# Supporting Information
# for

# Synthesis of aryl sulfides via radical–radical cross coupling of electron-rich arenes using visible light photoredox catalysis

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## Experimental details, LFP data and NMR spectra of all compounds

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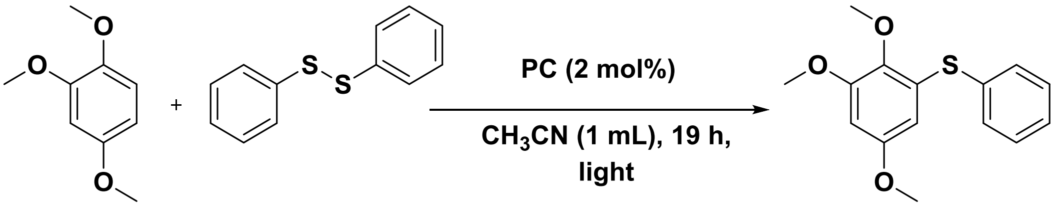
# General information

Solvents and reagents were obtained from commercial sources and used without further purification. Spectroscopic grade DMF and DMSO were dried with 3 Å molecular sieves according to a reported procedure.[1] $[Ir(dF(CF_3)ppy)_2(dtbbpy)]PF_6$ was synthesized according to the general procedure.[2] Proton NMR spectra were recorded on a Bruker Avance 300 MHz spectrometer and 600 MHz spectrometer in $CDCl_3$ solution with internal solvent signal peak at 7.26 ppm. Carbon NMR were recorded at 75 MHz spectrometer and 151 MHz spectrometer in $CDCl_3$ solution and referenced to the internal solvent signal at 77.26 ppm. Proton NMR data are reported as follows: chemical shift (ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, dd = doublet of doublets, ddd = doublet of doublet of doublets, td = triplet of doublets, qd = quartet of doublets, m = multiplet, br. s. = broad singlet), and coupling constants (Hz). High resolution mass spectra (HRMS) were obtained from the central analytic mass spectrometry facilities of the Faculty of Chemistry and Pharmacy, Regensburg University and are reported according to the IUPAC recommendations 2013. All reactions were monitored by thin-layer chromatography using Merck silica gel plates 60 F254; visualization was accomplished with short wave length UV light (254 nm). UV–Vis and fluorescence measurements were performed with Varian Cary 50 UV–vis spectrophotometer and FluoroMax-4 spectrofluorometer, respectively. For laser flash experiments, UV–vis spectra were recorded using an analytikjena SPECORD 5 PLUS spectrometer. Laser-flash photolysis (LFP) experiments were conducted with a Nd:YAG-laser (Continuum, Surelight SL I-10) using its third harmonics (355 nm, 58 mW and 40 mW output) and an "Applied Photophysics" spectrometer with monochromator and 5 stage photomultiplier. Digitalization was achieved with a Tektronix MDO 3034 Oscilloscope (50 Ω for ns time-scales and 1 kΩ for μs time-scales). The system was operated with the Applied Photophysics kinetic workbench program "Pro-Data LKS" (version 3.0.1). The probe and pulse light were arranged in an orthogonal setup. Transient spectra were recorded with 10 000 data points in the range from 300 nm to 620 nm, omitting the area of the pump wavelength (340–370 nm) and with a spectral resolution of 5 nm. All recordings of transient spectra were done performing four independent runs of the same sample that were then averaged. Kinetic traces were obtained by using an automated base line correction "internal dual" settings with four averages.

Spectra were analyzed and converted using the “Pro-Data Viewer” software. For further analysis of transient spectra and kinetics Origin 2017 was used. Experiments were conducted in acetonitrile (Acros, “extra dry”) in a sealed, nitrogen flushed quartz cuvette with glass neck (10 mm by 10 mm). The solvent was analyzed by UV–vis spectroscopy and under the described LFP conditions to ensure its optical purity. Electrochemical studies were carried out under argon atmosphere. The measurements were performed in dimethylformamide (DMF) containing 0.1 M tetra-*n*-butylammonium tetrafluoroborate using ferrocene/ferrocenium (Fc/Fc+) as an internal reference. A glassy carbon electrode (working electrode), platinum wire (counter electrode), and silver wire (quasi-reference electrode) were employed. Spectroelectrochemical studies were carried out in an optically transparent thin layer electrochemical cell (OTTLE). Suitable crystals were selected and mounted on a MITIGEN holder oil on a GV1000/SuperNova, TitanS2 diffractometer or Atlas diffractometer. Using **Olex2**[3], the structure was solved with the **ShelXT**[4] structure solution program, using the Intrinsic Phasing solution method. The model was refined with ShelXL using Least Squares minimisation. Standard flash chromatography was performed using silica gel of particle size 40−63 µm using petroleum ether (boiling range: 42–62 °C) and ethylacetate (boiling point: 77.1°C) as the eluent. Photoreduction and annulation reactions were performed with 455 nm LEDs (OSRAM Oslon SSL 80 royal-blue LEDs ($\lambda$ = 455 nm (± 15 nm), 3.5 V, 700 mA).

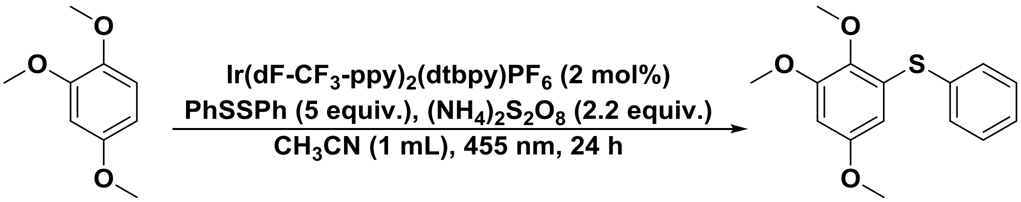
# Optimization reactions and control experiments

## Table S1:



| Entry | Photocatalyst | Oxidant | Light source | Air / $N_2$ | Comments |
|---|---|---|---|---|---|
| 1 | Ir(dF-$CF_3$-ppy)$_2$(dtbpy)$^{3+}$ | $(NH_4)_2S_2O_8$ | 455 nm | $N_2$ | Full conversion to product was observed in 6 hours |
| 2 | Ir(dF-$CF_3$-ppy)$_2$(dtbpy)$^{3+}$ | air | 455 nm | air | Degradation of catalyst is observed upon irradiation |
| 3 | 4-CzIPN | air | 455 nm | air | Degradation of catalyst is observed upon irradiation |
| 4 | 4-CzIPN | $(NH_4)_2S_2O_8$ | 455 nm | $N_2$ | 30% conversion of the starting material was observed |
| 5 | Eosin Y | air | 530 nm | air | PC bleached in 2 hours |
| 6 | Eosin Y | $(NH_4)_2S_2O_8$ | 530 nm | $N_2$ | Degradation of catalyst is observed upon irradiation |
| 7 | Eosin Y-$Na_2$ | air | 530 nm | air | Degradation of catalyst is observed upon irradiation |
| 8 | Eosin Y-$Na_2$ | $(NH_4)_2S_2O_8$ | 530 nm | $N_2$ | 10% conversion of the starting material was observed |

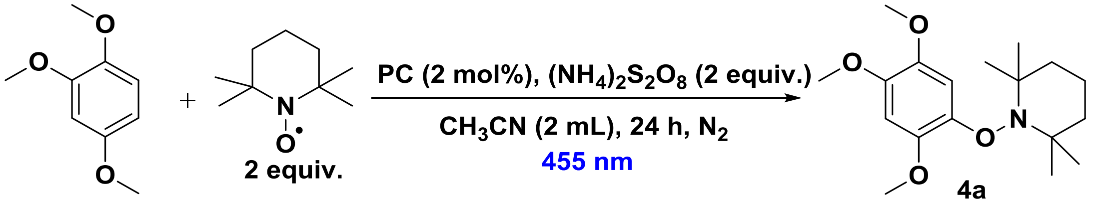
**Table S2:**



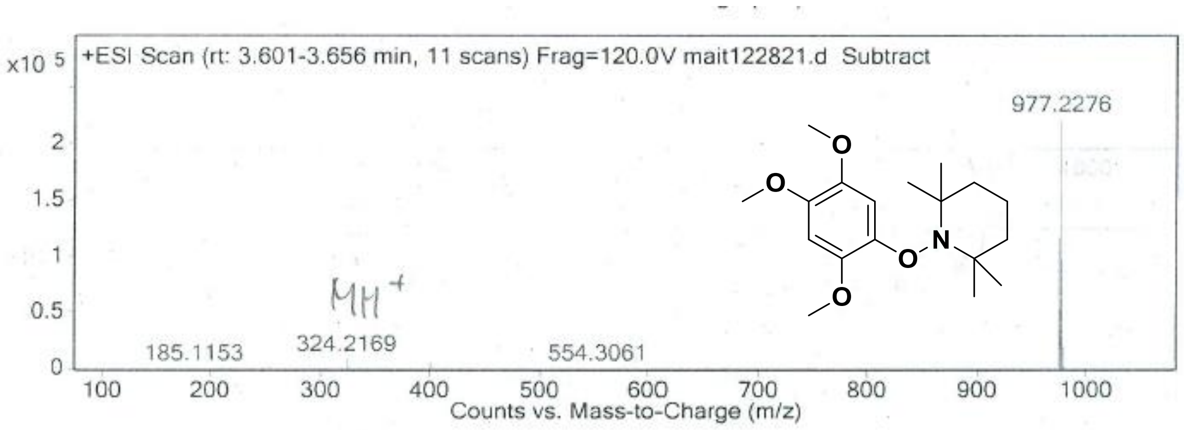
| Entry | Photocatalyst | Oxidant | $N_2$/ air | Light/ dark | Comments |
|---|---|---|---|---|---|
| 1 | ✓ | ✓ | $N_2$ | dark | Only Starting material, no conversion |
| 2 | ✓ | ✓ | $N_2$ | 455 nm | Full conversion to product |
| 3 | ✓ | ✓ | air | dark | Only Starting material, some oxidative side reactions of the disulphide, no product formation |
| 4 | ✓ | ✓ | air | 455 nm | Catalyst bleached immediately |
| 5 | ✓ | ✗ | $N_2$ | dark | Only Starting material, no conversion |
| 6 | ✓ | ✗ | $N_2$ | 455 nm | 10% conversion by GC |
| 7 | ✓ | ✗ | air | dark | Only Starting material, no conversion |
| 8 | ✓ | ✗ | air | 455 nm | Catalyst bleached immediately |

## HRMS analysis of the TEMPO adduct

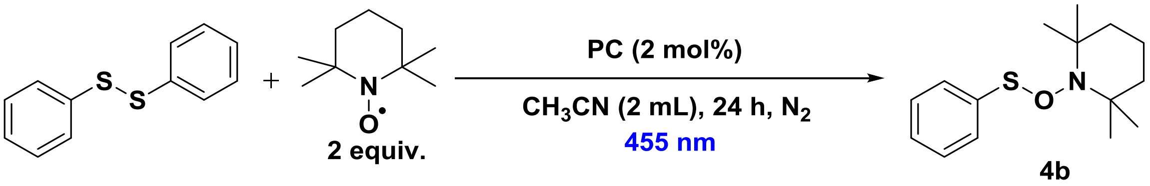
A solution of 1,2,4 trimethoxybenzene in $CH_3CN$ with 2 mol % $(Ir[dF(CF_3)ppy]_2(dtbpy))PF_6$, 2.2 equivalents $(NH_4)_2S_2O_8$ and 2 equivalents TEMPO was irradiated with a 455 nm LED under $N_2$ at 25 ºC. The reaction mixture was analyzed by HRMS, which showed the exact molecular ion indicating the formation of the proposed TEMPO adduct to the aryl radical cation intermediate.



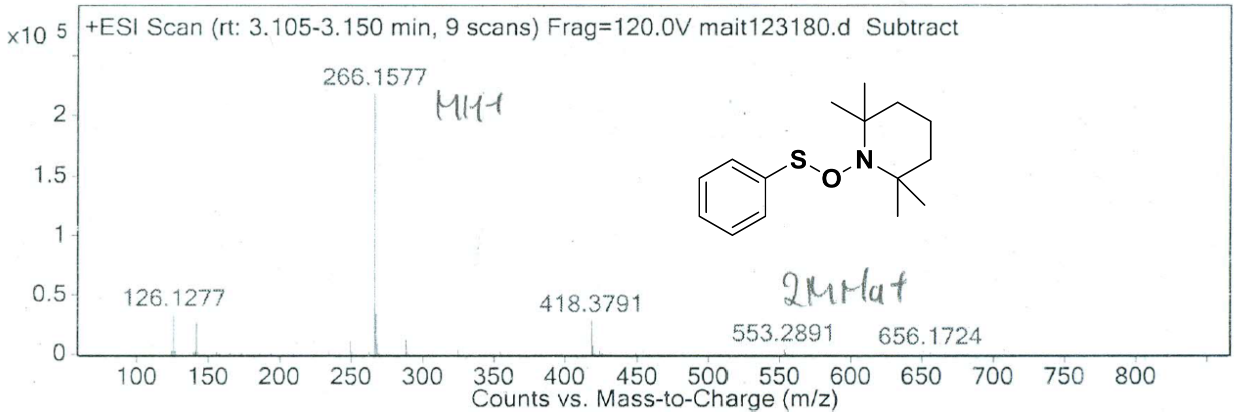
**HRMS [M+H]+** $C_{18}H_{29}NO_4$ calculated 324.2175 found 324.2169



A solution of diphenyl disulfide in $CH_3CN$ with 2 mol % $(Ir[dF(CF_3)ppy]_2(dtbpy))PF_6$ and 2 equivalents TEMPO was irradiated with a 455 nm LED under $N_2$ at 25 ºC. The reaction mixture was analyzed by HRMS, which showed the exact molecular ion indicating the formation of the proposed TEMPO adduct to the aryl radical cation intermediate.

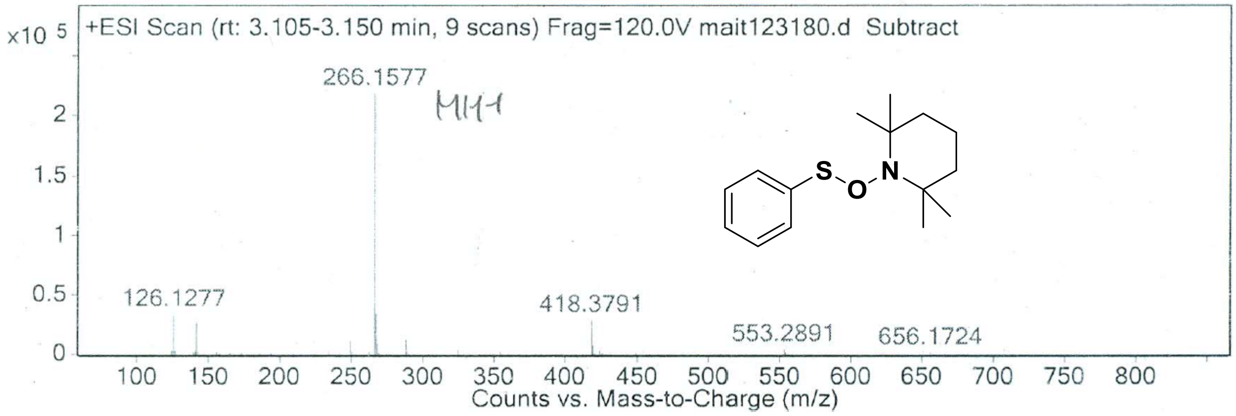


**HRMS [M+H]+** $C_{15}H_{23}NOS$ calculated 266.1579 found 266.1577



A solution of diphenyl disulfide in $CH_3CN$ and 2 equivalents TEMPO was irradiated with a 455 nm LED under $N_2$ at 25 ºC. The reaction mixture was analyzed by HRMS, which showed the exact molecular ion indicating the formation of the proposed TEMPO adduct to the aryl radical cation intermediate.

**HRMS [M+H]+** $C_{15}H_{23}NOS$ calculated 266.1579 found 266.1577



## UV–vis spectra of the catalyst and 1,3,5 trimethoxybenzene

Prior to experiments samples have been degassed by threefold execution of the freeze-pump-thaw procedure. Concentration of reagents in samples was: (Ir[dF($CF_3$)ppy]$_2$(dtbpy))$PF_6$ = $3.4 \cdot 10^{-5}$ mol/L (**solution I**) TMB = $50.5 \cdot 10^{-3}$ mol/L (**solution II**) and diphenyl disulfide = $8.1 \cdot 10^{-4}$ mol/L (**solution III**). This is equal to equivalents of 1, 1500 and 25 respectively in the reaction mixtures **A** (cat + TMB) and **B** [cat + TMB + $(PhS)_2$]. During and after measurements, ground states of the samples were confirmed *via* UV-Vis spectroscopy to ensure no change in the sample had taken place. The UV-Vis spectrum of the (Ir[dF($CF_3$)ppy]$_2$(dtbpy))$PF_6$-catalyst (cat, **Figure 1**) has a significant absorbance at 355 nm mandatory for the LFP experiments. 1,3,5-Trimehoxybenzene (TMB) is transparent at the pump wavelength and hence could be used in high excess (1500 equiv). The absorption spectrum of the mixture of catalyst and TMB was equal to the catalyst spectrum. Although diphenyl disulfide does not absorb significantly at the pump wavelength (355 nm) a change in the UV-vis spectrum occurred due to the LFP experiments even without catalyst and substrate.

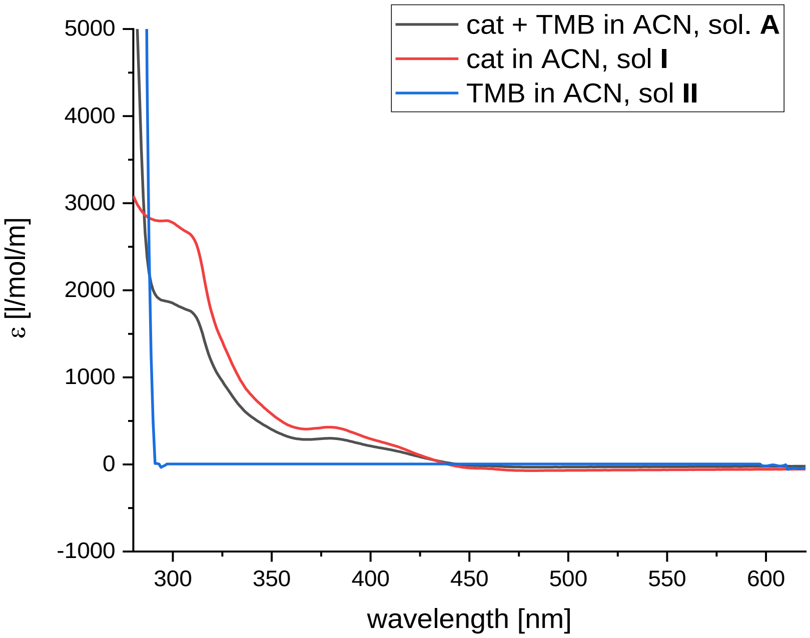


**Figure S1:** UV–vis of single components: catalyst, 1,3,5-TMB and mixture **A** (cat + 1500 equiv 1,3,5-TMB) in degassed acetonitrile.

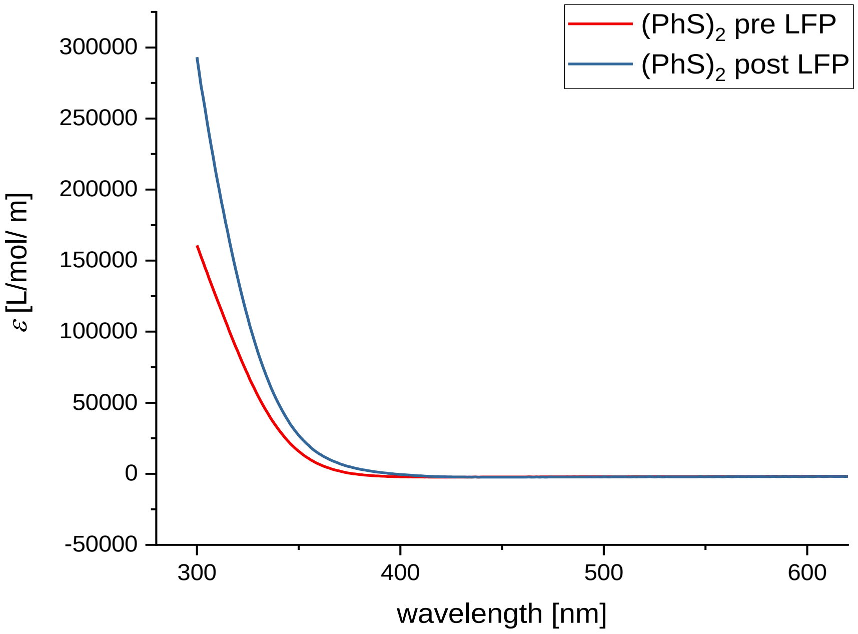


**Figure S2:** UV–vis spectra of diphenyl disulfide in degassed acetonitrile before (red line) and after (blue line) single laser flash experiment.

## Laser flash photolysis experiments

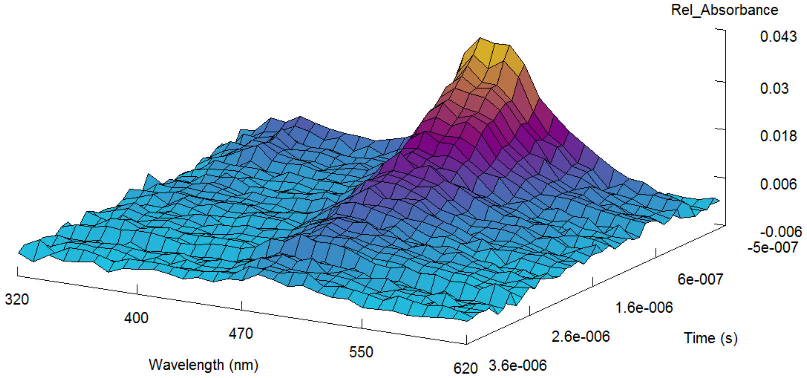


**Figure S3:** Spectra kinetics (400 ps/div), catalyst solution **I**.

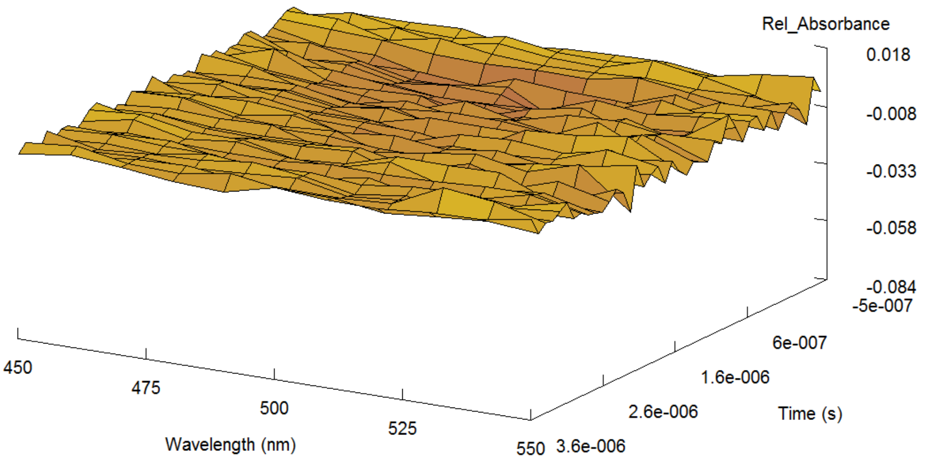


**Figure S4:** Spectra kinetics (400 ps/div), 1,3,5-TMB solution **II**.

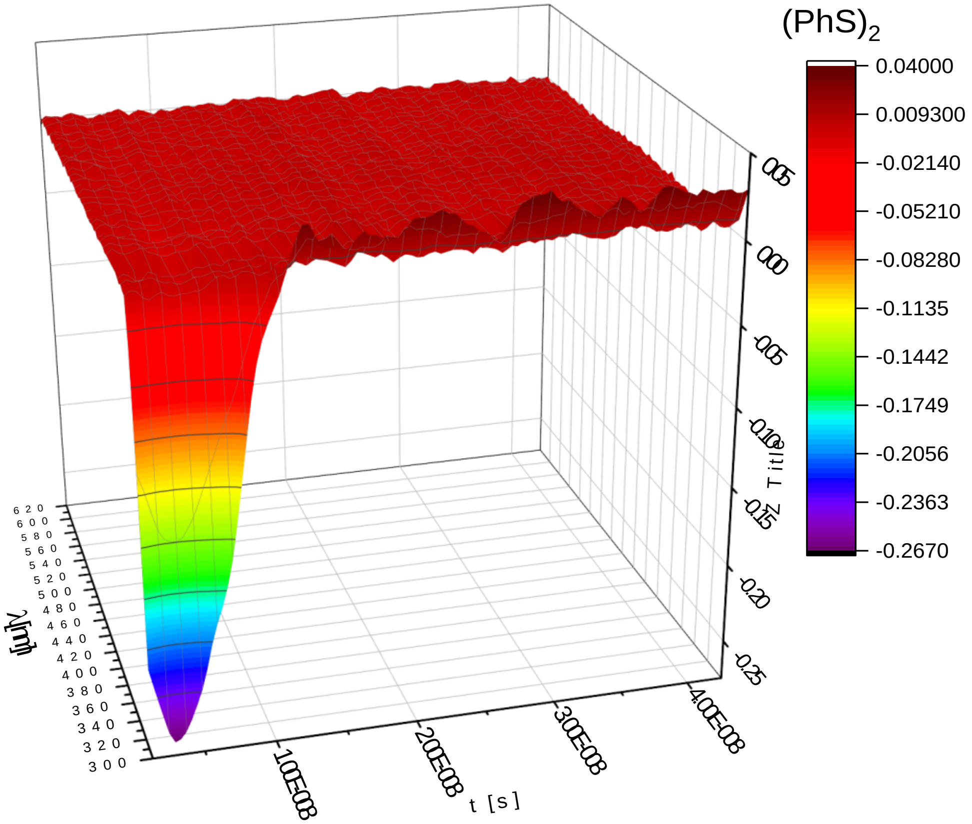


**Figure S5:** Spectra kinetics (400 ps/div), $(PhS)_2$ solution **III**.

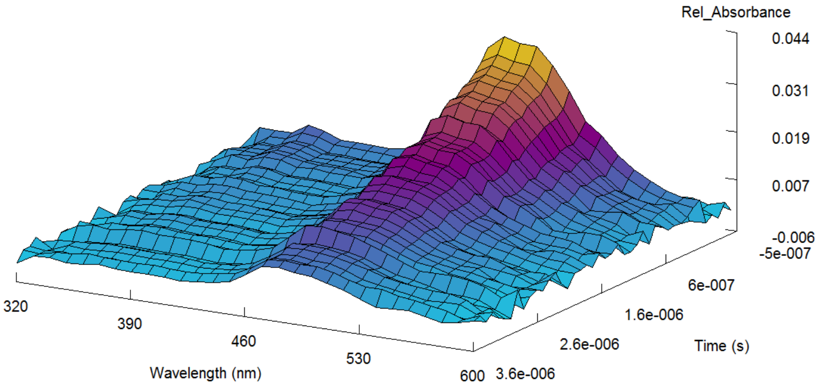


**Figure S6:** Spectra kinetics (400 ps/div), solution **A**.

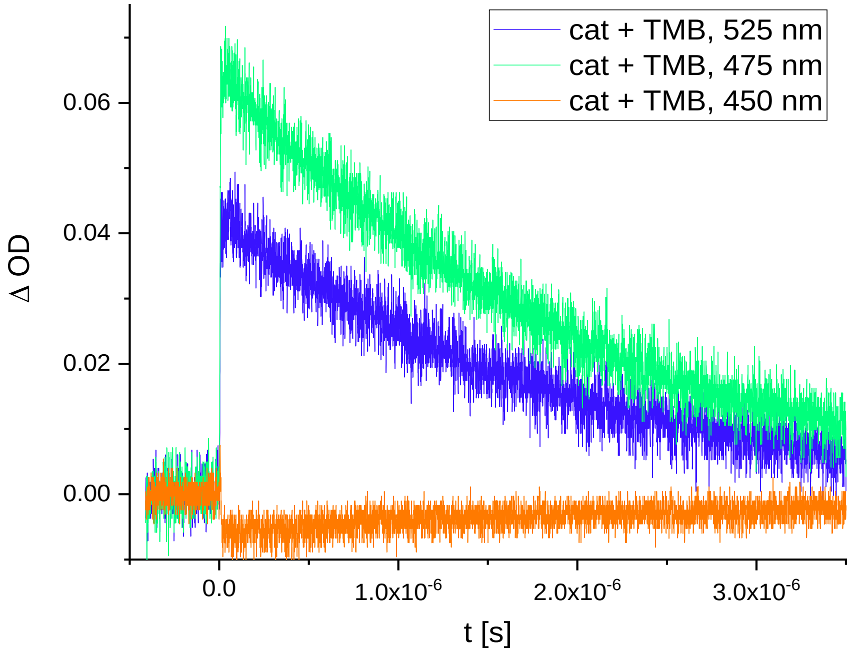


**Figure S7:** Kinetic traces recorded of (Ir[dF($CF_3$)ppy]$_2$(dtbpy))$PF_6$ - TMB mixture at 450 nm, 475 nm and 525 nm in degassed ACN (solution **A**) with 400 ps /div.

**Figure S6** and S**7** show the differences at the indicative wavelength for transient species. At 475 nm the maximum of the TMB•+ is observed leading to a higher change in optical density in solution **A** compared to solution **I**. The half-life of TMB•+ was determined of the decay traces in **Figure S8** to be 2.2 µs which is comparable to what has been observed for related compounds.[3] At 525 nm only the catalyst's emission should contribute significantly to the change in optical density (Δ OD) and indeed no proper kinetic signature is observed in the kinetic trace derived of the differences spectrum at 525 nm (**Figure 9**).

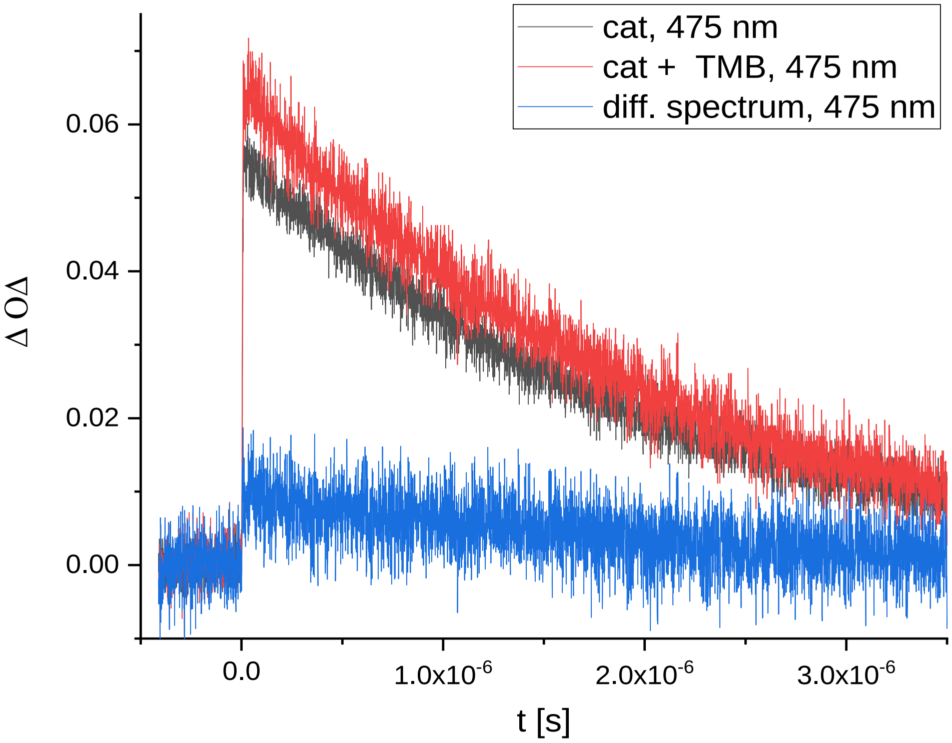


**Figure S8:** Kinetic trace at 475 nm recorded of solution **I** and **A** in degassed ACN (A) with 400 ps /div and the trace derived of subtracting the traces. Monoexponential fits of these decays were obtained: $k_\mathrm{I} = 4.86 \pm 0.04\ \mathrm{s}^{-1}$, $k_\mathrm{A} = 4.61 \pm 0.04\ \mathrm{s}^{-1}$, $k_\mathrm{Diff} = 3.2 \pm 0.2\ \mathrm{s}^{-1}$. With the latter describing the decay of TMB•+.

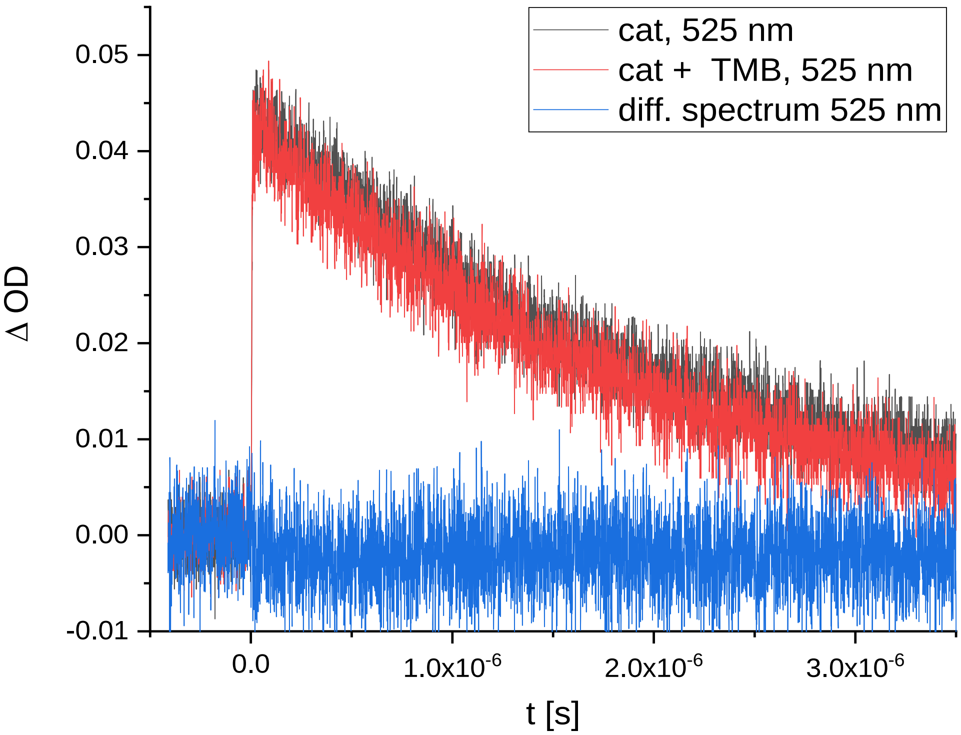
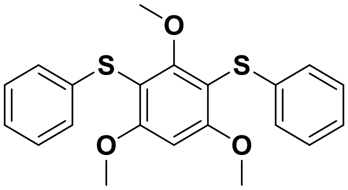


**Figure S9:** Mono-exponential fit of the kinetic trace at 525 nm recorded of Ir[dF($CF_3$)ppy]$_2$(dtbpy))$PF_6$ + TMB in degassed ACN (**A**) with 400 ps /div.

## General procedure for C–H sulfenylation

In a 5 mL snap vial with magnetic stirring bar, the arene (0.1 mmol, 1.0 equiv), the aryl disulfide (2.0 equiv), $(NH_4)_2S_2O_8$ (1.7 equiv) and $(Ir[dF(CF_3)ppy]_2(dtbpy))PF_6$ (0.002 mmol, 0.02 equiv) were added. Dry $CH_3CN$ (2.0 mL) were added under $N_2$ and the mixture was degassed by "pump-freeze-thaw" cycles (×3) via a syringe needle. This reaction mixture was irradiated through the plane bottom side of the snap vial using a 455 nm LED under nitrogen at 25 °C. The reaction progress was monitored by GC analysis. After 6 h to 24 h of irradiation, the reaction mixture was transferred to separating funnel, diluted with ethyl acetate and washed with 15 mL of water. The aqueous layer was washed three times (3 × 15 mL) with ethyl acetate. The combined organic phases were dried over $MgSO_4$, filtered and concentrated in vacuum. Purification of the crude product was achieved by flash column chromatography using petrol ether/ethyl acetate as eluent.

### Synthesis of (2,4,6-trimethoxy-1,3-phenylene)bis(phenylsulfane) (3a)[5]



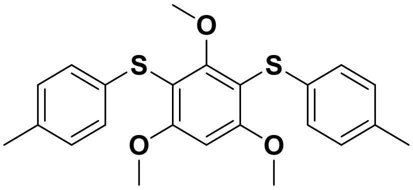
The compound was prepared according to the general procedure using 16.8 mg of 1,3,5-trimethoxybenzene, 2.2 mg of $[Ir(dF(CF_3)ppy)_2(dtbpy)]PF_6$, 43.6 mg of diphenyl disulfide, 40 mg of $(NH_4)_2S_2O_8$ and 2.0 mL dry $CH_3CN$. The reaction mixture was irradiated for 6 hours under $N_2$. Purification of the crude product was achieved by flash column chromatography using petrol ether/ethylacetate (85:15) as eluent to yield the desired compound as white solid (20.4 mg, 53%).

**$^1$H NMR** ($CDCl_3$, 300 MHz, ppm): δ 7.25-7.15 (m, 4H), 7.08-7.05 (m, 4H), 6.43 (s, 1H), 3.87 (s, 6H), 3.76 (s, 3H).

**$^{13}$C NMR** ($CDCl_3$, 75 MHz, ppm): δ 166.3, 163.7, 138.4, 128.8, 126.2, 125.0, 106.8, 92.5, 62.5, 56.5.

**HRMS [$M^{+\cdot}$]** $C_{21}H_{20}O_3S_2$ calculated 384.0848 found 384.0852.

### Synthesis of (2,4,6-trimethoxy-1,3-phenylene)bis(p-tolylsulfane) (3b)



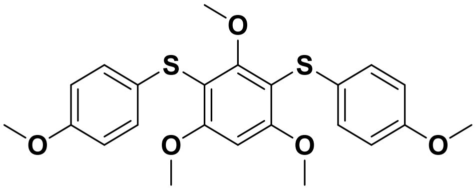
The compound was prepared according to the general procedure using 16.8 mg of 1,3,5-trimethoxybenzene, 2.2 mg of [Ir(dF(CF$_3$)ppy)$_2$(dtbpy)]PF$_6$, 49.2 mg of 1,2-di-*p*-tolyldisulfane, 40 mg of $(NH_4)_2S_2O_8$ and 2.0 mL dry $CH_3CN$. The reaction mixture was irradiated for 6 h under $N_2$. Purification of the crude product was achieved by flash column chromatography using petrol ether/ ethylacetate (85:15) as eluent to yield the desired compound as white solid (23.1 mg, 56%).

**$^1$H NMR** ($CDCl_3$, 300 MHz, ppm): δ 6.99 (s, 8H), 6.41 (s, 1H), 3.86 (s, 6H), 3.76 (s, 3H), 2.26 (s, 6H).

**$^{13}$C NMR** ($CDCl_3$, 75 MHz, ppm): δ 166.1, 163.5, 134.8, 129.6, 126.6, 107.4, 92.5, 62.5, 56.5, 21.1.

**HRMS [M$^{+\cdot}$]** $C_{23}H_{24}O_3S_2$ calculated 412.1161 found 412.1170.

### Synthesis of (2,4,6-trimethoxy-1,3-phenylene)bis((4-methoxyphenyl)sulfane) (3c)



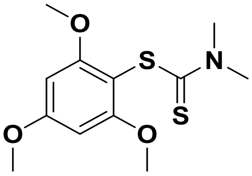
The compound was prepared according to the general procedure using 16.8 mg of 1,3,5-trimethoxybenzene, 2.2 mg of [Ir(dF(CF$_3$)ppy)$_2$(dtbpy)]PF$_6$, 55.6 mg of 1,2-bis(4-methoxyphenyl)disulfane, 40 mg of $(NH_4)_2S_2O_8$ and 2.0 mL dry $CH_3CN$. The reaction mixture was irradiated for 6 hours under $N_2$. Purification of the crude product was achieved by flash column chromatography using petrol ether/ ethylacetate (85:15) as eluent to yield the desired compound as white solid (24.0 mg, 54%).

**$^1$H NMR** ($CDCl_3$, 300 MHz, ppm): δ 7.11-7.08 (m, 4H), 6.75-6.72 (m, 4H), 6.36 (s, 1H), 3.84 (s, 6H), 3.79 (s, 3H), 3.73 (s, 6H).

**$^{13}$C NMR** ($CDCl_3$, 75 MHz, ppm): δ 165.6, 163.1, 158.0, 129.3, 128.9, 114.5, 108.6, 92.6, 62.5, 56.5, 55.5.

**HRMS [M+H]+** $C_{23}H_{24}O_5S_2$ calculated 445.1138 found 445.1140.

**Synthesis of 2,4,6-trimethoxyphenyl dimethylcarbamodithioate (3d)**



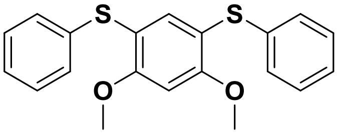
The compound was prepared according to the general procedure using 16.8 mg of 1,3,5-trimethoxybenzene, 2.2 mg of [Ir(dF($CF_3$)ppy)$_2$(dtbpy)]$PF_6$, 47.8 mg of tetramethylthiuramdisulfid, 40 mg of $(NH_4)_2S_2O_8$ and 2.0 mL dry $CH_3CN$. The reaction mixture was irradiated for 24 hours under $N_2$. Purification of the crude product was achieved by flash column chromatography using petrol ether/ ethylacetate (80:20) as eluent to yield the desired compound as white solid (19.6 mg, 68%).

**$^1$H NMR** ($CDCl_3$, 300 MHz, ppm): δ 6.21 (s, 2H), 3.85 (s, 3H), 3.83 (s, 6H), 3.54 (s, 6H).

**$^{13}$C NMR** ($CDCl_3$, 75 MHz, ppm): δ 197.6, 164.0, 162.7, 100.1, 91.4, 56.6, 55.5.

**HRMS [M+H]+** $C_{12}H_{17}NO_3S_2$ calculated 288.0723 found 288.0727.

**Synthesis of (4,6-dimethoxy-1,3-phenylene)bis(phenylsulfane) (3e)**



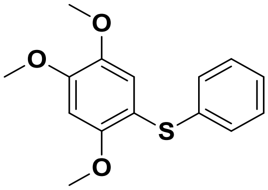
The compound was prepared according to the general procedure using 12.7 µL of 1,2-dimethoxybenzene, 2.2 mg of (Ir[dF($CF_3$)ppy]$_2$(dtbpy))$PF_6$, 43.6 mg of diphenyl disulfide, 40 mg of $(NH_4)_2S_2O_8$ and 2.0 mL dry $CH_3CN$. The reaction mixture was irradiated for 6 hours under $N_2$. Purification of the crude product was achieved by flash column chromatography using petrol ether/ ethylacetate (85:15) as eluent to yield the desired compound as yellowish white solid (14.2 mg, 40%).

**$^1$H NMR** ($CDCl_3$, 300 MHz, ppm): δ 7.39 (s, 1H), 7.25-7.10 (m, 10H), 6.55 (s, 1H), 3.88 (s, 6H).

**$^{13}$C NMR** ($CDCl_3$, 75 MHz, ppm): δ 160.82, 141.35, 136.74, 129.01, 128.59, 126.04, 113.44, 96.22, 56.39.

**HRMS[$M^{+\cdot}$]** $C_{20}H_{18}O_2S_2$ calculated 354.0742 found 354.0743.

### Synthesis of phenyl(2,4,5-trimethoxyphenyl)sulfane (3f)[6]



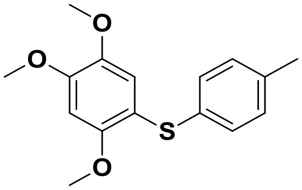
The compound was prepared according to the general procedure using 15.0 µL of 1,2,4-trimethoxybenzene, 2.2 mg of [Ir(dF(CF$_3$)ppy)$_2$(dtbpy)]PF$_6$, 43.6 mg of diphenyl disulfide, 40 mg of $(NH_4)_2S_2O_8$ and 2.0 mL dry $CH_3CN$. The reaction mixture was irradiated for 6 hours under $N_2$. Purification of the crude product was achieved by flash column chromatography using petrol ether/ ethylacetate (85:15) as eluent to yield the desired compound as pale yellow liquid (11.2 mg, 40%).

**$^1$H NMR** ($CDCl_3$, 300 MHz, ppm): δ 7.26-7.22 (m, 3H), 7.20-7.11 (m, 2H), 6.95 (s, 1H), 6.59 (s, 1H), 3.93 (s, 3H), 3.82 (s, 3H), 3.78 (s, 3H)

**$^{13}$C NMR** ($CDCl_3$, 75 MHz, ppm): δ 154.6, 150.9, 143.6, 137.9, 129.0, 127.7, 119.0, 110.0, 98.1, 57.2, 56.7, 56.3.

**HRMS[$M^{+\cdot}$]** $C_{15}H_{16}O_3S$ calculated 276.0814 found 276.0817.

### Synthesis of p-tolyl(2,4,5-trimethoxyphenyl)sulfane (3g)[6]



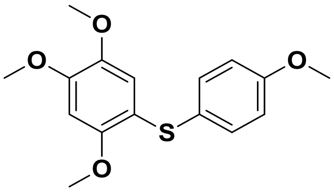
The compound was prepared according to the general procedure using 15.0 µL of 1,2,4-trimethoxybenzene, 2.2 mg of [Ir(dF(CF$_3$)ppy)$_2$(dtbpy)]PF$_6$, 49.2 mg of 1,2-di-*p*-tolyldisulfane, 40 mg of $(NH_4)_2S_2O_8$ and 2.0 mL dry $CH_3CN$. The reaction mixture was irradiated for 24 hours under $N_2$. Purification of the crude product was achieved by flash column chromatography using petrol ether/ ethylacetate (85:15) as eluent to yield the desired compound as white solid (12.5 mg, 43%).

**$^1$H NMR** ($CDCl_3$, 300 MHz, ppm): δ 7.10-7.02 (m, 4H), 6.87 (s, 1H), 6.57 (s,1H), 3.91 (s, 3H), 3.81 (s, 3H), 3.75 (s, 3H), 2.28 (s, 3H).

**$^{13}$C NMR** ($CDCl_3$, 75 MHz, ppm): δ 154.0, 150.0, 143.5, 135.9, 133.6, 129.8, 128.8, 118.2, 98.1, 57.1, 56.7, 56.3, 21.1.

**HRMS[$M^{+\cdot}$]** $C_{16}H_{18}O_3S$ calculated 290.0971 found 290.0977.

### Synthesis of (4-methoxyphenyl)(2,4,5-trimethoxyphenyl)sulfane (3h)[7]



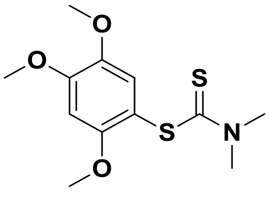
The compound was prepared according to the general procedure using 15.0 µL of 1,2,4-trimethoxybenzene, 2.2 mg of $[Ir(dF(CF_3)ppy)_2(dtbpy)]PF_6$, 55.6 mg of 1,2-bis(4-methoxyphenyl)disulfane, 40 mg of $(NH_4)_2S_2O_8$ and 2.0 mL dry $CH_3CN$. The reaction mixture was irradiated for 6 hours under $N_2$. Purification of the crude product was achieved by flash column chromatography using petrol ether/ ethylacetate (86:14) as eluent to yield the desired compound as pale yellow liquid (26.0 mg, 85%).

**$^1$H NMR** ($CDCl_3$, 300 MHz, ppm): δ 7.25-7.22 (m, 2H), 6.83-6.80 (m, 2H), 6.71 (s, 1H), 6.53 (s, 1H), 3.87 (s, 3H), 3.82 (s, 3H), 3.76 (s, 3H), 3.69(s, 3H).

**$^{13}$C NMR** ($CDCl_3$, 75 MHz, ppm): δ 159.0, 152.8, 149.7, 143.6, 132.5, 126.4, 116.5, 114.8, 114.4, 98.1, 57.0, 56.7, 56.3, 55.5.

**HRMS[$M^{+\cdot}$]** $C_{16}H_{18}O_4S$ calculated 306.0920 found 306.0926.

### Synthesis of 2,4,5-trimethoxyphenyl dimethylcarbamodithioate (3i)



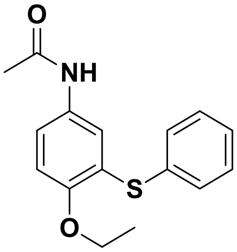
The compound was prepared according to the general procedure using 15.0 µL of 1,2,4-trimethoxybenzene, 2.2 mg of $[Ir(dF(CF_3)ppy)_2(dtbpy)]PF_6$, 47.8 mg of tetramethylthiuramdisulfid, 40 mg of $(NH_4)_2S_2O_8$ and 2.0 mL dry $CH_3CN$. The reaction mixture was irradiated for 24 hours under $N_2$. Purification of the crude product was achieved by flash column chromatography using petrol ether/ ethylacetate (80:20) as eluent to yield the desired compound as yellow solid (12.7 mg, 44%).

**$^1$H NMR** ($CDCl_3$, 300 MHz, ppm): δ 6.89 (s, 1H), 6.61 (s, 1H), 3.94 (s, 3H), 3.86 (s, 3H), 3.84 (s, 3H), 3.54 (d, *J* = 11.1 Hz, 6H).

**$^{13}$C NMR** ($CDCl_3$, 75 MHz, ppm): δ 197.8, 156.0, 152.4, 143.3, 121.1, 109.5, 97.7, 57.3, 56.6, 56.1, 45.9, 42.1.

**HRMS [M+H]+** $C_{12}H_{17}NO_3S_2$ calculated 288.0723 found 288.0724.

### Synthesis of *N*-(4-ethoxy-3-(phenylthio)phenyl)acetamide (3j)



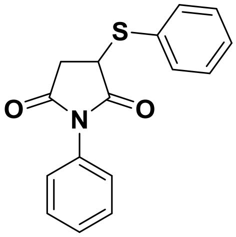
The compound was prepared according to the general procedure using 17.9 mg of *N*-(4-ethoxyphenyl)acetamide, 2.2 mg of $[Ir(dF(CF_3)ppy)_2(dtbpy)]PF_6$, 43.6 mg of diphenyl disulfide, 40 mg of $(NH_4)_2S_2O_8$ and 2.0 mL dry $CH_3CN$. The reaction mixture was irradiated for 24 hours under $N_2$. Purification of the crude product was achieved by flash column chromatography using petrol ether/ ethylacetate (85:15) as eluent to yield the desired compound as white solid (5.8 mg, 20%)

**$^1$H NMR** ($CDCl_3$, 600 MHz, ppm): δ 8.23 (d, *J* = 9 Hz, 1H), 7.86 (bs, 1H), 7.33-7.29 (m, 1H), 7.25-7.24 (m, 1H), 7.17 (t, *J* = 7.2 Hz, 1H), 7.11 (d, *J* = 7.5 Hz, 2H), 7.07 (d, *J* = 2.8 Hz, 1H), 6.96 (dd, *J* = 9 Hz, 2.8 Hz, 1H), 3.98 (q, *J* = 6.9 Hz, 2H), 2.00 (s, 3H), 1.38 (t, *J* = 7 Hz, 3H).

**$^{13}$C NMR** ($CDCl_3$, 150 MHz, ppm): δ 168.2, 155.5, 135.6, 133.0, 129.5, 127.7, 126.6, 122.8, 122.1, 121.4, 116.8, 64.0., 24.6, 14.9.

**HRMS [M+H]+** $C_{16}H_{17}NO_2S$ calculated 288.1053 found 288.1046.

### Synthesis of 1-phenyl-3-(phenylthio)pyrrolidine-2,5-dione (3k)



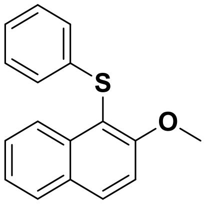
The compound was prepared according to the general procedure using 17.3 mg of 1-phenyl-3-(phenylthio)pyrrolidine-2,5-dione, 2.2 mg of [Ir(dF(CF$_3$)ppy)$_2$(dtbpy)]PF$_6$, 43.6 mg of diphenyl disulfide, 40 mg of $(NH_4)_2S_2O_8$ and 2.0 mL dry $CH_3CN$. The reaction mixture was irradiated for 24 hours under $N_2$. Purification of the crude product was achieved by flash column chromatography using petrol ether/ ethylacetate (85:15) as eluent to yield the desired compound as white solid (16.3 mg, 58%).

**$^1$H NMR** ($CDCl_3$, 600 MHz, ppm): δ 7.59-7.56 (m, 2H), 7.45-7.36 (m, 7H), 7.06-7.03 (m, 2H).

**$^{13}$C NMR** ($CDCl_3$, 151 MHz, ppm): δ 174.7, 173.7, 135.3, 133.8, 131.7, 129.9, 129.7, 129.3, 129.0, 126.5, 44.3, 36.6.

**HRMS [M+H]+** $C_{16}H_{13}NO_2S$ calculated 284.0740 found 284.0734.

### Synthesis of (2-methoxynaphthalen-1-yl)(phenyl)sulfane (3l)



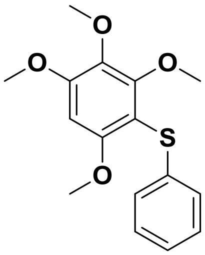
The compound was prepared according to the general procedure using 15.8 mg of (2-methoxynaphthalen-1-yl)(phenyl)sulfane, 2.2 mg of [Ir(dF(CF$_3$)ppy)$_2$(dtbpy)]PF$_6$, 43.6 mg of diphenyl disulfide, 40 mg of $(NH_4)_2S_2O_8$ and 2.0 mL dry $CH_3CN$. The reaction mixture was irradiated for 24 hours under $N_2$. Purification of the crude product was achieved by flash column chromatography using petrol ether/ ethylacetate (85:15) as eluent to yield the desired compound as white solid (8 mg, 30%).

**$^1$H NMR** ($CDCl_3$, 300 MHz, ppm): δ 8.48 (d, *J* = 8.4 Hz, 1H), 7.98 (d, *J* = 9.0 Hz, 1H), 7.84 (d, *J* = 8.1 Hz, 1H), 7.54-7.48 (m, 1H), 7.42-7.37 (m, 2H), 7.17-7.14 (m, 5H), 3.97 (s, 3H).

**$^{13}$C NMR** ($CDCl_3$, 75 MHz, ppm): δ 159.4, 138.3, 136.5, 132.3, 129.7, 128.9, 128.5, 127.9, 126.4, 125.6, 124.9, 124.3, 113.6, 113.1, 57.1.

**HRMS[M$^{+\cdot}$]** $C_{17}H_{14}OS$ calculated 266.07599 found 266.0752.

### Synthesis of phenyl(2,3,4,6-tetramethoxyphenyl)sulfane (3m)



The compound was prepared according to the general procedure using 19.8 mg of phenyl(2,3,4,6-tetramethoxyphenyl)sulfane, 2.2 mg of $[Ir(dF(CF_3)ppy)_2(dtbpy)]PF_6$, 43.6 mg of diphenyl disulfide, 40 mg of $(NH_4)_2S_2O_8$ and 2.0 mL dry $CH_3CN$. The reaction mixture was irradiated for 24 hours under $N_2$. Purification of the crude product was achieved by flash column chromatography using petrol ether/ ethylacetate (85:15) as eluent to yield the desired compound as white solid (12.2 mg, 40%).

**$^1$H NMR** ($CDCl_3$, 300 MHz, ppm): δ 7.199-7.149 (m, 2H), 7.072-7.021 (m, 3H), 6.375 (s, 1H), 3.936 (s, 3H), 3.831 (s, 3H), 3.801 (s, 3H), 3.796 (s, 3H).

**$^{13}$C NMR** ($CDCl_3$, 75 MHz, ppm): δ 157.7, 156.5, 155.6, 138.9, 137.2, 128.8, 126.2, 124.9, 92.9, 61.8, 61.4, 56.8, 56.2.

**HRMS[M$^{+\cdot}$]** $C_{16}H_{18}O_4S$ calculated 306.0920 found 306.0922.

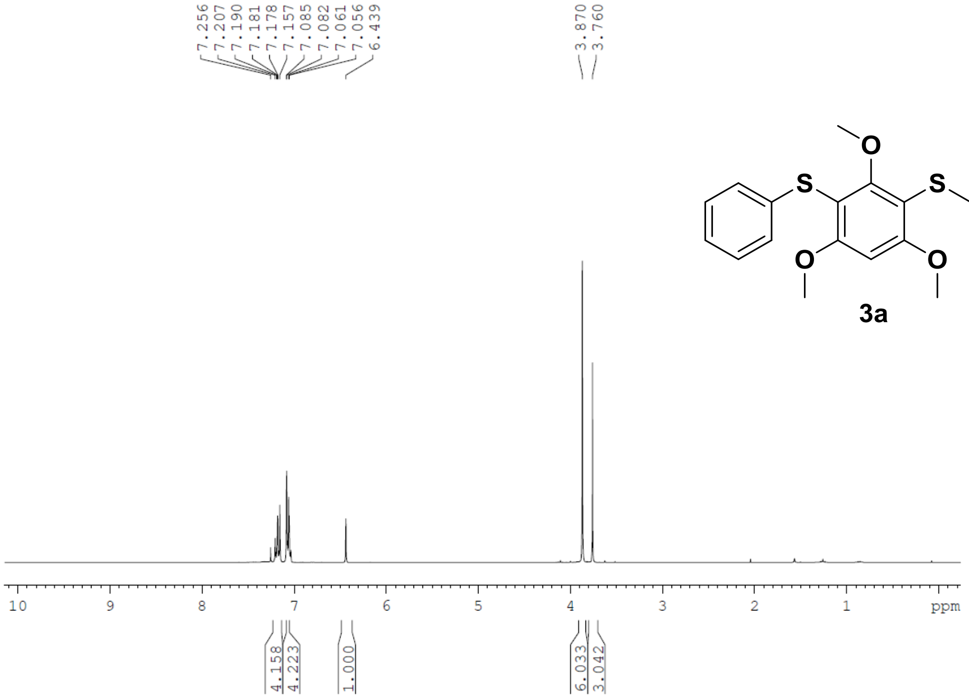
## Crystallographic Data

Single crystals of **3d**, **3e** and **3i** were obtained by recrystallisation from DCM/PE and Single crystals of **3a** was obtained by recrystallisation from EA/PE.

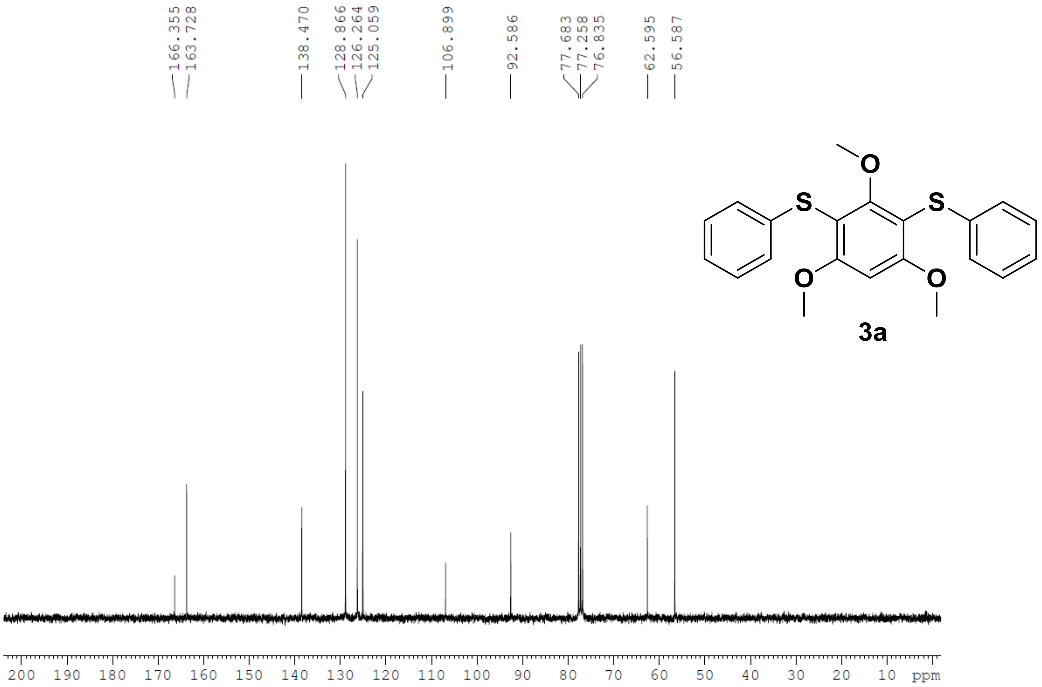
| **Compound** | **3a** | **3d** | **3e** | **3i** |
|---|---|---|---|---|
| | | | | |
| CCDC No | 1847083 | 1847084 | 1847085 | 1847086 |
| Formula | $C_{21}H_{20}O_3S_2$ | $C_{12}H_{17}NO_3S_2$ | $C_{20}H_{18}O_2S_2$ | $C_{12}H_{17}NO_3S_2$ |
| $D_{calc.}$/ g cm$^{-3}$ | 1.324 | 1.420 | 1.363 | 1.343 |
| $\mu$/mm$^{-1}$ | 2.645 | 3.604 | 2.863 | 3.410 |
| Formula Weight | 384.49 | 287.38 | 354.46 | 287.38 |
| Colour | clear colourless | clear colourless | clear colourless | Clear colourless |
| Shape | plate | block | plate | plate |
| Max Size/mm | 0.28 | 0.12 | 0.19 | 0.13 |
| Mid Size/mm | 0.17 | 0.10 | 0.14 | 0.08 |
| Min Size/mm | 0.07 | 0.08 | 0.06 | 0.02 |
| $T$/K | 122.99(10) | 123.01(11) | 122.9(2) | 122.9(2) |
| Crystal System | monoclinic | monoclinic | monoclinic | triclinic |
| Space Group | $P2_1/c$ | P2$_1$/n | P2$_1$/c | P-1 |
| $a$/Å | 14.5868(3) | 7.51380(10) | 10.3054(4) | 7.3374(3) |
| $b$/Å | 17.6123(3) | 7.37880(10) | 11.0809(4) | 10.3449(5) |
| $c$/Å | 7.5316(2) | 24.3461(4) | 15.6403(5) | 10.3830(8) |
| $\alpha/^\circ$ | 90 | 90 | 90 | 74.208(6) |
| $\beta/^\circ$ | 94.518(2) | 95.064(2) | 104.792(4) | 75.907(5) |
| $\gamma/^\circ$ | 90 | 90 | 90 | 72.065(4) |
| V/Å$^3$ | 1928.91(7) | 1344.55(3) | 1726.82(11) | 710.46(8) |
| $Z$ | 4 | 4 | 4 | 2 |
| $Z'$ | 1 | 1 | 1 | 1 |
| Wavelength/Å | 1.54184 | 1.54184 | 1.54184 | 1.54184 |
| Radiation type | CuK$_\alpha$ | CuK$_\alpha$ | CuK$_\alpha$ | CuK$_\alpha$ |
| $\Theta_{min}/^\circ$ | 3.942 | 3.645 | 4.437 | 4.494 |
| $\Theta_{max}/^\circ$ | 73.926 | 73.882 | 74.823 | 75.226 |
| Measured Refl. | 40564 | 17615 | 24757 | 2858 |
| Independent Refl. | 3891 | 2702 | 3513 | 2858 |
| Reflections Used | 3496 | 2472 | 3070 | 2321 |
| $R_{int}$ | 0.0555 | 0.0299 | 0.0465 | 0.0469 |
| Parameters | 238 | 168 | 219 | 169 |
| Restraints | 0 | 0 | 0 | 0 |
| Largest Peak | 0.259 | 0.321 | 0.242 | 0.564 |
| Deepest Hole | -0.232 | -0.303 | -0.325 | -0.392 |
| GooF | 1.032 | 1.042 | 1.050 | 1.090 |
| $wR_2$ (all data) | 0.0759 | 0.0703 | 0.0798 | 0.1515 |
| $wR_2$ | 0.0718 | 0.0676 | 0.0763 | 0.1391 |
| $R_1$ (all data) | 0.0344 | 0.0297 | 0.0372 | 0.0749 |
| $R_1$ | 0.0296 | 0.0263 | 0.0306 | 0.0614 |

# $^1$H- and $^{13}$C NMR spectra of synthesized compounds

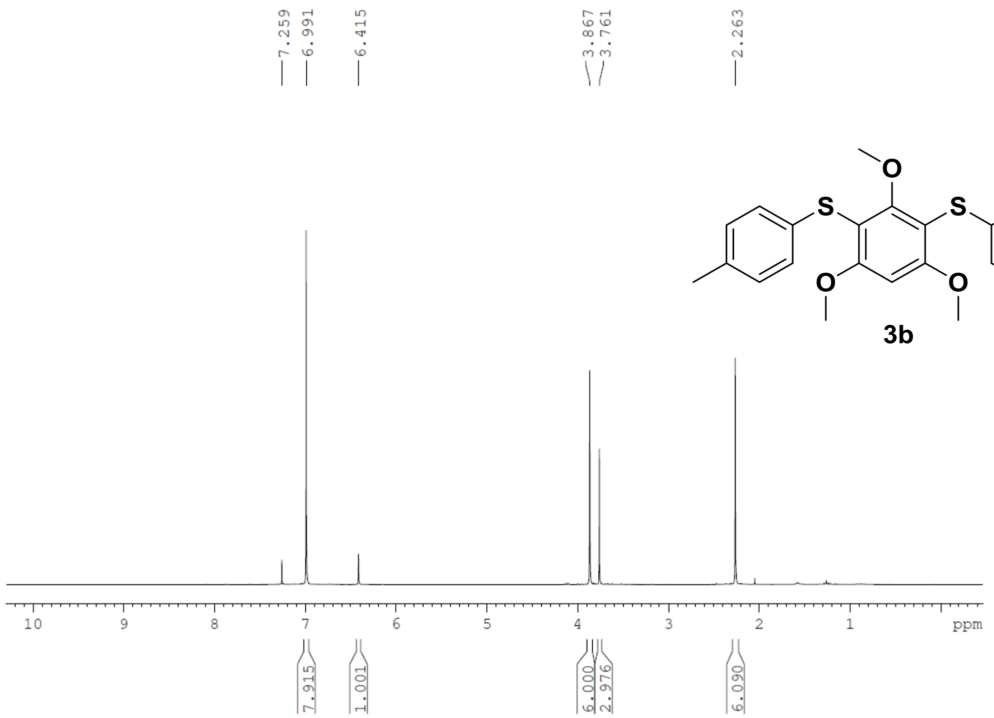
## $^1$H spectra of compound 3a (CDCl$_3$, 300 MHz)



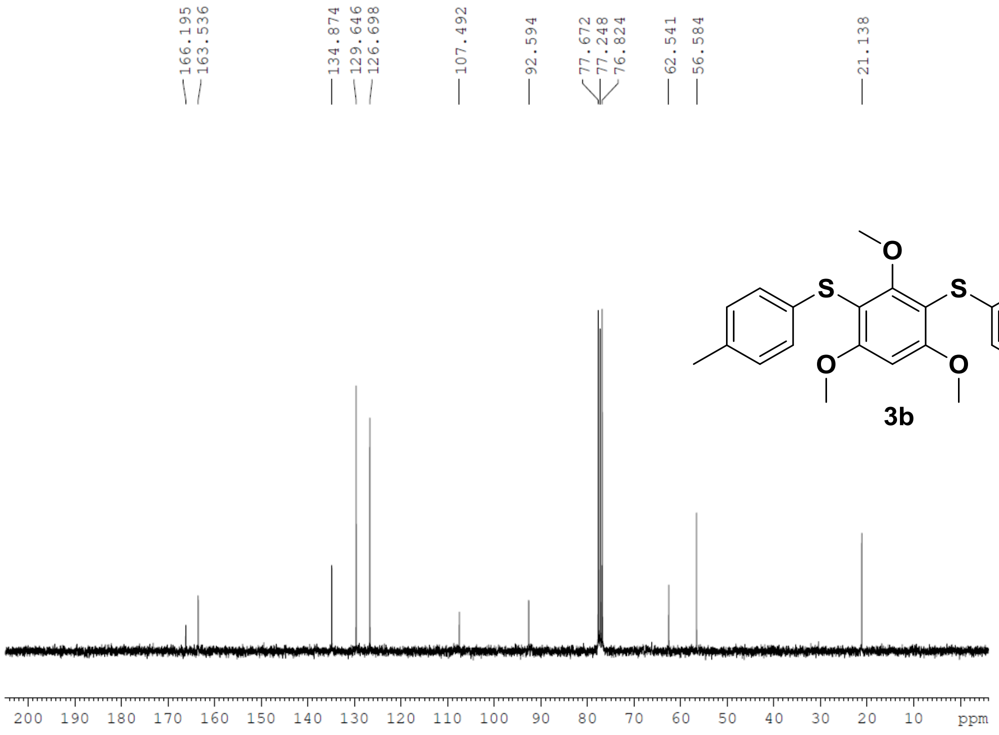
## $^{13}$C spectra of compound 3a (CDCl$_3$, 75 MHz)



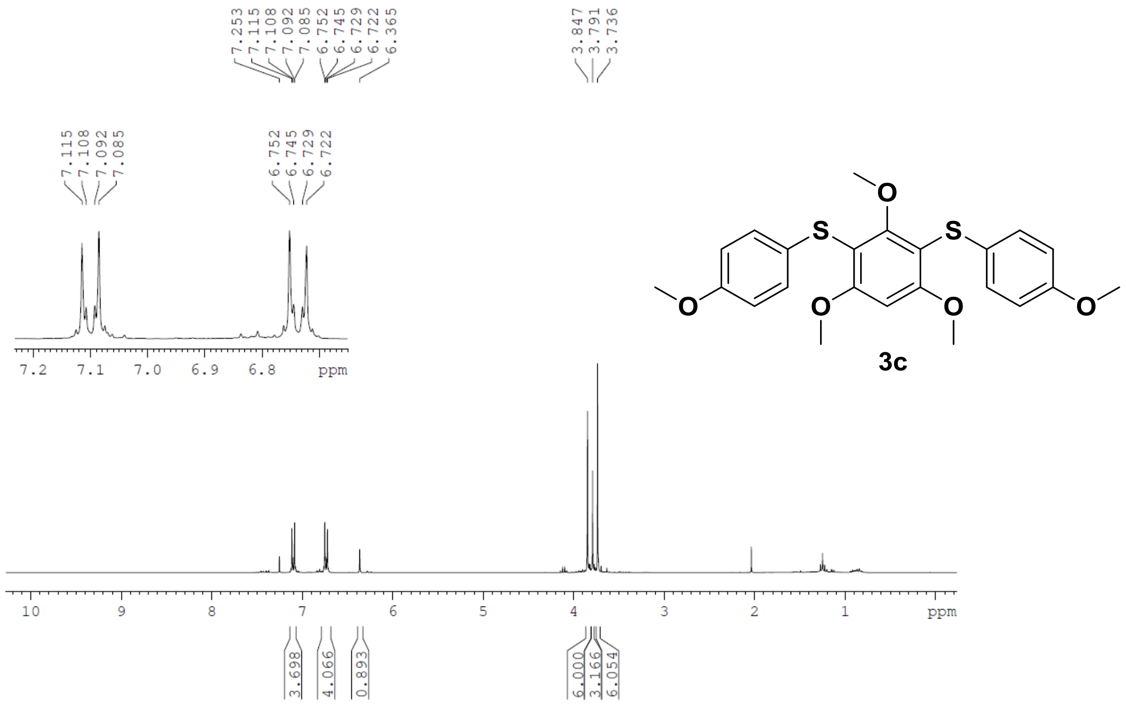
## $^{1}$H spectra of compound 3b ($CDCl_3$, 300 MHz)



## $^{13}$C spectra of compound 3b ($CDCl_3$, 75 MHz)

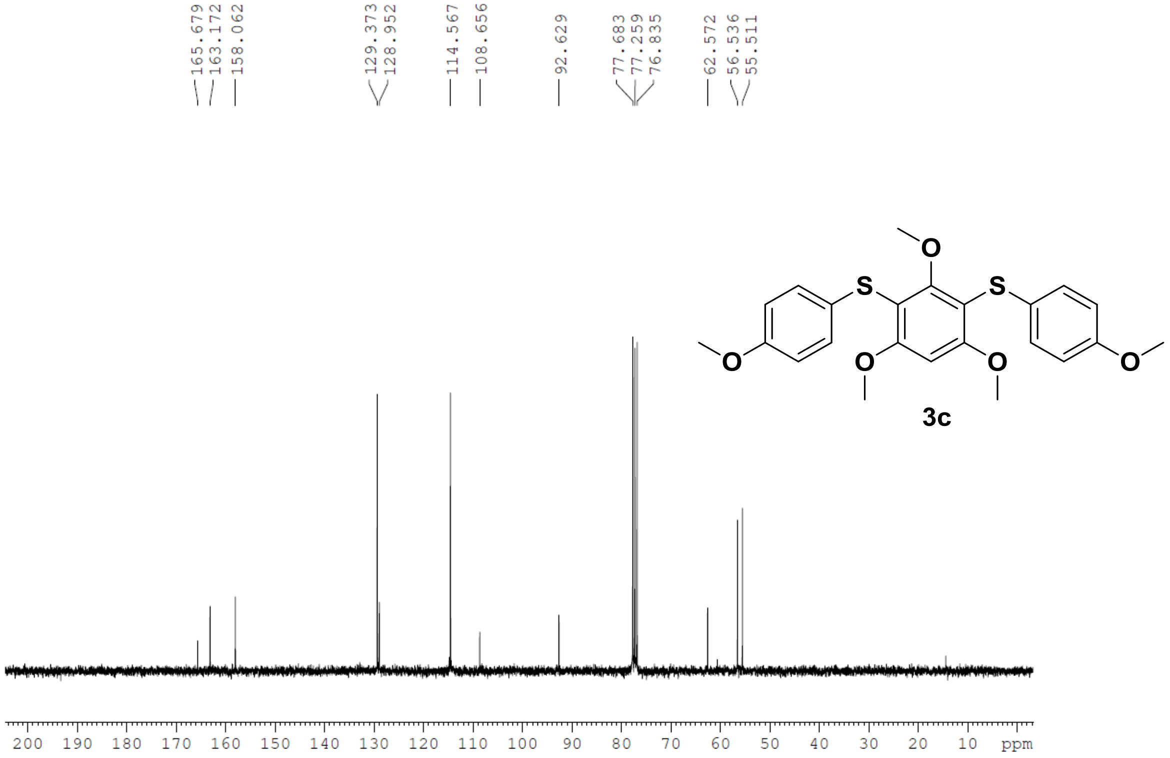


## $^{1}H$ spectra of compound 3c ($CDCl_3$, 300 MHz)



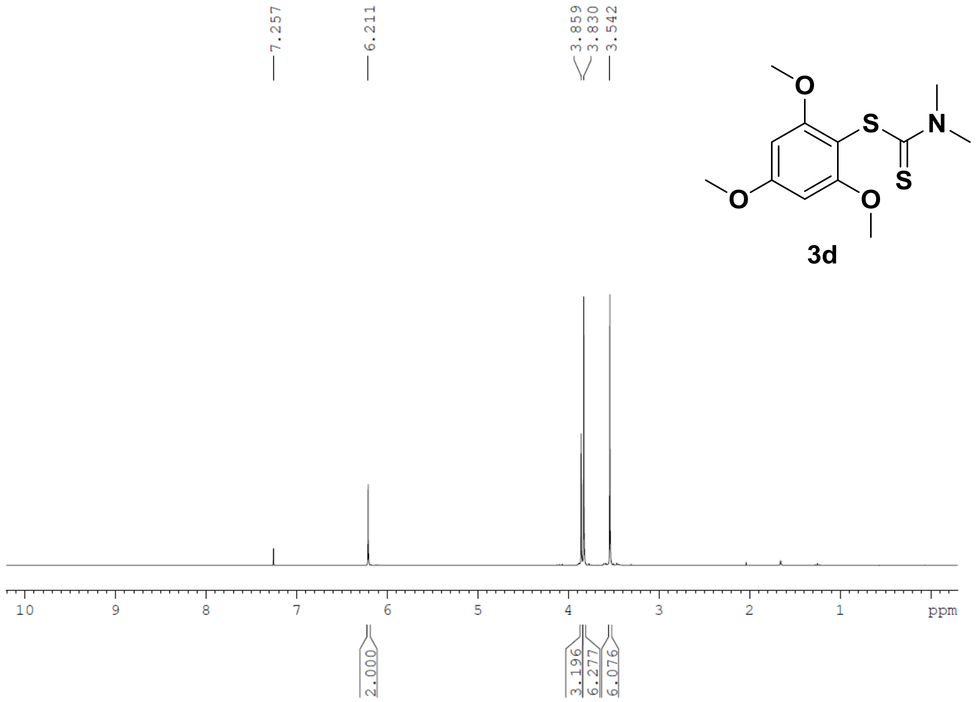
3c

## $^{13}C$ spectra of compound 3c ($CDCl_3$, 75 MHz)

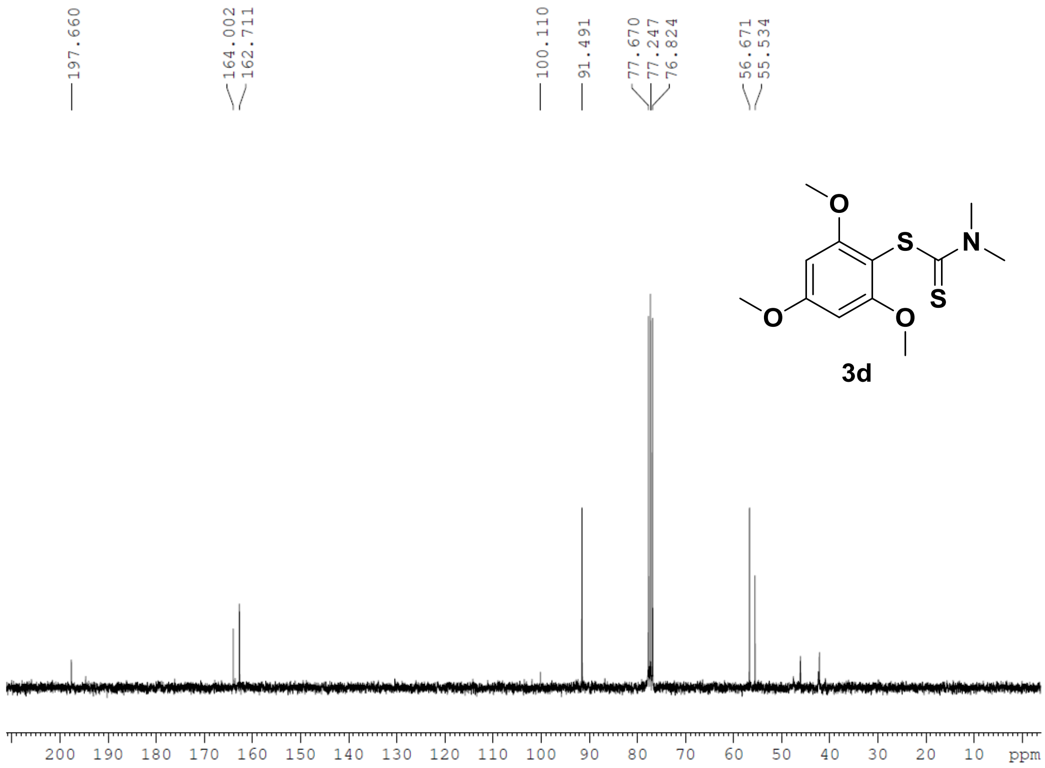


3c

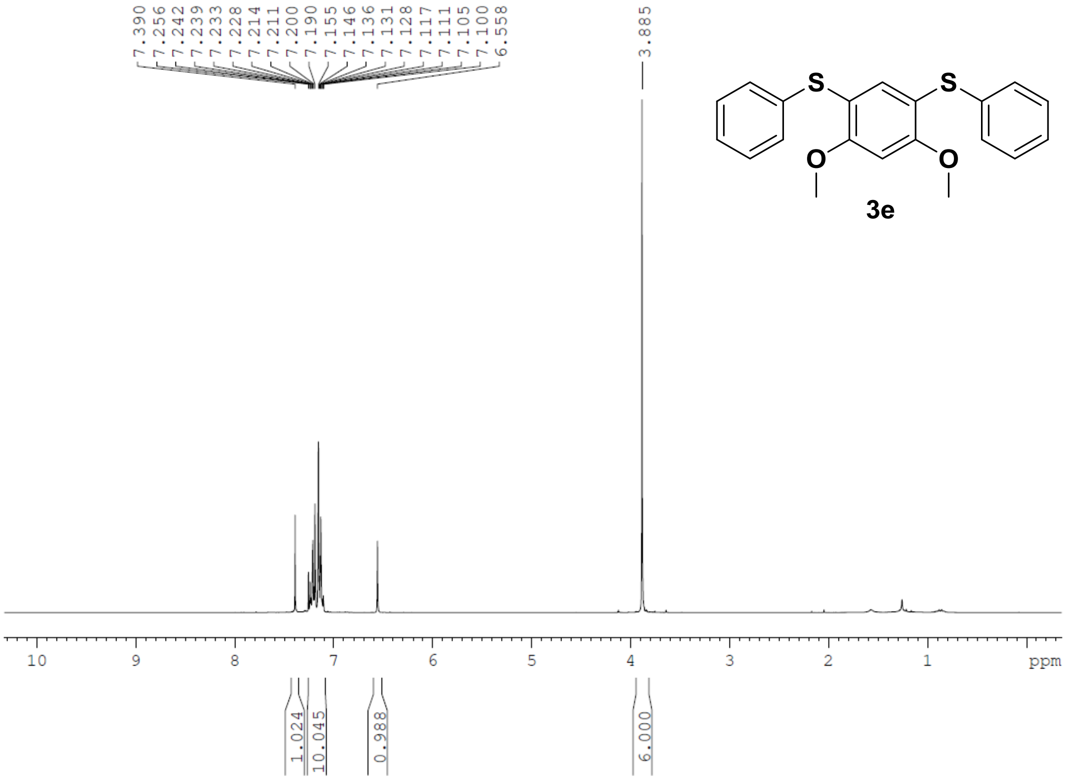
## $^1$H spectra of compound 3d ($CDCl_3$, 300 MHz)



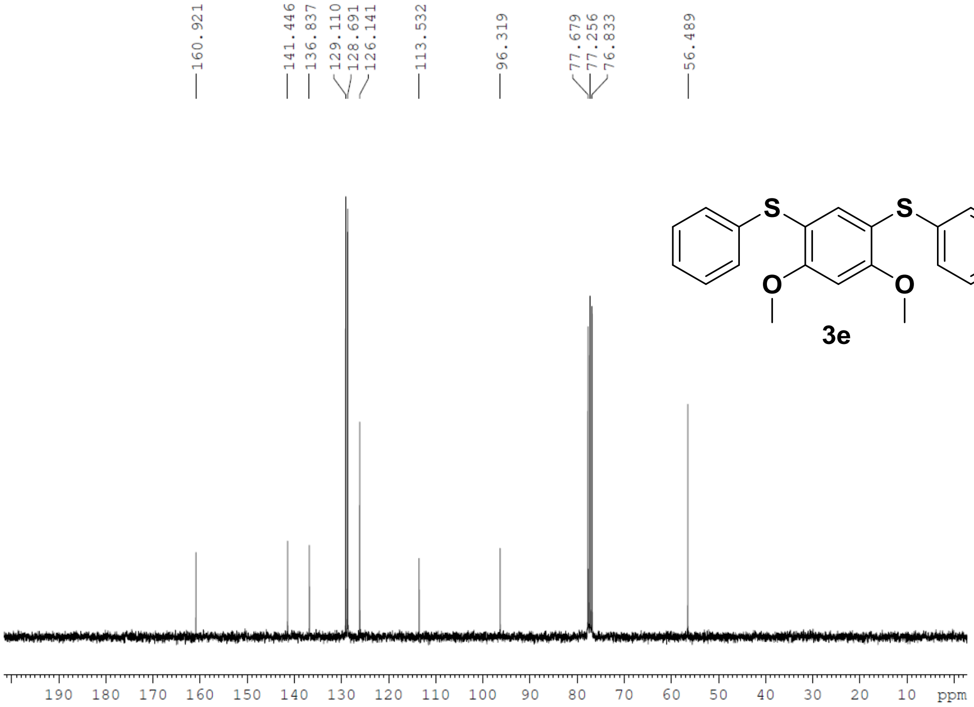
## $^{13}$C spectra of compound 3d ($CDCl_3$, 75 MHz)



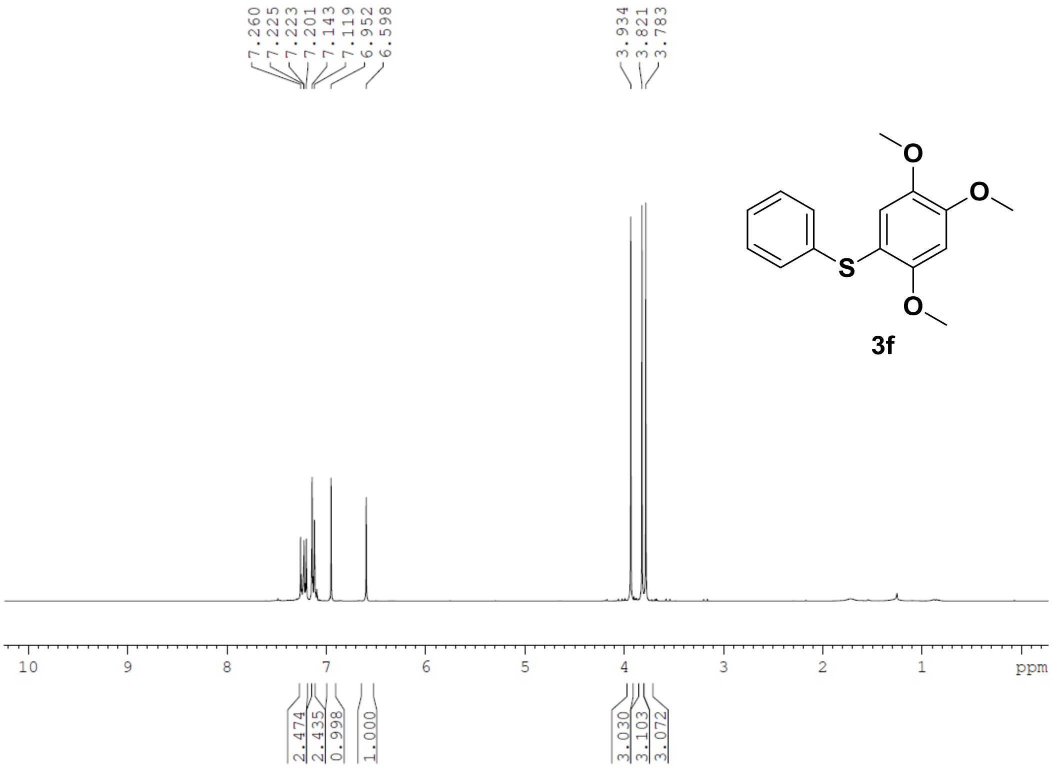
## $^1$H spectra of compound 3e (CDCl$_3$, 300 MHz)



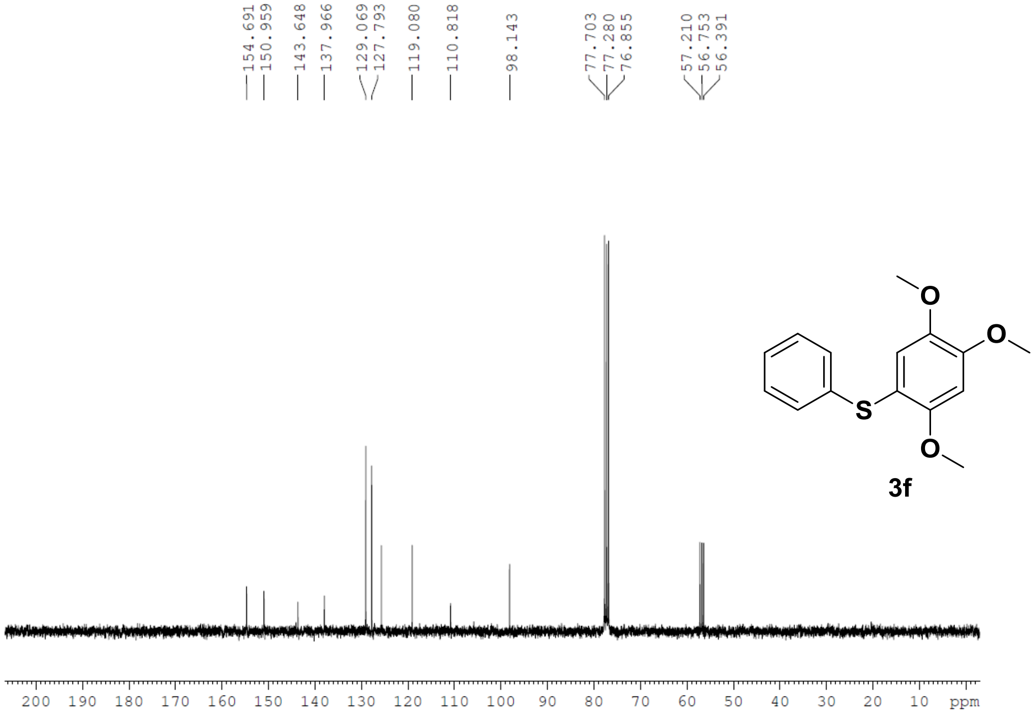
## $^{13}$C spectra of compound 3e (CDCl$_3$, 75 MHz)



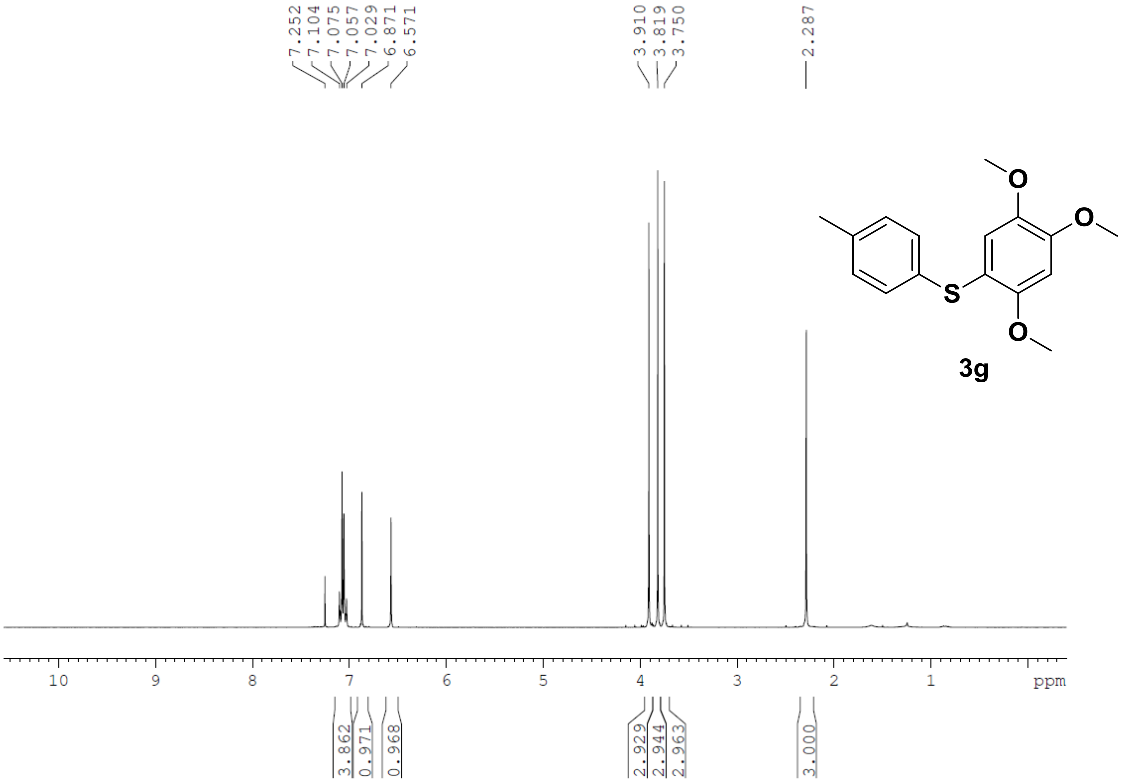
## $^{1}$H spectra of compound 3f ($CDCl_3$, 300 MHz)



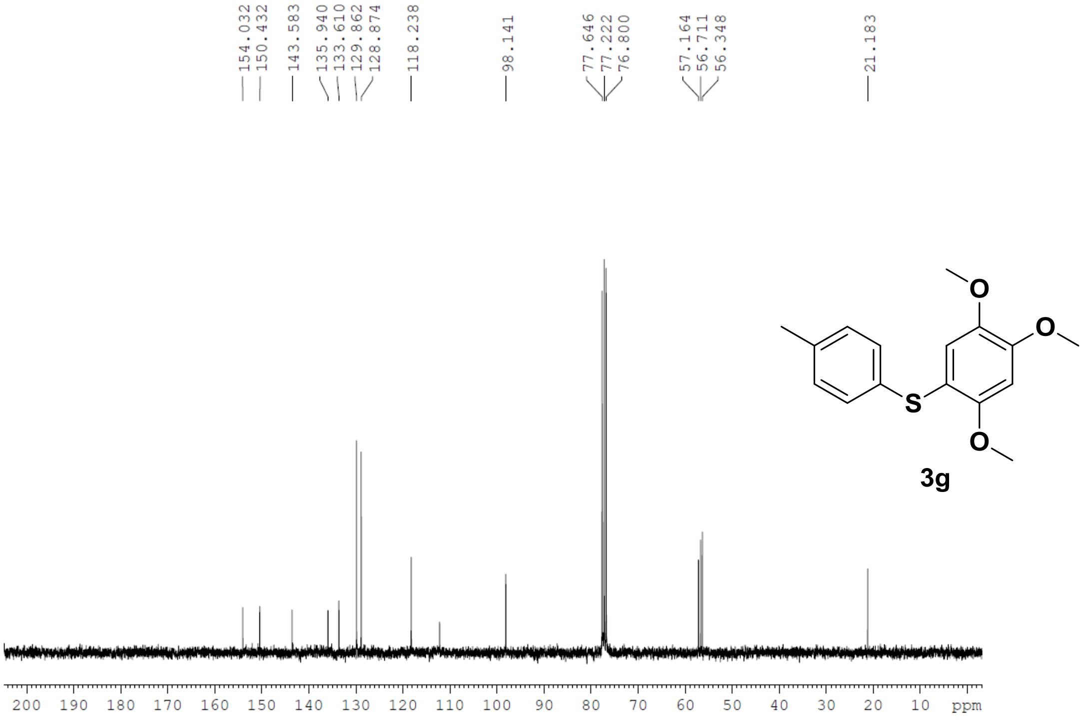
## $^{13}$C spectra of compound 3f ($CDCl_3$, 75 MHz)



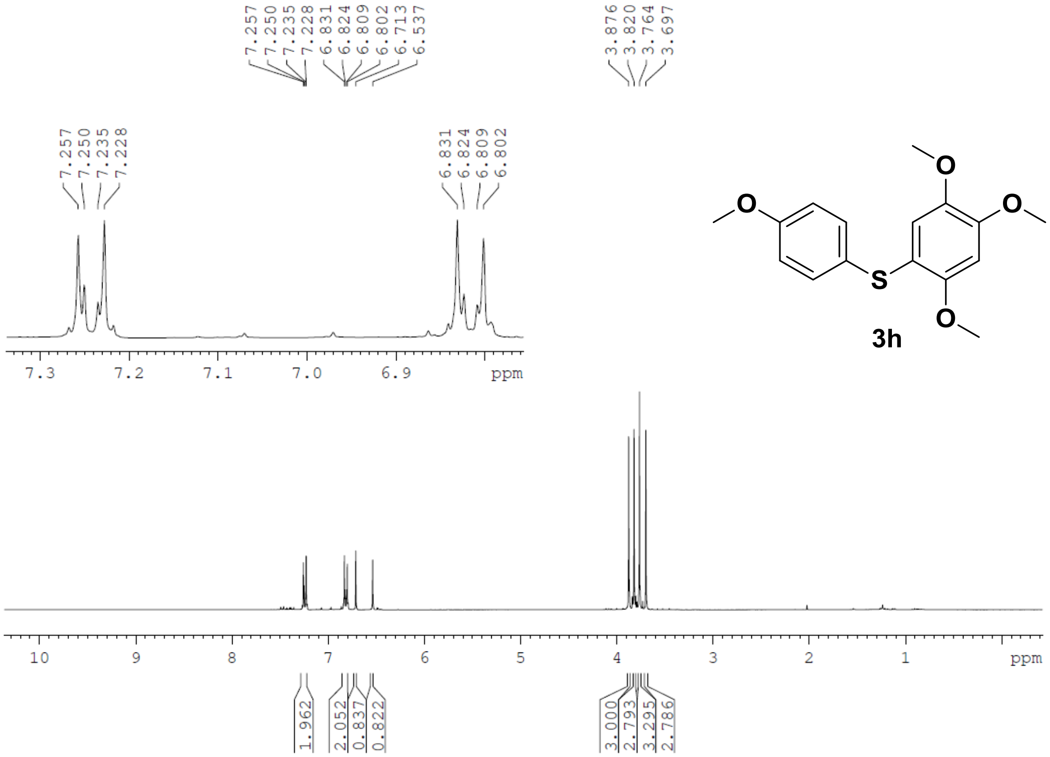
### $^{1}$H spectra of compound 3g ($CDCl_3$, 300 MHz)



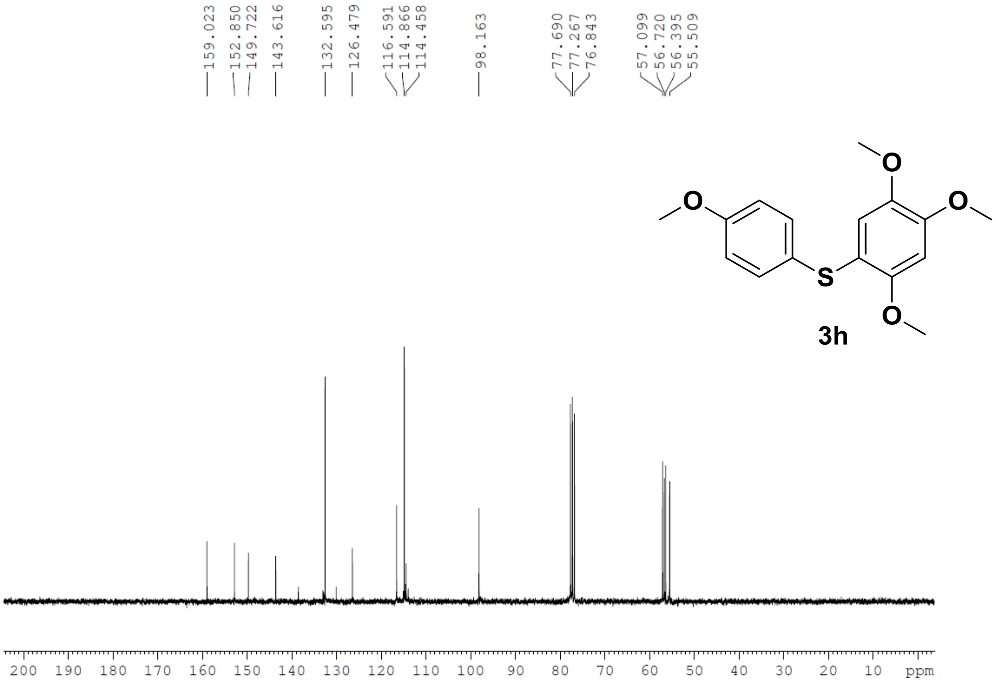
### $^{13}$C spectra of compound 3g ($CDCl_3$, 75 MHz)



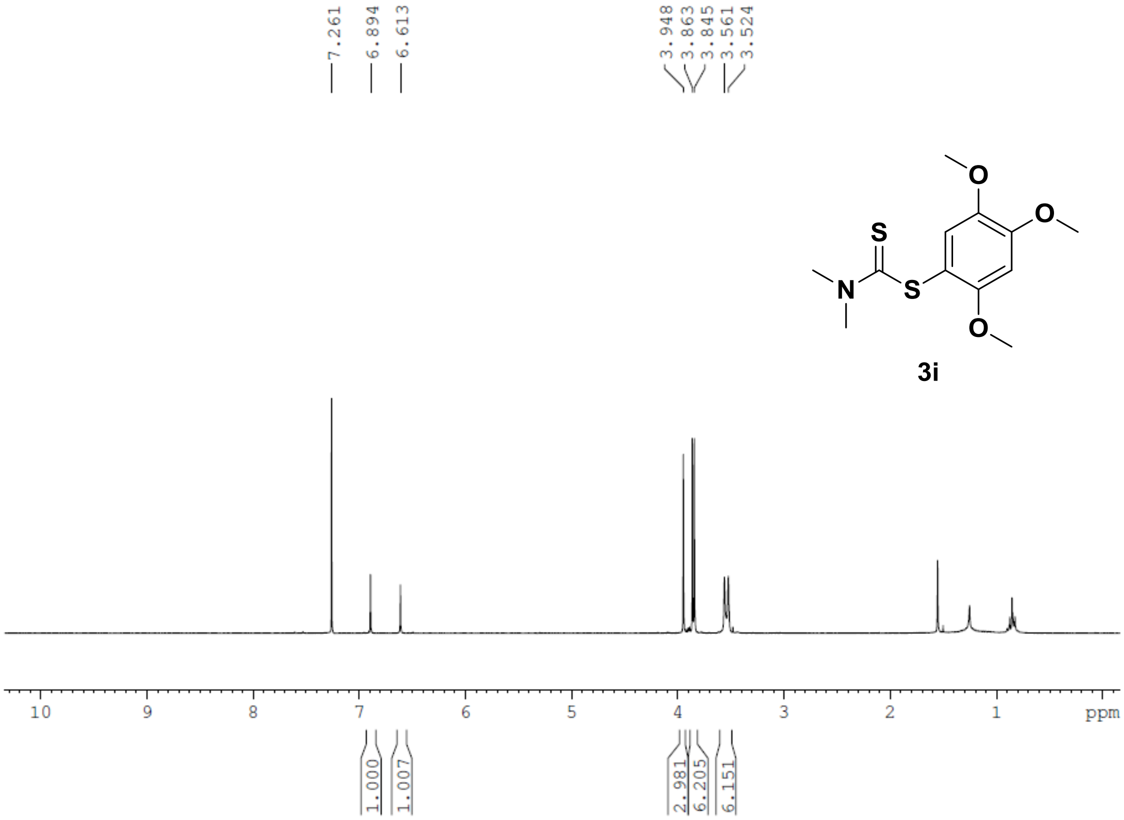
## $^1$H spectra of compound 3h ($CDCl_3$, 300 MHz)



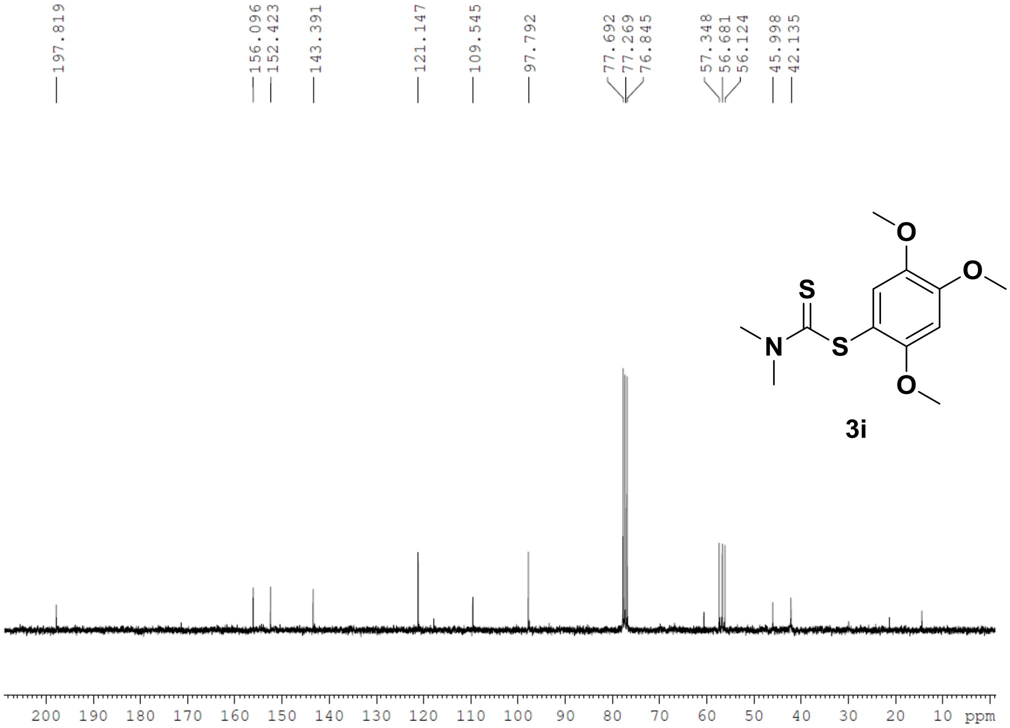
## $^{13}$C spectra of compound 3h ($CDCl_3$, 75 MHz)



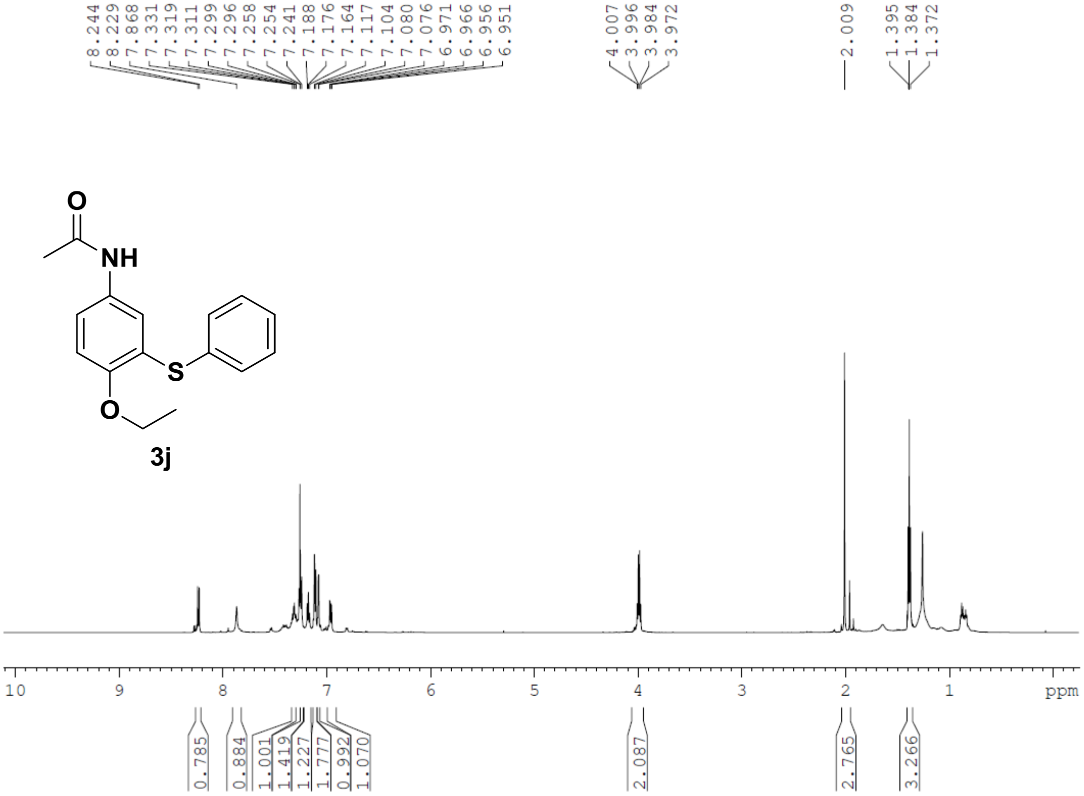
## $^1$H spectra of compound 3i (CDCl$_3$, 300 MHz)



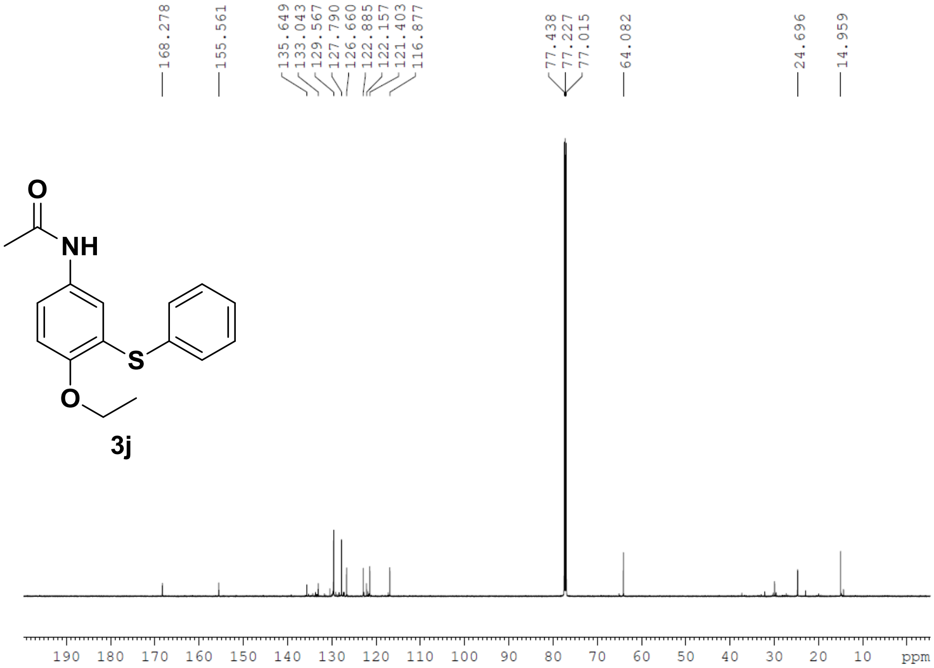
## $^{13}$C spectra of compound 3i (CDCl$_3$, 75 MHz)



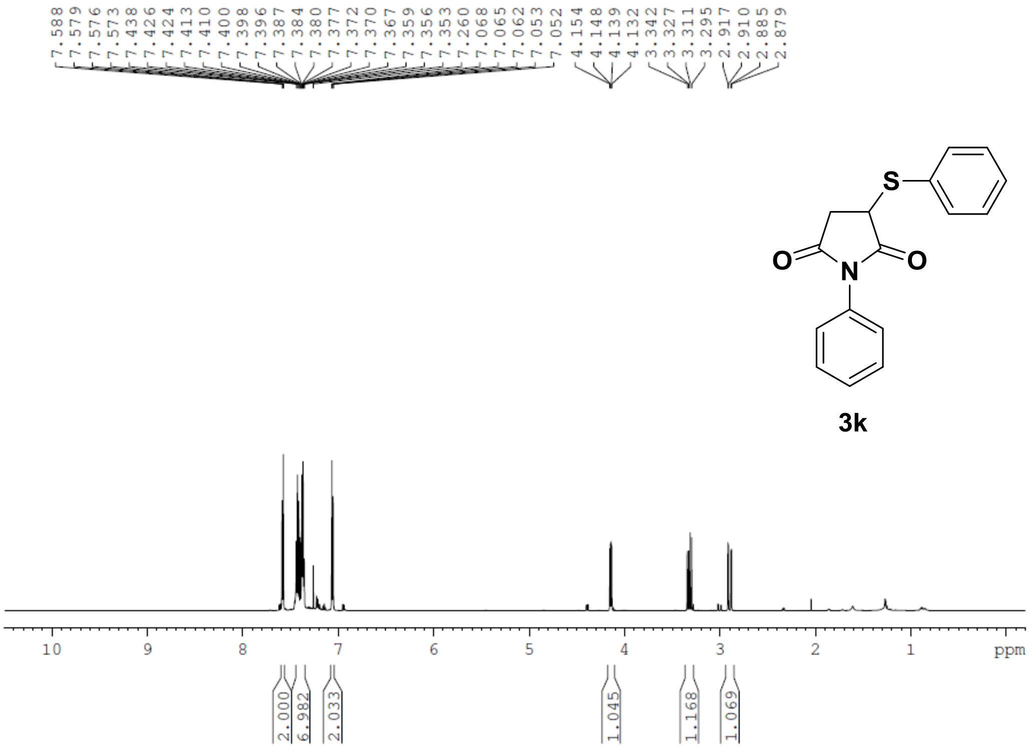
## $^1$H spectra of compound 3j ($CDCl_3$, 600 MHz)



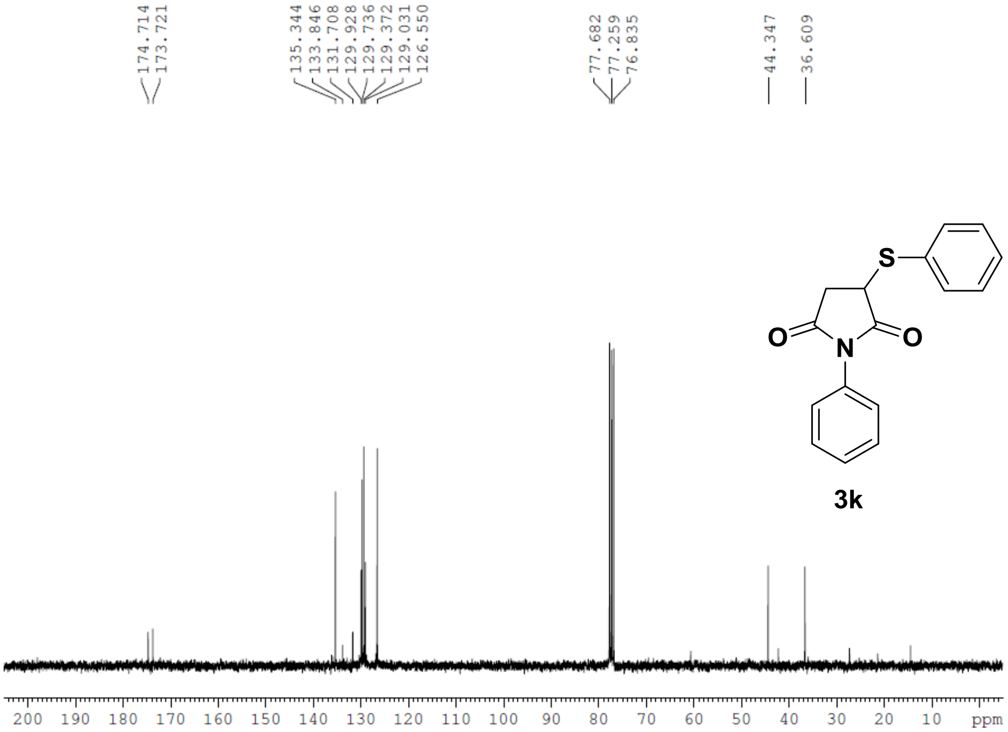
## $^{13}$C spectra of compound 3j ($CDCl_3$, 151 MHz)



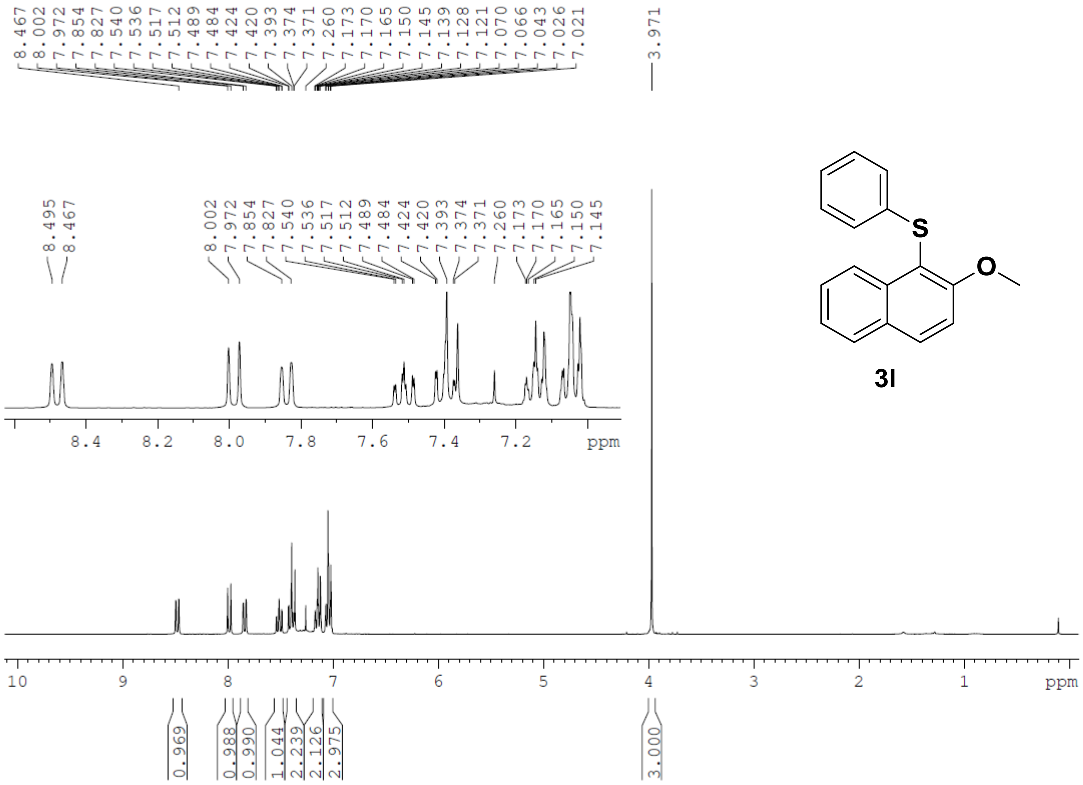
## $^1$H spectra of compound 3k (CDCl$_3$, 600 MHz)



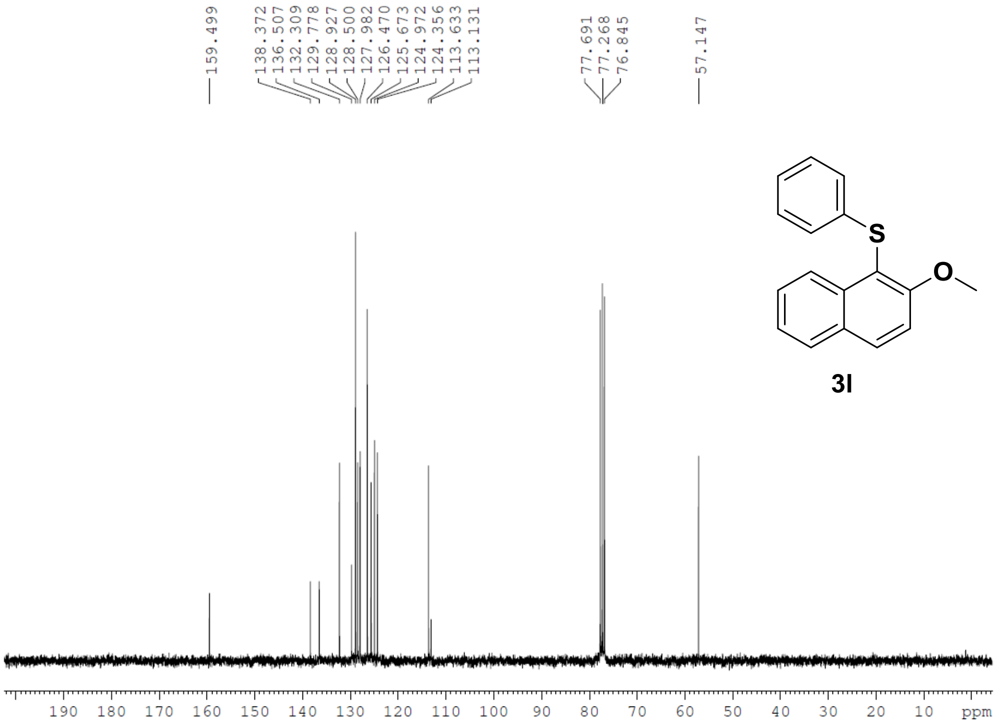
## $^{13}$C spectra of compound 3k (CDCl$_3$, 151 MHz)



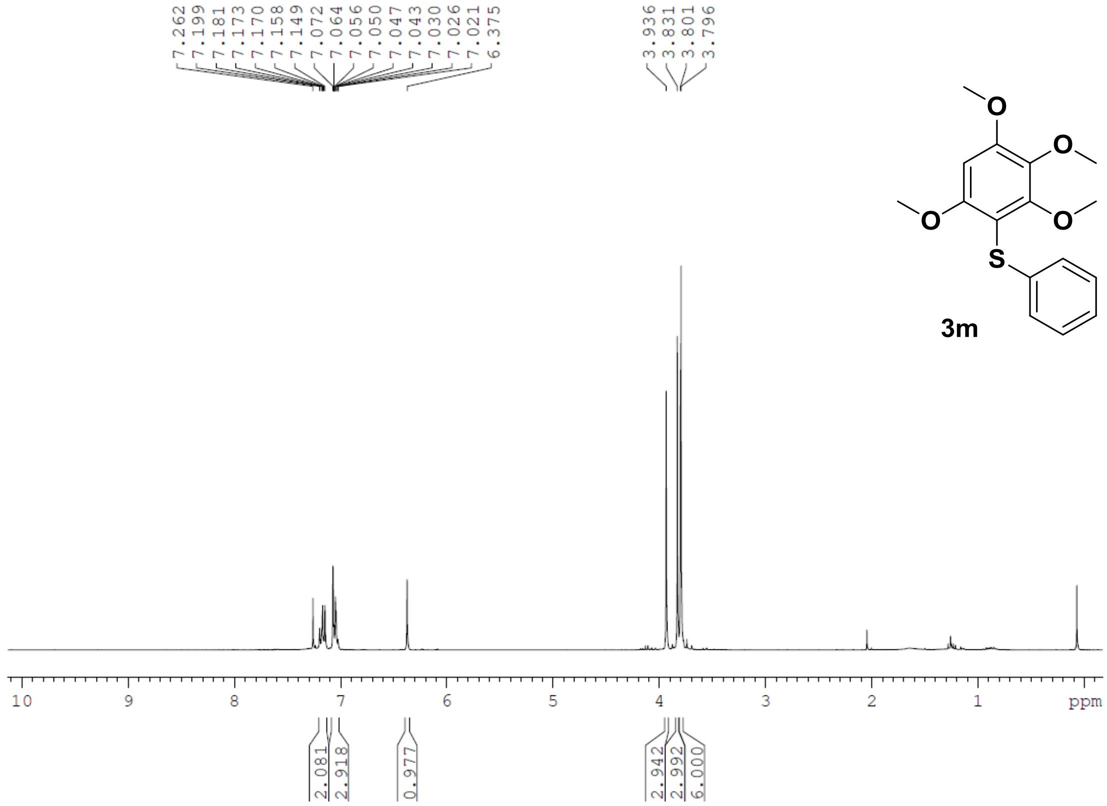
## $^{1}H$ spectra of compound 3l ($CDCl_3$, 300 MHz)



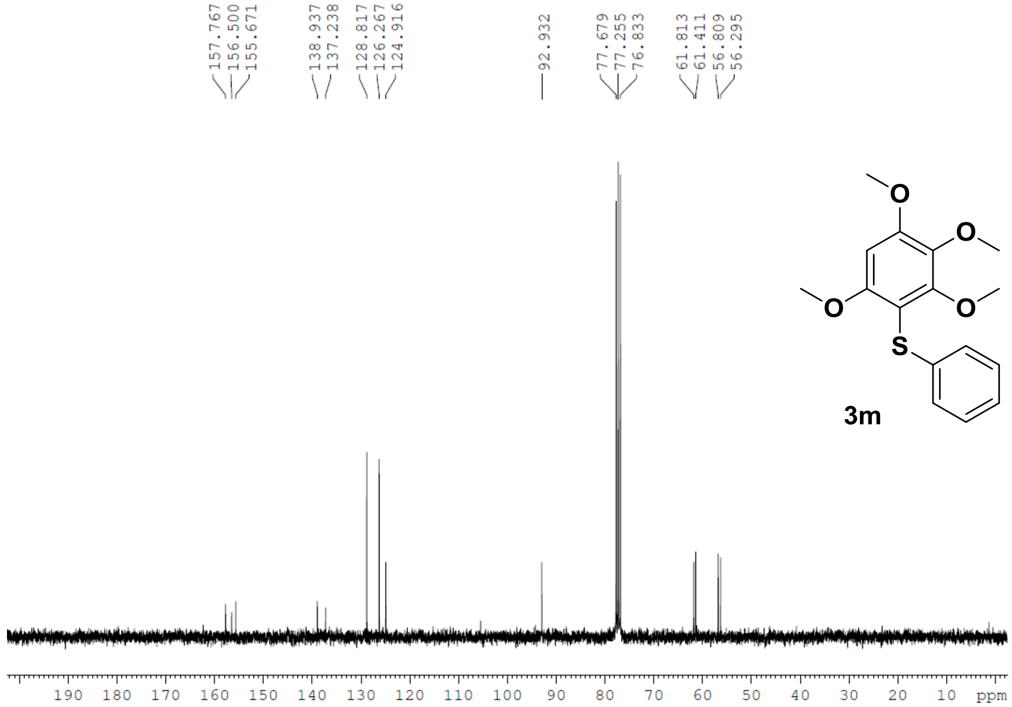
## $^{13}C$ spectra of compound 3l ($CDCl_3$, 75 MHz)



## $^1$H spectra of compound 3m ($CDCl_3$, 300 MHz)



## $^{13}$C spectra of compound 3m ($CDCl_3$, 75 MHz)



# References

1. D. B. G. Williams, M. J.  Lawton, *J. Org. Chem*. **2010**, *75*, 8351-8354.
2. M. S. Lowry, J. I. Goldsmith, J. D. Slinker, R. Rohl, R. A. Pascal, G. G. Malliaras, *Chem. Mater*. **2005**, *17*, 5712–5719.
3. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl. Crystallogr*. **2009**, *42*, 339-341.
4. G. M. Sheldrick, *Acta Crystallogr. C*, **2015**, *71*, 3-8.
5. L. Chen, P. Liu, J. Wu, B. Dai, *Tetrahedron.* **2018**, *74*, 1513-1519.
6. K. Yan, D. Yang, P. Sun, W. Wei, Y. Liu, G. Li, S. Lu, H. Wang, *Tetrahedron. Lett*. **2015**, *56,* 4792-4795.
7. M. R. Reddy, G. S Kumar, H. M. Meshram, *Tetrahedron. Lett*. **2016**, *57,* 3622-3624.