Supplementary data for:

Synthesis of a 6-aryloxymethyl-5-hydroxy-2,3,4,5-tetrahydro-[1*H*]-2-benzazepin-4-one: a muscarinic (M_3) antagonist

Paul Evans, Alan T. L. Lee and Eric J. Thomas*

The School of Chemistry, The University of Manchester, Manchester, M13 9PL, UK

e-mail: e.j.thomas@manchester.ac.uk

Experimental

General

Low resolution mass spectra were recorded on a Micromass Trio 200 spectrometer; high resolution mass spectra were recorded on a Kratos Concept IS spectrometer. Modes of ionisation were electron impact (EI), chemical ionisation (CI) using ammonia, or electrospray in positive or negative mode (ES±). For halogenated compounds, characteristic groups of peaks due to different isotopes were observed. Infrared spectra were recorded on a Genesis FTIR spectrometer as evaporated films (from deuterochloroform or dichloromethane) on sodium chloride plates. Nuclear magnetic resonance spectra were performed using deuterated chloroform ($CDCl_3$) as the solvent unless otherwise stated. Proton nuclear magnetic resonance spectra (^{1}H NMR) were recorded on a Varian INOVA Unity 500 and 300 (500 and 300 MHz) spectrometers. Residual non-deuterated solvent was used as the internal standard. Coupling constants (*J*) are quoted in Hertz (Hz). Carbon nuclear magnetic resonance spectra (^{13}NMR) were recorded on a Varian INOVA Unity 300 (75MHz) spectrometer.

Flash column chromatography was carried out using Merck silica gel 60H (40-60 nm, 230-300 mesh). Thin layer chromatography (TLC) was carried out using plastic plates coated with Merck HF254/366 silica gel. All reagents and solvents were purified by standard techniques and reactions in non-aqueous solvents were carried out under an atmosphere of nitrogen or argon.

2-Bromo-1,3-bis(bromomethyl)benzene 6[5]

N-Bromsuccinimide (106 g, 595 mmol) and azobisisobutyronitrile (*ca*. 50 mg) were added to a solution of 2-bromo-*m*-xylene **5** (50 g, 270 mmol) in carbon tetrachloride (500 cm^3) and the reaction mixture was stirred under reflux for 16 h. The mixture was filtered, the precipitate washed with ether (2 x 100 cm^3), and the filtrate and washings were concentrated under reduced pressure. Chromatography of the residue using light petroleum as eluent gave the tribromide **6** (49.22 g, 54 %), as a white solid, m.p. 101-103 °C (lit.,[5] 97-98 °C); υ_{max} 2358, 1427, 1261, 1209, 1116, 1025, 866, 800 and 724 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 7.46 (2 H, d, *J* 7.5, ArH), 7.33 (1 H, m, ArH) and 4.69 (4 H, s, 2 x CH_2); *m/z* (EI) 344 (M^+, 3%), 342, (M^+, 3), 265 (36), 263 (74), 261 (38), 182 (38), 184 (40) and 103 (100).

2-Bromo-3-(bromomethyl)-1-(2,6-dimethoxyphenoxymethyl)benzene 7

2,6-Dimethoxyphenol (24.61 g, 54.3 mmol) in tetrahydrofuran (100 cm^3) was added dropwise to a cooled (0 °C) suspension of sodium hydride (2.61 g, 54.3 mmol, 60 % w/w dispersion in mineral oil) in tetrahydrofuran (278 cm^3) and the mixture was stirred vigorously for 30 mins, before adding the bromide **6** (24.61 g, 72.4 mmol) in tetrahydrofuran (100 cm^3). The reaction was stirred under reflux for 16 h then cooled (0 °C), and saturated aqueous ammonium chloride (500 cm^3) was added. The mixture was extracted with ether (3 x 500 cm^3) and the organic extracts were washed with brine, dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography of the residue using ether : light petroleum (0 : 100 → 50 : 50) as eluent gave the *title compound* **7** (15.35 g, 51 %) as a white solid, m.p. 106-108 °C (Found: M^+, 413.9459. $C_{16}H_{16}O_3{}^{79}Br_2$ requires *M*, 413.9461); υ_{max} 1596, 1494, 1478, 1435, 1296, 1256, 1218, 1111, 1046, 1027, 791, 767 and 720 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 7.81 (1 H, br. dd, *J* 7.5, 2, ArH), 7.47-7.34 (2 H, m, ArH), 7.06 (1 H, t, *J* 8.5, ArH), 6.63 (2 H, d, *J* 8.5, ArH), 5.15 and 4.71 (each 2 H, s, CH_2) and 3.86 (6 H, s, 2 x OCH_3); δ_C (75 MHz, $CDCl_3$) 153.96, 139.54, 137.13, 130.34, 129.76, 127.84, 124.35, 105.54, 74.40, 56.41 and 34.40; *m/z* (CI) 434 (M^++18, 100%) and 417 (22).

[2-Bromo-3-(2,6-dimethoxyphenoxymethyl)phenyl]methanol 8

The dibromide **7** (15.78 g, 38 mmol) and potassium carbonate (1.49 g, 11 mmol) were heated under reflux in dioxane:water (1 : 1, 180 cm^3) for 16 h. The reaction mixture was then cooled and extracted with ethyl acetate (4 x 200 cm^3). The organic extracts were washed with brine, dried (Na_2SO_4) and concentrated under reduced pressure to give the *title compound* **8** (13.72 g, 99%), as a white solid, m.p. 101-102 °C (Found: M^++H, 353.0380. $C_{16}H_{18}O_4{}^{79}Br$ requires *M*, 353.0383); υ_{max} 3401, 1597, 1495, 1478, 1297, 1256, 1217, 1111, 1022, 777 and 765 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 7.78 (1 H, br. dd, *J* 7.5, 2, ArH), 7.48-7.35 (2 H, m, ArH), 7.05 (1 H, t, *J* 8.5, ArH), 6.63 (2 H, d, *J* 8.5, ArH), 5.15 and 4.79 (each 2 H, s, CH_2), 3.85 (6 H, s, 2 x CH_3) and 2.31 (1 H, br. s, OH); δ_C (75 MHz, $CDCl_3$) 153.99, 139.98,

138.42, 137.20, 128.90, 127.99, 127.65, 124.30, 122.60, 105.60, 74.36, 65.63 and 56.41; *m/z* (CI) 372 (M^++18, 90%), 370 (M^++18, 100), 353 (34) and 355 (32).

2-[2-(2,6-Dimethoxyphenoxymethyl)-6-(hydroxymethyl)phenyl]propan-2-ol 9

n-Butyllithium (1.6 M in hexanes, 19.0 cm^3, 31 mmol) was added dropwise to a cooled (-78 ºC) solution of the bromide **8** (5.0 g, 14 mmol) in tetrahydrofuran (50 cm^3) and the mixture was stirred for 45 mins before acetone (5.19 cm^3, 71 mmol) was added dropwise. After a further 2 h at -78 ºC, saturated methanolic ammonium chloride (20 cm^3) and water (50 cm^3) were added. The mixture was extracted with ethyl acetate (4 x 50 cm^3) and the organic extracts were washed with brine, dried (Na_2SO_4) and concentrated under reduced pressure. Chromatography of the residue using ethyl acetate : light petroleum (1 : 3) as eluent gave the *title compound* **9** (3.51 g, 75%), as a white solid, m.p. 99-101 °C (Found: M^++NH_4, 350.1963. $C_{19}H_{28}NO_5$ requires *M*, 350.1962) υ_{max} 3451, 1597, 1494, 1478, 1296, 1255, 1112, 1031, 961, 771 and 732 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 7.56 and 7.36 (each 1 H, dd, *J* 7.5, 1.5, ArH), 7.24 (1 H, t, *J* 7.5, ArH), 7.05 (1 H, t, *J* 8.5, ArH), 6.57 (2 H, d, *J* 8.5, ArH), 5.26 and 4.86 (each 2 H, s, CH_2), 3.88 (6 H, s, 2 x OCH_3) and 1.93 (6 H, s, 2 x CH_3); δ_C (75 MHz, $CDCl_3$) 153.94, 146.92, 138.24, 136.72, 135.20, 133.77, 132.70, 126.83, 124.32, 105.44, 75.76, 75.10, 66.40, 56.27 and 33.29; *m/z* (CI) 332 (5%), 315 (3), 297 (21) and 154 (100).

2-[2-(*tert*-Butyldimethylsilyloxymethyl)-6-(2,6-dimethoxyphenoxymethyl)phenyl]propan-2-ol 10

tert-Butyldimethylsilyl chloride (2.33 g, 15.5 mmol) was added to a cooled (0 °C) solution of the diol **9** (3.44 g, 10.4 mmol) and imidazole (1.76 g, 25.9 mmol) in anhydrous dichloromethane (43.3 cm^3) and the mixture stirred for 2 h at room temperature. Water (50 cm^3) was added and the mixture was extracted with dichloromethane (3 x 50 cm^3). The organic extracts were washed with brine, dried (Na_2SO_4) and concentrated under reduced pressure. Chromatography of the residue using ethyl acetate : light petroleum (1 : 3) as eluent gave the *title compound* **10** (4.58 g, 99%) as a colourless oil (Found: M^++Na, 469.2382. $C_{25}H_{38}O_5SiNa$ requires *M*, 469.2381); υ_{max} 3503, 1597, 1494, 1478, 1255, 1113, 838 and 775 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 7.62 and 7.33 (each 1 H, dd, *J* 7.5, 2, ArH), 7.23 (1 H, t, *J* 7.5, ArH), 7.05 (1 H, t, *J* 8.5, ArH), 6.63 (2 H, d, *J* 8.5, ArH), 5.47 (1 H, s, OH), 5.27 and 5.00 (each 2 H, s, CH_2), 3.89 (6 H, s, 2 x OCH_3), 1.81 (6 H, s, 2 x CH_3), 0.96 [9 H, s, $OSiC(CH_3)_3$] and 0.15 [6 H, s, $OSi(CH_3)_2$]; δ_C (75 MHz, $CDCl_3$) 154.04, 147.03, 137.39, 136.90, 135.33, 133.55, 131.81, 126.44, 124.22, 105.43, 75.37, 74.84, 67.31, 56.28, 32.95, 26.17, 18.51 and -4.80; *m/z* (ES) 469 (M^++23, 100%).

2-[2-(*tert*-Butyldimethylsilyloxymethyl)-6-(2,6-dimethoxyphenoxymethyl)phenyl]propene 11

Methane sulfonyl chloride (3.89 cm^3, 50.3 mmol) was added dropwise to a cooled (0 °C) solution of the alcohol **10** (4.48 g, 10.1 mmol), triethylamine (14.00 cm^3, 100.5 mmol) and 4-dimethylaminopyridine (45.1 mg, 0.4 mmol) in dichloromethane (50.5 cm^3) and the mixture was stirred for 16 h at room temperature. Water (50 cm^3) added and the mixture extracted with dichloromethane (3 x 50 cm^3). The organic extracts were washed with brine, dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography of the residue using ethyl acetate : light petroleum (1 : 10 → 1 : 3) as eluent gave the *title compound* **11** (2.82 g, 66%) as a colourless oil (Found: M^+, 428.2378. $C_{25}H_{36}O_4Si$ requires *M*, 428.2377); υ_{max} 1596, 1493, 1478, 1254, 1114, 838 and 774 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 7.67 and 7.53 (each 1 H, d, *J* 7.5, ArH), 7.36 (1 H, t, *J* 7.5, ArH), 7.04 (1 H, t, *J* 8.5, ArH), 6.62 (2 H, d, *J* 8, ArH), 5.30 (1 H, m, 1-H), 4.96 and 4.94 (each 1 H, d, *J* 11, ArHC*H*), 4.82 (1 H, m, 1-H'), 4.78 and 4.71 (each 1 H, d, *J* 13.5, ArHC*H*), 3.85 (6 H, s, 2 x OCH_3), 2.09 (3 H, s, 2-CH_3), 0.99 [9 H, s, $OSiC(CH_3)_3$] and 0.15 and 0.14 (each 3 H, s, $SiCH_3$); δ_C (75 MHz, $CDCl_3$) 154.23, 142.80, 140.61, 137.71, 137.58, 134.68, 128.03, 127.11, 126.20, 123.97, 116.13, 105.66, 72.36, 62.91, 56.34, 26.28, 25.00, 18.71 and -4.99; *m/z* (CI) 446 (M^++18, 24%), 429 (1), 297 (34) and 143 (100).

2-[6-(2,6-Dimethoxyphenoxymethyl)-2-(hydroxymethyl)phenyl]propene 12

Tetra-*n*-butylammonium fluoride (1 M in tetrahydrofuran, 9.22 cm^3, 9.22 mmol) was added dropwise to the silyl ether **11** (3.29 g, 7.68 mmol) in tetrahydrofuran (76.8 cm^3) and the mixture stirred for 1 h at room temperature. After concentration under reduced pressure, chromatography of the residue using ether : light petroleum (1 : 4) gave the *title compound* **12** (2.08 g, 86%) as a pale oil (Found: M^++H, 315.1593. $C_{19}H_{23}O_4$ requires *M*, 315.1591); υ_{max} 3409, 1640, 1596, 1493, 1478, 1296, 1254, 1112, 902 and 773 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 7.74 (1 H, dd, *J* 7.5, 1, ArH), 7.46-7.32 (2 H, m, ArH), 7.05 (1 H, t, *J* 8, ArH), 6.63 (2 H, d, *J* 8.5, ArH), 5.36 (1 H, m, 1-H), 5.07 and 4.95 (each 1 H, d, *J* 11, ArHC*H*), 4.88 (1 H, m, 1-H'), 4.72 and 4.65 (each 1 H, d, *J* 12.5, ArHC*H*), 3.85 (6 H, s, 2 x OCH_3), 2.13 (3 H, s, 2-CH_3) and 1.91 (1 H, br. s, OH); δ_C (75 MHz, $CDCl_3$) 154.18, 143.46, 141.76, 137.49, 135.35, 128.94, 128.63, 127.64, 127.49, 124.08, 116.56, 105.64, 72.30, 63.54, 56.38 and 25.52; *m/z* (CI) 332 (M^++18, 39%), 315 (5), 297 (12), 178 (62), 172 (64), 161 (99) and 143 (100).

3-(2,6-Dimethoxyphenoxymethyl)-2-propen-2-ylbenzaldehyde 13

Dimethyl sulfoxide (1.41 cm^3, 19.9 mmol) in dichloromethane (2 cm^3) was added dropwise to a cooled (-78 °C) solution of oxalyl chloride (0.87 cm^3, 9.96 mmol) in dichloromethane (13 cm^3) and the mixture stirred for 30 mins before adding the alcohol **12** (2.08 g, 6.64 mmol) in dichloromethane (10 cm^3). The reaction was stirred for a further 30 mins then triethylamine (5.55 cm^3, 39.8 mmol) was added dropwise and the mixture was allowed to warm to 0 °C and stirred for 30 mins. Saturated aqueous ammonium

chloride (50 cm^3) was added and the mixture was extracted with dichloromethane (3 x 50 cm^3). The organic extracts were washed with brine, dried (Na_2SO_4) and concentrated under reduced pressure. Chromatography of the residue using ether : light petroleum (1 : 3) as eluent gave the *title compound* **13** (1.80 g, 87%) as a pale yellow oil (Found: M^++H, 313.1441. $C_{19}H_{21}O_4$ requires *M*, 313.1434); υ_{max} 1691, 1596, 1494, 1478, 1297, 1254, 1216, 1113 and 774 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 10.25 (1 H, s, C*H*O), 8.06 and 7.93 (each 1 H, dd, *J* 7.5, 1, ArH), 7.48 (1 H, t, *J* 8, ArH), 7.06 (1 H, t, *J* 8.5, ArH), 6.62 (2 H, d, *J* 8.5, ArH), 5.51 (1 H, pent, *J* 1.5, 1'-H), 5.12 and 4.99 (each 1 H, d, *J* 11.5, ArHC*H*), 4.99 (1 H, q, *J* 1, 1'-H'), 3.85 (6 H, s, 2 x OCH_3) and 2.20 (3 H, t, *J* 1, 2'-CH_3); δ_C (75 MHz, $CDCl_3$) 192.89, 154.07, 146.78, 140.65, 137.04, 136.39, 135.43, 132.91, 127.61, 127.15, 124.33, 118.91, 105.47, 71.41, 56.26 and 26.74; *m/z* (CI) 332 (35%), 313 (85) and 295 (100).

***N*-[3-(2,6-Dimethoxyphenoxymethyl)-2-(propen-2-yl)phenylmethyl]prop-2-enylamine 14**

Prop-2-enylamine (0.80 cm^3, 10.7 mmol), was added to magnesium sulfate (9.19 g) and the aldehyde **13** (1.67 g, 5.34 mmol) in dichloromethane (55 cm^3), and the mixture strirred for 18 h at room temperature then filtered and concentrated under reduced pressure. The residue was dissolved in anhydrous methanol (36 cm^3), the solution was cooled to 0 °C, and sodium borohydride (304.5 mg, 8.01 mmol) was added. The suspension was stirred for 2 h at 0 °C and for a further 1 h at room temperature, then concentrated under reduced pressure and dichloromethane (50 cm^3) and water (50 cm^3) were added. Aqueous sodium hydroxide (2 M) was added until the pH was *ca*. 10 and the aqueous phase was extracted with dichloromethane (3 x 50 cm^3). The organic extracts were washed with brine, dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography of the residue using ether : light petroleum (6 : 4 → 100 : 0) as eluent gave the *title compound* **14** (1.69 g, 90%) as a pale yellow oil (Found: M^++H, 354.2062. $C_{22}H_{28}NO_3$ requires *M*, 354.2064); υ_{max} 3073, 1641, 1596, 1494, 1478, 1296, 1254, 1218, 1113 and 773 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 7.68 and 7.38 (each 1 H, dd, *J* 7.5, 1.5, ArH), 7.32 (1 H, t, *J* 7.5, ArH), 7.03 (1 H, t, *J* 8.5, ArH), 6.61 (2 H, d, *J* 8.5, ArH), 5.97 (1 H, ddt, *J* 17, 10, 6, 2-H), 5.33 (1 H, m, 2''-H), 5.22 (1 H, dq, *J* 17, 1.5, 3-H), 5.13 (1 H, dq, *J* 10, 1.7, 3-H'), 5.05 and 4.93 (each 1 H, d, *J* 11, ArHC*H*O), 4.85 (1 H, m, 2''-H'), 3.85 (6 H, s, 2 x OCH_3), 3.83 and 3.75 (each 1 H, d, *J* 13, ArHC*H*N), 3.29 (2 H, dt, *J* 6, 1.5, 1-H_2), 2.11 (3 H, t, *J* 1.5, 1''-CH_3) and 1.70 (1 H, br. s, NH); δ_C (75 MHz, $CDCl_3$) 154.21, 143.54, 142.33, 137.58, 137.21, 136.64, 135.27, 128.47, 128.21, 127.17, 123.99, 116.28, 116.12, 105.66, 72.51, 56.34, 52.05, 50.89 and 25.52; *m/z* (CI) 354 (M^++1, 100%).

***N*-[3-(2,6-Dimethoxyphenoxymethyl)-2-(propen-2-yl)phenylmethyl]-*N*-prop-2-enyl 2-nitrobenzene sulfonamide 4**

2-Nitrobenzene sulfonyl chloride (1.19 g, 5.38 mmol) was added to the amine **14** (1.58 g, 4.49 mmol), triethylamine (0.94 cm^3, 6.73 mmol) and 4-dimethylaminopyridine (11 mg) in dichloromethane (56 cm^3) and the reaction stirred at room temperature for 16 h. Water (50 cm^3) was added and the aqueous phase extracted with ether (3 x 50 cm^3). The organic extracts were washed with brine, dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography of the residue using ether : light petroleum (1 : 1) as eluent gave the *title compound* **4** (2.21 g, 92%) as a pale yellow oil (Found: M^++Na, 561.1666. $C_{28}H_{30}N_2O_7SNa$ requires *M*, 561.1666); υ_{max} 3078, 1642, 1596, 1545, 1493, 1478, 1438, 1372, 1354, 1296, 1254, 1164, 1112, 906, 774 and 735 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 8.05 (1 H, dt, *J* 7, 1.5, ArH), 7.75 – 7.64 (4 H, m, ArH), 7.32 - 7.24 (2 H, m, ArH), 7.04 (1 H, t, *J* 8.5, ArH), 6.61 (2 H, d, *J* 8.5, ArH), 5.62 (1 H, ddt, *J* 17, 10.5, 6.5, 2-H), 5.31 (1 H, m, 1"-H), 5.12 (2 H, m, 3-H_2), 5.04 and 4.89 (each 1 H, d, *J* 11, ArHC*H*), 4.82 (1 H, m, 1"-H'), 4.64 (2 H, s, $ArCH_2$), 3.97 (2 H, d, *J* 6, 1-H_2), 3.85 (6 H, s, 2 x OCH_3) and 2.05 (3 H, t, *J* 1.5, 2"-CH_3); δ_C (75 MHz, $CDCl_3$) 154.13, 148.09, 142.33, 142.15, 137.37, 135.53, 134.36, 133.74, 132.37, 132.05, 131.85, 131.36, 128.82, 127.46, 126.75, 124.43, 124.10, 119.60, 117.03, 105.55, 72.24, 56.30, 49.80, 48.23 and 25.07; *m/z* (ES) 561 (M^++23, 100%).

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