A Publication of Reliable Methods for the Preparation of Organic Compounds

Organic Syntheses

Working with Hazardous Chemicals

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September 2014: The paragraphs above replace the section "Handling and Disposal of Hazardous Chemicals" in the originally published version of this article. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

DIASTEREOSELECTIVE SYNTHESIS OF PROTECTED VICINAL AMINO ALCOHOLS: (S)-2-[(4S)-N-tert-BUTOXYCARBONYL-2,2-DIMETHYL-1,3-OXAZOLIDINYL]-2-tert-BUTYLDIMETHYLSILOXYETHANAL FROM A SERINE-DERIVED ALDEHYDE

[3-Oxazolidinecarboxylic acid, 4-[1-[[(1,1-dimethylethyl)dimethylsilyl]oxy]-2-oxoethyl]-2,2-dimethyl-, 1,1-dimethylethyl ester, [S-(R*,R*)]-]
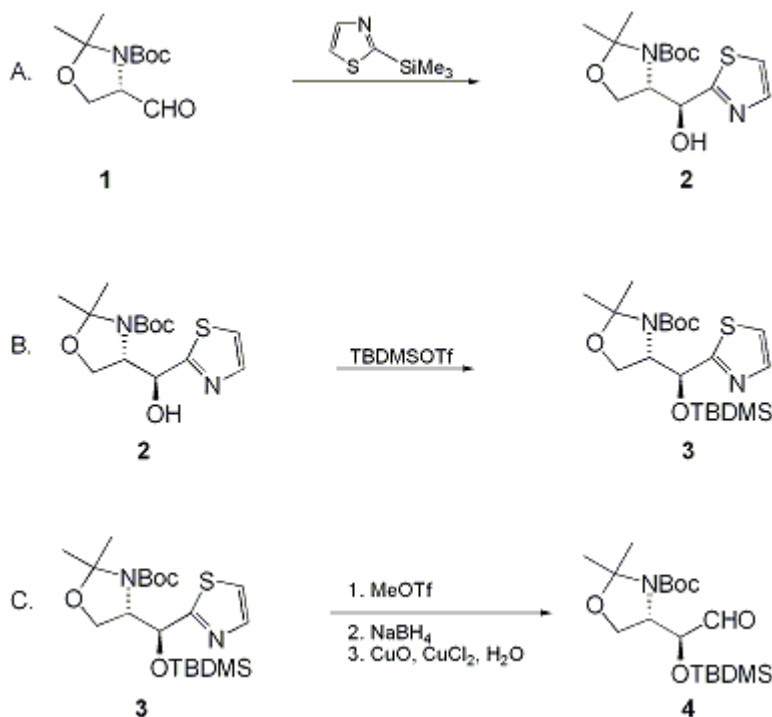
Submitted by Alessandro Dondoni and Daniela Perrone[1] .
Checked by Hou Chen and William R. Roush.

1. Procedure

A. *(S)-2-{[(4S)-N-tert-Butoxycarbonyl-2,2-dimethyl-1,3-oxazolidin-4-yl]hydroxymethyl}-1,3-thiazole* **(2)** . A 100-mL, two-necked, round-bottomed flask, containing a magnetic stirring bar, is equipped with a low-temperature thermometer and one equalizing dropping funnel (Note 1). The funnel is charged with a solution of 2-(trimethylsilyl)thiazole (2-TST, 6.17 g, 39.2 mmol, (Note 2)) in 10 mL of methylene chloride (Note 3) and connected to a nitrogen flow line. The flask is charged with a solution of aldehyde **1** (7.5 g, 32.7 mmol, (Note 4)) in 65 mL of methylene chloride , then cooled to −35°C in a CryoCool bath and 2-TST is added dropwise over 15 min (Note 5). After completion of the addition, the funnel is washed with two 1-mL portions of methylene chloride , then replaced with a rubber septum. The flask is allowed to stand at −20°C (freezer) overnight (15 hr, (Note 6)), then allowed to warm to room temperature and concentrated under reduced pressure. To the residue dissolved in 40 mL of tetrahydrofuran is added, in one portion, tetrabutylammonium fluoride trihydrate (12.3 g, 39.0 mmol), and the brown reaction mixture is stirred at room temperature for 30 min (Note 7) and (Note 8). The solvent is removed under reduced pressure and the residue is partitioned between ethyl acetate (200 mL) and aqueous saturated sodium bicarbonate solution (2 × 250 mL). The aqueous phase is extracted with ethyl acetate (3 × 80 mL); then the combined organic phases are dried with anhydrous sodium

sulfate and concentrated under reduced pressure using a 1-L flask to give 9.76 g (95% crude yield) of a clear brown solid. Analysis of crude product by ^{1}H NMR indicates a chemical purity of 90-95% and a diastereomeric ratio of 92% (anti-adduct). To the same 1-L flask equipped with a reflux condenser is added 475 mL of cyclohexane . The mixture is warmed at 80°C (water bath) until an homogeneous solution is obtained (Note 9). The hot solution is quickly filtered and allowed to cool to room temperature and to stand at this temperature overnight, at which time a white precipitate is formed. The precipitate is collected by filtration and washed with three 10-mL portions of cold cyclohexane to give 7.15-7.50 g (70-73% yield) of **2** as a white solid: mp 171-173°C (Note 10). The filtrate is concentrated under reduced pressure and purified by flash chromatography with a 5 × 14-cm column of silica gel (Note 11), (cyclohexane-ethyl acetate (2:3) and 0.2% of triethylamine), to give an additional 1.20-1.40 g (11.6-13.6% yield) of a mixture of syn- and anti- **(2)** adducts (Note 12). Analysis of this mixture by ^{1}H NMR indicates a syn/anti diastereomeric ratio of 1.2:1.

B. (S)-2-{[(4S)-N-tert-Butoxycarbonyl-2,2-dimethyl-1,3-oxazolidin-4-yl]-tert-butyldimethylsiloxy}-1,3-thiazole **(3)** . A 100-mL, one-necked, round-bottomed flask (Note 1) equipped with a magnetic stirring bar and a rubber septum is charged with a solution of the alcohol **2** (4.0 g, 12.7 mmol), 99% triethylamine (3.54 mL, 25.5 mmol), and 4-dimethylaminopyridine (DMAP, 0.12 g, 0.98 mmol) in 30 mL of N,N-dimethylformamide (Note 13) and (Note 14). While the solution is stirred at room temperature, tert-butyldimethylsilyl trifluoromethanesulfonate (4.38 mL, 19.1 mmol, (Note 15)) is introduced into the reaction flask through the rubber septum using a syringe over a period of 1 min. *Caution! tert-Butyldimethylsilyl trifluoromethanesulfonate is a toxic compound that should be handled in a well-ventilated fume hood.* After stirring at room temperature for 1 hr (Note 16), 4 mL of methanol is added via syringe. The reaction solution is stirred for an additional 30 min, then the solvent is removed under reduced pressure. The residue is dissolved in 60 mL of hexanes-ethyl acetate (4:1) and washed with 100 mL of aqueous saturated sodium chloride (NaCl). The organic phase is dried over anhydrous sodium sulfate and concentrated under reduced pressure to give 5.18-5.30 g (95-97% crude yield) of **3** as a colorless syrup (Note 17). Analysis of crude product by ^{1}H NMR indicates a chemical purity of > 98%.

C. (S)-2-[(4S)-N-tert-Butoxycarbonyl-2,2-dimethyl-1,3-oxazolidin-4-yl]-2-tert-butyldimethylsiloxyethanal **(4)** . A 100-mL, one-necked, round-bottomed flask, equipped with a 2-cm egg-shaped magnetic stirring bar (Note 18), is charged with a mixture of the O-silyl ether **3** (2.0 g, 4.66 mmol), activated 4 Å powdered molecular sieves (9.33 g), and 47 mL of acetonitrile (Note 19) and (Note 20). The suspension is stirred at room temperature for 10 min, then methyl triflate (0.63 mL, 5.6 mmol, (Note 21)) is added via syringe. *Caution! Methyl triflate is toxic and a suspected carcinogen that should be handled in a well-ventilated fume hood.* The mixture is vigorously stirred for 15 min and concentrated to dryness under reduced pressure (Note 22). To the residue suspended in 47 mL of 1:1 methanol/diethyl ether and cooled with an ice-water bath is added under vigorous stirring sodium borohydride (0.39 g, 10.3 mmol, (Note 23)). Upon completion of the addition, the flask is removed from the ice bath and the solution is stirred at room temperature for 15 min, diluted with acetone (4 mL) and filtered through a Celite pad. The pad is rinsed with three 47-mL portions of acetone and the filtrate is concentrated under reduced pressure (Note 24). The residue is dissolved in 47 mL of acetonitrile-water (10:1) and the flask is placed in an ultrasonic cleaning bath and treated with 98% copper(II) oxide (2.97 g, 37.3 mmol, (Note 25)) and then with 95% copper(II) chloride dihydrate (0.79 g, 4.63 mmol, (Note 25)). After 10 min, the mixture is filtered through a Celite pad that is rinsed with four 47-mL portions of acetonitrile . The filtrate is concentrated under reduced pressure (Note 24) to give a brown syrup. The brown residue is sonicated for 5 min each with five 47-mL portions of diethyl ether , in an ultrasonic cleaning bath. The liquid layer is pipetted and filtered through a 1 × 6.5-cm (h × d) Florisil (100-200 mesh) pad. The filtrate appears almost colorless and is concentrated under reduced pressure (Note 24), to give 1.4-1.52 g (80-87% crude yield) of crude aldehyde **4** as a clear yellow oil (Note 26). Analysis of the crude product by ^{1}H NMR indicates a chemical purity of 90-95%. Crude **4** can be purified by flash chromatography over a 4.5 × 15-cm column of Silica Gel 60 (Note 11) eluting with cyclohexane-ethyl acetate (9:1) to give 1.3-1.4 g (75-80% yield) of pure aldehyde (Note 27).

2. Notes

1. The glass components of the apparatus were dried overnight in a 150°C oven and allowed to cool in a

desiccator over a drying agent before assembly.

2. 2-(Trimethylsilyl)thiazole (2-TST) is prepared according to the *Organic Syntheses* procedure;[2] it is also commercially available (Acros Chimica or Aldrich Chemical Company, Inc.). The commercial product was purified by distillation prior to use.

3. Methylene chloride was dried before use by distillation from calcium hydride under an atmosphere of nitrogen.

4. The preparation of the N-Boc-L-serinal acetonide is described in the accompanying procedure, p. 64. The crude aldehyde was used without further purification.

5. During the addition the clear yellow solution became red-orange.

6. After standing for 15 hr at −20°C the reaction solution returned to clear yellow.

7. Tetrahydrofuran was dried before use by distillation from sodium metal and benzophenone under an atmosphere of nitrogen.

8. Tetrabutylammonium fluoride trihydrate was purchased from Acros Chimica and used without further purification.

9. The checkers found it necessary to heat the solution to reflux to dissolve the solid. The hot solution was filtered by pouring into a preheated glass funnel containing a plug of glass wool to remove insoluble materials.

10. The product exhibits the following properties: $[\alpha]_D$ −51.2° (CHCl$_3$, *c* 1.7), IR (KBr) cm^{-1}: 3230, 1695, 1656 ; ^{1}H NMR (300 MHz, DMSO-d$_6$, 120°C) δ: 1.38 (s, 9 H), 1.46 (s, 3 H), 1.56 (s, 3 H), 3.82 (dd, 1 H, J = 9.0, 6.8), 3.95 (dd, 1 H, J = 9.0, 3.0), 4.26 (ddd, 1 H, J = 6.4, 4.1, 3.0), 5.15 (dd, 1 H, J = 5.5, 4.1), 6.11 (d, 1 H, J = 5.5, ex D$_2$O), 7.55 (d, 1 H, J = 3.0), 7.71 (d, 1 H, J = 3.0) ; ^{13}C NMR (75 MHz, CDCl$_3$) δ: 24.5, 25.7, 28.2, 62.2, 64.4, 73.4, 81.5, 94.6, 119.0, 142.4, 154.5, 172.6 ; HRMS, calcd for C$_{14}$H$_{23}$N$_2$O$_4$S [M+H]$^+$ 315.1378, found 315.1379 Purification with flash chromatography on silica gel eluting with (1:1) cyclohexane-ethyl acetate gave a product with a maximum rotation of $[\alpha]_D$ −54.1° (CHCl$_3$, *c* 1.0) and a mp of 174-175°C.

11. Silica Gel 60 (230-400 mesh) was obtained from Merck & Company, Inc.

12. Recrystallization of this mixture from cyclohexane (70 mL) gave ca. 0.40 g of **2** (4%).

13. Triethylamine (99%) and 4-dimethylaminopyridine were purchased from Acros Chimica and used without further purification.

14. N,N-Dimethylformamide was purchased from Acros Chimica and dried over activated 4 Å molecular sieves (8-12 mesh, Acros) before use.

15. tert-Butyldimethylsilyl trifluoromethanesulfonate was purchased from Acros Chimica and used as received under an atmosphere of nitrogen.

16. TLC analysis on Silica Gel 60F-254 plates eluting with cyclohexane-ethyl acetate (7:3) showed the clean formation of product with R$_f$ = 0.69, at the expense of the starting material with R$_f$ = 0.3. If a small amount of starting material was still present at this time, more tert-butyldimethylsilyl trifluoromethanesulfonate (0.22 mL, 0.95 mmol) and 0.2 mL of triethylamine were added and the reaction mixture was stirred for a further 30 min, at which time the TLC analysis generally showed the reaction to be complete.

17. The crude product exhibits the following properties: $[\alpha]_D$ −46° (CHCl$_3$, *c* 0.65); IR (KBr) cm^{-1} 1705, 1685 ; ^{1}H NMR (300 MHz, DMSO-d$_6$, 120°C) δ: −0.04 (s, 3 H), 0.10 (s, 3 H), 0.94 (s, 9 H), 1.41 (s, 9 H), 1.45 (s, 3 H), 1.60 (s, 3 H), 3.80 (dd, 1 H, J = 8.9, 7.0), 4.09 (dd, 1 H, J = 8.9, 3.5), 4.17 (dt, 1 H, J = 7.0, 3.5), 5.55 (d, 1 H, J = 3.5), 7.60 (d, 1 H, J = 3.1), 7.75 (d, 1 H, J = 3.1) ; HRMS, calcd for C$_{20}$H$_{37}$N$_2$O$_4$SSi [M+H]$^+$ 429.2243, found 429.2229 . Purification with flash chromatography on silica gel eluting with cyclohexane-ethyl acetate (9:1) gave a product with a maximum rotation of $[\alpha]_D$ −47.6° (CHCl$_3$, *c* 0.60). Upon cold storage a chromatographed sample of **3** crystallized: mp 53-55°C.

18. For efficient stirring a powerful magnetic stirrer should be used.

19. Activated 4 Å molecular sieves (powder, < 5 micron) were purchased from Aldrich Chemical Company, Inc., and used as received.

20. Acetonitrile was purchased from Acros Chimica and dried over activated 4 Å molecular sieves (8-12 mesh, Acros) before use.

21. Methyl triflate was purchased from Aldrich Chemical Company, Inc. , and used as received.

22. TLC analysis on Silica Gel 60F-254 plates eluting with cyclohexane-ethyl acetate (9:1) showed the formation of product with R$_f$ = 0, at the expense of the starting material.

23. Sodium borohydride was purchased from Aldrich Chemical Company, Inc. , and used without further purification.

24. Bath temperature should not exceed 40°C.

25. Copper(II) oxide and copper(II) chloride dihydrate were purchased from Acros Chimica and used without further purification. The checkers found that the yield of Step C was substantially reduced (64-65%) when an old bottle of CuO was used. Results identical to those reported by the submitters were obtained using a new bottle of this reagent.

26. The crude product exhibits the following properties: $[\alpha]_D$ −40.7° (CHCl$_3$, c, 0.6); IR (neat) cm^{-1}: 1740, 1712, 1690 ; ^{1}H NMR (300 MHz, DMSO-d$_6$, 120°C) δ: 0.1 (s, 6 H), 0.95 (s, 9 H), 1.44 (s, 9 H), 1.49 (s, 3 H), 1.54 (s, 3 H), 3.88 (dd, 1 H, J = 9.0, 2.5), 3.95 (dd, 1 H, J = 9.0, 5.9), 4.07 (dt, 1 H, J = 6.0, 2.5), 4.26 (dd, 1 H, J = 6.0, 2.0), 9.55 (d, 1 H, J = 2.0) ; HRMS, calcd for C$_{18}$H$_{36}$NO$_5$Si [M+H]$^+$ 374.2362, found 374.2357 .

27. After flash chromatography the product showed a maximum rotation of $[\alpha]_D$ −45.7° (CHCl$_3$, c 0.7).

Waste Disposal Information

All toxic materials were disposed of in accordance with "Prudent Practices in the Laboratory"; National Academic Press; Washington, DC, 1995.

3. Discussion

The 2-amino-1,3-diol moiety is a structural unit featured by numerous natural products and synthetic analogues. For instance it is present at the polar head of sphingosines,[3] and at the non-reducing end of aza sugars.[4] Therefore chiral 3-amino-2,4-dihydroxybutanals are potential building blocks for the synthesis of those biologically active compounds.[5] [6] [7] Since either R or S configuration at the stereocenters may be required, it is advisable to rely on a synthetic method that allows one to obtain these building blocks with all possible absolute and relative stereochemical arrangements. Accordingly, the submitters have approached the synthesis of these compounds by two routes (Scheme 1), which are both centered on the use of the thiazole ring as a convenient precursor of the formyl group (Thiazole Aldehyde Synthesis).[8] [9] [10] These routes are complementary in the sense that starting from the same L-serine derived oxazolidine methyl ester **I** they lead to either R or S diastereomer oxazolidine alcohol **VI**. The S-configuration of the amino ester is employed for the construction of the new stereocenter through internal asymmetric induction. Thus, in one route ester **I** is reduced to the oxazolidine aldehyde **II**, which then undergoes stereoselective anti-addition of the thiazole-bearing organosilane **III** to give the S-oxazolidine alcohol **VIa** as major product (aldehyde route).[5,11] In the other route the same ester **I** is first converted into the oxazolidine ketone **V** through nucleophilic substitution with another metalated thiazole **IV**. Ketone **V** is then reduced stereoselectively to give the R-oxazolidine alcohol **VIb** as the major product (ketone route).[7,12] The opposite stereochemical outcome observed in this case is determined by the stereoselective hydride anti-addition to the carbonyl. The thiazole bearing diastereomeric oxazolidine alcohols **VIa** and **VIb**, after suitable protection of the hydroxy group, are converted into the corresponding aldehydes **VIIa** and **VIIb** by the usual thiazole-to-formyl cleavage protocol.[13] Evidently the antipodes of these aldehydes can also be prepared by the same routes starting from the D-serine derived enantiomer of ester **I**. Both routes can be scaled-up for the synthesis of gram quantities of these aldehydes. The thiazole ring serves as a convenient auxiliary in this methodology as well, since it tolerates different types of reaction conditions without any interference, and when needed it is readily converted into the formyl group. The thiazole-to-formyl cleavage occurs under mild and neutral conditions that do not affect the stereochemical integrity and chemical stability of the resulting aldehyde. Crude compound **VII** obtained by either the aldehyde or the ketone route is pure enough for use as a synthetic chiral building block.
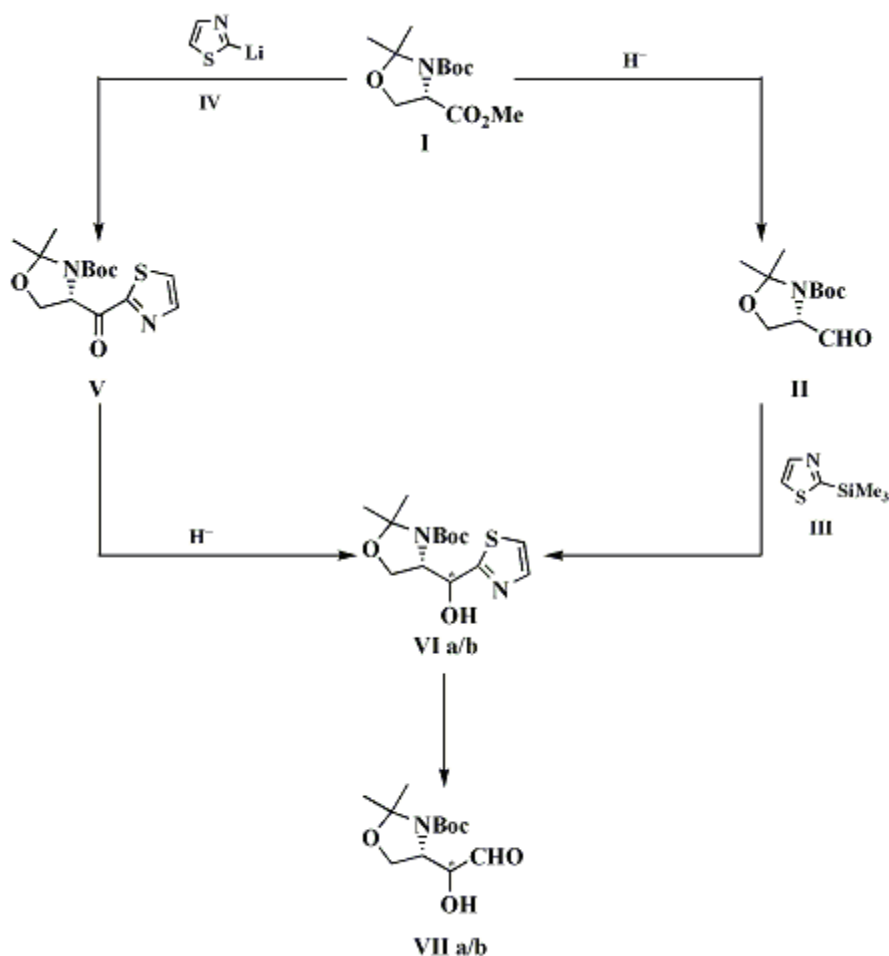
This procedure describes an example of the "aldehyde route". The addition of 2-(trimethylsilyl) thiazole (2-TST) to aldehydes occurs readily and does not require the presence of a fluoride ion source.[14] The resulting secondary alcohol is as a rule isolated in very good yield. The sense of the diastereofacial selectivity of the addition reaction to chiral α-amino aldehydes can be controlled by differential protection of the amino group. Specifically, compounds with double protection afford anti-amino alcohols, whereas those with single protection give syn-diastereomers.[5,11] Accordingly the addition of 2-TST to aldehyde **1** affords alcohol **2** as almost a single product (Step A). Rapid purification of this compound from the syn-isomer (≤ 8%) is carried out by crystallization from cyclohexane. Pure alcohol **2** is then converted almost quantitatively into the tert-butyldimethylsilyl ether **3** (Step B). Other types of protection of the hydroxy group of **3** can also be applied. Finally crude O-silyl ether **3** is subjected to the conventional thiazole-to-formyl deblocking protocol[13] (Step C) that is carried out through a sequence of very effective reactions, i.e., N-methylation, reduction, and metal-catalyzed hydrolysis. This aldehyde liberation requires no more than 4 hr of work. Isolated crude compound **4** is obtained in 52-59% yield from aldehyde **1**.

References and Notes

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Appendix
Chemical Abstracts Nomenclature (Collective Index Number);
(Registry Number)

2-(Trimethylsilyl)thiazole:
Thiazole, 2-(trimethylsilyl)- (10); (79265-30-8)

(S)-2-{[(4S)-N-tert-Butoxycarbonyl-2,2-dimethyl-1,3-oxazolidin-4-yl]hydroxymethyl}-1,3-thiazole:
3-Oxazolidinecarboxylic acid, 4-(hydroxy-2-thiazolylmethyl)-2,2-dimethyl-, 1,1-dimethylethyl ester,
[(S-(R,R)]- (12); (115822-48-5)

1,1-Dimethylethyl (S)-4-formyl-2,2-dimethyloxazolidinecarboxylate:
3-Oxazolidinecarboxylic acid, 4-formyl-2,2-dimethyl-, 1,1-dimethylethyl ester, (S)- (11); (102308-32-7)

Tetrabutylammonium fluoride trihydrate:
Ammonium, tetrabutyl-, fluoride, hydrate (8,9); (22206-57-1)

(S)-2-{[(4S)-N-tert-Butoxycarbonyl-2,2-dimethyl-1,3-oxazolidin-4-yl]-tert-butyldimethylsiloxy}-1,3-thiazole:
3-Oxazolidinecarboxylic acid, 4-[[[(1,1-dimethylethyl)dimethylsilyl]oxy]-2-thiazolylmethyl]2,2-dimethyl-, 1,1-dimethylethyl ester, [S-(R,R)]- (13) (168326-00-9)

Triethylamine (8);
Ethanamine, N,N-diethyl- (9); (121-44-8)

4-Dimethylaminopyridine: HIGHLY TOXIC:
Pyridine, 4-(dimethylamino)- (8);
4-Pyridinamine, N,N-dimethyl- (9); (1122-58-3)

N,N-Dimethylformamide: CANCER SUSPECT AGENT:
Formamide, N,N-dimethyl- (8,9); (68-12-2)

tert-Butyldimethylsilyl trifluoromethanesulfonate:
Methanesulfonic acid, trifluoro-, (1,1-dimethylethyl)dimethylsilyl ester (10); (69739-34-0)

(S)-2-2-[(4S)-N-tert-Butoxycarbonyl-2,2-dimethyl-1,3-oxazolidin-4-yl-2-tert-butyldimethylsiloxyethanal:
3-Oxazolidinecarboxylic acid, 4-[1-[[(1,1-dimethylethyl)dimethylsilyl]oxy]-2-oxoethyl]-2,2-dimethyl-, 1,1-dimethylethyl ester, [S-(R*,R*)]- (13); (192119-88-3)

Acetonitrile (8,9); (75-05-8)

Methyl triflate:
Methyl trifluoromethanesulfonate:
Methanesulfonic acid, trifluoro-, methyl ester (8,9); (333-27-7)

Sodium borohydride:
Borate (1−), tetrahydro-, sodium (8,9); (16940-66-2)

Copper(II) oxide:
Copper oxide (8,9); (1317-38-0)

Copper(II) chloride dihydrate:
Copper chloride dihydrate (8);
Copper chloride, dihydrate (9); (10125-13-0)