

Electronic Supporting Information

On the nucleophilic derivatization of 4,7-dibromo-[1,2,5]thiadiazolo[3,4-c]pyridine: basis for biologically interesting species and building blocks for organic materials.

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Materials, solvents and instrumentation.

All starting materials were purchased from Aldrich and used without further purification. Solvents were dried by standard methods or distilled prior to use. Reactions were monitored by TLC on precoated silica gel plates (ALUGRAM SIL G/UV254) and revealed by exposure to a UV254 lamp.

^1H , ^{13}C , NMR spectra were recorded using a Bruker 400 spectrometers. Chemical shifts (δ/ppm) are reported relative to $\text{Si}(\text{CH}_3)_4$, CDCl_3 .

FTIR spectra were measured on Agilent series Cary Spectrum 600 FT-IR spectrophotometer, units are cm^{-1} .

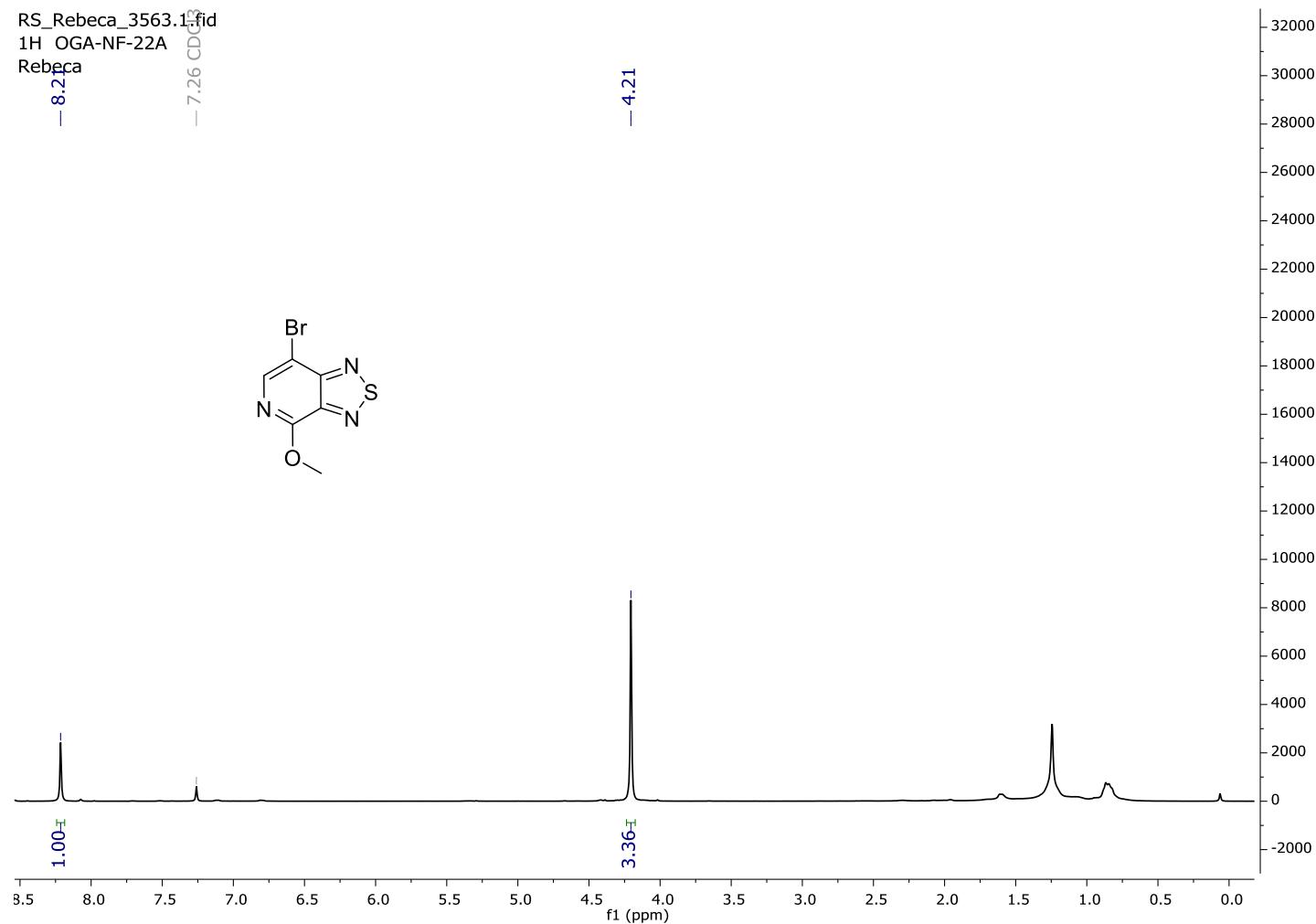
Mass spectra were acquired with an Agilent Technologies ESI TOF spectrometer.

Also a Gas Chromatographer 7890B coupled to a Mass Spectrometer 5977A MSD of simple quadrupole 5977A MSD both from Agilent Thecnologies.

A column HP-5MS-UI, 30m x 0.250 mm, 0.25um was chosen. Helium with a flow of 1 mL/min was used.

Experimental UV-visible spectra were determined using a Thermo Scientific Evolution 220 double beam spectrophotometer.

NMR spectra for the synthesized compounds.

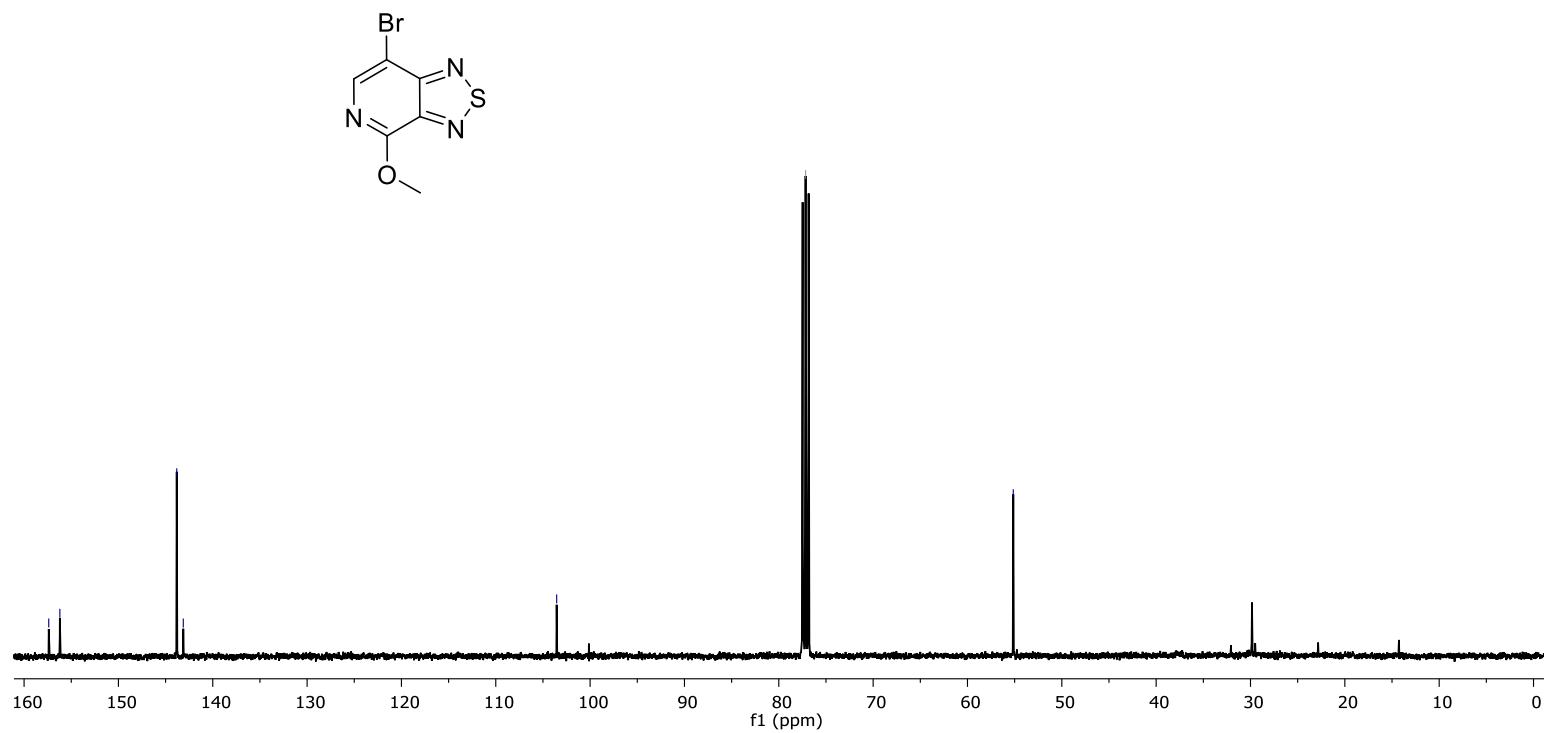
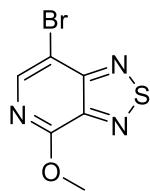


[3]

RS_Rebeca_3563.2.fid
13C OGA-NF-22A
Rebeca

✓ 157.71
✓ 156.62
✓ 143.82
✓ 143.12

— 103.54 —
— 77.16 CDCl₃ —
— 55.14 —



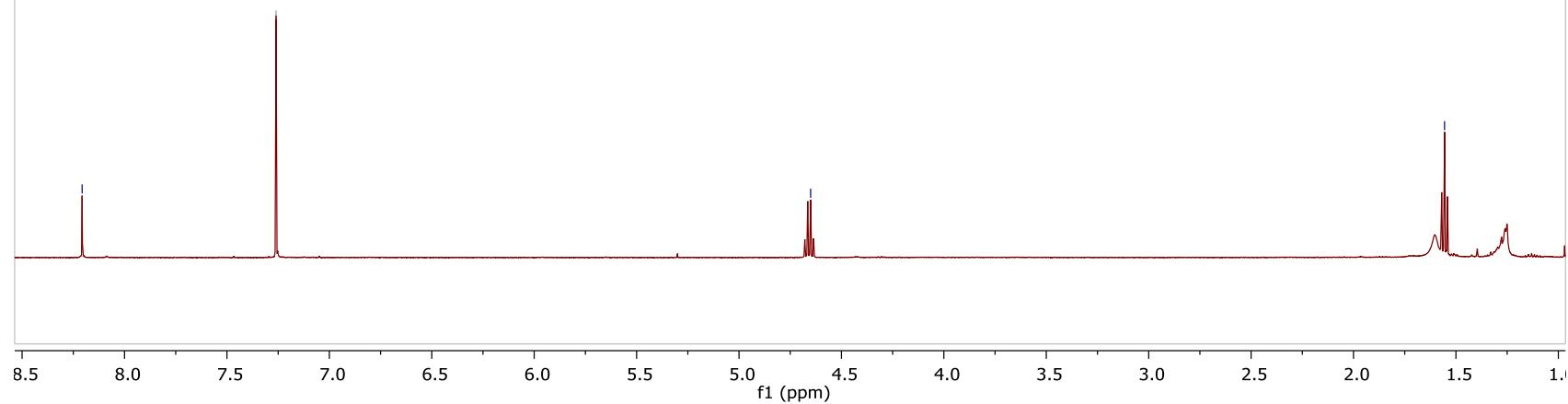
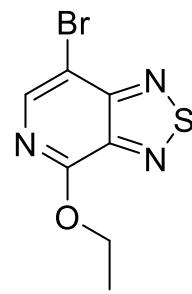
2489
single_pulse

- 8.21

- 7.26 CDCl₃

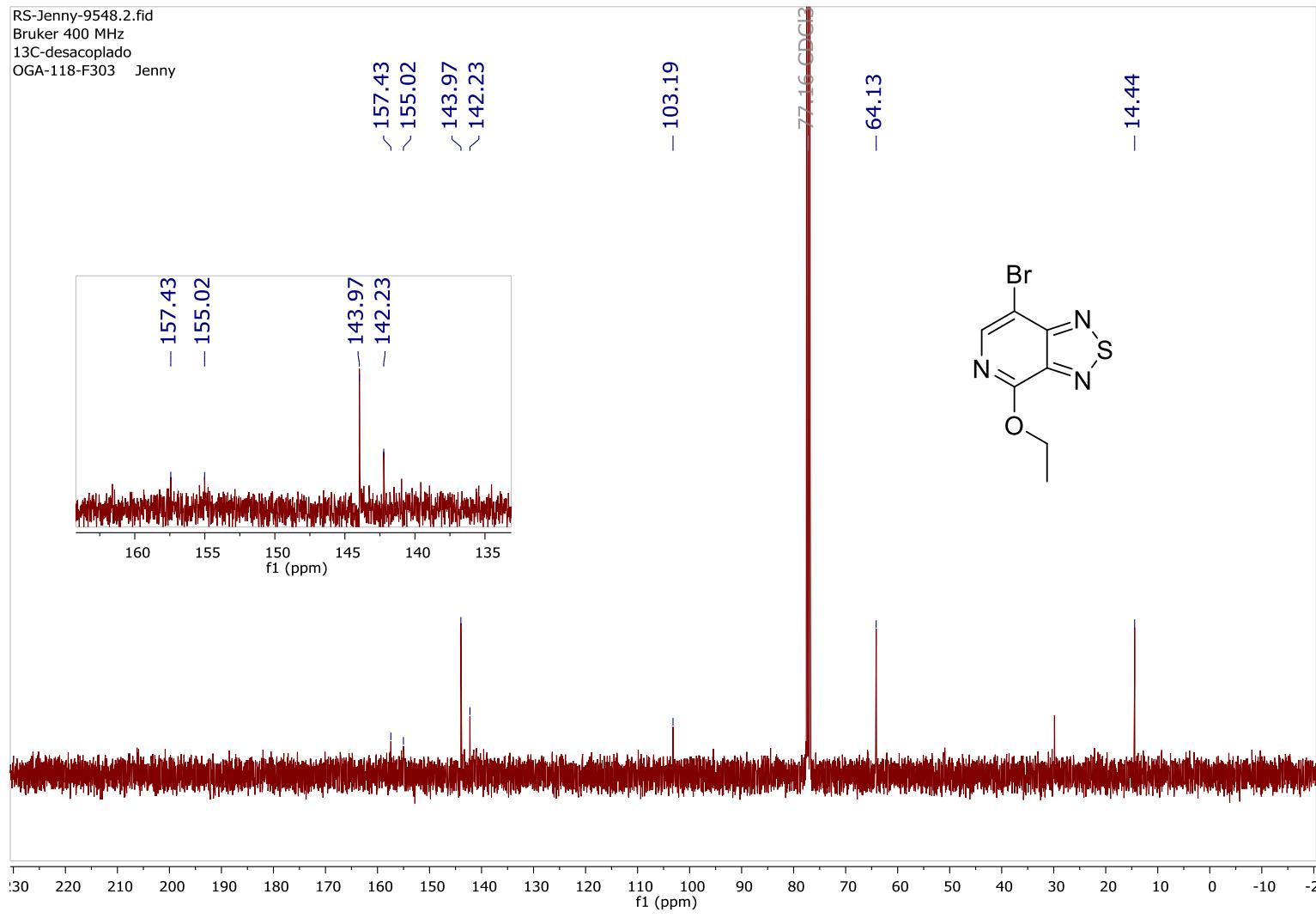
- 4.65

- 1.56

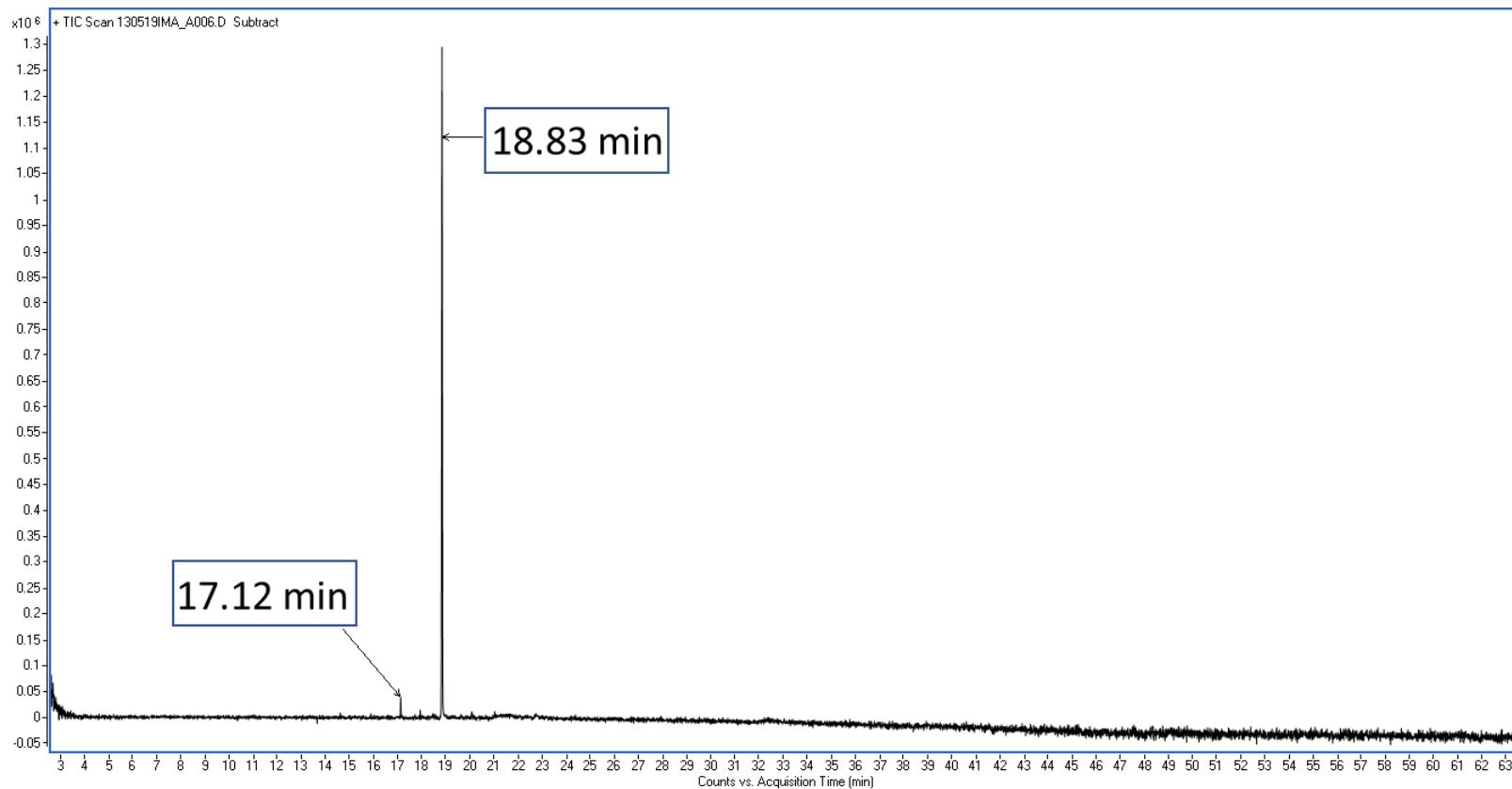


[5]

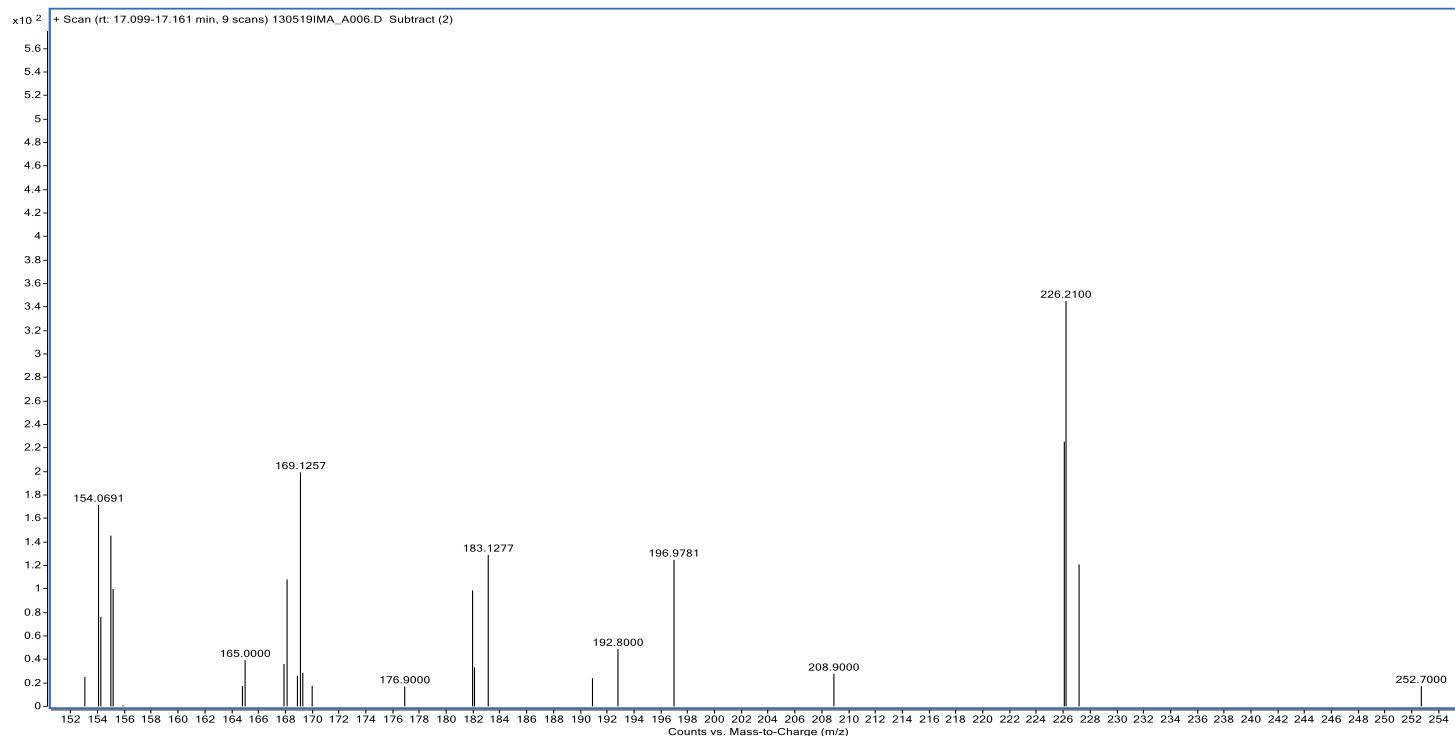
RS-Jenny-9548.2.fid
Bruker 400 MHz
13C-desacoplado
OGA-118-F303 Jenny



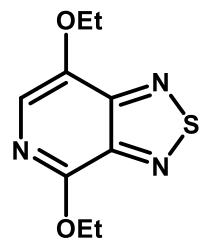
Gas chromatography for an impure sample of Compound 2.



Mass Spectrometry for Peak 1 (17.21min) of the previous chromatogram

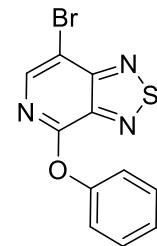
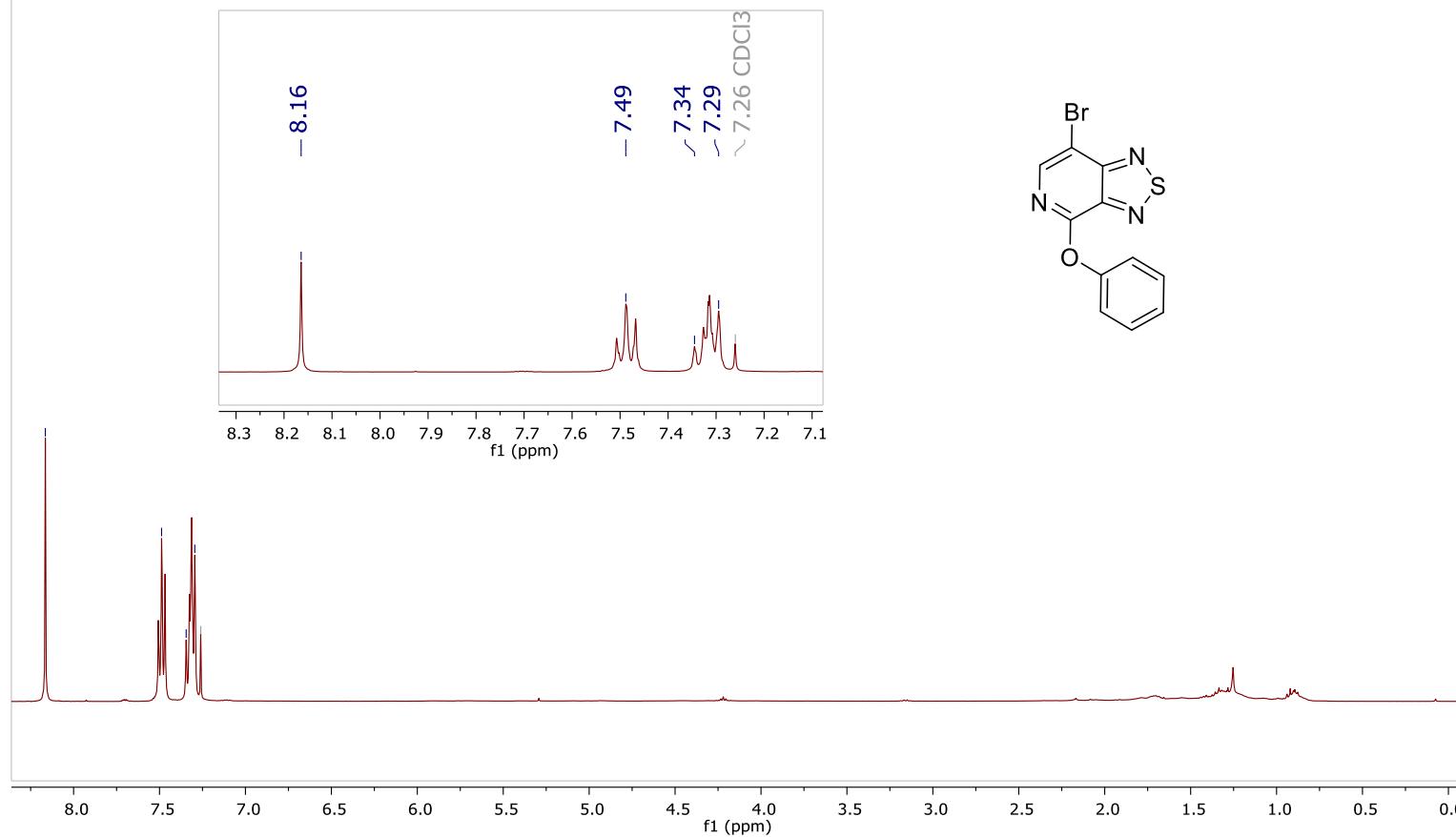


Base peak: 226.2100 m/z which corresponds to the diethoxylated species in its $[M + H^+]$ ⁺ form



RS-Jenny-9178.1.fid
Bruker 400MHz
1H 06A-92 F285
Jenny

7.49
7.34
7.29
7.26 CDCl₃



RS-Jenny-9178.2.fid

Bruker 400MHz

13C-desacoplado

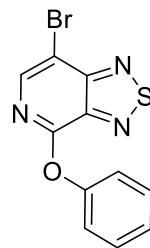
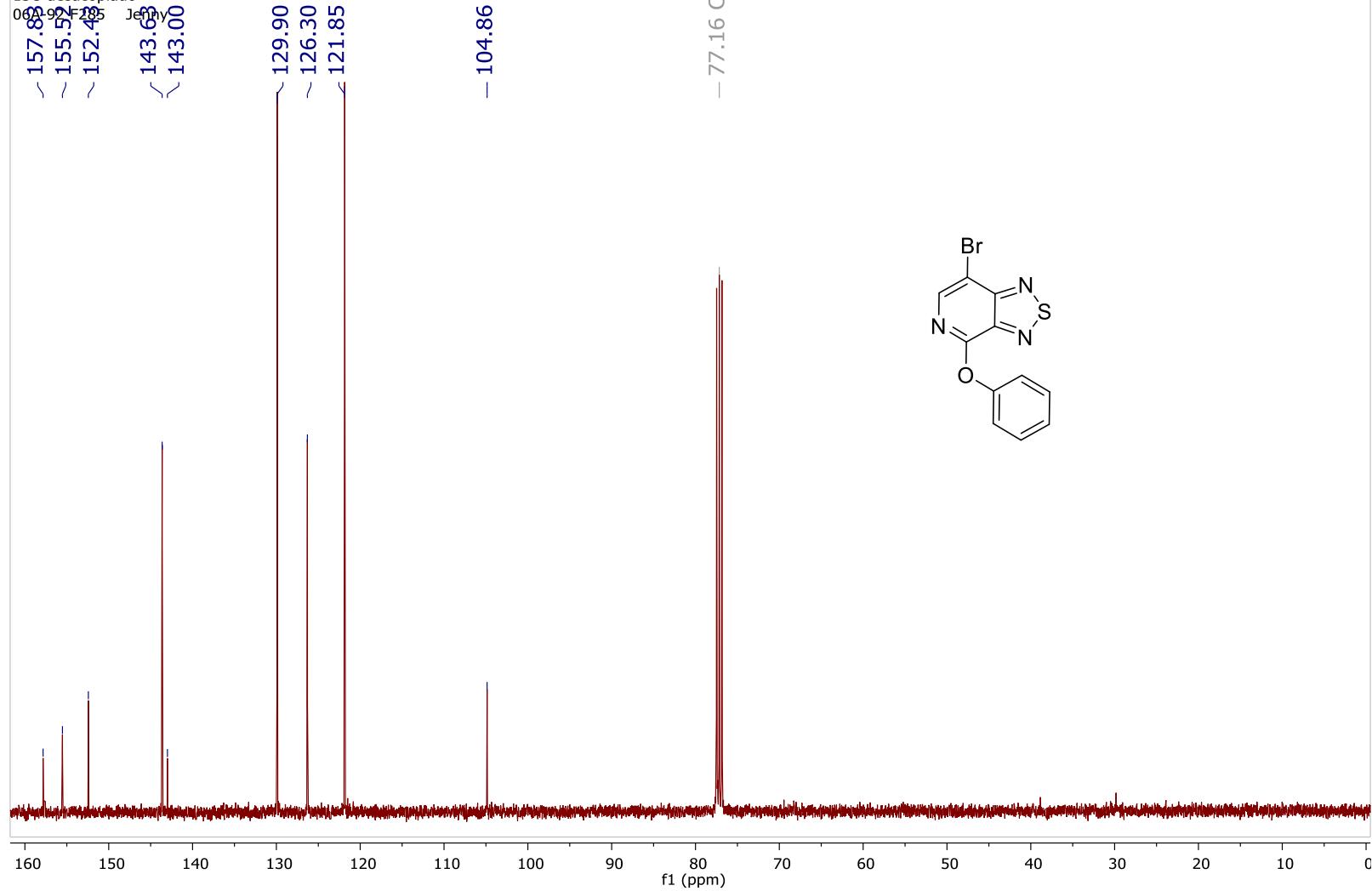
06A90 F185 Jenny

~ 157.88
~ 155.52
~ 152.44
~ 143.63
~ 143.00

129.90
~ 126.30
121.85

— 104.86

— 77.16 CDCl₃



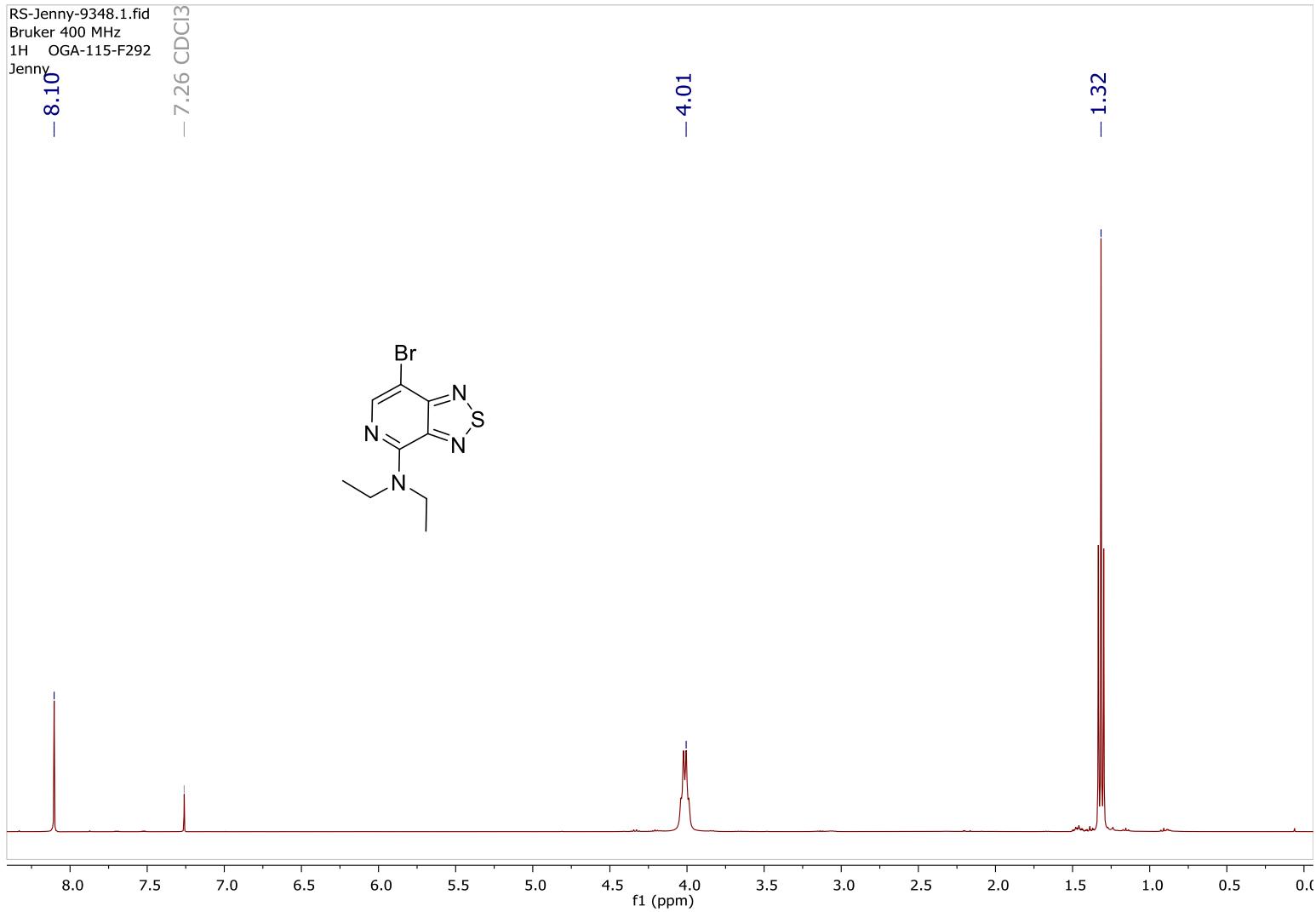
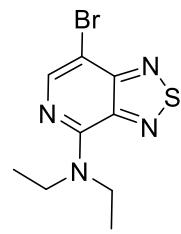
RS-Jenny-9348.1.fid
Bruker 400 MHz
1H OGA-115-F292
Jenny

- 7.26 CDCl₃

- 8.10

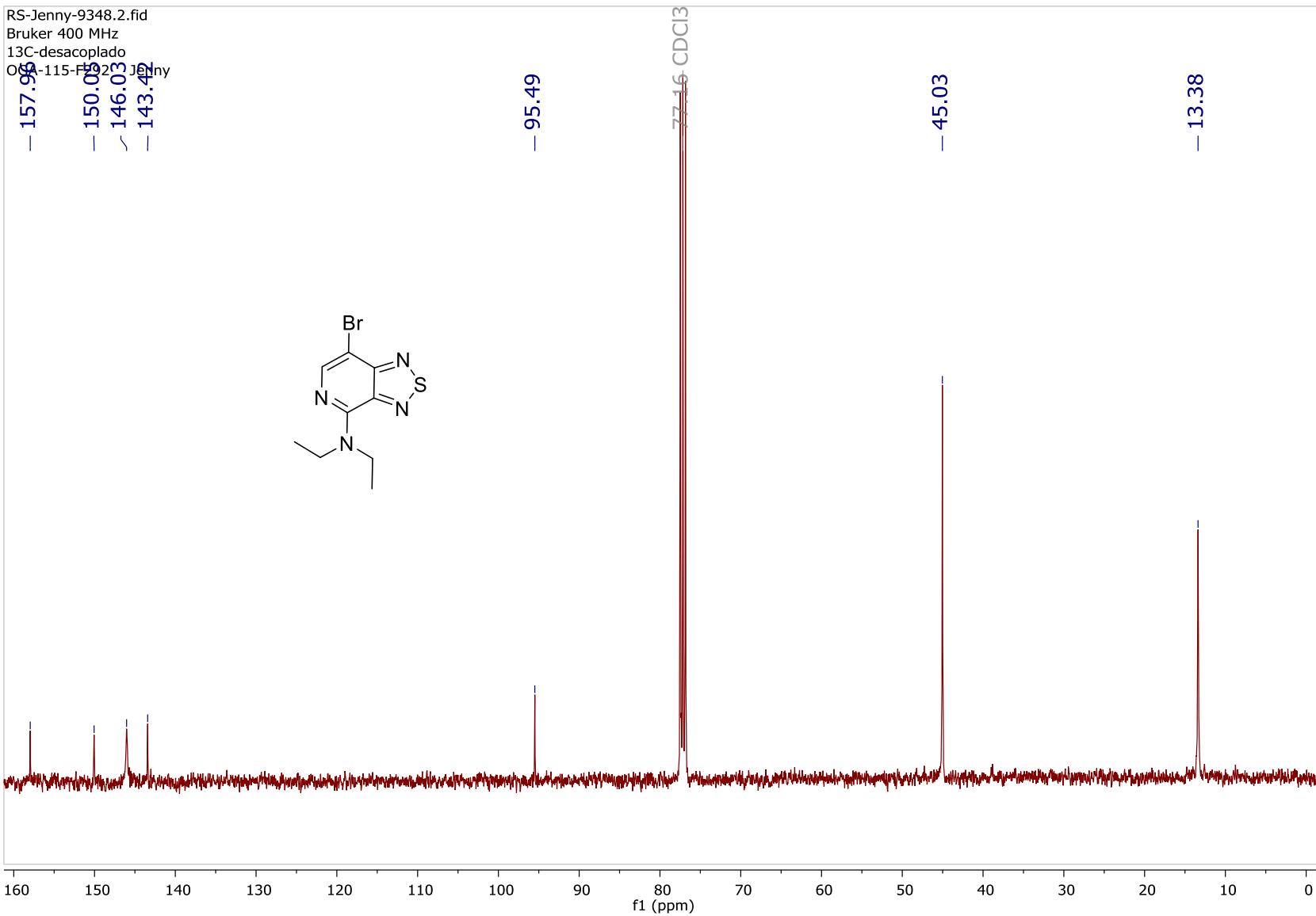
- 4.01

- 1.32

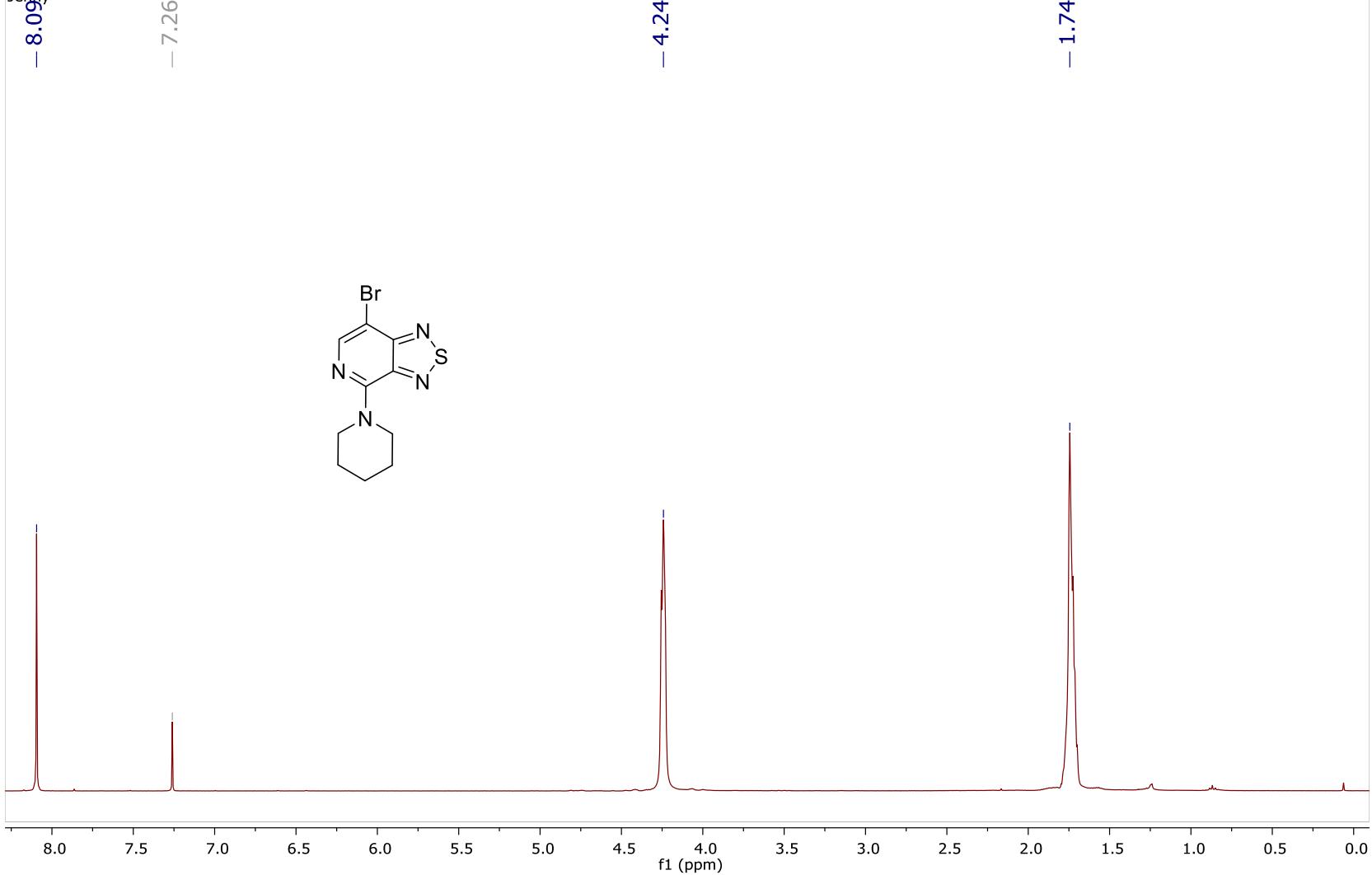


[11]

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Bruker 400 MHz
13C-desacoplado
Ole-115-FID Jenny

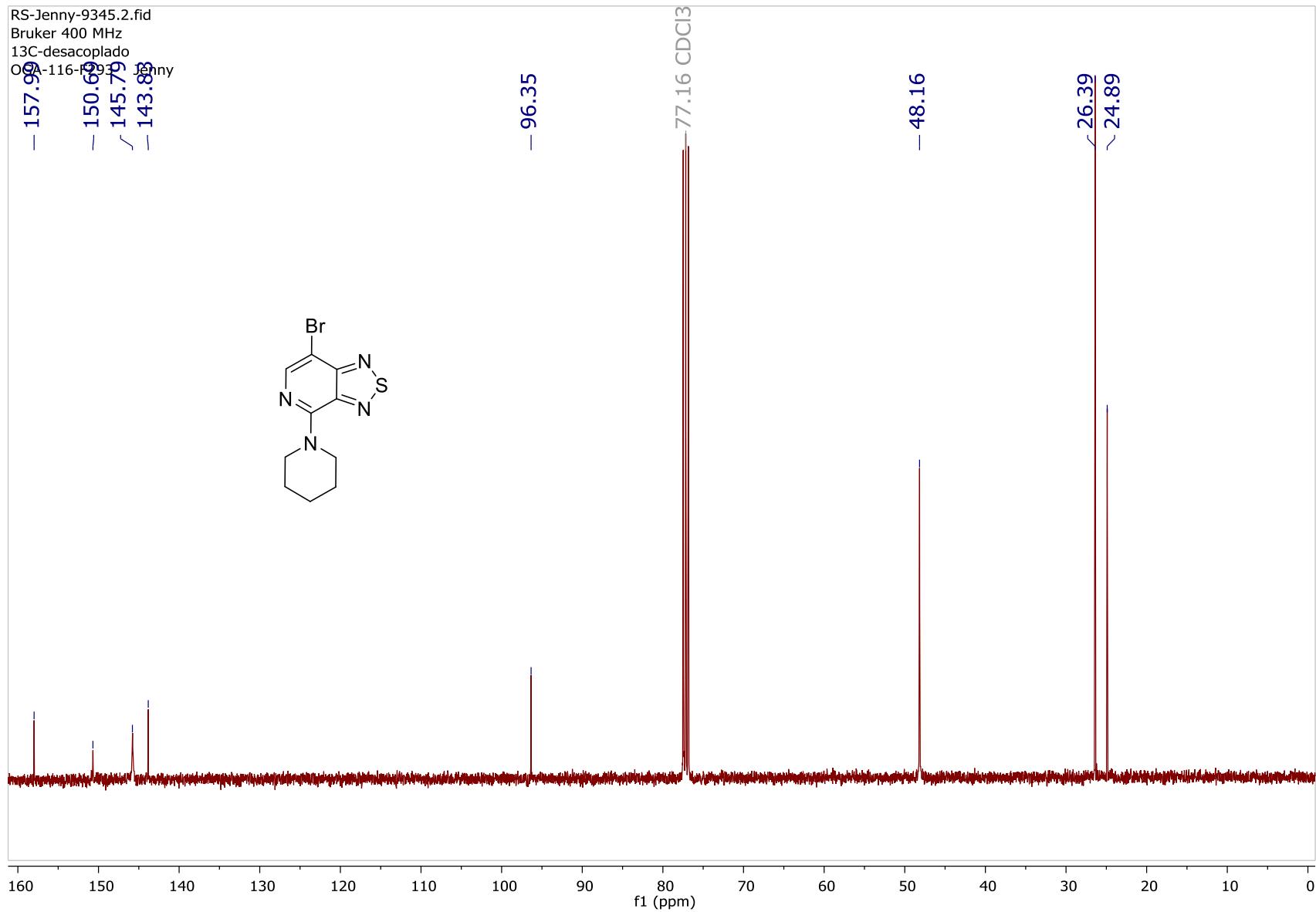
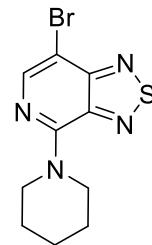


RS-Jenny-9345.1.fid
Bruker 400 MHz
1H OGA-116-F293
Jenny



RS-Jenny-9345.2.fid
Bruker 400 MHz
13C-desacoplado
OCA-116-1203 Jenny

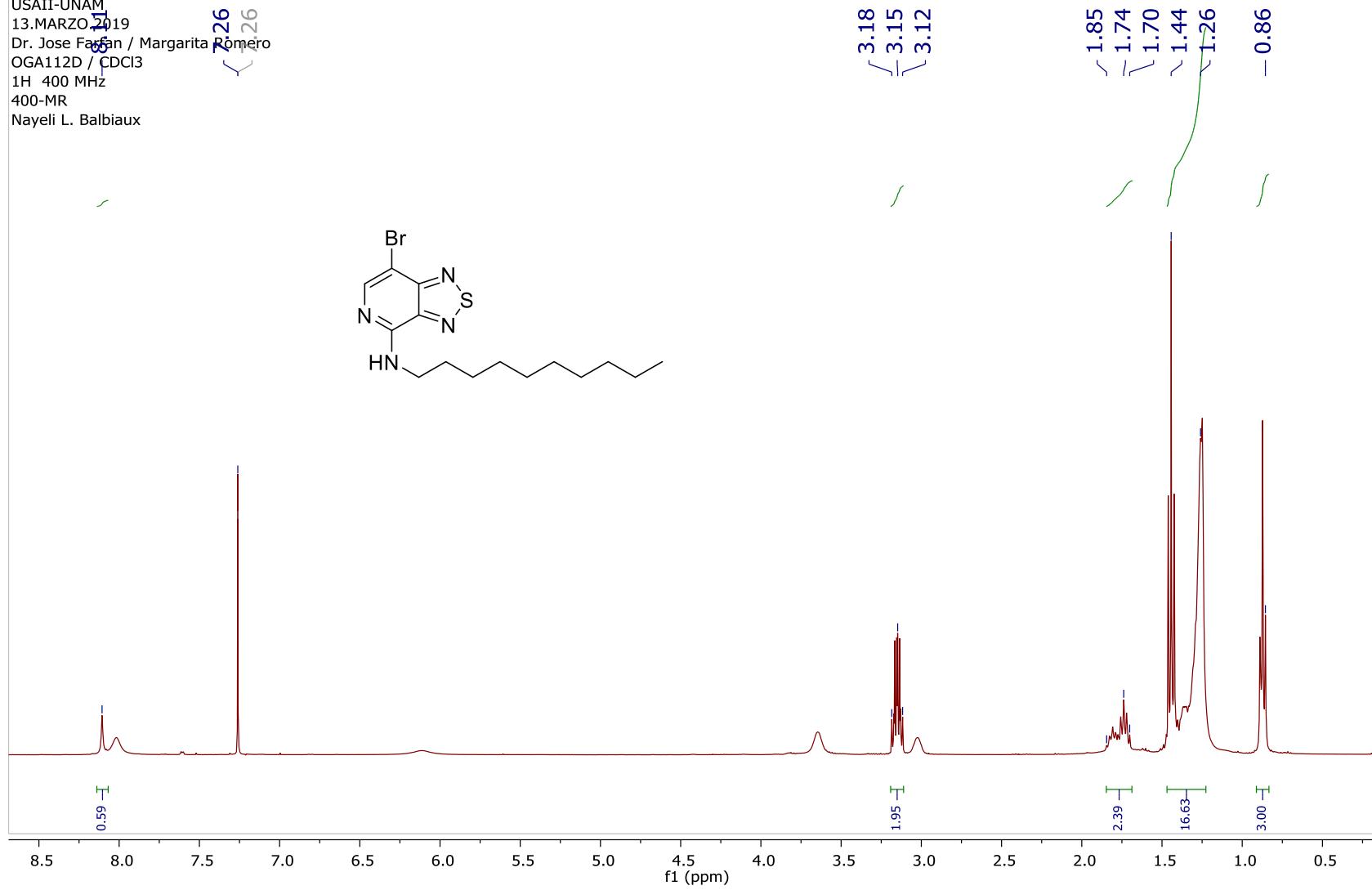
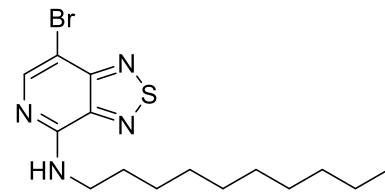
- 157.98
- 150.69
✓ 145.79
- 143.89



0760-1H_OGA112D
0760

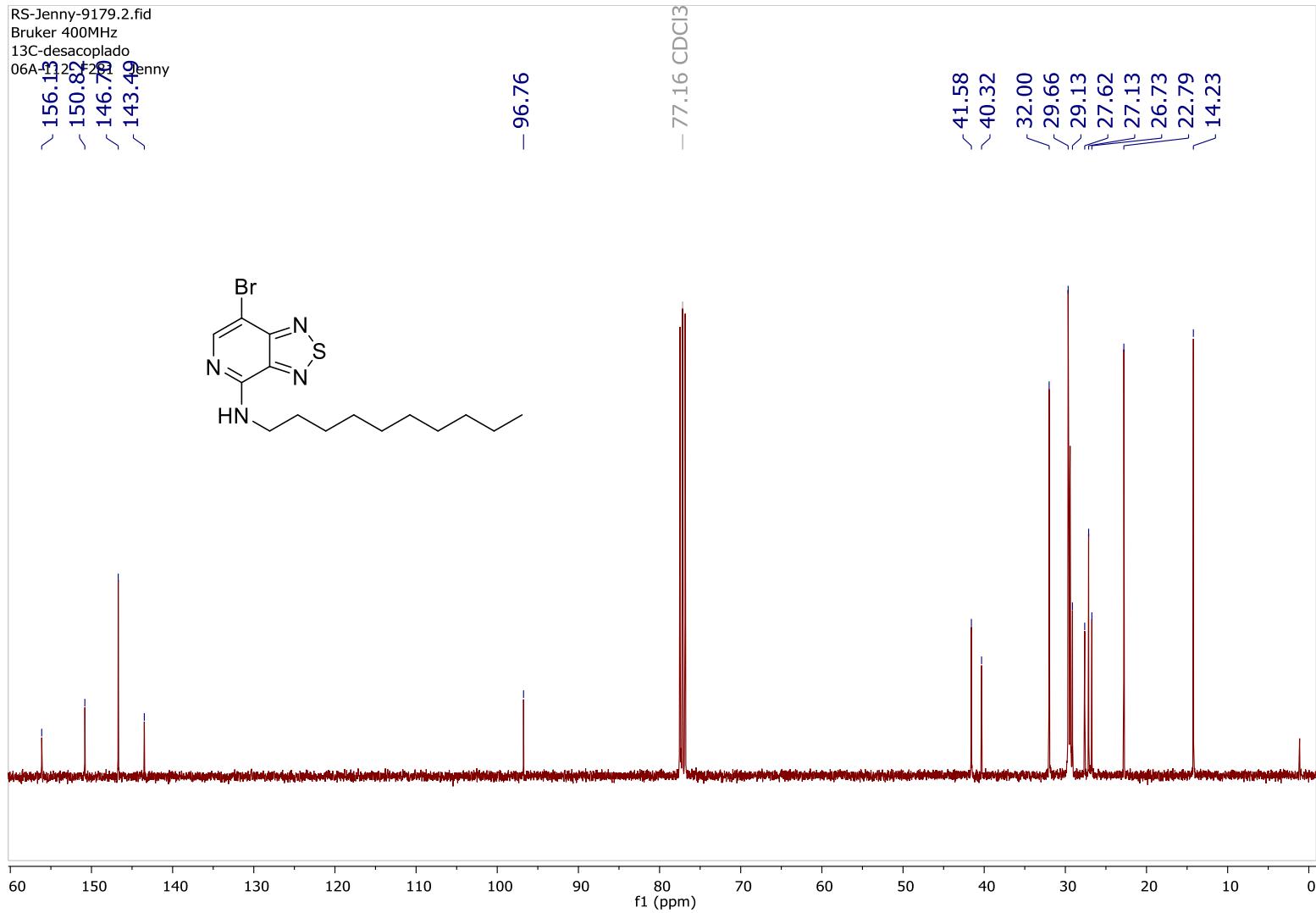
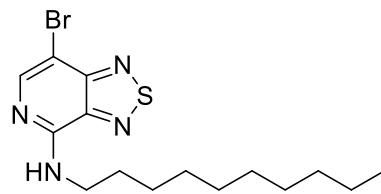
USAIU-UNAM
13.MARZO.2019
Dr. Jose Fagan / Margarita Romero
OGA112D / CDCl₃
1H 400 MHz
400-MR
Nayeli L. Balbiaux

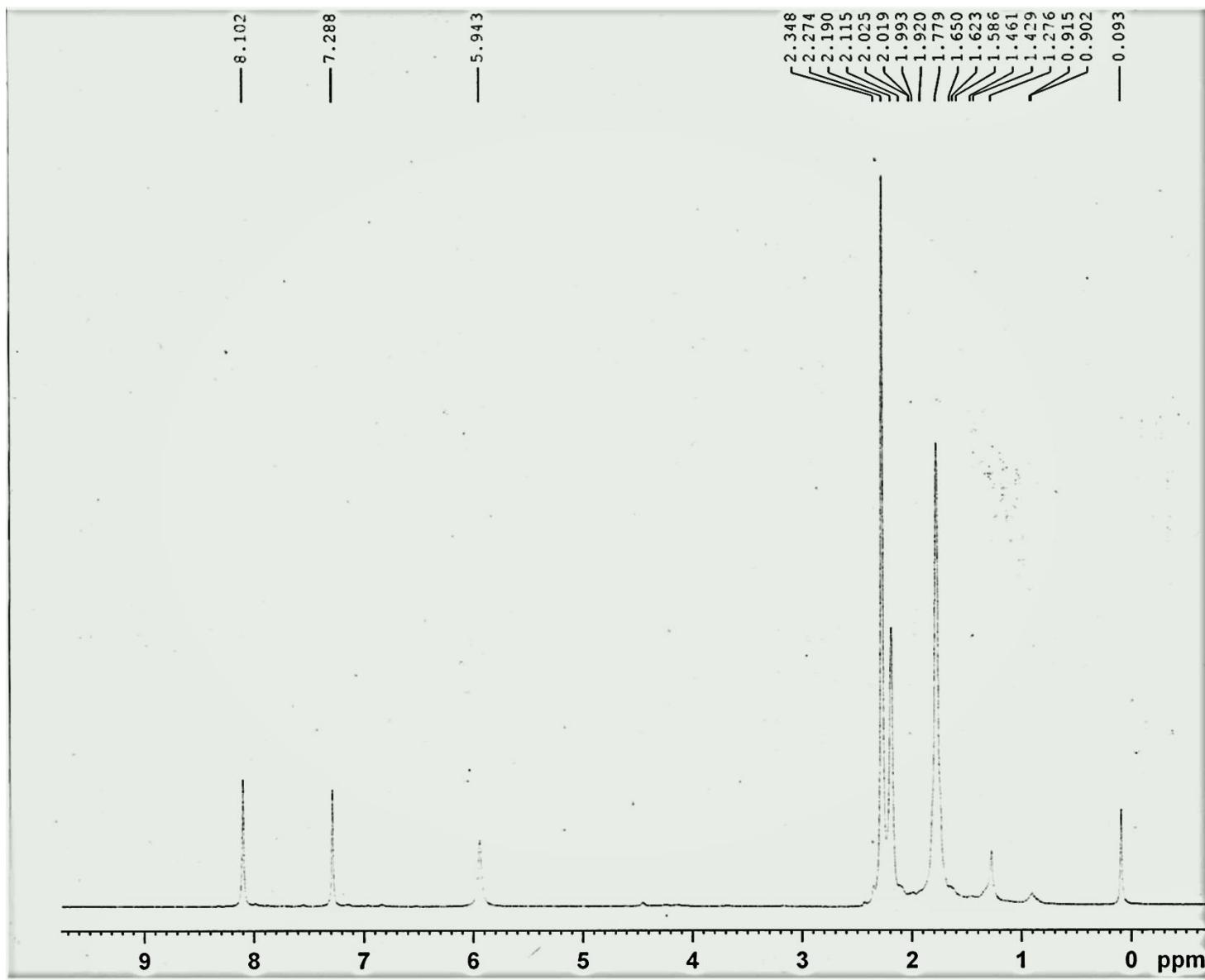
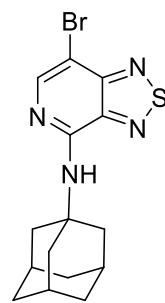
R: 26
R: 26 CDCl₃



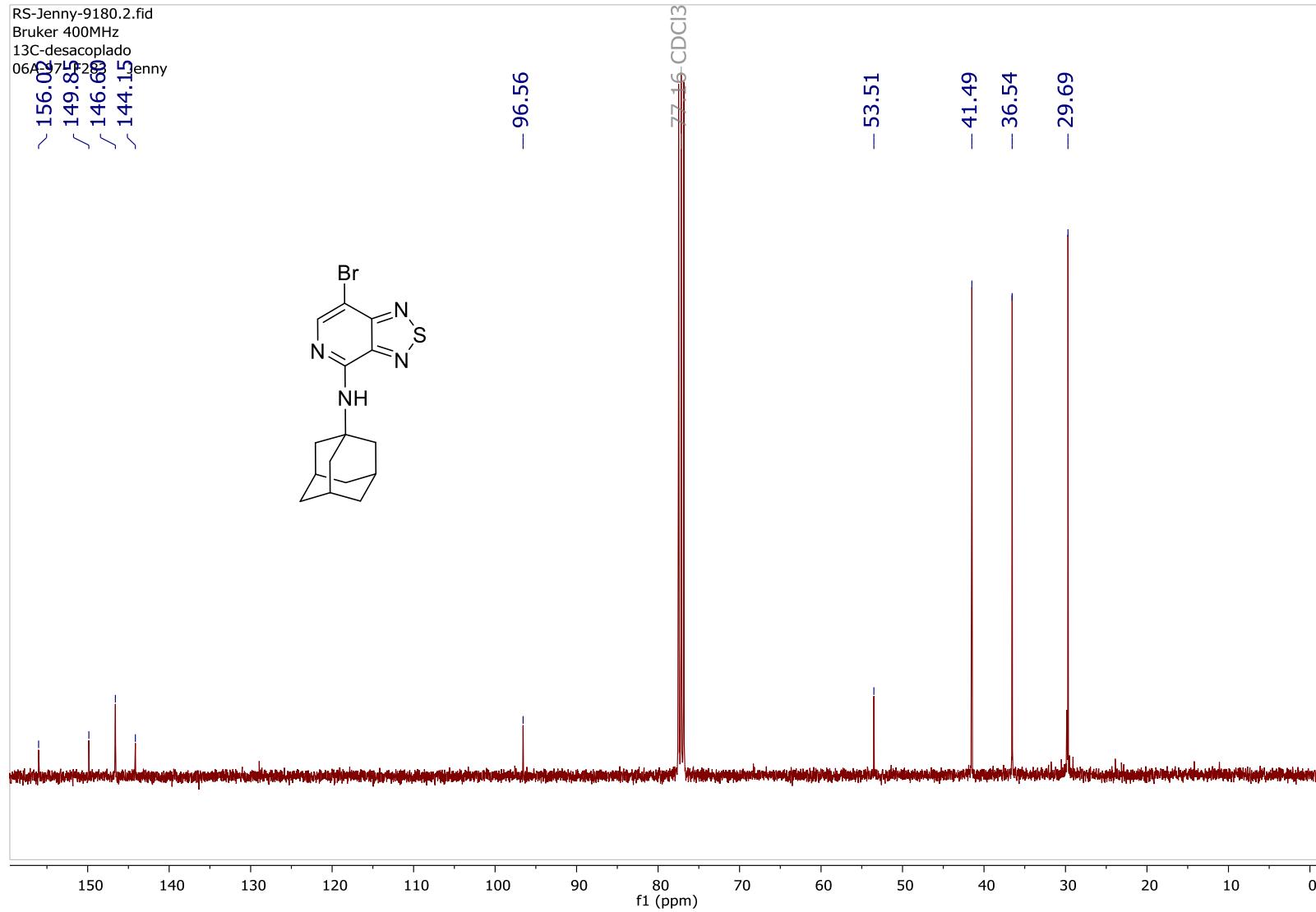
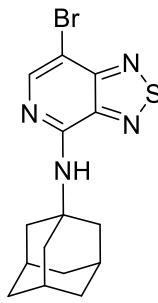
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Bruker 400MHz
13C-desacoplado
06A-1120-129 Jenny

✓ 156.11 ✓ 150.87 ✓ 146.79 ✓ 143.49





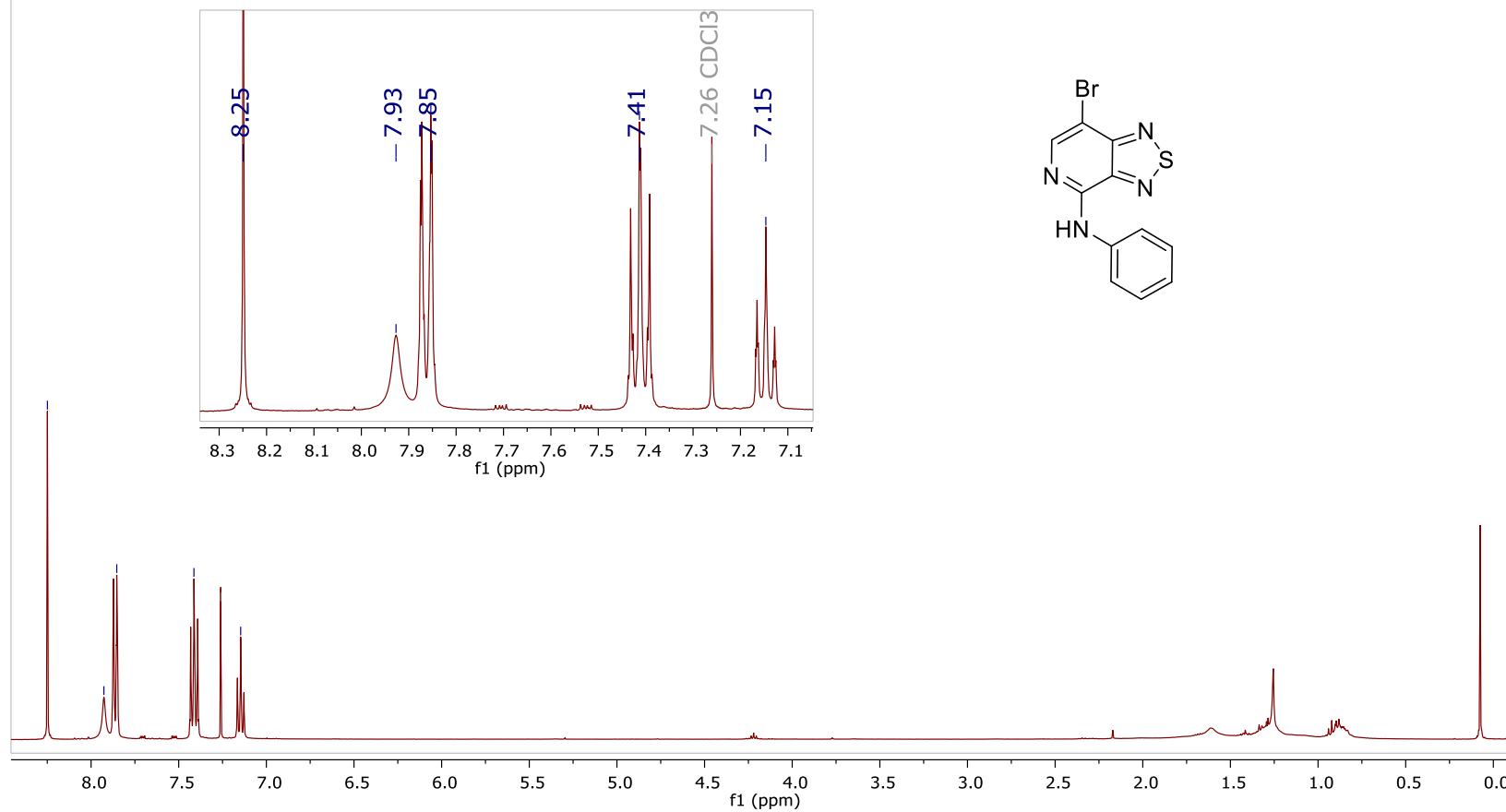
RS-Jenny-9180.2.fid
Bruker 400MHz
13C-desacoplado
06A¹⁷₁₈¹⁹₂₀ Jenny
✓ 156.00
✓ 149.85
✓ 146.69
✓ 144.15



RS-Jenny-9197.1.fid
Bruker 400MHz
1H MNV-68A-F287

Jenny
~ 8.25
~ 7.93
~ 7.85

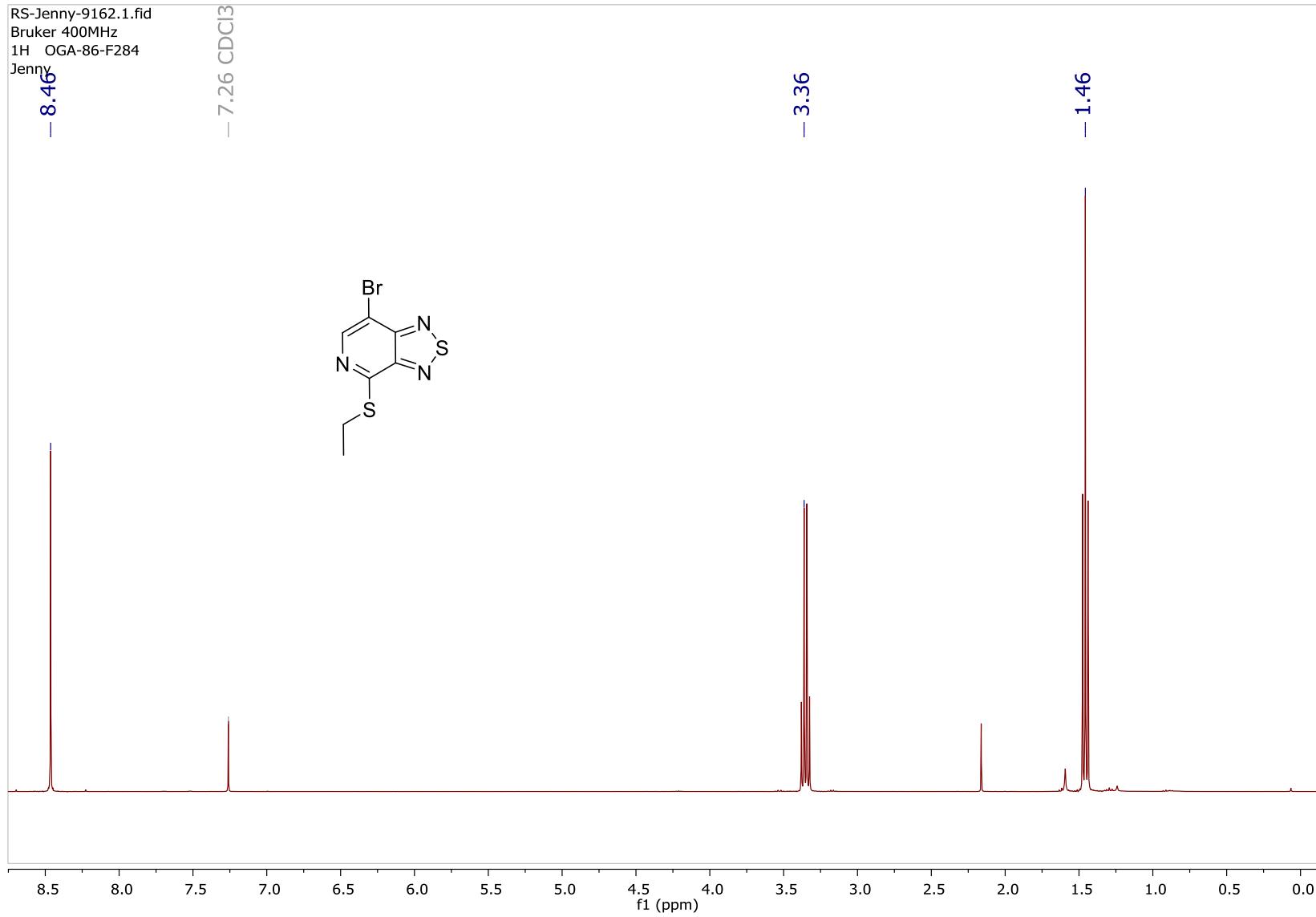
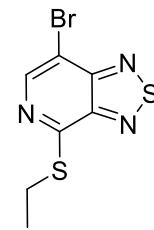
✓ 7.41
~ 7.26 CDCl3
~ 7.15



RS-Jenny-9162.1.fid
Bruker 400MHz
1H OGA-86-F284
Jenny

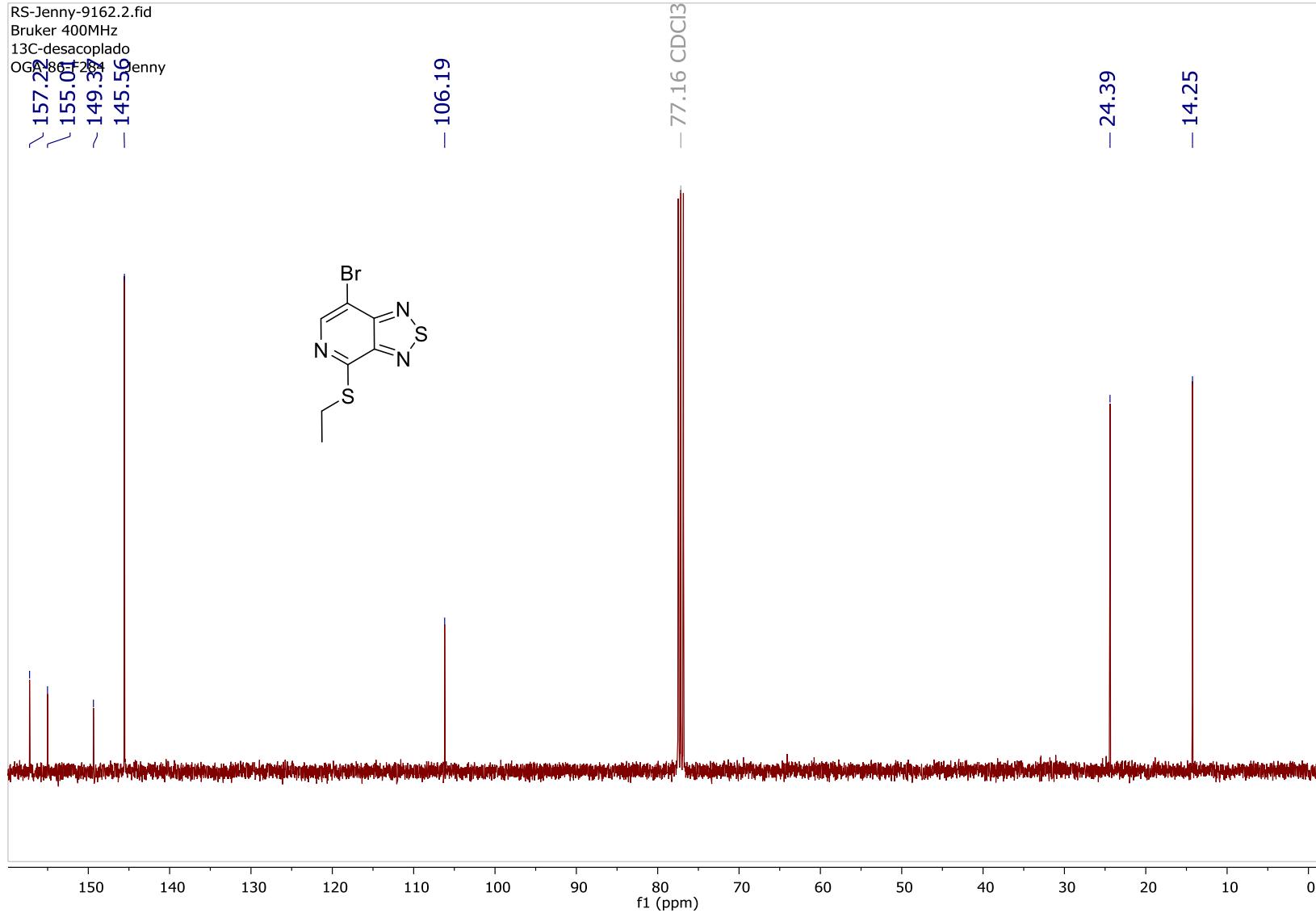
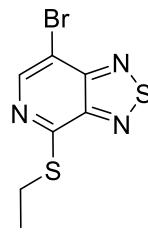
- 8.46

- 7.26 CDCl₃



RS-Jenny-9162.2.fid
Bruker 400MHz
13C-desacoplado
OGN88F24 Jenny

~ 157.29
~ 155.01
~ 149.35
- 145.56



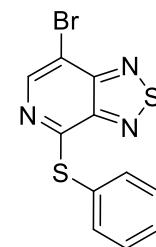
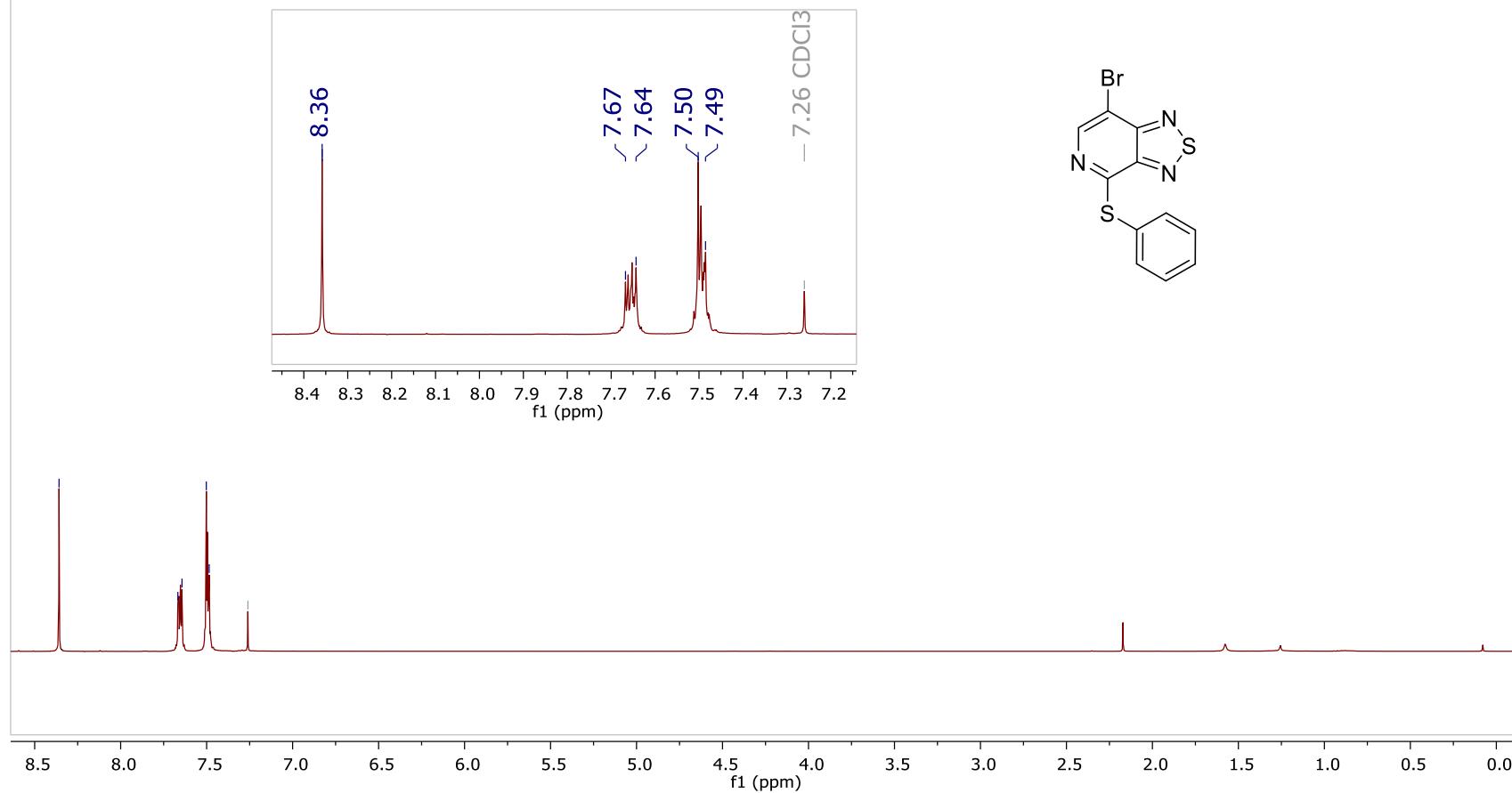
RS-Jenny-9163.1.fid

Bruker 400MHz

1H OGA-88-F286

Jenny

- 8.36
7.67
7.64
7.50
7.49
7.26 CDCl₃



RS-Jenny-9163.2.fid

Bruker 400MHz

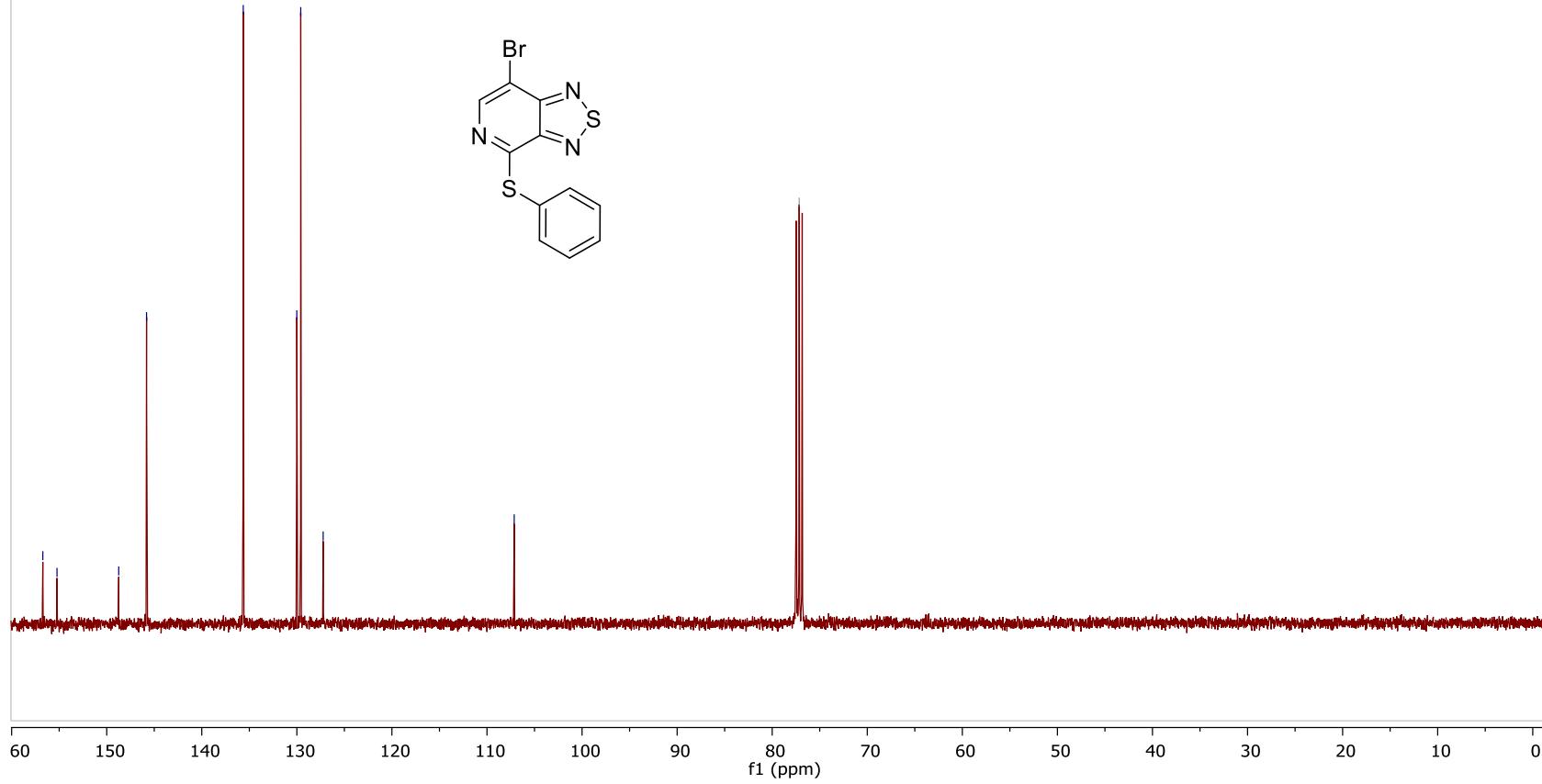
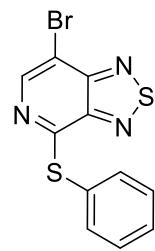
13C-desacoplado

OQ180FF36 Jenny

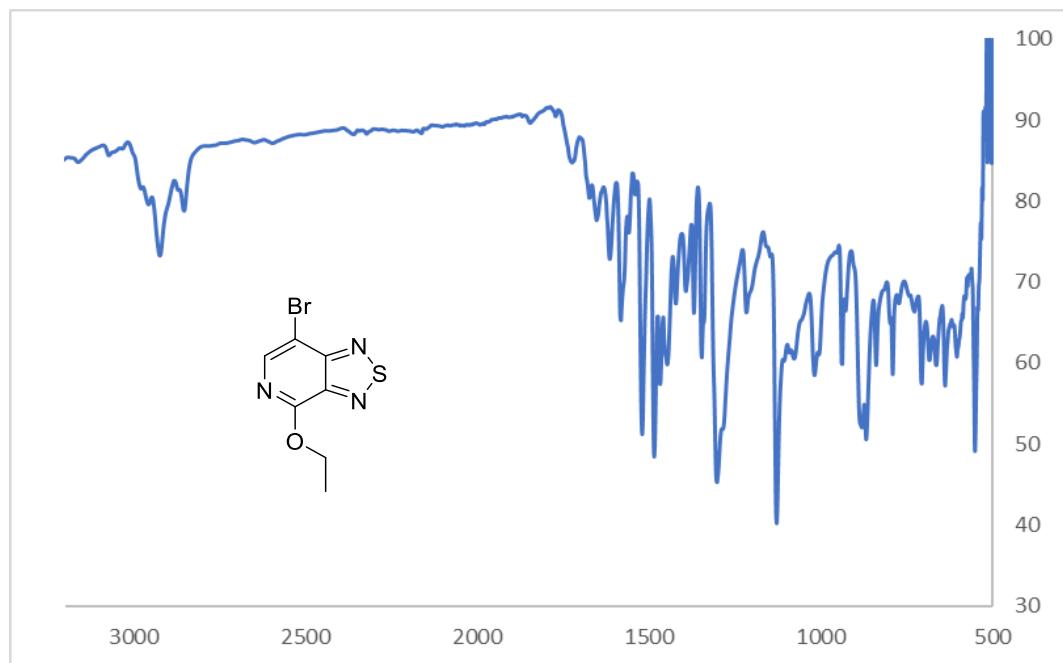
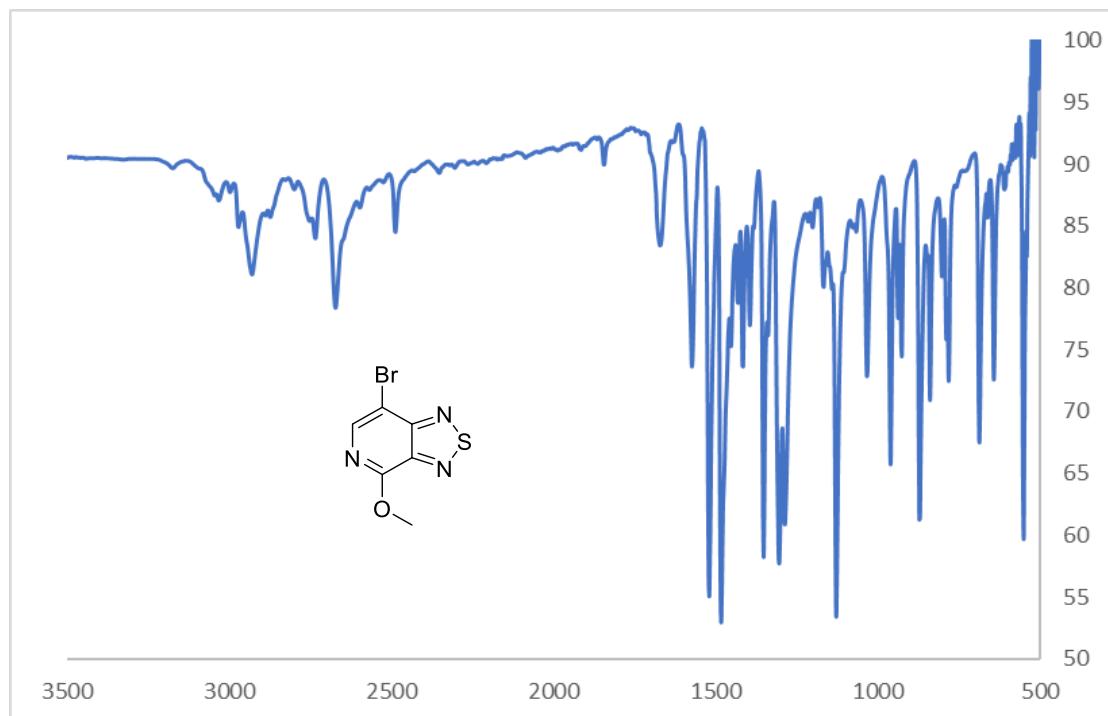
~ 156.74
~ 155.28
~ 148.78
~ 145.81
~ 127.23

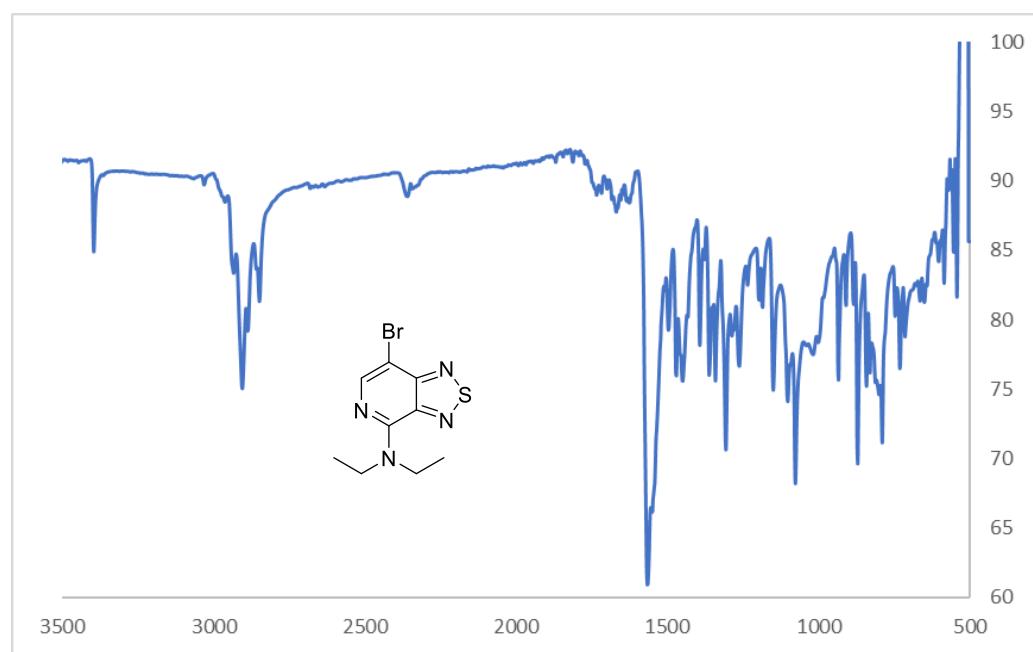
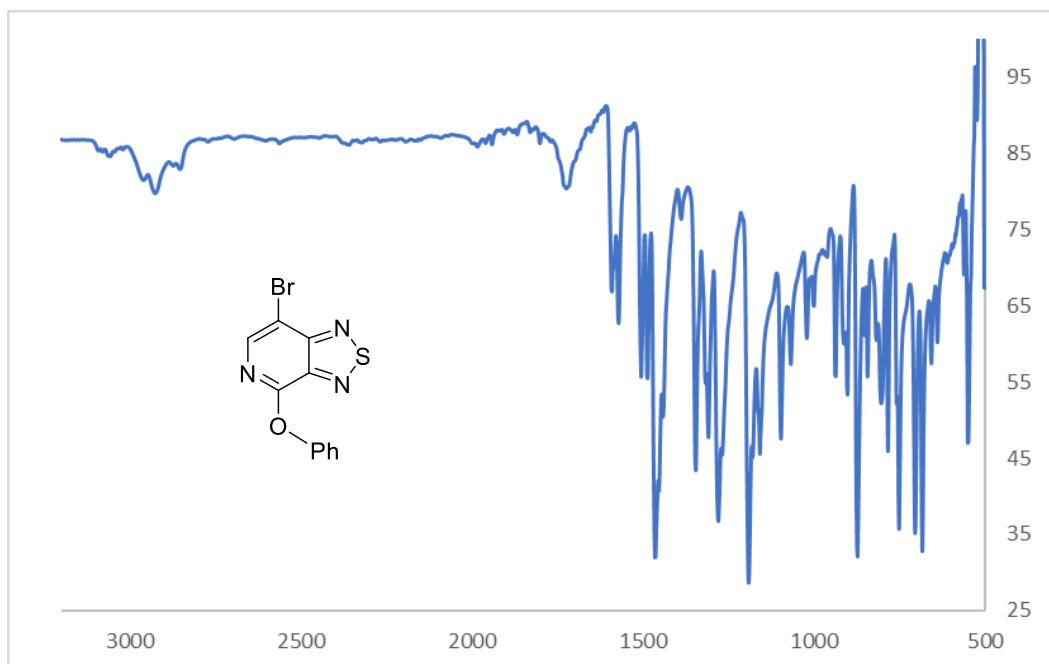
— 135.64
— 130.01
— 129.59
— 107.14

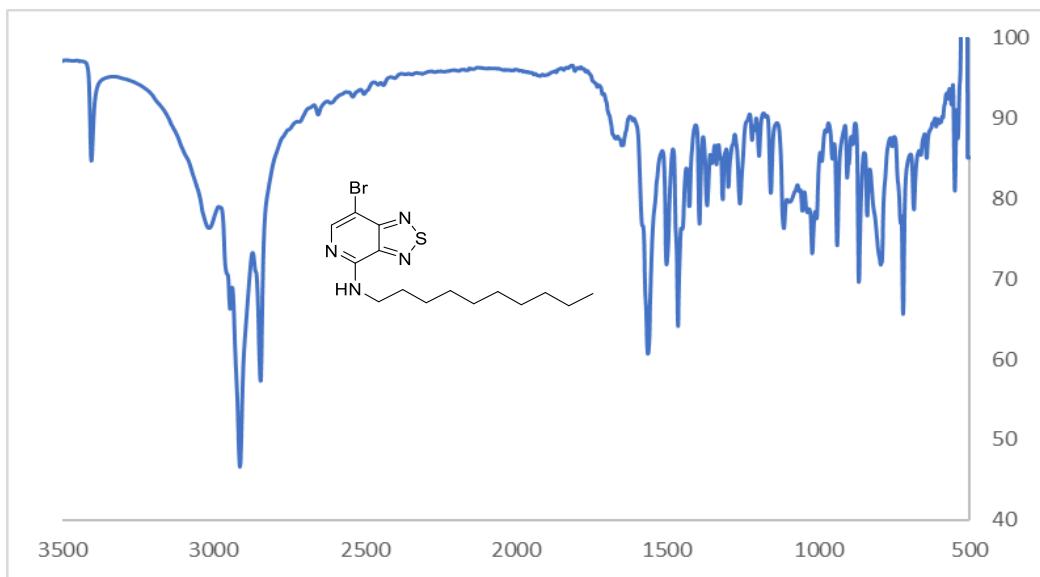
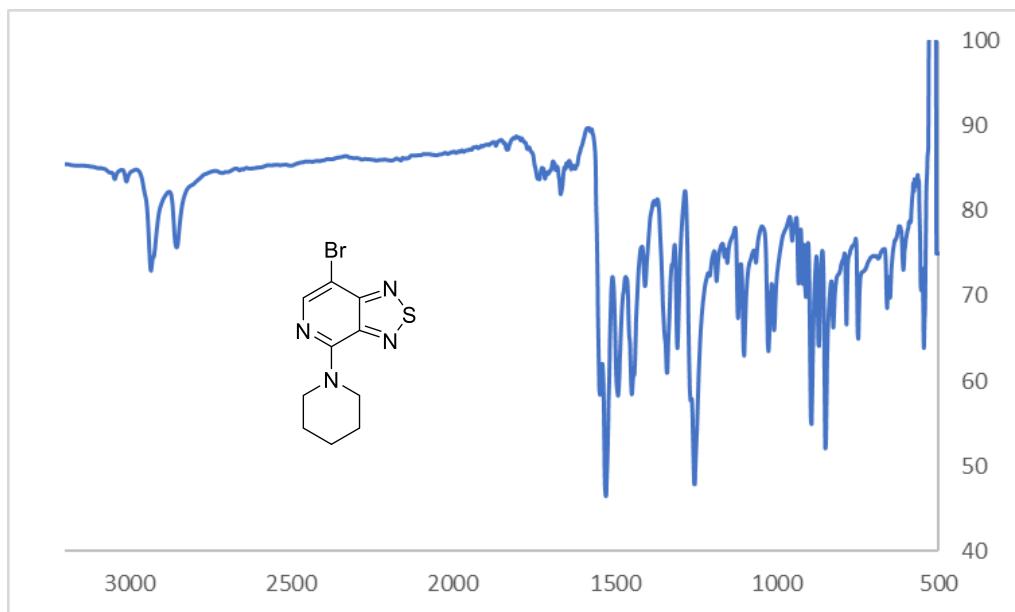
— 77.16 CDCl₃

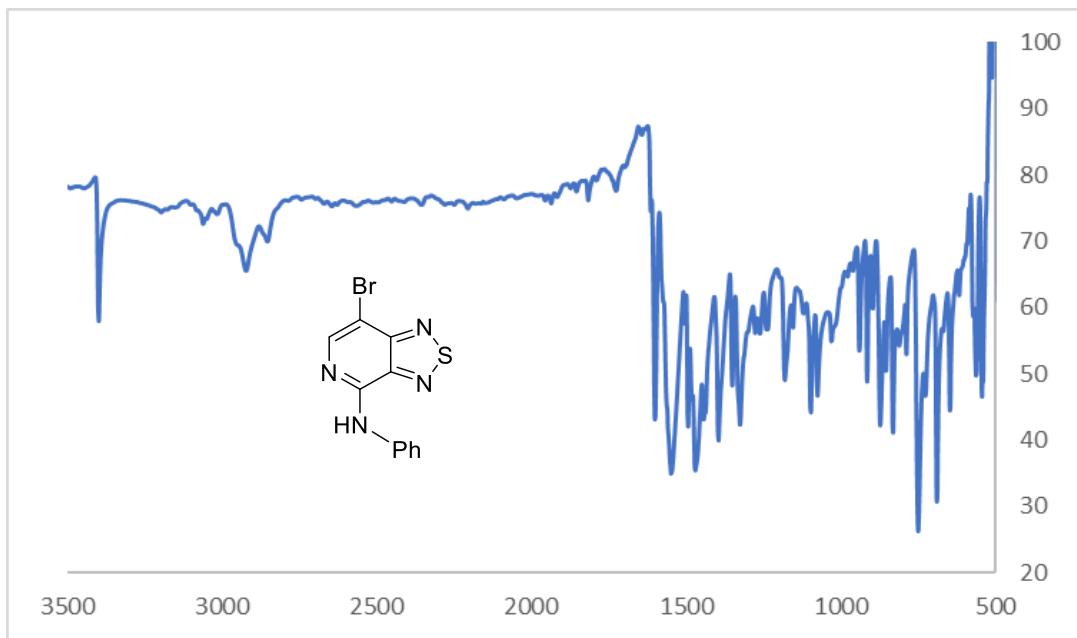
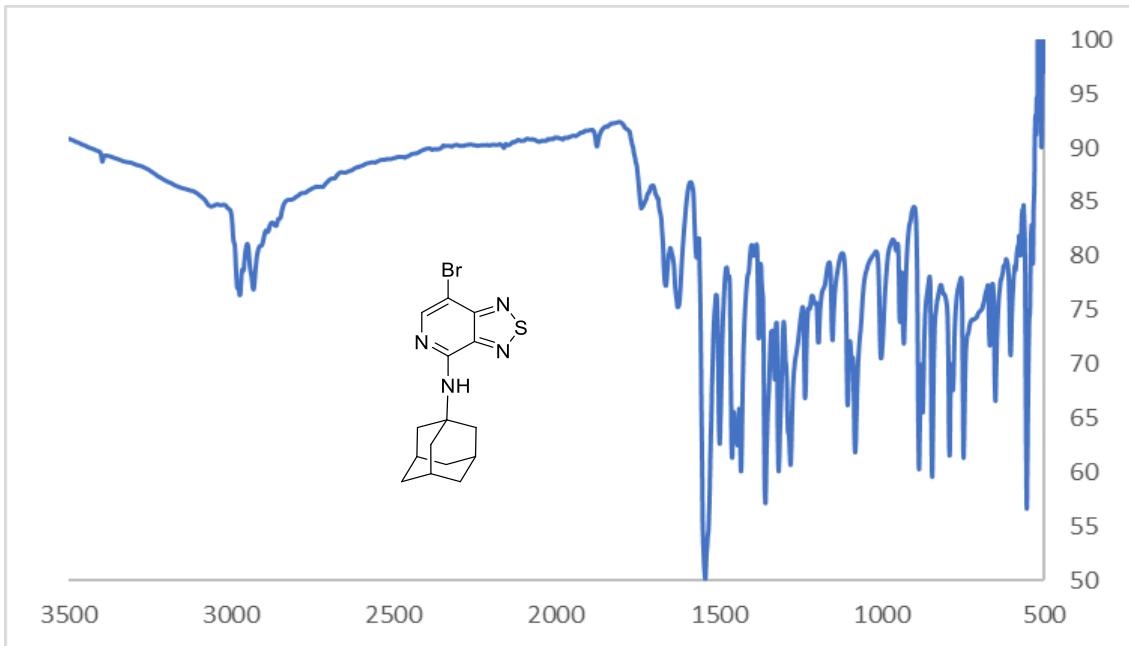


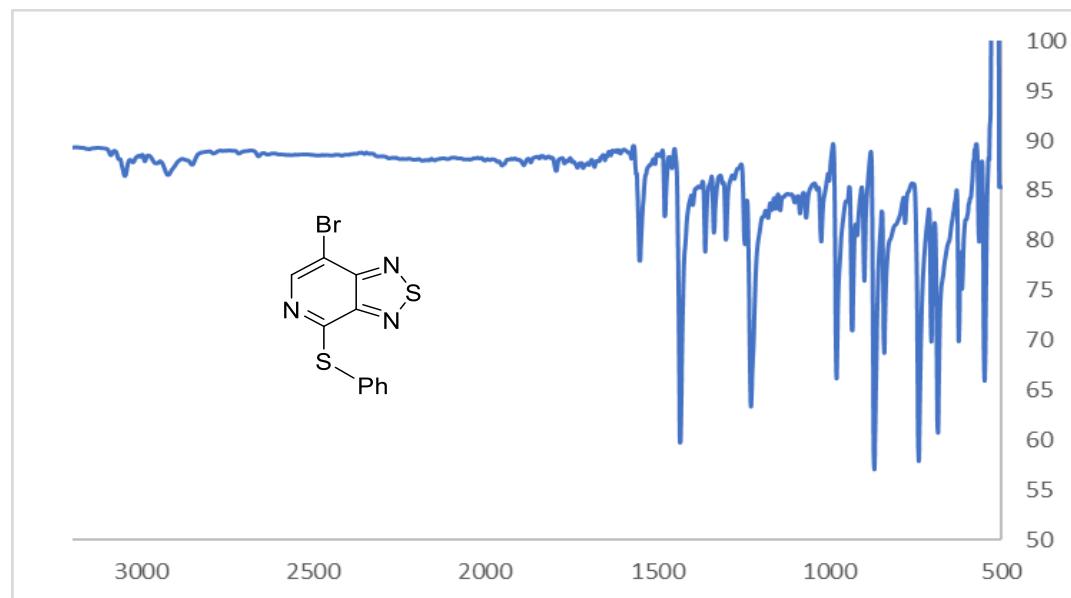
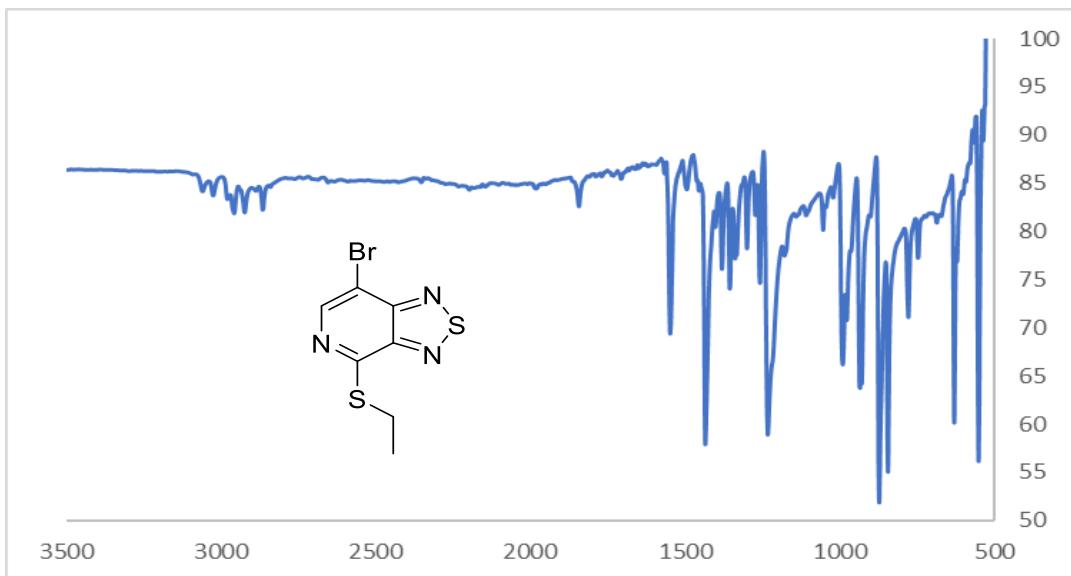
FTIR spectra for the synthesized compounds.

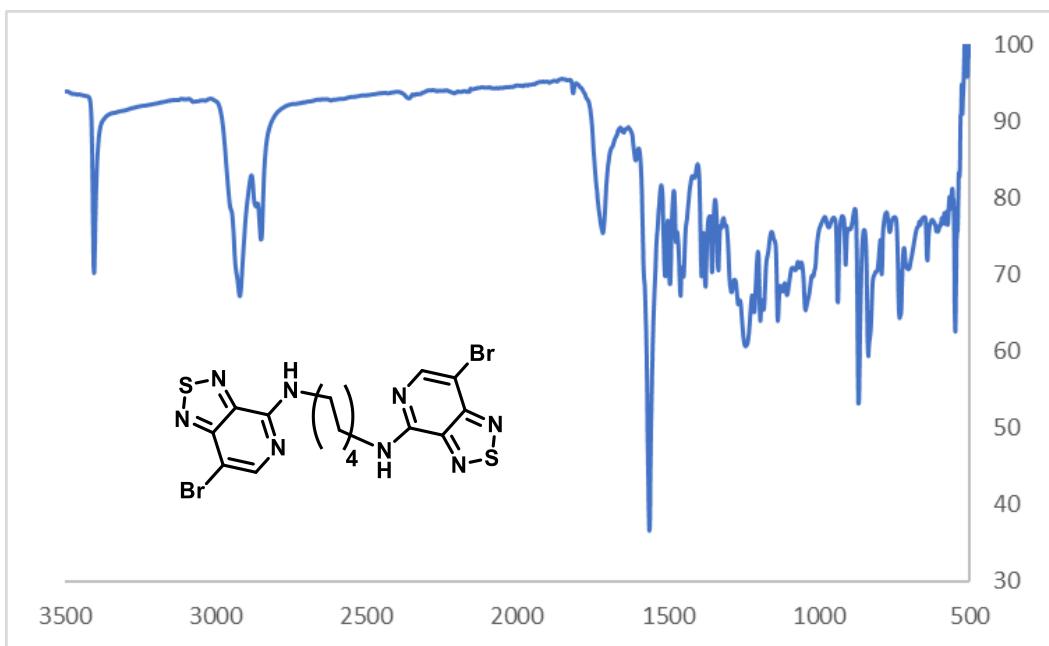




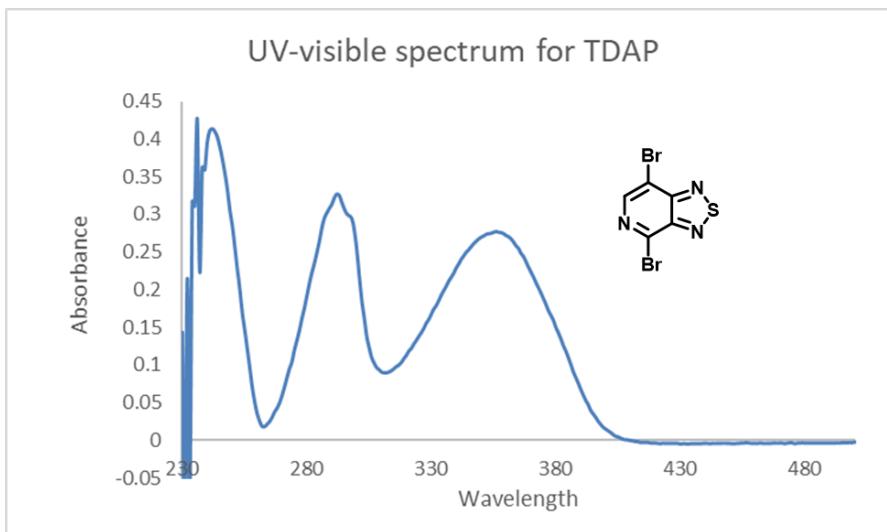






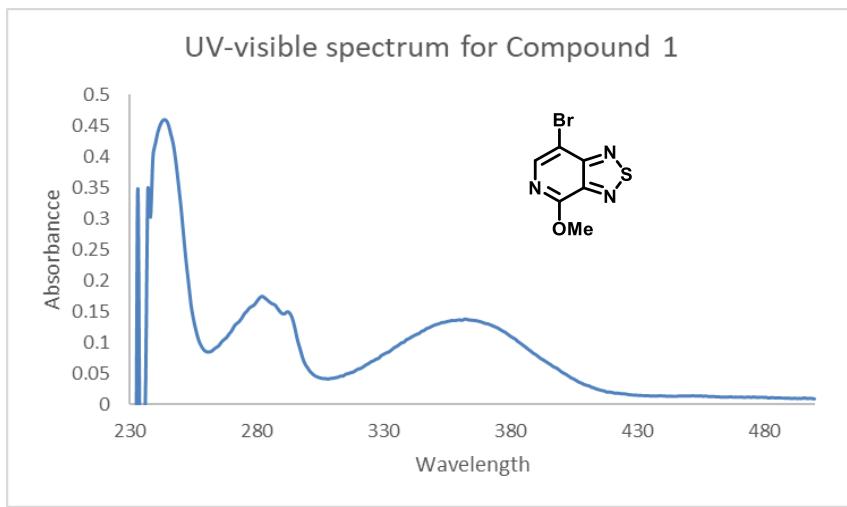


UV-Visible spectra of the synthesized compounds and tables for the determination of molar absorptivity coefficients.



Abs	Conc
0.004001	0.00000137
0.026883	0.0000068
0.054277	0.0000137
0.133626	0.000034
0.276804	0.000068
0.703585	0.00017

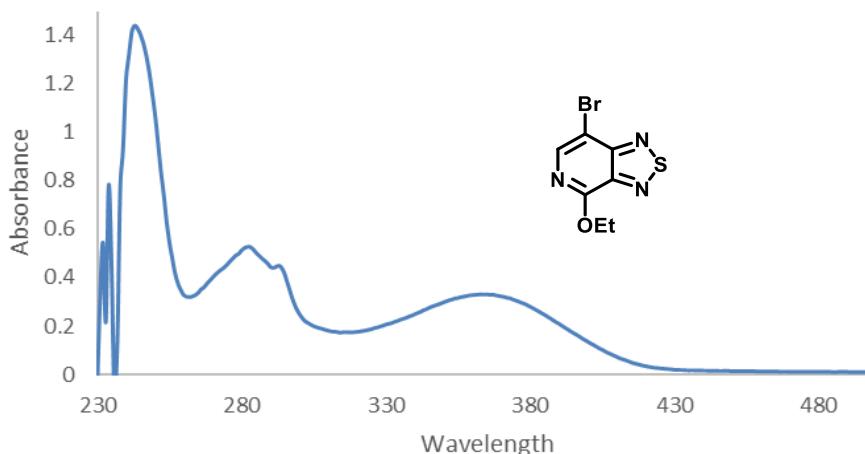
Max Abs =	356 nm	
ϵ =	4150 M ⁻¹	
E _{H-L} (opt) =	3.12 eV	397 nm



Absorbance	Concentration
0.027096	0.000005
0.036418	0.00001
0.137844	0.00005
0.219903	0.00008
0.250372	0.0001
0.506676	0.000209

Max Abs =	362	nm
ϵ =	2354	M ⁻¹
E _{H-L} (opt) =	2.97 eV	418 nm

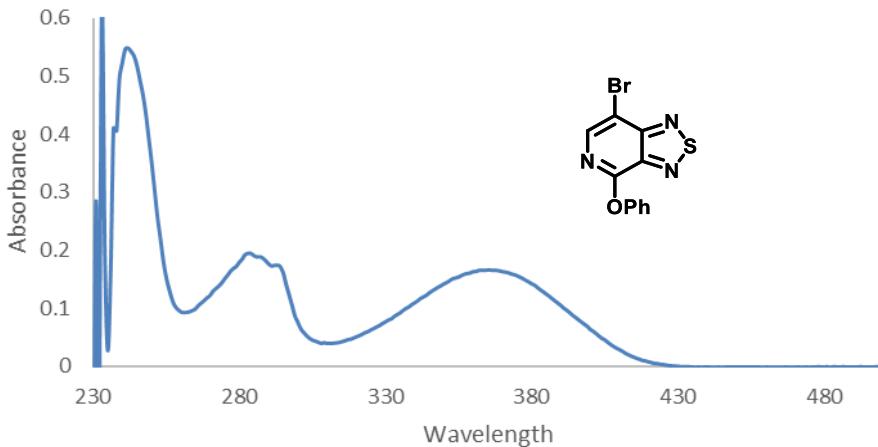
UV-visible spectrum for Compound 2



Absorbance	Concentration
0.076806	0.00006
0.089526	0.0001
0.329651	0.00038
0.509626	0.00051
0.759697	0.00076

Max Abs =	363	nm
ϵ =	1000	M ⁻¹
E _{H-L} (opt) =	2.98	416 nm

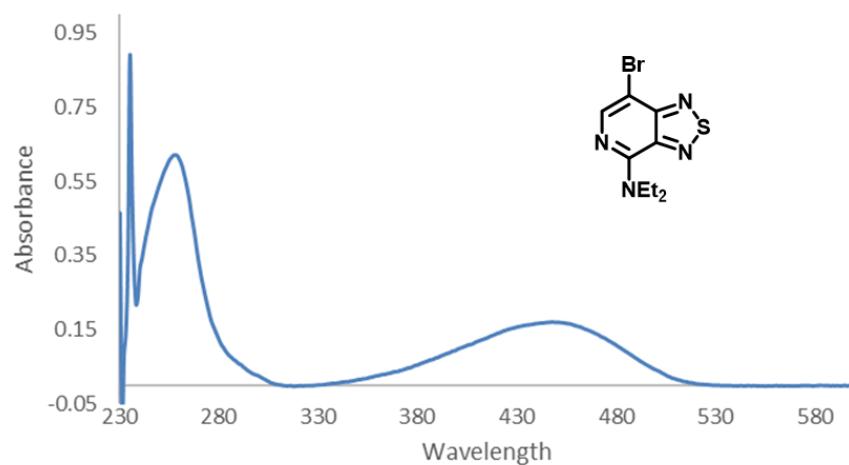
UV-visible spectrum for Compound 3



Absorbance	Concentration
0.020502	0.000005
0.047801	0.00001
0.165528	0.00005
0.288019	0.000066
0.415084	0.0001

Max Abs =	364	nm
ϵ =	4135	M ⁻¹
E _{H-L} (opt) =	2.97 eV	418 nm

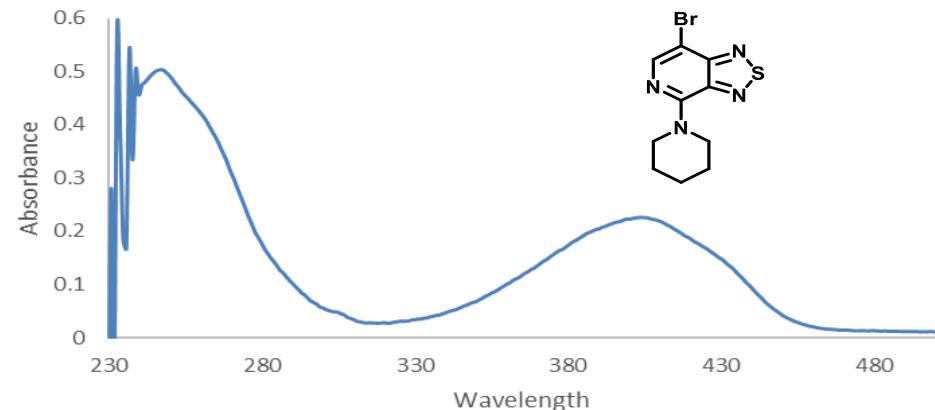
UV-visible spectrum for Compound 4



Absorbance	Concentration
0.006192	0.0000072
0.015179	0.0000146
0.029243	0.0000072
0.07322	0.0000143
0.170414	0.000036
0.409436	0.000072

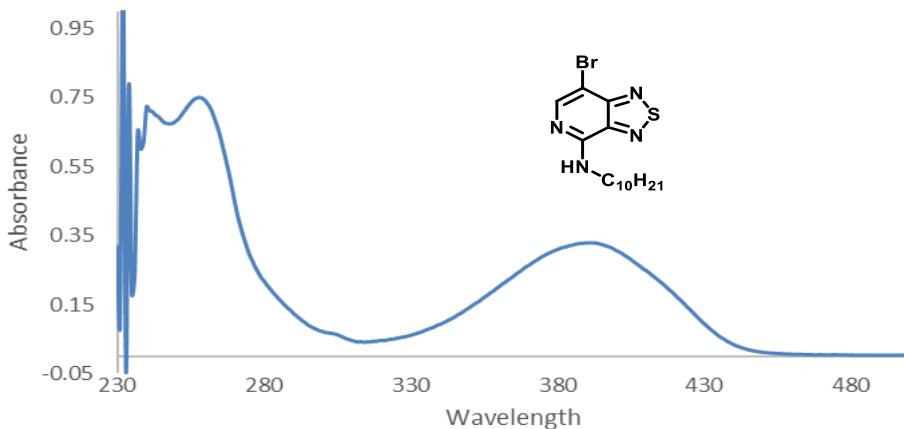
Max. Abs =	448	nm
$\epsilon =$	5574	M^{-1}
$E_{H-L}(\text{opt}) =$	2.42 eV	513 nm

UV-visible spectrum for Compound 5



Max Abs =	403	nm
$\epsilon =$	3956	M^{-1}
$E_{H-L}(\text{opt}) =$	2.70 eV	459 nm

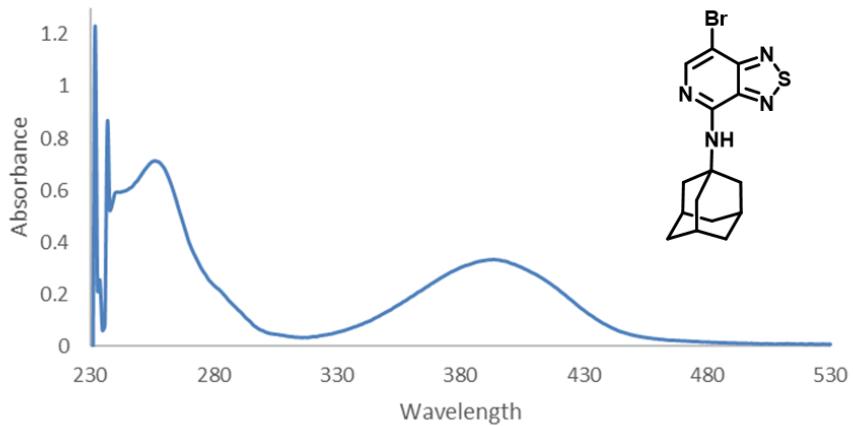
UV-visible spectrum for Compound 6



Absorbance	Concentration
0.022839	0.000005
0.047894	0.00001
0.200392	0.00005
0.328157	0.00008
0.430772	0.0001

Max. Abs. =	390	nm
ϵ =	4198	M ⁻¹
E _{H-L} (opt) =	2.79 eV	444 nm

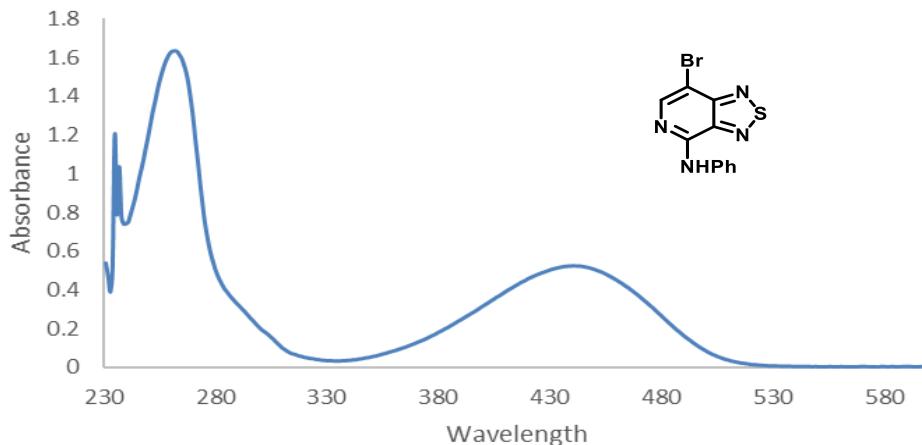
UV-visible spectrum for Compound 7



Absorbance	Concentration
0.034012	0.000005
0.051782	0.000008
0.060289	0.00001
0.213353	0.00005
0.333565	0.00008
0.949177	0.000187

Max Abs =	395	nm
ϵ =	4960	M ⁻¹
E _{H-L} (opt) =	2.74 eV	453 nm

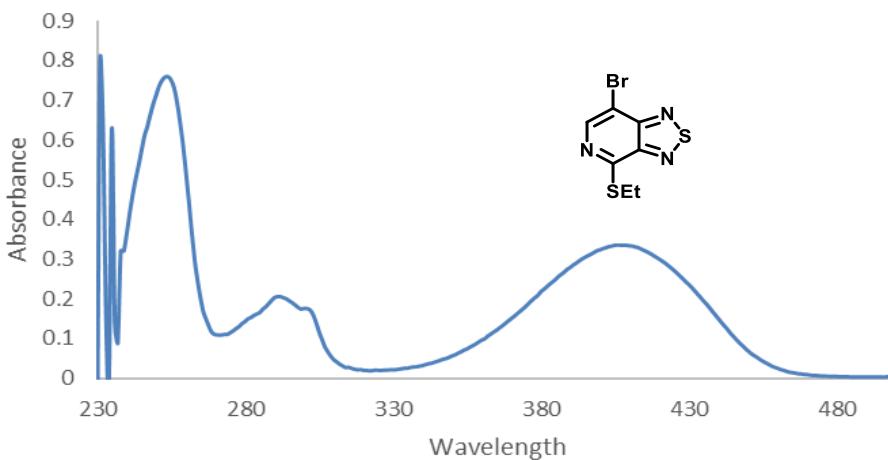
UV-visible spectrum for Compound 8



Absorbance	Concentration
0.055616	0.000005
0.14637	0.00001
0.236961	0.00002
0.522209	0.00004
0.665329	0.00005
1.20079	0.00008

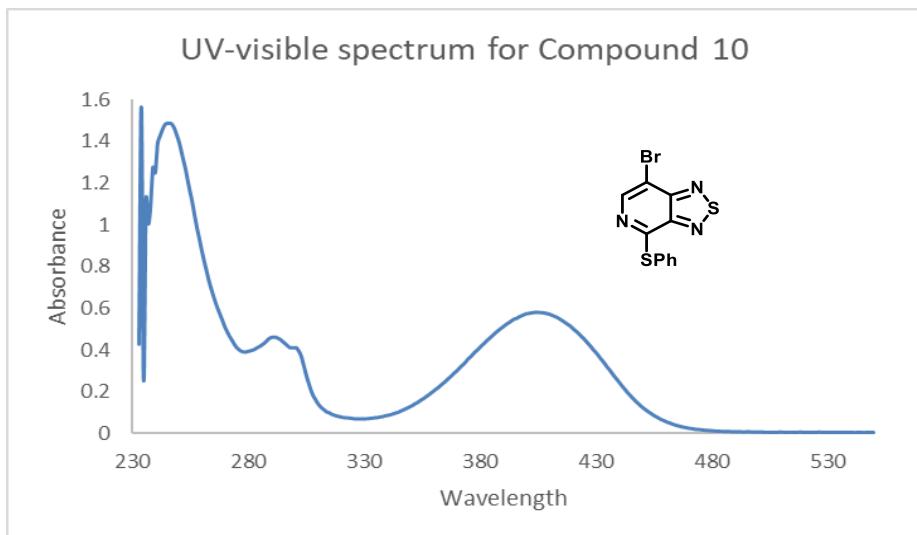
Max. Abs. =	442	nm
ϵ =	14947	M ⁻¹
E _{H-L} (opt) =	2.42 eV	512 nm

UV-visible spectrum for Compound 9



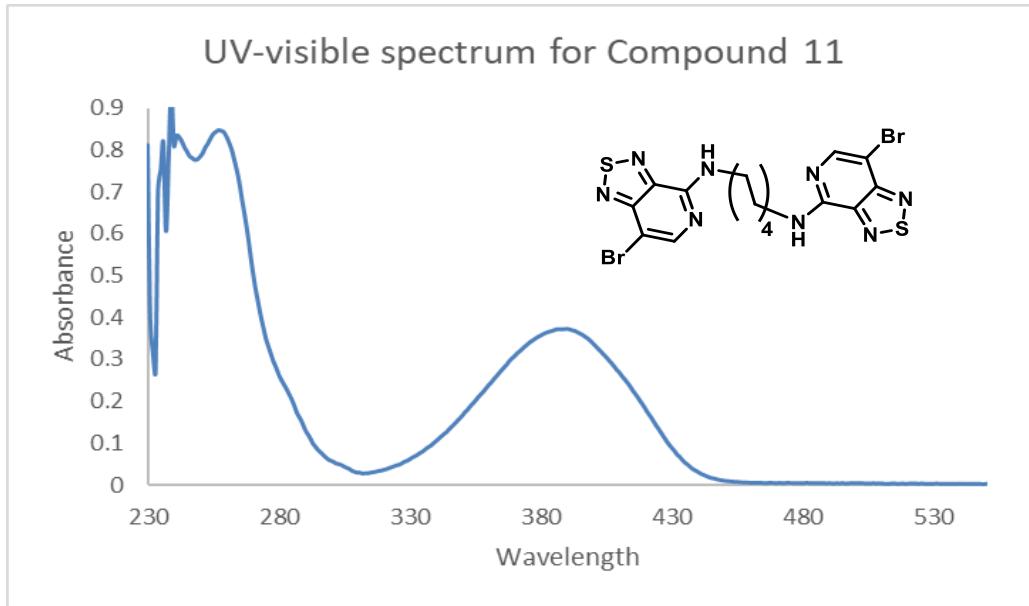
Absorbance	Concentration
0.017864	0.000005
0.047075	0.00001
0.150299	0.00005
0.261262	0.00008
0.335093	0.0001

Max. Abs. =	408	nm
ϵ =	3236	M ⁻¹
E _{H-L} (opt) =	2.69 eV	461 nm



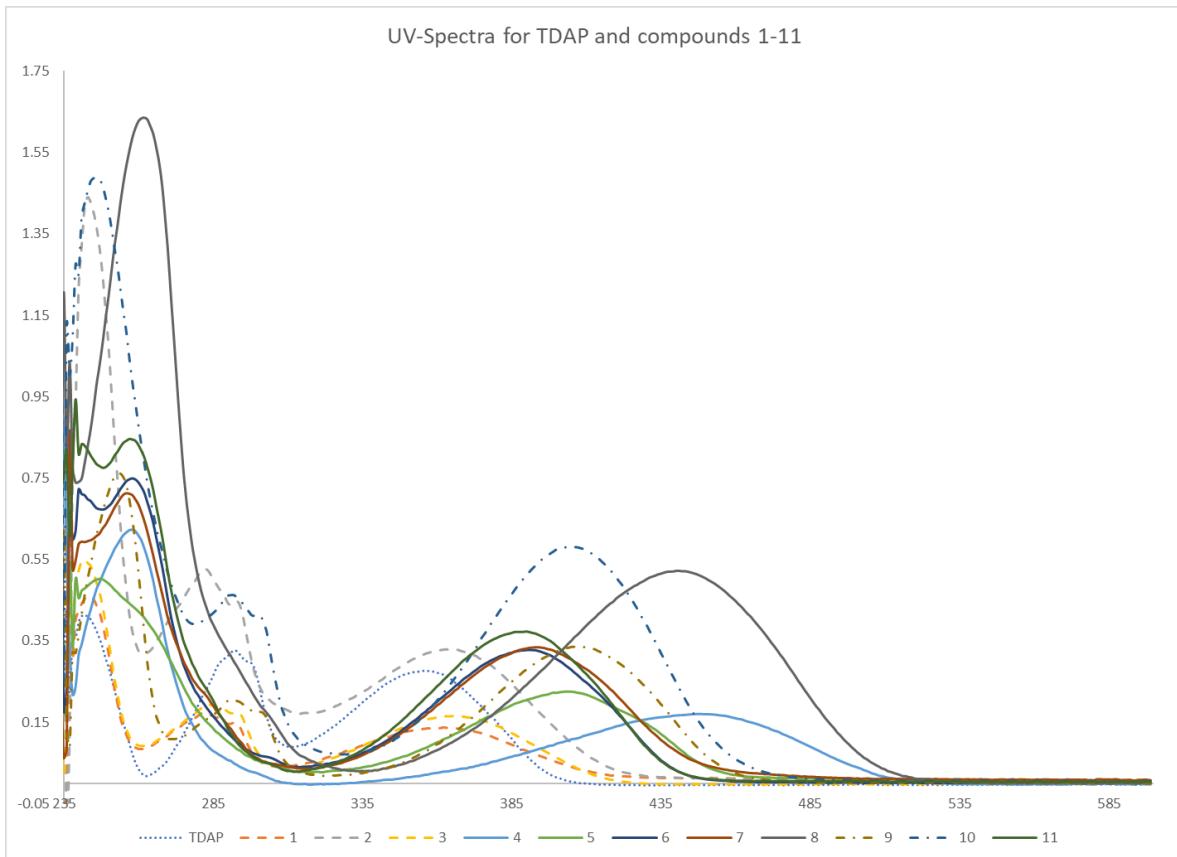
Absorbance	Concentration
0.066798	0.000005
0.271996	0.000025
0.42481	0.00004
0.581537	0.00005
0.831046	0.00008

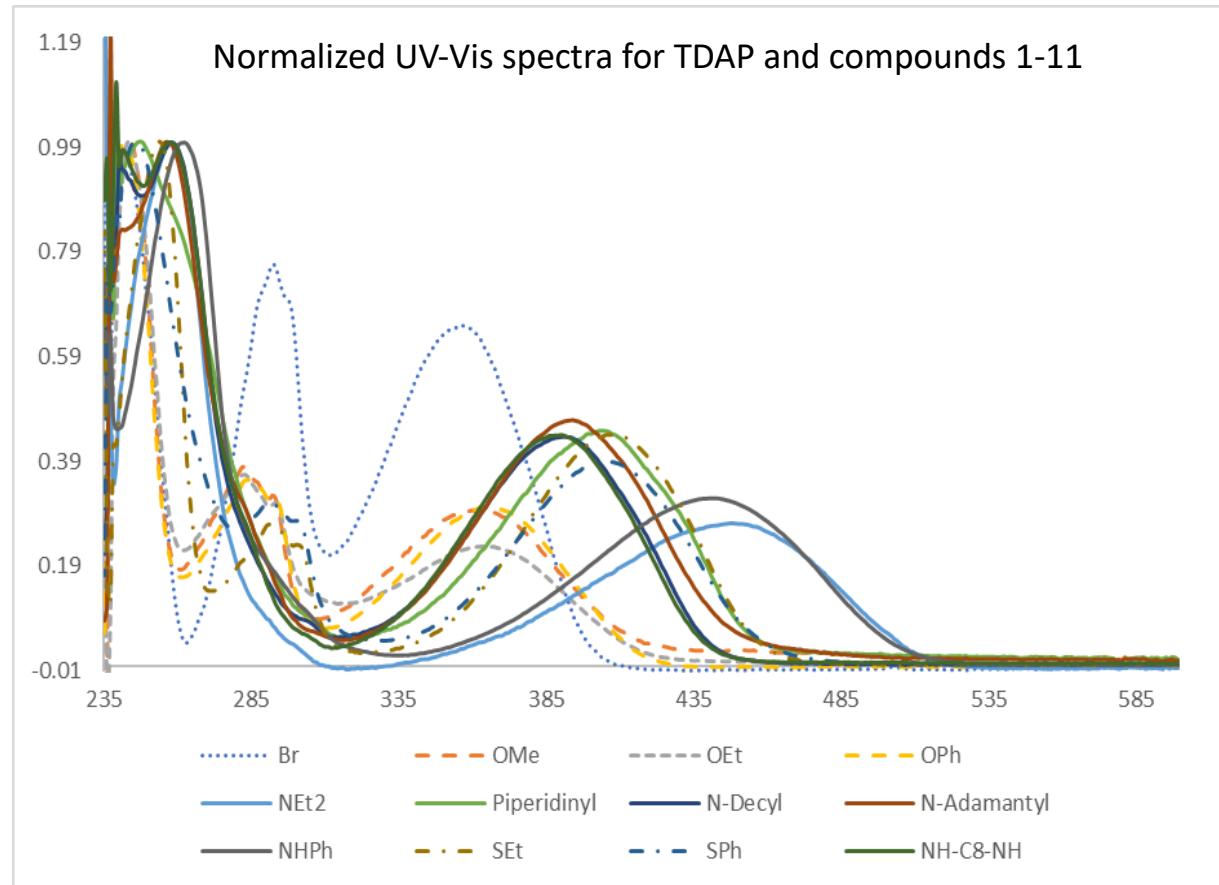
Max. Abs. =	405	nm
$\epsilon =$	10362	M ⁻¹
E _{H-L} (opt) =	2.71 eV	458 nm



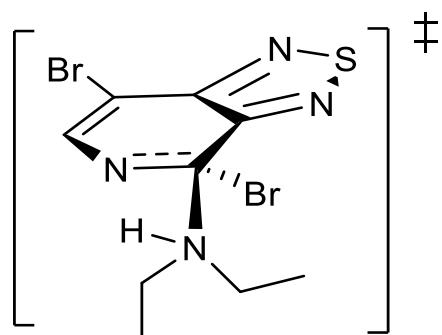
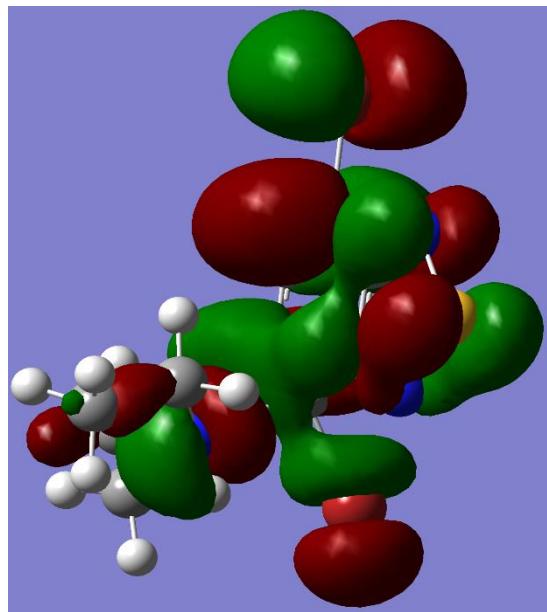
Absorbance	Concentration
0.020366	0.000005
0.030924	0.00001
0.070709	0.000025
0.102543	0.00004
0.373001	0.000115

Max Abs =	390	nm
$\epsilon =$	3246	M ⁻¹
E _{H-L} (opt) =	2.81 eV	442nm



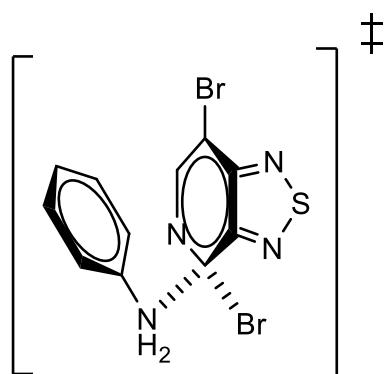
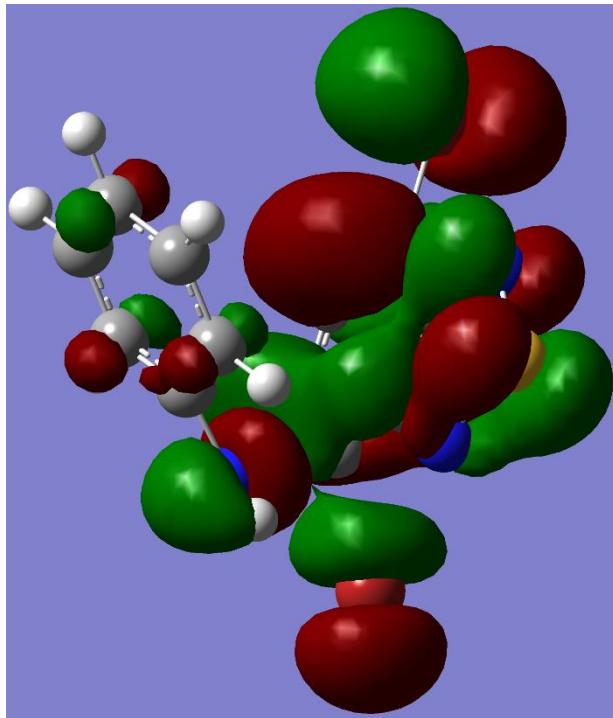


Geometry and electronic structure of the transition states taken into account for the mechanistic study



$$\Delta Q_{\text{thiadiazole}} = -0.105 \text{ au}$$

Nucleophile attack angle: 116.6°



$$\Delta Q_{\text{thiadiazole}} = -0.114 \text{ au}$$

$$\Delta Q_{\text{aniline}} = 0.116 \text{ au}$$

Nucleophilic attack angle: 121.7°

