

## Supplementary Material

# Substituent Effects in $\pi$ -Stacking of Activated Benzotriazoles

**Daniel S. Wenzholz<sup>1</sup>, Mohan Bhadbhade<sup>2</sup>, Hakan Kandemir<sup>1</sup>, Junming Ho<sup>1</sup>, Naresh  
Kumar<sup>1</sup> and David StC Black<sup>\*,1</sup>.**

<sup>1</sup>School of Chemistry, UNSW Sydney, Australia

<sup>2</sup>Mark Wainwright Analytical Centre, UNSW Sydney, Australia

\* *Corresponding author: Tel: +61 2 9385 4657; Fax: +61 2 9385 6141; E-mail:  
[d.black@unsw.edu.au](mailto:d.black@unsw.edu.au)*

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## **General**

Reagents and solvents were purchased from Ajax Finechem, Alfa Aesar, Chem-Supply, Chem-Impex and Sigma-Aldrich, and used without further purification. Anhydrous acetonitrile, dichloromethane and toluene were obtained from a PureSolv MD Solvent Purification System. Flash column chromatography was performed using Grace Davisil LC60A 40-63  $\mu\text{m}$  silica gel. Reaction progress was monitored by thin layer chromatography (TLC) using Merck TLC Silica gel 60 F254 aluminium sheets.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were recorded on Bruker Avance III 300 MHz and Bruker Avance III HD 400 MHz spectrometers. Melting points were measured using a SRS MPA100 OptiMelt instrument and are reported without correction. IR spectra were acquired on a Cary 630 ATR FTIR spectrophotometer. HRMS spectra were acquired using a Thermo Scientific LTQ Orbitrap XL MS (electrospray ionization mode).

## **Experimental Procedures and Characterisation Data**

### ***N*-Acetyl-4,6-dimethoxy-1*H*-benzo[1,2,3]triazole (1)**

Acetamide **5** (4.30 g, 20.4 mmol) was suspended in 5 M hydrochloric acid (30 mL) and cooled on ice. An ice cooled solution of  $\text{NaNO}_2$  (2.18 g, 30.7 mmol) in water (18 mL) was added slowly dropwise. After stirring for 10 min at 0  $^\circ\text{C}$  the white product was filtered, washed with water and recrystallised from acetonitrile to afford *N*-acetyl-4,6-dimethoxy-1*H*-benzo[1,2,3]triazole **1** (3.92 g, 87%) as white crystals. Mp 195-196  $^\circ\text{C}$ . (Found: C, 54.22; H, 5.07; N, 18.83;  $\text{C}_{10}\text{H}_{11}\text{N}_3\text{O}_3$  requires C, 54.29; H, 5.01; N, 19.0%).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  2.88 (s, 3H, Me), 3.82 (s, 3H, OMe), 3.99 (s, 3H, OMe), 6.36 (d,  $J = 1.96$  Hz, 1H, H5), 7.13 (d,  $J = 1.96$  Hz, 1H, H7).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  23.79 (Me), 56.53, 56.82 (OMe), 88.21 (C5), 98.64 (C7), 133.86, 134.33, 152.15, 164.22 (aryl C), 170.46 (C=O). IR (KBr):  $\nu_{\text{max}}$  1740, 1613, 1508, 1421, 1365, 1290, 1207, 1157, 1037, 944, 671  $\text{cm}^{-1}$ . UV-vis (MeOH):  $\lambda_{\text{max}}$  217 nm ( $\epsilon$  35,600  $\text{cm}^{-1}\text{M}^{-1}$ ), 272 (8,920). HRMS (+ESI): Found  $m/z$  222.0870  $[\text{M}+\text{H}]^+$ ;  $\text{C}_{10}\text{H}_{11}\text{N}_3\text{O}_3$  required 222.0879.

### ***N*-(3,5-Dimethoxyphenyl)acetamide (3)**

3,5-Dimethoxyaniline **2** (8.37 g, 54.6 mmol) was added to ice cooled acetic anhydride (30 mL) and stirred for 2 h. After confirmation of consumption of starting material by TLC, the reaction mixture was poured into 300 mL of ice water and stirred for 30 min before collecting solid *via* filtration to yield *N*-(3,5-dimethoxyphenyl)acetamide **3** (9.99 g, 94%) as grey crystals. Mp 155-156 °C (lit 157 °C).<sup>1</sup> <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): □ 2.15 (s, 3H, Me), 3.76 (s, 6H, OMe), 6.23 (t, *J* = 1.80 Hz, 1H, H4), 6.74 (d, *J* = 1.80 Hz, 2H, H2, H6), 7.30 (bs, 1H, NH). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): □ 24.88 (Me), 55.50 (OMe), 96.71 (C4), 98.19 (C2, C6), 139.78 (C1), 161.16 (C3, C5), 168.51 (C=O).

### ***N*-(3,5-Dimethoxy-2-nitrophenyl)acetamide (4)**

A suspension of Acetamide **3** (5.91 g, 30.3 mmol) in acetic anhydride (100 mL) was cooled in a salt/ice slurry. A separate solution of 70% nitric acid (3.0 mL, 46 mmol) in acetic anhydride (50 mL) was likewise cooled before being added slowly dropwise to this suspension over half an hour with stirring. After all of the nitric acid solution was added, the mixture was left to stir whilst being cooled for a further half an hour. After this time, the mixture was poured into 0.5 L of ice water and stirred overnight. The resulting precipitate was collected by filtration, washed with excess water and recrystallised from dichloromethane/light petroleum to obtain *N*-(3,5-dimethoxy-2-nitrophenyl)acetamide **4** (4.30 g, 59%) as yellow needles. Mp 146-147 °C (lit 148-149 °C).<sup>2</sup> <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): □ 2.21 (s, 3H, Me), 3.87 (s, 3H, OMe), 3.88 (s, 3H, OMe), 6.27 (d, *J* = 2.40, 1H, H4), 7.69 (d, *J* = 2.40, 1H, H6), 9.17 (bs, 1H, NH). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): □ 25.52 (Me), 56.06, 56.78 (OMe), 95.77 (C4), 97.84 (C6), 135.40, 155.57, 163.66 (aryl C), 169.01 (C=O).

### ***N*-(2-Amino-3,5-dimethoxyphenyl)acetamide (5)**

Nitroacetamide **4** (6.32 g, 26.3 mmol) and 10 % Pd/C (0.63 g) were suspended in absolute ethanol (250 mL) under nitrogen and brought to reflux. Hydrazine monohydrate (12.8 mL, 263 mmol) was added dropwise over 15 min, after which the mixture was refluxed for a further 2 h. The solution was filtered and filtrate collected. The solvent was removed *in vacuo* and the residue dissolved in dichloromethane before being washed with brine and dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure to yield *N*-(2-amino-3,5-dimethoxyphenyl)acetamide **5** (5.40 g, 98%) as a brown solid. Mp 86-88 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): □ 2.07 (s, 3H, Me), 3.67 (s, 3H, OMe), 3.77 (s, 3H, OMe), 3.83 (s, 2H, NH<sub>2</sub>), 6.28 (d, *J* = 1.89, 1H, H<sub>4</sub>), 6.57 (d, *J* = 1.89, 1H, H<sub>6</sub>), 8.02 (br s, 1H, NH). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): □ 23.55 (Me), 55.51, 55.65 (OMe), 96.66 (C<sub>4</sub>), 100.19 (C<sub>6</sub>), 122.57, 126.15, 150.06, 153.16 (aryl C), 168.85 (C=O). IR (KBr):  $\nu_{\max}$  3459, 3424, 3321, 3226, 1652, 1601, 1544, 1459, 1371, 1276, 1205, 1150, 1051, 800 cm<sup>-1</sup>. UV-vis (MeOH):  $\lambda_{\max}$  211 nm ( $\epsilon$  52,400 cm<sup>-1</sup>M<sup>-1</sup>), 299 nm (7,700). HRMS (+ESI): Found *m/z* 211.1028 [M+Na]<sup>+</sup>; C<sub>8</sub>H<sub>7</sub>N<sub>3</sub>O<sub>3</sub>Na required 211.1077.

### **4,6-Dimethoxy-1*H*-benzo[1,2,3]triazole (6)**

A solution of benzotriazole **1** (0.98 g, 4.4 mmol) in methanol (20 mL) was stirred with potassium hydroxide (0.50 g, 8.9 mmol) at room temperature for 30 min. The mixture was then diluted with ice water and pH adjusted to pH-5 with 10% H<sub>3</sub>PO<sub>4</sub>. The resulting precipitate was filtered, washed with water and dried to yield 4,6-dimethoxy-1*H*-benzo[1,2,3]triazole **6** (0.73 g, 86%) as a white solid. Single crystal obtained from acetonitrile. Mp 209-211 °C. <sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>): □ 3.84 (s, 3H, OMe), 3.98 (s, 3H, OMe), 6.36 (d, *J* = 1.63 Hz, 1H, H<sub>5</sub>), 6.73 (s, 1H, H<sub>7</sub>). <sup>13</sup>C NMR (75 MHz, DMSO-*d*<sub>6</sub>): □ 56.05, 56.28 (OMe), 83.67 (C<sub>5</sub>), 96.67 (C<sub>7</sub>), 132.57, 135.72, 151.13, 160.65 (aryl C). IR

(KBr):  $\nu_{\max}$  3319, 1627, 1524, 1469, 1432, 1154, 933, 828  $\text{cm}^{-1}$ . UV-vis (MeOH):  $\lambda_{\max}$  217 nm ( $\epsilon$  29,500  $\text{cm}^{-1}\text{M}^{-1}$ ), 273 (7,490). HRMS (+ESI):  $\text{C}_8\text{H}_9\text{N}_3\text{O}_2$   $[\text{M}+\text{Na}]^+$  requires 202.0587, found 202.0600.

#### ***N*-Acetyl-1*H*-benzo[1,2,3]triazole (8)**

Benzotriazole **7** (0.80 g, 6.7 mmol) was dissolved under nitrogen in dry dichloromethane (16 mL) and the solution cooled in an ice bath before adding triethylamine (1.1 mL, 8.0 mmol) followed by acetyl chloride (0.52 mL, 7.4 mmol). The mixture was stirred at 0 °C for 30 min before being warmed to room temperature and washed with 2 M hydrochloric acid (3 x 10 mL), water (2 x 50 mL) and brine (10 mL). The organic phase was dried over anhydrous sodium sulfate before the solvent was removed *in vacuo*, affording *N*-acetyl-1*H*-benzo[1,2,3]triazole **8** (0.84 g, 78%) as white opaque crystals. Single crystal obtained from light petroleum. Mp 47-48 °C (lit 49 °C).<sup>3</sup>  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  3.01 (s, 3H, Me), 7.51 (t,  $J = 7.7$  Hz, 1H), 7.66 (t,  $J = 7.6$  Hz, 1H), 8.12 (d,  $J = 8.3$  Hz, 1H), 8.29 (d,  $J = 8.2$  Hz, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  23.37 (Me), 114.56, 120.31, 126.32, 130.57 (aryl CH), 131.17, 146.43 (aryl C), 169.76 (C=O).

#### ***N*-Acetyl-4,6-dihydroxy-1*H*-benzo[1,2,3]triazole (9)**

*N*-acetyl triazole **1** (0.80 g, 3.6 mmol) was dissolved in dried toluene (8 mL) and anhydrous aluminium chloride (1.94 g, 14.5 mmol) was added under a nitrogen atmosphere and the mixture heated to 150 °C for 1.5 h. After cooling to room temperature, the mixture was diluted with ice water (80 mL) and extracted with ethyl acetate (3 x 25 mL). The combined organic layers were with 2M hydrochloric acid (2 x 20 mL) and brine (20 mL) before being dried over anhydrous sodium sulfate. Solvent was removed *in vacuo* and product purified by column chromatography (ethyl acetate/*n*-hexane) to obtain *N*-acetyl-4,6-dihydroxy-1*H*-benzo[1,2,3]triazole **9** (0.22 g, 31%) as a brown solid. Single crystal was obtained from

tetrahydrofuran. Mp 213 °C. <sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>): □ 2.84 (s, 3H, Me), 6.37 (d, *J* = 2.10 Hz, 1H, H5), 6.96 (d, *J* = 2.10 Hz, 1H, H7), 10.25 (bs, 1H, OH), 11.01 (bs, 1H, OH). <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>): □ 23.16, 89.47 (C5), 100.47 (C7), 131.88, 133.59, 150.34, 161.82 (aryl C), 169.83 (C=O). IR (neat):  $\nu_{\max}$  3287, 3135, 1713, 1627, 1407, 1288, 1160, 1085, 949, 815 cm<sup>-1</sup>. UV-vis (MeCN):  $\lambda_{\max}$  234 nm ( $\epsilon$  14,900 cm<sup>-1</sup>M<sup>-1</sup>), 352 nm (4,640). HRMS (+ESI): Found *m/z* 216.0380, [M+Na]<sup>+</sup>; C<sub>8</sub>H<sub>7</sub>N<sub>3</sub>O<sub>3</sub>Na required 216.0380.

#### **4,6-Dimethoxy-*N*-formyl-1*H*-benzo[1,2,3]triazole (10)**

A mixture of acetic anhydride (0.20 mL, 2.1 mmol) and formic acid (0.16 mL, 4.2 mmol) was heated with stirring to 55 °C for 3 h. After cooling to room temperature, the mixture was added slowly dropwise to a salt ice bath cooled suspension of parent benzotriazole **6** (0.27 g, 1.4 mmol) in dry tetrahydrofuran (3 mL) under nitrogen. The resulting mixture was stirred for 1 h while being kept cooled in a salt ice bath, after which the solvent was removed *in vacuo* and the residue diluted with ice water (30 mL) and stirred for 15 min. The white precipitate formed was collected via filtration, washed with water and recrystallised from acetonitrile yielding 4,6-dimethoxy-*N*-formyl-benzo[1,2,3]triazole **10** (0.20 g, 66%) as white crystals. Mp 172-173 °C. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>): □ 3.90 (s, 3H, OMe), 4.03 (s, 3H, OMe), 6.69 (d, *J* = 1.6 Hz, 1H, H5), 7.14 (d, *J* = 1.6 Hz, 1H, H7), 9.93 (s, 1H, CHO). <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>): □ 56.21, 56.51 (OMe), 86.86 (C5), 98.65 (C7), 132.55, 132.58, 151.58, 161.72 (aryl C), 163.56 (C=O). IR (neat):  $\nu_{\max}$  3113, 1738, 1721, 1598, 1427, 1277, 1077, 834, 802 cm<sup>-1</sup>. UV-vis (MeCN):  $\lambda_{\max}$  285 nm ( $\epsilon$  12,500 cm<sup>-1</sup>M<sup>-1</sup>), 313 nm (9,480). HRMS (+ESI): Found *m/z* 202.0583, [M+Na-CO]<sup>+</sup>; C<sub>8</sub>H<sub>9</sub>N<sub>3</sub>O<sub>2</sub>Na required 202.0592.

#### **Methyl *N*-carboxylate-4,6-dimethoxy-1*H*-benzo[1,2,3]triazole (11)**

Parent benzotriazole **6** (0.10 g, 0.52 mmol) was dissolved in dry tetrahydrofuran (5 mL) and triethyl amine (0.16 g, 1.6 mmol) was added, followed by triphosgene (0.16 g, 0.52 mmol).

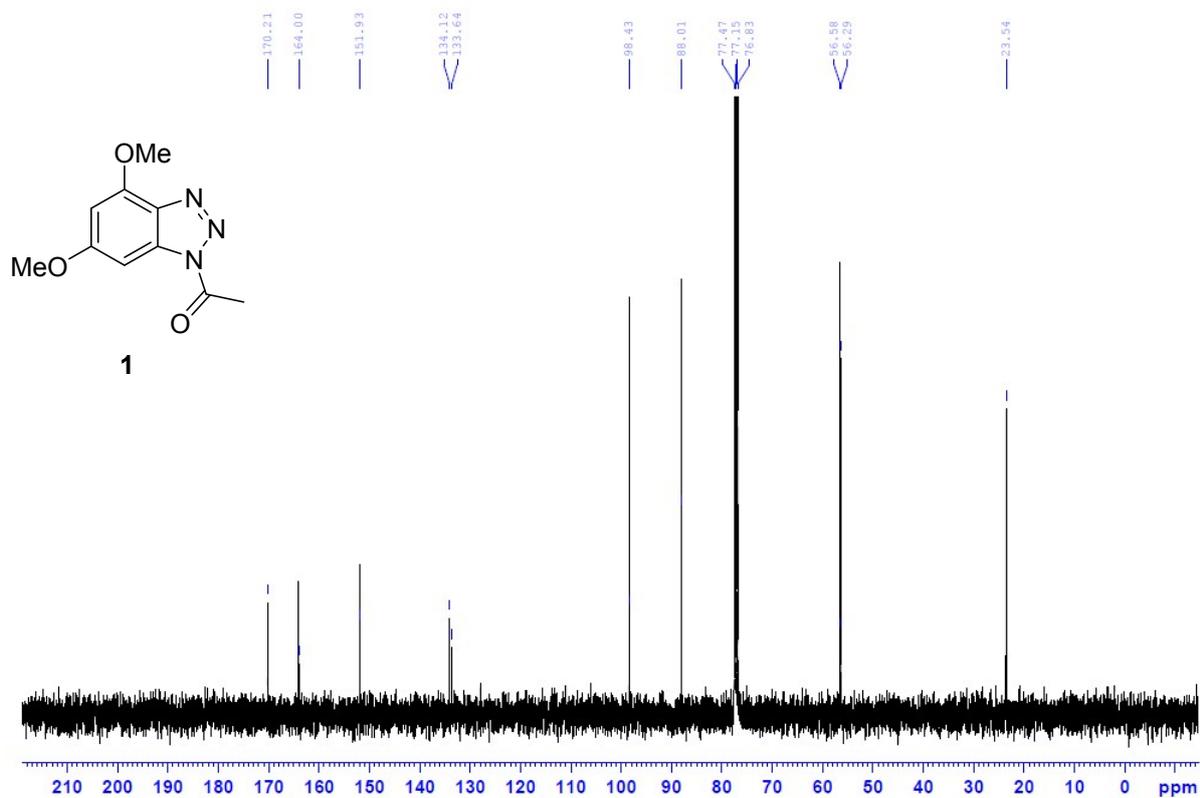
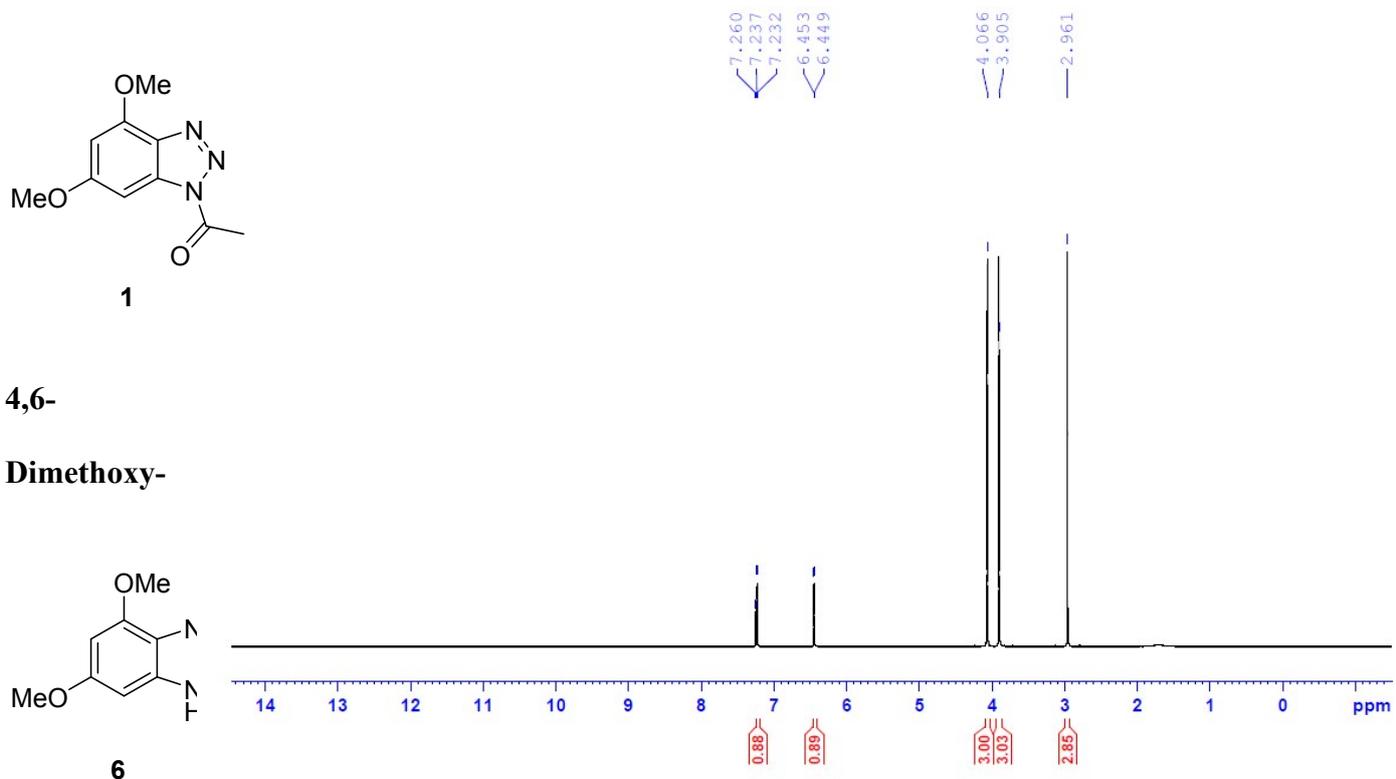
The reaction was left to stir at room temperature for 1 h, upon which it was quenched with excess methanol. The crude mixture was purified *via* column chromatography (ethyl acetate/*n*-hexane) to yield *methyl N-carboxylate-4,6-dimethoxy-benzo[1,2,3]triazole 11* (0.080 g, 65%) as a white solid. Single crystal was obtained from acetonitrile. Mp 171 °C. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>): □ 3.90 (s, 3H, OMe), 4.02 (s, 3H, OMe), 4.13 (s, 3H, OMe), 6.64 (d, *J* = 2.0 MHz, 1H, H5), 7.02 (d, *J* = 2.0 MHz, 1H, H7). <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>): □ 55.29, 56.12, 56.42 (OMe), 87.05 (C5), 97.66 (C7), 132.27, 134.31, 149.13, 151.58 (aryl C), 163.18 (C=O). IR (neat):  $\nu_{\max}$  3123, 2951, 2850, 1742, 1601, 1505, 1451, 1423, 1292, 1205, 1157, 1026, 829, 801, 756. UV-vis (MeCN):  $\lambda_{\max}$  215 nm ( $\epsilon$  52,800 cm<sup>-1</sup>M<sup>-1</sup>), 273 (22,600). HRMS (+ESI): Found *m/z* 260.0640, [M+Na]<sup>+</sup>; C<sub>10</sub>H<sub>11</sub>N<sub>3</sub>O<sub>4</sub>Na required 260.0642.

#### ***N*-Chloroacetyl-4,6-dimethoxy-1*H*-benzo[1,2,3]triazole (12)**

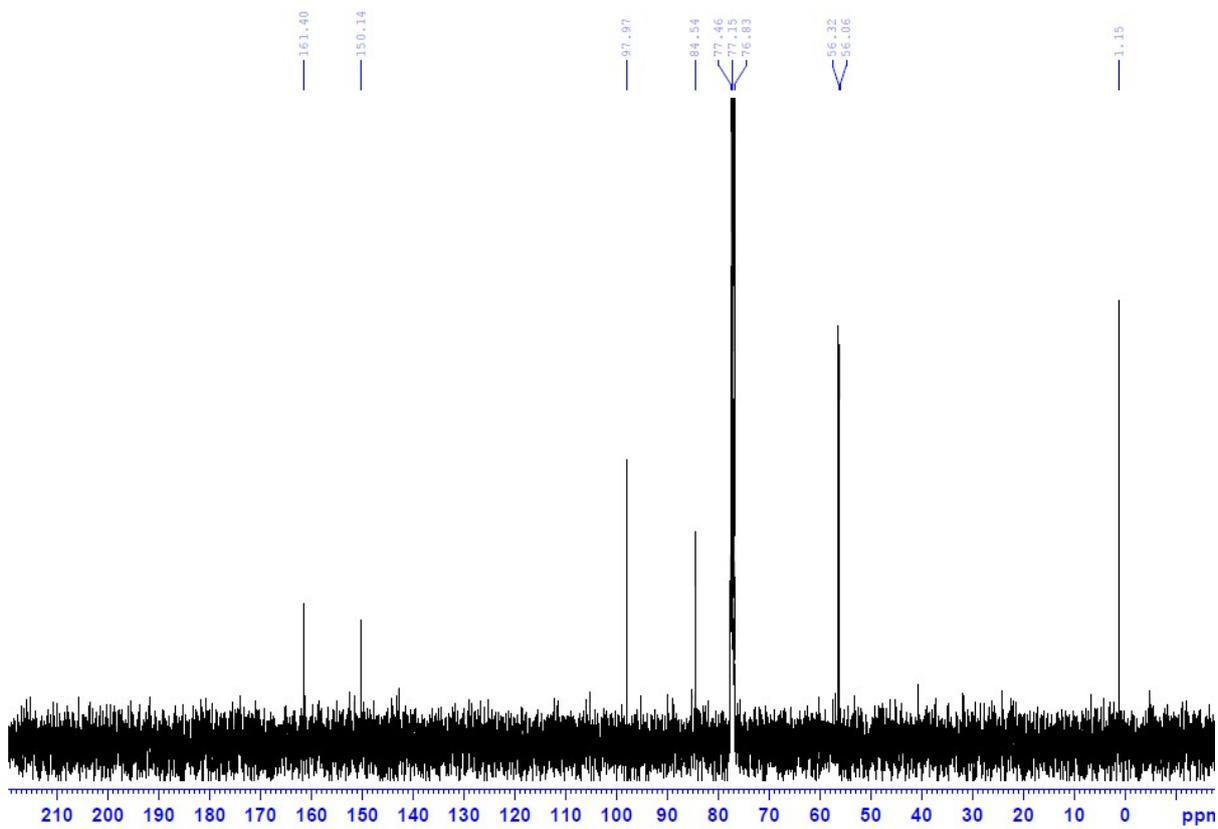
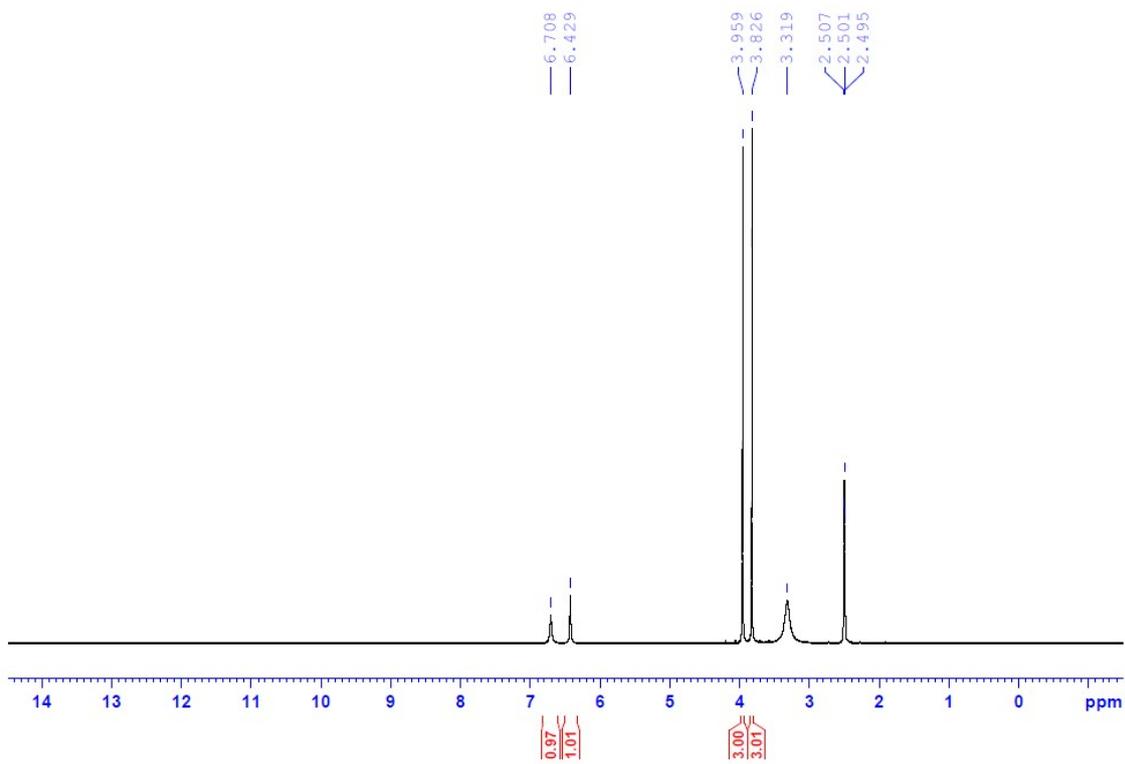
A suspension of parent benzotriazole **6** (0.26 g, 1.4 mmol) and anhydrous potassium carbonate (0.22 g, 1.6 mmol) in anhydrous acetone was cooled on ice under an atmosphere of nitrogen. Chloroacetyl chloride (0.13 mL, 1.6 mmol) was added dropwise and the mixture warmed to room temperature. After stirring for 3 h at room temperature, the solvent was removed *in vacuo* and the residue was recrystallised from chloroform/diethyl ether to yield *N-chloroacetyl-4,6-dimethoxy-benzo[1,2,3]triazole 12* (0.31 g, 86%) as white crystals. Mp 171-172 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): □ 3.92 (s, 3H, OMe), 4.08 (s, 3H, OMe), 5.16 (s, 2H, CH<sub>2</sub>), 6.49 (d, *J* = 2.0 Hz, 1H, H5), 7.24 (d, *J* = 2.0 Hz, 1H, H7). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): □ 42.90 (methylene C), 56.37, 56.71 (OMe), 87.90 (C5), 98.99 (C7), 133.40, 134.21, 152.22 164.59 (aryl C), 165.52 (C=O). IR (neat):  $\nu_{\max}$  3122, 2958, 1749, 1600, 1504, 1424, 1328, 1261, 1223, 1202, 1162, 968, 789, 751. UV-vis (MeCN):  $\lambda_{\max}$  216 nm ( $\epsilon$  40,600 cm<sup>-1</sup>M<sup>-1</sup>), 271 (14,900). HRMS (+ESI): Found *m/z* 278.0298, [M+Na]<sup>+</sup>; C<sub>10</sub>H<sub>10</sub>ClN<sub>3</sub>O<sub>3</sub>Na required 278.0303.

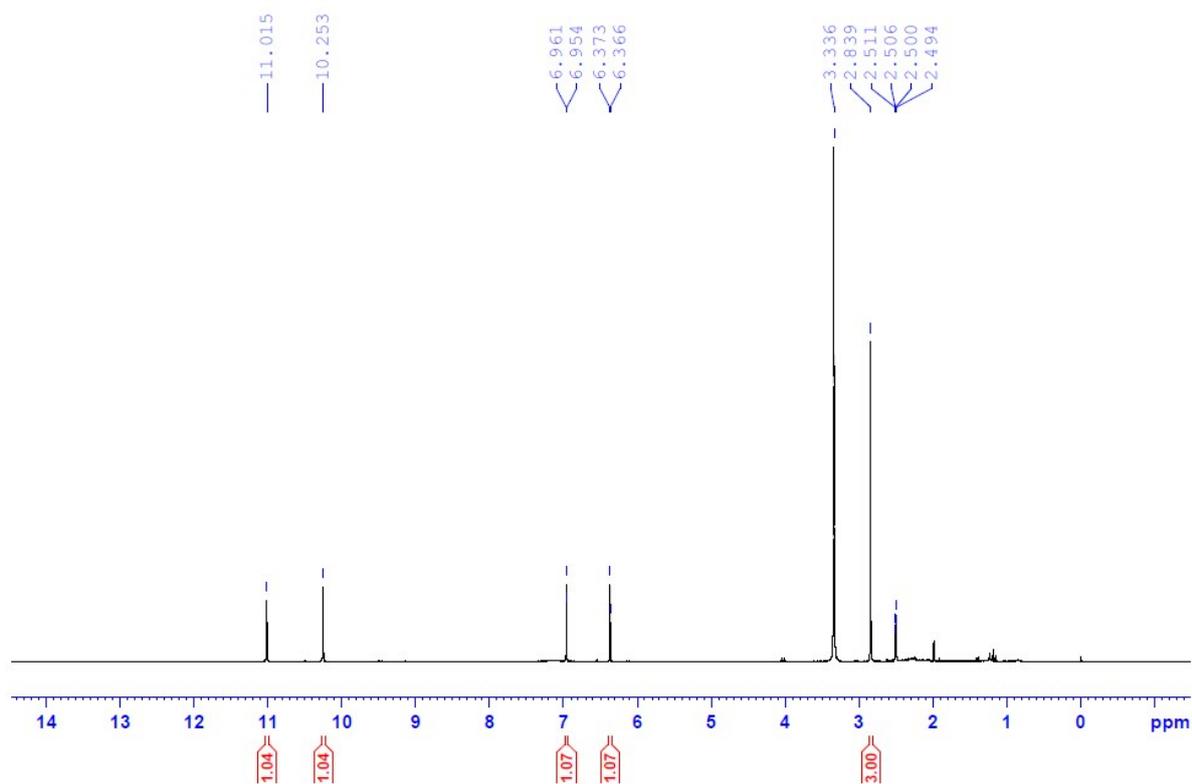
# H<sup>1</sup> NMR and C<sup>13</sup> NMR Spectra

## *N*-Acetyl-4,6-dimethoxy-1*H*-benzo[1,2,3]triazole (1)

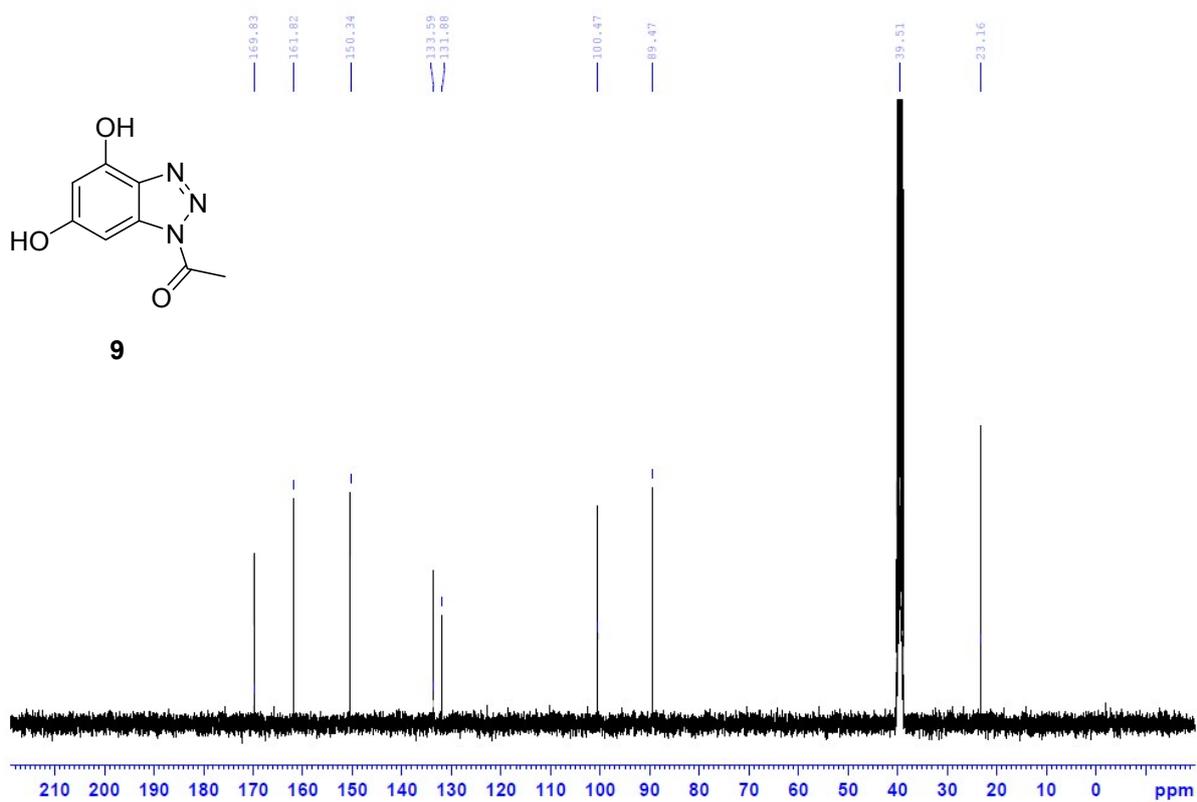
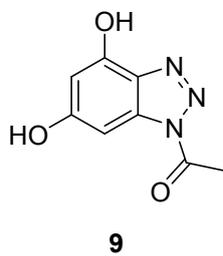


## *1H*-benzo[1,2,3]triazole (6)



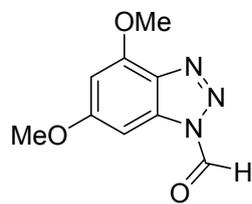


***N*-Acetyl-4,6-dihydroxy-1*H*-benzo[1,2,3]triazole (9)**

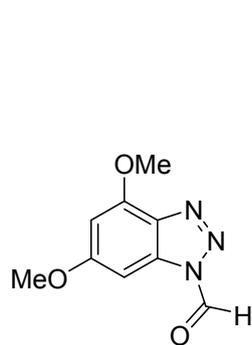
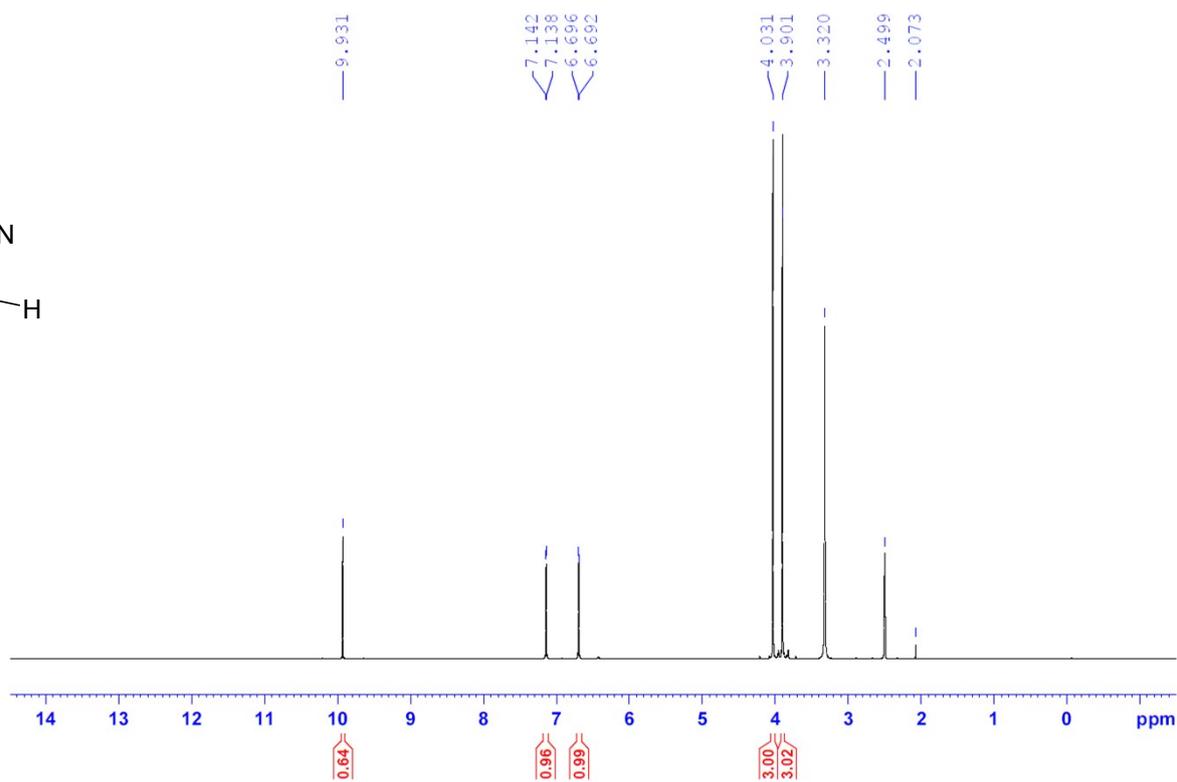


# 4,6-Dimethoxy-*N*-formyl-

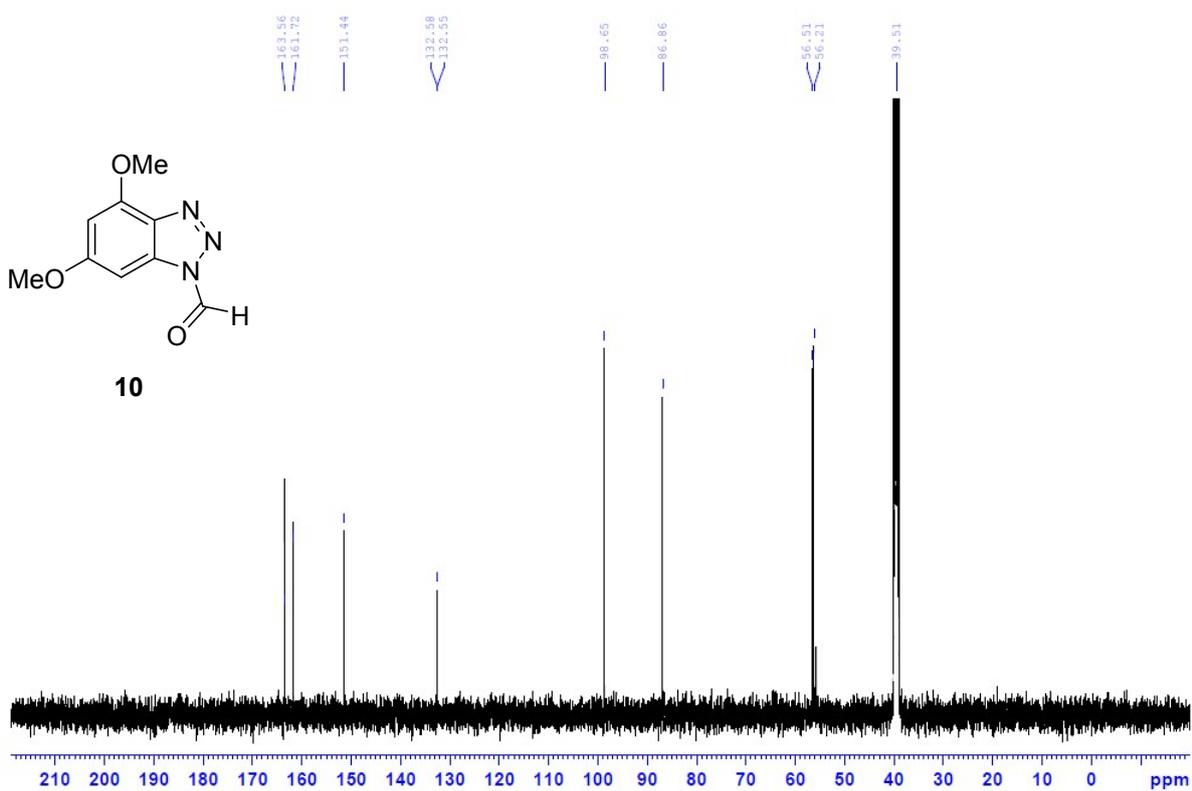
## 1*H*-benzo[1,2,3

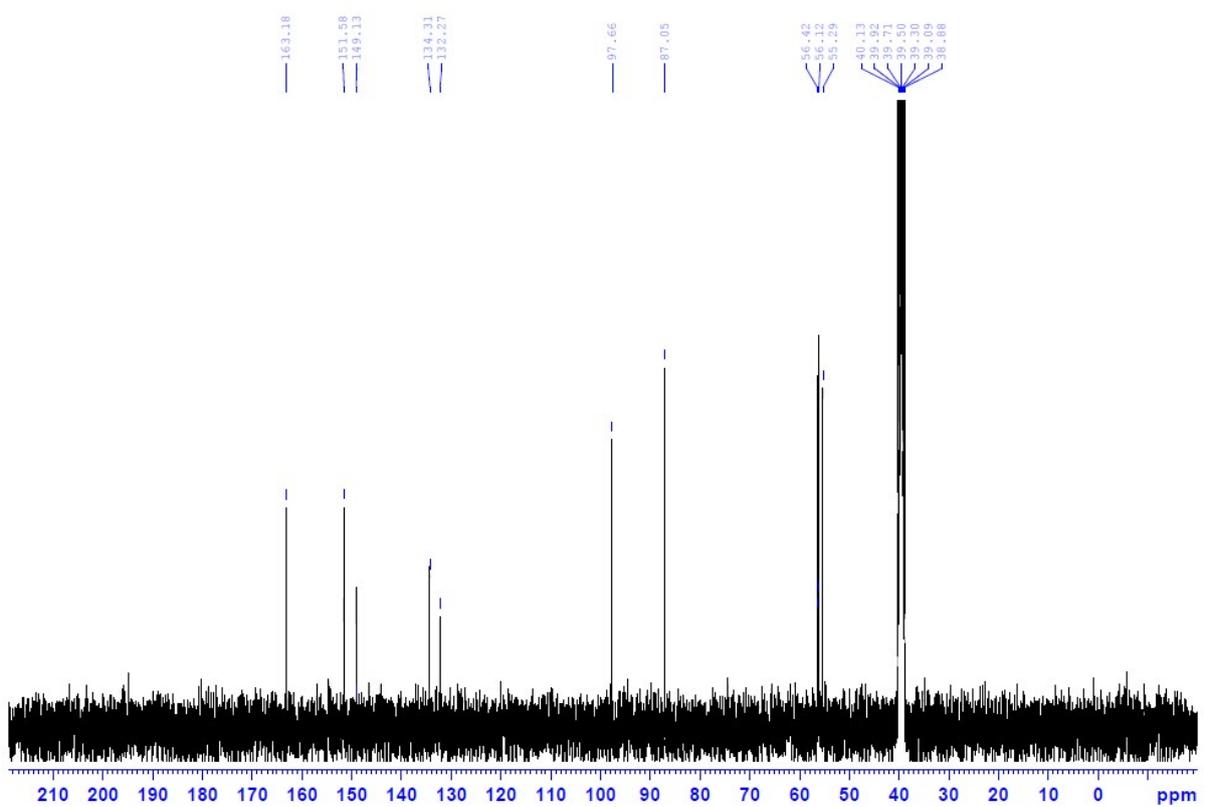
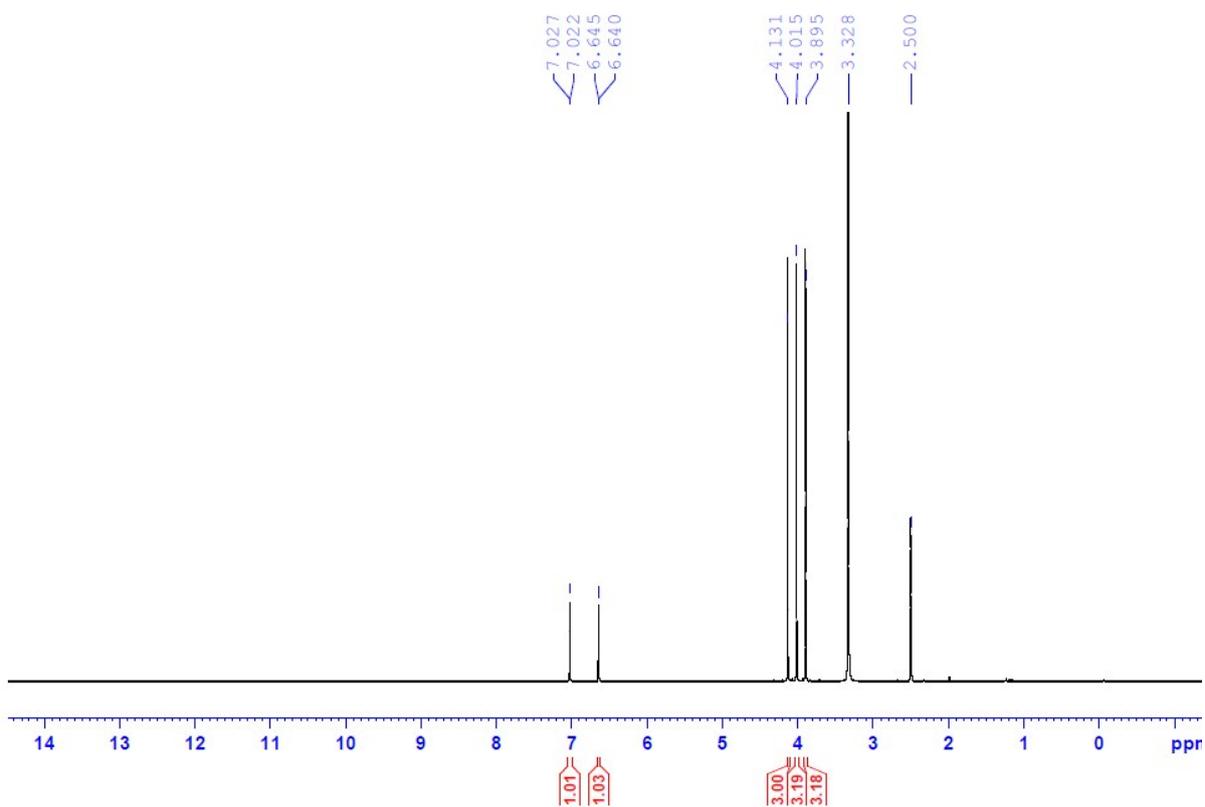


10

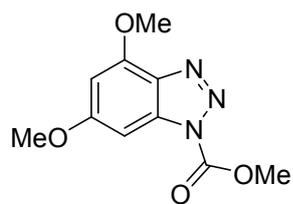


10

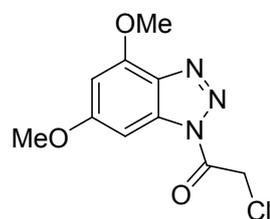




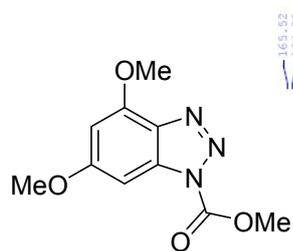
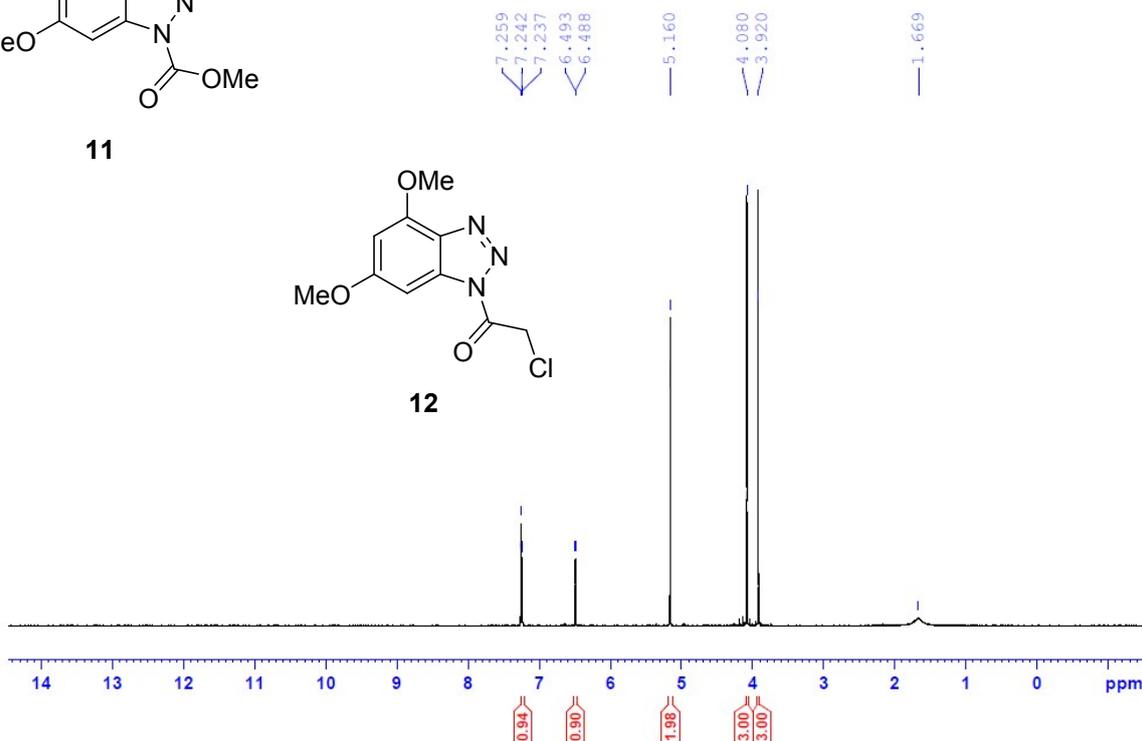
Methyl *N*-carboxylate-4,6-dimethoxy-1*H*-benzo[1,2,3]triazole (11)



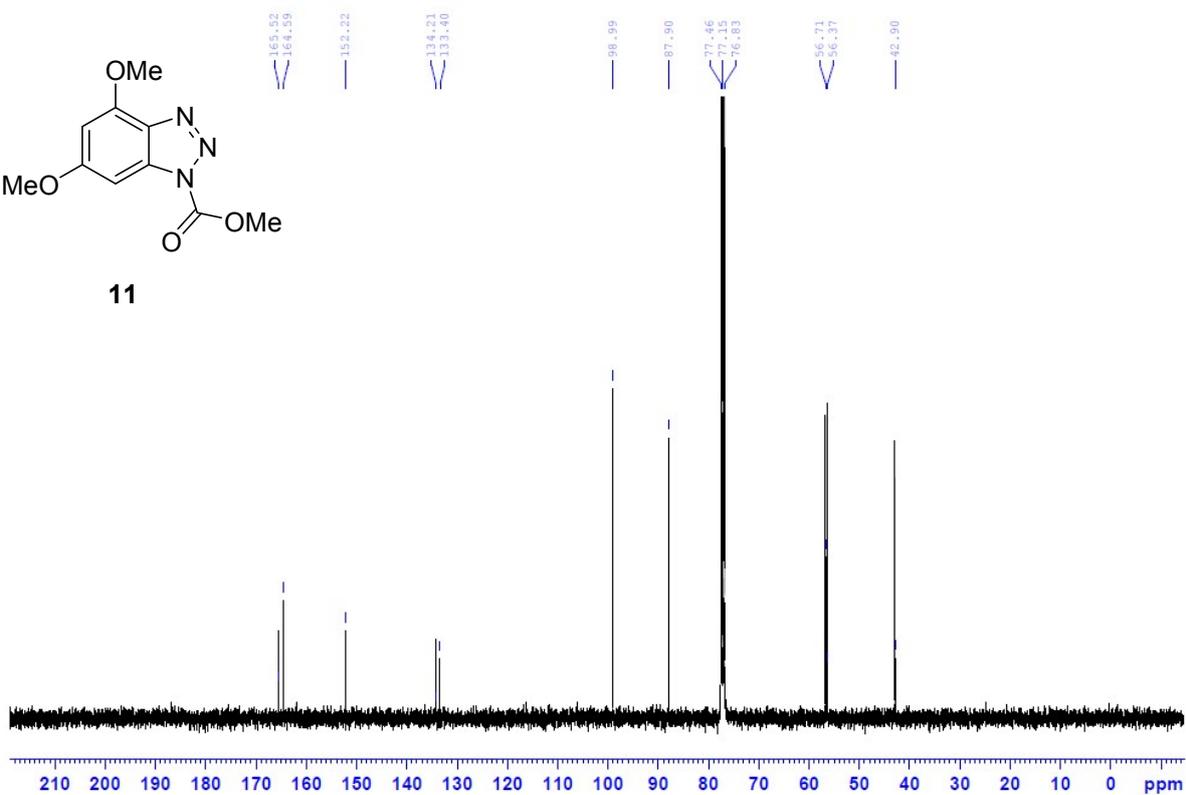
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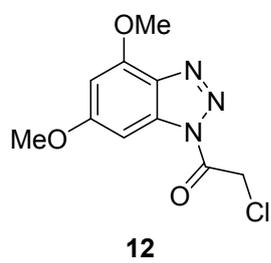
12



11



***N*-Chloroacetyl-4,6-dimethoxy-1*H*-benzo[1,2,3]triazole (12)**



## X-Ray Crystallography Experimental Details

### **N-Acetyl-4,6-dimethoxy-1H-benzo[1,2,3]triazole (1)**

N-Acetyl-4,6-dimethoxy-1H-benzo[1,2,3]triazole (1)	
Crystal data	
Chemical formula	0.5(C <sub>20</sub> H <sub>22</sub> N <sub>6</sub> O <sub>6</sub> )
<i>M<sub>r</sub></i>	221.22
Crystal system, space group	Orthorhombic, <i>Pnma</i>
Temperature (K)	150
<i>a</i> , <i>b</i> , <i>c</i> (Å)	9.9817 (12), 6.6498 (8), 15.4052 (18)
<i>V</i> (Å <sup>3</sup> )	1022.5 (2)
<i>Z</i>	4
Radiation type	Mo <i>K</i> α
μ (mm <sup>-1</sup> )	0.11
Crystal size (mm)	0.14 × 0.12 × 0.02
Data collection	
Diffractometer	Bruker <i>APEX-II</i> CCD
Absorption correction	Multi-scan <i>SADABS2016/2</i> (Bruker,2016/2) was used for absorption correction. <i>wR2(int)</i> was 0.0558 before and 0.0443 after correction. The Ratio of minimum to maximum transmission is 0.8748. The λ/2 correction factor is Not present.
<i>T<sub>min</sub></i> , <i>T<sub>max</sub></i>	0.653, 0.746
No. of measured, independent and observed [ <i>I</i> > 2σ( <i>I</i> )] reflections	2950, 964, 835
<i>R<sub>int</sub></i>	0.053
(sin θ/λ) <sub>max</sub> (Å <sup>-1</sup> )	0.595
Refinement	
<i>R</i> [ <i>F</i> <sup>2</sup> > 2σ( <i>F</i> <sup>2</sup> )], <i>wR</i> ( <i>F</i> <sup>2</sup> ), <i>S</i>	0.039, 0.109, 1.11
No. of reflections	964
No. of parameters	100
No. of restraints	3
H-atom treatment	H-atom parameters constrained
Δρ <sub>max</sub> , Δρ <sub>min</sub> (e Å <sup>-3</sup> )	0.20, -0.25

Computer programs: *SAINT* v7.46A (Bruker, 2008), *XT* (Sheldrick, 2015), *SHELXL* (Sheldrick, 2015), *Olex2* (Dolomanov *et al.*, 2009).

### **4,6-Dimethoxy-1H-benzo[1,2,3]triazole (6)**

	4,6-Dimethoxy-1H-benzo[1,2,3]triazole ( <b>6</b> )
Crystal data	
Chemical formula	C <sub>8</sub> H <sub>8</sub> N <sub>3</sub> O <sub>2</sub>
<i>M</i> <sub>r</sub>	179.18
Crystal system, space group	Monoclinic, <i>C2/c</i>
Temperature (K)	149
<i>a</i> , <i>b</i> , <i>c</i> (Å)	13.5266 (18), 10.2411 (14), 13.4172 (17)
β (°)	116.838 (4)
<i>V</i> (Å <sup>3</sup> )	1658.4 (4)
<i>Z</i>	8
Radiation type	Mo <i>K</i> α
μ (mm <sup>-1</sup> )	0.11
Crystal size (mm)	0.45 × 0.28 × 0.15
Data collection	
Diffractometer	Bruker <i>APEX-II</i> CCD
Absorption correction	Multi-scan <i>SADABS2016/2</i> (Bruker,2016/2) was used for absorption correction. <i>wR2(int)</i> was 0.0907 before and 0.0590 after correction. The Ratio of minimum to maximum transmission is 0.9029. The λ/2 correction factor is Not present.
<i>T</i> <sub>min</sub> , <i>T</i> <sub>max</sub>	0.673, 0.746
No. of measured, independent and observed [ <i>I</i> > 2σ( <i>I</i> )] reflections	11936, 1900, 1315
<i>R</i> <sub>int</sub>	0.054
(sin θ/λ) <sub>max</sub> (Å <sup>-1</sup> )	0.650
Refinement	
<i>R</i> [ <i>F</i> <sup>2</sup> > 2σ( <i>F</i> <sup>2</sup> )], <i>wR</i> ( <i>F</i> <sup>2</sup> ), <i>S</i>	0.047, 0.136, 1.06
No. of reflections	1900
No. of parameters	120
H-atom treatment	H-atom parameters constrained
Δρ <sub>max</sub> , Δρ <sub>min</sub> (e Å <sup>-3</sup> )	0.28, -0.23

Computer programs: *SAINT* v8.37A (Bruker, 2015), *SHELXT* 2014/5 (Sheldrick, 2014), *SHELXL* (Sheldrick, 2015), *Olex2* (Dolomanov *et al.*, 2009).

**N-Acetyl-1H-benzo[1,2,3]triazole (8)**

N-Acetyl-1H-benzo[1,2,3]triazole (8)	
Crystal data	
Chemical formula	2(C <sub>8</sub> H <sub>7</sub> N <sub>3</sub> O)
<i>M<sub>r</sub></i>	322.33
Crystal system, space group	Monoclinic, <i>P2<sub>1</sub>/c</i>
Temperature (K)	150
<i>a</i> , <i>b</i> , <i>c</i> (Å)	9.3151 (3), 4.9197 (2), 16.7332 (6)
β (°)	95.356 (1)
<i>V</i> (Å <sup>3</sup> )	763.49 (5)
<i>Z</i>	2
Radiation type	Mo <i>K</i> α
μ (mm <sup>-1</sup> )	0.10
Crystal size (mm)	0.54 × 0.36 × 0.17
Data collection	
Diffractometer	Bruker <i>APEX-II</i> CCD
Absorption correction	Multi-scan <i>SADABS2016/2</i> (Bruker,2016/2) was used for absorption correction. <i>wR2(int)</i> was 0.1059 before and 0.0490 after correction. The Ratio of minimum to maximum transmission is 0.9046. The λ/2 correction factor is Not present.
<i>T<sub>min</sub></i> , <i>T<sub>max</sub></i>	0.675, 0.746
No. of measured, independent and observed [ <i>I</i> > 2σ( <i>I</i> )] reflections	15481, 1710, 1590
<i>R<sub>int</sub></i>	0.033
(sin θ/λ) <sub>max</sub> (Å <sup>-1</sup> )	0.651
Refinement	
<i>R</i> [ <i>F</i> <sup>2</sup> > 2σ( <i>F</i> <sup>2</sup> )], <i>wR</i> ( <i>F</i> <sup>2</sup> ), <i>S</i>	0.039, 0.098, 1.04
No. of reflections	1710
No. of parameters	110
H-atom treatment	H-atom parameters constrained
Δρ <sub>max</sub> , Δρ <sub>min</sub> (e Å <sup>-3</sup> )	0.26, -0.16

Computer programs: *SAINT* V8.38A (? , 2016), *SHELXT* 2014/5 (Sheldrick, 2014), *SHELXL* (Sheldrick, 2015), *Olex2* (Dolomanov *et al.*, 2009).

**N-Acetyl-4,6-dihydroxy-1H-benzo[1,2,3]triazole (9)**

	N-Acetyl-4,6-dihydroxy-1H-benzo[1,2,3]triazole ( <b>9</b> )
Crystal data	
Chemical formula	2(C <sub>8</sub> H <sub>7</sub> N <sub>3</sub> O <sub>3</sub> )
<i>M</i> <sub>r</sub>	386.33
Crystal system, space group	Triclinic, <i>P</i> 1
Temperature (K)	150
<i>a</i> , <i>b</i> , <i>c</i> (Å)	6.0180 (7), 7.3930 (9), 9.3115 (10)
α, β, γ (°)	77.213 (7), 82.358 (7), 86.071 (8)
<i>V</i> (Å <sup>3</sup> )	400.09 (8)
<i>Z</i>	1
Radiation type	Mo <i>K</i> α
μ (mm <sup>-1</sup> )	0.13
Crystal size (mm)	0.10 × 0.07 × 0.04
Data collection	
Diffractometer	Bruker <i>APEX-II</i> CCD
Absorption correction	Multi-scan <i>SADABS2016/2</i> (Bruker,2016/2) was used for absorption correction. <i>wR2(int)</i> was 0.1449 before and 0.0733 after correction. The Ratio of minimum to maximum transmission is 0.6381. The λ/2 correction factor is Not present.
<i>T</i> <sub>min</sub> , <i>T</i> <sub>max</sub>	0.476, 0.746
No. of measured, independent and observed [ <i>I</i> > 2σ( <i>I</i> )] reflections	7324, 1852, 1142
<i>R</i> <sub>int</sub>	0.091
(sin θ/λ) <sub>max</sub> (Å <sup>-1</sup> )	0.654
Refinement	
<i>R</i> [ <i>F</i> <sup>2</sup> > 2σ( <i>F</i> <sup>2</sup> )], <i>wR</i> ( <i>F</i> <sup>2</sup> ), <i>S</i>	0.058, 0.145, 1.03
No. of reflections	1852
No. of parameters	130
H-atom treatment	H-atom parameters constrained
Δρ <sub>max</sub> , Δρ <sub>min</sub> (e Å <sup>-3</sup> )	0.31, -0.36

Computer programs: *SAINT* v8.37A (Bruker, 2015), *SHELXT* 2014/5 (Sheldrick, 2014), *SHELXL* (Sheldrick, 2015), *Olex2* (Dolomanov *et al.*, 2009).

#### 4,6-Dimethoxy-N-formyl-1H-benzo[1,2,3]triazole (**10**)

	4,6-Dimethoxy-N-formyl-1H-benzo[1,2,3]triazole ( <b>10</b> )
Crystal data	

Chemical formula	2(C <sub>5</sub> H <sub>5</sub> N <sub>3</sub> O <sub>3</sub> )
<i>M<sub>r</sub></i>	414.38
Crystal system, space group	Monoclinic, <i>P</i> 2 <sub>1</sub> / <i>n</i>
Temperature (K)	150
<i>a</i> , <i>b</i> , <i>c</i> (Å)	8.595 (7), 4.645 (4), 22.624 (18)
β (°)	91.293 (18)
<i>V</i> (Å <sup>3</sup> )	903.1 (13)
<i>Z</i>	2
Radiation type	Mo <i>K</i> α
μ (mm <sup>-1</sup> )	0.12
Crystal size (mm)	0.26 × 0.06 × 0.02
Data collection	
Diffractometer	Bruker <i>APEX-II</i> CCD
Absorption correction	Multi-scan <i>SADABS2016/2</i> (Bruker,2016/2) was used for absorption correction. <i>wR2(int)</i> was 0.1709 before and 0.0889 after correction. The Ratio of minimum to maximum transmission is 0.5147. The λ/2 correction factor is Not present.
<i>T<sub>min</sub></i> , <i>T<sub>max</sub></i>	0.384, 0.745
No. of measured, independent and observed [ <i>I</i> > 2σ( <i>I</i> )] reflections	8737, 1735, 718
<i>R<sub>int</sub></i>	0.281
(sin θ/λ) <sub>max</sub> (Å <sup>-1</sup> )	0.615
Refinement	
<i>R</i> [ <i>F</i> <sup>2</sup> > 2σ( <i>F</i> <sup>2</sup> )], <i>wR</i> ( <i>F</i> <sup>2</sup> ), <i>S</i>	0.094, 0.209, 0.99
No. of reflections	1735
No. of parameters	138
H-atom treatment	H-atom parameters constrained
Δρ <sub>max</sub> , Δρ <sub>min</sub> (e Å <sup>-3</sup> )	0.33, -0.33

Computer programs: *SAINT* v8.37A (Bruker, 2015), *SHELXT* 2014/5 (Sheldrick, 2014), *SHELXL* (Sheldrick, 2015), *Olex2* (Dolomanov *et al.*, 2009).

### Methyl N-carboxylate-4,6-dimethoxy-1H-benzo[1,2,3]triazole (11)

	Methyl N-carboxylate-4,6-dimethoxy-1H-benzo[1,2,3]triazole (11)
Crystal data	
Chemical formula	C <sub>10</sub> H <sub>11</sub> N <sub>3</sub> O <sub>4</sub>
<i>M<sub>r</sub></i>	237.22

Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	150
$a, b, c$ (Å)	13.073 (6), 4.901 (2), 16.934 (8)
$\beta$ (°)	106.837 (13)
$V$ (Å <sup>3</sup> )	1038.5 (8)
$Z$	4
Radiation type	Mo $K\alpha$
$\mu$ (mm <sup>-1</sup> )	0.12
Crystal size (mm)	0.35 × 0.08 × 0.07
Data collection	
Diffractometer	Bruker <i>APEX-II</i> CCD
Absorption correction	Multi-scan <i>SADABS2016/2</i> (Bruker,2016/2) was used for absorption correction. $wR2(int)$ was 0.1564 before and 0.0944 after correction. The Ratio of minimum to maximum transmission is 0.5158. The $\lambda/2$ correction factor is Not present.
$T_{min}, T_{max}$	0.385, 0.746
No. of measured, independent and observed [ $I > 2\sigma(I)$ ] reflections	9996, 2383, 1422
$R_{int}$	0.146
$(\sin \theta/\lambda)_{max}$ (Å <sup>-1</sup> )	0.649
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.088, 0.191, 1.04
No. of reflections	2383
No. of parameters	157
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}, \Delta\rho_{min}$ (e Å <sup>-3</sup> )	0.37, -0.31

Computer programs: *SAINT* v8.37A (Bruker, 2015), *SHELXT* 2014/5 (Sheldrick, 2014), *SHELXL* (Sheldrick, 2015), *Olex2* (Dolomanov *et al.*, 2009).

### **N-Chloroacetyl-4,6-dimethoxy-1H-benzo[1,2,3]triazole (12)**

	N-Chloroacetyl-4,6-dimethoxy-1H-benzo[1,2,3]triazole ( <b>12</b> )
Crystal data	
Chemical formula	$C_{10}H_{10}ClN_3O_3$
$M_r$	255.66
Crystal system, space group	Orthorhombic, $P2_12_12_1$

Temperature (K)	150
$a, b, c$ (Å)	4.669 (5), 8.554 (8), 28.15 (3)
$V$ (Å <sup>3</sup> )	1124 (2)
$Z$	4
Radiation type	Mo $K\alpha$
$\mu$ (mm <sup>-1</sup> )	0.34
Crystal size (mm)	0.71 × 0.22 × 0.09
Data collection	
Diffractometer	Bruker <i>APEX-II</i> CCD
Absorption correction	Multi-scan <i>SADABS2016/2</i> (Bruker, 2016/2) was used for absorption correction. $wR2(\text{int})$ was 0.1767 before and 0.0999 after correction. The Ratio of minimum to maximum transmission is 0.5845. The $\lambda/2$ correction factor is Not present.
$T_{\min}, T_{\max}$	0.436, 0.746
No. of measured, independent and observed [ $I > 2\sigma(I)$ ] reflections	11920, 2523, 1834
$R_{\text{int}}$	0.104
$(\sin \theta/\lambda)_{\text{max}}$ (Å <sup>-1</sup> )	0.649
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.063, 0.148, 1.06
No. of reflections	2523
No. of parameters	156
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e Å <sup>-3</sup> )	0.61, -0.71
Absolute structure	Flack $x$ determined using 540 quotients [(I+)-(I-)]/[(I+)+(I-)] (Parsons, Flack and Wagner, <i>Acta Cryst.</i> B69 (2013) 249-259).
Absolute structure parameter	0.04 (8)

Computer programs: *SAINT* V8.38A (?, 2016), *SHELXT* 2014/5 (Sheldrick, 2014), *SHELXL* (Sheldrick, 2015), *Olex2* (Dolomanov *et al.*, 2009).

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