Supporting Information for

Thiophosphoramides as Cooperative Catalysts for Copper-Catalyzed Arylation of Carboxylates with Diaryliodonium Salts

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General Information

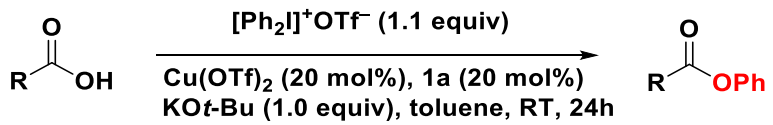
Methods and Reagents:

All the reagents were purchased from the commercial sources and used without further purification. All iodonium salts were purchased from TCI America. Abietic acid (technical, ~75% by GC) was purchased from Sigma Aldrich. All reactions were carried out under an atmosphere of nitrogen in flame or oven dried glassware with a magnetic stirrer. Heating was achieved by use of a silicone bath with heating controlled by electronic contact thermometer. Deionized water was used in the preparation of all aqueous solutions and for all aqueous extractions. Solvents used for purification and extraction were ACS or HPLC grade. toluene, dichloromethane, diethyl ether, tetrahydrofuran, and dimethylformamide were filtered through a column of activated alumina under nitrogen atmosphere (Innovative Technology PS-MD-5). Thin-layer chromatography (TLC) was conducted on precoated glass plates with 230-400 mesh silica gel impregnated with fluorescent indicator (250 nm) for routine monitor of reaction progress and visualized using the combination of UV and ceric ammonium molybdate. All products were purified by flash column chromatography using SiliCycle Silica Flash P60 (230-400 mesh) silica gel.

Instrumentation:

NMR spectra were recorded on Varian vnmrs 700 (700MHz), Varian vnmrs 500 (500 MHz), or Varian Inova 500 (500 MHz) spectrometers and chemical shifts are reported in parts per million (ppm) downfield from tetramethylsilane with solvent resonance as the internal standard ($CDCl_3$ at δ 7.26, DMSO-d6 at δ 2.5). Proton coupling patterns are described as singlet (s), doublet (d), triplet (t), quarted (q), and multiplet (m). High resolution mass spectra (HRMS) were obtained from Micromass AutoSpec Ultima or VG (Micromass) 70-250-S Magnetic Sector mass spectrometers at the University of Michigan mass spectrometry facility. Infrared spectra (IR) were recorded as thin films on NaCl plates on a Perkin Elmer Spectrum BX FT-IR spectrophotometer and were reported in wavenumbers (cm^{-1}).

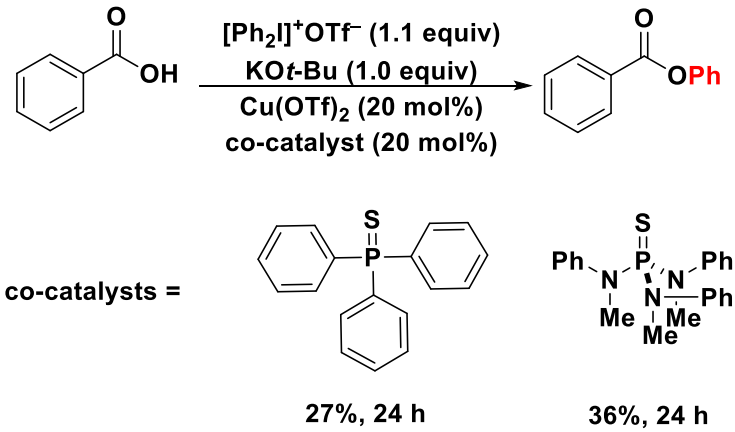
Synthesis and spectra data of compounds 3



General Procedure:

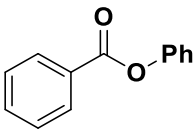
Potassium *tert*-butoxide (22mg, 0.2mmol), Copper(II) trifluoromethanesulfonate (15mg, 0.04), and benzoic acid (24mg, 0.2mmol) were added to an oven dried and nitrogen flushed 10mL vial charged with 3 mL dry dichloromethane at rt and then left to stir for 10 minutes. Diaryliodonium salt (95mg, 0.22mmol) and **1a** (30mg, 0.04mmol) were added in one portion and reaction was stirred for 24 hrs. The reaction was then quenched with H_2O. The product was extracted with diethyl ether and the organic layer was dried over Na_2SO_4, filtered and concentrated *in vacuo*. Crude material was purified by flash chromatography to give corresponding ester.

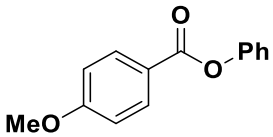
Control experiments:



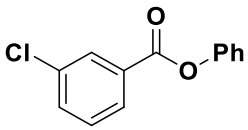
Spectroscopic data of compounds **3a-m**

Purification by flash chromatography (99:1→9:1Hexanes: Et_2O) to afford the above compound **3a** (33mg, 84%) as white crystal. ^{1}H NMR (700 MHz, $CDCl_3$) δ 8.22 (d, *J* = 7.14 Hz, 2H), 7.65 (t, *J* = 7.5 Hz, 1H), 7.52 (t, *J* = 7.8 Hz, 2H), 7.44 (t, *J* = 7.9 Hz, 2H), 7.28 (t, *J* = 7.5 Hz, 1H), 7.22 (d, *J* = 7.7 Hz, 2H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 165.34, 151.09, 133.73, 130.32, 129.72, 129.64, 128.71, 126.04, 121.86; IR (film, cm^{-1}): 2918, 1727, 1598, 1589, 1485, 1449, 1256, 1195, 1177, 1062, 1024; HRMS (ESI+) *m/z* calcd for $C_{13}H_{10}O_2$ [M+H]+ 199.0754, found 199.0750;

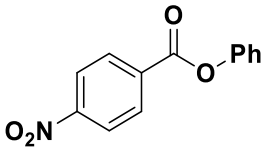




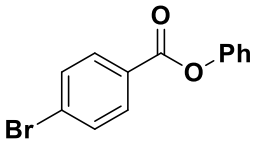
Purification by flash chromatography (99:1→9:1Hexanes: Et_2O) to afford the above compound **3b** (43mg, 93%) as white crystal. ^{1}H NMR (700 MHz, $CDCl_3$) δ 8.16 (d, J = 8.75 Hz, 2H), 7.42 (t, *J* = 7.1 Hz, 2H), 7.26 (t, J = 7.46 Hz, 1H), 7.21 (d, *J* = 7.8 Hz, 2H), 6.99 (d, J = 8.82 Hz, 2H), 3.90 (s, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 165.06, 164.01, 151.20, 132.43, 129.58, 125.86, 122.02, 121.95, 113.97, 55.67; IR (film, cm^{-1}): 2929, 1724, 1605, 1509, 1485, 1449, 1318, 1255, 1193, 1178, 1162, 1074, 1024; HRMS (ESI+) *m/z* calcd for $C_{14}H_{12}O_3$ [M+H]+229.0859, found 229.0868, calcd [M+Na]+ 251.0679, found 251.0672;



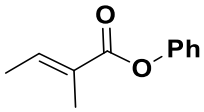
Purification by flash chromatography (95:5→8:2Hexanes: Et_2O) to afford the above compound **3c** (40 mg, 86%) as white solid. ^{1}H NMR (700 MHz, $CDCl_3$) δ 8.20 (s, 1H), 8.10 (d, *J* = 7.8 Hz, 1H), 7.62 (d, *J* = 7.98 Hz, 1H), 7.49 – 7.42 (m, 3H), 7.30 (t, *J* = 7.5 Hz, 1H), 7.22 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR (175 MHz, $CDCl_3$) δ164.13, 150.84, 134.89, 133.74, 131.46, 130.32, 130.04, 129.71, 128.42, 126.25, 121.70,; IR (film, cm^{-1}): 3068, 2922, 1732, 1590, 1484, 1248, 1195, 1075; HRMS (EI) *m/z* calcd for $C_{13}H_9ClO_2$ [M]+232.0291, found 232.0292;



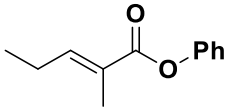
Purification by flash chromatography (9:1→7:3Hexanes: Et_2O) to afford the above compound **3d** (32mg, 67%) as yellow solid. ^{1}H NMR (700 MHz, $CDCl_3$) δ 8.38 (m, 4H), 7.47 (t, *J* = 8.0 Hz, 2H), 7.32 (t, *J* = 7.5 Hz, 1H), 7.24 (d, *J* = 7.7 Hz, 2H); ^{13}C NMR (175 MHz, $CDCl_3$) δ163.46, 151.03, 150.63, 135.11, 131.44, 129.83, 126.56, 123.87, 121.55; IR (film, cm^{-1}): 2923, 1738, 1518, 1265, 1182, 1077; HRMS (EI) *m/z* calcd for $C_{13}H_9NO_4$ [M]+243.0532, found 243.0535;



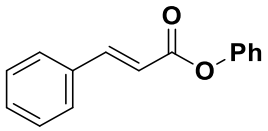
Purification by flash chromatography (95:5→9:1Hexanes: Et_2O) to afford the above compound **3e** (44mg, 80%) as white crystal. ^{1}H NMR (700 MHz, $CDCl_3$) δ 8.07 (d, *J* = 8.61 Hz, 2H), 7.66 (d, *J* = 8.61 Hz, 2H), 7.44 (t, *J* = 7.56 Hz, 2H), 7.29 (t, *J* = 7.46 Hz, 1H), 7.21 (d, *J* = 7.56 Hz, 2H); ^{13}C NMR (175 MHz, $CDCl_3$) δ164.64, 150.89, 132.10, 131.80, 129.69, 128.98, 128.62, 126.20, 121.75; IR (film, cm^{-1}): 2922, 2852, 1728, 1583, 1484, 1394, 1265, 1192, 1174, 1155, 1074; HRMS (EI) *m/z* calcd for $C_{13}H_9BrO_2$ [M]+275.9786, found 275.9789;



Purification by flash chromatography (99:1→9:1Hexanes: Et_2O) to afford the above compound **3f** (27mg, 73%) as colorless liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 (t, *J* = 7.9 Hz, 2H), 7.22 (t, *J* = 7.4 Hz, 1H), 7.15 – 7.08 (m, 3H), 1.96 (s, 3H), 1.89 (d, *J* = 7.1 Hz, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ166.71, 151.28, 139.50, 129.49, 128.32, 125.66, 121.86, 14.78, 12.32; IR (film, cm^{-1}): 2926, 1722, 1650, 1592, 1494, 1485, 1388, 1258, 1242, 1194, 1161, 1110, 1056, 1001; HRMS (ESI) *m/z* calcd for $C_{11}H_{12}O_2$ [M+H]+177.0910, found 177.0906;

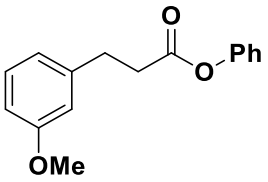


Purification by flash chromatography (99:1→9:1Hexanes: Et_2O) to afford the above compound **3g** (31mg, 83%) as yellow liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 (t, *J* = 7.8 Hz, 2H), 7.22 (t, *J* = 7.1 Hz, 1H), 7.11 (d, *J* = 7.7 Hz, 2H), 7.01 (td, *J* = 7.4, 1.1 Hz, 1H), 2.28 (p, *J* = 7.5 Hz, 2H), 1.95 (s, 3H), 1.11 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 166.87, 151.29, 146.22, 129.47, 126.80, 125.65, 121.86, 22.38, 13.11, 12.48; IR (film, cm^{-1}): 2965, 1725, 1646, 1593, 1487, 1231, 1195, 1162, 1126, 1089, 1066; HRMS (ESI) *m/z* calcd for $C_{12}H_{14}O_2$ [M+H]+ 191.1067, found 191.1067;

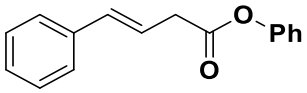


Purification by flash chromatography (99:1→9:1Hexanes: Et_2O) to afford the above compound **3h** (39mg, 89%) as white crystal. ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.88 (d, *J* = 16.0 Hz, 1H), 7.62 – 7.57 (m, 2H), 7.46 – 7.39 (m, 5H), 7.28 – 7.24 (m, 1H), 7.18 (d, *J* = 7.6 Hz, 2H), 6.65 (d, *J* = 16.0 Hz, 1H); ^{13}C NMR (175 MHz, $CDCl_3$) δ165.54, 150.92, 146.71, 134.30, 130.84, 129.58, 129.13, 128.44, 125.93,

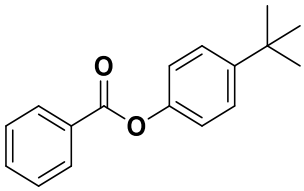
121.77, 117.44; IR (film, cm^{-1}): 2923, 1724, 1635, 1483, 1305, 1202, 1139; HRMS (APCI+) *m/z* calcd for $C_{15}H_{12}O_2$ [M+H]+225.0910, found 225.0899;



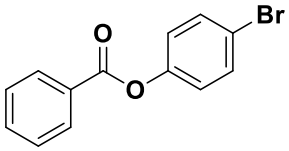
Purification by flash chromatography (95:5→9:1Hexanes: Et_2O) to afford the above compound **3i** (34mg, 67%) as colorless liquid. ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.37 (t, *J* = 7.56 Hz, 2H), 7.27 – 7.21 (m, 2H), 7.04 (d, J = 7.56 Hz, 2H), 6.87 (d, J=7.56 Hz, 1H), 6.82 (s, 1H), 6.79 (dd, *J* = 8.2, 2.4 Hz, 1H), 3.81 (s, 3H), 3.06 (t, *J* = 7.8 Hz, 2H), 2.89 (t, *J* = 7.8 Hz, 2H); ^{13}C NMR (175 MHz, $CDCl_3$) δ171.52, 159.89, 150.76, 141.86, 129.72, 129.54, 125.94, 121.66, 120.84, 114.26, 111.93, 55.31, 36.06, 31.13; IR (film, cm^{-1}): 2940, 1755, 1593, 1584, 1491, 1454, 1259, 1192, 1161, 1126, 1041; HRMS (APCI+) *m/z* calcd for $C_{16}H_{16}O_3$ [M+H]+257.1172, found 257.1172;



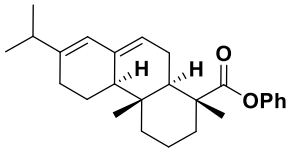
Purification by flash chromatography (99:1→9:1Hexanes: Et_2O) to afford the above compound **3j** (35mg, 71%) as off-white crystal. ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.43 – 7.36 (m, 4H), 7.33 (t, *J* = 7.7 Hz, 2H), 7.27 – 7.22 (m, 2H), 7.11 (d, *J* = 7.7 Hz, 2H), 6.61 (d, *J* = 15.9 Hz, 1H), 6.41 (dt, *J* = 15.7, 7.1 Hz, 1H), 3.50 (d, *J* = 7.07 Hz, 2H); ^{13}C NMR (175 MHz, $CDCl_3$) δ170.18, 150.80, 136.84, 134.21, 129.59, 128.74, 127.87, 126.50, 126.06, 121.65, 121.13, 38.60; IR (film, cm^{-1}): 3034, 1742, 1591, 1492, 1364, 1201, 1133; HRMS (APCI+) *m/z* calcd for $C_{16}H_{14}O_2$ [M+H]+ 239.1067, found 239.1060;



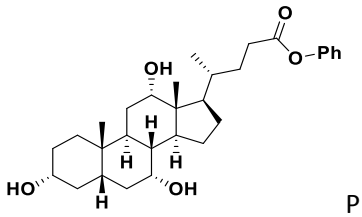
Purification by flash chromatography (99:1→9:1Hexanes: Et_2O) to afford the above compound (42mg, 84%) as white crystal. ^{1}H NMR (700 MHz, $CDCl_3$) δ 8.21 (d, *J* = 7.1 Hz, 2H), 7.64 (t, *J* = 7.4 Hz, 1H), 7.52 (t, *J* = 7.7 Hz, 2H), 7.45 (d, *J* = 8.8 Hz, 2H), 7.15 (d, *J* = 8.8 Hz, 2H), 1.35 (s, 9H); ^{13}C NMR (175 MHz, $CDCl_3$) δ165.49, 148.83, 148.71, 133.64, 130.29, 129.83, 128.67, 126.53, 121.13, 34.66, 31.58; IR (film, cm^{-1}): 2964, 1730, 1508, 1262, 1203, 1170, 1076, 1060, 1021; HRMS (ESI+) *m/z* calcd for $C_{17}H_{18}O_2$ [M+H]+255.1380, found 255.1378;



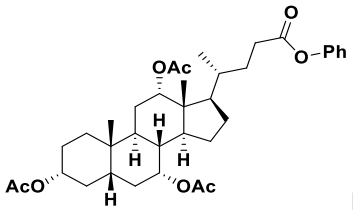
Purification by flash chromatography (99:1→9:1Hexanes: Et_2O) to afford the above compound (38mg, 70%) as white crystal. ^{1}H NMR (700 MHz, $CDCl_3$): δ 8.19 (d, J = 7.1 Hz, 2H), 7.65 (t, *J* = 7.5 Hz, 1H), 7.57 – 7.50 (m, 4H), 7.12 (d, J = 8.82, 2H); ^{13}C NMR (175 MHz, $CDCl_3$) δ165.01, 150.10, 133.95, 132.68, 130.35, 129.30, 128.78, 123.69, 119.13; IR (film, cm^{-1}): 2923, 1730, 1482, 1259, 1198, 1160, 1057; HRMS (EI) *m/z* calcd for $C_{13}H_9BrO_2$ [M]+275.9786, found 275.9787;



Potassium *tert*-butoxide (22mg, 0.2mmol), copper(II) trifluoromethanesulfonate (15mg, 0.04mmol), and abietic acid (60mg of 75% abietic acid, 0.15 mmol) were added to an oven dried and nitrogen flushed 10 mL vial charged with 3 mL dry dichloromethane at rt and then left to stir for 10 minutes. Diaryliodonium salt (95mg, 0.22mmol) and **1a** (30mg, 0.04mmol) were added in one portion and reaction was stirred for 24 hrs at 40°C. The reaction was then quenched with H_2O. The product was extracted with diethyl ether and the organic layer was dried over Na_2SO_4, filtered and concentrated. Purification by flash chromatography (95:5→9:1 Hexanes: EtOAc) to afford the above compound **3k** (40 mg, 71%) as yellow viscous liquid. Some impurities from the starting material (75% abietic acid) was also observed in the product and was inseparable by accessible purification process. ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.36 (t, *J* = 7.8 Hz, 2H), 7.21 (t, *J* = 7.3 Hz, 1H), 7.01 (d, *J* = 7.9 Hz, 2H), 5.81 (s, 1H), 5.43 (s, 1H), 2.31 - 2.27 (m, 1H), 2.26 – 2.21 (m, 1H), 2.11 (d, *J* = 2.7 Hz, 2H), 2.03 – 1.99 (m, 2H), 1.94 (d, *J* = 13.1 Hz, 1H), 1.86 – 1.82 (m, 2H), 1.70 – 1.63 (m, 2H), 1.39 (s, 3H), 1.29 – 1.19 (m, 4H), 1.03 (t, *J* = 6.7 Hz, 6H), 0.89 (s, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ177.26, 151.30, 145.62, 135.71, 129.45, 125.68, 122.46, 121.67, 120.57, 51.03, 46.99, 45.20, 38.42, 37.20, 35.04, 34.74, 27.59, 25.92, 22.62, 21.55, 20.97, 18.29, 17.27, 14.20; IR (film, cm^{-1}):2928, 1743, 1594, 1492, 1458, 1385, 12766, 1227, 1190, 1162, 1129, 1101, 1025, 1000; HRMS (ESI+) *m/z* calcd for $C_{26}H_{34}O_2$ [M+H]+ 379.2632, found 379.2635;



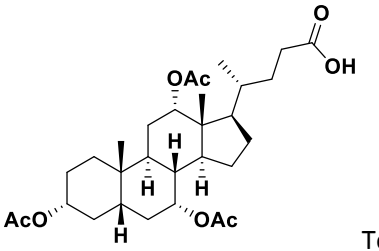
Purification by flash chromatography (1:1→0:1Hexanes: EtOAc) to afford the above compound **3l** (33mg, 34%) as light yellow solid. ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.37 (t, *J* = 7.9 Hz, 2H), 7.22 (t, *J* = 7.4 Hz, 1H), 7.07 (d, *J* = 7.7 Hz, 2H), 4.00 (s, 1H), 3.85 (s, *J* = 2.5 Hz, 1H), 3.48 (s, 1H), 3.47 – 3.43 (m, 1H), 2.64 – 2.59 (m, 1H), 2.52 – 2.48 (m, 1H), 2.26 – 2.18 (m, 1H), 1.98 – 1.88 (m, 5H), 1.85 – 1.81 (m, 1H), 1.78 (d, *J* = 14.4 Hz, 1H), 1.75 – 1.66 (m, 4H), 1.63 – 1.59 (m, 1H), 1.58 – 1.46 (m, 6H), 1.40 (d, *J* = 12.1 Hz, 2H), 1.37 – 1.32 (m, 1H), 1.14 (dd, *J* = 12.2, 6.1 Hz, 1H), 1.05 (d, *J* = 6.1 Hz, 3H), 1.01 – 0.96 (m, 1H), 0.89 (s, 3H), 0.71 (s, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 172.86, 150.91, 129.53, 125.84, 121.70, 73.15, 72.08, 68.57, 47.28, 46.67, 42.04, 41.58, 39.80, 39.71, 35.36, 35.34, 34.86, 34.77, 31.53, 31.01, 30.64, 28.47, 27.65, 26.73, 23.35, 22.66, 17.53, 12.70; IR (film, cm^{-1}): 3392, 2924, 1755, 595, 1456, 1376, 1259, 1234, 1194, 1076, 1036; HRMS (ESI+) *m/z* calcd for $C_{30}H_{44}O_5$ [M+NH_4]+ 502.3527, found 502.3526;



Purification by flash chromatography (9:1→7:3 Hexanes: EtOAc) to afford the above compound **3m** (108 mg, 89%) as colorless solid. ^{1}H NMR (700 MHz, $CDCl_3$) δ(t, J = 7.98, 2H),

7.22 (t, *J* = 7.4 Hz, 1H), 7.06 (d, *J* = 7.6 Hz, 2H), 5.11 (s, 1H), 4.91 (s, 1H), 4.59 – 4.57 (m, 1H), 2.60 (ddd, *J* = 15.0, 9.6, 5.1 Hz, 1H), 2.47 (ddd, *J* = 15.8, 9.1, 7.0 Hz, 1H), 2.15 (s, 3H), 2.09 (s, 3H), 2.05 (s, 3H), 1.98 – 1.91 (m, 3H), 1.90 – 1.87 (m, 1H), 1.81 – 1.74 (m, 2H), 1.70 (d, *J* = 5.6 Hz, 1H), 1.68 (d, *J* = 13.1 Hz, 1H), 1.65 – 1.62 (m, 1H), 1.61 – 1.58 (m, 2H), 1.53 – 1.48 (m, 3H), 1.46 – 1.41 (m, 2H), 1.38 – 1.32 (m, 1H), 1.30 – 1.22 (m, 3H), 1.16 – 1.11 (m, 1H), 1.07 (td, *J* = 14.4, 3.3 Hz, 1H), 0.92 (s, 3H), 0.89 (d, *J* = 6.4 Hz, 3H), 0.75 (s, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ172.52, 170.48, 170.32, 150.65, 129.38, 125.73, 121.48, 77.25, 77.06, 76.88, 75.35, 74.05, 70.65, 47.36, 45.07, 43.39, 40.90, 37.70, 34.66, 34.61, 34.59, 34.31, 31.21, 31.19, 30.69, 29.66, 28.86, 27.22, 26.86, 25.56, 22.79, 22.54, 21.61, 21.48, 21.43, 17.54, 12.23; IR (film, cm^{-1}): 2922, 1727, 1446, 1379, 1239, 1199, 1136, 1022; HRMS (EI) *m/z* calcd for $C_{36}H_{50}O_8$ [M+NH_4]+ 628.3844, found 628.3848;

Synthesis of **3α, 7α, 12α-Triacetoxy-5β-Cholan-24-oic acid**



To an ice cooled solution of cholic acid (1 gm; 2.45 mmol) in pyridine (3ml) and acetic anhydride (2 ml), DMAP (180 mg; 1.47 mmol) was added. The reaction mixture was stirred at rt for 3 hrs. The solution was concentrated *in vacuo*, dissolved in 50 ml diethyl ether, washed with 0.1 M HCl, $NaHCO_3$, and brine. The organic layer was dried over $MgSO_4$, filtered and concentrated *in vacuo* to give the crude product. Purification *via* flash chromatography (8:2→1:1Hexanes: EtOAc) to afford the above compound (831 mg, 63%) as colorless solid. ^{1}H NMR (700 MHz, $CDCl_3$) δ5.09 (s, 1H), 4.91 (s, 1H), 4.59 – 4.56 (m, 1H), 2.42 – 2.36 (m, 1H), 2.27 – 2.22 (m, 1H), 2.14 (s, 3H), 2.09 (s, 3H), 2.05 (s, 3H), 2.04 – 1.99 (m, 1H), 1.97 – 1.93 (m, 1H), 1.90 – 1.84 (m, 2H), 1.82 – 1.72 (m, 3H), 1.68 – 1.64 (m, 2H), 1.63 – 1.59 (m, 2H), 1.54 – 1.48 (m, 2H), 1.45 – 1.41 (m, 2H), 1.34 – 1.25 (m, 4H), 1.14 – 1.08 (m, 1H), 1.08 – 1.03 (m, 1H), 0.92 (s, 3H), 0.87 (dt, *J* = 14.4, 7.0 Hz, 2H), 0.83 (d, *J* = 6.6 Hz, 3H), 0.73 (s, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 179.36, 170.58, 170.54, 170.42, 75.37, 74.08, 70.70, 47.31, 45.04, 43.37, 40.89, 37.71, 34.58, 34.52, 34.30, 31.56, 31.21, 30.75, 30.51, 28.86, 27.14, 26.86, 25.55, 22.63, 22.53, 21.60, 21.47, 17.46, 14.10, 12.21; IR (film, cm^{-1}): 2936, 2013, 1730, 1441, 1374, 1230, 1023; HRMS (EI) *m/z* calcd for $C_{30}H_{46}O_8$ [M+NH_4]+ 552.3531, found 552.3530; Calcd [M+Na]+ 557.3085, found 557.3081;

References:

1. For the synthesis of $[Ph_2I]^+BF4^-$
   Bielawski, M.; Aili, D.; Olofsson, B. *J. Org. Chem.,* **2008**, 73, 4602
2. For Synthesis of 1a and 1b,
   Rodriguez, A. A.; Yoo, H.; Ziller, J. W.; Shea, K. J. *Tetrahedron Lett.,* **2009**, 50, 6830
3. Synthesis of $Cu(BF_4)_2$ is based on the synthesis of $Cu(SbF_6)_2$ by
   Evans, D.A.; Murry, J.A.; von Matt, P.; Norcross, R.D.; Miller, S.J. *Angew. Chem. Int. Ed. Engl.* **1995,** *34,* 798
4. Synthesis of 3α, 7α, 12α-Triacetoxy-5β-Cholan-24-oic acid
   Gao, H.; Dias, J.R. *J. Prakt. Chem*. **1997**, 339, 187