Supporting Information

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

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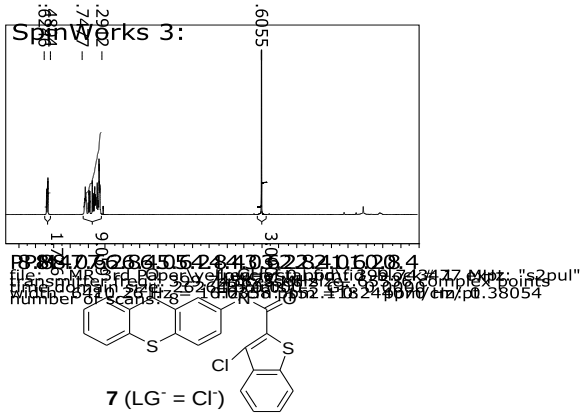
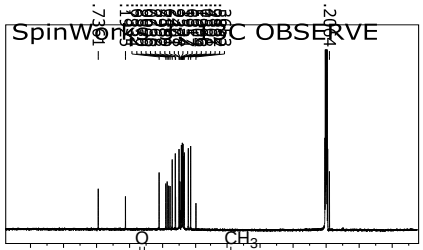
Table of Contents

List of NMR Spectra



7 ($LG^- = Cl^-$)

Figure 1. ^1H NMR spectrum of 3-Chloro-benzo[b]thiophene-2-carboxylic acid methyl-(9-oxo-9H-thioxanthen-2-yl)-amide[1] (**7**) ($LG^- = Cl^-$) in $CDCl_3$



7 ($LG^- = Cl^-$)

Figure 2. ^{13}C NMR spectrum of 3-Chloro-benzo[b]thiophene-2-carboxylic acid methyl-(9-oxo-9H-thioxanthen-2-yl)-amide[1] (**7**) ($LG^- = Cl^-$) DMSO-d_6

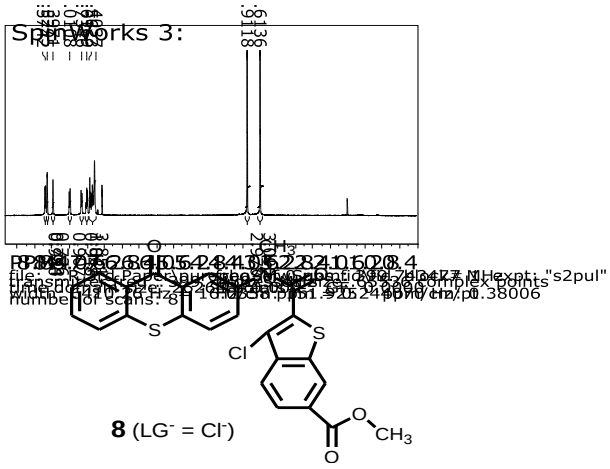


Figure 3, ^{1}H NMR spectrum of 3-Chloro-2-[methyl-(9-oxo-9H-thioxanthen-2-yl)-carbamoyl]-benzo[b]thiophene-6-carboxylic acid methyl ester (**8**) ($LG^{-} = Cl^{-}$) in $CDCl_3$

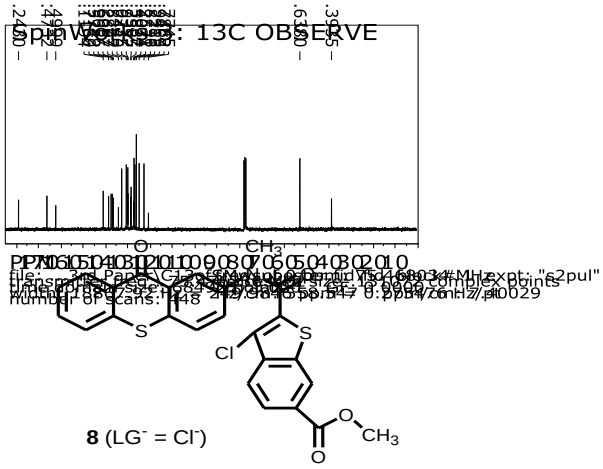


Figure 4, ^{13}C NMR spectrum of 3-Chloro-2-[methyl-(9-oxo-9H-thioxanthen-2-yl)-carbamoyl]-benzo[b]thiophene-6-carboxylic acid methyl ester (**8**) ($LG^- = Cl^-$) in $CDCl_3$

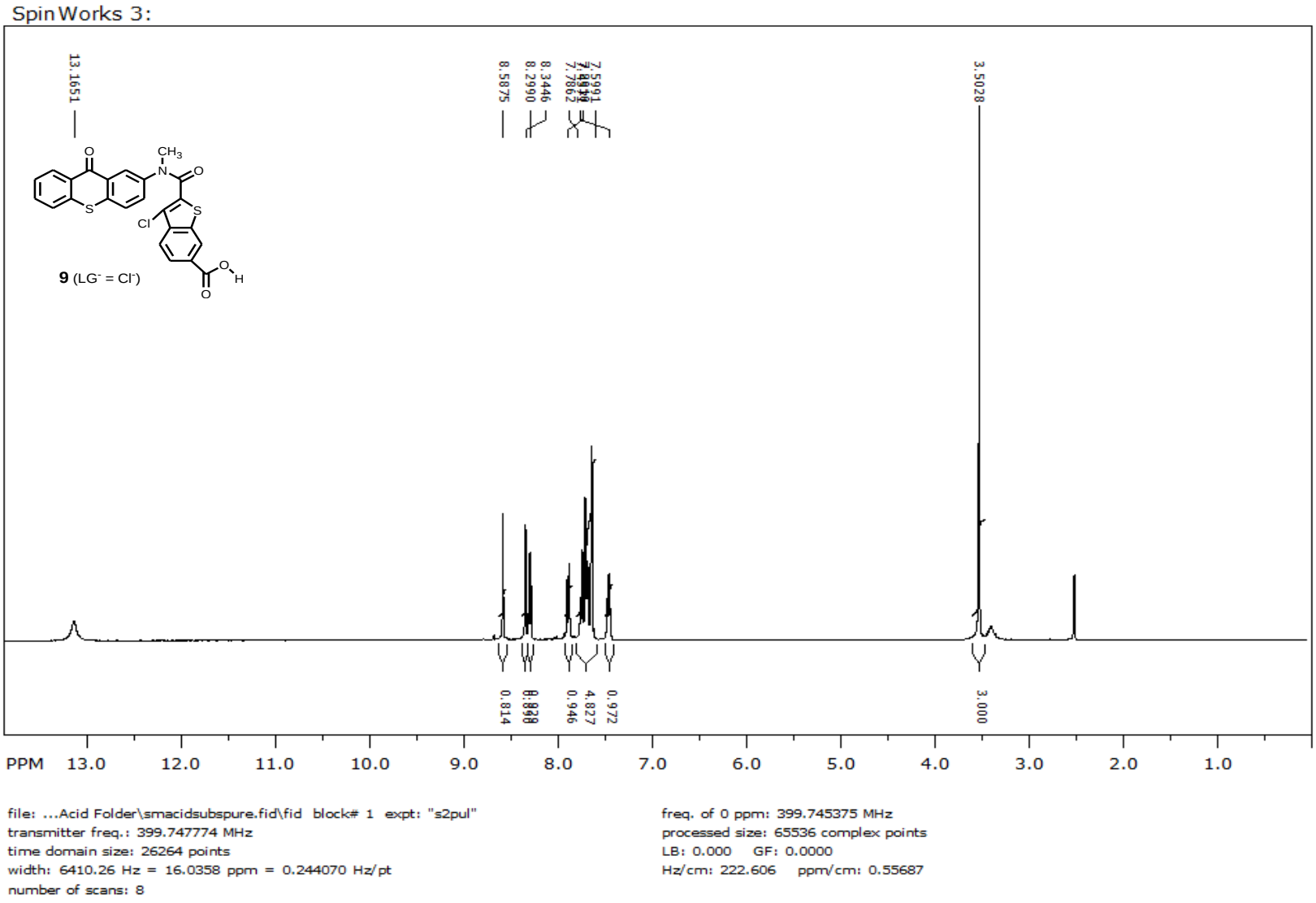


Figure 5, ^{1}H NMR spectrum of 3-Chloro-2-[methyl-(9-oxo-9H-thioxanthen-2-yl)-carbamoyl]-benzo[b]thiophene-6-carboxylic acid (**9**) ($LG^{-} = Cl^{-}$) in DMSO-d_6

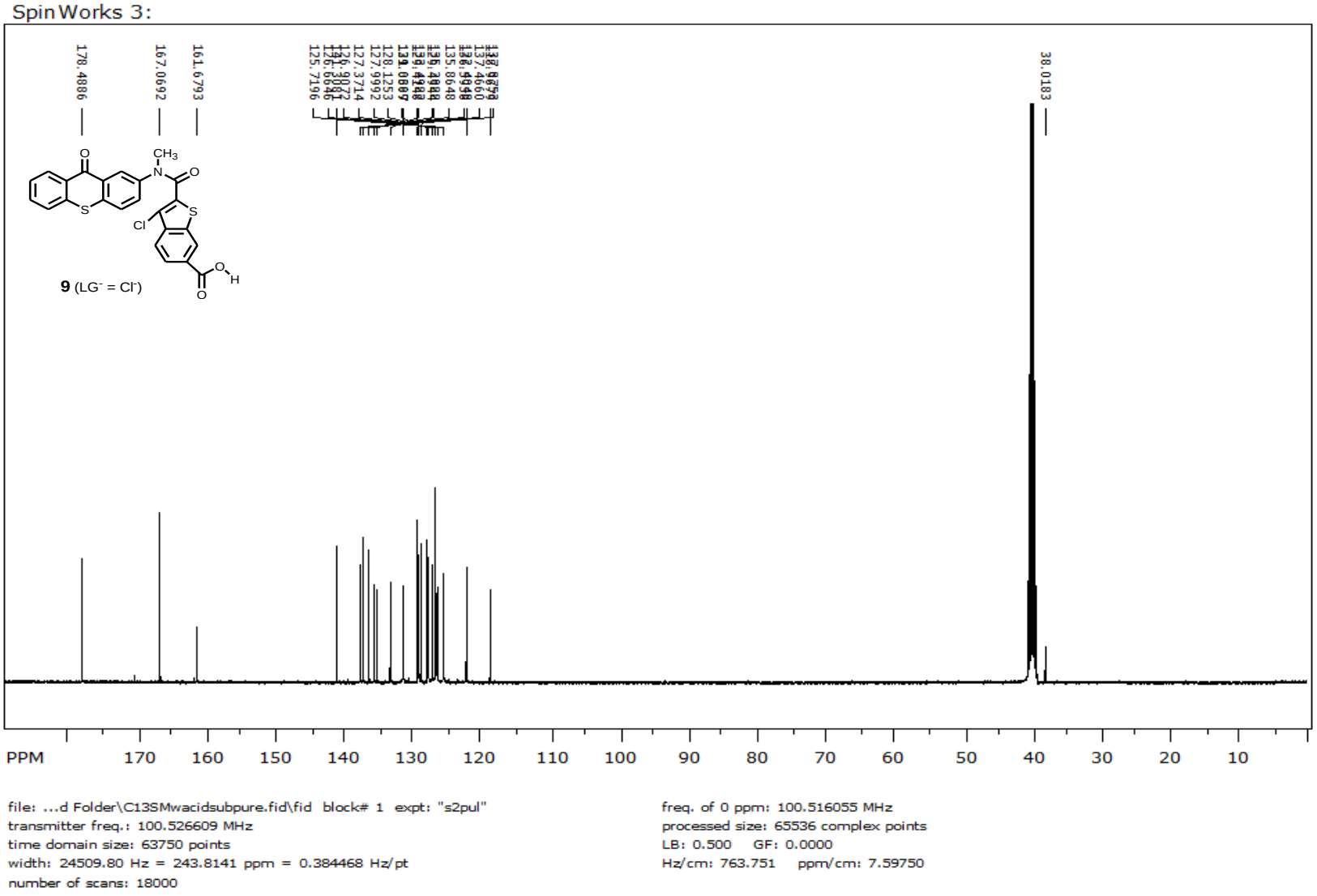
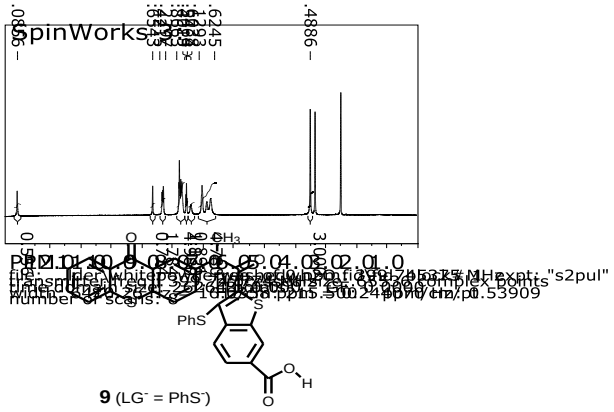


Figure 6, ^{13}C NMR spectrum of 3-Chloro-2-[methyl-(9-oxo-9H-thioxanthen-2-yl)-carbamoyl]-benzo[b]thiophene-6-carboxylic acid (**9**) ($LG^- = Cl^-$) in DMSO-d_6



DMSO

H_2O

Figure 7, ^{1}H 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-d_6

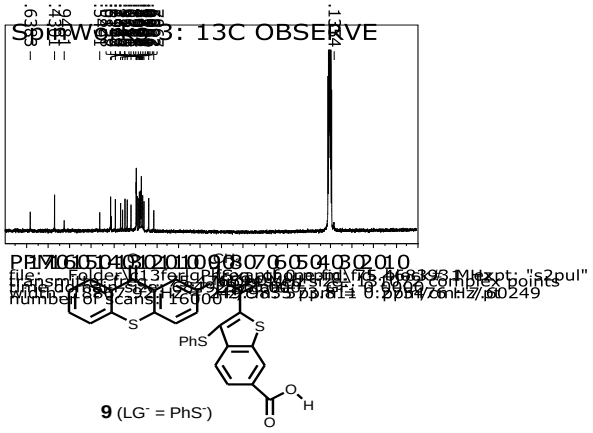


Figure 8, ^{13}C NMR spectrum of 2-[Methyl-(9-oxo-9H-thioxanthen-2-yl)-carbamoyl]-3-phenylsulfanyl-benzo[b]thiophene-6-carboxylic acid (**9**) ($LG^- = PhS^-$) in DMSO-d_6

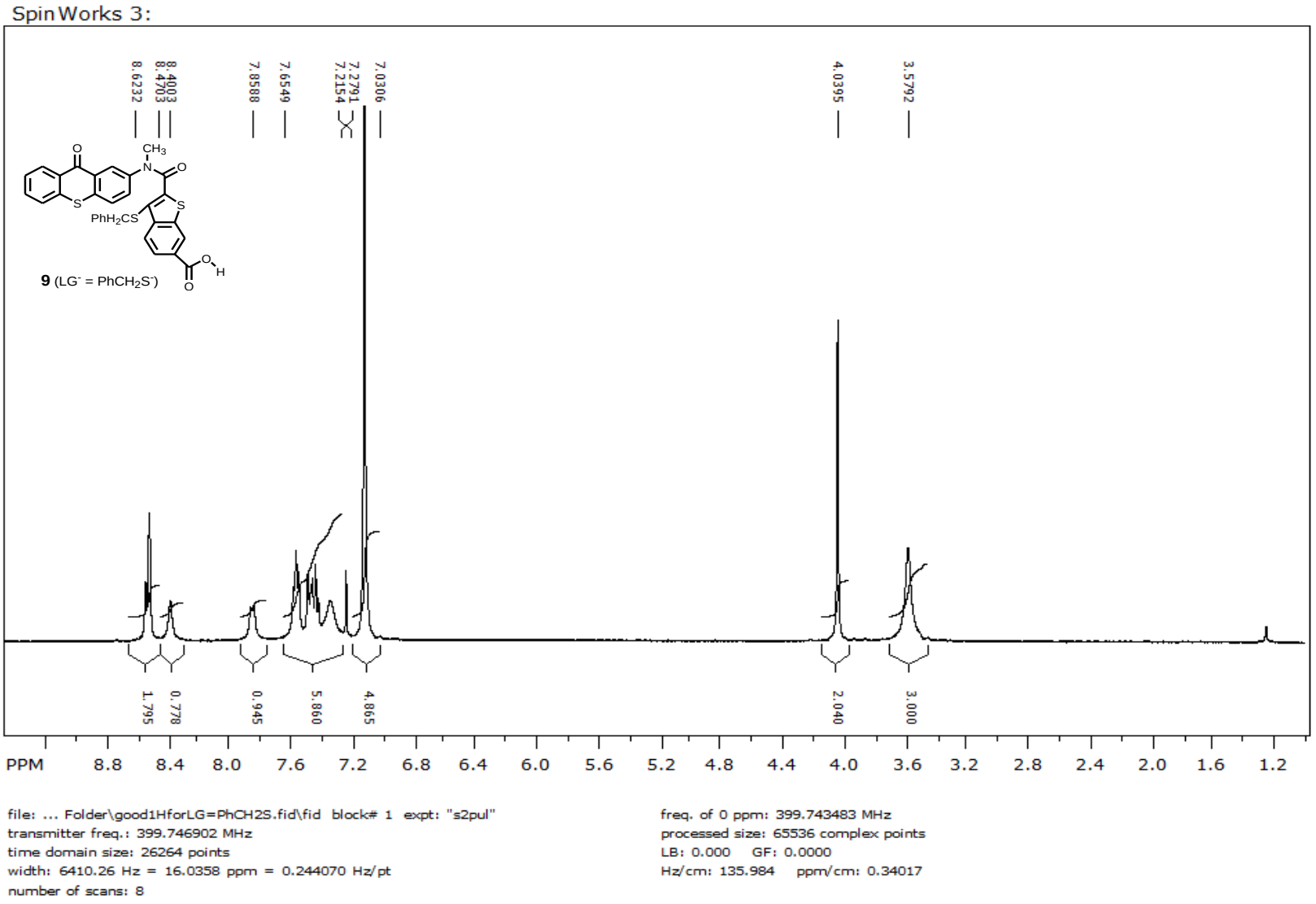


Figure 9, ^{1}H NMR spectrum of 3-Benzylsulfanyl-2-[methyl-(9-oxo-9H-thioxanthen-2-yl)-carbamoyl]-benzo[b]thiophene-6-carboxylic acid (9) (LG^{-} = $PhCH_2S^{-}$) in DMSO-d_6

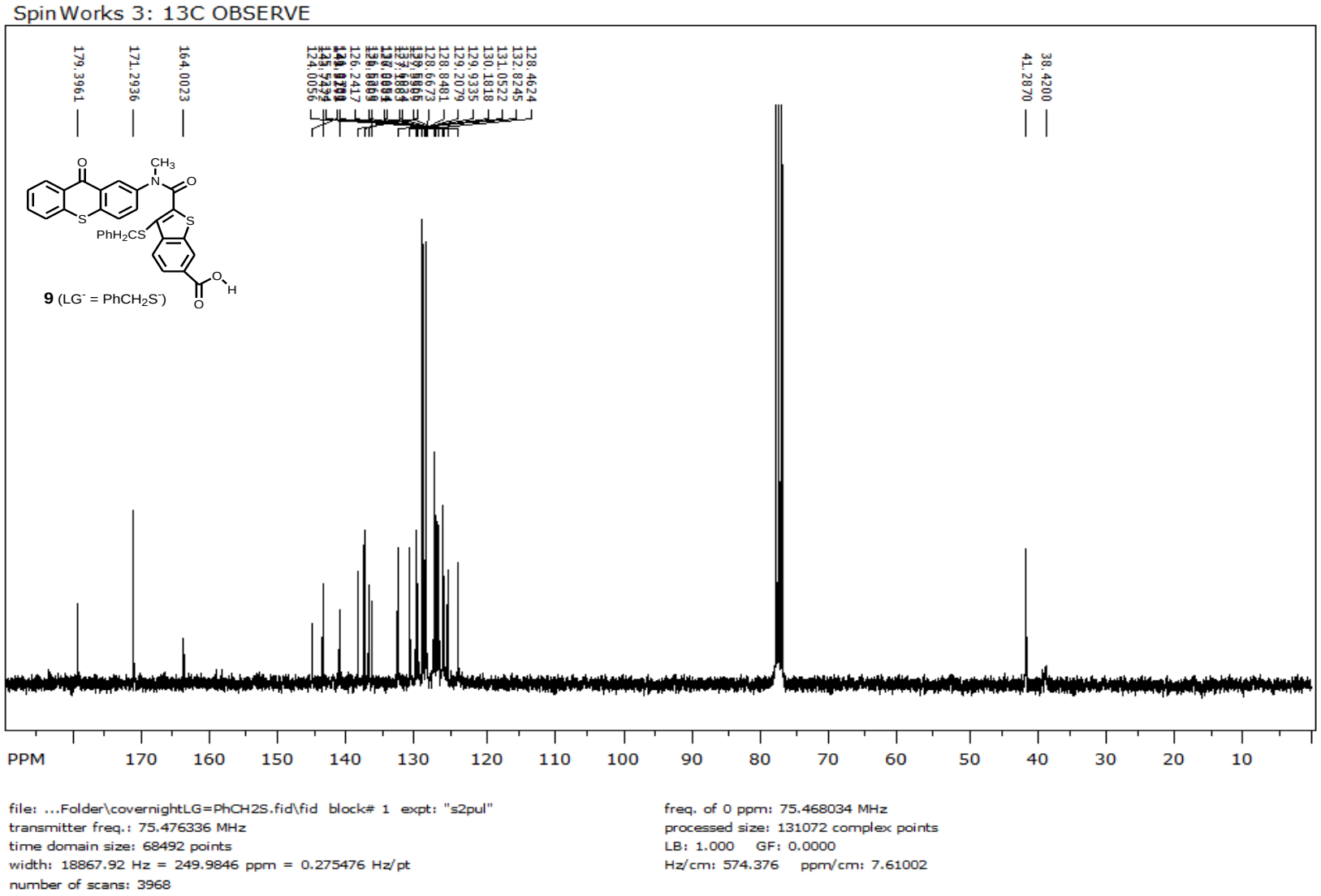


Figure 10, ^{13}C NMR spectrum of 3-Benzylsulfanyl-2-[methyl-(9-oxo-9H-thioxanthen-2-yl)-carbamoyl]-benzo[b]thiophene-6-carboxylic acid (**9**) (LG^- = $PhCH_2S^-$) in DMSO-d_6

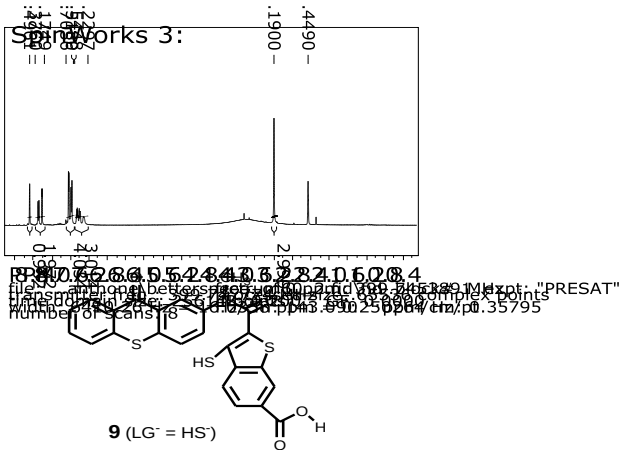


Figure 11, ^{1}H NMR spectrum of 3-Mercapto-2-[methyl-(9-oxo-9H-thioxanthen-2-yl)-carbamoyl]-benzo[b]thiophene-6-carboxylic acid (**9**) ($LG^{-} = HS^{-}$) in DMSO-d_6

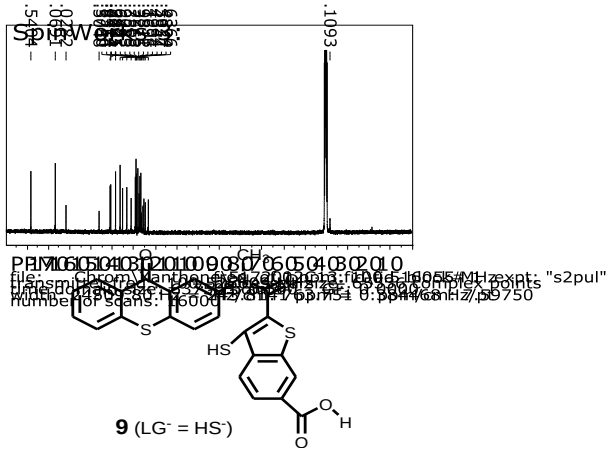


Figure 12, ^{1}3C NMR spectrum of 3-Mercapto-2-[methyl-(9-oxo-9H-thioxanthen-2-yl)-carbamoyl]-benzo[b]thiophene-6-carboxylic acid (**9**) ($LG^{-} = HS^{-}$) in DMSO-d_6

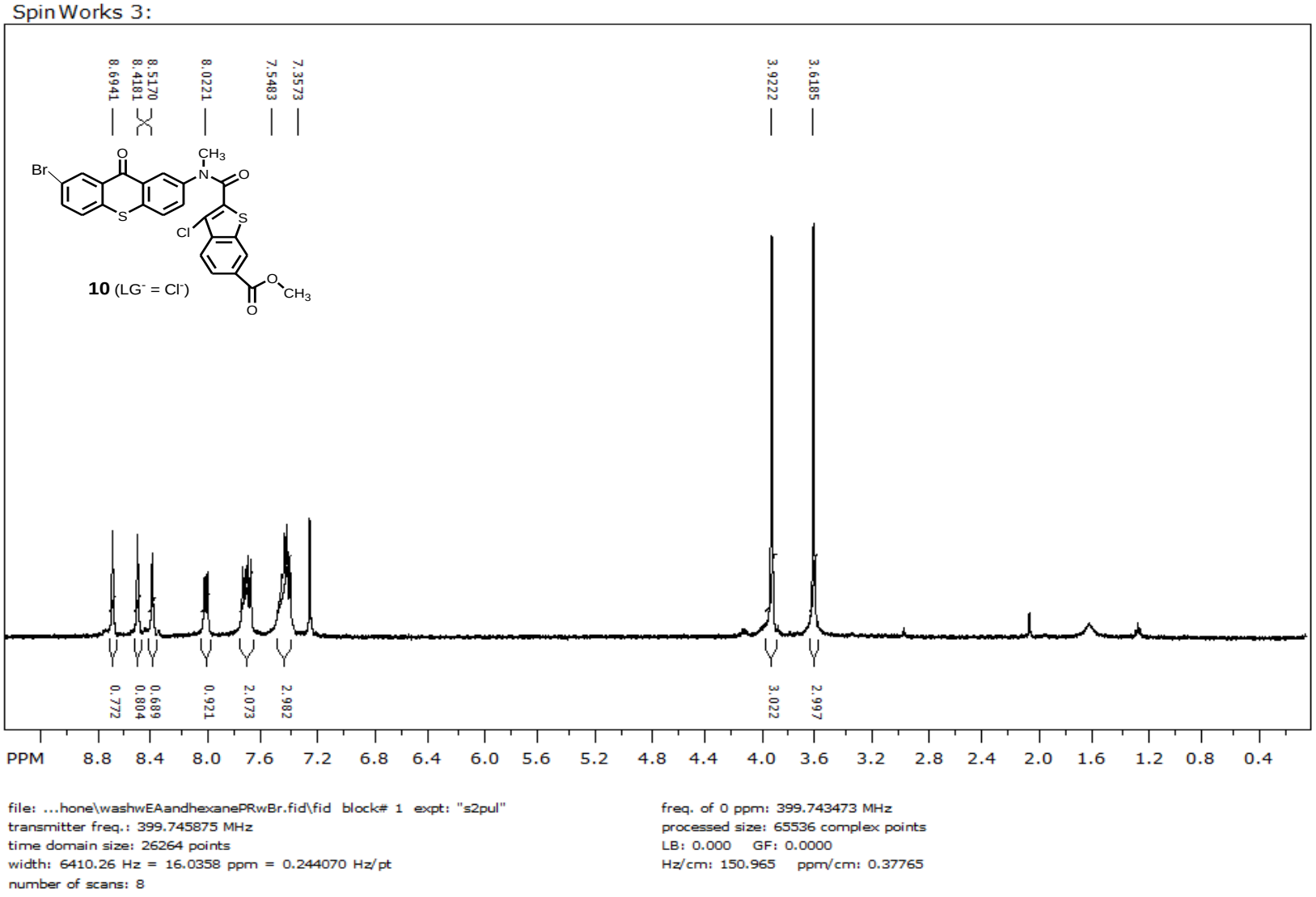
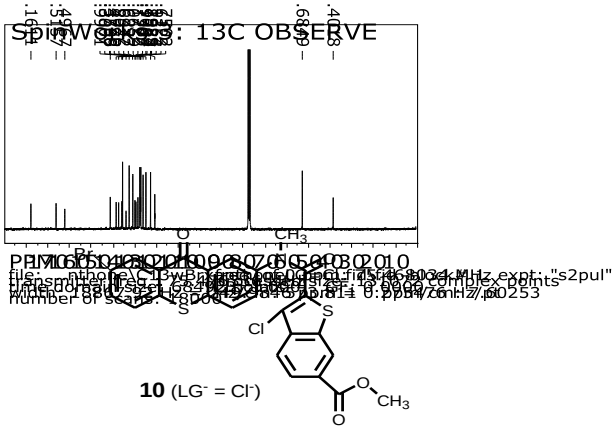


Figure 13, ^{1}H NMR spectrum of 2-[(7-Bromo-9-oxo-9H-thioxanthen-2-yl)-methyl-carbamoyl]-3-chloro-benzo[b]thiophene-6-carboxylic acid methyl ester (**10**) ($LG^{-} = Cl^{-}$) in $CDCl_3$



10 ($LG^- = Cl^-$)

Figure 14, ^{13}C 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 $CDCl_3$

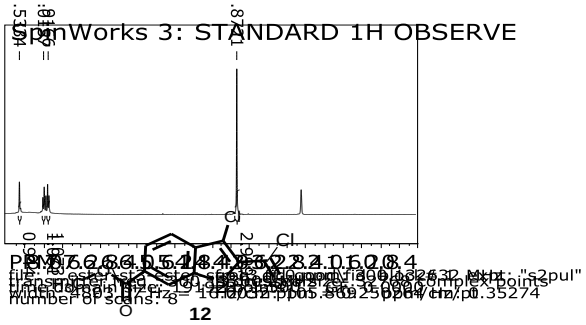


Figure 15, ^{1}H NMR spectrum of 3-Chloro-2-chlorocarbonyl-benzo[b]thiophene-6-carboxylic acid methyl ester (**12**) in DMSO-d_6

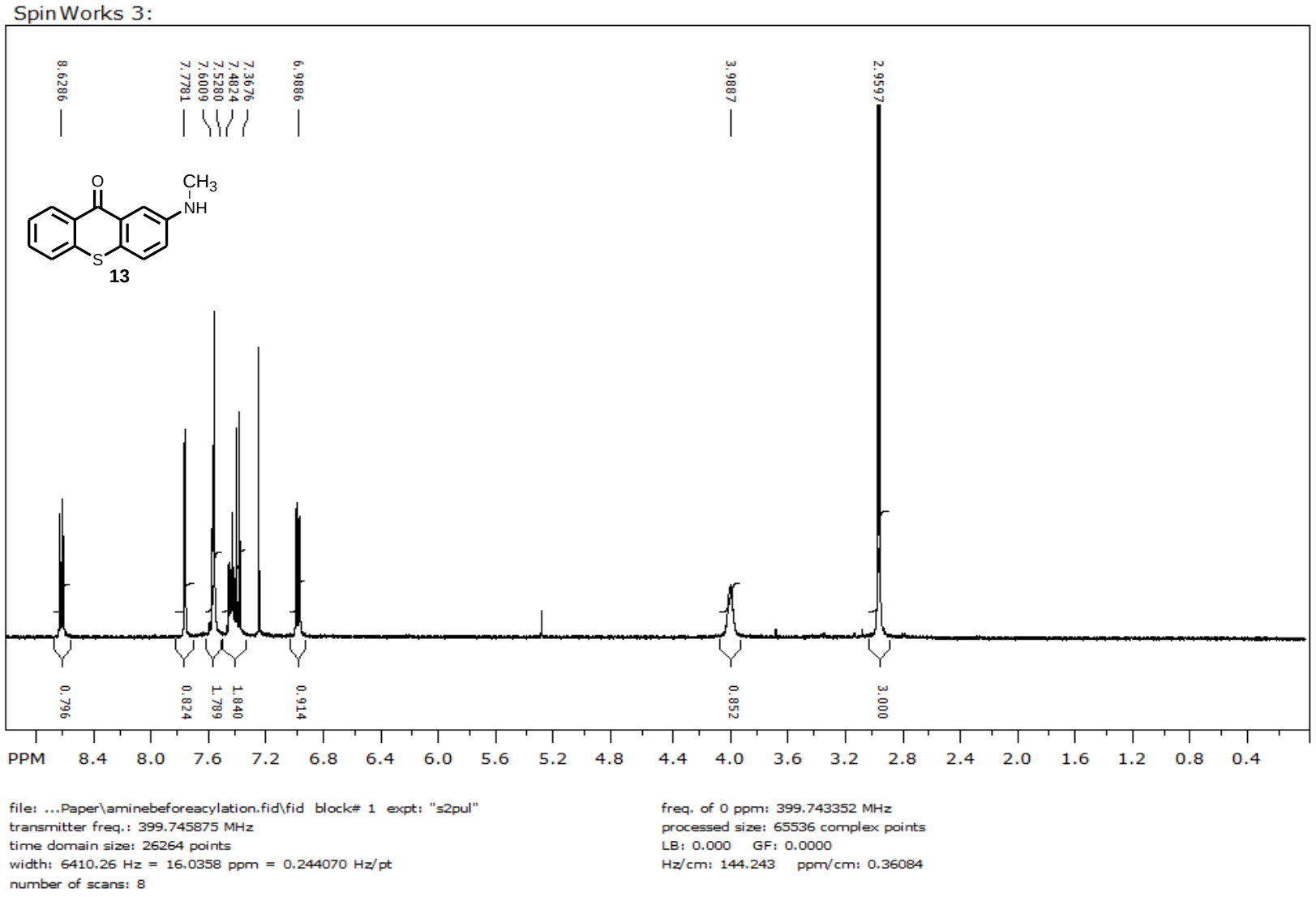


Figure 16, ^{1}H NMR spectrum of 2-Methylamino-thioxanthen-9-one (**13**) in $CDCl_3$

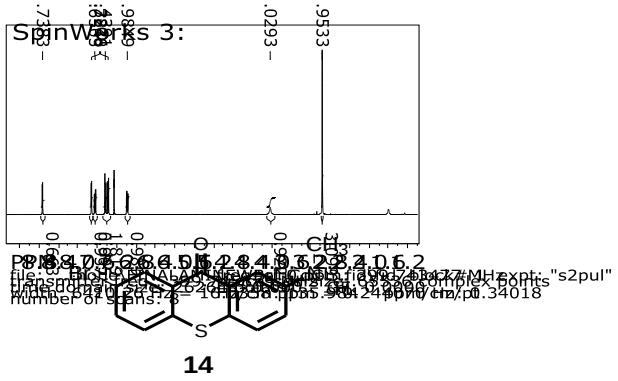
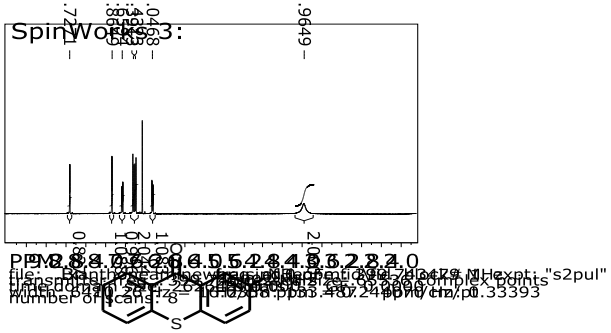
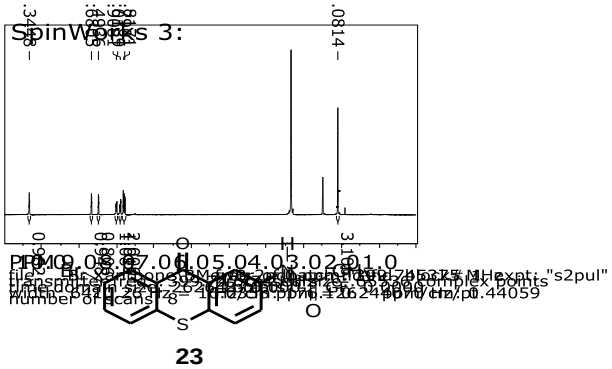


Figure 17, ^{1}H NMR spectrum of 2-Bromo-7-methylamino-thioxanthen-9-one (**14**) in $CDCl_3$



21

Figure 18, ^{1}H NMR spectrum of 2-Amino-7-bromo-thioxanthen-9-one (**21**) in $CDCl_3$



23

H_2O

DMSO

Figure 19, ^{1}H NMR spectrum of N-(7-Bromo-9-oxo-9H-thioxanthen-2-yl)-acetamide (**23**) in DMSO-d_6

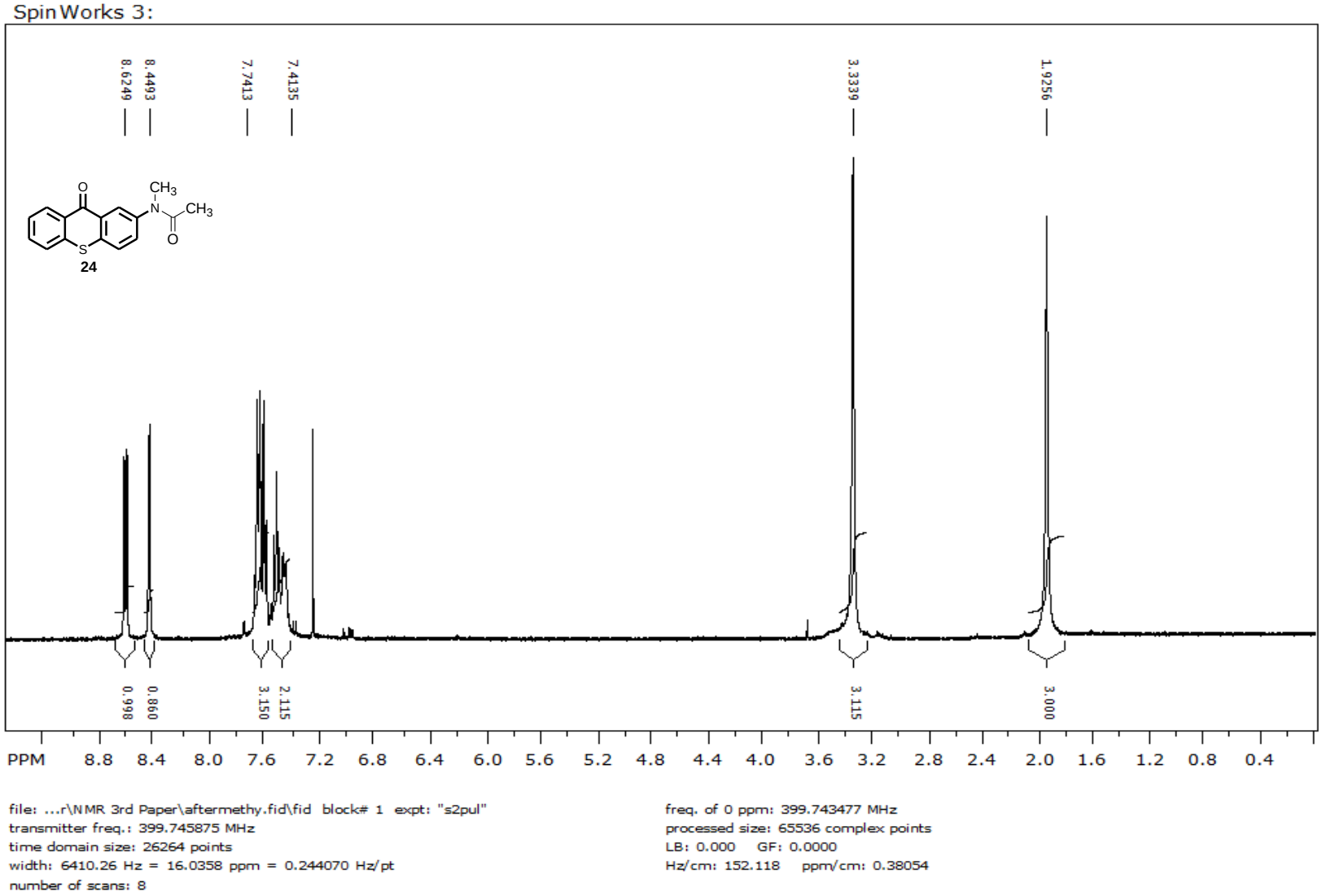


Figure 20, ^{1}H NMR spectrum of N-Methyl-N-(9-oxo-9H-thioxanthen-2-yl)-acetamide (**24**) in $CDCl_3$

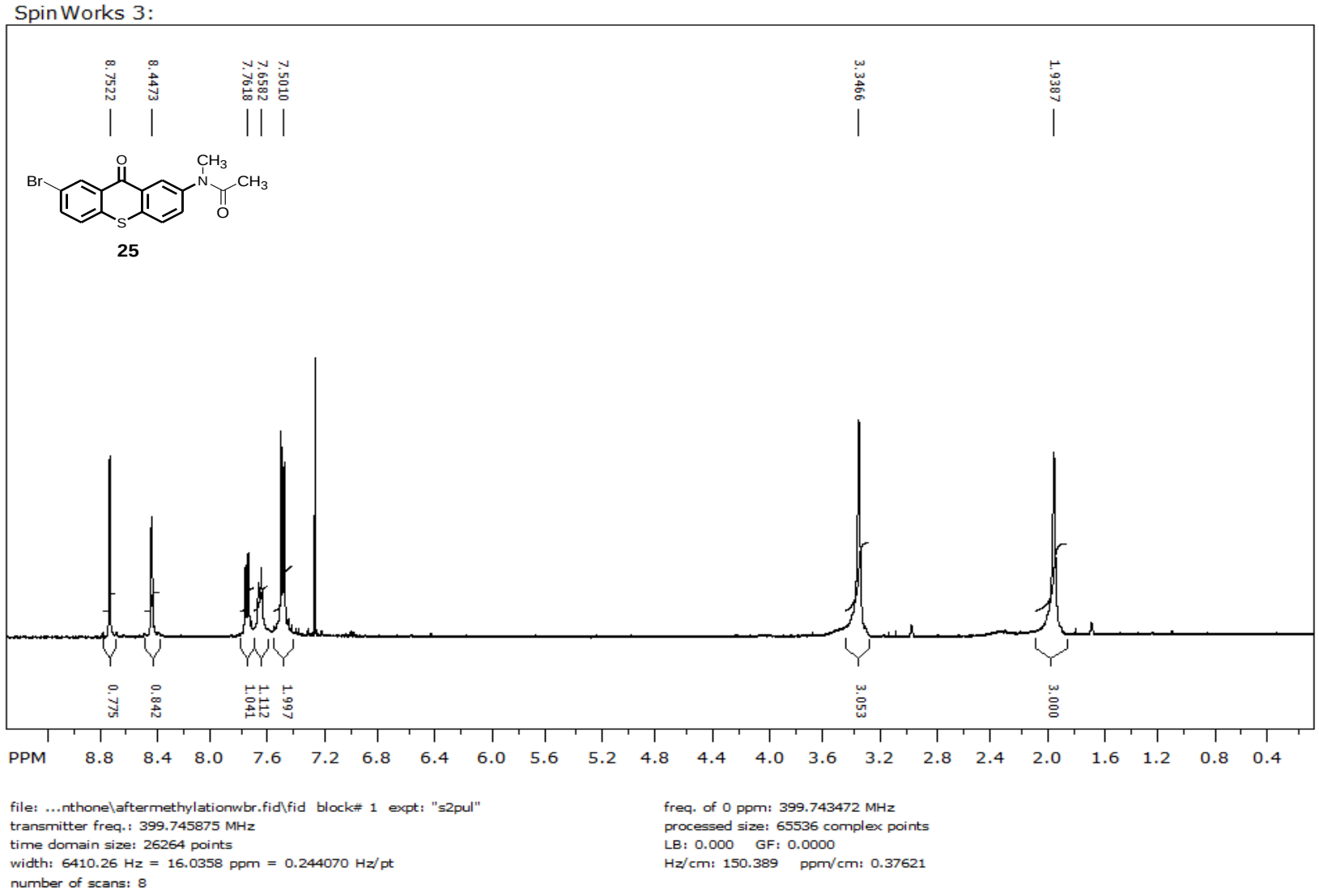


Figure 21, ^{1}H NMR spectrum of N-(7-Bromo-9-oxo-9H-thioxanthen-2-yl)-N-methyl-acetamide (**25**) in $CDCl_3$

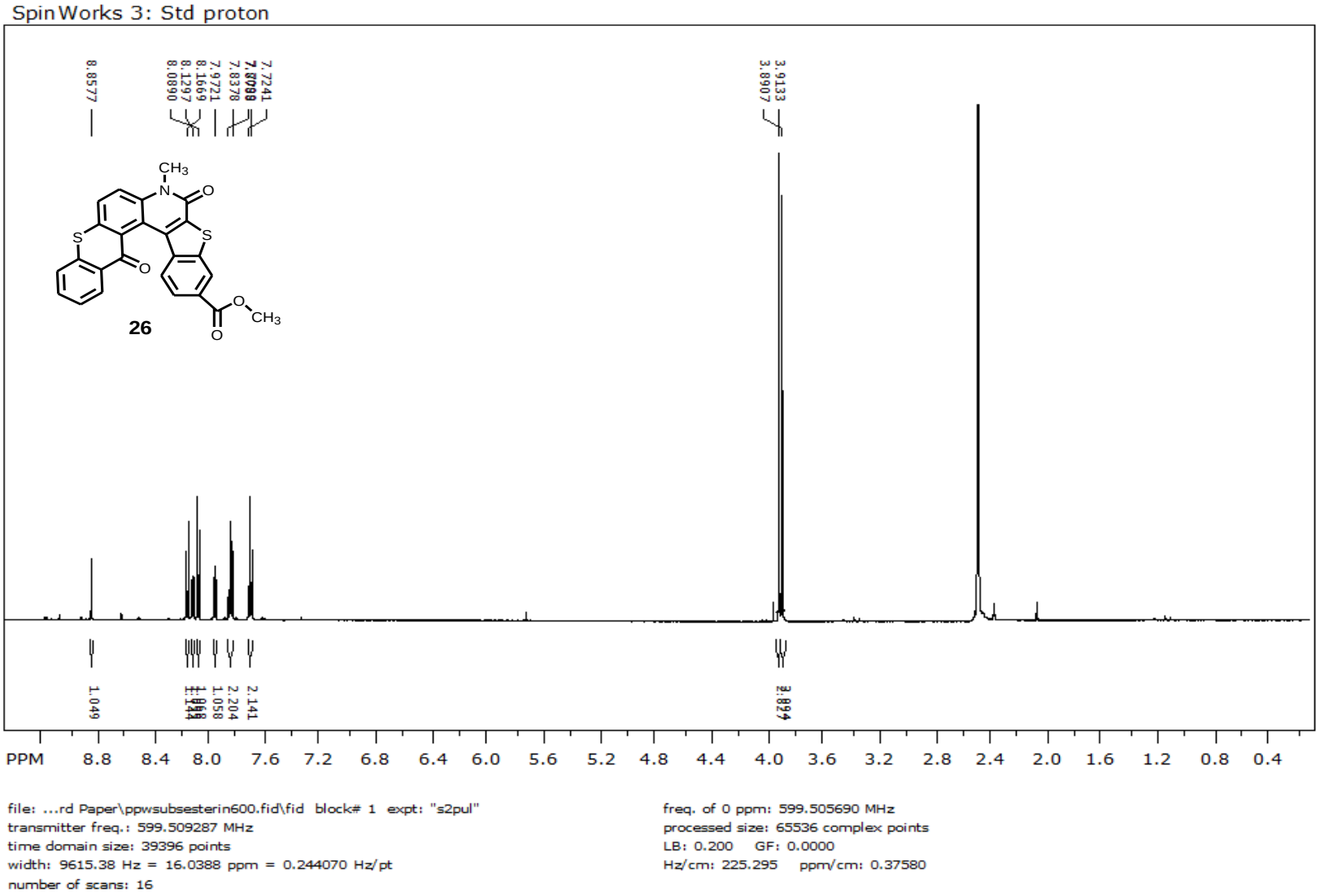


Figure 22, ^{1}H NMR spectrum of 6-methylcarboxylate-[1]benzothiopheno[2,3-c]benzo[a]anthracene-4-methyl-4*H*-7-thia-4-aza-3,12-dione **(26)** in DMSO-d_6

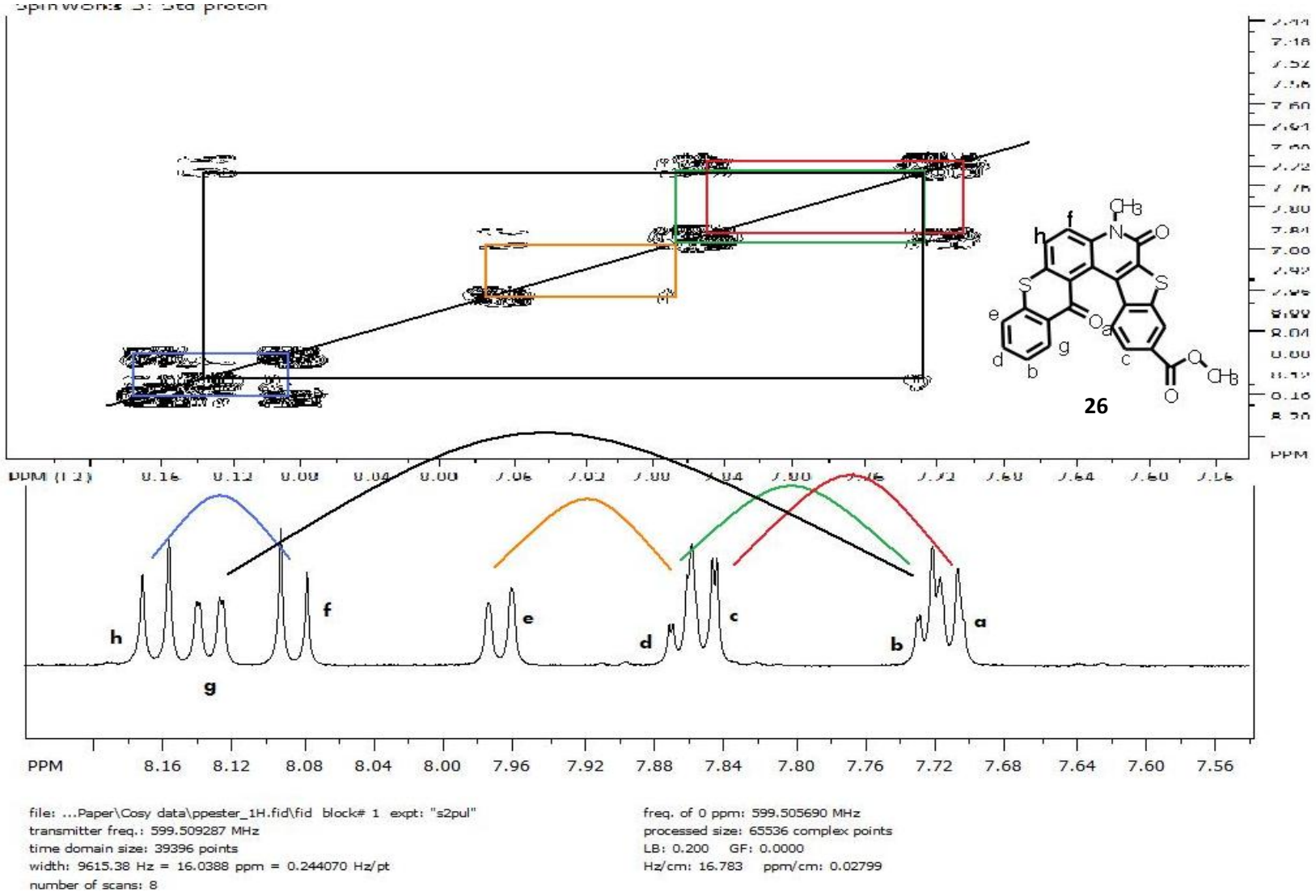


Figure 23, ^{1}H COSY NMR spectrum of 6-methylcarboxylate-[1]benzothiopheno[2,3-c]benzo[a]anthracene-4-methyl-4*H*-7-thia-4-aza-3,12-dione (**26**).

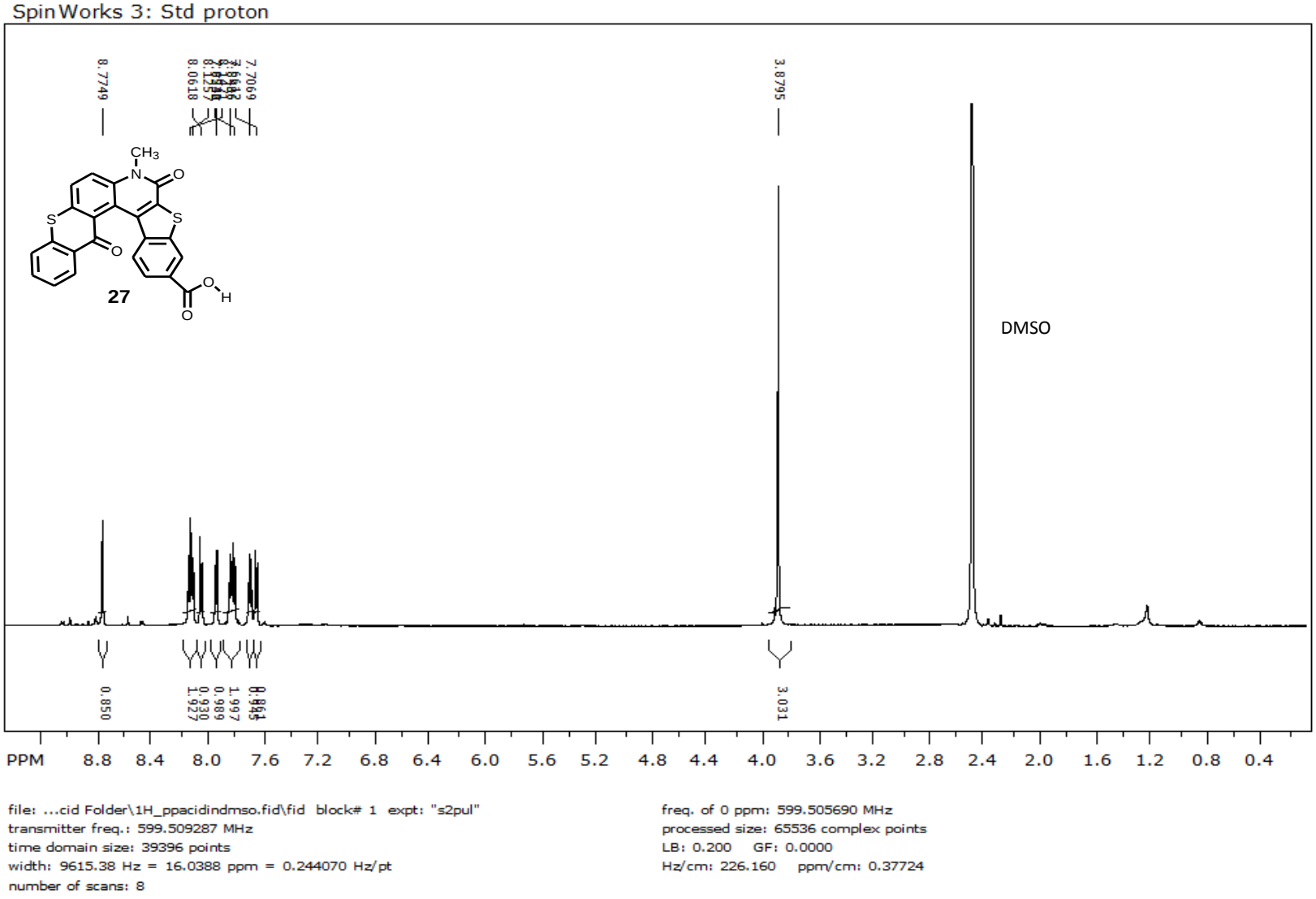


Figure 24, ^{1}H NMR spectrum of [1]benzothiopheno-6-carboxylicacid[2,3-c]benzo[a]anthracene-10-bromo-4-methyl-4*H*-7-thia-4-aza-3,12-dione (**27**) in DMSO-d_6.

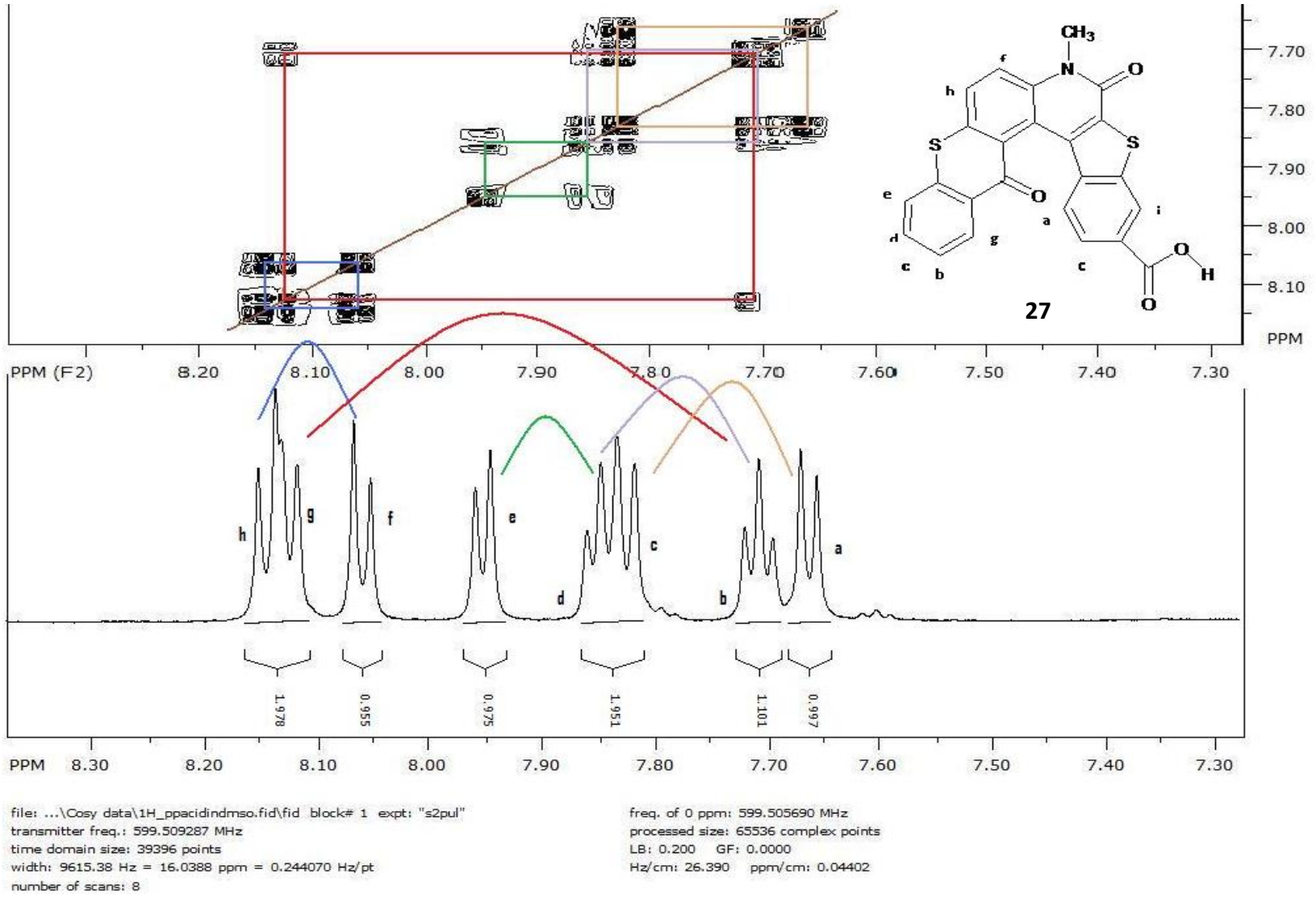


Figure 25, ^{1}H COSY NMR spectrum of [1]benzothiopheno-6-carboxylicacid[2,3-c]benzo[a]anthracene-10-bromo-4-methyl-4*H*-7-thia-4-aza-3,12-dione (**27**) in DMSO-d_6.

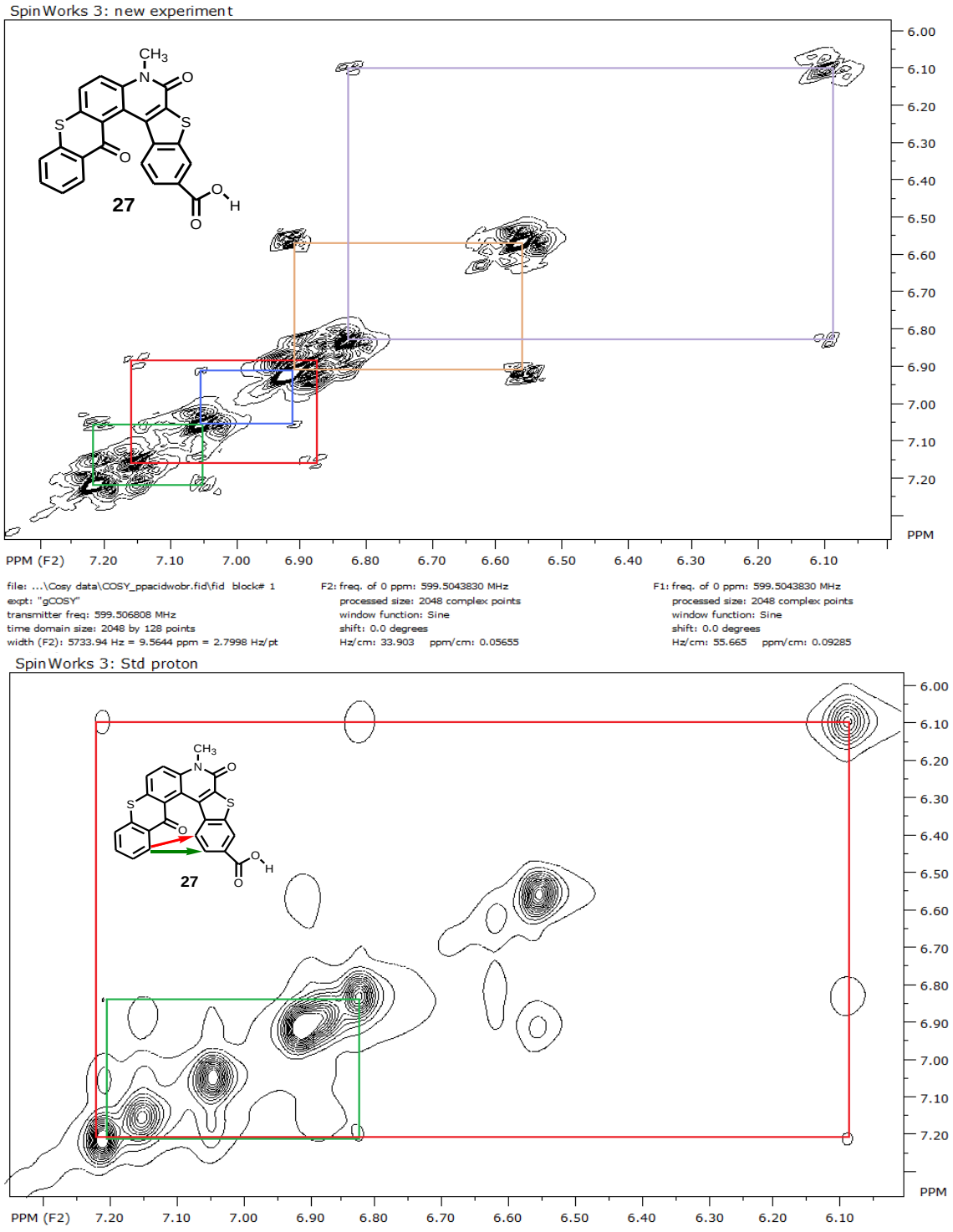


Figure 26, ^{1}H COSY and NOESY NMR spectrum of [1]benzothiopheno-6-carboxylicacid[2,3-c]benzo[a]anthracene-10-bromo-4-methyl-4*H*-7-thia-4-aza-3,12-dione (**27**) in D_2O

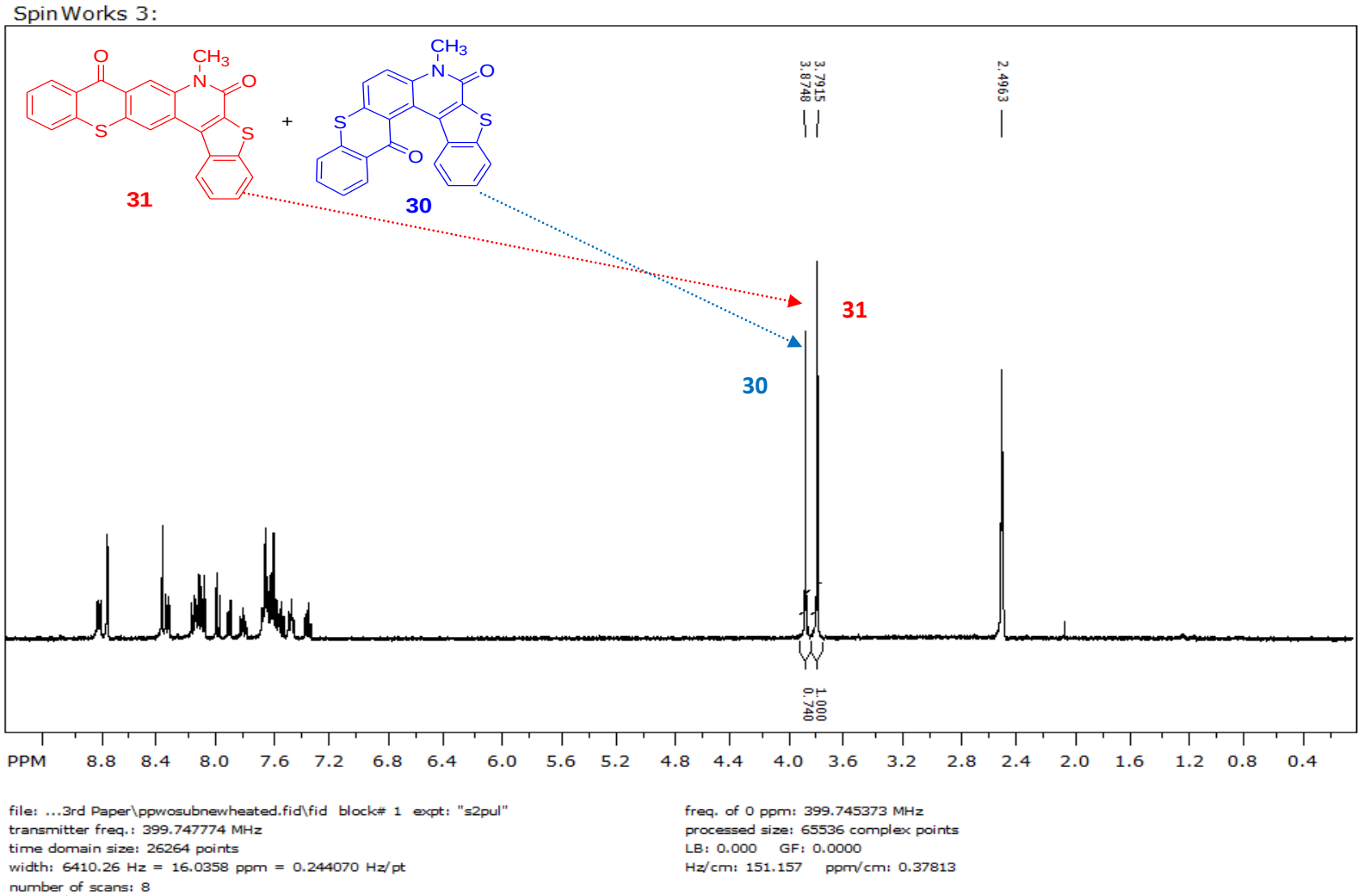


Figure 27, ^{1}H NMR spectrum of mixture of Photoproducts (**30** and **31**) by photolysis of 3-Chloro-benzo[b]thiophene-2-carboxylic acid methyl-(9-oxo-9H-thioxanthen-2-yl)-amide[1] (**7**) (LG^{-} = Cl^{-}) in DMSO-d_6

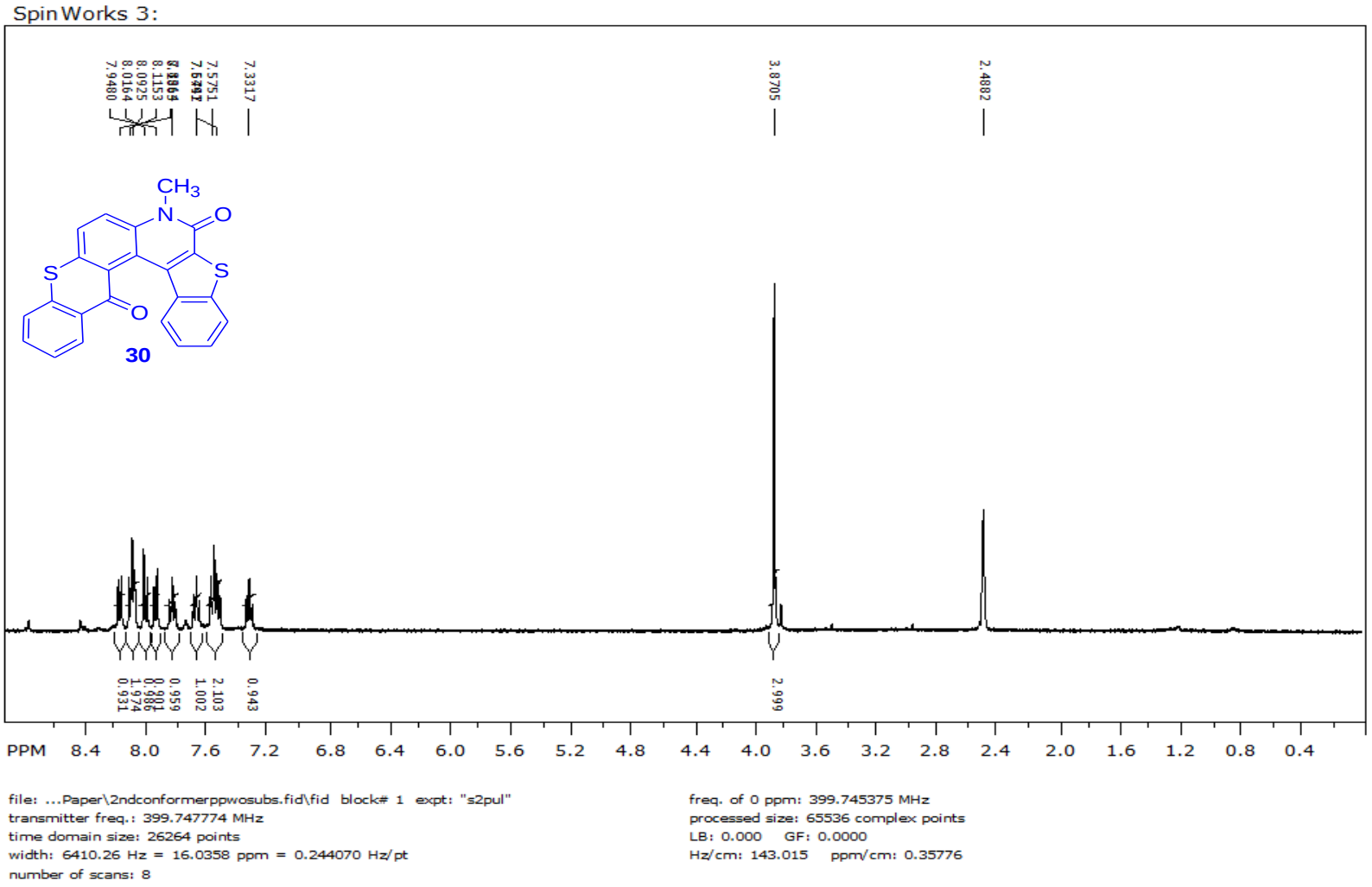


Figure 28, ^{1}H NMR spectrum of [1]benzothieno[2,3-c]benzo[a]anthracene-4-methyl-4*H*-7-thia-4-aza-3,12-dione **(30)** in DMSO-d_6.

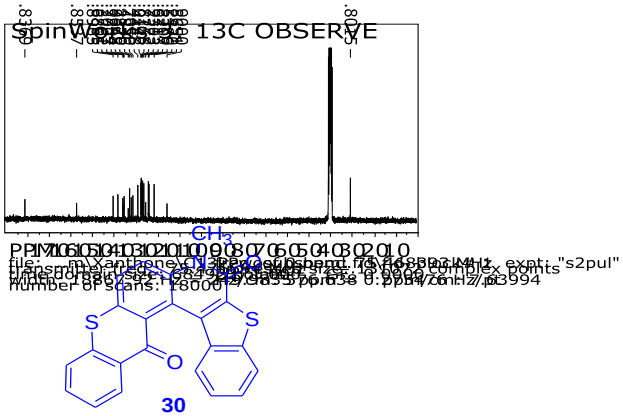


Figure 29, ^{13}C NMR spectrum of [1]benzothieno[2,3-c]benzo[a]anthracene-4-methyl-4*H*-7-thia-4-aza-3,12-dione **(30)** in DMSO-d_6.

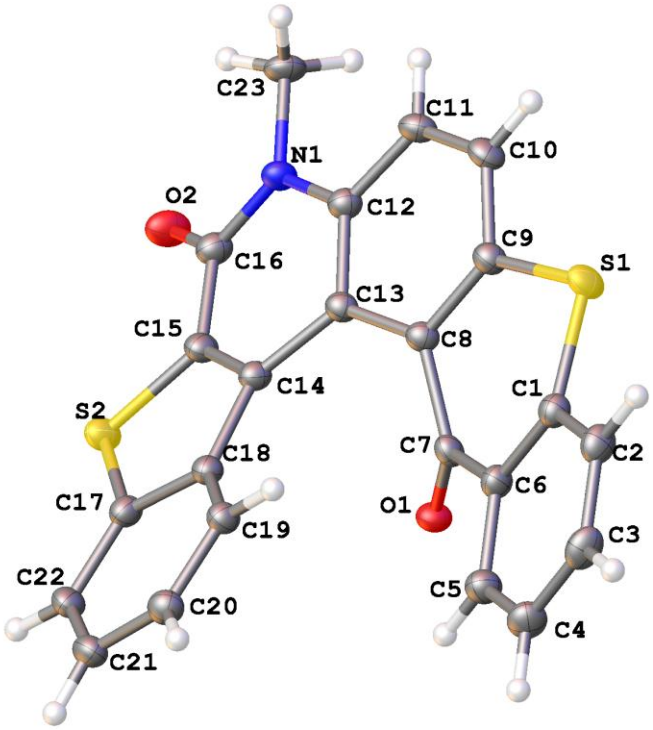


Figure 30, Crystal Structure of [1]benzothieno[2,3-c]benzo[a]anthracene-4-methyl-4*H*-7-thia-4-aza-3,12-dione **(30)**.

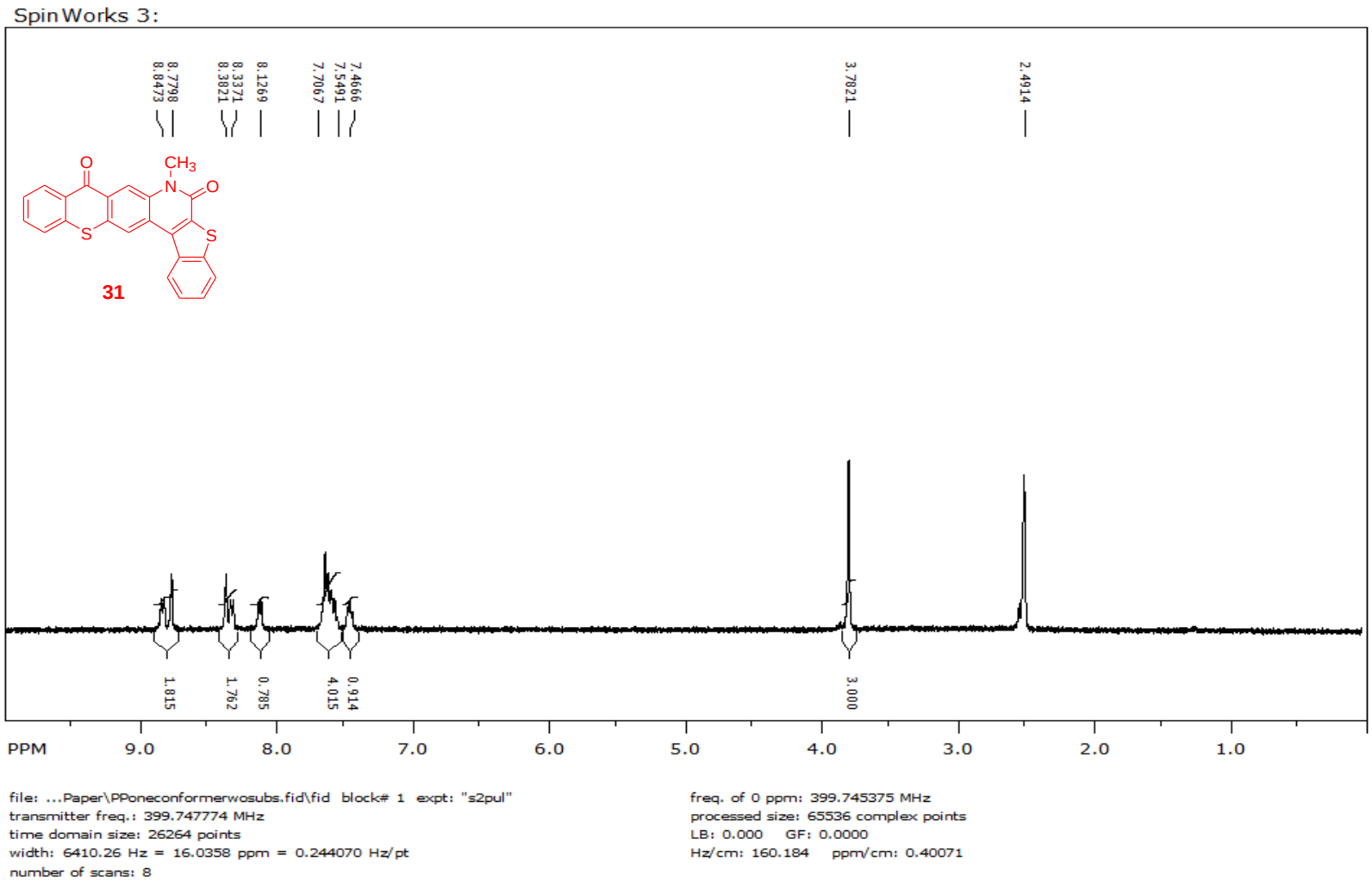


Figure 31, ^{1}H NMR spectrum of [1]benzothieno[2,3-c]naphthacene-1-methyl-1*H*-6-thia-1-aza-2,11-dione (**31**) in DMSO-d_6.

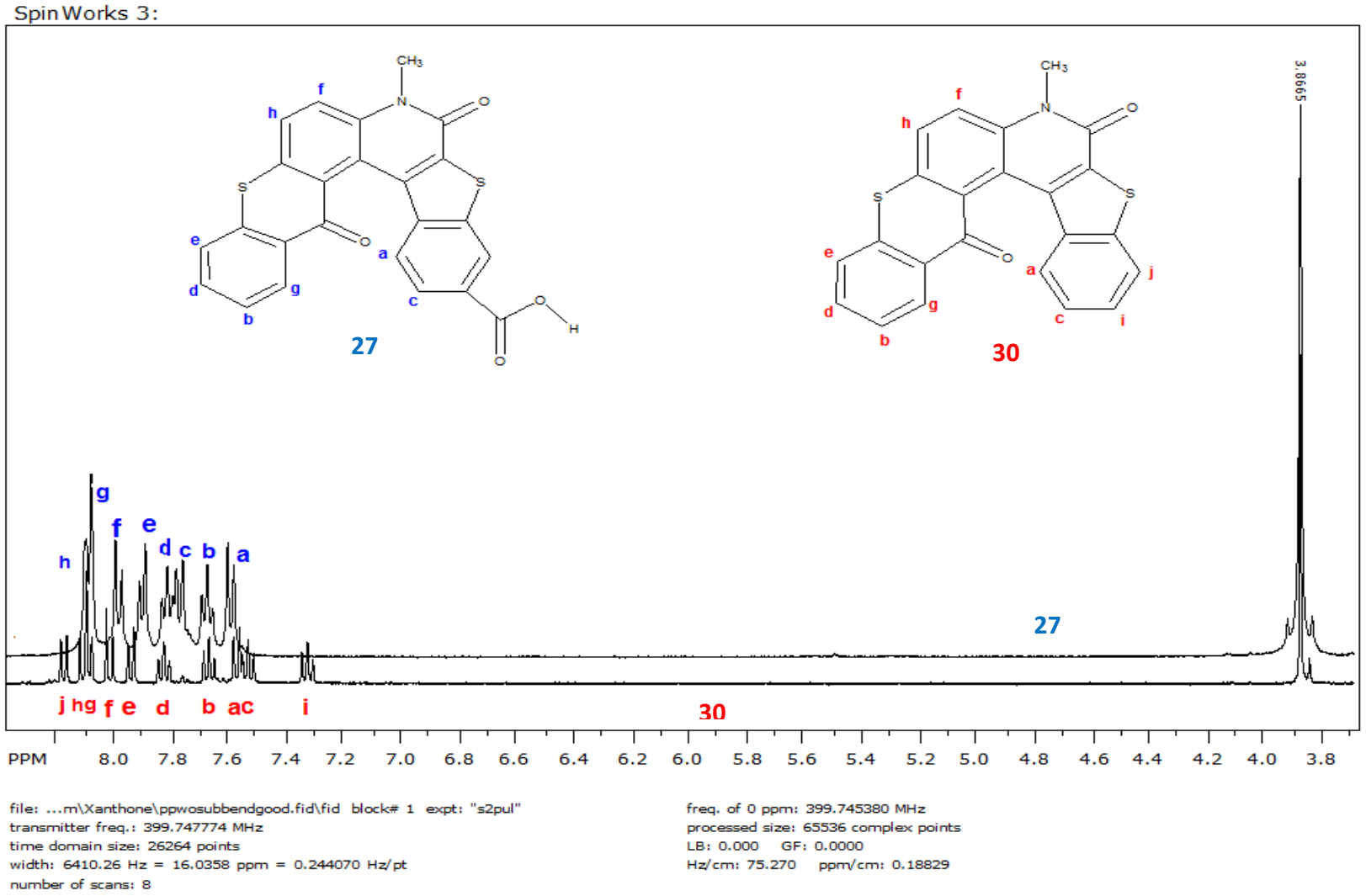


Figure 32, ^{1}H NMR spectrum comparison between Photoproduct **27** and **30** in DMSO-d_6.

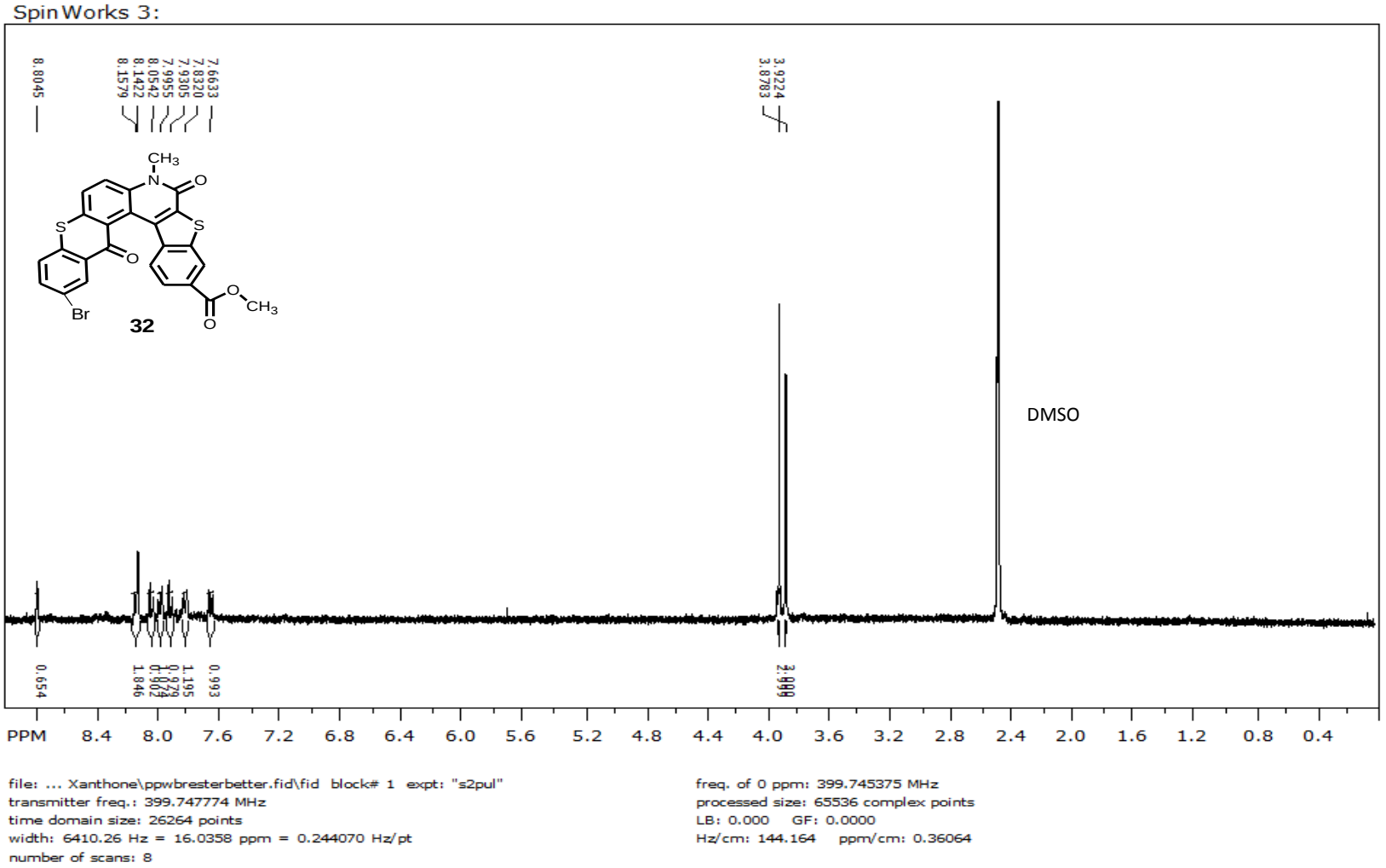


Figure 33, ^{1}H NMR spectrum of 6-methylcarboxylate-[1]benzothiopheno[2,3-c]benzo[a]anthracene-10-bromo-4-methyl-4*H*-7-thia-4-aza-3,12-dione (**32**) in DMSO-d_6.

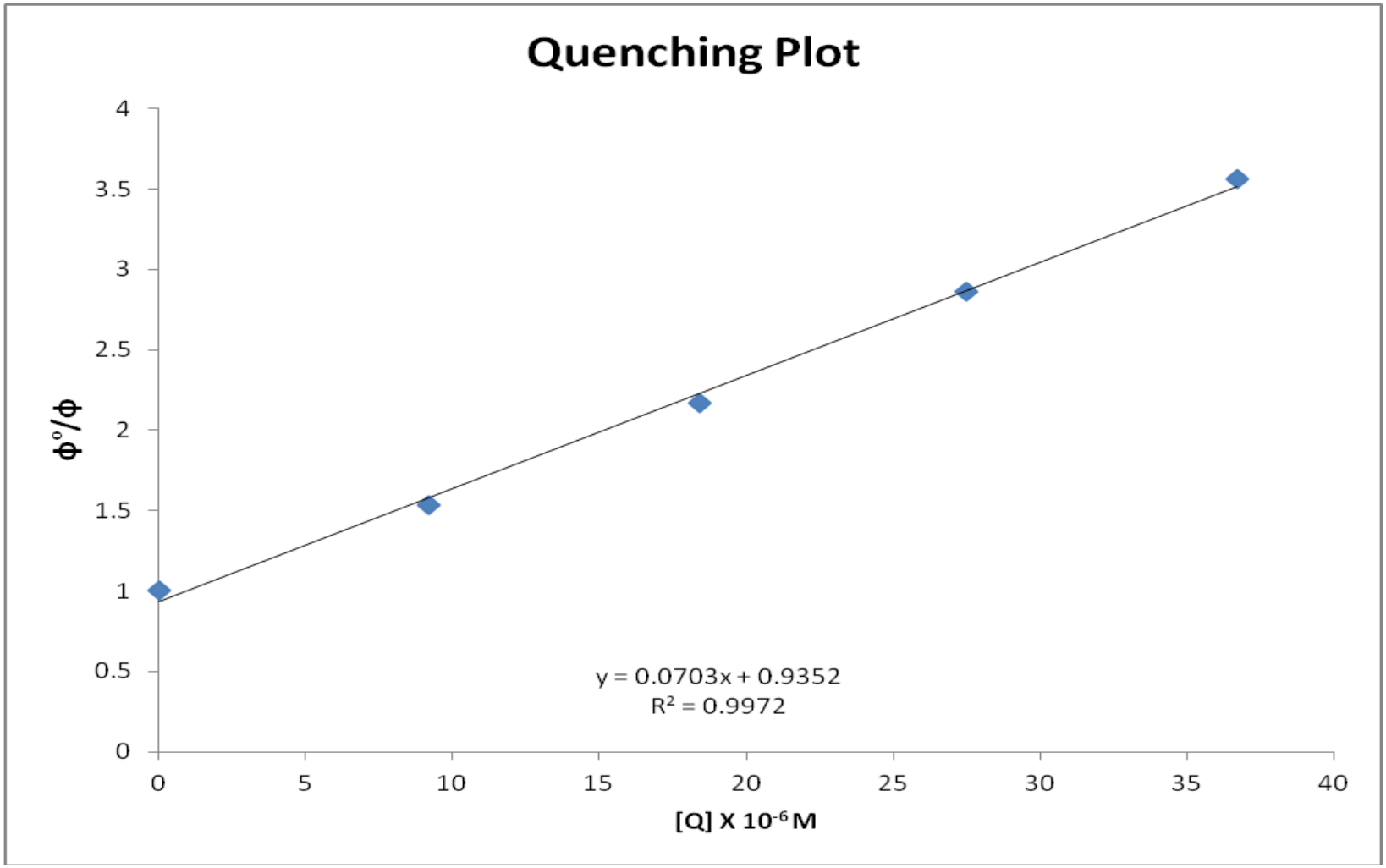
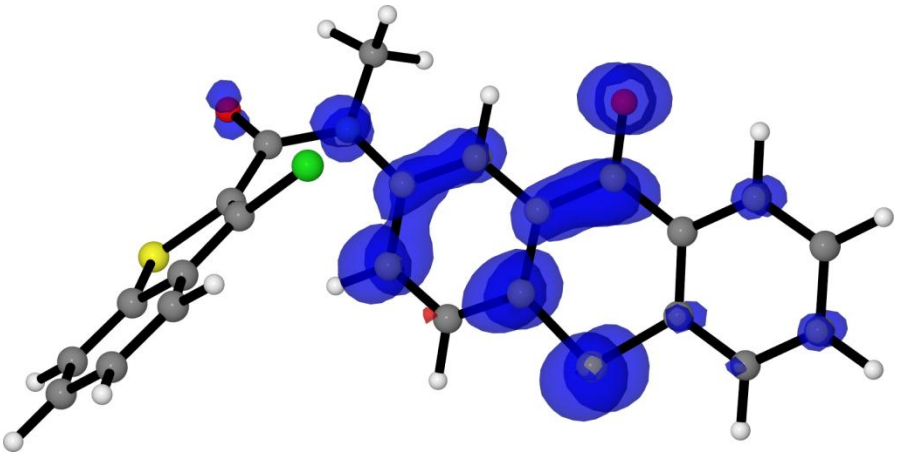
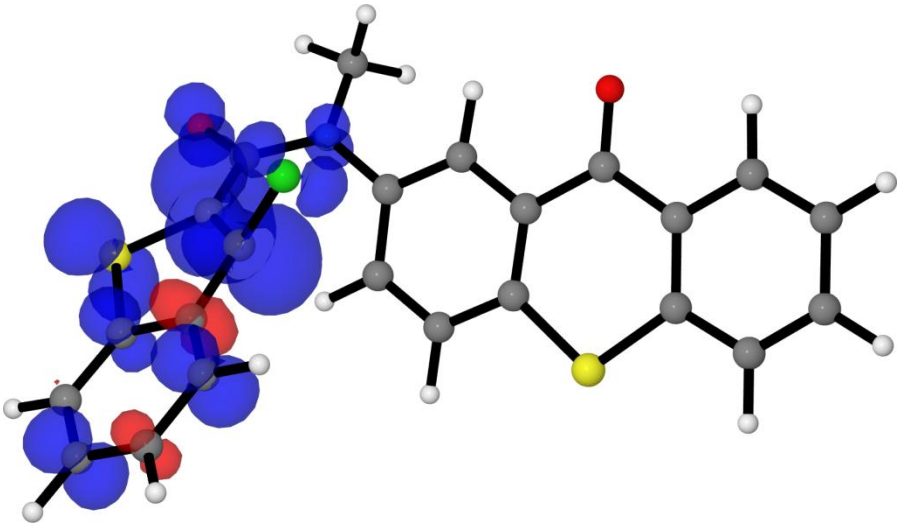


Figure 34, Stern-Volmer plot Φ^0/Φ vs [Q] of Quenching of ester **8** ($LG^- = Cl^-$) by piperylene as quencher Q

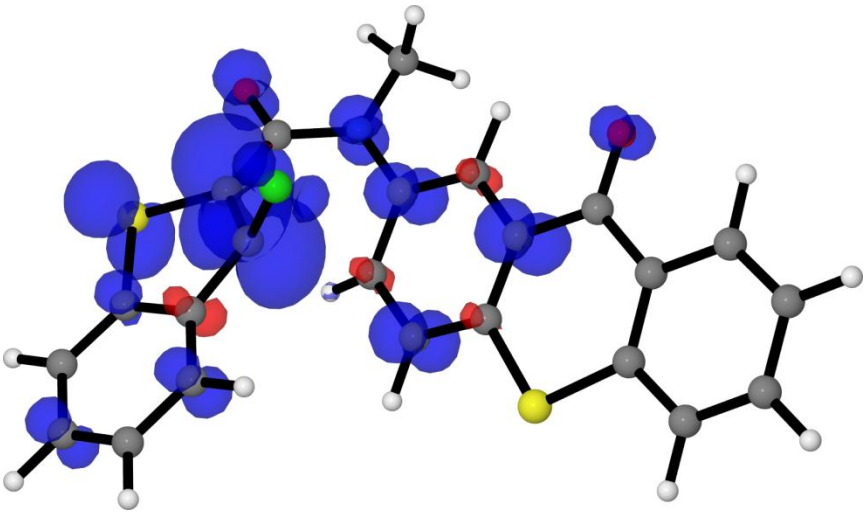
Computed Structures in Figure 3.



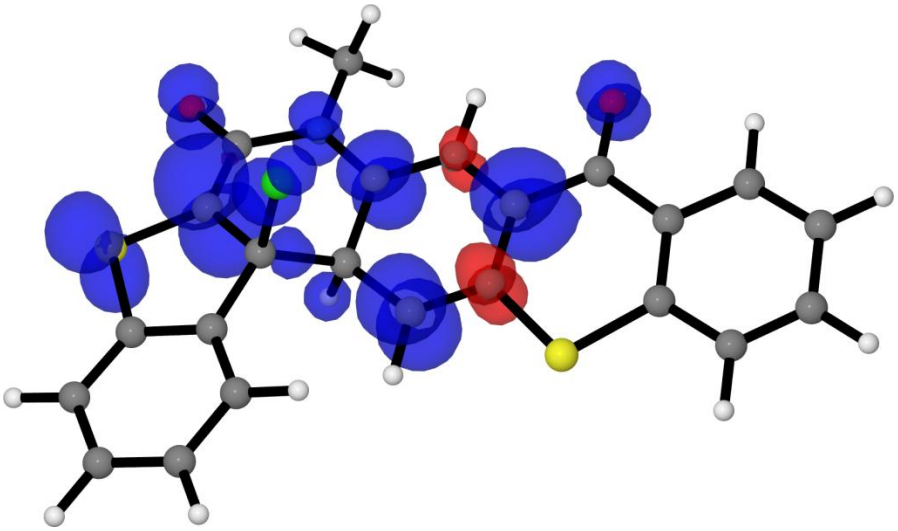
^{3}Thiox



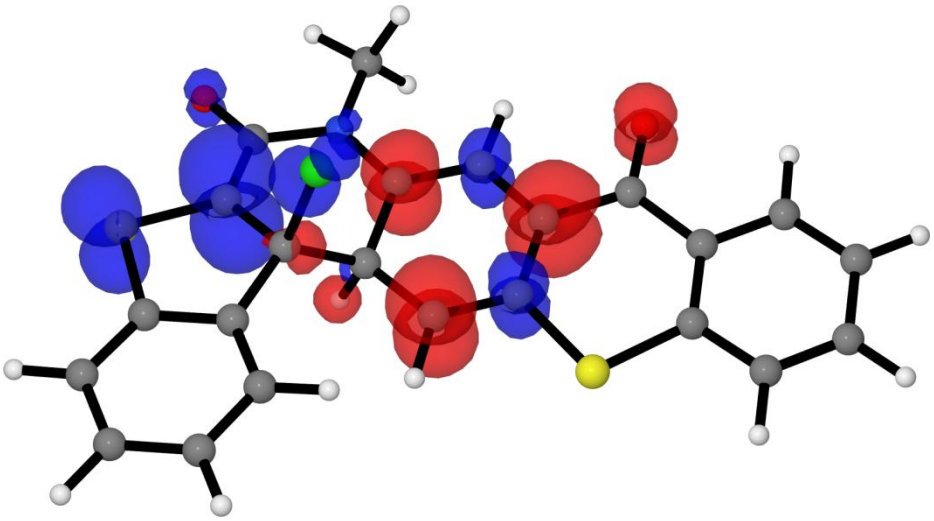
^{3}Bzt



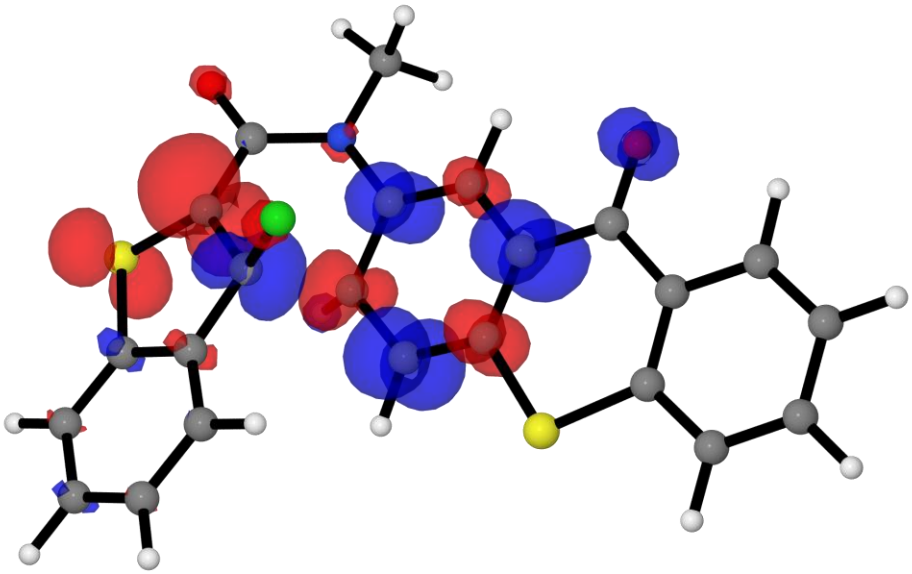
^{3}TS



^{3}I



$^1I_{DR}$



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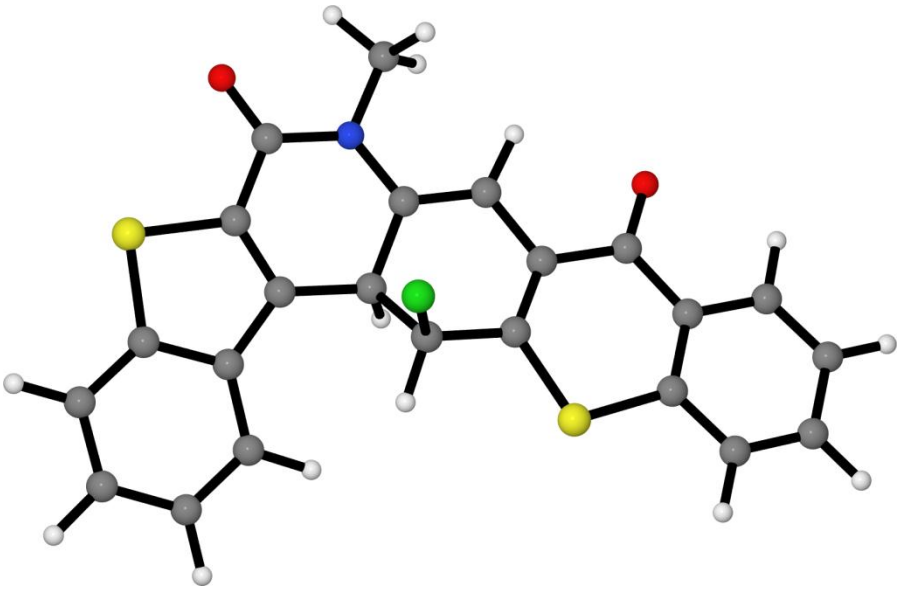
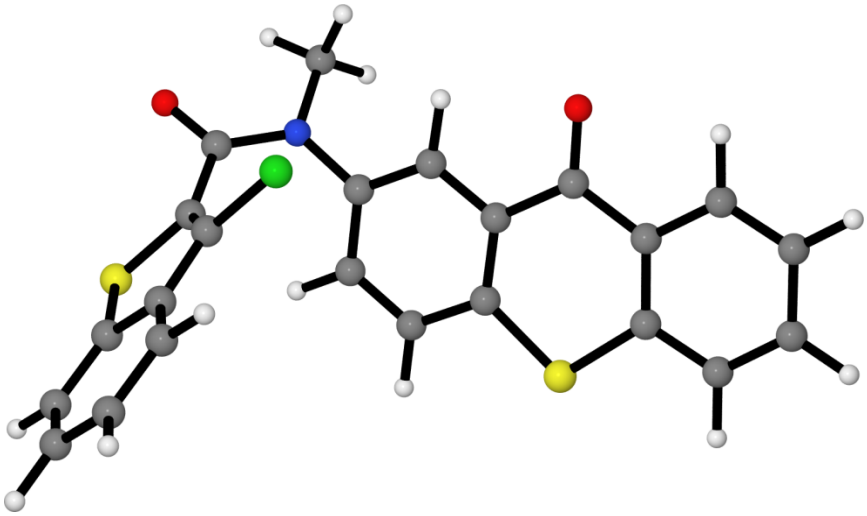
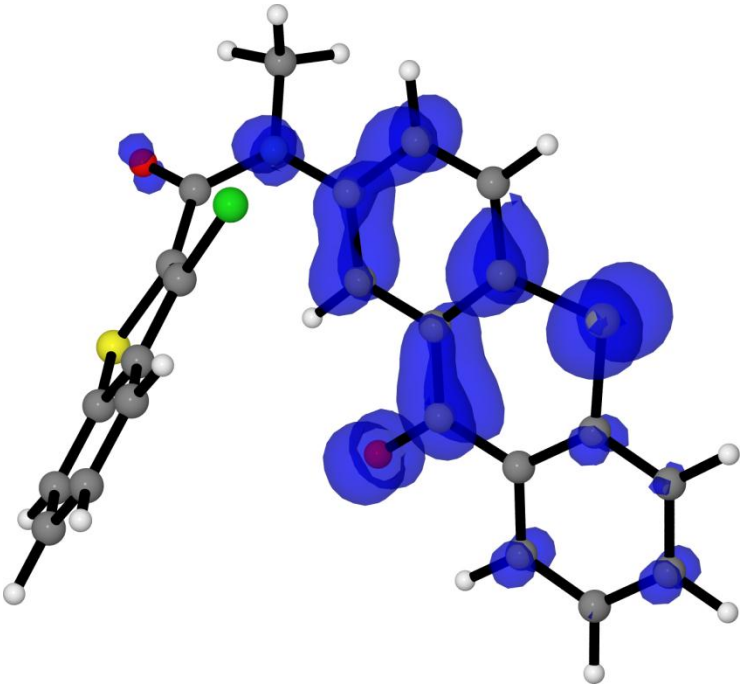


P-L

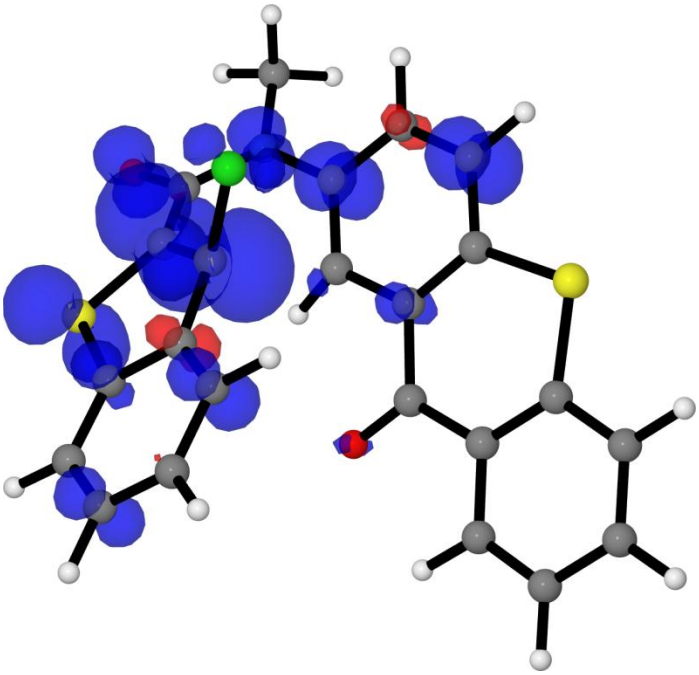


Thiox

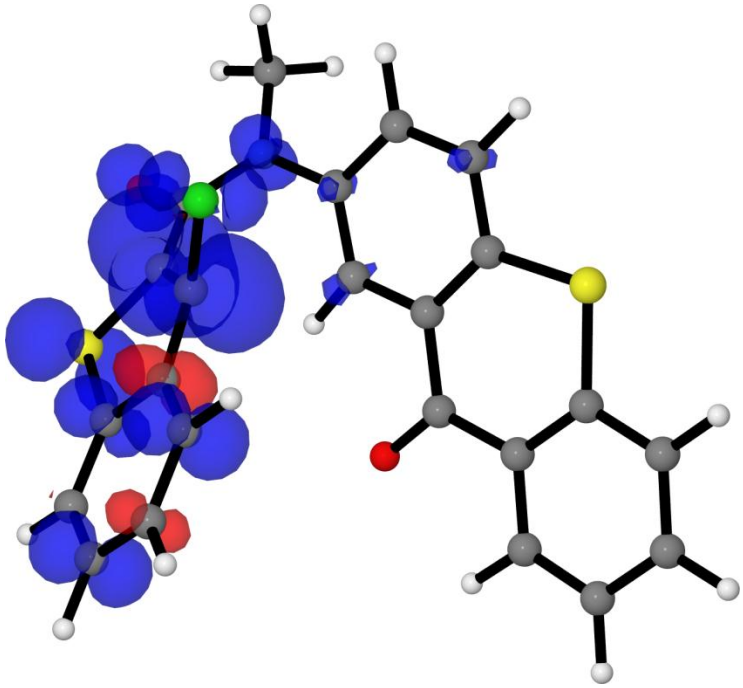
Computed Structures in Figure 4.



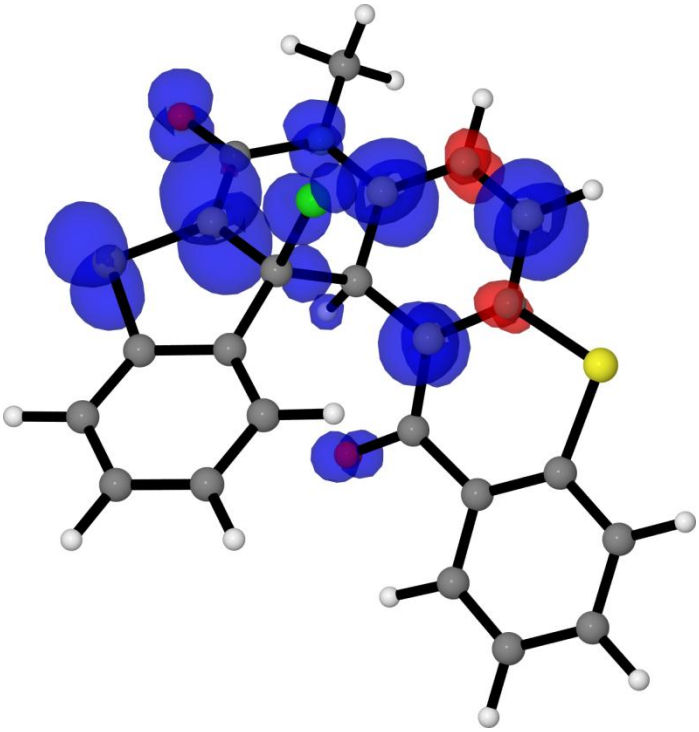
^{3}Thiox



^{3}Bzt



^{3}TS



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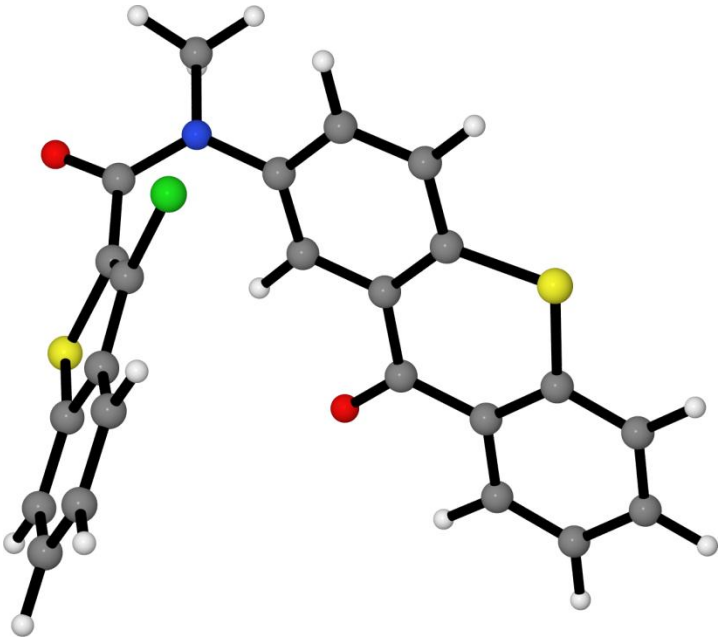

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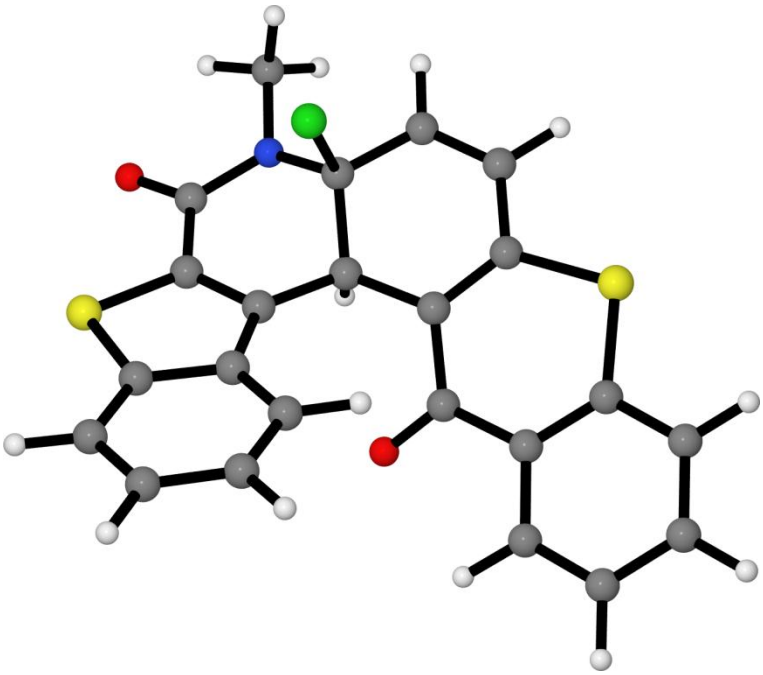

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