Photochromic Coenzyme Q Derivatives: Switching Redox Potentials with Light

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Supporting Information

Contents

1. General preliminary remarks

a) General working methods

All reactions were performed using magnetic stirring under ambient atmosphere unless otherwise specified. Reactions requiring anhydrous conditions were carried out under dry nitrogen or argon atmosphere using standard Schlenk techniques. Oxygen sensitive reactions were degassed under vacuum and performed under nitrogen or argon atmosphere or deaerated through argon bubbling.

All reagents and solvents were obtained from commercial suppliers and used without further purification if not otherwise stated.

For TLC, silica coated aluminum plates (Merck $60F^{254}$ silica gel, 0.2 mm) were utilized. Visualization was done with UV light at 254 or 366 nm or through suitable staining.

b) Isolation of compounds

For MPLC a Biotage Isolera One Flash Purification System with manually packed columns using Merck Geduran SI 60 (70-230 grain diameter) or Macherey- Nagel GmbH & Co. KG 60M (0.04-0.063 mm, 230-400 grain diameter) was utilized.

c) Analysis

Nuclear magnetic resonance spectroscopy (NMR) was carried out using a Bruker Avance 300 MHz spectrometer (^{1}H: 300 MHz, ^{13}C: 75 MHz, T = 300 K), a Bruker Avance 400 MHz spectrometer (^{1}H: 400 MHz, ^{13}C: 101 MHz, T = 300K) or a Bruker Avance 600 MHz spectrometer (^{1}H: 600 MHz, ^{13}C: 151 MHz, T = 300 K). Chemical shifts are reported in δ [ppm] relative to an internal standard (solvent residual peak). The used solvents are indicated for each spectrum. Coupling constants are reported in Hertz [Hz]. Characterization of the signals: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, bs = broad singlet, dd = doublet of doublet, dt = doublet of triplet. Integration is directly proportional to the number of the protons. Characterization of the ^{13}C-NMR signals: (+) for CH3 or CH, (-) for CH2 and (q) for quaternary C-atoms. The assignment resulted from DEPT135, ATP, HMBC, HSQC and NOESY experiments.

CV measurements and spectroelectrochemical studies were carried out under argon atmosphere. All measurements were performed in MeCN containing 0.1 M tertra ^{n}butylammonium tertra fluoroborate using ferrocene/ferrocenium (Fc/Fc+) as an internal reference. A glassy carbon electrode (working electrode), platinum wire counter electrode, and Ag quasi-reference electrode were employed for CV measurements. The scan rate was 50 mV/s, a step potential of 5.0 mV was applied. Spectroelectrochemical studies were carried out in an optically transparent thin layer electrochemical cell (OTTLE). The scan rate was 2 mV/s, a step potential of 0.02 V was applied.

IR spectroscopy was done using an Agilent Cary 630 FTIR. Melting points were recorded on a Stanford Research Systems OptiMelt (MPA100).

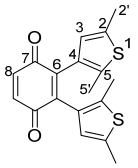
Steady state absorption measurements were carried out on a Varian Cary Bio 50 UV/Vis spectrometer. The used solvent is stated for each experiment. UV-induced isomerizations were performed at ambient temperature using a Herolab hand-lamp (254 nm, 2x8W or 312 nm, 1x6W) or an OSRAM Oslon SSL 80 single-spot LED (590 nm, 0.7 W). Sample volume was 2.5 mL. Photo stationary distribution as well as monitoring of photoactivated oxidation experiments was analyzed through separation on an 1220 Infinity LC System from Agilent with a reverse phase Phenomenex Luna® 3µ C18(2) column (150 × 2.0 mm, 100 Å) thermostatted at 40 °C. HPLC conditions were the following: solvent A = water (Millipore)/TFA (0.05% v/v), solvent B = MeCN (Fisher scientific, gradient grade); flow rate = 0.3 mL/min; injection volume 0.5 µL, elution with a gradient of 30% to 98% MeCN in 25 min for purity (220 nm, VWD detector) and 40% to 98% MeCN in 20 min for photoactivated oxidation monitoring and PSS (isosbestic point @317 nm, VWD detector).

2. Synthesis

2.1. Compound **1a**: 2,3-Bis(2,5-dimethylthiophen-3-yl)cyclohexa-2,5-diene-1,4-dione

Chemical Formula: $C_{18}H_{16}O_2S_2$

Molecular Weight: 328.44



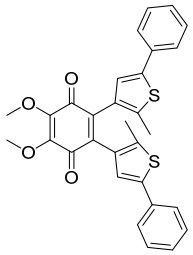
A crimp top vial was equipped with **8a** (97 mg, 0.36 mmol), **6a** (591 mg, 1.47 mmol), CuI (30 mg, 0.16 mmol) and dry toluene (7 mL) under nitrogen. The vial was deaerated through argon bubbling for five minutes. Then $Pd(PPh_3)_4$ (173 mg, 0.15mmol) was added and the vial was sealed and heated to 85 °C for 16h. The reaction mixture was cooled to room temperature and the solvent was removed *in vacuo*. The residue was dissolved in EtOAc (5 mL), a saturated KF solution (aq, 5 mL) was added and the mixture was stirred for one hour. The reaction mixture was filtered to remove precipitated Bu_3SnF and the organic layer was isolated. The aqueous layer was extracted with EtOAc (2 x 10 mL). The combined organic layers were dried over $MgSO_4$ and the solvent was removed *in vacuo*. The crude product was purified through MPLC (PE : EtOAc = 0 to 20%). The pure product was isolated as brown solid.

Yield:	12 mg, 0.04 mmol, 10%.
^{1}H-NMR:	δ_H(400 MHz, CDCl3): 6.76 (s, 2H, H8), 6.63 (d, *J* = 1.3 Hz, 2H, H3), 2.46 (s, 6H, H2'), 2.34 (s, 6H, H5').
^{13}C-NMR:	δ_C(101 MHz, CDCl3): 146.4 (s, C7) , 137.6 (s, C2), 134.8 (s, C5), 132.3 (s, C4) , 126.9 (s, C3), 123.4 (s, C6), 116.4 (s, C8), 15.2 (s, C2') , 13.8 (s, C5').
ESI-MS:	found: 331.08 (reduced form; MH^+, 100%).
HR-MS:	found: 329.0665 (MH^+, 100%).
R_f:	0.85 (30% PE in EA).

2.2. Compound **1b**^{o}: 2,3-Dimethoxy-5,6-bis(2-methyl-5-phenylthiophen-3-yl)cyclohexa-2,5-diene-1,4-dione

Chemical Formula: $C_{30}H_{24}O_4S_2$

Molecular Weight: 512.11



Compounds **5b** (1.42 g, 3.97 mmol), **8a** (522 mg, 1.59 mmol) and CuI (30 mg, 0.16 mmol) were dissolved in dry toluene (25 mL) under Argon atmosphere. The solution was deaerated through Argon bubbling for 5 min and $Pd(PPh)_3$ (183 mg, 0.16 mmol) was added. The vial was sealed and the reaction mixture was refluxed for 16h. The reaction mixture was cooled to room temperature and the solvent was removed *in vacuo*. The residue was dissolved in EtOAc (10 mL), a saturated KF solution (aq, 10 mL) was added and the mixture stirred for one hour. The reaction mixture was filtered to remove precipitated Bu_3SnF and the organic layer was isolated. The aqueous layer was extracted with EtOAc (2 x 20 mL). The organic layers were combined and dried over Na_2SO_4. The volatiles were removed *in vacuo* and the crude product was purified through MPLC (EA (0-55%) in PE) to give a red solid. For biological testing the sample was further purified through reversed phase MPLC (C18, 0.05% TFA in H_2O/MeCN, gradient 65 to 100%).

Yield: 560 mg, 1.04 mmol, 29%.

^{1}H-NMR: δ_H(600 MHz, CDCl3): 7.44 – 7.40 (m, 4H, phenyl), 7.34 – 7.28 (m, 4H), 7.24 (d, J = 7.3 Hz, 4H, phenyl), 6.83 (s, 2H, thiophene), 4.11 (s, 6H, methoxy), 2.07 (s, 6H, methyl).

^{13}C-NMR: δ_C(151 MHz, CDCl3): 183.2 (+), 144.6 (+), 140.3 (+), 139.6 (+), 138.00 (+), 134.0 (+), 130.1 (+), 128.8 (+), 127.3 (+), 125.7 (+), 125.3 , (+) 61.4 (+, methoxy), 14.9 (+, methyl).

FTIR: $\tilde{\nu}$(cm^{-1}): 2937, 1655, 1592, 1256, 1070, 757, 693.

HR-MS: found: 513.1187 (100%).

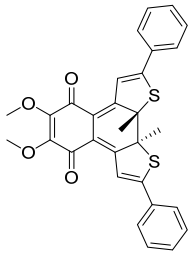
Melting point: 137 °C.

R_f: 0.65 (PE: EA = 1:1).

2.3. Compound **1b**[c]: (10a,10b)-5,6-Dimethoxy-10a,10b-dimethyl-2,9-diphenyl-10a,10b-dihydronaphtho[2,1-b:3,4-b']dithiophene-4,7-dione

Chemical Formula: $C_{30}H_{24}O_4S_2$

Molecular Weight: 512.11



Compound **9b**[o] (29 mg, 0.06 mmol) was dissolved in DMSO (5 mL) and effused into a Petri dish. The solution was irradiated for 4h with a 312 nm hand-lamp and then directly injected onto a reversed phase column. The compound could be isolated through elution with 0.05% TFA in H_2O/MeCN (reversed phase MPLC, C18, gradient 65 to 100%) to give a blue solid.

Yield: 9 mg, 0.01 mmol, 13%.

^{1}H-NMR: δ_H(400 MHz, CDCl3): 8.24 (s, 2H, thiophene), 7.83 – 7.61 (m, 4H, phenyl), 7.45 (dd, *J* = 5.2, 1.9 Hz, 6H, phenyl), 4.08 (s, 6H, methoxy), 2.09 (s, 3H, methyl).

HR-MS: found: 513.1185 (100%).

2.4- Compound **5a**: 3-Bromo-2,5-dimethylthiophene

Molecular formula: C_6H_7BrS

Molecular weight: 191.09 g/mol

Compound **2** (2.0 mL, 17.54 mmol, 1.0 eq) was dissolved in glacial acetic acid (50 mL). NBS (3120 mg, 17.54 mmol, 1.0 eq) was added in portions. The reaction mixture was stirred for 2h at ambient temperature. The solution was poured onto ice water (50 mL) and extracted with DCM (3 x 8 mL). The combined organic phases were dried over $MgSO_4$. The solvent was evaporated *in vacuo*. The crude product was purified through MPLC (PE). The pure product was obtained as translucent oil.

Yield: 2213 mg (11.58 mmol), 66%.

^{1}H-NMR: δ_H (300 MHz, $CDCl_3$): 2.35 (s, 3H, CH3 thiophene), 2.42 (s, 3H, CH3 thiophene), 6.57 (s, 1H, CH thiophene).

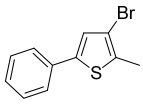
R_f: 0.92 (PE).

The analytical data were in agreement with published data.[1]

2.5. Compound **5b**: 3-Bromo-2-methyl-5-phenylthiophene

Chemical Formula: $C_{11}H_9BrS$

Molecular Weight: 253.16



A crimp top vial was equipped with **4** (3390 mg, 13.25 mmol), phenyl boronic acid (1651 mg, 13.52 mmol), $Pd(PPh_3)_2Cl_2$ (88 mg, 0.13 mmol), $AsPh_3$ (69 mg, 0.23 mmol), THF (39 mL) and a Na_2CO_3 solution (aq, 2M, 16 mL) and sealed. The vial was purged with argon for five minutes and the reaction mixture was heated to 80 °C for 16h. The mixture was cooled to room temperature and extracted with EtOAc (2 x 40 mL). The organic layers were combined and dried over $MgSO_4$. The solvent was removed *in vacuo* and the crude product was purified through MPLC (PE). The pure product was isolated as white crystalline powder.

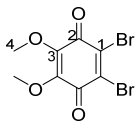
Yield: 2700 mg, 10.67 mmol, 80%

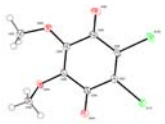
The analytical data were in agreement with published data.[2]

2.6. Compound **9b**: 2,3-Dibromo-5,6-dimethoxycyclohexa-2,5-diene-1,4-dione

Chemical Formula: $C_8H_6Br_2O_4$

Molecular Weight: 325.94





Compound **8b** (768 mg, 4.57 mmol) was dissolved in dry Et_2O (21 mL) under nitrogen atmosphere. Bromine (2773 mg, 17.35 mmol, 0.90 mL) was dissolved in a mixture of $CHCl_3$ (10 mL) and dry Et_2O (2.3 mL) and added dropwise to the reaction mixture at 0 °C. The reaction mixture was stirred for one hour at ambient temperature; then, concentrated sulfuric acid (23 mL) was added dropwise at 0 °C. The reaction mixture was stirred at ambient temperature for another hour and then poured onto ice. The mixture was extracted with Et_2O (3 x 50 mL). Ag_2O (5503 mg, 23.75 mmol) was added to the combined organic layers and stirred for 20 min. The solids were filtered off and the solvent was removed *in vacuo*. The crude product was purified through reversed phase MPLC (C18; H_2O/0.05% TFA : MeCN = 30 to 65 %). The pure product was obtained as red powder and crystallized for analytical purpose from $CHCl_3$/PE.

Yield: 826 mg, 2.54 mmol, 55%.

^{1}H-NMR: δ_H(600 MHz, CDCl3): 4.04 (s, 6H, H4).

^{13}C-NMR: δ_C(101 MHz, CDCl3): 174.7 (s, C2), 145.0 (C3) , 137.2 (C1), 61.7 (s, C4).

FTIR: $\tilde{\nu}$(cm^{-1}): 2948, 1625, 1662, 1562, 936, 731.

APCI-MS: found: 324.87 (MH^+, ^{79}Br, 50%), 326.87 (MH^+, $^{79}Br/^{81}Br$, 100%), 328.87 (MH^+, ^{81}Br, 50%)

HR-MS: 323.8625 ($M^{+\bullet}$,^{79}Br).

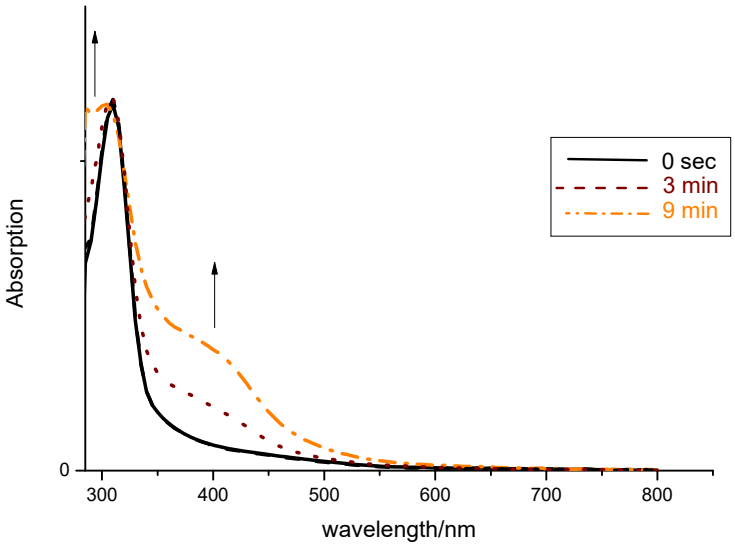
Melting point: 102 °C.

R_f: 0.74 (PE : EA = 1:1).

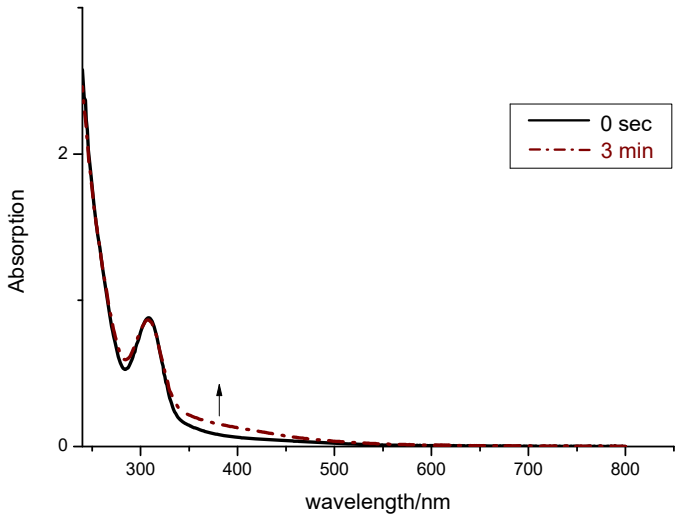
3. UV/Vis Spectroscopy: Further spectra

Compound **1a**^{o}

- Compound **1a**^{o} in toluene



- Compound **1a**^{o} in DCM

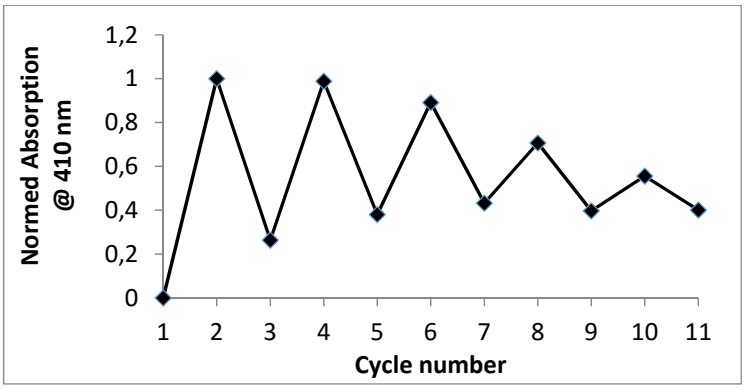


Compound **1b^o**

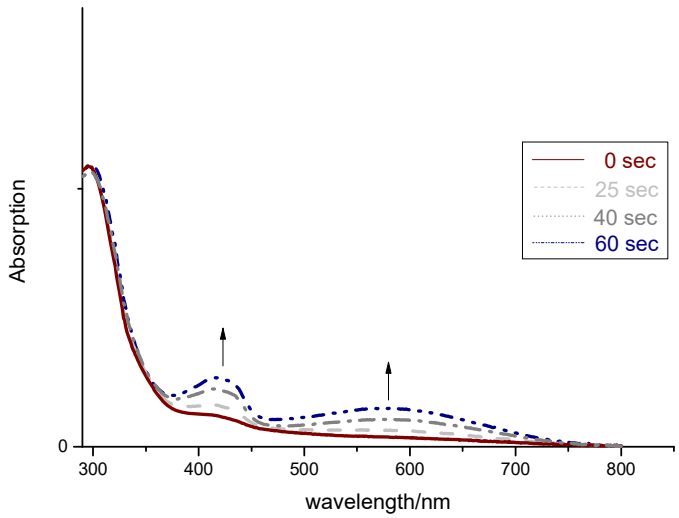
Table 1: Overview of spectroscopic properties of compound **1b^o** determined by UV/Vis spectroscopy and analytical HPLC.

Solvent	λ_{max} 1b^o [nm]	λ_{max} 1b^c [nm]	PSS [%]
MeCN	247, 297	307, 415, 582	20
DMSO	302	304, 410, 594	52
Toluene	298	296, 413, 580	47
Dioxane	301	294, 399, 595	42

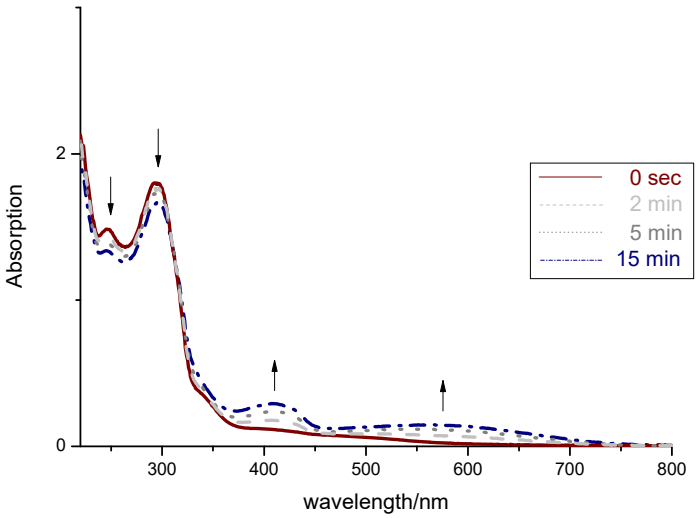
- Compound **1b^o** in DMSO, fatigue resistance



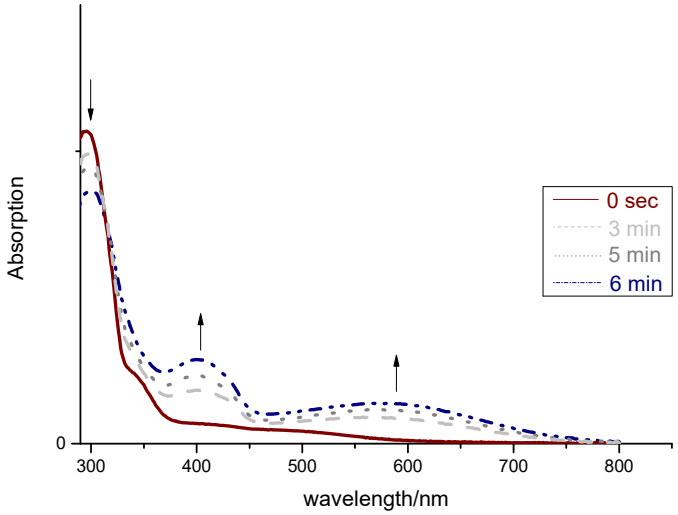
- Compound **1b^o** in toluene



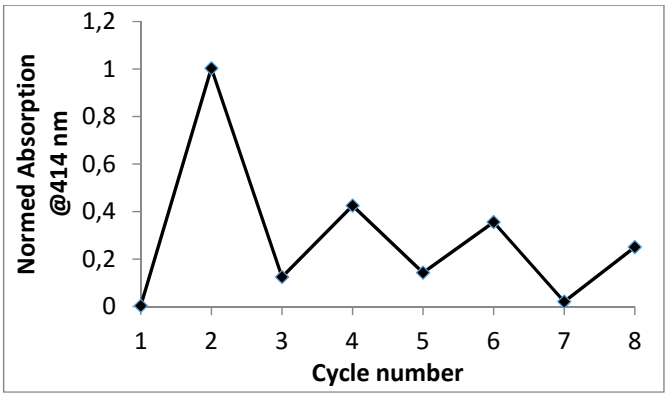
- Compound **1b**^{o} in MeCN



- Compound **1b**^{o} in toluene



- Compound **1b**^{o} in toluene, fatigue resistance

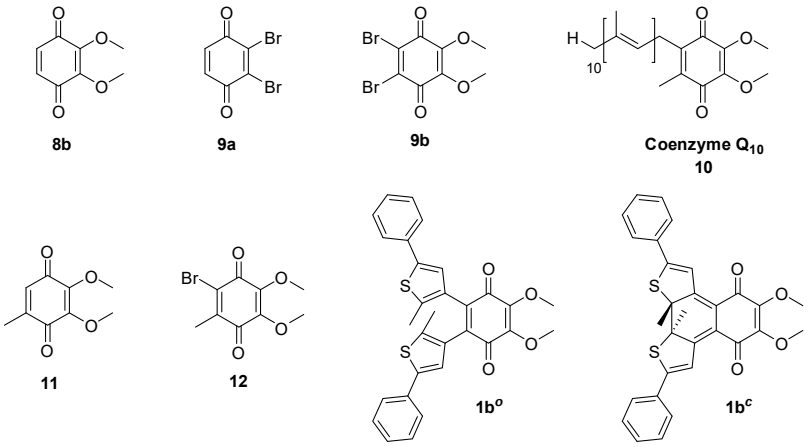


- Extinction coefficients

Compound	Solvent	Extinction coefficient [L/(mol*cm)]
1b^{o}	DMSO	ε_{300} = 582
1b^{o}	MeCN	ε_{296} =2539
1b^{c}	MeCN	ε_{579} =4928

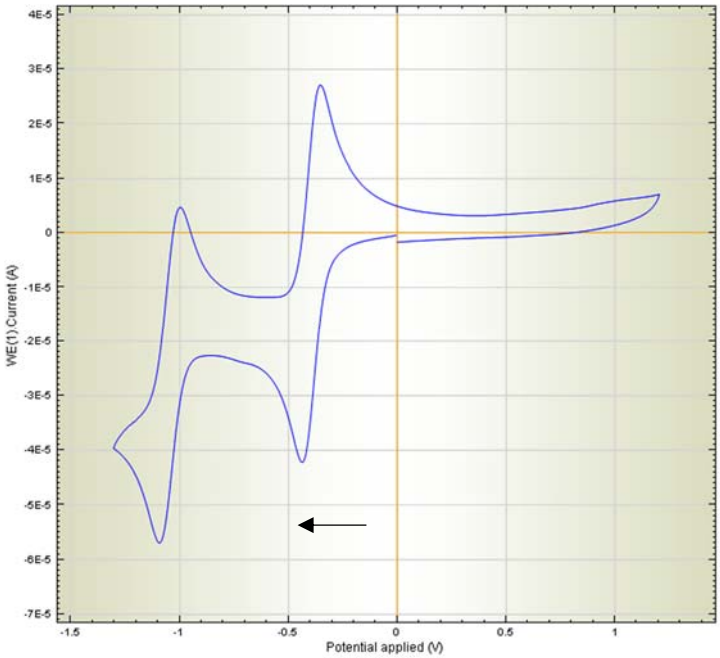
4. Cyclic Voltammery and Spectroelectrochemical Studies (further material)

Molecules included in the study:



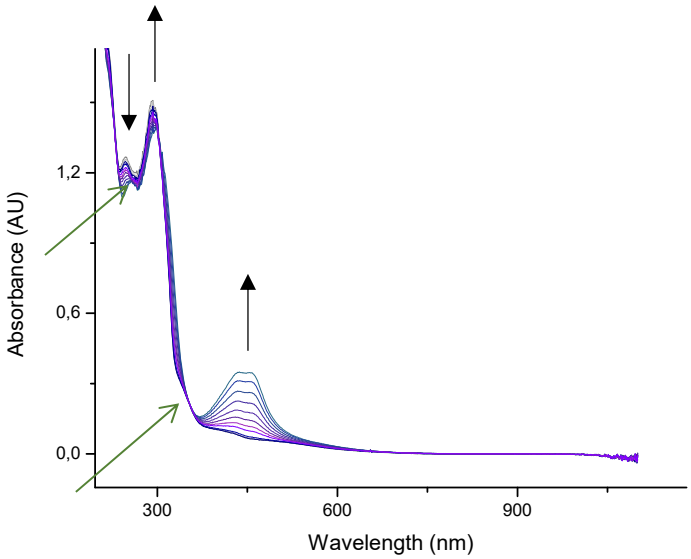
4.1. Compound **1b^o**

- Cyclic Voltammetry

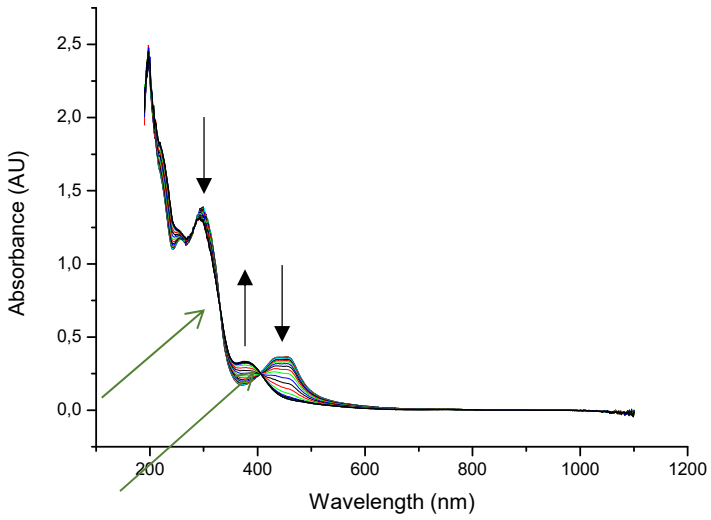


- Spectroelectrochemical studies

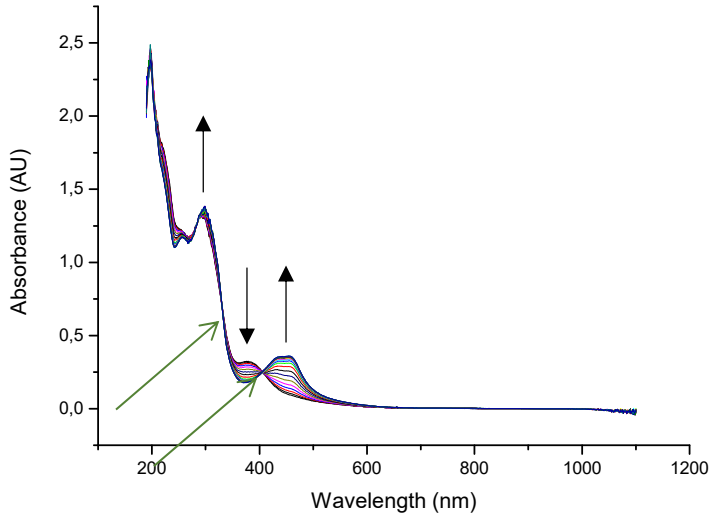
Peak 1



Peak 2



Peak 2 (invers)



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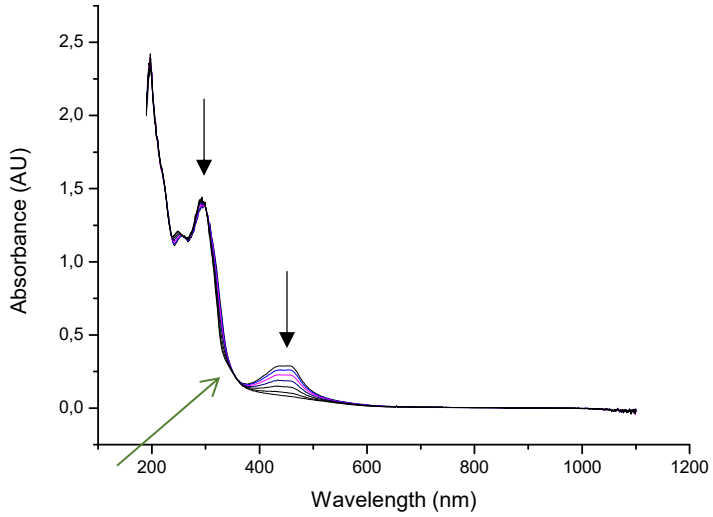
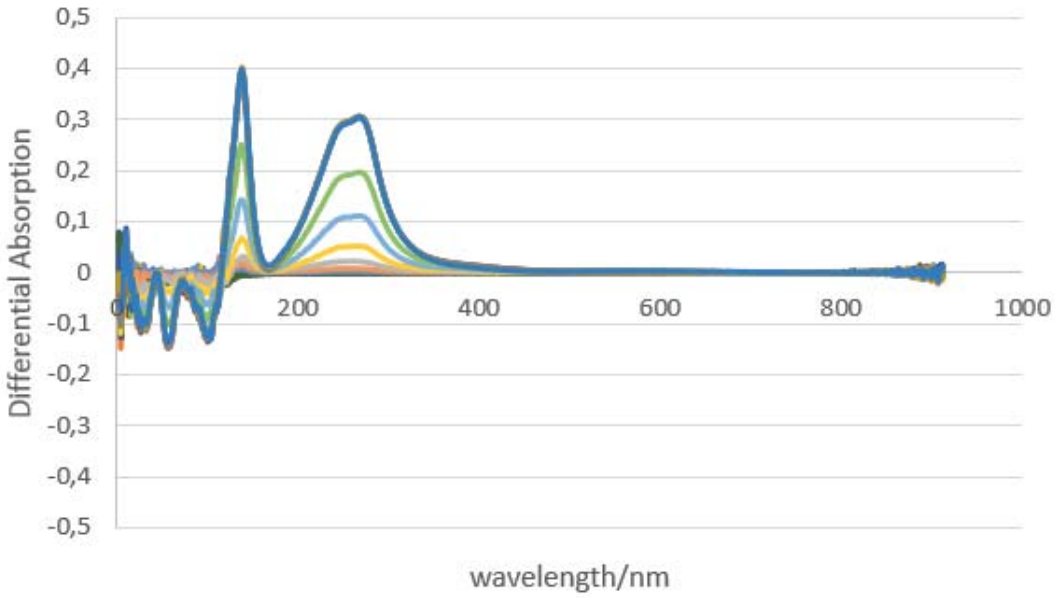
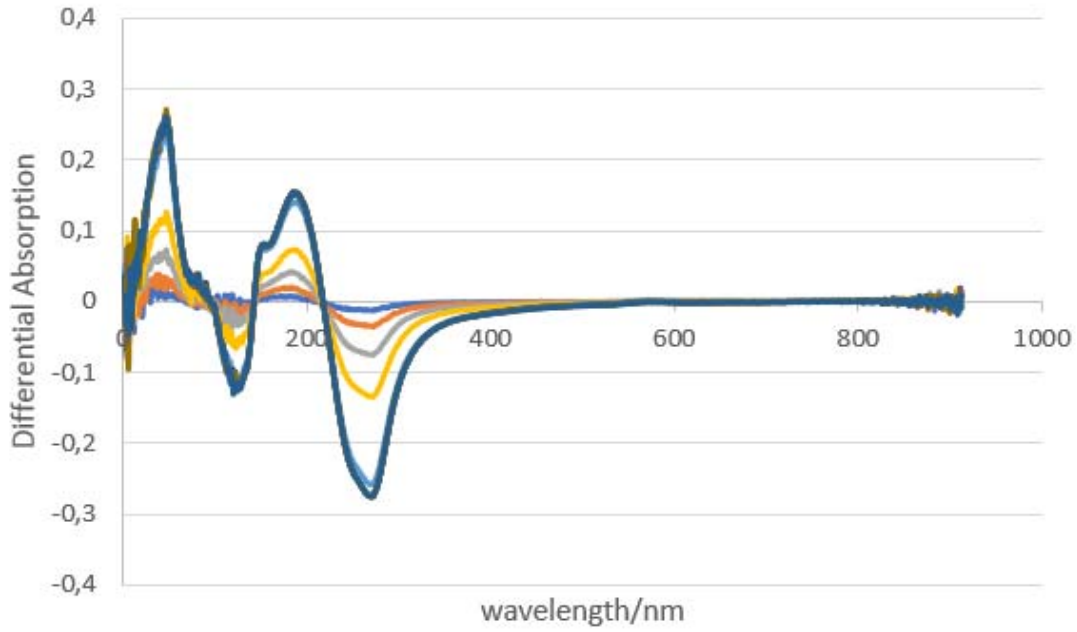


- Difference Spectra

Peak 1

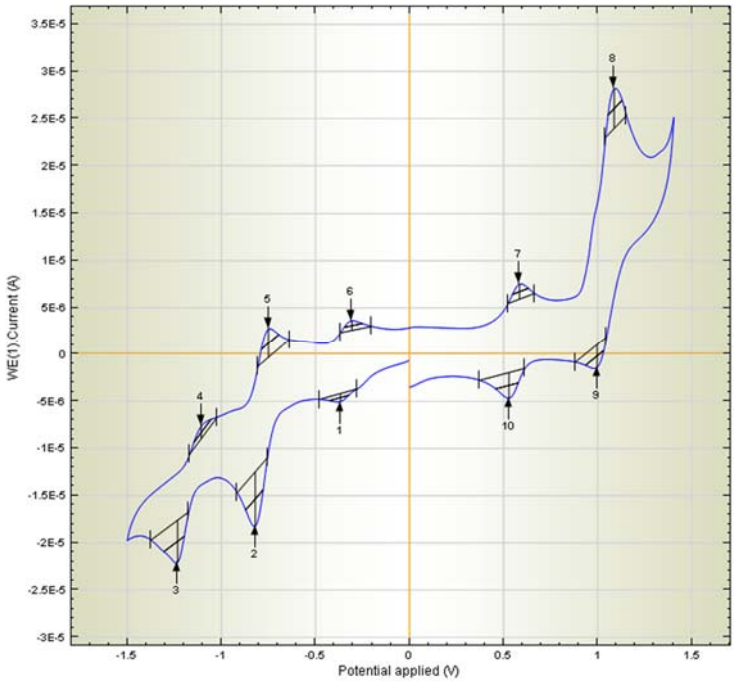


Peak 2

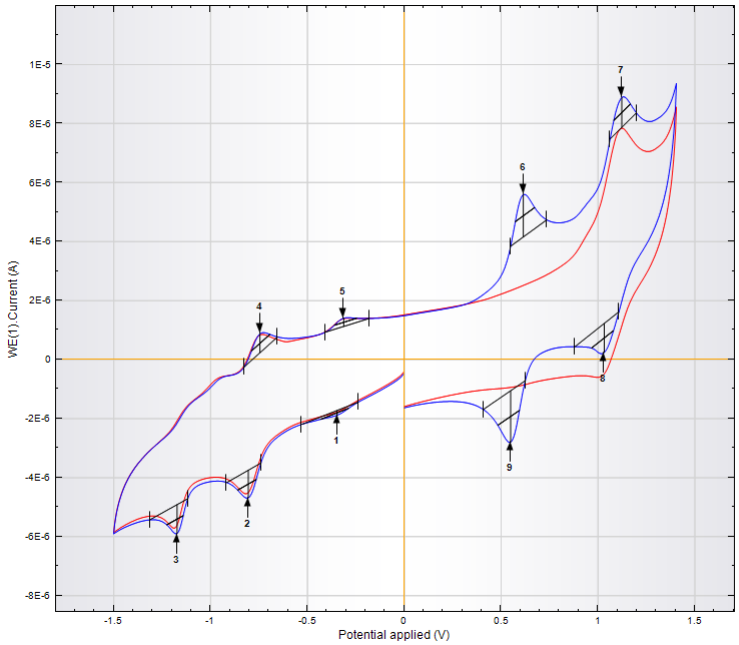


4.2. Compound **1b**^{c}

- Cyclic Voltammetry



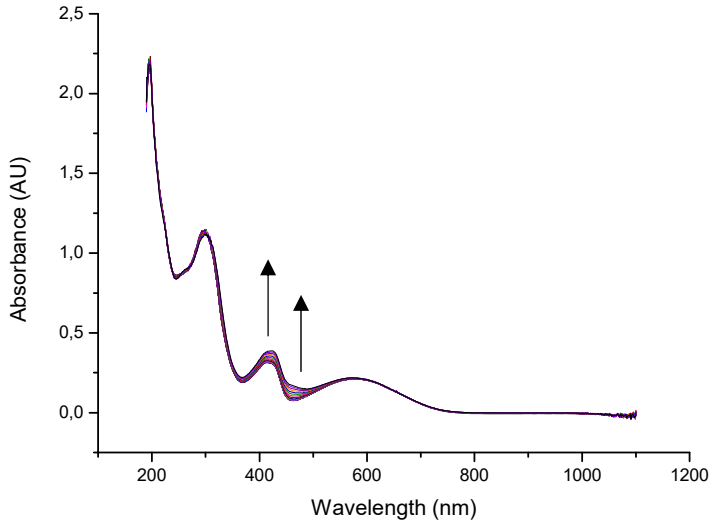
Compound **1b**^{c} with Ferrocene (peaks 7 and 10) as internal standard.



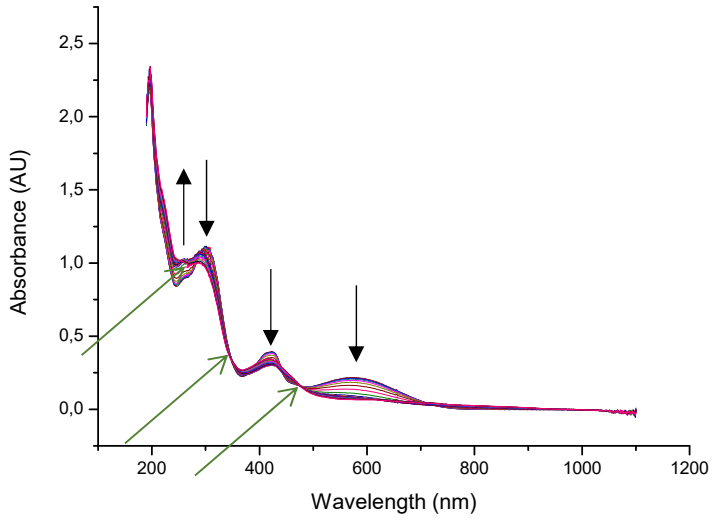
Two consecutive measurements of compound **1b**^{c}: Red: First round, without internal standard; Blue: Second round, after addition of ferrocene (peaks 6 and 9) as internal standard.

- Spectroelectrochemical studies

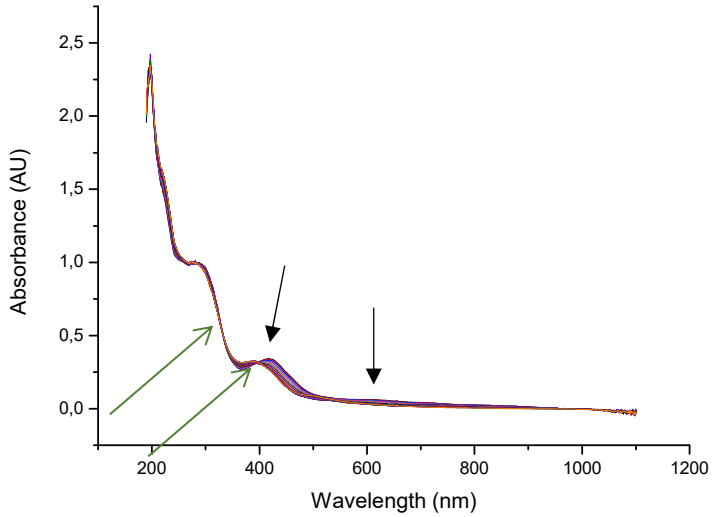
Peak 1 (0- -0.5 V)



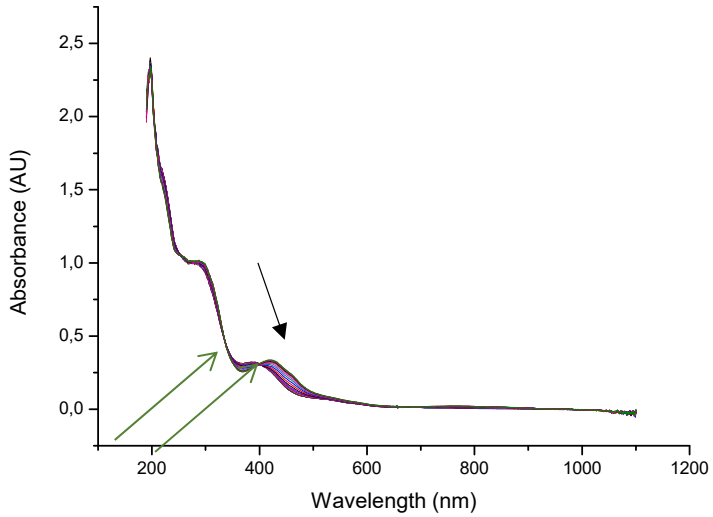
Peak 2 (-0.5 - -1.0V)



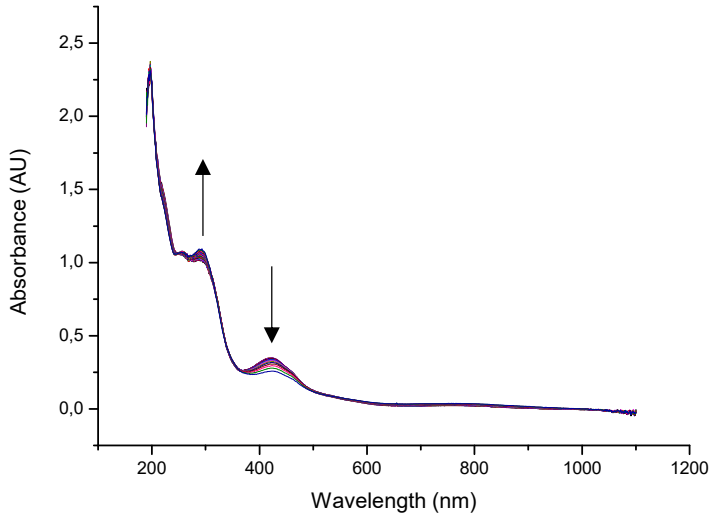
Peak 3 (-1.0 - -1.5V)



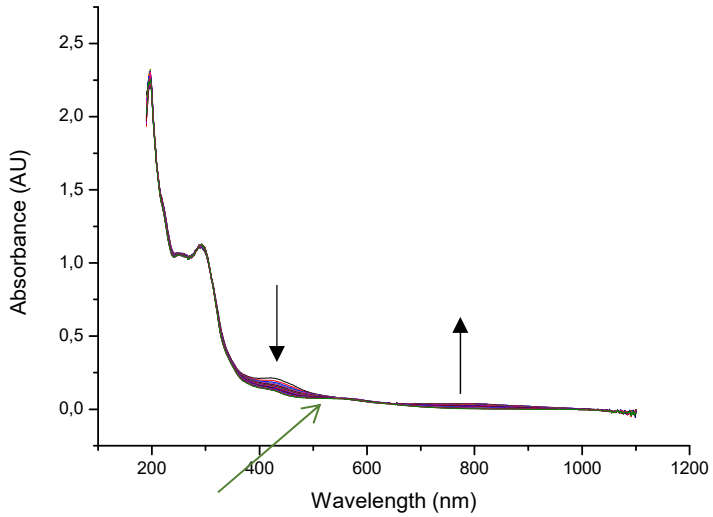
Peak 3 (invers, -1.5V - -1.0V)



Peak 2 (invers, -1.0 - -0.5V)

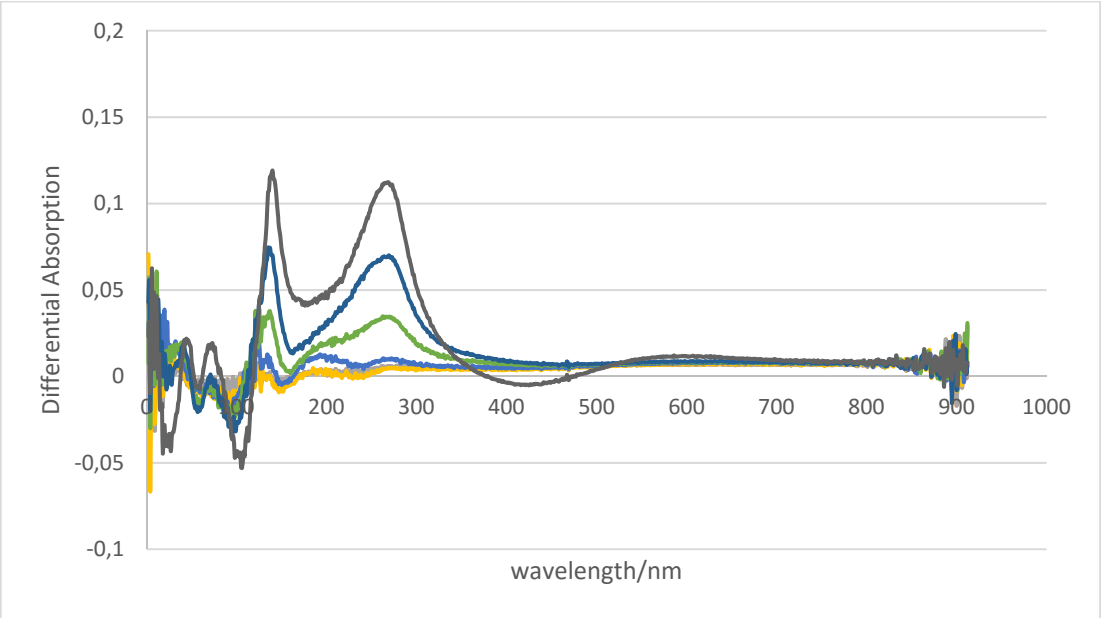


Peak 1 (invers, -0.5 – 0V)

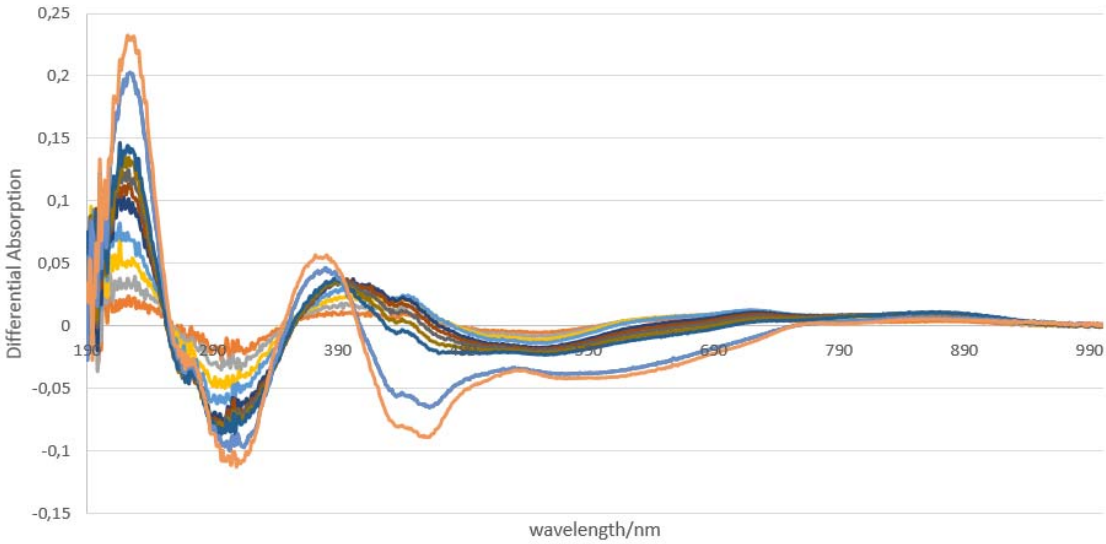


- Difference Spectra

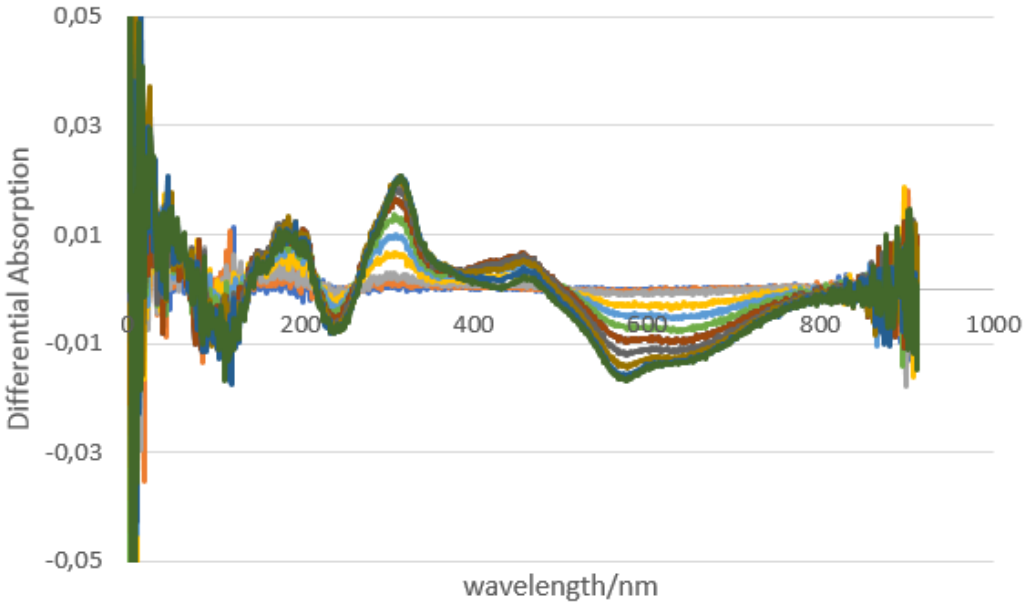
Peak 1



Peak 2

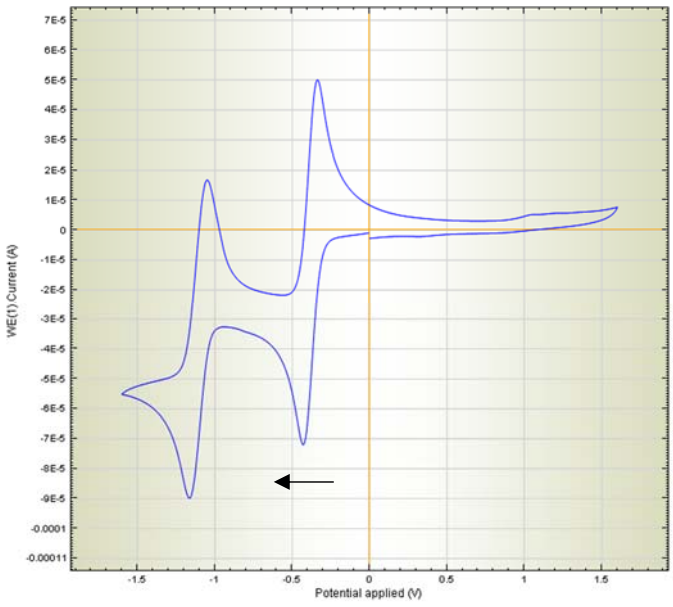


Peak 3



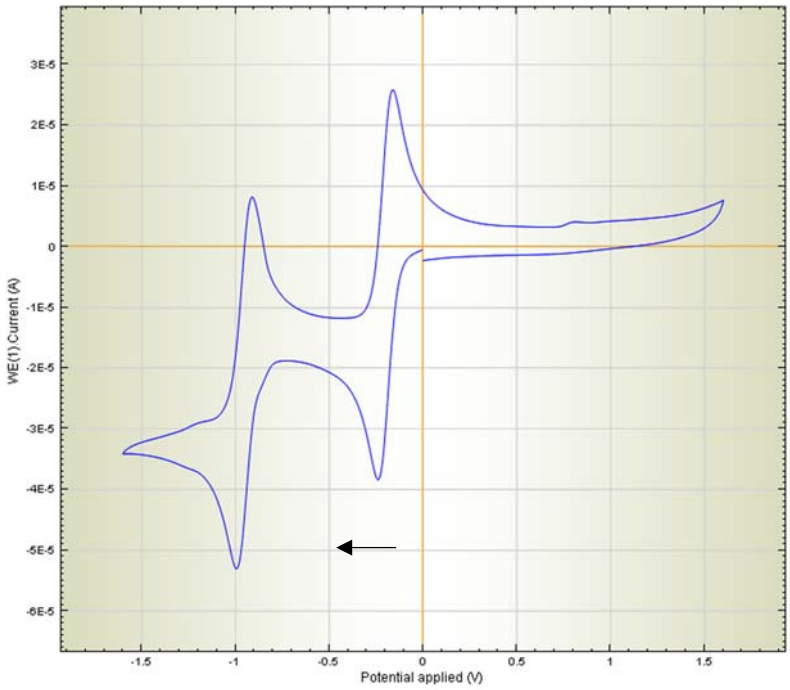
4.3. Compound **8b**

- Cyclic Voltammetry



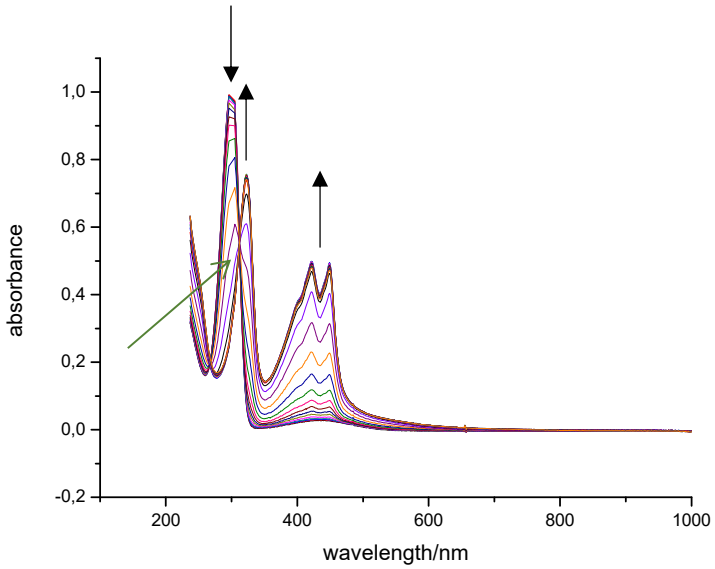
4.4. Compound **9b**

- Cyclic Voltammetry

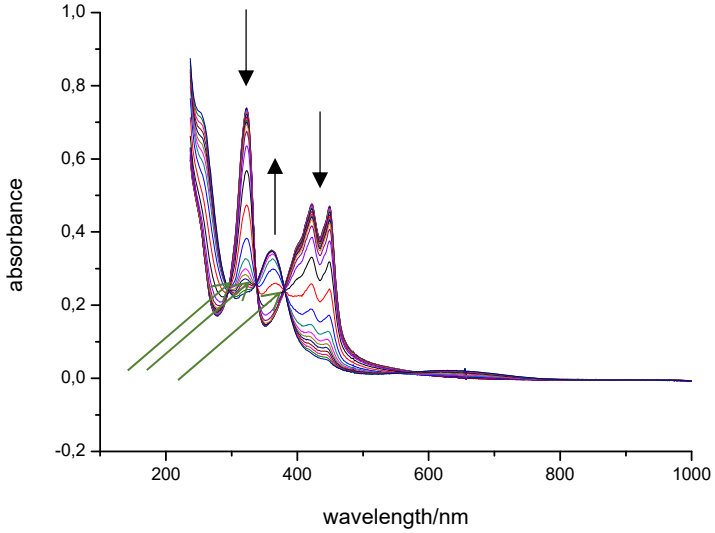


- Spectroelectrochemical studies

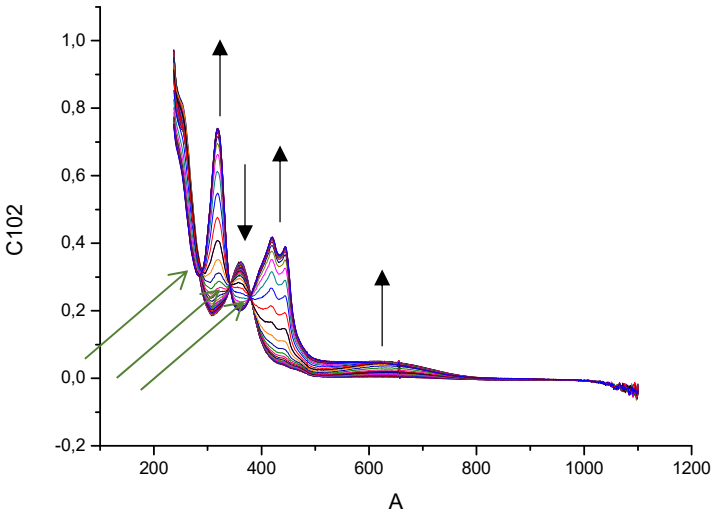
Peak 1 (0- -0.5V)



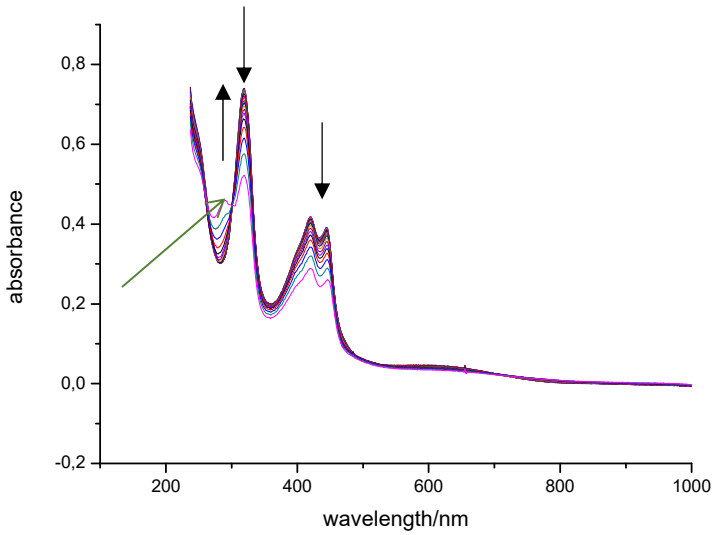
Peak 2 (-0.5 - -1.5V)



Peak 2 (invers, -1.5V - -0.5V)

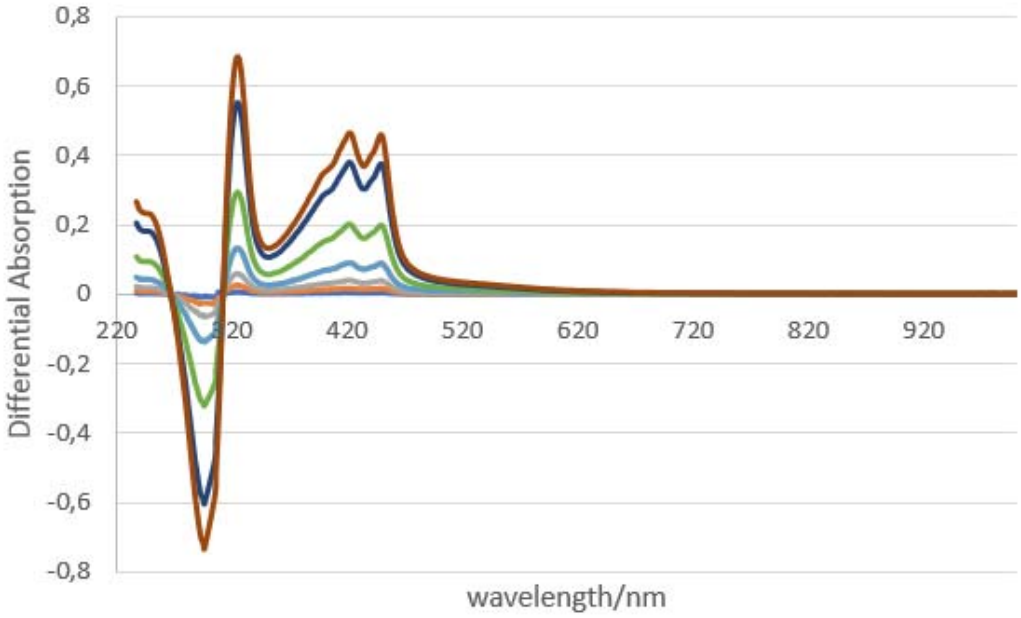


Peak 1 (invers, -0.5 – 0V, incomplete re-oxidation)

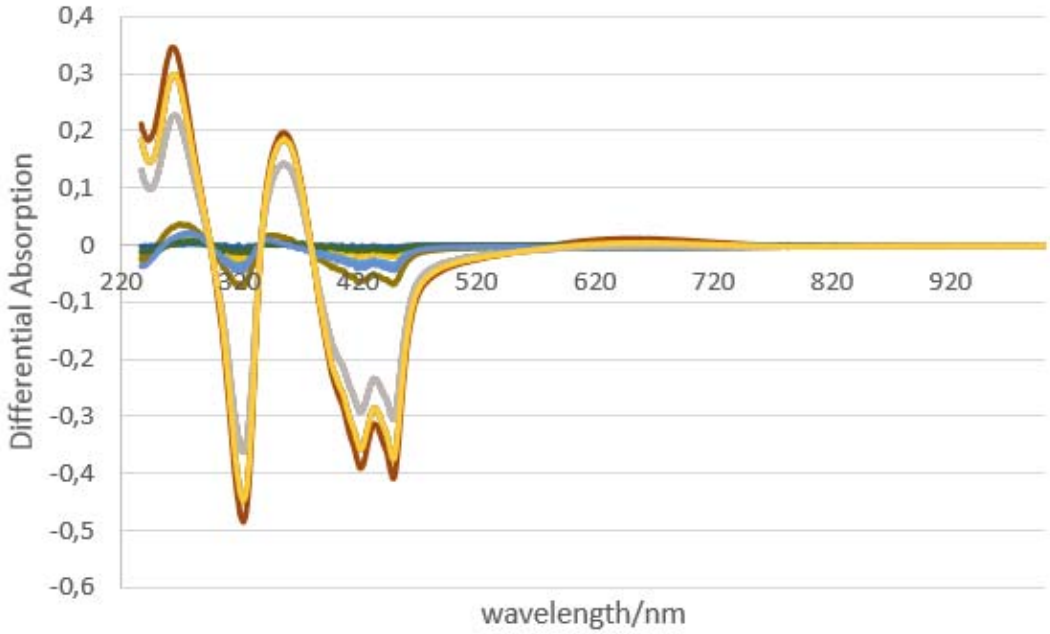


- Difference Spectra

Peak 1



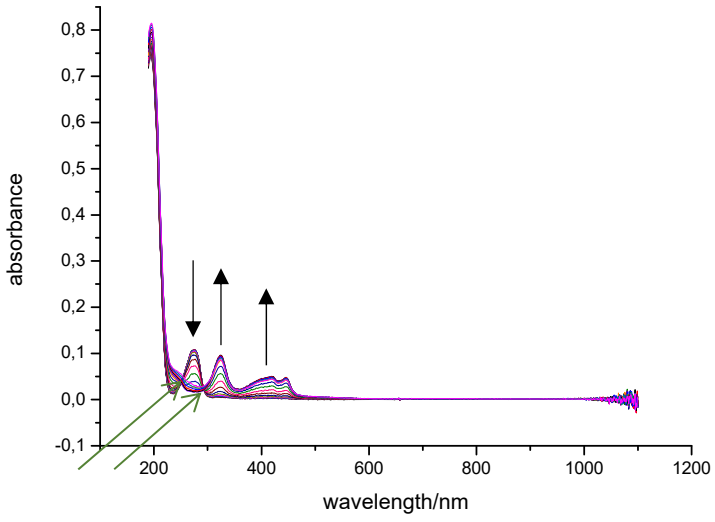
Peak 2



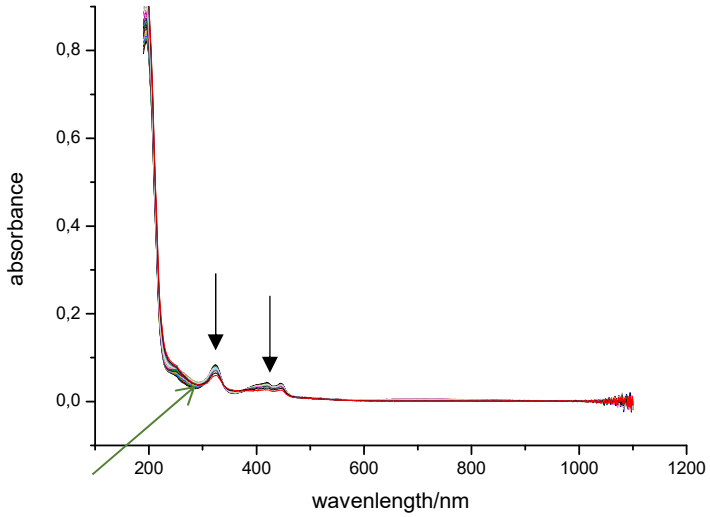
4.5. Compound **10** (CoQ_{10})

- Spectroelectric measurement

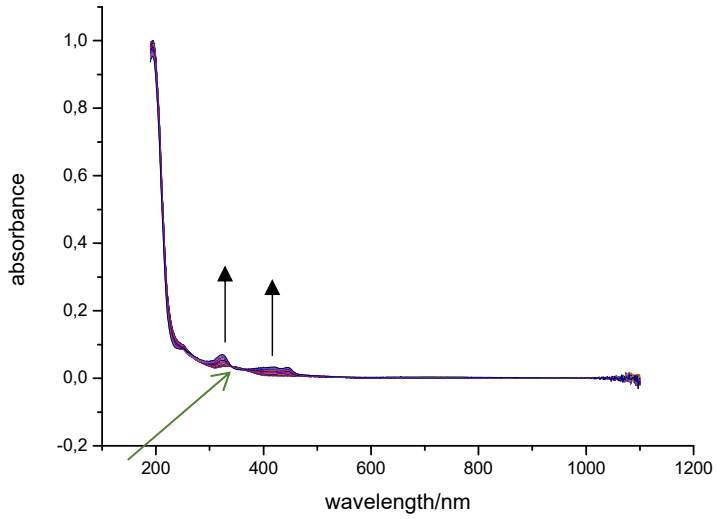
Peak 1



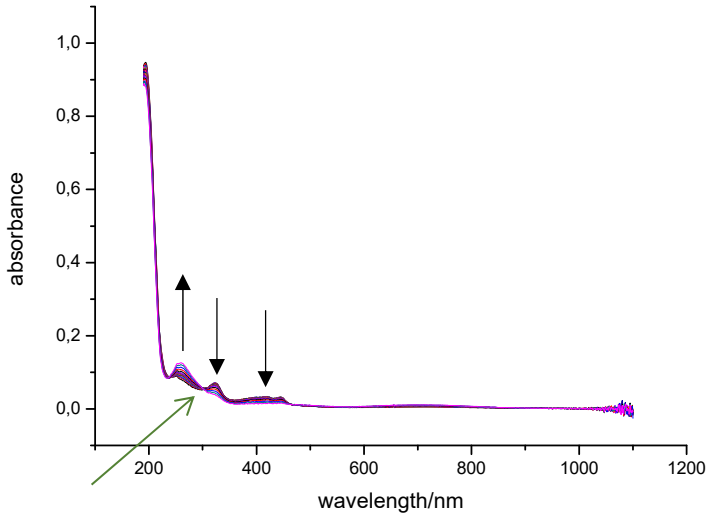
Peak 2



2nd peak (invers)

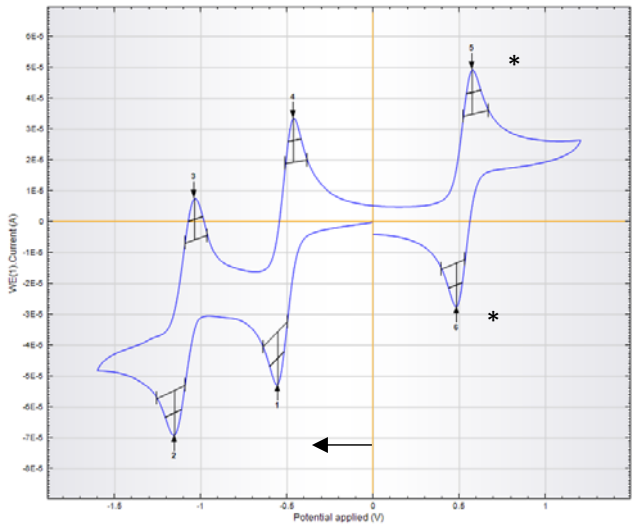


1st peak (invers)



4.6. Compound **11**

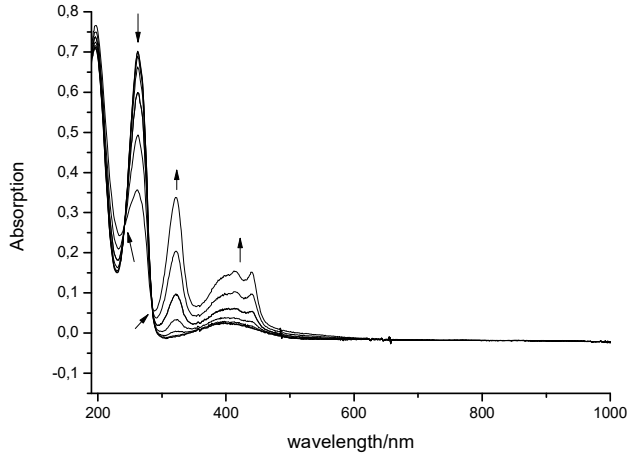
- Cyclic Voltammetry



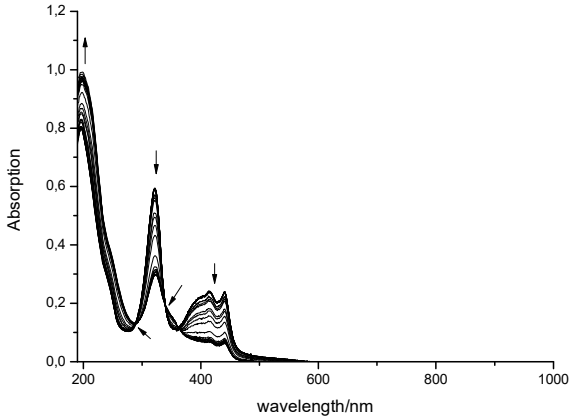
*Ferrocene as internal standard

- Spectroelectrochemical studies

Peak 1 (0- -0.7 V)

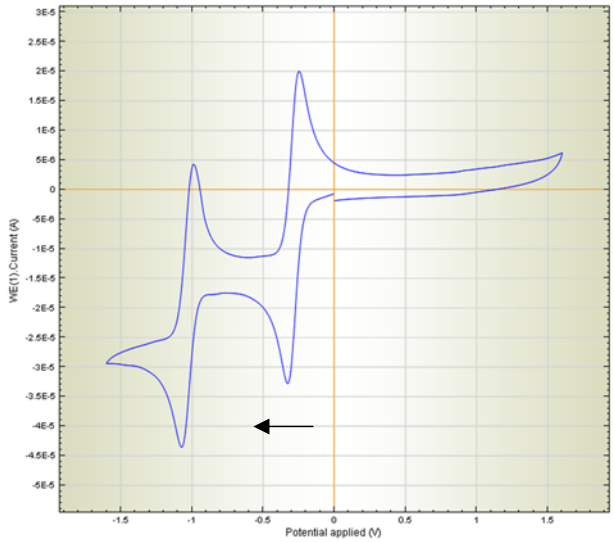


Peak 2 (-0.7- - 1.4V)



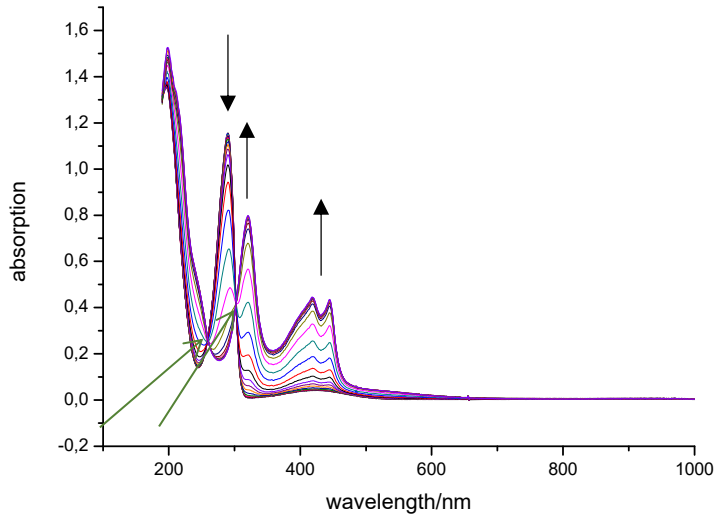
4.7. Compound **12**

- Cyclic Voltrammetry

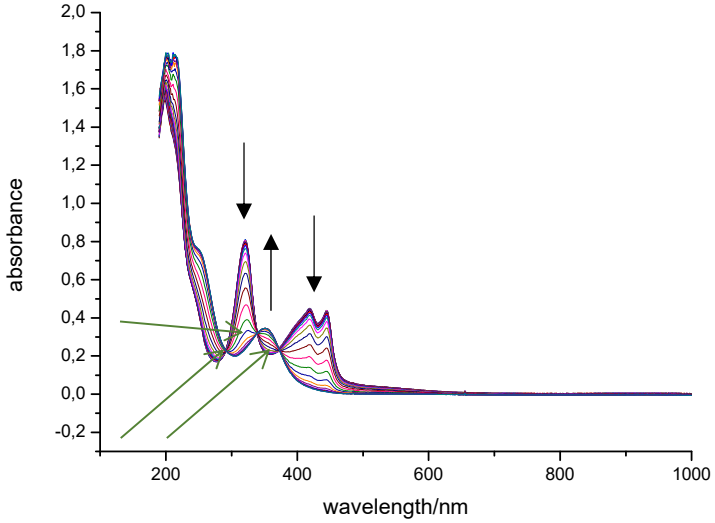


- Spectroelectrochemical studies

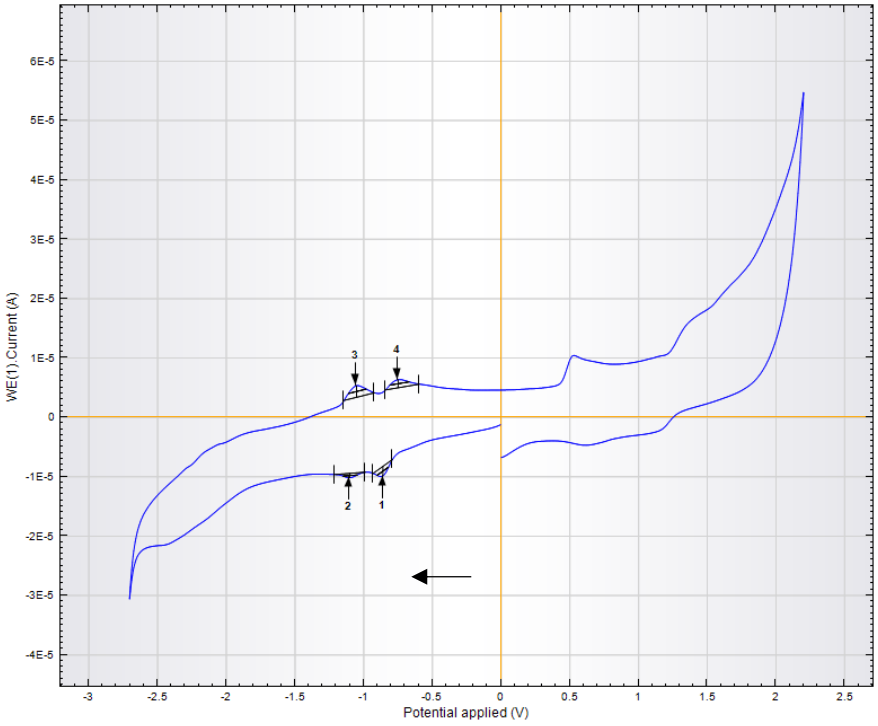
Peak 1 (0- -0.5V)



Peak 2 (-0.5 - -1.5V)

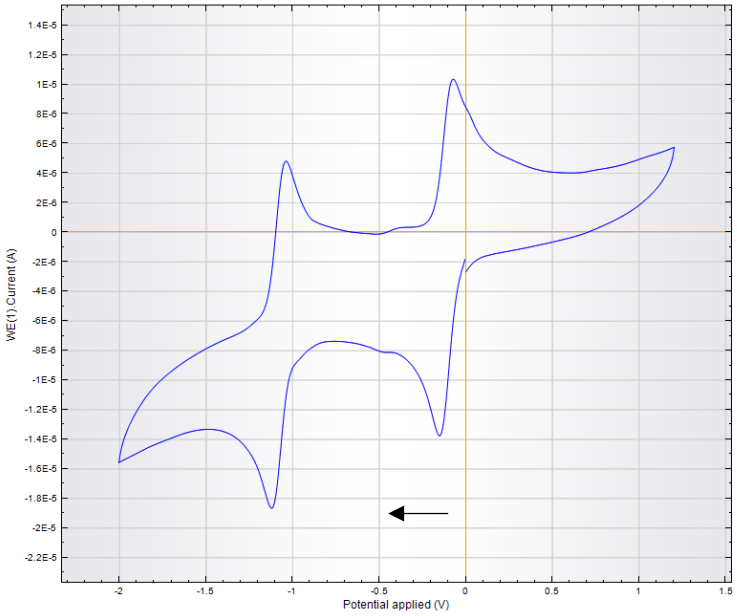


4.8. DCIP



Potentials vs. SCN: -0.96 V, -1.23 V.

4.9. PMS



Potentials vs SCN: -0.11 V, -1.08 V.

5. Photoactivated Oxidation

5.1. Experimental Approach:

A Reduction of **1b**^{o}: A solution of **1b**^{o} (5 mM or 10 mM, DMSO, 600 µL) was dissolved in DMSO (1200 µL) and treated with a saturated solution of Hantzsch ester **13** (12 mM, DMSO, 600 µL) and stirred at ambient temperature in the dark.

To monitor the reaction, samples (100 µL) were taken and diluted with DMSO (100 µL), filtered and injected into analytical HPLC.

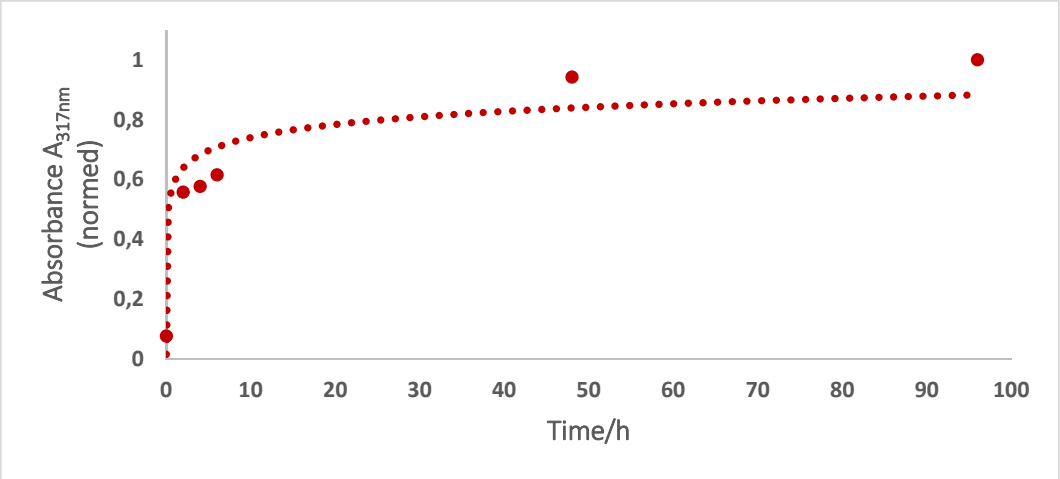
B Reduction of **1b**^{c}: A solution of **1b**^{c} (5 mM, DMSO, 50 µL) was dissolved in DMSO (100 µL) and treated with a saturated solution of Hantzsch ester **13** (12 mM, DMSO, 50 µL) and stirred at ambient temperature in the dark.

To monitor the reaction, samples (20 µL) were taken and diluted with DMSO (40 µL), filtered and injected into analytical HPLC.

C Reduction of **1b**^{c} and photoactivation: A solution of **1b**^{c} (10mM, DMSO, 50 µL) was dissolved in DMSO (100 µL) and treated with a saturated solution of Hantzsch ester **13** (12mM, DMSO, 50 µL) and stirred at ambient temperature in the dark. After three hours the sample was irradiated with a 590 nm single-spot LED for 10 min, then stirring was continued in the dark.

To monitor the reaction, samples (20 µL) were taken and diluted with DMSO (40 µL), filtered and injected into analytical HPLC.

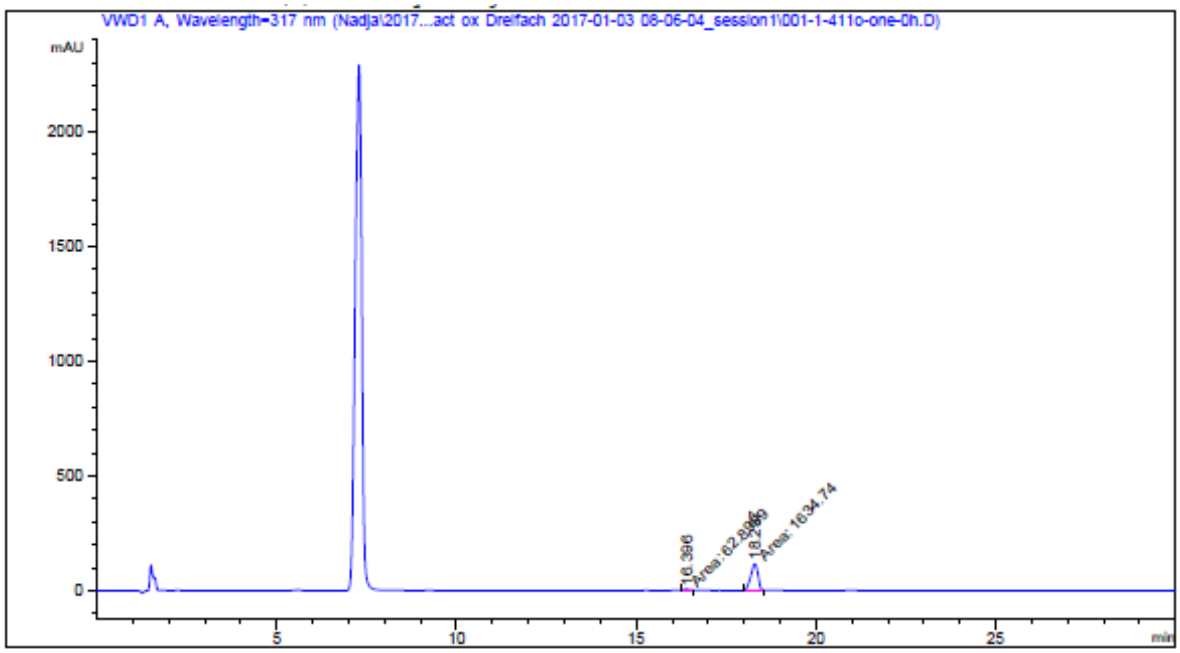
5.2. Formation of **1b**^{o,red} using **1b**^{o} (10 mM, DMSO)



5.3. Representative HPLC traces (for Main Text, Figure 6 **A** and **B**)

Peaks: 7.2 min Hantzsch ester **13** (at the applied gradient oxidized and reduced form show the same retention time); 16.3 min: **1b**^{o,red}; 18.3 min: **1b**^{o}; 21.0 min: **1b**^{c}.

A_0h



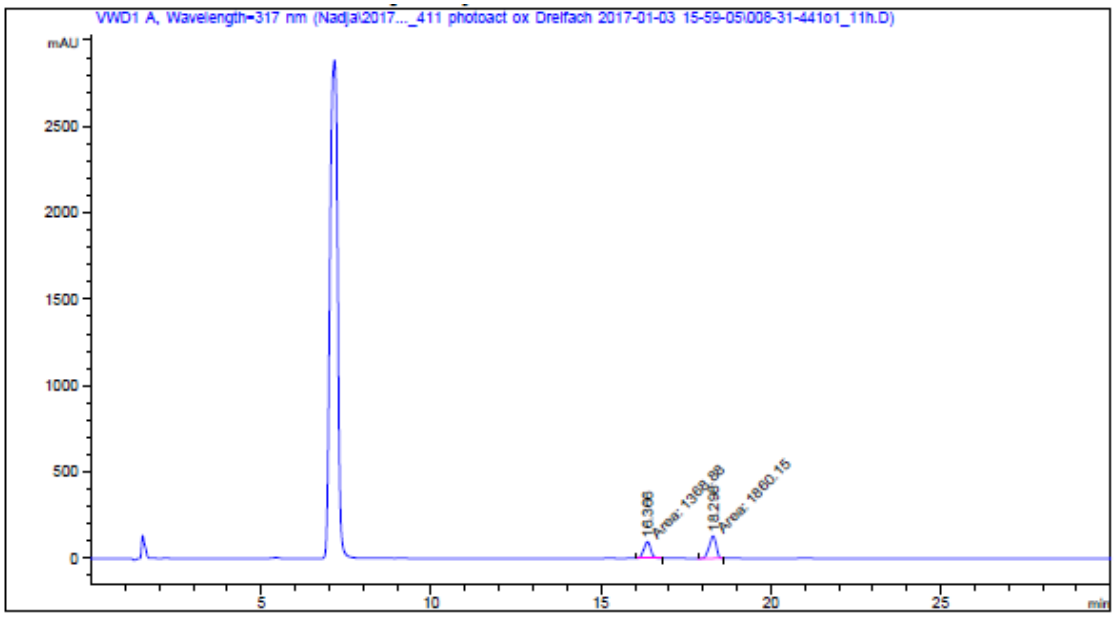

```
=====================================================================
                    Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=317 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  16.396 MM    0.2133   62.89994    4.91378   3.7051
   2  18.297 MM    0.2337 1634.74426  116.57957  96.2949
```

A_11h




```
=====================================================================
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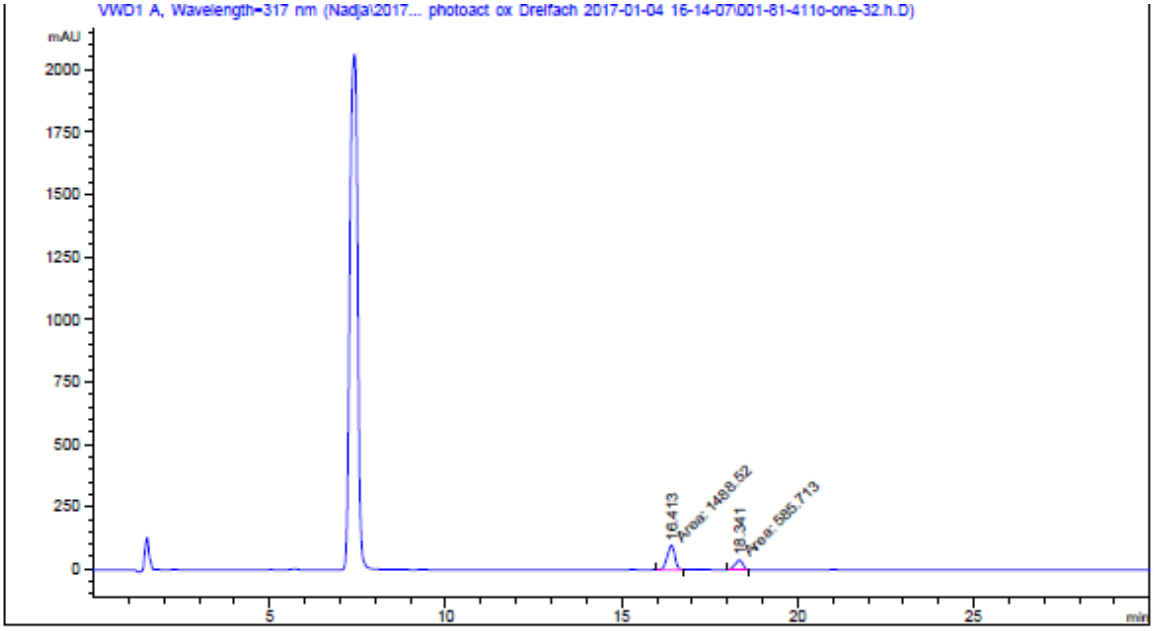
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=317 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  16.366 MM    0.2389 1368.88477   95.50758  42.3930
   2  18.298 MM    0.2382 1860.14685  130.17055  57.6070
```

A_32h



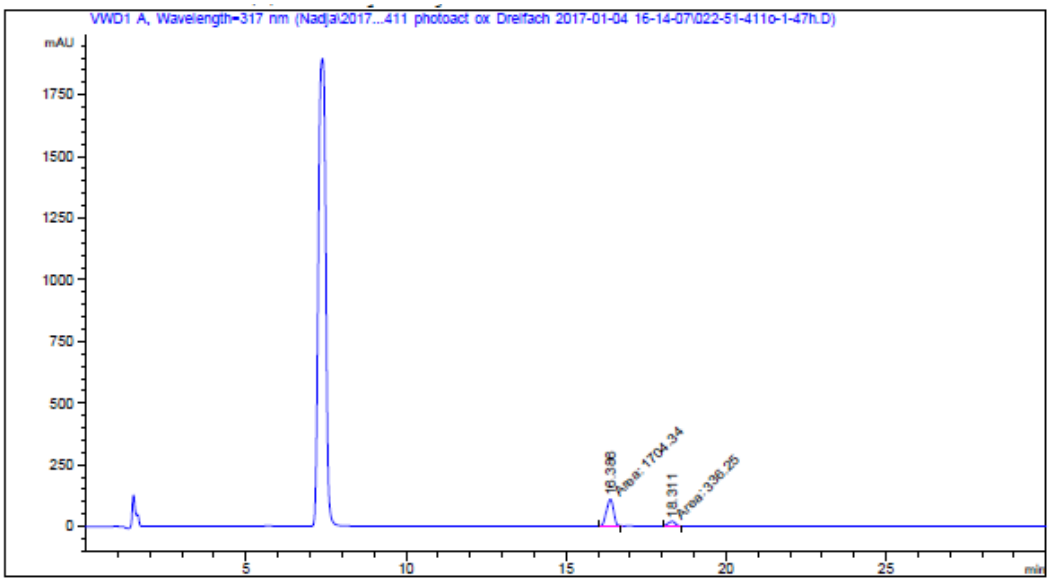

```
=====================================================================
                    Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=317 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  16.413 MM    0.2525 1488.51843   98.24986  71.7624
   2  18.341 MM    0.2508  585.71344   38.92433  28.2376
```

A_47h



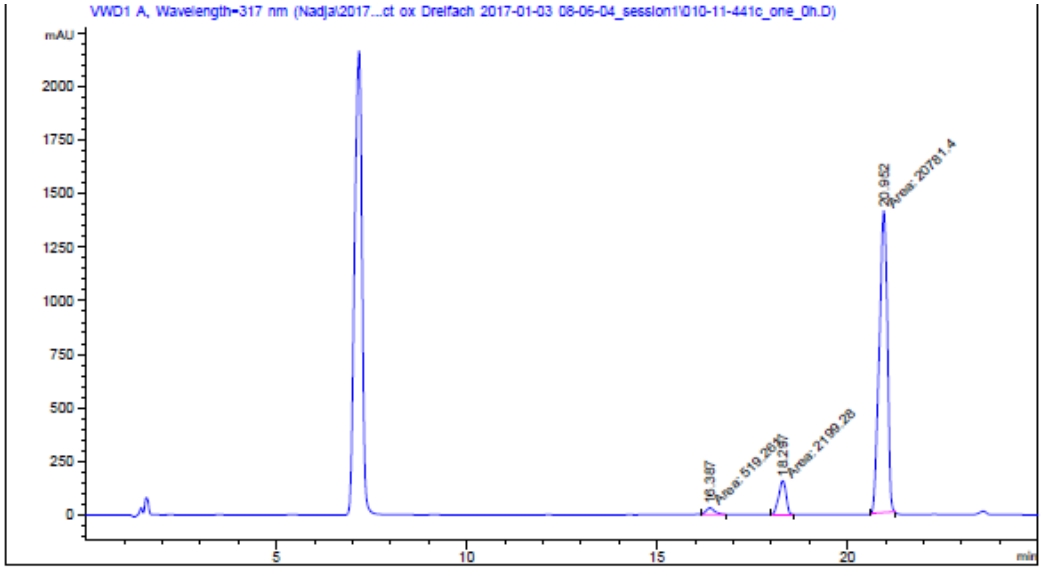

```
=====================================================================
                    Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=317 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  16.386 MM    0.2598 1704.33765  109.34824  83.5219
   2  18.311 MM    0.2752  336.25031   20.36510  16.4781
```

B_0h/C_0h



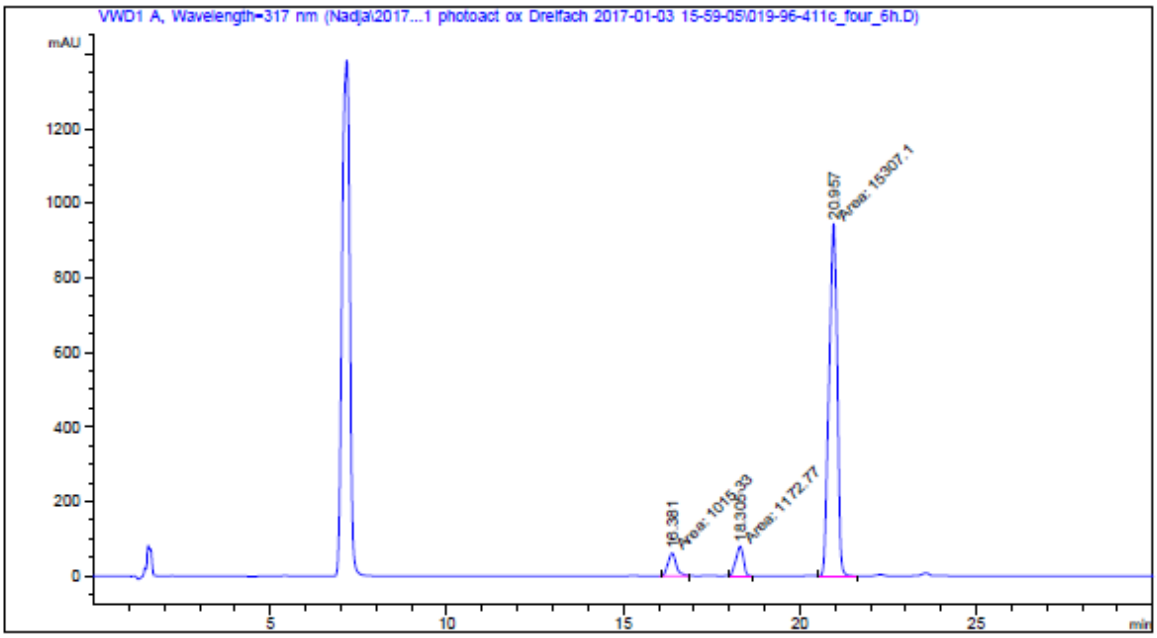

```
=====================================================================
                      Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=317 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  16.387 MM    0.2781  519.26062   31.12502   2.2096
   2  18.297 MM    0.2289 2199.28003  160.10457   9.3587
   3  20.952 MM    0.2459 2.07814e4  1408.44507  88.4317
```

B_6h



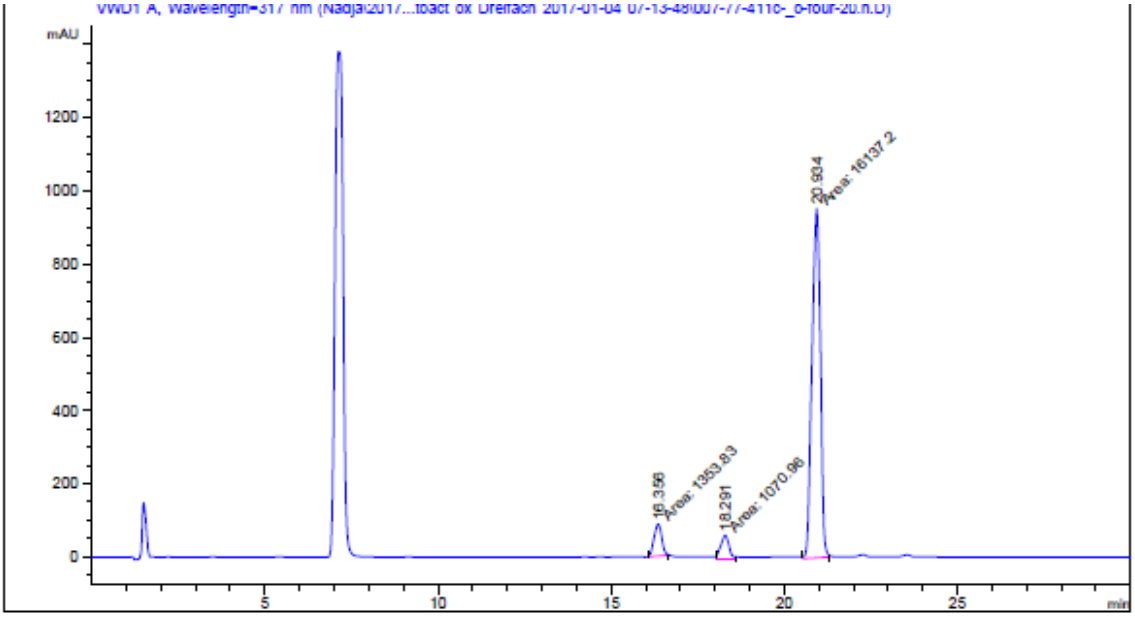

```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=317 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  16.381 MM    0.2752 1015.33301   61.48637   5.8035
   2  18.305 MM    0.2456 1172.76794   79.58045   6.7034
   3  20.957 MM    0.2697 1.53071e4   945.79211  87.4931
```

B_20h



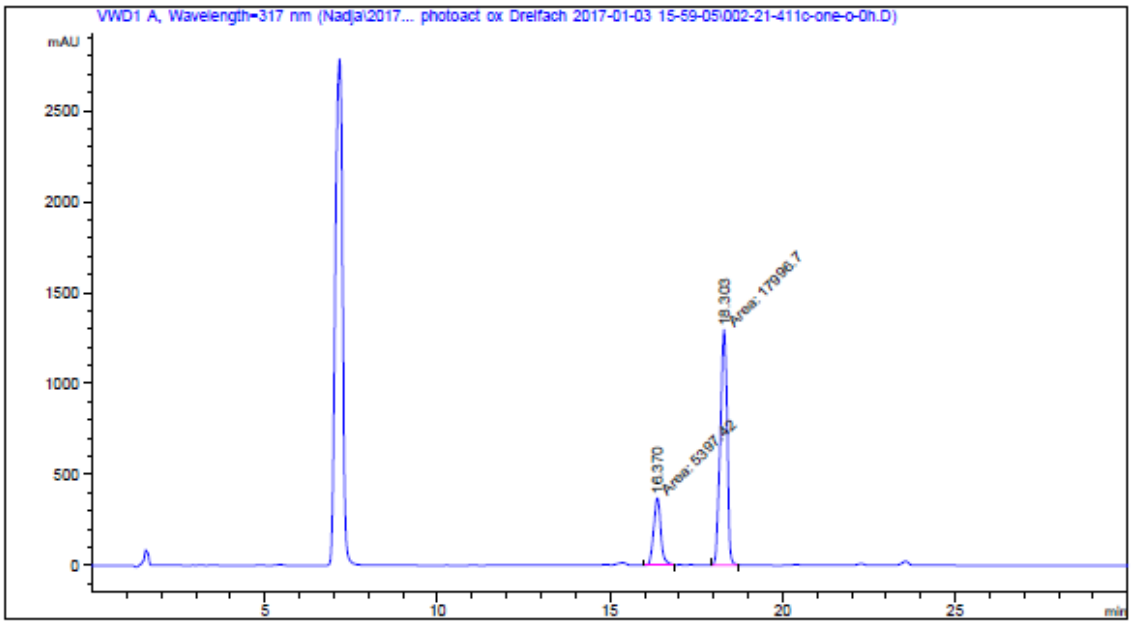

```
=====================================================================
                    Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=317 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  16.356 MM    0.2586 1353.82556   87.26817   7.2935
   2  18.291 MM    0.2799 1070.96094   63.77544   5.7696
   3  20.934 MM    0.2822 1.61372e4   953.15631  86.9368
```

C_3h

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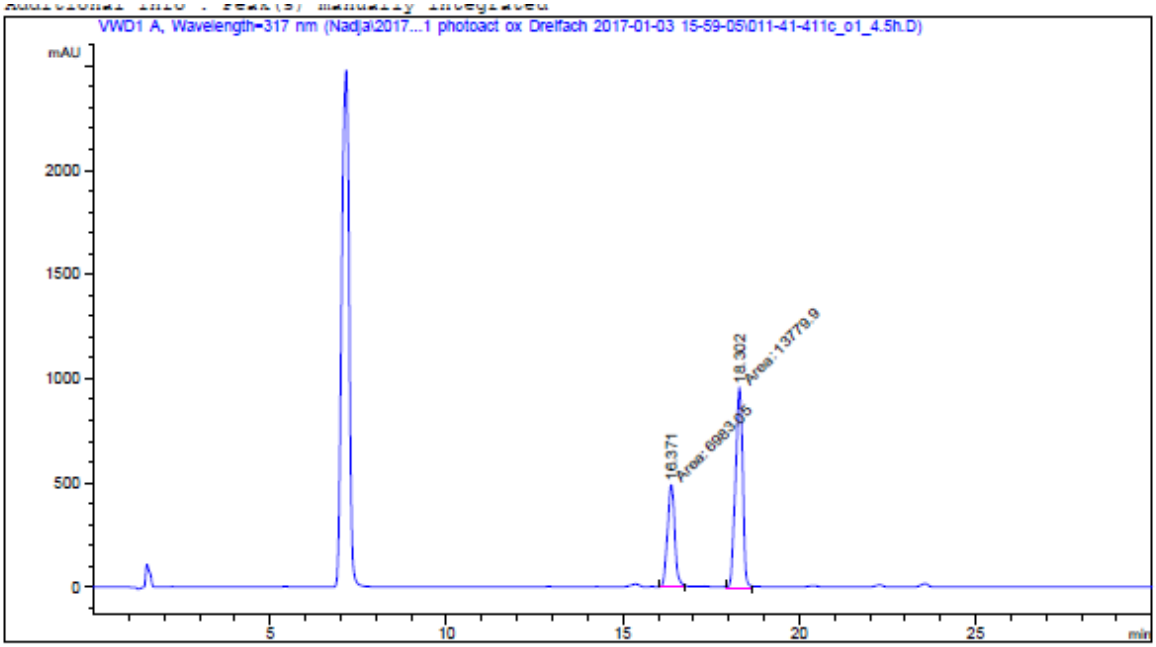
=====================================================================
                      Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=317 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  16.370 MM    0.2431 5397.41650  370.02362  23.0717
   2  18.303 MM    0.2320 1.79967e4  1292.72192  76.9283
```

C_7.5h



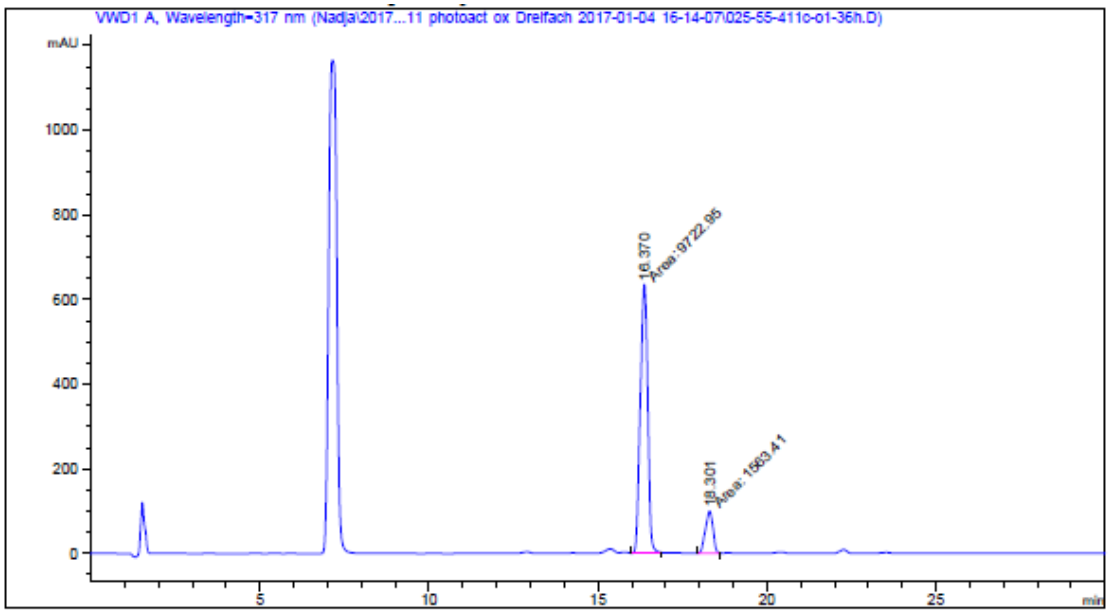

```
================================================================================
                          Area Percent Report
================================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=317 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  16.371 MM    0.2390 6983.05029  486.93979  33.6323
   2  18.302 MM    0.2388 1.37799e4   961.71655  66.3677
```

C_39h




```
=====================================================================
                      Area Percent Report
=====================================================================

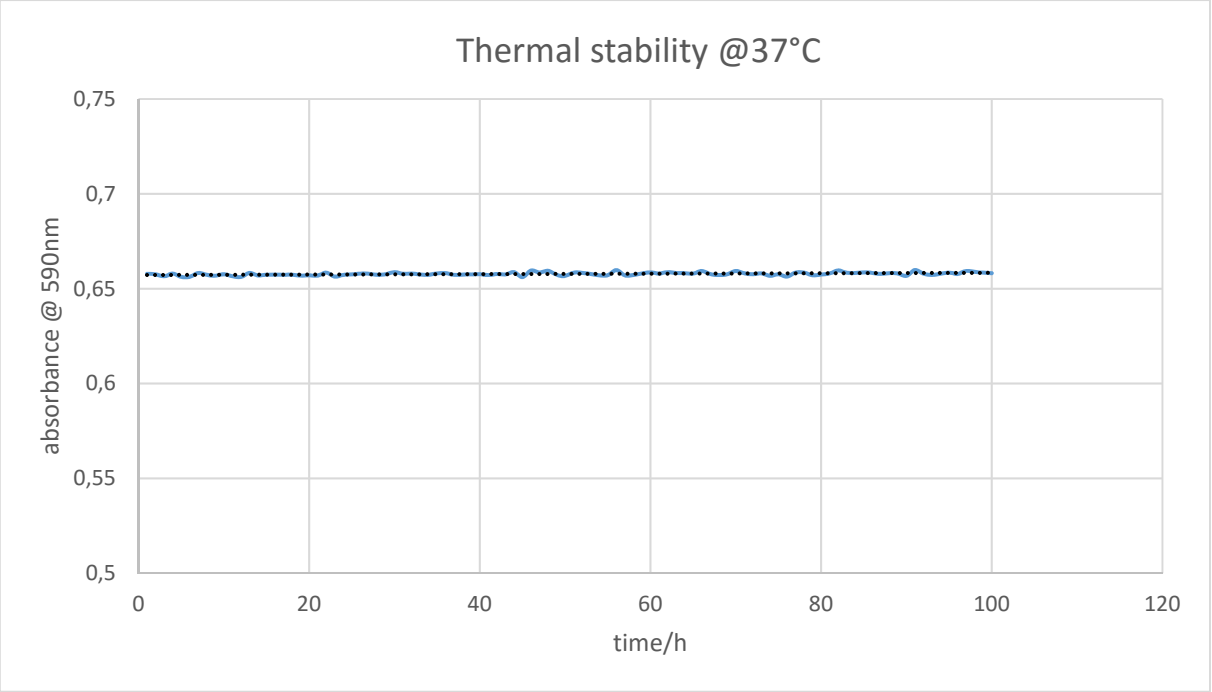
Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=317 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  16.370 MM    0.2555 9722.95117  634.16931  86.1478
   2  18.301 MM    0.2608 1563.40955   99.90733  13.8522
```

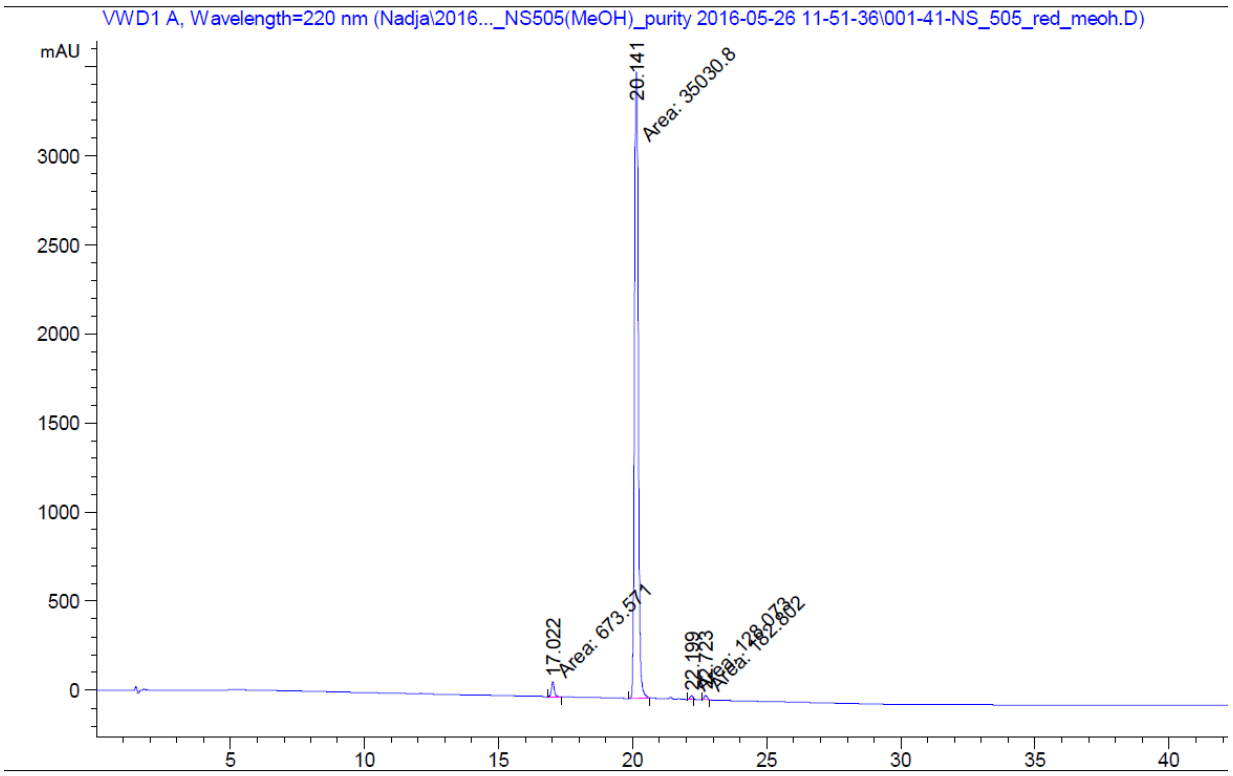
6. Activation of **1b**^{c} on isolated Mitochondria

- Stability of **1b**^{c} at elevated temperatures



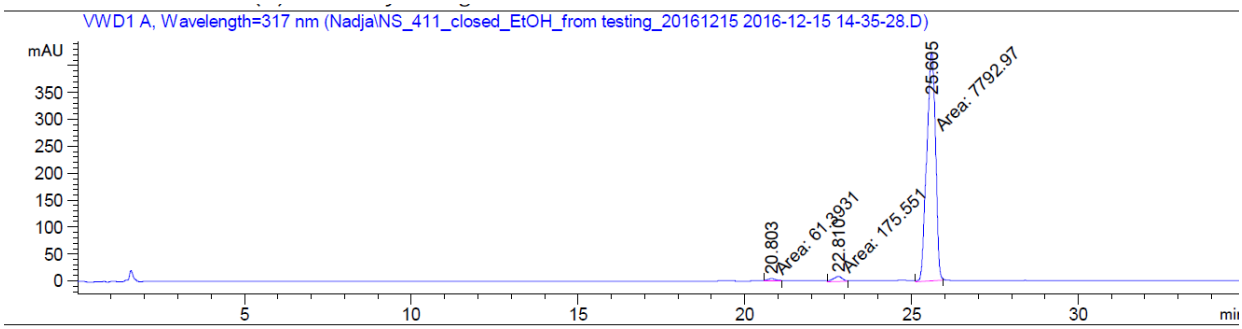
- Purity of compounds **1b**^{o} and **1b**^{c}

1b^{o}



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.022	MM	0.1302	673.57086	86.23805	1.8702
2	20.141	MM	0.1661	3.50308e4	3515.66992	97.2666
3	22.199	MM	0.1065	128.07347	20.05158	0.3556
4	22.723	MM	0.1231	182.80190	24.75809	0.5076

1b[c]



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.803	MM	0.2713	61.39307	3.77112	0.7646
2	22.810	MM	0.3193	175.55141	9.16268	2.1862
3	25.605	MM	0.3063	7792.96826	424.01196	97.0492
Totals :				8029.91273	436.94577	

- Isolation of mitochondria from yeast cells

A crude mitochondria extract was isolated from the wildtype yeast strain BY4742 (MATα his3Δ1 leu2Δ0 lys2Δ0 ura3Δ0), thankfully provided by the group of Herbert Tschochner, according to Gregg et al.[3] The protein concentration of the extract was determined with the Bradford assay[4] and the mitochondria were stored in 30 mM KP (pH 7.4), 2.2 mM EDTA and 0.1% (w/v) Thesit at -80 °C

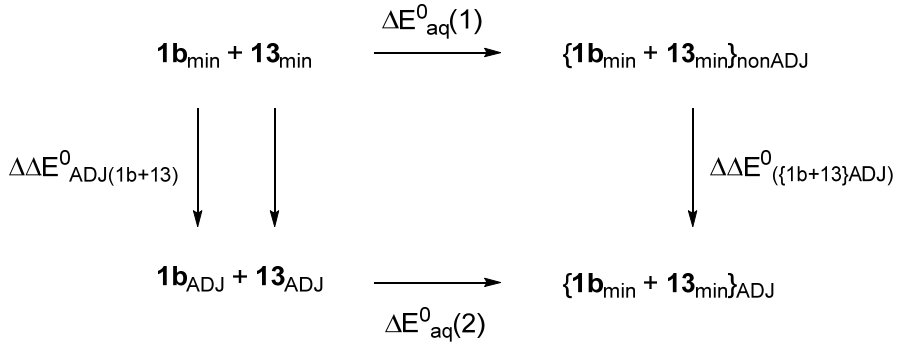
- Mitochondrial reduction of 2,6-dichlorophenol indophenol

Reduction of 2,6-dichlorophenol indophenol (DCIP) was measured using the succinate dehydrogenase activity (SDH) of mitochondria as described previously.[5] Prior to the assays, SDH was activated with 8 mM succinate for 15 min at 37 °C. Triplet measurements were carried out in a 96-well plate of assays containing 40 µM **1b**[c] and **1b**[o] dissolved in ethanol, respectively, 10 mM succinate, 100 µM DCIP and 0.2 g/L mitochondria in 50 mM KP (pH 7.6), 0.006% (w/v) Thesit, 0.2 mM EDTA at 37 °C. Reduction of DCIP was followed at 520 nm ($\varepsilon_{DCIP,520}$ = 6.8 mM^{-1} cm^{-1}) continuously for 30 min or with 10 min interruption in which the samples were irradiated with 590 nm in the same plate reader used for activity measurements with an integrated 10 W xenon flash lamp (Tecan Trading AG). The resulting data were plotted and fitted with a linear function in the time frame of 0-10 min as well as 20-30 min to visualize the difference in reactivity.

7. Computational Studies

All DFT-calculations (B3LAP/6–31G(d) level) were performed with the Gaussian 09, Revision D01 software package.[6] Optimized structures (**1b**$^{o}_{min}$, **1b**$^{c}_{min}$, **13**$_{min}$, {**1b**$^{o}_{min}$–**13**$_{min}$}$_{ADJ}$, {**1b**$^{c}_{min}$–**13**$_{min}$}$_{ADJ}$) were confirmed to be minima through frequency calculations. Single-point energies were calculated for **1b**$^{o}_{ADJ}$, **1b**$^{c}_{ADJ}$, **13**$_{ADJ}$, {**1b**$^{o}_{min}$–**13**$_{min}$}$_{nonADJ}$ and {**1b**$^{c}_{min}$–**13**$_{min}$}$_{nonADJ}$. All cartesian coordinates are given in paragraph 10. later in the Supporting Information.

Adapting a published strategy, an energy cycle to gain insight into the presence of a non-covalent π stacking between both photoisomers and **13** was calculated according to the following scheme.[7]



Then, the energies of the optimized structures (indicated with "min") of both photoisomers, the Hantzsch ester and the respective adduct complexes were compared with single point calculations of mixed structures, revealing the adjustment process (indicated with "ADJ") of the structures upon π stacking. The energy differences are given as follows:

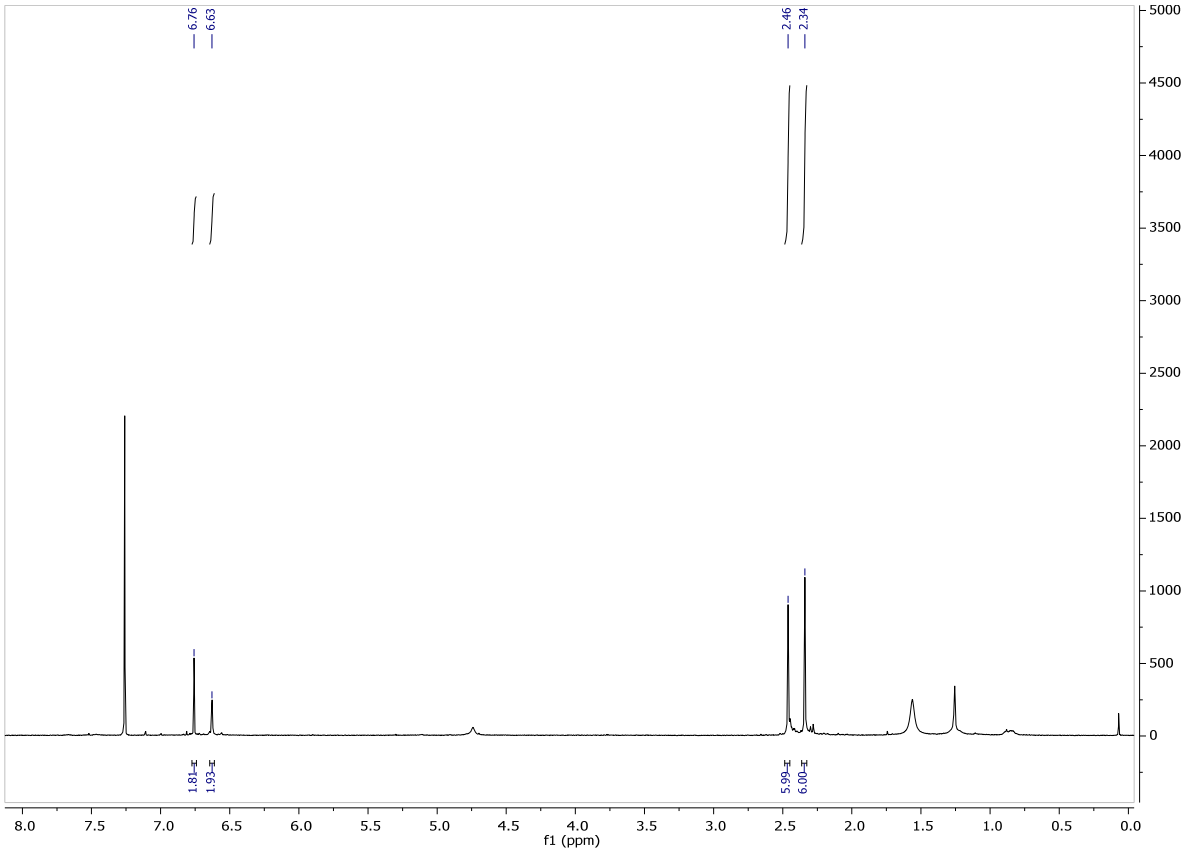
	1b^{o}	**1b**^{c}	ΔΔE^{0}(**1b**^{c}-**1b**^{o})
ΔE$^{0}_{aq}$(1)*	-0,38	1,38	
ΔE$^{0}_{aq}$(2)*	-16,5	-22,9	
ΔΔEG$^{0}_{ADJ(1b+13)}$*	1,07	1,75	
ΔΔE$^{0}_{(\{1b+13\}ADJ)}$*	-15,06	-22,53	-7,47

*Energy differences are expressed in Kcal/mol.

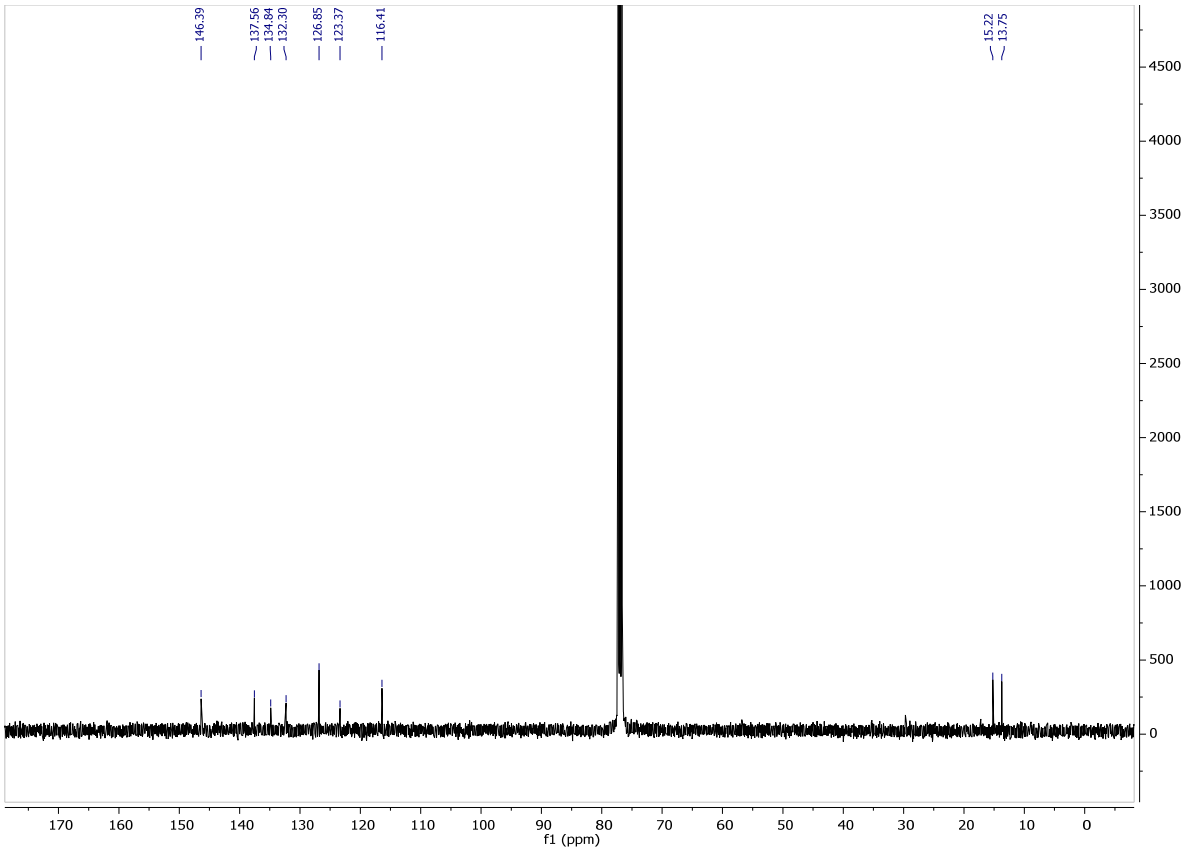
8. NMR spectra

- Compound **1a**^{o}

^{1}H NMR ($CDCl_3$, 400 MHz)

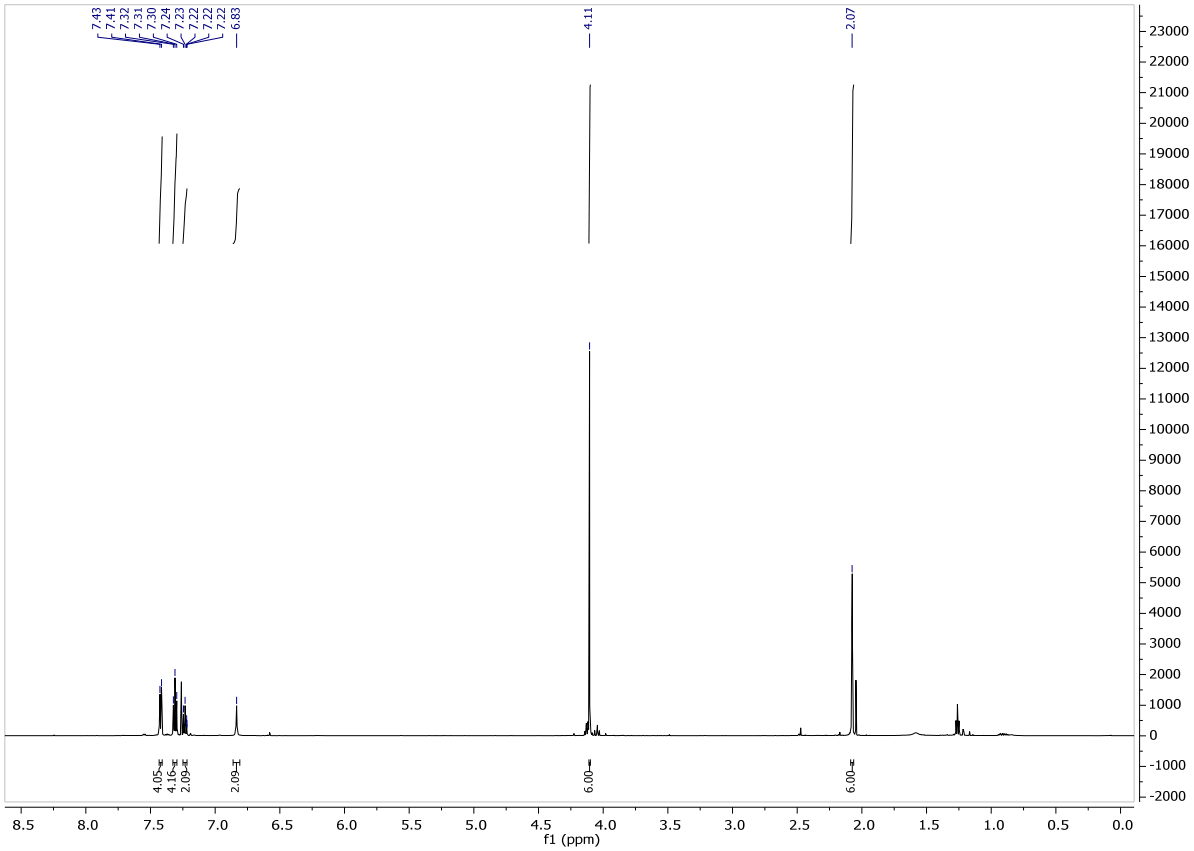


^{13}C NMR ($CDCl_3$, 101 MHz)

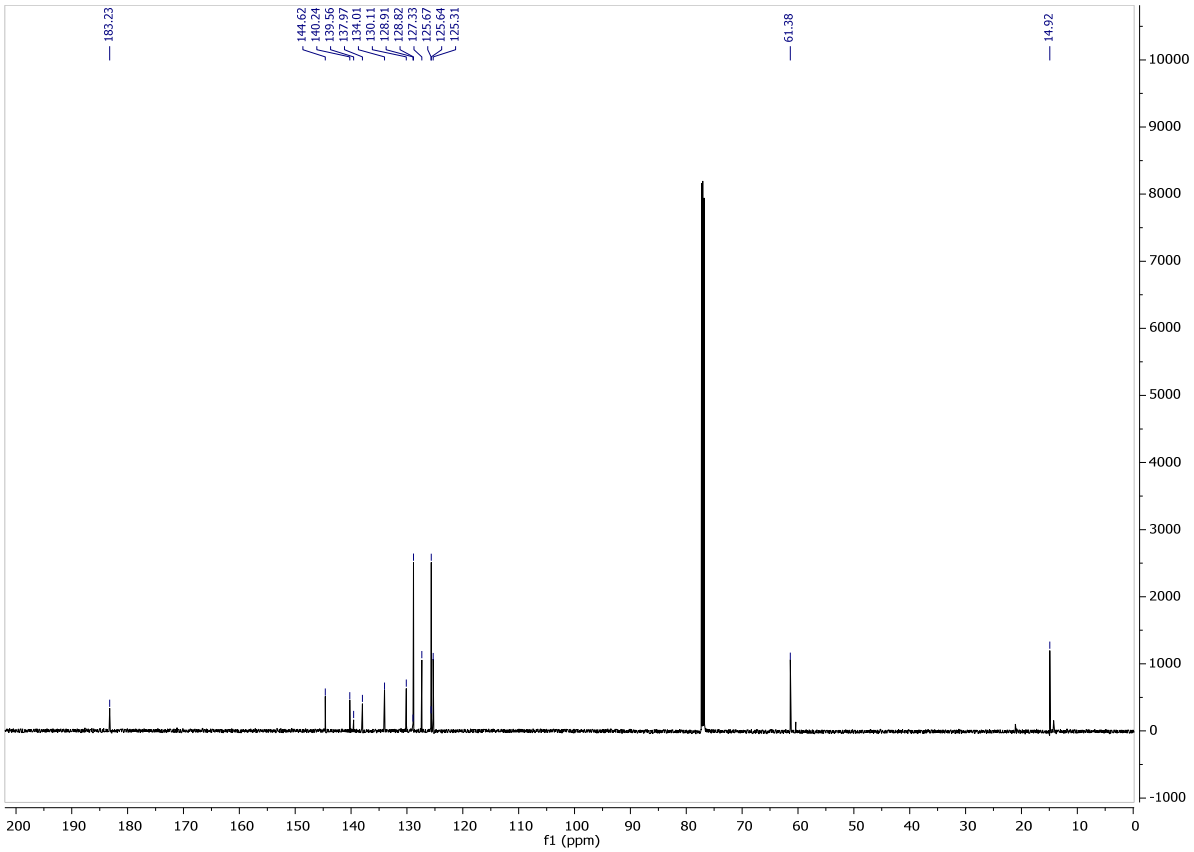


- Compound **1b'**

^{1}H ($CDCl_3$, 600 MHz)

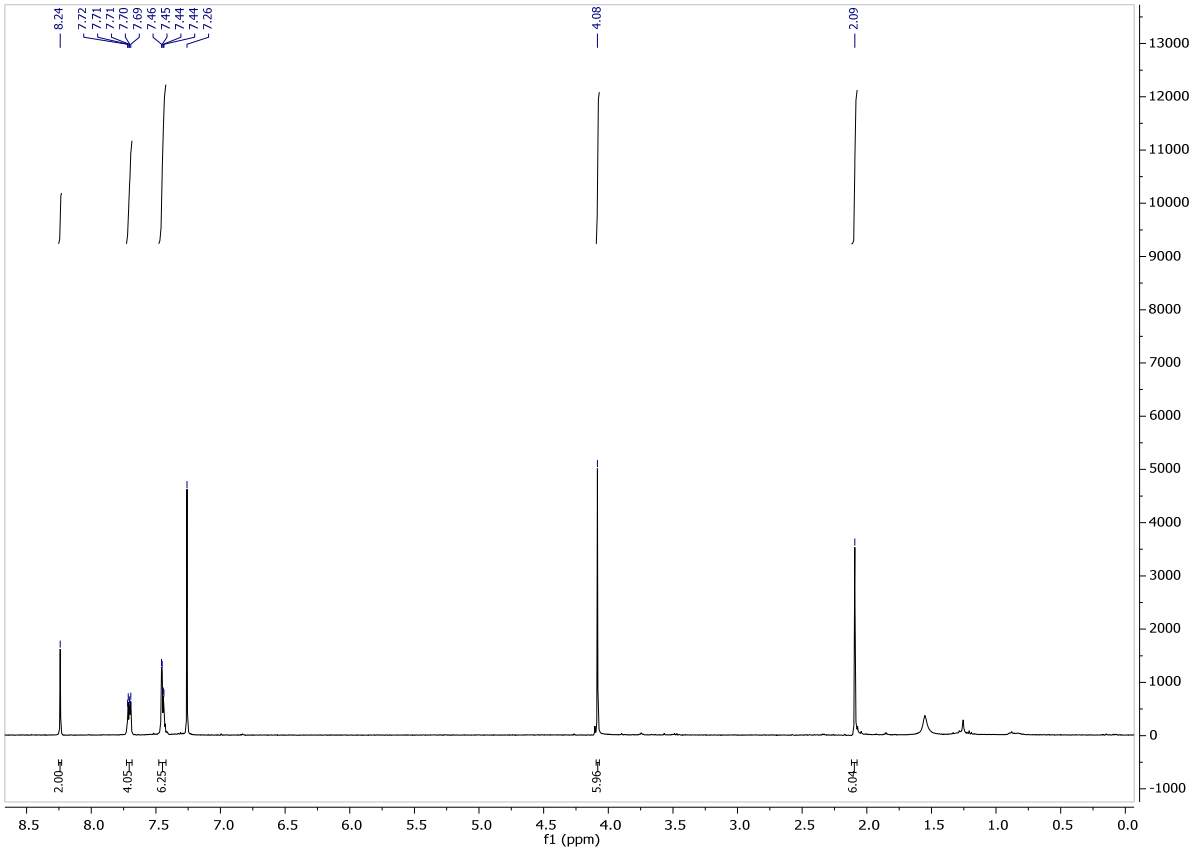


^{13}C ($CDCl_3$, 151 MHz)



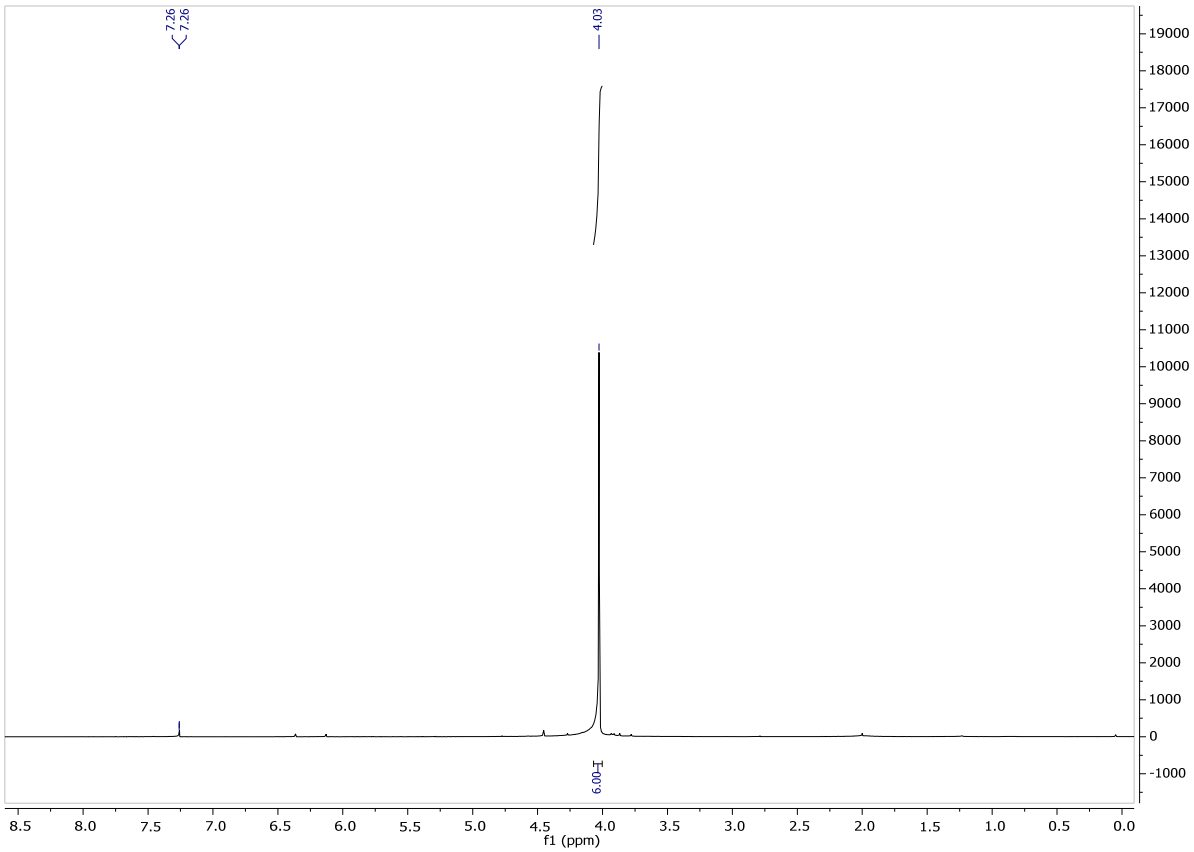
- Compound **1b**[c]

^{1}H NMR($CDCl_3$, 400MHz)

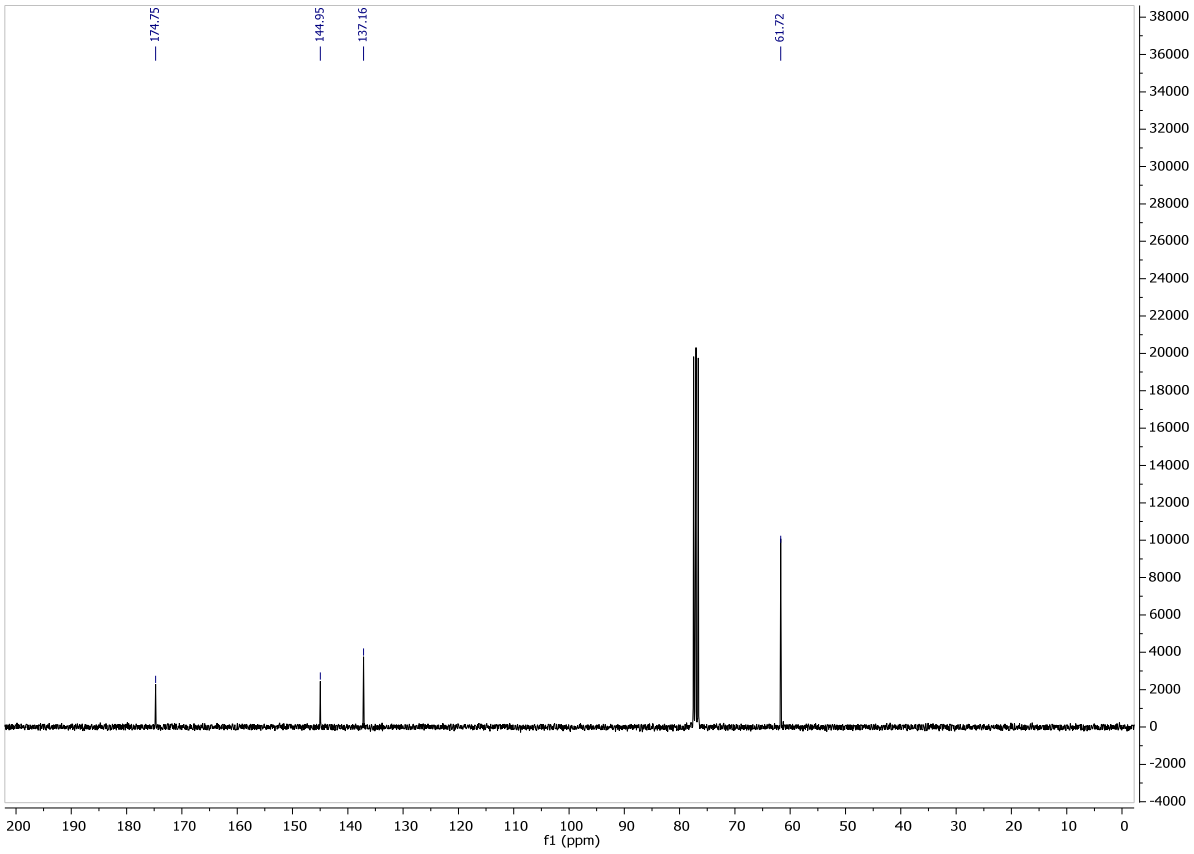


- Compound **9b**

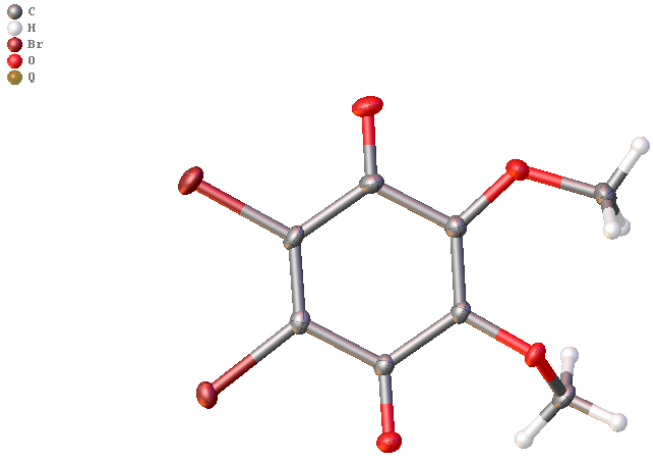
^{1}H ($CDCl_3$, 300 MHz)



^{13}C NMR ($CDCl_3$, 75MHz)



9. X-Ray Structure of 9b



Experimental. Single light red block-shaped crystals of (**O076**) were obtained by recrystallisation from .... A suitable crystal (0.25×0.18×0.10) mm³ was selected and mounted on ... on a GV1000, TitanS2 diffractometer. The crystal was kept at T = 123.01(10) K during data collection. Using **Olex2**, the structure was solved with the **ShelXT** structure solution program, using the Direct Methods solution method. The model was refined with version 2016/6 of **ShelXL** using Least Squares minimisation.[8]

Crystal Data. $C_8H_6Br_2O_4$, M_r = 325.95, monoclinic, $P2_1/c$ (No. 14), a = 8.56023(6) Å, b = 16.31960(16) Å, c = 6.91885(5) Å, □ = 94.8033(7)°, □ = □ = 90°, V = 963.165(14) Å³, T = 123.01(10) K, Z = 4, Z' = 1, □(CuK□) = 10.606, 13822 reflections measured, 1927 unique (R_{int} = 0.0288) which were used in all calculations. The final wR_2 was 0.0687 (all data) and R_1 was 0.0271 (I > 2(I)).

Compound	**O076**
Formula	$C_8H_6Br_2O_4$
$D_{calc.}$/ g cm^{-3}	2.248
□ /mm^{-1}	10.606
Formula Weight	325.95
Colour	light red
Shape	block
Size/mm³	0.25×0.18×0.10
T/K	123.01(10)
Crystal System	monoclinic
Space Group	$P2_1/c$
a/Å	8.56023(6)
b/Å	16.31960(16)
c/Å	6.91885(5)
□ /°	90
□ /°	94.8033(7)
□ /°	90
V/Å³	963.165(14)
Z	4
Z'	1
Wavelength/Å	1.54184
Radiation type	CuK□
□ $_{min}$/°	5.185
□ $_{max}$/°	73.474
Measured Refl.	13822
Independent Refl.	1927
Reflections Used	1907
R_{int}	0.0288
Parameters	129
Restraints	0
Largest Peak	0.519
Deepest Hole	-0.959
GooF	1.195
wR_2 (all data)	0.0687
wR_2	0.0685
R_1 (all data)	0.0276
R_1	0.0271

Structure Quality Indicators

Reflections:	d min (Cu) 0.80	I/σ 55.4	Rint 2.88%	complete at 2θ=134° 99%
Refinement:	Shift -0.001	Max Peak 0.5	Min Peak -1.0	GooF 1.195

A light red block-shaped crystal with dimensions 0.25×0.18×0.10 mm^3 was mounted on ....X-ray diffraction data were collected using a GV1000, TitanS2 diffractometer equipped with a n/a low-temperature device, operating at *T* = 123.01(10) K.

Data were measured using scans scans of 1.0 ° per frame for 1.0 s using CuK radiation (gradient vaccum rotating-anode X-ray tube, n/a kV, n/a mA). The total number of runs and images was based on the strategy calculation from the program CrysAlisPro (Agilent).The maximum resolution achieved was = 73.474. °

Cell parameters were retrieved using the CrysAlisPro (Agilent) software and refined using CrysAlisPro (Agilent) on 11290 reflections, 82 % of the observed reflections. Data reduction was performed using the CrysAlisPro (Agilent) software which corrects for Lorentz polarisation. The final completeness is 99.90 out to 73.474 in . The absorption coefficient of this material is 10.606 at this wavelength (= 1.54184) and the minimum and maximum transmissions are 0.634 and 0.800.

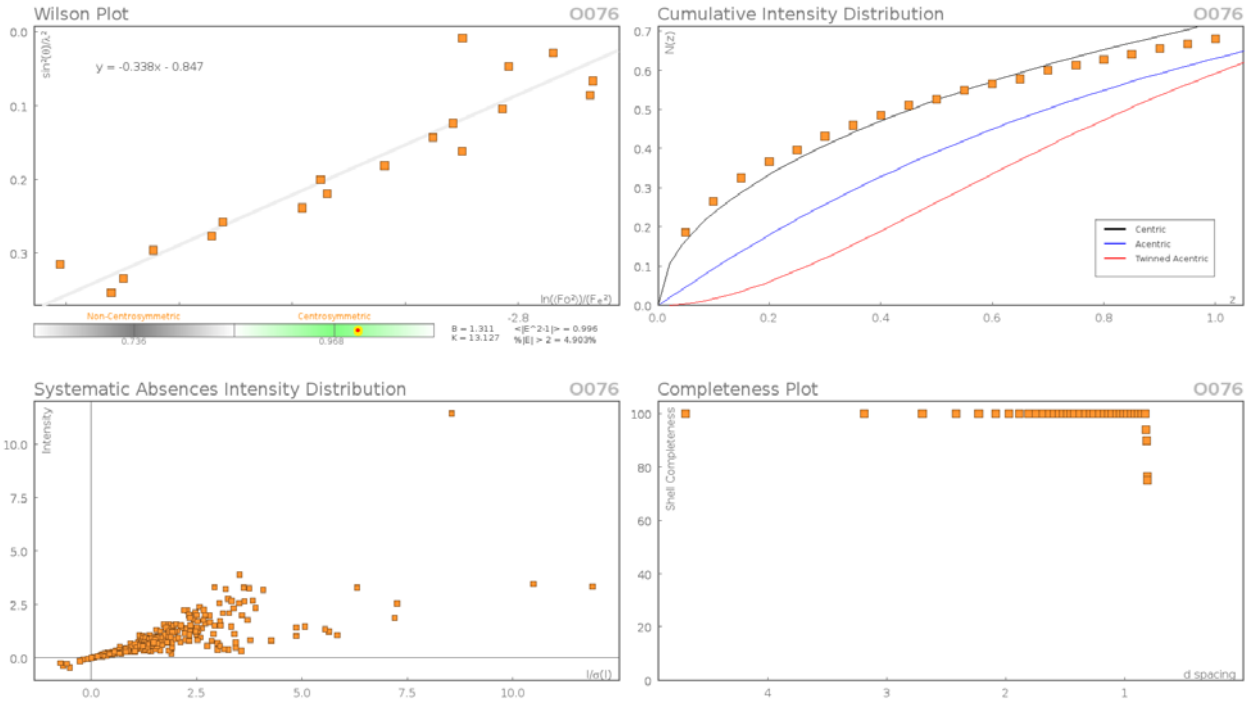
The structure was solved in the space group $P2_1/c$ (# 14) by Direct Methods using the **ShelXT** (Sheldrick, 2015) structure solution program and refined by Least Squares using version 2016/6 of **ShelXL** (Sheldrick, 2015). All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and refined using the riding model.

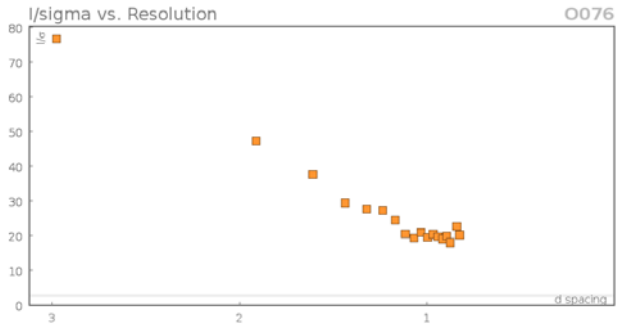
_refine_special_details: ?

_exptl_absorpt_special_details: ?

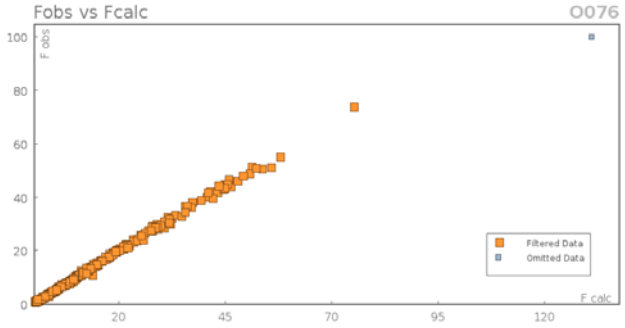
There is a single molecule in the asymmetric unit, which is represented by the reported sum formula. In other words: Z is 4 and Z' is 1.

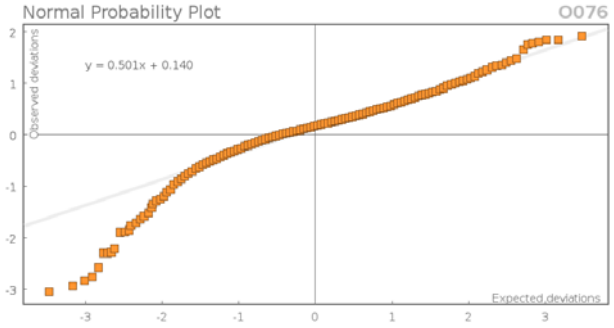
Data Plots: Diffraction Data





Data Plots: Refinement and Data





Reflection Statistics

Total reflections (after filtering)	14182	Unique reflections	1927
Completeness	0.993	Mean I/□	55.39
hkl_{max} collected	(10, 19, 8)	hkl_{min} collected	(-10, -19, -8)
hkl_{max} used	(10, 19, 8)	hkl_{min} used	(-10, 0, 0)
Lim d_{max} collected	100.0	Lim d_{min} collected	0.77
d_{max} used	8.53	d_{min} used	0.8
Friedel pairs	2829	Friedel pairs merged	1
Inconsistent equivalents	15	R_{int}	0.0288
R_{sigma}	0.0129	Intensity transformed	0
Omitted reflections	0	Omitted by user (OMIT hkl)	1
Multiplicity	(2411, 2142, 1154, 559, 246, 79, 11, 1)	Maximum multiplicity	20
Removed systematic absences	359	Filtered off (Shel/OMIT)	0

Images of the Crystal on the Diffractometer

Table 1: Fractional Atomic Coordinates (×10⁴) and Equivalent Isotropic Displacement Parameters (Å²×10³) for **O076**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij}.

Atom	x	y	z	U_{eq}
Br(01)	3602.1(3)	4478.8(2)	2540.8(4)	17.37(11)
Br(02)	6514.2(4)	3063.3(2)	2723.1(5)	24.33(11)
O(003)	5017(2)	6143.7(12)	2295(3)	20.8(4)
O(004)	7963(2)	6723.3(11)	2289(3)	16.2(4)
O(005)	10440(2)	5474.0(13)	2525(3)	25.2(5)
O(006)	9619(2)	3953.5(13)	2671(3)	25.2(4)
C(007)	5731(3)	4743.6(16)	2539(4)	14.6(5)

Atom	x	y	z	U_{eq}
C(008)	7777(3)	7205.3(16)	4007(4)	18.4(5)
C(009)	6066(3)	5643.1(16)	2439(4)	13.9(5)
C(00A)	8896(3)	5350.6(17)	2538(4)	16.3(5)
C(00B)	7721(3)	5902.3(16)	2490(4)	14.2(5)
C(00C)	11073(3)	6289.2(18)	2343(5)	23.6(6)
C(00D)	8556(3)	4448.2(17)	2611(4)	17.0(6)
C(00E)	6881(3)	4187.5(16)	2614(4)	15.7(5)

Table 2: Anisotropic Displacement Parameters (×10⁴) **O076**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2} \times U_{11} + ... + 2hka^* \times b^* \times U_{12}]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Br(01)	14.53(16)	17.29(18)	20.33(16)	-0.73(10)	1.67(10)	-4.12(10)
Br(02)	27.31(18)	10.36(17)	34.83(19)	-0.58(11)	-0.37(13)	-0.24(11)
O(003)	15.3(9)	14.4(10)	32.8(11)	-0.2(8)	1.7(8)	2.5(8)
O(004)	19.0(9)	9.2(9)	20.7(9)	0.9(7)	2.9(7)	-1.3(7)
O(005)	10.9(9)	16.7(11)	47.9(13)	-0.4(9)	2.3(9)	0.8(7)
O(006)	21.3(10)	17(1)	37.0(11)	-1.0(9)	1.7(9)	7.9(9)
C(007)	16.4(12)	13.4(13)	14.1(11)	-0.5(9)	0.9(9)	-2.3(10)
C(008)	21.7(13)	9.6(13)	24.1(13)	-3.1(10)	1.9(10)	0.6(10)
C(009)	14.4(12)	11.5(13)	15.6(11)	-1.2(9)	0.0(9)	-0.9(10)
C(00A)	13.6(12)	14.2(14)	20.9(13)	-1.1(10)	0.3(10)	-0.7(10)
C(00B)	15.2(12)	10.8(13)	16.5(11)	-0.7(9)	0.6(9)	-0.8(10)
C(00C)	12.7(12)	18.5(16)	39.7(17)	0.0(12)	2.2(12)	-2.2(10)
C(00D)	15.5(14)	13.5(14)	22.0(13)	-1.5(10)	0.4(10)	3.1(10)
C(00E)	19.7(13)	8.8(13)	18.4(12)	-1.0(9)	-0.2(10)	-0.9(10)

Table 3: Bond Lengths in Å for **O076**.

Atom	Atom	Length/Å
Br(01)	C(007)	1.873(3)
Br(02)	C(00E)	1.864(3)
O(003)	C(009)	1.212(3)
O(004)	C(008)	1.445(3)
O(004)	C(00B)	1.365(3)
O(005)	C(00A)	1.338(3)
O(005)	C(00C)	1.446(3)
O(006)	C(00D)	1.214(3)
C(007)	C(009)	1.498(4)
C(007)	C(00E)	1.336(4)
C(009)	C(00B)	1.476(4)
C(00A)	C(00B)	1.348(4)
C(00A)	C(00D)	1.503(4)
C(00D)	C(00E)	1.496(4)

Table 4: Bond Angles in ° for **O076**.

Atom	Atom	Atom	Angle/°
C(00B)	O(004)	C(008)	115.00(19)
C(00A)	O(005)	C(00C)	121.1(2)
C(009)	C(007)	Br(01)	114.59(19)
C(00E)	C(007)	Br(01)	123.8(2)
C(00E)	C(007)	C(009)	121.6(2)
O(003)	C(009)	C(007)	121.4(2)
O(003)	C(009)	C(00B)	120.8(2)
C(00B)	C(009)	C(007)	117.8(2)
O(005)	C(00A)	C(00B)	129.4(3)
O(005)	C(00A)	C(00D)	110.0(2)
C(00B)	C(00A)	C(00D)	120.6(2)
O(004)	C(00B)	C(009)	115.6(2)
C(00A)	C(00B)	O(004)	122.6(2)
C(00A)	C(00B)	C(009)	121.4(3)
O(006)	C(00D)	C(00A)	120.4(2)
O(006)	C(00D)	C(00E)	121.7(3)
C(00E)	C(00D)	C(00A)	117.8(2)
C(007)	C(00E)	Br(02)	123.0(2)
C(007)	C(00E)	C(00D)	120.6(2)
C(00D)	C(00E)	Br(02)	116.39(19)

Table 5: Torsion Angles in ° for **O076**.

Atom	Atom	Atom	Atom	Angle/°
Br(01)	C(007)	C(009)	O(003)	-2.7(3)
Br(01)	C(007)	C(009)	C(00B)	178.23(17)
Br(01)	C(007)	C(00E)	Br(02)	0.2(3)
Br(01)	C(007)	C(00E)	C(00D)	-179.90(18)
O(003)	C(009)	C(00B)	O(004)	-2.5(4)
O(003)	C(009)	C(00B)	C(00A)	-176.2(3)
O(005)	C(00A)	C(00B)	O(004)	4.4(4)
O(005)	C(00A)	C(00B)	C(009)	177.6(3)
O(005)	C(00A)	C(00D)	O(006)	0.9(4)
O(005)	C(00A)	C(00D)	C(00E)	-179.4(2)
O(006)	C(00D)	C(00E)	Br(02)	0.2(3)
O(006)	C(00D)	C(00E)	C(007)	-179.7(3)
C(007)	C(009)	C(00B)	O(004)	176.6(2)
C(007)	C(009)	C(00B)	C(00A)	2.9(4)
C(008)	O(004)	C(00B)	C(009)	77.4(3)
C(008)	O(004)	C(00B)	C(00A)	-109.0(3)
C(009)	C(007)	C(00E)	Br(02)	-179.57(19)
C(009)	C(007)	C(00E)	C(00D)	0.3(4)
C(00A)	C(00D)	C(00E)	Br(02)	-179.59(19)
C(00A)	C(00D)	C(00E)	C(007)	0.5(4)
C(00B)	C(00A)	C(00D)	O(006)	-179.3(3)
C(00B)	C(00A)	C(00D)	C(00E)	0.4(4)
C(00C)	O(005)	C(00A)	C(00B)	-3.5(5)
C(00C)	O(005)	C(00A)	C(00D)	176.3(2)
C(00D)	C(00A)	C(00B)	O(004)	-175.4(2)
C(00D)	C(00A)	C(00B)	C(009)	-2.2(4)
C(00E)	C(007)	C(009)	O(003)	177.1(3)
C(00E)	C(007)	C(009)	C(00B)	-2.0(4)

Table 6: Hydrogen Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for **O076**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij}.

Atom	x	y	z	U_{eq}
H(00A)	8012.63	7768.54	3756.18	28
H(00B)	8477.96	7006.09	5057.56	28
H(00C)	6715.55	7161.56	4347.64	28
H(00D)	10594.01	6543.84	1190.43	35
H(00E)	12185.38	6255.54	2261.98	35
H(00F)	10860.34	6609.39	3454.57	35

10. Cartesian Coordinates

1b$^{o}_{min}$

Atom	x	y	z
C	-15.038.100.939	29.044.368.258	-189.601.034
C	-27.435.818.052	33.607.833.909	22.455.777.594
C	-39.483.644.619	25.473.892.067	19.515.662.397
C	-38.125.147.164	13.217.392.807	10.870.653.103
C	-2.576.252.481	0.8477607128	-0.7641834582
C	-13.509.790.066	15.744.334.641	-1.256.123.951
O	-0.2383080914	10.701.232.635	11.349.367.055
O	-50.459.938.542	28.802.618.984	23.898.102.771
O	-0.4325081838	36.197.832.826	22.979.630.224
C	0.7948298695	36.068.501.912	15.553.350.439
O	-2.818.761.995	44.928.455.524	29.748.998.423
C	-39.449.364.116	53.770.868.513	28.651.658.533
C	-50.842.932.396	0.7028804489	-0.6524457487
C	-23.479.058.148	-0.4412971071	-0.0741639194
C	-14.918.574.954	-0.6393755093	0.9922912281
S	-14.901.899.315	23.122.883.649	14.790.583.114
C	-26.387.026.896	27.639.229.878	0.2294284537
C	-29.935.817.273	16.545.008.209	-0.4902655318
C	-61.044.376.093	0.2791332862	15.684.984.657
C	-72.049.223.768	-0.277954771	-0.9709561582
S	-7.005.242.547	-0.2534301354	0.7742924737
C	-54.365.875.455	0.4948582063	0.6671830293
C	-30.987.181.919	41.484.777.864	0.0647001844
C	-0.6441714635	0.3443262569	17.451.250.838
C	-46.821.095.016	0.8236038157	19.198.924.874
C	-84.101.279.334	-0.8308376157	16.019.459.192
C	-22.860.412.204	52.412.126.554	0.4149864988

C	-27.364.384.881	65.489.214.316	0.2457982109
C	-40.040.023.534	67.944.416.967	-0.2849181614
C	-48.212.553.485	57.179.097.126	-0.6375918169
C	-43.789.617.457	44.094.763.898	-0.4585127408
C	-83.591.030.278	13.176.178.816	29.216.306.093
C	-9.497.525.022	18.294.484.571	35.387.835.005
C	107.110.847.683	-1.882.857.121	28.493.570.635
C	107.739.515.051	14.136.011.685	15.362.696.475
C	-96.390.531.138	-0.8895972542	-0.9207379426
H	13.074.429.393	45.262.454.292	18.479.294.282
H	0.6092753166	36.220.328.858	-0.4761841457
H	14.008.099.011	27.357.157.635	18.052.892.644
H	-35.747.774.314	63.438.235.029	32.145.844.027
H	-47.760.520.319	50.396.779.586	34.847.652.858
H	-42.810.350.822	54.681.818.263	18.273.184.849
H	-36.745.408.446	16.948.162.683	13.320.383.054
H	-60.198.696.384	0.4167866968	26.389.952.116
H	-10.561.703.299	13.545.542.054	16.613.424.732
H	-0.5935361254	0.0933615491	2.810.197.747
H	0.3773905385	0.3715086119	13.503.716.398
H	-395.448.197	16.176.406.824	17.278.834.578
H	-53.554.136.741	11.650.417.704	27.133.608.564
H	-41.290.904.004	-0.0453958374	2.297.640.016
H	-1.286.808.125	50.636.277.705	0.803819406
H	-2.090.187.574	73.781.833.972	0.5211265312
H	-4.353.597.776	78.144.288.417	-0.4189620466
H	-58.144.081.268	58.965.178.191	-1.041.203.447
H	-50.354.668.474	35.794.197.657	-0.7027585332
H	-74.148.691.772	-130.864.812	34.579.220.506

H	-9.433.260.732	-21.989.061.367	-45.588.770.773
H	115.972.021.356	-22.882.190.083	-33.298.671.541
H	117.126.422.404	-14.461.927.739	-0.9895893764
H	-97.106.405.417	-0.5039002113	0.0927701535

$1b^{c}_{min}$

Atom	x	y	z
C	-99.299.507.049	0.8515276913	0.3104560882
C	-9.799.601.403	-0.3774949452	0.9124215544
C	-85.209.763.459	-11.240.964.334	0.9064322419
C	-74.118.857.808	-0.5779458306	0.0957963348
C	-76.070.160.456	0.6628158584	-0.6655290947
C	-88.175.122.792	14.819.437.539	-0.4335020165
O	-89.522.350.412	26.308.484.045	-0.8741646675
O	-84.208.107.706	-21.557.114.744	-15.841.985.308
O	110.936.788.922	-150.449.798	0.5131187105
C	116.498.259.109	-23.821.995.491	-0.4760374544
O	108.563.504.765	-0.8149636678	-16.286.791.853
C	111.488.222.257	-22.129.752.161	-1.763.784.573
C	-61.783.902.309	-12.046.479.283	0.0804706422
C	-66.629.593.781	10.560.956.137	-15.956.823.207
C	-55.232.731.308	0.0887480415	-19.359.982.381
S	-42.585.142.048	11.118.300.076	-28.540.863.606
C	-54.129.965.725	24.453.040.538	-30.443.010.807
C	-65.787.803.241	22.644.501.367	-23.489.638.241
C	-57.906.575.148	24.575.556.717	-0.6408409758
C	-45.539.989.842	29.120.006.676	-0.2658296033
S	-36.948.611.066	18.146.262.329	-0.8292329373
C	-50.051.265.181	-0.5011870533	-0.6109055868

C	-50.633.409.562	36.042.890.671	-38.702.366.783
C	-60.527.400.936	-0.9753659416	29.306.112.916
C	-44.261.803.413	0.5585422611	0.3614765013
C	-39.348.118.641	41.774.116.552	-0.6700137811
C	-37.285.484.284	38.699.153.094	-42.291.944.909
C	-34.046.678.488	4.980.131.529	-50.052.137.651
C	-44.063.903.743	58.480.317.862	-54.425.828.793
C	-57.373.742.475	55.947.414.109	-50.989.277.141
C	-60.643.301.434	44.865.669.309	-4.324.762.396
C	-28.748.098.053	47.395.830.213	-0.0657504085
C	-23.023.168.947	59.496.611.372	-0.31826395
C	-27.727.373.786	-6.622.539.203	144.710.653
C	-38.204.467.474	-6.073.475.399	-21.917.603.375
C	-43.946.850.654	48.651.238.686	-1.811.176.367
H	-127.163.469.673	24.242.945.433	-0.2398004384
H	-112.059.646.404	33.761.983.243	-0.4214991621
H	-115.155.880.529	19.829.136.198	-14.861.451.645
H	-122.161.054.717	22.508.135.592	-1.997.579.188
H	-109.603.648.518	27.534.757.167	-0.8310202284
H	-105.649.357.469	26.660.430.441	-25.647.769.676
H	-73.588.158.484	3.009.088.532	-2.293.621.331
H	-64.712.608.811	30.250.282.302	-1.257.319.064
H	-64.606.368.872	-0.4738728787	-3.811.894.655
H	-52.528.952.309	16.476.443.136	-32.485.045.908
H	-6.847.086.337	15.686.491.901	-24.689.963.013
H	-35.442.681.451	10.413.373.784	-0.0650127334
H	-51.748.138.542	1.324.813.868	-0.5811907574
H	-41.422.081.556	0.072605523	-12.983.075.582
H	-29.361.711.056	32.120.130.099	-38.834.124.641

H	-23.668.667.817	51.683.555.181	-52.657.902.009
H	-41.538.675.912	67.131.852.382	-60.493.101.268
H	-65.249.446.414	62.601.097.232	-54.417.028.366
H	-71.037.113.941	42.901.508.559	-40.828.642.511
H	-25.090.918.657	42.347.535.409	-0.9555257965
H	-14.888.083.156	63.684.425.302	-0.267557469
H	-23.244.309.932	-7.565.426.226	17.477.322.014
H	-41.865.885.379	65.853.613.407	-30.773.895.157
H	-51.923.066.729	44.376.896.015	-24.099.693.386

13_{min}

Atom	x	y	z
C	-85.237.231.944	1.845.144.961	4.174.231.402
C	-77.780.346.415	21.896.299.724	30.908.716.649
N	-81.506.540.571	32.977.214.779	23.413.124.614
C	-92.539.323.754	41.020.512.402	-25.944.422.176
C	100.454.531.568	38.176.506.418	-36.625.142.974
C	-9.747.192.847	26.479.033.066	-45.879.731.578
C	-9.415.863.433	52.244.436.921	-15.961.905.634
C	-65.410.991.917	1.501.336.992	-25.620.059.942
C	-8.253.060.874	0.7006881917	-50.554.962.711
O	-89.462.185.064	0.4373808372	-60.250.694.453
O	-71.639.854.711	-0.0488835437	-47.130.180.859
C	-6.876.094.058	11.777.251.462	-55.675.284.158
C	-76.910.744.956	24.020.238.852	-51.756.083.409
C	112.434.406.052	45.749.946.065	-405.108.193
O	119.165.696.212	42.868.234.045	-50.276.924.427
O	115.502.309.254	56.304.935.087	-32.401.975.122
C	127.236.746.206	63.906.951.862	-36.039.063.711
C	139.950.325.138	57.583.863.983	-30.559.912.087
H	-7.581.787.103	35.280.268.013	-15.418.089.482

H	-96.261.083.171	30.085.798.553	56.184.256.901
H	-106.227.808.678	19.880.074.937	46.474.682.686
H	-93.976.144.385	61.983.642.242	20.902.560.898
H	-86.127.758.779	51.992.431.914	-0.8509081237
H	-103.731.392.482	5.154.501.943	10.747.795.022
H	-67.516.544.558	0.4651798938	22.875.529.625
H	-61.560.348.187	2.022.458.262	16.780.265.618
H	-57.517.854.132	14.720.828.541	-33.163.175.257
H	-58.050.166.589	13.528.033.513	-54.324.532.253
H	-70.691.217.244	-0.894450874	-66.049.045.887
H	-73.940.140.343	32.602.539.391	-57.898.445.528
H	-87.569.772.832	22.181.141.287	-53.341.221.523
H	-75.271.645.494	26.598.050.961	-41.236.787.681
H	-125.512.293.378	73.790.101.728	-31.684.226.409
H	-127.663.967.788	64.766.248.819	-469.220.384
H	-148.569.275.142	63.971.248.661	-32.823.519.076
H	-141.626.825.298	47.796.413.135	-35.133.195.294
H	-139.338.937.304	56.372.314.043	-19.690.364.998

$1b^{o}_{ADJ}$

Atom	x	y	z
C	-0.80407314	349.775.721	-15.058.936
C	-207.115.394	392.368.047	-179.993.078
C	-322.183.471	299.959.576	-164.907.763
C	-297.730.862	160.333.084	-113.558.157
C	-17.214.937	118.960.893	-0.82168213
C	-0.56292178	214.493.641	-0.95931445
O	-0.5663618	180.110.869	-0.61935797

O	-436.514.137	-335.173.676	-192.783.693
O	-0.20629407	-438.781.774	-158.489.269
C	-147.873.499	-397.970.545	-212.489.828
O	-223.091.921	-521.771.558	-213.226.349
C	-328.437.918	-566.789.326	-30.035.809
C	-418.515.763	-0.75676409	-0.98184586
C	-140.187.753	-0.20360185	-0.42931895
C	-0.70252086	-0.58842619	-0.69755785
S	-0.52539417	-232.353.261	-0.74765049
C	-137.936.463	-253.891.817	-0.77136128
C	-177.984.733	-131.898.097	-124.905.733
C	-502.004.666	-0.36654462	-20.800.463
C	-607.039.379	-0.44389611	-172.961.582
S	-606.654.767	-0.69825946	-0.0080325
C	-463.006.119	-0.26218373	-0.22656528
C	-159.246.256	-386.514.017	-136.250.269
C	-0.1377374	-0.23915978	-181.482.925
C	-406.647.122	-0.45741426	-160.179.287
C	-709.883.527	-104.369.635	-258.867.137
C	-0.70309215	-492.966.732	-11.307.708
C	-0.91739511	-618.006.397	-170.760.516
C	-201.974.625	-639.542.017	-253.634.967
C	-291.298.897	-534.768.885	-27.740.735
C	-27.087.162	-409.958.779	-218.898.606
C	-738.860.876	-0.48460937	-384.860.303
C	-835.602.061	-105.280.301	-467.499.182

C	906.622.802	218.367.539	426.392.498
C	879.234.545	274.425.729	301.557.798
C	781.825.994	218.515.259	219.041.541
H	189.667.285	488.326.595	257.674.943
H	213.515.316	361.711.466	133.176.829
H	135.335.041	320.456.288	288.416.443
H	294.462.863	664.603.825	335.324.252
H	341.559.768	499.315.309	385.144.501
H	422.533.101	577.046.671	245.971.095
H	229.914.087	119.545.317	219.202.403
H	481.479.699	0.65910474	310.343.234
H	0.65281113	12.013.264	188.001.197
H	0.24486959	0.26788919	278.022.455
H	0.92429182	0.45131419	165.284.401
H	342.276.962	134.128.186	162.559.577
H	486.032.038	0.59726936	23.436.296
H	346.136.973	0.40244361	191.524.765
H	0.1722729	477.009.915	0.50667087
H	0.21505712	698.653.238	151.387.702
H	218.573.254	737.047.608	298.603.605
H	378.573.943	550.778.751	340.211.729
H	343.233.254	330.457.678	234.440.606
H	685.948.501	0.40494442	417.549.138
H	856.675.645	0.59878704	-56.401.158
H	982.593.525	261.927.032	490.707.675
H	933.387.407	362.568.899	268.231.005

	-	-	-
H	760.258.714	264.831.274	123.120.406

1b$^{c}_{ADJ}$

Atom	x	y	z
C	-907.836.258	112.179.091	0.17998013
C	-924.726.447	-0.12554757	0.73611198
C	-815.290.185	113.762.943	-0.69431059
C	-694.523.697	-0.80714238	-0.08928182
C	-681.491.236	0.51212176	-0.72062855
C	-779.981.716	156.271.355	-0.39190023
O	-760.456.436	277.328.926	-0.59725088
O	-828.416.733	220.368.065	-130.995.158
O	1.007.239.579	203.590.213	-0.34045185
C	1.058.567.529	263.598.508	-0.85540958
O	1.041.569.911	-0.33691453	-13.524.679
C	1.081.948.342	157.197.172	-196.805.019
C	-590.794.071	172.138.538	-0.19599324
C	-579.357.693	0.75600729	-161.673.319
C	-493.130.236	-0.4216981	-20.809.625
S	-344.228.685	0.34925571	-290.484.382
C	-423.119.303	193.936.034	-293.689.147
C	-540.923.105	197.989.552	-224.007.228
C	-584.738.595	308.113.521	-0.22444285
C	-475.985.164	378.697.737	-0.22381751
S	-365.035.195	283.206.065	-121.713.654
C	-459.226.653	126.455.115	-0.8373204

C	-360.215.613	305.280.399	-365.222.264
C	-570.017.456	-120.381.636	-317.548.716
C	-377.246.005	-0.49734521	-0.23249255
C	-447.822.781	-52.011.553	-0.03734703
C	-223.998.303	301.838.564	-400.493.006
C	-164.946.124	408.484.218	-467.827.892
C	-240.654.289	520.751.804	-501.701.297
C	-376.183.993	525.442.011	-467.827.806
C	-435.486.172	419.087.662	-400.629.632
C	-36.131.599	593.889.001	-0.79250987
C	-336.095.349	728.509.037	-0.54132164
C	-396.325.993	-79.214.929	-0.54553596
C	-481.979.987	720.023.733	-138.193.985
C	-507.446.994	585.533.758	-113.410.649
H	1.136.975.463	332.072.638	-0.52664653
H	-980.766.858	318.808.191	-138.854.447
H	1.102.407.398	18.720.126	-151.003.744
H	1.186.766.634	140.505.111	-222.473.308
H	1.072.259.874	242.219.114	-129.185.023
H	1.022.808.837	174.851.473	-286.923.586
H	-598.144.904	288.418.513	-209.069.091
H	-664.793.646	352.937.683	-0.79279585
H	-596.104.963	-0.52242689	-39.891.812
H	-509.090.056	-20.149.577	-358.014.319
H	-662.284.986	162.758.443	-276.815.284
H	-279.703.169	-0.20208691	-0.16000492

H	-430.955.962	0.40000828	0.55251205
H	-362.234.795	114.084.185	-110.288.635
H	-163.453.439	215.743.499	-373.562.874
H	-0.59520121	403.886.562	-493.651.851
H	-194.638.749	603.843.238	-554.438.435
H	-436.093.433	612.042.707	-494.586.719
H	-541.306.769	423.028.094	-376.914.255
H	-31.507.692	545.957.671	-16.508.906
H	-269.511.505	783.846.986	-119.756.157
H	-376.409.642	897.116.423	-0.74266624
H	-528.469.006	768.558.584	-223.549.721
H	-572.164.005	529.867.693	-180.416.326

13_{ADJ} ($1b^{o}_{ADJ}$)

Atom	x	y	z
C	-332.523.653	-112.640.897	-595.218.231
C	-373.679.825	-0.05903205	-647.753.197
N	-281.185.753	-109.658.568	-655.723.204
C	-163.430.425	-114.346.965	-581.132.136
C	-117.258.628	-0.01880182	-527.598.399
C	-185.112.604	-132.838.022	-564.276.888
C	-10.575.818	-25.313.566	-569.928.861
C	-509.435.731	-0.43450916	-701.053.062
C	-416.649.765	-231.097.563	-572.761.441
O	-369.721.778	-341.967.111	-552.139.705
O	-551.085.145	-207.932.769	-572.213.859

C	-635.699.566	-322.903.665	-546.312.813
C	-657.820.609	-406.611.306	-671.398.715
C	-0.01163158	-0.15642699	-438.089.312
O	0.40416624	-12.458.593	-401.017.209
O	0.54063086	-101.253.475	-397.261.373
C	-164.752.222	-0.91976797	-30.400.643
C	-29.672.539	-0.68045628	-375.832.946
H	-31.534.672	-197.763.282	-691.418.331
H	-17.346.154	-204.255.236	-482.634.193
H	-134.154.586	-179.646.156	-650.158.122
H	-133.390.529	-312.336.261	-658.073.629
H	-0.02650442	-250.818.585	-561.705.431
H	-14.418.571	-304.882.361	-4.811.661
H	-56.832.203	-0.96469009	-625.179.527
H	-566.121.351	-0.44195252	-731.506.027
H	-498.097.224	-110.063.647	-78.751.919
H	-729.266.496	-279.159.863	-51.058.124
H	-590.865.325	-381.569.159	-465.878.746
H	-727.893.207	-488.016.367	-649.451.136
H	-563.755.246	-450.516.034	-705.620.158
H	-700.271.806	-345.970.049	-752.163.472
H	-16.386.812	-188.577.485	-25.295.147
H	-143.568.847	-0.13009585	-231.640.933
H	-378.975.454	-0.69125868	-303.358.868
H	-296.323.201	-0.29197779	-425.811.232

H	315.701.375	-146.136.803	-450.294.775

13_{ADJ} ($1b^{c}_{ADJ}$)

Atom	x	y	z
C	-858.894.485	177.736.855	414.837.596
C	-781.522.972	215.470.864	309.330.355
N	-823.806.398	319.812.407	228.353.399
C	-93.690.116	397.307.762	250.985.741
C	-1.016.354.515	368.846.977	35.762.785
C	-993.018.507	244.137.926	441.715.315
C	-951.506.933	507.879.554	149.463.994
C	-647.450.968	159.199.649	268.090.001
C	-827.513.523	0.68962655	508.256.571
O	-901.981.727	0.35654175	599.322.778
O	-70.948.059	0.04373206	-483.870.319
C	-680.436.919	109.732.804	-567.294.204
C	-753.608.305	233.409.362	-517.005.536
C	-1.133.692.055	446.333.645	-400.078.054
O	-1.211.088.197	407.149.093	-486.119.307
O	-1.148.566.381	568.040.598	-339.311.403
C	-1.263.070.463	645.674.499	38.033.826
C	-138.897.768	604.920.765	304.968.868
H	-778.842.975	330.174.612	138.307.863
H	-1.001.029.288	269.037.575	-548.164.277
H	-1.074.693.359	172.189.025	-425.109.012
H	-897.268.742	597.763.854	181.646.125
H	-909.516.158	475.374.795	0.53494787
H	-105.559.387	535.855.672	135.538.856
H	-651.160.781	0.50857605	255.757.661
H	-614.059.746	204.670.668	174.160.888
H	-571.780.764	179.506.668	34.454.252
H	-571.968.373	121.904.003	-55.992.159
H	-707.021.525	-0.8699352	-670.874.972
H	-71.935.725	322.436.714	-571.111.588

H	-86.129.623	-223.066.138	533.041.365
H	-735.052.991	-248.177.418	410.031.823
H	1.235.048.877	-749.065.827	35.801.003
H	-127.681.889	634.311.073	488.186.614
H	1.472.403.035	-670.316.463	333.093.045
H	1.416.331.016	-501.899.827	329.486.782
H	1.374.128.279	-612.931.826	196.651.967

$(1b^{o}_{min}\text{-}13_{min})_{ADJ}$

Atom	x	y	z
C	-0.8040730809	34.977.569.396	-15.058.934.855
C	20.711.537.808	-39.236.801.652	-17.999.306.454
C	32.218.344.697	-29.995.955.349	-16.490.775.014
C	29.773.083.957	-16.033.307.134	-11.355.814.853
C	17.214.935.722	-11.896.088.458	-0.8216820681
C	-0.5629217323	21.449.362.409	-0.9593143737
O	0.5663617609	18.011.085.546	-0.6193579244
O	43.651.410.342	-33.517.365.036	-19.278.367.776
O	0.2062940576	43.878.173.992	-15.848.925.724
C	1.478.734.882	39.797.051.467	-21.248.981.172
O	-223.091.904	52.177.151.798	-21.322.633.273
C	32.843.789.287	-56.678.928.214	-30.035.806.748
C	41.851.573.121	0.7567640295	-0.9818457857
C	14.018.774.251	-0.2036018311	-0.4293189171
C	-0.7025208105	-0.5884261487	0.6975577944
S	-0.5253941271	23.235.324.344	-0.7476504392
C	13.793.645.274	-25.389.179.782	-0.7713612234

C	-17.798.471.965	-13.189.808.687	-12.490.572.345
C	-50.200.462.738	0.3665445912	-20.800.461.481
C	-60.703.933.248	-0.4438960709	-17.296.156.837
S	-60.665.472.163	-0.6982593997	0.0080324951
C	-46.300.608.387	0.2621837112	0.2265652618
C	-15.924.624.418	-38.651.398.723	-13.625.025.886
C	-0.1377373857	0.2391597656	-18.148.291.076
C	-4.066.470.907	0.4574142266	-16.017.927.455
C	-70.988.347.151	-10.436.962.684	-25.886.711.704
C	-0.70309209	-49.296.669.463	-11.307.707.087
C	-0.9173950396	-61.800.634.899	-17.076.050.223
C	-20.197.460.925	-63.954.196.599	-25.363.494.772
C	-29.129.887.545	-53.476.884.364	-27.740.732.856
C	-27.087.159.951	-40.995.874.779	-21.889.858.924
C	-7.388.608.182	-0.4846093346	-38.486.027.359
C	-83.560.199.847	-10.528.029.292	-46.749.914.647
C	-90.662.273.342	-21.836.752.202	-42.639.246.544
C	-87.923.447.993	-27.442.570.806	-30.155.777.422
C	-78.182.593.671	-21.851.524.226	-21.904.152.376
H	-18.966.727.034	-48.832.655.765	-25.767.492.377
H	-21.351.529.916	-36.171.143.877	-13.317.681.896
H	-13.533.503.084	-32.045.626.319	-28.841.642.061
H	-29.446.284.073	-66.460.377.151	-33.532.422.633
H	-34.155.974.254	-49.931.527.092	-3.851.444.711
H	-42.253.306.873	-57.704.662.793	-24.597.107.658
H	-22.991.406.982	-11.954.530.753	-21.920.238.583

	-		-
H	48.147.966.225	0.6591046902	31.034.320.972
H	-0.6528110757	12.013.263.058	1.880.011.825
H	-0.2448695742	-0.2678891665	27.802.243.357
H	0.9242917507	0.4513141603	16.528.438.905
H	- 34.227.693.644	13.412.817.565	16.255.956.418
H	- 48.603.200.133	0.5972693176	23.436.294.175
H	- 34.613.694.635	-0.4024435798	19.152.475.027
H	0.1722728827	-4.770.098.783	-0.5066708346
H	-0.2150571082	- 69.865.318.642	- 15.138.768.998
H	- 21.857.323.743	- 73.704.755.151	- 29.860.358.181
H	- 37.857.391.414	-550.778.711	- 34.021.170.262
H	- 34.323.322.744	-3.304.576.528	- 23.444.058.834
H	- 68.594.844.648	0.4049443936	- 41.754.910.626
H	- 85.667.557.943	-0.5987869915	- 56.401.153.734
H	- 98.259.344.754	- 26.192.701.153	- 49.070.763.801
H	- 93.338.733.456	- 36.256.887.201	- 26.823.098.438
H	- 76.025.865.778	- 26.483.125.433	- 12.312.039.622
C	- 33.252.362.744	11.264.088.874	- 59.521.818.802
C	- 37.367.979.609	-0.0590320503	- 64.775.314.575
N	- 28.118.573.178	- 10.965.855.975	- 65.572.315.158
C	- 16.343.041.307	- 11.434.695.599	- 58.113.209.227
C	- 11.725.861.921	0.0188018177	- 52.759.835.895
C	- 18.511.258.988	13.283.801.206	- 56.427.684.228
C	- 10.575.817.171	- 25.313.564.093	- 56.992.881.811
C	- 50.943.569.166	-0.4345091282	- 70.105.300.727
C	- 41.664.973.301	2.310.975.455	- 57.276.139.459
O	- 36.972.175.025	34.196.708.509	- 55.213.966.194

O	-55.108.510.385	20.793.275.293	-57.221.381.462
C	-63.569.951.875	32.290.363.991	-54.631.277.064
C	-65.782.055.933	40.661.127.557	-67.139.866.566
C	-0.0116315752	0.156426976	-43.808.927.846
O	0.4041662104	12.458.592.013	-40.101.717.818
O	0.5406308188	-10.125.346.773	-39.726.134.272
C	16.475.220.919	-0.9197679003	-30.400.640.635
C	29.672.536.738	-0.6804562234	-37.583.291.731
H	-31.534.669.658	-19.776.326.721	-69.141.827.849
H	-17.346.152.667	2.042.552.206	-48.263.415.644
H	-13.415.457.544	17.964.614.246	-6.501.580.742
H	-13.339.051.843	-31.233.623.744	-65.807.357.874
H	0.0265044204	-25.081.856.597	-56.170.538.846
H	-14.418.569.918	-30.488.233.777	-4.811.660.635
H	-56.832.198.695	-0.9646900149	-62.517.947.962
H	-56.612.130.977	0.4419524839	-73.150.596.965
H	-49.809.718.578	-11.006.363.899	-78.751.913.102
H	-7.292.664.396	27.915.984.229	-51.058.120.114
H	-59.086.528.017	38.156.913.048	-4.658.787.101
H	-72.789.315.292	48.801.632.997	-64.945.108.701
H	-56.375.520.202	45.051.599.964	-70.562.010.413
H	-70.027.175.365	34.597.002.253	-75.216.341.675
H	-16.386.810.753	-18.857.747.115	-25.295.145.088
H	-14.356.883.655	-0.1300958435	-23.164.091.522
H	-37.897.542.462	-0.6912586317	-30.335.884.474

H	29.632.317.837	0.2919777636	-42.581.119.928
H	31.570.135.069	-14.613.679.192	-45.029.474.075

$(1b^{c}_{min}\text{-}13_{min})_{ADJ}$

Atom	x	y	z
C	-97.004.469.697	11.576.897.879	0.3124094828
C	-96.367.747.974	-0.0725992805	0.9032082039
C	-8.369.992.332	-0.853820236	0.9330678212
C	-72.665.719.045	-0.3882003749	0.0780252081
C	-7.409.501.795	0.8596594826	-0.6882739918
C	-8.564.090.081	17.411.407.164	-0.4306143476
O	-86.524.835.066	29.073.832.319	-0.8495768174
O	-82.940.963.455	18.371.150.135	-16.861.499.779
O	108.219.976.372	19.147.453.412	0.4726162908
C	115.891.298.624	21.544.497.797	-0.7216801132
O	107.147.534.103	-0.4916692931	-15.997.650.728
C	110.869.669.311	-18.845.739.351	-15.957.561.444
C	-60.748.234.533	10.960.795.727	-0.01895636
C	-64.789.340.304	11.826.314.148	-16.601.043.835
C	-5.421.130.263	0.1402566161	-20.359.669.844
S	-41.297.769.162	10.738.866.989	-30.110.471.758
C	-52.037.908.655	24.744.741.388	-31.745.977.417
C	-63.511.412.018	23.741.181.215	-24.309.623.681
C	-57.507.387.119	23.689.069.234	-0.5670555965
C	-45.620.392.621	29.091.894.153	-0.1421003401
S	-36.796.372.163	-1.874.271.102	-0.9886767604
C	-48.895.326.143	-0.476415182	-0.7274773279
C	-48.165.168.158	35.974.742.122	-4.032.173.842
C	-60.592.222.038	-0.8917054556	-30.008.531.479
C	-41.989.833.546	0.5473818614	0.2109441763

C	-40.129.699.057	42.115.712.698	-0.5265194477
C	-34.763.226.776	37.924.129.352	-4.418.592.111
C	-31.164.928.337	48.694.841.887	-52.256.577.912
C	-4.087.272.242	57.715.777.437	-56.670.343.625
C	-54.232.315.032	55.873.157.682	-52.966.083.396
C	-5.786.549.858	45.129.565.057	-44.903.012.248
C	-30.136.234.073	48.381.848.144	-0.2433855735
C	-25.050.565.471	60.814.738.589	-0.1252635883
C	-29.803.084.036	67.227.899.626	-12.716.118.372
C	-39.679.088.423	61.100.180.832	-20.494.878.015
C	-44.789.399.459	48.684.143.827	-16.843.956.226
H	124.307.618.151	27.780.642.093	-0.4158762314
H	109.932.916.666	26.775.153.939	-14.727.876.097
H	119.636.878.949	1.208.001.244	-1.128.463.601
H	121.623.736.903	18.907.047.669	-17.860.717.567
H	108.873.510.952	23.413.740.794	-0.6223539253
H	105.591.290.922	24.338.067.834	-23.742.915.974
H	-70.815.994.911	31.664.738.293	-23.635.040.018
H	-64.367.757.693	28.939.216.187	-12.136.070.044
H	-64.733.590.783	-0.3700796361	-3.867.261.622
H	-53.173.682.679	16.139.317.323	-33.483.440.438
H	-68.695.688.315	14.326.682.549	-25.039.706.133
H	-33.031.676.691	0.9629042898	-0.2551566537
H	-488.168.138	13.673.305.686	0.4502036474
H	-39.127.706.277	0.0518516357	-11.420.295.489
H	-2.706.781.957	31.091.153.679	-40.704.632.918
H	-2.076.336.724	50.051.372.562	-55.071.376.252

H	-38.067.526.401	66.099.497.428	-62.980.338.718
H	-61.856.075.886	627.871.462	-56.436.601.848
H	-68.300.295.821	43.687.346.478	-42.302.489.529
H	-2.644.520.752	-43.599.827.098	-11.463.270.595
H	-17.390.068.173	65.503.997.801	-0.4852364572
H	-25.819.808.907	76.912.723.172	-15.598.373.443
H	-4.335.436.419	65.978.014.902	-29.475.783.977
H	-52.275.727.006	43.938.796.309	-23.100.092.374
C	-85.025.823.675	0.9349295655	45.679.407.988
C	-720.514.493	0.9566062251	4.148.707.563
N	-67.477.167.587	20.567.597.688	3.443.278.669
C	-75.195.791.971	31.362.451.098	30.456.849.665
C	-88.270.631.765	31.869.035.338	34.282.083.811
C	-94.401.494.038	21.016.344.697	4.299.212.831
C	-67.667.221.216	41.270.199.193	21.916.569.567
C	-61.561.946.349	-0.1117538286	43.352.947.644
C	-91.329.402.013	-0.1626215751	5.306.346.888
O	-102.986.234.548	-0.1145608577	-56.894.242.183
O	-83.382.256.494	12.379.752.313	-55.439.371.736
C	-89.177.397.186	23.329.784.286	-6.292.522.427
C	-96.646.973.597	32.979.682.576	-5.384.494.069
C	-97.718.661.345	42.475.333.545	-30.663.028.629
O	-109.264.794.642	42.712.344.255	-34.830.126.347
O	-92.819.446.205	52.049.143.658	-22.384.149.345
C	-101.877.742.957	62.628.430.607	-18.448.628.039
C	-11.037.548.424	58.502.094.106	0.6524218138
H	-57.832.499.964	20.441.226.771	31.453.698.935
H	-97.865.377.763	25.331.047.675	-52.507.439.849
H	-103.567.064.772	17.288.582.038	-38.242.552.097
H	-56.987.949.616	38.882.822.947	21.752.394.156
H	-71.410.269.223	4.107.993.249	11.636.339.144
H	-68.900.947.925	51.452.379.185	-25.624.565.058
H	-64.169.942.371	10.059.449.429	-37.613.235.534

H	-51.789.861.098	0.2446786852	39.955.487.063
H	-60.741.757.548	-0.4102206473	5.381.111.147
H	-80.608.510.431	28.181.845.165	-67.660.348.125
H	-95.730.497.734	19.265.791.347	-70.659.693.532
H	100.212.992.493	-41.547.700.352	-59.673.798.658
H	105.294.357.154	-28.084.179.423	-49.273.557.462
H	-9.009.190.832	36.712.830.961	-45.907.037.049
H	-95.305.394.883	70.986.113.547	-15.932.510.072
H	108.073.035.747	-65.383.028.373	-27.012.559.398
H	116.309.603.177	-67.036.002.943	-0.3053831617
H	117.205.633.769	-50.414.174.382	-0.9266289814
H	104.036.021.902	-55.086.211.599	-0.1720667971

($1b^{o}_{min}$-13_{min})$_{nonADJ}$

Atom	x	y	z
C	-150.381.032	290.443.727	-189.601.063
C	-274.358.222	336.078.391	-22.455.781
C	-394.836.507	254.738.959	-195.156.654
C	-38.125.153	132.173.948	-108.706.548
C	-257.625.287	-0.84776084	-0.76418358
C	-135.097.921	15.744.337	-125.612.414
O	-0.23830813	107.012.343	-113.493.688
O	-504.599.462	288.026.234	-238.981.064
O	-0.43250825	361.978.384	-229.796.337
C	0.79482999	360.685.073	-155.533.528
O	-281.876.242	449.284.623	-29.749.003
C	-394.493.701	537.708.766	-286.516.629

C	-508.429.402	0.70288055	-0.65244585
C	-234.790.618	-0.44129717	-0.07416394
C	-149.185.772	-0.63937561	0.99229139
S	-149.019.016	-231.228.872	147.905.853
C	-263.870.309	-276.392.341	0.22942849
C	-299.358.219	-165.450.108	-0.49026561
C	-610.443.856	0.27913333	-156.849.871
C	-720.492.346	-0.27795481	-0.9709563
S	-700.524.361	-0.25343017	0.77429259
C	-543.658.841	0.49485828	0.66718313
C	-309.871.867	-414.847.842	0.0647002
C	-0.64417156	0.34432631	174.512.535
C	-468.211.022	0.82360395	-191.989.278
C	-841.012.919	-0.83083775	-160.194.616
C	-228.604.157	-524.121.345	0.41498656
C	-273.643.891	-654.892.248	0.24579825
C	-400.400.296	-679.444.273	-0.2849182
C	-482.125.609	-571.791.057	-0.63759192
C	-437.896.242	-440.947.707	-0.45851282
C	-835.910.428	-131.761.808	-292.163.105
C	-949.752.647	-182.944.874	-353.878.404
C	-1.071.108.643	-188.285.742	-28.493.575
C	-1.077.395.317	-141.360.139	-153.626.988
C	-963.905.461	-0.88959739	-0.92073808
H	130.744.314	452.624.612	-184.792.971
H	0.60927541	362.203.344	-0.47618422
H	140.081.012	273.571.618	-180.528.954
H	-357.477.797	634.382.449	-32.145.849
H	-477.605.276	503.967.872	-348.476.582
H	-428.103.574	546.818.267	-182.731.876
H	-36.745.414	-169.481.653	-133.203.851

H	-601.987.059	0.41678676	-263.899.562
H	-105.617.049	135.455.441	166.134.273
H	-0.59353621	0.09336157	281.019.817
H	0.3773906	0.37150867	135.037.185
H	-395.448.257	161.764.093	172.788.372
H	-535.541.452	116.504.195	271.336.127
H	-412.909.103	-0.04539584	229.764.036
H	-128.680.832	-506.362.855	0.80381953
H	-209.018.789	-737.818.455	0.52112661
H	-435.359.844	-781.443.002	-0.41896211
H	-5.814.409	-589.651.868	-10.412.036
H	-503.546.762	-357.942.031	-0.70275864
H	-741.487.035	-130.864.832	-345.792.257
H	-943.326.218	-219.890.647	-455.887.778
H	-115.972.039	-228.821.935	-332.986.766
H	-1.171.264.402	-1.446.193	-0.98958952
H	-971.064.202	-0.50390029	-0.09277017
C	-561.317.887	1.086.924.755	-405.491.909
C	-649.644.335	1.156.754.287	-32.929.363
N	-785.721.933	1.136.871.922	-348.609.297
C	-841.606.419	1.048.735.118	-440.213.197
C	-759.285.583	-975.567.009	-519.908.751
C	-607.954.816	-988.537.863	-511.651.385
C	-992.649.793	1.047.366.237	-437.219.737
C	-618.963.258	1.257.796.692	-22.120.263
C	-415.035.688	1.097.333.695	-396.012.963
O	-339.657.846	1.033.274.349	-467.520.235
O	-369.206.577	1.184.415.448	-301.309.165
C	-225.656.075	-119.658.286	-290.412.321
C	-166.576.065	1.087.907.934	-201.719.937

C	-803.846.223	-878.473.348	-620.826.853
O	-725.926.414	-81.590.553	-69.091.901
O	-939.222.437	-863.326.869	-630.886.068
C	-985.351.482	-768.452.879	-729.590.945
C	-985.838.341	-626.366.544	-675.047.317
H	-848.904.072	-1.189.708.616	-290.515.712
H	-56.755.878	-1.017.407.975	-609.633.506
H	-56.311.754	-889.992.679	-493.347.424
H	-1.034.344.335	-1.074.173.966	-534.546.323
H	-1.030.586.417	-1.118.127.695	-362.627.927
H	-1.030.794.418	-94.791.679	-413.008.545
H	-560.360.417	-1.212.988.643	-140.637.472
H	-711.499.747	-1.298.079.125	-178.459.871
H	-560.005.026	-1.340.960.733	-26.039.769
H	-210.136.873	-1.295.903.513	-247.335.526
H	-182.170.495	-1.193.317.242	-390.586.557
H	-0.58922283	-1.104.441.396	-189.141.773
H	-181.199.148	-989.492.733	-247.014.512
H	-213.229.199	-1.088.741.304	-102.616.311
H	-1.086.515.322	-801.999.259	-754.127.073
H	-922.097.301	-776.136.992	-818.337.049
H	-1.028.436.872	-557.995.153	-749.422.116
H	-883.941.002	-593.689.516	-6.526.615
H	-1.046.149.766	-619.746.716	-583.846.524

$(1b^{c}_{min}\text{-}13_{min})_{nonADJ}$

Atom	x	y	z
C	-957.100.204	-174.607.876	-0.17104519
C	-944.065.278	-297.510.169	0.4309204
C	-81.620.274	-372.170.334	0.42493109
C	-705.293.655	-317.555.261	-0.385705
C	-724.806.685	-193.479.065	-114.703.061
C	-845.856.336	-111.566.256	-0.91500347
O	-859.328.612	0.03324235	-135.566.623
O	-806.186.182	-475.331.862	-110.269.755
O	-107.347.305	-109.310.834	0.03161747
C	-1.129.087.763	-0.21540657	-0.95753891
O	-1.049.740.201	-341.257.051	-114.717.821
C	-1.078.987.389	-481.058.238	-128.228.363
C	-581.944.068	-380.225.486	-0.40103069
C	-630.400.998	-15.415.108	-207.718.404
C	-516.432.348	-250.885.859	-241.750.003
S	-389.956.426	-148.577.639	-333.558.838
C	-505.404.691	-0.15230204	-352.580.314
C	-62.198.309	-0.33315601	-283.046.571
C	-543.170.791	-505.516.288	0.15933976
C	-41.950.491	-550.960.799	-0.2156717
S	-333.591.104	-441.223.331	-131.073.448
C	-464.617.673	-309.879.382	-109.240.709
C	-470.439.119	100.668.324	-435.173.892
C	-569.379.051	-357.297.281	-341.211.332
C	-406.723.043	-203.906.426	-0.12002477
C	-357.586.186	-677.501.928	0.18851257
C	-336.959.836	127.230.955	-471.069.682
C	-30.457.177	238.252.602	-548.671.626
C	-404.744.046	325.042.648	-592.408.549

C	-537.842.463	299.713.607	-558.043.021
C	-57.053.806	188.896.131	-480.626.475
C	-251.585.954	-733.719.078	-0.54725178
C	-19.433.665	-854.726.913	-0.16323733
C	-241.378.708	-922.014.737	0.96560551
C	-346.149.669	-867.108.343	171.025.948
C	-403.573.515	-746.273.163	132.967.542
H	-1.235.739.898	-0.17331155	-0.72130185
H	-108.470.163	0.77859244	-0.90300062
H	-1.115.663.976	-0.61469258	-196.764.686
H	-1.185.715.735	-484.842.073	-15.160.783
H	-1.060.141.641	-535.108.299	0.34951907
H	-1.020.598.728	-52.636.503	-20.832.762
H	-699.986.658	0.41148257	-277.512.321
H	-611.231.145	-562.263.559	0.775818
H	-610.168.748	-307.147.964	-429.339.689
H	-489.394.551	-424.525.135	-373.000.668
H	-6.488.137	-416.625.621	-295.049.822
H	-318.531.804	-155.626.904	-0.5465141
H	-481.586.412	-127.279.249	0.09968954
H	-378.325.818	-252.500.112	0.81680649
H	-257.722.085	0.61440709	-43.649.147
H	-200.791.639	257.075.004	-574.729.276
H	-379.491.762	411.558.014	-653.081.281
H	-616.599.521	366.250.448	-592.320.546
H	-674.476.214	169.254.519	-456.436.654
H	-215.014.153	-683.236.119	-143.702.737
H	-112.985.774	-896.605.069	-0.74905889
H	-19.654.806	-101.630.346	-126.623.124
H	-382.763.857	-918.296.949	-259.588.887
H	-483.335.694	-703.529.728	-192.846.854
C	-989.601.213	-600.006.919	-281.024.455

C	-871.306.731	-58.577.846	-346.506.305
N	-850.734.682	-472.855.385	-424.677.198
C	-942.933.701	-370.807.277	-44.385.983
C	-1.063.443.876	-378.291.396	-381.386.135
C	-1.099.199.386	-495.029.743	-290.660.542
C	-893.005.078	-261.755.667	-535.728.306
C	-753.403.595	-6.802.947	-346.195.893
C	-1.025.445.177	-71.389.156	-195.337.933
O	-1.132.697.484	-72.170.108	-13.759.137
O	-929.667.807	-810.656.722	-184.588.513
C	-96.255.297	-923.470.487	-100.534.027
C	-1.042.893.703	-1.028.368.744	-17.609.031
C	-1.170.641.863	-278.375.539	-39.246.359
O	-1.276.912.913	-288.994.582	-333.363.325
O	-1.142.726.747	-172.178.986	-473.706.218
C	-1.246.653.064	-0.72580841	-486.000.422
C	-1.349.025.509	-110.954.048	-591.883.159
H	-762.270.555	-465.070.944	-472.343.384
H	-1.124.360.004	-458.008.498	-190.350.061
H	-119.248.225	-541.645.216	-325.038.955
H	-892.536.074	-164.824.516	-485.392.551
H	-791.184.106	-2.834.904	-569.939.463
H	-957.389.057	-251.348.493	-623.351.263
H	-781.345.058	-778.534.605	-384.938.585
H	-671.856.172	-640.678.688	-407.784.937
H	-71.563.257	-696.065.635	-244.937.745

H	-865.530.532	-96.281.713	-0.68918552
H	1.017.380.493	-88.764.042	-0.13088681
H	1.059.487.238	1.115.863.557	-1.121.355
H	1.140.261.443	-988.167.576	205.319.993
H	-989.525.479	-106.117.433	265.947.784
H	1.193.340.358	0.1886951	513.497.589
H	1.294.253.152	-0.58894763	388.620.073
H	1.422.041.581	-0.30100494	604.222.143
H	1.402.635.618	-201.476.413	562.157.087
H	1.300.556.404	-128.453.987	-68.854.429

11. References

1. Fröhlich, J.; Hametner, C.; Kalt, W., Synthesis of trisubstituted thiophenesvia a halogen dance reaction at 2-bromo-5-methylthiophene. *Monatshefte für Chemie / Chemical Monthly* **1996,** *127* (3), 325-330.
2. Wang, R.; Pu, S.; Liu, G.; Cui, S.; Liu, W., Synthesis and photochromism of isomeric unsymmetrical diarylethenes bearing both naphthalene and thiophene moieties. *Journal of Photochemistry and Photobiology A: Chemistry* **2012,** *243*, 47-55.
3. Gregg, C.; Kyryakov, P.; Titorenko, V. I., Purification of Mitochondria from Yeast Cells. **2009,** (30), e1417.
4. Bradford, M. M., A rapid and sensitive method for the quantitation of microgram quantities of protein utilizing the principle of protein-dye binding. *Anal Biochem* **1976,** *72* (1), 248-254.
5. Reddy, C. A.; Beveridge, T. J.; Breznak, J. A.; Marzluf, G. A.; Schmidt, T. M.; Snyder, L. R., *Methods for General and Molecular Microbiology, Third Edition*. American Society of Microbiology: 2007.
6. (a) Becke, A. D., Density-functional thermochemistry. III. The role of exact exchange. *The Journal of Chemical Physics* **1993,** *98* (7), 5648-5652; (b) Lee, C.; Yang, W.; Parr, R. G., Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density. *Physical Review B* **1988,** *37* (2), 785-789; (c) Stephens, P. J.; Devlin, F. J.; Chabalowski, C. F.; Frisch, M. J., Ab Initio Calculation of Vibrational Absorption and Circular Dichroism Spectra Using Density Functional Force Fields. *The Journal of Physical Chemistry* **1994,** *98* (45), 11623-11627.
7. Kuhn, B.; Kollman, P. A., A Ligand That Is Predicted to Bind Better to Avidin than Biotin: Insights from Computational Fluorine Scanning. *Journal of the American Chemical Society* **2000,** *122* (16), 3909-3916.
8. (a) Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H., OLEX2: a complete structure solution, refinement and analysis program. *Journal of Applied Crystallography* **2009,** *42* (2), 339-341; (b) Sheldrick, G. M., Crystal structure refinement with SHELXL. *Acta Crystallographica. Section C, Structural Chemistry* **2015,** *71* (Pt 1), 3-8; (c) Linden, A., Chemistry and structure in Acta Crystallographica Section C. *Acta Crystallographica Section C* **2015,** *71* (1), 1-2.