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Synthesis of α-Hydrazino Ketones via Regio- and Stereoselective Electrophilic Amination of Manganese Enolates and Enamines

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Abstract: A straightforward procedure for the regio- and stereoselective synthesis of α-hydrazino ketones is described. Manganese enolates and manganese enamines derived from ketones and from the corresponding *N*-sulfinylimines react with azodicarboxylate esters (DTBAD and DEAD) in a regioselective fashion to afford in good to excellent yields the kinetic α-hydrazino ketones as sole or highly prevalent products. When enantiopure *N*-sulfinyl manganese enamines were used the stereoselectivity of these reactions ranged from 40% to 68% ee.

The α-alkylation of ketones is a challenging reaction in organic synthesis, and metal enolates have been used to this purpose extensively. Along with carbonyl compounds, alkyl halides are arguably the classical electrophiles. However, the two major problems encountered are the formation of polyalkylated side products and, in the case of unsymmetrical ketones, a poor control of the regioselectivity. Previous advances in the field of organomanganese chemistry have featured the possibility of preparing regioselectively, by treatment of ketones with Mn-amides[1] or by Li−, Mg−, and Na−Mn transmetalation,[2] Mn-enolates which react with C-electrophiles leading to α-substituted ketones. On the other hand, the electrophilic amination of nucleophiles is of considerable current interest as it provides a powerful method for introducing a nitrogen functionality at a carbanionic site.[3] Among the vast array of electrophilic amination reagents di-*tert*-butyl azodicarboxylate (DTBAD) and diethyl azodicarboxylate (DEAD), have been extensively used as aminating reagents. Conspicuous advantages offered by these reagents rely upon the very high diastereofacial selectivity in their reaction with chiral enolates[4] or with achiral enolates mediated by chiral metal complexes[5] and on the availability of well-established methods[6] for N−N bond cleavage under mild conditions.

The purpose of this paper is to report a new complementary approach to the formal synthesis of α-amino ketones via the electrophilic amination with azodicarboxylates of Mn-enolates prepared from manganese amides. The produced α-hydrazino ketones are versatile precursors for diverse α-amino ketone derivatives essential components of the Knorr pyrrole synthesis[7] and of considerable value as intermediates for the synthesis of adrenergic ethanolamine derivatives[8] and other biologically significant compounds.[9] Though numerous methods of preparing these compounds are known,[10] new processes to provide access need to be devised.

Organomanganese amides were easily prepared[1] in THF by reaction of 2 equiv of MeLi with a 1:1 mixture of the soluble $MnBr_4Li_2$ "ate" complex and the suitable R′R″NH. Exposure of various ketones to these organometallic reagents led to formation of the corresponding Mn-enolates. The strongly prevailing *Z* configuration of manganese enolates has been demonstrated by ^{1}H NMR measurements on the corresponding silyl enol ethers by Cahiez and others.[1b] These enolates react with azodicarboxylates under mild conditions to provide the α-hydrazino ketones **1**−**16** (Chart 1 and Table 1).

As shown from the results in Table 1, several interesting trends emerge. Regarding the amination efficiency of the two azodicarboxylates, DEAD appears to some extent superior to DTBAD (compare entries 1−2 and entries 9−10), and changing the amine in the Mn-amide led to major differences in either product yields or regio-

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(1) (a) Cahiez, G.; Figadère B.; Cléry, P. *Tetrahedron Lett*. **1994**, *35*, 3065−3068. (b) Cahiez, G.; Figadère, B.; Cléry, P. *Tetrahedron Lett*. **1994**, *35*, 6295−6298. (c) Cahiez, G.; Kanaan, M.; Cléry, P. *Synlett*, **1995**, 191−192.

(2) (a) Cahiez, G.; Cléry, P.; Lafitte, J. A. Fr. Pat. Appl. 90/16413, 1990; 91/11814, 1991; PCT Int. Appl. WO 93/06071, 1993. (b) Reetz, M. T.; Hanning, H. *Tetrahedron Lett*. **1993**, *34*, 7395−7398. (c) Cahiez, G.; Chau, K.; Cléry, P. *Tetrahedron Lett*. **1994**, *35*, 3069−3072. (d) Cahiez, G.; Clery, P.; Laffitte, J.-A. US Patent 5,426,201, 1995. (e) Cahiez, G.; Chau, K.; Blanchot, B. *Org. Synth.* **1998**, *76*, 239−251. (f) Inoue, R.; Shinokubo, H.; Oshima, K. *J. Org. Chem*. **1998**, *63*, 910−911. (g)-Maier, S.; Kazmaier, U. *Eur. J. Org. Chem*. **2000**, 1241−1245.

(3) Reviews: (a) Erdik, E.; Ay, M. *Chem. Rev*. **1989**, *89*, 1947−1980. (b) Boche, G. *Stereoselective Synthesis*; Houben-Weyl; G. Thieme: Stuttgart, 1995; Vol. E21, pp 5133−5157. (c) Genet, J. P.; Greck, C.; Lavergne, D. In *Modern Amination Methods*; Ricci, A., Ed.; Wiley-VCH: New York, 2000; pp 65−102. (d) Dembech, P.; Seconi, G.; Ricci, A. *Chem. Eur. J*. **2000**, *6*, 1281−1286.

(4) (a) Evans, D. A.; Britton, T. C.; Dorow, R. L.; Dellaria, J. F., Jr. *Tetrahedron* **1988**, *44*, 5525−5540. (b) Fernandez-Megia, E.; Paz, M. M.; Sardina, F. J. *J. Org. Chem*. **1994**, *59*, 7643−7652. (c) Greck, C.; Ferreira, F.; Genet, J. P. *Tetrahedron Lett*. **1996**, *37*, 2031−2034. (d) Seebach, D.; Sting, A. R. *Tetrahedron Lett.* **1996**, *37*, 279−290. (e) Aya, P.; Ben, R. N.; Qin, H. *Tetrahedron Lett*. **1998**, *39*, 6131−6134. (f) Bulman Page, P. C.; McKenzie, M. J.; Allin, S. M.; Buckle, D. R. *Tetrahedron* **2000**, *56*, 9683−9695. (g) Vicario, J. L.; Badia, D.; Carrillo, L.; Anakabe, E. *Tetrahedron*: *Asymmetry* **2002**, *13*, 754−751.

(5) (a) Evans, D. A.; Nelson, S. G.; *J. Am. Chem. Soc.* **1997**, *119*, 6452−6453. (b) Evans, D. A.; Johnson, D. S. *Org. Lett*. **1999**, *1*, 595−598. (c) Marigo, M.; Juhl, K.; Jørgensen, K. A. *Angew. Chem., Int. Ed*. **2003**, *42*, 1367−1369.

(6) (a) Gmeiner, P.; Hummel, E. *Synthesis* **1994**, 1026−1028.(b) Gmeiner, P.; Bollinger, B. *Tetrahedron* **1994**, 50, 10909−10922.

(7) (a) Gossauer, A. *Die Chemie der Pyrrole*; Springer-Verlag: New York, 1974; pp 210−220. (b) Jones, R. A.; Bean, G. P. *The Chemistry of Pyrroles*; Academic Press: London, 1977; pp 51−57.

(8) Tramontini, M. *Synthesis* **1982**, 605−644.

(9) Mayer D. *Houben-Weyl, Methoden der Organischen Chemie*, 4th ed.; G. Thieme: Stuttgart, 1977; Vol. 7/2C, p 2251.

(10) (a) Mayer, D. In *Houben-Weyl, Methoden der Organischen Chemie*, 4th ed.; G. Thieme: Stuttgart, 1977; Vol. 7/2c. (b) De Kimpe, N.; Verhe, R.; De Buyck, L.; Moens, L.; Sulmon, P.; Schamp. N. *Synthesis* **1982**, 765−766.(c) Pfaltz, A.; Anwar, S. *Tetrahedron Lett*. **1984**, *25*, 2977−2980. Azadi-Ardakani, M.; Alkhader, M. A.; Lippiatt, J. H.; Patel, D. I.; Smalley, R. K.; Higson, S. *J. Chem. Soc., Perkin Trans. 1* **1986**, 1107−1111.

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CHART 1

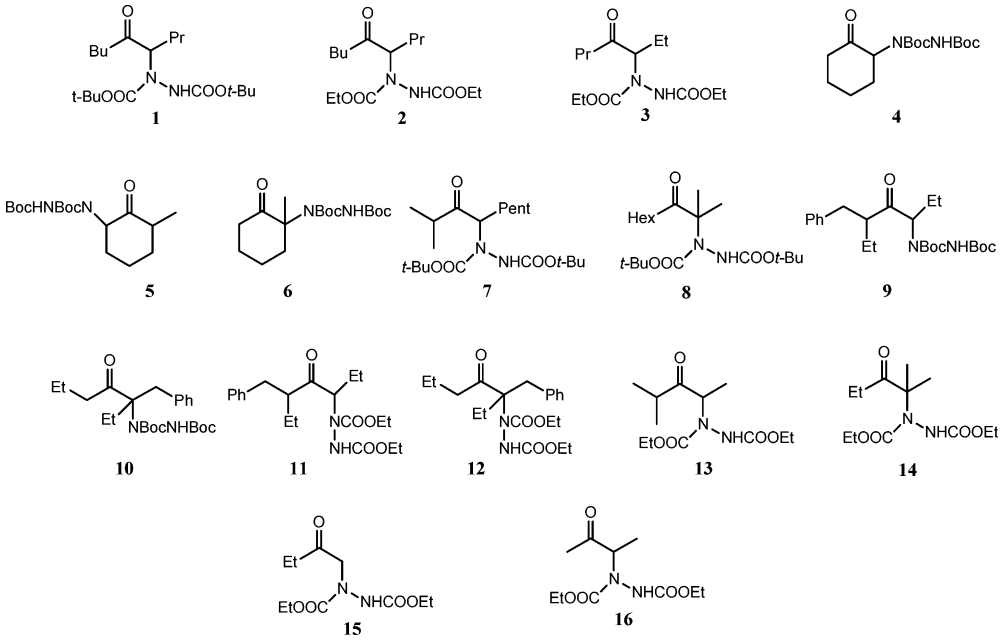
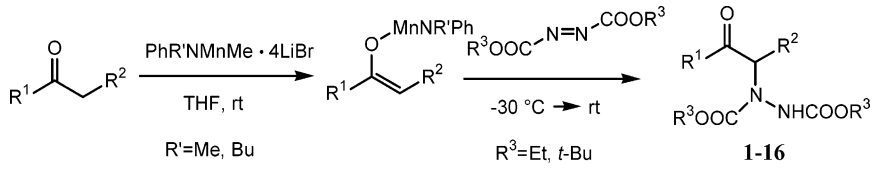


TABLE 1. Results of the Reaction of Azodicarboxylates with Ketones



entry	ketone[a]	M-amide	aminating reagent[b]	product (yield, %)[e]	regioselectivity kinetic/thermodynamic
1	BuCOBu	PhMeNMnMe	DTBAD	**1** (60)	
2	BuCOBu	PhMeNMnMe	DEAD	**2** (90)	
3	PrCOPr	PhMeNMnMe	DTBAD	**3** (60)	
4	cyclohexanone	PhMeNMnMe	DTBAD	**4** (25)	
5	2-Me-cyclohexanone	PhMeNMnMe	DTBAD	**5**[c]−**6**[d] (52)	40/60
6	2-Me-cyclohexanone	PhBuNMnMe	DTBAD	**5**[c]−**6**[d] (84)	91/9[f]
7	2-Me-cyclohexanone	LDA	DTBAD	**5**[c]−**6**[d] (52)	12/88
8	HexCO-*i*-Pr	PhBuNMnMe	DTBAD	**7**[c]−**8**[d] (60)	98/2
9	$PhCH_2$(Et)COPr	PhBuNMnMe	DTBAD	**9**[c]−**10**[d](75)	90/10
10	$PhCH_2$(Et)COPr	PhBuNMnMe	DEAD	**11**[c]−**12**[d](93)	98/2
11	EtCO-*i*Pr	PhBuNMnMe	DEAD	**13**[c]−**14**[d](72)	90/10
12	EtCOMe	PhBuNMnMe	DEAD	**15**[e]−**16**[d](50)	50/50

[a] The enolization was performed at 25 °C for 60 min. [b] The amination reaction started at −30 °C and was allowed to rise to 20 °C and resulted completed after 2.5 h. [c] Kinetic product. [d] Thermodynamic product. [e] Yield of isolated products. [f] Reducing the enolization time to 30 min, led to recovery of the expected amination product in 96% yield as a kinetic/thermodynamic mixture in the 88/12 ratio.

selectivity (entries 5−6). Comparison of results obtained in the electrophilic amination of Li- and Mn-enolates highlights the beneficial effect of the new methodology. Amination of the lithium enolate prepared with LDA from 2-methylcyclohexanone afforded (entry 7) in moderate overall yield (52%) the expected product, and a prevalence (88/12) of the thermodynamic regioisomer was observed. From the corresponding Mn-enolate (entry 6), the hydrazino ketone was obtained in 84% yield and with a high regioselectivity (91/9) in favor of the kinetic regioisomer. Good yields and high regiocontrol were finally observed using unsymmetrical open-chain ketones (entries 8−12). Throughout the work, the kinetic regioisomer gave highly favorable results with the exception of methyl ethyl ketone (entry 12), which gave in moderate yield a mixture of the kinetic and thermodynamic regioisomers in a 1:1 ratio. Finally, α-hydrazino ketones **5**, **9**, and **11** were obtained as 3:1 diastereomeric mixtures.

Inspired by these encouraging results, we extended the Mn-mediated enolization to imines for establishing the applicability of the kinetic regiocontrol to molecules containing a C=N moiety, and with the ultimate goal of moving toward interesting bifunctional compounds such as 1,2-diamines. To this purpose we focused our attention on ketone-derived sulfinimines (*N*-sulfinylimines) since these imines are quite stable compounds and the sulfinyl group activates the C=N bond to nucleophilic additions[11] and is easily removed from the product. Furthermore, in the presence of suitable bases, *N*-sulfinylimines from

(11) (a) Liu, G.; Cogan, D. A.; Owens, T. D.; Tang, T. P.; Ellman, J. A. *J. Org. Chem*. **1999**, *64*, 1278−1284. (b) Evans, J. W.; Ellman, J. A. *J. Org. Chem*. **2003**, *68,* 9948−9957.

SCHEME 1

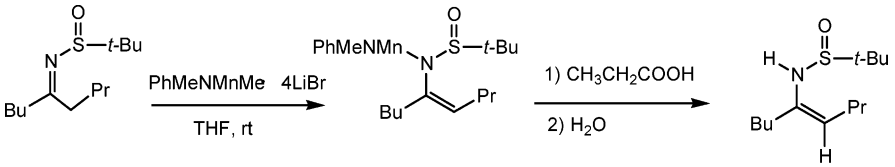
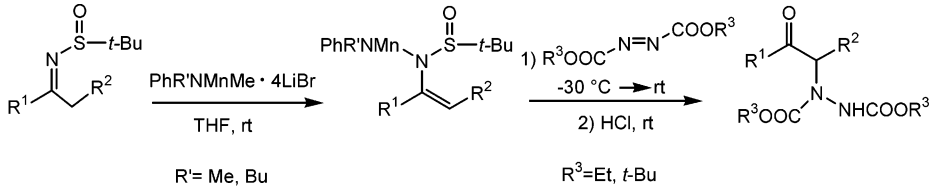
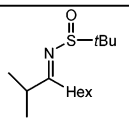
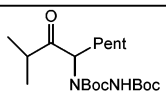
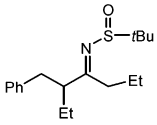
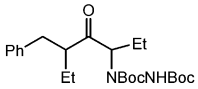
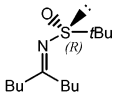
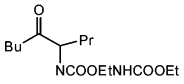
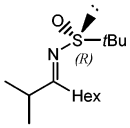
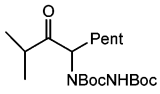
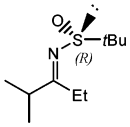
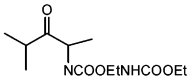


TABLE 2. Results of the Reaction of Azodicarboxylates with Sulfinimines



Entry	Sulfinimine	Product[a]	Yield(%)[b]	Regioselectivity Kinetic/Thermo dynamic	ee%
1	 (±)-(**17**)	 (**7**)	65	98/2	-
2	 (±)-(**18**)	 (**9**)	50	99/1	-
3	 (-)-(**19**)	 (**2**)	50	-	65
4	 (-)-(**17**)	 (**7**)	65	98/2	68
5	 (-)-(**20**)	 (**13**)	50	90/10	40

[a] Reaction conditions: sulfinimine (1 equiv), PhR′NMnMe/4LiBr (1.2 equiv), THF, 120 min, DEAD or TBAD (1.2 equiv), HCl 2 M. [b] Yields are referred to the isolated kinetic product.

aldehydes and ketones can enolize[12] but to date no studies have been performed regarding the regiochemical outcome under different conditions and the chemistry of metalloenamines.[13]

Several representative racemic (**17** and **18**) and homochiral ((−)-**19**, (−)-**17**, and (−)-**20**) *N*-sulfinylimines were synthesized from *tert*-butanesulfinamide. From NMR spectra only one species was detected which, in line with Ellman's findings,[11a] was assumed to be the *E* isomer. Enolization with Mn-amide led to the intermediate Mn-enamines. After quenching with 1 equiv of propionic acid the corresponding sulfinyl enamine **21** was obtained, whose *Z* configuration was demonstrated by ^{1}H NOE studies (Scheme 1).

In situ treatment with azodicarboxylates of the *N*-sulfinyl manganese enamines led after acidic hydrolysis of the intermediate imine, to the corresponding hydrazino ketones in satisfactory yields (Table 2).

(12) (a) Davis, F. A.; Reddy, R. E.; Szewczyk, J. M.; Reddy, G. V.; Portonovo, P. S.; Zhang, H.; Fanelli, D.; Reddy, R. T.; Zhou, P.; Carrol, P. J. *J. Org. Chem.* **1997**, *62*, 2555−2563. (b) Li, B.-F.; Yuan, K.; Zhang, M.-J.; Wu, H.; Dai, L.-X.; Wang, Q. R.; Hou, X.-L. *J. Org. Chem*. **2003**, *68*, 6264−6267.

(13) Martin, D. Metalloenamines. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon: Oxford, 1991; Vol. 2, pp 475−502.

The sole or the strongly prevailing kinetic regioisomer can be detected starting from imino derivatives when the enolization is promoted by a Mn-amide (entries 1, 2, 4, and 5 in Table 2). Taking into consideration that the sulfinyl group is also an excellent chiral auxiliary,[12] preliminary attempts were finalized at devising an asymmetric version of this regioselective amination reaction by using homochiral symmetrically (−)-**19** and unsymmetrically substituted (−)-**17** and (−)-**20** *N*-sulfinyl imines. Merging regiocontrolled enolization with an enantioselective bond construction would represent a highly desiderable breakthrough in selective synthesis. Employing the previously described procedure, the α-hydrazino ketones were formed in good yields (entries 3−5 in Table 2). The determination of the enantiomeric excess of **2**, **7**, and **13** was performed by HPLC using Chiracel OD and Chiralpak AD-H chiral columns (see the Experimental Section).

Significant enantiomeric enrichments, ranging from 40% to 68% ee, were observed (entries 3−5) for the α-hydrazino ketones **2**, **7**, and **13**, generated from the homochiral sulfinamides. Most interestingly, in the reaction starting from (−)-**17** and (−)-**20** the observed asymmetric induction combines with an excellent regiocontrol, thus highlighting the potentiality of this protocol to be exploited in highly selective synthesis.

In summary, the electrophilic amination of Mn-enolates and Mn-enamines with azodicarboxylates provides an expedient approach to the synthesis of kinetic α-hydrazino ketones. This methodology nicely complements among the others, the alternatives recently reported based on L-proline catalysis,[14] which provides α-hydrazino ketones as regioisomeric mixtures in which the thermodynamic product prevails and opens new interesting perspectives in the area of enolate functionalization.

Experimental Section

Typical Procedure for the Preparation of Mn-Amide RR′NMnMe·4LiBr: PhMeNMnMe·4LiBr. A suspension of dried $MnBr_2$ (1.2 mmol, 256 mg) and LiBr (2.4 mmol, 208 mg) in anhydrous THF (3 mL) was stirred at 20 °C under Ar atmosphere. After the mixture was stirred for 30 min at room temperature (clear solution), PhMeNH (0.13 mL, 1.2 mmol) was added. The solution was cooled to 0 °C, and then MeLi (1.6 M solution in hexane, 2.4 mmol, 1.5 mL) was added dropwise. The resulting solution was stirred at 0 °C for 15 min and then allowed to warm to room temperature.

Typical Procedure: *N,N′*-Bis(*tert*-butoxycarbonyl)-6-hydrazino-5-nonanone (1). To a solution of Mn-amide PhMeNMnMe·4LiBr (1.2 mmol) in anhydrous THF (3 mL) was added 0.17 mL of 5-nonanone (1 mmol) at room temperature. After 60 min, the reaction mixture was cooled to −30 °C, di-*tert*-butyl azodicarboxylate (276 mg, 1.2 mmol) was added, and the mixture was then allowed to warm to room temperature and stirred for 2.5 h. After quench with a 1 N HCl solution and extraction with diethyl ether, the combined organic layers were washed with brine, dried over $MgSO_4$, and filtered and the solvent removed under vacuum. Pure **1** (222 mg, 60%) was obtained as a yellow solid after flash chromatography on silica gel (Hex/AcOEt 9:1): mp 65−66 °C; ^{1}H NMR (C_6D_6, 300 MHz) δ 0.76 (t, J = 7.45 Hz, 3 H), 0.87 (t, J = 6.45 Hz, 3H), 1.06−1.22 (m, 2H) 1.25−1.76 (m, 6H), 1.36 (s, 9H), 1.41 (s, 9H), 2.02−2.40 (m, 2H), 4.85−4.96 (m, 1H), 6.53 (bs, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 14.0 (2C), 19.8, 22.4, 25.9, 28.3 (2C), 29.6, 39.7, 65.6, 80.7, 81.8, 155.1, 156.1, 210.3; ESIMS *m/z* 395 $(M + Na)^+$, 371 $(M - H)^-$. Anal. Calcd for $C_{19}H_{36}N_2O_5$: C, 61.26; H, 9.74; N, 7.52. Found: C, 61.29; H, 9.74; N, 7.48.

***N,N′*-Bis(*tert*-butoxycarbonyl)-2-hydrazino-2-methylcyclohexanone (6), via LDA.** To a stirred solution of diisopropylamine (0.17 mL, 1.2 mmol) in THF (1 mL) was added *n*-BuLi (1.6 M solution in hexane, 0.75 mL, 1.2 mmol) at −70 °C. The resulting solution was allowed to warm to 0 °C and then stirred for 1 h. 2-Methyl cyclohexanone (0.12 mL, 1 mmol) dissolved in of THF (1 mL) was added to the LDA solution at 0 °C and allowed to warm to room temperature. After 60 min, the reaction mixture was cooled to −30 °C, and di-*tert*-butyl azodicarboxylate (276 mg, 1.2 mmol) was added. The solution was stirred for 2.5 h at room temperature, then quenched with a 1 N HCl solution, and extracted with diethyl ether (3 × 10 mL). The combined organic layers were washed with NaCl saturated solution, dried over $MgSO_4$, and filtered, and the solvent was removed under vacuum. Flash chromatography on silica gel (Hex/AcOEt 9:1) afforded 157 mg (46%) of **6** as a yellow oil and 20 mg of **5** (6%) as white solid. For **6**: ^{1}H NMR (C_6D_6, 300 MHz) δ 1.12 (s, 3H), 1.31−1.45 (m, 2H), 1.36 (s, 9H), 1.39 (s, 9H), 1.74−1.86 (m, 2H), 2.13−2.26 (m, 2H), 2.48−2.64 (m, 2H), 6.29 (bs, 1H); ^{13}C NMR (C_6D_6, 75 MHz) δ 20.8, 21.5, 23.9, 27.9 (2C), 29.4, 38.2, 55.4, 80.4 (2C) 155.9, 156.0, 209.3; ESIMS *m/z* 365 $(M + Na)^+$. Anal. Calcd for $C_{17}H_{30}N_2O_5$: C, 59.63; H, 8.83; N, 8.12. Found: C, 59.70; H, 8.78; N, 8.20.

Typical Procedure: (*R*)-(−)-*N*-(1-Butylpentylidene)-2-methyl-2-propanesulfinamide (19). To a solution of 5-nonanone (0.25 mL, 1.5 mmol) and $Ti(OEt)_4$ (0.62 mL, 3 mmol) in THF (2.7 mL) under Ar atmosphere was added (*R*)-(+)-2-methyl-2-propanesulfinamide (200 mg, 1.65 mmol), and the mixture was heated to 60 °C. After 3 h, the reaction was cooled to room temperature and poured into an equal volume of brine with rapid stirring. The resulting suspension was filtered through a plug of Celite. The aqueous layer was extracted with EtOAc, and the combined organic portions were washed with brine, dried over $MgSO_4$, filtered, and concentrated under vacuum to afford the crude product. Purification by flash chromatography (Hex/AcOEt:10/1) afforded 220 mg (60%) of the imine (−)-**19** as a clear oil: $[\alpha]^{20}_D$ −157.1 (*c* 1.0 g/100 mL, $CHCl_3$); ^{1}H NMR (C_6D_6, 400 MHz) δ 0.71 (t, J = 7.41 Hz, 6H), 1.02−1.19 (m, 4H), 1.09 (s, 9H), 1.24−1.41 (m, 4H), 1.88−2.00 (m, 2H), 2.41−2.60 (m, 2H); ^{13}C NMR (C_6D_6, 100 MHz) δ 13.8, 14.00, 22.4 (2C), 23.1, 27.9, 29.8, 35.8, 40.7, 56.2, 186.7. Anal. Calcd for $C_{13}H_{27}NOS$: C, 63.62; H, 11.09; N, 5.71. Found: C, 63.58; H, 11.12; N, 5.75.

Typical Procedure: Amination of (*R*)-(−)-*N*-(1-Butylpentylidene)-2-methyl-2-propanesulfinamide (19). Imine (*R*)-(−)-**19** (200 mg, 0.82 mmol) dissolved in 1 mL of anhydrous THF was added to a solution of Mn-amide PhMeNMnMe·4LiBr (1.2 equiv) in THF (3 mL) at 20 °C. After 60 min, the mixture was cooled at −30 °C, and 0.15 mL (1.2 equiv) of diethyl azodicarboxylate was added. The solution was then allowed to warm to room temperature, stirred for 2.5 h, and hydrolyzed with 5 mL of 2 N HCl solution. After 1 h of stirring, the mixture was extracted with ether (3 × 10 mL). The combined organic portions were washed with saturated NH_4Cl, $NaHCO_3$ and brine, dried over $MgSO_4$, filtered, and concentrated under vacuum. Purification by flash silica gel chromatography afforded 129 mg (50%) of **2** as a thick yellow oil. The ee (65%) was determined by HPLC (Chiralcel OD column, Hex/*i*-PrOH 98:2, flow 0.5 mL/min, equipped with light scattering detector): t_{Rmajor} = 21.89 min, t_{Rminor} = 27.20 min.

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Supporting Information Available: Experimental procedures details and characterization data for compounds **2**−**5**, **7**, **9**, **11**, **13**, and **17**−**21**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(14) Kumaragurubaran, N.; Juhl, K.; Zhuang, W.; Bøgevig, A.; Jørgensen, K. A. *J. Am. Chem. Soc.* **2002**, *124*, 6254−6255.