Electronic Supplementary Information

Small isomeric push-pull chromophores based on thienothiophenes with tuneable optical (non)linearities

Jan Podlesný,[a,b] Oldřich Pytela,[a] Milan Klikar,[a] Veronika Jelínková,[b] Iwan V. Kityk,[c] Katarzyna Ozga,[c] Jaroslaw Jedryka,[c] Myron Rudysh[d,e] and Filip Bureš*[a]

[a.] Institute of Organic Chemistry and Technology, Faculty of Chemical Technology, University of Pardubice, Studentská 573, Pardubice, 53210, Czech Republic

[b.] Institute of Technology and Business in České Budějovice, Okružní 517/10, České Budějovice, 37001, Czech Republic

[c.] Institute of Optoelectronics and Measuring Systems, Faculty of Electrical Engineering, Czestochowa University of Technology, Armii Krajowej 17, Czestochowa, 42-200, Poland

[d.] Institute of Physics, Jan Długosz University, 13/15 Armii Krajowej Str., 42-201, Czestochowa, Poland

[e.] Faculty of Physics, Ivan Franko National University of Lviv, 8 Kyrylo and Mefodiy Str., 79005 Lviv, Ukraine

Email: Filip Bureš - filip.bures@upce.cz

* Corresponding author

Table of contents

Experimental procedures for synthesis of parent thieno[3,2-*b*]thiophene **3** 4

3-Bromothiophene-2-carboxaldehyde **8**[1] 4

Methyl thieno[3,2-*b*]thiophene-2-carboxylate **9**[2] 4

Thieno[3,2-*b*]thiophene-2-carboxylic acid **10**[1] 5

Thieno[3,2-*b*]thiophene **3**[1] 5

Experimental procedures for synthesis of parent thieno[2,3-*b*]thiophene **5** 6

2-(Thiophen-3-yl)-1,3-dioxolane **12**[3] 6

Methyl [3-(dioxolan-2-yl)-thiophen-2-ylthio]acetate **13**[4] 6

Methyl [(3-formylthiophen-2-yl)thio]acetate **14**[4] 7

Methyl thieno[2,3-*b*]thiophene-2-carboxylate **15**[4] 7

Thieno[2,3-*b*]thiophene-2-carboxylic acid **16**[5] 7

Thieno[2,3-*b*]thiophene **5**[6] 8

$^{1}H/^{13}C$ APT NMR and HR-MALDI-MS spectra of chromophore **1a** 9

$^{1}H/^{13}C$ APT NMR and HR-MALDI-MS spectra of chromophore **1b** 11

$^{1}H/^{13}C$ APT NMR and HR-MALDI-MS spectra of chromophore **1c** 13

$^{1}H/^{13}C$ APT NMR and HR-MALDI-MS spectra of chromophore **1d** 15

$^{1}H/^{13}C$ APT NMR and HR-MALDI-MS spectra of chromophore **1e** 17

$^{1}H/^{13}C$ APT NMR and HR-MALDI-MS spectra of chromophore **1f** 19

$^{1}H/^{13}C$ APT NMR and HR-MALDI-MS spectra of chromophore **1g** 21

$^{1}H/^{13}C$ APT NMR and HR-MALDI-MS spectra of chromophore **2a** 23

$^{1}H/^{13}C$ APT NMR and HR-MALDI-MS spectra of chromophore **2b** 25

$^{1}H/^{13}C$ APT NMR and HR-MALDI-MS spectra of chromophore **2c** 27

$^{1}H/^{13}C$ APT NMR and HR-MALDI-MS spectra of chromophore **2d** 29

$^{1}H/^{13}C$ APT NMR and HR-MALDI-MS spectra of chromophore **2e** 31

$^{1}H/^{13}C$ APT NMR and HR-MALDI-MS spectra of chromophore **2f** 33

$^{1}H/^{13}C$ APT NMR and HR-MALDI-MS spectra of chromophore **2g** 35

$^{1}H/^{13}C$ APT NMR spectra of compound **8** 37

$^{1}H/^{13}C$ APT NMR spectra of compound **9** 38

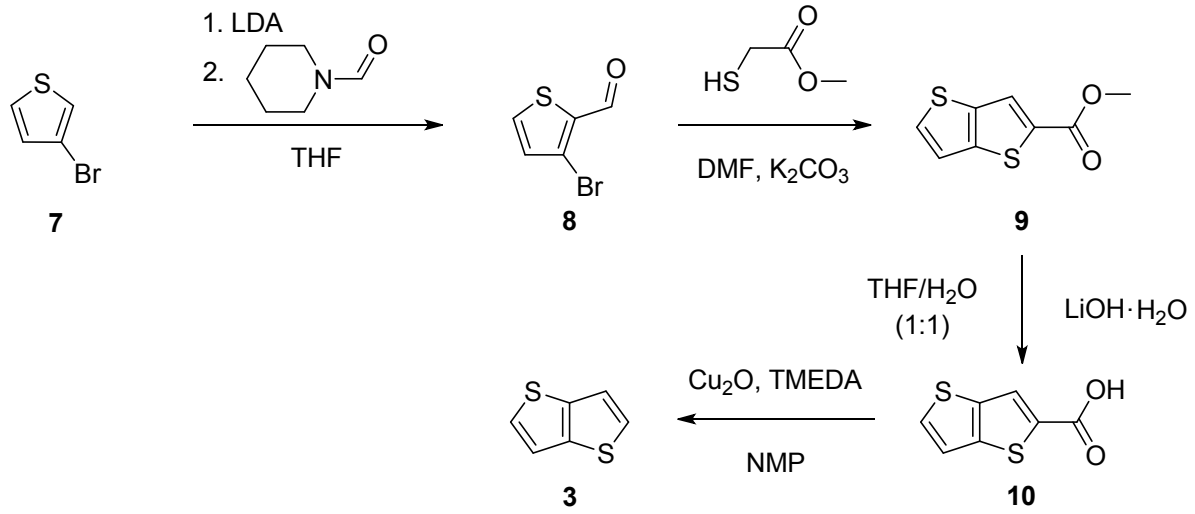
$^{1}H/^{13}C$ APT NMR spectra of compound **10** 39

$^{1}H/^{13}C$ APT NMR spectra of compound **3** 40

$^{1}H/^{13}C$ APT NMR spectra of compound **12** 41

$^{1}H/^{13}C$ APT NMR spectra of compound **13** 42
$^{1}H/^{13}C$ APT NMR spectra of compound **14** 43
$^{1}H/^{13}C$ APT NMR spectra of compound **15** 44
$^{1}H/^{13}C$ APT NMR spectra of compound **16** 45
$^{1}H/^{13}C$ APT NMR spectra of compound **5** 46
UV-VIS absorption spectra 47
HOMO and LUMO visualization created by Gaussian® 16 48
HOMO (up) and LUMO (down) localizations in **1a** 48
HOMO (up) and LUMO (down) localizations in **1b** 48
HOMO (up) and LUMO (down) localizations in **1c** 48
HOMO (up) and LUMO (down) localizations in **1d** 48
HOMO (up) and LUMO (down) localizations in **1e** 49
HOMO (up) and LUMO (down) localizations in **1f** 49
HOMO (up) and LUMO (down) localizations in **1g** 49
HOMO (up) and LUMO (down) localizations in **2a** 49
HOMO (up) and LUMO (down) localizations in **2b** 50
HOMO (up) and LUMO (down) localizations in **2c** 50
HOMO (up) and LUMO (down) localizations in **2d** 50
HOMO (up) and LUMO (down) localizations in **2e** 50
HOMO (up) and LUMO (down) localizations in **2f** 51
HOMO (up) and LUMO (down) localizations in **2g** 51
HOMO and LUMO visualization created by OPChem 8.6 52
Electrochemistry 56
NLO measurements 58

Experimental procedures for synthesis of parent thieno[3,2-*b*]thiophene 3



Scheme 2 Overall synthetic route towards thieno[3,2-*b*]thiophene **3**

3-Bromothiophene-2-carboxaldehyde 8[1]

3-Bromothiophene **7** (1.74 g, 10.67 mmol) was dissolved in dry THF (50 ml) in a flame-dried Schlenk flask. The solution was cooled in an ice bath to 0 °C and bubbled with argon for 5 minutes. LDA (8.1 ml, 16.09 mmol, 2M solution in the mixture of THF/heptane(ethylbenzene)) was added dropwise. The reaction mixture was stirred for 30 minutes at 0 °C, *N*-formylpiperidine (1.33 g, 11.74 mmol) was added and the reaction mixture was stirred for additional 2 hours at 25 °C. Saturated water solution of ammonium chloride (50 ml) was added and the crude product was extracted with diethyl ether (3 × 25 ml). Combined organic extracts were dried with sodium sulphate, filtered and the solvent was evaporated *in vacuo*. The crude product was purified by flash chromatography (silica gel, DCM/hexane, 1:1). Colourless liquid. Yield 1.57 g (77 %). R_f = 0.29 (silica gel, DCM/hexane, 1:1). ^{1}H-NMR (400 MHz, 25 °C, $CDCl_3$): δ = 7.11 (d, 1H, *J* = 4.8 Hz, Th), 7.69 (dd, 1H, *J* = 5.2 Hz, *J* = 1.6 Hz, Th), 9.93 ppm (d, 1H, *J* = 1.6 Hz, CHO). ^{13}C-NMR (100 MHz, 25 °C, $CDCl_3$): δ = 120.44; 132.14; 134.99; 136.99; 183.08 ppm. MS-EI (70 eV): *m/z* = 191 ([(M)$^+$], 100 %), 163 (3), 82 (10), 45 (5), 37 (4).

Methyl thieno[3,2-*b*]thiophene-2-carboxylate 9[2]

3-Bromothiophene-2-carbaldehyde **8** (374 mg, 1.96 mmol), methyl 2-sulphanylacetate (208 mg, 1.96 mmol) and potassium carbonate (366 mg, 2.65 mmol) were dissolved in DMF (100 ml). The reaction mixture was stirred for 3 hours at 25 °C and then poured onto ice. The yellow precipitate was filtered off and washed with water until all yellow impurities were removed. The pure product was dried in the vacuum oven. White solid. Yield 303 mg (78 %). m.p. = 95.7 – 96.9 °C. R_f = 0.49 (silica gel, DCM/hexane, 1:1). ^{1}H-NMR (400 MHz, 25 °C, $CDCl_3$): δ = 3.91 (s, 3H, *O*-CH3), 7.28 (dd, 1H, *J* = 5.2 Hz, *J* = 0.4 Hz, Th), 7.58 (d, 1H, *J* = 5.6 Hz, Th), 7.99

ppm (d, 1H, *J* = 0.4 Hz, Th). ^{13}C-NMR (100 MHz, 25 °C, $CDCl_3$): δ = 52.51; 119.93; 125.96; 131.94; 134.85; 138.96; 144.19; 163.27 ppm. MS-EI (70 eV): *m/z* = 198 ([(M)$^+$], 75 %), 167 (100), 139 (30), 95 (20), 69 (15).

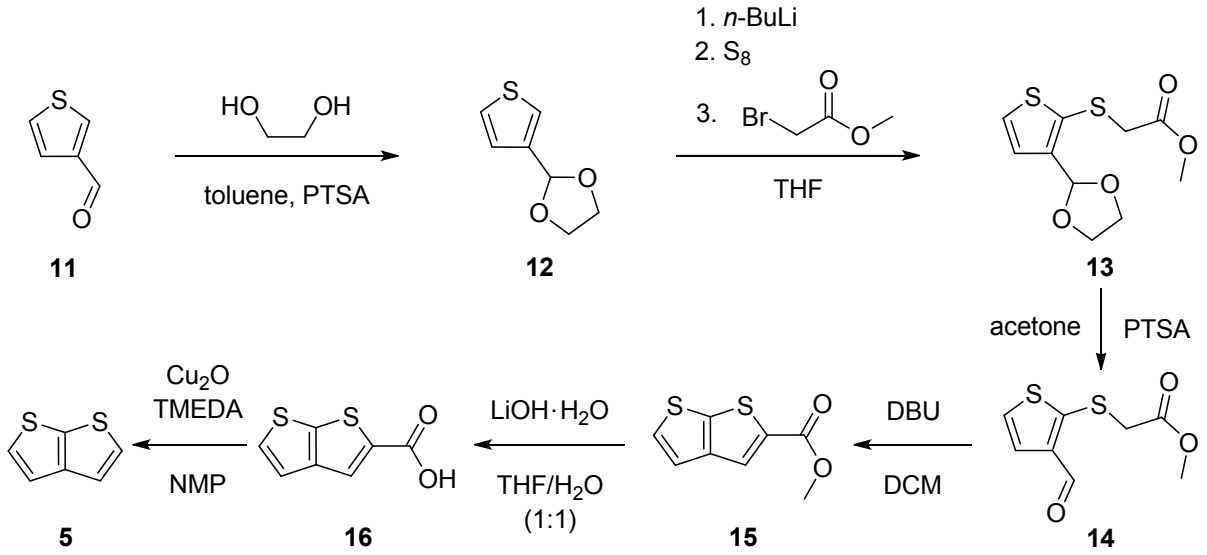
Thieno[3,2-*b*]thiophene-2-carboxylic acid 10[1]

Methyl thieno[3,2-*b*]thiophene-2-carboxylate **9** (197 mg, 0.99 mmol) and lithium hydroxide monohydrate (104 mg, 2.48 mmol) were dissolved in the mixture of THF/water (1:1) and heated to reflux at 100 °C for 4 hours. THF was evaporated *in vacuo* and water phase was washed with diethyl ether (3 × 50 ml). Water phase was cooled in ice bath and the crude product was precipitated with concentrated hydrochloric acid (36%). The white precipitate was filtered off and washed with water. The pure product was dried in vacuum oven. White solid. Yield 181 mg (99 %). m.p. = 220.1 – 222.0 °C. ^{1}H-NMR (400 MHz, 25 °C, d_6-DMSO): δ = 7.56 (d, 1H, *J* = 5.2 Hz, Th), 7.98 (d, 1H, *J* = 5.2 Hz, Th), 8.16 (s, 1H, Th), 13.30 ppm (br s, 1H, COOH). ^{13}C-NMR (100 MHz, 25 °C, *d6*-DMSO): δ = 120.28; 126.09; 132.94; 135.63; 138.55; 143.21; 163.39 ppm.

Thieno[3,2-*b*]thiophene 3[1]

Thieno[3,2-*b*]thiophene-2-carboxylic acid **10** (72 mg, 0.39 mmol) was dissolved in *N*-methylpyrrolidone (50 ml). Copper(I) oxide (56 mg, 0.39 mmol) and *N*,*N*,*N*'*N*'-tetramethylethylenediamine (5 mg, 0.04 mmol) were added and the reaction mixture was heated to reflux at 220 °C for 1 hour. After cooling to 25 °C, diethyl ether (25 ml) and diluted hydrochloric acid (25 ml, 1M) were added. The crude product was extracted with diethyl ether (3 × 25 ml). The combined organic extracts were dried with sodium sulphate, filtered and the solvent was evaporated *in vacuo*. The crude product was purified by flash chromatography (silica gel, hexane). White solid. Yield 48 mg (87 %). m.p. = 53.8 °C. R_f = 0.36 (silica gel, hexane). ^{1}H-NMR (500 MHz, 25 °C, $CDCl_3$): δ = 7.28 (d, 2H, *J* = 4.5 Hz, Th), 7.40 ppm (d, 2H, *J* = 5.0 Hz, Th). ^{13}C-NMR (125 MHz, 25 °C,$CDCl_3$): δ = 119.52; 127.50; 139.56 ppm. MS-EI (70 eV): *m/z* = 140 ([(M)$^+$], 100 %), 96 (25), 69 (20), 45 (10).

Experimental procedures for synthesis of parent thieno[2,3-*b*]thiophene 5



Scheme 3 Overall synthetic route towards thieno[2,3-*b*]thiophene **5**

2-(Thiophen-3-yl)-1,3-dioxolane 12[3]

Thiophene-3-carboxaldehyde **11** (1.28 g, 11.41 mmol) ethylene glycol (3.54 g, 57.07 mmol) and 4-methylbenzenesulphonic acid monohydrate (22 mg, 0.12 mmol) were dissolved in toluene (100 ml). The reaction mixture was heated to reflux at 165 °C for 6 hours and the resulting water was removed by Dean-Stark apparatus. After cooling to 25 °C, the reaction mixture was washed with saturated solution of sodium bicarbonate (3 × 50 ml). The organic phase was dried with sodium sulphate, filtered and the solvent was evaporated *in vacuo*. The crude product was purified by flash chromatography (silica gel, DCM/hexane, 1:1). Yellow liquid. Yield 1.76 g (99 %). R_f = 0.20 (silica gel, DCM/hexane, 1:1). ^{1}H-NMR (400 MHz, 25 °C, $CDCl_3$): δ = 3.92 – 3.98 (m, 2H, *O*-CH_2), 4.00 – 4.06 (m, 2H, *O*-CH_2), 5.88 (s, 1H, *O*-CH), 7.2 (dd, 1H, *J* = 5.2 Hz, *J* = 1.2 Hz, Th), 7.29 (dd, 1H, *J* = 5.2 Hz, *J* = 3.2 Hz, Th), 7.41 ppm (d, 1H, *J* = 2.8 Hz, Th). ^{13}C-NMR (100 MHz, 25 °C, $CDCl_3$): δ = 64.85; 100.20; 123.47; 125.49; 126.09; 139.96 ppm. MS-EI (70 eV): *m/z* = 155 ([$(M)^+$], 100 %), 111 (90), 97 (50), 84 (75), 73 (20).

Methyl [3-(dioxolan-2-yl)-thiophen-2-ylthio]acetate 13[4]

2-(Thiophen-3-yl)-1,3-dioxolane **12** (1.13 g, 7.26 mmol) was dissolved in dry THF (100 ml) in a flame-dried Schlenk flask. The solution was cooled to –20 °C and bubbled with argon for 5 minutes. *n*-Butyllithium (3.1 mml, 7.62 mmol, 2.5M solution in hexane) was added dropwise and the reaction mixture was stirred at –20 °C for 30 minutes. Elementary sulphur (233 mg, 7.26 mmol) was added in small portions and the reaction mixture was stirred at 25 °C for 1 hour. Methyl 2-bromoacetate (1.11 g, 7.26 mmol) was added and the reaction mixture was stirred at 25 °C for 2 hours. Saturated solution of ammonium chloride (50 ml) was added and the crude product was extracted with diethyl ether (3 × 25 ml). The combined organic extracts

were dried with sodium sulphate, filtered and the solvent was evaporated *in vacuo*. The crude product was purified by column chromatography (silica gel, diethyl ether/hexane, 1:1). Yellow liquid. Yield 680 mg (36 %). R_f = 0.20 (silica gel, diethyl ether/hexane, 1:1). ^{1}H-NMR (400 MHz, 25 °C, $CDCl_3$): δ = 3,51 (s, 2H, *S*-CH_2), 3,66 (d, 3H, *O*-CH_3), 3.98 – 4.02 (m, 2H, *O*-CH_2), 4.06 – 4.14 (m, 2H, *O*-CH_2), 6.03 (s, 1H, *O*-CH), 7.11 (d, 1H, *J* = 5.6 Hz, Th), 7.32 ppm (d, 1H, *J* = 5.6 Hz, Th). ^{13}C-NMR (100 MHz, 25 °C,$CDCl_3$): δ = 40.89; 52.59; 65.47; 99.07; 126.72; 129.70; 131.62; 144.24; 169.61 ppm. MS-EI (70 eV): *m/z* = 260 ([(M)$^+$], 17 %), 187 (100), 157 (40), 143 (35), 129 (15), 115 (10), 73 (15), 45 (20).

Methyl [(3-formylthiophen-2-yl)thio]acetate 14[4]

Methyl [3-(dioxolan-2-yl)-thiophen-2-ylthio]acetate **13** (200 mg, 0.77 mmol) and 4-methylbenzenesulphonic acid monohydrate (220 mg, 1.16 mmol) were dissolved in acetone (50 ml). The reaction mixture was stirred at 25 °C for 1 hour. The solvent was evaporated *in vacuo* and the crude product was extracted with diethyl ether (3 × 25 ml). The combined organic extracts were dried with sodium sulphate, filtered and the solvent was evaporated *in vacuo*. The crude product was purified by column chromatography (silica gel, diethyl ether/hexane, 1:1). White solid. Yield 123 mg (74 %). m.p. = 53.5 – 55.7 °C. R_f = 0.25 (silica gel, diethyl ether/hexane, 1:1). ^{1}H-NMR (400 MHz, 25 °C, $CDCl_3$): δ = 3.63 (s, 2H, *S*-CH_2), 3.66 (s, 3H, *O*-CH_3), 7.29 (d, 1H, *J* = 5.6 Hz, Th), 7.39 (d, 1H, *J* = 5.6 Hz, Th), 10.06 ppm (s, 1H, CHO). ^{13}C-NMR (100 MHz, 25 °C, $CDCl_3$): δ = 39.86; 52.87; 12.33; 128.33; 141.90; 145.85; 168.83; 184.88 ppm. MS-EI (70 eV): *m/z* = 216 ([(M)$^+$], 20 %), 184 (25), 157 (20), 143 (100), 129 (5), 111 (40), 85 (15), 71 (20), 45 (15).

Methyl thieno[2,3-*b*]thiophene-2-carboxylate 15[4]

Methyl [(3-formylthiophen-2-yl)thio]acetate **14** (158 mg, 0.73 mmol and DBU (11 mg, 0.07 mmol) were dissolved in DCM (25 ml). The reaction mixture was immediately cooled to 0 °C and stirred for 30 minutes. The solution was washed with water (3 × 25 ml) and the organic phase was dried with sodium sulphate, filtered and the solvent was evaporated *in vacuo*. The crude product was purified by column chromatography (silica gel, diethyl ether/hexane, 1:1). White solid. Yield 91 mg (63 %). m.p. = 105.4 – 107.1 °C. R_f = 0.47 (silica gel, diethyl ether/hexane, 1:1). ^{1}H-NMR (400 MHz, 25 °C, $CDCl_3$): δ = 3.91 (s, 3H, *O*-CH_3), 7.26 (d, 1H, *J* = 5.2 Hz, Th), 7.40 (d, 1H, *J* = 5.2 Hz, Th), 7.94 ppm (s, 1H, Th). ^{13}C-NMR (125 MHz, 25 °C, $CDCl_3$): δ = 52.55; 120.81; 126.33; 129.51; 136.09; 143.45; 146.29; 163.00 ppm. MS-EI (70 eV): *m/z* = 198 ([(M)$^+$], 50 %), 167 (100), 139 (25), 95 (20), 69 (18).

Thieno[2,3-*b*]thiophene-2-carboxylic acid 16[5]

Methyl thieno[2,3-*b*]thiophene-2-carboxylate **15** (49 mg, 0.25 mmol) and lithium hydroxide monohydrate (26 mg, 0.62 mmol) were dissolved in the mixture of THF/water (25 ml, 1:1).

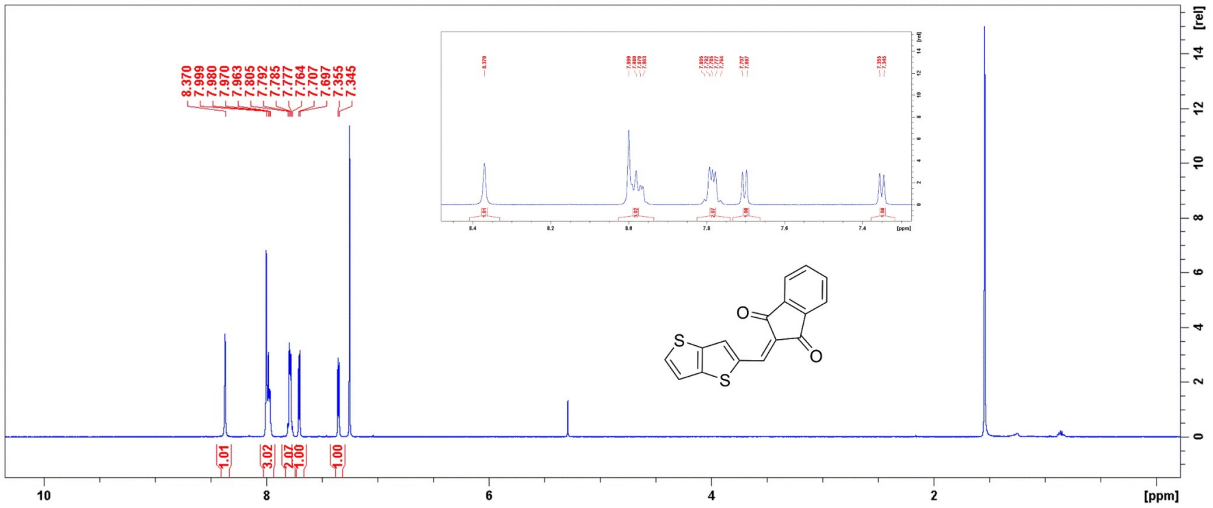
The reaction mixture was heated at 100 °C for 4 hours. THF was evaporated *in vacuo* and the water solution was washed with diethyl ether (3 × 25 ml). The water phase was cooled in ice bath and the product was precipitated with concentrated hydrochloric acid (36%). The white precipitate was filtered off and washed with water. The pure product was dried in vacuum oven. White solid. Yield 42 mg (92 %). m.p. = 243.1 – 245.7 °C. R_f = 0.47 (silica gel, diethyl ether/hexane, 1:1). ^{1}H-NMR (400 MHz, 25 °C, d_6-DMSO): δ= 7.43 (d, 1H, *J* = 5.2 Hz, Th), 7.45 (d, 1H, *J* = 5.2 Hz, Th), 8.00 (s, 1H, Th), 13.30 ppm (br s, 1H, COOH). ^{13}C- NMR (100 MHz, 25 °C, d_6-DMSO): δ = 120.82; 125.80; 130.87; 137.40; 142.30; 146.13; 163.22 ppm.

Thieno[2,3-*b*]thiophene 5[6]

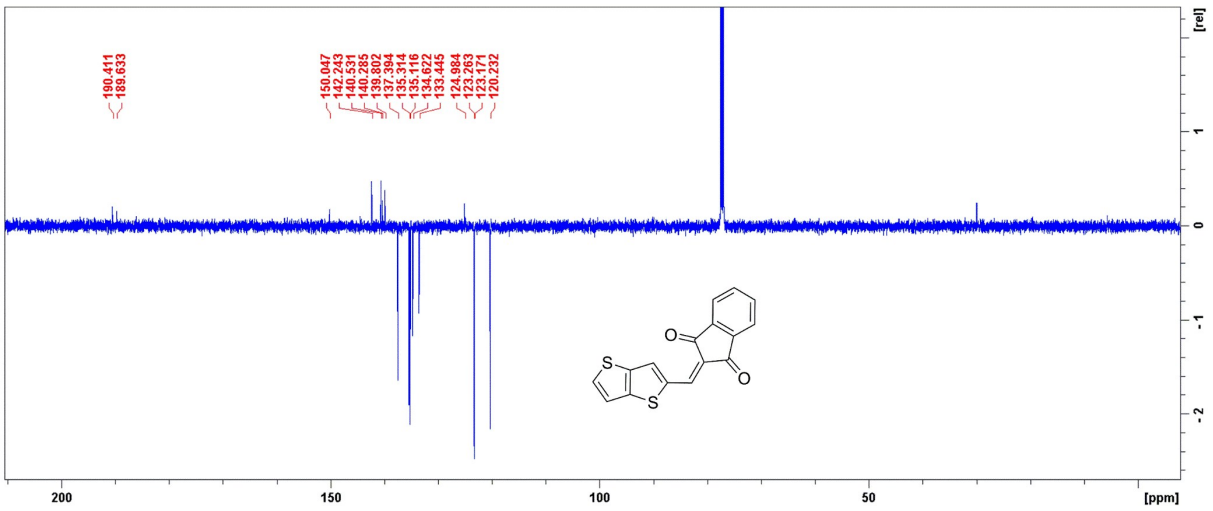
Thieno[2,3-*b*]thiophene-2-carboxylic acid **16** (213 mg, 1.16 mmol) was dissolved in *N*-methylpyrrolidone (25 ml). Copper(I) oxide (166 mg, 1.16 mmol) and *N*,*N*,*N*'*N*'-tetramethylethylenediamine (13 mg, 0.12 mmol) were added and the reaction mixture was heated to reflux at 220 °C for 1 hour. After cooling to 25 °C, the reaction mixture was diluted with diethyl ether (20 ml) and diluted hydrochloric acid (25 ml, 1M) was added. The crude product was extracted with diethyl ether (3 × 25 ml) and the combined organic extracts were dried with sodium sulphate, filtered and the solvent was evaporated *in vacuo*. The crude product was purified by flash chromatography (silica gel, hexane). Colourless liquid. Yield 133 mg (82 %). R_f = 0.37 (silica gel, hexane). ^{1}H-NMR (500 MHz, 25 °C, $CDCl_3$): δ= 7.23 (d, 2H, *J* = 5.5 Hz, Th), 7.35 ppm (d, 2H, *J* = 5.0 Hz, Th). ^{13}C- NMR (125 MHz, 25 °C,$CDCl_3$): δ = 119.98; 128.37; 137.46 147.18 ppm. MS-EI (70 eV): *m/z* = 140 ([(M)$^+$], 100 %), 96 (20), 69 (15), 63 (8), 45 (8).

$^{1}H/^{13}C$ APT NMR and HR-MALDI-MS spectra of chromophore 1a

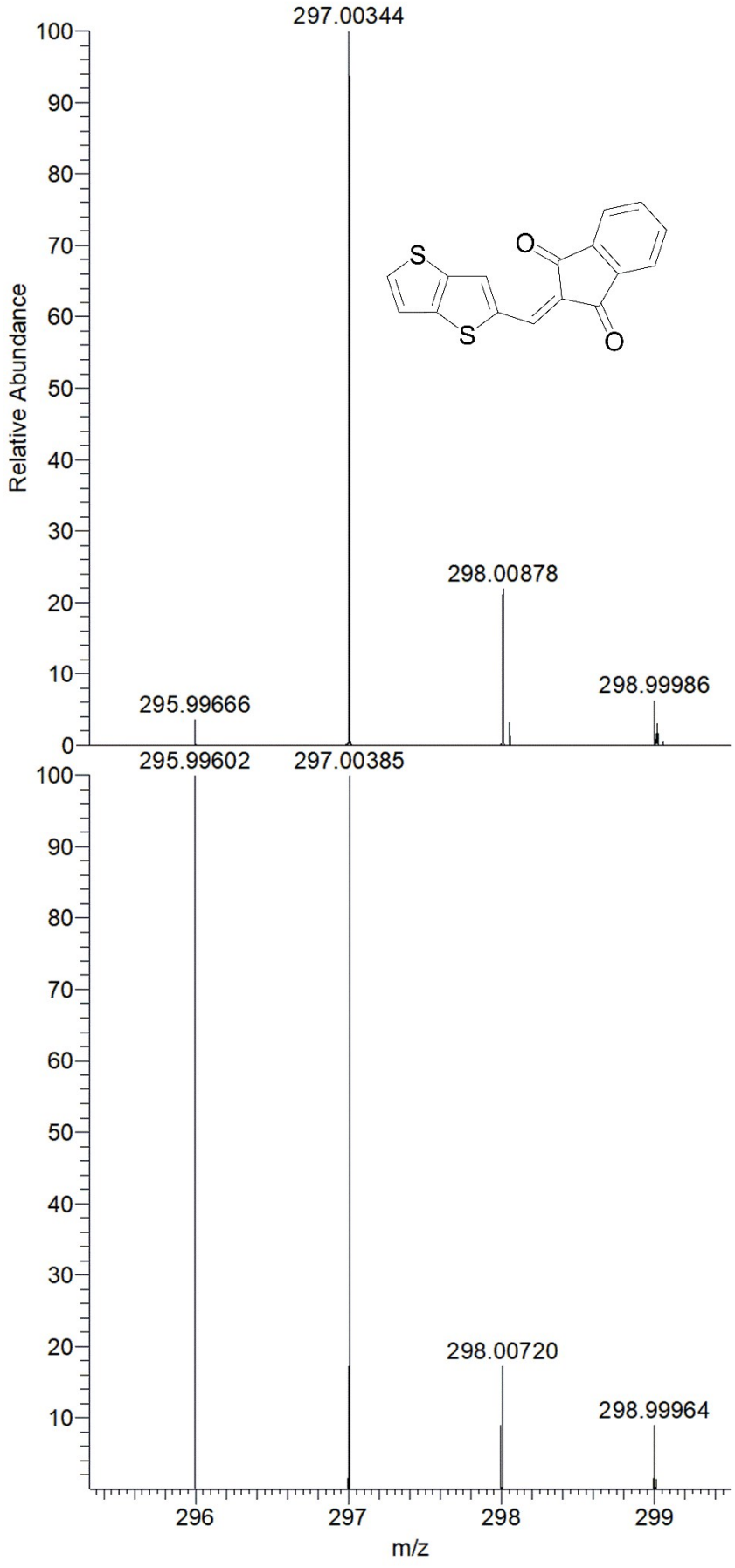
^{1}H NMR spectrum (500 MHz, 25 °C, $CDCl_3$) of **1a**



^{13}C APT NMR spectrum (125 MHz, 25 °C, $CDCl_3$) of **1a**

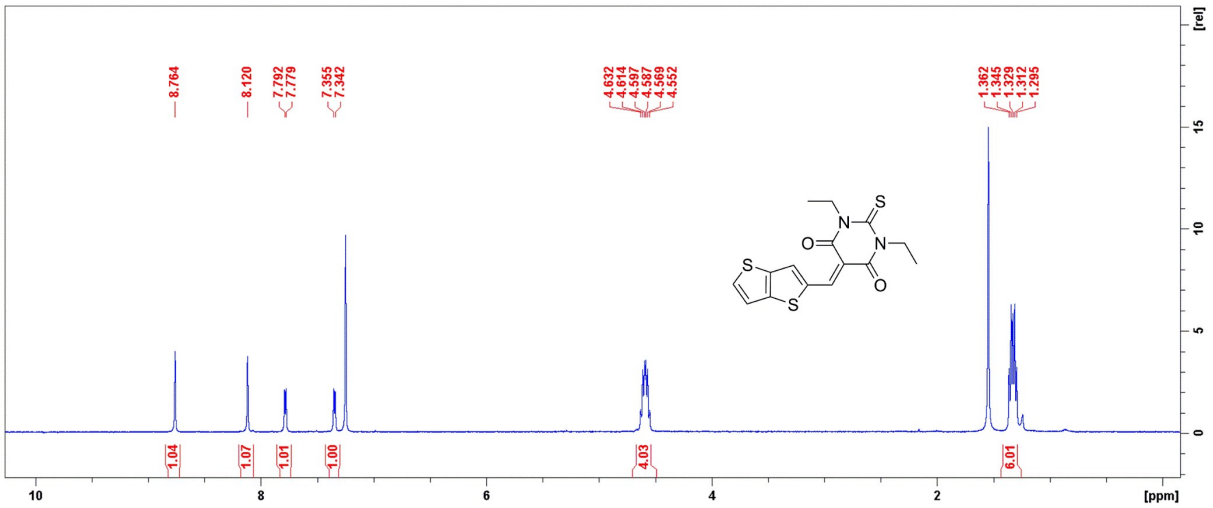


Experimental (up) and calculated (down) MALDI spectra of **1a**

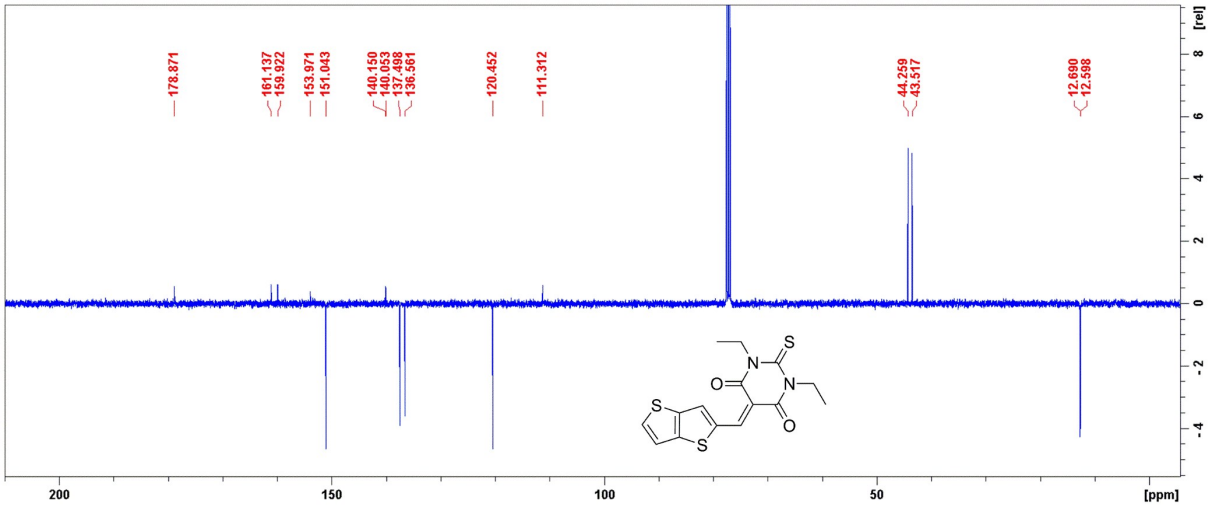


$^{1}H/^{13}C$ APT NMR and HR-MALDI-MS spectra of chromophore 1b

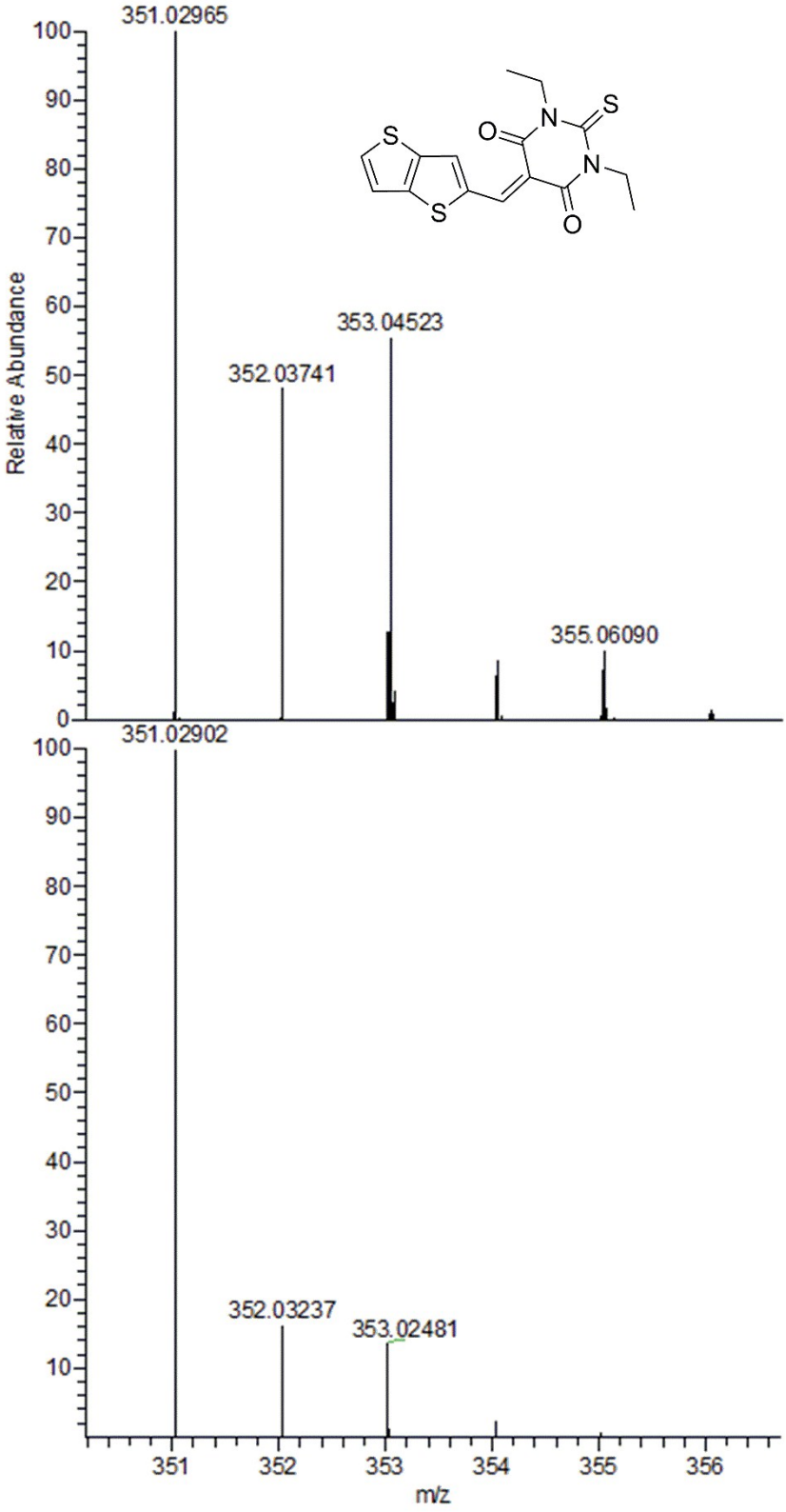
^{1}H NMR spectrum (400 MHz, 25 °C, $CDCl_3$) of **1b**



^{13}C APT NMR spectrum (100 MHz, 25 °C, $CDCl_3$) of **1b**

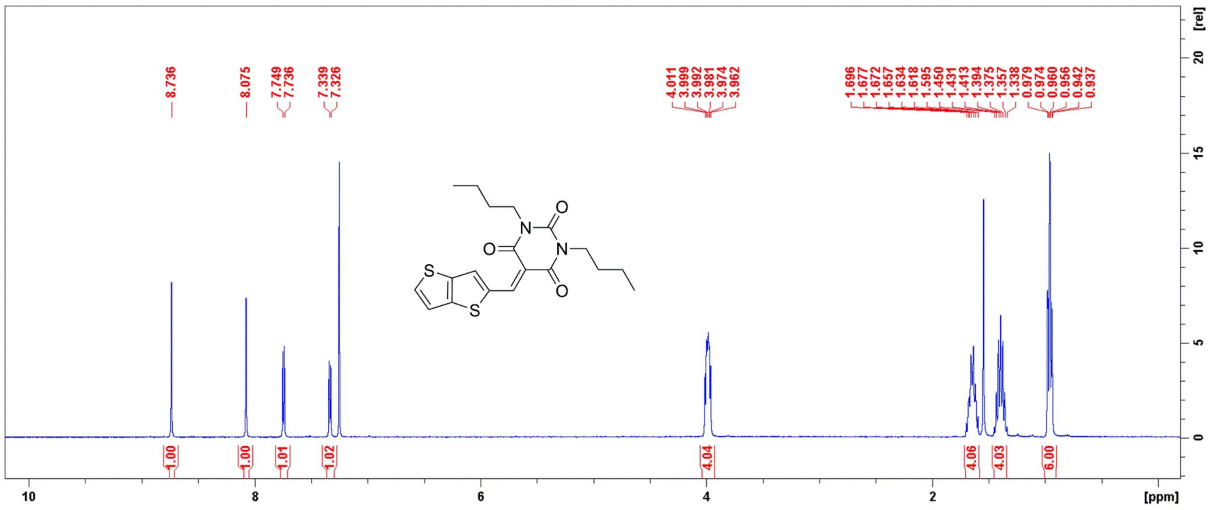


Experimental (up) and calculated (down) MALDI spectra of **1b**

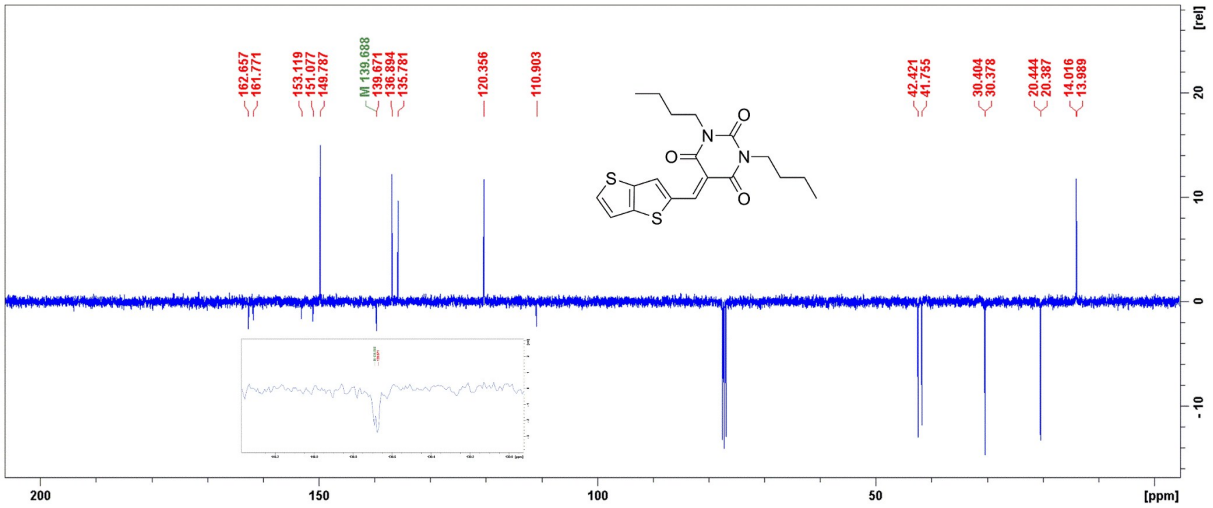


$^{1}H/^{13}C$ APT NMR and HR-MALDI-MS spectra of chromophore 1c

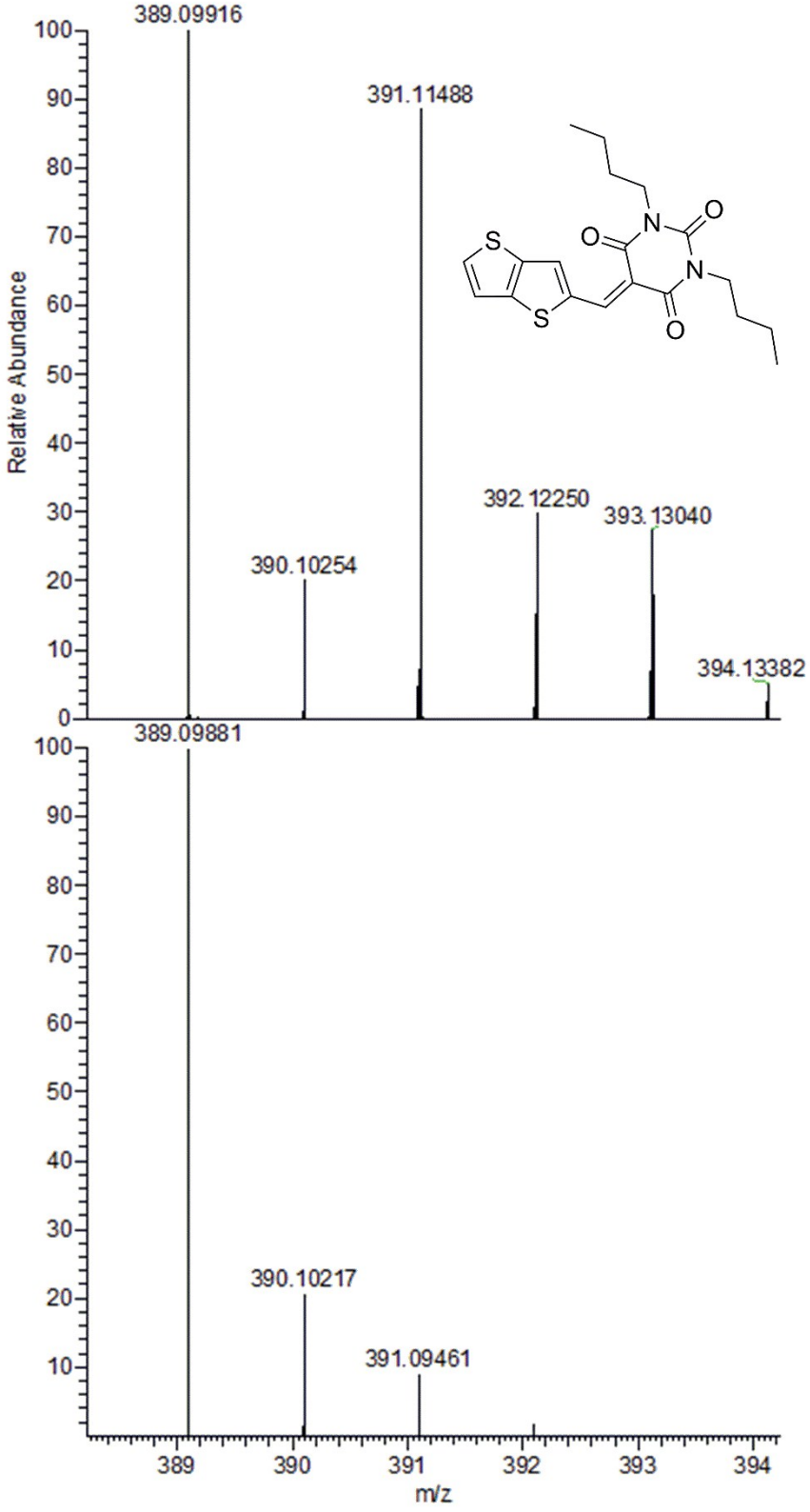
^{1}H NMR spectrum (400 MHz, 25 °C, $CDCl_3$) of **1c**



^{13}C APT NMR spectrum (100 MHz, 25 °C, $CDCl_3$) of **1c**

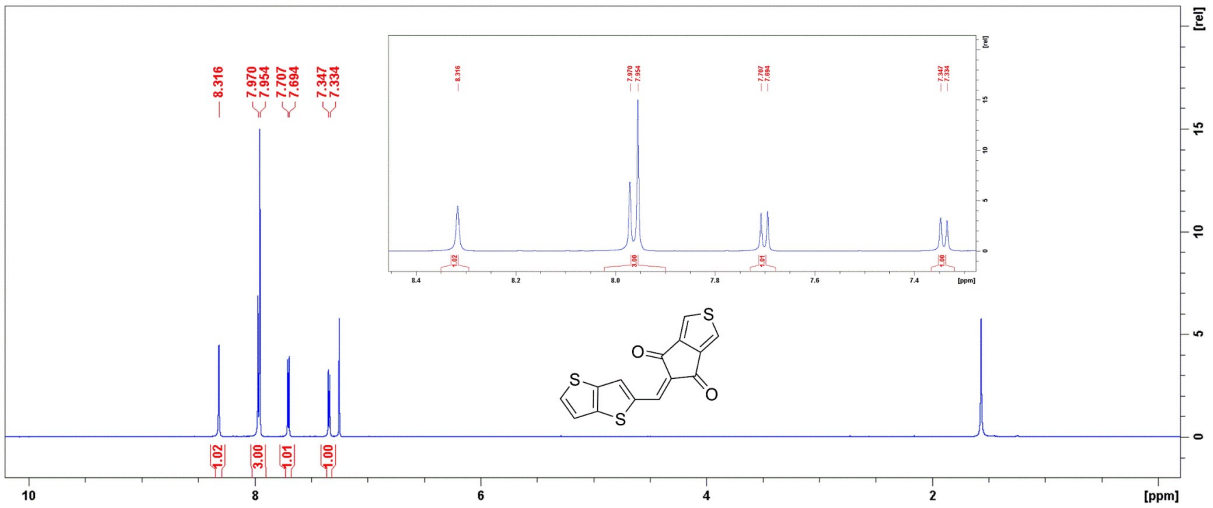


Experimental (up) and calculated (down) MALDI spectra of **1c**

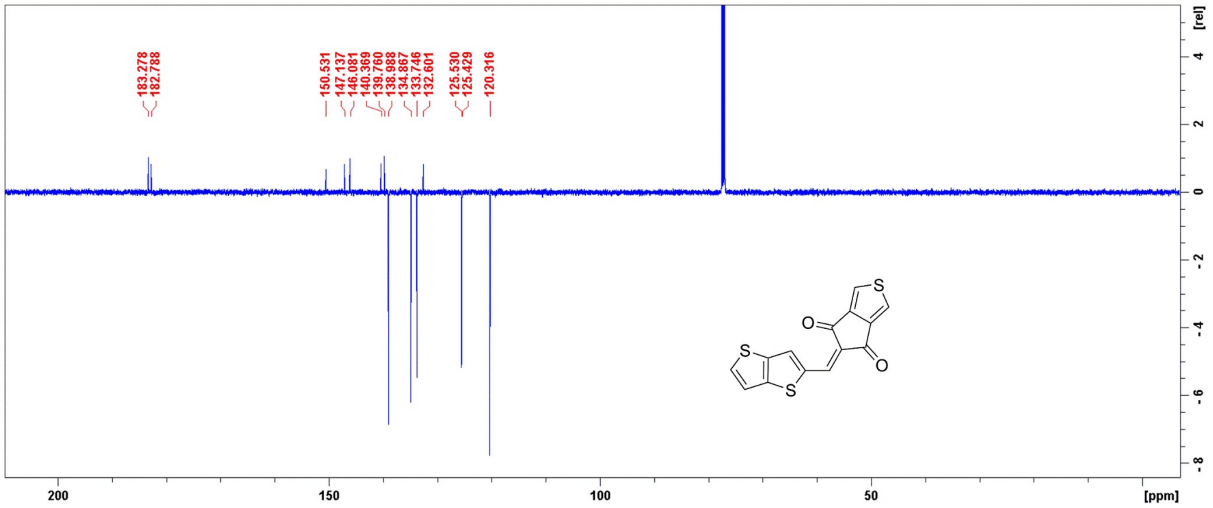


$^{1}H/^{13}C$ APT NMR and HR-MALDI-MS spectra of chromophore 1d

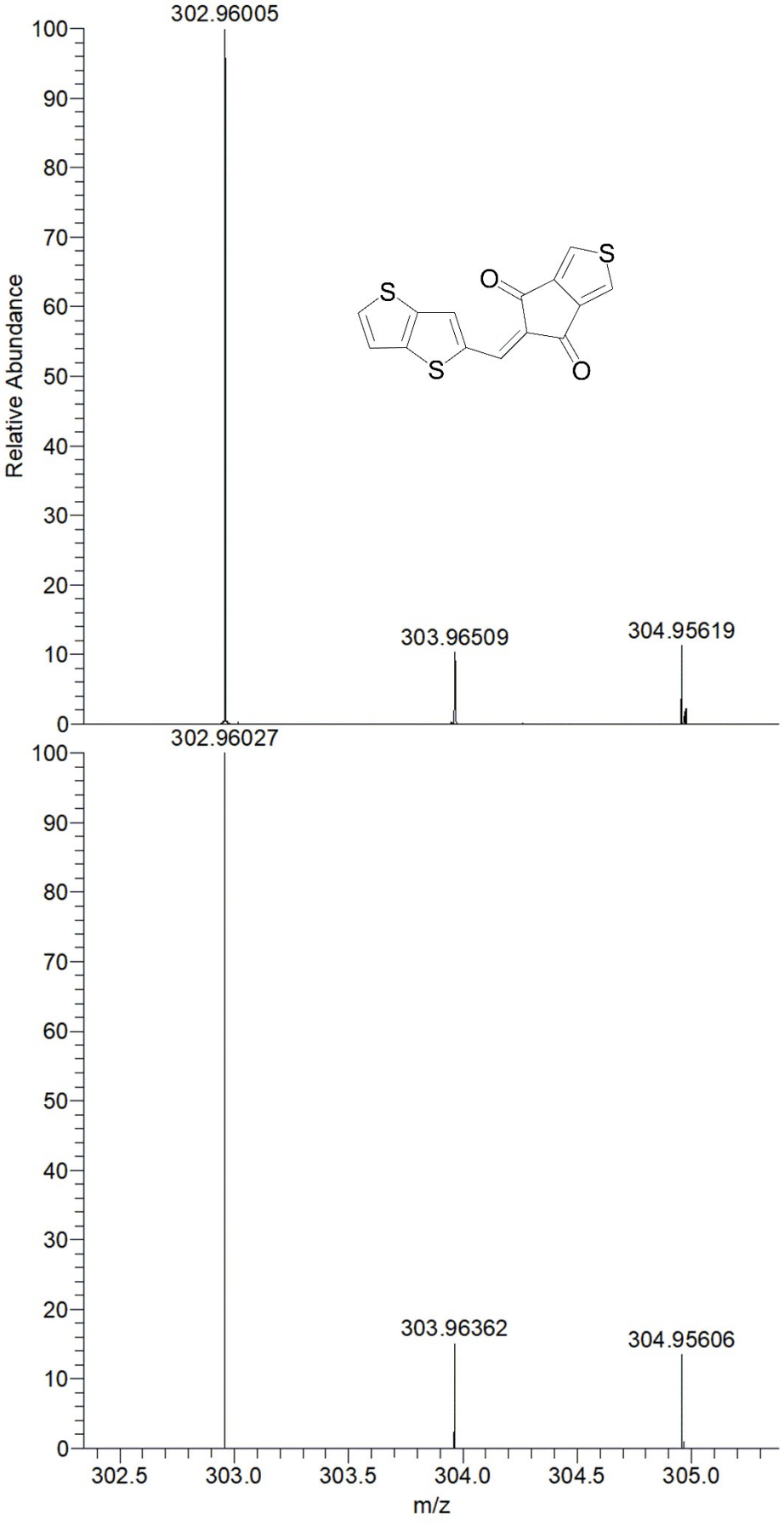
^{1}H NMR spectrum (400 MHz, 25 °C, $CDCl_3$) of **1d**



^{13}C APT NMR spectrum (125 MHz, 25 °C, $CDCl_3$) of **1d**

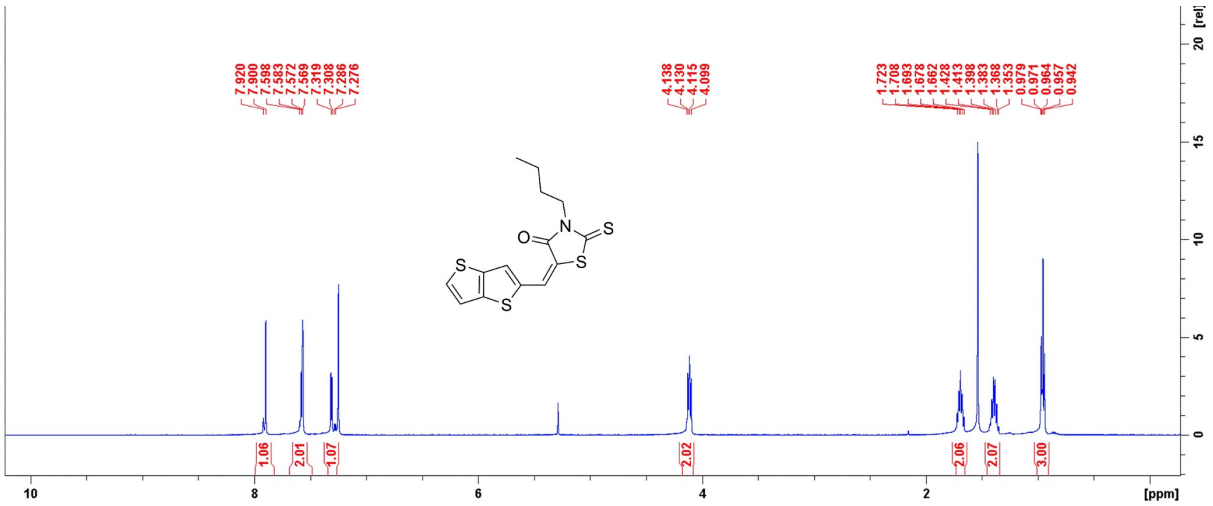


Experimental (up) and calculated (down) MALDI spectra of **1d**

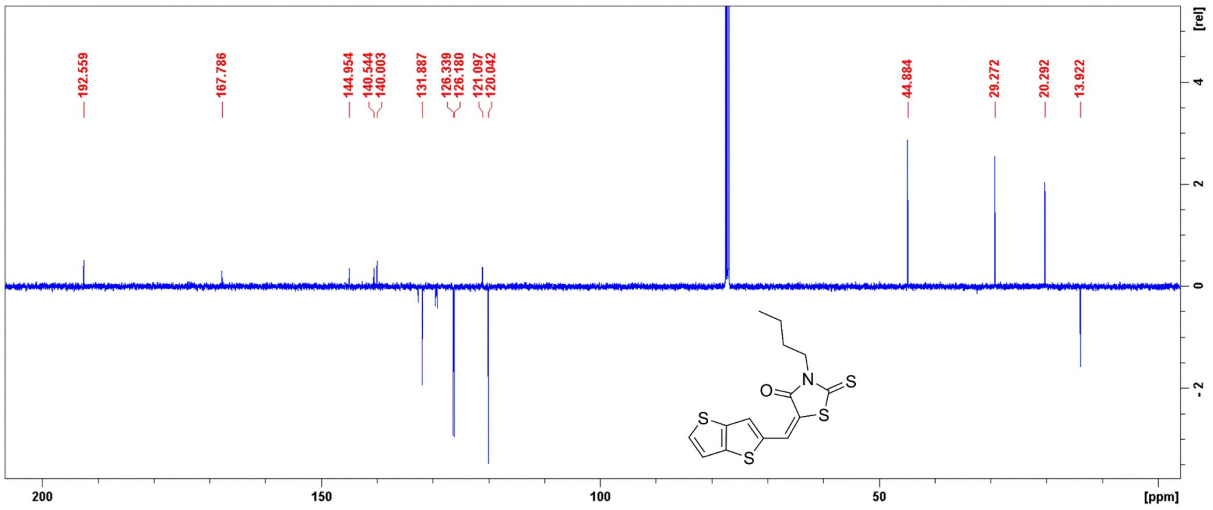


$^{1}H/^{13}C$ APT NMR and HR-MALDI-MS spectra of chromophore 1e

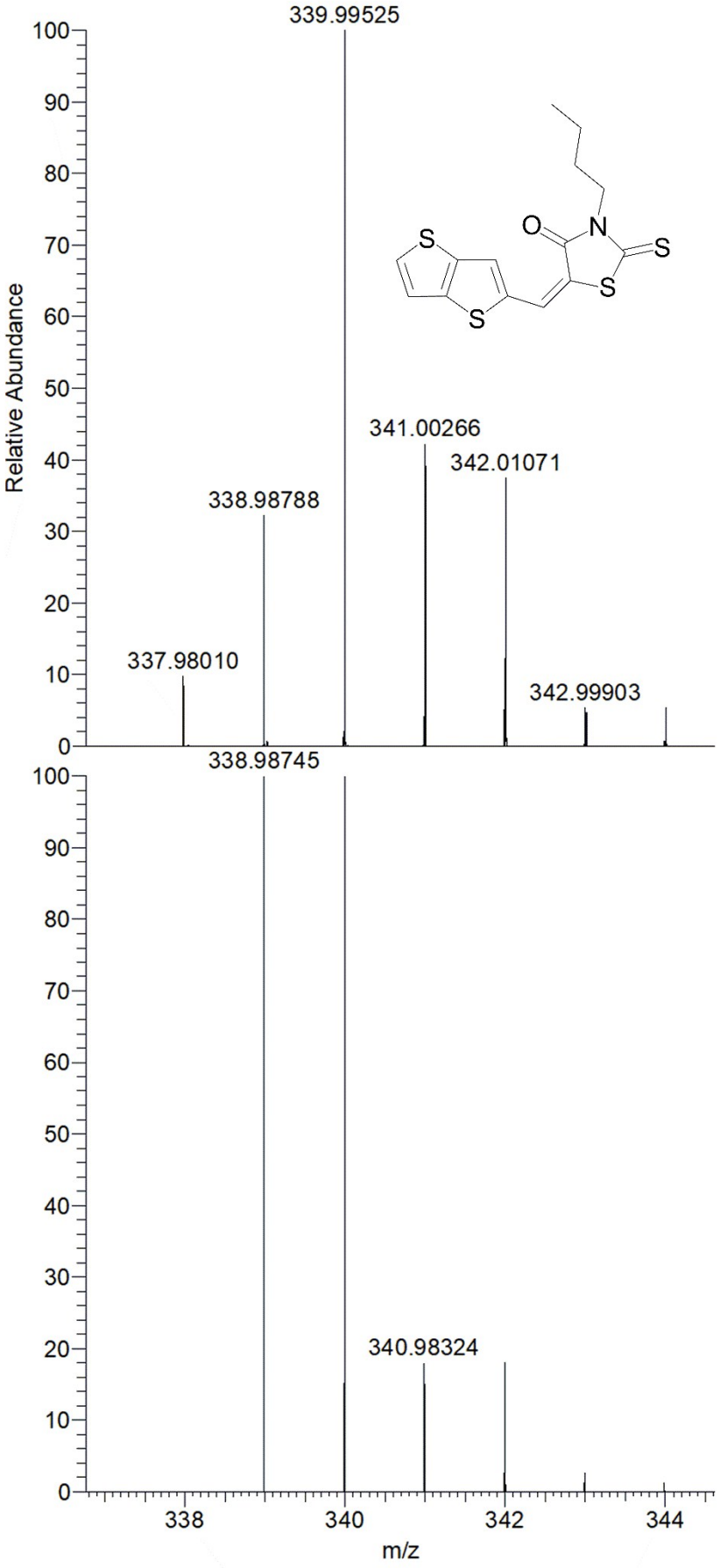
^{1}H NMR spectrum (500 MHz, 25 °C, $CDCl_3$) of **1e**



^{13}C APT NMR spectrum (125 MHz, 25 °C, $CDCl_3$) of **1e**

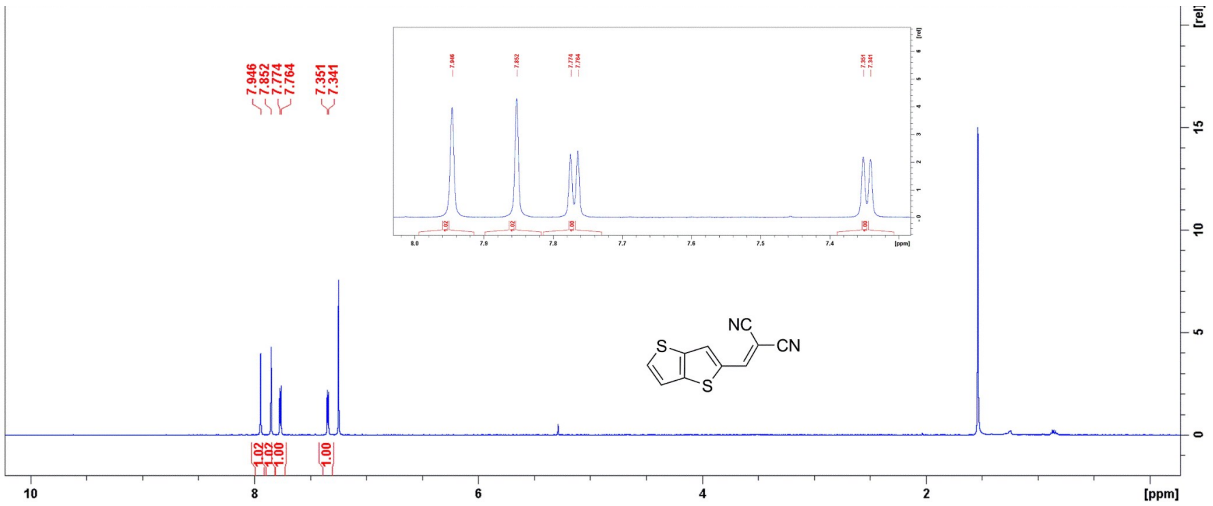


Experimental (up) and calculated (down) MALDI spectra of **1e**

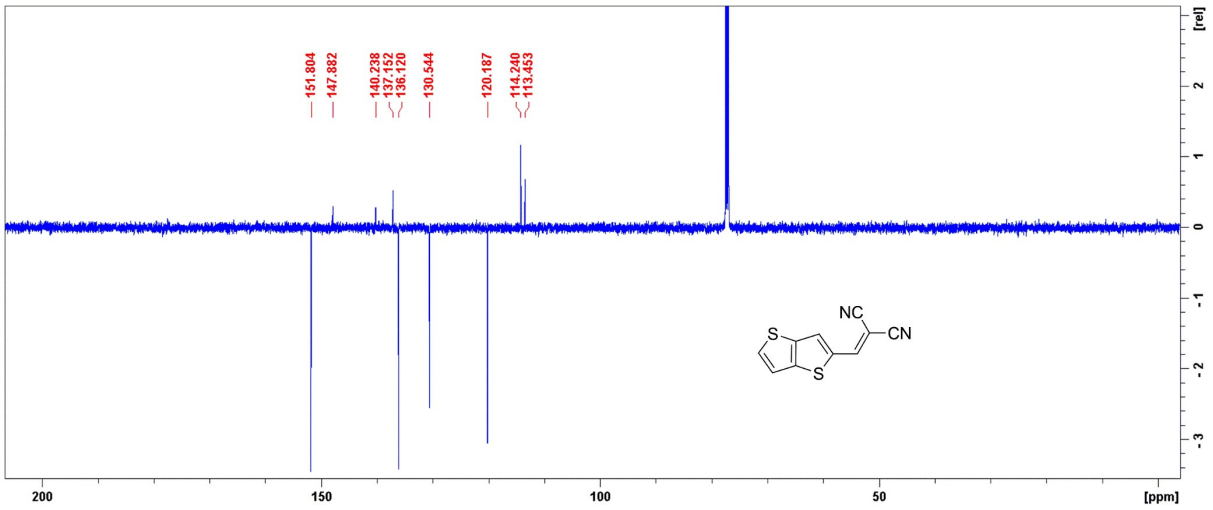


$^{1}H/^{13}C$ APT NMR and HR-MALDI-MS spectra of chromophore 1f

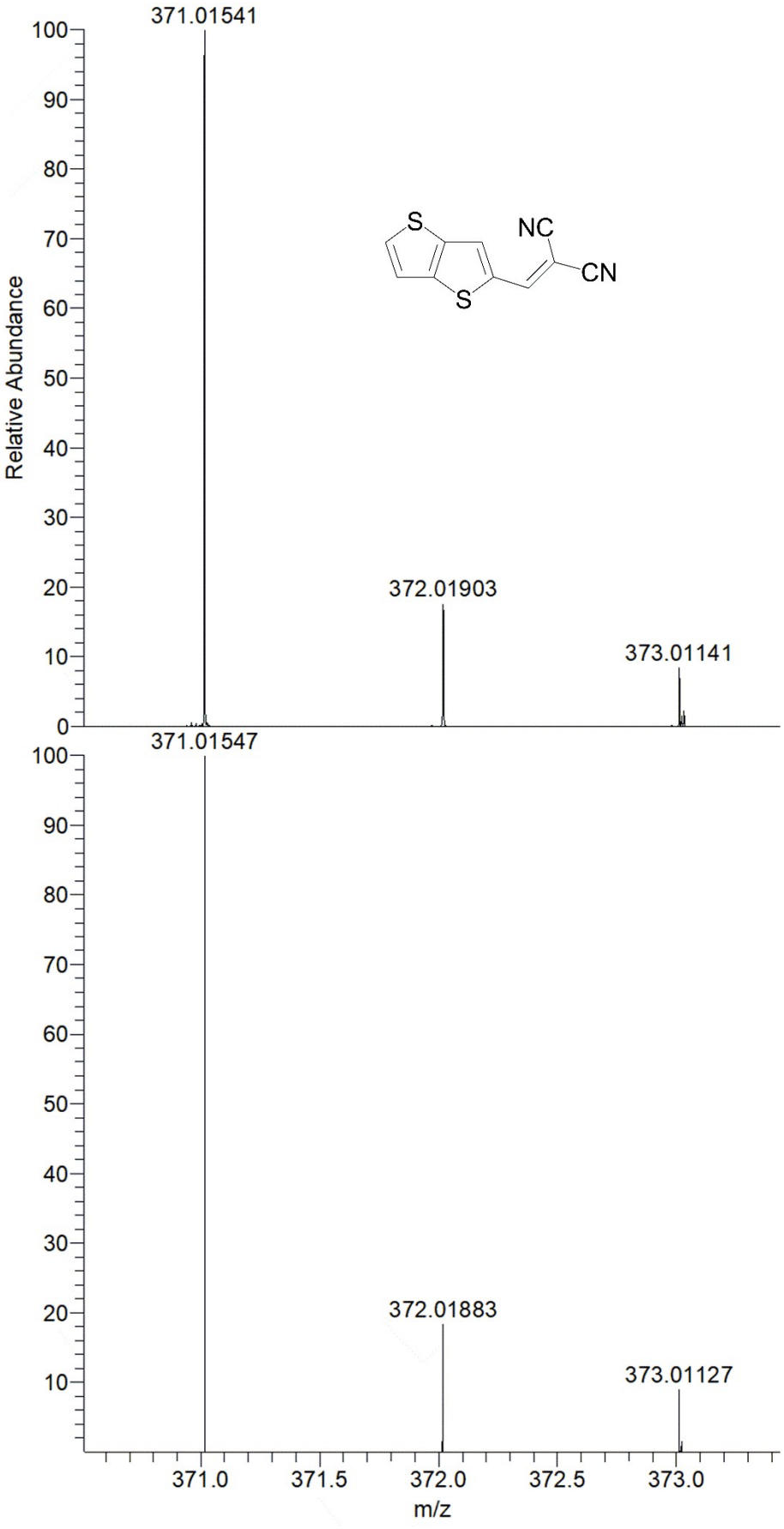
^{1}H NMR spectrum (500 MHz, 25 °C, $CDCl_3$) of **1f**



^{13}C APT NMR spectrum (125 MHz, 25 °C, $CDCl_3$) of **1f**

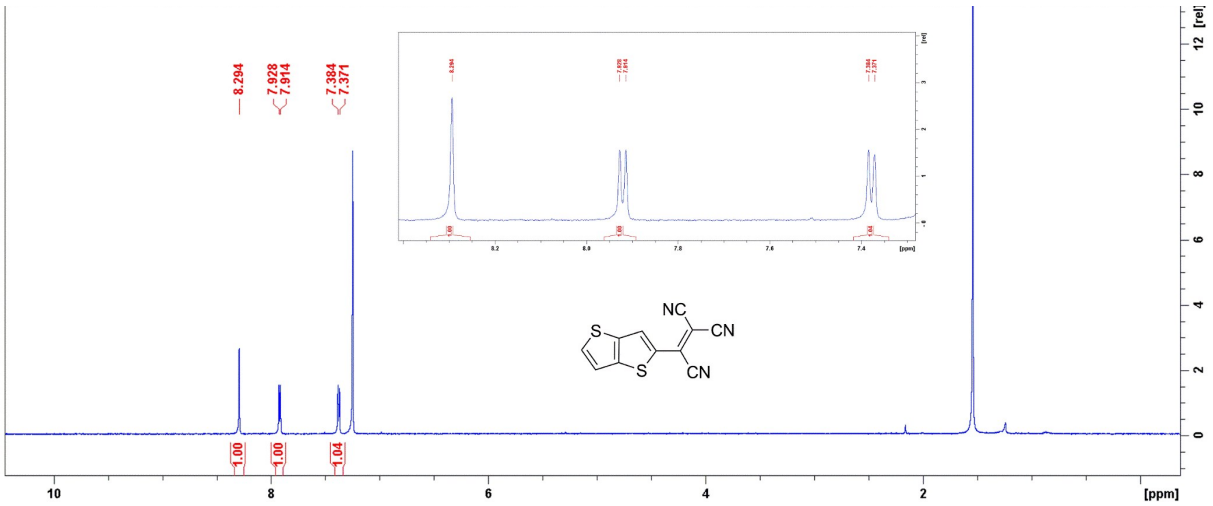


Experimental (up) and calculated (down) MALDI spectra of **1f**

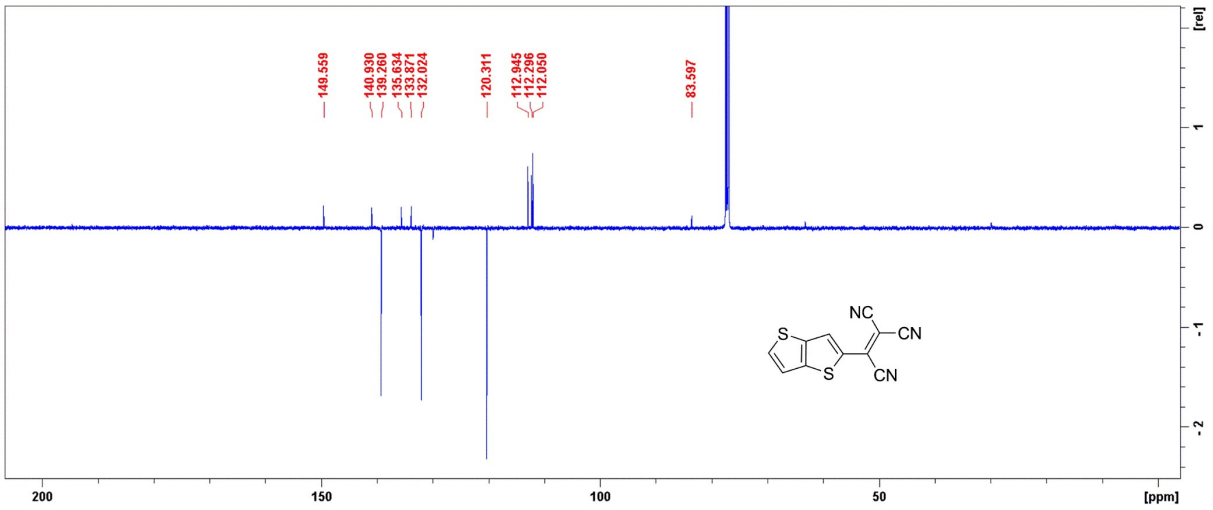


$^{1}H/^{13}C$ APT NMR and HR-MALDI-MS spectra of chromophore 1g

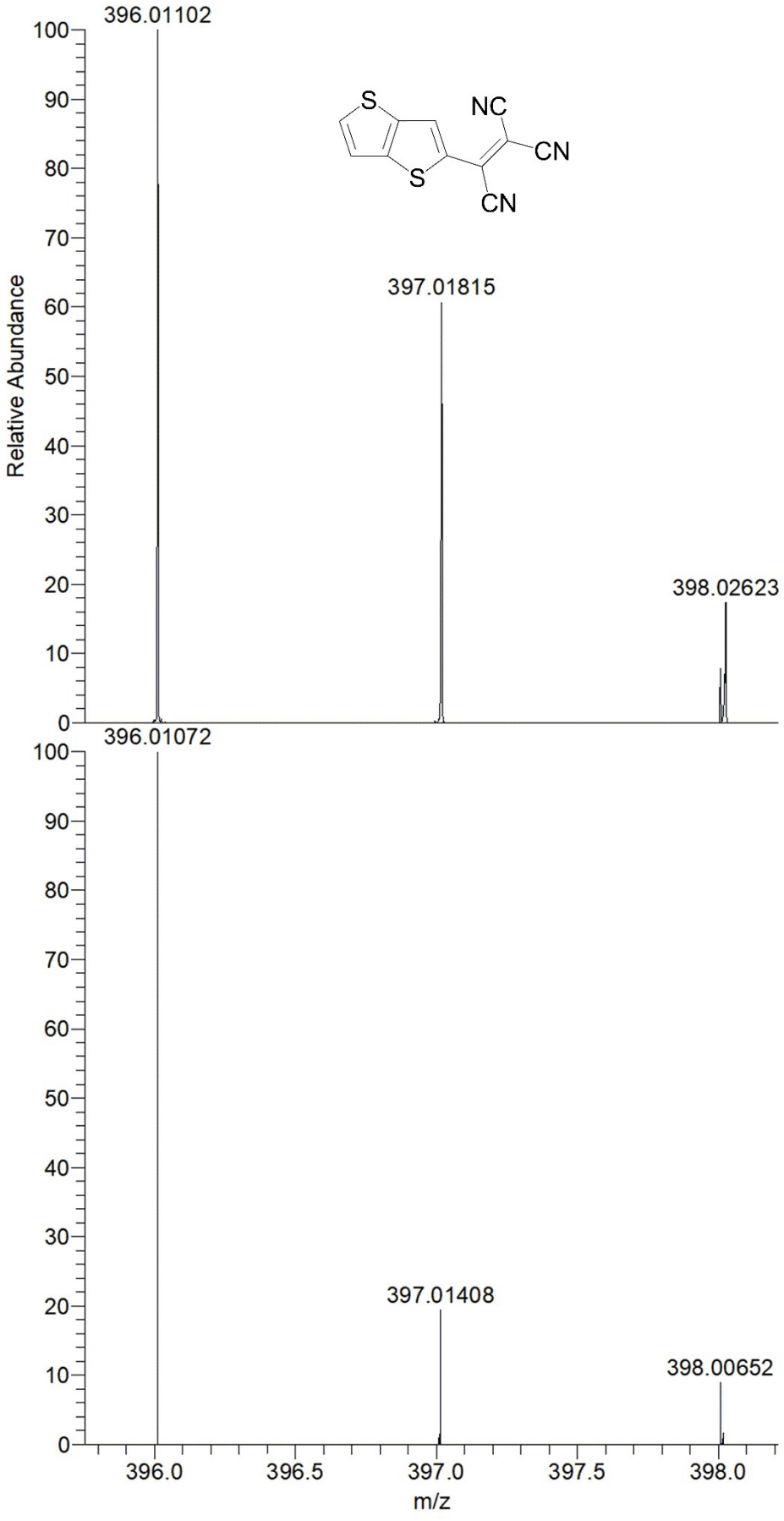
^{1}H NMR spectrum (400 MHz, 25 °C, $CDCl_3$) of **1g**



^{13}C APT NMR spectrum (125 MHz, 25 °C, $CDCl_3$) of **1g**

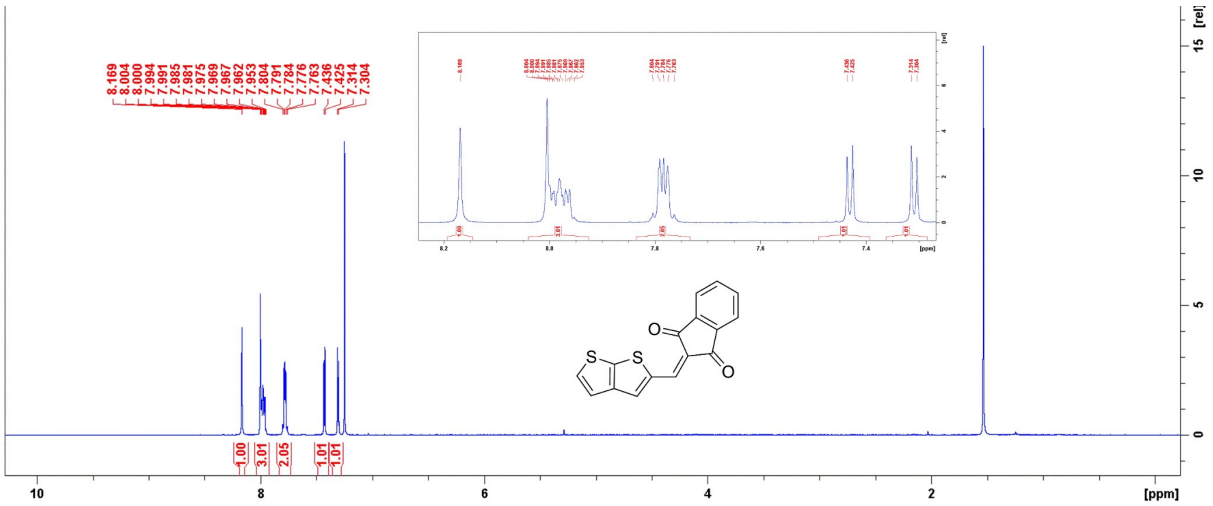


Experimental (up) and calculated (down) MALDI spectra of **1g**

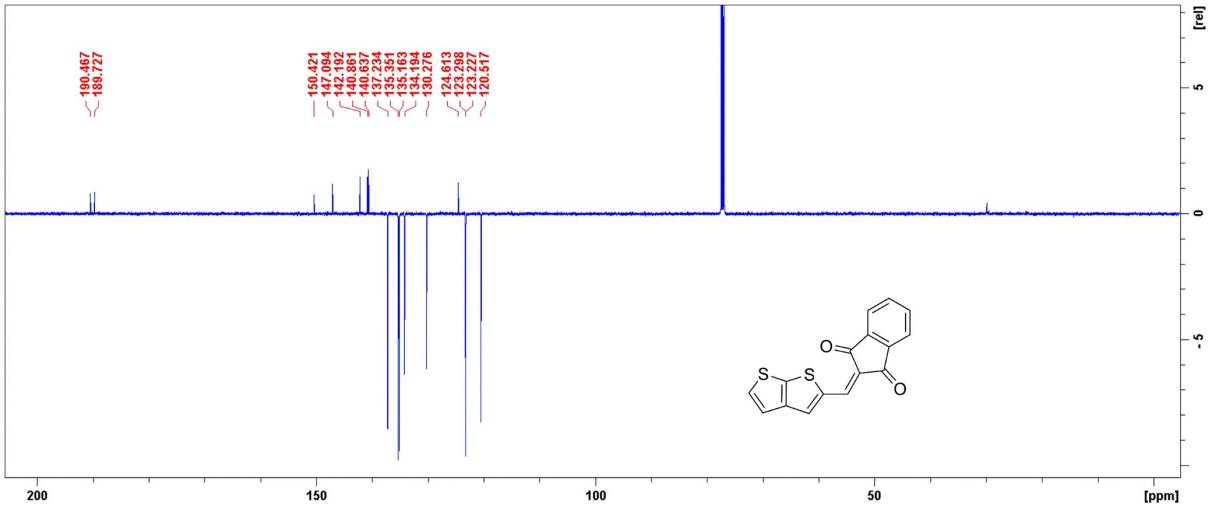


$^{1}H/^{13}C$ APT NMR and HR-MALDI-MS spectra of chromophore 2a

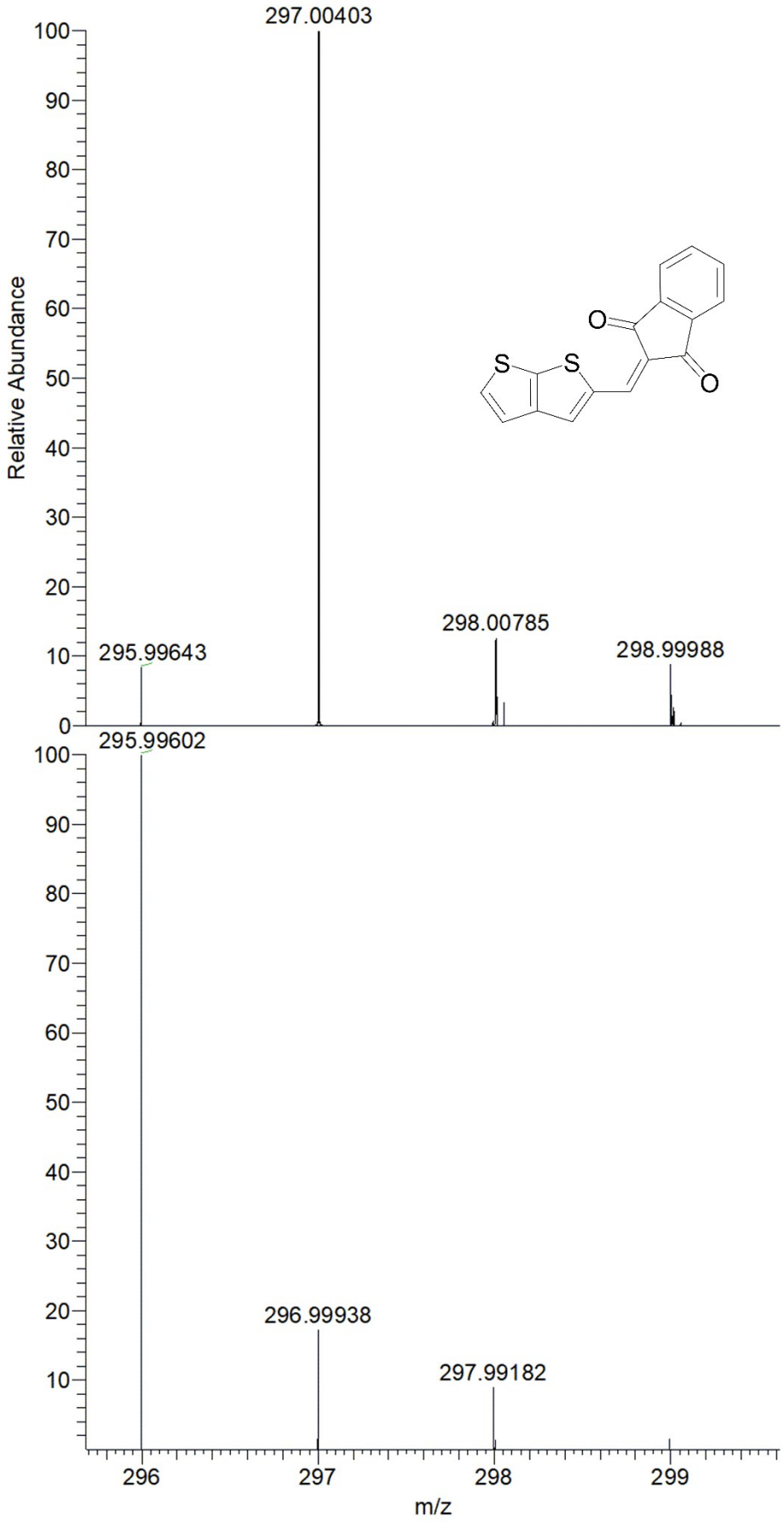
^{1}H NMR spectrum (500 MHz, 25 °C, $CDCl_3$) of **2a**



^{13}C APT NMR spectrum (125 MHz, 25 °C, $CDCl_3$) of **2a**

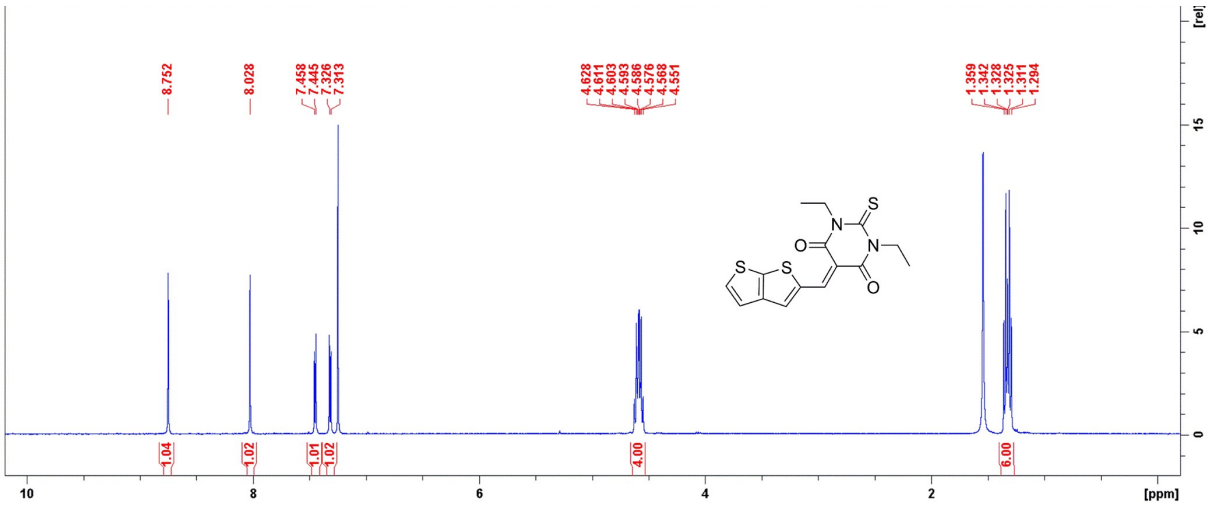


Experimental (up) and calculated (down) MALDI spectra of **2a**

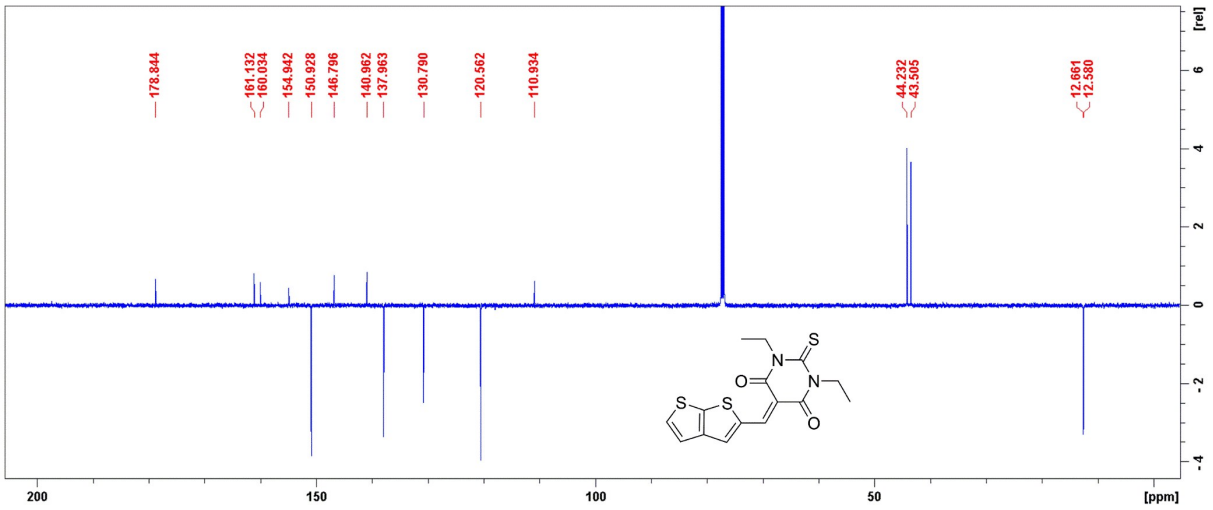


$^{1}H/^{13}C$ APT NMR and HR-MALDI-MS spectra of chromophore 2b

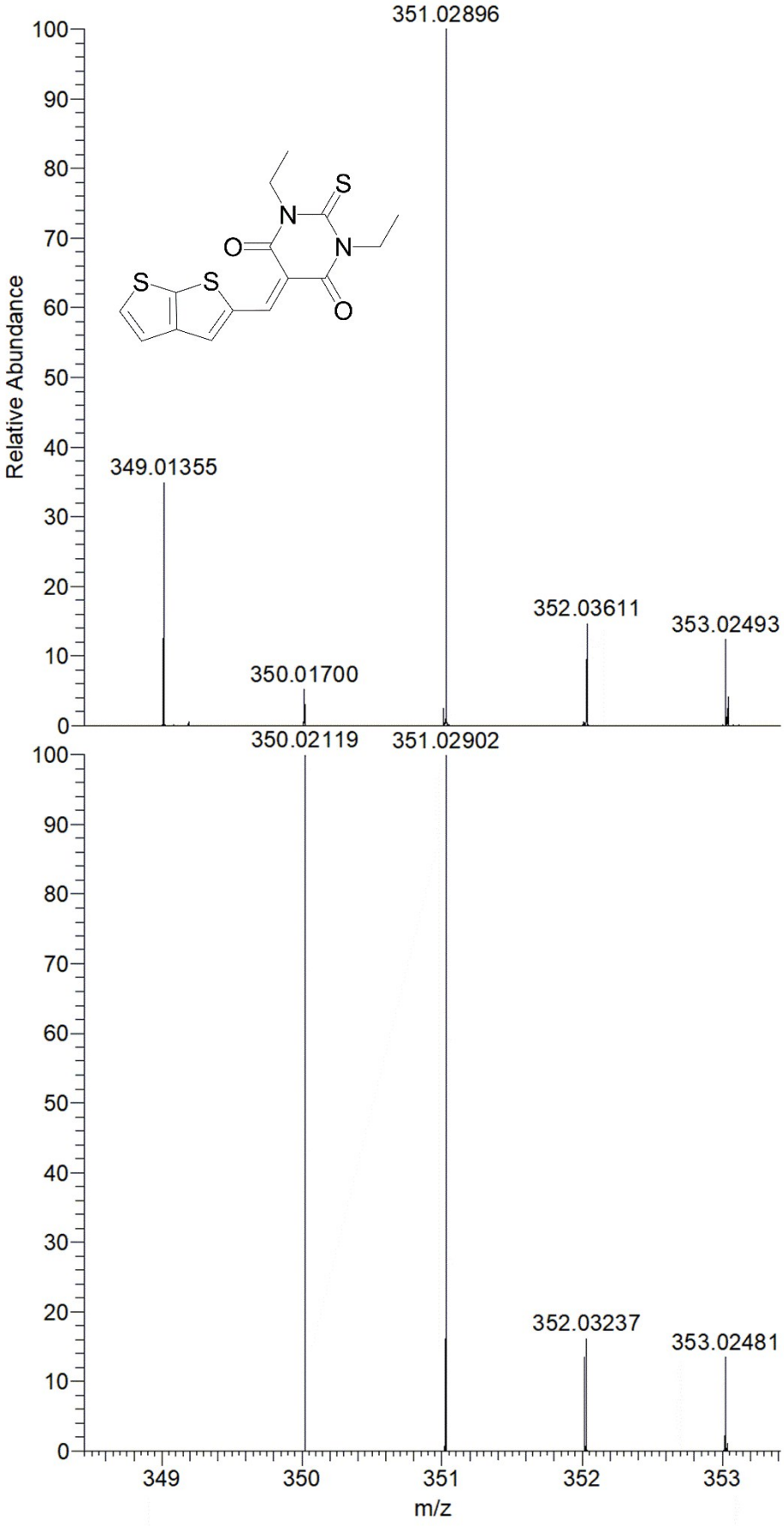
^{1}H NMR spectrum (400 MHz, 25 °C, $CDCl_3$) of **2b**



^{13}C APT NMR spectrum (125 MHz, 25 °C, $CDCl_3$) of **2b**

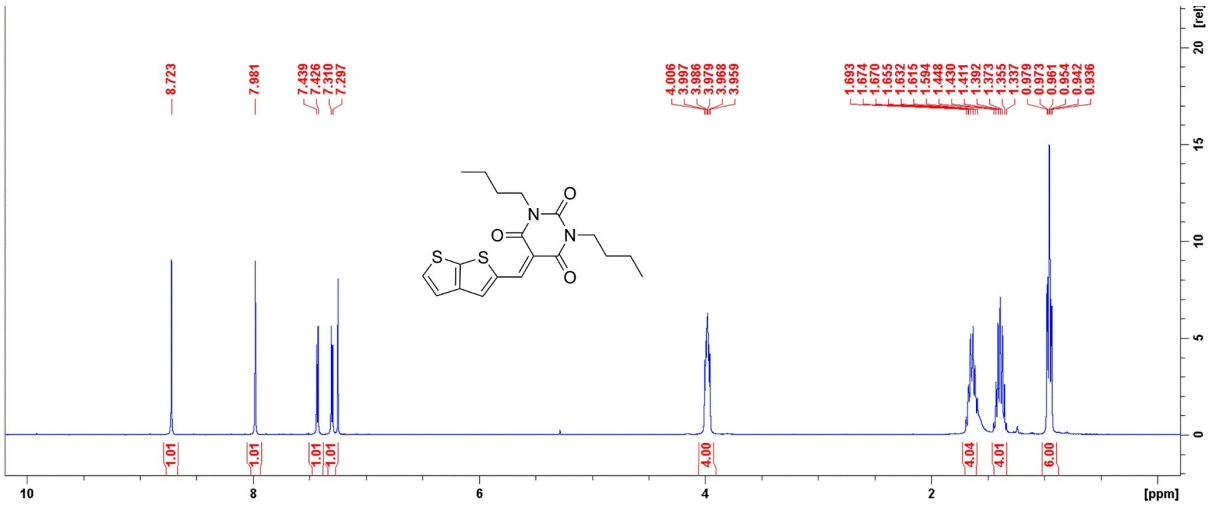


Experimental (up) and calculated (down) MALDI spectra of **2b**

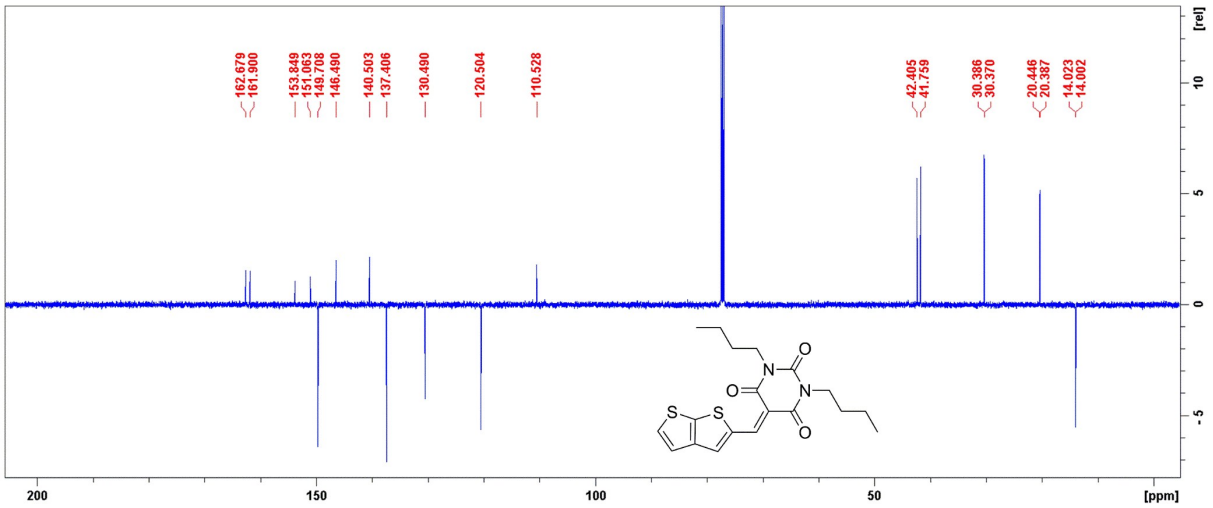


$^{1}H/^{13}C$ APT NMR and HR-MALDI-MS spectra of chromophore 2c

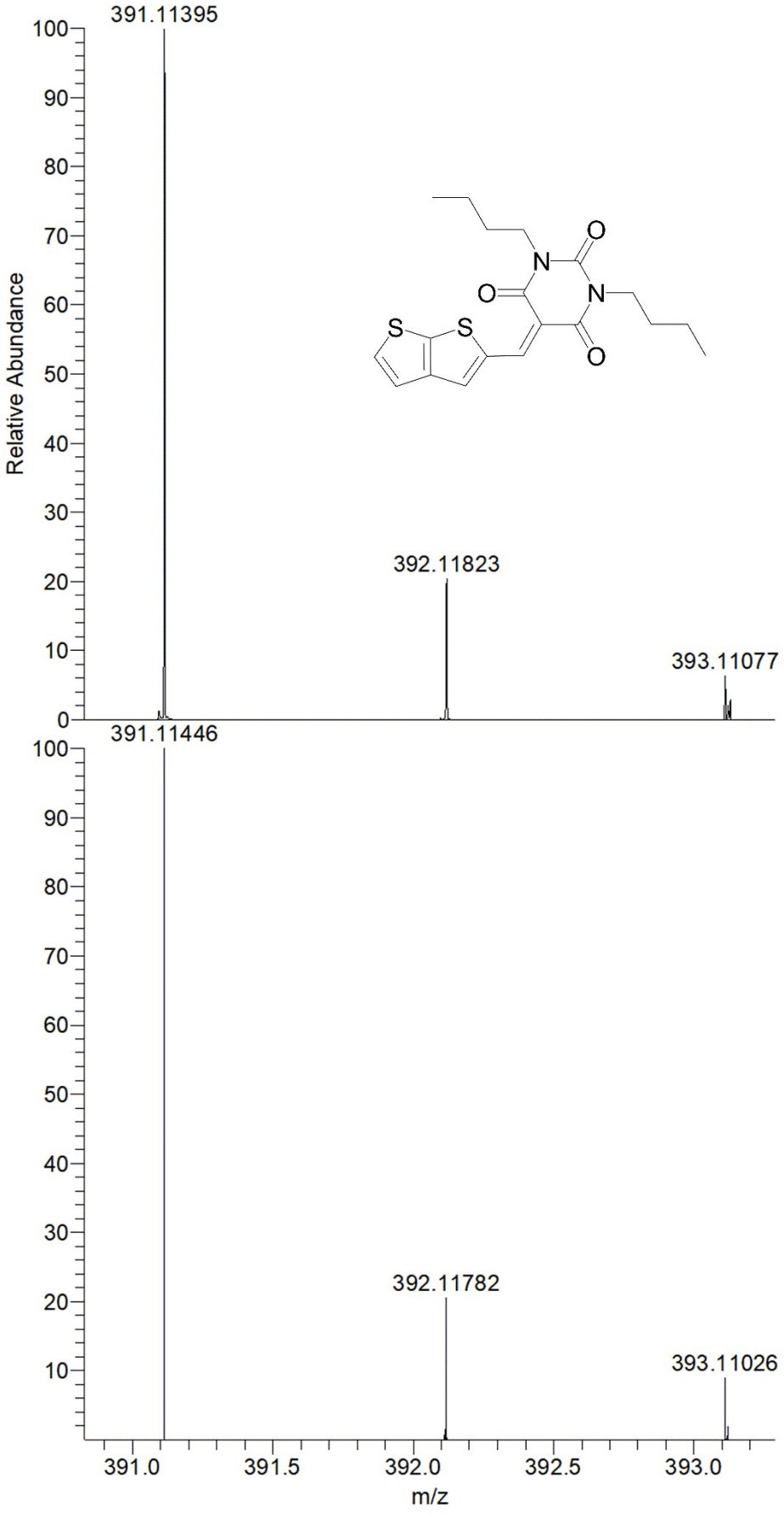
^{1}H NMR spectrum (400 MHz, 25 °C, $CDCl_3$) of **2c**



^{13}C APT NMR spectrum (125 MHz, 25 °C, $CDCl_3$) of **2c**

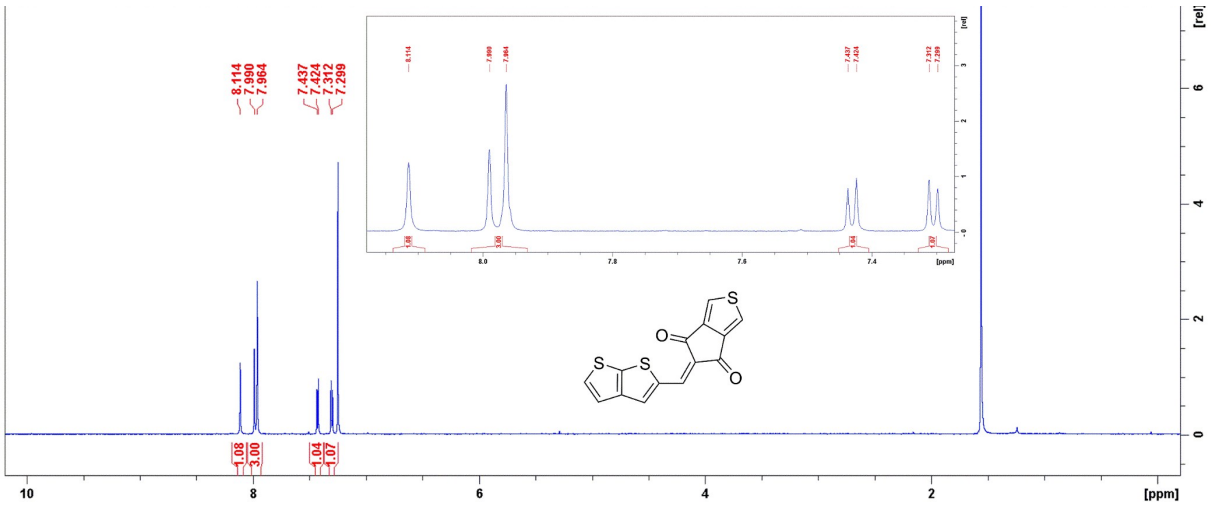


Experimental (up) and calculated (down) MALDI spectra of **2c**

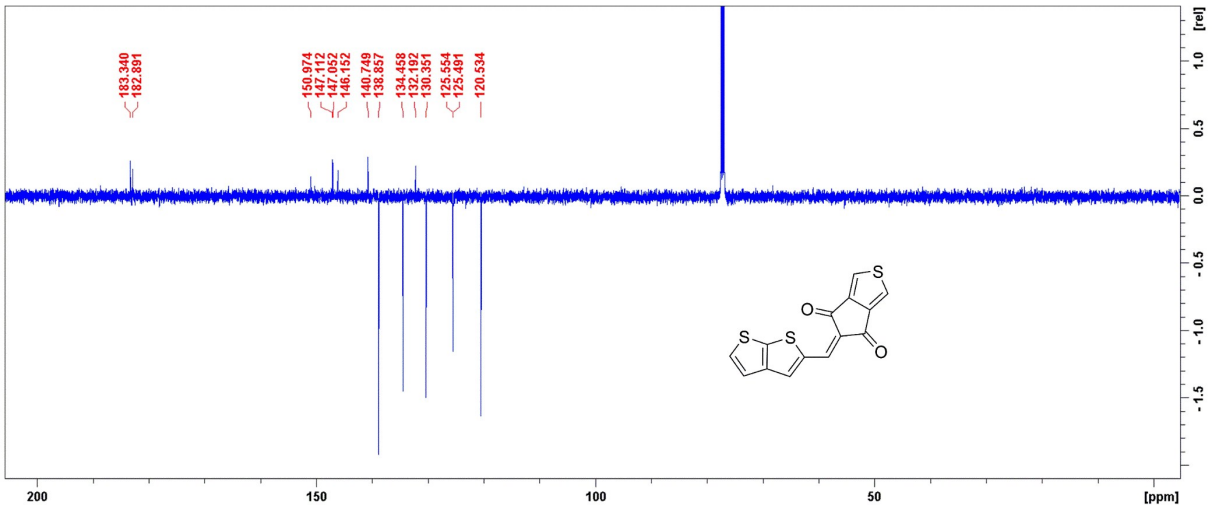


$^{1}H/^{13}C$ APT NMR and HR-MALDI-MS spectra of chromophore 2d

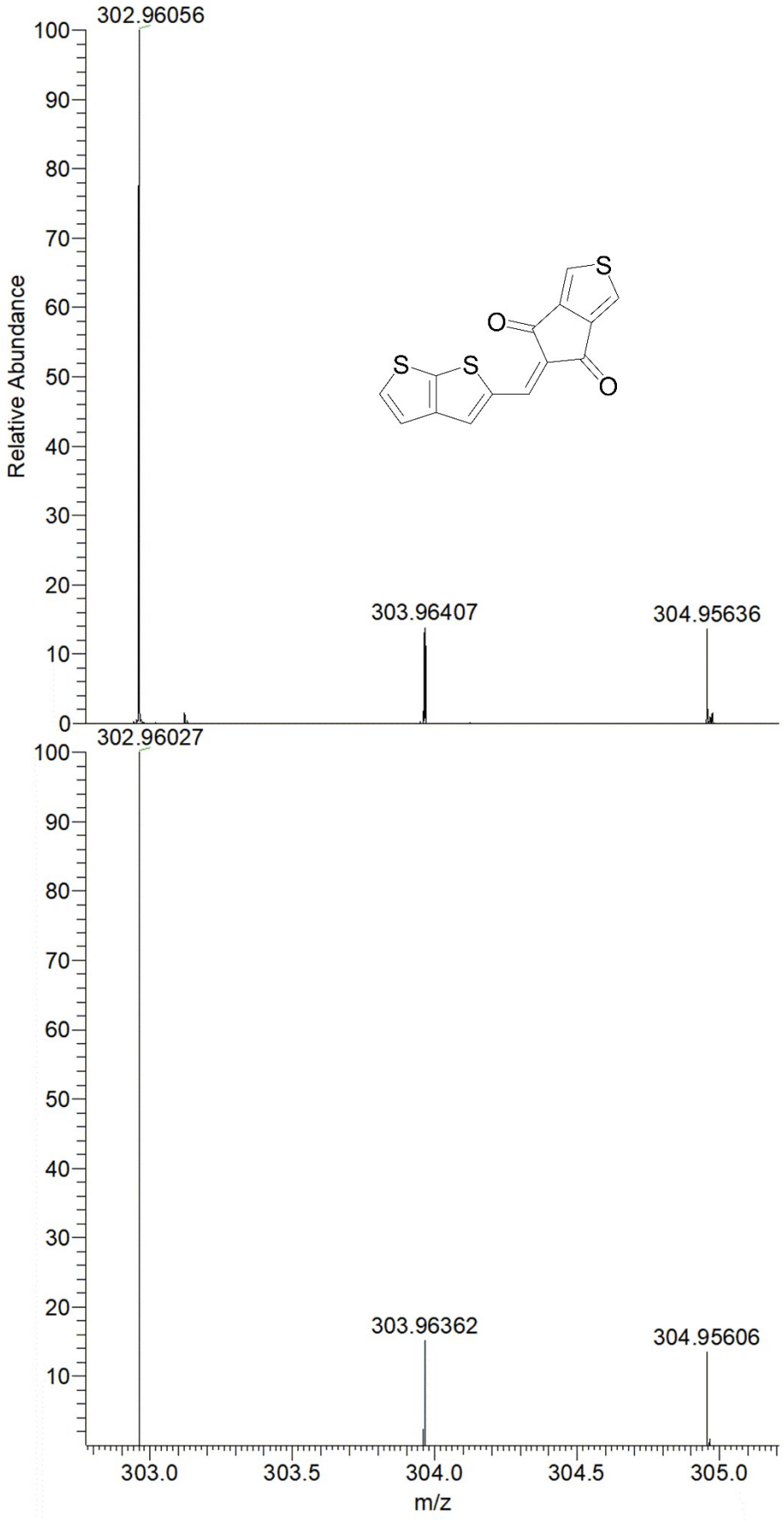
^{1}H NMR spectrum (400 MHz, 25 °C, $CDCl_3$) of **2d**



^{13}C APT NMR spectrum (125 MHz, 25 °C, $CDCl_3$) of **2d**

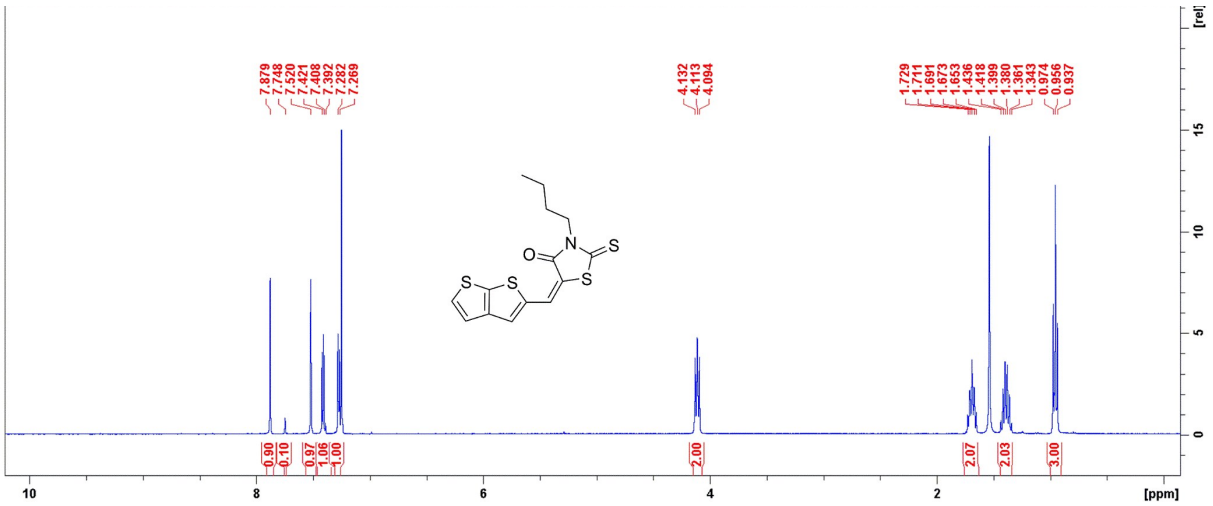


Experimental (up) and calculated (down) MALDI spectra of **2d**

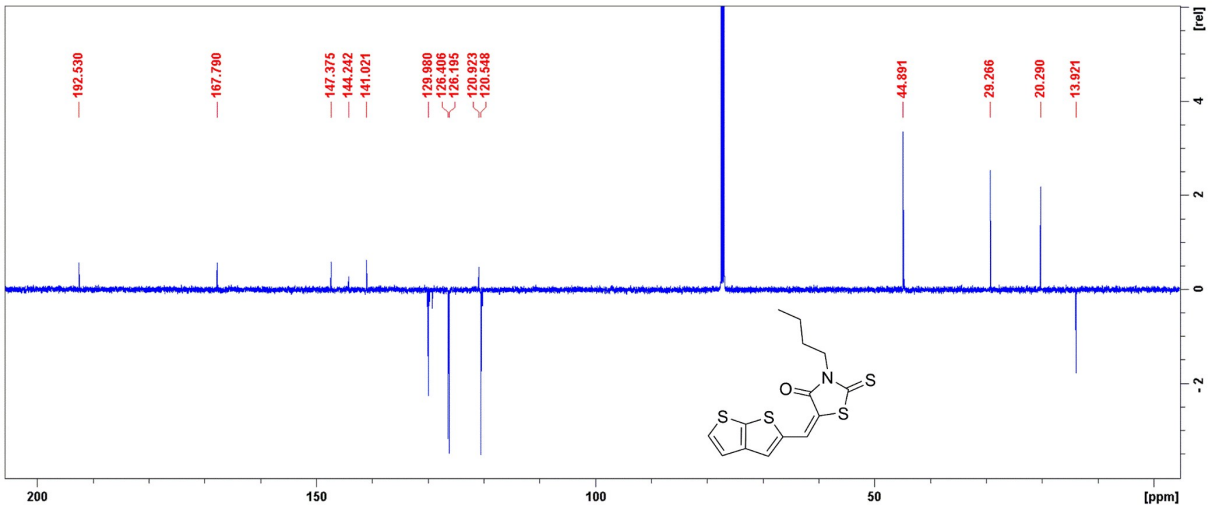


$^{1}H/^{13}C$ APT NMR and HR-MALDI-MS spectra of chromophore 2e

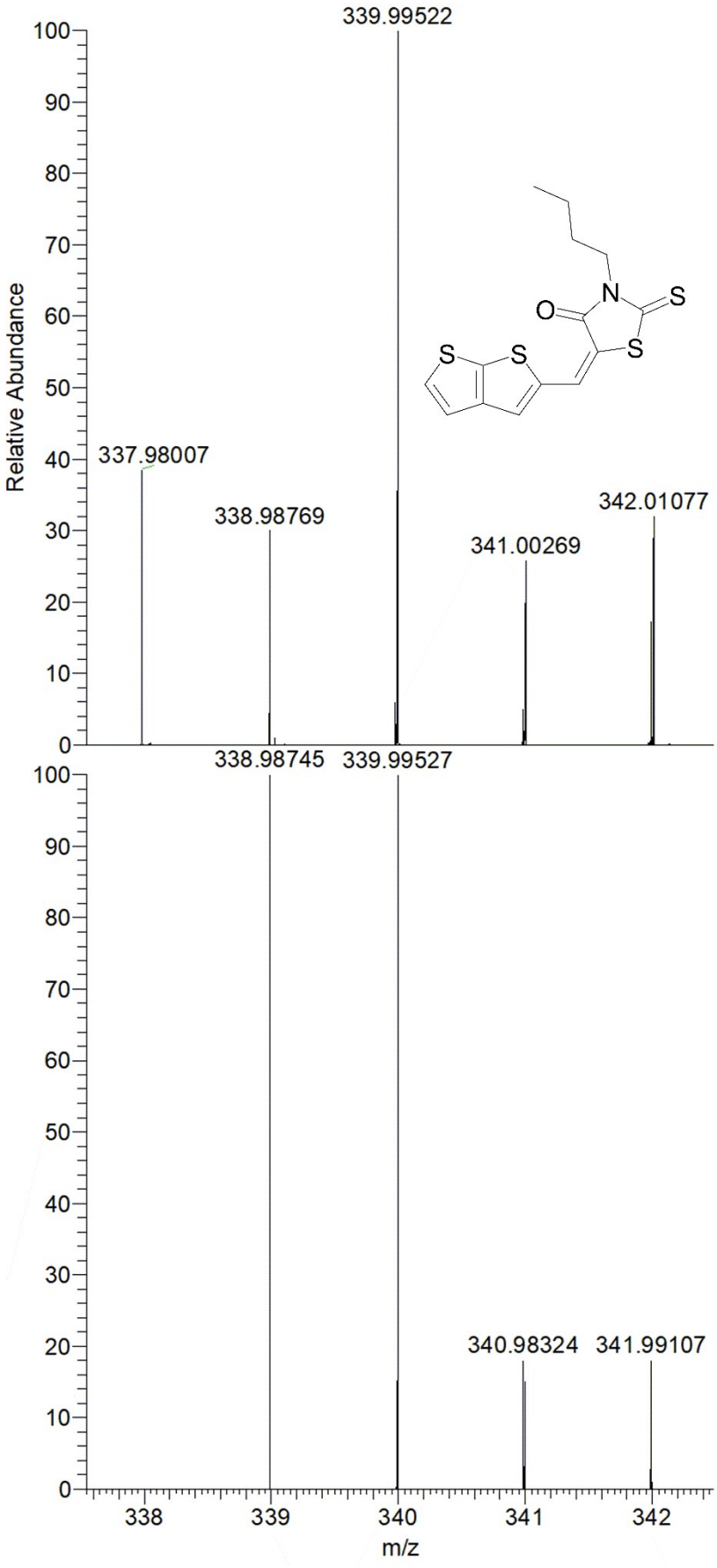
^{1}H NMR spectrum (400 MHz, 25 °C, $CDCl_3$) of **2e**



^{13}C APT NMR spectrum (125 MHz, 25 °C, $CDCl_3$) of **2e**

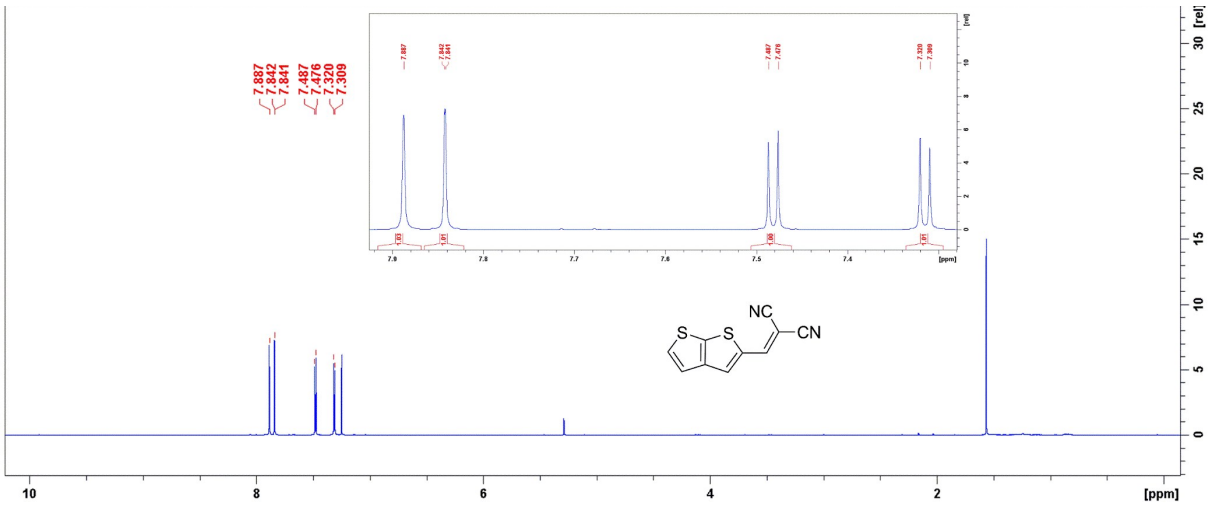


Experimental (up) and calculated (down) MALDI spectra of **2e**

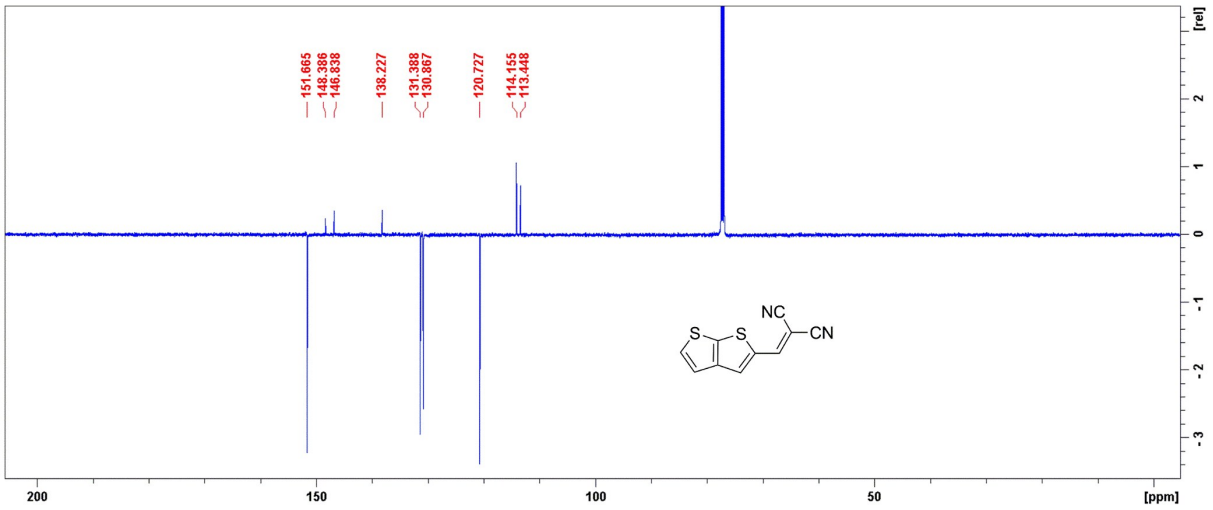


$^{1}H/^{13}C$ APT NMR and HR-MALDI-MS spectra of chromophore 2f

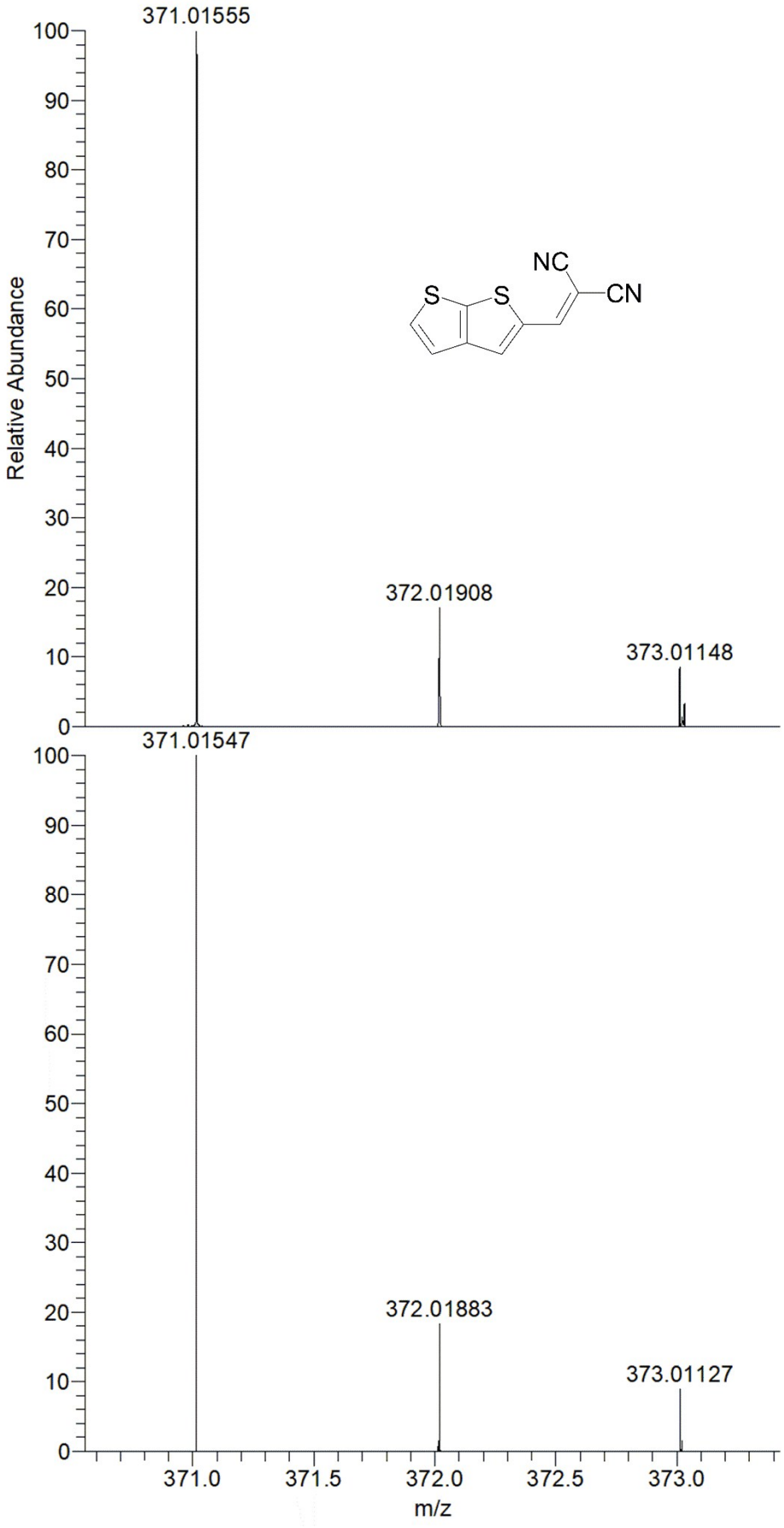
^{1}H NMR spectrum (500 MHz, 25 °C, $CDCl_3$) of **2f**



^{13}C APT NMR spectrum (125 MHz, 25 °C, $CDCl_3$) of **2f**

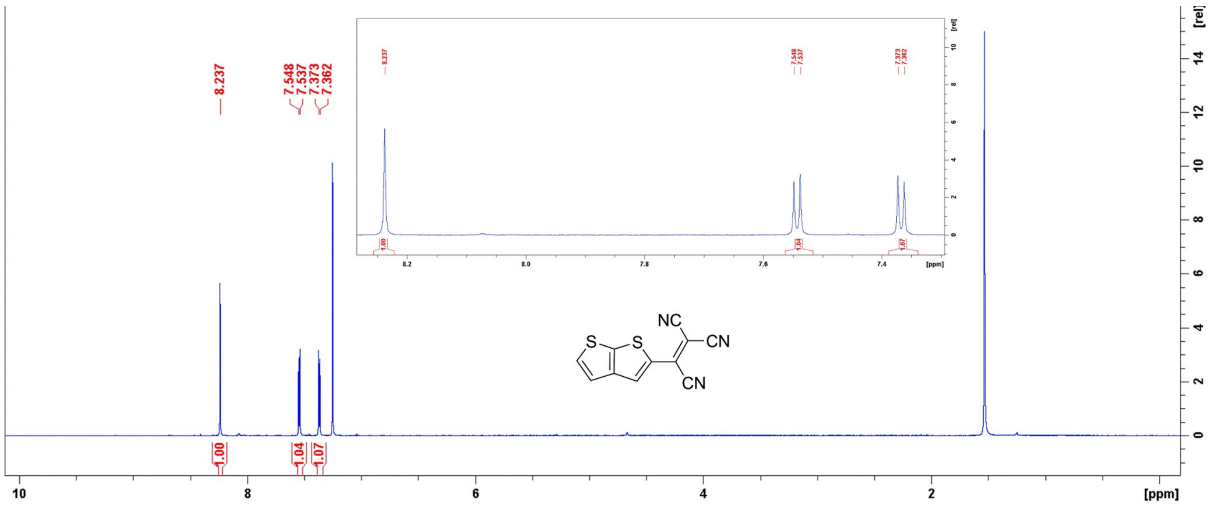


Experimental (up) and calculated (down) MALDI spectra of **2f**

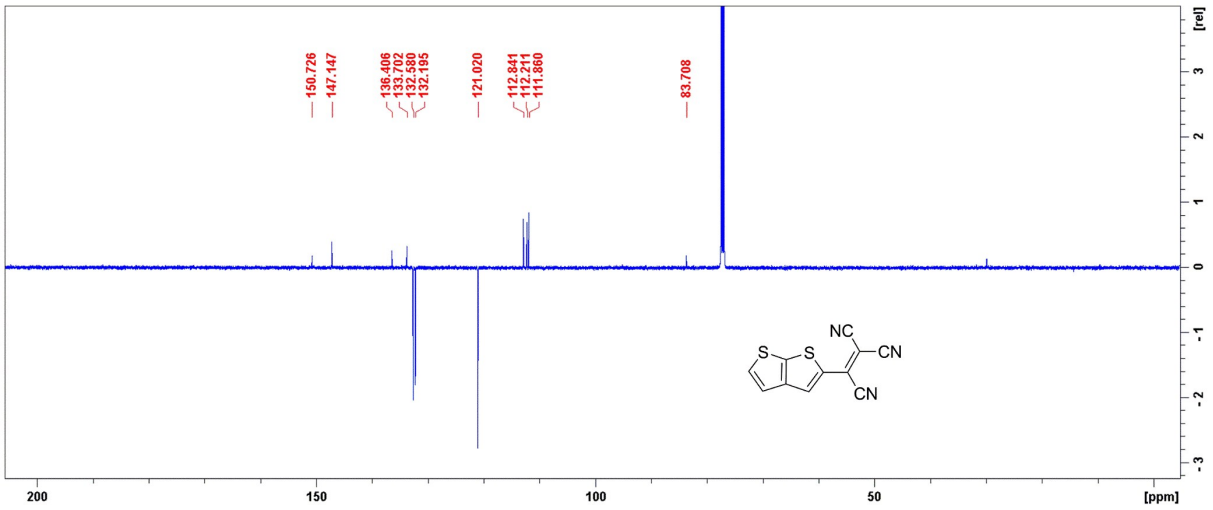


$^{1}H/^{13}C$ APT NMR and HR-MALDI-MS spectra of chromophore 2g

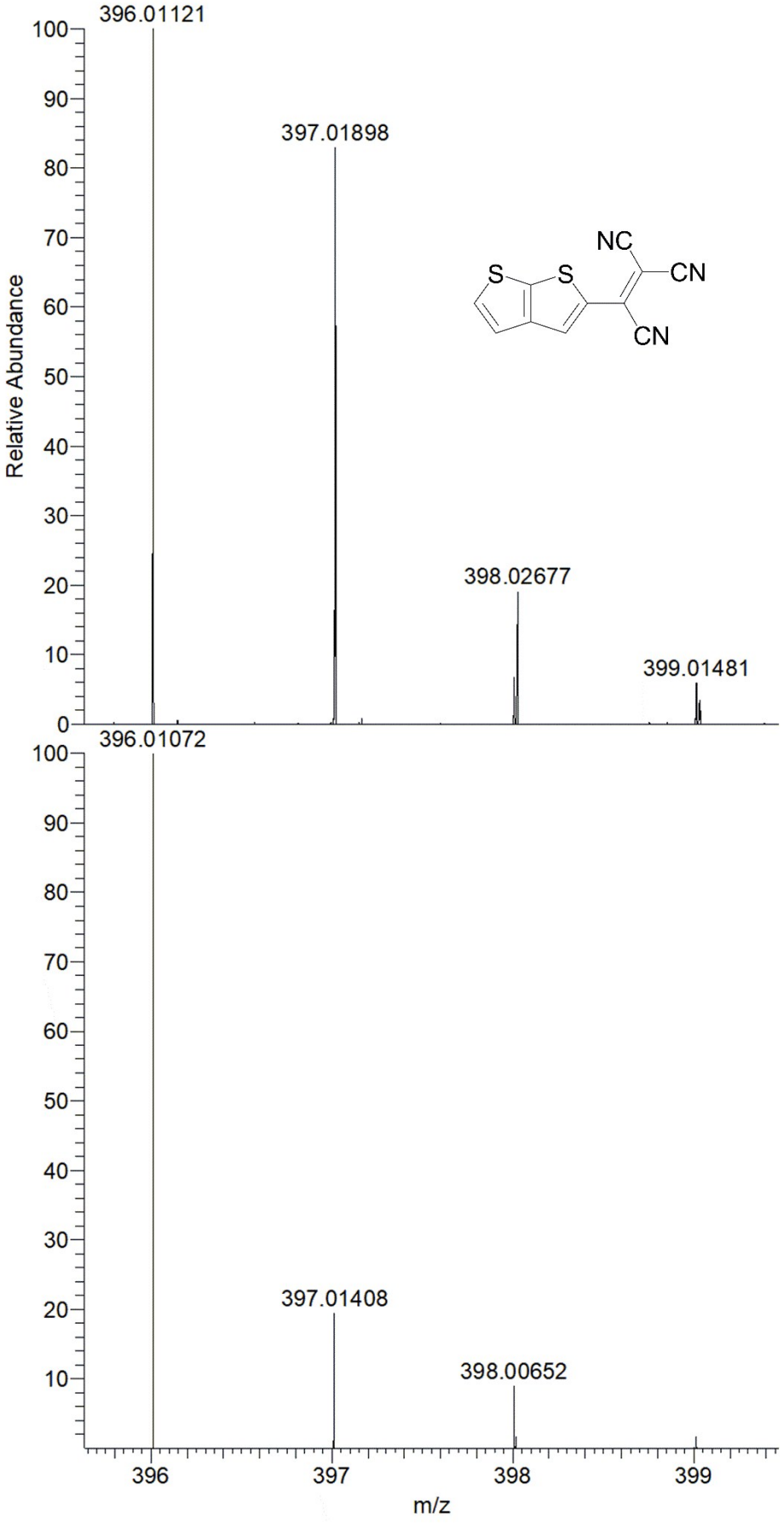
^{1}H NMR spectrum (400 MHz, 25 °C, $CDCl_3$) of **2g**



^{13}C APT NMR spectrum (125 MHz, 25 °C, $CDCl_3$) of **2g**

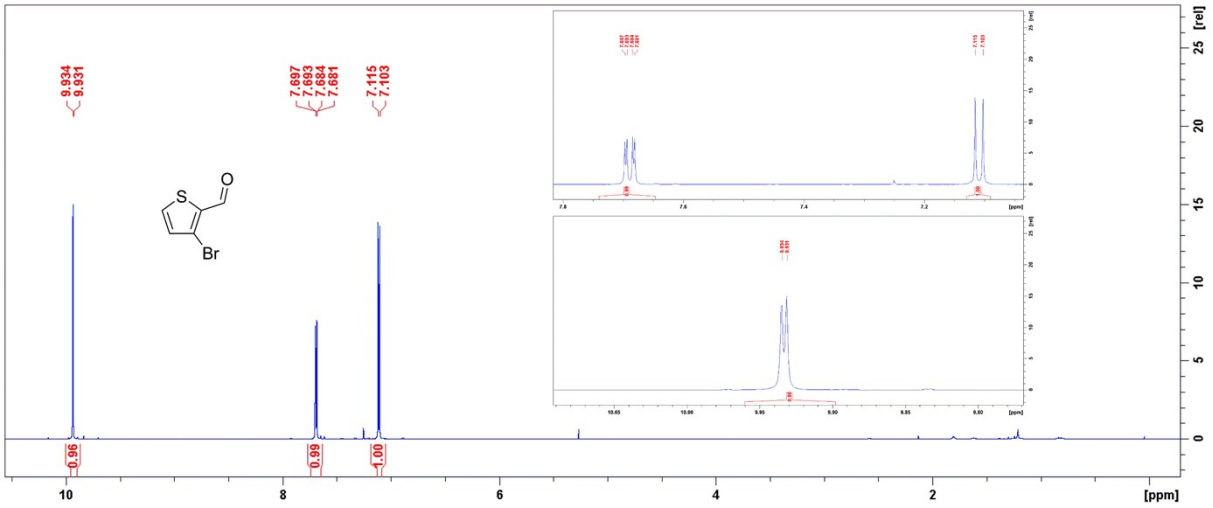


Experimental (up) and calculated (down) MALDI spectra of **2g**

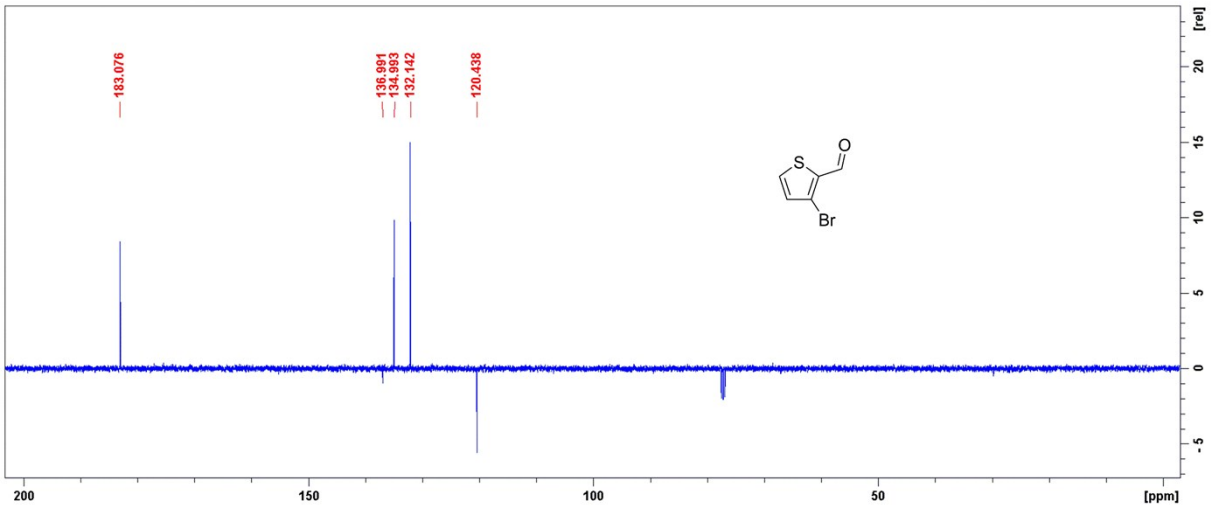


$^{1}H/^{13}C$ APT NMR spectra of compound 8

^{1}H NMR spectrum (400 MHz, 25 °C, $CDCl_3$) of **8**

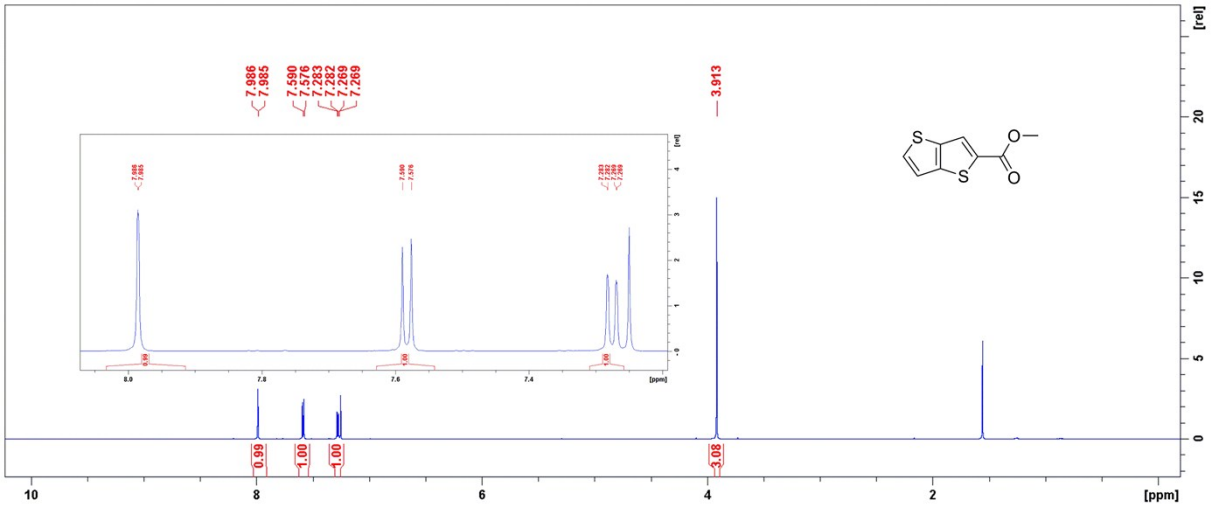


^{13}C APT NMR spectrum (100 MHz, 25 °C, $CDCl_3$) of **8**

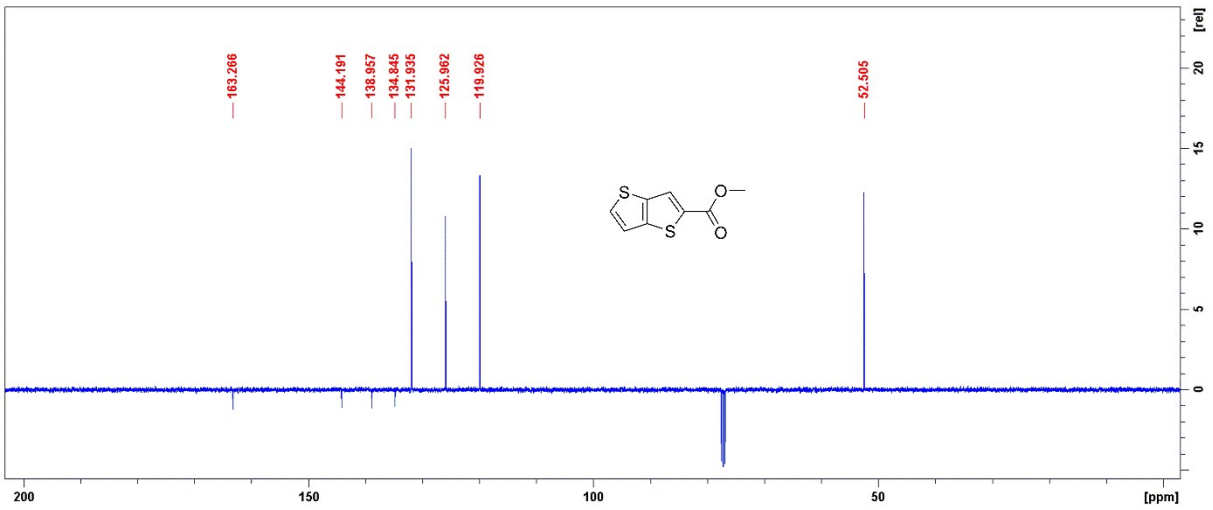


$^{1}H/^{13}C$ APT NMR spectra of compound 9

^{1}H NMR spectrum (400 MHz, 25 °C, $CDCl_3$) of **9**

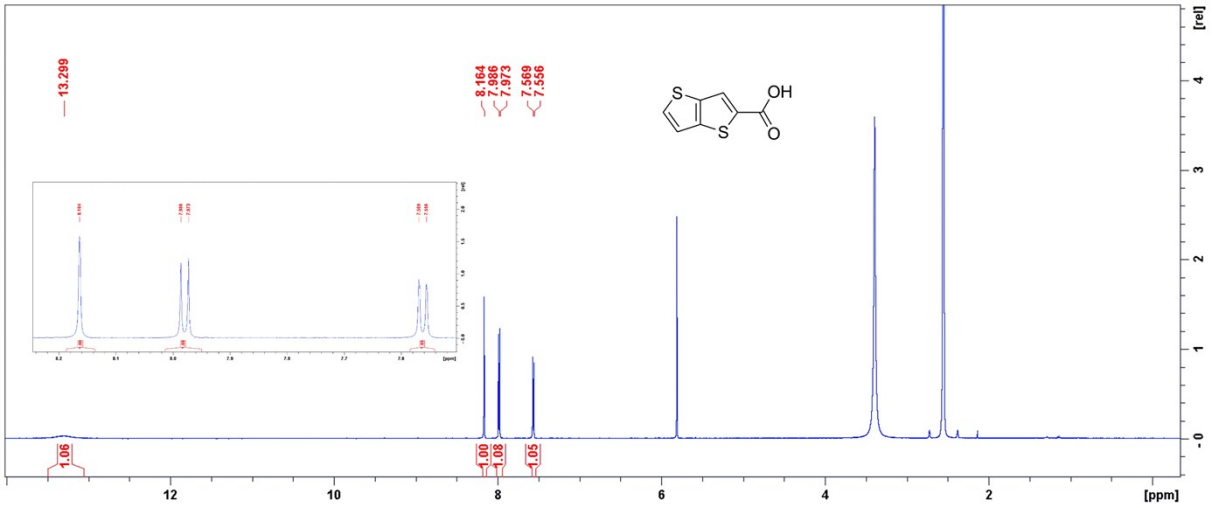


^{13}C APT NMR spectrum (100 MHz, 25 °C, $CDCl_3$) of **9**

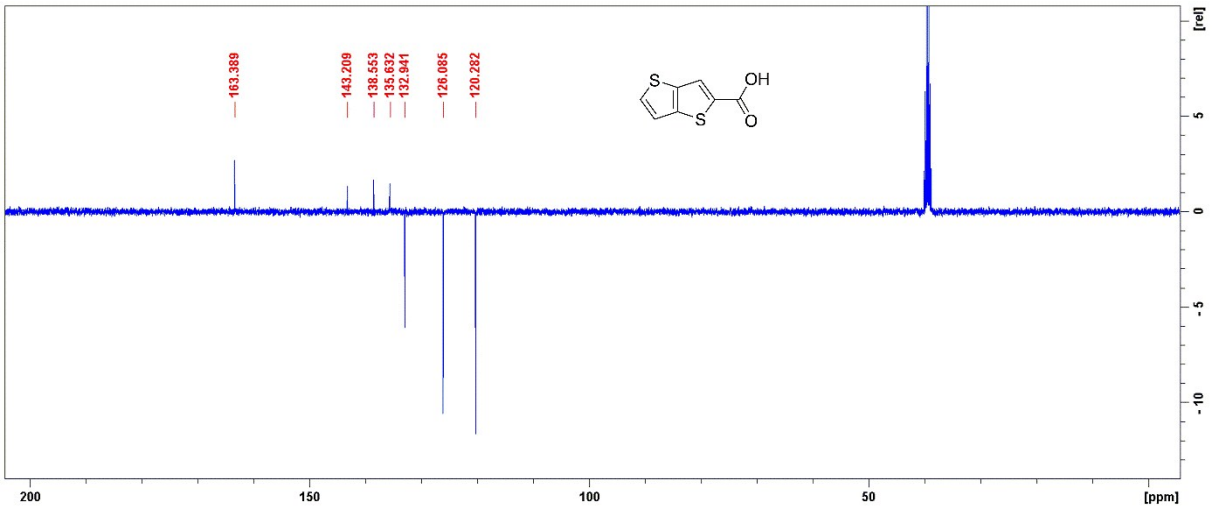


$^{1}H/^{13}C$ APT NMR spectra of compound 10

^{1}H NMR spectrum (400 MHz, 25 °C, d_6-DMSO) of **10**

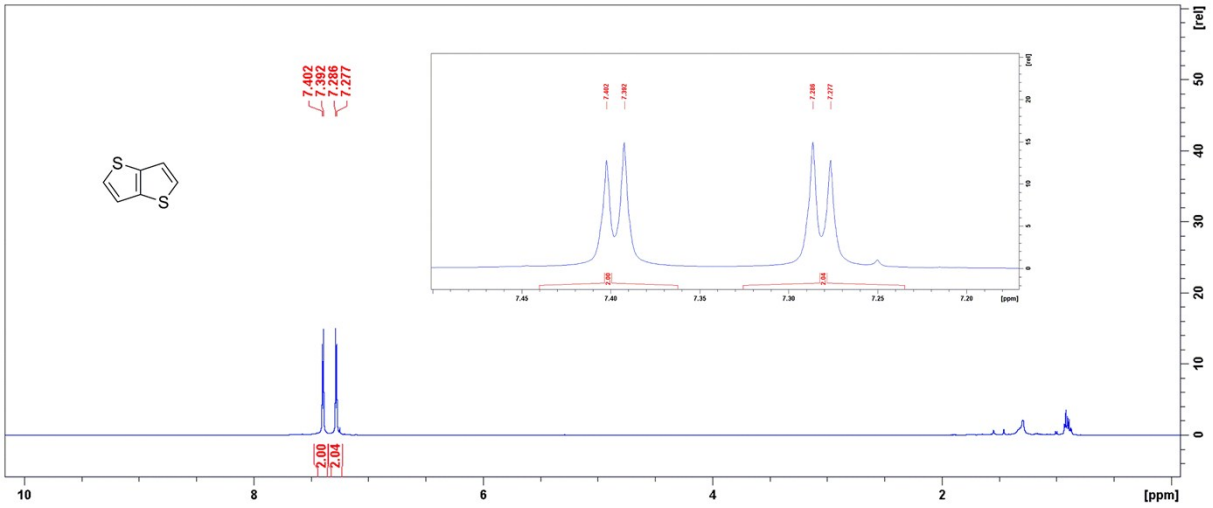


^{13}C APT NMR spectrum (100 MHz, 25 °C, d_6-DMSO) of **10**

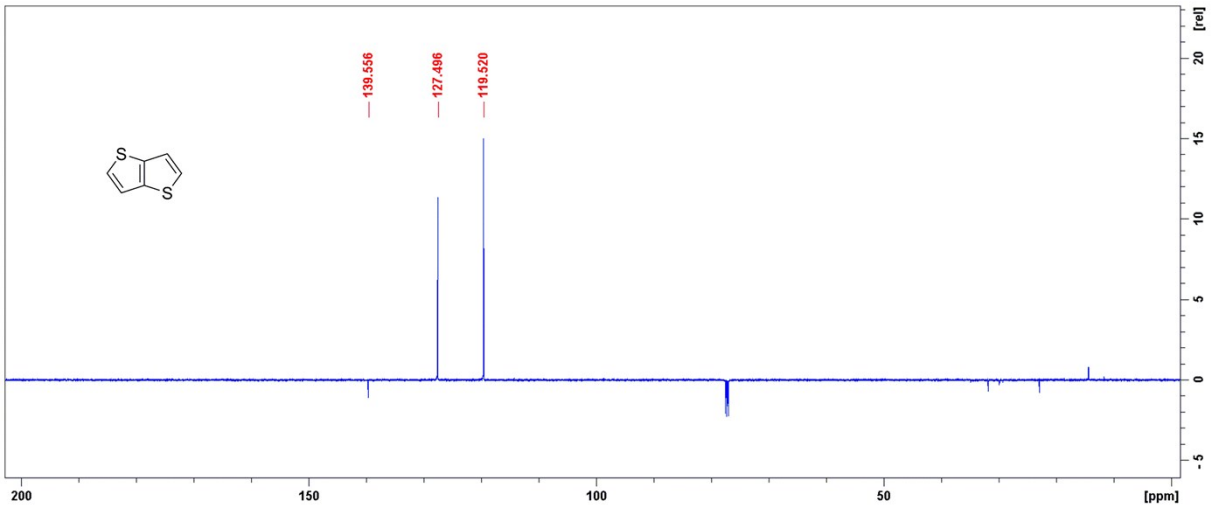


$^{1}H/^{13}C$ APT NMR spectra of compound 3

^{1}H NMR spectrum (500 MHz, 25 °C, $CDCl_3$) of **3**

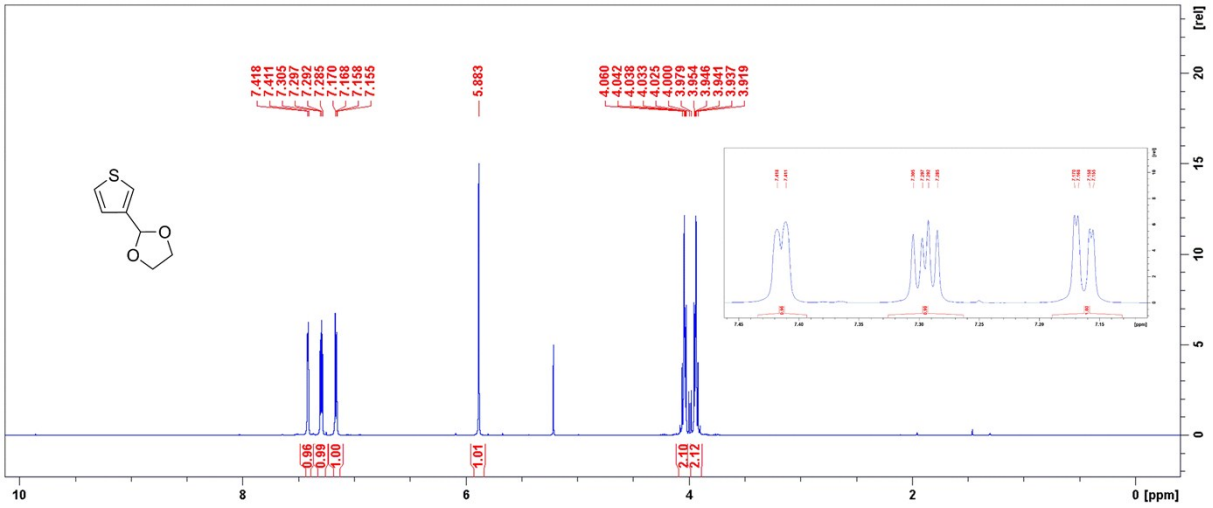


^{13}C APT NMR spectrum (125 MHz, 25 °C, $CDCl_3$) of **3**

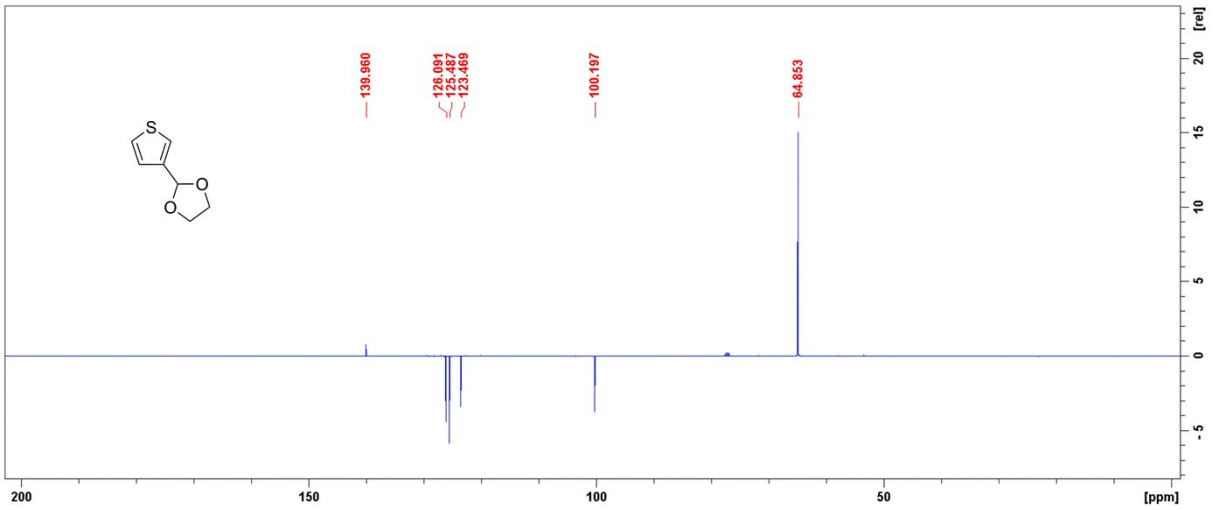


$^{1}H/^{13}C$ APT NMR spectra of compound 12

^{1}H NMR spectrum (400 MHz, 25 °C, $CDCl_3$) of **12**

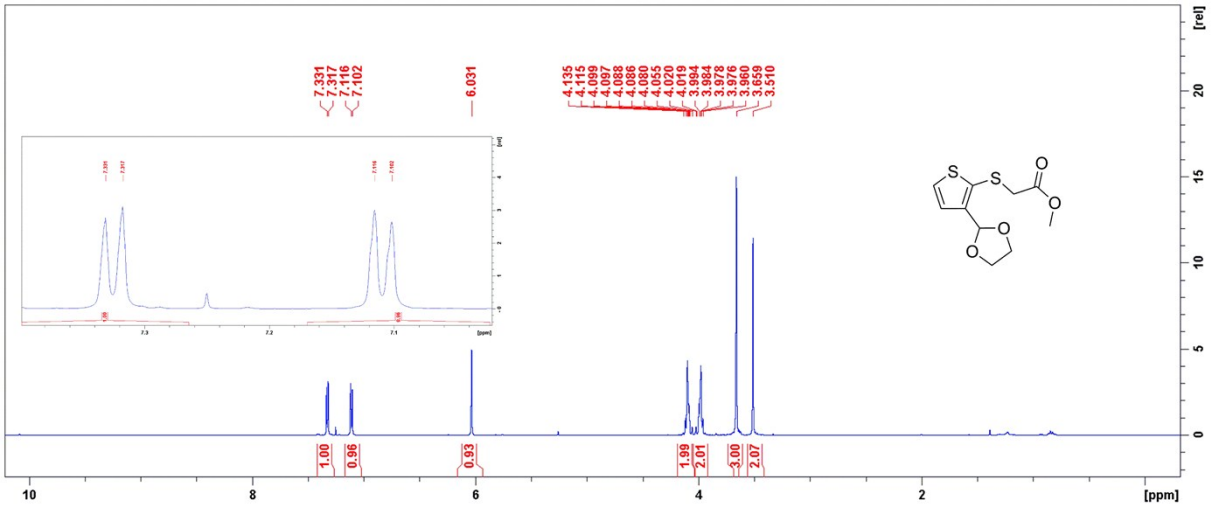


^{13}C APT NMR spectrum (100 MHz, 25 °C, $CDCl_3$) of **12**

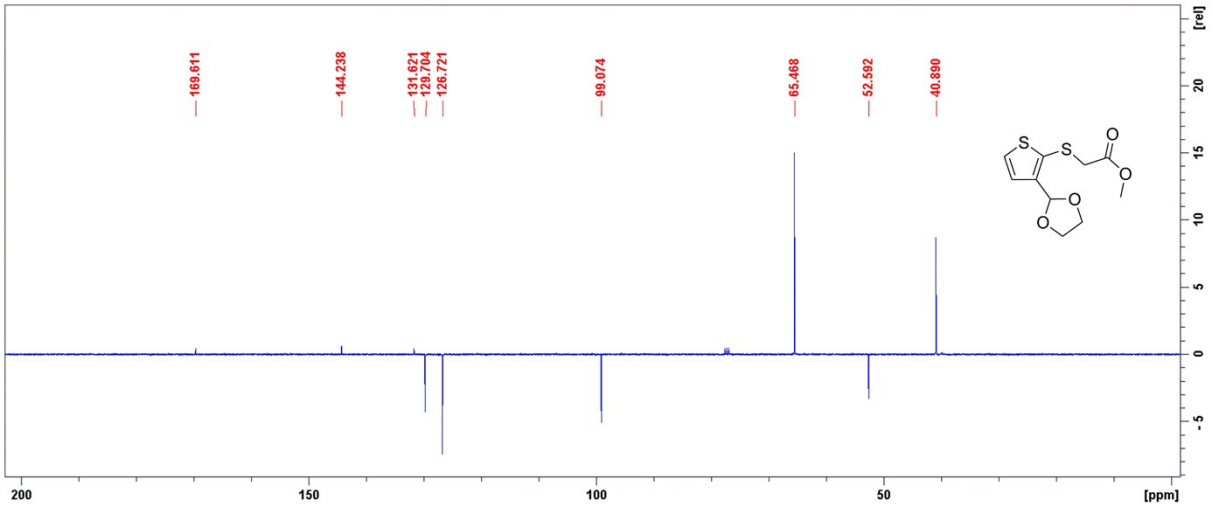


$^{1}H/^{13}C$ APT NMR spectra of compound 13

^{1}H NMR spectrum (400 MHz, 25 °C, $CDCl_3$) of **13**

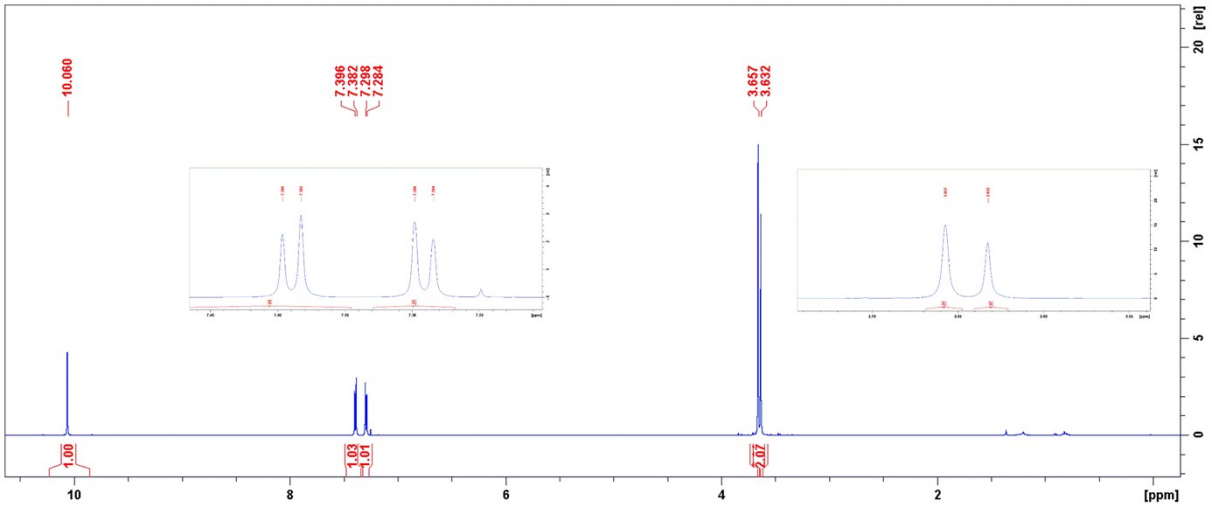


^{13}C APT NMR spectrum (100 MHz, 25 °C, $CDCl_3$) of **13**

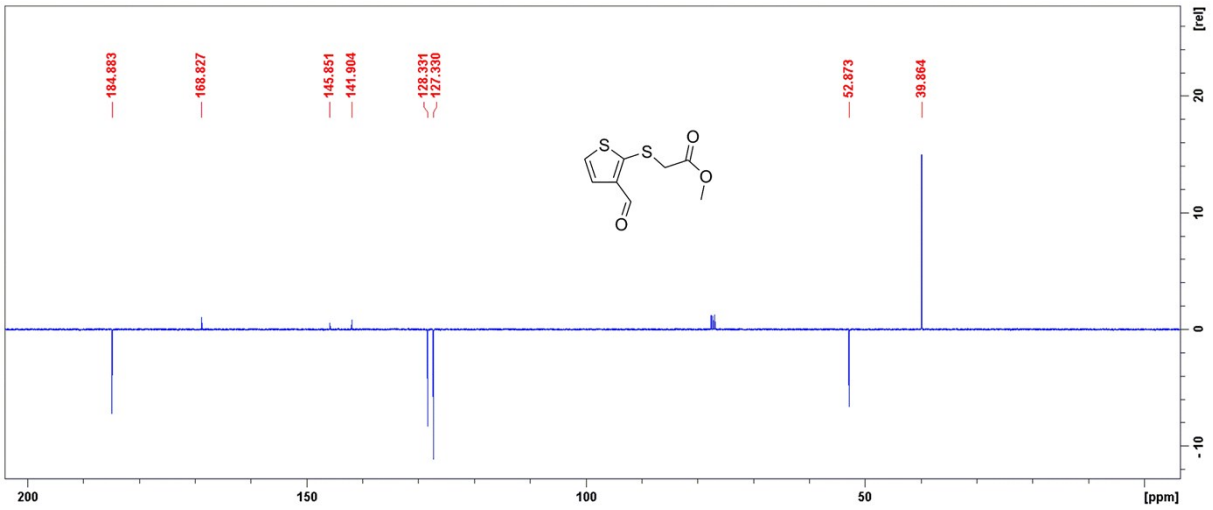


$^{1}H/^{13}C$ APT NMR spectra of compound 14

^{1}H NMR spectrum (400 MHz, 25 °C, $CDCl_3$) of **14**

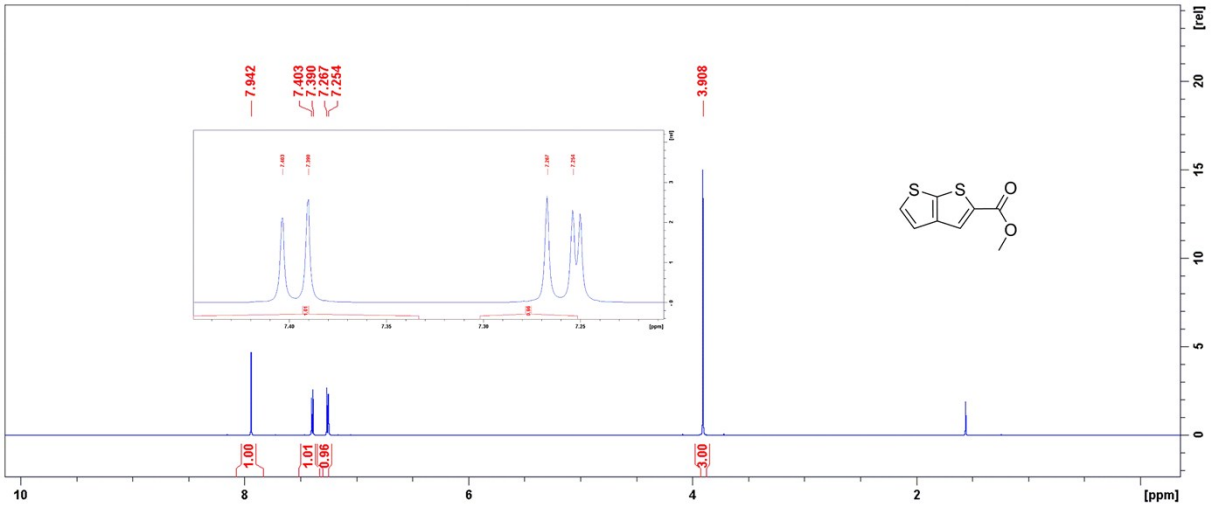


^{13}C APT NMR spectrum (100 MHz, 25 °C, $CDCl_3$) of **14**

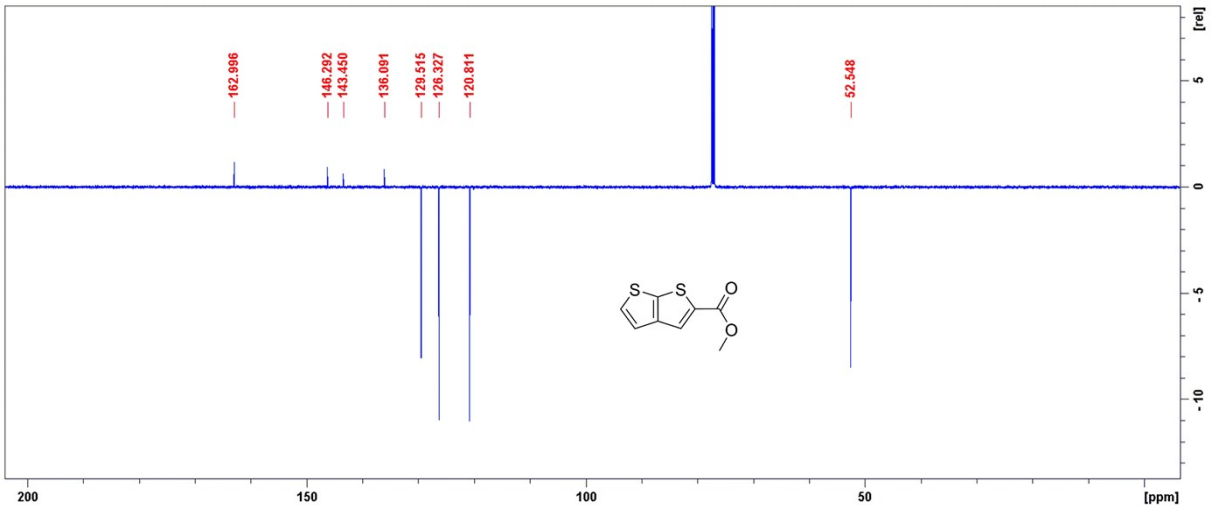


$^{1}H/^{13}C$ APT NMR spectra of compound 15

^{1}H NMR spectrum (400 MHz, 25 °C, $CDCl_3$) of **15**

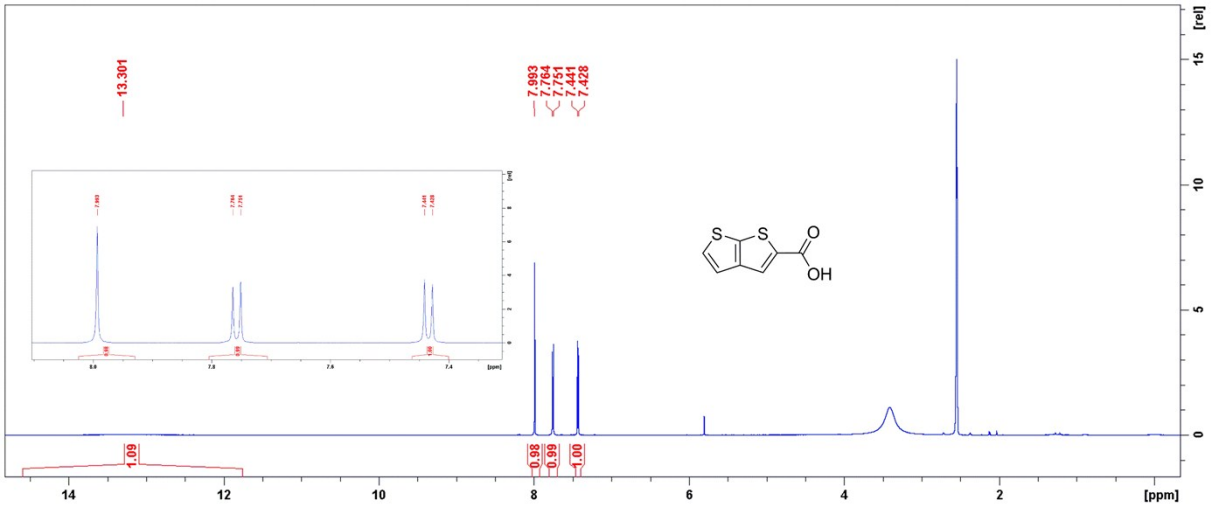


^{13}C APT NMR spectrum (125 MHz, 25 °C, $CDCl_3$) of **15**

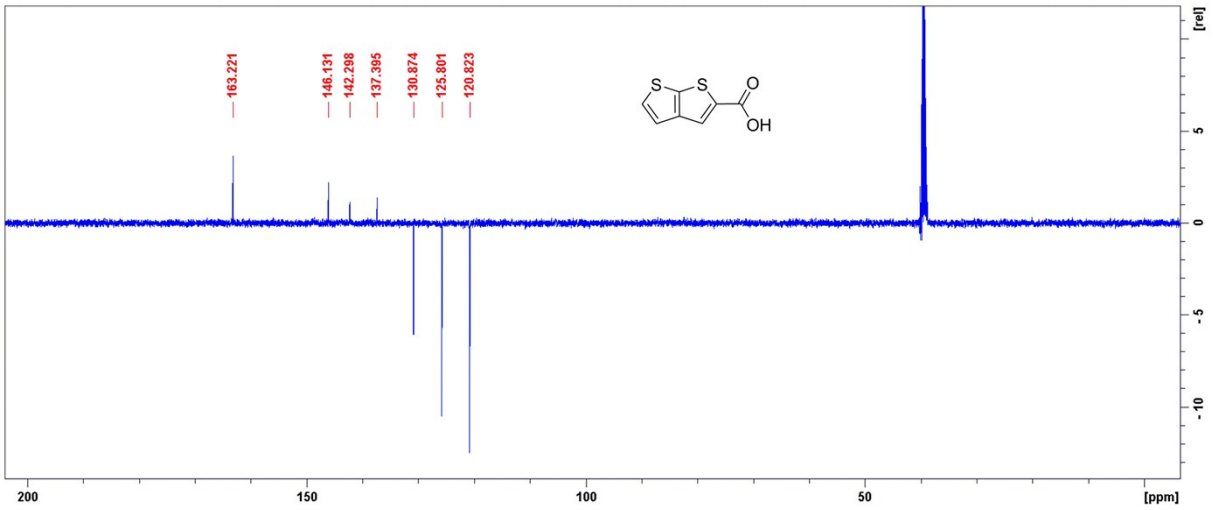


$^{1}H/^{13}C$ APT NMR spectra of compound 16

^{1}H NMR spectrum (400 MHz, 25 °C, d_6-DMSO) of **16**

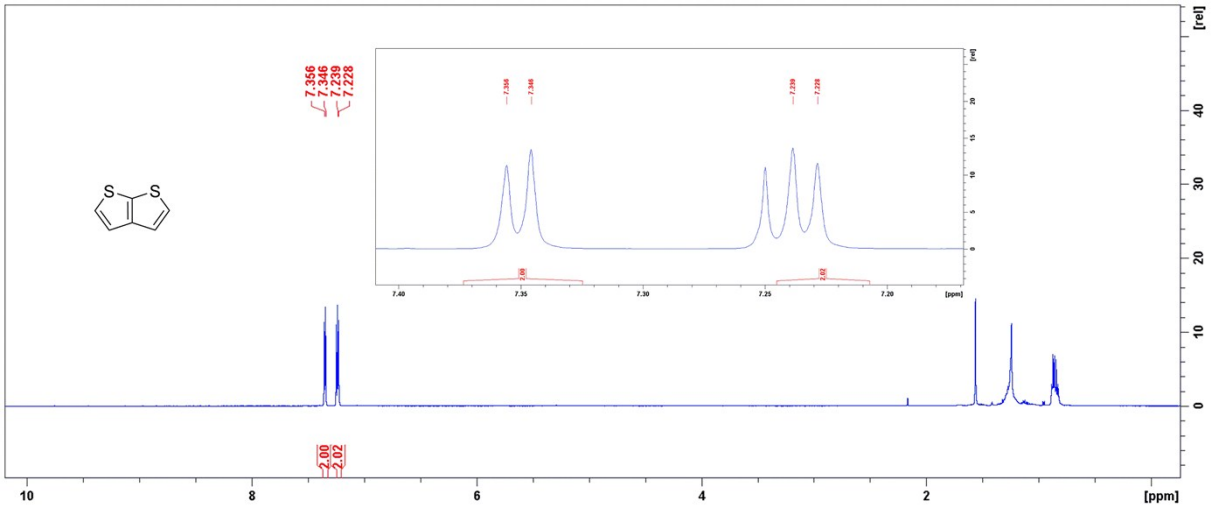


^{13}C APT NMR spectrum (100 MHz, 25 °C, d_6-DMSO) of **16**

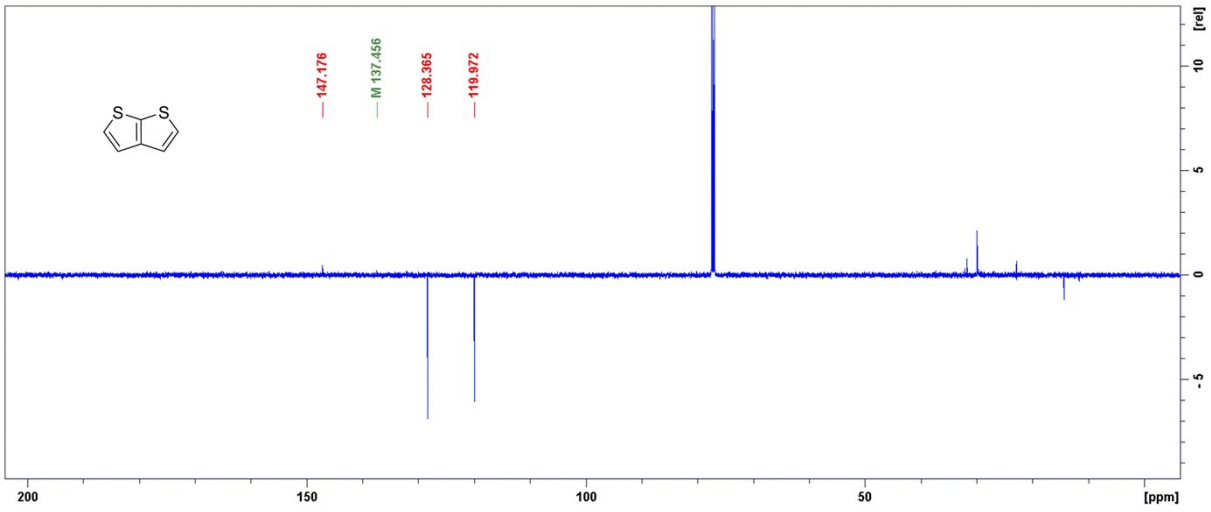


$^{1}H/^{13}C$ APT NMR spectra of compound 5

^{1}H NMR spectrum (500 MHz, 25 °C, $CDCl_3$) of **5**

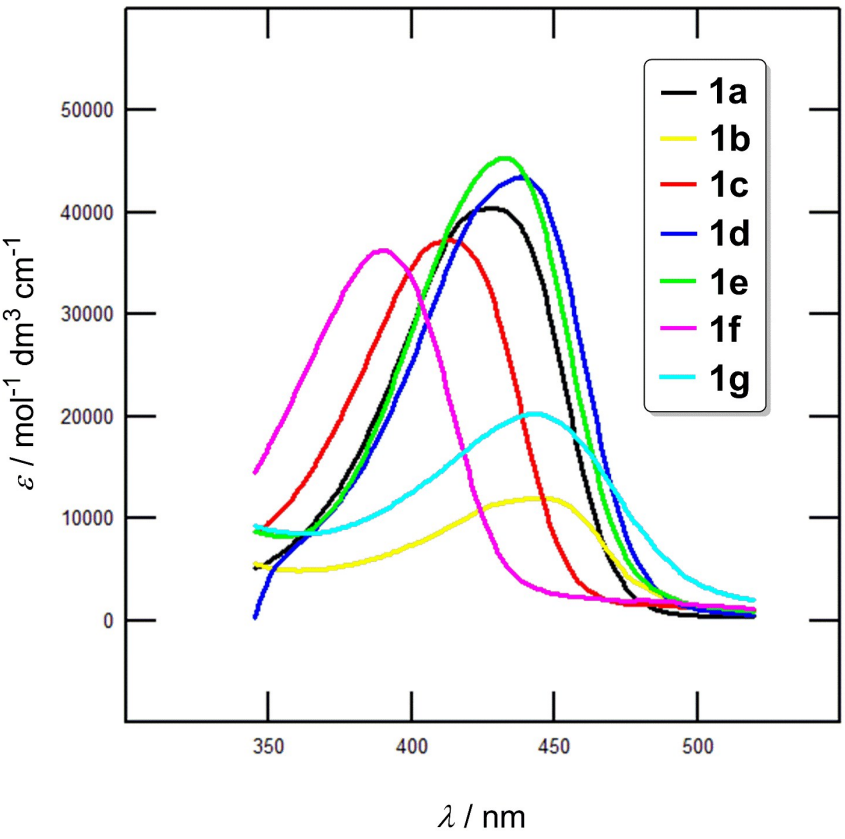


^{13}C APT NMR spectrum (125 MHz, 25 °C, $CDCl_3$) of **5**

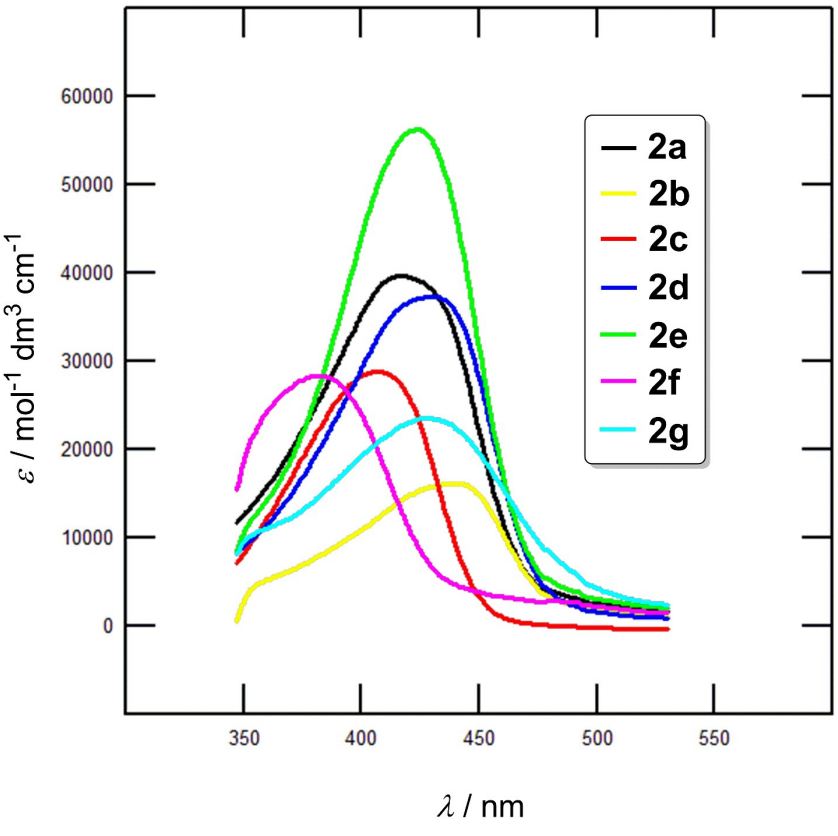


UV-VIS absorption spectra

UV-VIS absorption spectra of chromophores **1a** – **g** in DMF at concentration 1×10^{-5} M

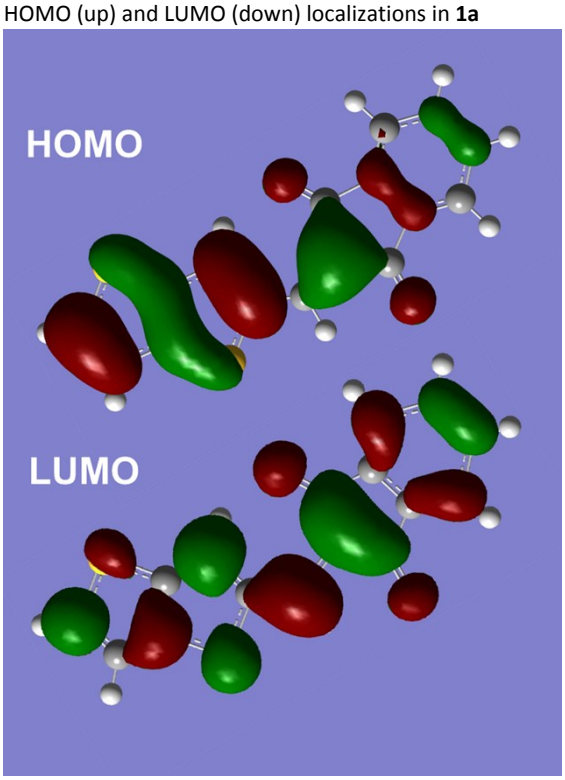


UV-VIS absorption spectra of chromophores **2a** – **g** in DMF at concentration 1×10^{-5} M

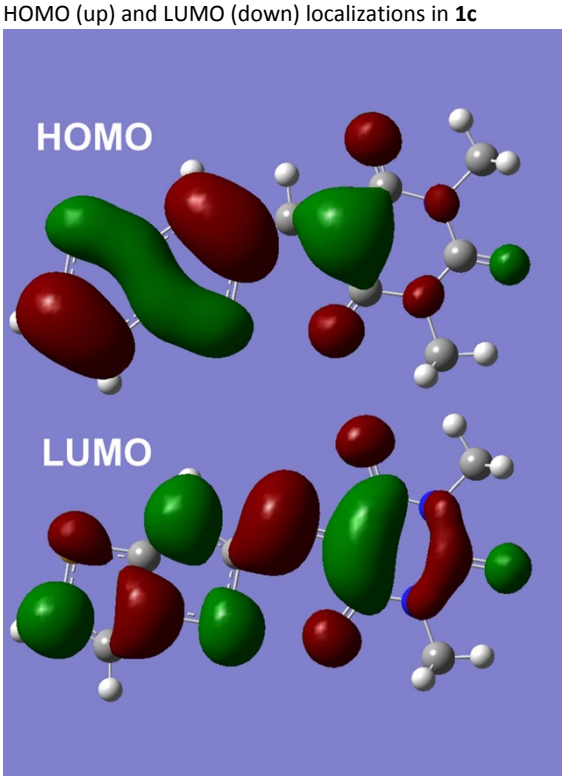


HOMO and LUMO visualization created by Gaussian® 16

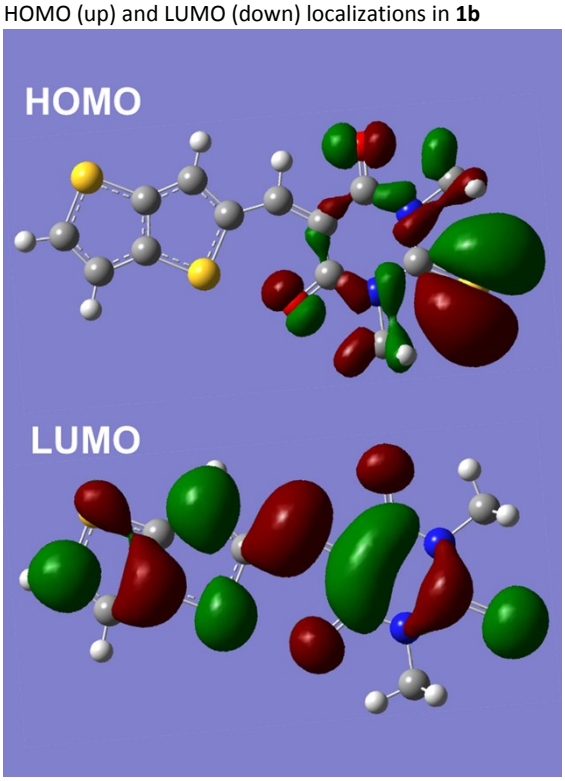
HOMO (up) and LUMO (down) localizations in **1a**



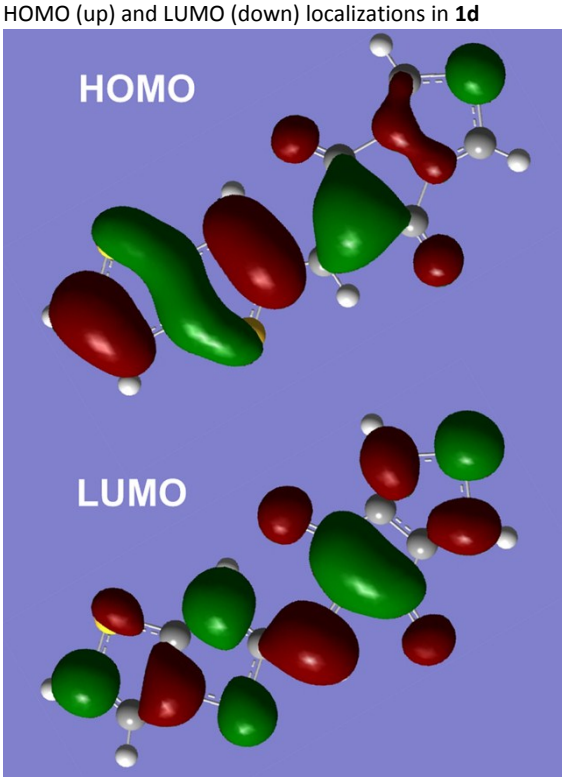
HOMO (up) and LUMO (down) localizations in **1c**



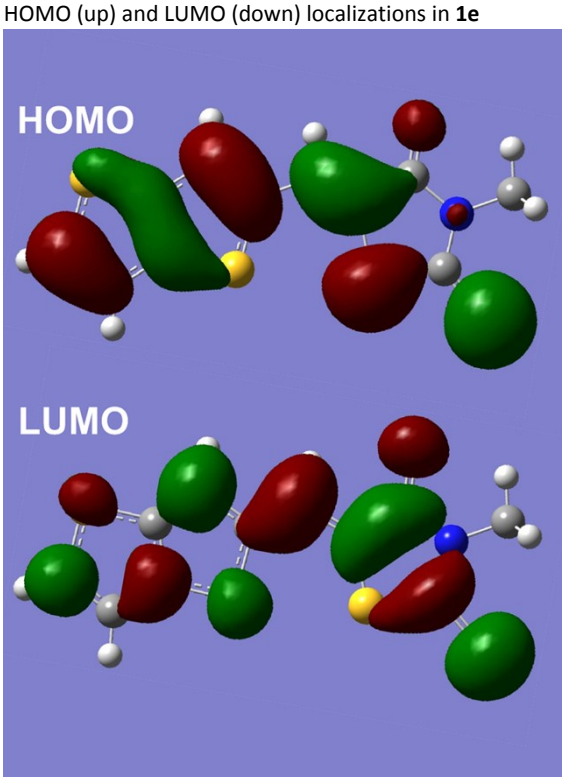
HOMO (up) and LUMO (down) localizations in **1b**



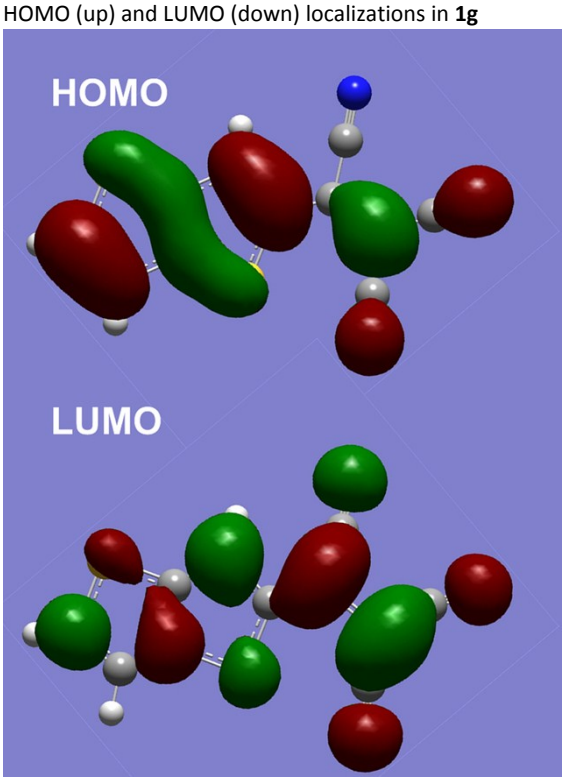
HOMO (up) and LUMO (down) localizations in **1d**



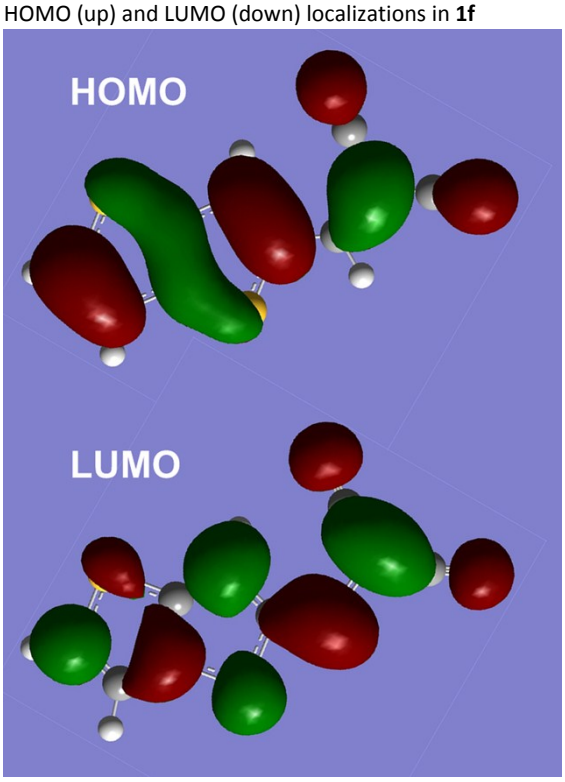
HOMO (up) and LUMO (down) localizations in **1e**



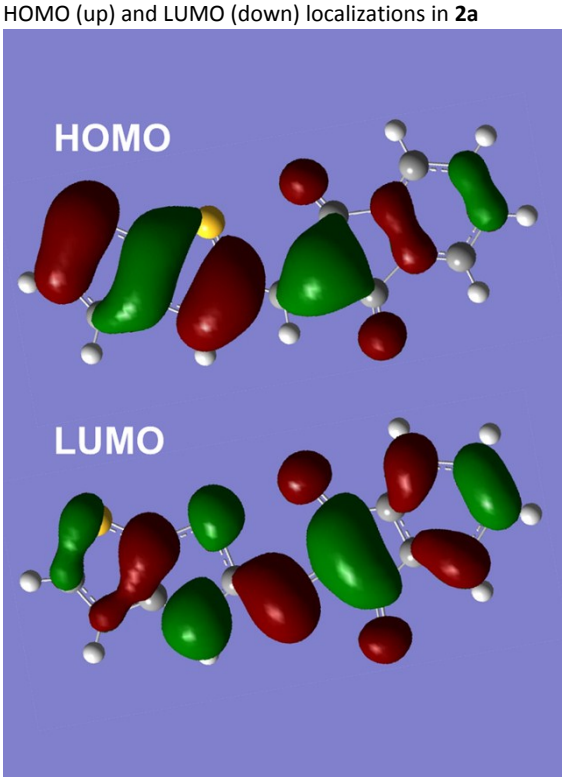
HOMO (up) and LUMO (down) localizations in **1g**



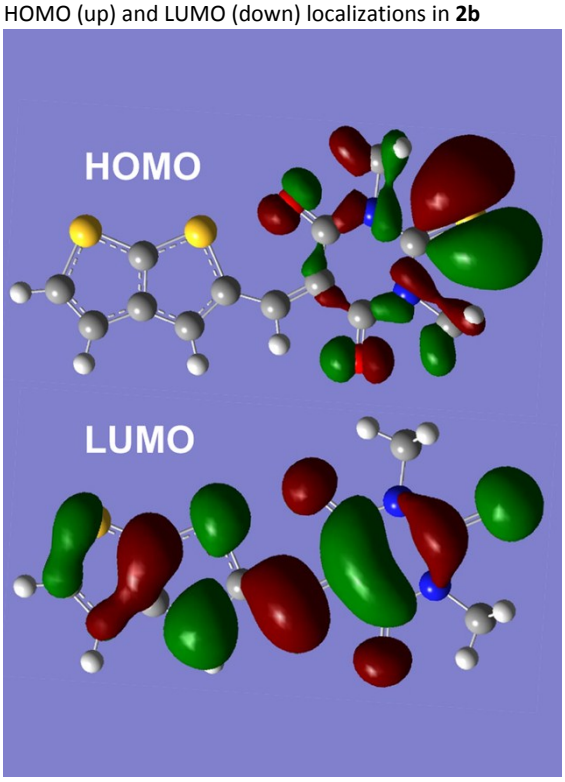
HOMO (up) and LUMO (down) localizations in **1f**



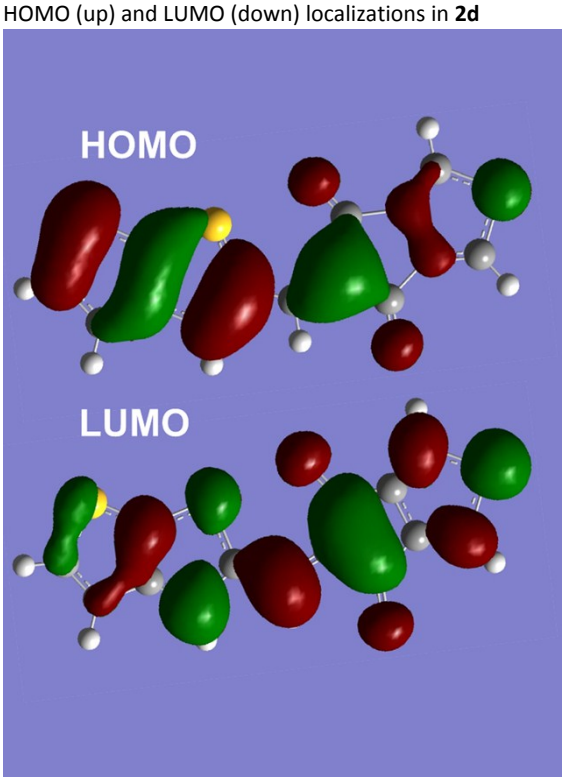
HOMO (up) and LUMO (down) localizations in **2a**



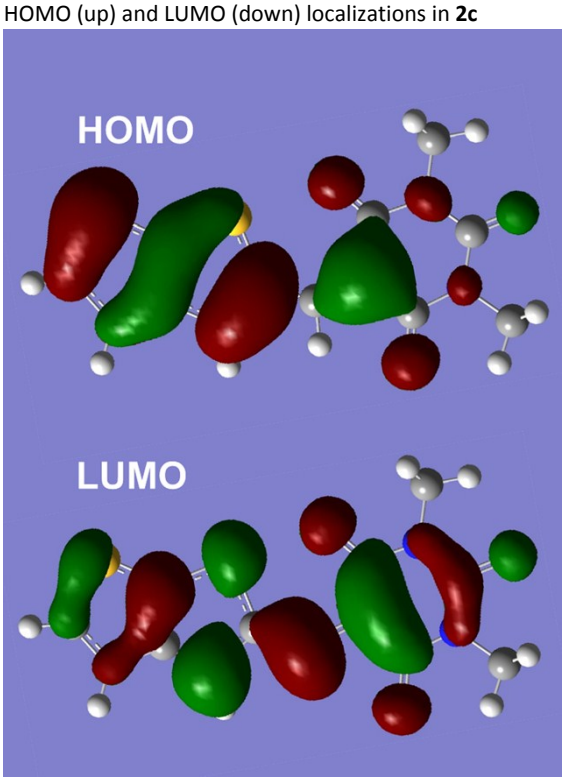
HOMO (up) and LUMO (down) localizations in **2b**



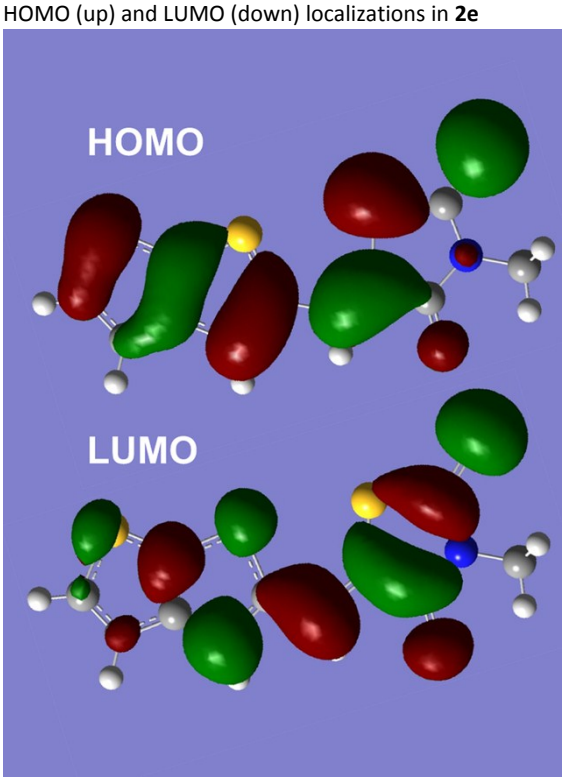
HOMO (up) and LUMO (down) localizations in **2d**



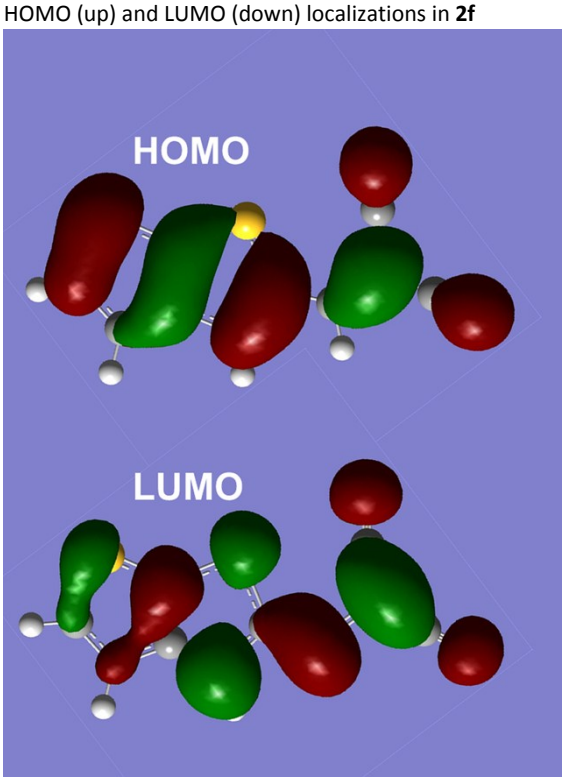
HOMO (up) and LUMO (down) localizations in **2c**



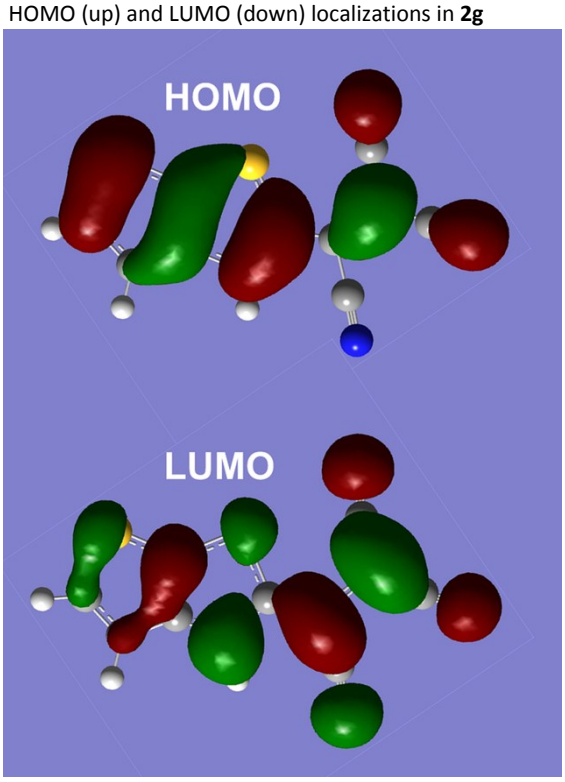
HOMO (up) and LUMO (down) localizations in **2e**



HOMO (up) and LUMO (down) localizations in **2f**

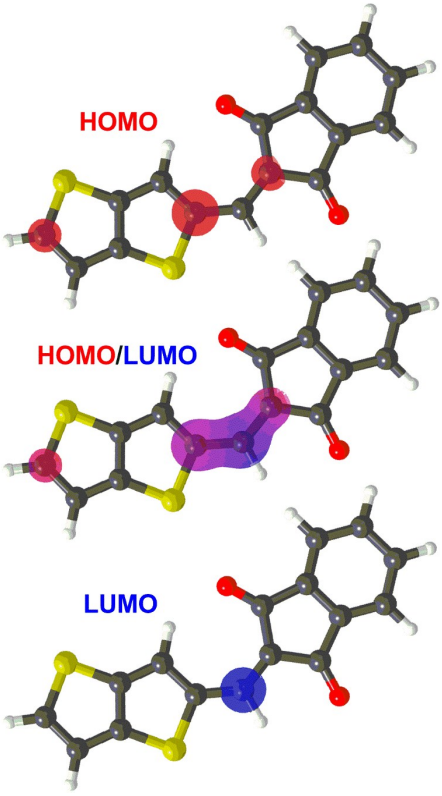


HOMO (up) and LUMO (down) localizations in **2g**

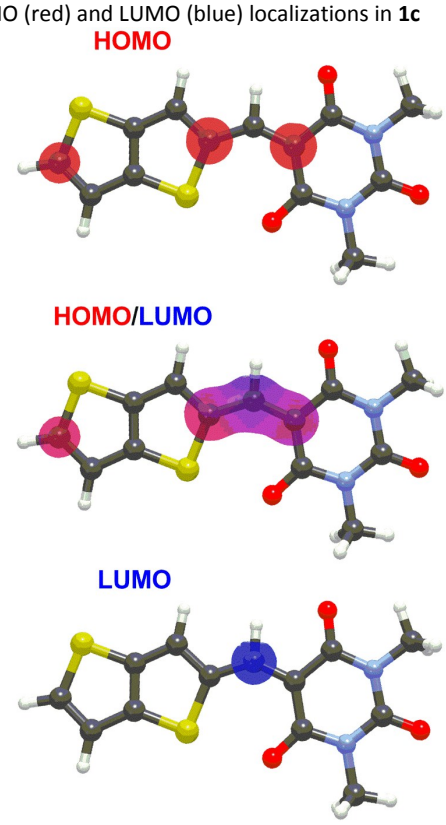


HOMO and LUMO visualization created by OPChem 8.6

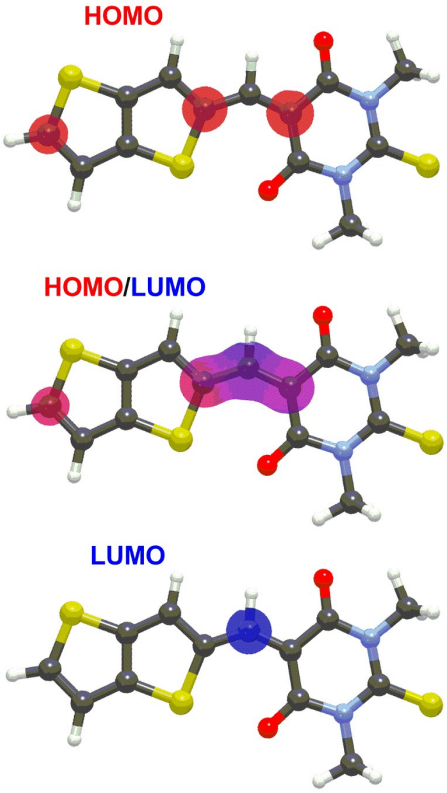
HOMO (red) and LUMO (blue) localizations in **1a**



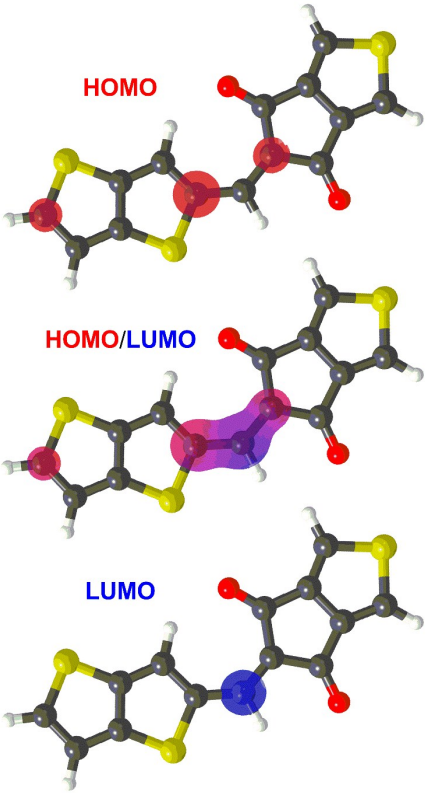
HOMO (red) and LUMO (blue) localizations in **1c**



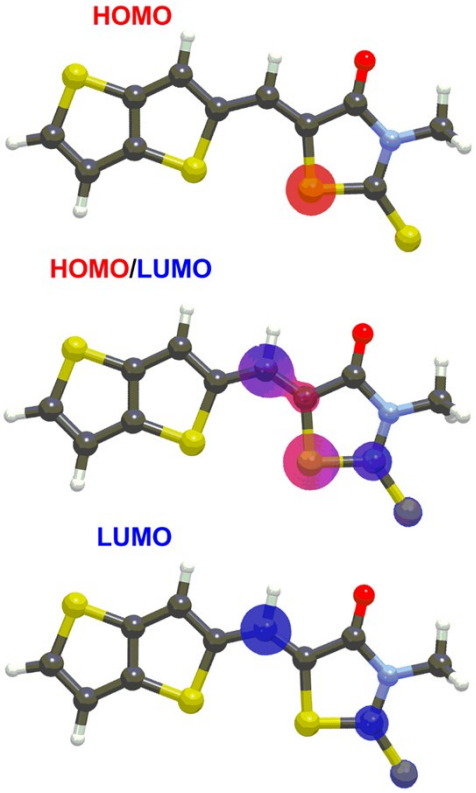
HOMO (red) and LUMO (blue) localizations in **1b**



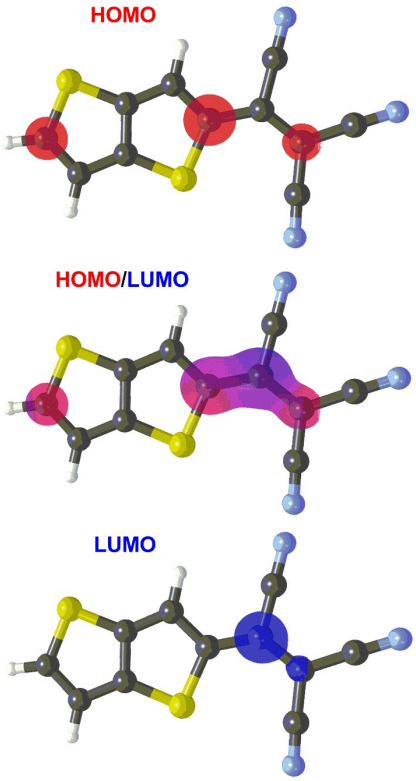
HOMO (red) and LUMO (blue) localizations in **1d**



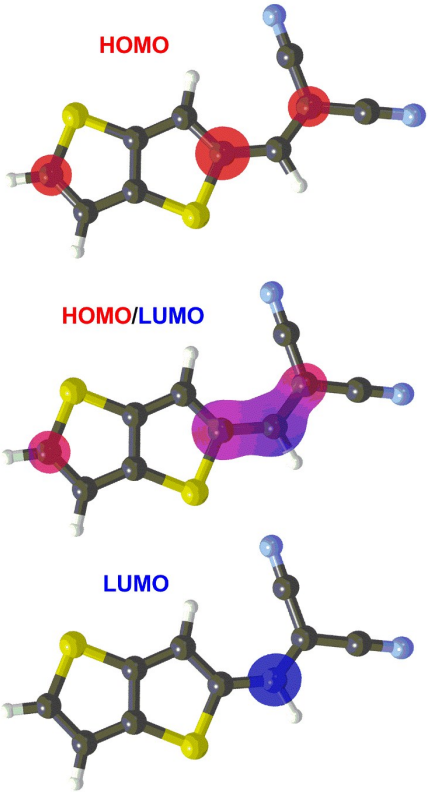
HOMO (red) and LUMO (blue) localizations in **1e**



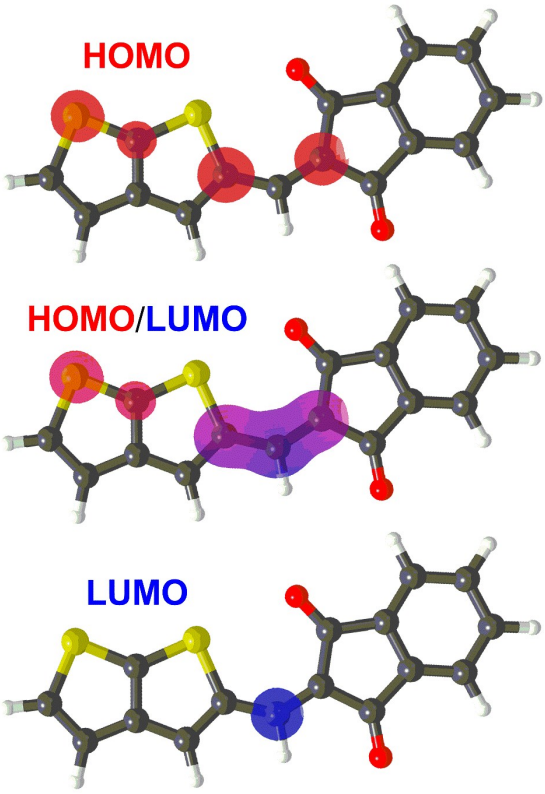
HOMO (red) and LUMO (blue) localizations in **1g**



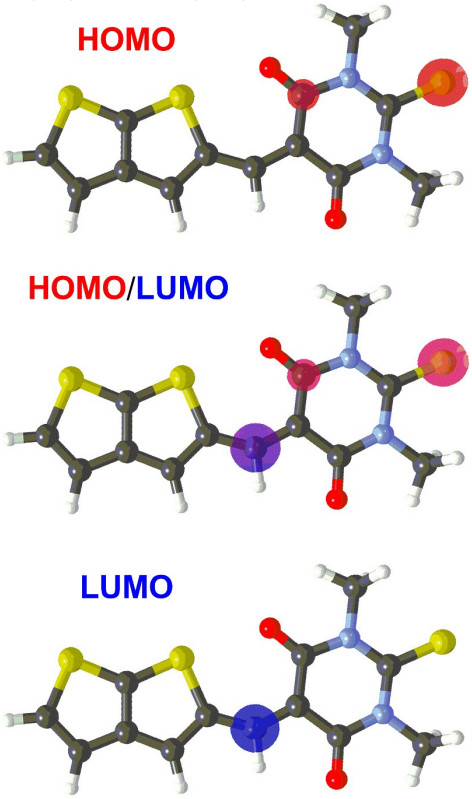
HOMO (red) and LUMO (blue) localizations in **1f**



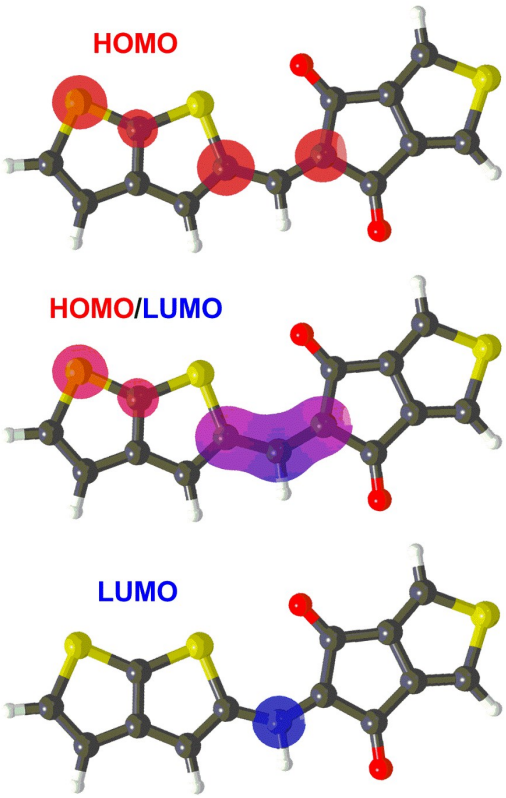
HOMO (red) and LUMO (blue) localizations in **2a**



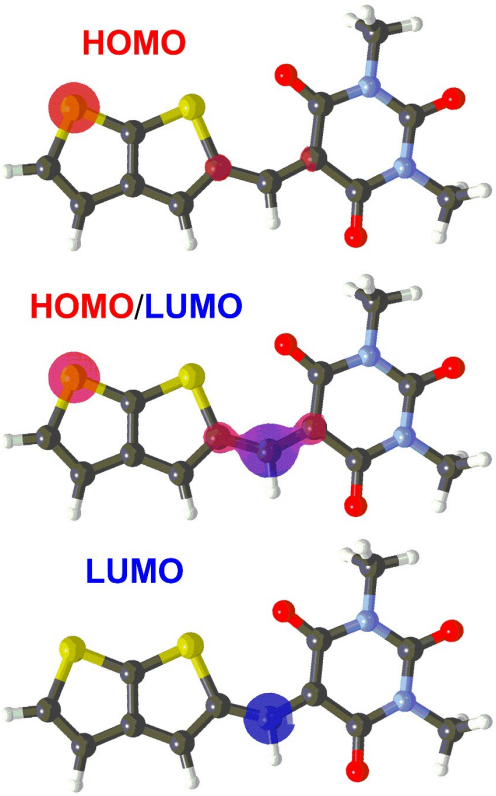
HOMO (red) and LUMO (blue) localizations in **2b**



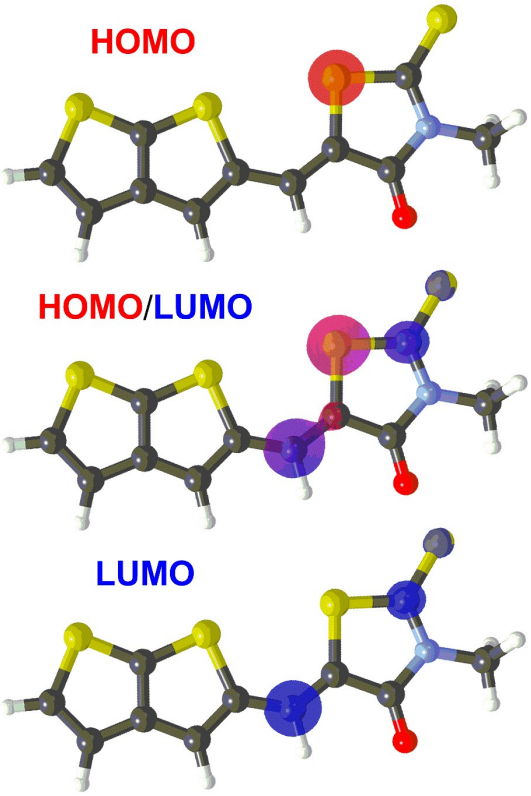
HOMO (red) and LUMO (blue) localizations in **2d**



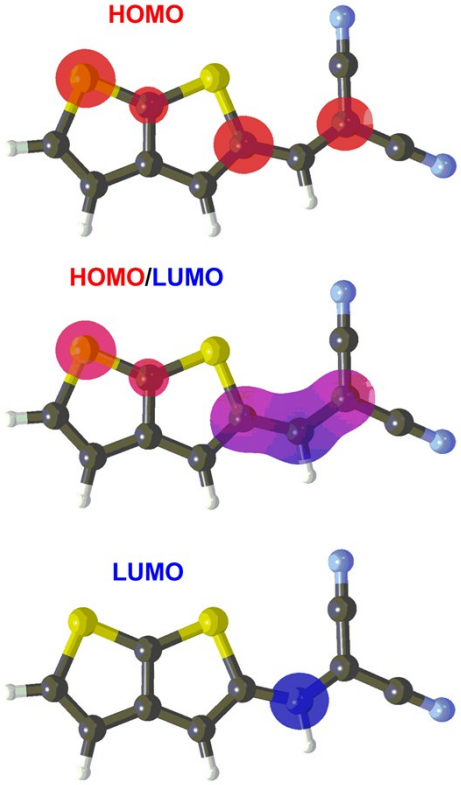
HOMO (red) and LUMO (blue) localizations in **2c**



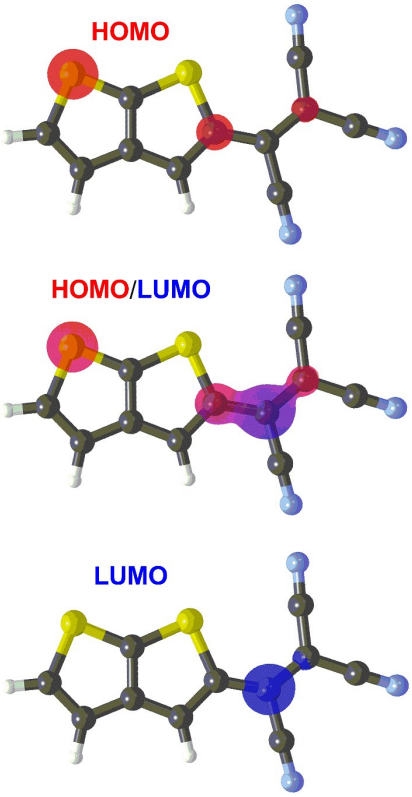
HOMO (red) and LUMO (blue) localizations in **2e**



HOMO (red) and LUMO (blue) localizations in **2f**

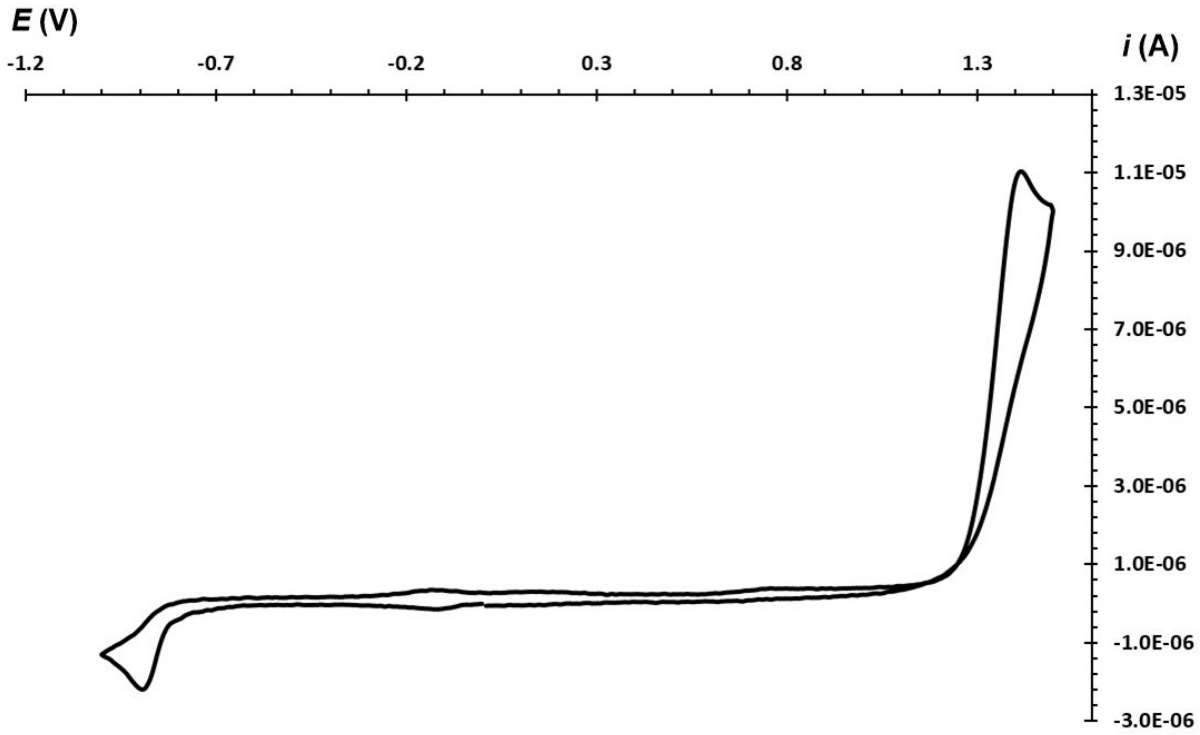


HOMO (red) and LUMO (blue) localizations in **2g**

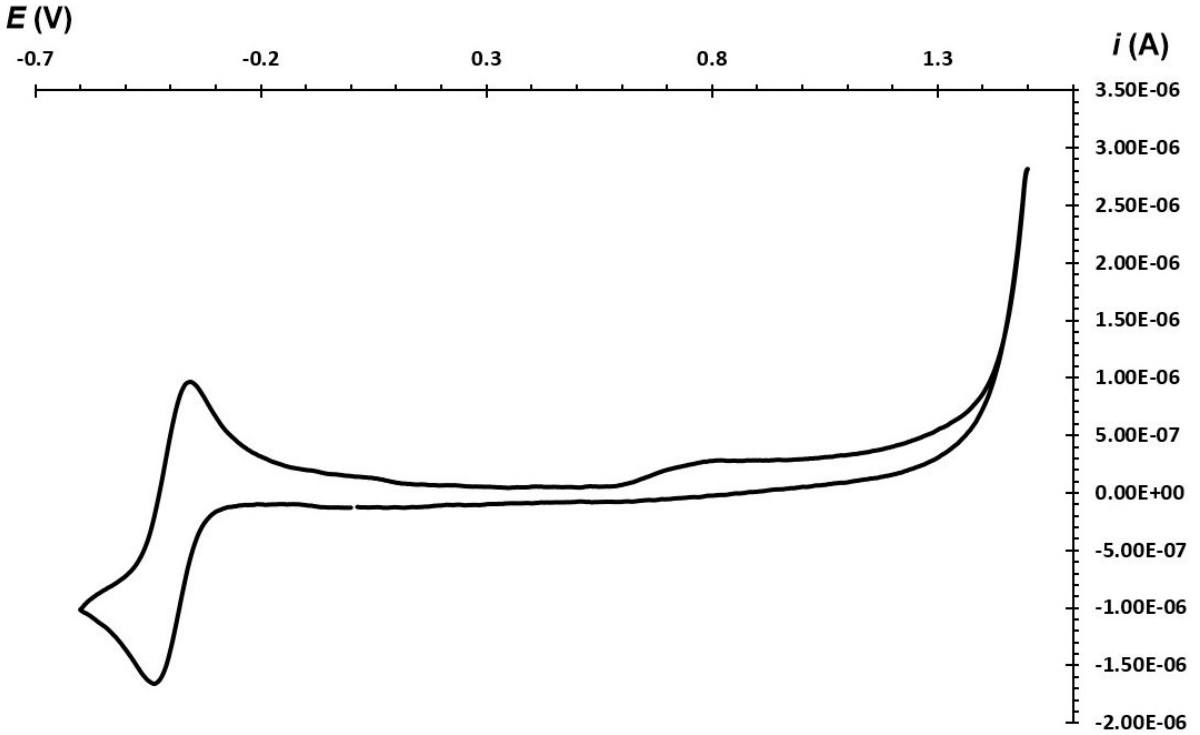


Electrochemistry

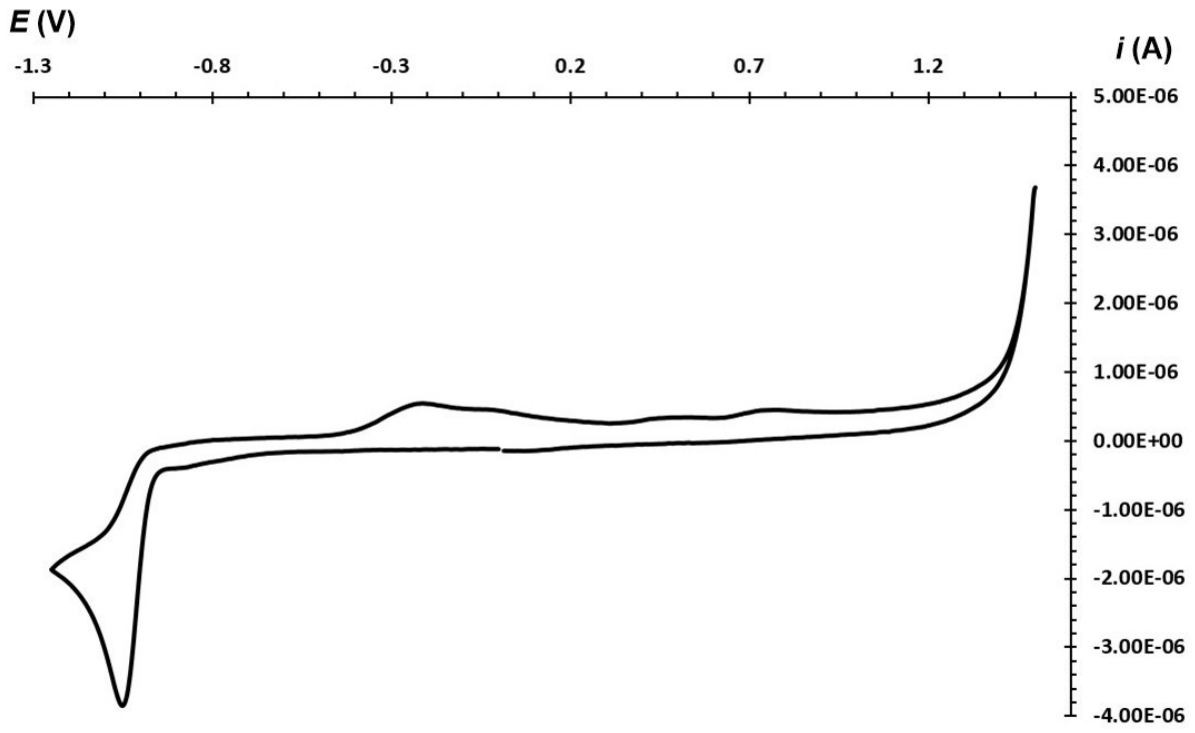
Representative CV curve of the irreversible oxidation and irreversible reduction of compound **1d** at glassy C electrode in *N*,*N*-dimethylformamide containing 0.1 M Bu_4NBF_4; scan rate 50 mV/s



Representative CV curve of the reversible reduction of compound **1g** at glassy C electrode in *N*,*N*-dimethylformamide containing 0.1 M Bu_4NBF_4; scan rate 50 mV/s (oxidation out of DMF potential window)

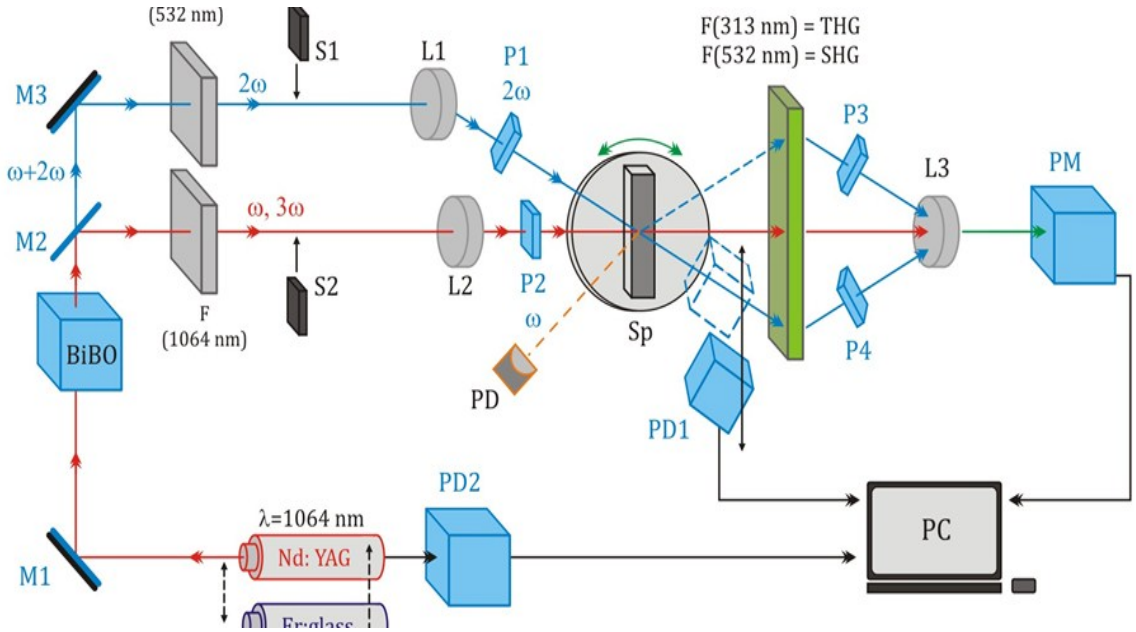


Representative CV curve of the irreversible reduction of compound **2f** at glassy C electrode in *N*,*N*-dimethylformamide containing 0.1 M Bu_4NBF_4; scan rate 50 mV/s (oxidation out of DMF potential window)



NLO measurements

Experimental set-up for measuring NLO properties



Nanosecond pulsed lasers have been used as the fundamental lasers for photo induced SHG and THG. For convenience of readers, these two methods are depicted jointly in the figure above. The fundamental laser beam of pulsed Nd:YAG laser (7 ns, power energy up to 90 mJ; with beam diameters varying within 2 – 4 mm) has been used for the photoinduced second harmonic generation (PISHG). It has been formed by a set of mirrors **M1**, **M2** and **M3**. This fundamental beam was split into two channels and in one of them it was doubled by frequency using α-BiB_3O_6 SHG crystals.[7] Both coherent beams have been propagated by two coherent channels after they have been propagated through a set of mirrors **M2** and **M3**. A set of interferometer filters at 528, 532 and 536 nm for writing channel (2ω) as well as fundamental 1064 nm (ω) allowed elimination of parasitic scattering background. A set of lenses **L1** and **L2** and Glan polarizer **P1** and **P2** formed a nonlinear interference of the mentioned beams on the surfaces of the specimens **Sp**. A laser treatment of the samples has been done for several minutes; the process was monitored by intensities of the diffraction maxima. Finally, diffraction space gratings patterns were occurred as monitored by continuous wave He-Ne laser at 633 nm (15 mW). Additionally, the Ge-photodiode controlled scattering background in space was applied. As a rule, the optically polarized treatment was saturated after 3 min and the relaxation process was observed during several upcoming hours. After the formation of the gratings, the writing 2ω channel was closed by shutter **S1** and the SHG was detected by usual method for the nonlinear optical acentric crystals. The photodetectors **PD** with relaxation time of 1 ns and **CCD** have been applied for intensity and space monitoring of the SHG. The temporary metrics of the pulses was analyzed using an oscilloscope Tektronix, which allows to perform control of SHG kinetics with 1.5 ns time resolution. In order to eliminate some parasitic background from the fundamental laser, due to filter power density limitation, we have performed angle dependent SHG studies of

the **PM** remote sensing with respect to the output beam propagation. The treatment by two bicolor coherent beams at 1064 nm and 532 nm with different intensities has been done up to 3 min.

The THG was measured using only channel **M2** and **L3**. Nanosecond Er:glass laser at wavelength 1540 nm and filters at 514 nm were used to separate the THG signal. The maximal output signals for the SHG and THG were obtained for the s-p light polarization. The Er:Yb glass laser EY-13-2014 was manufactured as a variable pulsed module with passive Q switching, which allowed to vary the laser pulse duration time within 25 – 180 ns and pulse frequency repetition within 120 – 900 Hz. The diameter of the beam was varied within 0.8 – 1.7 mm. The samples were prepared in a form of the powders embedded between the optical glasses. Additionally, chromophore placed into the photopolymer oligoether matrices (size up to 70 μm) with the applied dc-aligned electric field were also measured. So, we have measured effective integrated changes of the THG intensities $I(3\omega)$, which are proportional to the output third order optical susceptibilities similarly to that described in our earlier work.[8]

References:

1 L. S. Fuller, B. Iddon and K. a Smith, *J. Chem. Soc., Perkin Trans.*, 1997, **1**, 3465–3470.

2 M. M. M. Raposo, C. Herbivo, V. Hugues, G. Clermont, M. C. R. Castro, A. Comel and M. Blanchard-Desce, *Eur. J. Org. Chem.*, 2016, 5263–5273.

3 L. J. Nurkkala, R. O. Steen and S. J. Dunne, *Synthesis*, 2006, 1295–1300.

4 J. D. Prugh, G. D. Hartman, P. J. Mallorga, B. M. Mckeever, S. R. Michelson, M. A. Murcko, H. Schwam, R. L. Smith, J. M. Sondey, J. P. Springer and M. F. Sugrue, *J. Med. Chem.*, 1991, 1805–1818.

5 M. S. Egbertson, J. J. Cook, B. Bednar, J. D. Prugh, R. A. Bednar, S. L. Gaul, R. J. Gould, G. D. Hartman, C. F. Homnick, M. A. Holahan, L. A. Libby, J. J. Lynch, R. J. Lynch, G. R. Sitko, M. T. Stranieri and L. M. Vassallo, *J. Med. Chem.*, 1999, **42**, 2409–2421.

6 A. Comel and G. Kirsch, *J. Heterocycl. Chem.*, 2001, 1167–1171.

7 V. Petrov, M. Ghotbi, O. Kokabee, A. Esteban-Martin, F. Noack, A. Gaydardzhiev, I. Nikolov, P. Tzankov, I. Buchvarov, K. Miyata, A. Majchrowski, I. V. Kityk, F. Rotermund, E. Michalski and M. Ebrahim-Zadeh, *Laser Photonics Rev.*, 2010, **4**, 53–98.

8 Y. Slyvka, A. A. Fedorchuk, E. Goreshnik, G. Lakshminarayana, I. V. Kityk, P. Czaja and M. Mys'kiv, *Chem. Phys. Lett.*, 2018, **694**, 112–119.