Supplementary Material (ESI) for Chemical Communications

Direct Intramolecular Arylation of Unactivated Arenes : Application to the Synthesis of Aporphine Alkaloids

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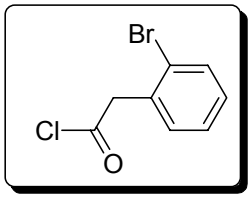
Supporting Information

General Methods. All experiments were carried out under an atmosphere of nitrogen. ^{1}H and ^{13}C NMR were recorded in $CDCl_3$ solutions using a Bruker AVANCE 300 spectrometer with Me_4Si as an internal standard. High-resolution mass spectra were obtained on a Kratos Concept IIH. Infra-Red analysis was performed with a Bruker EQUINOX 55. Unless otherwise specified, all reagents and solvents were used as is from commercial sources.

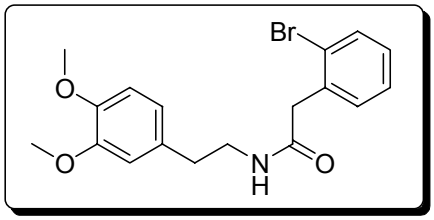
2-Bromophenylacetyl chloride[1]



To a solution of 2-bromo phenylacetic acid **6** (6g, 28mmol, 1eq.) in 60mL of dry dichloromethane (DCM) was added oxallyl chloride (2.68mL, 31mmol, 1.1eq.) in a 100mL round bottom flask equipped with a magnetic stir bar. To the mixture was added 1 drop of dimethylformamide (DMF) and the resulting mixture was stirred at 23°C for 4h. The reaction was then concentrated to produce the corresponding acid chloride as a pale yellow oil (6.51g, 99%). The crude product was pure by ^{1}H NMR and was consequently used without further purification. ^{1}H NMR (300MHz, $CDCl_3$, 293K, TMS): 4.32 (2H, s), 7.18-7.37 (3H, m), 7.59-7.63 (1H, m).

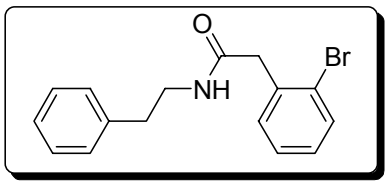
[1] Kuo, R.-Y.; Wu C.-C.; Chang, F.-R.; Yeh, J.-L.; Chen I.- J.; Wu, Y.- C.; *Bioorganic & Medicinal Chemistry Letters*, **2003**, *13*, 821-23.

2-(2-Bromophenyl)-N-[2-(3,4-dimethoxy-phenyl)-ethyl]-acetamide[1] (7a)



To a mixture of 3,4-Dimethoxy-phenylethylamine (8.0g, 44mmol, 1.0 eq.) and triethylamine (6.8mL, 51mmol, 1.1 eq.) in 150mL of dry DCM was added 2-bromo phenylacetyl chloride (10.86g, 47mmol, 1.05eq.) to a 250mL round bottom flask equipped with a magnetic stir bar at 0°C. The resulting mixture was stirred at 23°C for 8h during which time the reaction mixture turned yellow. It was then extracted with DCM and water and then recrystallized using a minimum of DCM followed by addition of Et_2O until precipitation occurs and was left at 0°C for 2 hours to afford **7a** as white needles (17.70g, 99%) R_f = 0.59 on silica gel (10% MeOH:DCM); mp = 127-129°C ($CHCl_3$); ^{1}H NMR (300MHz, $CDCl_3$, 293K, TMS): 2.71 (2H, t, *J*=6.9Hz), 3.47 (2H, q, *J*=6.9Hz), 3.67 (2H, s), 3.84 (3H, s), 3.86 (3H, s), 5.42 (1H, s), 6.58-6.74 (3H, m), 7.11-7.19 (1H, m), 7.27-7.28 (2H, m), 7.55 (1H, d, *J*=7.9Hz); ^{13}C NMR (75MHz, $CDCl_3$, 293K, TMS) : 35.0, 40.8, 44.1, 55.8, 55.9, 111.2, 111.6, 120.5, 124.9, 127.9, 129.1, 131.0, 131.6, 133.1, 134.7, 147.5, 148.9, 169.4; IR (nujol): 3313 (s), 3062 (w), 1647 (s), 1551 (s), 1235 (s), 1141 (s), 1027 (s) cm^{-1}. HRMS calculated for $C_{18}H_{20}BrNO_3$ (M+) 377.0627; Found : 377.0616.

2-(2-Bromophenyl)-N-phenethyl-acetamide[2](7b)

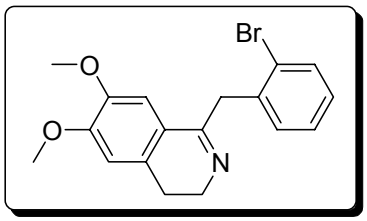


Following the experimental procedure described for the preparation of **7a**, **7b** was obtained as white solid in 95% yield. R_f = 0.49 on silica gel (100% EtOAc with TEA); mp = 111-112°C ($CHCl_3$); ^{1}H NMR (300MHz, $CDCl_3$, 293K, TMS): 2.75 (2H, t, *J*=6.8Hz), 3.47 (2H, q, *J*=6.7Hz), 3.66 (2H, s), 5.49 (1H, s), 7.05-7.28 (8H, m), 7.55 (1H, d, *J*=7.8Hz); ^{13}C NMR (75MHz, $CDCl_3$, 293K, TMS) : 35.5, 40.7, 44.0, 125.0, 126.4, 128.0, 128.6, 128.7, 129.1, 131.7, 133.1, 134.8, 138.6, 169.4; IR (KBr): 3269 (s), 3084

[2] Pandney, G. D.; Tiwari, Kamala P.; *Tetrahedron*, **1981,** *37 (6)*, 1213-14.

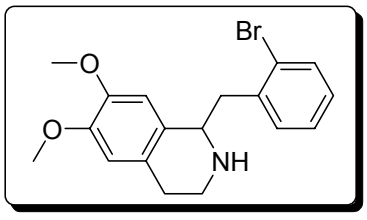
(m), 1643 (s), 1562 (s), 1026 (s) cm^{-1}. HRMS calculated for $C_{16}H_{16}BrNO$ (M+) 317.0415; Found : 317.0423;

1-(2-Bromobenzyl)-6,7-dimethoxy-3,4-dihydro-isoquinoline[1](8a)



To a solution of 2-(2-Bromophenyl)-N-[2-(3,4-dimethoxy-phenyl)-ethyl]-acetamide **7a** (6.0g, 16mmol, 1.0 eq.) in 80mL of dried DCM was added phosphorous oxychloride (5.8mL, 63mmol, 4.0eq.) in a 250mL round bottom flask equipped with a magnetic stir bar and a condenser at 0°C. The resulting mixture was refluxed for 6h. The reaction mixture turned yellow and was cooled to 0°C then made basic by adding slowly a 10% NaOH aqueous solution followed by extraction with DCM to afford **8a** (5.76g, 99%) as a pale yellow solid. The product was found to be pure by ^{1}H NMR and was used without further purification. R_f = 0.37 on silica gel (10% MeOH:DCM); mp = 115-117°C ($CHCl_3$); ^{1}H NMR (300MHz, $CDCl_3$, 293K, TMS): 2.67 (2H, t, *J*=7.8Hz), 3.73 (2H, t, *J*=7.7Hz), 3.79 (3H, s), 3.88 (3H, s), 4.19 (2H, s), 6.66 (1H, s), 6.91 (1H, s), 7.05 (1H, td, *J*=7.4, 1.5Hz), 7.18 (1H, td, *J*=7.4, 1.2Hz), 7.28 (1H, dd, *J*= 7.7, 1.6Hz), 7.57 (1H, dd, *J*=8.0, 1.2Hz); ^{13}C NMR (75MHz, $CDCl_3$, 293K, TMS) : 25.7, 42.6, 47.4, 56.9, 56.1, 109.0, 110.2, 121.4, 124.5, 127.6, 128.2, 130.2, 131.5, 132.8, 137.7, 147.3, 150.6, 164.9; IR (nujol): 2820 (w), 1515 (m), 1466 (s), 1267 (m), 1144 (m) cm^{-1}. HRMS calculated for $C_{18}H_{18}BrNO_2$ (M+) 359.0521; Found: 359.0476;

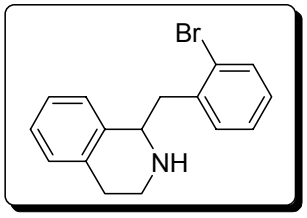
1-(2-Bromobenzyl)-6,7-dimethoxy-1,2,3,4-tetrahydro-isoquinoline[1]



To a solution of dihydroisoquinoline **8a** (5.76g, 16mmol, 1.0 eq.) in 80mL of MeOH at 0°C, was added slowly sodium borohydride (0.79g, 21mmol, 1.3eq.) in a 250mL round bottom flask equipped with a magnetic stir bar. The resulting mixture was stirred for 3h at 23°C. The reaction mixture was then cooled to 0°C and a brine solution was added and then extracted with DCM. Chromatography on silica gel neutralized with triethylamine (100% EtOAc) afforded the amine (5.71g, 99%) as a clear oil. R_f = 0.19 on silica

gel (100% EtOAc with 1% TEA); ^{1}H NMR (300MHz, $CDCl_3$, 293K, TMS): 2.67 (2H, t, *J*=7.8Hz), 3.73 (2H, t, *J*=7.7Hz), 3.79 (3H, s), 3.88 (3H, s), 4.19 (2H, s), 6.66 (1H, s), 6.91 (1H, s), 7.05 (1H, td, *J*=7.4, 1.5Hz), 7.18 (1H, td, *J*=7.4, 1.2Hz), 7.28 (1H, dd, *J*= 7.7, 1.6Hz), 7.57 (1H, dd, *J*=8.0, 1.2Hz); ^{13}C NMR (75MHz, $CDCl_3$, 293K, TMS) : 29.4, 40.0, 43.2, 54.8, 55.8, 55.9, 109.6, 111.6, 124.9, 127.1, 127.4, 128.2, 130.5, 132.0, 133.0, 138.8, 147.0, 147.4; IR: 3335 (w), 2933 (s), 2832 (s), 1523 (s), 1471 (s), 1254 (s), 1220 (s), 1108 (m), 1025 (s) cm^{-1}. HRMS calculated for $C_{18}H_{20}BrNO_2$ (M^+-C_7H_6Br) 192.1025; Found: 192.1032. MS (CI): m/z (%) = 362 (38), 302 (21), 280 (28), 192 (100), 176 (41), 132 (90);

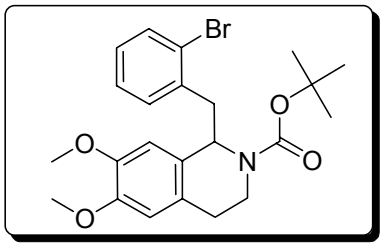
1-(2-bromobenzyl)-1,2,3,4-tetrahydroisoquinoline



To a solution of 2-(2-Bromophenyl)-N-phenethyl-acetamide **7b** (4.0g, 13mmol, 1.0 eq.) in a 100mL round bottom flask equipped with a magnetic stirrer was added polyphosphoric acid (33.27g, 332.7mmol, 25.6 eq.) and the resulting mixture was heated to 150^{o}C overnight. The reaction was then allowed to cool to room temperature and a solution of 10% NaOH was added until basic. The resulting mixture was extracted with Et_2O to afford **8b** (3.91g, 99%) as a brownish oil. The product was found to be pure by ^{1}H NMR and was used without any further purification. This compound was found to be unstable and decomposes on sitting or exposure to silica gel. It was therefore reduced to the amine immediately. R_f = 0.35 on silica gel (30% EtOAc neutralized with TEA); ^{1}H NMR (300MHz, $CDCl_3$, 293K, TMS): 2.73 (2H, t, *J*=7.5Hz), 3.74 (2H, t, *J*=7.4Hz), 4.19 (3H, s), 7.03-7.09 (1H, m), 7.16-7.25 (4H, m), 7.32 (1H, td, *J*=7.4, 1.1Hz), 7.43 (1H, d, *J*= 7.5Hz), 7.57 (1H, d, *J*=7.8 Hz); ^{13}C NMR (75MHz, $CDCl_3$, 293K, TMS) : 26.0, 42.3, 47.2, 124.8, 125.2, 126.9, 127.4, 127.5, 128.0, 128.8, 130.4, 130.6, 132.7, 137.6, 137.8, 165.2; To a solution of the crude dihydroisoquinoline (3.91g, 13mmol, 1.0 eq.) in 100mL of methanol (MeOH) at 0^{o}C, was added slowly sodium borohydride (0.64g, 17mmol, 1.3eq.) in a 250mL round bottom flask equipped with a magnetic stir bar. The resulting mixture was stirred for 3h at 23^{o}C. The reaction mixture was then

cooled to 0°C and a brine solution was added and then extracted with DCM. Chromatography on silica gel neutralized with triethylamine (30% EtOAc) afforded the amine (3.62g, 92%) as a pale yellow oil. R_f = 0.32 on silica gel (30% EtOAc with 1% TEA); ^{1}H NMR (300MHz, $CDCl_3$, 293K, TMS): 1.44 (1H, s), 2.81-2.87 (2H, ,m), 2.94-3.02 (2H, m), 3.23-3.31 (1H, m), 3.43 (1H, dd, *J*=13.7, 3.3 Hz), 4.35 (1H, dd, *J*=10.6, 3.1 Hz), 7.10-7.20 (4H, m), 7.28-7.30 (2H, m), 7.35-7.38 (1H, m), 7.60 (1H, d, *J*= 7.8 Hz); ^{13}C NMR (75MHz, $CDCl_3$, 293K, TMS) :30.1, 40.3, 43.2, 55.4, 125.2, 126.1, 126.5, 126.8, 127.7, 128.5, 129.5, 132.2, 133.4, 135.4, 138.8, 139.0; IR: 3336 (w), 3061 (m), 2927 (s), 2832 (m), 1469 (m), 1126 (m), 1025 (m) cm^{-1}. HRMS calculated for $C_9H_{10}N$ (M^+-C_7H_6Br) 132.0813; Found : 132.0800. MS (CI): m/z (%) = 302 (35), 220 (27), 132 (100);

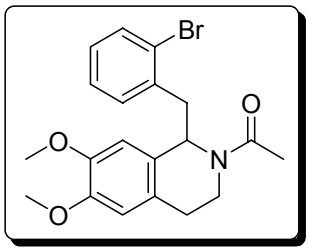
1-(2-Bromobenzyl)-6,7-dimethoxy-3,4-dihydro-1H-isoquinoline-2-carboxylic acid tert-butyl ester (9a)



To a solution of 1-(2-Bromobenzyl)-6,7-dimethoxy-1,2,3,4-tetrahydro-isoquinoline (1.4g, 3.9mmol, 1.0 eq.), diisopropylethylamine (1.35mL, 7.8mmol, 2.0 eq.) and 3mg of dimethylamino pyridine (DMAP) in DCM (40mL) was added slowly di-*tert*-butyl dicarbonate (1.07mL, 4.7mmol, 1.2 eq.) and the resulting mixture was stirred overnight at 23°C. The reaction was then quenched by adding a solution of NH_4Cl and was extracted with DCM. Chromatography on triethylamine neutralized silica gel (100% Ethyl Acetate) afforded **9a** as a white crystalline solid (1.44g, 80%). R_f = 0.51 on silica gel (100% EtOAc with 1% TEA); mp = 108-109°C ($CHCl_3$); ^{1}H NMR (300MHz, DMSO *d*-6, 383K): 1.21 (9H, s), 2.49-2.8 (2H, m), 3.07-3.23 (2H, m), 3.32-3.41 (1H, m), 3.70 (3H, s), 3.76 (3H, s), 4.00-4.07 (1H, m), 5.29-5.33 (1H, m), 6.70 (2H, d, *J*=12.9 Hz), 7.12-7.29 (3H, m), 7.56 (1H, d, *J*=7.9Hz); ^{13}C NMR (75MHz, DMSO *d*-6, 383K): 28.3, 28.7, 38.2, 42.7, 54.8, 57.1, 79.5, 112.9, 114.5, 125.6, 127.8, 128.1, 129.0, 130.1, 132.9, 133.1, 138.9, 148.8, 149.4, 154.5; IR: 3063 (w), 2931 (s), 1686 (s), 1519 (m), 1420 (m), 1228

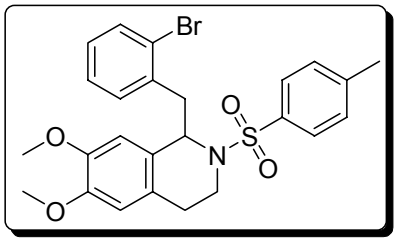
(m), 1161 (s), 1099 (m) cm^{-1}. HRMS calculated for $C_{23}H_{28}BrNO_4$ (M^+-C_4H_9O) 388.0548; Found: 388.0559.

1-[1-(2-Bromobenzyl)-6,7-dimethoxy-3,4-dihydro-1H-isoquinolin-2-yl]-ethanone (9b)



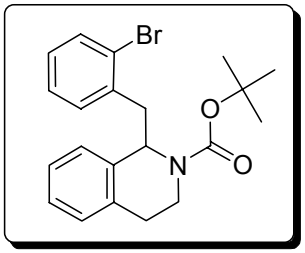
To a solution of 1-(2-Bromobenzyl)-6,7-dimethoxy-1,2,3,4-tetrahydro-isoquinoline (1.4g, 3.9mmol, 1.0 eq.), diisopropylethylamine (1.35mL, 7.8mmol, 2.0 eq.) and 3mg of DMAP in dry DCM was added slowly acetic anhydride (0.80mL, 7.8mmol, 2.0 eq.) and the resulting mixture was stirred overnight at 23°C. The reaction was then quenched by adding a solution of NH_4Cl and was extracted with DCM. Chromatography on TEA neutralized silica gel (100% Ethyl Acetate) afforded **9b** as a white solid (1.22g, 78%). mp = 122-123°C ($CHCl_3$); R_f = 0.30 on silica gel (100% EtOAc with 1% TEA); ^{1}H NMR (300MHz, $CDCl_3$, 293K, TMS, mixture of rotomers): 1.49 (2H, s), 2.09 (1H, s), 2.66-2.95 (2H, m), 3.08-3.31 (2.7H, m), 3.34-3.40 (1H, m), 3.62-3.79 (0.6H, m), 3.64 (1H, s), 3.85 (3.5H, s), 3.87 (1.5H, s), 4.80-4.86 (0.6H, m), 5.02-5.07 (0.7H, m), 5.80 (0.3H, t, *J*=7.2Hz), 6.29 (0.3H, s), 6.59 (0.3H, s), 6.63 (0.7H, s), 6.76 (0.7H, s), 7.02-7.29 (3H, m), 7.48 (0.3H, d, *J*=7.9Hz), 7.60 (0.7H, d, *J*=7.9Hz); ^{13}C NMR (75MHz, $CDCl_3$, 293K, TMS, mixture of rotomers) : 20.9, 22.3, 28.3, 28.9, 35.3, 41.7, 41.8, 43.3, 53.1, 56.1, 56.2, 56.3, 56.3, 56.9, 110.0, 110.7, 111.2, 111.8, 125.0, 125.9, 126.1, 127.0, 127.5, 128.3, 128.3, 128.5, 129.3, 132.0, 132.6, 132,9, 133.2, 137.5, 138.2, 147.6, 147.8, 148.1, 148.5, 169.6, 170.1; IR: 3017 (w), 3011 (s), 2956 (s), 1637 (s), 1519 (m), 1422 (s), 1253 (m), 1122 (m) cm^{-1}. HRMS calculated for $C_{20}H_{22}BrNO_3$ (M^+-C_7H_6Br) 234.1130; Found: 234.1094. MS (CI): m/z (%) = 404 (51), 302 (20), 234 (99), 220 (21), 192 (93), 176 (27), 132 (100);]

1-(2-Bromobenzyl)-6,7-dimethoxy-2-(toluene-4-sulfonyl)-1,2,3,4-tetrahydro-isoquinoline (9c)



To a solution of 1-(2-Bromobenzyl)-6,7-dimethoxy-1,2,3,4-tetrahydro-isoquinoline (1.4g, 3.9mmol, 1.0 eq.) and pyridine (0.47mL, 5.8 mmol, 1.5 eq.) in dichloromethane (DCM) was added slowly *p*-toluenesulfonyl chloride (0.81g, 4.3mmol, 1.1 eq.) and the resulting mixture was stirred overnight at 23^{o}C. The reaction was then quenched by adding a solution of NH_4Cl and was extracted with DCM. The product was then purified by silica chromatography (100% EtOAc) to afford **9c** as a white crystalline solid (1.04g, 54%). R_f = 0.58 on silica gel (100% EtOAc); mp = 132-133^{o}C ($CHCl_3$); ^{1}H NMR (300MHz, $CDCl_3$, 293K, TMS): 2.29 (3H, s), 2.53-2.59 (1H, m), 2.67-2.78 (1H, m), 3.16 (2H, d, *J*= 7.2Hz), 3.57 (1H, dd, *J*= 14.4, 4.4Hz), 3.64 (3H, s), 3.77 (3H, s), 3.88 (1H, dd, *J*= 13.4, 4.6Hz), 5.22 (1H, t, *J*= 7.2Hz), 6.30 (1H, s), 6.45 (1H, s), 7.05 (4H, t, *J*= 8.0Hz), 7.15 (1H, t, *J*=7.2Hz) 7.44 (3H, d, *J*=7.9Hz); ^{13}C NMR (75MHz, $CDCl_3$, 293K, TMS) : 21.1, 26.3, 38.8, 43.0, 55.4, 55.5, 109.5, 111.0, 124.8, 124.9, 126.7, 127.0, 127.1, 128.0, 129.0, 132.0, 132.3, 136.9, 137.0, 142.5, 146.6, 147.6; IR: 2968 (w), 2937 (s), 1517 (m), 1463 (m), 1251 (m), 1156 (m), 1107 (m), 1021 (m) cm^{-1}. HRMS calculated for $C_{25}H_{26}BrSNO_4$ (M^+-C_7H_6Br) 346.1113; Found : 346.1145. MS (CI): m/z (%) = 516 (31), 436 (5), 346 (100), 282 (21), 192 (63);

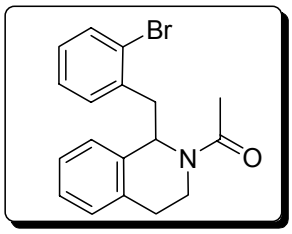
tert-butyl 1-(2-bromobenzyl)-3,4-dihydroisoquinoline-2(1H)-carboxylate (10a)



Following the experimental procedure described for the preparation of **9a**, **10a** was obtained as a clear crystalline solid in 88% yield after silica gel chromatography (10% EtOAc/Hexane). (R_f = 0.59 on silica gel (30% EtOAc); mp = 108-110 ^{o}C ($CHCl_3$); ^{1}H NMR (300MHz, $CDCl_3$, 293K, TMS, mixture of rotomers): 1.08 (7.5H, s), 1.32 (1.5H, s), 2.72-3.13 (3H, m), 3.25-3.35 (1.8H, m), 3.40-3.50 (0.2H, m), 3.98 (0.2H, dt, *J*=12.9, 5.0Hz), 4.41 (0.8H, dd, *J*=13.3, 5.0Hz), 5.46-5.56 (1H, m), 7.07-7.26 (6.20H, m), 7.40-7.43 (0.8H, m), 7.50 (0.2H, d, *J*=7.9Hz), 7.57 (0.8H, d,

J=7.9 Hz); ^{13}C NMR (75MHz, $CDCl_3$, 293K, TMS, mixture of rotomers) : 28.3, 28.7, 29.0, 29.2, 36.5, 39.1, 42.6, 43.2, 54.3, 54.4, 79.9, 125.8, 126.5, 126.6, 127.0, 127.1, 127.4, 127.5, 127.8, 127.9, 128.4, 128.7, 129.0, 129.6, 131.9, 132.3, 133.0, 134.9, 137.7, 138.5, 154.7; HRMS calculated for $C_9H_{10}N$ (M^+-C_4H_9O) 328.0337; Found : 328.0345. IR: 2977 (w), 2930 (m), 1690 (s), 1451 (m), 1158 (m) cm^{-1}.

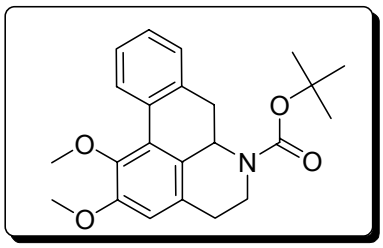
1-[1-(2-Bromobenzyl)-3,4-dihydro-1H-isoquinolin-2-yl]-ethanone (10b)



Following the experimental procedure described for the preparation of **9b**, tetrahydroisoquinoline **10b** was obtained as a pale yellow oil in 81% yield after a silica gel chromatography (30% EtOAc/Hexane). R_f = 0.16 on silica gel (30% EtOAc/Hex with 1% TEA); ^{1}H NMR (300MHz, $CDCl_3$, 293K, TMS, mixture of rotomers): 1.41 (2.1H, s), 2.02 (0.9H, s), 2.73-2.99 (2H, m), 3.05-3.20 (1.7H, m), 3.27-3.39 (1H, m), 3.64-3.68 (0.6H, m), 4.79-4.85 (0.7H, m), 5.10-5.14 (0.7H, m), 5.80 (0.3H, t, *J*=6.4Hz), 7.01-7.25 (6.3H, m), 7.38 (0.7H, d, *J*=6.1Hz), 7.45 (0.3H, d, *J*=7.7Hz), 7.56 (0.7H, d, *J*=7.6Hz); ^{13}C NMR (75MHz, $CDCl_3$, 293K, TMS, mixture of rotomers) : 20.8, 22.3, 28.7, 29.37, 35.3, 41.8, 42.0, 43.3, 53.4, 57.2, 125.1, 125.7, 126.7, 127.2, 127.3, 127.5 127.6, 127.9, 128.3, 128.6, 128.8, 129.4, 129.7, 131.9, 132.5, 132.9, 133.2, 134.3, 134.9, 136.7, 136.8, 137.5, 138.0, 169.3, 169.8; IR: 3063 (w), 2932 (s), 1636 (s), 1421 (m), 1026 (m) cm^{-1}. HRMS calculated for $C_9H_{10}N$ (M^+-C_7H_6Br) 174.0919; Found : 174.0936. MS (CI): m/z (%) = 344 (72), 264 (31), 174 (97), 144 (39), 132 (100);

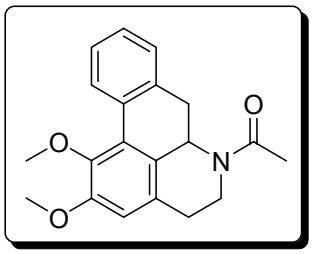
General procedure:

1-(1,2-Di1,2-Dimethoxy-4,5,6a,7-tetrahydro-dibenzoquinoline-6-carboxylic acid tert-butyl ester (11a)



To a oven dried flask was added tetrahydroisoquinoline **9a** (0.101g, 0.22mmol, 1.0 eq.), palladium (II) acetate (0.0025g, 0.011mmol, 0.05 eq.), potassium acetate (0.040g, 0.44mmol, 2.0eq.) and 2-(diphenylphosphino)-2'-(N,N-dimethylamino)biphenyl (0.0084g, 0.022mmol, 0.1 eq.) followed by rigorous purging with nitrogen. Dimethylacetamide (DMA)(2mL) was then added and the mixture was heated to 135^{o}C for 4.5h in a preheated oil bath. The product was then loaded on a silica gel column (20% EtOAc/Hex) to afford **11a** as a white solid (0.075g, 90%). (R_f = 0.57 on silica gel (100% EtOAc); mp = 149-151^{o}C ($CHCl_3$); ^{1}H NMR (300MHz, $CDCl_3$, 293K, TMS): 1.49 (9H, s), 2.63-3.00 (5H, m), 3.66 (3H, s), 3.89 (3H, s), 4.41-4.44 (1H, m), 4.64-4.69 (1H, m), 6.67 (1H, s), 7.21-7.34 (3H, m), 8.44 (1H, d, *J*=7.8 Hz); ^{13}C NMR (75MHz, $CDCl_3$, 293K, TMS) : 28.8, 30.7, 35.7, 38.7, 51.9, 56.2, 60.3, 80.2, 111.7, 126.8, 127.3, 127.9, 128.0, 128.4, 128.7, 130.1, 132.0, 137.3, 145.8, 152.2, 155.0; IR: 3070 (s), 2930 (s), 1687 (s), 1406 (m), 1249 (m), 1163 (m), 1106 (m) cm^{-1}. HRMS calculated for $C_{23}H_{27}NO_4$ (M+) 381.1940; Found : 381.1943.

methoxy-4,5,6a,7-tetrahydro-dibenzo[de,g]quinolin-6-yl)-ethanone (N-Acetyl nornuciferine)[3] (11b)

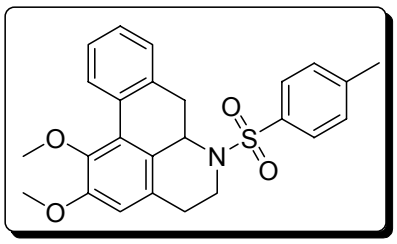


Following the general procedure, **11b** was obtained as a white solid in 99% yield after a column on silica (100% EtOAc). R_f = 0.17 on silica gel (100% EtOAc with TEA); mp = 223-224^{o}C ($CHCl_3$); ^{1}H NMR (300MHz, $CDCl_3$, 293K, TMS, mixture of rotormers): 2.16

[3] Kupchan, M. S.; Moniot, J. L.; Kanojia, R. M.; O'Brien, J. B.; *J. Org. Chem.*, **1971**, *36 (17)*, 2413-18.

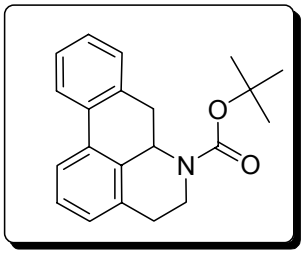
(1.3H, s), 2.22 (1.7H, s), 2.64-2.93 (3.4, m), 3.03-3.15 (1.0H, m), 3.31 (0.5H, t, *J*=12.3 Hz), 3.67 (3H, s), 3.90 (3H, m), 4.01 (0.6H, d, *J*=12.1Hz), 4.57 (0.5H, d, *J*=12.5Hz), 4.97 (0.5H, d, *J*=9.1Hz), 5.10 (0.6H, d, *J*=12.6Hz), 6.67 (0.6H, s), 6.70 (0.4H, s), 7.27-7.33 (3H, m), 8.42-8.48 (1H, m); ^{13}C NMR (75MHz, $CDCl_3$, 293K, TMS, mixture of rotomers) : 21.6, 22.6, 29.9, 30.7, 34.0, 36.3, 36.5, 41.9, 50.3, 53.7, 55.9, 59.9, 111.2, 111.6, 125.4, 126.4, 126.9, 127.3, 127.4, 127.7, 127.7, 127.8, 128.0, 128.3, 128.6, 128.6, 128.9, 130.1, 131.5, 131.6, 136.1, 136.8, 145.5, 145.7, 152.0, 152.2, 169.64; IR: 2935 (s), 2892 (m), 1625 (s), 1443 (m), 1423 (m), 1029 (m) cm^{-1}. HRMS calculated for $C_{20}H_{21}NO_3$ (M+) 323.1521; Found : 323.1527.

1,2-Dimethoxy-6-(toluene-4-sulfonyl)-5,6,6a,7-tetrahydro-4H-dibenzo[de,g]quinoline (11c)



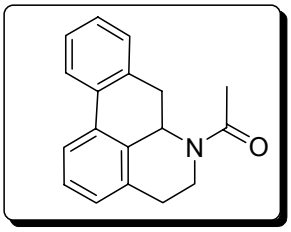
Following the general procedure, 11c was obtained as a white solid in 99% yield after a column on silica (20% EtOAc/Hexane). (R_f = 0.38 on silica gel (30% EtOAc); mp = 179-181^{o}C ($CHCl_3$); ^{1}H NMR (300MHz, $CDCl_3$, 293K, TMS): 2.32-2.48 (2H, m), 2.37 (3H, s), 3.02 (1H, t, *J*=13.8Hz), 3.16 (1H, dd, *J*=13.9, 4.4Hz), 3.24-3.33 (1H, m), 3.63 (3H, s), 3.90 (3H, s), 3.84 (3H, s), 4.06-4.13 (1H, m), 4.59 (1H, dd, *J*=13.7, 4.2 Hz), 6.53 (1H, s), 7.23 (2H, d, *J*=8.1 Hz), 7.26-7.36 (3H, m), 7.69 (2H, d, *J*=8.2Hz), 8.41(1H, d, *J*=7.7Hz); ^{13}C NMR (75MHz, $CDCl_3$, 293K, TMS) : 21.8, 29.0, 38.2, 41.2, 53.4, 56.2, 60.4, 111.6, 125.6, 127.2, 127.5, 128.2, 128.2, 128.7, 128.8, 129.2, 130.2, 131.7, 136.7, 138.2, 143.6, 146.0, 152.5; IR: 2928 (s), 2851 (m), 1452 (m), 1319 (m), 1149 (s), 1091 (m) cm^{-1}. HRMS calculated for $C_{25}H_{25}SNO_4$ (M+) 435.1504; Found : 435.1488.

4,5,6a,7-tetrahydro-dibenzoquinoline-6-carboxylic acid tert-butyl ester (13a)



Following the general procedure, **13a** was obtained as a white solid in 99% yield after a column on silica (10% ether/Hexane). (R_f = 0.76 on silica gel (70% EtOAc); mp = 153-155^{o}C ($CHCl_3$); ^{1}H NMR (300MHz, $CDCl_3$, 293K, TMS): 1.51 (9H, s), 2.71-2.79 (1H, m), 2.84-3.01 (3H, m), 3.1 (1H, dd, *J*=13.9, 4.1 Hz), 4.44-4.46 (1H, m), 3.89 4.86-4.91 (1H, m), 7.10 (1H, d, *J*=7.5 Hz), 7.24-7.35 (4H, m), 7.61 (1H, d, *J*=7.7 Hz), 7.77 (1H, d, *J*=7.6 Hz); ^{13}C NMR (75MHz, $CDCl_3$, 293K, TMS) : 28.8, 30.7, 34.6, 39.0, 51.8, 80.2, 122.6, 124.0, 127.1, 127.6, 128.1, 128.2, 129.0, 133.0, 134.2, 134.7, 135.3, 136.0, 155.0; IR: 2963 (m), 2929 (s), 1677(s), 1414 (m), 1212 (s), 1113 (m) cm^{-1}. HRMS calculated for $C_{21}H_{23}NO_2$ (M^+-C_4H_9); 264.102 Found : 264.0968.

1-(4,5,6a,7-tetrahydro-dibenzo[de,g]quinolin-6-yl)-ethanone[3] (13b)



Following the general procedure, **13b** was obtained as a white solid in 76% yield after a column on silica (100% EtOAc). R_f = 0.29 on silica gel (100% EtOAc); mp = 205 -207 ^{o}C ($CHCl_3$); 300MHz, $CDCl_3$, 293K, TMS, mixture of rotormers): 2.20 (1.1H, s), 2.24 (1.9H, s), 2.72-2.97 (3.4, m), 3.1-3.22 (1.0H, m), 3.31 (0.6H, t, *J*=11.9 Hz), 4.01-4.05 (0.6H, m), 4.74-4.79 (0.4H, m), 4.98-5.02 (0.4H, m), 5.26-5.32 (0.6H, m), 7.08-7.15 (1H, m), 7.25-7.36 (4H, m), 7.61-7.63 (1H, m), 7.75-7.82 (1H, m); ^{13}C NMR (75MHz, $CDCl_3$, 293K, TMS, mixture of rotomers) : 21.9, 23.0, 30.2, 31.0, 33.2, 35.8, 36.9, 42.5, 50.6, 53.9, 122.8, 122.9, 123.9, 124.2, 127.1, 127.6, 127.8, 128.1, 128.2, 128.3, 128.3, 128.4, 128.8, 129.4, 132.2, 132.9, 133.9, 134.1, 134.3, 134.6, 134.9, 135.1 135.6, 135.8, 169.5, 170.0; IR: 2959 (w), 2925 (s), 1730 (s), 1434 (m), 1417 (m) cm^{-1}. HRMS calculated for $C_{18}H_{17}NO$ (M+) 263.1310; Found : 263.1298.