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

James C. Anderson, Amit P. Jathoul and Aisha J. Syed

Department of Chemistry, University College London, 20 Gordon Street, London, WC1H 0AJ, UK.

and

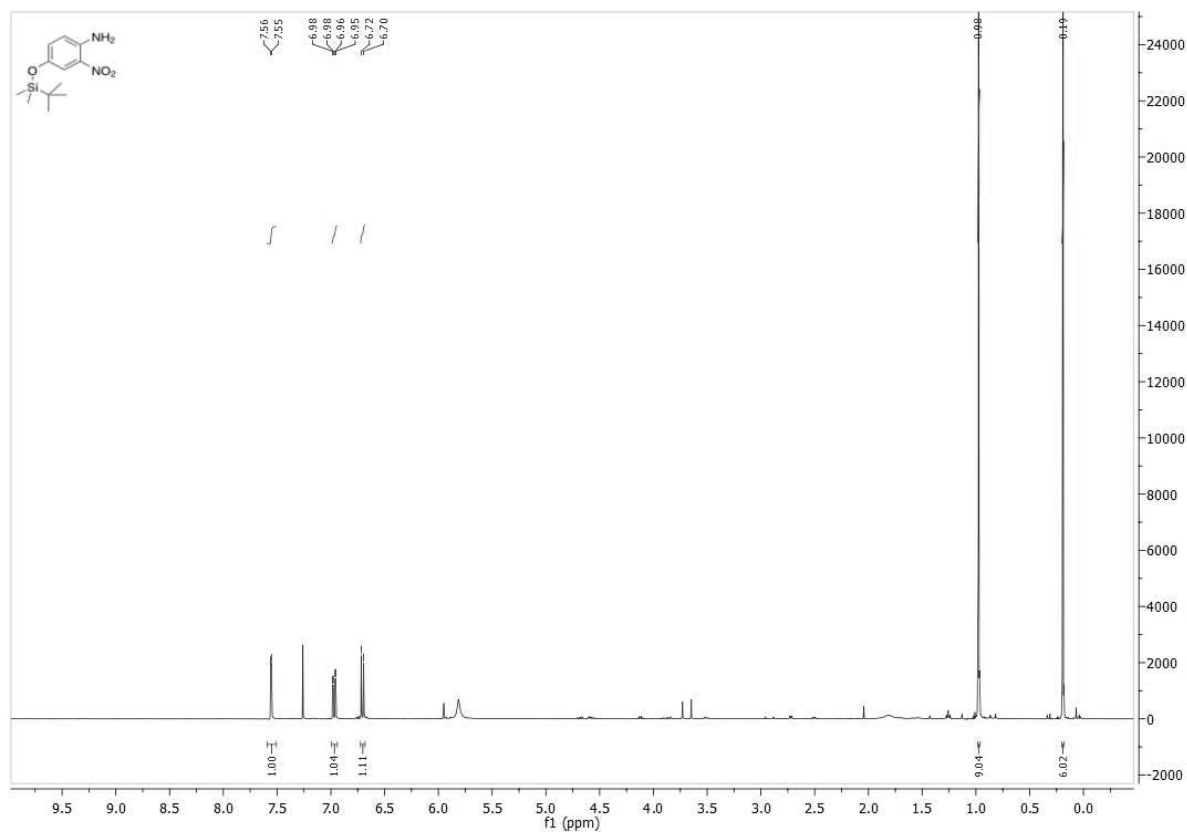
School of Biosciences, University of Cardiff, Sir Martin Evans Building, Museum Avenue, Cardiff, CF10 3AX, UK

Supplementary Information

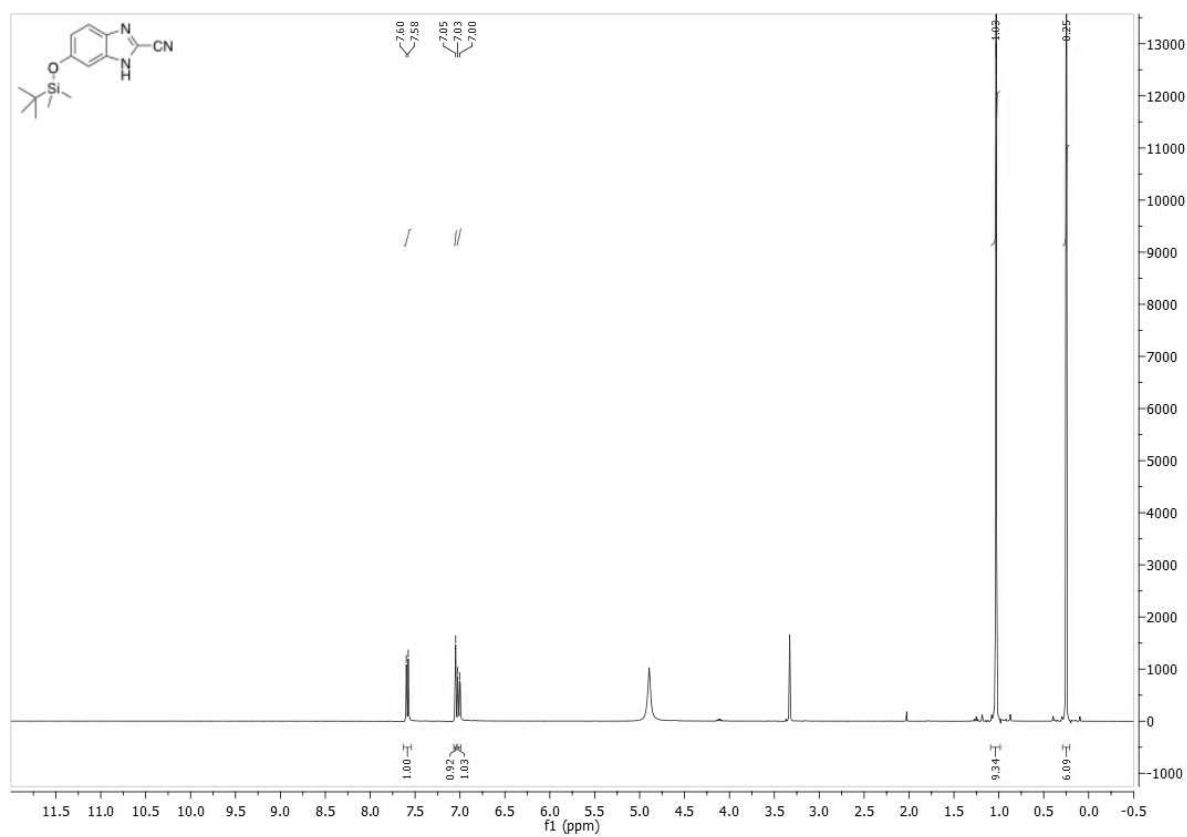
Copies of ^1H and ^{13}C NMR spectra

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

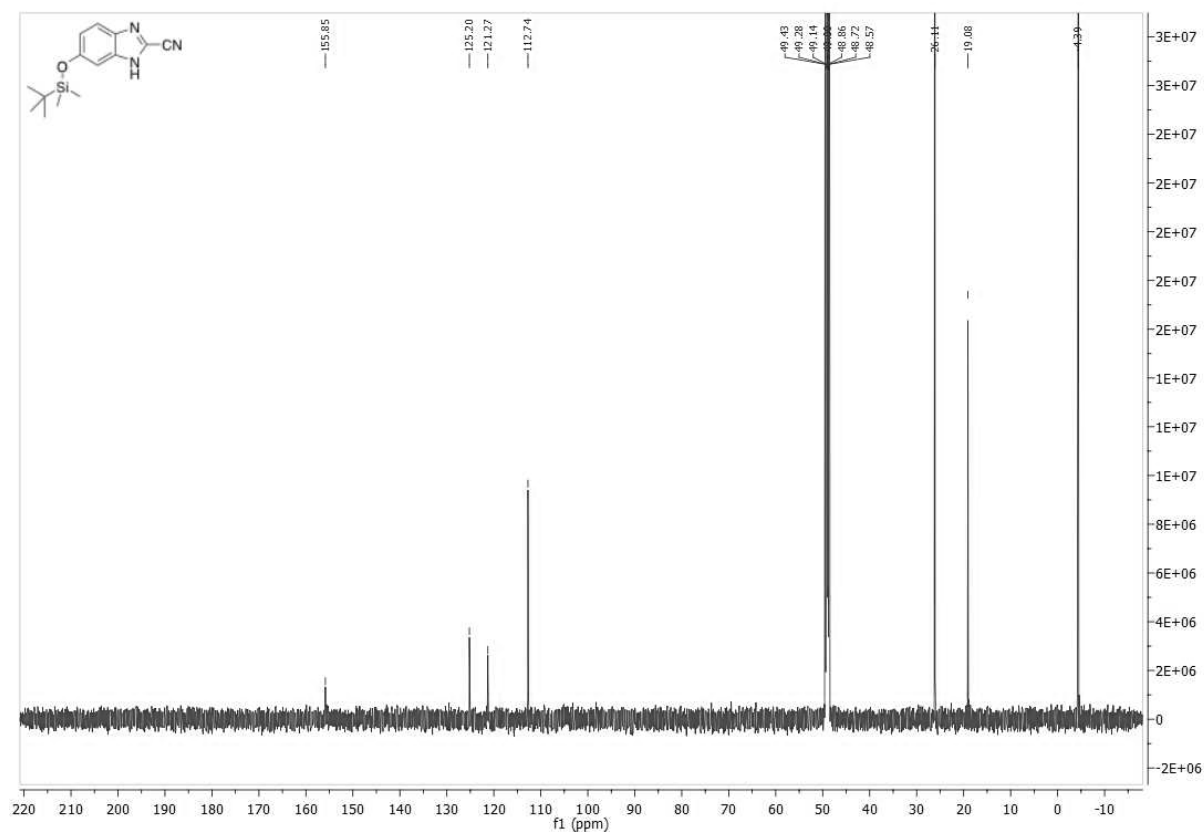
¹H – NMR: 4-((*tert*-butyldimethylsilyl)oxy)-2-nitroaniline (15)



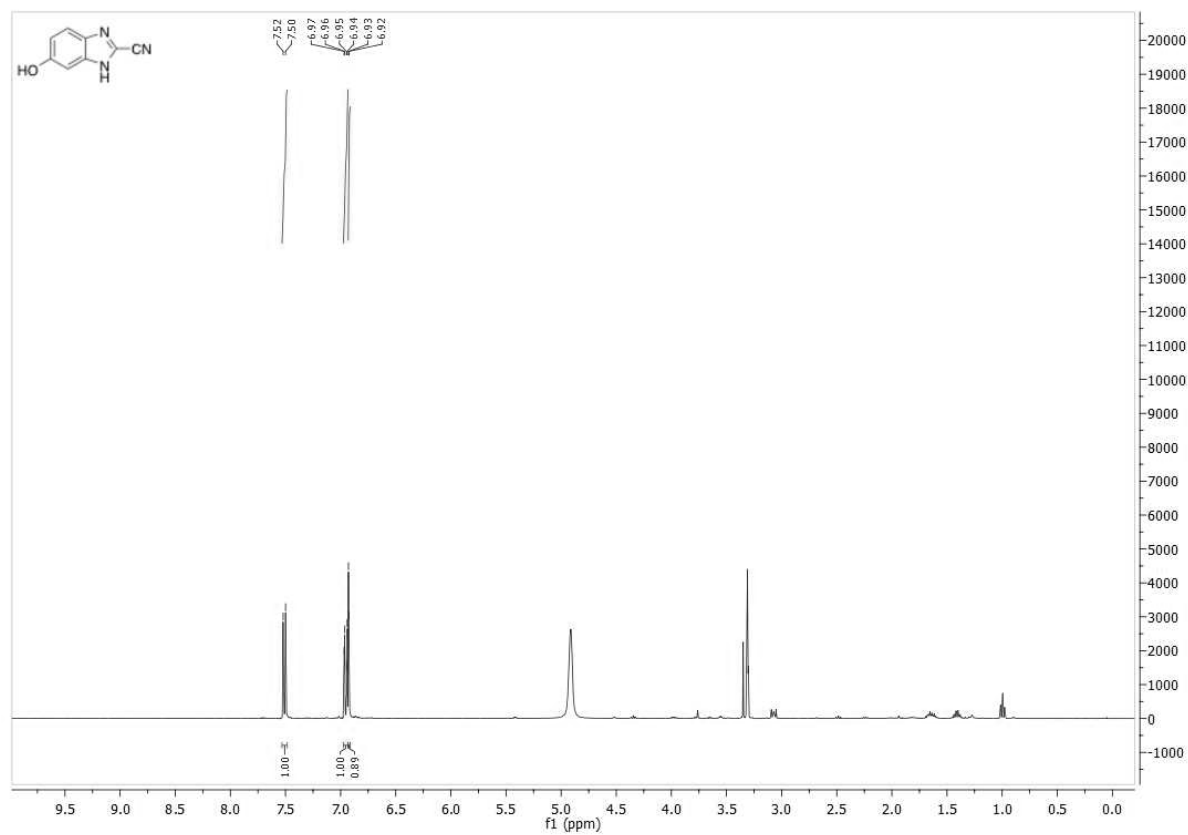
¹H – NMR: 6-((*tert*-butyldimethylsilyl)oxy)-1H-benzo[d]imidazole-2-carbonitrile (16)



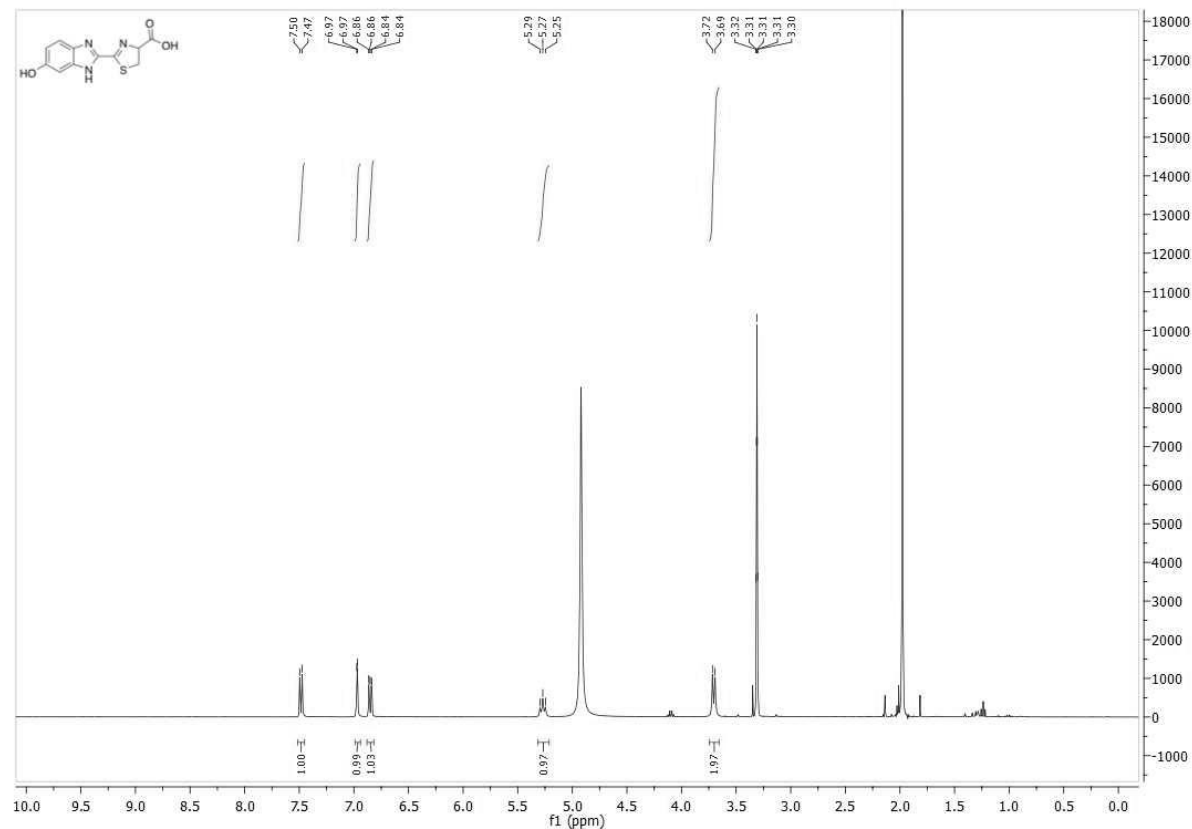
¹³C – NMR: 6-((tert-butyldimethylsilyl)oxy)-1H-benzo[d]imidazole-2-carbonitrile (16)



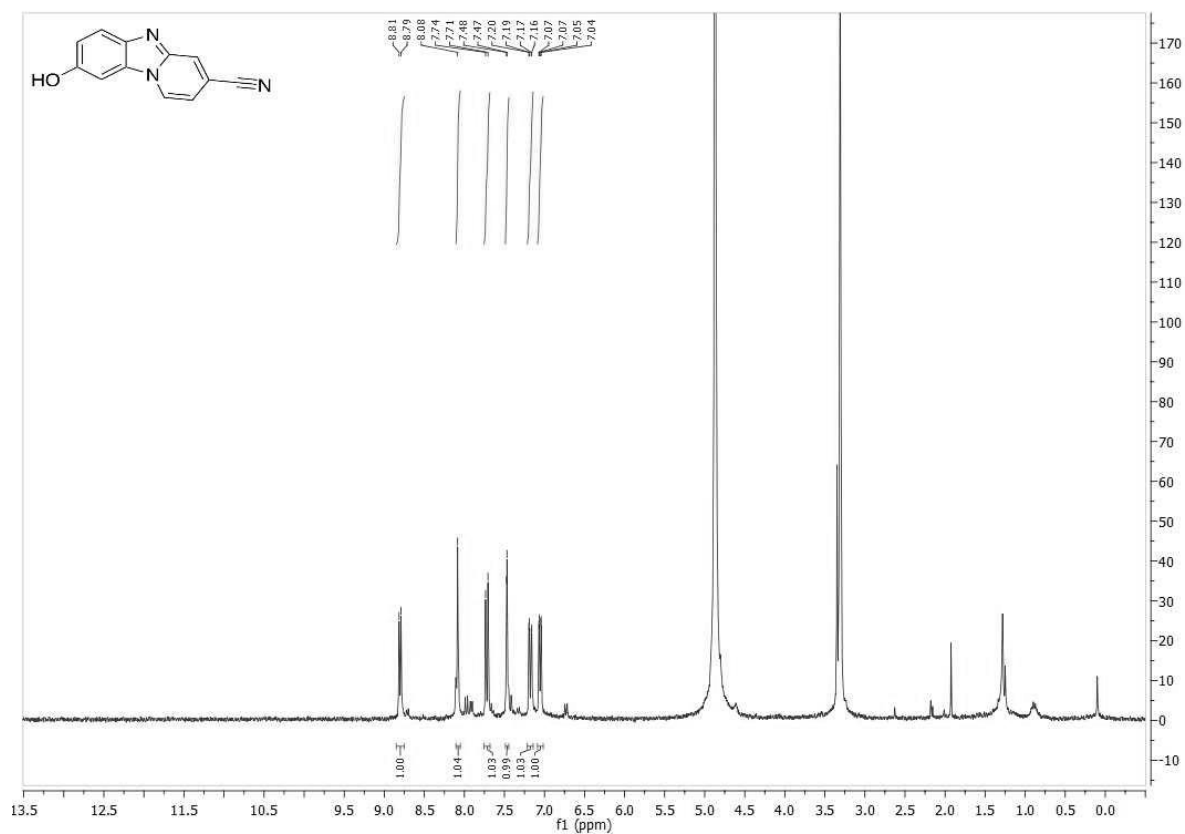
¹H – NMR: 6-hydroxy-1H-benzo[d]imidazole-2-carbonitrile (17)



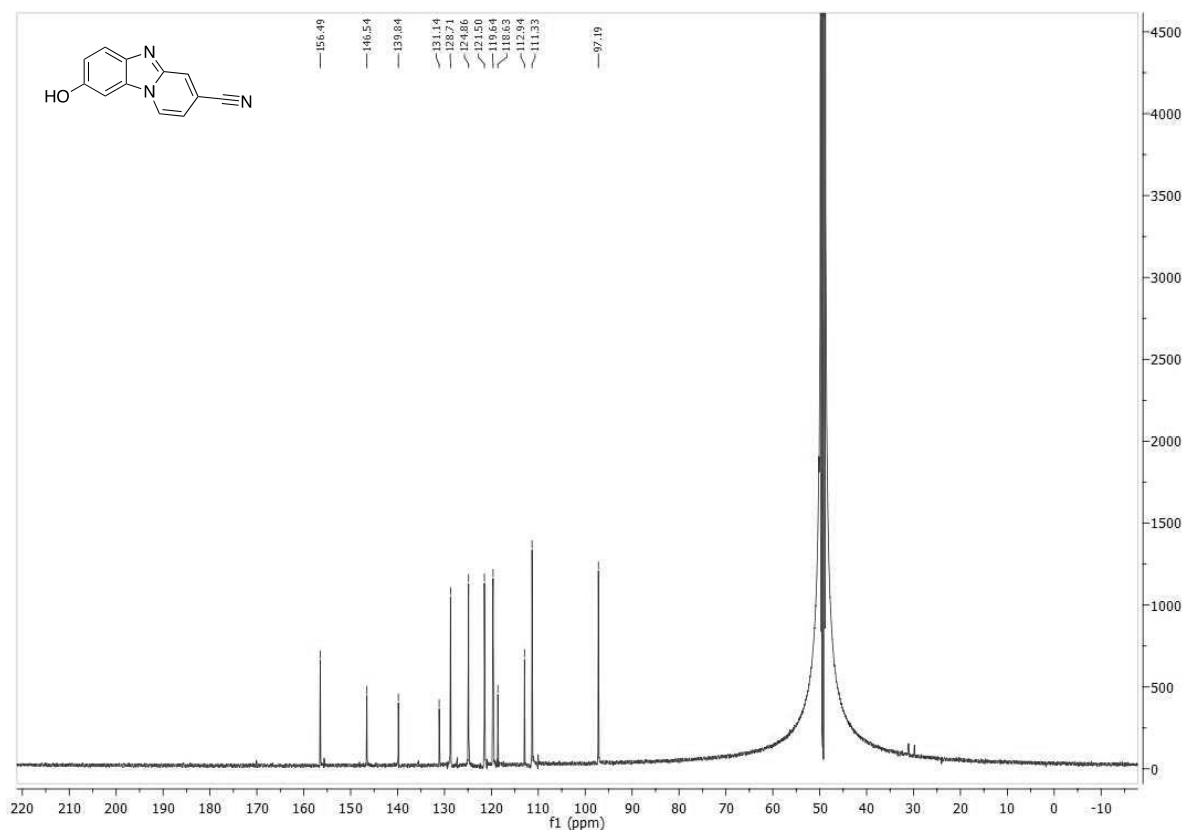
¹H – NMR: 2-(6-hydroxy-1*H*-benzo[*d*]imidazol-2-yl)-4,5-dihydrothiazole-4-carboxylic acid (10)



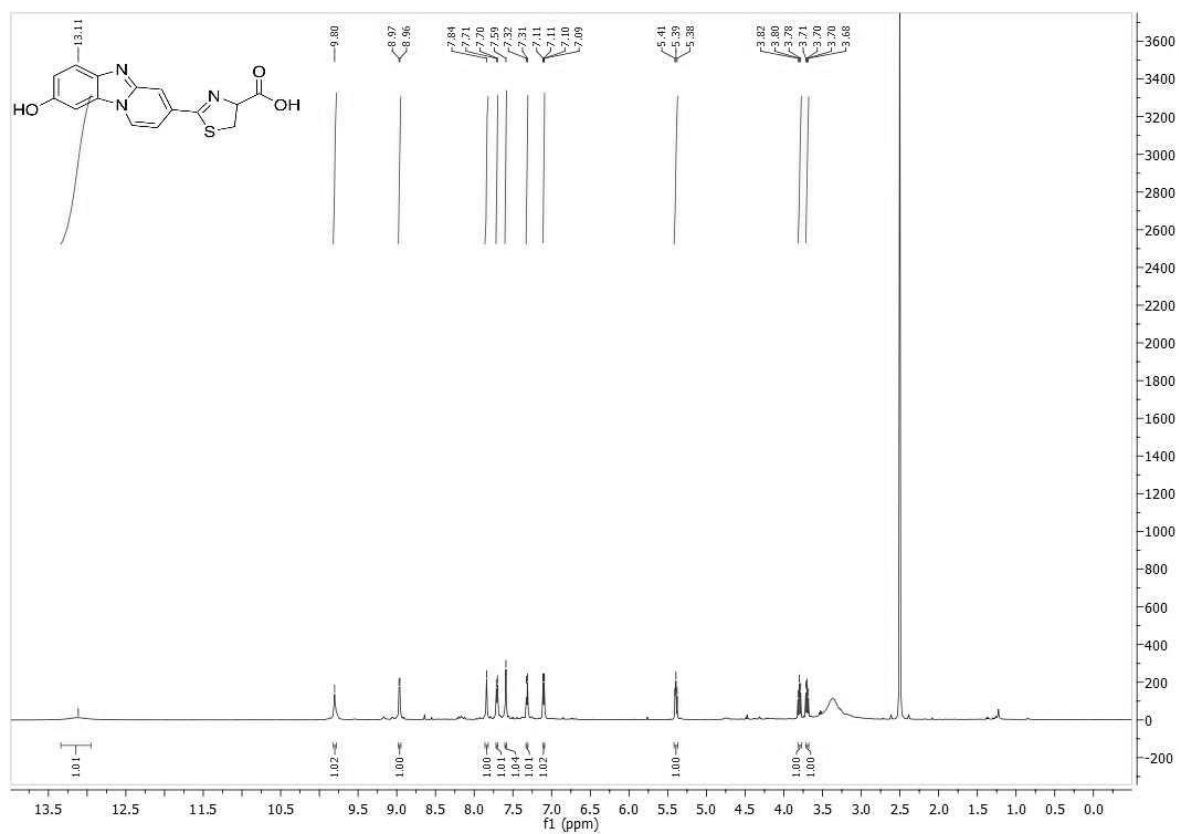
¹H – NMR: 8-hydroxybenzo[4,5]imidazo[1,2-*a*]pyridine-3-carbonitrile (20)



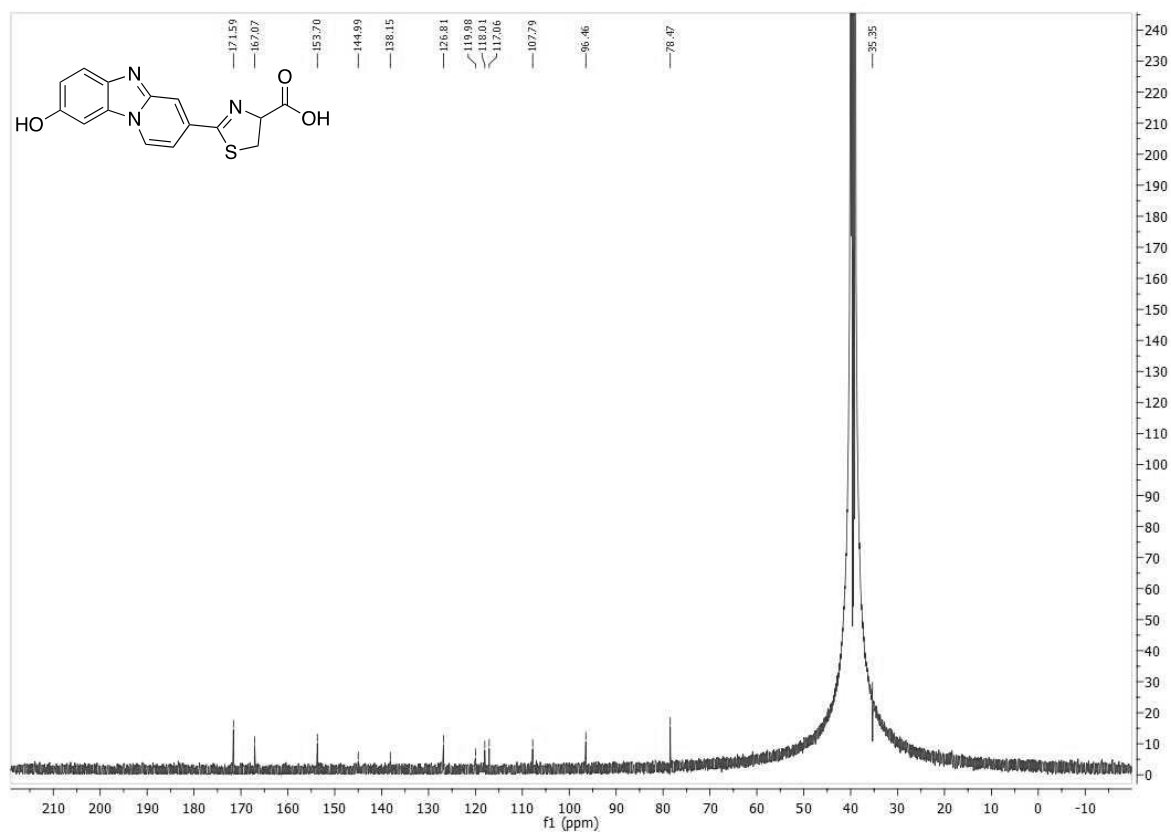
¹³C-NMR: 8-hydroxybenzo[4,5]imidazo[1,2-a]pyridine-3-carbonitrile (20)



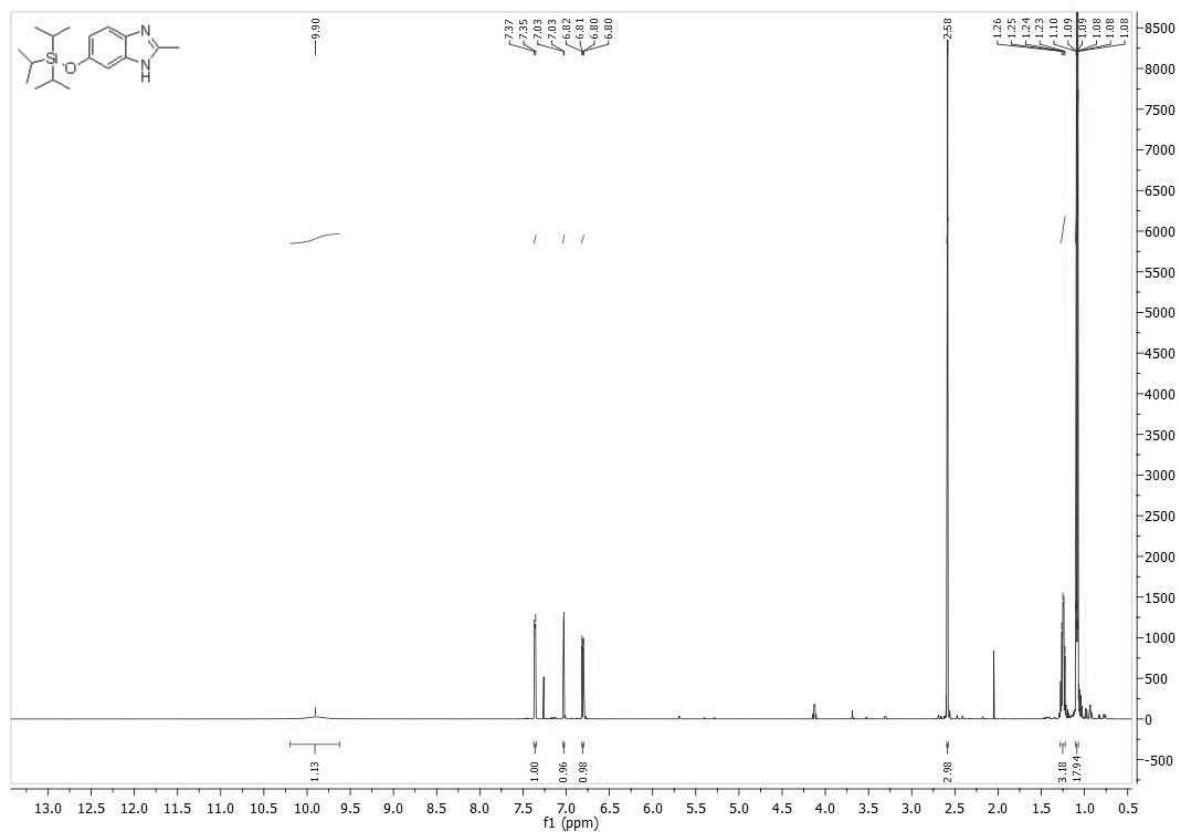
¹H - NMR: 2-(8-hydroxybenzo[4,5]imidazo[1,2-a]pyridin-3-yl)-4,5-dihydrothiazole-4-carboxylic acid (12)



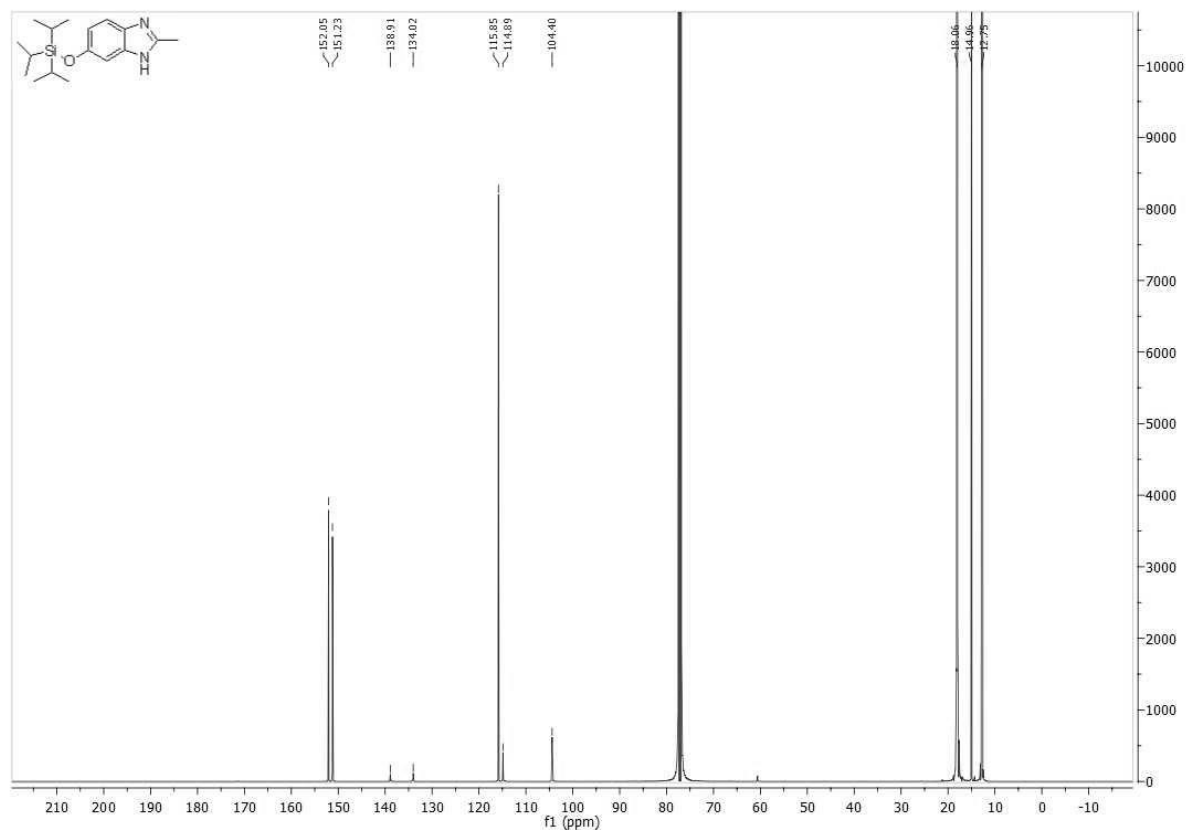
¹³C-NMR: 2-(8-hydroxybenzo[4,5]imidazo[1,2-a]pyridin-3-yl)-4,5-dihydrothiazole-4-carboxylic acid (12)



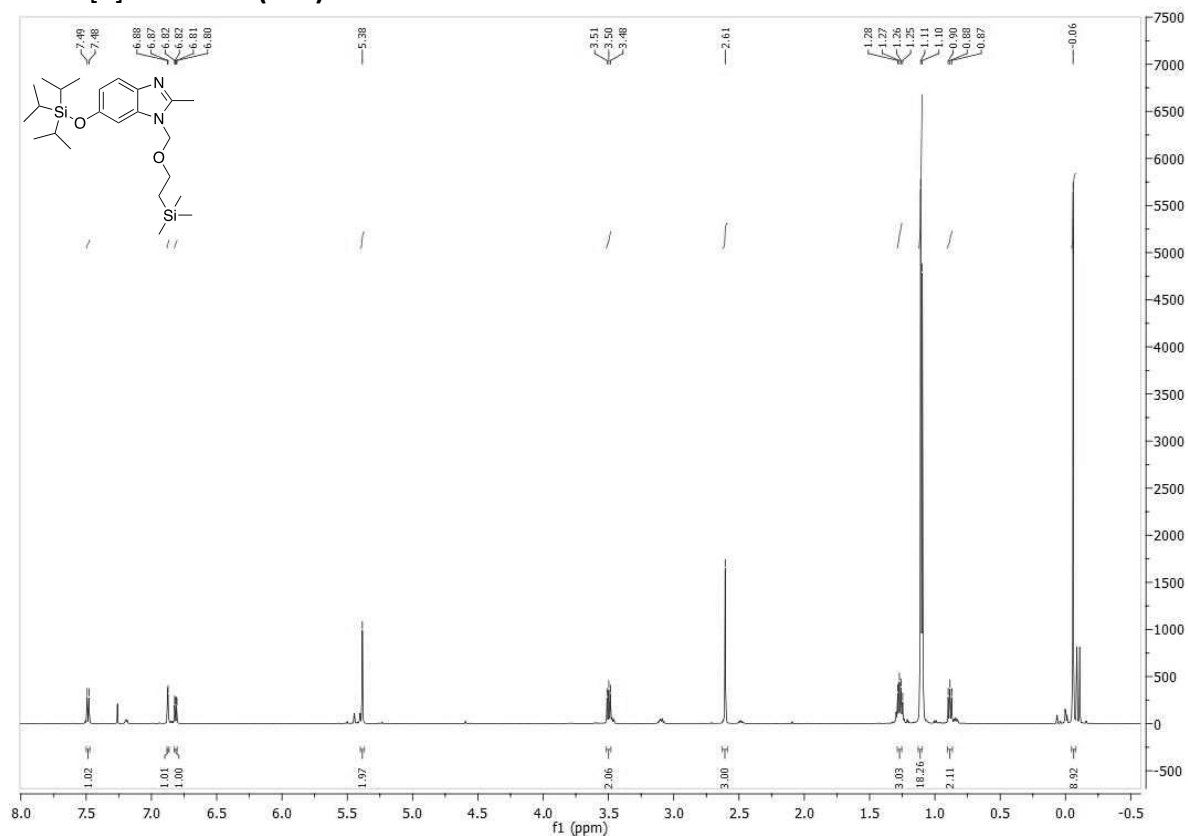
¹H – NMR: 2-methyl-6-((triisopropylsilyl)oxy)-1H-benzo[d]imidazole (22)



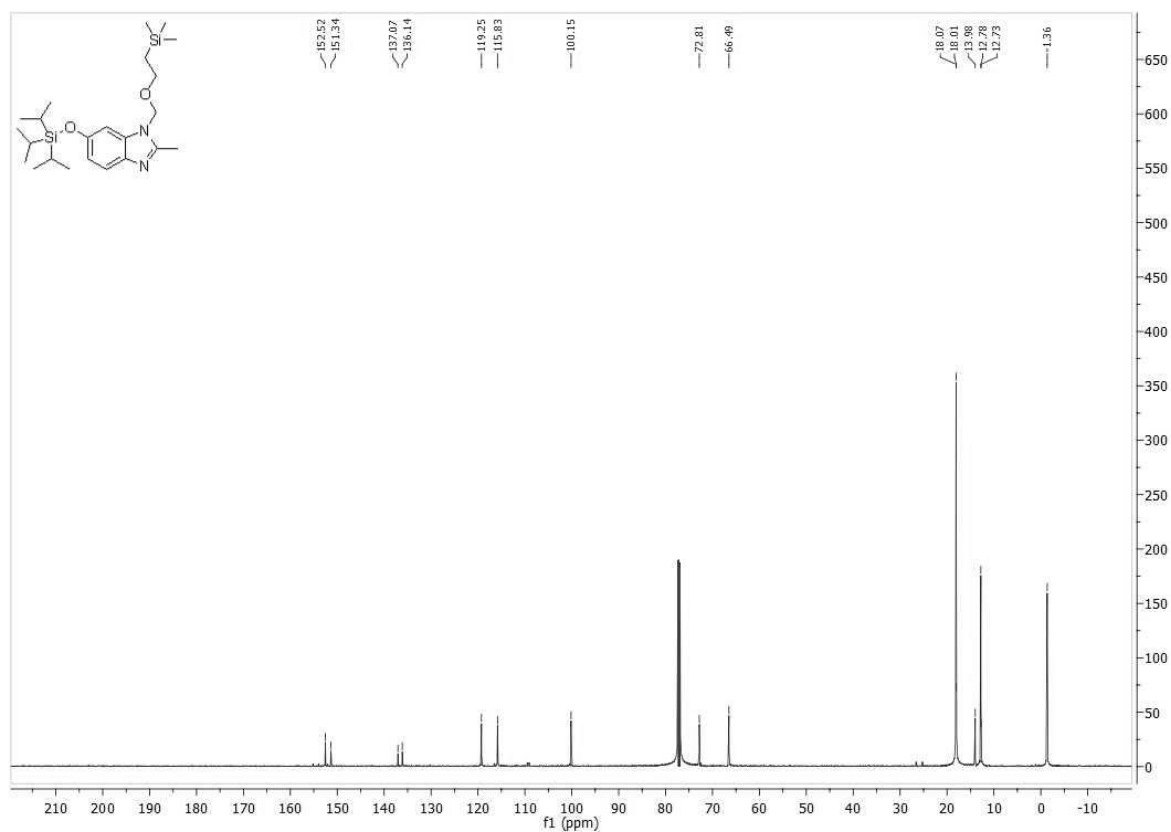
¹³C-NMR: 2-methyl-6-((triisopropylsilyl)oxy)-1H-benzo[d]imidazole (22)



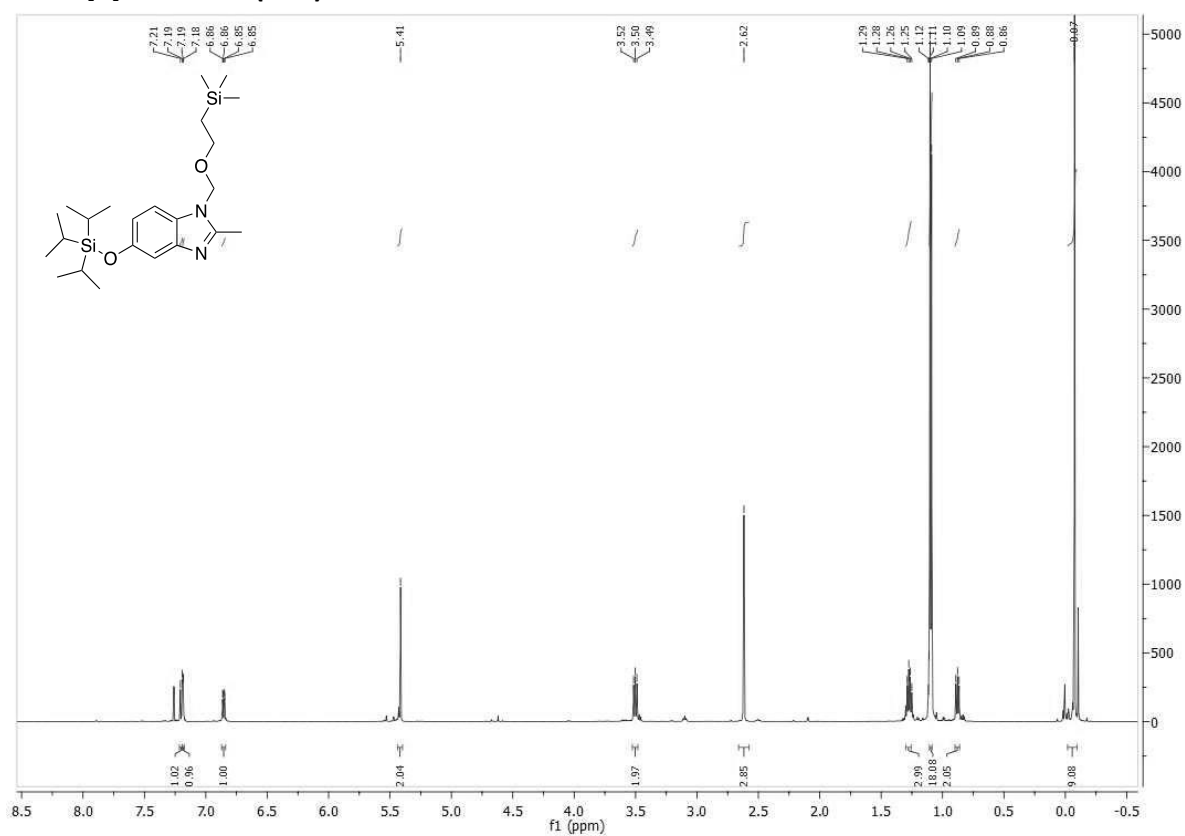
¹H-NMR: 2-methyl-6-((triisopropylsilyl)oxy)-1-((2-(trimethylsilyl)ethoxy)methyl)-1H-benzo[d]imidazole (23a)



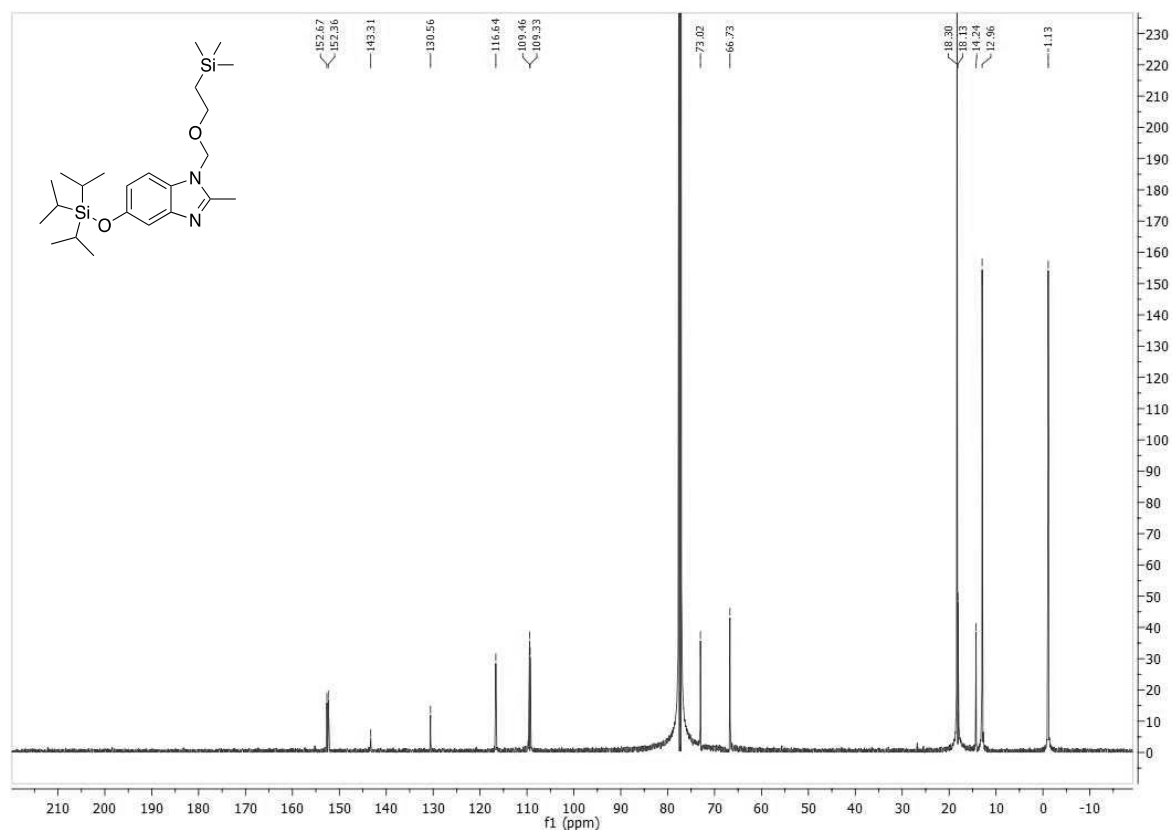
¹³C-NMR: 2-methyl-6-((triisopropylsilyl)oxy)-1-((2-(trimethylsilyl)ethoxy)methyl)-1H-benzo[d]imidazole (**23a**)



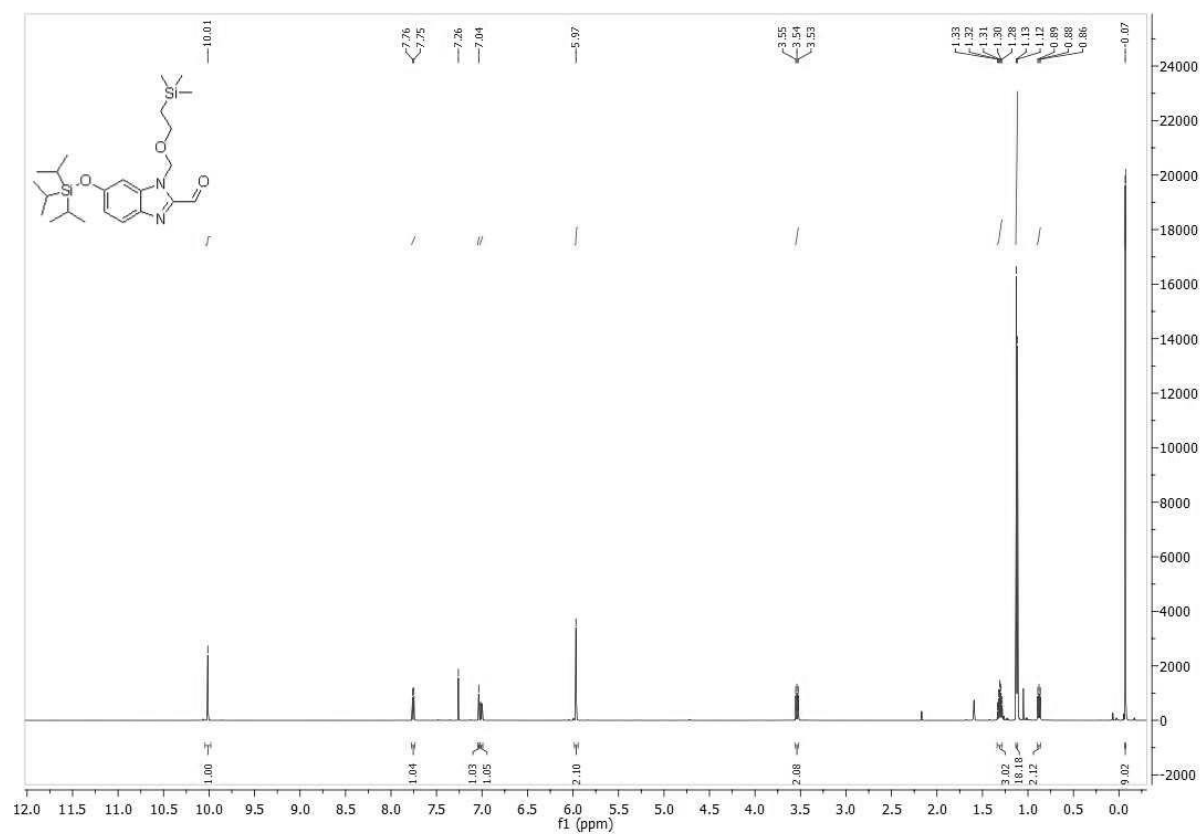
¹H-NMR: 2-methyl-5-((triisopropylsilyl)oxy)-1-((2-(trimethylsilyl)ethoxy)methyl)-1H-benzo[d]imidazole (**23b**)



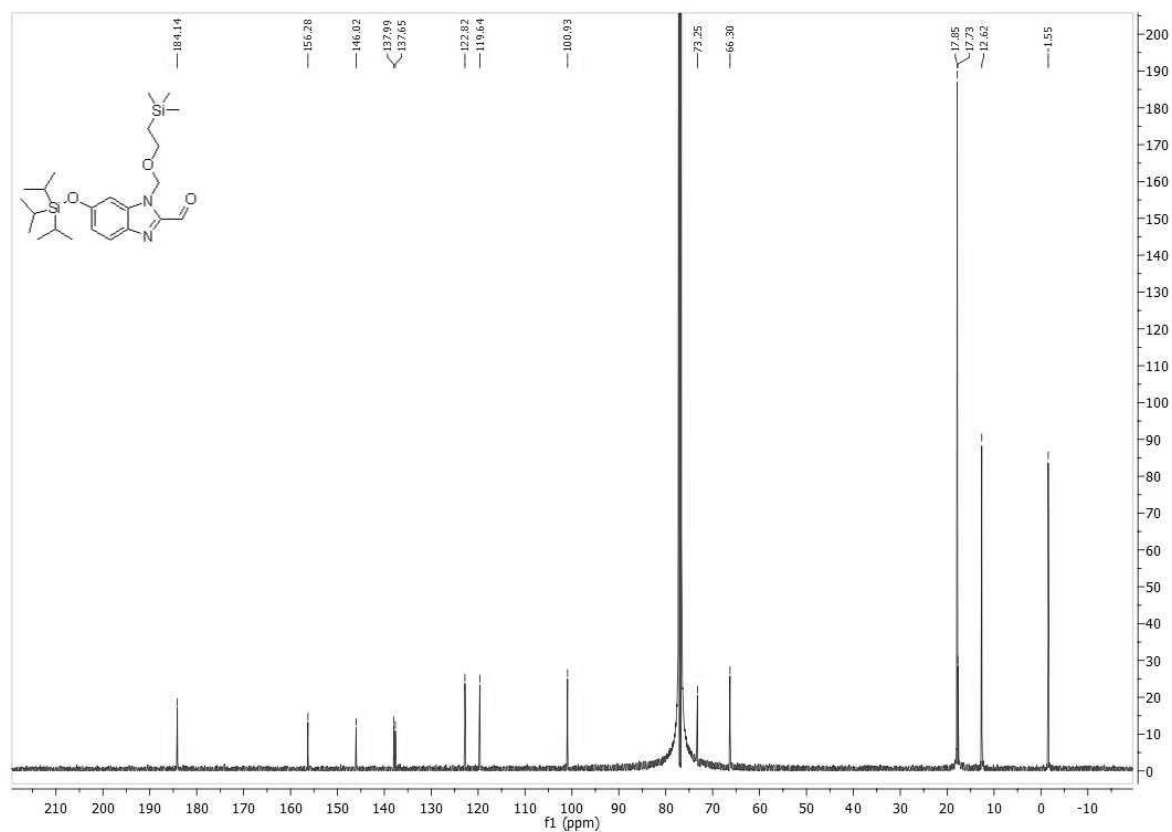
¹³C-NMR: 2-methyl-5-((triisopropylsilyl)oxy)-1-((2-(trimethylsilyl)ethoxy)methyl)-1H-benzo[d]imidazole (**23b**)



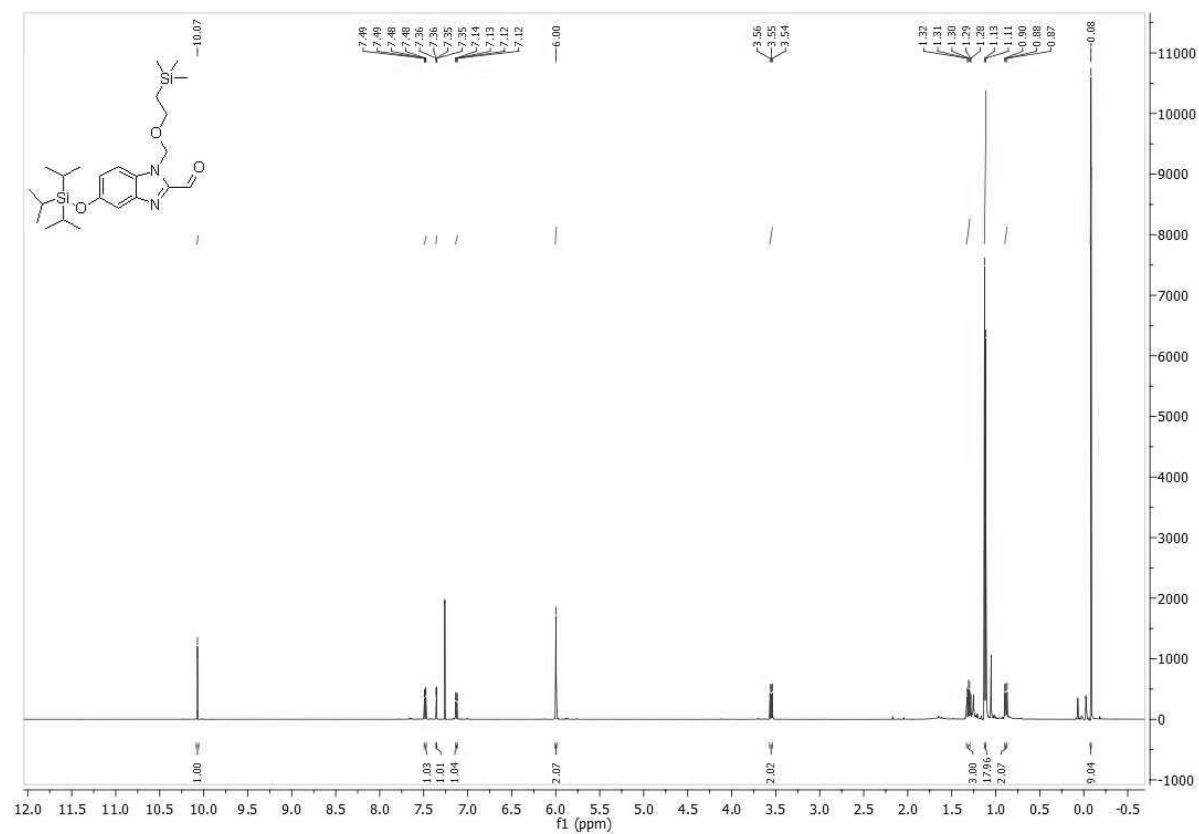
¹H – NMR: 6-((triisopropylsilyl)oxy)-1-((2-(trimethylsilyl)ethoxy)methyl)-1H-benzo[d]imidazole-2-carbaldehyde (**24a**)



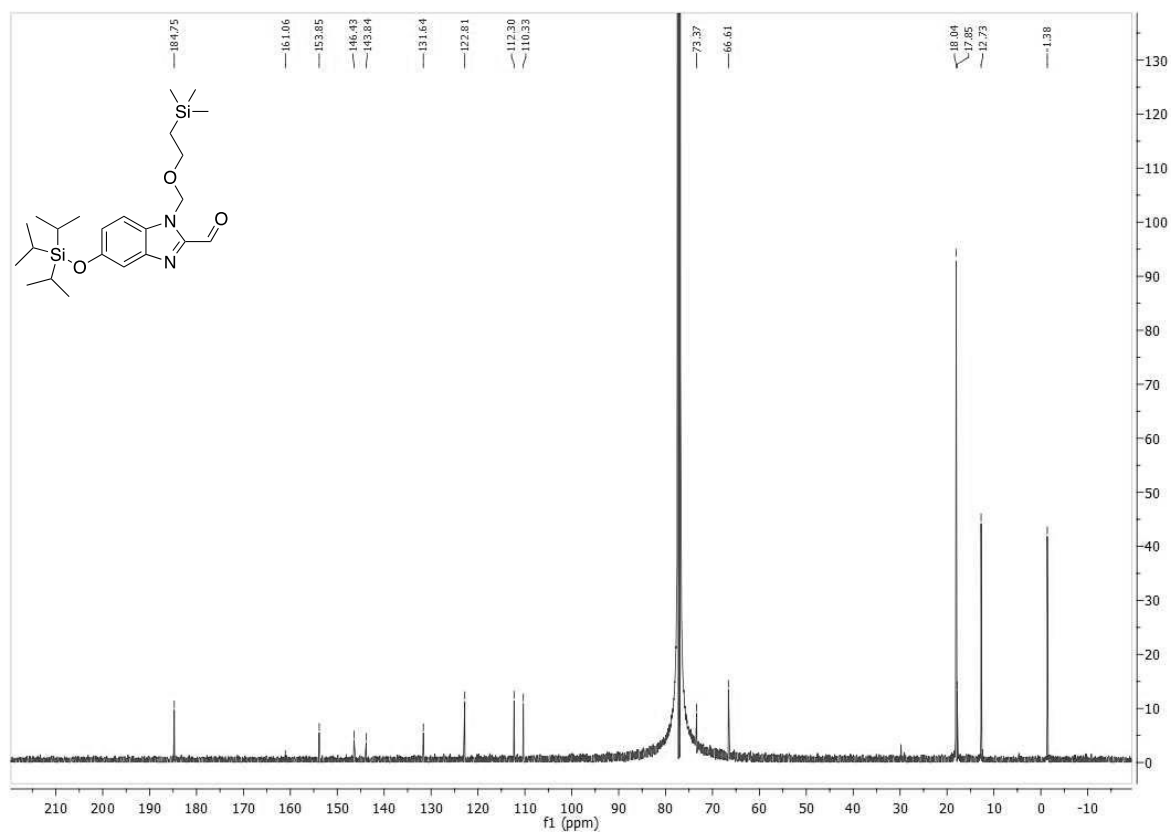
¹³C-NMR: 6-((triisopropylsilyl)oxy)-1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-benzo[*d*]imidazole-2-carbaldehyde (**24a**)



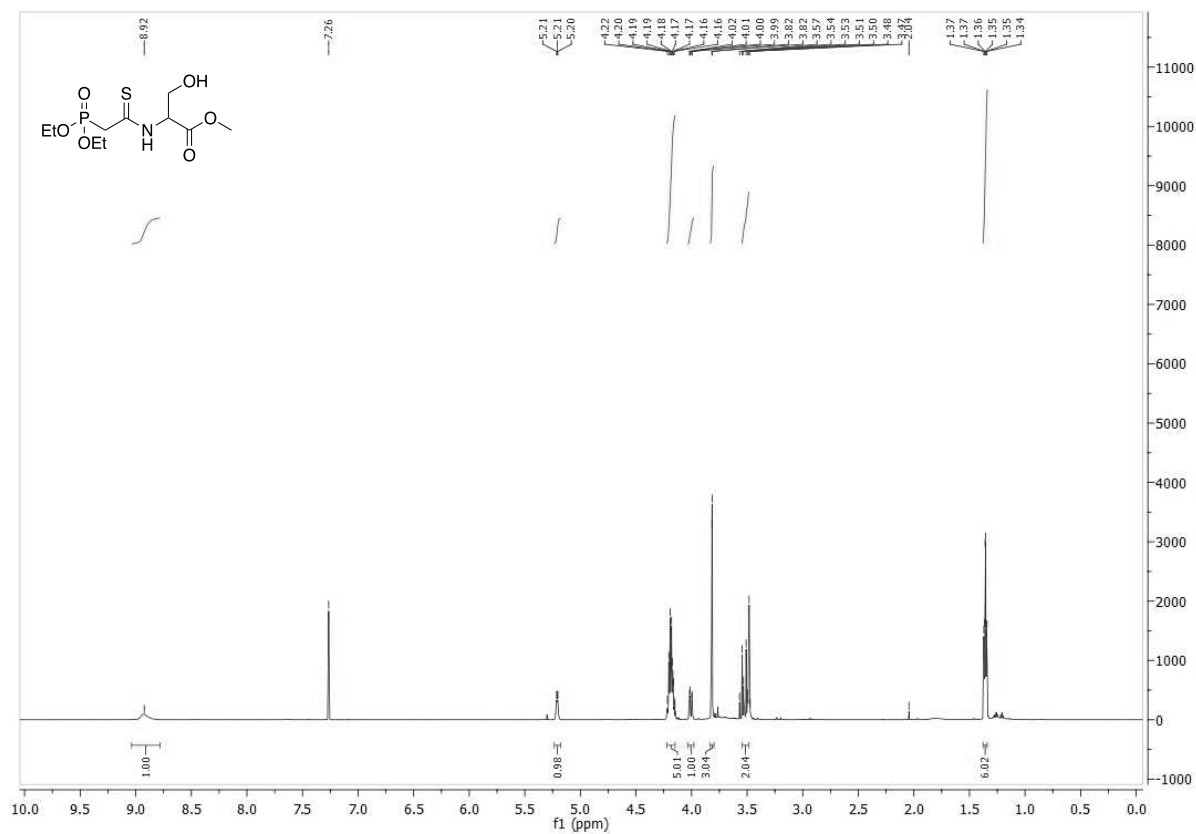
¹H-NMR: 5-((triisopropylsilyl)oxy)-1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-benzo[*d*]imidazole-2-carbaldehyde (**24b**)



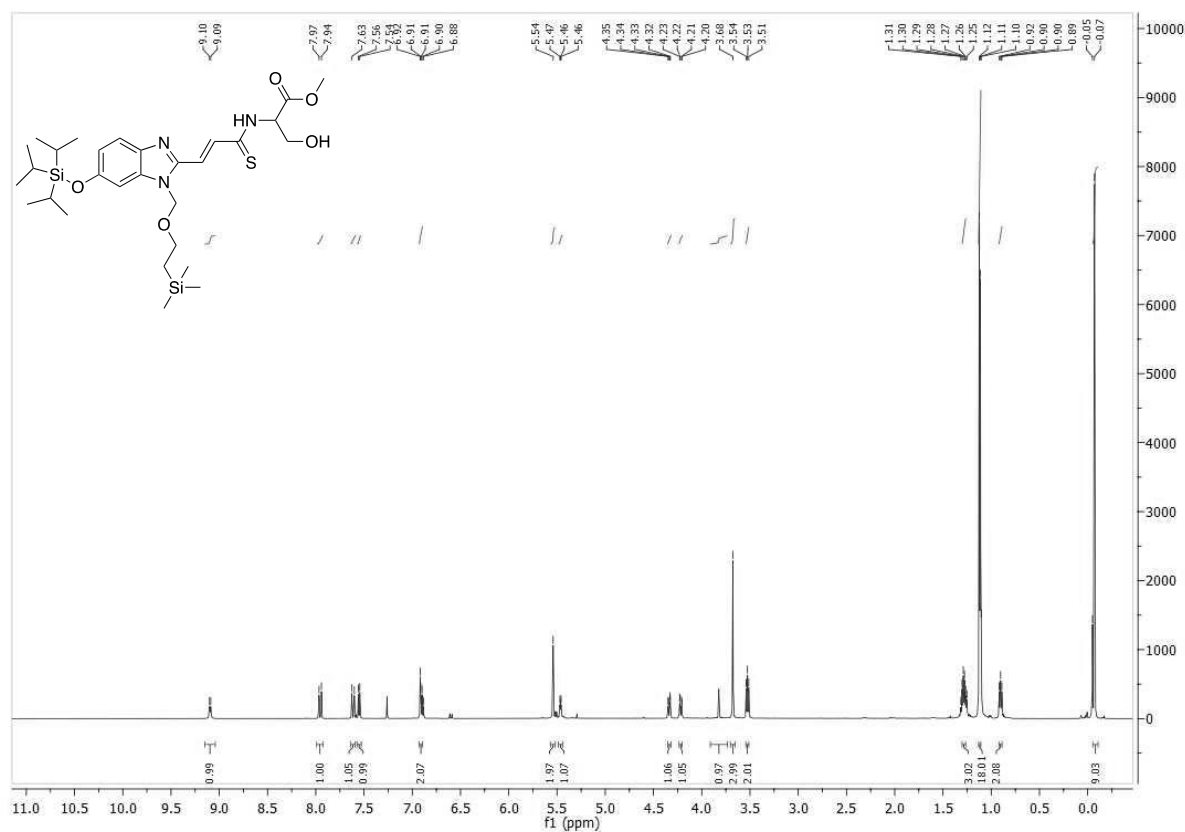
¹³C-NMR: 5-((triisopropylsilyloxy)-1-((2-(trimethylsilyl) ethoxy) methyl)-1H-benzo[d]imidazole-2-carbaldehyde (24b)



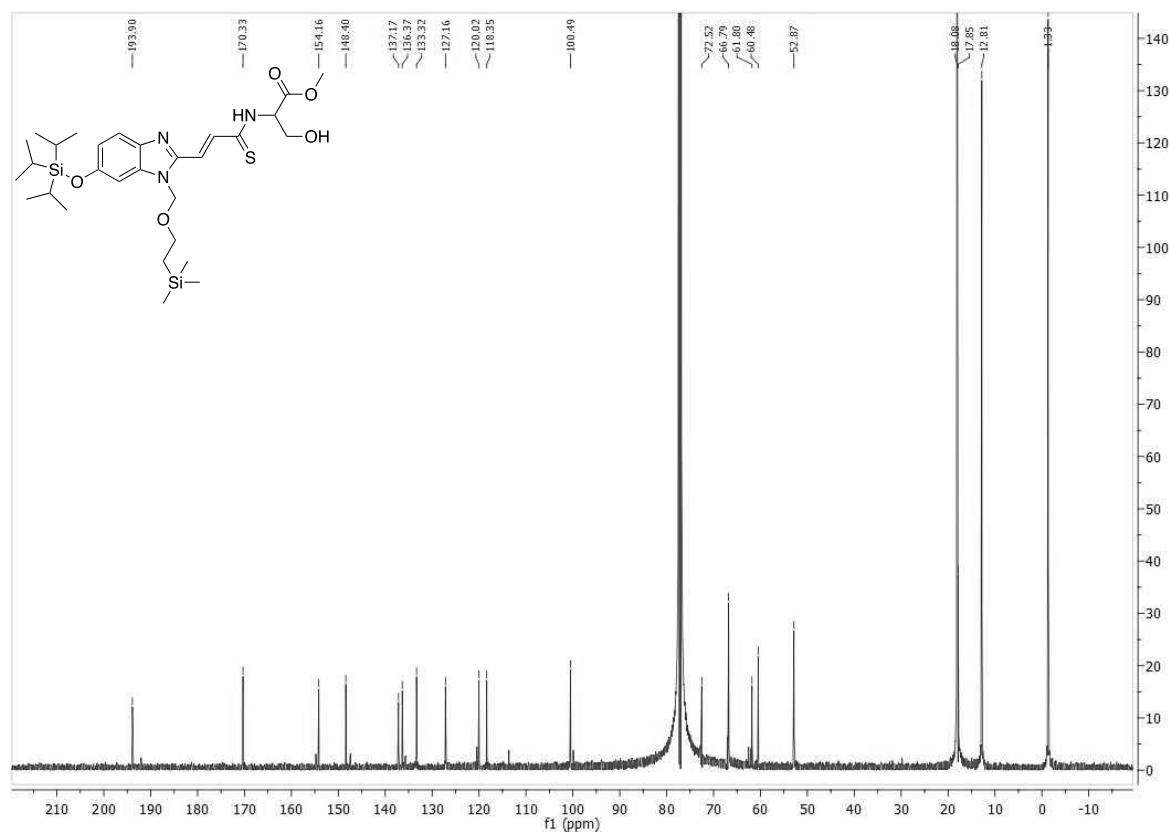
¹H - NMR: methyl (2-(diethoxyphosphoryl)ethanethioyl)serinate (25)



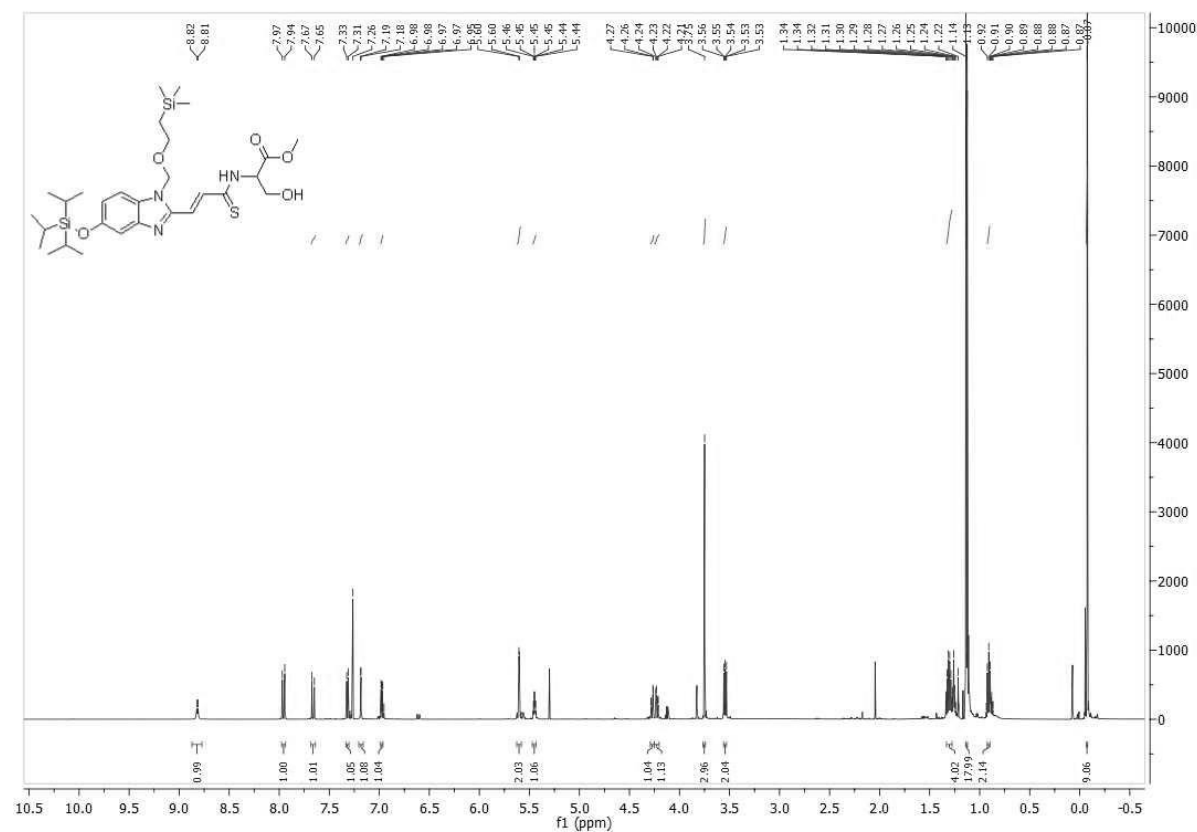
¹H – NMR: methyl (*E*)-3-(6-((triisopropylsilyloxy)-1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-benzo[*d*]imidazol-2-yl)prop-2-enethioyl)serinate (**26a**)



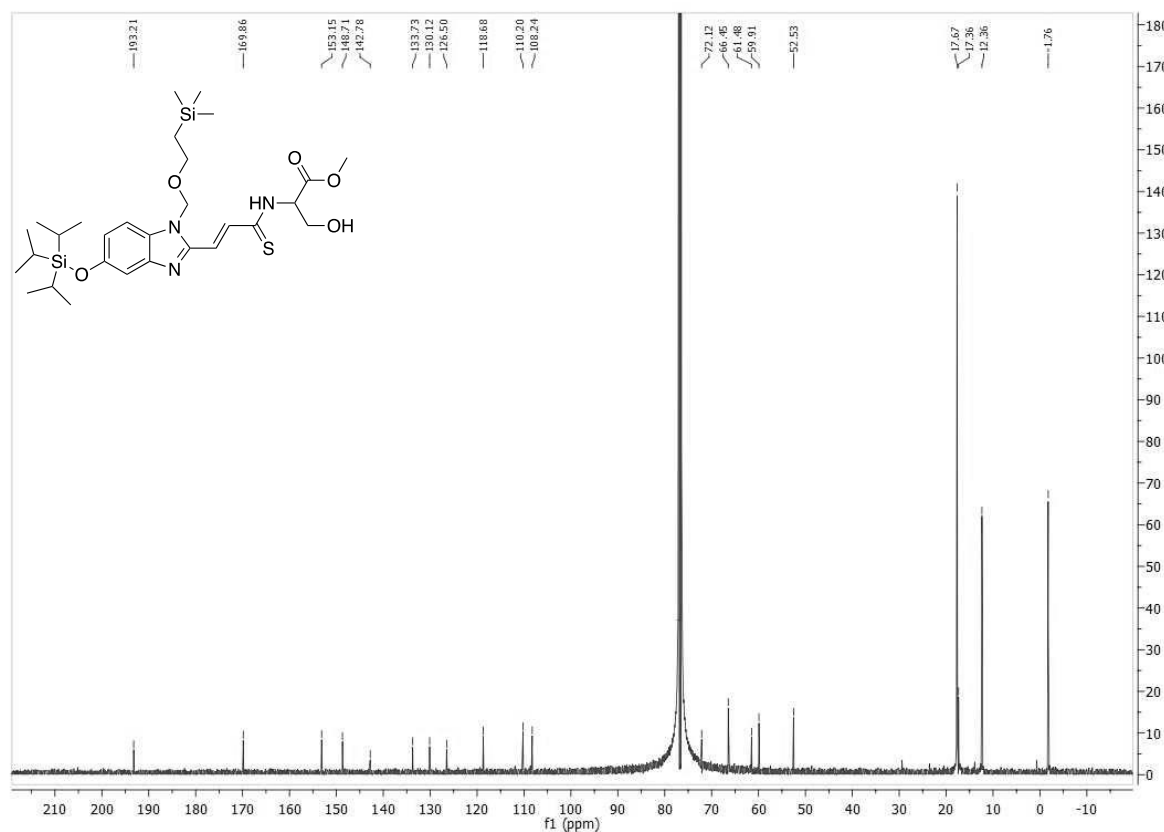
¹³C-NMR: methyl (*E*)-3-(6-((triisopropylsilyloxy)-1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-benzo[*d*]imidazol-2-yl)prop-2-enethioyl)serinate (**26a**)



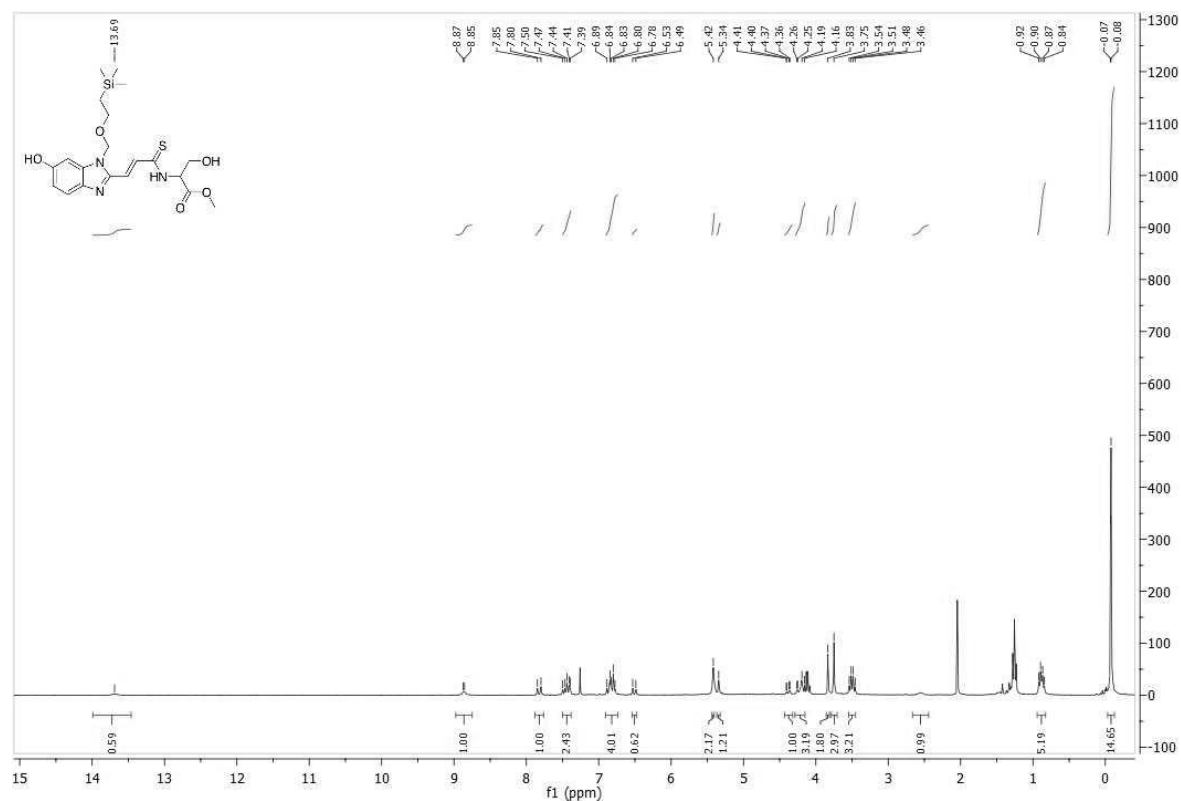
¹H – NMR: methyl(*E*)-(3-(5-((triisopropylsilyl)oxy)-1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-benzo[*d*]imidazol-2-yl)prop-2-enethioyl)serinate (**26b**)



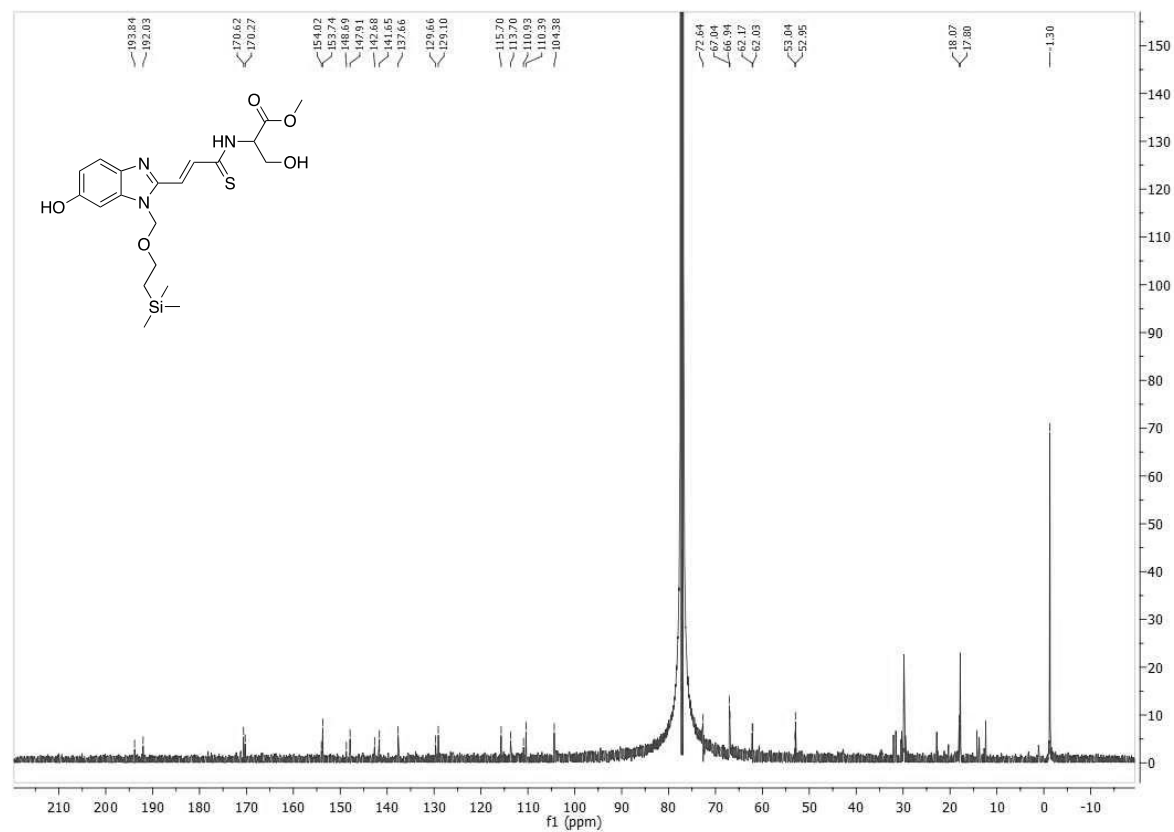
¹³C-NMR: methyl(*E*)-(3-(5-((triisopropylsilyl)oxy)-1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-benzo[*d*]imidazol-2-yl)prop-2-enethioyl)serinate (**26b**)



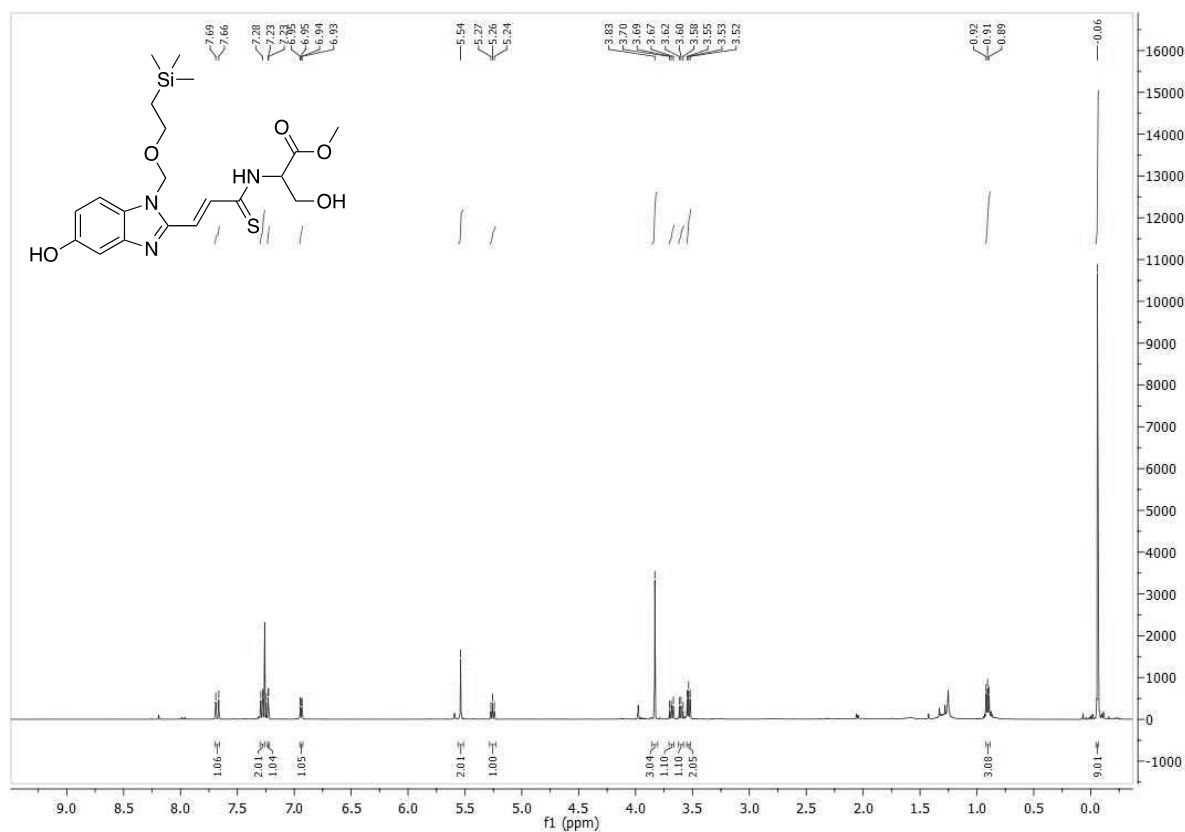
¹H – NMR: methyl (*E*)-(3-(6-hydroxy-1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-benzo[*d*]imidazol-2-yl)prop-2-enethioyl)serinate (**27a**)



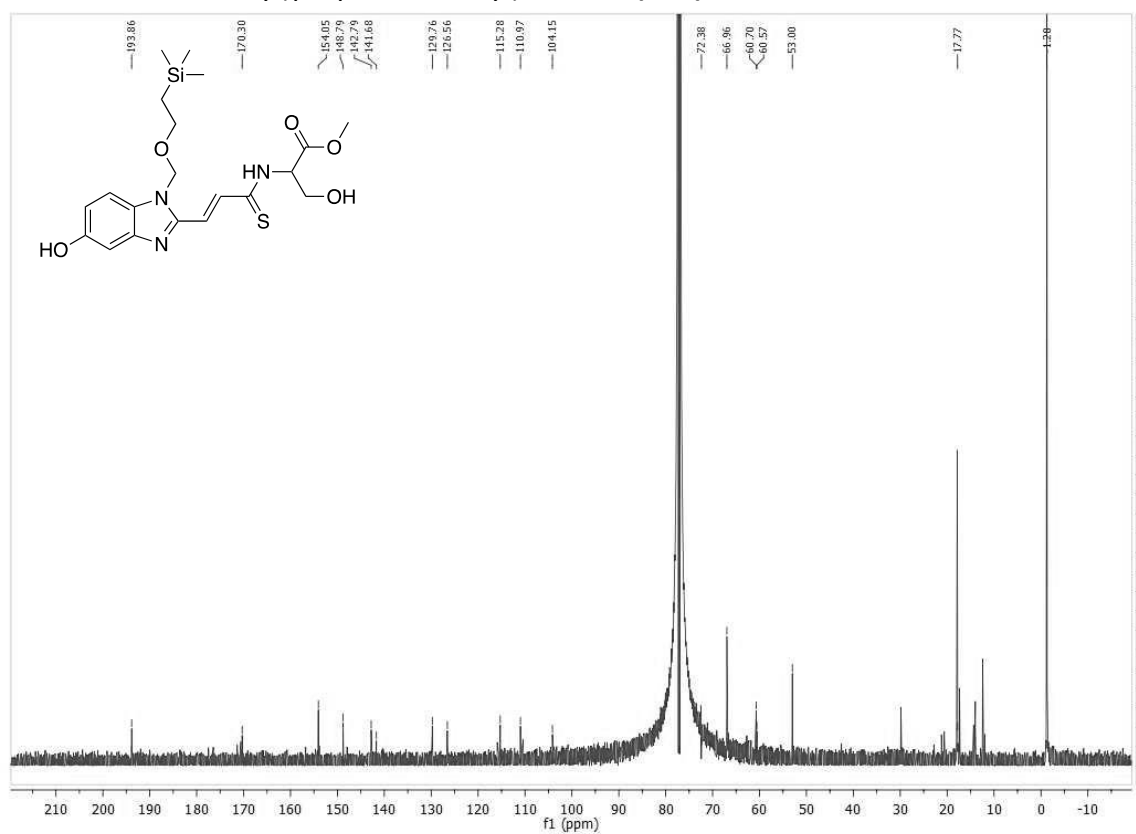
¹³C-NMR: methyl (*E*)-(3-(6-hydroxy-1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-benzo[*d*]imidazol-2-yl)prop-2-enethioyl)serinate (**27a**)



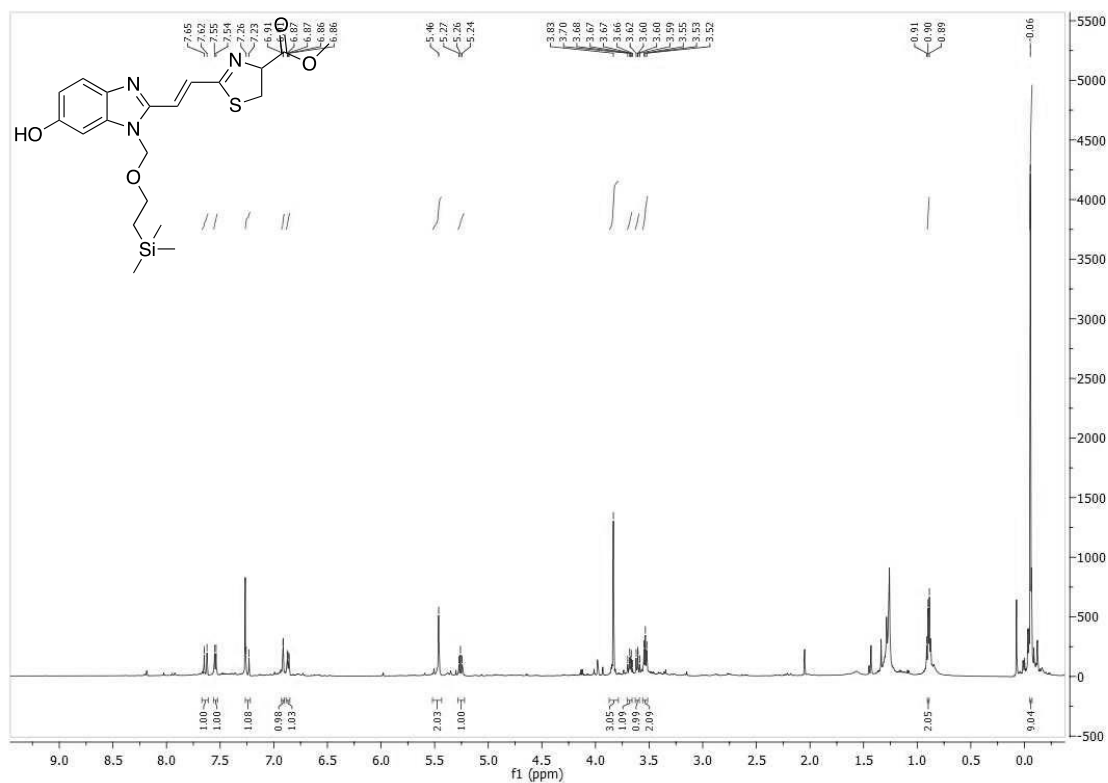
¹H – NMR: methyl (*E*)-(3-(5-hydroxy-1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-benzo[*d*]imidazol-2-yl)prop-2-enethioyl)serinate (**27b**)



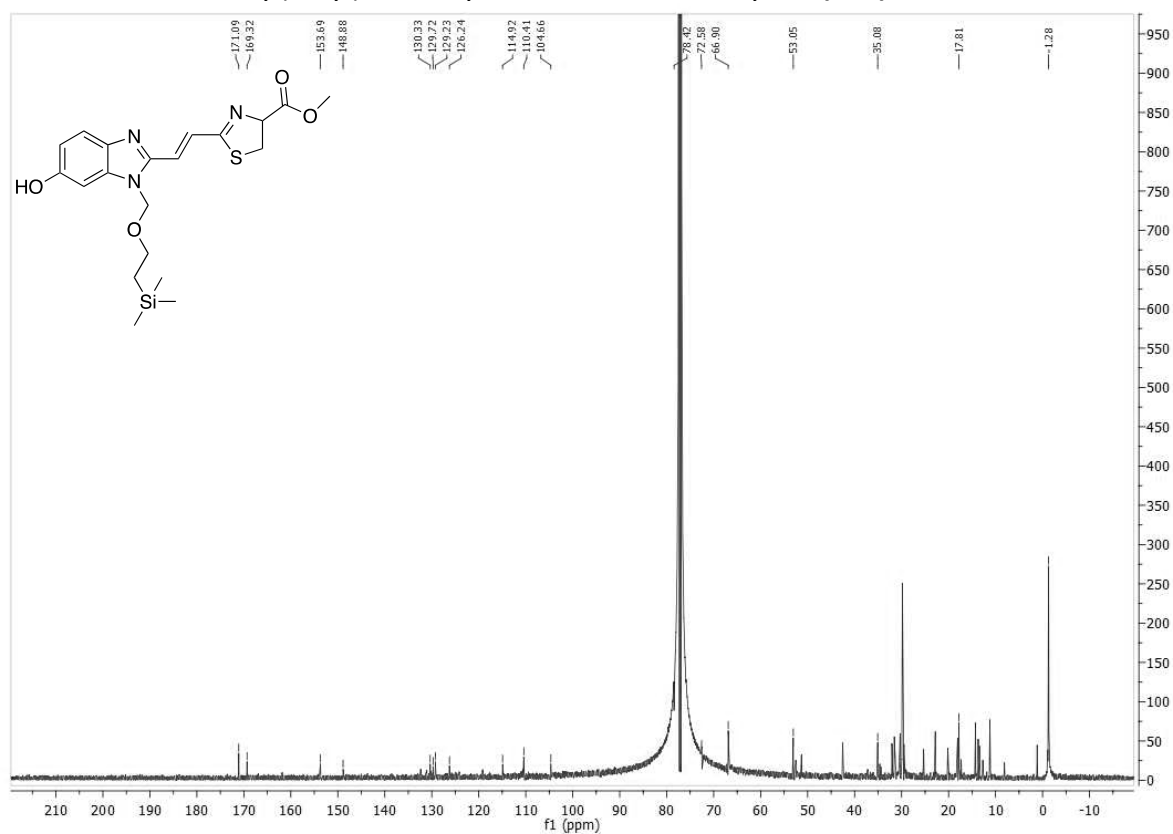
¹³C-NMR: methyl (*E*)-(3-(5-hydroxy-1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-benzo[*d*]imidazol-2-yl)prop-2-enethioyl)serinate (**27b**)



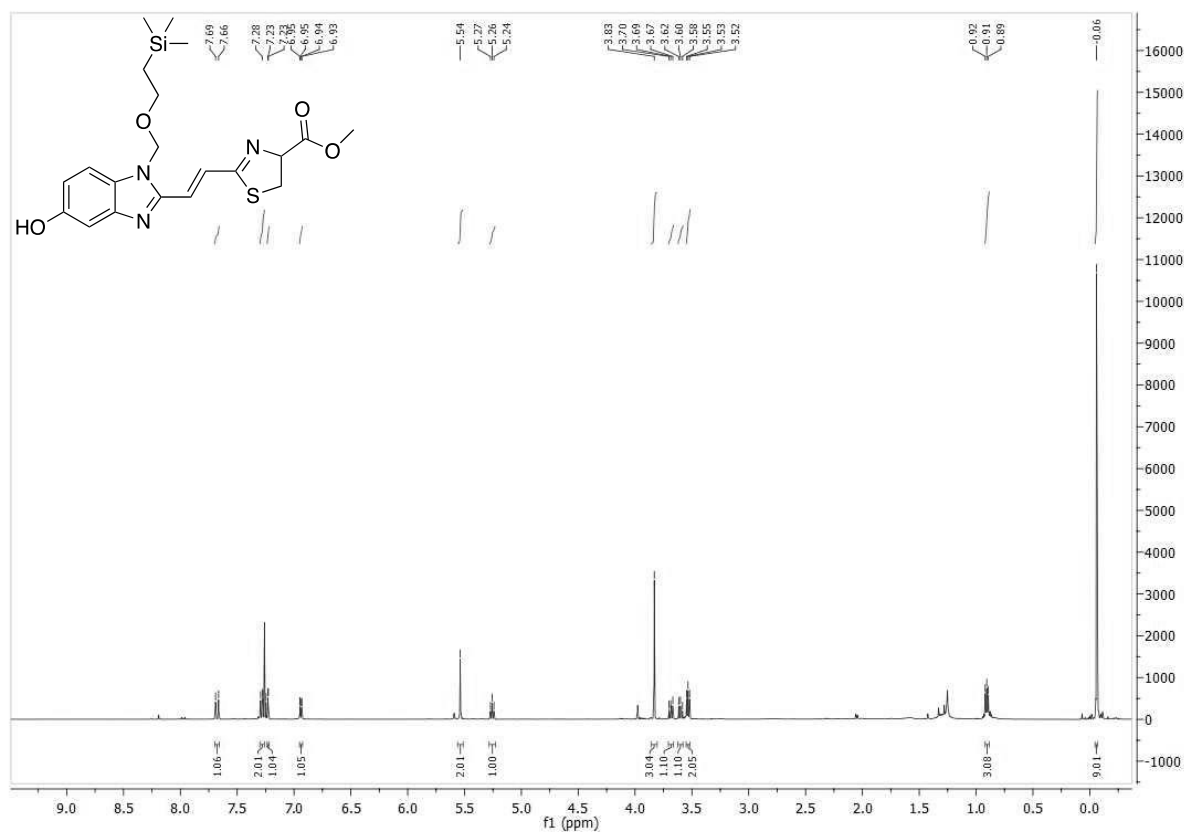
¹H – NMR: methyl (*E*)-2-(2-(6-hydroxy-1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-benzo[*d*]imidazol-2-yl)vinyl)-4,5-dihydrothiazole-4-carboxylate (**28a**)



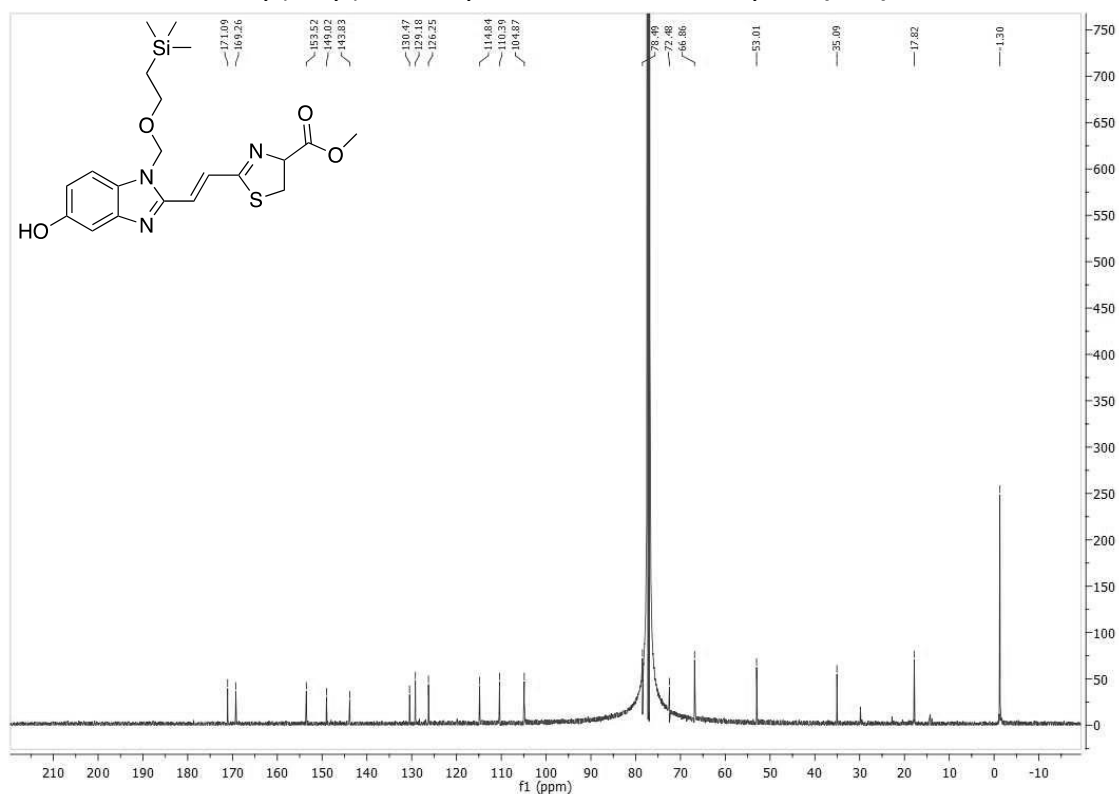
¹³C-NMR: methyl (*E*)-2-(2-(6-hydroxy-1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-benzo[*d*]imidazol-2-yl)vinyl)-4,5-dihydrothiazole-4-carboxylate (**28a**)



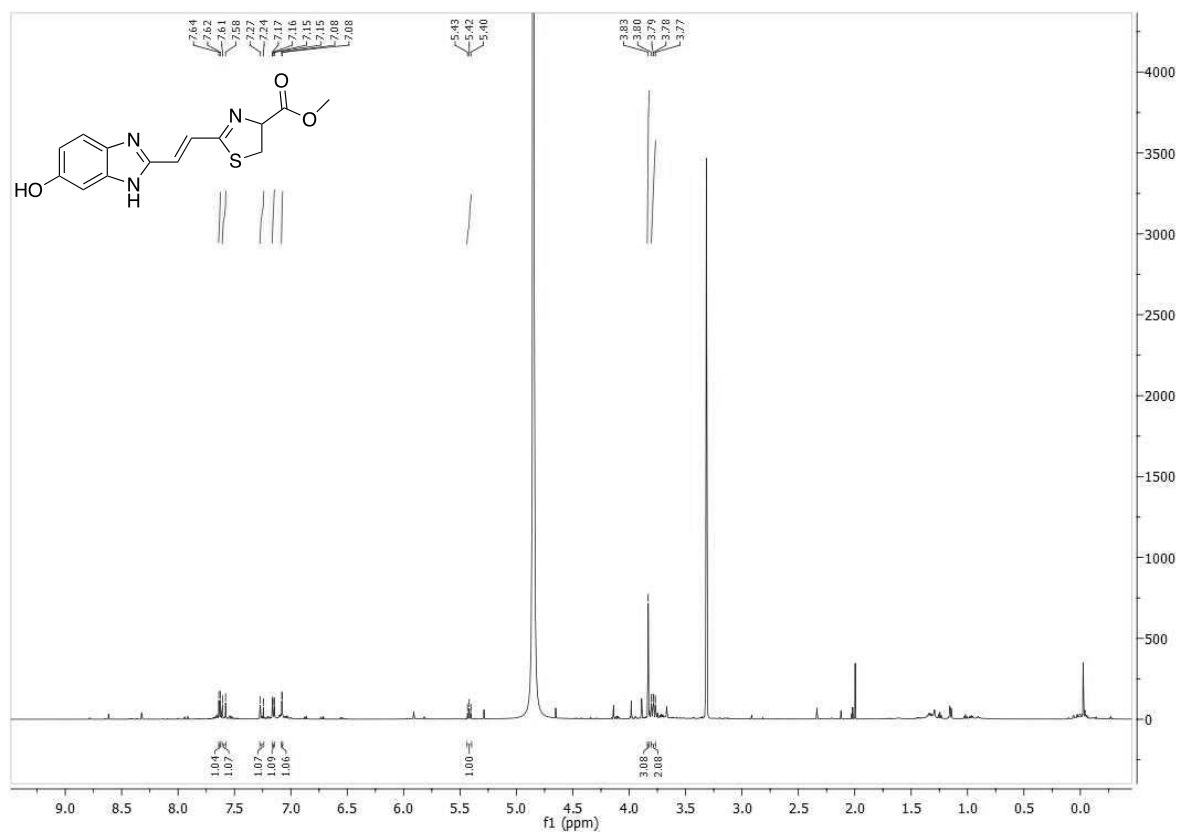
¹H – NMR: methyl (*E*)-2-(2-(5-hydroxy-1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-benzo[*d*]imidazol-2-yl)vinyl)-4,5-dihydrothiazole-4-carboxylate (**28b**)



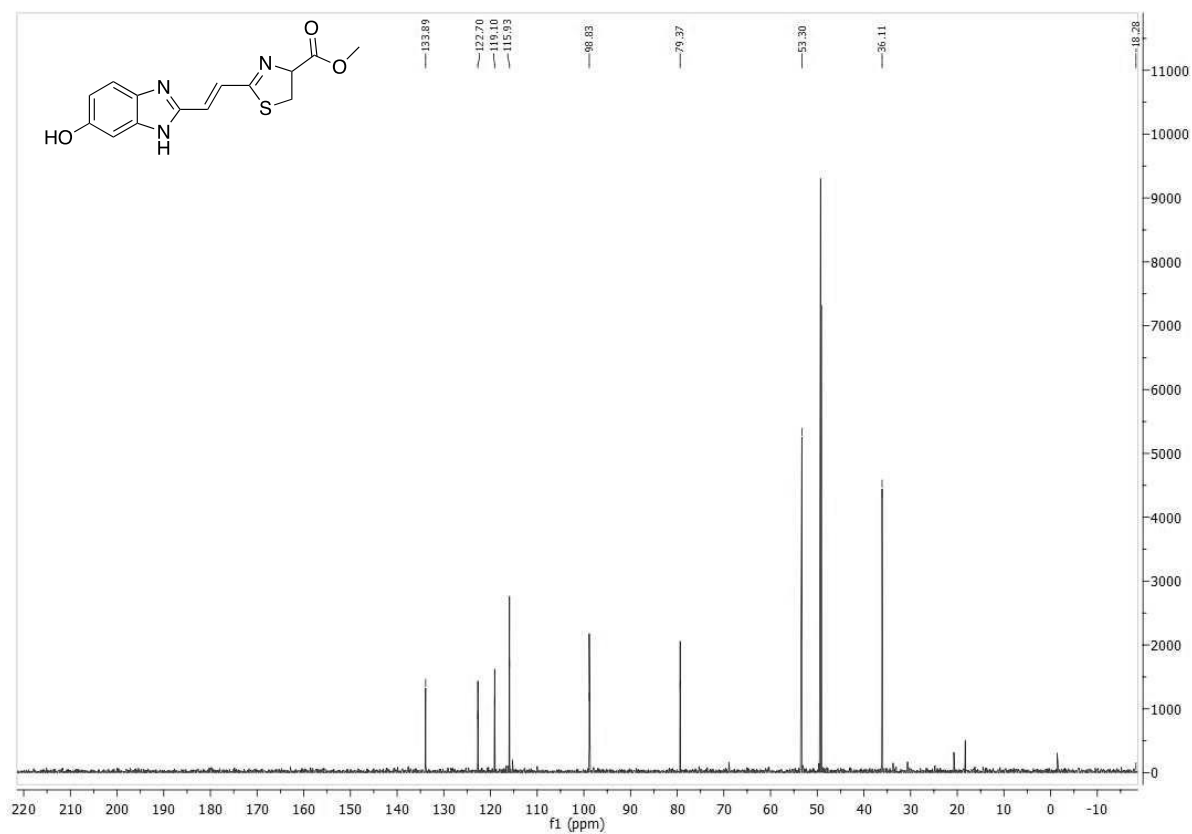
¹³C-NMR: methyl (*E*)-2-(2-(5-hydroxy-1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-benzo[*d*]imidazol-2-yl)vinyl)-4,5-dihydrothiazole-4-carboxylate (**28b**)



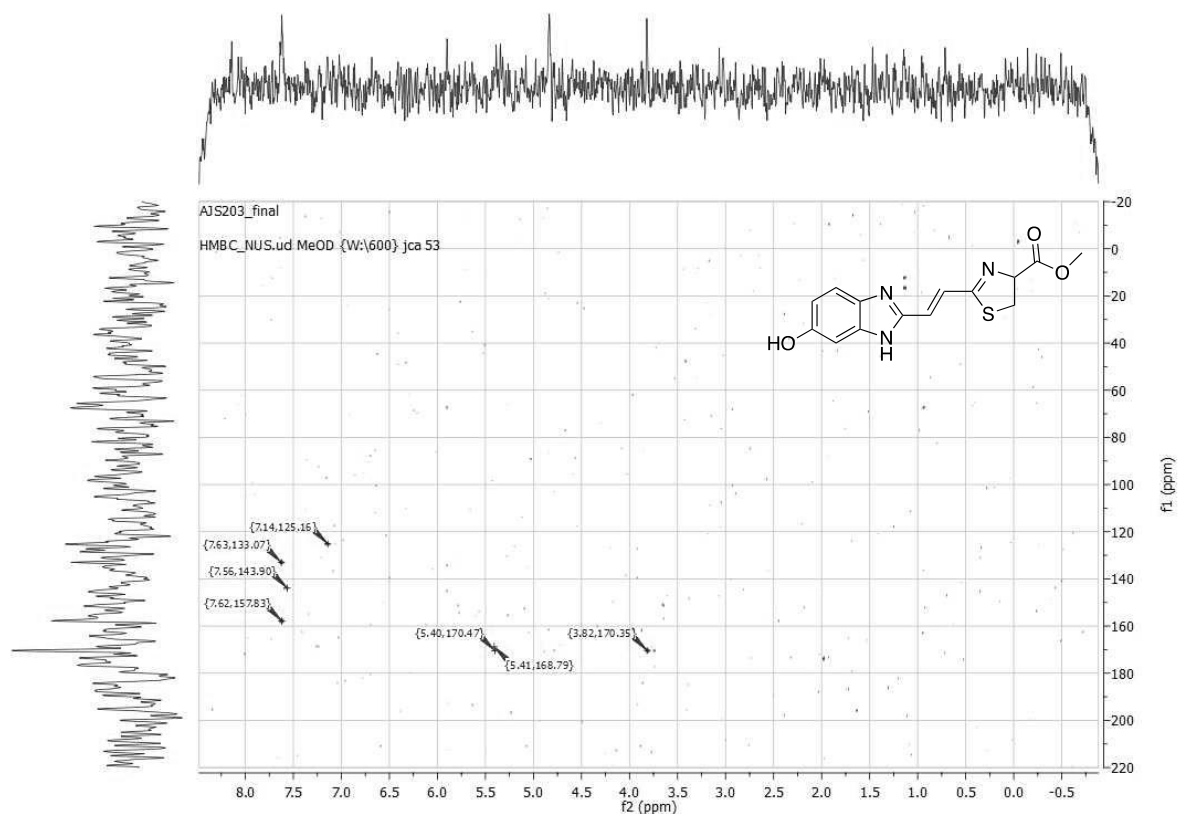
¹H – NMR: methyl (*E*)-2-(2-(6-hydroxy-1*H*-benzo[*d*]imidazol-2-yl)vinyl)-4,5-dihydrothiazole-4-carboxylate



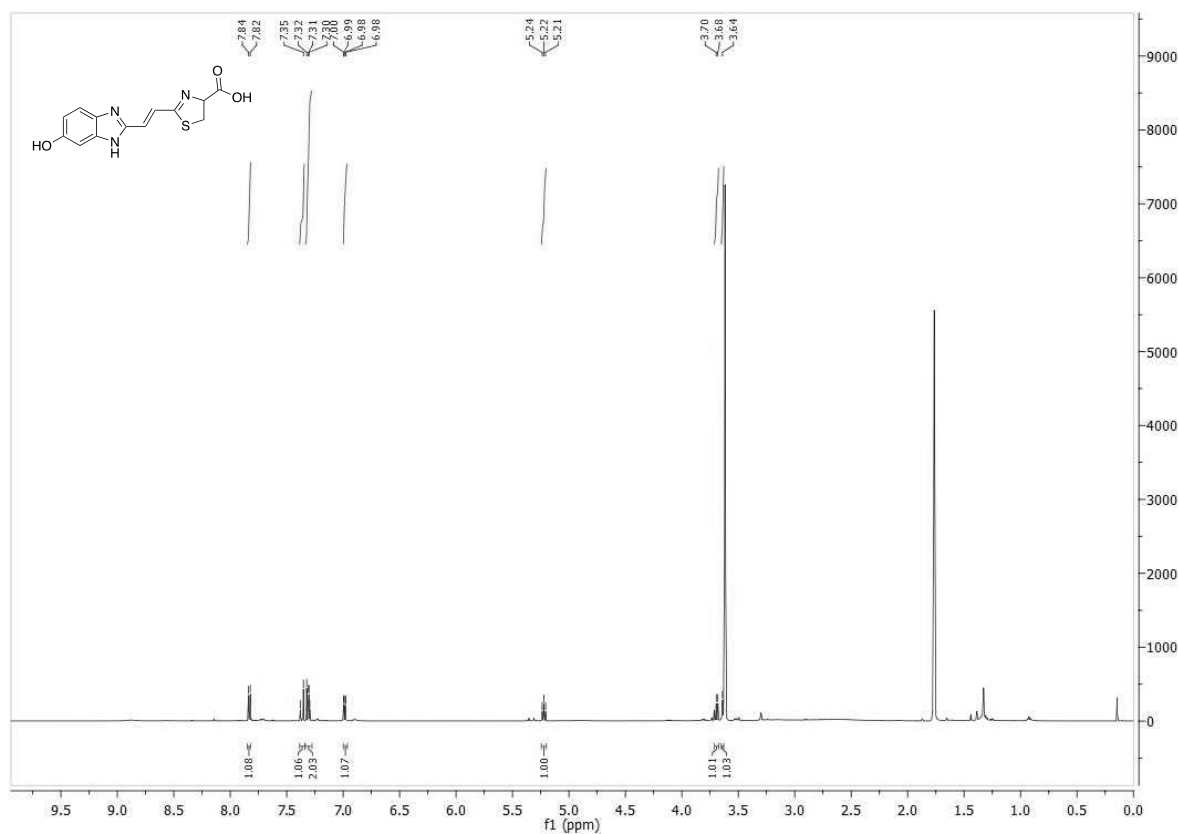
¹³C-NMR: methyl (*E*)-2-(2-(6-hydroxy-1*H*-benzo[*d*]imidazol-2-yl)vinyl)-4,5-dihydrothiazole-4-carboxylate



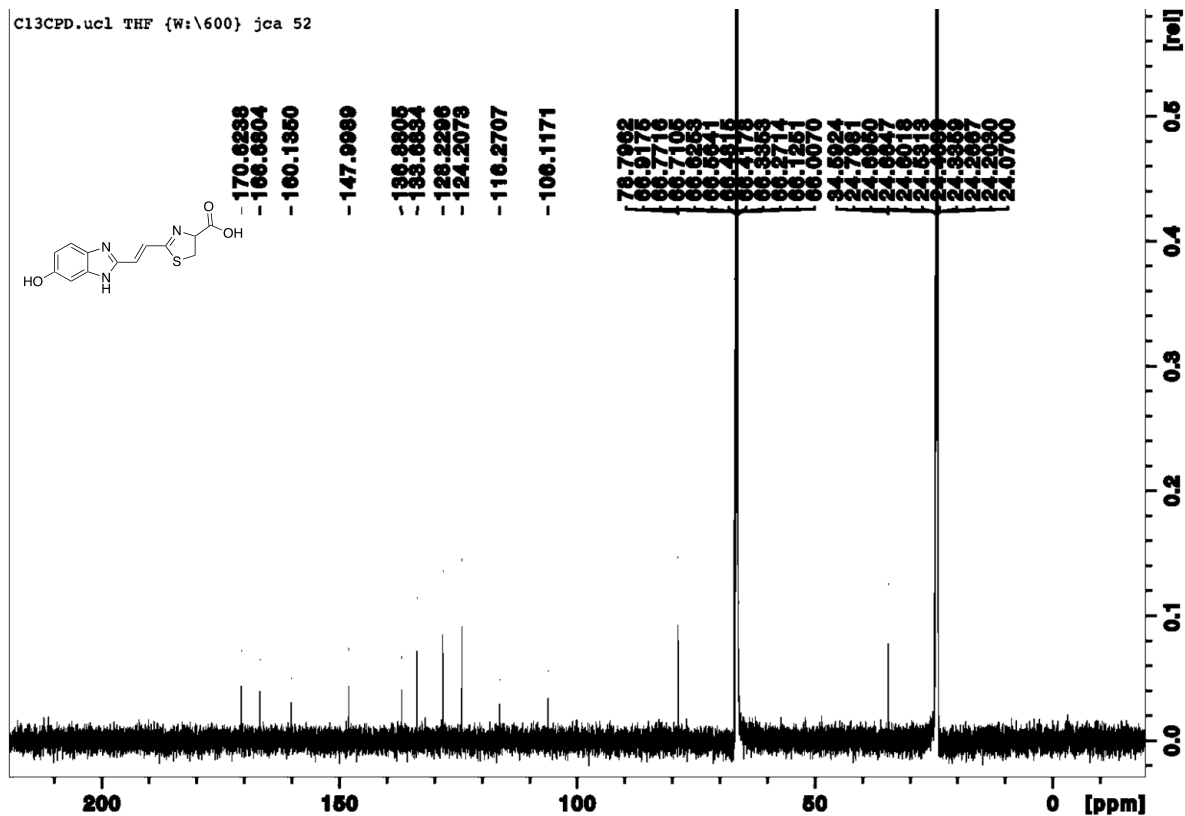
HMBC spectrum: methyl (*E*)-2-(2-(6-hydroxy-1*H*-benzo[*d*]imidazol-2-yl)vinyl)-4,5-dihydrothiazole-4-carboxylate



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



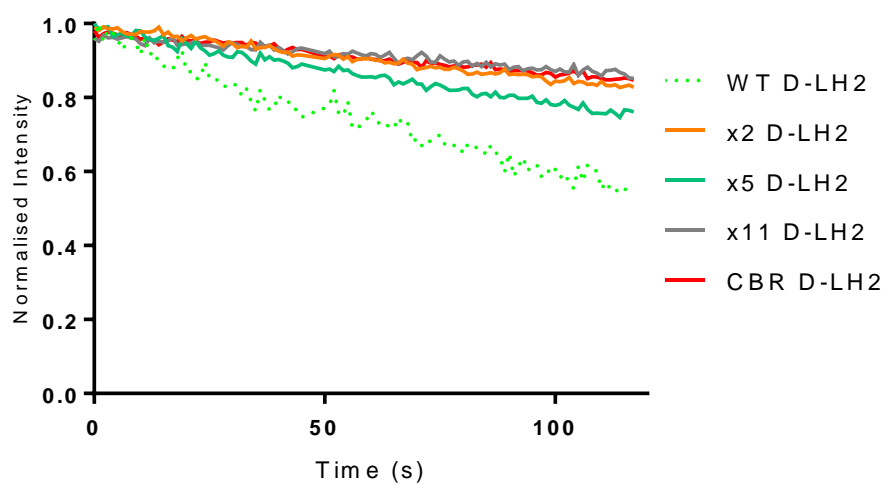
¹³C-NMR: (*E*)-2-(2-(6-hydroxy-1*H*-benzo[*d*]imidazol-2-yl)vinyl)-4,5-dihydrothiazole-4-carboxylic acid (**13**)



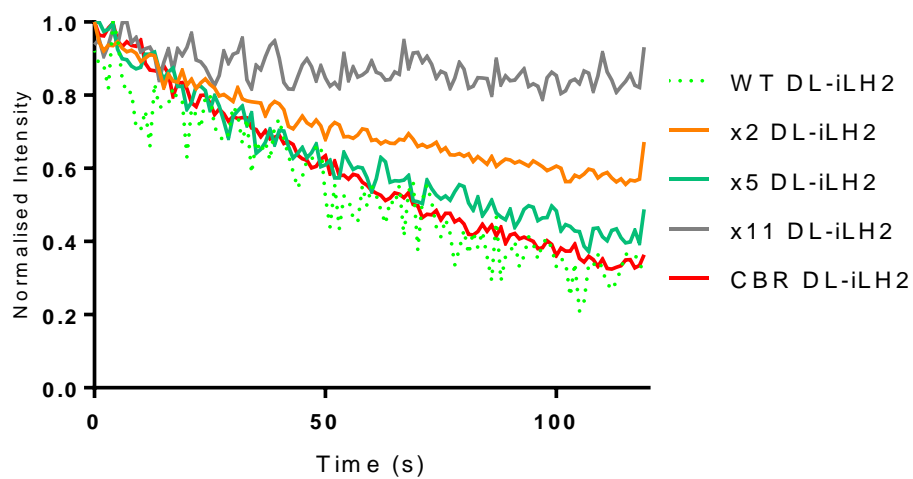
Emission kinetics of enzymes with different compounds acquired in the PIO

SI Figure:

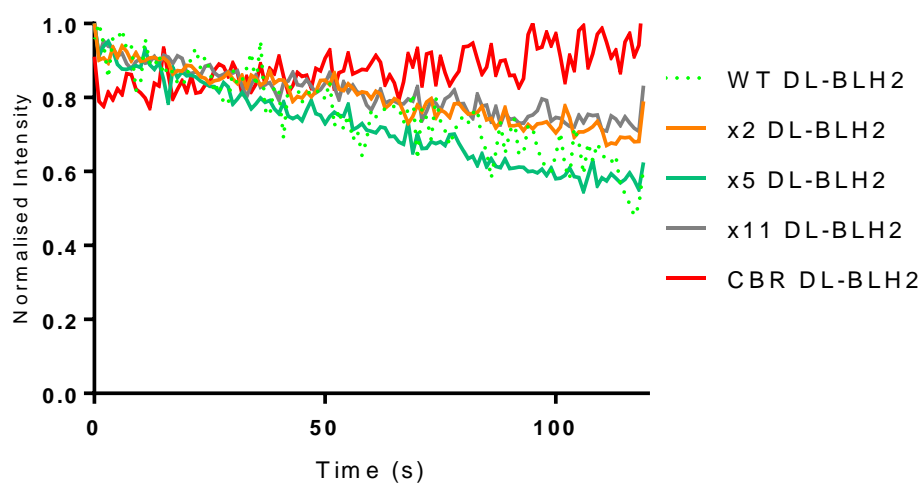
A



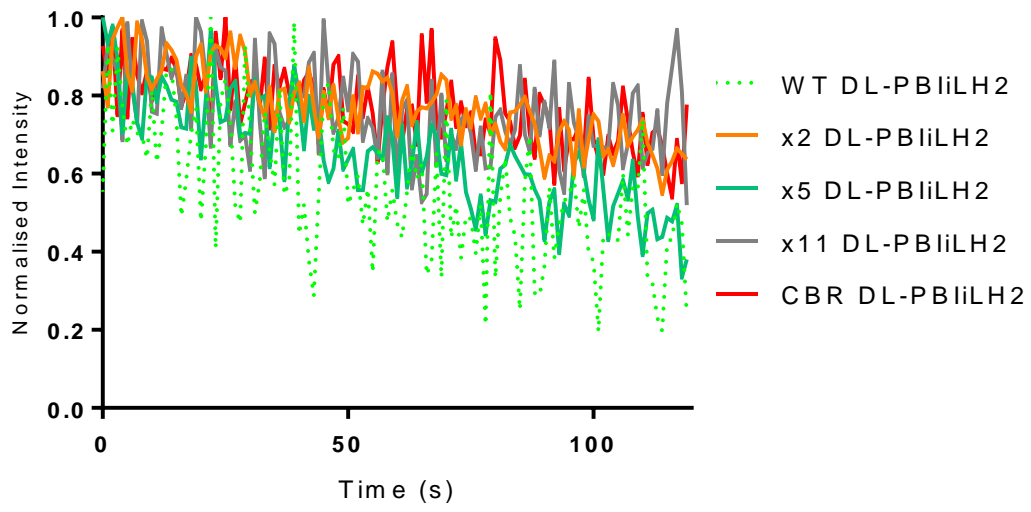
B



C



D



E

