

# Supporting Information

for

## On the mechanism of photocatalytic reactions with eosin Y

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### Experimental and analytical data

## General methods

Commercial chemicals were used as obtained from Sigma-Aldrich or Fisher. Solvents were used without further purification. For most reactions, DMSO dried over molecular sieves (certified <0.005% water content, Sigma-Aldrich) was used. TLC was performed on commercial silica gel coated aluminium plates (DC60 F254, Merck). Visualization was done with UV light. Product yields were determined by quantitative GC-FID. Authentic product samples were synthesized according to the cited literature reports [1-7]. Purity and structure were confirmed based on  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR, GCMS and  $^{19}\text{F}$  NMR (where appropriate). NMR spectral data were collected on a Bruker Avance 400 (400 MHz for  $^1\text{H}$ ; 100 MHz for  $^{13}\text{C}$ ) spectrometer at 25 °C. Chemical shifts are reported in  $\delta/\text{ppm}$ , and coupling constants  $J$  are given in Hertz. Solvent residual peaks were used as internal reference for all NMR measurements. Abbreviations: s – singlet, d – doublet, t – triplet, q – quartet, m – multiplet, dd – doublet of doublet.

## Synthesis of the chemical actinometer

Potassium Reineckate: Attempts to reproduce the one-step synthesis by Szyclinski et al. [8] were not successful (operation was discontinued after formation of copious almond-smelling gases was observed during synthesis). Therefore, the synthesis was performed via a two-step procedure:

**A:** Synthesis of ammonium Reineckate by a modified protocol according to Dakin:[9] Ammonium thiocyanate (100 g, 1.3 mol) was heated in a beaker in an oil bath (oil bath temperature 150 °C) until a homogenous molten mass was formed. Then, a finely powdered mixture of ammonium dichromate (20 g, 68 mmol), and ammonium thiocyanate (20 g, 0.26 mol) was added in small portions during which the mixture

was rapidly stirred with a glass rod. Vigorous evolution of gas was observed when approx. 1/10 of the dichromate–thiocyanate mixture has been added. After the completion of addition (~20 min), the reaction was agitated with a glass rod for another 30 min, after which the heating was stopped. The mixture was further vigorously stirred and solidified on cooling. (Stirring prevents the formation of an indivisible solid!) The cooled solids were finely powdered in a mortar and added to an ice-water mixture (80 mL). The resultant mixture was stirred for 10 min, then the insoluble portion was filtered off. The collected precipitates were dissolved in hot water (60 °C, 200 mL), and the resultant mixture quickly filtered to remove any residual precipitate. The filtrate was placed in a refrigerator (6 °C) for 12 h. The formed crystals were filtered and washed on the filter with copious amounts of cold water until the filtrate was free of  $\text{SCN}^-$  ions (checked by reaction with  $\text{Fe}^{\text{III}}$ ). After drying on air, ammonium Reineckate monohydrate (ammonium tetrathiocyanato-diamminechromate(III) monohydrate) was obtained as deep violet crystals (34.7 g, 72% yield). The dried product obtained by this method can be stored at room temperature under ambient light conditions for several months without decomposition. Attempts to further purify the crystals by crystallization from water–ethanol mixtures were unsuccessful but formed toxic HCN gas.

**B:** Synthesis of potassium Reineckate:

All operations were carried under red light (11 W, from Osram, bought in the Slovak Republic) in a dark room with exclusion of other forms of irradiation. An aqueous solution of  $\text{KNO}_3$  (50 mL, saturated at ambient temperature) was heated up to 50 °C. Then, ammonium Reineckate monohydrate (2.0 g, 5.6 mmol) was added in one portion and the mixture was stirred for 5 min. The resultant solution was cooled to 6 °C in a refrigerator upon which crystals formed. The crystals were filtered and

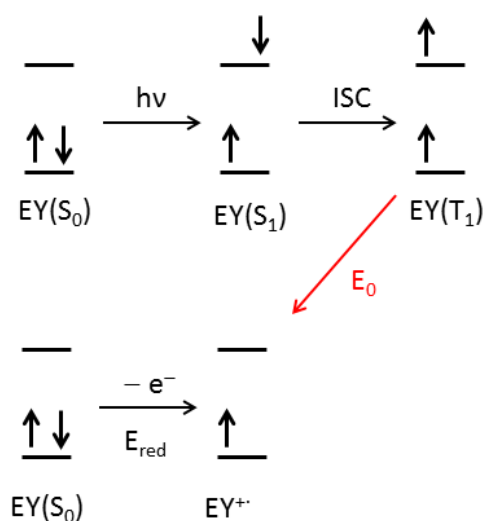
washed with a minimal amount of cold water. After drying on air, potassium Reineckate (potassium tetrathiocyanatodiamminechromate(III) monohydrate) was obtained as deep violet crystals (1.7 g, 84% yield). Potassium Reineckate readily decomposes upon exposure to ambient light, even in the solid phase.

### **Chemical actinometry and quantum yield measurements:**

Actinometry measurements were performed using a method according to Wegner and Adamson [10,11] with potassium Reineckate. Quantum-yield measurements were performed in the regime of total absorption of the incoming light by the dye. Irradiation was performed with a green high-power LED (Luxeon Rebel, Canada,  $P = 3.8 \text{ W}$ ,  $\lambda_{\text{max}} = 535 \text{ nm}$ ). The photon flux interacting with the sample was determined to be  $1.5 \cdot 10^8$  photons per second (corresponding to irradiance of  $0.55 \mu\text{W}/\text{m}^2$  at the point of intercept of radiation with cuvette wall) which did not drift over the time of the measurements as confirmed by repetitive experiments. The individual reaction times were chosen so that conversion was kept below 10% as required by the used protocol [10,11]. The substrate conversions were determined by quantitative GC-FID analysis with *n*-pentadecane as internal standard. All quantum yields were determined as an average of at least three subsequent measurements.

### **Redox potential of eosin Y:**

Knowledge of the exact redox potential of the pair eosin  $\text{Y}^+/\text{eosin Y}^*$  ( $T_1$ ) is central to the discussion of reaction mechanisms involving redox steps. This value is experimentally not available as both of the compounds are short-lived intermediates. However, the redox potential can be obtained indirectly via analysis of the following thermodynamic cycle:



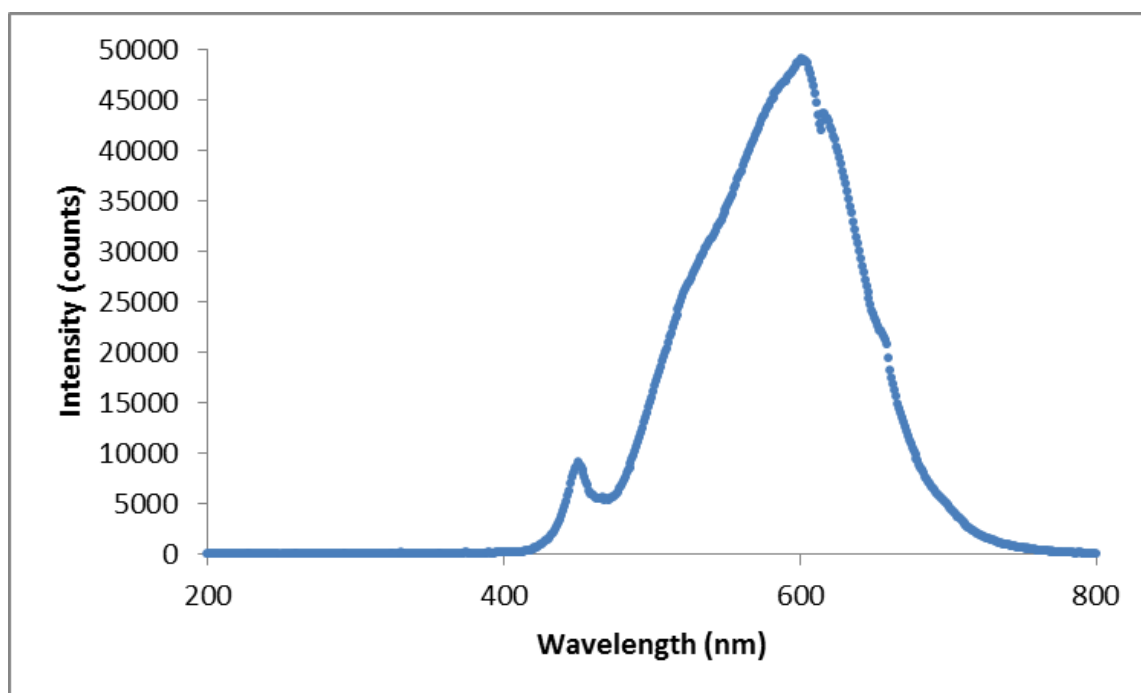
The energy of the triplet state eosin Y\* ( $T_1$ ) is derived from fluorescence measurements [12]:  $\Delta E(\text{triplet}) = E(\text{eosin Y}(T_1)) - E(\text{eosin Y}(S_0)) = 1.89 \text{ eV}$ .

The energy of the radical cation eosin Y<sup>+</sup> is derived from cyclic voltammetric experiments [13]:  $\Delta E_{\text{red}} = E(\text{Eosin Y}^{+\bullet}) - E(\text{eosin Y}(S_0)) = 0.78 \text{ eV}$ .

The combination of both values according to the aforementioned thermodynamic cycle allows the calculation of  $E_0$ :

$\Delta E_0 = \Delta E(\text{triplet}) - \Delta E_{\text{red}}$  so that  **$E_0 = 1.11 \text{ eV}$** , therefore the redox potential of the eosin Y<sup>+</sup>/eosin Y\* ( $T_1$ ) couple is  $-1.11 \text{ V}$ .

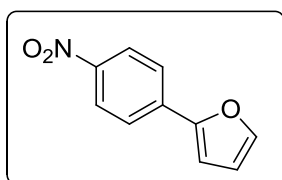
## Emission spectrum of the white LED light source



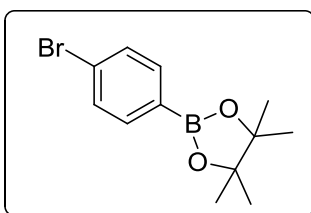
A white LED lamp with the upper spectrum was used for experiments that involved irradiation with white light.

## Spectral data of the synthesized compounds

All products used as calibration standards for GC-FID quantification were synthesized by literature methods [1-7]. Stilbene was used as internal reference (Sigma–Aldrich).

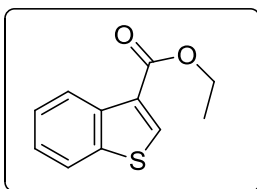


**2-(4-Nitrophenyl)furan:** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm) δ 8.25 (d, *J* = 9.0 Hz, 2H), 7.79 (d, *J* = 9.0 Hz, 2H), 7.58 (dd, *J* = 1.7 Hz, *J* = 0.5 Hz, 1H), 6.88 (dd, *J* = 3.5 Hz, *J* = 0.5 Hz, 1H), 6.56 (dd, *J* = 3.5 Hz, *J* = 1.7 Hz, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, ppm) δ 151.8 (C), 146.5 (C), 144.2 (CH), 136.5 (C), 124.4 (CH), 124.0 (CH), 112.5 (CH), 109.0 (CH). GC-MS (EI) *m/z* (relative intensity): 189 (100) [M<sup>+</sup>], 159 (68), 131 (36), 115 (68), 89 (23).



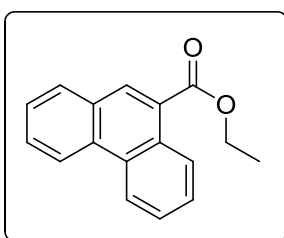
**2-(4-Bromophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane:**

**borolane:**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  7.66 (d,  $J = 8.3$  Hz, 2H), 7.51 (d,  $J = 8.3$  Hz, 2H), 1.34 (s, 12H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  136.4 (CH), 131.0 (C), 131.0 (CH), 126.3 (C), 84.1 (C), 24.9 ( $\text{CH}_3$ ). GC-MS (EI)  $m/z$  (relative intensity): 284 (56) [ $\text{M}^+$ ], 282 (56), 269 (100), 267 (100), 198 (73), 196 (74), 185 (84), 186(95), 103(33).



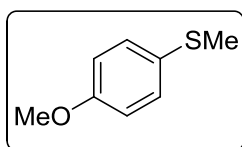
**Ethyl benzo[*b*]thiophene-3-carboxylate:**

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  8.06 (s, 1H), 7.88 – 7.83 (m, 2H), 7.47 – 7.38 (m, 2H), 4.41 (q,  $J = 7.1$  Hz, 2H), 1.42 (t,  $J = 7.1$  Hz, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  162.9 (CO), 142.2 (C), 138.8 (C), 133.9 (C), 130.4 (CH), 126.9 (CH), 125.5 (CH), 124.9 (CH), 122.8 (CH), 61.6 ( $\text{CH}_2$ ), 14.4 ( $\text{CH}_3$ ). GC-MS (EI)  $m/z$  (relative intensity): 206 (57) [ $\text{M}^+$ ], 177 (50), 161 (100), 133 (24), 89 (40).



**Ethyl phenanthrene-9-carboxylate:**

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  8.94 – 8.90 (m, 1H), 8.76 – 8.72 (m, 1H), 8.70 (d,  $J = 8.3$  Hz, 1H), 8.47 (s, 1H), 7.98 (d,  $J = 8.0$  Hz, 1H), 7.78 – 7.62 (m, 4H), 4.53 (q,  $J = 7.1$  Hz, 2H), 1.51 (t,  $J = 7.1$  Hz, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  167.7 (CO), 132.1 (C), 132.1 (CH), 130.8 (C), 130.2 (C), 130.0 (CH), 129.1 (C), 128.9 (CH), 127.4 (CH), 127.0 (CH), 126.9 (CH), 126.7 (C), 126.7 (CH) 122.9 (CH), 122.7 (CH), 61.3 ( $\text{CH}_2$ ), 14.5 ( $\text{CH}_3$ ). GC-MS (EI)  $m/z$  (relative intensity): 250 (100) [ $\text{M}^+$ ], 205 (87), 177 (71), 151 (16).



**(4-Methoxy)thioanisole:**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  7.28

(d,  $J = 8.8$  Hz, 2H), 6.86 (d,  $J = 8.8$  Hz, 2H), 3.79 (s, 3H), 2.45 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  157.2 (C), 129.2 (CH),

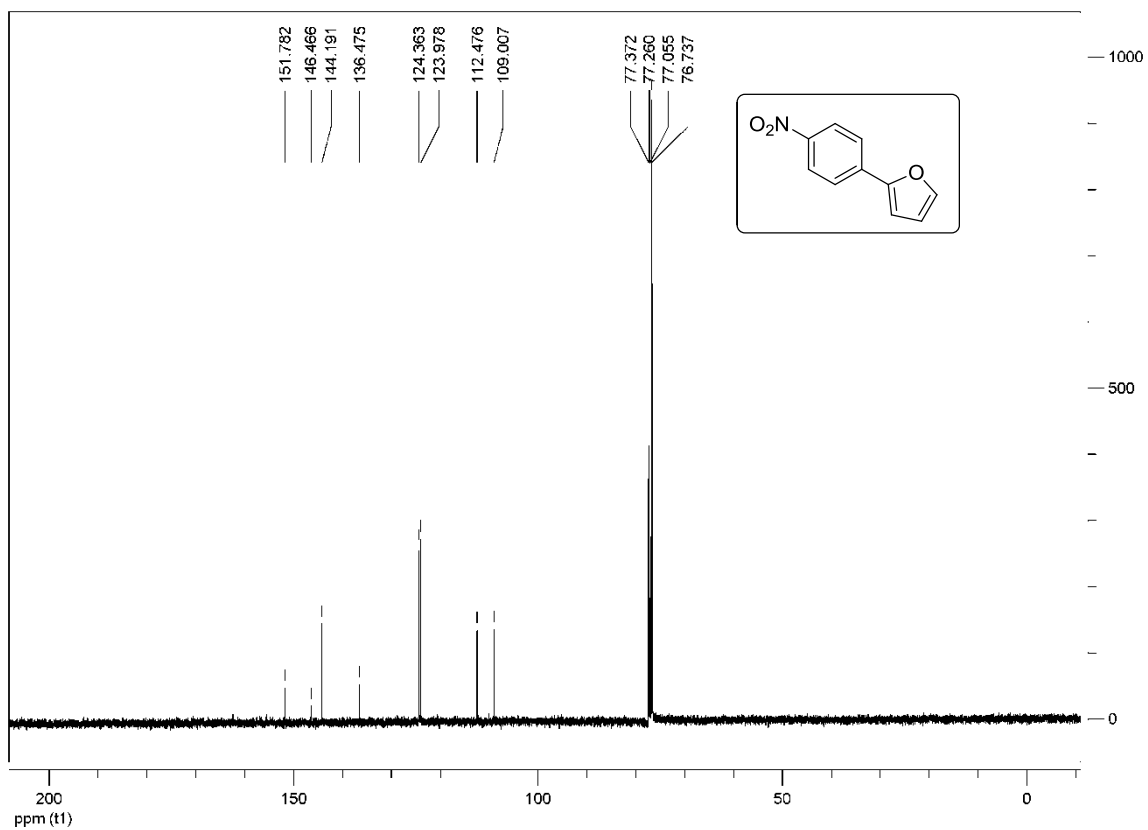
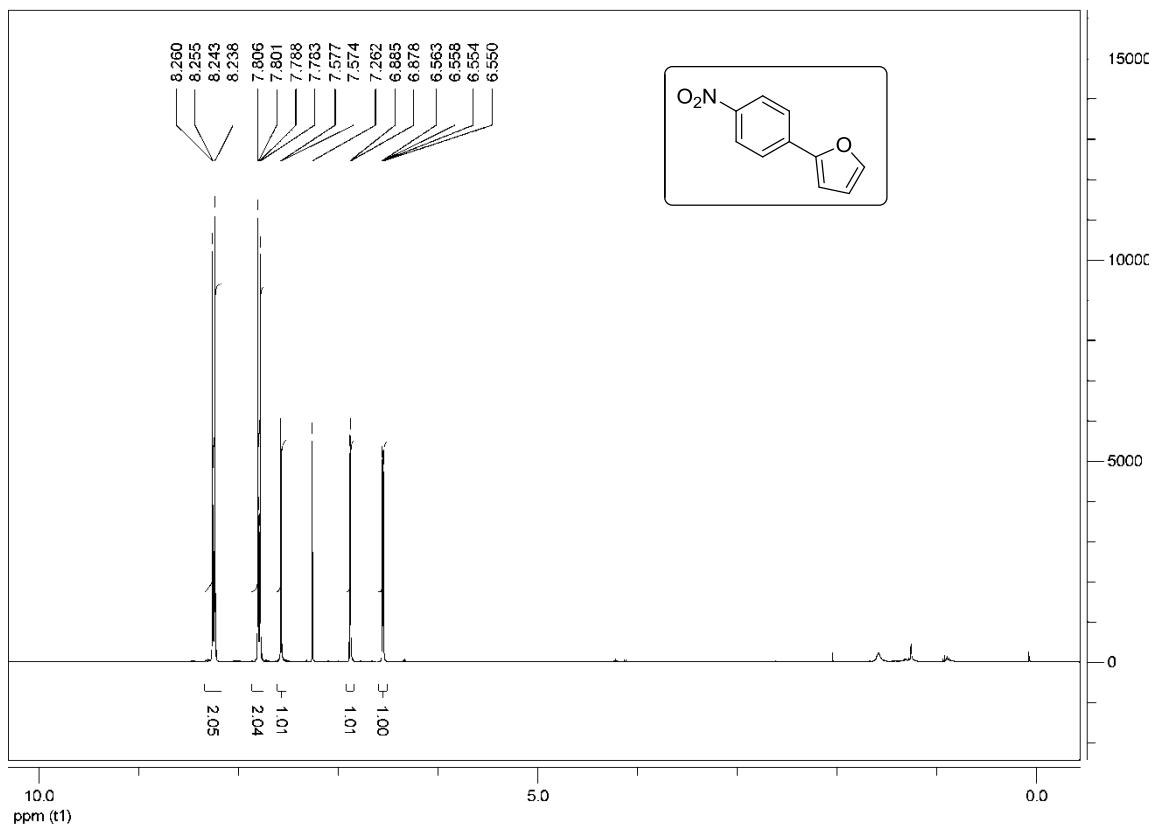
127.8 (C), 113.6 (CH), 54.3 ( $\text{CH}_3$ ), 17.1 ( $\text{CH}_3$ ). GC-MS (EI)  $m/z$  (relative intensity): 154 (81) [ $\text{M}^+$ ], 139 (100), 124 (7), 111 (18).

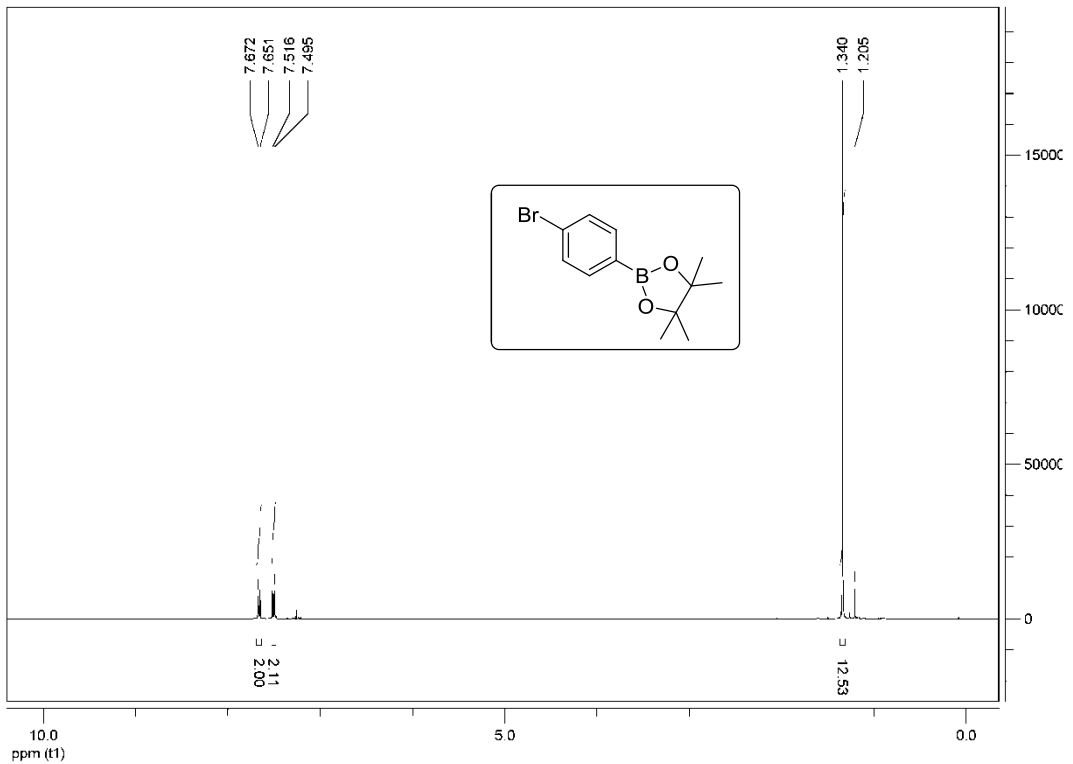
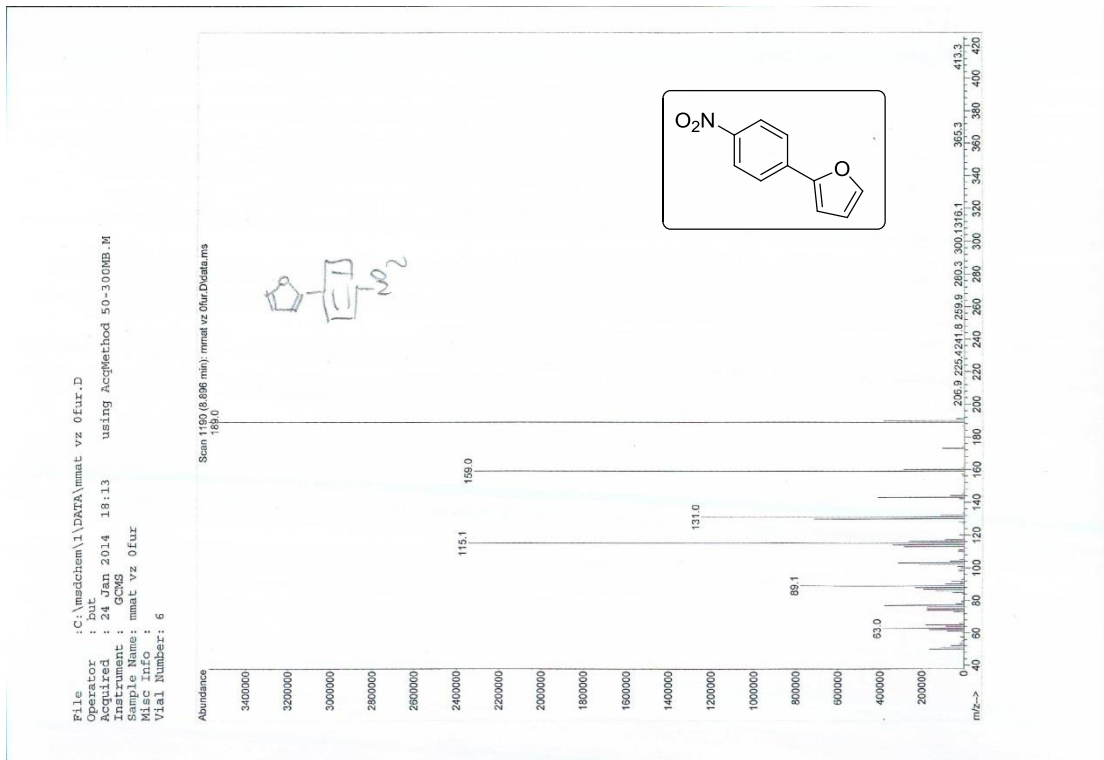
## References

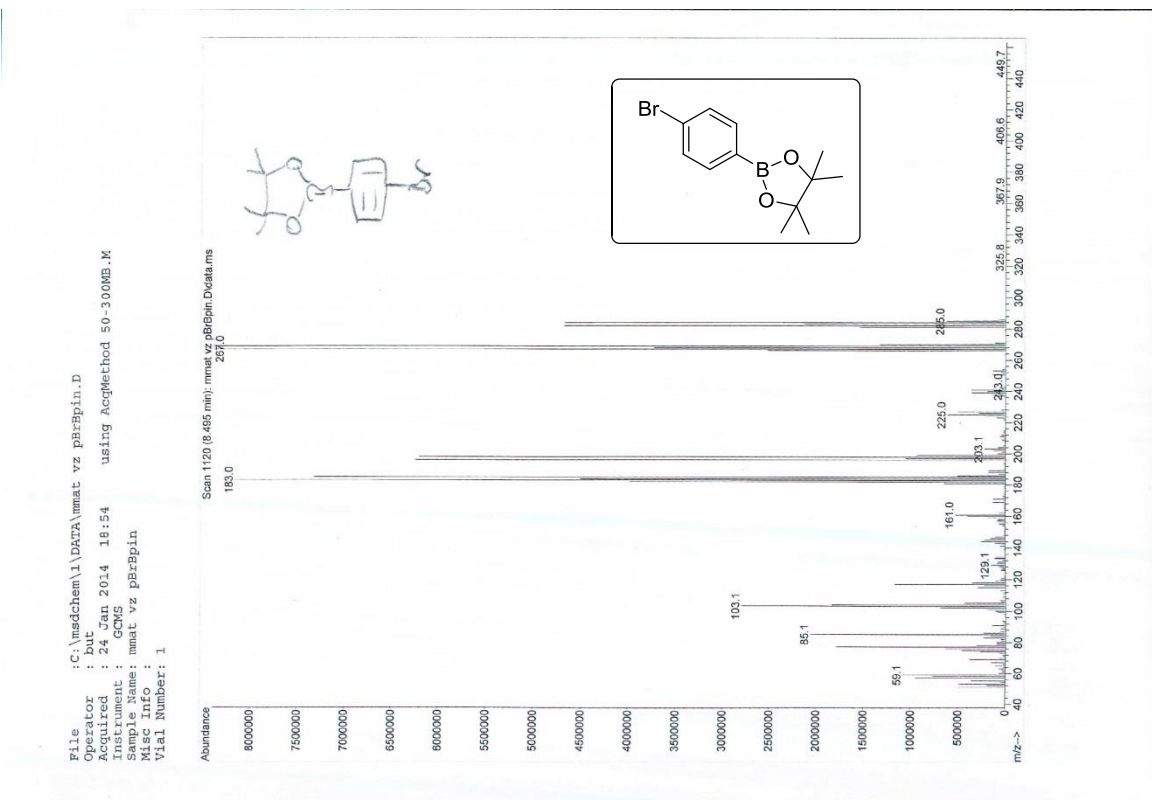
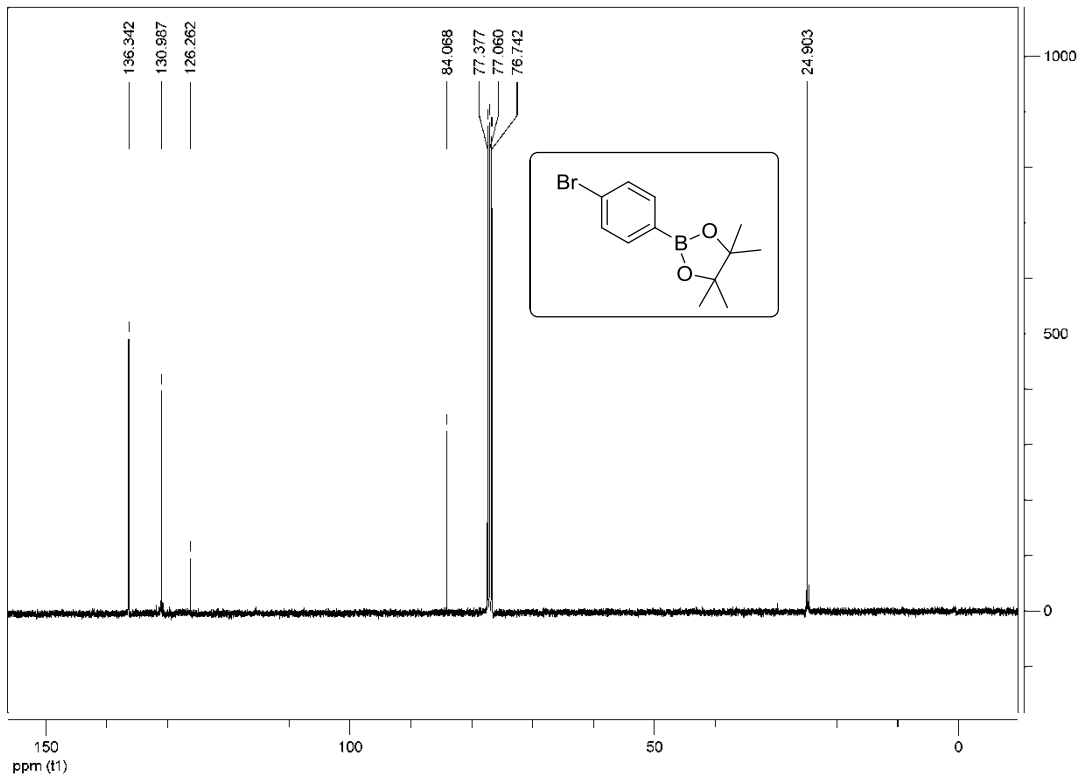
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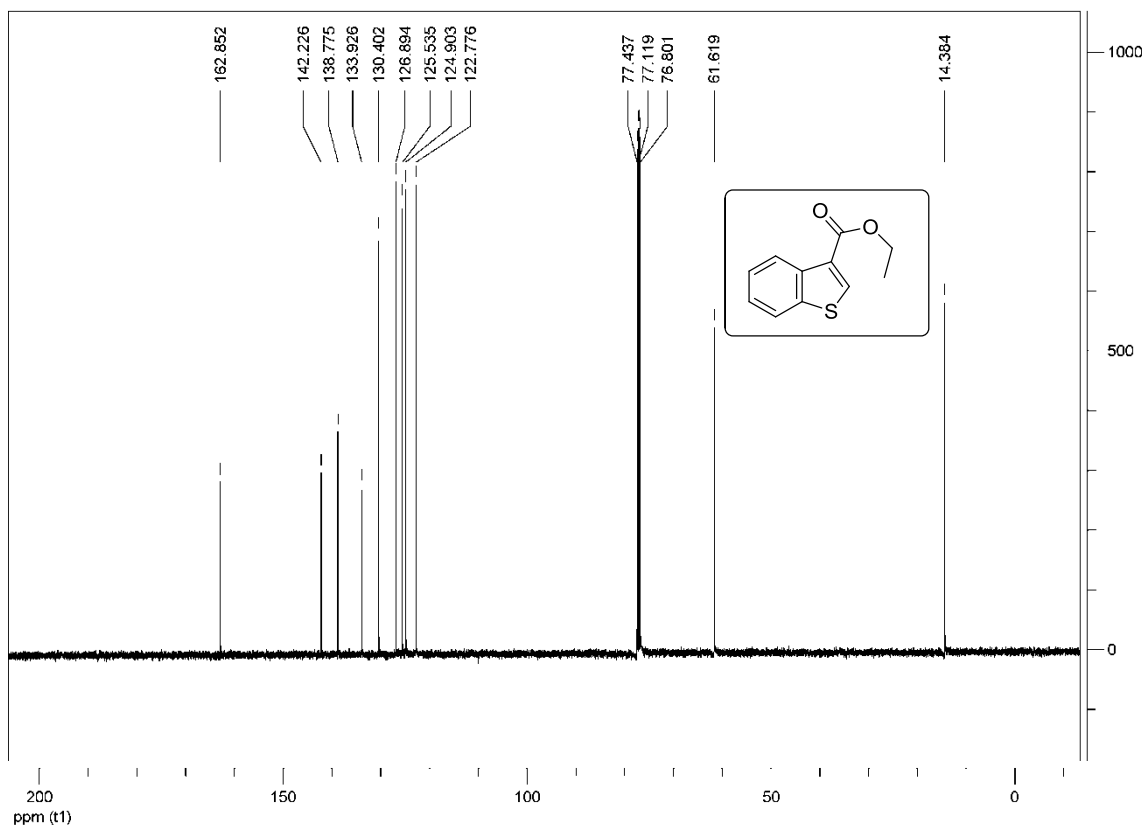
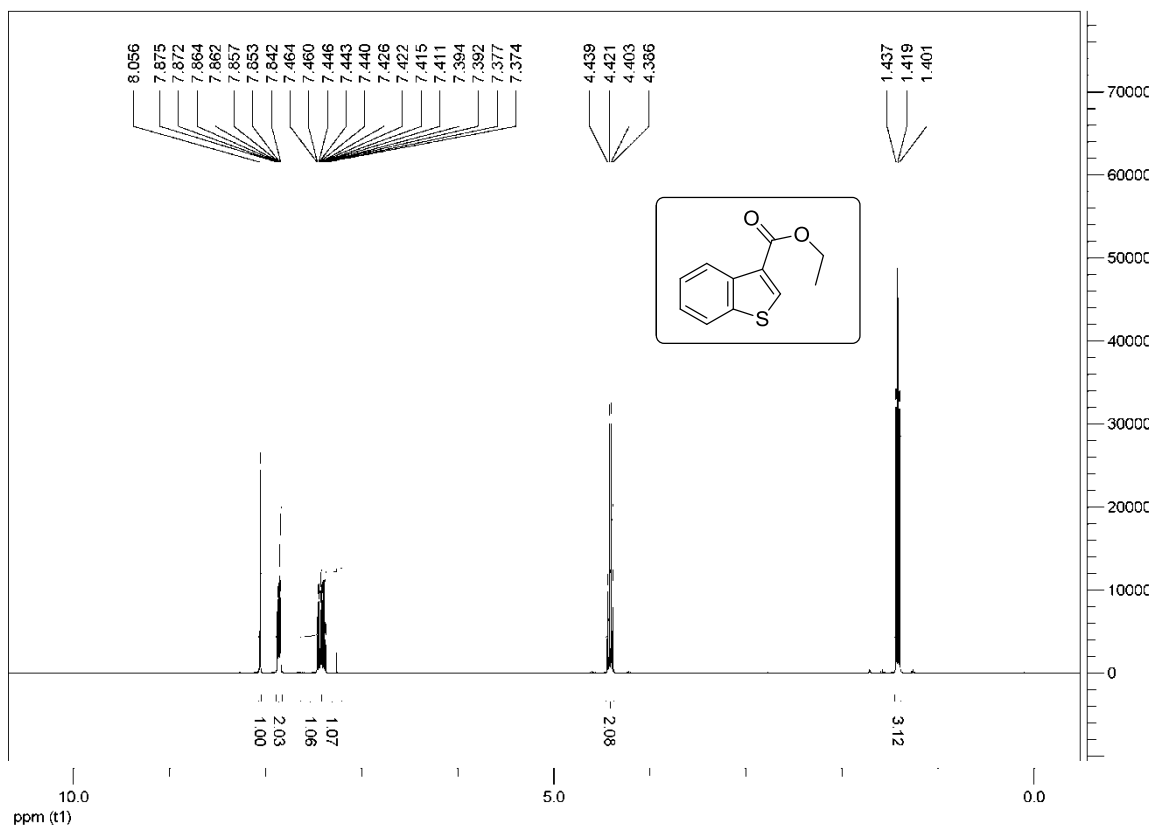


### Selected spectra:

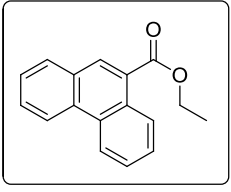
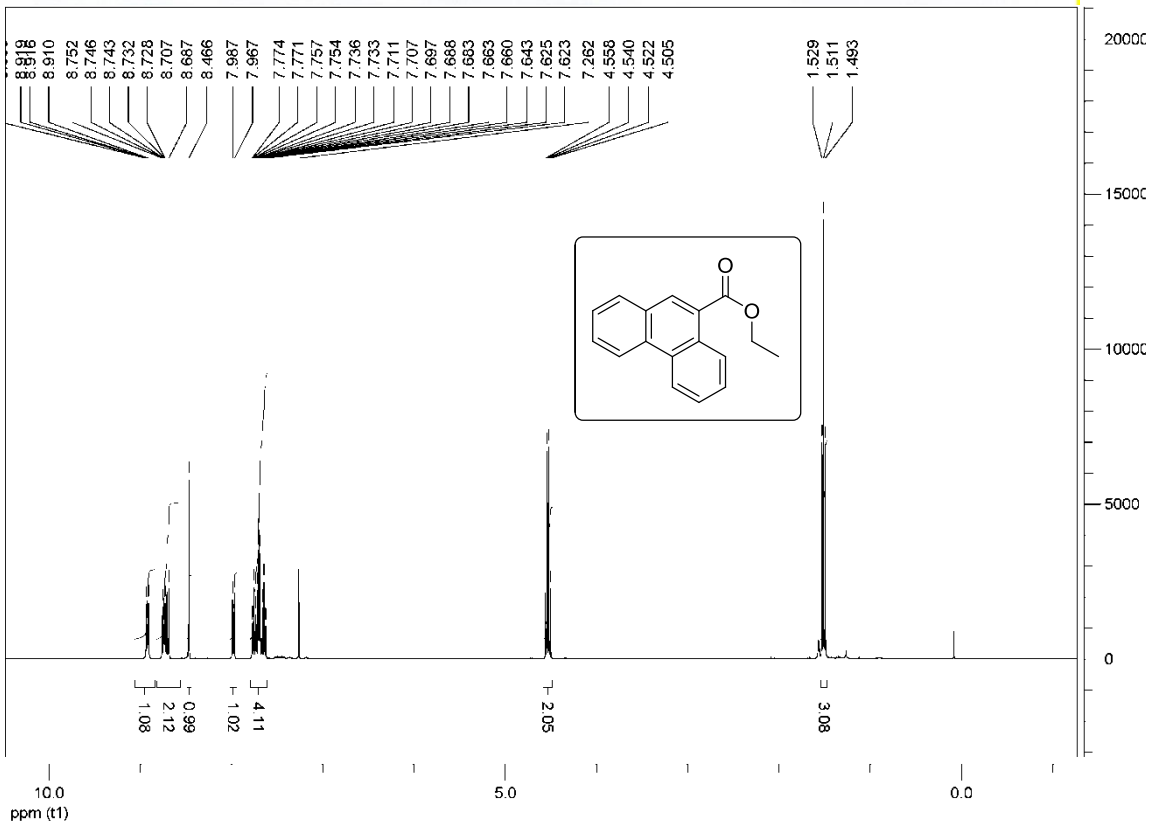
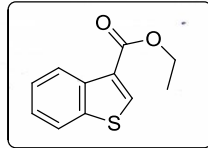
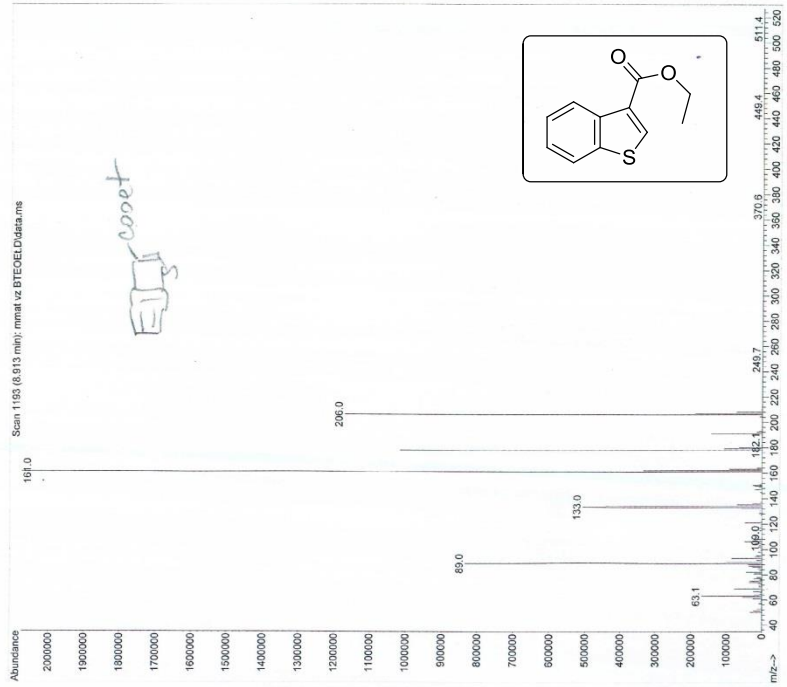


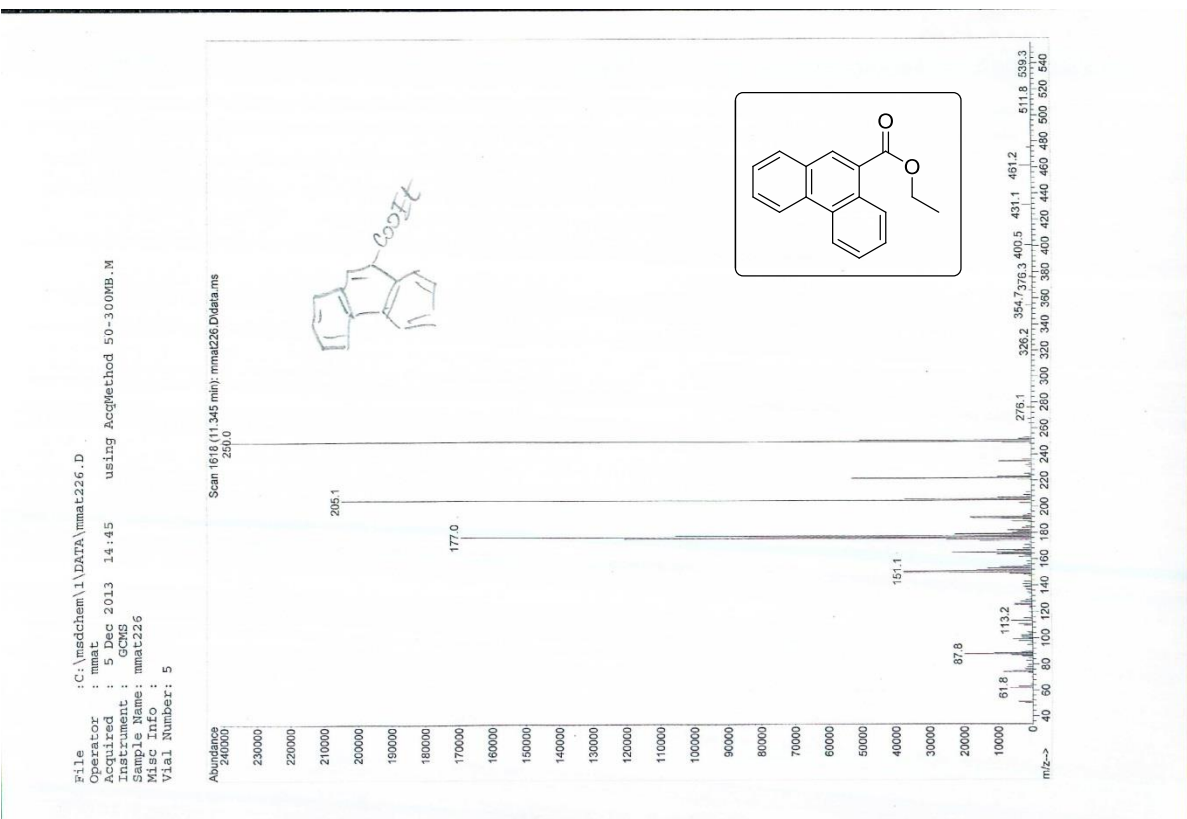
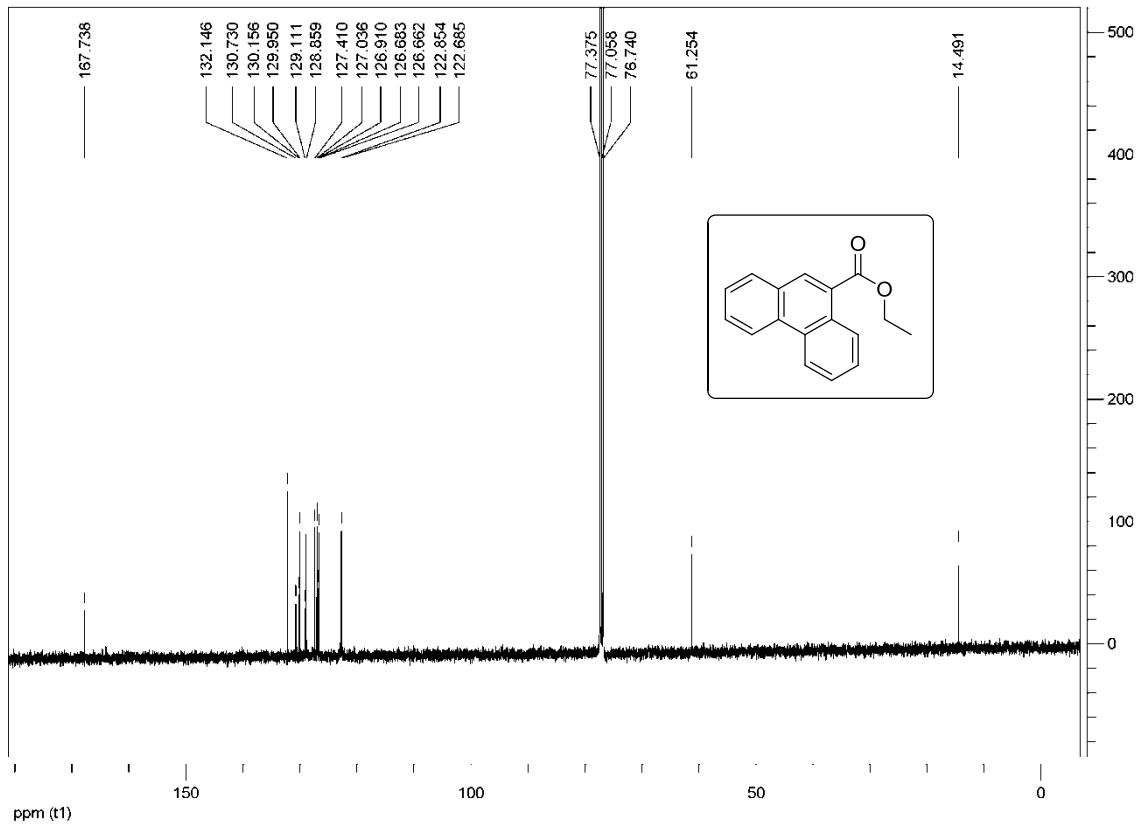






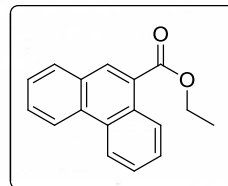
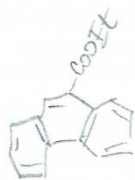
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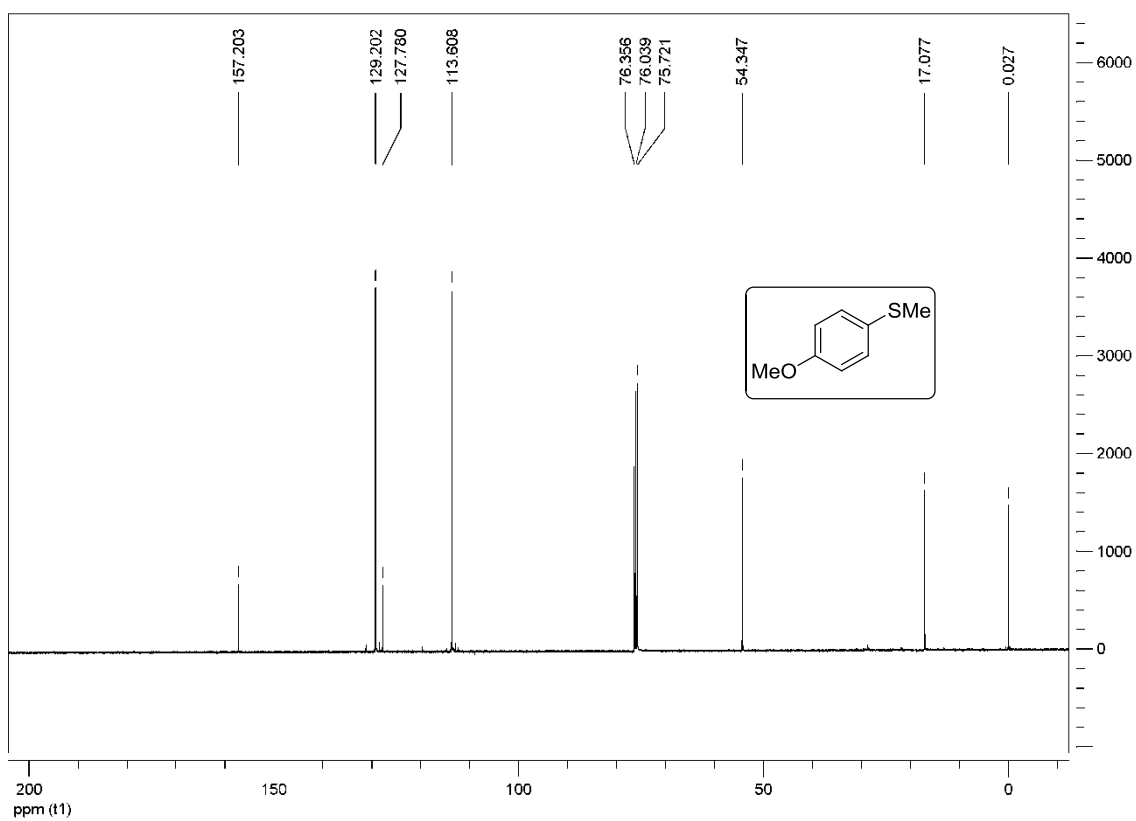
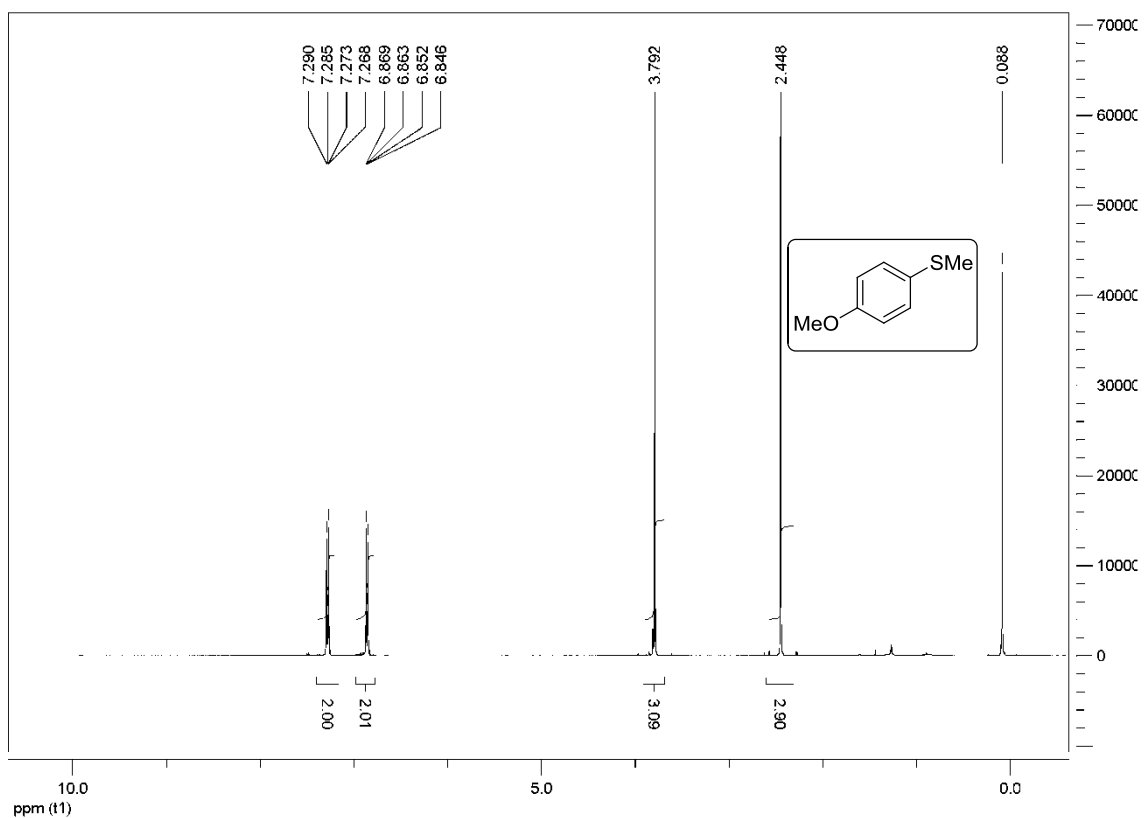




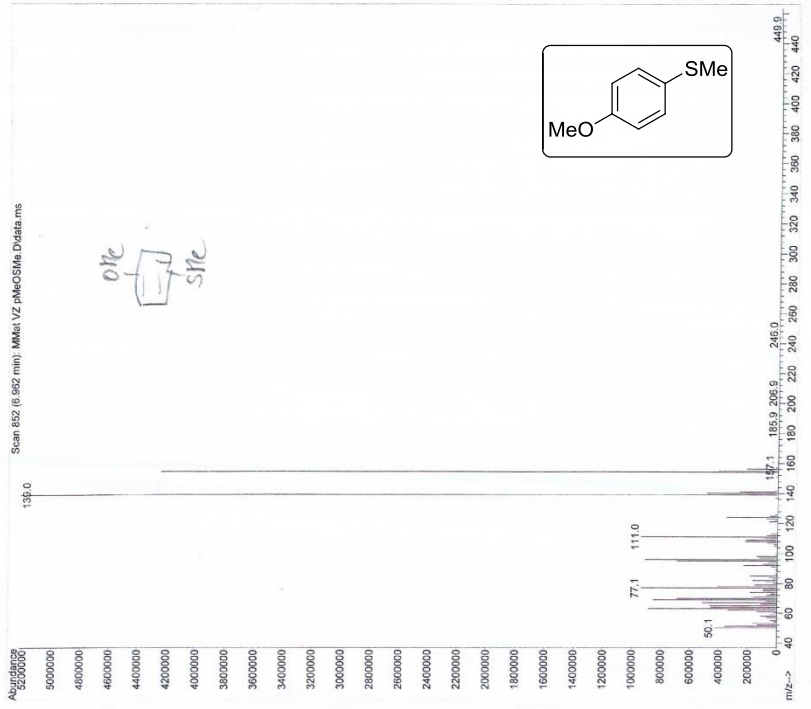
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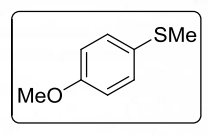




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**Results of direct photolysis of *ortho*-biphenyldiazonium tetrafluoroborate in acetonitrile with broad spectrum CFL irradiation source.**

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