Supporting information

Practical and Scalable Entry to Halogenated 1,4-Thiazines Through a Domino Morin-Rearrangement/Halogenation of *N,S*-Acetals and their Arylation Based on Suzuki-Miyaura Coupling

Fanny Danton,[a] Kouceila Abdelli,[a] Mohamed Othman,[a,*] Ata Martin Lawson,[a] Hassan Oulyadi,[b] Sergiu Shova,[c] Ján Moncol,[d] Alina Ghinet,[e,f,g] and Adam Daïch[a,*,†]

[a.] Université Le Havre Normandie, Normandie Univ, URCOM UR 3221, INC3M, FR CNRS 3038, 25 rue Philippe Lebon, BP 1123, F-76063, Le Havre Cedex, France
[b.] Normandie Univ, UNIROUEN, INSA Rouen, CNRS, UMR 6014-CARMeN, F-76000 Rouen, France
[c.] Petru Poni' Institute of Macromolecular Chemistry, Iasi, Romania
[d.] Department of Inorganic Chemistry, Faculty of Chemical and Food Technology, Slovak University of Technology, SK-81237 Bratislava, Slovakia
[e.] Univ. Lille, Inserm, CHU Lille, Institut Pasteur de Lille, UMR 1167 – RID-AGE – Risk Factors and Molecular Determinants of Aging-Related Diseases, F-59000 Lille, France
[f.] Faculty of Chemistry, 'Al. I. Cuza' University of Iasi, B-dul Carol I, Nr. 11, Corp A, Ro-700506, Iasi, Romania
[g.] Laboratoire de Chimie Durable et Santé, JUNIA, 16 rue Colson, F-59000 Lille Cedex, France

†Corresponding author

Phone (+0033) 232-744-403,
E-mail: adam.daich@univ-lehavre.fr,
ORCID: Adam Daïch 0000-0002-6942-0519

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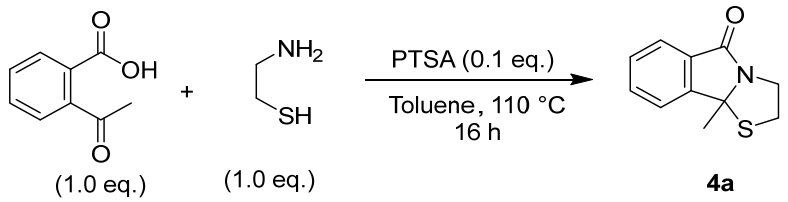
II. Full Experimental Details.

General remarks

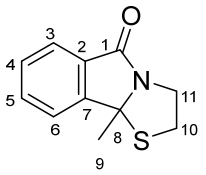
Unless otherwise specified, reagents and starting materials were purchased from commercial sources and were used without further purification. Reactions were carried out in standard glassware. NMR spectra were recorded at room temperature on a Bruker Advance 300 spectrometer (^{1}H: 300 MHz, ^{13}C: 75 MHz) in deuterated chloroform ($CDCl_3$), deuterated acetonitrile (CD_3CN) or deuterated dimethyl sulfoxide (C_2D_6OS) using TMS as internal standard ($\delta = 0$). High resolution ESI mass spectra were measured on 6530 Q-TOF Agilent System spectrometer. Separation procedure was carried out using Interchim Puriflash 430 System equipped with UV detector. Silicon dioxide (SiO_2) (30 to 50 µm) from Macherey-Nagel was used as the solid phase and a mixture of cyclohexane / ethyl acetate or dichlormethane / methanol has served as eluent. Melting points were recorded on a Stuart Scientific analyzer SMP 10 apparatus and are uncorrected. Infrared spectra were performed as neat on Perkin Elmer FT-IR spectrophotometer and only broad or strong signals are reported. Specific rotations were measured on a Jasco P-2000 polarimeter for compounds never described before.

II. General procedure for the synthesis of *N,S*-acetals as starting materials.

Synthesis of 9*b*-Methyl-2,3-dihydrothiazolo[2,3-*a*]isoindol-5(9*bH*)-one (4a)



To a previously stirred solution of 2-acetylbenzoic acid (2.00 g, 12.2 mmol, 1.0 eq.) and *p*-toluene-sulfonic acid monohydrate (PTSA, 230 mg, 1.22 mmol, 0.1 eq.) in toluene (60 mL), was added the aminothiol (1.11 g, 14.4 mmol, 1.2 eq.) and the mixture was heated at 110 °C for 16 h. After cooling at room temperature, the solvent was evaporated under reduced pressure and purification on flash chromatography (*Silica 60*) was performed to get 2.02 g (84%) of the corresponding *N,S*-acetal **4a**.



White solid, $R_f = 0.40$, eluent (ethyl acetate / cyclohexane = 3/7), mp = 64–66 °C, 2.00 g scale reaction (in 60 mL of toluene), 2.02 g was isolated, 84% yield.

IR (ν_{max} / cm^{-1}): 1698, 1347, 740, 698.

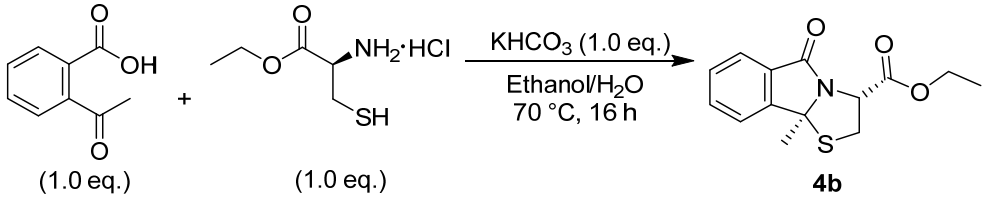
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.76 (dt, *J* = 7.4, 1.0 Hz, 1H), 7.65 – 7.53 (m, 1H), 7.47 (ddd, *J* = 8.4, 7.5, 1.7 Hz, 2H), 4.65 – 4.48 (m, 1H), 3.56 – 3.22 (m, 3H), 1.91 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ_C 170.6, 150.7, 133.1, 129.3, 129.0, 124.4, 121.8, 75.7, 43.3, 37.8, 28.8.

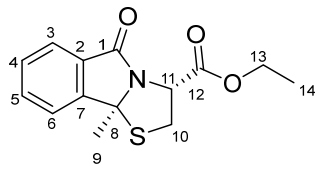
HRMS (ESI$^+$): Calcd for $C_{11}H_{12}NOS$ $[M+H]^+$ 206.0634, found 206.0655.

The synthesis of this product was reported in the following reference: F. Danton, M. Othman, A. M. Lawson, J. Moncol, A. Ghinet, B. Rigo, A. Daïch, *Chem. Eur. J.* **2019**, *25*, 6113–6118.

Synthesis of ethyl 9*b*-methyl-5-oxo-2,3,5,9*b*-tetrahydrothiazolo[2,3-*a*]isoindole-3-carboxylate (4b)



To a stirred solution of the ketoacid (2.00 g, 12.2 mmol, 1.0 eq.) in ethanol (40 mL), was added a solution of ethyl ester aminoethanthiol hydrochloride (1.67 g, 12.2 mmol, 1.0 eq.) and $KHCO_3$ (1.22 g, 12.2 mmol, 1.0 eq.) in water (20 mL). The mixture was then heated at 70 °C for 16 h. After cooling at room temperature, the solvent was evaporated and a purification on flash chromatography was performed to get the corresponding *N,S*-acetal **4b** in 85% yield.



Colorless pasty, R_f = 0.33, eluent (ethyl acetate / cyclohexane = 1/4), 2.00 g scale reaction (in 60 mL of toluene), 2.87 g was isolated, 85% yield.

IR (ν_{max} / cm^{-1}): 1745, 1694, 1341, 1326, 752.

^{1}H NMR (300 MHz, $CDCl_3$): δ_H 7.80 (d, *J* = 7.3 Hz, 1H, H-3), 7.62 (td, *J* = 7.5, 1.2 Hz, 1H, H-5), 7.56 – 7.44 (m, 2H, H-4, H-6), 5.14 (dd, *J* = 8.7, 6.4 Hz, 1H, H-11), 4.36 – 4.22 (m, 2H, H-13), 3.93 (dd, *J* = 11.8, 6.4 Hz, 1H, H-10), 3.82 (dd, *J* = 11.8, 8.7 Hz, 1H, H-10), 1.96 (s, 3H, H-9), 1.33 (t, *J* = 7.1 Hz, 3H, H-14).

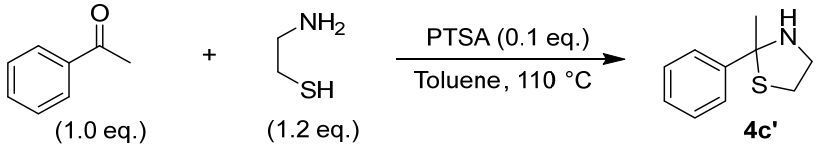
^{13}C NMR (75 MHz, $CDCl_3$): δ_C 170.7 ($Cq_{C=O}$, C-1), 170.5 ($Cq_{C=O}$, C-12), 149.2 (Cq, C-7), 133.4 (Cq, C-5), 129.5 (CH, C-4), 129.2 (Cq, C-2), 124.8 (CH, C-3), 122.0 (CH, C-6), 77.4 (Cq, C-8), 62.2 (CH_2, C-13), 58.2 (CH, C-11), 40.4 (CH_2, C-10), 28.3 (CH_3, C-9), 14.3 (CH_3, C-14).

HRMS (ESI$^+$): Calcd for $C_{14}H_{16}NO_3S$ $[M+H]^+$ 278.0845, found 278.0875.

The synthesis of this product was reported in the following reference: F. Danton, M. Othman, A. M. Lawson, J. Moncol, A. Ghinet, B. Rigo, A. Daïch, *Chem. Eur. J.* **2019**, *25*, 6113–6118. For specific rotation, see the following reference, Allin, S. M.; Vaidya, D. G.; Page, M. I.; Slawin, A. M. Z.; Smith, T. *Tetrahedron Lett.* **2000**, *41*, 2219–2222.

Synthesis of 1-(2-Methyl-2-phenylthiazolidin-3-yl)ethanone (4c)

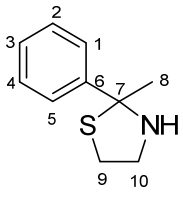
Step 1. Synthesis of 2-Methyl-2-phenylthiazolidine (4c')



(1.0 eq.) (1.2 eq.) **4c'**

To a stirred solution of acetophenone (2.00 g, 16.6 mmol, 1.0 eq.) and PTSA (0.316 g, 1.66 mmol, 0.1 eq.) in toluene, was added the cysteamine (1.54 g, 19.9 mmol, 1.2 eq.) before heating the mixture at 110 °C for 16 h. After cooling the reaction at room temperature, the solvent was evaporated under reduced pressure and a purification on flash chromatography was performed to get the corresponding *N,S*-acetals **4c'** in 43% yield.

2-Methyl-2-phenylthiazolidine (4c')



Colorless oil, R_f = 0.44, eluent (ethyl acetate / cyclohexane = 1/4), 2.00 g scale reaction (in 60 mL of toluene), 1.28 g was isolated, 43% yield.

IR (ν_{max} / cm^{-1}): 3296, 1444, 1062, 762, 699.

^{1}H NMR (300 MHz, $CDCl_3$): δ_H 7.66 (d, *J* = 7.7 Hz, 2H, Har), 7.33 (t, *J* = 7.5 Hz, 2H, Har), 7.22 (d, *J* = 7.3 Hz, 1H, Har), 3.59 – 3.42 (m, 1H, H-10), 3.16 – 3.03 (m, 3H, H-10, H-9), 2.27 – 2.18 (bs, 1H, NH), 1.90 (s, 3H, H-8).

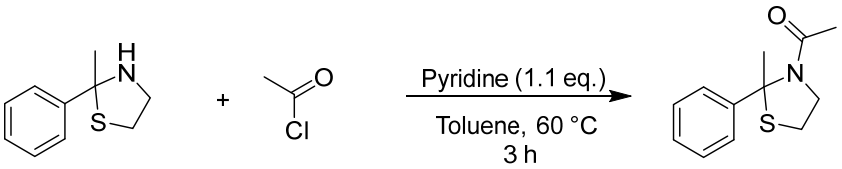
^{13}C NMR (75 MHz, $CDCl_3$): δ_C 147.4 (Cq, C-6), 128.0 (x2 CH, C-1, C-5), 126.8 (CH, C-3), 125.9 (x2 CH, C-2, C-4), 82.5 (Cq, C-7), 51.5 (CH_2, C-10), 37.4 (CH_2, C-9), 33.4 (CH_3, C-8).

HRMS (ESI$^+$): Calcd for $C_{10}H_{14}NS$ $[M+H]^+$ 180.0841, found 180.0850.

The synthesis of this product was reported in the following reference: F. Danton, M. Othman, A. M. Lawson, J. Moncol, A. Ghinet, B. Rigo, A. Daïch, *Chem. Eur. J.* **2019**, *25*, 6113–6118.

Step 2. Synthesis of 1-(2-Methyl-2-phenylthiazolidin-3-yl)ethanone (4c)

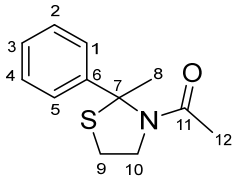
To a solution of *N,S*-acetal **4c'** (0.20 g, 1.85 mmol, 1.0 eq.) in 3 mL of toluene at 60 °C were added pyridine (0.16 g, 2.03 mmol, 1.1 eq.) and acetyl chloride (0.16 g, 2.03 mmol, 1.1 eq.) and the reaction was allowed to stir for 3 h. After filtration and concentration under reduced pressure, the resulting mixtures led to pure *N*-acetyl-*N,S*-acetal compound **4c** in 89% after purification on silica gel column chromatography.



4c' (1.0 eq.) (1.1 eq.) **4c**

NMR spectra of product **4c** was recorded at 50 °C in deuterated acetonitrile in order to simplify the analysis. Indeed, at room temperature, spectra were difficult to interpret due to the presence of rotamers probably.

1-(2-Methyl-2-phenylthiazolidin-3-yl)ethanone (4c)



White solid, R_f = 0.43, eluent (ethyl acetate / cyclohexane = 4/6), mp = 94–96 °C (*Bull. Soc. Chim. Fr.* **1964**, 2493-2499, 91 °C), 200 mg scale reaction (in 2 mL of toluene), 220 mg were isolated, 89% yield.

IR (ν_{max} / cm^{-1}): 1635, 1394, 1348, 728, 699.

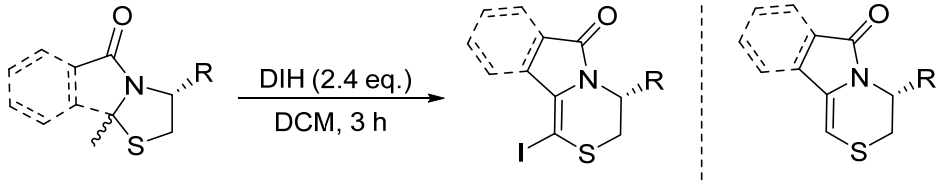
^{1}H NMR (300 MHz, CD_3CN 50 °C): δ_H 7.43 (d, *J* = 7.7 Hz, 2H, H-1, H-5), 7.36 (t, *J* = 7.5 Hz, 2H, H-2,H-4), 7.27 (dd, *J* = 13.6, 6.8 Hz, 1H, H-3), 4.15 (dt, *J* = 12.2, 6.0 Hz, 2H, H-10), 3.14 (dt, *J* = 12.0, 6.0 Hz, 1H, H-9), 3.02 (dt, *J* = 12.0, 6.3 Hz, 1H, H-9), 2.25 (s, 3H, H-8), 2.24 – 1.94 (bs, 3H, H-12).

^{13}C NMR (75 MHz, CD_3CN, 50 °C): δ_C 168.5 ($Cq_{C=O}$, C-11), 147.0 (Cq, C-6), 129.1 (x2 CH, C-2, C-4), 127.8 (CH, C-3), 126.1 (x2 CH, C-1, C-5), 75.8 (CH, C-7), 55.5 (CH_2, C-10), 29.7 (CH_2, C-9), 27.8 (CH_3, C-8), 25.5 (CH_3, C-12).

HRMS (ESI$^+$): Calcd for $C_{12}H_{16}NOS$ $[M+H]^+$ 222.0947, found 222.0944.

The synthesis of this product was reported in the following reference: F. Danton, M. Othman, A. M. Lawson, J. Moncol, A. Ghinet, B. Rigo, A. Daïch, *Chem. Eur. J.* **2019**, *25*, 6113–6118.

III. General procedure for the synthesis in domino process of iodothiazine compounds 7aA, 7bA and 7cA.



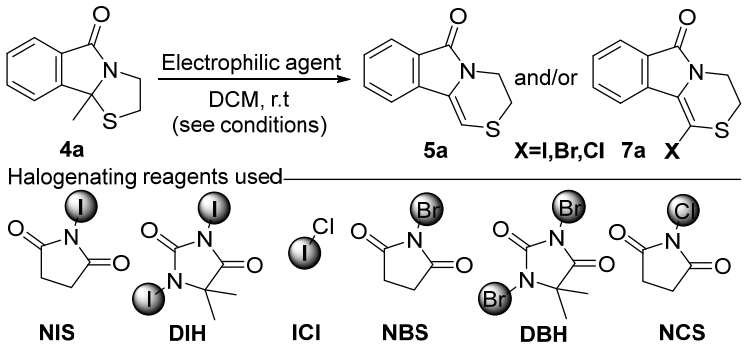
4a,b,c **7a,b,c(A)** **5a,b,c**

To 100 mg (1 eq.) of *N,S*-acetal substrate **4a**, **4b** or **4c**, described by our group in previous work, was dissolved in dry DCM (15 mL) and 2.4 equivalents of 1,3-diiodo-5,5-dimethylhydantoin (DIH) was then added dropwise at room temperature and the reaction mixture was stirred for 3 hours. After completion of the reaction (TLC), an aqueous solution of sodium thiosulfate ($Na_2S_2O_3$ 0.2 M, 10 mL) was then added to

quench the reaction. After extraction with DCM three times (3x10 mL), the organic layers were collected and dried on $MgSO_4$. The solvent was evaporated under reduced pressure and a purification on flash chromatography (ethyl acetate/cyclohexane = 3/7 up to 4/6) was performed to provide the expected iodinated compounds **7aA** (87 mg), **7bA** (87 mg) and **7cA** (95 mg) in an isolated yield of 54%, 57% and 50%, respectively.

Important remark: Following the same protocol, but when 1 up to 1.4 equivalents of *N*-iodosuccinimide (NIS) or 1 equivalent of DIH was used (see the following details in **Table 1**), only the Morin-rearrangement compound **5a** was isolated in yields of 38% up to 57% yield.

Table 1. Optimization of domino Morin-transposition/ halogenation of **4a** into 1,4-thiazines **7a (X=I), 7aB (X=Br)** and **7aC (X=Cl)**.[a]

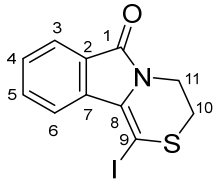


Entry	Halogenating reagent (eq.)	X	Product % **5a**	Product % **7a(A,B,C)**	Product **7a**	Time (h)	Yield (%)[a]
1	NIS (1.0 eq.)	I	100%	-		4	38
2	NIS (1.4 eq.)	I	100%	-		4	51
3	DIH (1.0 eq.)	I	100%	-		4	57
4	**DIH (2.4 eq.)**	**I**	**-**	**100%**	**7aA**	**3**	**54**
5	NBS (1.0 eq.)	Br	56%	44%	**7aB**	4	-[b]
6	NBS (2.0 eq.)	Br	-	100%	**7aB**	4	69
7	**DBH (1.1 eq.)**	**Br**	**-**	**100%**	**7aB**	**0.5**	**88**
8	+BHT (2.2 eq.)	Br	-	100%	**7aB**	0.5	79
9	NCS (1.4 eq.)	Cl	-	-	**7aC**	4	-[c]
10	**ICl (4.2 eq.)**	**Cl**	**-**	**100%**	**7aC**	**3**	**88**
11	ICl (1.4 eq.)	Cl	100%	-	**7aC**	4	96

[a] **7a (X=I)**, **7aB (X=Br)** and **7aC (X=I)**.
[b] Isolated yield.
[c] Ratio determined by ^{1}H NMR.
[d] Complex mixture containing traces of **5a** and **7aC**.

1-Iodo-3,4-dihydro-6*H*-[1,4]thiazino[3,4-*a*]isoindol-6-one (7aA)

This product was isolated pure as yellow solid, R_f = 0.60, eluent (ethyl acetate / cyclohexane = 4/6), mp = 165–167 °C, 100 mg scale reaction (in 3 mL of dichloromethane), 87 mg was isolated, 54% yield.



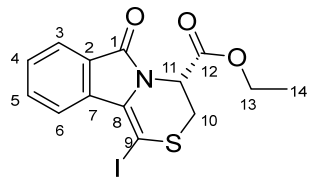
IR (ν_{max} / cm^{-1}): 1666, 1349, 1032, 755, 686.

^{1}H NMR (300 MHz, $CDCl_3$): δ_H 8.69 (d, *J* = 7.9 Hz, 1H, H-6), 7.85 (d, *J* = 7.3 Hz, 1H, H-3), 7.62 (t, *J* = 7.6 Hz, 1H, H-5), 7.50 (t, *J* = 7.5 Hz, 1H, H-4), 4.38 – 4.29 (m, 2H, H-11), 3.19 – 3.10 (m, 2H, H-10).

^{13}C NMR (75 MHz, $CDCl_3$): δ_C 165.0 ($Cq_{C=O}$, C-1), 135.3 (Cq, C-7), 131.8 (CH, C-3), 130.8 (Cq, C-8), 129.2 (CH, C-4), 128.8 (Cq, C-2), 123.5 (CH, C-6), 122.4 (CH, C-3), 61.7 (Cq, C-9), 39.4 (CH_2, C-11), 31.7 (CH_2, C-10).

HRMS (ESI$^+$): Calcd for $C_{11}H_9INOS$ $[M+H]^+$ 329.9444, found 329.9458.

Ethyl (*R*)-1-Iodo-6-oxo-3,4-dihydro-6*H*-[1,4]thiazino[3,4-*a*]isoindole-4-carboxylate (7bA)



This product was isolated pure as yellow oil, R_f = 0.42, eluent (ethyl acetate / cyclohexane = 3/7), 100 mg scale reaction (in 3 mL of dichloromethane), 83 mg was isolated, 57% yield.

IR (ν_{max} / cm^{-1}): 1743, 1683, 1198, 760, 692.

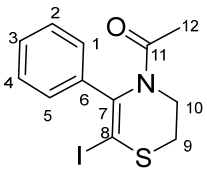
^{1}H NMR (300 MHz, $CDCl_3$): δ_H 8.70 (d, *J* = 8.0 Hz, 1H, H-6), 7.87 (d, *J* = 7.5 Hz, 1H, H-3), 7.70 – 7.57 (m, 1H, H-5), 7.57 – 7.45 (m, 1H, H-4), 5.74 (t, *J* = 3.3 Hz, 1H, H-11), 4.24 (qd, *J* = 7.3, 1.4 Hz, 2H, H-13), 3.48 (dd, *J* = 13.1, 3.5 Hz, 1H, H-10), 3.36 (dd, *J* = 13.1, 3.0 Hz, 1H, H-10), 1.25 (t, *J* = 7.2 Hz, 3H, H-14).

^{13}C NMR (75 MHz, $CDCl_3$): δ_C 167.6 ($Cq_{C=O}$, C-11), 165.1 ($Cq_{C=O}$, C-1), 135.6 (Cq, C-7), 132.2 (Cq, C-5), 130.2 (Cq, C-2), 129.3 (Cq, C-4), 128.4 (Cq, C-9), 123.9 (CH, C-3), 122.6 (CH, C-6), 62.5 (CH_2, C-13), 60.2 (Cq, C-9), 50.8 (CH, C-11), 33.2 (CH_2, C-10), 14.3 (CH_3, C-14).

HRMS (ESI$^+$): Calcd for $C_{14}H_{13}INO_3S$ $[M+H]^+$ 401.9655, found 401.9652.

$[\alpha]_D^{25}$= -295.7 (c 0.210 g/100 mL, CH_2Cl_2).

1-(6-Iodo-5-phenyl-2,3-dihydro-4*H*-1,4-thiazin-4-yl)ethan-1-one (7cA)



This product was isolated pure as yellow solid, R_f = 0.68, eluent (ethyl acetate / cyclohexane = 4/6), mp = 152–154 °C, 70 mg scale reaction (in 2 mL of dichloromethane), 67 mg was isolated, 50% yield.

IR (ν_{max} / cm^{-1}): 1663, 1372, 1219, 750, 697.

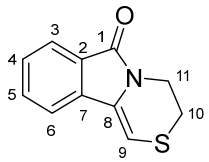
^{1}H NMR (300 MHz, $CDCl_3$): δ_H 7.43 – 7.28 (m, 5H, Har), 4.17 (t, *J* = 5.5 Hz, 2H, H-10), 3.26 (t, *J* = 5.5 Hz, 2H, H-9), 1.59 (s, 3H, H-12).

^{13}C NMR (75 MHz, $CDCl_3$): δ_C 170.6 ($Cq_{C=O}$, C-11), 139.5 (Cq, C-6), 138.6 (Cq, C-7), 129.5 (x2 CH, C-2, C-4), 128.6 (CH, C-3), 128.2 (x2 CH, C-1, C-5), 79.7 (Cq, C-8), 41.8 (CH_2, C-9), 36.2 (CH_2, C-10), 24.4 (CH_3, C-9).

HRMS (ESI$^+$): Calcd for $C_{12}H_{13}INOS$ $[M+H]^+$ 345.9757, found 345.9773.

Important remark: Following the same protocol, but when 1 up to 1.4 equivalents of *N*-iodosuccinimide (NIS) or 1 equivalent of DIH were used (see the following details in **Table 1**), only the Morin-rearrangement compound **5a** (in 38% up to 57% yield), **5b** (in 56% yield) or **5c** (in 96% yield) was isolated.

3*H*-[1,4]Thiazino[3,4-*a*]isoindol-6(4*H*)-one (5a)



This product was isolated pure as white solid, R_f = 0.31, eluent (ethyl acetate / cyclohexane = 3/7), mp = 107–109 °C, was isolated in 38% up to 57% yield.

IR (ν_{max} / cm^{-1}): 1698, 1351, 1242, 745.

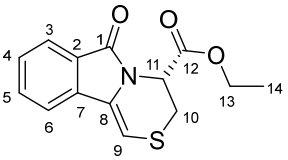
^{1}H NMR (300 MHz, $CDCl_3$): δ_H 7.77 (d, *J* = 7.5 Hz, 1H, Har), 7.54 – 7.45 (m, 2H, Har), 7.38 (ddd, *J* = 8.0, 6.4, 2.1 Hz, 1H, Har), 6.24 (s, 1H, H-9), 4.18 – 4.06 (m, 2H, H-11), 3.15 – 3.03 (m, 2H, H-10).

^{13}C NMR (75 MHz, $CDCl_3$): δ_C 165.6 ($Cq_{C=O}$, C-1), 134.7 (Cq, C-8), 131.7 (CH, Car), 130.7 (Cq, Car), 128.3 (CH, Car), 127.8 (Cq, Car), 123.1 (CH, Car), 118.7 (CH, Car), 99.7 (CH, C-9), 39.3 (CH_2, C-11), 26.0 (CH_2, C-10).

HRMS (ESI$^+$): Calcd for $C_{11}H_{10}NOS$ $[M+H]^+$ 204.0478, found 204.0478.

The synthesis of this product was reported in the following reference: F. Danton, M. Othman, A. M. Lawson, J. Moncol, A. Ghinet, B. Rigo, A. Daïch, *Chem. Eur. J.* **2019**, *25*, 6113–6118.

Ethyl 6-oxo-4,6-dihydro-3*H*-[1,4]thiazino[3,4-*a*]isoindole-4-carboxylate (5b)



This product was isolated pure as yellow solid, R_f = 0.38, eluent (ethyl acetate / cyclohexane = 3/7), mp = 124–127 °C, was isolated after separation in 56% yield.

IR (ν_{max} / cm^{-1}): 1732, 1687, 1202, 763.

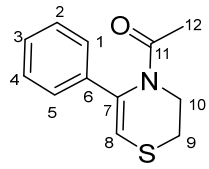
^{1}H NMR (300 MHz, $CDCl_3$): δ_H 7.83 (d, *J* = 7.6 Hz, 1H, Har), 7.63 – 7.50 (m, 2H, Har), 7.43 (ddd, *J* = 8.0, 6.5, 1.9 Hz, 1H, Har), 6.25 (d, *J* = 1.9 Hz, 1H, H-9), 5.47 (t, *J* = 3.3 Hz, 1H, H-11), 4.22 (q, *J* = 7.1 Hz, 2H, H-13), 3.50 (dt, *J* = 13.1, 2.6 Hz, 1H, H-10), 3.27 (dd, *J* = 13.1, 3.6 Hz, 1H, H-10), 1.24 (t, *J* = 7.1 Hz, 3H, H-14).

^{13}C NMR (75 MHz, $CDCl_3$): δ_C 167.8 ($Cq_{C=O}$, C-12), 165.9 ($Cq_{C=O}$, C-1), 135.0 (Cq, C-8), 132.2 (Cq, Car), 130.4 (Cq, Car), 128.6 (CH, Car), 127.4 (Cq, Car), 123.6 (CH, Car), 119.1 (CH, Car), 99.0 (CH, C-9), 62.3 (CH_2, C-13), 50.8 (CH, C-11) 28.1 (CH_2, C-10), 14.2 (CH_3, C-14).

HRMS (ESI$^+$): Calcd for $C_{14}H_{14}NO_3S$ $[M+H]^+$ 276.0689, found 276.0693.

$[\alpha]_D^{25}$ = -64.82 (c 0.218 g/100 mL, CH_2Cl_2).

1-(5-Phenyl-2*H*-1,4-thiazin-4(3*H*)-yl)ethanone (5c)



This product was isolated pure as white solid, R_f = 0.42, eluent (ethyl acetate / cyclohexane = 3/7), mp = 193–195 °C, was isolated in 96% yield.

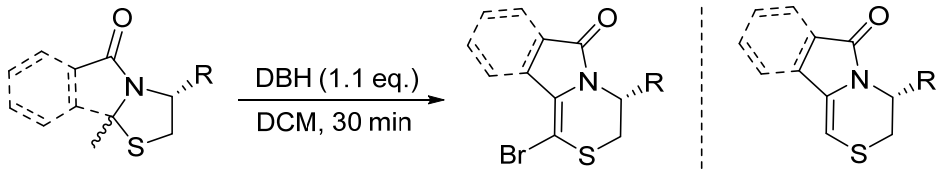
IR (ν_{max} / cm^{-1}): 1664, 1363, 1223, 946, 812, 756, 693.

^{1}H NMR (300 MHz, $CDCl_3$): δ_H 7.40 – 7.26 (m, 5H, Har), 6.15 (s, 1H, H-8), 4.03 – 3.93 (m, 2H, H-10), 3.16 – 3.08 (m, 2H, H-9), 1.70 (s, 3H, H-12).

^{13}C NMR (75 MHz, $CDCl_3$): δ_C 171.4 ($Cq_{C=O}$, C-11), 138.9 (Cq, C-7), 135.9 (Cq, C-6), 129.1 (x2 CH, C-2, C-4), 127.8 (CH, C-3), 124.6 (x2 CH, C-1, C-5), 113.2 (CH, C-8), 40.5 (CH_2, C-10), 28.4 (CH_2, C-9), 24.4 (CH_3, C-12).

HRMS (ESI$^+$): Calcd for $C_{12}H_{14}NOS$ $[M+H]^+$ 220.0791, found 220.0797.

IV. General procedure for the synthesis in domino process of bromothiazine compounds 7aB, 7bB and 7cB.



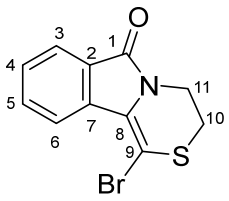
4a,b,c **7a,b,c(B)** **5a,b,c**

To 100 mg (1 eq.) of *N,S*-acetal substrate **4a**, **4b** or **4c**, described by our group in previous work, was dissolved in dry DCM (15 mL) and 1.1 equivalents of DBH was then added dropwise at room temperature and the reaction mixture was stirred for 30 minutes. After completion of the reaction (TLC), an aqueous solution of saturated sodium bicarbonate ($NaHCO_3$ 10 mL) was then added to quench the reaction. After three times extractions with DCM (3x10 mL), the organic layers were collected and dried on $MgSO_4$. The solvent was evaporated under reduced pressure and and a purification on flash chromatography (ethyl

acetate/cyclohexane = 4/6) was performed to provide the expected brominated compounds **7aB** (121 mg)**, 7bB** (108 mg) and **7cB** (91 mg) in an isolated yield of 88%, 85% and 55%, respectively.

Important remarks: Following the same protocol, but when 1.0 equivalent of *N*-bromosuccinimide (NBS) was used with *N,S*-acetal substrate **4a** (see the following details in **Table 1**), the brominated product **7aB** accompanied with the Morin-rearrangement compound **5a** were isolated in yields of 44% up to 56% yield, respectively. However, when 2.0 equivalents of *N*-bromosuccinimide (NBS) were used, only the Morin-rearrangement compound **5a** was isolated in 69% yield after 6 hours of the reaction (see details in **Table 1** and **entry 6**). Of interest, by using other conditions depending on the number of equivalents of NBS, we also isolate the Morin-rearrangement compounds **5b** and **5c** when starting with *N,S*-acetal substrates **4b** and **4c**, respectively.

1-Bromo-3,4-dihydro-6*H*-[1,4]thiazino[3,4-*a*]isoindol-6-one (7aB)



Yellow solid, R_f = 0.61, eluent (ethyl acetate / cyclohexane = 4/6), mp = 155–157 °C, 100 mg scale reaction (in 3 mL of dichloromethane), 121 mg was isolated, 88% yield.

IR (ν_{max} / cm^{-1}): 1677, 1352, 1032, 754, 682.

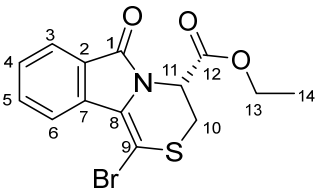
^{1}H NMR (300 MHz, $CDCl_3$): δ_H 8.44 (d, *J* = 7.9 Hz, 1H, H-6), 7.85 (d, *J* = 7.5 Hz, 1H, H-3), 7.60 (t, *J* = 7.2 Hz, 1H, H-5), 7.49 (t, *J* = 7.4 Hz, 1H, H-4), 4.26 – 4.19 (m, 2H, H-11), 3.26 – 3.18 (m, 2H, H-10).

^{13}C NMR (75 MHz, $CDCl_3$): δ_C 165.1 ($Cq_{C=O}$, C-1), 134.6 (Cq, C-7), 132.2 (CH, C-5), 129.1 (Cq, C-8), 129.0 (CH, C-4), 128.7 (Cq, C-2), 123.5 (CH, C-3), 123.4 (CH, C-6), 96.8 (Cq, C-9), 39.3 (CH_2, C-9), 30.0 (CH_2, C-10).

HRMS (ESI$^+$): Calcd for $C_{11}H_9BrNOS$ $[M+H]^+$ 281.9583, found 281.9596.

Ethyl (*R*)-1-bromo-6-oxo-3,4-dihydro-6*H*-[1,4]thiazino[3,4-*a*]isoindole-4-carboxylate (7bB)

Brown oil, R_f = 0.66, eluent (ethyl acetate / cyclohexane = 4/6), 100 mg scale (in 3 mL of dichloromethane), 108 mg was isolated, 85% yield.



IR (ν_{max} / cm^{-1}): 1747, 1687, 1193, 761, 691.

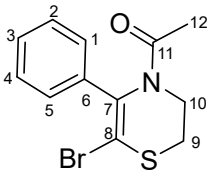
^{1}H NMR (300 MHz, $CDCl_3$): δ_H 8.46 (d, *J* = 8.0 Hz, 1H, H-6), 7.88 (d, *J* = 7.3 Hz, 1H, H-3), 7.63 (td, *J* = 7.7, 1.3 Hz, 1H, H-5), 7.51 (td, *J* = 7.5, 1.0 Hz, 1H, H-4), 5.60 (t, *J* = 3.3 Hz, 1H, H-11), 4.24 (q, *J* = 7.1 Hz, 2H, H-13), 3.55 – 3.43 (m, 2H, H-10), 1.26 (t, *J* = 7.1 Hz, 1H, H-14).

^{13}C NMR (75 MHz, $CDCl_3$): δ_C 167.5 ($Cq_{C=O}$, C-12), 165.2 ($Cq_{C=O}$, C-1), 134.9 (Cq, C-7), 132.6 (CH, C-5), 129.2 (CH, C-4), 128.6 (Cq, C-2), 128.2 (Cq, C-8), 123.8 (CH, C-3), 123.6 (CH, C-6), 95.6 (Cq, C-9), 62.6 (CH_2, C-13), 50.7 (CH, C-11), 31.6 (CH_2, C-10) 14.3 (CH_3, C-14).

HRMS (ESI$^+$): Calcd for $C_{14}H_{13}BrNO_3S$ $[M+H]^+$ 353.9794, found 353.9809.

$[\alpha]_D^{25}$= -177.8 (c 0.190 g/100 mL, CH_2Cl_2).

1-(6-Bromo-5-phenyl-2,3-dihydro-4*H*-1,4-thiazin-4-yl)ethan-1-one (7cB)



Yellow solid, R_f = 0.73, eluent (ethyl acetate / cyclohexane = 4/6), mp = 148–150 °C, 70 mg scale reaction (in 2 mL of dichloromethane), 64 mg was isolated, 55% yield.

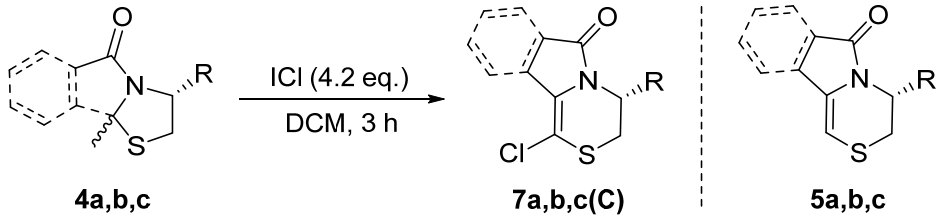
IR (ν_{max} / cm^{-1}): 1662, 1374, 1219, 779, 705.

^{1}H NMR (300 MHz, $CDCl_3$): δ_H 7.49 – 7.28 (m, 5H, Har), 4.10 (t, *J* = 5.8 Hz, 2H, H-10), 3.31 (t, *J* = 5.6 Hz, 2H, H-9), 1.61 (s, 3H, H-12).

^{13}C NMR (75 MHz, $CDCl_3$): δ_C 170.9 ($Cq_{C=O}$, C-11), 137.4 (Cq, C-6), 135.6 (Cq, C-7), 129.1 (x2 CH, C-2, C-4), 128.6 (CH, C-3), 128.3 (x2 CH, C-1, C-5), 109.6 (Cq, C-8), 41.6 (CH_2, C-10), 34.7 (CH_2, C-9), 24.2 (CH_3, C-12).

HRMS (ESI$^+$): Calcd for $C_{12}H_{13}BrNOS$ $[M+H]^+$ 297.9896, found 297.9915.

V. General procedure for the synthesis in domino process of chlorothiazine compounds 7aC, 7bC and 7cC.

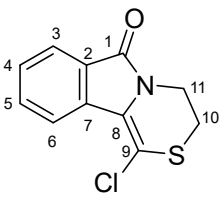


4a,b,c **7a,b,c(C)** **5a,b,c**

To 100 mg (1 eq.) of *N,S*-acetal substrate **4a**, **4b** or **4c**, described by our group in previous work, was dissolved in dry DCM (15 mL) and 4.2 equivalents of ICl (2.0 M solution of acetic acid) was then added dropwise at room temperature and the reaction mixture was stirred for 3 hours. After completion of the reaction (TLC), an aqueous solution of sodium thiosulfate ($Na_2S_2O_3$ 0.2 M, 10 mL) was then added to quench the reaction. After three times extractions with DCM (3x10 mL), the organic layers were collected and dried on $MgSO_4$. The solvent was evaporated under reduced pressure and and a purification on flash chromatography (ethyl acetate/cyclohexane = 4/6) was performed to provide the expected brominated compounds **7aC** (102 mg)**, 7bC** (102 mg) and **7cC** (87 mg) in an isolated yield of 88%, 91% and 54%, respectively.

Important remark: Following the same protocol, but when 1 equivalent of *N*-iodosuccinimide (ICl) was used (see the following details in **Table 1**), only the Morin-rearrangement compound **5a** was isolated in 96% yield. No reaction was conducted with *N,S*-acetal substrate **4b** or **4c** using these reaction conditions.

1-Chloro-3,4-dihydro-6*H*-[1,4]thiazino[3,4-*a*]-isoindol-6-one (7aC)



Yellow solid, R_f = 0.45, eluent (ethyl acetate / cyclohexane = 4/6), mp = 158–160 °C, 100 mg scale reaction (in 3 mL of dichloromethane), 102 mg was isolated, 88% yield.

IR (ν_{max} / cm^{-1}): 1678, 1352, 1034, 751, 685.

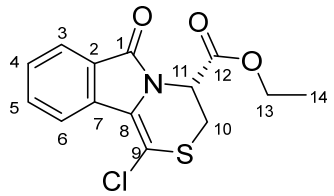
^{1}H NMR (300 MHz, $CDCl_3$): δ_H 8.24 (d, *J* = 7.9 Hz, 1H, H-6), 7.85 (d, *J* = 7.6 Hz, 1H, H-3), 7.59 (td, *J* = 7.6, 1.3 Hz, 1H, H-5), 7.47 (td, *J* = 7.5, 0.9 Hz, 1H, H-4), 4.18 – 4.13 (m, 2H, H-11), 3.26 – 3.20 (m, 2H, H-10).

^{13}C NMR (75 MHz, $CDCl_3$): δ_C 165.1 ($Cq_{C=O}$, C-1), 133.9 (Cq, C-7), 132.4 (CH, C-5), 128.9 (CH, C-4), 128.4 (Cq, C-2), 128.3 (Cq, C-8), 123.6 (CH, C-6), 123.5 (CH, C-3), 110.8 (Cq, C-9), 39.2 (CH_2, C-9), 29.0 (CH_2, C-10).

HRMS (ESI$^+$): Calcd for $C_{11}H_9ClNOS$ $[M+H]^+$ 238.0088, found 238.0098.

Ethyl (*R*)-1-chloro-6-oxo-3,4-dihydro-6*H*-[1,4]thiazino[3,4-*a*]isoindole-4-carboxylate (7bC)

Yellow oil, R_f = 0.64, eluent (ethyl acetate / cyclohexane = 4/6), 100 mg scale reaction (in 3 mL of dichloromethane), 102 mg was isolated, 91% yield.



IR (ν_{max} / cm^{-1}): 1747, 1693, 1199, 762, 692.

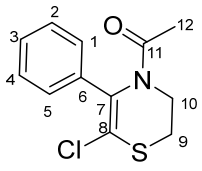
^{1}H NMR (300 MHz, $CDCl_3$): δ_H 8.24 (d, *J* = 8.0 Hz, 1H, H-6), 7.86 (d, *J* = 7.7 Hz, 1H, H-3), 7.60 (td, *J* = 7.9, 1.3 Hz, 1H, H-5), 7.48 (td, *J* = 7.5, 1.0 Hz, 1H, H-4), 5.50 (t, *J* = 3.3 Hz, 1H, H-11), 4.22 (q, *J* = 7.1 Hz, 2H, H-13), 3.54 (dd, *J* = 13.1, 3.0 Hz, 1H, H-10), 3.45 (dd, *J* = 13.2, 3.5 Hz, 1H, H-10), 1.24 (t, *J* = 7.1 Hz, 3H, H-14).

^{13}C NMR (75 MHz, $CDCl_3$): δ_C 167.4 ($Cq_{C=O}$, C-12), 165.1 ($Cq_{C=O}$, C-1), 134.1 (Cq, C-7), 132.8 (CH, C-5), 129.0 (CH, C-4), 127.9 (Cq, C-2), 127.8 (Cq, C-8), 123.7 (x2 CH, C-3, C-6), 109.7 (Cq, C-9), 62.5 (CH_2, C-13), 50.5 (CH, C-11), 30.7 (CH_2, C-10), 14.2 (CH_3, C-14).

HRMS (ESI$^+$): Calcd for $C_{14}H_{13}ClNO_3S$ $[M+H]^+$ 310.0299, found 310.0316.

$[\alpha]_D^{25}$= -160.8 (c 0.260 g/100 mL, CH_2Cl_2).

1-(6-Chloro-5-phenyl-2,3-dihydro-4*H*-1,4-thiazin-4-yl)ethan-1-one (7cC)



Yellow solid, R_f = 0.63, eluent (ethyl acetate / cyclohexane = 4/6), mp = 151–153 °C, 70 mg scale reaction (in 2 mL of dichloromethane), 61 mg was isolated, 54% yield.

IR (ν_{max} / cm^{-1}): 1659, 1371, 1218, 775, 705.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.50 – 7.28 (m, 5H, Har), 4.07 (t, *J* = 5.6 Hz, 2H, H-10), 3.51 – 3.18 (m, 2H, H-9), 1.63 (s, 3H, H-12).

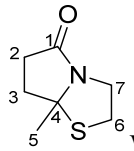
^{13}C NMR (75 MHz, $CDCl_3$): δ_C 171.2 ($Cq_{C=O}$, C-11), 136.2 (Cq, C-6), 134.1 (Cq, C-7), 128.8 (x2 CH, C-2, C-4), 128.6 (CH, C-3), 128.5 (x2 CH, C-1, C-5), 121.8 (Cq, C-8), 41.6 (CH_2, C-10), 33.5 (CH_2, C-9), 24.2 (CH_3, C-12).

HRMS (ESI$^+$): Calcd for $C_{12}H_{13}ClNOS$ $[M+H]^+$ 254.0401, found 254.0398.

VI. General procedure for the synthesis of 3,4-dihydro-6*H*-pyrrolo[2,1-*c*][1,4]thiazin-6-one (9) and 8-bromo-3,4-dihydro-6*H*-pyrrolo[2,1-*c*][1,4]thiazin-6-one (7dB).

Step 1: 7*a*-Methyltetrahydropyrrolo[2,1-*b*]thiazol-5(6*H*)-one (4d)

To a stirred solution of Levulinic acid, or 4-oxopentanoic acid (2.32 g, 20 mmol) and PTSA (0.35 g, 2 mmol, 0.1 eq.) in toluene (50 mL), was added the aminothiol (1.18 g, 24 mmol, 1.2 eq.) and the mixture was heated at 110 °C for 16 h. After cooling at room temperature, the solvent was evaporated and purification on flash chromatography was performed to get the corresponding *N,S*-acetal **4d** in only 37% yield.



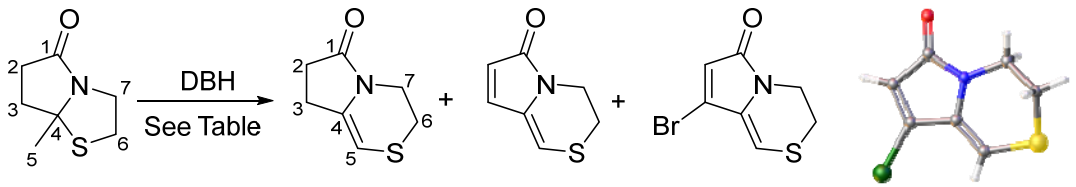
White solid, R_f = 0.32, eluent (ethyl acetate / cyclohexane = 3/7), mp = 42–44 °C, 2.32 g scale reaction (in 50 mL of toluene), 1.151 g was isolated, 37% yield.

IR (ν_{max} / cm^{-1}): 1695, 1349, 1174, 826.

^{1}H NMR (300 MHz, $CDCl_3$): δ_H 4.43 – 4.24 (m, 1H), 3.19 – 2.89 (m, 3H), 2.71 – 2.28 (m, 3H), 2.28 – 2.03 (m, 1H), 1.60 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ_C 177.1, 77.2, 43.2, 33.4, 32.7, 31.5, 31.3.
HRMS (ESI$^+$): Calcd for $C_7H_{12}NOS$ $[M+H]^+$ 158.0634, found 158.0636.

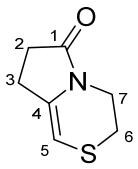
Step 2: *N,S*-Acetal substrate **4d** (50 mg, 0.318 mmol) was dissolved in DCM, then DBH (see number of equivalents in the table below) was added and the reaction mixture was stirred during 30 min. After that, a saturated solution of $NaHCO_3$ (2 x 10 mL) was added and a three times extraction with DCM was done. After drying the combined organic layers on dry Mg_2SO_4 and evaporation of solvent under reduced pressure, the compounds **4d**, **9**, **19** or **7dB** were recovered after a flash chromatography depending on the number of equivalents of DBH used (for details, see the following Table.



Entry	DBH (numer of equivalents)	Time	Products **4d/9/10/7dB** (in %)[a]
1	0.55	30 min	10/26/00/00
2	0.70	30 min	00/39/18/00
3	1.10	30 min	00/04/72/12
4	1.40	30 min	00/00/21/41
5	1.60	30 min	00/00/24/56
6	2.00	30 min	Complex mixture

[a] Estimated yield after flash chromatography.

7,8-Dihydro-3*H*-pyrrolo[2,1-*c*][1,4]thiazin-6(4*H*)-one (9): Morin product



White solid, R_f = 0.18, eluent (ethyl acetate / cyclohexane = 3/7), mp = 49–51 °C 100 mg scale reaction (in 3 mL of dioxane) for 3 h, 11 mg was isolated, 11% yield.

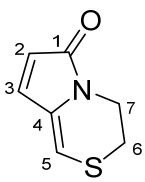
IR (ν_{max} / cm^{-1}): 1645, 1402, 1353, 867.

^{1}H NMR (300 MHz, $CDCl_3$): δ_H 5.02 (s, 1H, H-5), 3.96 – 3.84 (m, 2H, H-7), 2.91 – 2.83 (m, 2H, H-6), 2.77 – 2.69 (m, 2H, H-2), 2.52 – 2.44 (m, 2H, H-3).

^{13}C NMR (75 MHz, $CDCl_3$): δ_C 175.0 ($Cq_{C=O}$, C-1), 134.7 (Cq, C-4), 89.2 (CH, C-5), 41.1 (CH_2, C-7), 28.9 (CH_2, C-3), 24.3 (CH_2, C-2), 24.1 (CH_2, C-6).

HRMS (ESI$^+$): Calcd for $C_7H_{10}NOS$ $[M+H]^+$ 156.0478, found 156.0483.

3,4-Dihydro-6*H*-pyrrolo[2,1-*c*][1,4]thiazin-6-one (10): Oxidized Morin product



Colored patous product, R_f = 0.32 eluent (ethyl acetate / cyclohexane = 3/7). Only few amounts of this product were isolated pure after many separations by flash chromatography on silica gel column.

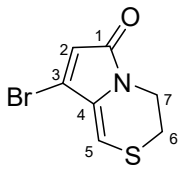
IR (ν_{max} / cm^{-1}): 1654, 1406, 1351, 868.

^{1}H NMR (300 MHz, $CDCl_3$): δ_H 6.83 (d, J = 5.6 Hz, 1H, H-2), 6.03 (s, 1H, H-5), 5.99 (d, J = 5.7 Hz, 1H, H-3), 3.95 – 3.84 (m, 2H, H-7), 3.08 – 2.97 (m, 2H, H-6).

^{13}C NMR (75 MHz, $CDCl_3$): δ_C 168.9 ($Cq_{C=O}$, C-1), 134.7 (Cq, C-4), 133.1 (CH, C-3), 121.0 (CH, C-2), 108.8 (CH, C-5), 38.1 (CH_2, C-7), 26.4 (CH_2, C-6).

HRMS (ESI$^+$): Calcd for C_7H_8NOS $[M+H]^+$ 154.0321, found 154.0319.

8-Bromo-3,4-dihydro-6*H*-pyrrolo[2,1-*c*][1,4]thiazin-6-one (7dB)



Yellow solid, R_f = 0.56 eluent (ethyl acetate / cyclohexane = 3/7), mp = 127–129 °C (decomposition).

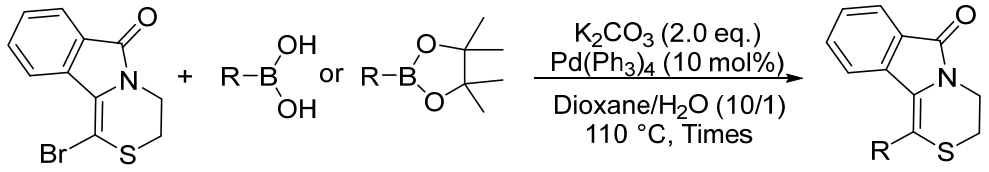
IR (ν_{max} / cm^{-1}): 1699, 1314, 1062, 786.

^{1}H NMR (300 MHz, $CDCl_3$): δ_H 6.33 (s, 1H, H-5), 6.26 (s, 1H, H-2), 4.00 – 3.93 (m, 2H, H-7), 3.12 – 3.04 (m, 2H, H-8).

^{13}C NMR (75 MHz, $CDCl_3$): δ_C 166.9 ($Cq_{C=O}$, C-1), 133.6 (Cq, C-4), 126.0 (Cq, C-3), 122.0 (CH, C-2), 109.8 (CH, C-5), 38.4 (CH_2, C-7), 26.4 (CH_2, C-6).

HRMS (ESI$^+$): Calcd for C_7H_7BrNOS $[M+H]^+$ 231.9426, found 231.9425.

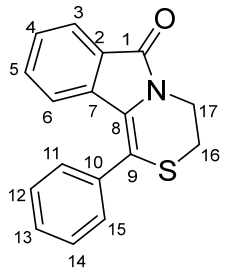
VII. General procedure for the synthesis of 3,4-dihydro-6*H*-pyrrolo[2,1-*c*][1,4]thiazin-6-ones (8a-n, q) by the Suzuki-Miyaura coupling of halogenated substrate 7aB and boronic acids or esters (16).



The reactions were carried out in sealed tubes. Thus, bromothiazine compound **7aB** (100 mg, 0.36 mmol) was dissolved in 4 mL of toluene or dioxane and 0.4 mL of water. To this solution, boronic acid or boronic acid ester (1.1 eq.), K_2CO_3 (98.4 mg, 2.0 eq.) and tetrakis-(triphenylphosphine)-palladium(0) ($Pd(Ph_3)_4$, , 41.1 mg, 10 mol%) were added under stirring and argon atmosphere. The reaction mixture was stirred at 110 °C and the reaction was monitored by NMR ^{1}H. After completion of the reaction (7 up to 21 hours), direct purification of the crude by flash chromatography by using the mixture of ethyl acetate/ cyclohexane = 3/7 up to 4/6 was performed to furnish the expected arylated thiazines **8a-n** in yields ranging from 55% up to 99%. With 2-furanylboronic acid (**16i**), the product **8i** obtained partially decomposed during attempts of purification. When allylboronic acid pinacol ester (**16o**) or *n*-butylboronic acid *(***16p***)* were used, the reaction conditions have not allowed to furnish the coupling products **8o** and **8p** and only traces were detected even if the reaction time is extended up to 21 hours.

1-Phenyl-3*H*-[1,4]thiazino[3,4-*a*]isoindol-6(4*H*)-one (8a)

Yellow solid, R_f = 0.34, eluent (ethyl acetate / cyclohexane = 3/7), mp= 89–91 °C, 100 mg scale reaction (in 3 mL of dioxane) for 3 h, 77 mg was isolated, 78% yield.



IR (ν_{max} / cm^{-1}): 1690, 1196, 749.

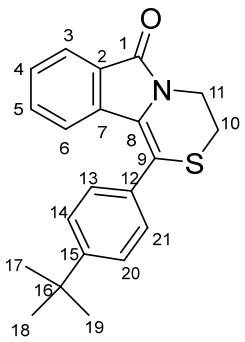
^{1}H NMR (300 MHz, $CDCl_3$): δ_H 7.81 (d, *J* = 7.6 Hz, 1H, H-3), 7.59 – 7.41 (m, 5H, Har), 7.30 (t, *J* = 7.4 Hz, 1H, H-4), 7.18 (td, *J* = 7.9, 1.3 Hz, 1H, H-5), 6.59 (d, *J* = 7.9 Hz, 1H, H-6), 4.36 – 4.13 (m, 2H, H-17), 3.31 – 3.14 (m, 2H, H-18).

^{13}C NMR (75 MHz, $CDCl_3$): δ_C 165.7 ($Cq_{C=O}$, C-1), 136.3 (Cq, C-8), 134.6 (Cq, C-8), 131.4 (CH, C-5), 130.4 (x2 C-12, C-14), 129.5 (CH, Car), 129.0 (x2 C-11, C-15), 128.4 (Cq, Car), 127.8 (CH, C-4), 126.7 (CH, Car), 123.0 (CH, C-3), 121.9 (CH, C-6), 119.5 (Cq, C-9), 39.2 (CH_2, C-17), 27.7 (CH_2, C-16).

HRMS (ESI$^+$): Calcd for $C_{17}H_{14}NOS$ $[M+H]^+$ 280.0791, found 280.0712.

The physicochemical characteristics of this product ware identical to the one synthesized before by our group and reported in the following reference by direct *N,S*-acetal transposition: F. Danton, M. Othman, A. M. Lawson, J. Moncol, A. Ghinet, B. Rigo, A. Daïch, *Chem. Eur. J.* **2019**, *25*, 6113–6118.

1-(4-(*Tert*-butyl)phenyl)-3,4-dihydro-6*H*-[1,4]thiazino[3,4-*a*]isoindol-6-one (8b)



Yellow solid, R_f = 0.63, eluent (ethyl acetate / cyclohexane = 4/6), mp = 190–192 °C, 50 mg scale reaction, 43 mg was isolated, 72% yield.

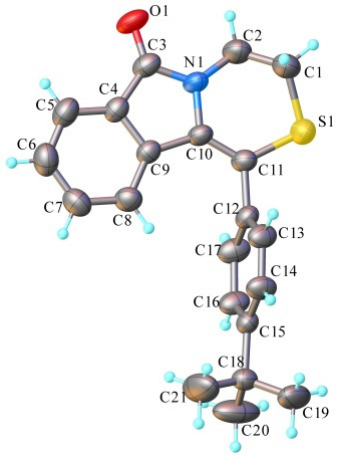
IR (ν_{max} / cm^{-1}): 1679, 1355, 1296, 976, 760, 694.

^{1}H NMR (300 MHz, $CDCl_3$): δ_H 7.81 (d, *J* = 7.5 Hz, 1H, H-3), 7.53 – 7.39 (m, 4H, Har), 7.35 – 7.27 (td, *J* = 7.6, 1.3 Hz, 1H, H-4), 7.21 (td, *J* = 7.6, 1.3 Hz, 1H, H-5), 6.67 (d, *J* = 7.8 Hz, 1H, H-6), 4.38 – 4.16 (m, 2H, H-11), 3.33 – 3.14 (m, 2H, H-10), 1.39 (s, 9H, H-17, H-18, H-19).

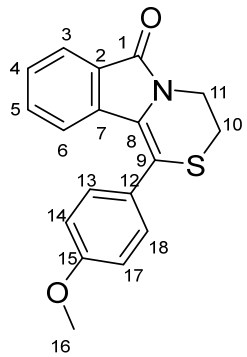
^{13}C NMR (75 MHz, $CDCl_3$): δ_C 165.7 (Cq $_{C=O}$, C-1), 152.8 (Cq, C-12), 134.7 (Cq, C-7), 133.2 (Cq, C-15), 131.4 (CH, C-5), 130.0 (x2 CH, C-13, C-21), 128.4 (Cq, C-2), 127.7 (CH, C-4), 126.6 (Cq, C-8), 126.0 (x2 CH, C-14, C-20), 123.0 (CH, C-3), 122.0 (CH, C-6), 119.9 (Cq, C-9), 39.2 (CH_2, C-11), 35.0 (Cq, C-16), 31.5 (3x CH_3, C-17, C-18, C-19), 27.7 (CH_2, C-10).

HRMS (ESI$^+$): Calcd for $C_{21}H_{22}NOS$ $[M+H]^+$ 336.1417, found 336.1432.

X-ray of compound **8b**: CCDC 2433572



1-(4-Methoxyphenyl)-3,4-dihydro-6*H*-[1,4]thiazino[3,4-*a*]isoindol-6-one (8c)



Yellow solid, R_f = 0.43, eluent (ethyl acetate / cyclohexane = 4/6), mp = 182–184 °C, 50 mg scale reaction, 39 mg was isolated, 70% yield.

IR (ν_{max} / cm^{-1}): 1698, 1349, 1244, 974, 761, 692.

^{1}H NMR (300 MHz, $CDCl_3$): δ_H 7.81 (d, *J* = 7.5 Hz, 1H, H-3), 7.43 (d, *J* = 8.7 Hz, 2H, H-13, H-18), 7.31 (td, *J* = 7.5, 1.0 Hz, 1H, H-4), 7.21 (td, *J* = 7.6, 1.3 Hz, 1H, H-5), 6.98 (d, *J* = 8.7 Hz, 2H, H-14, H-17), 6.71 (d, *J* = 7.7 Hz, 1H, H-6), 4.29 – 4.19 (m, 2H, H-11), 3.88 (s, 3H, H-16), 3.25 – 3.17 (m, 1H, H-10).

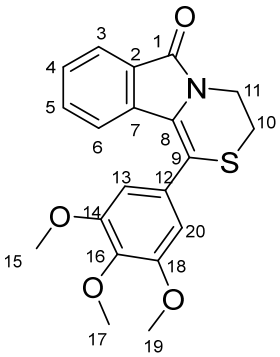
^{13}C NMR (75 MHz, $CDCl_3$): δ_C 165.7 ($Cq_{C=O}$, C-1), 160.6 ($Cq_{C=O}$, C-15), 134.6 (Cq, C-7), 131.7 (CH, C-5), 131.4 (x2 CH, C-13, C-18), 128.3 (Cq, C-12), 128.3 (Cq, C-2), 127.7 (CH, C-4), 126.5 (Cq, C-8), 123.0 (CH, C-3), 121.9 (CH, C-6), 119.7 (Cq, C-9), 114.4 (x2 CH, C-14, C-17), 55.5 (CH_3, C-16), 39.2 (CH_2, C-11), 27.7 (CH_2, C-10).

HRMS (ESI$^+$): Calcd for $C_{18}H_{16}NO_2S$ $[M+H]^+$ 310.0896, found 310.0905.

1-(3,4,5-Trimethoxyphenyl)-3,4-dihydro-6*H*-[1,4]thiazino[3,4-*a*]isoindol-6-one (8d)

Yellow solid, R_f = 0.30, eluent (ethyl acetate / cyclohexane = 4/6), mp = 153–155 °C, 50 mg scale reaction, 59 mg was isolated, 78% yield.

IR (ν_{max} / cm^{-1}): 1676, 1328, 1234, 947, 755, 692.

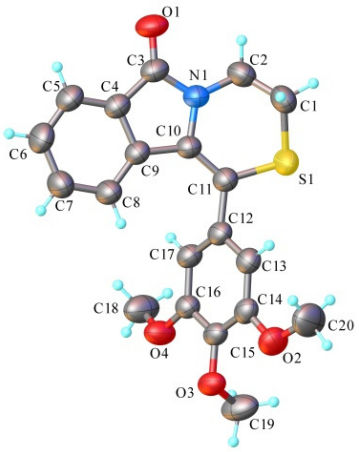


^{1}H NMR (300 MHz, CDCl$_3$): δ_H 7.82 (d, *J* = 7.4 Hz, 1H, H-3), 7.33 (td, *J* = 7.4, 1.1 Hz, 1H, H-4), 7.32 – 7.19 (m, 1H, H-5), 6.78 (d, *J* = 7.8 Hz, 1H, H-6), 6.74 (s, 2H, H-13, H-20), 4.27 – 4.22 (m, 2H, H-11), 3.94 (s, 3H, H-17), 3.84 (s, 6H, H-15, H-19), 3.25 – 3.20 (m, 2H, H-10).

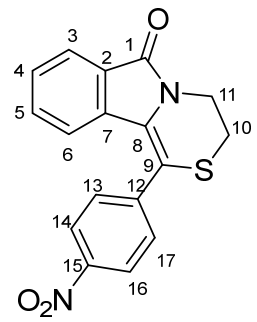
^{13}C NMR (75 MHz, CDCl$_3$): δ_C 165.7 (Cq$_{C=O}$, C-1), 153.7 (Cq, C-15), 139.0 (Cq, C-14, C-18), 134.5 (Cq, C-7), 131.6 (Cq, C-12), 131.5 (CH, C-5), 128.4 (Cq, C-2), 128.0 (CH, C-4), 126.7 (Cq, C-8), 123.1 (CH, C-3), 122.2 (CH, C-6), 119.4 (Cq, C-9), 107.3 (2x CH, C-13, C-20), 61.2 (CH_3, C-17), 56.4 (2x CH3, C-15, C-19), 39.2 (CH_2, C-9), 27.7 (CH_2, C-10).

HRMS (ESI$^+$): Calcd for $C_{20}H_{20}NO_4S$ $[M+H]^+$ 370.1108, found 370.1116.

X-ray of compound **8d**: CCDC 2433573



1-(4-Nitrophenyl)-3,4-dihydro-6*H*-[1,4]thiazino[3,4-a]isoindol-6-one (8e)



Red solid, R_f = 0.45, eluent (ethyl acetate / cyclohexane = 4/6), mp = 262–264 °C, 50 mg scale reaction (in 60 mL of toluene), 45 mg was isolated, 78% yield.

IR (ν_{max} / cm^{-1}): 1688, 1338, 1259, 971, 763, 691.

^{1}H NMR (300 MHz, CDCl$_3$): δ_H 8.34 (d, *J* = 8.8 Hz, 2H, H-14, H-16), 7.84 (d, *J* = 7.6 Hz, 1H, H-3), 7.74 (d, *J* = 8.7 Hz, 2H, H-13, H-17), 7.38 (t, *J* = 7.4 Hz, 1H, H-4), 7.27 – 7.21 (m, 1H, H-5), 6.63 (d, *J* = 7.9 Hz, 1H, H-6), 4.35 – 4.22 (m, 2H, H-11), 3.34 – 3.22 (m, 2H, H-10).

^{13}C NMR (75 MHz, CDCl$_3$): δ_C 165.7 (Cq$_{C=O}$, C-1), 148.4 (Cq, C-15), 143.3 (Cq, C-12), 134.1 (Cq, C-7), 131.8 (2x CH, C-13, C-17), 131.7 (CH, C-5), 128.7 (Cq, C-8), 128.5 (CH, C-4), 127.9 (Cq, C-2), 124.3 (2x CH, C-14, C-16), 123.5 (CH, C-3), 121.7 (CH, C-6), 116.3, 100.1 (Cq, C-9), 39.3 (CH_2, C-11), 27.6 (CH_2, C-10).

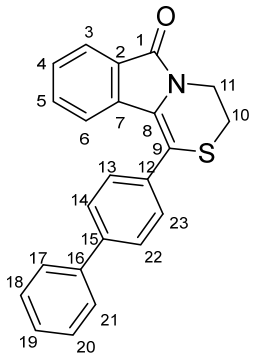
HRMS (ESI$^+$): Calcd for $C_{17}H_{13}N_2O_3S$ $[M+H]^+$ 325.0641, found 325.0651.

1-([1,1'-Biphenyl]-4-yl)-3,4-dihydro-6*H*-[1,4]thiazino[3,4-*a*]isoindol-6-one (8f)

Yellow solid, R_f = 0.64, eluent (ethyl acetate / cyclohexane = 4/6), mp = 228–230 °C, 50 mg scale reaction, 59 mg was isolated, 93% yield.

IR (ν_{max} / cm^{-1}): 1691, 1357, 1240, 974, 760, 693.

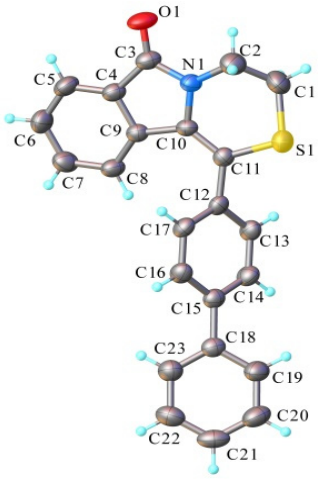
^{1}H NMR (300 MHz, $CDCl_3$): δ_H 7.84 (d, *J* = 7.5 Hz, 1H, H-3), 7.71 (t, *J* = 7.8 Hz, 4H, H-13, H-14, H-22, H-23), 7.61 (d, *J* = 8.0 Hz, 2H, H-17, H-21), 7.50 (t, *J* = 7.5 Hz, 2H, H-18, H-20), 7.40 (t, *J* = 7.3 Hz, 1H, H-19), 7.33 (t, *J* = 7.4 Hz, 1H, H-4), 7.22 (t, *J* = 7.5 Hz, 1H, H-5), 6.79 (d, *J* = 7.9 Hz, 1H, H-6), 4.36 – 4.20 (m, 2H, H-11), 3.34 – 3.19 (m, 2H, H-10).



^{13}C NMR (75 MHz, $CDCl_3$): δ_C 165.7 (Cq $_{C=O}$, C-1), 142.2 (Cq, C-15), 140.2 (Cq, C-16), 135.2 (Cq, C-12), 134.6 (Cq, C-8), 131.5 (CH, C-5), 130.9 (x2 CH, C-18, C-20), 129.1 (x2 CH, C-13, C-23), 128.4 (Cq, C-7), 127.9 (Cq, C-2), 127.9 (CH, C-4), 127.6 (x2 CH, C-17, C-21), 127.2 (x2 CH, C-14, C-22), 126.8 (Cq, C-8), 123.1 (CH, C-3), 122.0 (CH, C-6), 119.3 (Cq, C-10), 39.2 (CH_2, C-11), 27.7 (CH_2, C-10).

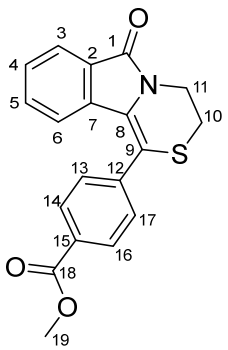
HRMS (ESI$^+$): Calcd for $C_{23}H_{18}NOS$ $[M+H]^+$ 356.1104, found 356.1118.

X-ray of compound **8f**: CCDC 2433574



Methyl 4-(6-oxo-3,4-dihydro-6*H*-[1,4]thiazino[3,4-*a*]isoindol-1-yl)benzoate (8g)

Yellow solid, R_f = 0.43, eluent (ethyl acetate / cyclohexane = 4/6), mp = 200–202 °C, 50 mg scale reaction, 44 mg was isolated, 74% yield.



IR (ν_{max} / cm^{-1}): 1686, 1357, 1219, 760, 691.

^{1}H NMR (300 MHz, $CDCl_3$): δ_H 8.14 (d, *J* = 8.4 Hz, 2H, H-14, H-15), 7.82 (d, *J* = 7.5 Hz, 1H, H-3), 7.62 (d, *J* = 8.4 Hz, 2H, H-13, H-19), 7.33 (td, *J* = 7.4, 0.9 Hz, 1H, H-4), 7.20 (td, *J* = 7.7, 1.2 Hz, 1H, H-5), 6.61 (d, *J* = 7.9 Hz, 1H, H-6), 4.35 – 4.17 (m, 2H, H-11), 3.97 (s, 3H, H-17), 3.31 – 3.16 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$): δ_C 166.7 ($Cq_{C=O}$, C-18), 165.8 ($Cq_{C=O}$, C-1), 141.1 (Cq, C-15), 134.3 (Cq, C-12), 131.6 (Cq, C-7), 131.0 (CH, C-5), 130.6 (2xCH, C-13, C-17), 130.3 (2xCH, C-14, C-16), 128.4 (Cq, C-8), 128.3 (CH, C-4), 127.2 (Cq,

C-2), 123.2 (CH, C-3), 121.9 (CH, C-6), 118.0 (Cq, C-9), 52.5 (CH_3, C-19), 39.3 (CH_2, C-11), 27.6 (CH_2, C-10).

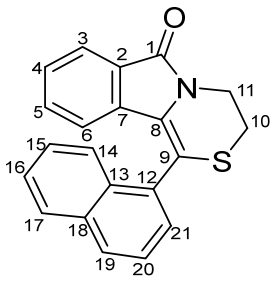
HRMS (ESI$^+$): Calcd for $C_{19}H_{15}NO_3S$ $[M+H]^+$ 338.0845, found 338.0852.

1-(Naphthalen-1-yl)-3,4-dihydro-6*H*-[1,4]thiazino[3,4-*a*]isoindol-6-one (8h)

Yellow solid, R_f = 0.39, eluent (ethyl acetate / cyclohexane = 3/7), mp = 175–177 °C, 50 mg scale reaction, 55 mg was isolated, 94% yield.

IR (ν_{max} / cm^{-1}): 1694, 1355, 1238, 966, 763, 691.

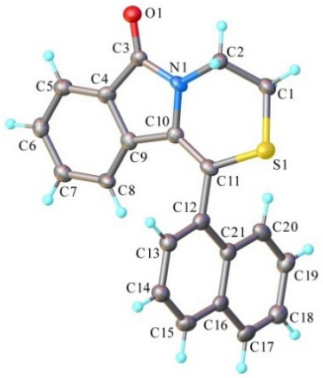
^{1}H NMR (300 MHz, $CDCl_3$): δ_H 8.04 – 7.90 (m, 3H, H-14, H-17, H-19), 7.80 (d, *J* = 7.6 Hz, 1H, H-3), 7.62 – 7.55 (m, 2H, Har), 7.55 – 7.49 (m, 1H, Har), 7.49 – 7.42 (m, 1H, Har), 7.26 – 7.19 (m, 1H, H-4), 7.03 – 6.93 (m, 1H, H-5), 5.93 (d, *J* = 7.9 Hz, 1H, H-6), 4.45 (ddd, *J* = 13.4, 6.3, 3.7 Hz, 1H, H-11), 4.29 (ddd, *J* = 13.4, 7.3, 3.8 Hz, 1H, H-11), 3.47 – 3.26 (m, 2H, H-10).



^{13}C NMR (75 MHz, $CDCl_3$): δ_C 166.0 ($Cq_{C=O}$, C-1), 134.4 (Cq, C-7), 134.0 (Cq, Car), 133.5 (Cq, Car), 131.9 (Cq, Car), 131.7 (CH, C-5), 129.9 (CH, Car), 128.7 (CH, Car), 128.6 (CH, Car), 128.4 (Cq, C-8), 128.3 (Cq, C-2), 127.9 (CH, C-4), 127.1 (CH, Car), 126.7 (CH, Car), 125.9 (CH, Car), 125.2 (CH, Car), 123.0 (CH, C-3), 122.1 (CH, C-6), 116.3 (Cq, C-9), 39.4 (CH_2, C-9), 27.8 (CH_2, C-10).

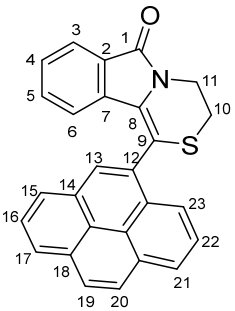
HRMS (ESI$^+$): Calcd for $C_{21}H_{16}NOS$ $[M+H]^+$ 330.0947, found 330.096.

X-ray of compound **8h**: CCDC 2433575



1-(Pyren-4-yl)-3,4-dihydro-6*H*-[1,4]thiazino[3,4-*a*]isoindol-6-one (8i)

Yellow solid, R_f = 0.62, eluent (ethyl acetate / cyclohexane = 4/6), mp = 279–281 °C, 50 mg scale reaction, 56 mg was isolated, 79% yield.



IR (ν_{max} / cm^{-1}): 1678, 1355, 1244, 980, 727, 695.

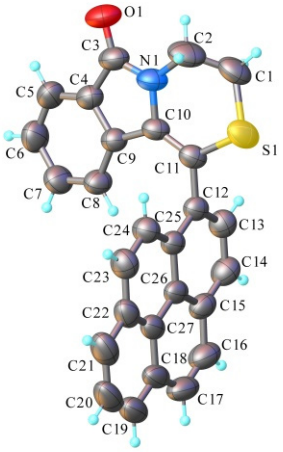
^{1}H NMR (300 MHz, $CDCl_3$): δ_H 8.33 – 8.17 (m, 3H, Har), 8.22 – 8.09 (m, 3H, Har), 8.13 – 7.98 (m, 3H, Har), 7.81 (d, *J* = 7.6 Hz, 1H, H-3), 7.19 (t, *J* = 7.5 Hz, 1H, H-4), 6.81 (t, *J* = 7.7 Hz, 1H, H-5), 5.71 (d, *J* = 8.0 Hz, 1H, H-6), 4.44 (t, *J* = 5.2 Hz, 2H, H-11), 3.43 (q, *J* = 4.6 Hz, 2H, H-10).

^{13}C NMR (75 MHz, $CDCl_3$): δ_C 166.0 ($Cq_{C=O}$, C-1), 134.4 (Cq, C-7), 132.2 (Cq, Car), 131.7 (CH, C-5), 131.3 (Cq, Car), 131.1 (Cq, Car), 130.4 (Cq, Car), 130.0 (Cq, Car), 128.8 (Cq, C-8), 128.6 (x2 Cq, Car; CH, Car), 128.4 (CH, Car), 128.4

(Cq, C-2), 127.9 (CH, C-4), 127.4 (CH, Car), 126.5 (CH, Car), 125.8 (CH, Car), 125.8 (CH, Car), 125.3 (Cq, Car), 125.1 (Cq, Car), 124.8 (Cq, Car), 124.4 (CH, Car), 123.0 (CH, C-3), 121.9 (CH, C-6), 116.9 (Cq, C-10), 39.4 (CH_2, C-9), 28.0 (CH_2, C-10).

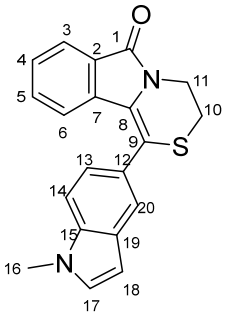
HRMS (ESI$^+$): Calcd for $C_{27}H_{18}NOS$ $[M+H]^+$ 404.1104, found 404.1119.

X-ray of compound **8i**: CCDC 2433576



1-(1-Methyl-1H-indol-5-yl)-3,4-dihydro-6*H*-[1,4]thiazino[3,4-*a*]isoindol-6-one (8k)

Yellow solid, R_f = 0.27, eluent (ethyl acetate / cyclohexane = 3/7), mp = 238–240 °C, 50 mg scale reaction, 45 mg was isolated, 55% yield.



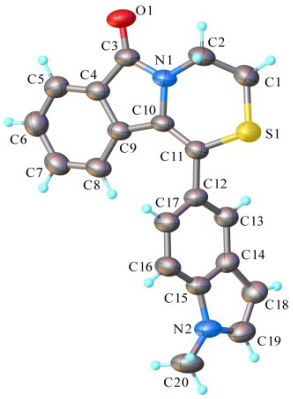
IR (ν_{max} / cm^{-1}): 1671, 1353, 1241, 980, 763, 693.

^{1}H NMR (300 MHz, $CDCl_3$): δ_H 7.85 – 7.78 (m, 2H, H-3, H-20), 7.41 (d, *J* = 8.5 Hz, 1H, H-14), 7.35 (dd, *J* = 8.5, 1.6 Hz, 1H, H-13), 7.34 – 7.24 (m, 1H, H-4), 7.17 – 7.07 (m, 2H, H-5, H-17), 6.61 (d, *J* = 7.9 Hz, 1H, H, H-6), 6.54 (d, *J* = 3.0 Hz, 1H, H-18), 4.29 (q, *J* = 4.8 Hz, 2H), 3.87 (s, 3H), 3.26 (t, *J* = 5.2 Hz, 2H).

^{13}C NMR (75 MHz, $CDCl_3$): δ_C 165.7 ($Cq_{C=O}$, C-1), 137.2 (Cq, C-15), 134.9 (Cq, C-7), 131.3 (CH, C-5), 130.1 (CH, C-17), 128.8 (Cq, C-15), 128.3 (Cq, C-2), 127.5 (CH, C-4), 127.0 (Cq, C-12), 126.4 (Cq, C-8), 123.8 (CH, C-13), 123.1 (CH, C-20), 122.9 (CH, C-3), 122.1 (CH, C-6), 121.7, 109.8 (CH, C-14), 101.8 (CH, C-18), 39.3 (CH_2, C-11), 33.2 (CH_3, C-16), 28.0 (CH_2, C-10).

HRMS (ESI$^+$): Calcd for $C_{20}H_{17}N_2OS$ $[M+H]^+$ 333.1056, found 333.1072.

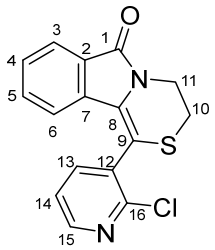
X-ray of compound **8k**: CCDC 2433577



1-(6-Chloropyridin-2-yl)-3,4-dihydro-6*H*-[1,4]thiazino[3,4-*a*]isoindol-6-one (8l)

Yellow solid, R_f = 0.54, eluent (ethyl acetate / cyclohexane = 4/6), mp = 185–187 °C, 50 mg scale reaction, 30 mg was isolated, 54% yield.

IR (ν_{max} / cm^{-1}): 1685, 1355, 1237, 973, 767, 696.

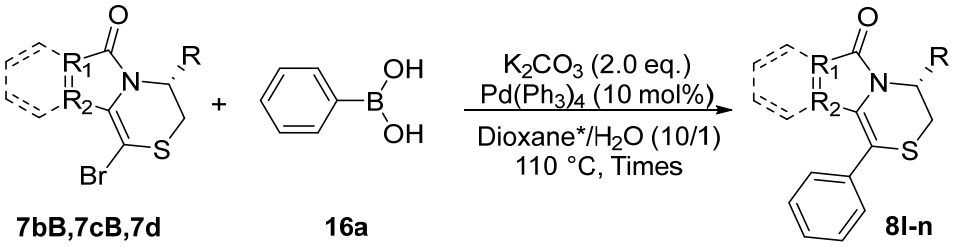


^{1}H NMR (300 MHz, $CDCl_3$): δ_H 8.56 (dd, *J* = 4.8, 2.0 Hz, 1H, H-15), 7.87 – 7.77 (m, 2H, H-3, H-16), 7.43 – 7.33 (m, 2H, H-4, H-14), 7.28 – 7.20 (m, 1H, H-5), 6.28 (d, *J* = 7.8 Hz, 1H, H-6), 4.36 (ddd, *J* = 13.5, 6.1, 3.7 Hz, 1H, H-11), 4.19 (ddd, *J* = 13.4, 7.1, 4.0 Hz, 1H, H-11), 3.37 – 3.20 (m, 2H, H-10).

^{13}C NMR (75 MHz, $CDCl_3$): δ_C 165.9 ($Cq_{C=O}$, C-1), 151.8 (Cq, C-12), 150.5 (CH, C-15), 141.2 (CH, C-13), 134.1 (Cq, C-7), 132.1 (CH, C-5), 131.8 (Cq, C-16), 129.0 (Cq, C-8), 128.6 (CH, C-4), 128.4 (Cq, C-2), 123.4 (CH, C-3), 123.0 (CH, C-14), 121.3 (CH, C-6), 112.4 (Cq, C-9), 39.4 (CH_2, C-11), 27.5 (CH_2, C-10).

HRMS (ESI$^+$): Calcd for $C_{16}H_{12}ClN_2OS$ $[M+H]^+$ 315.0353, found 315.0365.

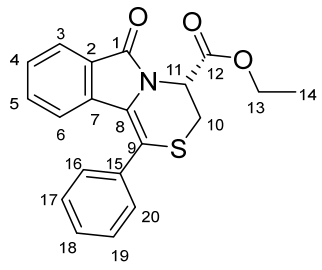
VIII. General procedure for the synthesis of 3,4-dihydro-6*H*-pyrrolo[2,1-*c*][1,4]thiazin-6-ones (8l-n) by the Suzuki-Miyaura coupling of halogenated substrate 7bB, 7cB or 7dB and phenylboronic acid (16a).



7bB,7cB,7d **16a** **8l-n**

The experimental procedure used herein with **7bB**, **7cB** and **7dB** as starting materials is same as the one drecibed before starting from the bromothiazine compound **7aB**.

Ethyl (*R*)-6-oxo-1-phenyl-3,4-dihydro-6*H*-[1,4]thiazino[3,4-*a*]isoindole-4-carboxylate (8m)



Yellow solid, R_f = 0.61, eluent (ethyl acetate / cyclohexane = 4/6), mp = 181–183 °C, 50 mg scale reaction in toluene, 30 mg was isolated, 60% yield.

*This reaction was performed in toluene instead of dioxane.

IR (ν_{max} / cm^{-1}): 1740, 1701, 1206, 1018, 748, 698.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.84 (d, *J* = 7.5 Hz, 1H, H-3), 7.45 (dt, *J* = 15.7, 7.9 Hz, 5H, Har), 7.33 (t, *J* = 7.4 Hz, 1H, H-4), 7.25 – 7.18 (m, 1H, H-5), 6.62 (d, *J* = 7.9 Hz, 1H, H-6), 5.62 (t, *J* = 3.3 Hz, 1H, H-11), 4.42 – 4.13 (m, 2H, H-13), 3.59 (dd, *J* = 13.0, 3.1 Hz, 1H, H-10), 3.44 (dd, *J* = 13.0, 3.6 Hz, 1H, H-10), 1.27 (t, *J* = 7.1 Hz, 3H, H-14).

^{13}C NMR (75 MHz, $CDCl_3$): δ_C 167.9 ($Cq_{C=O}$, C-12), 165.9 ($Cq_{C=O}$, C-1), 135.9 (Cq, C-15), 134.9 (Cq, C-7), 131.8 (CH, C-5), 130.6 (CH, Car), 130.1 (CH, Car), 129.6 (CH, Car), 129.3 (CH, Car), 128.8 (CH, Car), 128.0 (CH, C-4), 128.0 (Cq, Car), 126.2 (Cq, C-8), 123.4 (CH, C-3), 122.1 (CH, C-6), 118.7 (Cq, C-9), 62.3 (CH_2, C-13), 50.6 (CH, C-11), 29.6 (CH_2, C-10), 14.3 (CH_3, C-14).

HRMS (ESI$^+$): Calcd for $C_{20}H_{18}NO_3S$ $[M+H]^+$ 352.1002, found 352.1016.

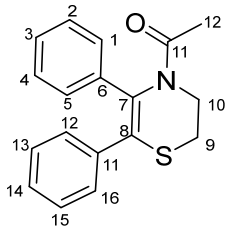
$[\alpha]_D^{25}$= - 64.2 (c 0.105 g/100 mL, CH_2Cl_2).

1-(5,6-Diphenyl-2,3-dihydro-4*H*-1,4-thiazin-4-yl)ethan-1-one (8n)

Orange solid, R_f = 0.72, eluent (ethyl acetate / cyclohexane = 4/6), mp = 124–126 °C, 50 mg scale reaction, 46 mg was isolated, 93% yield.

IR (ν_{max} / cm^{-1}): 1663, 1371, 691.

^{1}H NMR (300 MHz, $CDCl_3$): δ_H 7.24 – 7.18 (m, 3H, Har), 7.14 – 7.07 (m, 5H, Har), 7.02 – 6.97 (m, 2H, Har), 4.12 (t, *J* = 5.5 Hz, 2H, H-10), 3.33 – 3.23 (m, 2H, H-11), 1.64 (s, 3H, H-12).

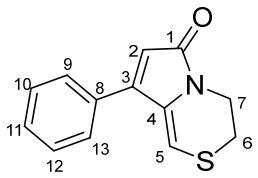


^{13}C NMR (75 MHz, $CDCl_3$): δ_C 171.6 ($Cq_{C=O}$, C-1), 138.4 (Cq, Car), 137.9 (Cq, Car), 132.9 (Cq, C-7), 129.7 (x2 CH, Car), 129.0 (x2 CH, Car), 128.4 (x2 CH, Car), 128.2 (x2 CH, Car), 127.9 (CH, Car), 127.3 (CH, Car), 127.0 (Cq, C-8), 40.8 (CH_2, C-10), 31.6 (CH_2, C-9), 24.6 (CH_3, C-12).

HRMS (ESI$^+$): Calcd for $C_{18}H_{18}NOS$ $[M+H]^+$ 296.1104, found 296.1115 .

8-Phenyl-3,4-dihydro-6*H*-pyrrolo[2,1-*c*][1,4]thiazin-6-one (8o)

Light brown solid, R_f = 0.44, eluent (ethyl acetate / cyclohexane = 4/6), mp = 103–105 °C, 50 mg scale reaction, 49 mg was isolated, 99% yield.



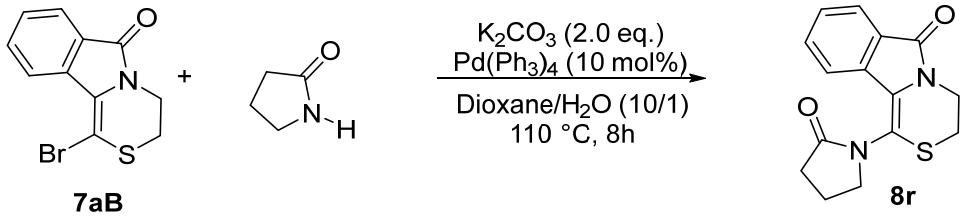
IR (ν_{max} / cm^{-1}): 1665, 1353, 1095, 765, 697.

^{1}H NMR (300 MHz, $CDCl_3$): δ_H 7.47 – 7.36 (m, 5H, Har), 6.20 (s, 1H, H-5), 6.12 (s, 1H, H-2), 4.10 – 4.00 (m, 2H, H-7), 3.19 – 3.07 (m, 2H, H-6).

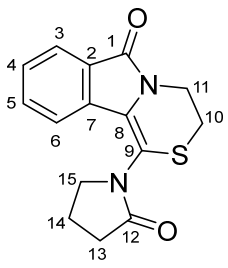
^{13}C NMR (75 MHz, $CDCl_3$): δ_C 168.3 ($Cq_{C=O}$, C-1), 147.2 (Cq, C-8), 134.0 (Cq, C-3), 131.9 (Cq, C-4), 129.5 (CH, C-11), 129.0 (x2 CH, C-10, C-12), 128.5 (x2 CH, C-9, C-13), 117.6 (CH, C-2), 109.3 (CH, C-5), 38.5 (CH_2, C-7), 26.2 (CH_2, C-6).

HRMS (ESI$^+$): Calcd for $C_{13}H_{12}NOS$ $[M+H]^+$ 230.0634, found 230.0640.

IX. Typical procedure for the synthesis of 1-(2-Oxo-pyrrolidin-1-yl)-3,4-dihydro-6*H*-[1,4]thiazino [3,4-*a*]isoindol-6-one (8r).



Ta a solution of 50 mg (0.177 mmol) of 1-bromo-3,4-dihydro-6*H*-[1,4]thiazino[3,4-*a*]isoindol-6-one (**7aB**) dissolved in 4 mL of toluene was added under stirring 0.4 mL of water. To this solution, pyrrolidin-2-one (16.59 mg, 1.1 eq.), K_2CO_3 (48.92 mg, 2.0 eq.) and tetrakis(triphenylphosphine)-palladium(0) ($Pd(Ph_3)_4$, 20.45 mg, 10 mol%) were added under stirring and argon atmosphere. The reaction mixture was stirred at 110 °C and the reaction was monitored by NMR ^{1}H. After completion of the reaction (8 hours), direct purification of the crude by flash chromatography to furnish the expected product, 1-(2-oxopyrrolidin-1-yl)-3,4-dihydro-6*H*-[1,4]thiazino[3,4-*a*]isoindol-6-one (**8r**), whose structure has been proven by X-ray analysis.



Orange solid, R_f = 0.51, eluent (ethyl acetate / cyclohexane = 4/6), mp = 258–260 °C (decomposition), 50 mg scale reaction, 34 mg was isolated, 67% yield.

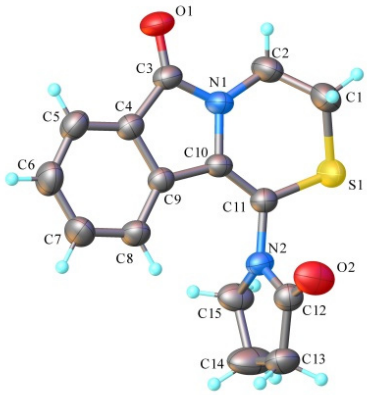
IR (ν_{max} / cm^{-1}): 2952, 2895, 1682, 1631, 1470, 1398, 1287, 1180, 1096, 691.

^{1}H NMR (300 MHz, $CDCl_3$): δ_H 7.84 (dt, *J* = 7.6 Hz and *J* = 3.2 Hz, 1H, H-3), 7.54 (td, *J* = 8.0 Hz and *J* = 3 Hz, 1H, H-6), 7.44 (dt, *J* = 7.6 Hz and *J* = 3.2 Hz, 1H, H-4), 7.42 (td, *J* = 8.0 Hz and *J* = 3.2 Hz, 1H, H-5), 4.31 – 4.39 (m, 1H, H-11), 4.02 – 3.93 (m, 1H, H-11), 3.91 – 3.92 (m, 1H, H-10), 3.62 – 3.69 (m, 1H, H-10), 3.15 – 3.30 (m, 2H, H-15), 2.53 – 2.59 (m, 2H, H-13), 2.23 – 2.36 (m, 2H, H-14).

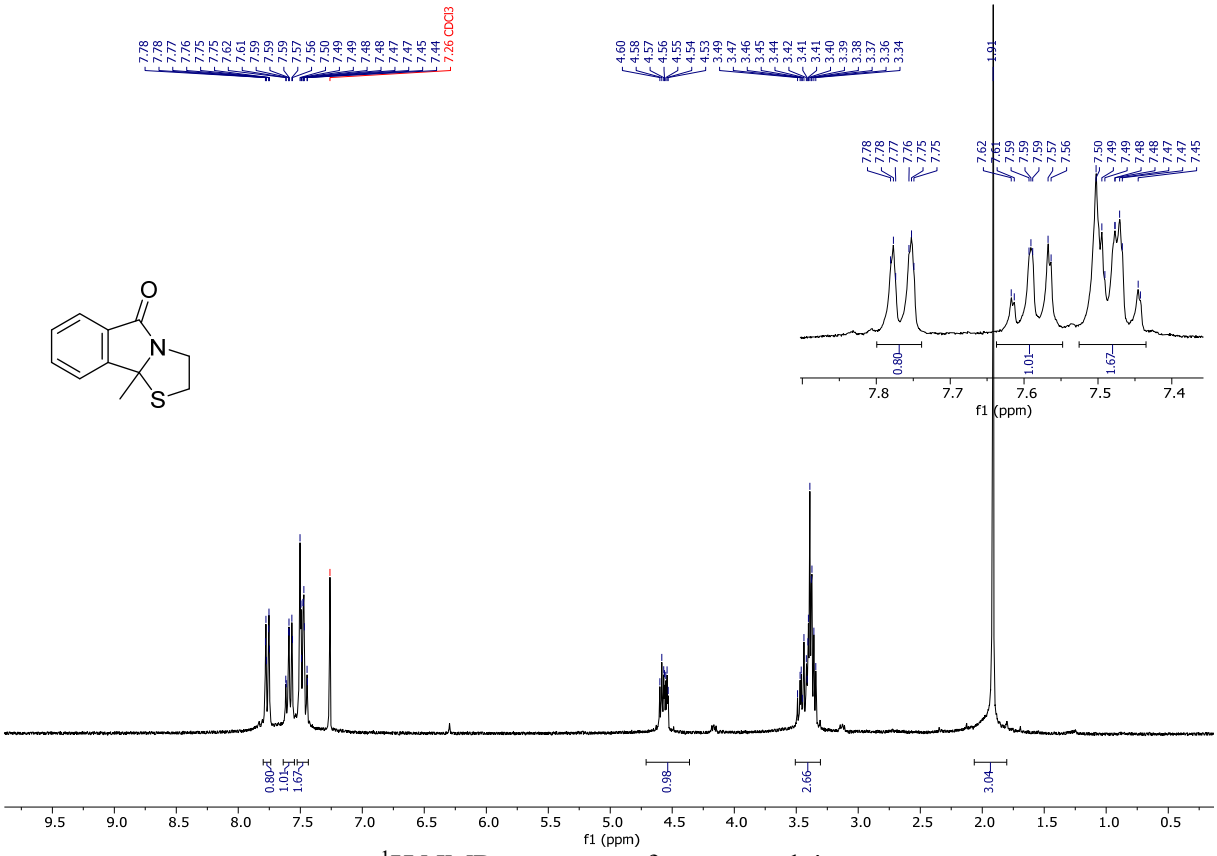
^{13}C NMR (75 MHz, $CDCl_3$): δ_C 175.3 ($Cq_{C=O}$, C-12), 165.4 ($Cq_{C=O}$, C-1), 133.1 (Cq, C-7), 132.6 (Cq, C-5), 129.5 (Cq, C-2), 128.8 (CH, C-3), 128.4 (CH, C-9), 123.5 (CH, C-4), 121.6 (CH, C-6), 114.8 (CH, C-8), 48.9 (CH_2, C-15), 39.2 (CH_2, C-11), 31.2 (CH_2, C-13), 27.3 (CH_2, C-10), 18.9 (CH_2, C-14).

HRMS (ESI$^+$): Calcd for $C_{15}H_{14}N_2O_2S$ $[M+H]^+$ 287.0849, found 288.0882.

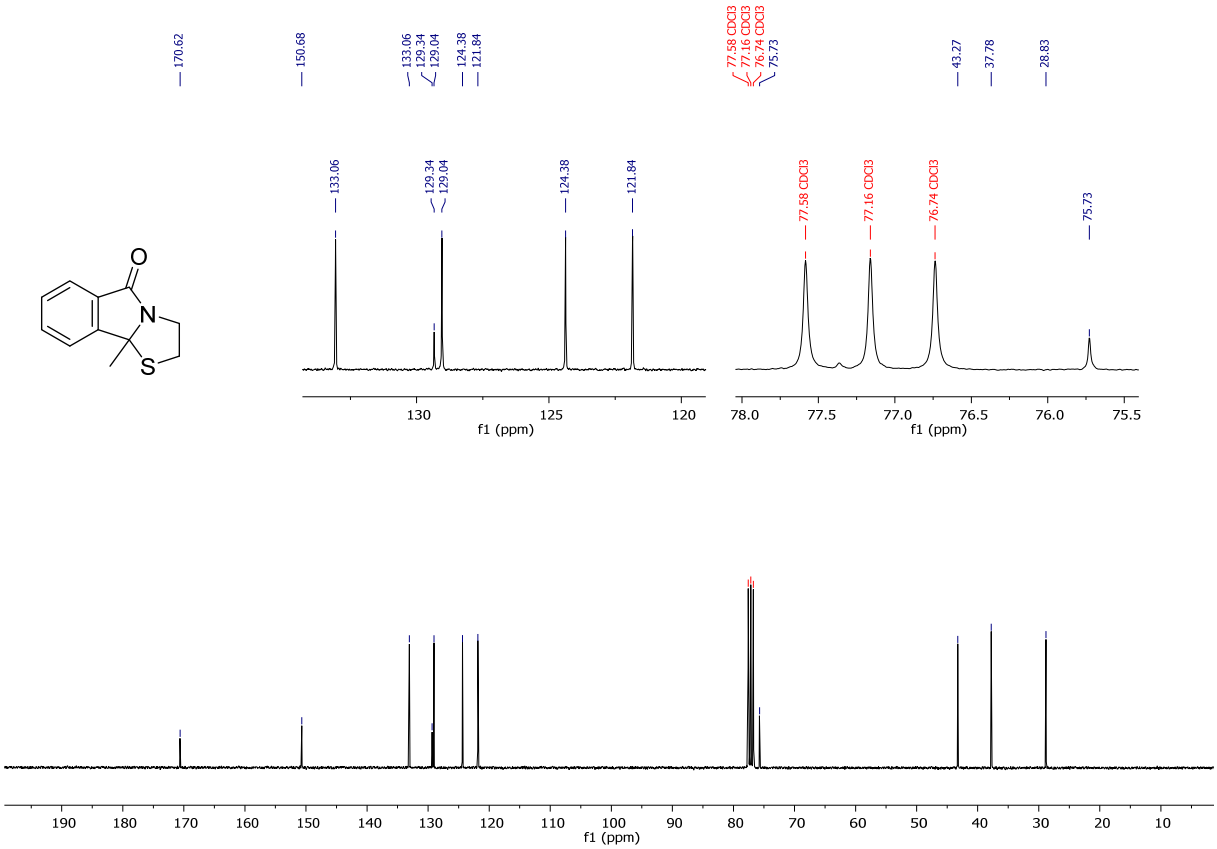
X-ray of compound **8r**: CCDC 2433578



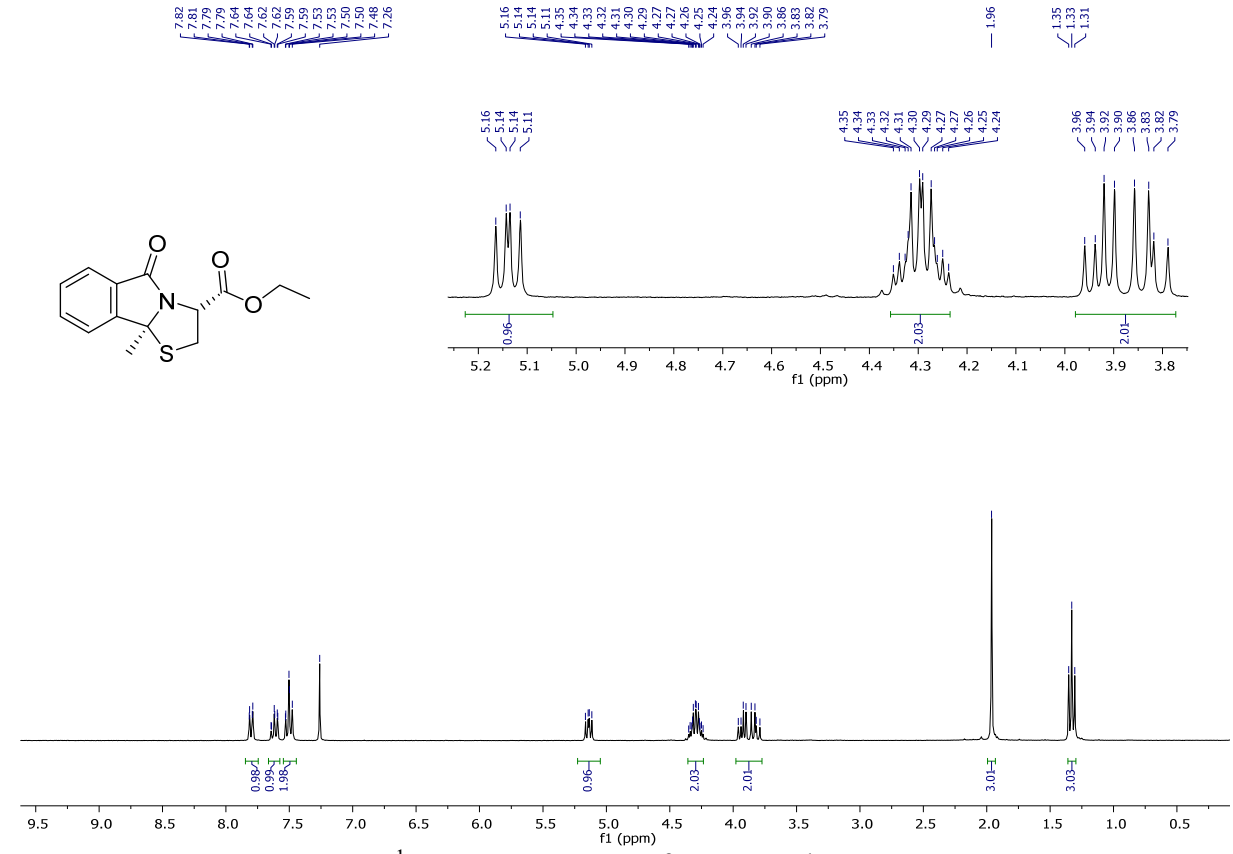
X. Copies of NMR spectra



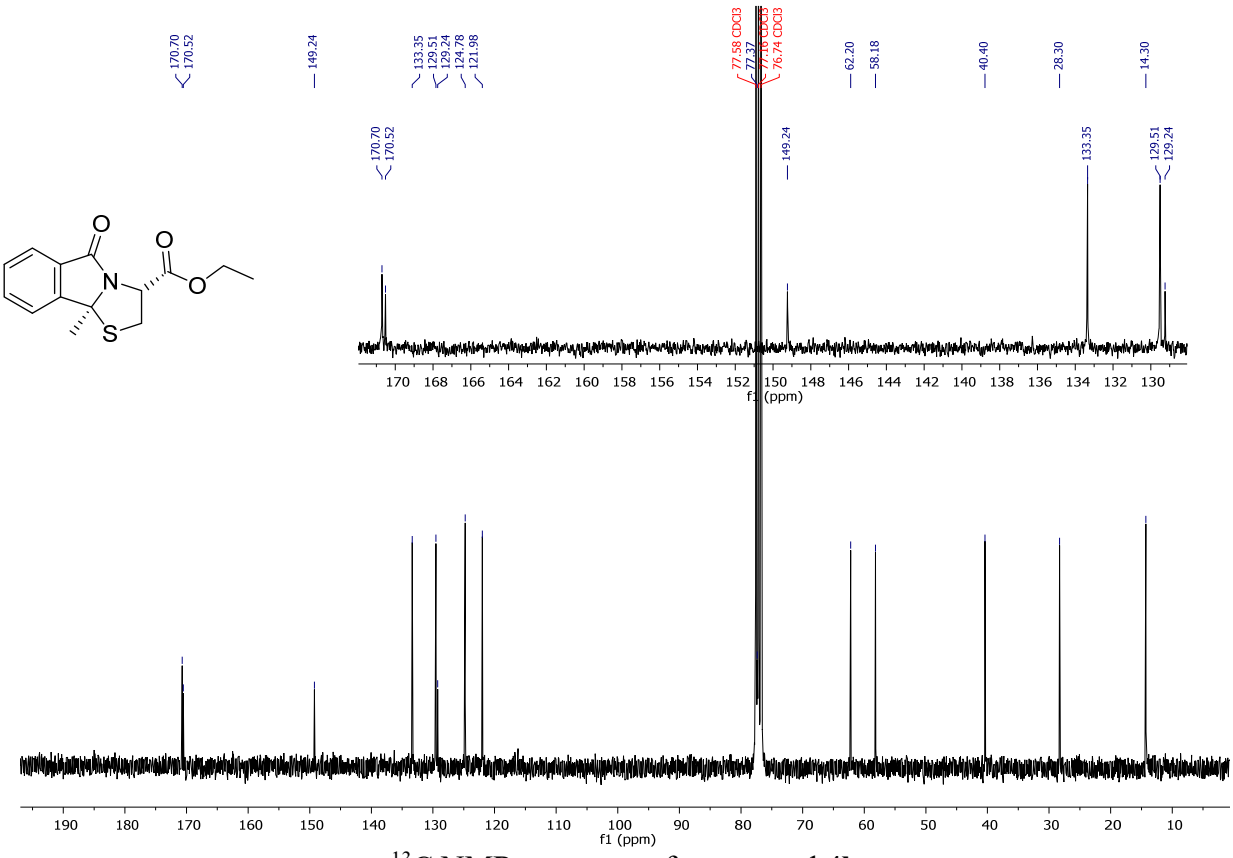
^{1}H NMR spectrum of compound **4a**



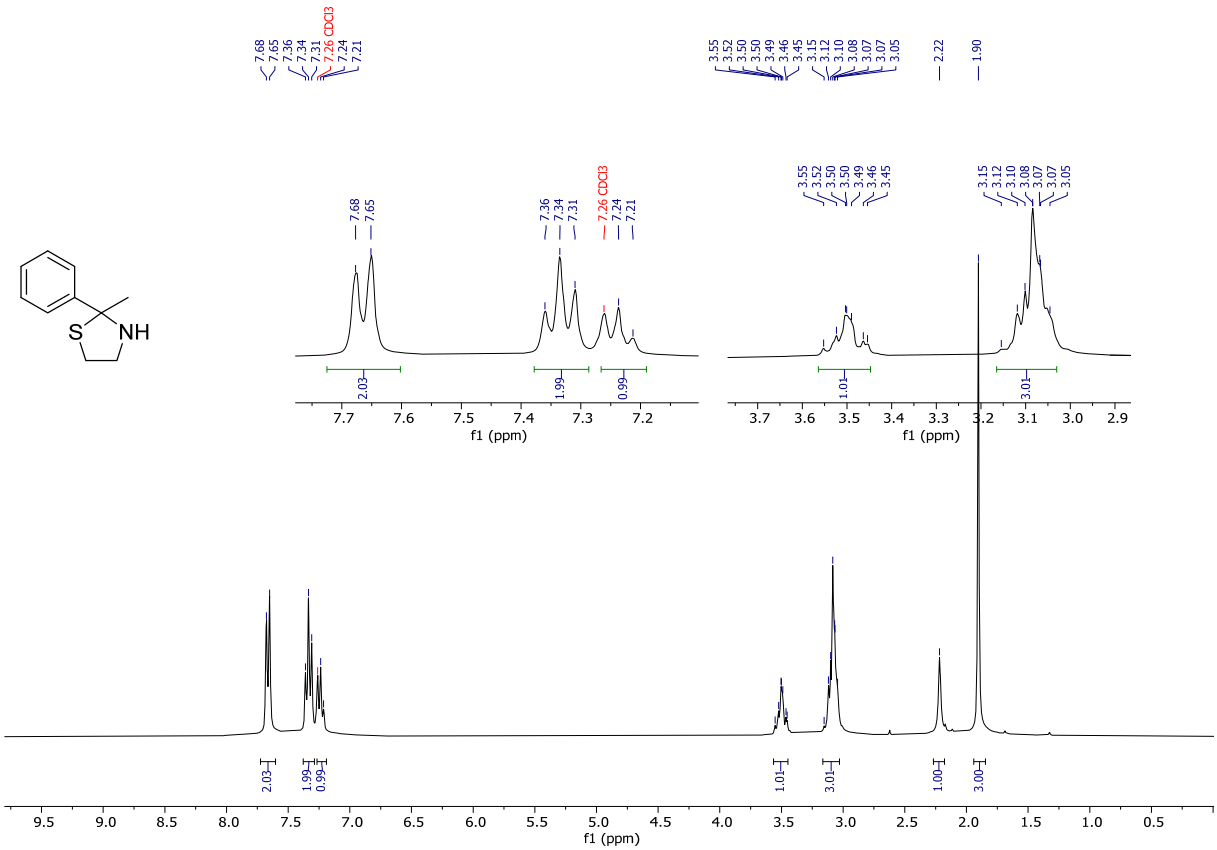
^{13}C NMR spectrum of compound **4a**



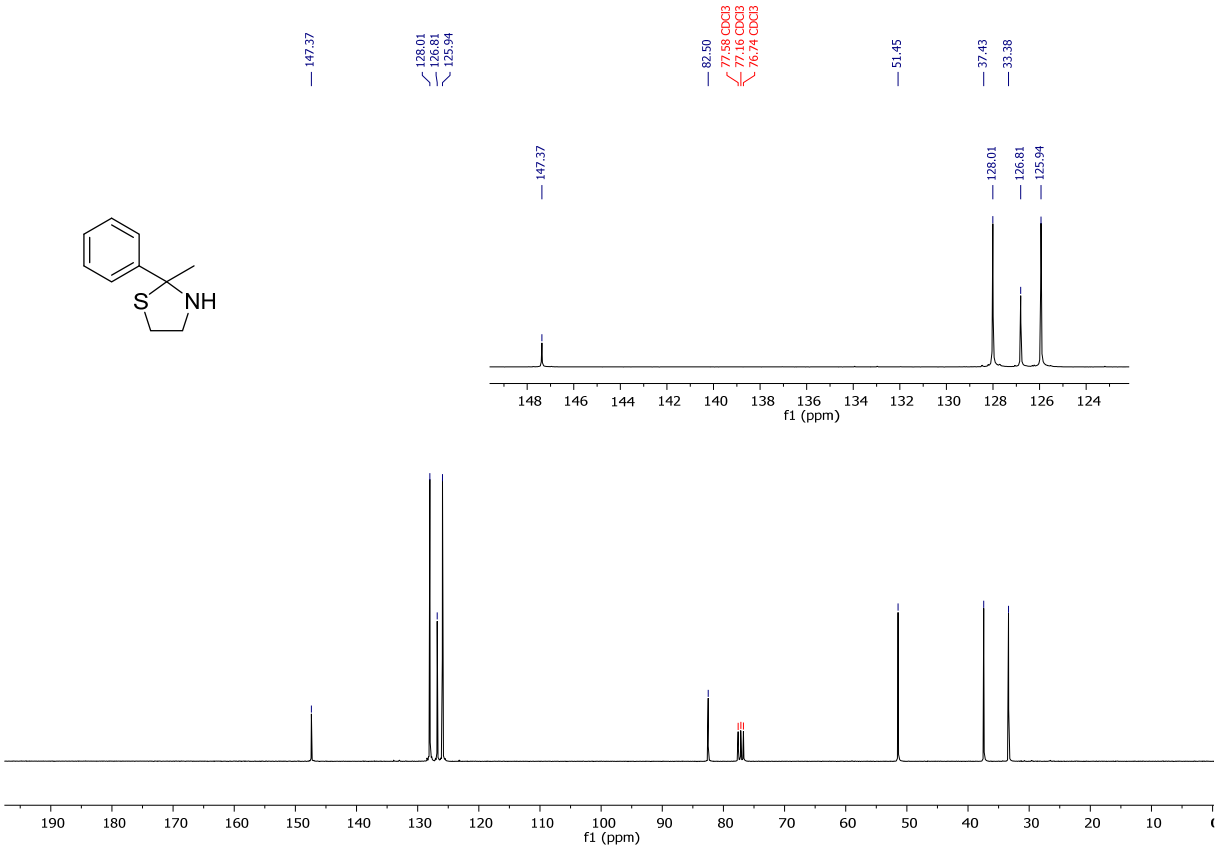
^{1}H NMR spectrum of compound **4b**



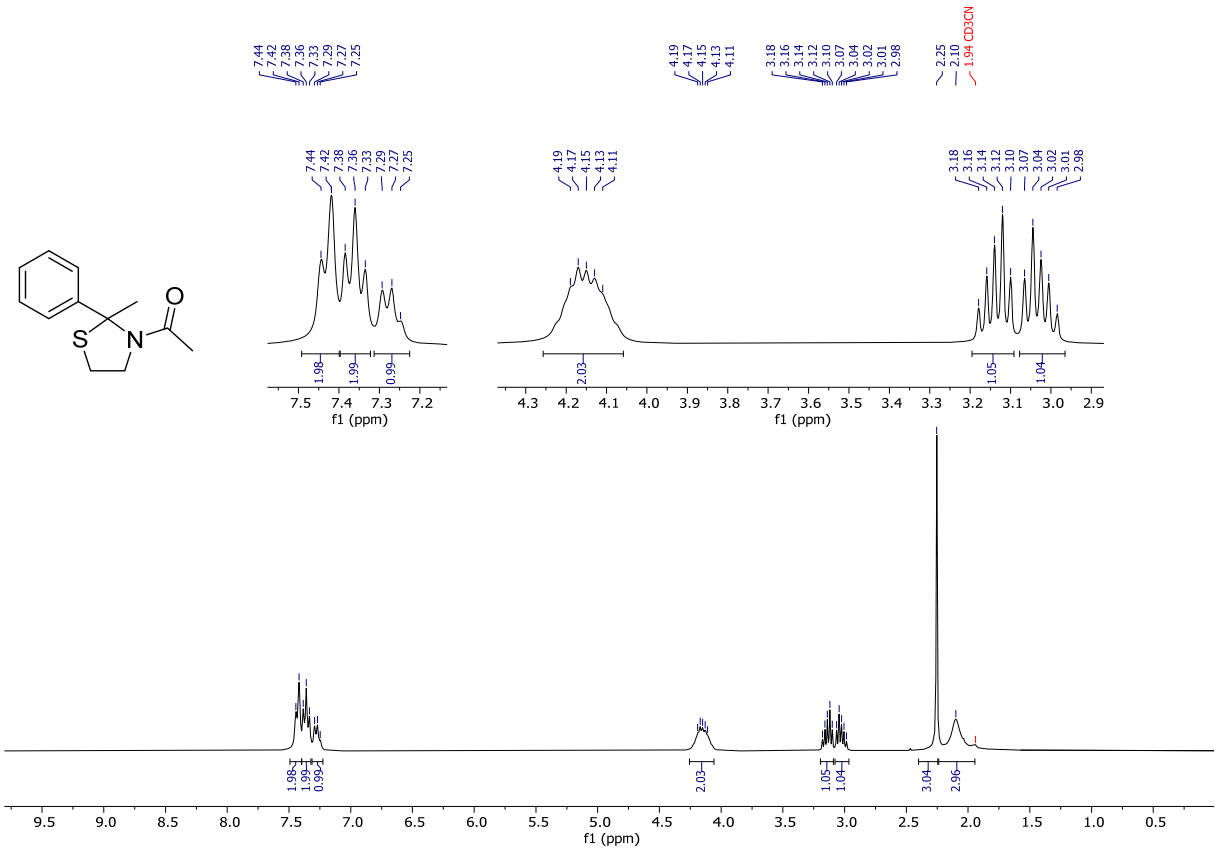
^{13}C NMR spectrum of compound **4b**



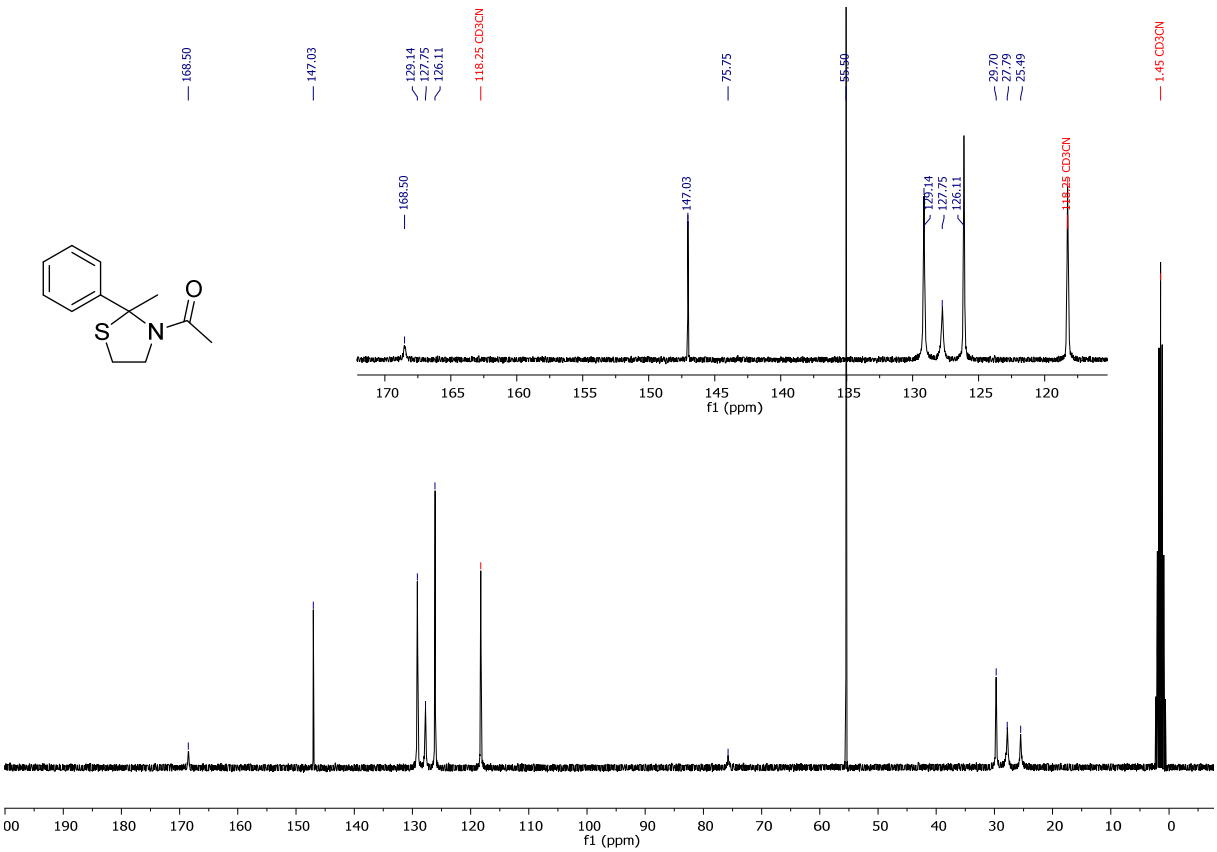
^{1}H NMR spectrum of compound **4'c**



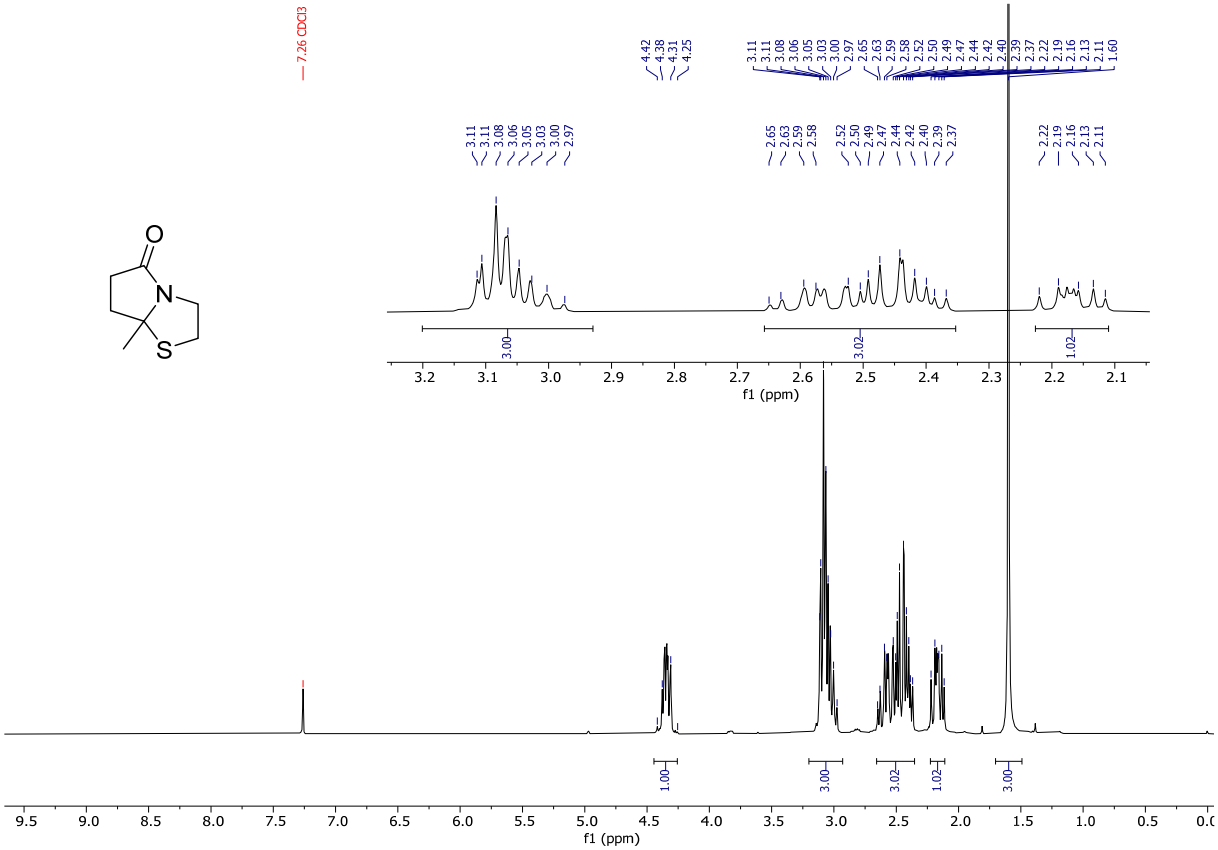
^{13}C NMR spectrum of compound **4'c**



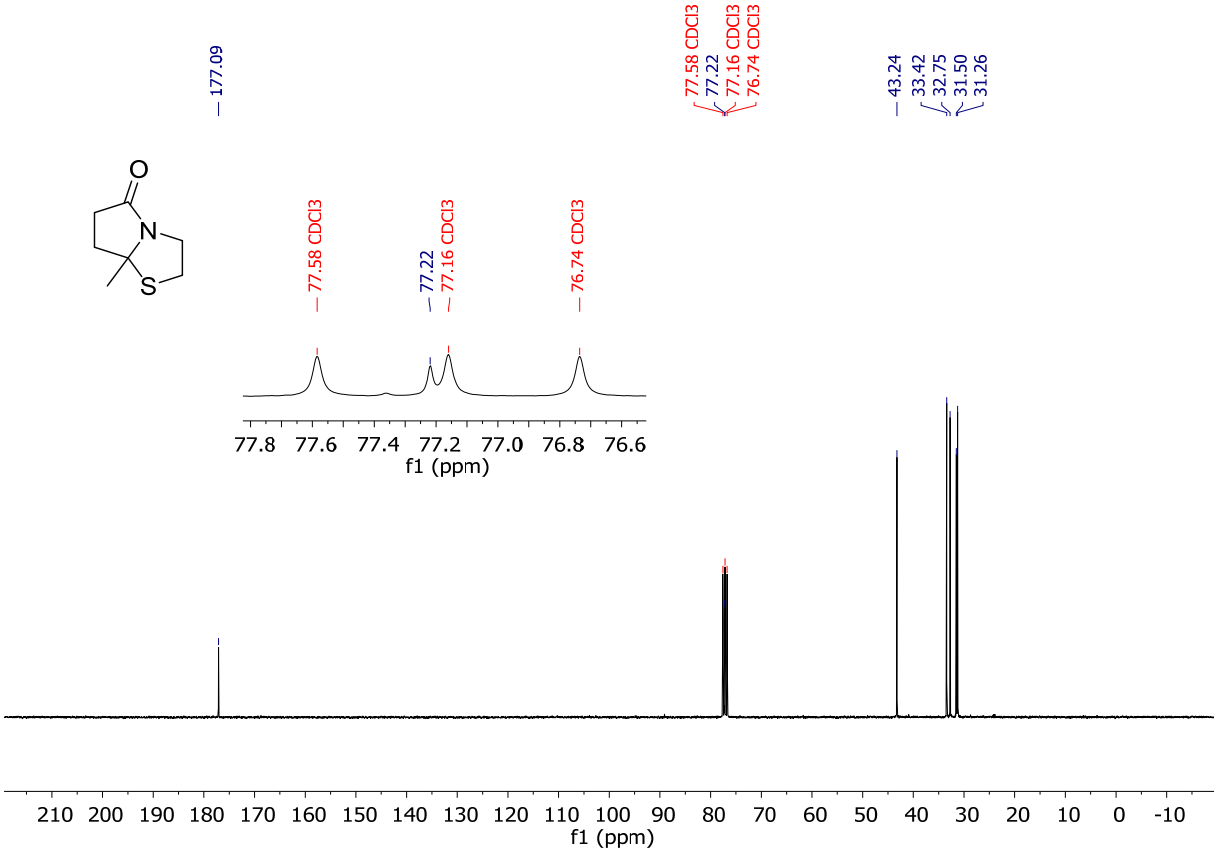
^{1}H NMR spectrum of compound **4c**



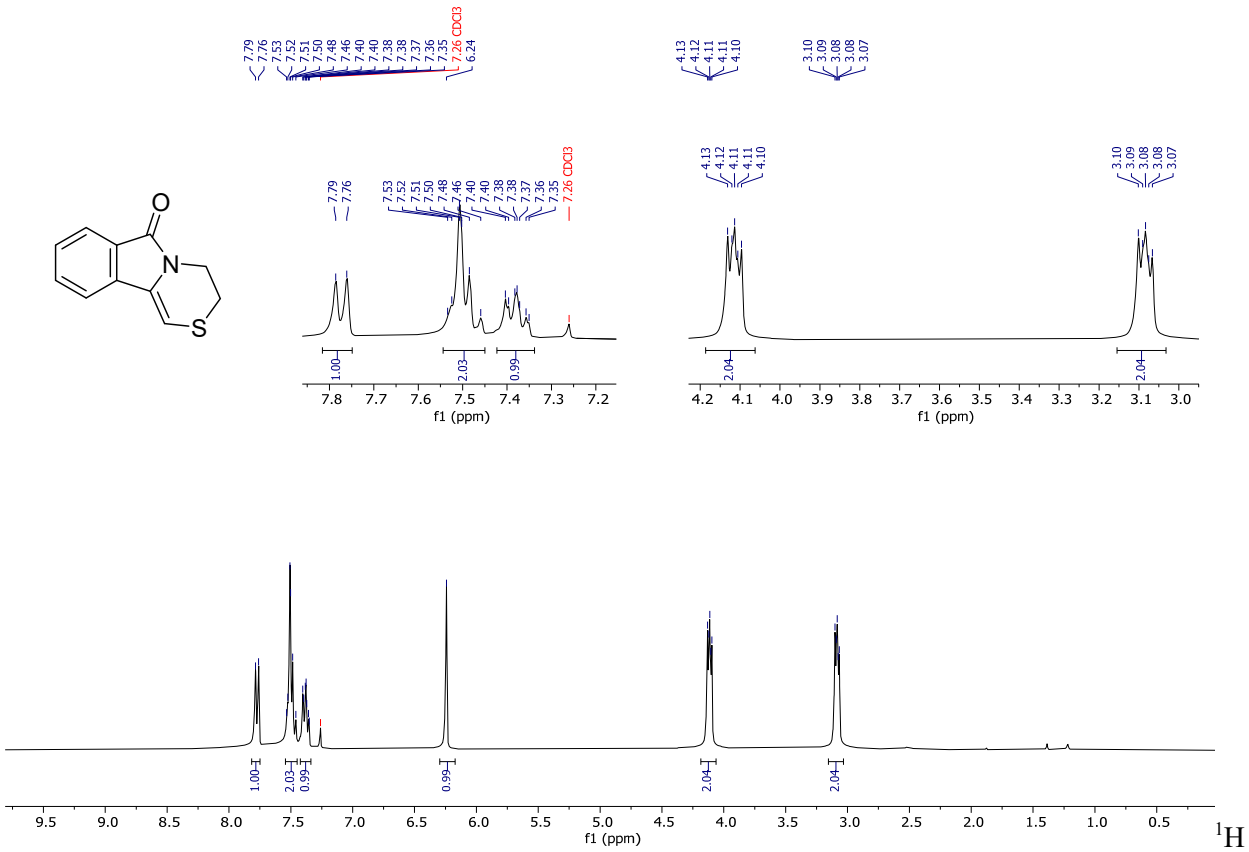
^{13}C NMR spectrum of compound **4c**



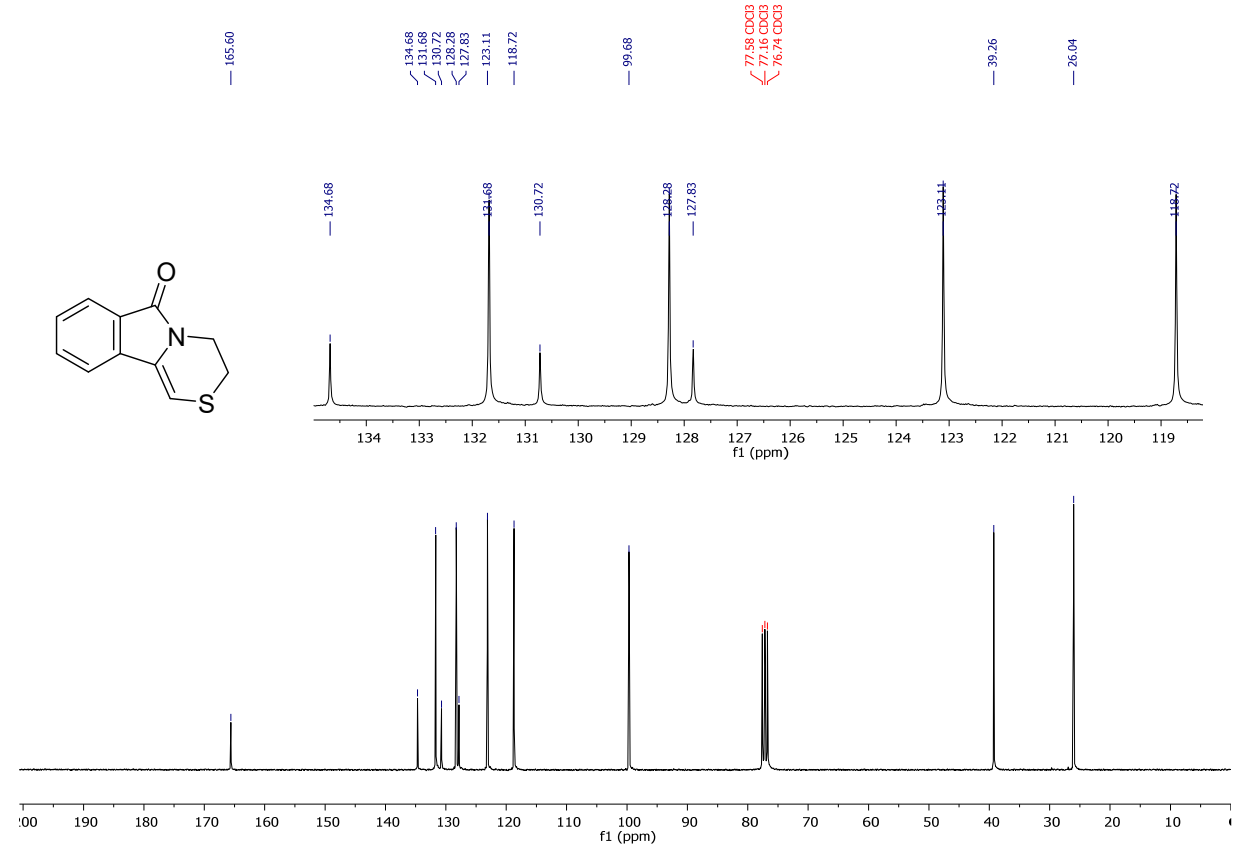
^{1}H NMR spectrum of compound **4d**



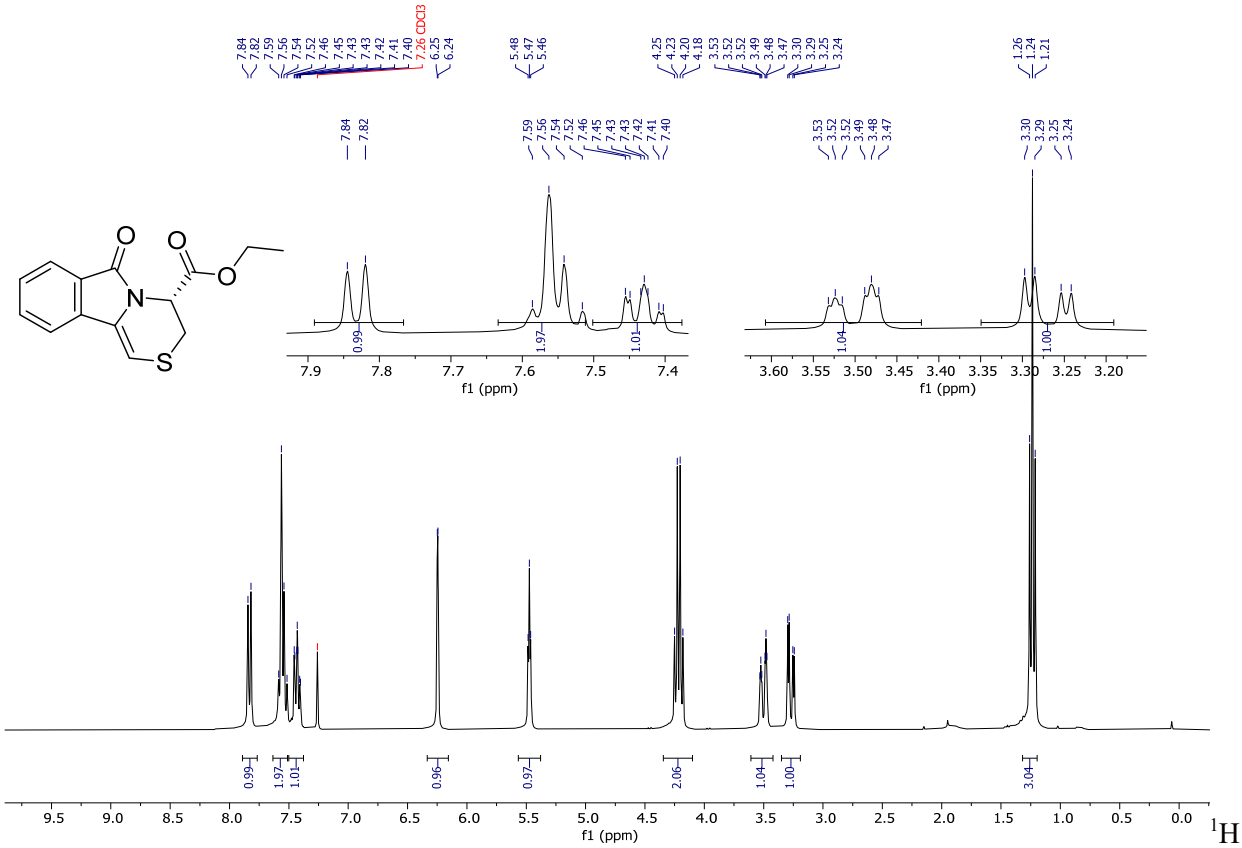
^{13}C NMR spectrum of compound **4d**



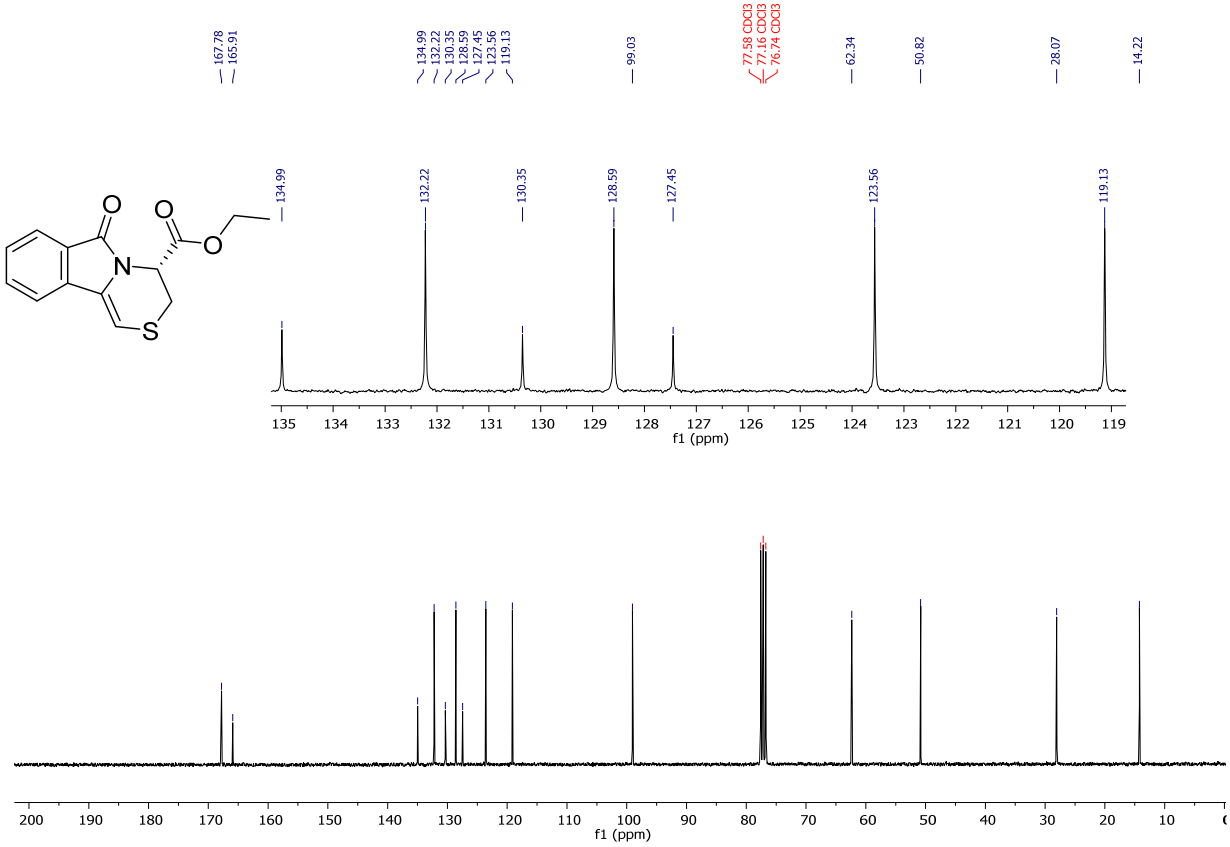
^{1}H NMR spectrum of compound **5a**



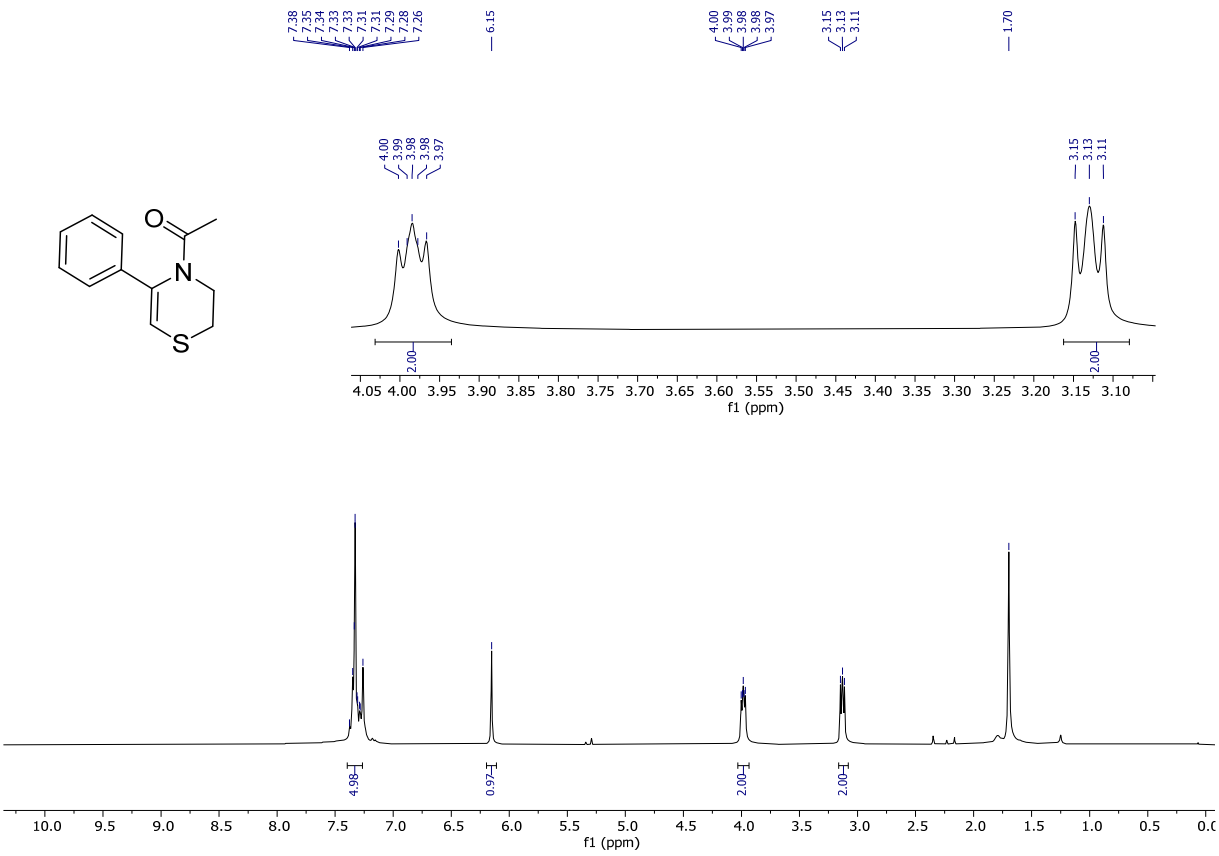
^{13}C NMR spectrum of compound **5a**



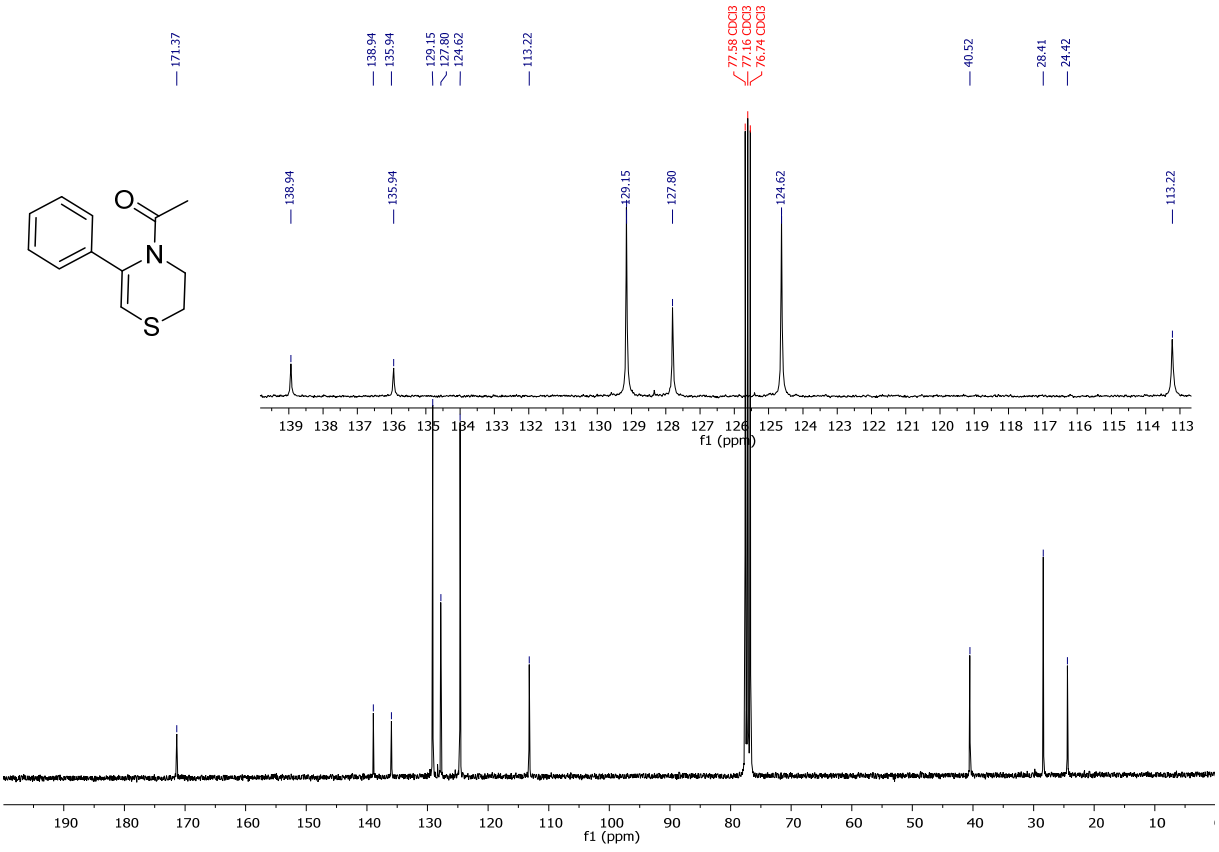
^{1}H NMR spectrum of compound **5b**



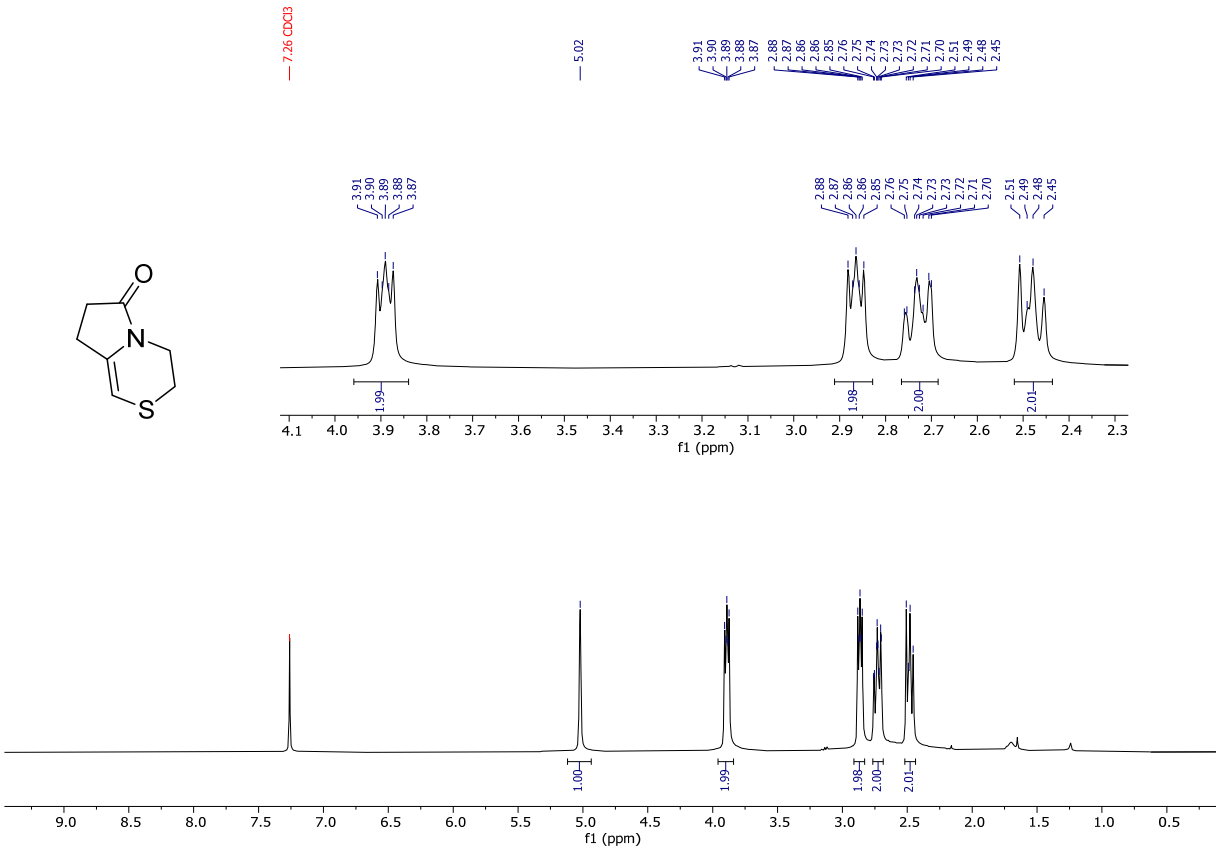
^{13}C NMR spectrum of compound **5b**



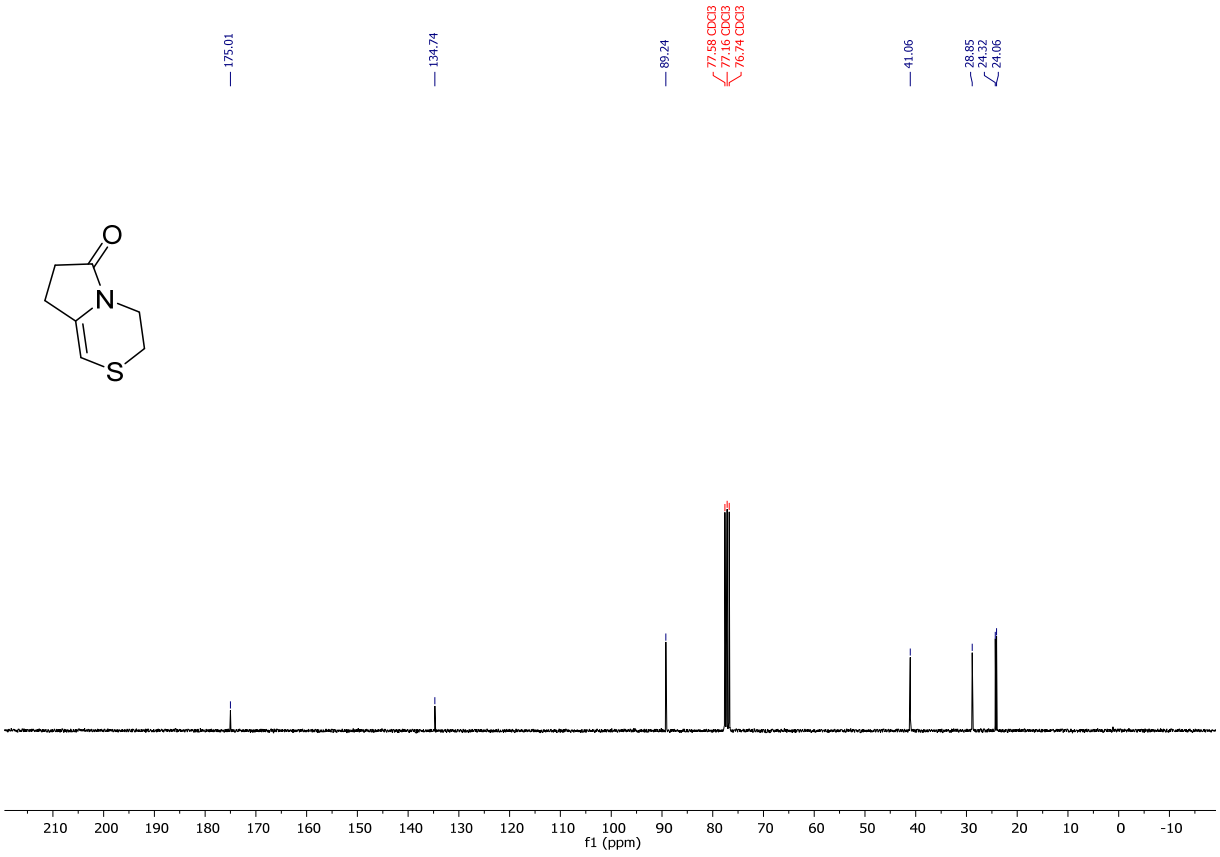
^{1}H ^{1}H NMR spectrum of compound **5c**



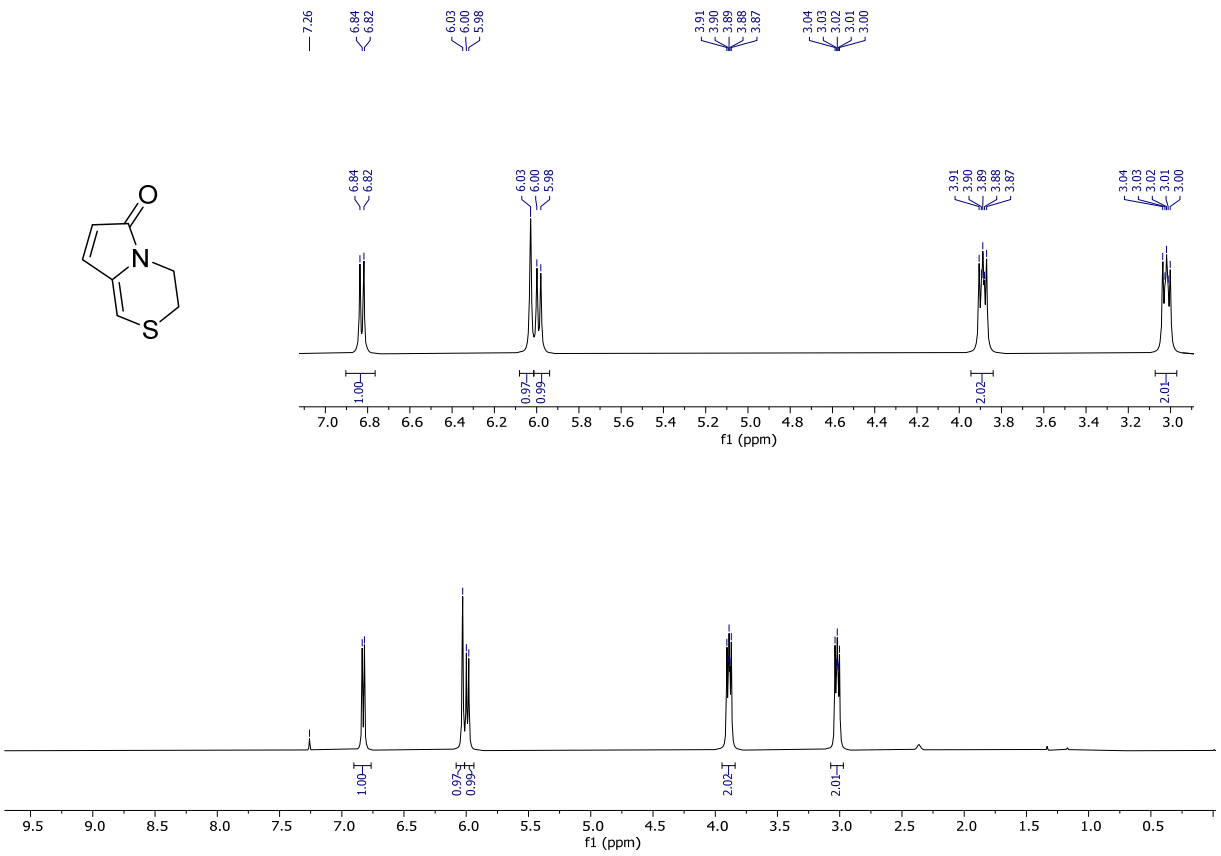
^{13}C NMR spectrum of compound **5c**



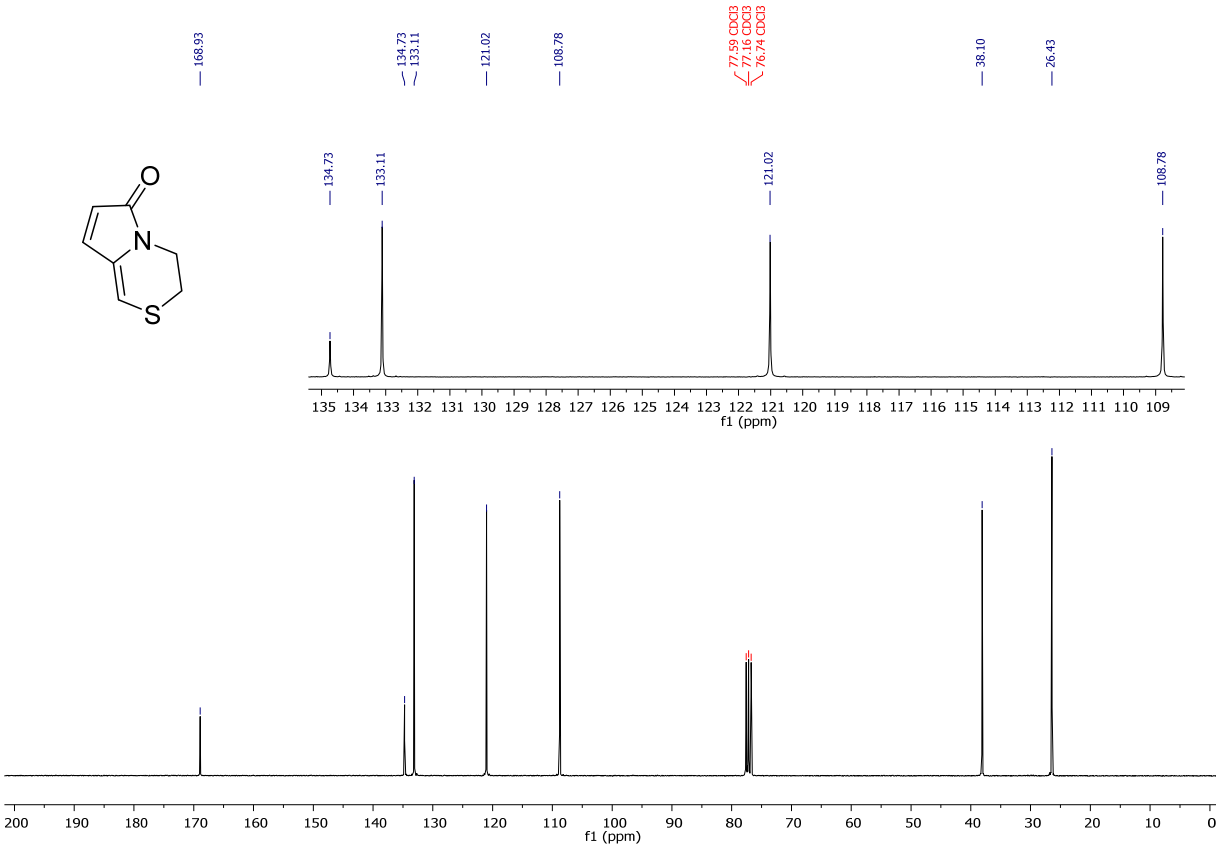
^{1}H ^{1}H NMR spectrum of compound **9**



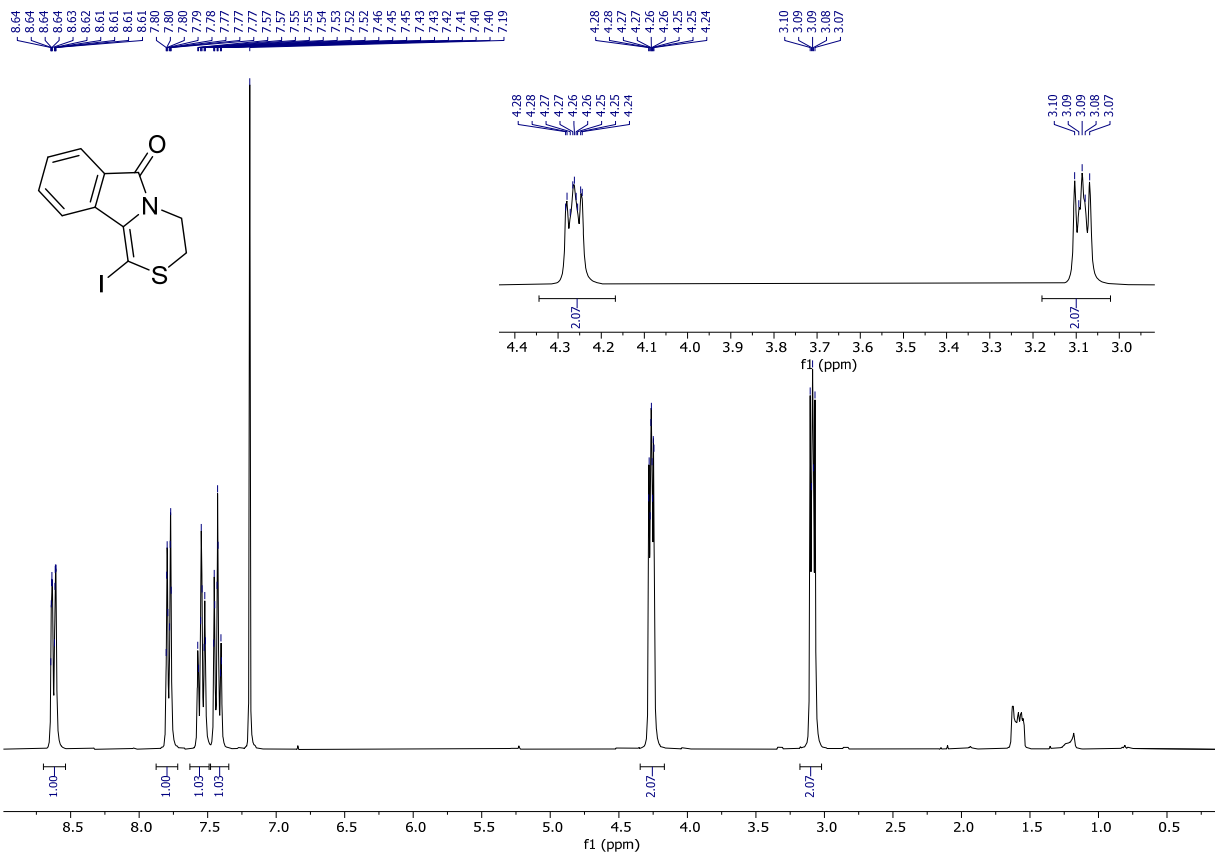
^{13}C NMR spectrum of compound **9**



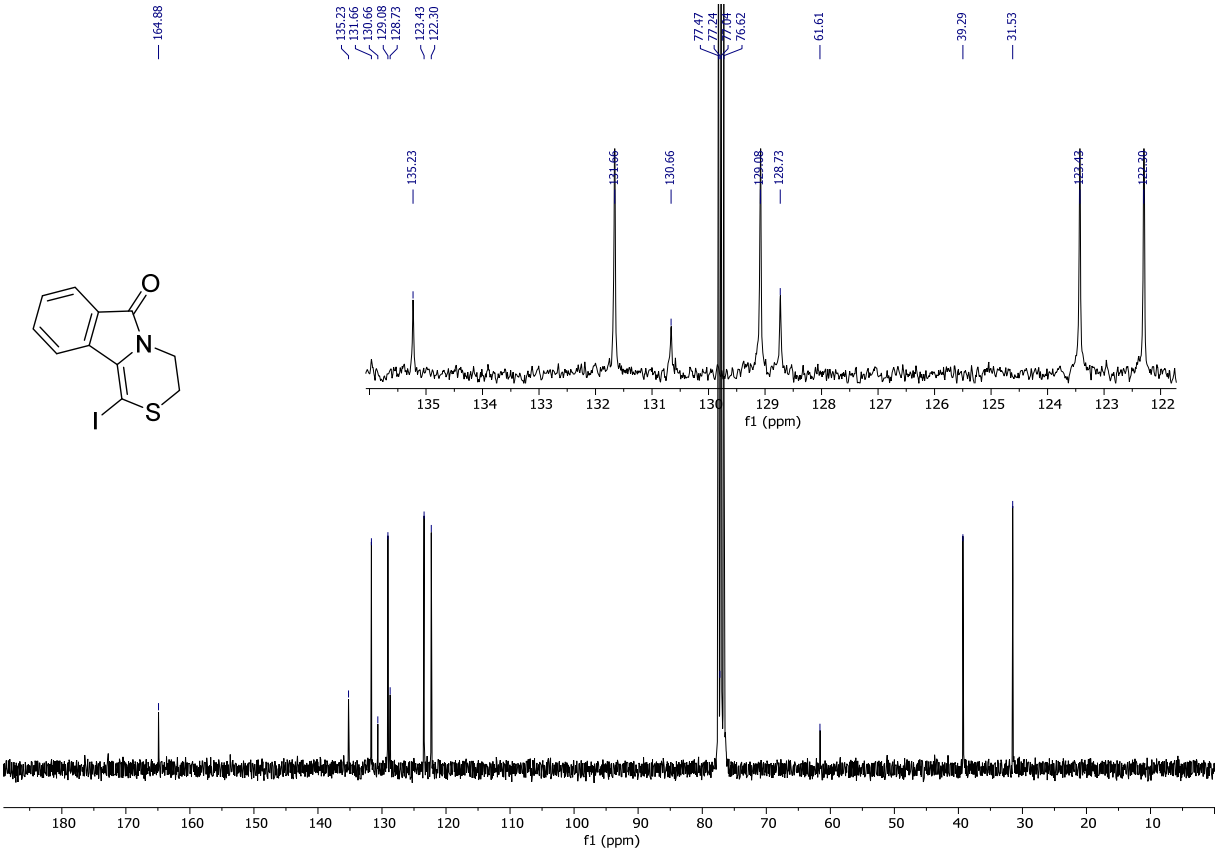
^{1}H ^{1}H NMR spectrum of compound **10**



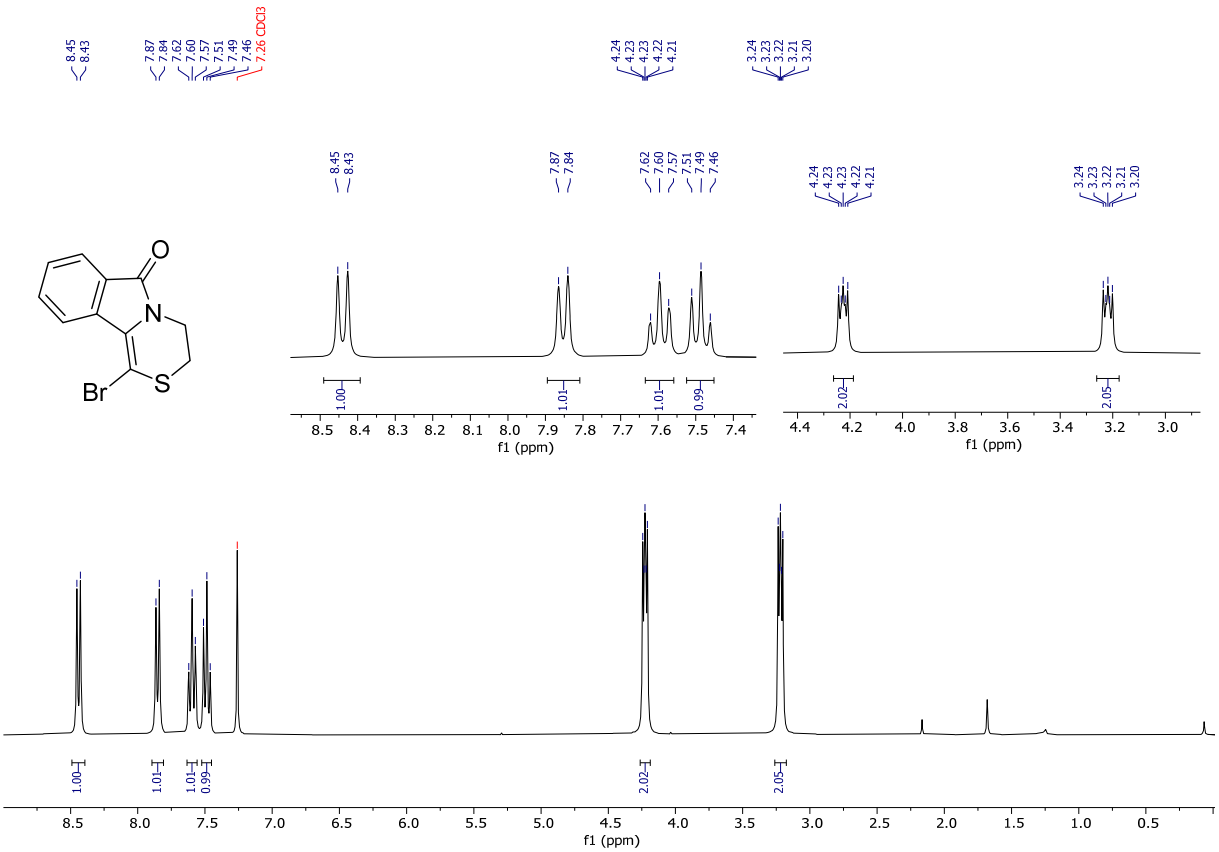
^{13}C NMR spectrum of compound **10**



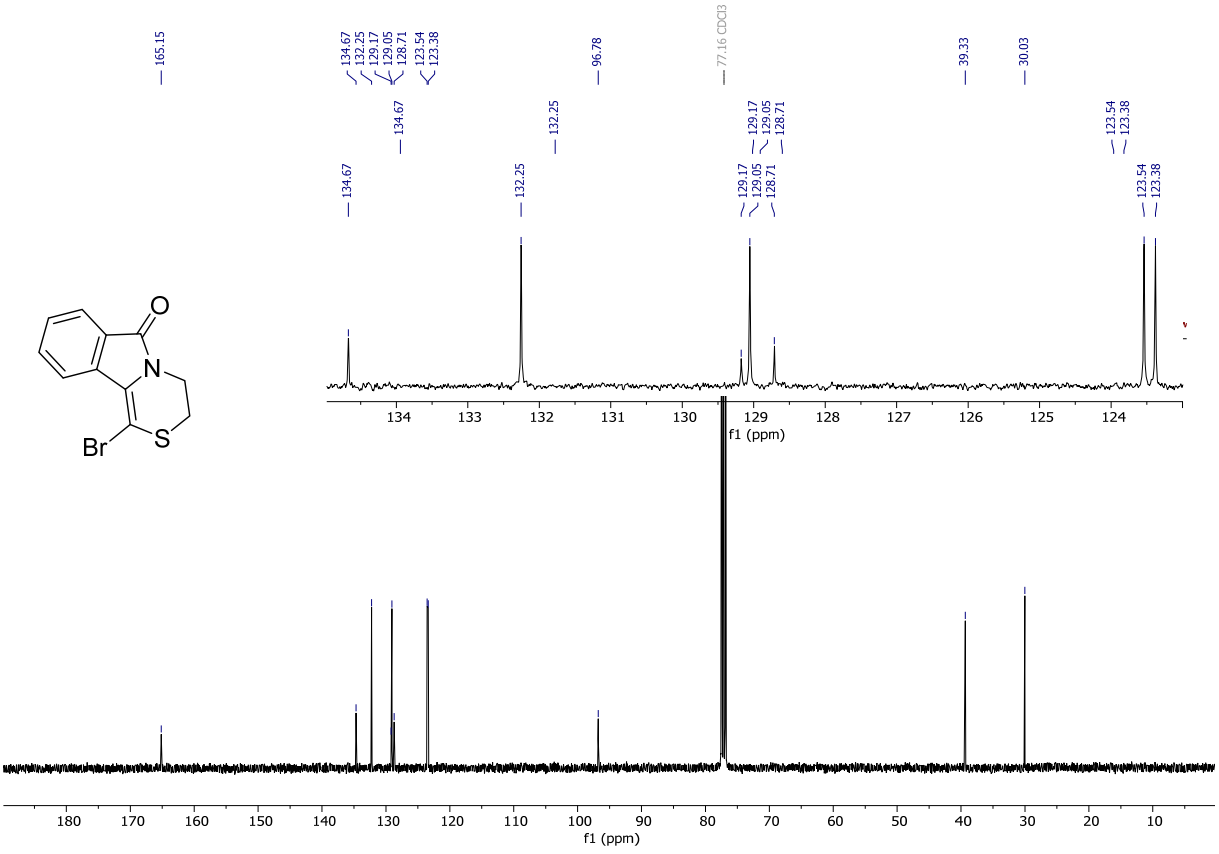
^{1}H NMR spectrum of compound **7aA**



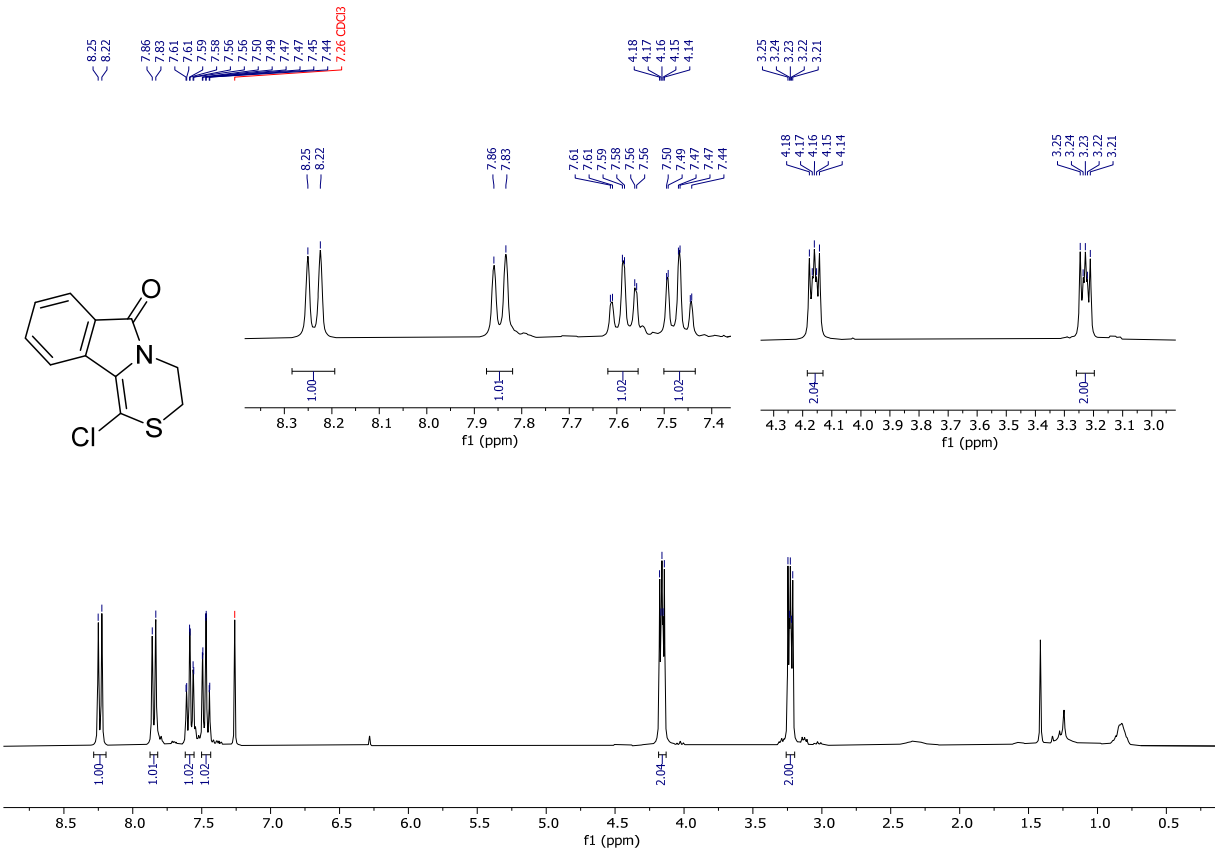
^{13}C NMR spectrum of compound **7aA**



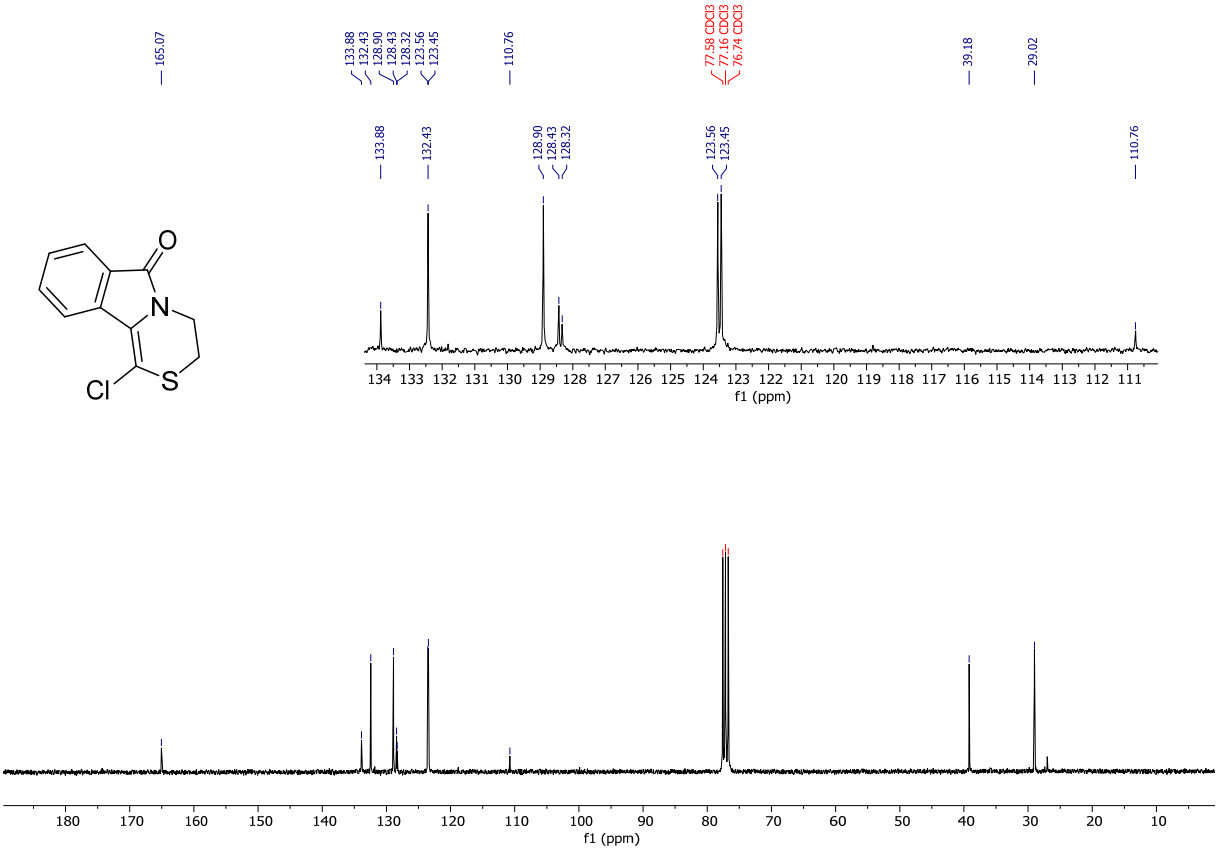
^{1}H NMR spectrum of compound **7aB**



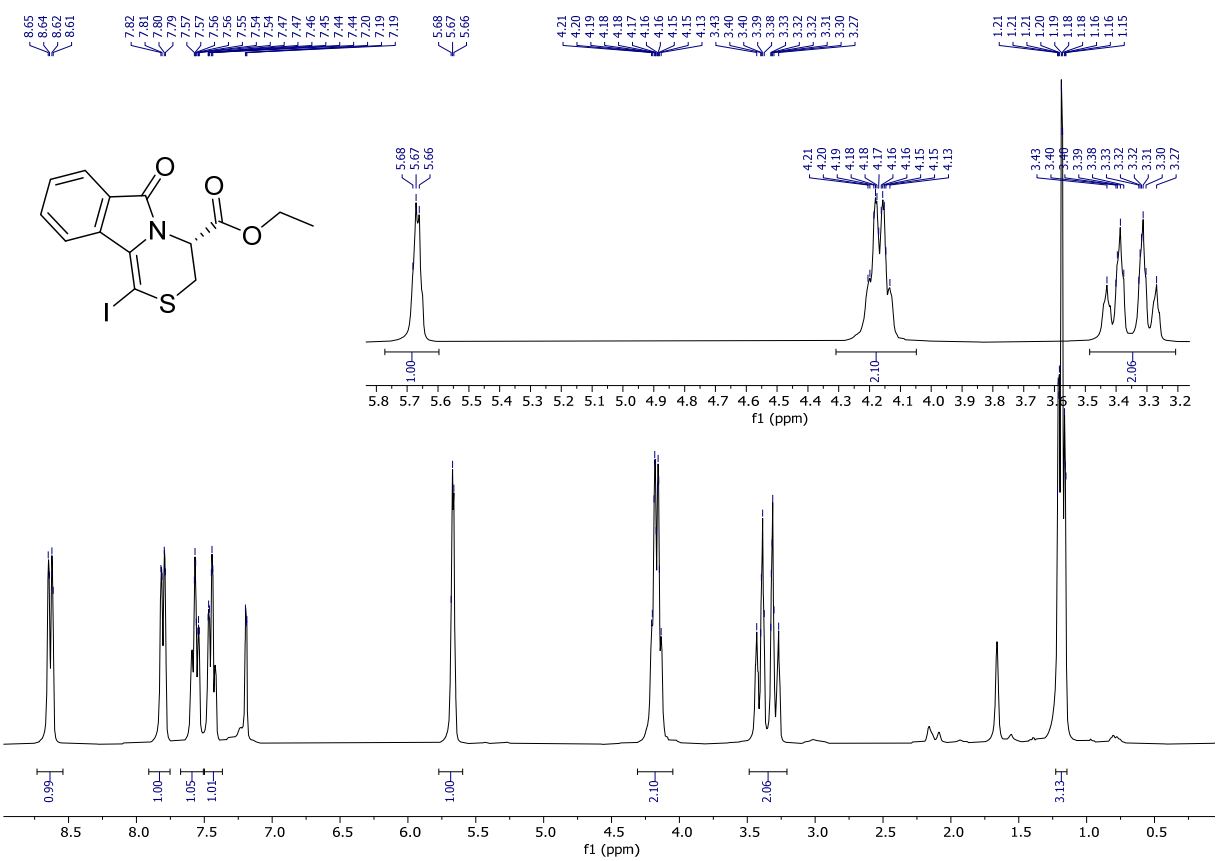
^{13}C NMR spectrum of compound **7aB**



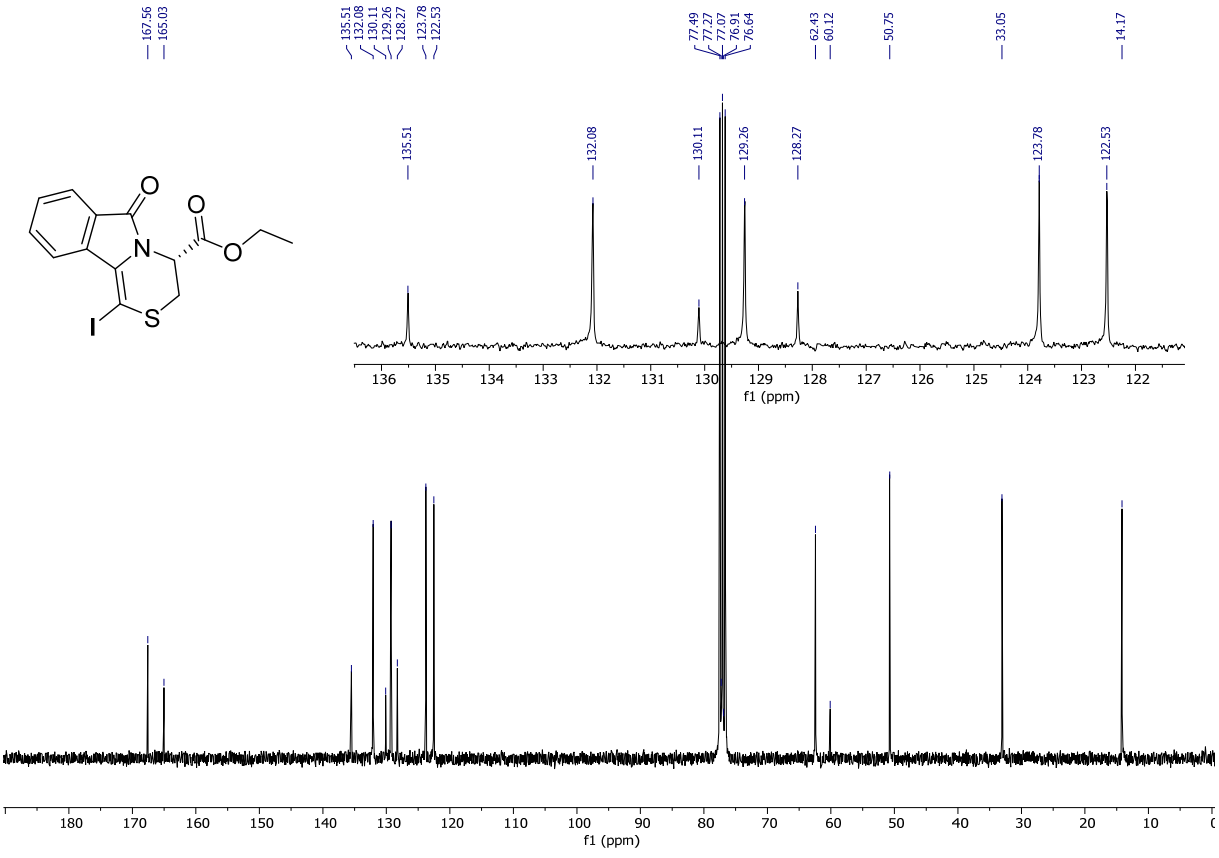
^{1}H NMR spectrum of compound **7aC**



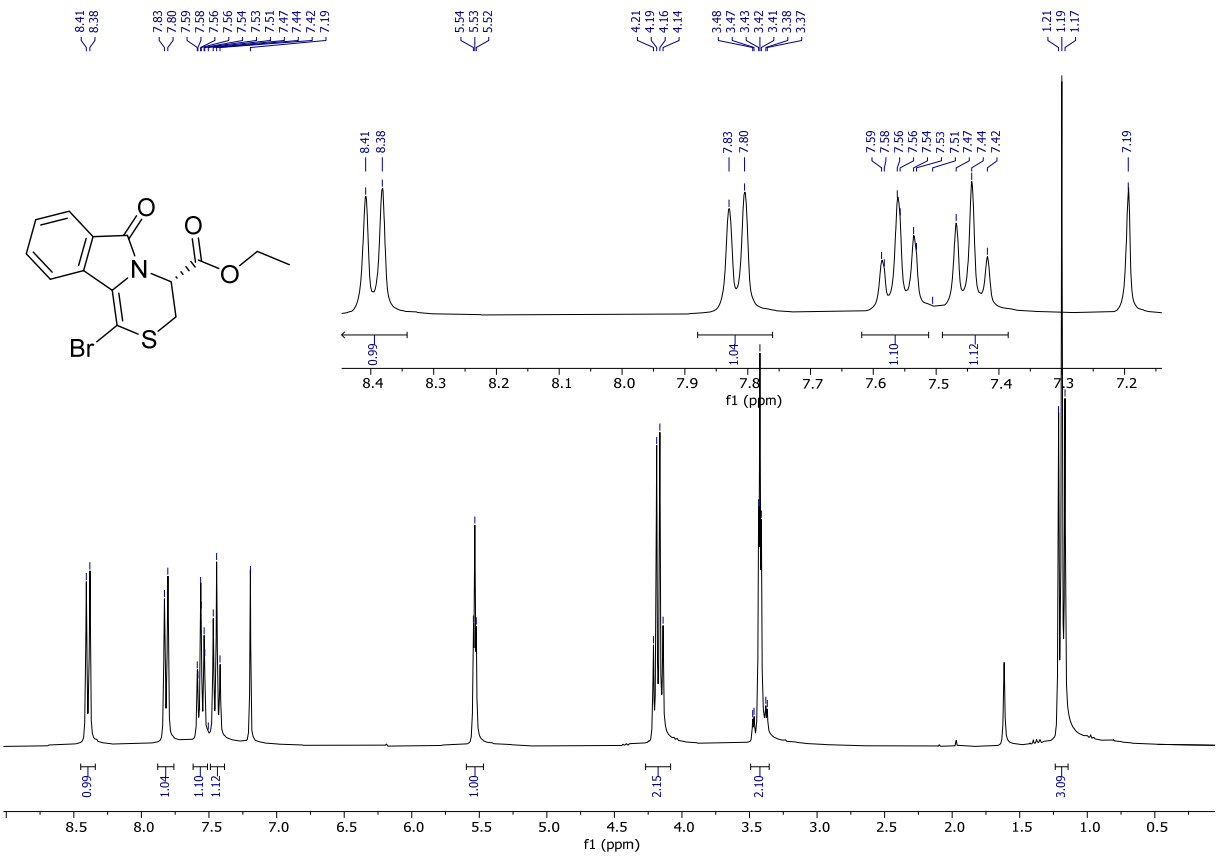
^{13}C NMR spectrum of compound **7aC**



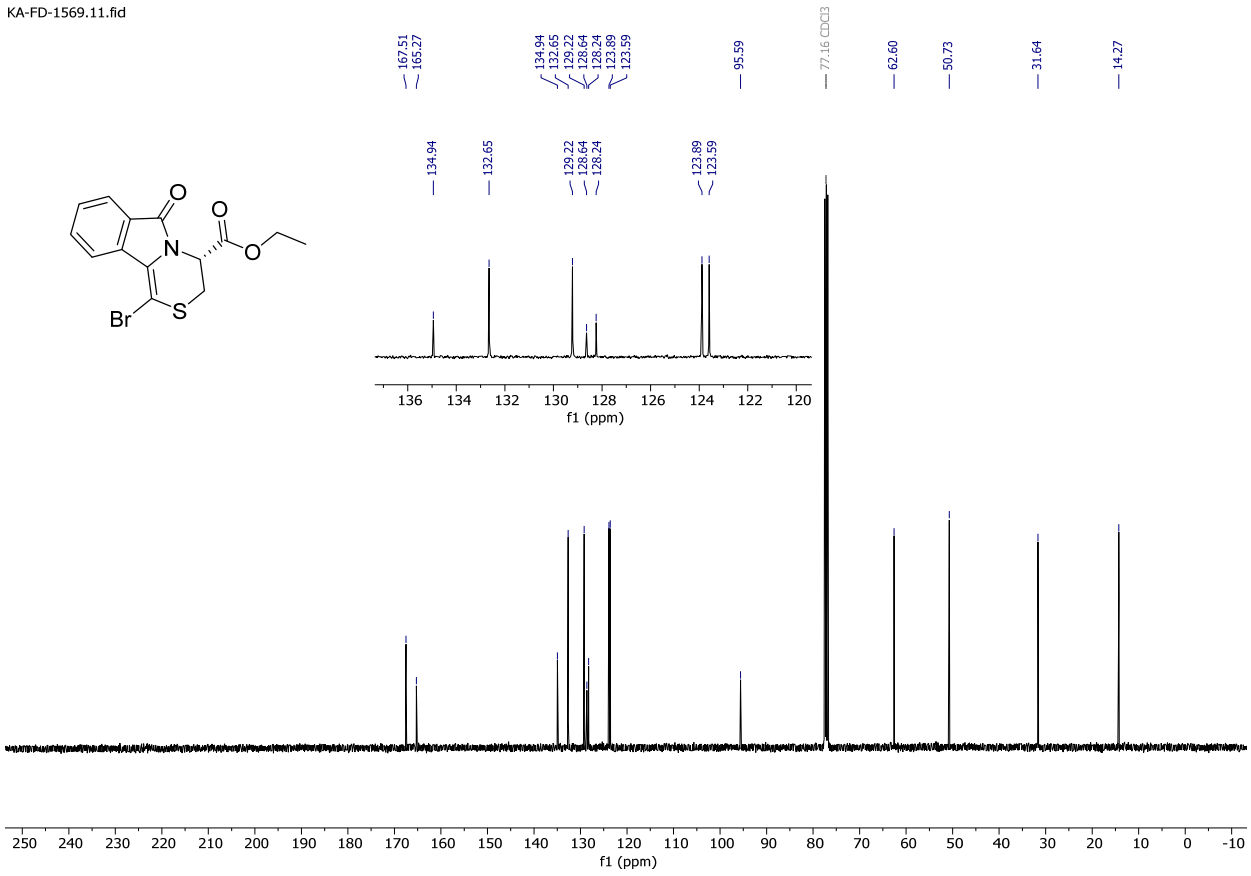
^{1}H NMR spectrum of compound **7bA**



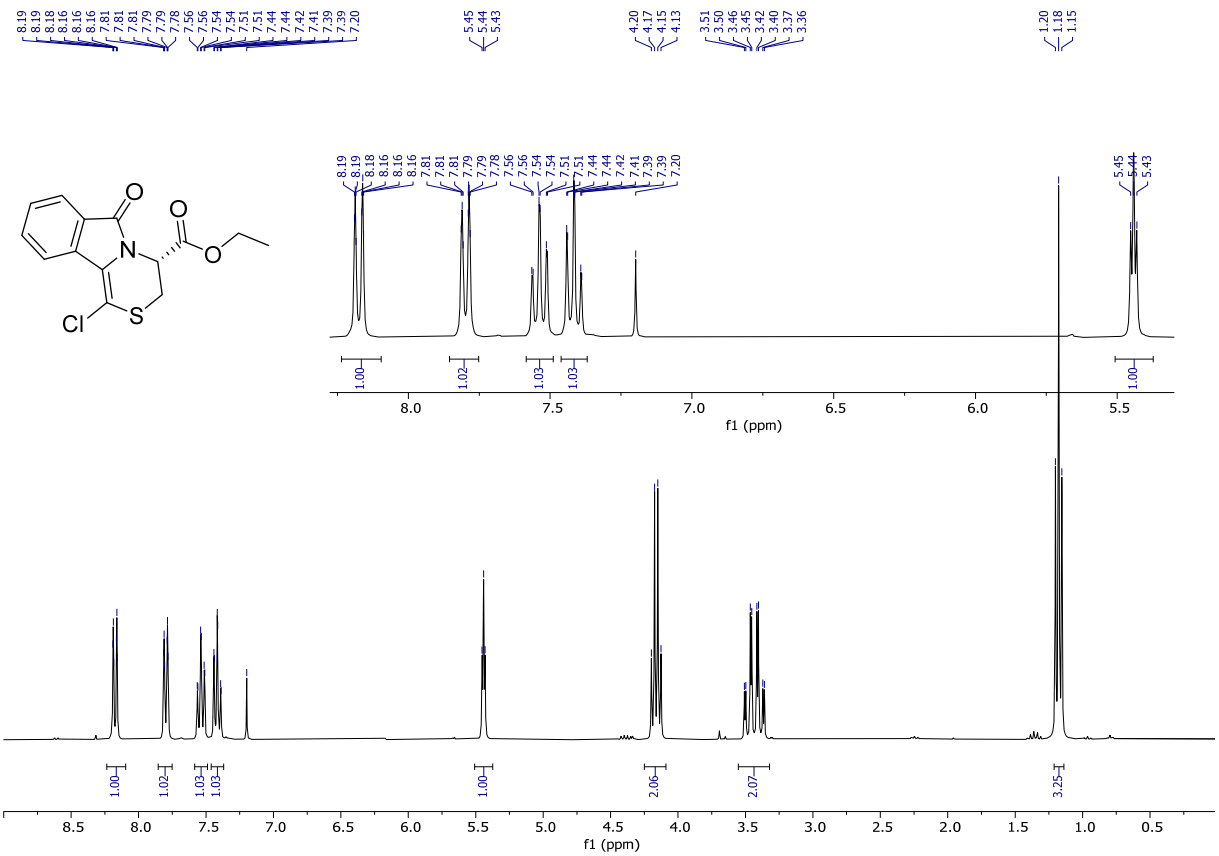
^{13}C NMR spectrum of compound **7bA**



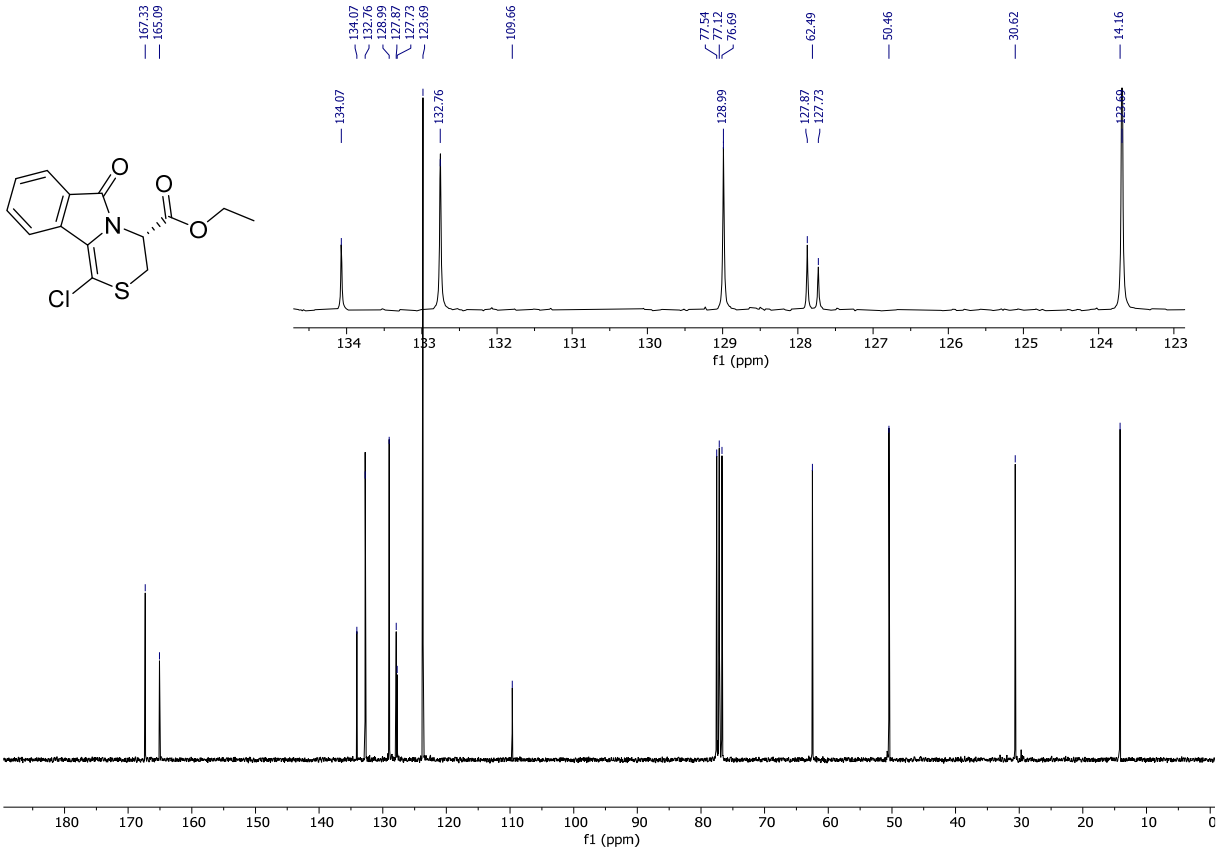
^{1}H NMR spectrum of compound **7bB**



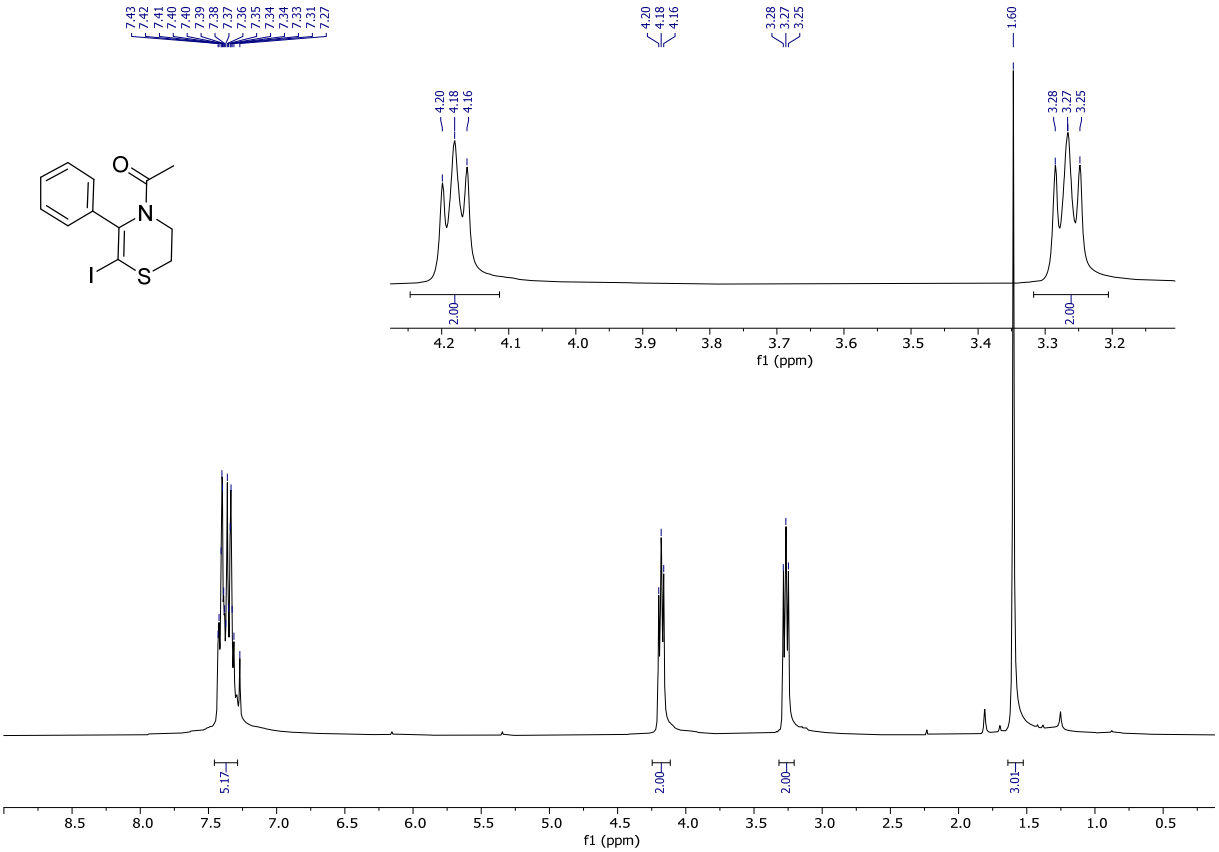
^{13}C NMR spectrum of compound **7bB**



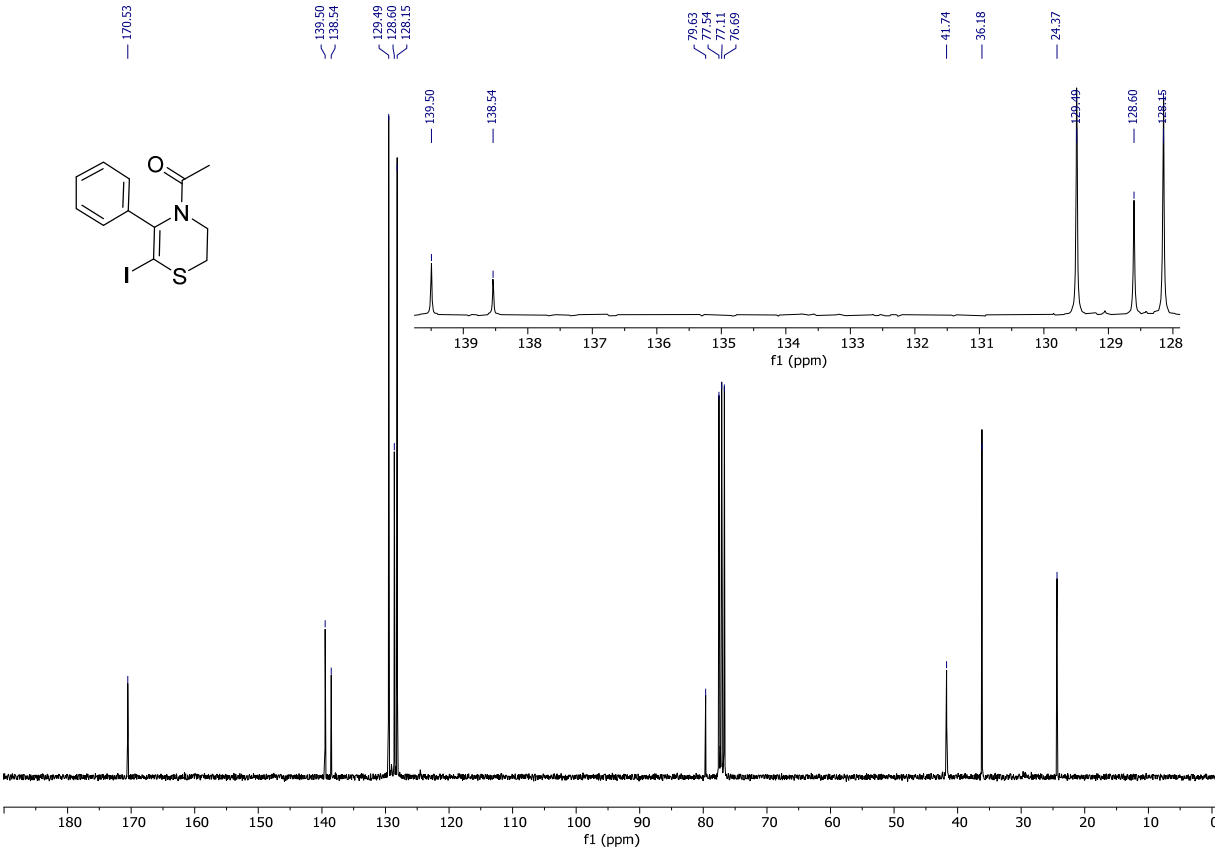
^{1}H NMR spectrum of compound **7bC**



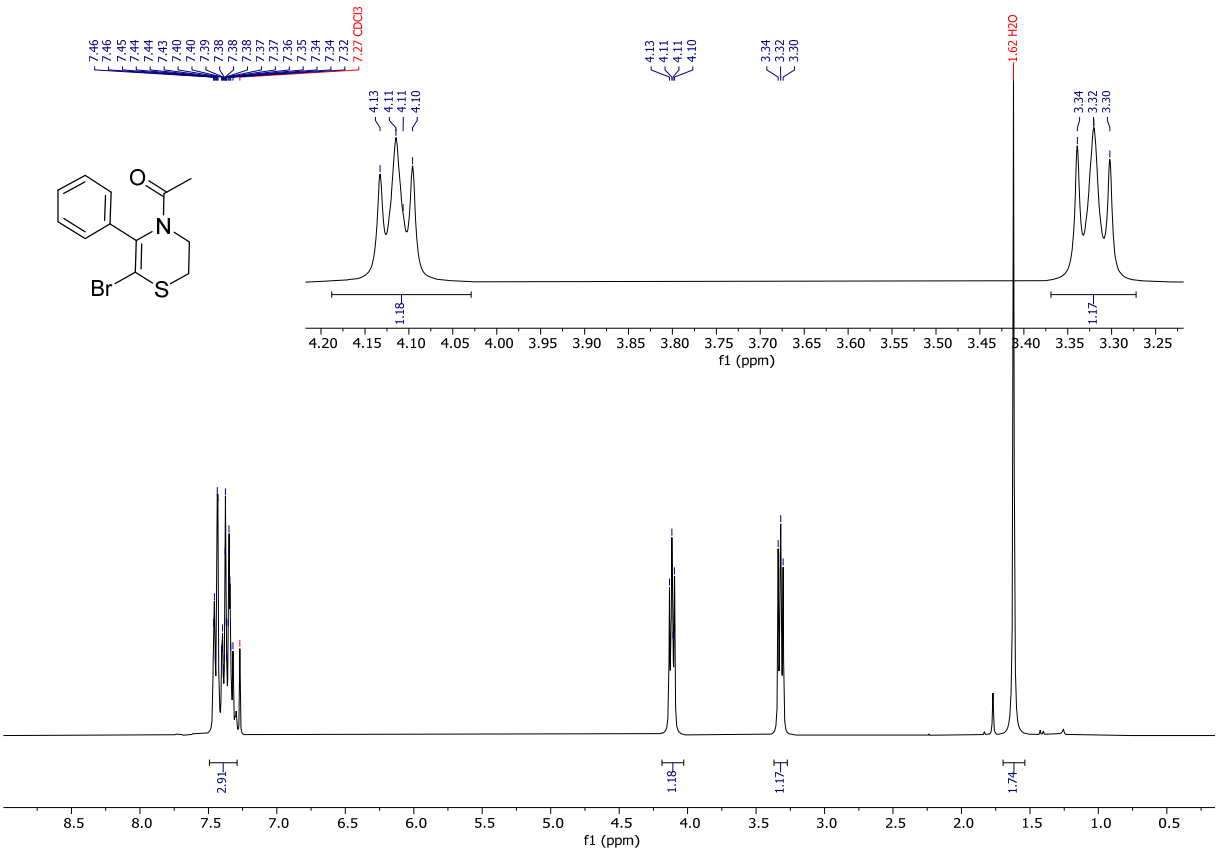
^{13}C NMR spectrum of compound **7bC**



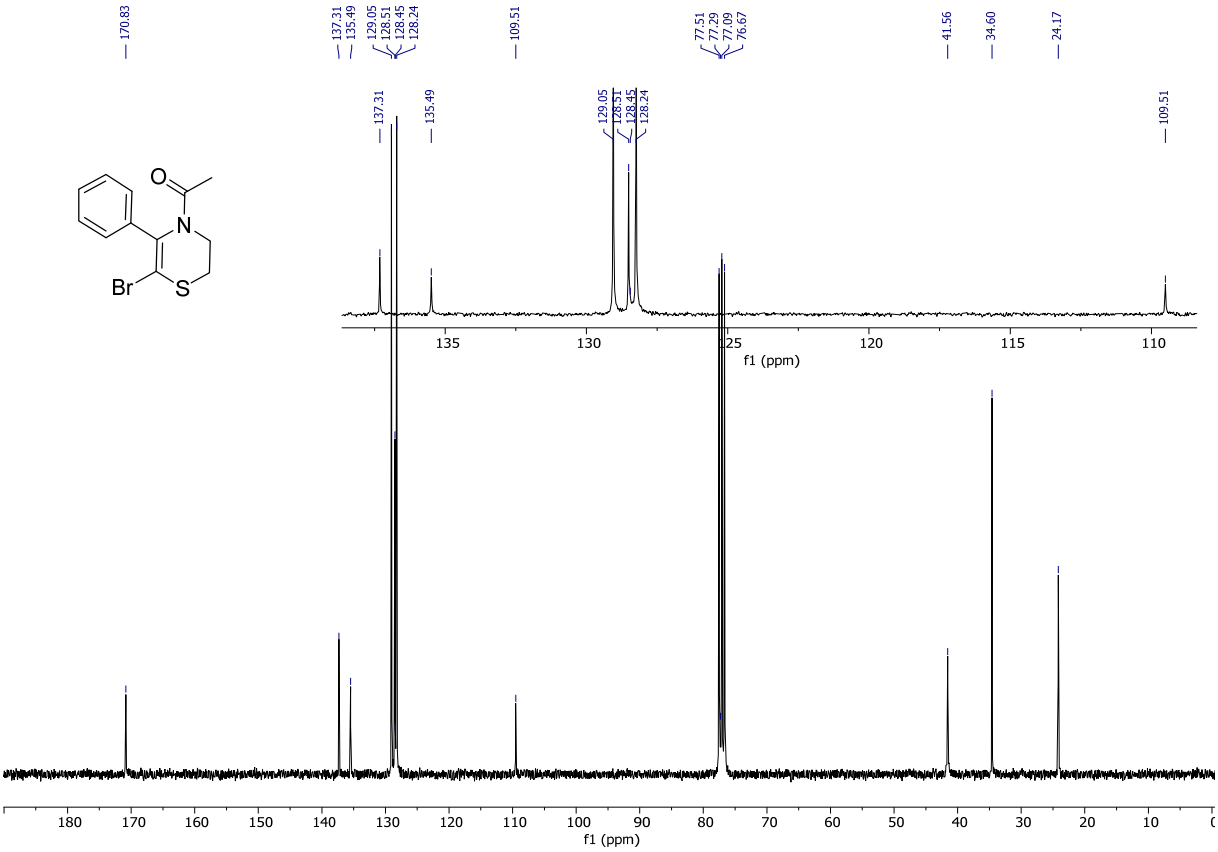
^{1}H NMR spectrum of compound **7cA**



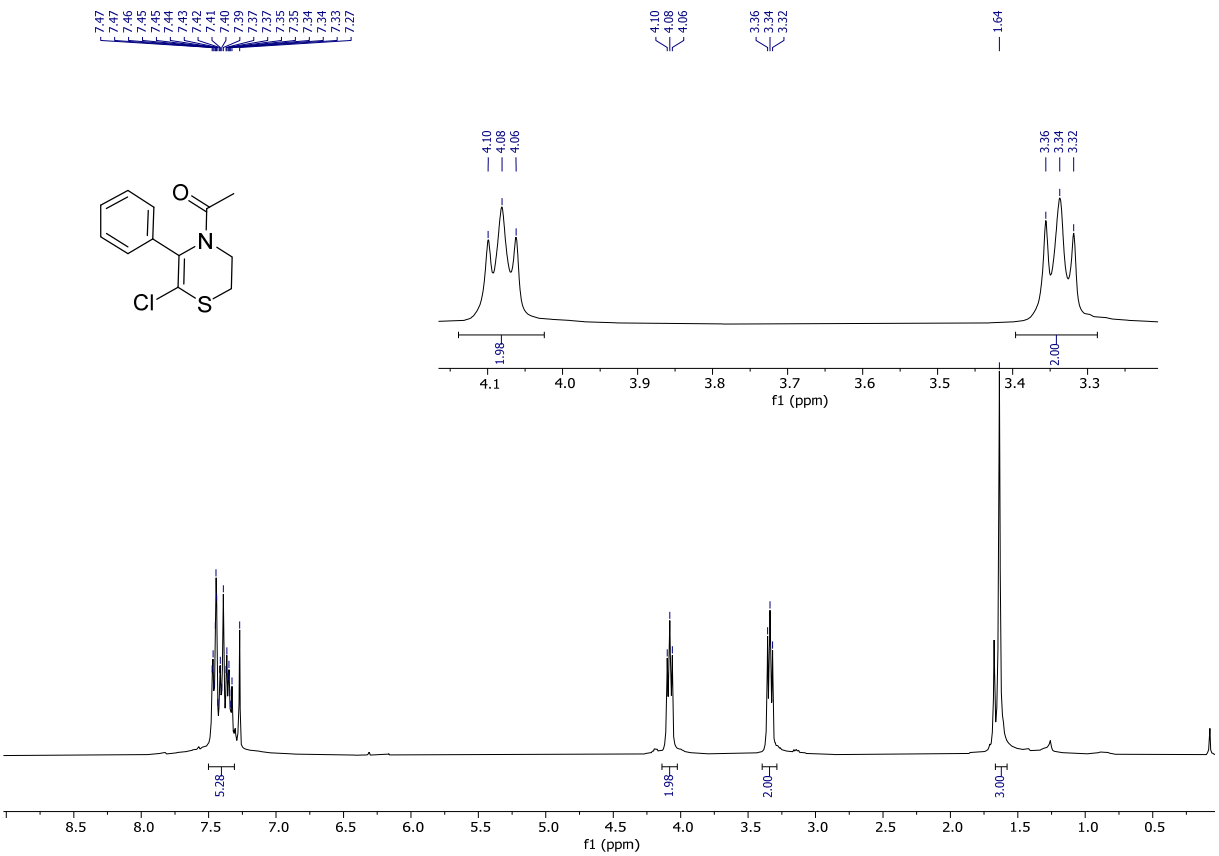
^{13}C NMR spectrum of compound **7cA**



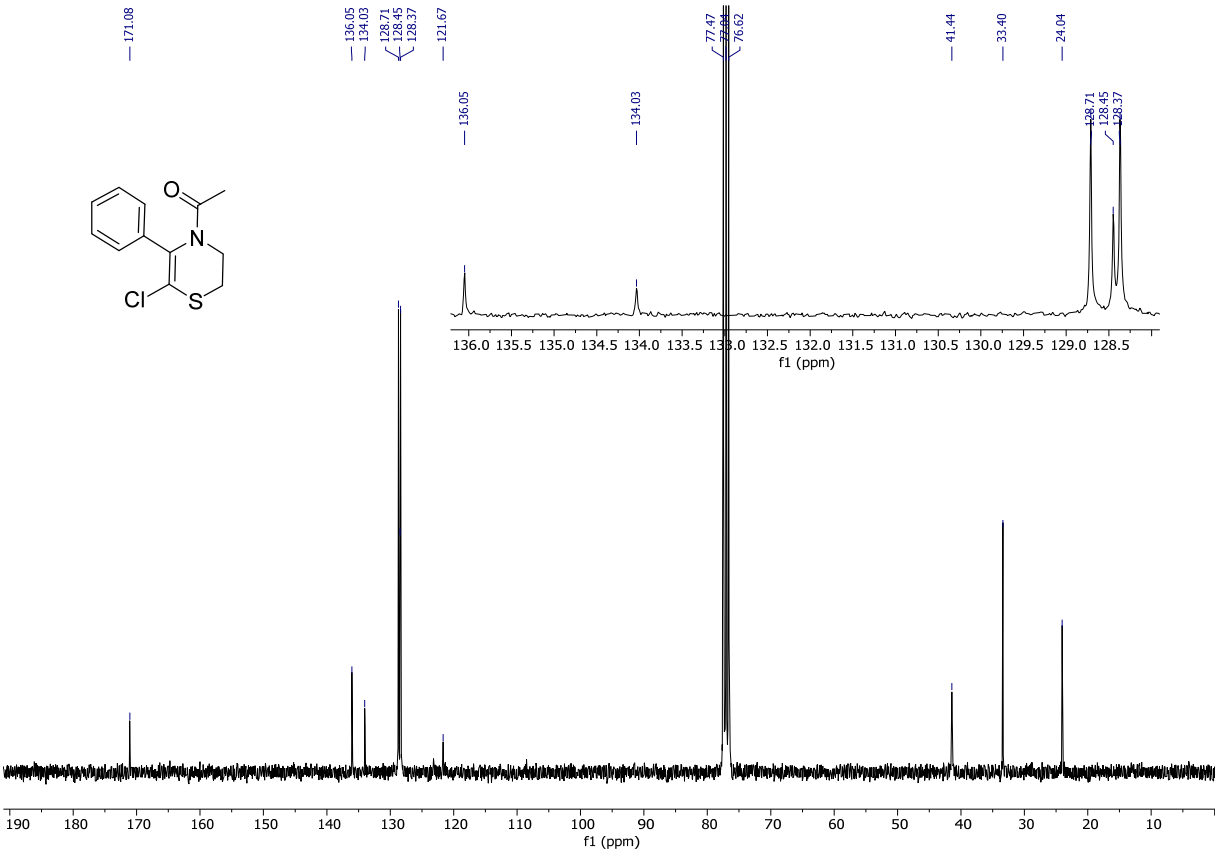
^{1}H NMR spectrum of compound **7cB**



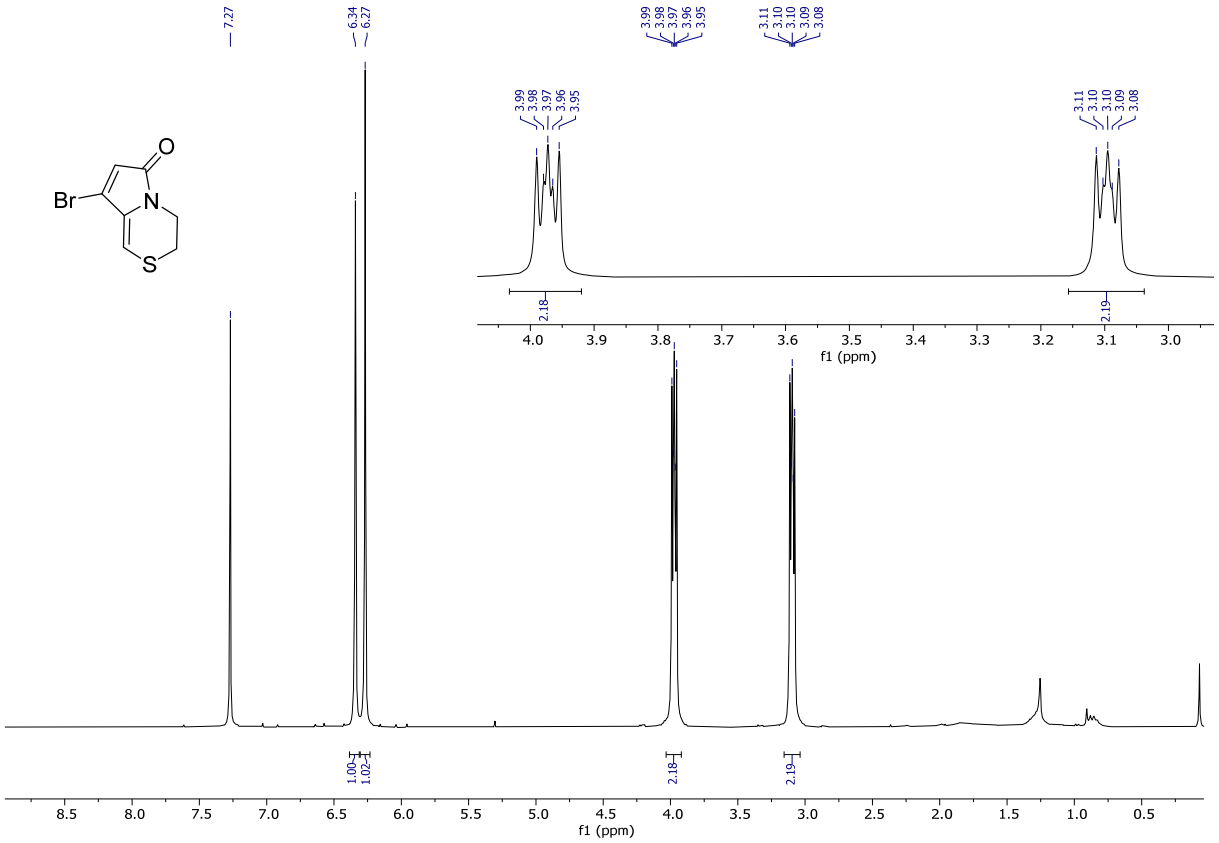
^{13}C NMR spectrum of compound **7cB**



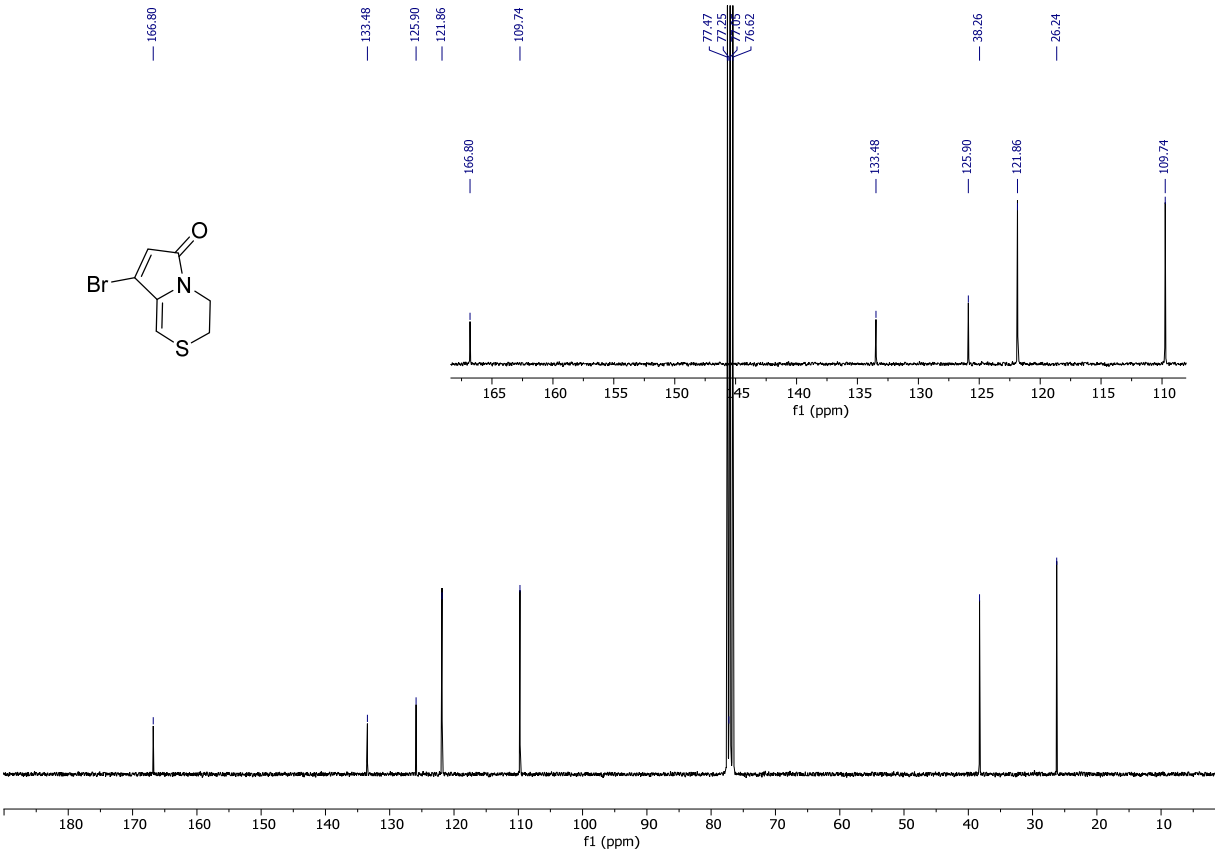
^{1}H NMR spectrum of compound **7cC**



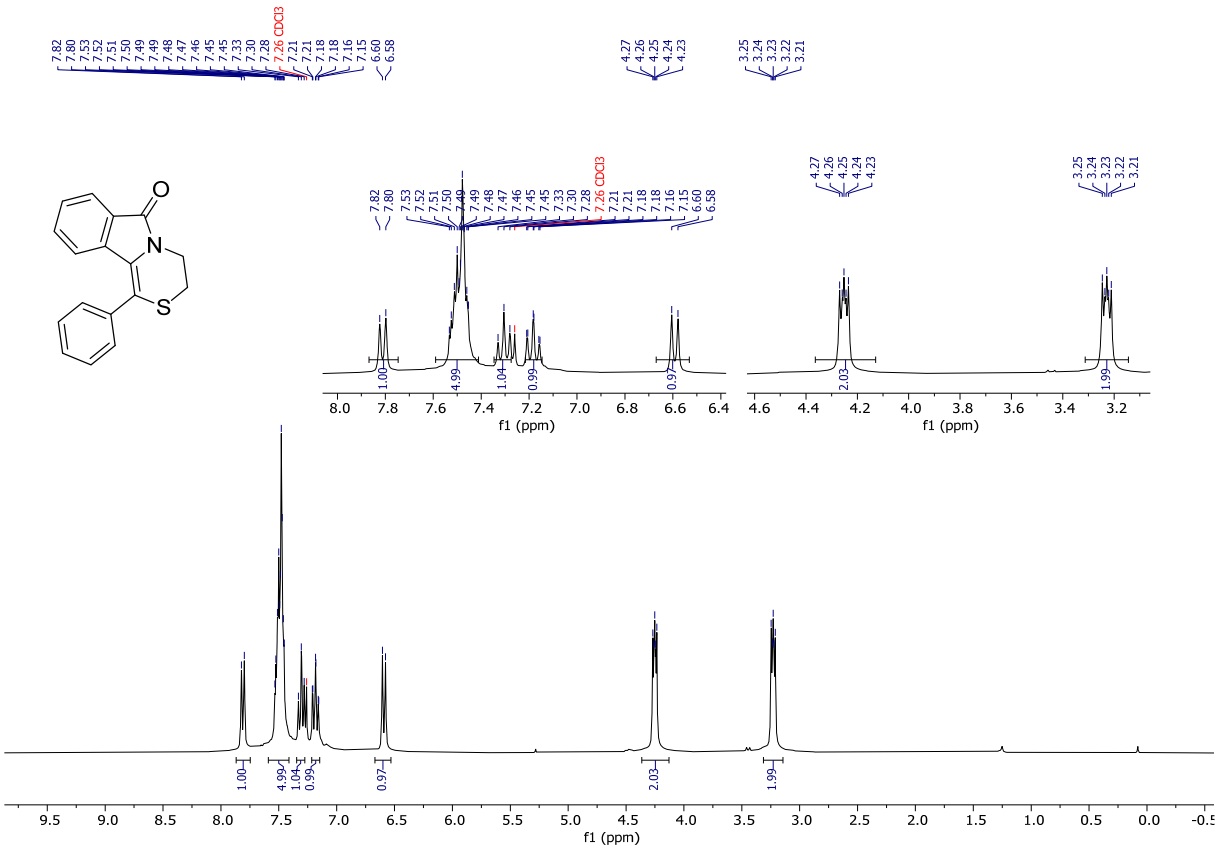
^{13}C NMR spectrum of compound **7cC**



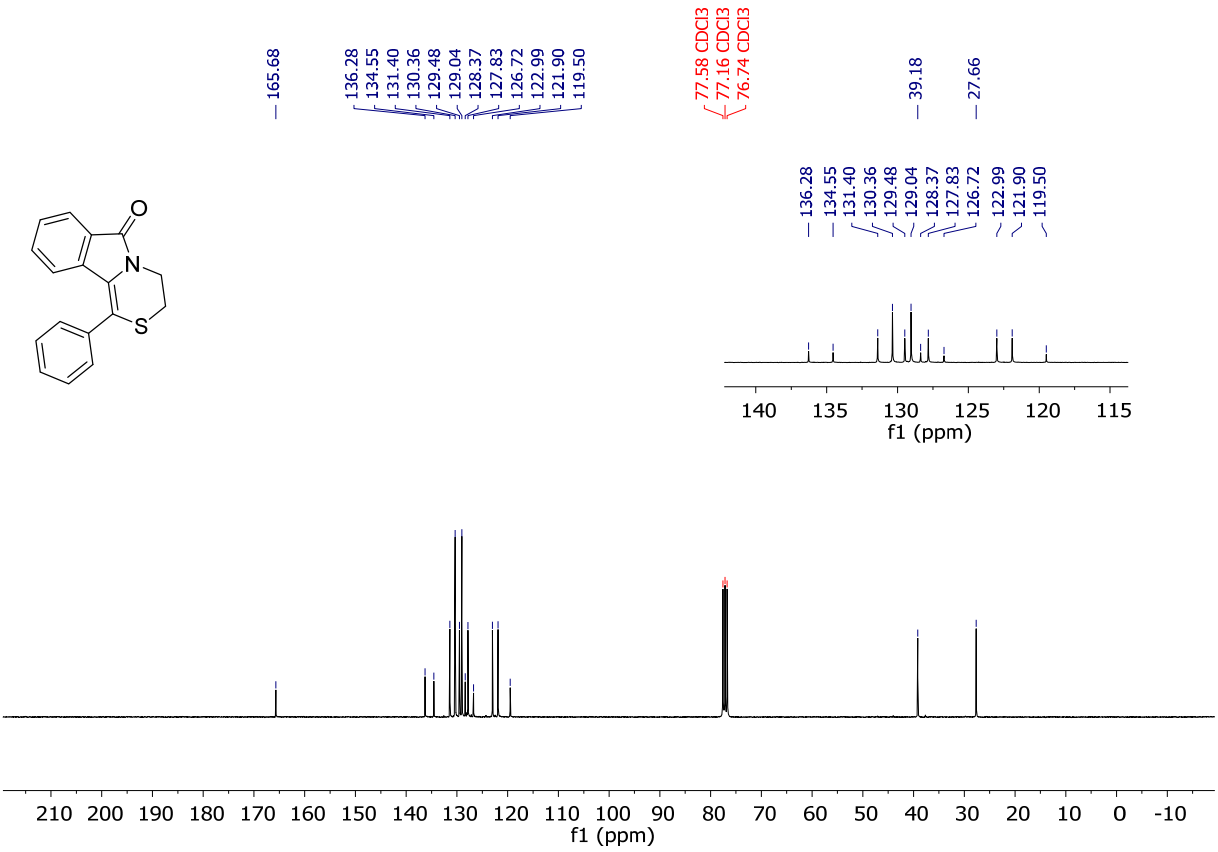
^{1}H NMR spectrum of compound **7dB**



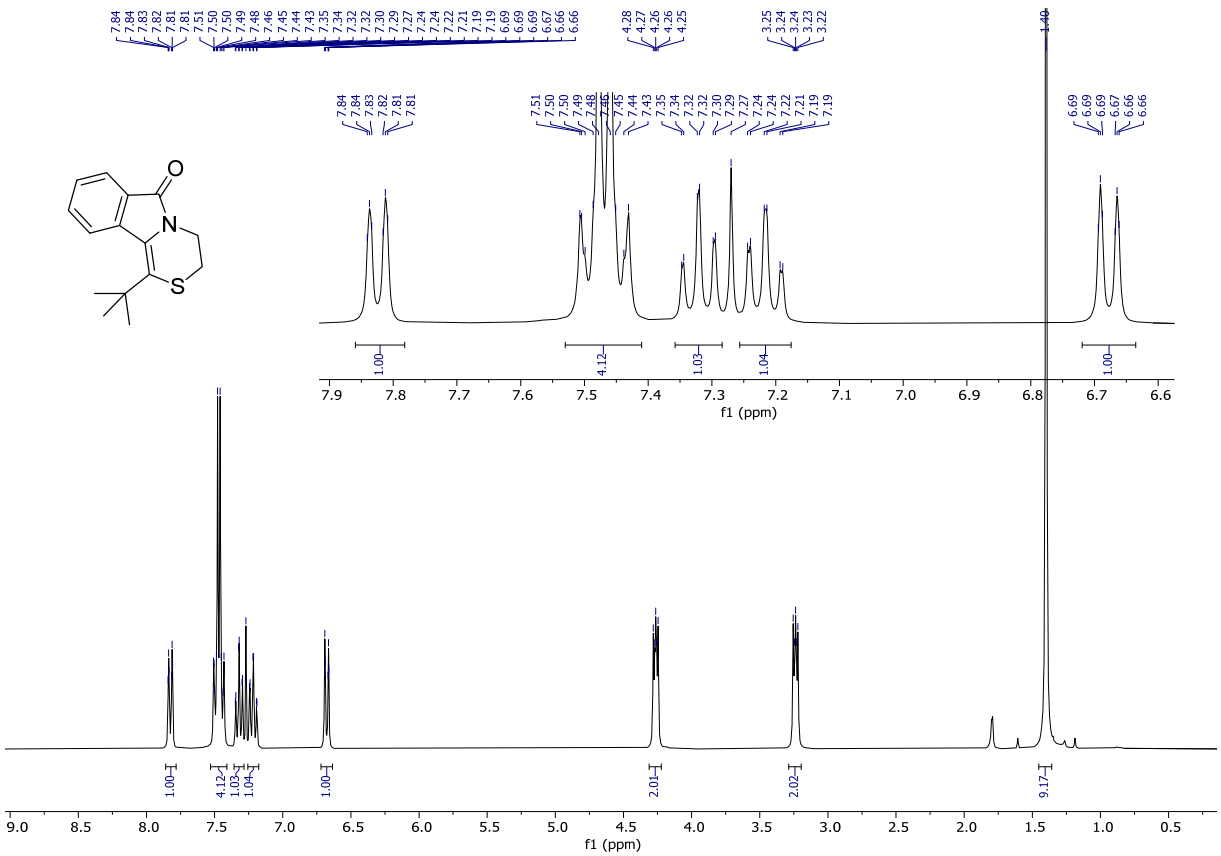
^{13}C NMR spectrum of compound **7dB**



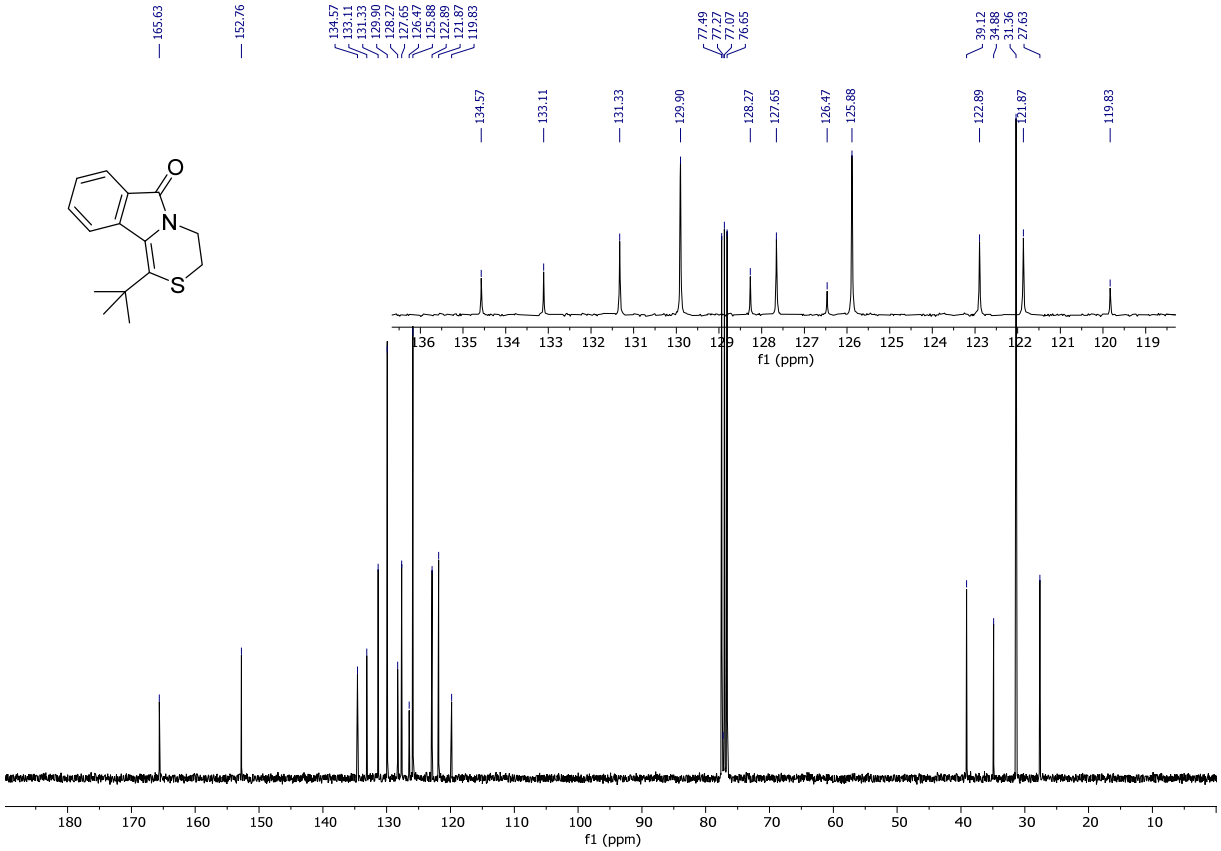
^{1}H NMR spectrum of compound **8a**



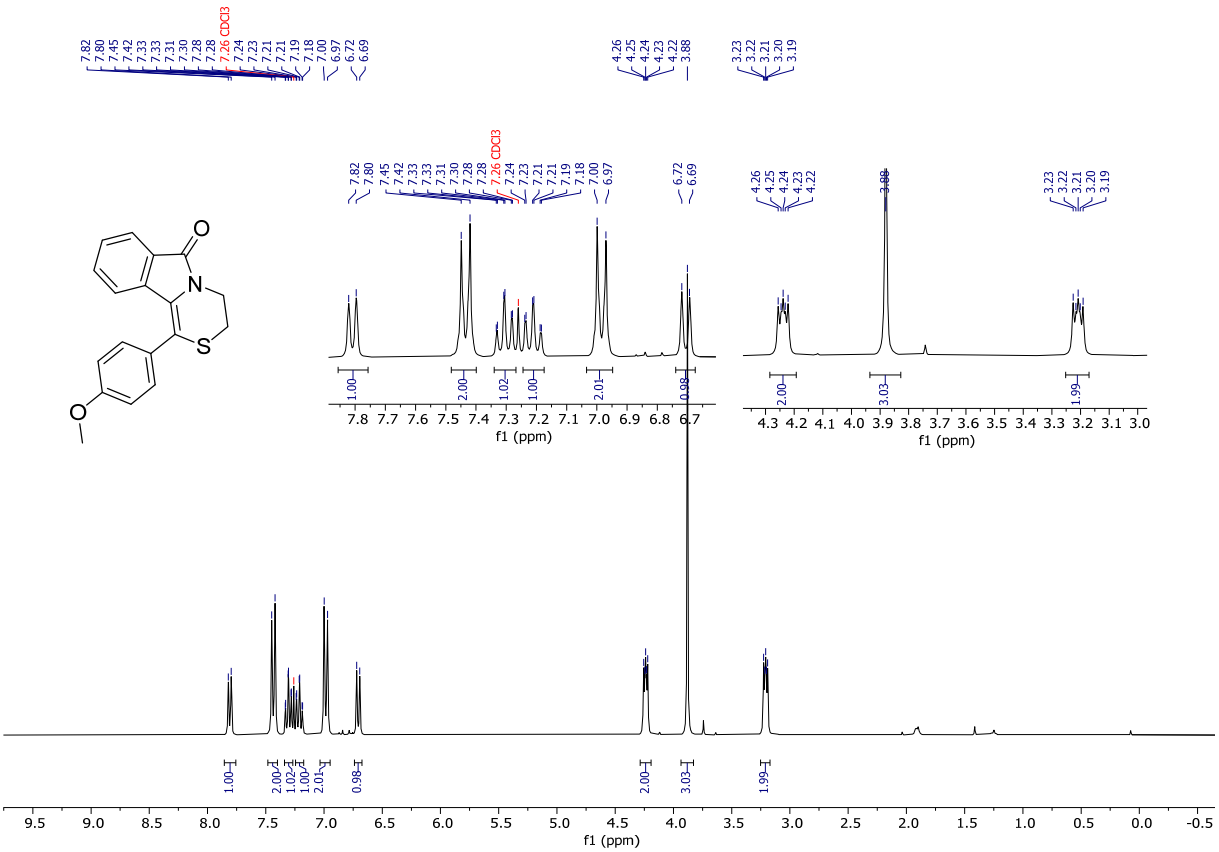
^{13}C NMR spectrum of compound **8a**



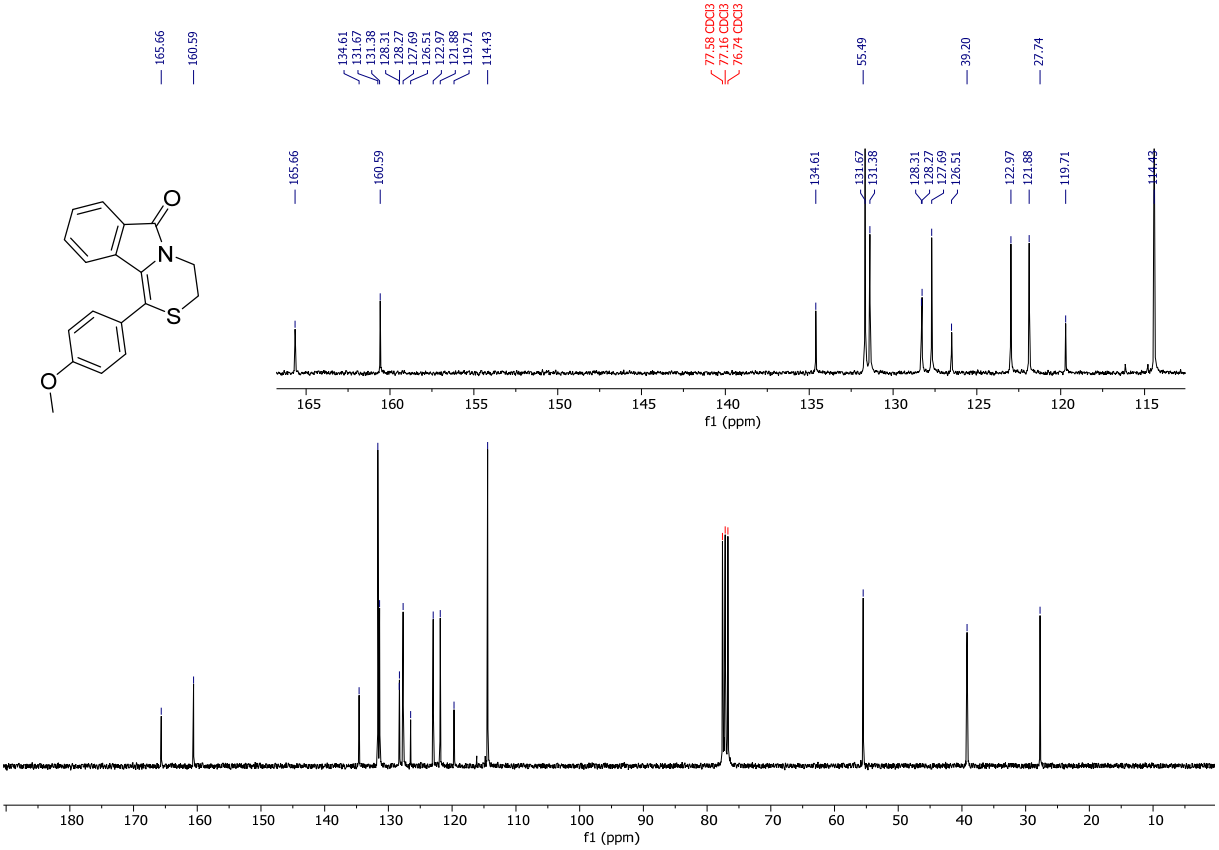
^{1}H NMR spectrum of compound **8b**



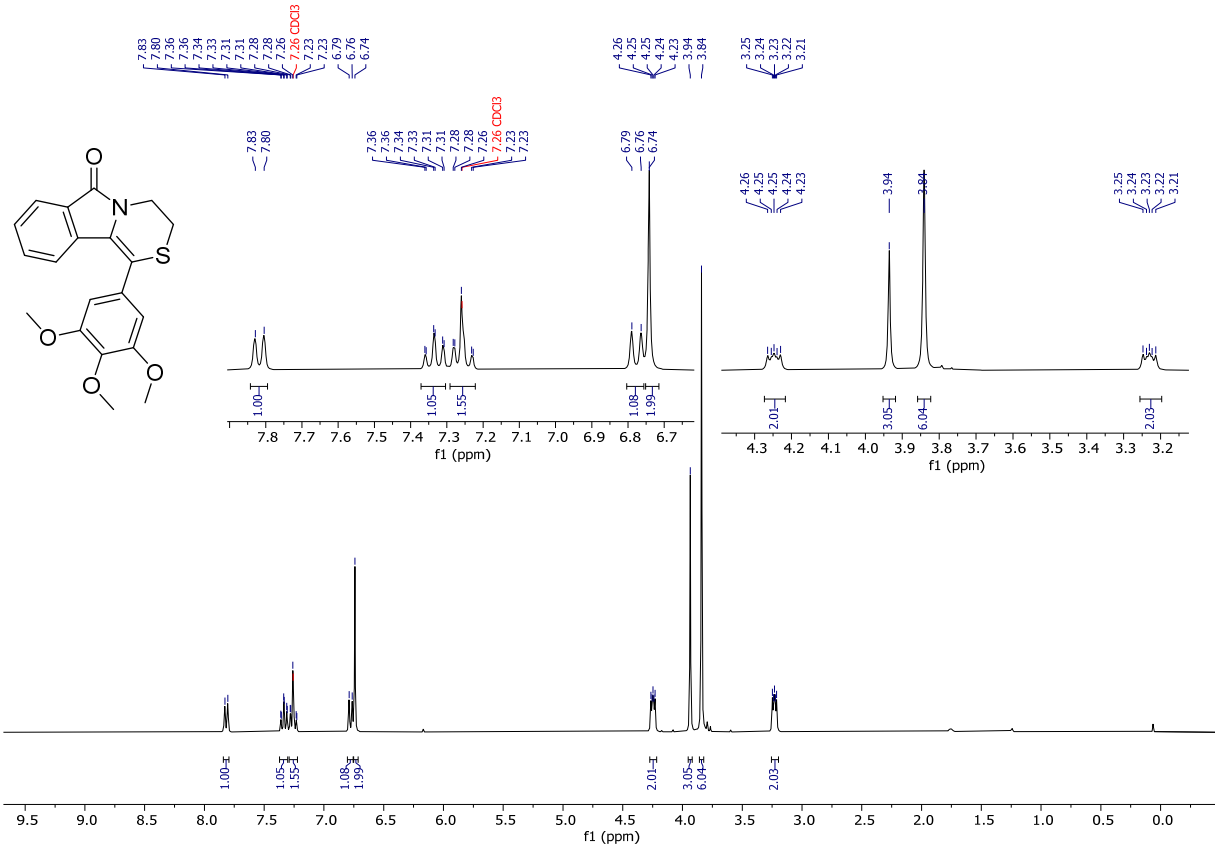
^{13}C NMR spectrum of compound **8b**



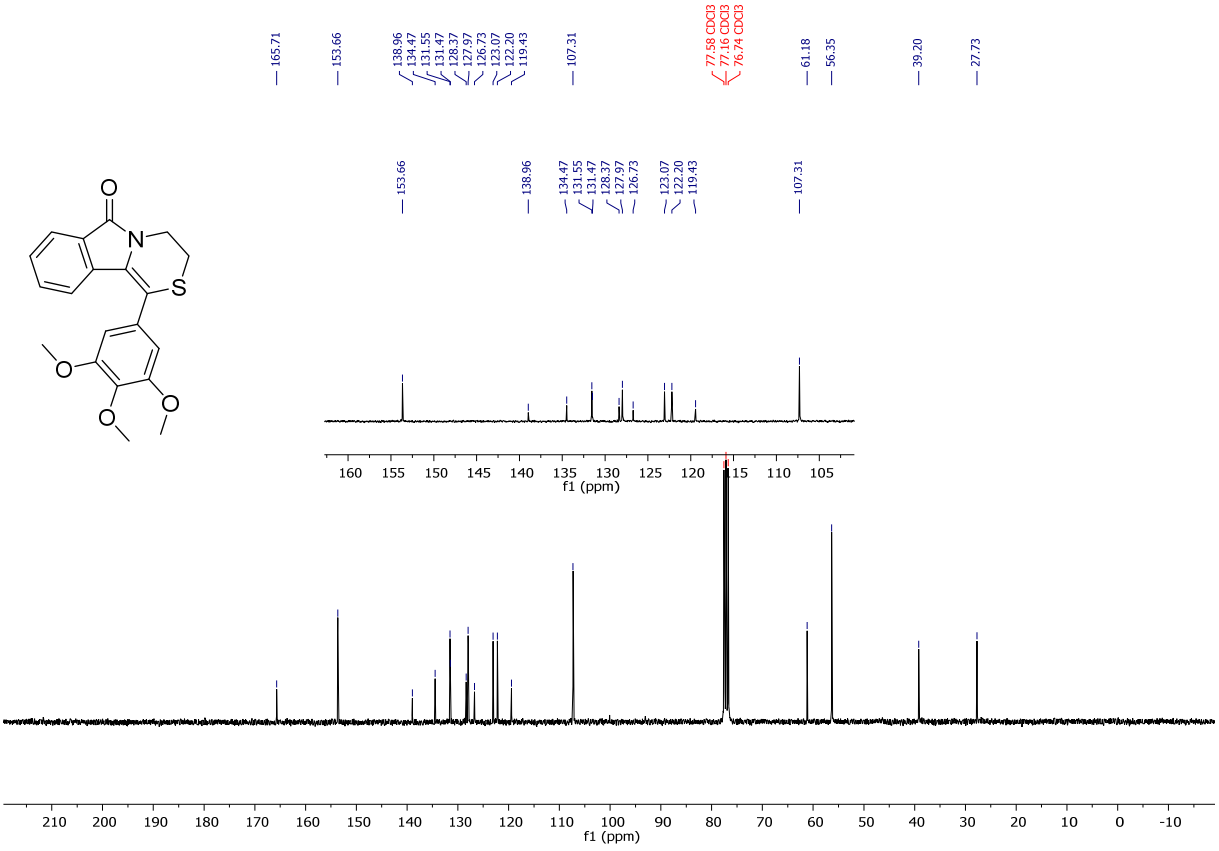
^{1}H NMR spectrum of compound **8c**



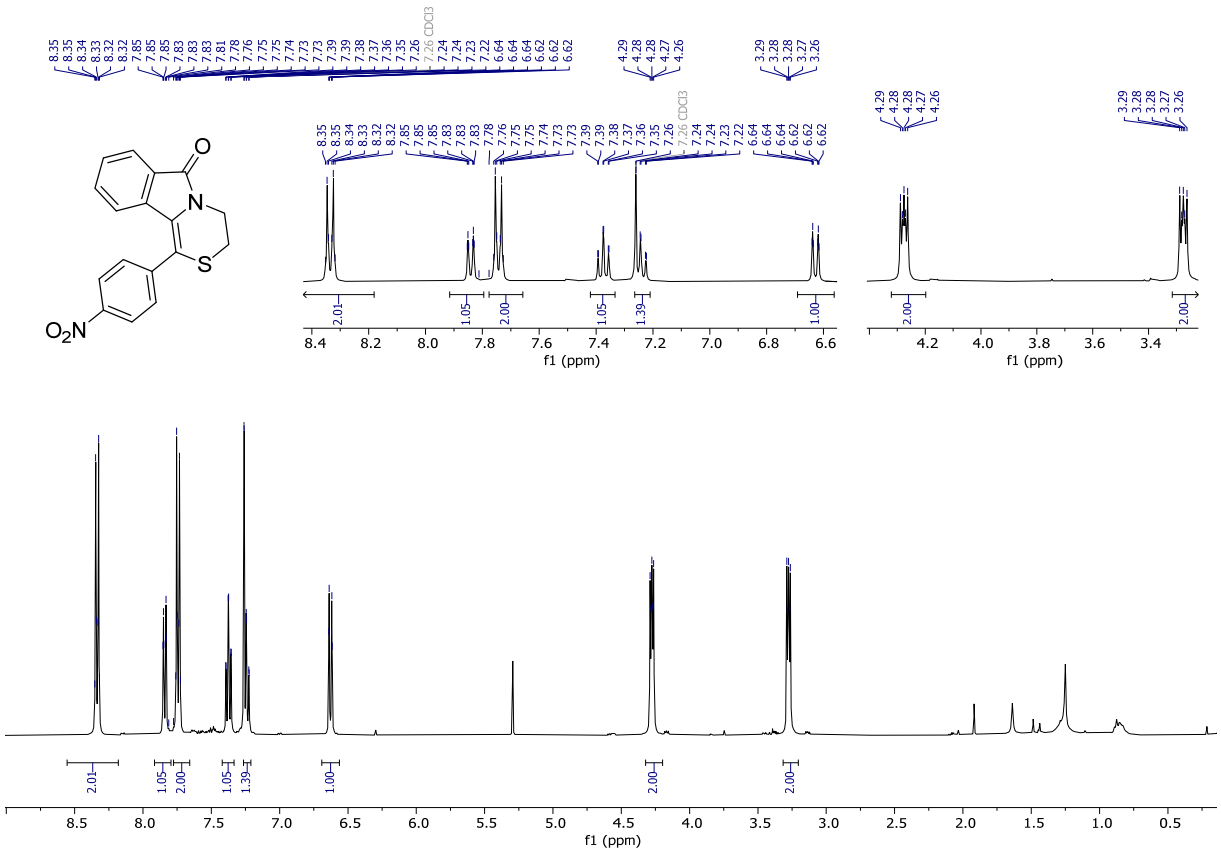
^{13}C NMR spectrum of compound **8c**



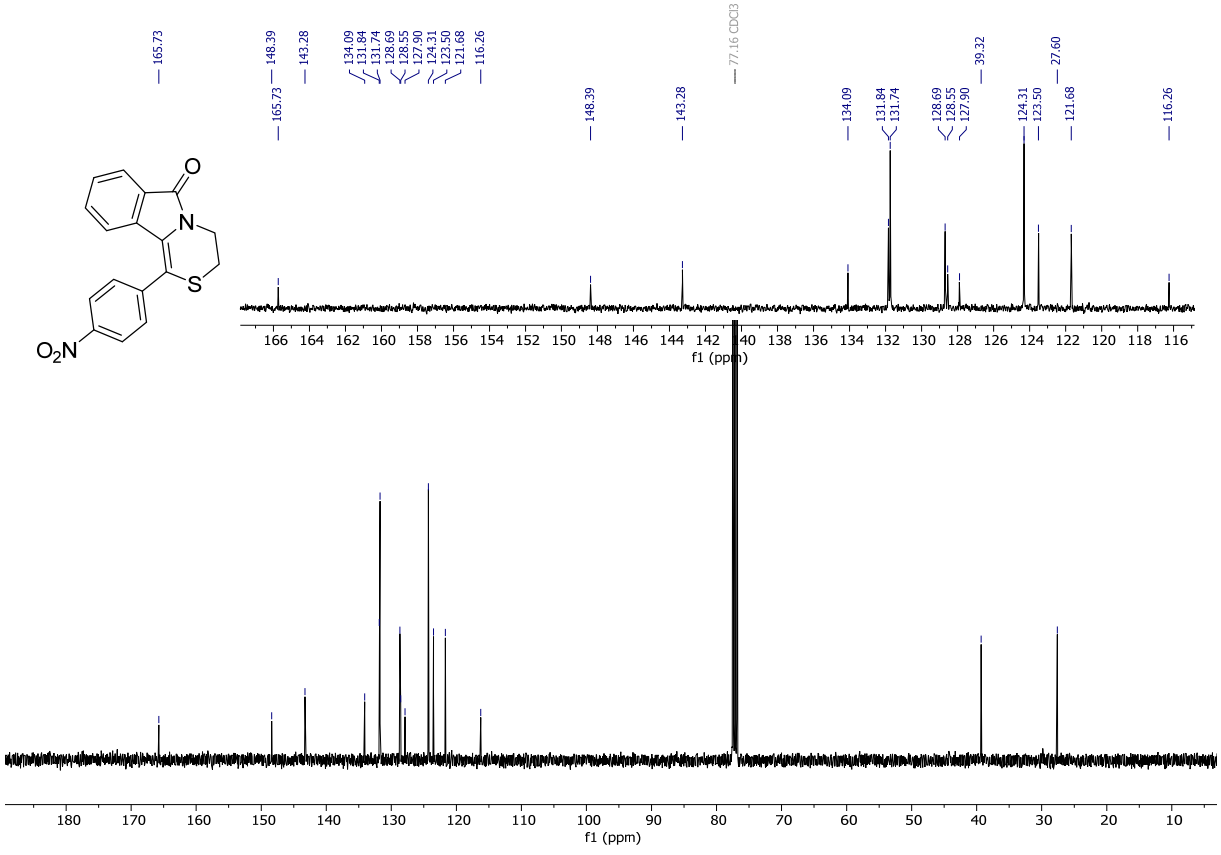
^{1}H NMR spectrum of compound **8d**



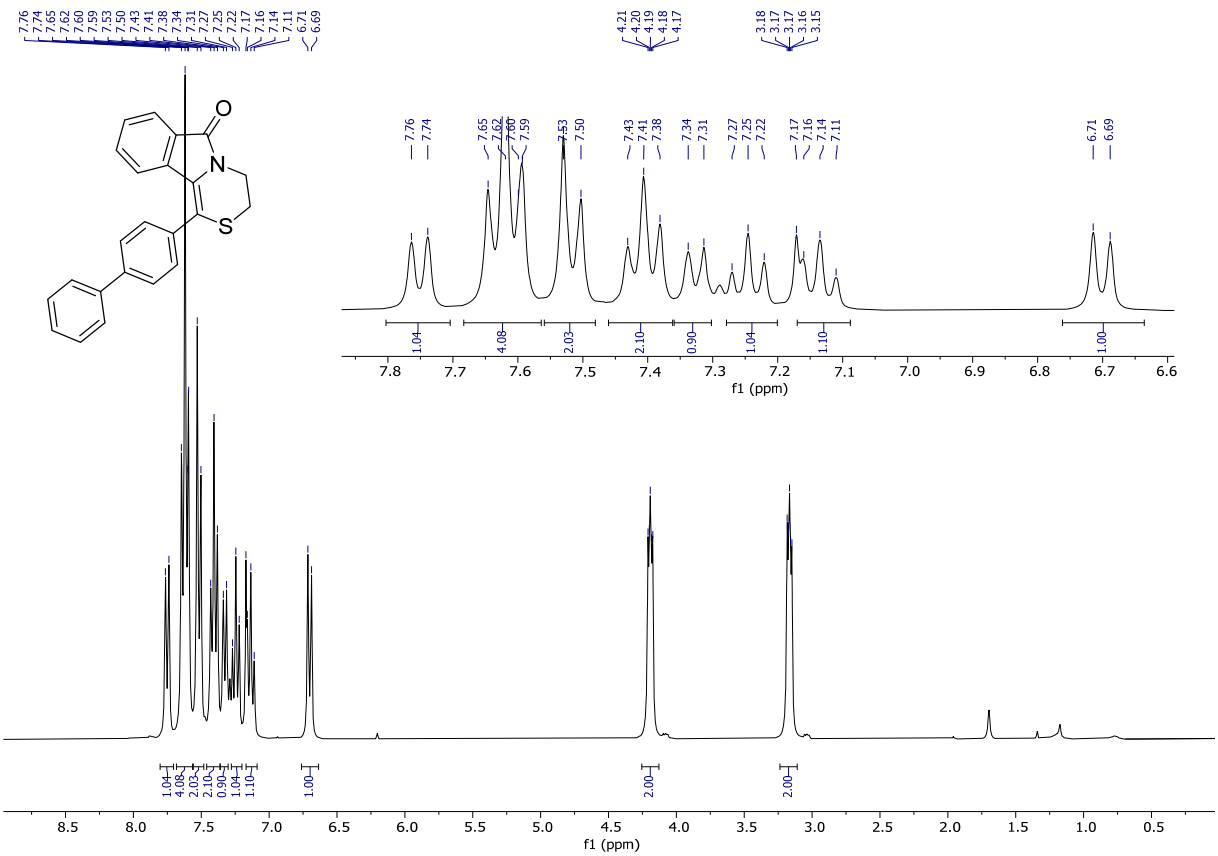
^{13}C NMR spectrum of compound **8d**



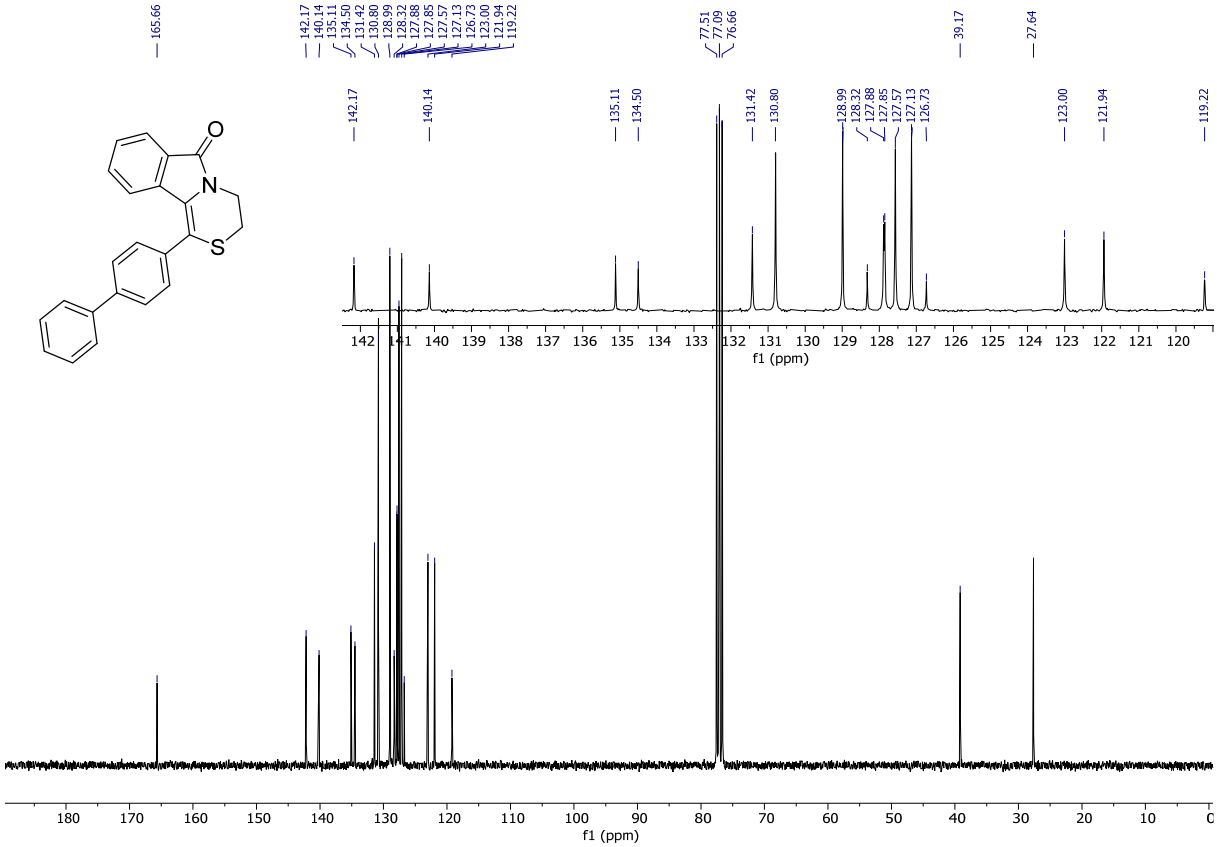
^{1}H NMR spectrum of compound **8e**



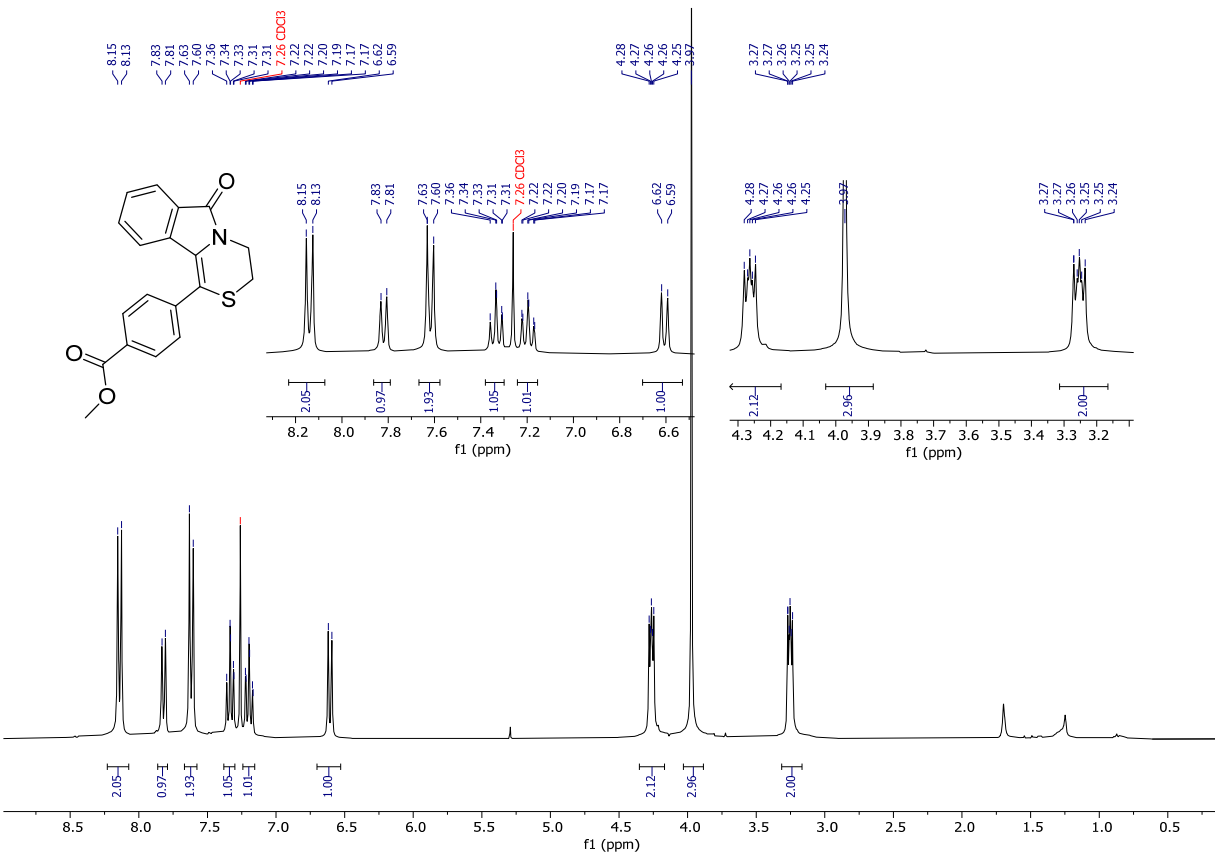
^{13}C NMR spectrum of compound **8e**



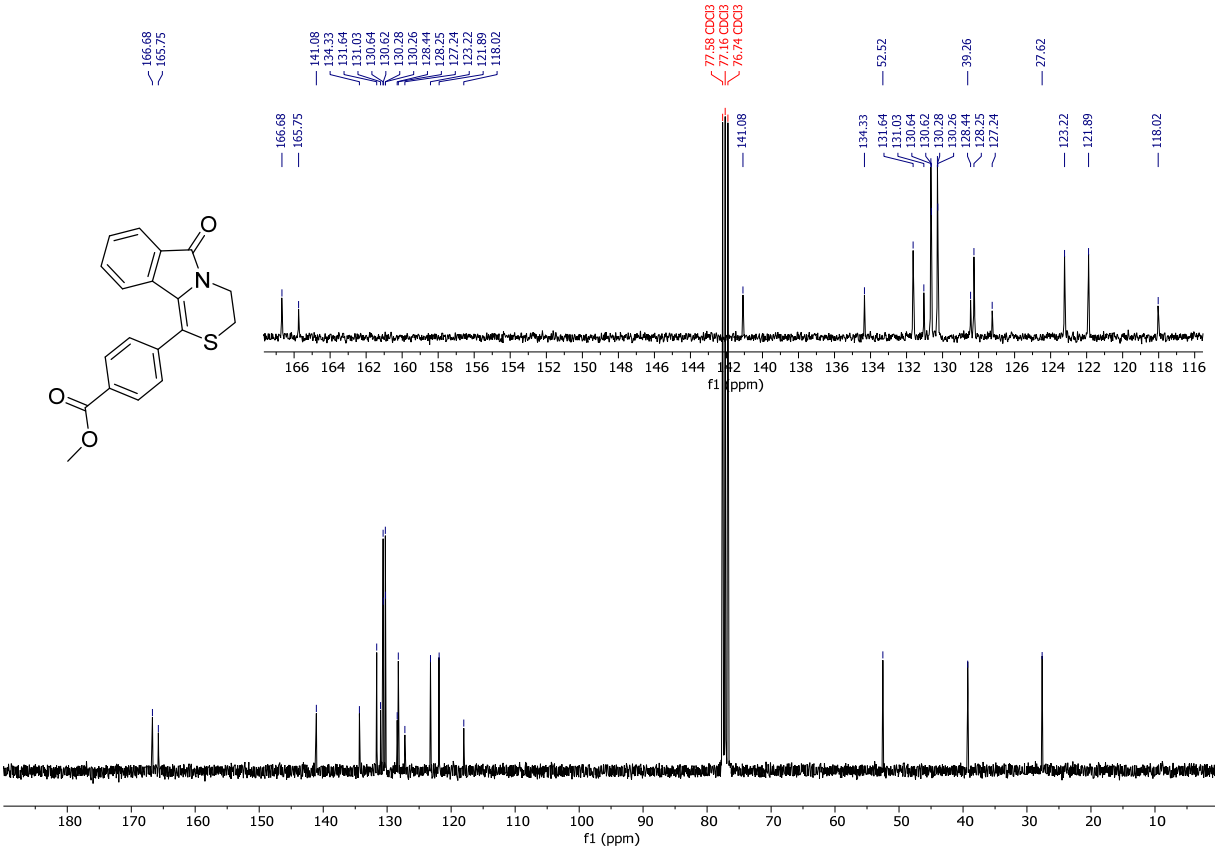
^{1}H NMR spectrum of compound **8f**



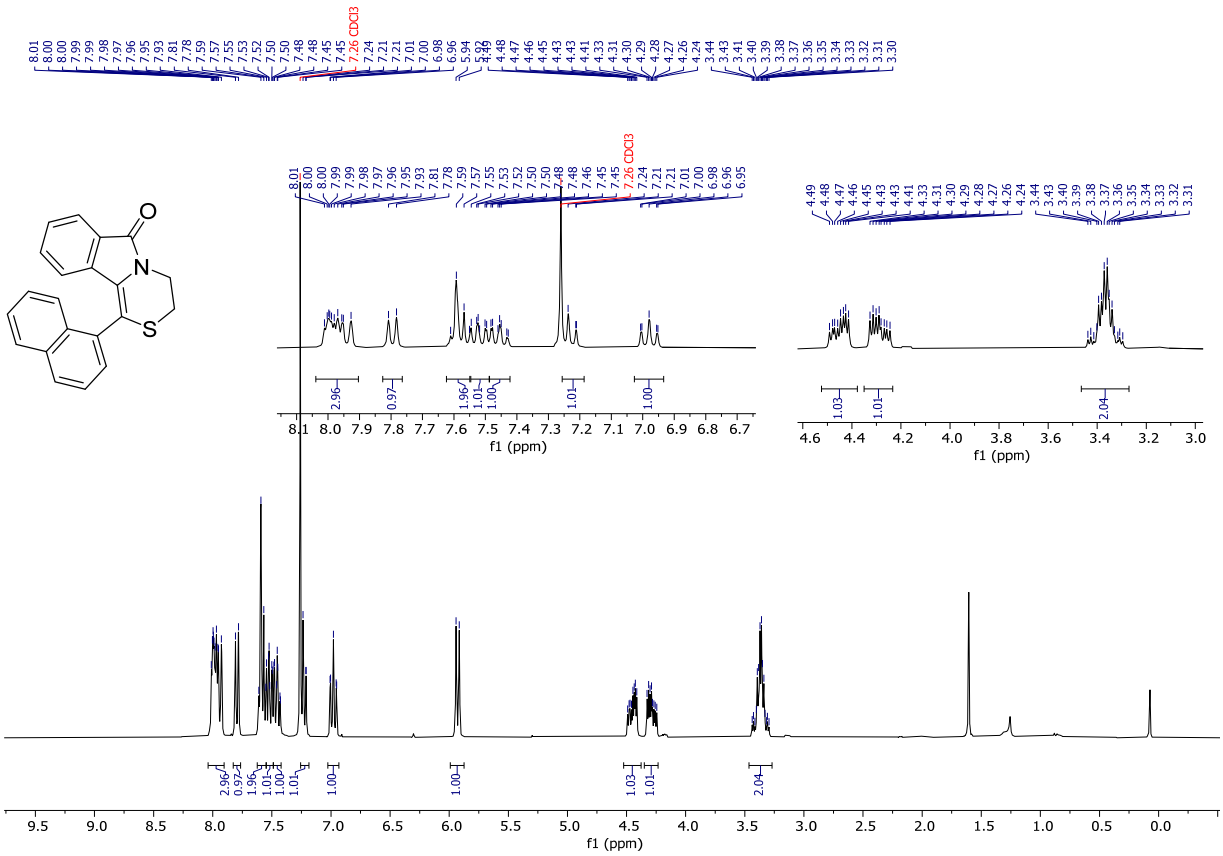
^{13}C NMR spectrum of compound **8f**



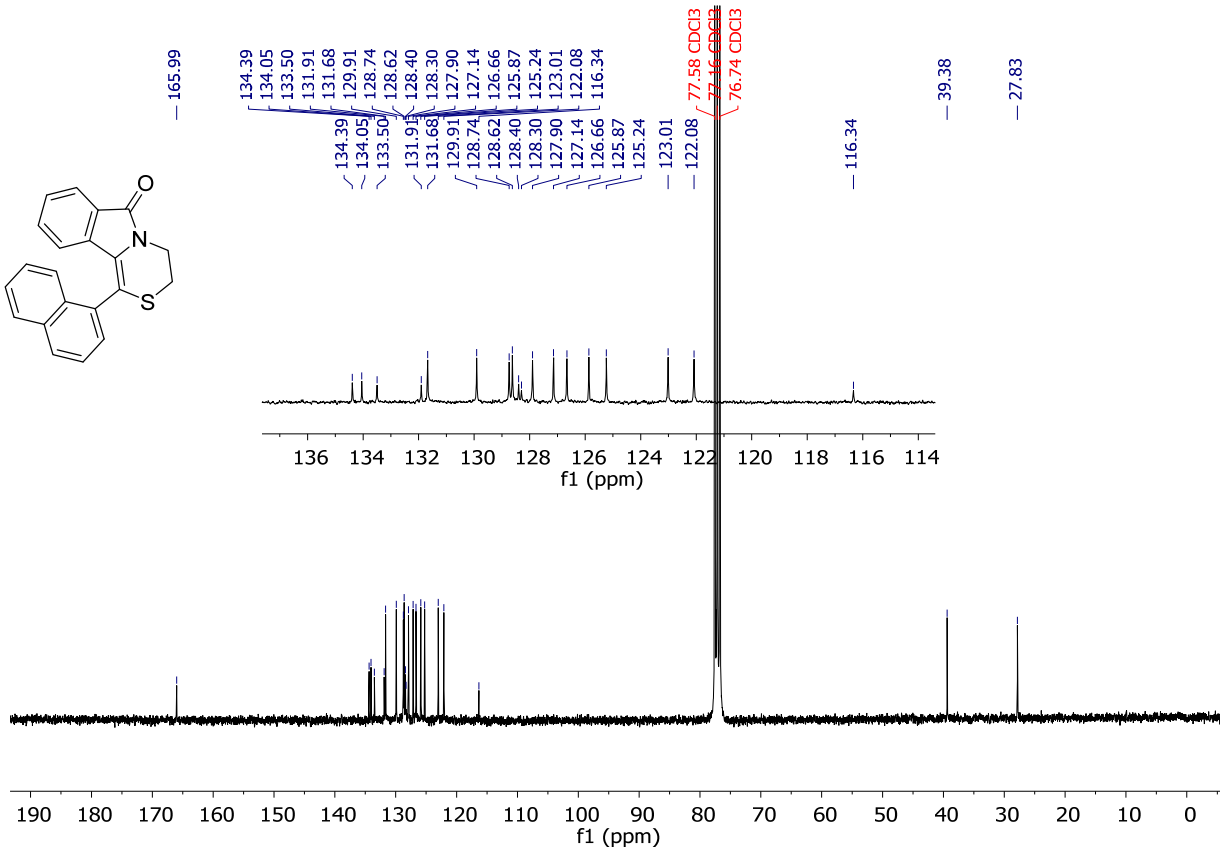
^{1}H NMR spectrum of compound **8g**



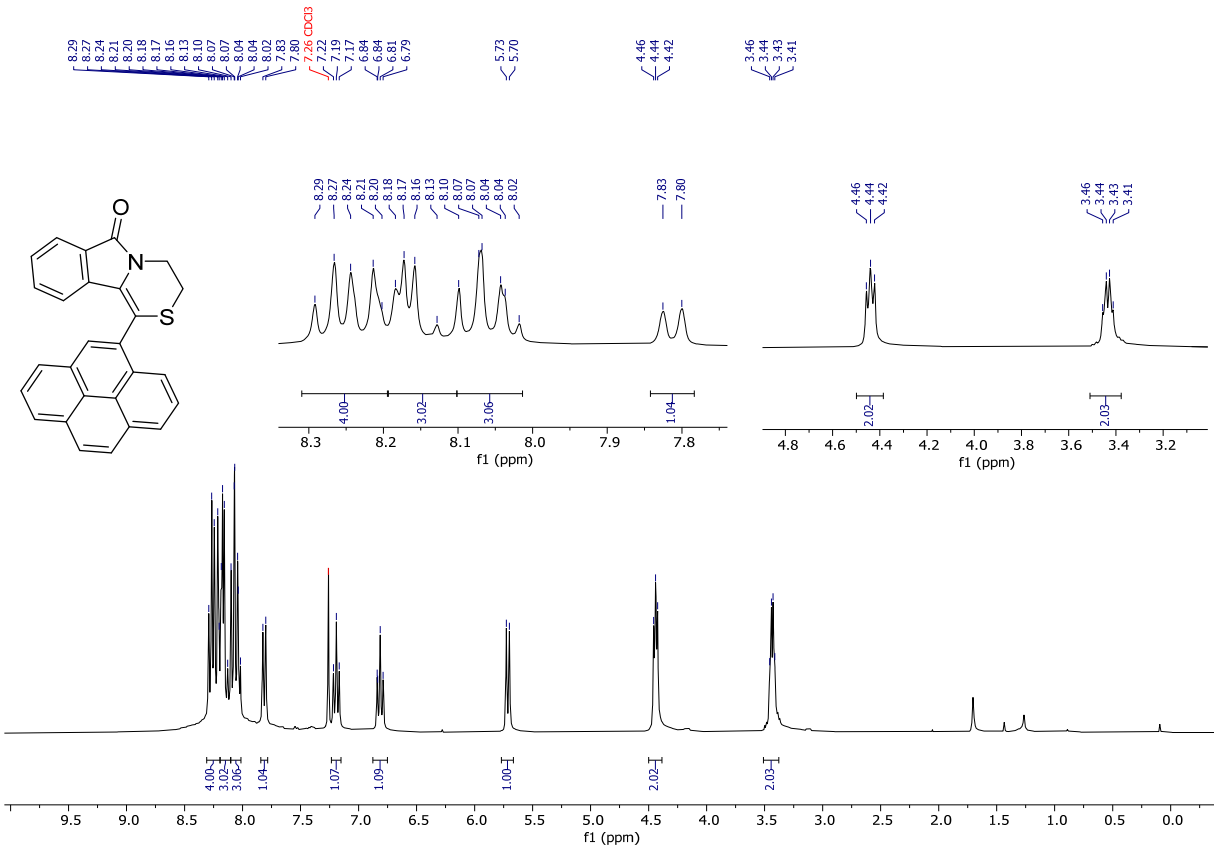
^{13}C NMR spectrum of compound **8g**



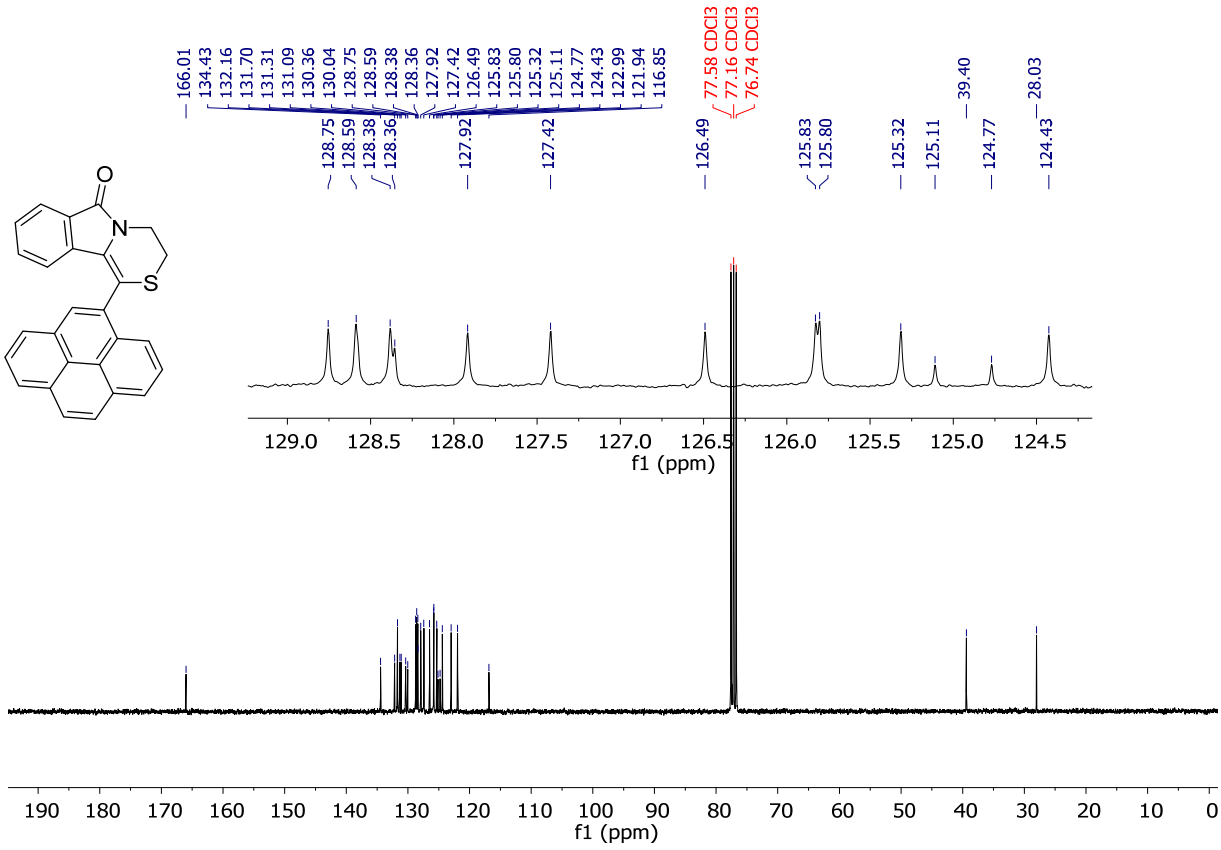
^{1}H NMR spectrum of compound **8h**



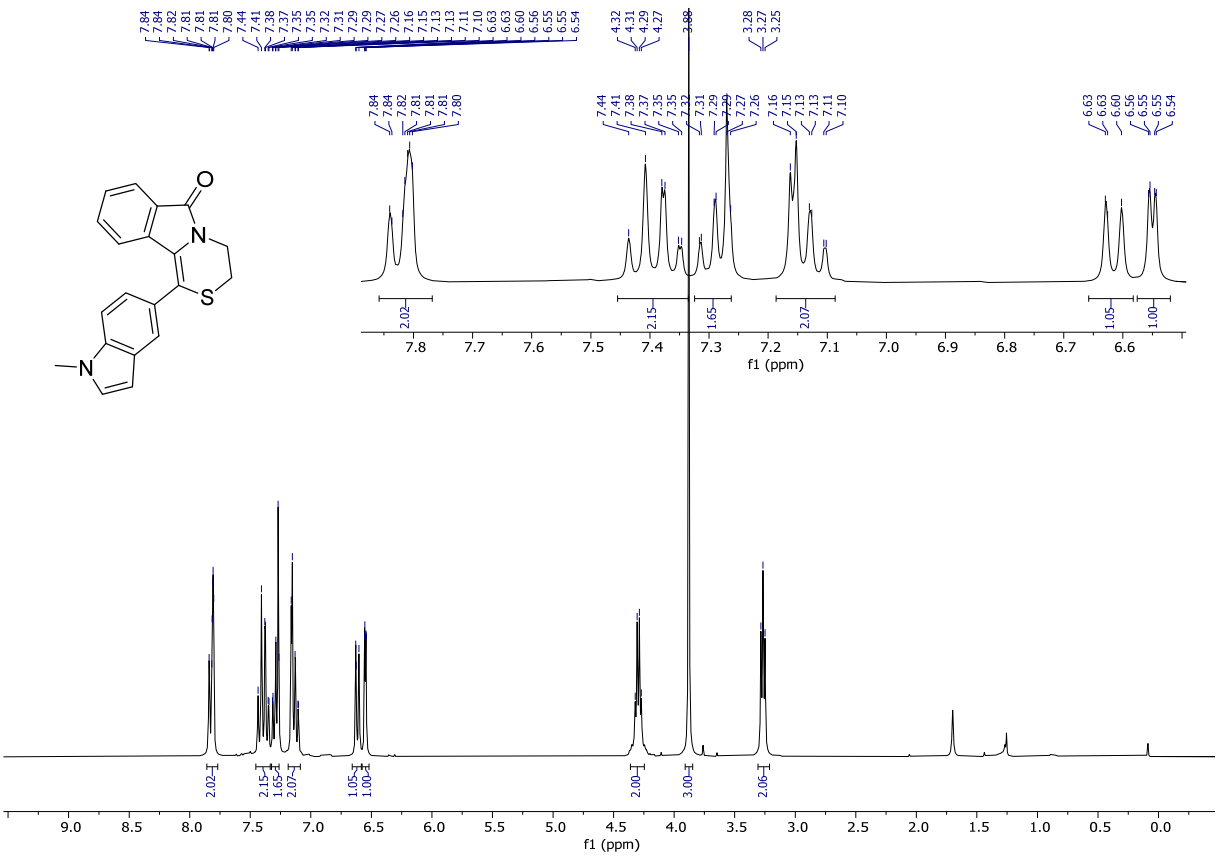
^{13}C NMR spectrum of compound **8h**



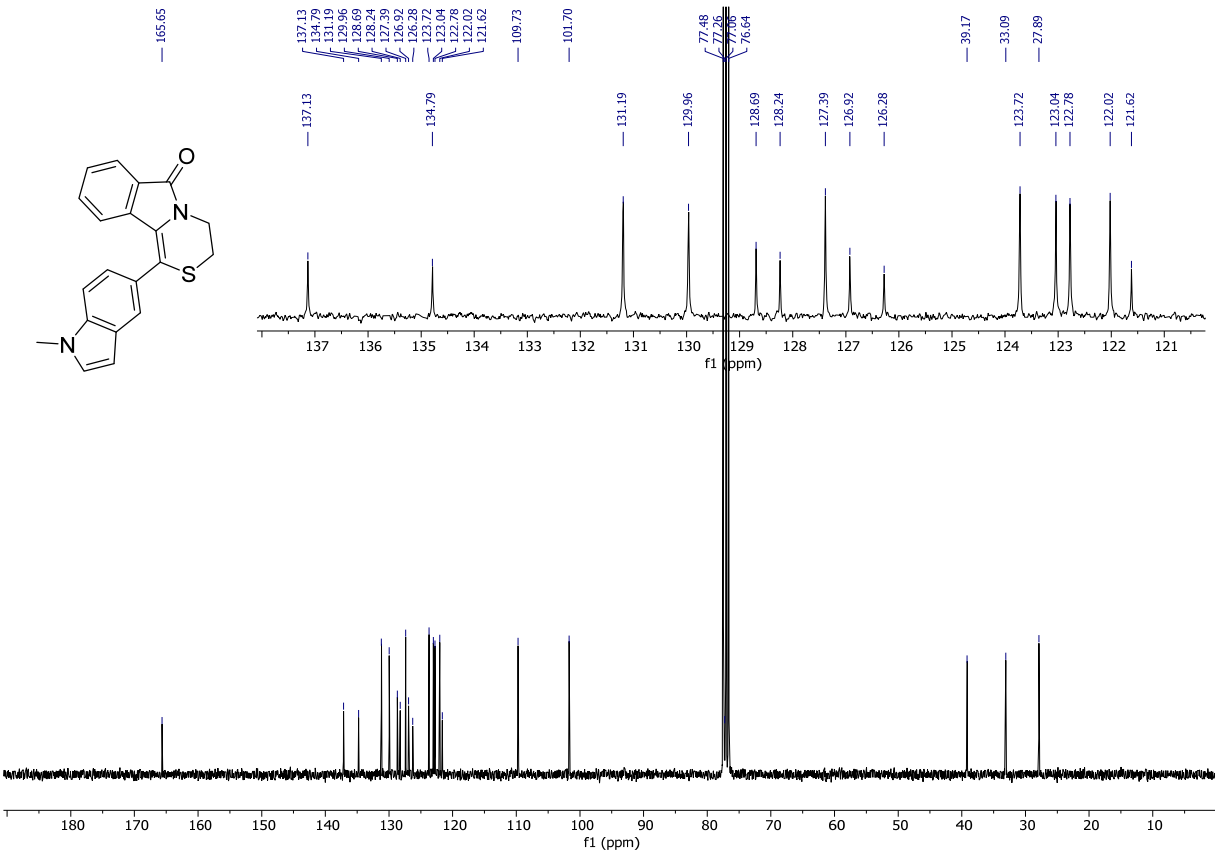
^{1}H NMR spectrum of compound **8i**



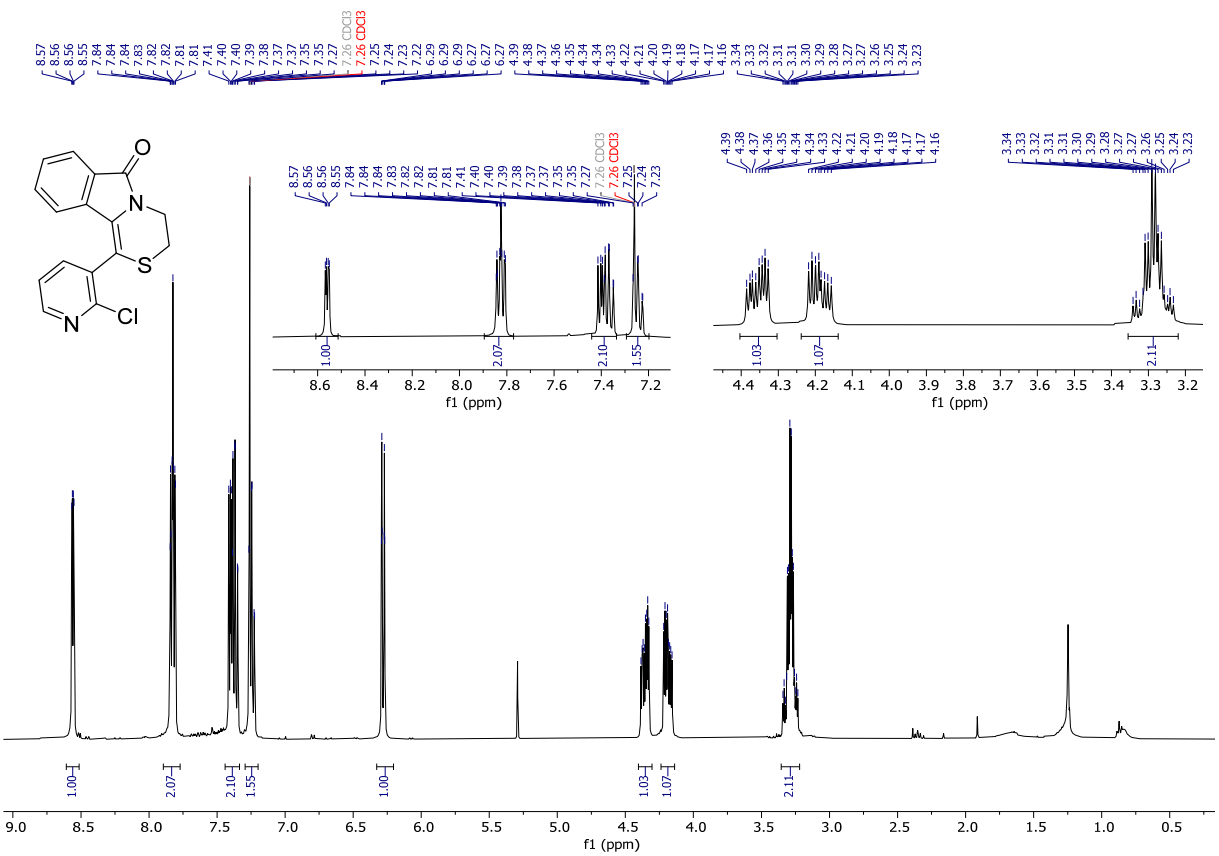
^{1}H NMR spectrum of compound **8i**



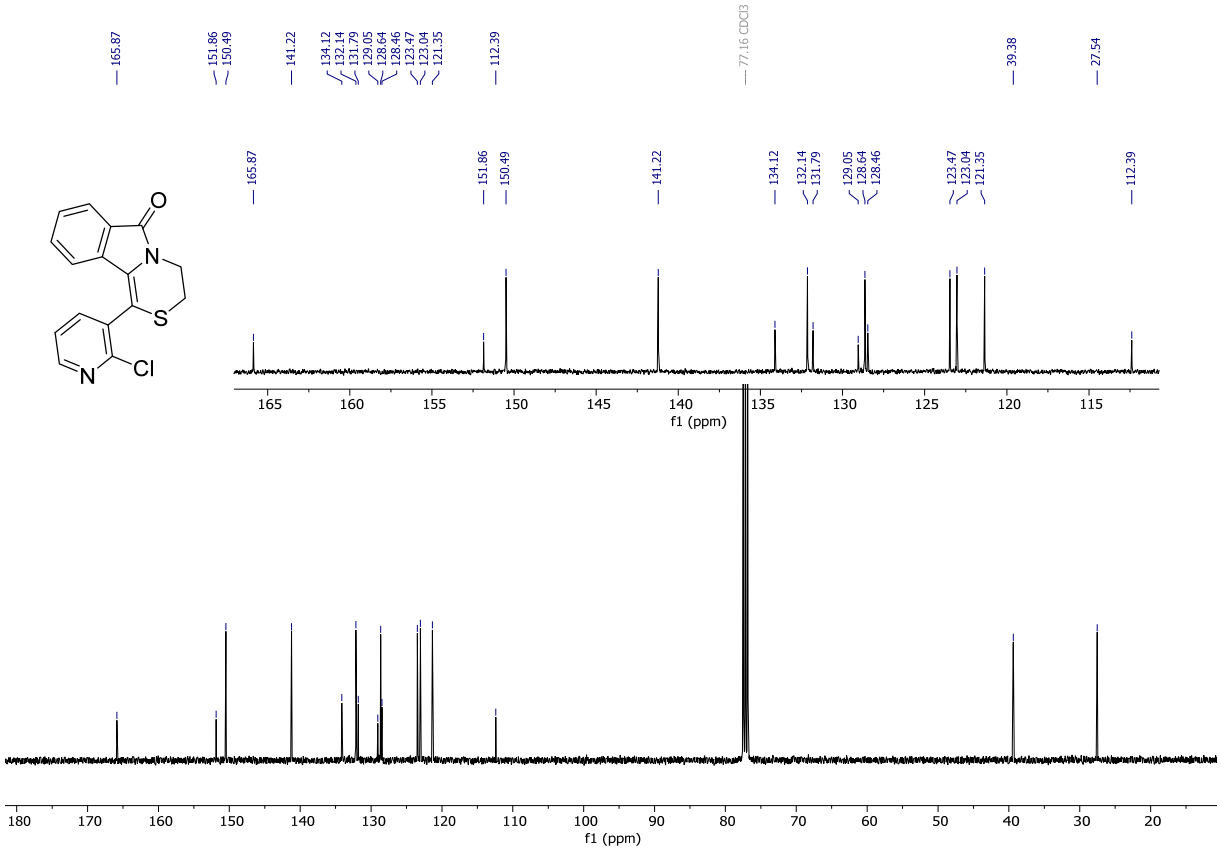
^{1}H NMR spectrum of compound **8k**



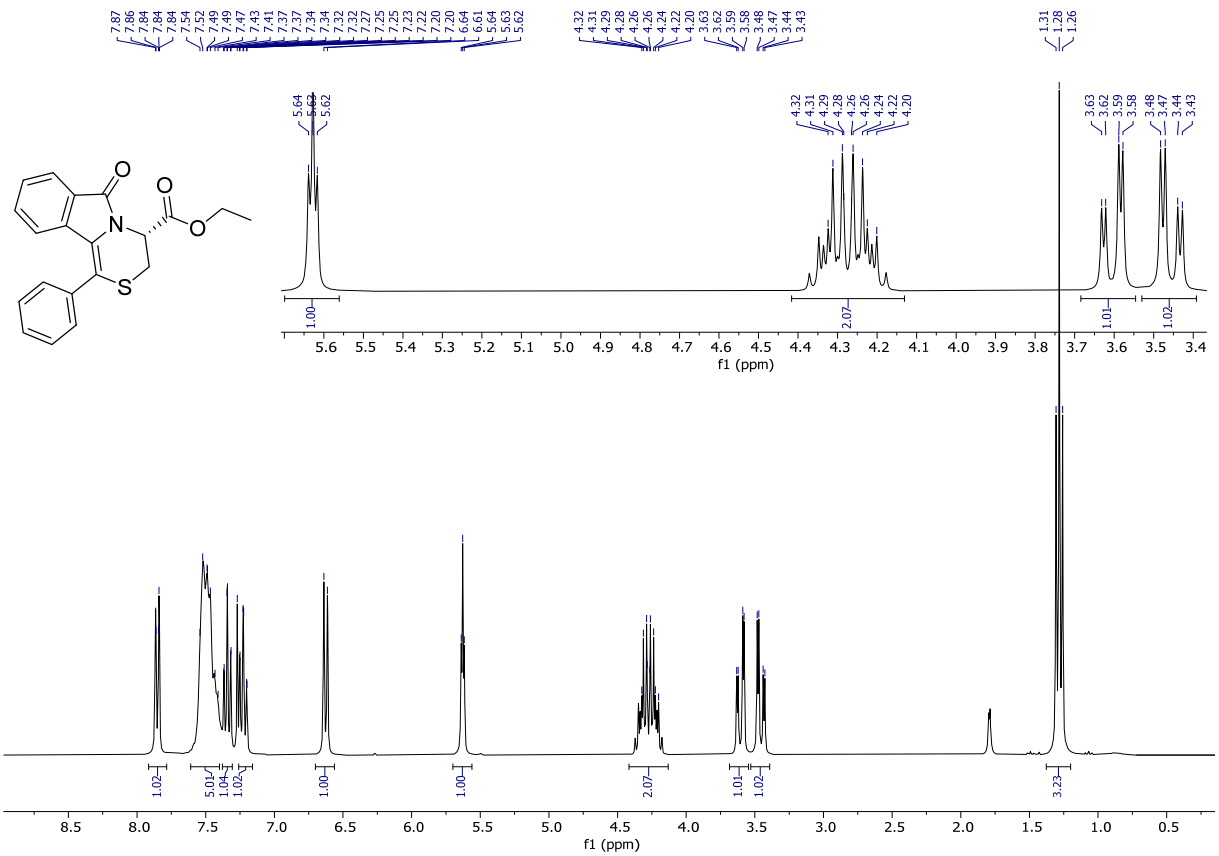
^{13}C NMR spectrum of compound **8k**



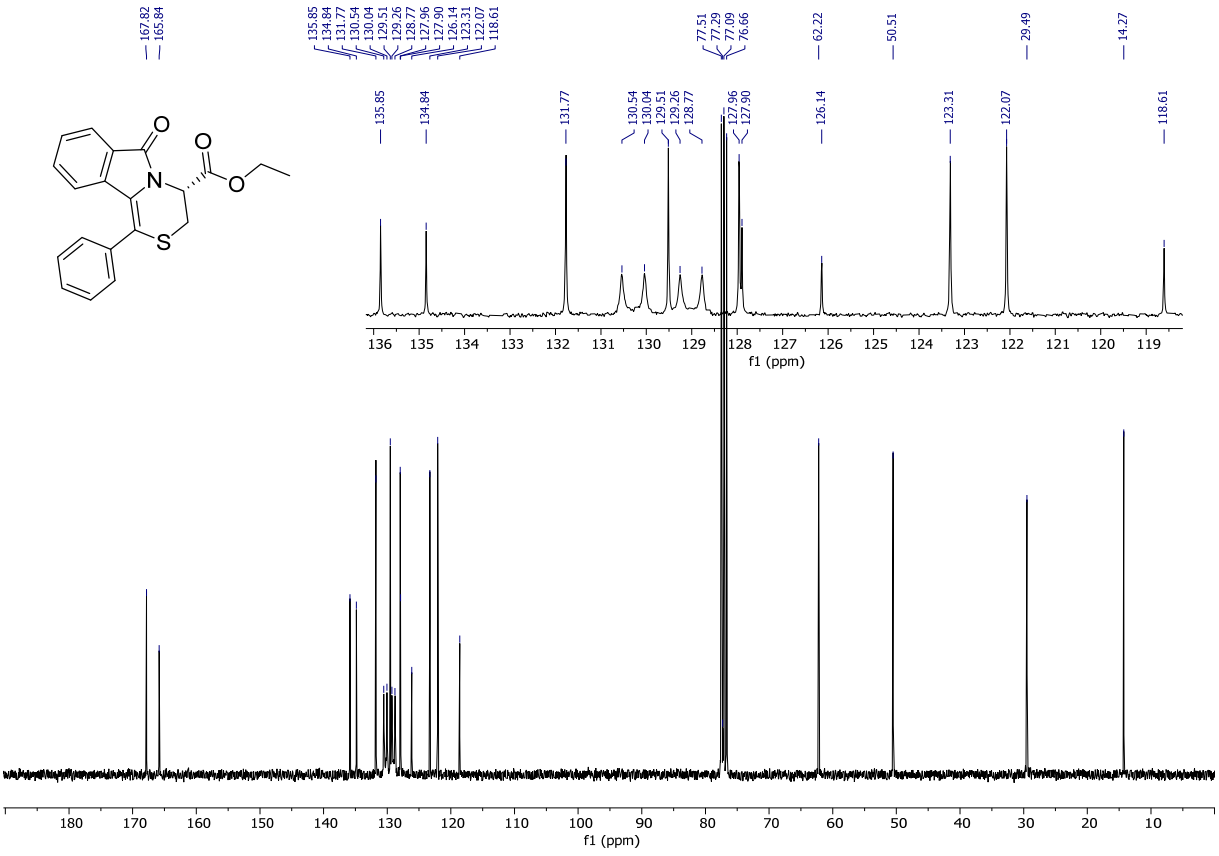
^{1}H NMR spectrum of compound **8l**



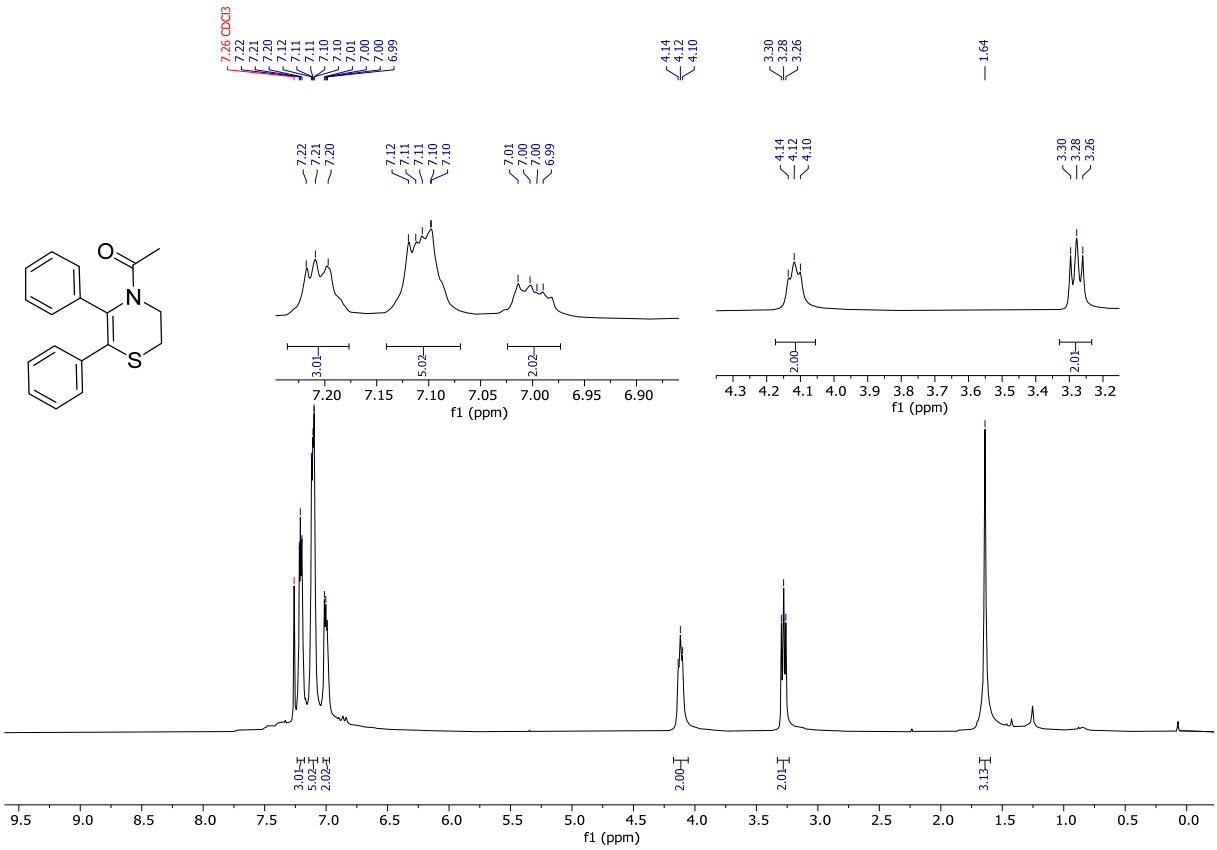
^{13}C NMR spectrum of compound **8l**



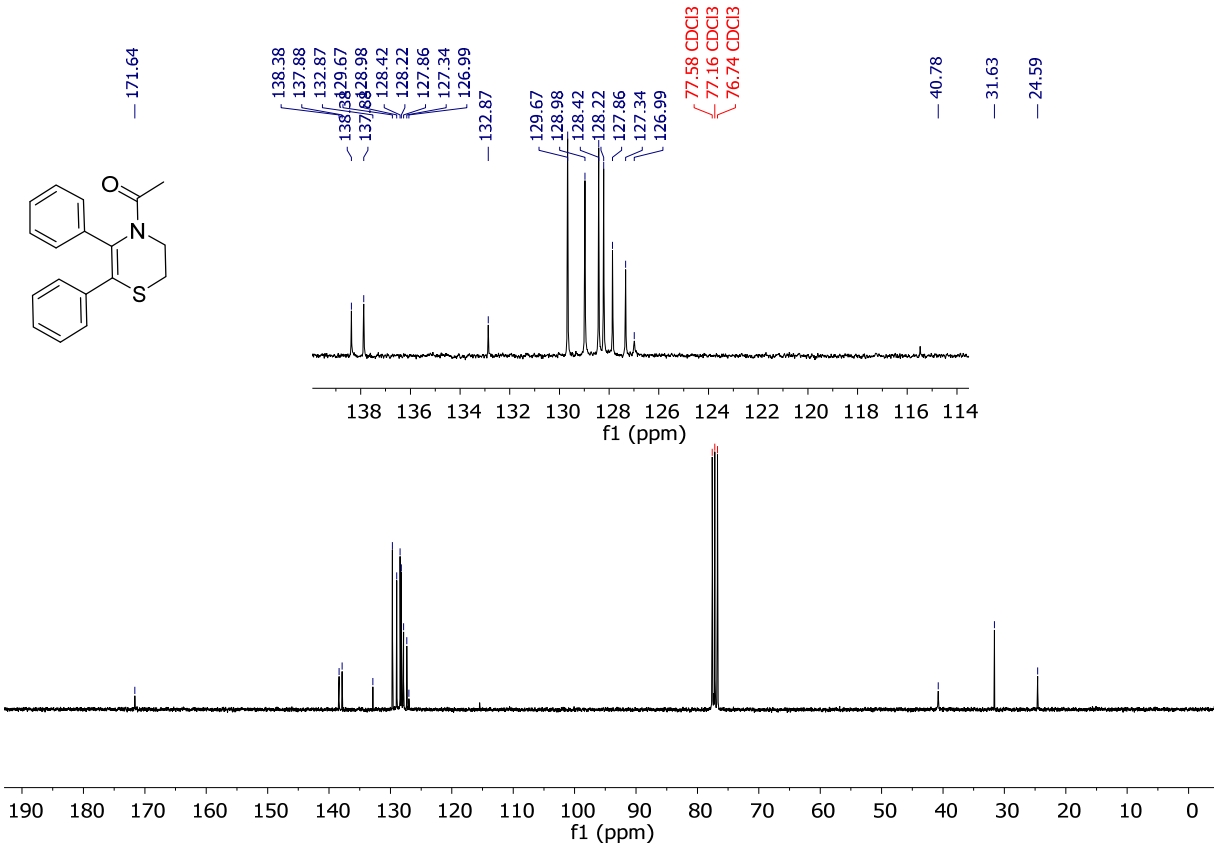
^{1}H NMR spectrum of compound **8m**



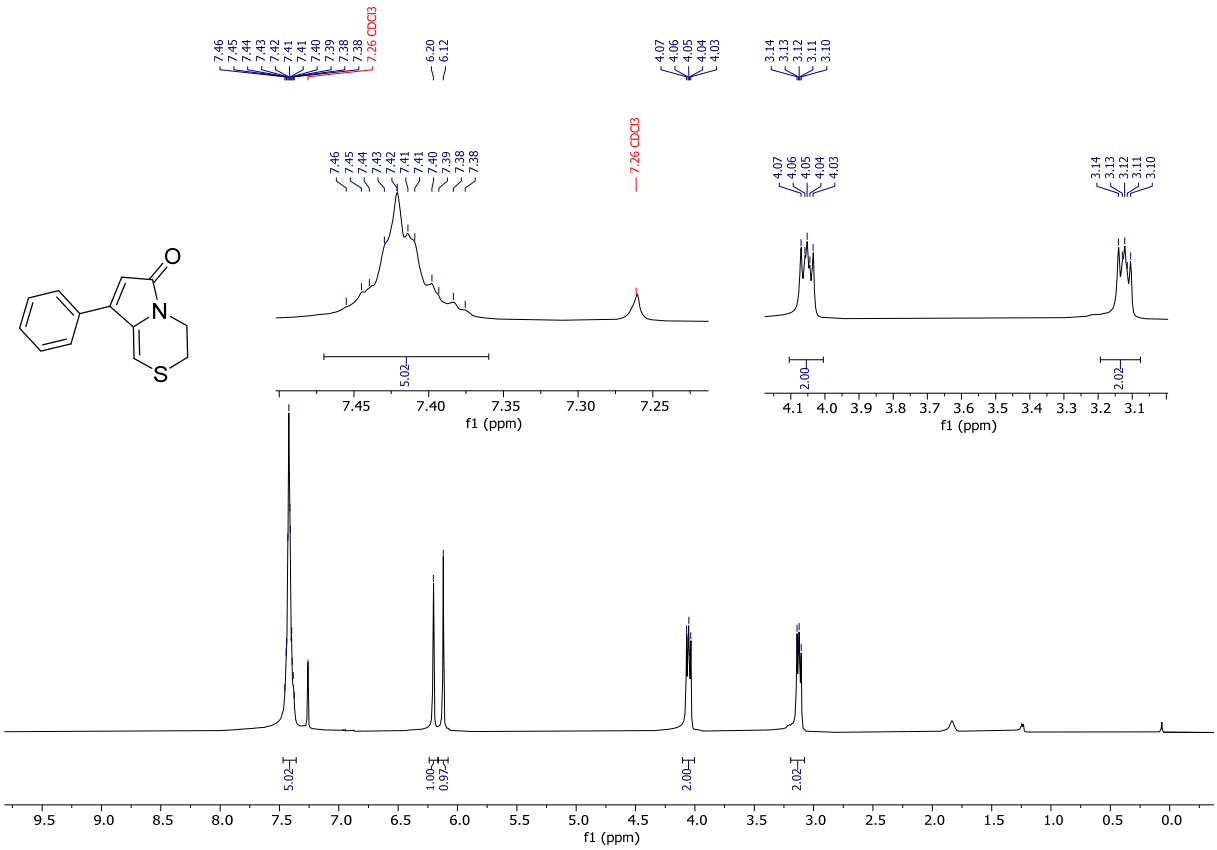
^{13}C NMR spectrum of compound **8m**



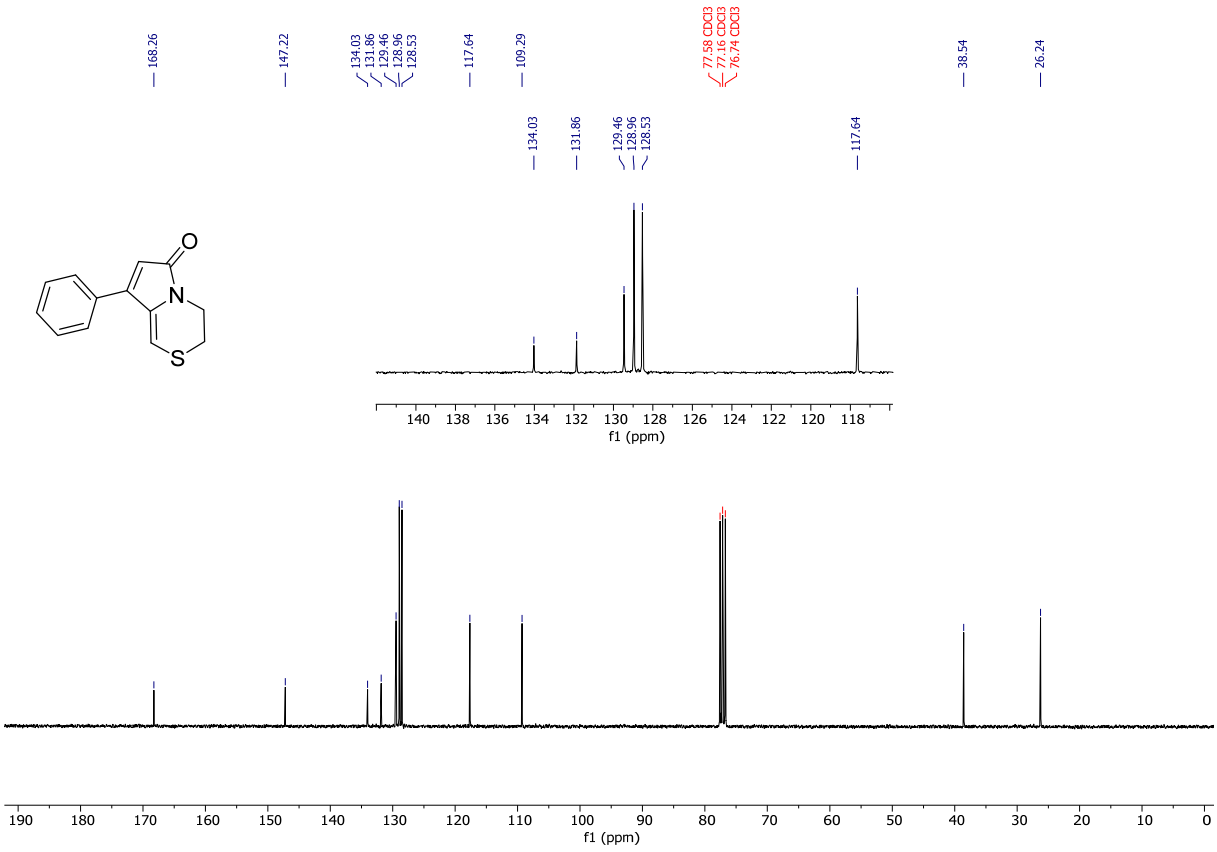
^{1}H NMR spectrum of compound **8n**



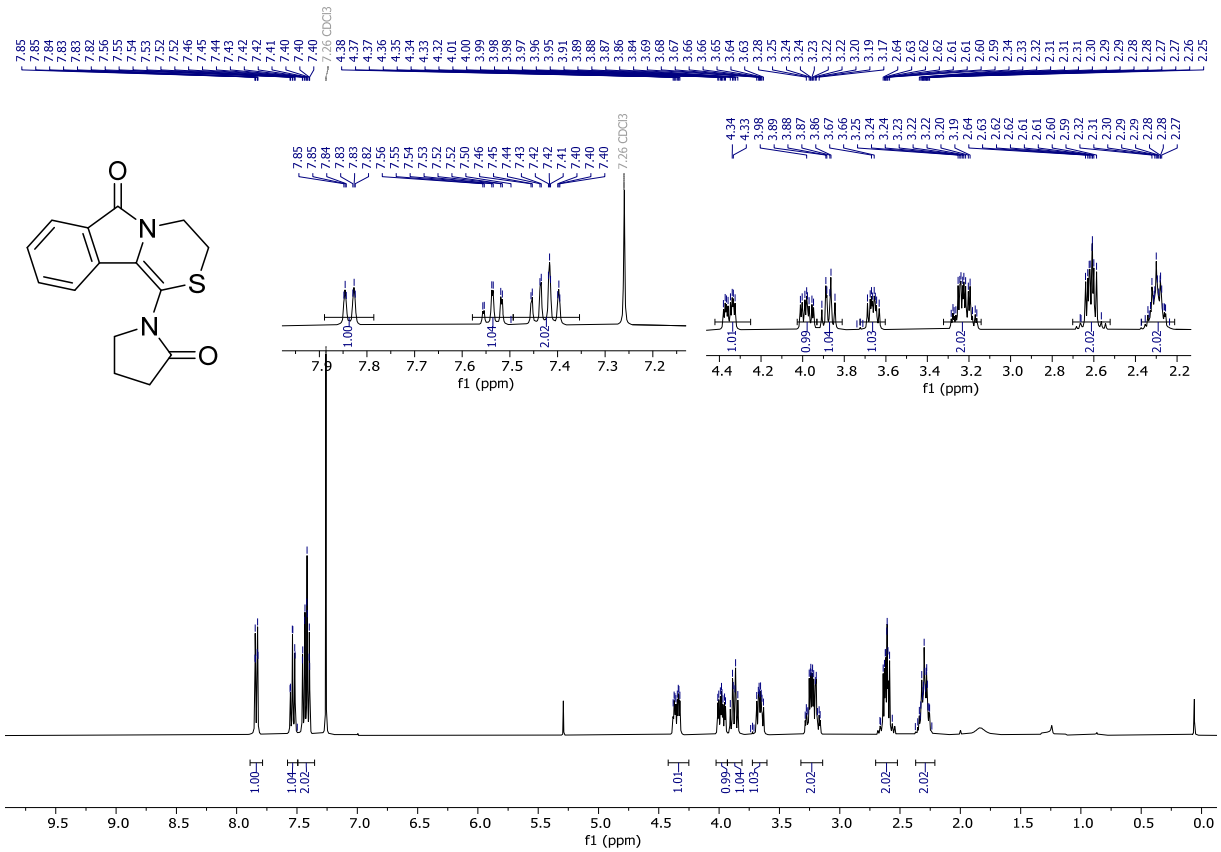
^{13}C NMR spectrum of compound **8n**



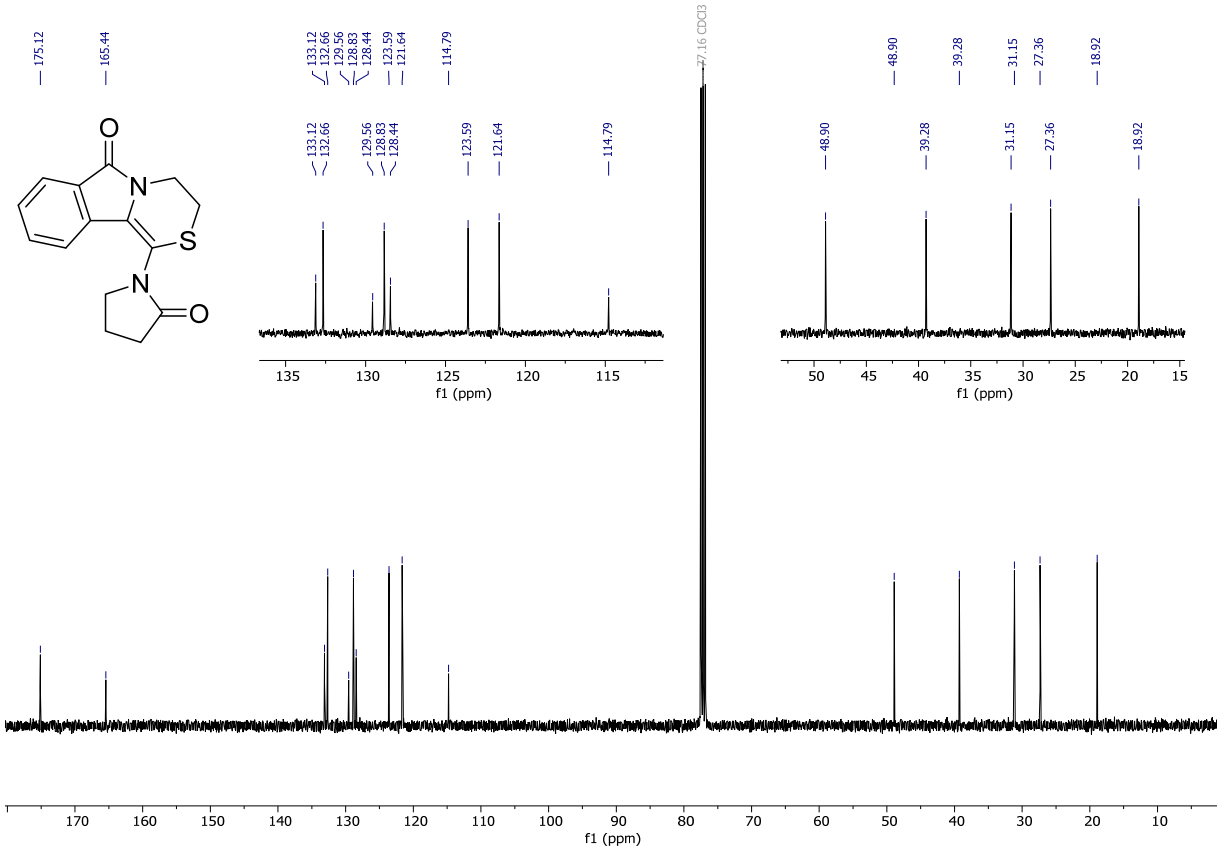
^{1}H NMR spectrum of compound **8o**



^{13}C NMR spectrum of compound **8o**



^{1}H NMR spectrum of compound **8r**



^{13}C NMR spectrum of compound **8r**

XI. Structural crystallographic data

checkCIF/PLATON report

Structure factors have been supplied for datablock(s) fd1551

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: fd1551 (Product 7dB)

```
Bond precision:   C-C = 0.0036 A          Wavelength=1.54186

Cell:             a=12.0292(4)     b=4.1018(1)         c=15.6950(4)
                  alpha=90         beta=92.149(2)      gamma=90
Temperature:      100 K

                 Calculated                Reported
Volume           773.87(4)                 773.87(4)
Space group      P 21/c                    P 1 21/c 1
Hall group       -P 2ybc                   -P 2ybc
Moiety formula   C7 H6 Br N O S            C7 H6 Br N O S
Sum formula      C7 H6 Br N O S            C7 H6 Br N O S
Mr               232.09                    232.10
Dx,g cm-3        1.992                     1.992
Z                4                         4
Mu (mm-1)        9.242                     9.242
F000             456.0                     456.0
F000'            455.45
h,k,lmax         14,5,19                   14,5,18
Nref             1508                      1465
Tmin,Tmax        0.304,0.630               0.065,0.214
Tmin'            0.045

Correction method= # Reported T Limits: Tmin=0.065 Tmax=0.214
AbsCorr = MULTI-SCAN

Data completeness= 0.971           Theta(max)= 72.162

R(reflections)= 0.0313( 1439)                    wR2(reflections)=
                                                 0.0825( 1465)
S = 1.070                  Npar= 100
```

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level C

```
PLAT911_ALERT_3_C Missing FCF Refl Between Thmin & STh/L=    0.600         10 Report
              -10   3   6, -10   3   7,   -8   3   8,    5   0 16,    6   0 16,    6   1 16,
                7   0 16,   -1   0 18,    2   0 18,    3   0 18,
```

Alert level G

```
PLAT912_ALERT_4_G Missing # of FCF Reflections Above STh/L=  0.600         33 Note
PLAT941_ALERT_3_G Average HKL Measurement Multiplicity .....              4.7 Low
PLAT969_ALERT_5_G The 'Henn et al.' R-Factor-gap value .....          7.036 Note
              Predicted wR2: Based on SigI**2  1.17 or SHELX Weight  7.71
PLAT978_ALERT_2_G Number C-C Bonds with Positive Residual Density.          3 Info
```

0 **ALERT level A** = Most likely a serious problem - resolve or explain
0 **ALERT level B** = A potentially serious problem, consider carefully
1 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight
4 **ALERT level G** = General information/check it is not something unexpected

0 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
1 ALERT type 2 Indicator that the structure model may be wrong or deficient
2 ALERT type 3 Indicator that the structure quality may be low
1 ALERT type 4 Improvement, methodology, query or suggestion
1 ALERT type 5 Informative message, check

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Publication of your CIF in IUCr journals

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Publication of your CIF in other journals

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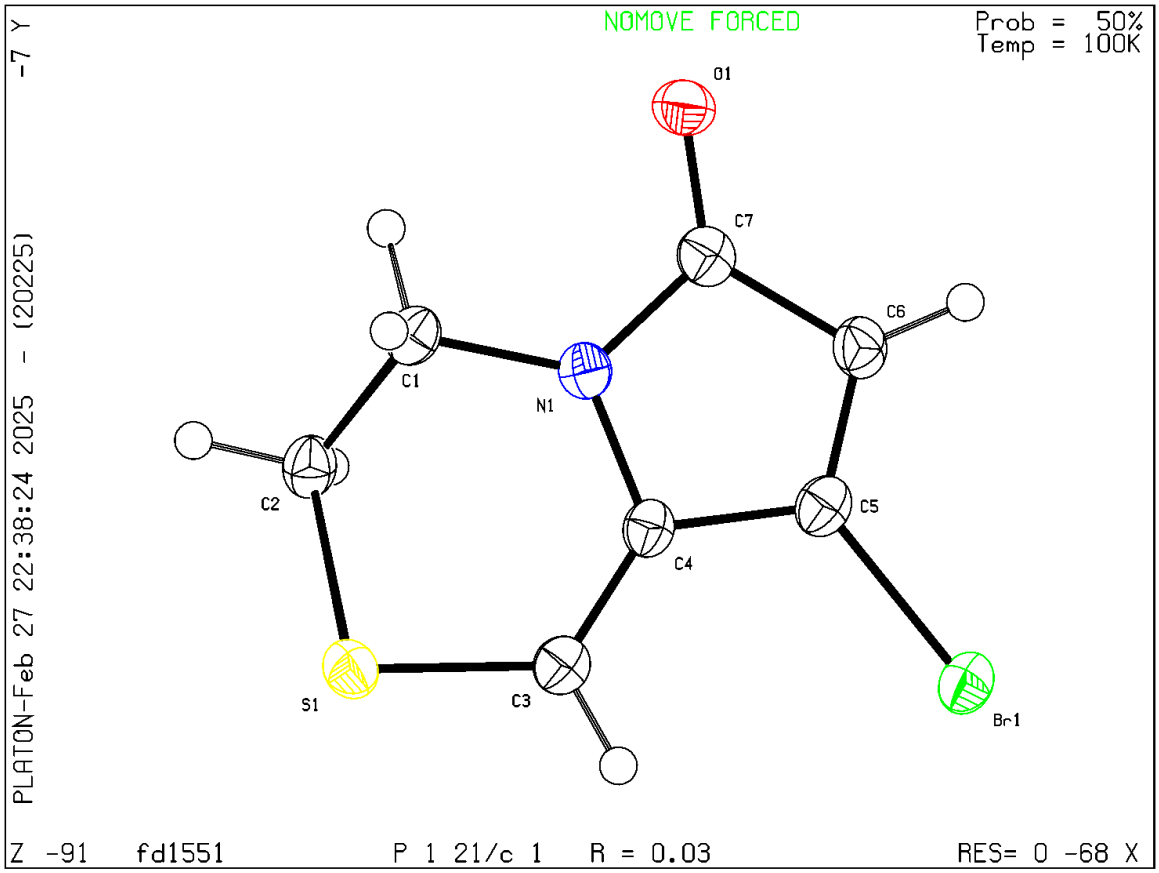
PLATON version of 02/02/2025; check.def file version of 02/02/2025

Datablock fd1551 - ellipsoid plot



checkCIF/PLATON report

Structure factors have been supplied for datablock(s) shs_6530_algh_auto

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: shs_6530_algh_auto (Prodcut 8b)

```
Bond precision:   C-C = 0.0047 A           Wavelength=0.71073

Cell:           a=9.8420(7)         b=13.3225(9)      c=15.5328(12)
                alpha=108.055(6)    beta=93.614(6)    gamma=108.512(6)
Temperature:    293 K

                 Calculated                 Reported
Volume           1806.5(3)                  1806.5(2)
Space group      P -1                       P -1
Hall group       -P 1                       -P 1
Moiety formula   C21 H21 N O S              2(C21 H21 N O S)
Sum formula      C21 H21 N O S              C42 H42 N2 O2 S2
Mr               335.45                     670.89
Dx,g cm-3        1.233                      1.233
Z                4                          2
Mu (mm-1)        0.186                      0.186
F000             712.0                      712.0
F000'            712.75
h,k,lmax         11,15,18                   11,15,18
Nref             6397                       6394
Tmin,Tmax        0.989,0.991
Tmin'            0.982

Correction method= Not given

Data completeness= 1.000            Theta(max)= 25.026

R(reflections)= 0.0608( 3637)                wR2(reflections)=
                                             0.1383( 6394)
S = 1.013                  Npar= 441
```

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level C

```
PLAT041_ALERT_1_C Calc. and Reported SumFormula    Strings  Differ     Please Check
             Calc: C21 H21 N O S
             Rep.: C42 H42 N2 O2 S2
PLAT042_ALERT_1_C Calc. and Reported MoietyFormula Strings  Differ     Please Check
             Calc: C21 H21 N O S
             Rep.: 2(C21 H21 N O S)
PLAT052_ALERT_1_C Info on Absorption Correction Method   Not Given     Please Do !
PLAT230_ALERT_2_C Hirshfeld Test Diff for    C18A     --C20A     .        6.0 s.u.
PLAT242_ALERT_2_C Low    'MainMol' Ueq as Compared to Neighbors of       C18B Check
PLAT242_ALERT_2_C Low    'MainMol' Ueq as Compared to Neighbors of       C18A Check
PLAT340_ALERT_3_C Low Bond Precision on  C-C Bonds ..............    0.00474 Ang.
PLAT906_ALERT_3_C Large K Value in the Analysis of Variance ......     15.496 Check
PLAT906_ALERT_3_C Large K Value in the Analysis of Variance ......      3.455 Check
PLAT911_ALERT_3_C Missing FCF Refl Between Thmin & STh/L=    0.595          2 Report
               1 -7  2,   1 -2  5,
```

Alert level G

```
PLAT002_ALERT_2_G Number of Distance or Angle Restraints on AtSite          7 Note
PLAT045_ALERT_1_G Calculated and Reported Z Differ by a Factor ...          2 Check
PLAT154_ALERT_1_G The s.u.'s on the Cell Angles are Equal ..(Note)       0.006 Degree
PLAT171_ALERT_4_G The CIF-Embedded .res File Contains EADP Records          1 Report
PLAT176_ALERT_4_G The CIF-Embedded .res File Contains SADI Records          1 Report
PLAT191_ALERT_3_G A Non-default SADI Restraint Value has been used      0.0100 Report
PLAT199_ALERT_1_G Reported _cell_measurement_temperature ..... (K)        293 Check
PLAT200_ALERT_1_G Reported   _diffrn_ambient_temperature ..... (K)        293 Check
PLAT230_ALERT_2_G Hirshfeld Test Diff for    C18B     --C19B     .       17.3 s.u.
PLAT230_ALERT_2_G Hirshfeld Test Diff for    C18B     --C20B     .       25.0 s.u.
PLAT230_ALERT_2_G Hirshfeld Test Diff for    C18B     --C21B     .       14.3 s.u.
PLAT230_ALERT_2_G Hirshfeld Test Diff for    C18B     --C19X     .       14.7 s.u.
PLAT230_ALERT_2_G Hirshfeld Test Diff for    C18B     --C20X     .       20.3 s.u.
PLAT230_ALERT_2_G Hirshfeld Test Diff for    C18B     --C21X     .       23.3 s.u.
PLAT301_ALERT_3_G Main Residue  Disorder .............(Resd    1)        13% Note
PLAT412_ALERT_2_G Short Intra XH3 .. XHn     H14B     ..H21A     .       2.11 Ang.
                                                      x,y,z  =      1_555 Check
PLAT720_ALERT_4_G Number of Unusual/Non-Standard Labels .........          8 Note
             H1BA    H1BB    H2BA    H2BB    H1AA    H1AB    H2AA    H2AB
PLAT860_ALERT_3_G Number of Least-Squares Restraints ............         15 Note
PLAT910_ALERT_3_G Missing # of FCF Reflection(s) Below Theta(Min).          1 Note
               0  0  1,
PLAT933_ALERT_2_G Number of HKL-OMIT Records in Embedded .res File          2 Note
               1 -7  2,   1 -2  5,
PLAT941_ALERT_3_G Average HKL Measurement Multiplicity ...........        2.7 Low
PLAT969_ALERT_5_G The 'Henn et al.' R-Factor-gap value ...........      2.305 Note
             Predicted wR2: Based on SigI**2  6.00 or SHELX Weight 13.66
PLAT978_ALERT_2_G Number C-C Bonds with Positive Residual Density.          3 Info
```

0 **ALERT level A** = Most likely a serious problem - resolve or explain
0 **ALERT level B** = A potentially serious problem, consider carefully

```
 10 ALERT level C = Check. Ensure it is not caused by an omission or oversight
 23 ALERT level G = General information/check it is not something unexpected

  7 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
 13 ALERT type 2 Indicator that the structure model may be wrong or deficient
  9 ALERT type 3 Indicator that the structure quality may be low
  3 ALERT type 4 Improvement, methodology, query or suggestion
  1 ALERT type 5 Informative message, check
```

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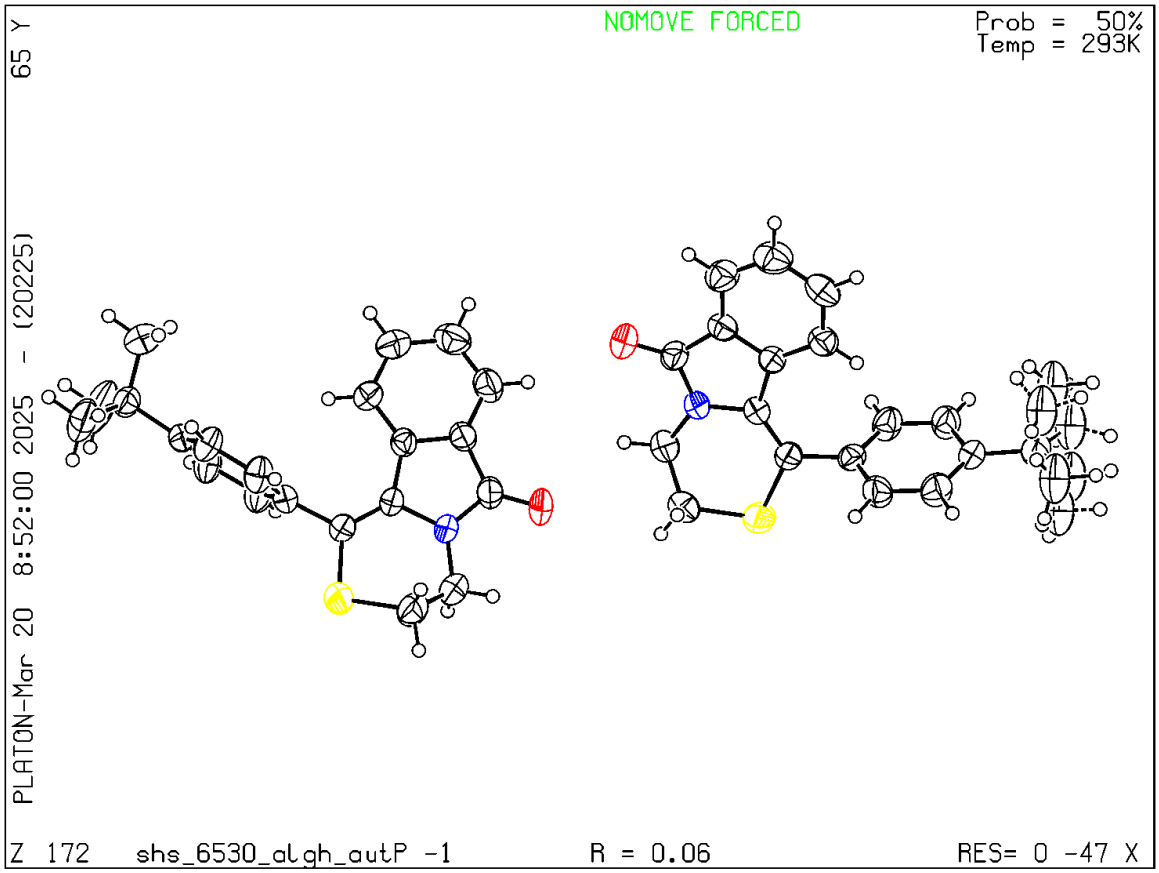
PLATON version of 02/02/2025; check.def file version of 02/02/2025

Datablock shs_6530_algh_auto - ellipsoid plot



checkCIF/PLATON report

Structure factors have been supplied for datablock(s) shs_871_algh_auto

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No syntax errors found. CIF dictionary Interpreting this report

Datablock: shs_871_algh_auto (Product 8d)

```
Bond precision:   C-C = 0.0034 A          Wavelength=1.54184

Cell:             a=28.9306(7)     b=8.7354(2)         c=14.5461(5)
                  alpha=90         beta=98.643(3)      gamma=90
Temperature:      293 K
```

	Calculated	Reported
Volume	3634.35(18)	3634.36(17)
Space group	C 2/c	C 1 2/c 1
Hall group	-C 2yc	-C 2yc
Moiety formula	C20 H19 N O4 S	C20 H19 N O4 S
Sum formula	C20 H19 N O4 S	C20 H19 N O4 S
Mr	369.42	369.42
Dx,g cm-3	1.350	1.350
Z	8	8
Mu (mm-1)	1.798	1.798
F000	1552.0	1552.0
F000'	1559.20	
h,k,lmax	34,10,17	34,10,17
Nref	3213	3210
Tmin,Tmax	0.879,0.931	0.515,1.000
Tmin'	0.764	

```
Correction method= # Reported T Limits: Tmin=0.515 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 0.999           Theta(max)= 66.584

R(reflections)= 0.0451( 2374)                    wR2(reflections)=
                                                 0.1403( 3210)
S = 1.037                 Npar= 238
```

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level C

```
PLAT911_ALERT_3_C Missing FCF Refl Between Thmin & STh/L=    0.595          3 Report
               -8 10  3,  -1  1  3,   4  4 15,
```

Alert level G

```
PLAT012_ALERT_1_G No       _shelx_res_checksum Found in CIF ......     Please Check
PLAT199_ALERT_1_G Reported _cell_measurement_temperature ..... (K)        293 Check
PLAT200_ALERT_1_G Reported   _diffrn_ambient_temperature ..... (K)        293 Check
PLAT909_ALERT_3_G Percentage of I>2sig(I) Data at Theta(Max) Still        46% Note
PLAT933_ALERT_2_G Number of HKL-OMIT Records in Embedded .res File          1 Note
               -1  1  3,
PLAT969_ALERT_5_G The 'Henn et al.' R-Factor-gap value ...........      2.863 Note
              Predicted wR2: Based on SigI**2  4.90 or SHELX Weight 13.54
PLAT978_ALERT_2_G Number C-C Bonds with Positive Residual Density.          3 Info
```

0 **ALERT level A** = Most likely a serious problem - resolve or explain
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1 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight
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3 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
2 ALERT type 2 Indicator that the structure model may be wrong or deficient
2 ALERT type 3 Indicator that the structure quality may be low
0 ALERT type 4 Improvement, methodology, query or suggestion
1 ALERT type 5 Informative message, check

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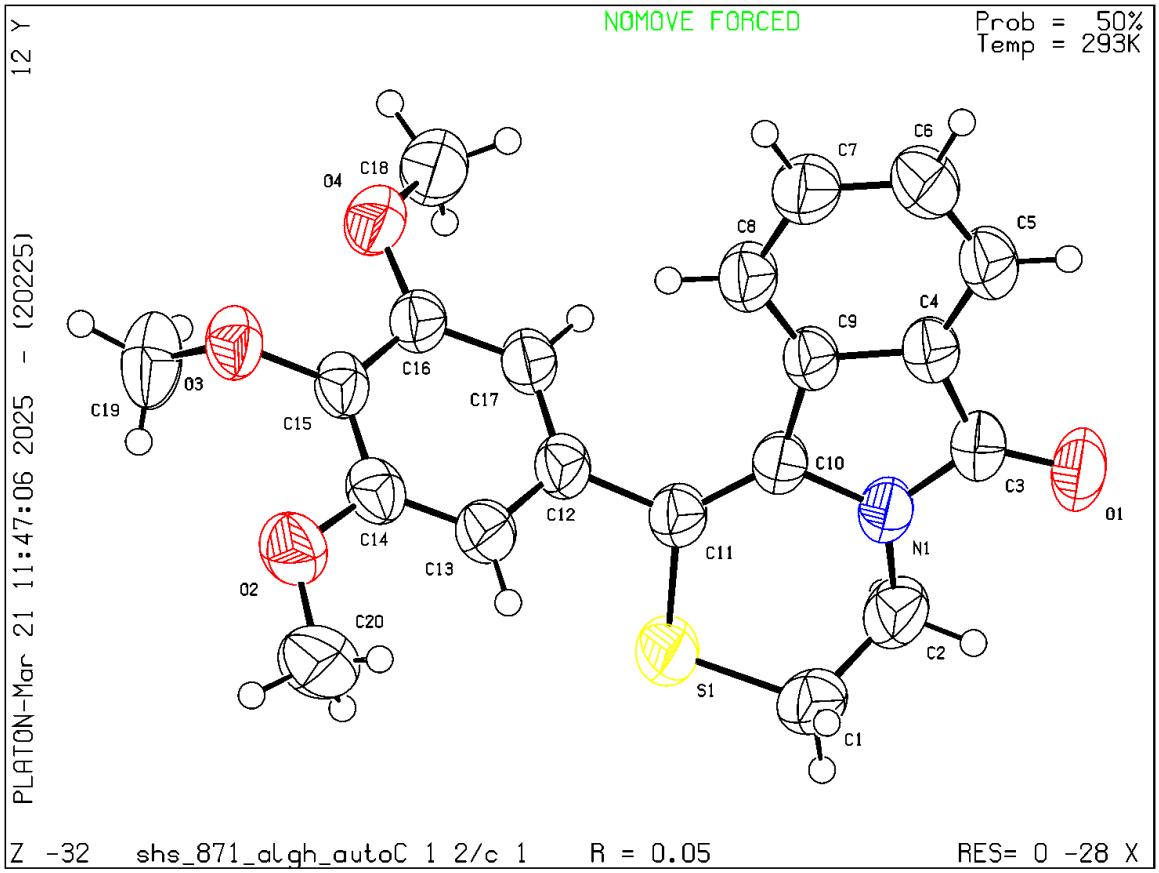
PLATON version of 02/02/2025; check.def file version of 02/02/2025

Datablock shs_871_algh_auto - ellipsoid plot



checkCIF/PLATON report

Structure factors have been supplied for datablock(s) shi_6529_algh_autored

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: shi_6529_algh_autored (Product 8f)

Bond precision: C-C = 0.0041 A Wavelength=0.71073

Cell: a=9.2246(4) b=9.9792(5) c=38.1166(18)
alpha=90 beta=90 gamma=90
Temperature: 293 K

	Calculated	Reported
Volume	3508.8(3)	3508.8(3)
Space group	P b c a	P b c a
Hall group	-P 2ac 2ab	-P 2ac 2ab
Moiety formula	C23 H17 N O S	C23 H17 N O S
Sum formula	C23 H17 N O S	C23 H17 N O S
Mr	355.44	355.43
Dx,g cm-3	1.346	1.346
Z	8	8
Mu (mm-1)	0.196	0.196
F000	1488.0	1488.0
F000'	1489.53	
h,k,lmax	10,11,45	10,11,45
Nref	3090	3088
Tmin,Tmax	0.988,0.990	
Tmin'	0.981	

Correction method= Not given

Data completeness= 0.999 Theta(max)= 25.027

R(reflections)= 0.0582(2286) wR2(reflections)= 0.1205(3088)

S = 1.090 Npar= 236

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level C

```
PLAT052_ALERT_1_C Info on Absorption Correction Method   Not Given     Please Do !
PLAT230_ALERT_2_C Hirshfeld Test Diff for    N1       --C2       .        6.5 s.u.
PLAT340_ALERT_3_C Low Bond Precision on  C-C Bonds ..............    0.00408 Ang.
PLAT906_ALERT_3_C Large K Value in the Analysis of Variance ......     16.890 Check
PLAT906_ALERT_3_C Large K Value in the Analysis of Variance ......      2.744 Check
```

Alert level G

```
PLAT199_ALERT_1_G Reported _cell_measurement_temperature ..... (K)        293 Check
PLAT200_ALERT_1_G Reported   _diffrn_ambient_temperature ..... (K)        293 Check
PLAT909_ALERT_3_G Percentage of I>2sig(I) Data at Theta(Max) Still        48% Note
PLAT910_ALERT_3_G Missing # of FCF Reflection(s) Below Theta(Min).          1 Note
                  0  0  2,
PLAT933_ALERT_2_G Number of HKL-OMIT Records in Embedded .res File          1 Note
                  2  7 24,
PLAT969_ALERT_5_G The 'Henn et al.' R-Factor-gap value ...........      2.772 Note
               Predicted wR2: Based on SigI**2  4.35 or SHELX Weight 11.05
PLAT978_ALERT_2_G Number C-C Bonds with Positive Residual Density.          0 Info
```

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1 ALERT type 5 Informative message, check

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Publication of your CIF in IUCr journals

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Publication of your CIF in other journals

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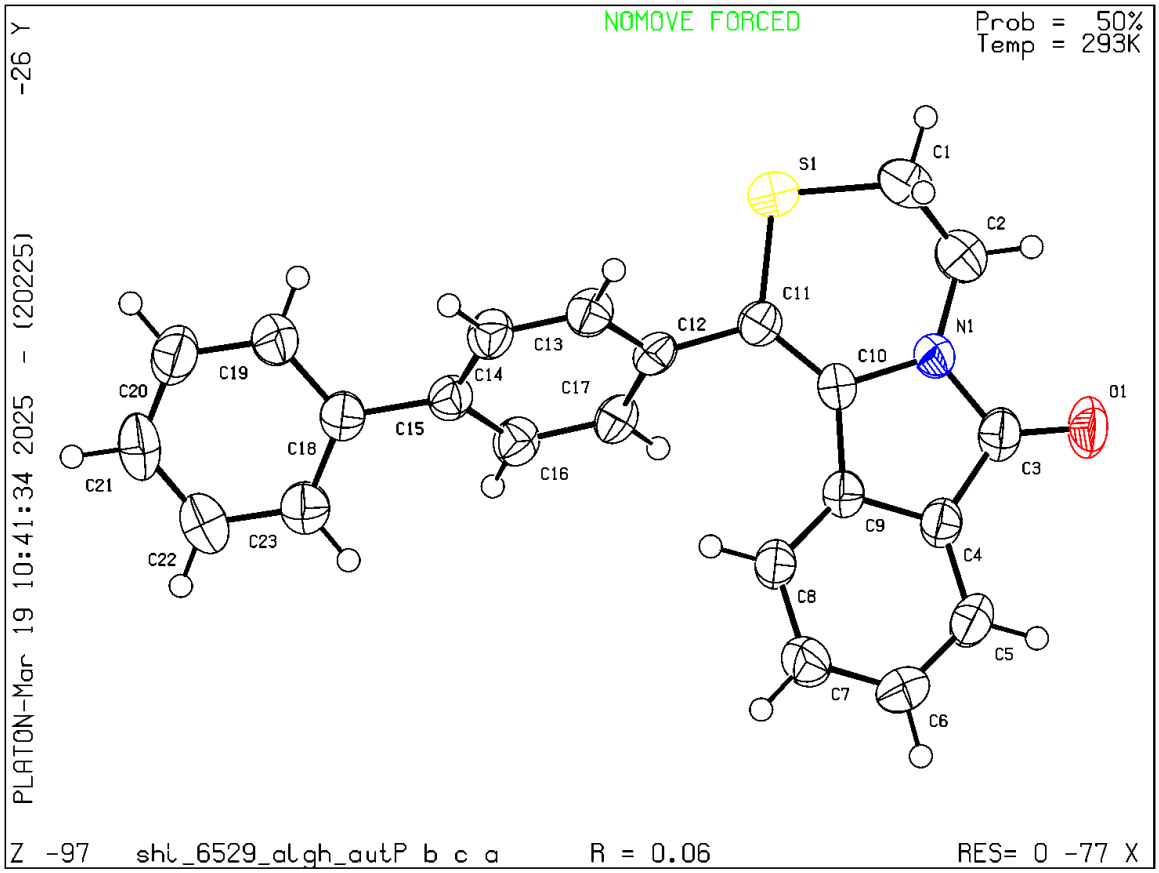
PLATON version of 02/02/2025; check.def file version of 02/02/2025

Datablock shi_6529_algh_autored - ellipsoid plot



checkCIF/PLATON report

Structure factors have been supplied for datablock(s) shs_867_algh_auto

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: shs_867_algh_auto (Product 8h)

Bond precision: C-C = 0.0064 A Wavelength=1.54184

Cell: a=7.5769(2) b=27.7136(7) c=8.1552(3)
alpha=90 beta=115.488(4) gamma=90
Temperature: 193 K

	Calculated	Reported
Volume	1545.79(10)	1545.79(10)
Space group	P 21/n	P 1 21/n 1
Hall group	-P 2yn	-P 2yn
Moiety formula	C21 H15 N O S	C21 H15 N O S
Sum formula	C21 H15 N O S	C21 H15 N O S
Mr	329.40	329.40
Dx,g cm-3	1.415	1.415
Z	4	4
Mu (mm-1)	1.901	1.901
F000	688.0	688.0
F000'	691.09	
h,k,lmax	9,32,9	9,32,9
Nref	2721	2596
Tmin,Tmax	0.796,0.945	0.654,1.000
Tmin'	0.796	

Correction method= # Reported T Limits: Tmin=0.654 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 0.954 Theta(max)= 66.587

R(reflections)= 0.0666(2275) wR2(reflections)= 0.1790(2596)

S = 1.088 Npar= 218

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level B

PLAT029_ALERT_3_B _diffrn_measured_fraction_theta_full value Low . 0.954 Why?

Alert level C

PLAT230_ALERT_2_C Hirshfeld Test Diff for C19 --C20 . 5.7 s.u.
PLAT340_ALERT_3_C Low Bond Precision on C-C Bonds ..... 0.00641 Ang.
PLAT906_ALERT_3_C Large K Value in the Analysis of Variance ..... 5.455 Check
PLAT911_ALERT_3_C Missing FCF Refl Between Thmin & STh/L= 0.595 125 Report

4	3	0,	4	28	0,	0	30	0,	0	32	0,	-3	28	1,	-1	30	1,
0	11	2,	4	12	2,	-4	24	2,	-5	26	2,	-5	27	2,	-3	9	3,
4	16	3,	5	16	3,	4	17	3,	5	17	3,	3	18	3,	5	18	3,
4	20	3,	3	21	3,	4	21	3,	-5	23	3,	-6	24	3,	-6	3	4,
4	11	4,	-5	22	4,	3	0	5,	2	1	5,	4	1	5,	4	2	5,
4	3	5,	4	4	5,	4	8	5,	4	9	5,	4	10	5,	4	11	5,
4	13	5,	4	14	5,	-4	19	5,	-5	21	5,	4	0	6,	2	1	6,
3	1	6,	3	2	6,	3	3	6,	2	4	6,	3	4	6,	3	5	6,
3	6	6,	3	8	6,	3	9	6,	-8	12	6,	-1	13	6,	-6	16	6,
-7	18	6,	-6	19	6,	0	24	6,	-6	1	7,	2	1	7,	-6	2	7,
2	2	7,	2	3	7,	-6	4	7,	2	4	7,	2	5	7,	1	6	7,
2	6	7,	1	7	7,	1	8	7,	-2	11	7,	-2	12	7,	-7	13	7,
-6	13	7,	-2	13	7,	-6	14	7,	-3	14	7,	-3	15	7,	-2	15	7,
-3	16	7,	-2	16	7,	-3	18	7,	-3	19	7,	-4	20	7,	-3	20	7,
-5	21	7,	-4	21	7,	-3	21	7,	-4	22	7,	-6	0	8,	0	0	8,
-6	1	8,	1	1	8,	1	5	8,	0	6	8,	1	6	8,	1	7	8,

Alert level G

PLAT083_ALERT_2_G SHELXL Second Parameter in WGHT Unusually Large 7.89 Why ?
PLAT909_ALERT_3_G Percentage of I>2sig(I) Data at Theta(Max) Still 73% Note
PLAT933_ALERT_2_G Number of HKL-OMIT Records in Embedded .res File 26 Note

-6	2	7,	-6	3	4,	-6	4	7,	-6	16	6,	-6	19	6,	-6	24	3,
-5	21	5,	-5	22	4,	-5	23	3,	-4	19	5,	-3	9	3,	-3	28	1,
-2	8	9,	-1	13	6,	0	6	8,	0	11	2,	2	1	6,	2	4	6,
3	4	6,	3	8	6,	3	18	3,	3	21	3,	4	3	0,	4	11	4,
4	12	2,	5	17	3,														

PLAT941_ALERT_3_G Average HKL Measurement Multiplicity ..... 4.1 Low
PLAT969_ALERT_5_G The 'Henn et al.' R-Factor-gap value ..... 6.812 Note
Predicted wR2: Based on SigI**2 2.63 or SHELX Weight 16.45
PLAT978_ALERT_2_G Number C-C Bonds with Positive Residual Density. 3 Info

0 **ALERT level A** = Most likely a serious problem - resolve or explain
1 **ALERT level B** = A potentially serious problem, consider carefully
4 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight
6 **ALERT level G** = General information/check it is not something unexpected

0 ALERT type 1 CIF construction/syntax error, inconsistent or missing data

```
  4 ALERT type 2 Indicator that the structure model may be wrong or deficient
  6 ALERT type 3 Indicator that the structure quality may be low
  0 ALERT type 4 Improvement, methodology, query or suggestion
  1 ALERT type 5 Informative message, check
```

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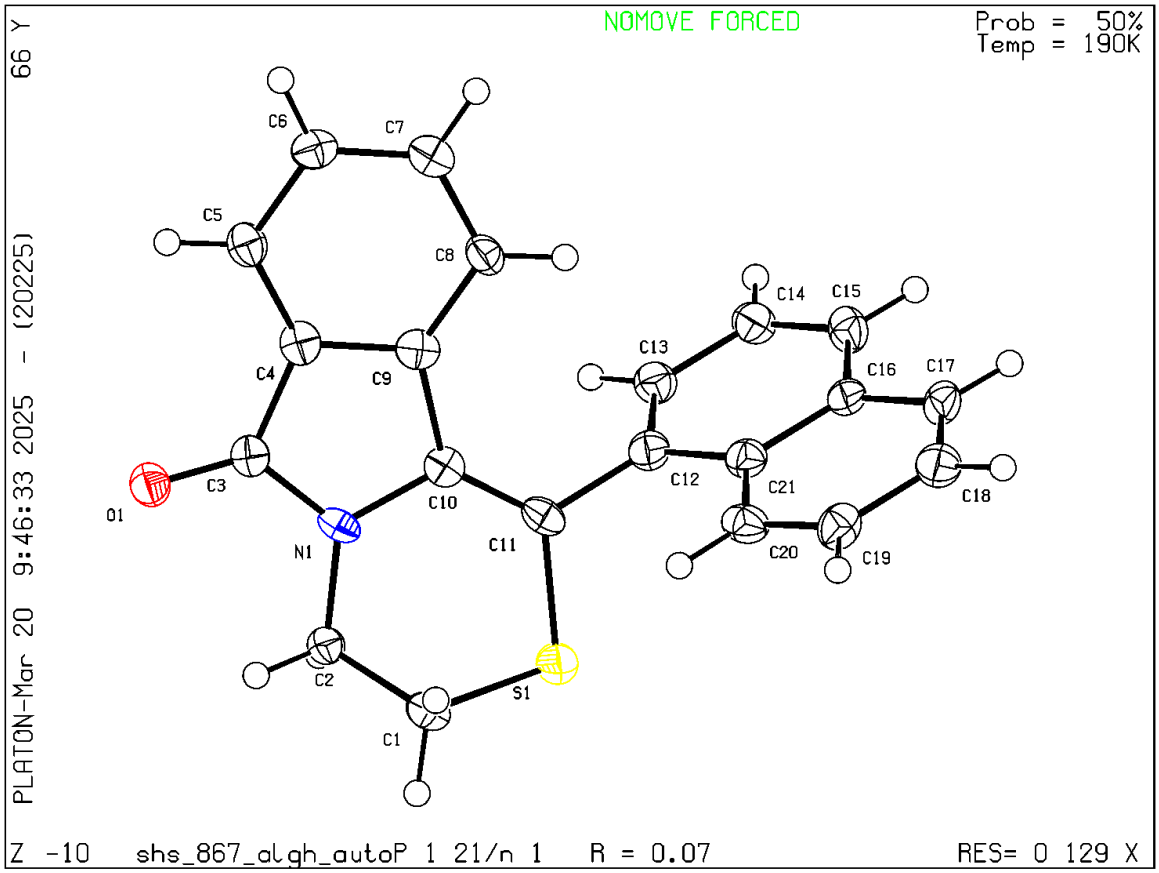
PLATON version of 02/02/2025; check.def file version of 02/02/2025

Datablock shs_867_algh_auto - ellipsoid plot



checkCIF/PLATON report

Structure factors have been supplied for datablock(s) shs_869_algh_auto

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: shs_869_algh_auto (Product 8i)

Bond precision: C-C = 0.0029 A Wavelength=1.54184

Cell: a=6.0141(1) b=24.4546(3) c=13.3223(2)
alpha=90 beta=91.490(1) gamma=90
Temperature: 293 K

	Calculated	Reported
Volume	1958.68(5)	1958.68(5)
Space group	P 21/n	P 1 21/n 1
Hall group	-P 2yn	-P 2yn
Moiety formula	C27 H17 N O S	C27 H17 N O S
Sum formula	C27 H17 N O S	C27 H17 N O S
Mr	403.48	403.48
Dx,g cm-3	1.368	1.368
Z	4	4
Mu (mm-1)	1.610	1.610
F000	840.0	840.0
F000'	843.50	
h,k,lmax	7,29,15	7,29,15
Nref	3449	3438
Tmin,Tmax	0.926,0.938	0.965,1.000
Tmin'	0.879	

Correction method= # Reported T Limits: Tmin=0.965 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 0.997 Theta(max)= 66.591

R(reflections)= 0.0418(3023) wR2(reflections)= 0.1197(3438)

S = 1.034 Npar= 275

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level C

```
PLAT241_ALERT_2_C High   'MainMol' Ueq as Compared to Neighbors of         C2 Check
PLAT906_ALERT_3_C Large K Value in the Analysis of Variance ......      2.252 Check
PLAT911_ALERT_3_C Missing FCF Refl Between Thmin & STh/L=    0.595         11 Report
                  1  3  0,   2  4  0,   1  5  0,   1 11  0,  -3  4  1,   1  6  2,
                  1  2  4,   1  9  4,  -1 10  4,  -2  0  8,  -1 22 10,
```

Alert level G

```
PLAT002_ALERT_2_G Number of Distance or Angle Restraints on AtSite          4 Note
PLAT012_ALERT_1_G No       _shelx_res_checksum Found in CIF ......     Please Check
PLAT171_ALERT_4_G The CIF-Embedded .res File Contains EADP Records          1 Report
PLAT176_ALERT_4_G The CIF-Embedded .res File Contains SADI Records          2 Report
PLAT191_ALERT_3_G A Non-default SADI Restraint Value has been used     0.0100 Report
PLAT191_ALERT_3_G A Non-default SADI Restraint Value has been used     0.0100 Report
PLAT199_ALERT_1_G Reported _cell_measurement_temperature ..... (K)        293 Check
PLAT200_ALERT_1_G Reported   _diffrn_ambient_temperature ..... (K)        293 Check
PLAT230_ALERT_2_G Hirshfeld Test Diff for    C1       --C2       .         6.3 s.u.
PLAT301_ALERT_3_G Main Residue  Disorder ..............(Resd    1)         3% Note
PLAT720_ALERT_4_G Number of Unusual/Non-Standard Labels ..........          6 Note
              H2AA    H2AB    H2BC    H2BD    H1XA    H1XB
PLAT860_ALERT_3_G Number of Least-Squares Restraints .............          2 Note
PLAT909_ALERT_3_G Percentage of I>2sig(I) Data at Theta(Max) Still         76% Note
PLAT933_ALERT_2_G Number of HKL-OMIT Records in Embedded .res File         10 Note
               -3  4  1,  -2  0  8,  -1 10  4,   1  2  4,   1  3  0,   1  5  0,
                1  6  2,   1  9  4,   1 11  0,   2  4  0,
PLAT941_ALERT_3_G Average HKL Measurement Multiplicity ...........        3.7 Low
PLAT969_ALERT_5_G The 'Henn et al.' R-Factor-gap value ...........      6.577 Note
              Predicted wR2: Based on SigI**2  1.82 or SHELX Weight 11.58
PLAT978_ALERT_2_G Number C-C Bonds with Positive Residual Density.          9 Info
PLAT992_ALERT_5_G Repd & Actual _reflns_number_gt Values Differ by          6 Check
```

```
   0 ALERT level A = Most likely a serious problem - resolve or explain
   0 ALERT level B = A potentially serious problem, consider carefully
   3 ALERT level C = Check. Ensure it is not caused by an omission or oversight
  18 ALERT level G = General information/check it is not something unexpected

   3 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
   5 ALERT type 2 Indicator that the structure model may be wrong or deficient
   8 ALERT type 3 Indicator that the structure quality may be low
   3 ALERT type 4 Improvement, methodology, query or suggestion
   2 ALERT type 5 Informative message, check
```

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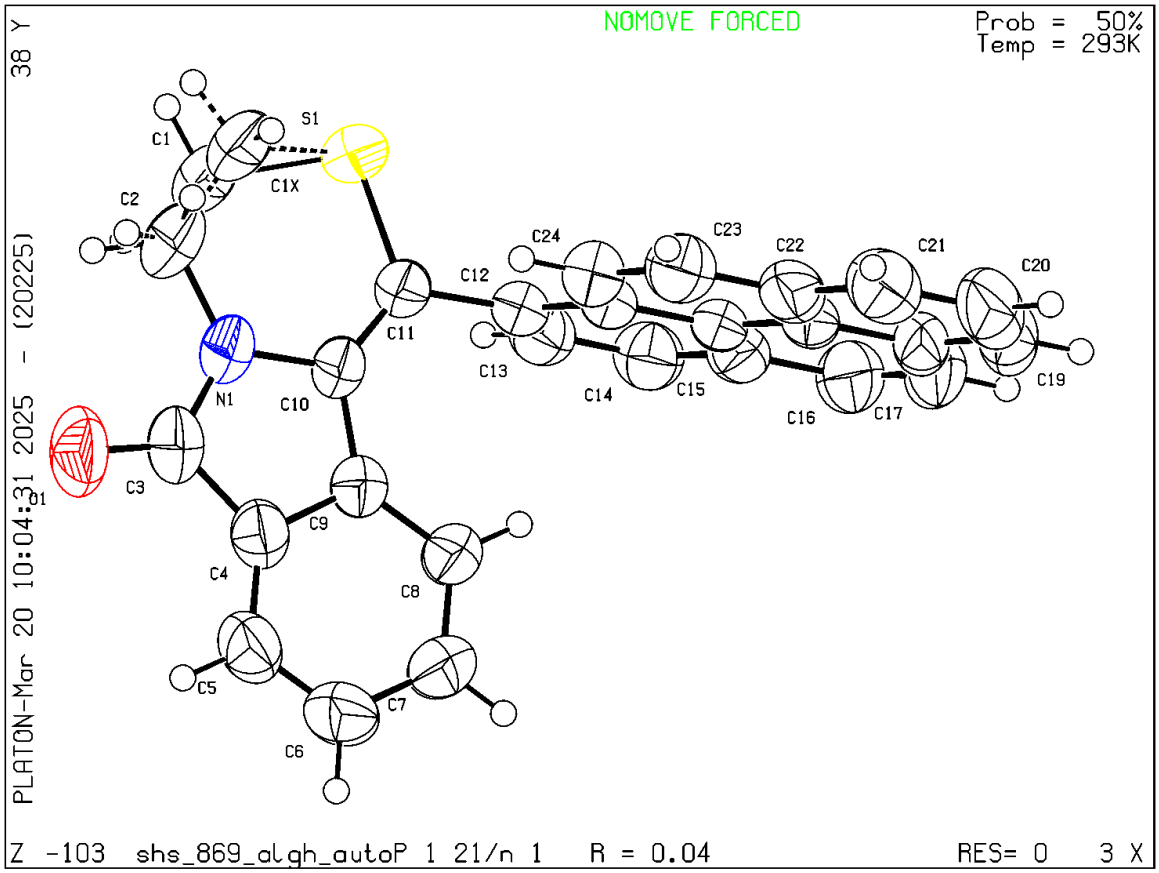
PLATON version of 02/02/2025; check.def file version of 02/02/2025

Datablock shs_869_algh_auto - ellipsoid plot



checkCIF/PLATON report

Structure factors have been supplied for datablock(s) shs_821_algh_auto

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No syntax errors found. CIF dictionary Interpreting this report

Datablock: shs_821_algh_auto (Product 8k)

Bond precision: C-C = 0.0041 A Wavelength=1.54184

Cell: a=8.1298(5) b=8.5574(4) c=12.2507(7)
alpha=73.319(5) beta=88.673(5) gamma=80.899(5)
Temperature: 293 K

	Calculated	Reported
Volume	805.91(8)	805.91(8)
Space group	P -1	P -1
Hall group	-P 1	-P 1
Moiety formula	C20 H16 N2 O S	C20 H16 N2 O S
Sum formula	C20 H16 N2 O S	C20 H16 N2 O S
Mr	332.41	332.41
Dx,g cm-3	1.370	1.370
Z	2	2
Mu (mm-1)	1.844	1.843
F000	348.0	348.0
F000'	349.56	
h,k,lmax	9,10,14	9,10,14
Nref	2848	2825
Tmin,Tmax	0.915,0.929	0.624,1.000
Tmin'	0.758	

Correction method= # Reported T Limits: Tmin=0.624 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 0.992 Theta(max)= 66.578

R(reflections)= 0.0698(2397) wR2(reflections)= 0.2150(2825)

S = 1.075 Npar= 218

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level C

```
PLAT340_ALERT_3_C Low Bond Precision on  C-C Bonds ..............    0.00405 Ang.
PLAT911_ALERT_3_C Missing FCF Refl Between Thmin & STh/L=    0.595         23 Report
               -3 -8  1,  -9  2  1,  -9  2  2,  -4  8  3,  -8 -5  4,  -8  3  4,
               -8  4  4,  -3 -7  5,   0 -7  6,   8 -1  6,  -7  5  6,   7  1  7,
               -6  6  7,  -1 -6  8,   3 -4  8,  -7  4  8,   2 -5  9,   3 -4  9,
                4  4 10,   5  5 10,   3 -3 11,   3  8 11,   2  0 13,
PLAT918_ALERT_3_C Reflection(s) with I(obs) much Smaller I(calc) .          1 Check
```

Alert level G

```
PLAT072_ALERT_2_G SHELXL First  Parameter in WGHT  Unusually Large       0.15 Report
PLAT154_ALERT_1_G The s.u.'s on the Cell Angles are Equal ..(Note)      0.005 Degree
PLAT199_ALERT_1_G Reported _cell_measurement_temperature ..... (K)        293 Check
PLAT200_ALERT_1_G Reported   _diffrn_ambient_temperature ..... (K)        293 Check
PLAT909_ALERT_3_G Percentage of I>2sig(I) Data at Theta(Max) Still        73% Note
PLAT941_ALERT_3_G Average HKL Measurement Multiplicity ...........        3.1 Low
PLAT969_ALERT_5_G The 'Henn et al.' R-Factor-gap value ...........      4.211 Note
             Predicted wR2: Based on SigI**2  5.11 or SHELX Weight 19.99
PLAT978_ALERT_2_G Number C-C Bonds with Positive Residual Density.          1 Info
```

0 **ALERT level A** = Most likely a serious problem - resolve or explain
0 **ALERT level B** = A potentially serious problem, consider carefully
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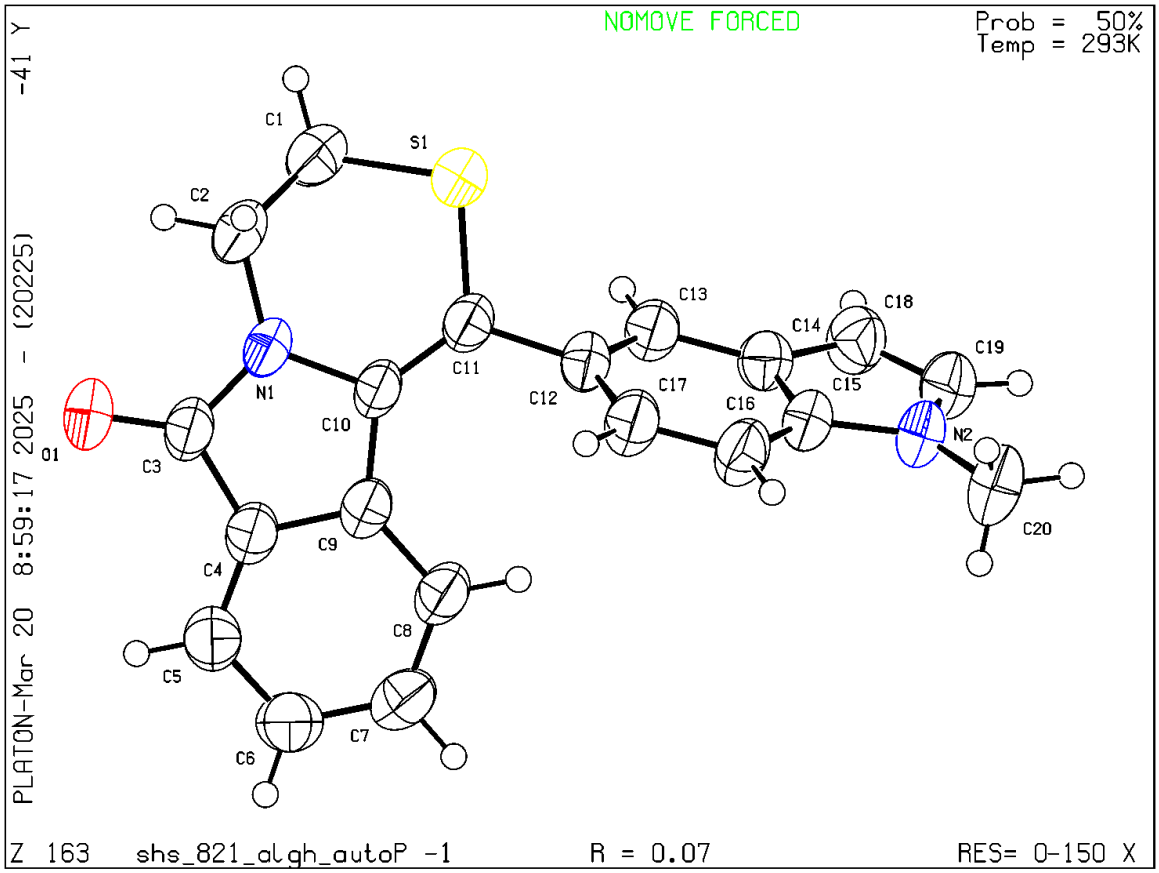
PLATON version of 02/02/2025; check.def file version of 02/02/2025

Datablock shs_821_algh_auto - ellipsoid plot



checkCIF/PLATON report

Structure factors have been supplied for datablock(s) shs_870_algh_auto

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: shs_870_algh_auto (Product 8r)

Bond precision: C-C = 0.0028 A Wavelength=1.54184

Cell: a=10.85284(13) b=10.61071(12) c=11.79455(14)
alpha=90 beta=100.8736(12) gamma=90
Temperature: 293 K

	Calculated	Reported
Volume	1333.83(3)	1333.83(3)
Space group	P 21/n	P 1 21/n 1
Hall group	-P 2yn	-P 2yn
Moiety formula	C15 H14 N2 O2 S	C15 H14 N2 O2 S
Sum formula	C15 H14 N2 O2 S	C15 H14 N2 O2 S
Mr	286.34	286.34
Dx,g cm-3	1.426	1.426
Z	4	4
Mu (mm-1)	2.184	2.184
F000	600.0	600.0
F000'	602.97	
h,k,lmax	12,12,14	12,12,14
Nref	2355	2323
Tmin,Tmax	0.757,0.721	0.739,1.000
Tmin'	0.686	

Correction method= # Reported T Limits: Tmin=0.739 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 0.986 Theta(max)= 66.598

R(reflections)= 0.0400(2204) wR2(reflections)= 0.1087(2323)

S = 1.061 Npar= 181

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level C

```
PLAT241_ALERT_2_C High   'MainMol' Ueq as Compared to Neighbors of        C14 Check
PLAT906_ALERT_3_C Large K Value in the Analysis of Variance ......      2.134 Check
PLAT911_ALERT_3_C Missing FCF Refl Between Thmin & STh/L=    0.595         31 Report
               12   0   0,    6   3   0,    0 12   0, -11   0   1,   11   0   1,   -4   4   1,
               -2   4   1, -12   0   2,   10   0   2,   12   0   2,    4 11   2,    5 11   2,
              -11   0   3,   11   0   3, -12   0   4,   10   0   4,   -2 12   4, -11   0   5,
              -12   0   6, -10   0   6,   10   0   6, -11   0   7, -10   0   8,   -8   8   8,
              -11   0   9,   -9   6   9, -10   0 10,    6   4 10,   -3   0 11,   -4   0 12,
               -3   0 13,
```

Alert level G

```
PLAT012_ALERT_1_G No       _shelx_res_checksum Found in CIF ......     Please Check
PLAT199_ALERT_1_G Reported _cell_measurement_temperature ..... (K)        293 Check
PLAT200_ALERT_1_G Reported   _diffrn_ambient_temperature ..... (K)        293 Check
PLAT909_ALERT_3_G Percentage of I>2sig(I) Data at Theta(Max) Still        88% Note
PLAT933_ALERT_2_G Number of HKL-OMIT Records in Embedded .res File          2 Note
               -4   4   1,   -2   4   1,
PLAT955_ALERT_1_G Reported (CIF) and Actual (FCF) Lmax Differ by .          1 Units
PLAT969_ALERT_5_G The 'Henn et al.' R-Factor-gap value ...........      6.864 Note
             Predicted wR2: Based on SigI**2  1.58 or SHELX Weight 10.24
PLAT978_ALERT_2_G Number C-C Bonds with Positive Residual Density.          7 Info
```

0 **ALERT level A** = Most likely a serious problem - resolve or explain
0 **ALERT level B** = A potentially serious problem, consider carefully
3 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight
8 **ALERT level G** = General information/check it is not something unexpected

4 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
3 ALERT type 2 Indicator that the structure model may be wrong or deficient
3 ALERT type 3 Indicator that the structure quality may be low
0 ALERT type 4 Improvement, methodology, query or suggestion
1 ALERT type 5 Informative message, check

It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

Publication of your CIF in IUCr journals

A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica*, *Journal of Applied Crystallography*, *Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E* or *IUCrData*, you should make sure that full publication checks are run on the final version of your CIF prior to submission.

Publication of your CIF in other journals

Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

PLATON version of 02/02/2025; check.def file version of 02/02/2025

Datablock shs_870_algh_auto - ellipsoid plot