

# **Photochemical Aerobic Oxidation of Sulfides to Sulfoxides: The Crucial Role of Wavelength Irradiation**

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## **SUPPORTING INFORMATION**

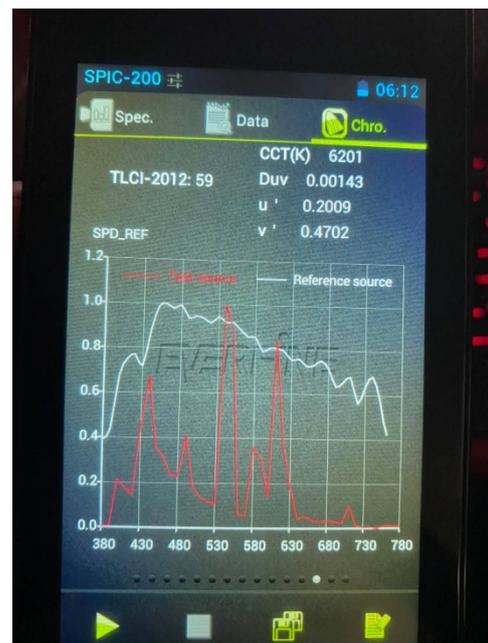
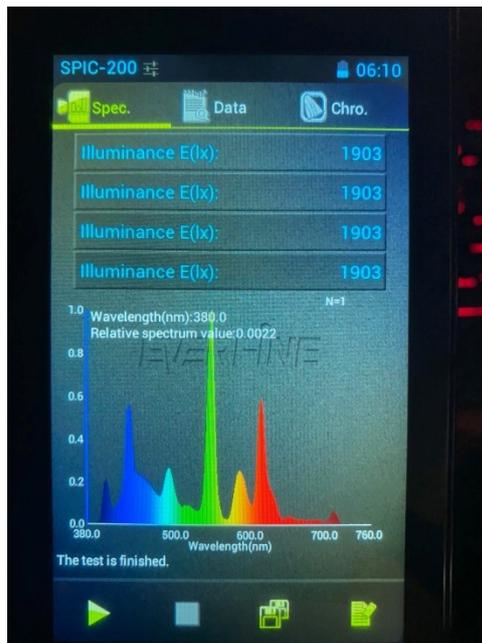
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## General Remarks

Chromatographic purification of products was accomplished using forced-flow chromatography on Merck® Kieselgel 60 70-230 mesh. Thin-layer chromatography (TLC) was performed on aluminum backed silica plates (0.2 mm, 60 F<sub>254</sub>). Visualization of the developed chromatogram was performed by fluorescence quenching using phosphomolybdic acid, anisaldehyde or potassium permanganate stains. Melting points were determined on a Buchi® 530 hot stage apparatus and are uncorrected. Mass spectra (ESI) were recorded on a Finningan® Surveyor MSQ LC-MS spectrometer. HRMS spectra were recorded on a Bruker® Maxis Impact QTOF spectrometer. <sup>1</sup>H-NMR, <sup>19</sup>F-NMR and <sup>13</sup>C-NMR spectra were recorded on a Varian® Mercury (200 MHz, 188 MHz and 50 MHz, respectively) or on an Avance III HD Bruker 400 MHz (400 MHz, 376 MHz and 100 MHz, respectively), and are internally referenced to residual solvent signals. Data for <sup>1</sup>H-NMR are reported as follows: chemical shift ( $\delta$  ppm), integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br s = broad signal), coupling constant and assignment. Data for <sup>19</sup>F-NMR are reported in terms of chemical shift ( $\delta$  ppm) and are internally referenced to trifluoroacetic acid (188 MHz) or fluoroform (376 MHz). Data for <sup>13</sup>C-NMR are reported in terms of chemical shift ( $\delta$  ppm). Mass spectra and conversions of the reactions were recorded on a Shimadzu® GCMS-QP2010 Plus Gas Chromatograph Mass Spectrometer utilizing a MEGA® column (MEGA-5, F.T: 0.25  $\mu$ m, I.D.: 0.25 mm, L: 30 m, T<sub>max</sub>: 350 °C, Column ID# 11475). A Varian® Cary 50 UV-Vis spectrophotometer was used for the quantum yield measurements and the UV-Vis data. A Scinco® FS-2 fluorescence spectrometer was used for the fluorescence studies. Kessil lamps PR160L were used as the irradiation source. For all experiments, the intensity of the Kessil lamps was controlled in the maximum level with power consumption: 370 nm (max 43W), 390 nm (max 52W), 427 nm (max 45W), 440 nm (max 45W), 456 nm (max 50W), 467 nm (max 44W) and 525 nm (max 44W). Photon flux for every irradiation source was calculated. CFL ( $3.39 \times 10^{-9}$  einstein s<sup>-1</sup>), 370 nm ( $2.85 \times 10^{-8}$  einstein s<sup>-1</sup>), 390 nm ( $7.09 \times 10^{-8}$  einstein s<sup>-1</sup>), 427 nm ( $8.56 \times 10^{-8}$  einstein s<sup>-1</sup>), 440 nm ( $11.06 \times 10^{-8}$  einstein s<sup>-1</sup>), 456 nm ( $16.57 \times 10^{-8}$  einstein s<sup>-1</sup>).

## Emission Spectrum of the Light Source

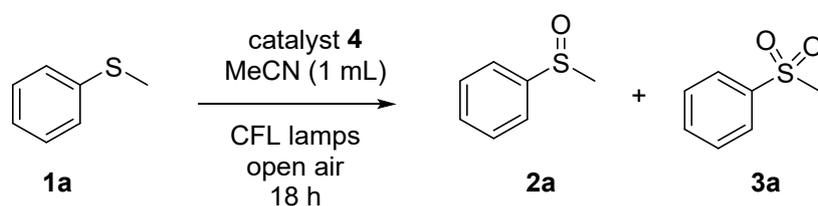
The emission spectrum of the lamps was measured with a SPIC-200 spectral irradiance colorimeter. The lamp was placed in a dark room in a 30 cm distance from the lamp.

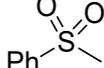
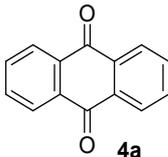
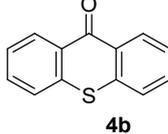
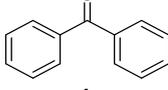


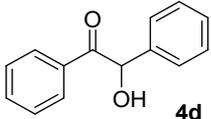
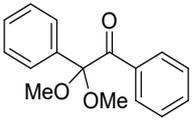
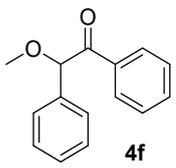
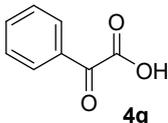
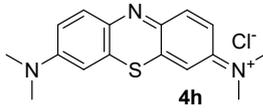
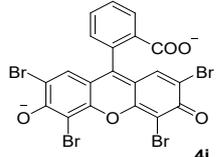
## PART A: Optimization Experiments

### Optimization of the Reaction Conditions for the Photochemical Oxidation of Sulfides to Sulfoxides

#### Catalyst Optimization for the Photochemical Oxidation under CFL Irradiation

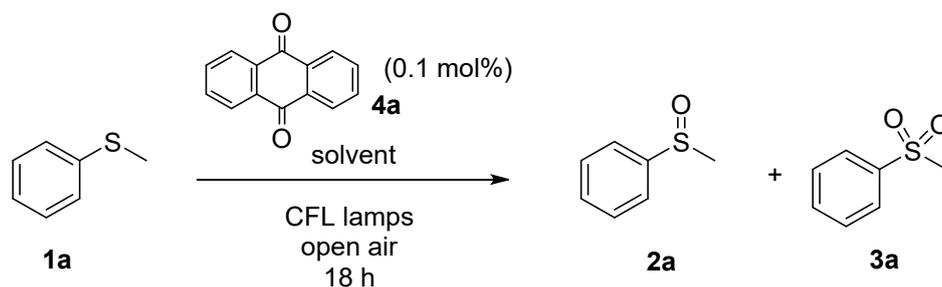


Entry	Catalyst	Catalyst loading (mol%)	Conversion %		
					
1	No catalyst	0	89	11	0
2	Anthraquinone	20	0	92	8
3	 <b>4a</b>	10	0	99	1
4		2	0	97	3
5		1	0	98	2
6		0.5	35	65	0
7		0.1	71	29	0
8	Thioxanthen-9-one	20	0	60	40
9	 <b>4b</b>	10	0	80	20
10		2	0	82	18
11		1	0	83	17
12	Benzophenone  <b>4c</b>	20	69	31	0

13	Benzoin	20	12	88	0
14	 4d	10	86	14	0
2,2-Dimethoxy-2-phenylacetophenone					
15	 4e	10	28	72	0
Benzoin methyl ether					
16	 4f	10	68	32	0
Phenylglyoxylic acid					
17	 4g	10	76	24	0
Methylene blue					
18	 4h	5	51	49	0
Eosin Y					
19	 4i	5	7	93	0

The reaction was performed with phenyl methyl sulfide (1a) (25 mg, 0.20 mmol) and catalyst 4 in MeCN (1.0 mL), under household bulb irradiation for 18 h. Conversion was determined by <sup>1</sup>H-NMR.

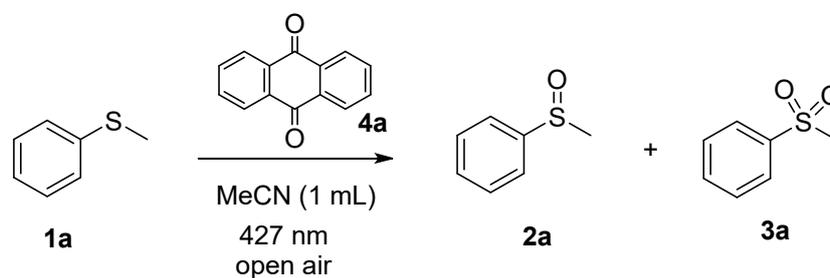
## Optimization Experiments under CFL Irradiation – Solvents



CFL lamps		Conversion (%)		
Entry	Solvent			
1	MeCN	71	29	0
2	MeOH	61	39	0
3 <sup>a</sup>	MeOH	69	31	0
4 <sup>b</sup>	MeOH	71	29	0
5 <sup>c</sup>	MeOH	75	25	0
6 <sup>d</sup>	MeOH	0	100	0
7	CH <sub>2</sub> Cl <sub>2</sub>	96	4	0
8	EtOAc	95	5	0
9	Pet. Ether	100	0	0
10	EtOH	69	31	0
11	CHCl <sub>3</sub>	96	4	0
12	Benzene	93	7	0
13	DMF	67	26	7
14	DMSO-d <sub>6</sub>	87	13	0
15	H <sub>2</sub> O	100	0	0
16 <sup>e</sup>	MeOH	0	95	5
17 <sup>f</sup>	MeOH	0	100	0

The reaction was performed with phenyl methyl sulfide (**1a**) (25 mg, 0.20 mmol) and catalyst **4a** (0.1 mol%, 0.0002 mmol) in solvent (1.0 mL) and H<sub>2</sub>O (40 μL), under household bulb irradiation for 18 h. Conversions were determined by <sup>1</sup>H-NMR. <sup>a</sup> The reaction was performed under O<sub>2</sub> atmosphere. <sup>b</sup> The reaction was performed with MeOH (0.5 mL). <sup>c</sup> The reaction was performed with MeOH (2 mL). <sup>d</sup> The reaction was performed with 0.5 mol% (0.001 mmol) catalyst **4a**. <sup>e</sup> The reaction was performed in 0.50 mmol scale without the addition of H<sub>2</sub>O. <sup>f</sup> The reaction was performed in 0.50 mmol scale.

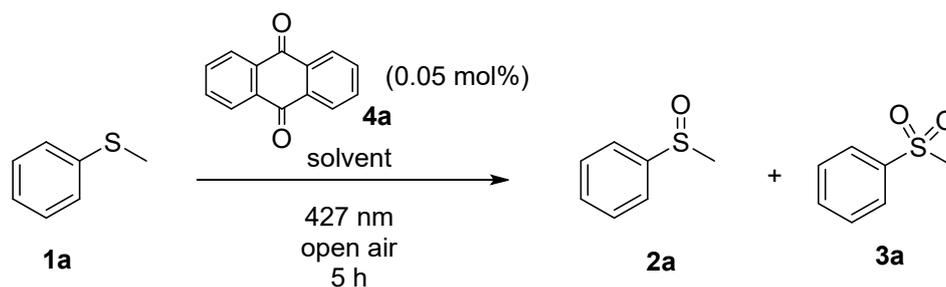
## Optimization Experiments under 427 nm Irradiation – Catalyst Loading (mol%)



Entry	427 nm		Conversion (%)		
	Catalyst loading (mol%)	Reaction time	<chem>CSc1ccccc1</chem>	<chem>COS(=O)c1ccccc1</chem>	<chem>CS(=O)(=O)c1ccccc1</chem>
1	-	30 min	100	0	0
2	0.1	30 min	88	12	0
3	-	5 h	98	2	0
4	0.1	5 h	0	95	5
5	-	18 h	0	81	19
6	0.1	18 h	0	69	31
7	0.05	5 h	36	64	0
8	0.01	5 h	93	7	0
9 <sup>a</sup>	0.01	5 h	87	13	0

The reaction was performed with phenyl methyl sulfide (**1a**) (25 mg, 0.20 mmol) and catalyst **4a** in MeCN (1.0 mL), under blue LED (Kessil PR160L, 427 nm) irradiation. Conversions were determined by <sup>1</sup>H-NMR. <sup>a</sup> The reaction was performed in MeOH, instead of acetonitrile.

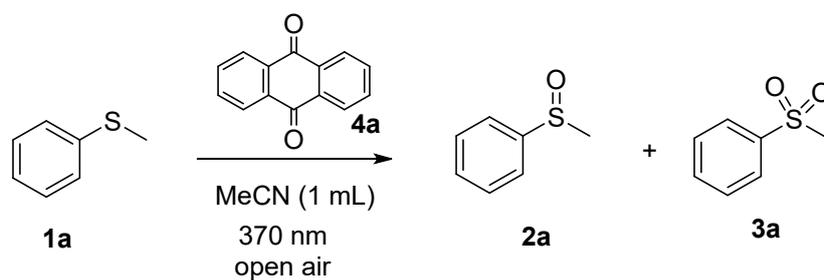
## Optimization Experiments under 427 nm Irradiation – Solvents



427 nm		Conversion (%)		
Entry	Solvent	Ph-S-	Ph-S(=O)-	Ph-S(=O) <sub>2</sub> -
1 <sup>a</sup>	MeCN	36	64	0
2	MeCN	35	65	0
3 <sup>a</sup>	MeOH	29	71	0
4	MeOH	0	100	0
5	Pet. Ether	93	7	0
6	EtOAc	11	89	0
7	CH <sub>2</sub> Cl <sub>2</sub>	20	80	0
8	CHCl <sub>3</sub>	85	15	0
9	EtOH	23	15	62
10	iPrOH	79	21	0
11	Benzene	72	28	0
12	DMF	50	50	0
13	DMAc	100	0	0

The reaction was performed with phenyl methyl sulfide (**1a**) (25 mg, 0.20 mmol) and catalyst **4a** (0.05 mol%, 0.0001 mmol) in solvent (0.5 mL), under blue LED (Kessil PR160L, 427 nm) irradiation for 5 h. Conversions were determined by <sup>1</sup>H-NMR. <sup>a</sup>The reaction was performed with 1.0 mL solvent.

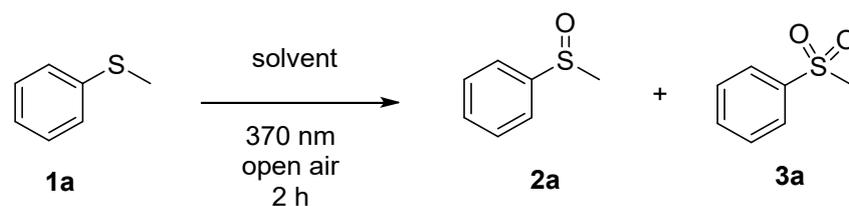
## Optimization Experiments under 370 nm Irradiation – Catalyst Loading (mol%)



Entry	370 nm		Conversion (%)		
	Catalyst loading (mol%)	Reaction time	Ph-S-	Ph-S(=O)-	Ph-S(=O) <sub>2</sub> -
1	0.1	30 min	52	48	0
2	0.1	1 h	40	60	0
3	0.1	4 h	0	83	17
4	0.1	8 h	0	70	30
5	0.1	18 h	0	29	71
6	0.01	2 h	4	90	6
7	-	30 min	89	11	0
8	-	1 h	56	44	0
9	-	2 h	11	89	0
10	-	3 h	0	85	15
11	-	on	0	61	39
12 <sup>a</sup>	-	on	0	88	12

The reaction was performed with phenyl methyl sulfide (**1a**) (25 mg, 0.20 mmol) in MeCN (1.0 mL), under UVA LED (Kessil PR160L, 370 nm) irradiation. Conversions were determined by <sup>1</sup>H-NMR. <sup>a</sup> 40 μL of H<sub>2</sub>O were added to the reaction mixture.

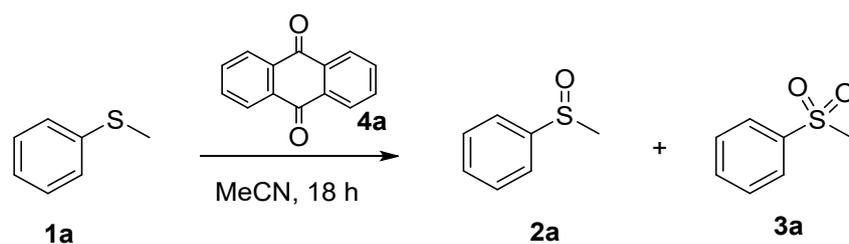
### Optimization Experiments under 370 nm Irradiation – Solvents



370 nm		Conversion (%)		
Entry	Solvent	<chem>CS(=O)c1ccccc1</chem>	<chem>CS(=O)(=O)c1ccccc1</chem>	<chem>CS(=O)(=O)c1ccccc1</chem>
1	MeOH	20	80	0
2 <sup>a</sup>	MeOH	10	90	0
3	MeCN	11	89	0
4 <sup>b</sup>	MeCN	10	90	0
5 <sup>c</sup>	MeCN	0	85	15
6 <sup>a</sup>	MeCN	0	99	1
7 <sup>d</sup>	MeCN	0	99	1
8	Pet. Ether	94	6	0
9	EtOAc	80	20	0
10	CH <sub>2</sub> Cl <sub>2</sub>	81	19	0
11	CHCl <sub>3</sub>	37	63	0
12	EtOH	11	89	0
13	iPrOH	17	83	0
14	Benzene	93	17	0
15	DMF	72	28	0

The reaction was performed with phenyl methyl sulfide (**1a**) (25 mg, 0.20 mmol) in solvent (1.0 mL), under UVA LED (Kessil PR160L, 370 nm) irradiation for 2 h. Conversions were determined by <sup>1</sup>H-NMR. <sup>a</sup> The reaction time was 3 h and 40 μL of H<sub>2</sub>O were added. <sup>b</sup> 40 μL of H<sub>2</sub>O were added to the reaction mixture. <sup>c</sup> The reaction time was 3 h. <sup>d</sup> The reaction was performed with 0.5 mL solvent for 3 h and 40 μL of H<sub>2</sub>O were added.

## Control Mechanistic Experiments and Various Irradiation Sources



Entry	Variations	Catalyst loading (mol%)	Oxidant	Ph-S-	Ph-S(=O)-	Ph-S(=O) <sub>2</sub> -
1 <sup>a</sup>	Sunlight/ 4 h	0.5	air	0	100	0
2	Dark	0.5	air	100	0	0
3	Heating at 60 °C	0.5	air	100	0	0
5	Under Argon	0.5	-	92	8	0
6	370 nm	-	air	0	61	39
7	390 nm	-	air	0	56	44
8	427 nm	-	air	0	81	19
9	440 nm	-	air	60	40	0
10	456 nm	-	air	98	2	0
11	467 nm	-	air	99	1	0
12	525 nm	-	air	100	0	0
13	370 nm/ 2 h	0.05	air	0	99	1
14	390 nm/ 2 h	0.05	air	0	85	15
15	427 nm/ 5 h	0.05	air	0	89	11
16	440 nm/ 5 h	0.05	air	0	100	0
17	456 nm/ 5 h	0.05	air	72	28	0
18	456 nm	0.05	air	0	87	13
19	467 nm/ 5 h	0.05	air	97	3	0
20	467 nm	0.05	air	48	52	0

21	525 nm/ 5 h	0.05	air	100	0	0
22	525 nm	0.05	air	100	0	0

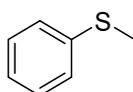
<sup>a</sup>The reaction was performed with phenyl methyl sulfide (**1a**) (25 mg, 0.20 mmol) in MeCN (1.0 mL). Conversions were determined by <sup>1</sup>H-NMR.

## PART B: Experimental Procedures

### General Procedure for the Synthesis of Sulfides

Thiol (12.00 mmol) was dissolved in dry methanol (40 mL) at -10 °C, followed by the addition of sodium methoxide (864 mg, 16.00 mmol). The reaction mixture was stirred for 10 min at -10 °C, and then the corresponding bromide (14.00 mmol) was slowly added. After stirring for 1 h at room temperature, the solvent was removed *in vacuo*. The crude residue was diluted with water (100 mL) and extracted with chloroform (4 x 70 mL). The combined organic layers were dried (Na<sub>2</sub>SO<sub>4</sub>) and the solvent was removed *in vacuo*. The desired sulfide was isolated after purification by column chromatography eluting with petroleum ether:ethyl acetate (100:0-95:5) depending on the substrate.

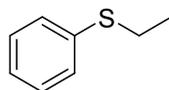
#### Methyl(phenyl)sulfane (1a)<sup>1</sup>



Colorless oil; (**92%**); Eluent: Petroleum ether; NMR data in accordance with reported literature.<sup>1</sup>

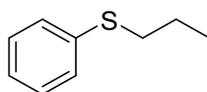
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 7.32 (5H, m, ArH), 2.52 (3H, s, SCH<sub>3</sub>); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 138.4, 128.8, 126.6, 125.0, 15.8.

#### Ethyl(phenyl)sulfane (1b)<sup>1</sup>



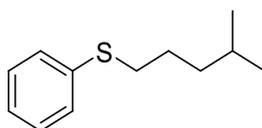
Colorless oil; (**94%**); Eluent: Petroleum ether; NMR data in accordance with reported literature.<sup>1</sup>

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 7.41-7.31 (5H, m, ArH), 3.00 (2H, q, *J* = 7.4 Hz, SCH<sub>2</sub>), 1.37 (3H, t, *J* = 7.4 Hz, CH<sub>3</sub>); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 136.6, 128.9, 128.7, 125.7, 27.5, 14.3.

**Phenyl(propyl)sulfane (1c)<sup>2</sup>**

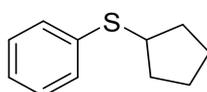
Colorless oil; (**81%**); Eluent: Petroleum ether; NMR data in accordance with reported literature.<sup>2</sup>

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 7.40-7.35 (2H, m, ArH), 7.34-7.28 (2H, m, ArH), 7.22-7.17 (1H, m, ArH), 2.94 (2H, t,  $J = 7.3$  Hz, SCH<sub>2</sub>), 1.72 (2H, sext,  $J = 7.3$  Hz, CH<sub>2</sub>), 1.07 (3H, t,  $J = 7.3$  Hz, CH<sub>3</sub>); **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 136.9, 128.9, 128.8, 125.6, 35.6, 22.5, 13.4.

**(4-Methylpentyl)(phenyl)sulfane (1d)<sup>3</sup>**

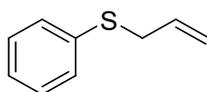
Colorless oil; (**92%**); Eluent: Petroleum ether; NMR data in accordance with reported literature.<sup>3</sup>

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 7.37 (2H, d,  $J = 7.1$  Hz, ArH), 7.31 (2H, t,  $J = 7.1$  Hz, ArH), 7.20 (1H, t,  $J = 7.1$  Hz, ArH), 2.95 (2H, t,  $J = 7.2$  Hz, SCH<sub>2</sub>), 1.74-1.65 (2H, m, CH<sub>2</sub>) 1.64-1.54 [1H, m, CH(CH<sub>3</sub>)<sub>2</sub>], 1.40-1.32 (2H, m, CH<sub>2</sub>), 0.92 (6H, d,  $J = 6.6$  Hz, 2 x CH<sub>3</sub>); **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 137.0, 128.8, 128.8, 125.6, 38.1, 33.8, 27.7, 27.0, 22.5.

**Cyclopentyl(phenyl)sulfane (1e)<sup>4</sup>**

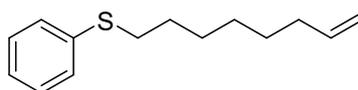
Colorless oil; (**89%**); Eluent: Petroleum ether / Ethyl acetate 95:5; NMR data in accordance with reported literature.<sup>4</sup>

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 7.39 (2H, d,  $J = 7.5$  Hz, ArH), 7.30 (2H, t,  $J = 7.5$  Hz, ArH), 7.20 (1H, t,  $J = 7.5$  Hz, ArH), 3.68-3.57 (1H, m, SCH), 2.17-2.02 (2H, m, CH<sub>2</sub>), 1.87-1.76 (2H, m, CH<sub>2</sub>), 1.69-1.57 (4H, m, 2 x CH<sub>2</sub>); **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 137.3, 129.9, 128.7, 125.8, 45.9, 33.5, 24.8.

**Allyl(phenyl)sulfane (1f)<sup>1</sup>**

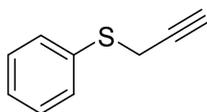
Colorless oil; (**93%**); Eluent: Petroleum ether; NMR data in accordance with reported literature.<sup>1</sup>

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 7.38 (2H, d,  $J = 7.5$  Hz, ArH), 7.31 (2H, t,  $J = 7.5$  Hz, ArH), 7.22 (1H, t,  $J = 7.5$  Hz, ArH), 5.92 (1H, ddt,  $J = 16.9, 10.0$  and  $6.9$  Hz, =CH), 5.17 (1H, d,  $J = 16.9$  Hz, =CHH), 5.11 (1H, d,  $J = 10.0$  Hz, =CHH), 3.59 (2H, d,  $J = 6.9$  Hz, SCH<sub>2</sub>); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 135.9, 133.6, 129.8, 128.8, 126.2, 117.6, 37.1.

**Oct-7-en-1-yl(phenyl)sulfane (1g)<sup>5</sup>**

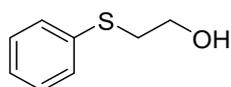
Colorless oil; (**77%**); Eluent: Petroleum ether; NMR data in accordance with reported literature.<sup>5</sup>

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 7.28 (2H, m, ArH), 7.04 (2H, m, ArH), 6.94 (1H, m, ArH), 5.73 (1H, ddt,  $J = 17.2, 10.2$  and  $6.6$  Hz, =CH), 5.05 (2H, m, =CH<sub>2</sub>), 2.66 (2H, t,  $J = 7.2$  Hz, SCH<sub>2</sub>), 1.92 (2H, m, CH<sub>2</sub>), 1.48 (2H, m, CH<sub>2</sub>), 1.21 (4H, m, 2 x CH<sub>2</sub>), 1.09 (m, 2H, CH<sub>2</sub>); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 139.1, 137.9, 129.2, 129.1, 125.8, 114.6, 34.1, 33.7, 29.4, 29.1, 28.9, 28.9.

**Phenyl(prop-2-yn-1-yl)sulfane (1h)<sup>6</sup>**

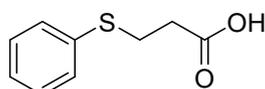
Yellowish oil; (**84%**); Eluent: Petroleum ether / Ethyl acetate 95:5; NMR data in accordance with reported literature.<sup>6</sup>

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 7.49 (2H, d,  $J = 7.7$  Hz, ArH), 7.36 (2H, t,  $J = 7.7$  Hz, ArH), 7.31-7.28 (1H, m, ArH), 3.64 (2H, d,  $J = 2.6$  Hz, CH<sub>2</sub>), 2.27 (1H, t,  $J = 2.6$  Hz,  $\equiv$ CH); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 134.9, 130.1, 129.0, 126.9, 79.8, 71.5, 22.5.

**2-(Phenylthio)ethan-1-ol (1i)**<sup>7</sup>

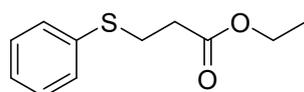
Colorless oil; (**79%**); Eluent: Petroleum ether / Ethyl acetate 95:5; NMR data in accordance with reported literature.<sup>7</sup>

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 7.44-7.11 (5H, m, ArH), 3.71 (2H, t,  $J = 6.1$  Hz, OCH<sub>2</sub>), 3.11 (2H, t,  $J = 6.1$  Hz, SCH<sub>2</sub>), 2.04 (1H, br, OH); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 134.9, 129.9, 128.8, 126.5, 60.3, 36.9.

**3-(Phenylthio)propanoic acid (1j)**<sup>8</sup>

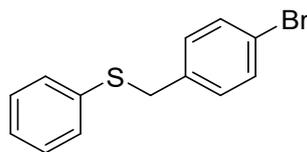
White solid; m.p.: 58-60 °C; (**87%**); Eluent: Ethyl acetate; NMR data in accordance with reported literature.<sup>8</sup>

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 11.75 (1H, br s, COOH), 7.43 (2H, d,  $J = 8.2$  Hz, ArH), 7.35 (2H, t,  $J = 8.2$  Hz, ArH), 7.34-7.30 (1H, m, ArH), 3.21 (2H, t,  $J = 7.3$  Hz, CH<sub>2</sub>), 2.73 (2H, t,  $J = 7.3$  Hz, CH<sub>2</sub>); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 178.2, 134.8, 130.1, 128.9, 126.5, 34.1, 28.5.

**Ethyl 3-(phenylthio)propanoate (1k)**<sup>1</sup>

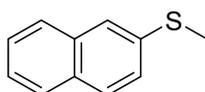
Yellowish oil; (**83%**); Eluent: Petroleum ether / Ethyl acetate 95:5; NMR data in accordance with reported literature.<sup>1</sup>

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 7.39 (2H, d,  $J = 7.5$  Hz, ArH), 7.31 (2H, t,  $J = 7.5$  Hz, ArH), 7.22 (1H, t,  $J = 7.5$  Hz, ArH), 4.15 (2H, q,  $J = 7.1$  Hz, OCH<sub>2</sub>), 3.18 (2H, t,  $J = 7.2$  Hz, CH<sub>2</sub>), 2.63 (2H, t,  $J = 7.2$  Hz, CH<sub>2</sub>), 1.27 (3H, t,  $J = 7.1$  Hz, CH<sub>3</sub>); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 171.8, 135.3, 130.1, 129.0, 126.5, 60.7, 34.5, 29.1, 14.2.

**(4-Bromobenzyl)(phenyl)sulfane (1l)**<sup>9</sup>

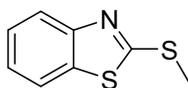
White solid; m.p.: 73-75 °C; (**77%**); Eluent: Petroleum ether / Ethyl acetate 95:5; NMR data in accordance with reported literature.<sup>9</sup>

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 7.42 (2H, d,  $J$  = 8.4 Hz, ArH), 7.33-7.26 (4H, m, ArH), 7.24-7.21 (1H, m, ArH), 7.17 (2H, d,  $J$  = 8.4 Hz, ArH), 4.07 (2H, s, CH<sub>2</sub>); **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 136.7, 135.6, 131.5, 130.4, 130.2, 128.9, 126.7, 121.0, 38.6.

**Methyl(naphthalen-2-yl)sulfane (1m)**<sup>3</sup>

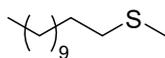
Colorless oil; (**67%**); Eluent: Petroleum ether; NMR data in accordance with reported literature.<sup>3</sup>

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 7.80 (1H, d,  $J$  = 7.4 Hz, ArH), 7.76 (2H, d,  $J$  = 8.7 Hz, ArH), 7.64-7.62 (1H, m, ArH), 7.51-7.38 (3H, m, ArH), 2.61 (3H, s, CH<sub>3</sub>); **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 136.1, 133.9, 131.3, 128.2, 127.7, 126.7, 126.5, 125.7, 125.2, 123.4, 15.8.

**2-(Methylthio)benzothiazole (1n)**<sup>10</sup>

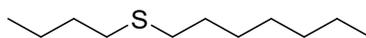
White solid; m.p.: 43-45 °C; (**96%**); Eluent: Petroleum ether / Ethyl acetate 95:5; NMR data in accordance with reported literature.<sup>10</sup>

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 7.90 (1H, d,  $J$  = 8.0 Hz, ArH), 7.77 (1H, d,  $J$  = 8.0 Hz, ArH), 7.43 (1H, t,  $J$  = 8.0 Hz, ArH), 7.31 (1H, t,  $J$  = 8.0 Hz, ArH), 2.81 (3H, s, CH<sub>3</sub>); **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 168.0, 153.3, 135.1, 126.0, 124.0, 121.3, 120.9, 15.9.

**Dodecyl(methyl)sulfane (1q)<sup>11</sup>**

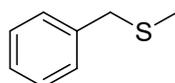
Colorless oil; (**89%**); Eluent: Petroleum ether; NMR data in accordance with reported literature.<sup>11</sup>

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 2.48 (2H, t,  $J = 7.1$  Hz, SCH<sub>2</sub>), 2.08 (3H, s, SCH<sub>3</sub>), 1.65-1.50 (2H, m, CH<sub>2</sub>), 1.43-1.13 (18H, m, 9 x CH<sub>2</sub>), 0.87 (3H, t,  $J = 6.2$  Hz, CH<sub>3</sub>); **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 34.3, 31.9, 29.6, 29.6, 29.6, 29.5, 29.3, 29.2, 29.2, 28.8, 22.6, 15.5, 14.0.

**Butyl(heptyl)sulfane (1r)<sup>3</sup>**

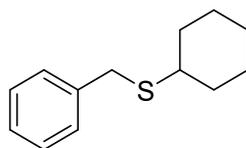
Colorless oil; (**80%**); Eluent: Petroleum ether; NMR data in accordance with reported literature.<sup>3</sup>

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 2.56-2.48 (4H, m, 2 x SCH<sub>2</sub>), 1.65-1.54 (4H, m, 2 x CH<sub>2</sub>), 1.48-1.37 (4H, m, 2 x CH<sub>2</sub>), 1.36-1.25 (6H, m, 3 x CH<sub>2</sub>), 0.96-0.87 (6H, m, 2 x CH<sub>3</sub>); **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 32.2, 31.8, 31.8, 31.7, 29.7, 28.9, 22.6, 22.0, 14.0, 13.7.

**Benzyl(methyl)sulfane (1v)<sup>1</sup>**

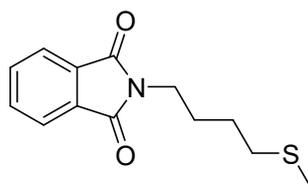
Colorless oil; (**92%**); Eluent: Petroleum ether; NMR data in accordance with reported literature.<sup>1</sup>

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 7.43-7.24 (5H, m, ArH), 3.73 (2H, s, CH<sub>2</sub>), 2.05 (3H, s, CH<sub>3</sub>); **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 138.2, 128.7, 128.3, 126.8, 38.2, 14.8.

**Benzyl(cyclohexyl)sulfane (1x)**<sup>12</sup>

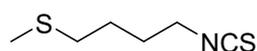
Colorless oil; (**87%**); Eluent: Petroleum ether; NMR data in accordance with reported literature.<sup>12</sup>

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 7.38-7.29 (5H, m, ArH), 3.78 (2H, s, SCH<sub>2</sub>), 2.66-2.56 (1H, m, SCH), 2.00-1.94 (2H, m, 2 x CHH), 1.83-1.73 (2H, m, 2 x CHH), 1.66-1.57 (1H, m, CHH), 1.44-1.23 (5H, m, 5 x CHH); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 138.9, 128.7, 128.4, 126.7, 42.9, 34.6, 33.3, 25.9, 25.8.

**2-(4-(Methylthio)butyl)isoindoline-1,3-dione (5)**<sup>13</sup>

White solid; m.p.: 57-59 °C; (**87%**); Eluent: Petroleum ether / Ethyl acetate 70:30; NMR data in accordance with reported literature.<sup>13</sup>

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 7.86 (2H, dd,  $J = 5.4$  and  $3.1$  Hz, ArH), 7.73 (2H, dd,  $J = 5.4$  and  $3.1$  Hz, ArH), 3.73 (2H, t,  $J = 7.1$  Hz, NCH<sub>2</sub>), 2.61-2.50 (2H, m, SCH<sub>2</sub>), 2.11 (3H, s, SCH<sub>3</sub>), 1.87-1.77 (2H, m, CH<sub>2</sub>), 1.71-1.61 (2H, m, CH<sub>2</sub>); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 168.4, 133.9, 132.1, 123.2, 37.5, 33.6, 27.7, 26.4, 15.5.

**Methyl(4-thiocyanatobutyl)sulfane (6)**<sup>13</sup>

2-(4-(Methylthio)butyl)isoindoline-1,3-dione (**1z**) (950 mg, 3.81 mmol) was dissolved in ethanol (2 mL) and hydrazine hydrate (4 mL) was slowly added to the solution. The reaction mixture was heated at 70 °C for 5 h. After completion of the reaction, the reaction mixture was cooled down at 0 °C and solid precipitated. The crude mixture

was filtered and the filtrate was evaporated until dry to afford the corresponding amine (450 mg), which was used without further purification.

The corresponding amine was dissolved in THF (10 mL) and Et<sub>3</sub>N (1.46 mL, 10.5 mmol) was added. The reaction mixture was cooled down at 0 °C and a solution of CS<sub>2</sub> (229 mg, 3.00 mmol) in THF (1 mL) was added dropwise, so as the temperature did not exceed 5 °C. When the addition was completed, the reaction mixture was stirred for 1 h at room temperature. The resulting gray suspension was cooled down at 0 °C and MsCl (255 μL, 3.30 mmol) was added in one portion. The reaction mixture was stirred for 1 h at room temperature. The resulting yellow suspension was diluted with Et<sub>2</sub>O (60 mL), washed successfully with 1 M HCl (2 x 20 mL), H<sub>2</sub>O (30 mL) and brine (30 mL), dried (Na<sub>2</sub>SO<sub>4</sub>) and evaporated until dry. The crude product was purified by column chromatography (Petroleum ether / Ethyl acetate 9:1) to afford 400 mg. Yield (2 steps): **66 %**.

Colorless oil; NMR data in accordance with reported literature.<sup>13</sup>

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ: 3.53 (2H, t, *J* = 6.6 Hz, CH<sub>2</sub>NCS), 2.50 (2H, t, *J* = 6.6 Hz, SCH<sub>2</sub>), 2.07 (3H, s, SCH<sub>3</sub>), 1.84-1.75 (2H, m, CH<sub>2</sub>), 1.74-1.65 (2H, m, CH<sub>2</sub>); **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ: 129.9, 44.5, 33.0, 28.6, 25.6, 15.2.

## **General Procedures for the Photochemical Aerobic Oxidation of Sulfides to Sulfoxides**

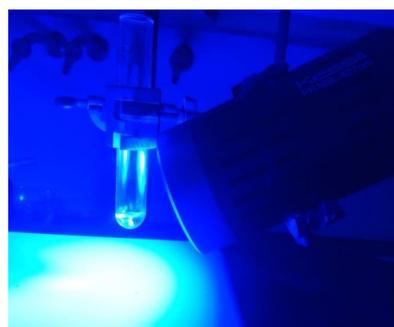
### **General Procedure for the Photochemical Aerobic Oxidation of Sulfides under Household Bulb Irradiation**

In a glass vial containing sulfide (1.0 eq., 0.50 mmol) and anthraquinone (0.5 mol%, 0.0025 mmol, 0.5 mg) in methanol (1.5 mL), water (100  $\mu$ L) was added. The reaction mixture was left stirring under household bulb irradiation ( $2 \times 85$ W household lamps) for 18-48 h. The desired product was purified by column chromatography (Pet. Ether/AcOEt: 6:4)



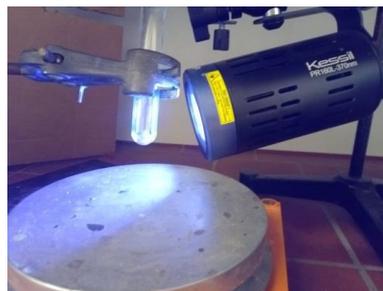
### **General Procedure for the Photochemical Aerobic Oxidation of Sulfides under 427 nm Blue LED Irradiation**

In a glass vial containing sulfide (1.0 eq., 0.50 mmol), anthraquinone (0.05 mol%,  $0.25 \times 10^{-3}$  mmol, 0.05 mg) in methanol (1.0 mL) was added (catalyst was added from stock solution in methanol). The reaction mixture was left stirring under Blue LED (Kessil PR 160L, 427 nm) irradiation for 5-20 h. The desired product was purified by column chromatography (Pet. Ether/AcOEt: 6:4)

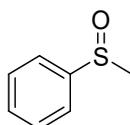


### General Procedure for the Photochemical Aerobic Oxidation of Sulfide under 370 nm UVA LED Irradiation

In a glass vial containing sulfide (1.0 eq., 0.50 mmol) in acetonitrile (1.0 mL), water (100  $\mu$ L) was added. The reaction mixture was left stirring under UVA LED (Kessil PR 160L, 370 nm) irradiation for 3-20 h. The desired product was purified by column chromatography (Pet. Ether/AcOEt: 6:4).



#### (Methylsulfinyl)benzene (2a)<sup>1</sup>

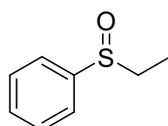


CFL lamps		427 nm		370 nm	
18 h	99 %	5 h	100 %	3 h	99 %

Colorless oil; Eluent: Petroleum ether / Ethyl acetate 6:4; NMR data in accordance with reported literature.<sup>1</sup>

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 7.70-7.66 (2H, m, ArH), 7.59-7.51 (3H, m, ArH), 2.75 (3H, s, CH<sub>3</sub>); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 145.7, 131.0, 129.3, 123.5, 43.9; ESI-MS [M+H<sup>+</sup>]: 141 m/z.

#### (Ethylsulfinyl)benzene (2b)<sup>14</sup>

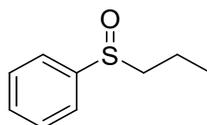


CFL lamps		427 nm		370 nm	
18 h	95 %	5 h	94 %	3 h	99 %

Yellowish solid; m.p.: 119-121 °C; Eluent: Petroleum ether / Ethyl acetate 6:4; NMR data in accordance with reported literature.<sup>14</sup>

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 7.63 (2H, dd,  $J = 7.4$  and  $2.1$  Hz, ArH), 7.57-7.50 (3H, m, ArH), 2.93 (1H, dq,  $J = 14.7$  and  $7.3$  Hz, SCHH), 2.79 (1H, dq,  $J = 14.7$  and  $7.3$  Hz, SCHH), 1.22 (3H, t,  $J = 7.3$  Hz, CH<sub>3</sub>); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 143.3, 130.9, 129.1, 124.2, 50.3, 5.9; ESI-MS [M+H<sup>+</sup>]: 155 m/z.

**(Propylsulfinyl)benzene (2c)<sup>3</sup>**

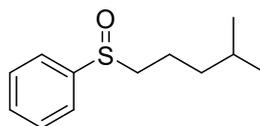


CFL lamps		427 nm		370 nm	
18 h	97 %	5 h	97 %	4 h	95 %

White solid; m.p.: 96-98 °C; Eluent: Petroleum ether / Ethyl acetate 6:4; NMR data in accordance with reported literature.<sup>3</sup>

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 7.63-7.62 (2H, d,  $J = 7.6$  Hz, ArH), 7.55-7.45 (3H, m, ArH), 2.84-2.71 (2H, m, 2 x SCHH), 1.74-1.86 (1H, m, CHH), 1.60-1.72 (1H, m, CHH), 1.04 (3H, t,  $J = 7.4$  Hz, CH<sub>3</sub>); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 144.0, 130.8, 129.1, 123.9, 59.2, 15.8, 13.2; ESI-MS [M+H<sup>+</sup>]: 169 m/z.

**((4-Methylpentyl)sulfinyl)benzene (2d)<sup>3</sup>**



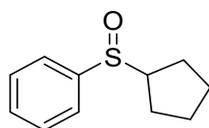
CFL lamps		427 nm		370 nm	
18 h	87 %	5 h	94 %	4 h	99 %

Colorless oil; Eluent: Petroleum ether / Ethyl acetate 6:4; NMR data in accordance with reported literature.<sup>3</sup>

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 7.65-7.60 (2H, m, ArH), 7.55-7.48 (3H, m, ArH), 2.81-2.74 (2H, m, SCH<sub>2</sub>), 1.80-1.71 (1H, m, CHH), 1.69-1.59 (1H, m, CHH), 1.59-1.50 (1H, m, CH), 1.36-1.29 (1H, m, CHH), 1.28-1.21 (1H, m, CHH), 0.86 (6H, d,  $J =$

6.6 Hz, 2 x CH<sub>3</sub>); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 144.0, 130.8, 129.1, 124.0, 57.6, 37.7, 27.7, 22.3, 22.3, 20.1; ESI-MS [M+H<sup>+</sup>]: 211 m/z.

**(Cyclopentylsulfinyl)benzene (2e)**

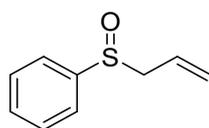


CFL lamps		427 nm		370 nm	
18 h	70 %	12 h	83 %	12 h	85 %

Pale yellow oil; Eluent: Petroleum ether / Ethyl acetate 6:4;

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 7.64-7.57 (2H, m, ArH), 7.50-7.41 (3H, m, ArH), 3.09 (1H, quint, *J* = 7.7 Hz, SCH), 2.12-2.01 (1H, m, CHH), 1.83-1.75 (2H, m, 2 x CHH), 1.73-1.52 (5H, m, 5 x CHH); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 143.5, 130.7, 128.9, 124.4, 64.2, 27.5, 25.9, 25.5, 24.7; HRMS: calculated for C<sub>11</sub>H<sub>15</sub>OS<sup>+</sup> (M+H)<sup>+</sup>: 195.0838, found: 195.0836.

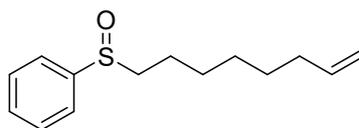
**(Allylsulfinyl)benzene (2f)<sup>1</sup>**



CFL lamps		427 nm		370 nm	
20 h	72 %	20 h	83 %	20 h	85 %

Colorless oil; Eluent: Petroleum ether / Ethyl acetate 6:4; NMR data in accordance with reported literature.<sup>14</sup>

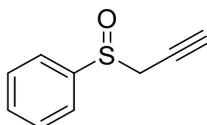
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 7.66-7.61 (2H, m, ArH), 7.58-7.49 (3H, m, ArH), 5.68 (1H, ddt, *J* = 17.0, 10.2 and 7.5 Hz, =CH), 5.36 (1H, d, *J* = 10.2 Hz, =CHH), 5.22 (1H, d, *J* = 17.0 Hz, =CHH), 3.60 (1H, dd, *J* = 12.8 and 7.5 Hz, SCHH), 3.54 (1H, dd, *J* = 12.8 and 7.5 Hz, SCHH); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 143.0, 131.1, 129.0, 125.3, 124.4, 123.9, 60.9; ESI-MS [M+H<sup>+</sup>]: 167 m/z.

**(Oct-7-en-1-ylsulfinyl)benzene (2g)**<sup>15</sup>

CFL lamps		427 nm		370 nm	
18 h	88 %	5 h	93 %	3 h	97 %

Colorless oil; Eluent: Petroleum ether / Ethyl acetate 6:4; NMR data in accordance with reported literature.<sup>15</sup>

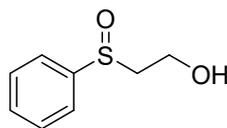
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 7.65-7.56 (2H, m, ArH), 7.55-7.46 (3H, m, ArH), 5.77 (1H, ddt,  $J$  = 17.0, 10.3 and 6.4 Hz, =CH), 4.95 (2H, m, =CH<sub>2</sub>), 2.79 (2H, t,  $J$  = 7.7 Hz, SCH<sub>2</sub>), 2.06-1.98 (2H, m, CH<sub>2</sub>), 1.82-1.70 (1H, m, CHH), 1.68-1.56 (1H, m, CHH), 1.46-1.28 (6H, m, 3  $\times$  CH<sub>2</sub>); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 144.0, 138.7, 130.8, 129.1, 123.9, 114.3, 57.2, 33.5, 28.5, 28.5, 28.4, 22.0; ESI-MS [M+H<sup>+</sup>]: 237 m/z.

**(Prop-2-yn-1-ylsulfinyl)benzene (2h)**<sup>16</sup>

CFL lamps		427 nm		370 nm	
18 h	90 %	5 h	78 %	20 h	100 %

Colorless oil; Eluent: Petroleum ether / Ethyl acetate 6:4; NMR data in accordance with reported literature.<sup>16</sup>

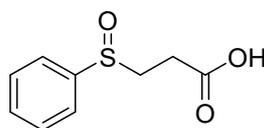
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 7.76-7.72 (2H, m, ArH), 7.58-7.55 (3H, m, ArH), 3.68 (1H, dd,  $J$  = 15.7 and 2.7 Hz, SCHH), 3.66 (1H, dd,  $J$  = 15.7 and 2.7 Hz, SCHH), 2.36 (1H, t,  $J$  = 2.7 Hz,  $\equiv$ CH); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 142.7, 131.8, 129.1, 124.5, 76.4, 72.7, 47.7; ESI-MS [M+H<sup>+</sup>]: 165 m/z.

**2-(Phenylsulfinyl)ethan-1-ol (2i)**<sup>17</sup>

CFL lamps		427 nm		370 nm	
18 h	80 %	6 h	67 %	4 h	70 %

Colorless oil; Eluent: Petroleum ether / Ethyl acetate 6:4; NMR data in accordance with reported literature.<sup>17</sup>

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 7.67 (2H, dd,  $J = 7.9$  and  $1.6$  Hz, ArH), 7.60-7.51 (3H, m, ArH), 4.19 (1H, ddd,  $J = 12.1, 8.8$  and  $3.2$  Hz, OCHH), 4.03 (1H, ddd,  $J = 12.1, 5.4$  and  $4.1$  Hz, OCHH), 3.19 (2H, m, S(O)CHH and OH), 2.91 (1H, ddd,  $J = 13.6, 5.4$  and  $3.2$  Hz, S(O)CHH); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 143.0, 131.2, 129.4, 123.9, 58.3, 57.0; ESI-MS [M+H<sup>+</sup>]: 171 m/z.

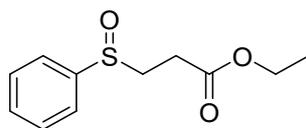
**3-(Phenylsulfinyl)propanoic acid (2j)**

CFL lamps		427 nm		370 nm*	
18 h	63 %	5 h	62 %	5 h	70 %

\*The reaction was performed in methanol due to poor solubility of 3-(phenylthio)propanoic acid in acetonitrile

White solid; m.p.: 95-97 °C; Eluent: Ethyl acetate

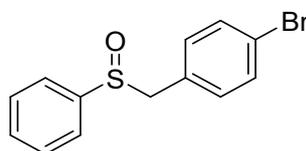
<sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>OD)  $\delta$ : 7.75-7.69 (2H, m, ArH), 7.65-7.58 (3H, m, ArH), 3.25 (1H, dt,  $J = 14.4$  and  $7.2$  Hz, CHH), 3.10 (1H, dt,  $J = 14.4$  and  $7.2$  Hz, CHH), 2.64 (1H, dt,  $J = 15.9$  and  $7.2$  Hz, CHH), 2.41 (1H, dt,  $J = 15.9$  and  $7.2$  Hz, CHH); <sup>13</sup>C NMR (100 MHz, CD<sub>3</sub>OD)  $\delta$ : 177.8, 143.9, 132.6, 130.6, 125.4, 54.1, 30.0; HRMS: calculated for C<sub>9</sub>H<sub>10</sub>NaO<sub>3</sub>S<sup>+</sup> (M+Na)<sup>+</sup>: 221.0243, found: 221.0241.

**Ethyl 3-(phenylsulfinyl)propanoate (2k)<sup>1</sup>**

CFL lamps		427 nm		370 nm	
18 h	82 %	8 h	80 %	7 h	80 %

Colorless oil; Eluent: Petroleum ether / Ethyl acetate 6:4; NMR data in accordance with reported literature.<sup>1</sup>

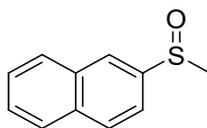
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 7.65-7.59 (2H, dd,  $J = 7.4$  and  $1.8$  Hz, ArH), 7.56-7.48 (3H, m, ArH), 4.11 (2H, q,  $J = 7.1$  Hz, OCH<sub>2</sub>), 3.23 (1H, ddd,  $J = 13.7, 8.5$  and  $6.9$  Hz, CHH), 2.97 (1H, ddd,  $J = 13.7, 8.5$  and  $5.8$  Hz, CHH), 2.82 (1H, ddd,  $J = 16.9, 8.5$  and  $6.9$  Hz, CHH), 2.53 (1H, ddd,  $J = 16.9, 8.5$  and  $5.8$  Hz, CHH), 1.23 (3H, t,  $J = 7.1$  Hz, CH<sub>3</sub>); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 171.1, 142.9, 131.1, 129.2, 124.0, 61.0, 51.1, 26.1, 14.0; ESI-MS [M+H<sup>+</sup>]: 227 m/z.

**1-Bromo-4-((phenylsulfinyl)methyl)benzene (2l)<sup>18</sup>**

CFL lamps		427 nm		370 nm	
18 h	78 %	5 h	81 %	3 h	74 %

White solid; m.p.: 177-179 °C; Eluent: Petroleum ether / Ethyl acetate 6:4; NMR data in accordance with reported literature.<sup>18</sup>

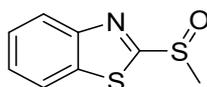
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 7.51-7.44 (3H, m, ArH), 7.39 (4H, d,  $J = 8.2$  Hz, ArH), 6.85 (2H, d,  $J = 8.2$  Hz, ArH), 4.03 (1H, d,  $J = 12.8$  Hz, CHH), 3.98 (1H, d,  $J = 12.8$  Hz, CHH); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 142.3, 131.9, 131.5, 131.3, 129.0, 127.9, 124.4, 122.6, 62.5; ESI-MS [M+H<sup>+</sup>]: 295 m/z.

**2-(Methylsulfinyl)naphthalene (2m)<sup>3</sup>**

CFL lamps		427 nm		370 nm	
18 h	97 %	5 h	94 %	3 h	98 %

White solid; m.p.: 105-107 °C; Eluent: Petroleum ether / Ethyl acetate 6:4; NMR data in accordance with reported literature.<sup>3</sup>

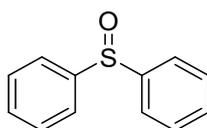
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 8.23 (1H, s, ArH), 8.00 (1H, d, *J* = 8.6, ArH), 7.99-7.88 (2H, m, ArH), 7.65-7.57 (3H, m, ArH), 2.81 (3H, s, CH<sub>3</sub>); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 142.7, 134.4, 132.9, 129.5, 128.4, 128.0, 127.7, 127.3, 124.0, 119.4, 43.7; ESI-MS [M+H<sup>+</sup>]: 191 m/z.

**2-(Methylsulfinyl)benzo[d]thiazole (2n)<sup>19</sup>**

CFL lamps		427 nm		370 nm	
48 h	92 %	20 h	55 %	20 h	56 %

Yellowish solid; m.p.: 69-71 °C; Eluent: Petroleum ether / Ethyl acetate 6:4; NMR data data in accordance with reported literature.<sup>19</sup>

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 8.08 (1H, d, *J* = 7.9 Hz, ArH), 8.02 (1H, d, *J* = 7.9 Hz, ArH), 7.58 (1H, t, *J* = 7.9 Hz, ArH), 7.51 (1H, t, *J* = 7.9 Hz, ArH), 3.09 (3H, s, CH<sub>3</sub>); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 178.3, 153.7, 136.0, 126.9, 126.2, 123.9, 122.3, 43.1; ESI-MS [M+H<sup>+</sup>]: 198 m/z.

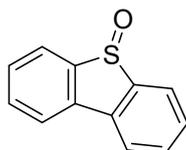
**Sulfinyldibenzene (2o)<sup>3</sup>**

CFL lamps		427 nm		370 nm	
18 h	90 %	18 h	65 %	10 h	70 %

White solid; m.p.: 70-72 °C; Eluent: Petroleum ether / Ethyl acetate 6:4; NMR data in accordance with reported literature.<sup>3</sup>

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 7.70-7.64 (4H, m, ArH), 7.51-7.43 (6H, m, ArH); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 145.6, 131.0, 129.3, 124.8; ESI-MS [M+H<sup>+</sup>]: 203 m/z.

### Dibenzo[b,d]thiophene 5-oxide (2p)<sup>10</sup>

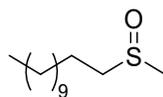


CFL lamps		427 nm		370 nm	
18 h	78 %	5 h	76 %	5 h	75 %

White solid; m.p.: 188-190 °C; Eluent: Petroleum ether / Ethyl acetate 6:4; NMR data in accordance with reported literature.<sup>10</sup>

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 7.99 (2H, d,  $J$  = 7.6 Hz, ArH), 7.81 (2H, d,  $J$  = 7.6 Hz, ArH), 7.60 (2H, t,  $J$  = 7.6 Hz, ArH), 7.50 (2H, t,  $J$  = 7.6 Hz, ArH); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 145.1, 137.0, 132.5, 129.5, 127.4, 121.8; ESI-MS [M+H<sup>+</sup>]: 201 m/z.

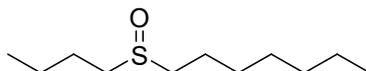
### 1-(Methylsulfinyl)dodecane (2q)<sup>16</sup>



CFL lamps		427 nm		370 nm	
18 h	70 %	5 h	85 %	18 h	100 %

White solid; m.p.: 62-64 °C; Eluent: Petroleum ether / Ethyl acetate 6:4; NMR data in accordance with reported literature.<sup>16</sup>

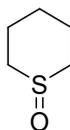
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 2.79-2.72 (1H, m, SCHH), 2.70-2.62 (1H, m, SCHH), 2.57 (3H, s, SCH<sub>3</sub>), 1.77 (2H, qu,  $J$  = 7.2 Hz, CH<sub>2</sub>), 1.51-1.26 (18H, m, 9 x CH<sub>2</sub>), 0.89 (3H, t,  $J$  = 6.7 Hz, CH<sub>3</sub>); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 54.8, 38.5, 31.9, 29.6, 29.5, 29.3, 29.3, 29.2, 28.8, 22.6, 22.5, 14.1; ESI-MS [M+H<sup>+</sup>]: 121 m/z.

**1-(Butylsulfinyl)heptane (2r)<sup>3</sup>**

CFL lamps		427 nm		370 nm	
18 h	74 %	5 h	71 %	18 h	70 %

Colorless oil; Eluent: Petroleum ether / Ethyl acetate 6:4; NMR data data in accordance with reported literature.<sup>3</sup>

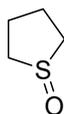
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 2.76-2.60 (4H, m, 2 x SCH<sub>2</sub>), 1.83-1.72 (4H, m, 2 x CH<sub>2</sub>), 1.58-1.40 (4H, m, 2 x CH<sub>2</sub>), 1.39-1.26 (6H, m, 3 x CH<sub>2</sub>), 0.98 (3H, t,  $J$  = 7.3 Hz, CH<sub>3</sub>), 0.90 (3H, t,  $J$  = 6.8 Hz, CH<sub>3</sub>); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 52.4, 52.1, 31.5, 28.8, 28.8, 24.6, 22.6, 22.5, 22.1, 14.0, 13.6; ESI-MS [M+H<sup>+</sup>]: 205 m/z.

**Tetrahydro-2H-thiopyran 1-oxide (2s)<sup>20</sup>**

CFL lamps		427 nm		370 nm	
18 h	77 %	5 h	84 %	20 h	77 %

White solid; m.p.: 60-62 °C; Eluent: Petroleum ether / Ethyl acetate 6:4; NMR data in accordance with reported literature.<sup>20</sup>

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 2.90 (2H, t,  $J$  = 10.9 Hz, SCH<sub>2</sub>), 2.78 (2H, t,  $J$  = 10.9 Hz, SCH<sub>2</sub>), 2.32-2.18 (2H, m, CH<sub>2</sub>), 1.73-1.58 (4H, m, 2 x CH<sub>2</sub>); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 48.9, 24.6, 19.1; ESI-MS [M+H<sup>+</sup>]: 119 m/z.

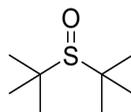
**Tetrahydrothiophene 1-oxide (2t)<sup>21</sup>**

CFL lamps		427 nm		370 nm	
18 h	90 %	5 h	91 %	20 h	90 %

Colorless oil; Eluent: Petroleum ether / Ethyl acetate 6:4; NMR data in accordance with reported literature.<sup>21</sup>

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 2.91-2.74 (4H, m, 2 x  $\text{SCH}_2$ ), 2.48-2.35 (2H, m,  $\text{CH}_2$ ), 2.05-1.93 (2H, m,  $\text{CH}_2$ );  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 54.3, 25.3; **ESI-MS**  $[\text{M}+\text{H}^+]$ : 105 m/z.

**2-(*tert*-Butylsulfinyl)-2-methylpropane (2u)<sup>3</sup>**

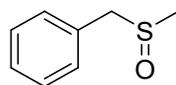


CFL lamps		427 nm		370 nm	
18 h	60 %	5 h	78 %	18 h	80 %

Colorless solid; Eluent: Petroleum ether; NMR data in accordance with reported literature.<sup>3</sup>

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 1.35 (18H, s, 6 x  $\text{CH}_3$ );  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 57.2, 25.5; **ESI-MS**  $[\text{M}+\text{H}^+]$ : 163 m/z.

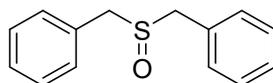
**((Methylsulfinyl)methyl)benzene (2v)<sup>16</sup>**



CFL lamps		427 nm		370 nm	
18 h	75 %	9 h	71 %	6 h	90 %

White solid; m.p: 54-56 °C; Eluent: Petroleum ether / Ethyl acetate 6:4; data in accordance with reported literature.<sup>16</sup>

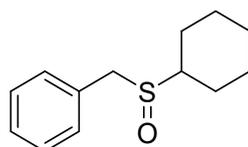
$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.43-7.33 (3H, m, ArH), 7.32-7.28 (2H, m, ArH), 4.08 (1H, d,  $J = 12.8$  Hz,  $\text{SCHH}$ ), 3.94 (1H, d,  $J = 12.8$  Hz,  $\text{SCHH}$ ), 2.47 (3H, s,  $\text{SCH}_3$ );  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 130.0, 129.6, 128.9, 128.4, 60.2, 37.2; **ESI-MS**  $[\text{M}+\text{H}^+]$ : 155 m/z.

**(Sulfinylbis(methylene))dibenzene (2w)<sup>14</sup>**

CFL lamps		427 nm		370 nm	
18 h	84 %	5 h	83 %	3 h	84 %

White solid; m.p.: 132-134 °C; Eluent: Petroleum ether / Ethyl acetate 6:4; NMR data in accordance with reported literature.<sup>14</sup>

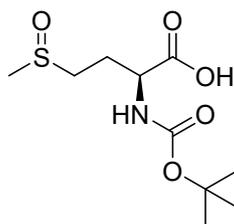
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 7.42-7.36 (6H, m, ArH), 7.34-7.30 (4H, m, ArH), 3.97 (2H, d, *J* = 13.0 Hz, SCHH), 3.93 (2H, d, *J* = 13.0 Hz, SCHH); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 130.1, 130.0, 128.9, 128.3, 57.1; ESI-MS [M+H<sup>+</sup>]: 231 m/z.

**((Cyclohexylsulfinyl)methyl)benzene (2x)<sup>22</sup>**

CFL lamps		427 nm		370 nm	
18 h	85 %	12 h	80 %	3 h	85 %

White solid; m.p.: 82-84 °C; Eluent: Petroleum ether / Ethyl acetate 6:4; NMR data in accordance with reported literature.<sup>22</sup>

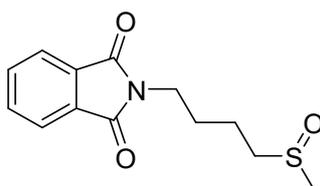
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 7.47-7.29 (5H, m, ArH), 4.01 (1H, d, *J* = 13.1 Hz, SCHH), 3.93 (1H, d, *J* = 13.1 Hz, SCHH), 2.54-2.44 (1H, m, SCH), 2.16-2.07 (1H, m, CHH), 1.99-1.82 (3H, m, 3 x CHH), 1.75-1.67 (1H, m, CHH), 1.63-1.47 (2H, m, 2 x CHH), 1.39-1.24 (3H, m, 3 x CHH); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 130.6, 129.9, 128.6, 128.1, 56.9, 54.7, 26.9, 25.4, 25.4, 25.1, 23.9; ESI-MS [M+H<sup>+</sup>]: 223 m/z.

**(2S)-2-((tert-Butoxycarbonyl)amino)-4-(methylsulfinyl)butanoic acid (2y)**<sup>23</sup>

CFL lamps		427 nm		370 nm*	
18 h	90 %	5 h	91 %	5 h	90 %

\*The reaction was performed in methanol due to poor solubility of *N*-Boc L-methionine in acetonitrile. Yellowish solid; m.p.: 114-116 °C;  $[\alpha]_{\text{D}}^{25} = +4.8$  (c 1.25, CH<sub>3</sub>OH); Eluent: Ethyl acetate; NMR data in accordance with reported literature (1:1 mixture of diastereoisomers).<sup>23</sup>

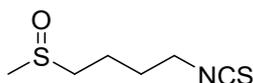
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 6.85 (1H, br s, OH), 5.65-5.51 (1H, m, NH), 4.49-4.37 (1H, m, NCH), 3.02-2.84 (2H, m, SCH<sub>2</sub>), 2.74 (1.5H, s, SCH<sub>3</sub>), 2.69 (1.5H, s, SCH<sub>3</sub>), 2.46-2.31 (1H, m, CHH), 2.29-2.15 (1H, m, CHH), 1.46 (9H, s, 3 x CH<sub>3</sub>); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 173.2, 173.1, 155.6, 155.6, 80.3, 52.4, 52.2, 49.3, 37.6, 37.3, 28.7, 28.3, 27.0, 26.2, 25.7; ESI-MS [M+H<sup>+</sup>]: 266 m/z.

**2-(4-(Methylsulfinyl)butyl)isoindoline-1,3-dione (7)**<sup>13</sup>

CFL lamps		427 nm		370 nm	
18 h	93 %	5 h	91 %	4 h	79 %

White solid; m.p.: 132-133 °C; Eluent: Petroleum ether / Ethyl acetate 6:4; NMR data in accordance with reported literature.<sup>13</sup>

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 7.86 (2H, dd,  $J = 5.4$  and  $3.1$  Hz, ArH), 7.76-7.71 (2H, m, ArH), 3.76 (2H, t,  $J = 6.6$  Hz, NCH<sub>2</sub>), 2.81-2.75 (2H, m, SCH<sub>2</sub>), 2.59 (3H, s, CH<sub>3</sub>), 1.92-1.81 (4H, m, 2 x CH<sub>2</sub>); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 168.3, 134.0, 132.0, 123.3, 53.8, 38.5, 37.1, 27.7, 19.8; ESI-MS [M+H<sup>+</sup>]: 266 m/z.

**1-(Methylsulfinyl)-4-thiocyanatobutane (8)**<sup>13</sup>

CFL lamps		427 nm		370 nm*	
18 h	75 %	5 h	97 %	4 h	87 %

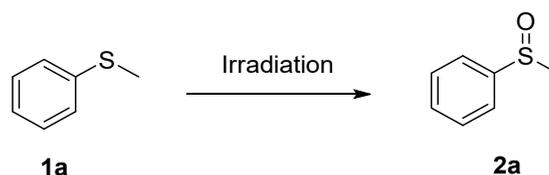
\*The reaction was performed using anthraquinone (0.5 mol%, 0.0025 mmol, 0.5 mg) to accelerate the reaction to avoid decomposition of sulforaphane.

Colorless oil; Eluent: Petroleum ether / Ethyl acetate 6:4; NMR data in accordance with reported literature.<sup>13</sup>

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 3.61 (2H, t,  $J$  = 6.0 Hz, CH<sub>2</sub>NCS), 2.80-2.67 (2H, m, SCH<sub>2</sub>), 2.61 (3H, s, SCH<sub>3</sub>), 2.00-1.84 (4H, m, 2 x CH<sub>2</sub>); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 130.9, 53.4, 44.6, 38.6, 28.9, 20.0; ESI-MS [M+H<sup>+</sup>]: 178 m/z.

## PART C: Mechanistic Studies

### Quenching Studies on the Alkyl Aryl Sulfide Oxidation



Source of Irradiation	Quenchers				
	DABCO	NaN <sub>3</sub>	Co(acac) <sub>3</sub>	DMB (1,4-dimethoxybenzene)	Benzoquinone
CFL lamps <sup>a</sup>	28 %	23 %	- (decomposition)	89 %	0 %
LED 370 nm <sup>b</sup>	28 %	12 %	14 %	84 %	6 %
LED 427 nm <sup>c</sup>	28 %	31 %	0 %	75 %	6 %

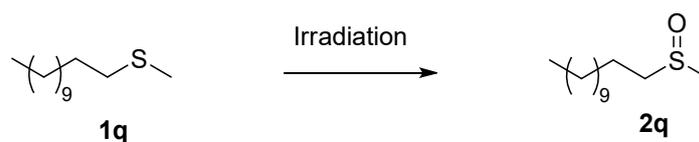
<sup>a</sup> In a glass vial containing sulfide (1.0 eq., 0.20 mmol), quencher (1.0 eq.) and anthraquinone (0.5 mol%, 0.001 mmol, 0.2 mg) in methanol (1 mL), water (40  $\mu$ L) was added. The reaction mixture was left stirring under household bulb irradiation (2  $\times$  85W household lamps) for 18 h. Conversions were determined by <sup>1</sup>H-NMR. All reactions were performed in triplicates, the average yield is provided.

<sup>b</sup> In a glass vial containing sulfide (1.0 eq., 0.20 mmol) in acetonitrile (0.5 mL) and quencher (1.0 eq.), water (40  $\mu$ L) was added. The reaction mixture was left stirring under UVA LED (Kessil PR 160L, 370 nm) irradiation for 3 h. Conversions were determined by <sup>1</sup>H-NMR. All reactions were performed in triplicates, the average yield is provided.

<sup>c</sup> In a glass vial containing sulfide (1.0 eq., 0.20 mmol), quencher (1.0 eq.) and anthraquinone (0.05 mol%, 0.1  $10^{-3}$  mmol, 0.02 mg) (from stock solution), methanol (0.5 mL) was added. The reaction mixture was left stirring under Blue LED (Kessil PR 160L, 427 nm) irradiation for 5 h. Conversions were determined by <sup>1</sup>H-NMR. All reactions were performed in triplicates, the average yield is provided.

Green: No quenching, Orange: Quenching, Grey: Not applicable due to fluorescence quenching studies, Gold: Not applicable due to oxidation potential vs sulfide radical cation.

## Quenching Studies on the Dialkyl Sulfide Oxidation



Source of Irradiation \ Quenchers	Quenchers				
	DABCO	NaN <sub>3</sub>	Co(acac) <sub>3</sub>	DMB	Benzoquinone
CFL lamps <sup>a</sup>	0 %	0 %	0 %	100 %	0 %
LED 370 nm <sup>b</sup>	0 %	5 %	0 %	88 %	21 %
LED 427 nm <sup>c</sup>	0 %	19 %	4 %	88 %	10 %

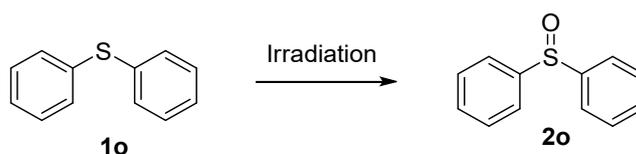
<sup>a</sup> In a glass vial containing sulfide (1.0 eq., 0.20 mmol), quencher (1.0 eq.) and anthraquinone (0.5 mol%, 0.001 mmol, 0.2 mg) in methanol (1 mL), water (40  $\mu$ L) was added. The reaction mixture was left stirring under household bulb irradiation ( $2 \times 85$ W household lamps) for 18 h. Conversions were determined by <sup>1</sup>H-NMR. All reactions were performed in triplicates, the average yield is provided.

<sup>b</sup> In a glass vial containing sulfide (1.0 eq., 0.20 mmol) in acetonitrile (0.5 mL) and quencher (1.0 eq.), water (40  $\mu$ L) was added. The reaction mixture was left stirring under UVA LED (Kessil PR 160L, 370 nm) irradiation for 18 h. Conversions were determined by <sup>1</sup>H-NMR. All reactions were performed in triplicates, the average yield is provided.

<sup>c</sup> In a glass vial containing sulfide (1.0 eq., 0.20 mmol), quencher (1.0 eq.) and anthraquinone (0.05 mol%, 0.1  $10^{-3}$  mmol, 0.02 mg) (from stock solution), methanol (0.5 mL) was added. The reaction mixture was left stirring under Blue LED (Kessil PR 160L, 427 nm) irradiation for 5 h. Conversions were determined by <sup>1</sup>H-NMR. All reactions were performed in triplicates, the average yield is provided.

Green: No quenching, Orange: Quenching, Grey: Not applicable due to fluorescence quenching studies, Gold: Not applicable due to oxidation potential vs sulfide radical cation.

## Quenching Studies on the Diaryl Sulfide Oxidation



Source of Irradiation \ Quenchers	Quenchers				
	DABCO	NaN <sub>3</sub>	Co(acac) <sub>3</sub>	DMB	Benzoquinone
CFL <sup>a</sup>	0 %	2 %	0 %	5 %	5 %
LED 370 nm <sup>b</sup>	0 %	4 %	8 %	6 %	0 %
LED 427 nm <sup>c</sup>	0 %	4 %	7 %	19 %	6 %

<sup>a</sup> In a glass vial containing sulfide (1.0 eq., 0.20 mmol), quencher (1.0 eq.) and anthraquinone (0.5 mol%, 0.001 mmol, 0.2 mg) in methanol (1 mL), water (40  $\mu$ L) was added. The reaction mixture was left stirring under household bulb irradiation ( $2 \times 85$ W household lamps) for 18 h. Conversions were determined by <sup>1</sup>H-NMR. All reactions were performed in triplicates, the average yield is provided.

<sup>b</sup> In a glass vial containing sulfide (1.0 eq., 0.20 mmol) in acetonitrile (0.5 mL) and quencher (1.0 eq.), water (40  $\mu$ L) was added. The reaction mixture was left stirring under UVA LED (Kessil PR 160L, 370 nm) irradiation for 10 h. Conversions were determined by <sup>1</sup>H-NMR. All reactions were performed in triplicates, the average yield is provided.

<sup>c</sup> In a glass vial containing sulfide (1.0 eq., 0.20 mmol), quencher (1.0 eq.) and anthraquinone (0.05 mol%, 0.1  $10^{-3}$  mmol, 0.02 mg) (from stock solution), methanol (0.5 mL) was added. The reaction mixture was left stirring under Blue LED (Kessil PR 160L, 427 nm) irradiation for 18 h. Conversions were determined by <sup>1</sup>H-NMR. All reactions were performed in triplicates, the average yield is provided.

Green: No quenching, Orange: Quenching, Grey: Not applicable due to fluorescence quenching studies, Gold: Not applicable due to oxidation potential vs sulfide radical cation.

## Determination of the Quantum Yield

### Determination of the photon flux

A ferrioxalate actinometer solution was prepared following the Hammond variation of the Hatchard and Parker procedure<sup>24</sup> outlined in the *Handbook of Photochemistry*.<sup>25</sup> Ferrioxalate actinometer solution measures the decomposition of ferric ions to ferrous ions, which are complexed by 1,10-phenanthroline and monitored by UV/Vis absorbance at 510 nm. The moles of iron-phenanthroline complex formed are related to moles of photons absorbed. The values of the quantum yield of potassium ferrioxalate are related to the concentration and wavelength.

The solutions were prepared and stored under dark:

1. **Potassium ferrioxalate solution 0.012M:** 147.4 mg of potassium ferrioxalate and 69.5  $\mu$ L of sulfuric acid (96%) were added to a 25 mL volumetric flask and filled to the mark with water (HPLC grade).
2. **Phenanthroline solution:** 0.2% by weight of 1,10-phenanthroline in water (100 mg in 50 mL volumetric flask or 50 mg in 25 mL).
3. **Buffer solution:** to a 100 mL volumetric flask 4.94 g of NaOAc and 1.0 mL of sulfuric acid (96%) were added and filled to the mark with water (HPLC grade).

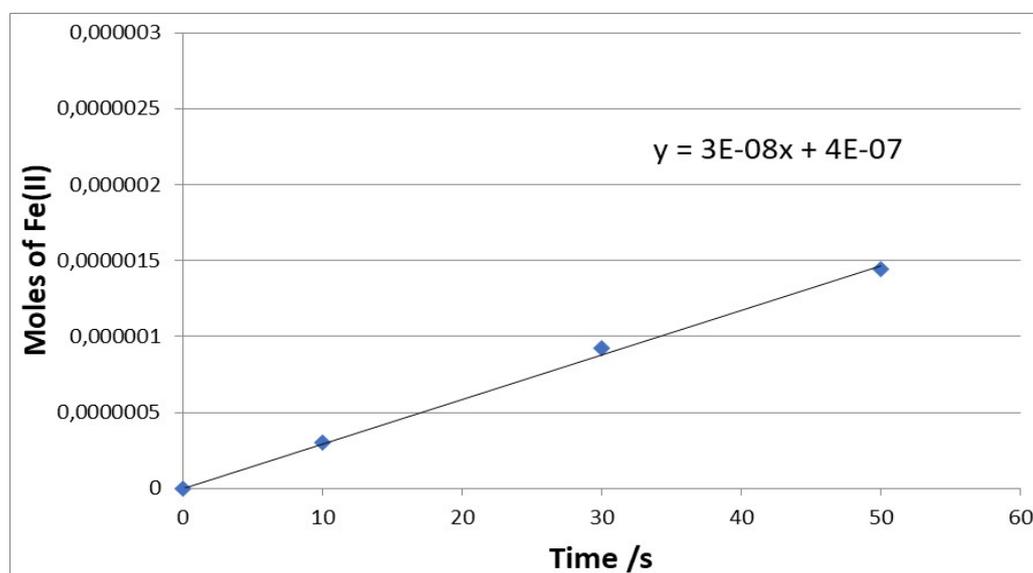
A cuvette was loaded with 1.0 mL of potassium ferrioxalate solution and placed under Kessil 427 nm lamp irradiation. Three different actinometer solutions were irradiated in sequence for 10 s, 30 s and 50 s, respectively. After each irradiation, the actinometer solutions were carefully transferred into a 10 mL volumetric flask, then

0.5 mL of phenanthroline solution and 2.0 mL of buffer solution were added and the flask was filled up with water. The absorbance of the final solution was measured at 510 nm. A non-irradiated sample was also prepared and the absorbance at 510 nm was measured.

The moles of  $\text{Fe}^{2+}$  formed for each sample are determined using Beer's Law (Eq. 1):

$$\text{Moles of Fe (II)} = \frac{V_1 \times V_3 \times \Delta A (510 \text{ nm})}{10^3 \times V_2 \times l \times \varepsilon (510 \text{ nm})} \quad (\text{Eq. 1})$$

where  $V_1$  is the irradiated volume (1 mL),  $V_2$  is the aliquot of the irradiated solution taken for the determination of the ferrous ions (1 mL),  $V_3$  is the final volume after complexation with phenanthroline (10 mL),  $l$  is the optical path-length of the irradiation cell (1 cm),  $\Delta A (510 \text{ nm})$  is the optical difference in absorbance between the irradiated solution and the one stored in the dark,  $\varepsilon (510 \text{ nm})$  is the extinction coefficient the complex  $\text{Fe}(\text{phen})_3^{2+}$  at 510 nm ( $11100 \text{ L mol}^{-1} \text{ cm}^{-1}$ ). The moles of  $\text{Fe}^{2+}$  formed ( $x$ ) are plotted as a function of time ( $t$ ).



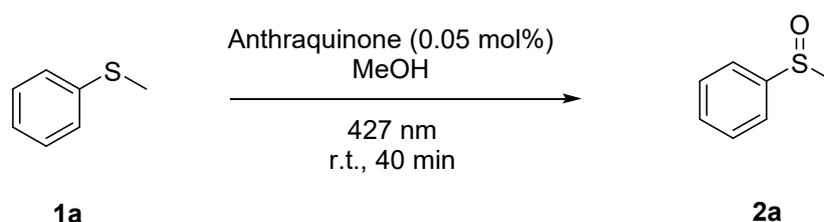
The slope of this line was correlated to the moles of incident photons by unit of time ( $q_{n,p}^0$ ) by the use of the following Equation 2:

$$\Phi(\lambda) = \frac{dx/dt}{q_{n,p}^0 \times [1 - 10^{-A(\lambda)}]} \quad (\text{Eq. 2})$$

where  $dx/dt$  is the rate of change of a measurable quantity (spectral or any other property), the quantum yield ( $\Phi$ ) for  $\text{Fe}^{2+}$  at 427 nm is 1.11,<sup>26</sup>  $[1 - 10^{-A(\lambda)}]$  is the ratio of absorbed photons by the solution, and  $A(\lambda)$  is the absorbance of the actinometer at the wavelength used to carry out the experiments (427 nm). The absorbance at 427 nm ( $A(427)$ ) was 0.16461.

The photon flux, which is  $q_{n,p}^0$ , was determined to be  $8,56 \times 10^{-8}$  einstein  $\text{s}^{-1}$ .

Determination of the quantum yield for the photochemical reaction of thioanisole **1a** at 427 nm

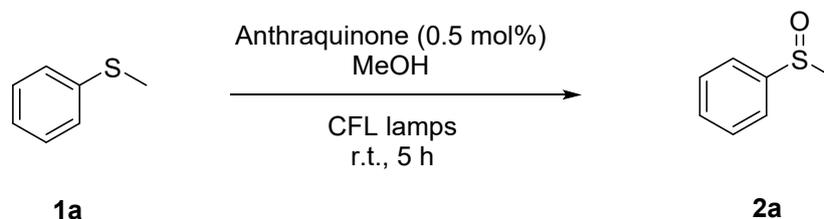


In a glass vial containing thioanisole (1.0 eq., 0.20 mmol, 25 mg) anthraquinone (0.05 mol%,  $0.1 \times 10^{-3}$  mmol, 0.02 mg) in methanol (0.5 mL) was added (catalyst was added from stock solution in methanol). The reaction mixture was left stirring under Blue LED (Kessil PR 160L, 427 nm) irradiation for 2400 s (40 min). After irradiation, the solvent was removed and the yield of the product was determined by  $^1\text{H}$  NMR (65%). The quantum yield was determined with the following equation:

$$\Phi = \frac{\text{mol product}}{\text{flux} \times t \times f} = \frac{0.130 \times 10^{-3} \text{ mol}}{8.56 \times 10^{-8} \text{ einstein s}^{-1} \times 2400 \text{ s} \times 0.3155} = 2.0$$

### Determination of the quantum yield for the photochemical reaction of thioanisole **1a** at CFL lamps

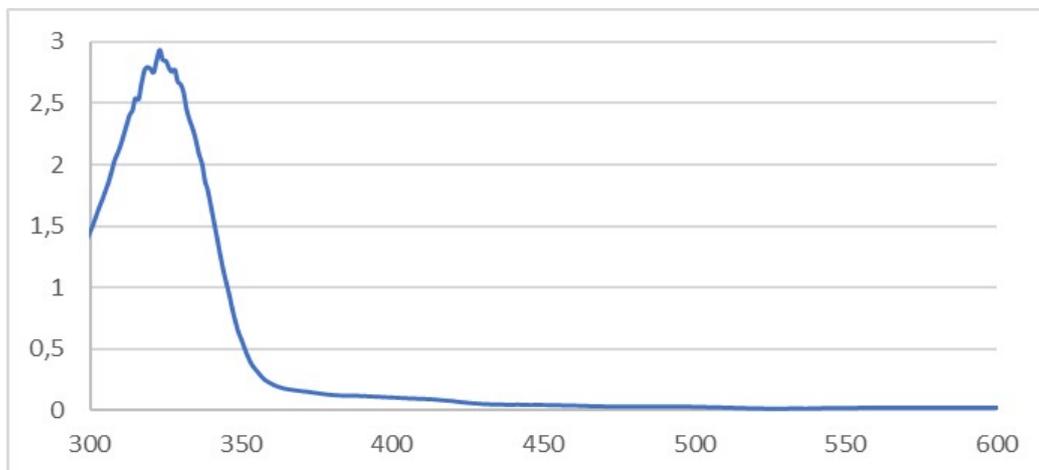
In the case where CFL lamps were used as irradiation source, the photon flux was calculated as above and found to be  $3.39 \times 10^{-9}$  einstein  $s^{-1}$ .



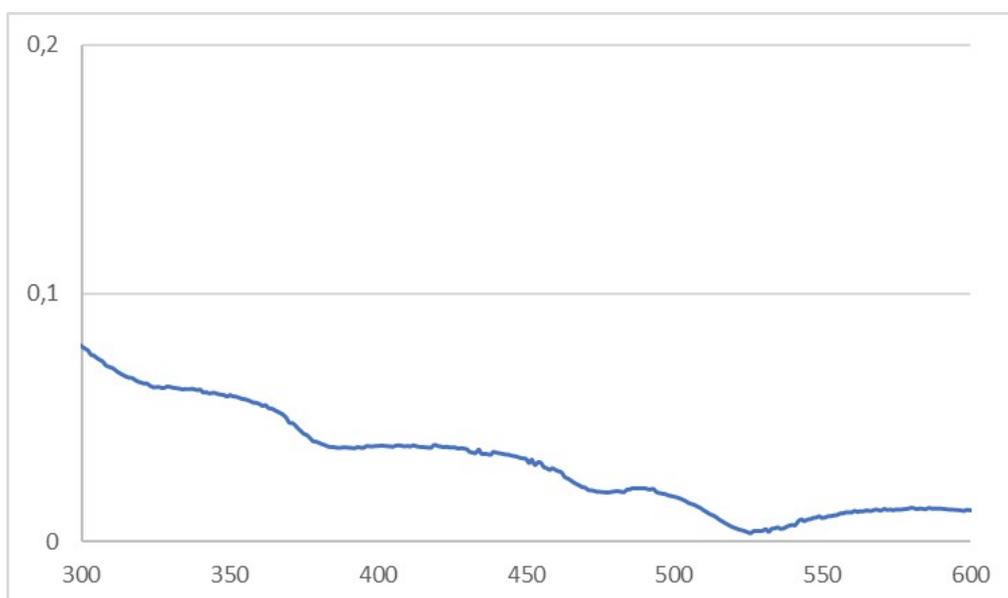
In a glass vial containing thioanisole (1.0 eq., 0.20 mmol, 25 mg) and anthraquinone (0.5 mol%, 0.001 mmol, 0.2 mg) in methanol (1.0 mL), water (40  $\mu\text{L}$ ) was added. The reaction mixture was left stirring under household bulb irradiation ( $2 \times 85\text{W}$  household lamps) for 18000 s (5 h). After irradiation, the solvent was removed and the yield of the product was determined by  $^1\text{H}$  NMR (63%). The quantum yield was determined with the following equation:

$$\Phi = \frac{\text{mol product}}{\text{flux} \times t \times f} = \frac{0.126 \times 10^{-3} \text{ mol}}{3.39 \times 10^{-9} \text{ einstein s}^{-1} \times 18000 \text{ s} \times 0.99999} = 2.1$$

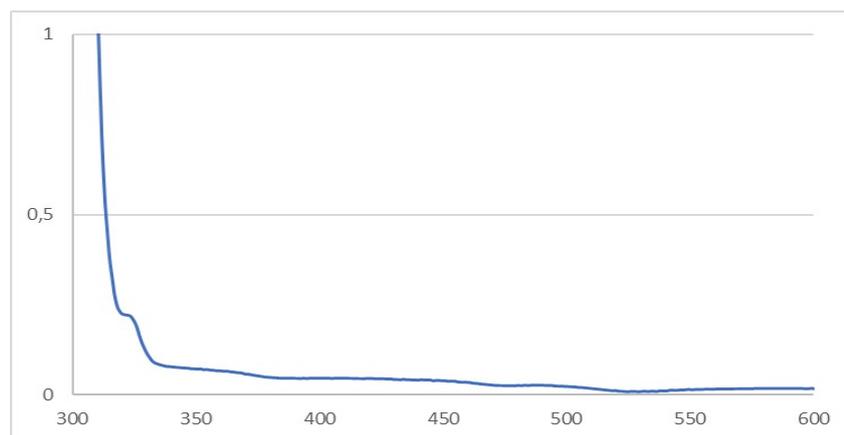
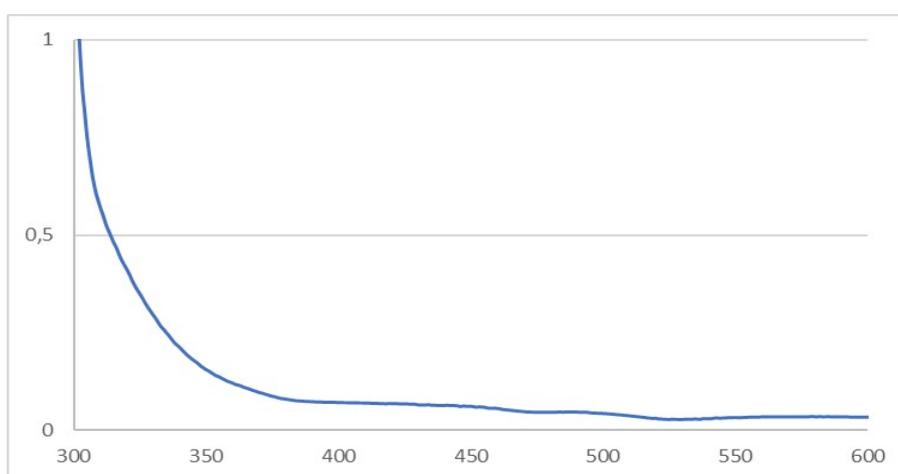
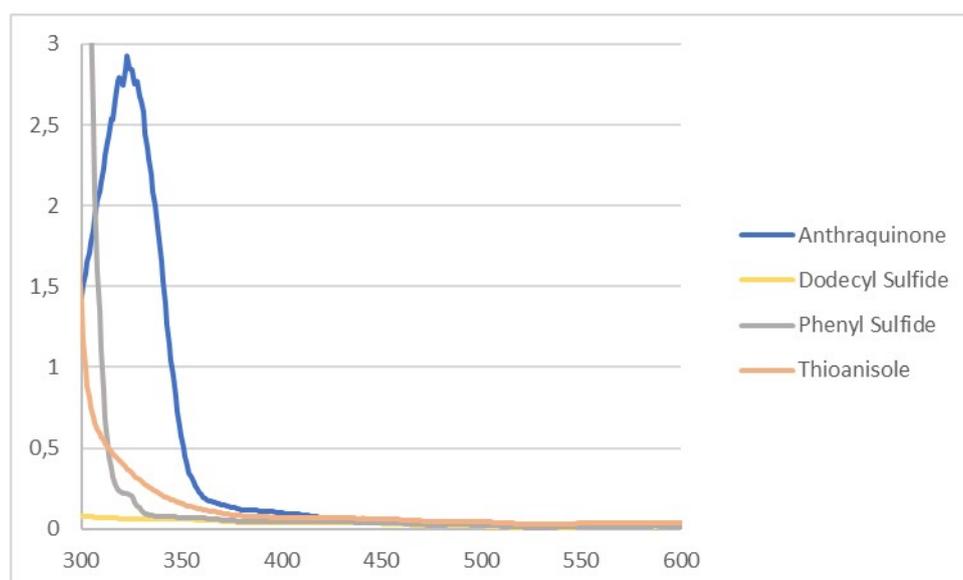
### Mechanistic Investigation with UV-Vis



Anthraquinone  $10^{-3}$ M in MeCN

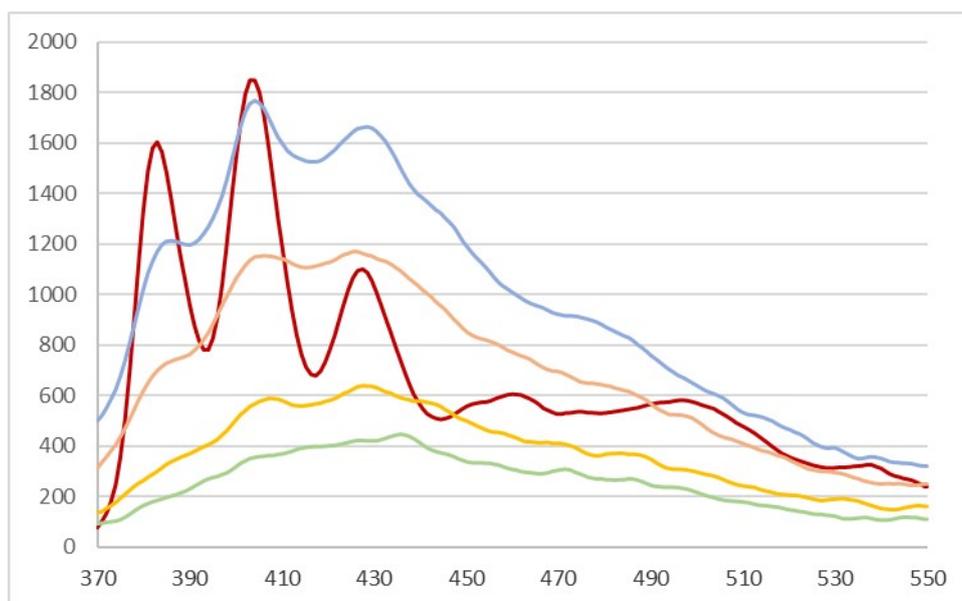


Dodecyl methyl sulfide  $10^{-2}$ M in MeCN

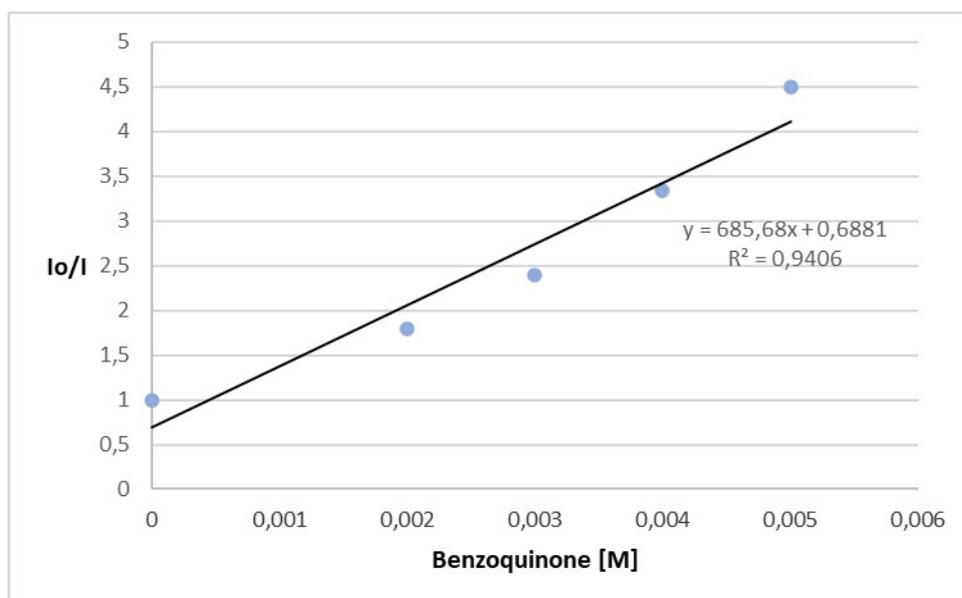
Diphenyl sulfide  $10^{-2}$ M in MeCNThioanisole  $10^{-2}$  M in MeCNAnthraquinone  $10^{-3}$ M, dodecyl methyl sulfide  $10^{-2}$ M, diphenyl sulfide  $10^{-2}$ M and thioanisole  $10^{-2}$ M in MeCN

## Fluorescence Quenching Studies

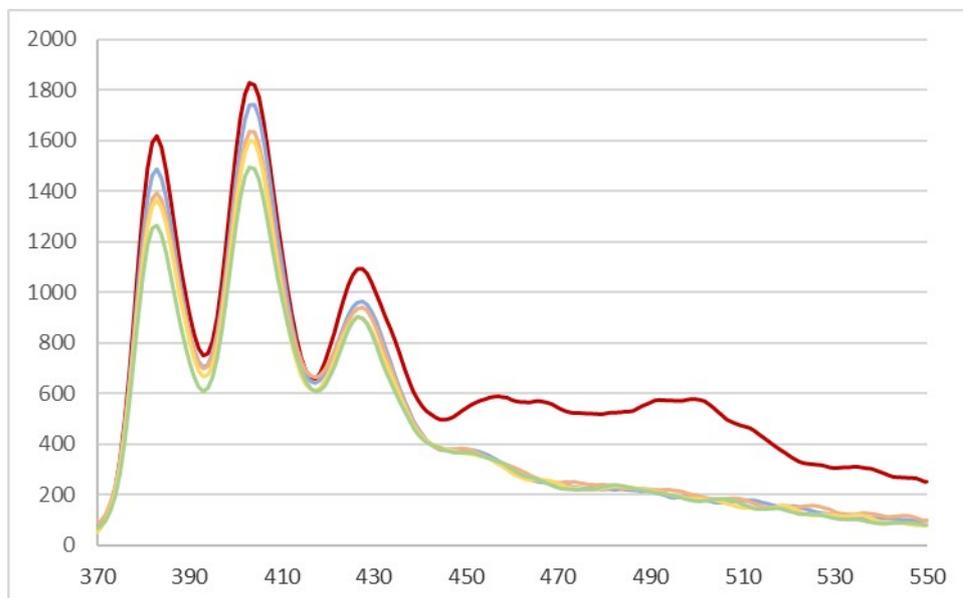
After irradiation of anthraquinone (**4a**) (1 mM in MeCN) at 358 nm, its fluorescence was measured at 404 nm. Increasing the added amount of benzoquinone, there is a decrease in the fluorescence.



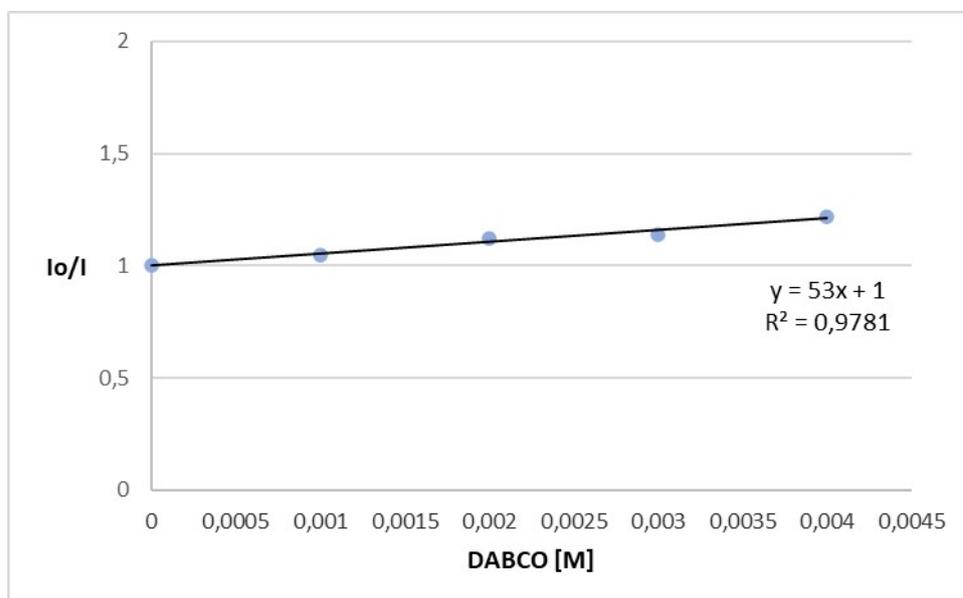
The corresponding Stern-Volmer plot is presented below.



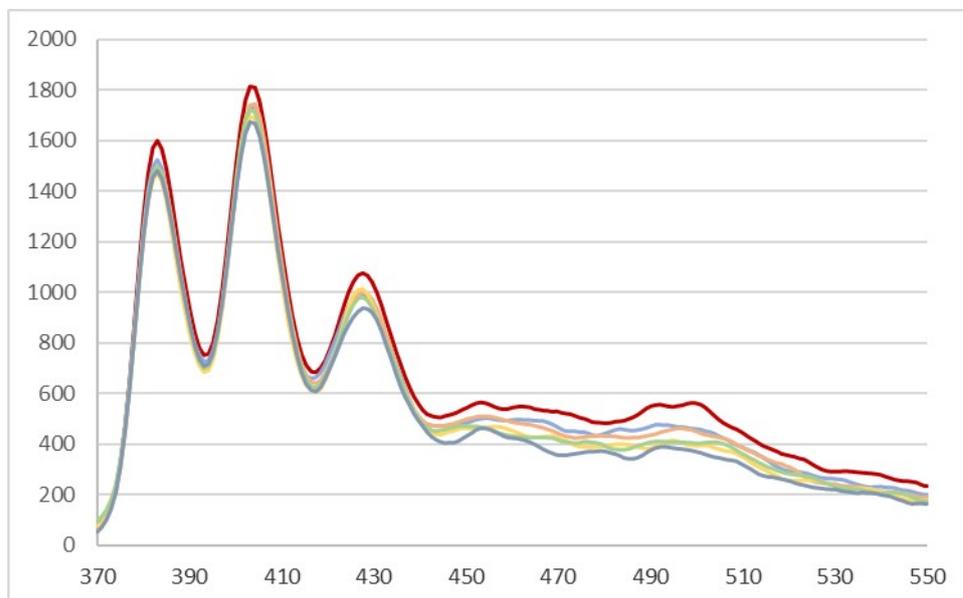
After irradiation of anthraquinone (**4a**) (1 mM in MeCN) at 358 nm, its fluorescence was measured at 404 nm. Increasing the added amount of DABCO, there is no significant decrease in the fluorescence.



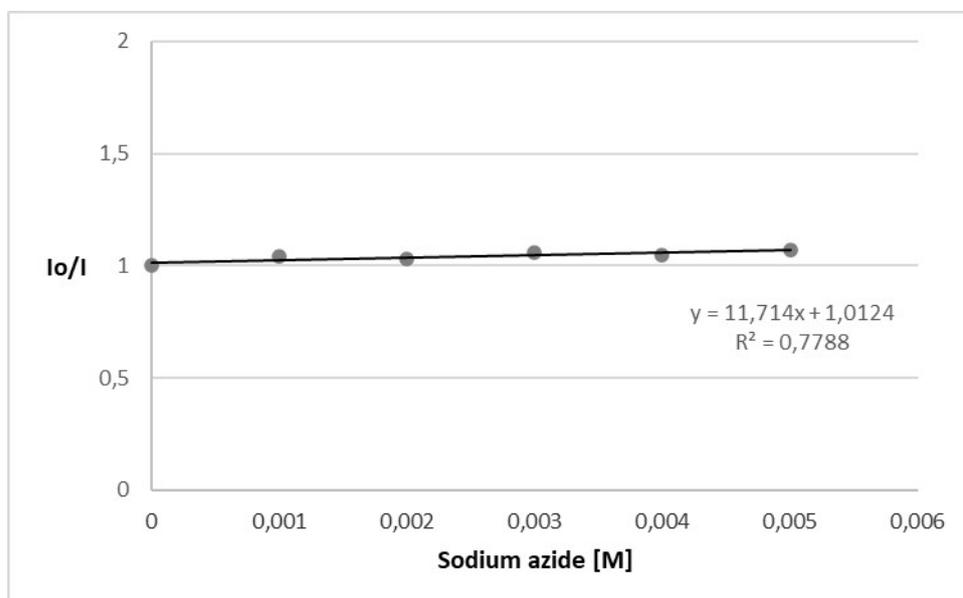
The corresponding Stern-Volmer plot is presented below.



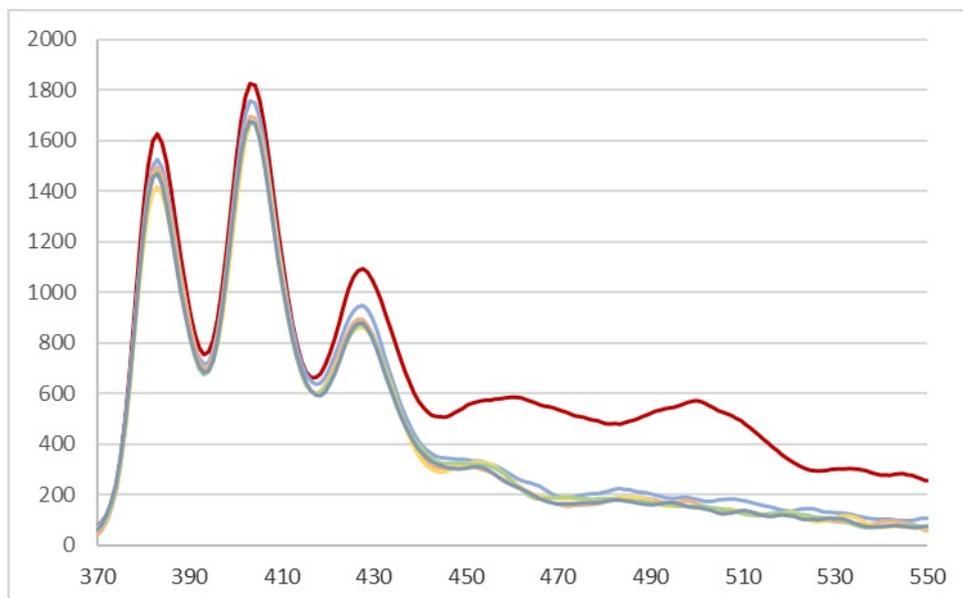
After irradiation of anthraquinone (**4a**) (1 mM in MeCN) at 358 nm, its fluorescence was measured at 404 nm. Increasing the added amount of sodium azide, there is no significant decrease in the fluorescence.



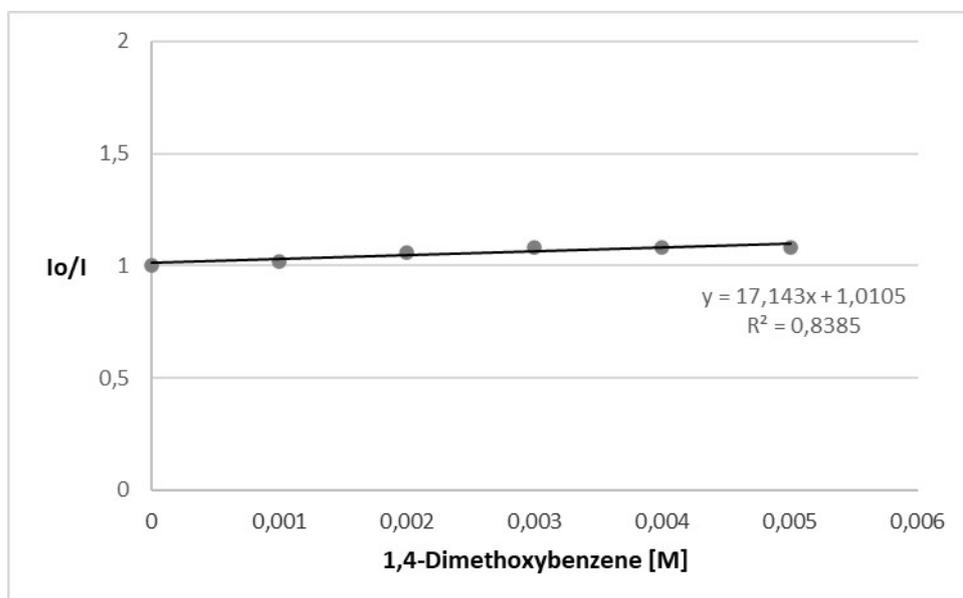
The corresponding Stern-Volmer plot is presented below.



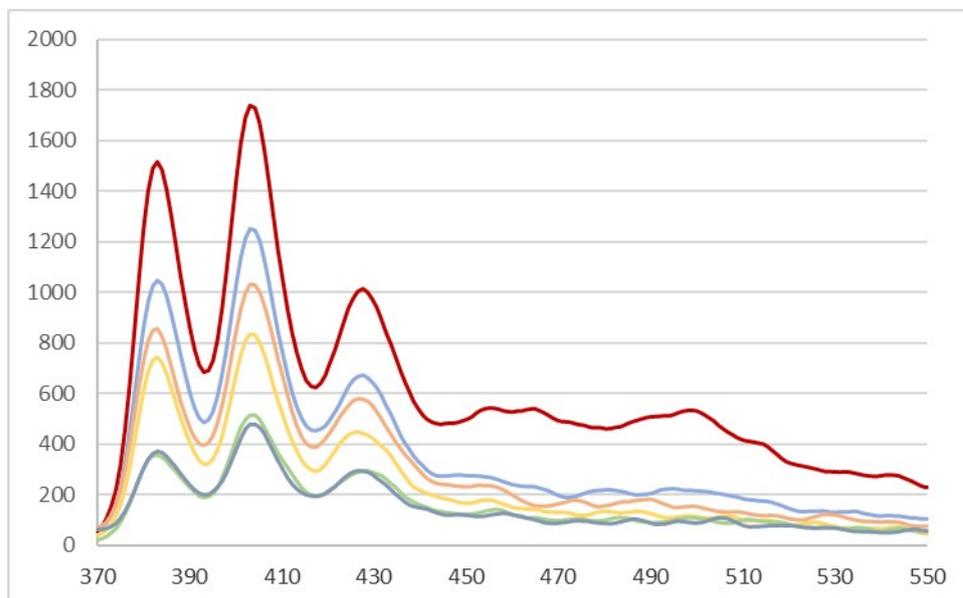
After irradiation of anthraquinone (**4a**) (1 mM in MeCN) at 358 nm, its fluorescence was measured at 404 nm. Increasing the added amount of 1,4-dimethoxybenzene, there is no significant decrease in the fluorescence.



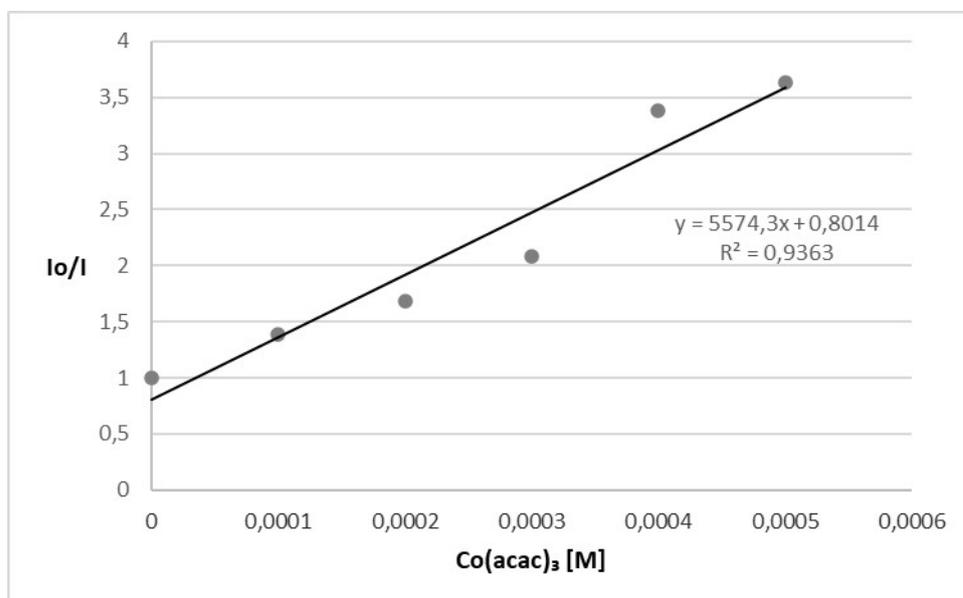
The corresponding Stern-Volmer plot is presented below.



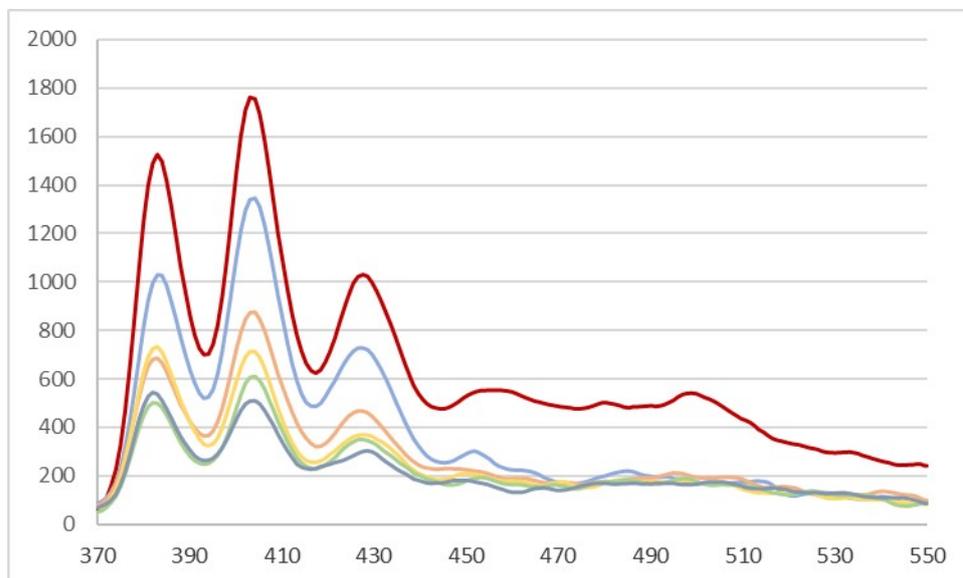
After irradiation of anthraquinone (**4a**) (1 mM in MeCN) at 358 nm, its fluorescence was measured at 404 nm. Increasing the added amount of  $\text{Co}(\text{acac})_3$ , there is a decrease in the fluorescence.



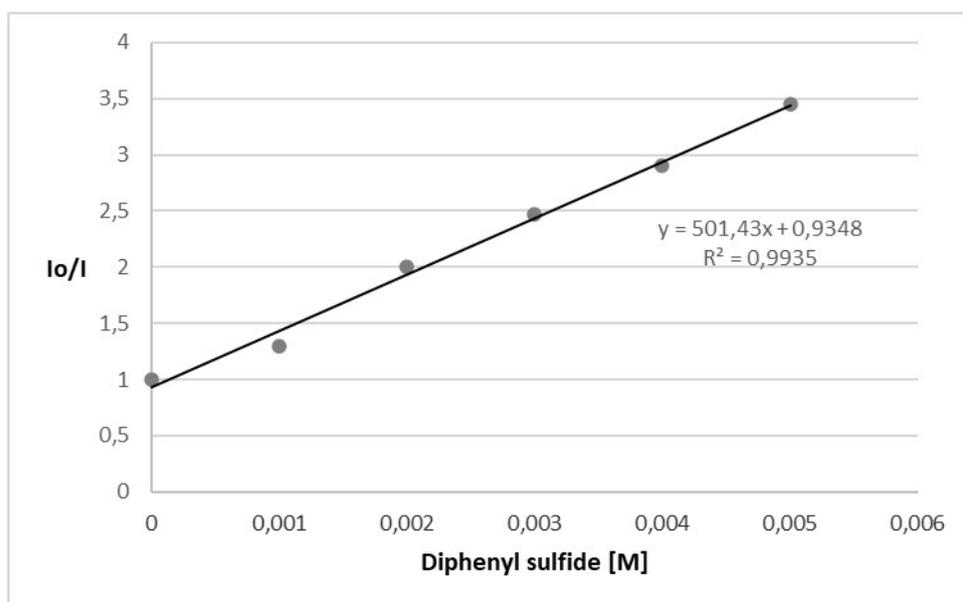
The corresponding Stern-Volmer plot is presented below.



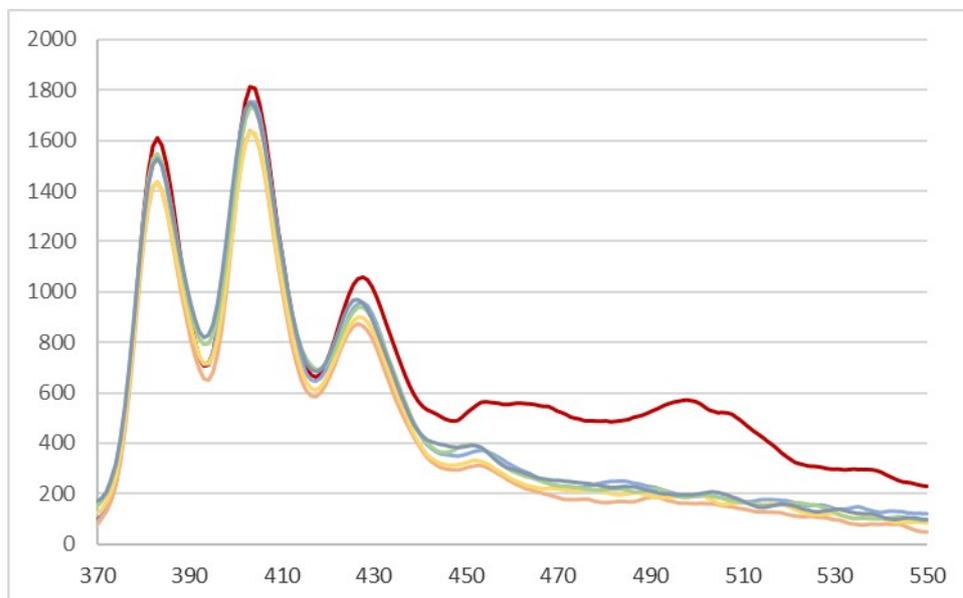
After irradiation of anthraquinone (**4a**) (1 mM in MeCN) at 358 nm, its fluorescence was measured at 404 nm. Increasing the added amount of diphenyl sulfide, there is a decrease in the fluorescence.



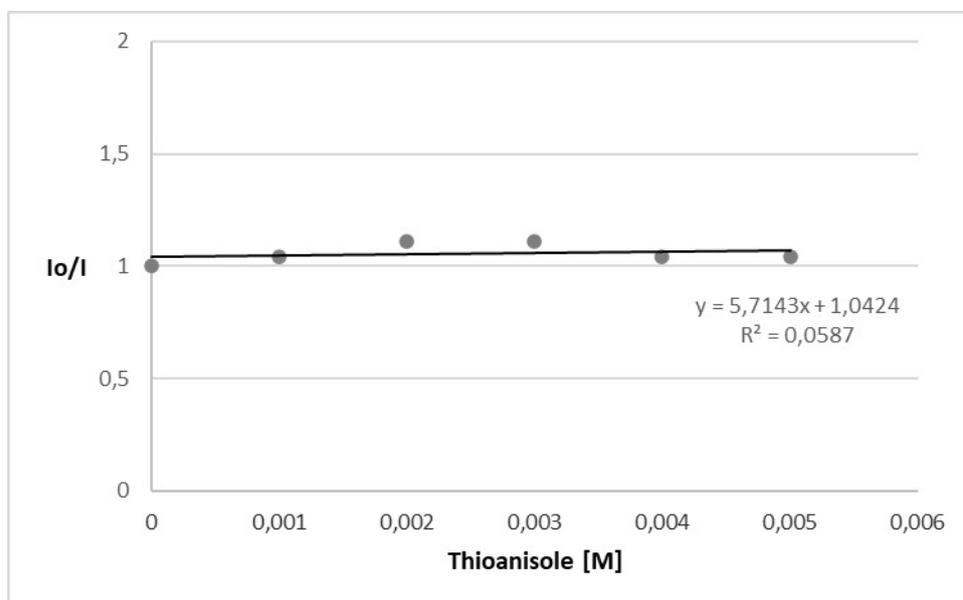
The corresponding Stern-Volmer plot is presented below.



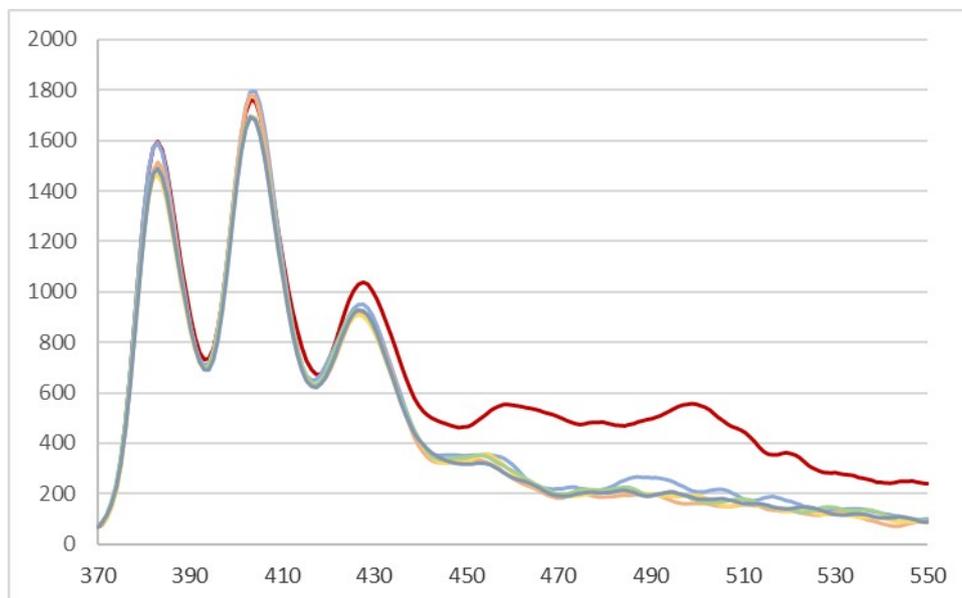
After irradiation of anthraquinone (**4a**) (1 mM in MeCN) at 358 nm, its fluorescence was measured at 404 nm. Increasing the added amount of thioanisole, there is no significant decrease in the fluorescence.



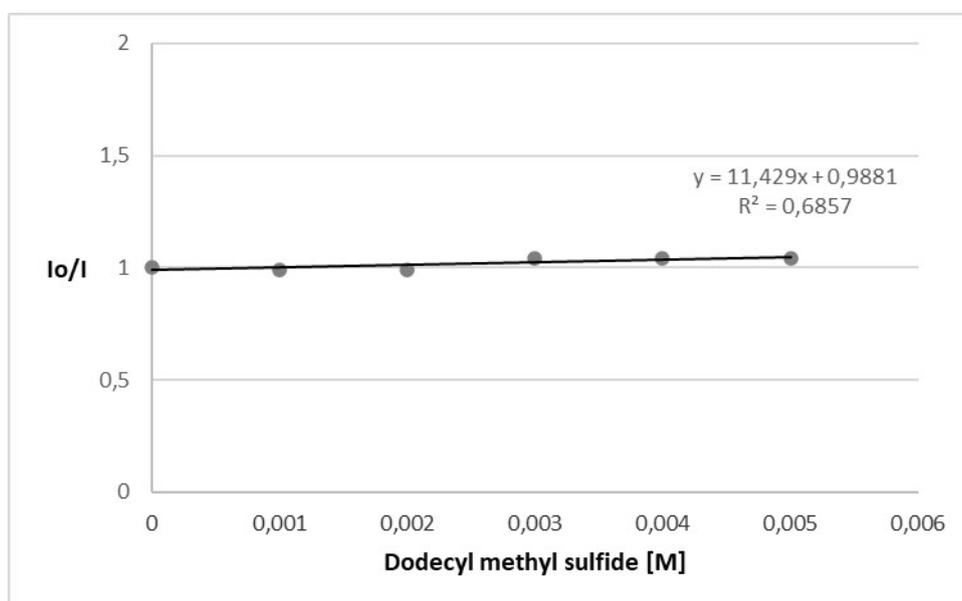
The corresponding Stern-Volmer plot is presented below.



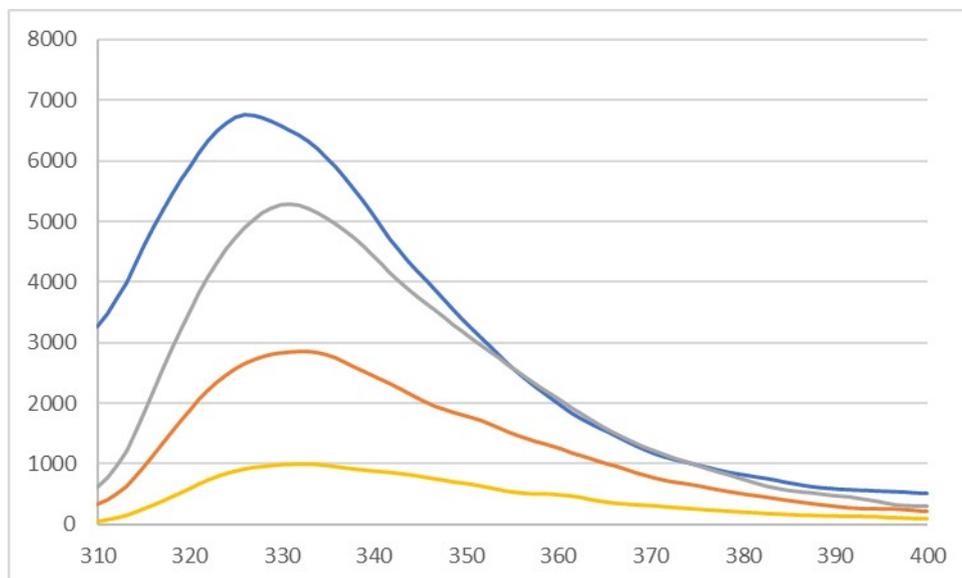
After irradiation of anthraquinone (**4a**) (1 mM in MeCN) at 358 nm, its fluorescence was measured at 404 nm. Increasing the added amount of dodecyl methyl sulfide, there is no significant decrease in the fluorescence.



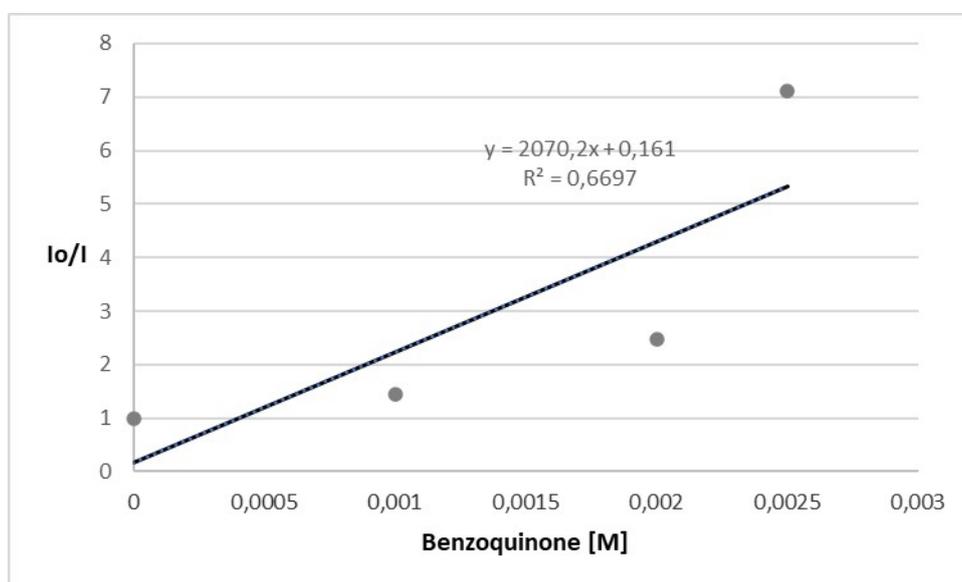
The corresponding Stern-Volmer plot is presented below.



After irradiation of thioanisole (**1a**) (1 mM in MeCN) at 293 nm, its fluorescence was measured at 327 nm. Increasing the added amount of benzoquinone, there is a decrease in the fluorescence.



The corresponding Stern-Volmer plot is presented below.



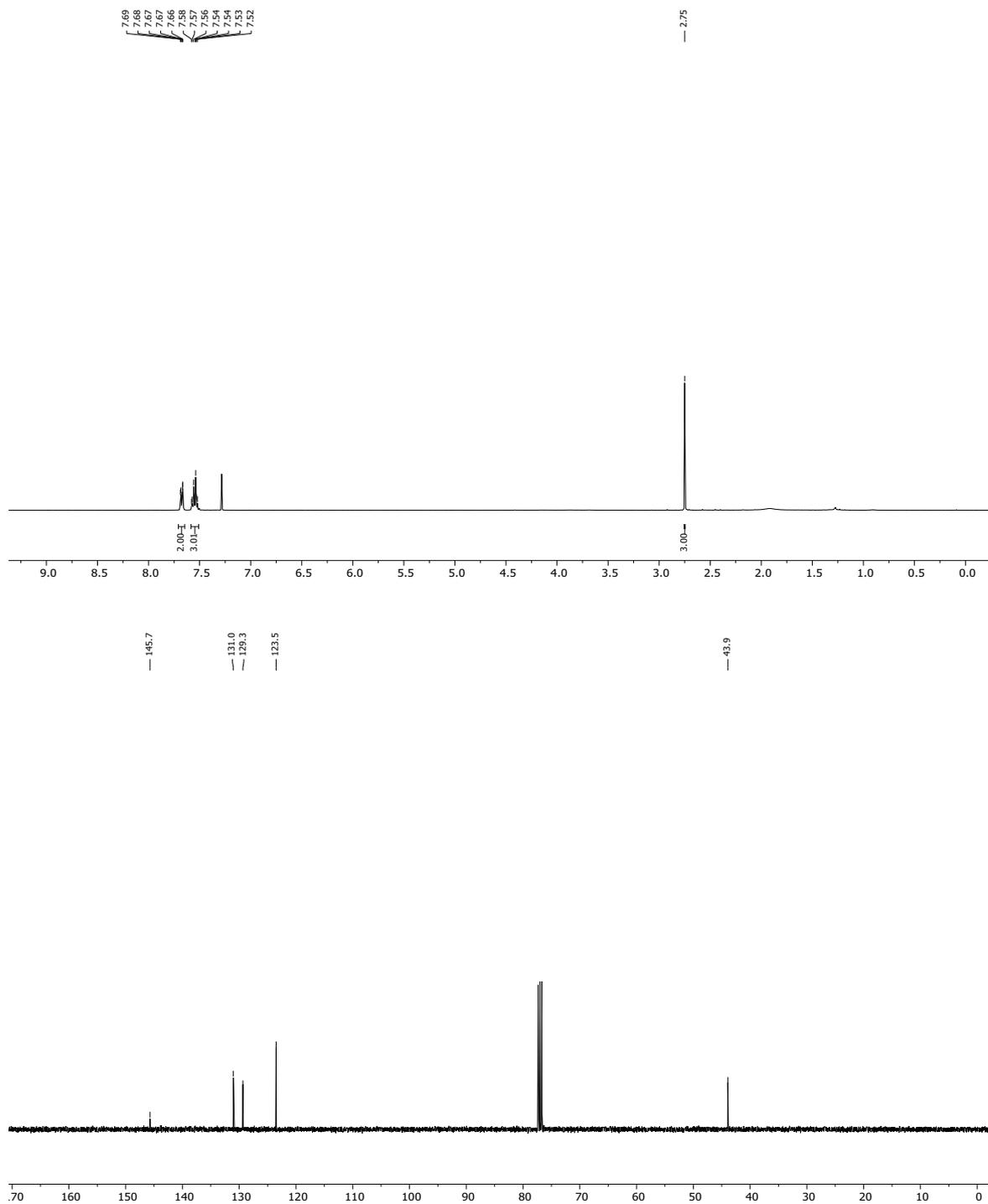
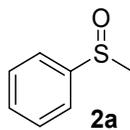
## References

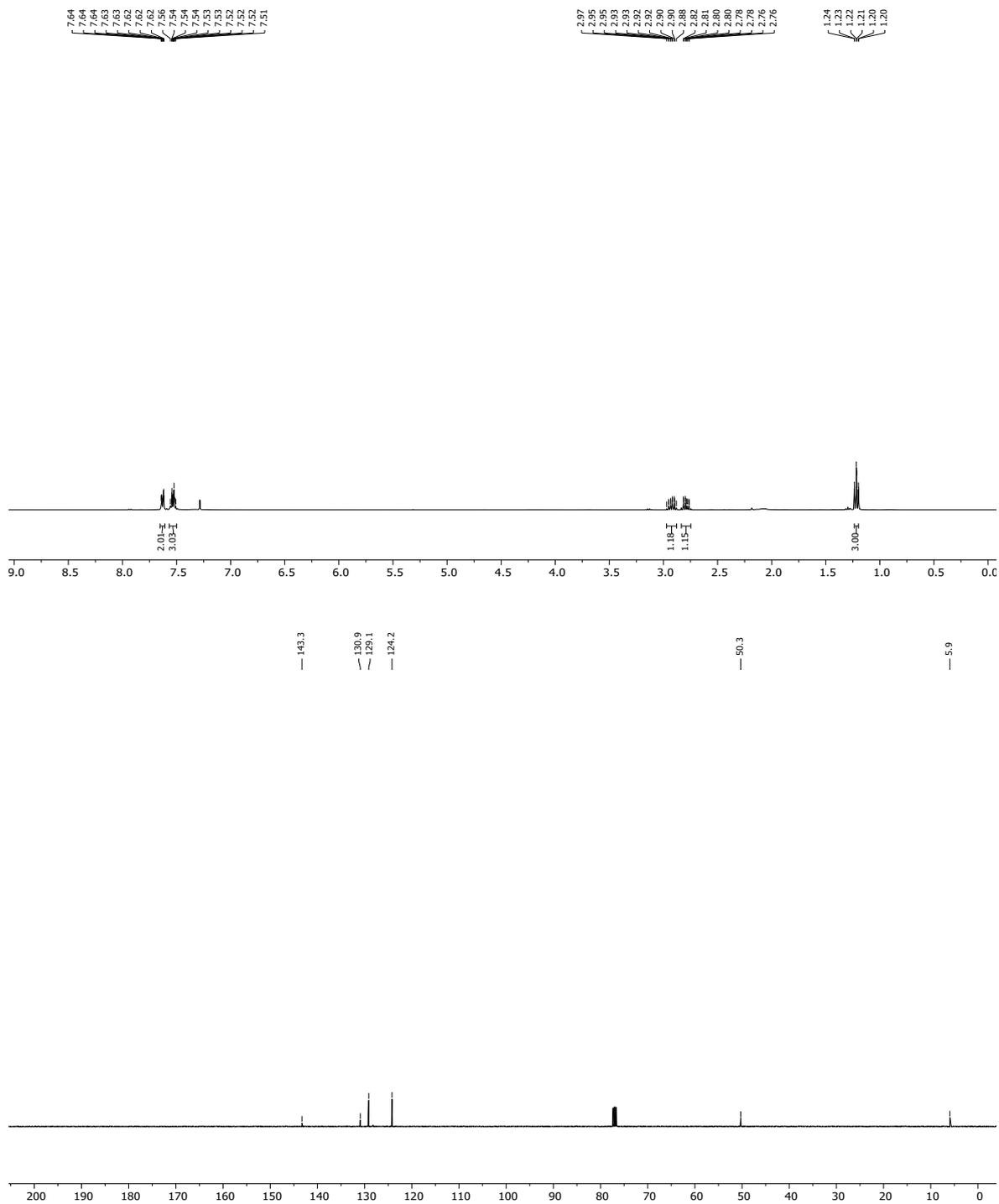
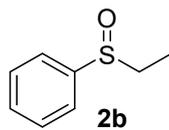
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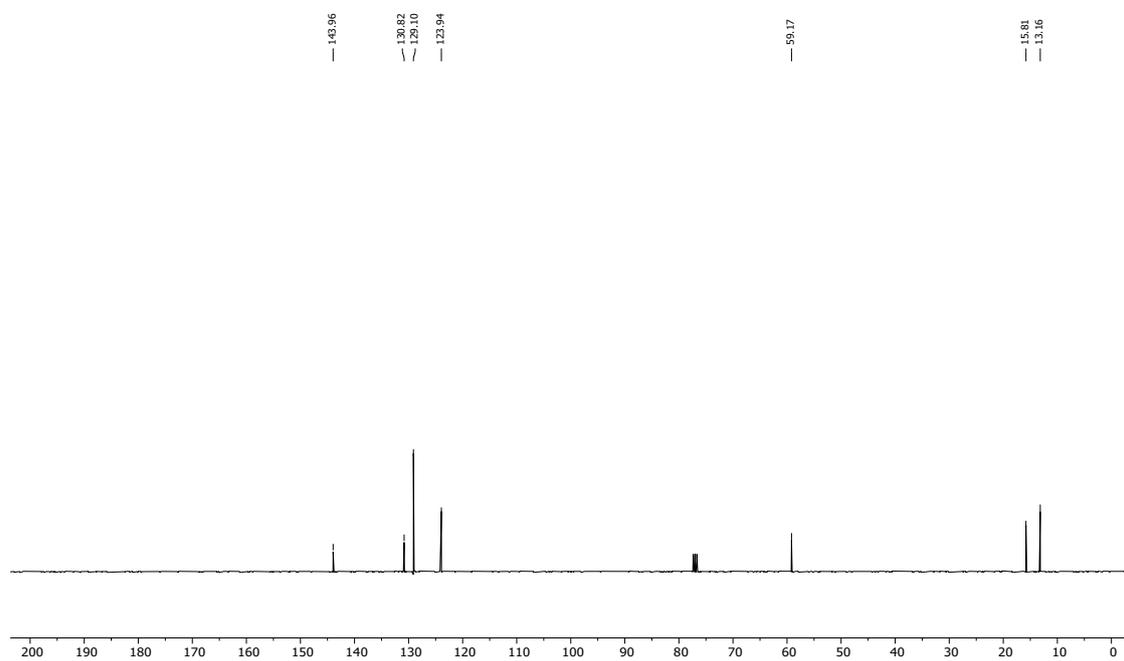
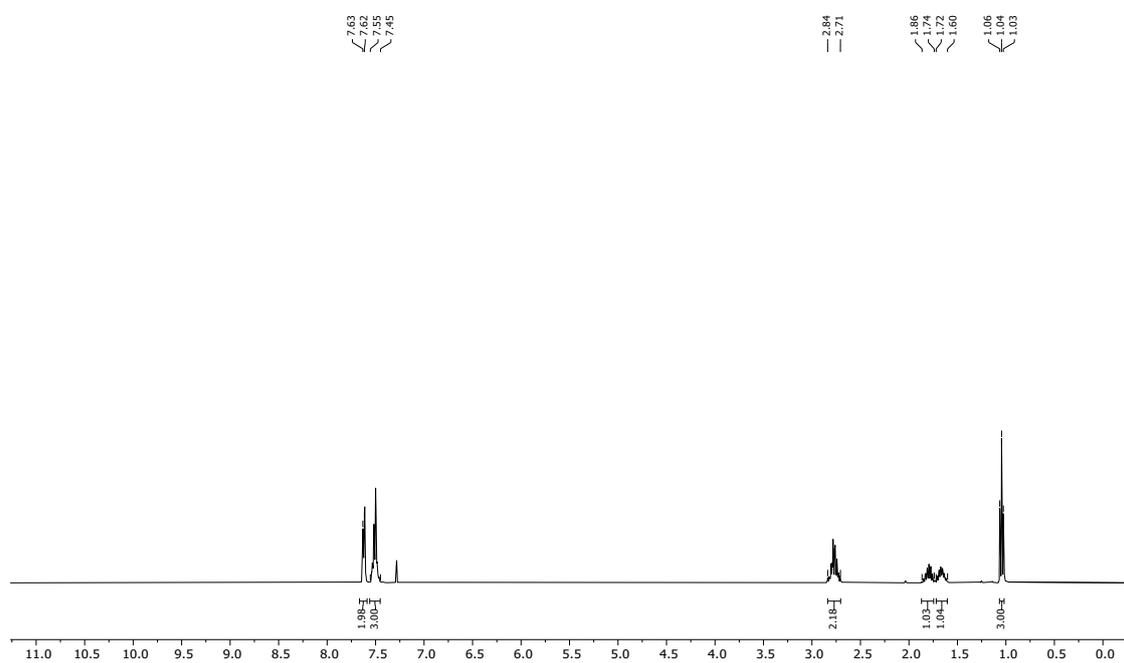
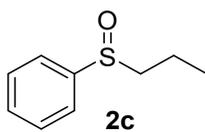
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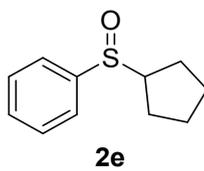
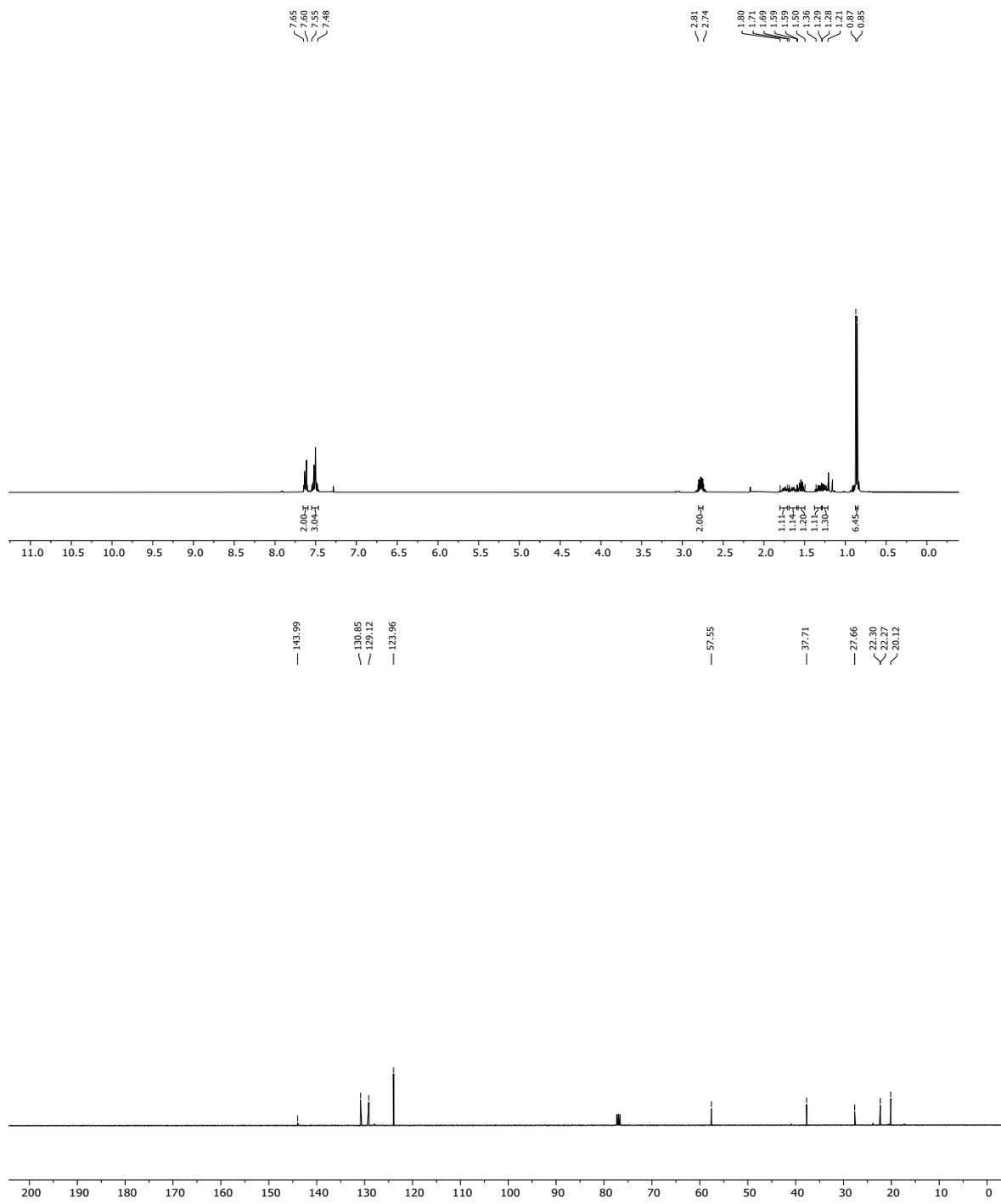
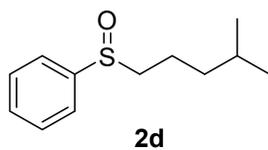
# PART D: NMR INDEX

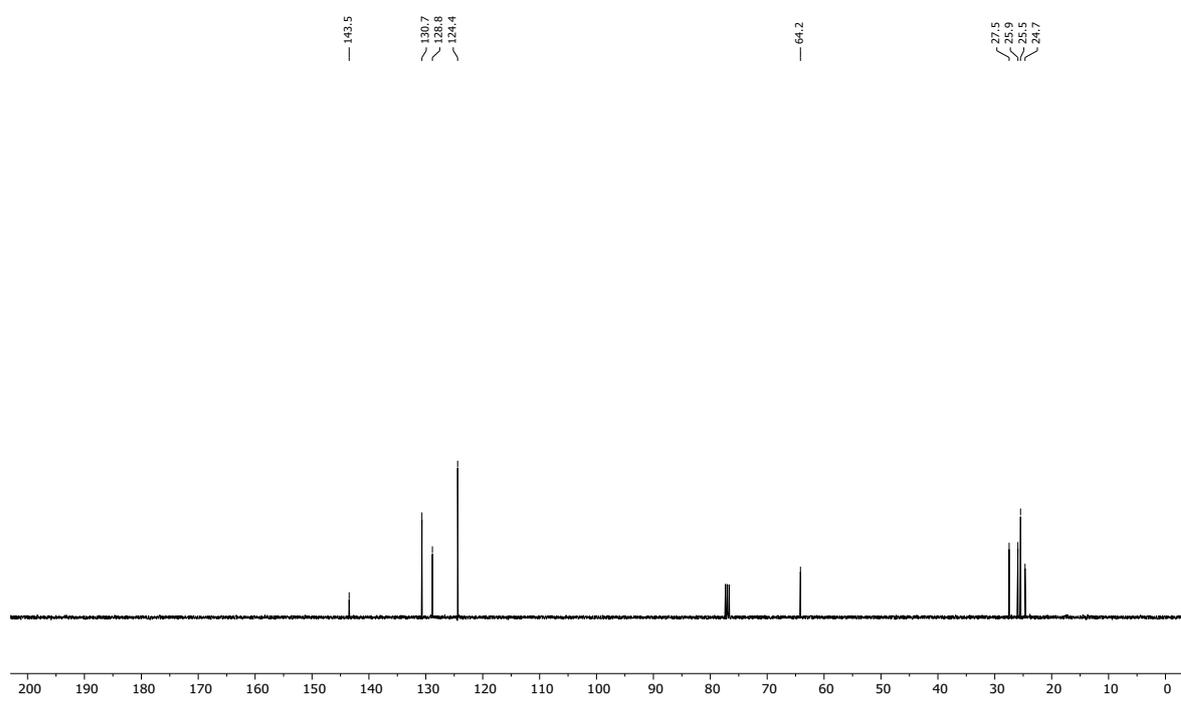
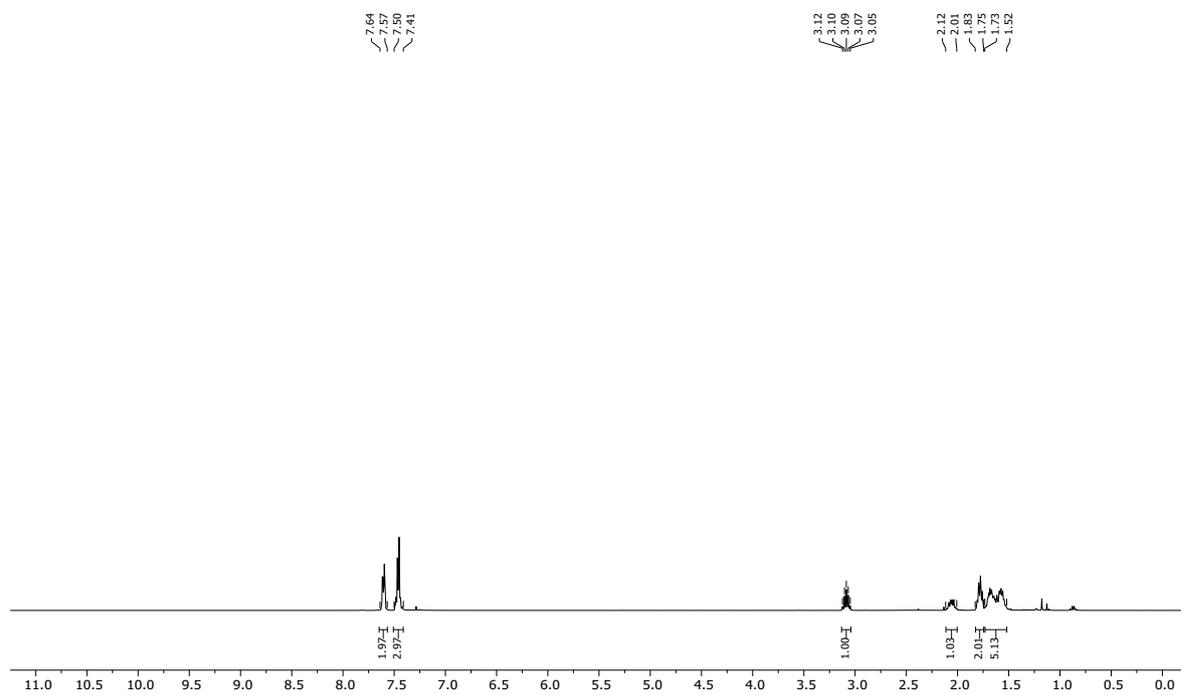
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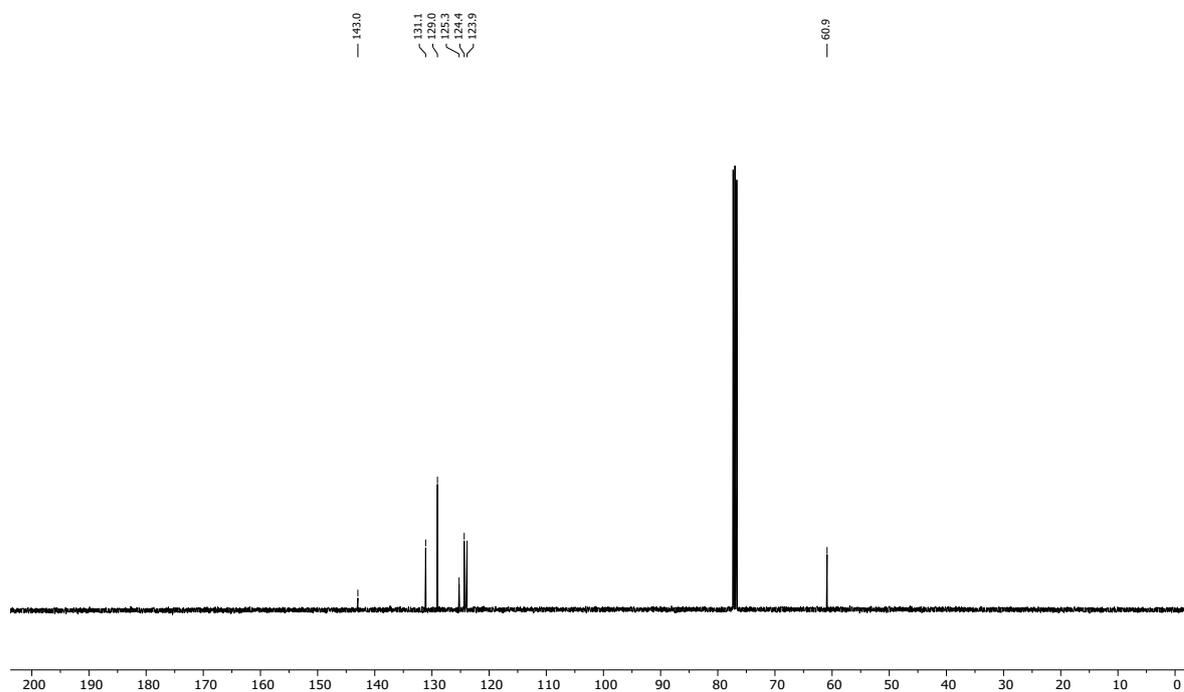
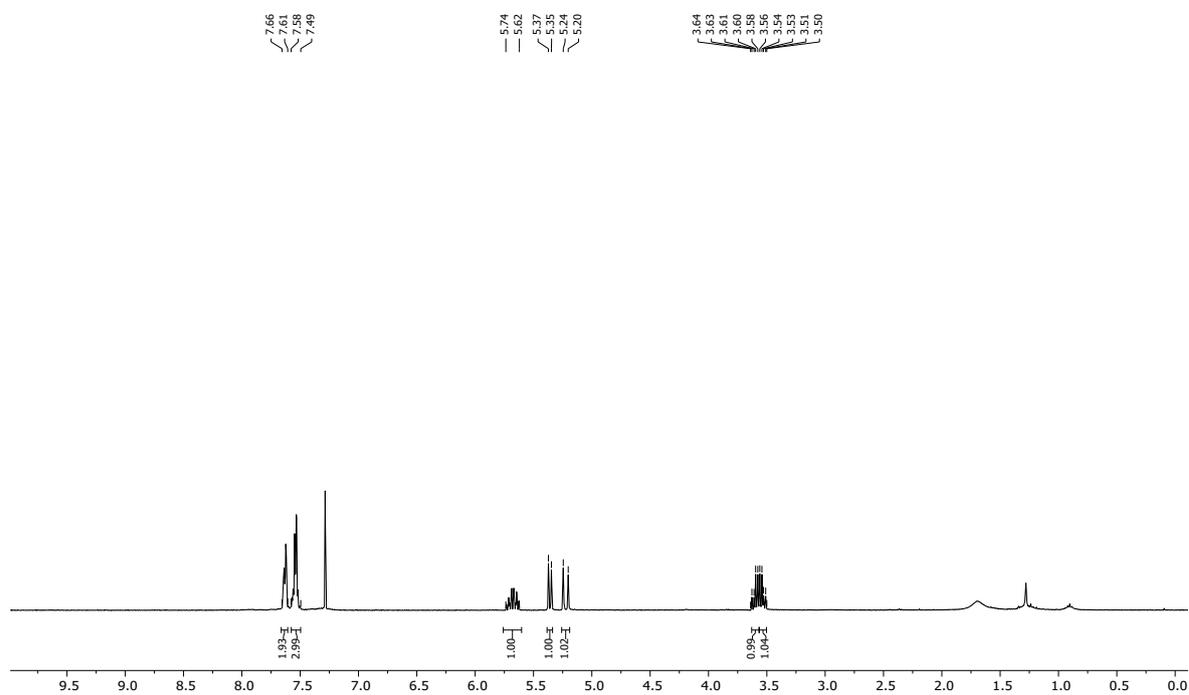
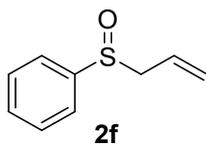


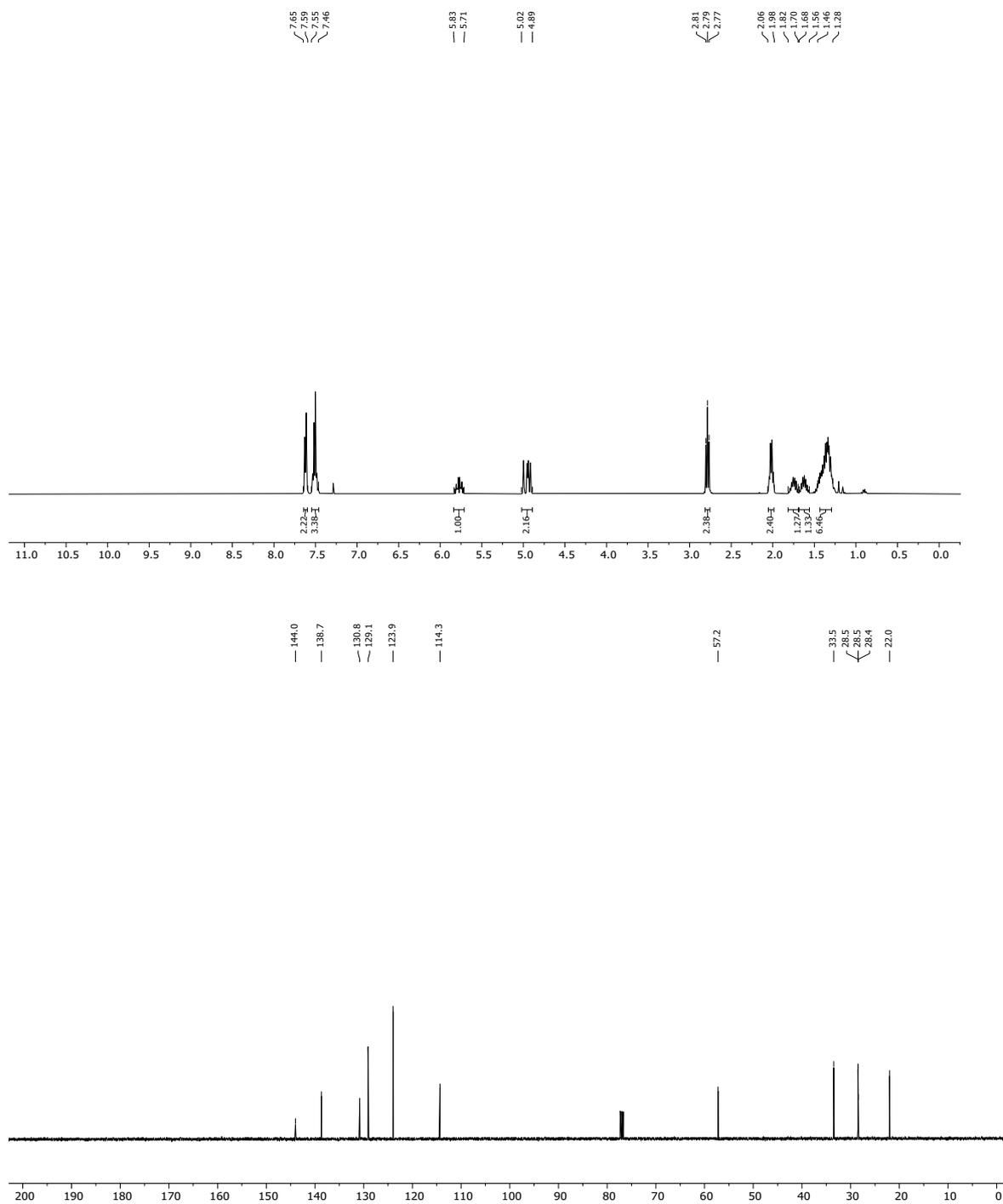
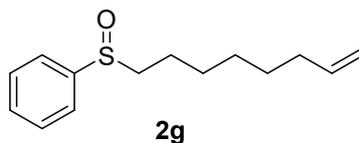


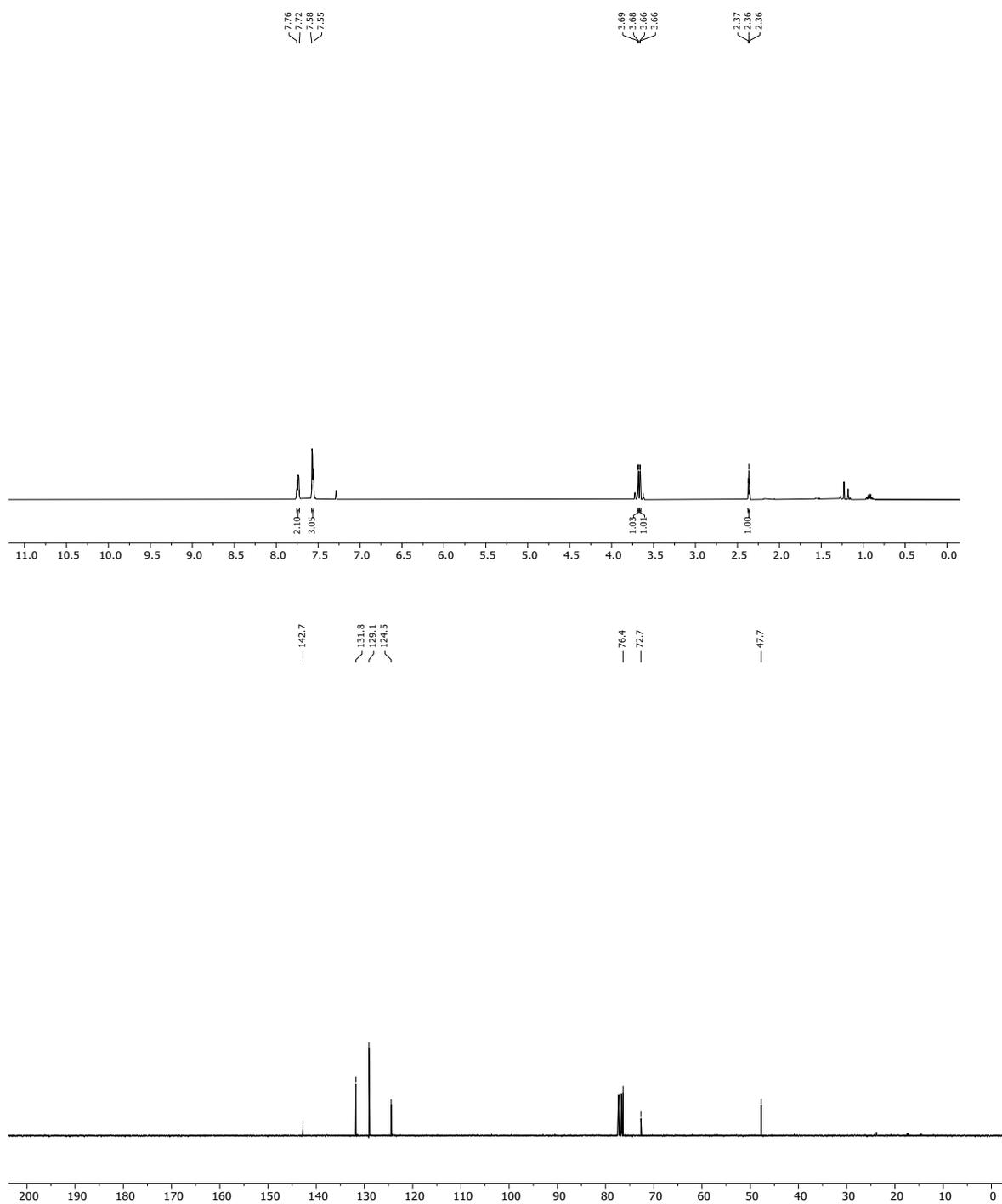
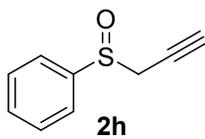


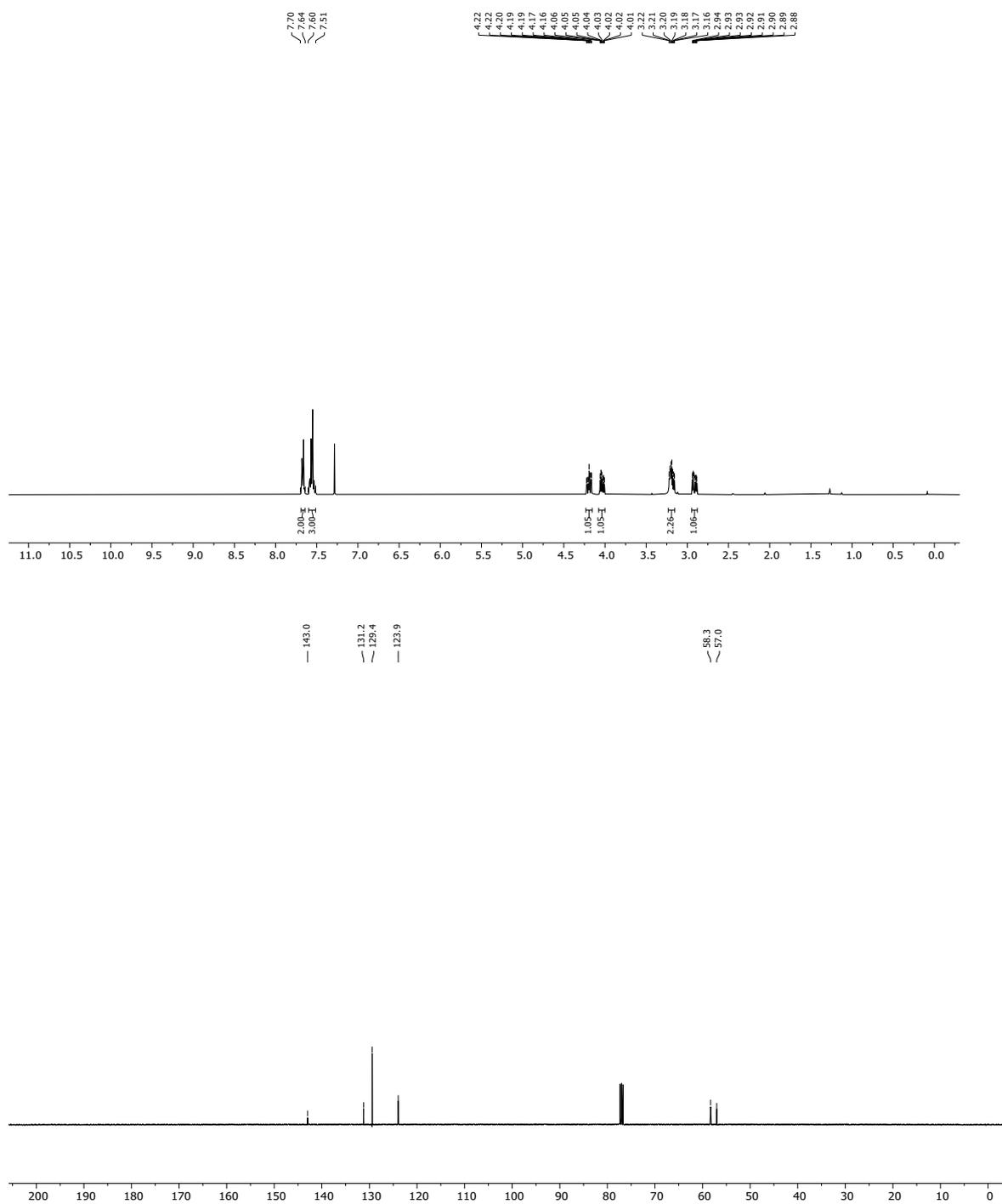
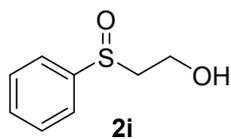


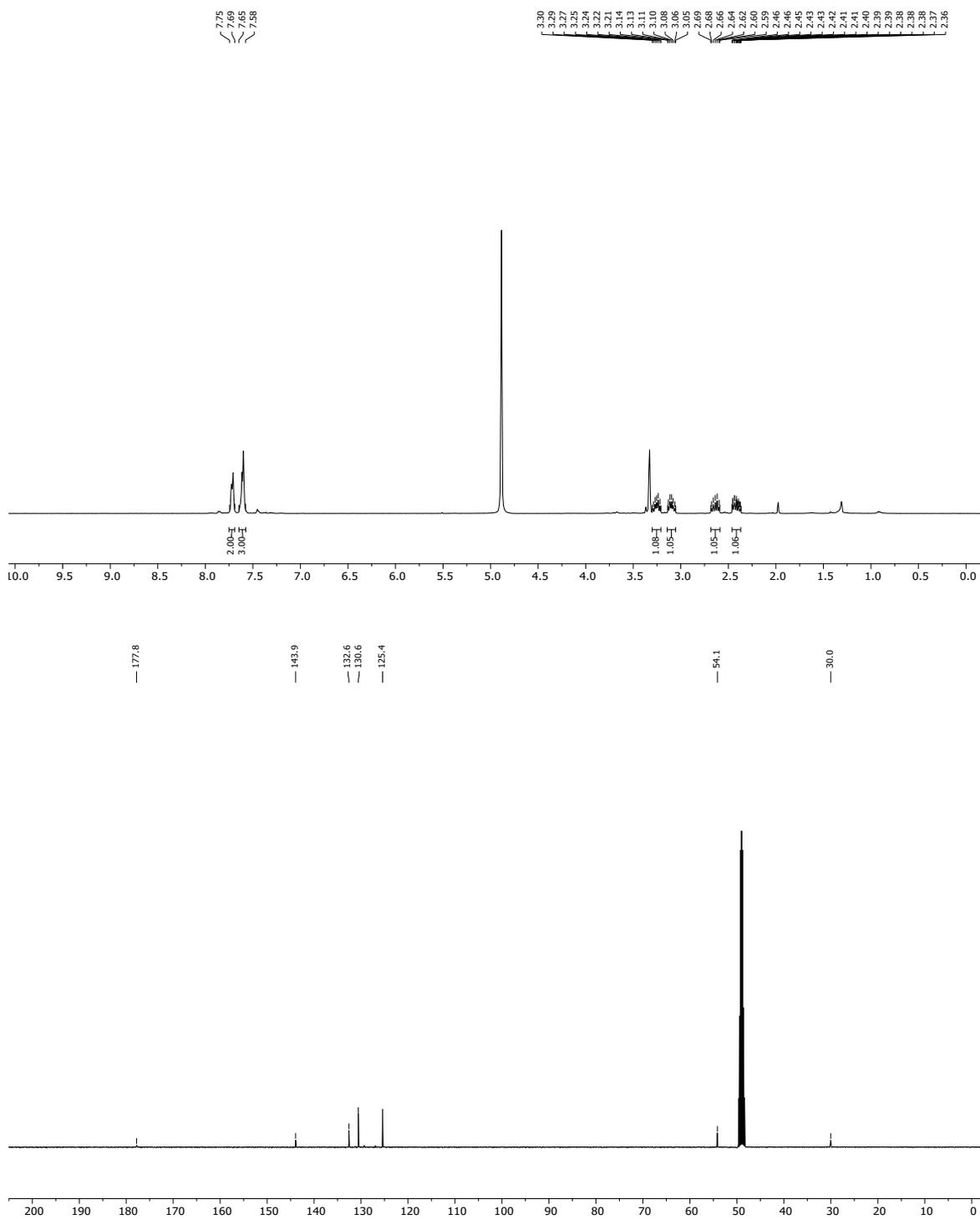
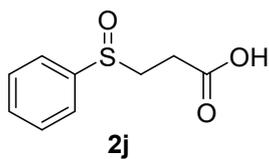


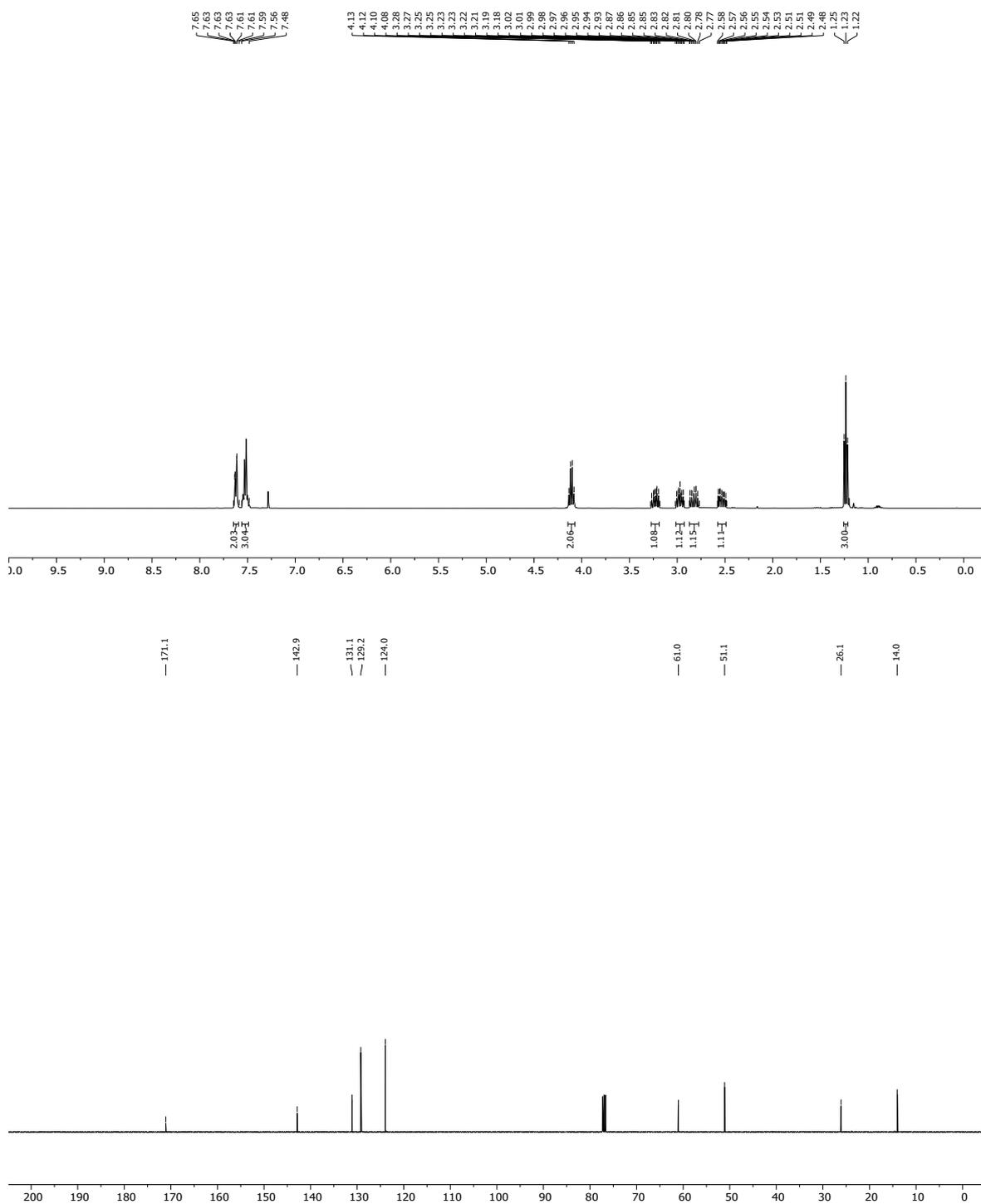
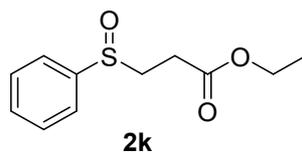


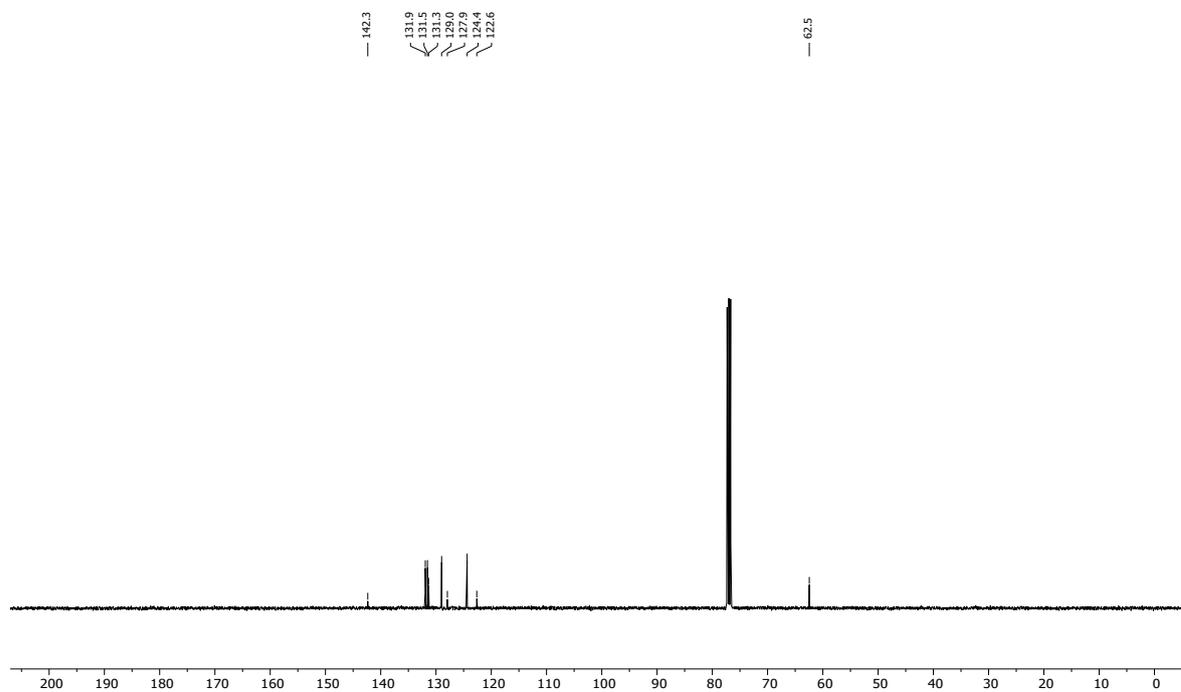
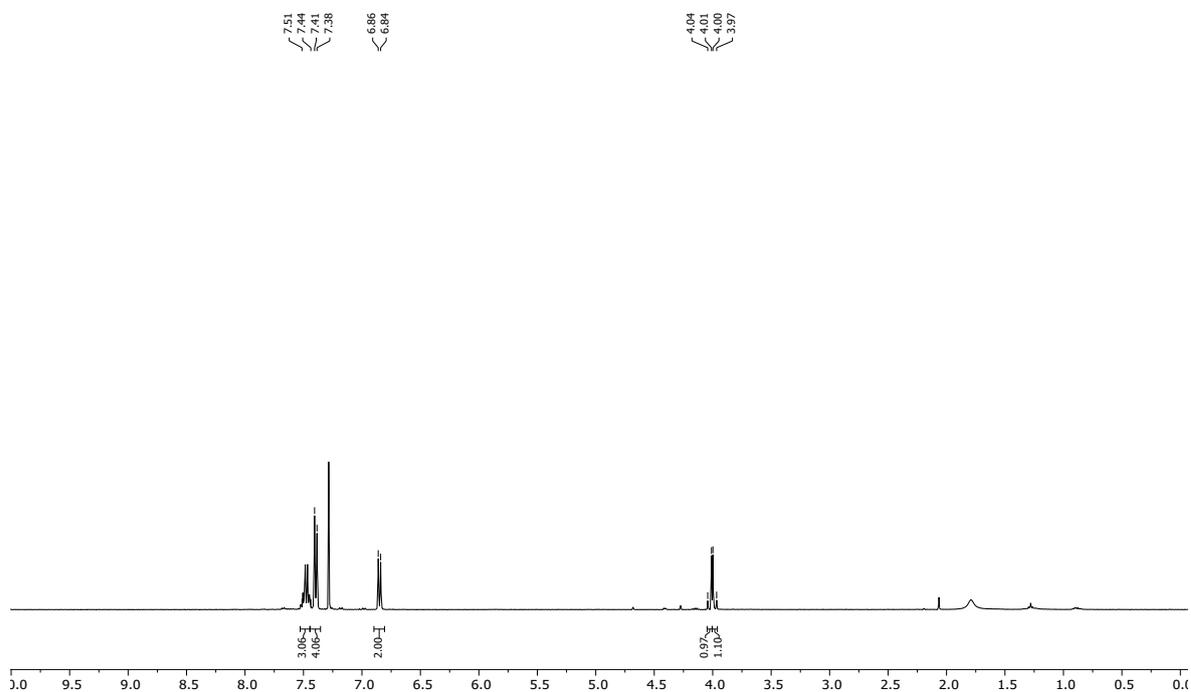
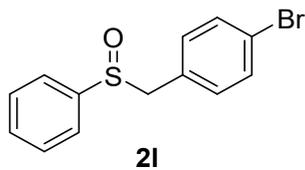


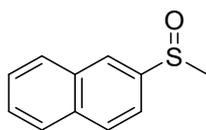




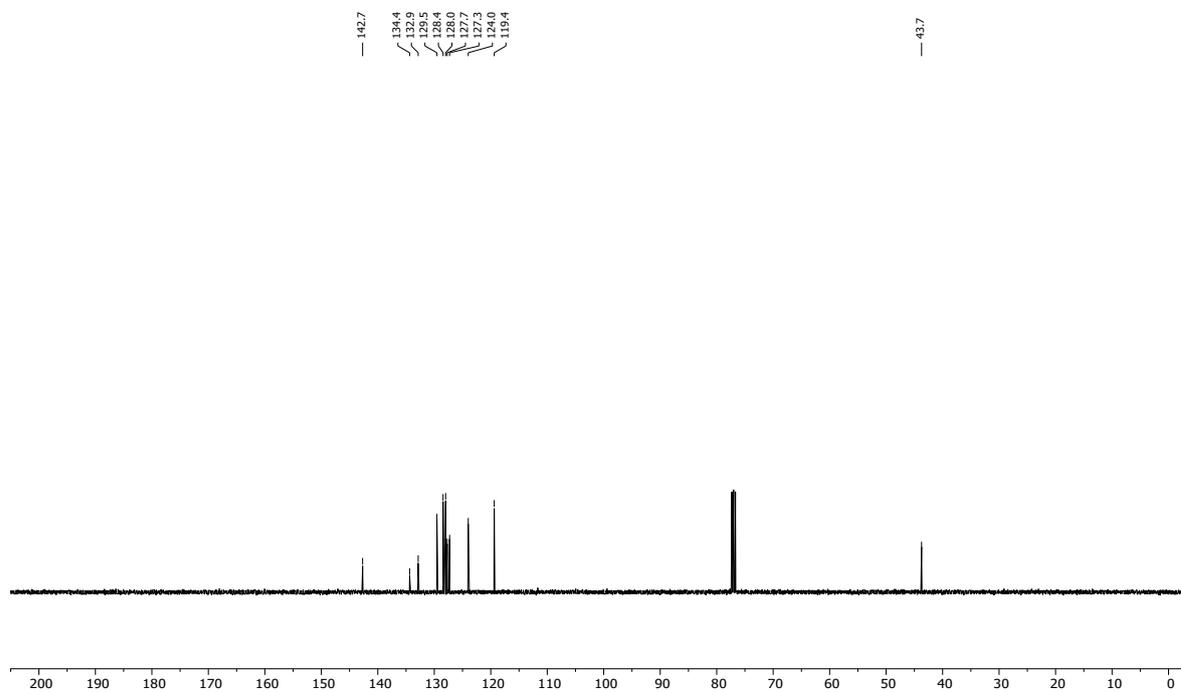
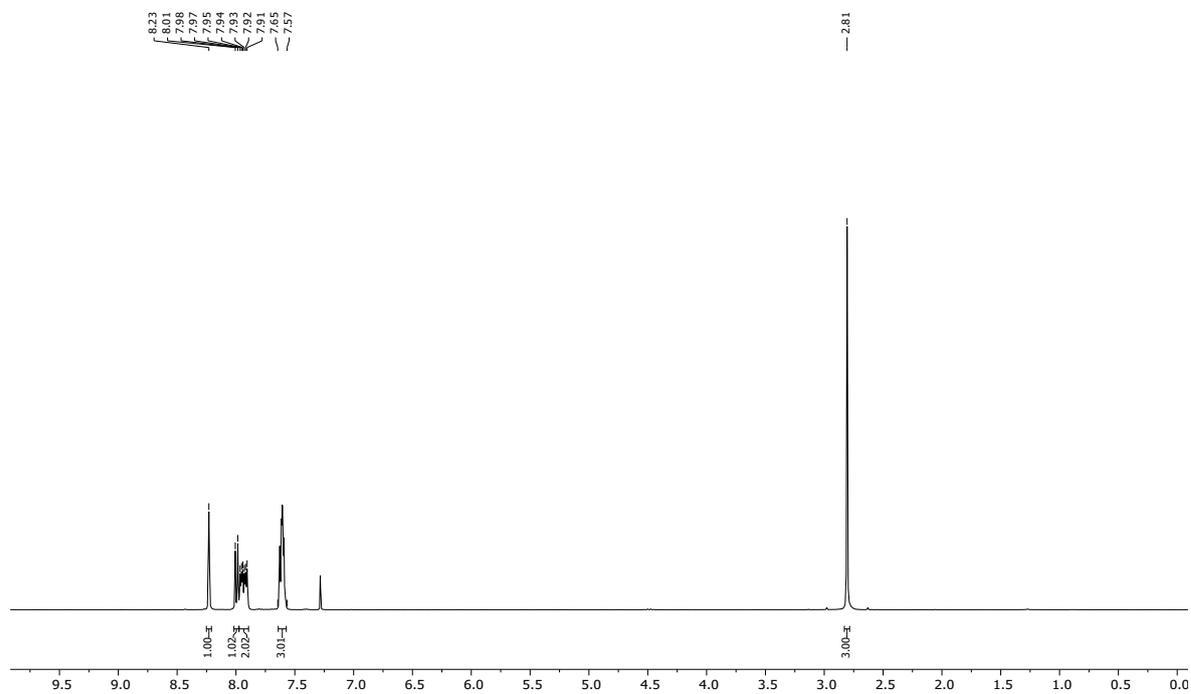


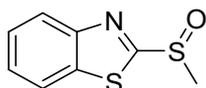
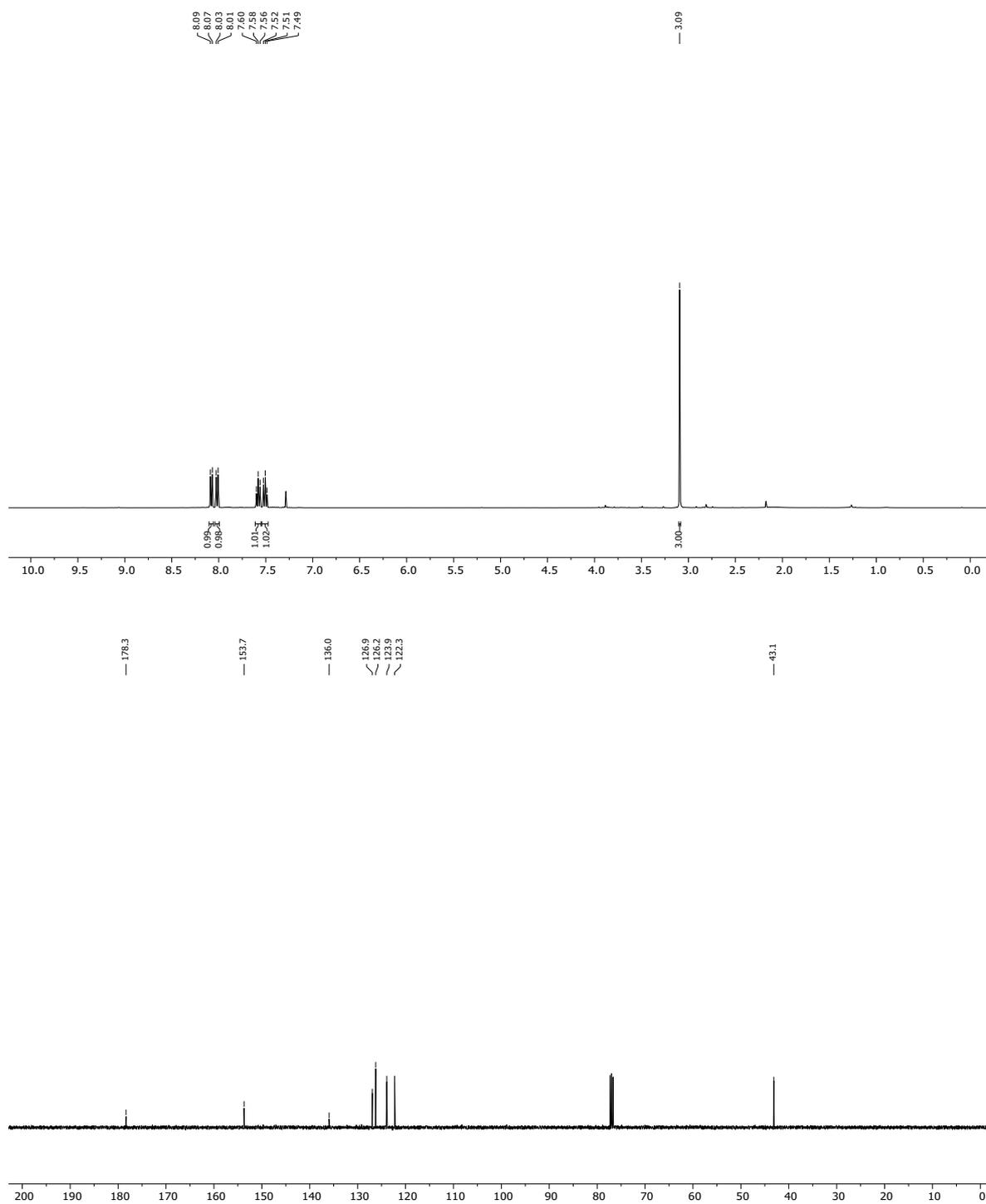


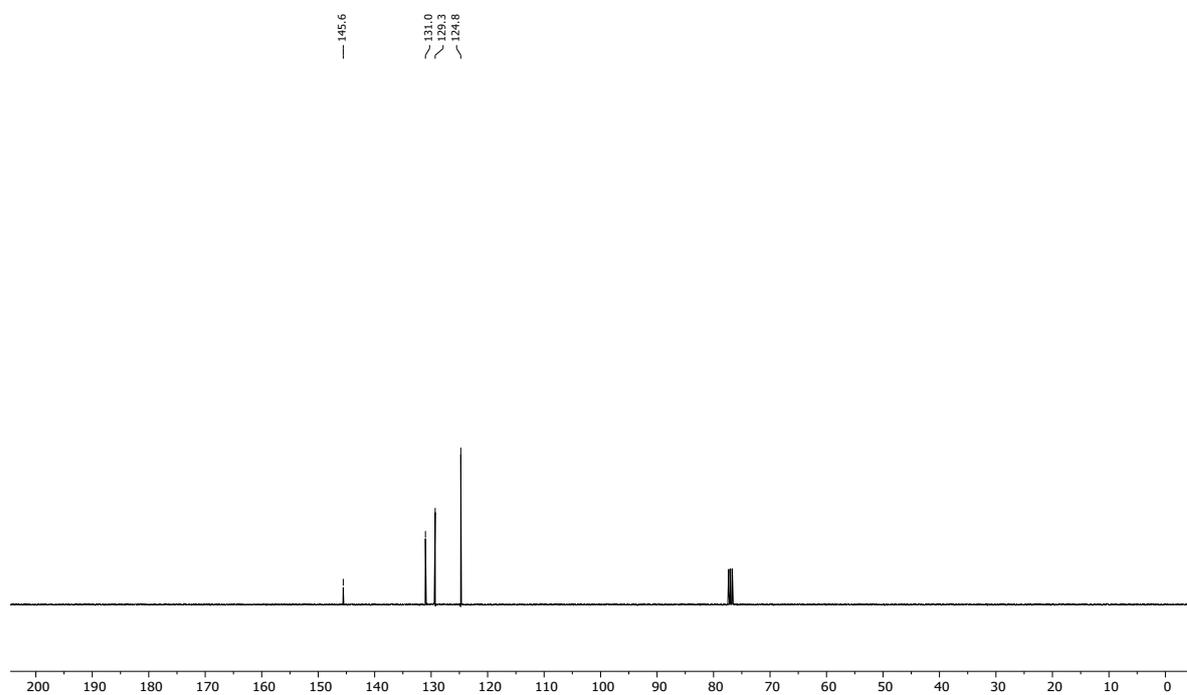
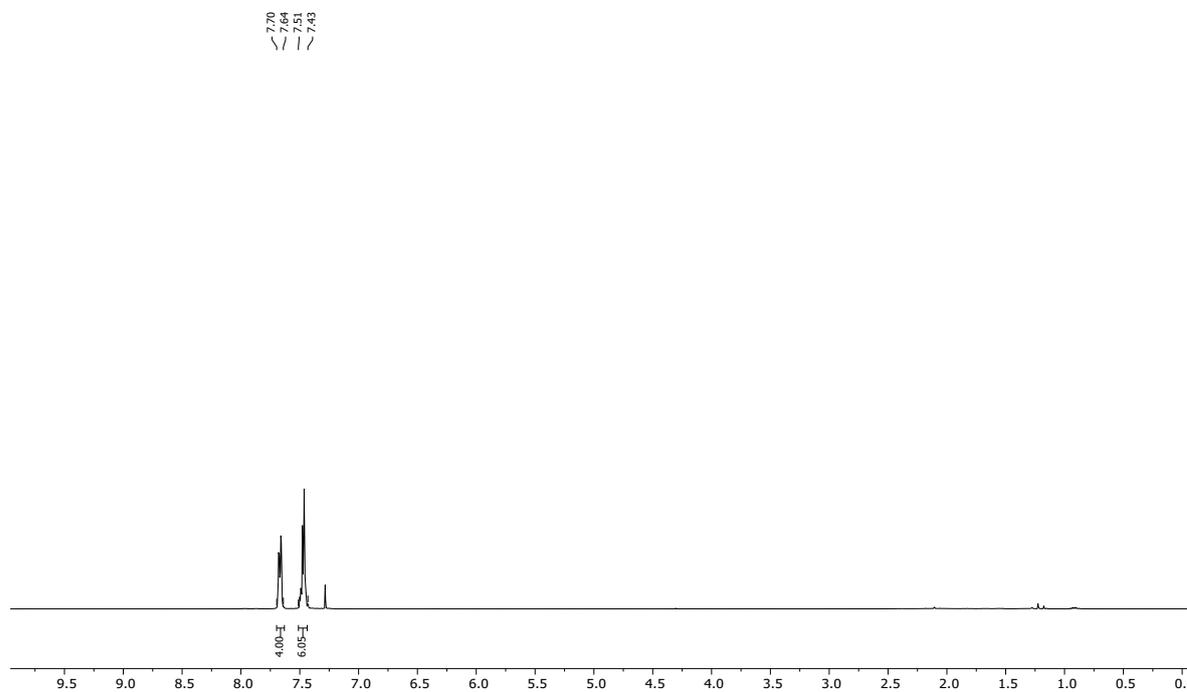
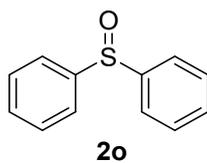


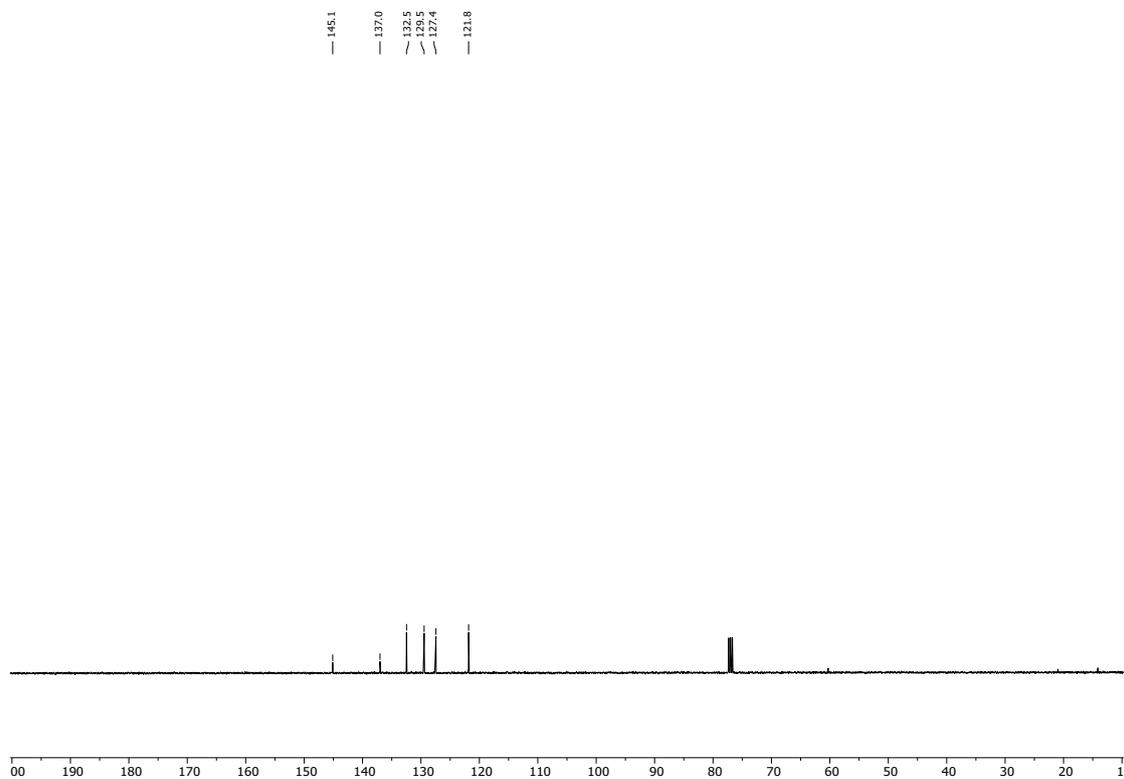
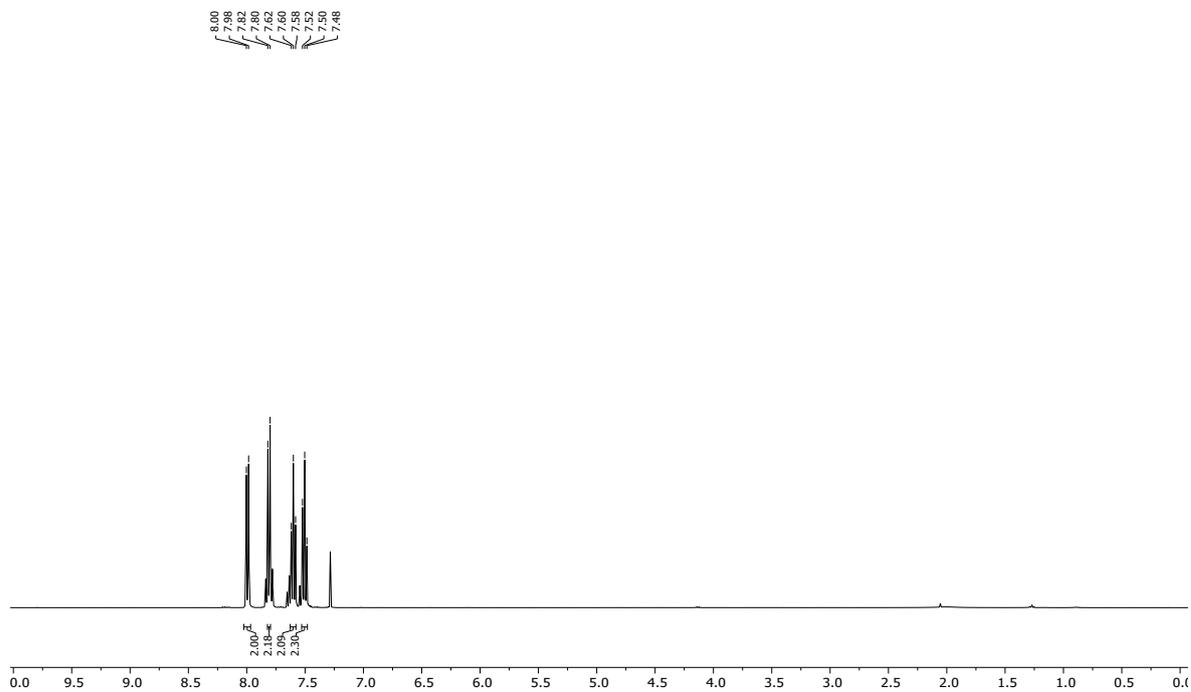
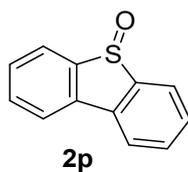


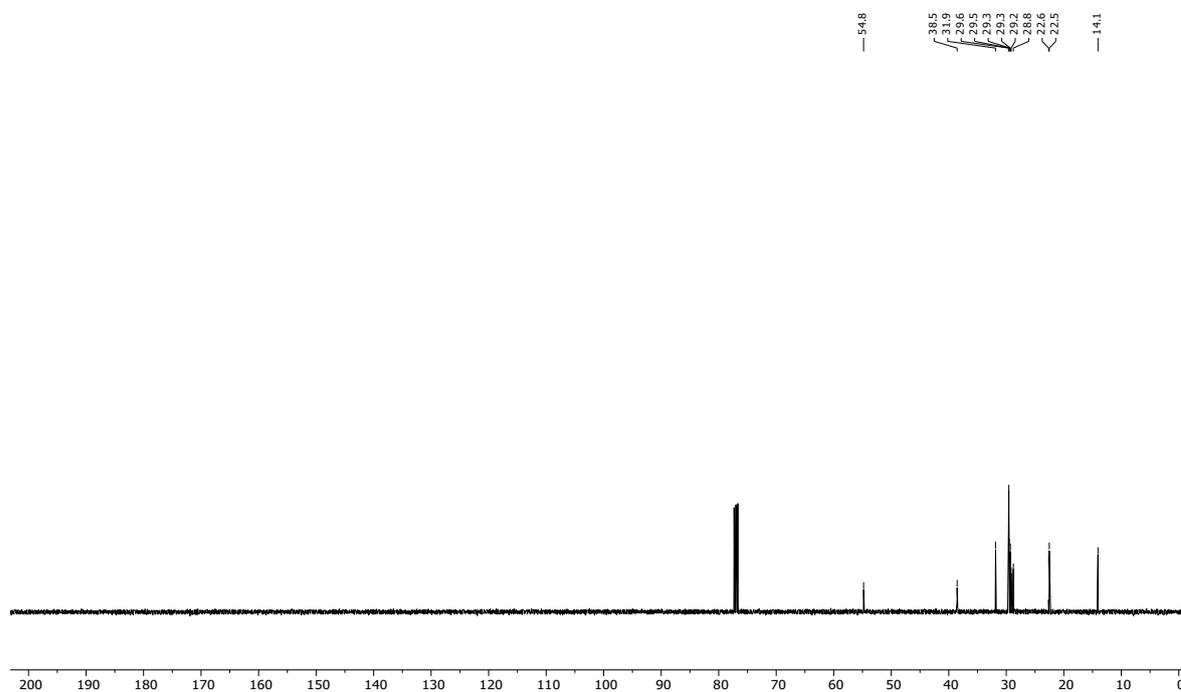
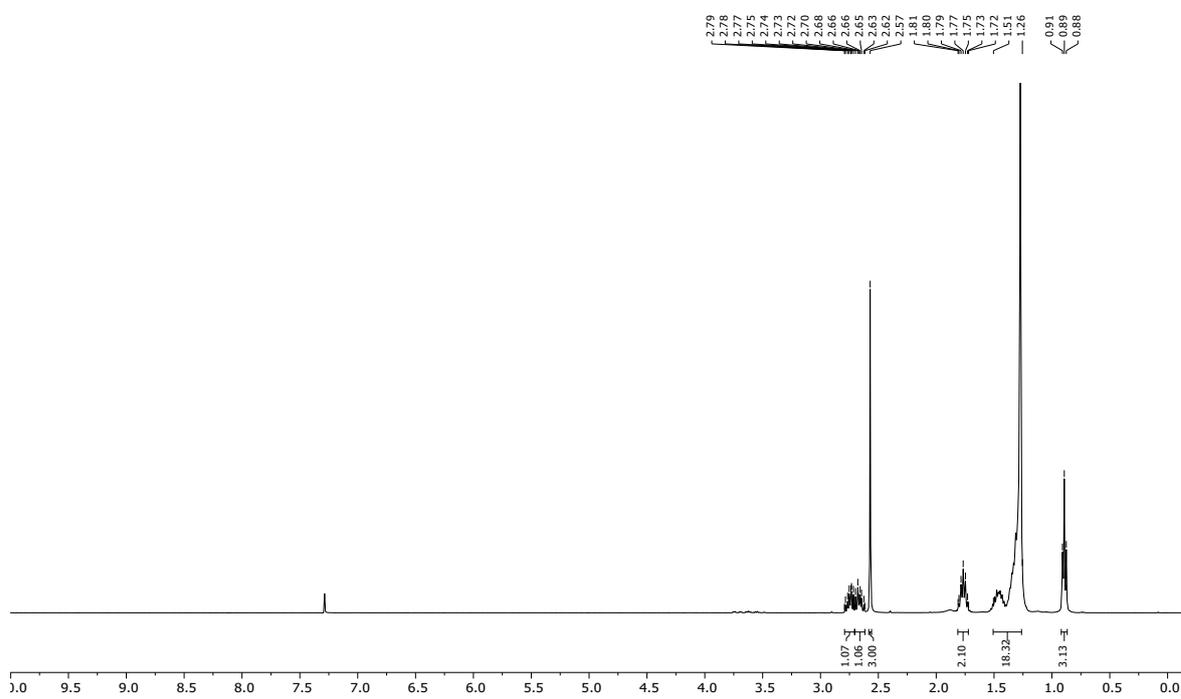
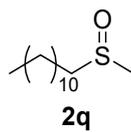
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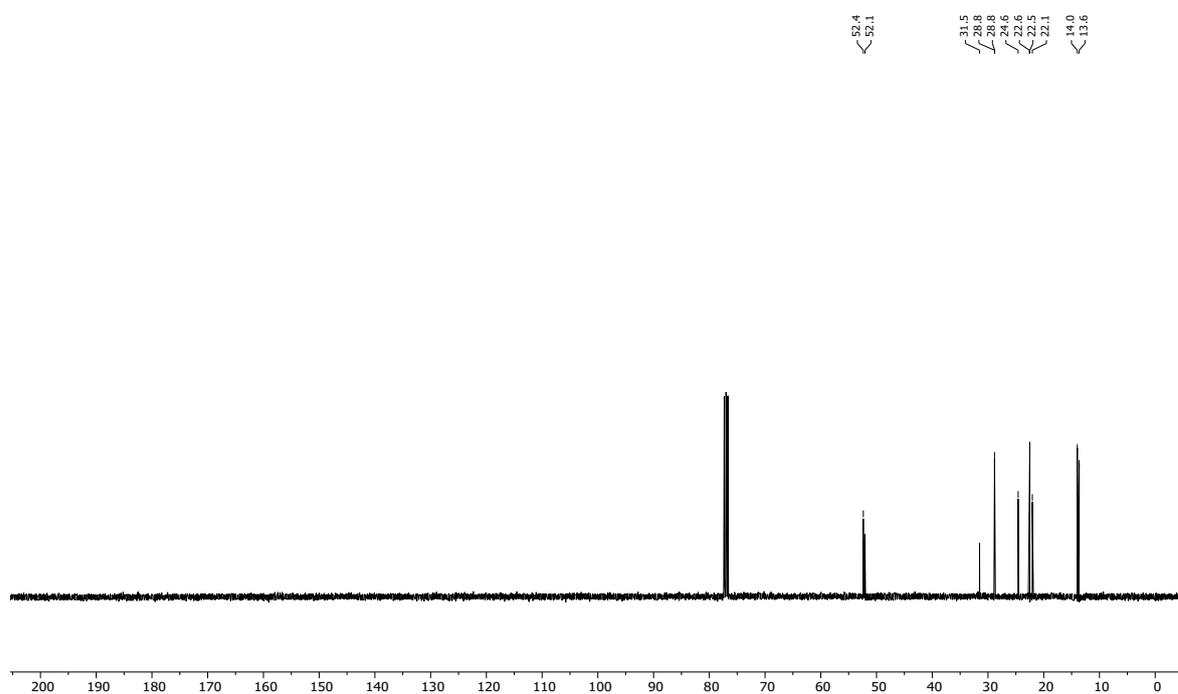
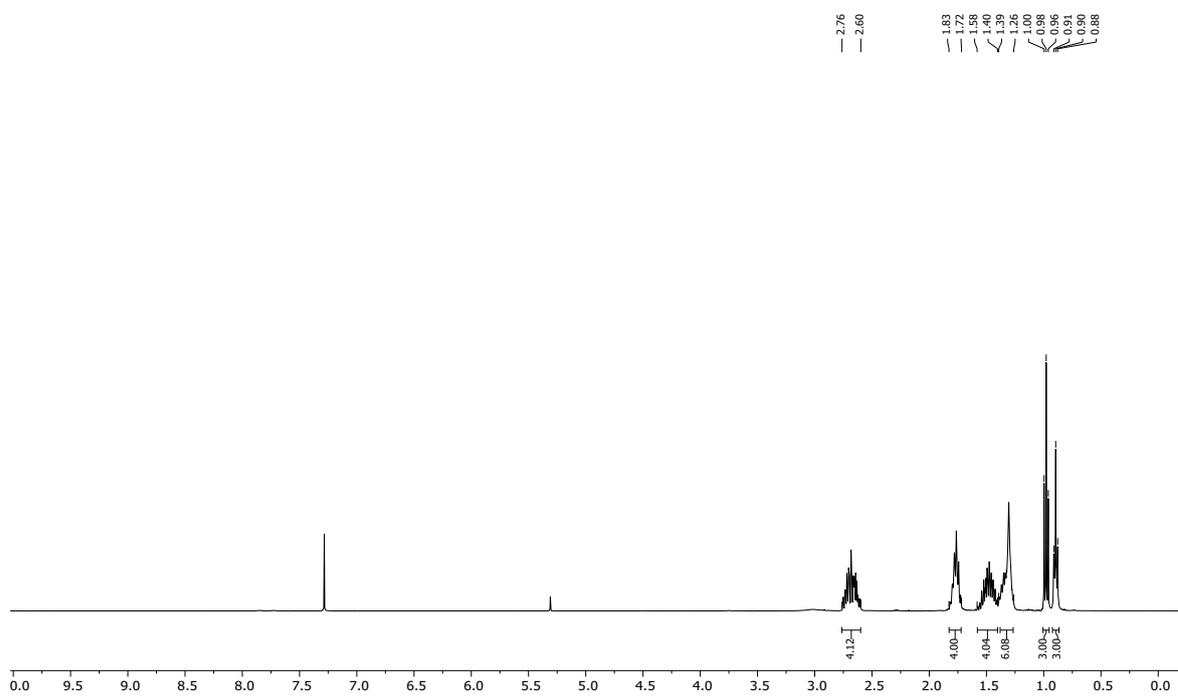
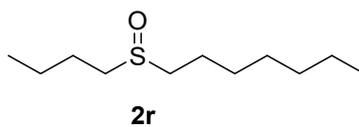


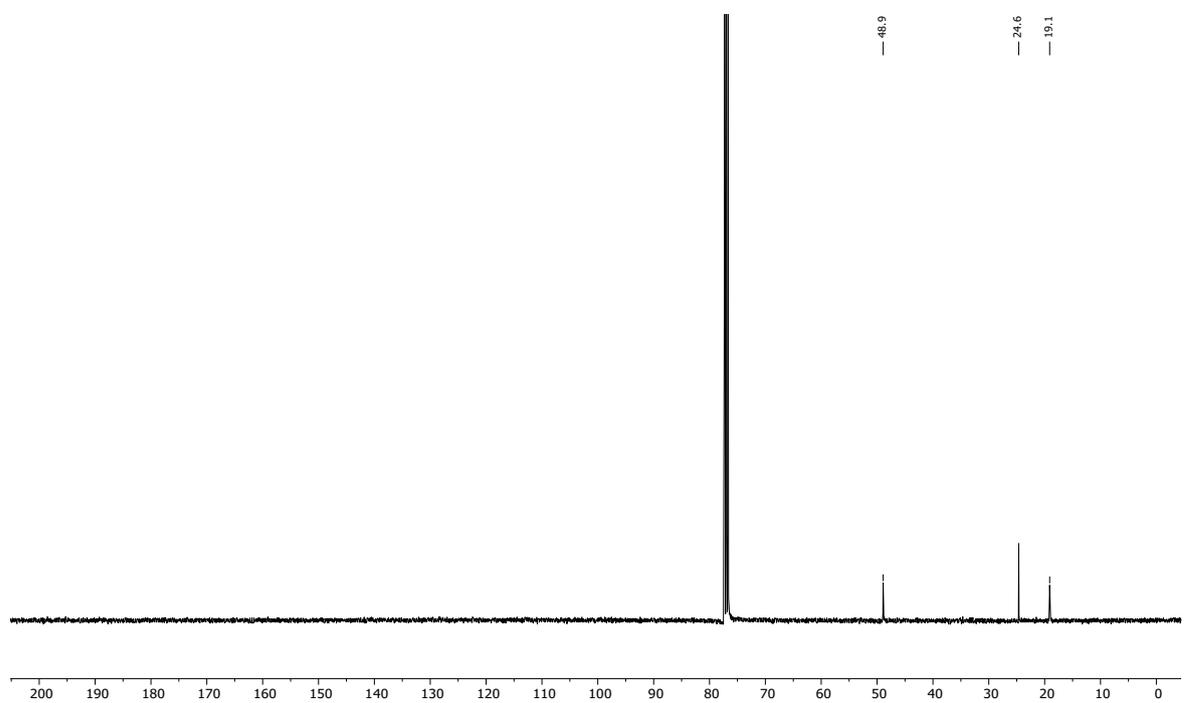
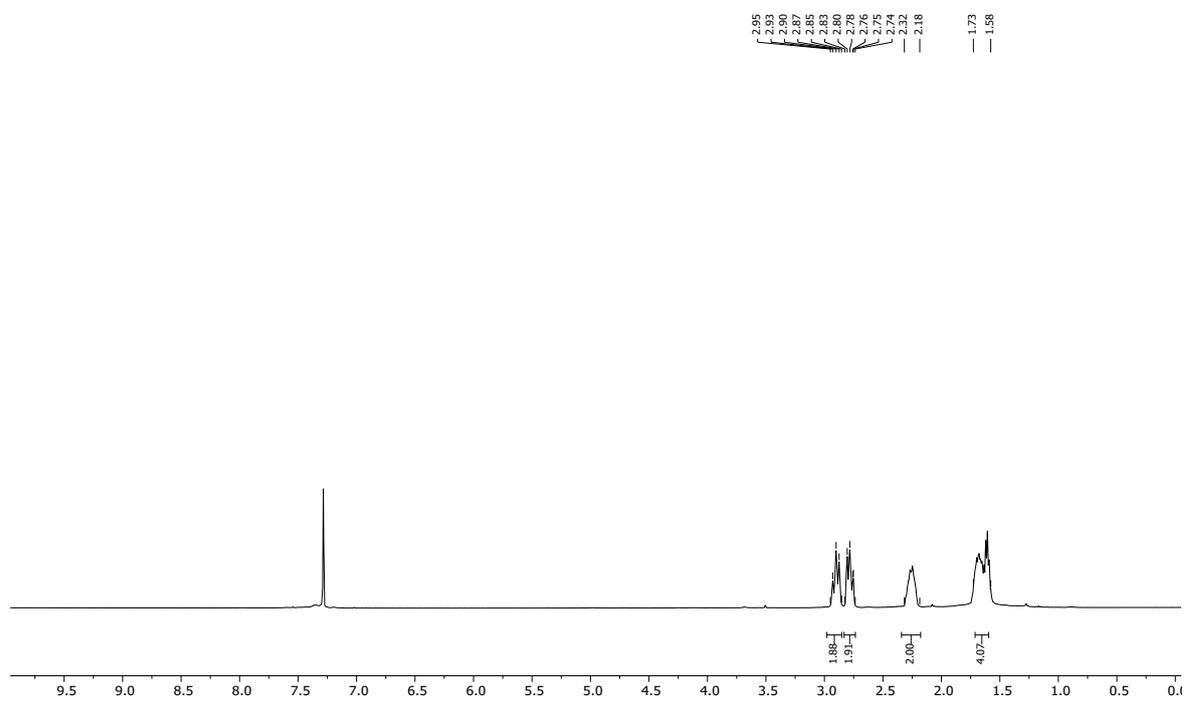
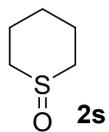
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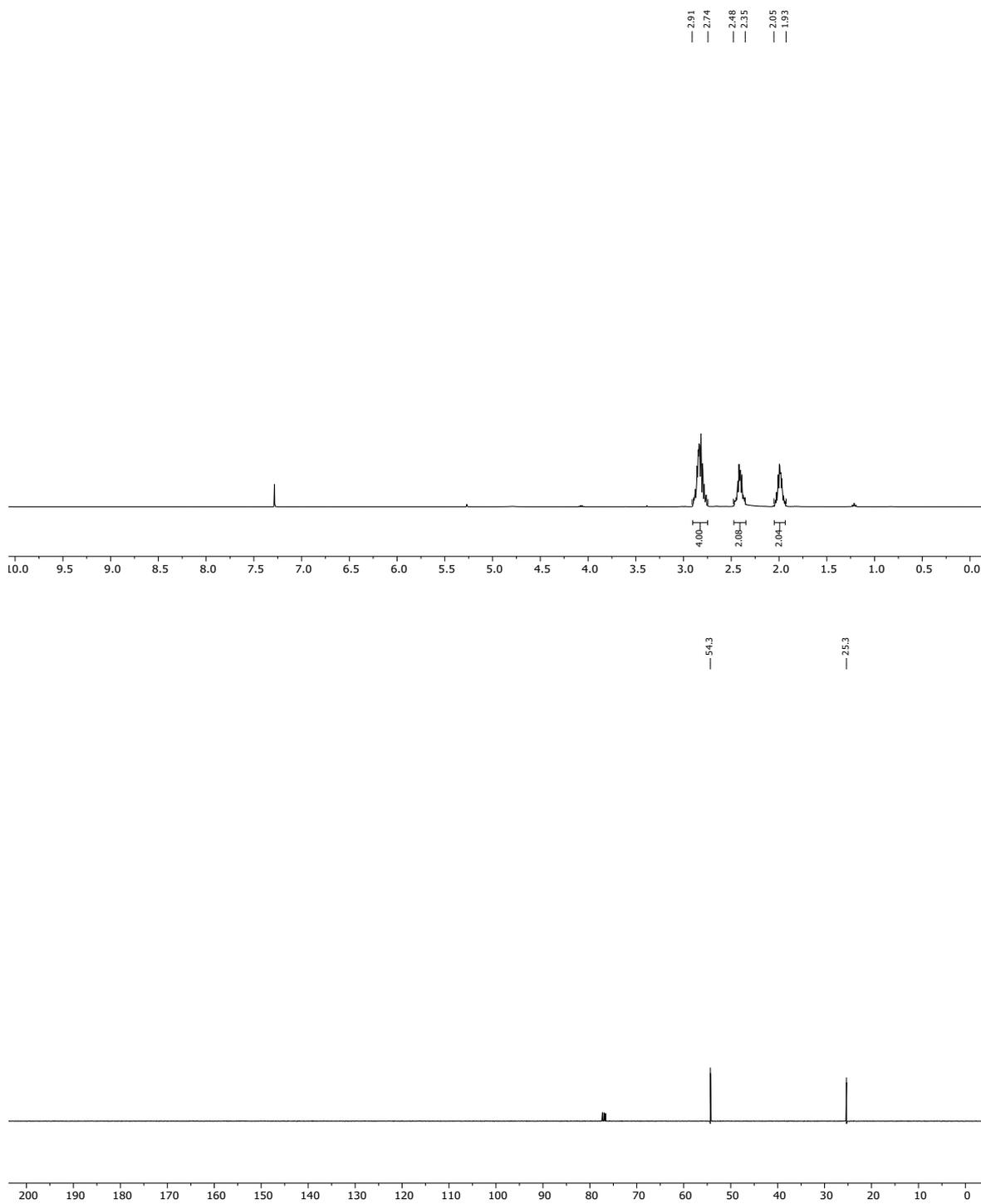
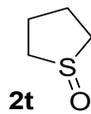


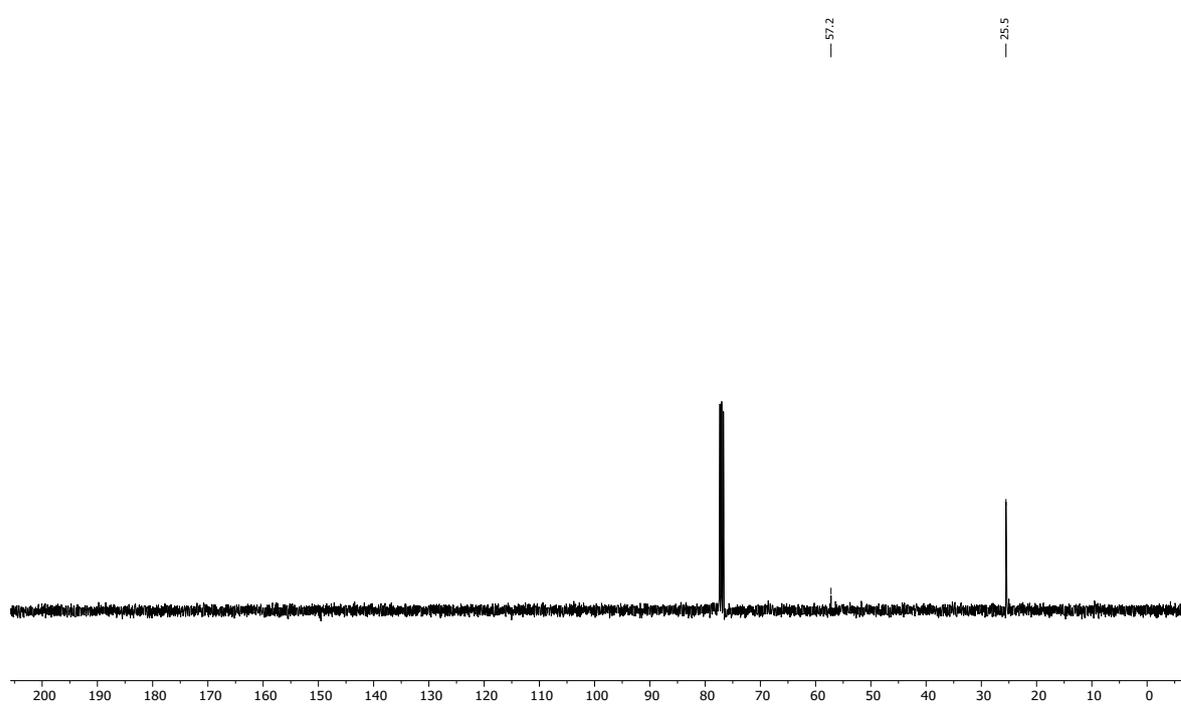
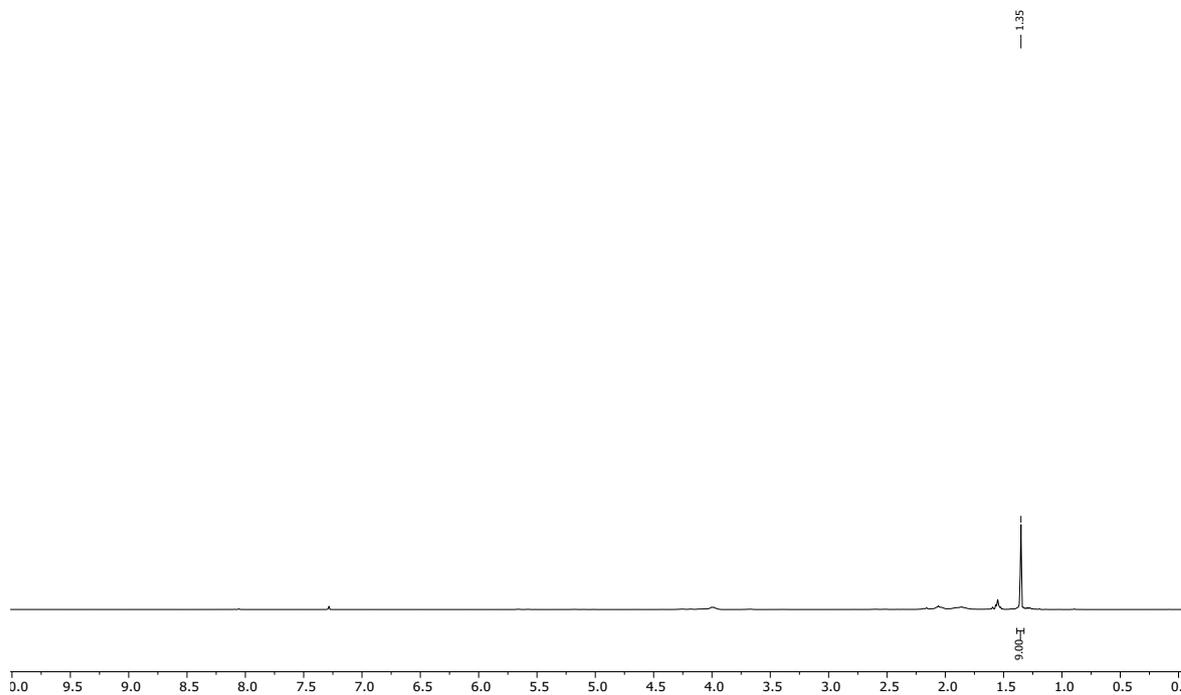
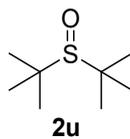


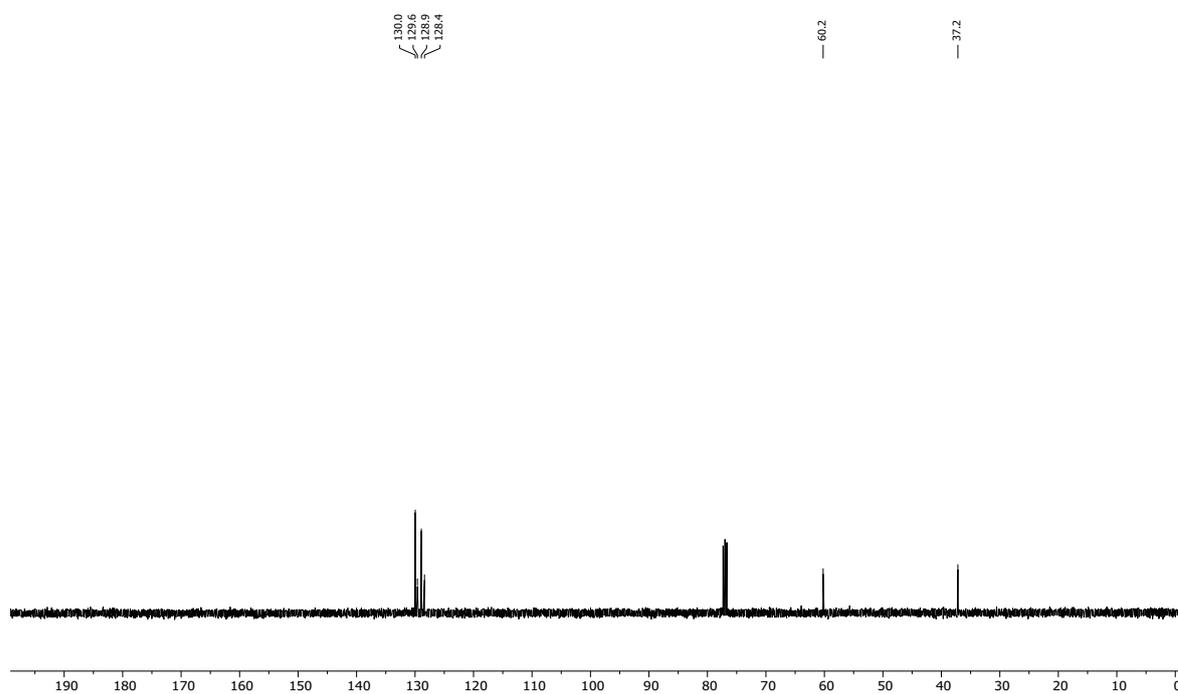
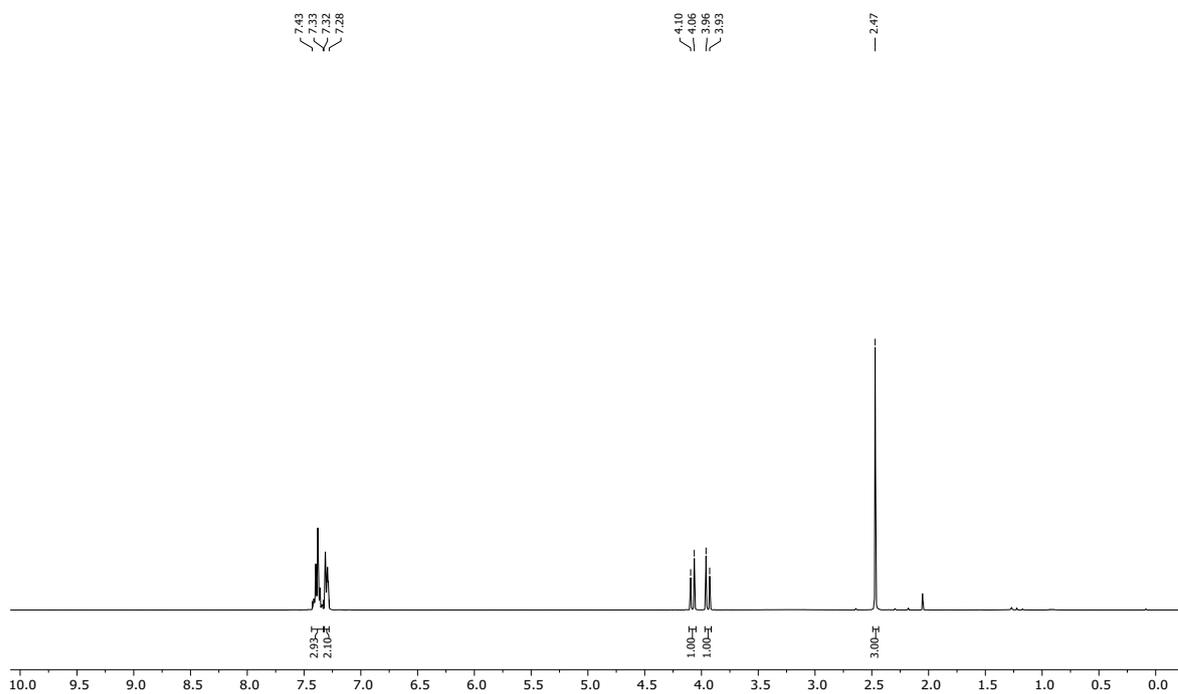
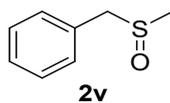


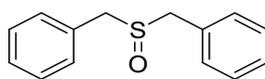










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