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CONVERGENT SYNTHESIS OF THE CDEF RING FRAGMENT OF YESSOTOXIN VIA α-CYANO ETHERS

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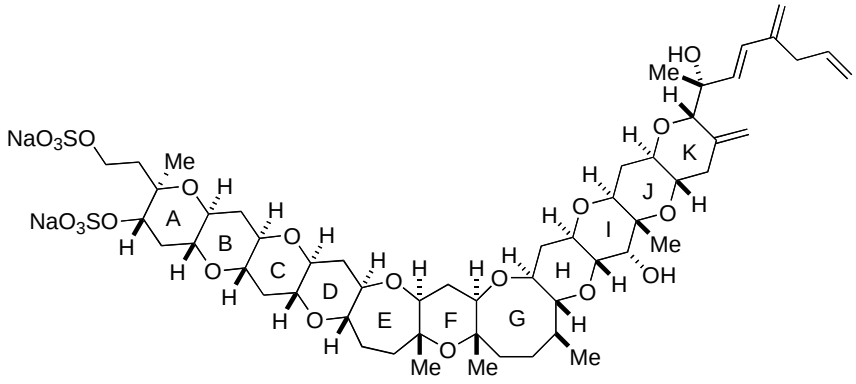
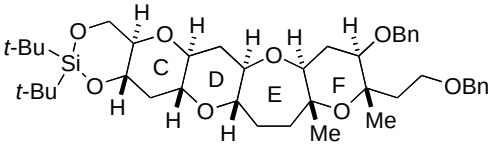
Abstract – The synthesis of the CDEF ring fragment of yessotoxin, a marine ladder polyether, has been achieved. Union of three components, the C ring aldehyde, the F ring diol, and trimethylsilyl cyanide, was accomplished by treatment with $Sc(OTf)_3$ to afford the α-cyano ether both in stepwise and one-pot reactions. The DE ring system was constructed through a ring closing metathesis reaction and reductive etherification sequence.

Yessotoxin (**1**) [1] is a marine polyether toxin produced by the dinoflagellate *Protoceratium* and other species.[2] Bivalve mollusks, such as scallops and mussels, accumulate **1** and its analogs[3] by filter feeding in waters containing blooms of the algae. Besides the potent acute toxicity against mice (LD_{50} = 286 μg/kg, i.p.),[4] yessotoxins have recently been shown to exhibit intriguing biological activities in humans, i.e., (i) modulation of cytosolic calcium levels of human lymphocytes,[5] (ii) activation of caspases,[6] and (iii) cytotoxicity against human tumor cell lines.[7] The broad spectrum of biological activities of **1**, coupled with the unique arched molecular structure, prompted us to target its synthesis, although significant advancements[8,9] in the synthesis of **1** have already been reported by Nakata,[10] Mori,[11] and Kadota.[12] During the course of our synthetic studies of **1**,[13] we developed an efficient method for convergent synthesis of polycyclic ethers[14,15] via α-cyano ethers,[16] and the methodology was successfully applied to the convergent synthesis of the FGHI ring system via construction of the central GH ring.[17] Herein, we describe a convergent synthesis of the CDEF ring fragment (**2**) of **1** via α-cyano ethers based on our methodology.

§ Dedicated to Professor Satoshi Omura on occasion of his 70th birthday

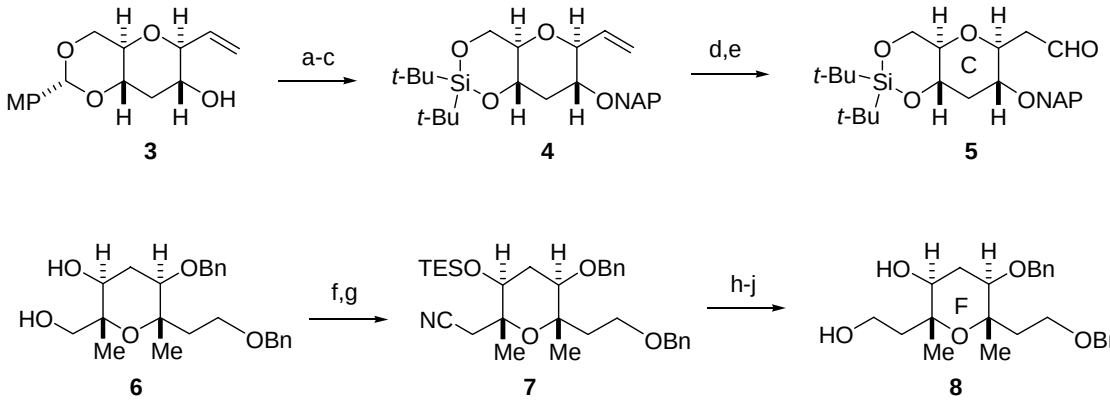


yessotoxin (**1**)



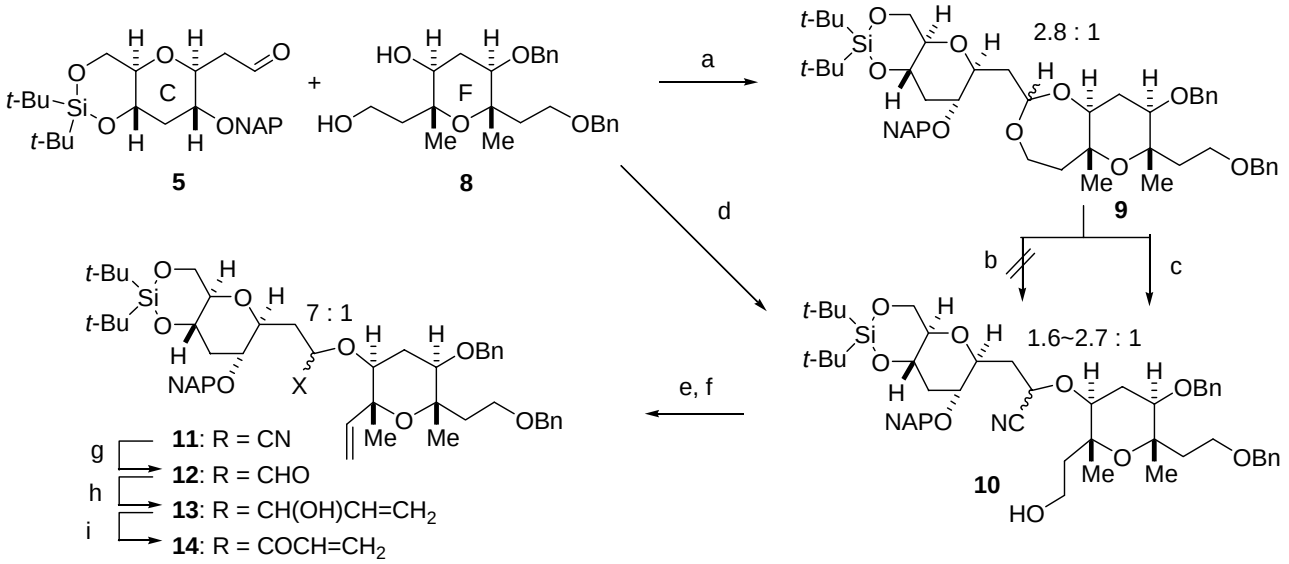
CDEF ring fragment (**2**)

Synthesis of the C (**5**) and F ring (**8**) fragments commenced with known tetrahydropyran derivatives (**3**)[18] and (**6**)[19] prepared from 2-deoxy-D-ribose (Scheme 1). To prepare aldehyde (**5**), protection of the secondary alcohol (**3**) as NAP (2-naphthylmethyl) ether,[20] followed by conversion of the *p*-methoxybenzylidene to the corresponding di-*tert*-butylsilylene gave olefin (**4**). Hydroboration with 9-BBN gave the primary alcohol, which was oxidized with Dess-Martin periodinane to yield aldehyde (**5**). For the diol (**8**), regioselective one-pot triflation and silylation[21] of the diol (**6**) followed by treatment with NaCN afforded nitrile (**7**). Sequential reduction of the nitrile (**7**) with DIBAL-H and $NaBH_4$ gave the corresponding primary alcohol and subsequent removal of the TES group afforded the diol (**8**) in 78% yield.



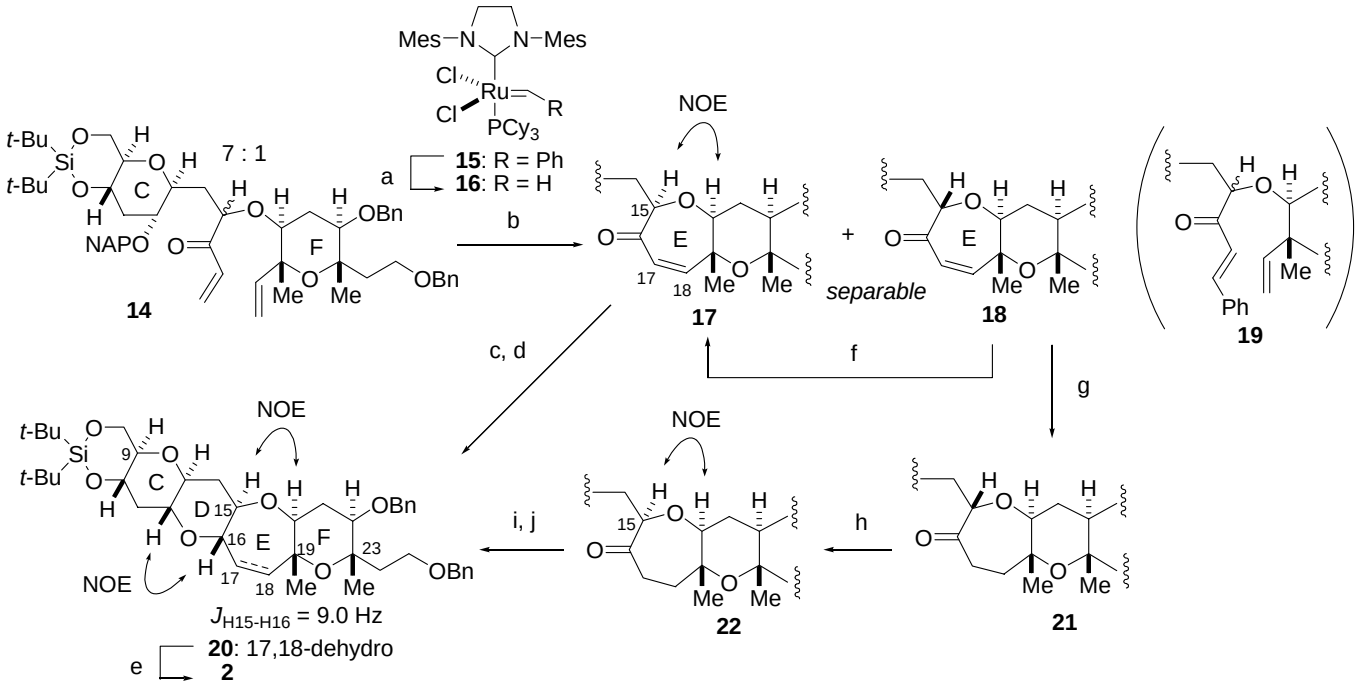
Scheme 1. *Reagents and conditions:* (a) NAPBr, NaHMDS, THF, DMF, rt, 2 h; (b) *p*-TsOH·H_2O, H_2O, MeOH, THF, rt, 45 min; (c) *t*-$Bu_2Si(OTf)_2$, 2,6-lutidine, THF, DMF, 0 °C , 10 min, 86% (3 steps); (d) 9-BBN, sonication, THF, rt, 3 h, then 30%H_2O_2, $NaHCO_3$ (aq), rt, 1 h; (e) Dess-Martin periodinane, CH_2Cl_2, rt, 35 min, 99% (2 steps); (f) Tf_2O, 2,6-lutidine, CH_2Cl_2, -70 °C, then TESOTf, 20 min; (g) NaCN, 18-crown-6, DMF, 45 °C, 3.5 h, 80% (2 steps); (h) DIBAL-H, CH_2Cl_2, -78 °C, 40 min; (i) $NaBH_4$, EtOH, rt, 1.5 h; (j) TBAF, THF, rt, 1 h, 78% (3 steps).

We then moved on to coupling of the fragments and synthesis of the α-cyano ethers as shown in Scheme 2. Condensation of **5** using two equivalents of **8** was successfully achieved by treatment with $Sc(OTf)_3$[22] in benzene to give seven-membered ring acetal (**9**) in 78% yield as a mixture of diastereomers (2.8:1) with respect to the stereogenic center on the acetal carbon. Attempts to obtain α-cyano ether **10** by means of regioselective opening of the acetal (**9**) under conditions using TMSCN and TMSOTf, which was previously successful for a model system[16] lacking angular methyl groups on the F ring, failed with recovery of the starting material. After considerable experimentation, we found that $Sc(OTf)_3$ was effective for the acetal cleavage, affording α-cyano ether (**10**) as a mixture of diastereomers (1.6:1).[17] The finding that the common Lewis acid $Sc(OTf)_3$ was effective for both acetal formation and subsequent cleavage suggested that one-pot synthesis of the α-cyano ether (**10**) should be possible from the aldehyde (**5**), the diol (**8**), and TMSCN. As expected, union of the three components was achieved by treatment with $Sc(OTf)_3$ using 1.2 equivalents of the diol (**8**) to afford the α-cyano ether (**10**) (2.7:1) in a single step. The resulting primary alcohol (**10**) was converted to terminal olefin (**11**) via 2-nitrobenzenselenide through elimination of the selenoxide.[23] Nitrile (**11**) was reduced with DIBAL-H at –78 °C to afford aldehyde (**12**) (89%), which was treated with vinyl lithium at –78 to -20 °C to afford alcohol (**13**) (76%). Oxidation of **13** with Dess-Martin periodinane gave the α,β-unsaturated ketone (**14**) (94%).



Scheme 2. *Reagents and conditions:* (a) $Sc(OTf)_3$, benzene, rt, 14 h, 78%; (b) TMSCN, TMSOTf, MS4A, CH_2Cl_2, rt to 40 °C; (c) $Sc(OTf)_3$, TMSCN, CH_2Cl_2, rt, 9.5 h, then K_2CO_3, MeOH, rt, 30 min, 92%; (d) $Sc(OTf)_3$, TMSCN, CH_2Cl_2, rt, 18 h, then K_2CO_3, MeOH, 53% (recovery of **8**, 41%); (e) 2-$NO_2C_6H_4SeCN$; Bu_3P, THF, rt, 25 min; (f) 30%H_2O_2, $NaHCO_3$ (aq), THF, 45 °C, 3.5 h, 77% (2 steps); (g) DIBAL-H, CH_2Cl_2, -78 °C, 30 min, 89%; (h) $(CH_2=CH)_4Sn$, MeLi, THF, -78 to -20 °C, 1 h, 76%; (i) Dess-Martin periodinane, CH_2Cl_2, rt, 1 h, 94%.

Next, ring closing metathesis (RCM)[24] reaction of the diene (**14**) was examined as shown in Scheme 3. In the case of micro-scale experiments (< 5 mg), which require a relatively greater amount of catalyst loading, concomitant formation of byproduct (**19**) resulting from the Grubbs catalyst (**15**)[25] was problematic. Therefore, ruthenium ethylidene complex (**16**), prepared from **15** by treatment with ethylene gas, was subjected to the RCM. As expected, no undesirable byproduct (**19**) was formed under the reaction conditions, and seven-membered enone (**17**) and its C15[26] epimer (**18**) were obtained in 9% and 67% yields, respectively. The structure of the desirable isomer (**17**) was determined by NOE experiments. Construction of the D ring was successfully achieved through removal of the NAP group of **17** with DDQ, followed by reductive etherification with Et_3SiH in the presence of TMSOTf to give 6/6/7/6 tetracyclic ether (**20**) as a single isomer. Finally, hydrogenation of the double bond of **20** using PtO_2 afforded the CDEF ring fragment (**2**) in 94% yield, whose structure was unambiguously determined by NOE experiments and coupling constants.[27]



Scheme 3. *Reagents and conditions:* (a) CH_2=CH_2 (bubbling), toluene, rt, 30 min, then Ar (bubbling); (b) **16** (38 mol%), toluene, 100 °C, **17**: 9%, **18**: 67%; (c) DDQ, CH_2Cl_2, H_2O, rt, 45%; (d) Et_3SiH, TMSOTf, CH_2Cl_2, -55 °C, 20 min, 83%; (e) H_2, PtO_2, AcOEt, rt, 3 h, 94%; (f) DBU, toluene, 100 °C, 3 h, 40%; (g) H_2, PtO_2, AcOEt, rt, 3 h, 73%; (h) DBU, toluene, 100 °C, 92 h, 84%, **22**:**21** = 4.7:1; (i) DDQ, CH_2Cl_2, H_2O; (j) Et_3SiH, TMSOTf, CH_2Cl_2, -50 °C, 56% (2 steps).

Alternatively, conversion of the undesirable isomer (**18**) into **2** was carried out. Epimerization of **18** by treatment with DBU in toluene at 100 °C for 3 h gave **17** in 40% yield. The moderate yield was due to the partial decomposition of the enones, which might result from their ability as Michael acceptors under the

basic conditions. Therefore, epimerization was examined using a saturated ketone (**21**) derived from the α,β-unsaturated ketone (**18**) by hydrogenation using PtO_2. As expected, treatment of **21** with DBU in toluene at 100 °C for 92 h give a separable mixture of **22** and **21** (4.7:1) in good yield (84%) without any decomposition products. Removal of the NAP group of **22**, followed by reductive etherification afforded **2** in 56% yield for two steps.

In conclusion, convergent synthesis of the CDEF ring fragment has been achieved through union of the C and F ring fragments to give the α-cyano ethers, followed by construction of the central DE ring system through the ring closing metathesis and reductive etherification. Further studies directed towards the total synthesis of yessotoxin via α-cyano ethers based on our methodology are currently in progress in our laboratory.

ACKNOWLEDGEMENTS

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26. The carbon numbering of compounds in this article corresponds to that of yessotoxin.
27. Spectral data of **2**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32-7.25 (10H, m, Ph), 4.62 (1H, d, J = 11.5 Hz,

benzyl), 4.45 (1H, d, *J* = 12.0 Hz, benzyl), 4.42 (1H, d, *J* = 11.5 Hz, benzyl), 4.41 (1H, d, *J* = 11.5 Hz, benzyl), 4.12 (1H, dd, *J* = 10.5, 5.0 Hz, H8eq), 3.79 (1H, ddd, *J* = 10.0, 10.0, 4.5 Hz, H10), 3.79 (1H, dd, *J* = 10.0, 10.0 Hz, H8ax), 3.56 (1H, ddd, *J* = 15.0, 8.0 Hz, H25a), 3.52 (1H, ddd, *J* = 14.5, 8.5 Hz, H25b), 3.41 (1H, dd, *J* = 12.0, 4.0 Hz, H20), 3.29 (1H, ddd, *J* = 10.0, 10.0, 5.0 Hz, H9), 3.20 (1H, dd, *J* = 12.0, 3.5 Hz, H22), 3.15-3.26 (2H, m, H15, H16), 3.04 (1H, ddd, *J* = 10.0, 10.0, 4.0 Hz, H13), 2.94 (1H, ddd, *J* = 10.0, 10.0, 4.0 Hz, H12), 2.37 (1H, ddd, *J* = 11.5, 4.0, 4.0 Hz, H11eq), 2.27 (1H, ddd, *J* = 11.5, 4.0, 4.0 Hz, H14eq), 2.10 (1H, ddd, *J* = 12.5, 4.5, 4.5 Hz, H21eq), 1.94-2.00 (1H, m, H17), 1.71-1.91 (5H, m, H17, H18, H24), 1.71 (1H, q, *J* = 12.0 Hz, H21ax), 1.45 (1H, q, *J* = 11.0 Hz, H11ax), 1.40 (1H, q, *J* = 11.0 Hz, H14ax), 1.21 (3H, s, Me), 1.20 (3H, s, Me), 1.01 (9H, s, ^{t}Bu), 0.96 (9H, s, ^{t}Bu); ^{13}C NMR (125.7 MHz, $CDCl_3$) δ 127.58 (Ph), 127.33 (Ph), 127.30 (Ph), 81.45 (C22), 80.41 (C16), 79.74 (C15), 79.59 (C20), 77.54 (C9), 76.86 (C19 or C23), 76.69 (C13), 75.89 (C12), 75.42 (C19 or C23), 72.85 (benzyl), 72.75 (C10), 70.92(benzyl), 66.80 (C8), 66.30 (C25), 41.58 (C18 or C24), 39.70 (C18 or C24), 38.42 (C11), 36.89 (C14), 29.23 (C17), 28.79 (C21), 27.50 (^{t}Bu), 27.13 (^{t}Bu), 22.84 (Me), 22.69 (^{t}Bu), 22.39 (Me), 20.00 (^{t}Bu); ESI MS 745 ($M+Na^{+}$).