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Photochemical Metal-free Aerobic Oxidation of Thiols to Disulfides

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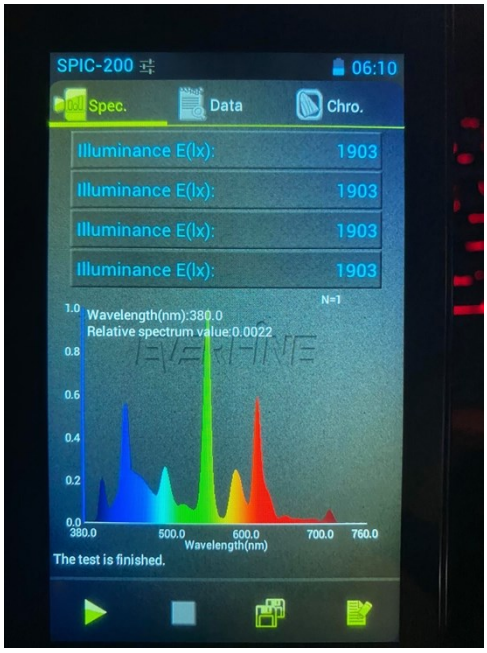
SUPPORTING INFORMATION

General Remarks

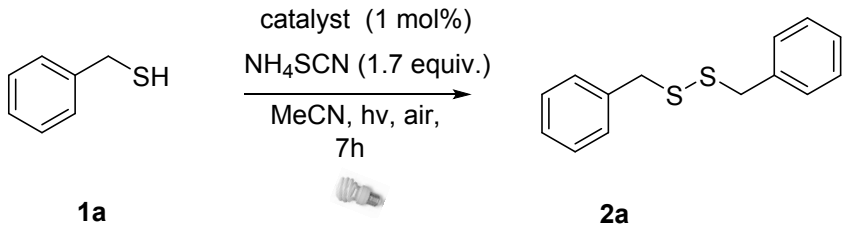
Chromatographic purification of products was accomplished using forced-flow chromatography on Merck® Kieselgel 60 F_{254} 230-400 mesh. Thin-layer chromatography (TLC) was performed on aluminum backed silica plates (0.2 mm, 60 F_{254}). Visualization of the developed chromatogram was performed by fluorescence quenching using phosphomolybdic acid, anisaldehyde or potassium permanganate stains. Mass spectra (ESI) were recorded on a Finningan® Surveyor MSQ LC-MS spectrometer. HRMS spectra were recorded on Bruker® Maxis Impact QTOF spectrometer. ^{1}H and ^{13}C NMR spectra were recorded on Varian® Mercury (200 MHz and 50 MHz, respectively) or an Avance III HD Bruker 400 MHz (400 MHz and 100 MHz, respectively) and are internally referenced to residual solvent signals. Data for ^{1}H NMR are reported as follows: chemical shift (δ ppm), integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br s = broad signal), coupling constant and assignment. Data for ^{13}C NMR are reported in terms of chemical shift (δ 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 μm, I.D.: 0.25 mm, L: 30 m, T_{max}: 350 °C, Column ID# 11475). A Varian® Cary 50 UV-Vis spectrophotometer was used as the light source for the quantum yield measurements and the UV-Vis data. A Scinco® FS-2 fluorescence spectrometer was used for the fluorescence studies.

Emission Spectrum of the Light Source

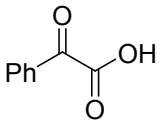
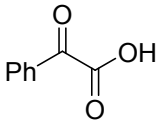
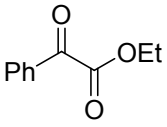
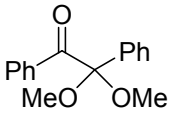
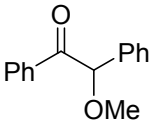
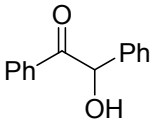
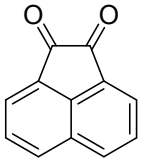
The emission spectrum of the lamps was measured with a SPIC-200 spectral irradiance colorimeter. The lamp was placed in a dark room in a 30 cm distance from the lamp.

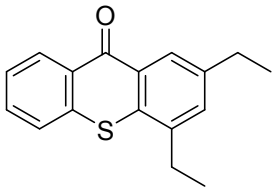
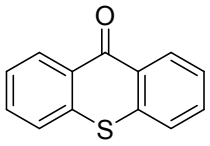
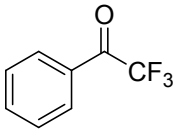
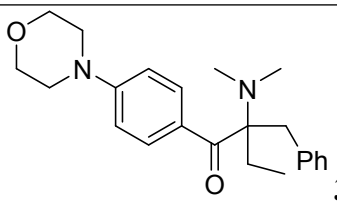
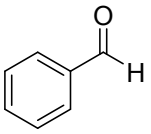
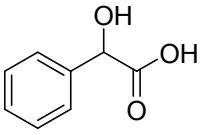


Optimization of the Reaction Conditions for the Photochemical Metal-free Aerobic Oxidation of Benzyl Mercaptan



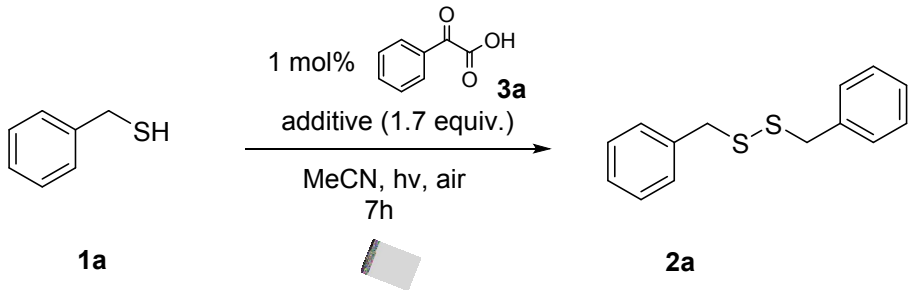
1a **2a**

Entry	Catalyst	Catalyst Loading (mol%)	Yield (%)[a]
1	 **3a**	1	100 (92)
2[b]	 **3a**	1	traces
3	 **3b**	1	94
4	 **3c**	1	97
5	 **3d**	1	92
6	 **3e**	1	74
7	 **3f**	1	100

8	 **3g**	1	98
9	 **3h**	1	97
10	 **3i**	1	50
11	 **3j**	1	42
12	 **3k**	1	10
13	 **3l**	1	25
14	-	-	9

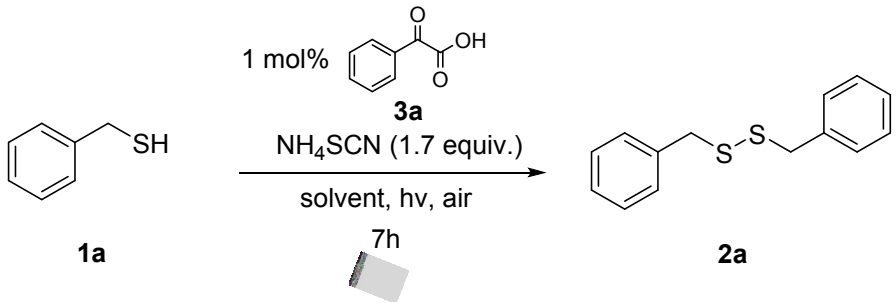
[a] Yield determined by GC-MS, yield of product after isolation by column chromatography in parenthesis.

[b] Reaction was kept in the dark. The same outcome was obtained when the reaction was performed under dark at 50 ^{o}C.



Entry	Additive	Yield (%)[a]
1	NH_4SCN	100
2	KSCN	95
3	PhSCN	30
4	-	44
5	TBDMS-CN	7
6	KCN	96
7	NaCN	93
8	PhCN	10
9	Ethyl Cyanoacetate	19
10	1,4-$Ph(CN)_2$	33
11	KBr	25
12	KI	23
13	KCl	15
14	TMEDA	55

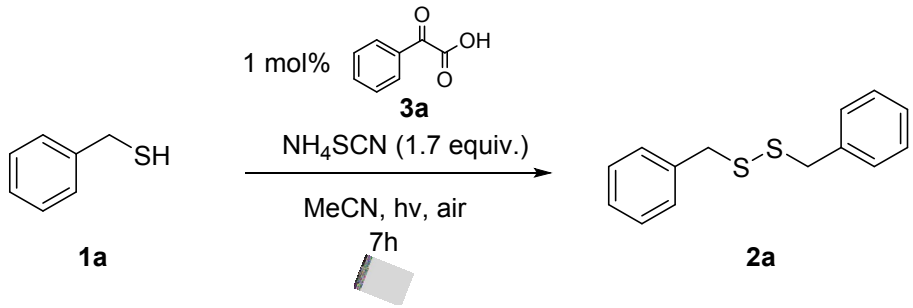
[a] Yield determined by GC-MS.



Entry	Solvent	Yield (%)[a]
1	H_2O	5
2	MeOH	93
3	Glycerol	55
4	DMSO	-
5	Acetone	54
6	toluene	4
7	Pet. Ether	15
8	MeCN	100
9	Et_2O	19
10	THF	41
11	$CHCl_3$	9
12	CH_2Cl_2	19
13	EtOAc	54

[a] Yield determined by GC-MS.

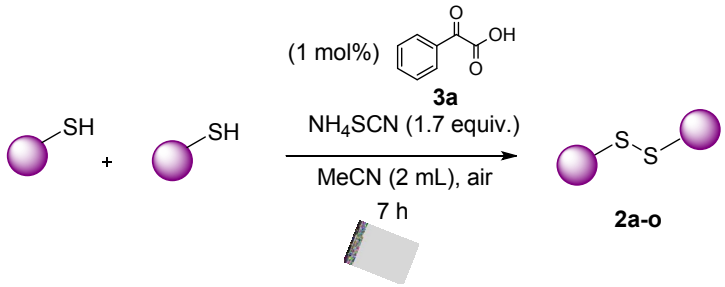
Mechanistic Studies on the Photochemical Metal-free Aerobic Oxidation of Benzyl Mercaptan



Entry	Quencher (equiv.)	Notes	Yield (%)[a]
1	BHT (1.0)	Radical Scavenger	0
2	TEMPO (1.0)	Radical Scavenger	0
3	$CuCl_2$ (1.0)	Electron Scavenger	87
4	DABCO (1.0)	Singlet Oxygen Scavenger	30
5	NaN_3 (1.0)	Singlet Oxygen Scavenger	10
6	Benzoquinone (1.0)	Superoxide Radical Anion Scavenger	37
7	Ar atmosphere	-	24

[a] Yield determined by GC-MS.

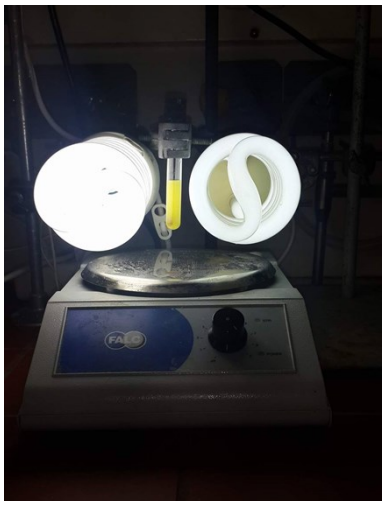
General Procedure for the Photochemical Metal-free Synthesis of Symmetrical Disulfides from Thiols



In a glass vial containing phenylglyoxylic acid (0.8 mg, 0.005 mmol) and ammonium thiocyanate (65 mg, 0.85 mmol) in acetonitrile (2 mL), thiol (0.50 mmol) was added. The reaction mixture was irradiated under open air with 2 x 85W household lamps (see photos below) with vigorous stirring for 7 h. The desired product was isolated either after dilution with CH_2Cl_2 (5 mL), wash with 10% aq. $NaHCO_3$ (2 x 5 mL) and the organic layer was dried over Na_2SO_4 and the solvent was removed *in vacuo* or after purification by column chromatography.

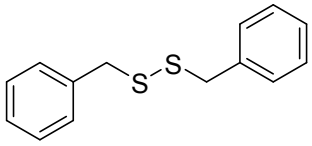
A

B



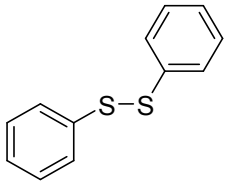
Scheme **A**: 2 x 85W fluorescent household lamps utilized for the photocatalytic reaction. Bulbs are placed symmetrically 3 cm away from the reaction tube. **B**: Beginning of the reaction.

1,2-Dibenzyldisulfane (2a)[1]



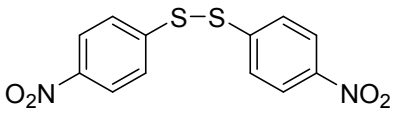
Colorless solid; 92% yield; m.p.: 60-62 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ: 7.31-7.25 (10H, m, ArH), 3.61 (4H, s, 2 x SCH_2); ^{13}C NMR (50 MHz, $CDCl_3$) δ: 137.3, 129.4, 128.4, 127.4, 43.2; MS (ESI) m/z 247 $[M+H]^+$.

1,2-Diphenyldisulfane (2b)[2]



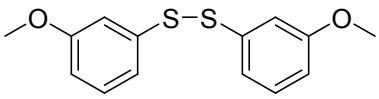
Colorless solid; 96% yield; m.p.: 58-60 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ: 7.56-7.50 (4H, m, ArH), 7.37-7.23 (6H, m, ArH); ^{13}C NMR (50 MHz, $CDCl_3$) δ: 137.0, 129.0, 127.4, 127.1; MS (ESI) m/z 219 $[M+H]^+$.

1,2-Bis(4-nitrophenyl)disulfane (2c)[3]



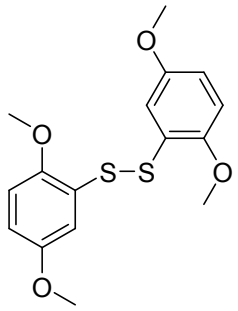
White solid; 64% yield; m.p.: 174-176 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ: 8.16 (4H, d, J = 9.0 Hz, ArH), 7.59 (4H, d, J = 9.0 Hz, ArH); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 147.0, 144.1, 126.4, 124.5; MS (ESI) m/z 308 $[M+H]^+$.

1,2-Bis(3-methoxyphenyl)disulfane (2d)[3]



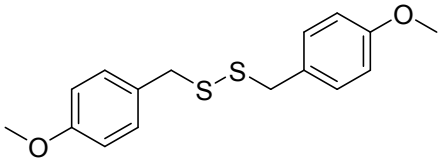
Colorless oil; 58% yield; ^{1}H NMR (200 MHz, $CDCl_3$) δ: 7.22 (2H, t, J = 8.1 Hz, ArH), 7.11-7.05 (4H, m, ArH), 6.76 (2H, ddd, J = 8.1, 2.3 and 1.2 Hz, ArH), 3.77 (6H, s, 2 x OCH_3); ^{13}C NMR: (50 MHz, $CDCl_3$) δ: 160.0, 138.2, 129.9, 119.5, 113.1, 112.5, 55.3; MS (ESI) m/z 279 $[M+H]^+$.

1,2-Bis(2,5-dimethoxyphenyl)disulfane (2e)[4]



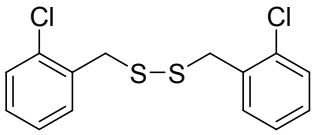
Colorless oil; 33% yield; ^{1}H NMR (200 MHz, $CDCl_3$) δ: 7.15 (2H, d, J = 2.8 Hz, ArH), 6.77 (2H, d, J = 8.8 Hz, ArH), 6.67 (2H, dd, J = 8.8 and 2.8 Hz, ArH), 3.85 (6H, s, 2 x OCH_3), 3.70 (6H, s, 2 x OCH_3); ^{13}C NMR: (100 MHz, $CDCl_3$) δ: 154.3, 150.9, 125.8, 113.6, 112.5, 111.8, 56.6, 55.7; MS (ESI) m/z 339 $[M+H]^+$.

1,2-Bis(4-methoxybenzyl)disulfane (2f)[5]



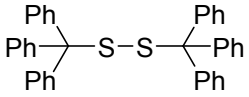
Colorless oil; 97% yield; ^{1}H NMR (200 MHz, $CDCl_3$) δ: 7.19 (4H, d, J = 8.8 Hz, ArH), 6.87 (4H, d, J = 8.8 Hz, ArH), 3.80 (6H, s, 2 x OCH_3), 3.60 (4H, s, 2 x SCH_2); ^{13}C NMR: (50 MHz, $CDCl_3$) δ: 158.9, 130.4, 129.3, 133.8, 55.2, 42.7; MS (ESI) m/z 307 $[M+H]^+$.

1,2-Bis(2-chlorobenzyl)disulfane (2g)[1]



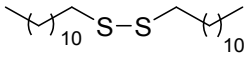
Colorless oil; 57% yield; ^{1}H NMR (200 MHz, $CDCl_3$) δ: 7.29 (4H, d, J = 8.5 Hz, ArH), 7.15 (4H, d, J = 8.5 Hz, ArH), 3.57 (4H, s, 2 x SCH_2); ^{13}C NMR: (50 MHz, $CDCl_3$) δ: 139.6, 135.8, 133.4, 130.6, 128.7, 128.6, 42.4; MS (ESI) m/z 314 $[M+H]^+$.

1,2-Ditrityldisulfane (2h)[6]



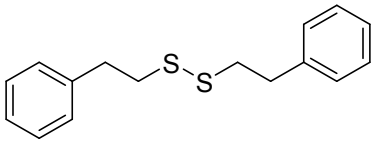
Colorless oil; 45% yield; ^{1}H NMR (200 MHz, $CDCl_3$) δ: 7.32-7.21 (30H, m, ArH); ^{13}C NMR (50 MHz, $CDCl_3$) δ: 143.5, 130.3, 127.8, 126.9, 72.6; MS (ESI) m/z 551 $[M+H]^+$.

1,2-Didodecyldisulfane (2i)[7]



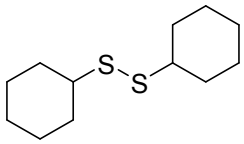
Colorless oil; 50% yield; ^{1}H NMR (200 MHz, $CDCl_3$) δ: 2.68 (4H, t, J = 7.4 Hz, 2 x SCH_2), 1.74-1.60 (4H, m, 2 x CH_2), 1.37-1.27 (36H, m, 18 x CH_2), 0.88 (6H, t, J = 6.3 Hz, 2 x CH_3); ^{13}C NMR (50 MHz, $CDCl_3$) δ: 39.2, 31.9, 29.8, 29.7, 29.6, 29.5, 29.4, 29.3, 29.2, 28.5, 22.7, 14.1; MS (ESI) m/z 403 $[M+H]^+$.

1,2-Diphenethyldisulfane (2j)[1]



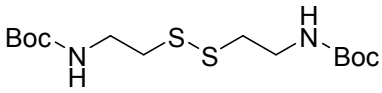
Colorless oil; 98% yield; ^{1}H NMR (200 MHz, $CDCl_3$) δ: 7.38-7.13 (10H, m, ArH), 3.04-2.99 (8H, m, 2 x CH_2); ^{13}C NMR: (50 MHz, $CDCl_3$) δ: 139.4, 128.6, 128.5, 126.3, 40.1, 35.7; MS (ESI) m/z 275 $[M+H]^+$.

1,2-Dicyclohexyldisulfane (2k)[1]



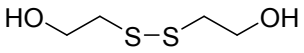
Colorless oil; 100% yield; ^{1}H NMR (200 MHz, $CDCl_3$) δ: 2.72-2.60 (2H, m, 2 x SCH), 2.06-2.01 (4H, m, 2 x CH_2), 1.81-1.77 (4H, m, 2 x CH_2), 1.31-1.26 (12H, m, 6 x CH_2); ^{13}C NMR: (50 MHz, $CDCl_3$) δ: 49.9, 32.8, 26.0, 25.7; MS (ESI) m/z 231 $[M+H]^+$.

Di-*tert*-butyl (disulfanediylbis(ethane-2,1-diyl))dicarbamate (2l)[8]



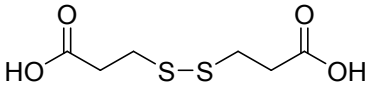
Colorless solid; 75% yield; m.p.: 103-104 ^{o}C; ^{1}H NMR (200 MHz, $CDCl_3$) δ: 5.08 (2H, br s, 2 x NH), 3.54-3.23 (4H, m, 2 x NCH_2), 2.83-2.55 (4H, t, J = 6.4 Hz, 2 x SCH_2), 1.40 (18H, s, 6 x CH_3); ^{13}C NMR (50 MHz, $CDCl_3$) δ: 155.8, 79.5, 39.3, 38.3, 28.3; MS (ESI) m/z 353 $[M+H]^+$.

2,2'-Disulfanediylbis(ethan-1-ol) (2m)[9]



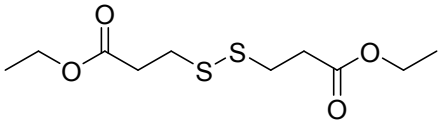
Colorless oil; 93% yield; ^{1}H NMR (200 MHz, $CDCl_3$) δ: 3.87 (4H, t, J = 5.9 Hz, 2 x OCH_2), 3.05 (2H, s, 2 x OH), 2.85 (4H, t, J = 5.9 Hz 2 x SCH_2); ^{13}C NMR (50 MHz, $CDCl_3$) δ: 60.3, 41.1; MS (ESI) m/z 153 $[M+H]^+$.

3,3'-Disulfanediyldipropionic acid (2n)[2]



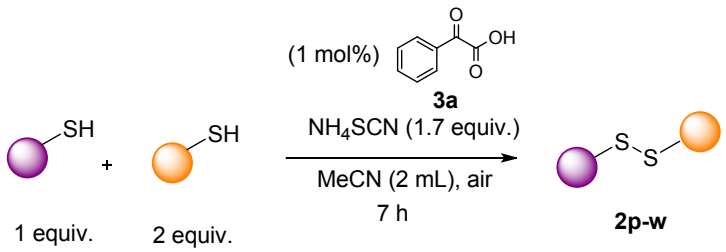
Colorless solid; 100% yield; m.p.: 153-155 ^{o}C; ^{1}H NMR (200 MHz, DMSO) δ: 2.85 (4H, t, J = 6.9 Hz, 2 x CH_2CO), 2.58 (4H, t, J = 6.9 Hz, 2 x SCH_2); ^{13}C NMR (50 MHz, DMSO) δ: 172.8, 33.6, 33.1; MS (ESI) m/z 209 $[M-H]^-$.

Diethyl 3,3'-disulfanediyldipropionate (2o)



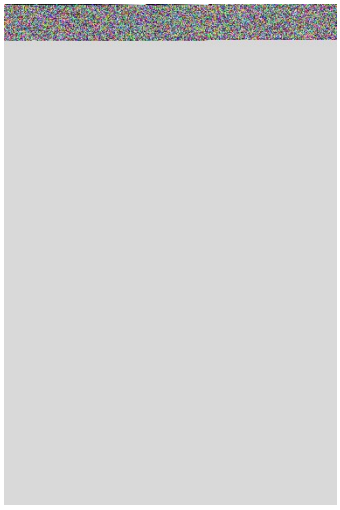
Colorless oil; 65% yield; ^{1}H NMR (200 MHz, $CDCl_3$) δ: 4.12 (4H, q, J = 7.1 Hz, 2 x OCH_2), 2.91 (4H, t, J = 6.8 Hz, 2 x SCH_2), 2.70 (4H, t, J = 6.8 Hz, $COCH_2$), 1.28 (6H, t, J = 7.1 Hz, 2 x CH_3); ^{13}C NMR: (50 MHz, $CDCl_3$) δ: 171.6, 60.7, 34.1, 33.1, 14.2; HRMS exact mass calculated for $[M+Na]^+$ ($C_{10}H_{18}O_4S_2Na^+$) requires *m/z* 289.0539, found *m/z* 289.0540.

General Procedure for the Photochemical Metal-free Synthesis of Non-Symmetrical Disulfides from Thiols

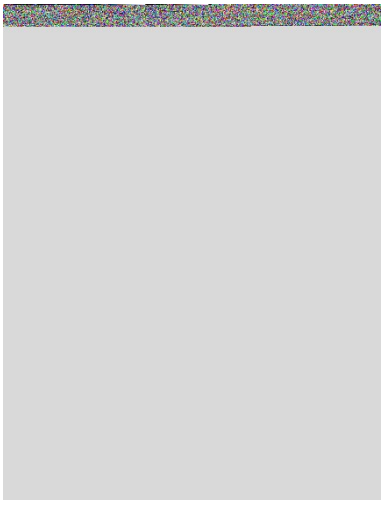


In a glass vial containing phenylglyoxylic acid (0.8 mg, 0.005 mmol) and ammonium thiocyanate (65 mg, 0.85 mmol) in acetonitrile (2 mL), simple thiol (0.50 mmol) and thiol bearing polar group (1.00 mmol) was added. The reaction mixture was irradiated under open air with 2 x 85W household lamps (see photos below) with vigorous stirring for 7 h. The desired product was isolated after purification by column chromatography.

A

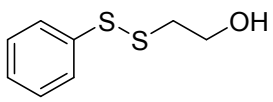


B



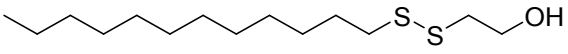
Scheme **A**: 2 x 85W fluorescent household lamps utilized for the photocatalytic reaction. Bulbs are placed symmetrically 3 cm away from the reaction tube. **B**: Beginning of the reaction.

2-(Phenyldisulfanyl)ethan-1-ol (2p)



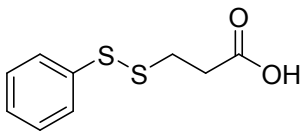
Colorless oil; 38% yield; ^{1}H NMR (200 MHz, $CDCl_3$) δ: 7.55 (2H, d, J = 6.7 Hz, ArH), 7.39-7.19 (3H, m, ArH), 3.85 (2H, t, J = 5.8 Hz, OCH_2), 2.89 (2H, t, J = 5.8 Hz, SCH_2), 2.01 (1H, br s, OH); ^{13}C NMR: (50 MHz, $CDCl_3$) δ: 136.9, 129.1, 127.8, 127.2, 59.8, 41.1; HRMS exact mass calculated for $[M+Na]^+$ ($C_8H_{10}OS_2Na^+$) requires *m/z* 209.0065, found *m/z* 209.0062.

2-(Dodecyldisulfanyl)ethan-1-ol (2q)[10]



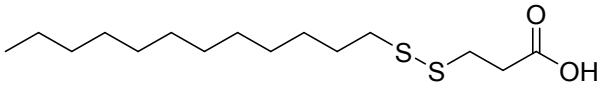
Colorless oil; 32% yield; ^{1}H NMR (200 MHz, $CDCl_3$) δ: 3.88 (2H, t, J = 5.8 Hz, OCH_2), 2.84 (2H, t, J = 5.8 Hz, SCH_2), 2.70 (2H, t, J = 7.5 Hz, SCH_2), 2.08 (1H, br s, OH), 1.71-1.60 (2H, m, 2 x CH*H*), 1.34-1.18 (18H, m, 9 x CH_2), 0.87 (3H, t, J = 6.2 Hz, CH_3); ^{13}C NMR: (50 MHz, $CDCl_3$) δ: 60.2, 41.1, 39.0, 31.9, 29.6, 29.5, 29.4, 29.3, 29.2, 29.1, 28.9, 28.5, 22.7, 14.1; MS (ESI) m/z 279 $[M+H]^+$.

3-(Phenyldisulfanyl)propanoic acid (2r)[11]



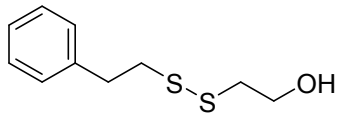
White solid; 50% yield; m.p.: 56-58 ^{o}C; ^{1}H NMR (200 MHz, $CDCl_3$) δ: 10.49 (1H, br s, COOH), 7.58-7.45 (2H, m, ArH), 7.38-7.19 (3H, m, ArH), 2.95 (2H, t, J = 7.0 Hz, CH_2), 2.79 (2H, t, J = 7.0 Hz, CH_2); ^{13}C NMR: (50 MHz, $CDCl_3$) δ: 178.1, 136.6, 129.1, 127.7, 127.1, 33.5, 32.6; MS (ESI) m/z 213 $[M-H]^-$.

3-(Dodecyldisulfanyl)propanoic acid (2s)[12]



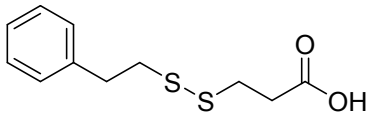
White solid, 45% yield; m.p.: 110-112 ^{o}C; ^{1}H NMR (200 MHz, $CDCl_3$) δ: 9.05 (1H, br s, CO_2H), 2.92-2.77 (4H, m, 2 x CH_2), 2.68 (2H, t, J = 7.2 Hz, SCH_2), 1.69-1.58 (2H, m, CH_2), 1.31-1.21 (18H, m, 9 x CH_2), 0.87 (3H, t, J= 6.2 Hz, CH_3); ^{13}C NMR: (50 MHz, $CDCl_3$) δ: 178.1, 39.0, 33.9, 32.6, 31.9, 29.6, 29.5, 29.4, 29.3, 29.2, 29.1, 28.5, 22.7, 14.1; MS (ESI) m/z 305 $[M-H]^-$.

2-(Phenethyldisulfanyl)ethan-1-ol (2t)



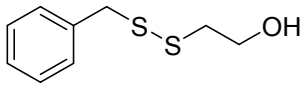
Colorless oil, 90% yield; ^{1}H NMR (200 MHz, $CDCl_3$) δ: 7.35-7.17 (5H, m, ArH), 3.91-3.83 (2H, m, OCH_2), 3.01-2.79 (6H, m, 3 x CH_2), 2.52 (1H, br s, OH); ^{13}C NMR: (50 MHz, $CDCl_3$) δ: 139.9, 128.5, 128.4, 126.4, 60.3, 41.1, 40.1, 35.6; HRMS exact mass calculated for $[M+Na]^+$ ($C_{10}H_{14}OS_2Na^+$) requires *m/z* 237.0378, found *m/z* 237.0384.

3-(Phenethyldisulfanyl)propanoic acid (2u)



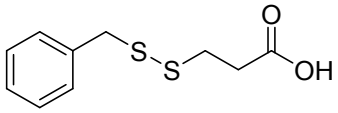
White solid, 51% yield; Low melting point solid; ^{1}H NMR (200 MHz, $CDCl_3$) δ: 9.78 (1H, br s, COOH), 7.31-7.18 (5H, m, ArH), 2.98-2.80 (8H, m, 4 x CH_2); ^{13}C NMR: (50 MHz, $CDCl_3$) δ: 178.1, 139.8, 128.6, 128.5, 126.4, 40.1, 35.6, 33.9, 32.6; HRMS exact mass calculated for $[M-H]^-$ ($C_{11}H_{14}O_2S_2^-$) requires *m/z* 241.0351, found *m/z* 241.0359.

2-(Benzyldisulfanyl)ethan-1-ol (2v)[13]



Colorless oil, 45% yield; ^{1}H NMR (200 MHz, $CDCl_3$) δ: 7.34-7.24 (5H, m, ArH), 3.90 (2H, s, $PhCH_2$), 3.71 (2H, t, J = 5.8 Hz, OCH_2), 2.52 (2H, t, J = 5.8 Hz, SCH_2), 2.01 (1H, s, OH); ^{13}C NMR: (50 MHz, $CDCl_3$) δ: 137.1, 129.3, 128.5, 127.5, 60.0, 43.3, 40.7; MS (ESI) m/z 201 $[M+H]^+$.

3-(Benzyldisulfanyl)propanoic acid (2w)



White solid, 48% yield; m.p.: 45-47 ^{o}C; ^{1}H NMR (200 MHz, $CDCl_3$) δ: 10.00 (1H, br s, COOH), 7.62-7.02 (5H, m, ArH), 3.90 (2H, s, $PhCH_2S$), 2.64-2.59 (4H, m, 2 x CH_2); ^{13}C NMR: (50 MHz, $CDCl_3$) δ: 178.1, 137.1, 129.2, 128.5, 127.5, 43.4, 36.7, 32.2; HRMS exact mass calculated for $[M-H]^-$ ($C_{10}H_{12}O_2S_2^-$) requires *m/z* 227.0195, found *m/z* 227.0203.

Determination of the Quantum Yield

Determination of the photon flux of the lamps

The photon flux of the CFL lamps was determined following the procedure described in *Green Chem.,* **2019***, 21,* 669-674. A 0.006M solution of potassium ferrioxalate was prepared by dissolving 120 mg of potassium ferrioxalate hydrate in 40 mL of 0.05M H_2SO_4. A buffered solution of phenanthroline was prepared by dissolving 10 mg of phenanthroline and 2.25 g of sodium acetate in 250 mL of 0.5 M H_2SO_4. Both solutions were stored in the dark. To determine the photon flux of the lamps, 2.0 mL of the solution of potassium ferrioxalate was placed in the cuvette, UV-Vis absorbance recorded (absorbance of interest at 510 nm), and irradiated for 90 seconds at lamps. After irradiation, 0.35 mL of the phenanthroline solution was added to the cuvette. The solution was allowed to rest for 1 h (complete coordination of ferrous ions to phenanthroline). The absorbance of the solution was then measured at 510 nm.

The fraction of light absorbed (f) by this solution was calculated, using this absorbance (A):

$$f = 1 - 10^{-A} = 1 - 10^{-4.9987} = 0.9999$$

In order to measure the photon flux, the mol of Fe^{2+} are required:

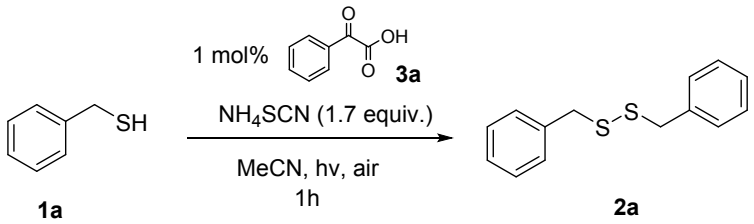
$$\text{Mol } Fe^{2+} = \frac{V \times \Delta A}{l \times \varepsilon} = \frac{0.00235\ \text{L} \times 0.382}{1.0\ \text{cm} \times 11.100\ \text{L mol}^{-1}\ \text{cm}^{-1}} = 8.09 \times 10^{-8}\ \text{mol}$$

In this equation, V is the total volume of the solution after addition of the phenanthroline (0.00235 L), ΔA is the difference in the absorbance at 510 nm between the irradiated and the non-irradiated solutions, l is the path length (1.0 cm), and ε is the molar absorptivity at 510 nm (11.100 L mol^{-1} cm^{-1}). The photon flux is then calculated:

$$\text{Mol Fe}^{2+} = \frac{\text{Mol Fe}^{2+}}{\Phi \times t \times f} = \frac{8.09 \times 10^{-8}\ \text{mol}}{1.35 \times 90\ \text{sec} \times 0.9999} = 6.66 \times 10^{-10}\ \text{einstein}^{\ s^{-1}}$$

In this equation, Φ is the quantum yield of the ferrioxalate actinometer, t is the time of the irradiation (90 seconds), and f is the fraction of the light absorbed at lamps (that is calculated above). Thus, the photon flux of the spectrophotometer was calculated to be 6.66×10^{-10} einstein s^{-1}.

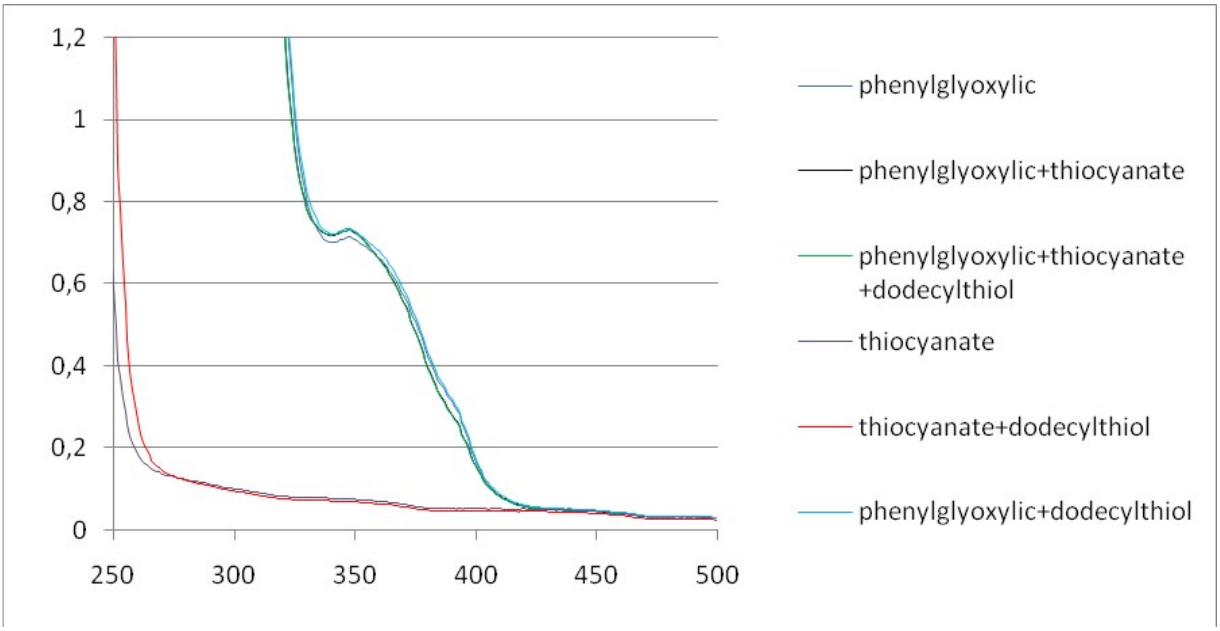
Determination of the quantum yield



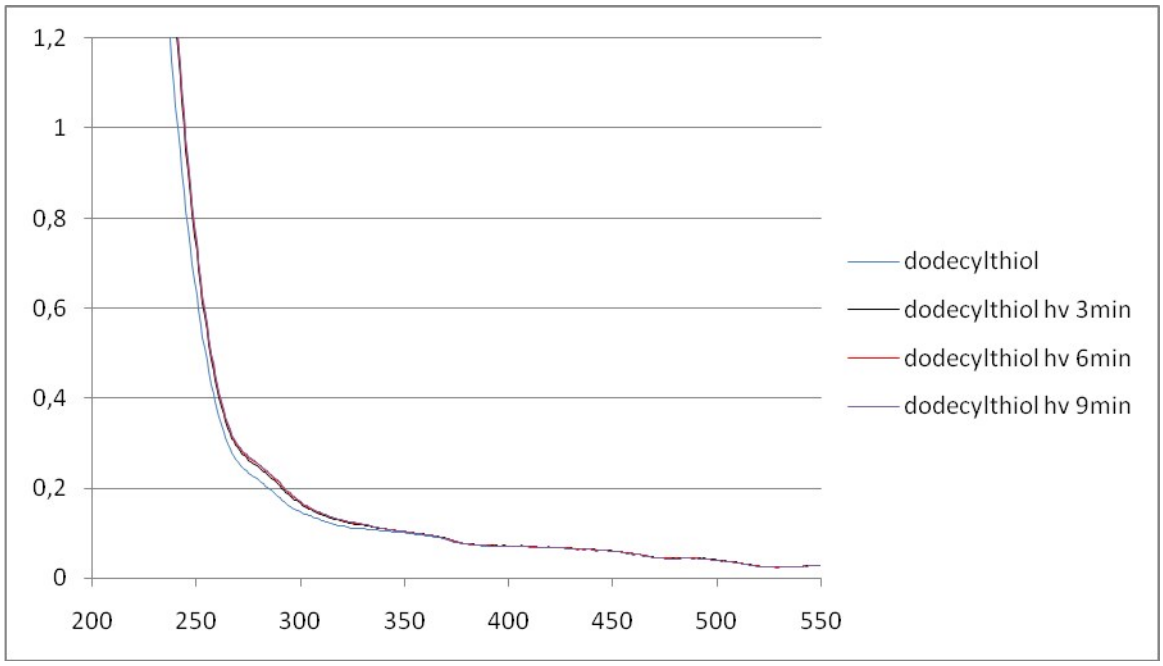
A cuvette was charged with benzyl mercaptan (**1a**) (62 mg, 0.50 mmol), phenylglyoxylic (**3a**) acid (0.8 mg, 0.005 mmol) and ammonium thiocyanate (65 mg, 0.85 mmol) in acetonirile (2 mL). The sample was stirred and then irradiated under CFL irradiation for 3600 s (1 h). After irradiation, the solvent was removed and the yield of the product was determined by GC-MS (36%). The quantum yield was determined with the following equation:

$$\Phi = \frac{\text{mol product}}{\text{flux} \times t \times f} = \frac{0.09 \times 10^{-3}\ \text{mol}}{6.66 \times 10^{-10}\ \text{einstein}\ s^{-1} \times 3600\ \text{s} \times 0.9999} = 38$$

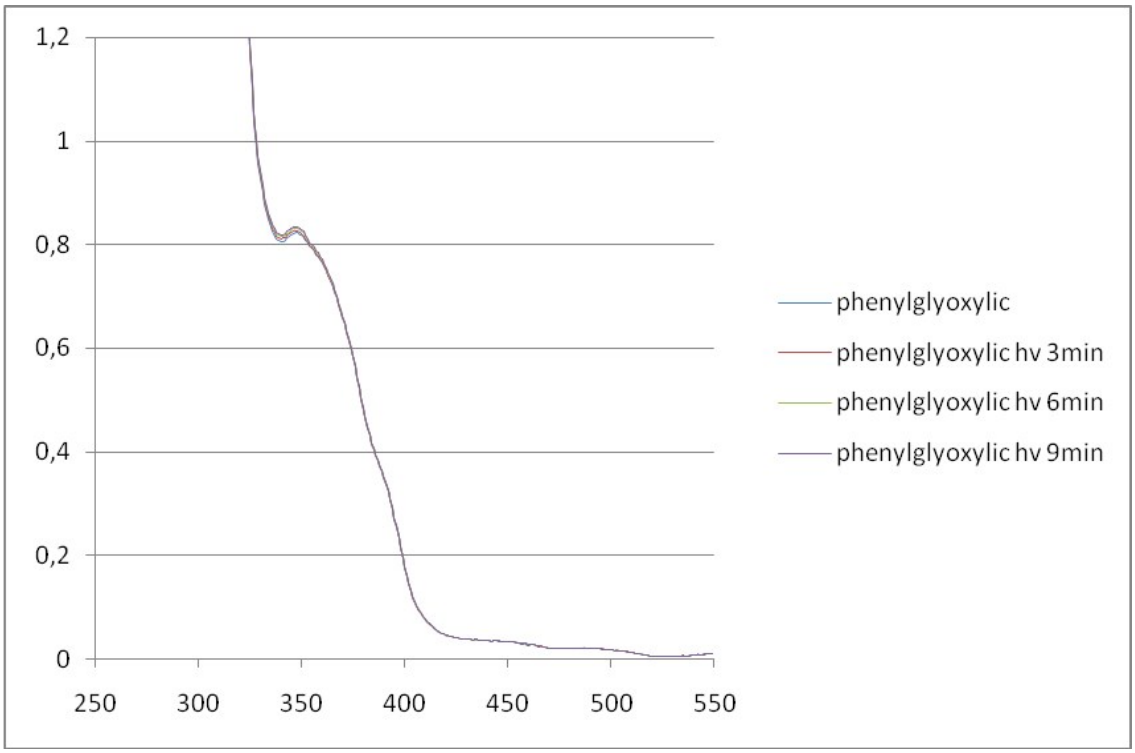
Mechanistic Investigations with UV-Vis Absorption Spectra



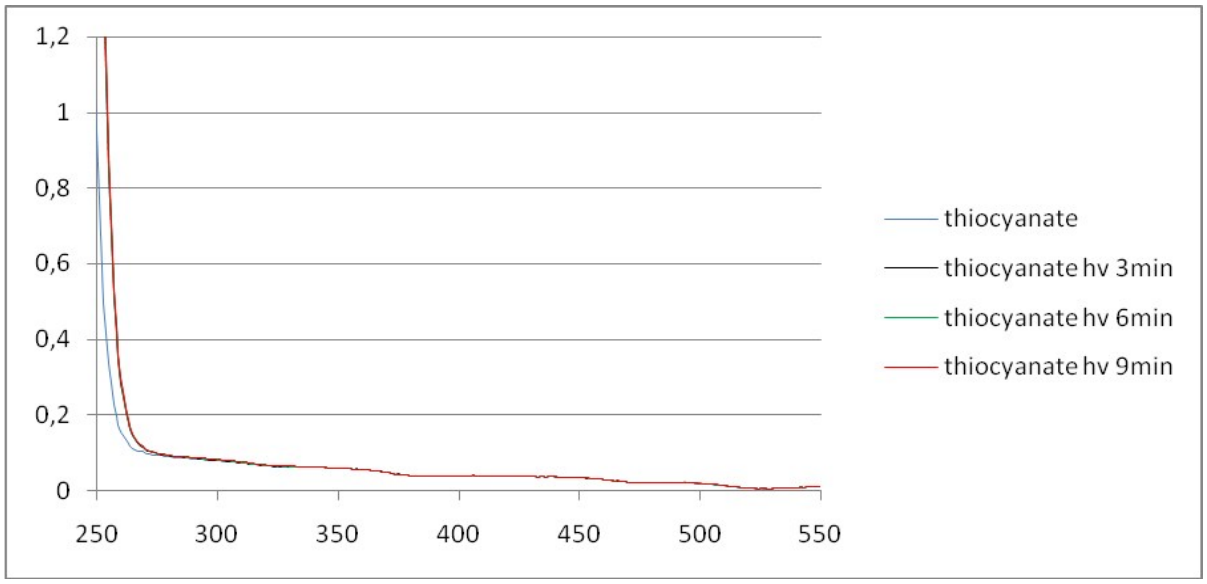
UV-VIS spectra of phenylglyoxylic acid (10^{-2} M in MeCN), phenylglyoxylic acid (10^{-2} M in MeCN) and ammonium thiocyanate (10^{-2} M in MeCN), phenylglyoxylic acid (10^{-2} M in MeCN), ammonium thiocyanate (10^{-2} M in MeCN) and dodecylthiol (10^{-2} M in MeCN), ammonium thiocyanate (10^{-2} M in MeCN), ammonium thiocyanate (10^{-2} M in MeCN) and dodecylthiol (10^{-2} M in MeCN), phenylglyoxylic acid (10^{-2} M in MeCN) and dodecylthiol (10^{-2} M in MeCN).



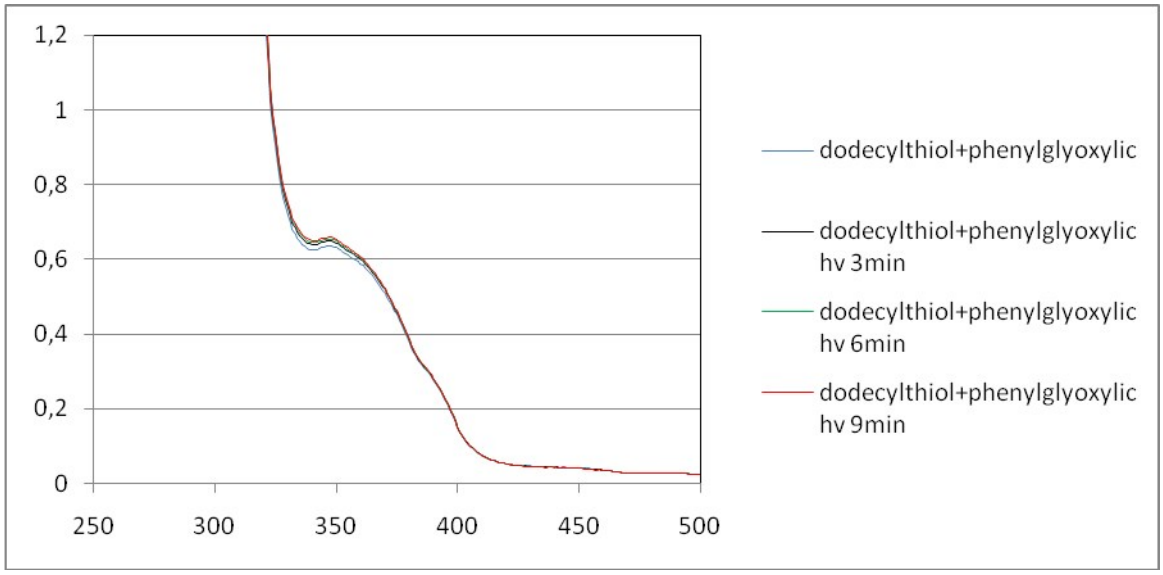
Dodecylthiol (10^{-2} M) in MeCN, after consecutive irradiation.



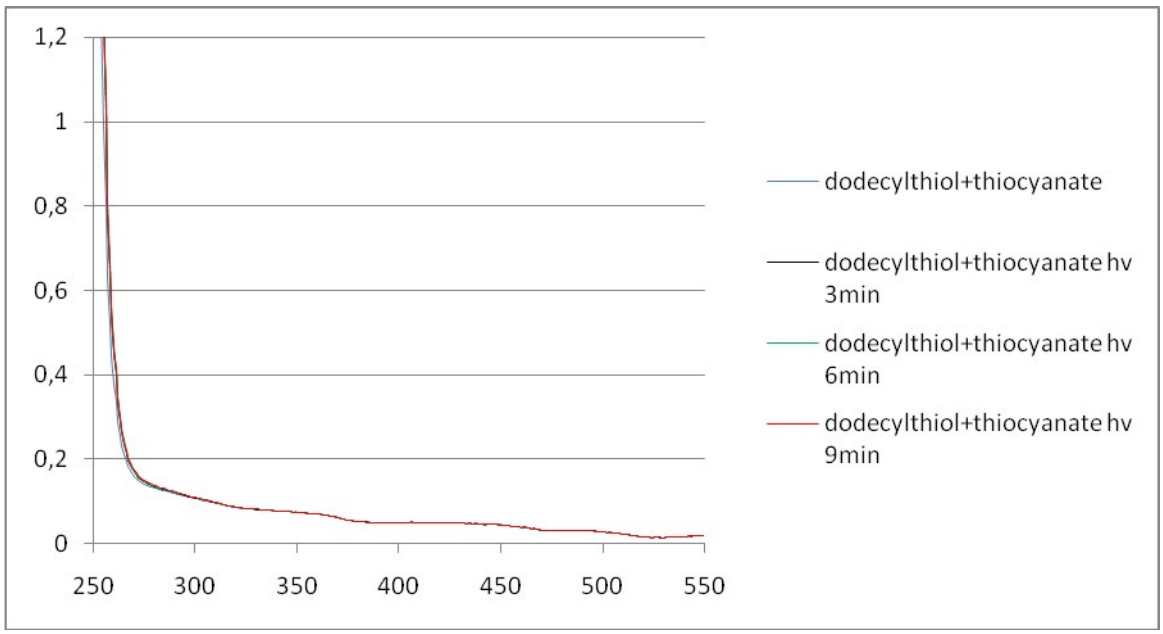
Phenylglyoxylic acid (10^{-2} M) in MeCN, after consecutive irradiation.



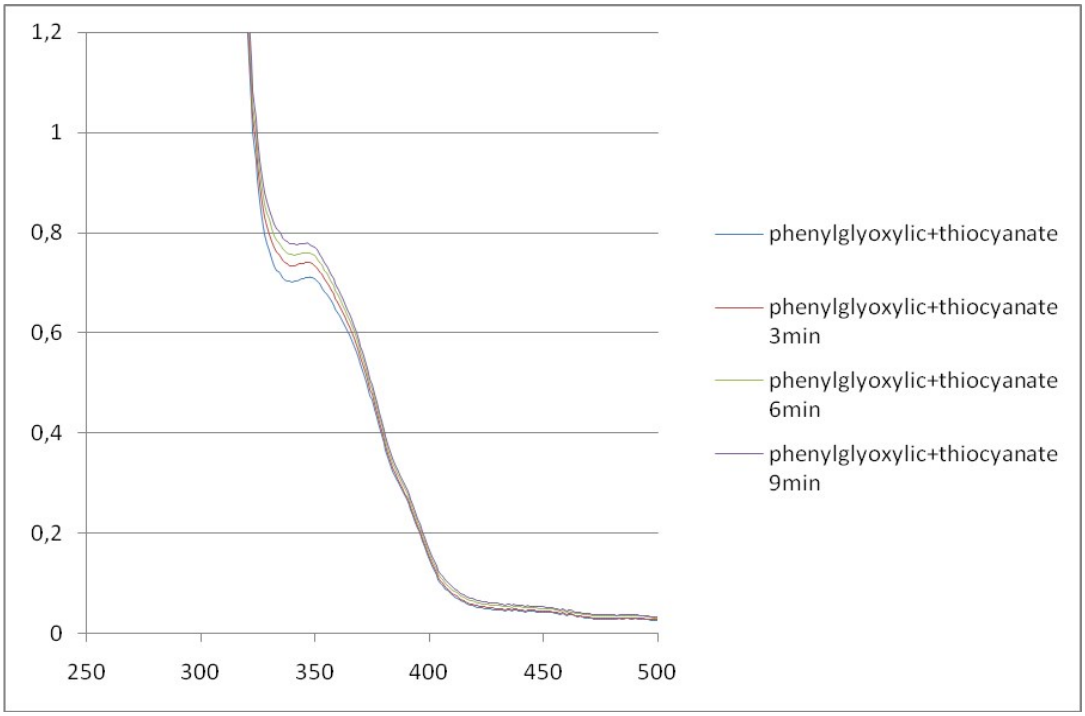
Ammonium thiocyanate (10^{-2} M) in MeCN, after consecutive irradiation.



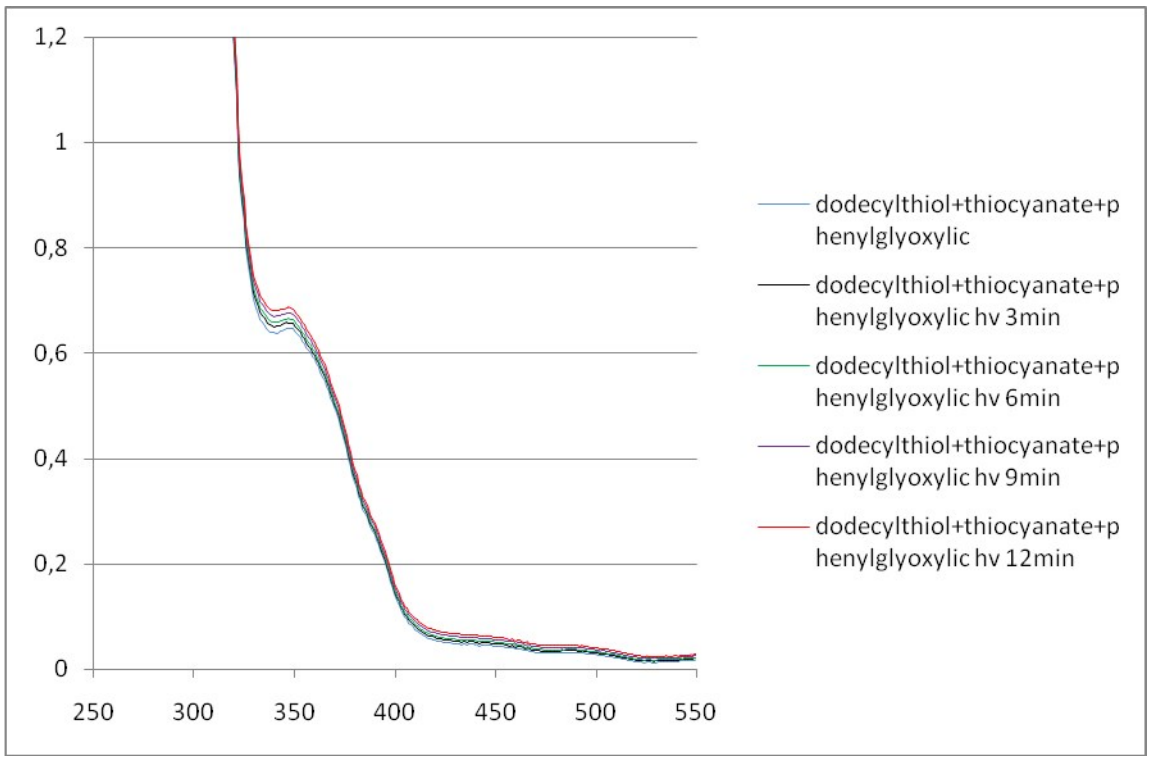
Dodecylthiol (10^{-2} M) and phenylglyoxylic acid (10^{-2} M) in MeCN, after consecutive irradiation.



Dodecylthiol (10^{-2} M) and ammonium thiocyanate (10^{-2} M) in MeCN, after consecutive irradiation.



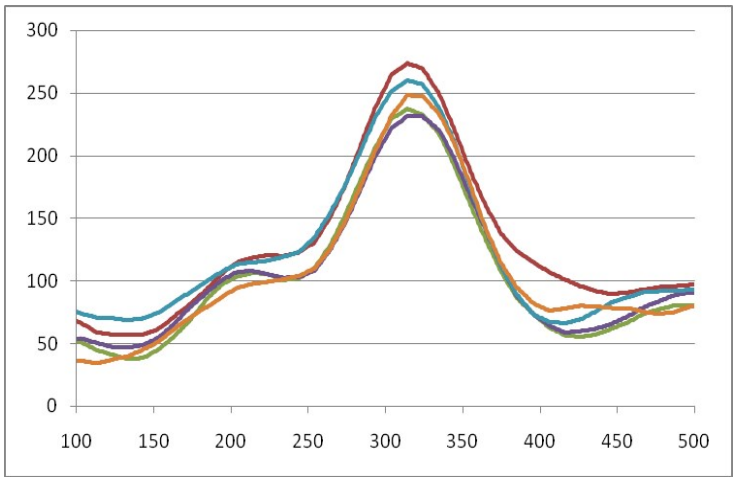
Ammonium thiocyanate (10^{-2} M) and phenylglyoxylic acid (10^{-2} M) in MeCN, after consecutive irradiation.

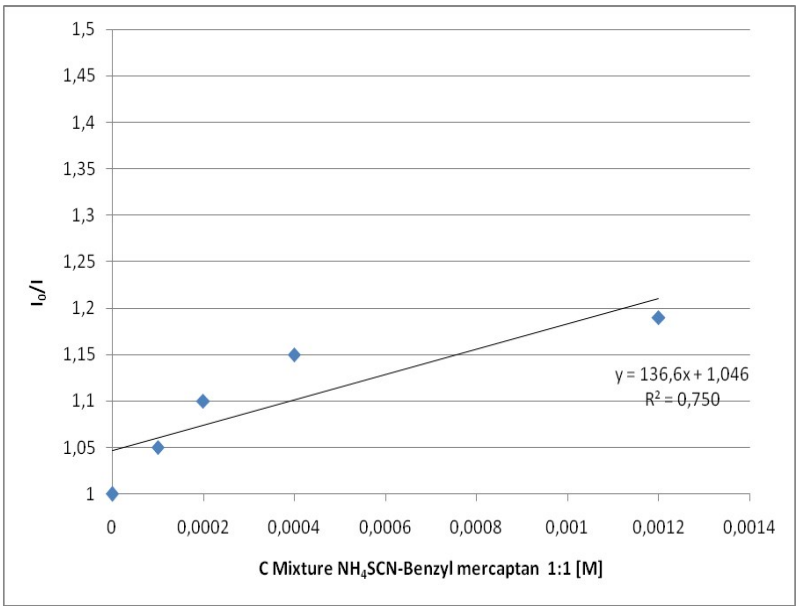


Dodecylthiol (10^{-2} M), ammonium thiocyanate (10^{-2} M) and phenylglyoxylic acid (10^{-2} M) in MeCN, after consecutive irradiation.

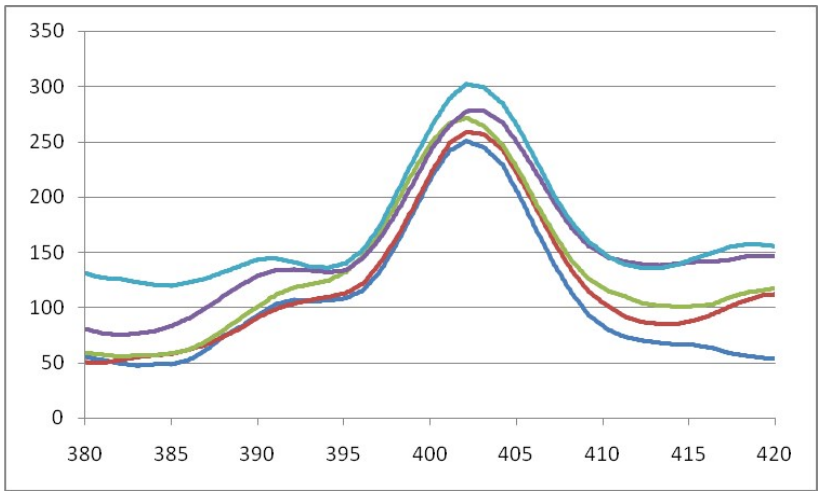
Fluorescence Quenching Studies

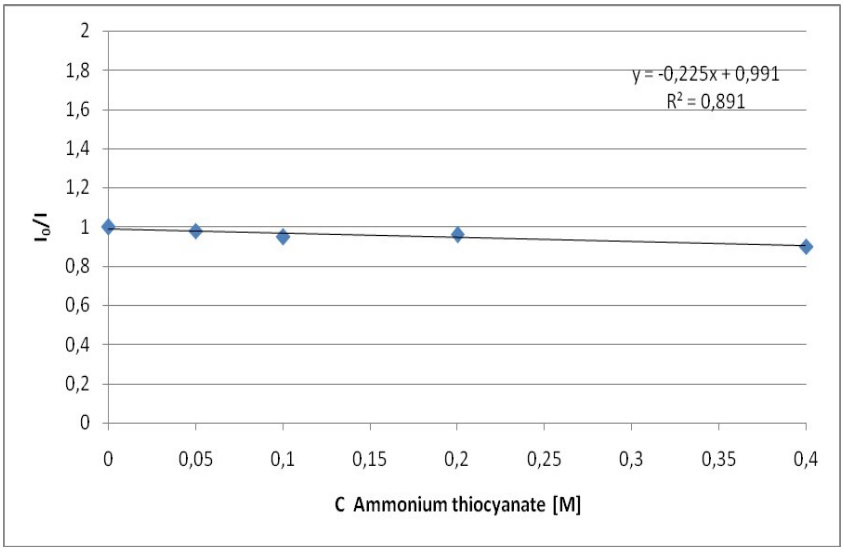
After irradiation of phenylglyoxylic acid (10^{-3} M in MeCN) at 360 nm, its fluorescence was measured at 402 nm. Increasing the amount of the added mixture of ammonium thiocyanate and benzyl mercaptan, a constant decrease in the fluorescence was observed.

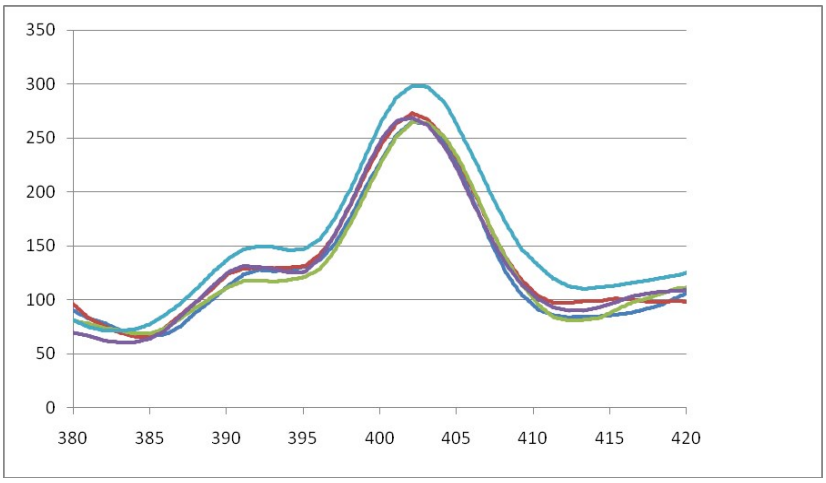


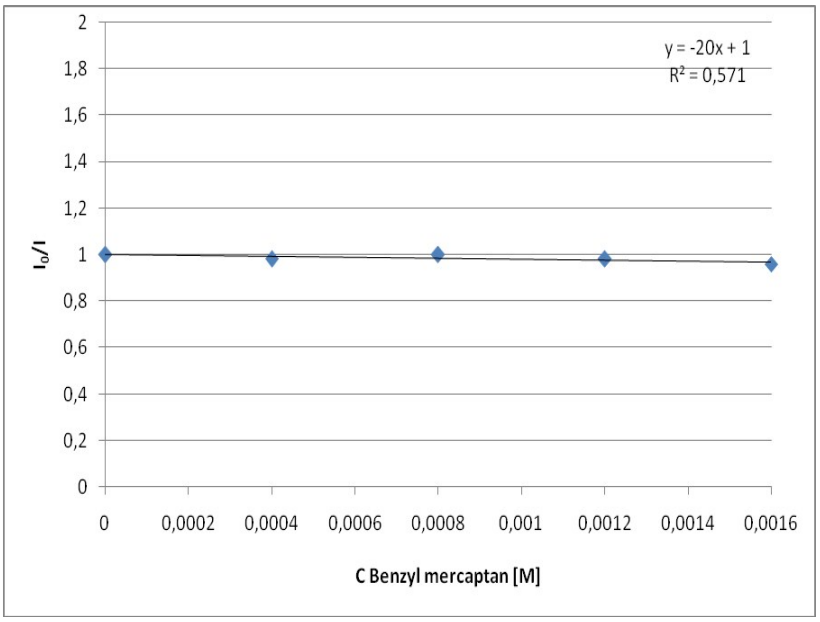


Similarly, fluorescence quenching experiments took place with ammonium thiocyanate and benzyl mercaptan.



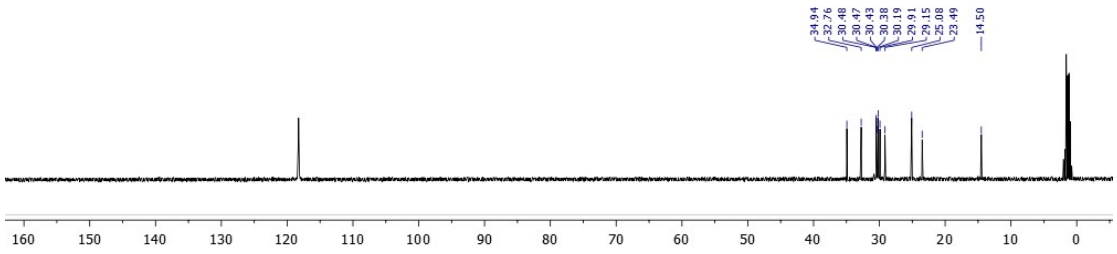



350
300
250
200
150
100
50
0
380
385
390
395
400
405
410
415
420

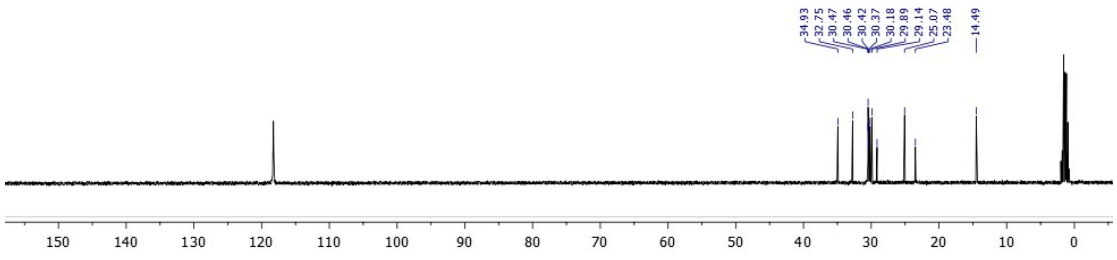

y = -20x + 1
R² = 0,571
I0/I
2
1,8
1,6
1,4
1,2
1
0,8
0,6
0,4
0,2
0
0
0,0002
0,0004
0,0006
0,0008
0,001
0,0012
0,0014
0,0016
C Benzyl mercaptan [M]

^{13}C-NMR Mechanistic Experiments

The ^{13}C-NMR spectra of dodecanethiol in CD_3CN were recorded before and after irradiation for 7 h.

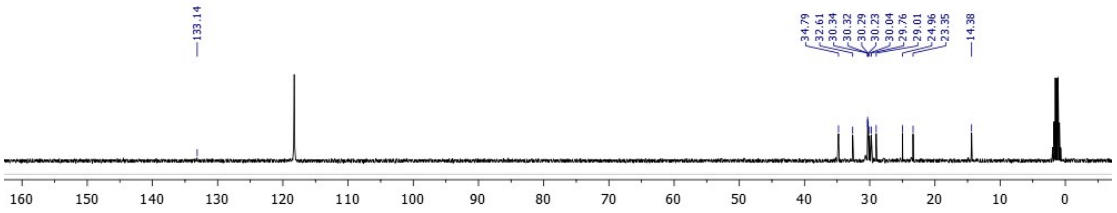


^{13}C-NMR spectrum of dodecylthiol in CD_3CN

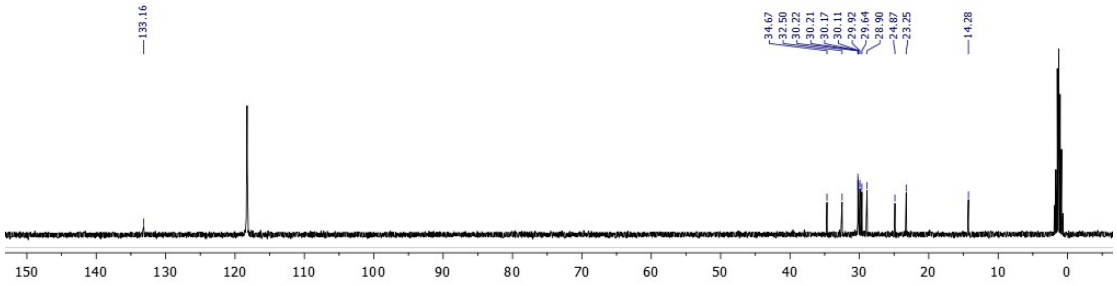


^{13}C-NMR spectrum of dodecylthiol in CD_3CN, after irradiation for 7 h in CD_3CN

^{13}C-NMR spectra in CD_3CN of dodecylthiol and ammonium thiocyanate, before and after irradiation for 7 h.

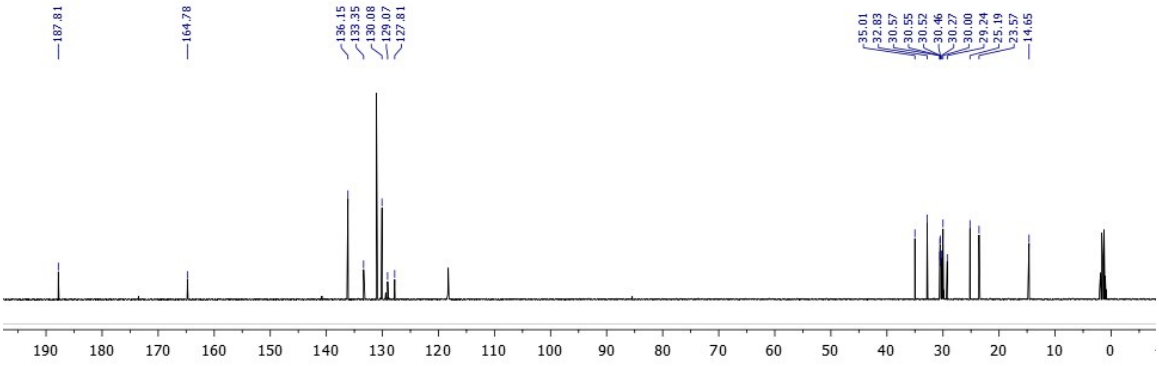


^{13}C-NMR spectrum of dodecylthiol and ammonium thiocyanate in CD_3CN

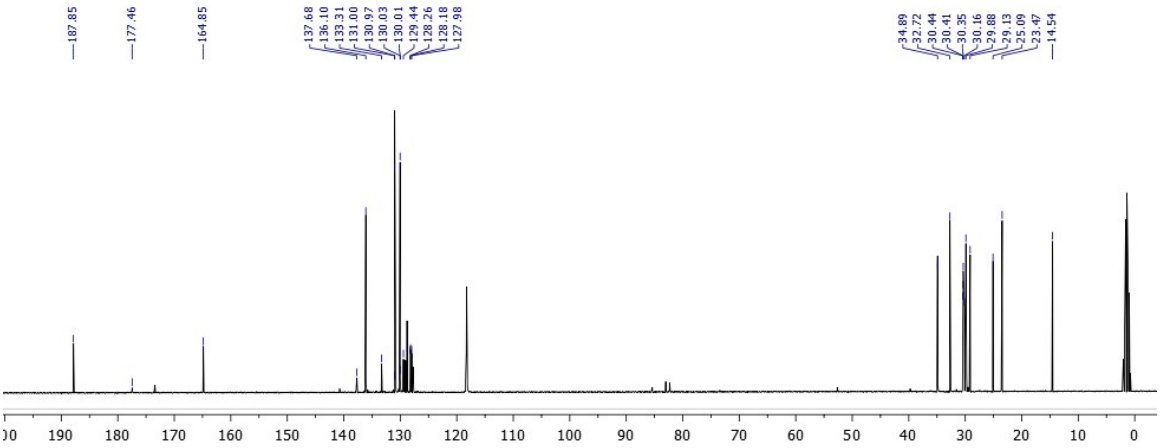


^{13}C-NMR spectrum of dodecylthiol and ammonium thiocyanate in CD_3CN, after irradiation for 7 h

^{13}C-NMR spectra in CD_3CN of dodecylthiol and phenylglyoxylic acid, before and after irradiation for 7 h.

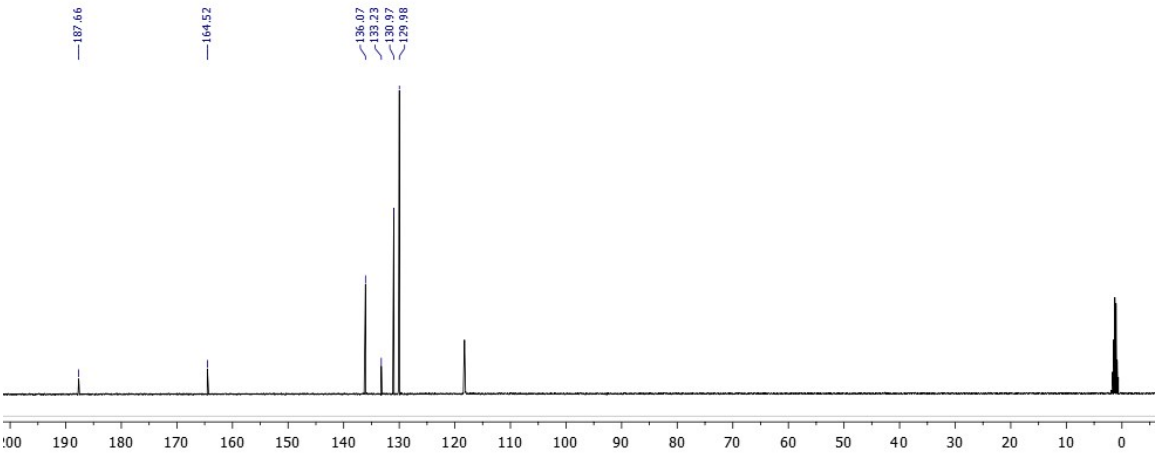


^{13}C-NMR spectrum of dodecylthiol and phenylglyoxylic acid in CD_3CN

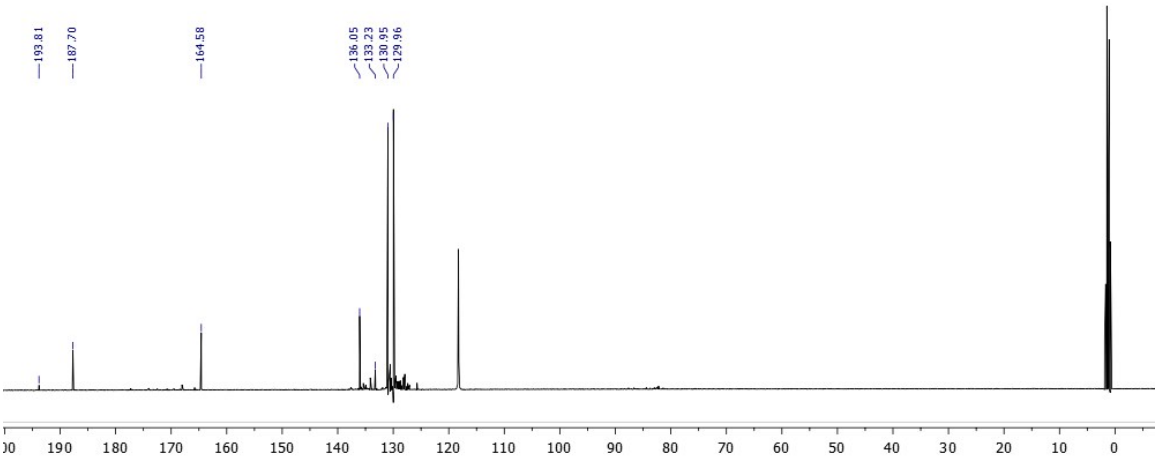


^{13}C-NMR spectrum of dodecylthiol and phenylglyoxylic acid in CD_3CN, after irradiation for 7 h

^{13}C-NMR spectra in CD_3CN of PhCOCOOH, before and after irradiation for 7 h were recorded. After irradiation, photodecomposition to benzaldehyde is observed (193.8 ppm).

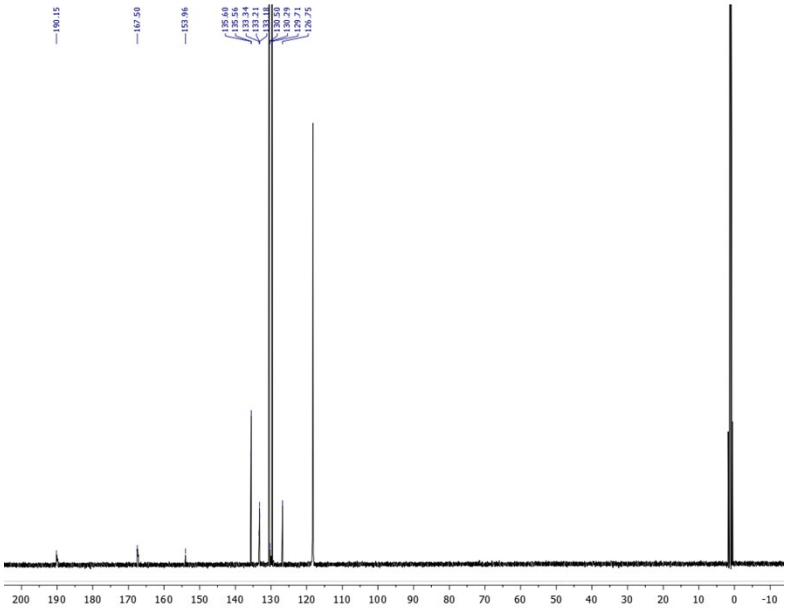


^{13}C-NMR spectrum of phenylglyoxylic acid in CD_3CN

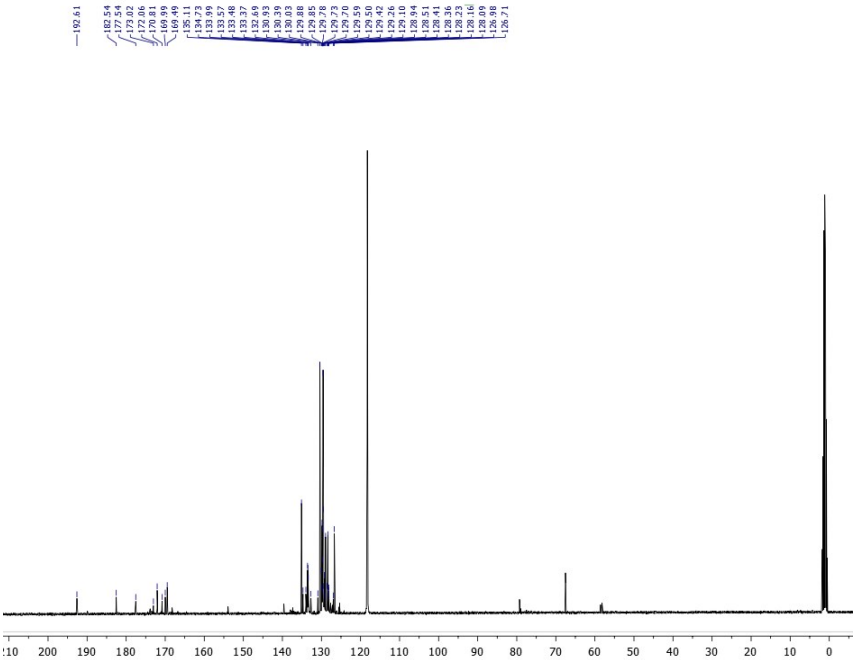


^{13}C-NMR spectrum of phenylglyoxylic acid in CD_3CN, after irradiation for 7 h

^{13}C-NMR spectra in CD_3CN of phenylglyoxylic acid and ammonium thiocyanate, before and after irradiation for 7 h were recorded. Salt formation (PhCOCOOH with NH_4SCN) is observed. Faster photodecomposition to benzaldehyde (192.6 ppm) is also occurring, along with other products.

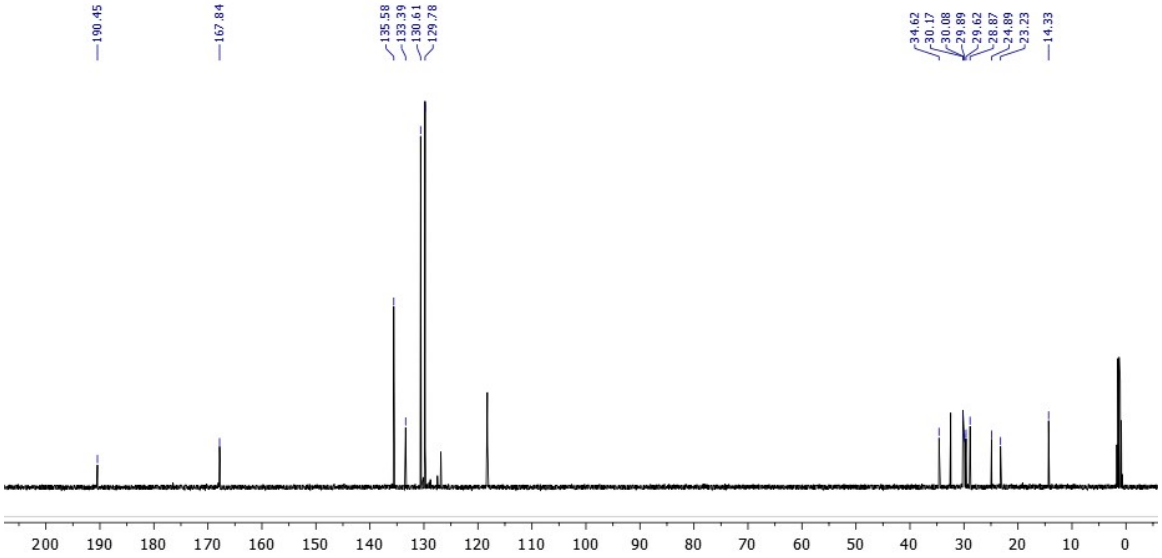


^{13}C-NMR spectrum of phenylglyoxylic acid and ammonium thiocyanate in CD_3CN

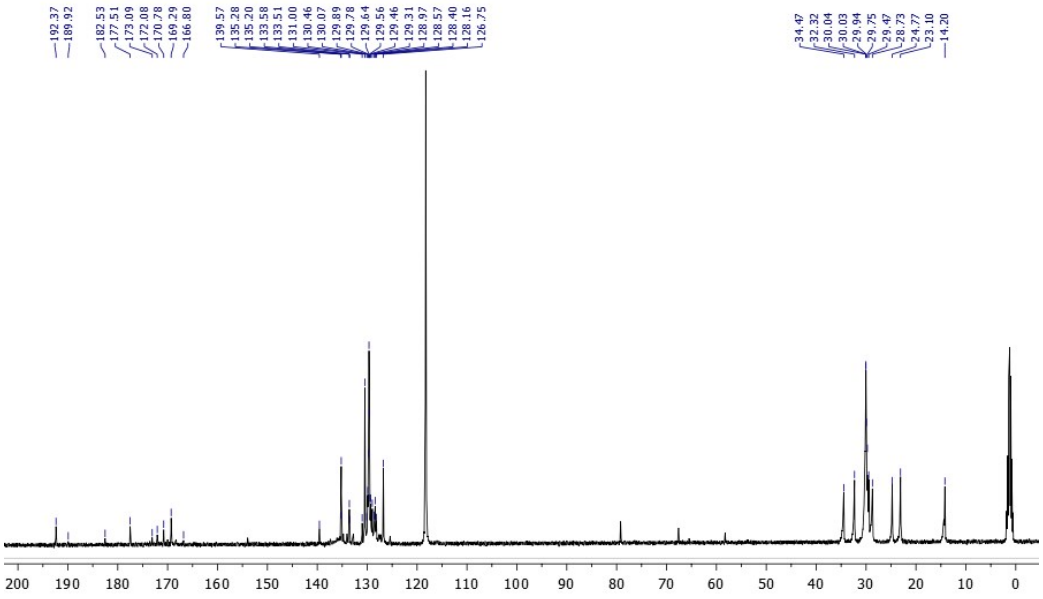


^{13}C-NMR spectrum of phenylglyoxylic acid and ammonium thiocyanate in CD_3CN, after irradiation for 7 h

Finally, the reaction mixture (dodecylthiol, phenylglyoxylic acid and ammonium thiocyanate) (in CD_3CN) presented all expected signals. As it was expected after 7 h of irradiation of the reaction, photodecomposition of PhCOCOOH (192.4 ppm) to benzaldehyde was observed and the product has also formed.



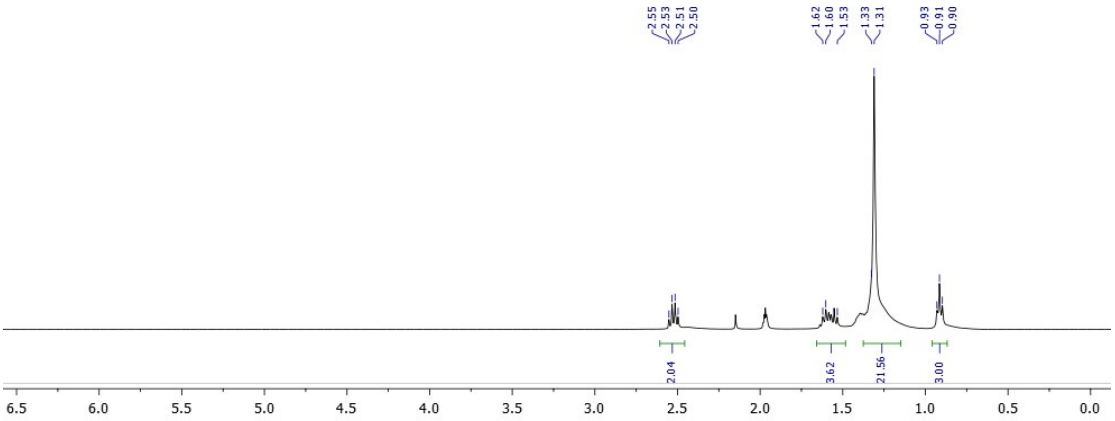
^{13}C NMR spectrum of the reaction mixture in CD_3CN



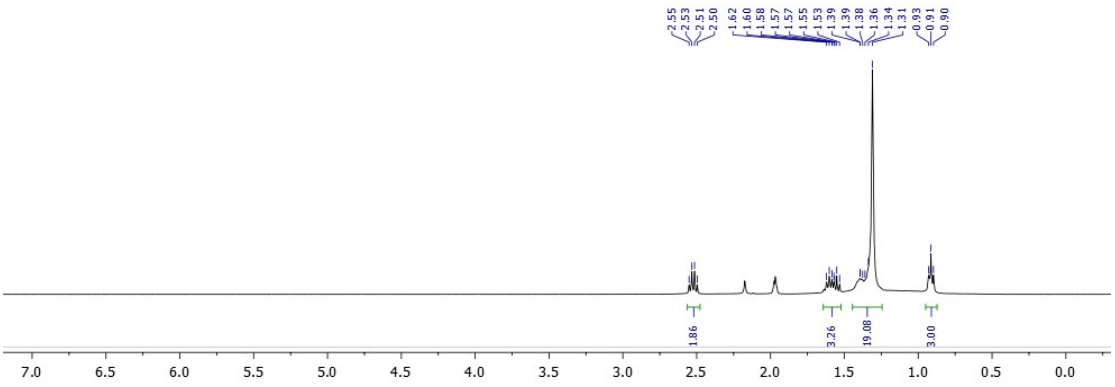
^{13}C NMR spectrum of the reaction mixture in CD_3CN, after irradiation for 7 h

^{1}H-NMR Mechanistic Experiments

The ^{1}H-NMR spectra of dodecylthiol in CD_3CN were recorded before and after irradiation for 7 h

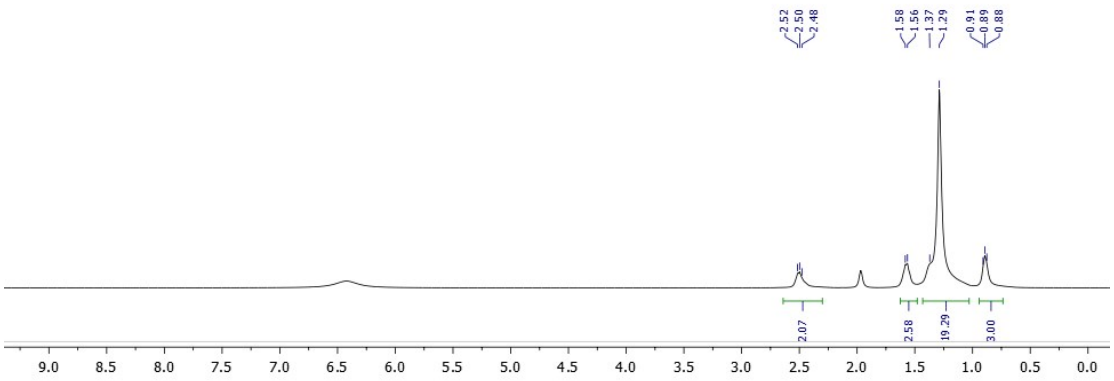


^{1}H NMR spectrum of dodecylthiol in CD_3CN

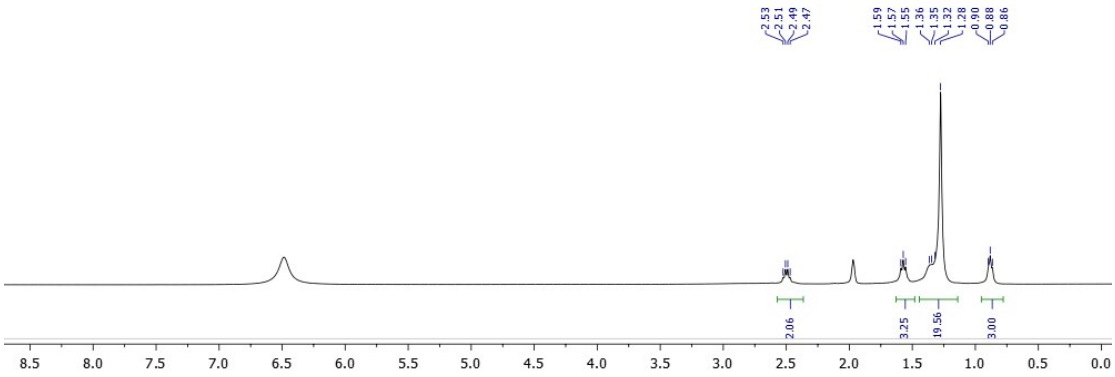


^{1}H NMR spectrum of dodecylthiol in CD_3CN, after irradiation for 7 h

^{1}H-NMR spectra in CD_3CN of dodecylthiol and ammonium thiocyanate, before and after irradiation for 7 h were recorded.

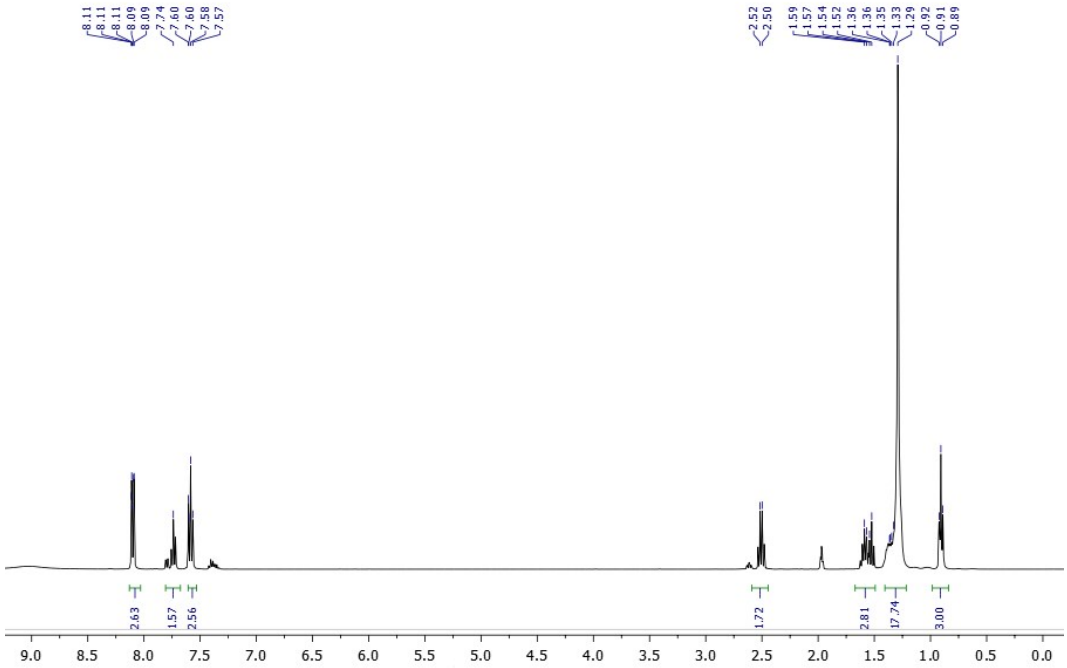


^{1}H NMR spectrum of dodecylthiol and ammonium thiocyanate in CD_3CN

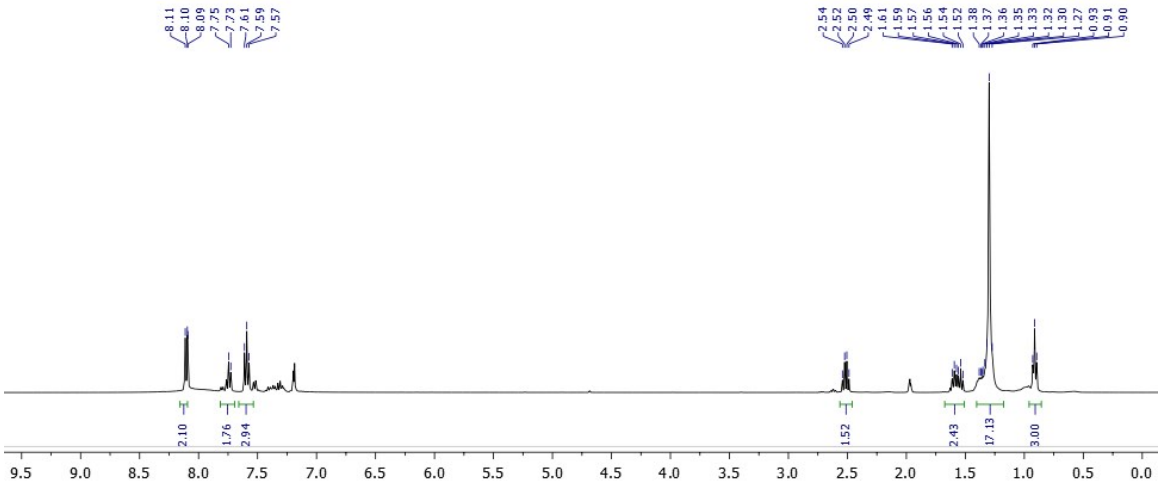


^{1}H NMR spectrum of dodecylthiol and ammonium thiocyanate in CD_3CN, after irradiation for 7 h

^{1}H-NMR spectra in CD_3CN of dodecylthiol and phenylglyoxylic acid, before and after irradiation for 7 h were recorded.

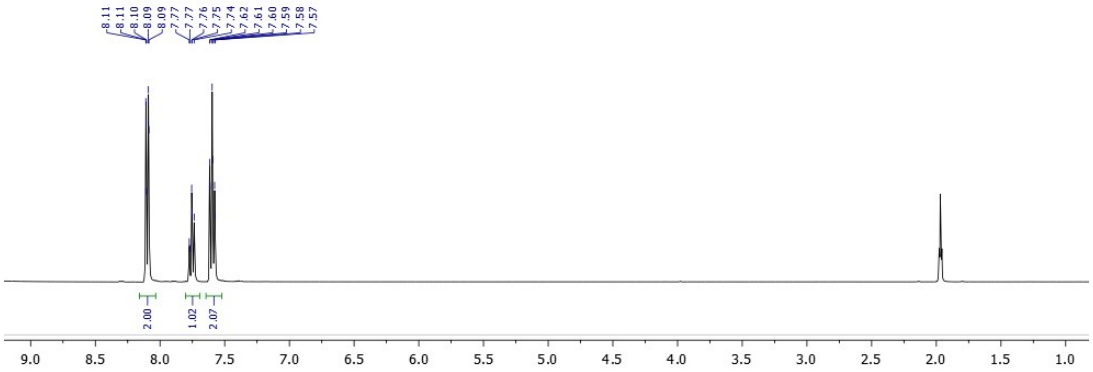


^{1}H NMR spectrum of dodecylthiol and phenylglyoxylic acid in CD_3CN

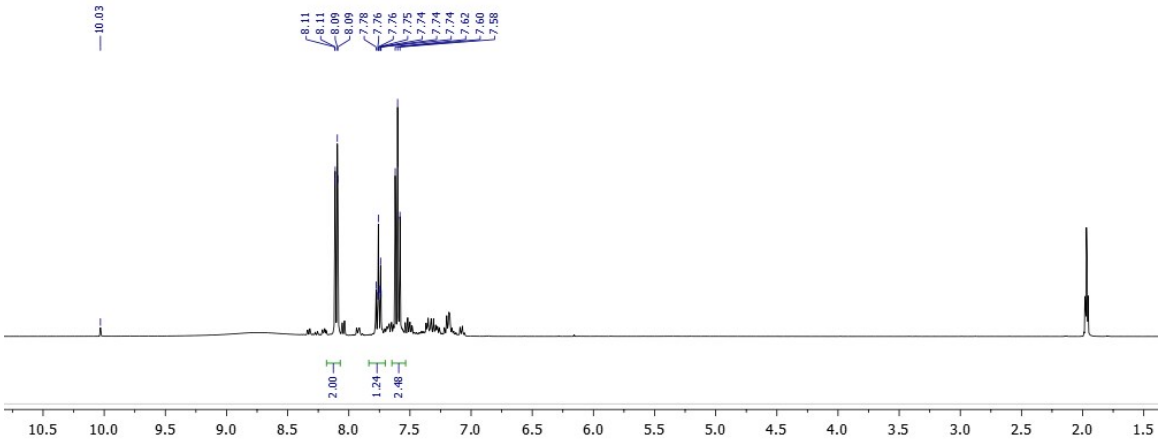


^{1}H NMR spectrum of dodecylthiol and phenylglyoxylic acid in CD_3CN, after irradiation for 7 h

^{1}H-NMR spectra in CD_3CN of phenylglyoxylic acid, before and after irradiation for 7 h were recorded. Photodecomposition of PhCOCOOH to benzaldehyde (10.03 ppm) is observed.

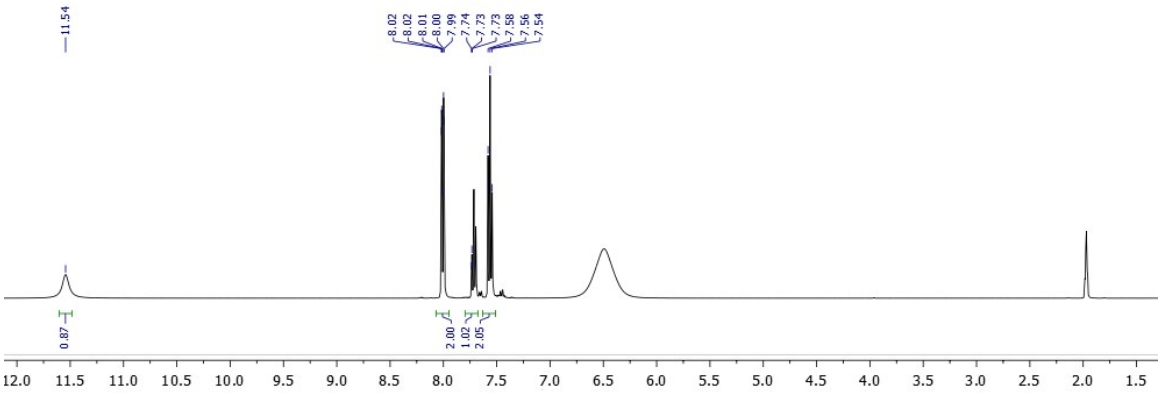


^{1}H-NMR spectra of phenylglyoxylic acid in CD_3CN

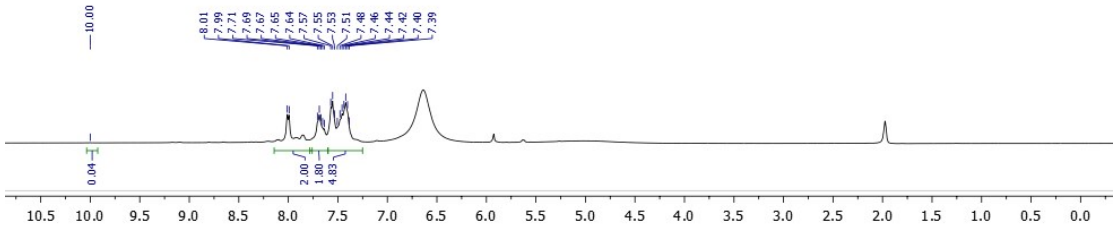


^{1}H NMR spectrum of phenylglyoxylic acid in CD_3CN, after irradiation for 7 h

^{1}H-NMR spectra in CD_3CN of phenylglyoxylic acid and ammonium thiocyanate, before and after irradiation for 7 h were recorded. Photodecomposition of PhCOCOOH to benzaldehyde (10.00 ppm) is observed.

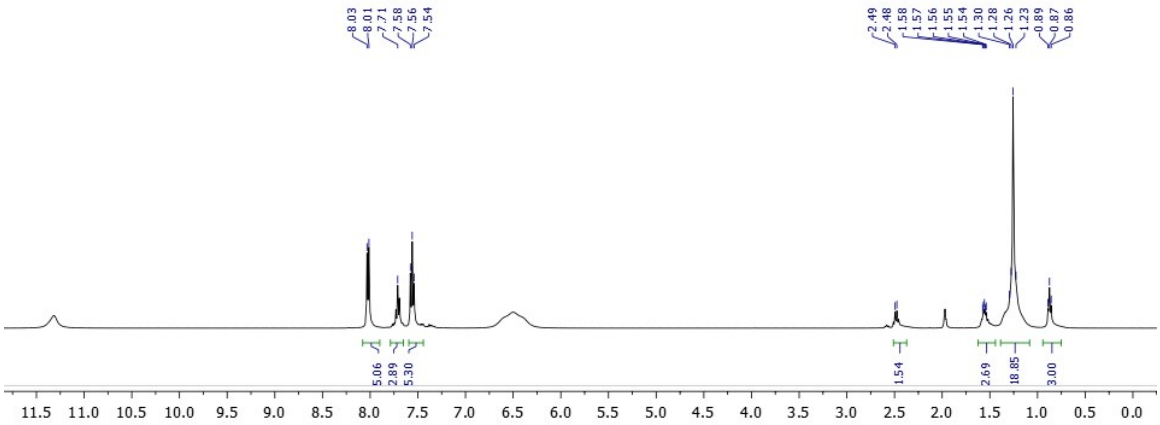


^{1}H NMR spectrum of phenylglyoxylic acid and ammonium thiocyanate in CD_3CN

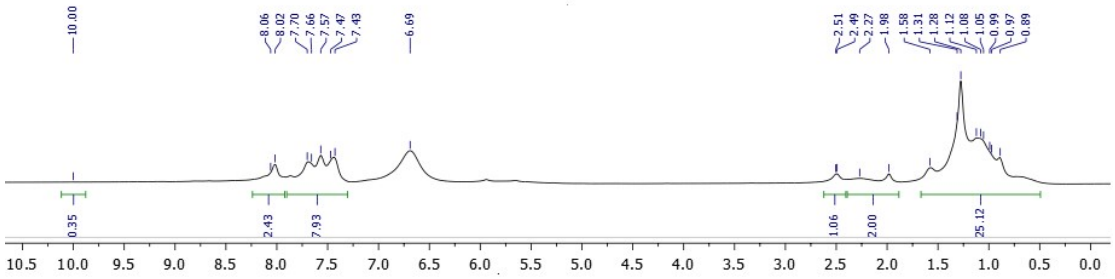


^{1}H NMR spectrum of phenylglyoxylic acid and ammonium thiocyanate in CD_3CN after irradiation for 7 h

Finally, the reaction mixture (dodecylthiol, phenylglyoxylic acid and ammonium thiocyanate) (in CD_3CN) presented all expected signals. As it was expected after 7 h of irradiation of the reaction, photodecomposition of PhCOCOOH to benzaldehyde (10.00 ppm) is observed.



^{1}H NMR spectrum of the reaction mixture in CD_3CN



^{1}H NMR spectrum of the reaction mixture in CD_3CN after irradiation for 7 h

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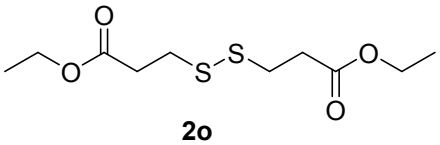

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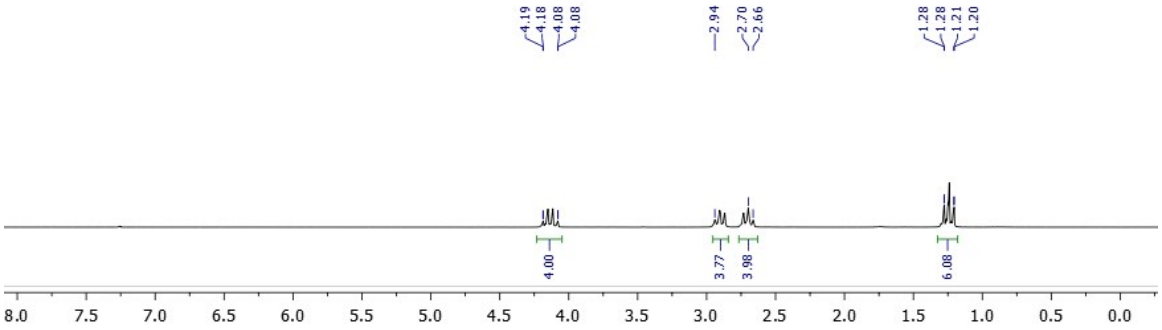
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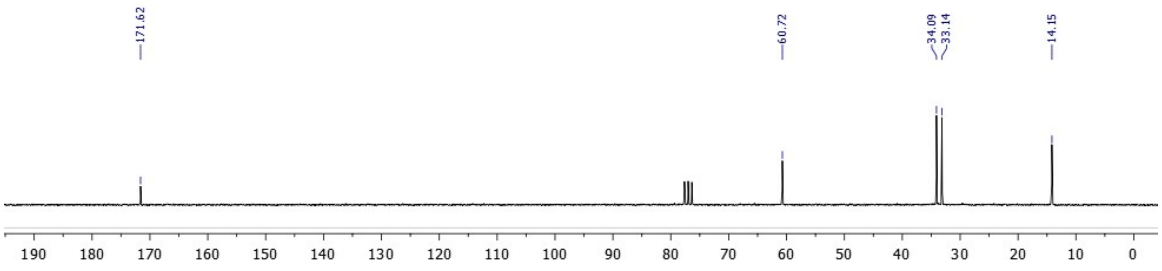
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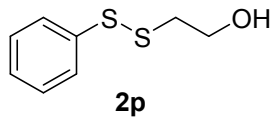
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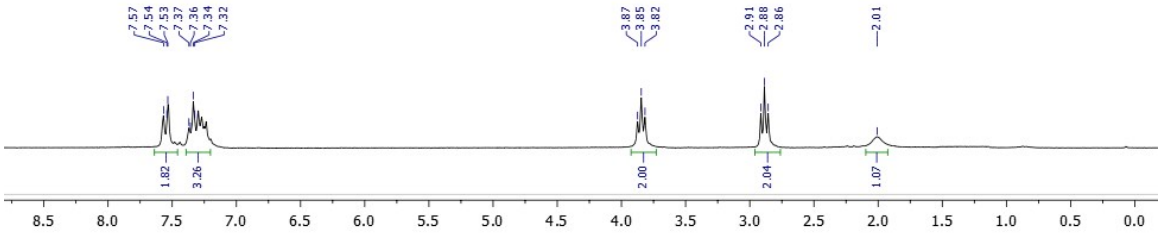
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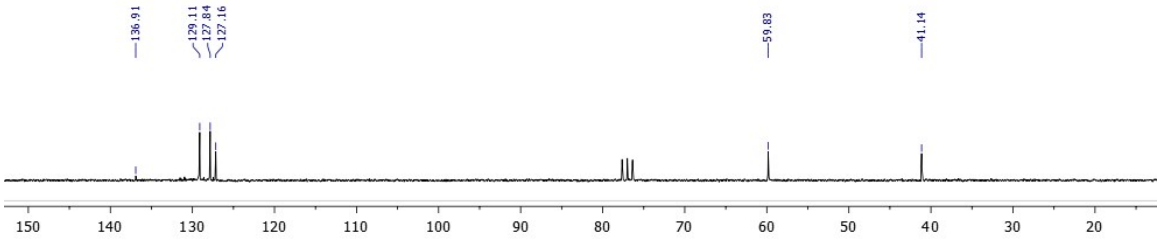
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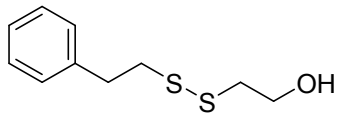
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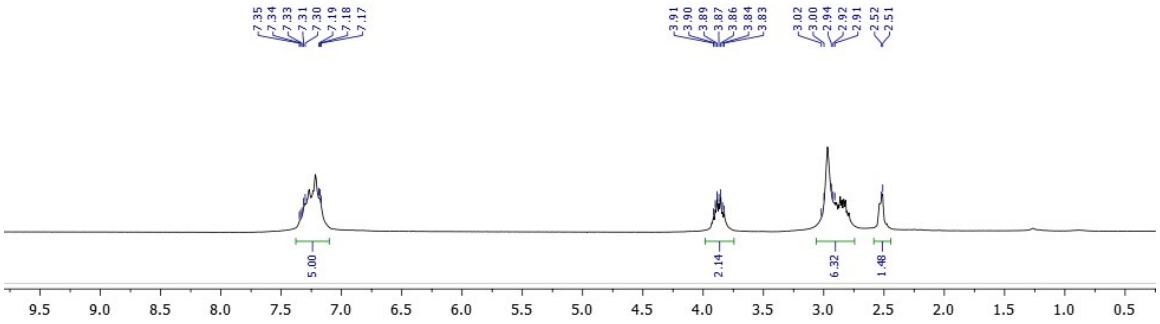
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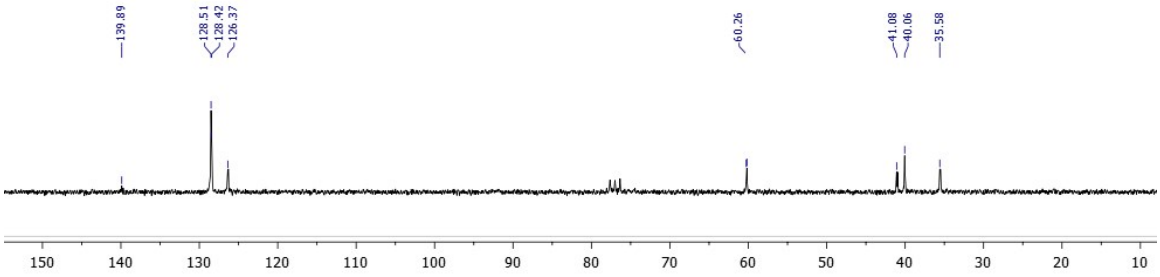
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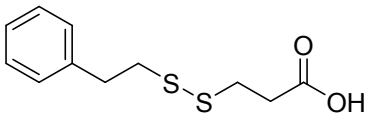
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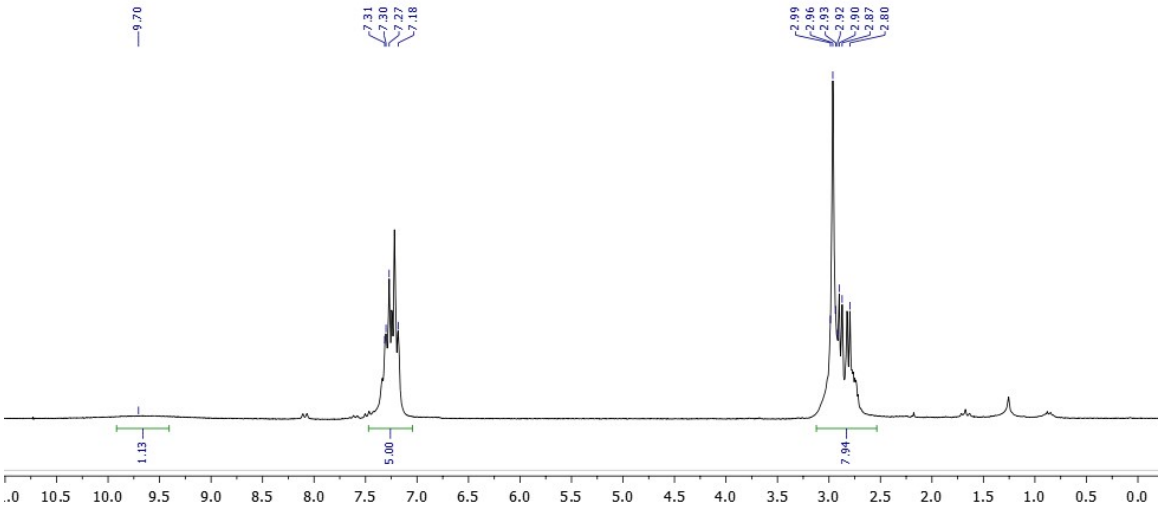
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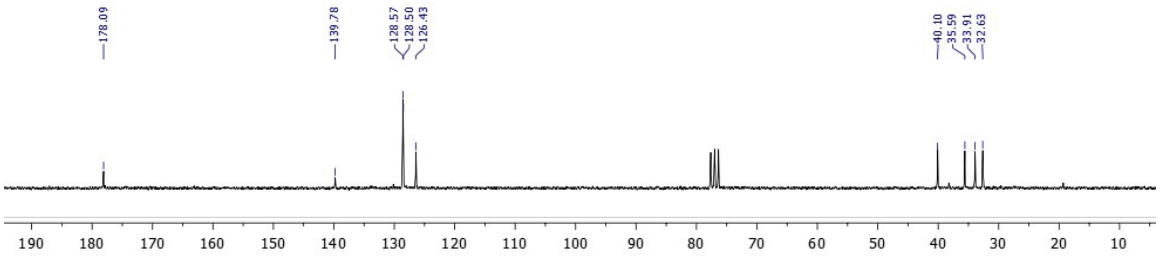
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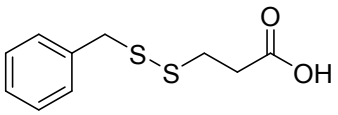
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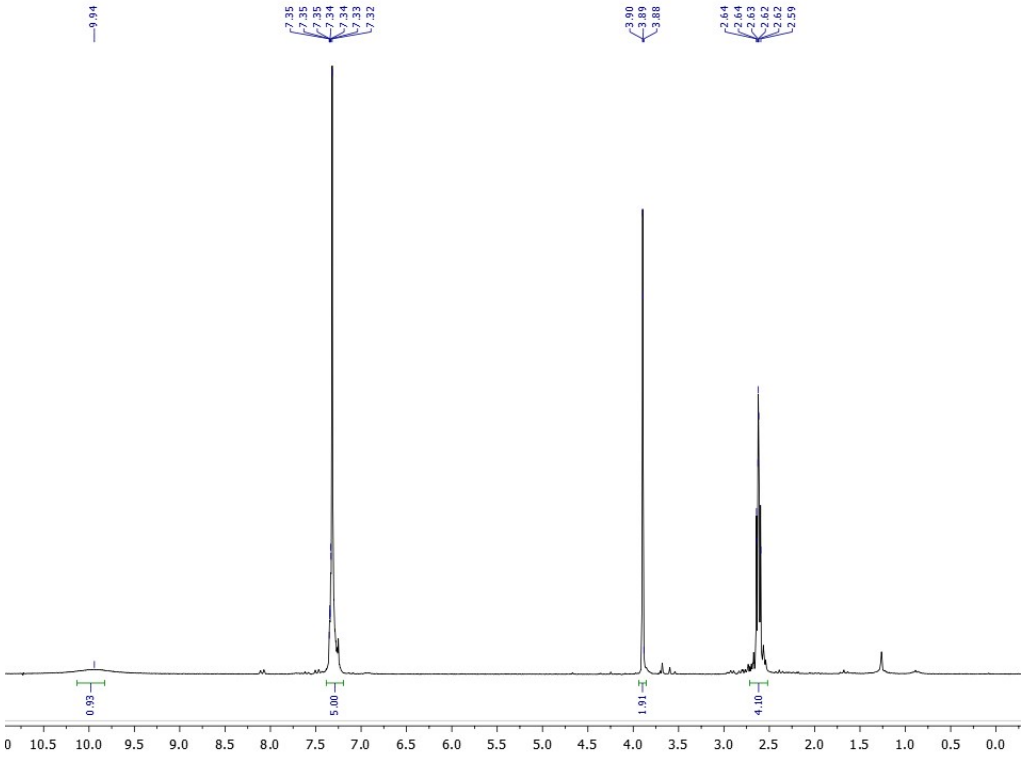
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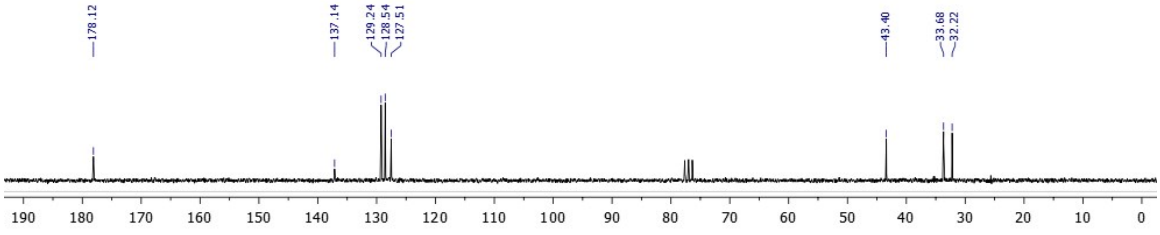
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