Supporting Information

Photochemical Electrocyclic Ring Closure and Leaving Group Expulsion from *N*-(9oxothioxanthenyl)benzothiophene Carboxamides.

Majher Sarker, Tasnuva Shahrin, Mark G. Steinmetz*, and Qadir Timerghazin*

Department of Chemistry, Marquette University, Milwaukee, Wisconsin 532011881

Mark.steinmetz@marquette.edu, Qadir.timerghazin@marquette.edu

Table of Contents

List of NMR Spectra

¹ H NMR spectrum 3 -Chloro-benzo[b]thiophene-2-carboxylic acid methyl-(9-oxo-9H-	
thioxanthen-2-yl)-amide (7) (LG ⁻ = Cl ⁻)	5
¹³ C NMR spectrum of 3-Chloro-benzo[b]thiophene-2-carboxylic acid methyl-(9-oxo-9H-	•
thioxanthen-2-yl)-amide (7) (LG ⁻ = Cl ⁻))	6
¹ H NMR spectrum of 3-Chloro-2-[methyl-(9-oxo-9H-thioxanthen-2-yl)-carbamoyl]-	
benzo[b]thiophene-6-carboxylic acid methyl ester (8) $(LG^{-} = Cl^{-})$	7
¹³ C NMR spectrum of 3-Chloro-2-[methyl-(9-oxo-9H-thioxanthen-2-yl)-carbamoyl]-	
benzo[b]thiophene-6-carboxylic acid methyl ester (8) $(LG^{-} = CI^{-})$	8
¹ H NMR spectrum of 3-Chloro-2-[methyl-(9-oxo-9H-thioxanthen-2-yl)-carbamoyl]-	
benzo[b]thiophene-6-carboxylic acid (9) $(LG^{-} = Cl^{-})$	9

¹³ C NMR spectrum of 3-Chloro-2-[methyl-(9-oxo-9H-thioxanthen-2-yl)-carbamoyl]-	
benzo[b]thiophene-6-carboxylic acid (9) $(LG^{-} = Cl^{-})$	10
¹ H NMR spectrum of 2-[Methyl-(9-oxo-9H-thioxanthen-2-yl)-carbamoyl]-3-phenylsulfan	nyl-
benzo[b]thiophene-6-carboxylic acid (9) $(LG^{-} = PhS^{-})$	11
¹³ C NMR spectrum of 2-[Methyl-(9-oxo-9H-thioxanthen-2-yl)-carbamoyl]-3-phenylsulfa	nyl-
benzo[b]thiophene-6-carboxylic acid (9) $(LG^- = PhS^-)$	12
¹ H NMR spectrum of 3-Benzylsulfanyl-2-[methyl-(9-oxo-9H-thioxanthen-2-yl)-carbamog	yl]-
benzo[b]thiophene-6-carboxylic acid (9) ($LG^- = PhCH_2S^-$)	13
¹³ C NMR spectrum of 3-Benzylsulfanyl-2-[methyl-(9-oxo-9H-thioxanthen-2-yl)-carbamo	oyl]-
benzo[b]thiophene-6-carboxylic acid (9) ($LG^- = PhCH_2S^-$)	14
¹ H NMR spectrum of 3-Mercapto-2-[methyl-(9-oxo-9H-thioxanthen-2-yl)-carbamoyl]-	
have $[h]$ this phase f as the multiplication (0) (I, C^2, IIS^2)	15
benzo[b]thtophene-o-carboxytic actid (9) (LG = HS)	15
13 C NMR 3-Mercapto-2-[methyl-(9-oxo-9H-thioxanthen-2-yl)-carbamoyl]-benzo[b]thiop]	15 hene-6-
¹³ C NMR 3-Mercapto-2-[methyl-(9-oxo-9H-thioxanthen-2-yl)-carbamoyl]-benzo[b]thiop carboxylic acid (9) (LG ⁻ = HS ⁻).	15 hene-6- 16
¹³ C NMR 3-Mercapto-2-[methyl-(9-oxo-9H-thioxanthen-2-yl)-carbamoyl]-benzo[b]thiop carboxylic acid (9) (LG ⁻ = HS ⁻)	hene-6- 16 loro-
¹³ C NMR 3-Mercapto-2-[methyl-(9-oxo-9H-thioxanthen-2-yl)-carbamoyl]-benzo[b]thiop carboxylic acid (9) (LG ⁻ = HS ⁻) ¹ H NMR spectrum of 2-[(7-Bromo-9-oxo-9H-thioxanthen-2-yl)-methyl-carbamoyl]-3-chl benzo[b]thiophene-6-carboxylic acid methyl ester (10) (LG ⁻ = Cl ⁻)	15 hene-6- 16 loro- 17
¹³ C NMR 3-Mercapto-2-[methyl-(9-oxo-9H-thioxanthen-2-yl)-carbamoyl]-benzo[b]thiop carboxylic acid (9) (LG ⁻ = HS ⁻) ¹ H NMR spectrum of 2-[(7-Bromo-9-oxo-9H-thioxanthen-2-yl)-methyl-carbamoyl]-3-chl benzo[b]thiophene-6-carboxylic acid methyl ester (10) (LG ⁻ = Cl ⁻) ¹³ C NMR spectrum of 2-[(7-Bromo-9-oxo-9H-thioxanthen-2-yl)-methyl-carbamoyl]-3-chl	hene-6- 16 loro- 17 lloro-
benzo[b]thiophene-6-carboxylic acid (9) (LG = HS). ¹³ C NMR 3-Mercapto-2-[methyl-(9-oxo-9H-thioxanthen-2-yl)-carbamoyl]-benzo[b]thiophene-6-carboxylic acid (9) (LG ⁻ = HS ⁻). ¹ H NMR spectrum of 2-[(7-Bromo-9-oxo-9H-thioxanthen-2-yl)-methyl-carbamoyl]-3-chl benzo[b]thiophene-6-carboxylic acid methyl ester (10) (LG ⁻ = Cl ⁻). ¹³ C NMR spectrum of 2-[(7-Bromo-9-oxo-9H-thioxanthen-2-yl)-methyl-carbamoyl]-3-chl benzo[b]thiophene-6-carboxylic acid methyl ester (10) (LG ⁻ = Cl ⁻).	15 hene-6- 16 loro- 17 lloro- 18
benzo[b]thiophene-6-carboxylic acid (9) (LG = HS) ¹³ C NMR 3-Mercapto-2-[methyl-(9-oxo-9H-thioxanthen-2-yl)-carbamoyl]-benzo[b]thiophene carboxylic acid (9) (LG ⁻ = HS ⁻) ¹ H NMR spectrum of 2-[(7-Bromo-9-oxo-9H-thioxanthen-2-yl)-methyl-carbamoyl]-3-chl benzo[b]thiophene-6-carboxylic acid methyl ester (10) (LG ⁻ = Cl ⁻) ¹³ C NMR spectrum of 2-[(7-Bromo-9-oxo-9H-thioxanthen-2-yl)-methyl-carbamoyl]-3-chl benzo[b]thiophene-6-carboxylic acid methyl ester (10) (LG ⁻ = Cl ⁻) ¹³ C NMR spectrum of 2-[(7-Bromo-9-oxo-9H-thioxanthen-2-yl)-methyl-carbamoyl]-3-chl benzo[b]thiophene-6-carboxylic acid methyl ester (10) (LG ⁻ = Cl ⁻) ¹⁴ H NMR spectrum of 3-Chloro-2-chlorocarbonyl-benzo[b]thiophene-6-carboxylic acid m	15 hene-6- 16 loro- 17 lloro- 18 ethyl
benzo[b]thiophene-6-carboxylic acid (9) (LG = HS) ¹³ C NMR 3-Mercapto-2-[methyl-(9-oxo-9H-thioxanthen-2-yl)-carbamoyl]-benzo[b]thiophene-6-carboxylic acid (9) (LG ⁻ = HS ⁻) ¹ H NMR spectrum of 2-[(7-Bromo-9-oxo-9H-thioxanthen-2-yl)-methyl-carbamoyl]-3-chl benzo[b]thiophene-6-carboxylic acid methyl ester (10) (LG ⁻ = Cl ⁻) ¹³ C NMR spectrum of 2-[(7-Bromo-9-oxo-9H-thioxanthen-2-yl)-methyl-carbamoyl]-3-chl benzo[b]thiophene-6-carboxylic acid methyl ester (10) (LG ⁻ = Cl ⁻) ¹³ C NMR spectrum of 2-[(7-Bromo-9-oxo-9H-thioxanthen-2-yl)-methyl-carbamoyl]-3-chl benzo[b]thiophene-6-carboxylic acid methyl ester (10) (LG ⁻ = Cl ⁻) ¹⁴ H NMR spectrum of 3-Chloro-2-chlorocarbonyl-benzo[b]thiophene-6-carboxylic acid methyl ester (12)	15 hene-6- 16 loro- 17 lloro- 18 ethyl 19
benzo[b]thiophene-o-carboxylic acid (9) (LG = HS) ¹³ C NMR 3-Mercapto-2-[methyl-(9-oxo-9H-thioxanthen-2-yl)-carbamoyl]-benzo[b]thiophene- carboxylic acid (9) (LG ⁻ = HS ⁻) ¹ H NMR spectrum of 2-[(7-Bromo-9-oxo-9H-thioxanthen-2-yl)-methyl-carbamoyl]-3-chl benzo[b]thiophene-6-carboxylic acid methyl ester (10) (LG ⁻ = Cl ⁻) ¹³ C NMR spectrum of 2-[(7-Bromo-9-oxo-9H-thioxanthen-2-yl)-methyl-carbamoyl]-3-chl benzo[b]thiophene-6-carboxylic acid methyl ester (10) (LG ⁻ = Cl ⁻) ¹⁴ H NMR spectrum of 2-[(7-Bromo-9-oxo-9H-thioxanthen-2-yl)-methyl-carbamoyl]-3-chl benzo[b]thiophene-6-carboxylic acid methyl ester (10) (LG ⁻ = Cl ⁻) ¹⁴ H NMR spectrum of 3-Chloro-2-chlorocarbonyl-benzo[b]thiophene-6-carboxylic acid methyl ester (12)	15 hene-6- 16 loro- 17 lloro- 18 ethyl 19 20
 ¹³C NMR 3-Mercapto-2-[methyl-(9-oxo-9H-thioxanthen-2-yl)-carbamoyl]-benzo[b]thiop⁷ carboxylic acid (9) (LG⁷ = HS⁷). ¹H NMR spectrum of 2-[(7-Bromo-9-oxo-9H-thioxanthen-2-yl)-methyl-carbamoyl]-3-chl ¹³C NMR spectrum of 2-[(7-Bromo-9-oxo-9H-thioxanthen-2-yl)-methyl-carbamoyl]-3-chl ¹⁴H NMR spectrum of 2-[(7-Bromo-9-oxo-9H-thioxanthen-2-yl)-methyl-carbamoyl]-3-chl ¹⁵C NMR spectrum of 2-[(7-Bromo-9-oxo-9H-thioxanthen-2-yl)-methyl-carbamoyl]-3-chl ¹⁶H NMR spectrum of 2-[(7-Bromo-9-oxo-9H-thioxanthen-2-yl)-methyl-carbamoyl]-3-chl ¹⁷H NMR spectrum of 2-[(7-Bromo-9-oxo-9H-thioxanthen-2-yl]-methyl-carbamoyl]-3-chl ¹⁸H NMR spectrum of 2-[(7-Bromo-9-oxo-9H-thioxanthen-2-yl]-methyl-carbamoyl]-3-chl ¹⁹H NMR spectrum of 2-[(7-Bromo-9-oxo-9H-thioxanthen-9-one (13). ¹¹H NMR spectrum of 2-Methylamino-thioxanthen-9-one (14). 	15 hene-6- 16 loro- 17 lloro- 18 ethyl 19 20 21

¹ H NMR spectrum of N-(7-Bromo-9-oxo-9H-thioxanthen-2-yl)-acetamide (23)	.23	
¹ H NMR spectrum of N-Methyl-N-(9-oxo-9H-thioxanthen-2-yl)-acetamide (24)	24	
¹ H NMR spectrum of N-(7-Bromo-9-oxo-9H-thioxanthen-2-yl)-N-methyl-acetamide (25)).25	
¹ H NMR spectrum of 6-methylcarboxylate-[1]benzothiopheno[2,3-c]benzo[a]anthracene	-4-	
methyl-4 <i>H</i> -7-thia-4-aza-3,12-dione (26)	26	
¹ H NMR COSY spectrum of 6-methylcarboxylate-[1]benzothiopheno[2,3-c]benzo[a]anth	nracene-	
4-methyl-4 <i>H</i> -7-thia-4-aza-3,12-dione (26)	27	
¹ H NMR spectrum of [1]benzothiopheno-6-carboxylicacid[2,3-c]benzo[a]anthracene-10-	bromo-	
4-methyl-4 <i>H</i> -7-thia-4-aza-3,12-dione (27)	28	
¹ H NMR COSY spectrum of [1]benzothiopheno-6-carboxylicacid[2,3-c]benzo[a]anthrace	ene-10-	
bromo-4-methyl-4 <i>H</i> -7-thia-4-aza-3,12-dione (27)	29	
¹ H NMR COSY and NOESY spectrum of [1]benzothiopheno-6-carboxylicacid[2,3-		
c]benzo[a]anthracene-10-bromo-4-methyl-4 <i>H</i> -7-thia-4-aza-3,12-dione (27)	30	
¹ H NMR spectrum of mixture of Photoproducts (30 and 31) by photolysis of 3-Chloro-		
benzo[b]thiophene-2-carboxylic acid methyl-(9-oxo-9H-thioxanthen-2-yl)-amide (7) (LC	$b^{-} = Cl^{-}$	
	31	
¹ H NMR spectrum of [1]benzothieno[2,3-c]benzo[a]anthracene-4-methyl-4 <i>H</i> -7-thia-4-az	a-3,12-	
dione (30)	32	
¹³ C NMR spectrum of [1]benzothieno[2,3-c]benzo[a]anthracene-4-methyl-4H-7-thia-4-az	za-3,12-	
dione (30)	33	
Crystal Structure of [1]benzothieno[2,3-c]benzo[a]anthracene-4-methyl-4H-7-thia-4-aza-	3,12-	
dione (30)	34	
¹ H NMR spectrum of [1]benzothieno[2,3-c]naphthacene-1-methyl-1 <i>H</i> -6-thia-1-aza-2,11-dione		

(31)	35
¹ H NMR spectrum comparison between Photoproduct 27 and 30	36
¹ H NMR spectrum of 6-methylcarboxylate-[1]benzothiopheno[2,3-c]benzo[a]anthracene	-10-
bromo-4-methyl-4 <i>H</i> -7-thia-4-aza-3,12-dione (32)	37
Stern-Volmer plot Φ^0/Φ vs [Q] of Quenching of ester 8 by piperylene as quencher Q	38
Computed Structures in Figure 3	39
Computed Structures in Figure 4	43



Figure

1. ¹H NMR spectrum of 3-Chloro-benzo[b]thiophene-2-carboxylic acid methyl-(9-oxo-9H-thioxanthen-2-yl)-amide¹ (7) (LG⁻ = Cl⁻) in CDCl₃



2. ¹³C NMR spectrum of 3-Chloro-benzo[b]thiophene-2-carboxylic acid methyl-(9-oxo-9H-thioxanthen-2-yl)-amide¹ (7) (LG⁻ = Cl⁻) DMSO-d₆

Figure



Figure 3, ¹H NMR spectrum of 3-Chloro-2-[methyl-(9-oxo-9H-thioxanthen-2-yl)-carbamoyl]-benzo[b]thiophene-6-carboxylic acid methyl ester (8) (LG⁻ = Cl⁻) in CDCl₃



Figure 4, ¹³C NMR spectrum of 3-Chloro-2-[methyl-(9-oxo-9H-thioxanthen-2-yl)-carbamoyl]-benzo[b]thiophene-6-carboxylic acid methyl ester (8) (LG⁻ = Cl⁻) in CDCl₃





Spin Works 3:







DMSO

 H_2O





Figure 8, ¹³C NMR spectrum of 2-[Methyl-(9-oxo-9H-thioxanthen-2-yl)-carbamoyl]-3-phenylsulfanyl-benzo[b]thiophene-6-carboxylic acid (9) (LG⁻ = PhS⁻) in DMSO-d₆





SpinWorks 3: 13C OBSERVE







 H_2O

Figure 11, ¹H NMR spectrum of 3-Mercapto-2-[methyl-(9-oxo-9H-thioxanthen-2-yl)-carbamoyl]-benzo[b]thiophene-6-carboxylic acid (**9**) (LG⁻ = HS⁻) in DMSO-d₆



Figure 12, ¹3C NMR spectrum of 3-Mercapto-2-[methyl-(9-oxo-9H-thioxanthen-2-yl)-carbamoyl]-benzo[b]thiophene-6-carboxylic acid (9) (LG⁻ = HS⁻) in DMSO-d₆



Figure 13, ¹H NMR spectrum of 2-[(7-Bromo-9-oxo-9H-thioxanthen-2-yl)-methyl-carbamoyl]-3-chloro-benzo[b]thiophene-6-carboxylic acid methyl ester (10) (LG⁻ = Cl⁻) in CDCl₃



Figure 14, ¹³C NMR spectrum of 2-[(7-Bromo-9-oxo-9H-thioxanthen-2-yl)-methyl-carbamoyl]-3-chloro-benzo[b]thiophene-6-carboxylic acid methyl ester (10) $(LG^{-} = CI^{-})$ in CDCl₃



Figure 15, ¹H NMR spectrum of 3-Chloro-2-chlorocarbonyl-benzo[b]thiophene-6-carboxylic acid methyl ester (12) in DMSO-d₆



Figure 16, ¹H NMR spectrum of 2-Methylamino-thioxanthen-9-one (13) in CDCl₃



Figure 17, ¹H NMR spectrum of 2-Bromo-7-methylamino-thioxanthen-9-one (14) in CDCl₃



Figure 18, ¹H NMR spectrum of 2-Amino-7-bromo-thioxanthen-9-one (21) in CDCl₃



Figure 19, ¹H NMR spectrum of N-(7-Bromo-9-oxo-9H-thioxanthen-2-yl)-acetamide (23) in DMSO-d₆



Figure 20, ¹H NMR spectrum of N-Methyl-N-(9-oxo-9H-thioxanthen-2-yl)-acetamide (24) in CDCl₃



Figure 21, ¹H NMR spectrum of N-(7-Bromo-9-oxo-9H-thioxanthen-2-yl)-N-methyl-acetamide (25) in CDCl₃

SpinWorks 3: Std proton







Figure 23, ¹H COSY NMR spectrum of 6-methylcarboxylate-[1]benzothiopheno[2,3-c]benzo[a]anthracene-4-methyl-4*H*-7-thia-4-aza-3,12-dione (**26**).

Spin Works 3: Std proton











Figure 26, ¹H COSY and NOESY NMR spectrum of [1]benzothiopheno-6-carboxylicacid[2,3c]benzo[a]anthracene-10-bromo-4-methyl-4*H*-7-thia-4-aza-3,12-dione (**27**) in D₂O



thioxanthen-2-yl)-amide¹ (7) (LG⁻ = Cl⁻) in DMSO-d₆



Figure 28, ¹H NMR spectrum of [1]benzothieno[2,3-c]benzo[a]anthracene-4-methyl-4H-7-thia-4-aza-3,12-dione (30) in DMSO-d₆.



Figure 29, ¹³C NMR spectrum of [1]benzothieno[2,3-c]benzo[a]anthracene-4-methyl-4H-7-thia-4-aza-3,12-dione (30) in DMSO-d₆.



Figure 30, Crystal Structure of [1]benzothieno[2,3-c]benzo[a]anthracene-4-methyl-4*H*-7-thia-4-aza-3,12-dione (30).



Figure 31, ¹H NMR spectrum of [1]benzothieno[2,3-c]naphthacene-1-methyl-1*H*-6-thia-1-aza-2,11-dione (31) in DMSO-d₆.

Spin Works 3:



Figure 32, ¹H NMR spectrum comparison between Photoproduct 27 and 30 in DMSO-d₆.



Figure 33, ¹H NMR spectrum of 6-methylcarboxylate-[1]benzothiopheno[2,3-c]benzo[a]anthracene-10-bromo-4-methyl-4*H*-7-thia-4-aza-3,12-dione (32) in DMSO-d₆.



Figure 34, Stern-Volmer plot Φ^0/Φ vs [Q] of Quenching of ester 8 (LG⁻ = Cl⁻) by piperylene as quencher Q

Computed Structures in Figure 3.



³Thiox



³Bzt



³TS



³I



 \mathbf{I}_{DR}





P-L



Thiox

Computed Structures in Figure 4.



³Thiox



³Bzt



³TS



³I



Thiox



P-U