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SUPPORTING INFORMATION

Title: Combined Metalation–Cross Coupling Strategies: Biaryl *O*-Carbamate Remote Anionic Fries Rearrangement – Synthesis of Schumanniophytine
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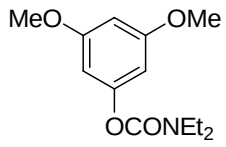
Ref. No.: O200701116

General Methods

Melting points are uncorrected. Infrared spectra were recorded as neat or KBr discs using a BOMEM MB-100 FTIR spectrophotometer. ^{1}H and ^{13}C NMR spectra were recorded using a Bruker 400 MHz spectrometer. When peak multiplicities are given, the following abbreviations are used: s, singlet; d, doublet; t, triplet; q, quartet; qn, quintet; sx, sextet; dd, doublet of doublet; td, triplet of doublet; m, multiplet; bs, broad singlet. GC-MS analyses were performed with an *Agilent 6890N* GC coupled with an *Agilent 5973 inert* MS under EI conditions. THF was freshly distilled from sodium benzophenone ketyl under argon and *N,N*-diethylcarbamoyl chloride was distilled from CaH_2 and stored over 4 Å molecular sieves prior to use. *n*- and *s*-Butyllithium were purchased from Aldrich as solutions in hexanes and cyclohexane, stored in a resealable container, and titrated periodically against *N*-benzylbenzamide. LDA was freshly prepared before reactions by stirring a 1:1 mixture of diisopropylamine and *n*-BuLi at 0 ^{o}C in THF (1 M) for 10 min. *N,N,N',N'*-tetramethylethylenediamine (TMEDA) was stored over solid KOH prior to use. All reactions involving alkyllithiums were carried out in oven or flame-dried glassware cooled under argon using syring-septum cap techniques. The -105, -78, and 0 ^{o}C temperatures designated are approximate as achieved by a liquid nitrogen-ethanol, dry ice-acetone, and ice-salt bath, respectively. When internal temperature readings were essential, a Barnant Dual J stainless steel-sheathed thermocouple thermometer was employed. $[Pd(PPh_3)_4]$ was freshly prepared according to a literature procedure[1] and solutions were pre-degassed using sonication associated with argon bubbling. Eaton's reagent[2] was prepared by stirring 1:10 mass ratio of P_2O_5 and freshly distilled MsOH under argon for 4-8 h. Reaction monitoring was done by TLC and GC where appropriate. Flash column chromatography was carried out using Merck silica gel 60 (particle size: 32-63).

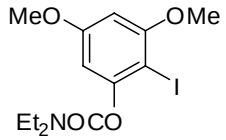
[1] D. R. Coulson, *Inorg. Synth.* **1972**, *13*, 121–123.
[2] P. E. Eaton, G. R. Carlson, J. T. Lee, *J. Org Chem.* **1973**, *38*, 4071–4073.

3,5-Dimethoxyphenyl diethylcarbamate (8)



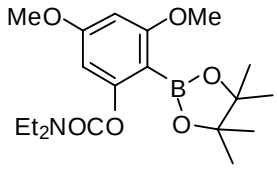
A solution of 3,5-dimethoxyphenol (20 g, 0.13 mol) in MeCN (250 mL), was added K_2CO_3 (27 g, 0.195 mol), $ClCONEt_2$ (25 mL, 0.195 mol) and the whole was heated to reflux for 12 h. The mixture was then diluted with water (625 mL) and extracted with Et_2O (3x). The combined extracts were then washed with NaOH (2M), water (2x), brine (2x), dried (Na_2SO_4), and concentrated in vacuo affording a brown oil which was distilled under high vacuum to yield **8** (26.3 g, 80%) as a colourless oil, bp 183 ^oC at 1.13 mmHg; IR (neat) ν_{max} 2974, 2937, 1719, 1599, 1473, 1415, 1270, 1205, 1155, 1059 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 6.33 (s, 3H), 3.78 (s, 6H), 3.41 (q, 4H, J = 6.3 Hz), 1.23 (t, 6H, J = 7.9 Hz) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.0, 154.0, 153.2, 100.4, 97.8, 55.4, 42.2, 41.9, 14.2, 13.4 ppm; EIMS (*m/z*(%)) 253[M^+](60), 100(100), 72(40); HRMS (EI) calculated for $C_{13}H_{19}NO_4$ 253.1314: found 253.1304.

2-Iodo-3,5-dimethoxyphenyl diethylcarbamate (9a)



A solution of **8** (1 g, 3.95 mmol) in THF (50 mL) containing TMEDA (0.78 mL, 5.1 mmol) was treated via syring with *s*-BuLi (3.6 mL, 5.1 mmol, 1.4 M in cyclohexane) maintaining an internal temperature <-72 ^oC. The mixture was allowed to metalate for 10 min and then treated with a solution of I_2 (1.5 g, 5.9 mmol, in 10mL THF) via canula maintaining an internal temperature <-72 ^oC. The reaction is then warmed to room temperature and treated with saturated aqueous NH_4Cl (20 mL) followed by saturated aqueous $Na_2S_2O_3$ (20 mL). The layers were then separated, aqueous phase extracted with EtOAc (2 x 20 mL), dried (Na_2SO_4), and concentrated in vacuo affording a yellow solid. Flash column chromatography (1:1 hexanse:EtOAc) yielded **9a** (1.3 g, 86%) as a yellow solid, mp 67-68 ^oC (hexanes); IR (neat) ν_{max} 2972, 2934, 1720, 1593, 1458, 1403, 1268, 1217, 1154, 1094 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 6.47 (d, 1H, J = 2.6 Hz), 6.33 (d, 1H, J = 2.5 Hz), 3.87 (s, 3H), 3.81 (s, 3H), 3.55 (q, 2H, J = 7.1 Hz), 3.42 (q, 2H, J = 7.1 Hz), 1.34 (t, 3H, J = 7.1 Hz), 1.24 (t, 3H, J = 7.1 Hz) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.8, 159.9, 153.8, 153.2, 101.2, 96.8, 73.2, 56.9, 56.0, 42.6, 42.4, 14.7, 13.6 ppm; EIMS (*m/z*(%)) 379[M^+](1), 253(22), 252(81), 137(14), 100(65), 72(100); HRMS (EI) calculated for $C_{13}H_{18}INO_4$ 379.0281: found 379.0286.

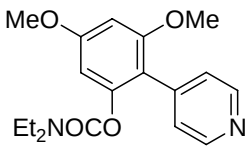
3,5-Dimethoxy-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl diethylcarbamate (9b)



A solution of freshly prepared LDA (23.1 mL, 2.15 M) was added via canula to a solution of **8** (5 g, 19.8 mmol), $B(OiPr)_3$ (11.9 mL, 51.5 mmol), in THF (40 mL) at –78 ^oC maintaining an internal temperature of < -72 ^oC. After the addition the mixture was stirred at –78 ^oC for 1 h and allowed to warm to 0 ^oC before acidification to < pH 5 with 1M HCl. The layers were then separated and the aqueous phase was extracted with EtOAc (3 x 20 mL), extracts combined, washed with brine, dried (Na_2SO_4), and

concentrated in vacuo, then heated to 80 °C under high vacuum for 1 h to yield 2-(diethylcarbamoyloxy)-3,5-dimethoxyphenylboronic acid (5.7g, 97%) as a colourless powder. This boronic acid (50 mg, 0.17 mmol) and pinacol (22 mg, 0.18 mmol) were dissolved in EtOAc (10 mL) and concentrating in vacuo affording **9b** (64 mg, quantitative, purity 98%, by GC peak area) as a colourless solid; mp 82-83 °C; IR (KBr) ν_{max} 2980, 2976, 1727, 1599, 1515, 1327, 1270, 1142, 1112, 823 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 6.26 (d, 1H, J = 2.1 Hz), 6.22 (d, 1H, J = 2.1 Hz), 3.44 (q, 2H, J = 7.1 Hz), 3.36 (q, 2H, J = 7.1 Hz), 3.78 (s, 3H), 3.76 (s, 3H), 1.30 (s, 12H), 1.25 (t, 3H, J = 7.1 Hz), 1.18 (t, 3H, J = 7.1Hz) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.0, 163.5, 158.1, 155.0, 100.5, 96.5, 83.8, 56.7, 56.0, 42.5, 42.3, 25.5, 14.8, 14.1 ppm; EIMS (*m/z*(%)) 379[M^+](1), 364(68), 321(100), 278(100), 250(27), 180(32), 151(47), 100(100), 72(96); HRMS (EI) calculated for $C_{19}H_{30}BNO_6$ [M – CH_3]$^+$ 364.1931: found 364.1936.

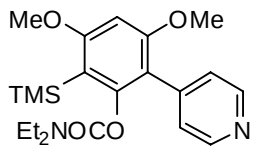
3,5-Dimethoxy-2-(pyridin-4-yl)phenyl diethylcarbamate (10)



A solution of freshly prepared LDA (47.4 mL, 47.4 mmol, 1M in THF) was added via canula to a solution of **8** (10 g, 39.5 mmol), $B(OiPr)_3$ (23.7 mL, 102.7 mmol), and THF (80 mL) at –78 °C maintaining an internal temperature of < -72 °C. After the addition the mixture was stirred at –78 °C for 1 h and allowed to warm to 0 °C before acidification to < pH 5 with 1M HCl. The layers were separated and the aqueous phase was extracted with EtOAc (3 x 20 mL), extracts combined, washed with brine (50 mL), dried (Na_2SO_4), added to a flask containing pinacol (5.14 g, 43.5 mmol), and concentrated in vacuo to yield **9b** as a dark oil. To this flask was then added 4-bromopyridine hydrochloride (7.7 g, 39.5 mmol), Na_2CO_3 (8.4 g, 80 mmol), and [$Pd(PPh_3)_4$] (1.8 g, 1.6 mmol). The flask was then fitted with a reflux condenser, purged with Ar, added degassed DME (70 mL), degassed Na_2CO_3 (40 mL, 2M), and heated to 90 °C for 20 h. The mixture was allowed to cool, the residual DME was removed in vacuo, the resultant aqueous phase was extracted with CH_2Cl_2 (3 x 20 mL), extracts combined, washed with brine (50 mL), dried (Na_2SO_4), and concentrated in vacuo to afford the crude product as a brown oil. Flash column chromatography (EtOAc) yielded **10** (13 g, 99%) as a yellow solid. This compound was also prepared in a less efficient manner from the reaction of **9a** (150 mg, 0.41 mmol), 4-tributylstannylpyridine (225 mg, 0.61 mmol), and $PdCl_2(PPh_3)_2$ (17 mg, 0.04 mmol) in degassed DMF (0.5 mL) heated to reflux for 1 h. The reaction was allowed to cool, diluted and sonicated with aqueous NaF (5 mL, 0.01 M), extracted with CH_2Cl_2 (3 x 5 mL), organic extracts combined, washed with water (10 mL), brine (10 mL), dried (Na_2SO_4), and concentrated to dryness in vacuo to afford the crude product as a brown oil. Flash column chromatography (EtOAc) yielded **10** (100 mg, 73%) as a yellow solid. Recrystallization gave the product as light yellow crystals, mp 113-114 °C (5:1 heptane:EtOAc); IR (KBr) ν_{max} 2979, 2938, 1721, 1622, 1410, 1273, 1220, 1197, 1155, 1096, 1060, 843, 569 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.60 (d, 2H, J = 5.1 Hz), 7.27 (d, 2H, J = 5.3 Hz), 6.45 (s, 1H), 6.43 (s, 1H), 3.86 (s, 3H), 3.75 (s, 3H), 3.23 (q,

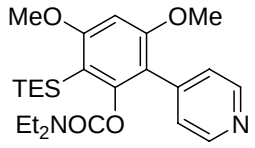
2H, J = 7.0 Hz), 3.13 (q, 2H J = 7.0 Hz), 1.03 (t, 3H, J = 7.0 Hz), 0.93 (t, 3H, J = 7.0 Hz) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.1, 158.1, 153.8, 150.5, 149.5, 142.8, 126.2, 115.1, 100.4, 96.8, 56.2, 55.9, 42.3, 41.9, 14.1, 13.4 ppm; EIMS (*m/z*(%)) 330[M^+](40), 277(50), 100(100), 72(18); HRMS (EI+) calculated for $C_{18}H_{22}N_2O_4$ [M^+] 330.1580: found 330.1581.

3,5-Dimethoxy-2-(pyridin-4-yl)-6-(triethylsilyl)phenyl diethylcarbamate (11a)



A solution of **10** (250 mg, 0.76 mmol) and Me_3SiCl (0.43 mL, 3.4 mmol in THF (25 mL) was cooled to -78 °C and treated via syring a solution of freshly prepared LDA (3.8 mL, 2.7 mmol, 0.7 M in THF) maintaining an internal temperature of < -72 °C. The resulting yellow solution was left to warm slowly to room temperature and stirred for 10 h. The mixture was then treated with saturated aqueous NH_4Cl (20 mL), layers separated, aqueous phase extracted with EtOAc (2 x 20 mL), dried (Na_2SO_4), and concentrated in vacuo affording a yellow solid. Flash column chromatography (EtOAc) yielded **11a** (290 mg, 94%) as a colourless solid. Recrystallization gave the product as colourless crystals; mp 105-106 °C (hexanes:EtOAc); IR (KBr) ν_{max} 2980, 1710, 1604, 1378, 1103 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 (bs, 2H), 7.22 (d, 2H, J = 4.6 Hz), 6.40 (s, 1H), 3.85 (s, 3H), 3.74 (s, 3H), 3.20-2.97 (m, 4H), 0.90 (t, 3H, J = 7.0 Hz), 0.81 (t, 3H, J = 7.1 Hz), 0.26 (s, 9H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.2, 159.5, 154.8, 153.5, 149.5, 143.8, 126.6, 115.4, 112.6, 92.8, 56.1, 55.7, 41.6, 41.3, 13.7, 13.0, 1.3 ppm; EIMS (*m/z*(%)) 401[M^+](1), 387(100), 100(100), 72(58); HRMS (EI) calculated for $C_{21}H_{30}N_2O_4Si$ 402.1975: found 402.1981.

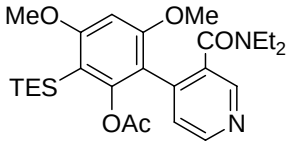
3,5-Dimethoxy-2-(pyridin-4-yl)-6-(triethylsilyl)phenyl diethylcarbamate (11b)



A solution of 3,5-dimethoxy-2-(pyridin-4-yl)phenyl diethylcarbamate (1.98 g, 6 mmol) in THF (15 mL) was cooled to < -105 °C and treated via syring a solution of *n*-BuLi (2.9 mL, 7.2 mmol, 2.47M in hexanes) maintaining an internal temperature of < -104 °C. The resulting yellow solution was stirred for 5 min and then TESCl (2.5 mL, 15 mmol) was added via syring (int temp < -104 °C). The mixture was stirred for 1.5 h (int temp < -101 °C), warmed to room temperature, diltued with saturated aqueous Na_2CO_3, and rapidly stirred for 4 h. The layers were then separated and the aqueous layer was extracted with CH_2Cl_2 (2 x 20mL), extracts combined, dried (Na_2SO_4), and concentrated in vacuo to afford a yellow oil. Flash column chromatography (EtOAc) yielded **11b** (2.22 g, 91%) as a colourless solid which would precipitate from hexanes as an amorphous powder; mp 117-118 °C (hexanes); IR (KBr) ν_{max} 2954, 2872, 2365, 1730, 1595, 1458, 1376, 1325, 1268, 1211, 1148, 1097, 723 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57 (s, 2H), 7.24 (s, 2H), 6.40 (s, 1H), 3.85 (s, 3H), 3.77 (s, 3H), 3.11-2.99 (m, 4H), 0.95 (t, 9H, J = 7.7 Hz), 0.88-0.79 (m, 12H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.1, 159.0, 155.2, 153.4, 149.0, 143.4,

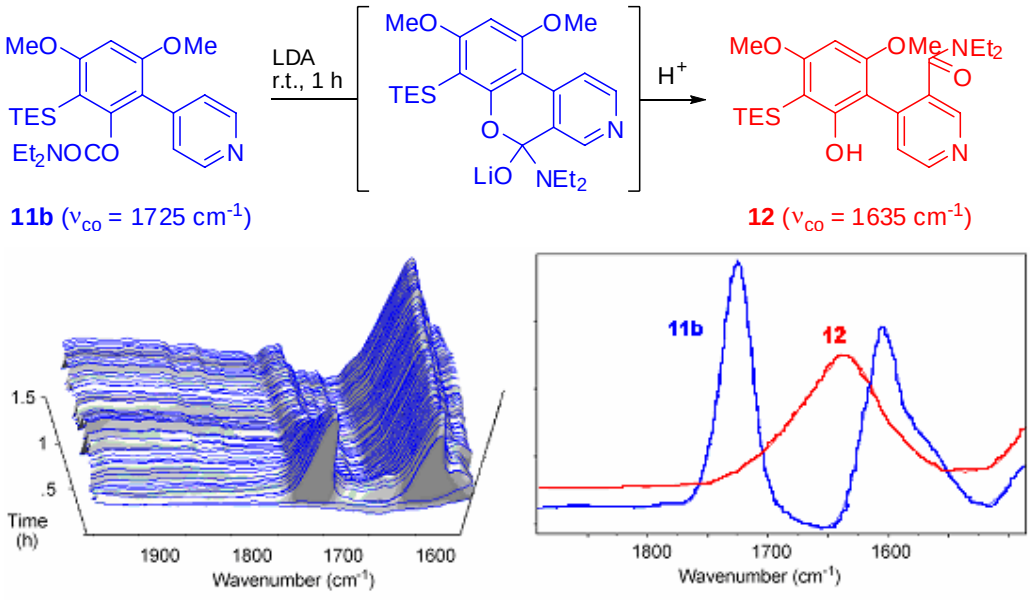
126.3, 115.3, 110.2, 92.1, 55.7, 55.2, 40.9, 40.7, 13.4, 12.5, 7.8, 4.6 ppm; EIMS (*m/z*(%)) M^+ not found, 415[M^+-C_2H_5](100), 100(15), 72(10); HRMS (EI) calculated for $C_{24}H_{36}N_2O_4Si$ 444.2444: found 444.2443.

2-(3-(Diethylcarbamoyl)pyridin-4-yl)-3,5-dimethoxy-6-(triethylsilyl)phenyl acetate (12a)

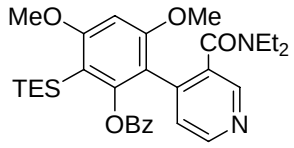


A solution of freshly prepared LDA (1.5 mL, 1.5 mmol, 1M in THF) was added via syring to a flask containing a solution of **11b** (166 mg, 0.37 mmol) in THF (3.7 mL) at 0 °C. The mixture was then warmed to room temperature, stirred for 1 h, re-cooled to 0 °C, quenched with an excess of Ac_2O, warmed to room temperature, neutralized with saturated aqueous $NaHCO_3$, layers separated, aqueous phase extracted with CH_2Cl_2 (3 x 5 mL), extracts combined, dried (Na_2SO_4), and concentrated in vacuo to afford the crude titled compound as a dark oil. Flash column chromatography (EtOAc) yielded **12a** (135 mg, 75%) as tan solid. Recrystallization from hexanes gave tan beads; mp 142-143 °C (hexanes); IR (KBr) ν_{max} 2948, 2878, 2365, 2339, 1763, 1630, 1604, 1471, 1433, 1370, 1319, 1211, 1116, 1085, 736 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.64 (s, 1H), 8.60 (d, 1H, J = 4.2), 7.22 (d, 1H, J = 3.9), 6.41 (s, 1H), 3.85 (s, 3H), 3.80 (s, 3H), 3.70-2.50 (broad m, 4H), 1.88 (s, 3H), 0.92 (t, 13H, J = 7.3 Hz), 0.77 (octet, 8H, J = 7.5 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.5; 167.3; 166.7; 149.2; 133.7; 126.9; 112.7; 92.2; 55.2; 38.4; 20.9; 12.5; 7.7; 4.6 ppm; EIMS (*m/z*(%)) M^+ not found, 457[M^+-C_2H_5](100), 415(15), 342(20), 256(17); HRMS (EI) calculated for $C_{19}H_{22}N_2O_5$ 486.2550: found 486.2550.

React IR Monitoring of DreM of 11b

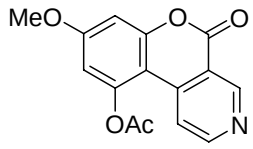


2-(3-(Diethylcarbamoyl)pyridin-4-yl)-3,5-dimethoxy-6-(triethylsilyl)phenyl benzoate (12b)



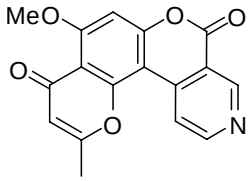
A solution of freshly prepared LDA (6.6 mL, 6.6 mmol, 1M in THF) was added via syring to a flask containing a solution of **11b** (734 mg, 1.65 mmol) in THF (33 mL) at 0 ^{o}C. The mixture was then warmed to room temperature, stirred for 1 h, re-cooled to 0 ^{o}C, quenched with BzCl (1 mL, 8.25 mmol), warmed to room temperature and stirred for 1 h, and neutralized with saturated aqueous $NaHCO_3$. The layers were then separated, aqueous phase extracted with EtOAc (2 x 20mL), extracts combined, dried (Na_2SO_4), and concentrated in vacuo to afford a dark red oil. Flash column chromatography (EtOAc) yielded **12b** (590 mg, 65%) as a yellow foam; mp 58-62 ^{o}C; IR (KBr) ν_{max} 2953, 2883, 1738, 1636, 1598, 1463, 1316, 1246, 1207, 1099, 709 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52 (s, 1H), 8.40 (d, 1H, J = 4.9 Hz), 8.09 (d, 1H, J = 7.6 Hz), 8.00 (bs, 1H), 7.49 (t, 1H, J = 6.9 Hz), 7.35 (t, 2H, J = 7.5 Hz), 7.19 (d, 1H, J = 4.9 Hz), 6.43 (s, 1H), 3.86 (s, 3H), 3.78 (s, 3H), 3.50-2.60 (m, 4H), 0.95-0.85 (m, 15H), 0.72 (q, 3H, J = 7.9 Hz), 0.70 (q, 3H, J = 7.9 Hz) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.2, 166.8, 165.9, 148.8, 146.8, 134.3, 133.3, 132.6, 130.1, 129.9, 129.2, 128.3, 128.2, 126.6, 112.6, 92.1, 55.5, 55.3, 42.2, 38.4, 14.1, 12.4, 7.7, 4.8 ppm; EIMS (*m/z*(%)) M^+ not found, 519[M^+-C_2H_5](100), 105(22); HRMS (EI+) calculated for $C_{31}H_{40}N_2O_5Si$ 547.2628: found 547.2626.

8-Methoxy-5-oxo-5*H*-chromeno[3,4-*c*]pyridine-10-yl acetate (13)



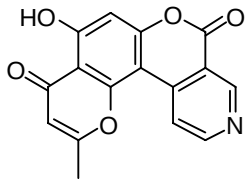
A flamed dried, argon flushed flask containing **12b** (3.9 g, 7.12 mmol) in CH_2Cl_2 (320 mL) cooled to 0 ^{o}C was added BCl_3 (35.6 mL, 35.6 mmol, 1 M in heptane) via syring. The mixture was stirred for 30 min, quenched with water, layers separated, aqueous phase washed with CH_2Cl_2, extracts combined, dried (Na_2SO_4), and concentrated in vacuo affording a colourless solid. This crude material was heated to 90 ^{o}C in a mixture of conc. HCl (47 mL, 564 mmol) and EtOH (47 mL) for 12 h before concentration in vacuo affording a tan solid that was dissolved in CH_2Cl_2 (50 mL), Ac_2O (3.4 mL, 35.6 mmol), and treated dropwise with NEt_3 (4.9 mL 35.6 mmol) at 0 ^{o}C. After the addition the whole was warmed to room temperature and stirred for 1 h, washed with water (50 mL), washed with saturated aqueous $NaHCO_3$ (2 x 50 mL), dried (Na_2SO_4), and concentrated in vacuo affording a tan solid. Flash column chromatography (EtOAc) yielded **13** (1.71 g, 84%) as a colourless solid. Recrystallization gave the product as transparent needles; mp 189-190 ^{o}C (EtOAc); IR (KBr) ν_{max} 1762, 1629, 1585, 1195, 1148, 1054 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.55 (s, 1H), 8.89 (d, 1H, J = 5.1 Hz), 8.15 (d, 1H, J = 5.0 Hz), 6.82 (s, 1H), 6.71 (s, 1H), 3.91 (s, 3H), 2.53 (s, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.0, 162.3, 159.6, 154.9, 154.4, 153.1, 150.0, 140.1, 117.4, 115.3, 108.2, 103.1, 100.3, 56.1, 21.6 ppm; EIMS (*m/z*(%)) 285[M^+](15), 243(100); HRMS (EI+) calculated for $C_{15}H_{11}NO_5$ 285.0637: found 285.0633.

10-Methyoxy schumanniophytine (14)



A solution of **13** (50 mg, 0.18 mmol), saturated aqueous $NaHCO_3$ (2 mL), water (1 mL) and MeOH (3 mL) was stirred at room temperature for 4 h, cooled to 0 ^oC, neutralized with conc. HCl, and then concentrated to dryness in vacuo. To this crude phenol was added 2-butynoic acid (30 mg, 0.36 mmol) and the flask was purged with argon before treatment with Eaton's reagent[2] (3 mL, 1:10 $MsOH:P_2O_5$). The reaction was stirred at 80 ^oC for 12 h, cooled to 0 ^oC, carefully basified with saturated aqueous $NaHCO_3$, extracted with $CHCl_3$ (3 x 5 mL), organic phase washed with 2M NaOH, dried (Na_2SO_4), and concentrated in vacuo affording a light brown solid. Flash column chromatography deactivated with 1% Et_3N (CH_2Cl_2, 3-6% MeOH) yielded **14** (28 mg, 52%) as a colourless solid; Recrystallization from CH_2Cl_2 gave the product as a colourless amorphous solid; mp 288-289 ^oC (decomp); IR (KBr) ν_{max} 2926, 2847, 1740, 1668, 1589, 1338, 1107, 861 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 9.53 (s, 1H), 8.92 (d, 1H, J = 5.1 Hz), 8.56 (d, 1H, J = 5.4 Hz), 6.77 (s, 1H), 6.20 (s, 1H), 4.01 (s, 3H), 2.49 (s, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.2, 162.9, 159.0, 157.6, 156.9, 155.0, 153.0, 139.6, 118.5, 115.0, 113.4, 112.1, 98.9, 96.9, 57.1, 19.8 ppm; EIMS (*m/z*(%)) 309[M^+](100), 280(45), 263(25), 239(8) ppm; HRMS (EI+) calculated for $C_{17}H_{11}NO_5$ [M^+] 309.0637: found 309.0637.

Schumanniophytine (1)



A solution of **14** (20 mg, 0.065 mmol) in CH_2Cl_2 (2 mL) at 0 ^oC was added BCl_3 (0.26 mL, 0.26 mmol, 1 M in heptane) via syring. The mixture was stirred for 30 min, quenched with water (5 mL), layers separated, aqueous phase washed with $CHCl_3$ (3 x 5 mL), extracts combined, dried (Na_2SO_4), and concentrated in vacuo yielding analytically pure schumanniophytine **(1)** (18.4 mg, 96%) as a yellow solid. Recrystallization from $CHCl_3$ gave the product as light yellow crystals; mp 295-298 ^oC (decomp), (lit.[3] mp 293-296 ^oC); IR (KBr) ν_{max} 2922, 1749, 1663, 1589, 1415, 1172, 1056, 871 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 13.47 (s, 1H), 9.58 (s, 1H), 8.97 (d, 1H, J = 5.7 Hz), 8.48 (d, 1H, J = 5.7 Hz), 6.81 (s, 1H), 6.34 (s, 1H), 2.65 (s, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 182.6, 175.7, 167.3, 164.6, 159.5, 158.4, 156.0, 155.2, 153.4 (d, 1C, J = 7.3 Hz), 139.8, 118.4 (d, 1C, J = 19.7 Hz), 115.1, 110.9, 108.6, 101.6, 97.8, 21.0 ppm; EIMS (*m/z*(%)) 295[M^+](31), 255(1), 149(100); HRMS (EI+) calculated for $C_{16}H_9NO_5$ [M^+] 295.0481: found 295.0486.

[3] T. R. Kelly, M. H. Kim, *J. Org. Chem.* **1992**, *57*, 1593–1597.