# Supporting Information

# for

# A Mild and Simple Method for Making MIDA Boronates

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**General Procedures**

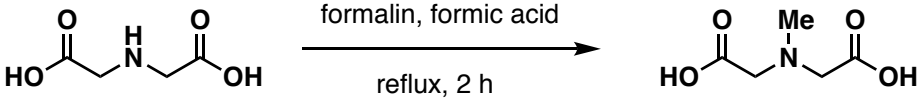
*Materials.* Commercially available materials were purchased from Millipore Sigma, Alfa-Aesar, TCI America, Combi-Blocks, Frontier Scientific, or Thermo-Fisher Scientific and were used without further purification unless stated otherwise. Unless stated otherwise, all of the solvents were dispensed from a solvent purification system that passes solvents through packed columns according to the method described by Pangborn and coworkers (THF, $Et_2O$, $CH_3CN$, $CH_2Cl_2$: dry neutral alumina; hexanes, toluene: dry neutral alumina and Q5 reactant; DMSO, DMF, $CH_3OH$: activated molecular sieves) and stored in Strauss flasks over 3A molecular sieves. Pyridine was freshly distilled under an atmosphere of nitrogen over $CaH_2$.

$^1H$ NMR spectra were recorded at 23 °C on a Bruker 500-MHz spectrometer with broad-band CryoProbe. Chemical shifts (δ) are reported in parts per million (ppm) downfield from tetramethylsilane and referenced to residual proton signals in the NMR solvent (DMSO, δ = 2.50, acetonitrile, δ = 1.94). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, sext = sextet, m = multiplet, br = broad, app = apparent), coupling constant (*J*) in Hertz (Hz), and integration. Solution $^{13}C$ NMR spectra were recorded at 23 °C on a Bruker 500-MHz spectrometer with broad-band CryoProbe. Chemical shifts (δ) are reported in ppm downfield from tetramethylsilane and referenced to carbon resonances in the NMR solvent (DMSO, δ = 39.5, acetonitrile, δ = 1.32). Carbons bearing boron substituents were typically not observed (quadrupolar relaxation). High resolution mass spectra (HRMS) were performed by Furong Sun and Haijun Yao at the University of Illinois School of Chemical Sciences Mass Spectrometry Laboratory.

Unless noted, all reactions were performed in flame dried round bottom flasks, Schlenk flasks fitted with rubber septa, or glass vials under a positive pressure of argon or nitrogen. Organic solutions were concentrated via rotary evaporation under reduced pressure with a bath temperature of 35-40 °C.

## Experimental Procedures

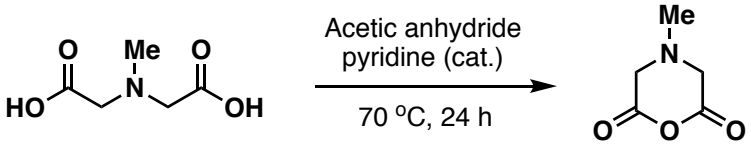
### Synthesis of *N*-Methyliminodiacetic acid (MIDA)




According to the previously reported procedure (*OL*, **2010**, *12*, 2314) to a 3-neck 3 L round bottom flask equipped with a large stir bar was added iminodiacetic acid (1.0 kg, 7.5 mol), water (840 mL) and formic acid (850 mL, 23 mol). The flask was fitted with a thermometer, a 500 mL pressure-equalizing addition funnel charged with formalin (430 mL, 5.7 mol), and a water-cooled Friedrichs condenser vented to ambient atmosphere. The mixture was heated to a gentle reflux. To the stirred mixture was added dropwise the formalin at a rate necessary to control the effervescence (ca. 30 mL/min). Following the addition, the mixture was maintained at reflux for an additional 2 h. The solution was cooled to room temperature. Under air the reaction mixture was layered underneath 20 L of acetone in a 25 L plastic distilled water container with the assistance of a rubber hose, washing with water (200 mL), such that the organic phase remained undisturbed and the phases did not mix. The mixture was allowed to stand undisturbed in the sealed plastic container for 7 days during which time the product crystallized as large colorless needle-like crystals. The crystals were agitated with a large metal rod and collected via filtration, washed with acetone (2 x 1 L), and residual solvent was removed *in vacuo* to afford *N*-methyliminodiacetic acid in quantitative yield (1.1 kg).

Spectral data were consistent with previous reports (*OL*, **2010**, *12*, 2314).

### 4-Methylmorpholine-2,6-dione (MIDA Anhydride) 1




A mixture of MIDA (500 g, 3.4 mol, 1 eq.), acetic anhydride (1.7 L, 18 mol, 5.3 eq.) and pyridine (40 mL, 0.51 mol, 0.15 eq.) were heated at 70 °C for 24 h. Upon cooling to room temperature, the reaction mixture was concentrated in vacuo. The removal of excess acetic anhydride, acetic acid, and pyridine was performed with toluene azeotrope (12 x 1L). The residue was suspended in $Et_2O$ (4 L), stirred with activated carbon (100 g) for 15 mins at room temperature and filtered through celite. The filtrate was concentrated in vacuo to afford a pale yellow solid, which was dissolved in refluxing $Et_2O$ (350 mL) under an $N_2$ atmosphere. Upon cooling, the crystallization flask was left to stand at room temperature for 48 h at which point the large colorless shards of MIDA anhydride had formed which were collected by filtration under a blanket of $N_2$ (211 g, 48%).

**$^1$H NMR** (500 MHz, DMSO-$d_6$) δ 2.31 (s, 3H), 3.60 (s, 4H).

**$^{13}$C NMR** (126 MHz, DMSO-$d_6$) δ 42.4, 54.2, 165.8.

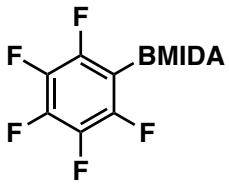
**GP1** – **General Procedure for Dean-Stark Complexation of MIDA with Boronic Acids (Figure 3)**

Boronic acid (0.5 mmol. 1 eq.) and MIDA (0.6 mmol, 1.2 eq.) were suspended in toluene/DMSO (10:1, 6 mL) and heated at reflux using a Dean-Stark apparatus. After 6 h the reaction vessel was cooled to room temperature and diluted with water (70 mL) and extracted with EtOAc (3 x 30 mL). The organics were combined, washed with brine (20 mL), dried over $MgSO_4$, filtered and concentrated *in vacuo* to afford the MIDA boronate product.

**GP2 - General Procedure for Reaction of MIDA Anhydride with Boronic Acids (Figure 3)**

MIDA anhydride **1** (1.5 mmol, 3 eq.) and boronic acid (0.5 mmol, 1 eq.) were added to a 7 mL vial, sealed with a PTFE septum cap and the vial was evacuated and backfilled with $N_2$ (x3). Anhydrous dioxane (1.5 mL) was added and the vial was placed in a pre-equilibrated 70 $^oC$ heating block for 24 h. The vial was removed from the heating block and cooled to room temperature. The crude material was diluted with water (10 mL) and extracted with EtOAc (3 x 5 mL). The organics were combined, dried over $MgSO_4$, filtered and concentrated in vacuo to afford the MIDA boronate product.

***Tips*** – If trace impurities are present or the reaction is found to be incomplete these can be removed *via* trituration with $Et_2O$. Alternatively the impure mixture can be dissolved in the minimum volume of acetone followed by addition of hexanes/$Et_2O$ (1:1) which will cause precipitation of the MIDA boronate for collection by filtration.




**Pentafluorophenylboronic acid MIDA Ester 4**

Prepared in 81% yield (130 mg) using **GP2** with pentafluorophenylboronic acid (106 mg, 0.5 mmol), following **GP1** no product was detected.

**$^1$H NMR** (500 MHz, Acetonitrile-$d_3$) δ 2.76 (s, 3H), 3.97 (d, *J* = 17.2 Hz, 2H), 4.15 (d, *J* = 17.2 Hz, 2H)

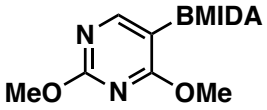
**$^{13}$C NMR** (126 MHz, Acetonitrile-$d_3$) δ 48.1, 63.1, 130-155 (multiple weak signals),* 168.3

**$^{11}$B NMR** (128 MHz, Acetonitrile-$d_3$) δ 10.4.

**$^{19}$F NMR** (376 MHz, Acetonitrile-$d_3$) δ -164.5 (td, J = 21.5, 9.2 Hz), -155.1 (t, J = 19.6 Hz), -134.2 (dd, J = 22.9, 9.1 Hz).

**HRMS** (ESI, $M+H^+$) $C_{11}H_7BF_5NO_4$ Found 324.0461, Calc. 324.0467.

*Multiple couplings to fluorine bound carbons rendered them unresolvable from noise when using a saturated solution of **4** in acetonitrile-$d_3$ on a 500 MHz spectrometer equipped with a cryoprobe. $^1$H , $^{19}$F and HRMS data are consistent with the proposed structure.




**(2,4-Dimethoxypyrimidin-5-yl)boronic acid MIDA Ester 5**

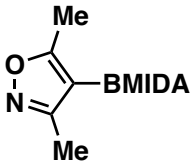
Prepared in 36% yield (54 mg) using **GP1** and 61% yield (90 mg) using **GP2** with (2,4-dimethoxypyrimidin-5-yl)boronic acid (92 mg, 0.5 mmol).

**$^{1}$H NMR** (500 MHz, DMSO-$d_6$) δ 2.64 (s, 3H), 3.86 (s, 3H), 3.90 (s, 3H), 4.04 (d, *J* = 17.2 Hz, 2H), 4.37 (d, *J* = 17.2 Hz, 2H), 8.27 (s, 1H).

**$^{13}$C NMR** (126 MHz, DMSO-$d_6$) δ 47.2, 53.6, 54.3, 62.7, 163.1, 163.3, 166.2, 169.0, 173.3.

**$^{11}$B NMR** (161 MHz, DMSO-$d_6$) δ 15.3.

**HRMS** (ESI, M+H$^+$) $C_{11}H_{15}BN_3O_6$ Found 296.1052, Calc. 296.1054.




**(3,5-Dimethylisoxazol-4-yl)boronic acid MIDA Ester 6**

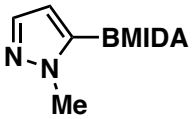
Prepared in 55% yield (69 mg) using **GP1** and 75% yield (94 mg) using **GP2** with (3,5-dimethylisoxazol-4-yl)boronic acid (71 mg, 0.5 mmol).

**$^{1}$H NMR** (500 MHz, DMSO-$d_6$) δ 2.13 (s, 3H), 2.32 (s, 3H), 2.65 (s, 3H), 4.13 (d, *J* = 17.3 Hz, 2H), 4.34 (d, *J* = 17.4 Hz, 2H).

**$^{13}$C NMR** (126 MHz, DMSO-$d_6$) δ 11.8, 12.5, 47.1, 61.8, 162.3, 169.0, 173.3.

**$^{11}$B NMR** (161 MHz, DMSO-$d_6$) δ 15.3

**HRMS** (ESI, M+H$^+$) $C_{10}H_{14}BN_2O_5$ Found 253.0998, Calc. 253.0996




**(1-methyl-1*H*-pyrazol-5-yl)boronic acid MIDA Ester 7**

Prepared in 24% yield (28 mg) using **GP1** and 68% yield (80 mg) using **GP2** with (3,5-dimethylisoxazol-4-yl)boronic acid (63 mg, 0.5 mmol).

**$^{1}$H NMR** (500 MHz, Acetonitrile-$d_3$) δ 2.60 (s, 3H), 3.89 – 3.96 (m, 5H), 4.08 (d, *J* = 17.2 Hz, 2H), 6.35 (d, *J* = 1.9 Hz, 1H), 7.40 (d, *J* = 1.9 Hz, 1H).

**$^{13}$C NMR** (126 MHz, Acetonitrile-$d_3$) δ 39.8, 48.0, 62.6, 114.3, 138.7, 169.0.

**$^{11}$B NMR** (128 MHz, Acetonitrile-$d_3$) δ 9.6.

**HRMS** (ESI, M+H$^+$) $C_9H_{13}BN_3O_4$ Found 238.0991, Calc. 238.0999


**Ethynylboronic acid MIDA Ester 8**

Prepared in 80% yield (147 mg) using **GP2** with ethynylboronic acid (1 mmol)* following **GP1** no product was detected.

* Ethynylboronic acid was freshly prepared via dropwise addition of ethynylmagnesium bromide (2 mL, 1 eq. 0.5 M in THF) to trimethylborate (0.067 mL, 0.6 mmol, 1.2 eq.) in THF (0.75 mL) at -78 °C. The reaction mixture was stirred at RT for 2 h followed by addition of 1M HCl (1 mL, 2 eq.). The reaction mixture was diluted with $Et_2O$ (5 mL) and the organic layer quickly separated. The aqueous layer was extracted with two further portions of $Et_2O$ (5 mL). The combined organics were dried over $Na_2SO_4$, transferred to a round bottomed flask and concentrated to ~3 mL. The solution was then transferred portion wise to a 7 mL vial containing DMSO (**GP1**, 0.54 mL) or dioxane (**GP2**, 1.5 mL) and concentrated *in vacuo* to remove any $Et_2O$/THF to leave freshly prepared solution of ethynyl boronic acid which was immediately used in **GP1** and **GP2**.

**$^1$H NMR** (500 MHz, Acetonitrile-$d_3$) δ 2.68 (s, 1H), 3.03 (s, 3H), 3.87 (d, $J$ = 17.1 Hz, 2H), 3.99 (d, $J$ = 17.1 Hz, 2H).

**$^{13}$C NMR** (126 MHz, Acetonitrile-$d_3$) δ 48.8, 62.4, 90.2 (broad), 168.6.

**$^{11}$B NMR** (128 MHz, Acetonitrile-$d_3$) δ 5.7.

Data were consistent with literature – J. R. Struble, S. J. Lee, M. D. Burke, *Tetrahedron*, **2010**, *66*, 4710.

## General Procedure for MIDA Boronate Maker Kit (Figure 5)

## Contents of Kit

*Reactionware*

1 x **7 mL glass vial** containing 1.5 mmol of MIDA anhydride and a magnetic stir bar

*Purification*

1 x **10 mL centrifuge column** packed with 350 mg of silica gel, 2 plastic frits and 1.5g of celite

3 x **50 mL conical tubes**

*Solvents*

**Solvent 1** Dioxane (1.5 x mL)

**Solvent 2** Hexanes (1 x 10 mL)

**Solvent 3** Hexanes:$Et_2O$ 1:1 (1 x 10 mL)

**Solvent 4** THF:MeCN 3:2 (1 x 1.5 mL)

**Solvent 5** $Et_2O$ (3 x 10 mL)

**Solvent 6** Acetone:MeOH 99:1 (1x10 mL)

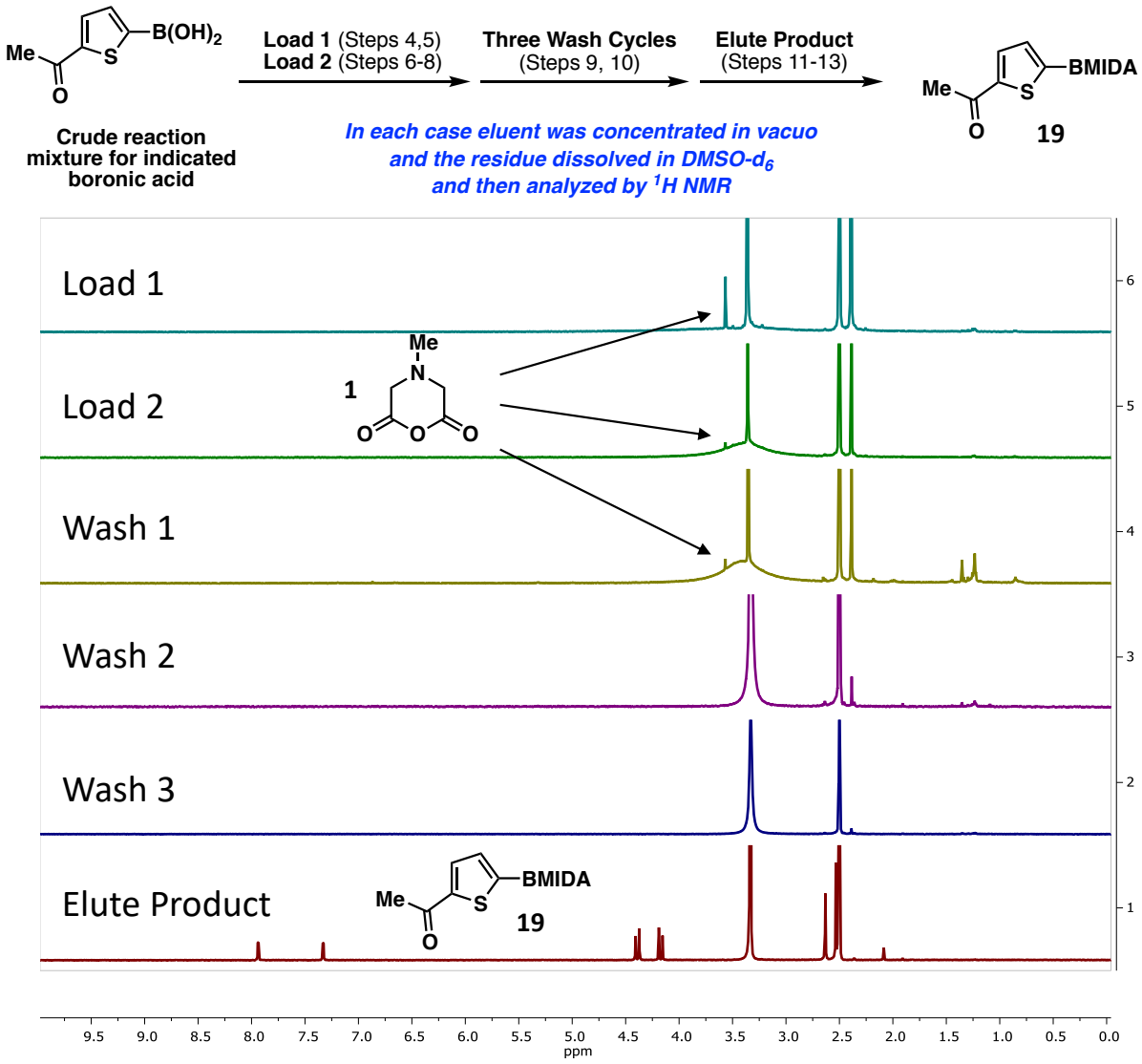
**Solvent 7** Hexane (2 x 20 mL)

## Protocol

1. Weigh out boronic acid (0.5 mmol) and add to 7mL glass vial.
2. Add **Solvent 1**, then cap the 7 mL vial and stir for 24 hours at 70 °C.
3. Add **Solvent 2** to 10 mL centrifuge column
4. Once the 7 mL vial has cooled to room temperature pour contents into centrifuge column.
5. Uncap the bottom of the column and centrifuge for 30 seconds at 250xG. **Discard the eluent**.
6. Re-cap the bottom of the column and add **Solvent 3**.
7. Add **Solvent 4** to the 7 mL vial and scrape any residue off the sides of the vessel.
8. Pour contents of 7 mL vial into column, uncap the column and centrifuge for 30 seconds at 250xG. **Discard the eluent**.
9. Add **Solvent 5** (x1) to column then centrifuge for 30 seconds at 250xG. **Discard the eluent**.
10. Repeat step 9 two additional times.
11. Place the column in a clean 50 ml conical tube. Cap the bottom of the column and add **Solvent 6**. Cap the top of the column and shake vigorously for 1 min.
12. Uncap the column and centrifuge for 2 minutes at 250xG. **Keep the eluent**.
13. Add **Solvent 7** (x1) into a clean 50 ml conical tube.
14. Pour the eluent into the labeled tube, then add a **Solvent 7** (x1).
15. Vortex until the supernatant becomes clear and precipitate has formed.
16. Centrifuge for 2 minutes at 1000xG. Decant the supernatant to **retrieve pellet** of MIDA boronate.

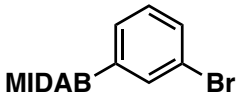
Product is retrieved by air drying overnight in the conical tube or can be transferred to a separate vessel with acetone.

## Representative $^{1}$H NMR Analysis of Centrifuge Purification Protocol




**Supplementary Figure 1** $^{1}$H NMR analysis (500 MHz, DMSO-$d_6$) of the elution profile of the reaction of 5-Acetyl-2-thienylboronic acid with MIDA anhydride when subject to centrifuge column purification. Each eluent stream for Load, Wash and Elute Product were individually collected and concentrated in vacuo, then dissolved in DMSO-$d_6$ for analysis. During the loading phase and the first wash cycle excess MIDA anhydride **1** was eluted. Washes 2 and 3 removed additional impurities. The eluted product was analytically pure 5-Acetyl-2-thienylboronic acid MIDA Ester **19**, containing no trace of anhydride, boronic acid or free diacid MIDA.

## Synthesis using MIDA Boronate Maker Kit




**3-Bromophenylboronic acid MIDA Ester 3**

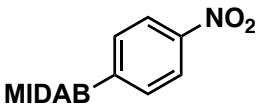
Prepared in 93% yield (145 mg) according to the MIDA boronate maker kit procedure using 3-bromophenylboronic acid (100 mg, 0.5 mmol, 1 eq.).

**$^{1}$H NMR** (500 MHz, DMSO-$d_6$) δ 2.55 (s, 3H), 4.15 (d, *J* = 17.2 Hz, 2H), 4.35 (d, *J* = 17.2 Hz, 2H), 7.33 (t, *J* = 7.6 Hz, 1H), 7.43 (d, *J* = 7.4 Hz, 1H), 7.54 – 7.62 (m, 2H).

**$^{13}$C NMR** (126 MHz, DMSO-$d_6$) δ 47.7, 62.0, 121.9, 130.0, 131.4, 131.7, 134.9, 169.2.

**$^{11}$B NMR** (161 MHz, DMSO-$d_6$) δ 10.4.

**HRMS** (ESI, M+H$^+$) $C_{11}H_{12}B^{79}BrNO_4$ Found 312.0055, Calc. 312.0043.




**4-Nitrophenylboronic acid MIDA Ester 9**

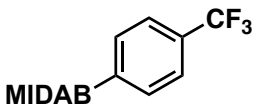
Prepared in 66% yield (92 mg) according to the MIDA boronate maker kit procedure using 4-nitrophenylboronic acid (84 mg, 0.5 mmol, 1 eq.).

**$^{1}$H NMR** (500 MHz, DMSO-$d_6$) δ 2.55 (s, 3H), 4.18 (d, *J* = 17.1 Hz, 2H), 4.41 (d, *J* = 17.1 Hz, 2H), 7.75 (d, *J* = 8.6 Hz, 2H), 8.21 (d, *J* = 8.7 Hz, 2H).

**$^{13}$C NMR** (126 MHz, DMSO-$d_6$) δ 48.2, 62.6, 122.7, 134.4, 148.6, 169.6.

**$^{11}$B NMR** (161 MHz, DMSO-$d_6$) δ 10.5.

**HRMS** (ESI, M+H$^+$) $C_{11}H_{12}BN_2O_6$ Found 278.0798, Calc. 278.0788




**4-trifluoromethylboronic acid MIDA Ester 10**

Prepared in 65% yield (98 mg) according to the MIDA boronate maker kit procedure using 4-trifluoromethylboronic acid (90 mg, 0.5 mmol, 1 eq.).

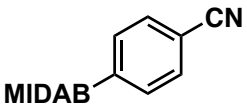
**$^{1}$H NMR** (500 MHz, DMSO-$d_6$) δ 2.52 (s, 3H), 4.15 (d, *J* = 17.2 Hz, 2H), 4.38 (d, *J* = 17.2 Hz, 2H), 7.67 (d, *J* = 8.0 Hz, 2H), 7.71 (d, *J* = 8.1 Hz, 2H).

**$^{13}$C NMR** (126 MHz, DMSO-$d_6$) δ 47.7, 61.9, 124.1 (q, *J* = 3.8 Hz), 124.4 (q, *J* = 271.9 Hz), 129.3 (q, *J* = 31.5 Hz), 133.3, 169.2.

**$^{11}$B NMR** (161 MHz, DMSO-$d_6$) δ 10.5.

**$^{19}$F NMR** (471 MHz, DMSO-$d_6$) δ -61.2.

**HRMS** (ESI, M+H$^+$) $C_{12}H_{12}BF_3NO_4$ Found 302.0814, Calc. 302.0811




**4-Cyanophenylboronic acid MIDA Ester 11**

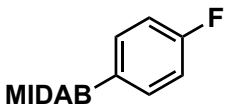
Prepared in 71% yield (92 mg) according to the MIDA boronate maker kit procedure using 4-cyanophenylboronic acid (74 mg, 0.5 mmol, 1 eq.).

**$^{1}$H NMR** (500 MHz, DMSO-$d_6$) δ 2.52 (s, 3H), 4.16 (d, *J* = 17.2 Hz, 2H), 4.38 (d, *J* = 17.2 Hz, 2H), 7.64 (d, *J* = 8.0 Hz, 2H), 7.81 (d, *J* = 8.1 Hz, 2H).

**$^{13}$C NMR** (126 MHz, DMSO-$d_6$) δ 47.7, 62.0, 111.5, 119.0, 131.1, 133.3, 169.2.

**$^{11}$B NMR** (161 MHz, DMSO-$d_6$) δ 10.4.

**HRMS** (ESI, M+H$^+$) $C_{12}H_{12}BN_2O_4$ Found 259.0890, Calc. 259.0890




**4-Fluorophenylboronic acid MIDA Ester 12**

Prepared in 75% yield (95 mg) according to the MIDA boronate maker kit procedure using 4-fluorophenylboronic acid (70 mg, 0.5 mmol, 1 eq.).

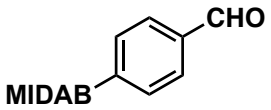
**$^{1}$H NMR** (500 MHz, DMSO-$d_6$) δ 2.51 (s, 3H), 4.12 (d, *J* = 17.2 Hz, 2H), 4.34 (d, *J* = 17.2 Hz, 2H), 7.18 (dd, *J* = 9.4, 8.6 Hz, 2H), 7.48 (dd, *J* = 8.5, 6.3 Hz, 2H).

**$^{13}$C NMR** (126 MHz, DMSO-$d_6$) δ 48.0, 62.3, 115.0 (d, *J* = 19.8 Hz), 135.1 (d, *J* = 7.8 Hz), 163.4 (d, *J* = 244.8 Hz), 169.8.

**$^{11}$B NMR** (161 MHz, DMSO-$d_6$) δ 10.8.

**$^{19}$F NMR** (471 MHz, DMSO-$d_6$) δ -113.02.

**HRMS** (ESI, M+H$^+$) $C_{11}H_{12}BFNO_4$ Found 253.0846, Calc. 253.0843




**4-Formylphenylboronic acid MIDA Ester 13**

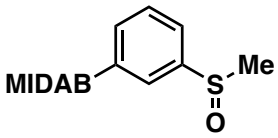
Prepared in 63% yield (83 mg) according to the MIDA boronate maker kit procedure using 4-formylphenylboronic acid (75 mg, 0.5 mmol, 1 eq.).

**$^{1}$H NMR** (500 MHz, DMSO-$d_6$) δ 2.52 (s, 3H), 4.16 (d, *J* = 17.2 Hz, 2H), 4.38 (d, *J* = 17.2 Hz, 2H), 7.68 (d, *J* = 7.9 Hz, 2H), 7.89 (d, *J* = 8.0 Hz, 2H), 10.03 (s, 1H).

**$^{13}$C NMR** (126 MHz, DMSO-$d_6$) δ 47.7, 62.0, 128.5, 133.1, 136.5, 169.3, 193.4.

**$^{11}$B NMR** (161 MHz, DMSO-$d_6$) δ 10.8.

**HRMS** (ESI, M+H$^+$) $C_{12}H_{13}BNO_5$ Found 262.0892, Calc. 262.0887




**(3-(methylsulfinyl)phenyl)boronic acid MIDA Ester 14**

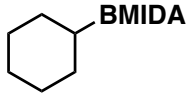
Prepared in 41% yield (64 mg) according to the MIDA boronate maker kit procedure using ((3-(methylsulfinyl)phenyl)boronic acid (100 mg, 0.5 mmol, 1 eq.).

**$^{1}$H NMR** (500 MHz, DMSO-$d_6$) δ 2.53 (s, 3H), 2.74 (s, 3H), 4.16 (dd, *J* = 17.2 Hz, 2H), 4.37 (dd, *J* = 17.3 Hz, 2H), 7.52 – 7.63 (m, 2H), 7.69 (dt, *J* = 7.2, 1.8 Hz, 1H), 7.74 (s, 1H).

**$^{13}$C NMR** (126 MHz, DMSO-$d_6$) δ 43.8, 48.3, 62.5, 124.5, 127.8, 129.0, 135.2, 146.1, 169.8.

**$^{11}$B NMR** (161 MHz, DMSO-$d_6$) δ 10.9.

**HRMS** (ESI, M+H$^+$) $C_{12}H_{15}BNO_5S$ Found 296.0775, Calc. 296.0764




**Cyclohexylboronic acid MIDA Ester 15**

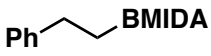
Prepared in 26% yield (31 mg) according to the MIDA boronate maker kit procedure using cyclohexylboronic acid (64 mg, 0.5 mmol, 1 eq.).

**$^{1}$H NMR** (500 MHz, DMSO-$d_6$) δ 0.67 (tt, *J* = 12.0, 2.8 Hz, 1H), 1.00 (q, *J* = 10.3, 9.3 Hz, 2H), 1.13 – 1.26 (m, 3H), 1.53 – 1.80 (m, 5H), 2.88 (s, 3H), 3.94 (d, *J* = 17.2 Hz, 2H), 4.16 (d, *J* = 17.2 Hz, 2H).

**$^{13}$C NMR** (126 MHz, DMSO-$d_6$) δ 27.0, 27.6, 27.9, 45.7, 62.5, 169.5.

**$^{11}$B NMR** (161 MHz, DMSO-$d_6$) δ 12.3.

**HRMS** (ESI, M+H$^+$) $C_{11}H_{19}BNO_4$ Found 240.1415, Calc. 240.1407




**2-Phenylethylboronic acid MIDA Ester 16**

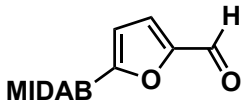
Prepared in 34% yield (45 mg) according to the MIDA boronate maker kit procedure using 2-phenylethylboronic acid (75 mg, 0.5 mmol, 1 eq.).

**$^1$H NMR** (500 MHz, DMSO-$d_6$) δ 0.84 (m, 2H),2.56 (m, 2H), 4.01 (d, *J* = 17.0 Hz, 2H), 4.21 (d, *J* = 17.0 Hz, 2H), 7.13 (m, 1H), 7.21 (m, 2H), 7.26 (t, *J* = 7.5 Hz, 2H).

**$^{13}$C NMR** (126 MHz, DMSO-$d_6$) δ 30.5, 46.0, 62.1, 125.8, 128.2, 128.6, 145.6, 169.5.

**$^{11}$B NMR** (161 MHz, DMSO-$d_6$) δ 12.9.

**HRMS** (ESI, M+H$^+$) $C_{13}H_{17}BNO_4$ Found 262.1261, Calc. 262.1251




**5-Formyl-2-furylboronic acid MIDA Ester 17**

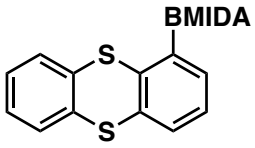
Prepared in 83% yield (104 mg) according to the MIDA boronate maker kit procedure using 5-formyl-2-furylboronic acid (70 mg, 0.5 mmol, 1 eq.).

**$^1$H NMR** (500 MHz, DMSO-$d_6$) δ 2.67 (s, 3H), 4.17 (d, *J* = 17.2 Hz, 2H), 4.41 (d, *J* = 17.3 Hz, 2H), 6.91 (d, *J* = 3.5 Hz, 1H), 7.51 (d, *J* = 3.5 Hz, 1H), 9.64 (s, 1H).

**$^{13}$C NMR** (126 MHz, DMSO-$d_6$) δ 47.4, 61.8, 120.3, 122.8, 155.2, 168.8, 178.6.

**$^{11}$B NMR** (161 MHz, DMSO-$d_6$) δ 8.3.

**HRMS** (ESI, M+H$^+$) $C_{10}H_{11}BNO_6$ Found 252.0680, Calc. 252.0679




**Thianthren-1-ylboronic acid MIDA Ester 18**

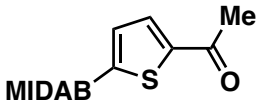
Prepared in 35% yield (65 mg) according to the MIDA boronate maker kit procedure using thianthren-1-ylboronic acid (130 mg, 0.5 mmol, 1 eq.).

**$^1$H NMR** (500 MHz, DMSO-$d_6$) δ 2.65 (s, 3H), 4.31 (d, *J* = 17.4 Hz, 2H), 4.49 (d, *J* = 17.5 Hz, 2H), 7.32 – 7.41 (m, 3H), 7.52 (dd, *J* = 7.4, 1.4 Hz, 1H), 7.61 (dd, *J* = 7.1, 2.0 Hz, 1H), 7.65 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.72 – 7.77 (m, 1H).

**$^{13}$C NMR** (126 MHz, DMSO-$d_6$) δ 48.4, 64.1, 127.1, 128.2, 128.4, 128.6, 129.3, 130.4, 134.0, 134.3, 134.8, 136.4, 140.1, 169.4.

**$^{11}$B NMR** (161 MHz, DMSO-$d_6$) δ 15.5.

**HRMS** (ESI, M+H$^+$) $C_{17}H_{15}BNO_4S_2$ Found 372.0546, Calc. 372.0536.




**5-Acetyl-2-thienylboronic acid MIDA Ester 19**

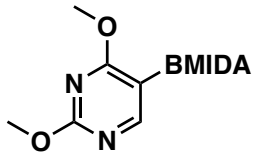
Prepared in 81% yield (113 mg) according to the MIDA boronate maker kit procedure using 5-Acetyl-2-thienylboronic acid (85 mg, 0.5 mmol, 1 eq.).

**$^1$H NMR** (500 MHz, DMSO-$d_6$) δ 2.53 (s, 3H), 2.64 (s, 3H), 4.17 (d, *J* = 17.2 Hz, 2H), 4.39 (d, *J* = 17.2 Hz, 2H), 7.33 (d, *J* = 3.7 Hz, 1H), 7.94 (d, *J* = 3.7 Hz, 1H).

**$^{13}$C NMR** (126 MHz, DMSO-$d_6$) δ 27.4, 48.0, 62.2, 134.6, 135.0, 147.5, 169.2, 191.0.

**$^{11}$B NMR** (161 MHz, DMSO-$d_6$) δ 9.5.

**HRMS** (ESI, M+H$^+$) $C_{11}H_{13}BNO_5S$ Found 282.0612, Calc. 282.0607




**(2,4-Dimethoxypyrimidin-5-yl)boronic acid MIDA Ester 5**

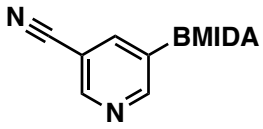
Prepared in 68% yield (100 mg) according to the MIDA boronate maker kit procedure using (2,4-dimethoxypyrimidin-5-yl)boronic acid (92 mg, 0.5 mmol, 1 eq.).

**$^1$H NMR** (500 MHz, DMSO-$d_6$) δ 2.64 (s, 3H), 3.86 (s, 3H), 3.90 (s, 3H), 4.04 (d, *J* = 17.2 Hz, 2H), 4.37 (d, *J* = 17.2 Hz, 2H), 8.27 (s, 1H).

**$^{13}$C NMR** (126 MHz, DMSO-$d_6$) δ 47.2, 53.6, 54.3, 62.7, 163.2, 166.2, 169.0, 173.3.

**$^{11}$B NMR** (161 MHz, DMSO-$d_6$) δ 15.3.

**HRMS** (ESI, M+H$^+$) $C_{11}H_{15}BN_3O_6$ Found 296.1052, Calc. 296.1054.




**(5-Cyanopyridin-3-yl)boronic acid MIDA Ester 20**

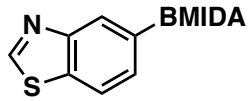
Prepared in 51% yield (66 mg) according to the MIDA boronate maker kit procedure using (5-cyanopyridin-3-yl)boronic acid (74 mg, 0.5 mmol, 1 eq.).

**$^{1}$H NMR** (500 MHz, DMSO-$d_6$) δ 2.62 (s, 3H), 4.19 (d, *J* = 17.1 Hz, 2H), 4.40 (d, *J* = 17.1 Hz, 2H), 8.30 (t, *J* = 2.0 Hz, 1H), 8.87 (d, *J* = 1.8 Hz, 1H), 9.02 (d, *J* = 2.2 Hz, 1H).

**$^{13}$C NMR** (126 MHz, DMSO-$d_6$) δ 48.4, 62.7, 109.1, 117.8, 144.7, 153.1, 157.1, 169.5.

**$^{11}$B NMR** (161 MHz, DMSO-$d_6$) δ 10.5.

**HRMS** (ESI, M+H$^+$) $C_{11}H_{11}BN_3O_4$ Found 260.0849, Calc. 260.0843.




**Benzo[*d*]thiazol-6-ylboronic acid MIDA Ester 21**

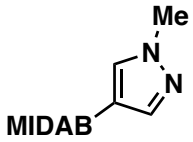
Prepared in 59% yield (86 mg) according to the MIDA boronate maker kit procedure using benzo[d]thiazol-6-ylboronic acid (90 mg, 0.5 mmol, 1 eq.).

**$^{1}$H NMR** (500 MHz, DMSO-$d_6$) δ 2.53 (s, 3H), 4.18 (d, *J* = 17.2 Hz, 2H), 4.39 (d, *J* = 17.2 Hz, 2H), 7.61 (dd, *J* = 8.2, 1.3 Hz, 1H), 8.08 (d, *J* = 8.1 Hz, 1H), 8.21 (s, 1H), 9.41 (s, 1H).

**$^{13}$C NMR** (126 MHz, DMSO-$d_6$) δ 48.2, 62.4, 122.7, 127.0, 130.6, 133.8, 154.0, 156.8, 169.8.

**$^{11}$B NMR** (161 MHz, DMSO-$d_6$) δ 11.4.

**HRMS** (ESI, M+H$^+$) $C_{12}H_{12}BN_2O_4S$ Found 291.0613, Calc. 291.0611




**(1-methyl-1*H*-pyrazol-4-yl)boronic acid MIDA Ester 22**

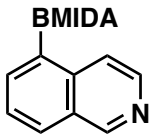
Prepared in 33% yield (39 mg) according to the MIDA boronate maker kit procedure using (1-methyl-1H-pyrazol-4-yl)boronic acid (63 mg, 0.5 mmol, 1 eq.).

**$^{1}$H NMR** (500 MHz, DMSO-$d_6$) δ 2.59 (s, 3H), 3.82 (s, 3H), 4.03 (d, *J* = 17.1 Hz, 2H), 4.26 (d, *J* = 17.1 Hz, 2H), 7.37 (s, 1H), 7.57 (s, 1H).

**$^{13}$C NMR** (126 MHz, DMSO-$d_6$) δ 38.1, 47.3, 61.2, 134.7, 142.7, 169.2.

**$^{11}$B NMR** (161 MHz, DMSO-$d_6$) δ 15.8.

**HRMS** (ESI, M+H$^+$) $C_9H_{13}BN_3O_4$ Found 238.0992, Calc. 238.0999




**isoquinolin-5-ylboronic acid MIDA Ester 23**

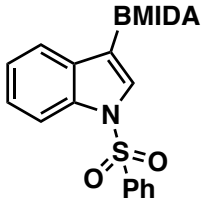
Prepared in 61% yield (87 mg) according to the MIDA boronate maker kit procedure using (isoquinolin-5-ylboronic acid (87 mg, 0.5 mmol, 1 eq.).

**$^1$H NMR** (500 MHz, DMSO-$d_6$) δ 2.51 (s, 3H), 4.23 (d, *J* = 17.3 Hz, 2H), 4.43 (d, *J* = 17.4 Hz, 2H), 7.53 (dd, *J* = 8.7, 4.1 Hz, 1H), 7.66 (dd, *J* = 7.0, 1.4 Hz, 1H), 7.77 (dd, *J* = 8.4, 7.0 Hz, 1H), 8.06 (dt, *J* = 8.4, 1.1 Hz, 1H), 8.63 (dt, *J* = 8.7, 1.2 Hz, 1H), 8.90 (dd, *J* = 4.1, 1.6 Hz, 1H).

**$^{13}$C NMR** (126 MHz, DMSO-$d_6$) δ 47.6, 62.5, 129.2, 131.4, 131.4, 133.9, 135.9, 148.6, 150.1, 169.9.

**$^{11}$B NMR** (161 MHz, DMSO-$d_6$) δ 11.5.

**HRMS** (ESI, M+H$^+$) $C_{14}H_{14}BN_2O_4$ Found 285.1042, Calc. 285.1047.




**(1-(phenylsulfonyl)-1*H*-indol-3-yl)boronic acid MIDA Ester 24**

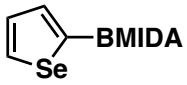
Prepared in 31% yield (64 mg) according to the MIDA boronate maker kit procedure using ((1-(phenylsulfonyl)-1H-indol-3-yl)boronic acid (151 mg, 0.5 mmol, 1 eq.).

**$^1$H NMR** (500 MHz, DMSO-$d_6$) δ 2.54 (s, 3H), 4.18 (d, *J* = 17.2 Hz, 2H), 4.38 (d, *J* = 17.2 Hz, 2H), 7.23 (td, *J* = 7.5, 1.1 Hz, 1H), 7.31 (t, *J* = 7.2 Hz, 1H), 7.47 – 7.62 (m, 3H), 7.67 (t, *J* = 7.5 Hz, 1H), 7.72 (s, 1H), 7.89 (d, *J* = 8.4 Hz, 1H), 8.01 (d, *J* = 7.2 Hz, 2H).

**$^{13}$C NMR** (126 MHz, DMSO-$d_6$) δ 47.3, 61.8, 113.0, 122.2, 123.5, 124.3, 126.8, 129.7, 132.0, 133.3, 134.6, 135.2, 136.9, 169.3.

**$^{11}$B NMR** (161 MHz, DMSO-$d_6$) δ 15.0

**HRMS** (ESI, M+H$^+$) $C_{19}H_{18}BN_2O_6S$ Found 413.0986, Calc. 413.0979




**Selenophen-2-ylboronic acid MIDA Ester 25**

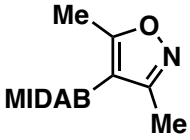
Prepared in 42% yield (60 mg) according to the MIDA boronate maker kit procedure using selenophen-2-ylboronic acid (60 mg, 0.5 mmol, 1 eq.).

**$^{1}$H NMR** (500 MHz, DMSO-$d_6$) δ 2.63 (s, 3H), 4.14 (d, *J* = 17.2 Hz, 2H), 4.36 (d, *J* = 17.2 Hz, 2H), 7.43 (dd, *J* = 5.2, 3.5 Hz, 1H), 7.49 (d, *J* = 3.5 Hz, 1H), 8.37 (d, *J* = 5.2 Hz, 1H).

**$^{13}$C NMR** (126 MHz, DMSO-$d_6$) δ 48.0, 62.0, 131.5, 135.5, 135.5, 169.3.

**$^{11}$B NMR** (161 MHz, DMSO-$d_6$) δ 11.0.

**HRMS** (ESI, M+H$^+$) $C_9H_{11}BNO_4Se$ Found 287.9937, Calc. 286.9946.




**(3,5-Dimethylisoxazol-4-yl)boronic acid MIDA Ester 6**

Prepared in 54% yield (68 mg) according to the MIDA boronate maker kit procedure using (3,5-dimethylisoxazol-4-yl)boronic acid (72 mg, 0.5 mmol, 1 eq.).

**$^{1}$H NMR** (500 MHz, DMSO-$d_6$) δ 2.13 (s, 3H), 2.32 (s, 3H), 2.65 (s, 3H), 4.13 (d, *J* = 17.3 Hz, 2H), 4.34 (d, *J* = 17.4 Hz, 2H).

**$^{13}$C NMR** (126 MHz, DMSO-$d_6$) δ 11.8, 12.5, 47.1, 61.8, 162.3, 169.0, 173.3.

**$^{11}$B NMR** (161 MHz, DMSO-$d_6$) δ 15.3

**HRMS** (ESI, M+H$^+$) $C_{10}H_{14}BN_2O_5$ Found 253.0998, Calc. 253.0996

## Gram Scale Synthesis of MIDA Boronates (Figure 5)

## Materials

*Reactionware*

1 x **40 mL glass vial** containing 15 mmol of MIDA anhydride and a magnetic stir bar

*Purification*

4 x **10 mL centrifuge column** packed with 350 mg of silica gel, 2 plastic frits and 1.5g of celite

16 x **50 mL conical tubes**

*Solvents*

**Solvent 1** Dioxane (1 x 15mL)

**Solvent 2** Hexanes (8 x 10 mL)

**Solvent 3** THF:MeCN 3:2 (1 x 15 mL)

**Solvent 4** Hexanes:$Et_2O$ 1:1 (8 x 10 mL)

**Solvent 5** $Et_2O$ (16 x 10 mL)

**Solvent 6** Acetone:MeOH 99:1 (4 x 5 mL)

**Solvent 7** Acetone:MeOH 99:1 (8 x 10 mL)

**Solvent 8** Hexane (8 x 10 mL)

**Solvent 9** Hexane (16 x 20 mL)

## Protocol

1. Weigh out boronic acid (5 mmol) and add to 40 mL glass vial.
2. Add **Solvent 1**, then cap the 40 mL vial and stir for 24 hours at 70 °C.
3. Add **Solvent 2** (x1) to each of the 4 10 mL centrifuge columns.
4. Once the 40 mL vial has cooled to room temperature, add 2 mL of the contents of the 40 mL vial into each centrifuge column.
5. Uncap the bottom of the column and centrifuge for 30 seconds at 250xG. **Discard the eluent**.
6. Re-cap the bottom of the columns and repeat steps 3-5. (x1)
7. Add **Solvent 3** to the 40 mL vial and scrape any residue off the sides of the vessel.
8. Re-cap the bottom of the columns and add **Solvent 4** (x1) to each column.
9. Add 2 mL portion from 40 mL vial into each column, uncap the columns and centrifuge for 30 seconds at 250xG. **Discard the eluent**.
10. Repeat steps 8 and 9. (x1)
11. Add **Solvent 5** (x1) to each column then centrifuge for 30 seconds at 250xG. **Discard the eluent**.
12. Repeat step 9. (x3)
13. Place each column in a clean 50 mL conical tube. Cap the bottom of each column and add **Solvent 6** (x1). Cap the top of each column and shake vigorously for 1 min.
14. Uncap the bottom of each column and centrifuge for 2 minutes at 250xG. **Keep the eluent**.

15. Place each column in a clean 50 mL conical tube. Cap the bottom of the column and add **Solvent 7** (x1). Cap the top of the column and shake vigorously for 1 min.
16. Uncap the bottom of the column and centrifuge for 2 minutes at 250xG. **Keep the eluent.**
17. Repeat steps 15 and 16. (x1)
18. Combine the retained eluents into 1 conical tube per column (4 total).
19. Add **Solvent 8** (x1) into 4 clean 50 mL conical tubes.
20. Add 5 mL of the eluent to each tube containing **Solvent 8**, then add additional **Solvent 8** (x1) to each tube.
21. Add **Solvent 9** (x1) to 8 clean 50 mL conical tubes.
22. Add 10 mL of the eluent into the labeled tubes, then add **Solvent 9** (x1) to each tube.
23. Vortex all of the conical tubes until the supernatant becomes clear and precipitate has formed.
24. Centrifuge for 2 minutes at 1000xG. Decant the supernatant to **retrieve pellet** of MIDA boronate.

Product is retrieved by air drying overnight in the conical tube or can be transferred to a separate vessel with acetone.

## X-Ray Crystal Structure of 1

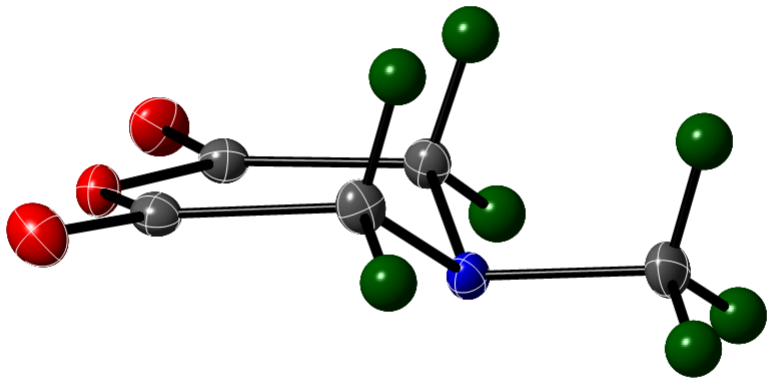


Table 1. Crystal data and structure refinement for dd53zs.

| | | |
|---|---|---|
| Identification code | dd53zs | |
| Empirical formula | C5 H7 N O3 | |
| Formula weight | 129.12 | |
| Temperature | 100(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Monoclinic | |
| Space group | $P2_1/c$ | |
| Unit cell dimensions | a = 7.1941(2) Å | a= 90°. |
| | b = 11.5580(4) Å | b= 106.7923(17)°. |
| | c = 7.5263(3) Å | g = 90°. |
| Volume | 599.12(4) $Å^3$ | |
| Z | 4 | |
| Density (calculated) | 1.431 $Mg/m^3$ | |
| Absorption coefficient | 0.119 $mm^{-1}$ | |
| F(000) | 272 | |
| Crystal size | 0.237 x 0.235 x 0.148 $mm^3$ | |
| Theta range for data collection | 2.958 to 28.291°. | |
| Index ranges | -9<=h<=9, -15<=k<=15, -10<=l<=10 | |

| | |
|---|---|
| Reflections collected | 10214 |
| Independent reflections | 1489 [R(int) = 0.0261] |
| Completeness to theta = 25.242° | 99.8 % |
| Absorption correction | Semi-empirical from equivalents |
| Max. and min. transmission | 0.7457 and 0.6855 |
| Refinement method | Full-matrix least-squares on $F^2$ |
| Data / restraints / parameters | 1489 / 0 / 83 |
| Goodness-of-fit on $F^2$ | 1.080 |
| Final R indices [I>2sigma(I)] | R1 = 0.0320, wR2 = 0.0857 |
| R indices (all data) | R1 = 0.0349, wR2 = 0.0881 |
| Extinction coefficient | n/a |
| Largest diff. peak and hole | 0.328 and -0.199 e.$Å^{-3}$ |

Table 2. Atomic coordinates ( x $10^4$) and equivalent isotropic displacement parameters ($Å^2$x $10^3$) for dd53zs. U(eq) is defined as one third of the trace of the orthogonalized $U^{ij}$ tensor.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| O(1) | 4873(1) | 3157(1) | 6404(1) | 18(1) |
| O(2) | 2778(1) | 4116(1) | 7482(1) | 24(1) |
| O(3) | 7032(1) | 2150(1) | 5508(1) | 26(1) |
| N(1) | 7133(1) | 5116(1) | 6645(1) | 16(1) |
| C(1) | 4327(1) | 4137(1) | 7206(1) | 17(1) |
| C(2) | 5770(1) | 5104(1) | 7747(1) | 17(1) |
| C(3) | 8112(1) | 4004(1) | 6820(1) | 19(1) |
| C(4) | 6691(1) | 3035(1) | 6175(1) | 17(1) |
| C(5) | 8548(2) | 6051(1) | 7258(2) | 23(1) |

Table 3. Bond lengths [Å] and angles [°] for dd53zs.

| | |
|---|---|
| O(1)-C(4) | 1.3748(11) |
| O(1)-C(1) | 1.3925(12) |
| O(2)-C(1) | 1.1917(12) |
| O(3)-C(4) | 1.1959(12) |
| N(1)-C(3) | 1.4531(12) |
| N(1)-C(2) | 1.4552(12) |
| N(1)-C(5) | 1.4646(12) |
| C(1)-C(2) | 1.4999(13) |
| C(2)-H(2A) | 0.9900 |
| C(2)-H(2B) | 0.9900 |
| C(3)-C(4) | 1.4990(13) |
| C(3)-H(3A) | 0.9900 |
| C(3)-H(3B) | 0.9900 |
| C(5)-H(5A) | 0.9800 |
| C(5)-H(5B) | 0.9800 |
| C(5)-H(5C) | 0.9800 |
| | |
| C(4)-O(1)-C(1) | 122.34(7) |
| C(3)-N(1)-C(2) | 109.23(7) |
| C(3)-N(1)-C(5) | 110.43(8) |
| C(2)-N(1)-C(5) | 110.41(8) |
| O(2)-C(1)-O(1) | 117.01(9) |
| O(2)-C(1)-C(2) | 125.24(9) |
| O(1)-C(1)-C(2) | 117.65(8) |
| N(1)-C(2)-C(1) | 112.32(8) |
| N(1)-C(2)-H(2A) | 109.1 |
| C(1)-C(2)-H(2A) | 109.1 |
| N(1)-C(2)-H(2B) | 109.1 |
| C(1)-C(2)-H(2B) | 109.1 |
| H(2A)-C(2)-H(2B) | 107.9 |
| N(1)-C(3)-C(4) | 111.32(8) |
| N(1)-C(3)-H(3A) | 109.4 |
| C(4)-C(3)-H(3A) | 109.4 |
| N(1)-C(3)-H(3B) | 109.4 |

| | |
|---|---|
| C(4)-C(3)-H(3B) | 109.4 |
| H(3A)-C(3)-H(3B) | 108.0 |
| O(3)-C(4)-O(1) | 117.24(9) |
| O(3)-C(4)-C(3) | 124.83(9) |
| O(1)-C(4)-C(3) | 117.91(8) |
| N(1)-C(5)-H(5A) | 109.5 |
| N(1)-C(5)-H(5B) | 109.5 |
| H(5A)-C(5)-H(5B) | 109.5 |
| N(1)-C(5)-H(5C) | 109.5 |
| H(5A)-C(5)-H(5C) | 109.5 |
| H(5B)-C(5)-H(5C) | 109.5 |

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Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for dd53zs. The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{23}$ | $U^{13}$ | $U^{12}$ |
|---|---|---|---|---|---|---|
| O(1) | 16(1) | 16(1) | 21(1) | -1(1) | 5(1) | -1(1) |
| O(2) | 17(1) | 32(1) | 26(1) | -1(1) | 10(1) | -1(1) |
| O(3) | 27(1) | 22(1) | 29(1) | -6(1) | 7(1) | 5(1) |
| N(1) | 15(1) | 17(1) | 16(1) | -1(1) | 6(1) | -3(1) |
| C(1) | 17(1) | 19(1) | 15(1) | 1(1) | 5(1) | 1(1) |
| C(2) | 18(1) | 17(1) | 18(1) | -3(1) | 7(1) | -1(1) |
| C(3) | 14(1) | 22(1) | 22(1) | -2(1) | 6(1) | 0(1) |
| C(4) | 17(1) | 18(1) | 15(1) | 1(1) | 3(1) | 3(1) |
| C(5) | 22(1) | 24(1) | 22(1) | -3(1) | 5(1) | -9(1) |

Table 5. Hydrogen coordinates ( x $10^4$) and isotropic displacement parameters ($Å^2$x $10^3$) for dd53zs.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| H(2A) | 5068 | 5851 | 7588 | 20 |
| H(2B) | 6500 | 5024 | 9075 | 20 |
| H(3A) | 8856 | 3875 | 8133 | 23 |
| H(3B) | 9042 | 4010 | 6073 | 23 |
| H(5A) | 7866 | 6793 | 7145 | 35 |
| H(5B) | 9433 | 6061 | 6483 | 35 |
| H(5C) | 9292 | 5924 | 8556 | 35 |

Table 6. Torsion angles [°] for dd53zs.

| | |
|---|---|
| C(4)-O(1)-C(1)-O(2) | -173.87(8) |
| C(4)-O(1)-C(1)-C(2) | 2.84(13) |
| C(3)-N(1)-C(2)-C(1) | -56.66(10) |
| C(5)-N(1)-C(2)-C(1) | -178.28(8) |
| O(2)-C(1)-C(2)-N(1) | -157.58(10) |
| O(1)-C(1)-C(2)-N(1) | 26.01(12) |
| C(2)-N(1)-C(3)-C(4) | 59.15(10) |
| C(5)-N(1)-C(3)-C(4) | -179.25(8) |
| C(1)-O(1)-C(4)-O(3) | 178.43(9) |
| C(1)-O(1)-C(4)-C(3) | -0.08(13) |
| N(1)-C(3)-C(4)-O(3) | 150.27(10) |
| N(1)-C(3)-C(4)-O(1) | -31.35(12) |

Symmetry transformations used to generate equivalent atoms: