# **Supporting Information for**

#### Nickel-Catalyzed Carboxylation of Organoboronates

Yusuke Makida, Enrico Marelli, Alexandra M. Z. Slawin and Steven P. Nolan\*

EaStCHEM School of Chemistry, University of St Andrews, North Haugh, KY16 9ST, UK Fax: +44(0) 1334 463 808, E-mail: snolan@st-andrews.ac.uk

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## **Instrumentation and Chemicals**

NMR spectra were recorded on a Bruker AVANCE 300 spectrometer, operating at 300 MHz for <sup>1</sup>H NMR and 75 MHz for <sup>13</sup>C NMR, or a Bruker AVANCE III 500 spectrometer, operating at 500 MHz for <sup>1</sup>H NMR and 125 MHz for <sup>13</sup>C NMR at 25 °C. Chemical shifts are reported in  $\delta$  ppm. Chemical shift values for <sup>1</sup>H and <sup>13</sup>C are referenced to the residual solvent resonances. The chemical shifts in the <sup>19</sup>F NMR spectra were recorded relative to trichlorofluoromethane ( $\delta$  = 0.00 ppm). Elemental analyses were performed at London Metropolitan University 166-220 Holloway Road, London, N7 8DB. Mass spectrometry was performed by EPSCR National Mass Spectrometry Service Center at Swansea University, Grove building, Singleton Park, Swansea, SA2 8PP, Wales, UK. TLC analysis was performed on commercial polyester sheets bearing 0.20mm layer of silica gel with fluorescent indicater UV<sub>254</sub>. Flash chromatography was performed on silica gel 60 Å pore diameter and 40-63 µm particules size.

All reactions were setted up under a dry argon atmosphere by using standard dry box technics unless otherwise stated. [Ni(cod)<sub>2</sub>] was purchased from Strem Chemicals or Alfa Aesar and stored at -30°C, inside the glovebox. NHC salts and free NHCs were prepared by previously described procedures.<sup>1</sup> Nickel complexes were prepared following literature procedures.<sup>2</sup> KO'Bu and CsF were purchased from Aldrich and Acros Organics, respectively. Anhydrous solvents (1,4-dioxane, tetrahydrofuran (THF), 1,2-dichloroethane (DCE), dimethylacetamide (DMA), toluene, cyclopentylmethylether (CPME)) were purchased from commerchial suppliers, and stored over 4Å molecular sieves under argon. Boronates **2b** and **2j** were obtained from commercial suppliers. Boronates **2a**, **2c-e**, **2g-r** and **4a-c** were synthesized by the esterification

of the corresponding boronic acids. Characterization data for **2a-2c**, **2e-2r** and **4a-c** were reported previously.<sup>3</sup> All carboxylation products are well known, and their spectroscopic data correspond to those previously reported.<sup>3-13</sup>

### **Preparation of Boronates**

Preparation of **2a** is descrived as a representative. In a dry vial, 4-methoxyphenylboronic acid (398 mg, 2.5 mmol), neopentylglycole (286 mg, 2.75 mmol, 1.10 equiv.) and MgSO<sub>4</sub> (ca. 2 g) were suspended in DCM (2.0 mL) and stirred overnight at room temperature. The reaction mixture was filtered through silica gel, washed with hexane/DCM and dried under vacuum, affording **2a** (528 mg, 2.40 mmol, 96%) as a white solid.



#### Typical Procedure for the Nickel-Catalyzed Carboxylation.

(Table 2, entry 1) In a glovebox, [Ni(IPr\*)(allyl)Cl] (1e) (21.0 mg, 0.02 mmol, 5 mol %), boronate 2a (88.0 mg, 0.4 mmol, 1.0 equiv.) and KO'Bu (53.9 mg, 1.2 equiv.) were placed in a Schlenk flask with a stirring bar. Toluene (2.0 mL) was added to the Schlenk and caped with glass stopper. Outside the glovebox, the Schlenk was freezed with liquid N<sub>2</sub>, then under vacuum, followed by purged with CO<sub>2</sub> flow for three times. A balloon was filled with CO<sub>2</sub> (the number of equivalents of CO<sub>2</sub> was estimated at 10 by approximate calculation based on the volume of the balloon) and connected to the Schlenk inlet. Then the schlenk was put in an oil bath at 100°C and stirred for 15 hours. The solution was then cooled to room temperature, diluted with EtOAc and treated with 3 mL of HCl (ca. 3 M). The aqueous phase were extracted with EtOAc (4 mL x 4), dried over MgSO<sub>4</sub> and concentrated under vacuum. The crude was purified by column chromatography on silica gel (hexane/DCM/MeOH 1:2:0 to 0:20:1) to afford **3a** (58.4 mg, 0.38 mmol) in 96% yield as a white solid.



## **Reactions with Other Boron Reagents.**

Following the above typical procedure, reactivities of phenylboronic acid, phenylboronic acid pinacol ester and potassium phenyltrifluoroborate were investigated. Reactions were analysed by <sup>1</sup>H NMR spectroscopy of crude material after acidic work up. None of these afforded carboxylation product.



### **Synthesis of Borates**

NMR monitering of the convertion of 2h into 6h. Inside a glovebox, boronate 2h (25.8 mg, 0.1 mmol) and KO'Bu (11.2 mg, 0.1 mmol) were placed in a vial and dissolved in 0.6 mL benzene- $d_6$ . Then the mixture was transferred to an NMR tube equipped with *J*-Young valve. All NMR mesurements were conducted at room temperature after mechanical stirring for 30 minutes. Spectroscopic data indicate complete consumption of 2h.



**Isolation of borate 6f**. Inside a glovebox, boronate **2f** (208.0 mg, 1.0 mmol) and KO'Bu (112.2 mg, 1.0 mmol) were dissolved in 5 mL THF in a round bottomed flask equipped with a stirring bar and let react for 1 hour. The product was precipitated adding cold pentane and cooling the mixture in the fridge, then the supernatant was removed and the product was washed with cold pentane. The solid was dried under vacuum to afford **6f** (303.0 mg) in 95% yield.



**Characterisation of the borate 6f.** Elemental analysis and mass spectrometry did not yields satisfactory results to enable the unambiguous characterization of **6f**. We resorted to grow crystals by slow diffusion of pentane in concentrate solution of the compound in diethyl ether, and crystals of **6f**  $\cdot \frac{1}{2}$ THF were obtained. The structure of this species and the crystal structure are presented below.



The <sup>1</sup>H, <sup>13</sup>C, <sup>11</sup>B and <sup>19</sup>F NMR spectra obtained by analyzing the crystals were superimposable to those obtained previously and are reported here, thus demonstrating the identity of **6f** as a potassium arylborate salt. The presence of a solvation molecule suggests that this species has a propensity to aggregate, especially in a non-coordinating solvent such as toluene. We propose that the aggregate is cleaved at the reaction temperature, leading to the reactive monomer that is then activated by the catalyst.

#### **Reactivity Experiments of Borate 6f**

Using precatalyst 1e with KO'Bu. Inside a glovebox, [Ni(IPr\*)(allyl)Cl] (21.0 mg, 0.020 mmol, 5 mol %), borate 6f (128.1 mg, 0.4 mmol) and KO'Bu (3.0 mg, 0.028 mmol, 7 mol %) were weighted in a Schlenk flask equipped with a stirring bar and a cap, and dissolved in toluene (2.0 mL). The typical procedure for the carboxylation was then followed. <sup>1</sup>H NMR spectroscopic analysis of crude reaction mixture showed >95% conversion from 6f into 3f.



Using precatalyst 1e without KO'Bu. Inside a glovebox, [Ni(IPr\*)(allyl)Cl] (21.0 mg, 0.020 mmol, 5 mol %) and borate 6f (128.1 mg, 0.4 mmol) were weighted in a Schlenk flask equipped with a stirring bar and a cap, and dissolved in toluene (2.0 mL). The typical

procedure for the carboxylation was then followed. <sup>1</sup>H NMR spectroscopic analysis of crude reaction mixture showed 82% conversion from **6f** into **3f**.



Using precatalyst 1e with KO'Bu. Inside a glovebox,  $[Ni(cod)_2]$  (5.5 mg, 0.020 mmol, 5 mol %), free IPr\* (21.9 mg, 0.024 mmol, 6 mol %) and borate 6f (128.1 mg, 0.4 mmol) were weighted in a Schlenk flask equipped with a stirring bar and a cap, and dissolved in toluene (2.0 mL). The typical procedure for the carboxylation was then followed. <sup>1</sup>H NMR spectroscopic analysis of crude reaction mixture showed 61% conversion of 6f into 3f.



Characterization Data.

# 2-(4-tert-Butyldimethylsilyloxyphenyl)-5,5-dimethyl-1,3,2-dioxaborinane (2d)



White solid.

<sup>1</sup>**H NMR** (300 MHz, CDCl<sub>3</sub>) *δ* 7.79 (d, *J* = 8.4 Hz, 2H), 6.83 (d, *J* = 8.4 Hz, 2H), 3.75 (s, 4H), 1.02 (s, 6H), 0.98 (s, 9H), 0.20 (s, 6H).

<sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  158.06, 135.40, 119.44, 72.24, 31.87, 25.68, 21.93, 18.23, 4.39.

**HRMS–ESI** (m/z):  $[M+H]^+$  calcd for  $[C_{17}H_{30}BO_3Si]^+$ , 321.2052; found, 321.2055.

p-Anisic acid (3a)<sup>3</sup>



White solid.

<sup>1</sup>**H NMR** (300 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  12.64 (bs, 1H), 7.89 (d, *J* = 9.0 Hz, 2H), 7.01 (d, *J* = 9.0 Hz, 2H), 3.82 (s, 3H).

<sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, DMSO-*d*<sub>6</sub>) δ 166.99, 162.82, 131.33, 122.96, 113.79, 55.42.

Benzoic acid (3b)<sup>3</sup>

White solid.

<sup>1</sup>**H** NMR (300 MHz, DMSO- $d_6$ )  $\delta$  8.00–7.87 (m, 2H), 7.62 (tt, J = 7.5, 1.5 Hz, 1H), 7.50–7.43 (m, 2H).

<sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, DMSO-*d*<sub>6</sub>) δ 167.30, 132.84, 130.75, 129.25, 128.55.

p-Toluic acid (3c)<sup>6</sup>



White solid.

<sup>1</sup>**H NMR** (500 MHz, CDCl<sub>3</sub>)  $\delta$  8.02 (d, J = 8.0 Hz, 2H), 7.28 (d, J = 8.0 Hz, 2H), 2.44 (s, 3H).

<sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, DMSO-*d*<sub>6</sub>) δ167.30, 144.64, 130.30, 129.19, 126.56, 21.76.

4-tert-Butyldimethylsilyloxybenzoic acid (3d)<sup>10</sup>

Yellow solid.

<sup>1</sup>**H** NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  8.34 (d, J = 8.7 Hz, 2H), 6.90 (d, J = 8.7 Hz, 2H), 1.00 (s, 9H), 0.25 (s, 6H).

<sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, CDCl<sub>3</sub>) δ 172.13, 160.85, 132.30, 122.30, 119.92, 91.61, 25.57, 18.24, -4.38.

4-N,N-Dimethylaminobenzoic acid (3e)<sup>9</sup>



Brown solid.

<sup>1</sup>**H NMR** (300 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  12.13 (bs, 1H), 7.75 (d, *J* = 9.0 Hz, 2H), 6.70(d, *J* = 9.0 Hz, 2H), 2.92 (s, 6H).

<sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, DMSO-*d*<sub>6</sub>) δ 167.56, 153.07, 130.07, 116.90, 110.78, 39.66.

4-Fluorobenzoic acid (3f)<sup>3</sup>



White solid.

<sup>1</sup>**H NMR** (500 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  8.01 (dd, *J* = 8.5, 5.5 Hz, 2H), 7.31 (t, *J* = 8.5 Hz, 2H), 3.88 (s, 3H).

<sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, DMSO- $d_6$ )  $\delta$  164.91 (d, J = 249 Hz), 166.34, 132.12 (d, J = 9.45 Hz), 127.38, 115.10 (d, J = 21.83).

<sup>19</sup>F{<sup>1</sup>H} NMR (282.3 MHz, DMSO- $d_6$ )  $\delta$  –102.65.

4-Chlorobenzoic acid (3g)<sup>9</sup>



White solid.

<sup>1</sup>**H** NMR (300 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  7.94 (d, *J* = 8.6 Hz, 2H), 7.56 (d, *J* = 8.6 Hz, 2H). <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  166.44, 137.77, 131.13, 129.63, 128.73.

4-Trifluoromethylbenzoic acid (3h)<sup>3</sup>



White solid.

<sup>1</sup>**H** NMR (500 MHz, DMSO- $d_6$ )  $\delta$  8.12 (d, J = 8.3 Hz, 2H), 7.85 (d, J = 8.4 Hz, 2H). <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, DMSO- $d_6$ )  $\delta$  166.22, 134.61, 132.50 (q, J = 31.8 Hz), 130.16, 125.58 (q, J = 3.4 Hz), 123.82 (q, J = 271.1 Hz).

<sup>19</sup>F{<sup>1</sup>H} NMR (470.5 MHz, DMSO- $d_6$ )  $\delta$ -61.67.

4-Methoxycarbonylbenzoic acid (3i)<sup>3</sup>



White solid.

<sup>1</sup>**H NMR** (300 MHz, DMSO-*d*<sub>6</sub>) δ 8.06 (s, 4H), 3.87 (s, 3H).

<sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, DMSO-*d*<sub>6</sub>) δ 166.55, 165.59, 134.82, 133.14, 129.57, 129.32, 52.44.

4-Cyanobenzoic acid (3j)<sup>6</sup>



Brown solid.

<sup>1</sup>**H** NMR (300 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  8.08 (d, *J* = 8.6 Hz, 2H), 7.97 (d, *J* = 8.6 Hz, 2H). <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  166.08, 134.85, 132.70, 129.94, 118.21, 115.08.

*m*-Anisidic acid (3k) <sup>9</sup>



White solid.

<sup>1</sup>**H NMR** (300 MHz, CDCl<sub>3</sub>) *δ* 7.73(dt, *J* = 8.1, 1.1 Hz, 1H), 7.63 (dd, *J* = 2.6, 1.1 Hz, 1H), 7.39 (t, *J* = 8.1 Hz, 1H), 7.16 (ddd, *J* = 8.1, 2.6, 1.1 Hz, 1H), 3.87 (s, 3H).

<sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, CDCl<sub>3</sub>) *δ* 172.23, 159.56, 130.53, 129.51, 122.67, 120.48, 114.34, 55.44.

3-Fluorobenzoic acid (3l)<sup>7</sup>



Yellow solid.

<sup>1</sup>**H NMR** (300 MHz, CDCl<sub>3</sub>) *δ* 7.92 (ddd, *J* = 7.5, 1.5, 0.9 Hz, 1H), 7.80 (dm, *J* = 9.0 Hz, 1H), 7.49 (m, 1H), 7.33 (m, 1H).

<sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  170.88, 164.19, 130.20 (d, J = 7.7 Hz), 125.99, 120.95 (d, J = 53.9 Hz), 117.12 (d, J = 52.1 Hz) (Some signals were not observed).

<sup>19</sup>F{<sup>1</sup>H} NMR (282.3 MHz, CDCl<sub>3</sub>) δ-112.48.

3-Trifluoromethylbenzoic acid (3m) 11

White solid.

<sup>1</sup>**H NMR** (300 MHz, CDCl<sub>3</sub>) *δ* 12.31 (bs, 1H), 8.39 (s, 1H), 8.32 (d, *J* = 8.0 Hz, 1H), 7.88 (d, *J*=7.5 Hz, 1H), 7.64 (dd, *J*= 8.0, 7.5 Hz, 1H).

<sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  171.24, 133.38, 131.28 (q, J = 31.9 Hz), 130.44 (q, J = 1.4 Hz), 130.05, 129.48, 127.15 (q, J = 3.8 Hz), 123.35 (q, J = 270.9 Hz).

<sup>19</sup>F{<sup>1</sup>H} NMR (470.5 MHz, CDCl<sub>3</sub>) δ-62.91.

3-Methoxycarbonylbenzoic acid (3n)<sup>3</sup>



White solid.

<sup>1</sup>**H NMR** (300 MHz, DMSO- $d_6$ )  $\delta$  8.47 (d, J = 1.2 Hz, 1H), 8.23–8.13 (m, 2H), 7.65 (t, J = 7.5 Hz, 1H), 3.88 (s, 3H).

<sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, DMSO-*d*<sub>6</sub>) δ 166.47, 165.55, 133.78, 133.21, 131.37, 130.04, 129.78, 129.36, 52.43.

o-Anisidic acid (30)<sup>3</sup>



White solid.

<sup>1</sup>**H NMR** (300 MHz, CDCl<sub>3</sub>)  $\delta$  8.10 (dt, J = 7.8, 1.8 Hz, 1H), 7.57–7.50 (m, 1H), 7.12–7.00 (m, 2H), 4.03 (s, 3H).

<sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, CDCl<sub>3</sub>) δ165.93, 158.06, 133.99, 133.40, 121.81, 117.36, 111.60, 56.50.

2-Fluorobenzoic acid (3p)<sup>12</sup>



Yellow solid.

<sup>1</sup>**H NMR** (300 MHz, CDCl<sub>3</sub>) *δ* 11.74 (bs, 1H), 8.06 (m, 1H), 7.61 (m, 1H), 7.29–7.14 (m, 2H).

<sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  169.92, 162.62 (d, J = 260.6 Hz), 135.61 (d, J = 9.2 Hz), 132.73, 124.11 (d, J = 3.9 Hz), 117.34 (d, J = 8.9 Hz), 117.15 (d, J = 22.0 Hz).

<sup>19</sup>**F**{<sup>1</sup>**H**} **NMR** (282.3 MHz, CDCl<sub>3</sub>): *δ*-108.61.

3-Thenoic acid (3q)<sup>9</sup>



Brown solid.

<sup>1</sup>**H** NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  11.15 (bs, 1H), 8.25 (dd, J = 3.0, 1.1 Hz, 1H), 7.61 (dd, J = 5.4, 1.1 Hz, 1H), 7.34 (dd, J = 5.4, 3.0 Hz, 1H).

<sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, CDCl<sub>3</sub>) δ168.14, 134.60, 132.85, 128.10, 126.34.

2-Furoic acid (3r)<sup>5</sup>



White solid.

<sup>1</sup>**H** NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  10.74 (bs, 1H), 7.65 (dd, J = 1.8, 0.9 Hz, 1H) 7.61 (dd, J = 3.5, 0.9 Hz, 1H), 7.3-7.1 (dd, J = 3.5, 1.8 Hz, 1H).

<sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, CDCl<sub>3</sub>): δ163.68, 147.45, 143.76, 120.19, 112.28.

(*E*)-Cinnamic acid  $(5a)^5$ 



Off white solid.

<sup>1</sup>**H NMR** (300 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  12.43 (bs, 1H), 7.75–7.63 (m, 2H), 7.58 (d, *J* = 16.2 Hz, 1H), 7.47–7.34 (m, 3H), 6.53 (d, *J* = 16.2 Hz, 1H).

<sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, DMSO-*d*<sub>6</sub>) δ 167.55, 143.91, 134.21, 130.20, 128.88, 128.18, 119.21.

(E)-4-Phenyl-2-butenoic acid (5b)<sup>13</sup>



White solid.

<sup>1</sup>**H NMR** (300 MHz, CDCl<sub>3</sub>)  $\delta$  7.33–7.15 (m, 6H), 5.87 (dt, J = 15.6, 1.4 Hz, 1H), (dd, J = 6.6, 1.4 Hz, 2H).

<sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, CDCl<sub>3</sub>) δ171.82, 150.24, 137.78, 128.78, 128.73, 126.77, 121.59, 38.53.



White solid.

<sup>1</sup>**H NMR** (300 MHz, CDCl<sub>3</sub>) *δ*7.50–7.35 (m, 5H), 6.57 (d, *J* = 1.2 Hz, 1H), 6.04 (d, *J* = 1.2 Hz, 1H).

<sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, CDCl<sub>3</sub>) δ172.20, 140.54, 136.04, 129.55, 128.44, 128.35, 128.23.

**Borate 6f** 



White solid.

<sup>1</sup>**H NMR** (500 MHz, THF- $d_8$ )  $\delta$  7.46 (t, J = 7.5 Hz, 2H), 6.74 (t, J = 7.5 Hz, 2H), 3.25 (d, J = 10.0 Hz, 2H) 3.21(d, J = 10.0 Hz, 2H), 1.05 (s, 12 H), 0.52 (s, 3H).

<sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, THF- $d_8$ )  $\delta$  161.86 (d, J = 236.6 Hz), 137.92, 135.30 (d, J = 6.1Hz), 112.78 (d, J = 17.9 Hz), 73.06, 67.21, 33.40, 32.77, 24.74, 23.02.

<sup>19</sup>**F**{<sup>1</sup>**H**} **NMR** (470.5 MHz, THF- $d_8$ )  $\delta$ -122.54.

<sup>11</sup>**B NMR** (160.5 MHz, THF-*d*<sub>8</sub>) δ 3.31.

**Borate 6h** 



<sup>1</sup>**H** NMR (300 MHz, benzene- $d_6$ )  $\delta$  7.65 (d, J = 7.5 Hz, 2H), 6.75 (d, J = 7.5 Hz, 2H), 3.35 (d, J = 10.0 Hz, 2H), 3.29 (d, J = 10.0 Hz, 2H), 1.09 (bs, 9 H), 0.96 (s, 3H), 0.82 (s, 3H).

<sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, benzene- $d_6$ )  $\delta$  133.64, 124.18 (d, J = 3.5 Hz), 72.05, 68.68, 32.85, 32.71, 24.70, 23.41 (Some signals were not observed).

<sup>19</sup>**F**{<sup>1</sup>**H**} **NMR** (282.3 MHz, benzene- $d_6$ )  $\delta$ -61.83.

<sup>11</sup>**B** NMR (96.3 MHz, benzene- $d_6$ )  $\delta$  3.21.

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![](_page_21_Figure_1.jpeg)

![](_page_22_Figure_0.jpeg)

10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240 -250

![](_page_23_Figure_0.jpeg)

![](_page_24_Figure_0.jpeg)

220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1

![](_page_25_Figure_0.jpeg)

![](_page_25_Figure_1.jpeg)

![](_page_26_Figure_0.jpeg)

![](_page_27_Figure_0.jpeg)

0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240 -25

![](_page_28_Figure_0.jpeg)

![](_page_28_Figure_1.jpeg)

![](_page_29_Figure_0.jpeg)

b

--62.911

-10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -2

![](_page_30_Figure_0.jpeg)

![](_page_30_Figure_1.jpeg)

![](_page_31_Figure_0.jpeg)

![](_page_31_Figure_1.jpeg)

![](_page_32_Figure_0.jpeg)

![](_page_32_Figure_1.jpeg)

![](_page_33_Picture_0.jpeg)

0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240 -25

![](_page_34_Figure_0.jpeg)

![](_page_35_Figure_0.jpeg)

0 -1 

![](_page_36_Figure_0.jpeg)

![](_page_37_Figure_0.jpeg)

![](_page_37_Figure_1.jpeg)

![](_page_38_Figure_0.jpeg)

![](_page_38_Figure_1.jpeg)

-1 

![](_page_39_Figure_0.jpeg)

![](_page_39_Figure_1.jpeg)

![](_page_40_Figure_0.jpeg)

10

0 -10 -20 -30 -40

-50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240 -250

90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140

![](_page_41_Figure_0.jpeg)

![](_page_42_Figure_0.jpeg)

![](_page_43_Picture_0.jpeg)

After crystallization.

![](_page_43_Figure_2.jpeg)

![](_page_44_Figure_0.jpeg)