O-Methylephedrine: A Versatile and Highly Efficient *ortho*-Directing Group. Synthesis of Enantiopure 1,2-Disubstituted Ferrocene Derivatives

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Received July 19, 2001

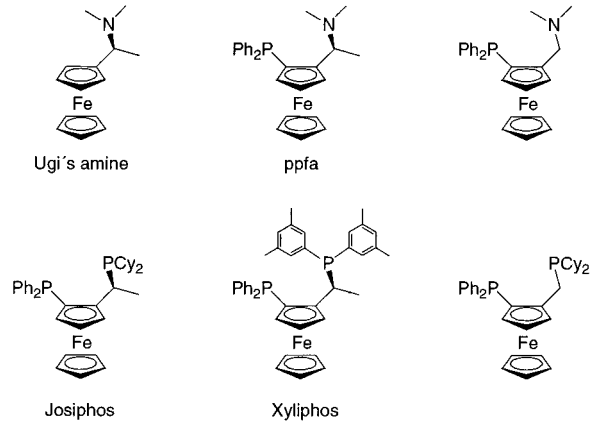
O-Methylephedrine was identified as a very efficient chiral auxiliary for *ortho*-lithiation reactions of ferrocenes. (1*R*,2*S*)-*O*-Methylephedrine [$CH_3NHCH(CH_3)CH(Ph)OCH_3$] was reacted with *N*-ferrocenylmethyl-*N*,*N*,*N*-trimethylammonium iodide [$FcCH_2N(CH_3)_3I$; Fc = ferrocenyl] to give (1*R*,2*S*)-*N*-ferrocenylmethyl-*O*-methylephedrine. Treatment of this compound with *t*-BuLi in pentane followed by quenching with the electrophiles iodine, dibromotetrafluoroethane, chlorodiphenylphosphine or benzophenone gave 2-substituted ferrocenes in 98% de and with the (R_p)-ferrocene configuration. Subsequently, the chiral auxiliary could be replaced by systems including dimethylamine, acetate, diaryl- or dialkylphosphines to give a number of enantiopure bifunctional 1,2-disubstituted ferrocene derivatives such as (R_p)-*N*-2-iodo- or (R_p)-*N*-2-bromoferrocenylmethyldimethylamine or (R_p)-2-acetoxymethyl-1-diphenylphosphinoferrocene. As an application, ferrocenyl diphosphines possessing a planar (R_p)-ferrocene configuration only {1,2-(PPh_2)$FcCH_2PR_2$, R = Cy, Ph, [3,5-$(CF_3)_2$Ph]} were synthesized in three steps from *O*-methylephedrine and *N*-ferrocenylmethyl-*N*,*N*,*N*-trimethylammonium iodide in up to 77% overall yield.

Introduction

Enantiopure 1,2-disubstituted ferrocene derivatives are widely used as ligands in homogeneous transition metal catalysts.[1] Typical examples are the aminophosphine ppfa,[2] the diphosphine Josiphos[3] and the industrially important Xyliphos[4] (Scheme 1). On the basis of common synthetic protocols, e.g., *ortho*-lithiation with *n*- or *sec*-BuLi and quenching with an electrophile[2] followed by nucleophilic displacement of the dimethylamino group,[2,3] hundreds of bi- and multifunctional catalyst ligands have been prepared from commercially available (*S*)- or (*R*)-1-(*N*,*N*-dimethylamino)ethylferrocene[5] (Ugi's amine, Scheme 1).

Common characteristics of these ligands include the ferrocenylethyl backbone and the presence of both central and planar chirality. Although these systems have been known for quite some time,[2] until recently comparably little attention has been paid to ligands based on a ferrocenylmethyl backbone or, more generally, to ferrocene ligands possessing planar chirality only. Reported examples include ppfa[2,6] and Josiphos analogues[7] (Scheme 1).

Scheme 1



In general, the synthesis of enantiopure or enantiomerically enriched 1,2-disubstituted ferrocenes involves either a traditional resolution[2,6] of racemic intermediates or a stereoselective *ortho*-metalation step. However, while the course of the metalation of Ugi's amine is directed by the configuration of the stereogenic center, the related ferrocenylmethyl derivatives require a chiral auxiliary to achieve stereoselectivity. The stereoselective *ortho*-metalations reported to date include cyclopalladation of

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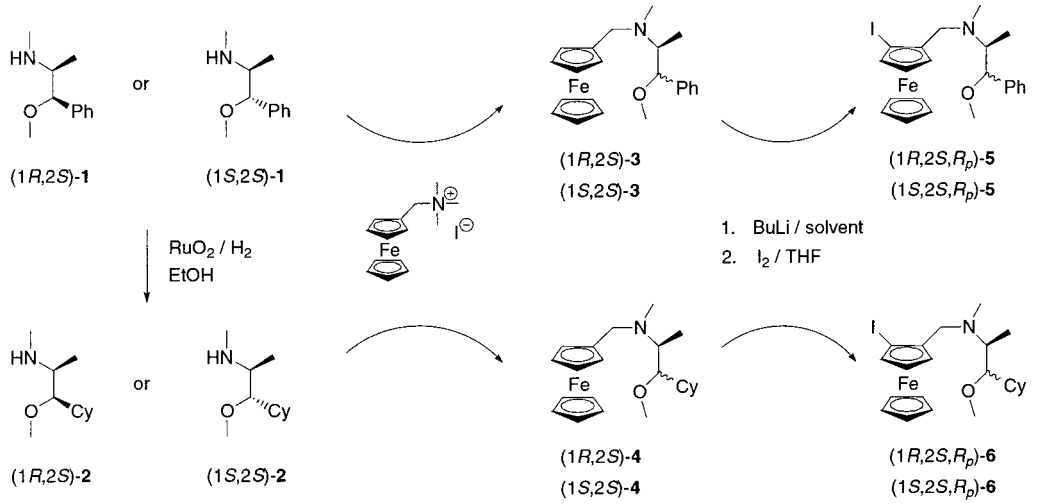
10.1021/jo015949y CCC: $20.00
Published on Web 11/29/2001

Scheme 2



(dimethylaminomethyl)ferrocene,[8] *ortho*-metalation of ferrocenyl sulfoxides or dioxanes,[9] amines,[10] amides,[11] phosphineoxides,[12] ferrocenyl oxazolines,[13] ferrocenylhydrazones,[14] azepines,[15] methoxy-[16] or methoxymethylpyrrolidine derivatives.[6,17]

Recently, we reported briefly on *O*-methylephedrine as a readily available and highly efficient new *ortho*-directing group.[18] Herein, we describe the potential of *O*-methylephedrine and three related *O*-methylated amino alcohols in the synthesis of enantiopure 1,2-disubstituted planar chiral ferrocene derivatives. Several synthetic protocols are given for the synthesis of diphosphines that possess only planar chirality.

Results and Discussion

(1*R*,2*S*)-*O*-Methylephedrine [(1*R*,2*S*)-*N*-methyl-1-methoxy-1-phenylprop-2-ylamine, (1*R*,2*S*)-**1**] and its diastereomer (1*S*,2*S*)-*O*-methyl-*pseudo*-ephedrine [(1*S*,2*S*)-*N*-methyl-1-methoxy-1-phenylprop-2-ylamine, (1*S*,2*S*)-**1**] are easily accessible by *O*-methylation[19,20] of (1*R*,2*S*)-ephedrine or (1*S*,2*S*)-*pseudo*-ephedrine (KH, CH_3I, THF, 86% and 64% yield, respectively). Hydrogenation of both diastereomers of **1** in EtOH/H_2O with RuO_2 as the catalyst cleanly gave the cyclohexyl derivatives (1*R*,2*S*)-**2** (74%) and (1*S*,2*S*)-**2** (80%) with full retention of configuration (Scheme 2).

Each diastereomer of **1** and **2** was considered to be a potential *ortho*-directing chiral auxiliary and was reacted with *N*-ferrocenylmethyl-*N*,*N*,*N*-trimethylammonium iodide ([$FcCH_2N(CH_3)_3$]I) to give ferrocene derivatives (1*R*,2*S*)-**3** and (1*S*,2*S*)-**3** as well as (1*R*,2*S*)-**4** and (1*S*,2*S*)-**4**. All four ferrocenyl intermediates were subjected to *ortho*-lithiation reactions under different reaction conditions. The lithiation reagent, solvent, and the general reaction conditions were varied. Iodine, which is a very reactive electrophile, was found to work best for screening purposes. In a typical reaction (1*R*,2*S*)-**3** was reacted in diethyl ether at −78 °C with *sec*-BuLi. The reaction mixture was stirred for 1.5 h at −78 °C and 1.5 h at −30 °C, and the resulting suspension was reacted at −78 °C with a solution of iodine in THF. This procedure gave rise to products (1*R*,2*S*,R_p)-**5** and (1*R*,2*S*,S_p)-**5** in a ratio of 1:9 [only the products with the (R_p)-configuration are represented in Scheme 2]. Table 1 summarizes selected *ortho*-lithiation results obtained in the reaction of each diastereomer of **3** and **4** with iodine as the electrophile to give products **5** and **6**.

The results listed in Table 1 show that the outcome of the reaction depends strongly on the lithiation agent, solvent and chiral auxiliary. In general, acceptable to very high conversions were obtained with *sec*-BuLi and *t*-BuLi in diethyl ether or pentane but the use of *n*-BuLi as the lithiating agent or THF as the solvent (entries 1 and 6) led to a lithiation reaction that was very slow or did not occur at all. The best result was obtained with (1*R*,2*S*)-**3** and *t*-BuLi in pentane, which gave product **5** in 98% de and with the (R_p)-ferrocene configuration (entry 7). Changing the solvent to diethyl ether reduced the diastereoselectivity to 86% but did not alter the ferrocene configuration (entry 4). The reaction of the same substrate, (1*R*,2*S*)-**3**, with *sec*-BuLi is heavily dependent on the solvent used. The use of pentane gives

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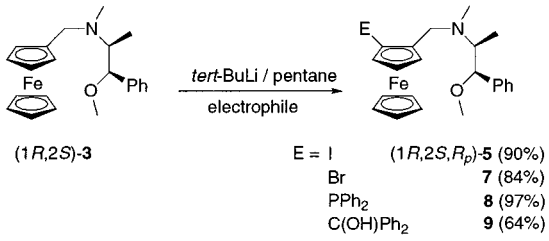
Table 1. *ortho*-Lithiation of Ferrocene Derivatives 3 and 4[a]

entry	substrate	lithiation agent	solvent	isolated yield[b] (%)	de (%)	main product
1	(1*R*,2*S*)-**3**	*n*-BuLi	ether	0		
2	(1*R*,2*S*)-**3**	*sec*-BuLi	ether	66	80	(1*R*,2*S*,S_p)-**5**
3	(1*R*,2*S*)-**3**	*sec*-BuLi	pentane	79	79	(1*R*,2*S*,R_p)-**5**
4	(1*R*,2*S*)-**3**	*t*-BuLi	ether	65	86	(1*R*,2*S*,R_p)-**5**
5[c]	(1*R*,2*S*)-**3**	*t*-BuLi	ether	65	85	(1*R*,2*S*,R_p)-**5**
6	(1*R*,2*S*)-**3**	*t*-BuLi	THF	<10	n.d.[d]	n.d.[d]
7	(1*R*,2*S*)-**3**	*t*-BuLi	pentane	91	98	(1*R*,2*S*,R_p)-**5**
8	(1*S*,2*S*)-**3**	*sec*-BuLi	ether	63	64	(1*S*,2*S*,S_p)-**5**
9	(1*S*,2*S*)-**3**	*t*-BuLi	pentane	84	49	(1*S*,2*S*,R_p)-**5**
10	(1*R*,2*S*)-**4**	*sec*-BuLi	ether	27	17	(1*R*,2*S*,R_p)-**6**
11	(1*R*,2*S*)-**4**	*t*-BuLi	pentane	86	78	(1*R*,2*S*,S_p)-**6**
12	(1*S*,2*S*)-**4**	*sec*-BuLi	ether	67	16	(1*S*,2*S*,S_p)-**6**
13	(1*S*,2*S*)-**4**	*t*-BuLi	pentane	70	40	(1*S*,2*S*,R_p)-**6**

[a] General reaction conditions (except for entry 5): addition of BuLi at −78 °C, 1.5 h at −78 °C; 2.5 (pentane) or 1.5 (ether, THF) h at −30 °C; addition of iodine in THF at −78 °C. [b] Of the mixture of diastereomers; for isolated yields of the main product see Experimental Section. [c] Addition of BuLi at −78 °C, 3 h at −40 °C; addition of iodine in THF at −78 °C. [d] Because of low conversion these values were not determined.

Scheme 3



(1*R*,2*S*)-**3**

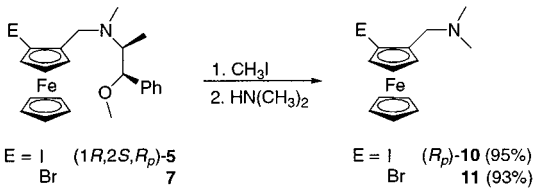
the product in 79% de and with the (R_p)-ferrocene configuration (entry 3), while in diethyl ether the reaction gave **5** in 80% de but with the (S_p)-configuration. It is interesting to note that, for all substrates listed, a change of configuration was found when the reaction was carried out with *t*-BuLi in pentane as compared to *sec*-BuLi in diethyl ether (entries 2/7, 8/9, 10/11, 12/13).

The above results guided our choice of chiral auxiliary and reaction conditions for the subsequent investigations. Since the *O*-methylephedrine derivative (1*R*,2*S*)-**3** gave superior results with *t*-BuLi in pentane and with I_2 as the electrophile (entry 7), it was of interest to try additional electrophiles and to find suitable reaction conditions to replace the *O*-methylephedrine unit by other functional groups.

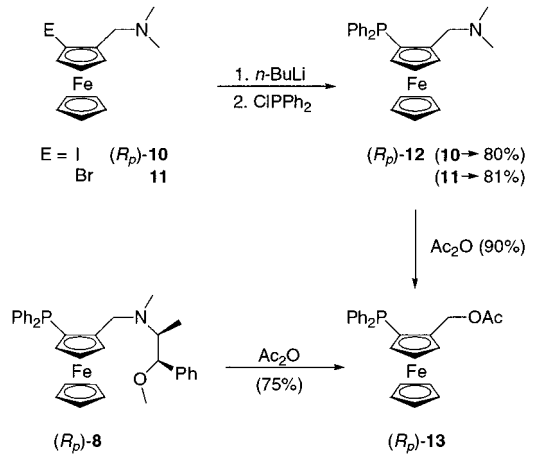
As shown in Scheme 3, and in a similar way as for I_2, the use of electrophiles $F_2BrC-CBrF_2$, $ClPPh_2$ or benzophenone gave products **7**, **8**, and **9** in high chemical yield (84%, 97%, and 64%, respectively) and with 98% de. These results indicate that, at least when rather reactive electrophiles are used, the high diastereoselectivity observed is already established in the initial lithiation step.

Different methods for the replacement of the chiral auxiliary were tried, and the choice of method depended on the nature of the *ortho*-substituent. In the case of iodo- and bromo-derivatives **5** and **7** (Scheme 4), *N*-methylation with CH_3I and subsequent nucleophilic substitution with $(CH_3)_2NH$ led to 2-iodo(bromo)(dimethylaminomethyl)-ferrocenes **10** and **11** in almost quantitative yield[6] (95% and 93%, respectively). In some respects derivatives **10** and **11** are chemical equivalents of Ugi's amine (Scheme 1), since treatment with *n*-BuLi leads to removal of the

Scheme 4



Scheme 5



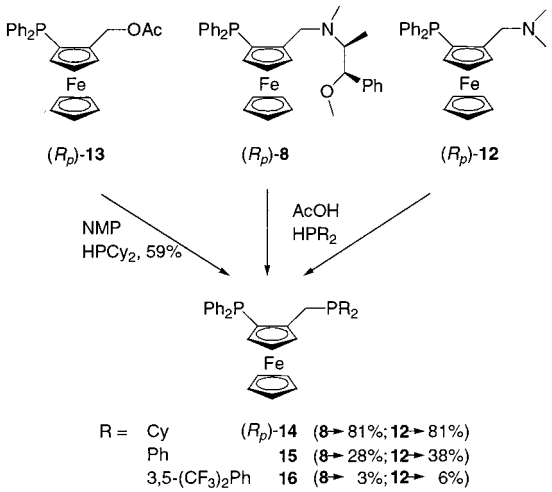
halides. These metalated derivatives can subsequently be reacted with different electrophiles, as exemplified by the transformations of **10** and **11** (*n*-BuLi, Et_2O, $ClPPh_2$) to **12** (Scheme 5).

Enantiopure aminophosphine **12** represents the ppfa analogue with planar chirality only. Compound **12** was previously prepared by classical resolution of racemic precursors with tartaric acid or ephedrine[2,6] or, alternatively, in a diastereoselective manner with (methoxymethyl)pyrrolidine[6] as the chiral auxiliary. As is the case with ppfa, the dimethylamino group of **12** can be exchanged by other nucleophiles,[2,3] thus allowing further functional group variations. For example, reaction of **12** with Ac_2O gave acetate **13** in 90% yield. Acetate **13** is also directly accessible in 75% yield by reacting **8** with Ac_2O, thus providing a second route for the replacement of the chiral auxiliary by a reactive functional group. However, in comparison to the reaction **12** → **13** a higher temperature and a longer reaction time is required.

The absolute configurations of all intermediates and products were established by chemical correlation of the appropriate precursors with (+)- or (−)-**10**, where the configuration is known to be (R_p) for (−)-**10**.[6,7] For example, the main diastereomer obtained in the reaction of (1*R*,2*S*)-**3** with *t*-BuLi in pentane and iodine, i.e., (1*R*,2*S*,R_p)-**5** (entry 7), correlates to (−)-**10** by the reaction **5** → **10**. Similar correlations were carried out for the main products of the reactions given in entries 8, 10, and 12, i.e., (1*S*,2*S*,S_p)-**5**, (1*R*,2*S*,R_p)-**6**, and (1*S*,2*S*,S_p)-**6**, respectively.

Having shown that the chiral auxiliary *O*-methylephedrine not only directs *ortho*-lithiations with very high diastereoselectivity but also that it can be replaced easily by other functional groups, we applied this methodology to the synthesis of ferrocenyl diphosphines. As mentioned above, ferrocenyl diphosphines such as Josiphos or Xyliphos (Scheme 1) have been investigated extensively as ligands in homogeneous catalysts, but only very recently have Kagan and co-workers reported the

Scheme 6



synthesis (together with a few catalytic experiments) of Josiphos analogues lacking central chirality.[7] Diphosphines with R = Cy (**14**), Ph (**15**), *t*-Bu, cyclopentyl (and a *P*-chiral derivative) were synthesized in 30−52% yield from enantiopure acetate **13** (Scheme 6). The acetate precursor **13** was obtained in 6 steps from ferrrocenylcarbaldehyde using a chiral acetal as the *ortho*-directing group.[9]

Although the transformation of **13** (accessible in three steps through the reaction sequence **1** → **3** → **8** → **13**) to diphosphine **14**[9] could be slightly improved (by using NMP as the solvent and 1.2 equiv of phosphine), a direct replacement of *O*-methylephedrine by phosphine was attempted. Recently, Consiglio, Togni and co-workers reported that, like Josiphos from ppfa, racemic **14** can be prepared by reacting racemic **12** with dicyclohexylphosphine in acetic acid.[21] By using similar conditions, not only enantiomerically pure **12** but also **8** could be transformed to diphosphines **14**−**16**. However, in both cases a strong dependence of the chemical yields upon the type of phosphine was observed. The use of dicyclohexylphosphine gave a yield of 81% (**14**), whereas the use of diphenylphosphine and bis(3,5-ditrifluoromethylphenyl)phosphine led to lower yields: 28% (**15**) and 3% (**16**), respectively. In contrast to ppfa, only very nucleophilic phosphines seem to react efficiently under the given reaction conditions. In summary, the chiral auxiliary can be replaced not only by dimethylamine or acetate but also by certain phosphines, thus allowing the synthesis of **14** (and analogues) in three steps from *O*-methylephedrine (**1**) and commercially available $[FcCH_2N(CH_3)_3]I$, through the reaction sequence **1** → **3** → **8** → **14**, in up to 77% (**14**) overall yield.

Conclusion

In conclusion, we have identified *O*-methylephedrine as a very versatile and efficient chiral auxiliary for the *ortho*-lithiation of ferrocene. Reaction of *N*-ferrocenylmethyl-*O*-methylephedrine, (1*R*,2*S*)-**3**, with *t*-BuLi in pentane followed by treatment with electrophiles allowed the introduction of different functional groups into the ferrocenyl *ortho*-position with a diastereoselectivity of 98%. Replacement of the chiral auxiliary *O*-methylephedrine was achieved with dimethylamine, acetate, diaryl- and dialkylphosphines. As an application, ferrocenyl diphosphines possessing planar chirality only were synthesized in three steps with an overall chemical yield of up to 77%. Further applications of this methodology, such as the synthesis of new catalyst ligands based on biferrocene and biferrocenoazepine backbones, will be reported in due course.

Experimental Section

General Methods. Melting points were determined on a Kofler melting point apparatus and are uncorrected. ^1H (400.132 MHz), ^{13}C (100.624 MHz) and ^{31}P (161.975 MHz) NMR spectra were recorded in $CDCl_3$. Chemical shifts (δ) are reported in ppm relative to $CHCl_3$ (7.26, ^1H), $CDCl_3$ (77.0, ^{13}C) and 85% H_3PO_4 (0.0, ^{31}P). The coupling constants given for ^{13}C spectra refer to $^{13}C-^{31}P$ couplings. Mass spectra were measured on a Finnigan 900S (EI, 70 eV). Optical rotations were measured on a Perkin-Elmer 241 polarimeter at 20 °C. All reactions requiring inert conditions were carried out under Ar using standard Schlenk techniques. Pentane and Et_2O were distilled from lithium aluminum hydride, acetonitrile was distilled from calcium hydride, and THF was distilled from potassium and benzophenone under Ar prior to use. 1-Methyl-2-pyrrolidinone (NMP) was dried over 4Å molecular sieves, acetic acid and acetic anhydride were freshly distilled, and Ar was bubbled through each for 12 h prior to use. The mineral oil present in the potassium hydride (35% in mineral oil) was removed with hexane. (1*R*,2*S*)-Ephedrine and (1*S*,2*S*)-*pseudo*-ephedrine were used as purchased from Aldrich. Chromatographic separations were performed under gravity either on silica gel (MERCK, 40−63 μm) or alumina (MERCK, activity II−III, 0.063−0.200 mm). The enantiomeric purity of amines **10** and **11** was established by HPLC (Hewlett-Packard HP1090 liquid chromatograph) on Daicel Chiralcel-OD (250 × 4.6 mm); eluent 0.2% Et_2NH, 0.5% 2-PrOH, 99.3% *n*-hexane, rt. **10**: t_R 14.3 (S_p), 18.4 (R_p) min. **11**: t_R 15.6 (S_p), 19.3 (R_p) min.

(1*R*,2*S*)-*N*-Methyl-1-methoxy-1-phenylprop-2-ylamine [(1*R*,2*S*)-*O*-Methylephedrine, (1*R*,2*S*)-1].[19,22] A dried 2-L three-necked round-bottomed flask was charged with potassium hydride (11.0 g, 275 mmol) and THF (300 mL). To this suspension was added dropwise a solution of (1*R*,2*S*)-ephedrine (32.5 g, 197 mmol) in THF (300 mL) at room temperature within 2 h. The reaction mixture was stirred for 16 h, and a solution of CH_3I (26.7 g, 188 mmol) in THF (200 mL) was added dropwise. After stirring for a further 16 h the reaction was carefully quenched by the addition of ice/water (200 mL). The organic phase was separated, and the aqueous phase was extracted with Et_2O (3 × 300 mL). The combined organic layers were washed with brine, dried over $MgSO_4$, and concentrated in vacuo. The residue was distilled under reduced pressure to give the product, which distilled over at 78 °C (1 Torr) as a colorless liquid (30.5 g, 86%). ^1H NMR δ: 1.02 (d, J = 6.3 Hz, 3H), 1.26 (br s, 1H), 2.38 (s, 3H), 2.72 (dq, J = 5.0 and 6.3 Hz, 1H), 3.26 (s, 3H), 4.13 (d, J = 5.0 Hz, 1H), 7.25−7.32 (m, 3H), 7.33−7.37 (m, 2H). ^{13}C NMR δ: 14.8, 33.9, 57.2, 60.0, 86.3, 127.3, 127.5, 128.3, 139.7. MS (20 °C) *m*/*z*: 179 (0.3) [M^+], 121 (5), 105 (5), 58 (100). HRMS: calcd for $C_{11}H_{17}ON$ 179.1310, found 179.1314. $[\alpha]^{20}_D = -86.8$ (c = 1.0, CH_2Cl_2) [lit.: $[\alpha]^{20}_D = -84.4$ (c = 1.0, $CHCl_3$)].[19a]

(1*S*,2*S*)-*N*-Methyl-1-methoxy-1-phenylprop-2-ylamine [(1*S*,2*S*)-*O*-Methyl-*pseudo*-ephedrine, (1*S*,2*S*)-1].[20,22] (1*S*,2*S*)-**1** was prepared from (1*S*,2*S*)-*pseudo*-ephedrine (7.0 g, 4.2 mmol) using the same procedure as described above for (1*R*,2*S*)-**1**. The product distilled at 94 °C (1 Torr) as a colorless liquid (4.9 g, 64%). ^1H NMR δ: 0.74 (d, J = 6.3 Hz, 3H), 2.40 (s, 3H), 2.72 (dq, J = 6.3 and 8.3 Hz, 1H), 3.15 (s, 3H), 3.83 (d, J = 8.3 Hz, 1H), 7.24−7.37 (m, 5H). ^{13}C NMR δ: 15.0, 33.3,

(21) (a) Bronco, S.; Consiglio, G.; Di Benedetto, S.; Fehr, M.; Spindler, F.; Togni, A. *Helv. Chim. Acta* **1995**, *78*, 883. (b) Bronco, S.; Consiglio, G.; Di Benedetto, S.; Drent, E.; Heeres, H. J. (Shell Internationale Research Maatschappij B.V., Netherlands) Brit. UK Pat. Appl. GB 2289855 A1 19951206, 1995.

(22) The procedure described in ref 19a was slightly modified.

56.3, 59.8, 87.9, 127.5, 127.6, 127.9, 139.2. MS (20 °C) *m*/*z*: 179 (1) [M^+], 121 (27), 105 (17), 58 (100). HRMS: calcd for $C_{11}H_{17}ON$ 179.1310, found 179.1315. $[\alpha]^{20}_D = +105.0$ (*c* = 2.0, CH_2Cl_2) [lit. for (1*R*,2*R*)-**1**: $[\alpha]^{20}_D = -104.5$ (*c* = 1.7, THF)].[20]

(1*R*,2*S*)-*N*-Methyl-1-cyclohexyl-1-methoxyprop-2-ylamine [(1*R*,2*S*)-2]. A 100-mL autoclave with a glass inlet was charged with (1*R*,2*S*)-*O*-methylephedrine, (1*R*,2*S*)-**1**, (3.0 g, 16.8 mmol), RuO_2 (170 mg, 1.3 mmol), EtOH (25 mL) and H_2O (25 mL). The suspension was hydrogenated for 2 h at 90 °C under a hydrogen pressure of 90 bar. The mixture was cooled to room temperature, and the catalyst was removed by filtration over a layer of Celite. Ethanol was removed under reduced pressure, and the aqueous phase was extracted with CH_2Cl_2 (6 × 20 mL). The combined organic layers were washed with brine and dried over $MgSO_4$, and the solvent was removed in vacuo. The residue was purified by Kugelrohr distillation at 150 °C (1 Torr) to give the product as a colorless liquid (2.3 g, 74%). ^{1}H NMR *δ*: 1.00 (d, *J* = 6.6 Hz, 3H), 0.94−1.77 (m, 11H), 1.92−1.96 (m, 1H), 2.42 (s, 3H), 2.66 (dq, *J* = 3.5 and 6.6 Hz, 1H), 2.90 (dd, *J* = 3.5 and 7.6 Hz, 1H), 3.48 (s, 3H). ^{13}C NMR *δ*: 13.7, 26.1, 26.2, 26.5, 29.4, 29.9, 34.0, 40.6, 56.1, 61.51, 88.6. MS (20 °C) *m*/*z*: 185 (1) [M^+], 127 (2), 95 (4), 58 (100). HRMS: calcd for $C_{11}H_{23}ON$ 185.1780, found 185.1778. $[\alpha]^{20}_D = -6.1$ (*c* = 1.0, CH_2Cl_2).

(1*S*,2*S*)-*N*-Methyl-1-cyclohexyl-1-methoxyprop-2-ylamine [(1*S*,2*S*)-2]. (1*S*,2*S*)-*O*-Methyl-*pseudo*-ephedrine, (1*S*,2*S*)-**1**, (2.0 g, 12.1 mmol) was hydrogenated as described above for (1*R*,2*S*)-**2** to give (1*S*,2*S*)-**2** as a colorless liquid (150 °C at 1 Torr, 1.7 g, 80%). ^{1}H NMR *δ*: 0.93 (d, *J* = 6.0 Hz, 3H), 1.00−1.24 (m, 6H), 1.46−1.66 (m, 6H, CH_2), 2.31 (s, 3H), 2.55 (dq, *J* = 4.0 and 6.0 Hz, 1H), 2.62 (dd, *J* = 6.0 and 7.0 Hz, 1H), 3.48 (s, 3H). ^{13}C NMR *δ*: 16.0, 26.3, 26.5, 26.6, 27.1, 31.0, 33.9, 40.1, 56.1, 61.6, 90.7. MS (20 °C) *m*/*z*: 185 (4) [M^+], 127 (4), 95 (8), 58 (100). HRMS: calcd for $C_{11}H_{23}ON$ 185.1780, found 185.1775. $[\alpha]^{20}_D = +19.3$ (*c* = 1.0, CH_2Cl_2).

Preparation of Derivatives 3 and 4. General Procedure. A degassed suspension of *N*-ferrocenylmethyl-*N*,*N*,*N*-trimethylammonium iodide[23] (3.85 g, 10 mmol) and the appropriate diastereomer of amine **1** or **2** (11 mmol) in anhydrous acetonitrile (100 mL) was refluxed under Ar for 3−4 days progress of the reaction was monitored by TLC). After the reaction mixture cooled to room temperature, the solvent was evaporated under reduced pressure, and the residue was purified by chromatography on silica with PE/Et_2O/Et_3N (10/3/1) as eluent, except where stated otherwise.

(1*R*,2*S*)-*N*-Ferrocenylmethyl-*N*-methyl-1-methoxy-1-phenylprop-2-ylamine [(1*R*,2*S*)-3]. This reaction was also carried out on a 50-mmol scale; (1*R*,2*S*)-**3** was obtained as a red oil (17.0 g, 90%) from (1*R*,2*S*)-**1** (9.85 g, 55 mmol). ^{1}H NMR *δ*: 1.03 (d, *J* = 6.8 Hz, 3H), 2.27 (s, 3H), 2.84 (dq, *J* = 4.6 and 6.8 Hz, 1H), 3.28 (s, 3H), 3.43 (d, *J* = 13.1 Hz, 1H), 3.51 (d, *J* = 13.1 Hz, 1H), 4.09 (m, 4H), 4.11 (s, 5H), 4.29 (d, *J* = 4.6 Hz, 1H), 7.24−7.29 (m, 3H), 7.33−7.37 (m, 2H). ^{13}C NMR *δ*: 8.4, 37.9, 53.9, 56.7, 62.4, 67.6, 67.8, 68.4, 69.7, 69.9, 85.1, 85.6, 127.0, 127.0, 128.0, 141.3. MS (80 °C) *m*/*z*: 377 (3) [M^+], 256 (12), 199 (100). HRMS: calcd for $C_{22}H_{27}ONFe$ 377.1442, found 377.1436. $[\alpha]^{20}_\lambda = -8.7$ (589 nm), −8.1 (578 nm), −6.5 (546 nm) (*c* = 1.0, CH_2Cl_2) (corrected value[18]).

(1*S*,2*S*)-*N*-Ferrocenylmethyl-*N*-methyl-1-methoxy-1-phenylprop-2-ylamine [(1*S*,2*S*)-3]. (1*S*,2*S*)-**3** was prepared from (1*S*,2*S*)-**1** (1.97 g). Chromatography on silica gel with PE/Et_2O/Et_3N (30/3/1) as eluent gave the desired product as a yellow solid (2.64 g, 70% yield). Mp: 31 °C. ^{1}H NMR *δ*: 0.66 (d, *J* = 6.8 Hz, 3H), 2.30 (s, 3H), 3.03 (dq, *J* = 8.6 and 6.8 Hz, 1H), 3.17 (s, 3H), 3.44 (d, *J* = 12.9 Hz, 1H), 3.66 (d, *J* = 12.9 Hz, 1H), 4.05 (d, *J* = 8.6 Hz, 1H), 4.07−4.10 (m, 2H), 4.11 (s, 5H), 4.17 (m, 1H), 4.25 (m, 1H), 7.24−7.29 (m, 3H), 7.31−7.35 (m, 2H). ^{13}C NMR *δ*: 11.7, 37.3, 54.0, 56.4, 61.6, 67.6, 67.9, 68.4, 69.9, 70.0, 85.6, 86.6, 127.5, 127.8, 128.2, 140.9. MS (80 °C) *m*/*z*: 377 (2) [M^+], 256 (7), 199 (100). HRMS: calcd for $C_{22}H_{27}ONFe$ 377.1442, found 377.1429. $[\alpha]^{20}_\lambda = +76.3$ (589 nm), +79.7 (578 nm), +94.3 (546 nm) (*c* = 1.0, CH_2Cl_2).

(23) Lednicer, D.; Hauser, C. R. *Organic Syntheses*; Wiley: New York, 1973; Collect. Vol. V, p 434.

(1*R*,2*S*)-*N*-Ferrocenylmethyl-*N*-methyl-1-cyclohexyl-1-methoxyprop-2-ylamine [(1*R*,2*S*)-4]. (1*R*,2*S*)-**4** was obtained as a red oil (3.52 g, 92% yield) from (1*R*,2*S*)-**2** (2.04 g). ^{1}H NMR *δ*: 0.95 (d, *J* = 6.6 Hz, 3H), 0.99−1.26 (m, 5H), 1.49−1.75 (m, 6H), 2.10 (s, 3H), 2.71 (dq, *J* = 7.6 and 6.6 Hz, 1H), 2.81 (dd, *J* = 3.6 and 7.6 Hz, 1H), 3.30 (d, *J* = 12.9 Hz, 1H), 3.38 (d, *J* = 12.9 Hz, 1H), 3.42 (s, 3H), 4.07 (m, 2H), 4.10 (s, 5H), 4.12 (m, 1H), 4.16 (m, 1H). ^{13}C NMR *δ*: 8.4, 26.5, 26.7, 26.7, 26.9, 30.7, 36.7, 39.9, 54.2, 57.5, 60.8, 67.6, 67.7, 68.4, 69.7, 70.0, 85.5, 88.8. MS (80 °C) *m*/*z*: 383 (4) [M^+], 256 (17), 199 (100). HRMS: calcd for $C_{22}H_{33}ONFe$ 383.1912, found 383.1901. $[\alpha]^{20}_\lambda = +11.0$ (589 nm), +11.4 (578 nm), +13.6 (546 nm) (*c* = 1.0, CH_2Cl_2).

(1*S*,2*S*)-*N*-Ferrocenylmethyl-*N*-methyl-1-cyclohexyl-1-methoxyprop-2-ylamine [(1*S*,2*S*)-4]. (1*S*,2*S*)-**4** was obtained from (1*S*,2*S*)-**2** (2.04 g). Chromatography on silica with PE/Et_2O/Et_3N (30/3/1) as eluent gave the desired product as a red oil (2.87 g, 75%). ^{1}H NMR *δ*: 0.91 (d, *J* = 6.8 Hz, 3H), 1.00−1.28 (m, 5H), 1.51−1.80 (m, 6H), 2.15 (s, 3H), 2.68 (dd, *J* = 6.0 and 5.8 Hz, 1H), 2.81 (dq, *J* = 6.0 and 6.8 Hz, 1H), 3.30 (d, *J* = 13.1 Hz, 1H), 3.45 (s, 3H), 3.51 (d, *J* = 13.1 Hz, 1H), 4.06 (m, 2H), 4.09 (s, 5H), 4.14 (m, 1H), 4.19 (m, 1H). ^{13}C NMR *δ*: 9.1, 26.4, 26.5, 26.7, 27.9, 30.4, 37.2, 40.4, 54.9, 58.3, 61.8, 67.4, 67.5, 68.4, 69.8, 69.8, 86.1, 89.7. MS (60 °C) *m*/*z*: 383 (3) [M^+], 256 (11), 199 (100). HRMS: calcd for $C_{22}H_{33}ONFe$ 383.1912, found 383.1924. $[\alpha]^{20}_\lambda = +2.8$ (589 nm), +2.7 (578 nm), +2.0 (546 nm) (*c* = 2.0, CH_2Cl_2).

Preparation of Derivatives 5 and 6. General Procedure. To a degassed solution of each diastereomer of **3** or **4** (1 mmol) in 10 mL of an anhydrous solvent (Et_2O, THF or pentane) was added dropwise BuLi (either 0.75 mL of a 1.6 M solution of *n*-BuLi in hexane or 0.92 mL of a 1.3 M solution of *sec*-BuLi in cyclohexane or 0.71 mL of a 1.7 M solution of *t*-BuLi in pentane, 1.2 mmol) under Ar at −78 °C. The reaction mixture was stirred for 1.5 h at −78 °C and then for 2.5 h (pentane) or 1.5 h (ether) at −30 °C, during which time the yellow suspension turned orange. The temperature was again lowered to −78 °C, and a solution of iodine (381 mg, 1.5 mmol) in THF (5 mL) was added dropwise; stirring was continued at this temperature for additional 20 min. The reaction was quenched with saturated $NaHCO_3$ (10 mL), the organic phase was separated, and the aqueous layer was extracted three times with Et_2O (20 mL). The combined organic layers were washed with aqueous $Na_2S_2O_3$ and brine and dried over $MgSO_4$. After removal of the solvent the residue was purified by chromatography on silica gel with PE/Et_2O/Et_3N (100/20/1) as eluent, unless stated otherwise.

(1*R*,2*S*,R_p)-*N*-(2-Iodoferrocenylmethyl)-*N*-methyl-1-methoxy-1-phenylprop-2-ylamine [(1*R*,2*S*,R_p)-5]. This reaction was also carried out on a 20-mmol scale. (1*R*,2*S*,R_p)-**5** was obtained as the major product when (1*R*,2*S*)-**3** (7.54 g, 20 mmol) was reacted in pentane with *t*-BuLi. Chromatography with PE/Et_2O/Et_3N (100/20/3) gave (1*R*,2*S*,R_p)-**5** as a red oil (9.1 g, 90%, 98% de). ^{1}H NMR *δ*: 1.07 (d, *J* = 6.8 Hz, 3H), 2.25 (s, 3H), 2.90 (dq, *J* = 4.8 and 6.8 Hz, 1H), 3.27 (s, 3H), 3.46 (d, *J* = 13.6 Hz, 1H), 3.50 (d, *J* = 13.6 Hz, 1H), 4.07 (s, 5H), 4.09 (m, 1H), 4.13 (m, 1H), 4.29 (d, *J* = 4.8 Hz, 1H), 4.38 (m, 1H), 7.22−7.27 (m, 3H), 7.30−7.34 (m, 2H). ^{13}C NMR *δ*: 9.2, 37.1, 45.7, 54.2, 56.7, 63.5, 68.5, 68.7, 71.5, 74.4, 85.2, 86.5, 127.0, 127.0, 128.0, 141.5. MS (80 °C) *m*/*z*: 503 (1) [M^+], 382 (23), 325 (100). HRMS: calcd for $C_{22}H_{26}ONFeI$ 503.0408, found 503.0419. $[\alpha]^{20}_\lambda = -35.7$ (589 nm), −38.3 (578 nm), −52.6 (546 nm) (*c* = 2.0, CH_2Cl_2).

(1*R*,2*S*,S_p)-*N*-(2-Iodoferrocenylmethyl)-*N*-methyl-1-methoxy-1-phenylprop-2-ylamine [(1*R*,2*S*,S_p)-5]. (1*R*,2*S*,S_p)-**5** was obtained as the main product when (1*R*,2*S*)-**3** (377 mg) was reacted in diethyl ether with *sec*-BuLi. Chromatography with PE/Et_2O/Et_3N (100/20/3) as the eluent yielded the product as a red oil (297 mg, 59%, 80% de). ^{1}H NMR *δ*: 1.08 (d, *J* = 6.7 Hz, 3H), 2.24 (s, 3H), 2.83 (dq, *J* = 5.3 and 6.7 Hz, 1H), 3.24 (s, 3H), 3.42 (d, *J* = 13.2 Hz, 1H), 3.48 (d, *J* = 13.2 Hz, 1H), 4.03 (m, 1H), 4.07 (s, 5H), 4.12 (m, 1H), 4.24 (d, *J* = 5.3 Hz, 1H), 4.36 (m, 1H), 7.20−7.25 (m, 3H), 7.29−7.34 (m, 2H). ^{13}C NMR *δ*: 8.4, 37.6, 46.2, 53.7, 56.7, 62.6, 68.8, 68.9, 71.5, 74.3, 84.5, 86.4, 127.0, 127.1, 128.0, 141.4. MS

(80 °C) *m*/*z*: 503 (2) [M$^+$], 382 (38), 325 (100). HRMS: calcd for $C_{22}H_{26}ONFeI$ 503.0408, found 503.0421. $[\alpha]^{20}_{\lambda} = +0.2$ (589 nm), +2.6 (578 nm), +11.4 (546 nm) (*c* = 0.5, CH_2Cl_2).

(1*S*,2*S*,*R*$_p$)-*N*-(2-Iodoferrocenylmethyl)-*N*-methyl-1-methoxy-1-phenylprop-2-ylamine [(1*S*,2*S*,*R*$_p$)-5]. (1*S*,2*S*,*R*$_p$)-**5** was obtained as the major product when (1*S*,2*S*)-**3** (377 mg) was reacted in pentane with *t*-BuLi. Red oil (317 mg, 63%, 49% de). ^{1}H NMR δ: 0.72 (d, *J* = 6.6 Hz, 3H), 2.30 (s, 3H), 3.12−3.20 (m, 1H), 3.17 (s, 3H), 3.62 (d, *J* = 13.6 Hz, 1H), 3.72 (d, *J* = 13.6 Hz, 1H), 4.11 (d, *J* = 8.6 Hz, 1H), 4.12 (s, 5H), 4.17 (m, 1H), 4.29 (m, 1H), 4.40 (m, 1H), 7.26−7.36 (m, 5H). ^{13}C NMR δ: 13.4, 36.2, 45.8, 55.6, 56.4, 63.7, 68.5, 68.9, 71.5, 74.6, 86.0, 86.6, 127.6, 127.8, 128.2, 141.0. MS (70 °C) *m*/*z*: 503 (2) [M$^+$], 382 (21), 325 (100). HRMS: calcd for $C_{22}H_{26}ONFeI$ 503.0408, found 503.0391. $[\alpha]^{20}_{\lambda} = +51.8$ (589 nm), +53.0 (578 nm), +53.0 (546 nm) (*c* = 2.0, CH_2Cl_2).

(1*S*,2*S*,*S*$_p$)-*N*-(2-Iodoferrocenylmethyl)-*N*-methyl-1-methoxy-1-phenylprop-2-ylamine [(1*S*,2*S*,*S*$_p$)-5]. (1*S*,2*S*,*S*$_p$)-**5** was obtained as the major product when (1*S*,2*S*)-**3** (377 mg) was reacted in Et_2O with *sec*-BuLi. Red oil (262 mg, 52%, 64% de). ^{1}H NMR δ: 0.75 (d, *J* = 6.8 Hz, 3H), 2.32 (s, 3H), 2.99 (dq, *J* = 6.8 and 8.4 Hz, 1H), 3.20 (s, 3H), 3.50 (d, *J* = 13.4 Hz, 1H), 3.71 (d, *J* = 13.4 Hz, 1H), 4.09−4.12 (m, 1H), 4.11 (s, 5H), 4.18 (m, 1H), 4.35 (m, 1H), 4.39 (m, 1H), 7.25−7.35 (m, 5H). ^{13}C NMR δ: 12.0, 37.6, 46.2, 53.4, 56.5, 61.9, 68.9, 69.0, 71.5, 74.3, 86.7, 86.8, 127.6, 127.8, 128.2, 140.9. MS (70 °C) *m*/*z*: 503 (2) [M$^+$], 382 (27), 325 (100). HRMS: calcd for $C_{22}H_{26}ONFeI$ 503.0408, found 503.0387. $[\alpha]^{20}_{\lambda} = +65.6$ (589 nm), +69.3 (578 nm), +87.2 (546 nm) (*c* = 1.0, CH_2Cl_2).

(1*R*,2*S*,*R*$_p$)-*N*-(2-Iodoferrocenylmethyl)-*N*-methyl-1-cyclohexyl-1-methoxyprop-2-ylamine [(1*R*,2*S*,*R*$_p$)-6]. (1*R*,2*S*,*R*$_p$)-**6** was obtained as the major product when (1*R*,2*S*)-**4** (383 mg) was reacted in Et_2O with *sec*-BuLi. Chromatography eluent PE/Et_2O/Et_3N (80/20/1). Red oil (81 mg, 16%, 17% de). ^{1}H NMR δ: 0.99 (d, *J* = 6.3 Hz, 3H), 0.88−1.26 (m, 6H), 1.51−1.74 (m, 5H), 2.14 (s, 3H), 2.74 (dq, *J* = 6.3 and 8.3 Hz, 1H), 2.79 (dd, *J* = 2.8 and 8.3 Hz, 1H), 3.36 (d, *J* = 13.2 Hz, 1H), 3.40 (d, *J* = 13.2 Hz, 1H), 3.41 (s, 3H), 4.09 (s, 5H), 4.14 (m, 1H), 4.18 (m, 1H), 4.19 (m, 1H). ^{13}C NMR δ: 8.5, 26.1, 26.5, 26.8, 26.9, 30.8, 36.4, 39.5, 45.8, 54.3, 56.5, 60.9, 68.4, 69.2, 71.4, 74.7, 86.5, 88.7. MS (70 °C) *m*/*z*: 509 (2) [M$^+$], 382 (14), 325 (64), 85 (100). HRMS: calcd for $C_{22}H_{32}ONFeI$ 509.0878, found 509.0854. $[\alpha]^{20}_{\lambda} = +11.8$ (589 nm), +11.2 (578 nm), +5.1 (546 nm) (*c* = 2.0, CH_2Cl_2).

(1*R*,2*S*,*S*$_p$)-*N*-(2-Iodoferrocenylmethyl)-*N*-methyl-1-cyclohexyl-1-methoxyprop-2-ylamine [(1*R*,2*S*,*S*$_p$)-6]. (1*R*,2*S*,*S*$_p$)-**6** was obtained as the major product when (1*R*,2*S*)-**4** (383 mg) was reacted in pentane with *t*-BuLi. Chromatography eluent PE/Et_2O/Et_3N (80/20/1). Red oil (392 mg, 77%, 78% de). ^{1}H NMR δ: 1.02 (d, *J* = 6.7 Hz, 3H), 0.88−1.26 (m, 6H), 1.52−1.76 (m, 5H), 2.10 (s, 3H), 2.72 (dq, *J* = 6.7 and 7.6 Hz, 1H), 2.80 (dd, *J* = 2.8 and 7.6 Hz, 1H), 3.38 (d, *J* = 13.2 Hz, 1H), 3.41 (d, *J* = 13.2 Hz, 1H), 3.42 (s, 3H), 4.10 (s, 5H), 4.17 (m, 1H), 4.26 (m, 1H), 4.39 (m, 1H). ^{13}C NMR δ: 8.5, 26.4, 26.5, 26.7, 26.9, 31.1, 36.4, 39.5, 46.0, 54.3, 57.7, 70.0, 68.7, 69.1, 71.5, 74.5, 86.6, 89.1. MS (70 °C) *m*/*z*: 509 (2) [M$^+$], 382 (13), 325 (77), 83 (100). HRMS: calcd for $C_{22}H_{32}ONFeI$ 509.0878, found 509.0887. $[\alpha]^{20}_{\lambda} = +25.8$ (589 nm), +27.7 (578 nm), +37.4 (546 nm) (*c* = 2.0, CH_2Cl_2).

(1*S*,2*S*,*R*$_p$)-*N*-(2-Iodoferrocenylmethyl)-*N*-methyl-1-cyclohexyl-1-methoxyprop-2-ylamine [(1*S*,2*S*,*R*$_p$)-6]. (1*S*,2*S*,*R*$_p$)-**6** was obtained as the major product when (1*S*,2*S*)-**4** (383 mg) was reacted in pentane with *t*-BuLi. Red oil (249 mg, 49%, 40% de). ^{1}H NMR δ: 0.94 (d, *J* = 6.8 Hz, 3H), 0.98−1.79 (m, 11H), 2.20 (s, 3H), 2.66 (t, *J* = 6.1 Hz, 1H), 2.89 (dq, *J* = 6.1 and 6.8 Hz, 1H), 3.43 (s, 3H), 3.44 (d, *J* = 13.4 Hz, 1H), 3.48 (d, *J* = 13.4 Hz, 1H), 4.09 (s, 5H), 4.16 (m, 1H), 4.26 (m, 1H), 4.38 (m, 1H). ^{13}C NMR δ: 9.3, 26.4, 26.6, 26.7, 27.9, 30.4, 36.3, 40.3, 46.0, 55.8, 57.8, 61.9, 68.4, 68.9, 71.5, 74.4, 86.9, 89.8. MS (70 °C) *m*/*z*: 509 (3) [M$^+$], 382 (23), 325 (100). HRMS: calcd for $C_{22}H_{32}ONFeI$ 509.0878, found 509.0864. $[\alpha]^{20}_{\lambda} = -8.7$ (589 nm), −9.7 (578 nm), −20.0 (546 nm) (*c* = 1.0, CH_2Cl_2).

(1*S*,2*S*,*S*$_p$)-*N*-(2-Iodoferrocenylmethyl)-*N*-methyl-1-cyclohexyl-1-methoxyprop-2-ylamine [(1*S*,2*S*,*S*$_p$)-6]. (1*S*,2*S*,*S*$_p$)-**6** was obtained as the major product when (1*S*,2*S*)-**4** (383 mg) was reacted in Et_2O with *sec*-BuLi. Red oil (199 mg, 39%, 16% de). ^{1}H NMR δ: 0.99 (d, *J* = 6.6 Hz, 3H), 0.84−1.84 (m, 11H), 2.20 (s, 3H), 2.67 (t, *J* = 6.1 Hz, 1H), 2.89 (dq, *J* = 6.1 and 6.6 Hz, 1H), 3.31 (d, *J* = 13.4 Hz, 1H), 3.46 (s, 3H), 3.61 (d, *J* = 13.4 Hz, 1H), 4.10 (s, 5H), 4.16 (m, 1H), 4.35 (m, 1H), 4.37 (m, 1H). ^{13}C NMR δ: 9.3, 26.4, 26.5, 26.7, 28.1, 30.4, 36.9, 40.3, 45.9, 54.4, 57.6, 62.0, 68.5, 69.1, 71.6, 74.2, 87.3, 90.3. MS (70 °C) *m*/*z*: 509 (3) [M$^+$], 382 (21), 325 (100). HRMS: calcd for $C_{22}H_{32}ONFeI$ 509.0878, found 509.0891. $[\alpha]^{20}_{\lambda} = +30.5$ (589 nm), +32.8 (578 nm), +45.4 (546 nm) (*c* = 1.0, CH_3CN).

Preparation of Derivatives 7−9. General Procedure. (1*R*,2*S*)-**3** was reacted in pentane with *t*-BuLi and quenched with the appropriate electrophile as described in the general preparation procedure for (1*R*,2*S*,*R*$_p$)-**5**. In the cases of **8** and **9**, after addition of the electrophile the reaction mixture was allowed to warm to room temperature and stirring was continued for 16 h before workup. The workup procedure was similar to that described for **5**. Products (1*R*,2*S*,*R*$_p$)-**7**, **8**, and **9** were purified by chromatography on silica with PE/Et_2O/Et_3N (100/20/1) as the eluent, unless stated otherwise.

(1*R*,2*S*,*R*$_p$)-*N*-(2-Bromoferrocenylmethyl)-*N*-methyl-1-methoxy-1-phenylprop-2-ylamine [(1*R*,2*S*,*R*$_p$)-7]. Reaction of (1*R*,2*S*)-**3** (4.54 g, 12 mmol) and 1,2-dibromotetrafluoroethane (4.69 g, 18 mmol) gave (1*R*,2*S*,*R*$_p$)-**7** as a red oil (4.60 g, 84%, 98% de). ^{1}H NMR δ: 1.06 (d, *J* = 6.8 Hz, 3H), 2.26 (s, 3H), 2.90 (dq, *J* = 4.6 and 6.8 Hz, 1H), 3.27 (s, 3H), 3.49 (d, *J* = 13.6 Hz, 1H), 3.63 (d, *J* = 13.6 Hz, 1H), 4.03 (m, 1H), 4.05 (m, 1H), 4.10 (s, 5H), 4.30 (d, *J* = 4.6 Hz, 1H), 4.37 (m, 1H), 7.23−7.26 (m, 3H), 7.30−7.34 (m, 2H). ^{13}C NMR δ: 9.0, 37.4, 52.4, 56.7, 63.7, 66.0, 68.2, 70.0, 71.0, 80.3, 84.2, 85.3, 126.9, 128.0, 126.9, 141.5. MS (50 °C) *m*/*z*: 457/455 (1) [M$^+$], 336/334 (22), 279/277 (100). HRMS: calcd for $C_{22}H_{26}ONFeBr$ 455.0547, found 455.0556. $[\alpha]^{20}_{\lambda} = -45.3$ (589 nm), −48.4 (578 nm), −60.6 (546 nm) (*c* = 0.66, $CHCl_3$).

(1*R*,2*S*,*R*$_p$)-*N*-(2-Diphenylphosphinoferrocenylmethyl)-*N*-methyl-1-methoxy-1-phenylprop-2-ylamine [(1*R*,2*S*,*R*$_p$)-8]. (1*R*,2*S*)-**3** (3.77 g, 10 mmol) and chlorodiphenylphosphine (3.32 g, 15 mmol) yielded (1*R*,2*S*,*R*$_p$)-**8** as an orange viscous oil (5.44 g, 97%, 98% de). ^{1}H NMR δ: 0.79 (d, *J* = 6.8 Hz, 3H), 2.01 (s, 3H), 2.75 (dq, *J* = 3.8 and 6.8 Hz, 1H), 3.22 (s, 3H), 3.44 (d, *J* = 13.4 Hz, 1H), 3.74 (m, 1H), 3.79 (dd, *J* = 1.5 and 13.4 Hz, 1H), 3.94 (s, 5H), 4.18 (m, 2H), 4.29 (m, 1H), 7.17−7.26 (m, 8H), 7.30−7.37 (m, 5H), 7.54−7.58 (m, 2H). ^{13}C NMR δ: 8.2, 36.4, 53.7 (d, *J* = 8.4 Hz), 56.5, 64.4, 68.7, 69.6, 71.3 (d, *J* = 4.6 Hz), 72.7 (d, *J* = 4.6 Hz), 75.7 (d, *J* = 8.4 Hz), 85.2, 92.2 (d, *J* = 24.3 Hz), 126.7, 126.8, 127.5, 127.7 (d, *J* = 6.1 Hz), 128.0, 128.0, 128.9, 132.5 (d, *J* = 18.2 Hz), 135.1 (d, *J* = 21.3 Hz), 138.1 (d, *J* = 8.4 Hz), 140.2 (d, *J* = 9.9 Hz), 142.0. ^{31}P NMR δ: −22.0. MS (150 °C) *m*/*z*: 561 (2) [M$^+$], 440 (24), 383 (100). HRMS: calcd for $C_{34}H_{36}ONFeP$ 561.1884, found 561.1878. $[\alpha]^{20}_{\lambda} = +213.7$ (589 nm), +225.6 (578 nm), +278.5 (546 nm) (*c* =1.0, CH_2Cl_2).

(1*R*,2*S*,*R*$_p$)-*N*-[2-(Diphenyl-hydroxymethyl)ferrocenylmethyl]-*N*-methyl-1-methoxy-1-phenylprop-2-ylamine [(1*R*,2*S*,*R*$_p$)-9]. (1*R*,2*S*)-**3** (377 mg, 1.0 mmol) and a solution of benzophenone (273 mg, 1.5 mmol) in THF (5 mL) gave (1*R*,2*S*,*R*$_p$)-**9** as an orange viscous oil (376 mg, 64%, 98% de). ^{1}H NMR δ: 0.85 (d, *J* = 6.8 Hz, 3H), 1.56 (br s, 1H), 2.11 (s, 3H), 2.76 (dq, *J* = 2.0 and 6.8 Hz, 1H), 3.03 (d, *J* = 13.6 Hz, 1H), 3.19 (s, 3H), 3.79 (d, *J* = 13.6 Hz, 1H), 3.83 (m, 1H), 3.93 (s, 5H), 4.08 (m, 2H), 4.22 (m, 1H), 7.10−7.36 (m, 12 H), 7.47−7.60 (m, 3H). ^{13}C NMR δ: 6.9, 36.3, 52.1, 56.6, 63.0, 65.4, 69.8, 70.7, 70.8, 77.7, 82.7, 83.9, 126.2, 126.4, 126.5, 127.0, 127.3, 127.4, 127.6, 128.1, 130.1, 140.9, 147.7, 149.9 (2 C signals not determined). MS (150 °C) *m*/*z*: 559 (5) [M$^+$ + 1], 438 (31), 381 (96), 243 (100). HRMS: calcd for $C_{35}H_{37}O_2NFe$ 558.2174, found 558.2248. $[\alpha]^{20}_{\lambda} = +155.7$ (589 nm), +168.1 (578 nm), +232.3 (546 nm) (*c* = 1.0, CH_2Cl_2).

(*R*$_p$)-1-Iodo-2-(dimethylaminomethyl)ferrocene [(*R*$_p$)-10]. To a solution of (1*R*,2*S*,*R*$_p$)-**5** (8.57 g, 17 mmol) in CH_3CN (60 mL) was added CH_3I (4.83 g, 34 mmol). After the mixture stirred for 30 min at room temperature, Et_2O (300 mL) was added slowly. The resulting yellow precipitate was filtered off

and dried in vacuo [10.5 g, 96% yield, mp 183 °C (dec)]. The dry ammonium iodide salt, 40% aqueous dimethylamine solution (100 mL) and benzene (100 mL) were placed in a 500-mL steel autoclave and heated to 110 °C for 16 h. After the reaction cooled to room temperature, the benzene layer was separated, and the aqueous phase was extracted with three portions of Et_2O (50 mL). The combined organic layers were washed with water and brine and dried with $MgSO_4$. After removal of the solvent, the residue was purified by chromatography on silica gel. Elution with PE/Et_2O/Et_3N (10/10/1) afforded (R_p)-**10** as a red oil [5.92 g, 99% yield; 95% overall based on (1*R*,2*S*,R_p)-**5**] in >99% ee as determined by HPLC.

(R_p)-1-Bromo-2-(dimethylaminomethyl)ferrocene [(R_p)-11]. (R_p)-**11** was prepared in exactly the same way as (R_p)-**10** (see above) starting from (1*R*,2*S*,R_p)-**7** (4.32 g, 9.5 mmol). The respective ammonium iodide intermediate was obtained as a yellow solid (5.42 g, 96% yield, mp 178 °C). Product (R_p)-**11** was isolated as a red liquid [2.83 g, 97% yield; 93% based on (1*R*,2*S*,R_p)-**7**] in >99% ee as determined by HPLC.

(R_p)-1-Diphenylphosphino-2-(dimethylaminomethyl)-ferrocene [(R_p)-12]. To a solution of (R_p)-**10** (2.58 g, 7 mmol) or (R_p)-**11** (2.25 g, 7 mmol) in Et_2O (70 mL) was added *n*-BuLi (5.3 mL of a 1.6 M solution in hexane, 8.5 mmol) at −40 °C, and the resulting mixture was stirred for 2 h. Subsequently, Ph_2PCl (2.3 g, 10.5 mmol) was added at −78 °C, the mixture was allowed to warm to room temperature, and stirring was continued overnight. After the reaction was quenched with aqueous $NaHCO_3$, the organic layer was separated, washed with brine, and dried over $MgSO_4$. The solvent was evaporated, and the residue was purified by chromatography on silica. Elution with PE/Et_2O/Et_3N (12/4/1) afforded (R_p)-**12** as a yellow solid (from **10**: 2.39 g, 80%; from **11**: 2.42 g, 81% yield).

The spectral data of **10**−**12** are in accordance with the values reported in ref 6.[24]

(R_p)-2-Acetoxymethyl-1-diphenylphosphinoferrocene [(R_p)-13].[7,17] A solution of (R_p)-**8** (561 mg, 1 mmol) or (R_p)-**12** (427 mg, 1 mmol) in acetic anhydride (5 mL) was degassed and heated for 3.5 h at 120 °C in the case of **8** or 30 min at 80 °C in the case of **12**. After the mixture cooled to room temperature, the acetic anhydride was removed in vacuo (directly from the Schlenk tube), and the residue was dissolved in CH_2Cl_2, washed with 2 N NaOH, water, and brine, and dried over $MgSO_4$. Removal of the solvent and chromatography on silica with PE/Et_2O/Et_3N (24/4/1) as eluent gave acetate (R_p)-**13** as a yellow solid [from (R_p)-**8**: 332 mg, 75%; from (R_p)-**12**: 398 mg, 90% yield]. Mp: 139 °C. ^{1}H NMR δ: 1.60 (s, 3H), 3.77 (m, 1H), 4.08 (s, 5H), 4.32 (m, 1H), 4.52 (m, 1H), 4.97 (d, J = 11.9 Hz, 1H), 5.15 (dd, J = 2.3 and 11.9 Hz, 1H), 7.15−7.24 (m, 5H), 7.37−7.40 (m, 3H), 7.51−7.56 (m, 2H). ^{13}C NMR δ: 20.4, 61.8 (d, J = 9.9 Hz), 69.6, 70.0, 72.3 (d, J = 3.8 Hz), 73.0 (d, J = 3.0 Hz), 77.7 (d, J = 9.1 Hz), 86.3 (d, J = 24.3 Hz), 127.8 (d, J = 5.3 Hz), 127.9 (d, J = 6.1), 128.2 (d, J = 8.4 Hz), 129.2, 132.5 (d, J = 18.2 Hz), 134.9 (d, J = 21.3 Hz), 137.0 (d, J = 9.1 Hz), 139.7 (d, J = 9.9 Hz), 170.6. ^{31}P NMR δ: −22.1. MS (110 °C) *m*/*z*: 442 (75) [M$^+$], 399 (8), 262 (100). HRMS: calcd for $C_{25}H_{23}O_2FeP$ 442.0785, found 442.0790. $[\alpha]^{20}_{\lambda}$ = +238.7 (589 nm), +251.0 (578 nm), +303.8 (546 nm) (c = 0.53).

Preparation of Ligands 14−16. General Procedure. A solution of 1 mmol of (R_p)-**8** (561 mg) or (R_p)-**12** (427 mg) in freshly distilled acetic acid (5 mL) was degassed, and the appropriate dialkyl- or diarylphosphine (1.2 mmol) was added by syringe. The resulting mixture was degassed again (careful exclusion of oxygen is crucial to obtain a good yield of the product) and reacted at elevated temperature (the course of the reaction was monitored by TLC). After completion, the reaction mixture was cooled to room temperature, and acetic acid was removed in vacuo directly from the Schlenk tube. The residue was dissolved in CH_2Cl_2, washed with saturated $NaHCO_3$, water, and brine, and dried over $MgSO_4$. Removal of the solvent and purification on alumia led to diphosphines **14**−**16**.

(24) The specific rotation of (R_p)-**11** given in ref 6 should read: $[\alpha]^{20}_{\lambda}$ = +337.6 (589 nm), 359.0 (578 nm), +457.6 (546 nm) (c = 0.5, $CHCl_3$).

(R_p)-2-[(Dicyclohexylphosphino)methyl]-1-diphenylphosphinoferrocene [(R_p)-14]. From (R_p)-**8** or (R_p)-**12**: dicyclohexylphosphine (238 mg) as nucleophile. From (R_p)-**8**: heating at 130 °C for 12 h. From (R_p)-**12**: heating at 100 °C for 40 h. Chromatography with PE (to remove unreacted phosphine) followed by PE/Et_2O (25/1) as eluent gave the product as a yellow solid [479 mg, 81% yield from both (R_p)-**8** and (R_p)-**12**]. From (R_p)-**13**: a solution of (R_p)-**13** (442 mg, 1 mmol) in 1-methyl-2-pyrrolidinone (NMP) (5 mL) was degassed, and dicyclohexylphosphine (238 mg, 1.2 mmol) was added by syringe. The resulting mixture was degassed again and heated to 130 °C for 60 h. Subsequently, the reaction mixture was cooled to room temperature, washed with saturated aqueous NH_4Cl, water, and brine, and dried over $MgSO_4$. Removal of the solvent and purification on alumina (as described above) gave the desired product (342 mg, 59%). Mp: 115 °C (from ethanol). ^{1}H NMR δ: 0.84−1.80 (m, 22H), 2.66 (dd, J = 3.3 and 15.4 Hz, 1H), 2.70 (dd, J = 2.3 and 15.4 Hz, 1H), 3.73 (m, 1H), 3.97 (d, 5H), 4.22 (m, 1H), 4.55 (m, 1H), 7.17−7.26 (m, 5H), 7.38 (m, 3H), 7.54−7.58 (m, 2H). ^{13}C NMR δ: 21.3 (dd, J = 9.9 and 19.0 Hz), 26.4, 26.6, 27.1, 27.3 (d, J = 9.1 Hz), 27.3 (d, J = 9.1 Hz), 27.4, 29.4 (d, J = 7.6 Hz), 29.5 (d, J = 6.8 Hz), 29.6 (d, J = 12.2 Hz), 30.0 (d, J = 12.9 Hz), 33.4 (d, J = 14.4 Hz), 34.1 (d, J = 14.4 Hz), 68.7, 69.8, 70.6 (d, J = 3.8 Hz), 72.3 (dd, J = 3.8 and 10.6 Hz), 75.5 (dd, J = 3.8 and 6.0 Hz), 93.3 (dd, J = 18.2 and 25.9 Hz), 127.6, 127.9 (d, J = 5.3 Hz), 128.0 (d, J = 7.6 Hz), 129.0, 132.5 (d, J = 17.5 Hz), 135.2 (d, J = 20.5 Hz), 138.1 (d, J = 9.1 Hz), 139.9 (d, J = 9.1 Hz). ^{31}P NMR δ: −22.6 (d, J = 5.1 Hz), −1.0 (d, J = 5.1 Hz). MS (140 °C) *m*/*z*: 580 (3) [M$^+$], 497 (100), 415 (4). HRMS: calcd for $C_{35}H_{42}FeP_2$ 580.2112, found 580.2130. $[\alpha]^{20}_{\lambda}$ = +164.7 (589 nm), +174.3 (578 nm), +218.0 (546 nm) (c = 0.43, $CHCl_3$) [lit. for (S_p)-**14**: $[\alpha]^{20}_{\lambda}$ = −160 (589 nm) (c = 1.0, $CHCl_3$)].[7]

(R_p)-1-Diphenylphosphino-2-[(diphenylphosphino)-methyl]ferrocene [(R_p)-15]. From (R_p)-**8** or (R_p)-**12**: diphenylphosphine (223 mg) as nucleophile. From (R_p)-**8**: heating at 80 °C for 4 h. From (R_p)-**12**: heating at 100 °C for 40 h. Chromatography with PE (to remove unreacted phosphine) followed by PE/Et_2O (20/1) as eluent gave the product as a yellow solid [159 mg, 28% yield from (R_p)-**8**; 216 mg, 38% yield from (R_p)-**12**]. Mp: 55 °C. ^{1}H NMR δ: 3.35 (s, 2H), 3.75 (m, 1H), 3.96 (s, 5H), 4.07 (m, 1H), 4.14 (m, 1H), 7.17−7.45 (m, 18H), 7.56−7.61 (m, 2H). ^{13}C NMR δ: 28.8 (dd, J = 10.6 and 16.0 Hz), 69.0, 69.9, 70.7 (d, J = 3.8 Hz), 71.9 (dd, J = 3.8 and 7.6 H), 75.8 (dd, J = 3.8 and 6.1 Hz), 90.5 (dd, J = 16.0 and 25.9 Hz), 127.7, 127.9, 128.0 (d, J = 6.1 Hz), 128.1 (d, J = 3.0 Hz), 128.2 (d, J = 6.8 Hz), 128.3 (d, J = 6.8 Hz), 128.8, 129.1, 132.2 (d, J = 17.5 Hz), 132.5 (d, J = 17.5 Hz), 133.5 (d, J = 19.8 Hz), 135.2 (d, J = 20.5 Hz), 138.0 (d, J = 8.4 Hz), 140.0 (d, J = 16.0 Hz), 139.3 (d, J = 16.0 Hz), 140.0 (d, J = 9.1 Hz). ^{31}P NMR δ: −22.5 (d, J = 8.0 Hz), −14.0 (d, J = 8.0 Hz). MS (140 °C) *m*/*z*: 568 (31) [M$^+$], 497 (33), 414 (25), 383 (32), 57 (100). HRMS: calcd for $C_{35}H_{30}FeP_2$ 568.1173, found 568.1161. $[\alpha]^{20}_{\lambda}$ = +177.9 (589 nm), +187.0 (578 nm), +214.3 (546 nm) (c = 0.44, $CHCl_3$) [lit. for (S_p)-**15**: $[\alpha]^{20}_{\lambda}$ = −178 (589 nm) (c = 1.0, $CHCl_3$)].[7]

(R_p)-1-Bis[3,5-bis(trifluoromethyl)phenyl]phosphino-methyl-2-diphenyl-phosphinoferrocene [(R_p)-16]. From (R_p)-**8** or (R_p)-**12**: bis[3,5-bis(trifluoromethyl)phenyl]phosphine (413 mg) as the nucleophile. From (R_p)-**8**: heating at 80 °C for 4 h. From (R_p)-**12**: heating at 100 °C for 40 h. Chromatography with PE (to remove unreacted phosphine) followed by PE/Et_2O (30/1) as eluent gave the product as a yellow solid [50 mg, 6% yield from (R_p)-**8**; 25 mg, 3% yield from (R_p)-**12**]. Mp: 47 °C. ^{1}H NMR δ: 3.29 (dd, J = 2.8 and 13.9 Hz, 1H), 3.67 (ddd, J = 2.5, 5.0 and 13.9 Hz, 1H), 3.86 (m, 1H), 3.90 (m, 1H), 3.97 (s, 5H), 4.20 (m, 1H), 7.14−7.19 (m, 2H), 7.24 (m, 3H), 7.39 (m, 3H), 7.55−7.60 (m, 2H), 7.68 (d, J = 5.8 Hz, 4H), 7.78 (s, 1H), 7.87 (s, 1H). ^{13}C NMR δ: 29.3 (dd, J = 9.9 and 16.7 Hz), 69.6, 70.1, 71.7−71.8 (m, 2C), 76.0 (dd, J = 2.3 and 8.4 Hz), 87.7 (dd, J = 16.0 and 27.4 Hz), 122.9−123.0 (m), 123.02 (d, J = 271.2 Hz), 123.04 (d, J = 271.2 Hz), 123.4−123.5 (m), 128.1 (d, J = 6.8 Hz), 128.1, 128.2 (d, J = 7.6 Hz), 129.3, 131.5 (d, J = 27.0 Hz), 131.8−132.1 (m), 131.9 (d, J =

33.4 Hz), 132.6 (dd, J = 1.5 and 16.7 Hz), 133.3−133.5 (m), 135.0 (d, J = 20.5 Hz), 137.4 (d, J = 7.6 Hz), 139.5 (d, J = 7.6 Hz), 140.5 (d, J = 23.6 Hz), 141.1 (d, J = 23.6 Hz). The quoted coupling constants refer to $^{13}C-^{31}P$ and $^{13}C-^{19}F$. ^{31}P NMR δ: −24.6 (d, J = 20.0 Hz), −12.0 (d, J = 20.0 Hz). MS (120 °C) m/z: 840 (86) [M^+], 627 (9), 519 (11), 383 (100). HRMS: calcd for $C_{39}H_{26}FeP_2F_{12}$ 840.0668, found 840.0649. $[\alpha]^{20}_{\lambda}$ = +147.7 (589 nm), +153.6 (578 nm), +177.2 (546 nm) (c = 0.39, $CHCl_3$).

Acknowledgment. This work was kindly supported by Österreichische Nationalbank (project 7516). A PhD grant from Bundesministerium für Auswärtige Angelegenheiten (Nord-Süd-Dialog Stipendienprogramm) is kindly acknowleged by L.X.

JO015949Y