87463-40-9; **40**, 87463-33-0; **41**, 87463-34-1; (±)-**43**, 87481-47-8; (±)-**44**, 87463-56-7; **45**, 7493-75-6; (±)-**46**, 87463-57-8; (±)-**47**, 87463-58-9; (±)-yohimbaniminium ion, 87481-45-6; (*E*)-2,4-pentadienoic acid, 21651-12-7; (*E*)-*N*-methyl-3,5-hexadien-1-amine, 87463-59-0; phenethylamine, 64-04-0; tryptophyl bromide, 55982-76-8; allylamine, 107-11-9; *N*-allyl-*N*-methylamine, 627-37-2; acryloyl chloride, 814-68-6; diisopropylethylamine, 7087-68-5; methyltriphenylphosphonium bromide, 1779-49-3.

A Series of (2*S*)-2-*O*-Protected-2-hydroxypropanals (L-Lactaldehydes) Suitable for Use as Optically Active Intermediates

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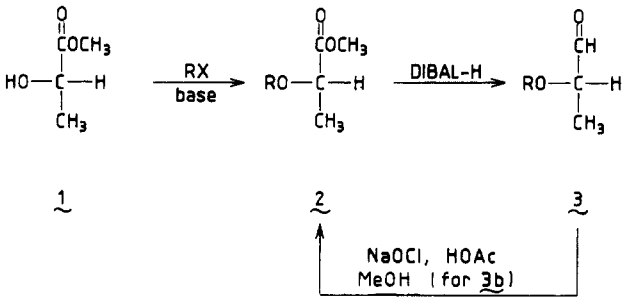
The synthesis and properties of a series of (2*S*)-2-*O*-protected-2-hydroxypropanals, where the protecting groups are *tert*-butyldimethylsilyl (**3a**), *tert*-butyldiphenylsilyl (**3b**), and (methoxyethoxy)methyl (**3c**), are described. A ^{1}H NMR spectroscopic method of determining the optical purity of methyl L-lactate is described.

Short-chain, highly functionalized, optically active compounds are in considerable demand as starting materials in the synthesis of complex natural products via the newer methods developed in the area of stereochemically controlled organic reactions.[1-3] In this laboratory the need for both enantiomers of a protected 2-hydroxypropanal for the synthesis of the possible diastereomers of EHNA,[4,5] a semi-tight-binding inhibitor of adenosine deaminase, was satisfied by deriving both (2*S*)- and (2*R*)-2-benzyloxypropanals from L-rhamnose and D-mannose, respectively. Upon the identification of the biologically more potent isomer as the 2*S*,3*R* isomer,[4] an acute need for its precursor, an *O*-protected (2*S*)-hydroxypropanal developed. Hence a shorter route to this intermediate was sought.

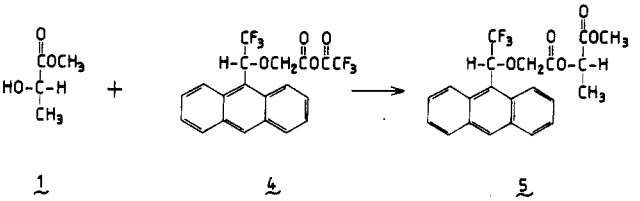
The most logical source of (2*S*)-2-hydroxypropanal derivatives is from (2*S*)-2-hydroxypropionic acid (L-lactic acid), which is available from fermentation of D-glucose using *Lactobacillus delbrueckii*.[6] We chose for our studies a commercial preparation of 2-hydroxypropanoic acid methyl ester (**1**, methyl L-lactate).[7] Inasmuch as the optical rotations for both L-lactic acid and its methyl ester **1** are reported to be low [i.e., $[\alpha]^{22}_D$ +2.67° (*c* 2.5, water)[8] and $[\alpha]^{26}_D$ −8.25° (neat),[9] respectively, for L-lactic acid and **1**], optical methods for determination of the optical purity of the commercial sample were abandoned in favor of a more direct method. Based on the work of Pirkle and Simmons,[10] the optically active mixed anhydride **4** was reacted with **1** in pyridine to give the (trifluoromethyl)anthrylmethyl derivative **5** (Scheme I and II). The product **5** was isolated from the crude reaction mixture by column chromatography, with care being taken to include all material that eluted in the zone for **5** (or its possible diastereomeric contaminant) so that no possible diastereomeric separations would occur.[11] Examination of **5** by

Scheme I



Series	R
a	$Me_2(Me_3C)Si$
b	$Ph_2(Me_3C)Si$
c	$MeOCH_2CH_2OCH_2$
d	$PhCH_2$ (for 3 only)

Scheme II



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(7) Our starting materials (**1** and L-lactic acid) were kindly donated by the Pettibone Corporation, Chicago, IL, and were scrutinized carefully as described in the text for optical purity. Both L-lactic acid and its methyl ester were considered to be >99% optically pure by the ^{1}H NMR technique. It is worth noting that sulfuric acid and boron trifluoride etherate catalyzed esterifications of L-lactic acid resulted in ca. 4% racemization.
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(11) The precautions taken in the chromatographic step cannot be overemphasized. Both diastereomeric products (i.e., **5** and its diastereomer from (2*R*)-hydroxypropanoic methyl ester) have been shown to be inseparable by both silica gel (adsorption) and octadecylsilyl (reverse-phase) high-pressure liquid chromatography. This column chromatographic step is necessary to purify **5** from **1** and **4**, as well as decomposition products of **4** and **5**.

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200-MHz Fourier-transform ^1H NMR spectroscopy, using deuterated benzene as solvent, revealed signals for only a single diastereomer, a fact determined by deliberate addition of a D,L mixture prepared from **4** and D,L-**1**. By making use of the methyl ($-OCH_3$) resonance at δ 3.11 and the A,B pattern for the methylene ($-OCH_2C{=}O$) protons at δ 3.81, one could ascertain that the (2S)-2-hydroxypropionic acid methyl ester (**1**) was indeed >99% optically pure. (Compare δ 3.22 and 3.84 for the methyl and methylene resonances, respectively, for the 2R isomer of **5** prepared from D,L-methyl lactate). Such a procedure was found superior to traditional spectropolarimetric techniques, including the use of the molybdate complex[6] that has been recommended for lactic acid.[12]

Protection of the hydroxy group presented some difficulties, as benzylation of **1** using sodium hydride–benzyl bromide in *N,N*-dimethylformamide invariably gave low yields of the benzyl ether **2d**. However, derivitization using *tert*-butylchlorodimethylsilane[13] or *tert*-butylchlorodiphenylsilane[14] in tetrahydrofuran containing triethylamine and 4-(dimethylamino)pyridine gave high yields of both silyl derivatives **2a** and **2b**. Similarly (methoxyethoxy)methyl chloride (MEM-Cl)[15] in dichloromethane with ethylbis(2-propyl)amine gave the analogous MEM derivative **2c**[16] in 90% yield.

Reduction of each of the ester derivatives **2a–2c** was carried out at −78 °C with diisobutylaluminum hydride in hexane,[17] with water quenching at −40 °C, to give the respective aldehydes **3a–3c** in high yield after column chromatography. The products were all distillable oils[18,19] that, as previously noted with **3d**,[5] rapidly hydrated in moist solvent (or handling in the open air) to give the hydrated aldehydes (i.e., the *gem*-diols), a phenomenon well documented for such aldehydes.[20] As the hydration products show much lower optical rotations than their *aldehydo* counterparts, and the latter products are nearly impossible to maintain in the *aldehydo* form in solution, optical rotations were most reliably determined as fully equilibrated solutions in 95% ethanol. As such, the values obtained for each sample were reproducible within the limits of experimental error (ca. ±2%). As the question of possible racemization of **3a–3c** is always of importance, one derivative, **3b**, was oxidized directly to the methyl ester **2b** using sodium hypochlorite in acetic acid–methanol.[21] Examination of this product (**2b**) by ^1H NMR and polarimetry confirmed that little, if any, racemization had taken place during the steps **1** → **2b** → **3b** → **2b**. Thus these optically active aldehydes, as pointed out earlier for the benzyl-protected derivative **3d**,[5] appear to be stable, useful intermediates perhaps for stereocontrolled syntheses such as aldol reactions where racemic **3a**, **3b**, and **3d** have been used.[18]

Experimental Section

General. All solutions were evaporated at 40 °C under aspirator vacuum. Chromatography was carried out using E. Merck Silica Gel-60 products (cat. no. 7734, 0.073–0.20 mm particle size, for open columns; cat. no. 5539 aluminum-backed plates for TLC) with the solvents indicated. Gas–liquid chromatography was conducted on a Hewlett-Packard 5710A flame-ionization instrument equipped with capillary columns, either a 0.25 mm × 7 m OV-101 or a 0.25 mm × 30 m SE-54 column. Proton nuclear magnetic resonance (^1H NMR) was carried out using a Nicolet NT-200 instrument in the indicated solvent with internal tetramethylsilane as standard (δ Me_4Si 0.0). Chemical shifts are reported as δ (ppm), with coupling constants in hertz (Hz) being apparent, first-order values. Mass spectra (MS) were determined using the appropriate GLC column on a Hewlett-Packard 5985A GLC-MS instrument operating at 70 eV in the electron-impact mode. Optical rotations were measured at the indicated wavelength and concentration on a Perkin-Elmer Model 241 digital spectropolarimeter in 1-dm tubes. All reagents and solvents were of reagent grade and were used directly as supplied except those noted as follows: dry tetrahydrofuran (distilled from potassium benzophenone ketyl); dichloromethane (dried over a column of aluminum oxide, activity I).

(2*S*)-2-[(*tert*-Butyldimethylsilyl)oxy]propanoic Acid Methyl Ester (2a). A solution of 15.6 g (0.149 mol) of (2S)-2-hydroxypropanoic acid methyl ester (**1**), 30.0 g (0.199 mol) of *tert*-butylchlorodimethylsilane (Petrarch), 38.7 g (0.382 mol) of triethylamine, and 1.83 g (0.015 mol) of 4-(dimethylamino)pyridine (Reilly) in 150 mL of anhydrous tetrahydrofuran was stirred under a dry nitrogen atmosphere for 12 h, at the end of which time the solvent was evaporated. The residue was triturated in ether, the salts removed by filtration, and the filtrate was washed sequentially with 15% acetic acid, water, saturated aqueous sodium bicarbonate, and water and then dried over anhydrous magnesium sulfate. Evaporation of the ether gave the crude oily product that was purified by distillation to yield 30.0 g (90%) of pure **2a**: bp 95 °C (30 torr); $[\alpha]^{21}_D$ −31.7° (*c* 0.66, 95% ethanol); IR (neat) 2870, 1760, 1740, and 1125 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.07, 0.09 (s, s, 3 H, 3 H, CH_3Si), 0.90 [s, 9 H, $(CH_3)_3C$], 1.4 (d, 3 H, $J_{3,2}$ = 7, H-3), 3.75 (s, 3 H, $-CO_2CH_3$), 4.23 (q, 1 H, $J_{2,3}$ = 6.88, H-2).

Anal. Calcd for $C_{10}H_{22}O_3Si$: C, 55.0; H, 10.15. Found: C, 55.12; H, 10.19.

(2*S*)-2-[(*tert*-Butyldiphenylsilyl)oxy]propanoic Acid Methyl Ester (2b). By analogy with the same procedure as for **2a**, 10.0 g (0.096 mol) of **1**, 34.3 g (0.125 mol) of *tert*-butylchlorodiphenylsilane (Silar), 33.4 mL (24.3 g, 0.240 mol) of triethylamine, and 1.17 g (0.010 mol) of 4-(dimethylamino)pyridine (Reilly) were reacted in 100 mL of anhydrous tetrahydrofuran to give upon workup a crude product that was purified in 7-g lots by chromatography over a column of 200 g of silica gel using 1:1 dichloromethane–hexane to yield a total of 26.6 g (81%) of pure **2b** as indicated by TLC and ^1H NMR, R_f 0.63 (dichloromethane). An analytical sample was obtained by short-path distillation: $[\alpha]^{21}_D$ −51.8° (*c* 0.78, 95% ethanol); IR (neat) 2870, 1760, 1740, 1117, and 1140 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.07 [s, 9 H, $(CH_3)_3C$], 1.36 (d, 3 H, $J_{3,2}$ = 6.93, H-3), 3.55 (s, 3 H, CO_2CH_3), 4.28 (q, 1 H, $J_{2,3}$ = 6.76, H-2), 7.29–7.48, 7.56–7.77 (m, m, 5 H, 5 H, aryl, aryl).

Anal. Calcd. for $C_{20}H_{26}O_3Si$: C, 70.13; H, 7.66. Found: C, 70.09; H, 7.68.

(2*S*)-2-[((Methoxyethoxy)methyl)oxy]propanoic Acid Methyl Ester (2c). To a solution of 10.0 g (0.096 mol) of **1** and 18.6 g (0.144 mol) of ethylbis(2-propyl)amine (Aldrich) in 100 mL of dry dichloromethane maintained under a dry nitrogen atmosphere was added 17.9 g (0.144 mol) of (methoxyethoxy)methyl chloride (Aldrich). After the solution was stirred for 12 h, it was washed sequentially with 1 N HCl, water, saturated aqueous sodium bicarbonate, and water and then dried over magnesium sulfate. Evaporation of the solvent gave a crude product that was

(12) An older method based on ^1H NMR techniques (See Dale, J. A.; Dull, D. L.; Mosher, H. S. *J. Org. Chem.* **1969**, *34*, 2543.), which makes use of α-methoxy-α-(trifluoromethyl)phenylacetyl derivatives, has been used to determine the optical purity of **1**; however, a europium shift reagent was required to achieve separation of the signals of interest. See Yasuhara, F.; Yamaguchi, S. *Tetrahedron Lett.* **1980**, *21*, 2827–2830.

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(16) Racemic **2c** is reported (no data) by Heathcock, C. H.; Hagen, J. P.; Jarvi, E. T.; Pirrung, M. C.; Young, S. D. *J. Am. Chem. Soc.* **1981**, *103*, 4972–4974.

(17) Compare Heathcock, C. H.; Pirrung, M. C.; Lampe, J.; Buse, C. T.; Young, S. D. *J. Org. Chem.* **1981**, *46*, 2290–2300, who report the reduction of racemic **2d** to give racemic **3d**.

(18) Racemic **3a**, **3b**, and **3d** have been previously reported. See Heathcock, C. H.; Young, S. D.; Hagen, J. P.; Pirrung, M. C.; White, C. T.; VanDerveer, D. *J. Org. Chem.* **1980**, *45*, 3846–3856 for (±)-**3a**, ref. 16 for (±)-**3b**, and ref. 17 for (±)-**3d**.

(19) **Note Added in Proof**: After submission of this manuscript, **3c** was described. See: Kelly, T. R.; Kaul, P. N. *J. Org. Chem.* **1983**, *48*, 2775–2776.

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purified by distillation to yield 17.4 g (90%) of pure **2c**:[16] bp 125–129 °C (30–32 torr); $[\alpha]^{21}_D$ −74.9° (*c* 0.64, 95% ethanol); IR (neat) 1760, 1460, 1370, and 1110 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.43 (d, 3 H, $J_{3,2}$ = 6.75, H-3), 3.38 (s, 3 H, CH_3OCH_2), 3.54 (m, 2 H, CH_3OCH_2), 3.67–3.83 (m, 5 H, OCH_2CH_2O, $-CO_2CH_3$), 4.29 (q, 1 H, $J_{2,3}$ = 6.84, H-2), 4.79 (s, 2 H, OCH_2O).

Anal. Calcd for $C_8H_{16}O_5$: C, 49.98; H, 8.39. Found: C, 49.84; H, 8.44.

(2*S*)-2-[(*tert*-Butyldimethylsilyl)oxy]propanal (3a). To a solution of 10.0 g (0.053 mol) of (2*S*)-2-[(*tert*-butyldimethylsilyl)oxy]propanoic acid methyl ester (**2a**) in 60 mL of dry hexane cooled to −78 °C was added with stirring 50 mL of a 20% solution (0.071 mol) of diisobutylaluminum hydride in hexane[17] (Aldrich) over a period of 30 min. When GLC analysis (SE-54) indicated the completion of reaction, 40 mL of water was added, and the mixture was allowed to warm to room temperature. After filtration to remove insolubles, the aldehyde was extracted with ether, the ether extract was dried over magnesium sulfate, and the solvent was evaporated to yield the crude aldehyde. Purification of the product on a column of 200 g of silica gel that was eluted with 1:1 dichloromethane–hexane gave 7.95 g (92%) of **3a** as an oil that was pure by ^{1}H NMR and GLC analysis.[18] An analytical sample was purified by short-path distillation: bp 79 °C (28 torr); $[\alpha]^{21}_D$ −6.13° (*c* 1, 95% ethanol), $[\alpha]_{578}$ +6.17°, $[\alpha]_{365}$ +21.1°; IR (neat) 1760, 1450, and 1360 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.09, 0.11 (s, s, 3 H, 3 H, CH_3Si), 0.92 [s, 9 H, $(CH_3)_3C$], 1.27 (d, 3 H, $J_{3,2}$ = 6.9, H-3), 4.1 (q, 1 H, $J_{2,3}$ = 6.6, H-2), 9.62 (s, 1 H, H-1); MS(EI), *m/z* (relative intensity), 173 (1.4) M^+ – Me, 131 (100) M^+ – *t*-Bu, 103 (19.1), 75 (13.9), 73 (27.0), 59 (5.7), 45 (4.1).

Anal. Calcd for $C_9H_{20}O_2Si$: C, 57.44 H, 10.72. Found: C, 57.22; H, 10.7.

(2*S*)-2-[(*tert*-Butyldiphenylsilyl)oxy]propanal (3b). By the procedure described for **3a**, 5.5 g (0.016 mol) of methyl (2*S*)-2-[(*tert*-butyldiphenylsilyl)oxy]propanoic acid methyl ester was reduced with 30 mL (0.020 mol) of diisobutylaluminum hydride, and the crude aldehyde **3b** was purified on a column of 100 g of silica gel eluted with 1:1 dichloromethane–hexane to yield 4.8 g (87%) of **3b** that was pure by TLC and ^{1}H NMR.[18] An analytical sample was prepared by short-path distillation: bp 108–110 °C (0.05 torr); $[\alpha]^{21}_D$ −10.2° (*c* 1.2, 95% ethanol); R_f 0.44 (1:1 dichloromethane:hexane); IR (neat) 2870, 1740, and 1115 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.1 [s, 9 H, $(CH_3)_3C$], 1.21 (d, 3 H, $J_{3,2}$ = 6.76, H-3), 4.1 (q, 1 H, $J_{2,3}$ = 6.72, H-2), 7.29–7.54, 7.54–7.78 (m, m, 5 H, 5 H, aryl, aryl), 9.64 (s, 1 H, *H*-1); MS (EI), *m/z* (relative intensity) 255 (100) M^+ – *t*-Bu, 181 (4.5), 178 (12.9), 177 (90.7), 135 (20.1), 117 (18.1), 105 (16.6), 77 (5.5).

Anal. Calcd for $C_{19}H_{24}SiO_2$: C, 73.04; H, 7.73. Found: C, 73.02; H, 7.77.

(2*S*)-2-[((Methoxyethoxy)methyl)oxy]propanal (3c).[19] By the procedure for **3a** and with the solvent 95:5 hexane–tetrahydrofuran, 10.0 g (0.052 mol) of 2-[((methoxyethoxy)methyl)oxy]propanoic acid methyl ester (**2c**) was reduced with 48 mL (0.068 mol) of 20% diisobutylaluminum hydride in hexane to give, after purification by distillation, 7.81 g (92%) of pure **3c** (GLC/SE-54): bp 37 °C (1 torr), 95 °C (15 torr); $[\alpha]^{21}_D$ −28.8° (*c* 1, 95% ethanol); $[\alpha]_{365}$ −82.0°; IR (neat) 1725, 1450, and 1360 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.33 (d, 3 H, $J_{3,2}$ = 6.93, H-3), 3.39 (s, 3 H, CH_3O), 3.55 (t, 2 H, CH_3OCH_2), 3.76 (m, 2 H, OCH_2CH_2O), 4.1 (q, 1 H, $J_{2,3}$ = 6.63, H-2), 4.83 (s, 2 H, OCH_2O), 9.65 (s, 1 H, H-1); MS (EI), *m/z* (relative intensity) 133 (10.7) M^+ – CHO, 117 (26.1), 103 (3.5), 89 (100), 88 (21.9), 59 (20.6), 45 (9.0).

Anal. Calcd for $C_7H_{14}O_4$: C, 51.85; H, 8.70. Found: C, 51.62; H, 8.75.

Oxidation of (2*S*)-2-[(*tert*-Butyldiphenylsilyl)oxy]propanal (3b) to (2*S*)-2-[(*tert*-Butyldiphenylsilyl)oxy]propanoic Acid Methyl Ester (2b). Approximately 1.5 mL of a cold 1.5 M solution of sodium hypochlorite was added dropwise to a solution of 0.60 g (1.9 mmol) of aldehyde **3b** and 0.2 g (3.33 mmol) of acetic acid in 2 mL of methanol at 0 °C. After 20 min at 0 °C, the mixture was warmed to room temperature and stirred for 12 h.[21] To the mixture was added 50 mL of ether, and the ether extract was washed with saturated aqueous sodium sulfite, saturated aqueous sodium bicarbonate, and water, followed by drying over magnesium sulfate. The ether was evaporated to give the crude product which was purified as described in the foregoing preparation of **2b** to give a low yield of pure **2b** (20%), identical with the authentic product by ^{1}H NMR, TLC, and optical rotation; $[\alpha]^{21}_D$ −50.2° (*c* 0.7, 95% ethanol).

(2*S*)-2-[(+)-α-[(1-(9-Anthryl)-2,2,2-trifluoroethoxy)-acetyl]oxy]propanoic Acid Methyl Ester (5). The method of Pirkle and Simmons[10] was followed whereby the mixed anhydride **4**, prepared from 150 mg (0.45 mmol) of (+)-α-[1-(9-anthryl)-2,2,2-trifluoroethoxy]acetic acid and 620 mg (2.94 mmol) of trifluoroacetic anhydride, was reacted under reflux with 200 mg (1.92 mmol) of methyl (2*S*)-lactate (**1**)[7] in 15 mL of dry tetrahydrofuran containing 0.5 mL of dry pyridine. After 5 h at reflux, the cooled mixture was washed sequentially with 1 N hydrochloric acid, water, saturated aqueous sodium bicarbonate, and water, followed by drying over magnesium sulfate. The viscous oily product that was obtained upon evaporation of the solvent was purified by column chromatography over 20 g of silica gel with 2:1 dichloromethane–carbon tetrachloride. Care was exercised to collect all the zone indicated to be the desired adduct in order not to fractionate a possible diastereomeric mixture: yield, 73 mg (9.8%) of pure **5** as an oil that can be stored at −20 °C; ^{1}H NMR (C_6D_6) δ 0.9 (d, 3 H, $J_{3,2}$ = 7, H-3), 3.11 (s, 3 H, CO_2CH_3), 3.81 (dd, 2 H, $J_{a,b}$ = 16.5, $OCH_2C{=}O$), 4.86 (1 H, $J_{2,3}$ = 7.03, H-2), 6.81 (q, 1 H, $J_{H,F}$ = 7.64, $HCCF_3$), 7.16–7.39, 7.65–81, 8.0–8.3 (m, m, aryl, aryl); MS (EI), *m/z* 420 (75) M^+·, 351 (100) M^+· – CF_3, 259 (69) [M^+· – $C_6H_9O_5$], 206 (31) [anthryl – CHO]$^+$·, 177 (9) [anthryl]$^+$·.

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Registry No. 1, 27871-49-4; **2a**, 87681-24-1; **2b**, 87681-25-2; **2c**, 87681-26-3; **3a**, 87727-28-4; **3b**, 87696-33-1; **3c**, 86163-01-1; **4**, 81408-52-8; **5**, 87681-27-4; *tert*-butylchlorodimethylsilane, 18162-48-6; *tert*-butylchlorodiphenylsilane, 58479-61-1; (methoxyethoxy)methyl chloride, 3970-21-6; (+)-α-[1-(9-anthryl)-2,2,2-trifluoroethoxy]acetic acid, 87727-29-5; trifluoroacetic anhydride, 407-25-0.