New Shelf-Stable Halo- and Alkoxy-Substituted Pyridylboronic Acids and their Suzuki Cross-Coupling Reactions to Yield Heteroarylpyridines

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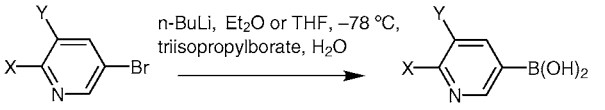
Abstract: New shelf-stable pyridylboronic acids have been synthesized: bromine–lithium exchange followed by reaction with triisopropylborate (TIPB) yielded 2-fluoro-5-pyridylboronic acid (**4**), 3-bromo-5-pyridylboronic acid (**5**) and 2-ethoxy-5-pyridylboronic acid (**6**); directed lithiation followed by reaction with trimethylborate (TMB) or TIPB afforded 2-methoxy-3-pyridylboronic acid (**8**), 3-bromo-6-methoxy-4-pyridylboronic acid (**11**) and 3-bromo-6-ethoxy-4-pyridylboronic acid (**12**). Cross-coupling of pyridylboronic acids **4**, **6**, **8**, and **11** with 3-bromoquinoline [Cs_2CO_3, $Pd(PPh_3)_2Cl_2$, 1,4-dioxane, 95 °C] gave pyridinylquinoline derivatives **13**, **15**–**17** in 50–77% yields: the analogous reaction of **5** was low yielding due to further in situ reactions of the product **14**. Cross-coupling of **12** with 2-bromo-5-nitrothiophene gave 3-bromo-4-(5-nitro-2-thienyl)-6-ethoxypyridine (**18**).

Key words: pyridine, boronic acids, cross-coupling, Suzuki reaction, heterobiaryl

In the context of biaryl and heterobiaryl synthesis, metal-mediated cross-coupling reactions continue to be of paramount importance.[1] Within this field the Suzuki–Miyaura protocol for palladium-catalyzed cross-coupling of aryl/heteroaryl boronic acids (or esters) with aryl/heteroaryl halides (or triflates) is particularly versatile.[2] Although the use of halopyridines as cross-coupling partners is widespread,[1a,3] far fewer reactions of pyridylboronic acids (or esters) have been reported.[3a,4] This is no doubt partly due to the difficulties in purification of the parent pyridylboronic acids[5] which are highly polar molecules and are water-soluble (especially 2-pyridylboronic acid which readily deboronates)[6] although a new and efficient synthesis of 3-pyridylboronic acid has been published.[7] 3-Pyridylboronic acid[8] and 4-pyridylboronic acid[9] have also been used as bifunctional ligands in the assembly of polynuclear metal complexes, coordinating through N and O atoms.

Recent attention has been directed towards functionalized pyridylboronic acids and esters, especially halogenated derivatives which are shelf-stable.[10–13] For example, 2-bromo- and 2-chloro-5-pyridylboronic acids have been synthesized independently by Rault et al.[10] and by ourselves.[11] We now report new halo- and alkoxy-pyridylboronic acids **4**–**6**, **8**, **11**, and **12**, and establish that they are suitable partners in Suzuki cross-coupling reactions. During the preparation of this manuscript, Rault et al. reported similar syntheses of **4**[10] and **5**[11] and used each of them in a cross-coupling reaction different from those reported herein.

Bromine–lithium exchange reactions on 2-fluoro-5-bromopyridine (**1**), 3,5-dibromopyridine (**2**) and 2-ethoxy-5-bromopyridine (**3**) were performed in diethyl ether or tetrahydrofuran at –78 °C using butyllithium, followed by reaction with TIPB and aqueous workup, to afford 2-fluoro-5-pyridylboronic acid (**4**) (51% yield), 3-bromo-5-pyridylboronic acid (**5**) (74% yield) and 2-ethoxy-5-pyridylboronic acid (**6**) (61% yield) (Scheme 1).



1 X = F; Y = H
2 X = H; Y = Br
3 X = OEt; Y = H

4 X = F; Y = H (51%)
5 X = H; Y = Br (74%)
6 X = OEt; Y = H (61%)

Scheme 1

An alternative strategy involving directed metallation[14] was applied for the synthesis of pyridylboronic acid derivatives **8**, **11**, and **12**. Thus, reaction of 2-methoxypyridine **7** with LDA in THF at 0 °C[15] followed by addition of trimethylborate (TMB) and aqueous workup gave 2-methoxy-3-pyridylboronic acid (**8**) (13% yield) (Scheme 2). Numerous attempts to improve the yield of **8** using the same protocol at –78 °C with lithiation in the presence of TMB, or with prior addition of TMB, were unsuccessful. 2-Methoxy- and 2-ethoxy-5-bromopyridine (**9** and **10**), respectively, were lithiated at C(4) by reaction with LDA in THF at –78 °C,[16] and then treated with triisopropylborate (TIPB) to afford 3-bromo-6-methoxy-4-pyridylboronic acid (**11**) (39% yield) and 3-bromo-6-ethoxy-4-pyridylboronic acid (**12**) (23% yield) respectively (Scheme 3). All the boronic acids **4**–**6**, **8**, **11**, and **12** were isolated as shelf-stable solids after straightforward workup procedures.[17]

To confirm their suitability as partners in cross-coupling reactions, pyridylboronic acids **4**–**6**, **8**, and **11** were each treated with 3-bromoquinoline using caesium carbonate as base and bis(triphenylphosphino)palladium dichloride as catalyst in 1,4-dioxane at 95 °C to give the correspond-

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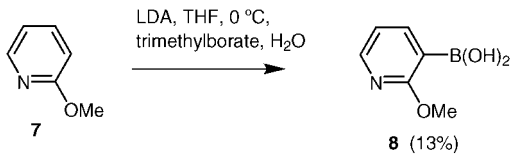
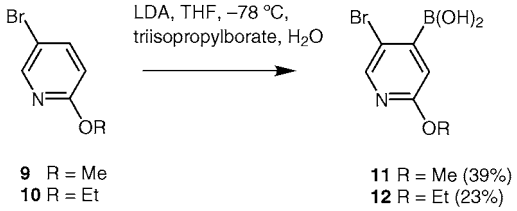
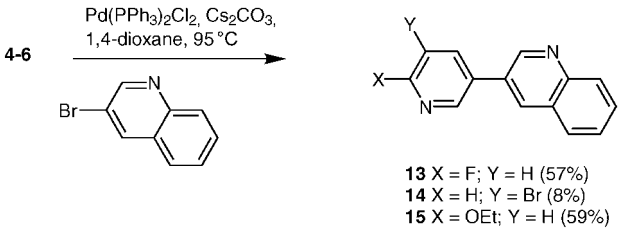


Scheme 2

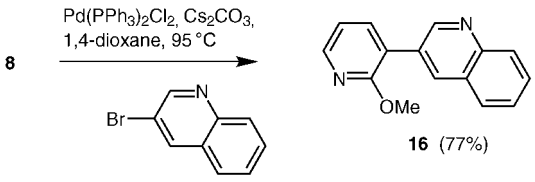


Scheme 3

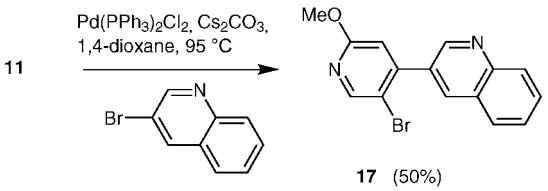
ing pyridinylquinoline products (Schemes 4–6). Compounds **13** and **15**–**17** were isolated in synthetically useful yields (50–77%); the low yield (8%) of product **14** obtained from the boronic acid **5** is due to the formation of numerous other products (TLC evidence) which probably arise from further couplings of the reactive bromine substituent of **14**. No such couplings were observed with **17** and **18**, presumably due to the steric effect of the heterocyclic substituent adjacent to the bromine.



Scheme 4

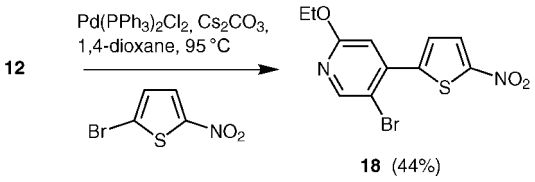


Scheme 5



Scheme 6

To establish the scope for using alternative heteroarylbromides in the coupling reactions, boronic acid **12** was treated with 2-bromo-5-nitrothiophene under the same conditions to give product **18** (44% yield) (Scheme 7).



Scheme 7

In summary, this paper describes new shelf-stable pyridylboronic acid derivatives which should prove to be versatile as bifunctional ligands for metal complexation,[8,9] and reagents for the synthesis of arylpyridine and heteroarylpyridine systems of importance as pharmaceutical and agrochemical compounds[1] and optoelectronic materials.[3c,18] The bromo and/or alkoxy substituents on the pyridine ring of products **15**–**18** offer scope for further synthetic transformations.

2-Fluoro-5-pyridylboronic Acid (4)

To a solution of 2-fluoro-5-bromopyridine (**1**) (599 mg, 3.4 mmol) and TIPB (1.3 g, 6.9 mmol) in anhyd THF (10 mL) at –78 °C was added *n*-BuLi (1.6 M in hexane, 2.2 mL, 3.5 mmol) dropwise. The reaction mixture was stirred for 4 h at –78 °C then quenched with H_2O (10 mL) and allowed to warm to 20 °C with stirring overnight. The solvent was evaporated in vacuo and the aqueous layer was taken to pH 10 with 5% NaOH and was then washed with Et_2O. The aqueous layer was then acidified to pH 4 with 48% aq HBr to precipitate compound **4** as a white solid (245 mg, 51%); mp 170–171 °C (lit.[8] 172 °C).

^{1}H NMR [$(CD_3)_2C(O)$–TMS]: δ = 8.52 (d, 1 H, *J* = 2.0 Hz), 8.41 (s, 2 H, OH), 8.25 (m, 1 H), 7.13 (m, 1 H).

^{13}C NMR [$(CD_3)_2C(O)$–TMS]: δ = 166.39, 164.49, 154.08, 153.97, 147.54, 147.48, 108.91, 108.62.

Anal. Calcd for $C_5H_5BFNO_2$ (140.9): C, 42.62; H, 3.58; N, 9.94. Found: C, 42.32; H, 3.57; N, 9.81.

3-Bromo-5-pyridylboronic Acid (5)

To a solution of 3,5-dibromopyridine (**2**) (2.0 g, 8.4 mmol) in anhyd Et_2O (30 mL) at –78 °C was added *n*-BuLi (1.6 M in hexane, 6.0 mL, 10.0 mmol) dropwise. The reaction mixture was stirred for 2 h at –78 °C. TIPB (3.3 g, 17.3 mmol) was then added quickly. The reaction mixture was stirred for 2 h at –78 °C, allowed to warm to 20 °C and quenched with H_2O (50 mL). After stirring overnight, work-up as described for **4** gave **5** as a hygroscopic white solid (1.3 g, 74%); mp >300 C (lit.[9] 210 °C, dec.).

^{1}H NMR [$(CD_3)_2S(O)$–TMS]: δ = 8.80 (d, 1 H, *J* = 1.4 Hz), 8.68 (d, 1 H, *J* = 2.4 Hz), 8.56 (s, 2 H, OH), 8.24 (m, 1 H).

^{13}C NMR [$(CD_3)_2S(O)$–TMS]: δ = 153.76, 152.15, 144.79, 121.38.

Anal. Calcd for $C_5H_5BBrNO_2$ (201.8): C, 29.76; H, 2.50; N, 6.49. Found: C, 29.48; H, 1.75; N, 6.77.

2-Ethoxy-5-pyridylboronic Acid (6)

Following the procedure used for compound **5**, 2-ethoxy-5-bromopyridine (**3**) (200 mg, 1.0 mmol), Et_2O (5 mL), *n*-BuLi (1.6 M in hexane, 0.6 mL, 1.0 mmol) and TIPB (375 mg, 2.0 mmol) gave **6** as a white solid (101 mg, 61%); mp 131–134 °C.

^{1}H NMR [$(CD_3)_2C(O)$–TMS]: δ = 8.59 (d, 1 H, *J* = 1.8 Hz), 8.03 (dd, 1 H, *J* = 2.1, 1.8 Hz), 7.18 (s, 2 H, OH), 6.69 (d, 1 H, *J* = 8.1 Hz), 4.35 (q, 2 H, *J* = 4.2 Hz), 1.33 (t, 3 H, *J* = 5.1 Hz).

^{13}C NMR [$(CD_3)_2C(O)$–TMS]: δ = 165.56, 153.79, 144.38, 110.16, 61.25, 14.27.

Anal. Calcd for $C_7H_{10}BFNO_2$ (167.0): C, 50.35; H, 6.04; N, 8.39. Found: C, 50.09; H, 6.10; N, 8.26.

2-Methoxy-3-pyridylboronic Acid (8)

To a solution of 2-methoxypyridine (**7**) (1.2 mL, 11.4 mmol) in anhyd THF (10 mL) at 0 °C was added LDA (2.0 M in heptane–THF–ethylbenzene, 6.9 mL, 13.8 mmol) dropwise. The reaction mixture was stirred for 3 h at –78 °C, then TMB (2.4 g, 23.2 mmol) was added dropwise. The mixture was allowed to warm to 20 °C, quenched with H_2O (10 mL) and stirred overnight. Workup as for compound **4** gave **8** as a white solid (235 mg, 13%); mp 143–145 °C.

^{1}H NMR [$(CD_3)_2C(O)$–TMS]: δ = 8.24 (dd, 1 H, *J* = 2.1, 2.1 Hz), 8.12 (dd, 1 H, *J* = 2.1, 1.8 Hz), 7.10 (s, 2 H, OH), 7.00 (m, 1 H), 3.99 (s, 3 H).

^{13}C NMR [$(CD_3)_2C(O)$–TMS]: δ = 168.26, 150.09, 146.70, 118.08, 53.56.

Anal. Calcd for $C_6H_8BNO_3$ (152.9): C, 47.12; H, 5.27; N, 9.16, Found: C, 46.78; H, 5.18; N, 8.94.

3-Bromo-6-methoxy-4-pyridylboronic Acid (11)

To a solution of 5-bromo-2-methoxypyridine (**9**) (727 mg, 3.9 mmol) in anhyd THF (10 mL) at –78 °C was added LDA (2.0 M in heptane–THF–ethylbenzene, 2.0 mL, 4.0 mmol) dropwise. The reaction mixture was stirred for 1 h at –78 °C, then TIPB (1.5 g, 7.8 mmol) was added dropwise. The mixture was stirred for 1 h at –78 °C then quenched with H_2O (10 mL) and allowed to warm to 20 °C overnight. Workup as for compound **4** gave **11** as a white solid (351 mg, 39%); mp 97–99 °C.

^{1}H NMR [$(CD_3)_2C(O)$–TMS]: δ = 8.16 (s, 1 H), 7.76 (s, 2 H, OH), 6.84 (s, 1 H), 3.85 (s, 3 H)

^{13}C NMR [$(CD_3)_2C(O)$–TMS]: δ = 162.79, 147.44, 115.67, 114.92, 53.17.

Anal. Calcd for $C_6H_7BBrNO_3$ (231.8): C, 31.08; H, 3.04; N, 6.04. Found: C, 31.09; H, 2.90; N, 6.00.

3-Bromo-6-ethoxy-4-pyridylboronic Acid (12)

Following the procedure used for compound **12**, 5-bromo-2-ethoxypyridine (**10**) (261 mg, 1.3 mmol), THF (10 mL) and LDA (2.0 M in heptane–THF–ethylbenzene, 0.8 mL, 1.5 mmol) gave **12** as a white solid (74 mg, 23%); mp 103–105 °C.

^{1}H NMR [$(CD_3)_2C(O)$–TMS]: δ = 8.15 (s, 1 H), 7.70 (s, 2 H, OH), 6.81 (s, 1 H), 4.30 (q, 2 H, *J* = 7.2 Hz), 1.32 (t, 3 H, *J* = 6.8 Hz).

^{13}C NMR [$(CD_3)_2C(O)$–TMS]: δ = 162.48, 147.45, 115.86, 114.67, 61.72, 14.15

Anal. Calcd for $C_7H_9BBrNO_3$ (245.9): C, 34.20; H, 3.69; N, 5.70. Found: C, 34.90; H, 3.25; N, 5.90.

Cross-Coupling Reactions; General Procedure

The boronic acid (1.0 equiv.), 3-bromoquinoline (or for compound **18** 2-bromo-5-nitrothiophene) (1.2–1.8 equiv), and $Pd(PPh_3)_2Cl_2$ (5 mol%) were sequentially added to degassed 1,4-dioxane (10 mL) and the mixture was stirred at 20 °C for 30 min. Degassed aqueous Cs_2CO_3 solution (1 M, 3.0 equiv) was added and the reaction mixture was heated under nitrogen at 95 °C until TLC monitoring showed that the reaction had finished. Solvent was removed in vacuo then EtOAc was added and the organic layer was washed with brine, separated, and dried over $MgSO_4$. The product was purified by chromatography on a silica gel column.

3-(6-Fluoro-pyridin-3-yl)-quinoline (13)

Compound **4** (100 mg, 0.7 mmol), 3-bromoquinoline (199 mg, 1.0 mmol), $Pd(PPh_3)_2Cl_2$ and Cs_2CO_3 in dioxane were reacted according to the general procedure. The reaction was complete in 67 h. Purification by column chromatography (CH_2Cl_2–EtOAc, 1:1) gave compound **13** as a white solid (91 mg, 57%); mp 126–127 °C.

^{1}H NMR [$(CD_3)_2C(O)$–TMS]: δ = 9.12 (d, 1 H, *J* = 2.4 Hz), 8.60 (m, 1 H), 8.52 (d, 1 H, *J* = 2.0 Hz), 8.34 (m, 1 H), 7.95 (m, 2 H), 7.68 (m, 1 H), 7.54 (m, 1 H), 7.17 (m, 1 H).

^{13}C NMR [$(CD_3)_2C(O)$–TMS]: δ = 164.94, 162.58, 149.43, 147.99, 146.60, 146.45, 140.86, 140.78, 133.67, 132.25, 132.21, 130.00, 129.77, 129.42, 128.57, 128.09, 127.43, 110.16, 109.78.

Anal. Calcd $C_{14}H_9FN_2$ (224.2): C, 74.99; H, 4.05; N, 12.49, Found: C, 74.54; H, 4.16; N, 12.38.

MS(EI): *m*/*z* (%) = 224 (M^+, 100).

3-(5-Bromo-pyridin-3-yl)-quinoline (14)

Compound **5** (100 mg, 0.4 mmol), 3-bromoquinoline (153 mg, 0.7 mmol), $Pd(PPh_3)_2Cl_2$ and Cs_2CO_3 in dioxane were reacted according to the general procedure. The reaction was complete in 68 h. Purification by column chromatography (EtOAc–CH_2Cl_2, 7:3) gave compound **14** as a white solid (11 mg, 8%); mp 180–182 °C.

^{1}H NMR ($CDCl_3$–TMS): δ = 9.07 (s, 1 H), 8.86 (s, 1 H), 8.71 (s, 1 H), 8.27 (s, 1 H), 8.11 (d, 2 H, *J* = 8.0 Hz), 7.86 (d, 1 H, *J* = 8.5 Hz), 7.73 (t, 1 H, *J* = 7.0 Hz), 7.58 (t, 1 H, *J* = 7.5 Hz).

^{13}C NMR ($CDCl_3$–TMS): δ = 149.20, 147.79, 146.87 (2 C), 145.44, 136.12, 133.10, 129.39, 128.38 (3 C), 127.11, 126.60 (2 C).

MS (EI): *m*/*z* (%) = 284 (M^+, 100%).

HRMS: *m*/*z* calcd for $C_{14}H_9BrN_2$, 283.99491; found, 283.99310.

3-(6-Ethoxy-pyridin-3-yl)-quinoline (15)

Compound **6** (12 mg, 0.07 mmol), 3-bromoquinoline (21 mg, 0.1 mmol), $Pd(PPh_3)_2Cl_2$ and Cs_2CO_3 in dioxane were reacted according to the general procedure. The reaction was complete in 63 h. Purification by column chromatography (CH_2Cl_2–EtOAc, 9:1) gave compound **15** as a white solid (10 mg, 59%); mp 104–105 °C.

^{1}H NMR [$(CD_3)_2C(O)$–TMS]: δ = 9.21 (d, 1 H, *J* = 2.5 Hz), 8.63 (d, 1 H, *J* = 2.0 Hz), 8.54 (d, 1 H, *J* = 2.0 Hz), 8.16 (dd, 1 H, *J* = 2.8, 2.5 Hz), 8.05 (m, 2 H), 7.76 (m, 1 H), 7.64 (m, 1 H), 6.93 (d, 1 H, *J* = 8.0 Hz), 4.43 (q, 2 H, *J* = 7.0 Hz), 1.39 (t, 3 H, *J* = 7.0 Hz).

^{13}C NMR [$(CD_3)_2C(O)$–TMS]: δ = 164.95, 150.34, 148.58, 146.66, 138.81, 133.38, 131.82 (2C), 130.36 (2C), 129.30, 128.11, 127.87, 122.31, 62.62, 15.18

MS(EI): *m*/*z* (%) = 250 (M^+, 55), 235 (100).

HRMS: *m*/*z* calcd for $C_{16}H_{14}N_2O$, 250.11061; found, 250.11059.

3-(2-Methoxy-pyridin-3-yl)-quinoline (16)

Compound **8** (100 mg, 0.7 mmol), 3-bromoquinoline (153 mg, 0.7 mmol), $Pd(PPh_3)_2Cl_2$ and Cs_2CO_3 in dioxane were reacted according to the general procedure. The reaction was complete in 95 h. Purification by column chromatography (CH_2Cl_2–EtOAc, 1:1) gave compound **15** as a white solid (86 mg, 77%); mp 89–90 °C.

^{1}H NMR [$(CD_3)_2C(O)$–TMS]: δ = 9.12 (d, 1 H, *J* = 2.0 Hz), 8.48 (d, 1 H, *J* = 2.0 Hz), 8.26 (dd, 1 H, *J* = 2.0, 2.0 Hz), 8.08 (m, 1 H), 8.01 (m, 1 H), 7.95 (dd, 1 H, *J* = 2.0, 2.0 Hz), 7.78 (m, 1 H), 7.64 (m, 1 H), 7.16 (m, 1 H), 3.98 (s, 3 H).

^{13}C NMR [$(CD_3)_2C(O)$–TMS]: δ = 161.21, 151.35, 147.52, 147.03, 139.33, 135.42, 130.25, 129.64, 129.33, 128.44, 128.06, 127.00, 121.40, 117.77, 53.21.

MS(EI): *m*/*z* (%) = 236 (M^+, 100).

HRMS: *m*/*z* calcd for $C_{15}H_{12}N_2O$, 236.09496; found, 236.09500.

3-(5-Bromo-2-methoxy-pyridin-4-yl)-quinoline (17)
Compound **11** (100 mg, 0.4 mmol), 3-bromoquinoline (123 mg, 0.6 mmol), $Pd(PPh_3)_2Cl_2$ and Cs_2CO_3 in dioxane were reacted according to the general procedure. The reaction was complete in 98 h. Purification by column chromatography (CH_2Cl_2–EtOAc, 9:1) gave compound **17** as a white solid (68 mg, 50%); mp 120–123 °C.

^{1}H NMR [$(CD_3)_2C(O)$–TMS]: δ = 9.14 (d, 1 H, *J* = 2.0 Hz), 8.54 (d, 1 H, *J* = 2.4 Hz), 8.33 (d, 1 H, *J* = 2.8 Hz), 8.12 (d, 1 H, *J* = 2.4 Hz), 8.09 (m, 1 H), 8.03 (m, 1 H), 7.81 (m, 1 H), 7.65 (m, 1 H), 3.99 (s, 3 H).

^{13}C NMR [$(CD_3)_2C(O)$–TMS]: δ = 160.32, 151.04, 147.73, 147.17, 141.32, 135.92, 130.01, 129.35, 128.81, 128.57, 127.94, 127.15, 123.56, 112.09, 53.78.

MS(EI): *m*/*z* (%) = 314 (M^+, 100).

HRMS: *m*/*z* calcd for $C_{15}H_{11}BrN_2O$, 314.00547; found, 314.00539.

3-Bromo-4-(5-nitro-2-thienyl)-6-ethoxypyridine (18)
Compound **12** (20 mg, 0.08 mmol), 2-bromo-5-nitrothiophene (20 mg, 0.1 mmol), $Pd(PPh_3)_2Cl_2$ and Cs_2CO_3 in dioxane were reacted according to the general procedure. The reaction was complete in 59 h. Purification by column chromatography (CH_2Cl_2) gave compound **18** as a yellow solid (11 mg, 44%); mp 84–86 °C.

^{1}H NMR [$(CD_3)_2C(O)$–TMS]: 8.32 (s, 1 H), 7.99 (d, 1 H, *J* = 4.0 Hz), 7.51 (d, 1 H, *J* = 4.5 Hz), 6.96 (s, 1 H), 4.25 (q, 2 H, *J* = 4.5 Hz), 1.24 (t, 3 H, *J* = 7.0 Hz).

^{13}C NMR [$(CD_3)_2C(O)$–TMS]: δ = 163.80, 152.95, 150.44, 145.21, 142.44, 129.32, 129.00, 112.96, 110.31, 62.57, 14.10.

HRMS: *m*/*z* calcd for $C_{11}H_9BrN_2O_3S$, 327.95173; found, 327.95169.

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