Synthesis of 2-[*N*-(9-Phenylfluoren-9-yl)amino]-1-indanones by Anionic Cyclization of Phenylalanine-Derived Oxazolidinones[1]

M. Rita Paleo, Luis Castedo,* and Domingo Domínguez

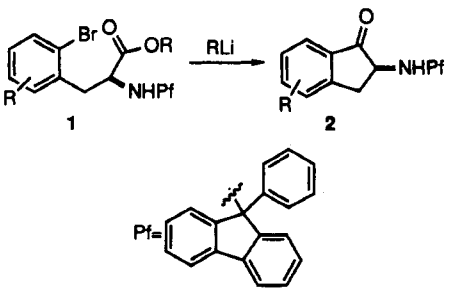
Departamento de Química Orgánica, Facultad de Química, Universidad de Santiago y Sección de Alcaloides del CSIC, 15706 Santiago de Compostela, Spain

Received November 16, 1992

A novel preparation of *N*-(phenylfluorenyl)-2-amino-1-indanones is described. The key step is the cyclization of aryl-substituted *o*-bromophenylalanine-derived oxazolidinones with *n*-BuLi by halogen–metal exchange followed by in situ intramolecular acylation of the aryllithium intermediate. When this method was applied to an optically pure oxazolidinone derived from an amino acid, cyclization occurred with complete retention of the integrity of the chiral center.

Cyclic vicinal amino ketones and amino alcohols are of great interest as medicinal agents and as intermediates in natural product syntheses. In connection with our interest in the development of total syntheses of ribasine alkaloids,[2] we needed an efficient procedure for the preparation of N-protected 2-amino-5,6-(methylenedioxy)-1-indanone. A number of approaches to the synthesis of 2-amino-1-indanones are known, but there is no generally useful method for the preparation of derivatives with substituents on the aryl ring. Chiral 2-amino-1-indanones have been obtained by Friedel–Crafts cyclization of N-protected phenylalanines (*N*-(methoxycarbonyl) or *N*-phthaloyl),[3] but this method is only useful for the synthesis of indanones that have no alkoxy substituents on the aryl ring; cyclization of the methyl ether derived from tyrosine has been unsuccessful[3b] or given poor yields.[3c] Alternatively, racemic 2-aminoindanones with donor substituents on the benzene ring can be prepared as their hydrochloride salts by α-nitrosation of 1-indanones followed by hydrogenation,[4] but this method has not been extended to the synthesis of chiral compounds and cannot be used for the preparation of N-protected 2-aminoindanones, as release of the base from the hydrochloride leads to an extremely labile α-amino indanone which decomposes to highly colored products.[5]

We therefore planned an alternative synthesis of N-protected 2-amino-1-indanones by anionic cyclization of the *o*-bromophenylalanine derivatives **1** by lithium–bromine exchange followed by internal trapping of the lithiated intermediate by the carboxyl group.[6] For this approach to be successful, a nitrogen-protecting group was needed which would both stabilize the labile α-amino ketone group and protect against enolization of the cyclopentanone. Reasoning that these requirements would be well fulfilled by the N-protecting group recently introduced by Rapoport, 9-phenylfluoren-9-yl (Pf),[7] we began studies directed at efficient preparation of the 2-[*N*-(Pf)amino]-1-indanones **2**. Protection of the nitrogen atom by the Pf group would also prevent deprotonation of the α-carbon from interfering with the aminoacylation process.[7]



1 2 (1)

Our first target was 5,6-(methylenedioxy)-2-[*N*-(Pf)-amino]-1-indanone (**2a**), which we needed for the synthesis of ribasine alkaloids. The substrate required for the cyclization was prepared in good yield by alkylation[8] of the glycinate **3** with dibromide **4a**, which after imine hydrolysis gave an 80% yield of the amino ester hydrochloride **5a**. Nitrogen protection was then carried out under the conditions recommended by Rapoport[7] to give the N-protected-amino ester **6a**.

Low-temperature lithium–bromine exchange carried out by treating a cooled THF solution (−95 °C) of the bromide **6a** with various amounts of *t*-BuLi (100–300 M %) produced a mixture of indanol **8a** and recovered starting material (eq 2); surprisingly, no desired aminoindanone was observed, suggesting that cyclization to **2a** was followed by attack by the organolithium reagent. Moreover, the recovery of starting material showed that addition to the

(1) Part of this work was presented at the 203rd American Chemical Society National Meeting, San Francisco, April 1992.

(2) (a) Boente, J. M.; Castedo, L.; Cuadros, R.; Saá, J. M.; Suau, R.; Perales, A.; Martínez-Ripoll, M.; Fayos, J. *Tetrahedron Lett.* **1983**, *24*, 2029. (b) Allais, D. P.; Guinaudeau, H.; Freyer, A. J.; Shamma, M.; Ganguli, N. C.; Talapatra, B.; Talapatra, S. K. *Tetrahedron Lett.* **1983**, *24*, 2445. (c) Boente, J. M.; Campello, M. J.; Castedo, L.; Domínguez, D.; Saá, J. M.; Suau, R.; Vidal, M. C. *Tetrahedron Lett.* **1983**, *24*, 4481. (d) Alonso, R.; Castedo, L.; Domínguez, D. *Tetrahedron Lett.* **1986**, *27*, 3539. (e) Allais, D. P.; Guinaudeau, H. *J. Nat. Prod.* **1990**, *53*, 1280.

(3) (a) McClure, D. E.; Arison, B. H.; Jones, J. H.; Baldwin, J. J. *J. Org. Chem.* **1981**, *46*, 2431. (b) McClure, D. E.; Lumma, P. K.; Arison, B. H.; Jones, J. H.; Baldwin, J. J. *J. Org. Chem.* **1983**, *48*, 2675. (c) Effenberger, F.; Steegmüller, D.; Null, V.; Ziegler, T. *Chem. Ber.* **1988**, *121*, 125. (d) Dornhege, E. *Liebigs. Ann. Chem.* **1971**, *743*, 42.

(4) Rimek, H.-J.; Yupraphat, T.; Zymalkowski, F. *Liebigs Ann. Chem.* **1969**, *725*, 116.

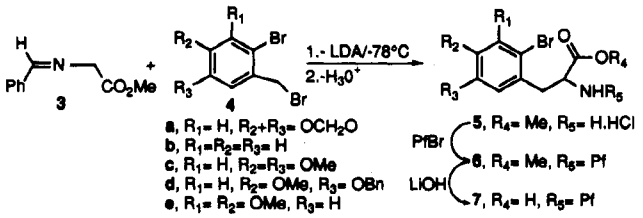
(5) We have carried out the catalytic hydrogenation of 2-hydroximino-5,6-(methylenedioxy)-1-indanone to give the corresponding 2-aminoindanone hydrochloride, but upon attempted acylation under alkaline conditions it decomposed to a dark purple solution.

(6) We have recently reported a related anionic cyclization for the synthesis of phthalides using a carbamate as the internal trapping agent: Paleo, M. R.; Lamas, C.; Castedo, L.; Domínguez, D. *J. Org. Chem.* **1992**, *57*, 2029.

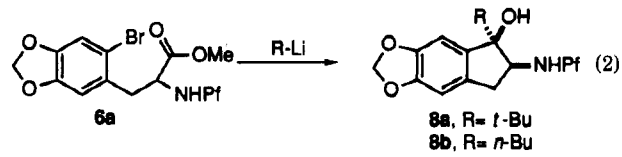
(7) (a) Christie, B. D.; Rapoport, H. *J. Org. Chem.* **1985**, *50*, 1239. (b) Lubell, W. D.; Rapoport, H. *J. Am. Chem. Soc.* **1987**, *109*, 236. (c) Lubell, W. D.; Rapoport, H. *J. Am. Chem. Soc.* **1988**, *110*, 7447.

0022-3263/93/1958-2763$04.00/0

Scheme I



indanone was faster than metal–halogen interchange.[9] Treatment of **6a** with 200 M % of *n*-BuLi led similarly to a mixture of indanol **8b** and **6a** (eq 2); under treatment with 100 M % of *n*-BuLi the starting material was recovered, indicating that kinetic deprotonation of the *N*-(Pf)amine took place in preference to metal–halogen exchange or nucleophilic addition to the ester group.[10]

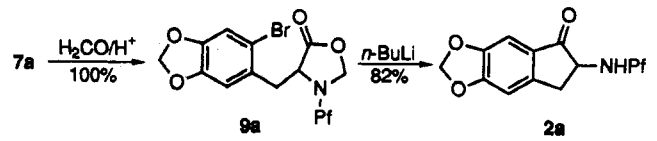


(2)

In an attempt to avoid addition of the organometal to the carbonyl group after the aminoacylation step, we turned our attention to the acid **7a**, reasoning that a lithium carboxylate would act as an internal trap for the arylmetal derivative to give a tetrahedral addition product which would withstand the reaction conditions.[11] The amino acid **7a** (Scheme I) was obtained quantitatively by hydrolysis of **6a** with LiOH.[12] However, treatment of a cold (−95 °C) THF solution of **7a** or its sodium carboxylate with various amounts of *n*-BuLi (200–300 M %) led to complex mixtures from which only a low yield of indanone **2a** could be isolated (12%).[13]

The above results led us to the conclusion that it is necessary to protect the acidic hydrogen of the amine and also to use an acylating group which generates an intermediate that is stable enough to survive until metal–halogen exchange is complete, so as to avoid the formation of the undesired aminoindanols **8**. These two conditions were well fulfilled by converting the amino acid **7a** into the corresponding oxazolidinone **9a**, which can be seen as an N,O-diprotected amino acid. Compound **9a** was obtained quantitatively as a white solid by reaction of **7a** with excess aqueous formaldehyde (37%) and catalytic *p*-TsOH.[14]

The cyclization of the oxazolidinone **9a** required a careful study of the reaction conditions to avoid the formation of the undesired addition product **8b**. Treatment of a THF



(3)

solution of **9a** (0.1 N, the limit of solubility) with just 100 M % of *n*-BuLi (titrated prior to use) at between −95 and −105 °C afforded the desired aminoindanone **2a** in a very good 82% yield. It is worth noting that **2a** is remarkably stable for an indanone substituted by a basic secondary nitrogen at the α-position.[15]

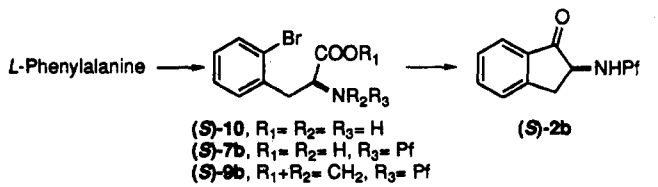
To explore the generality of this process, we have also prepared 2-[*N*-(Pf)amino]-1-indanones **2** with different substitution patterns (see Scheme II and Table I). The oxazolidinones **9** were prepared following the same procedure as for **9a**, with only the substitution pattern of the dibromides **4** being varied (see Scheme I).

The cyclization of the unsubstituted oxazolidinone **9b** is a very clean reaction, as the ^{1}H-NMR of the crude product shows only the signals of the desired product **2b**. The dimethoxy derivative **2c** was also obtained in good yield under the same conditions. Similarly, **2d** was prepared by treatment of **9d** with 115 M % of *n*-BuLi; in this case the yield was 67%, which would probably be improved by protecting the phenoxy group with a group with no acidic protons.[16] Like **9b**, **9e** was obtained in quantitative yield.

The anionic cyclization of **9** is believed to take place by lithium–halogen exchange followed by intramolecular atack on the oxazolidinone carbonyl to give a stable lithium alkoxide, which releases formaldehyde upon workup (Scheme II). This mechanism is reminiscent of the oxazolinone intermediate hypothesized by Rapoport for intramolecular amino acylation reactions between aryl ether Grignards and *N*-(alkoxycarbonyl)alanyl chlorides.[17]

To check whether the integrity of the chiral center is preserved under the cyclization conditions used, we decided to apply the method to the synthesis of (*S*)-**2b**, starting from L-phenylalanine.

Bromination of L-phenylalanine (neat bromine, in vacuum, 24 h, followed by chromatography on Sephadex LH-20)[18] afforded optically active (*S*)-**10**. N-Phenylfluorenylation[7b] under the usual conditions, followed by oxazolidinone formation, occurred uneventfully to give (*S*)-**9b**, which was cyclized under the conditions described for racemic **2b** to give (*S*)-**2b**, $[\alpha]^{20}_D$ = −149° (*c* = 0.7, CH_2Cl_2), in quantitative yield (eq 4). ^{1}H-NMR experi-



(4)

ments with chiral (+)-Eu(hfc)$_3$ shift reagent[19] revealed

(8) (a) Stork, G.; Leong, A. Y. W.; Touzin, A. M. *J. Org. Chem.* **1976**, *41*, 3491. (b) Oguri, T.; Shioiri, T.; Yamada, S.-I. *Chem. Pharm. Bull.* **1977**, *25*, 2287. (c) Bey, P.; Vevert, J. P. *Tetrahedron Lett.* **1977**, *17*, 1455. (d) Bey, P.; Vevert, J.-P.; Dorsselaer, V. V.; Kolb, M. *J. Org. Chem.* **1979**, *44*, 2732.

(9) A recent report shows that lithium–halogen exchange is possible in the presence of a ketone which then acts as an internal trap for the aryllithium: Kihara, M.; Kashimoto, M.; Kobayashi, Y. *Tetrahedron* **1992**, *48*, 67.

(10) Sardina, F. J.; Paz, M. M.; Fernández-Megía, E.; Boer, R. F.; Alvarez, M. P. *Tetrahedron Lett.* **1992**, *33*, 4637.

(11) Anionic cyclization of β-(*o*-bromophenyl)propanoic acid promoted by *n*-BuLi (200 M%) gives a good yield of indanone: (a) Parham, W. E.; Jones, L. D.; Sayed, Y. *J. Org. Chem.* **1975**, *40*, 2394. (b) Boatman, R. J.; Whitlock, B. J.; Whitlock, H. W., Jr. *J. Am. Chem. Soc.* **1977**, *99*, 4822.

(12) Gerspacher, M.; Rapoport, H. *J. Org. Chem.* **1991**, *56*, 3700.

(13) Rapoport has reported unsuccessful attempts at intermolecular aminoacylation of organometallics with *N*-(Pf)-alanine (see ref 7c).

(14) Lubell, W. D.; Jamison, T. F.; Rapoport, H. *J. Org. Chem.* **1990**, *55*, 3511.

(15) We are not aware of any other N-substituted-2-aminoindanones with a basic nitrogen.

(16) (a) Beak, P.; Musik, T. J.; Chen, C. *J. Am. Chem. Soc.* **1988**, *110*, 3538. (b) Gallagher, D. J.; Beak, P. *J. Am. Chem. Soc.* **1991**, *113*, 7984.

(17) Buckley, T. F.; Rapoport, H. *J. Am. Chem. Soc.* **1981**, *103*, 6157.

(18) Faulstich, H.; Smith, H. O.; Zobeley, S. *Liebigs Ann. Chem.* **1973**, 765.

(19) Parker, D. *Chem. Rev.* **1991**, *91*, 1441.

none of the opposite enantiomer, its enantiomeric ratio was >99/1 (the limit of detection), whereas racemic **2b** showed the expected splitting of signals of the two enantiomers. The key to this preservation of chirality is the use of the 9-phenylfluorenyl group for nitrogen protection, since this group is known to hinder deprotonation of the α-carbon.

To sum up, we have developed a novel and preparatively useful approach to the synthesis of 2-[*N*-(Pf)amino]-1-indanones based on the cyclization of a bromophenylalanine oxazolidinone with *n*-BuLi by halogen–metal exchange followed by in situ intramolecular acylation of the aryllithium intermediate. When this method was applied to an optically pure oxazolidinone derived from an amino acid, cyclization occurred with complete preservation of the integrity of the chiral center.

Experimental Section

General Methods. ^1H and ^{13}C NMR spectra were recorded at 250 and 62.83 MHz in $CDCl_3$. Mass spectra were recorded at an ionization voltage of 70 eV. Melting points are uncorrected. All air-sensitive reactions were carried out under dried deoxygenated Ar in oven-dried glassware, with magnetic stirring; reagents were added by syringe through septa. All solvents for air- or moisture-sensitive reactions were dried by standard procedures.[20] The concentration of commercial solutions of *n*-BuLi in hexane (Aldrich) was determined immediately prior to use by titration with diphenylacetic acid.[21]

Dibromide **4b** is commercially available, the known **4a** and **4c** were obtained from commercial piperonyl and veratryl alcohols, respectively, and bromine,[22] and **4d** and **4e** were obtained from the corresponding *o*-bromobenzylic alcohols[6] and HBr/toluene.

Esterification of glycine with methanol saturated with dry hydrochloric acid,[8d] followed by treatment of the intermediate amino ester hydrochloride with benzaldehyde in methylene chloride in the presence of triethylamine and anhydrous $MgSO_4$, afforded the Schiff base methyl ester derivative **3**.[8a]

Preparation of α-Amino Esters 5. General Procedure. A 50-mL round-bottomed flask equipped with a stirring bar, septum cap, and Ar inlet was flame-dried under a stream of dry Ar and then cooled to rt. An LDA solution was prepared by treating diisopropylamine (0.87 mL, 6.16 mmol) in anhydrous THF (1 mL) with *n*-BuLi (1.6 M in hexane, 6.16 mmol) at −78 °C, the cooling bath was removed, and the mixture was stirred for 15 min. The LDA solution was then cooled again to −78 °C, and the Schiff base **3** (1.0 g, 5.6 mmol) was added in THF. The dark orange solution obtained was stirred for 50 min, a solution of the dibromide **4** (5.6 mmol) in anhydrous THF (5 mL) was added, and the resulting mixture was stirred at −78 °C for 1 h, slowly warmed to rt, and stirred for another 4 h. Ice-cold aqueous ammonium chloride ether (10:10 mL) was added, the organic layer was separated, and the aqueous layer was extracted with ether (3 × 5 mL). The combined organic layers were dried with anhydrous Na_2SO_4, and the solvent was evaporated to leave an oil which was immediately partially hydrolyzed to the α-amino ester by treatment with 5% HCl (5 mL) for 1–2 h at rt. Ether was added, and the aqueous layer was separated, treated with solid K_2CO_3 in an ice–water bath till basic, and extracted with CH_2Cl_2 (3 × 10 mL). The organic extract was dried with anhydrous Na_2SO_4, and evaporation of the solvent gave an oil which was treated with HCl-saturated ether to precipitate the hydrochloride **5**. In some cases the final treatment with HCl/ether was not necessary, and addition of a few mL of 5% HCl to the oil gave a solid which was filtered out, dried, and recrystallized from methanol.

Methyl 2-Amino-3-[2-bromo-4,5-(methylenedioxy)phenyl]propanoate Hydrochloride (5a). Recrystallization from methanol gave 1.52 g (80%): mp 197–198 °C; IR (KBr) 1750 cm^{-1}; ^1H NMR (MeOD) δ 3.15 (dd, 1 H, *J* = 14.2, 8.1 Hz), 3.40 (dd, 1 H, *J* = 14.2, 7.2 Hz), 3.82 (s, 3 H), 4.30 (t, 1 H, *J* = 7.6 Hz), 6.04 (s, 2 H), 6.85 (s, 1 H), 7.13 (s, 1 H); ^{13}C NMR (MeOD) δ 37.64, 53.75, 53.94, 103.71, 112.01, 113.98, 116.16, 127.93, 149.55, 150.03, 170.26 (CO).

Scheme II

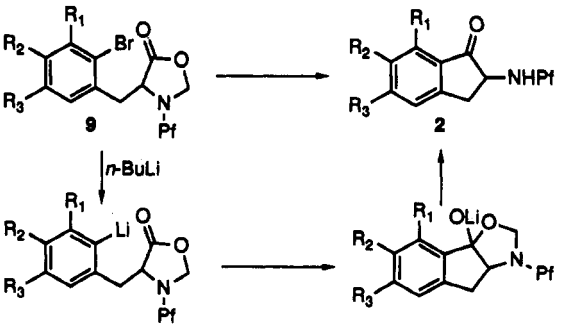


Table I. Cyclization of Oxazolidinones 9 to Aminoindanones 2

	R_1	R_2	R_3	2 (%)	mol % *n*-BuLi
a	H	O	CH_2O	82	100
b	H	H	H	98	105
c	H	OMe	OMe	85	100
d	H	OMe	OBn	67	115
e	OMe	OMe	H	98	105

Methyl 2-Amino-3-(2-bromophenyl)propanoate Hydrochloride (5b). Recrystallization from methanol gave 1.06 g (65%): mp 174–176 °C; IR (KBr) 1745 cm^{-1}; ^1H NMR (MeOD) δ 3.25 (dd, 1 H, *J* = 14.1, 7.7 Hz), 3.44 (dd, 1 H, *J* = 14.1, 7.7 Hz), 3.75 (s, 3 H), 4.34 (t, 1 H, *J* = 7.7 Hz), 7.25 (m, 1 H), 7.37 (m, 2 H), 7.64 (d, 1 H, *J* = 7.7 Hz); ^{13}C NMR (MeOD) δ 37.95, 53.67, 53.82, 125.70, 129.39, 131.03, 132.98, 134.53, 135.26, 170.33 (CO).

Methyl 2-Amino-3-(2-bromo-4,5-dimethoxyphenyl)propanoate Hydrochloride (5c). Recrystallization from 2-propanol–ether gave 1.49 g (75%): mp 200–202 °C; IR (KBr) 1745 cm^{-1}; ^1H NMR (MeOD) δ 3.17 (dd, 1 H, *J* = 14.2, 8.0 Hz), 3.39 (dd, 1 H, *J* = 14.2, 7.2 Hz), 3.79 (s, 3 H), 3.83 (s, 3 H), 3.84 (s, 3 H), 4.31 (t, 1 H, *J* = 7.6 Hz), 6.92 (s, 1 H), 7.17 (s, 1 H); ^{13}C NMR (MeOD) δ 37.46, 53.78, 54.02, 56.84 (2 × OMe), 115.90, 115.98, 117.62, 126.95, 150.61, 151.30, 170.42 (CO).

Methyl 2-Amino-3-[2-bromo-4-methoxy-5-(phenylmethoxy)phenyl]propanoate Hydrochloride (5d). Recrystallization from 2-propanol–ether gave 1.63 g (68%): mp 225–227 °C; IR (KBr) 1745 cm^{-1}; ^1H NMR (MeOD) δ 3.15 (dd, 1 H, *J* = 14.1, 7.8 Hz), 3.34 (dd, 1 H, *J* = 14.1, 7.5 Hz), 3.72 (s, 3 H), 3.85 (s, 3 H), 4.27 (t, 1 H, *J* = 7.6 Hz), 5.10 (s, 2 H), 6.98 (s, 1 H), 7.20 (s, 1 H), 7.31–7.47 (m, 5 H); ^{13}C NMR (MeOD) δ 37.41, 53.72, 54.02, 57.01, 72.72, 116.67, 118.23, 118.88, 127.02, 128.81, 129.15, 129.59, 138.31, 149.60, 152.07, 170.28 (CO).

Methyl 2-Amino-3-(2-bromo-3,4-dimethoxyphenyl)propanoate Hydrochloride (5e). Recrystallization from 2-propanol-ether gave 1.67 g (85%): mp 192–193 °C; IR (KBr) 1745 cm^{-1}; ^1H NMR (MeOD) δ 3.21 (dd, 1 H, *J* = 14.1, 8.1 Hz), 3.42 (dd, 1 H, *J* = 14.1, 7.2 Hz), 3.78 (s, 3 H), 3.83 (s, 3 H), 3.89 (s, 3 H), 4.31 (t, 1 H, *J* = 7.7 Hz), 7.05 (d, 1 H, *J* = 10.1 Hz), 7.06 (d, 1 H, *J* = 10.1 Hz); ^{13}C NMR (MeOD) δ 37.66, 53.70, 53.92, 56.70, 60.81, 113.24, 121.15, 127.71, 127.91, 148.37, 154.98, 170.43 (CO).

Preparation of *N*-(9-Phenylfluoren-9-yl)-α-amino Esters 6. General Procedure. To a stirred suspension of α-amino esters **5** (3 mmol) in dry CH_3CN (5 mL) at rt in a Morton flask were added anhydrous $Pb(NO_3)_2$ (0.74 g, 2.4 mmol) and anhydrous K_3PO_4 (1.3 g, 6.3 mmol) followed by 9-bromo-9-phenylfluorene bromide (1.2 g, 3.75 mmol) in dry CH_3CN (2 mL). The suspension was stirred for 48–96 h and then filtered through Celite, and the residue was washed with CH_2Cl_2 (3 × 15 mL). The solvent of the combined filtrate and washings was evaporated, and the residue was chromatographed (CH_2Cl_2–hexane (1:1)).

Methyl 2-[*N*-(Pf)amino]-3-[2-bromo-4,5-(methylenedioxy)phenyl]propanoate (6a). Recrystallization from CH_2Cl_2–hexane gave 1.46 g (90%): mp 156–157 °C; IR (KBr) 1740 cm^{-1};

(20) Perrin, D. D.; Armarego, W. L. F. *Purification of Laboratory Chemicals*; Pergamon Press: Oxford, 1988.
(21) Kofron, W. G.; Baclawsky, L. M. *J. Org. Chem.* **1976**, *41*, 1879.
(22) Dai-ho, G.; Mariano, P. S. *J. Org. Chem.* **1988**, *53*, 5113.

^{1}H NMR δ 2.70–2.84 (m, 3 H), 3.21 (s, 3 H), 5.95 (d, 1 H, J = 1.3 Hz), 5.97 (d, 1 H, J = 1.3 Hz), 6.60 (s, 1 H), 6.69 (d, 1 H, J = 7.6 Hz), 6.91 (s, 1 H), 6.98 (m, 1 H), 7.14–7.39 (m, 9 H), 7.60–7.69 (m, 2 H); ^{13}C NMR δ 41.22, 51.48, 55.88, 72.93, 101.58, 111.57, 112.54, 115.52, 119.75, 119.99, 125.06, 126.20, 127.26, 127.81, 128.17, 128.30, 130.32, 139.98, 141.28, 144.43, 147.04, 147.16, 148.56, 148.78, 176.23 (CO).

Methyl 2-[*N*-(Pf)amino]-3-(2-bromophenyl)propanoate (6b). Recrystallization from CH_2Cl_2–hexane gave 1.2 g (80%): mp 85–86 °C; IR (KBr) 1730 cm^{-1}; ^{1}H NMR δ 2.84–2.98 (m, 3 H), 3.20 (s, 3 H), 6.49 (d, 1 H, J = 7.6 Hz), 6.92 (td, 1 H, J = 7.5, 1.0 Hz), 7.09–7.48 (m, 13 H), 7.61 (d, 1 H, J = 7.5 Hz), 7.68 (dd, 1 H, J = 6.7, 0.7 Hz); ^{13}C NMR δ 41.50, 51.40, 55.55, 72.90, 119.69, 119.97, 124.95, 125.36, 126.22, 126.94, 127.20, 127.97, 128.08, 128.13, 128.25, 132.40, 132.74, 137.37, 139.91, 141.31, 144.60, 148.62, 148.75, 176.42 (CO).

Methyl 2-[*N*-(Pf)amino]-3-(2-bromo-4,5-dimethoxyphenyl)propanoate (6c). Recrystallization from CH_2Cl_2–hexane gave 1.34 g (80%): mp 178–179 °C; IR (KBr) 1730 cm^{-1}; ^{1}H NMR δ 2.72 (dd, 1 H, J = 10.0, 2.5 Hz), 2.85 (m, 2 H), 3.23 (s, 3 H), 3.78 (s, 3 H), 3.88 (s, 3 H), 6.53 (s, 1 H), 6.54 (d, 1 H, J = 7.9 Hz), 6.93 (m, 1 H), 6.95 (s, 1 H), 7.17–7.39 (m, 9 H), 7.60 (d, 1 H, J = 7.4 Hz), 7.67 (d, 1 H, J = 7.4 Hz); ^{13}C NMR δ 40.74, 51.48, 55.90, 56.20, 56.27, 72.95, 114.41, 115.27, 115.39, 119.66, 119.96, 125.11, 126.21, 127.24, 127.78, 128.06, 128.24, 128.35, 129.35, 139.95, 141.25, 144.42, 148.60, 148.75, 148.87, 176.27 (CO).

Methyl 2-[*N*-(Pf)amino]-3-[2-bromo-4-methoxy-5-(phenylmethoxy)phenyl]propanoate (6d). Recrystallization from CH_2Cl_2–hexane gave 1.7 g (90%): mp 62–64 °C; IR (KBr) 1735 cm^{-1}; ^{1}H NMR δ 2.69 (m, 1 H), 2.84 (m, 2 H), 3.18 (s, 3 H), 3.86 (s, 3 H), 4.96 (d, 1 H, J = 11.8 Hz), 5.00 (d, 1 H, J = 11.8 Hz), 6.58 (d, 1 H, J = 7.6 Hz), 6.63 (s, 1 H), 6.95 (m, 2 H), 7.16–7.46 (m, 14 H), 7.60 (d, 1 H, J = 7.4 Hz), 7.67 (d, 1 H, J = 7.4 Hz); ^{13}C NMR δ 40.81, 51.45, 56.14, 56.30, 71.20, 72.94, 115.88, 116.01, 117.04, 119.69, 119.97, 120.12, 124.82, 125.13, 125.45, 126.21, 127.24, 127.43, 127.81, 128.05, 128.25, 128.32, 128.49, 128.65, 129.13, 129.30, 136.80, 139.99, 141.22, 144.45, 147.45, 148.56, 148.83, 149.13, 176.29 (CO).

Methyl 2-[*N*-(Pf)amino]-3-(2-bromo-3,4-dimethoxyphenyl)propanoate (6e). Recrystallization from CH_2Cl_2–hexane gave 1.37 g (82%): mp 187–188 °C; IR (KBr) 1730 cm^{-1}; ^{1}H NMR δ 2.80–2.88 (m, 3 H), 3.20 (s, 3 H), 3.81 (s, 3 H), 3.89 (s, 3 H), 6.58 (d, 1 H, J = 7.5 Hz), 6.81 (d, 1 H, J = 8.5 Hz), 6.91 (m, 2 H), 7.16–7.37 (m, 9 H), 7.60 (d, 1 H, J = 7.5 Hz), 7.66 (d, 1 H, J = 7.5 Hz); ^{13}C NMR δ 41.09, 51.37, 55.77, 56.18, 60.35, 72.89, 110.86, 119.74, 119.96, 120.12, 125.44, 126.19, 126.86, 127.17, 127.21, 127.81, 128.11, 128.24, 128.49, 129.13, 130.32, 139.96, 141.24, 146.56, 148.60, 148.75, 152.39, 176.45 (CO).

Synthesis of *N*-(9-Phenylfluoren-9-yl)-α-amino Acids 7. General Procedure. A solution of α-amino ester 6 (2 mmol) in 40 mL of 1:1 dioxane–water was treated with lithium hydroxide (LiOH–H_2O, 1.2 g, 28 mmol), and the mixture was stirred for 20 h at 60 °C and then cooled to rt. The pH was brought to 2 by addition of 5% HCl. The solution was extracted with EtOAc (2 × 25 mL), the combined organic layers were washed with water and brine and dried, and the solvent was evaporated to leave a white solid in quantitative yield.

2-[*N*-(Pf)amino]-3-[2-bromo-4,5-(methylenedioxy)phenyl]-propanoic Acid (7a). Recrystallization from EtOAc–hexane gave 1 g (95%): mp 216–219 °C; IR (KBr) 1710 cm^{-1}; ^{1}H NMR δ 2.78 (dd, 1 H, J = 9.6, 4.6 Hz), 2.89 (m, 2 H), 5.97 (d, 1 H, J = 1.3 Hz), 6.00 (d, 1 H, J = 1.3 Hz), 6.36 (s, 1 H), 6.51 (d, 1 H, J = 7.6 Hz), 6.93 (s, 1 H), 6.94 (m, 1 H), 7.19–7.38 (m, 9 H), 7.65 (m, 2 H); ^{13}C NMR δ 39.20, 57.09, 72.64, 101.85, 110.90, 112.63, 115.21, 119.77, 120.28, 124.14, 125.92, 126.30, 127.54, 127.92, 127.99, 128.38, 128.58, 129.11, 129.18, 140.57, 140.79, 143.25, 146.46, 147.78, 147.91, 148.34, 175.38 (CO).

2-[*N*-(Pf)amino]-3-(2-bromophenyl)propanoic Acid (7b). Recrystallization from Cl_2CH_2–hexane gave 0.92 g (95%): mp 195–197 °C; IR (KBr) 1710 cm^{-1}; ^{1}H NMR δ 2.93 (m, 3 H), 6.31 (d, 1 H, J = 7.5 Hz), 6.83 (t, 1 H, J = 7.5 Hz), 7.07–7.36 (m, 12 H), 7.48 (d, 1 H, J = 7.7 Hz), 7.64 (m, 2 H); ^{13}C NMR δ 39.61, 56.42, 72.84, 119.81, 120.16, 124.14, 125.19, 125.94, 126.33, 127.59, 127.78, 127.92, 128.36, 128.48, 128.56, 128.80, 129.20, 132.02, 133.15, 136.04, 140.57, 140.81, 143.08, 146.27, 147.71, 175.19 (CO).

2-[*N*-(Pf)amino]-3-(2-bromo-4,5-dimethoxyphenyl)propanoic Acid (7c). Recrystallization from CH_2Cl_2–hexane gave 1.07 g (98%): mp 169–171 °C; IR (KBr) 1755 cm^{-1}; ^{1}H NMR δ 2.77 (dd, 1 H, J = 10.8, 3.6 Hz), 2.88 (dd, 1 H, J = 14.0, 3.6 Hz), 3.08 (m, 1 H), 3.63 (s, 3 H), 3.91 (s, 3 H), 6.27 (s, 1 H), 6.30 (d, 1 H, J = 7.6 Hz), 6.81 (t, 1 H, J = 7.5 Hz), 6.96 (s, 1 H), 7.20–7.39 (m, 9 H), 7.60 (d, 1 H, J = 7.5 Hz), 7.65 (d, 1 H, J = 7.5 Hz); ^{13}C NMR δ 38.58, 55.79, 56.24, 57.70, 72.66, 113.58, 114.67, 115.20, 119.50, 120.23, 124.22, 125.87, 126.37, 127.54, 127.97, 128.05, 128.24, 128.54, 129.19, 140.52, 140.76, 143.11, 146.29, 148.18, 148.91, 149.05, 175.84 (CO).

2-[*N*-(Pf)amino]-3-[2-bromo-4-methoxy-5-(phenylmethoxy)phenyl]propanoic Acid (7d). Recrystallization from EtOAc–hexane gave 1.18 g (95%): mp 186–187 °C; IR (KBr) 1710 cm^{-1}; ^{1}H NMR δ 2.76 (dd, 1 H, J = 10.5, 3.8 Hz), 2.90 (m, 2 H), 3.90 (s, 3 H), 4.77 (d, 1 H, J = 11.8 Hz), 4.84 (d, 1 H, J = 11.8 Hz), 6.30 (d, 1 H, J = 7.5 Hz), 6.34 (s, 1 H), 6.85 (t, 1 H, J = 7.5 Hz), 6.98 (s, 1 H), 7.20–7.44 (m, 14 H), 7.61 (d, 1 H, J = 7.5 Hz), 7.65 (d, 1 H, J = 7.5 Hz); ^{13}C NMR δ 38.54, 56.36, 57.62, 70.81, 72.63, 115.13, 115.77, 115.90, 119.55, 120.29, 124.14, 125.87, 126.35, 127.43, 127.57, 127.81, 128.06, 128.13, 128.24, 128.59, 128.68, 129.25, 136.51, 140.68, 143.08, 146.18, 148.26, 149.78, 174.84 (CO).

2-[*N*-(Pf)amino]-3-(2-bromo-3,4-dimethoxyphenyl)propanoic Acid (7e). Recrystallization from CH_2Cl_2–hexane gave 1.01 g (93%): mp 196–197 °C; IR (KBr) 1700 cm^{-1}; ^{1}H NMR δ 2.89 (m, 2 H), 3.03 (m, 1 H), 3.84 (s, 3 H), 3.90 (s, 3 H), 6.43 (d, 1 H, J = 7.5 Hz), 6.77 (m, 2 H), 6.90 (t, 1 H, J = 7.5 Hz), 7.20–7.38 (m, 9 H), 7.65 (m, 2 H); ^{13}C NMR δ 39.07, 56.16, 56.79, 60.36, 72.90, 111.59, 119.86, 120.31, 120.98, 124.21, 125.94, 126.32, 126.57, 127.64, 128.03, 128.16, 128.61, 128.77, 129.30, 140.66, 140.80, 142.90, 146.06, 146.84, 147.65, 152.86, 152.97, 174.96 (CO).

Synthesis of Oxazolidinones 9. General Procedure. Amino acid 7 (1.8 mmol), formaldehyde (37 wt % solution in water, 27 mmol), and *p*-toluenesulfonic acid monohydrate (0.11 mmol) were dissolved in 15 mL of THF and stirred for 16 h at rt. The solution was washed with saturated $NaHCO_3$ (15 mL) and brine (15 mL) and dried, and the solvent was evaporated to leave a white solid in quantitative yield.

3-(9-Phenylfluoren-9-yl)-4-[[2-bromo-4,5-(methylenedioxy)phenyl]methyl]oxazolidin-5-one (9a). Recrystallization from CH_2Cl_2–hexane gave 0.96 g (98%): mp 193 °C; IR (KBr) 1775 cm^{-1}; ^{1}H NMR δ 2.78 (m, 1 H), 3.01 (m, 2 H), 5.45 (d, 1 H, J = 8.0 Hz), 5.49 (d, 1 H, J = 8.0 Hz), 5.98 (d, 1 H, J = 1.3 Hz), 5.99 (d, 1 H, J = 1.3 Hz), 6.37 (s, 1 H), 6.69 (d, 1 H, J = 7.6 Hz), 6.83 (m, 1 H), 6.99 (s, 1 H), 7.16–7.49 (m, 9 H), 7.56 (d, 1 H, J = 7.5 Hz), 7.69 (d, 1 H, J = 7.5 Hz); ^{13}C NMR δ 35.35, 59.60, 77.33, 84.00, 101.77, 110.92, 112.67, 115.72, 119.69, 120.39, 125.33, 126.27, 127.03, 127.76, 127.88, 128.35, 128.90, 129.43, 129.67, 139.24, 141.71, 142.48, 144.38, 146.95, 147.59, 147.69, 176.10 (CO).

3-(9-Phenylfluoren-9-yl)-4-[(2-bromophenyl)methyl]oxazolidin-5-one (9b). Recrystallization from CH_2Cl_2–hexane gave 0.87 g (97%): mp 186–188 °C; IR (KBr) 1780 cm^{-1}; ^{1}H NMR δ 2.94 (dd, 1 H, J = 12.5, 3.9 Hz), 3.10 (m, 2 H), 5.44 (d, 1 H, J = 8.0 Hz), 5.47 (d, 1 H, J = 8.0 Hz), 6.49 (d, 1 H, J = 7.6 Hz), 6.72 (t, 1 H, J = 7.5 Hz), 7.05 (dd, 1 H, J = 7.2, 2.1 Hz), 7.11–7.56 (m, 13 H), 7.68 (m, 1 H); ^{13}C NMR δ 35.50, 59.05, 77.24, 83.86, 119.61, 120.31, 125.00, 125.48, 126.27, 126.92, 127.58, 127.81, 128.24, 128.53, 128.82, 129.59, 132.02, 133.00, 136.36, 139.15, 141.70, 142.54, 144.35, 146.67, 176.08 (CO).

3-(9-Phenylfluoren-9-yl)-4-[(2-bromo-4,5-dimethoxyphenyl)methyl]oxazolidin-5-one (9c). Recrystallization from CH_2Cl_2–hexane gave 0.97 g (97%): mp 178 °C; IR (KBr) 1765 cm^{-1}; ^{1}H NMR δ 2.73 (dd, 1 H, J = 13.4, 3.5 Hz), 2.96 (dd, 1 H, J = 10.9, 3.5 Hz), 3.13 (dd, 1 H, J = 13.4, 10.9 Hz), 3.62 (s, 3 H), 3.94 (s, 3 H), 5.50 (d, 1 H, J = 8.6 Hz), 5.51 (d, 1 H, J = 8.6 Hz), 6.22 (s, 1 H), 6.52 (d, 1 H, J = 7.6 Hz), 6.71 (t, 1 H, J = 7.6 Hz), 7.07 (s, 1 H), 7.12–7.60 (m, 10 H), 7.69 (d, 1 H, J = 7.4 Hz); ^{13}C NMR δ 34.73, 55.71, 56.25, 60.30, 77.33, 84.20, 113.33, 115.32, 119.37, 120.30, 125.41, 126.33, 127.02, 127.86, 128.11, 128.30, 128.57, 128.84, 129.62, 139.12, 141.71, 142.52, 144.34, 147.02, 148.79, 176.38 (CO).

3-(9-Phenylfluoren-9-yl)-4-[(2-bromo-4-methoxy-5-phenylmethoxy)methyl]oxazolidin-5-one (9d). Recrystallization from CH_2Cl_2–hexane gave 1.1 g (97%): mp 123–125 °C; IR (KBr) 1775 cm^{-1}; ^{1}H NMR δ 2.72 (dd, 1 H, J = 12.6, 2.9 Hz),

3.03 (m, 2 H), 3.93 (s, 3 H), 4.77 (d, 1 H, J = 11.8 Hz), 4.83 (d, 1 H, J = 11.8 Hz), 5.46 (d, 1 H, J = 8.0 Hz), 5.49 (d, 1 H, J = 8.0 Hz), 6.34 (s, 1 H), 6.57 (d, 1 H, J = 7.6 Hz), 6.77 (t, 1 H, J = 7.6 Hz), 7.08 (s, 1 H), 7.11–7.49 (m, 14 H), 7.53 (d, 1 H, J = 7.3 Hz), 7.69 (d, 1 H, J = 7.3 Hz); ^{13}C NMR δ 34.77, 56.33, 60.15, 70.83, 77.30, 84.15, 115.63, 115.83, 119.42, 120.31, 125.42, 126.30, 127.00, 127.40, 127.81, 127.90, 128.09, 128.30, 128.44, 128.65, 128.84, 129.60, 136.58, 139.12, 141.67, 142.49, 144.35, 147.00, 148.05, 149.40, 176.36 (CO).

3-(9-Phenylfluoren-9-yl)-4-[(2-bromo-3,4-dimethoxyphenyl)methyl]oxazolidin-5-one (9e). Recrystallization from CH_2Cl_2–hexane gave 0.98 g (98%): mp 193 °C; IR (KBr) 1770 cm^{-1}; ^{1}H NMR δ 2.91 (dd, 1 H, J = 12.3, 3.9 Hz), 3.05 (m, 2 H), 3.86 (s, 3 H), 3.90 (s, 3 H), 5.39 (d, 1 H, J = 8.0 Hz), 5.45 (d, 1 H, J = 8.0 Hz), 6.66 (d, 1 H, J = 7.6 Hz), 6.77 (m, 3 H), 7.15–7.47 (m, 9 H), 7.54 (d, 1 H, J = 7.5 Hz), 7.68 (d, 1 H, J = 7.5 Hz); ^{13}C NMR δ 35.31, 56.14, 59.36, 60.33, 77.29, 83.85, 111.38, 119.67, 120.31, 121.28, 125.23, 126.21, 126.54, 126.95, 127.81, 127.93, 128.25, 128.38, 128.82, 129.28, 129.58, 139.23, 141.67, 142.57, 144.51, 146.61, 146.83, 152.73, 176.18 (CO).

Preparation of 2-[*N*-(9-Phenylfluoren-9-yl)amino]-1-indanones 2. General Procedure. In a 25-mL round-bottomed flask equipped with a stirring bar, septum cap, and Ar inlet, that had previously been flame-dried under a stream of dry Ar, the oxazolidinone **9** (0.5 mmol) was dissolved in 5 mL of anhydrous THF, cooled to −95–105 °C, and treated dropwise with 100–120 M % (see Table I) of n-BuLi (1.6 M in hexane). The yellowish solution obtained was further stirred for 30 min and then quenched by addition of a few drops of AcOH. The reaction vessel was taken out of the cooling bath, saturated $NaHCO_3$ and CH_2Cl_2 were added, the organic layer was separated, washed with brine, and dried, and the solvent was evaporated. In the scaled-up reaction with 4 g (7.4 mmol) of **9a**, a precipitate of **2a** formed when saturated $NaHCO_3$ was added and was filtered out, dried, and recrystallized.

2-[*N*-(9-Phenylfluoren-9-yl)amino]-5,6-(methylenedioxy)indan-1-one (2a). Recrystallization from DME gave 177 mg (82%): mp 230 °C; IR (KBr) 1700 cm^{-1}; ^{1}H NMR δ 2.16 (dd, 1 H, J = 16.6, 7.2 Hz), 2.46 (dd, 1 H, J = 16.6, 4.5 Hz), 2.80 (br m, 1 H), 3.02 (dd, 1 H, J = 7.2, 4.5 Hz), 5.97 (d, 1 H, J = 1.1 Hz), 5.98 (d, 1 H, J = 1.1 Hz), 6.53 (s, 1 H), 6.99 (s, 1 H), 7.20–7.46 (m, 11 H), 7.70 (m, 2 H); ^{13}C NMR δ 37.46, 60.46, 73.26, 102.04, 102.44, 105.63, 119.69, 119.97, 125.01, 126.18, 126.29, 127.27, 127.73, 128.35, 128.42, 128.44, 128.54, 129.07, 139.72, 141.66, 144.59, 148.16, 149.31, 150.04, 150.10, 154.47, 203.87 (CO).

2-[*N*-(9-Phenylfluoren-9-yl)amino]indan-1-one (2b). Recrystallization from CH_2Cl_2–hexane gave 190 mg (98%): mp 171–172 °C; IR (KBr) 1710 cm^{-1}; ^{1}H NMR δ 2.29 (dd, 1 H, J = 16.6, 7.5 Hz), 2.59 (dd, 1 H, J = 16.6, 5.1 Hz), 3.05 (dd, 1 H, J = 7.5, 5.1 Hz), 7.14–7.45 (m, 14 H), 7.62–7.72 (m, 3 H); ^{13}C NMR δ 37.47, 60.53, 73.25, 119.72, 120.01, 123.82, 124.95, 126.19, 126.30, 126.41, 127.30, 127.35, 127.78, 128.38, 128.45, 128.57, 134.69, 134.99, 139.70, 141.68, 144.59, 149.29, 150.05, 152.32, 206.04 (CO).

2-[*N*-(9-Phenylfluoren-9-yl)amino]-5,6-dimethoxyindan-1-one (2c). Recrystallization from DME–hexane gave 190 mg (85%): mp 110–113 °C; IR (KBr) 1710 cm^{-1}; ^{1}H NMR δ 2.19 (dd, 1 H, J = 16.2, 7.1 Hz), 2.50 (dd, 1 H, J = 16.2, 4.6 Hz), 3.03 (dd, 1 H, J = 7.1, 4.6 Hz), 3.84 (s, 6 H), 6.60 (s, 1 H), 7.07 (s, 1 H), 7.22–7.47 (m, 11 H), 7.70 (m, 2 H); ^{13}C NMR δ 37.16, 56.01, 56.08, 60.22, 73.19, 104.44, 107.42, 119.69, 119.96, 125.01, 126.23, 126.30, 127.27, 127.68, 128.36, 128.43, 128.54, 139.75, 141.65, 144.57, 147.91, 149.29, 149.44, 150.07, 155.79, 204.58 (CO).

2-[*N*-(9-Phenylfluoren-9-yl)amino]-4-methoxy-5-(phenylmethoxy)indan-1-one (2d). Recrystallization from DME–hexane gave 175 mg (67%): mp 180–182 °C; IR (KBr) 1700 cm^{-1}; ^{1}H NMR δ 2.15 (dd, 1 H, J = 16.4, 7.1 Hz), 2.47 (dd, 1 H, J = 16.4, 4.5 Hz), 3.00 (dd, 1 H, J = 7.1, 4.5 Hz), 3.84 (s, 3 H), 5.08 (d, 1 H, J = 12.5 Hz), 5.11 (d, 1 H, J = 12.5 Hz), 6.60 (s, 1 H), 7.09 (s, 1 H), 7.21–7.47 (m, 16 H), 7.69 (m, 2 H); ^{13}C NMR δ 37.20, 56.06, 60.35, 70.72, 73.30, 104.82, 109.23, 119.68, 119.96, 125.03, 126.19, 126.30, 127.08, 127.25, 127.53, 127.68, 128.15, 128.35, 128.40, 128.51, 128.70, 136.01, 139.71, 141.65, 144.65, 147.56, 149.32, 149.88, 150.12, 154.93, 204.55 (CO).

2-[*N*-(9-Phenylfluoren-9-yl)amino]-6,7-dimethoxyindan-1-one (2e). Recrystallization from CH_2Cl_2–hexane gave 219 mg (98%): mp 152–153 °C; IR (KBr) 1710 cm^{-1}; ^{1}H NMR δ 2.19 (dd, 1 H, J = 16.1, 7.7 Hz), 2.50 (dd, 1 H, J = 16.1, 5.6 Hz), 3.03 (dd, 1 H, J = 7.7, 4.6 Hz), 3.81 (s, 3 H), 3.95 (s, 3 H), 6.79 (d, 1 H, J = 8.2 Hz), 7.04 (d, 1 H, J = 8.2 Hz), 7.22–7.48 (m, 11 H), 7.69 (m, 2 H); ^{13}C NMR δ 36.66, 56.87, 61.39, 61.83, 73.15, 119.66, 119.96, 120.51, 120.80, 124.93, 126.16, 126.27, 127.16, 127.25, 127.72, 128.35, 128.47, 128.51, 139.69, 141.61, 144.62, 144.76, 147.15, 149.35, 150.09, 151.19, 203.44 (CO).

(*S*)-*N*-(9-Phenylfluoren-9-yl)-*o*-bromophenylalanine [(*S*)-7b]. In a 25-mL Morton flask previously flame-dried under a stream of dry Ar was prepared a suspension of (*S*)-*o*-bromophenylalanine[18] (**10**) (300 mg, 1.2 mmol) in 3 mL of anhydrous $CHCl_3$, and $(CH_3)_3SiCl$ (164 μL, 1.29 mmol) was added at rt. The mixture was heated under reflux for 2 h, allowed to cool to rt, and treated with Et_3N (360 μL, 2.58 mmol), $Pb(NO_3)_2$ (227 mg, 0.74 mmol), and a solution of PfBr (427 mg, 1.48 mmol) in $CHCl_3$ (1 mL). The resulting mixture was vigorously stirred for 4 days at rt, and then excess MeOH (0.3 mL) was added. Filtration followed by evaporation gave a residue which was chromatographed on silica gel.

Recrystallization from ether–hexane gave 565 mg, 95%: mp 160–162 °C.

(*S*)-3-(9-Phenylfluoren-9-yl)-4-[(2-bromophenyl)methyl]oxazolidin-5-one [(*S*)-9b]. Prepared in the same way as racemic **9b**. Recrystallization from CH_2Cl_2–hexane gave 804 mg, 90%: mp 174–175 °C. The spectroscopic data are identical to those of racemic **9b**.

(*S*)-2-[*N*-(9-Phenylfluoren-9-yl)amino]indan-1-one [(*S*)-2b]. Obtained following the general procedure for the preparation of racemic **2b**.

Recrystallization from CH_2Cl_2–hexane gave 190 mg (98%): mp 100–101 °C; $[\alpha]^{20}_D$ = −149° (c = 0.7, CH_2Cl_2). The spectroscopic data are identical to those of racemic **2b**.

Acknowledgment. This work was supported by the Spanish Ministry of Education and Science under DGICYT Project No. PB90-0764 and through an FPI predoctoral fellowship awarded to M.R.P.

Supplementary Material Available: Elemental analysis data for all compounds and full characterization data for (*S*)-**7b**, (*S*)-**9b**, and (*S*)-**2b** (5 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.