JOC*Note*

Synthesis of Alkylated Aminofluorenes by Palladium-Catalyzed Substitution at Halofluorenes†

Ginagunta Saroja, Zhang Pingzhu, Nikolaus P. Ernsting, and Jürgen Liebscher*

Department of Chemistry, Humboldt University, Brook-Taylor Strasse 2, 12489 Berlin, Germany

liebscher@chemie.hu-berlin.de

Received August 16, 2003

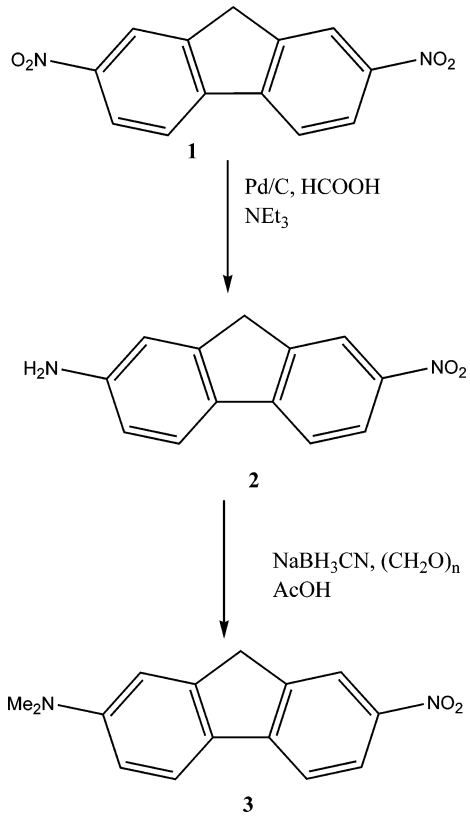
Abstract: New N-substituted 2-amino-9,9-dialkylfluorenes optionally bearing electron-withdrawing substituents such as nitro or cyano in position 7 can be synthesized starting from 2-halo-9,9-dialkylfluorenes by Pd-catalyzed substitution with amines. Chiral amino groups can be introduced by this method too. 2-*N*,*N*-Dimethylamino-7-nitro-9*H*-fluorene was obtained in a convenient way by reductive amination. The *N*-substituted 2-amino-7-nitro-9*H*-fluorenes are promising candidates for fluorescence probes for femtosecond solvation dynamics.

p,*p*′-Aminonitrofluorene (ANF, IUPAC name: 7-nitro-9*H*-fluoren-2-amine) was found to be a faithful probe for investigation of dynamics in liquid acetonitrile by femtosecond measurements.[1] We follow up the target to develop modified ANFs useful as solvation probes in a variety of environments, biopolymers included.

The only members in this series which have been described so far are 2-(dimethylamino)-7-nitrofluorene **3**,[2] 2-(dimethylamino)-9,9-dimethyl-7-nitrofluorene,[3] and 2-(dimethylamino)-fluorene-7-carbonitrile.[4] Generally, the products were obtained by methylation of the corresponding aminofluorenes, but in some cases experimental procedures were not provided. Since the known synthesis of 2-(dimethylamino)-7-nitrofluorene **3** gave an unsatisfactory yield, we developed a more useful route by reductive amination with paraformaldehyde. The starting 2-amino-7-nitrofluorene **2** was so far reductively available from 2,7-dinitrofluorene **1** with $(NH_4)_2S$.[5] The Pd-catalyzed reduction with formic acid turned out to be a more useful way as far as reaction conditions and yields are concerned (Scheme 1).

Aromatic substitution of halides in halofluorenes by amines is another, more versatile option. For benzene derivatives, such substitutions are possible by addition/elimination pathway if the ring is activated by an electron-withdrawing group such as nitro or cyano,

SCHEME 1



eventually under high-pressure conditions.[6] A more versatile method to introduce amino groups into arenes is the Buchwald−Hartwig reaction, i.e., the Pd-catalyzed substitution of halide in haloarenes.[7−12] This reaction does not require activating substituents attached to the ring. It was successfully applied to introduce arylamines into fluorenes.[13] 9,9-Didecyl-2-nitro-7-diphenylaminofluorene was synthesized by Cu-mediated Ullmann reaction.[14]

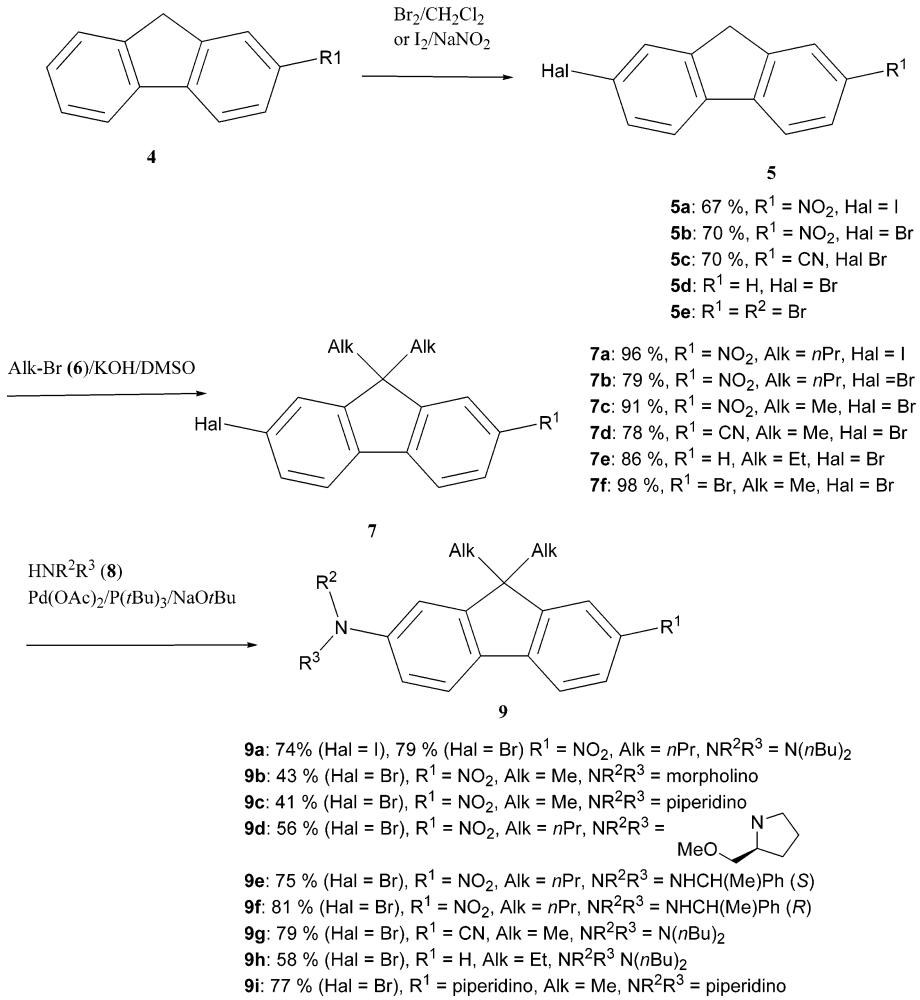
Our effort concentrated on the introduction of alkylamines into fluorenes. We applied high-pressure conditions (10 kbar, neat) or Pd-catalysis [$Pd(OAc)_2$, $P(t\text{-}Bu)_3$ and NaO-*t*-Bu in toluene at 100 °C] to achieve the envisaged substitution of halide in 2-bromo- and 2-iodo-7-nitrofluorene by dibutylamine, but unreacted starting materials were recovered. We suppose that the acidity at position 9 could be responsible for the failure of the substitution. Deprotonation of this position by a basic

† Dedicated to Prof. Dr. Wolfgang Steglich on the occasion of his 70th birthday.

(1) Ruthmann, J.; Kovalenko, S. A.; Ernsting, N. P.; Ouw, D. *J. Chem. Phys.* **1998**, *109*, 5466.
(2) Fletcher, T. L.; Namkung, M. J. *J. Org. Chem.* **1958**, *23*, 680.
(3) van Walree, C. A.; Maarsman, A. W.; Marsman, A. W.; Flipse, M. C.; Jenneskens, L. W.; Smeets, W. J. J.; Spek, A. L. *J. Chem. Soc., Perkin Trans. 2* **1997**, 809.
(4) Maus, M.; Rettig, W.; Bonafoux, D.; Lapouyade, R. *J. Phys. Chem. A* **1999**, *103*, 3388.
(5) Cui, X.-S.; Bergman, J.; Moller, L. *Mutat. Res. Genetic Toxicol.* **1996**, *369*, 147.
(6) Ibata, T.; Isogami, Y.; Toyoda, J. *Bull. Chem. Soc. Jpn.* **1991**, *64*, 42.
(7) Wolfe, J. P.; Wagaw, S.; Mascoux, J.-F.; Buchwald, S. L. *Acc. Chem. Res.* **1998**, *31*, 805.
(8) Hartwig, J. B. *Synlett* **1997**, 329.
(9) Hartwig, J. B. *Pure Appl. Chem.* **1999**, *71*, 1417
(10) Prim, D.; Campagne, J-M.; Joseph, D.; Andrioletti, B. *Tetrahedron* **2002**, *58*, 2041.
(11) Littke, A.; Fu, G. C. *Angew. Chem., Int Ed.* **2002**, *41*, 4176.
(12) Schnyder, A.; Indolese, A. F.; Studer, M.; Blaser, H.-U. *Angew. Chem., Int Ed.* **2002**, *41*, 3668.
(13) Wong, K.-T.; Wang, Z.-J.; Chien, Y.-Y.; Wang, C.-L. *Org. Lett.* **2001**, *3*, 2285.
(14) Belfield, K. D.; Schafer, K. J.; Mourad, W.; Reinhardt, B. A. *J. Org. Chem.* **2000**, *65*, 4475.

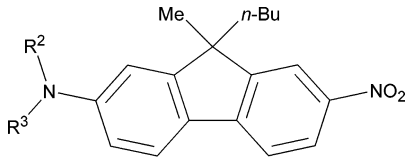
10.1021/jo035204n CCC: $27.50
Published on Web 01/07/2004

SCHEME 2



reactant (amine **8**) or reagent (NaO-*t*-Bu) generates the corresponding fluorenyl anion which is deactivated in nucleophilic substitution reactions. In this context, it is worth mentioning that 2-bromo-9,9-dialkylfluorene-7-boronic acids can undergo Pd-catalyzed Suzuki-reactions.[15,16] The new route which we followed here (Scheme 2) therefore started with blocking the acidic position 9 of 7-acceptor-substituted 2-halofluorenes **5** by dialkylation adapting known procedures.[14] The resulting 2-halo-9,9-dialkylfluorenes **7** reacted with secondary aliphatic amines in the presence of $Pd(OAc)_2$, tri-*tert*-butylphosphine, and NaO-*t*-Bu to afford the target aminofluorenes **9**. Iodide and bromide could be used as leaving groups. The synthesis tolerates various substituents in position 7 of the 2-bromofluorenes and varying chain lengths of the alkyl substituents in position 9. In the case of 2,7-dibromo-9,9-dimethylfluorene **7f**, both bromo atoms are replaced by di(*n*-butyl)amine under these conditions. For future use of products **9** to probe the ultrafast dynamics of polar environments it is particularly interesting that also optically active 2-amino-7-nitro-9,9-dialkyl-9*H*-fluorenes **9d**, **9e**, and **9f** could be synthesized when (*S*)-*O*-methylprolinol, (*R*)-phenethylamine, or (*S*)-phenethylamine, respectively, were applied. Such optically active donor−acceptor-substituted fluorescence probes can be expected to respond to the chirality of the environment under investigation. It should be mentioned that formation of products **9e** and **9f** proves that the Pd-catalyzed substitution can also be applied to primary amines.

In a similar manner, chiral 2-amino-7-nitro-9*H*-fluorenes **10** with two different substituents at position 9 were obtained by reaction of the corresponding 9-(*n*-butyl)-2-iodo-9-methyl-7-nitro-9*H*-fluorene with amines. The phenethylamino derivative **10b** obtained with (*S*)-phenethylamine was formed as a diastereomeric mixture. Compound **10b**, after separation of the diastereomers, is interesting for the further transformation into optically active *N*-unsubstituted 2-amino-9-(*n*-butyl)-9-methyl-7-nitro-9*H*-fluorene by reductive removal of the phenethyl substitutent and thus giving access to fluorenes where



10a: 78% $NR^2R^3 = N(nBu)_2$
10b: 54 % NR^2R^3 = NHCH(Me)Ph (*S*)

(15) Rehan, M.; Schlüter, A.-D.; Wegner, G.; Feast, W. *J. Polymer* **1989**, *30*, 1054.
(16) Schlüter, A.-D. *J. Polym. Sci. Part A., Polymer Chem.* **2001**, *32*, 1533.

the chirality center is not found at the amine substituent but at the fluorene ring.

In summary, Pd-catalyzed substitution of 2-halo-9,9-dialkylfluorenes gives straightforward access to donor−acceptor-substituted fluorenes whose polarity and solubility can easily be tuned by the length of the alkyl substituents at the amino group and at position 9. Optically active fluorenes are also accessible in this way. Long lipophilic substituents can be expected to serve as anchors to fix such fluorenes in membranes, micelles, and vesicles, allowing femtosecond dynamic polarity measurements in close proximity of such supramolecular assemblies. Detailed physicochemical investigations of these products are currently underway. Preliminary femtosecond measurements with 2-(dimethylamino)-7-nitrofluorene show that N-alkylated aminofluorenes should be better probes of solvation dynamics than the parent 2-amino-7-nitrofluorene, mainly by virtue of a larger Stokes shift. [17]

Experimental Section

7-Nitro-9*H*-fluoren-2-ylamine (2). A mixture of 2,7-dinitrofluorene (4 g, 0.015 mol), 10% palladium on carbon (0.25 g), and triethylamine (20 mL, 0.14 mol) was placed in a two-necked round-bottomed flask which was equipped with a reflux condenser. The mixture was heated to boiling, and formic acid (3.06 g, 2.56 mL, 0.067 mol) was added dropwise with stirring. The mixture was boiled for about 30−40 min. The reaction mixture turned a dark reddish color a few minutes after addition of formic acid. After, the reaction mixture was cooled, dichloromethane was added and the catalyst was removed by filtration. The solvent and excess triethylamine were removed under reduced pressure, and the reddish residue was chromatographed on silica gel with dichloromethane to give a bright red solid of 1.94 g (57% yield): mp 228−230 °C (lit.[18] mp 232 °C); ^{1}H NMR (DMSO-d_6) δ 3.93 (s, 2H), 5.74 (s, 2H), 6.71 (d, J = 7.9 Hz, 1H), 6.85 (s, 1H), 7.74 (d, J = 8.3 Hz, 1H), 7.82 (d, J = 8.7 Hz, 1H), 8.23 (d, J = 7.9 Hz, 1H), 8.31 (s, 1H). Anal. Calcd for $C_{13}H_{10}N_2O_2$: C, 69.02; H, 4.46; N, 12.38. Found: C, 69.04; H, 4.32; N, 12.09.

***N*,*N*-Dimethyl-(7-nitro-9*H*-fluoren-2-yl)amine (3).** To the stirred mixture of 7-nitro-9*H*-fluoren-2-ylamine (100 mg, 0.442 mmol) and paraformaldehyde (148 mg, 0.005 mmol) in 99% glacial acetic acid (4 mL) at 25 °C under argon was added $NaCNBH_3$ (140 mg, 2.25 mmol) in one portion. The resulting mixture was stirred at 25 °C for 24 h and then poured into cold water. A bright orange-red solid precipitated. It was filtered off and recrystallized from MeCN/water: yield 91 mg (81%); ^{1}H NMR ($CDCl_3$) δ 3.05 (s, 6H), 3.88 (s, 2H), 6.75 (dd, J_1 = 2.6 Hz, J_2 = 2.2 Hz, 1H), 6.89 (d, J = 1.9 Hz, 1H), 7.61 (d, J = 8.7 Hz, 1H), 7.67 (d, J = 8.7 Hz, 1H), 8.22 (d, J = 8.7 Hz, 1H), 8.26 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 36.9 (CH_2), 40.6 (CH_3), 108.2 (CH), 111.7 (CH), 117.7 (CH), 120.1 (CH), 122.2 (CH), 123.5 (CH), 128.1 (C), 142.2 (C), 144.2 (C), 147.2 (C), 149.2 (C), 151.4 (C). Anal. Calcd for $C_{15}H_{14}N_2O_2$: C, 70.85; H, 5.55; N, 11.02. Found: C, 70.36; H, 5.85; N, 10.70.

2-Amino-9,9-dialkylfluorenes 9 and 10: General Procedure. To a solution of 2-bromo- or 2-iodo-9,9-dialkyl-9*H*-fluorene **7** (2 mmol) or 2-iodo-9-(*n*-butyl)-9-methyl-7-nitro-9*H*-fluorene (2 mmol), the corresponding amine **8** (4 mmol), and NaO-*t*-Bu (520 mg, 5 mmol) in dry toluene (16 mL) were added $Pd(OAc)_2$ (26 mg, 1 mmol) and tri-*tert*-butylphosphine (80 mg, 0.4 mmol) under argon atmosphere. The solution was heated to 100 °C under inert conditions for 15 h (6h for **9a**), during which time the color changed to reddish brown. After being cooled to rt, the mixture was mixed with AcOEt (50 mL) and washed with brine (100 mL). The organic layer was dried over $MgSO_4$, filtered, and concentrated. The crude product was purified by column chromatography on silica gel with AcOEt/hexanes = 1:5) affording the products as crystalline or glassy material.

2-Dibutylamino-7-nitro-9,9-di(*n*-propyl)-9*H*-fluorene (9a). The dark red product **9a** was obtained in 74% yield starting from iodo compound **7a** and in 73% starting from bromo compound **7b**: ^{1}H NMR ($CDCl_3$) δ 0.69 (m, 10H). 0.98 (t, J = 7.2 Hz, 6H), 1.36 (t, J = 7.2 Hz, 2H), 1.43 (t, J = 7.5 Hz, 2H), 1.62 (m, 4H), 1.93 (m, 4H), 3.36 (t, J = 7.5 Hz, 4H), 6.56 (d, J = 2.3 Hz, 1H), 6.65 (d, J = 8.3 Hz, 1H), 7.52 (d, J = 8.3 Hz, 1H), 7.56 (d, J = 8.3 Hz, 1H), 8.11 (d, J = 2.3 Hz, 1H), 8.18 (d, J_1 =8.3 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 14.0 (CH_3), 14.4 (CH_3), 17.1 (CH_2), 20.4 (CH_2), 29.4 (CH_2), 42.7 (CH_2), 51.0 (CH_2), 55.3 (C), 105.4 (CH), 111.1 (CH), 117.3 (CH), 117.9 (CH), 122.3 (CH), 123.7 (CH), 126.3 (C), 144.8 (C), 149.0 (C), 149.6 (C), 150.4 (C), 154.6 (C); MS (CI) m/z 422 (M^+, 59), 379 (100). Anal. Calcd for $C_{27}H_{38}N_2O_2$: C, 76.74; H, 9.06; N, 6.63. Found: C, 77.10; H, 9.06; N, 6.52.

9,9-Dimethyl-2-morpholino-7-nitro-9*H*-fluorene (9b). The dark red product **9b** was obtained in 43% yield starting from the bromo compound **7c**: mp 120−125 °C; ^{1}H NMR ($CDCl_3$) δ 1.51 (s, 6H, CH), 3.29 (t, J = 4.89 Hz, 4H, CH_2), 3.90 (t, J = 4.89 Hz, 4H, CH_2), 6.96 (dd, J = 6.8 Hz, 1H, CH), 6.94 (dd, J = 8.3 Hz, 1H, CH), 7.66 (d, J = 6.8 Hz, 1H, CH), 7.66 (t, 1H, J = 8.3 Hz, CH), 8.22 (dd, 2H, J = 6.8 Hz, CH); ^{13}C NMR ($CDCl_3$) δ 26.99 (CH_3), 47.20 (C), 49.01 (CH_2), 66.79 (CH_2), 109.24 (CH), 114.75 (CH), 118.10 (CH), 118.76 (CH), 122.39 (CH), 123.65 (CH), 128.62 (C), 146.00 (C), 146.13 (C), 152.69 (C), 153.90 (C), 156.98 (C). Anal. Calcd for $C_{19}H_{20}N_2O_3$: C, 70.35; H, 6.21; N, 8.64; O, 14.80. Found: C, 70.16; H, 6.26; N, 8.37.

9,9-Dimethyl-7-nitro-2-piperidino-9*H*-fluorene (9c). The dark red product **9c** was obtained in 41% yield starting from the bromo compound **7c**: mp 136−139 °C; ^{1}H NMR ($CDCl_3$) δ 1.49 (s, 6H, CH_3), 1.64 (m, 2H CH_2), 1.74 (m, 4H, CH_2), 3.30 (t, J = 5.25 Hz, 4H, CH_2), 6.97 (m, 2H, CH), 7.62 (q, 2H, CH), 8.2 (dd, J = 7.1 Hz, CH); ^{13}C NMR ($CDCl_3$) δ 24.3 (CH_2), 25.7 (CH_2), 27.0 (CH_3), 47.1 (C), 50.2 (CH_2), 109.6 (CH), 115.2 (CH), 118.0 (CH), 118.4 (CH), 122.3 (CH), 123.7 (CH), 127.4 (C), 145.7 (C), 146.5 (C), 153.4 (C), 153.8 (C), 157. (C); MS (CI) m/z 322 (M^+, 62), 224 (100). Anal. Calcd for $C_{20}H_{22}N_2O_2$: C, 74.51; H, 6.88; N, 8.69. Found: C, 73.84; H, 6.66; N, 8.43.

2-[(2*S*)-2-(Methoxymethyl)-1-pyrrolidino]-7-nitro-9,9-di(*n*-propyl)-9*H*-fluorene (9d). The deeply orange product **9d** was obtained in 56% yield starting from the bromo compound **7b**: mp 51−53 °C; $[\alpha]^{21}_D$ = −131 (c 0.1, CH_2Cl_2); ^{1}H NMR ($CDCl_3$) δ 0.68 (m, 10H, CH, CH_3), 1.99 (m, 8H, CH_2), 3.27 (t, 2H, J = 8.3 Hz, CH_2), 3.30 (s, 3H, CH_3), 3.53 (m, 2H, CH_2), 4.00 (d, 1H, J = 3.8 Hz, CH), 6.59 (d, 1H, J = 1.9 Hz, CH), 6.67 (dd, 1H, J = 8.3 Hz, CH), 7.54 (d, J = 8.3 Hz, 1H, CH), 7.59 (d, 1H, J = 8.3 Hz, CH), 8.11 (d, 1H, J = 2.3 Hz, CH), 8.19 (dd, 1H, J = 8.3 Hz, CH); ^{13}C NMR ($CDCl_3$) δ 14.4 (CH_3), 17.1 (CH_2), 17.1 (CH_2), 23.2 (CH_2), 28.9 (CH_2), 42.7 (CH_2), 48.7 (CH_2), 55.4 (C), 58.4 (CH_3), 59.2 (CH), 73.0 (CH_2), 106.0 (CH), 11.6 (CH), 117.4 (CH), 117.9 (CH), 122.3 (CH), 123.7 (CH), 127.2 (C), 145.1 (C), 148.8 (C), 148.9 (C), 150.5 (C), 1547 (C); HRMS calcd for $C_{25}H_{32}N_2O_2$ 408.24129, found 408.24124.

7-Nitro-2-[(*R*)-1-phenylethylamino]-9,9-dipropyl-9*H*-fluorene (9e). The red product **9e** was obtained in 75% yield starting from the bromo compound **7b**: mp 49−51 °C; ^{1}H NMR ($CDCl_3$) δ 0.43 (m, 2H) 0.52 (m, 3H), 0,67 (m, 5H), 1.59 (t, 3H, J = 6.8 Hz, CH_3), 1.64 (m, 1H, CH_2), 1.84 (m, 3H, CH_2), 4.42 (s, 1H, CH), 4.61 (q, 1H, J = 6.8 Hz, CH), 6.41 (d, 1H, J = 1.9 Hz, CH), 6.55 (dd, 1H, J = 8.3 Hz, CH), 7.22 (m, 1H, J = 6.8 Hz, CH), 7.30 (d, 1H, J = 7.9 Hz, CH), 7.33 (d, 2H, J = 6.9 Hz, CH), 7.36 (d, 1H, J = 6.4 Hz, CH), 7.48 (t, 2H, CH), 8.06 (d, 1H, J = 1.9 Hz, CH), 8.15 (dd, 1H, J = 8.3 Hz, CH); ^{13}C NMR ($CDCl_3$) δ 14.2 (CH_3), 14.4 (CH_3), 16.9 (CH_2), 17.1 (CH_2), 24.8 (CH_3), 42.4 (CH_2), 42.5 (CH_2), 53.5 (CH), 55.2 (C), 107.6 (CH), 113.1 (CH), 117.6 (CH), 117.9 (CH), 122.2 (CH), 123.6 (CH), 125.8 (CH), 127.0 (CH), 128.7 (CH), 128.3 (C), 144.4 (C), 145.3 (C), 148.6 (C), 150.6 (C), 154.4 (C). HRMS calcd for $C_{27}H_{30}N_2O_2$ 414.23073, found 414.23069. Anal. Calcd for $C_{27}H_{30}N_2O_2$: C, 78.23; H, 7.29; N, 6.76. Found: C, 77.80; H, 7.49; N, 6.55.

(17) Saroja, G.; Lustres, L.; Ernsting, N. P.; Liebscher, J. Manuscript in preparation.

(18) Fletcher, T. L.; Namkung, M. J. *J. Org. Chem.* **1960**, *25*, 740.

7-Nitro-*2*-[(*S*)-1-phenylethylamino]-9,9-dipropyl-9*H*-fluorene (9f). The red product **9e** was obtained in 81% yield starting from the bromo compound **7b**: mp 48−50 °C; $[\alpha]^{21}_D$ = −188 (*c* 0.1, CH_2Cl_2); ^{1}H NMR ($CDCl_3$) δ 0.40 (m, 2H), 0.5 (m, 3H), 0.67 (m, 5H), 1.58 (t, *J* = 6.8 Hz, 3H), 1.79 (m, 1H), 1.83 (m, 3H), 4.42 (s, 1H), 4.61 (q, *J* = 6.8 Hz, 1H), 6.41 (d, *J* = 2.1 Hz, 1H), 6.55 (t, *J* = 8.3 Hz, 1H), 7.22 (m, 1H), 7.30 (d, *J* = 2.9 Hz, 1H), 7.36 (m, 3H), 7.48 (t, *J* = 8.3 Hz, 2H), 8.06 (d, *J* = 2.1 Hz, 1H), 8.15 (dd, J_1 = 8.3 Hz, J_2 = 2.1 Hz, 1H); ^{13}C NMR ($CDCl_3$) 14.2 (CH_3), 14.4 (CH_3), 16.9 (CH_2), 17.1 (CH_2), 24.8 (CH_3), 42,4 (CH_2), 42.5 (CH_2), 53.5 (CH), 55.2 (C), 107.6 (CH), 113.1 (CH), 117.6 (CH), 117.9 (CH), 122.2 (CH), 123.6 (CH), 125.8 (CH), 127.0 (CH), 128.3 (C), 128.7 (C), 144.4 (C), 145.3 (C), 148.7 (C), 150.7 (C), 154.4 (C). Anal. Calcd for $C_{27}H_{30}N_2O_2$: C 78.23; H, 7.29; N, 6.76. Found: C, 78.16; H, 7.59; N, 6.37.

2-Dibutylamino-7-cyano-9,9-dimethyl-9*H*-fluorene (9g). The deeply orange product **9g** was obtained in 79% yield starting from bromo compound **7d**: ^{1}H NMR ($CDCl_3$) δ 0.98 (t, 6H, *J* = 7.5 Hz, CH_3), 1.40 (m, 4H, CH_2), 1.44 (s, 6H, CH_3), 1.61 (m, 4H, CH_2), 3.34 (t, *J* = 7.5 Hz, 4H, CH_2), 6.64 (m, 2H, CH), 7.53 (m, 4H, CH); ^{13}C NMR ($CDCl_3$) δ 14.0 (CH_3), 20.3 (CH_2), 27.1 (CH_3), 29.4 (CH_2), 46.8 (C), 51.0 (CH_2), 105.0 (CH), 106.8 (C), 110.9 (CH), 118.4 (CH), 122.1 (CH), 124.6 (C), 125.7 (CH), 131.5 (CH), 144.9 (C), 149.4 (C), 153.0 (C), 156.3 (C). Anal. Calcd for $C_{24}H_{30}N_2$: C, 83.19; H, 8.73; N, 8.08. Found: C, 80.99; H, 8.33; N, 7.78.

2-Dibutylamino-9,9-diethyl-9*H*-fluorene (9h). The product **9h** was obtained as brownish oil in 58% yield starting from the bromo compound **7e**: ^{1}H NMR ($CDCl_3$) δ 0.37 (t, 6H, CH_3), 0.96 (t, *J* = 7.2 Hz, CH_2), 1.33 (m, *J* = 6.8 Hz, 2H, CH_2), 1.38 (m, 2H, *J* = 7.2 Hz, CH_2), 1.58 (m, 2H, CH_2), 1.95 (m, 4H, CH_2), 3.30 (t, 4H, CH_2), 6.61 (d, *J* = 11.7 Hz, 1H, CH), 7.13 (t, *J* = 7.2 Hz, 1H, CH), 7.22 (t, *J* = 7.2 Hz, 2H, CH), 7.24 (d, *J* = 7.2 Hz, CH_2), 7.54 (t, *J* = 7.9 Hz, 2H, CH); ^{13}C NMR ($CDCl_3$) δ 8.6 (CH_3), 14.0 (CH_3), 20.4 (CH_2), 29.5 (CH_2), 33.0 (CH_2), 51.1 (CH_2), 55.7 (C), 106.4 (CH), 110.8 (CH), 117.9 (CH), 120.3 (CH), 122.5 (CH), 124.6 (CH), 126.6 (CH), 129.6 (C), 142.4 (C), 148.2 (C), 148.9 (C), 151.4 (C). Anal. Calcd for $C_{25}H_{35}N$: C, 85.90; H, 10.09; N, 4.01. Found: C, 84.84; H, 9.89; N, 4.03.

9,9-Dimethyl-2,7-dipiperidino-9*H*-fluorene (9i). The product **9i** was obtained as brownish glass in 77% yield starting from the dibromo compound **7f**: mp 137−140 °C; ^{1}H NMR ($CDCl_3$) δ 1.43 (s, 6H, CH_3), 1.58 (m, 4H, $2CH_2$), 1.74 (m, 8H, $4CH_2$), 3.17 (t, *J* = 5.3 Hz, 8H, CH_2), 6.86 (dd, *J* = 8.3 Hz, 2H, CH), 6.99 (d, *J* = 1.9 Hz, 2H, CH), 7.45 (d, *J* = 8.3 Hz, 2H, CH); ^{13}C NMR ($CDCl_3$) δ 24.3 (CH_2), 26.1(CH_2), 27.6 (CH_3), 46,7 (C), 51.6 (CH_2), 111.6 (CH), 115.4 (CH), 119.4 (CH), 131.6 (C), 151.3 (C), 154.4 (C). Anal. Calcd for $C_{25}H_{32}N_2$: C, 83.28; H, 8.95; N, 7.77. Found: C, 81.10; H, 8.98; N, 7.25.

9-(*n*-Butyl)-2-di(*n*-butylamino)-9-methyl-7-nitro-9*H*-fluorene (10a). The product **10a** was obtained as orange glassy material in 78% starting from the 2-iodo precursor: ^{1}H NMR ($CDCl_3$) δ 0.71 (m, 5H), 0.98 (t, 6H), 1.11 (m, 2H, CH_2), 1.39 (m, 4H, $2CH_2$), 1.46 (s, 3H, CH_3), 1.62 (m, 5H), 1.95 (m, 2H, CH_2), 3.36 (m, 4H, $2CH_2$), 6.60 (d, *J* = 1.9 Hz, 1H, CH), 6.65 (dd, J_1 = 2.3 Hz, J_2 = 2.2 Hz, 1H, CH), 8.13 (d, *J* = 1.9 Hz, 1H, CH), 8.18 (dd, J_1 = 8.9 Hz, J_2 = 2.0, 1H, CH); ^{13}C NMR ($CDCl_3$) δ 13.8 (CH_3), 4.0 (CH_3), 20.4 (CH_2), 22.9 (CH_2), 26.4 (CH_2), 26.8 (CH_3), 29.4 (CH_2), 40.4 (CH_2), 50.8 (C), 51.0 (CH_2), 105.3 (CH), 111.1 (CH), 117.1 (CH), 118.0 (CH), 122.5 (CH), 123.8 (CH), 125.3 (C), 145.0 (C), 148.0 (C), 149.6 (C), 151.9 (C), 156.0 (C). Anal. Calcd for $C_{26}H_{36}N_2O_2$: C, 76.43; H, 8.88; N, 6.86. Found: C, 76.00; H, 8.74; N, 6.88.

9-(*n*-Butyl)-9-methyl-7-nitro-*2*-[(*S*)-1-phenylethylamino]-9*H*-fluorene (10b). The deeply orange glass was obtained as diastereomeric mixture in 54% yield from the 2-iodo precursor: ^{1}H NMR ($CDCl_3$) δ 0.32 (m, 1H), 0.51 (t, *J* = 7.1 Hz, 2H), 0.61 (m, 1H), 0.86 (m, 1H), 1.01 (m, 1H), 1.22 (s, 1H), 1.30 (s, 2H), 1.49 (d, *J* = 6.8 Hz, 3H), 1.59 (m, 1H), 1.76 (m, 1H), 4.37 (s, 1H), 4.51 (t, 1H), 6.43 (m, 2H), 7.25 (m, 5H), 8.02 (m, 1H), 8.07 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 13.7 (CH_3), 13.8 (CH_3), 22.8 (CH_2), 22.9 (CH_2), 24.7 (CH_3), 24.9 (CH_3), 26.2 (CH_2), 26.4 (CH_2), 26.5 (CH_3), 26.7 (CH_3), 40.3 (CH_2), 50.7 (C), 53.6 (CH), 107.4 (CH), 112.8 (CH); 113.1 (CH), 117.7 (CH), 117.8 (CH), 117.9 (CH), 118.0 (CH), 122.4 (CH), 122.5 (CH), 123.6 (CH), 125.8 (CH), 125.9 (CH), 127.0 (CH), 127.1 (CH), 127.2 (CH), 128.7 (CH), 128.8 (C), 144.5 (C), 144.6 (C), 145.3 (C), 147.8 (C), 148.8 (C), 149.0 (C), 151.0 (C), 152.1 (C), 155.8 (C), 155.9 (C). Anal. Calcd for $C_{26}H_{28}N_2O_2$: C, 77.97; H, 7.05; N, 6.99. Found: C, 77.79; H, 7.07; N, 6.81.

Acknowledgment. G.S. gratefully acknowledges an Alexander-von-Humboldt scholarship. Z. P. thanks the Service Center for Experts and Scholars of Hebei Province China for sponsoring a scholarship. This work was further supported by the Deutsche Forschungsgemeinschaft, the VW-Foundation, and the Fonds der Chemischen Industrie.

Supporting Information Available: Experimental procedures and spectroscopic data (^{1}H NMR, ^{13}C NMR, MS) of 9*H*-fluorene-2-carbonitrile, compounds **1**, **5b**, **5c**, and 9,9-dialkyl-9*H*-fluorenes **7**. This material is available free of charge via the Internet at http://pubs.acs.org.

JO035204N