4. EXPERIMENTAL

4.1 GENERAL INFORMATION

Column chromatography was performed using silica gel 60 (particle size: 0.063-0.2 mm). The TLC was performed on aluminium-backed Alugram Sil G/UV_{245} plates pre-coated with 0.20 mm silica gel 60.

Infra red spectra were recorded using a Bruker Vector 22. Routine NMR spectra were recorded on a Bruker AC-200, a Bruker 300 and a Bruker 400 spectrometers. $CDCl_3$ solvent was used in most cases using TMS as internal standard and d_8-toluene and d_6-benzene were used to monitor isomerisation reactions. All ^{13}C NMR spectroscopic signals in the aromatic and other regions have been assigned as quaternary (C) or non-quaternary (CH).

The mass spectra were done on VG 70 SEQ machine under a high resolution and low resolution with the following settings:
Ionization: EI, Resolution: 7500, Mass Range: 3.00 amu (8\kv), Scan Rate: 5 Secs /decade (external).

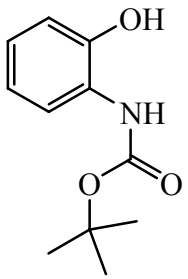
All reactions were done in flame dried glassware and under nitrogen gas. The solvents used in the reaction were distilled before use.

Melting points were determined on a Reichert hot stage microscope apparatus and are uncorrected.

4.2. EXPERIMENTAL PROCEDURE FOR THE SYNTHESIS OF 6-MEMBERED BENZO-FUSED HETEROCYCLIC COMPOUNDS

4.2.1 EXPERIMENTAL PROCEDURES FOR THE SYNTHESIS *TERT*-BUTYL 4*H*-1,4-BENZOXAZINE-4-CARBOXYLATE **91**

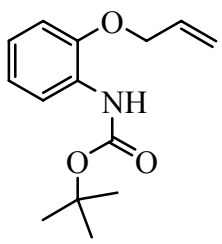
(a) Synthesis of *tert*-butyl 2-hydroxyphenylcarbamate **22**[51]



22

A mixture of aminophenol (0.50 g, 4.6 mmol, 1.0 equiv.), di-*tert*-butyl dicarbonate (1.99 g, 9.16 mmol, 2.00 equiv.) in THF (10 mL), was stirred at room temperature for 18 hrs. The reaction was then extracted with ethyl acetate (4 × 100 mL), the solvent combined was dried with magnesium sulfate. The filtered crystals were then washed with carbon tetrachloride, filtered and dried to afford the desired compound as white crystals (0.61 g, 64% yield). The spectroscopic data of these crystals agreed with those in the literature. Mp: 140-141 °C, IR: ν_{cm}^{-1} 3226 (OH), 3292 (NH), 1691 (C=O); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.53 (s, 9H, 3×CH_3), 6.66 (bs, 1H, OH), 6.81-7.08 (m, 4H, 4×ArH), 8.12 (bs, 1H, NH).

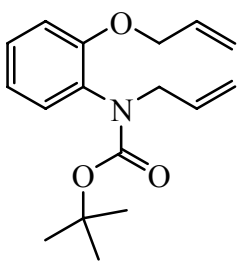
(b) Synthesis of *tert*-butyl 2-(allyloxy)phenylcarbamate **88**[68]



88

tert-Butyl 2-hydroxyphenylcarbamate (0.45 g, 2.2 mmol, 1.0 equiv.) was dissolved in DMF (10mL) and NaH (60% in oil, 192 mg, 4.84 mmol, 2.20 equiv.) was added and reaction stirred for one hour. Allyl bromide (0.42 mL, 4.8 mmol, 2.2 equiv.) was added and the reaction was stirred for a further 18 hrs at room temperature. Water (30 mL) was added and the reaction was then extracted with ethyl acetate (3 × 100 mL), the fraction combined were dried with magnesium sulfate after which the solvent was removed under vacuum. Column chromatography was then done on the residue using 10% ethyl acetate in hexane to afford the compound as a brown oil (84%, 0.459 g). *m/z* (EI): 249 (M^+, 28%), 218 (21), 193 (53), 152 (30), 108 (96), 57 (100); HRMS; calcd for $C_{14}H_{19}NO_3$ 249.1364, found 249.1341; IR: ν_{max} (film)/cm^{-1} 3429 (N-H), 2979 (C-H), 1729 (C=O), 1602 (C-C), 1157 (Ar-O), 745 (C=C); ^{1}H NMR (300MHz, $CDCl_3$): δ (ppm) = 1.52 (s, 9H, 3×CH_3), 4.57 (d, 2H, *J* = 4.3Hz, O-CH_2), 5.30 (d, 1H, *J* = 10.5Hz, OCH_2CH=C*H*H), 5.38 (d, 1H, *J* = 17.2Hz, OCH_2CH=C*H*H), 5.99-6.12 (m, 1H, O-CH_2*CH*=), 6.80-6.85 (m, 1H, ArH), 6.92-6.94 (m, 2H, 2×ArH), 7.10 (s, 1H, ArH), 8.09 (s, 1H, N-H); ^{13}C NMR (75MHz, $CDCl_3$): δ (ppm) = 28.2 (3×CH_3), 69.4 (O-CH_2), 80.1 (C-O), 111.2 (CH), 117.9 (CH), 118.1 (CH_2), 121.2 (CH), 122.1 (CH), 128.2 (C), 132.9 (CH), 146.3 (C), 152.6 (C=O).

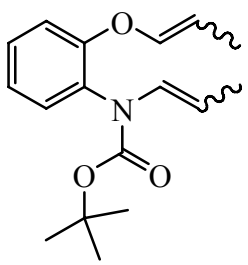
(c) Synthesis of tert-butyl allyl(2-allyloxy)phenylcarbamate **89**



89

tert-Butyl 2-(allyloxy)phenylcarbamate (0.36 g, 1.4 mmol, 1.0 equiv.) was dissolved in DMF 20mL and NaH (60% in oil, 0.07 g, 1.7 mmol, 1.2 equiv.) with allyl bromide (0.15 mL, 1.7 mmol, 1.2 equiv.) were added and reaction was then stirred at room temperature for a further 18 hrs. Water (20 mL) was added to the crude product after which it was extracted with ethyl acetate (3 × 100 mL) and the combined fraction was dried with magnesium sulfate and then the solvent was removed under vacuum. Column chromatography was done to afford a brown oil (0.25 g, 64%). *m/z* (EI), 289 (M^+, 19%), 233 (22), 148 (100), 57 (78), 41 (32); HRMS; calcd for $C_{17}H_{23}NO_3$ 289.1677, found 289.1679; IR: ν_{max} (film)/cm^{-1} 2979 (C-H), 1699 (C=O), 1280 (C-N), 1151 (Ar-O); ^1H NMR (300MHz, $CDCl_3$): δ (ppm) = 1.32 (s, 9H, 3×CH_3), 4.07-4.35 (bm, 2H, N-CH_2), 4.52-4.54 (m, 2H, O-CH_2), 5.00-5.09 (m, 2H, O-CH_2CH=CH_2), 5.25 (dd, 1H, *J* = 1.0Hz, 10.6Hz, N-CH_2CH=CH_2), 5.41 (dd, 1H, *J* = 1.5Hz, 17.3Hz, N-CH_2CH=CH_2), 5.81-5.92 (m, 1H, N-CH_2C*H*=), 5.95-6.08 (m, 1H, O-CH_2C*H*=), 6.86-6.91 (m, 2H, 2×ArH), 7.07-7.20 (m, 2H, 2×ArH); ^{13}C NMR (75MHz, $CDCl_3$): δ (ppm) = 28.2 (3×CH_3), 52.0 (CH_2), 68.0 (CH_2), 79.4 (C-O), 112.5 (CH_2), 116.5 (CH_2), 116.9 (CH), 120.3 (CH), 127.8 (CH), 129.6 (CH), 131.1 (C), 132.9 (CH), 134.4 (CH), 154.1 (C), 155.0 (C).

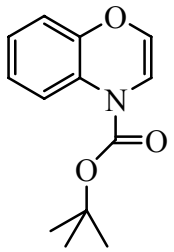
(d) Synthesis of *tert*-butyl 1-propenyl[2-(1-propenyloxy)phenyl]carbamate **90**



90

tert-Butyl allyl-2-(allyloxy)phenylcarbamate (106 mg, 0.37 mmol, 1.0 equiv.) was dissolved in d_8 toluene (2 mL) and ruthenium isomerisation catalyst (1 mol%, 2.9 mg, 0.01 mmol) was added and reaction was stirred at 90-100 °C for 98 hrs after which the solvent was removed from the crude product on a rotatory evaporator before passing it through a silica gel column using 20% ethyl acetate in hexane to afford the isomerised product as a brown oil (86 mg, 81% yield). *m/z* (EI): 289 (M^+, 8%), 160 (56), 120(93), 57 (100); HRMS calcd for $C_{17}H_{23}NO_3$ 289.1677, found 289.1675; IR: ν_{max} (film)/cm^{-1} 2976 (C-H), 1710 (C=O), 1669 (C=C), 1125 (Ar-O), 1018 (C-N); ^{1}H NMR (300MHz, d_8 Toluene): δ (ppm) = 1.32 (s, 12H, 4×CH_3), 1.43 (dd, 3H, J = 6.7Hz, 1.5Hz, CH_3), 4.30-4.41 (m, 1H, O-CH=), 4.58-4.68 (m, 1H, N-CH=), 6.14-6.17 (m, 1H, CH=C*H*-CH_3), 6.74-6.83 (m, 2H, 2×ArH), 6.97-7.12 (m, 3H, 2×ArH and CH=C*H*CH_3); ^{13}C NMR (75MHz, $CDCl_3$): δ (ppm) = 9.4 (CH_3), 12.0 (CH_3), 28.3 (3×CH_3), 80.5 (C-O), 108.8 (CH), 114.2 (CH), 118.6 (CH), 122.3 (CH), 122.9 (2×CH), 128.6 (C), 140.7 (CH), 145.5 (C), 152.6 (C=O).

(e) Synthesis of *tert*-butyl 4*H*-1,4-benzoxazine-4-carboxylate **91**[51]

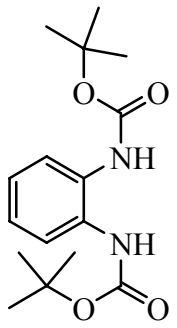


91

tert-Butyl 1-propenyl[2-(1-propenyloxy)phenyl]carbamate (69.5 mg, 0.24 mmol, 1.00 equiv.) was dissolved in toluene (15 mL) and Grubbs II catalyst (5 mol%, 0.01 mmol, 10.2 mg) was added and the reaction was reflux for 18 hrs after which the crude product was passed through a silica column using 10% ethyl acetate in hexane to afford the 6-membered benzo-fused compound as a brown oil (40.1 mg, 71% yield). m/z (EI): 233 (M^+, 10%), 133 (36), 57 (100); HRMS calcd for $C_{13}H_{15}NO_3$ 233.1051, found 233.1047; IR: ν_{max} (film)/cm^{-1} 2926 (C-H), 1714 (C=O), 1151 (Ar-O), 1060 (C-N); ^{1}H NMR (300MHz, $CDCl_3$): δ =1.55 (s, 9H, 3×CH_3), 5.98 (d, 1H, *J* = 4.6Hz, N-CH=), 6.19 (d, 1H, *J*= 4.6Hz, O-CH=), 6.71-6.74 (m, 1H, Ar-H), 6.92-6.96 (m, 2H, 2×ArH), 7.79 (bs, 1H, ArH); ^{13}C NMR (75MHz, $CDCl_3$): δ (ppm) = 28.2 (3×CH_3), 82.1 (C-O), 110.4 (CH), 116.2 (CH), 121.4 (CH), 123.5 (CH), 125.5 (CH), 127.7 (CH), 130.9 (C), 147.3 (C), 150.1 (C=O).

4.2.2 EXPERIMENTAL PROCEDURES FOR THE ATTEMPTED SYNTHESIS OF DI(*TERT*-BUTYL) 2,5-DIHYDRO-1,6-BENZODIAZOCINE-1,6-DICARBOXYLATE **96**

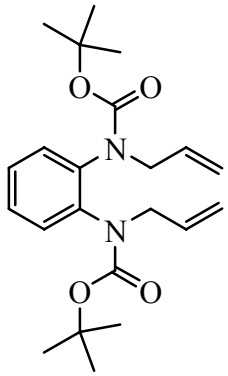
(a) Synthesis of *tert*-butyl 2-[(*tert*-butoxycarbonyl)amino]phenylcarbamate **93**[69]



93

o-Phenylenediamine (0.50 g, 4.6 mmol, 1.0 equiv.) was dissolved in THF (10 mL) and di-*tert*-butyl dicarbonate (2.30 mL, 10.2 mmol, 2.20 equiv.) was added and the reaction was stirred at room temperature for 18 hrs. Water (20 mL) was added and it was then extracted using ethyl acetate (3 × 100 mL), dried with magnesium sulfate and solvent was removed under high vacuum after which column chromatography was done using 5% ethyl acetate in hexane to give the desired compound as a white solid (1.33 g, 93% yield). *m/z* (EI): 308 (M^+, 22%), 196 (66), 108 (42), 57 (100); HRMS calcd for $C_{16}H_{24}N_2O_4$ 308.1736, found 308.1730; IR: ν_{max} (film)/cm^{-1} 3306 (ArC-H), 2980 (C-H), 1731 (C=O), 1601 (N-H) 1050 (Ar-O). Mp: 125-127 °C; ^{1}H NMR (300MHz, $CDCl_3$): δ (ppm) = 1.51 (s, 18H, 6×CH_3), 6.71 (bs, 2H, 2×ArH), 7.10-7.13 (m, 2H, 2×ArH), 7.45 (bs, 2H, 2×N-H); ^{13}C NMR (75MHz, $CDCl_3$): δ (ppm) = 28.2 (6×CH_3), 80.7 (2×C-O), 124.2 (2×CH), 125.3 (2×CH), 130.2 (2×C), 153.7 (2×C=O).

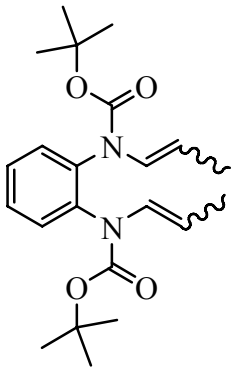
(b) Synthesis of *tert*-butyl allyl{2-[allyl(*tert*-butoxycarbonyl)amino]phenyl}carbamate **94**



94

tert-Butyl 2-[(*tert*-butoxycarbonyl)amino]phenylcarbamate (0.93 g, 3.2 mmol, 1.0 equiv.) was dissolved in DMF (20 mL) and NaH (60% in oil, 90.4 mg, 9.73 mmol, 3.00 equiv.) was added and allyl bromide (0.84 mL, 9.7 mmol, 3.0 equiv.) and reaction was stirred at room temperature for 18 hrs. Water (50 mL) was then added it was then extracted with ethyl acetate (4 × 100 mL) and column chromatography was done using 20% ethyl acetate in hexane to afford the product as a yellow oil (0.77 g, 60% yield). *m/z* (EI): 388 (M^+, 5%), 276 (21), 187 (30), 159 (33), 57 (100); HRMS calcd for $C_{22}H_{32}N_2O_4$ 388.2362 found 388.2370; IR: ν_{max} (film)/cm^{-1} 2931 (C-H), 1701 (C=O), 1149 (Ar-O). ^{1}H NMR (300MHz, $CDCl_3$): δ (ppm) = 1.36 (2×brs, 18H, 6×CH_3), 3.63 (bs, 2H, N-CH_2), 4.47 (bs, 2H, N-CH_2), 5.08-5.11 (m, 4H, 2×=CH_2), 5.89-5.91 (m, 2H, 2×NCH_2CH=), 7.06-7.09 (m, 2H, 2×ArH), 7.22 (bs, 2H, 2×ArH); ^{13}C NMR (75MHz, $CDCl_3$): δ (ppm) = 28.2 (6×CH_3), 51.3 (CH_2), 52.8 (CH_2), 80.2 (2×C-O), 117.4 (2×CH_2), 127.7 (2×CH), 131.0 (2×CH), 133.5 (2×CH), 154.3 (2×C=O).

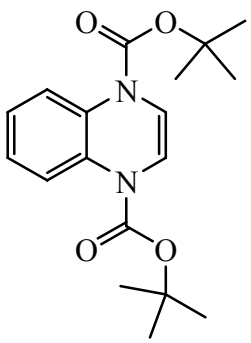
(c) Synthesis of *tert*-butyl 2-[*tert*-butoxycarbonyl(prop-1-enyl)amino]phenyl(prop-1-enyl)carbamate **95**



95

tert-Butyl allyl{2-[allyl(*tert*-butoxycarbonyl)amino]phenyl}carbamate (121 mg, 0.31 mmol, 1.00 equiv.) was dissolved in d_8-toluene (2 mL) and ruthenium isomerisation catalyst (2.86 mg, 0.01 mmol, 1.00 equiv.) was added and the reaction was stirred at 95 °C for 98 hrs. The solvent was removed on a high vacuum and column chromatography was done on the crude product using 5% ethyl acetate in hexane to give the expected compound as a brown oil (116 mg, 96% yield). *m/z* (EI): 388 (M^+, 3%), 236 (28), 207 (28), 192 (34), 57 (100); HRMS calcd for $C_{22}H_{32}N_2O_4$ 388.2362, found 388.2377; IR: ν_{max} (film)/cm^{-1} 2975 (C-H), 1709 (C=O), 1161 (C-N), 756 (HC=C); ^{1}H NMR (300MHz, d_8-Toluene): δ (ppm) = 1.38 (bs, 18H, 6×CH_3), 1.46-1.49 (m, 6H, 2×CH_3), 4.55 (bs, 2H, 2×N-C*H*=CH), 6.94-7.05 (m, 6H, 4×ArH and 2×N-CH=C*H*); ^{13}C NMR (75MHz, $CDCl_3$): δ (ppm) = 15.0 (2×CH_3), 28.1 (6×CH_3), 80.9 (2×C-O), 106.6 (2×CH), 128.1 (4×CH), 131.3 (2×CH), 136.3 (2×C), 152.0 (2×C=O).

(d) Attempted synthesis of di(*tert*-butyl) 1,4-quinoxaline dicarboxylate **96**

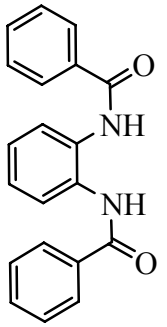


96

tert-Butyl 2-[*tert*-butoxycarbonyl(prop-1-enyl)amino]phenyl(prop-1-enyl)carbamate (96.5mg, 0.25 mmol, 1.00 equiv.) was dissolved in toluene (15 mL) and Grubbs II catalyst (21.2 mg, 0.02 mmol, 10 mol%) was added and the reaction was heated at 80 °C for 18 hrs after which the crude product was purified by column chromatography (20% ethyl acetate in hexane). We isolated the starting material as a brown oil (60.6 mg) instead of our desired 6-membered benzo-fused ring. The TLC proved it to be the starting material.

4.2.3 EXPERIMENTAL PROCEDURES FOR THE ATTEMPTED SYNTHESIS OF 1,4-DIBENZOYL-1,4-DIHYDROQUINOXALINE **100**

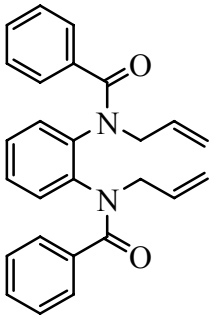
(a) Synthesis of *N*-[2-(benzoylamino)phenyl]benzamide **97**[68]



97

Benzoyl chloride (5.5 g, 4.5 mL, 2.1 equiv.) was added dropwise to a solution of o-phenylenediamine (2.00 g, 18.5 mmol) and pyridine (3.06 mL, 37.9 mmol, 2.10 equiv.) in of THF (50 mL). The solution was then stirred for 4 hrs at room temperature. The precipitate formed, was filtered and washed with diethyl ether (5 × 100 mL) and dried at 100 °C overnight to afford a white solid (5.89 g, 88% yield). *m/z* (EI): 316 (M^+, 44%), 218 (25), 194 (50), 105 (100), 77 (52); HRMS calculated for $C_{20}H_{16}N_2O_2$ 316.1211 found 316.1224; IR: ν_{max} (film)/cm^{-1} 1643 (C=O), 1600 (N-H) 1494 (C=C). Mp: 230 °C.

(b) Synthesis of *N*-allyl-*N*-{2-[allyl(benzoyl)amino]phenyl}benzamide **98**

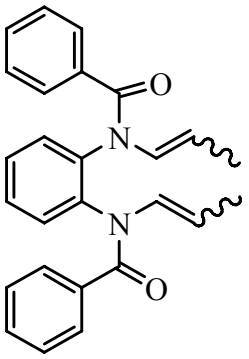


98

To a solution of *N*-[2-(benzoylamino)phenyl]benzamide (1.00 g, 3.16 mmol, 1.00 equiv.) in 20 mL of DMSO, NaH (60% in oil, 0.50 g, 13 mmol, 4.0 equiv.) and allyl bromide (1.09 mL, 12.4 mmol, 4.00 equiv.) was added. The reaction was stirred at room temperature for 20 hrs after which water (10 mL) was added and it was then extracted using ethyl acetate (3 x 100 mL) and the combined fraction was dried with magnesium sulfate. Column chromatography was done using 20% ethyl acetate in hexane to afford the product as a white solid (1.01 g, 88% yield). *m/z* (EI): 396 (M^+, 7%), 291 (45), 275 (98), 105 (100), 77 (57); HRMS calcd for $C_{26}H_{24}N_2O_2$ 396.1837, found 396.1842; IR: ν_{max} (film)/cm^{-1} 3066 (ArC-H), 3009 (HC=C) 2930 (C-H) 1651 (C=O), 1075 (C-N); Mp: 132-135 °C; ^{1}H NMR (300MHz, $CDCl_3$): δ (ppm) = 3.90-4.20 (bm, 2H, 2×NCH_2), 4.37 (bs, 2H, 2×N-CH_2), 5.11 (bs, 4H, 2×N-CH_2CH=CH_2), 5.86 (bs, 2H, 2×NCH_2CH=), 7.26-7.40 (m, 14H, 14×ArH); ^{13}C NMR (75MHz, $CDCl_3$): δ (ppm) = 52.1 (2×CH_2), 116.3

(2×CH_2), 126.9 (CH), 127.8 (2×CH), 129.4 (2×CH), 130.6 (CH) 134.2 (2×CH), 136.0 (2×C), 140.2 (2×C), 168.3 (2×C=O).

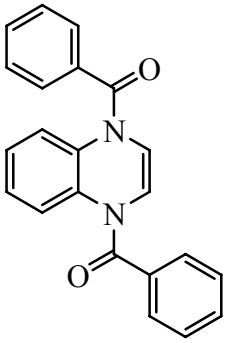
(c) Synthesis of *N*-{2-[benzoyl-(1-propenyl)amino]phenyl}-*N*-(1-propenyl)benzamide **99**



99

To a solution of *N*-allyl-*N*-{2-[allyl(benzoyl)amino]phenyl}benzamide (100 mg, 0.25 mmol, 1.00 equiv.) in d_8-toluene (2 mL), ruthenium isomerisation catalyst **12** (5 mol%, 11.9 mg, 0.01 mmol) was added and reaction was stirred for 18 hours at 80-90 °C and the solvent was removed under a high vacuum. Column chromatography was done on the crude product using 20% ethyl acetate in hexane to afford the desired compound as a brown solid (93.7 mg, 94% yield). *m/z* (EI): 396 (M^+, 9%), 340 (25), 275 (100), 105 (75), 77 (32); HRMS calcd for $C_{26}H_{24}N_2O_2$ 396.1837, found 396.1849; IR ν_{max} (film)/cm^{-1} 2924 (C-H), 2260 (C-N), 1651 (C=O); Mp: 174-177 °C; ^{1}H NMR (300MHz, $CDCl_3$): δ (ppm) = 1.36-1.62 (m, 6H, 2×CH_3), 4.86-5.18 (bm, 2H, 2×N-CH=), 6.50 (bs, 2H, 2×NCH=C*H*), 7.25-7.51 (m, 14H, 14×ArH); ^{13}C NMR (75MHz, $CDCl_3$): δ (ppm) = 15.0 (2×CH_3), 127.5 (CH), 128.0 (2×CH), 128.3 (CH), 129.0 (CH), 129.7 (CH), 130.4 (2×CH), 131.1 (CH), 135.2 (2×C), 137.3 (2×C), 169.1 (2×C=O).

(d) Attempted synthesis of 1,4-dibenzoyl-1,4-dihydroquinoxaline **100**



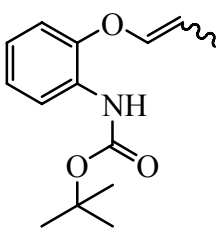
100

N-{2-[Benzoyl-(1-propenyl)amino]phenyl}-(1-propenyl)benzamide (76.2 mg, 0.19 mmol) was dissolved in toluene (10 mL) and Grubbs II catalyst (5 mol%, 0.01 mmol, 8.06 mg) was added and the reaction was stirred at room temperature for 20 hrs. Column chromatography was done on the crude product using 40% ethyl acetate in hexane to afford a brown oil (62.7 mg) which was the starting material.

4.3 EXPERIMENTAL PROCEDURE FOR THE SYNTHESIS OF 7-MEMBERED BENZO-FUSED HETEROCYCLIC COMPOUNDS

4.3.1 EXPERIMENTAL PROCEDURES FOR THE SYNTHESIS OF *TERT*-BUTYL 1,5-BENZOXAZEPINE-5(4*H*)-CARBOXYLATE **103**

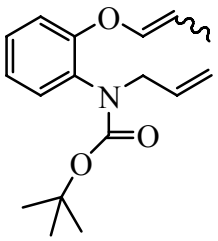
(a) Synthesis of *tert*-butyl allyl 2-(1-propenyloxy)phenylcarbamate **101**



101

tert-Butyl-2-(allyloxy)phenylcarbamate (200 mg, 0.80 mmol) was dissolved in toluene (8 mL) and ruthenium isomerisation catalyst (5 mol%, 38 mg, 0.40 mmol) was added and the reaction was heated at reflux at 80-100 °C for 18 hrs. The solvent was removed under vacuum and column chromatography was done on the crude product using 10% ethyl acetate in hexane to afford the product as a brown oil (196 mg, 98% yield). ^{1}H NMR showed that the compound was a 2:1 mixture of *E/Z* isomers. *m/z* (EI): 249 (M^+, 9%), 189 (20), 193 (60), 149 (31), 120 (37), 57 (100), HRMS; calcd for $C_{17}H_{19}NO_3$ 249.1364, found 249.1356; IR: ν_{max} (film)/cm^{-1} 3442 (N-H), 2987 (C-H), 1732 (C=O), 1671 (C=C), 1157 (ArC-O); ^{1}H NMR (300MHz, $CDCl_3$): δ (ppm) = 1.53 and 1.54 (2×s, 9H, 3×CH_3), 1.67 (bd, 1H, *J* = 6.7Hz, CH_3- *Z* isomer), 1.73 (bd, 1H, *J* = 6.7Hz, CH_3- *E* isomer), 4.95-5.00 (m, 1H, C*H*CH_3- *E* isomer), 5.35-5.46 (m, 1H, C*H*CH_3- *Z* isomer), 6.17-6.34 (m, H, OCH), 6.88-7.01 (m, 4H, 4×ArH), 8.09 (bs, 1H, N-H); ^{13}C NMR (75MHz, $CDCl_3$): δ (ppm) = 9.4 and 12.1 (CH_3), 28.3 (3×CH_3), 80.5 (*C*(CH_3)$_3$), 108.8 and 109.2 (CH), 114.2 and 114.7 (CH), 118.6 (CH), 122.3 and 122.4 (CH), 122.9 and 123.0 (CH), 128.9 (C), 140.7 (CH), 141.7 and 141.8 (C), 145.3 and 145.5 (C), 152.0 (C=O).

(b) Synthesis of *tert*-butyl allyl [2-(1-propenyloxy)phenyl]carbamate **102**

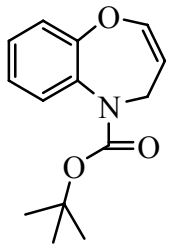


102

tert-Butyl allyl 2-(1-propenyloxy)phenylcarbamate (131 mg, 0.52 mmol) was dissolved in DMF (10 mL) and NaH (60% in oil, 25 mg, 0.63 mmol, 1.2 equiv.) was added, followed by allyl bromide (76 mg, 0.05 mL, 0.63 mmol, 1.2 equiv.). The reaction was stirred at room temperature for 18 hrs after which water (20 mL) was added and the crude product was extracted with ethyl acetate (4 × 100 mL) and column chromatography was done using 5% ethyl acetate in hexane to afford the product as a yellow oil (124 mg, 83%

yield) the product was found to be *E*/*Z* mixture. *m*/*z* (EI): 289 (M^+ 9%), 189 (20), 163 (35), 160 (25), 57 (100); HRMS calcd for $C_{17}H_{23}NO_3$ 289.1677, found 289.1669; IR: ν_{max} (film)/cm^{-1} 2927 (C-H), 1701 (C=O), 1255 (C-N), 1126 (ArC-O), 1526 (C=C); ^{1}H NMR (300MHz, $CDCl_3$): δ (ppm) = 1.34 (bs, 9H, 3×CH_3), 1.64 and 1.70 (2×bd, 3H, *J* = 6.8Hz, 6.7Hz, CHCHC*H*$_3$), 4.13 (bs, 2H, N-CH_2), 4.84-4.88 (m, 1H, OCHC*H*), 5.02-5.11 (m, 2H, N-CH_2-CH=C*H*$_2$), 5.27-5.33 (m, 1H, O-C*H*=CH-), 5.80-5.95 (m, 1H, CH_2C*H*CH_2), 6.31-6.34 (m, 1H, OC*H*CH), 6.96-7.01 (m, 2H, 2×ArH), 7.11-7.26 (m, 2H, 2×ArH); ^{13}C NMR (75MHz, $CDCl_3$): δ (ppm) = 9.4 and 12.1 (CH_3), 28.1 (3×CH_3), 52.2 (N-CH_2), 79.7 (C-O), 107.2 and 108.0 (CH_2), 115.7 and 116.3 (CH), 122.3 (CH), 128.0 (CH), 129.6 and 129.7 (CH), 134.2 (CH), 140.9 and 142.2 (CH), 153.3 (C), 154.7 and 159.8 (C=O).

(c) Synthesis of *tert*-butyl 1,5-benzoxazepine-5(4*H*)-carboxylate **103**



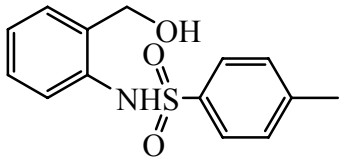
103

tert-Butyl allyl [2-(1-propenyloxy)phenyl]carbamate (97 mg, 0.33 mmol) was dissolved in toluene (5 mL) and Grubbs II catalyst (10 mol%, 14 mg, 0.04 mmol) was added. The reaction was then stirred at 60 °C for 18 hrs. The solvent was removed under vacuum and column chromatography was done on the crude residue using 10% ethyl acetate in hexane to afford the cyclised compound as a brown solid (36 mg, 60% yield). *m/z* (EI): 247 (M^+, 20%), 191 (50), 120 (21), 57 (100), HRMS calcd for $C_{14}H_{17}NO_3$ 247.1208, found 247.1203; IR: ν_{max} (film)/cm^{-1} 2976 (C-H), 1703 (C=O), 1380 (C-N), 1166 (C=C), 1067 (C-O); Mp: 59-61 °C; ^{1}H NMR (300MHz, $CDCl_3$): δ (ppm) = 1.38 (bs, 9H, 3×CH_3), 4.22 (bs, 2H, N-CH_2), 4.83 (bs, 1H, O-C*H*=CH), 6.42 (bd, 1H, *J* = 6.0Hz, N-CH_2-C*H*=CH), 7.07 (bs, 2H, 2×ArH), 7.17-7.20 (m, 2H, 2×ArH); ^{13}C NMR (75MHz,

$CDCl_3$): δ (ppm) = 28.2 (3×CH_3), 45.2 (CH_2), 80.6 (C-O), 105.2 (CH), 121.0 (CH), 123.7 (C), 123.9 (CH), 127.9 (CH), 129.8 (CH), 133.2 (C), 142.7 (CH), 154.3 (C=O).

4.3.2. EXPERIMENTAL PROCEDURES FOR THE ATTEMPTED SYNTHESIS OF 1-[(4-METHYLPHENYL)SULFONYL]-1,5-DIHYDRO-1,4-BENZOXAPINE **109**

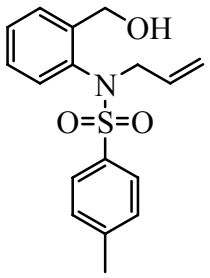
(a) Synthesis of *N*-[2-(hydromethyl)phenyl]-4-methylbenzenesulfonamide **105**[69]



105

Tosyl chloride (8.38 g, 44.7 mmol, 2.20 equiv.) was dissolved in pyridine (25 mL) at 0°C and 2-aminobenzyl alcohol (2.50 g, 20.3 mmol, 1.00 equiv.) was added and reaction was stirred at room temperature for further 18 hrs. The solvent was removed under high vacuum and column chromatography was done using 50% ethyl acetate in hexane to afford the product as a white solid (1.53 g, 28% yield). *m/z* (EI): 277 (M^+ , 57%), 194 (34), 122 (100), 93 (83), 77 (41); HRMS calcd for $C_{14}H_{15}NO_3S$ 277.0773 found 277.0765; IR: ν_{max} (film)/cm^{-1} 2924 (OH), 1655 (N-H), 1158 (O=S=O); Mp: 142-145 °C; ^{1}H NMR (300MHz, $CDCl_3$): δ (ppm) = 2.38 (s, 3H, CH_3), 4.39 (s, 2H, Ar-CH_2), 7.05-7.09 (m, 2H, 2×ArH), 7.20-7.28 (m, 3H, 3×ArH), 7.43 (d, 1H, *J* = 8.0Hz, ArH), 7.64 (d, 2H, *J* = 7.9Hz, 2×ArH), 7.88 (bs, 1H, O-H); ^{13}C NMR (75MHz, $CDCl_3$): δ (ppm) = 21.5 (CH_3), 63.9 (CH_2), 123.4 (CH), 125.3 (CH), 127.0 (2×CH), 129.0 (CH), 129.2 (CH), 129.6 (2×CH), 131.6 (C), 136.3 (C), 136.9 (C), 143.7 (C).

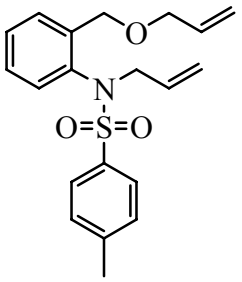
(b) Synthesis of *N*-allyl-*N*-[2-(hydroxymethyl)phenyl]-4-methylbenzenesulfonamide **106**[70]



106

N-[2-(Hydroxymethyl)phenyl]-4-methylbenzenesulfonamide (1.03 g, 3.95 mmol) was dissolved in acetone (45 mL) and potassium carbonate (2.19 g, 15.8 mmol, 4.00 equiv.) was added followed by allyl bromide (1.91 g, 15.8 mmol, 4.00 equiv.) and the reaction was then heated at 60 °C for 22 hrs. Water (20 mL) was then added and the crude product was then extracted with ethyl acetate (3 × 100 mL) and column chromatography was done using 30% ethyl acetate in hexane to afford the desired compound as a brown oil (1.13 g, 90%). *m/z* (EI): 317 (M^+, 1%), 162 (91), 144 (100), 134 (24), 91 (43); HRMS; calcd for $C_{17}H_{19}NO_3S$ 317.1085, found 317.1098; IR: ν_{max} (film)/cm^{-1} 3517 (O-H), 2924 (C-H), 1598 (C=C), 1341 (O=S=O), 1305 (C-N); ^{1}H NMR (300MHz, $CDCl_3$): δ (ppm) = 2.46 (s, 3H, CH_3), 3.03 (bs, 1H, NCH_2), 3.70-3.76 (m, 1H, NCH_2), 4.50 (bd, 2H, *J* = 10.0Hz, Ar-CH_2), 4.94-5.03 (m, 3H, N-CH_2CH=C*H*$_2$ and OH), 5.64-5.78 (m, 1H, N-CH_2C*H*=), 6.45 (d, 1H, *J* = 7.9Hz, ArH), 7.11-7.16 (m, 1H, ArH), 7.26-7.36 (m, 3H, 3×ArH), 7.54-7.60 (m, 3H, 3×ArH); ^{13}C NMR (75MHz, $CDCl_3$): δ (ppm) = 21.5 (CH_3), 55.0 (CH_2), 61.1 (CH_2), 119.1 (CH_2), 127.5 (CH), 128.0 (2×CH), 128.2 (CH), 129.0 (CH), 129.5 (2×CH), 131.1 (CH), 131.8 (CH), 134.6 (C), 137.0 (C), 142.3 (C), 143.9 (C).

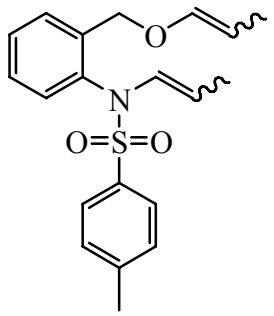
(c) Synthesis of *N*-allyl-*N*-{2-[(allyloxy)methyl]phenyl}-4-methylbenzenesulfonamide **107**



107

N-Allyl-*N*-[2-(hydroxymethyl)phenyl]-4-methylbenzenesulfonamide (1.07 g, 3.38 mmol, 1.00 equiv.) was dissolved in THF (40 mL) and NaH (60% in oil, 99.5 mg, 4.15 mmol, 1.20 equiv.) was added at 0 °C followed by allyl bromide (0.37 mL, 502 mg, 4.15 mmol, 1.30 equiv.) and the reaction was then stirred at room temperature for 18 hrs. Water (10 mL) was added and the product was extracted with ethyl acetate (4 × 100 mL) and the combined solvent was dried with magnesium sulfate and the solvent was removed under a high vacuum. Column chromatography was done on the crude product using 20% ethyl acetate in hexane to afford the desired compound as a brown oil (949 mg, 78% yield). *m/z* (EI): 202 (M^+- Ts, 65%), 144 (100), 91 (36); HRMS calcd for $C_{13}H_{16}NO$ 202.1223 found 202.1232; IR: ν_{max} (film)/cm^{-1} 2858 (C-H), 1646 (C=C), 1347 (O=S=O), 1164 (C-N), 1090 (ArC-O); ^{1}H NMR (300MHz, $CDCl_3$): δ (ppm) = 2.44 (s, 3H, CH_3), 3.85 (bs, 1H, O-CH_2), 4.06 (d, 2H, *J* = 5.5Hz, N-CH_2), 4.35 (bs, 1H, O-CH_2), 4.69-4.76 (m, 2H, Ar-CH_2), 4.95-5.01 (m, 2H, *J* = 5.7Hz, 13.7Hz, N-CH_2CH=CH_2), 5.21 (d, 1H, *J* = 10.5Hz, O-CH_2CH=CH_2), 5.33 (dd, 1H, *J* = 1.5Hz, 17.2Hz, O-CH_2CH=CH_2), 5.67-5.80 (m, 1H, NCH_2C*H*=), 5.91-6.04 (m, 1H, OCH_2C*H*=), 6.54 (d, 1H, *J* = 7.9Hz, ArH), 7.09-7.14 (m, 1H, ArH), 7.26-7.34 (m, 3H, 3×ArH), 7.54 (d, 2H, *J* = 8.2Hz, 2×ArH), 7.61 (d, 1H, *J* = 7.7Hz, ArH); ^{13}C NMR (75MHz, $CDCl_3$): δ (ppm) = 21.5 (CH_3), 54.7 (CH_2), 68.1 (CH_2), 71.5 (CH_2), 116.8 (CH_2), 119.5 (CH_2), 127.4 (CH), 127.7 (CH), 128.0 (2×CH), 128.5 (CH), 128.8 (CH), 129.4 (2×CH), 132.2 (CH), 134.7 (CH), 135.4 (C), 136.8 (C), 140.4 (C), 143.5 (C).

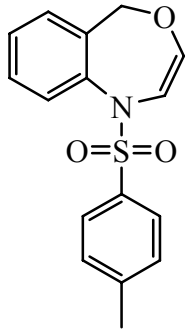
(d) Synthesis of 4-methyl-*N*-(1-propenyl)-*N*-{[2-(1-propenyloxy)methyl] phenyl}benzenesulfonamide **108**



108

N-Allyl-*N*-{2-[(allyloxy)methyl]phenyl}-4-methylbenzenesulfonamide (100 mg, 0.33 mmol) was dissolved in d_8-toluene. Ruthenium isomerisation catalyst (3 mol%, 9.5 mg, 0.01 mmol) was then added and the reaction was stirred at 70-80 °C for 20 hrs. The solvent was removed under a high vacuum and column chromatography was done on the crude product using 10% ethyl acetate in hexane to afford the desired compound as a complex mixture of *E*/*Z* isomers as a yellow oil (93.8 mg, 94%). *m/z* (EI): 368 (M^+,10%), 247 (45), 105 (100), 77 (49), HRMS calcd for $C_{24}H_{20}N_2O_4S$ 368.1524, found 368.1539; IR: ν_{max} (film)/cm^{-1} 2972 (C-H), 1658 (C=C), 1352 (O=S=O), 1166 (C-N), 1089 (C-O); ^{1}H NMR (300MHz, $CDCl_3$): δ (ppm) = 1.53-1.65 (m, 6H, 2×CH_3), 2.44 (s, 3H, CH_3), 4.21-4.33 and 4.30-4.40 (2×m, 1H, O-CH=C*H*), 4.72 and 4.80-4.85 (s and m, 2H, $ArCH_2$), 5.91 and 6.22 (dd and dd, 1H, *J* = 6.2Hz and 1.6Hz, *J* = 12.5Hz and 1.3Hz), 6.50-6.55 (m, 1H, OC*H*=CH), 6.89 (bd, 1H, *J* = 13.9Hz, N-CH=), 7.14-7.19 (m, 1H, ArH), 7.26-7.31 (m, 3H, 3×ArH), 7.36-7.42 (m, 1H, ArH), 7.58-7.63 (m, 3H, 3×ArH).

(e) Attempted synthesis of 1-[(4-methylphenyl)sulfonyl]-1,5-dihydro-1,4-benzoxapine **109**

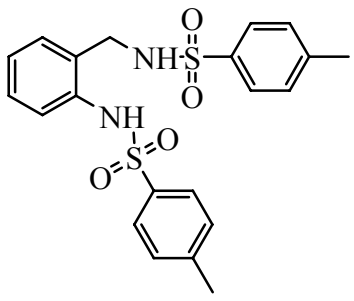


109

4-Methyl-*N*-(1-propenyl)-*N*-{[2-(1-propenyloxy)methyl]phenyl}benzenesulfonamide (77.8 mg, 0.22 mmol) was dissolved in toluene (9 mL) and Grubbs II catalyst (10 mol%, 0.02 mmol, 18.4 mg) was added and the reaction was heated at reflux at 80°-100 °C for 20 hrs. Column chromatography was performed on the crude product to afford a yellow oil (60 mg) which was the starting material.

4.3.3 EXPERIMENTAL PROCEDURES FOR THE ATTEMPTED SYNTHESIS OF 1,4-BIS[(4-METHYLPHENYL)SULFONYL]-4,5-DIHYDRO-1*H*-1,4-BENZODIAZEPINE **114**

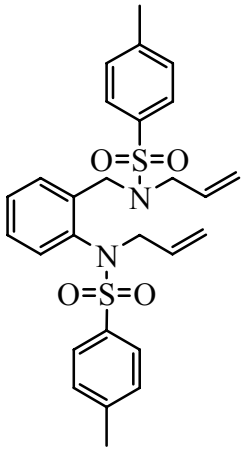
(a) Synthesis of 4-methyl-*N*-[2-({[(4-methylphenyl)sulfonyl]amino}methyl)phenyl]benzenesulfonamide **111**[71]



111

To a mixture of tosyl chloride (8.6 g, 45 mmol, 2.2 equiv.) in pyridine (25 mL) at 0 °C, 2-aminobenzylamine (2.5 g, 21 mmol) was added and reaction was stirred at room temperature for 20 hrs. The solvent was removed under vacuum and column chromatography was done using 50% ethyl acetate in hexane to afford the product as a white solid (5.1 g, 59% yield). *m/z* (EI): 430 (M^+, 13%), 275 (100), 120 (68), 91 (41); HRMS calcd for $C_{21}H_{22}N_2O_4S_2$ 430.1021 found 430.1023; IR: ν_{max} (film)/cm^{-1} 3268 (N-H), 1494 (C-H), 1405 (ArC=C), 1328 (O=S=O); Mp: 127-129 °C; ^{1}H NMR (300MHz,$CDCl_3$): δ (ppm) = 2.39 (s, 3H, CH_3), 2.44 (s, 3H, CH_3), 3.81 (d, 2H, *J* = 6.6Hz, Ar-CH_2), 5.10-5.14 (m, 1H, NH), 7.08-7.33 (m, 6H, 6×ArH), 7.21-7.33 (m, 2H, 2×ArH), 7.56 (d, 2H, *J* = 8.2Hz, 2×ArH), 7.72 (d, 2H, *J* = 8.2Hz, 2×ArH); ^{13}C NMR (75MHz, $CDCl_3$): δ (ppm) = 21.5 (2×CH_3), 43.9 (CH_2), 125.8 (CH), 126.7 (CH), 127.1 (2×CH), 127.3 (2×CH), 129.2 (CH), 129.5 (2×CH), 129.8 (2×CH), 130.7 (CH), 130.9 (C), 134.9 (C), 136.0(C), 136.2 (C), 143.8 (C), 143.8 (C).

(b) Synthesis of *N*-Allyl-*N*-[2-({allyl[(4-methylphenyl)sulfonyl]amino}methyl)phenyl]-4-methylbenzenesulfonamide **112**

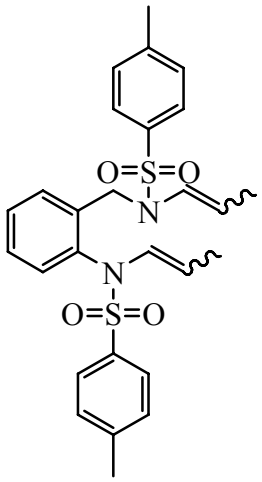


112

4-Methyl-*N*-[2-{[(4-methylphenyl)sulfonyl]amino}methyl)phenyl)benzenesulfonamide (4.0 g, 9.3 mmol, 1.0 equiv.) was dissolved in acetone (160 mL) and potassium carbonate (4.88 g, 35.4 mmol, 4.00 equiv.) was added with allyl bromide (4.83 g, 35.9 mmol, 4.30

equiv.) and the reaction was stirred for 18 hrs at 60 °C. Water (200 mL) was added and the crude product was extracted with ethyl acetate (4 × 200 mL) and dried with magnesium sulfate. The solvent was removed under high vacuum and column chromatography was done using 30% ethyl acetate in hexane to afford the desired compound as a white solid (3.8 g, 80% yield). *m/z* (EI): 511 (M^++ 1, 73%), 355 (52), 300 (44), 144 (100), 91 (50); HRMS; calcd for $C_{27}H_{30}N_2O_4S_2$ 510.1647, found 511.1680 (M^++1); IR: ν_{max} (film)/cm^{-1} 3029 (ArC-H), 1598 (C=C), 1345 (O=S=O), 1091 (ArC-N); Mp: 117-119 °C; ^{1}H NMR (300MHz, $CDCl_3$): δ (ppm) = 2.45 (bs, 6H, 2×CH_3), 3.72-3.79 (m, 2H, Ar-CH_2), 3.89 (dd, 1H, *J* = 6.2Hz, 15.2Hz, N-C*H*H), 4.39 (dd, 1H, *J* = 5.6Hz, 13.8Hz, N-C*H*H), 4.51 (d, 1H, *J* = 17.2Hz, N-CH_2), 4.76 (d, 1H, *J* = 17.0Hz, N-CH_2), 4.94-5.07 (m, 4H, 2×NCH_2CH=C*H*$_2$), 5.52-5.73 (m, 2H, 2×NCH_2C*H*=), 6.41 (d, 1H, *J* = 7.9Hz, ArH), 7.06-7.11 (m, 1H, ArH), 7.34-7.36 (m, 5H, *J* = 8.3Hz, 16.9Hz, 5×ArH), 7.50 (d, 2H, *J* = 7.7Hz, 2×ArH), 7.74 (d, 1H, *J* = 7.8Hz, ArH), 7.77 (d, 2H, *J* = 7.7Hz, 2×ArH); ^{13}C NMR (75MHz, $CDCl_3$): δ (ppm) = 21.5 (2×CH_3), 47.5 (CH_2), 51.2 (CH_2), 54.8 (CH_2), 118.8 (CH_2), 119.9 (CH_2), 127.2 (4×CH), 128.1 (2×CH), 128.5 (CH), 128.8 (CH), 129.4 (2×CH), 129.7 (2×CH), 132.0 (CH), 132.5 (CH), 134.6 (C), 137.1 (2×C), 138.9 (C), 143.2 (C), 143.8 (C).

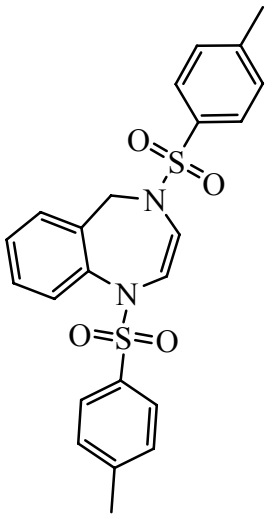
(c) Synthesis of 4-methyl-*N*-(2{[(4-methylphenyl)sulfonyl][1,2-{[1- propenyl] benzyl)-*N*-[1-propenyl]benzenesulfonamide **113**



113

To a mixture of *N*-allyl-*N*-[2-{(ally[(4-methylphenyl)sulfonyl]amino}methyl)phenyl]-4-methylbenzenesulfonamide (100 mg, 0.19 mmol) was dissolved in DCM (8 mL) and ruthenium isomerisation catalyst (3mol%, 9.5 mg, 0.01 mmol) was added and the reaction was reflux at 80 °C for 48 hrs. The solvent was removed under high vacuum and column chromatography was done on the crude product using 20% ethyl acetate in hexane to afford a white solid (94.6 mg, 95% yield). ^{1}H NMR spectroscopy proved that compound to be a mixture of *E*/*Z* isomers. *m/z* (EI): 355 (M^+ - Ts, 100%), 144 (81), 91 (71); HRMS for $C_{20}H_{23}N_2O_2S$ 355.1480 found 355.1463; IR: ν_{max} (film)/cm^{-1} 1701 (C=C), 1597 (ArC=C), 1355 (O=S=O), 1090 (C-N); Mp: 140-143 °C; ^{1}H NMR (300MHz, $CDCl_3$): δ (ppm) = 1.53-1.65 (m, 6H, 2×CH_3), 2.45 (bs, 6H, 2×CH_3), 4.70-4.77 (m, 2H, N-CH_2), 6.24-6.89 (m, 3H, 3×N-C*H*=C*H*), 7.08-7.11 (m, 1H, NC*H*-CH), 7.26-7.35 (m, 6H, 6×ArH), 7.52-7.59 (m, 3H, 3×ArH), 7.69-7.71 (m, 3H, 3×ArH).

(d) Attempted synthesis of 1,4-*bis*[(4-methylphenyl)sulfonyl]-4,5-dihydro-1*H*-1,4-benzodiazepine **114**

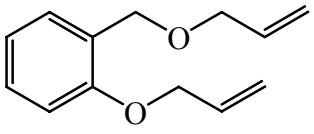


114

4-Methyl-*N*-(2{[4-methylphenyl)sulfonyl][1,2{[1-propenyl]benzyl)-*N*-[1-propenyl]bezenesulfonamide (74 mg, 0.14 mmol) was dissolved in DCM (6 mL) and Grubbs II catalyst (5 mol%, 0.01 mmol, 8.5 mg) was added. The reaction was then heated at reflux at 100-110 °C for 40 hrs after which the solvent was removed under vacuum. Column chromatography was performed on the crude product using 10% ethyl acetate in hexane to afford white solid (32 mg) which is the starting material.

4.3.4 EXPERIMENTAL PROCEDURES FOR THE ATTEMPTED SYNTHESIS OF 5*H*-1,4-BENZODIOXEPINE **118**

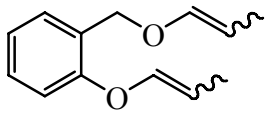
(a) Synthesis of 1-(allyloxy)-2-[(allyloxy)methyl]benzene **116**[72]



116

2-(Hydroxymethyl) phenol (2.00 g, 16.1 mmol) in 20 mL of DMF was cooled to 0 °C, NaH (60% in oil, 1.14 g, 35.4 mmol, 2.20 equiv.) and allyl bromide (8.39 g, 64.4 mmol, 4.00 equiv.) was added and the reaction was stirred at room temperature for 17 hrs. Water (20 mL) was added and the crude product was extracted with ethyl acetate (5 × 100 mL). The combine filtrate was then dried with magnesium sulfate and the solvent evapourated after which column chromatography was then done using 10% ethyl acetate in hexane to afford the product as a yellow oil (1.2 g, 60% yield). *m/z* (EI): 204 (M^+ - 1, 17%), 147 (62), 121 (47), 106 (46), 91 (40), 78 (52) 55 (23), 41 (100); HRMS calcd for $C_{13}H_{18}O_2$ 204.1150 found 203.1079; IR: ν_{max} (film)/cm^{-1} 1650 (C=C), 1494 (ArC=C), 1084 (C-O); ^{1}H NMR (300MHz, $CDCl_3$) : δ (ppm) = 4.08 (d, 2H, *J* = 5.5Hz, O-CH_2), 4.54 (d, 2H, *J* = 4.9Hz, O-CH_2), 4.60 (s, 2H, Ar-CH_2), 5.17-5.43 (m, 4H, 2×OCH_2CH=CH_2), 5.91-6.10 (m, 2H, 2×O-CH_2C*H*=CH_2), 6.84 (d, 1H, *J* = 8.2Hz, ArH), 6.93-6.98 (m, 1H, ArH), 7.19-7.24 (m, 1H, ArH), 7.41 (d, 1H, *J* = 7.5Hz, ArH); ^{13}C NMR (75MHz, $CDCl_3$): δ (ppm) = 66.8 (CH_2), 68.7 (CH_2), 71.4 (CH_2), 111.4 (CH), 116.7 (CH_2), 116.9 (CH_2), 120.6 (CH), 127.1 (C), 128.3 (CH), 128.7 (CH), 133.3 (CH), 134.9 (CH), 155.9 (C).

(b) Synthesis of 1-(1-propenyloxy)-2-[(1-propenyloxy)methyl]benzene **117**

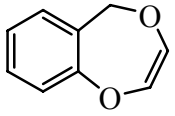


117

1-(Allyloxy)-2-[(allyloxy)methyl]benzene (150 mg, 0.97 mmol, 1.00 equiv.) was dissolved in d_8-toluene and ruthenium isomerisation catalyst (4 mol%, 9.6 mg, 0.01 mmol) was added. The reaction was then stirred at 80 °C for 18 hrs. The solvent was removed from the crude product under high vacuum and column chromatography was done on the crude product, using 10% ethyl acetate in hexane to afford the desired compound as a yellow oil (86.4 mg, 72% yield). From the NMR spectrum, it was clear that the compound was a complex mixture of *E*/*Z* isomers. *m/z* (EI): 204 (M^+, 4%), 147 (100), 90 (95), 77 (21); HRMS; calcd for $C_{13}H_{16}O_3$ 204.1150, found 204.1129; IR: ν_{max}

(film)/cm^{-1} 1669 (C=C), 1357 (-C-H) 1126 (C-O); ^{1}H NMR (300MHz, $CDCl_3$): δ (ppm) = 1.54-1.72 (m, 6H, 2×CH_3), 4.41-4.46 (m, 1H, Ar-CH_2), 4.82-4.94 (m, 3H, 2×OCH=C*H*- and ArCH_2), 6.04-6.09 (m, 1H, O–C*H*=), 6.31-6.40 (m, 1H, O-C*H*=), 6.87 (d, 1H, *J* = 8.1Hz, ArH), 7.03-7.08 (m, 1H, ArH), 7.23-7.28 (m, 1H, ArH), 7.42 (d, 1H, *J* = 7.2Hz, ArH).

(c) Attempted synthesis of 5*H*-1,4-benzodioxepine **118**

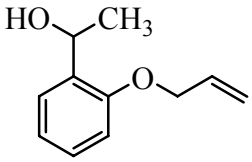


118

1-(1-Propenyloxy)-2-[(1-propenyloxy)methyl]benzene (60 mg, 0.29 mmol, 1.00 equiv) was dissolved in toluene (10mL) and Grubbs II catalyst (8.49 mg, 0.01 mmol, 3 mol%) was added and the reaction was heated at 80°-120 °C for 40 hrs. The solvent was removed under vacuum and column chromatography was done on the crude product using 5% ethyl acetate in hexane to afford a yellow oil (23.6 mg) which is the starting material.

4.3.5. EXPERIMENTAL PROCEDURES FOR THE ATTEMPTED SYNTHESIS OF 5-METHYL-5*H*-1,4-BENZODIOXEPINE **123**

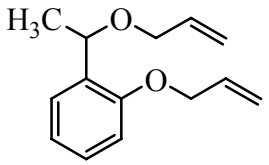
(a) Synthesis of 1-[2-(allyloxy)phenyl]ethanol **120**



120

Methylmagnesium iodide was made by suspending magnesium metal turnings (112 mg, 24.3 mmol, 1.50 equiv.) in diethyl ether (30 mL) at 0 °C and methyl iodide (0.23 mL, 525 mg, 3.70 mmol) was added when magnesium metal turnings had all dissolved. 2-(allyloxy)benzaldehyde (500 mg, 3.08 mmol, 1.00 equiv.) was then added dropwise to the solution and the reaction was stirred at room temperature for a further 18 hrs. It was then quenched with ammonium chloride (20 mL), extracted using ethyl acetate (3 × 100 mL) and then dried with magnesium sulfate. The solvent was removed under vacuum and column chromatography was done using 10% ethyl acetate in hexane to afford the product as a colourless oil (420 mg, 77% yield). *m/z* (EI): 178 (M^+, 86%), 163 (67), 135 (68), 120 (100), 107 (64), 91 (57), 77 (33), 65 (28); HRMS; calcd for $C_{11}H_{14}O_2$ 240.1150, found 240.1160; IR: ν_{max} (film)/cm^{-1} 3389 (OH), 3076 (ArC=C), 1601 (C=C), 1489 (C-H), 1076 (C-O); ^{1}H NMR (300MHz, $CDCl_3$): δ (ppm) = 1.52 (d, 3H, *J* = 6.5Hz, CH_3), 2.66 (bs, 1H, O-H), 4.59 (dd, 2H, *J* = 1.5Hz, 3.6Hz, O-CH_2), 5.14 (bd, 1H, *J* = 3.0Hz, CH_3CHOH), 5.30 (d, 1H, CH_2, *J* = 10.5Hz, O-$CH_2CH=CH_2$), 5.42 (d, 1H, *J* = 17.3Hz, O-$CH_2CH=CH_2$), 6.00-6.12 (m, 1H, O-CH_2CH=), 6.86 (d, 1H, *J* = 8.2Hz, ArH), 6.94-6.99 (m, 1H, ArH), 7.19-7.26 (m, 1H, ArH), 7.36 (d, 1H, *J* = 7.4Hz, ArH); ^{13}C NMR (75MHz, $CDCl_3$): δ (ppm) = 23.8 (CH_3), 66.5 (CH_2), 68.7 (CHOH), 111.6 (CH), 117.5 (CH), 120.9 (CH), 126.1 (CH), 128.1 (CH), 132.9 (CH), 133.7 (C), 155.4 (C).

(b) Synthesis of 1-(allyloxy)-2-[1-(allyloxy)ethyl]benzene **121**

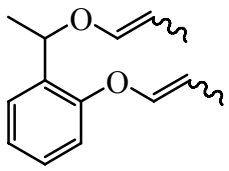


121

1-[2-(Allyloxy)phenyl]ethanol (619 mg, 3.49 mmol) was dissolved in DMF (30 mL) and NaH (60% in oil, 280 mg, 6.99 mmol, 2.00 equiv.) followed by allyl bromide (0.61 mL, 6.99 mmol, 2.00 equiv.) was added and the reaction was stirred at room temperature for 18 hrs. Water (50 mL) was then added and the crude product was extracted with ethyl acetate (3 × 100 mL) which was dried with magnesium sulfate. Column chromatography

was then done using 10% ethyl acetate in hexane to afford the desired compound as a yellow oil (647 mg, 81% yield). *m/z* (EI): 218 (M^+, 21%), 203 (100), 174 (81), 161 (62), 145 (24), 133 (48), 120 (60), 107 (69), 91 (92), 77 (34); HRMS; calcd for $C_{14}H_{18}O_2$ 218.1306, found 218.1306; IR: ν_{max} (film)/cm^{-1} 2976 (C-H), 1600 (C=C), 1082 (C-O); ^{1}H NMR (300MHz, $CDCl_3$): δ (ppm) = 1.42 (d, 3H, *J* = 6.4Hz, CH_3), 3.84-3.92 (m, 2H, O-CH_2), 4.54 (d, 2H, *J* = 4.8Hz, O-CH_2), 4.96 (q, 1H, *J* = 6.4Hz, C*H*-CH_3), 5.13-5.15 (m, 1H, OCH_2CH=CH_2), 5.24-5.28 (m, 2H, OCH_2CH=CH_2), 5.40 (dd, 1H, J = 1.5Hz, 17.3Hz, OCH_2CHCH_2), 5.87-6.10 (m, 2H, 2×CH_2-C*H*=CH_2), 6.38 (d, 1H, *J* = 8.2Hz, ArH), 6.96-7.01 (m, 1H, ArH), 7.16-7.22 (m, 1H, ArH), 7.45 (dd, 1H, *J* = 1.3Hz, 7.5Hz, ArH); ^{13}C NMR (75MHz, $CDCl_3$): δ (ppm) = 22.6 (CH_3), 68.6 (OCH_2), 69.5 (OCH_2), 70.9 (CH_3), 111.5 (CH_2), 116.3 (CH), 116.9 (CH), 120.9 (CH), 126.0 (CH), 127.8 (CH), 132.4 (CH), 133.3 (CH), 135.1 (C), 155.5 (C).

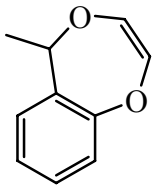
(c) Synthesis of 1-(1-propenyloxy)-2-[1-(1-propenyloxy)ethyl] benzene **122**



122

1-(Allyloxy)-2-[1-(allyloxy)ethyl]benzene (100 mg, 0.46 mmol) was dissolved in d_8-benzene and Isomerisation catalyst (5 mol%, 22 mg, 0.02 mmol) was added. The reaction was heated at 100 °C for 18 hrs after which the solvent was removed under vacuum. The crude compound was not purified and NMR spectroscopy on the material showed that it was a complex mixture of *E*/*Z* isomers. *m/z* (FAB): 161 (M^+, $C_{11}H_{12}{}^+O$), 154 (100), 136 (98), 107 (26), 91 (24), 54 (20); IR: ν_{max} (film)/cm^{-1} 3042 (ArC-H), 2871 (C-H), 1525 (C=C), 1043 (C-O); ^{1}H NMR (300MHz, C_6D_6): δ (ppm) = 1.50 (d, 3H, *J* = 6.4Hz, CH_3), 1.61-1.66 (m, 3H, CH_3), 1.77 (dd, 3H, *J* = 1.5Hz, 6.8Hz, CH_3), 4.34-4.38 (m, 1H, O-CH=C*H*), 4.60-4.70 (m, 1H, O-CH=C*H*), 5.18-5.28 (m, 1H, PHCH), 5.91 (dt, 1H, *J* = 1.4Hz, 5.9Hz, O-CH=), 6.08-6.13 (m, 1H, O-CH=), 6.70-6.76 (m, 1H, ArH), 6.88-7.02 (m, 2H, 2×ArH), 7.55-7.58 (m, 1H, ArH).

(d) Attempted synthesis of 5-methyl-5*H*-1,4-benzodioxepine **123**

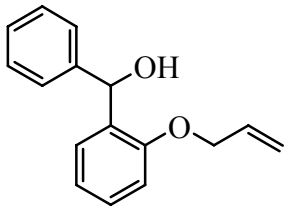


123

Crude 1-(1-Propenyl)-2-[1-(1-propenyloxy)ethyl]benzene (100 mg) was dissolved in d_8-benzene and Grubbs II catalyst (10 mol%, 22 mg, 0.05 mmol) was added. The reaction was then reflux for 40 hrs after which the NMR spectroscopy was done on the crude product. We isolated the starting material.

4.3.6 EXERIMENTAL PROCEDURES FOR THE ATTEMPTED SYNTHESIS OF 5-PHENYL-5*H*-1,4-BENZODIOXEPINE **127**

(a) Synthesis of [2-(allyloxy)phenyl](phenyl)methanol **124**

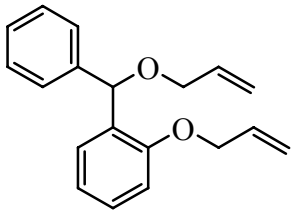


124

Phenylmagnesium bromide was prepared by dissolving magnesium metal turning (112 mg, 24.3 mmol, 1.50 equiv.) in THF (30 mL) at 0 °C after which bromobenzene (0.8 mL, 1.2 g, 7.4 mmol, 2.4 equiv.) was added. 2-(Allyloxy)benzaldehyde (500 mg, 3.08 mmol, 1.00 equiv.) was then added dropwise to the solution and the reaction was stirred at room temperature for a further 18 hrs. The reaction was then quenched with ammonium chloride (20 mL), extracted with ethyl acetate (3 × 100 mL) and the combined filtrate was dried with magnesium sulfate. The solvent was removed under vacuum and column

chromatography was done on the crude product using 5% ethyl acetate in hexane to afford the compound as a colourless oil (281 mg, 38% yield). *m/z* (EI): 240 (M^+, 38%), 199 (91), 181 (100), 152 (21), 121 (55), 105 (29), 77 (35); HRMS; calcd for $C_{16}H_{16}O_2$ 240.1150 found, 240.1160; IR: ν_{max} (film)/cm^{-1} 3408 (OH), 3066 (ArC=C), 1600 (C=C), 1489 (-C-H), 1113 (C-O); ^{1}H NMR (300MHz, $CDCl_3$): δ (ppm) = 2.97 (d, 1H, *J* = 4.5Hz, O-H), 4.42 (d, 2H, *J* = 5.1Hz, O-CH_2), 5.12-5.24 (m, 2H, $OCH_2CH=CH_2$), 5.78-5.91 (m, 1H, $OCH_2CH=$), 5.99 (d, 1H, *J* = 3.4Hz, PhC*H*), 6.77 (d, 1H, *J* = 8.2Hz, ArH), 6.85-6.95 (m, 1H, ArH), 7.12-7.32 (m, 7H, 7×ArH), 7.31 (d, 2H, *J* = 7.2Hz, 2×ArH); ^{13}C NMR ($CDCl_3$): δ (ppm) = 68.8 (CH_2), 72.3 (CHOH), 111.9 (CH), 112.0 (CH), 117.5 (CH), 117.5 (CH), 120.9 (CH), 126.4 (CH), 127.0 (CH), 127.8 (CH), 128.0 (CH), 128.5 (CH), 132.8 (C), 132.9 (CH), 143.3 (C), 155.6 (C).

(b) Synthesis of 1-(allyloxy)-2-[(allyloxy)(phenyl)methyl]benzene **125**

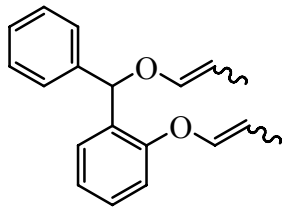


125

[2-(Allyloxy)phenyl](phenyl)methanol (411 mg, 1.71 mmol) was dissolved in DMF (20 mL) and NaH (60% in oil, 137 mg, 3.42 mmol, 2.00 equiv.) was added, followed by allyl bromide (0.29 mL, 414 mg, 2.00 equiv.) and the reaction was stirred at room temperature for 18 hrs. Water (30 mL) was added and the crude product was extracted with ethyl acetate (4 × 100 mL). The combined filtrate was dried with magnesium sulfate and the solvent was removed under vacuum. Column chromatography was then performed using 10% ethyl acetate in hexane to afford the compound as a colourless oil (452 mg, 86% yield). *m/z* (EI): 280 (M^+, 15%), 239 (43), 181 (100), 174 (24), 152 (26), 121 (34), 105 (99), 91 (36), 77 (24); HRMS; calcd for $C_{19}H_{20}O_2$ 280.1463, found 280.1458; IR: ν_{max} (film)/cm^{-1} 1599 (-C-H), 1488 (ArC=C), 1066 (C-O); ^{1}H NMR (300MHz, $CDCl_3$): δ (ppm) = 3.94 (d, 2H, *J* = 5.4Hz, O-CH_2), 4.43 (bs, 2H, O-CH_2), 5.07-5.30 (m, 4H,

2×$OCH_2CH{=}CH_2$), 5.82 (s, 1H, PhC*H*), 5.88-5.91 (m, 2H, 2×$OCH_2CH{=}CH_2$), 6.74 (d, 1H, *J* = 8.2Hz, ArH), 6.87-6.92 (m, 1H, ArH), 7.08-7.22 (m, 4H, 4×ArH), 7.23 (bd, 2H, *J* = 7.1Hz, 2×ArH), 7.44-7.46 (m, 1H, ArH); ^{13}C NMR (75MHz, $CDCl_3$): δ (ppm) = 68.8 (O-CH_2), 69.8 (O-CH_2), 76.2 (CH), 111.7 (CH_2), 116.5 (CH_2), 120.9 (CH) 127.9 (CH), 127.0 (2×CH), 127.1 (2×CH), 128.0 (2×CH), 128.1 (CH), 131.1 (C), 133.1 (CH), 135.0 (CH), 142.1 (C), 155.5 (C).

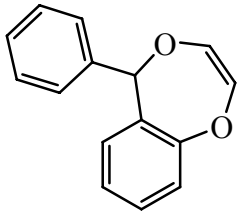
(c) Synthesis of 1-[phenyl(1-propenyloxy)methyl]-2-(1-propenyloxy)benzene **126**



126

To a mixture of 1-(allyloxy)-2-[(allyloxy)(phenyl)methyl]benzene (100 mg, 0.36 mmol) in d_8-benzene was added ruthenium isomerisation catalyst (5 mol%, 19.1 mg, 0.02 mmol). The reaction was then heated at reflux at 100 °C for 18 hrs after which the solvent was removed under vacuum. The crude compound was not purified and NMR spectroscopy on the material showed that it was a complex mixture of *E*/*Z* isomers. *m/z* (FAB): 279 (M^+, 21%), 190 (100), 154 (24), 136 (26), 40 (36); IR: ν_{max} (film)/cm^{-1} 3354 (ArC-H), 2871 (C-H), 1525 (C=C), 1043 (Ar-O); ^{1}H NMR (300MHz, $CDCl_3$): δ (ppm) = 1.48-1.70 (m, 6H, 2×CH_3), 4.42-4.46 (m, 1H, O-CH=), 4.85-4.90 (m, 1H, O-CH=), 6.04-6.33 (m, 3H, PhC*H* and O-CH=C*H*-), 6.89-6.91 (m, 1H, ArH), 7.04-7.08 (m, 1H, ArH), 7.19-7.54 (m, 6H, 6×ArH), 7.65 (d, 1H, *J* = 7.7Hz, ArH), 7.69 (d, 1H, *J* = 7.8Hz, ArH).

(d) Attempted synthesis of 5-phenyl-5*H*-1,4-benzodioxepine **127**

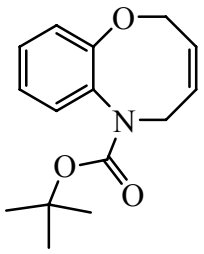


127

Crude 1-[phenyl(1-propenyloxy)methyl]-2-(1-propenyloxy)benzene (100 mg) was dissolved in toluene (8 mL) and Grubbs II catalyst (10 mol%, 0.03 mmol, 24.3 mg) was added. The reaction was reflux for 20 hrs after which NMR spectroscopy was done on the crude product. From the NMR we isolated the starting material.

4.4. EXPERIMENTAL PROCEDURE FOR THE SYNTHESIS OF 8-MEMBERED BENZO-FUSED HETEROCYCLIC COMPOUNDS

4.4.1 EXEPRIMENTAL PROCEDURE FOR THE SYNTHESIS OF *TERT*-BUTYL-2,5-DIHYDRO-6*H*-1,6-BENZOXAZOCINE-6-CARBOXYLATE **128**

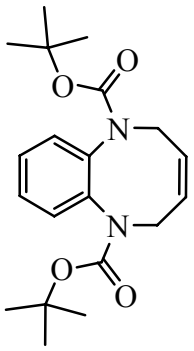


128

tert-Butyl allyl-2-(allyloxy)phenylcarbamate (80 mg, 0.27 mmol, 1.0 equiv.) was dissolved in toluene (3 mL) and Grubbs II catalyst (10 mol%, 22.9 mg, 0.27 mmol) was added and reaction was stirred for a further 18 hrs at room temperature. The crude product was then passed through a silica gel column to afford the cyclized product as a brown solid (42 mg, 69% yield). *m/z* (EI): 261 (M^+, 41%), 218 (3), 148 (48), 68 (56), 57 (62); HRMS; calcd for $C_{15}H_{19}NO_3$ 261.1364, found 261.1321; IR: ν_{max} (film)/cm^{-1} 2975

(C-H), 1239 (C-N), 1700 (C=O), 1160 (Ar-O); Mp: 65-68 °C; ^{1}H NMR (300MHz, $CDCl_3$): δ (ppm) = 1.41 (s, 9H, 3×CH_3), 4.34 (s, 2H, N-CH_2), 4.71 (d, 2H, *J* = 6.6Hz, O-CH_2), 5.76-5.92 (m, 2H, CH=CH), 6.92-6.97 (m, 2H, 2×ArH), 7.11-7.17 (m, 2H, 2×ArH); ^{13}C NMR (75MHz, $CDCl_3$) δ (ppm) = 28.2 (3×CH_3), 48.9 (CH_2), 65.1 (CH_2), 80.5 (C-O), 120.8 (CH), 121.8 (CH), 125.5 (C), 127.9 (CH), 129.8 (2×CH), 132.6 (CH), 136.6 (C), 154.7 (C=O).

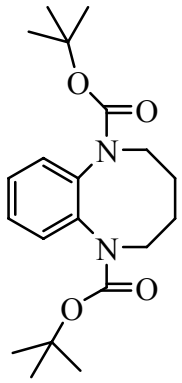
4.4.2 EXPERIMENTAL PROCEDURE FOR THE SYNTHESIS OF DI(*TERT*-BUTYL)-2,5-DIHYDRO-1,6-BENZODIAZOCINE-1,6-DICARBOXYLATE **129**



129

tert-Butyl allyl{2-[allyl(*tert*-butoxycarbonyl)aminophenyl]carbamate (120 mg, 0.31 mmol, 1.00 equiv.) was dissolved in toluene (5 mL) and Grubbs II catalyst (10 mol%, 16.9 mg, 0.01 mmol) was added and the reaction was stirred for 18 hrs at 60 °C. The solvent was removed on the high vacuum and column chromatography was then done on the crude product using 20% ethyl acetate in hexane to afford the cyclized compound as a white solid (55 mg, 64% yield). *m/z* (EI): 360 (M^+, 6%), 248 (29), 204 (48), 159 (33), 57 (100); HRMS calcd for $C_{20}H_{28}N_2O_4$ 360.2049, found 360.2069; IR: ν_{max} (film)/cm^{-1} 2975 (C-H), 1701 (C=O), 1165 (C-N), 1050 (Ar-O); Mp: 113-116 °C; ^{1}H NMR (300MHz, $CDCl_3$): δ (ppm) = 1.43 (s, 18H, 6×CH_3), 4.08 (bs, 4H, 2×N-CH_2), 5.86 (bs, 2H, CH=CH-), 7.12-7.14 (bm, 2H, 2×ArH), 7.15-7.30 (bm, 2H, 2×ArH); ^{13}C NMR (75MHz, $CDCl_3$): δ (ppm) = 28.2 (6×CH_3), 45.7 (2×CH_2), 80.6 (2×C-O), 125.3 (2×C), 128.5 (2×CH), 129.2 (2×CH), 136.5 (2×CH), 154.6 (2×C=O).

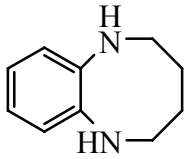
4.4.3. EXPERIMENTAL PROCEDURE FOR THE SYNTHESIS OF DI(*TERT*-BUTYL) 2,3,4,5-TETRAHYDRO-1,6-BENZODIAZOCINE-1,6-DICARBOXYLATE **130**



130

To a suspension of 10% Pd/C (70 mg, 0.05 equiv.) in ethanol (20 mL) was added di(*tert*-butyl) 2,5-dihydro-1,6-benzodiazocine-1,6-dicarboxylate (480 mg, 1.33 mmol, 1.00 equiv.) and the mixture was shaken at an atmosphere of 5 atm for 20 hrs. The crude product was then filtered under vacuum through a celite plug using ethanol (50 mL) and the solvent was removed under vacuum. Column chromatography was then done using 30% ethyl acetate in hexane to afford the product as a white solid (466 mg, 97% yield). *m/z* (EI): 362 (M^+, 27%), 206 (71), 162 (26), 57 (100); HRMS; calcd for $C_{20}H_{30}N_2O_4$ 362.2206, found 362.2203; IR: ν_{max} (film)/cm^{-1} 2976 (ArC-H), 2931 (C-H), 1699 (C=O), 1394 (C-N); Mp: 100-103 °C; ^{1}H NMR (300MHz, $CDCl_3$): δ (ppm) = 1.44 (bs, 18H, 6×CH_3), 1.67 (bs, 4H, 2×N-CH_2CH_2), 3.65 (bs, 4H, 2×N-CH_2), 7.23 (bs, 2H, 2×ArH), 7.33-7.39 (m, 2H, 2×ArH); ^{13}C NMR (75MHz, $CDCl_3$): δ (ppm) = 26.5 (2×CH_2), 28.2 (6×CH_3), 50.9 (bs, 2×N-CH_2), 79.7 (2×C-O), 128.0 (2×CH), 129.3 (2×CH), 140.4 (2×C), 154.8 (2×C=O).

4.4.4. EXPERIMENTAL PROCEDURES FOR THE ATTEMPTED SYNTHESIS OF 1,2,3,4,5,6-HEXAHYDRO-1,6-BENZODIAZOCINE **131**



131

METHOD ONE

Di(*tert*-butyl) 2,3,4,5-tetrahydro-1,6-benzodiazocine-1,6-dicarboxylate (226 mg, 0.55 mmol) was dissolved in THF (10 mL) AT 0 °C and TFA (1 mL) was added and reaction was stirred at room temperature for 1 hr and then 18 hrs. The reaction was neutralized with NaOH (5 mL) and the crude product was extracted with ethyl acetate and the extracts were dried with magnesium sulfate. Column chromatography was done using 40% ethyl acetate in hexane to afford a brown oil (22.8 6mg). Most of the compound had decomposed and from the ^{1}H NMR we isolated our starting material.

METHOD TWO

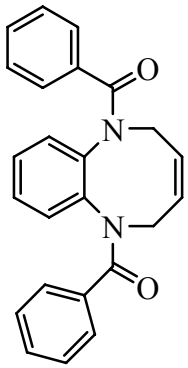
Silica (10 mg) was added to Di(*tert*-butyl) 2,3,4,5-tetrahydro-1,6-benzodiazocine-1,6-dicarboxylate (162.5 mg) and solvent was removed under vacuum. The mixture was then put in a microwave and swirl every 30 secs and TLC was taken every 30 secs for a total of 2 mins 30 secs. Column chromatography was then performed using 30% ethyl acetate in hexane to afford a brown oil (62.5 mg) which was the starting material.

METHOD THREE

Di(*tert*-butyl) 2,3,4,5-tetrahydro-1,6-benzodiazocine-1,6-dicarboxylate (85 mg, 0.24 mmole) was dissolved in DCM (20 mL) at 0 °C and $AlCl_3$ (71 mg, 0.53 mmole, 2.2 equiv.) was added and the reaction was checked by TLC after 15 mins. It was then left

overnight after which NMR spectroscopy was done on the crude product and the compound obtained was not characterisable.

4.4.5. EXPERIMENTAL PROCEDURE FOR THE SYNTHESIS OF1,6-DIBENZOYL-1,2,5,6-TETRAHYDRO-1,6-BENZODIAZOCINE **132**

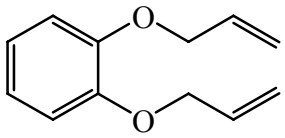


132

N-Allyl-*N*-{2-[allyl(benzoyl)amino]phenyl}benzamide (192 mg, 0.48 mmol, 1.00 equiv.) was dissolved in of toluene (20 mL) and PTSA (9.1 mg, 0.05 mmol, 10 mol%) was added followed by Grubbs II catalyst (10 mol%, 16.9 mg, 0.02 mmol) and the reaction was stirred for 23 hrs at room temperature after which the solvent was removed on the high vacuum. Column chromatography was done on the crude product using 30% ethyl acetate in hexane to give the product as a white solid (70 mg, 97% yield). *m/z* (EI): 368 (M^+, 10%), 247 (45), 105 (100), 77 (49); HRMS calcd for $C_{24}H_{20}N_2O_2$ 368.1524, found 368.1539; IR: ν_{max} (film)/cm^{-1} 1731 (C=O), 1642 (C=C), 1096 (C-N); Mp: 195-198 °C; ^{1}H NMR (300MHz, $CDCl_3$): δ (ppm) = 4.74 (bs, 4H, 2×N-CH_2), 5.79 (bs, 2H, CH=CH-), 6.89-7.00 (m, 6H, 6×ArH), 7.08-7.13 (m, 4H, 4×ArH), 7.22-7.27 (m, 4H, 4×ArH); ^{13}C NMR (75MHz, $CDCl_3$): δ (ppm) = 45.4 (2×CH_2), 126.9 (CH), 127.9 (2×CH), 128.7 (2×CH), 129.0 (CH), 129.8 (CH), 130.0 (CH), 135.5 (2×C), 137.4 (2×C), 169.6 (2×C=O).

4.4.6. EXPERIMENTAL PROCEDURES FOR THE SYNTHESIS OF ATTEMPTED 2,5-DIHYDRO-1,6-BENZODIOXACINE **133**[60]

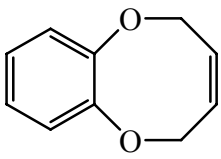
(a) Synthesis of 1,2-*bis*(allyloxy)benzene **47**[60]



47

Catechol (2.5 g, 23 mmol) in acetone (150 mL) was stirred at 60 °C and potassium carbonate (12.6 g, 90.8 mmol, 4.00 equiv.) was added followed by allyl bromide (10.9 g, 90.8 mmol, 4.00 equiv.) and the reaction was heated at 60 °C for 20 hrs. Water (50 mL) was added and the crude product was extracted using ethyl acetate (4 × 100 mL), and the combined filtrate were dried with magnesium sulfate and the solvent removed after which column chromatography was done using 20% ethyl acetate in hexane to afford the product as a yellow oil (3.99 g, 92% yield). *m/z* (EI): 190 (M^+, 55%), 149 (26), 119 (23), 41 (100); HRMS calcd for $C_{12}H_{14}O_2$ 190.0994 found 190.0990; IR: ν_{max} (film)/cm^{-1} 2857 (C-H), 1648 (C=C), 1124 (ArC-O); ^{1}H NMR (300MHz, $CDCl_3$): δ (ppm) = 4.59 (d, 4H, *J* = 5.3Hz, 2×O-CH_2), 5.26 (dd, 2H, *J* = 1.1Hz, 10.5Hz, 2×OCH_2CH=CH_2), 5.41 (dd, *J* = 1.5Hz, 17.3Hz, 2H, 2×OCH_2CH=CH_2), 6.01-6.14 (m, 2H, 2×O-CH_2C*H*=), 6.89 (bs, 4H, 4×ArH); ^{13}C NMR (75MHz, $CDCl_3$): δ = 69.8 (2×OCH_2), 114.3 (2×CH_2), 117.3 (2×CH), 121.2 (2×CH), 133.5 (2×CH), 148.5 (2×C).

(b) Attempted synthesis of 2,5-dihydro-1,6-benzodioxacine **133**



133

METHOD ONE

1,2-*Bis*(allyloxy)benzene (100 mg, 0.53 mmol) was dissolved in benzene (10 mL) and Grubbs II catalyst (5 mol%, 0.03 mmol, 25.6 mg) was added and reaction was stirred at room temperature for 20 hrs. The solvent was removed under vacuum and column chromatography was done using 10% ethyl acetate in hexane to afford a brown oil (38.9 mg) which is the starting material.

METHOD TWO

1,2-*Bis*(allyloxy)benzene (300 mg, 1.58 mmol) was dissolved in toluene (20 mL) and Grubbs II catalyst (10 mol%, 0.12 mmol, 101.9 mg) was added and reaction was heated at reflux at 80-100 °C at room temperature for 20 hrs. The solvent was removed under vacuum and column chromatography was done using 10% ethyl acetate in hexane to afford a brown oil (112 mg) which is the starting material.

METHOD THREE

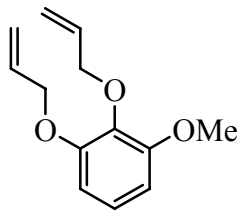
1,2-*Bis*(allyloxy)benzene (100 mg, 0.53 mmol) was dissolved in toluene (20 mL) and Hoveyda-Grubbs catalyst (2 mol%, 0.01 mmol, 6.64 mg) was added and reaction was stirred at room temperature for 20 hrs. The solvent was removed under vacuum and column chromatography was done using 10% ethyl acetate in hexane to afford a brown oil (40 mg) which is the starting material. Most of the material had decomposed.

METHOD FOUR

1,2-*Bis*(allyloxy)benzene (100 mg, 0.53 mmol) was dissolved in DCM (0.06 mL) and Grubbs II catalyst (10 mol%, 0.05 mmol, 44.6 mg) was added and reaction was heated in a pressure vial at 50 °C for 6 hrs. Column chromatography was performed on the crude product using 10% ethyl acetate in hexane to afford a brown oil (60 mg) which is the starting material.

4.4.7. EXPERIMENTAL PROCEDURES FOR THE SYNTHESIS OF 7-METHOXY-2,5-DIHYDRO-1,6-BENZODIOXACINE **137**[60]

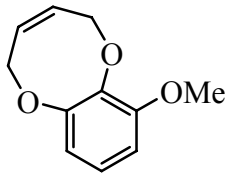
(a) Synthesis of 1,2-*bis*(allyloxy)-3-methoxybenzene **136**



136

3-Methoxy-1,2-benzenediol (498 mg, 3.56 mmol, 1.00 equiv.) was dissolved in acetone (20 mL) and potassium carbonate (1.98 g, 14.2 mmol, 4.00 equiv.) with allyl bromide (1.72 g, 14.2 mmol, 4.00 equiv.) was added and the reaction was reflux for 18 hrs. Water (30 mL) was added and the crude product was then extracted with ethyl acetate (3 × 100 mL), the combined filtrate was dried with magnesium sulfate to afford the product as a yellow oil which was purified by column chromatography 20% ethyl acetate in hexane to afford our compound (599 mg, 76% yield). *m/z* (EI): 220 (M^+, 65%), 205 (27), 179 (96), 41 (100); HRMS; calcd for $C_{13}H_{16}O_3$ 220.1099, found 220.1098; IR ν_{max} (film)/cm^{-1} 1647 (C=C), 1475 (ArC=C), 1104 (C-O); ^{1}H NMR (300MHz, $CDCl_3$): δ (ppm) = 3.83 (s. 3H, O-CH_3), 4.53 (d, 2H, *J* = 6.0Hz, O-CH_2), 4.57 (d, 2H, *J* = 5.2Hz, O-CH_2), 5.16-5.44 (m, 4H, 2×O-CH_2CH=CH_2), 5.99-6.18 (m, 2H, 2×O-CH_2-C*H*=), 6.67 (d, 2H, *J* = 8.6Hz, 2×ArH), 6.92-6.98 (m, 1H, ArH); ^{13}C NMR (75MHz, $CDCl_3$): δ (ppm) = 55.9 (O-CH_3), 69.8 (O-CH_2), 74.0 (O-CH_2), 105.4 (CH_2), 107.1 (CH_2), 117.1 (CH), 117.4 (CH), 123.4 (CH), 133.4 (CH), 134.5 (CH), 137.7 (C), 152.6 (C), 153.8 (C).

(b) Synthesis of 7-methoxy-2,5-dihydro-1,6-benzodioxocine **137**[60]

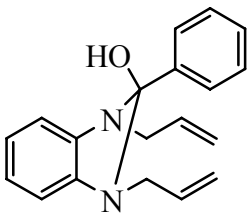


137

To a mixture of 1,2-*bis*(allyloxy)-3-methoxybenzene (137 mg, 0.62 mmol, 1.00 equiv.) in toluene (10 mL), Grubbs II catalyst (10 mol%, 51 mg, 0.06 mmol) was added and the reaction was stirred at 60 °C for a further 18 hrs. The solvent was removed under a high vacuum and column chromatography was done on the crude product using 10% ethyl acetate in hexane to afford the desired cyclized compound as a yellow oil (72 mg, 60% yield). *m/z* (EI): 192 (M^+, 87%), 151 (47), 110 (90), 94 (100); HRMS calcd for $C_{11}H_{12}O_3$ 192.0786 found 192.0785; IR: ν_{max} (film)/cm^{-1} 1585 (C=C), 1099 (Ar-O); ^1H NMR (300MHz, $CDCl_3$): δ (ppm) = 3.82-3.85 (bm, 3H, O-CH_3), 4.87-5.00 (m, 2H, O-CH_2), 4.96-4.99 (m, 2H, O-CH_2), 5.88-5.91 (m, 2H, C*H*=C*H*), 6.54-6.57 (m, 2H, 2×ArH), 6.86-6.92 (m, 1H, ArH); ^{13}C NMR (75MHz, $CDCl_3$): δ (ppm) = 55.9 (O-CH_3), 67.9 (CH_2), 70.8 (CH_2), 105.1 (CH), 113.6 (CH), 126.9 (CH), 132.1 (CH), 132.5 (CH), 136.6 (C), 149.2 (C), 153.5 (C).

4.4.8. EXPERIMENTAL PROCEDURES FOR THE ATTEMPTED SYNTHESIS OF 13-PHENYL-1,8-DIAZATRICYCLO[6.4.1.$0^{2,7}$]TRIDECA-2,4,6,10-TETRAEN-13-OL **139**

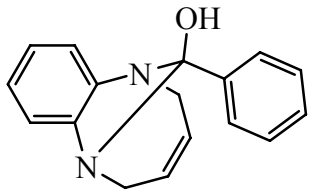
(a) Synthesis of 1,3-diallyl-2-phenyl-2,3-dihydro-1*H*-benzimidazol-2-ol **138**



138

N-Allyl-*N*-{2-[allyl(benzoyl)amino]phenyl}benzamide (0.38 g, 0.97 mmol, 1.00 equiv.) was dissolved in THF (20 mL) and $LiAlH_4$ (0.07 g, 1.9 mmol, 2 equiv.) was added and the reaction was stirred at room temperature for 18 hrs. Water (10 mL) was added to quench the $LiAlH_4$ and it was then extracted with ethyl acetate (2 × 100 mL) and the combined fraction was dried with magnesium sulfate after which column chromatography was performed on crude product using 5% ethyl acetate in hexane to afford the product as a brown oil (0.18 g, 25%). *m/z* (EI): 292 (M^+, 78%), 275 (100), 187 (60), 145 (31), 119 (76), 105 (96), 77 (61); HRMS calcd for $C_{19}H_{20}N_2O$ 292.1576, found 292.1583; IR: ν_{max} (film)/cm^{-1} 3730 (OH), 2923 (C-H), 1463 (ArC=C); ^1H NMR (300MHz, $CDCl_3$): δ (ppm) = 3.41-3.50 (m, 2H, N-CH_2), 3.64-3.61 (m, 2H, N-CH_2), 3.65-3.66 (m, 1H, CHOH), 5.09-5.18 (m, 4H, 2×N-CH_2CH=CH_2), 5.56 (s, 1H, O-H), 5.67-5.80 (m, 2H, 2×N-CH_2C*H*=), 6.39-6.42 (m, 2H, 2×ArH), 6.63-6.66 (m, 2H, 2×ArH), 7.37-7.39 (m, 3H, 3×ArH), 7.53-7.56 (m, 2H, 2×ArH); ^{13}C NMR (75MHz, $CDCl_3$): δ (ppm) = 48.4 (2×CH_2), 87.8 (C-OH), 105.3 (2×CH_2), 117.4 (2×CH), 118.7 (2×CH), 128.3 (2×CH), 128.9 (2×CH), 129.1 (CH), 129.9 (C), 133.2 (2×CH), 139.3 (C), 140.7 (C)

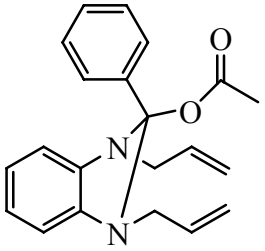
(b) Attempted synthesis of 13-phenyl-1,8-diazatricyclo[6.4.1.$0^{2,7}$]trideca-2,4,6,10-tetraen-13-ol **139**



139

1,3-Diallyl-2-phenyl-2,3-dihydro-1*H*-benzimidazol-2-ol (77.9 mg, 0.27 mmole, 1.00 equiv.) was dissolved in toluene (10 mL) and Grubbs II catalyst (5 mol%, 0.01 mmol, 114.6 mg) was added and the reaction was done at room temperature initially and then heated at 80 °C for 20 hrs. The solvent was removed under vacuum and column chromatography was done on the crude product using 20% ethyl acetate in hexane to afford a brown oil (58.8 mg) which was uncharacterisable.

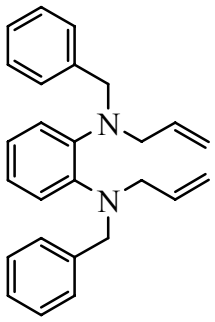
(c) Attempted synthesis of 1,3-diallyl-2-phenyl-2,3-dihydro-1*H*-benzimidazol-2-yl acetate **140**



140

1,3-Diallyl-2-phenyl-2,3-dihydro-1*H*-benzimidazol-2-ol (113.4 mg, 0.39 mmol, 1.00 equiv.) was dissolved in pyridine (10 mL) and acetic anhydride (0.09 mL, 101.7 mg, 0.47 mmol, 1.2 equiv.) was added and the reaction was stirred at room temperature for 18 hrs after which the solvent was removed under vacuum. Column chromatography was then done on the crude product using 5% ethyl acetate in hexane to afford a brown oil (22.9 mg) which was uncharacterisable.

(d) Attempted synthesis of N^{1},N^{11}-diallyl-N^{1},N^{11}-dibenzyl-1,2-benzenediamine **142**



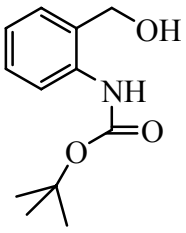
142

N-Allyl-*N*-{2-[allyl(benzoyl)amino]phenyl}benzamide (0.38 g, 0.97 mmol, 1.00 equiv.) was dissolved in THF (20 mL) and $LiAlH_4$ (0.07 g, 1.9 mmol, 2 equiv.) was added and the reaction was stirred at room temperature for 18 hrs. Water (10 mL) was added to quench the $LiAlH_4$ and it was then extracted with ethyl acetate (2 × 100 mL) and the

combined fraction was dried with magnesium sulfate after which column chromatography was performed on crude product using 5% ethyl acetate in hexane but 1,3-diallyl-2-phenyl-2,3-dihydro-1*H*-benzimidazol-2-ol (0.18 mg, 25%) was isolated instead of N^1,N^2-diallyl-N^1,N^2-dibenzyl-1,2-benzenediamine.

4.4.9. EXPERIMENTAL PROCEDURES FOR THE ATTEMPTED SYNTHESIS OF *TERT*-BUTYL 1,4-DIHYDRO-6*H*-5,1-BENZOXAZOCINE-1-(6*H*)-CARBOXYLATE **149**

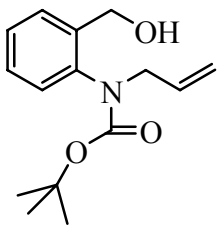
(a) Synthesis of *tert*-butyl 2-(hydroxymethyl)phenylcarbamate **145**



145

2-Aminobenzyl alcohol (800 mg, 6.49 mmol, 1.00 equiv.) was dissolved in THF (30 mL) and Boc_2O (4.47 mL, 19.5 mmol, 3.00 equiv.) was added. The reaction was then stirred at room temperature for 20 hrs. Water (20 mL) was then added and the crude product was then extracted with ethyl acetate (4 × 100 mL) which was dried with magnesiun sulfate. Column chromatography was then performed using 20% ethyl acetate in hexane to afford the desired compound as a yellow oil (1.15 g, 76% yield). *m/z* (EI): 223 (M^+, 16%), 167 (36), 132 (27), 105 (51), 57 100); HRMS; calcd for $C_{12}H_{17}NO_3$ 223.1208, found 223.1356; IR: ν_{max} (film)/cm^{-1} 3360 (O-H), 2979 (ArC-H), 2933 (C-H), 1704 (C=O), 1590 (N-H); ^{1}H NMR 300MHz, $CDCl_3$): δ (ppm) = 1.50 (s, 3H, 3×CH_3) 2.96 (bs, 1H, N-H), 4.56 (s, 2H, Ar-CH_2), 6.96-7.01 (m, 1H, ArH), 7.10 (d, 1H, *J* = 7.1Hz, ArH), 7.24-7.26 (m, 1H, ArH), 7.70 (bs, 1H, O-H), 7.82 (d, 1H, *J* = 8.1Hz, ArH); ^{13}C NMR (75MHz, $CDCl_3$): δ (ppm) = 28.2 (3×CH_3), 63.8 (CH_2), 80.3 (C-O), 121.0 (CH), 123.1 (CH), 128.7 (CH), 128.8 (CH), 129.1 (C), 137.7 (C), 153.4 (C=O).

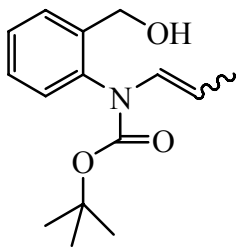
(b) Synthesis of *tert*-butyl allyl[2-(hydroxymethyl)phenyl]carbamate **146**



146

tert-Butyl-2-(hydroxymethyl)phenylcarbamate (994 mg, 4.26 mmol) was dissolved in acetone (30 mL) and potassium carbonate (2.35 g, 17.1 mmol, 4.00 equiv.) was added followed by allyl bromide (1.08 g, 1.46 mL, 4.00 equiv.). The reaction was then stirred at 60 °C for 18 hrs. Water (20 mL) was added and the crude product was extracted with ethyl acetate (4 × 100 mL). The solvent was removed under a vacuum and column chromatography was done using 10% ethyl acetate in hexane to afford the desired compound as a yellow oil (745mg, 67% yield). *m/z* (EI): 263 (M^+, 25%), 218 (62), 207 (32), 122 (45), 68 (64), 57 (100); HRMS; calcd for $C_{15}H_{21}NO_3$ 263.1521, found 263.1507; IR: ν_{max} (film)/cm^{-1} 3372 (O-H), 2979 (ArC-H), 2931 (C-H), 1731 (C=O), 1367 (C-N); ^{1}H NMR (300MHz, $CDCl_3$): δ (ppm) = 1.52 (s, 9H, 3×CH_3), 3.99 (d, 2H, *J* = 5.5Hz, N-CH_2), 4.56 (s, 2H, Ar-CH_2), 5.24 (d, 1H, *J* = 10.5Hz, $NCH_2CH=CH_2$), 5.32 (d, 1H, *J* = 17.2Hz, $NCH_2CH=CH_2$), 5.87-6.00 (m, 1H, N-CH_2-C*H*=), 6.95-6.99 (m, 1H, ArH), 7.12 (d, 1H, *J* = 7.3Hz, ArH), 7.28-7.33 (m, 1H, ArH), 7.80 (bs, 1H, O-H), 8.00 (d, 1H, *J* = 8.1Hz, ArH); ^{13}C NMR (75MHz, $CDCl_3$): δ (ppm) = 28.3 (3×CH_3), 70.4 (CH_2), 71.0 (CH_2), 80.0 (C-O), 117.7 CH_2), 120.1 (CH), 122.4 (CH), 125.3 (C), 129.1 (CH), 129.3 (CH), 138.4 (CH), 138.8 (C), 152.9 (C=O).

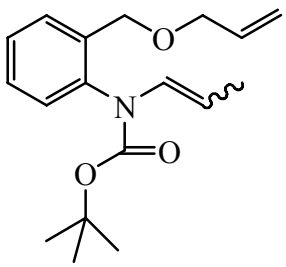
(c) Synthesis of *tert*-butyl 2-(hydroxymethyl)phenyl (1-propenyl) carbamate **147**



147

tert-Butyl allyl[2-(hydroxymethyl)phenyl]carbamate (370 mg, 1.33 mmol) in toluene (10 mL) and ruthenium isomerisation catalyst (5 mol%, 63 mg, 0.07 mmol) was added and the reaction was then stirred at 60 °C for 18 hrs. The solvent was removed under vacuum and the crude product was then passed through a silica gel column using 10% ethyl acetate in hexane to afford the product as a yellow oil (331 mg, 90% yield) NMR spectroscopy showed that this compound consist of approximately a 65:35 mixture of *E*/*Z* isomers. *m/z* (EI): 263 (M^+, 25%), 150 (100), 132 (62), 106 (26), 57 (51); HRMS; calcd for $C_{15}H_{21}NO_3$ 263.1521, found 263.1533; IR: ν_{max} (film)/cm^{-1} 3396 (O-H), 2978 (C-H), 1732 (C=O), 1669 (C=C), 1159 (C-O), 1072 (C-N); ^{1}H NMR (300MHz, $CDCl_3$): δ (ppm) = 1.52 (s, 9H, 3×CH_3), 1.56-1.63 (m, 3H, CH_3), 4.47-4.56 (2×m, 1H, CHC*H*), 4.70 and 4.79 (s, 1H, Ar-CH_2), 5.98 and 6.29 (dd, 1H, *J* = 1.4Hz, 6.0Hz and 12.9Hz, N-C*H*=CH-), 6.97-7.03 (m, 1H, ArH), 7.13-7.19 (m, 1H, ArH), 7.25-7.34 (m, 1H, ArH), 7.58 (bs, 1H, O-H), 7.98 and 8.01 (d and d, 1H, *J* = 8.1Hz and 8.1Hz, ArH); ^{13}C NMR (75MHz, $CDCl_3$, *E*-isomer): δ (ppm) = 12.4 (CH_3), 28.2 (3×CH_3), 72.6 (CH_2), 80.2 (C-O), 101.3 (CH), 103.3 (CH), 120.3 (CH), 122.5 (CH), 129.1 (CH), 129.4 (CH), 137.9 (C), 138.2 (C), 143.6 (CH), 152.9 (C=O). *Z*-isomers 9.1 (CH_3), 28.3 (3×CH_3), 70.3 (CH_2), 80.4 (C-O), 101.4 (CH), 120.9 (CH), 122.9 (CH), 129.4 (CH), 138.0 (C), 145.0 (C)

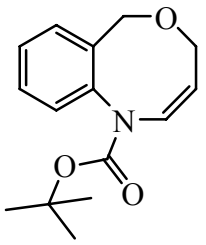
(d) Synthesis of *tert*-butyl 2-[(allyloxy)methyl]phenyl(1-propenyl)carbamate **148**



148

tert-Butyl 2-(hydroxymethyl)phenyl(1-propenyl)carbamate (230 mg, 0.87 mmol) was dissolved in DMF (15 mL) and NaH (60% in oil, 46 mg, 1.1 mmol, 1.3 equiv.) was added at 0°C followed by allyl bromide (0.15 mL, 1.75 mmol, 2.00 equiv.). The reaction was then stirred at room temperature for 19 hrs. Water (80mL) was then added and the crude product was extracted using ethyl acetate (2 × 100 mL) and the combined extracts were then dried with magnesium sulfate and the solvent removed. Purification was done by silica gel chromatography using 10% ethyl acetate in hexane to afford the product as a yellow oil (210 mg, 79% yield). By NMR the product seems to be a mixture of *E*/*Z* isomers with the ratio being difficult to determine. *m/z* (EI): 303 (M^+, 1%), 190 (100), 146 (43), 57 (44); HRMS; calcd for $C_{18}H_{25}NO_3$ 303.1834, found 303.1838; IR: ν_{max} (film)/cm^{-1} 2977 (ArC-H), 1699 (C=O), 1612 (C=C), 1151 (ArC-O), 1080 (C-N); ^{1}H NMR (300MHz, $CDCl_3$): δ (ppm) = 1.39 (bs, 9H, 3×CH_3), 1.49-1.64 (m, 3H, CH_3), 3.96 (bs, 1H, Ar-C*H*H), 4.24-4.32 (m, 1H, Ar-C*H*H), 4.63-4.90 (m, 3H, O-CH_2 and NCHC*H*), 5.87-5.98 (m, 1H, O-CH=C*H*-CH_2), 5.87-5.98 and 6.28 (m and d, 1H, *J* = 12.0Hz. NCHC*H*CH_3), 7.09 (bs, 1H, ArH), 7.26-7.28 (m, 2H, 2×ArH), 7.45-7.48 (m, 1H, ArH); ^{13}C NMR (75MHz, $CDCl_3$): δ (ppm) = 9.3 and 12.5 (CH_3), 28.2 (3×CH_3), 52.8 and 52.9 (CH_2), 67.0 and 69.5 (CH_2), 80.2 (C-O), 99.4 and 101.5 (CH), 127.3 (CH), 128.0 (CH), 128.1 (CH), 133.0 and 133.5 (CH), 135.6 (C) 145.3 and 146.3 (C), 153.0 (C=O).

(e) Attempted synthesis of *tert*-butyl 4*H*-5,1-benzoxazocine-1-(6*H*)-carboxylate **149**

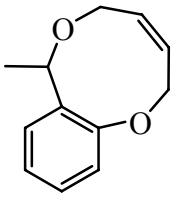


149

tert-Butyl 2-[(allyoxy)methyl]phenyl(1-propenyl)carbamate (120 mg, 0.39 mmol) was dissolved in toluene (8 mL) and Grubb II catalyst (10 mol%, 0.04 mmol, 33.6 mg) was added and the reaction was heated at reflux at 80 °C for 36 hrs. The solvent was removed under vacuum and column chromatography was performed using 5% ethyl acetate in hexane to afford a brown oil (10 mg). The compound had decomposed and the recovered material was the starting material.

4.5. EXPERIMENTAL PROCEDURES FOR THE SYNTHESIS OF 9-MEMBERED BENZO-FUSED HETEROCYCLIC COMPOUNDS

4.5.1. EXPERIMENTAL PROCEDURE FOR THE ATTEMPTED SYNTHESIS OF 7-METHYL-2,5-DIHYDRO-7*H*-1,6-BENZODIOXONINE **150**

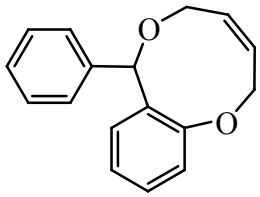


150

1-(Allyloxy)-2-[(allyloxy)(phenyl)methyl]benzene (100 mg, 0.68 mmol) was dissolved in toluene (10 mL) and Grubbs II catalyst (10 mol%, 0.07 mmole, 57.9 mg) and reaction was heated at reflux for 18 hrs. The solvent was removed under vacuum and column

chromatography was performed using 5% ethyl acetate in hexane to afford a brown oil (13.9 mg). Most of the compound had decomposed and the material recovered was the starting material.

4.5.2. EXPERIMENTAL PROCEDURE FOR THE ATTEMPTED SYNTHESIS OF 7-PHENYL-2,5-DIHYDRO-7*H*-1,6-BENZODIOXONINE **151**

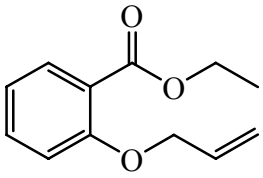


151

1-(Allyloxy)-2-[1-(allyloxy)ethyl]benzene (100 mg, 0.36 mmol) was dissolved in toluene (10 mL) and Grubbs II catalyst (10 mol%, 0.04 mmol, 30.3 mg) was added. The reaction was reflux for 18 hrs after which the solvent was removed under vacuum and column chromatography was done using 5% ethyl acetate in hexane to afford a brown oil (44 mg). The material isolated was the starting material.

4.5.3. EXPERIMENTAL PROCEDURES FOR THE ATTEMPTED SYNTHESIS OF 7,7-DIPHENYL-2,5-DIHYDRO-7*H*-1,6-BENZODIOXONINE **156**

(a) Synthesis of ethyl 2-(allyoxy)benzoate **153**

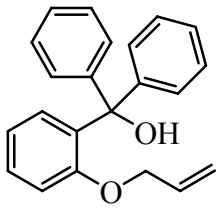


153

Ethyl 2-hydroxybenzoate (1.3 g, 6.3 mmol) was dissolved in acetone (50 mL) and potassium carbonate (3.33 g, 24.1 mmol, 4.00 equiv.) was added followed by allyl

bromide (2.1 mL, 2.9 g, 4.0 equiv.). The reaction was reflux for 18 hrs after which water (30 mL) was added and the crude product was extracted with ethyl acetate (4 × 100 mL) and column chromatography was done using 5% ethyl acetate in hexane to afford the product as a colourless oil (1.28 g, 96% yield). *m/z* (EI): 206 (M^+, 43%), 161 (75), 162 (26), 57 (100); HRMS; calcd for $C_{12}H_{14}O_3$ 206.0943, found 206.0993; IR: ν_{max} (film)/cm^{-1} 2983 (C-H), 1726 (C=O), 1601 (C=C), 1080 (ArC-O); ^{1}H NMR (300MHz, $CDCl_3$): δ (ppm) = 1.38 (t, 3H, *J* = 7.1Hz, CH_3), 4.36 (q, 2H, *J* = 7.1Hz, OCH_2CH_3), 4.61 (dd, 2H, *J* = 1.4Hz, 3.3Hz, O-CH_2CH), 5.29 (d, 1H, *J* = 10.6Hz, $OCH_2CH=CH_2$), 5.51 (dd, 1H, *J* = 1.4Hz, 17.2Hz, $OCH_2CH=CH_2$), 6.01-6.07 (m, 1H, OCH_2CH=), 6.93-6.97 (m, 2H, 2×ArH), 7.40-7.45 (m, 1H, ArH), 7.79 (dd, 1H, *J* = 1.4Hz, 7.7Hz, ArH); ^{13}C NMR (75MHz, $CDCl_3$): δ (ppm) = 14.2 (CH_3), 60.6 CH_2), 69.3 (CH_2), 113.5 (CH_2), 117.2 (CH), 120.2 (CH), 120.9 (C), 131.4 (CH), 132.6 (CH), 133.0 (CH), 157.8 (C), 166.2 (C=O).

(b) Synthesis of [2-(allyloxy)phenyl](diphenyl)methanol **154**

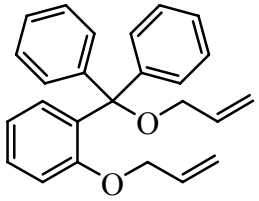


154

The Grignard reagent was prepared by dissolving magnesium turnings (266 mg, 10.9 mmol, 2.50 equiv.) in THF (20 mL) at 0 °C followed by addition of bromobenzene (3.43 g, 2.29 mL, 5.00 equiv.) after which ethyl-2-(allyoxy)benzoate (900 mg, 4.37 mmol, 1.00 equiv.) was then added to the solution. The reaction was then stirred at room temperature for 18 hrs after which ammonium chloride solution (20 mL) was added to quench the reaction. The crude product was extracted with ethyl acetate (4 ×100 mL), dried with magnesiun sulfate and column chromatography was done using 5% ethyl acetate in hexane to afford the product as a white solid (642 mg, 44% yield). *m/z* (EI): 316 (M^+, 32%), 239 (77), 121 (26), 105 (100), 77 (26); HRMS; calcd for $C_{22}H_{20}O_2$ 316.1463 found

316.1467; IR: ν_{max} (film)/cm^{-1} 3515 (O-H), 3058 (ArC-H), 2926 (C-H), 1679 (C=C), 1018 (Ar-O); Mp: 99-101 °C; ^{1}H NMR (300MHz, $CDCl_3$): δ (ppm) = 4.36 (d, 2H, *J* = 5.0Hz, O-CH_2), 5.00-5.09 (m, 2H, OCH_2CHCH_2), 5.25 (s, 1H, O-H), 5.51-5.63 (m, 1H, OCH_2CHCH_2), 6.53 (d, 1H, *J* = 6.7Hz, ArH), 6.80-6.82 (m, 1H, ArH), 6.93 (d, 1H, *J* = 8.1Hz, ArH), 7.26-7.32 (m, 11H, 11×ArH); ^{13}C NMR (75MHz, $CDCl_3$): δ (ppm) = 69.3 (O-CH_2), 81.8 (C), 113.3 (CH_2), 117.1 (CH), 120.6 (CH), 126.9 (2×CH), 127.6 (4×CH), 127.7 (4×CH), 128.8 (CH), 130.1 (CH), 132.1 (2×C), 135.9 (C), 146.5 (CH), 156.3 (C).

(c) Synthesis of 1-(allyloxy)-2-[allyloxy(diphenyl)methyl]benzene **155**

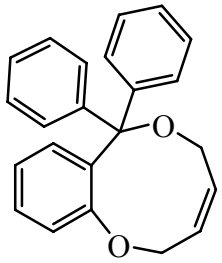


155

[2-(Allyloxy)phenyl](diphenyl)methanol (316 mg, 1.00 mmol, 1.00 equiv.) was dissolved in DMF (20 mL) at 0 °C and NaH (60% in oil, 79.2 mg, 1.98 mmol, 1.98 equiv.) was added. This was then followed by addition of allyl bromide (0.17 mL, 2.0 mmol, 2.0 equiv.) and the reaction was stirred for 18 hrs at room temperature. Water (20 mL) was then added and the crude product was extracted with ethyl acetate (4 × 100 mL), which was then dried with magnesium sulfate. Purification was done by silica gel chromatography using 5% ethyl acetate in hexane to afford the desired product as a white solid (234 mg, 66% yield). *m/z* (EI): 356 (M^+, 15%), 299 (38), 259 (36), 257 (44), 218 (100), 181 (26), 130 (34), 105 (75), 68 (77); HRMS; calcd for $C_{25}H_{24}O_2$ 356.1776, found 356.1772; IR: ν_{max} (film)/cm^{-1} 3583 (ArC-H), 1680 (C=C), 1367 (C-O), 1017 (Ar-O); Mp: 98-100 °C. ^{1}H NMR (300MHz, $CDCl_3$): δ (ppm) = 3.55 (d, 2H, *J* = 4.7Hz, O-CH_2), 4.19 (d, 2H, *J* = 4.9Hz, O-CH_2), 4.84 (dd, 1H, *J* = 1.2Hz, 17.2Hz, O-CH_2CH=C*H*H), 4.96 (dd, 1H, *J* = 1.0Hz, 10.6Hz, O-CH_2CH=C*H*H), 5.14 (dd, 1H, *J* = 1.2Hz, 10.5Hz, O-CH_2CH=C*H*H), 5.36-5.51 (m, 2H, O-CH_2CH=CH_2 and OCH_2CH=CH_2), 5.87-5.93 (m, 1H, O-CH_2CH=CH_2), 6.77 (d, 1H, *J* = 8.1Hz, ArH), 6.98-7.03 (m, 1H, ArH), 7.21-7.27

(m, 8H, 8×ArH), 7.50 (bd, 3H, *J* = 7.1Hz, 3×ArH), 7.87 (d, 1H, *J* = 6.7Hz, ArH); ^{13}C NMR (75MHz, $CDCl_3$): δ (ppm) = 64.7 (O-CH_2), 68.6 (O-CH_2), 85.2 (C), 113.3 (CH_2), 112.9 (CH), 115.1 (CH_2), 116.6 (CH), 120.7 (CH), 126.6 (2×CH), 127.2 (2×CH), 127.8 (CH), 128.5 (CH), 128.6 (2×CH), 132.8 (C), 133.0 (C), 135.2 (C), 142.7 (CH), 155.4 (C).

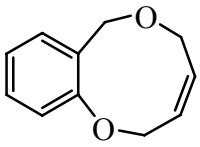
(d) Attempted synthesis of 7,7-diphenyl-2,5-dihydro-7*H*-1,6-benzodioxonine **156**



156

1-(alloxy)-2-[allyoxy(diphenyl)methyl]benzene (146 mg, 0.42 mmol) was dissolved in toluene (10 mL) and Grubbs II catalyst (10 mol%, 0.04 mmol, 35.7 mg) was added. The reaction was the reflux at 80 °C for 18 hrs to afford a yellow oil (13.4 mg). The material had decomposed.

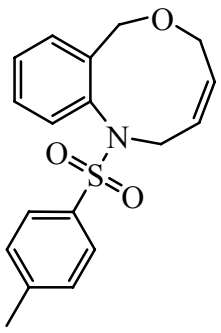
4.5.4. EXPERIMENTAL PROCEDURE FOR THE ATTEMPTED SYNTHESIS OF 2,5-DIHYRO-7*H*- *1*,6-BENZODIOXONINE **157**



157

1-(Allyloxy)-2-[(allyloxy)methyl]benzene (100 mg, 0.49 mmol) was dissolved in toluene (15mL) and Grubbs II catalyst (5 mol%, 20.8 mg, 0.03 mmol) was added and reaction was heated at reflux at 80 °C for 4 hrs. Column chromatography was performed using 19% ethyl acetate in hexane to afford a yellow oil (30 mg) which is the starting material.

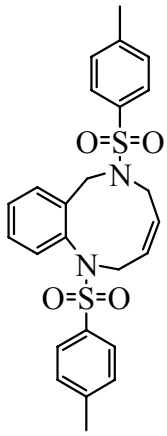
4.5.5. EXPERIMENTAL PROCEDURE FOR ATTEMPTED SYNTHESIS OF 1[(4-METHYLPHENYL)SULFONYL]-1,2,5,7-TETRAHYDRO-6,1-BENZOXAZONINE **158**



158

N-Allyl-*N*-[2-(allyloxy)methylphenyl]-4-methylbenzenesulfonamide (100 mg, 0.28 mmole) was dissolved in toluene (8 mL) and Grubbs II catalyst (10 mol%, 0.03 mmol, 23.7 mg) was then added after which the reaction was reflux for 18 hrs. The solvent was removed under vacuum and column chromatography was performed on the crude product using 20% ethyl acetate in hexane to afford a brown oil (28.6 mg). We suspect the compound had polymerized.

4.5.6. EXPERIMENTAL PROCEDURE FOR THE SYNTHESIS OF 1,6-*BIS*[(4-METHYLPHENYL)SULFONYL]-2,5,6,7-TETRAHYDRO-1*H*-1,6-BENZODIAZONINE **159**

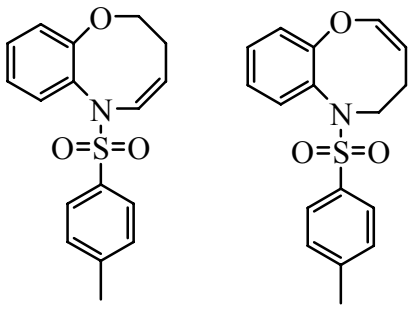


159

N-Allyl-*N*-[2-({ally[(4-methylphenyl)sulfonyl]amino}methyl)phenyl]-4-methylbenzenesulfonamide (100 mg, 0.19 mmol) was added to DCM (10 mL) and Grubbs II catalyst (10 mol%, 17 mg, 0.02 mmol) was added and reaction was stirred for 18 hrs at 60 °C. The solvent was removed under high vacuum and column chromatography was done on the crude product using 20% ethyl acetate in hexane to afford the cyclized product as a white solid (88 mg, 96% yield). *m/z* (EI): 482 (M^+, 13%), 222 (41), 171 (46), 156 (50), 106 (100); HRMS; calcd for $C_{25}H_{26}N_2O_4S_2$ 482.1334, found 482.1338; IR: ν_{max} (film)/cm^{-1} 2852 (C-H), 1648 (C=C), 1491 (ArC=C), 1341 (O=S=O), 1159 (C-N); Mp: 84-89 °C; ^{1}H NMR (300MHz, $CDCl_3$): δ = 2.46 (s, 6H, 2×CH_3), 3.53-3.60 (m, 2H, Ar-CH_2), 4.05-4.12 (m, 1H, N-CH_2), 4.31 (d, 1H, *J* = 13.9Hz, N-CH_2), 4.56-4.65 (m, 2H, N-CH_2), 5.56-5.59 (m, 2H, N-C*H*$_2$=C*H*), 6.47 (d, 1H, *J* = 7.9Hz, ArH), 7.15-7.19 (m, 1H, ArH), 7.26-7.35 (m, 5H, 5×ArH), 7.55-7.61 (m, 3H, 3×ArH), 7.73 (bd, 2H, *J* = 8.2Hz, 2×ArH); ^{13}C NMR (75MHz, $CDCl_3$): δ (ppm) = 21.5 (CH_3), 21.6 (CH_3), 44.7 (CH_2), 47.7 (CH_2), 48.0 (CH_2), 126.8 (2×CH), 126.9 (CH), 127.6 (CH), 127.9 (2×CH), 129.1 (CH), 129.4 (CH), 129.6 (2×CH), 129.8 (2×CH), 130.7 (CH), 132.4 (CH), 135.0 (C), 137.6 (C), 138.3 (C), 139.2 (C), 143.3 (C), 143.9 (C).

4.6. EXPERIMENTAL PROCEDURES FOR THE INTERNAL ISOMERISATION OF 8- AND 9-MEMBERED BENZO-FUSED HETEROCYCLIC COMPOUNDS

4.6.1. EXPERIMENTAL PROCEDURE FOR THE SYNTHESIS OF A MIXTURE OF 6-[(4-METHYLPHENYL)SULFONYL]-3,6-DIHYDRO-2*H*-1,6-BENZOXAZOCINE **161** AND 6-[(4-METHYLPHENYL)SULFONYL]-5,6-DIHYDRO-4*H*-1,6,-BENZOXAZOCINE **162**

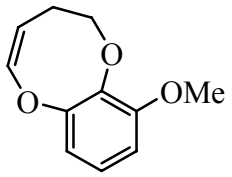


161 **162**

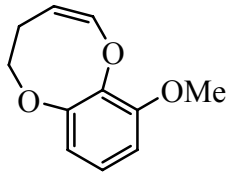
6-[(4-Methylphenyl)sulfonyl]-5,6-dihydro-2*H*-1,6-benzoxazocine (37 mg, 0.12 mmol, 1.0 equiv.) was dissolved in d_8-toluene at room temperature and ruthenium isomerisation catalyst **12** (9.5 mg, 0.01 mmol) was added. The reaction was then stirred at 60-70 °C for a further 18 hrs after which the solvent was removed under a high vacuum. Column chromatography was done on the crude product to afford the desired product as a mixture of regioisomers as a white solid (28.6 mg, 77%). *m/z* (EI): 315 (M^+, 36%), 160 (100); HRMS; calcd for $C_{17}H_{17}NO_3S$ 315.0929, found 315.0914; IR: ν_{max} (film)/cm^{-1} 2922 (C-H), 1350 (O=S=O), 1165 (C-N), 1086 (ArC-O), 1025 (C-S); Mp: 101-104 °C; ^{1}H NMR (300MHz, $CDCl_3$): δ (ppm) = 2.41 (d, 3H, *J* = 7.8Hz, CH_3), 3.42 (t, 2H, *J* = 5.8Hz, O-CH_2 OR N-CH_2), 3.73 (t, 2H, *J* = 5.5Hz, O-*CH*$_2$*CH*$_2$ or N-*CH*$_2$*CH*$_2$), 4.46 (dd,1H, *J* = 8.4Hz, 16.2Hz, N-CH=C*H*), 4.84 (dd, IH, *J* = 7.8Hz, 17.6Hz, O-CH=C*H*)], 6.14 (d, 1H, *J* = 7.5Hz, N-CH= or O-CH=), 6.86-7.27 (m, 4H, 4×ArH), 7.48 (dt, 2H, *J* = 12.0Hz, 7.4Hz, 2×ArH), 7.67 (t, 2H, *J* = 9.4Hz, 2×ArH); ^{13}C NMR (75MHz, $CDCl_3$): 21.5 and 21.6 (CH_3), 22.1 and 22.7 (CH_2), 45.7 (N-CH_2), 71.2 (O-CH_2), 100.9 (CH), 106.7 (CH), 121.1 (CH), 123.4 (CH), 124.6 and 124.9 (CH), 127.5 and 127.6 (CH), 129.1 (CH), 129.3

(CH), 129.9 (CH), 130.0 (CH), 130.8 (CH), 131.6 (CH), 132.1 (CH), 135.8 (C), 137.9 (C), 143.2 (C), 143.6 (C), 144.0 (C), 154.3 (C).

4.6.2. EXPERIMENTAL PROCEDURE FOR THE SYNTHESIS OF A MIXTURE OF 10-METHOXY-2,3-DIHYDRO-1,6-BENZODIOXOCINE **163** AND 7-METHOXY-2,3- DIHYDRO-1,6-BENZODIOXOCINE **164**



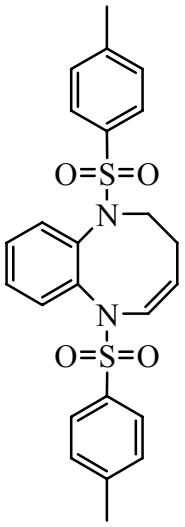
163



164

7-Methoxy-2,5-dihydro-1,6-benzodioxacine (59 mg, 0.33 mmol) was dissolved in toluene (4 mL) and ruthenium isomerisation catalyst (5 mol%, 16 mg, 0.02 mmol) was added. The reaction was then heated for 48 hrs. The solvent was removed under a high vacuum and column chromatography was done on the crude product using 20% ethyl acetate in hexane to afford a mixture of regioisomers as a yellow oil (37 mg, 63% yield). *m/z* (EI): 192 (M^+, 29%), 153 (39), 136 (30), 107 (42), 89 (49), 77 (100), 51 (38); HRMS calcd for $C_{11}H_{12}O_3$ 192.0786 found 192.0781; IR: ν_{max} (film)/cm^{-1} 2969 (C-H), 1651 (C=C), 1247 (Ar-O), 1090 (C-O); ^{1}H NMR (300MHz, $CDCl_3$): δ (ppm) = 2.18-2.29 (m, 2H, O-$CH_2C\mathit{H}_2$), 3.77 and 3.78 (s, 3H, O-CH_3), 4.04 and 4.18 (t, 2H, *J* = 5.6Hz, O-CH_2), 4.57-4.69 and 4.75-4.81 (m, 1H, OCH=C*H*), 6.36 and 6.47 (d, 1H, *J* = 7.1Hz, OC*H*=CH), 6.55-6.61 (m, 2H, 2×ArH), 6.84-6.93 (m, 1H, ArH); ^{13}C NMR (75MHz, $CDCl_3$): δ (ppm) = 23.9 (CH_2), 25.3 (CH_2), 56.1 (O-CH_3), 66.0 (CH_2), 68.6 (CH_2), 103.7 (CH), 106.7 (CH), 107.3 (CH), 107.8 (CH), 113.5 (CH), 114.6 (CH), 123.6 (CH), 124.2 (CH), 126.8 (C), 132.1 (C), 136.7 (C), 145.2 (2×CH), 149.5 (C), 152.4 (C), 153.8 (C).

4.6.3. EXPERIMENTAL PROCEDURE FOR THE SYNTHESIS OF 1,6-*BIS*[(4-METHYLPHENYL)SULFONYL]-1,2,3,6-TETRAHYDRO-1,6-BENZODIAZOCINE **166**

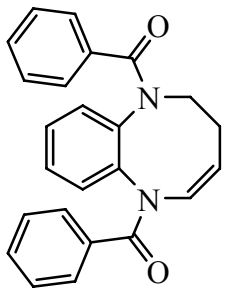


166

1,6-*Bis*[(4-methylphenyl)sulfonyl]-1,2,5,6-tetrahydro-1,6-benzodiazocine (279 mg, 0.53 mmol, 1.00 equiv.) was dissolved in toluene (5 mL) at room temperature and ruthenium isomerisation catalyst (22 mg, 0.02 mmol, 4 mol%) was added and the reaction was then stirred for a further 20 hrs at 100 °C. The solvent was removed under high vacuum and column chromatography was done on the crude product using 30% ethyl acetate in hexane afford the desired compound as a brown solid (168 mg, 60% yield). *m/z* (EI): 468 (M^+, 12%), 313 (38), 159 (100), 131 (21), 91 (41); HRMS calcd for $C_{24}H_{24}N_2O_4S_2$ 468.1177, found 468.1172; IR: ν_{max} (film)/cm^{-1} 2923 (C-H), 1654 (C=C), 1351 (O=S=O), 1163 (C-S), 1084 (C-N); Mp: 134-138 °C; ^{1}H NMR (300MHz, $CDCl_3$): δ (ppm) = 1.72-1.79 (m, 2H, NCH_2CH_2), 2.39 (s, 3H, CH_3), 2.44 (s, 3H, CH_3), 3.18 (t, 2H, *J* = 5.7Hz, N-CH_2), 4.66 (td, 1H, *J* = 8.2Hz, 10.0Hz, N-CH=C*H*), 6.69 (d, 1H, *J* = 10.0Hz, N-C*H*=CH), 7.07-7.10 (m, 1H, ArH), 7.26-7.36 (m, 6H, 6×ArH), 7.48-7.51 (m, 1H, ArH), 7.66 (d, 2H, *J* = 8.3Hz, 2×ArH), 7.88 (d, 2H, *J* = 8.3Hz, 2×ArH); ^{13}C NMR (75MHz, $CDCl_3$): δ (ppm) = 21.5 (2×CH_3), 22.0 (CH_2), 48.7 (CH_2), 104.2 (CH), 128.2 (2×CH), 128.3 (2×CH), 128.7 (CH), 128.8 (CH), 129.2 (CH), 129.5 (2×CH), 129.7 (CH),

129.8 (2×CH), 130.4 (CH), 135.3 (C), 136.1 (C), 136.5 (C), 137.3 (C), 143.6 (C), 144.2 (C).

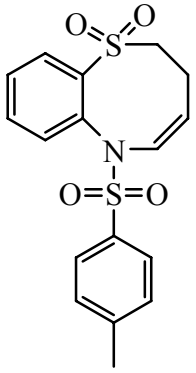
4.6.4. EXPERIMENTAL PROCEDURE FOR THE ATTEMPTED SYNTHESIS OF 1,6-DIBENZOYL-1,2,3,6-TETRAHYDRO-1,6-BENZODIAZOCINE **167**



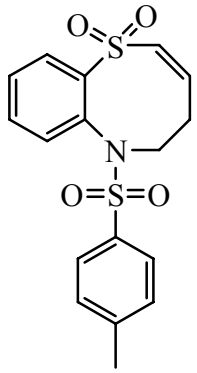
167

1,6-Dibenzoyl-1,2,5,6-tetrahydro-1,6-benzodiazocine (82 mg, 0.22 mmol) was dissolved in d_8-toluene and ruthenium isomerisation catalyst (9.5 mg, 5 mol%, 0.01 mmol) was added. The reaction was then heated at 70-100 °C for 20 hrs. H NMR spectroscopy was done on the crude product but the spectra was too broad and we could not characterized the compound.

4.6.5. EXPERIMENTAL PROCEDURE FOR THE ATTEMPTED SYNTHESIS OF A MIXTURE 6-[(4-METHYLPHENYL) SULFONYL]-3,6-DIHYDRO-2*H*-1,6-BENZOTHIAZOCINE 1,1-DIOXIDE **168** AND 6-[(4-METHYLPHENYL) SULFONYL]-5,6-DIHYDRO-4*H*-1,6-BENZOTHIAZOCINE 1,1-DIOXIDE **169**



168



169

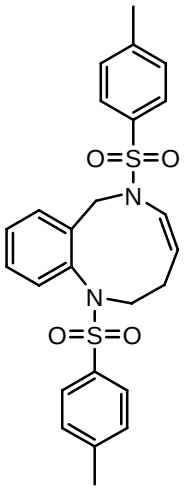
METHOD ONE

6-[(4-Methylphenyl)sulfonyl]-5,6-dihydro-2*H*-1,6-benzothiazocine 1,1-dioxide (40.3 mg, 0.11 mmol) was added to d_8-toluene in an NMR tube at 100 °C Grubbs II catalyst (10 mol%, 0.01 mmol, 10.5 mg) was added but, 6-[(4-methylphenyl) sulfonyl]-5,6-dihydro-2*H*-1,6-benzothiazocine was insoluble in d_8-toluene.

METHOD TWO

6-[(4-Methylphenyl)sulfonyl]-5,6-dihydro-2*H*-1,6-benzothiazocine 1,1-dioxide (34.9 mg, 0.09 mmol) was added to DCM (5 mL) and Grubbs II catalyst (10 mol%, 0.01 mmol, 9.5 mg) was added and the reaction was reflux for 34 hrs. The solvent was removed under vacuum and column chromatography was performed on the crude compound using 70% ethyl acetate in hexane to afford brown solid (30 mg) which is 6-[(4-methylphenyl) sulfonyl]-5,6-dihydro-2*H*-1,6-benzothiazocine 1,1-dioxide.

4.6.6. EXPERIMENTAL PROCEDURE FOR THE SYNTHESIS OF 1,6-*BIS*[(4-METHYLPHENYL)SULFONYL]-2,3,6,7-TETRAHYDRO-1*H*-1,6-BENZODIAZONINE **170**



170

1,6-*Bis*[(4-methylphenyl)sulfonyl]-2,5,6,7-tetrahydro-1*H*-1,6-benzodiazonine (30 mg, 0.06 mmol) was dissolved in d_8-benzene and ruthenium isomerisation catalyst (10mol%, 9.5mg, 0.01mmol) was added and the reaction was stirred at 90 °C for 40 hrs. The solvent was removed under high vacuum and column chromatography was done using 30% ethyl acetate in hexane to afford the product as a brown solid (29 mg, 97% yield). *m/z* (EI): 482 (M^+, 2%), 327 (62), 277 (100), 183 (23), 144 (55), 91 (49); HRMS calcd for $C_{25}H_{26}N_2O_4S_2$ 482.1334 found 482.1341; IR: ν_{max} (film)/cm^{-1} 2959 (C-H), 1648 (C=C), 1345 (O=S=O), 1089 (C-N); Mp: 192-196 °C; ^{1}H NMR (300MHz, $CDCl_3$): δ (ppm) = 1.76-1.99 (m, 1H, NCH_2CH_2), 2.04-2.17 (m, 1H, NCH_2CH_2), 2.35 (s, 3H, CH_3), 2.37 (s, 3H, CH_3), 3.05 (d, 1H, *J* = 12.5Hz, N-CH_2CH_2), 3.95 (t, 1H, *J* = 12.0Hz, NCH_2), 4.46-4.59 (m, 2H, Ar-CH_2), 5.61-5.65 (m, 1H, NCH=C*H*), 6.09 (d, IH, *J* = 7.1Hz, NC*H*=CH), 6.34 (d, 1H, *J* = 7.8Hz, ArH), 7.08-7.13 (m, 1H, ArH), 7.19-7.23 (m, 4H, 4×ArH), 7.29-7.34 (m, 1H, ArH), 7.44 (d, 2H, *J* = 7.9Hz, 2×ArH), 7.62 (d, 2H, *J* = 7.9Hz, 2×ArH), 7.73 (d, 1H, *J* = 7.6Hz, ArH); ^{13}C NMR (75MHz, $CDCl_3$): δ (ppm) = 21.5 (CH_3), 21.6 (CH_3), 25.2 (CH_2), 51.8 (CH_2), 52.9 (CH_2), 127.3 (CH), 127.4 (2×CH),

127.6 (2×CH), 129.0 (CH), 129.3 (CH), 129.5 (2×CH), 129.6 (2×CH), 130.3 (CH), 132.0 (CH), 132.8 (CH), 135.4 (C), 136.0 (C), 137.9 (C), 140.1 (C), 143.6 (C), 143.6 (C).