**Combined Experimental and Computational Investigations of the Fluorosolvatochromism of Chromeno[4,3-b]pyridine Derivatives: Effect of the Methoxy Substituent**

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**EXPERIMENTAL**

**General**

All reagents including the salicylaldehydes, ethyl 3-aminocrotonate and solvents and were purchased from Sigma-Aldrich and VWR international and were used as received without additional purification. Reactions monitored by thin-layer chromatography (TLC) on silica gel 60 F254 using UV light. 1H spectra were recorded on a JOEL 600 MHz spectrometer. 1H NMR spectra were internally referenced to the residual solvent signal (CHCl3 = 7.24 ppm). Data are reported as follows: chemical shifts, multiplicity (s=singlet, d=doublet, t=triplet, q=quartet, br=broad, dd=double doublet, m=multiplet), integration, coupling constant (in Hz). Mass spectra were recorded on Agilent 7890B GC/ 5975C MS.

**Procedure for the synthesis of 7- and 8-Methoxy- chromeno[4,3-b]pyridine-3-carboxylates**

**Following a reported procedure**

(P.A. Navarrete-Encina, R. Salazar, C. Vega-Retter, K. Pérez, J.A. Squella, L.J. Nuñez-Vergara, *J. Braz. Chem. Soc*. 21 (**2010**) 413–418)

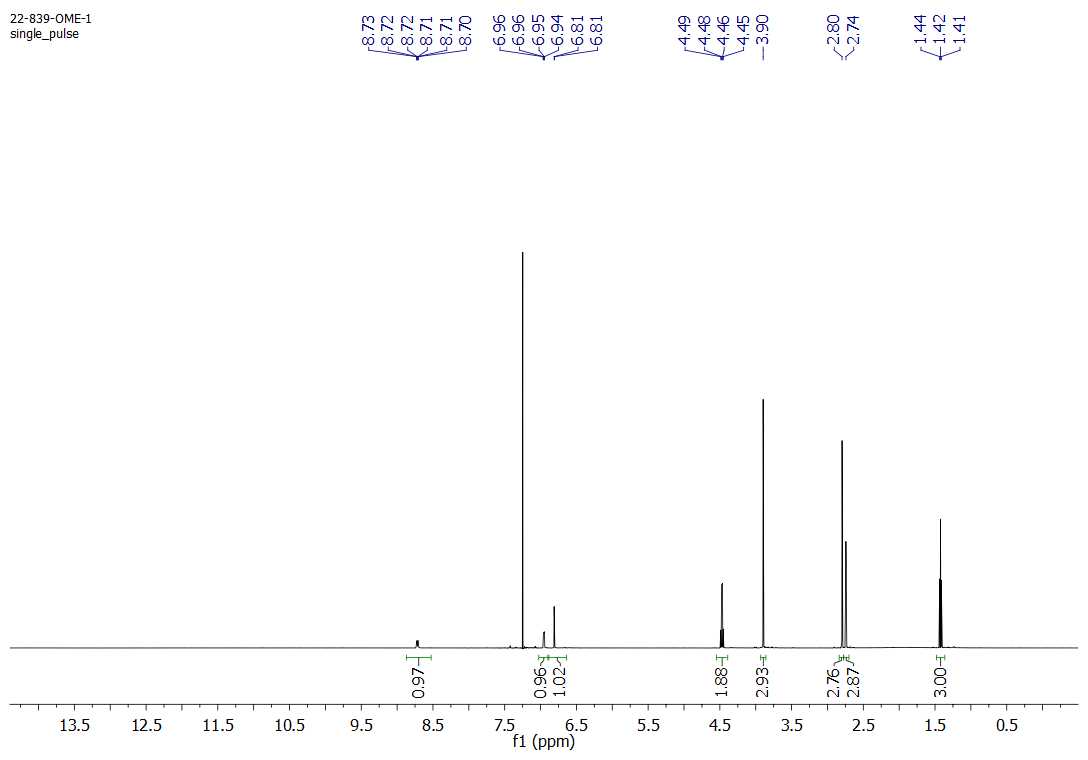


A solution of substituted salicyldehyde **2** (5 mmol) and ethyl 3-aminocrotonate **1** (10 mmol) in 10 ml of acetic acid was heated at 60 oC for 24 hours during which a precipitate was formed. After, cooling the reaction mixture to room temperature, the precipitate was isolated by vacuum filtration and then purified by recrystallization from ethanol or acetonitrile to provide the pure chromeno[4,3-b]pyridine-3-carboxylates **3**.

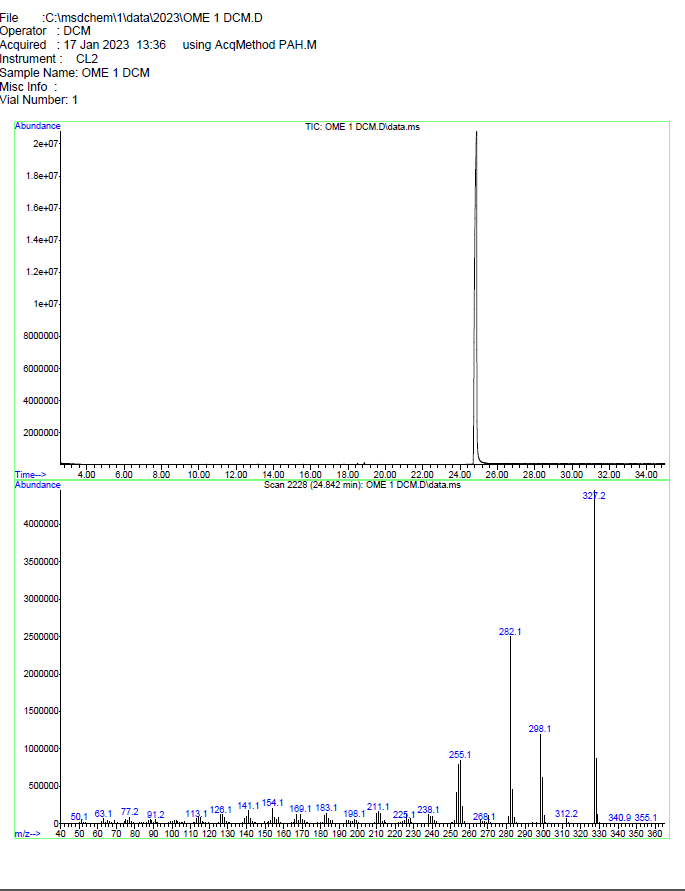
**Ethyl 8-methoxy-2,4-dimethyl-5-oxo-5H-chromeno[4,3-b]pyridine-3-carboxylate (3b):**



1H NMR (600 MHz, ) δ 8.87 – 8.53 (m, 1H), 6.95 (dd, *J* = 8.9, 2.5 Hz, 1H), 6.81 (d, *J* = 2.4 Hz, 1H), 4.47 (q, *J* = 7.2 Hz, 2H), 3.90 (s, 3H), 2.80 (s, 3H), 2.74 (s, 3H), 1.42 (t, *J* = 7.1 Hz, 3H).



1HNMR spectrum for compound **3b**

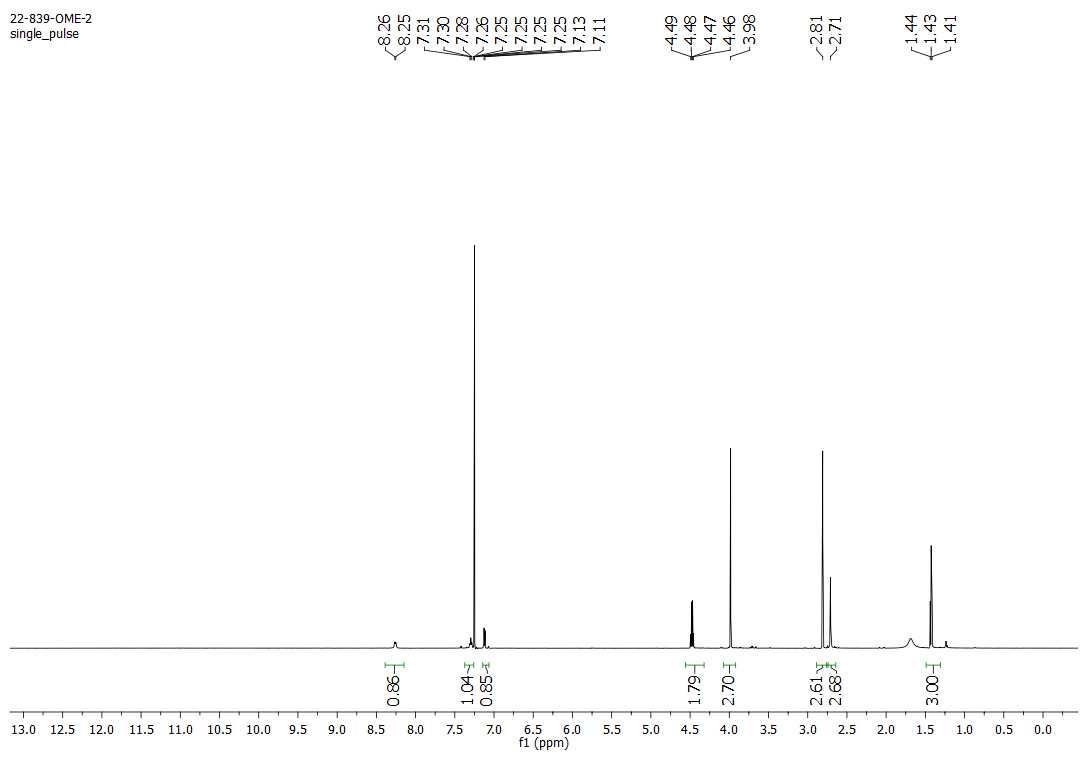


GCMS spectrum of compound **3b**

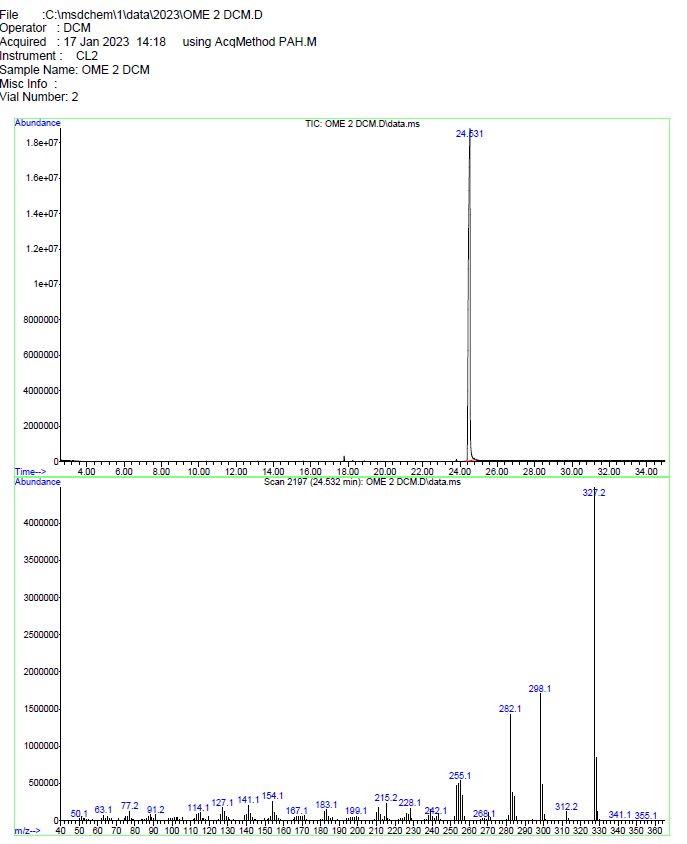
Ethyl 7-methoxy-2,4-dimethyl-5-oxo-5H-chromeno[4,3-b]pyridine-3-carboxylate (**3c**)



Pale yellow solid. 42% yield. m.p. 130-132 OC. 1H NMR (600 MHz, ) δ 8.26 (d, *J* = 7.5 Hz, 1H), 7.30 (t, *J* = 7.6 Hz, 1H), 7.12 (d, *J* = 8.0 Hz, 1H), 4.47 (q, *J* = 7.1 Hz, 2H), 3.98 (s, 3H), 2.81 (s, 3H), 2.71 (s, 3H), 1.43 (t, *J* = 7.1 Hz, 3H).



1HNMR spectrum for **3c**



GCMS spectrum of compound **3b**