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Polymerisation resistant synthesis of methacrylamido phenylboronic acids

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ABSTRACT

Acrylamido boronic acids are important building blocks for functional polymers but suffer from poor synthetic strategies and unwanted polymerisation. A two-step deprotection of pinacolato methacrylamido phenylene boronic esters to generate 2-, 3- and 4-methacrylamido phenylboronic acids in good yield and purity is reported. Boronic acid containing methacrylamido monomers are now available in good yields for incorporation into polymers.

1. Introduction

We are currently engaged in a program of research utilising boronic acids in polymer constructs [1], and wanted to rapidly access a range of phenylboronic acid methacrylamides, exemplified by **1a–c**, Fig. 1. Existing syntheses for this class of compound face a number of drawbacks: Boronic acid must be robustly protected (pinacol) since the usual syntheses employ reactions of anilines with acid chlorides. Deprotection often results in low purity compounds (contamination with diol) and is reliant on multiple extractions or chromatographic techniques on a case by case basis to isolate products. Whilst these compounds are often used for polymer/hydrogel synthesis unwanted polymerisation during their synthesis often significantly reduces yield [2–7]. Additionally, Qin et al. [8] and Cambre et al. [9] described routes to well-defined boronic acid polymers, albeit by deprotection of boronic ester polymers as apposed to the using deprotected monomers.

Yuen and Hutton have reported two hydrolyses of potassium trifluoroborates as expeditious routes to boronic acids [10], a strategy which has also been employed in the synthesis of novel saccharide sensors [11]. Treatment of potassium trifluoroborate salts with either TMS-Cl or $LiOH_{(aq)}$ resulted in hydrolysis to the respective boronic acids in high yield. Whilst no acrylamido boronic acids were prepared carbamates were readily generated incorporated by their TMS-Cl route.

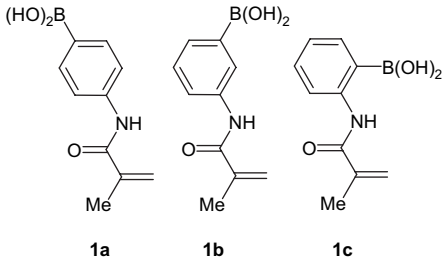

Fig. 1. *Para*, *meta* and *ortho* methacrylamido phenylboronic acids **1a–c**.

The strategy of deprotecting a pinacolato boronic ester to its corresponding boronic acid *via* potassium boron trifluoride seemed attractive to us since high temperatures and acidic conditions could be avoided suggesting polymerisation would not detrimentally affect overall yield.

Therefore we set about the synthesis of **6a–c** to test the efficacy of this deprotection method with polymerisation sensitive substrates. Other than pinacol protection, reactions of *ortho* boronates were a little lower yielding than *meta* and *para*, Scheme 1.

Particularly of interest to us are the sensing opportunities offered by the *ortho* interaction possible in **1c** (Fig. 2); the resultant modification of boron's Lewis acidity and ligand exchange rates by this "*ortho effect*" [2,12–15] makes the *ortho* acrylamido boronic

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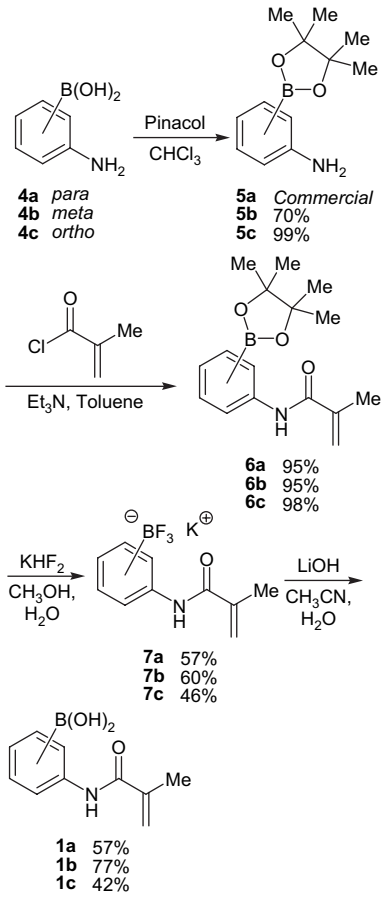

Scheme 1. Synthesis of 4-, 3- and 2-methacrylamido phenylboronic acids, **1a–c**.

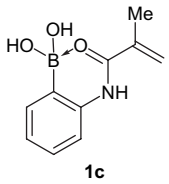

Fig. 2. Six-membered rings formed by *ortho* methacrylamide **1c**.

acid **1c** as the most useful in terms of carbohydrate sensing [16–18]. It is noteworthy that the synthesis of such compounds *via* direct hydrolysis of diol protected boronic esters is extremely low yielding and impractical for accessing these and related compounds in useful yields.

Pinacol protected **6a–c** were easily converted to their corresponding trifluoroborates (**7a–c**) by treatment with KHF_2 in methanol/water. In our hands subsequent treatment of **7b** with TMS-Cl failed to give easily isolable acrylamido boronic acids, and was not investigated further. Lithium hydroxide in acetonitrile/water, on the other hand, quantitatively converted trifluoroborates **7a–c** to the corresponding boronic acids [19].

Isolated yields are below 80% for this two-step deprotection of methacrylamido boronic esters to the corresponding boronic acids but it represents a great improvement over other general methods, further exploitation in synthetic and polymer chemistry of these versatile monomers can now be achieved.

2. Conclusions

We have demonstrated efficient general monomer syntheses of methacrylamido phenylboronic acids, exemplified by **1a–c**, in three or four steps from commercially available starting materials without concomitant polymer formation.

The versatile nature of this deprotection strategy initially reported by Yuen and Hutton [10] for non-polymerisable substrates is ideally suited to acrylamide preparation. These monomers will be used by us in the preparation of functional polymers for carbohydrate recognition.

3. Experimental

3.1. General procedure 1 pinacol protection (*5b* and *5c*)

Aminophenylboronic acids (**4b** and **c**) and pinacol (1 equiv) were suspended in chloroform (0.2 M) and stirred at room temperature for 8 h (ensuring complete dissolution), the generated water and chloroform solvent are strongly immiscible as such droplets of water can be observed at the end of the reaction [20,21]. Solvent was evaporated, the resulting residues could be purified by column chromatography [SiO_2, toluene (neat) to toluene:ethyl acetate (9:1)] if required, and evaporated to dryness to give crystalline solids.

3.2. General procedure 2 amide preparation (*6a–c*)

Aminophenyl boronic esters (**5a–c**) were stirred at 0 °C in toluene or dichloromethane (0.03 M) with triethylamine (1 equiv) under an atmosphere of dry nitrogen. Solutions of methacryloyl chloride (0.9 M in toluene, 1 equiv) were added slowly (0.2 mL/min). The mixtures were stirred at 0 °C for a further 20 min and then allowed to warm to room temperature. The reaction mixtures were washed with water, dried over magnesium sulphate, filtered and dried *in vacuo*, to give white solids (**6a–c**).

3.3. General procedure 3 potassium trifluoroborate derivative preparation (*7a–c*)

In plastic apparatus methacrylamido phenyl boronic esters (**6a–c**) were stirred at room temperature in a 1:1 mixture of methanol and water (0.05 M). KHF_2 (6 equiv) was added in one portion and the slurries were stirred overnight at room temperature. The slurry solutions were evaporated to dryness (<30 °C), redissolved in hot acetone and filtered. The filtrate was evaporated *in vacuo*; the residue was triturated with ether for three times. The solid was then redissolved in acetone, filtered and dried *in vacuo*, to give white solids (**7a–c**).

3.4. General procedure 4 boronic acid preparation (*1a–c*)

Methacrylamido phenyl trifluoroborates (**7a–c**) were stirred at room temperature in a 2:1 mixture of acetonitrile and water (0.05 M). $LiOH \cdot H_2O$ (8 equiv) was added in one portion and the mixtures were stirred overnight at room temperature. To the solutions equal volumes of saturated ammonium hydrochloride (30 mL/mmol **7a–c**) and 1 N hydrochloric acid (8 mL/mmol **7a–c**) were added. The solution was extracted four times with ethyl acetate (4 × 40 mL/mmol **7a–c**); the combined organic extracts were dried over sodium sulphate, filtered, evaporated and dried *in vacuo*, to give white solids (**1a–c**).

3.5. 3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)benzenamine *5b* [5]

IR (ν, neat, cm^{-1}) 3466, 3377, 2991, 1629, 1579, 1444, 1360, 1141, 851 and 706. ^1H NMR (δ; 300 MHz; $CDCl_3$) 1.30 (12H, s, Pin CH_3), 6.80 (1H, ddd, $J = 7.5$, 2.7 and 1.5, Ar C*H*), 7.15 (1H, d, $J = 2.7$, Ar C*H*), 7.19 (1H, d, $J = 7.5$, Ar C*H*), 7.23 (1H, td, $J = 7.5$, 1.5, Ar C*H*). $^{13}C\{^1H\}$

NMR (δ; 75 MHz; $CDCl_3$) 25.3 (Pin CH_3), 84.1 (Pin Cq), 118.5 (Ar CH), 121.6 (Ar CH), 125.5 (Ar CH), 129.1 (Ar CH), 146.0 (Ar C–N), (C–B not detected). $^{11}B\{^1H\}$ NMR (δ; 96 MHz; $CDCl_3$) 31.4 (bs). MS (ESI, positive, CH_3OH) found m/z 220.1527, $C_{12}H_{18}{}^{11}BNO_2$ requires m/z 220.15088.

3.6. 2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)benzenamine **5c** [6]

IR (ν, neat, cm^{-1}) 3488, 3384, 2994, 1606, 1457, 1354, 1137, 1088, 760 and 656. ^1H NMR (δ; 300 MHz; $CDCl_3$) 1.3 (12H, s, Pin C*H*$_3$), 6.53 (1H, d, $J = 8.1$, Ar C*H*), 6.61 (1H, td, $J = 7.5$ and 0.9 Ar C*H*), 7.2 (1H, m, Ar C*H*), 7.5 (1H, dd, $J = 7.5$ and 1.8, Ar C*H*). $^{13}C\{^1H\}$ NMR (δ; 75 MHz; $CDCl_3$) 25.3 (Pin CH_3), 83.9 (Pin Cq), 115.3 (Ar CH), 117.4 (Ar CH), 133.1 (Ar CH), 137.2 (Ar CH), 153.8 (Ar C–N), (C–B not detected). $^{11}B\{^1H\}$ NMR (δ; 96 MHz; $CDCl_3$) 31.3 (bs). MS (ESI, positive, CH_3OH) found m/z 220.1509, $C_{12}H_{18}{}^{11}BNO_2$ requires m/z 220.15088.

3.7. N-(4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)methacrylamide **6a**

IR (ν, neat, cm^{-1}) 3315, 2979, 1668, 1607, 1523, 1399, 1361, 1144, 1090, 860 and 655. ^1H NMR (δ; 300 MHz; $CDCl_3$) 1.30 (12H, s, Pin C*H*$_3$), 2.05 (3H, s, methacryl C*H*$_3$), 5.41 (1H, dd, $J = 0.9$ and 0.6, methacryl C=C*H*), 5.73 (1H, dd, $J = 0.9$, 0.6, methacryl C=C*H*), 7.52 (2H, d, $J = 8.5$, Ar C*H*), 7.72 (2H, d, $J = 8.5$, Ar C*H*). $^{13}C\{^1H\}$ NMR (δ; 75 MHz; $CDCl_3$) 19.2 (methacryl CH_3), 25.3 (Pin CH_3), 84.2 (Pin Cq), 119.1 (2 Ar CH), 120.4 (methacryl CH_2), 136.2 (2 Ar CH), 140.8 (Ar C–N), 141.3 (methacryl Cq), 166.8 (amide Cq) (C–B not detected). $^{11}B\{^1H\}$ NMR (δ; 96 MHz; $CDCl_3$) 31.1 (bs). MS (ESI, positive, CH_3OH) found m/z 288.1760, $C_{16}H_{23}{}^{11}BNO_3$ requires m/z 288.1771; found m/z 310.1585, $C_{16}H_{22}{}^{11}BNO_3Na$ requires m/z 310.1590. MS (ESI, negative, CH_3OH) found m/z 286.1603, $C_{16}H_{21}{}^{11}BNO_3$ requires m/z 286.1614.

3.8. N-(3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)methacrylamide **6b**

IR (ν, neat, cm^{-1}) 3314, 2978, 1663, 1626, 1540, 1426, 1358, 1143 and 706. ^1H NMR (δ; 300 MHz; $CDCl_3$) 1.30 (12H, s, Pin C*H*$_3$), 2.05 (3H, s, methacryl C*H*$_3$), 5.37 (1H, dd, $J = 0.9$ and 0.6, methacryl C=C*H*), 5.71 (1H, dd, $J = 0.9$ and 0.6, methacryl C=C*H*), 7.30 (1H, t, $J = 7.5$, Ar C*H*), 7.44 (1H, bs N*H*), 7.48 (1H, dt, $J = 7.5$ and 1.2, Ar C*H*), 7.59 (1H, d, $J = 2.1$, Ar C*H*), 7.93 (1H, ddd, $J = 8.1$, 2.4 and 1.2, Ar C*H*). $^{13}C\{^1H\}$ NMR (δ; 75 MHz; $CDCl_3$) 19.1 (methacryl CH_3), 25.3 (Pin CH_3), 84.4 (Pin Cq), 120.2 (methacryl CH_2), 123.5 (Ar CH), 126.2 (Ar CH), 129.1 (Ar CH), 131.1 (Ar CH), 137.7 (Ar C–N), 141.3 (methacryl Cq), 166.8 (amide Cq) (C–B not detected). $^{11}B\{^1H\}$ NMR (δ; 96 MHz; $CDCl_3$) 31.3 (bs). MS (ESI, positive, CH_3OH) found m/z 288.1747, $C_{16}H_{23}{}^{11}BNO_3$ requires m/z 288.1771; found m/z 310.1563, $C_{16}H_{22}{}^{11}BNO_3Na$ requires m/z 310.1590. MS (ESI, negative, CH_3OH) found m/z 286.1612, $C_{16}H_{21}{}^{11}BNO_3$ requires m/z 286.1614.

3.9. N-(2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)methacrylamide **6c**

IR (ν, neat, cm^{-1}) 3343, 2969, 1627, 1548, 1479, 1158, 1021 and 757. ^1H NMR (δ; 300 MHz; $CDCl_3$) 1.30 (12H, s, Pin C*H*$_3$), 2.05 (3H, s, methacryl C*H*$_3$), 5.41 (1H, m, $J = 0.9$, methacryl C=C*H*), 5.90 (1H, m, $J = 0.9$, methacryl C=C*H*), 7.01 (1H, td, $J = 7.5$ and 0.9, Ar C*H*), 7.41 (1H, td, $J = 7.5$ and 1.5, Ar C*H*), 7.71 (1H, dd, $J = 7.5$ and 1.5, Ar C*H*), 8.54 (1H, d, $J = 8.4$, Ar C*H*), 9.8 (1H, bs, N*H*). $^{13}C\{^1H\}$ NMR (δ; 75 MHz; $CDCl_3$) 19.1 (methacryl C*H*$_3$), 25.3 (Pin C*H*$_3$), 84.8 (Pin Cq), 119.6 (Ar C*H*), 120.7 (methacryl CI_2), 123.4 (Ar C*H*), 133.4 (Ar C*H*), 136.7 (Ar C*H*), 141.3 (methacryl Cq), 145.1 (Ar CN), 166.6 (amide Cq) (C–B not detected). $^{11}B\{^1H\}$ NMR (δ; 96 MHz; $CDCl_3$) 30.8 (bs). MS (ESI, positive, CH_3OH) found m/z 288.1762, $C_{16}H_{23}{}^{11}BNO_3$ requires m/z 288.1771; found m/z 310.1583, $C_{16}H_{22}{}^{11}BNO_3Na$ requires m/z 310.1590. MS (ESI, negative, CH_3OH) found m/z 286.1600, $C_{16}H_{21}{}^{11}BNO_3$ requires m/z 286.1614.

3.10. Potassium trifluoro(4-methacrylamido phenyl)borate **7a**

IR (ν, KBr, cm^{-1}) 3468, 2925, 2421, 1654, 1618, 1521, 1441, 1390, 1241, 982, 924 and 828. ^1H NMR (δ; 300 MHz; CD_3OD) 2.05 (3H, s, methacryl C*H*$_3$), 3.30 (2H, s, *H*$_2$O), 5.46 (1H, m, $J = 0.9$, methacryl C=C*H*), 5.77 (1H, m, $J = 0.9$, methacryl C=C*H*), 7.38 (2H, d, $J = 8.0$, Ar C*H*), 7.48 (2H, d, $J = 8.0$, Ar C*H*). $^{13}C\{^1H\}$ NMR (δ; 75 MHz; CD_3OD) 19.4 (methacryl CH_3), 120.6 (methacryl CH_2), 121.5 (2 Ar CH), 133.2 (2 Ar CH), 137.8 (Ar C–N), 142.8 (methacryl Cq), 170.3 (amide Cq) (C–B not detected). $^{11}B\{^1H\}$ NMR (δ; 96.3 MHz; CD_3OD) 5.3 (bs). ^{19}F NMR (δ; 377 MHz, CD_3OD) −143.6 (s). MS (ESI, negative, CH_3OH) found m/z 228.0814, $C_{10}H_{10}{}^{11}BF_3NO$ requires m/z 228.0808; compound hydrolyses during analysis to the corresponding boronic acid, found m/z 204.0838, $C_{10}H_{11}{}^{11}BNO_3$ requires m/z 204.0832.

3.11. Potassium trifluoro(3-methacrylamido phenyl)borate **7b**

IR (ν, KBr, cm^{-1}) 3644, 3598, 3556, 3483, 2412, 1648, 1623, 1587, 1488, 1459, 1420, 1291, 1231, 1162, 945 and 800. ^1H NMR (δ; 300 MHz; CD_3OD) 2.05 (3H, s, methacryl C*H*$_3$), 3.30 (2H, s, H_2O), 5.46 (1H, m, $J = 0.9$, methacryl C=C*H*), 5.78 (1H, m, $J = 0.9$, methacryl C=C*H*), 7.18 (1H, dd, $J = 8.0$ and 7.2, Ar C*H*), 7.31 (1H, d, $J = 7.2$, Ar C*H*), 7.44 (1H, dd, $J = 8.0$ and 1.2, Ar C*H*), 7.54 (1H, d, $J = 1.2$, Ar C*H*). $^{13}C\{^1H\}$ NMR (δ; 75 MHz; CD_3OD) 19.4 (methacryl CH_3), 120.6 (methacryl CH_2), 121.2 (Ar CH), 126.2 (Ar CH), 128.6 (Ar CH), 129.6 (Ar CH), 138.3 (Ar C–N), 142.7 (methacryl Cq), 170.4 (amide Cq) (C–B not detected). $^{11}B\{^1H\}$ NMR (δ; 96 MHz; CD_3OD) 4.9 (bs). ^{19}F NMR (δ; 377 MHz, CD_3OD) −143.7 (s). MS (ESI, negative, CH_3OH) found m/z 228.0802, $C_{10}H_{10}{}^{11}BF_3NO$ requires m/z 228.0808.

3.12. Potassium trifluoro(2-methacrylamido phenyl)borate **7c**

IR (ν, KBr, cm^{-1}) 3431, 1668, 1627, 1611, 1580, 1544, 1442, 1184, 950, 758, 741 and 483. ^1H NMR (δ; 300 MHz; CD_3OD) 2.05 (3H, s, methacryl C*H*$_3$), 3.30 (2H, s, *H*$_2$O), 5.90 (1H, m, methacryl C=C*H*), 6.30 (1H, m, methacryl C=C*H*), 7.40 (3H, m, Ar C*H*), 7.60 (1H, m, Ar C*H*). $^{13}C\{^1H\}$ NMR (δ; 75 MHz; $CDCl_3$) 18.2 (methacryl CH_3), 118.3 (methacryl CH_2), 128.7 (Ar CH), 129.9 (Ar CH), 132.7 (Ar CH), 136.9 (Ar CH), (Ar C–N, methacryl Cq, amide Cq, C–B not detected). $^{11}B\{^1H\}$ NMR (δ; 96 MHz; CD_3OD) 4.0 (bs). ^{19}F NMR (δ; 377 MHz, CD_3OD) −139.9 (s, maj) −133.4, −138.9, −148.9, −151.0 (min). MS (ESI, negative, CH_3OH) found m/z 228.0803, $C_{10}H_{10}{}^{11}BF_3NO$ requires m/z 228.0808.

3.13. 4-Methacrylamido phenylboronic acid **1a** [22]

IR (ν, KBr, cm^{-1}) 3359, 2569, 2474, 1652, 1623, 1606, 1524, 1509, 1434, 1399, 1368, 1113, 999 and 832. ^1H NMR (δ; 300 MHz; CD_3OD) 2.05 (3H, s, methacryl C*H*$_3$), 5.51 (1H, s, methacryl C=C*H*), 5.79 (1H, s, methacryl C=C*H*), 7.57 (2H, d, $J = 8.1$, Ar C*H*), 7.78 (2H, d, $J = 8.1$, Ar C*H*). $^{13}C\{^1H\}$ NMR (δ; 75 MHz; $CDCl_3$) 18.0 (methacryl CH_3), 120.0 (2 Ar CH), 120.1 (methacryl CH_2), 134.7 (2 Ar CH), 140.5 (Ar C–N), 141.1 (methacryl Cq), 169.2 (amide Cq) (C–B not detected). $^{11}B\{^1H\}$ NMR (δ; 96 MHz; CD_3OD) 28.7 (bs). MS (ESI, negative, CH_3OH) found m/z 204.0822, $C_{10}H_{11}{}^{11}BNO_3$ requires m/z 204.0832.

3.14. 3-Methacrylamido phenylboronic acid **1b** [4]

IR (ν, KBr, cm^{-1}) 3436, 2361, 1626, 1552, 1480, 1446, 1357, 1219, 1117, 993 and 763. ^1H NMR (δ; 300 MHz; CD_3OD) 2.05 (3H, s, methacryl C*H*$_3$), 5.38 (1H, m, $J = 0.9$, methacryl C=C*H*), 5.69 (1H, m,

$J = 0.9$, methacryl C=C*H*), 7.20 (1H, m, Ar C*H*), 7.41 (1H, m, Ar C*H*), 7.60 (1H, m, Ar C*H*), 7.74 (1H, bs, Ar C*H*). $^{13}C\{^1H\}$ NMR (δ; 75 MHz; CD_3OD) 19.4 (methacryl CH_3), 121.1 (methacryl CH_2), 121.2 (Ar CH), 128.3 (Ar CH), 129.9 (Ar CH), 139.2 (Ar C–N), 142.6 (methacryl Cq), 170.4 (amide Cq) (C–B not detected). $^{11}B\{^1H\}$ NMR (δ; 96 MHz; CD_3OD) 29.9 (bs). MS (ESI, negative, CH_3OH) found m/z 204.0819, $C_{10}H_{11}{}^{11}BNO_3$ requires m/z 204.0832.

3.15. 2-Methacrylamido phenylboronic acid **1c**

IR (ν, KBr, cm^{-1}) 3313, 2473, 1654, 1621, 1541, 1432, 1390, 1033, 800 and 699. ^1H NMR (δ; 300 MHz; CD_3OD) 2.05 (3H, s, methacryl C*H*$_3$), 5.76 (1H, m, methacryl C=C*H*), 6.16 (1H, m, methacryl C=C*H*), 7.20 (3H, m, Ar C*H*), 7.40 (1H, m, Ar C*H*). $^{13}C\{^1H\}$ NMR (δ; 75.0 MHz; $CDCl_3$) 18.4 (methacryl C*H*$_3$), 118.2 (methacryl C*H*$_2$), 127.3 (Ar C*H*), 128.4 (Ar C*H*), 129.5 (Ar C*H*), 133.4 (Ar C*H*), 137.25 (Ar C–N), 139.3 (methacryl Cq), 169.1 (amide Cq) (C–B not detected). $^{11}B\{^1H\}$ NMR (δ; 96 MHz; CD_3OD) 7.2 (bs). MS (ESI, negative, CH_3OH) found m/z 204.0831, $C_{10}H_{11}{}^{11}BNO_3$ requires m/z 204.0832.

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