matographed on silica gel (water-saturated ethyl acetate) to yield the product, 0.36 g (31% yield): $[\alpha]^{25}_D$ -21.8° (c 0.40, H_2O); ^1H NMR (200 MHz, D_2O) δ 1.03, 1.20 (s, 6 H, CH_3), 1.37 (dd, J = 13 Hz, J = 11.8 Hz, 1 H, C5-H_{ax}), 1.83 (dd, J = 13 Hz, J = 4.7 Hz, 1 H, C5-H_{eq}), 3.15, 3.42 (d, J = 11.8 Hz, 2 H, CH_2OD), 3.27 (d, J = 9.8 Hz, 1 H, C3), 3.91 (ddd, J = 9.8 Hz, J = 11.8 Hz, J = 4.7 Hz, 1 H, C4); ^{13}C NMR (50 MHz, D_2O) δ 27.14, 31.11 (CH_3), 43.66 (C5), 64.21, 65.82, 72.06, 75.08 (C1,3,4,6), 98.92 (C2). Anal. Calcd for $C_8H_{16}O_5$: C, 50.04; H, 8.40. Found: C, 50.02; H, 8.40. All data are consistent with those reported.

To prepare D-fructose, the condition was essentially the same except that no aldehyde was used. Triosephosphate isomerase (500 units) was added to the mixture in addition to the aldolase. The product was identified with HPLC and compared with that of authentic D-fructose.

Fuculose-1-phosphate Aldolase Catalyzed Reaction: Preparation of D-Ribulose. To a Tris buffer solution (85 mL, 10 mM, pH 7.5, containing 6 mM KCl, 6 mM $Co(NO_3)_2$) were added sodium arsenate (200 mmol), glycoaldehyde (1.7 g, 14.2 mmol), and dihydroxyacetone (3.2 g, 17.8 mmol). The solution was adjusted to pH 7.5 followed by adding 100 mg of the enzyme-containing *E. coli* cells and 1 mg of lysozyme (51 000 μm) to break the cells. The mixture was stirred for 24 h. TLC showed no glycoaldehyde was present, R_f 0.75. The mixture was lyophilized and triturated with 4 × 75 mL of methanol and filtered, and the filtrate was evaporated. The product was purified on Dowex 50 (Ba^{2+}) column with water as a mobile phase to give 1.70 g of product, which was identical with authentic D-ribulose (from Aldrich) by HPLC (t_R = 4.9 min) and NMR analyses.

Rhamnulose-1-phosphate Aldolase Catalyzed Reactions. The *E. coli* cells containing this enzyme were used to prepared L-xylulose from DHA and glycoaldehyde under the same conditions as that for the preparation of D-ribulose. The product obtained (1.60 g, 76% yield based on glycoaldehyde) was identical with authentic L-xylulose (from Aldrich) by HPLC (t_R = 5.0 min) and NMR analyses. When L-lactaldehyde (4.75 mmol, prepared by acid hydrolysis of the dimethyl acetal precursor)[16] was used as acceptor and dihydroxyacetone (5.56 mmol) as donor, a mixture of L-rhamnulose and L-rhamnose (0.61 g, 71% yield) was obtained based on ^1H NMR, ^{13}C NMR, and HPLC analyses (t_R rhamnose = 5.2 min; t_R rhamnulose = 4.8 min; the ratio of aldose to ketose is 0.6:0.4).

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A Synthetic Approach to Rocaglamide via Reductive Cyclization of δ-Keto Nitriles

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The anticancer agent rocaglamide contains a novel bicyclo[3.3.0]octanol structure. The approach to this molecule involved the preparation of a hydroxy ketone intermediate via a samarium-mediated cyclization. This ketone was then converted into an excellent Michael acceptor via novel chemistry. Subsequent steps led to the preparation of an isomer of rocaglamide. An X-ray determination supported our view that cuprate addition occurred with unusual concave selectivity.

Rocaglamide (1) is a novel natural product which was isolated from *Aglaia elliptifolia* Merr. in 1982.[1] Its structure was elucidated by McPhail. Rocaglamide exhibits significant activity against P388 lymphocytic leukemia in CDF_1 mice and inhibitory activity in vitro against cells derived from human epidermoid carcinoma of the nasopharynx.[2] Its challenging structure and potent activity combine to make rocaglamide an attractive synthetic objective. Two approaches have recently been reported. An approach by Trost and co-workers uses a clever trimethylenemethane–palladium(0) cyclization to form a cyclopentene precursor.[3] The approach by Taylor and Davey utilizes an intramolecular dithiane cyclization to form the cyclopentane ring.[4]

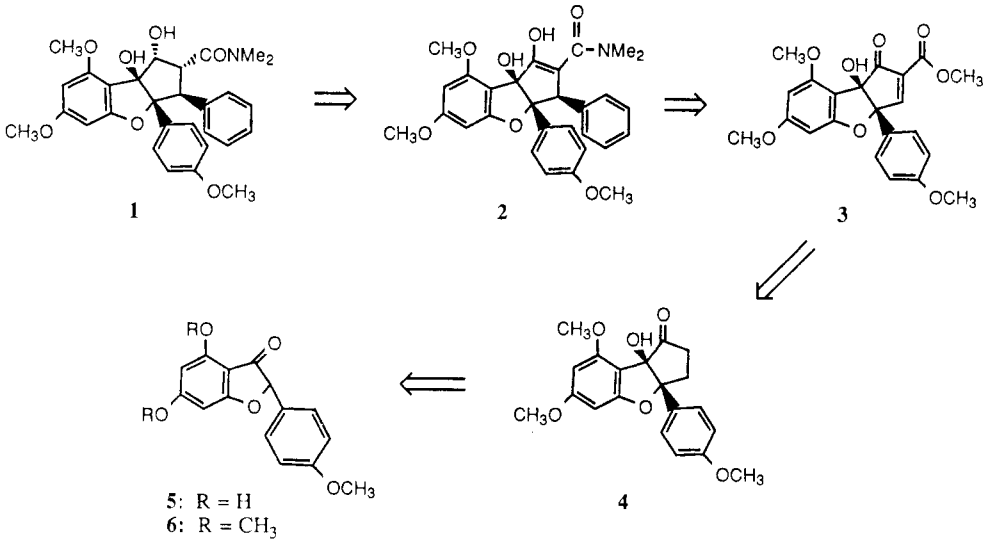
Our approach features a samarium-mediated cylization of a keto nitrile. The retrosynthetic analsyis is illustrated in Scheme I. Our expectation was that nucleophiles would add to the convex face of the bicyclo[3.3.0]octane subunits in **2** and **3**. The starting point in our synthesis is the known ketone **5**. It can be prepared in one step by a Hoesch reaction on phloroglucinol.[5] Methylation of **5** provided ketone **6**. Trimethylation to afford a 3,4,6-trimethoxybenzofuran can occur if the conditions are not carefully monitored. Michael addition of ketone **6** with acrylonitrile to form **7** could be achieved by using a catalytic amount of Triton B in *tert*-butyl alcohol. Rigorous exclusion of oxygen was necessary to prevent the formation of byproduct **8**. This byproduct had also been observed by Taylor and Davey (Scheme II).

Initially, the cyclization of **7** to **4** was attempted by using the Zn/Me_3SiCl protocol developed by Corey.[6] These conditions had already been used for the cyclization of a simple keto nitrile. The only product isolated was alcohol **9**. The same result was obtained with the Mg/Me_3SiCl conditions used by Hutchinson.[7] However, when conditions similar to those developed by Molander for the cyclization of halo ketones were used, a good yield of hydroxy ketone **4** was obtained.[8] Alcohol **9** was also obtained. The

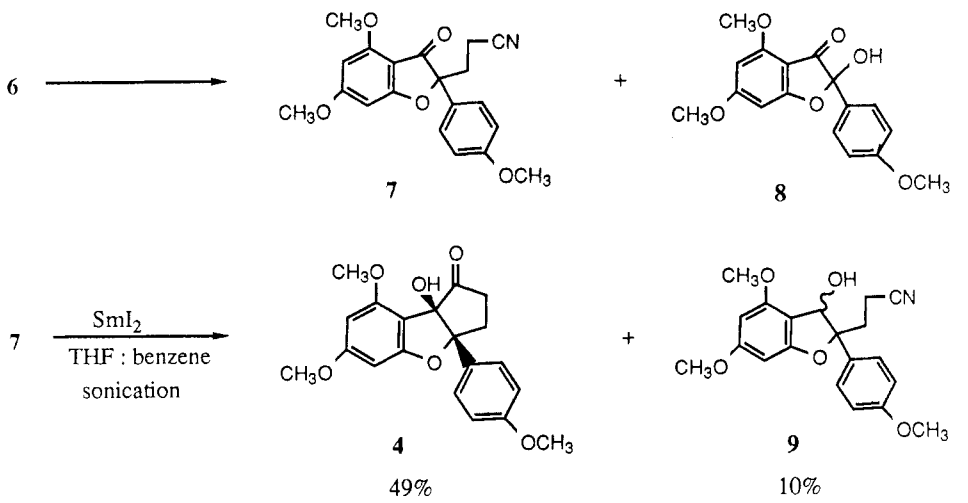
(1) McPhail, A. T.; King, M. L.; Chiang, C. C.; Ling, H. C.; Fujita, E.; Ochiai, M. *Chem. Commun.* **1982**, 1150.
(2) King, M. L.; Ling, C. H.; Wang, C. B.; Leu, S. C. *Med. Sci.* **1975**, *1*, 11.
(3) Trost, B. M.; Saulnier, M. G. Presented at the 192nd National Meeting of the American Chemical Society, Anaheim, CA, Sept 7–12, 1986; Abstract 144.
(4) Taylor, R. J. K.; Davey, A. E. *Chem. Commun.* **1987**, 25.
(5) Katamna, C. *Bull. Soc. Chim. Fr.* **1970**, 2309.
(6) Corey, E. J.; Pyne, S. G. *Tetrahedron Lett.* **1983**, *24*, 2821.
(7) Hutchinson, C. R.; Ikeda, T.; Yue, S. *J. Org. Chem.* **1985**, *50*, 5193.
(8) Molander, G. A.; Etter, J. B.; Zinke, P. W. *J. Am. Chem. Soc.* **1987**, *109*, 453. Molander, G. A.; Etter, J. B. *J. Org. Chem.* **1986**, *51*, 1778.

0022-3263/89/1954-0077$01.50/0

Scheme I



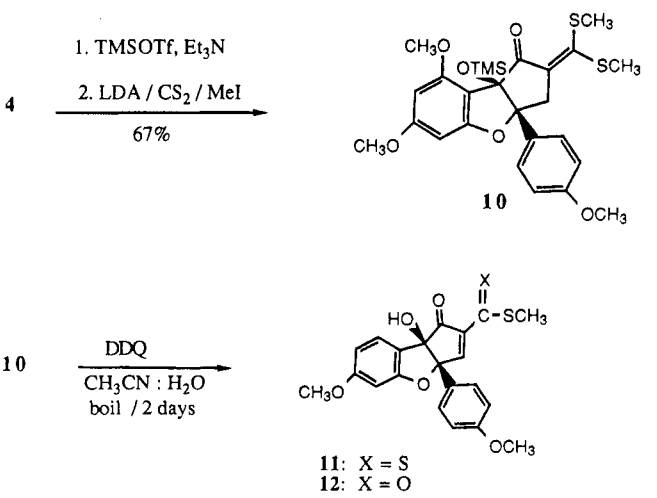
Scheme II



ratio of **4** to **9** depended on the reaction solvents. If the reaction was conducted in 1:10 THF/benzene using sonication, a 49% yield of **4** was realized, along with a 10% yield of **9**. As the percentage of THF was increased, the yield of **9** also increased.

With ketone **4** in hand, the next objective became the preparation of enone **3**. The most direct route to **3** seemed to involve the carboalkoxylation of **4** followed by dehydrogenation using selenium methodology. Unfortunately, the introduction of the ester could not be achieved. Conditions such as dimethyl carbonate/NaH or KH gave only unreacted **4**. Formation of the thioester with COS and base[9] was briefly examined with no success. However, reaction of **4** with LDA, carbon disulfide, and then excess methyl iodide[10] provided compound **10** in 67% isolated yield (Scheme III). The dehydrogenation of **10** to **11** was next investigated. Although there was no good literature precedent for this reaction, it seemed reasonable that a hydride abstracting reagent might generate **11**. While trityl tetrafluoroborate produced a complex mixture of products, DDQ in boiling benzene afforded a low yield of **12**. This reaction was difficult to reproduce until the solvent was changed to acetonitrile/water. Apparently, traces of water in the benzene were responsible for the

Scheme III

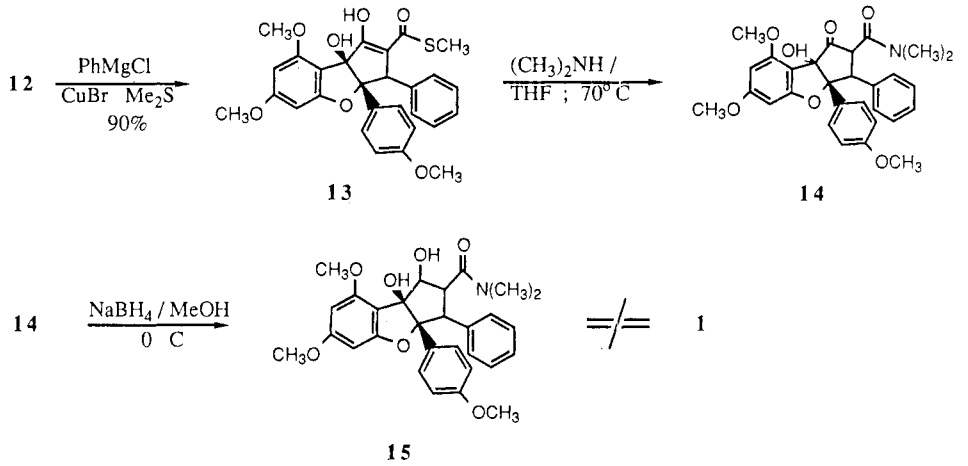


production of **12**. The use of a 45:1 ratio of acetonitrile to water resulted in a 56% yield of **12**.

Since **12** was expected to be a reasonable Michael acceptor, it was treated at −78 °C with the complex formed from equimolar amounts of phenylmagnesium bromide and CuBr–Me_2S (Scheme IV). The product, thioester **13**, was obtained in 90% yield. While the addition of the

(9) Vedejs, E.; Nader, B. *J. Org. Chem.* **1982**, *47*, 3193.
(10) Dieter, R. K. *Tetrahedron* **1986**, *42*, 3029.

Scheme IV



organometallic was expected to occur from the convex face of the bicyclic system, the experience with the unsuccessful carboalkoxylation reactions produced some doubt as to the actual stereochemistry of **13**. Since we were only two steps from the completion of the route and **13** was now readily available, we reacted **13** with dimethylamine in refluxing THF. While keto amide **14** was produced in 92% yield, it is not clear whether the reaction proceeded via the direct displacement of the thiomethyl group or a ketene intermediate was involved. Keto amide **14** was not enolic and was homogeneous as evidenced by proton NMR. Reduction of **14** with sodium borohydride in methanol at 0 °C afforded a dihydroxy amide **15** in quantitative yield.

The mass spectrum, IR spectrum, and proton NMR spectrum supported the overall structure of **15**. Unfortunately, the NMR spectrum of authentic rocaglamide kindly provided by Professor McPhail was not identical. Additionally, the ^{13}C NMR spectra were also different. The major differences are summarized in Table I. In view of these discrepancies, an X-ray structure of an advanced intermediate was imperative. While this work was proceeding, a parallel route was also examined. It is shown in Scheme V. The Michael addition to cinnamonitrile produced two isomers in a 5:1 ratio. The major isomer was taken on to afford **17**. This reacted with carbon disulfide to afford **18**. Compound **18** was then converted to **15**. The structure of **18** was determined by X-ray diffraction (Table II). It clearly indicates that the phenyl and *p*-methoxyphenyl groups are trans. Assuming that the carbomethoxyl group would equilibrate trans to the bulky *p*-methoxyphenyl group and that the hydride delivery would afford a *trans*-diol, the structure of **15** is as shown in Scheme VI. The structure assignments at C-1 and C-2 are tentative but very reasonable.

The synthetic routes described above produce the rocaglamide carbon framework very efficiently. We are currently modifying our routes to obtain the desired stereochemistry.

Experimental Section

Unless otherwise noted, materials were obtained from commercial suppliers and were used without purification. Dichloromethane was distilled from phosphorus pentoxide. Infrared spectra were determined on a Perkin-Elmer 1320 spectrometer. Nuclear magnetic resonance spectra were determined on a Nicolet 300-MHz instrument. Carbon-13 NMR spectra were determined on a Nicolet 300-MHz instrument. High-resolution mass spectra were determined on a Kratos mass spectrometer. Elemental analyses were performed by Galbraith Laboratories, Inc. The purity of all titled compounds was shown to be at least 95% by proton NMR and TLC analyses.

Table I

partial comparison of NMR data[a]		
	rocaglamide	amide **15**
proton H-1	5.01	4.82
coupling constant[b]	J = 6.8	J = 10
proton H-2	3.88	3.57
coupling constant	J = 6.8, 14	J = 10, 12
proton H-3	4.32	4.25
coupling constant	J = 14	J = 12
amide methyl groups		
CH_3	3.31	2.99
CH_3	2.94	2.89

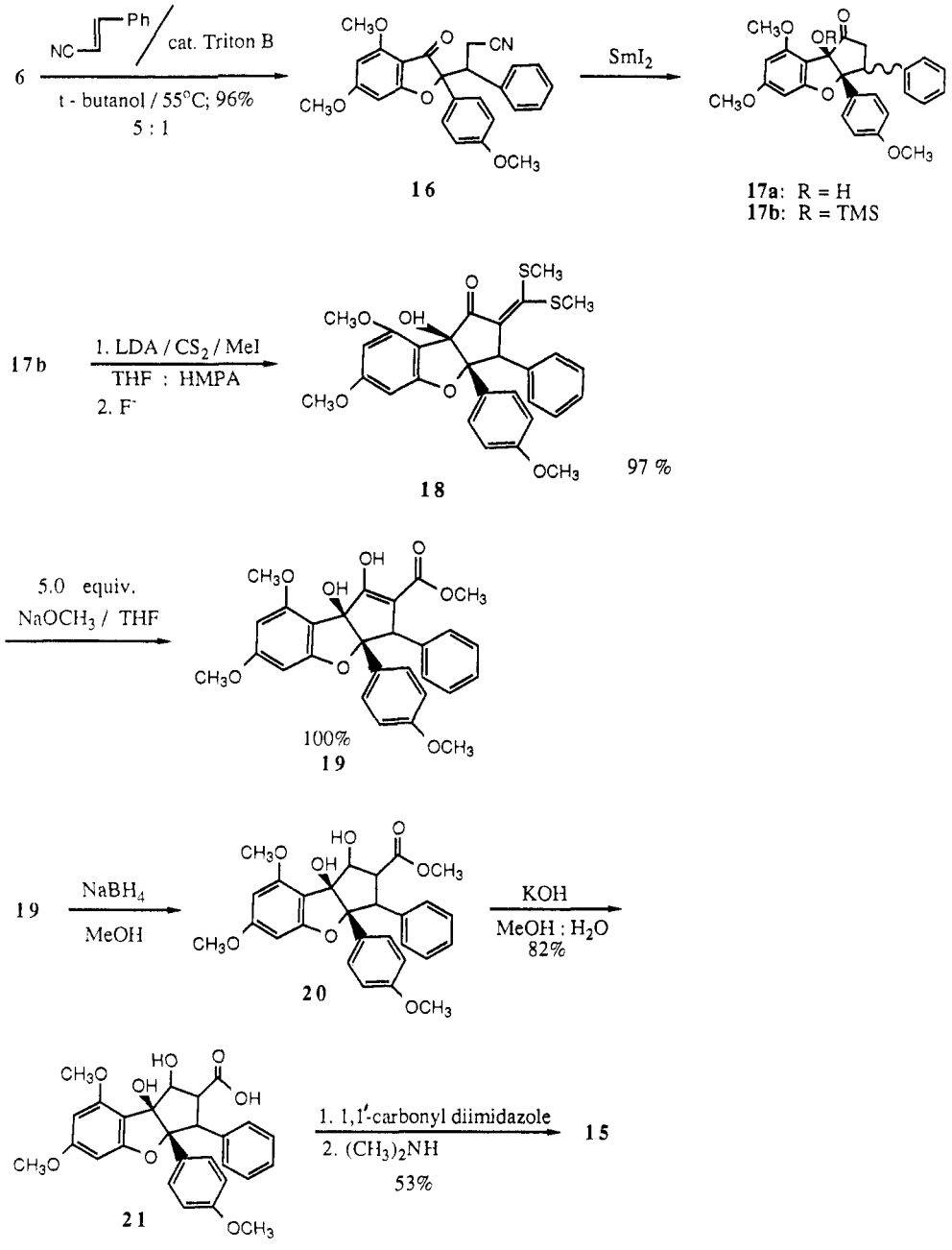
comparison of ^{13}C NMR data			
rocaglamide	amide **15**	rocaglamide	amide **15**
169	171.5	93.8	92.3
163.5	163.5	92.8	91.7
161	161.8	89	88.6
158	159.1		84.6
157.5	157.9	78.5	77.3
138.3	135.7	56	
129	129.3	56	55.7
128	129.2	55.5	55.2
128	128.2	55	54.7
126.5	127.1	47	47.3
112.8	113.4	36.9	37.5
108	105.7	35.7	36.0
101.5	99.9		

[a] We thank Dr. McPhail for permission to publish his NMR data ($CDCl_3$). [b] Coupling constants in hertz.

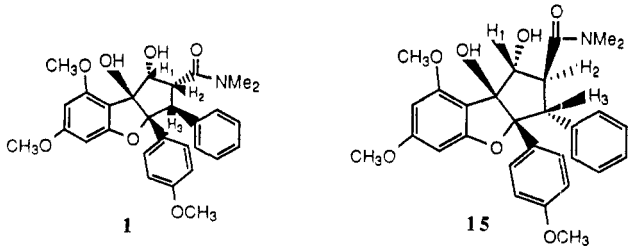
4,6-Dimethoxy-2-(4-methoxyphenyl)-3-benzofuranone (6). To a solution of compound **5** (30.0 g, 110 mmol) in acetone (250 mL) were added solid potassium carbonate (34.2 g, 247 mmol) and dimethyl sulfate (20.7 mL, 220 mmol) in one portion. After being stirred for 2 h at reflux, the suspension was cooled and the acetone layer was separated from the excess solid potassium carbonate by filtration. The filter cake was washed thoroughly with ether (2 × 150 mL). The combined filtrate was treated successively with dilute hydrochloric acid, water, and finally saturated sodium chloride. The organic layer was dried over anhydrous sodium sulfate and concentrated in vacuo. The residue was triturated with a 5:1 hexanes/ether mixture and recrystallized in chloroform to give 28.35 g (86% yield) of compound **6**. It is a light beige solid and melts at 127 °C: NMR ($CDCl_3$) δ 7.30 (d, J = 6 Hz, 2 H), 6.90 (d, J = 6 Hz, 2 H), 6.20 (d, J = 2 Hz, 1 H), 6.00 (d, J = 2 Hz, 1 H), 5.40 (s, 1 H), 3.93 (s, 3 H), 3.90 (s, 3 H), 3.78 (s, 3 H); IR ($CDCl_3$) 2940, 2830, 1690, 1610, 1590, 1508, 1460, 1250, 1210, 1150, 1100 cm^{-1}; high-resolution mass spectrum for $C_{17}H_{16}O_3$ requires 300.099 78, measured 300.099 92; MS, m/e 300 (M^+), 282, 272, 257, 241, 192, 163, 135, 106.

4,6-Dimethoxy-2-(4-methoxyphenyl)-2-(2-cyanoethyl)-3-benzofuranone (7). To a solution of compound **6** (9.00 g, 30.0 mmol) in *tert*-butyl alcohol (10 mL) under an argon atmosphere was added trimethylbenzylammonium hydroxide (3.2 mL, 90

Scheme V



Scheme VI[a]

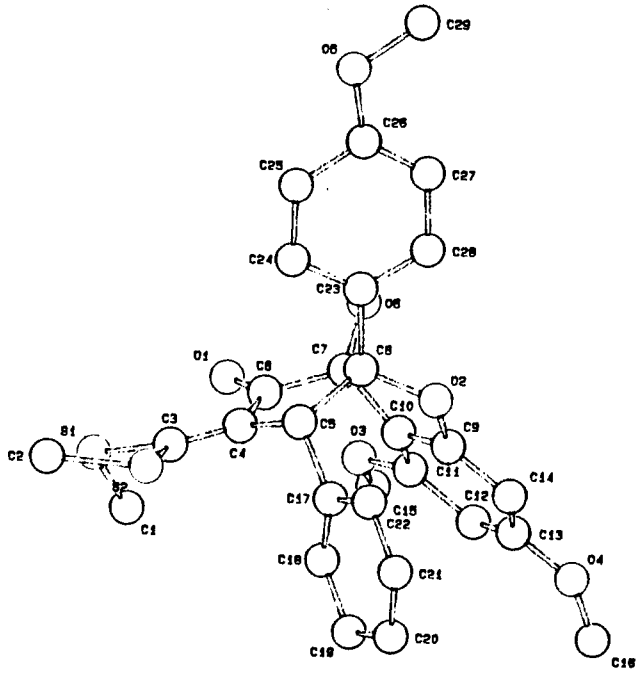


[a] On the basis of the coupling constants of H-1 (10 Hz), H-2 (10 and 12 Hz), and H-3 (12 Hz), we believe that the rocaglamide isomer we synthesized has the relative stereochemistry shown. The all-axial arrangement of the three protons would explain the large coupling constants observed.

mmol), followed immediately by the slow addition of acrylonitrile (28.3 mL, 430 mmol). After being stirred for 4 h, the reddish solution was neutralized with dilute hydrochloric solution and poured into a separatory funnel containing water (50 mL). The combined organic layer obtained after extraction of the aqueous layer with ether was washed with saturated sodium chloride. It was then dried and concentrated in vacuo, and the crude product was purified via flash column chromatography using 2:1 hexanes/ethyl acetate as eluent to obtain compound **7** (9.70 g, 91%) as a foam: NMR ($CDCl_3$) δ 7.48 (d, J = 7 Hz, 2 H), 6.85 (d, J = 7 Hz, 2 H), 6.25 (d, J = 2 Hz, 1 H), 6.0 (d, J = 2 Hz, 1 H), 3.89 (s, 3 H), 3.85 (s, 3 H), 3.75 (s, 3 H), 2.55–2.28 (m, 4 H); IR (film) 2940, 2830, 2240, 1690, 1610, 1585, 1500, 1460, 1420, 1250, 1210, 1150, 1050, 900 cm^{-1}; high-resolution mass spectrum for $C_{20}H_{19}NO_5$ requires 353.126 33, measured 353.126 42; ^{13}C NMR ($CDCl_3$) δ 194.40, 173.76, 170.17, 159.56, 159.30, 127.73, 125.82, 118.57, 113.91, 102.81, 93.30, 90.29, 88.85, 55.86, 55.81, 55.03, 33.56, 11.90.

Tricyclic α-Hydroxy Ketone 4. A solution of 1,2-diiodoethane (3.20 g, 11.4 mmol) in dry THF (10 mL) was added over 10 min to a round-bottom flask containing flame-dried samarium metal (3.04 g, 20.3 mmol) under an argon atmosphere. The immediate formation of a dark-blue color was observed. The solution was stirred at room temperature for 1 h and subjected to sonication for 3 h to insure complete formation of samarium diiodide. A solution of compound **7** (3.82 g, 10.8 mmol) in benzene (100 mL) was introduced rapidly. The resulting blue solution was subjected

Table II. Crystal Parameters for the X-ray Diffraction Study of Compound 18[a]



formula	$C_{28}H_{28}O_6S_2$
mol wt, g/mol	536.66
crystal system	monoclinic
space group	$P2_1/n$ (no. 14)
lattice constants, Å	
a	15.40 (1)
b	10.76 (1)
c	16.12 (1)
lattice angles, deg	
β	104.2 (1)
unit cell vol, Å^3	2590 (4)
Z	4
D_{calcd}, g/cm^3	1.38
radiation: Mo Kα (λ, Å)	0.710 69
temperature	−75 °C
monochromater	graphite
reflctns collected	5062
reflctns obsd [$I > 3\sigma(I)$]	1373
residue factor (after isotropic thermal parameter refinement)	
R^b	0.203
R_w^c	0.244

[a] Intensity data collection was carried out on a RIGAKU AFC6 four-circle diffractometer. Both room (25 °C) and low (−75 °C) temperature data collection have been tried. Due to the quality of the crystal, the thermal parameter refinement could only be carried out on an isotropic level, on which C-1 still showed non-positive-definite. Anisotropic thermal parameter refinement resulted in many more (~10) atoms being non-positive-definite before the R factor was lowered to 0.177. [b] $R = \sum(|F_o| - |F_c|)/\sum|F_o|$. [c] $R_w = [\sum(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$.

to ultrasonication for 1 day. This solution was quenched with dilute hydrochloric acid and extracted twice with ether. The combined organic layer was washed with water and saturated sodium chloride. The organic layer was then dried and concentrated in vacuo. The crude product was purified by flash column chromatography using 2:1 hexanes/ethyl acetate as eluent to yield compound **4** (1.90 g, 49%) as a colorless oil: NMR ($CDCl_3$) δ 7.30 (d, J = 6 Hz, 2 H), 6.90 (d, J = 6 Hz, 2 H), 6.20 (d, J = 2 Hz, 1 H), 6.00 (d, J = 2 Hz, 1 H), 3.87 (s, 3 H), 3.84 (s, 3 H), 3.76 (s, 3 H), 3.30 (s, br, 1 H), 2.90–2.43 (m, 4 H); IR ($CDCl_3$) 3490, 2960, 2840, 1750, 1615, 1600, 1460, 1420, 1245, 1210, 1150, 1040 cm^{-1}; high-resolution mass spectrum for $C_{20}H_{20}O_6$ requires 356.125 99, measured 356.125 45; ^{13}C NMR ($CDCl_3$) δ 211.14, 164.19, 161.92, 159.17, 158.08, 129.73, 127.17, 118.90, 105.53, 96.86, 92.19, 88.71, 86.51, 55.46, 55.32, 55.03, 33.97, 33.81.

The above reaction also gave a minor product, **9**, identified as the uncyclized alcohol (0.35 g, 9%): NMR ($CDCl_3$) δ 7.20 (d, J = 6 Hz, 2 H), 6.80 (d, J = 6 Hz, 2 H), 5.98 (d, J = 2 Hz, 1 H), 5.71 (d, J = 2 Hz, 1 H), 5.0 (d, J = 6 Hz, 1 H), 3.87 (s, 3 H), 3.81 (s, 3 H), 3.76 (s, 3 H), 2.50–2.03 (m, 4 H); IR (film) 3350, 3000, 2925, 2820, 2238, 1615, 1580, 1500, 1450, 1400, 1240, 1200, 1105, 1030, 815, 750 cm^{-1}; high-resolution mass spectrum for $C_{20}H_{21}NO_5$ requires 355.141 98, measured 355.141 57.

Tricyclic α-Trimethylsiloxy Ketone. To a solution of ketone **4** (0.28 g, 0.79 mmol) in dry benzene (10 mL) at 5 °C under an argon atmosphere was added diisopropylethylamine (0.35 mL, 1.97 mmol), followed by the dropwise addition of trimethylsilyl trifluoromethanesulfonate (0.25 mL, 1.30 mmol). The solution was stirred at 5 °C for 6 h and then allowed to warm to room temperature over a 6-h period. The solution was diluted with hexanes (60 mL) and filtered. The filtrate was concentrated in vacuo to give 0.33 g (98%) as a colorless oil of high purity: NMR ($CDCl_3$) δ 7.23 (d, J = 7 Hz, 2 H), 6.83 (d, J = 7 Hz, 2 H), 6.20 (d, J = 2 Hz, 1 H), 6.00 (d, J = 2 Hz, 1 H), 3.83 (s, 3 H), 3.80 (s, 3 H), 3.74 (s, 3 H), 2.70–2.30 (m, 4 H), −0.40 (s, 9 H); IR ($CDCl_3$) 2950, 2830, 1745, 1608, 1590, 1508, 1460, 1435, 1245, 1150, 1100, 1035 cm^{-1}; high-resolution mass spectrum for $C_{23}H_{28}O_3Si$ requires 428.165 58, measured 428.165 52; ^{13}C NMR ($CDCl_3$) δ 209.34, 164.54, 162.50, 159.01, 158.43, 131.19, 127.53, 113.31, 106.11, 97.57, 91.92, 89.27, 88.88, 55.51, 55.23, 55.12, 34.19, 34.12, 0.807.

Tricyclic Keto Disulfide 10. n-Butyllithium (4.96 mL, 12.1 mmol) was added dropwise to a solution of diisopropylamine (1.80 mL, 12.8 mmol) in dry tetrahydrofuran (30 mL) at −40 °C under an argon atmosphere. The resulting solution of lithium diisopropylamide was stirred for 15 min, and then the tricyclic ketone (1.20 g, 2.80 mmol) in THF (10 mL) was added dropwise. The yellow solution was stirred for 75 min, after which neat carbon disulfide (4.56 mL, 75.9 mmol) was added rapidly. The reaction mixture was stirred for 5 h, and iodomethane (4.73 mL, 75.9 mmol) was added. The resulting solution was stirred while being warmed from −40 °C to room temperature overnight. It was diluted with hexanes (200 mL) and filtered. The filtrate was concentrated in vacuo. The crude product was purified via flash column chromatography using 2:1 hexanes/ethyl acetate as eluent to give a bright yellow solid (0.92 g, 62%). The compound has a melting point range of 69.5–72 °C: NMR ($CDCl_3$) δ 7.22 (d, J = 6 Hz, 2 H), 6.84 (d, J = 6 Hz, 2 H), 6.21 (d, J = 2 Hz, 1 H), 6.00 (d, J = 2 Hz, 1 H), 3.86 (s, 3 H), 3.83 (s, 3 H), 3.73 (s, 3 H), 3.60 (d, 1 H), 2.93 (d, 1 H), 2.50 (s, 3 H), 2.45 (s, 3 H), −0.35 (9 H); IR ($CDCl_3$) 2920, 2825, 1685, 1607, 1587, 1503, 1460, 1430, 1242, 1215, 1170, 1120, 1100, 1035 cm^{-1}; high-resolution mass spectrum for $C_{26}H_{32}O_6SiS_2$ requires 532.140 97, measured 532.140 63; ^{13}C NMR ($CDCl_3$) δ 193.03, 164.42, 161.83, 159.17, 158.63, 151.90, 131.22, 130.44, 127.41, 113.33, 107.27, 95.90, 92.26, 91.57, 89.29, 55.65, 55.38, 55.00, 44.96, 19.02, 17.53, 1.29. Elemental analysis calcd for $C_{26}H_{32}O_6SiS_2$: C, 58.62; H, 6.06. Found: C, 59.04; H, 6.53.

Treatment of the compound (0.10 g, 0.19 mmol) with tetra-n-butylammonium fluoride (2.2 equiv) gave the deprotected keto disulfide **10** (0.08 g, 93%) as a bright yellow solid which melts at 179 °C: NMR ($CDCl_3$) δ 7.26 (d, J = 8 Hz, 2 H), 6.85 (d, J = 8 Hz, 2 H), 6.19 (d, J = 2 Hz, 1 H), 6.01 (d, J = 2 Hz, 1 H), 3.79 (s, 3 H), 3.76 (s, 3 H), 3.72 (s, 3 H), 3.61 (d, J = 18 Hz, 1 H), 3.38 (s, 1 H, 3.00 (d, J = 18 Hz, 1 H), 2.48 (s, 3 H), 2.46 (s, 3 H); IR ($CDCl_3$) 3480, 2920, 2825, 1672, 1603, 1590, 1502, 1460, 1430, 1245, 1211, 1195, 1145, 1050, 1032, 905, 780 cm^{-1}; high-resolution mass spectrum for $C_{23}H_{24}O_6S_2$ requires 460.101 44, measured 460.101 27; ^{13}C NMR ($CDCl_3$) δ 194.15, 164.22, 161.56, 159.25, 148.23, 154.88, 129.79, 128.34, 126.91, 113.62, 106.83, 94.75, 92.54, 89.22, 89.16, 55.65, 55.42, 55.20, 45.25, 19.41, 17.44. Elemental analysis calcd for $C_{23}H_{24}O_6S_2$: C, 59.98; H, 5.25. Found: C, 59.83; H, 5.18.

Tricyclic Enone 12. To a solution of keto disulfide **10** (0.40 g, 0.75 mmol) in acetonitrile/water (45:1) was added 2,3-dichloro-5,6-dicyanobenzoquinone (0.30 g, 1.28 mmol) in one portion. The resulting dark red solution was boiled for 2 days. It was then concentrated in vacuo. The crude product was purified via flash column chromatography using 2.5:1 hexanes/ethyl acetate as eluent, giving compound **12** (0.18 g, 56%). This compound is a yellow powdery solid and melts at 68–70 °C: NMR ($CDCl_3$) δ 7.92 (s, 1 H), 7.27 (d, J = 7 Hz, 2 H), 6.95 (d, J = 7 Hz, 2 H), 6.18 (d, J = 2 Hz, 1 H), 6.03 (d, J = 2 Hz, 1 H), 3.83 (s, 3 H), 3.80 (s, 3

H), 3.77 (s, 3 H), 2.42 (s, 3 H); IR ($CDCl_3$) 3435, 2920, 2830, 1730, 1715, 1615, 1590, 1500, 1460, 1435, 1300, 1250, 1105, 1030 cm^{-1}; high-resolution mass spectrum for $C_{22}H_{20}O_7$ requires 428.092 98, measured 428.092 72; ^{13}C NMR ($CDCl_3$) δ 196.06, 185.64, 164.41, 160.56, 160.05, 158.40, 156.86, 140.54, 127.74, 125.07, 113.93, 105.21, 94.60, 92.82, 88.63, 86.59, 55.57, 55.19, 54.74, 11.38.

Tricyclic Thioester 13. To a suspension of CuBr–Me_2S (0.066 g, 0.32 mmol) in diethyl ether (5 mL) under argon at 0 °C was added phenylmagnesium bromide solution (0.32 mL, 0.64 mmol). The yellow suspension was stirred at 0 °C for 25 min and then cooled to −78 °C. A solution of compound **12** (0.11 g, 0.26 mmol) in ether (5 mL) was added dropwise. The reaction mixture was stirred at −78 °C for 1 h and then slowly warmed up to room temperature over a 3-h period. It was quenched with dilute HCl (2 mL), poured into saturated ammonium chloride, and extracted twice with ether (2 × 25 mL). The combined organic layer was washed with water, followed by saturated sodium chloride, dried, and concentrated in vacuo. Recrystallization from a 10:1 hexanes/ether mixture gave a tan powder (0.12 g, 90%), which melted at 92–94 °C. The compound exists as an 80:20 mixture of enol ester/keto ester forms: NMR ($CDCl_3$) δ 10.60 (s, br, 1 H), 7.43 (d, J = 8 Hz, 2 H), 7.22 (m, 3 H), 7.06 (m, 2 H), 6.87 (d, J = 8 Hz, 2 H), 6.01 (d, J = 2 Hz, 1 H), 5.60 (d, J = 2 Hz, 1 H), 4.78 (s, 1 H), 3.84 (s, 3 H), 3.79 (s, 3 H), 3.64 (s, 3 H), 2.25 (s, 3 H); IR ($CDCl_3$) 3400 (enol), 2922, 2830, 1750 (keto), 1670, 1617, 1595, 1505, 1495, 1460, 1250, 1215, 1150, 905 cm^{-1}; high-resolution mass spectrum for $C_{28}H_{24}O_6S$ ($M^+ - H_2O$) requires 488.129 36, measured 488.128 69; MS (CI, isobutane), m/e 507 (MH^+), 489, 433, 415, 339, 311, 300, 223, 209.

Tricyclic Keto Amide 14. To a solution of thioester **13** (0.12 g, 0.24 mmol) in tetrahydrofuran (3 mL) was added excess dimethylamine (1.2 mL), and the solution was heated in a culture tube at 75 °C for 2 days. The reaction mixture was concentrated in vacuo and the residue recrystallized in 5:1 hexanes/ethyl ether to give a light yellow-orange powder (0.11 g, 92%). The compound exists entirely as a keto amide (no enol amide is detected): NMR ($CDCl_3$) δ 7.35 (d, J = 8 Hz, 2 H), 7.20 (m, 3 H), 7.07 (m, 2 H), 6.86 (d, J = 8 Hz, 2 H), 6.16 (d, J = 3 Hz, 1 H), 6.03 (d, J = 3 Hz, 1 H), 4.74 (d, J = 13 Hz, 1 H), 4.53 (d, J = 13 Hz, 1 H), 3.80 (s, 3 H), 3.78 (s, 3 H), 3.76 (s, 3 H), 2.95 (s, 3 H), 2.86 (s, 3 H); IR ($CDCl_3$) 3350, 2920, 2830, 1743, 1635, 1610, 1590, 1505, 1460, 1250, 1215, 1145, 1030 cm^{-1}; high-resolution mass spectrum for $C_{29}H_{27}NO_6$ ($M^+ - H_2O$) requires 485.183 84, measured 485.183 48; mass spectrum (chemical ionization, isobutane), m/e 504 (MH^+), 486, 455, 311, 300, 223, 177; ^{13}C NMR ($CDCl_3$) 204.84, 166.37, 164.56, 162.08, 159.26, 158.14, 135.24, 128.89, 128.23, 128.03, 127.36, 113.37, 104.86, 97.51, 96.17, 92.59, 88.59, 87.08, 55.71, 55.19, 55.24, 54.08, 37.19, 35.99.

Tricyclic Hydroxy Amide 15. Sodium borohydride (0.031 g, 0.81 mmol) was suspended in methanol (3 mL) under argon at 0 °C. A solution of keto amide **14** (0.0465 g, 0.092 mmol) in methanol (2 mL) was added dropwise. The resulting solution was stirred at 0 °C for 10 h and then slowly allowed to warm to room temperature over 2 h. The reaction mixture was quenched with dilute HCl (2 mL) and poured into brine. The mixture was extracted twice with ether. The combined organic layer was dried and concentrated in vacuo. Recrystallization in 5:1 hexanes/ethyl ether gave a white crystalline powder (0.0436 g, 93%): mp 108 °C; NMR ($CDCl_3$) δ 7.37 (d, J = 8 Hz, 2 H), 7.14 (m, 3 H), 7.03 (m, 2 H), 6.87 (d, J = 8 Hz, 2 H), 6.19 (d, J = 2 Hz, 1 H), 6.09 (d, J = 2 Hz, 1 H), 4.80 (d, J = 10 Hz, 1 H), 4.23 (d, J = 12 Hz, 1 H), 3.81 (s, 6 H), 3.77 (s, 3 H), 3.56 (dd, J = 10 and 12 Hz, 1 H), 2.99 (s, 3 H), 2.84 (s, 3 H); IR ($CDCl_3$) 3560, 3490, 2930, 2830, 1632, 1605, 1503, 1490, 1450, 1435, 1250, 1197, 1143, 1120, 1030, 910, 730 cm^{-1}; high-resolution mass spectrum for $C_{29}H_{31}NO_7$ requires 505.210 06, measured 505.209 30; ^{13}C NMR ($CDCl_3$) see Table I.

Benzofuranone 16. Compound **6** (7.30 g, 24.3 mmol) was suspended in *tert*-butyl alcohol (150 mL) and maintained under an argon atmosphere. The suspension was heated at 60 °C until most of the solid material went into solution. Benzyltrimethylammonium hydroxide (1.10 mL, 2.43 mmol) was added to the solution, followed by the slow addition of cinnamonitrile (3.29 mL, 24.94 mmol). The reaction mixture was heated at 60 °C for 2 days. It was cooled, and the copious chalky precipitate was separated from the *tert*-butyl alcohol solution via filtration. The collected precipitate was triturated twice with ether. The filtrate was partitioned twice in ether and once in dilute HCl solution. The combined organic layer was treated with brine and concentrated in vacuo. The residue left after concentrating in vacuo was combined with the initial copious precipitate and carried on to the next reaction without further purification or separation of diastereomers. The spectroscopic data of the major isomer are reported: NMR ($CDCl_3$) δ 7.38 (d, J = 8 Hz, 2 H), 7.45–7.15 (m, 5 H), 6.72 (d, J = 8 Hz, 2 H), 6.33 (d, J = 2 Hz, 1 H), 6.02 (d, J = 2 Hz, 1 H), 3.89 (s, 3 H), 3.85 (s, 3 H), 3.82–3.78 (m, 1 H), 3.75 (s, 3 H), 2.92–2.84 (m, 1 H), 2.70–2.64 (m, 1 H); IR (Nujol) 2925, 2840, 2240, 1687, 1612, 1580, 1455, 1425, 1320, 1235, 1115, 1020 cm^{-1}; high-resolution mass spectrum for $C_{26}H_{23}O_5N$ requires 429.157 63, measured 429.156 94.

Tricyclic Ketone 17b. To a solution of compound **17a** (0.85 g, 1.96 mmol) in dry benzene (30 mL) at 5 °C under an argon atmosphere was added diisopropylethylamine (0.88 mL, 4.92 mmol) dropwise, followed by the slow addition of TMSOTf (0.63 mL, 3.25 mmol). The reaction mixture was stirred at 5 °C for 6 h and then slowly allowed to warm to room temperature. It was diluted with hexanes (140 mL) and filtered. The filtrate was concentrated in vacuo to give compound **17b** (0.84 g, 85%) in high purity; NMR ($CDCl_3$) δ 7.25 (d, J = 8 Hz, 2 H), 7.19 (m, 2 H), 6.92 (m, 2 H), 6.86 (d, J = 8 Hz, 2 H), 6.04 (d, J = 2 Hz, 1 H), 5.99 (d, J = 2 Hz, 1 H), 3.97 (m, 1 H), 3.81 (s, 3 H), 3.77 (s, 3 H), 3.74 (s, 3 H), 3.18 (t, J = 16 Hz, 1 H), 2.55 (dd, J = 8, 18 Hz, 1 H), −0.35 (s, 9 H); IR ($CDCl_3$) 2950, 2830, 1750, 1608, 1590, 1460, 1435, 1248, 1200, 1150, 1110, 1035 cm^{-1}; high-resolution mass spectrum for $C_{29}H_{32}O_6Si$ requires 504.196 83; measured 504.196 35; ^{13}C NMR ($CDCl_3$) 207.20, 164.48, 162.82, 158.85, 157.98, 136.20, 131.67, 128.47, 128.41, 128.19, 113.15, 112.96, 105.82, 97.80, 91.75, 89.38, 88.00, 55.54, 55.23, 55.12, 52.53, 39.10, 1.32.

Tricyclic Keto Disulfide 18. *n*-Butyllithium (2.60 mL, 6.35 mmol) was added dropwise to a solution of diisopropylamine (0.94 mL, 6.67 mmol) in dry THF (25 mL) under an argon atmosphere at −40 °C. The resulting lithium diisopropylamide was stirred for 15 min, and then hexamethylphosphoramide (6.50 mL, 37.4 mmol) was added rapidly. After 30 min, a solution of compound **17b** (0.80 g, 1.60 mmol) in dry tetrahydrofuran (10 mL) was added dropwise. The orange solution was stirred for $1^1/_4$ h, and then carbon disulfide (2.87 mL, 47.6 mmol) was added rapidly. The reaction mixture was stirred for 5 h, after which methyl iodide (4.0 mL, 63.5 mmol) was introduced rapidly. The reaction mixture was allowed to warm to room temperature overnight. It was diluted with hexanes (120 mL) and washed four times with water and once with brine. The organic layer was dried and concentrated in vacuo. The crude product was purified via flash column chromatography using 2:1 hexanes/ethyl acetate as eluent to yield a compound (0.64 g, 67%): NMR ($CDCl_3$) δ 7.34 (d, J = 8 Hz, 2 H), 7.30–6.85 (m, 5 H), 6.85 (d, J = 8 Hz, 2 H), 5.88 (d, J = 2 Hz, 1 H), 5.29 (d, J = 2 Hz, 1 H), 4.76 (s, 1 H), 3.82 (s, 3 H), 3.76 (s, 3 H), 3.55 (s, 3 H), 2.55 (s, 3 H), 2.22 (s, 3 H), −0.35 (s, 9 H); IR (film) 2942, 2812, 1680, 1605, 1590, 1457, 1430, 1240, 1215, 1175, 1092, 1035 cm^{-1}; high-resolution mass spectrum for $C_{32}H_{36}O_6SiS_2$ requires 608.172 28, measured 608.170 71; ^{13}C NMR ($CDCl_3$) δ 192.62, 164.20, 162.02, 158.82, 157.64, 159.19, 138.59, 133.19, 132.85, 127.05, 126.83, 113.33, 113.14, 107.26, 96.74, 91.91, 91.82, 90.56, 88.01, 60.18, 55.38, 55.24, 55.14, 19.54, 17.89, 0.77.

Treatment of the compound (0.20 g, 0.33 mmol) with tetra-*n*-butylammonium fluoride (2.2 equiv) gave deprotected keto disulfide **18** (0.17 g, 96%) as a yellow solid which melts at 220 °C: NMR ($CDCl_3$) δ 7.37 (d, J = 8 Hz, 2 H), 7.35–6.90 (m, 5 H), 6.96 (d, J = 8 Hz, 2 H), 5.95 (d, J = 2 Hz, 1 H), 5.37 (d, J = 2 Hz, 1 H), 4.91 (br s, 1 H), 3.84 (s, 3 H), 3.79 (s, 3 H), 3.58 (s, 3 H), 2.62 (s, 3 H), 2.36 (s, 3 H); IR ($CDCl_3$) 3500, 3000, 2920, 2825, 1715, 1605, 1590, 1490, 1460, 1435, 1250, 1140, 1100, 1055, 1032, 910, 730 cm^{-1}; high-resolution mass spectrum for $C_{29}H_{28}O_6S_2$ requires 536.132 74, measured 536.133 47. Elemental analysis calcd for $C_{29}H_{28}O_6S_2$: C, 64.91; H, 5.26. Found: C, 64.57; H, 5.26.

Tricyclic Keto Ester 19. To a solution of tricyclic disulfide **18** (0.12 g, 0.20 mmol) in dry THF (6 mL) at 0 °C under an argon atmosphere was added a solution of sodium methoxide (0.054 g, 1.00 mmol) in THF (2 mL). The reaction mixture was stirred for $1^1/_2$ days. Dilute HCl solution (3 mL) was added, and the mixture was stirred for 5 min. It was poured into ether (60 mL) and washed twice with saturated NaCl. The organic layer was

dried and concentrated in vacuo. The crude product (0.101 g, 97%) was a light yellow foamy solid of high purity, mp 30 °C. It exists as an 80:20 enol ester/keto ester mixture: NMR ($CDCl_3$) δ 10.65 (br, s), 7.42 (d, J = 8 Hz, 2 H), 7.09 (m, 3 H), 6.90 (d, J = 8 Hz, 2 H), 6.79 (m, 2 H), 5.98 (d, J = 2 Hz, 1 H), 5.61 (d, J = 2 Hz, 1 H), 4.67 (s, 1 H), 3.81 (s, 3 H), 3.78 (s, 3 H), 3.62 (s, 3 H), 3.58 (s, 3 H); IR ($CDCl_3$) 3420, 2940, 2825, 1755, 1655, 1608, 1592, 1455, 1420, 1245, 1212, 1142, 1120, 1055, 1030, 910 cm^{-1}; high-resolution mass spectrum for $C_{28}H_{24}O_7$ requires 472.152 21, measured 472.152 59.

Tricyclic Ester 20. To sodium borohydride (0.081 g, 2.14 mmol) in dry methanol (3 mL) at 0 °C under argon was added a solution of compound **19** (0.078 g, 0.14 mmol) in methanol (5 mL) dropwise. The reaction mixture was stirred at 0 °C for 10 h. It was concentrated in vacuo. The resiude was taken up in ether (25 mL) and treated with dilute HCl solution (2 mL). The organic layer was washed with brine, dried, and concentrated. The crude product was recrystallized in ether/hexanes (3:1) to give ester **20** (0.0706 g, 100%) as a light yellow foamy solid which melts at 78–80 °C: NMR ($CDCl_3$) δ 7.33 (d, J = 8 Hz, 2 H), 7.16 (m, 3 H), 6.94 (m, 2 H), 6.87 (d, J = 8 Hz, 2 H), 6.12 (d, J = 2 Hz, 1 H), 6.05 (d, J = 2 Hz, 1 H), 4.77 (d, J = 11 Hz, 1 H), 4.03 (d, J = 13 Hz, 1 H), 3.81 (s, 3 H), 3.78 (s, 3 H), 3.76 (s, 3 H), 3.60 (s, 3 H), 3.24 (dd, 1 H, J = 11 and 13 Hz); IR ($CDCl_3$) 3472, 2940, 2825, 1720, 1610, 1590, 1450, 1430, 1270, 1175, 1120, 1025, 910 cm^{-1}; high-resolution mass spectrum for $C_{28}H_{28}O_8$ requires 492.178 43, measured 492.178 03; ^{13}C NMR ($CDCl_3$) 172.95, 163.93, 161.89, 159.24, 159.79, 134.84, 128.99, 128.25, 127.82, 127.15, 113.45, 105.03, 99.35, 92.53, 91.23, 88.67, 83.79, 77.25, 55.66, 55.23, 54.70, 52.12, 50.80.

Tricyclic Acid 21. To ester **20** (0.17 g, 0.35 mmol) in a methanol/water mixture (24:4) was added solid potassium hydroxide. The solution was heated at 44 °C for 10 h. It was then neutralized with dilute HCl solution and poured into brine (50 mL). The aqueous layer was extracted three times with diethyl ether. The combined organic layer was treated with brine, dried, and concentrated in vacuo. Recrystallization in chloroform gave acid **21** (0.14 g, 82%) as a white crystalline powder, which melts between 259–261 °C: NMR ($CDCl_3$) δ 7.34 (d, J = 8 Hz, 2 H), 7.19 (m, 3 H), 6.97 (m, 2 H), 6.90 (d, J = 8 Hz, 2 H), 6.14 (d, J = 2 Hz, 1 H), 6.07 (d, J = 2 Hz, 1 H), 4.79 (d, J = 11 Hz, 1 H), 4.00 (d, J = 13 Hz, 1 H), 3.79 (s, 6 H), 3.77 (s, 3 H), 3.24 (dd, J = 11 and 13 Hz, 1 H); IR ($CDCl_3$) 3460, 3550–2650 (br), 2920, 1700, 1620, 1500, 1440, 1250, 1210, 1135, 905, 730 cm^{-1}; high-resolution mass spectrum for $C_{27}H_{26}O_8$ requires 478.162 78, measured 478.162 74; ^{13}C NMR ($CDCl_3$) δ 176.34, 163.90, 161.83, 159.17, 157.81, 134.68, 129.01, 128.90, 128.24, 127.90, 113.43, 104.84, 99.25, 92.52, 91.19, 88.56, 83.56, 77.28, 55.69, 55.55, 55.23, 50.45.

Tricyclic Amide 15. To a stirred solution of acid **21** (90 mg, 0.19 mmol) in methylene chloride (3 mL) at 0 °C under an argon atmosphere was added pyridine (0.076 mL, 0.94 mmol). The solution was stirred for 3 min, and 1,1'-carbonyldiimidazole (0.16 g, 0.94 mmol) in methylene chloride (2 mL) was added. It was stirred at 0 °C for 5 h and then allowed to slowly warm to room temperature. The mixture was quenched with dilute HCl solution and poured into brine. The aqueous layer was extracted twice with methylene chloride (20 mL). The combined organic layer was dried and concentrated in vacuo. Recrystallization in ethyl ether/hexanes (1:5) gave a white crystalline powder (50 mg, 53%) whose physical properties are identical with those of amide **15**.

Registry No. **4**, 117828-35-0; **4** Me_3Si ether, 117828-36-1; **5**, 117828-32-7; **6**, 117828-33-8; **7**, 117828-34-9; **9**, 117828-37-2; **10**, 117828-38-3; **10** detrimethylsilated, 117828-39-4; **12**, 117828-40-7; **13**, 117828-41-8; **14**, 117828-42-9; **15**, 117894-34-5; **16** (isomer 1), 117828-43-0; **16** (isomer 2), 117828-44-1; **17a**, 117828-45-2; **17b**, 117828-46-3; **18**, 117828-48-5; **18** Me_3Si ether, 117828-47-4; **19**, 117828-49-6; **20**, 117828-50-9; **21**, 117828-51-0; acrylonitrile, 107-13-1; cinnamonitrile, 4360-47-8.

Supplementary Material Available: Positional parameters and isotropic temperature factors for compound **18** (1 page). Ordering information is given on any current masthead page.

Diastereoselective Crossed Aldol Reactions with Chiral Fluorinated Aldehydes

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Lewis acid catalyzed crossed aldol reactions were carried out between optically active α-fluoro aldehydes (*S*)- and (*R*)-**2**, prepared from (*S*)-monoethyl 2-fluoro-2-methylmalonate by asymmetric enzymatic hydrolysis, and enol silyl ethers or silyl ketene acetals. Moderate to excellent diastereoselectivity was observed, depending on the nature of the Lewis acid employed. The α-fluoro substituent has little effect on the diastereoselectivity of these Lewis acid catalyzed aldol condensations.

The diastereo- and/or enantioselective construction of molecules is an important current topic in organic chemistry. A wide variety of highly stereoselective reactions have been developed, which seem to afford useful solutions toward this problem.[1] Among these, the crossed aldol reaction has especially attracted the interest of synthetic chemists. Since Mukaiyama's discovery[2] of the Lewis acid mediated reaction of enol silyl ethers with aldehydes, much work has led to the development of methods for the assembly of contiguous stereocenters with high relative as well as absolute stereocontrol.[3]

However, in the field of fluorine chemistry, only a few methods are known for the stereoselective preparation of fluorinated compounds.[4] The exploration of new methodologies is necessary, because the inherent characteristics

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