Engineering crystals that facilitate acyl transfer reaction: insight from a comparison of crystal structures of *myo*-inositol-1,3,5-orthoformate derived benzoates and carbonates. Endurance

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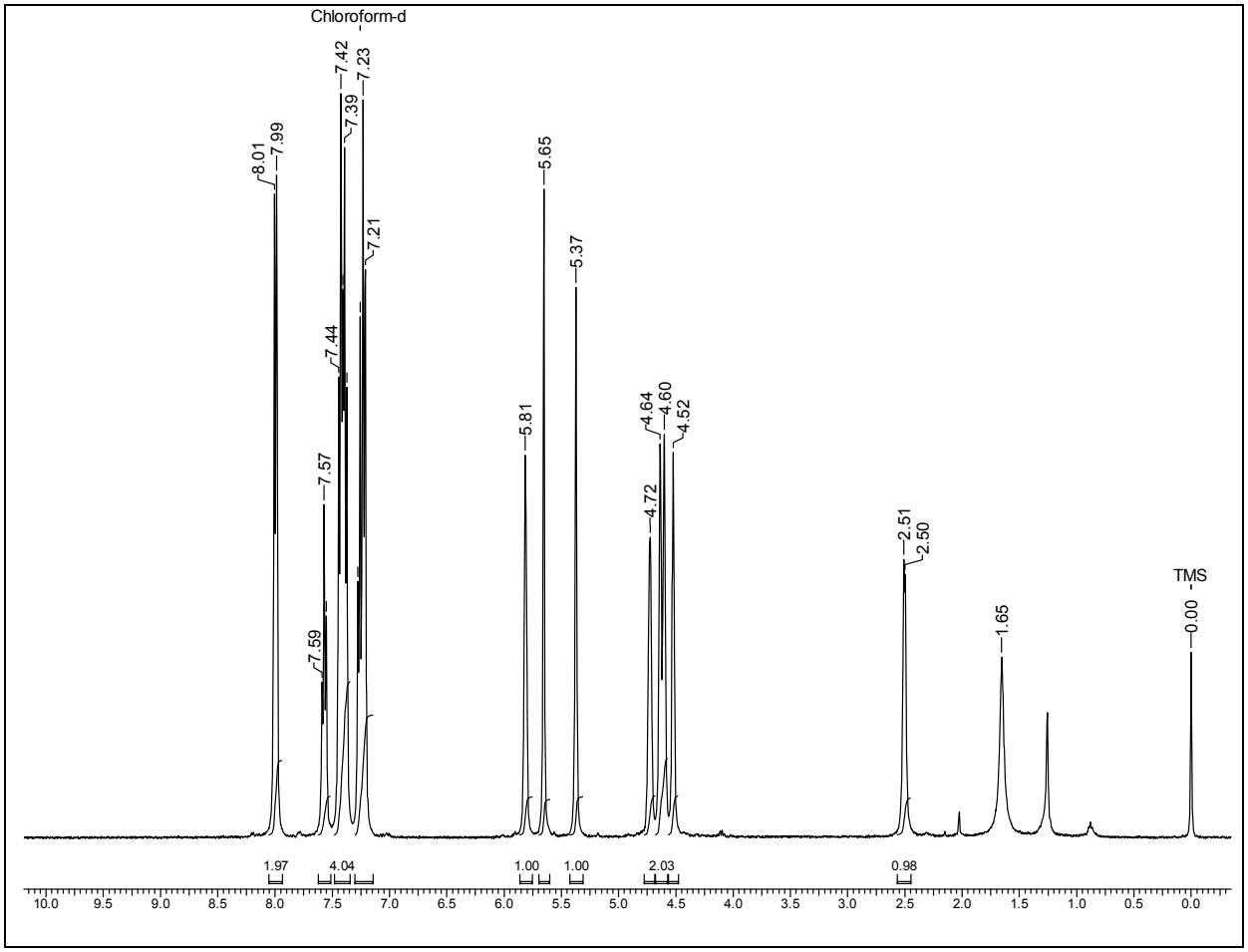


Figure S1: ^{1}H NMR spectrum of the carbonate **2** in chloroform-*d*.

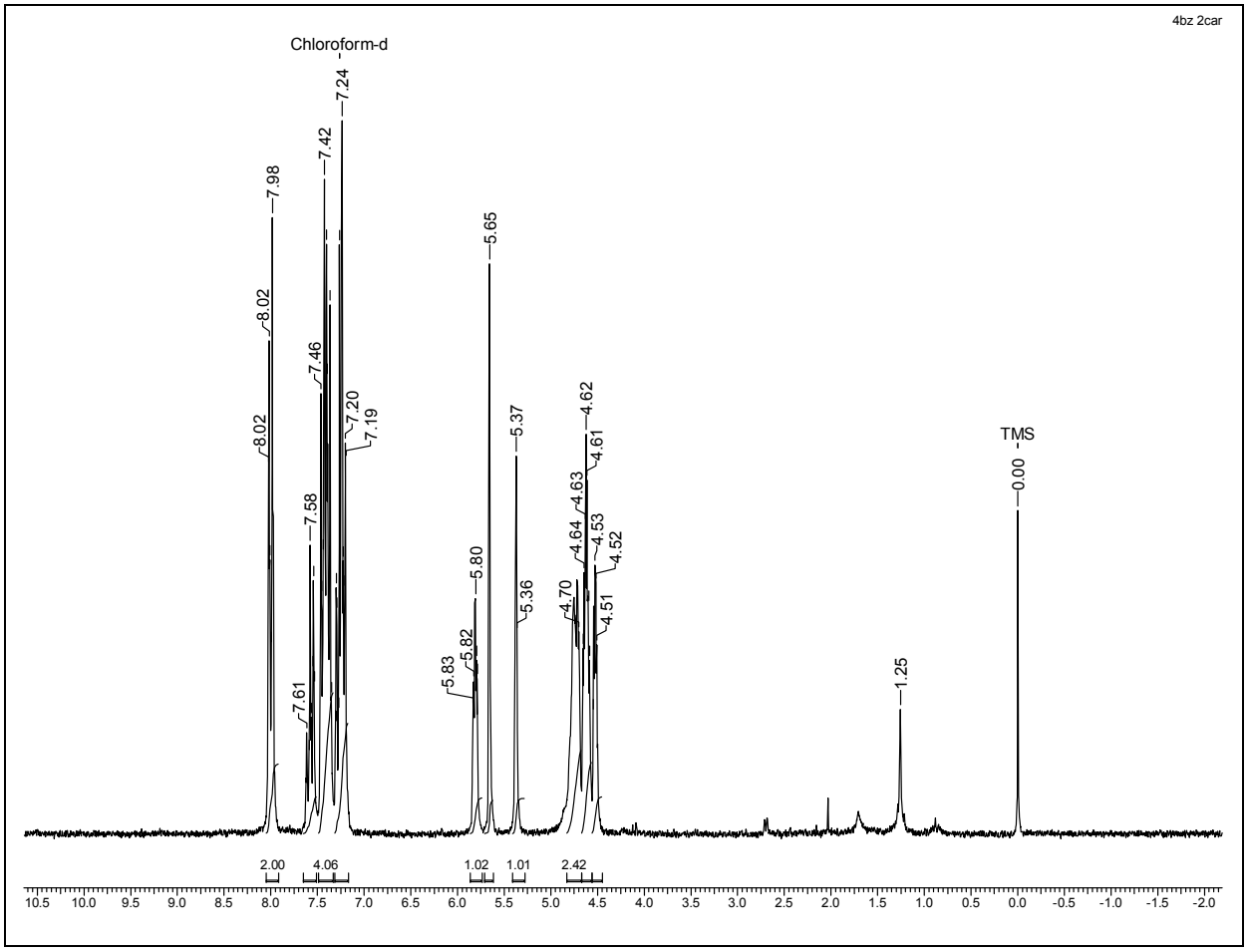


Figure S2: ^{1}H NMR spectrum of the carbonate **2** in chloroform-*d*- D_2O.

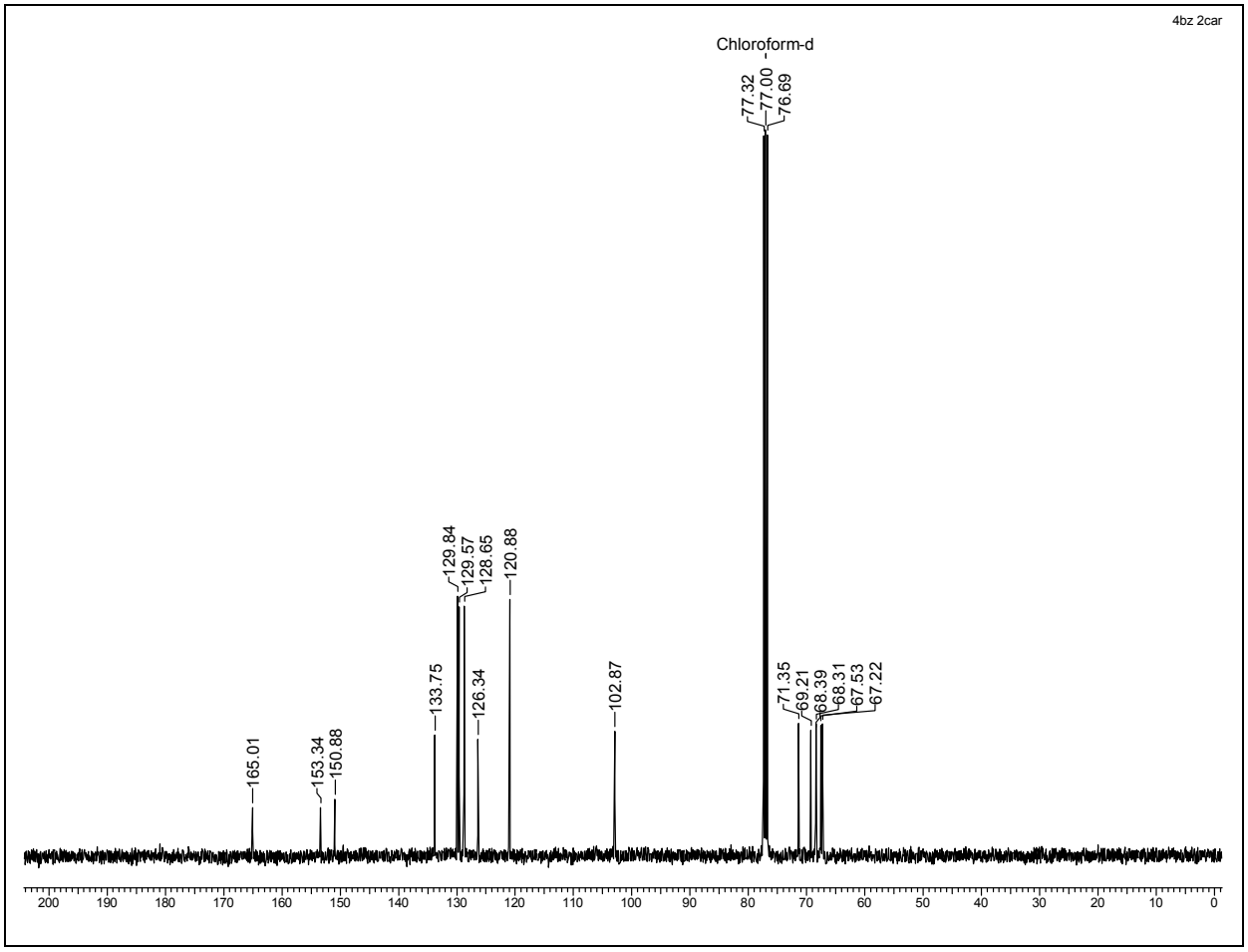


Figure S3: ^{13}C NMR spectrum of the carbonate **2** in chloroform-*d*.

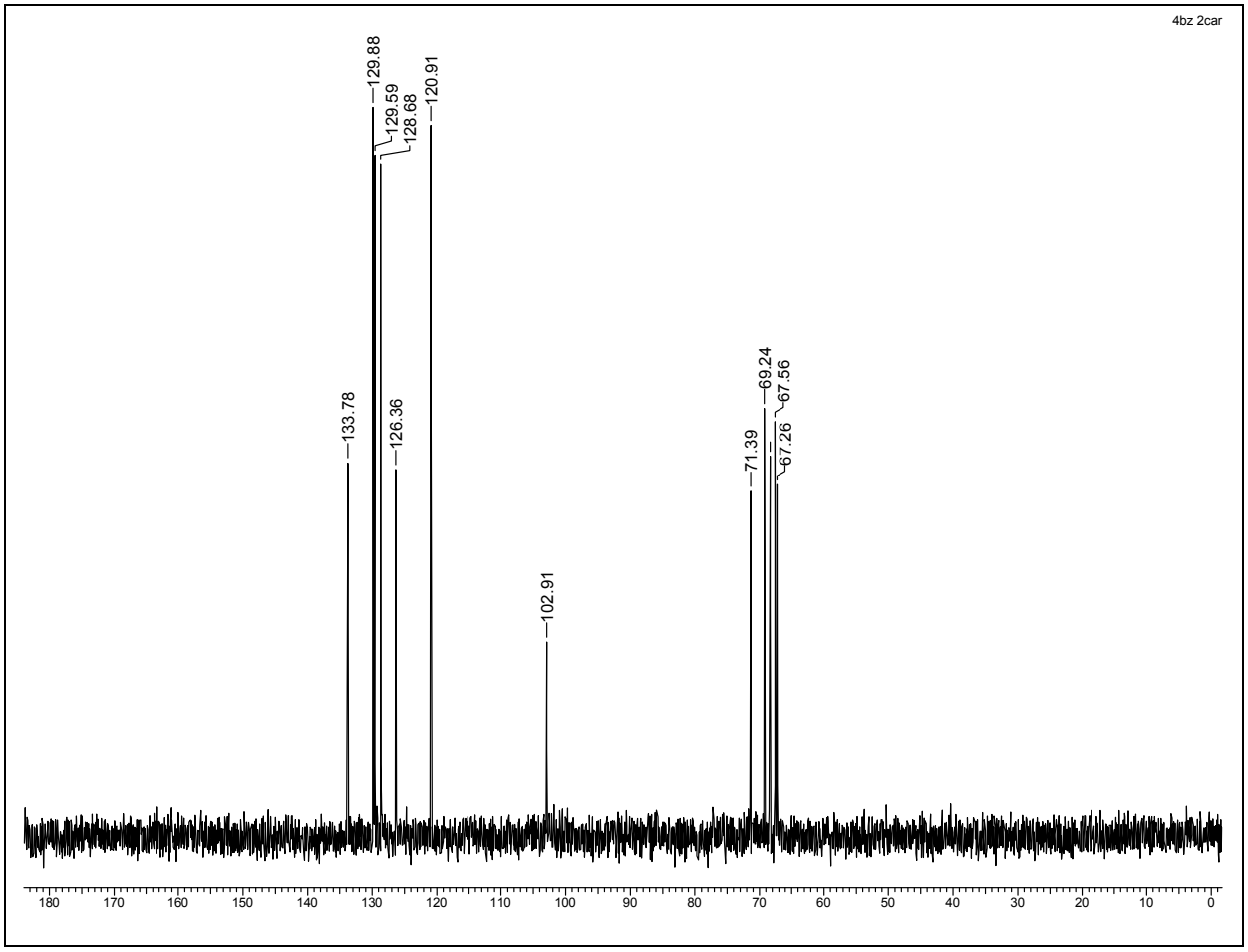


Figure S4: ^{13}C NMR (DEPT) spectrum of the carbonate **2** in chloroform-*d*.

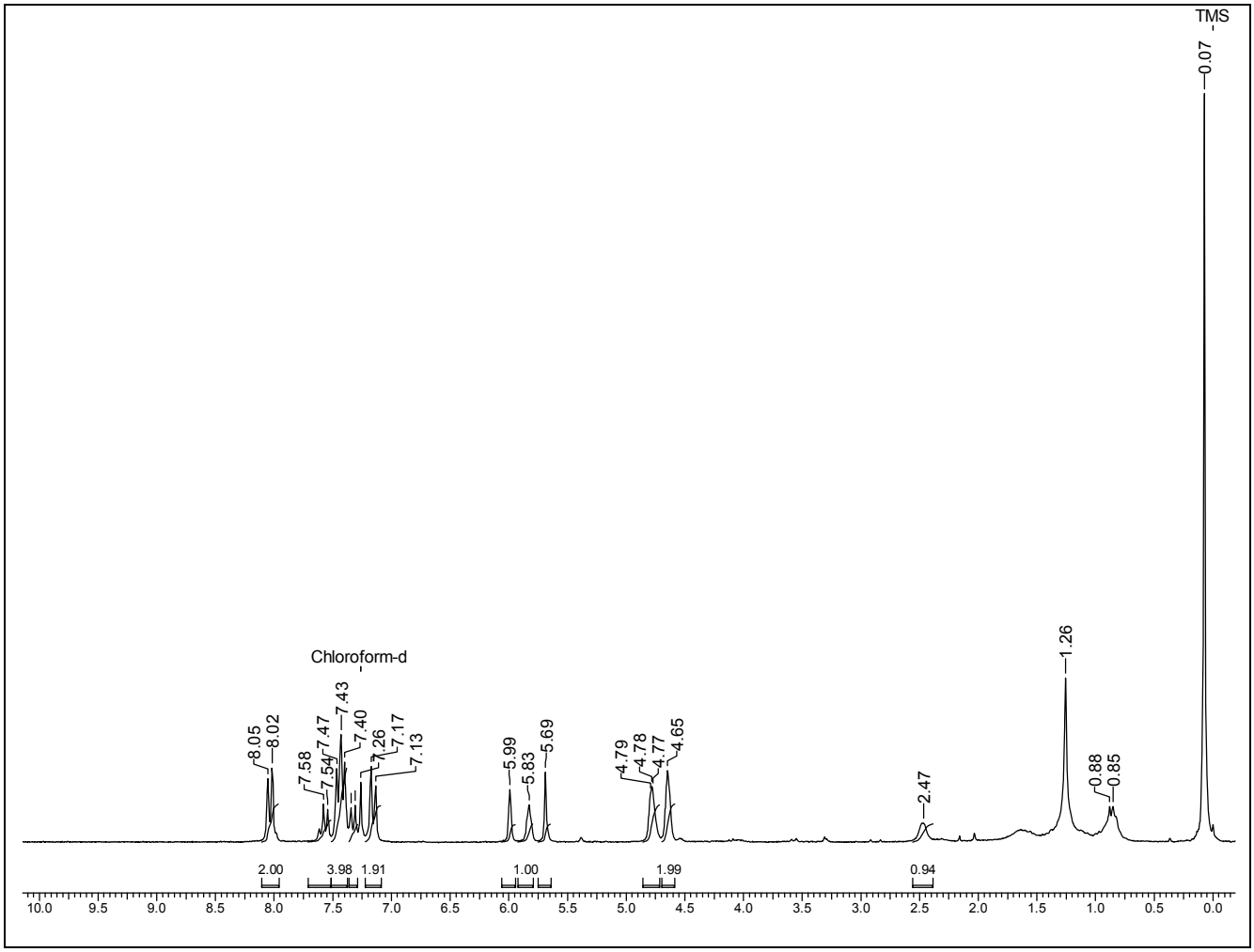


Figure S5: ^{1}H NMR spectrum of the thiocarbonate **3** in chloroform-*d*.

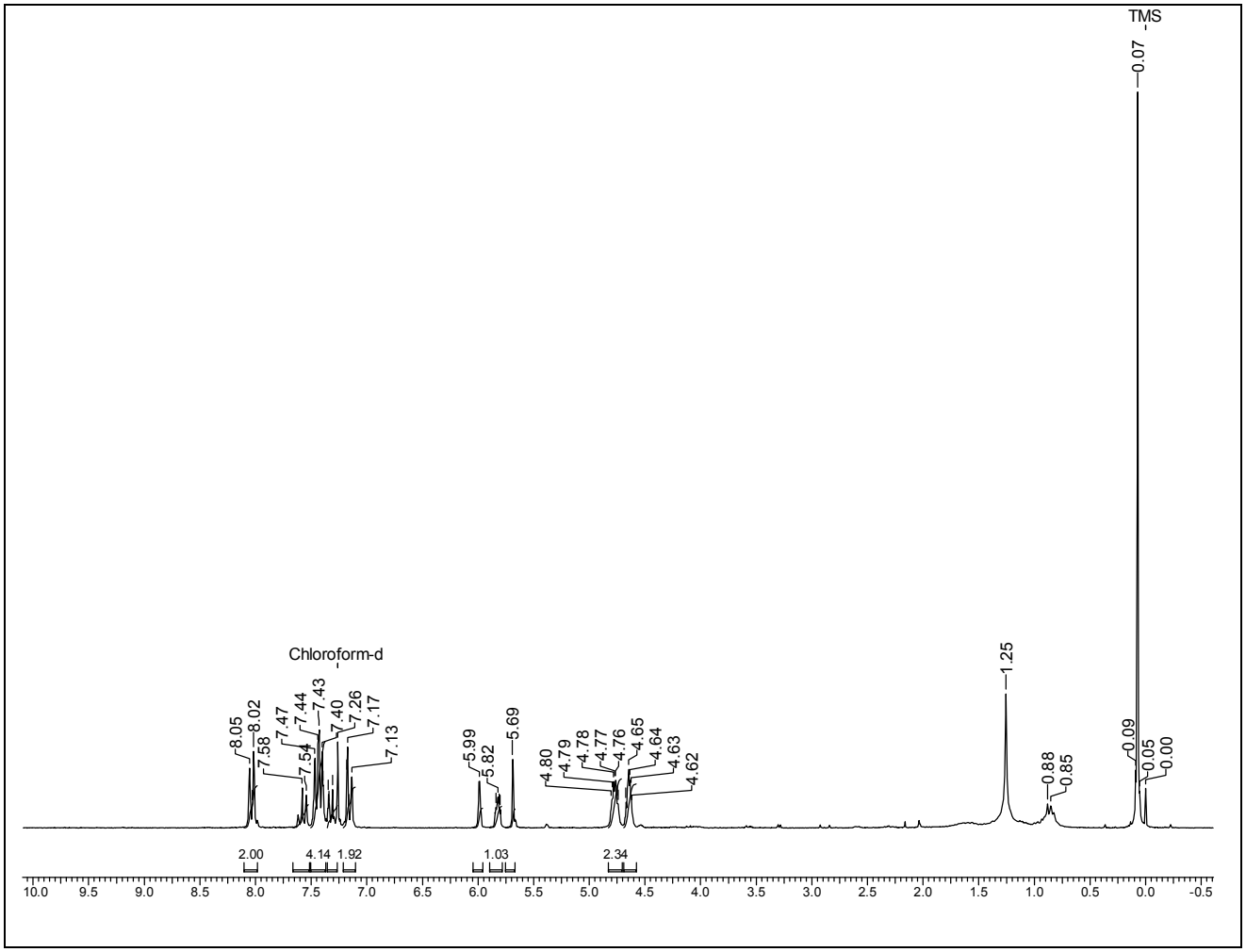


Figure S6: ^{1}H NMR spectrum of the thiocarbonate **3** in chloroform-*d*- D_2O.

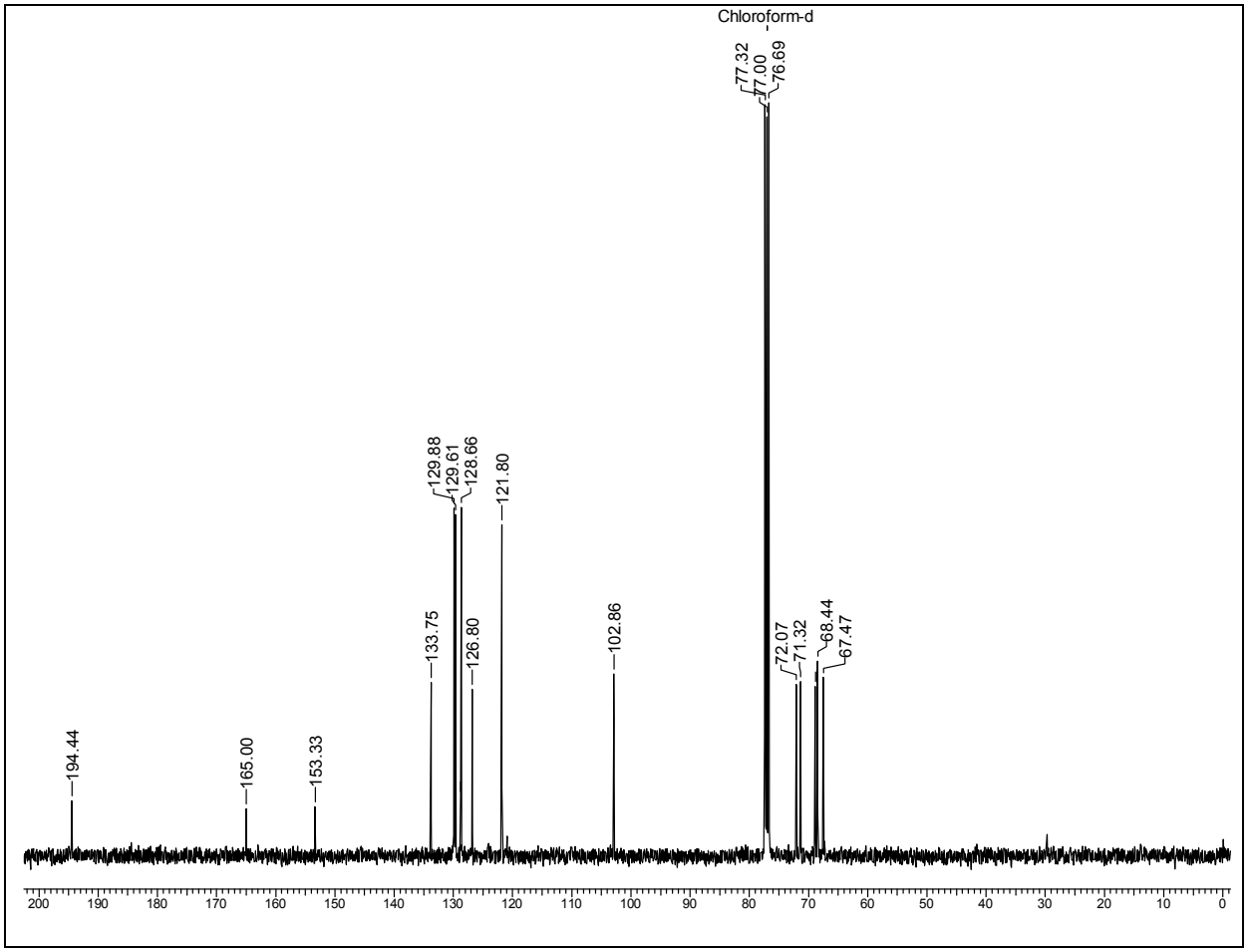


Figure S7: ^{13}C NMR spectrum of the thiocarbonate **3** in chloroform-*d*.

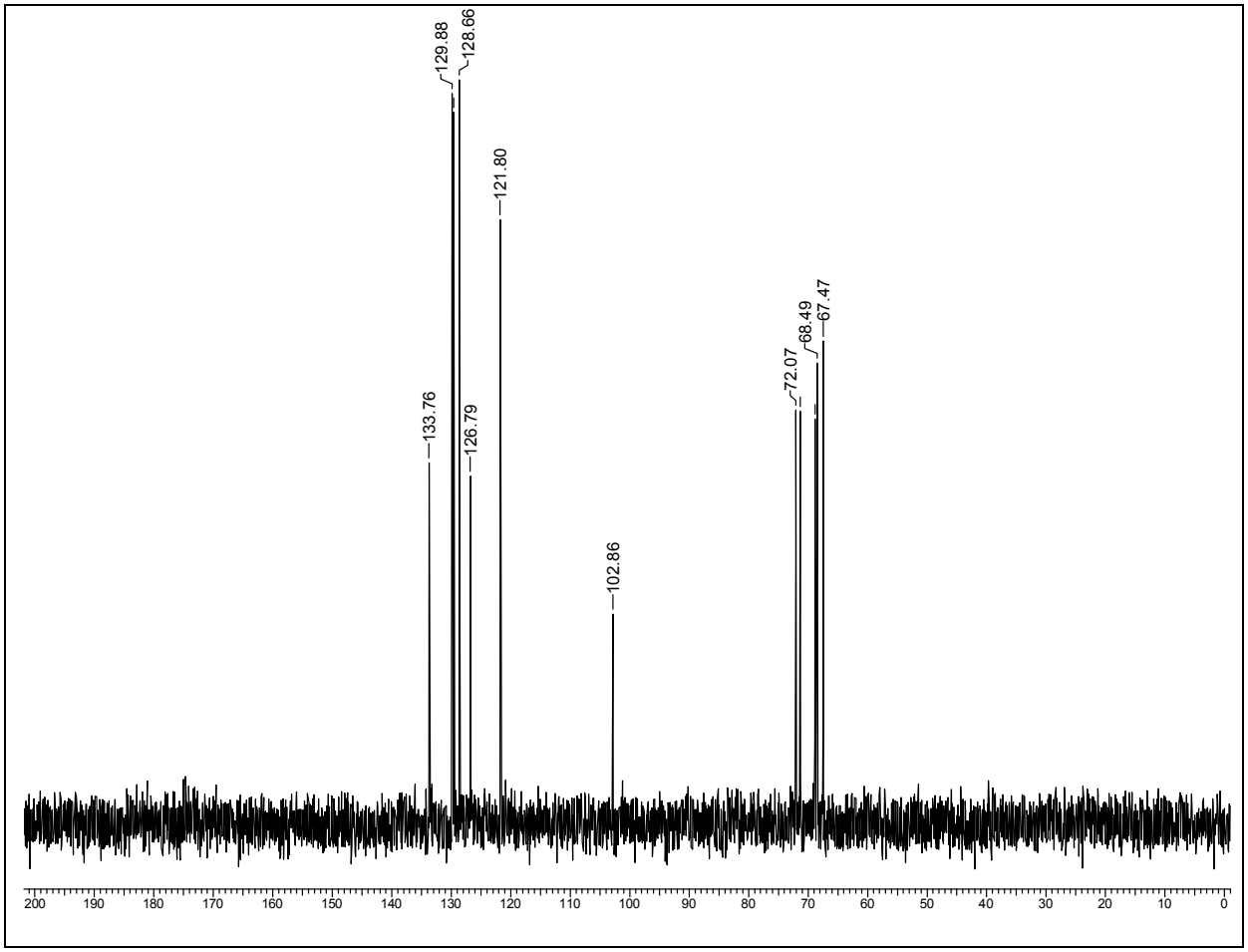


Figure S8: ^{13}C NMR (DEPT) spectrum of the thiocarbonate **3** in chloroform-*d*.

DSC Analysis:

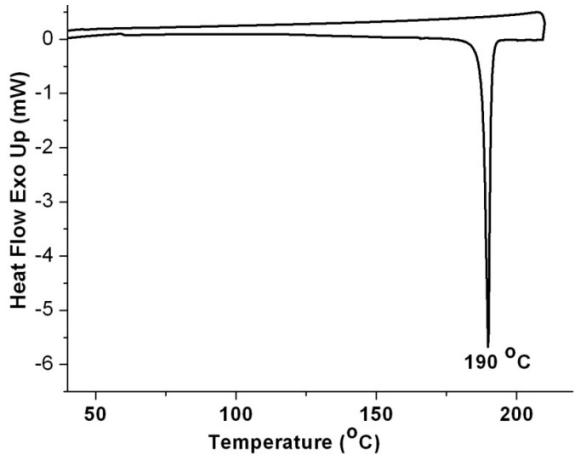


Figure S9: DSC of crystals of the carbonate **2**.

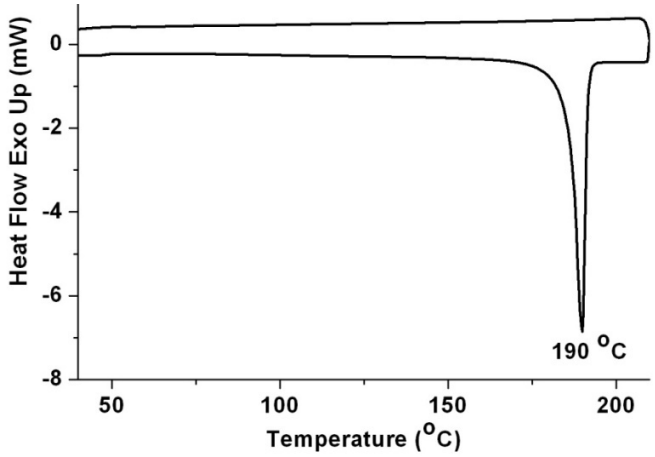


Figure S10: DSC of crystals of the thiocarbonate **3**.

Powder X-ray Diffraction Studies:

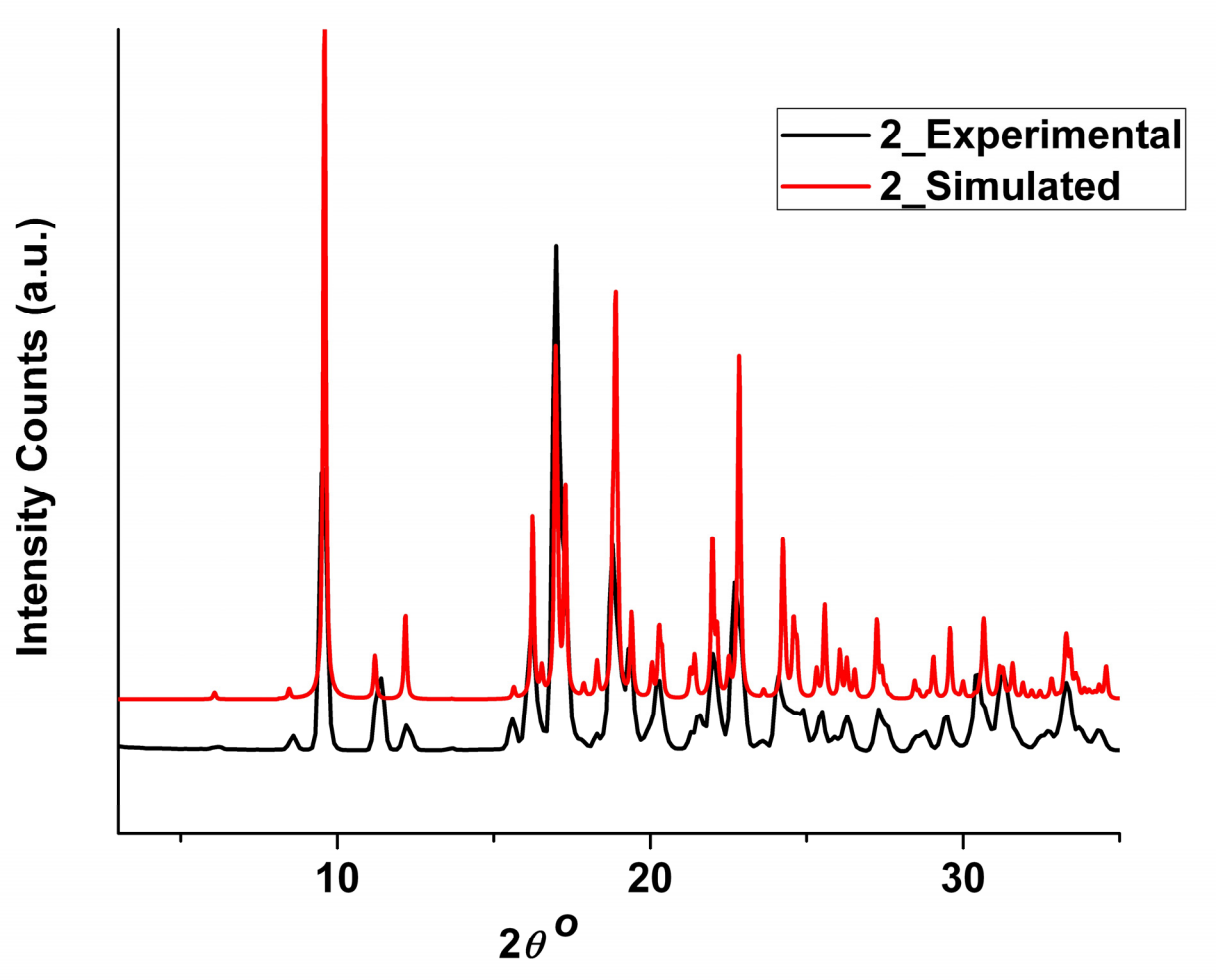


Figure S11. PXRD pattern of crystals of the carbonate **2**.

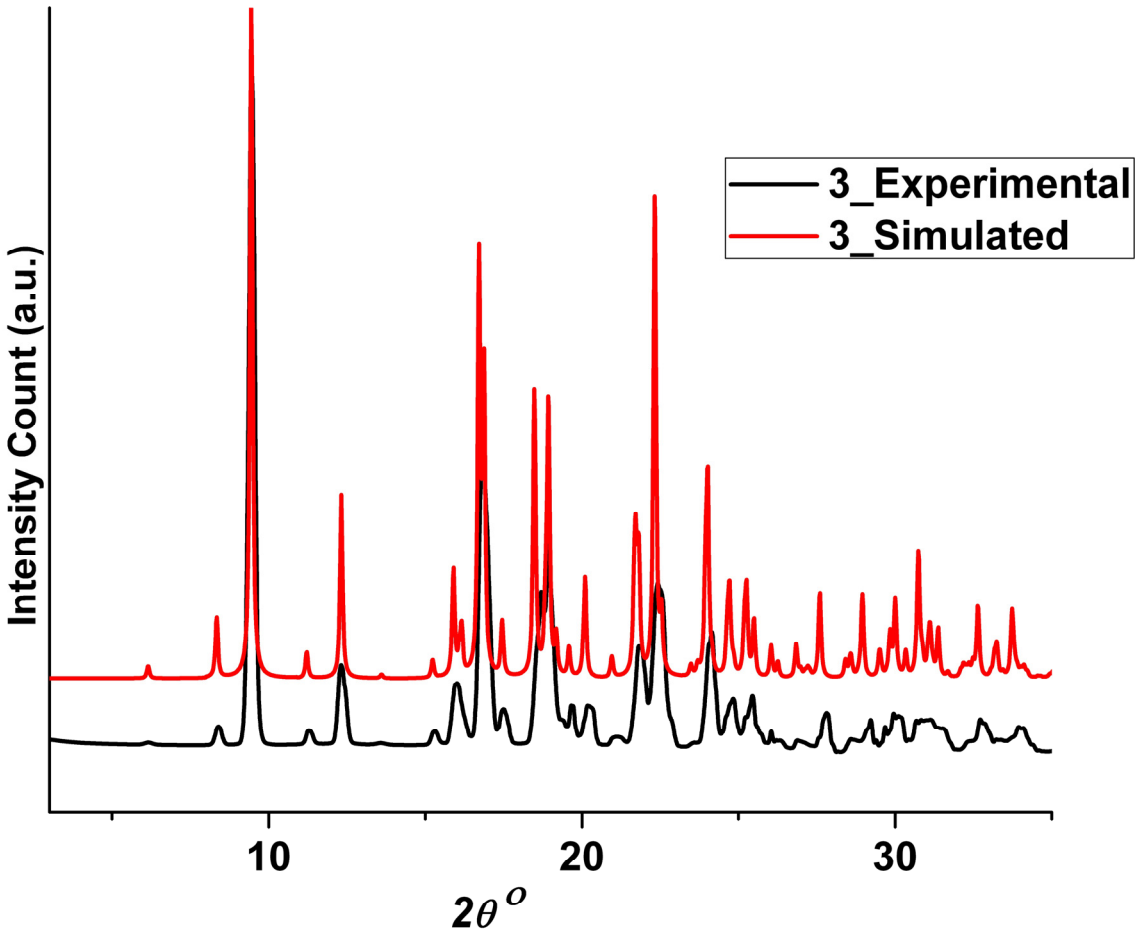


Figure S12. PXRD pattern of crystals of the thiocarbonate **3**.

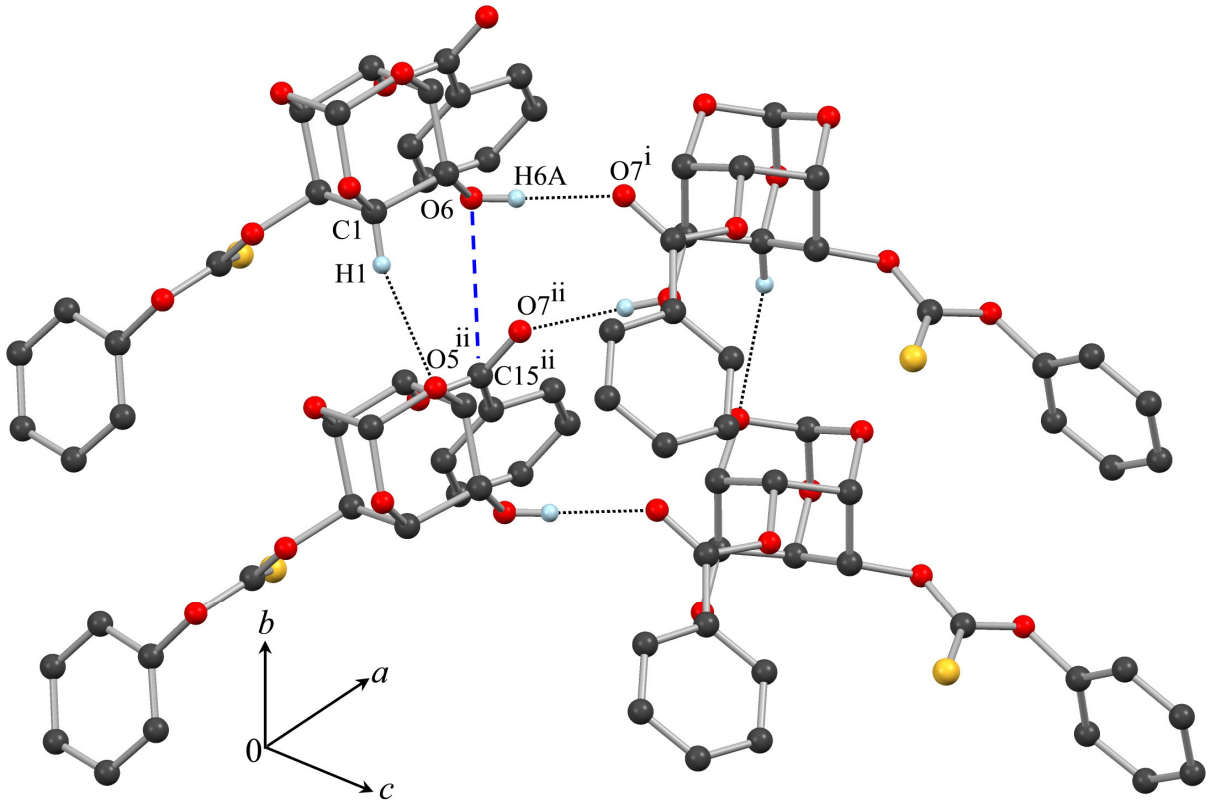
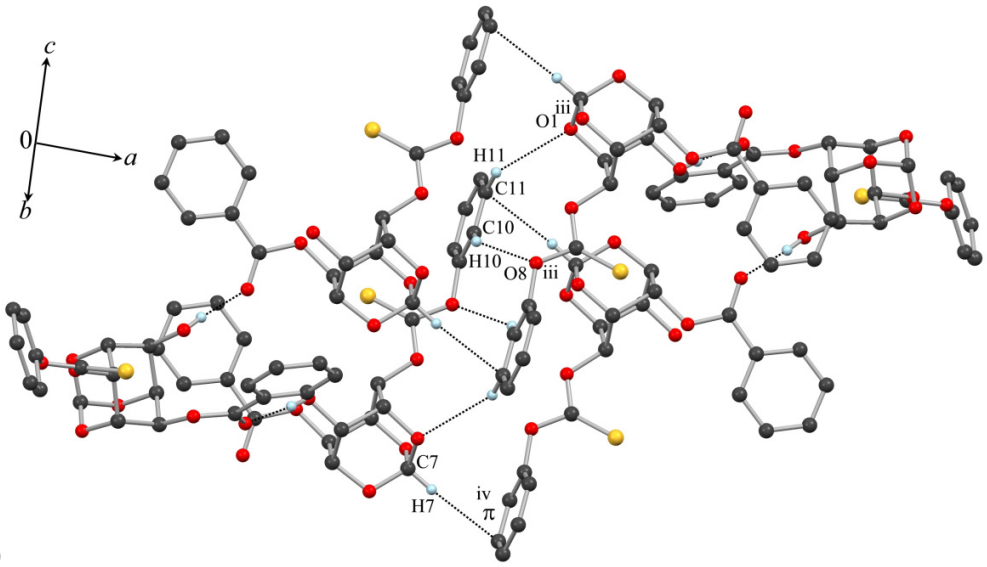
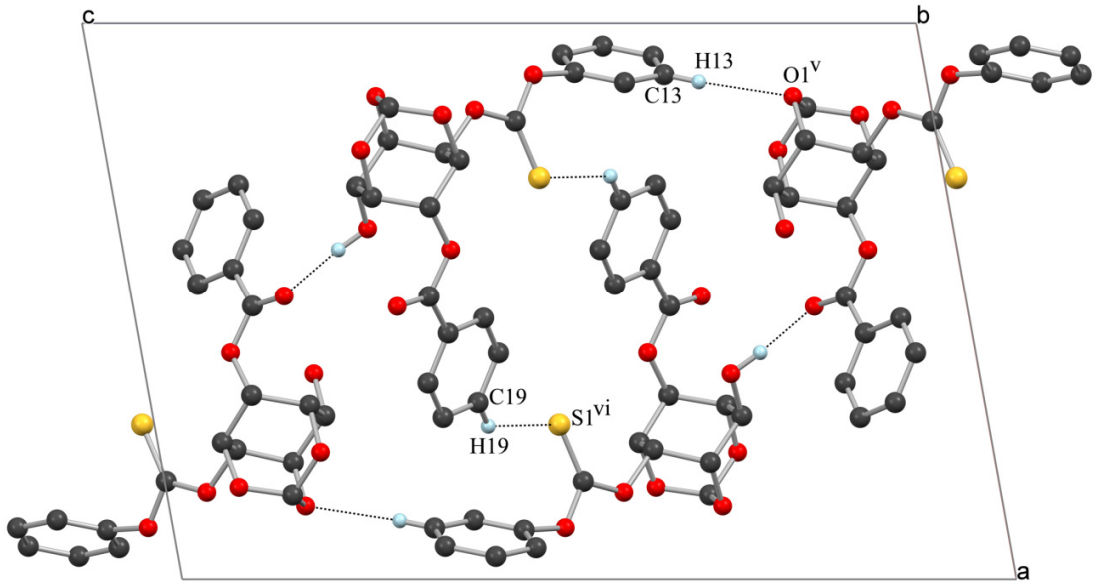


Figure S13. Helical association of molecules of the thiocarbonate **3** linked through O6-H6A···O7^{i} interactions shown in dotted lines. The helical assembly is supplemented by unit-translated C1-H1···O5^{ii} interactions. The relative positioning of the El···Nu groups (C15^{ii} =O7^{ii} ···O6-H6A) is shown by a dashed blue line [Symmetry codes: (i) −*x*+1, *y*−1/2, −*z*+3/2; (ii) x, y-1, z].

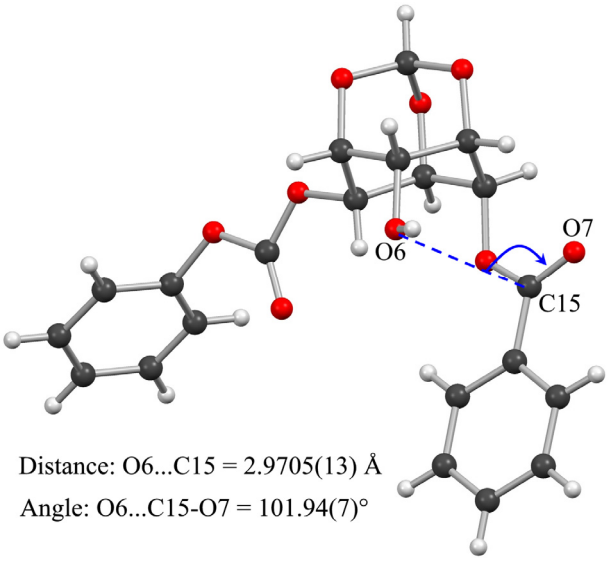


(a)

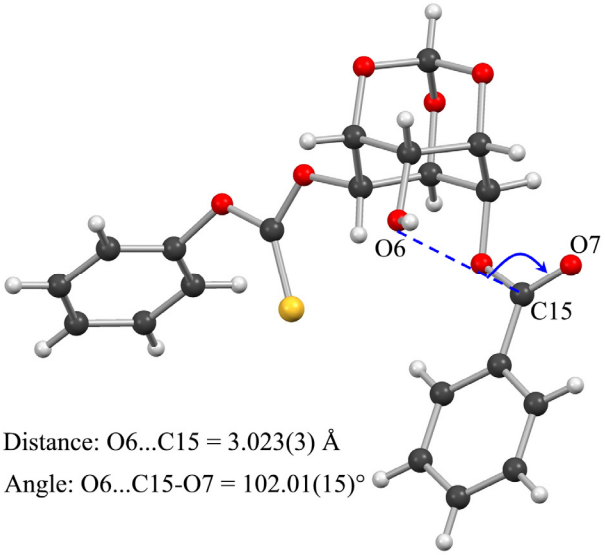


(b)

Figure S14. (a) The packing of thiocarbonate molecules **3** in its crystal connected through C10-H10···O8^{iii}, C11-H11···O1^{iii} and C7-H7···π^{iv} interactions (dotted lines). (b) View of the packing of molecules of **3** along the *b*-axis reveals joining of adjacent molecules through C13-H13...O1^{v} and C19-H19···S1^{vi} interactions. [Symmetry codes: (iii) −*x*, −*y*, −*z*+1; (iv) −*x*, −*y*+1, −*z*+1; (v) –x, -y+1/2, z-1/2; (vi) −*x*+1, −*y*, −*z*+1.].



(a)



(b)

Figure S15. Intramolecular geometry of the electrophile (C=O) and nucleophile (OH) in crystals of (a) carbonate **2** (b) thiocarbonate **3**. Although the geometry for the intramolecular addition of the hydroxy group to the benzoate carbonyl group is good in crystals of **2** and **3**, it does not lead to a cyclized product. Cyclization involving the axial benzoate and the axial hydroxy group results in the formation of an orthoester type structure which is not stable and reverts back to the starting material.