Synthetic Studies towards Maoecrystal V

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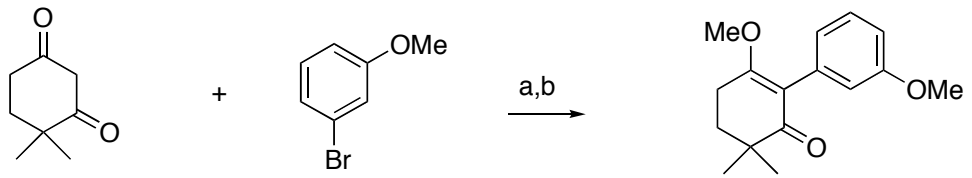
Supporting Information

Experimental Procedure

General information

Unless otherwise noted, all reactions were performed under an argon atmosphere using flame-dried glassware. Toluene, hexanes and CH_2Cl_2 were distilled over CaH_2. THF and Et_2O were distilled over sodium/benzophenone ketyl. All reagents were commercially available and used without further purification unless indicated otherwise. Thin layer chromatography (TLC) was performed on Silica Gel 60 F254 plates and was visualized with UV light and $KMnO_4$ stain. Preparative thin layer chromatography was performed with Merck silica gel 60-F254 coated 0.50 mm plates. Flash chromatography was performed with Sorbent Tech. silica gel 60. Yields reported are for isolated, spectroscopically pure compounds. NMR spectra were recorded on 300, 400 or 500 MHz instruments. The residual solvent protons (^1H) or the solvent carbons (^{13}C) were used as internal standards. ^1H NMR data are presented as follows: chemical shift in ppm downfield from tetramethylsilane (multiplicity, coupling constant, integration). The following abbreviations are used in reporting NMR data: s, singlet; br s, broad singlet; d, doublet; t, triplet; q, quartet; qt, quartet of triplets; dd, doublet of doublets; dt, doublet of triplets; AB, AB quartet; m, multiplet. High-resolution mass spectra were recorded by

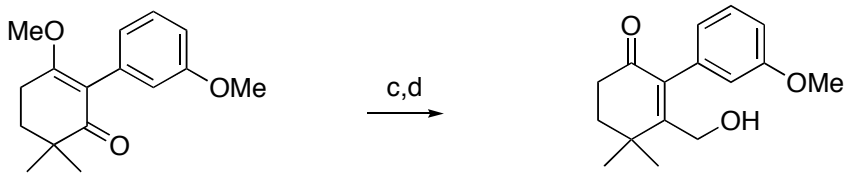
the Columbia University Mass Spectrometry Core facility on a JEOL HX110 spectrometer.



6 **7** **8**

(a) $Pd(OAc)_2$, 2-di-t-butylphosphino-2'-methylbiphenyl, K_3PO_4,, THF, 80 °C, 12 h, 91%; (b) $TMSCHN_2$, Hunig's base, CH_3CN/MeOH = 9:1, 6 h, 100%

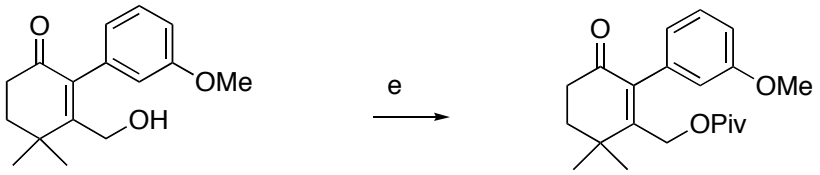
Compound 8: An oven-dried, 250 mL round bottom high-pressure flask containing a stirbar was capped with a rubber septum. This flask was then charged with 1,3-diketone **6** (5.1 g, 36 mmol), $Pd(OAc)_2$ (67 mg, 0.3 mmol), 2-di-t-butylphosphino-2'-methylbiphenyl (206 mg, 0.6 mmol), and K_3PO4 (14.6 g, 69 mmol). The flask was evacuated and backfilled with argon. 100 mL of THF and aryl bromide **7** (3.8 mL, 30 mmol) were sequentially injected, and the septum was replaced with a Teflon screw cap. The flask was sealed and heated at 80 °C for 12 hours. The reaction mixture was then diluted with MeOH and filtered. The filtrate was concentrated and dissolved in 27 mL of CH_3CN and 3 ml of MeOH under argon. To this mixture, Hunig's base (7.5 mL, 43 mmol) and a solution of $TMSCHN_2$ (21 mL, 2M) in hexane were added sequentially at 0 °C. The reaction mixture was stirred at room temperature for additional 12 hours. Solvents were removed under reduced pressure using rotavap. The residues were purified by flash chromatography to give a colourless oil. (7.1g, 91% yield). ^1H NMR ($CDCl_3$, 300 MHz): δ 7.24 (dd, *J* = 7.8, 7.8 Hz, 1H), 6.81-6.70 (m, 3H), 3.79 (s, 3H), 3.70 (s, 3H), 2.70 (dd, *J* = 6.3, 6.3 Hz, 2H), 1.93 (dd, *J* = 6.3, 6.3 Hz, 2H), 1.18 (s, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 201.7, 170.0, 158.9, 135.3, 128.4, 123.2, 118.4, 116.3, 112.3, 55.5, 55.1, 39.6, 34.0, 24.5, 22.7; HRMS (FAB, *m/z*) calcd for $C_{16}H_{21}O_3$ $[M+H]^+$ 261.1491, found 261.1485.



8 **9**

(c) Bu_3SnCH_2OMOM, BuLi, THF, -78 ºC to -40 ºC, 30 min, 0.5% HCl work-up, 75%; (d) HCl/MeOH, 50 ºC, 75%

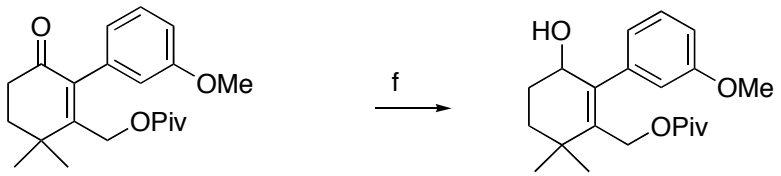
compound 9: A solution of Bu_3SnCH_2OMOM (5.9 g, 16 mmol) in 40 mL of anhydrous THF was cooled to -78 ºC under argon. BuLi in hexane (6.45 ml, 2.5 M) was added dropwise in 5 mins. The reaction mixture was stirred at this temperature for additional 10 min and a solution of **8** (2.6 g, 10 mmol) in 10 mL of THF was injected quickly. The reaction mixture was slowly warmed up to -40 ºC in 30 min and stirred for additional 1 hour at this temperature. Then the reaction mixture was warmed up to 0 ºC and acidified with 0.5% HCl solution until pH = 3. 30 min later, the reaction mixture was neutralized with saturated $NaHCO_3$ solution, extracted with ethyl acetate (3 x 20 mL) , and dried over $MgSO_4$. The extract was filtered over cotton and the solvent was removed under reduced pressure. The residue was put on a short silica gel column. The nonpolar impurity was removed by hexane and the polar part was collected using ethyl acetate as eluent. The ethyl acetate was removed under reduced pressure and the residue was dissolved in 50 mL of MeOH. 8 drops of concentrated HCl (37%) was added dropwise and the reaction mixture was stirred at 50 ºC for 3 hours. Then the mixture was cooled to room temperature, neutralized with saturated $NaHCO_3$ solution, and extracted with ethyl acetate (3 x 30 mL). The extract was dried over $MgSO_4$, filtered and the solvent was removed using rotovap. The residue was purified using flash chromatography to give a colorless oil (1.5 g, 56% for two steps). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.26 (dd, *J* = 7.6, 7.6 Hz, 2H), 6.84 (dd, *J* = 8.0, 2.4 Hz, 1H), 6.63 (d, *J* = 7.6 Hz, 1H), 6.60 (s, 1H), 4.08 (d, *J* = 5.6 Hz, 2H), 3.77 (s, 3H), 2.61 (dd, *J* = 6.4, 6.4 Hz, 2H), 1.95 (dd, *J* = 6.3, 6.3 Hz, 2H), 1.33 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 198.5, 162.7, 159.4, 138.5, 136.9, 129.3, 121.7, 115.1, 113.1, 60.4, 55.1, 37.6, 35.3, 34.6, 26.8; IR (neat): cm^{-1} 3441, 2960, 2926, 1701, 1670, 1596, 1484, 1466, 1287, 1256, 1047; HRMS (FAB, *m/z*) calcd for $C_{16}H_{20}O_3$ $[M+H]^+$ 261.1412, found 261.1417.



9 **10**

(e) PivCl, Py, DCM, 12 h, 96%;

Compound 10: compound **9** (1.3 g, 5 mmol) was dissolved in 20 mL of anhydrous DCM under argon at 0 ºC. Pyridine (2.4 mL, 30 mmol) was injected into this solution and 5 min later pivaloyl chloride (2.4 mL, 20 mmol) was injected into the mixture. The reaction mixture was stirred at this temperature for 12 hours, quenched with water, extracted with ether (3 x 20 mL) and dried over $MgSO_4$. After filtration of the drying agent, the solvent was removed under reduced pressure and the residue was purified by flash chromatography (1.65 g, 96%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.22 (dd, *J* = 8.0, 8.0 Hz, 1H), 6.82 (dd, *J* = 8.4, 2.0 Hz, 1H), 6.61 (d, *J* = 7.6 Hz, 1H), 6.58 (br s, 1H), 4.43 (s, 2H), 3.76 (s, 3H), 2.66 (dd, *J* = 6.4, 6.4 Hz, 2H), 2.13 (dd, *J* = 6.8, 6.8 Hz, 2H), 1.28 (s, 6H), 1.19 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 197.9, 177.6, 159.1, 157.3, 141.4, 136.2, 128.8, 122.0, 115.6, 113.1, 62.3, 55.1, 38.6, 37.5, 35.3, 34.7, 27.1; IR (neat): cm^{-1} 2952, 1724, 1667, 1453, 1437, 1301, 1259, 1156, 1034; HRMS (FAB, *m/z*) calcd for $C_{21}H_{28}O_4$ $[M]^+$ 344.1988, found 344.2001.

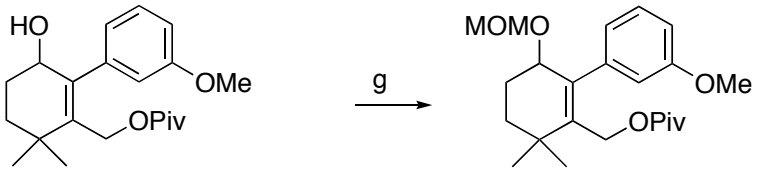


10 **10a**

(f) $NaBH_4$, $CeCl_3$, MeOH, 0 ºC, 2 h, 93%;

Compound 10a: compound 10 (3.4g, 10 mmol) and cerium chloride heptahydrate (5g, 13 mmol) were dissolved in 20 mL of methanol at 0 ºC. 5 min later $NaBH_4$ (600 mg, 15 mmol) was added carefully in three portions. The reaction mixture was stirred at 0 ºC for two hours and quenched with water. The product was extracted with ethyl acetate (3 x 30 mL) and dried over $MgSO_4$. After filtration of the drying agent, the solvent was removed under reduced pressure and the residue was purified using flash chromatography (3.22 g,

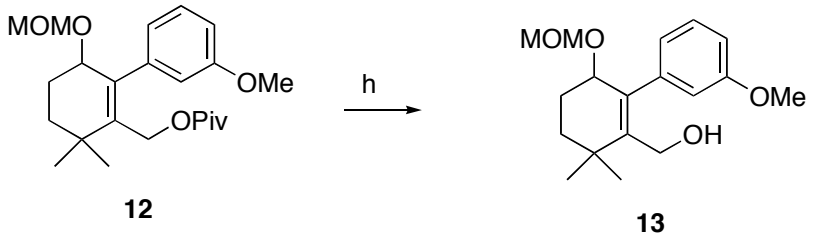
93%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.20 (dd, *J* = 7.6, 7.6 Hz, 2H), 6.79 (dd, *J* = 7.6 Hz, 1H), 6.75 (d, *J* = 7.6 Hz, 1H), 6.71 (s, 1H), 4.42 (d, *J* = 11.2 Hz, 1H), 4.32 (s, 1H), 4.11 (d, *J* = 11.2 Hz, 1H), 3.77 (s, 3H), 2.02-1.74 (m, 4H), 1.16 (s, 9H), 1.14 (s, 3H), 1.08 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 178.1, 159.4, 143.1, 140.7, 138.3, 129.2, 121.4, 114.8, 112.6, 69.1, 62.0, 55.1, 38.5, 34.7, 34.4, 28.3, 27.5, 27.2, 27.1; IR (neat): cm^{-1} 3435, 2960, 2936, 2870, 1724, 1597, 1577, 1480, 1285; HRMS (FAB, *m/z*) calcd for $C_{21}H_{30}O_4$ $[M]^+$ 346.2144, found 346.2158.



10a **11**

(g) MOMCl, Hunig's base, DCM, 12 h, 95%;

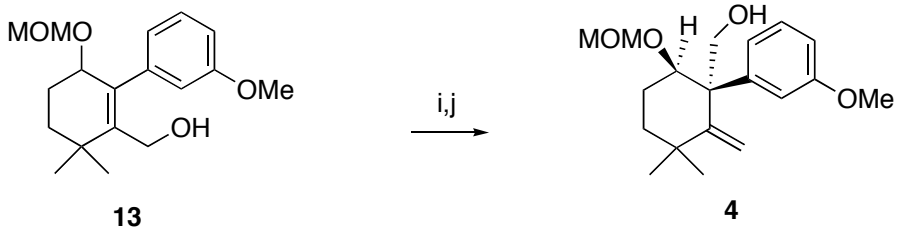
Compound 11: compound **10a** (1.8 g, 5.2 mmol) and Hunig's base (2.72 mL, 15.6 mmol) were dissolved in anhydrous DCM under argon at room temperature. MOMCl (775 mL, 11 mmol) was injected into the solution and the reaction mixture was stirred at room temperature for 12 hours. Then the reaction was quenched with 2 drops of water. The solvent was removed under reduced pressure and the residue was purified using flash chromatography (1.93 g, 95%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.16 (dd, *J* = 7.6, 7.6 Hz, 1H), 6.79-6.74 (m, 3H), 4.53 (d, *J* = 7.2 Hz, 1H), 4.46 (d, *J* = 11.6 Hz, 1H), 4.27-4.25 (m, 1H), 4.24 (d, *J* = 7.2 Hz, 1H), 4.10 (d, *J* = 11.6 Hz, 1H), 3.76 (s, 3H), 2.85 (s, 3H), 1.94-1.77 (m, 3H), 1.49-1.44 (m, 1H), 1.16 (s, 9H), 1.13 (s, 3H), 1.09 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 178.1, 159.1, 143.8, 141.6, 139.4, 128.6, 121.7, 114.8, 112.3, 94.9, 73.4, 62.0, 55.2, 54.8, 38.5, 34.4, 34.3, 28.4, 27.1, 26.7, 25.1; IR (neat): cm^{-1} 2959, 2935, 1724, 1577, 1480, 1284, 1152, 1032; HRMS (FAB, *m/z*) calcd for $C_{23}H_{34}O_5$ $[M]^+$ 390.2406, found 390.2418.



12 **13**

(h) DIBAL-H, -78 ºC, DCM, 30 min, 95%;

Compound 13 : compound **12** (1.95 g, 5 mmol) was dissolved in anhydrous DCM under argon and cooled to -78 ºC. 7.5 mL of DIBAL-H in hexane (2 M) was injected into the reaction mixture slowly and the reaction mixture was stirred for 30 min at this temperature. Then the reaction was quenched with 0.5 mL of methanol and 5 g of sodium sulfate decahydrate. After warming up to room temperature, the mixture was stirred for additional 1 hour and filtered. The solvent was removed using rotovap and the residue was purified with flash chromatography (1.45, 95%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.22 (dd, *J* = 7.6, 7.6 Hz, 1H), 6.82-6.79 (m, 3H), 4.53 (d, *J* = 7.2 Hz, 1H), 4.25 (d, *J* = 7.2 Hz, 1H), 4.21 (dd, *J* = 4.0, 4.0 Hz, 1H), 4.05 (dd, *J* = 12.0, 4.4 Hz, 1H), 3.86 (dd, *J* = 12.0, 5.6 Hz, 1H), 3.80 (s, 3H), 2.88 (s, 3H), 1.93-1.76 (m, 3H), 1.48-1.43 (m, 1H), 1.22 (s, 3H), 1.14 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 159.5, 144.7, 142.5, 138.3, 129.2, 121.3, 114.4, 112.6, 94.9, 73.8, 59.7, 55.2, 54.9, 34.5, 34.4, 28.4, 26.8, 25.2; IR (neat): cm^{-1} 3458, 2936, 1597, 1577, 1483, 1149, 1027; HRMS (FAB, *m/z*) calcd for $C_{18}H_{26}O_4$ $[M]^+$ 306.1831, found 306.1836.



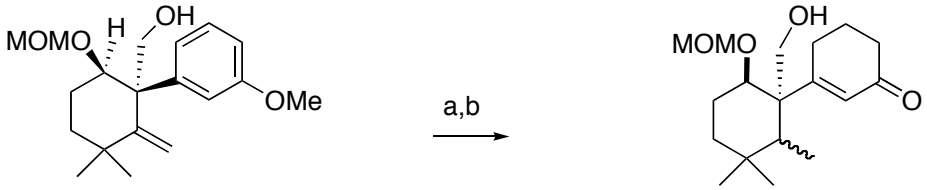
13 **4**

(i) KH, 18-crown-6, ICH_2SnBu_3, 0 ºC, THF, 6 h, 90%; (j) BuLi, -78 ºC to -20 ºC, THF, 6 h, 88%.

Compound 4: an oven-dried round-bottomed flask was charged with KH (360 mg, 9 mmol) and 20 mL of THF under argon at 0 ºC. A solution of compound **4** (920 mg, 3 mmol) in 5 mL of THF was injected slowly into the flask. 30 mins later, 18-crown-6 (780 mg, 3 mmol) was added. The reaction mixture was stirred for additional 5 min and then α-iodomethyl tributylstanne (3.9 g, 9 mmol) was injected and the reaction mixture was

stirred at this temperature for 6 hours. After quenched with water carefully, the product was extracted with ether (3 x 20 mL) and dried over $MgSO_4$. The drying agent was removed by filtration and the solvent was concentrated using rotovap. The residue was purified by flash chromatograph. And the desired product was dissolved in THF under argon. The mixture was cooled to -78 ºC and BuLi in hexane (3.6 mL, 9 mmol) was injected dropwise. The temperature was slowly warmed up to -20 ºC in 6 hours and the reaction was quenched with saturated NH_4Cl solution, extracted with ether (3 x 30 mL), and dried over $MgSO_4$. After filtration, the extract was concentrated and the residue was purified by chromatography (0.78g, 80% for 2 steps).

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.25-7.14 (m, 3H), 6.75-6.71 (m, 1H), 5.37 (s, 1H), 5.34 (s, 1H), 4.78 (d, *J* = 10.4 Hz, 2H), 3.96 (dd, *J* = 16.0, 6.4 Hz, 1H), 3.84-3.79 (m, 2H), 3.78 (s, 3H), 3.45 (s, 3H), 3.26 (dd, *J* = 9.6, 9.6 Hz, 1H), 2.27 (dddd, *J* = 16.4, 16.4, 16.4, 6.8 Hz, 1H), 1.96 (dddd, *J* = 17.6, 6.0, 6.0, 6.0 Hz, 1H), 1.46-1.31 (m, 2H), 1.10 (s, 3H), 0.52 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 159.0, 154.6, 143.0, 128.5, 121.4, 115.4, 110.8, 110.7, 96.8, 80.5, 66.5, 56.3, 55.9, 55.0, 38.5, 36.9, 31.3, 30.1, 24.9; IR (neat): cm^{-1} 3485, 2953, 1606, 1579, 1485, 1464, 1053, 1027; HRMS (FAB, *m/z*) calcd for $C_{19}H_{28}O_4$ $[M+Na]^+$ 343.1885, found 343.1868.

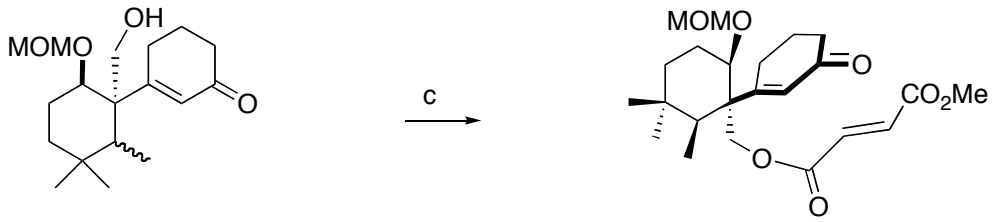


4 **13**

(a) Li, NH_3(l), *t*-BuOH/THF, -78 ºC, 20 min, - 33 ºC, 40min; (b) 1 N HCl, 0 ºC, THF/MeOH (10/1), 8 h, 2 steps, 78%;

Compound 13: an oven-dried three-neck flash equipped with a dry ice acetone condenser was charged with 30 mg of compound **4**, 1 mL of THF, 1 mL of tertbutylol, and 2 mL of liquid ammonia. Then 20 mg of lithium was added and the reaction mixture was stirred at -78 ºC for 20 mins and -33 ºC for 40 mins. Then ammonium chloride solid was added to quench the reaction until the blue color disappeared. The reaction mixture was then

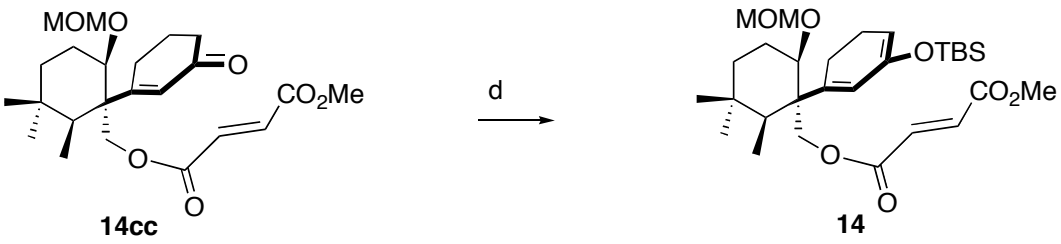
slowly warmed up to room temperature to vaporize the ammonia. The residue was extracted with ethyl acetate (3 x 20 mL) and dried over magnesium sulfate. After filtration of the drying agent, the solvent was removed under the reduced pressure and the residue was dissolved in THF/MeOH mixed solvent (THF/MeOH = 10: 1). The mixture was cooled to 0 ºC and 2 drop of 1N HCl solution was added. The reaction mixture was stirred at 0 ºC for 12 hours and quenched with saturated $NaHCO_3$. The extract was dried over $MgSO_4$. After filtration, the solvent was removed using rotovap and the residue was used without purification in the next step.



13 **14**

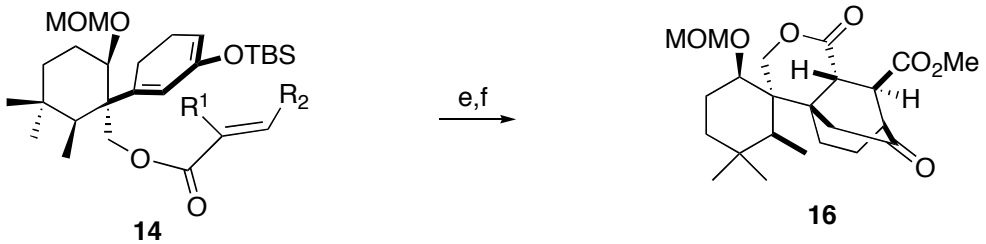
(c) **14**, Py, DCM, 0 ºC;

Compound 14: **13** (28 mg) and pyridine (73 υL, 0.9 mmol) was dissolved in DCM under argon at 0 ºC. Acyl chloride (65 mg, 0.4 mmol) in 1 mL of DCM was injected slowly. After addition of acyl chloride solution, the reaction mixture was stirred at this temperature for 12 hours. The reaction was then quenched with methanol and the solvent was removed under the reduced pressure. The residue was purified using preparation TLC. **14cc**: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 6.88 (d, *J* =15.6 Hz, 2H), 6.52 (s, 1H), 4.68 (d, *J* = 6.8 Hz, 1H), 4.52 (d, *J* = 7.2 Hz, 1H), 4.45 (d, *J* = 11.2 Hz, 1H), 4.22 (d, *J* = 11.2 Hz, 1H), 3.82 (s, 3H), 3.74 (dd, *J* = 12, 4 Hz, 1H), 3.29 (s, 3H), 2.63-2.56 (m, 1H), 2.52-2.29 (m, 3H), 2.13 (dddd, *J* = 13.2, 13.2, 13.2, 4 Hz, 1H), 2.00-1.97 (m, 1H), 1.92-1.84 (m, 2H), 1.67 (ddd, *J* = 7.2, 7.2, 7.2 Hz, 1H), 1.53 (ddd, *J* = 13.6, 3.6, 3.6 Hz, 1H), 1.37 (ddd, *J* = 13.2, 13.2, 4 Hz, 1H), 1.04 (d, *J* = 7.6 Hz, 3H), 0.89 (s, 3H), 0.84 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 199.8, 165.3, 164.5, 163.7, 133.7, 133.3, 131.4, 96.2, 80.1, 65.2, 55.9, 52.4, 52.1, 45.2, 40.1, 37.6, 34.4, 32.0, 29.1, 25.0, 23.7, 21.2, 12.4 ; IR (neat): cm^{-1} 2967, 1728, 1680, 1579, 1480, 1280, 1256, 1147; HRMS (FAB, *m/z*) calcd for $C_{23}H_{35}O_7$ $[M + H]^+$ 423.2383, found 423.2400.



(d) TBSOTf, TEA, DCM, 0 ºC, 15 h, 81%;

Compound 14: an oven-dried flask was charged with starting material (22 mg, 0.05 mmol), TEA (22 μL, 0.15 mmol), and 5 mL of DCM under argon at 0 ºC. TBSOTf (27 μL, 0.1 mmol) was added and the reaction mixture was stirred at this temperature for 12 hours. The product was purified using preparation TLC. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 6.88 (d, *J* =15.6 Hz, 2H), 6.18 (s, 1H), 4.91-4.89 (m, 1H), 4.69 (d, *J* = 6.8 Hz, 1H), 4.52 (d, *J* = 6.8 Hz, 1H), 4.45 (d, *J* = 11.6 Hz, 1H), 4.7 (d, *J* = 11.2 Hz, 1H), 3.82 (s, 3H), 3.74 (dd, *J* = 12.4, 4 Hz, 1H), 3.30 (s, 3H), 2.25-2.01 (m, 5H), 1.89-1.84 (m, 1H), 1.56 (ddd, *J* = 7.2, 7.2, 7.2 Hz, 1H), 1.49 (ddd, *J* = 13.6, 3.6, 3.6 Hz, 1H), 1.35 (ddd, *J* = 13.2, 13.2, 4 Hz, 1H), 1.01 (d, *J* = 7.6 Hz, 3H), 0.92 (s, 9H), 0.89 (s, 3H), 0.86 (s, 3H), 0.12 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 165.4, 164.8, 148.9, 138.7, 133.8, 133.2, 127.4, 102.5, 96.5, 81.0, 65.5, 55.6, 52.3, 50.8, 44.8, 40.9, 34.3, 32.3, 26.4, 25.7, 25.3, 22.7, 20.6, 18.1, 12.1; IR (neat): cm^{-1} 2952, 2360, 1725, 1721, 1667, 1455, 1300, 1258, 1155, 1035; HRMS (FAB, *m/z*) calcd for $C_{29}H_{49}O_7Si$ $[M + H]^+$ 537.3248, found 537.3237.



(e) 180 ºC, sealed tube, toluene, 12 h; (f) TBAF, 0 ºC, THF, 2 steps, 48%.

Compound 16: compound **14** (37 mg, 0.07 mmol) was dissolved in 5 mL of anhydrous toluene in a high-pressure tube. The reactor was wash with BSA first and dried in oven for 12 hours. The reaction mixture was degassed with argon and then stirred at 180 ºC for 16 hours. After cooling to room temperature and the mixture was transfer to a round bottom flask. The mixture was further cooled to 0 ºC and TBAF in THF (70 μL, 0.07 mmol) was added. 5 mins later the reaction was quenched with saturated ammonium chloride solution. After extracting with ethyl acetate (3 x 10 mL), the solution was dried over $MgSO_4$. The drying agent was removed by filtration and the solvent was removed under reduced pressure. The residue was purified using flash chromatography (14 mg, 48%) ^{1}H NMR ($CDCl_3$, 400 MHz): δ 4.76 (d, *J* = 7.2 Hz, 1H), 4.68 (d, *J* = 12.0 Hz, 1H), 4.62 (d, *J* = 6.8 Hz, 1H), 4.12 (br s, 1H), 3.94 (dd, *J* = 3.2, 3.2 Hz, 1H), 3.88 (d, *J* = 12.0 Hz, 1H), 3.67 (s, 3H), 3.48 (dd, *J* = 18.8, 3.2 Hz, 1H), 3.44 (s, 3H), 3.11 (dd, *J* = 12.4, 4.8 Hz, 1H), 2.93 (d, *J* = 18.4 Hz, 1H), 2.74 (br s, 1H), 2.04-1.72 (m, 5H), 1.60-1.55 (m, 2H), 1.40-1.29 (m, 2H), 1.19 (d, *J* = 7.6 Hz, 3H), 0.97 (s, 3H), 0,88 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 212.5, 175.7, 173.5, 96.0, 84.1, 78.0, 56.8, 56.6, 52.5, 48.7, 47.0, 44.7, 43.9, 43.3, 41.6, 40.7, 34.1, 32.7, 27.2, 25.9, 23.1, 21.9, 13.9; IR (neat): cm^{-1} 2952, 2850, 1740, 1665, 1461, 1311, 1184, 1023; HRMS (FAB, *m/z*) calcd for $C_{23}H_{35}O_7$ $[M + H]^+$ 423.2383, found 423.2396.