Enantiospecific Synthesis of *N*-(9-Phenylfluoren-9-yl)-α-amino Ketones†

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Enantiomerically pure *N*-(9-phenylfluoren-9-yl)-α-amino ketones were prepared in excellent yields by acylation of organolithium reagents with *N*-(9-phenylfluoren-9-yl)-α-amino acid-derived oxazolidinones. The method is not applicable for the acylation of Grignard reagents as they attack the methylenic carbon of the oxazolidinone to give the corresponding *N*-alkylated amino acids **13** in excellent yields. The resulting *N*-(9-phenylfluoren-9-yl)-α-amino ketones **8** could be stereoselectively reduced to the corresponding *syn*- or *anti*-*β*-amino alcohols depending upon the nature of the reducing agent.

Introduction

The synthesis of enantiomerically pure α-amino ketones is of general interest and wide applicability in asymmetric organic synthesis as it provides a direct route to the preparation of a large variety of heterocyclic systems, as well as natural and pharmacologically interesting products.[1] In this regard the preparation of α-amino aryl ketones is particularly important.[2] Several different methods for the synthesis of α-amino ketones have been reported.[3] A number of them use α-amino acids as precursors since they are generally inexpensive compounds and readily available in many structural types and in enantiomerically pure form. An attractive approach for the preparation of enantiomerically pure α-amino ketones is the reaction of suitably *N*-protected (with benzenesulfonyl, ethoxycarbonyl, acetyl, or benzoyl groups) α-amino acids with alkyllithium or Grignard reagents,[4] although the removal of the *N*-protecting group usually requires harsh conditions. *N*-Blocked α-amino ketones can also be prepared by acylation of organometallic reagents with carboxyl-activated α-amino acid derivatives: isoxazolidides,[5] *N*-methyl-*N*-methoxyamides,[6,7] thiopyridyl esters,[8] and acid chlorides.[4a] Intra- and intermolecular versions of the Friedel−Crafts acylation[4a,9] provide α-amino aryl ketones. The Dakin−West reaction[10] and other reported methods that do not use amino acids as starting materials, such as the Neber rearrangement,[11] the reaction of α-halo ketones with amines,[12] and the reaction of metalated α-amino nitriles with aldehydes,[13] do not afford enantiomerically pure compounds and/or suffer from unsatisfactory yields and lack of regioselectivity.

We now report an alternative synthesis of enantiomerically pure *N*-protected α-amino ketones **8** based on the reaction of *N*-(9-phenylfluoren-9-yl)amino acid-derived oxazolidinones **6** with organolithium reagents,[14] which avoids the use of difficult-to-remove *N*-protecting groups and expensive carboxyl activation schemes.

Results and Discussion

We have shown recently that treatment of certain cyclic *N*-(9-phenylfluoren-9-yl)-α-amino esters, such as **1**, with organolithium reagents afforded the corresponding enantiomerically pure α-amino ketones in high yields.[15] We attribute the success of this transformation to the unusual stability of the intermediate **2**, which would stem from the electron-withdrawing effect of the α-nitrogen and the lithium-complexing ability of the fluorenyl ring of the Pf group.[14] If it were possible to extend such transformation to acyclic *N*-Pf-α-amino esters, then a very convenient synthesis of α-amino ketones would be in hand. To study the feasibility of this proposal, we studied the acylation of alkyllithium reagents with *N*-Pf-α-amino esters, and even with *N*-Pf-α-amino acids, but to no avail: only when the acids were treated with 300 mol % of alkyllithium were the corresponding ketones isolated in moderate yields (<50%). All other nucleophile−electrophile combinations afforded low yields, at best, of the desired ketones. These failures were possibly

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† Dedicated to the memory of Prof. Ignacio Ribas.

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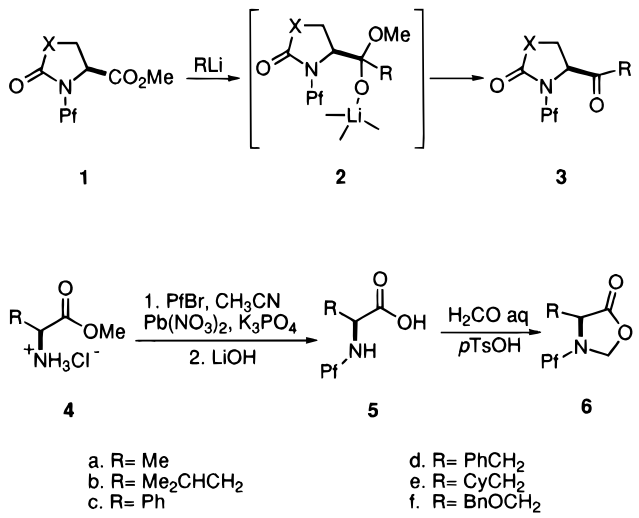
Scheme 1



due to the acidic hydrogen of the NH group, which could be transferred to the alkoxide intermediate, leading to its collapse and the subsequent formation of tertiary alcohols, the major reaction products observed. Thus we turned our attention toward other aminoacylating electrophiles that would lack the offending NH group. Oxazolidinones **6** were an obvious alternative: *N*,*N*-diprotected α-amino esters which were obtained in excellent yields by treatment of the corresponding *N*-Pf- amino acid **5** with aqueous formaldehyde in the presence of *p*-TsOH.[16]

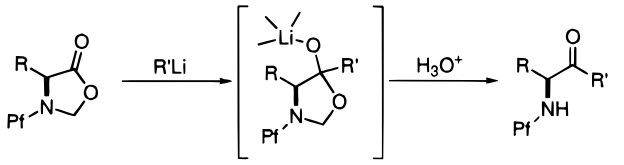
To our delight, when alanine-derived oxazolidinone **6a** was treated with MeLi (150 mol %, THF, −78 °C), methyl ketone **8a** was isolated in 92% yield after purification (Table 1). Detailed analysis of the ^{1}H NMR spectrum of the crude reaction mixture showed no traces of the corresponding tertiary alcohol. Remarkably, the addition of MeLi to **6a** to provide ketone **8a** could be carried out successfully even at 0 °C (72% yield, no tertiary alcohol detected in the crude reaction mixture), attesting to the robustness of the addition intermediate **7**.

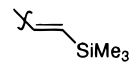
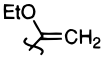
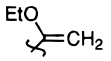
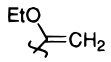
The question of whether the reaction had occurred without racemization was addressed by transforming **8a** into the tertiary alcohol **9** (MeLi, −78 °C, 62% yield) followed by reaction with (*R*)- and (*S*)-phenylethyl isocyanate (Scheme 2). ^{1}H NMR analysis of the crude diastereomeric carbamates **10a**,**b** and of mixtures of them of known composition showed that their ratios of diastereomers (dr) were >99/1; thus the ratios of enantiomers (er) of **9** and **8a** must be >99/1.

As can be seen from Table 1, other alkyllithium, aryllithium, and vinyllithium reagents were successfully added to oxazolidinone **6a** to provide the corresponding ketones in excellent yields (entries 2−6).

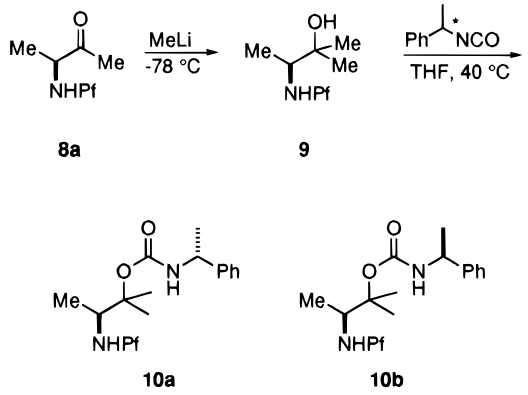
The stability of the intermediate **7**, the key factor that determines the output of these nucleophilic additions, is partly due to the Pf group, since the reaction of the Cbz-protected analogue of oxazolidinone **6a** with MeLi gave a complex mixture of products, none of them being the expected amino ketone. The beneficial effect of the Pf group probably stems from its ability to act as a Li^+ ligand in intermediate **7**, through a cation−π interaction.[17] In fact, semiempirical calculations on **7** (R = R′ = Me, monomeric species, Li^+ coordinated to two molecules of dimethyl ether, PM3) showed that its most stable conformation places the Li^+ snugly within the fluorenyl π cloud.[18]

Table 1



entry	R	R'	compound	yield (%)
1	Me	Me	**8a**	92
2	Me	nBu	**8b**	90
3	Me	tBu	**8c**	94
4	Me	Ph	**8d**	94
5	Me		**8e**	92
6	Me		**8f**	84
7	Me_2CHCH_2-	Me	**8g**	91
8	Me_2CHCH_2-	Ph	**8h**	96
9	Me_2CHCH_2-		**8i**	85
10	Ph	Ph	**8j**	85
11	$PhCH_2$-	Ph	**8k**	91
12	$PhCH_2$-		**8l**	58
13	$PhCH_2$-	tBu	**8m**	57
14	$CyCH_2$-		**8n**	85
15	$BnOCH_2$-	Ph	**8o**	87

Scheme 2



To test the scope of this α-amino ketone preparation, we studied the reaction of lithium reagents with oxazolidinones derived from leucine, phenylglycine, phenylalanine, cyclohexylalanine, and serine[19] (**6b**−**f**). Starting from leucine oxazolidinone **6b**, the corresponding methyl

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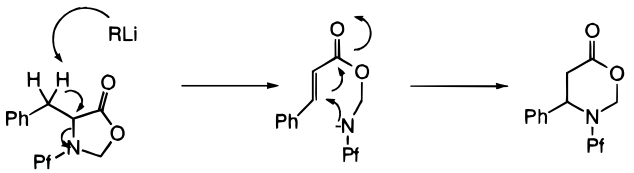
(18) The intramolecular acylation of *N*-Pf-*o*-lithiophenylalanine-derived oxazolidinones to give (*N*-Pf-amino)indanones has been reported.[16] In this case extremely low temperatures (−90 °C) and strict stoichiometric control had to be employed to avoid overaddition of the organolithium reagent (used to generate the *o*-lithiophenylalanine) to the carboxyl group. MNDO calculations on these systems showed that the Li^+ in the corresponding intermediates cannot bind to the fluorenyl ring of the Pf group.

(19) Lubell, W.; Rapoport, H. *J. Org. Chem.* **1989**, *54*, 3824.

Scheme 3



and phenyl ketones **8g**,**h** were obtained in excellent yields (91% and 96%, respectively) using the same reaction conditions as for alanine. Next we investigated the reaction with α-ethoxyvinyllithium,[20] a readily prepared acyl anion equivalent of considerable synthetic value. When **6b** was treated with this lithium reagent at −78 °C and then stirred at 0 °C for 4 h, the amino ketone **8i** was isolated in 85% yield.

The addition of organolithium compounds to D-phenylglycine oxazolidinone provided a more stringent test of our methodology, due to the highly sensitive nature of the resulting benzyl ketones to acidic or basic conditions. Unfortunately, attempted acylations of MeLi and *n*-BuLi with **6c** gave complex mixtures of products, among which was 9-phenylfluorene (PfH). The presence of this compound indicated that the hydrogen of the chiral center was being abstracted by these highly basic nucleophiles.[21] In stark contrast, the reaction of **6c** with the less basic PhLi (THF, −40 °C) afforded ketone **8j** in 85% yield.

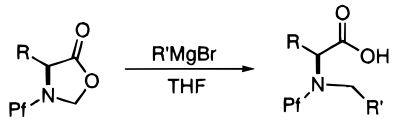
When phenylalanine-derived oxazolidinone **6d** was treated with PhLi at −40 °C for 4 h, the corresponding ketone **8k** was isolated in 91% yield, but when **6d** was treated with α-ethoxyvinyllithium at 0 °C for 4 h, the amino ketone **8l** was isolated only in a modest 58% yield.

In the crude product from this reaction, a very unstable byproduct was detected and tentatively identified as **12**. A plausible mechanism for its formation is shown in Scheme 3. Molecular mechanics (MM3) calculations showed that in the lowest energy conformation of **6d** the carbonyl oxygen lies very close to one of the benzylic hydrogens, which has an antiperiplanar relationship with the *N*-Pf group. Complexation of the organolithium nucleophile to the carbonyl oxygen prior to addition should place the basic reagent very close to the aforementioned hydrogen and lead to elimination to give amide **11**.[22] Ring reclosure in **11** would lead to the observed compound. **12** was also detected when **6d** was treated with LDA (150 mol %) at −40 °C, which argues in favor of the base-promoted elimination mechanism shown above.

Our MM calculations suggested that bulky nucleophiles should be less prone to give this side reaction. Thus, while MeLi failed to give any of the corresponding methyl ketone, when we used a more basic but also bulkier reagent such as *t*-BuLi, at −20 °C for 1.5 h, the corresponding amino ketone **8m** was isolated in 57% yield.

Cyclohexylalanine oxazolidinone **6e** afforded the corresponding ketone **8n** in 85% yield when treated with α-ethoxyvinyllithium in THF at 0 °C, showing that the problems encountered with phenylalanine-derived oxazolidinone **6d** were not due to steric hindrance.

Table 2



6 **13**

entry	R	R'	compound	yield (%)
1	Me	Me	**13a**	92
2	Me_2CHCH_2-	Ph	**13b**	94
3	$BnOCH_2$-	Me	**13c**	84
4	MeO_2CCH_2-	Me	**13d**	90
5	Me	H	**13e**	92[a] 94[b]

[a] $LiBH_4$. [b] DIBALH.

The acylation of serine-derived oxazolidinone **6f** was particularly interesting, since the resulting ketones are precursors of chloramphenicol and its analogues[23] and of dopamine agonists.[24] **6f** was prepared by benzylation of *N*-Pf-serine[19] (BnBr, NaH, DMF) followed by reaction of the resulting acid with aq formaldehyde and *p*-TsOH. Treatment of a THF solution of **6f** with PhLi at −78 °C for 2 h afforded the amino ketone **8o** in 87% yield.

The reaction of the oxazolidinones **6** with Grignard reagents was also studied, since they are often more convenient to prepare than the equivalent lithium reagents. Addition of MeMgBr or PhMgBr to a cold solution (−78 °C) of the corresponding oxazolidinone in THF proceeded smoothly to give new products which were isolated in very good yield and unambiguously identified as the amino acids **13** (Table 2). Surprisingly, no amino ketones **8** were detected in the crude reaction mixture. This behavior resembles the Lewis acid-promoted ring opening of chiral oxazolidines.[25] This reaction is quite general, as can be seen from Table 2. The same mode of addition was obtained when a solution of oxazolidinone was treated with reducing agents such as DIBALH or $LiBH_4$ (entry 5).

A natural corollary to any new method of preparation of *N*-protected α-amino ketones is to study the stereoselectivity of their reductions to β-amino alcohols[26] (Scheme 4). To study this transformation we chose the amino ketones **8d**, since they should provide the ephedrine-type systems, and **8f**, a chiral ferrocene derivative which could be seen as a precursor of chiral ferrocenyl catalysts.[27] After extensive optimization of the reaction conditions (reducing agent, solvent, and temperature), we found that both **8d**,**f** could be stereodivergently reduced to give either **14d**,**f** or **15d**,**f**.

The configurational assignment of **14d** and **15d** was carried out as follows: treatment of the β-amino alcohols **14d** and **15d** with aqueous formaldehyde and catalytic *p*-TsOH in THF afforded the oxazolidines **16** and **17** in 92% and 96% yield, respectively. **16** showed a strong

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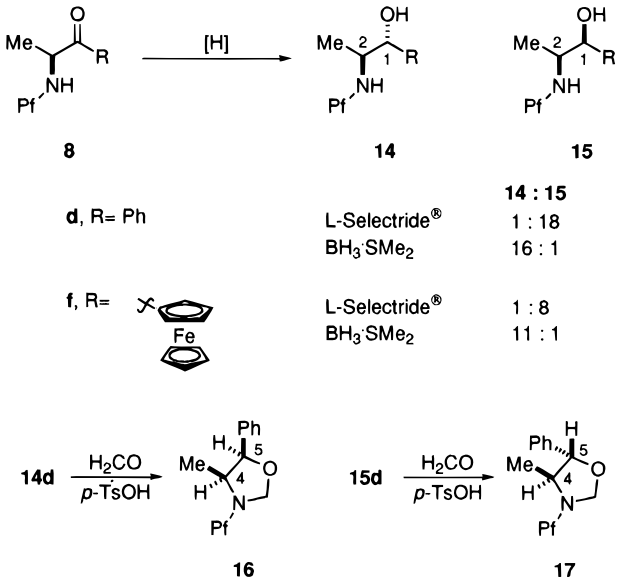
Scheme 4



NOE between H4 and H5, while **17b** did not show an NOE between H4 and H5; this allowed us to assign the configurations shown for **14d** and **15d**. The stereochemistry of ferrocenyl alcohols **14d** ($J_{1,2}$ = 3.3 Hz) and **15d** ($J_{1,2}$ = 7.0 Hz) was established by ^{1}H NMR analysis and comparison of coupling constants $J_{1,2}$ with those shown by the closely related phenyl alcohols **14d** ($J_{1,2}$ = 3.1 Hz) and **15d** ($J_{1,2}$ = 8.3 Hz).

In conclusion, we report a useful method for the enantiospecific synthesis of α-amino ketones based on the acylation of organolithium reagents by *N*-(9-phenylfluoren-9-yl)amino acid-derived oxazolidinones. The reaction proceeds with no detectable racemization. The method is not applicable for the acylation of Grignard reagents as they attack the methylenic carbon of the oxazolidinone to give the corresponding *N*-alkylated amino acids **13** in excellent yields. The resulting *N*-(9-phenylfluoren-9-yl)-α-amino ketones **8** can be stereoselectively reduced to the corresponding *syn*- or *anti*-*β*-amino alcohols depending upon the nature of the reducing agent.

Experimental Section

General.[15b] *N*-Pf-L-alanine,[21] *N*-Pf-L-aspartic acid *β*-methyl ester,[28] and *N*-Pf-L-serine[19] were prepared as described in the literature. *J* values are reported in hertz (Hz).

Preparation of *N*-(9-Phenylfluoren-9-yl)-L-amino Acids 5. General Procedure. Thionyl chloride (2.4 mL, 33.0 mmol) was added dropwise to a suspension of commercial L-amino acid (25.0 mmol) in dry MeOH (25 mL) at 0 °C. The bath was removed and the resulting solution allowed to stir at rt for 20 h; then it was concentrated to an oily residue which was triturated with ether, and the resulting white crystalline solid was filtered, washed with cold ether, and dried to give **4** in 95−97% yield. To a stirred suspension of **4** (12 mmol) in CH_3CN (20 mL) were added sequentially anhydrous $Pb(NO_3)_2$ (3.18 g, 9.6 mmol), K_3PO_4 (5.35 g, 25.2 mmol), and a solution of PfBr (4.81 g, 15 mmol) in CH_3CN (10 mL). Additional PfBr (320 mg, 1 mmol) in CH_3CN (1 mL) was added after 24 h. After being stirred for a total of 48 h, the reaction mixture was filtered through a pad of Celite, and the residue was thoroughly washed with CH_2Cl_2 and MeOH. The combined filtrate and washings were concentrated, and the residue was dissolved in a (1:1) dioxane:H_2O mixture (200 mL); $LiOH·H_2O$ (5 g, 120 mmol) was added, and the resulting solution was stirred at rt for 24 h. Toluene (100 mL) was added, and the layers were separated; the aqueous layer was acidified to pH 2 with 10% H_3PO_4 and extracted with EtOAc (3 × 80 mL). The combined organic layer was washed with water (50 mL) and brine (50 mL), dried, and concentrated. The residue was purified by column chromatography (CH_2Cl_2−MeOH, 5%) or crystallized from the appropriate solvent to give the product as white crystals.

***N*-(9-Phenylfluoren-9-yl)-L-leucine (5b):** 4.23 g, 95% yield; mp 165−167 °C (EtOAc−hexane); $[\alpha]^{20}_D$ −36 (*c* 1.0, $CHCl_3$); IR 1715 cm^{-1}; ^{1}H NMR *δ* 0.52 (d, *J* = 6.5, 3H), 0.75 (d, *J* = 6.5, 3H), 1.35 (m, 2H), 1.71 (m, 1H), 2.60 (dd, *J* = 5.8, 7.9, 1H), 6.16 (bs, 1H), 7.14−7.44 (m, 11H), 7.69 (t, *J* = 7.5, 2H); ^{13}C NMR *δ* 21.8, 22.6, 24.3, 43.8, 54.2, 72.8, 120.0, 120.1, 125.0, 126.0, 126.2, 127.5, 127.8, 128.1, 128.5, 128.8, 128.9, 140.7, 140.8, 143.7, 147.4, 148.7, 178.6. Anal. Calcd for $C_{25}H_{25}NO_2$: C, 80.83; H, 6.78; N, 3.77. Found: C, 80.52; H, 6.92; N, 3.70.

***N*-(9-Phenylfluoren-9-yl)-L-phenylglycine (5c):** 4.13 g, 88% yield; mp 150−153 °C (EtOH); $[\alpha]^{20}_D$ −131 (*c* 1.0, CH_2Cl_2); IR 1735 cm^{-1}; ^{1}H NMR *δ* 3.64 (s, 1H), 6.85−7.37 (m, 16H), 7.74 (t, *J* = 6.4, 2H); ^{13}C NMR *δ* 60.4, 73.0, 119.8, 119.9, 125.6, 125.7, 126.1, 127.3, 127.5, 127.7, 127.9, 128.2, 128.3, 128.4, 128.8, 139.2, 140.2, 141.0, 143.6, 147.6, 148.0, 176.7. Anal. Calcd for $C_{27}H_{21}NO_2$: C, 82.89; H, 5.42; N, 3.58. Found: C, 83.04; H, 5.68; N, 3.72.

***N*-(9-Phenylfluoren-9-yl)-L-phenylalanine (5d):** 4.71 g, 97% yield; mp 185 °C (EtOH); $[\alpha]^{20}_D$ +128 (*c* 1.1, CH_2Cl_2); IR 1702 cm^{-1}; ^{1}H NMR *δ* 2.65−2.80 (m, 3H), 6.63 (d, *J* = 7.5, 1H), 6.97−7.31 (m, 15H), 7.63 (d, *J* = 7.5, 2H); ^{13}C NMR *δ* 39.7, 57.1, 72.7, 119.8, 120.1, 124.6, 125.9, 126.0, 127.0, 127.4, 127.8, 128.0, 128.4, 128.5, 128.6, 128.8, 129.6, 136.4, 140.5, 140.6, 143.6, 147.2, 148.2, 177.9. Anal. Calcd for $C_{28}H_{23}NO_2$: C, 83.03; H, 5.73; N, 3.46. Found: C, 82.83; H, 5.82; N, 3.39.

***N*-(9-Phenylfluoren-9-yl)-L-cyclohexylalanine (5e):** 4.1 g, 82% yield; mp 156−161 °C (EtOH); $[\alpha]^{20}_D$ +138 (*c* 1.3, CH_2Cl_2); IR 1714 cm^{-1}; ^{1}H NMR *δ* 0.52−0.7 (m, 1H), 0.74−0.98 (m, 1H), 1.02−1.63 (m, 11H), 2.61 (m, 1H), 7.12−7.42 (m, 11H), 7.67 (t, *J* = 7.9, 2H); ^{13}C NMR *δ* 26.0, 26.2, 26.3, 32.3, 33.4, 33.5, 42.3, 53.4, 72.8, 120.1, 120.2, 124.8, 126.0, 126.2, 127.5, 127.8, 128.1, 128.5, 128.7, 128.9, 140.7, 140.8, 143.7, 147.3, 148.8, 178.7. Anal. Calcd for $C_{28}H_{29}NO_2$: C, 81.72; H, 7.10; N, 3.40. Found: C, 81.67; H, 7.29; N, 3.43.

Preparation of Oxazolidinones 6. General Procedure. *N*-Pf-amino acid **5** (5.0 mmol), formaldehyde (26 wt % solution in water, 100 mmol), and *p*-TsOH·H_2O (95 mg, 0.5 mmol) were dissolved in THF (50 mL) and stirred at rt, under Ar, for 24 h. The reaction mixture was then partitioned between satd $NaHCO_3$ and CH_2Cl_2 (2 × 75 mL), and the combined organic layer was washed with water (50 mL) and brine (50 mL), dried, and then concentrated to give a white solid in quantitative yield. The products were not stable under chromatographic conditions, and the residues were recrystallized from the appropriate solvents to give **6** as white crystals.

(4*S*)-4-Methyl-3-*N*-(9′-phenylfluoren-9′-yl)oxazolidin-5-one (6a): recrystallization from CH_2Cl_2−hexane gave 1.6 g, 94% yield; mp 179−180 °C; $[\alpha]^{20}_D$ −92 (*c* 1.0, $CHCl_3$); IR 1780 cm^{-1}; ^{1}H NMR *δ* 1.25 (d, *J* = 7.3, 3H), 3.12 (q, *J* = 7.3, 1H), 5.11 (d, *J* = 7.5, 1H), 5.23 (d, *J* = 7.5, 1H), 7.23−7.46 (m, 11H), 7.69 (m, 2H); ^{13}C NMR *δ* 16.4, 54.7, 77.1, 82.8, 120.3, 125.5, 125.8, 127.0, 127.9, 128.2, 128.4, 128.8, 129.1, 129.4, 140.0, 141.1, 142.5, 145.9, 147.1, 177.6. Anal. Calcd for $C_{23}H_{19}NO_2$: C, 80.92; H, 5.61; N, 4.10. Found: C, 80.78; H, 6.00; N, 4.23.

(4*S*)-4-Isobutyl-3-*N*-(9′-phenylfluoren-9′-yl)oxazolidin-5-one (6b): recrystallization from EtOAc−hexane gave 1.84 g, 96% yield; mp 179−181 °C; $[\alpha]^{20}_D$ −260 (*c* 1.0, $CHCl_3$); IR 1780 cm^{-1}; ^{1}H NMR *δ* 0.43 (d, *J* = 6.5, 3H), 0.72 (d, *J* = 6.5, 3H), 1.28−1.55 (m, 2H), 1.72 (m, 1H), 2.84 (dd, *J* = 6.5, 8.2, 1H), 5.31 (d, *J* = 7.9, 1H), 5.38 (d, *J* = 7.9, 1H), 7.18−7.74 (m, 13H); ^{13}C NMR *δ* 21.8, 22.4, 24.1, 39.3, 56.7, 77.3, 83.6, 120.0, 120.3, 125.9, 126.2, 127.0, 127.9, 128.2, 128.4, 128.8, 128.9, 129.6, 139.7, 141.5, 142.5, 144.9, 147.4, 177.4. Anal. Calcd for $C_{26}H_{25}NO_2$: C, 81.43; H, 6.57; N, 3.65. Found: C, 81.31; H, 6.53; N, 3.59.

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(4*R*)-4-Phenyl-3-*N*-(9′-phenylfluoren-9′-yl)oxazolidin-5-one (6c): recrystallization from CH_2Cl_2−hexane gave 1.6 g, 80% yield; mp 160−162 °C; $[\alpha]^{20}_D$ −9.2 (*c* 1.0, $CHCl_3$); IR 1770 cm^{-1}; ^1H NMR δ 4.16 (s, 1H), 5.32 (d, J = 7.7, 1H), 5.36 (d, J = 7.7, 1H), 7.12−7.57 (m, 16H), 7.68 (d, J = 7.5, 1H), 7.77 (d, J = 7.5, 1H); ^{13}C NMR δ 61.3, 77.4, 83.5, 120.1, 120.4, 125.5, 126.0, 126.5, 126.9, 128.0, 128.3, 128.5, 128.7, 128.9, 129.1, 129.6, 134.7, 139.7, 141.3, 142.2, 145.4, 146.9, 175.0. Anal. Calcd for $C_{28}H_{21}NO_2$: C, 83.35; H, 5.25; N, 3.47. Found: C, 82.91; H, 5.20; N, 3.41.

(4*S*)-4-Benzyl-3-*N*-(9′-phenylfluoren-9′-yl)oxazolidin-5-one (6d): recrystallization from CH_2Cl_2−hexane gave 1.98 g, 95% yield; mp 167−169 °C; $[\alpha]^{20}_D$ −205 (*c* 1.02, $CHCl_3$); IR 1775 cm^{-1}; ^1H NMR δ 2.67 (dd, J = 5.3, 13.4, 1H), 2.87 (dd, J = 5.8, 13.4, 1H), 3.07 (t, J = 5.5, 1H), 4.54 (d, J = 7.5, 1H), 5.17 (d, J = 7.5, 1H), 6.99−7.44 (m, 16H), 7.59 (d, J = 7.5, 1H), 7.68 (d, J = 7.5, 1H); ^{13}C NMR δ 37.1, 60.1, 77.3, 84.1, 119.9, 120.2, 125.3, 125.7, 126.8, 126.9, 127.8, 128.1, 128.4, 128.5, 128.6, 128.8, 129.5, 129.8, 136.6, 139.3, 141.5, 142.6, 145.0, 147.0, 176.7. Anal. Calcd for $C_{29}H_{23}NO_2$: C, 83.52; H, 5.57; N, 3.36. Found: C, 83.28; H, 5.54; N, 3.35.

(4*S*)-4-(Cyclohexylmethyl)-3-*N*-(9′-phenylfluoren-9′-yl)oxazolidin-5-one (6e): recrystallization from CH_2Cl_2−hexane gave 1.9 g, 90% yield; mp 180−182 °C; $[\alpha]^{20}_D$ −232 (*c* 1.1, CH_2Cl_2); IR 1777 cm^{-1}; ^1H NMR δ 0.55−1.67 (m, 13H), 2.92 (dd, J = 5.6, 9.0, 1H), 5.34 (d, J = 7.9, 1H), 5.42 (d, J = 7.9, 1H), 7.23−7.50 (m, 11H), 7.67 (d, J = 7.5, 1H), 7.75 (d, J = 7.9, 1H); ^{13}C NMR δ 26.0, 26.1, 26.2, 32.2, 33.2, 33.3, 37.6, 56.0, 76.5, 77.0, 77.2, 77.5, 83.5, 119.9, 120.3, 125.8, 126.3, 127.0, 127.9, 128.2, 128.3, 128.7, 128.8, 129.5, 139.5, 141.5, 142.5, 144.8, 147.4, 177.6. Anal. Calcd for $C_{29}H_{29}NO_2$: C, 82.24; H, 6.90; N, 3.30. Found: C, 81.95; H, 6.79; N, 3.24.

(4*S*)-4-[(Benzyloxy)methyl]-3-*N*-(9′-phenylfluoren-9′-yl)oxazolidin-5-one (6f): recrystallization from Et_2O−CH_2Cl_2−hexane gave 2.06 g, 92% yield; mp 139−141 °C; $[\alpha]^{20}_D$ −120 (*c* 1.0, $CHCl_3$); IR 1780 cm^{-1}; ^1H NMR δ 2.97 (t, J = 2.7, 1H), 3.47 (dd, J = 2.8, 9.5, 1H), 3.68 (dd, J = 2.7, 9.4, 1H), 4.48 (d, J = 12.3, 1H), 4.60 (d, J = 12.3, 1H), 5.28 (d, J = 6.7, 1H), 5.41 (d, J = 6.7, 1H), 7.14−7.49 (m, 16H), 7.64 (d, J = 7.5, 1H), 7.71 (d, J = 7.5, 1H); ^{13}C NMR δ 59.7, 71.5, 73.3, 77.4, 85.5, 120.2, 120.3, 125.4, 125.7, 127.0, 127.6, 127.7, 127.9, 128.2, 128.4, 128.6, 128.8, 128.9, 129.5, 137.9, 139.6, 141.3, 142.5, 145.3, 147.3, 175.9. Anal. Calcd for $C_{30}H_{25}NO_3$: C, 80.51; H, 5.63; N, 3.13. Found: C, 80.11; H, 5.67; N, 3.06.

(4*S*)-[5-Oxo-3-*N*-(9′-phenylfluoren-9′-yl)oxazolidin-4-yl]acetic acid methyl ester (6g): recrystallization from CH_2Cl_2−hexane gave 1.84 g, 92% yield; mp 169−171 °C; $[\alpha]^{20}_D$ −258 (*c* 1.0, $CHCl_3$); IR 1730, 1785 cm^{-1}; ^1H NMR δ 2.28 (dd, J = 5.0, 16.6, 1H), 2.63 (dd, J = 4.0, 16.6, 1H), 3.06 (t, J = 4.5, 1H), 3.72 (s, 3H), 5.37 (s, 2H), 7.21−7.50 (m, 11H), 7.66 (d, J = 7.5, 1H), 7.74 (d, J = 7.5, 1H); ^{13}C NMR δ 37.2, 52.0, 55.1, 77.5, 84.4, 120.3, 120.4, 125.5, 125.6, 126.9, 128.1, 128.2, 128.8, 129.0, 129.1, 129.7, 139.3, 141.8, 142.3, 144.8, 147.2, 171.0, 176.1. Anal. Calcd for $C_{25}H_{21}NO_4$: C, 75.17; H, 5.30; N, 3.51. Found: C, 75.02; H, 5.41; N, 3.43.

Preparation of *N*-(9-Phenylfluoren-9-yl)amino Ketones 8. General Procedure. A solution of **6** (0.35 mmol) in THF (4 mL) was cooled to −78 °C and treated with R′Li (0.525 mmol). After the mixture stirred at −78 °C for 2 h, the reaction was quenched by addition of HCO_2Et (0.525 mmol), the resulting mixture was stirred for 2−3 min, and then AcOH (5.25 mmol) was added. The cooling bath was removed, the reaction mixture was further stirred for 12 h and then partitioned between satd $NaHCO_3$ and EtOAc (25 mL), and the organic layer was washed with water (10 mL) and brine (10 mL), dried, and concentrated. The residue was purified by column chromatography (CH_2Cl_2−hexane, 1:1) to give the product as a white solid.

(3*S*)-3-[*N*-(9′-Phenylfluoren-9′-yl)amino]butan-2-one (8a): 105 mg, 92% yield; mp 117−118 °C (CH_2Cl_2−hexane); $[\alpha]^{20}_D$ −200 (*c* 1.0, $CHCl_3$); IR 1710 cm^{-1}; ^1H NMR δ 0.98 (d, J = 7.1, 3H), 1.62 (s, 3H), 2.70 (q, J = 7.1, 1H), 3.40 (bs, 1H), 7.10−7.43 (m, 11H), 7.67 (bd, J = 7.2, 2H); ^{13}C NMR δ 20.5, 26.7, 57.6, 73.2, 119.7, 119.9, 125.4, 126.2, 126.3, 127.2, 127.8, 128.0, 128.3, 140.2, 141.0, 144.7, 149.8, 150.2, 212.0. Anal. Calcd for $C_{23}H_{21}NO$: C, 84.37; H, 6.46; N, 4.28. Found: C, 84.31; H, 6.87; N, 4.40.

(2*S*)-2-[*N*-(9′-Phenylfluoren-9′-yl)amino]heptan-3-one (8b): 117 mg, 90% yield; mp 56−58 °C (lit.[29] 56−57 °C); $[\alpha]^{20}_D$ −200 (*c* 1.2, $CHCl_3$); IR (CH_2Cl_2) 1710 cm^{-1}; ^1H NMR δ 0.78 (t, J = 7.0, 3H), 1.00 (d, J = 7.1, 3H), 1.13 (m, 4H), 1.53 (m, 1H), 2.06 (m, 1H), 2.70 (q, J = 7.1, 1H), 7.13−7.48 (m, 11H), 7.70 (m, 2H); ^{13}C NMR δ 13.6, 20.8, 22.0, 25.3, 39.4, 56.8, 73.1, 119.6, 119.8, 125.4, 126.1, 126.3, 127.1, 127.7, 127.9, 128.1, 128.2, 140.1, 141.0, 144.8, 149.8, 150.1, 214.2.

(4*S*)-2,2-Dimethyl-4-[*N*-(9′-phenylfluoren-9′-yl)amino-]pentan-3-one (8c): 122 mg, 94%; mp 170−172 °C (CH_2Cl_2−hexane); $[\alpha]^{20}_D$ −227 (*c* 1.3, $CHCl_3$); IR 1695 cm^{-1}; ^1H NMR δ 0.63 (s, 9H), 1.01 (d, J = 6.9, 3H), 3.10 (q, J = 6.9, 1H), 3.58 (bs, 1H), 7.06−7.41 (m, 11H), 7.66 (d, J = 7.3, 2H); ^{13}C NMR δ 22.7, 26.7, 42.8, 52.2, 73.0, 119.6, 119.8, 125.3, 126.1, 126.5, 127.0, 127.9, 128.0, 128.2, 139.9, 141.2, 145.3, 149.8, 150.2, 219.8. Anal. Calcd for $C_{26}H_{27}NO\cdot{}^1/_2H_2O$: C, 82.50; H, 7.46; N, 3.70. Found: C, 82.80; H, 7.15; N, 3.68.

(2*S*)-1-Phenyl-2-[*N*-(9′-phenylfluoren-9′-yl)amino]propan-1-one (8d). To a −78 °C solution of PhBr (72 μL, 0.7 mmol) in THF (0.5 mL) was added *n*-BuLi (2.5 M, 240 μL, 0.6 mmol); the reaction mixture was stirred for 30 min and then transferred via cannula to a solution of **6a** (0.35 mmol) in THF (3 mL) at −78 °C. After 2 h at −78 °C, quenching and workup were performed as above. Column chromatography (CH_2Cl_2−hexane, 1:1) afforded 128 mg, 94% yield; mp 134−136 °C (Et_2O−MeOH); $[\alpha]^{20}_D$ −288 (*c* 1.05, $CHCl_3$); IR 1680 cm^{-1}; ^1H NMR δ 0.99 (d, J = 7.0, 3H), 3.55 (q, J = 7.0, 1H), 3.61 (bs, 1H), 6.90−7.44 (m, 16H), 7.59 (d, J = 7.4, 2H); ^{13}C NMR δ 22.2, 52.4, 73.2, 119.5, 119.8, 125.5, 126.2, 126.5, 127.1, 127.7, 127.8, 128.0, 128.1, 128.3, 132.7, 135.2, 140.1, 140.8, 144.6, 149.5, 150.1, 205.2. Anal. Calcd for $C_{28}H_{23}NO$: C, 86.34; H, 5.95; N, 3.60. Found: C, 85.98; H, 5.94; N, 3.65.

(4*S*)-4-[*N*-(9′-Phenylfluoren-9′-yl)amino]-1-(trimethylsilanyl)pent-1-en-3-one (8e). A solution of (2-bromovinyl)trimethylsilane[30] (90 μL, 0.58 mmol) in Et_2O (1 mL) at −78 °C was treated with *t*-BuLi (0.5 mL, 0.75 mmol, 1.5 M in pentane) and then warmed to −20 °C for 2 h. The reaction mixture was cooled to −78 °C, treated with a solution of **6a** (100 mg, 0.29 mmol) in THF (4 mL), and slowly warmed to 10 °C over a period of 4 h. HCO_2Et (60 μL, 0.75 mmol) was added followed by AcOH (430 μL, 7.5 mmol) after 3 min; the resulting mixture was stirred for 10 h. Workup as above followed by column chromatography (CH_2Cl_2−hexane, 1:1, to CH_2Cl_2) afforded **8e** as a white foam in 92% yield (110 mg): $[\alpha]^{20}_D$ −190 (*c* 1.2, $CHCl_3$); IR 1685 cm^{-1}; ^1H NMR δ 0.06 (s, 9H), 1.02 (d, J = 7.0, 3H), 3.14 (q, J = 7.0, 1H), 3.45 (bs, 1H), 6.10 (d, J = 19.1, 1H), 6.53 (d, J = 19.1, 1H), 7.07−7.48 (m, 11H), 7.64 (d, J = 7.5, 1H), 7.70 (d, J = 7.5, 1H); ^{13}C NMR δ 1.4, 21.1, 53.6, 73.1, 119.5, 119.7, 124.8, 125.4, 126.2, 126.7, 127.1, 127.7, 128.0, 128.1, 128.3, 139.3, 140.2, 140.9, 144.6, 146.6, 149.6, 150.1, 204.0. Anal. Calcd for $C_{27}H_{29}NOSi$: C, 78.79; H, 7.10; N, 3.40. Found: C, 78.63; H, 7.29; N, 3.52.

(2*S*)-1-Ferrocenyl-2-[*N*-(9′-phenylfluoren-9′-yl)-amino]propan-1-one (8f). A solution of (tri-*n*-butylstannyl-)ferrocene[31] (560 mg, 1.18 mmol) in THF (10 mL) at −78 °C was treated with *n*-BuLi (2.5 M in hexane, 470 μL, 1.18 mmol) and then stirred at −78 °C for 30 min as a precipitate of monolithioferrocene appeared. A solution of **6a** (350 mg, 1.0 mmol) in THF (12 mL) was then added via cannula, and the reaction mixture was stirred for 1.5 h; then HCO_2Et (95 μL, 1.18 mmol) and AcOH (300 μL, 5.2 mmol) were added, the cooling bath was removed, and the mixture was allowed to reach rt. EtOAc (30 mL) was added, and the organic layer was washed with satd $NaHCO_3$, water, and brine, dried, and concentrated. Short column chromatography (CH_2Cl_2−hexane, 1:1, to CH_2Cl_2) afforded the product as a brick-red solid in 84% yield (428 mg): mp 169−172 °C (EtOH); $[\alpha]^{20}_D$ −155 (*c* 1.0, CH_2Cl_2); IR 1660 cm^{-1}; ^1H NMR δ 1.16 (d, J = 6.9, 3H), 3.16 (q, J = 6.9, 1H), 3.72 (bs, 1H), 3.91 (s, 5H), 4.33 (m, 3H), 4.42 (s, 1H), 7.19−7.44 (m, 11H), 7.62 (d, J = 7.1, 1H), 7.70

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(d, J = 7.3, 1H); ^{13}C NMR δ 24.0, 54.6, 68.9, 69.6, 69.9, 71.5, 71.6, 72.8, 77.2, 119.7, 119.9, 125.8, 126.2, 127.0, 127.8, 128.1, 128.2, 128.4, 140.1, 140.9, 145.3, 150.1, 150.2, 208.0. Anal. Calcd for $C_{32}H_{27}FeNO$: C, 77.27; H, 5.47; N, 2.82. Found: C, 77.31; H, 5.84; N, 2.65.

(3*S*)-5-Methyl-3-[*N*-(9′-phenylfluoren-9′-yl)amino]hexan-2-one (8g): same procedure as for **6a** but starting with **6b** (0.35 mmol) and with a reaction time of 5 h at −78 °C afforded 118 mg, 91% yield; mp 88−90 °C (Et_2O−EtOH); $[\alpha]^{20}_D$ −226 (*c* 1.0, $CHCl_3$); IR 1710 cm^{-1}; ^{1}H NMR δ 0.27 (d, J = 6.5, 3H), 0.73 (d, J = 6.5, 3H), 0.81 (m, 1H), 1.07 (m, 1H), 1.33 (s, 3H), 1.75 (m, 1H), 2.51 (dd, J = 3.1, 9.7, 1H), 3.18 (bs, 1H), 6.96−7.60 (m, 13H); ^{13}C NMR δ 21.2, 23.6, 24.1, 27.2, 43.1, 59.5, 73.0, 119.5, 119.6, 125.8, 126.2, 127.2, 127.4, 127.6, 128.1, 128.2, 128.3, 140.0, 141.2, 144.5, 149.7, 149.8, 213.3. Anal. Calcd for $C_{26}H_{27}NO$: C, 84.51; H, 7.37; N, 3.79. Found: C, 84.23; H, 7.33; N, 3.88.

(2*S*)-4-Methyl-1-phenyl-2-[*N*-(9′-phenylfluoren-9′-yl)amino]pentan-1-one (8h): same procedure as for **8d** with a stirring time in the presence of AcOH of only 4 h afforded 145 mg, 96% yield; mp 130−132 °C; $[\alpha]^{20}_D$ −332 (*c* 1.0, $CHCl_3$); IR 1680 cm^{-1}; ^{1}H NMR δ 0.37 (d, J = 6.5, 3H), 0.80 (d, J = 6.5, 3H), 0.89 (m, 1H), 1.29 (m, 1H), 2.01 (m, 1H), 3.53 (dd, J = 2.6, 10.4, 1H), 3.63 (bs, 1H), 6.87−7.51 (m, 17H), 7.63 (d, J = 7.3, 1H); ^{13}C NMR δ 21.0, 23.7, 24.3, 44.4, 54.4, 73.0, 119.3, 119.5, 126.1, 126.2, 127.1, 127.3, 127.4, 127.5, 128.0, 128.1, 128.3, 132.5, 135.3, 140.1, 141.0, 144.7, 149.3, 149.9, 205.6. Anal. Calcd for $C_{31}H_{29}NO$: C, 86.27; H, 6.77; N, 3.24. Found: C, 85.99; H, 7.06; N, 3.12.

(4*S*)-2-Ethoxy-6-methyl-4-[*N*-(9′-phenylfluoren-9′-yl)amino]hept-1-en-3-one (8i). To a solution of ethyl vinyl ether (72 μL, 0.75 mmol) in THF (1 mL) at −78 °C was added *t*-BuLi (0.75 mmol); the resulting solution was stirred while slowly warmed to 0 °C, stirred for 45 min at that temperature, cooled to −78 °C, and treated via cannula with a solution of **6b** (96 mg, 0.25 mmol) in THF (2 mL). The resulting solution was stirred at 0 °C for 4 h, and then the reaction was quenched by addition of a buffer solution of pH 8.6 (KH_2PO_4−NaOH). The cooling bath was removed and the reaction mixture stirred for 30 min. The solution was partitioned between EtOAc (10 mL) and water (10 mL); the organic layer was washed with water (10 mL) and brine (10 mL), dried, and concentrated. The residue was chromatographed through a short column of alumina, grade III (CH_2Cl_2−hexane, 1:1), to give **8i** in 85% yield (90 mg): mp 85−86 °C (EtOH); $[\alpha]^{20}_D$ −285 (*c* 1.1, $CHCl_3$); IR 1700 cm^{-1}; ^{1}H NMR δ 0.31 (d, J = 6.5, 3H), 0.81 (d, J = 6.7, 3H), 0.85 (m, 1H), 1.08 (t, J = 6.8, 3H), 1.14 (m, 1H), 1.91 (m, 1H), 3.26−3.53 (m, 4H), 3.97 (d, J = 2.3, 1H), 4.61 (d, J = 2.3, 1H), 6.97 (d, J = 7.5, 1H), 7.08−7.48 (m, 10H), 7.58 (d, J = 7.5, 1H), 7.63 (d, J = 7.5, 1H); ^{13}C NMR δ 14.0, 20.8, 23.7, 24.3, 43.7, 53.4, 63.1, 73.0, 90.5, 119.2, 119.3, 125.9, 126.3, 127.1, 127.4, 127.6, 127.9, 128.1, 128.2, 140.2, 141.4, 144.7, 149.5, 149.9, 156.0, 202.9. Anal. Calcd for $C_{29}H_{31}NO_2$: C, 81.83; H, 7.36; N, 3.29. Found: C, 81.53; H, 7.57; N, 3.24.

(2*R*)-1,2-Diphenyl-2-[*N*-(9′-phenylfluoren-9′-yl)amino]-1-ethanone (8j). To a solution of PhBr (57 μL, 0.56 mmol) in THF (0.8 mL) at −78 °C was added *n*-BuLi (2.5 M, 208 μL, 0.52 mmol), and the reaction mixture was stirred for 30 min and then transferred via cannula to a solution of **6c** (0.35 mmol) in THF (1.5 mL) at −40 °C. After 3 h the reaction was quenched by addition of a pH 8.6 buffer solution, and then workup was done as above. Column chromatography (CH_2Cl_2−hexane, 1:1) afforded 134 mg of **8j**, 85%: mp 132−134 °C (Et_2O−hexane); $[\alpha]^{20}_D$ +142 (*c* 1.0, $CHCl_3$); IR 1684 cm^{-1}; ^{1}H NMR δ 4.2 (bs, 1H), 4.6 (s, 1H), 6.93−7.6 (m, 22H), 7.7 (d, J = 7.5, 1H); ^{13}C NMR δ 61.4, 73.4, 119.5, 119.7, 126.0, 126.4, 126.5, 127.1, 127.2, 127.6, 127.7, 127.8, 127.9, 128.1, 128.2, 128.3, 128.4, 132.6, 135.7, 140.0, 140.3, 141.1, 144.5, 149.2, 149.6, 201.2. Anal. Calcd for $C_{33}H_{25}NO$: C, 87.88; H, 5.60; N, 3.12. Found: C, 87.88; H, 5.58; N, 3.10.

(2*S*)-1,3-Diphenyl-2-[*N*-(9′-phenylfluoren-9′-yl)amino]propan-1-one (8k). To a solution of PhBr (68 μL, 0.66 mmol) in THF (3 mL) at −78 °C was added *n*-BuLi (2.5 M, 252 μL, 0.63 mmol); the reaction mixture was stirred for 30 min and then transferred via cannula to a solution of **6d** (0.35 mmol) in THF (6 mL) at −40 °C. The reaction mixture was stirred for 4 h at −40 °C, and then the reaction was quenched by addition of a pH 8.6 buffer solution. The resulting mixture was partitioned between CH_2Cl_2 and H_2O (10 mL). The organic layer was washed with water and brine (10 mL), dried, and concentrated. Column chromatography (CH_2Cl_2−hexane, 1:2) afforded **8k** as a white solid (148 mg, 91% yield): mp 111−113 °C (CH_2Cl_2−hexane); $[\alpha]^{20}_D$ −249 (*c* 1.2, $CHCl_3$); IR 1680 cm^{-1}; ^{1}H NMR δ 2.5−2.67 (m, 2H), 3.56 (bs, 1H), 3.66 (dd, J = 4.5, 8.5, 1H), 6.65 (d, J = 7.5, 1H), 6.87−7.41 (m, 21H), 7.57 (d, J = 7.4, 1H); ^{13}C NMR δ 41.5, 58.2, 73.0, 119.3, 125.5, 126.2, 127.0, 127.1, 127.5, 127.7, 127.8, 127.9, 128.0, 128.1, 128.2, 129.9, 132.6, 135.5, 138.2, 139.7, 141.0, 144.7, 149.1, 149.2, 204.7. Anal. Calcd for $C_{34}H_{27}NO$: C, 87.70; H, 5.86; N, 3.01. Found: C, 87.47; H, 5.84; N, 3.11.

(4*S*)-2-Ethoxy-5-phenyl-4-[*N*-(9′-phenylfluoren-9′-yl)amino]pent-1-en-3-one (8l). The same procedure as for **8i** was used but starting from **6d** (0.25 mmol) and using HCO_2Et (60 μL, 0.75 mmol) and AcOH (100 μL) for the quench. The reaction mixture was then stirred for 10 min followed by aqueous workup as above. The residue was chromatographed through a short column (CH_2Cl_2−hexane, 1:3 to 1:1) to give **8l** in 58% yield (67 mg) as an oil: $[\alpha]^{20}_D$ −186 (*c* 1.0, $CHCl_3$); IR 1708 cm^{-1}; ^{1}H NMR δ 1.11 (t, J = 6.9, 3H), 2.39 (dd, J = 9.2, 13.2, 1H), 2.62 (dd, J = 4.1, 13.2, 1H), 3.29−3.55 (m, 4H), 3.99 (d, J = 2.4, 1H), 4.64 (d, J = 2.4, 1H), 6.49 (d, J = 7.6, 1H), 6.80 (t, J = 7.5, 1H), 6.99−7.37 (m, 14H), 7.55 (d, J = 7.4, 2H); ^{13}C NMR δ 14.0, 40.7, 57.3, 63.2, 72.9, 90.9, 119.0, 119.2, 125.3, 126.0, 126.3, 127.0, 127.6, 127.8, 127.9, 128.0, 128.1, 129.9, 138.5, 139.7, 141.3, 144.7, 149.2, 149.3, 156.1, 201.9. Anal. Calcd for $C_{32}H_{29}NO_2 \cdot {}^2/_3H_2O$: C, 81.49; H, 6.49; N, 2.97. Found: C, 81.25; H, 6.53; N, 2.61.

(2*S*)-4,4-Dimethyl-1-phenyl-2-[*N*-(9′-phenylfluoren-9′-yl)amino]pentan-3-one (8m). To a solution of **6d** (104 mg, 0.25 mmol) in THF (3 mL) at −20 °C was slowly added *t*-BuLi (0.38 mmol). The resulting yellow solution was stirred for 90 min at −20 °C; then the reaction was quenched by addition of HCO_2Et (31 μL, 0.38 mmol) and AcOH (50 μL). The cooling bath was removed and the reaction mixture stirred for an additional 15 min. Workup as above and column chromatography (CH_2Cl_2−hexane, 1:2) afforded 64 mg of **8m**, 57% yield; mp 158−160 °C (CH_2Cl_2−hexane); $[\alpha]^{20}_D$ −219 (*c* 1.1, $CHCl_3$); IR 1697 cm^{-1}; ^{1}H NMR δ 0.65 (s, 9H), 2.24 (dd, J = 9.8, 13.2, 1H), 2.71 (dd, J = 2.2, 13.2, 1H), 3.25 (dd, J = 2.6, 9.8, 1H), 3.36 (bs, 1H), 6.09 (d, J = 7.6, 1H), 6.71 (t, J = 7.5, 1H), 7.08−7.29 (m, 14H), 7.54 (d, J = 7.5, 1H), 7.62 (d, J = 7.2, 1H); ^{13}C NMR δ 26.8, 41.6, 43.1, 58.5, 72.7, 119.1, 119.5, 125.4, 126.1, 126.3, 126.9, 127.1, 127.6, 127.8, 127.9, 128.1, 128.2, 130.3, 138.8, 139.2, 141.4, 145.8, 148.9, 149.1, 218.9. Anal. Calcd for $C_{32}H_{31}NO$: C, 86.24; H, 7.03; N, 3.14. Found: C, 86.03; H, 7.03; N, 3.04.

(4*S*)-5-Cyclohexyl-2-ethoxy-4-[*N*-(9′-phenylfluoren-9′-yl)amino]-1-penten-3-one (8n). To a solution of ethyl vinyl ether (74 μL, 0.77 mmol) in THF (1 mL) at −78 °C was added *t*-BuLi (0.75 mmol); the resulting solution was stirred while allowed to warm slowly to 0 °C, stirred for 45 min at that temperature, then cooled to −78 °C, and treated via cannula with a solution of **6e** (106 mg, 0.25 mmol) in THF (2 mL). The resulting solution was stirred at 0 °C for 4 h and then the reaction quenched by addition of a buffer solution of pH 8.6 (KH_2PO_4−NaOH). The cooling bath was removed and the reaction mixture stirred for 45 min. The solution was partitioned between EtOAc (10 mL) and water (10 mL); the organic layer was washed with water (10 mL) and brine (10 mL), dried, and concentrated. The residue was chromatographed through a short column of alumina grade III (EtOAc−hexane, 1:6) to give **8n** as an oil in 85% yield (99 mg): $[\alpha]^{20}_D$ −218 (*c* 1.2, CH_2Cl_2); IR 1708 cm^{-1}; ^{1}H NMR δ 0.35−0.41 (m, 1H), 0.76−1.64 (m, 14H), 3.29−3.49 (m, 4H), 3.98 (d, J = 2.4, 1H), 4.61 (d, J = 2.4, 1H), 6.98 (d, J = 7.5, 1H), 7.09−7.49 (m, 10H), 7.57 (d, J = 7.5, 1H), 7.62 (d, J = 7.5, 1H); ^{13}C NMR δ 14.0, 26.1, 26.5, 26.6, 31.5, 33.6, 34.5, 42.0, 52.6, 63.1, 73.0, 90.6, 119.1, 119.2, 125.8, 126.2, 127.0, 127.3, 127.5, 127.7, 127.8, 127.9, 128.1, 140.0, 141.2, 144.5, 149.3, 149.8, 155.8. Anal. Calcd for $C_{32}H_{35}NO_2 \cdot {}^1/_4H_2O$: C, 81.74; H, 7.62; N, 2.98. Found: C, 81.96; H, 7.53; N, 3.09.

(2*S*)-3-(Benzyloxy)-1-phenyl-2-[*N*-(9′-phenylfluoren-9′-

yl)amino]propan-1-one (8o): same procedure as for **8d** but with a stirring time in the presence of AcOH of only 2 h afforded 151 mg of **8o** (87% yield) after chromatography (CH_2Cl_2−hexane, 1:1); mp 63−64 °C (Et_2O−EtOH); $[\alpha]^{20}_D$ −189 (*c* 1.0, $CHCl_3$); IR 1680 cm^{-1}; ^1H NMR δ 3.46 (m, 2H), 3.70 (bs, 1H), 3.80 (m, 1H), 4.25 (s, 2H), 6.90−7.45 (m, 22H), 7.65 (d, J = 7.4, 1H); ^{13}C NMR δ 56.1, 72.9, 73.0, 73.7, 119.5, 119.8, 125.6, 126.2, 126.4, 127.1, 127.2, 127.3, 127.7, 127.8, 127.9, 128.1, 128.3, 128.4, 132.5, 136.5, 138.0, 140.1, 140.9, 144.4, 149.3, 149.7, 204.4. Anal. Calcd for $C_{35}H_{29}NO_2$: C, 84.82; H, 5.90; N, 2.83. Found: C, 84.63; H, 5.83; N, 2.83.

2-Methyl-3-[*N*-(9-phenylfluoren-9-yl)amino]butan-2-ol (9). A solution of **8a** (180 mg, 0.55 mmol) in THF (6 mL) at −78 °C was treated with MeLi (690 mL, 1.1 mmol), the reaction mixture was stirred for 2 h at that temperature, and the reaction was quenched by addition of AcOH (500 μL, 8.7 mmol). EtOAc (10 mL) was added, the mixture was washed with satd $NaHCO_3$ (10 mL), H_2O (10 mL), and brine (10 mL), and the organic layer was dried, filtered and concentrated. The residue was purified by column chromatography (EtOAc−hexane, 1:5) to give **9** as a colorless oil in 64% yield (121 mg): $[\alpha]^{20}_D$ +285 (*c* 1.6, $CHCl_3$); ^1H NMR δ 0.52 (d, J = 6.5, 3H), 0.98 (s, 3H), 1.13 (s, 3H), 2.13 (q, J = 6.5, 1H), 7.21−7.45 (m, 11H), 7.70 (d, J = 7.5, 1H), 7.74 (d, J = 7.5, 1H); ^{13}C NMR δ 18.2, 23.4, 26.5, 57.0, 71.9, 72.4, 119.9, 120.0, 125.2, 125.7, 125.9, 127.2, 127.7, 128.2, 128.3, 128.4, 140.1, 140.8, 145.4, 148.6, 151.4. Anal. Calcd for $C_{24}H_{25}NO$: C, 83.93; H, 7.34; N, 4.08. Found: C, 83.99; H, 7.59; N, 3.87.

Preparation of 10a,b. A solution of **9** (85 mg, 0.25 mmol) in THF (3 mL) was treated with $CuBr{\cdot}SMe_2$ (155 mg, 0.75 mmol) and (*R*)-(+) or (*S*)-(−)-phenylethyl isocyanate (70 μL, 0.50 mmol) at rt. The resulting suspension was stirred at 40 °C for 24 h (**10a**) or 14 h (**10b**), diluted with EtOAc (25 mL), and washed with a pH 8 buffer solution (NH_3/NH_4Cl). The organic phase was washed with brine (2 × 15 mL), dried, and concentrated. The determination of the er was done with the crude product, but for analytical purposes the residue was purified by column chromatography. (*R*)-**10a**: column chromatography (CH_2Cl_2) afforded 91 mg, 74% yield; $[\alpha]^{20}_D$ +169 (*c* 1.0, $CHCl_3$); IR 1702 cm^{-1}; ^1H NMR (338 K) δ 0.44 (d, J = 6.4, 3H), 1.38 (d, J = 6.8, 3H), 1.40 (s, 3H), 1.44 (s, 3H), 1.99 (bs, 1H), 2.49 (q, J = 6.4, 1H), 4.62 (m, 1H), 4.68 (m, 1H), 7.11−7.38 (m, 16H), 7.64 (t, J = 7.6, 2H); ^{13}C NMR δ 17.3, 22.4, 22.8, 23.5, 50.3, 56.0, 72.6, 84.8, 119.8, 119.9, 125.5, 125.8, 125.9, 126.2, 127.0, 127.1, 127.4, 127.5, 128.0, 128.1, 128.2, 128.6, 140.2, 140.4, 144.0, 146.3, 149.0, 152.1, 155.0. Anal. Calcd for $C_{33}H_{34}N_2O_2{\cdot}H_2O$: C, 77.92; H, 7.13; N, 5.51. Found: C, 77.93; H, 6.88; N, 5.41. (*S*)-**10b**: column chromatography (EtOAc−hexane, 1:6) afforded 98 mg, 80% yield; $[\alpha]^{20}_D$ +118 (*c* 0.9, $CHCl_3$); IR 1700 cm^{-1}; ^1H NMR (338 K) δ 0.41 (bs, 3H), 1.41 (m, 9H), 2.09 (bs, 1H), 2.52 (q, J = 6.5, 1H), 4.61 (bs, 1H), 4.70 (bm, 1H), 7.10−7.40 (m, 16H), 7.65 (t, J = 6.5, 2H); ^{13}C NMR δ 17.2, 22.7, 23.5, 50.5, 55.8, 72.6, 84.9, 119.8, 119.9, 125.5, 125.8, 126.2, 126.3, 127.0, 127.1, 127.5, 127.6, 128.0, 128.1, 128.2, 128.6, 140.3, 140.4, 144.1, 146.5, 148.9, 152.2, 154.9. Anal. Calcd for $C_{33}H_{34}N_2O_2{\cdot}^3/_4H_2O$: C, 78.62; H, 7.10; N, 5.55. Found: C, 78.30; H, 7.05; N, 5.21.

Reaction of Oxazolidinones 6 with Grignard Reagents. General Procedure. To a solution of oxazolidinone **6** (0.25 mmol) in THF (5 mL) at −78 °C was added a commercial solution of RMgBr (0.5 mmol). After the mixture was stirred for 6 h at −78 °C, glacial AcOH (85 μL, 1.5 mmol) was added, the cooling bath was removed, and the reaction mixture was stirred for 15 min. The solution was partitioned between satd $NaHCO_3$ (10 mL) and EtOAc (10 mL), and the aqueous layer was extracted with EtOAc (2 × 10 mL). The combined organic layer was washed with water (10 mL) and brine (10 mL), dried, and concentrated. Column chromatography (CH_2Cl_2−MeOH, 2%) provided **13** as a white foam.

(2*S*)-2-[*N*-Ethyl-*N*-(9′-phenylfluoren-9′-yl)amino]propanoic acid (13a): 82 mg, 92% yield; mp 169−171 °C (CH_2Cl_2−hexane); $[\alpha]^{20}_D$ +486 (*c* 1.0, $CHCl_3$); IR 1707, 1760 cm^{-1}; ^1H NMR δ 0.77 (d, J = 7.2, 3H), 1.13 (t, J = 7.2, 3H), 3.00 (m, 1H), 3.11 (q, J = 7.2, 1H), 3.29 (m, 1H), 7.16−7.54 (m, 11H), 7.67 (d, J = 7.5, 1H), 7.79 (d, J = 7.6, 1H); ^{13}C NMR δ 10.1, 14.4, 40.7, 54.6, 79.2, 120.3, 120.8, 124.7, 126.0, 126.5, 127.6, 127.9, 128.7, 129.0, 129.1, 129.3, 139.4, 141.3, 141.9, 144.9, 147.2, 175.3. Anal. Calcd for $C_{24}H_{23}NO_2$: C, 80.64; H, 6.49; N, 3.92. Found: C, 80.49; H, 6.27; N, 3.92.

(2*S*)-2-[*N*-Benzyl-*N*-(9′-phenylfluoren-9′-yl)amino]-4-methylpentanoic acid (13b): 108 mg, 94% yield; $[\alpha]^{20}_D$ +179 (*c* 1.0, $CHCl_3$); IR 1703 cm^{-1}; ^1H NMR δ 0.24 (d, J = 6.5, 3H), 0.61 (d, J = 6.5, 3H), 0.79 (m, 1H), 1.29 (m, 1H), 1.56 (m, 1H), 3.24 (dd, J = 2.8, 10.0, 1H), 4.10 (d, J = 13.8, 1H), 4.41 (d, J = 13.8, 1H), 7.21−7.79 (m, 18H); ^{13}C NMR δ 20.7, 23.4, 25.3, 37.3, 50.9, 57.9, 79.7, 120.0, 120.6, 126.3, 126.9, 127.1, 127.4, 127.5, 127.8, 127.9, 128.2, 128.6, 128.7, 128.8, 129.4, 138.7, 140.1, 141.3, 143.3, 146.1, 147.4, 177.1. Anal. Calcd for $C_{32}H_{31}NO_2{\cdot}^1/_2H_2O$: C, 81.67; H, 6.85; N, 2.98. Found: C, 81.40; H, 6.98; N, 2.83.

(2*S*)-3-(Benzyloxy)-2-[*N*-ethyl-*N*-(9′-phenylfluoren-9′-yl)amino]propanoic acid (13c): 97 mg, 84% yield; $[\alpha]^{20}_D$ +350 (*c* 1.0, $CHCl_3$); IR 1710, 1760 cm^{-1}; ^1H NMR δ 1.21 (t, J = 7.0, 3H), 3.11−3.32 (m, 4H), 3.49 (m, 1H), 4.07 (d, J= 12.0, 1H), 4.19 (d, J = 12.0, 1H), 7.09−7.47 (m, 16H), 7.61 (d, J = 7.5, 1H), 7.73 (d, J = 7.5, 1H); ^{13}C NMR δ 15.1, 42.6, 60.6, 66.2, 73.0, 79.9, 120.3, 120.6, 125.2, 126.1, 126.6, 127.5, 127.7, 127.9, 128.0, 128.2, 128.6, 129.0, 129.1, 129.2, 137.6, 139.5, 141.2, 142.2, 145.1, 146.5, 172.6. Anal. Calcd for $C_{31}H_{29}NO_3$: C, 80.32; H, 6.31; N, 3.02. Found: C, 80.13; H, 6.20; N, 2.87.

(2*S*)-2-[*N*-Ethyl-*N*-(9′-phenylfluoren-9′-yl)amino]-3-[(methyloxy)carbonyl]propanoic acid (13d): 94 mg, 90% yield; $[\alpha]^{20}_D$ +341 (*c* 1.0, $CHCl_3$); IR 1708, 1736, 1769 cm^{-1}; ^1H NMR δ 1.11 (t, J = 7.1, 3H), 1.62 (dd, J = 2.6, 15.6, 1H), 2.48 (dd, J = 10.1, 15.6, 1H), 2.83 (m, 1H), 3.27 (m, 1H), 3.43 (s, 3H), 3.79 (dd, J = 2.5, 10.0, 1H), 7.17−7.48 (m, 11H), 7.67 (d, J = 7.4, 1H), 7.75 (d, J = 7.4, 1H); ^{13}C NMR δ 13.9, 30.8, 41.8, 51.6, 55.7, 79.1, 120.4, 120.9, 124.9, 126.1, 127.4, 127.7, 128.6, 128.8, 129.1, 129.2, 139.6, 141.5, 142.2, 144.8, 147.2, 171.1, 175.7. Anal. Calcd for $C_{26}H_{25}NO_4$: C, 75.16; H, 6.06; N, 3.37. Found: C, 74.76; H, 6.16; N, 3.15.

(2*S*)-2-[*N*-Methyl-*N*-(9′-phenylfluoren-9′-yl)amino]propanoic Acid (13e). (a) A solution of **6a** (50 mg, 0.15 mmol) in THF (2 mL) was cooled to 0 °C, and $LiBH_4$ (6.5 mg, 0.3 mmol) was added. The reaction mixture was stirred for 24 h while warming to rt; then 1 M H_3PO_4 (0.5 mL) was slowly added. The resulting mixture was partitioned between satd $NaHCO_3$ (10 mL) and EtOAc (2 × 10 mL); the combined organic phase was washed with water (10 mL) and brine (10 mL), dried, and concentrated. The residue was purified by column chromatography (CH_2Cl_2−MeOH, 2%) to give **13e** in 92% yield (47 mg). (b) A solution of **6a** (50 mg, 0.15 mmol) in THF (2 mL) at −78 °C was treated with DIBALH (220 μL, 0.22 mmol). The reaction mixture was stirred for 2 h at −78 °C, and HCO_2Et (20 mL, 0.25 mmol) was added; the resulting mixture was stirred for 10 min and then diluted with $CHCl_3$ (8 mL) and satd Na_2CO_3 (5 drops), stirring was continued until the solution became cloudy, and then KH_2PO_4 and Na_2SO_4 were added. The resulting mixture was stirred at rt for 1 h and then filtered. The residue was washed with $CHCl_3$, the combined clear filtrate and washings were concentrated, and the residue was purified by chromatography (CH_2Cl_2−MeOH, 2%) to give **13e** as a white foam (48 mg, 94% yield): $[\alpha]^{20}_D$ +383 (*c* 1.0, $CHCl_3$); IR 1714, 1757 cm^{-1}; ^1H NMR δ 0.73 (d, J = 7.1, 3H), 2.54 (s, 3H), 3.28 (q, J = 7.1, 1H), 7.18−7.53 (m, 11H), 7.65 (d, J = 7.6, 1H), 7.78 (d, J = 7.6, 1H); ^{13}C NMR δ 10.9, 32.0, 56.7, 77.7, 120.4, 120.9, 124.7, 126.6, 127.6, 128.0, 128.7, 128.9, 129.1, 129.3, 139.6, 140.9, 141.1, 145.1, 147.0, 174.5. Anal. Calcd for $C_{23}H_{21}NO_2{\cdot}^1/_2H_2O$: C, 78.38; H, 6.29; N, 3.97. Found: C, 78.71; H, 6.43; N, 3.82.

(1*R*,2*S*)-1-Phenyl-2-[*N*-(9′-phenylfluoren-9′-yl)-amino]propan-1-ol (14d). A solution of **8d** (50 mg, 0.13 mmol) in THF (4 mL) at −78 °C was treated with $BH_3{\cdot}SMe_2$ (0.02 mL, 0.2 mmol) and stirred for 36 h while slowly warming to rt. MeOH (0.3 mL) was slowly added to the reaction mixture, and after stirring for 5 min, the resulting mixture was concentrated to dryness and purified by column chromatography (EtOAc−hexane, 1:6) to give **14d** as a white foam (49 mg, 98% yield): $[\alpha]^{20}_D$ +189 (*c* 1.0, $CHCl_3$); ^1H NMR δ 0.46 (d, J = 6.0, 3H), 2.29 (m, 1H), 4.02 (d, J = 3.1, 1H), 6.80 (d, J = 7.4, 2H), 7.02−7.70 (m, 16H); ^{13}C NMR δ 15.8, 53.9, 72.9, 74.9, 120.0, 120.1, 124.6, 125.5, 125.7, 126.0, 126.7, 127.4,

127.9, 128.0, 128.1, 128.5, 128.6, 128.7, 139.9, 141.3, 141.4, 145.0, 149.5, 150.0. Anal. Calcd for $C_{28}H_{25}NO$: C, 85.90; H, 6.44; N, 3.58. Found: C, 85.83; H, 6.29; N, 3.72.

(1*S*,2*S*)-1-Phenyl-2-[*N*-(9′-phenylfluoren-9′-yl)-amino]propan-1-ol (15d). A solution of **8d** (50 mg, 0.13 mmol) in THF (5 mL) at −78 °C was treated with L-Selectride (260 μL, 0.26 mmol) and stirred for 7 h; then the reaction was quenched with AcOH (22 μL, 0.38 mmol). After 5 min of stirring, the reaction mixture was allowed to warm up to rt. $LiOH·H_2O$ (27 mg, 0.64 mmol) and H_2O_2 (30%, 1 mL) were added, and the resulting mixture was stirred for 30 min and then partitioned between CH_2Cl_2 (15 mL) and H_3PO_4 (1 M, 15 mL). The aqueous phase was washed with CH_2Cl_2 (15 mL), and the combined organic phase was washed with brine (20 mL), dried, and concentrated to give a residue that was purified by short column chromatography (EtOAc−hexane, 1:6) to give **15d** (49 mg, 98%) as a white foam: $[\alpha]^{20}_D$ +258 (*c* 1.0, CH_2Cl_2); ^{1}H NMR δ 0.36 (d, J = 6.3, 3H), 2.16 (m, 1H), 3.98 (d, J = 8.3, 1H), 6.90−7.62 (m, 18H); ^{13}C NMR δ 19.2, 55.0, 72.6, 78.6, 120.0, 120.1, 125.1, 125.8, 126.0, 127.2, 127.3, 127.5, 127.8, 128.1, 128.2, 128.4, 128.5, 140.3, 140.8, 142.3, 144.9, 148.7, 151.1. Anal. Calcd for $C_{28}H_{25}NO$: C, 85.90; H, 6.44; N, 3.58. Found: C, 85.78; H, 6.31; N, 3.62.

(4*S*,5*R*)-4-Methyl-5-phenyl-3-[*N*-(9′-phenylfluoren-9′-yl)amino]oxazolidine (16). A solution of **14d** (50 mg, 0.13 mmol) in THF (1 mL) was treated with H_2CO (26%, 0.2 mL) and *p*-TsOH (5 mg, 0.026 mmol). The reaction mixture was stirred at rt for 48 h and then partitioned between satd $NaHCO_3$ (15 mL) and CH_2Cl_2 (15 mL); the organic phase was washed with water (10 mL) and brine (10 mL), dried, and concentrated to give a residue which was purified by short column chromatography (EtOAc−hexane, 1:6) to give **16** as a white crystalline solid (47 mg, 92% yield): mp 142−144 °C (EtOAc−hexane); $[\alpha]^{20}_D$ −420 (*c* 0.7, $CHCl_3$); ^{1}H NMR δ 0.48 (d, J = 7.0, 3H), 2.98 (q, J = 6.8, 1H), 4.23 (d, J = 6.4, 1H), 5.01 (d, J = 6.3, 1H), 5.09 (d, J = 6.3, 1H), 6.97−7.71 (m, 18H); ^{13}C NMR δ 17.1, 58.2, 77.1, 81.1, 83.4, 119.8, 119.9, 125.5, 125.9, 126.7, 126.8, 127.1, 127.3, 127.9, 128.0, 128.1, 128.2, 128.5, 128.8, 139.3, 140.0, 141.6, 144.5, 148.0, 149.7. Anal. Calcd for $C_{29}H_{25}NO·{}^1/_2H_2O$: C, 84.43; H, 6.11; N, 3.39. Found: C, 84.09; H, 6.22; N, 3.37.

(4*S*,5*S*)-4-Methyl-5-phenyl-3-[*N*-(9′-phenylfluoren-9′-yl)amino]oxazolidine (17): same procedure as above but with a reaction time of 24 h provided **17** in 96% yield (49 mg); mp 120−121 °C (EtOH); $[\alpha]^{20}_D$ −440 (*c* 0.7, $CHCl_3$); ^{1}H NMR δ 0.77 (d, J = 6.2, 3H), 2.23 (m, 1H), 4.11 (d, J = 8.0, 1H), 4.78 (d, J = 7.3, 1H), 5.17 (d, J = 7.3, 1H), 6.54 (m, 2H), 6.98−7.69 (m, 16H); ^{13}C NMR δ 19.4, 62.1, 77.1, 84.1, 88.7, 119.7, 119.8, 126.5, 126.9, 127.2, 127.3, 127.4, 127.6, 127.7, 128.0, 128.1, 128.2, 128.5, 128.7, 139.1, 139.3, 142.3, 145.3, 147.5, 148.9. Anal. Calcd for $C_{29}H_{25}NO$: C, 86.32; H, 6.24; N, 3.47. Found: C, 86.33; H, 6.19; N, 3.52.

(1*R*,2*S*)-1-Ferrocenyl-2-[*N*-(9′-phenylfluoren-9′-yl)amino]propan-1-ol (14f): same procedure as for **14d** afforded **14f** in 84% yield (42 mg) as an orange foam after short column chromatography (CH_2Cl_2−hexane, 1:1 to 2:1); mp 139−140 °C (Et_2O−hexane); $[\alpha]^{20}_D$ −18 (*c* 1.0, CH_2Cl_2); ^{1}H NMR ($CDCl_3$ + D_2O) δ 0.52 (d, J = 6.6, 3H), 2.23 (m, 1H), 3.58 (s, 1H), 3.85 (d, J = 3.3, 1H), 3.95 (s, 1H), 4.04 (s, 6H), 4.21 (s, 1H), 7.18−7.43 (m, 11H), 7.71 (d, J = 7.0, 1H); ^{13}C NMR δ 26.5, 63.5, 75.5, 78.4, 82.2, 82.5, 86.4, 86.9, 87.4, 99.1, 129.8, 129.9, 134.8, 135.4, 135.9, 137.1, 137.7, 137.8, 138.2, 138.3, 150.0, 150.8, 155.0, 159.6, 160.3. Anal. Calcd for $C_{32}H_{29}FeNO·H_2O$: C, 74.27; H, 6.04; N, 2.71. Found: C, 73.91; H, 5.81; N, 2.75.

(1*S*,2*S*)-1-Ferrocenyl-2-[*N*-(9′-phenylfluoren-9′-yl)amino]propan-1-ol (15f). A solution of **8f** (200 mg, 0.4 mmol) in THF (5 mL) at −78 °C was treated with L-Selectride (800 μL, 0.8 mmol) and stirred for 24 h while slowly warming to rt; then it was quenched with AcOH (70 μL, 1.2 mmol). After 5 min of stirring, the reaction mixture was cooled to 0 °C, $LiOH·H_2O$ (85 mg, 2.0 mmol) and H_2O_2 (30%, 1.7 mL) were added, and the resulting mixture was stirred for 20 min and then partitioned between CH_2Cl_2 (15 mL) and H_3PO_4 (1 M, 15 mL). The aqueous phase was washed with CH_2Cl_2 (15 mL), and the combined organic phase was washed with brine (20 mL), dried, and concentrated to give a residue that was purified by short column chromatography (CH_2Cl_2−hexane, 1:1 to 2:1) to give **15f** (159 mg, 79%) as an orange foam: mp 148−149 °C (Et_2O−hexane); $[\alpha]^{20}_D$ +20 (*c* 1.0, CH_2Cl_2); ^{1}H NMR δ 0.44 (d, J = 6.3, 3H), 2.15 (quintuplet, J = 6.5, 1H), 3.93 (d, J = 7.0, 1H), 4.03 (m, 3H), 4.10 (s, 1H), 4.15 (s, 5H), 7.17−7.40 (m, 11H), 7.63 (m, 2H); ^{13}C NMR δ 18.9, 54.4, 65.3, 67.3, 67.4, 68.4, 68.5, 72.6, 74.2, 90.5, 119.8, 119.9, 125.2, 125.7, 126.0, 127.1, 127.6, 127.8, 128.2, 128.3, 140.2,140.5, 145.4, 149.0, 151.2. Anal. Calcd for $C_{32}H_{29}FeNO·H_2O$: C, 74.27; H, 6.04; N, 2.71. Found: C, 73.87; H, 5.77; N, 2.73.

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