Electronic Supplementary Information

Synthesis of 2,3-Di- and 2,3,4-Trisubstituted Furans From 1,2-Dioxines Generated by An Enyne-RCM / Diels-Alder Reaction Sequence

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CONTENTS

General Methods: THF and ether were distilled from sodium benzophenone ketyl under nitrogen just prior to use. For CH_2Cl_2, toluene, and benzene, the drying agent was calcium hydride. All reactions were performed under a N_2 atmosphere. All chromatographic purifications were performed on silica-gel (230-400 mesh) using the indicated solvent systems. All recorded melting points are uncorrected. IR spectra were recorded as a thin film. NMR spectra were recorded with reference to TMS as an internal standard. The organic extracts were dried over anhydrous $MgSO_4$.

1,2-Dioxines (**5a**–**c** and **5'd**) were synthesized starting from the corresponding acyclic enynes according to the published procedure.[1]

General procedure for the $FeSO_4$-catalyzed cleavage of O-O bonds: A THF-H_2O (1:1) solution (1 mL) of **5'd** (45 mg, 0.17 mmol) was treated with $FeSO_4 \cdot 7H_2O$ (72 mg, 0.26 mmol) at rt. After 5 h, the reaction solution was quenched with water (5 mL) and extracted with EtOAc (5 mL x 3). The combined organic layers were dried over anhydrous $MgSO_4$, removed under reduced pressure, and the residue was column chromatographed on silica gel (elution with 10% ethyl acetate in hexanes) to give 11 mg (26%) of **7'd** and 13 mg (30%) of **9'd**.

General procedure for the reductive cleavage of 1,2-dioxines: To a CH_2Cl_2 (1.5 mL) solution of **5b** (50 mg, 0.193 mmol) and zinc dust (50 mg , 0.78 mmol) was added acetic acid (0.02 mL) in CH_2Cl_2 (0.5 mL) at room temperature. The reaction mixture was stirred for two hours then filtered through celite pad and the solvent was concentrated under reduced pressure. The residue was column chromatographed on silica gel (EtOAc/MeOH = 1:1) to give **10b** (40 mg, 78%) and **7b** (7 mg, 15%) as colorless oil.

General procedures for the oxidations of the allylic diols:

Condition A (TPAP/NMO): To **10b** (300 mg, 1.16 mmol) in 10% acetonitrile-CH_2Cl_2 (6 ml) were added TPAP (33 mg, 0.093 mmol), 4-methylmorpholine *N*-oxide (339 mg, 2.90 mmol) and 4 Å molecular sieves (340 mg). The reaction mixture was stirred for 10 hr at room temperature. The solvent was removed under reduced pressure and the residue was column chromatographed on silica gel (elution with 20% ethyl acetate in hexanes) to afford 75 mg (27%) of **7b** as a colorless oil and 141 mg (54%) of **11b** as a colorless solid.

Condition B (PCC): The diol **10c** (500 mg, 1.83 mmol) in CH_2Cl_2 (4 mL) was treated with pyridinium chlorochromate (789 mg, 3.66 mmol) and 4 Å molecular sieves

(790 mg). The reaction mixture was stirred for 2 hr at room temperature. The solvent was removed under reduced pressure and the residue was column chromatographed on silica gel (elution with 10% ethyl acetate in hexanes) to give 426 mg (92%) of **7c** as a colorless oil.

Condition C (IBX, EtOAc): A EtOAc (2 mL) solution of **10a** (40 mg, 0.16 mmol) and IBX (135 mg, 0.48 mmol) was refluxed for 6 hr. The reaction mixture was loaded on silica gel and column chromatographed (elution with 20% ethyl acetate in hexanes) to give 29 mg (80%) of **7a** and 2 mg (5%) of **11a** as colorless solids.

Condition D (IBX, DMSO): A DMSO (2 mL) solution of **10a** (30 mg, 0.12 mmol) and IBX (101 mg, 0.36 mmol) was heated at 50 ^{o}C for 8 hr. The reaction solution was quenched with water (5 mL) and extracted with CH_2Cl_2 (5 mL x 3). The combined organic layers were dried over anhydrous $MgSO_4$, removed under reduced pressure, and the residue was column chromatographed on silica gel (elution with 10% ethyl acetate in hexanes) to give 11 mg (41%) of **7a** and 5 mg (15%) of **11a**.

Condition E (Pyr-SO_3, DMSO): A mixture of **10a** (20 mg, 0.08 mmol), Pyr-SO_3 (50%, 51 mg, 0.32 mmol), DMSO (50 mg, 0.64 mmol), and Et_3N (0.12 mL, 0.86 mmol) in CH_2Cl_2 (4 mL) was stirred for 10 hr at rt. The reaction solution was quenched with saturated NH_4Cl (5 mL) and extracted with CH_2Cl_2 (5 mL x 3). The combined organic layers were dried over anhydrous $MgSO_4$, removed under reduced pressure, and the residue was column chromatographed on silica gel (elution with 10% ethyl acetate in hexanes) to give 13 mg (64%) of **7a**.

4,7-Dihydro-1,5-dioxa-6-aza-indene-6-carboxylic acid *tert*-butyl ester (7a): colorless solids; R_f= 0.8 (silica gel, hexane/EtOAc = 1:1); mp 70-72 ^{o}C; ^{1}H NMR (250 MHz, $CDCl_3$) δ = 7.34-7.33 (m, 1H), 6.27-6.26 (m, 1H), 4.87 (s, 2H), 4.64 (s, 2H), 1.51 (s, 9H); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ = 155.3, 145.3, 142.3, 115.3, 107.8, 82.6, 68.1, 45.5, 28.7; IR (film, cm^{-1}) 2976, 2930, 2868, 2361, 1711, 1363, 1317, 1245, 1158, 1066, 1030; HRMS: *m/z* calcd. for $C_{11}H_{16}NO_4$ $(M+H)^+$: 226.1079; found: 226.1080.

7,8-Dihydro-4*H*-1,5-dioxa-6-aza-azulene-6-carboxylic acid *tert*-butyl ester (7b): colorless oil; R_f= 0.7 (silica gel, hexane/EtOAc = 2:1); ^{1}H NMR (250 MHz, $CDCl_3$) δ = 7.26-7.25 (m, 1H), 6.17-6.16 (m, 1H), 4.83 (s, 2H), 3.89 (t, *J* = 6.0 Hz, 2H), 3.00 (t, *J* = 6.0 Hz, 2H), 1.51 (s, 9H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ = 154.5, 150.0, 140.4, 118.6, 109.6, 81.4, 70.4, 47.4, 28.4, 28.0; IR (film, cm^{-1}) 2930, 2858, 1726, 1696, 1399, 1368,

1281, 1230, 1173, 1107; HRMS: *m/z* calcd. for $C_{12}H_{18}NO_4$ $(M+H)^+$: 240.1236; found: 240.1233.

4,7,8,9-Tetrahydro-1,5-dioxa-6-aza-cyclopentacyclooctene-6-carboxylic acid *tert*-butyl ester (7c): colorless oil; R_f= 0.8 (silica gel, hexane/EtOAc = 2:1); ^{1}H NMR (250 MHz, $CDCl_3$) δ = 7.16 (s, 1H), 6.11 (s, 1H), 4.75 (s, 2H), 3.45 (t, *J* = 5.2 Hz, 2H), 2.79 (t, *J* = 5.8 Hz, 2H), 1.83- 1.73 (m, 2H), 1.42 (s, 9H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ = 156.3, 152.2, 139.9, 116.3, 110.9, 81.2, 69.5, 50.6, 28.2, 26.6, 24.7; IR (film, cm^{-1}) 2976, 2930, 2863, 1716, 1455, 1404, 1363, 1281, 1250, 1158, 1112; HRMS: *m/z* calcd. for $C_{13}H_{20}NO_4$ $(M+H)^+$: 254.1392; found: 254.1391.

3-Methyl-4,7-dihydro-1,6-dioxa-5-aza-indene-5-carboxylic acid *tert*-butyl ester (7'd): colorless solids; R_f= 0.8 (silica gel, hexane/EtOAc = 2:1); mp 68-70 ^{o}C; ^{1}H NMR (250 MHz, $CDCl_3$) δ = 7.11 (s, 1H), 4.85 (s, 2H), 4.47 (s, 2H), 1.96 (s, 3H), 1.51 (s, 9H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ = 154.8, 145.9, 138.5, 117.9, 114.5, 82.0, 67.1, 43.2, 28.3, 7.9; IR (film, cm^{-1}) 2976, 2915, 2863, 2356, 2336, 1711, 1685, 1368, 1219, 1153, 1096, 1086; HRMS: *m/z* calcd. for $C_{12}H_{18}NO_4$ $(M+H)^+$: 240.1236; found: 240.1234.

2-Hydroxy-2,4,7,7a-tetrahydro-1,5-dioxa-6-aza-indene-6-carboxylic acid tert-butyl ester (9a): colorless oil; R_f = 0.1 (silica gel, hexane/EtOAc = 2:1); ^{1}H NMR (250 MHz, $CDCl_3$) δ = 6.18-6.14 (m, 1H), 5.82-5.73 (m, 1H), 4.81 (bs, 1H), 4.65-4.46 (m, 4H), 3.24-2.92 (m, 1H), 1.50 (s, 9H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ = 154.5, 140.2, 121.8, 102.8, 82.5, 76.2, 69.2, 54.5, 28.2; IR (film, cm^{-1}) 3415, 2984, 2926, 2864, 2360, 2248, 1705, 1478, 1451, 1370, 1232,1158, 1089; ESI-MS *m/z* 266 ($(M+Na)^+$). Anal. Calcd for $C_{11}H_{17}NO_5$: C, 54.31; H, 7.04. Found: C, 54.35; H, 7.02.

2-Hydroxy-3-methyl-2,4,7,7a-tetrahydro-1,6-dioxa-5-aza-indene-5-carboxylic acid *tert*-butyl ester (9'd): colorless oil; R_f = 0.1(silica gel, hexane / EtOAc = 2 : 1); ^{1}H NMR (250 MHz, $CDCl_3$) δ= 5.96-5.85 (m, 1H), 4.95 (bs, 1H), 4.80-4.75 (m, 1H), 4.40-4.30 (m, 1H), 3.90-3.83 (m, 1H), 3.63-3.29 (m, 1H), 3.05-3.02 (m, 1H), 1.82 (s, 3H), 1.49 (s, 9H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ = 155.0, 130.3, 129.4, 105.8, 82.5, 78.3, 77.0, 45.8, 28.3, 9.8; IR (film, cm^{-1}) 3415, 2976, 2926, 2876, 2360, 1728, 1709, 1482, 1455, 1370, 1251, 1162, 1131, 1062, 1031; ESI-MS *m/z* 280 ($(M+Na)^+$). Anal. Calcd for $C_{12}H_{19}NO_5$: C, 56.02; H, 7.44. Found: C, 56.11; H, 7.54.

4-Hydroxy-5-(2-hydroxy-ethylidene)-[1,2]oxazinane-2-carboxylic acid *tert*-butyl ester (10a): colorless oil; R_f= 0.1 (silica gel, hexane/EtOAc = 1:1); ^{1}H NMR (250 MHz,

$CDCl_3$) δ = 5.54 (s, 1H), 4.64 (d, *J* = 12.4 Hz, 1H), 4.52-4.51 (m, 1H), 4.35 (bs, 2H), 4.20-4.17 (m, 1H),4.07-3.92 (m, 4H), 3.40 (d, *J* = 13.9 Hz, 1H), 1.40 (s, 9H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ = 155.9, 135.2, 127.2, 82.0, 72.8, 62.1, 56.8, 52.8, 28.2; IR (film, cm^{-1}) 3406 (br), 2981, 2930, 1696, 1429, 1293, 1368, 1255, 1163, 1112, 1015; HRMS *m/z* calcd. for $C_{11}H_{20}NO_5$ $(M+H)^+$: 246.1341; found: 246.1341.

5-Hydroxy-6-(2-hydroxy-ethylidene)-[1,2]oxazepane-2-carboxylic acid *tert*-butyl ester (10b): colorless oil; R_f= 0.1 (silica gel, hexane/EtOAc = 1:1); ^{1}H NMR (250 MHz, $CDCl_3$) δ = 5.54 (t, *J* = 6.0 Hz, 1H), 4.83 (d, *J* = 4.4 Hz, 1H), 4.60 (d, *J* = 12.2 Hz, 1H), 4.29 (d, *J* = 12.3 Hz, 1H), 4.23-4.15 (m, 2H), 3.74-3.56 (m, 4H), 1.97-1.92 (m, 1H), 1.81-1.77 (m, 1H), 1.44 (s, 9H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ = 155.2, 140.5, 129.5, 81.5, 77.1, 68.6, 57.9, 45.2, 35.2, 28.3; IR (film, cm^{-1}) 3421 (br), 2981, 2930, 2879, 1696, 1486, 1450, 1393, 1363, 1301, 1245, 1163, 1117, 1066; HRMS *m/z* calcd. for $C_{12}H_{22}NO_5$ $(M+H)^+$: 260.1498; found: 260.1499.

6-Hydroxy-7-(2-hydroxy-ethylidene)-[1,2]oxazocane-2-carboxylic acid *tert*-butyl ester (10c): colorless oil; R_f= 0.2 (silica gel, hexane/EtOAc = 1:1); ^{1}H NMR (250 MHz, $CDCl_3$) δ = 5.62 (t, *J* = 6.2 Hz, 1H), 4.56-4.48 (m, 2H), 4.23-4.02 (m, 5H), 3.60-3.55 (m, 1H), 3.04 (t, *J* = 10.3 Hz, 1H), 1.95-1.89 (m, 2H), 1.72-1.64 (m, 1H), 1.39 (s, 9H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ = 156.5, 138.8, 134.7, 81.5, 75.9, 68.3, 57.6, 49.4, 33.6, 28.3, 21.7; IR (film, cm^{-1}) 3437 (br), 2991, 2935, 2868, 2254, 1696, 1450, 1404, 1260, 1158, 1112, 1025; HRMS *m/z* calcd. for $C_{13}H_{24}NO_5$ $(M+H)^+$: 274.1654; found: 274.1655.

5-Hydroxy-4-(2-hydroxy-1-methyl-ethylidene)-[1,2]oxazinane-2-carboxylic acid *tert*-butyl ester (10'd): colorless oil; R_f= 0.1 (silica gel, hexane/EtOAc = 1:1); ^{1}H NMR (250 MHz, $CDCl_3$) δ = 4.53-4.46 (m, 2H), 4.24 (d, *J* = 11.8 Hz, 1H), 4.01-3.90 (m, 2H), 3.82-3.78 (m, 2H), 1.69 (s, 3H), 1.33 (s, 9H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ = 155.1, 133.4, 127.0, 82.0, 75.5, 62.9, 61.4, 45.4, 28.1, 16.0; IR (film, cm^{-1}) 3386 (br), 2976, 2925, 2361, 2336, 1701, 1440, 1394, 1363, 1240, 1153, 1076, 1107, 1004; HRMS *m/z* calcd. for $C_{12}H_{22}NO_5$ $(M+H)^+$: 260.1498; found: 260.1494.

2-Oxo-2,6,7,7a-tetrahydro-4*H*-furo[3,2-c]pyran-6-carboxylic acid *tert*-butyl ester (11a): colorless solids; R_f= 0.6 (silica gel, hexane/EtOAc = 1:1); mp 121-123 ^{o}C; ^{1}H NMR (250 MHz, $CDCl_3$) δ = 6.05 (s, 1H), 4.93-4.66 (m, 4H), 3.14 (dd, *J* = 12.4, 9.8 Hz, 1H), 1.51 (s, 9H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ = 171.4, 162.4, 153.8, 115.7, 83.4, 74.5, 68.7, 53.6, 28.2; IR (film, cm^{-1}) 2981, 2940, 2366, 2336, 1788, 1757, 1726,

1450, 1373, 1327, 1240, 1153; HRMS: *m/z* calcd. for $C_{11}H_{16}NO_5$ $(M+H)^+$: 242.1028; found: 242.1023.

2-Oxo-2,7,8,8a-tetrahydro-4*H*-1,5-dioxa-6-aza-azulene-6-carboxylic acid *tert*-butyl ester (11b): colorless solids; R_f= 0.4 (silica gel, hexane/EtOAc = 1:1); mp 107-109 ^oC; ^1H NMR (250 MHz, $CDCl_3$) δ = 5.89 (s, 1H), 5.30-5.24 (m, 1H), 5.08-5.00 (m, 1H), 4.90-4.83 (m, 1H), 4.18-4.11 (m, 1H), 3.38-3.27 (m, 1H), 2.53-2.46 (m, 1H), 1.72-1.65 (m, 1H), 1.47 (s, 9H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ = 171.7, 171.1, 155.2, 115.3, 82.9, 82.5, 71.3, 46.6, 34.6, 28.2; IR (film, cm^{-1}) 2976, 2930, 1757, 1706, 1399, 1363, 1301, 1245, 1173, 1153, 1122, 1081, 1020; HRMS: *m/z* calcd. for $C_{12}H_{18}NO_5$ $(M+H)^+$: 256.1185; found: 256.1189.

2-Oxo-2,4,7,8,9,9a-hexahydro-1,5-dioxa-6-aza-cyclopentacyclooctene-6-carboxylic acid *tert*-butyl ester (11c): colorless solids; R_f= 0.2 (silica gel, hexane/EtOAc = 2:1); mp 100-102 ^oC; ^1H NMR (250 MHz, $CDCl_3$) δ = 6.08 (s, 1H), 5.17 (bs, 1H), 5.01 (d, *J* = 13.8 Hz, 1H), 4.50 (d, *J* = 13.7 Hz, 1H), 3.84-3.77 (m, 1H), 3.04-3.00 (m, 1H), 2.28-2.21 (m, 2H), 1.70-1.60 (m, 2H), 1.48 (s, 9H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ = 171.7, 166.1, 156.9, 122.5, 83.2, 82.4, 68.7, 50.0, 30.2, 28.3, 20.6; IR (film, cm^{-1}) 2976, 2925, 1757, 1706, 1450, 1363, 1265, 1168, 1107; HRMS: *m/z* calcd. for $C_{13}H_{20}NO_5$ $(M+H)^+$: 270.1341; found: 270.1337.

3-Methyl-2-oxo-2,4,7,7a-tetrahydro-1,6-dioxa-5-aza-indene-5-carboxylic acid *tert*-butyl ester (11'd): colorless oil; R_f= 0.3 (silica gel, hexane/EtOAc = 2:1); ^1H NMR (250 MHz, $CDCl_3$) δ = 5.01-4.93 (m, 2H), 4.60-4.52 (m, 1H), 4.05 (d, *J* = 14.4 Hz, 1H), 3.55 (t, *J* = 10.5 Hz, 1H), 1.91 (s, 3H), 1.47 (s, 9H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ = 173.2, 154.3, 152.4, 122.8, 83.3, 75.7, 74.2, 46.4, 28.1, 8.7; IR (film, cm^{-1}) 2976, 2930, 2382, 1762, 1731, 1716, 1696, 1455, 1373, 1342, 1240, 1153, 1086, 1030; HRMS : *m/z* calcd. for $C_{12}H_{18}NO_5$ $(M+H)^+$: 256.1185; found: 256.1185.

2-[4-(*tert*-Butyl-dimethyl-silanyloxy)-but-2-ynyloxy]-isoindole-1,3-dione (13): To a CH_2Cl_2 (20 mL) solution of **12** (2.00g, 10.0 mmol), PPh_3 (3.97 g, 15.0 mmol), and *N*-hydroxyphthalimide (1.78 g, 12.0 mmol) was added DIAD (2.95 mL, 15.0 mmol) at 0 °C. After 30 min, the cooling bath was removed and the reaction mixture was stirred for 5 hr at room temperature. The solvent was removed under reduced pressure and the residue was column chromatographed on silica gel (elution with 10% ethyl acetate in hexanes) to afford 3.10 g (89%) of **13** as a colorless solid: R_f = 0.5 (silica gel, hexane / EtOAc = 3 : 1); mp 32-34 ^oC; ^1H NMR (250 MHz, $CDCl_3$) δ = 7.78-7.73 (m, 4H), 4.85-4.83 (m, 2H), 4.25-4.24 (m, 2H), 0.75 (s, 9H), -0.04 (s, 6H); ^{13}C NMR (62.9 MHz,

$CDCl_3$) δ = 163.3, 134.6, 128.7, 123.6, 88.7, 77.4, 65.3, 51.6, 25.7, 18.1, -5.4; IR (film, cm^{-1}) 2953, 2929, 2887, 2856, 1794, 1732, 1613, 1578, 1470, 1374, 1328, 1255, 1189, 1143, 1085, 1016; HRMS: *m/z* calcd. for $C_{18}H_{24}NO_4Si$ $(M+H)^+$: 346.1475; found: 346.1474.

***O*-[4-(*tert*-Butyl-dimethyl-silanyloxy)-but-2-ynyl]-hydroxylamine-*N*-carboxylic acid *tert*-butyl ester (14):** To a CH_2Cl_2 (30 mL) solution of **13** (2.00g, 5.79 mmol) was added $NH_2NH_2{\cdot}H_2O$ (1.40 mL, 29.0 mmol) at 0 °C. After 10 min, the cooling bath was removed and the reaction mixture was stirred for 2 hr at room temperature. The reaction mixture was diluted with 5 % Na_2CO_3 (30 mL), extracted with EtOAc (30 mL x 3). The combined organic layers were dried over anhydrous $MgSO_4$, removed under reduced pressure to afford 1.20 g (96%) of the hydroxylamine. To the hydroxylamine (1.75 g, 8.13 mmol) in 1,4-dioxane (14 mL) and 1 N Na_2CO_3 (14 mL) was added $(Boc)_2O$ (2.71 g, 12.0 mmol) at 0 °C. After 10 min, the cooling bath was removed and the reaction mixture was stirred for 8 hr at room temperature. The reaction mixture was diluted with saturated NH_4Cl (30 mL), extracted with CH_2Cl_2 (30 mL x 3). The combined organic layers were dried over anhydrous $MgSO_4$, removed under reduced pressure, and the residue was column chromatographed on silica gel (elution with 15% ethyl acetate in hexanes) to give 2.41 g (94%) of **7a** as a colorless solid; R_f = 0.5 (silica gel, hexane / EtOAc = 3 : 1); mp 34-36 ^oC; ^1H NMR (250 MHz, $CDCl_3$) δ = 7.47 (s, 1H), 4.47-4.46 (m, 2H), 4.33-4.31 (m, 2H), 1.44 (s, 9H), 0.86 (s, 9H), 0.08 (s, 6H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ = 156.4, 86.2, 82.0, 79.3, 64.0, 51.7, 28.2, 25.8, 18.3, -5.1; IR (film, cm^{-1}) 3280, 2957, 2926, 2891, 2856, 1817, 1751, 1728, 1470, 1397, 1366, 1251, 1174, 1135, 1089, 1008; HRMS: *m/z* calcd. for $C_{15}H_{30}NO_4Si$ $(M+H)^+$: 316.1944; found: 316.1942.

***N*-Allyl-*O*-[4-(tert-butyl-dimethyl-silanyloxy)-but-2-ynyl]-*N*-carboxylic acid *tert*-butyl ester (15a):** A solution of **14** (3.00 g, 12.0 mmol), allyl bromide (1.24 mL, 14.0 mmol), and catalytic amount of *n*-Bu_4NI (20 mg) in THF (30 mL) was treated with 60% NaH (490 mg, 12.0 mmol) at 0 ^oC. The solution was stirred for 10 hr at 25 ^oC and quenched with saturated NH_4Cl (50 mL). It was extracted with EtOAc (50 mL x 3). The combined organic phases were dried and removed under reduced pressure. The residue was column chromatographed on silica gel (elution with 10% ethyl acetate in hexanes) to give 2.91 g (86 %) of **15a** a colorless oil; R_f = 0.6 (silica gel, hexane / EtOAc = 8 : 1); ^1H NMR (250 MHz, $CDCl_3$) δ= 5.85-5.79 (m, 1H), 5.22-5.12 (m, 2H), 4.47-4.46 (m, 2H), 4.32-4.30 (m, 2H), 4.07-4.04 (m, 2H), 1.44 (s, 9H), 0.86 (s, 9H), 0.07 (s, 6H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ = 156.6, 132.3, 118.1, 85.8, 81.7, 79.7, 62.8, 53.6, 51.8, 28.2, 25.8, 18.3, -5.2; IR (film, cm^{-1}) 3076, 2953, 2926, 2895, 2856, 2706, 2360, 1736,

1713, 1644, 1474, 1432, 1366, 1255, 1143, 1081; HRMS: *m/z* calcd. for $C_{18}H_{34}NO_4Si$ $(M+H)^+$: 356.2257; found: 356.2264.

***N*-But-3-enyl-*O*-[4-(*tert*-butyl-dimethyl-silanyloxy)-but-2-ynyl]-*N*-carboxylic acid *tert*-butyl ester (15b): 15b** was prepared in 63% as a colorless oil; R_f = 0.6 (silica gel, hexane / EtOAc = 5 : 1); ^{1}H NMR (250 MHz, $CDCl_3$) δ = 5.79-5.68 (m, 1H), 5.09-4.96 (m, 2H), 4.47-4.46 (m, 2H), 4.32-4.30 (m, 2H), 3.53 (t, *J* = 8.5 Hz, 2H), 2.38-2.33 (m, 2H), 1.44 (s, 9H), 0.86 (s, 9H), 0.07 (s, 6H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ = 156.5, 135.2, 116.8, 85.9, 81.5, 79.6, 62.6, 51.7, 49.9, 31.2, 28.2, 25.8, 18.3, -5.2; IR (film, cm^{-1}) 3079, 2955, 2931, 2859, 1710, 1642, 1472, 1460, 1368, 1255, 1141, 1085, 1002; HRMS : *m/z* calcd. for $C_{19}H_{36}NO_4Si$ $(M+H)^+$: 370.2414; found: 370.2404.

5-[1-(*tert*-Butyl-dimethyl-silanyloxymethyl)-vinyl]-3,6-dihydro-[1,2]oxazine-2-carboxylic acid *tert*-butyl ester (16a): A solution of **15a** (1.00 g, 2.81 mmol) and 1st generation Grubbs' catalyst (50 mg, 0.060 mmol) in CH_2Cl_2 (140 mL) was refluxed at 45 ^{o}C for 16 hr under N_2. The solvent was removed under reduced pressure and the residue mixture was column chromatographed on silica gel (hexane / EtOAc = 20:1) to give 950 mg (95%) of **16a** as a colorless oil; R_f = 0.5 (silica gel, hexane / EtOAc = 8 : 1); ^{1}H NMR (250 MHz, $CDCl_3$) δ = 5.80 (s, 1H), 5.21 (s, 1H), 4.87 (s, 1H), 4.52-4.51 (m, 2H), 4.27 (s, 2H), 4.10-4.09 (m, 2H), 1.44 (s, 9H), 0.86 (s, 9H), 0.01 (s, 6H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ = 154.8, 142.1, 132.1, 118.0, 109.8, 81.6, 68.5, 63.3, 44.7, 28.2, 25.8, 18.2, -5.4; IR (film, cm^{-1}) 2954, 2927, 2891, 2855, 2360, 2341, 1735, 1695, 1477, 1461, 1394, 1366, 1251, 1168, 1101; ESI-MS *m/z* 378 ($(M+Na)^+$). Anal. Calcd for $C_{18}H_{33}NO_4Si$: C, 60.81; H, 9.36. Found: C, 60.88; H, 9.31.

6-[1-(*tert*-Butyl-dimethyl-silanyloxymethyl)-vinyl]-4,7-dihydro-3H-[1,2]oxazepine-2-carboxylic acid *tert*-butyl ester (16b): 16b was prepared in 93% as a colorless oil; R_f = 0.5 (silica gel, hexane / EtOAc = 5 : 1); ^{1}H NMR (250 MHz, $CDCl_3$) δ = 5.84 (t, *J* = 6.8 Hz, 1H), 5.20 (s, 1H), 4.87 (s, 1H), 4.76 (s, 2H), 4.24 (s, 2H), 3.68 (t, *J* = 6.4Hz, 2H), 2.56-2.48 (m, 2H), 1.47 (s, 9H), 0.88 (s, 9H), 0.05 (s, 6H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ = 155.3, 143.9, 135.9, 122.8, 110.1, 81.0, 76.6, 63.8, 50.6, 28.4, 25.9, 23.4, 18.3, -5.4; IR (film, cm^{-1}) 2931, 2858, 1727, 1701, 1470, 1390, 1367, 1254, 1173, 1118; HRMS : *m/z* calcd. for $C_{19}H_{36}NO_4Si$ $(M+H)^+$: 370.2414; found: 370.2400.

4-(*tert*-Butyl-dimethyl-silanyloxymethyl)-3,5,8,8a-tetrahydro-1,2,6-trioxa-7-aza-naphthalene-7-carboxylic acid *tert*-butyl ester (17a): A 5% MeOH-CH_2Cl_2 solution (12 mL) of **16a** (30 mg, 0.080 mmol) and a catalytic amount of rose Bengal bengal sensitizer (5 mg) was irradiated using a 400-W tungsten lamp while a steady flow of

oxygen was passed though the solution. The reaction flask was cooled in an ice-bath during this procedure. After 6 h, the solvent was removed under reduced pressure and the residue mixture was column chromatographed on silica gel (elution with 5% ethyl acetate in hexanes) to give 22 mg (66%) of **17a** as a colorless oil; R_f = 0.4 (silica gel, hexane / EtOAc = 5 : 1); ^{1}H NMR (250 MHz, $CDCl_3$) δ = 4.85-4.73 (m, 3H), 4.48 (d, *J* = 16.9, 1H), 4.30-4.22 (m, 4H), 3.01 (dd, *J* = 12.6, 10.5 Hz, 1H), 1.49 (s, 9H), 0.87 (s, 9H), 0.05 (s, 6H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ = 154.4, 130.9, 125.4, 82.4, 72.1, 70.9, 67.0, 58.8, 48.4, 28.2, 25.7, 18.2, -5.4; IR (film, cm^{-1}) 2954, 2931, 2883, 2859, 1739, 1707, 1465, 1370, 1327, 1259, 1224, 1164, 1109, 1073; HRMS: *m/z* calcd. for $C_{18}H_{34}NO_6Si$ $(M+H)^+$: 388.2155; found: 388.2154.

4-(*tert*-Butyl-dimethyl-silanyloxymethyl)-3,8,9,9a-tetrahydro-5H-1,2,6-trioxa-7-aza-benzocycloheptene-7-carboxylic acid *tert*-butyl ester (17b): 17b was prepared in 42% as a colorless oil; R_f = 0.5 (silica gel, hexane / EtOAc = 5 : 1); ^{1}H NMR (250 MHz, $CDCl_3$) δ = 4.84-4.78 (m, 1H), 4.63-4.58 (m, 2H), 4.50-4.43 (m, 2H), 4.25-4.15 (m, 1H), 4.11-4.02 (m, 2H), 3.26 - 3.10 (m, 1H), 2.38- 2.21 (m, 1H), 2.15-2.07 (m, 1H), 1.49 (s, 9H), 0.88 (s, 9H), 0.05 (s, 6H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ = 155.8, 130.7, 130.2, 81.9, 77.7, 71.3, 70.0, 59.0, 46.2, 34.1, 28.4, 25.9, 18.4, -5.3; IR (film, cm^{-1}) ; 2960, 2930, 2887, 2856, 2560, 2394, 2352, 2210, 1709, 1667, 1540, 1474, 1393, 1362, 1289, 1255, 1162, 1112, 1070, 1004; HRMS : *m/z* calcd. for $C_{19}H_{36}NO_6Si$ $(M+H)^+$: 402.2312; found: 402.2307.

3-(*tert*-Butyl-dimethyl-silanyloxymethyl)-4,7-dihydro-1,5-dioxa-6-aza-indene-6-carboxylic acid *tert*-butyl ester (18a): colorless oil; R_f = 0.8 (silica gel, hexane / EtOAc = 5 : 1); ^{1}H NMR (250 MHz, $CDCl_3$) δ = 7.20 (s, 1H), 4.91-4.90 (m, 2H), 4.60 (s, 2H), 4.52 (s, 2H), 1.5 (s, 9H), 0.89 (s, 9H), 0.05 (s, 6H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ = 154.9, 145.5, 137.8, 123.2, 115.1, 82.1, 67.3, 56.5, 45.0, 28.3, 25.8, 18.2, -5.4; IR (film, cm^{-1}) 2962, 2927, 2851, 2360, 2345, 1703, 1549, 1469, 1366, 1263, 1160, 1069; ESI-MS *m/z* 369 (M^+). Anal. Calcd for $C_{18}H_{31}NO_5Si$: C, 58.51; H, 8.46. Found: C, 58.55; H, 8.45.

3-(*tert*-Butyl-dimethyl-silanyloxymethyl)-7,8-dihydro-4H-1,5-dioxa-6-aza-azulene-6-carboxylic acid *tert*-butyl ester (18b): colorless oil; R_f = 0.6 (silica gel, hexane / EtOAc = 5 : 1); ^{1}H NMR (250 MHz, $CDCl_3$) δ = 7.16 (s.1H), 4.87 (s, 2H), 4.46 (s, 2H), 3.88 (t, *J* = 6.1Hz, 2H), 2.98 (t, *J* = 6.0Hz, 2H), 1.51 (s, 9H), 0.88 (s, 9H), 0.07 (s, 6H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ = 154.5, 150.6, 137.1, 124.2, 118.5, 81.4, 69.6, 56.3, 47.3, 28.4, 28.0, 25.9, 18.4, -5.4; IR (film, cm^{-1}) 2958, 2923, 2855, 1731, 1699,

1691, 1457, 1382, 1255, 1164, 1109, 1069, 1042; ESI-MS *m/z* 406 ($(M+Na)^+$). Anal. Calcd for $C_{19}H_{33}NO_5Si$: C, 59.50; H, 8.67. Found: C, 59.56; H, 8.62.

5-[1-(*tert*-Butyl-dimethyl-silanyloxymethyl)-2-hydroxy-ethylidene]-4-hydroxy-[1,2]oxazinane-2-carboxylic acid *tert*-butyl ester (19a): colorless oil; R_f = 0.1 (silica gel, hexane / EtOAc = 5 : 1); ^{1}H NMR (250 MHz, $CDCl_3$) δ = 4.74-4.68 (m, 2H), 4.56-4.50 (m, 1H), 4.37-4.11 (m, 5H), 3.53-3.46 (m, 1H), 3.38 (bs, 1H), 3.08 (bs, 1H), 1.48 (s, 9H), 0.88 (s, 9H), 0.07 (s, 6H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ = 155.9, 135.7, 131.7, 81.9, 67.0, 62.6, 61.2, 59.4, 53.0, 28.2, 25.8, 18.2, -5.4; IR (film, cm^{-1}) 3410, 2958, 2935, 2887, 2855, 1699, 1469, 1438, 1390, 1370, 1255, 1156, 1101, 1061, 1002; ESI-MS *m/z* 412 ($(M+Na)^+$). Anal. Calcd for $C_{18}H_{35}NO_6Si$: C, 55.50; H, 9.06. Found: C, 55.52; H, 9.08.

6-[1-(*tert*-Butyl-dimethyl-silanyloxymethyl)-2-hydroxy-ethylidene]-5-hydroxy-[1,2]oxazepane-2-carboxylic acid *tert*-butyl ester (19b): colorless oil; R_f = 0.1 (silica gel, hexane / EtOAc = 1 : 1); ^{1}H NMR (250 MHz, $CDCl_3$) δ = 5.04 (s. 1H), 4.80 (d, *J* = 14.2 Hz, 1H), 4.59 (d, *J* = 14.2 Hz, 1H), 4.30-4.13 (m, 4H), 3.94-3.89 (m, 1H), 3.45-3.44 (m, 1H), 3.04 (bs, 1H), 2.66 (bs, 1H), 2.07-2.03 (m, 1H), 1.90-1.85 (m, 1H), 1.46 (s, 9H), 0.88 (s, 9H), 0.07 (s, 6H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ = 155.7, 137.0, 135.7, 81.8, 72.4, 69.6, 62.0, 60.4, 44.8, 35.2, 28.4, 25.9, 18.3, -5.3; IR (film, cm^{-1}) 3419, 2953, 2930, 2856, 2510, 2394, 2364, 2240, 1701, 1474, 1459, 1397, 1366, 1251, 1166, 1120, 1070, 1004; HRMS : *m/z* calcd. for $C_{19}H_{38}NO_6Si$ $(M+H)^+$: 404.2468; found: 404.2476.

3-(*tert*-Butyl-dimethyl-silanyloxymethyl)-2-oxo-2,4,7,7a-tetrahydro-1,5-dioxa-6-aza-indene-6-carboxylic acid *tert*-butyl ester (20a): colorless solid; R_f = 0.5 (silica gel, hexane / EtOAc = 3 :1); mp 39-41 ^{o}C; ^{1}H NMR (250 MHz, $CDCl_3$) δ = 5.36 (d, *J* = 13.0 Hz, 1H), 4.80-4.53 (m, 5H), 3.14 (dd, *J* = 10.9Hz, 1H), 1.50 (s, 9H), 0.88 (s, 9H), 0.08 (s, 6H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ = 171.1, 155.0, 153.0, 126.7, 83.1, 73.4, 67.8, 58.8, 53.2, 28.2, 25.8, 18.2, -5.6; IR (film, cm^{-1}) 2958, 2931, 2859, 1766, 1727, 1699, 1477, 1457, 1374, 1259, 1152, 1101, 1038; HRMS : *m/z* calcd. for $C_{18}H_{32}NO_6Si$ $(M+H)^+$: 386.1999; found: 386.1995.

3-(*tert*-Butyl-dimethyl-silanyloxymethyl)-2-oxo-2,7,8,8a-tetrahydro-4H-1,5-dioxa-6-aza-azulene-6-carboxylic acid *tert*-butyl ester (20b): colorless solid; R_f = 0.1 (silica gel, hexane / EtOAc = 5 : 1); mp 39-41 ^{o}C; ^{1}H NMR (250 MHz, $CDCl_3$) δ = 5.28-5.20 (m, 2H), 5.00-4.90 (m, 1H), 4.48 (s, 2H), 4.24-4.18 (m, 1H), 3.34-3.24 (m, 1H), 2.50-2.45 (m, 1H), 1.72-1.58 (m, 1H), 1.49 (s, 9H), 0.91 (s, 9H), 0.09 (s, 6H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ = 171.3, 164.0, 155.5, 126.3, 82.3, 81.9, 72.1, 58.7, 46.5,

34.8, 28.3, 26.0, 18.3, -5.5; IR (film, cm^{-1}) 2953, 2926, 2853, 1759, 1709, 1594, 1470, 1397, 1366, 1247, 1162, 1093, 1050, 1031; HRMS : *m/z* calcd. for $C_{19}H_{34}NO_6Si$ $(M+H)^+$: 400.2164; found: 400.2164.

General procedure for the cleavage of N-O bonds: To a solution of **7a** (10 mg, 0.04 mmol) in CH_3CN-H_2O (4:1, 2 mL) were added $Mo(CO)_6$ (2 mg, 0.008 mmol) and $NaBH_4$ (2 mg, 0.053 mmol). The reaction solution was heated at 85 ^oC for 2 hr, quenched with water (5 mL) and extracted with EtOAc (5 mL x 3). The combined organic layers were dried over anhydrous $MgSO_4$, removed under reduced pressure, and the residue was column chromatographed on silica gel (elution with 10% ethyl acetate in hexanes) to give 10 mg (98%) of **21a** a colorless oil.

(3-Hydroxymethyl-furan-2-ylmethyl)-carbamic acid *tert*-butyl ester (21a): colorless oil; R_f = 0.2 (silica gel, hexane / EtOAc = 2 : 1); ^1H NMR (250 MHz, $CDCl_3$) δ = 7.29-7.28 (m, 1H), 6.35 (s, 1H), 5.30 (bs, 1H), 4.53 (s, 2H), 4.26 (d, *J* = 6.1 Hz, 2H), 3.82 (bs, 1H), 1.41 (s, 9H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ = 156.5, 148.8, 141.6, 122.3, 111.6, 80.5, 56.0, 35.6, 28.4; IR (film, cm^{-1}) 3338, 2976, 2930, 2876, 2360, 1694, 1624, 1517, 1451, 1424, 1393, 1366, 1255, 1170, 1101, 1051, 1012; ESI-MS *m/z* 250 $((M+Na)^+)$. Anal. Calcd for $C_{11}H_{17}NO_4$: C, 58.14; H, 7.54. Found: C, 58.10; H, 7.57.

[2-(3-Hydroxymethyl-furan-2-yl)-ethyl]-carbamic acid *tert*-butyl ester(21b): colorless oil; R_f = 0.2 (silica gel, hexane / EtOAc = 2 : 1); ^1H NMR (250 MHz, $CDCl_3$) δ = 7.29-7.27 (m, 1H), 6.39-6.38 (m, 1H), 4.87 (bs, 1H), 4.47 (s, 2H), 3.39-3.34 (m, 2H), 2.84 (t, *J* = 6.2 Hz, 2H), 2.43 (bs, 1H), 1.41 (s, 9H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ = 156.2, 150.3, 141.3, 120.7, 111.3, 79.7, 56.3, 39.5, 28.5, 27.0; IR (film, cm^{-1}) 3342, 2976, 2930, 2872, 2394, 2360, 2229, 1694, 1624, 1517, 1455, 1393, 1370, 1282, 1251, 1166, 1143; ESI-MS *m/z* 264 $((M+Na)^+)$. Anal. Calcd for $C_{12}H_{19}NO_4$: C, 59.73; H, 7.94. Found: C, 59.80; H, 7.98.

[3-(3-Hydroxymethyl-furan-2-yl)-propyl]-carbamic acid *tert*-butyl ester (21c): colorless oil; R_f = 0.1 (silica gel, hexane / EtOAc = 3 : 1); ^1H NMR (250 MHz, $CDCl_3$) δ = 7.27-7.26(m, 1H), 6.38-6.37(m, 1H), 4.77(bs, 1H), 4.43(s, 2H), 3.10-3.05(m, 2H), 2.69(t, *J* = 6.8Hz, 2H), 1.88-1.78(m, 2H), 1.43(s, 9H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ =156.5, 151.8, 140.9, 128.6, 120.1, 111.2, 79.6, 56.2, 39.3, 28.5, 22.9; IR (film, cm^{-1})3353, 2976, 2926, 2872, 2726, 2564, 2352, 2325, 2202, 2059, 1694, 1540, 1517, 1455, 1393, 1362, 1278, 1255, 1174, 1047, 993; ESI-MS *m/z* 278 $((M+Na)^+)$. Anal. Calcd for $C_{13}H_{25}NO_4$: C, 61.16; H, 8.29. Found: C, 61.20; H, 8.28.

[4-(*tert*-Butyl-dimethyl-silanyloxymethyl)-3-hydroxymethyl-furan-2-ylmethyl]-carbamic acid *tert*-butyl ester (21d): colorless solid; R_f = 0.1 (silica gel, hexane / EtOAc = 5 : 1); mp 40-42 ^oC; ^1H NMR (250 MHz, $CDCl_3$) δ = 7.24(s ,1H) , 5.00(s, 1H) , 4.60 (s,2H), 4.53 (d, J = 6.3Hz, 2H), 4.26 (d, J = 6.0, 2H), 3.67 (s, 1H), 1.42 (s, 9H), 0.91 (s, 9H), 0.10 (s, 6H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ = 156.0, 149.1, 138.7, 125.1, 121.5, 80.1, 56.5, 54.6, 35.8, 28.3, 25.8, 18.3, -5.4; IR (film, cm^{-1}) 3378, 2966, 2927, 2855, 1941, 1695, 1529, 1509, 145, 1366, 1251, 1172,1049, 1006; ESI-MS *m/z* 394 ($(M+Na)^+$). Anal. Calcd for $C_{18}H_{33}NO_5Si$: C, 58.19; H, 8.95. Found: C, 58.23; H, 8.90.

[2-[4-(tert-Butyl-dimethyl-silanyloxymethyl)-3-hydroxymethyl-furan-2-yl]-ethyl]-carbamic acid *tert*-butyl ester (21e) : colorless oil; R_f = 0.2 (silica gel, hexane / EtOAc = 3 : 1); ^1H NMR (250 MHz, $CDCl_3$) δ = 7.23(s, 1H), 4.78(bs, 1H), 4.60(s, 2H), 4.45(s, 2H), 3.38-3.35(m, 2H), 3.27(bs, 1H), 2.82(t, J = 6.4 Hz, 2H), 1.43(s, 9H), 0.90(s, 9H), 0.11(s, 6H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ =156.0, 150.9, 138.3, 125.0, 120.8, 79.5 56.8, 55.0, 39.5, 28.5, 27.0, 26.0 18.4, -5.2; IR (film, cm^{-1}) 3357, 2953, 2930, 2856, 2360, 2337, 1697, 1543, 1520, 1470, 1393, 1366, 1259, 1174, 1112, 1058, 1004; ESI-MS *m/z* 408 ($(M+Na)^+$). Anal. Calcd for $C_{19}H_{35}NO_5Si$: C, 59.19; H, 9.15. Found: C, 59.23; H, 9.10.

Reference:

(1) Yang, Y.-K.; Lee, S.; Tae, J. *Bull. Kor. Chem. Soc.* **2004**, *25*, 1307.