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Synthesis and bioluminescence of electronically modified and rotationally restricted colour-shifting infraluciferins

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and

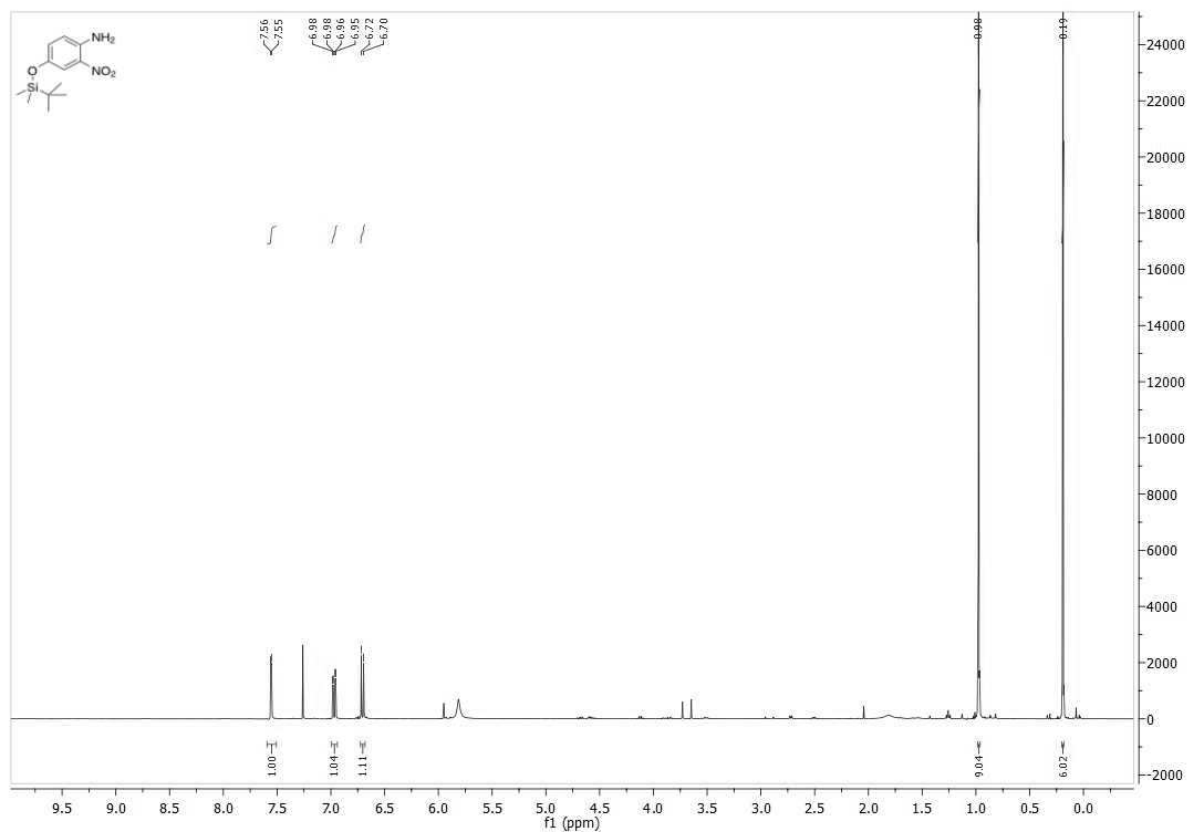
School of Biosciences, University of Cardiff, Sir Martin Evans Building, Museum Avenue, Cardiff, CF10 3AX, UK

Supplementary Information

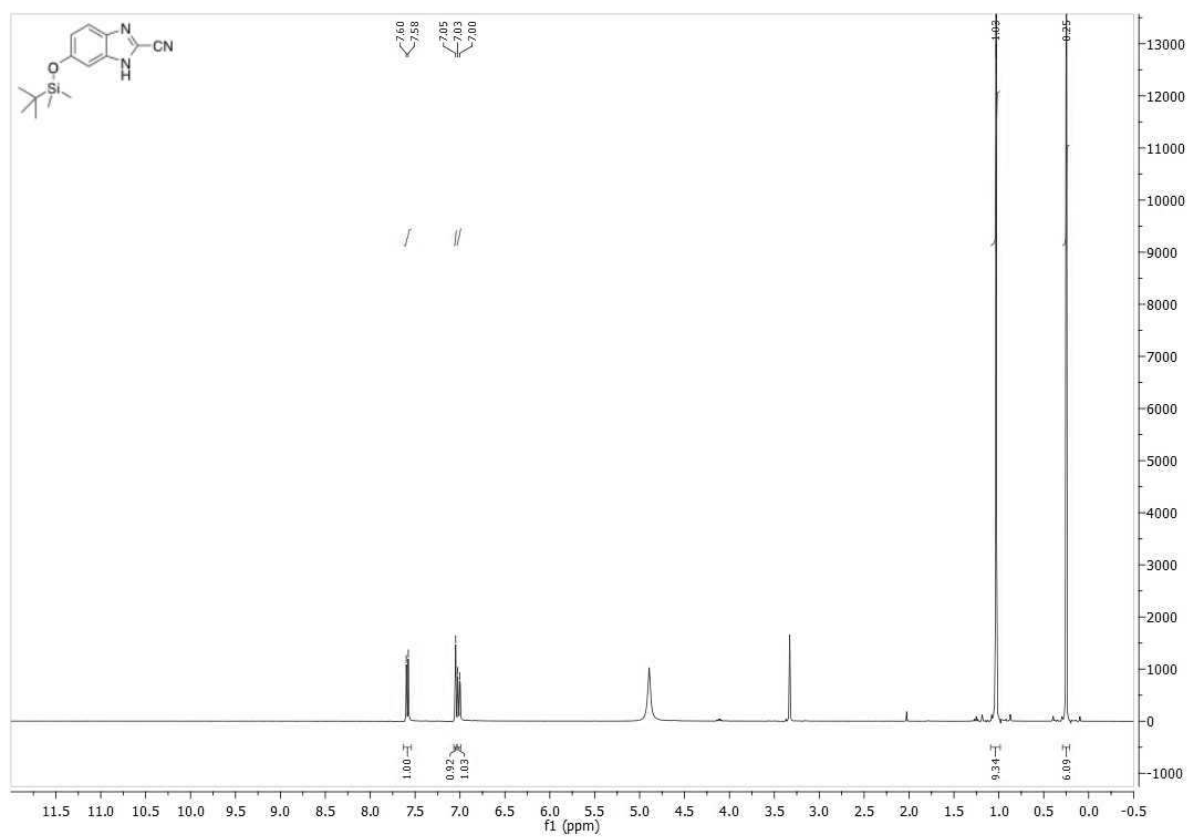
Copies of ^1H and ^{13}C NMR spectra

Graphs of emission kinetics of enzymes with different compounds acquired in the PIO

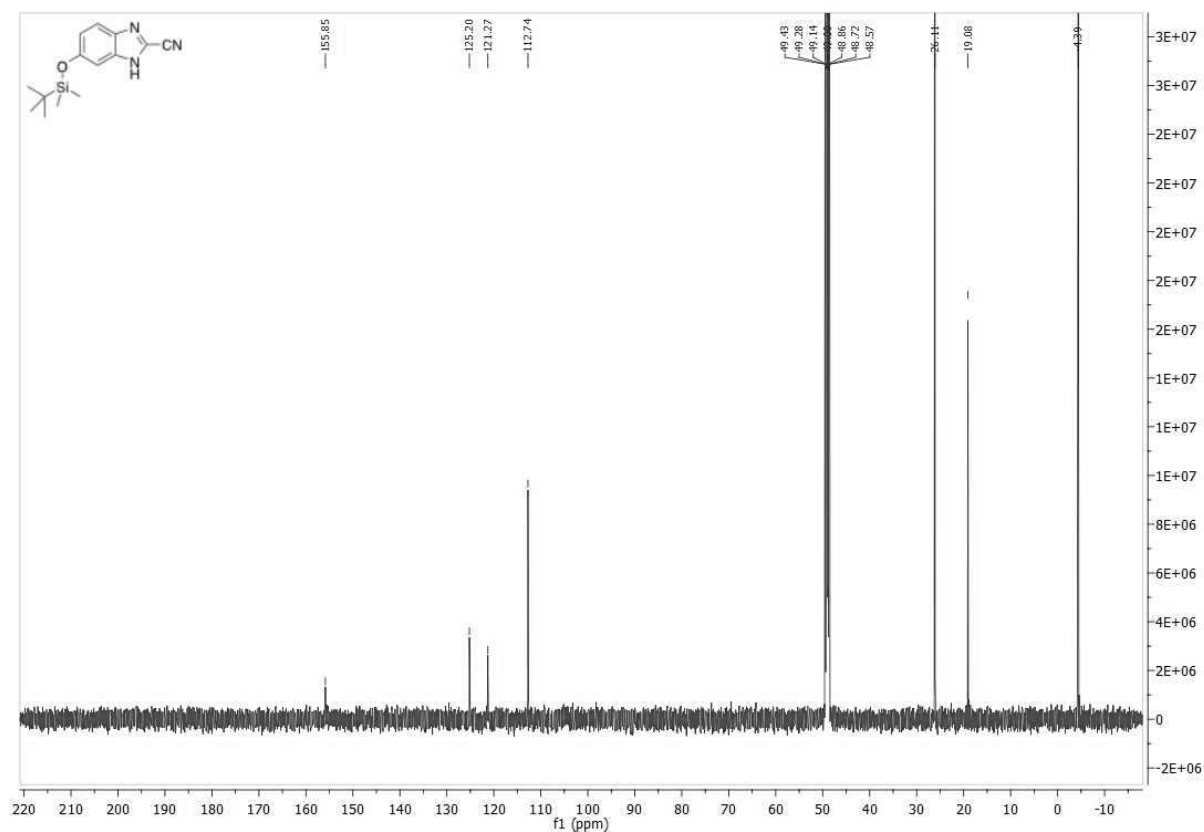
¹H – NMR: 4-((*tert*-butyldimethylsilyl)oxy)-2-nitroaniline (15)



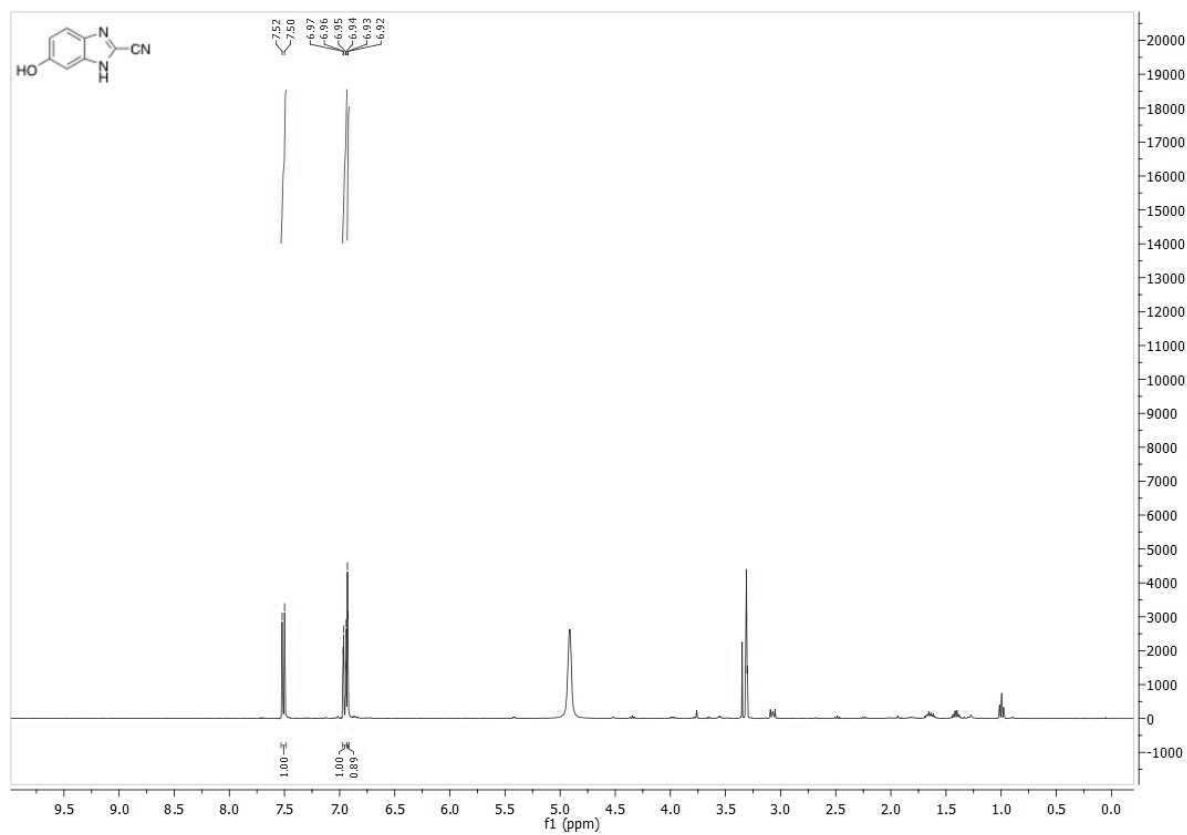
¹H – NMR: 6-((*tert*-butyldimethylsilyl)oxy)-1H-benzo[d]imidazole-2-carbonitrile (16)



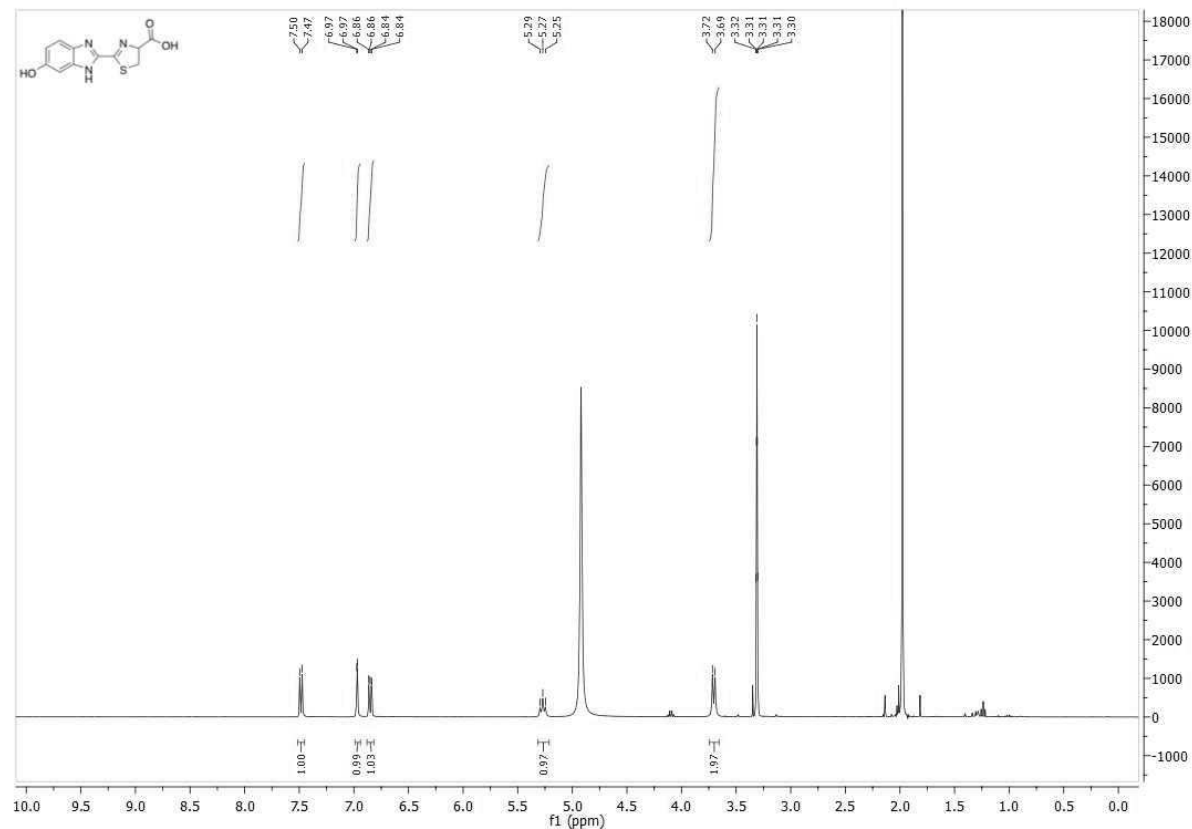
¹³C – NMR: 6-((tert-butyldimethylsilyloxy)-1H-benzo[d]imidazole-2-carbonitrile (16)



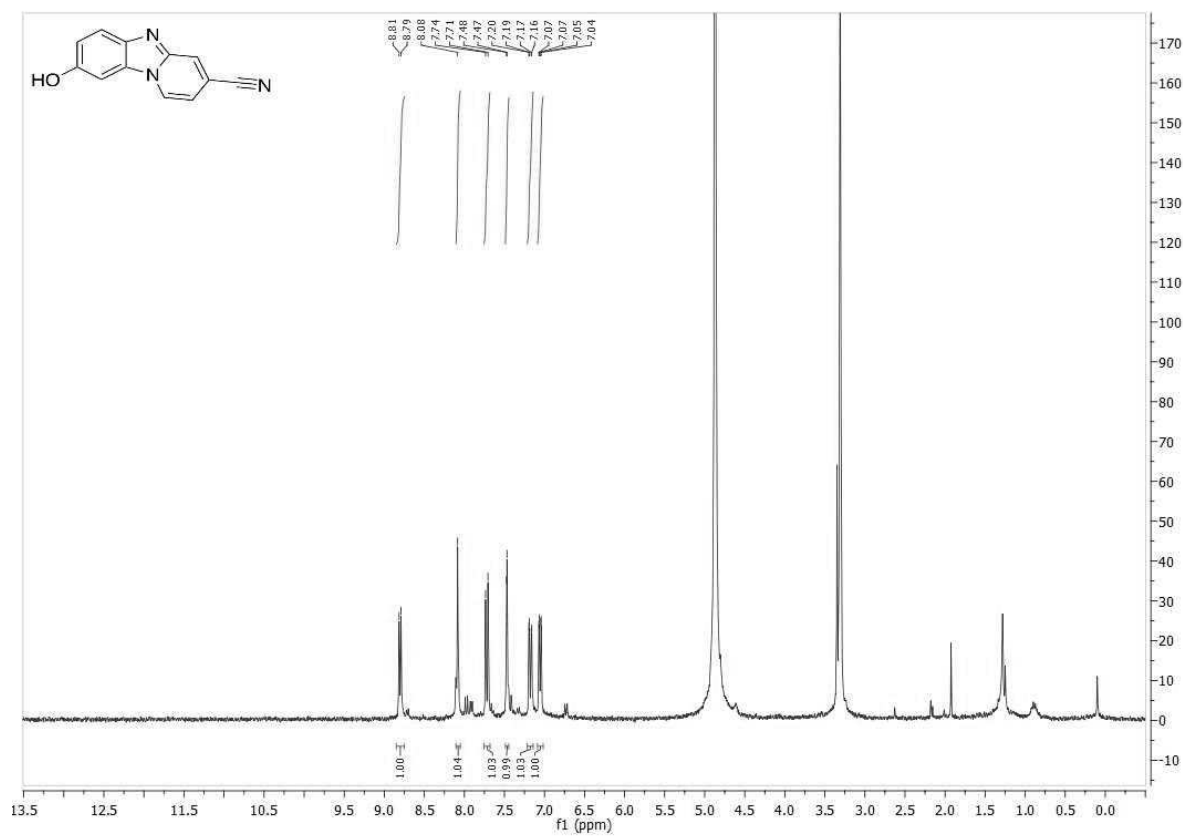
¹H – NMR: 6-hydroxy-1H-benzo[d]imidazole-2-carbonitrile (17)



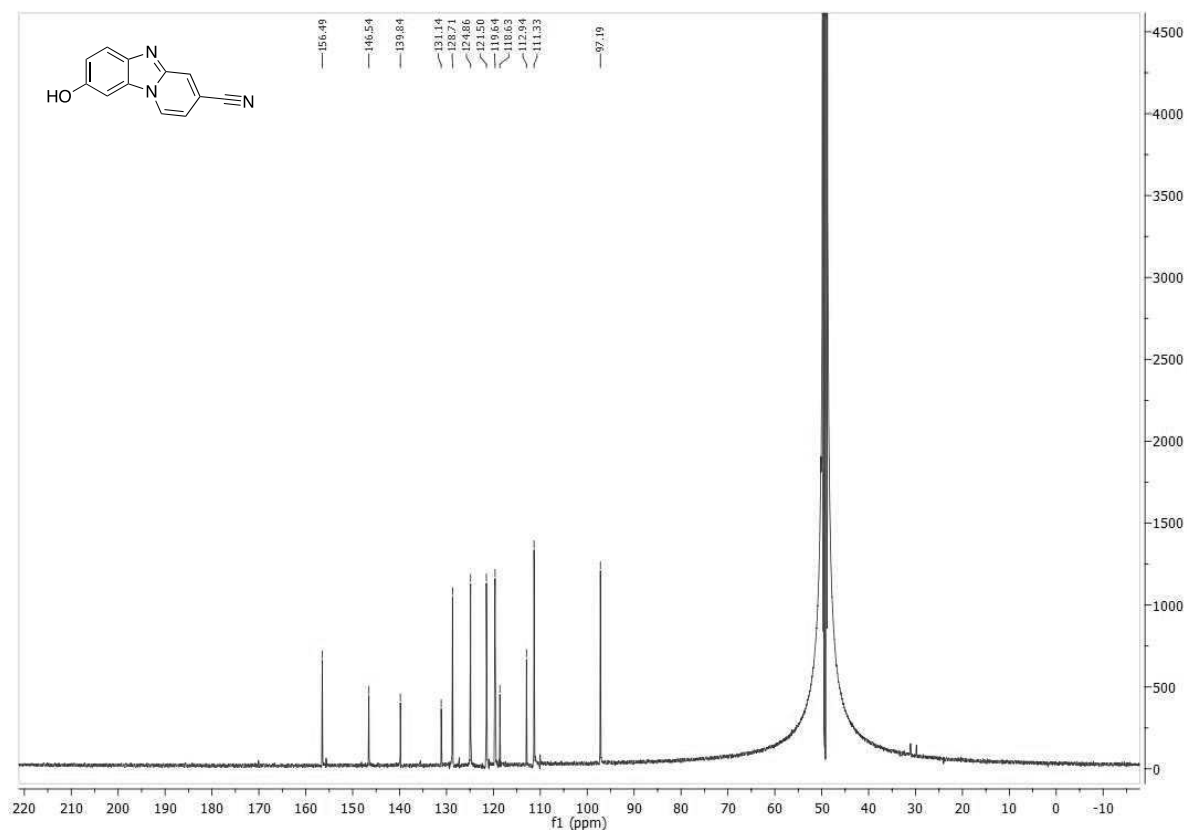
¹H – NMR: 2-(6-hydroxy-1*H*-benzo[*d*]imidazol-2-yl)-4,5-dihydrothiazole-4-carboxylic acid (10)



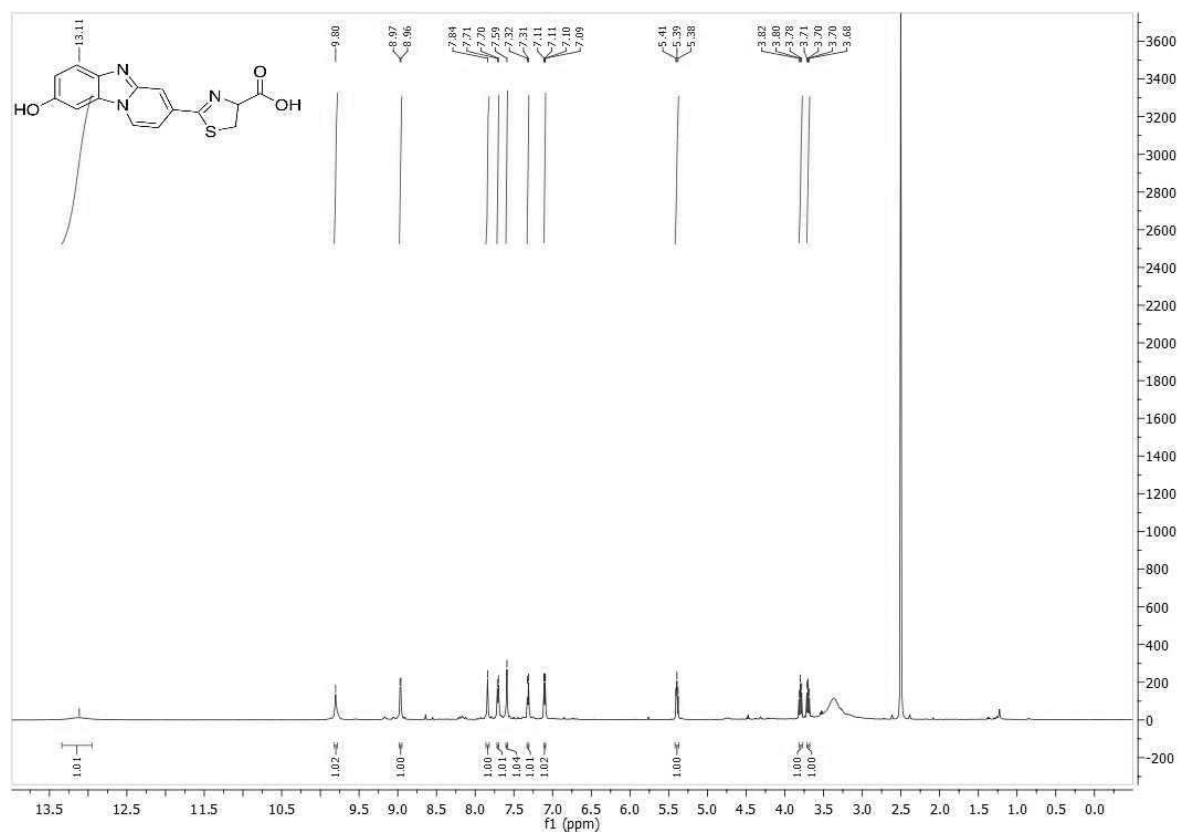
¹H – NMR: 8-hydroxybenzo[4,5]imidazo[1,2-*a*]pyridine-3-carbonitrile (20)



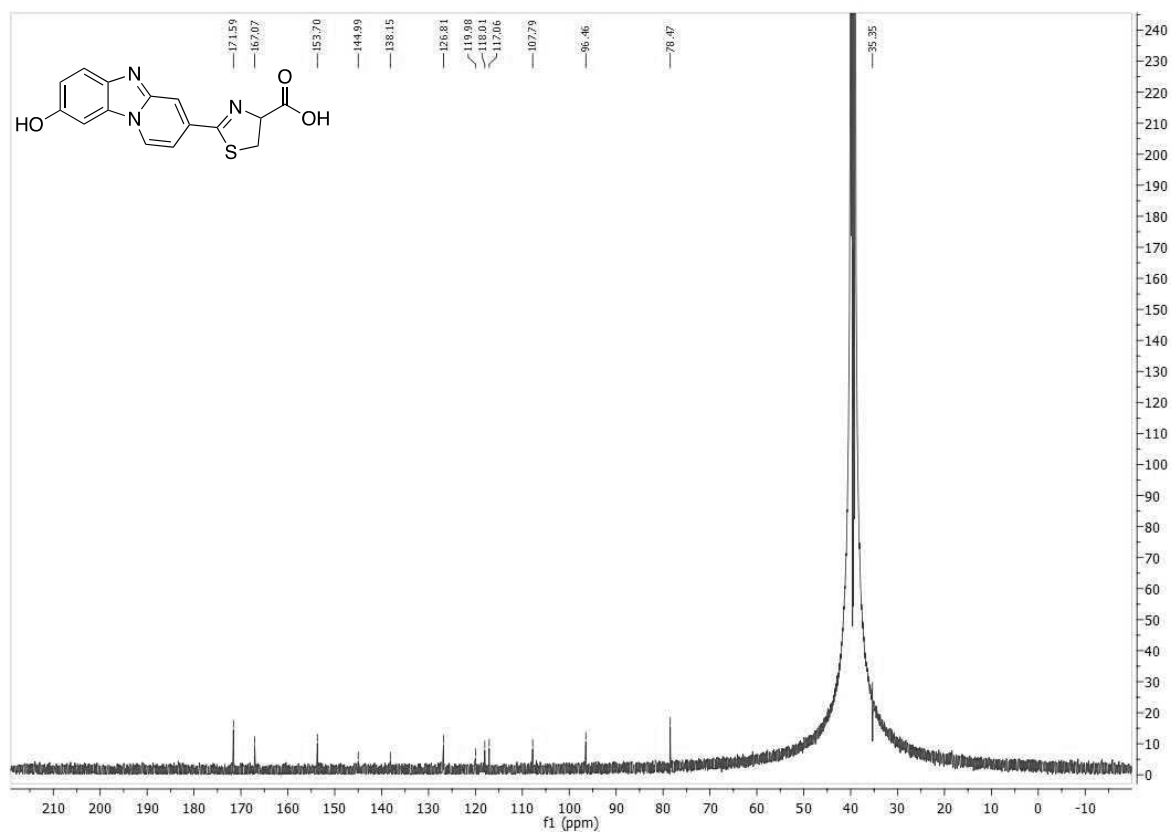
¹³C-NMR: 8-hydroxybenzo[4,5]imidazo[1,2-*a*]pyridine-3-carbonitrile (**20**)



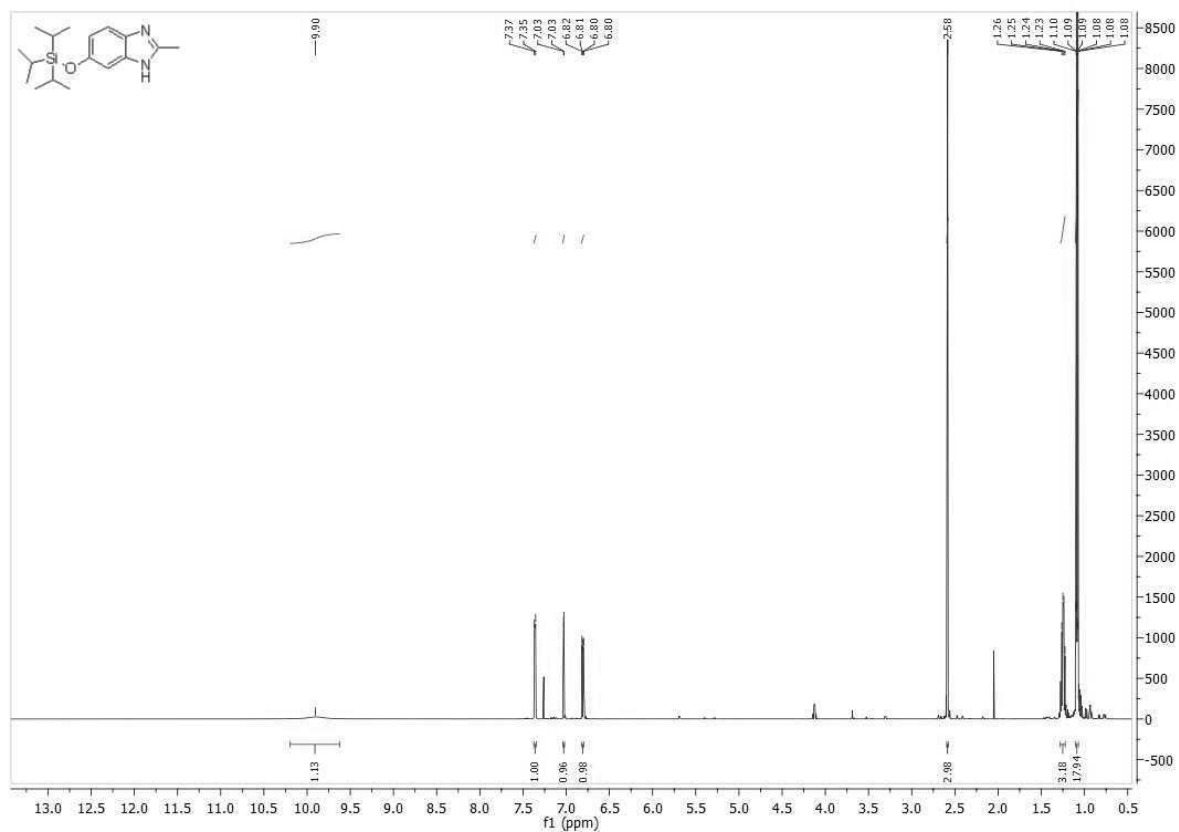
¹H – NMR: 2-(8-hydroxybenzo[4,5]imidazo[1,2-*a*]pyridin-3-yl)-4,5-dihydrothiazole-4-carboxylic acid (**12**)



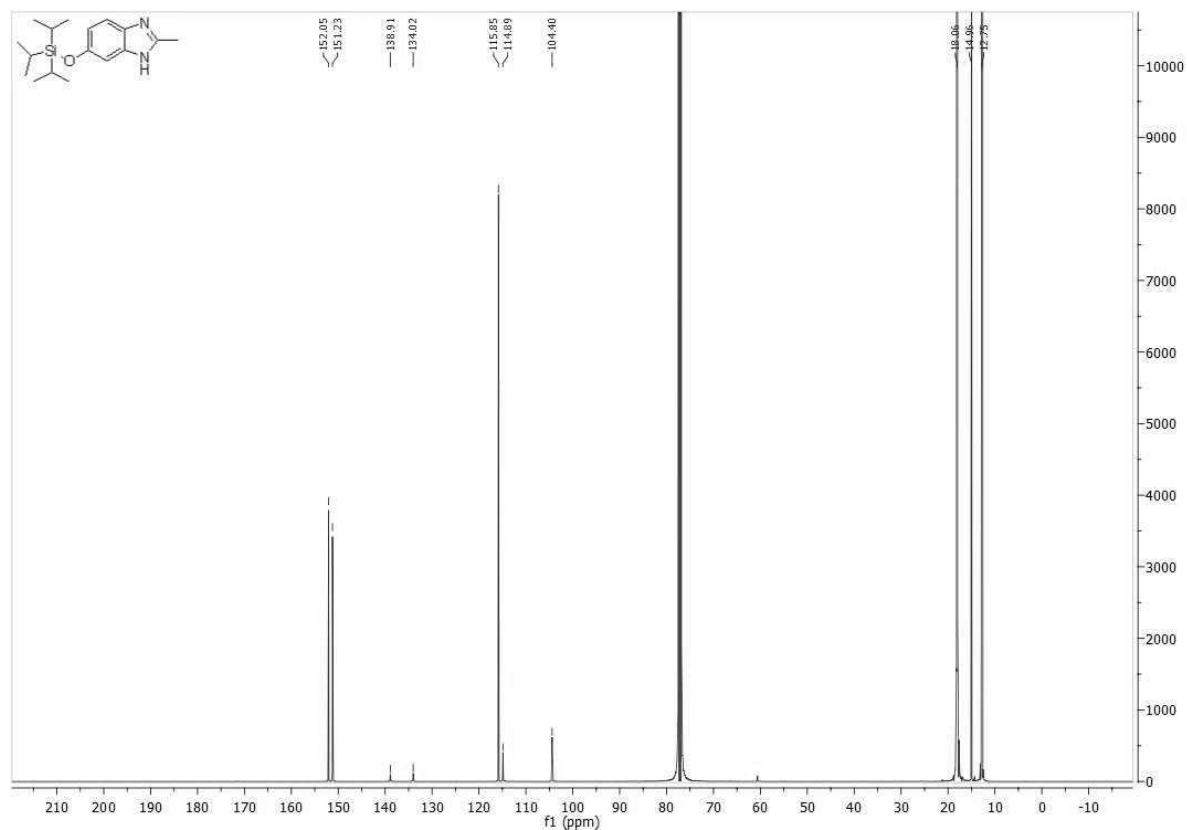
¹³C-NMR: 2-(8-hydroxybenzo[4,5]imidazo[1,2-a]pyridin-3-yl)-4,5-dihydrothiazole-4-carboxylic acid (12)



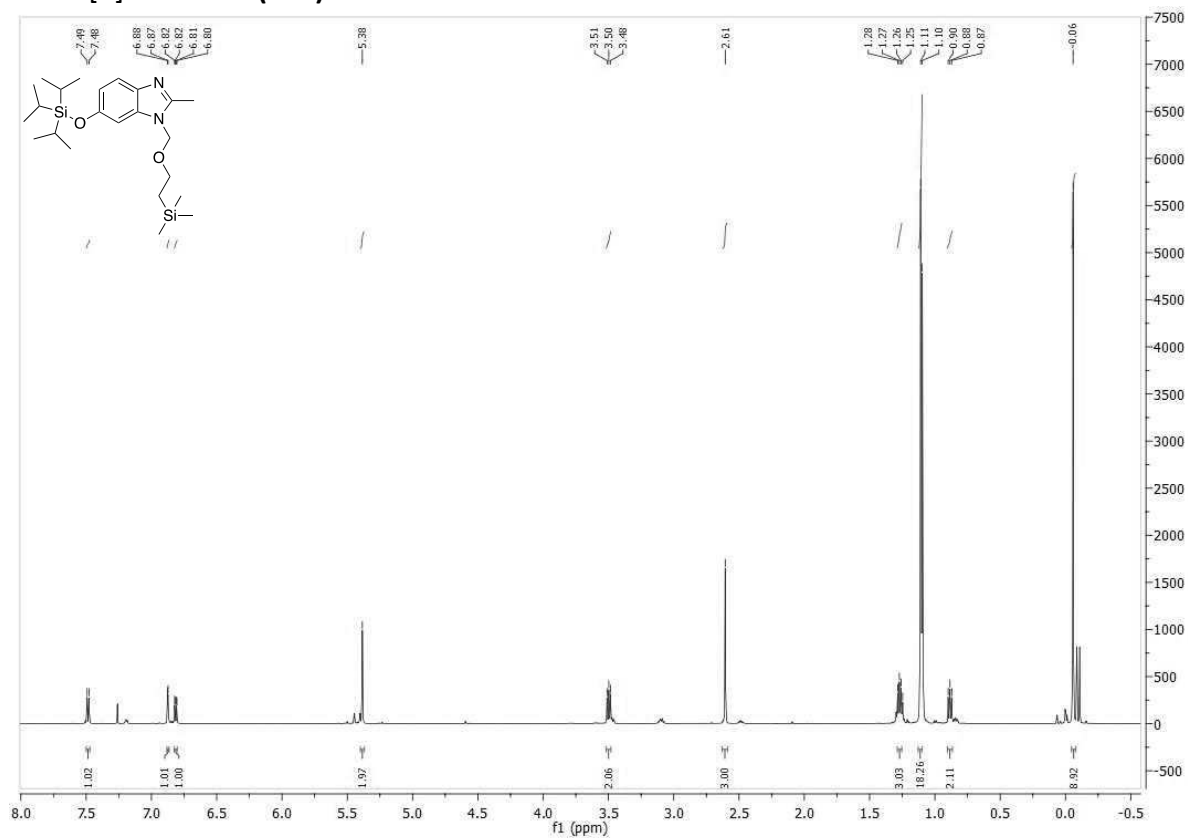
¹H – NMR: 2-methyl-6-((triisopropylsilyl)oxy)-1H-benzo[d]imidazole (22)



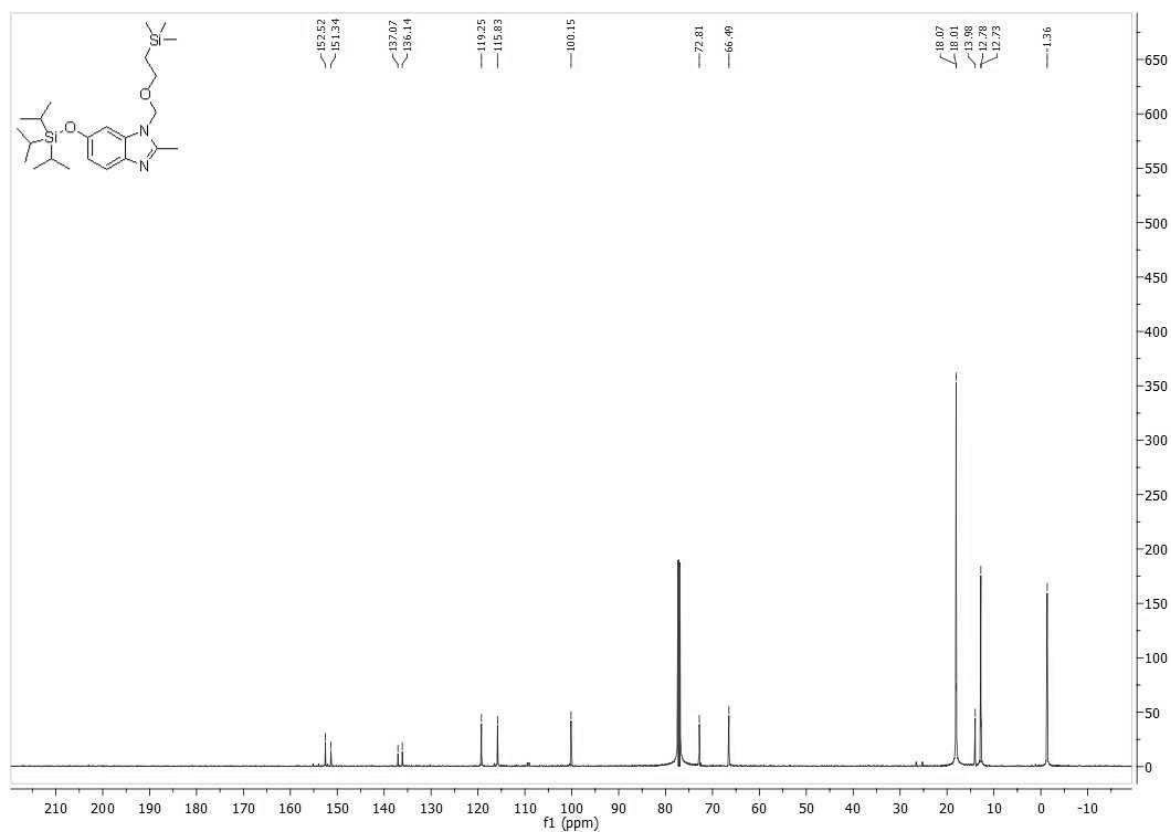
¹³C-NMR: 2-methyl-6-((triisopropylsilyl)oxy)-1H-benzo[d]imidazole (22)



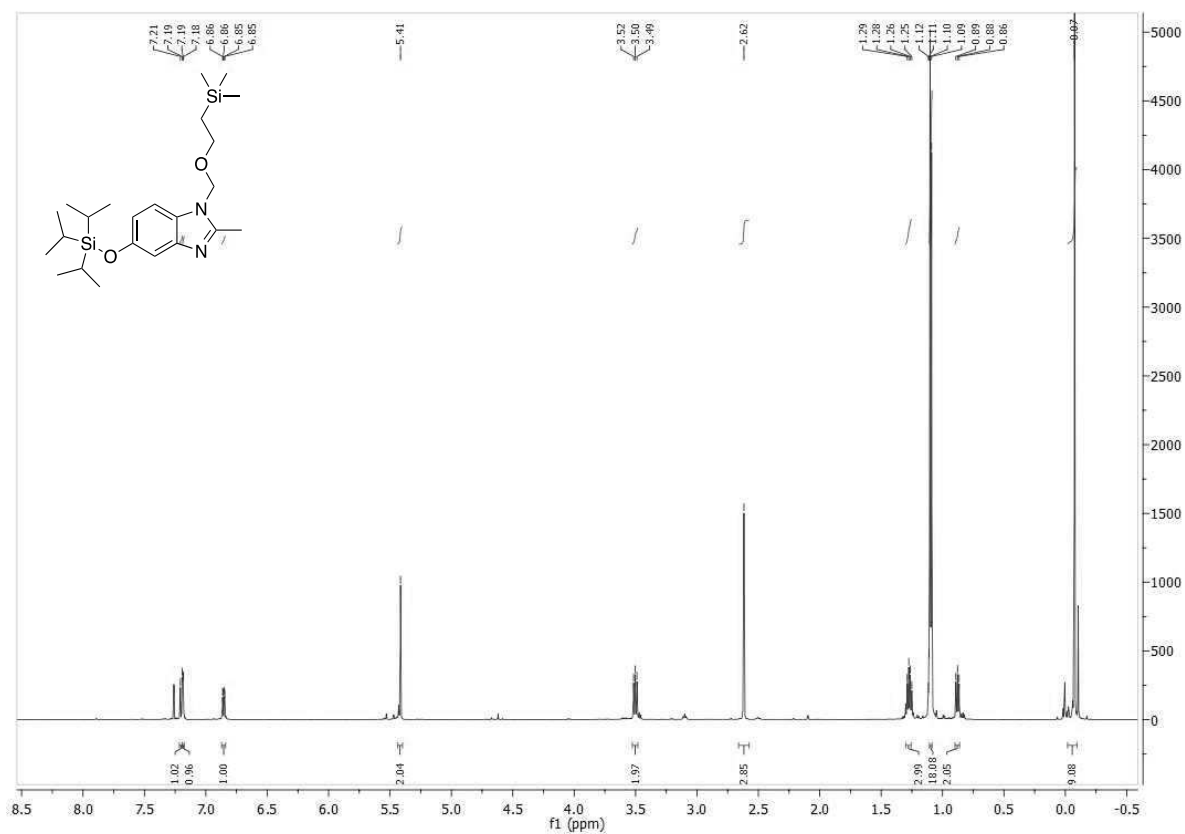
¹H-NMR: 2-methyl-6-((triisopropylsilyl)oxy)-1-((2-(trimethylsilyl)ethoxy)methyl)-1H-benzo[d]imidazole (23a)



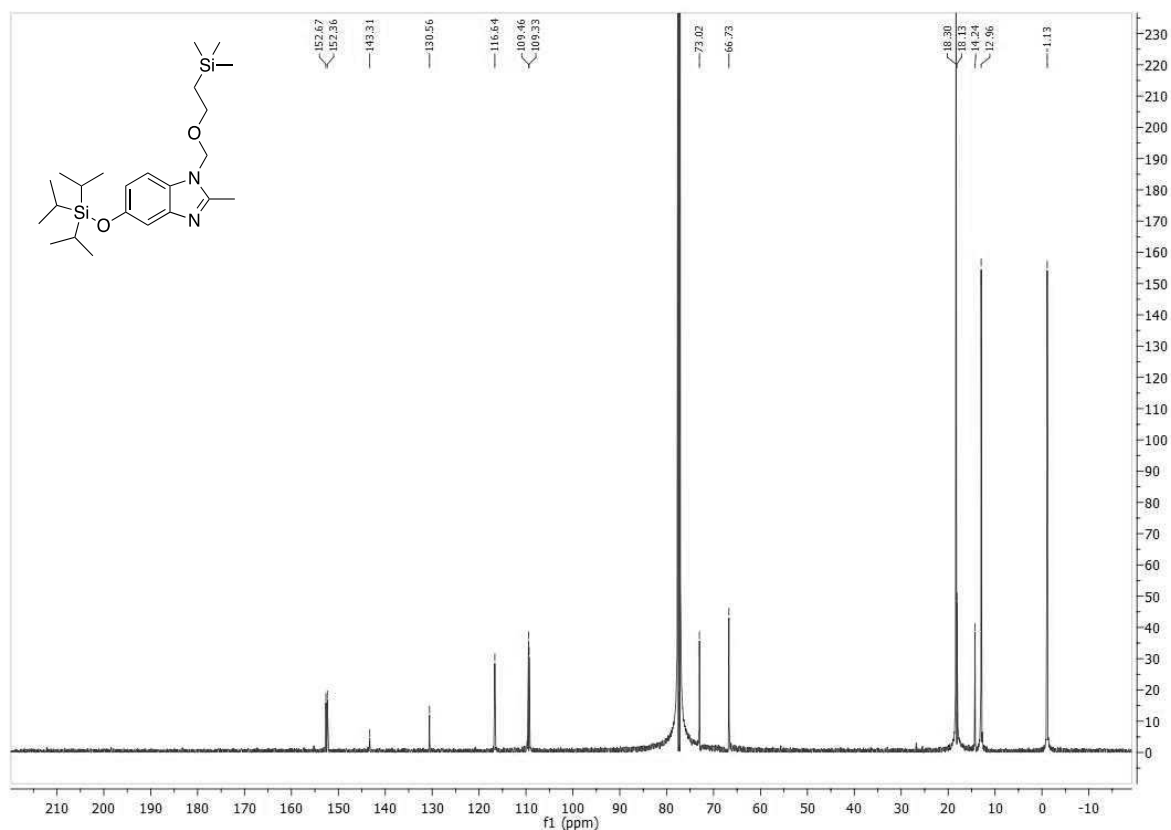
¹³C-NMR: 2-methyl-6-((triisopropylsilyl)oxy)-1-((2-(trimethylsilyl)ethoxy)methyl)-1H-benzo[d]imidazole (**23a**)



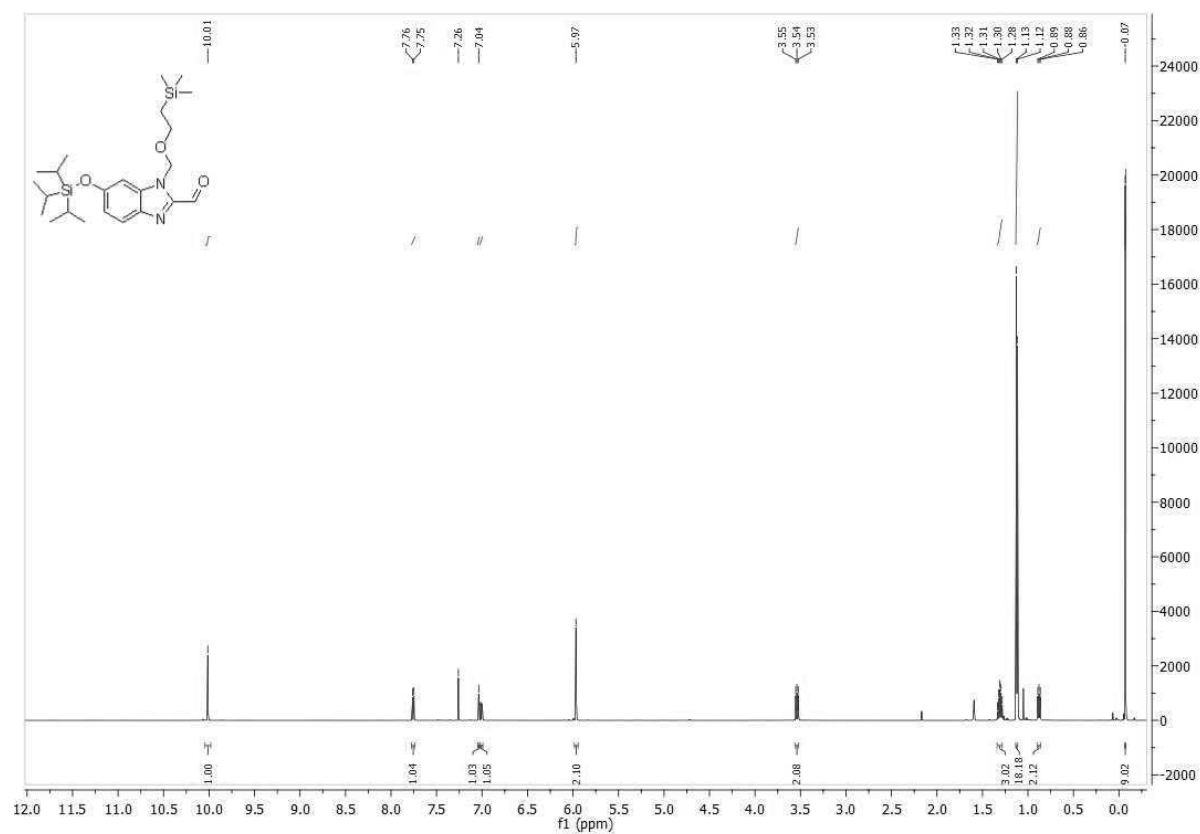
¹H-NMR: 2-methyl-5-((triisopropylsilyl)oxy)-1-((2-(trimethylsilyl)ethoxy)methyl)-1H-benzo[d]imidazole (**23b**)



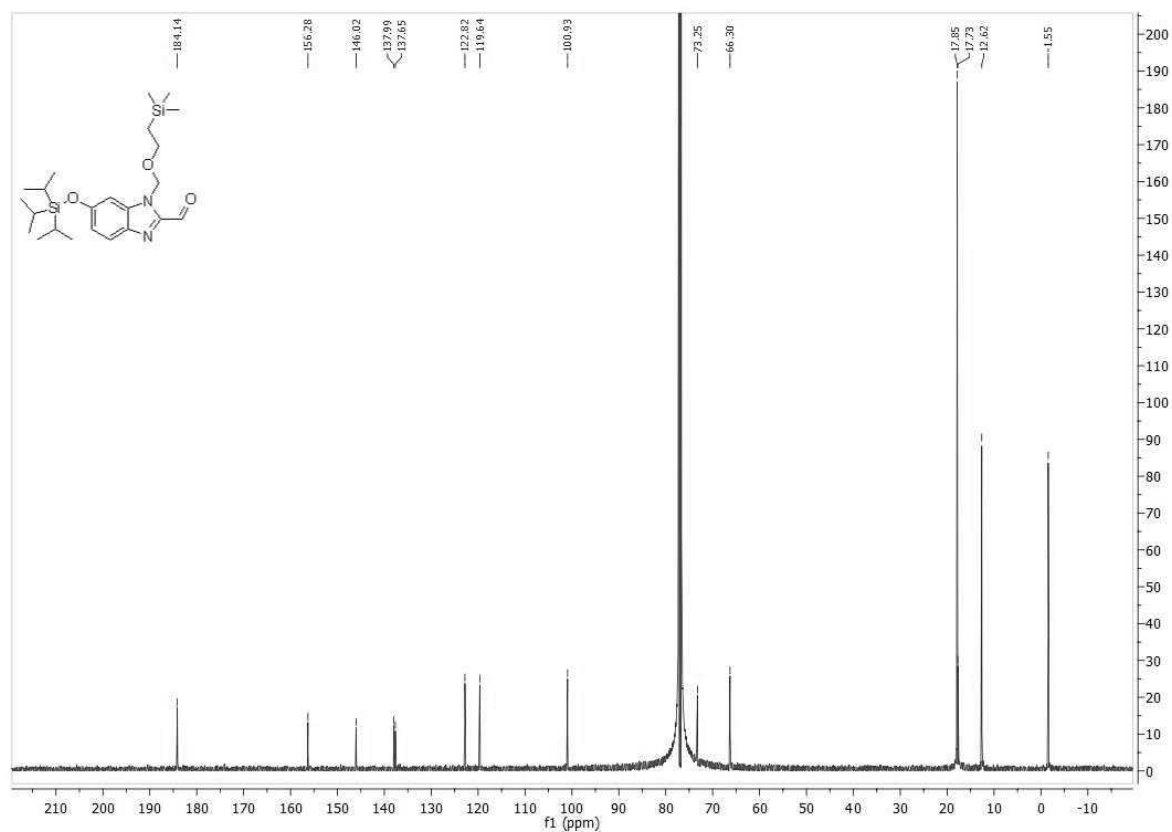
¹³C-NMR: 2-methyl-5-((triisopropylsilyl)oxy)-1-((2-(trimethylsilyl)ethoxy)methyl)-1H-benzo[d]imidazole (**23b**)



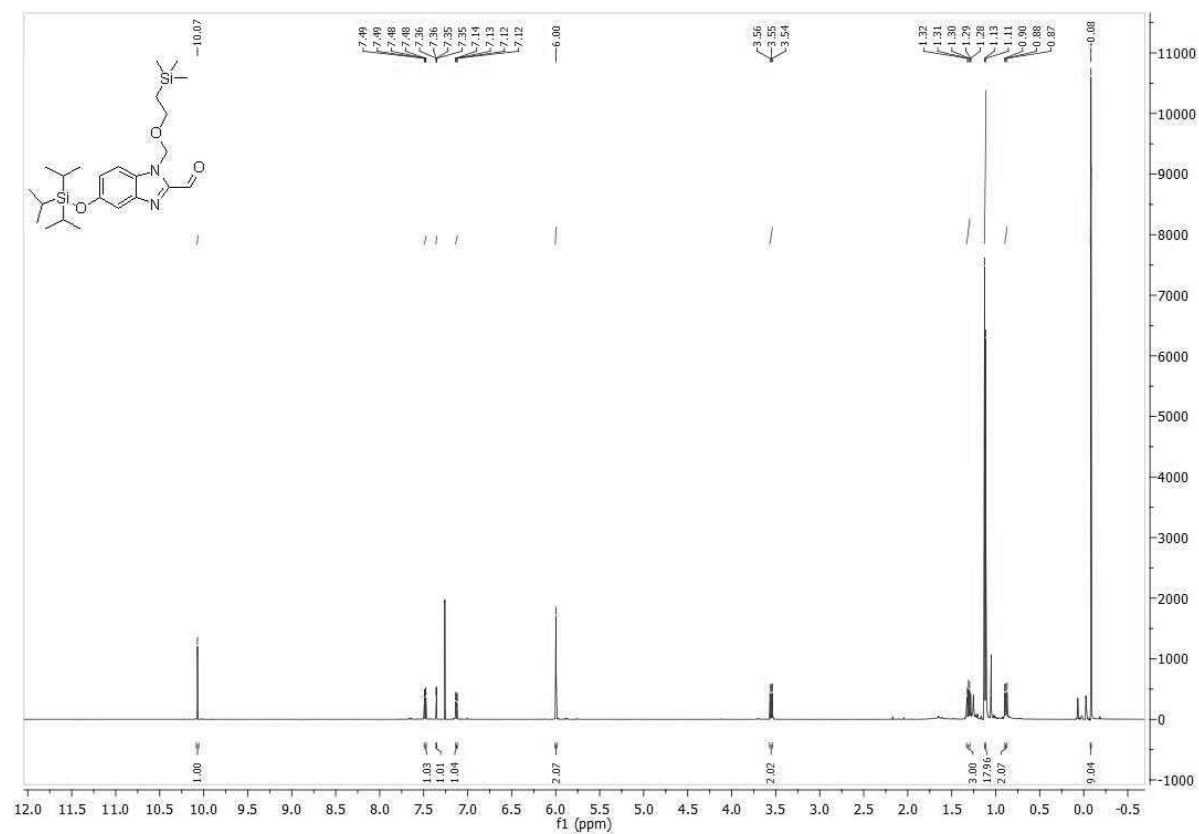
¹H – NMR: 6-((triisopropylsilyl)oxy)-1-((2-(trimethylsilyl)ethoxy)methyl)-1H-benzo[d]imidazole-2-carbaldehyde (**24a**)



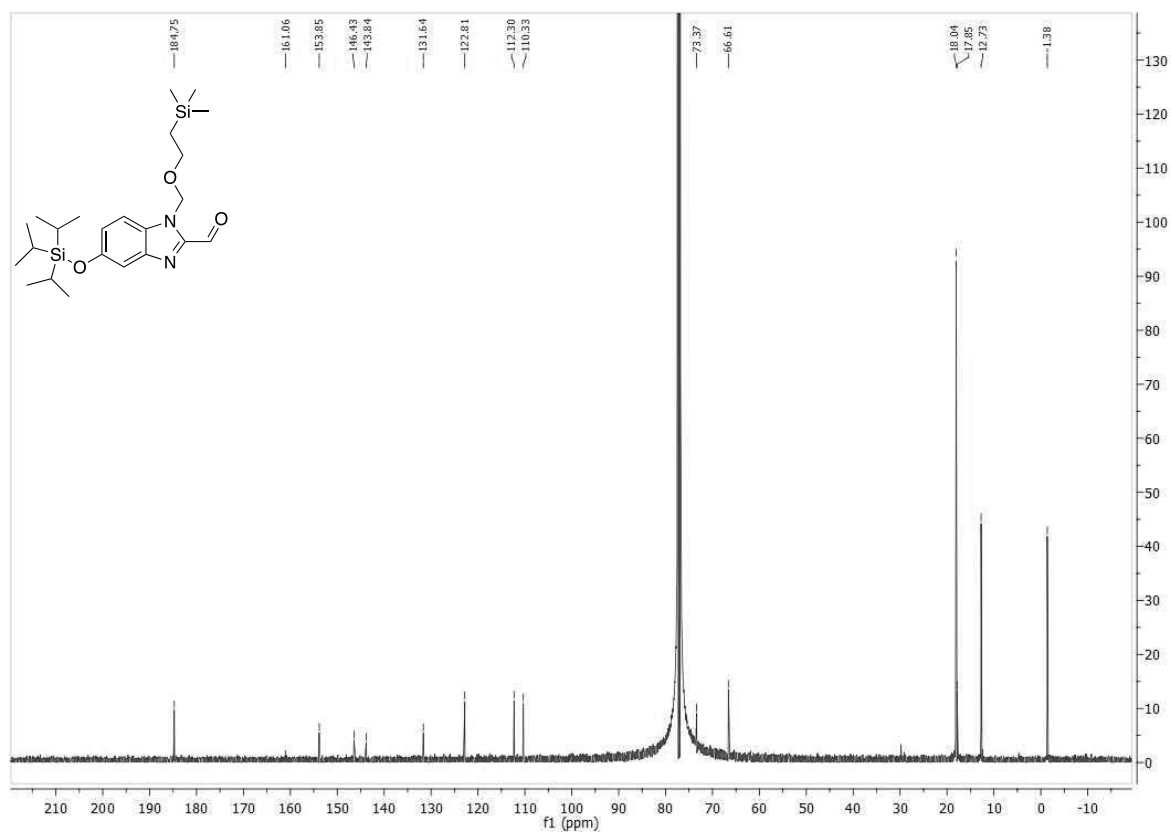
¹³C-NMR: 6-((triisopropylsilyl)oxy)-1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-benzo[*d*]imidazole-2-carbaldehyde (**24a**)



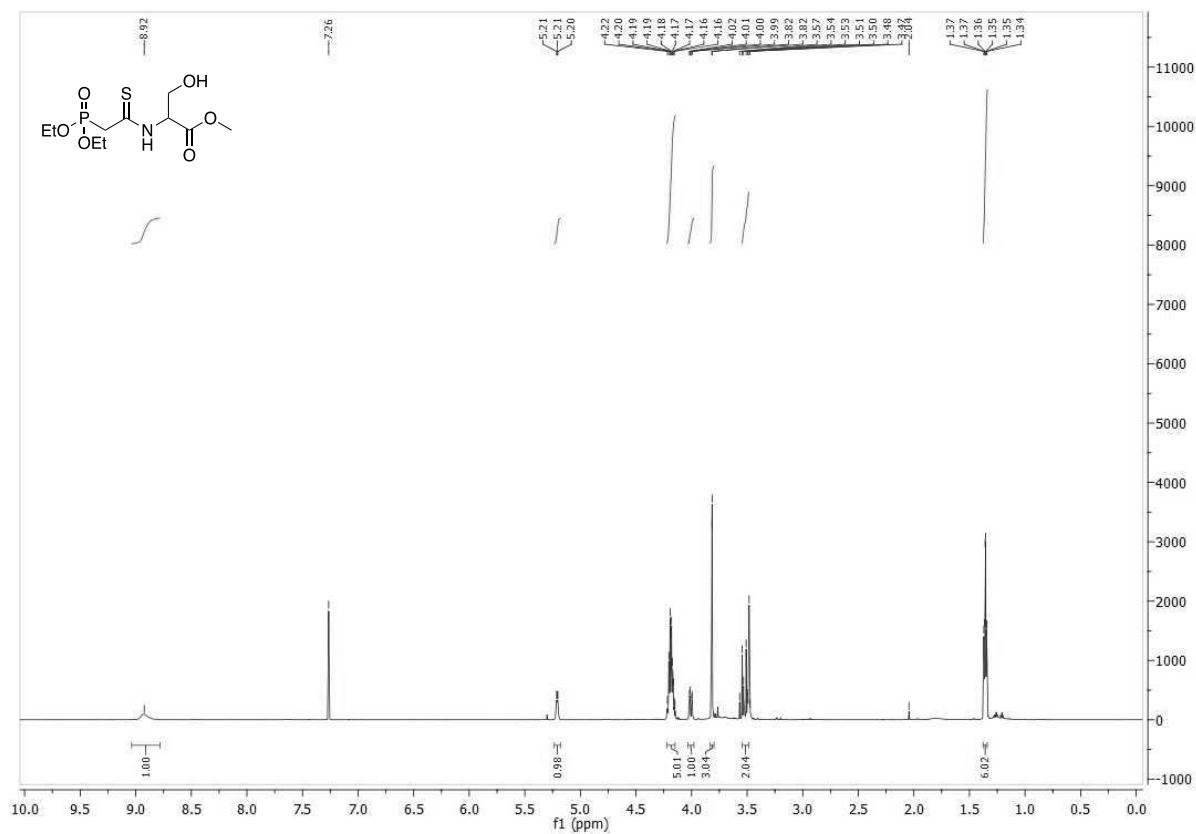
¹H-NMR: 5-((triisopropylsilyl)oxy)-1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-benzo[*d*]imidazole-2-carbaldehyde (**24b**)



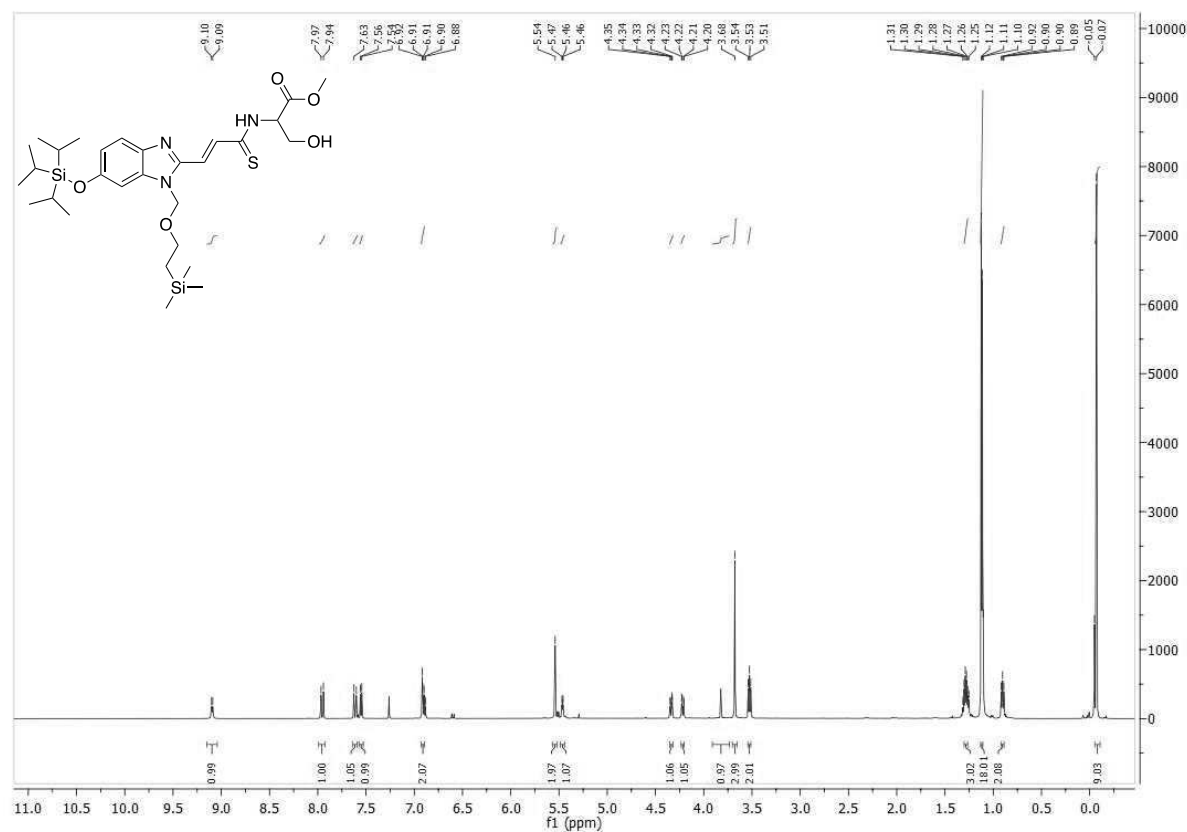
¹³C-NMR: 5-((triisopropylsilyloxy)-1-((2-(trimethylsilyl) ethoxy) methyl)-1H-benzo[d]imidazole-2-carbaldehyde (24b)



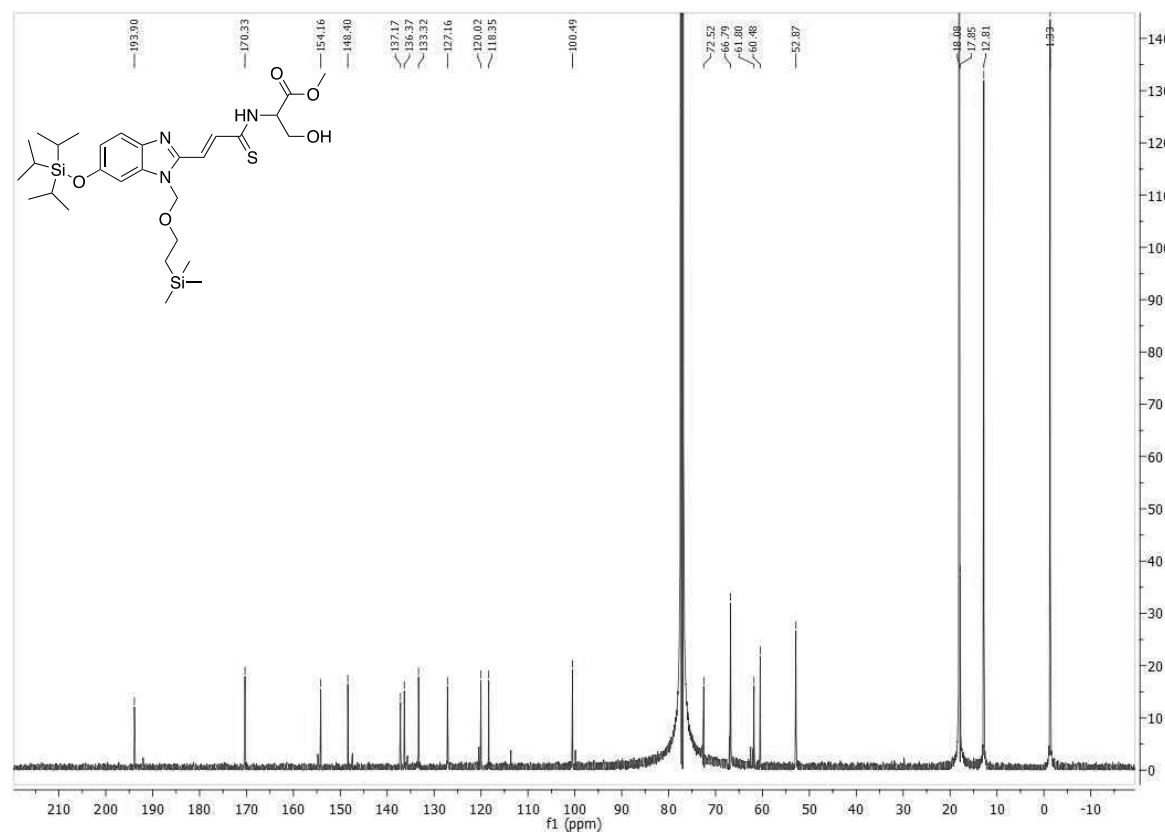
¹H - NMR: methyl (2-(diethoxyphosphoryl)ethanethioyl)serinate (25)



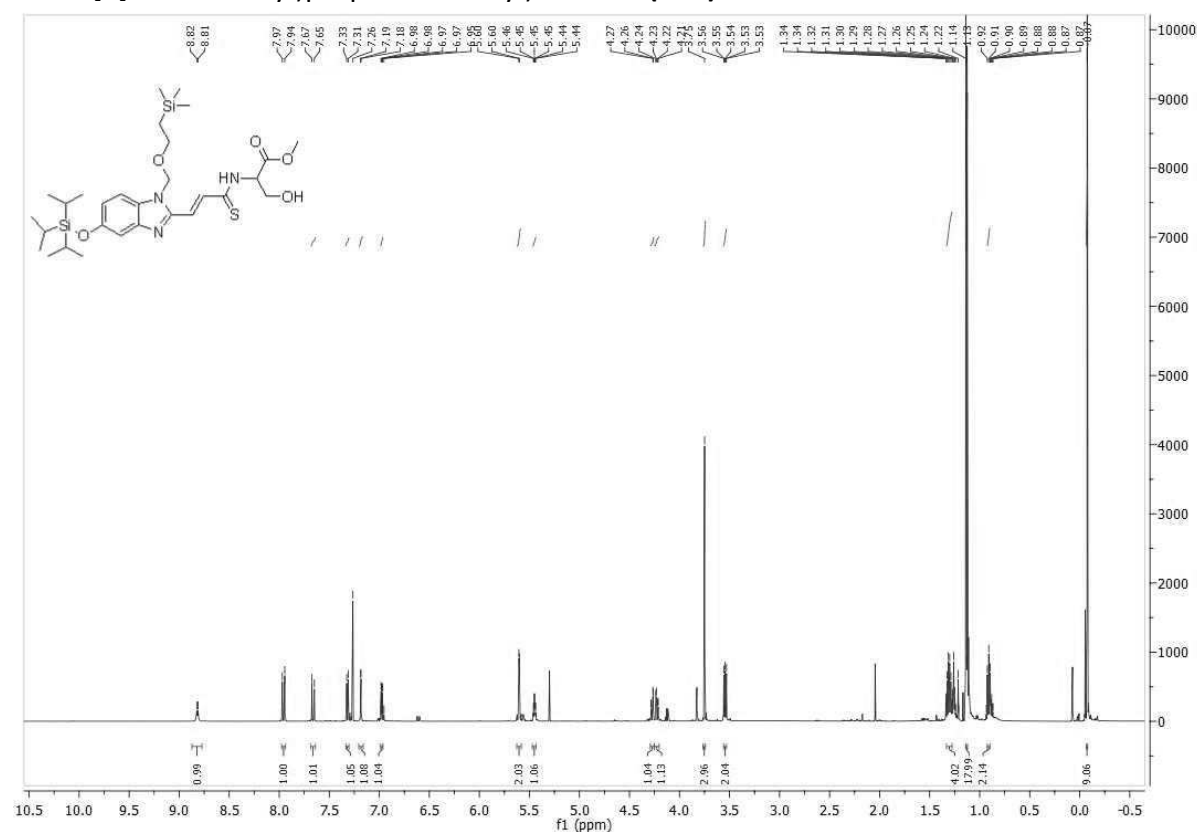
¹H – NMR: methyl (*E*)-3-(6-((triisopropylsilyloxy)-1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-benzo[*d*]imidazol-2-yl)prop-2-enethioyl)serinate (**26a**)



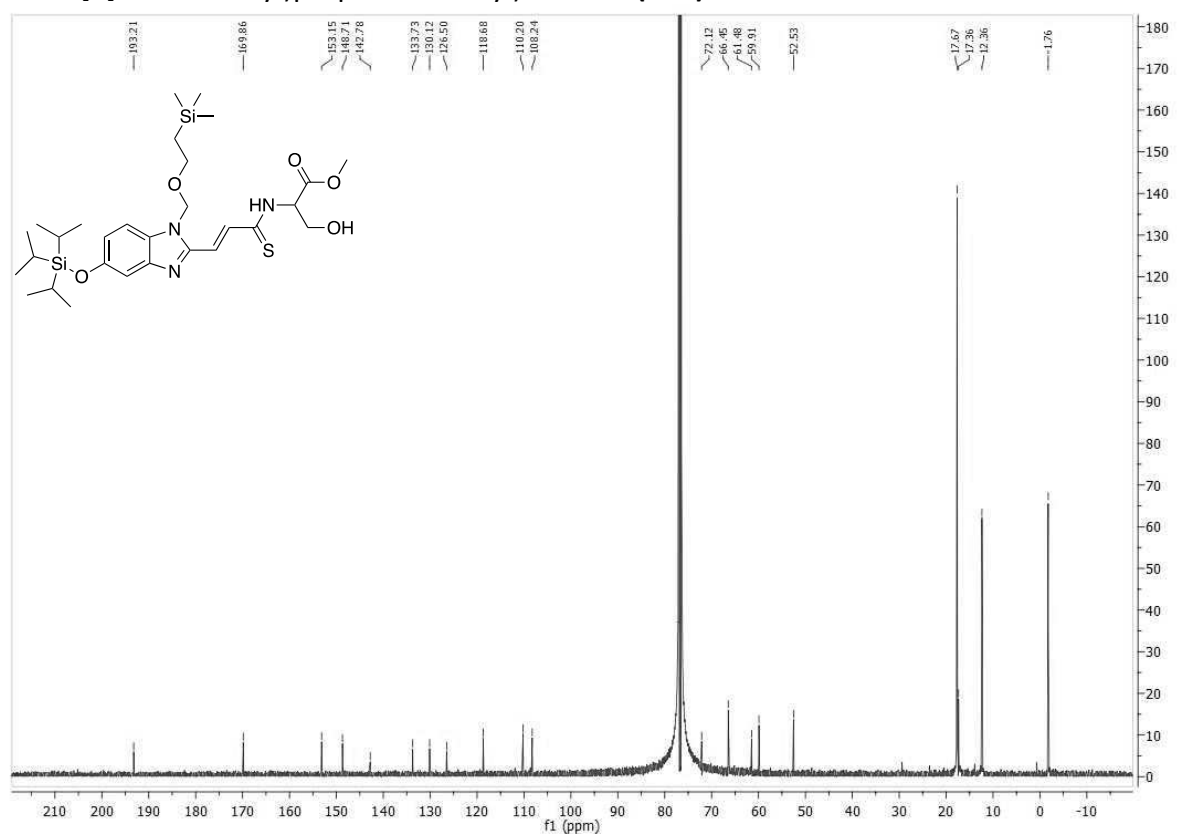
¹³C-NMR: methyl (*E*)-3-(6-((triisopropylsilyloxy)-1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-benzo[*d*]imidazol-2-yl)prop-2-enethioyl)serinate (**26a**)



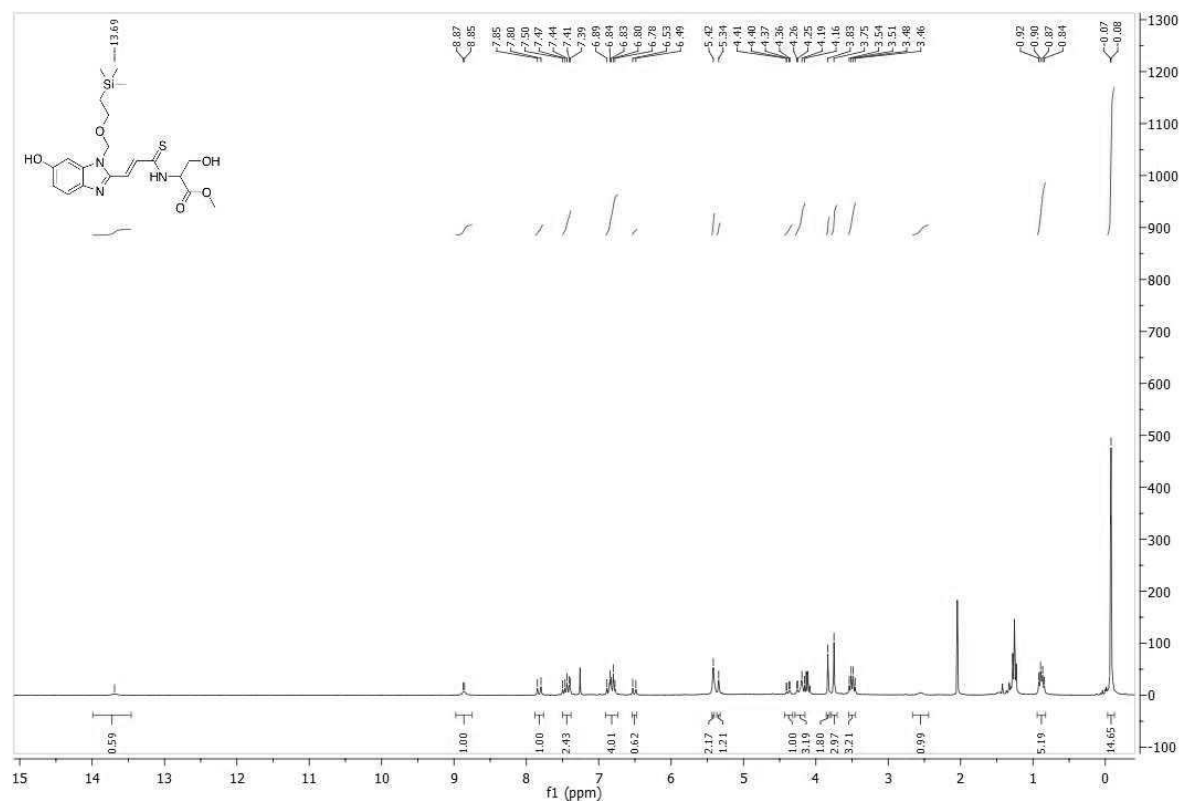
¹H – NMR: methyl(*E*)-(3-(5-((triisopropylsilyl)oxy)-1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-benzo[*d*]imidazol-2-yl)prop-2-enethioyl)serinate (**26b**)



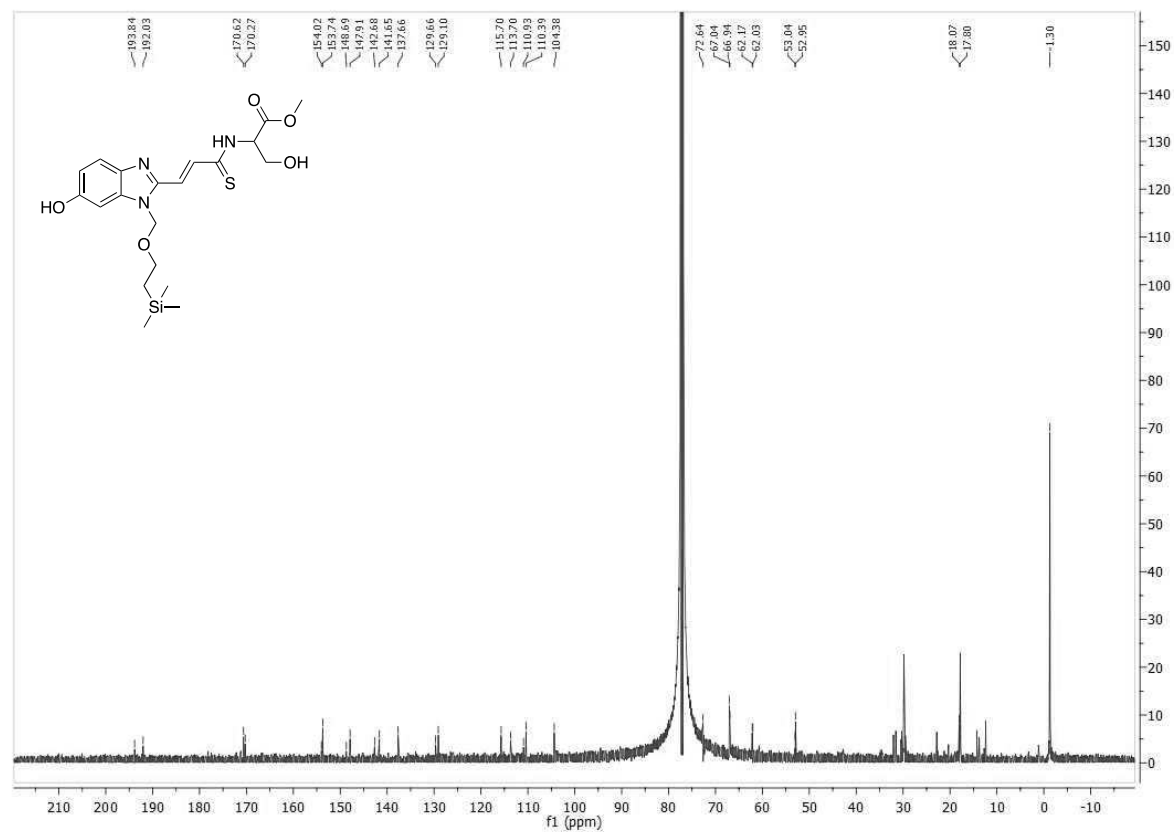
¹³C-NMR: methyl(*E*)-(3-(5-((triisopropylsilyl)oxy)-1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-benzo[*d*]imidazol-2-yl)prop-2-enethioyl)serinate (**26b**)



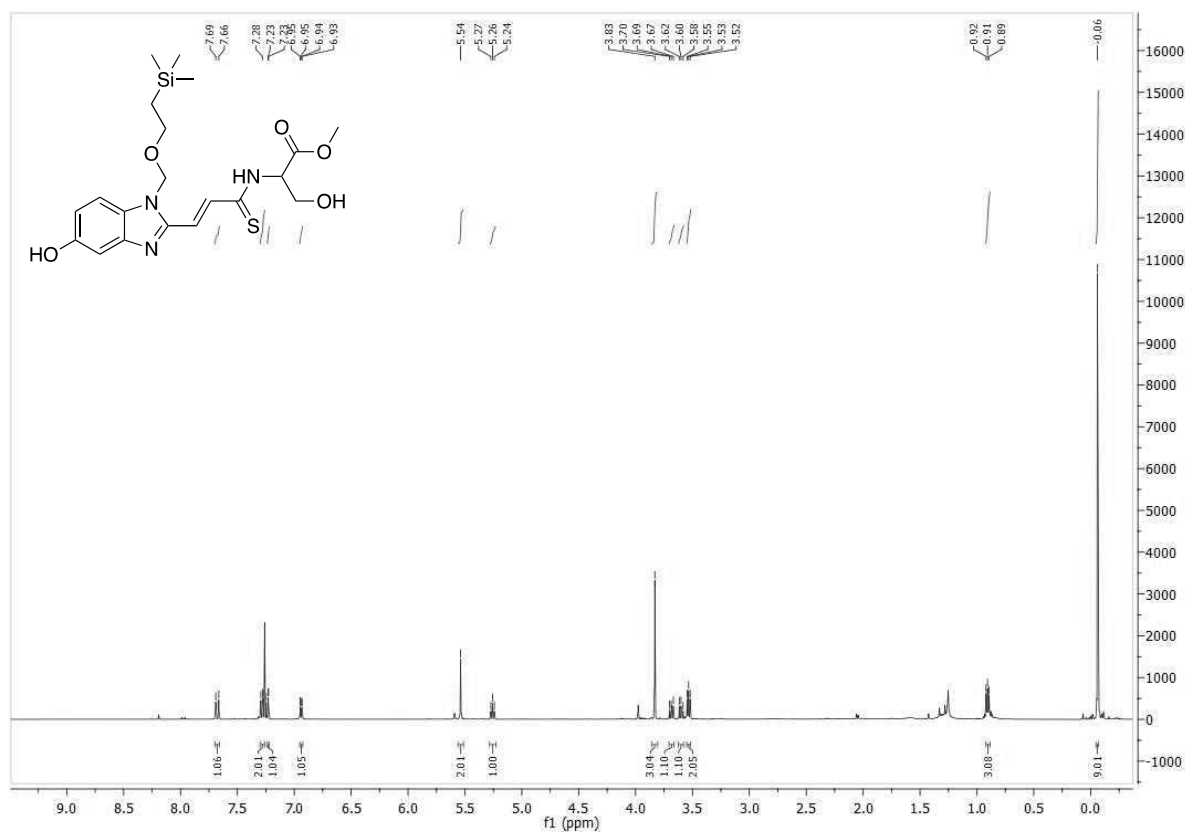
¹H – NMR: methyl (*E*)-(3-(6-hydroxy-1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-benzo[*d*]imidazol-2-yl)prop-2-enethioyl)serinate (**27a**)



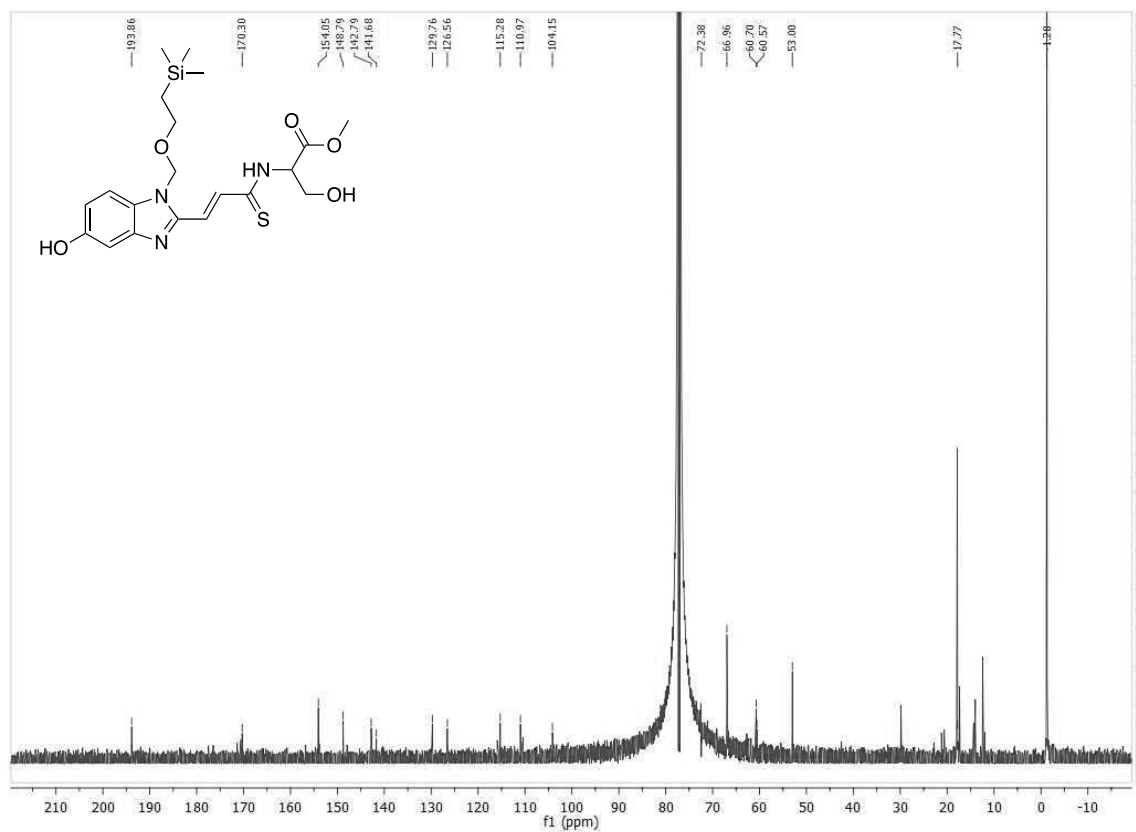
¹³C-NMR: methyl (*E*)-(3-(6-hydroxy-1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-benzo[*d*]imidazol-2-yl)prop-2-enethioyl)serinate (**27a**)



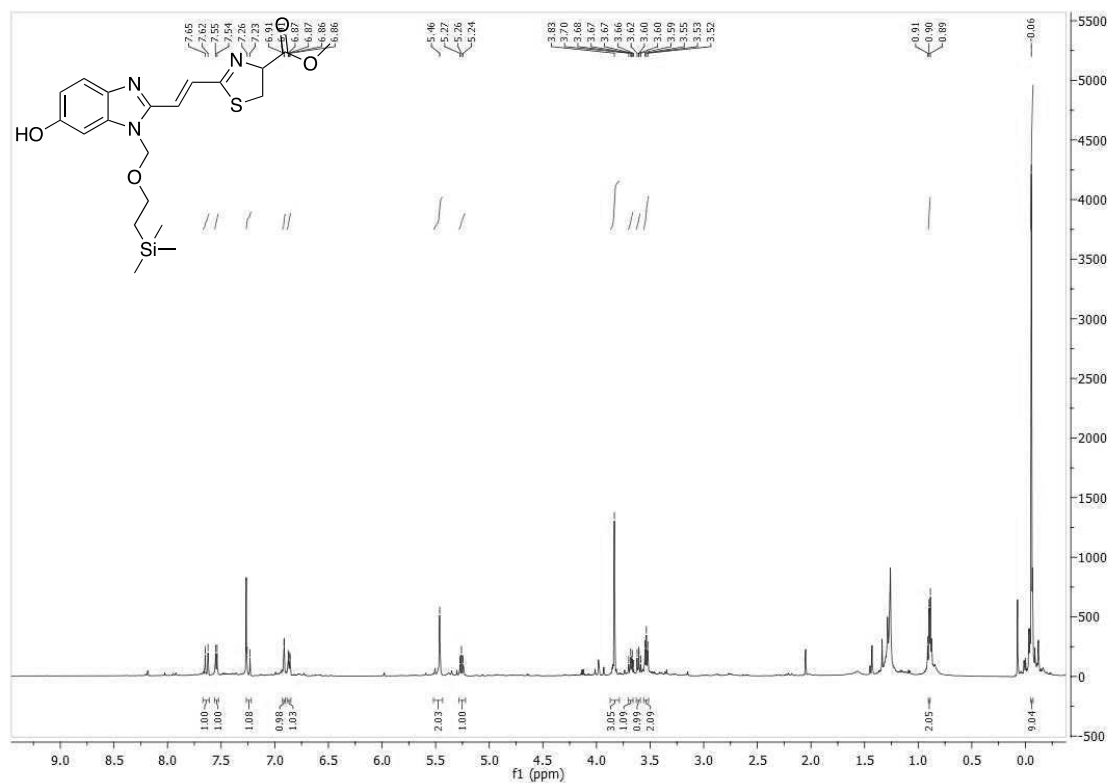
¹H – NMR: methyl (*E*)-(3-(5-hydroxy-1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-benzo[*d*]imidazol-2-yl)prop-2-enethioyl)serinate (27b**)**



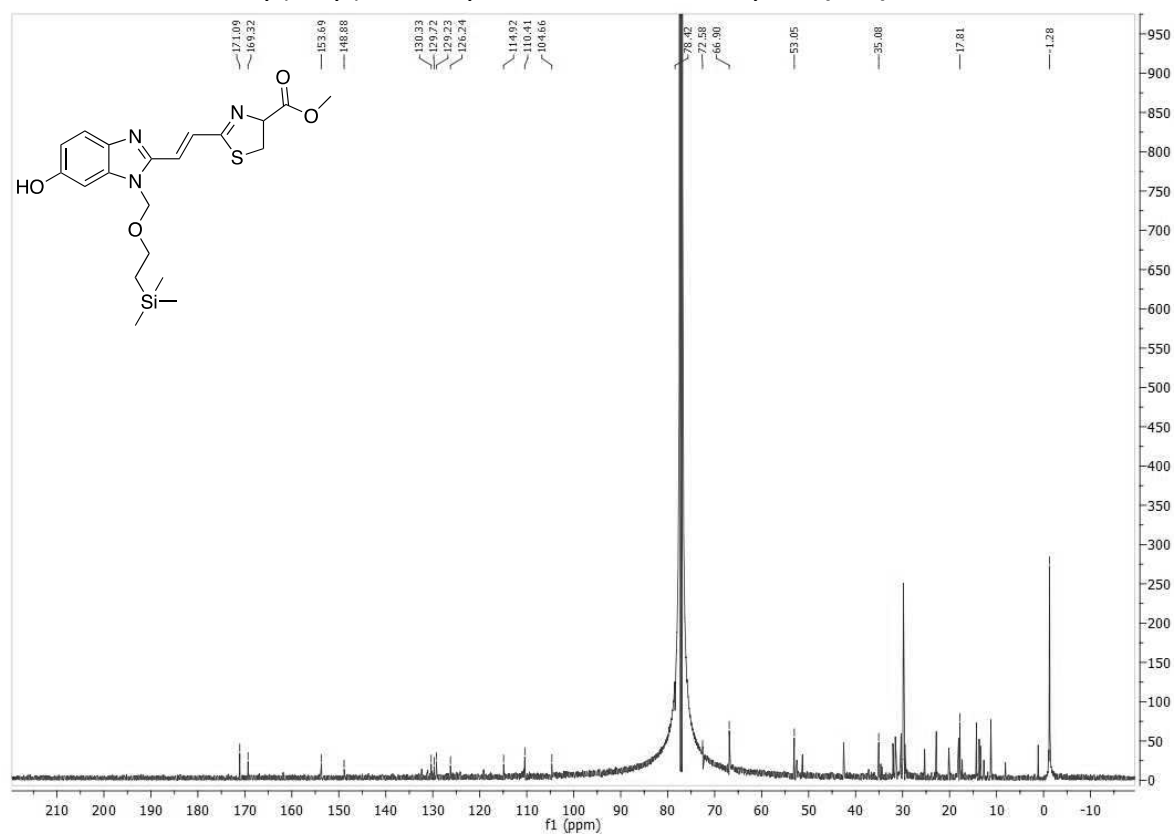
¹³C-NMR: methyl (*E*)-(3-(5-hydroxy-1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-benzo[*d*]imidazol-2-yl)prop-2-enethioyl)serinate (27b**)**



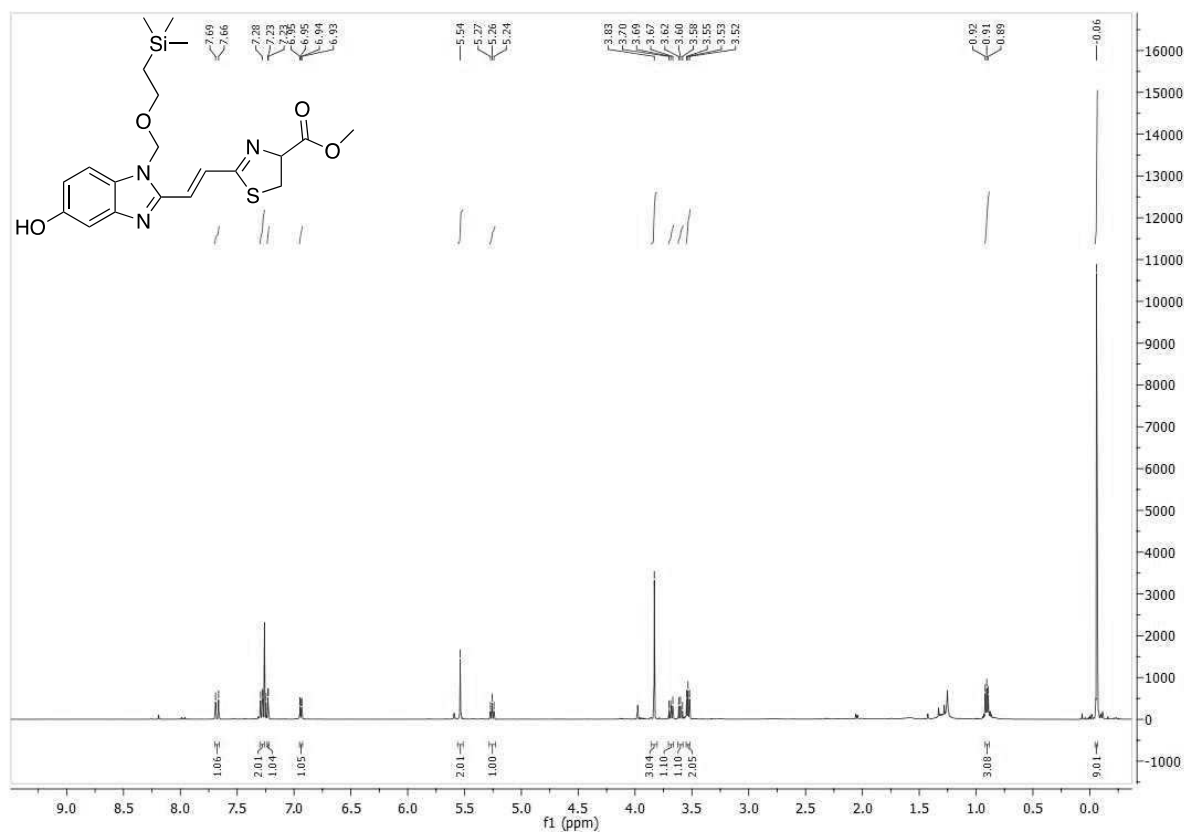
¹H – NMR: methyl (*E*)-2-(2-(6-hydroxy-1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-benzo[*d*]imidazol-2-yl)vinyl)-4,5-dihydrothiazole-4-carboxylate (**28a**)



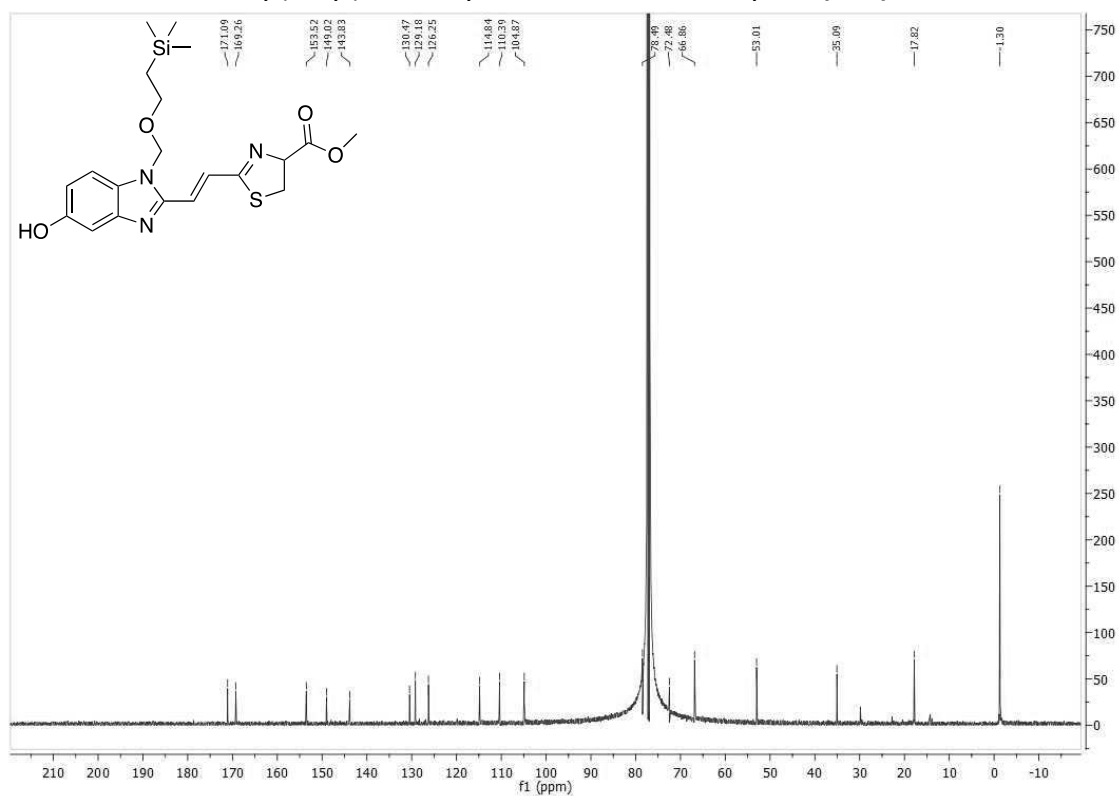
¹³C-NMR: methyl (*E*)-2-(2-(6-hydroxy-1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-benzo[*d*]imidazol-2-yl)vinyl)-4,5-dihydrothiazole-4-carboxylate (**28a**)



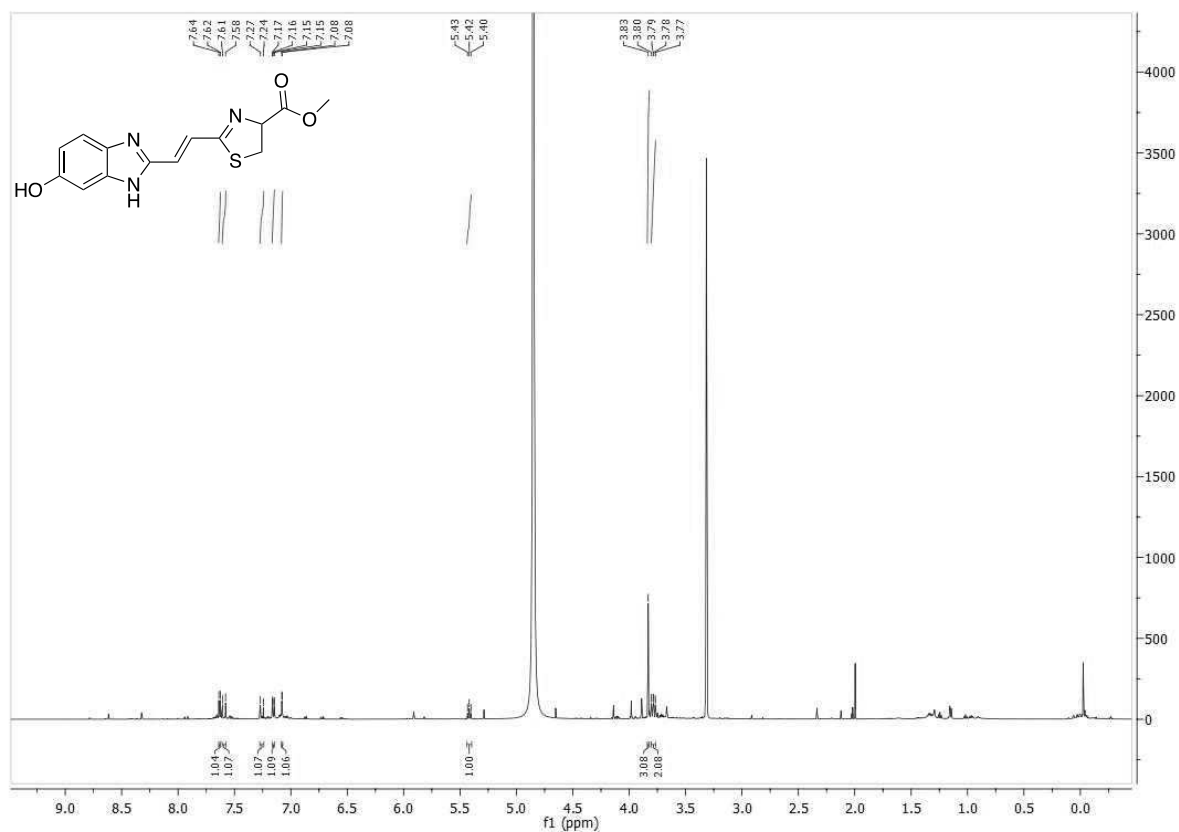
¹H – NMR: methyl (*E*)-2-(2-(5-hydroxy-1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-benzo[*d*]imidazol-2-yl)vinyl)-4,5-dihydrothiazole-4-carboxylate (**28b**)



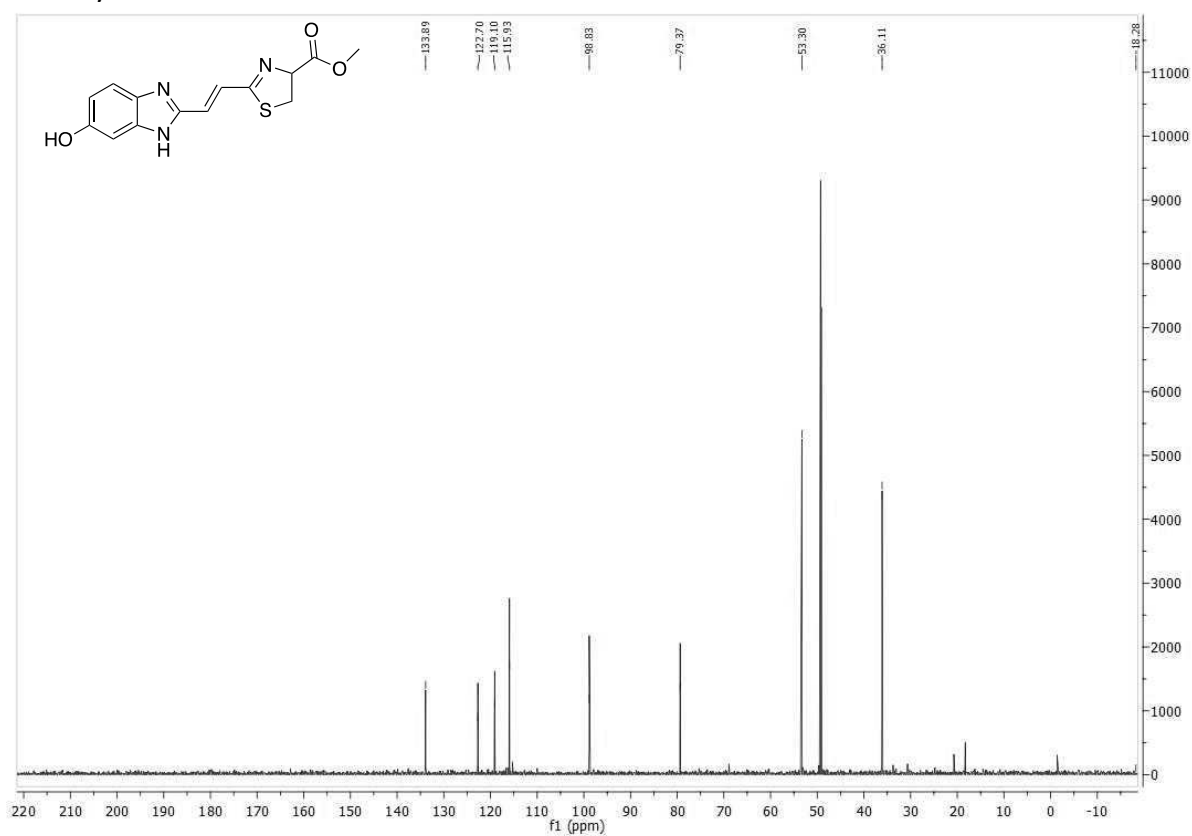
¹³C-NMR: methyl (*E*)-2-(2-(5-hydroxy-1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-benzo[*d*]imidazol-2-yl)vinyl)-4,5-dihydrothiazole-4-carboxylate (**28b**)



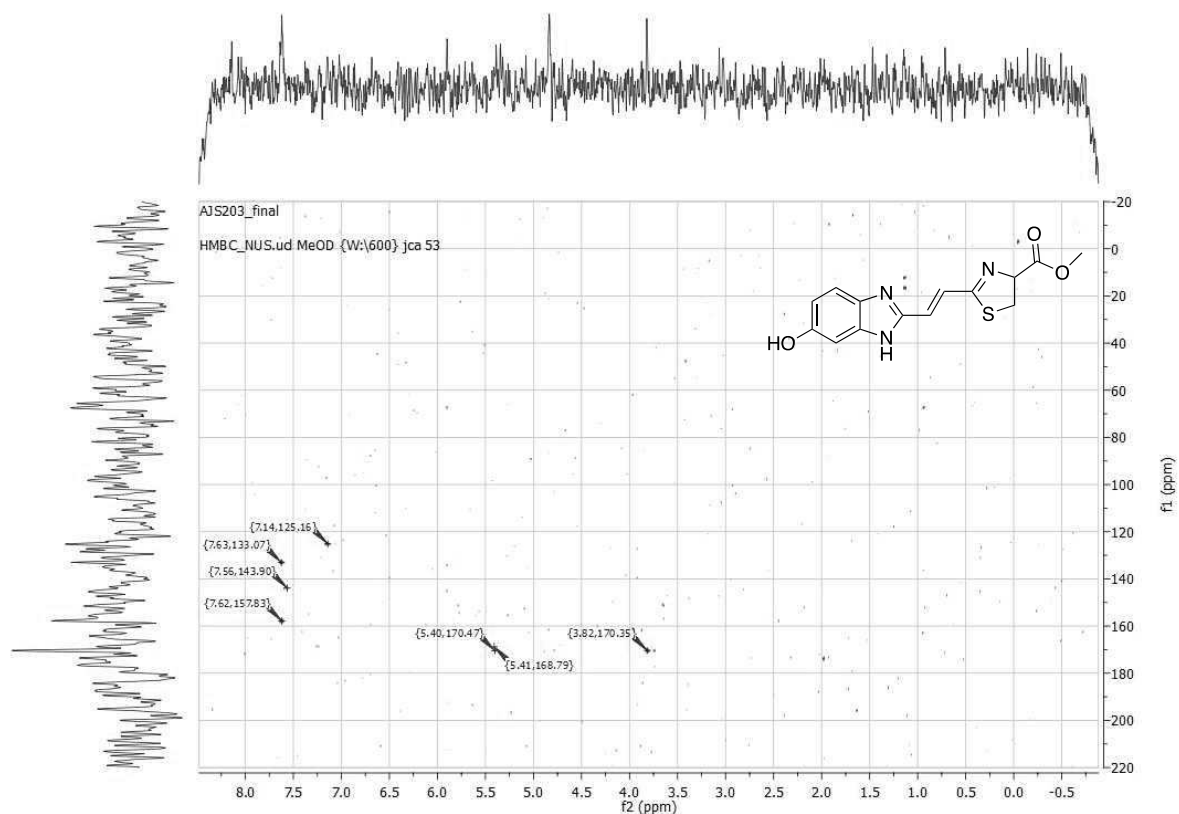
¹H – NMR: methyl (*E*)-2-(2-(6-hydroxy-1*H*-benzo[*d*]imidazol-2-yl)vinyl)-4,5-dihydrothiazole-4-carboxylate



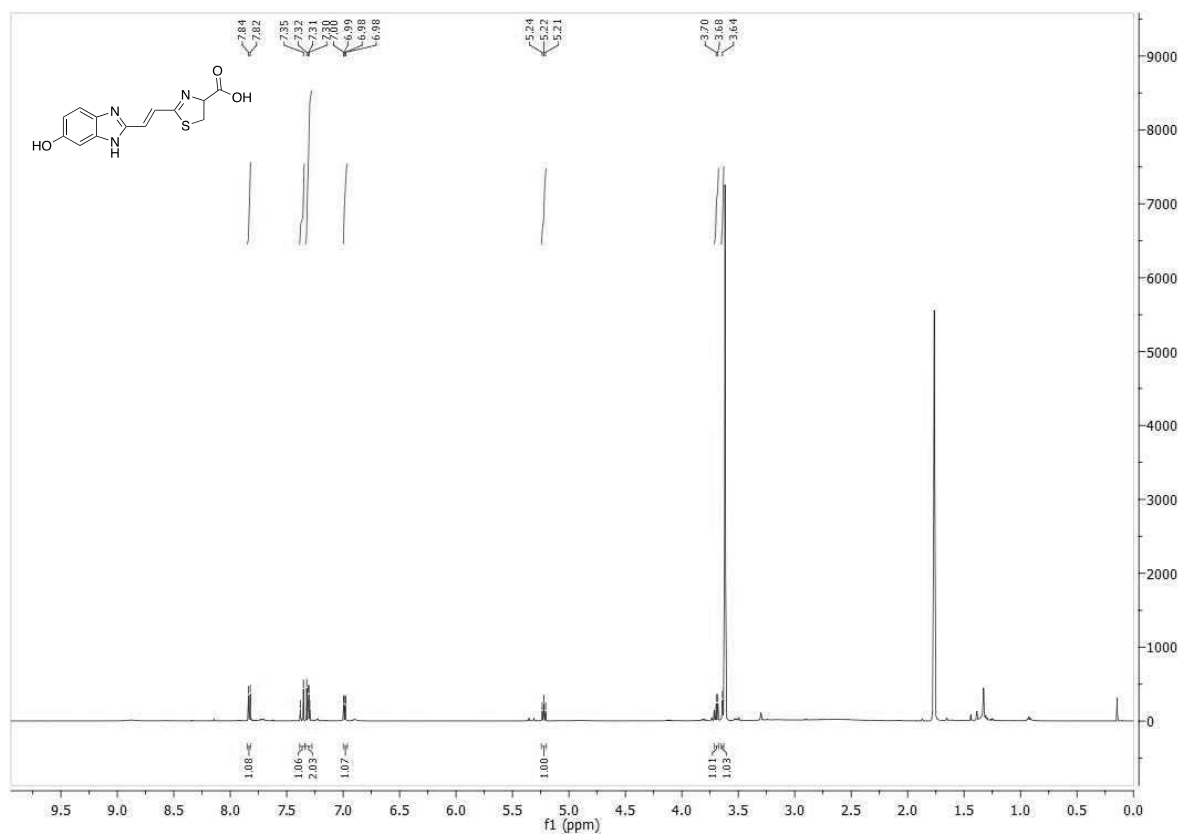
¹³C-NMR: methyl (*E*)-2-(2-(6-hydroxy-1*H*-benzo[*d*]imidazol-2-yl)vinyl)-4,5-dihydrothiazole-4-carboxylate



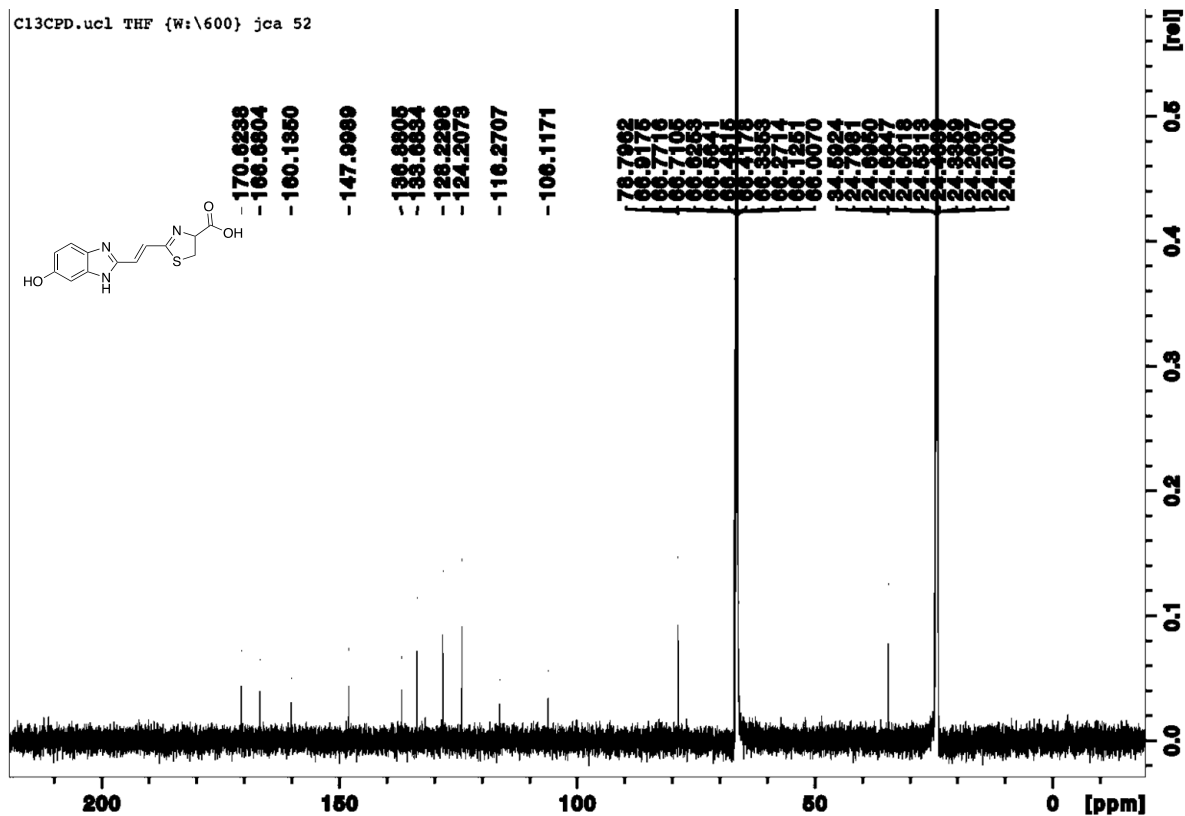
HMBC spectrum: methyl (*E*)-2-(2-(6-hydroxy-1*H*-benzo[*d*]imidazol-2-yl)vinyl)-4,5-dihydrothiazole-4-carboxylate



¹H – NMR: (*E*)-2-(2-(6-hydroxy-1*H*-benzo[*d*]imidazol-2-yl)vinyl)-4,5-dihydrothiazole-4-carboxylic acid (13**)**



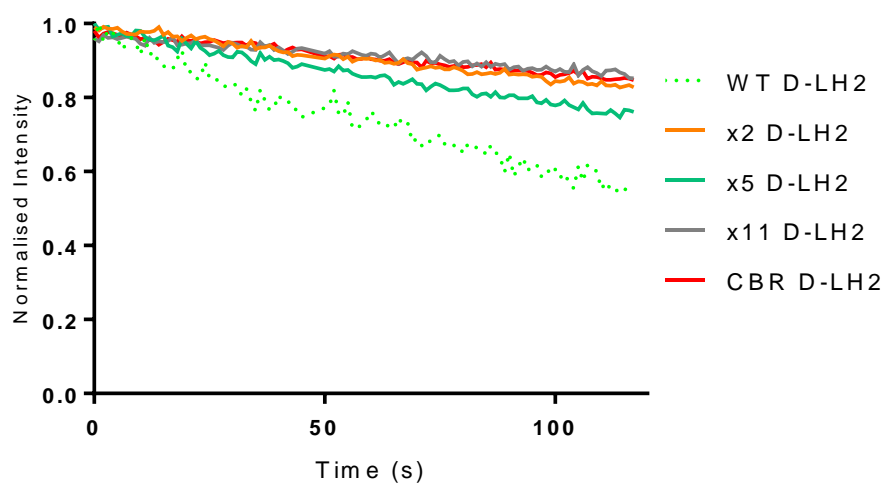
¹³C-NMR: (*E*)-2-(2-(6-hydroxy-1*H*-benzo[*d*]imidazol-2-yl)vinyl)-4,5-dihydrothiazole-4-carboxylic acid (**13**)



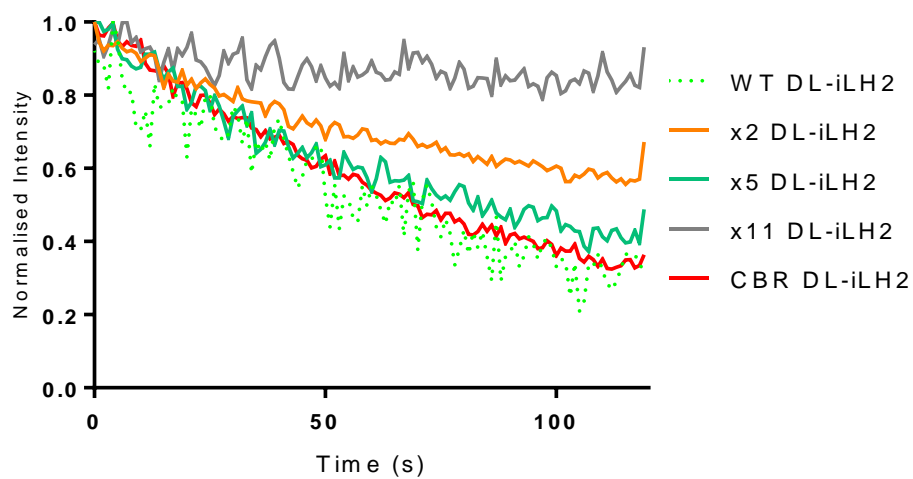
Emission kinetics of enzymes with different compounds acquired in the PIO

SI Figure:

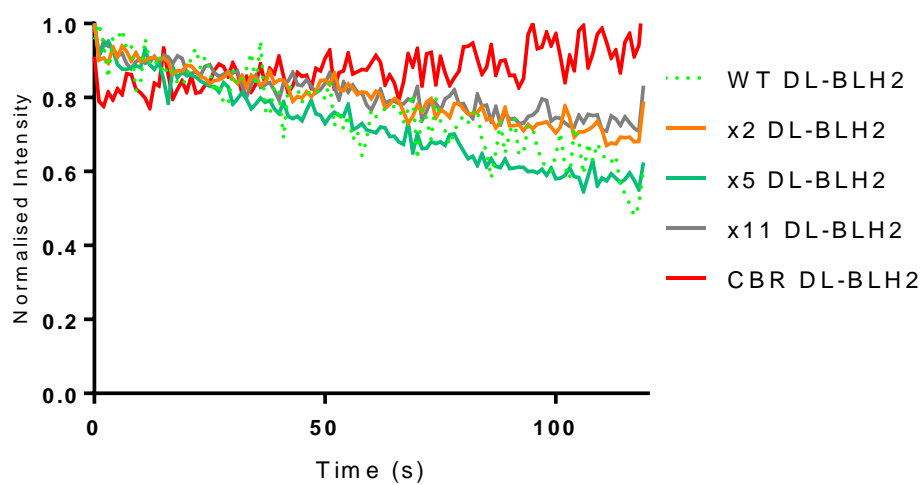
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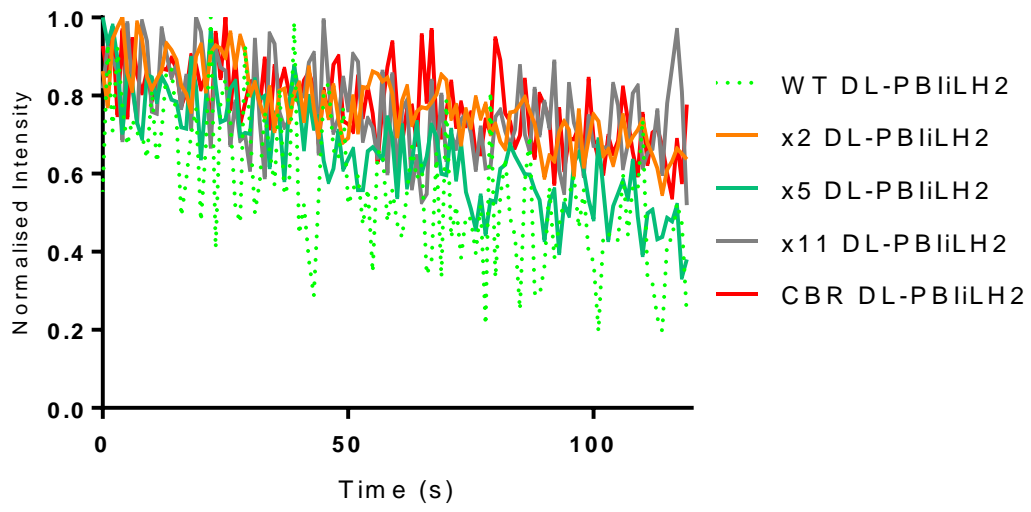
B



C



D



E

