Supporting Information

CO2 Improved the Synthesis of Benzimidazole with the Catalysis of a New Calcium 4-Amino-3-Hydroxybenzoate

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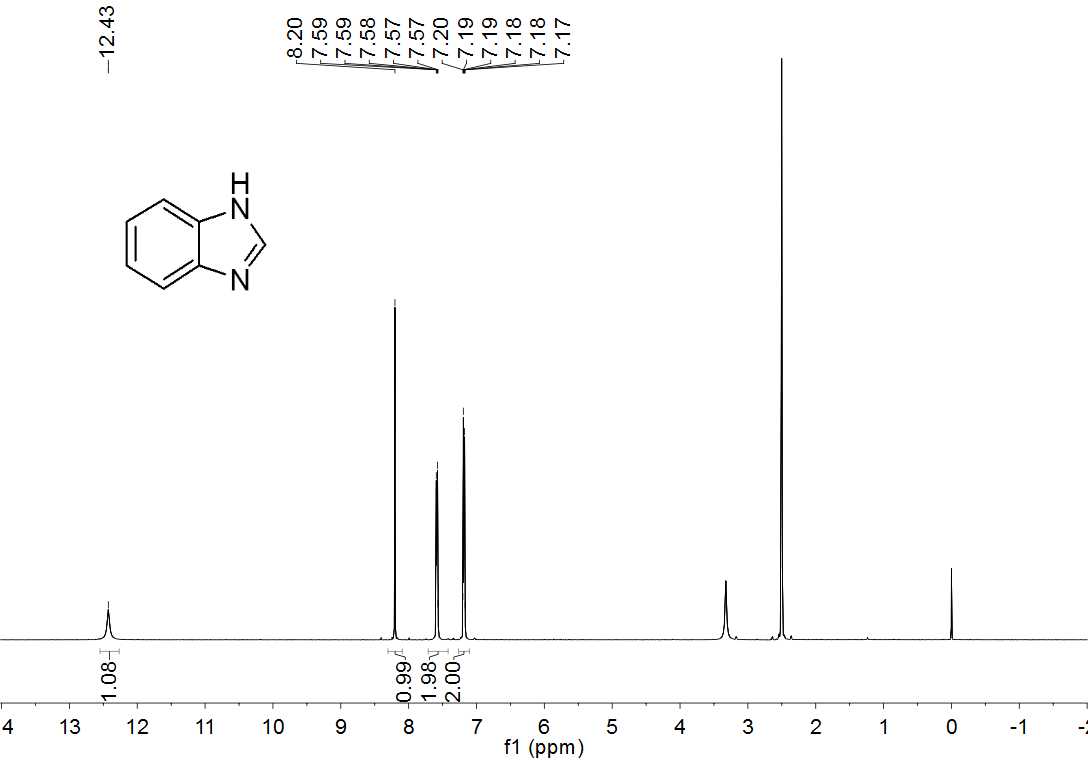
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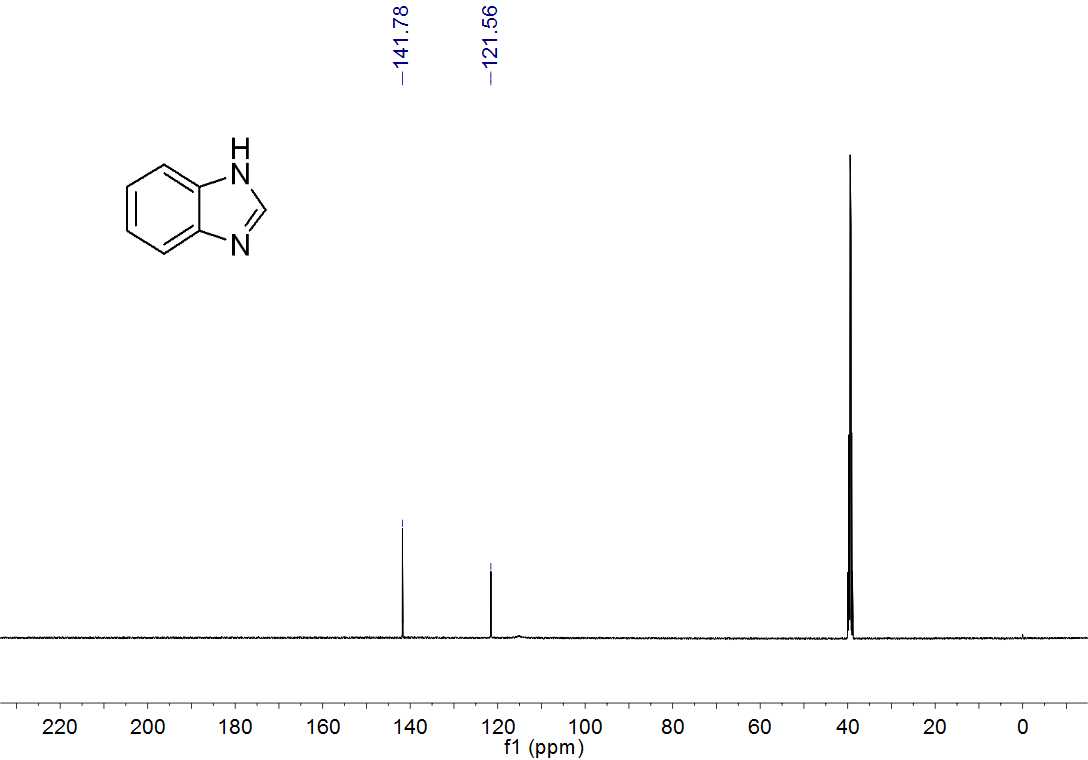
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1. **NMR data of isolated benzimidazole products**

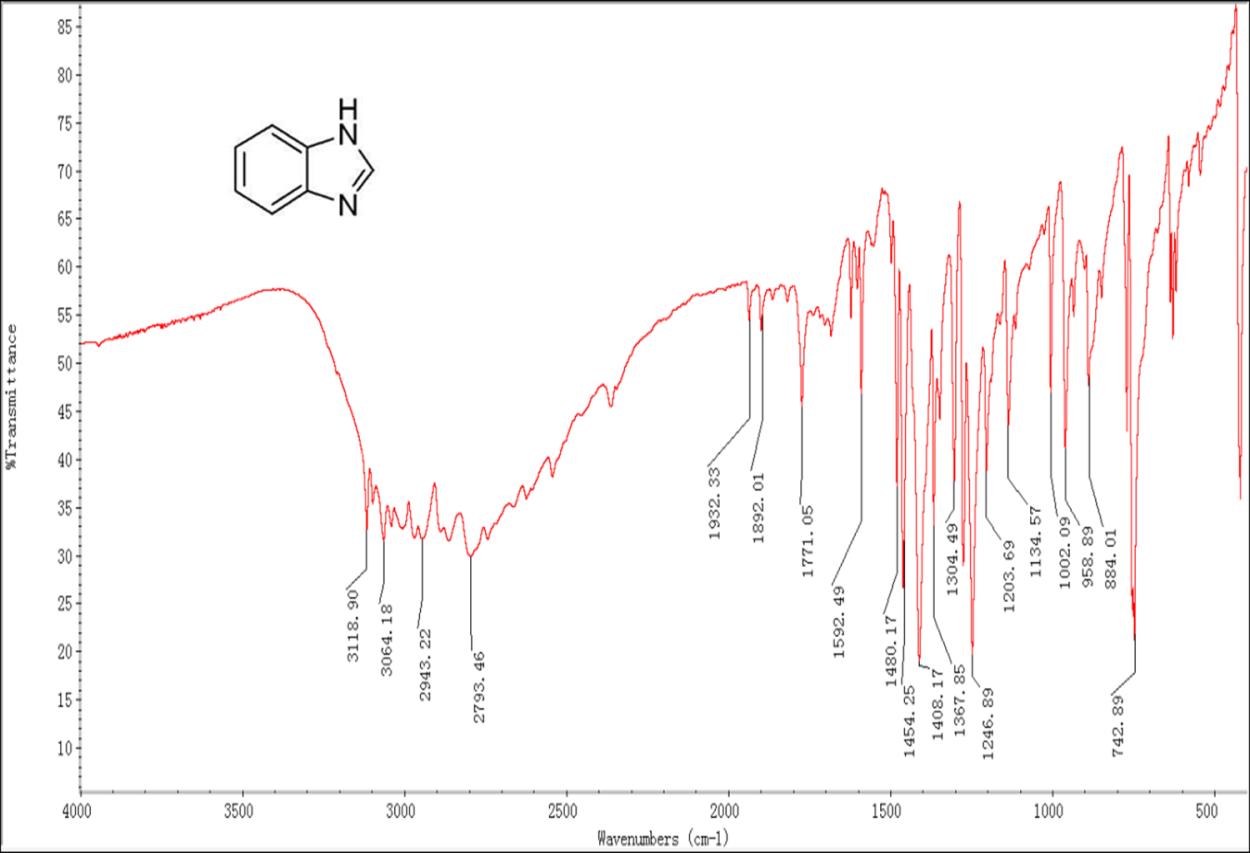


**Figure S1**. 1H NMR of benzimidazole in DMSO-*d6*.

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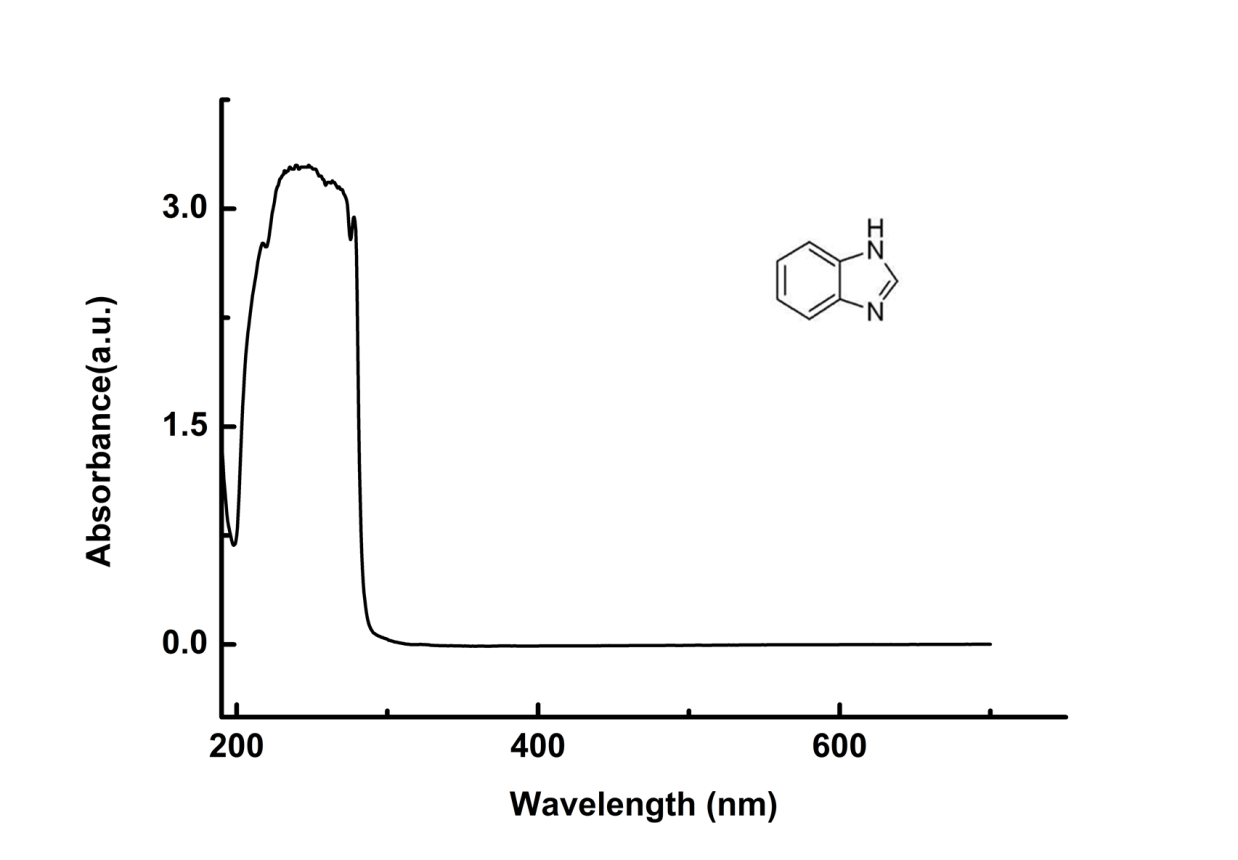
**Figure S2**. 13C NMR of benzimidazole in DMSO-*d6*.

1. **FT-IR data of isolated benzimidazole products**



**Figure S3**. FT-IR spectrum of benzimidazole.

1. **UV-Vis data of isolated benzimidazole products**

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**Figure S4**. UV-Vis spectrum of benzimidazole in CH3OH.

1. **X-ray structure data of calcium 4-amino-3-hydroxybenzoate**

**Table S1** Crystal data and structure refinement parameters for calcium 4-amino-3-hydroxybenzoate

|  |  |
| --- | --- |
| calcium 4-amino-3-hydroxybenzoate |  |
| Empirical formula  Formula weight  Temperature (K)  Wavelength (Å)  Crystal system  Space group  *a* (Å)  *b* (Å)  *c* (Å)  *α* (°)  *β* (°)  *γ* (°)  Calculated density (Mg/m3)  *µ*(mm-1)  *F*(000)  *θ* range (°)  Limiting indices  Reflections collected  Independent eflections  Completeness to  Data/restraints/Parameters  Goodness-of-fiton F2  Final Rindices[I > 2σ(I)]  R indices (all data) | C16H20CaN2O8  408.42  273(2)  0.71073  Monoclinic  *C2/c*  29.045(4)  8.2636(10)  7.7063(8)  90  96.624(6)  90  1.476  0.389  856  2.82 to 28.34  -38<=h<=38, -11<=k<=11, -10<=l<=10  40146  2292 [R(int) = 0.0279]  99.9%  2292 / 2 / 129  1.104  *R*1=0.0516,*wR*2=0.1510  *R*1=0.0563, *wR*2=0.1557 |

Symmetry operations used to generate equivalent atoms: (i)-x+1,y,-z+3/2 (ii)x,-y+1,z+1/2 (iii)-x+1,-y+1,-z+1 (iv)-x+1,-y+1,-z+2

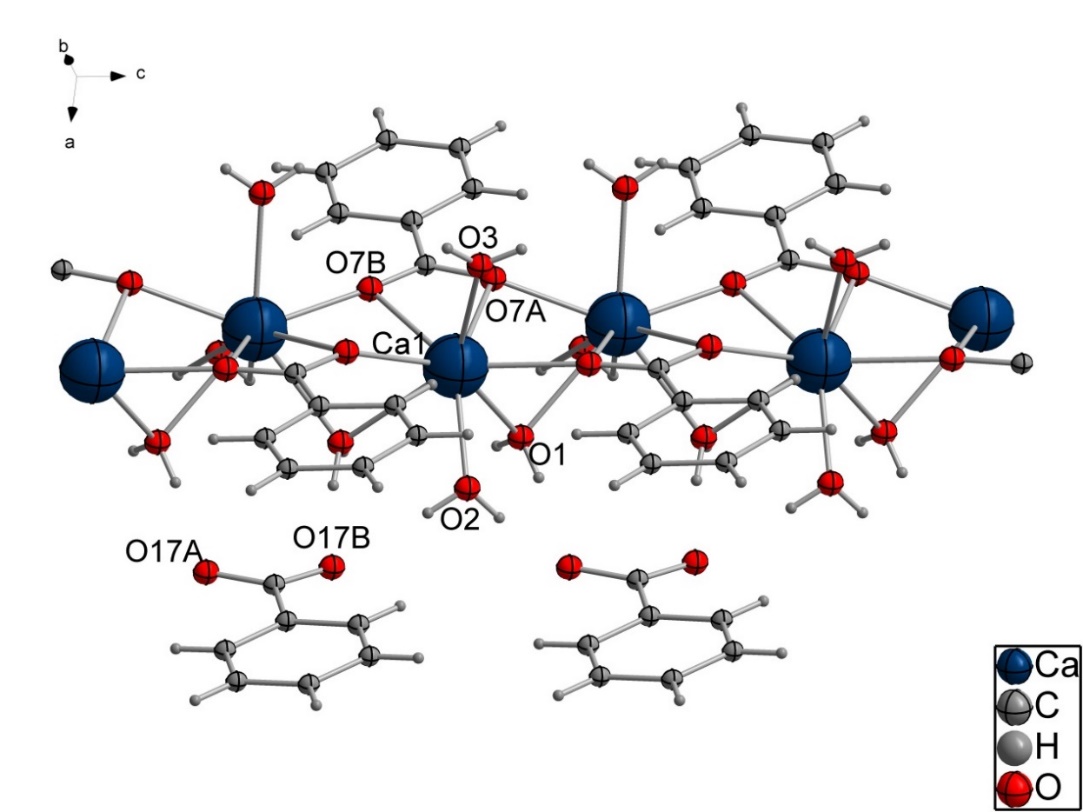
**Table S2** The selected bond lengths (Å), bond angles (º) of calcium 4-amino-3-hydroxybenzoate

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Bond | Dist. | Bond | Dist. | Bond | Dist. |
| Ca(1)-O(3)#1 | 2.3842(16) | N(1)-C(1) | 1.364(2) | C(3)-C(4) | 1.395(3) |
| Ca(1)-O(3) | 2.3842(16) | O(2)-C(5) | 1.252(3) | C(3)-H(3) | 0.9300 |
| Ca(1)-O(1)#1 | 2.401(2) | O(3)-C(5) | 1.260(3) | C(4)-C(8) | 1.390(3) |
| Ca(1)-O(1) | 2.401(2) | O(1)-C(6) | 1.381(4) | C(4)-C(5) | 1.500(3) |
| Ca(1)-O(3)#2 | 2.5046(16) | O(1)-H(1) | 0.845(10) | C(6)-H(6A) | 0.9600 |
| Ca(1)-O(3)#3 | 2.5047(16) | O(4)-C(2) | 1.419(3) | C(6)-H(6B) | 0.9600 |
| Ca(1)-O(2)#3 | 2.5172(18) | O(4)-H(4) | 0.8200 | C(6)-H(6C) | 0.9600 |
| Ca(1)-O(2)#2 | 2.5173(18) | C(1)-C(7) | 1.389(3) | C(7)-C(8) | 1.392(3) |
| N(1)-H(1A) | 0.8619 | C(1)-C(2) | 1.402(3) | C(7)-H(7) | 0.9300 |
| N(1)-H(1B) | 0.8620 | C(2)-C(3) | 1.389(3) | C(8)-H(8) | 0.9300 |
| Angle | (**°**) | Angle | (**°**) | Angle | (**°**) |
| O(3)#1-Ca(1)-O(3) | 155.90(10) | O(3)#3-Ca(1)-O(2)#3 | 51.84(5) | C(2)-C(3)-H(3) | 119.5 |
| O(3)#1-Ca(1)-O(1)#1 | 78.90(8) | O(3)#1-Ca(1)-O(2)#2 | 123.59(6) | C(4)-C(3)-H(3) | 119.5 |
| O(3)-Ca(1)-O(1)#1 | 84.39(7) | O(3)-Ca(1)-O(2)#2 | 75.37(6) | C(8)-C(4)-C(3) | 119.29(19) |
| O(3)#1-Ca(1)-O(1) | 84.39(7) | O(1)#1-Ca(1)-O(2)#2 | 96.87(9) | C(8)-C(4)-C(5) | 121.18(19) |
| O(3)-Ca(1)-O(1) | 78.90(8) | O(1)-Ca(1)-O(2)#2 | 151.77(6) | C(3)-C(4)-C(5) | 119.52(19) |
| O(1)#1-Ca(1)-O(1) | 91.93(14) | O(3)#2-Ca(1)-O(2)#2 | 51.84(5) | O(2)-C(5)-O(3) | 121.86(19) |
| O(3)#1-Ca(1)-O(3)#2 | 74.41(6) | O(3)#3-Ca(1)-O(2)#2 | 90.36(6) | O(2)-C(5)-C(4) | 119.27(19) |
| O(3)-Ca(1)-O(3)#2 | 116.50(7) | O(2)#3-Ca(1)-O(2)#2 | 87.92(9) | O(3)-C(5)-C(4) | 118.80(18) |
| O(1)#1-Ca(1)-O(3)#2 | 71.55(8) | C(1)-N(1)-H(1A) | 109.1 | O(1)-C(6)-H(6A) | 109.5 |
| O(1)-Ca(1)-O(3)#2 | 155.10(6) | C(1)-N(1)-H(1B) | 110.0 | O(1)-C(6)-H(6B) | 109.5 |
| O(3)#1-Ca(1)-O(3)#3 | 116.50(7) | H(1A)-N(1)-H(1B) | 109.1 | H(6A)-C(6)-H(6B) | 109.5 |
| O(3)-Ca(1)-O(3)#3 | 74.41(6) | C(6)-O(1)-H(1) | 109.7(19) | O(1)-C(6)-H(6C) | 109.5 |
| O(1)#1-Ca(1)-O(3)#3 | 155.11(6) | C(2)-O(4)-H(4) | 109.5 | H(6A)-C(6)-H(6C) | 109.5 |
| O(1)-Ca(1)-O(3)#3 | 71.55(8) | N(1)-C(1)-C(7) | 123.2(2) | H(6B)-C(6)-H(6C) | 109.5 |
| O(3)#2-Ca(1)-O(3)#3 | 129.71(9) | N(1)-C(1)-C(2) | 116.6(2) | C(1)-C(7)-C(8) | 120.1(2) |
| O(3)#1-Ca(1)-O(2)#3 | 75.37(6) | C(7)-C(1)-C(2) | 120.21(19) | C(1)-C(7)-H(7) | 120.0 |
| O(3)-Ca(1)-O(2)#3 | 123.59(6) | C(3)-C(2)-C(1) | 118.9(2) | C(8)-C(7)-H(7) | 120.0 |
| O(1)#1-Ca(1)-O(2)#3 | 151.77(6) | C(3)-C(2)-O(4) | 121.4(2) | C(4)-C(8)-C(7) | 120.2(2) |
| O(1)-Ca(1)-O(2)#3 | 96.87(9) | C(1)-C(2)-O(4) | 119.55(19) | C(4)-C(8)-H(8) | 119.9 |
| O(3)#2-Ca(1)-O(2)#3 | 90.35(6) | C(2)-C(3)-C(4) | 121.1(2) | C(7)-C(8)-H(8) | 119.9 |

**Table S3** Hydrogen bond for calcium 4-amino-3-hydroxybenzoate

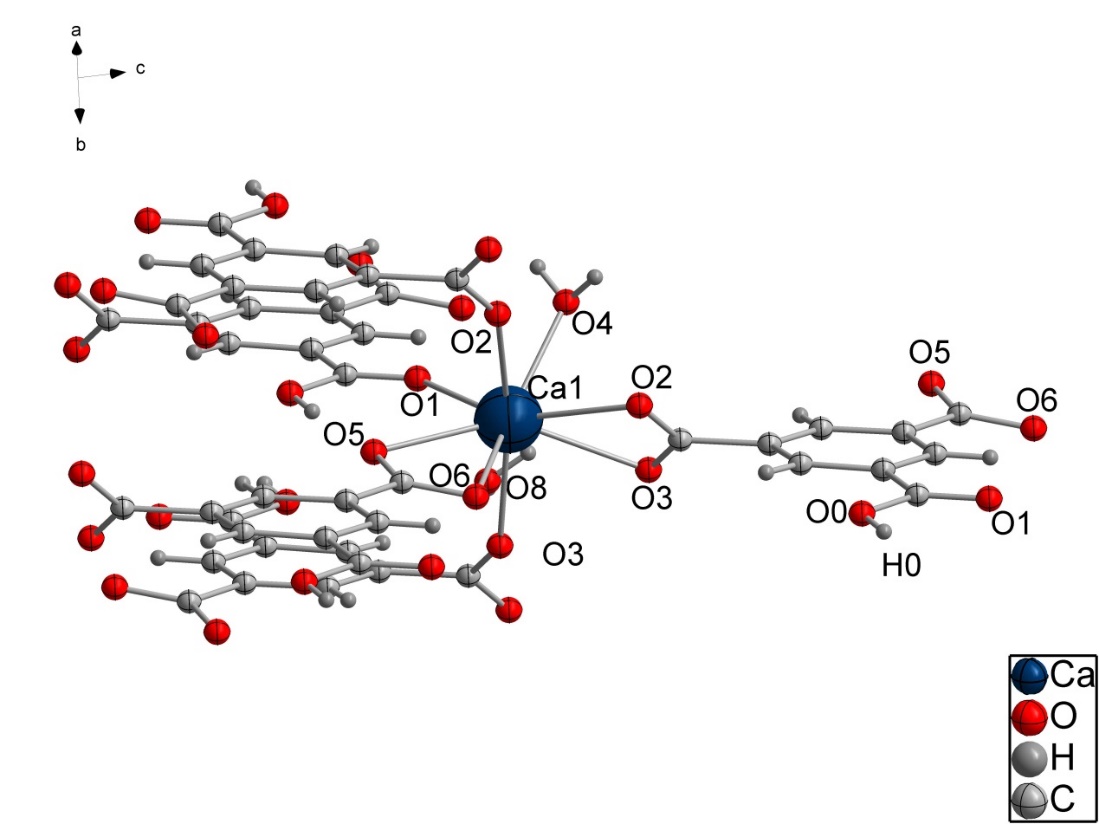
|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Donor--H…Acceptor | d(D‑-H) / Å | d(H…A) / Å | d(D…A) / Å | ∠(DHA) /**°** |
| O(1)--H(1)…O(2) | 0.84 | 1.92 | 2.7667 | 176 |
| N(1)--H(1B)…O(4) | 0.86 | 1.98 | 2.8322 | 167 |

1. **The molecular structure of calcium benzoate**

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**Figure S5**. The molecular structure of calcium benzoate.

1. **The molecular structure of calcium benzene-1,3,5-tricarboxylate**

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**Figure S6**. The molecular structure of calcium benzene-1,3,5-tricarboxylate.