Research Paper

Journal of Chemical Research

A synthetic route to 1-(4-boronobenzyl)-*1H*-pyrrole

Journal of Chemical Research
1–5

DOI: 10.1177/1747519820960692
journals.sagepub.com/home/chl
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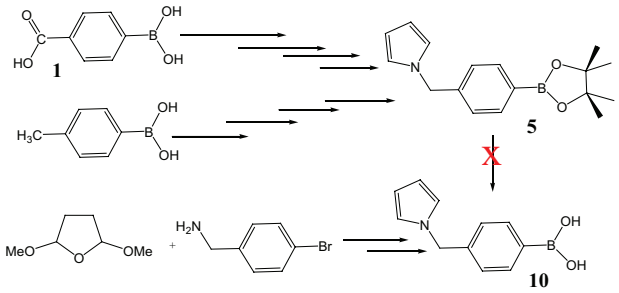
Abstract

The synthesis of 1-(4-boronobenzyl)-*1H*-pyrrole was investigated using three different routes. Two key routes that involved the introduction of the boronate group protected as the pinacol ester, failed, due to deprotection problems. The route involving the introduction of the boronate group as the final step of the reaction yielded 1-(4-boronobenzyl)-*1H*-pyrrole (**10**).

Keywords

boronate esters, boronic acid, lithiation, pinacol protection, pyrrole

Date received: 4 August 2020; accepted: 2 September 2020



Introduction

Pyrrole/pyrrole derivatives have been investigated for a variety of uses which include batteries,[1–3] an anti-corrosion film,[4–6] photoconductors,[6,7] conducting polymers,[1–3,8] electromagnetic shielding materials,[9] membranes,[10,11] ion-exchange chromatography resins,[12] modified electrodes for enantioselective recognition,[13] electrosynthesis,[14–16] displays,[17] tissue engineering scaffolds,[18,19] neural probes,[20] drug delivery devices,[21] biosensors[22–24] and sensors.[25] The preparation of *N*-substituted pyrroles traditionally has involved deprotonation of the 1-position of the pyrrole ring with Na, K[26–28]or n-BuLi[7,8] under nitrogen in a solution of tetrahydrofuran (TFH) or under phase transfer conditions with t-BuOK[29] or NaOH[30] followed by reaction of the alkali salt of pyrrole, with an equivalent amount of acyl or alkyl halide (Scheme 1(a)). The above reactions, due to the use of basic conditions, the reactivity of pyrrole and activation effects have synthetic limitations, low yields due to the formation of undesirable side products (2-substituted and disubstituted pyrroles)[26–28] and are unsuitable in the preparation of pyrroles containing base labile groups. Recently, we described a procedure to arylmethylene pyrroles based on the reduction of acylpyrroles with (BF_3.OEt_2)/$NaBH_4$ (Scheme 1(b))[31] and in a further paper[32] a high yield route to *N*-alkyl pyrroles using the Paal–Knorr method, involving the condensation of primary amines with 2,5-dimethoxytetrahydrofuran (DMT)[20,33,34] using acid-base organic solvent mixtures (Scheme 1(c)).

In an attempt to combine the thin film forming properties of pyrroles[25] with our interest in boronates[35,36] as receptors and sensors,[37,38] we now report strategies directed to the synthesis of 1-(4-boronobenzyl)-*1H*-pyrrole (**10**).

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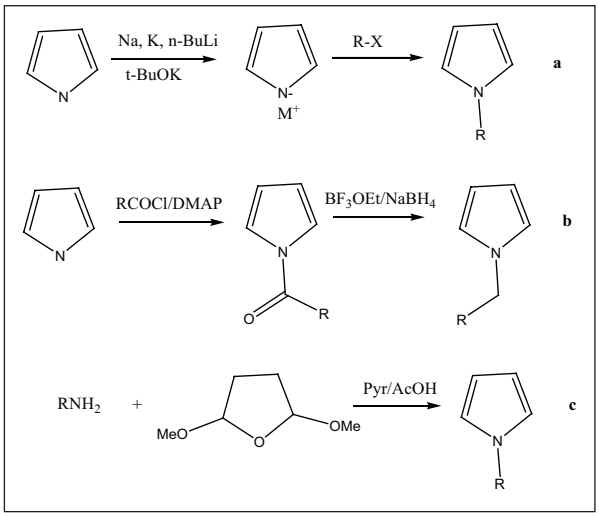
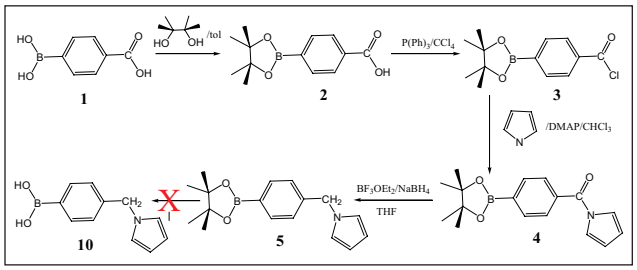


Scheme 1. Synthetic routes to *N*-alkyl pyrroles.
DMAP: dimethyaminopyridine; n-BuLi: n butyllithium; t-BuOK: potassium tert-butoxide; NaBH4: sodium borohydride; BF_3OEt: boron trifluoride diethyl etherate pyr-pyridine; AcOH: acetic acid.

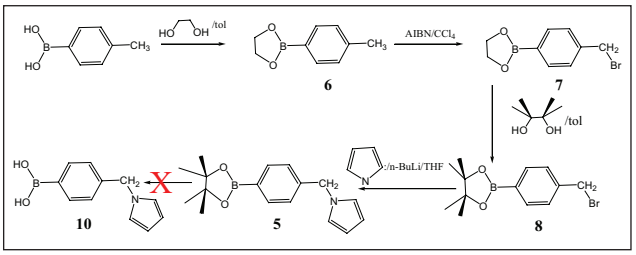


Scheme 2. A synthetic pathway to **10** via the reduction of acyl pyrrole.

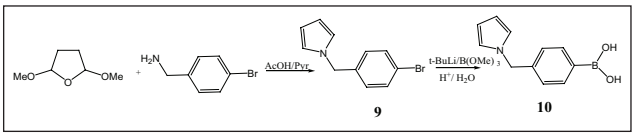
Results and discussion

The synthesis of pyrrole/boronate compounds is problematic due to the sensitivity of the pyrrole group to undergo oxidation under acidic conditions leading to uncontrolled polymerisation and decomposition[39] and the aqueous solubility of the boronate group which may necessitate its protection, to facilitate isolation and characterisation.

Our strategy to the synthesis of 1-(4-boronobenzyl)-*1H*-pyrrole (**10**) is outlined in Scheme 2, and involved the introduction of the boronate group early in the reaction, protected as a pinacol ester due to stability problems associated with the ethylene glycol group.[35] 4-Carboxybenzeneboronic acid (**1**) was converted to the pinacol ester in refluxing toluene (Dean–Stark apparatus) in quantitative yields to give the cyclic boronate ester **2** in high yield (98%). The attempted conversion of the pinacol protected acid **2**, to the acid chloride **(3)** using thionyl chloride or oxalyl chloride failed to yield the desired product due to the stability of the pinacol protecting group. The milder procedure of Lee[40] using triphenylphosphine/carbon tetrachloride yielded the crude acid chloride **3** on solvent evaporation as a mixture contaminated with the pinacol protected acid **2** and triphenylphosphine. Due to the moisture sensitivity of **3**, the compound was used as isolated and reacted with pyrrole, using dimethylaminopyridine (DMAP) as an acylation catalyst to yield the *N*-acylpyrrole **4**, in low yield (24%). The *N*-acylpyrrole **4** was successfully reduced to 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) benzyl)-*1H*-pyrrole (**5)** using $BF_3/OEt_2/NaBH_4$.[31] Cleavage of the cyclic boronate ester **5** was attempted using 4M HCl, RT, 18 h,[35] BBr_3/CH_2Cl_2[41] and MeOH/TsOH/reflux, but all methods failed to yield the desired product **10**, due to decomposition of the pyrrole group. Milder methods $SiO_2/CH_2Cl_2/(COOH)_2$,[42] basic hydrolysis (dioxane/NaOH(aq)) and oxidative cleavage ($NaIO_4/Me_2CO$/aq. NH_4OAc)[43] also failed to yield **10**.



Scheme 3. A synthetic pathway to **10** via the alkylation of the lithium salt of pyrrole.



Scheme 4. Synthesis of 1-(4-boronobenzyl)-*1H*-pyrrole (**10**).

In a parallel approach, the preparation 1-(4-boronobenzyl)-*1H*-pyrrole (**10)** was investigated as shown in Scheme 3. 4-Methylbenzeneboronic acid was protected with ethylene glycol as the cyclic boronate ester **6** and isolated in good yield (83%). Bromination of **6** with *N*-bromosuccinimide (NBS) in the presence of azoisobutyronitrile (AIBN) in refluxing carbon tetrachloride afforded 2-(4-(bromomethyl)phenyl)-1,3,2-dioxaborolane (**7**), in high yield (90%). 2-(4-(Bromomethyl) phenyl)-1,3,2-dioxaborolane (**7)** was converted to the cyclic pinacol ester **8** in moderate yield (50.5%) by exchange with pinacol, in refluxing toluene. 2-(4-(Bromomethyl)phenyl)-4,4,5,5-tetramethyl-1,3,2- dioxaborolane (**8**) was converted to 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzyl)-*1H*-pyrrole (**5)** in moderate yield (34%), by alkylation of the lithium salt of pyrrole in dimethyl sulfoxide (DMSO), prepared with n-BuLi/THF. Cleavage of the cyclic boronate ester (**5:** Scheme 3) as in the case of (**5:** Scheme 2) failed to yield **10** using similar procedures.

The inability of the synthetic routes depicted in Schemes 2 and 3 to produce 1-(4-boronobenzyl)-*1H*-pyrrole (**10**) led to the investigation of an alternative approach to the product, in which the boronate group was introduced late in the reaction, as shown in Scheme 4. In this approach, 4-bromobenzylamine was condensed with DMT under neutral conditions in an aqueous mixture of AcOH/pyr to give 1-(4-bromobenzyl)-*1H*-pyrrole (**9**).[32] Lithiation of **9** with t-butyllithium, quenching with trimethylborate followed by acid hydrolysis finally yielded 1-(4-boronobenzyl)-*1H*-pyrrole (**10**) (52%) in moderate yield. Confirmation of the structure of (**10**) using mass spectroscopic techniques proved inconclusive as the molecular ion was not directly observed based on the technique used, due to the elimination of H_2O from the $–B(OH)_2$ group.[35] In EIMS, a distinct peak was observed at 182 for (M^+-H_2O+1)

and in negative ion ESMS peaks at 437 for ($2M^+ + Cl$) and 236 ($M^+ + Cl$). Definitive confirmation of the structure of compound **10** was finally achieved by its conversion to the pinacol ester **5** (69%) in high yield.

In conclusion, a variety of methods have been investigated to synthesise 1-(4-boronobenzyl)-*1H*-pyrrole (**10**). It is clear based on the results reported here that the introduction of the boronate group, late in the reaction, is the most effective method for the preparation of this compound (Scheme 4) due to the lack of an adequate method for the removal of the pinacol protecting group from **5** (Schemes 2 and 3). Review of the literature identified that the carbazole analogue of **10**, 4-((*9H*-carbazol-9-yl)methyl)phenylboronic acid[44] had been prepared from the corresponding carbazole analogue of **9**, 9-(4-bromobenzyl)-*9H*-carbazole using a similar procedure to Scheme 4, but n-butyllithium(n-BuLi) replaced t-butyllithium(t-BuLi).

Experimental section

Trimethylborate, tert-butyllithium (1.7M in pentane), n-butyllithium (1.6M in hexane), pinacol, DMAP, 4-bromobenzylamine.HCl, pyrrole, pyridine, DMSO, THF (Aldrich), 4-Carboxybenzeneboronic acid (Lancaster). Commercial reagents were used as received with the exception of pyrrole, pyridine and THF, which were redistilled the latter from sodium and benzophenone under nitrogen. Reactions on exclusion of air or water were performed in oven-dried glassware and under an argon or N_2 atmosphere. Analytical thin-layer chromatography was performed on Merck silica gel 60F254 aluminium backed thin-layer chromatography (TLC) plates and was visualised by fluorescence quenching under UV light or I_2 staining. Preparative thin-layer chromatography (PTLC) was performed on Analtech silica gel GF 2000 μm and was visualised by fluorescence quenching under UV light. Melting points were determined on an electrothermal apparatus and were reported uncorrected. 1H and 13C-NMR spectra were recorded at 270.05 and 67.80 MHz, respectively, on a Joel 270 MHz FT-NMR spectrometer using TMS as an internal standard. Mass spectra were recorded by B. Stein at the EPSRC Mass Spectrometry Service Centre, Swansea for EI and CI (NH_3) spectra, on a VG quarto II triple quadropole mass spectrometer and accurate mass liquid secondary ion mass spectrometry (LSIMS) measurements on a Finnigan MAT 900 XLT using a Cs^+ ions to ionise. Elemental analysis was performed at the Micro Analytical Service, Manchester Univ, UK. Distance calculations in optimised structures were undertaken using the Alchemy 2000 (Tripos) molecular modelling package.

4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)benzoic acid **(2)**

A mixture of 4-carboxybenzeneboronic acid (0.5 g; 3.0 mmol) and 2,3-dimethyl-2,3-butanediol (0.36 g; 3.0 mmol) was suspended in toluene (100 mL) and refluxed in a Dean–Stark apparatus until the theoretical amount of water was removed. The solution was then evaporated to yield on recrystallisation from CH_3CN a colourless solid. Yield 0.78 g (98%); m.p. 230 °C–232 °C (lit.[45] 228 °C–231 °C); 1H NMR (270 MHz, $CDCl_3$): δ 1.5 (s, 12H), 7.9 (d, 2H, J=8.1), 8.15 (d, 2H, J=8.1); 13 C NMR (67.8 MHz, $CDCl_3$): δ 25.1, 85.5, 129.4, 131.7, 135.0; LRMS (CIMS (NH_3)) *m/z* (%): 266 (($M+NH_4$)$^+$, 77), 162 (22), 144 (27), 136 (100), 126 (16); calcd for $C_{13}H_{17}O_4$ B: C, 62.87; H, 6.91; found: C, 63.06; H, 7.15.

4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)benzoyl chloride **(3)**

A mixture of 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoic acid (**2**) (2 g; 8.1 mmol), triphenylphosphine (2.1 g; 8.1 mmol), in CCl_4 (50 mL) were refluxed for 20 h, then cooled, filtered and evaporated to give crude 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoyl chloride as an oil: Yield 2.24 g.

4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)(1H-pyrrol-1-yl)methanone **(4)**

Prepared by the DMAP (0.099 g; 0.81 mmol) catalysed condensation of crude 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoyl chloride (**3**) (2.24 g; 8.4 mmol) with pyrrole (0.62 g; 9.26 mmol) in the presence of triethylamine (TEA) (1.3 mL; 9.1 mmol)/CH_2Cl_2 (6 mL) overnight, according to the general procedure described by D'Silva and Iqbal.[31] After work up, the crude product was purified by PTLC ($CHCl_3$ /pet ether (40–60); 1:1) to give a colourless solid. Yield 0.59 g (24%); m.p. 99 °C–102 °C; 1H NMR (270 MHz, $CDCl_3$): δ 1.5 (s, 12H), 6.45 (t, 2H, J=2.5), 7.35 (t, 2H, J=2.5), 7.8 (d, 2H, J=8.8), 8.05 (d, 2H, J=8.8); 13 C NMR (67.8 MHz, $CDCl_3$) δ 24.89, 29.69, 113.1, 121.2, 128.4, 134.7; LRMS (CIMS (NH_3)) *m/z* (%): 315 (($M+NH_4$)$^+$, 37), 298 (($M+H^+$), 43), 279 (10), 247 (18), 231 (18), 198 (10), 189 (86), 172 (100), 158 (18), 152 (15), 144 (94), 136 (21), 128 (24); calcd for $C_{17}H_{20}NO_3$ B: C, 68.65; H, 6.78, N, 4.71; found: C, 68.73; H, 6.88; N, 4.67.

4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)benzyl)-1H-pyrrole **(5:** *Scheme 2)*

4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)(*1H*-pyrrol-1-yl)methanone(**4**) (0.5 g; 1.7 mmol) was reduced to (**5a**) in THF (3 mL) using $NaBH_4$ (0.3 g) in the presence of BF_3: OEt_2 (2.3 g; 16.3 mmol) in a sealed pressure tube.[31] The crude product was obtained as an oil which was purified by PTLC (EtOAc/$CHCl_3$ /pet ether (40–60); 1:4:5) to give a colourless crystalline solid. Yield 0.11 g (24%); m.p. 123 °C–125 °C; 1H NMR (270 MHz, $CDCl_3$): δ 1.3 (s, 12H), 5.1 (s, 2H), 6.2 (t, 2H, J=2.1), 6.7 (t, 2H, J=2.1), 7.1 (d, 2H, J=7.8), 7.8 (d, 2H, J=7.8); 13 C NMR (67.8 MHz, $CDCl_3$): δ 24.6, 53.2, 83.6, 108.3, 121.0, 126.1, 135.0, 141.0; LRMS (EIMS) *m/z* (%) 283 ((M^+) 38), 217 (100), 182 (10), 135 (11), 117 (55), 91 (10); HRMS (EIMS) calcd for $C_{17}H_{22}NO_2$ B 283.1744, found: 283.1744; calcd for $C_{17}H_{22}NO_2$ B: C, 72.04; H, 7.83, N, 4.95; found: C, 72.14; H, 8.02; N, 5.04.

4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)benzyl)-1H-pyrrole **(5:** *Scheme 3)*

To a stirred solution of pyrrole (0.4 g; 5.93 mmol) dissolved in dry THF (3 mL), under nitrogen at 0 °C was added n-BuLi (3.37 mL; 5.39 mmol) and the solution stirred for

2 h. The solvent was then removed and a solution of 2-(4-(bromomethyl)phenyl)-1,3,2-dioxaborolane (1.6 g; 5.39 mmol) added dropwise and left stirring for 8 h at 65 °C. Water was then added and the solution extracted with Et_2O, dried $MgSO_4$ and evaporated to yield an oil which was purified 2× by PTLC ($CHCl_3$) to yield a solid (0.52 g; 34%). 1H NMR (270 MHz, $CDCl_3$) δ 1.3 (s, 12H), 5.1 (s, 2H), 6.2 (t, 2H, *J*=2.1), 6.7 (t, 2H, *J*=2.1), 7.1 (d, 2H, *J*=7.8), 7.75 (d, 2H, *J*=7.8); 13 C NMR (67.8 MHz, $CDCl_3$) δ 24.6, 53.2, 83.6, 108.3, 121.0, 126.1, 135.0, 141.0; LRMS (EIMS) *m/z* (%) 283 ((M^+) 54), 217 (100), 182 (22), 135 (18), 117 (94), 91 (15); HRMS (EIMS) calcd for $C_{17}H_{22}NO_2$ B: 283.1744; found: 283.1744.

2-p-Tolyl[1,3,2]dioxaborolane **(6)**

A mixture of 4-methylphenylboronic acid (5.1 g; 38.0 mmol) and ethylene glycol (2.36 g; 38.0 mmol) was suspended in toluene (100 mL) and refluxed in a Dean–Stark apparatus until the theoretical amount of water was azeotroped. The solution was then evaporated to recover a colourless solid (5.13 g; 83%). m.p. 61 °C–63 °C. Lit.[46] 59 °C–60 °C. 1H (270 MHz, $CDCl_3$) δ 2.4 (s, 3H), 4.4 (s, 4H), 7.3 (d, 2H, *J*=7.5), 7.75 (d, 2H, *J*=7.5); 13 C NMR (67.8 MHz, $CDCl_3$) δ 22.1, 65.5, 128.8, 135.0, 140.1; LRMS (EIMS) *m/z* (%) 162 (($M+$), 100), 132 (30), 117 (70), 105 (40), 91 (37); calcd for $C_9H_{11}O_2B$: C, 66.63; H, 6.84; found: C, 66.9; H, 7.17.

2-(4-(Bromomethyl)phenyl)-1,3,2-dioxaborolane **(7)**

A mixture of 2-p-tolyl[1,3,2]dioxaborolane (**6**) (3.15 g; 19.4 mmol), NBS (3.8 g; 21.4 mmol) and AIBN (0.067 g; 0.19 mmol) in CCl_4 (125 mL) was refluxed for 18 h. The solution was then cooled, filtered and evaporated to give a brown solid which was decolourised with $CHCl_3$\charcoal to yield after hot filtration and evaporation a pale brown solid. Yield 4.21 g (90%); m.p. 142 °C–143 °C (lit[47] 84 °C–85 °C); 1H NMR (270 MHz, $CDCl_3$) δ 4.15 (s, 4H), 4.3 (s, 2H), 7.2 (d, 2H, *J*=7.9), 7.65 (d, 2H, *J*=7.9); 13 C NMR (67.8 MHz, $CDCl_3$) δ 33.1, 66.0, 128.3, 135.2, 140.8; LRMS (EIMS) *m/z* (%) 240 ((M^+), 2), 239 ((M^+-H)$^+$), 3), 161 (100), 117 (24), 105 (10), 91 (12), 86 (16); calcd for $C_9H_{10}O_2$ BBr: C, 44.9; H, 4.2; found: C, 44.73; H, 4.09.

2-(4-(Bromomethyl)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane **(8)**

A mixture of 2-(4-(bromomethyl)phenyl)-1,3,2-dioxaborolane (**7**) (1.94 g; 16.0 mmol) and pinacol (1.94 g; 16.0 mmol) was suspended in toluene (100 mL) and refluxed in a Dean–Stark apparatus for 20 h. The solution was then evaporated to recover a brown solid. Yield 2.4 g (51%); m.p. 71 °C–75 °C. Lit[48] 85 °C–89 °C. An analytical sample was prepared by decolourisation of the compound with charcoal in $CHCl_3$. 1H NMR (270 MHz, $CDCl_3$) δ 1.35 (s, 12H), 4.45 (s, 2H), 7.35 (d, 2H, *J*=8.1), 7.75 (d, 2H, *J*=8.1); 13 C NMR (67.8 MHz, $CDCl_3$) δ 24.8, 33.3, 76.5, 83.88, 128.3, 135.2, 140.6; LRMS (EIMS) *m/z* (%) 432 ((2 x M^+-2Br), 100), 333(25), 296 (45), 281/283 (55), 247/248/249 (22), 232/233 (62); HRMS (EIMS) calcd for $C_{13}H_{18}O_2$ BBr 296.0583; found: 296.0583; calcd for $C_{13}H_{18}O_2BBr$: C, 52.69; H, 6.13; found: C, 52.79; H, 6.22.

1-(4-Bromobenzyl)-1H-pyrrole **(9)**

Prepared by acid-base catalysed condensation of 4-bromobenzylamine.HCl (3 g; 16.1 mmol) with DMT (2.1 mL; 16.2 mmol) in pyridine/AcOH/H_2O at 70 °C for 50 h as described by D'Silva and Walker.[32]

1-(4-Boronobenzyl)-1H-pyrrole **(10)**

To a stirred solution of 1-(4-bromobenzyl)-*1H*-pyrrole (**9**) (2.0 g; 9.0 mmol), dissolved in THF (8 mL) under argon at −60 °C was added dropwise t-BuLi (11.0 mL; 19 mmol). After 1 h at −60 °C, THF (6 mL) and trimethyl borate (10 mL; 88 mmol) were added to the dark brown solution and it allowed to reach room temperature overnight. Then HCl (2M) was added and the solution left stirring for 4 h followed by extraction with $CHCl_3$. The $CHCl_3$ layer was then washed with NaOH (2M). The NaOH layer was then acidified and the product extracted into the $CHCl_3$ layer, washed with water, dried $MgSO_4$ and evaporated to yield a brown oil which was purified by PTLC ($CHCl_3$/EtOH: 25:1) to give on storage an off-white solid. Yield 0.92 g (52%); m.p. 131 °C–133 °C; 1H NMR (270 MHz, $CDCl_3$) δ 5.05 (s, 2H), 6.1 (t, 2H, *J*=2.3), 6.6 (t, 2H, *J*=2.3), 7.1 (d, 2H, *J*=8.2), 8.05 (d, 2H, *J*=8.2); 13 C NMR (67.8 MHz, $CDCl_3$) δ 53.4, 108.8, 121.3, 126.6, 128.8, 136.1, 143.0; LRMS (EIMS) *m/z* 182 ((M^+ -H_3O), 5), 157 (50), 117 (28), 91 (100); LRMS (ESMS) *m/z* (%) 437 ($2M^+$+Cl), 50), 282 (40), 254 (10), 236 (M^++Cl, 50), 127 (100), 81 (82). Confirmation of the structure of the compound was achieved by converting (7) (0.2 g; 1.0 mmol) into 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzyl)-*1H*-pyrrole **(5a)** by reaction with pinacol (0.11 g; 1.0 mmol) with removal of water using a Dean–Stark apparatus and PTLC (CH_2Cl_2). The compound was obtained as a colourless solid. Yield (69%); m.p. 117 °C–121 °C; 123 °C–125 °C (**5a**); LRMS (EIMS) *m/z* (%) 283 ((M^+) 53), 217 (100), 182 (22), 135 (18), 117 (100), 91 (15); HRMS calcd for $C_{17}H_{22}NO_2$ B: 283.1744; found: 283.1744.

Acknowledgement

The author thanks Dr. Deborah A Walker for her contribution to this paper.

Declaration of conflicting interests

The author(s) declared no potential conflicts of interest with respect to the research, authorship and/or publication of this article.

Funding

The author(s) disclosed receipt of the following financial support for the research, authorship and/or publication of this article: Financial support from EPSRC under Grant GR/F 20937 is gratefully acknowledged, and Dr. Ballantine and B. Stein of the EPSRC MS Service Centre, Swansea, for EI/CI, FAB and ESIMS measurements.

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Supplemental material

The 1H, 13C NMR, and microanalysis are available online.

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