ARYLLEAD(IV) REAGENTS IN SYNTHESIS: FORMATION OF THE C11 QUATERNARY CENTER OF *N*-METHYLWELWITINDOLINONE C ISOTHIOCYANATE

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Supporting Information

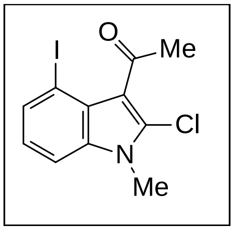
General Methods

Melting point determinations are uncorrected. Infrared spectra were recorded as thin films on salt plates on Perkin-Elmer 781 spectrophotometer, with ν_{max} in inverse centimeters. Proton (^{1}H NMR) and carbon (^{13}C NMR) magnetic resonance spectra were obtained in $CDCl_3$ at 500MHz and 62 MHz or 125MHz, respectively (unless otherwise noted). The following abbreviation were utilized to describe peak patterns when appropriate: br = broad, s = singlet, d = doublet, t = triplet, q = quartet and m = multiplet.

All air and moisture sensitive reactions were carried out under an atmosphere of dry argon or nitrogen using oven-dried or flame-dried glassware and standard syringe techniques. THF, Et_2O, benzene, toluene were distilled from sodium/benzophenone. Methylene chloride, TMSCl, Et_3N, diisopropylamine, $HN(TMS)_2$, DME, DMSO were distilled from CaH_2. DMF was pretreated with 4Å molecular sieves overnight and then distilled from 4Å molecular sieves below 70 ^{o}C under vacuum prior to the use. Acetone was pretreated and distilled as DMF but under an atmosphere of N_2. CuCN was oven-dried at 60^{o}C before use. $Pb(OAc)_4$ was dried over solid KOH under vacuum for 3 h before use.

General degassing procedure is ‘freeze-pump-thaw’. The solvent was frozen in a dry ice bath or liquid N_2, connected to high vacuum for 5 min, then allowed to thaw under a stream of N_2. This step was repeated 3 times. The reactions could then be run under N_2.

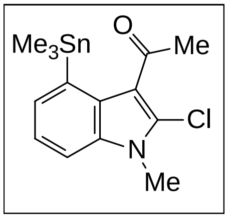
Flash chromatography was performed on Premium Grade 60, 40-75 mesh silica gel from Sorbent Technology using EtOAc-hexanes mixtures as solvent unless otherwise indicated. Thin layer chromatography TLC was carried out on Whatman silica gel plates with UV detection.



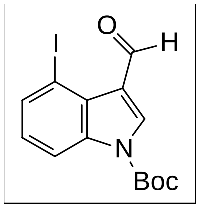
***N*-Methyl-2-chloro-3-acetyl-4-iodoindole (6).** To a stirred solution of ketone **11** (4.0 g, 19.3 mmol), in TFA (40 mL) was added freshly made thallium trifluouroacetate (10.8 g, 21.1 mmol). This solution was allowed to react for 2 h at room temperature. TFA was removed *in vacuo.* The resulting light brown solid was immediately utilized for iodination without further purification.

To a stirred solution of the above indole thallium trifluoroacetate intermediate in DMF (20 mL) was added CuI (5.5 g, 29 mmol) and I_2 (10 g, 39.4 mmol). This solution was allowed to stir for 1 h at RT and poured into $CHCl_3$/MeOH (9/1, 100 mL). The entire mixture was then filtered through celite. The resulting organic layer was successively washed with saturated Na_2SO_3 (3 x 20 mL), H_2O (20 mL), brine (20 mL), dried over $MgSO_4$, and concentrated. Purification on silica gel chromatography (EtOAc-hexanes

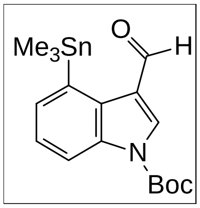
1/5) gave iodoindole **6** (white crystal, 2.6 g, 78%): R$_f$ 0.24 (EtOAc-hexanes 1/5); mp 100-102 ^{o}C; IR 3048, 2924, 2849, 1670, 1492, 1466, 1417, 1366, 1332, 1214, 1179, 1103, 999, 763, 734; ^{1}H-NMR δ 7.69 (d, *J* = 7.5Hz, 1H); 7.28 (d, *J* = 7.5Hz, 1H); 6.98 (t, *J* = 7.5Hz, 1H); 3.76 (s, 3H); 2.72 (s, 3H); ^{13}C-NMR δ 198.7, 135.9, 133.8, 127.6, 126.9, 124.3, 109.6, 84.8, 34.3, 30.9; Anal. calcd. for $C_{11}H_9ClNO$, C 39.61, H 2.72, found, C 39.75, H 2.61.



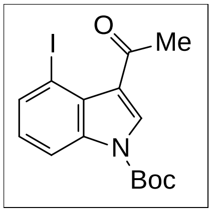
***N*-Methyl-2-chloro-3-acetyl-4-trimethylstannylindole (12)**: 4-Iodoindole **6** (33 mg, 0.1 mmol), hexamethylditin (30 μL, 0.15 mmol), $PdCl_2(PPh_3)_2$ (10 mg, 10 μmol) and toluene (3 mL) were added to a 10 mL round-bottom flask fitted with a refluxing condenser. The mixture was heated to reflux at 110^{o}C for 5h. The reaction was allowed to cool to RT, filtered through a bed a celite, and concentrated. Purification by silica gel chromatography (EtOAc-hexanes 1/8) affords **12** (off-white solid, 18 mg, 50%): R$_f$ 0.19 (EtOAc-hexanes 1/15); mp 166-168^{o}C; IR 3053, 2985, 2305, 1638, 1489, 1420, 1366, 1262, 895, 740, 698; ^{1}H-NMR δ 7.57 (dd, *J* = 8.5, 2, 1H), 7.30 (m, 2H), 3.81 (s, 3H), 2.69 (s, 3H), 0.3 (s, 9H) with 0.35 and 0.25 satellite peaks; ^{13}C-NMR δ 193.4, 137.8, 135.3, 132.8, 132.1, 131.8, 123.3, 114.8, 109.5, 30.6, 30.5, -4.6; HRMS for $C_{14}H_{18}NOSn$, calcd.(M^++1), 372.0179, found, 372.0177.



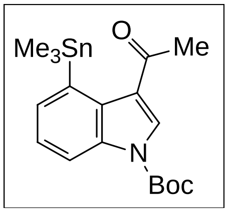
***N-tert*-butoxycarbonyl-4-Iodoindole-3-carboxaldehyde:** To a solution of 4-iodo-3-formylindole (103 mg, 0.4 mmol) in acetonitrile (5 mL), was added Boc_2O (88 mg, 0.5 mmol) and DMAP (5 mg, 0.04 mmol). The resulting mixture was kept at rt for 1.5h, and concentrated. The crude product can be purified on silica gel (EtOAc-hexanes 1/8) to yield desired iodoaldehyde (white solid, 1.33 g, 90%): R$_f$ 0.48 (EtOAc-hexanes 1/5); mp 118-119 ^{o}C; IR 3143, 2987, 2253, 1750, 1668, 1529, 1469, 1417, 1366, 1262, 1147, 1093, 908, 734, 648; ^{1}H-NMR δ 11.23 (s, 1H), 8.39 (s, 1H), 8.33 (d, *J* = 8.5Hz, 1H), 7.83 (d, *J* = 8Hz, 1H), 7.09 (t, *J* = 8.5, 8Hz, 1H), 1.67 (s, 3H); ^{13}C-NMR δ 186.1, 148.3, 137.1, 135.8 132.5, 130.5, 126.4, 120.9, 115.6, 86.2, 83.2, 28.1. Anal. calcd. for $C_{14}H_{14}INO_3$, C 45.30, H 3.80, found, C 45.20, H 3.93.



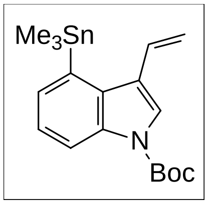
***N-tert*-butoxycarbonyl-4-trimethylstannylindole-3-carboxyaldehyde (13).** Following the same procedure used to prepare **12,** compound **13** can be prepared and purified by silica gel chromatography (CH_2Cl_2-hexanes 1/4) as a white thick oil (yield, 55%): R_f 0.22 (EtOAc-hexanes 1/15); IR 2982, 2917, 2252, 1728, 1678, 1548, 1416, 1370, 1338, 1261, 1149, 1102, 1049, 908, 733, 648; ^{1}H-NMR δ 9.91 (s, 1H), 8.28 (s, 1H), 8.20 (d, *J* = 13Hz, 1H), 7.62 (d, *J* = 6Hz, 1H), 7.39 (t, *J* = 7.5Hz, 1H), 1.72 (s, 9H), 0.34 (s, 9H); ^{13}C-NMR δ 185.4, 148.7, 138.6, 137.4, 136.1, 133.8, 132.1, 125.4, 123.2, 115.3, 85.8, 28.2, -5.2; HRMS for $C_{17}H_{23}NO_3Sn$, calcd., 409.0700, found, 409.0705.



***N-tert*-Butoxycarbonyl-3-acetyl-4-iodoindole**: Following the same procedure used above, desired iodoketone can be prepared and purified by silica gel chromatography as a white solid (yield, 77%): R_f 0.34 (EtOAc-hexanes 1/5); mp 102-103 °C; IR 3054, 2985, 2684, 2306, 1744, 1682, 1545, 1420, 1363, 1264, 1151, 895, 739; ^{1}H-NMR δ 8.23 (d, *J* = 8.5Hz, 1H), 8.04 (s, 1H), 7.84 (d, *J* = 7.5Hz, 1H), 7.05 (t, *J* = 8.5, 7.5Hz, 1H), 2.63 (s, 3H), 1.69 (s, 9H); ^{13}C-NMR δ 194.6, 148.6, 136.6, 136.5, 130.4, 130.3, 126.6, 123.9, 115.2, 94.9, 85.7, 31.8, 28.2, 27.4; Anal. calcd. for $C_{15}H_{16}INO_3$, C, 46.77, H, 4.19, found, C 46.90, H 4.32.

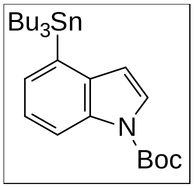


***N*-(*tert*-Butoxycarbonyl)-3-acetyl-4-trimethylstannyl indole (14)**: Following the same procedure used to prepare **12,** compound **14** can be prepared and purified by silica gel chromatography (CH_2Cl_2-hexanes 1/4) as a white thick oil (yield, 50%): R_f 0.3 (EtOAc-hexanes 1/15); IR 2982, 2910, 2252, 1739, 1660, 1544, 1472, 1412, 1352, 1271, 1129, 1076, 908, 733, 648; ^{1}H-NMR δ 8.31 (s, 1H), 8.16 (d, *J* = 7.5Hz, 1H), 7.61 (d, *J* = 7.5Hz, 1H), 7.35(t, *J* = 7.5Hz, 1H), 2.58 (s, 3H), 1.75 (s, 9H), 0.34 (s, 9H); ^{13}C-NMR δ 193.9, 149.1, 138.1, 135.5, 133.8, 133.6, 133.2, 124.8, 121.8, 115.2, 85.6, 28.1, 27.4, -4.8; HRMS for $C_{18}H_{25}NO_3Sn$, calcd., 423.0856, found, 423.0860.



***N*-*tert*-butoxycarbonyl-3-vinyl-4-trimethylstannyl indole (15).** To PPh_3CH_3Br (126 mg, 0.35 mmol) in THF (3 mL) at 0 °C was added LDA (0.36 mmol) solution in THF (1 mL). The resulting mixture was stirred and kept at 0 °C for 1.5 h to generate a yellow solution of $PPh_3{=}CH_2$. Compound **14** (130 mg, 0.32 mmol) was added and the resulting mixture was stirred for another 2 h. TLC showed the completion of the reaction. Saturated ammonium chloride solution was added to quench the reaction. The mixture was extracted with ether (3 x 5 mL). The combined organic layers were washed with brine, dried over sodium sulfate, filtered, and concentrated. The residue was purified by silica gel chromatography to afford **15** (colorless oil, 100mg, 76%): R_f 0.20 (EtOAc-hexanes 1/15); IR 2928, 2920, 2253, 1726, 1425, 1401, 1365, 1333, 1279, 1257, 1158, 1050, 908, 734, 649; ^{1}H-NMR δ 8.21 (d, *J* = 8.5Hz, 1H), 7.74 (s, 1H), 7.40 (d, *J* = 9Hz, 1H), 7.30 (t, *J* = 7Hz, 1H), 6.91 (dd, *J* = 10.5, 10.5Hz, 1H), 5.65 (d, *J* = 17Hz, 1H), 5.31 (d, *J* = 10.5Hz, 1H), 1.69 (s, 9H), 0.41 (s, 9H);

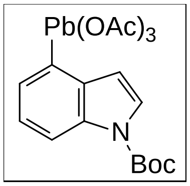
^{13}C-NMR δ 149.7, 135.3, 135.2, 131.4, 131.3, 128.8, 123.8, 122.6, 122.4, 116.1, 115.8, 83.8, 28.2, -6.5; HRMS for $C_{18}H_{25}NO_2Sn$, calcd., 407.0907, found, 407.0892.



***N*-(*tert*-butoxycarbonyl)-4-tributylstannyl indole (17)**. To potassium hydride (3.1 g, 35% in mineral oil, 27 mmol, washed with pentane three times) in dry ether (50 mL) at 0 °C was added 4-bromoindole (**16**, 5.0 g, 25.5 mmol) in ether (10 mL) dropwise over 10 min. The reaction was kept at the same temperature for 0.5 h, then cooled to –78 °C. *t*-Butyllithium solution (1.7*M* in hexane, 33 mL, 56 mmol) which was precooled to –78 °C in ether (30 mL) in another flask, was added through a cannula. A white participate formed and the reaction mixture was kept for 1 h at –78 °C. Tri-*n*-butylstannyl chloride (12.5 g, 38.25 mmol) in ether (10 mL) was added in one portion. The resulting mixture was kept for another hour at low temperature and then allowed to warm to room temperature. The reaction was quenched with ammonium chloride solution (30 mL). Standard extraction workup afforded a yellow liquid product.

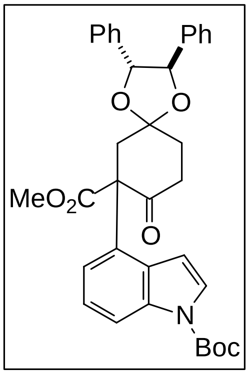
To this crude product in acetonitrile (30 mL) was added Boc_2O (8.3 g, 38.2 mmol) and DMAP (311 mg, 2.55 mmol). The resulting mixture was stirred at room temperature for 1 h and concentrated. The residue was diluted with methylene chloride, washed with water, sodium bicarbonate, and brine, dried over Na_2SO_4, filtered, and concentrated to give a sticky liquid. The residue was purified by column chromatography (EtOAc-hexanes 1/20) to afford **16** (colorless oil, 9.7 g. 76%): R_f 0.6 (EtOAc-hexanes 1/15); IR 2960, 2928, 2252, 1727, 1533, 1457, 1405, 1346, 1150, 1149, 1093, 1025, 908, 734; ^{1}H NMR δ 8.18 (d, *J* = 7Hz, 1H), 7.68 (d, *J* = 3Hz, 1H), 7.39 (dd, *J* = 7. 1Hz, 1H). 7.32 (dd, *J* = 8, 6.5Hz, 1H), 6.56 (d, *J* = 3.5Hz, 1H), 1.74 (s, 9H), 1.61 (m, 6H), 1.40 (m, 6H), 1.21 (t, *J* =

6Hz, 6H), 0.94 (t, *J* = 7Hz, 6H); ^{13}C NMR δ 149.9, 137.3, 134.8, 134.1, 131.1, 125.7, 123.8, 115.1, 109.4, 83.6, 30.9, 29.3, 28.3, 27.5, 13.6, 10.1; HRMS for $C_{20}H_{41}NO_2Sn$, calcd, 507.2159, found. 507.2154.

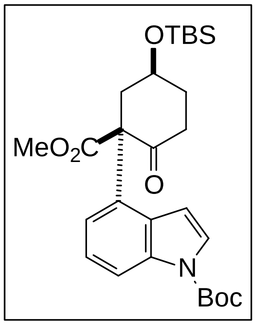


***N-tert*-butoxycarbonyl-4-indole lead triacetate (18)**. To indole stannane **17** (0.87 g, 1.72 mmol) in chloroform (10 mL) was added successively lead(IV) tetraacetate (0.8 g, 1.8 mmol) and mercury (II) trifluoroacetate (40 mg, 0.9 mmol). The reaction was warmed to 40 °C and kept for 2 h. The mixture was allowed to cool, filtered through a bed of celite. The filtrate was dried to give red solid product. The solid was washed with petroleum ether a few times to afford product **18** (light red solid, 1.02 g, 98%) that was pure enough for the next reaction: R_f 0 (EtOAc-hexanes 1/15); mp 64-68 °C; IR 3054, 2982, 1737, 1560, 1416, 1342, 1320, 1265, 1142, 1025, 737, 700; ^{1}H-NMR δ 8.34 (d, *J* = 8Hz, 1H), 7.72 (d, *J* = 3Hz, 1H), 7.51 (d, J = 8Hz, 1H), 7.46 (t, *J* = 8, 7.5Hz, 1H) 6.97 (d, *J* = 7.5Hz, 1H), 2.11 (s, 9H), 1.68 (s, 9H); ^{13}C-NMR δ 180.7, 153.5, 149.1, 137.2, 132.2, 128.5, 128.3, 125.5, 125.2, 119.0, 105.9, 84.9, 28.4, 20.6; Anal. for $C_{19}H_{23}NO_8Pb$, calcd, C 38.00, H 3.86, found, C 38.04, H 3.67.

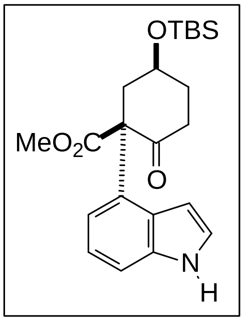
Gerneral procedure for organolead coupling reaction: To a crude product solution of indole lead triacetate **18** (1.4 equiv) at 40 °C was added the premixed solution of *β*-ketoester (1.0 equiv) and pyridine (4 equiv) in $CHCl_3$. The reaction was stirred for 5 h, and filtered through a bed of celite. 2*M* H_2SO_4 Solution was added into filtrate. The aqueous layer was extracted with $CHCl_3$ for three times. The combined organic layers were successively washed with 2*M* H_2SO_4 solution, H_2O, $NaHCO_3$ and brine, dried over Na_2SO_4, filtered, and concentrated to give a crude product. The residue can be purified by silica gel chromatography to furnish the pure product.



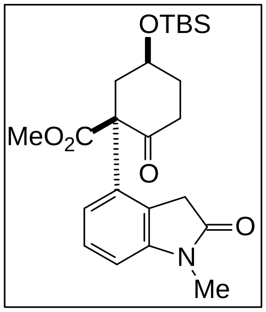
Methyl (1´*R*,2´*R*,2*RS*)-1-(*N*-*tert*-butoxycarbonylindol-4´-yl)-5-(1´,2´-diphenyl)ethylenedioxy-2-oxo-cyclohexan-1-carboxylate (19): White solid, 2:1 mixture of diastereomers, 98%: R_f 0.26 (EtOAc-hexanes 1/5); mp 108-118 ^{o}C; IR 3054, 2985, 2306, 1730, 1423, 1264, 1159, 1129, 896, 740, 699; ^{1}H NMR δ 8.23 (s, 1H), 8.26 (dd, *J* = 4, 6.5Hz, 1H), 7.36 (m, 10H), 7.28 (m, 1H), 7.12 (t, *J* = 3Hz, 1H), 6.41 (dd, *J* = 4, 3.5Hz, 1H), 4.88 (dd, *J* = 3.5, 4.5Hz), 3.5~3.58 (ds, 3H), 3.07 (dd, *J* = 19, 19Hz, 1H), 2.78 (m, 1H), 2.53 (m, 1H), 1.67 (s, 9H); ^{13}C NMR δ 204.2, 172.3, 149.7, 136.2, 135.6, 130, 128.8, 128.5, 127.6, 126.8, 126.5, 125.7, 124.1, 120.3, 115.5, 107.9, 107.2, 86.5, 83.8, 63.1, 53.1, 44.9, 37.9, 36.8, 28.3, 21.2, 14.3; HRMS for $C_{37}H_{39}NO_5$, calcd, 581.2413, found, 581.2413.



Methyl 1-(*N*-*tert*-butoxycarbonylindol-4´-yl)-5-*tert*-butyldimethylsilyloxy-2-oxo-cyclohexan-1-carboxylate (**23).** White solid, 98%: R_f 0.48 (EtOAc-hexanes 1/5); mp 68-70 ^{o}C; IR 2940, 2858, 2249, 1727, 1469, 1417, 1350, 1247, 1133, 1097, 1024, 907, 733; ^{1}H-NMR δ 8.21 (d, *J* = 8Hz, 1H), 7.57 (d, *J* = 4Hz, 1H), 7.32 (t, *J* = 7.5, 1H), 7.15 (d, *J* = 2Hz, 1H), 6.4 (d, *J* = 4Hz, 1H), 4.22 (m, 1H), 3.67 (s, 3H), 2.89 (m, 1H), 2.84 (d, *J* = 5.5Hz), 2.50 (m, 1H), 2.01 (m, 2H), 1.66 (s, 9H), 0.9 (s, 9), 0.10 (s, 3H), 0.08 (s, 3H); ^{13}C NMR δ 207.6, 171.5, 149.6, 136, 129.9, 129, 8, 126.0, 124.01, 120.7, 115.4, 106.9, 83.9, 76.9, 66.0, 64.1, 52.7, 42.9, 36.9, 35.8, 28.3, 25.9, 18.3, -4.5, -4.7; HRMS for $C_{27}H_{39}NO_6Si$, calcd., 501.2547, found, 501.2543.

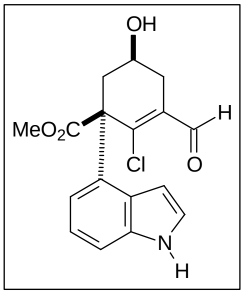


Methyl 1-(4´-indolyl)-2-oxo-cyclohexane-1-carboxylate (24). Compound **23** was added to a round-bottom flask and connected to high vacuum or N_2, placed into 200 °C oil bath for 4 h to give black solid. Purify by silica gel chromatography ((EtOAc-hexanes 1/4) afforded product **24** (white solid, mg, 90%): R_f 0.42 (EtOAc-hexanes 1/2); mp 68-70 °C; IR 3459, 3396, 2952, 2860, 2252, 1717, 1460, 1431, 1359, 1253, 1104, 908, 836, 732, 644; ^{1}H NMR δ 8.2 (s, 1H), 7.38 (d, *J* = 8Hz, 1H), 7.19 (dd, *J* = 5, 2Hz, 1H), 7.02 (d, *J* = 7.5Hz, 1H), 6.36 (m, 1H), 4.2 (m, 1H), 3.79 (s, 3H), 2.98 (dt, *J* = 16, 2Hz, 1H), 2.8 (m, 2H), 2.56 (m, 1H), 2.0 (m, 2H), 0.9 (s, 9H), 0.09 (s, 3H, 0.05 (s, 3H); ^{13}C NMR δ 207.9, 171.7, 136.6, 129.6, 126.9, 124.3, 121.7, 118.2, 111.4, 102.7, 66.1, 64.7, 52.6, 42.9, 37.2, 35.7, 25.9, 18.28, -4.5, -4.8; HRMS for $C_{22}H_{31}NO4Si$, calcd., 401.2022, found, 401.2021.



Methyl 1-(*N*-methyl-2´-oxo-indol-4´-yl)-2-oxo-cyclohexane-1-carboxylate (25). To indole compound **24** (0.25 g, 0.62 mmol) in dry THF (5 mL), was added MeI (57 µL, 0.93 mmol), tetrabutylammonium iodide (12 mg, 20 mg/mmol **24**) and powdered potassium hydroxide (52 mg, 0.93 mmol). The resulting mixture was stirred for 4 h, then filtered through celite. The filtrate was concentrated and diluted with CH_2Cl_2 (10 mL). The organic layer was washed with H_2O (3 mL), $NaHCO_3$ solution (3 mL) and brine (3 mL), dried over $MgSO_4$ and concentrated. The residue was purified by silica gel chromatography (EtOAc-hexanes 1/4) to give the desired compound (white solid, 0.22 mg, 85%): R_f 0.46 (EtOAc-hexanes 1/2); mp 108-110 °C; IR 2952, 2886, 2856, 2253, 1729, 1606, 1573, 1517, 1463, 1435, 1417, 1361, 1334, 1296, 1251, 1169, 1106, 1029, 908, 864, 835, 776, 732, 649; ^{1}H NMR δ 7.33(d, *J* = 7.5Hz, 1H), 7.25 (t, *J* = 8Hz, 1H), 7.05 (m, 2H), 6.3 (d, *J* = 3.5Hz, 1H), 4.23 (m, 1H), 3.77 (s, 3H), 3.66 (s, 3H), 3.03 (dt, *J* = 12.5, 2Hz, 1H), 2.82 (m. 1H), 2.58 (m, 1H), 2.41 (m, 1H), 2.03 (m, 2H), 0.92 (s, 9H), 0.13 (s, 3H), 0.08 (s, 3H); ^{13}C-NMR δ 207.9, 171.7, 137.4, 129.6, 128.9, 127.5, 121.3, 117.7, 109.6, 100.9, 66.2, 52.1, 43.0, 37.3, 35.7, 33.0, 26.0, 18.3, -4.3, -4.7; HRMS for $C_{23}H_{33}NO_4Si$, calcd., 415.2179, found, 415.2183.

This material (0.64 g, 1.55 mmol) was dissolved in *tert*-butanol (20 mL). NBS (0.3 g, 1.68 mmol) was added in small portions over 15 min. The reaction was kept for 4 h, concentrated and dissolved in CH_2Cl_2 (10 mL). The solution was washed with $NaHCO_3$ solution (5 mL) and brine (5 mL), dried over $NaSO_4$ and concentrated to give crude product. Purification by silica gel chromatography afforded pure **25** (white solid, 0.42 g, 65%): R$_f$ 0.47 (EtOAc-hexanes 1/2); mp 140-144 ^{o}C; IR 3053, 2950, 2857, 1713, 1604, 1464, 1343, 1257, 1219, 1036, 939, 838, 775, 736, 704; ^{1}H NMR δ 7.32 (t, *J* = 8Hz, 1H), 6.97 (d, *J* = 8Hz, 1H), 6.81 (d, *J* = 8Hz, 1H), 4.26 (m, 1H), 3.72 (s, 3H), 3.25 (q, *J* = 46.5, 24, 2H), 3.2 (s, 1H), 3.0 (m, 1H), 2.86 (m, 1H), 2.65 (d, *J* = 12.5Hz, 1H), 2.45 (m, 1H), 2.02 (m, 2H), 0.92 (s, 9H), 0.12 (s, 3H), 0.10 (s, 3H); ^{13}C-NMR δ 207.9, 171.7, 137.4, 129.6, 128.9, 127.5, 121.3, 117.7, 109.6, 100.94, 66.2, 52.08, 42.96, 37.26, 35.7, 33, 26, 18.3, -4.3, -4.7; HRMS for $C_{23}H_{33}NO_5Si$, calcd., 431.2128, found, 431.2127.



Methyl 1-(4´-indolyl)-2-chloro-3-formyl-5-hydroxy-cyclohex-2-ene-1-carboxylate (26): A solution of $POCl_3$ (56 µL, 0.6 mmol) in DMF (1 mL) was stirred at RT for 30 min. Compound **24** (120 mg, 0.3 mmol) in DMF (1 mL) was added and the resulting solution was stirred at RT for 1 h. Aqueous sodium carbonate (5 mL) was added. After stirring for 10 min, the mixture was extracted with ethyl acetate (4 x 5 mL). The combined organic layers were washed with brine (5mL), dried with $MgSO_4$, and concentrated. The residue was purified by silica gel chromatography to give **26** (white solid, 80 mg, 78%): R_f 0.16 (EtOAc-hexanes 1/1); mp 196-198 ^oC; IR 3465, 3395, 3054, 2985, 2361, 2299, 1728, 1423, 1265, 895, 741; ^1H-NMR (DMSO-d_6) δ 11.18 (s. 1H), 8.24 (s, 1H), 7.37 (d, *J* = 7.5Hz, 1H), 7.29 (s. 1H), 7.06 (t, *J* = 8, 7.5Hz, 1H), 6.85 (d, *J* = 8Hz, 1H), 6.10 (s, 1H), 5.19 (m, 1H), 3.17 (s, 3H), 3.07 (d, *J* = 24Hz, 1H), 2.77 (m, 2H), 2.19 (m, 1H), 2.04 (m, 1H); ^{13}C-NMR δ 205.2, 171.3, 161.5, 136.4, 128.4, 126.2, 125.2, 120.6, 120.6, 117.1, 111.7, 100.8, 94.3, 67.4, 63.7, 52.4, 48.6, 38.1, 36.3, 30.4.