 °C under argon. After 15 min, phenyl isothiocyanate (0.4 mL, 3.4 mmol) was added, and the resulting burgundy solution was stirred for 30 min at −78 °C. *s*-BuLi (2.6 mL, 3.4 mmol, 1.3 M solution) and TMEDA (0.5 mL, 3.4 mmol) were sequentially injected. The resulting maroon solution was stirred for a further 30 min at −78 °C and treated with MeI (0.5 mL, 8 mmol). The resulting brown solution was allowed to warm to ambient temperature overnight, worked up in the usual manner, and subjected to MPLC to afford 915 mg (63%) of **27** as yellow needles: mp 108–109 °C (Et_2O–hexane); IR ($CHCl_3$) ν(max) 3421, 1625, 1591 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.28 (s, 9 H), 1.07 (t, J = 7 Hz, 3 H), 1.28 (t, J = 7 Hz, 3 H), 2.08 (s, 3 H), 3.11–3.71 (m, 4 H), 3.85 (s, 3 H), 6.85–7.45 (m, 7 H, ArH and NH); MS m/e (rel intensity) 428 (M^+, 1), 383 (20), 382 (75), 381 (100), 183 (23).

Anal. Calcd for $C_{23}H_{32}N_2O_2SSi$: C, 64.44; H, 7.53; N, 6.54. Found: C, 64.63; H, 7.72; N, 6.56.

***N,N*-Diethyl-2,3-bis(diethylcarbamoyl)-5-methoxy-6-(trimethylsilyl)benzamide (28).** According to procedure A, a solution of benzamide **8d** (2.75 g, 7.3 mmol), *s*-BuLi (11.4 mL of a 1.4 M solution, 14.6 mmol), and TMEDA (2.4 mL, 14.6 mmol) was added diethylcarbamoyl chloride (1.7 mL, 14.6 mmol). Standard workup followed by MPLC afforded 2.29 g (66%) of **28** as a colorless powder: mp 140–141 °C (hexane); IR ($CHCl_3$) ν(max) 1630 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.26 (s, 9 H), 0.98–1.60 (m, 18 H), 3.15–3.40 (m, 12 H), 3.84 (s, 3 H), 6.69 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ (rel intensity) 0.6 (100), 12.4 (45), 12.8 (43), 12.9 (57), 13.0 (23), 13.1 (61), 13.2 (63), 38.7 (63), 38.8 (66), 39.0 (45), 43.4 (42), 43.6 (57), 44.3 (44), 55.3 (44), 106.8 (44), 124.2 (9), 125.1 (8), 137.3 (13), 141.2 (10), 164.2 (11), 167.8 (10), 168.3 (10), 168.9 (9); MS m/e (rel intensity) 477 (M^+, 2), 462 (26), 406 (51), 405 (29), 404 (32), 377 (69), 332 (25), 331 (100), 305 (24), 304 (30).

Anal. Calcd for $C_{25}H_{43}N_3O_4Si$: C, 62.86; H, 9.07; N, 8.80. Found: C, 62.49; H, 9.00; N, 8.51.

***N,N*-Diethyl-2,3-bis(diethylcarbamoyl)-5-methoxybenzamide (29).** Benzamide **28** (1.48 g, 3.1 mmol) was treated with an excess of CsF for 12 h according to procedure B. Workup in the usual manner followed by MPLC afforded 942 mg (75%) of **29** as a colorless solid: mp 88.5–89.5 °C (hexane); IR ($CHCl_3$) ν(max) 1637 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.97–1.62 (m, 18 H), 3.12–3.71 (m, 12 H), 3.84 (s, 3 H), 6.81 (s, 2 H); ^{13}C NMR ($CDCl_3$) δ (rel intensity) 12.7 (100), 13.2 (54), 14.0 (72), 38.8 (52), 39.1 (87), 43.3 (86), 44.2 (49), 55.6 (48), 111.8 (95), 124.2 (8), 136.6 (27), 159.1 (20), 167.3 (12), 168.5 (23); MS m/e (rel intensity) 405 (M^+, 2), 334 (91), 333 (39), 305 (81), 234 (21), 233 (100), 232 (41).

Anal. Calcd for $C_{22}H_{35}N_3O_4$: C, 65.16; H, 8.70; N, 10.36. Found: C, 64.80; H, 8.53; N, 10.31.

***N,N*-Diethyl-2,3-bis(diethylcarbamoyl)-5-methoxy-4,6-bis(trimethylsilyl)benzamide (30).** According to procedure A, to a solution of benzamide **28** (470 mg, 1 mmol), *s*-BuLi (2.6 mL of a 1.2 M solution, 3 mmol), and TMEDA (0.5 mL, 3 mmol) was added TMSCl (0.4 mL, 3 mmol). Standard workup followed by MPLC afforded 422 mg (78%) of **30** as a colorless powder: mp 120–121 °C (Et_2O–hexane); IR ($CHCl_3$) ν(max) 1631 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.32 (s, 18 H), 1.04–1.25 (m, 18 H), 3.06–3.31 (m, 12 H), 3.67 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ (rel intensity) 1.9 (100), 12.7 (46), 12.9 (46), 13.2 (50), 38.7 (28), 38.9 (51), 43.9 (48), 44.1 (26), 65.0 (23), 127.6 (7), 128.9 (12), 143.1 (14), 167.9 (7), 173.1 (5); MS m/e (rel intensity) 550 (M^+, 1), 534 (33), 477 (27), 476 (52), 450 (28), 449 (79), 404 (34), 403 (100), 377 (21).

Anal. Calcd for $C_{28}H_{51}N_3O_4Si_2$: C, 61.16; H, 9.35; N, 7.64. Found: C, 61.37; H, 9.58; N, 7.51.

X-ray Crystallographic Analysis of Compound 30. Crystals of **30**, $C_{28}H_{51}N_3O_4Si_2$, mol wt = 549.908, are orthorhombic, a = 11.728 (1) Å, b = 21.238 (3) Å, c = 26.408 (4) Å, V = 6578 (1) Å^3, space group $Pbca$, Z = 8, D_c = 1.111 g cm^{-3}, $F(000)$ = 2400, T = 294 ± 1 K, λ = 0.710 73 Å, μ(Mo Kα) = 1.44 cm^{-1}.

Data were collected from a crystal of dimensions 0.30 × 0.34 × 0.36 mm mounted on a Syntex $P2_1$ diffractometer. Accurate cell constants were derived from 15 general reflections well distributed in reciprocal space ($18 < 2\theta < 27°$). Data collection was by the $\theta - 2\theta$ scan method using variable scan rates (2.93–29.30 deg min^{-1}) and a scan width of 0.8° below Kα_1 to 0.8° above Kα_2. Background measurements were made at the beginning and end of each scan for a total of half the scantime. Crystal stability was monitored by the measurement of two standard reflections (02,11; 191) every 100 reflections; only statistical variation was observed. Data were corrected for Lorentz and polarization effects but not absorption. From a total of 4335 unique reflections measured ($2\theta \leq 45°$), 1842 with $I \geq 3\sigma(I)$ were considered observed. The structure was solved by direct methods (MULTAN80) and refined by full-matrix least-squares methods to final R and R_w values of 0.047 and 0.058, respectively ($R = \sum||F_o| - |F_c||/\sum|F_o|$; $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$).

All hydrogen atoms were located from a difference Fourier synthesis and included in the refinement but because of the limited amount of data, only the isotropic thermal parameters were refined. A final difference Fourier was featureless with maximum residuals of 0.16 e Å^{-3}. Scattering factors used were taken from the compilations of the International Tables,[51] and, for hydrogen, the data of Stewart et al.[52] were used. Computer programs used have been described elsewhere.[53]

Carbodesilylations Reactions: Preparations of Phthalides 31a–c. 3-Phenylphthalide (31a). A solution of benzamide **7a** (517 mg, 2.1 mmol) and freshly distilled benzaldehyde (0.3 mL, 3 mmol) in anhydrous DMF (20 mL) was treated with an excess of CsF, and the resulting mixture was refluxed for 12 h under argon. The solution was cooled, treated with Et_2O (100 mL), and subjected to filtration to remove the excess CsF. The organic phase was washed with saturated NaCl solution, dried (Na_2SO_4), and evaporated to dryness in vacuo. The residue was dissolved in toluene (100 mL) containing a catalytic amount of *p*-toluenesulfonic acid, and the resulting solution was refluxed for 12 h. Removal of the solvent in vacuo followed by MPLC afforded 242 mg (48%) of **31a** as colorless crysals: mp 113–114 °C (Et_2O-hexane) (lit.[54] mp 115 °C); IR ($CHCl_3$) ν(max) 1764 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.40 (s, 1 H), 7.27–8.02 (m, 9 H).

(50) Glev, K.; Nitzsche, S. *J. Prakt. Chem.* **1939**, *153*, 200.

(51) *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. 4.

(52) Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175.

(53) Carty, A. J.; Mott, G. N.; Taylor, N. J.; Yule, J. E. *J. Am. Chem. Soc.* **1978**, *100*, 3051.

(54) Narasimhan, N. S.; Paradkar, M. V. *Indian J. Chem.* **1969**, *7*, 536. Narasimhan, N. S.; Mali, R. S. *Tetrahedron* **1975**, *31*, 1005.

4,5-Dimethoxy-3-phenylphthalide (31b). Benzamide **7c** (1.14 g, 3.7 mmol) was treated under conditions identical with those used for the preparation of phthalide **31a** to give, after MPLC, 490 mg (49%) of phthalide **31b** as colorless crystals: mp 92.5–93 °C (Et_2O); IR ($CHCl_3$), ν(max) 1758 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.37 (s, 3 H), 3.94 (s, 3 H), 6.39 (s, 1 H), 7.10 (d, J = 8.3 Hz, 1 H), 7.33 (s, 5 H), 7.69 (d, J = 8.3 Hz, 1 H, C_6-H); MS m/e (rel intensity) 271 (42), 270 (M^+, 100), 255 (57), 193 (57), 166 (28), 165 (100), 139 (22).

Anal. Calcd for $C_{16}H_{14}O_4$: C, 71.10; H, 5.22. Found: C, 71.26; H, 5.05.

4-Chloro-7-methyl-3-phenlylphthalide (31c). Benzamide **8m** (750 mg, 2.5 mmol) was treated under conditions identical with those used for the preparation of phthalide **31a** to give, after MPLC, 295 mg (45%) of the phthalide **31c** as a colorless crystalline solid: mp 132–133 °C (Et_2O); IR ($CHCl_3$) ν(max) 1755 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.73 (s, 3 H), 6.32 (s, 1 H), 7.26–7.52 (m, 7 H); MS m/e (rel intensity) 260 (35), 258 (M^+, 100), 181 (21), 179 (23), 153 (65).

Anal. Calcd for $C_{15}H_{11}ClO_2$: C, 69.64; H, 4.29. Found: C, 69.31; H, 4.17.

Preparation of *o*-Toluamides 32a–c. *N,N*-Diethyl-2-methoxy-6-methylbenzamide (32a). According to procedure A, to a solution of *N,N*-diethyl-2-methoxybenzamide (5.13 g, 24.8 mmol), *s*-BuLi (22.7 mL of a 1.2 M solution, 27.3 mmol), and TMEDA (4.1 mL, 27.3 mmol) was added MeI (8.5 mL, 136 mmol). Workup in the usual manner followed by short-path distillation afforded 4.89 g (89%) of **32a** as a colorless oil: bp 104–106 °C (0.05 mm) [lit.[42] bp 99–100 °C (0.13 mm)]; identical IR, ^1H NMR, and MS with those reported.[42]

***N,N*-Diethyl-3-chloro-2-methylbenzamide (32b).** According to procedure A, a solution of *N,N*-diethyl-3-chlorobenzamide (5.30, 25 mmol), *s*-BuLi (23 mL of a 1.2 M solution, 27.5 mmol), and TMEDa (4.1 mL, 27.5 mmol) was treated with MeI (7.8 mL, 125 mmol). Workup in the usual manner followed by short-path distillation afforded 4.25 g (80%) of **32b** as a colorless oil: bp 88–90 °C (0.005 mm); IR (neat) ν(max) 1628 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.03 (t, J = 7 Hz, 3 H), 1.27 (t, J = 7 Hz, 3 H), 2.31 (s, 3 H), 3.12 (q, J = 7 Hz, 2 H), 3.34–3.74 (m, 2 H), 7.02–7.43 (m, 3 H); MS m/e (rel intensity) 225 (M^+, 25), 210 (27), 155 (32), 153 (100), 125 (58).

Anal. Calcd for $C_{12}H_{16}ClNO$: C, 60.47; H, 8.11; N, 4.70. Found: C, 60.61; H, 8.22; N, 4.98.

***N,N*-Diethyl-3-methoxy-2-methylbenzamide (32c).** According to procedure A, a solution of *N,N*-diethyl-3-methoxybenzamide (4.94 g, 28.8 mmol), *s*-BuLi (21.8 mL of a 1.2 M solution, 26.2 mmol), and TMEDA (4.0 mL, 26.2 mmol) was treated with MeI (7.5 mL, 119 mmol). Workup in the usual manner followed by MPLC afforded 4.51 g (86%) of **32c** as a colorless oil: bp 110–112 °C (0.01 mm); IR (neat) ν(max) 1620 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.02 (t, J = 7 Hz, 3 H), 1.26 (t, J = 7 Hz, 3 H), 2.14 (s, 3 H), 3.13 (q, J = 7 Hz, 2 H), 3.40–3.83 (m, 2 H), 3.83 (s, 3 H), 6.71–7.19 (m, 3 H); MS m/e (rel intensity) 221 (M^+, 5), 149 (100).

Anal. Calcd for $C_{13}H_{19}NO_2$: C, 70.55; H, 8.65; N, 6.33. Found: C, 70.33; H, 8.30; N, 6.03.

Preparation of α-Silyl-*o*-toluamides 33a–c. *N,N*-Diethyl-2-methoxy-6-[(trimethylsilyl)methyl]benzamide (33a). According to procedure A, a solution of benzamide **32a** (4.12 g, 18.6 mmol), *s*-BuLi (15.7 mL of a 1.3 M solution, 20.5 mmol), and TMEDA (3.2 mL, 20.5 mmol) was treated with TMSCl (7.2 mL, 55.9 mmol). Standard workup followed by MPLC afforded 3.68 g (80%) of **33a** as a colorless oil: bp 110–112 °C (0.05 mm); IR (neat) ν(max) 1639 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.06 (s, 9 H), 1.04 (t, J = 7 Hz, 3 H), 1.26 (t, J = 7 Hz, 3 H), 2.00 (s, 2 H), 3.25–3.75 (m, 4 H), 3.79 (s, 3 H), 6.59–6.73 (m, 2 H), 7.08–7.29 (m, 1 H); MS m/e (rel intensity) 293 (M^+, 7), 279 (26), 278 (100), 262 (51), 193 (26), 149 (44), 73 (71).

Anal. Calcd for $C_{16}H_{27}NO_2Si$: C, 65.47; H, 9.27; N, 4.77. Found: C, 65.41; H, 9.37; N, 4.75.

***N,N*-Diethyl-3-chloro-2-[(trimethylsilyl)methyl]benzamide (33b).** According to procedure A, a solution of benzamide **32b** (8.22 g, 36.4 mmol), *s*-BuLi (31.5 mL of a 1.3 M solution, 40 mmol), and TMEDA (6 mL, 40 mmol) was treated with TMSCl (13.9 mL, 109 mmol). Workup in the usual manner followed by short-path distillation afforded 8.96 g (83%) of **33b** as a colorless viscous oil: bp 114–116 °C (0.05 mm); IR (neat) ν(max) 1637 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.05 (s, 9 H), 1.04 (t, J = 7 Hz, 3 H), 1.25 (t, J = 7 Hz, 3 H), 1.99 (d, J = 13.2 Hz, 1 H), 2.46 (d, J = 13.2 Hz, 1 H), 3.06–3.15 (m, 2 H), 3.23–3.32 (m, 1 H), 3.76–3.84 (m, 1 H), 7.02–7.07 (m, 2 H), 7.30–7.34 (m, 1 H); MS m/e (rel intensity) 297 (M^+, 5), 284 (38), 283 (21), 282 (100), 153 (21).

Anal. Calcd for $C_{15}H_{24}ClNOSi$: C, 60.48; H, 8.36; N, 4.70. Found: C, 60.45; H, 8.13; N, 4.49.

***N,N*-Diethyl-3-methoxy-2-[(trimethylsilyl)methyl]benzamide (33c).** According to procedure A, a solution of benzamide **32c** (2.54 g, 13.3 mmol), *s*-BuLi (11.5 mL of a 1.3 M solution, 14.9 mmol), and TMEDA (2.2 mL, 14.9 mmol) was treated with TMSCl (5.6 mL, 43.8 mmol). Workup in the usual manner followed by MPLC afforded 2.65 g (68%) of **33c** as a colorless oil: bp 110–112 °C (0.03 mm); IR (neat) ν(max) 1636 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.19 (s, 9 H), 1.29 (t, J = 7 Hz, 3 H), 1.49 (t, J = 7 Hz, 3 H), 2.14 (br, 1 H), 2.38 (br, 1 H), 3.38 (q, J = 7 Hz, 2 H), 3.52 (br, 2 H), 4.05 (s, 3 H), 6.94–7.52 (m, 3 H); MS m/e (rel intensity) 292 (M^+, 20), 279 (22), 278 (100), 149 (21), 73 (28).

Anal. Calcd for $C_{16}H_{27}NO_2Si$: C, 65.47; H, 9.27; N, 4.77. Found: C, 65.82; H, 9.45; N, 4.61.

Preparation of Amide Alcohols 34a–d. *N,N*-Diethyl-2-(2′-hydroxy-2′-phenylethyl)benzamide (34a). To a solution of benzamide **16** (850 mg, 3.2 mmol) and freshly distilled benzaldehyde (0.7 mL, 6.4 mmol) in anhydrous THF (20 mL) was added anhydrous TBAF (3.5 mL, 3.5 mmol, 1 M in THF), and the resulting yellow solution was stirred at ambient temperature under argon overnight. Workup in the usual manner followed by MPLC afforded 749 mg (79%) of **34a** as a nondistillable viscous oil: IR (neat) ν(max) 3323, 1610 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.02 (t, J = 7 Hz, 3 H), 1.27 (t, J = 7 Hz, 3 H), 2.62–3.71 (m, 6 H), 4.89 (br, 1 H), 5.51 (br, 1 H, exchanged with D_2O), 7.23–7.34 (m, 9 H); MS m/e (rel intensity) 297 (M^+, 1), 191 (48), 190 (49), 178 (20), 176 (44), 119 (72), 118 (100), 90 (92); HRMS calcd for $C_{19}H_{23}NO_2$ 297.1729, found 297.1727.

***N,N*-Diethyl-2-(2′-hydroxy-2′-phenylethyl)-6-methoxybenzamide (34b).** Under the same conditions as those described for the preparation of **34a**, benzamide **33a** (1.43 g, 4.8 mmol), benzaldehyde (1 mL, 10 mmol) in THF (20 mL), and TBAF (6 mL, 6 mmol) gave, after standard workup and MPLC, 714 mg (46%) of **34b** as a viscous oil, which decomposed on attempted distillation: IR (neat) ν(max) 3327, 1610 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.97 (t, J = 7 Hz, 3 H), 1.27 (t, J = 7 Hz, 3 H), 2.59–3.66 (m, 6 H), 3.82 (s, 3 H), 4.74–4.86 (m, 1 H), 5.46 (d, J = 5 Hz, 1 H, exchanged with D_2O), 6.75–7.45 (m, 8 H); MS m/e (rel intensity) 327 (M^+, 1), 221 (63), 206 (100), 190 (20), 149 (89); HRMS calcd for $C_{20}H_{25}NO_3$ 327.18355, found 327.1818.

***N,N*-Diethyl-3-chloro-2-(2′-hydroxy-2′-phenylethyl)-benzamide (34c).** Use of benzamide **33b** (1.48 g, 4.9 mmol) and benzaldehyde (1 mL, 10 mmol) in THF (40 mL) and TBAF (6 mL, 6 mmol) under the conditions described for the preparation of **34a** afforded, after standard workup and MPLC, 1.4 g (85%) of **34c** as an off-white solid: mp 88.5–90 °C (hexane); IR ($CHCl_3$) ν(max) 3316, 1607 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.04 (t, J = 7 Hz, 3 H), 1.28 (t, J = 7 Hz, 3 H), 2.49–3.69 (m, 6 H), 4.96–5.23 (m, 1 H), 5.77 (d, J = 7 Hz, 1 H, exchanged with D_2O), 7.06–7.55 (m, 8 H); MS m/e (rel intensity) 331 (M^+, 2), 227 (31), 226 (32), 225 (97), 224 (65), 212 (33), 210 (100), 155 (20), 153 (60), 152 (23).

Anal. Calcd for $C_{19}H_{22}ClNO_2$: C, 68.78; H, 6.68; N, 4.22. Found: C, 68.70; H, 6.60; N, 4.11.

***N,N*-Diethyl-2-(2′-hydroxy-2′-phenylethyl)-3-methoxybenzamide (34d).** Under conditions described for the preparation of **33a**, benzamide **33c** (710 mg, 2.4 mmol) and benzaldehyde (0.5 mL, 5 mmol) in THF (20 mL) and TBAF (3 mL, 3 mmol) furnished, after standard workup and MPLC, 651 mg (82%) of **34d** as a viscous oil: bp 170 °C (0.1 mm); IR (neat) ν(max) 3328, 1637 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.02 (t, J = 7 Hz, 3 H), 1.26 (t, J = 7 Hz, 3 H), 2.31–3.63 (m, 6 H), 3.91 (s, 3 H), 4.95 (br, 1 H), 5.62 (d, J = 6 Hz, 1 H, exchanged with D_2O), 6.78–7.46 (m, 8 H); MS m/e (rel intensity) 327 (M^+, 1), 221 (100), 220 (61), 206 (90), 149 (55), 148 (42).

Anal. Calcd for $C_{20}H_{25}NO_3$: C, 73.37; H, 7.70; N, 4.28. Found: C, 73.52; H, 7.48; N, 4.35.

Peterson Olefination. Preparation of Stilbene 35. A solution of benzamide **17** (830 mg, 2.5 mmol) and 3,5-dimethoxybenzaldehyde (900 mg, 5.4 mmol) in anhydrous THF (50 mL) was

treated with TBAF (5.4 mL, 5.4 mmol, 1 M in THF), and the resulting yellow solution was stirred under argon at room temperature for 12 h. Removal of solvent in vacuo followed by standard workup and MPLC afforded 622 mg (74%) of **35** as a viscous oil: IR (neat) ν(max) 1626, 1597 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.97–1.34 (m, 6 H), 3.05–3.18 (m, 3 H), 3.62, 3.80 (2 s, 6 H), 3.82 (br, 1 H), 6.30–6.62 (m, 3 H), 7.01 (d, J = 16.2 Hz, 1 H), 7.10 (d, J = 16.2 Hz, 1 H), 7.14–7.40 (m, 3 H), 7.68 (d, J = 7.6 Hz, 1 H); MS m/e (rel intensity) 339 (M^+, 71), 268 (20), 168 (89), 142 (100), 139 (31).

Preparation of Tetralin Derivative 38. [2-[(Trimethylsilyl)methyl]benzyl]diethylamine (36). A solution of benzamide **16** (3.14 g, 11.9 mmol) in anhydrous THF (50 mL) was treated with BH_3 (60 mL, 60 mmol, 1 M in THF), and the mixture was refluxed under argon for 12 h. Standard workup afforded, after MPLC and short-path distillation, 1.93 g (65%) of **36** as a colorless oil: bp 68–76 °C (0.01 mm); IR (neat) ν(max) 1641 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.00 (s, 9 H), 1.03 (t, J = 7 Hz, 6 H), 2.27 (s, 2 H), 2.51 (q, J = 7 Hz, 4 H), 3.45 (s, 2 H), 6.89–7.36 (m, 4 H); MS m/e (rel intensity) 249 (M^+, 29), 234 (41), 177 (87), 161 (62).

Anal. Calcd for $C_{15}H_{27}NSi$: C, 72.22; H, 10.91; N, 5.61. Found: C, 72.16; H, 10.76; N, 5.85.

[2-[(Trimethylsilyl)methyl]benzyl]diethylmethylammonium Iodide (37). To a solution of amine **36** (3.14 g, 12.6 mmol) in anhydrous hexane (15 mL) was added MeI (4 mL, 67 mmol), and the mixture was stirred at room temperature for 24 h. The colorless crystalline material was collected by filtration and washed with cold hexane to afford 4.65 g (94%) of **37**: mp 122–124 °C; IR ($CHCl_3$) ν(max) 2435 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.02 (s, 9 H), 1.47 (t, J = 7 Hz, 6 H), 2.38 (s, 2 H), 3.15 (s, 3 H), 3.56–3.86 (m, 4 H), 4.65 (s, 2 H), 7.06–7.59 (m, 4 H); MS m/e (rel intensity) 289 (6), 249 (17), 234 (22), 177 (100).

Anal. Calcd for $C_{16}H_{30}INSi$: C, 49.10; H, 7.73; N, 3.58. Found: C, 49.14; H, 7.43; N, 3.58.

2-Carbomethoxy-1,2,3,4-tetrahydronaphthalene (38). To a solution of the salt **37** (624 mg, 1.6 mmol) and freshly distilled methyl acrylate (0.4 mL, 4.5 mmol) in anhydrous CH_3CN was added CsF (250 mg, 1.7 mmol), and the mixture was refluxed for 5 h under argon. The mixture was cooled, diluted with Et_2O (50 mL), and subjected to filtration to remove excess CsF. Evaporation to dryness followed by standard workup and MPLC afforded 256 mg (85%) of **38**[19f] as a colorless oil: IR (neat) ν(max) 1736 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.77–1.93 (m, 1 H), 2.16–2.26 (m, 1 H), 2.71–2.92 (m, 3 H), 3.01 (d, J = 8 Hz, 2 H), 3.73 (s, 3 H), 7.10 (s, 4 H); MS m/e (rel intensity) 190 (M^+, 27), 131 (39), 130 (100), 129 (27).

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Supplementary Material Available: Tables listing important bond lengths, bond angles, C–H bonds, least-squares planes, atomic coordinates, H-atom coordinates, and anisotropic thermal parameters for **30** (7 pages); table of structure factors for **30** (11 pages). Ordering information is given on any current masthead page.