Cationic Cyclizations and Rearrangements Promoted by a Heterogeneous Gold Catalyst

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Supporting Information

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General Methods

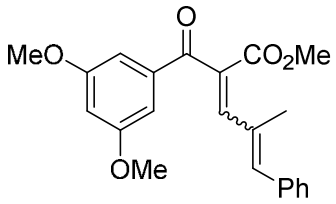
Reactions with gold were done in oven dried glassware using standard Schlenk techniques or in a nitrogen glovebox. All other reactions were done under an atmosphere of nitrogen. $AuCl_3$ and $AgSbF_6$ were purchased from Strem Chemicals. Dichloromethane-d_2, toluene-d_8, and deuterated chloroform were from Cambridge Isotope Laboratories. Dichloromethane, hexanes, toluene, and diethyl ether stored in the glovebox were purified according to the method described by Grubbs.[1] Solvents (dichloromethane, dichloroethane, toluene, THF, and ether) used for the preparation of aryl enones were purchased from Fisher and obtained from a Glass Contour solvent purification system. Reactions with $AgSbF_6$ were done with minimal light conditions using aluminum foil. If $AgSbF_6$ is not pure, rearrangement reactions are not efficient. Cyclizations were monitored by ^{1}H NMR using J-Young tubes or thin layer chromatography. Thin Layer Chromatography plates were visualized using a UV lamp, stained with *p*-anisaldehyde or potassium permanganate solution, and dried on a hot plate. Flash column chromatography was done on EM Science silica gel 60 (230-400 mesh). ^{1}H NMR, ^{13}C NMR, DEPT-135, COSY, and HSQC spectra were recorded on Bruker Avance 500 MHz or Bruker Avance 400 MHz spectrometer. ^{1}H and ^{13}C NMR chemical shifts (δ) are reported in parts per million after referencing to the appropriate solvent resonances.[2] An ATI Mattson Genesis FT-IR spectrometer was used to acquire infrared spectra. High Resolution Mass Spectra were obtained from the Chemistry Instrumentation Center of SUNY at Buffalo or the Mass Spectrometry Laboratory of University of Illinois at Urbana-Champaign.

Preparation of Nazarov Precursors

Nazarov precursors described in this paper were prepared according to known procedures using Knoevanagel condensation of *β*-ketoesters and aldehydes using acetic acid and piperidene in benzene at 100 °C, Lehnert modification of Knoevanagel condensation with $TiCl_4$/pyridine at 0 °C, or oxido-alkylidenation of alkynes.[3-6]

Reaction details are listed with all compounds (method of preparation, time, mmol of product, yield, purification method).

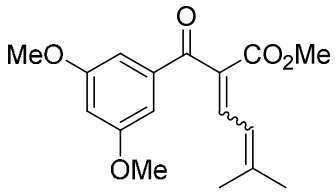
New Aryl Enones (Nazarov Precursors)



1

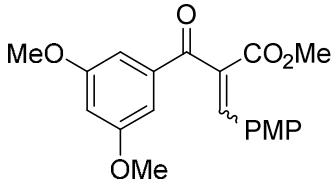
(Knoevanagel condensation, 16 h, 0.420 mmol of **1**, quantitative yield, flash column chromatography with ethyl acetate:hexanes = 1:4) **^{1}H NMR (500 MHz, $CDCl_3$, δ)**: 7.67 (m, 1H, CH), 7.33-7.30 (m, 2H, CH), 7.24-7.23 (m, 3H, CH), 7.10 (d, *J* = 2.3 Hz, 2H, CH), 6.97 (s, 1H, CH), 6.66 (t, *J* = 2.3 Hz, 1H, CH), 3.80 (s, 6H, OCH_3), 3.71 (s, 3H, OCH_3), 1.79 (s, 3H, CH_3). **^{13}C NMR (125 MHz, $CDCl_3$, δ)**: 195.2, 166.0, 161.1, 148.2, 142.2, 139.3, 136.2, 133.3, 129.6, 129.0, 128.3, 128.2, 106.9, 106.1, 55.6, 52.5, 16.4. **IR (neat, cm^{-1})**: 1714, 1666, 1588, 1456,

1426, 1351, 1315, 1296, 1245, 1196, 1172, 1155, 1065, 1018, 1007, 955, 925. **HRMS** calculated for $C_{22}H_{22}O_5$ $(M)^+$ 366.1462, found: 366.14581.



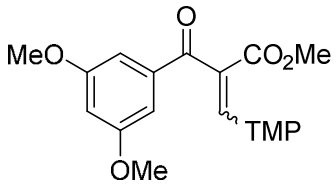
3

(Knoevanagel condensation, 16 h, 0.420 mmol of **3**, quantitative yield, flash column chromatography with Ethyl acetate:hexanes = 1:4) **^{1}H NMR (500 MHz, $CDCl_3$, δ)**: 7.79 (d, *J* = 12.5 Hz, 1H, CH), 7.032 (s, 1H, CH), 7.028 (s, 1H, CH), 6.67-6.66 (m, 1H, CH), 5.86 (d, *J* = 11.8 Hz, 1H, CH), 3.81 (s, 6H, OCH_3), 3.69 (s, 3H, OCH_3), 1.94 (s, 3H, CH_3), 1.81(s, 3H, CH_3). **^{13}C NMR (125 MHz, $CDCl_3$, δ)**: 194.8, 166.0, 161.1, 151.2, 139.8, 139.0, 128.4, 120.7, 107.1, 106.6, 106.4, 106.3, 55.7, 52.3, 27.1, 19.2. **IR (neat, cm^{-1})**: 2917, 1714, 1670, 1629, 1590, 1456, 1428, 1350, 1295, 1243, 1205, 1151, 1064, 1009, 926. **HRMS** calculated for $C_{17}H_{20}O_5$ $(M)^+$ 304.1305, found 304.13138.



5

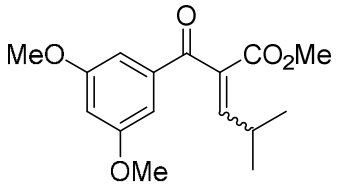
(Knoevanagel condensation, 16 h, 2.10 mmol of **5**, quantitative yield, flash column chromatography with ethyl acetate:hexanes = 1:2) **^{1}H NMR (500 MHz, $CDCl_3$, δ)**: 7.89 (s, 1H, CH), 7.29 (d, *J* = 8.7 Hz, 2H, CH), 7.11 (d, *J* = 2.4 Hz, 2H, CH), 6.75 (d, *J* = 8.9 Hz, 2H, CH), 6.64 (t, *J* = 2.3 Hz, 1H, CH), 3.78 (s, 6H, OCH_3), 3.74 (s, 3H, OCH_3), 3.73 (s, 3H, OCH_3). **^{13}C NMR (125 MHz, $CDCl_3$, δ)**: 195.9, 165.8, 161.5, 161.2, 142.7, 138.1, 132.4, 128.1, 125.5, 114.9, 114.4, 106.9, 106.6, 55.7, 55.4, 52.6. **IR (neat, cm^{-1})**: 1721, 1710, 1668, 1594, 1571, 1512, 1423, 1356, 1292, 1255, 1208, 1202, 1188, 1180, 1168, 1154, 1125, 1065, 1051, 1025, 1006, 928. **HRMS** calculated for $C_{20}H_{20}O_6$ $(M)^+$ 356.1254, found: 356.12555.



7

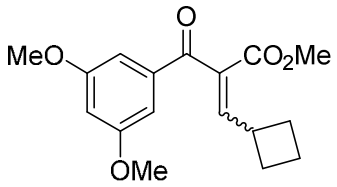
(Knoevanagel condensation, 16 h, 0.42 mmol of **7**, quantitative yield, flash column chromatography with ethyl acetate:hexanes = 1:2) **^{1}H NMR (400 MHz, $CDCl_3$, δ)**: 8.15 (s, 1H, CH), 7.08 (m, 2H, CH), 6.59 (t, *J* = 2.9 Hz, 1H, CH), 5.95 (s, 1H, CH), 3.78 (s, 6H, OCH_3), 3.77 (s, 3H, OCH_3), 3.70 (s, 3H, OCH_3), 3.50 (s, 6H, OCH_3). **^{13}C NMR (100 MHz, $CDCl_3$, δ)**: 193.3, 167.4, 163.8, 160.6, 159.8, 139.7, 136.0, 128.1, 107.1, 106.5, 105.5, 105.2, 90.3, 55.7, 55.5, 54.9,

52.3. **IR (neat, cm^{-1})**: 1717, 1672, 1591, 1455, 1426, 1336, 1315, 1295, 1250, 1234, 1204, 1152, 1124, 1087, 1061, 1033, 1005, 951, 925. **HRMS** calculated for $C_{22}H_{24}O_8$ $(M)^+$ 416.1466, found: 416.14597.



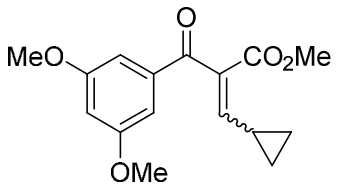
9

(Knoevanagel condensation, 16 h, 1.05 mmol of **9**, quantitative yield, flash column chromatography with ethyl acetate:hexanes = 1:4) **^{1}H NMR (500 MHz, $CDCl_3$, δ)**: 7.04 (m, 2H, CH), 6.94 (d, J = 11.0 Hz, 1H, CH), 6.67 (m or t, J = 2.2 Hz, 1H, CH), 3.81 (s, 6H, OCH_3), 3.69 (s, 3H, OCH_3), 2.40-2.32 (m, 1H, CH), 1.00 (d, J = 6.6 Hz, 6H, CH_3). **^{13}C NMR (125 MHz, $CDCl_3$, δ)**: 194.1, 165.2, 161.1, 154.0, 138.7, 131.1, 106.9, 106.4, 55.7, 52.4, 29.4, 21.9. **IR (neat, cm^{-1})**: 2964, 1717, 1671, 1639, 1602, 1467, 1457, 1426, 1356, 1335, 1318, 1305, 1242, 1205, 1195, 1176, 1159, 1149, 1061, 1038, 1011, 959. **HRMS** calculated for $C_{16}H_{20}O_5$ $(M)^+$ 292.1305, found: 292.12933.



11

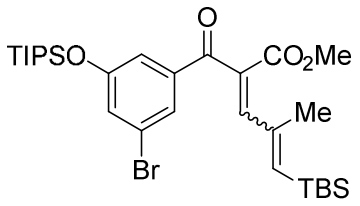
(Knoevanagel condensation including Lehnert modification, 2.10 mmol of the β-ketoester was used to obtain 1.68 to 1.89 mmol of **11**, 80-90% yield, 24 h, flash column chromatography with ethyl acetate:hexanes = 1:4 to 1:6) **^{1}H NMR (500 MHz, $CDCl_3$, δ)**: 7.28 (d, J = 10 Hz, 1H, CH), 7.03 (d, J = 2.0 Hz, 2H, CH), 6.70 (t, J = 2.25 Hz, 1H, CH), 3.85 (s, 6H, OCH_3), 3.73 (s, 3H, OCH_3), 3.00 (m, 1H, CH), 2.11-2.08 (m, 2H, CH_2), 2.03-1.99 (m, 2H, CH_2), 1.90-1.86 (m, 2H, CH_2). **^{13}C NMR (125 MHz, $CDCl_3$, δ)**: 193.9, 165.1, 161.0, 151.7, 138.5, 130.7, 106.8, 106.3, 55.6, 52.2, 35.4, 28.8, 28.5, 18.9. **IR (neat, cm^{-1})**: 2944, 1721, 1674, 1597, 1460, 1431, 1368, 1352, 1320, 1298, 1249, 1205, 1158, 1064, 1005, 925. **HRMS** calculated for $C_{17}H_{21}O_5$ $(M)^+$ 305.1389, found: 305.1397.



14

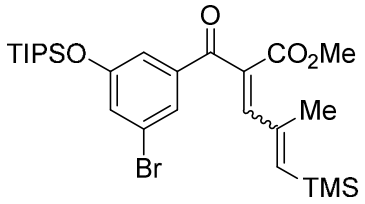
(Knoevanagel condensation, 16 h, 0.630 mmol of **14**, quantitative yield, flash column chromatography with ethyl acetate:hexanes = 1:4) **^{1}H NMR (500 MHz, $CDCl_3$, δ)**: 7.06 (m, 2H, CH), 6.64 (t, J = 2.3 Hz, 1H, CH), 6.50 (d, J = 11.4 Hz, 1H, CH), 3.79 (s, 6H, OCH_3), 3.64 (s,

3H, OCH_3), 1.45-1.37 (m, 1H, CH), 0.95-0.92 (m, 2H, CH_2), 0.73-0.70 (m, 2H, CH_2). **^{13}C NMR (125 MHz, $CDCl_3$, δ)**: 194.2, 165.1, 161.0, 154.0, 138.8, 130.4, 106.9, 106.3, 55.6, 52.1, 13.1, 9.7. **IR (neat, cm^{-1})**: 2917, 1717, 1676, 1626, 1593, 1452, 1434, 1422, 1356, 1288, 1242, 1200, 1149, 1063, 1050, 1010, 956, 933, 921. **HRMS** calculated for $C_{16}H_{18}O_5$ $(M)^+$ 290.1149, found 290.11472.



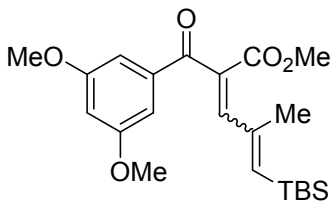
27a

(Oxido-alkylidenation, 24 h, 1.93 mmol of **27a**, 77% yield over two steps, flash column chromatography with ethyl acetate:hexanes = 1:19) **^{1}H NMR (400 MHz, $CDCl_3$, δ)**: 7.64 (s, 1H), 7.52 (s, 1H), 7.30 (s, 1H), 7.24 (s, 1H), 6.10 (s, 1H), 3.71 (s, 3H), 1.71 (s, 3H), 1.26 (m, 3H), 1.09 (d, *J* = 7.3 Hz, 18H), 0.85 (s, 9H), 0.05 (s, 6H). **^{13}C NMR (100 MHz, $CDCl_3$, δ)**: 193.6, 165.6, 157.2, 149.2, 147.4, 143.4, 139.3, 128.3, 128.2, 124.5, 123.2, 119.1, 52.5, 26.3, 20.3, 17.8, 17.1, 12.6, -4.8. **IR (neat, cm^{-1})**: 2951, 2866, 1728, 1682, 1589, 1562, 1435, 1285, 1169, 1088, 972, 918, 883, 849, 748, 690. **HRMS** calculated for $C_{29}H_{48}O_4BrSi_2$ $(M)^+$ 595.2269, found: 595.22589.



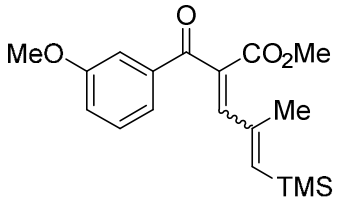
27b

(Oxido-alkylidenation, 24 h, 2.03 mmol of **27b**, 79% yield over two steps, flash column chromatography with ethyl acetate:hexanes = 1:19) **^{1}H NMR (400 MHz, $CDCl_3$, δ)**: 7.63 (s, 1H), 7.50 (s, 1H), 7.30 (s, 1H), 7.25 (s, 1H), 6.10 (s, 1H), 3.71 (s, 3H), 1.69 (s, 3H), 1.33 – 1.18 (m, 3H), 1.09 (d, *J* = 7.3 Hz, 18H), 0.09 (s, 9H). **^{13}C NMR (100 MHz, $CDCl_3$, δ)**: 193.6, 165.5, 157.2, 150.1, 148.9, 146.2, 139.4, 128.2, 128.1, 124.4, 123.1, 119.0, 52.4, 19.8, 17.8, 12.5, -0.67. **IR (neat, cm^{-1})**: 2947, 2893, 2866, 2360, 2341, 1728, 1681, 1654, 1589, 1562, 1434, 1365, 1284, 1238, 1164, 1091, 995, 972, 918, 845, 748, 686, 667. **HRMS** calculated for $C_{26}H_{42}O_4BrSi_2$ $(M)^+$ 553.1800, found: 553.18280.



27c

(Knoevanagel condensation, 16 h, 0.269 mmol of **27c**, 64% yield, flash column chromatography with ethyl acetate:hexanes = 1:5) **^{1}H NMR (500 MHz, $CDCl_3$, δ)**: 7.49 (s, 1H, CH), 7.06-7.05 (m, 2H, CH), 6.67-6.65 (m, 1H, CH), 6.05 (s, 1H, CH), 3.81 (s, 6H, OCH_3), 3.70 (s, 3H, OCH_3), 1.72 (s, 3H, CH_3), 0.92 (s, 3H, CH_3), 0.81 (s, 6H, CH_3), 0.22 (s, 3H, CH_3), 0.02 (s, 3H, CH_3). **^{13}C NMR (125 MHz, $CDCl_3$, δ)**: (both diastereomers) 195.2, 194.9, 166.0, 161.1, 148.8, 147.8, 145.5, 144.4, 142.3, 139.2, 139.0, 130.0, 128.9, 107.0, 106.3, 55.7, 53.5, 52.6, 26.6, 26.4, 25.6, 20.4, 17.2, 1.13, -3.80, -4.66. **IR (neat, cm^{-1})**: 2953, 2931, 1724, 1677, 1593, 1462, 1428, 1352, 1316, 1297, 1249, 1206, 1157, 1066, 1011. **HRMS** calculated for $C_{22}H_{33}O_5Si$ $(M)^+$ 405.2092, found: 405.20828.

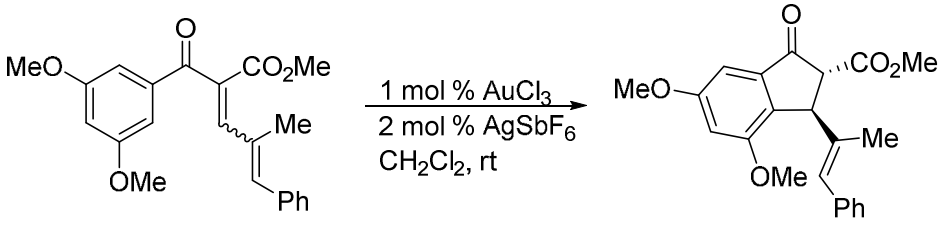


27d

(Oxido-alkylidenation, 24 h, 1.42 mmol of **27d**, 54% yield over two steps, flash column chromatography with ethyl acetate:hexanes = 1:4 to 1:6) **^{1}H NMR (500 MHz, $CDCl_3$, δ)**: 7.50 (s, 2H, CH), 7.45 (d, J = 7.5 Hz, 1H CH), 7.36 (t, J = 7.5 Hz, 1H, CH), 7.13 (d, J = 8.0 Hz, 1H, CH), 6.07 (s, 1H, CH), 3.84 (s, 3H, OCH_3), 3.687 (s, 3H, OCH_3), 1.70 (s, 3H, CH_3), 0.06 (s, 9H) **^{13}C NMR (125 MHz, $CDCl_3$, δ)**: 194.9, 165.8, 159.9, 149.6, 148.4, 145.4, 138.4, 129.7, 129.0, 122.2, 120.3, 112.5, 55.4, 52.3, 19.8, -0.548. **IR (neat, cm^{-1})**: 3006, 2954, 1722, 1701, 1680, 1599, 1583, 1487, 1464, 1452, 1435, 1361, 1319, 1216, 1174, 1043, 848. **HRMS** calculated for $C_{18}H_{25}O_4Si$ $(M)^+$ 333.1522, found 333.1523.

Cyclization Reactions with Au Catalyst

All cyclizations were done according to the procedure described for the cyclization of **1**. The cyclizations were monitored using Thin Layer Chromatography (TLC) and/or ^{1}H NMR spectroscopy. Aryl enone substrates are used as diastereomeric mixtures to obtain a single product.[7] Reaction details are listed with all compounds (temperature, solvent, time, mmol of product, yield, purification method).

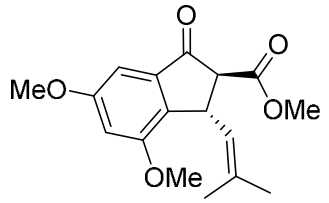


1 **2**

Gold(III) chloride (0.0008 g, 0.0026 mmol) was dissolved in CH_2Cl_2 (0.8 mL) in a 15 x 45 mm Amber Screw Cap Vial. Silver(I) hexafluoroantimonate (0.0019 g, 0.0055 mmol) was weighed under minimal light and added to the reaction mixture. The vial was capped, wrapped with aluminum foil, and the reaction mixture was stirred for 0.5 h at room temperature. Aryl

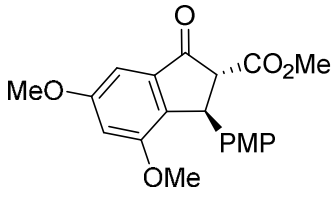
enone **1** (0.100 g, 0.273 mmol) was added to the mixture and stirred for 0.5 h at room temperature. Au and Ag were filtered through Celite using ethyl acetate and the removal of solvent provided aryl cyclopentenone **2** in >99% yield. **^{1}H NMR (500 MHz, $CDCl_3$, δ)**: 7.33-7.30 (m, 2H, CH), 7.23-7.29 (m, 3H, CH), 6.83 (d, *J* = 1.9 Hz, 1H, CH), 6.70 (d, *J* = 1.9 Hz, 1H, CH), 6.36 (s, 1H, CH), 4.48 (d, *J* = 3.1 Hz, 1H, CH), 3.85 (s, 3H, OCH_3), 3.82 (s, 3H, OCH_3), 3.80 (s, 3H, OCH_3), 3.55 (d, *J* = 3.1 Hz, 1H, CH), 1.71 (s, 3H, CH_3). **^{13}C NMR (125 MHz, $CDCl_3$, δ)**: 199.0, 169.3, 162.1, 158.2, 138.2, 138.0, 137.6, 137.1, 129.0, 128.2, 127.3, 126.5, 106.7, 96.8, 60.5, 56.0, 55.9, 53.0, 50.1. **IR (neat, cm^{-1})**: 1741, 1705, 1609, 1493, 1453, 1437, 1356, 1305, 1232, 1205, 1147, 1031, 982. **HRMS** calculated for $C_{22}H_{22}O_5$ $(M)^+$ 366.1462, found: 366.14682.

New Aryl Products (Nazarov and Lactone Products)



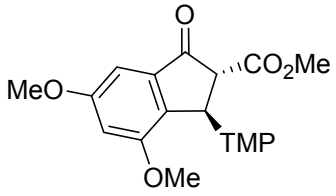
4

(room temperature, CH_2Cl_2, 1 h, 0.176 mmol of **4**, >99% yield, flash column chromatography with ethyl acetate:hexanes = 1:4) **^{1}H NMR (500 MHz, $CDCl_3$, δ)**: 6.77 (d, *J* = 2.1 Hz, 1H, CH), 6.66 (d, *J* = 2.1 Hz, 1H, CH), 4.94 (d, *J* = 9.5 Hz, 1H, CH), 4.53 (dd, *J* = 9.6 Hz, 2.8 Hz, 1H, CH), 3.82 (s, 3H, OCH_3), 3.81 (s, 3H, OCH_3), 3.77 (s, 3H, OCH_3), 3.40 (d, *J* = 2.8 Hz, 1H, CH), 1.79 (d, *J* = 1.3 Hz, 3H, CH_3), 1.71 (d, *J* = 1.4 Hz, 3H, CH_3). **^{13}C NMR (125 MHz, $CDCl_3$, δ)**: 199.5, 169.4, 161.7, 158.1, 139.5, 137.0, 134.2, 124.5, 106.8, 96.6, 61.9, 55.9, 55.8, 52.9, 39.9, 25.9, 18.5. **IR (neat, cm^{-1})**: 2955, 1736, 1711, 1592, 1495, 1454, 1435, 1359, 1308, 1236, 1205, 1150, 1040, 935. **HRMS** calculated for $C_{17}H_{20}O_5$ $(M)^+$ 304.1305, found 304.13058.



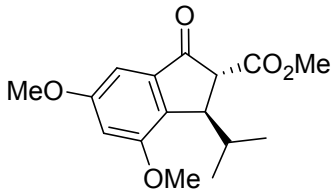
6

(room temperature, CH_2Cl_2, 0.5 h, 0.281 mmol of **6**, >99% yield, flash column chromatography with ethyl acetate:hexanes = 1:2) **^{1}H NMR (500 MHz, $CDCl_3$, δ)**: 6.97 (d, *J* = 8.7 Hz, 2H, CH), 6.85 (d, *J* = 2.0 Hz, 1H, CH), 6.79 (d, *J* = 8.7 Hz, 2H, CH), 6.66 (d, *J* = 2.0 Hz, 1H, CH), 4.88 (d, *J* = 2.8 Hz, 1H, CH), 3.85 (s, 3H, OCH_3), 3.78 (s, 3H, OCH_3), 3.77 (s, 3H, OCH_3), 3.65 (s, 3H, OCH_3), 3.58 (d, *J* = 2.9 Hz, 1H, CH). **^{13}C NMR (125 MHz, $CDCl_3$, δ)**: 199.3, 169.0, 162.1, 158.5, 157.9, 138.7, 137.6, 134.5, 128.3, 114.1, 107.1, 96.6, 64.4, 56.0, 55.8, 55.4, 53.0, 45.3. **IR (neat, cm^{-1})**: 1738, 1710, 1610, 1583, 1511, 1494, 1453, 1435, 1360, 1307, 1244, 1204, 1173, 1148, 1109, 1030, 987, 933. **HRMS** calculated for $C_{20}H_{20}O_6$ $(M)^+$ 356.1254, found: 356.12564.



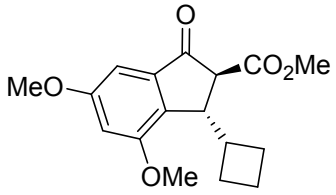
8

(room temperature, CH_2Cl_2, 0.5 h, 0.240 mmol of **8**, >99% yield, flash column chromatography with ethyl acetate:hexanes = 1:2) **^{1}H NMR (500 MHz, $CDCl_3$, δ)**: 6.81 (d, *J* = 2.1 Hz, 1H, CH), 6.54 (d, *J* = 2.1 Hz, 1H, CH), 6.17 (d, *J* = 2.2 Hz, 1H, CH), 5.97(d, *J* = 2.2 Hz, 1H, CH), 5.43 (d, *J* = 2.8 Hz, 1H, CH), 3.89 (s, 3H, OCH_3), 3.82 (s, 3H, OCH_3), 3.81(d, *J* = 2.8 Hz, 1H, CH), 3.78 (s, 3H, OCH_3), 3.73 (s, 3H, OCH_3), 3.61 (s, 3H, OCH_3), 3.38 (s, 3H, OCH_3). **^{13}C NMR (125 MHz, $CDCl_3$, δ)**: 200.5, 170.1, 160.9, 160.1, 159.1, 158.9, 157.4, 139.7, 137.6, 109.9, 106.1, 96.3, 91.3, 91.2, 60.8, 56.5, 55.7, 55.67, 55.2, 52.5, 35.6. **IR (neat, cm^{-1})**: 1736, 1704, 1604, 1590, 1497, 1467, 1461, 1432, 1428, 1356, 1333, 1301, 1228, 1206, 1113, 1151, 1059, 1036, 989, 950, 934. **HRMS** calculated for $C_{22}H_{24}O_8$ $(M)^+$ 416.1466, found: 416.14667.



10

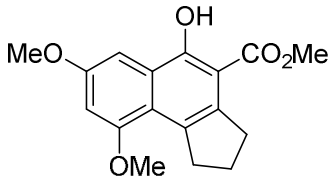
(room temperature, CH_2Cl_2, 0.5 h, 0.342 mmol of **10**, >99% yield, flash column chromatography with ethyl acetate:hexanes = 1:4) **^{1}H NMR (500 MHz, $CDCl_3$, δ)**: 6.77 (d, *J* = 2.1 Hz, 1H, CH), 6.67 (d, *J* = 2.1 Hz, 1H, CH), 3.85 (s, 3H, OCH_3), 3.82 (s, 3H, OCH_3), 3.80-3.78 (m, 1H, CH), 3.74 (s, 3H, OCH_3), 3.47 (d, *J* = 2.8 Hz, 1H, CH), 2.73-2.67 (m, 1H, CH), 1.04 (d, *J* = 6.9 Hz, 3H, CH_3), 0.51 (d, *J* = 7.0 Hz, 3H, CH_3). **^{13}C NMR (125 MHz, $CDCl_3$, δ)**: 199.9, 170.3, 161.6, 157.9, 139.3, 138.0, 106.5, 96.7, 55.9, 55.7, 54.9, 52.8, 47.3, 28.3, 21.7, 15.9. **IR (neat, cm^{-1})**: 2957, 1740, 1710, 1613, 1494, 1463, 1454, 1435, 1360, 1328, 1300, 1247, 1204, 1150, 1103, 1040, 1024, 935. **HRMS** calculated for $C_{16}H_{20}O_5$ $(M)^+$ 292.1305, found: 292.1305.



12

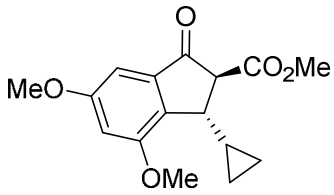
(room temperature, toluene, 16 h, 0.179 mmol of **12**, 64% yield, flash column chromatography with ethyl acetate:hexanes = 1:4) **^{1}H NMR (500 MHz, $CDCl_3$, δ)**: 6.81 (d, *J* = 2.0 Hz, 1H, CH), 6.70 (d, *J* = 1.5 Hz, 1H, CH), 3.89 (s, 3H, OCH_3), 3.87 (s, 3H, OCH_3), 3.80 (s, 3H, OCH_3), 3.77 (m, 1H, CH), 3.59 (d, *J* = 2.0 Hz, 1H, CH), 2.84 (m, 1H, CH), 2.10-2.03 (m, 2H, CH_2), 1.86-1.81 (m, 2H, CH_2), 1.80-1.77 (m, 2H, CH_2). **^{13}C NMR (125 MHz, $CDCl_3$, δ)**: 199.6, 169.8, 161.4, 157.8, 139.0, 137.5, 106.3, 96.6, 57.5, 55.7, 55.4, 52.7, 45.7, 39.2, 27.7, 25.1, 17.9. **IR (neat,**

cm^{-1}): 2955, 1742, 1712, 1613, 1495, 1464, 1454, 1435, 1361, 1308, 1205, 1151, 1038, 934. **HRMS** calculated for $C_{17}H_{21}O_5$ $(M)^+$ 305.1389, found 305.1388.



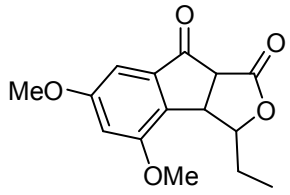
13

(room temperature, toluene, 16 h, 0.084 mmol of **13**, 30% yield, flash column chromatography with ethyl acetate:hexanes = 1:4)**^{1}H NMR (500 MHz, CDCl$_3$, δ)**: 12.34 (br, 1H, OH), 7.35 (d, *J* = 2.0 Hz, 1H, CH), 6.64 (d, *J* = 2.0 Hz, 1H, CH), 4.04 (s, 3H, OCH_3), 3.99 (s, 3H, OCH_3), 3.94 (s, 3H, OCH_3), 3.48 (t, *J* = 7.5 Hz, 2H, CH_2), 3.27 (t, *J* = 7.5 Hz, 2H, CH_2), 2.11 (m, 2H, CH_2). **^{13}C NMR (125 MHz, CDCl$_3$, δ)**: 172.9, 159.1, 157.7, 157.3, 136.9, 129.8, 126.1, 122.3, 105.2, 101.5, 94.6, 55.4, 55.4, 52.0, 35.0, 34.6, 24.4. **IR (neat, cm^{-1})**: 3392, 2921, 1730, 1655, 1595, 1502, 1439, 1407, 1341, 1213, 1156, 1079, 1053, 1012, 946. **HRMS** calculated for $C_{17}H_{19}O_5$ $(M)^+$ 303.1232, found 303.1241.



15

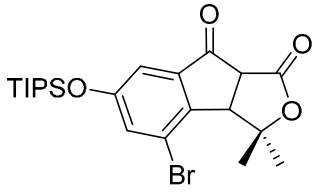
(room temperature, CH_2Cl_2, 16 h, 0.205 mmol of **15**, 68% yield, flash column chromatography with ethyl acetate:hexanes = 1:4) Product formation was observed within 2 h. However, the reaction was run for 16 h to see if more of **16** would form. **^{1}H NMR (500 MHz, CDCl$_3$, δ)**: 6.81 (d, *J* = 2.0 Hz, 1H, CH), 6.73 (d, *J* = 1.5 Hz, 1H, CH), 3.91 (s, 3H, OCH_3), 3.86 (m, 4H, OCH_3/CH), 3.78 (s, 3H, OCH_3), 3.56 (d, *J* = 2.5 Hz, 1H, CH), 3.30 (m, 1H, CH), 0.97-0.95 (m, 1H, CH), 0.66-0.62 (m, 1H, CH), 0.52-0.50 (m, 1H, CH), 0.28-0.22 (m, 1H, CH). **^{13}C NMR (125 MHz, CDCl$_3$, δ)**: 199.2, 169.5, 161.5, 158.2, 139.2, 137.4, 106.5, 96.5, 60.6, 55.7, 55.5, 52.7, 45.3, 15.8, 5.9, 2.9. **IR (neat, cm^{-1})**: 2954, 1742, 1712, 1613, 1494, 1459, 1435, 1360, 1310, 1266, 1230, 1206, 1154, 1035, 911. **HRMS** calculated for $C_{16}H_{19}O_5$ $(M)^+$ 291.1232, found 291.1239.



16

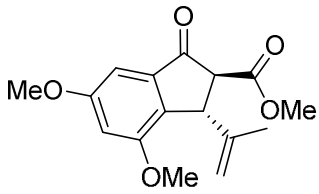
(room temperature, CH_2Cl_2, 16 h, 0.072 mmol of **16**, 24% yield, flash column chromatography with ethyl acetate:hexanes = 1:4) **^{1}H NMR (500 MHz, CDCl$_3$, δ)**: 6.82 (s, 1H, CH), 6.72 (s, 1H,

CH), 4.60-4.57 (m, 1H, CH), 3.89 (s, 3H, OCH_3), 3.86-3.85 (m, 1H, CH), 3.83 (s, 3H, OCH_3), 1.97-1.93 (m, 2H, CH_2), 1.11 (t, J = 7.4 Hz, 3H, CH_3). **^{13}C NMR (125 MHz, $CDCl_3$, δ)**: 195.0, 169.7, 162.7, 157.4, 137.4, 136.0, 106.7, 97.3, 85.2, 56.1, 55.9, 54.3, 42.7, 30.0, 9.23. **IR (neat, cm^{-1})**: 2968, 2940, 1774, 1715, 1613, 1464, 1491, 1436, 1355, 1324, 1307, 1206, 1167, 1099, 1034, 1027, 970. **HRMS** calculated for $C_{15}H_{16}O_5$ $(M)^+$ 276.0992, found 276.09930.



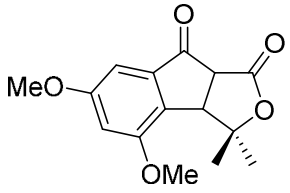
29a

(room temperature, toluene, 5 h, 0.023 mmol of **29a** from **27a**, 79% yield, preparatory TLC with ethyl acetate:hexanes = 1:4) **29a** formed within 5 h, however, the reaction mixture was monitored using TLC until 16 h to observe any further reaction. **^{1}H NMR (500 MHz, $CDCl_3$, δ)**: 7.40 (d, J = 2.2 Hz, 1H, CH), 7.19 (d, J = 2.2 Hz, 1H, CH), 4.14 (d, J = 8.7 Hz, 1H, CH), 3.97 (d, J = 8.6 Hz, 1H, CH), 1.85 (s, 3H, CH_3), 1.31-1.25 (m, 3H, CH), 1.10 (s, 3H, CH_3), 1.095 (d, J = 7.4 Hz, 18H, CH_3). **^{13}C NMR (125 MHz, $CDCl_3$, δ)**: 194.6, 167.6, 158.2, 144.3, 138.3, 131.7, 122.4, 113.8, 86.9, 57.2, 50.4, 31.4, 25.7, 17.9, 12.7. **IR (neat, cm^{-1})**: 2946, 2893, 2868, 1781, 1725, 1602, 1558, 1464, 1389, 1374, 1297, 1259, 1173, 1128, 983, 962. **HRMS** calculated for $C_{22}H_{31}O_4BrSiNa$ $(M+Na)^+$ 489.1067, found: 489.10648.



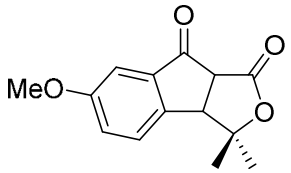
28b

(60 °C, CH_2Cl_2:toluene = 1:1, 24 h, 0.198 mmol of **28b**, 80% yield, column chromatography with ethyl acetate:hexanes = 1:4) **^{1}H NMR (500 MHz, $CDCl_3$, δ)**: 6.80 (m, 1H, CH), 6.68 (m, 1H, CH), 4.83 (m, 1H, CH), 4.71 (m, 1H, CH), 4.32 (d, J = 3.0 Hz, 1H, CH), 3.84 (s, 3H, CH_3), 3.82 (s, 3H, CH_3), 3.77 (s, 3H, CH_3), 3.45 (d, J = 3.5 Hz, 1H, CH), 1.62 (s, 3H, CH_3). **^{13}C NMR (125 MHz, $CDCl_3$, δ)**: 198.9, 169.1, 161.9, 157.9, 144.4, 137.8, 137.6, 112.4, 106.5, 96.6, 60.6, 55.8, 55.7, 52.8, 47.6, 20.1. **IR (neat, cm^{-1})**: 2956, 2925, 1739, 1714, 1495, 1453, 1436, 1360, 1310, 1206, 1152. **HRMS** calculated for $C_{16}H_{19}O_5$ $(M)^+$ 291.1232, found 291.1239.



29b

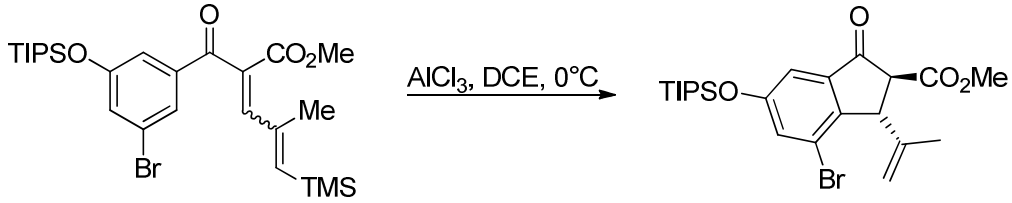
(60 °C, CH_2Cl_2:toluene = 1:1, 24 h, 0.205 mmol of **29b**, 83% yield, column chromatography with ethyl acetate:hexanes = 1:4) **^{1}H NMR (500 MHz, $CDCl_3$, δ)**: 6.90 (d, *J* = 2.0 Hz, 1H, CH), 6.77 (d, *J* = 2.0, 1H, CH), 4.13 (d = 8.0 Hz, 1H, CH), 3.96 (m, 4H, CH/OCH_3), 3.90 (s, 3H, OCH_3), 1.75 (s, 3H, CH_3), 1.16 (s, 3H, CH_3). **^{13}C NMR (125 MHz, $CDCl_3$, δ)**: 195.4, 168.3, 162.5, 157.6, 137.7, 134.1, 106.5, 97.3, 86.5, 56.2, 55.9, 55.7, 47.4, 30.7, 24.9. **IR (neat, cm^{-1})**: 3055, 2987, 1774, 1716, 1617, 1497, 1436, 1423, 1361, 1317, 1154, 1095, 1023, 896. **HRMS** calculated for calculated for $C_{15}H_{17}O_5$ $(M)^+$ 277.1076, found 277.1073.



29c

(60 °C, CH_2Cl_2:toluene = 1:1, 24 h, 0.265 mmol of **29c**, 88% yield, column chromatography with ethyl acetate:hexanes = 1:4) **^{1}H NMR (500 MHz, CD_2Cl_2, δ)**: 7.70 (d, *J* = 8.5 Hz, 1H, CH), 7.28 (dd, *J* = 8.5 Hz, 2.5 Hz, 1H, CH), 7.21 (d, *J* = 2.5 Hz, 1H CH), 3.95 (d, *J* = 3.5 Hz, 1H, CH), 3.91 (s, 3H, OCH_3), 3.62 (dd, *J* = 3.0 Hz, 1H, CH), 1.20 (s, 3H, CH_3), 1.14 (s, 3H, CH_3). **^{13}C NMR (125 MHz, CD_2Cl_2, δ)**: 198.7, 169.7, 160.0, 147.3, 137.4, 128.8, 124.1, 105.1, 76.8, 57.6, 50.9, 49.1, 22.7, 21.6. **IR (neat, cm^{-1})**: 3045, 2986, 1764, 1710, 1498, 1436, 1418, 1365, 1312, 1154, 1098, 1021, 902. **HRMS** calculated for $C_{14}H_{15}O_4$ $(M)^+$ 247.0970, found 247.0980.

Cyclization Reaction of 27b with $AlCl_3$

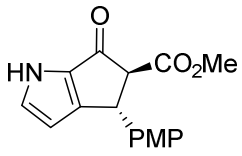


27b **28a**

This cyclization was performed according to the procedure of Sarpong.[8] To a 25 ml round-bottom flask was added dry $AlCl_3$ (0.231 g, 1.73 mmol, 1.1 eq) and DCE (15 ml). The flask was cooled to 0 °C. Aryl enone **27b** (0.869 g, 1.57 mmol, diastereomeric mixture) was added, and the reaction mixture turned deep red. The reaction mixture was stirred for 0.5 h at 0 °C and monitored by TLC. The reaction mixture was quenched with saturated aqueous potassium sodium tartrate solution, which turned the reaction mixture green, then yellow. The reaction mixture was extracted three times with Et_2O. The combined organic extracts were washed with brine, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude residue was purified by flash column chromatography (19:1 hexanes:ethyl acetate) to afford **28a** as a 3.6:1 mixture of *anti*:*syn* isomers (0.597 g, 1.24 mmol, 79% yield). **^{1}H NMR (400 MHz, $CDCl_3$, δ)**: 7.38 (d, *J* = 2.2 Hz, 1H), 7.16 (d, *J* = 2.2 Hz, 1H), 4.93 (s, 1H), 4.70 (s, 1H), 4.29 (d, *J* = 2.7 Hz, 1H), 3.79 (s, 3H), 3.51 (d, *J* = 2.7 Hz, 3H), 1.65 (s, 3H), 1.37 – 1.20 (m, 3H), 1.10 (d, *J* = 7.3 Hz, 18H). **^{13}C NMR (125 MHz, $CDCl_3$, δ)**: 197.6, 168.5, 157.2, 146.5, 143.3, 138.3, 131.7, 122.2, 114.1, 112.9, 61.0, 52.9, 50.3, 20.3, 17.8, 12.5. **IR (neat, cm^{-1})**: 2947, 2866, 2360, 2341, 1720, 1650, 1585, 1554, 1458, 1377, 1292, 1223, 1157, 1134, 1099, 1060, 960, 883, 798, 759, 729, 686, 667, 617. **HRMS** calculated for $C_{23}H_{34}O_4BrSi$ $(M)^+$ 483.1384, found: 483.13733.

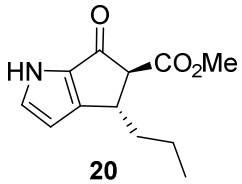
Known Cyclization and Rearrangement Products

Characterization and purification details for the following compounds have been previously reported.[3,6]



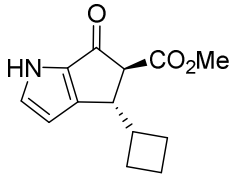
18

(room temperature, CH_2Cl_2, 12 h, 0.070 mmol of **18**, >99% yield)



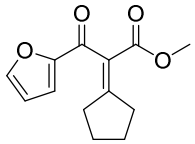
20

(60 °C, toluene, 16 h, 0.046 mmol of **20**, >99% yield)



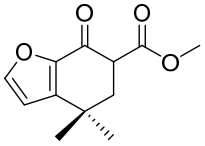
22

(80 °C, toluene, 4 h, 0.063 mmol of **22**, 74% yield)



24

(80 °C, toluene, 0.5 h, 0.406 mmol of **24**, 95% yield)



26

(80 °C, toluene, 18 h, 0.025 mmol of **26**, 50% yield)

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