

2,3-Diarylmaleate salts as a versatile class of diarylethenes with a full spectrum of photoactivity in water

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I. General information

Materials. Diarylethenes **1a-e,g,h** were synthesized according [S1]. 3,4-Bis(5-(3,5-bis(trifluoromethyl)phenyl)-2-methylthiophen-3-yl)furan-2,5-dione **1f** was synthesized according [S2]. Water was distilled before use as solvent for preparative photoreactions. All commercially available reagents were used without further purification. Column chromatography was performed using silica gel 60 (0.063-0.200 mm, pH 6.0 – 7.5) by Th.Geyer; TLC analysis was conducted on silica gel 60 F₂₅₄ plates.

Instrumentation. ¹H (400 MHz) and ¹³C (101 MHz) NMR spectra were recorded on a Bruker AV400 instrument in CDCl₃, D₂O, (CD₃)₂SO and CD₃CN. Chemical shifts are reported in ppm using the residual signals of CDCl₃, D₂O and (CD₃)₂SO as internal standards. HRMS were recorded using Agilent 1200/Agilent 6210 TOF HPLC instrument equipped with an electrospray ionization source (ESI). Melting points (uncorrected) were measured on a SMP10 apparatus (Stuart).

Photochemical studies. Electronic absorption spectra were recorded with a SF-56 spectrophotometer in 1 cm quartz cuvettes. The experimental measurements were performed in solutions of freshly distilled acetonitrile and water (buffer pH=7) in the presence of air. UV irradiation was performed with Vilber Lourmat lamps (254 nm (6 W), 365 nm (15 W), 313 nm (15 W)). Visible light irradiation was performed by blue ($\lambda_{\text{max}} = 465$ nm) and green ($\lambda_{\text{max}} = 512$ nm) LED sources. For photolysis with UV (365 nm) common glassware was used. For photolysis with UV (254 and 313 nm) quartz cuvette and round-bottom flask was used.

The extinction coefficients at the absorbance maxima (ϵ_{λ}) of **3a-A**, **3a-B**, **3b-A**, **3b-B**, **4b**, and **11a** were measured in three independent experiments for each value; the corresponding mean values were used for the calculations (Table S1). In the case of DAM's closed-ring isomers (**3a-B** and **3b-B**), NMR spectroscopy combined with electronic spectroscopy (in 1 mm cells) was used to determine conversion. The conversion of **4b** to **11a** upon UV irradiation was taken as 100% at the moment when further irradiation did not cause any changes in the spectrum.

Table S1. Photophysical properties of DAM salts.

| | λ_{max} , nm (ϵ , M ⁻¹ cm ⁻¹) of initial isomers | λ_{max} , nm (ϵ , M ⁻¹ cm ⁻¹) of photoisomers (3a-B , 3b-B) or photoproduct (11a) | Φ_{OC} (Φ for 4a) | Φ_{CO} |
|-----------|--|--|---|--------------------|
| 3a | 255 (26500), 300 (11400, shoulder) | 460 (5500) | 0.051 | 0.045 |
| 3b | 315 (24500) | 545 (10900) | 0.083 | 0.004 |
| 4a | 283 (20200) | 235 (50600) | 0.33 | - |

The quantum yields of cyclization and cycloreversion (Φ_{OC} and Φ_{CO} , respectively) for **3a** and **3b** were measured using the previously reported method [S3]. 1,2-Bis(2-methyl-1-benzothiophen-3-yl)perfluorocyclopentene in hexane solution was used as a chemical actinometer at 313, 465 and 512 nm [S3]. The photon numbers n_p were $\approx 8.7 \times 10^{15}$ photons / s at 313 nm, $\approx 7.6 \times 10^{16}$ photons / s at 465 nm, $\approx 4.6 \times 10^{16}$ photons / s at 512 nm.

The quantum yield of irreversible photorearrangement of **4a** in water was measured using the following equation:

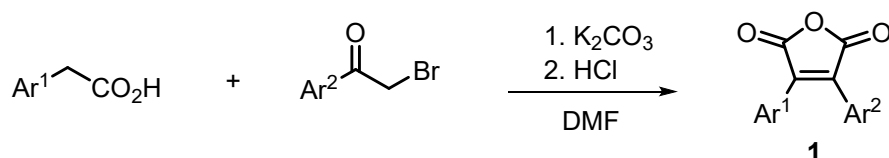
$$\Phi = \frac{\Delta A_{235}^B \cdot N_A \cdot v}{1000 \cdot \epsilon_{235}^B \cdot l \cdot n_p \cdot \frac{A_{313}^A(\Delta t)}{A_{313}(\Delta t)} (1 - 10^{-A_{313}(\Delta t)}) \cdot \Delta t}$$

, where ΔA_{235}^B is the change of absorbance of photoproduct **11a** at 235 nm during irradiation for Δt ; ϵ_{235}^B is the extinction coefficient of **11a** at 235 nm; l is the optical path; v is the solution volume; N_A is the Avogadro constant; $A_{313}^A(\Delta t)$ is the mean value of **4a** absorbance at 313 nm for during irradiation for Δt ; $A_{313}(\Delta t)$ is the total absorbance of solution at 313 nm.

II. Synthesis

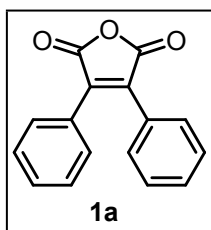
II.1. Synthesis of starting diarylethenes 1

Scheme S1.



General procedure. Arylacetic acid (1.5 mmol) and potassium carbonate (4.5 mmol) were suspended in *N,N*-dimethylformamide (DMF) (5 mL), and nitrogen was passed through the mixture for 15 min. Then 2-bromo-1-arylethanone (1.5 mmol) was added, and the suspension was stirred under nitrogen at room temperature for 1 h and at 80°C for 5 h. Next, the reaction mixture was heated at 80°C in an oxygen atmosphere until disappearance of organic components (TLC control, eluent petroleum ether / ethyl acetate 3:1). The mixture was cooled, poured into water (200 mL), and extracted with ethyl acetate (3 × 50 mL). The aqueous phase was acidified (HCl) to pH = 3-4. The mixture was kept overnight, then extracted with ethyl acetate (3 × 50 mL). The combined organic phases were washed with 5% sodium bicarbonate (150 mL), water (150 mL), dried over magnesium sulfate, and evaporated in vacuum.

3,4-Diphenylfuran-2,5-dione (**1a**).



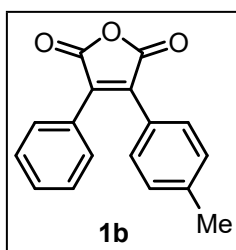
Yield 76% (0.29 g). Pale yellow powder, mp 159-160 °C.

^1H NMR (400 MHz, CDCl_3): δ = 7.60 – 7.51 (m, 4H), 7.51 – 7.37 (m, 6H). ^{13}C

NMR (101 MHz, CDCl_3): δ = 164.93, 138.30, 131.27, 129.82, 129.06, 127.32.

HRMS (ESI-TOF) m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{16}\text{H}_{10}\text{O}_3$ 251.0703, found 251.0708.

3-Phenyl-4-(*p*-tolyl)furan-2,5-dione (**1b**).



Yield 48% (0.19 g). Pale yellow powder, mp 127-128 °C.

^1H NMR (400 MHz, CDCl_3): δ = 7.63 – 7.51 (m, 2H), 7.50 – 7.38 (m, 5H),

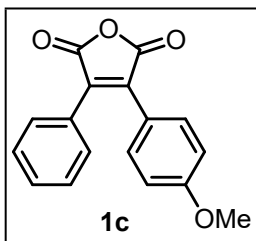
7.24 – 7.16 (m, 2H), 2.39 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3): δ = 165.09,

142.04, 138.39, 137.34, 131.08, 129.82, 129.80, 129.75, 129.03, 127.58,

124.44, 21.74. HRMS (ESI-TOF) m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{17}\text{H}_{12}\text{O}_3$ 265.0859,

found 265.0863.

3-(4-Methoxyphenyl)-4-phenylfuran-2,5-dione (1c).

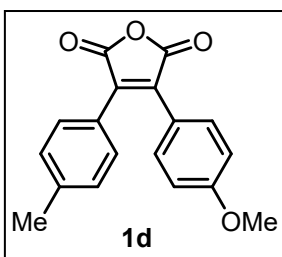


Yield 49% (0.21 g). Yellow powder, mp 132-134 °C.

^1H (400 MHz, CDCl_3): δ = 7.60 – 7.51 (m, 4H), 7.47 – 7.38 (m, 3H), 6.92 – 6.86 (m, 2H), 3.85 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3): δ = 165.35, 165.19, 162.14, 137.99, 135.86, 131.86, 130.90, 129.64, 129.08, 127.88, 119.64, 114.58, 55.57. HRMS (ESI-TOF) m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{17}\text{H}_{12}\text{O}_4$ 281.0808,

found 281.0812.

3-(4-Methoxyphenyl)-4-(*p*-tolyl)furan-2,5-dione (1d).

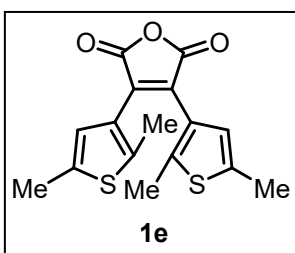


Yield 67% (0.30 g). Yellow powder, mp 142-143 °C.

^1H (400 MHz, CDCl_3): δ = 7.57 (d, J = 8.8 Hz, 2H), 7.46 (d, J = 8.1 Hz, 2H), 7.21 (d, J = 8.1 Hz, 2H), 6.90 (d, J = 8.8 Hz, 2H), 3.85 (s, 3H), 2.40 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3): δ = 165.47, 165.34, 161.97, 141.53, 137.09, 136.03, 131.72, 129.78, 129.60, 124.93, 119.84, 114.52, 55.54,

21.72. HRMS (ESI-TOF) m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{18}\text{H}_{14}\text{O}_4$ 295.0965, found 295.0969.

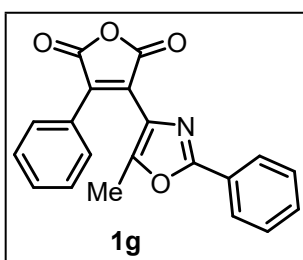
3,4-Bis(2,5-dimethylthiophen-3-yl)furan-2,5-dione (1e).



Yield 69% (0.33 g). Brown powder, mp 138-139 °C.

^1H NMR (400 MHz, CDCl_3): δ = 6.75 (s, 2H), 2.43 (s, 6H), 1.93 (s, 6H). ^{13}C NMR (101 MHz, CDCl_3): δ = 165.20, 141.47, 137.82, 134.54, 126.09, 125.55, 15.26, 14.97. HRMS (ESI-TOF) m/z $[\text{M}+\text{K}]^+$ calcd for $\text{C}_{16}\text{H}_{14}\text{O}_3\text{S}_2$ 357.0016, found 356.9927.

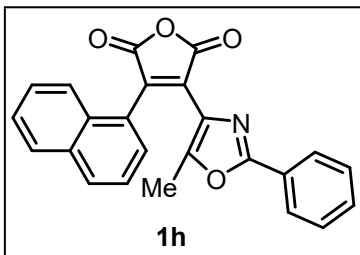
3-(5-Methyl-2-phenyloxazol-4-yl)-4-phenylfuran-2,5-dione (1g).



Yield 30% (0.14 g). Orange powder, mp 158-160 °C.

^1H NMR (400 MHz, CDCl_3): δ = 7.94 – 7.88 (m, 2H), 7.80 – 7.72 (m, 2H), 7.53 – 7.39 (m, 6H), 2.47 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3): δ = 164.82, 164.03, 160.99, 151.99, 139.21, 131.44, 130.98, 130.72, 130.55, 128.97, 128.48, 127.56, 126.66, 126.51, 125.91, 12.67. HRMS

(ESI-TOF) m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{20}\text{H}_{14}\text{NO}_4$ 332.0917, found 322.0924.



3-(5-Methyl-2-phenyloxazol-4-yl)-4-(naphthalen-1-yl) furan-2,5-dione (1h).

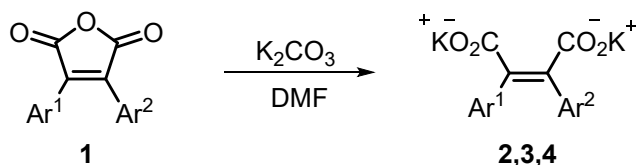
Yield 28% (0.16 g). Orange powder, mp 164-166 °C.

^1H NMR (400 MHz, CDCl_3): δ = 8.02 (d, J = 8.1 Hz, 1H), 7.92 (d, J = 8.1 Hz, 1H), 7.69 – 7.52 (m, 5H), 7.47 (t, J = 7.4 Hz, 1H), 7.42 – 7.27 (m, 4H), 2.23 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3): δ =

164.97, 163.74, 160.73, 152.94, 138.70, 134.15, 133.49, 131.30, 130.81, 130.51, 129.07, 128.83, 128.75, 126.94, 126.49, 126.38, 125.76, 125.12, 125.03, 12.61. HRMS (ESI-TOF) m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{24}\text{H}_{16}\text{NO}_4$ 382.1074, found 382.1085.

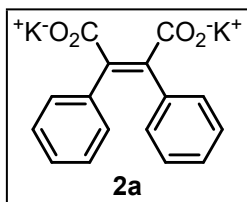
II.2. Synthesis of DAM salts

Scheme S2.



3,4-Diaryl substituted maleic anhydride **1** (2 mmol) and potassium carbonate (1.8 mmol) were suspended in DMF (5 mL) and the mixture was stirred at 80 °C for 16 h. The reaction was controlled by ¹³C NMR spectroscopy (disappearance of potassium carbonate: for details, see Section III.1). After completion of the reaction, the mixture was diluted with diethyl ether (50 mL), filtered on a glass funnel filter and dried in vacuo.

Potassium 2,3-diphenylmaleate (**2a**).



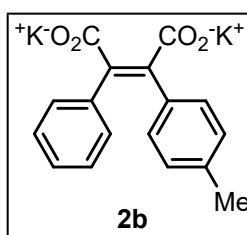
Yield 76% (0.47 g). White powder, mp >300 °C.

¹H NMR (400 MHz, D₂O): δ = 7.25 – 7.12 (m, 6H), 7.12 – 7.00 (m, 4H). ¹³C

NMR (101 MHz, D₂O): δ = 177.61, 139.49, 138.27, 129.74, 128.15, 127.17.

HRMS (ESI-TOF) *m/z* [M-2K+H]⁻ calcd for C₁₆H₁₀K₂O₄ 267.0663, found 267.0658.

Potassium 2-phenyl-3-(*p*-tolyl)maleate (**2b**).



Yield 58% (0.37 g). White powder, mp >300 °C.

¹H NMR (400 MHz, D₂O): δ = 7.25 – 7.18 (m, 3H), 7.13 – 7.07 (m, 2H),

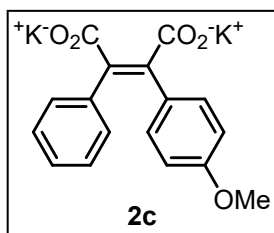
7.06 – 7.01 (m, 2H), 7.01 - 6.96 (m, 2H). 2.24 (s, 3H). ¹³C NMR (101 MHz,

D₂O): δ = 177.91, 177.65, 139.72, 138.78, 138.47, 137.40, 135.14, 129.76,

129.70, 128.67, 128.14, 127.07, 20.31. HRMS (ESI-TOF) *m/z* [M-2K+H]⁻

calcd for C₁₇H₁₂K₂O₄ 281.0819, found 281.0818.

Potassium 2-(4-methoxyphenyl)-3-phenylmaleate (**2c**).



Yield 73% (0.49 g). White powder, mp >300 °C.

¹H (400 MHz, D₂O): δ = 7.25 – 7.18 (m, 3H), 7.16 – 7.08 (m, 2H), 7.03 (d,

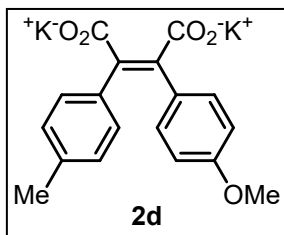
J = 7.7 Hz, 2H), 6.80 (d, *J* = 7.8 Hz, 2H), 3.77 (s, 3H). ¹³C NMR (101 MHz,

D₂O): δ = 177.94, 177.66, 157.87, 139.32, 138.63, 138.52, 131.13, 130.93,

129.80, 128.15, 127.03, 113.55, 55.30. HRMS (ESI-TOF) *m/z* [M-2K+H]⁻

calcd for C₁₇H₁₂K₂O₅ 297.0769, found 297.0770.

Potassium 2-(4-methoxyphenyl)-3-(*p*-tolyl) maleate (2d).

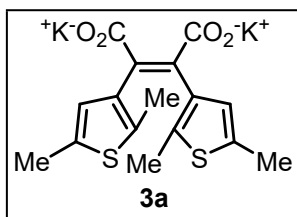


Yield 88% (0.61 g). Beige powder, mp >300 °C.

^1H (400 MHz, D_2O): $\delta = 7.07 - 6.94$ (m, 6H), 6.79 (d, $J = 8.4$ Hz, 2H), 3.76 (s, 3H), 2.25 (s, 3H). ^{13}C NMR (101 MHz, D_2O): $\delta = 177.87, 177.85, 157.70, 138.81, 138.54, 137.16, 135.27, 131.02, 129.63, 128.61, 113.46, 55.20, 20.22$. HRMS (ESI-TOF) m/z $[\text{M}-2\text{K}+\text{H}]^-$ calcd for $\text{C}_{18}\text{H}_{14}\text{K}_2\text{O}_5$

311.0925, found 311.0921.

Potassium 2,3-bis(2,5-dimethylthiophen-3-yl)maleate (3a).



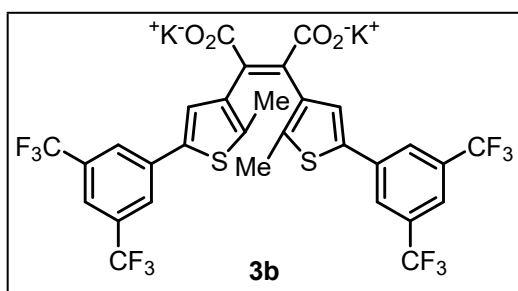
Yield 55% (0.41 g). Brown powder, mp >300 °C.

^1H NMR (400 MHz, D_2O): $\delta = 6.27$ (s, 1H), 2.27 (s, 3H), 2.00 (s, 3H). ^{13}C NMR (101 MHz, D_2O): $\delta = 177.27, 135.77, 135.28, 134.78, 134.62, 127.04, 14.19, 13.07$. HRMS (ESI-TOF) m/z $[\text{M}-2\text{K}+\text{H}]^-$ calcd for

$\text{C}_{16}\text{H}_{14}\text{K}_2\text{O}_4\text{S}_2$ 335.0417, found 335.0413.

3,4-Bis(5-(3,5-bis(trifluoromethyl)phenyl)2-methylthiophen-3-yl)furan-2,5-dione (3b).*

* The reaction was performed on 100 mg of substrate.

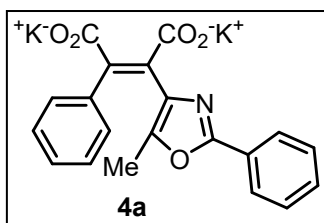


Yield 80% (0.09 g). White powder, mp >300 °C.

^1H NMR (400 MHz, $\text{D}_2\text{O}+\text{CD}_3\text{CN}$): δ = 8.40 (s, 4H), 8.29 (s, 2H), 7.59 (s, 2H), 2.75 (s, 6H). ^{13}C NMR (101 MHz, $\text{D}_2\text{O}+\text{CD}_3\text{CN}$): δ = 174.84, 139.34, 136.89, 136.27, 135.53, 134.37, 131.22 (q, J = 33.3 Hz), 128.38, 127.06, 124.77, 124.36, 121.66, 119.60, 118.95, 13.00.

HRMS (ESI-TOF) m/z $[\text{M}-2\text{K}+\text{H}]^-$ calcd for $\text{C}_{30}\text{H}_{14}\text{F}_{12}\text{O}_4\text{S}_2\text{K}_2$ 731.0226, found 731.0230.

Potassium 2-(5-methyl-2-phenyloxazol-4-yl)-3-phenylmaleate (4a).

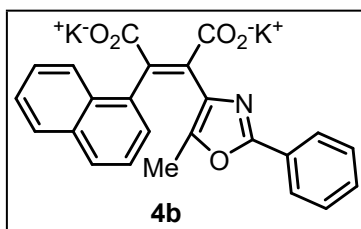


Yield 66% (0.51 g). Brown powder, mp >300 °C.

^1H NMR (400 MHz, D_2O): δ = 7.94 - 7.79 (m, 2H), 7.56 - 7.42 (m, 3H), 7.33 - 7.14 (m, 5H). ^{13}C NMR (101 MHz, D_2O): δ = 177.53, 174.48, 159.91, 147.55, 147.21, 137.79, 132.91, 130.72, 129.12, 128.57, 128.35, 126.60, 126.25, 125.95, 9.77.

HRMS (ESI-TOF) m/z $[\text{M}-2\text{K}+3\text{H}]^+$ calcd for $\text{C}_{20}\text{H}_{13}\text{K}_2\text{NO}_5$ 350.1023, found 350.1030.

3-(5-Methyl-2-phenyloxazol-4-yl)-4-(naphthalen-1-yl) furan-2,5-dione (4b).



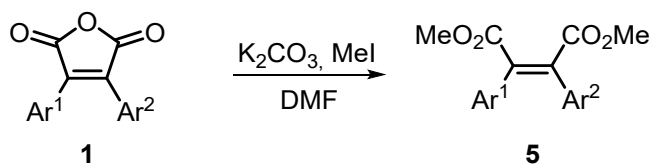
Yield 84% (0.72 g). Brown powder, mp = 262 °C.

^1H NMR (400 MHz, D_2O): δ = 8.10 (d, J = 8.2 Hz, 1H), 7.87 - 7.80 (m, 2H), 7.68 - 7.61 (m, 2H), 7.53 - 7.38 (m, 8H), 1.77 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3): δ = 176.32, 174.14, 158.79, 146.64, 143.31, 135.28, 132.72, 132.28, 130.15, 129.94, 129.80, 128.16,

127.56, 127.41, 126.24, 125.60, 125.33, 125.24, 125.09, 124.92, 9.75. HRMS (ESI-TOF) m/z $[\text{M}-2\text{K}+3\text{H}]^+$ calcd for $\text{C}_{24}\text{H}_{15}\text{K}_2\text{NO}_5$ 400.1180, found 400.1190.

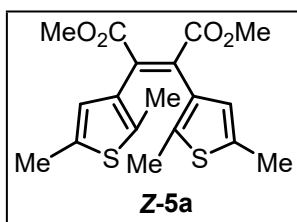
II.3. Trapping of DAM salts

Scheme S3.



Products 5a,b. 3,4-Aryl substituted maleic anhydride **1** (2 mmol) and potassium carbonate (6 mmol, 0.83 g) were suspended in DMF (5 mL), the mixture was stirred for 1 h at 80 °C and cooled down to RT. Then iodomethane (5 mmol, 42 μ L) or 2-bromo-1-phenylethan-1-one (5 mmol, 0.50 g) was added, and the suspension was stirred at room temperature for 24 h. The reaction mixture was poured into water (150 mL) and extracted with ethyl acetate (4 \times 40 mL). The combined organic phases were washed with water (150 mL), dried with magnesium sulfate, and evaporated in vacuum. The residue was purified by column chromatography eluting by petroleum ester/ethyl acetate (20:1).

Dimethyl 2,3-bis(2,5-dimethylthiophen-3-yl)maleate (**Z-5a**).

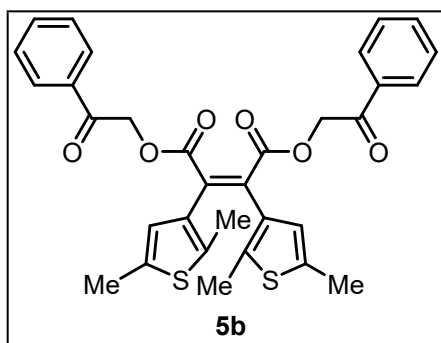


Yield 63% (0.46 g). Orange powder, mp 128 °C.

¹H NMR (400 MHz, CDCl₃): δ = 6.26 (s, 2H), 3.80 (s, 6H), 2.30 (s, 6H), 1.98 (s, 6H). ¹³C NMR (101 MHz, CDCl₃): δ = 168.46, 136.94, 135.84, 134.57, 131.05, 126.28, 52.69, 15.19, 13.98. HRMS (ESI-TOF) *m/z*

[M+H]⁺ calcd for C₁₈H₂₁O₄S₂ 365.0876, found 365.0886.

Bis(2-oxo-2-phenylethyl) 2,3-bis(2,5-dimethylthiophen-3-yl)maleate (**5b**).



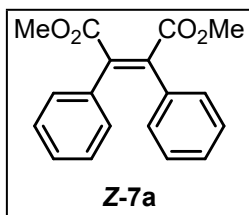
Yield 42% (0.48 g). Pale orange powder, mp 99-100 °C.

¹H NMR (400 MHz, CDCl₃): δ = 7.94 – 7.88 (m, 4H), 7.62-7.56 (m, 2H), 7.50-7.43 (m, 4H), 6.52 -6.47 (m, 2H), 5.42 (s, 4H), 2.35 – 2.32 (m, 6H), 2.06 (s, 6H). ¹³C NMR (101 MHz, CDCl₃): δ = 192.02, 167.24, 137.70, 135.74, 134.64, 134.54, 133.85, 130.91, 128.91, 128.01, 126.72, 67.23, 15.24, 14.22. HRMS (ESI-TOF) *m/z* [M+H]⁺ calcd for C₃₂H₂₈O₆S₂

573.1400, found 573.1408.

Products Z-7a and Z-7b. Corresponding DAM salt (2 mmol) was suspended in DMF (5 mL) with potassium carbonate (2 mmol, 0.28 g) and iodomethane (5 mmol, 42 μ L) was added. The suspension was stirred at room temperature for 24 h. The reaction mixture was poured into water (150 mL) and extracted with ethyl acetate (4×40 mL). The combined organic phases were washed with water (150 mL), dried with magnesium sulfate, and evaporated in vacuum. The residue was purified by column chromatography eluting by petroleum ester/ethyl acetate (20:1).

Dimethyl 2,3-diphenylmaleate (Z-7a).

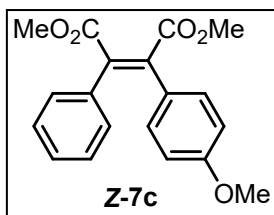


Yield 35% (0.21 g). Pale yellow powder, mp 108 °C.

^1H NMR (400 MHz, CDCl_3): δ = 7.23 – 7.15 (m, 6H), 7.12 – 7.07 (m, 4H), 3.83 (s, 6H). ^{13}C NMR (101 MHz, CDCl_3): δ = 168.48, 138.91, 134.53, 129.82, 128.47, 128.28, 52.84. HRMS (ESI-TOF) m/z $[\text{M}+\text{Na}]^+$ calcd for

$\text{C}_{18}\text{H}_{16}\text{O}_4$ 319.0941 found 319.0944.

Dimethyl 2-(4-methoxyphenyl)-3-phenylmaleate (Z-7c).



Yield 70% (0.46 g). Pale yellow powder, mp 87-88 °C.

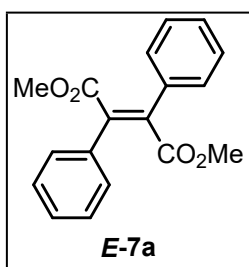
^1H NMR (400 MHz, CDCl_3): δ = 7.24 – 7.19 (m, 3H), 7.14 – 7.09 (m, 2H), 7.03 – 6.98 (m, 2H), 6.72 – 6.66 (m, 2H), 3.85 (s, 3H), 3.81 (s, 3H), 3.74 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3): δ = 169.01, 168.41, 159.75, 139.69,

136.52, 134.91, 131.22, 129.94, 128.34, 128.26, 126.54, 55.24, 52.76, 29.80. HRMS (ESI-TOF) m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{19}\text{H}_{18}\text{O}_5$ 327.1227 found 327.1236.

II.4. Preparative photoreactions of DAMs

Preparative photoreactions of DAMs. Potassium diarylmaleate (0.25 mmol) was dissolved in 200 mL of distilled water, and the reaction mixture was irradiated with appropriate light source (DAMs **2a-d**, **4a,b**: $\lambda = 365$ nm, 15 W; DAM **3a**: $\lambda = 313$ nm, 15 W) with stirring. After completion of the reaction (NMR control), the mixture was evaporated in vacuum. The residue was suspended in DMF (5 mL) and potassium carbonate (104 mg, 0.75 mmol) was added. The reaction mixture was stirred for 1 h at room temperature. Then iodomethane (40 μ L, 0.6 mmol) was added, and the suspension was stirred at room temperature for 24 h. The reaction mixture was poured into water (150 mL) and extracted with ethyl acetate (3×50 mL). The combined organic phases were washed with water (150 mL), dried with magnesium sulfate, and evaporated in vacuum. The residue was purified by column chromatography eluting by petroleum ester/ethyl acetate (20:1).

Dimethyl 2,3-diphenylmaleate (*E*-7a).

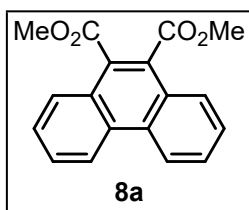


DAM: **2a**. Reaction time: 273 h.

Yield 28% (0.02 g). White powder, mp 145 °C.

^1H NMR (400 MHz, CDCl_3): $\delta = 7.46 - 7.32$ (m, 10H), 3.54 (s, 6H). ^{13}C NMR (101 MHz, CDCl_3): $\delta = 168.58, 137.74, 135.54, 128.98, 128.64, 128.14, 52.37$. HRMS (ESI-TOF) m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{18}\text{H}_{16}\text{O}_4$ 297.1121, found 297.1126.

Dimethyl phenanthrene-9,10-dicarboxylate (**8a**).



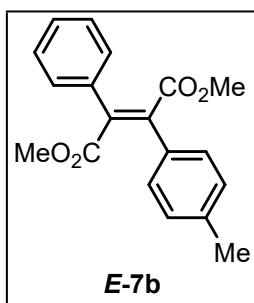
DAM: **2a**. Reaction time: 273 h.

Yield 57% (0.04 g). White powder, mp 133 °C.

^1H NMR (400 MHz, CDCl_3): $\delta = 8.73$ (d, $J = 8.4$ Hz, 2H), 8.21 – 8.14 (m, 2H), 7.82 – 7.71 (m, 2H), 7.71 – 7.63 (m, 2H), 4.04 (s, 6H). ^{13}C NMR (101

MHz, CDCl_3): $\delta = 168.50, 131.23, 130.04, 128.64, 127.82, 127.22, 127.05, 123.03, 52.94$. HRMS (ESI-TOF) m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{18}\text{H}_{14}\text{O}_4$ 295.0965, found 295.0971.

Dimethyl 2-phenyl-3-(p-tolyl)maleate (*E*-7b).

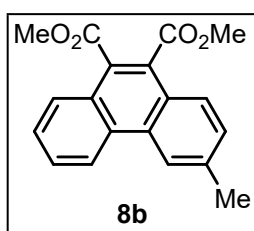


DAM: **2b**. Reaction time: 77.5 h.

Yield 31% (0.02 g). White powder, mp 106 °C.

¹H NMR (400 MHz, CDCl₃): δ = 7.44 – 7.33 (m, 5H), 7.32 – 7.27 (m, 2H), 7.23 – 7.14 (m, 2H), 3.57 (s, 3H), 3.54 (s, 3H), 2.37 (s, 3H). ¹³C NMR (101 MHz, CDCl₃): δ = 168.76, 168.74, 139.00, 137.80, 137.06, 135.71, 132.59, 129.39, 128.88, 128.61, 128.12, 127.99, 52.36, 52.31, 21.46. HRMS (ESI-TOF) *m/z* [M+H]⁺ calcd for C₁₉H₁₈O₄ 311.1278, found 311.1284

Dimethyl 3-methylphenanthrene-9,10-dicarboxylate (**8b**).

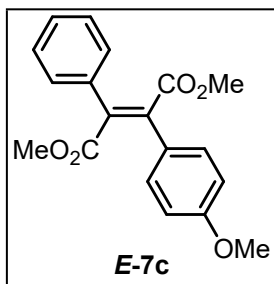


DAM: **2b**. Reaction time: 77.5 h.

Yield 55% (0.04 g). Pale yellow powder, mp 110 °C.

¹H NMR (400 MHz, CDCl₃): δ = 8.72 (d, *J* = 8.4 Hz, 1H), 8.51 (s, 1H), 8.17 (d, *J* = 9.1 Hz, 1H), 8.05 (d, *J* = 8.5 Hz, 1H), 7.77 – 7.70 (m, 1H), 7.69 – 7.62 (m, 1H), 7.50 (d, *J* = 9.6 Hz, 1H), 4.03 (s, 6H), 2.64 (s, 3H). ¹³C NMR (101 MHz, CDCl₃): δ = 168.64, 168.60, 138.79, 131.38, 130.93, 130.12, 129.59, 128.95, 128.38, 127.69, 127.43, 127.01, 126.90, 125.17, 123.00, 122.79, 52.88, 22.29. HRMS (ESI-TOF) *m/z* [M+H]⁺ calcd for C₁₉H₁₆O₄ 309.1121, found 309.1128.

Dimethyl 2-(4-methoxyphenyl)-3-phenylmaleate (*E*-7c).

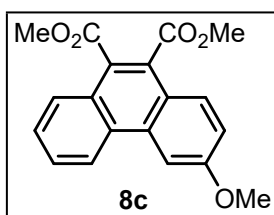


DAM: **2c**. Reaction time: 77.5 h.

Yield 24% (0.02 g). White powder, mp 109 °C.

¹H NMR (400 MHz, CDCl₃): δ = 7.58 – 7.17 (m, 7H), 7.02 – 6.81 (m, 2H), 3.83 (s, 3H), 3.58 (s, 3H), 3.53 (s, 3H). ¹³C NMR (101 MHz, CDCl₃): δ = 168.91, 168.88, 160.19, 137.39, 136.62, 135.78, 129.54, 128.85, 128.61, 128.12, 127.83, 114.12, 55.41, 52.40, 52.31. HRMS (ESI-TOF) *m/z* [M+H]⁺ calcd for C₁₉H₁₈O₅ 327.1227, found 327.1235.

Dimethyl 3-methoxyphenanthrene-9,10-dicarboxylate (**8c**).



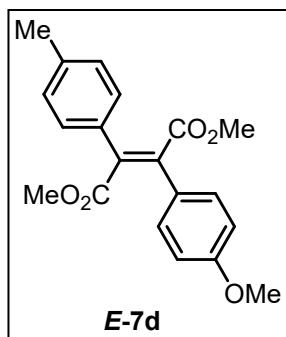
DAM: **2c**. Reaction time: 77.5 h.

Yield 66% (0.05 g). Pale yellow powder, mp 110 °C.

¹H NMR (400 MHz, CDCl₃): δ = 8.63 (d, *J* = 8.2 Hz, 1H), 8.20 (d, *J* = 8.1 Hz, 1H), 8.12 – 8.01 (m, 2H), 7.76 – 7.69 (m, 1H), 7.69 – 7.62 (m, 1H), 7.29 (dd, *J* = 9.1, 2.5 Hz, 1H), 4.05 – 4.01 (m, 9H). ¹³C NMR (101 MHz, CDCl₃): δ = 168.71, 168.57, 159.93, 133.11, 130.51, 130.28, 128.71, 128.12, 127.89, 127.72, 127.24, 127.05, 123.01,

121.69, 117.90, 104.32, 55.64, 52.89, 52.84. HRMS (ESI-TOF) m/z $[M+H]^+$ calcd for $C_{19}H_{16}O_5$ 325.1071, found 325.1083.

Dimethyl 2-(4-methoxyphenyl)-3-(*p*-tolyl)maleate (*E*-7d).



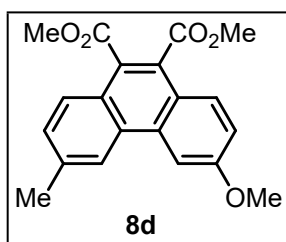
DAM: **2d**. Reaction time: 77.5 h.

Yield 28% (0.02 g). White powder, mp 118 °C.

1H (400 MHz, $CDCl_3$): δ = 7.32 (d, J = 8.7 Hz, 2H), 7.28 – 7.27 (m, 2H), 7.17 (d, J = 7.9 Hz, 2H), 6.89 (d, J = 8.7 Hz, 2H), 3.82 (s, 3H), 3.57 (d, J = 5.4 Hz, 6H), 2.36 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 169.07, 160.13, 138.86, 136.74, 132.85, 129.54, 129.38, 128.04, 127.99, 114.11, 55.41, 52.35, 52.32, 21.46. HRMS (ESI-TOF) m/z $[M+H]^+$ calcd for

$C_{20}H_{20}O_5$ 341.1384, found 341.1392.

Dimethyl 3-methoxy-6-methylphenanthrene-9,10-dicarboxylate (**8d**).

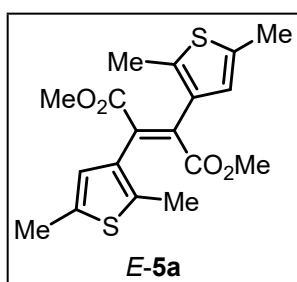


DAM: **2d**. Reaction time: 77.5 h.

Yield 58% (0.05 g). Pale yellow powder, mp 152 °C.

1H (400 MHz, $CDCl_3$): δ = 8.38 (s, 1H), 8.12 – 7.96 (m, 3H), 7.48 (d, J = 8.5 Hz, 1H), 7.29 – 7.26 (m, 1H), 4.09 – 3.94 (m, 9H), 2.62 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 168.80, 168.70, 159.75, 138.19, 132.75, 130.64, 129.66, 129.19, 128.64, 127.33, 126.89, 125.61, 122.69, 121.87, 117.77, 104.24, 55.65, 52.82, 52.77, 22.19. HRMS (ESI-TOF) m/z $[M+H]^+$ calcd for $C_{20}H_{18}O_5$ 339.1227, found 339.1236.

Dimethyl 2,3-bis(2,5-dimethylthiophen-3-yl)fumarate (*E*-5a).

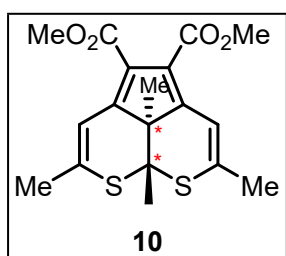


DAM: **3a**. Reaction time: 22.5 h.

Yield 24% (0.02 g). Pale yellow oil.

1H NMR (400 MHz, $(CD_3)_2SO$): δ = 6.51 (s, 2H), 3.52 (s, 6H), 2.35 (s, 6H), 2.23 (s, 6H). ^{13}C NMR (101 MHz, $(CD_3)_2SO$): δ = 167.10, 135.66, 134.92, 133.57, 131.08, 125.84, 52.20, 14.58, 13.26. HRMS (ESI-TOF) m/z $[M+Na]^+$ calcd for $C_{18}H_{20}O_4S_2$ 387.0695, found 387.0698.

Dimethyl (2a^{1s},5a^s)-2a¹,4,5a,7-tetramethyl-2a¹,5a-dihydro-5,6-dithiaacenaphthylene-1,2-dicarboxylate (**10**).

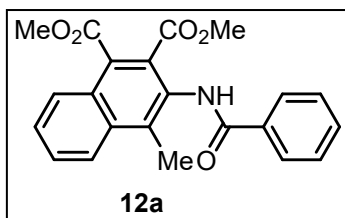


DAM: **3a**. Reaction time: 22.5 h.

Yield 58% (0.05 g). Orange oil.

^1H NMR (400 MHz, $(\text{CD}_3)_2\text{SO}$): δ = 6.44 – 6.40 (m, 2H), 3.69 (s, 6H), 2.23 (s, 3H), 2.19 (s, 3H), 1.95 (d, J = 1.1 Hz, 6H). ^{13}C NMR (101 MHz, $(\text{CD}_3)_2\text{SO}$): δ = 163.33, 148.83, 140.18, 126.04, 113.99, 63.88, 52.55, 51.54, 28.44, 22.85, 22.81. HRMS (ESI-TOF) m/z $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{18}\text{H}_{20}\text{O}_4\text{S}_2$ 387.0695, found 387.0700.

Dimethyl 3-benzamido-4-methylnaphthalene-1,2-dicarboxylate



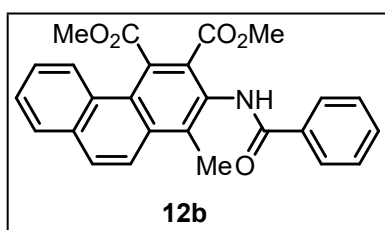
(12a).

DAM: **4a**. Reaction time: 5 h.

Yield 88% (0.08 g). White powder, mp 197 °C.

^1H NMR (400 MHz, CDCl_3): δ = 9.25 (s, 1H), 8.14 (d, J = 8.4 Hz, 1H), 8.07 (d, J = 8.4 Hz, 1H), 8.00 (d, J = 7.4 Hz, 2H), 7.67 (t, J = 7.6 Hz, 1H), 7.59 (t, J = 7.4 Hz, 2H), 7.53 (t, J = 7.4 Hz, 2H), 4.00 (s, 3H), 3.88 (s, 3H), 2.64 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3): δ = 168.40, 168.07, 165.56, 135.25, 134.43, 134.22, 132.20, 131.34, 129.31, 128.97, 128.63, 127.90, 127.61, 127.50, 126.54, 125.31, 125.21, 53.17, 52.85, 15.67. HRMS (ESI-TOF) m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{22}\text{H}_{19}\text{NO}_5$ 378.1336, found 378.1344.

Dimethyl 2-benzamido-1-methylphenanthrene-3,4-dicarboxylate (12b).



DAM: **4b**. Reaction time: 25 h.

Yield 69% (0.07 g). Beige powder, mp 194 °C.

^1H NMR (400 MHz, $(\text{CD}_3)_2\text{SO}$): δ = 10.33 (s, 1H), 8.22 – 8.04 (m, 5H), 8.01 (d, J = 7.3 Hz, 2H), 7.78 – 7.63 (m, 2H), 7.63 (t, J = 7.2 Hz, 1H), 7.57 (t, J = 7.3 Hz, 2H), 3.94 (s, 3H), 3.74 (s, 3H), 2.66 (s, 3H). ^{13}C NMR (101 MHz, $(\text{CD}_3)_2\text{SO}$): δ = 170.17, 166.77, 166.13, 135.81, 133.99, 132.73, 132.36, 131.71, 131.31, 129.92, 129.58, 128.90, 128.48, 128.34, 128.00, 127.60, 126.99, 125.32, 124.93, 122.81, 53.08, 52.65, 14.57. HRMS (ESI-TOF) m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{26}\text{H}_{21}\text{NO}_5$ 428.1493, found 428.1498.

III. NMR studies[†]

III.1. Experiments with potassium carbonate

For detection of potassium carbonate impurities in DAM salts, ¹³C NMR spectroscopy was applied. Figure S1 shows an experiment on addition of K₂CO₃ to DAM **2a**. The pristine sample contains six peaks of entire compound in the downfield region (spectrum 1). Upon addition of 0.1 equiv. of K₂CO₃ a signal of the carbonate anions emerges at 165.50 ppm. Further addition of the salt results in downfield shift of the peak to 167.42 (0.5 equiv.) and 167.93 (1 equiv.). The spectrum of pure potassium carbonate features a signal at 168.41 in accordance to the literature data [S4].

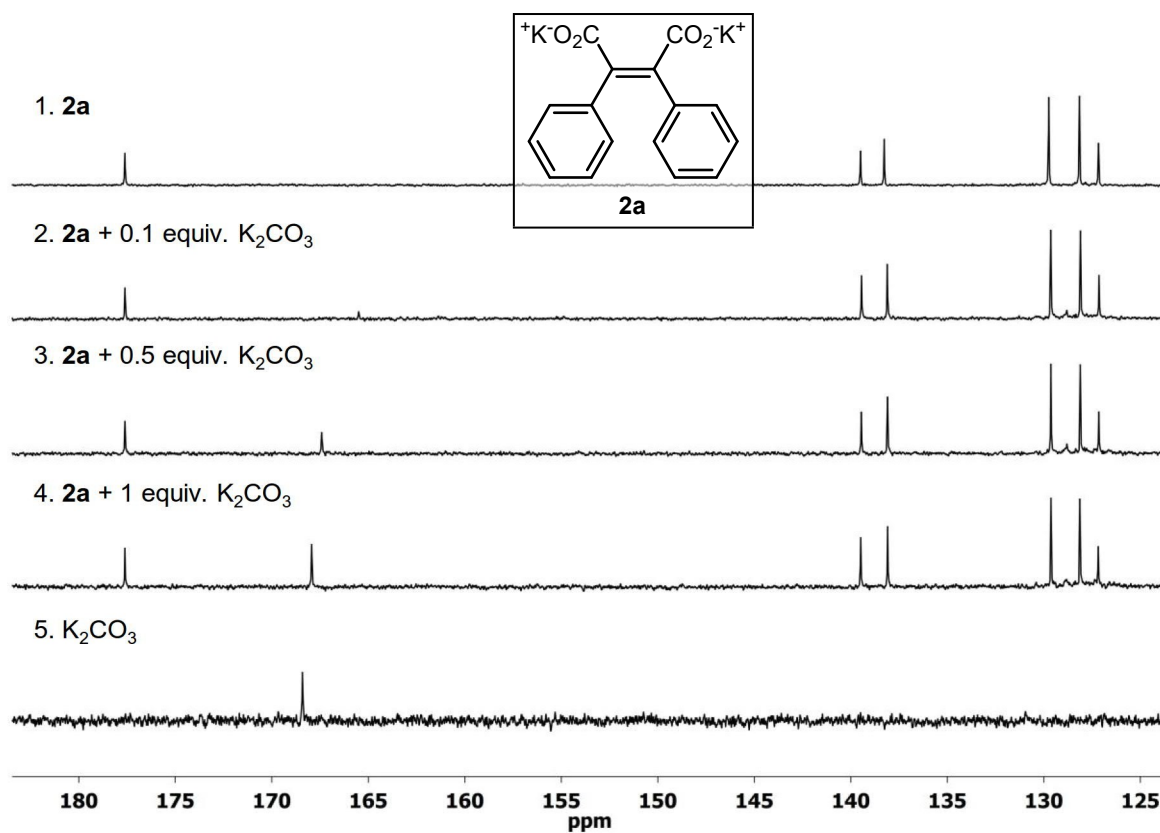


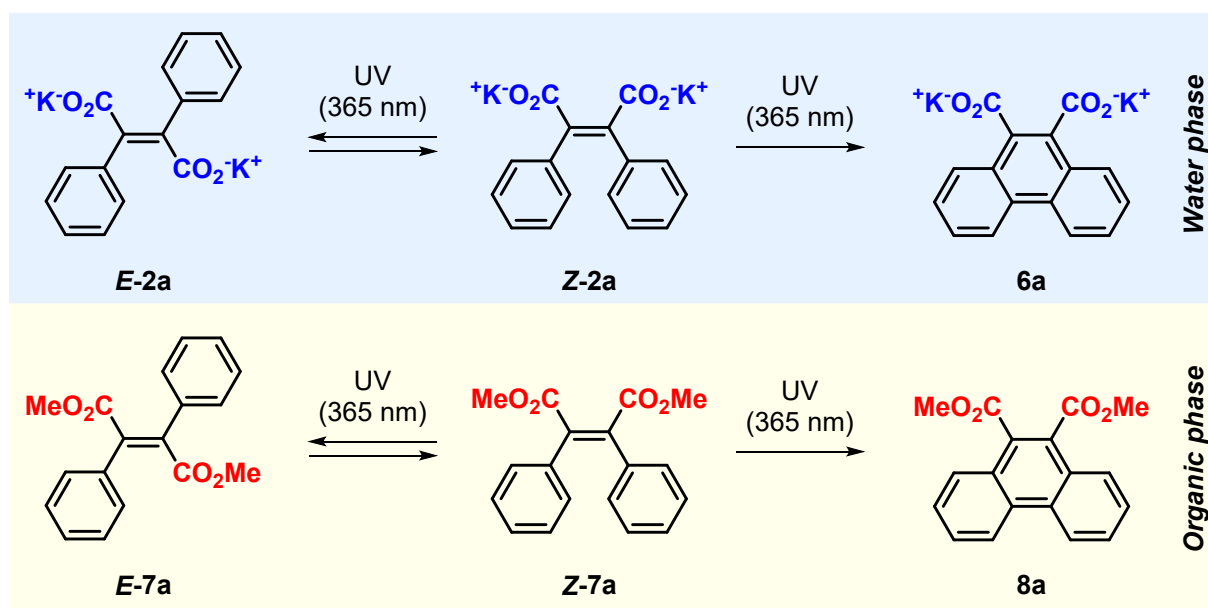
Figure S1. ¹³C NMR spectra of **2a** in D₂O upon addition of K₂CO₃.

[†] Please note, that all NMR stacks were aligned to certain peaks of organic molecules (peak of water was not used as reference).

III.2. *Z*/*E*-isomerization of DAMs salts 2

At the early stage of DAMs **2a-d** photolysis, a formation of *E*-isomer with relatively deshielded signals of phenyl protons was observed (Scheme S4). In the case of **Z-2a**, the product **E-2a** was found at 7.3-7.5 ppm (Figure S2). Further irradiation led to partial disappearance of this product and formation of final phenanthrene **6a**. Photolysis of alkylated derivative **Z-7a** for 2 h also led to the formation of **E-7a** with related downfield shift of phenyl signals (Figure S3). Note, both *Z*- and *E*-isomers of **7a** were isolated, the structure of **Z-7a** was confirmed by X-ray crystallography.

Scheme S4.



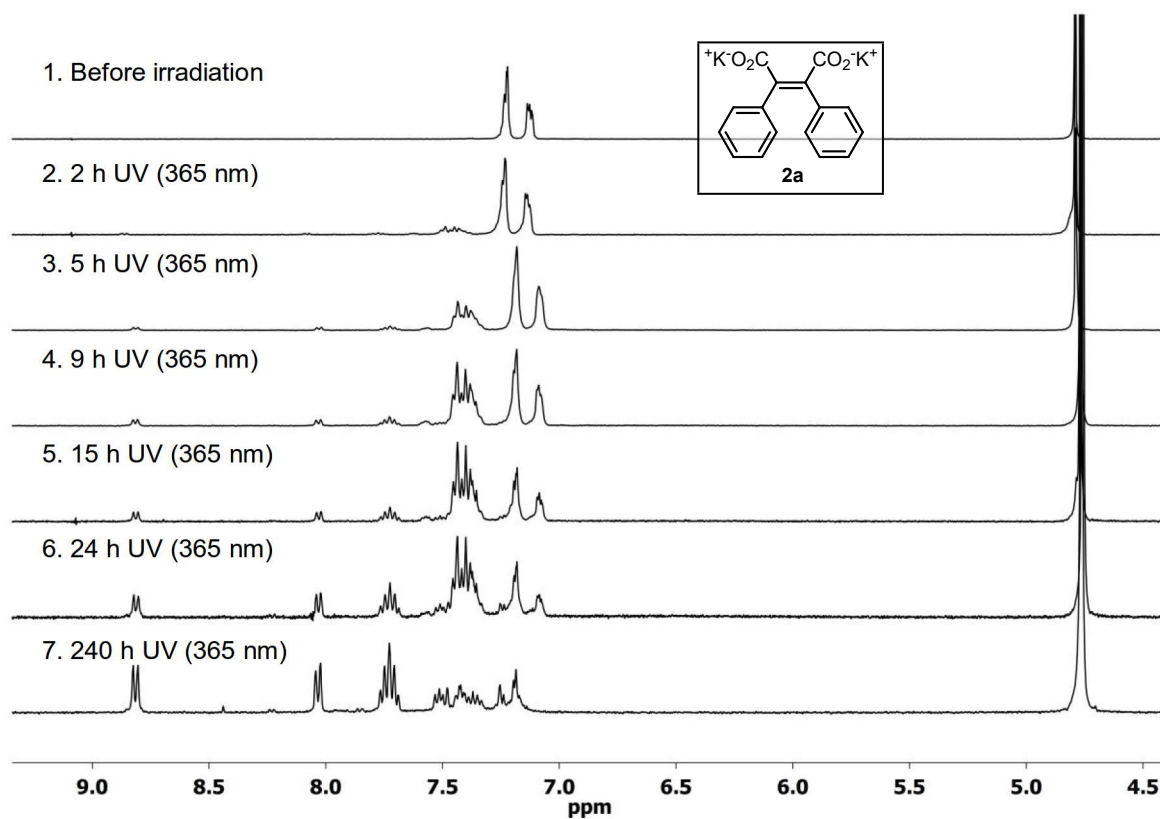


Figure S2. ^1H NMR spectra of **2a** in D_2O upon continuous irradiation with UV light (365 nm).

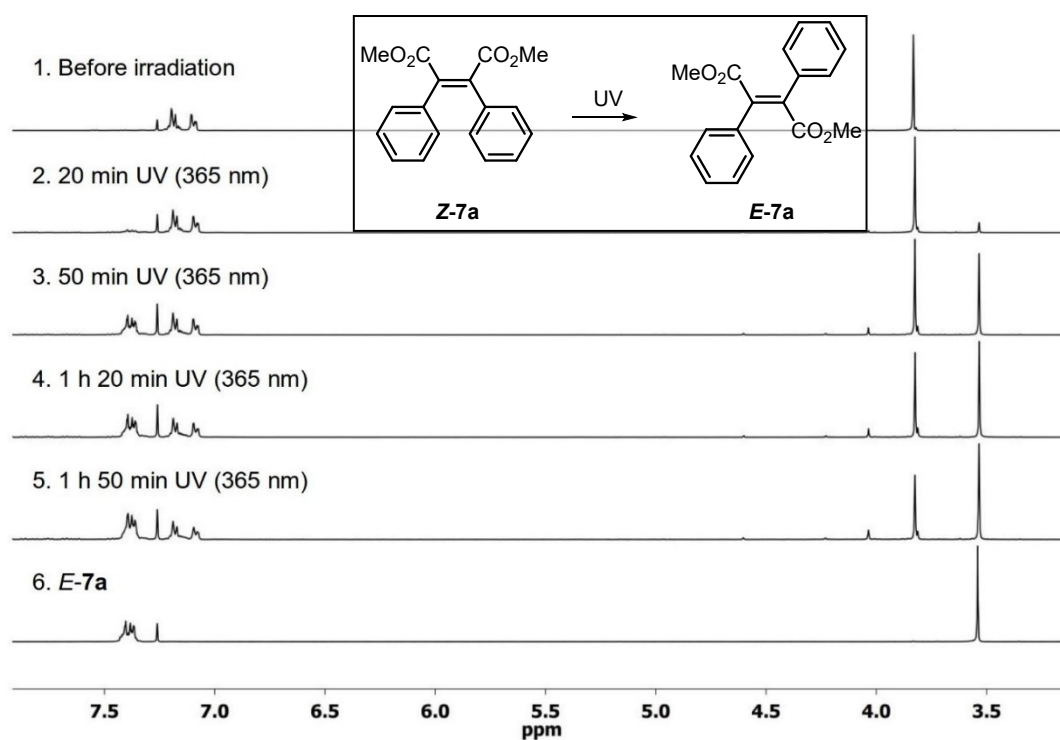


Figure S3. ^1H NMR spectra of **Z-7a** in CDCl_3 upon continuous irradiation with UV light (365 nm).

III.3. NMR monitoring of 2b-d photoreactions

According to preparative photochemical reactions, DAMs **2a-d** yield two main products, corresponding *E*-isomers as well as phenanthrenes **6a-d** (Schemes S5-S7). NMR monitoring experiments support these results (Figures S4-S6).

Scheme S5.

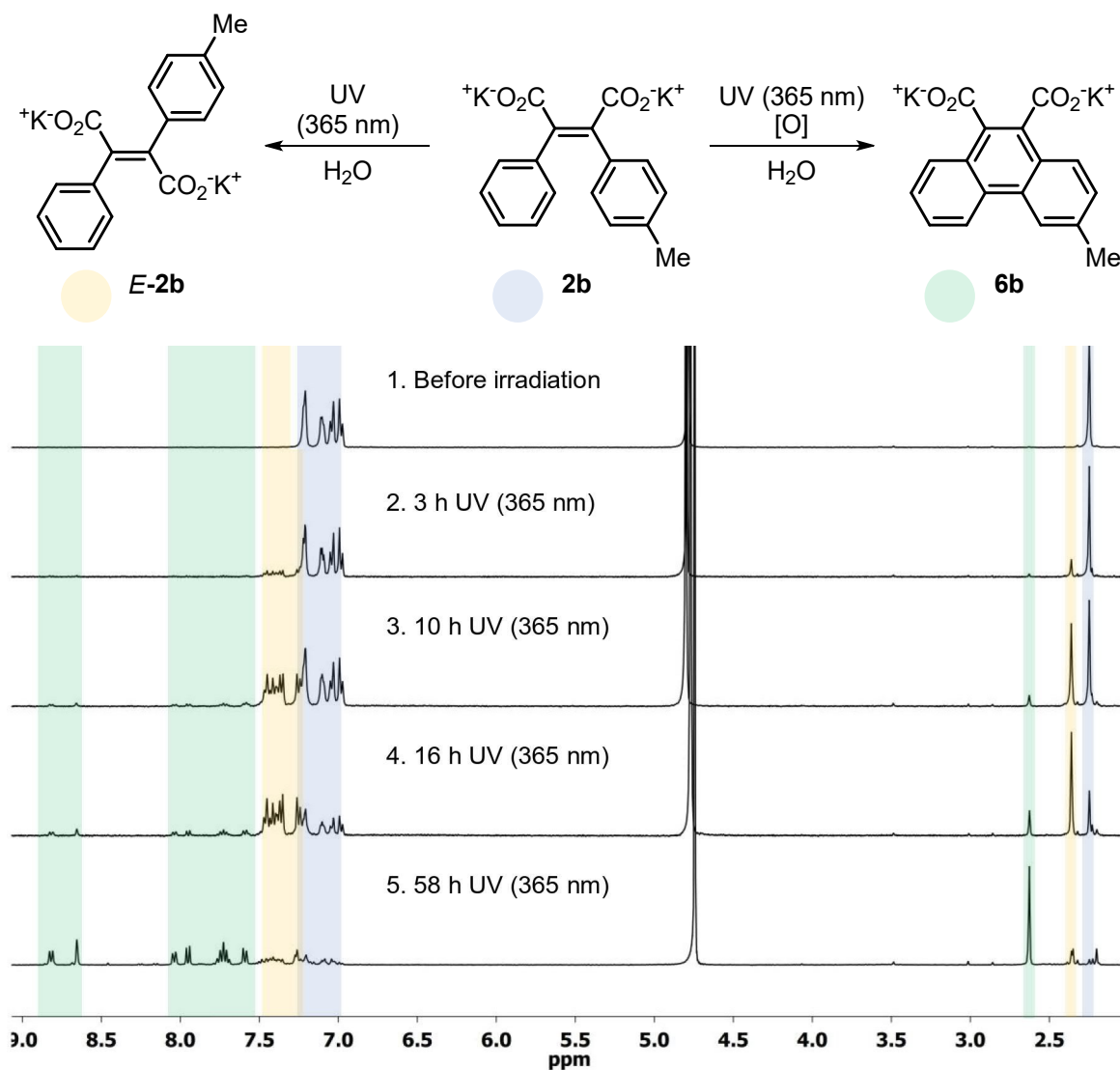


Figure S4. ^1H NMR spectra of **2b** in D_2O upon continuous irradiation with UV light (365 nm).

Scheme S6.

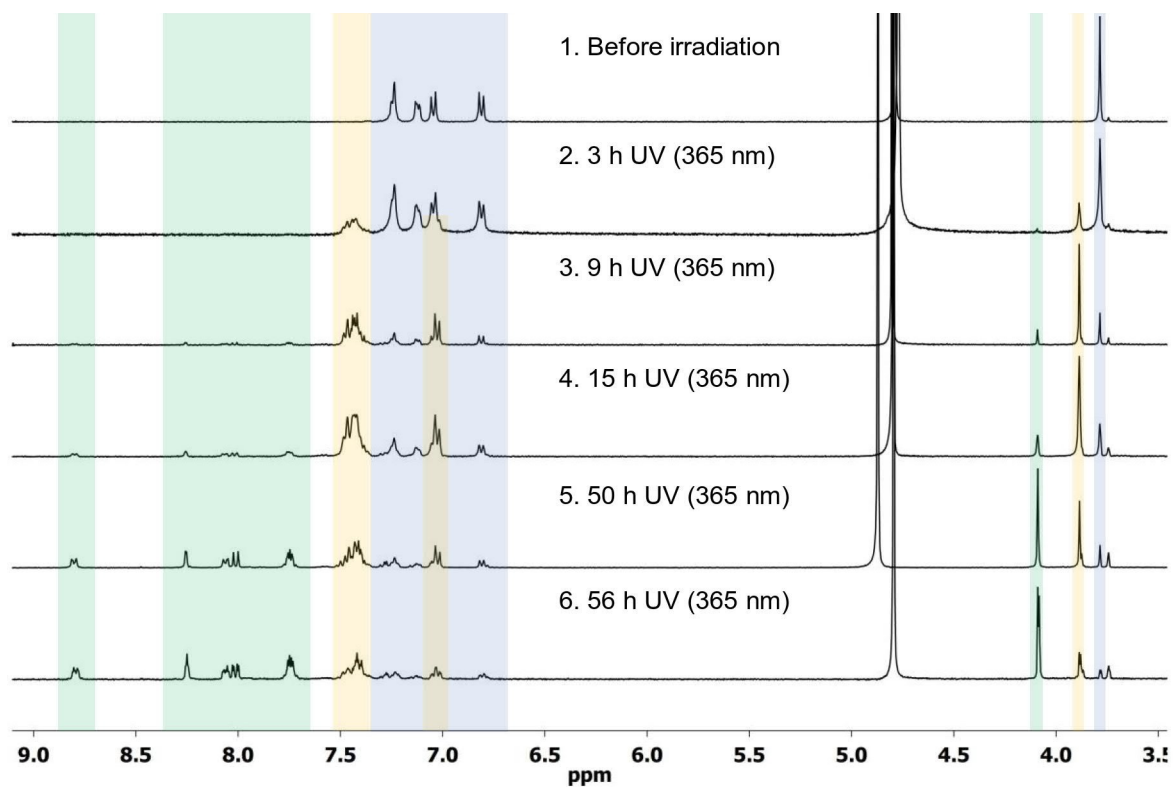
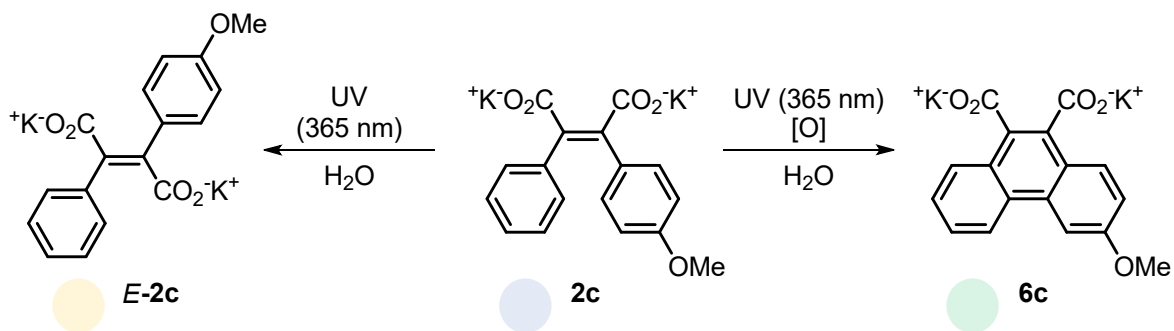


Figure S5. ^1H NMR spectra of **2c** in D_2O upon continuous irradiation with UV light (365 nm).

Scheme S7.

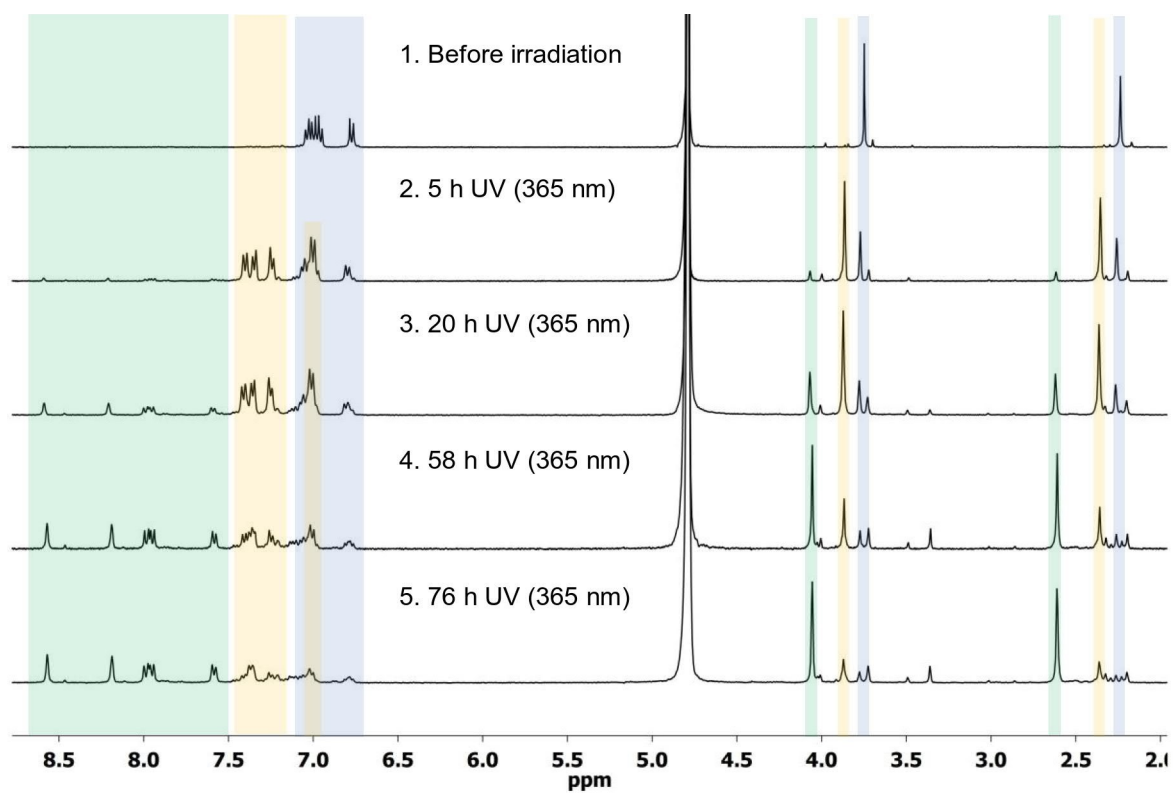
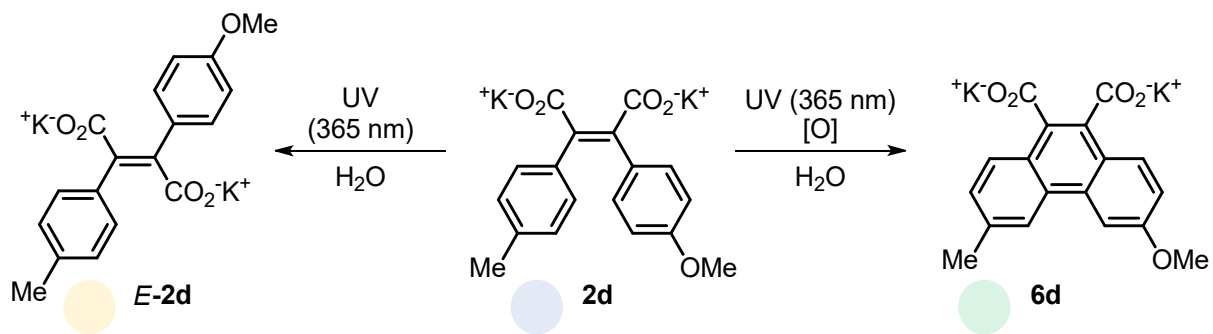
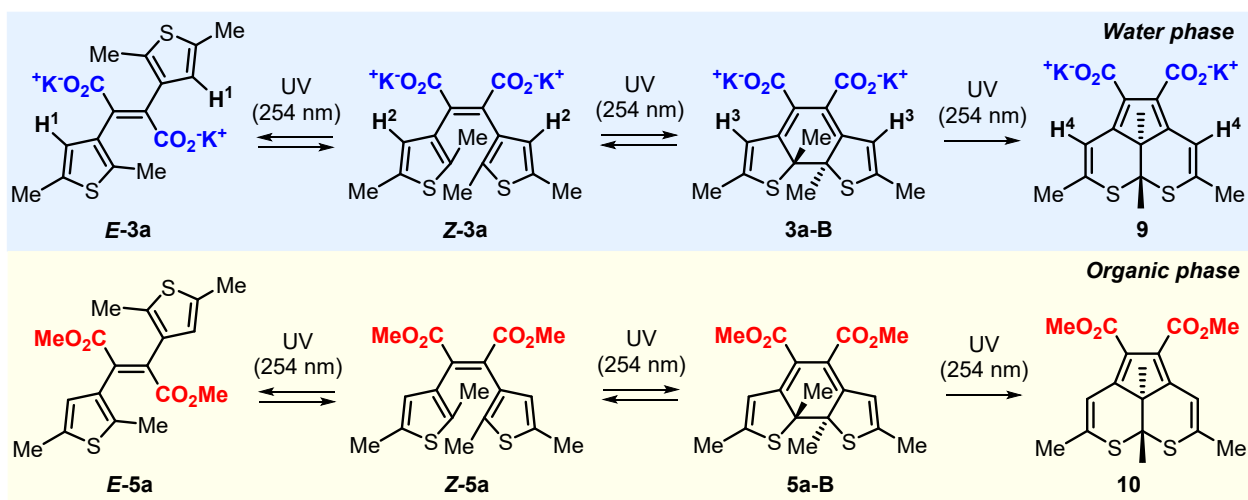


Figure S6. ¹H NMR spectra of **2d** in D₂O upon continuous irradiation with UV light (365 nm).

III.4. NMR monitoring of **3a,b** photoswitching

Photolysis of DAMs **Z-3a** for 9 h led to the formation of three products according to NMR spectroscopy (Figure S7). These compounds were recognized as **E-3a**, closed-ring isomer **3a-B** and product of formal 1,2-dyotropic rearrangement **9** [S5] (Scheme S8). To assign the corresponding NMR peaks, we performed a direct alkylation of **Z-3a** (towards **Z-5a**) and preparative photolysis followed by alkylation with iodomethane. The last experiment gave us pure **E-5a** and **10** (Figure S8). The structure of the latter was proved by ^{13}C NMR spectroscopy (peaks at 63.88 and 52.55 ppm of sp^3 -carbons bearing methyl groups in accordance to [S6-S9]) and UV-Vis spectroscopy (absorbance band in the visible region at 505 nm, Figure S26). The spectrum of **5a-B** was detected upon photolysis of **Z-5a** at the early stage (Figure S9). Comparison of the NMR spectra of water-soluble and alkylated products allowed us to assign the signals in the downfield region of as following: $\delta = 6.61$ (H^1 of **E-3a**), 6.34 (H^4 of **9**), 6.29 (H^2 of **Z-3a**), 6.22 (H^3 of **3a-B**) ppm.

Scheme S8.



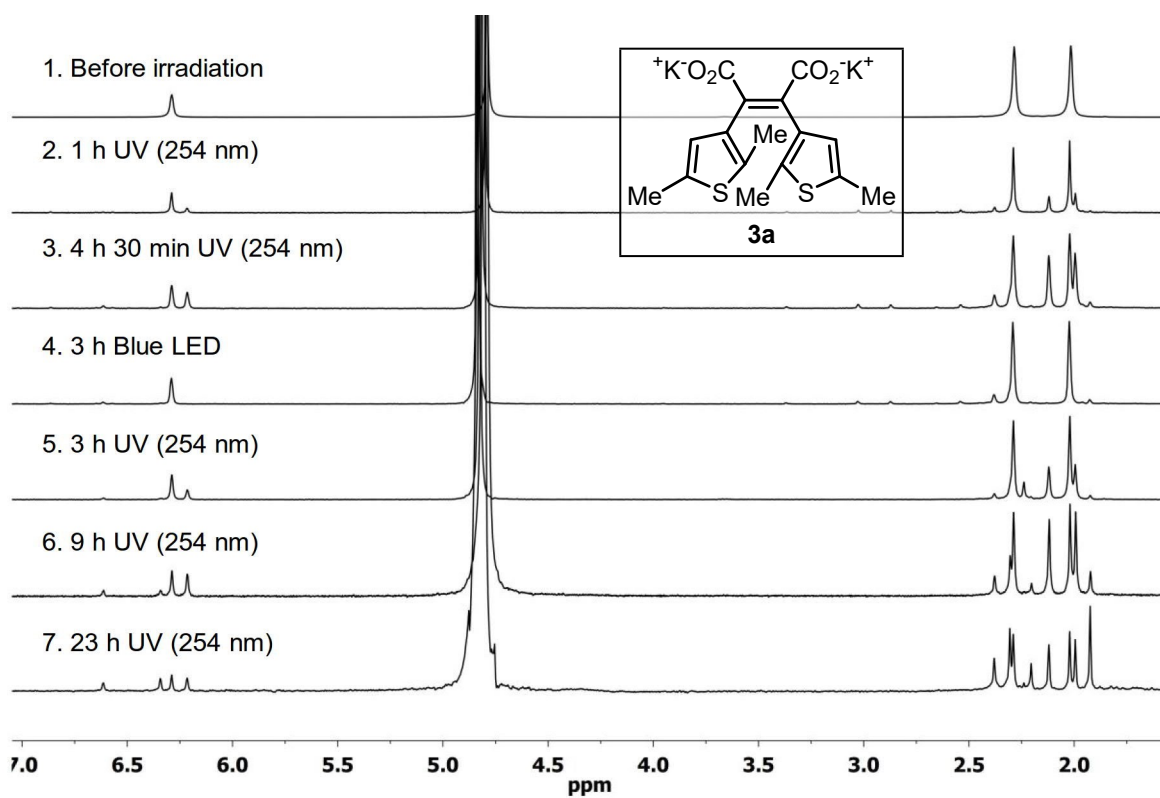


Figure S7. ^1H NMR spectra of **3a** in D_2O upon with UV light (254 nm) and visible light (blue LED, 465 nm).

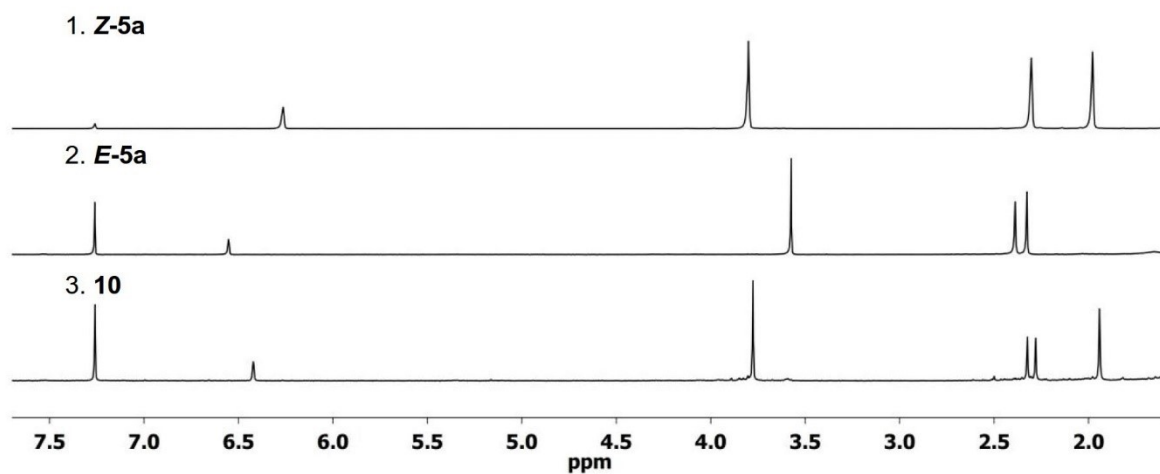


Figure S8. ^1H NMR spectra of **Z-5a**, **E-5a** and **10** in CDCl_3 .

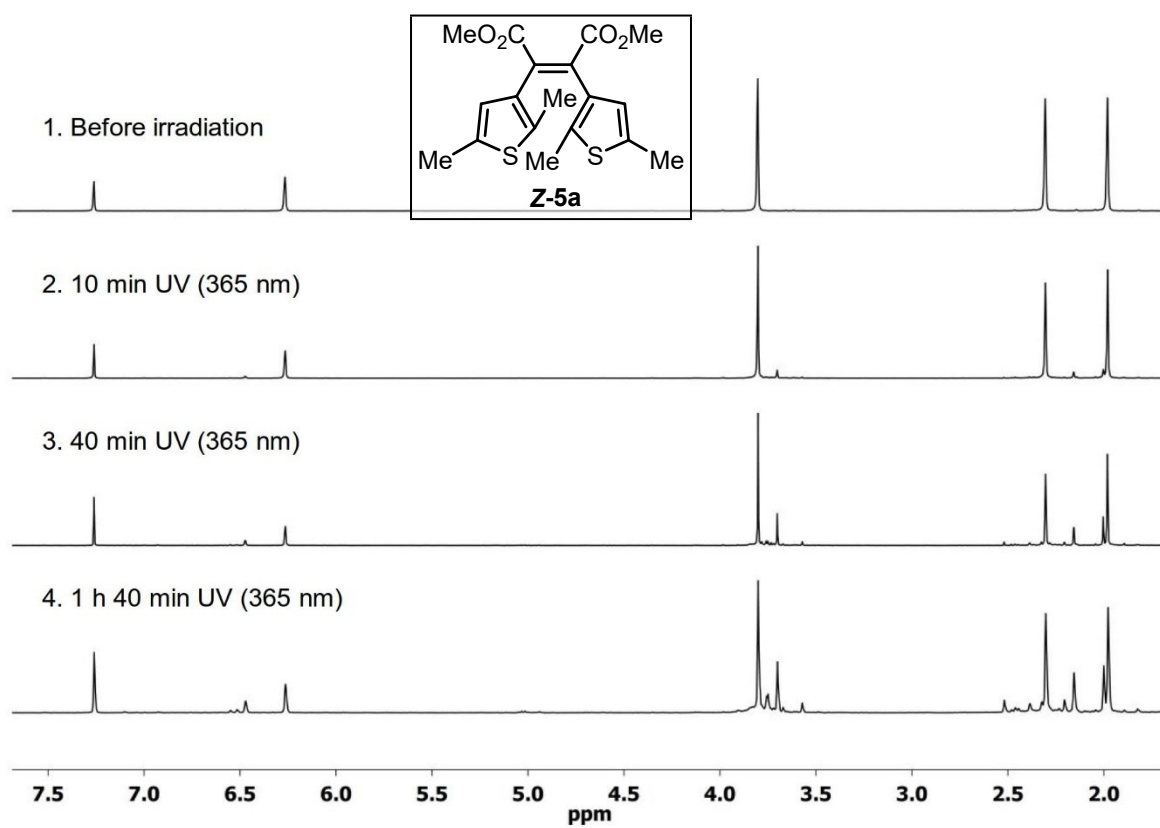


Figure S9. ^1H NMR spectra of **Z-5a** in CDCl_3 upon irradiation with UV light (365 nm).

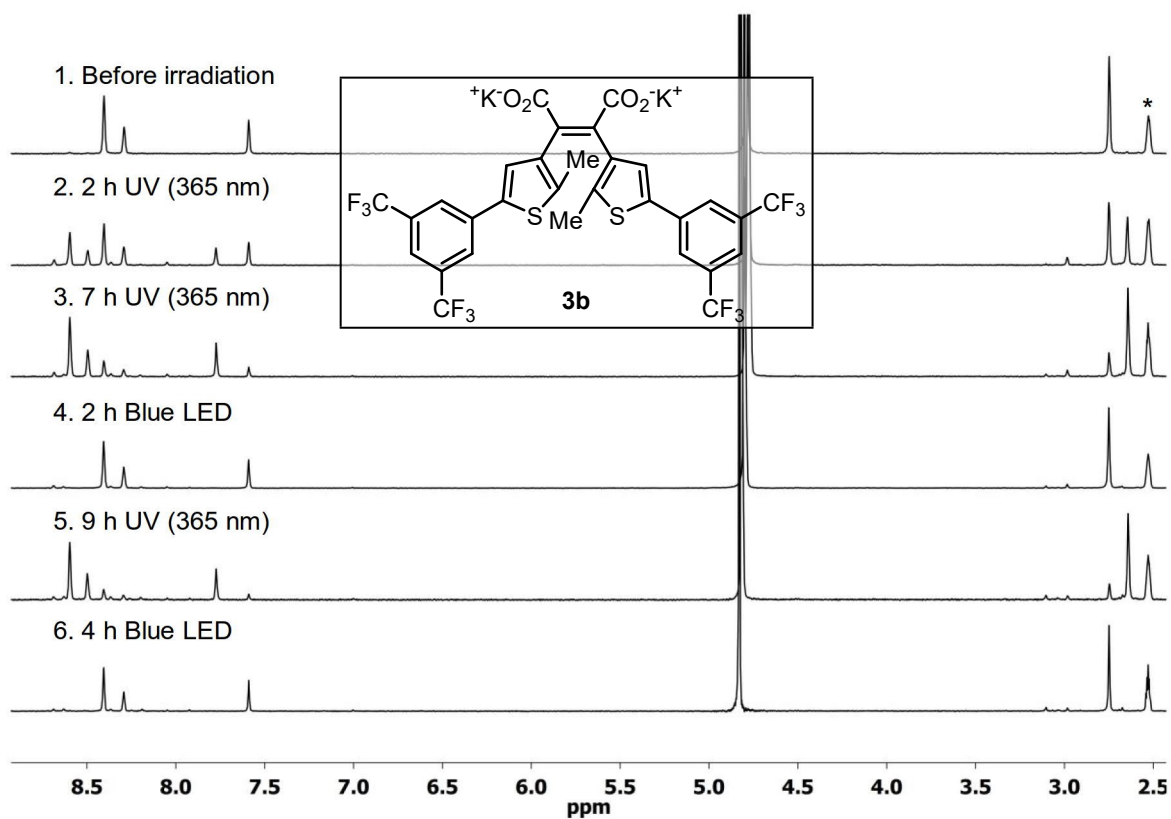


Figure S10. 1H NMR spectra of **3b** (D_2O / CD_3CN 1:1) upon continuous irradiation with UV light (365 nm) and visible light (465 nm). MeCN residual peak ($\delta = 2.53$) is marked by *.

III.5. NMR monitoring of 4a,b photorearrangement

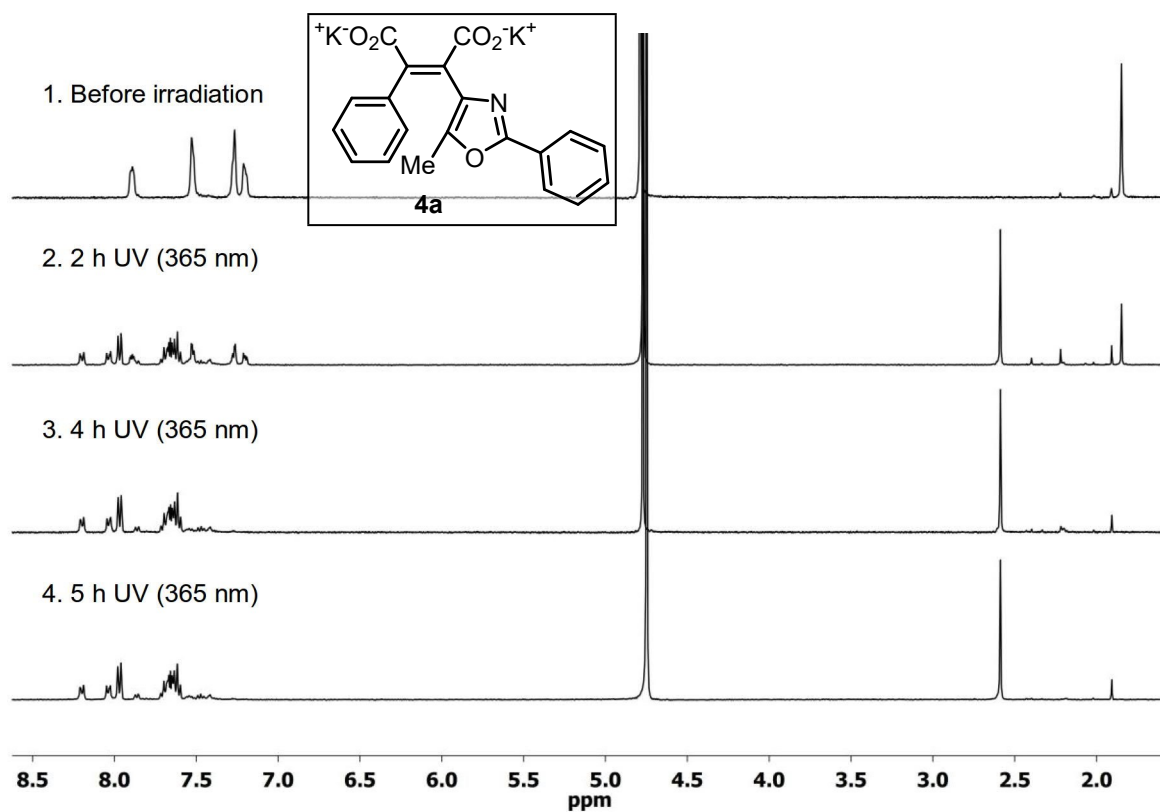


Figure S11. ^1H NMR spectra of **4a** in D_2O upon continuous irradiation with UV light (365 nm).

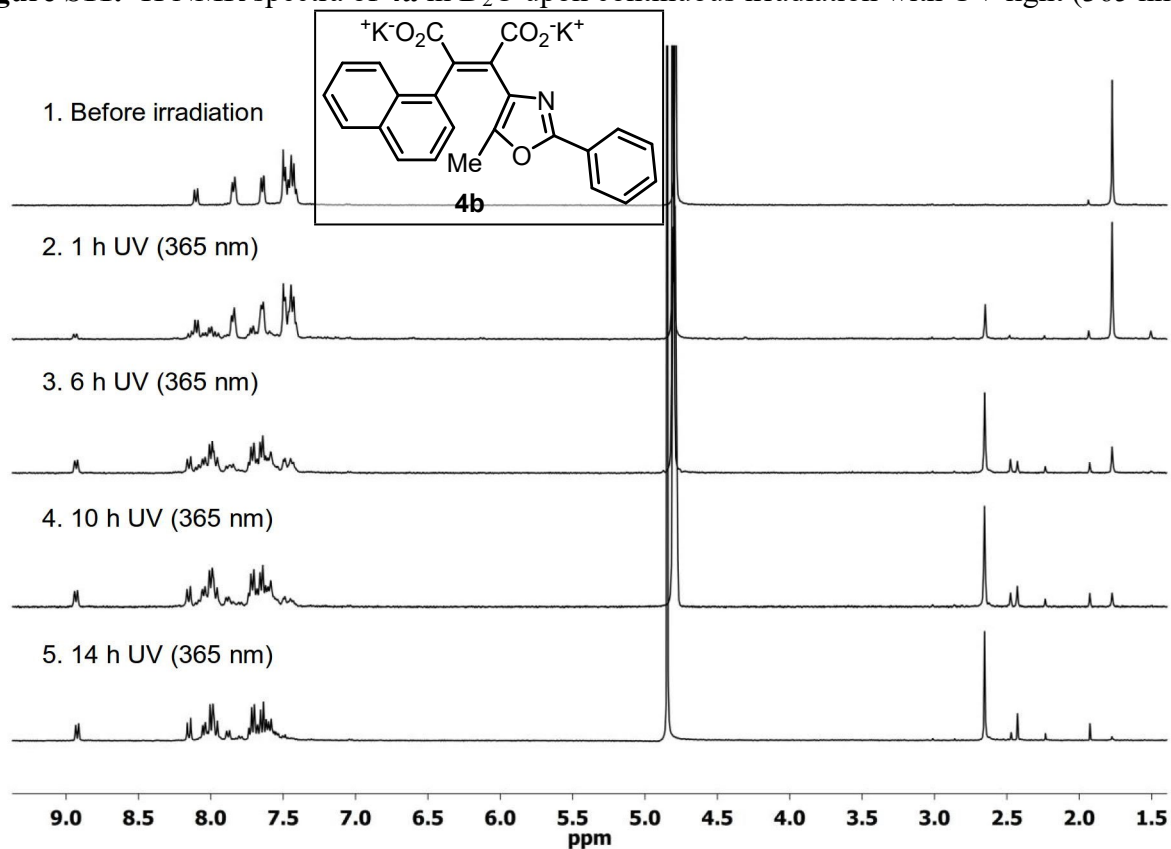


Figure S12. ^1H NMR spectra of **4b** in D_2O upon continuous irradiation with UV light (365 nm).

III.6. 2D NOESY for 4a

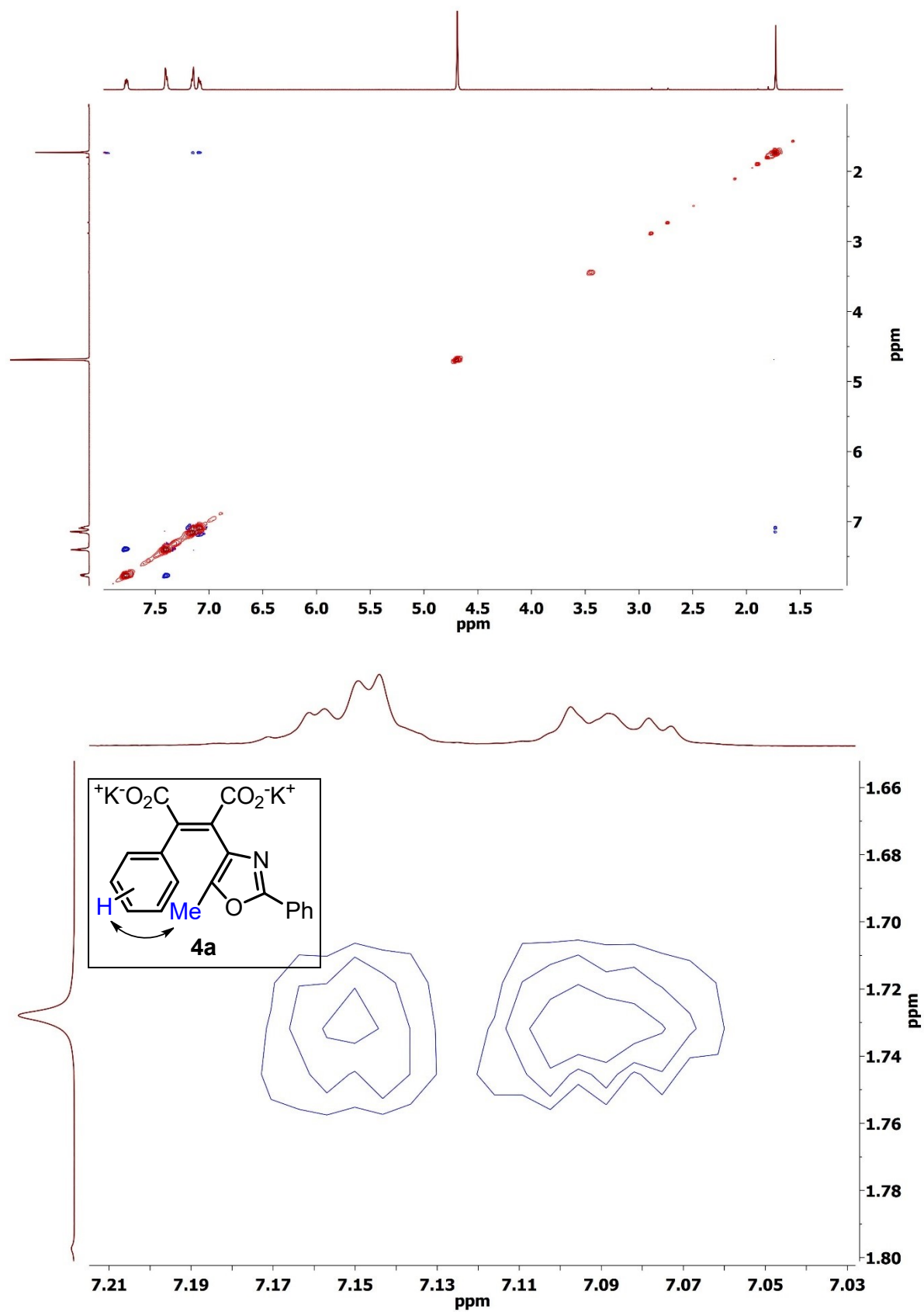


Figure S13. H-H NOESY spectrum of 4a.

IV. X-ray crystallography

Experimental intensities of reflections were measured on a Bruker D8 with Photon III detector, charge-integrating pixel array detector (CPAD), laterally graded multilayer (Goebel) mirror, microfocus Mo-target X-ray tube ($\lambda = 0.73071 \text{ \AA}$), and integrated Oxford Cryosystems 1000 liquid nitrogen cooling device (stability of 0.1 K). Data reduction and integration were performed with the Bruker software package SAINT (version 8.40B) platform [S10]. Absorption corrections based on measurements of equivalent reflections were carried out SADABS (multi-scan methods) [S11]. The structures were solved by direct methods with the SHELXT program and refined by full matrix least-squares on F^2 with SHELXL [S12]. Positions of all non-H atoms were found from electron difference density maps and refined with individual anisotropic displacement parameters. The H-atoms were positioned geometrically and refined as riding atoms with relative isotropic displacement parameters. A rotating group model was applied for methyl groups. Crystal data, data collection and structure refinement details are summarized in Table S2. The structures have been deposited at the Cambridge Crystallographic Data Center with the reference CCDC numbers 2255492-2255496, and they also contain the supplementary crystallographic data. These data can be obtained free of charge from the CCDC via http://www.ccdc.cam.ac.uk/data_request/cif.

Table S2. Crystal data, data collection and structure refinement details.

| | Z-7a | E-7b | E-7c | 8b | 8d | 12a |
|--|--|--|--|--|--|---|
| CCDC number | 2255492 | 2255495 | 2255494 | 2255496 | 2255493 | 2257444 |
| Formula | C ₁₈ H ₁₆ O ₄ | C ₁₉ H ₁₈ O ₄ | C ₁₉ H ₁₈ O ₅ | C ₁₉ H ₁₆ O ₄ | C ₂₀ H ₁₈ O ₅ | C ₂₂ H ₁₉ NO ₅ |
| M _w | 296.31 | 310.33 | 326.33 | 308.32 | 338.34 | 377.38 |
| T, K | 110 | 110 | 139 | 110 | 110 | 101 |
| Crystal system | Monoclinic | Monoclinic | Monoclinic | Orthorhombic | Triclinic | Monoclinic |
| Space group | P2 ₁ /n | P2 ₁ /n | P2 ₁ /n | Pbca | P-1 | P2 ₁ /c |
| Z(Z') | 4(1) | 4(1) | 4(1) | 8 | 2(1) | 4(1) |
| a, Å | 8.7095(4) | 10.583(8) | 9.538(2) | 9.0013(18) | 7.3855(18) | 10.4074(6) |
| b, Å | 8.6086(4) | 7.649(6) | 10.289(2) | 16.186(3) | 10.729(3) | 18.1894(10) |
| c, Å | 19.3283(8) | 20.107(14) | 16.613(4) | 21.094(4) | 12.101(4) | 9.8502(6) |
| a, ° | 90 | 90 | 90 | 90 | 65.688(10) | 90 |
| b, ° | 93.799(2) | 104.03(2) | 94.677(10) | 90 | 78.414(11) | 100.929(2) |
| g, ° | 90 | 90 | 90 | 90 | 71.301(9) | 90 |
| V, Å ³ | 1445.99(11) | 1579(2) | 1625.0(7) | 3073.3(11) | 825.1(4) | 1830.87(18) |
| d _{calc} , g cm ⁻³ | 1.361 | 1.305 | 1.334 | 1.333 | 1.362 | 1.369 |
| m, cm ⁻¹ | 0.96 | 0.91 | 0.97 | 0.93 | 0.98 | 0.98 |
| F(000) | 624 | 656 | 688 | 1296 | 356 | 792 |
| 2θ _{max} , °(compl, %) | 58(99.9) | 52(99.9) | 55 (100) | 54(100) | 58(99.4) | 58(99.9) |
| Number of measured reflections | 13735 | 11685 | 12180 | 21024 | 8082 | 26142 |
| Number of independent reflections | 3843 | 3098 | 3739 | 3355 | 4343 | 4868 |
| Number of observed reflections with I>2s(I) | 2727 | 1559 | 2695 | 2331 | 3137 | 4029 |
| Number of parameters | 201 | 209 | 217 | 213 | 281 | 329 |
| R1 | 0.0576 | 0.0893 | 0.0604 | 0.0667 | 0.0677 | 0.0548 |
| wR2 | 0.1457 | 0.2582 | 0.1416 | 0.1741 | 0.1743 | 0.1431 |
| GOF | 1.001 | 1.008 | 1.038 | 1.049 | 1.036 | 1.052 |
| Residual density, eÅ ⁻³ (d _{min} /d _{max}) | 0.336/-0.326 | 0.362/-0.462 | 0.240/-0.323 | 0.442/-0.402 | 0.233/-0.275 | 0.0403/-0.392 |

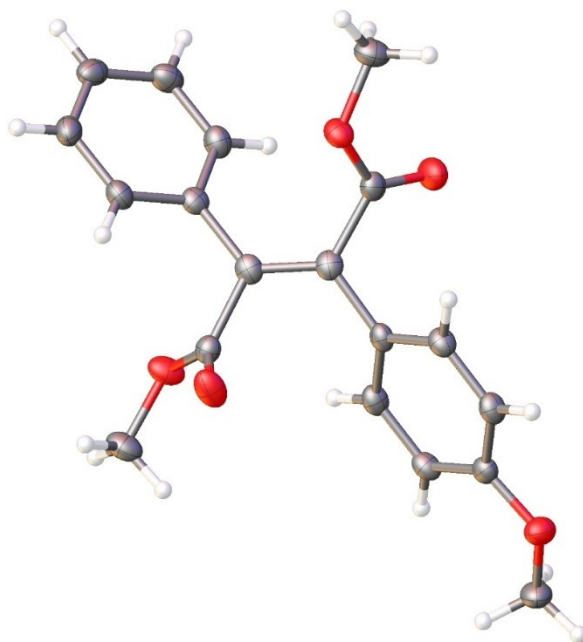


Figure S14. Molecular structure of *E*-7c. Thermal ellipsoids are drawn at the 50% probability level.

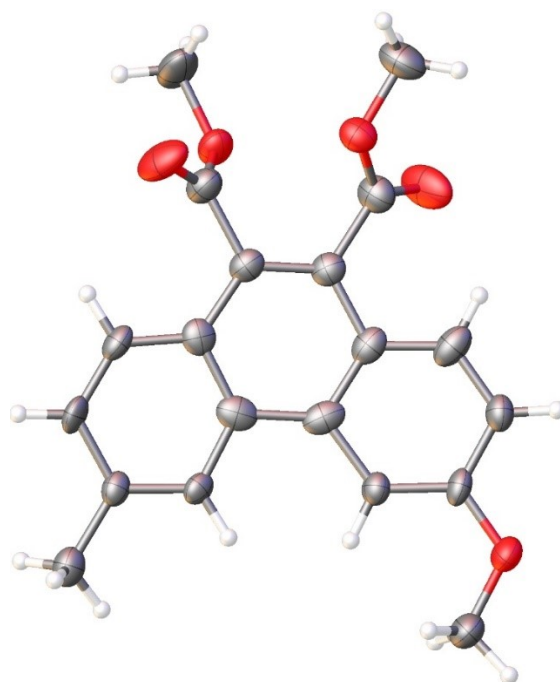


Figure S15. Molecular structure of 8d. Thermal ellipsoids are drawn at the 50% probability level.

V. Photochemical studies

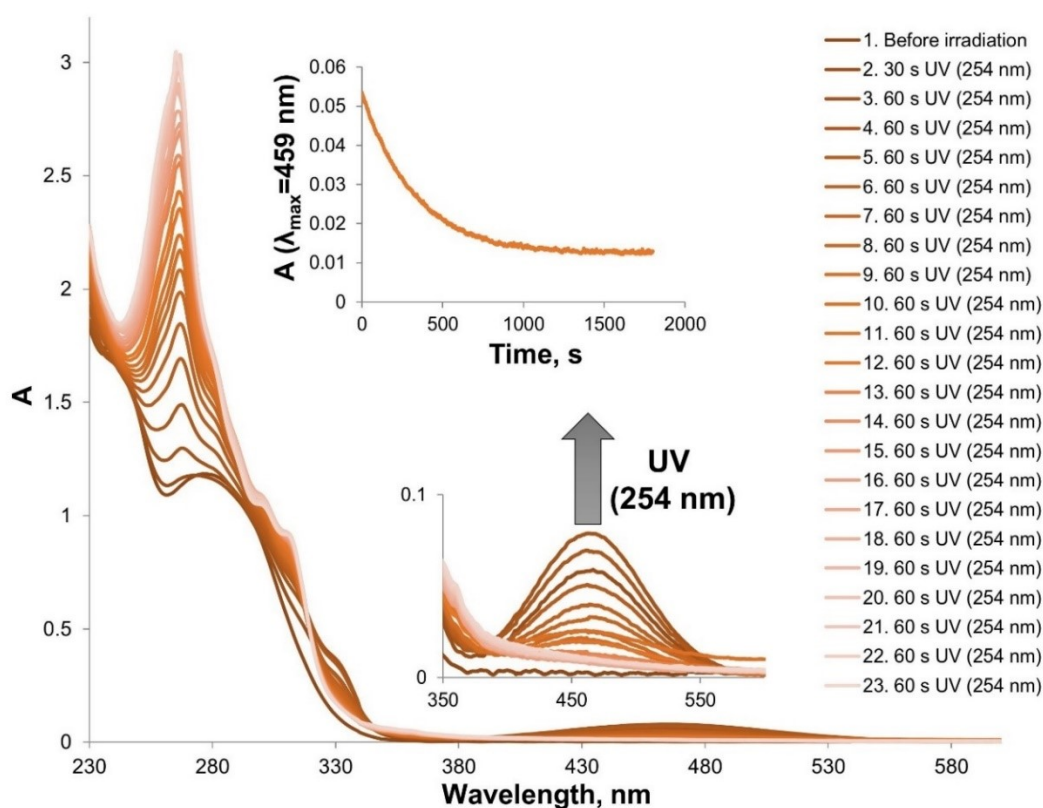


Figure S16. Spectral changes of water solution (buffer pH = 7) of **2a** ($c \approx 10^{-4}$ M) upon irradiation with UV ($\lambda_{\text{max}} = 254$ nm) and thermal bleaching of **2a-B** (on inset).

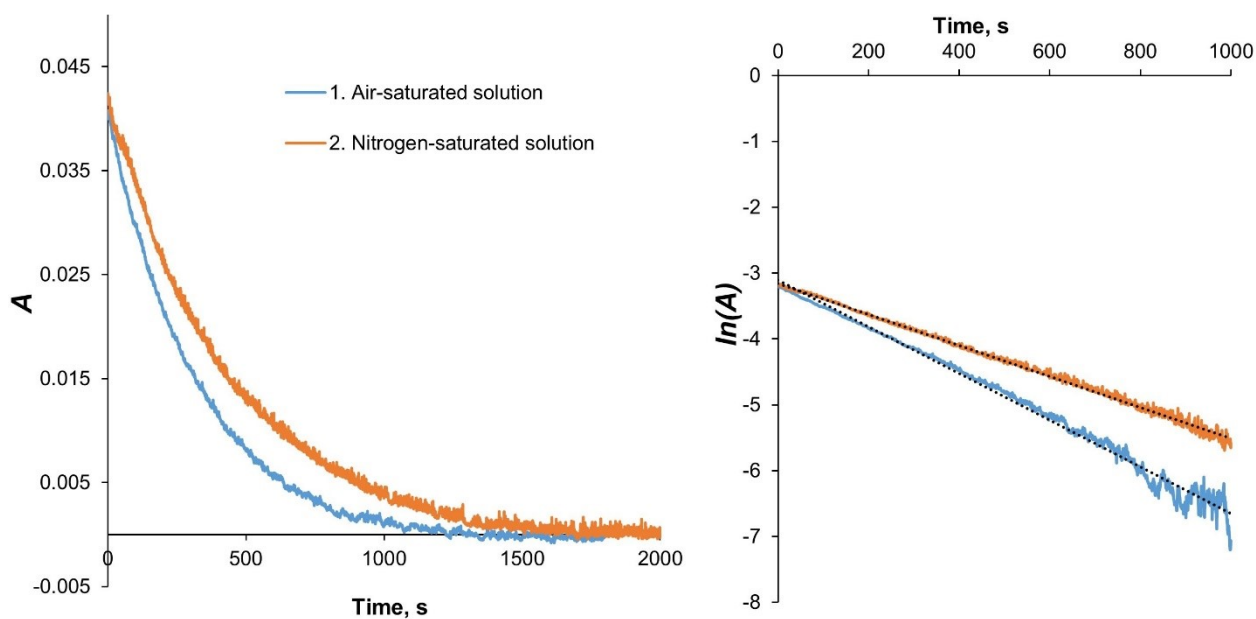


Figure S17. Thermal bleaching of **2a-B** species in the air- and nitrogen-saturated solutions in the ambient conditions.

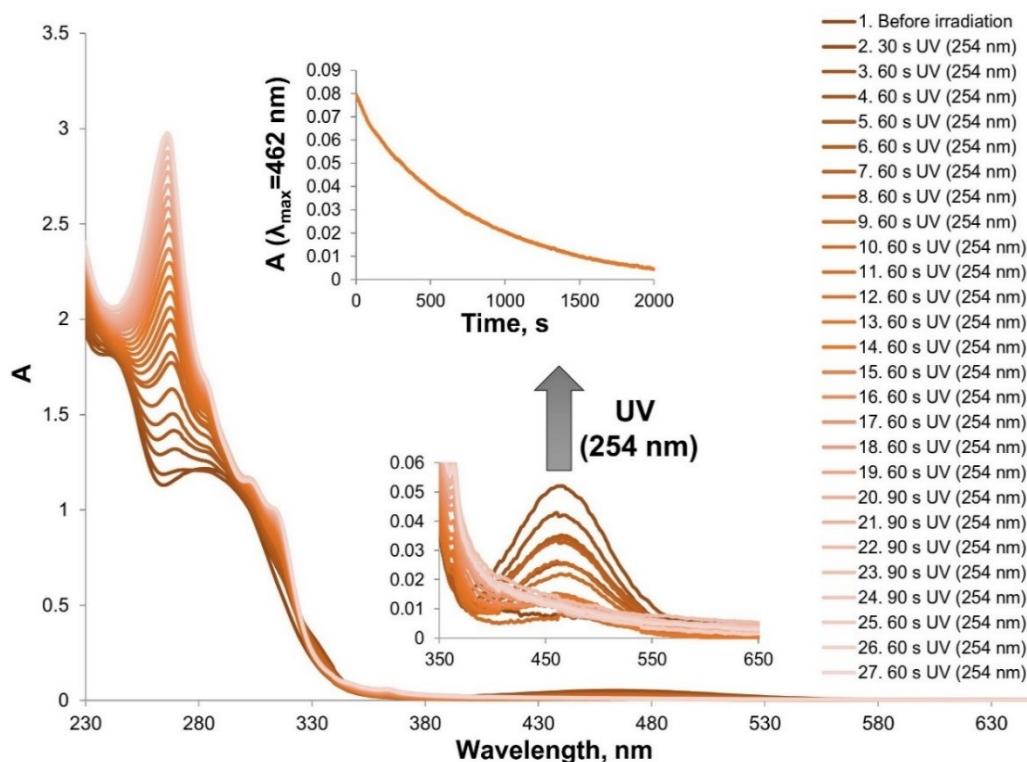


Figure S18. Spectral changes of water solution (buffer pH = 7) of **2b** ($c \approx 10^{-4}$ M) upon irradiation with UV ($\lambda_{\text{max}} = 254$ nm) and thermal bleaching of **2b-B** (on inset).

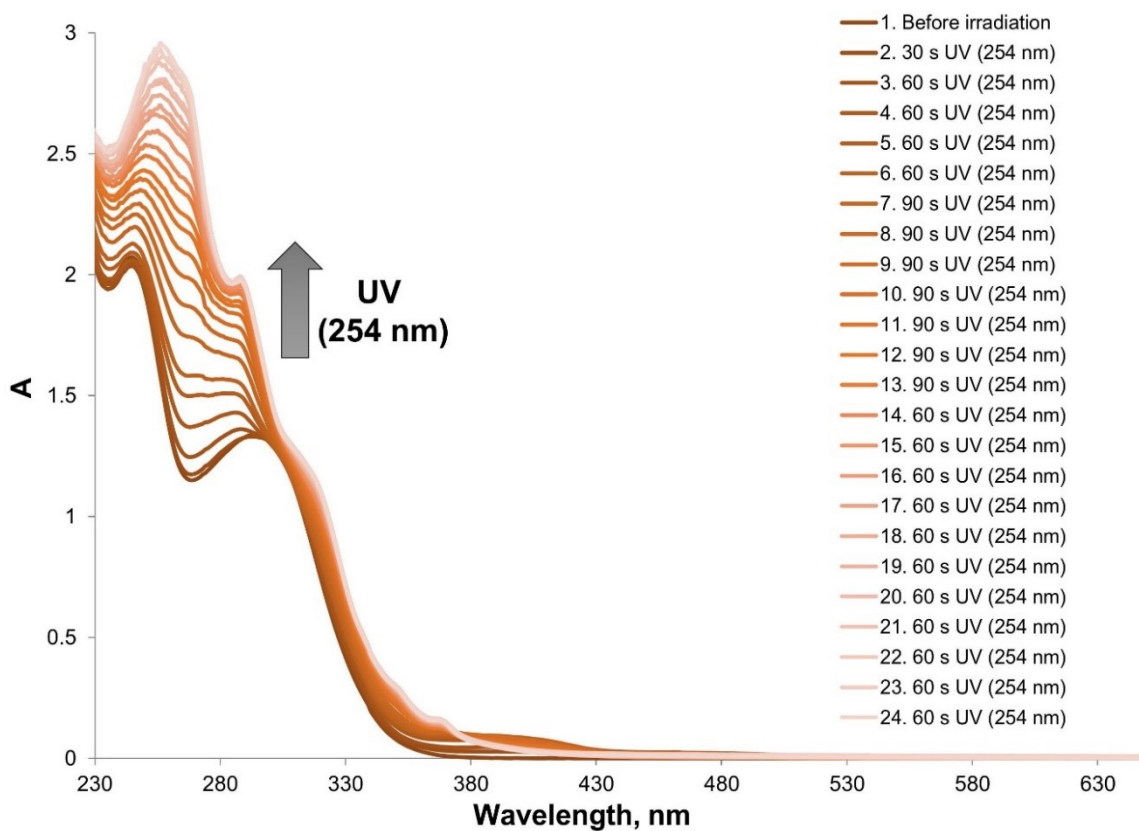


Figure S19. Spectral changes of water solution (buffer pH = 7) of **2c** ($c \approx 10^{-4}$ M) upon irradiation with UV ($\lambda_{\text{max}} = 254$ nm).

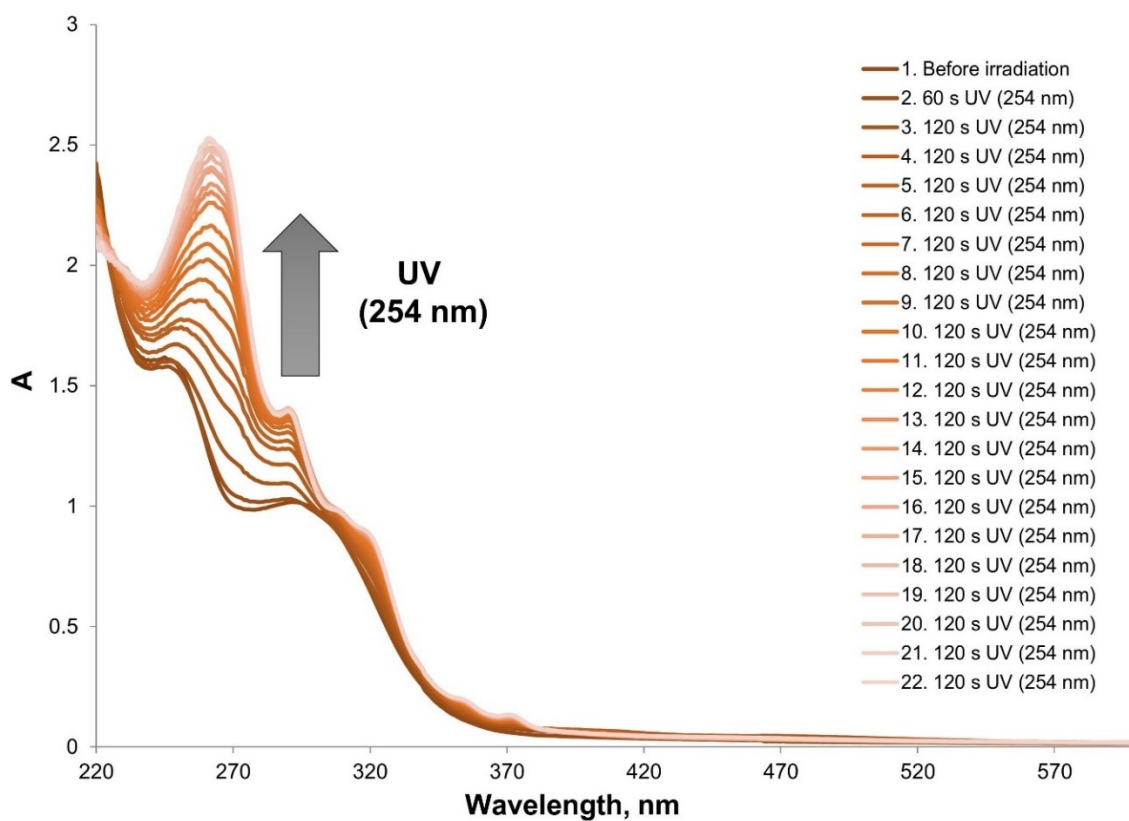


Figure S20. Spectral changes of water solution (buffer pH = 7) of **2d** ($c \approx 0.9 \cdot 10^{-4}$ M) upon irradiation with UV ($\lambda_{\text{max}} = 254$ nm).

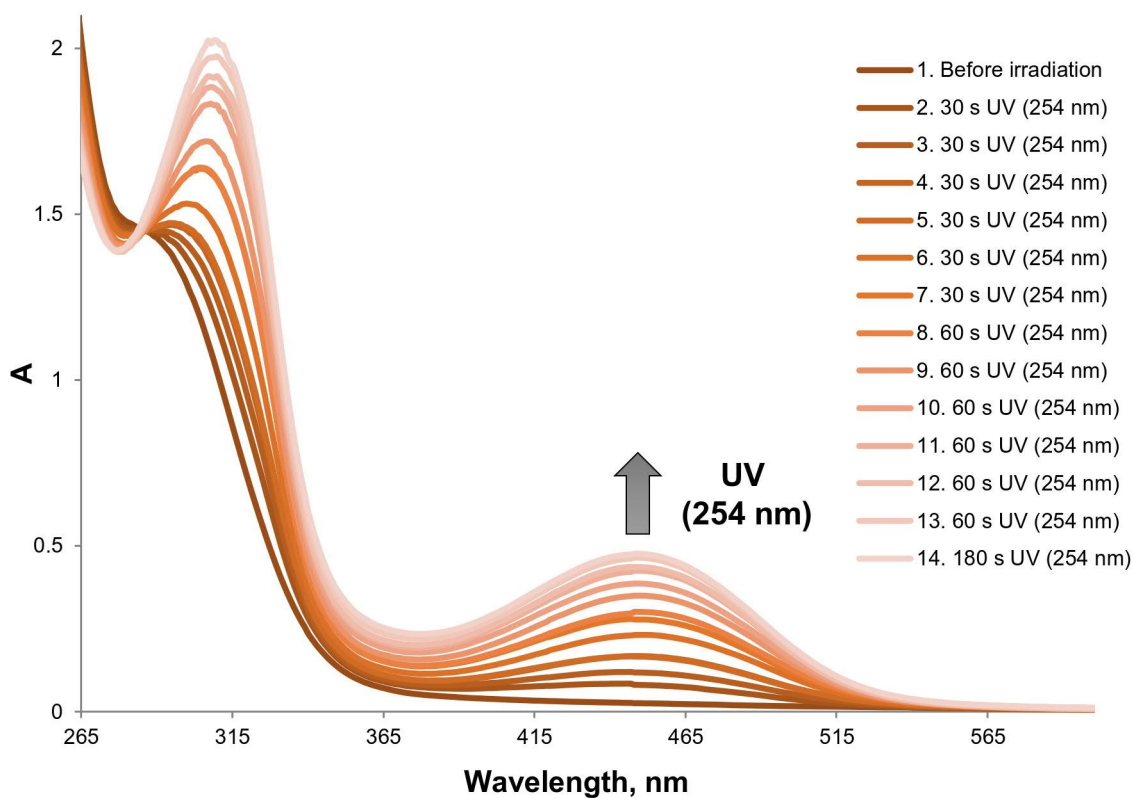


Figure S21. Spectral changes of water solution (buffer pH = 7) of **3a** ($c \approx 10^{-4}$ M) upon irradiation with UV ($\lambda_{\text{max}} = 254$ nm).

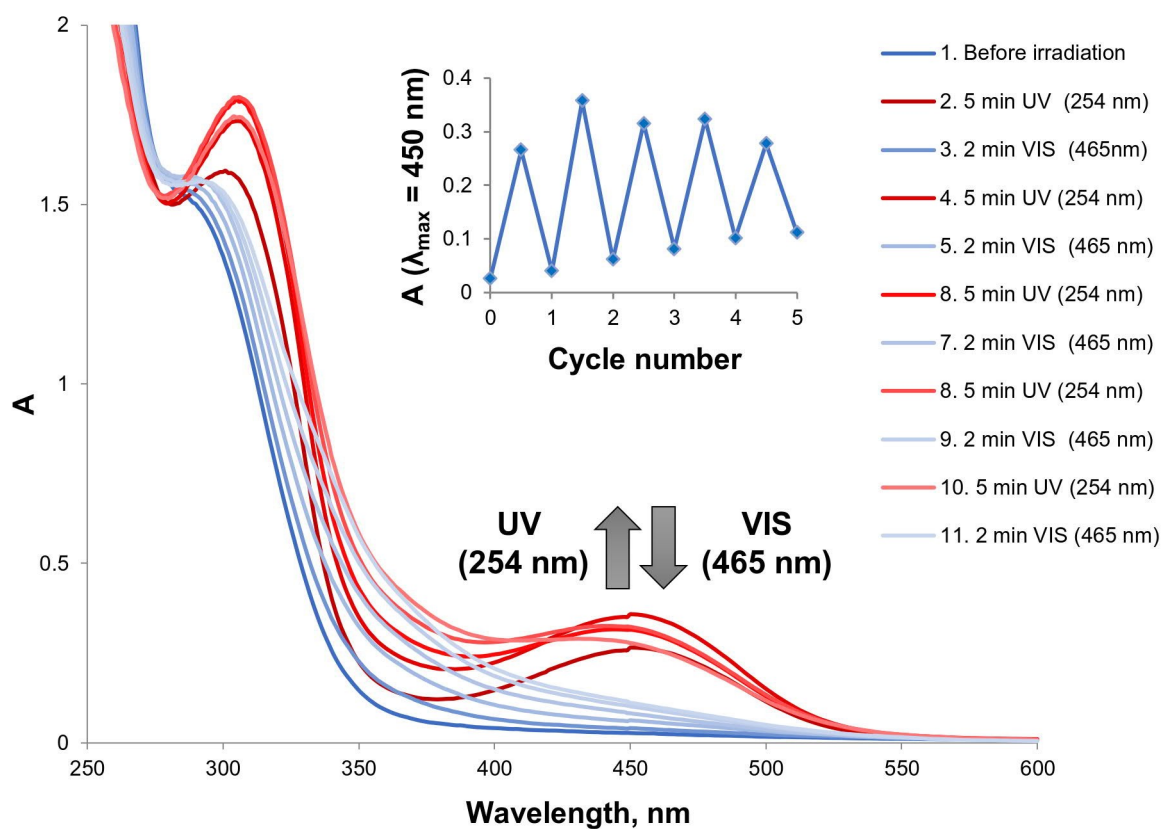


Figure S22. Spectral changes of water solution (buffer pH = 7) of **3a** ($c \approx 10^{-4}$ M) upon irradiation with UV ($\lambda_{\max} = 254$ nm) and visible light ($\lambda_{\max} = 465$ nm) and cyclicity (on inset).

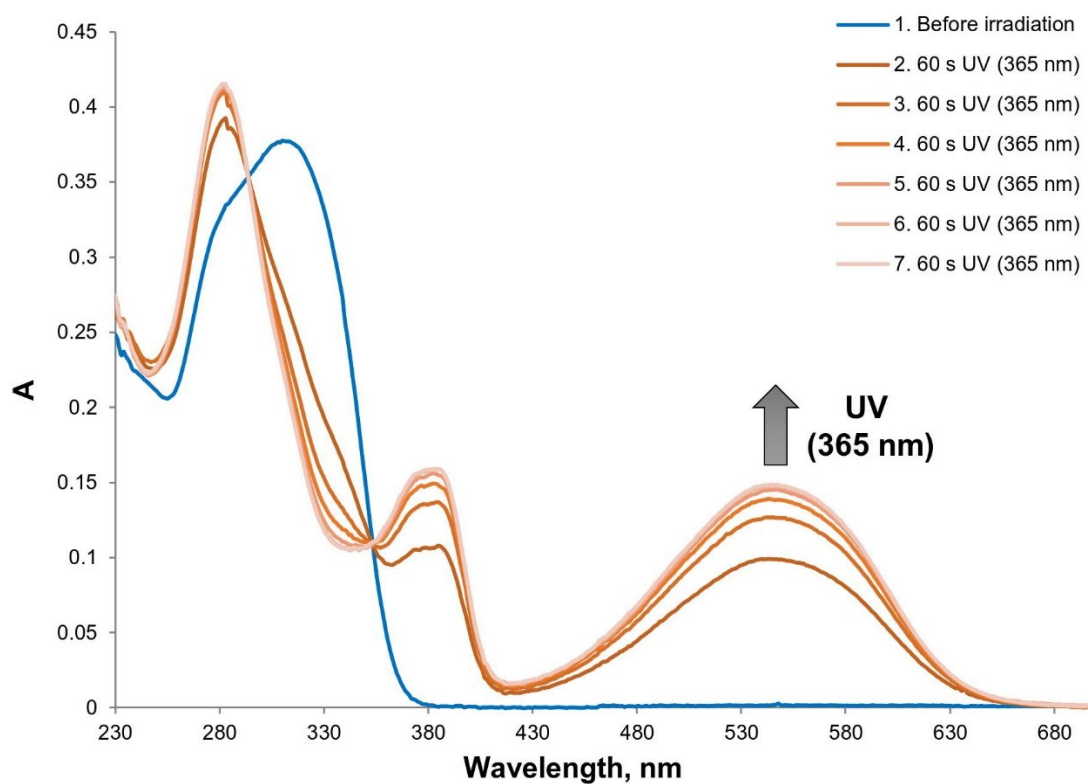


Figure S23. Spectral changes of water solution (buffer pH = 7) with acetonitrile (1:1) of **3b** ($c \approx 10^{-5}$ M) upon irradiation with UV ($\lambda_{\max} = 365$ nm).

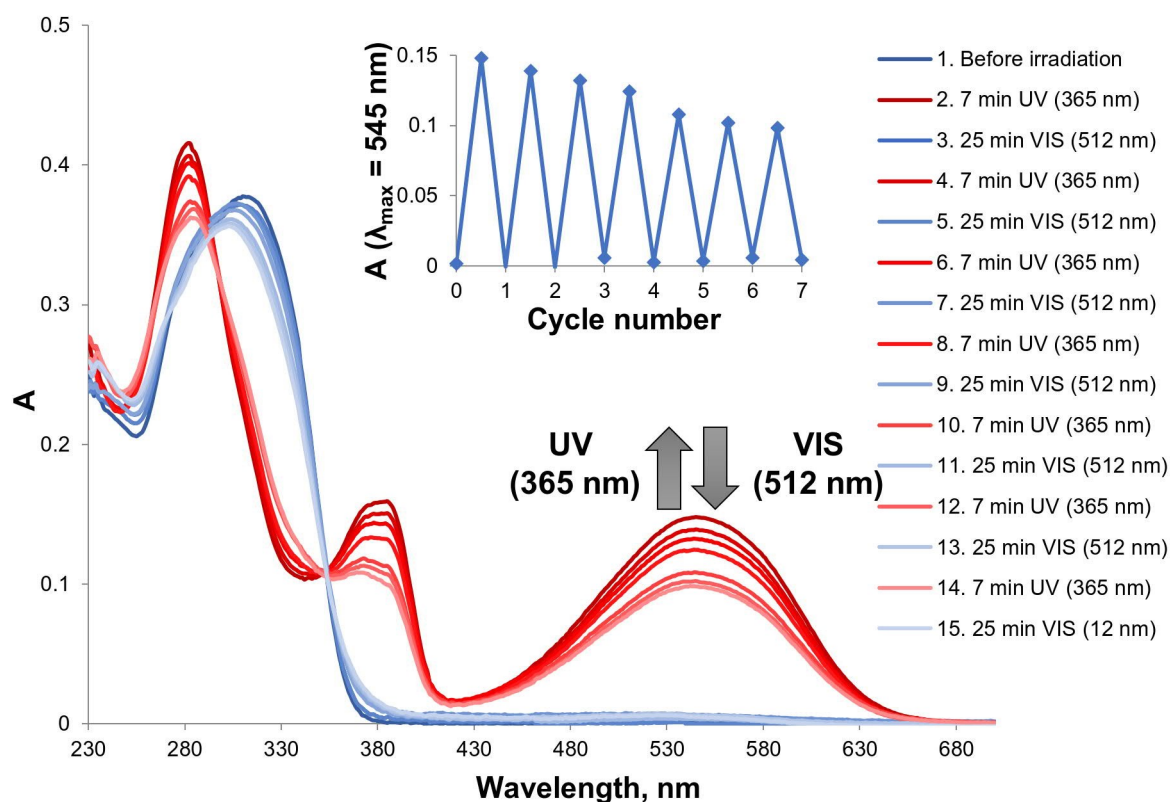


Figure S24. Spectral changes of water solution (buffer pH = 7) with acetonitrile (1:1) of **3b** ($c \approx 10^{-5}$ M) upon irradiation with UV ($\lambda_{\max} = 365$ nm) and visible light ($\lambda_{\max} = 512$ nm) and cyclicality (on inset).

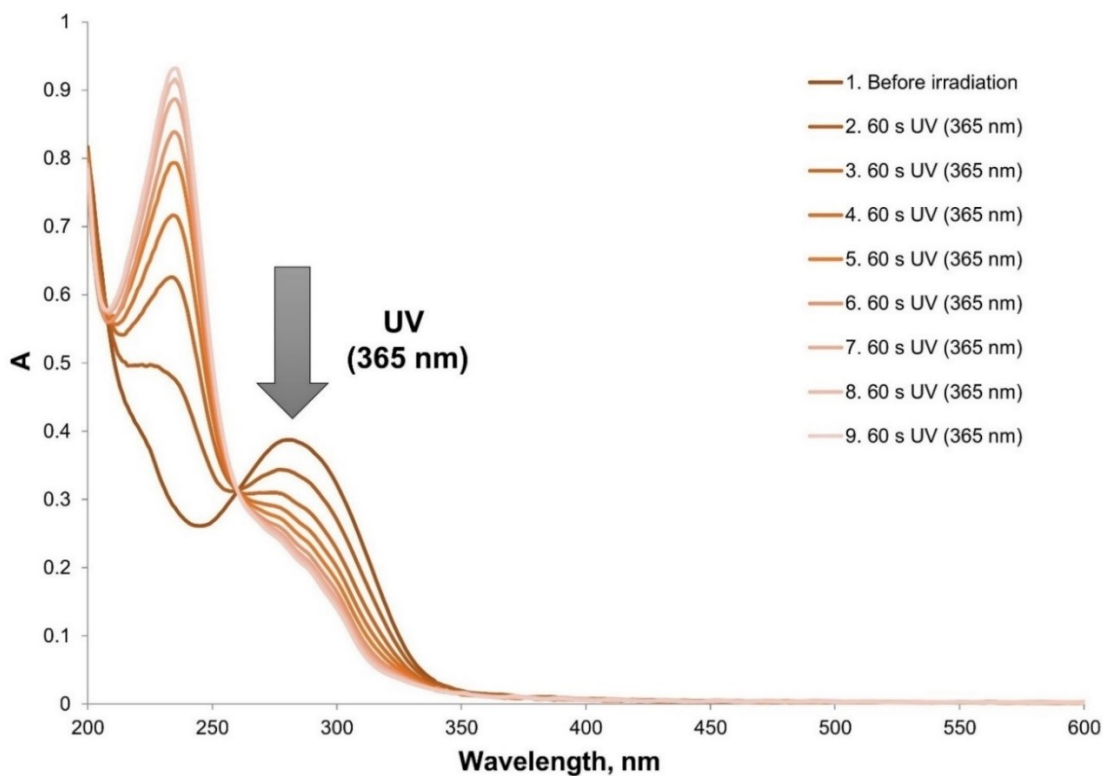


Figure S25. Spectral changes of water solution (buffer pH = 7) of **4a** ($c \approx 10^{-4}$ M) upon irradiation with UV ($\lambda_{\max} = 365$ nm).

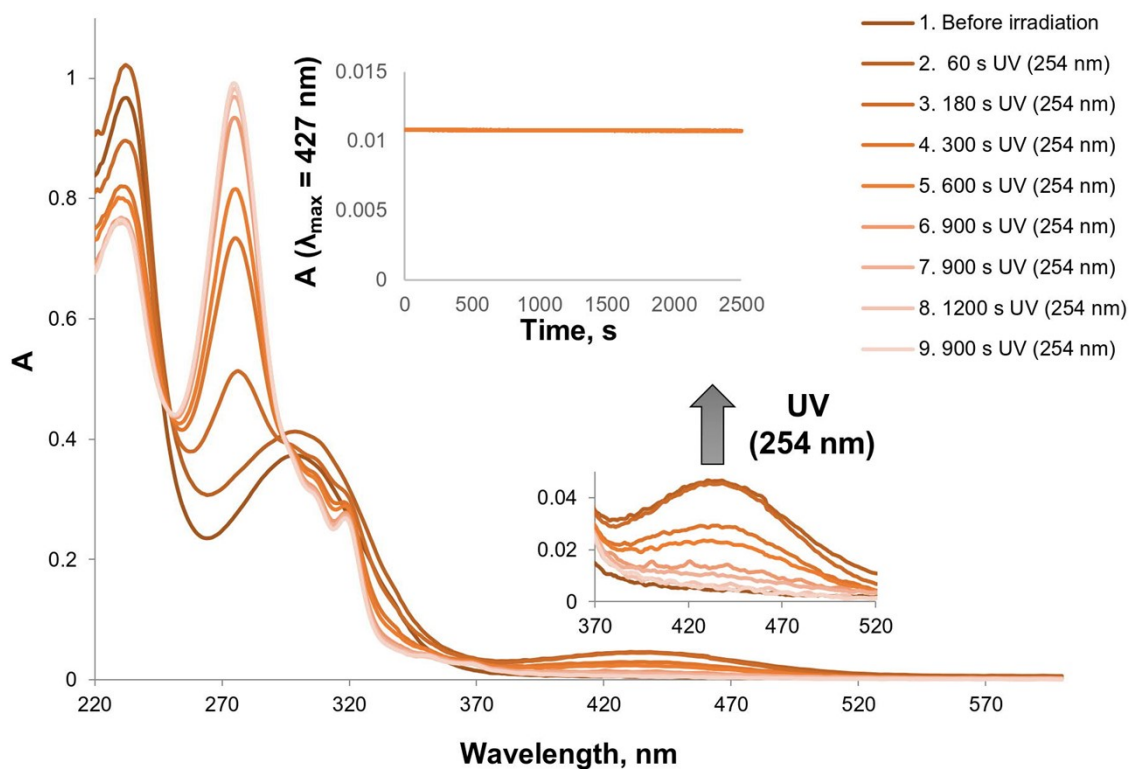


Figure S26. Spectral changes of water solution (buffer pH = 7) of **4b** ($c \approx 10^{-4}$ M) upon irradiation with UV ($\lambda_{\text{max}} = 365$ nm) and thermal bleaching of **4b-B** (on inset).

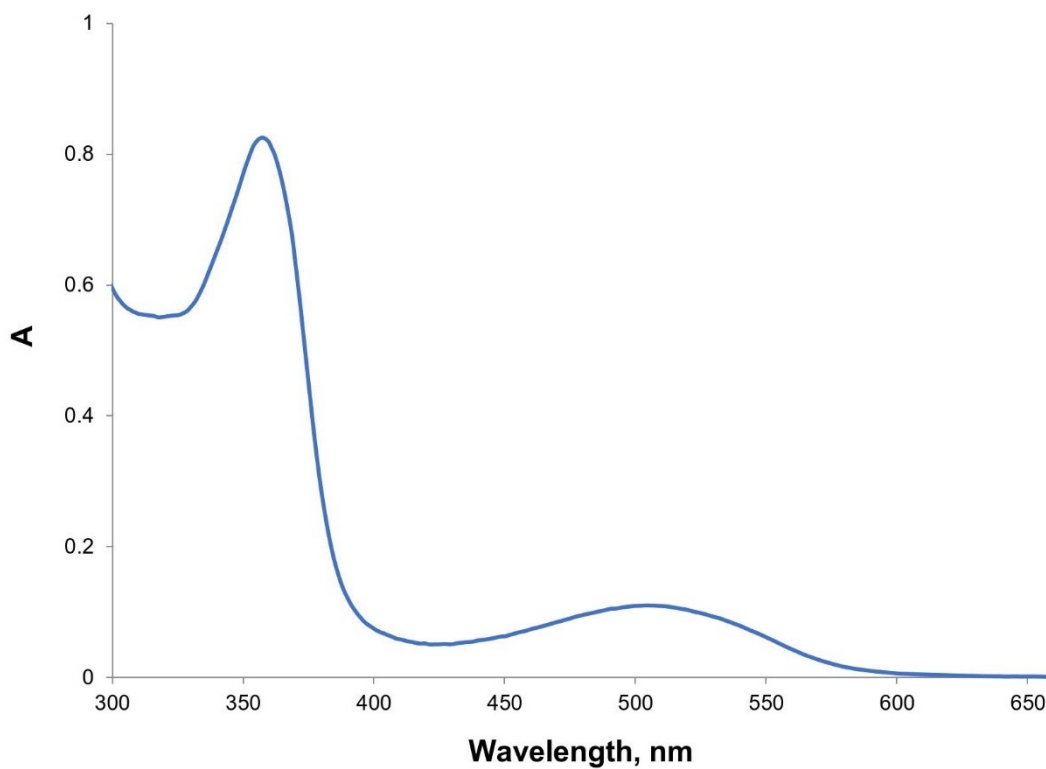


Figure S27. Absorbance spectrum of **10** in acetonitrile ($c \approx 1.2 \cdot 10^{-4}$ M).

VI. DFT calculations

Spectral properties of photogenerated closed-ring isomers **2a-B** and **3a-B** were simulated by the method of Patel and Masunov [S13]. All results were obtained using the Gaussian 09 program package [S14]. Density functional theory (DFT) calculations were performed using the M05-2x [S15] (structure optimization) and M05 [S16] (calculation of absorption spectra) functionals with the 6-31G(d) basis set [S17]. Calculation of vibrational frequencies was performed to prove that the optimized structure corresponds to a true minimum on the potential energy surface. The solvent influence was modeled using the polarizable continuum model (PCM) in water [S18]. The electronic excitations were calculated by linear-response time-dependent DFT (TD-DFT) [S19] at the TD-M05 level of theory.

Table S3. Calculated wavelength λ (nm) and oscillator strength f for **2a-B** (M05-2X/6-31G(d)/PCM // TD-M05 /6-31G(d)/PCM level of theory).

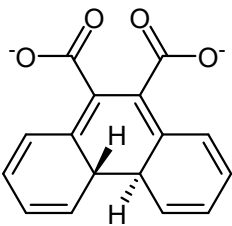
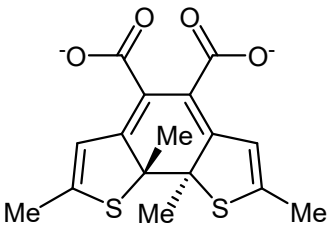
|  2a-B | Excited state | λ , nm (f) |
|---|-----------------|------------------------|
| | 1 | 489.98 (0.1406) |
| 2 | 395.78 (0.0237) | |
| 3 | 369.76 (0.0533) | |
| 4 | 365.30 (0.0099) | |
| 5 | 359.35 (0.0120) | |
| 6 | 345.49 (0.0891) | |
| 7 | 308.36 (0.1593) | |
| 8 | 306.69 (0.0320) | |
| 9 | 306.31 (0.0014) | |
| 10 | 285.83 (0.0264) | |

Table S4. Calculated wavelength λ (nm) and oscillator strength f for **3a-B** (M05-2X/6-31G(d)/PCM // TD-M05 /6-31G(d)/PCM level of theory).

|  3a-B | Excited state | λ , nm (f) |
|--|-----------------|------------------------|
| | 1 | 438.72 (0.1628) |
| 2 | 355.68 (0.0542) | |
| 3 | 339.23 (0.0154) | |
| 4 | 336.04 (0.0435) | |
| 5 | 333.82 (0.0043) | |
| 6 | 332.37 (0.0006) | |
| 7 | 305.23 (0.0099) | |
| 8 | 289.00 (0.0001) | |
| 9 | 279.50 (0.0011) | |
| 10 | 279.21 (0.0037) | |

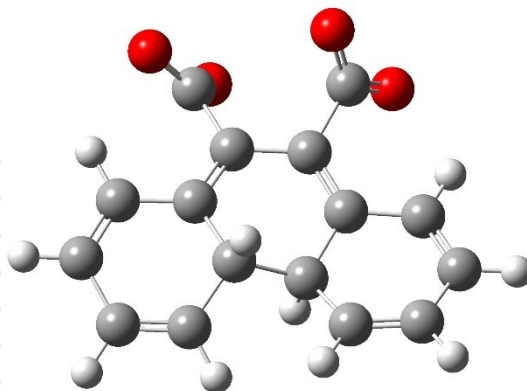
Cartesian coordinate columns of the optimized structure for compound 2a-B

(MO5-2X / 6-31G(d) / PCM (water))

Number of imaginary frequencies: 0

Computed total energy: -575266.1 kcal/mol

| | | | | |
|----|---|------------|------------|------------|
| 1 | C | 0.1747610 | 1.4419880 | 2.2716460 |
| 2 | C | -0.0207100 | 0.7308120 | 0.9273310 |
| 3 | C | -0.1747610 | -1.4419880 | 2.2716460 |
| 4 | C | 0.0207100 | -0.7308120 | 0.9273310 |
| 5 | C | -0.1309280 | 1.4241840 | -0.2381710 |
| 6 | C | -0.3261530 | 0.6921160 | -1.5566400 |
| 7 | C | 0.1309280 | -1.4241840 | -0.2381710 |
| 8 | C | 0.3261530 | -0.6921160 | -1.5566400 |
| 9 | C | -0.1747610 | 2.8777550 | -0.2773200 |
| 10 | C | -0.0388670 | 3.5552680 | -1.4370380 |
| 11 | C | 0.1415100 | 1.5096730 | -2.7385420 |
| 12 | C | 0.2261350 | 2.8449150 | -2.6827310 |
| 13 | C | 0.1747610 | -2.8777550 | -0.2773200 |
| 14 | C | 0.0388670 | -3.5552680 | -1.4370380 |
| 15 | C | -0.1415100 | -1.5096730 | -2.7385420 |
| 16 | C | -0.2261350 | -2.8449150 | -2.6827310 |
| 17 | O | 1.2087000 | 1.0921030 | 2.8901170 |
| 18 | O | -0.6633240 | 2.3102340 | 2.6167070 |
| 19 | O | 0.6633240 | -2.3102340 | 2.6167070 |
| 20 | O | -1.2087000 | -1.0921030 | 2.8901170 |
| 21 | H | -1.4168590 | 0.5319310 | -1.6748240 |
| 22 | H | 1.4168590 | -0.5319310 | -1.6748240 |
| 23 | H | -0.2859370 | 3.3908800 | 0.6676110 |
| 24 | H | -0.0552700 | 4.6383890 | -1.4443260 |
| 25 | H | 0.3785140 | 0.9892710 | -3.6592410 |
| 26 | H | 0.5257410 | 3.4141580 | -3.5550260 |
| 27 | H | 0.2859370 | -3.3908800 | 0.6676110 |
| 28 | H | 0.0552700 | -4.6383890 | -1.4443260 |
| 29 | H | -0.3785140 | -0.9892710 | -3.6592410 |
| 30 | H | -0.5257410 | -3.4141580 | -3.5550260 |



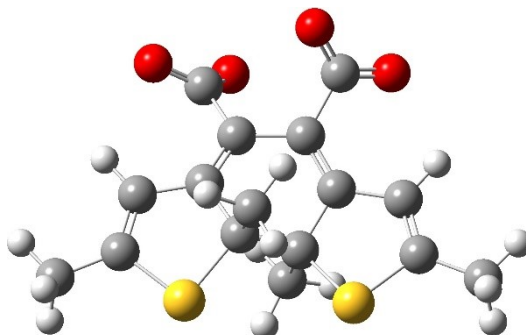
Cartesian coordinate columns of the optimized structure for compound 3a-B

(MO5-2X / 6-31G(d) / PCM (water))

Number of imaginary frequencies: 0

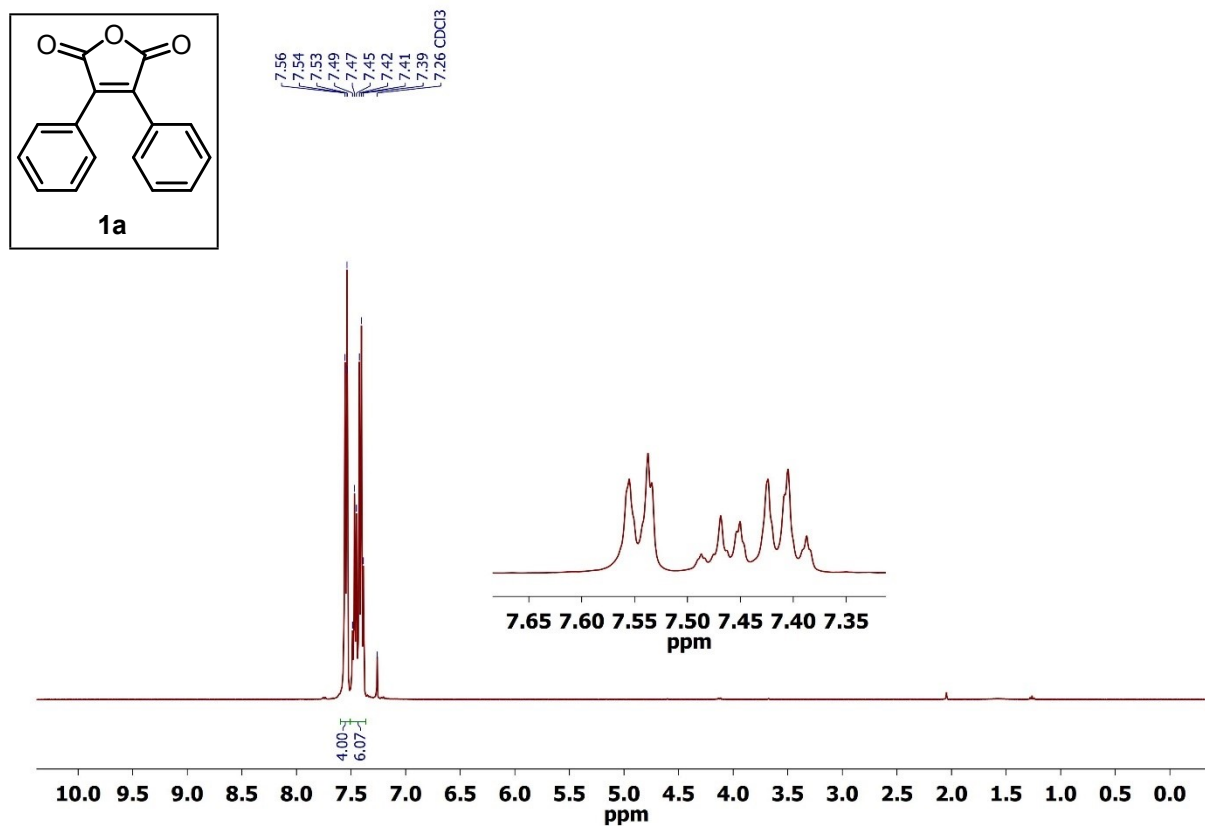
Computed total energy: -1076519.5 kcal/mol

| | | | | |
|----|---|------------|------------|------------|
| 1 | C | -0.7363920 | 1.4365920 | -0.0139070 |
| 2 | C | 0.7364070 | 1.4365830 | 0.0139140 |
| 3 | C | -1.4045230 | 0.2701900 | 0.1327240 |
| 4 | C | -0.6314880 | -1.0161800 | 0.4322360 |
| 5 | C | 1.4045220 | 0.2701720 | -0.1327210 |
| 6 | C | 0.6314720 | -1.0161940 | -0.4322110 |
| 7 | C | -2.8337050 | 0.0229270 | 0.0661320 |
| 8 | C | -3.1848500 | -1.2740160 | 0.0136000 |
| 9 | S | -1.8035790 | -2.3930550 | 0.0290620 |
| 10 | C | 2.8337010 | 0.0228980 | -0.0661470 |
| 11 | C | 3.1848300 | -1.2740500 | -0.0136020 |
| 12 | S | 1.8035540 | -2.3930680 | -0.0290090 |
| 13 | C | 4.5635760 | -1.8460590 | 0.0654530 |
| 14 | C | -4.5635870 | -1.8460280 | -0.0655540 |
| 15 | C | -0.3545020 | -1.0654750 | 1.9439020 |
| 16 | C | 0.3544890 | -1.0655130 | -1.9438790 |
| 17 | C | -1.4591920 | 2.7317160 | -0.3799070 |
| 18 | O | -0.9155970 | 3.3911280 | -1.2988380 |
| 19 | O | -2.5345060 | 2.9949480 | 0.2133620 |
| 20 | C | 1.4592230 | 2.7316960 | 0.3799140 |
| 21 | O | 2.5345340 | 2.9949200 | -0.2133740 |
| 22 | O | 0.9156420 | 3.3911310 | 1.2988300 |
| 23 | H | -3.5426490 | 0.8373470 | 0.0397720 |
| 24 | H | 3.5426520 | 0.8373130 | -0.0398030 |
| 25 | H | 4.7726790 | -2.4805410 | -0.7993070 |
| 26 | H | 5.2999230 | -1.0433260 | 0.0975600 |
| 27 | H | 4.6803230 | -2.4637040 | 0.9594930 |
| 28 | H | -4.6804050 | -2.4632680 | -0.9598660 |
| 29 | H | -4.7725790 | -2.4809120 | 0.7989350 |
| 30 | H | -5.2999650 | -1.0433050 | -0.0972280 |
| 31 | H | 0.2889590 | -0.2314470 | 2.2288180 |
| 32 | H | -1.3050290 | -0.9739030 | 2.4713190 |
| 33 | H | 0.1219550 | -2.0016840 | 2.2320170 |
| 34 | H | 1.3050190 | -0.9739540 | -2.4712920 |
| 35 | H | -0.1219700 | -2.0017260 | -2.2319770 |
| 36 | H | -0.2889670 | -0.2314870 | -2.2288080 |

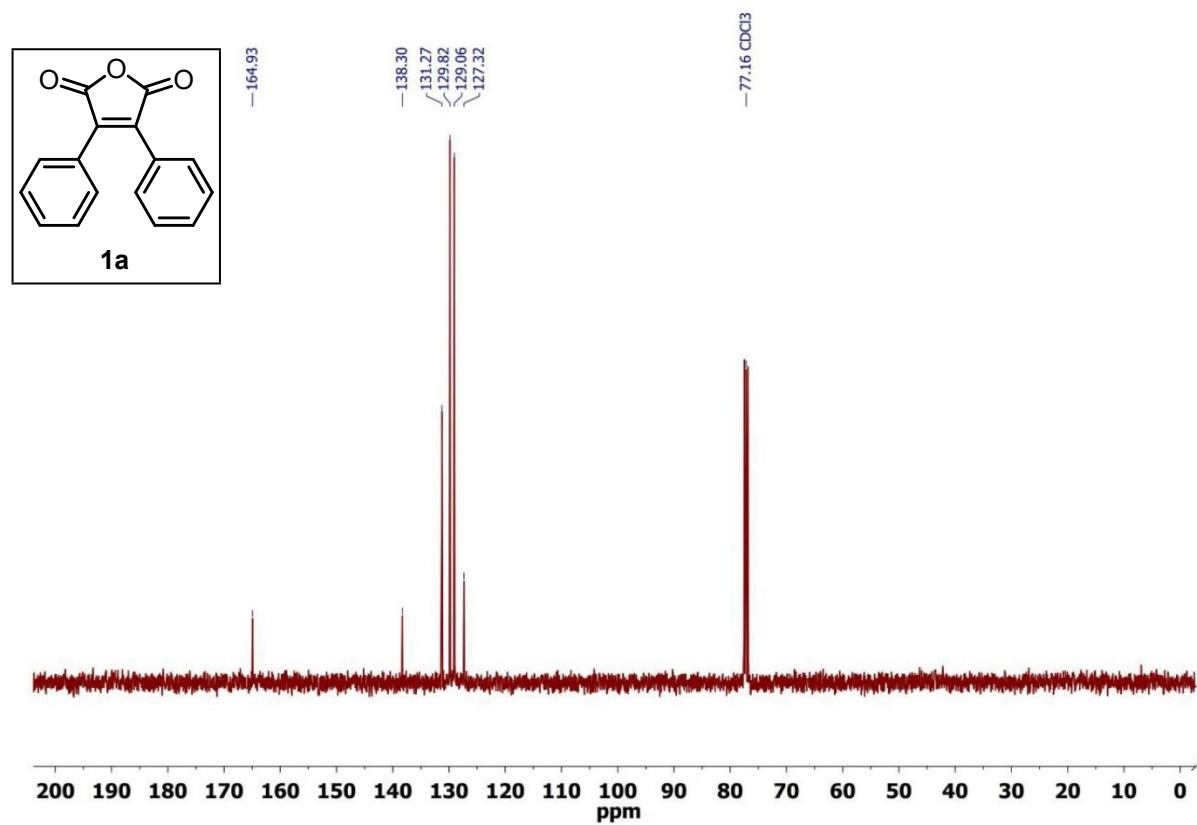


VII. Copies of NMR spectra

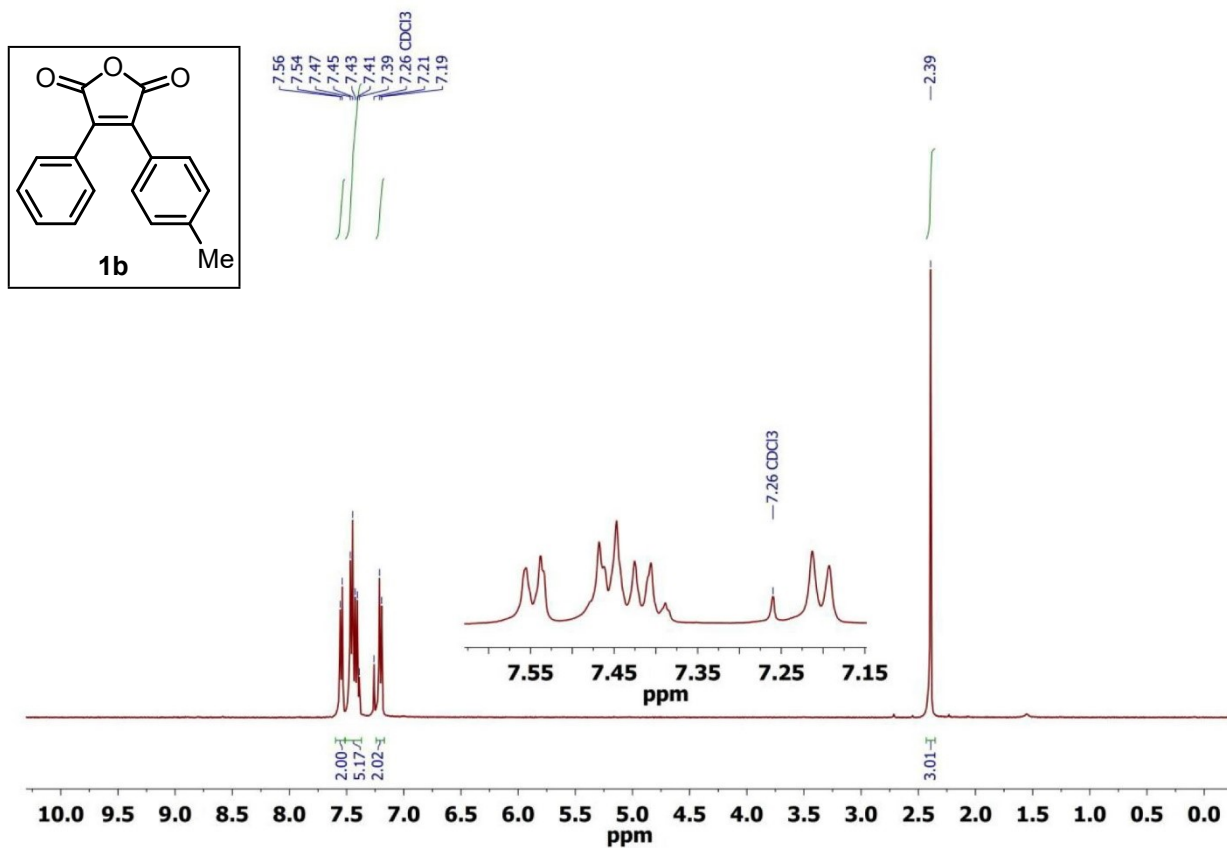
^1H NMR spectrum of **1a** in CDCl_3



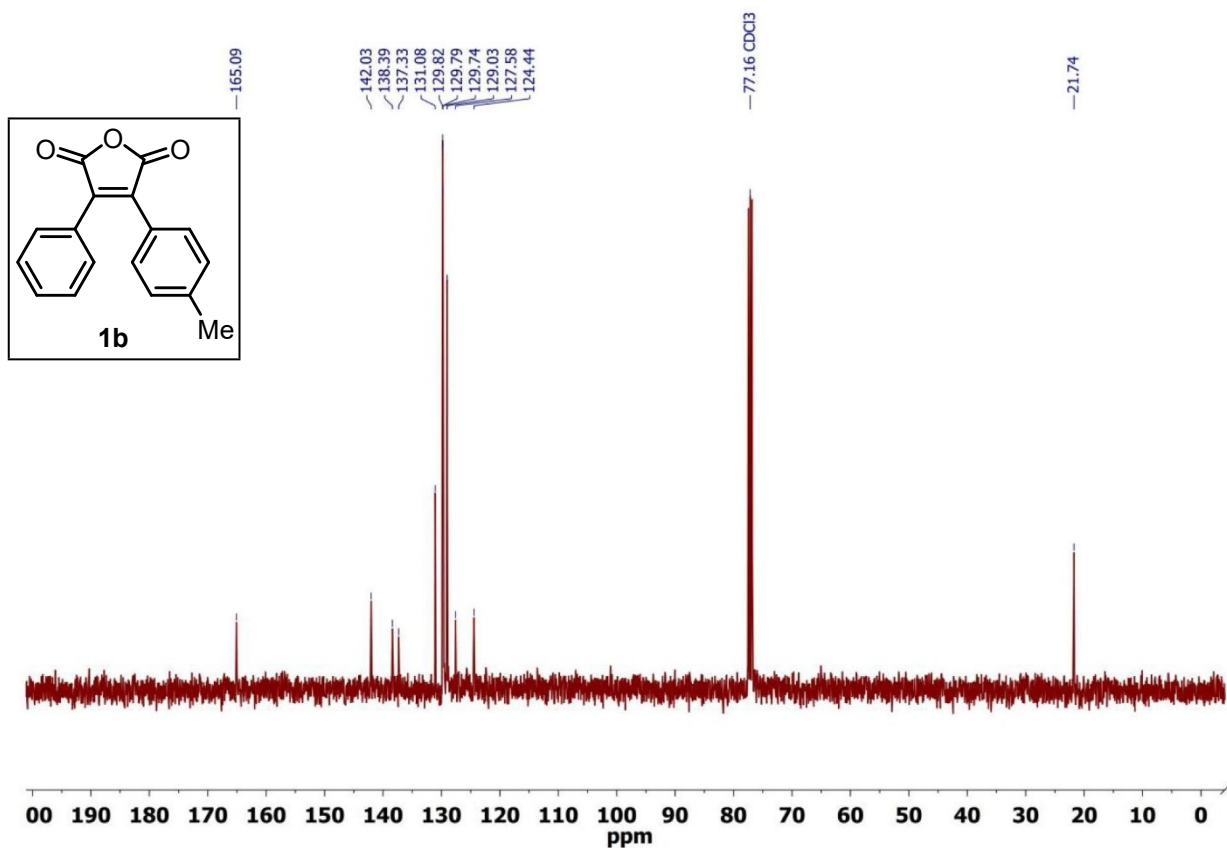
^{13}C NMR spectrum of **1a** in CDCl_3



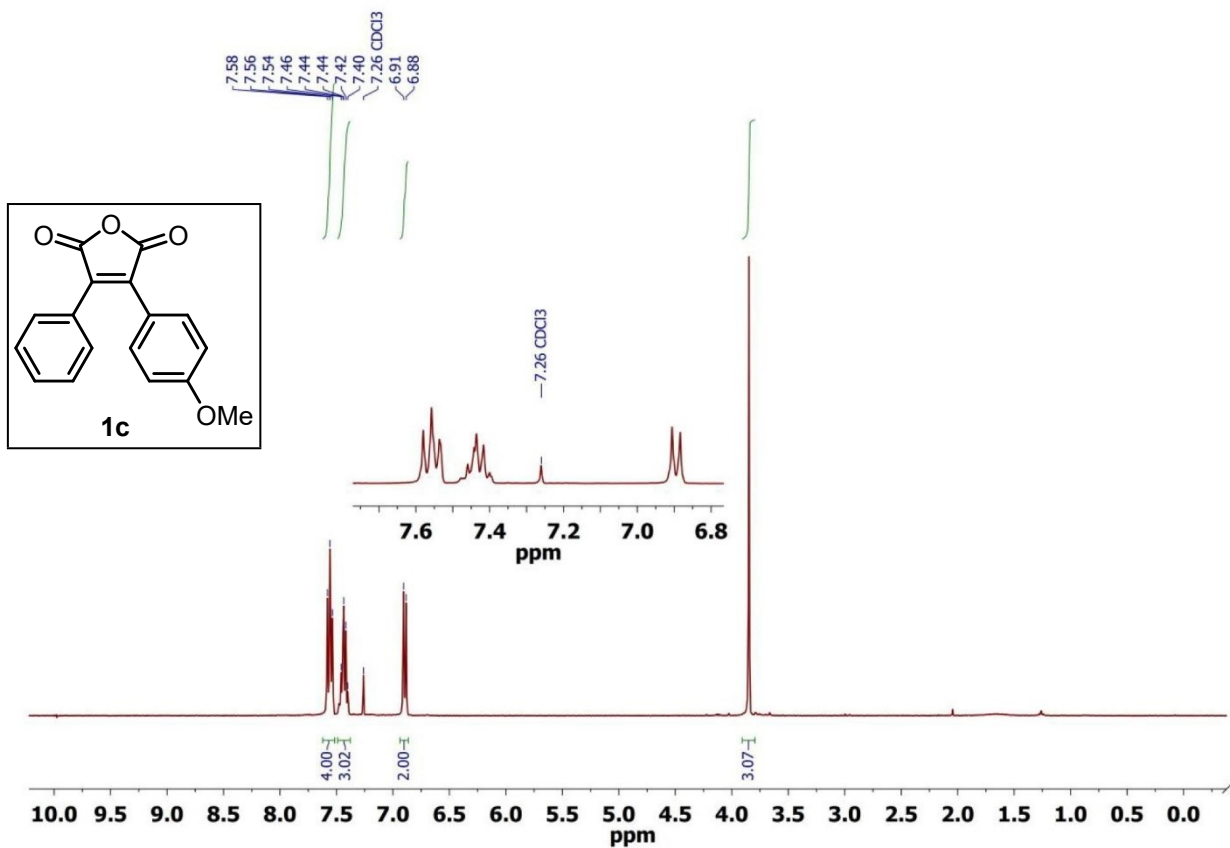
^1H NMR spectrum of **1b** in CDCl_3



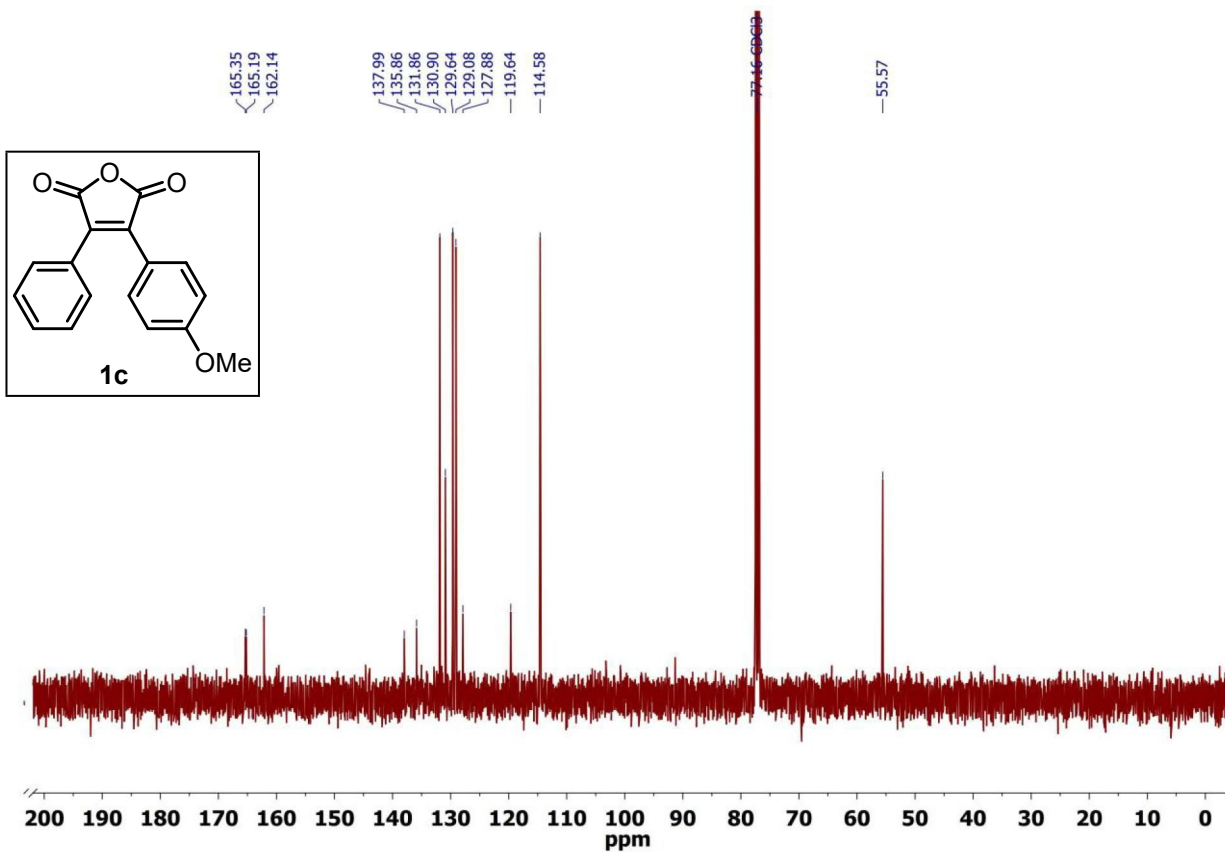
^{13}C NMR spectrum of **1b** in CDCl_3



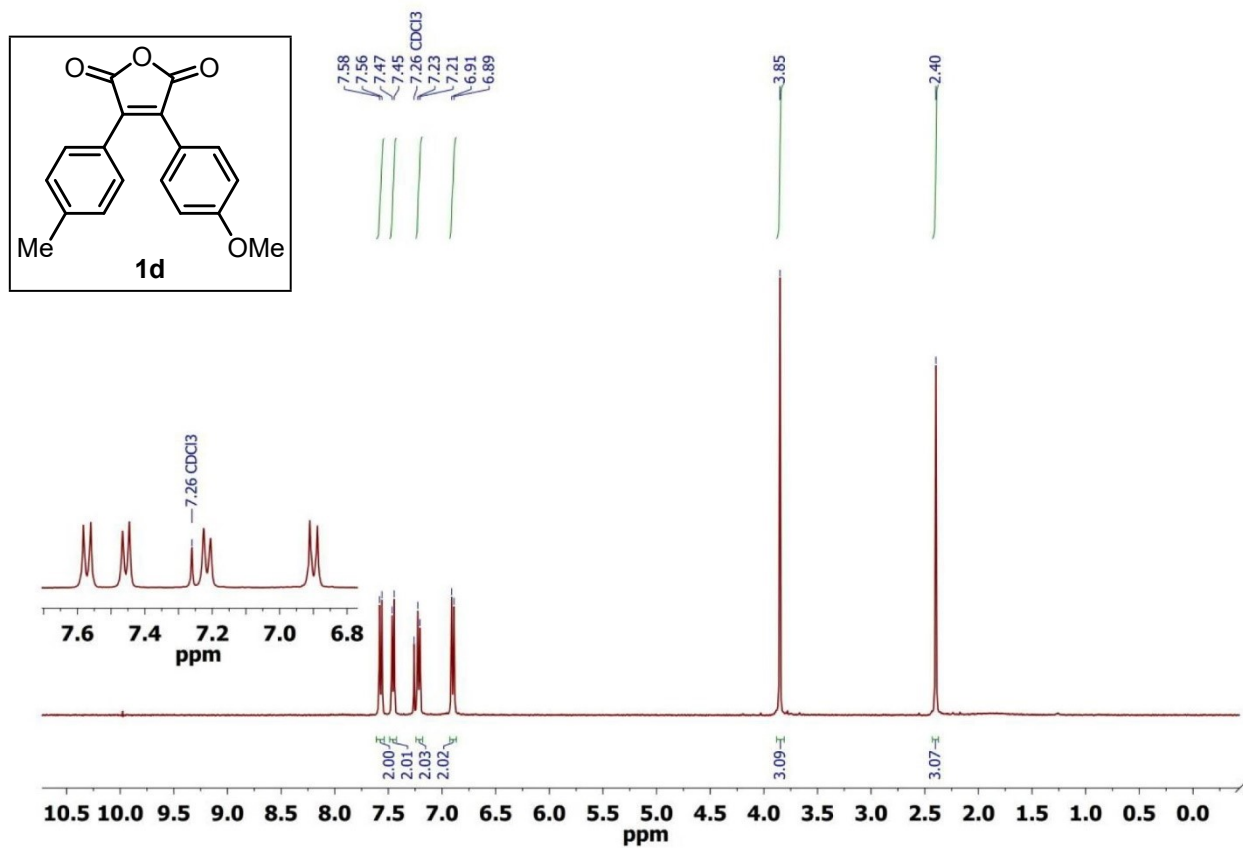
^1H NMR spectrum of **1c** in CDCl_3



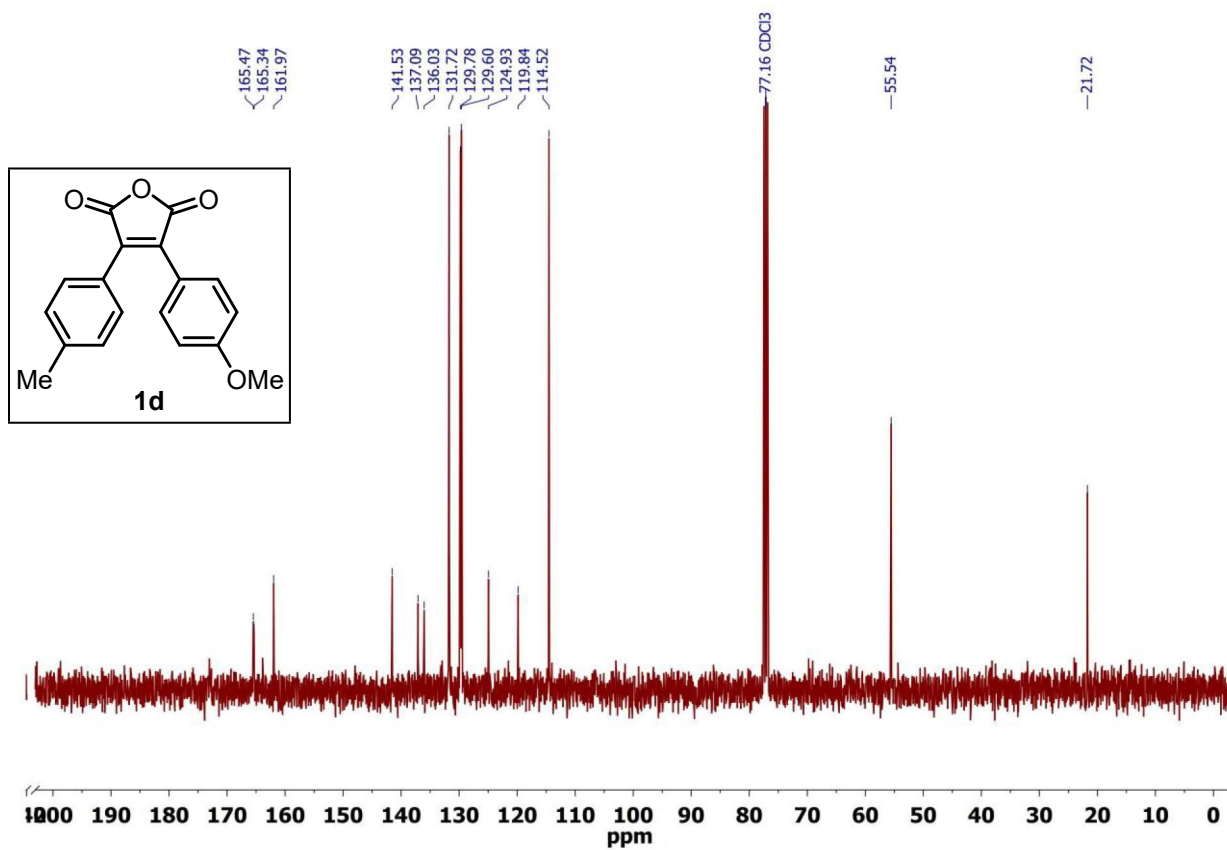
^{13}C NMR spectrum of **1c** in CDCl_3



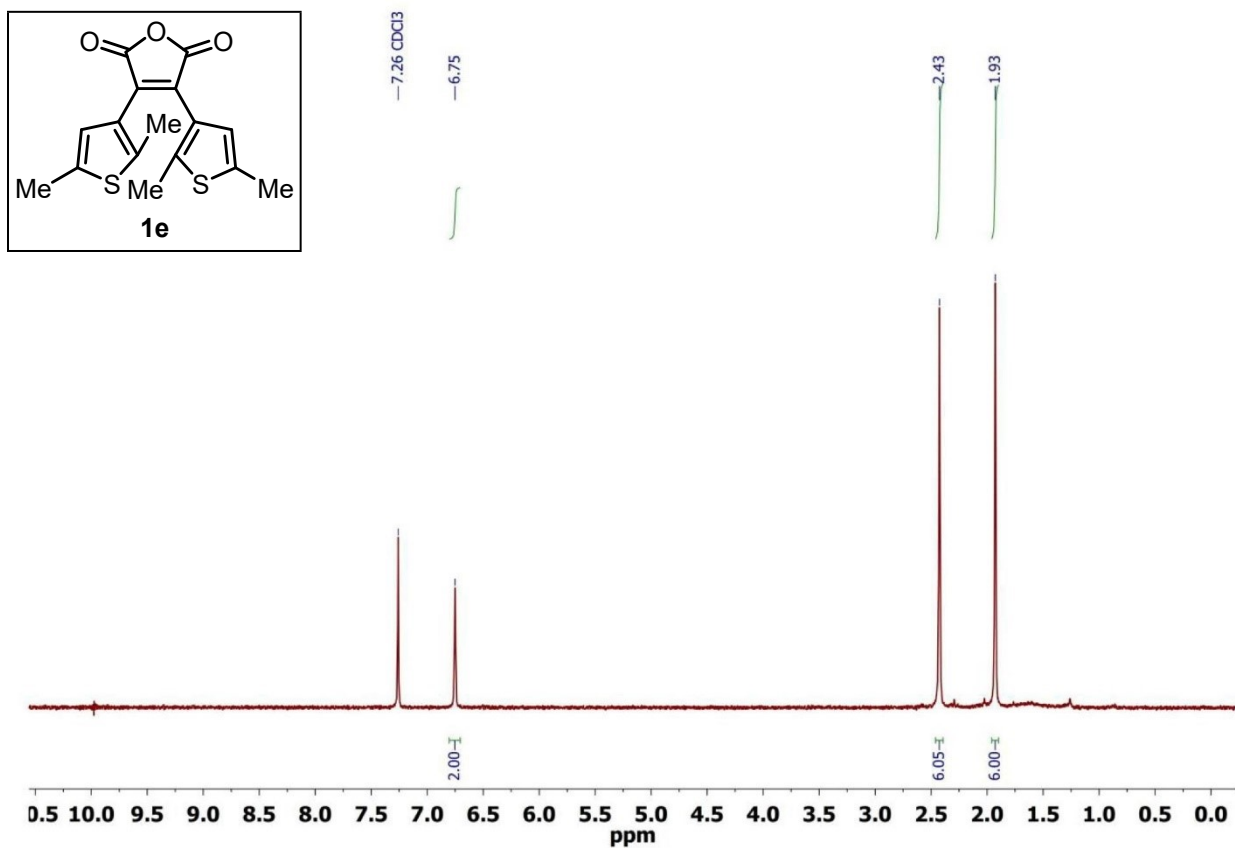
^1H NMR spectrum of **1d** in CDCl_3



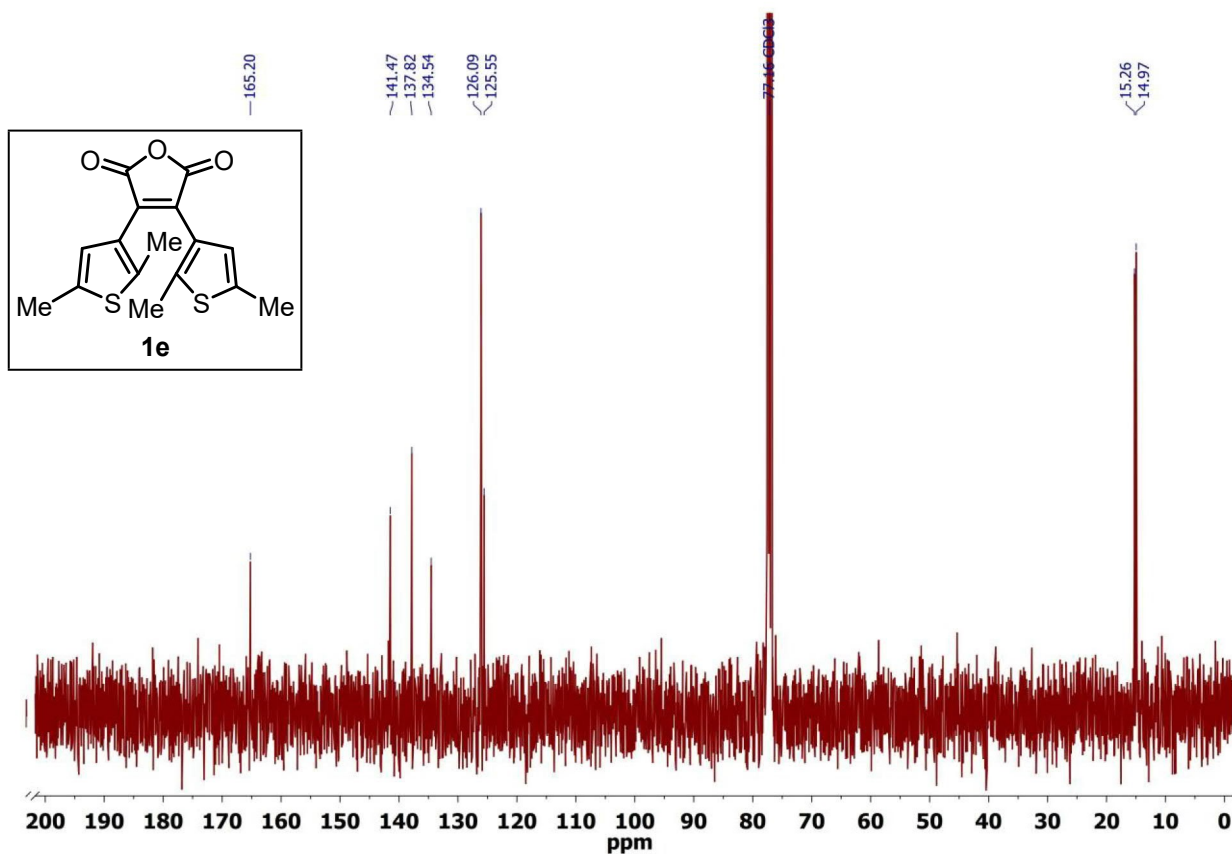
^{13}C NMR spectrum of **1d** in CDCl_3



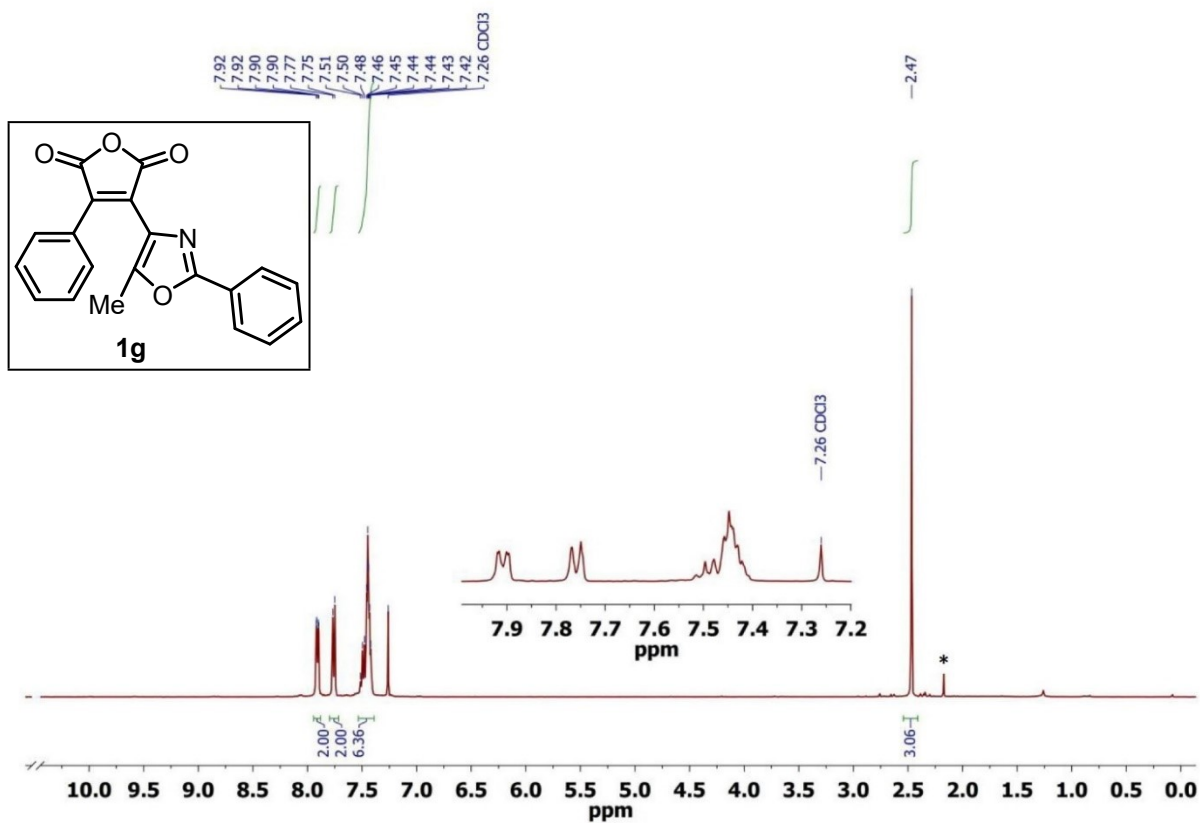
^1H NMR spectrum of **1e** in CDCl_3



^{13}C NMR spectrum of **1e** in CDCl_3

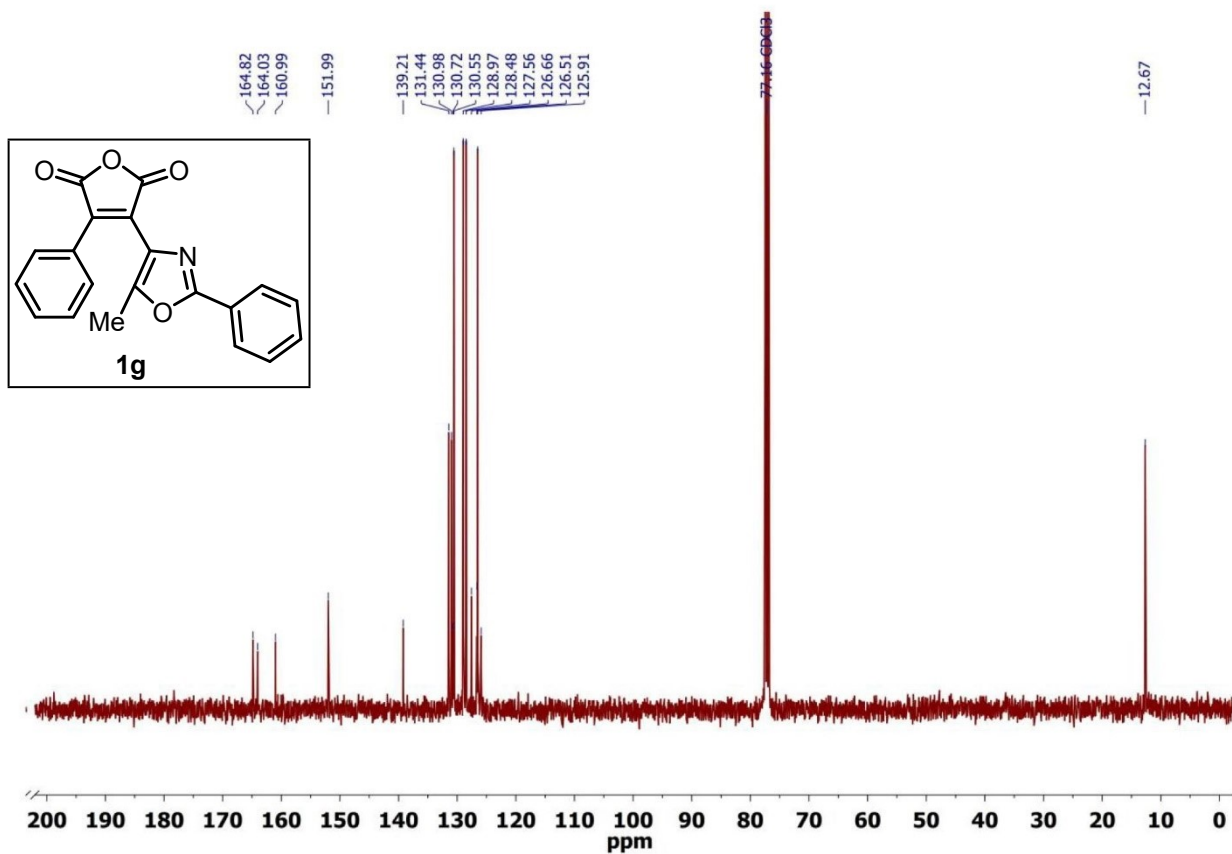


^1H NMR spectrum of **1g** in CDCl_3

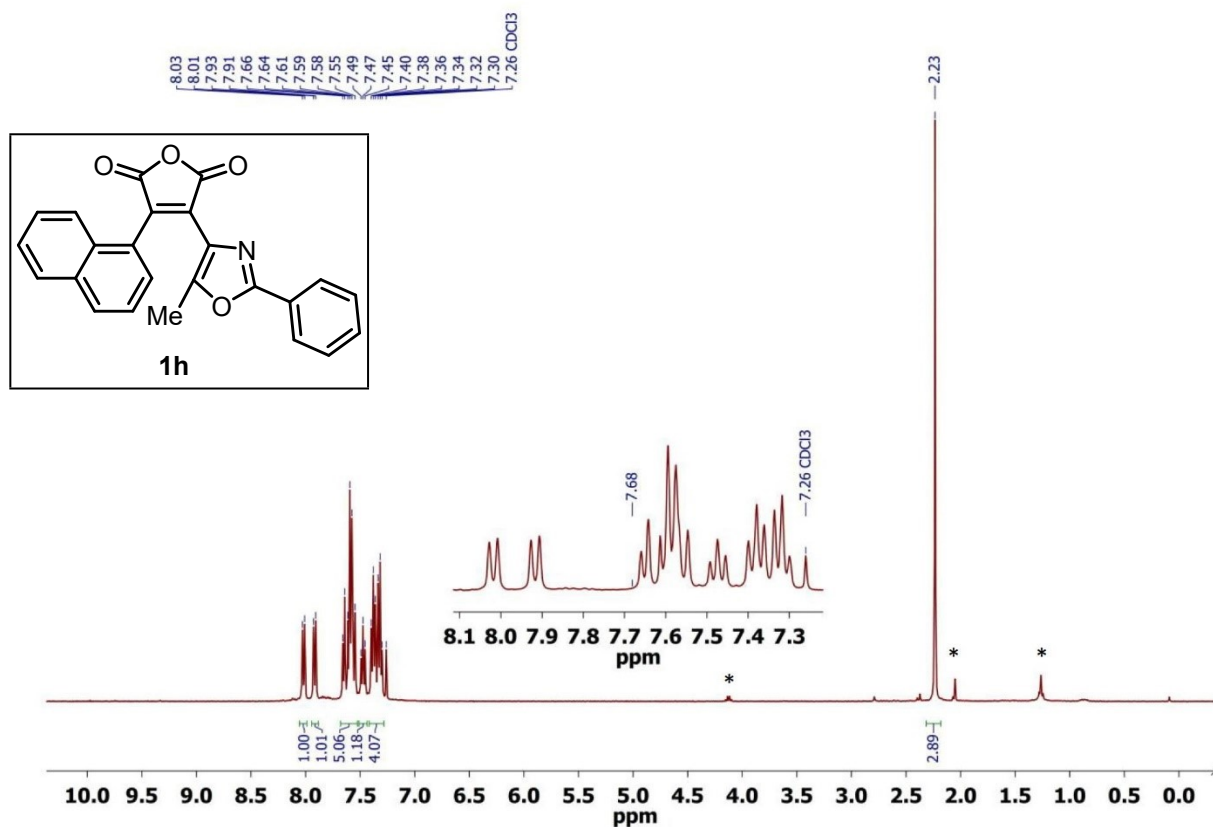


* - acetone ($\delta = 2.17$)

^{13}C NMR spectrum of **1g** in CDCl_3

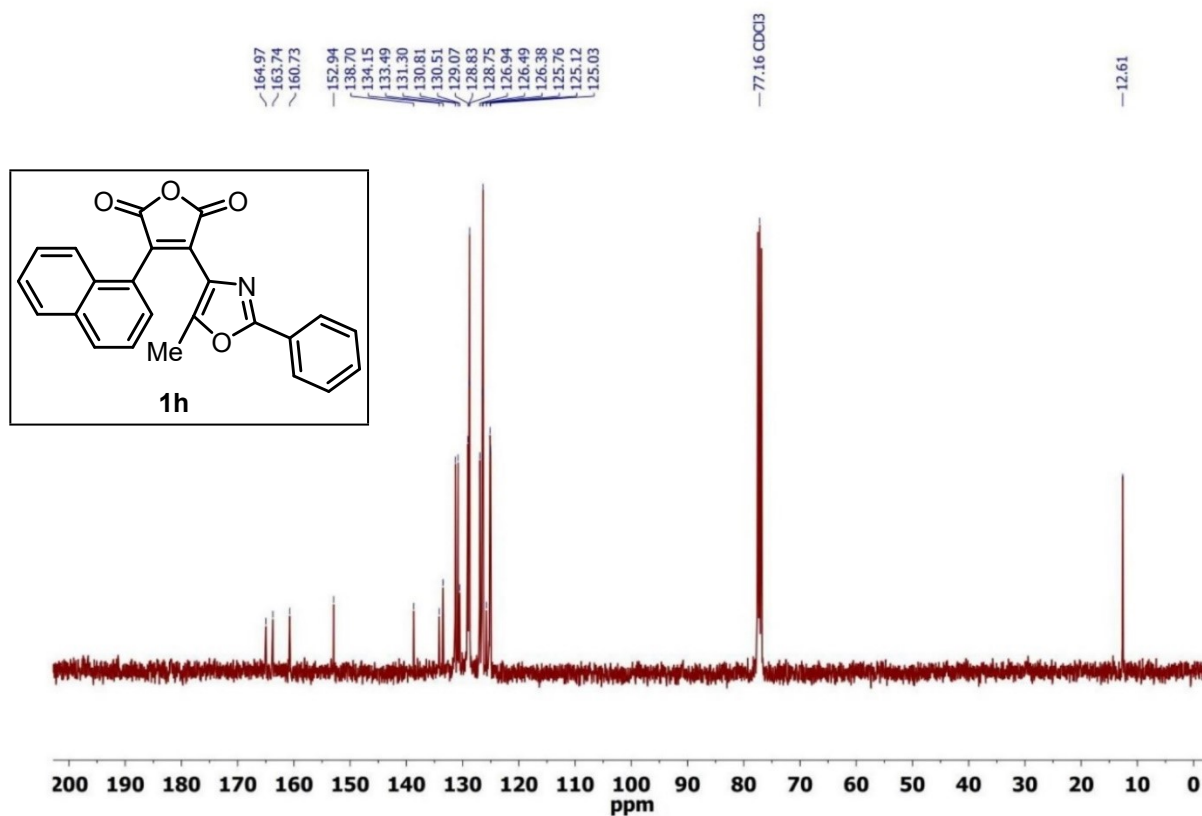


¹H NMR spectrum of **1h** in CDCl₃

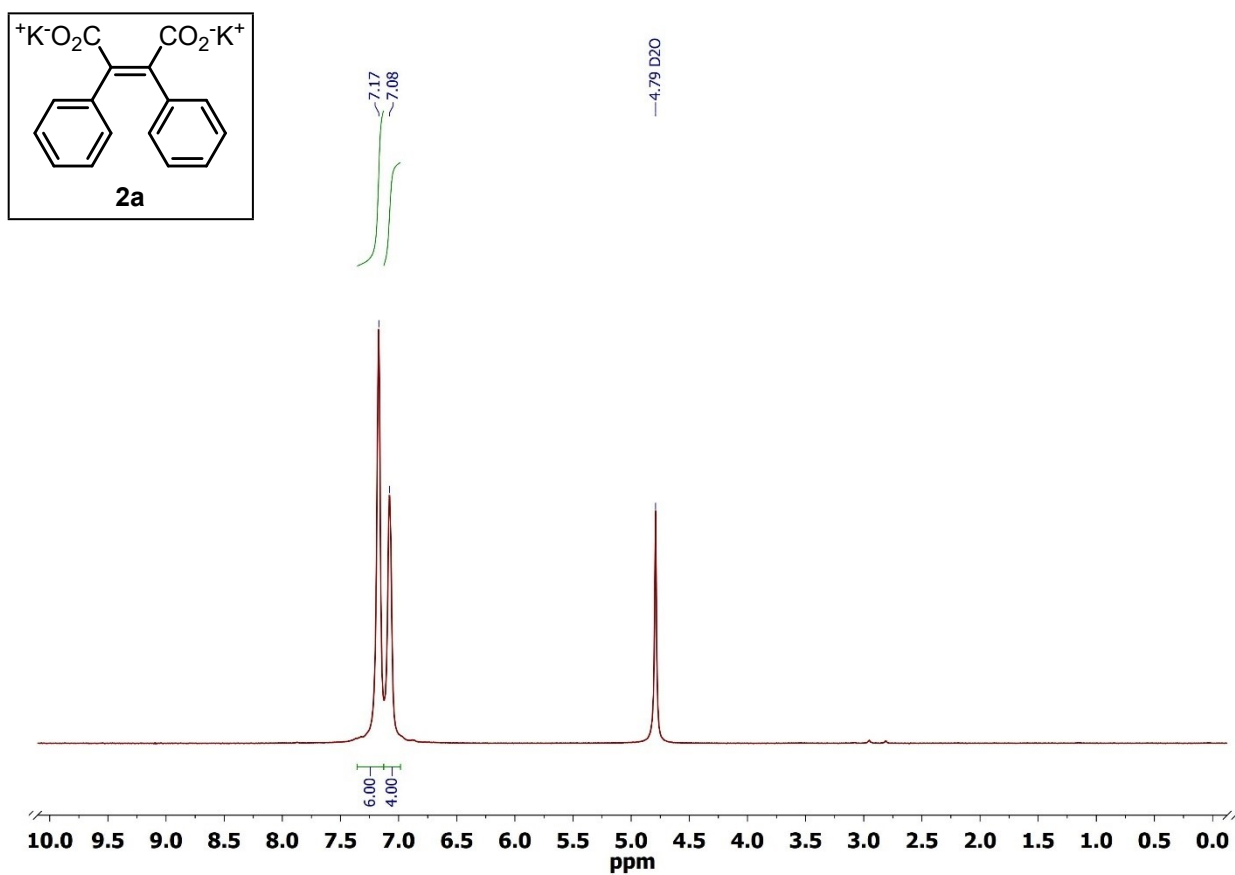


* - ethyl acetate ($\delta = 4.13$ (q, $J = 7.1$ Hz, 1H), 2.05 (s, 2H), 1.29 – 1.24 (m, 5H))

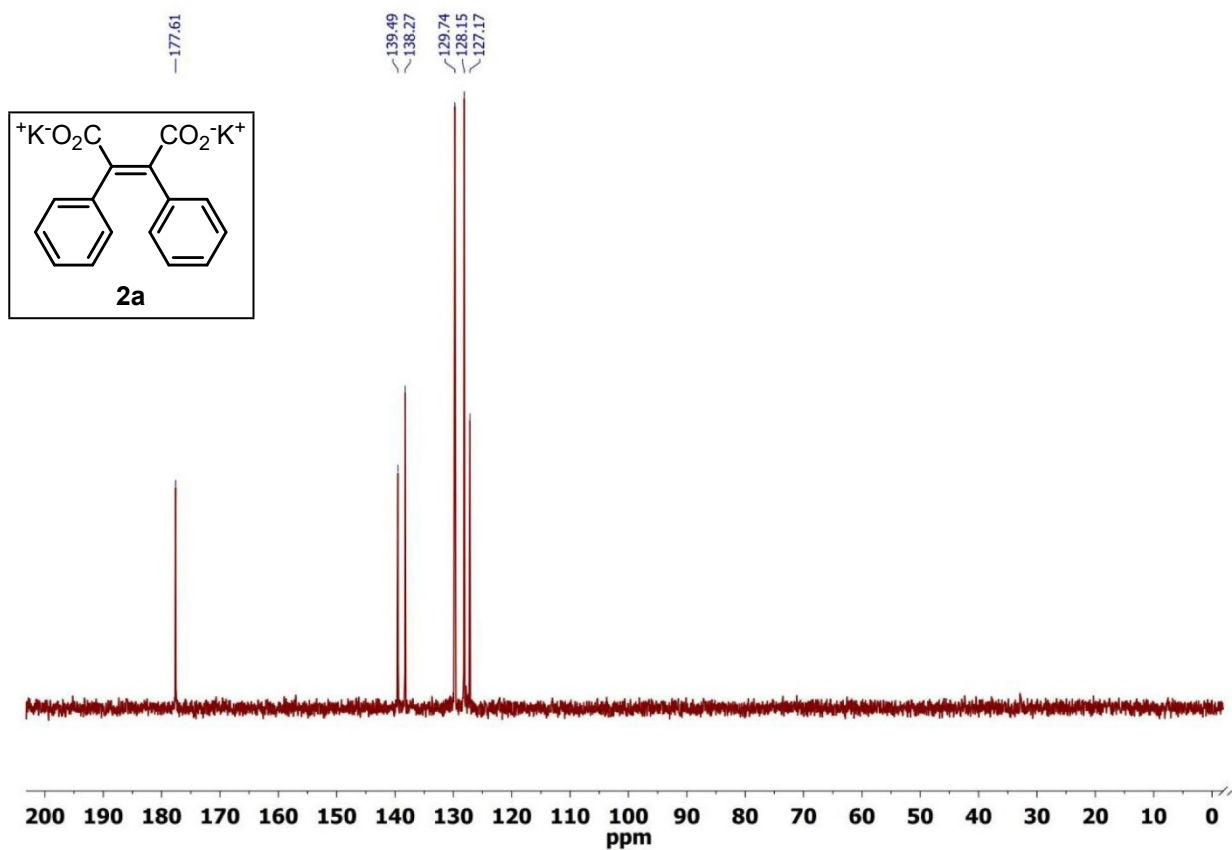
¹³C NMR spectrum of **1h** in CDCl₃



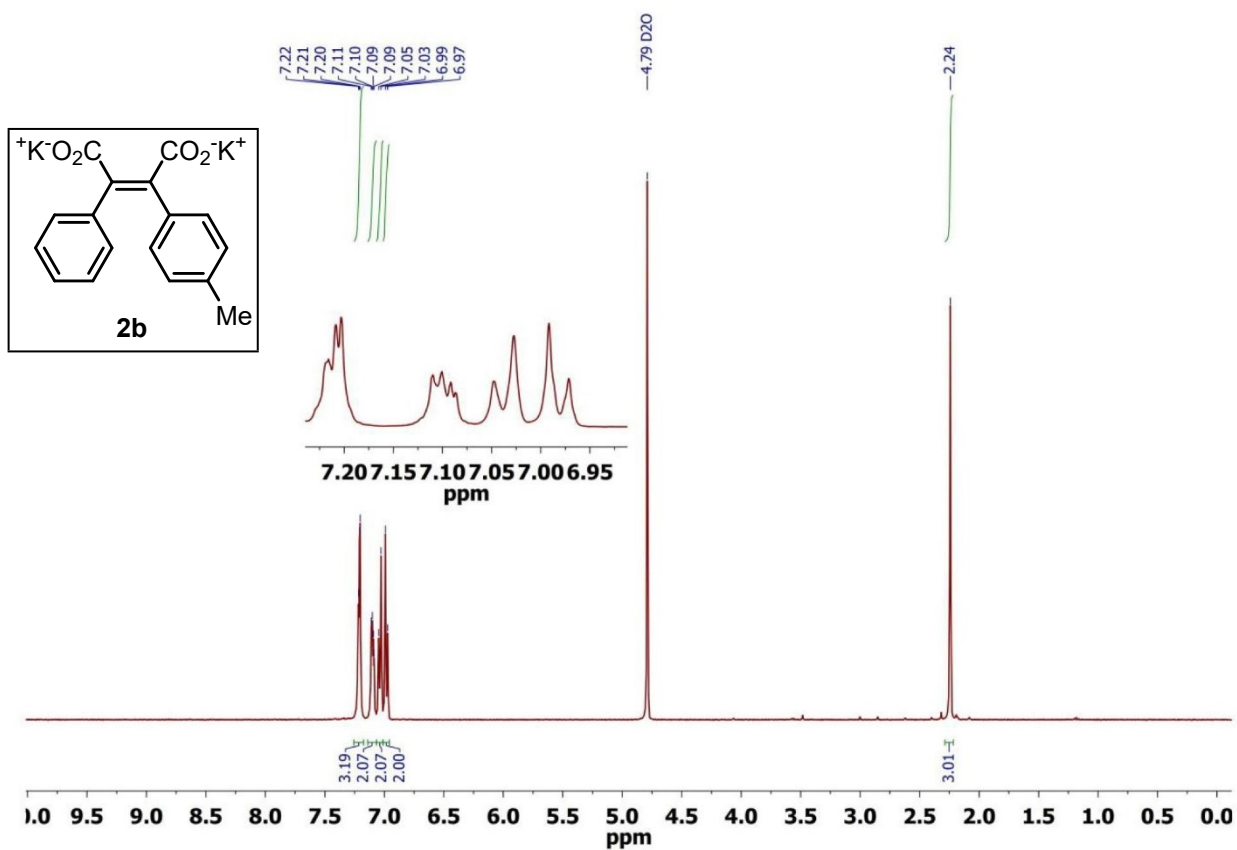
^1H NMR spectrum of **2a** in D_2O



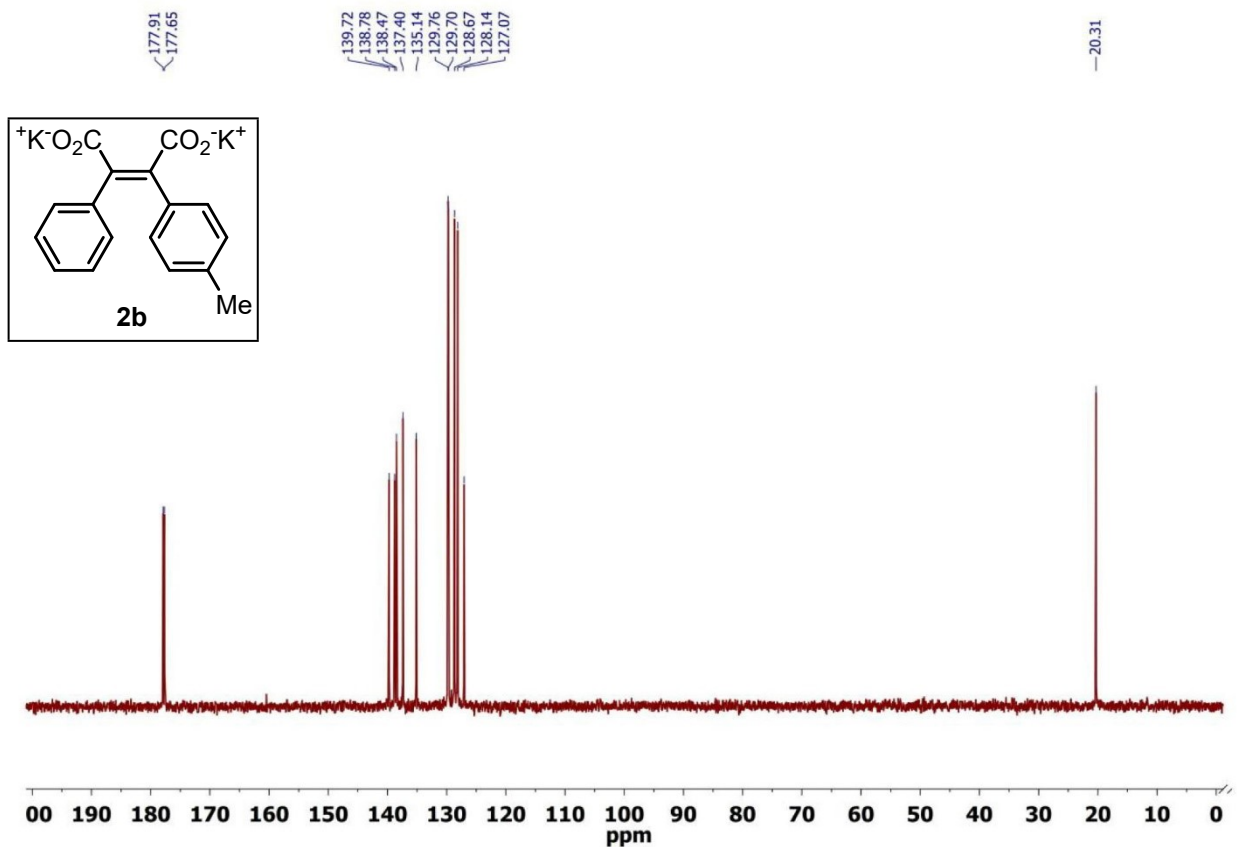
^{13}C NMR spectrum of **2a** in D_2O



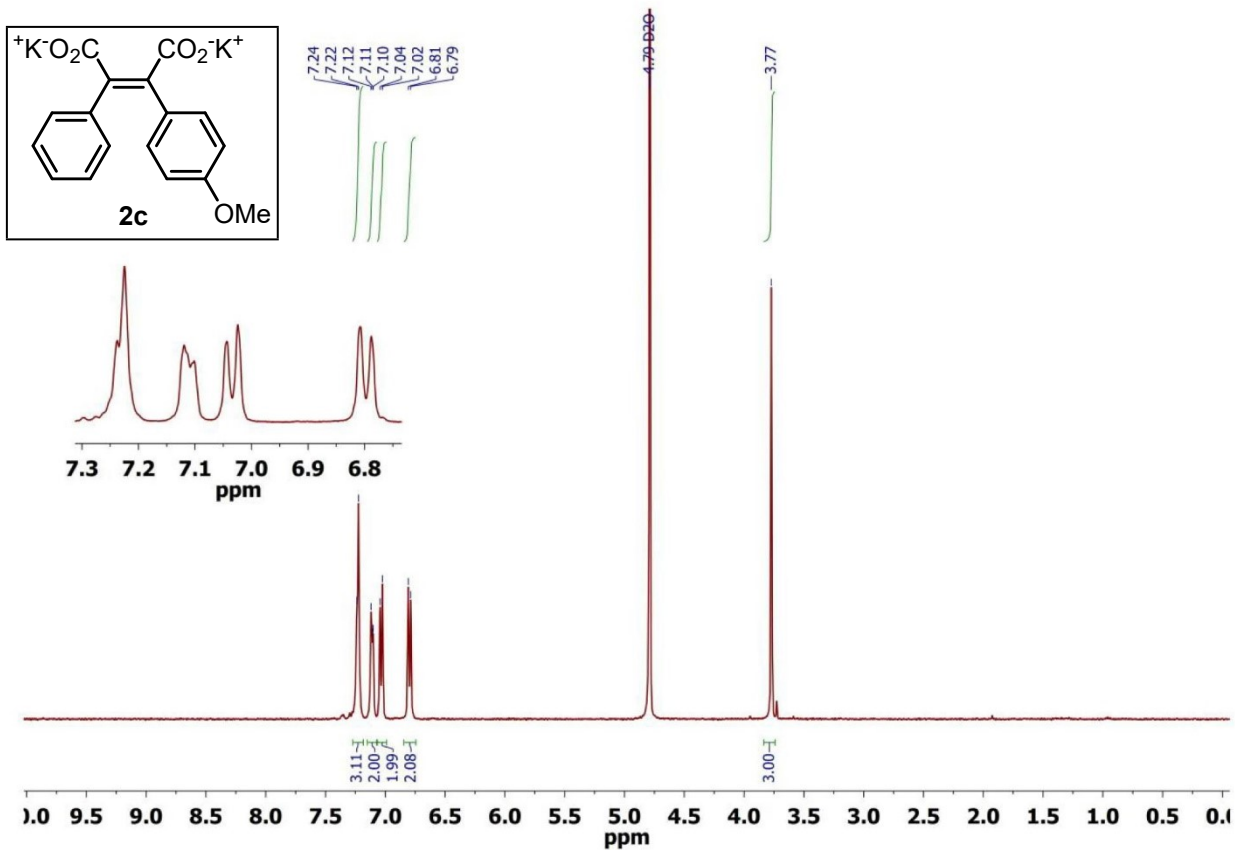
^1H NMR spectrum of **2b** in D_2O



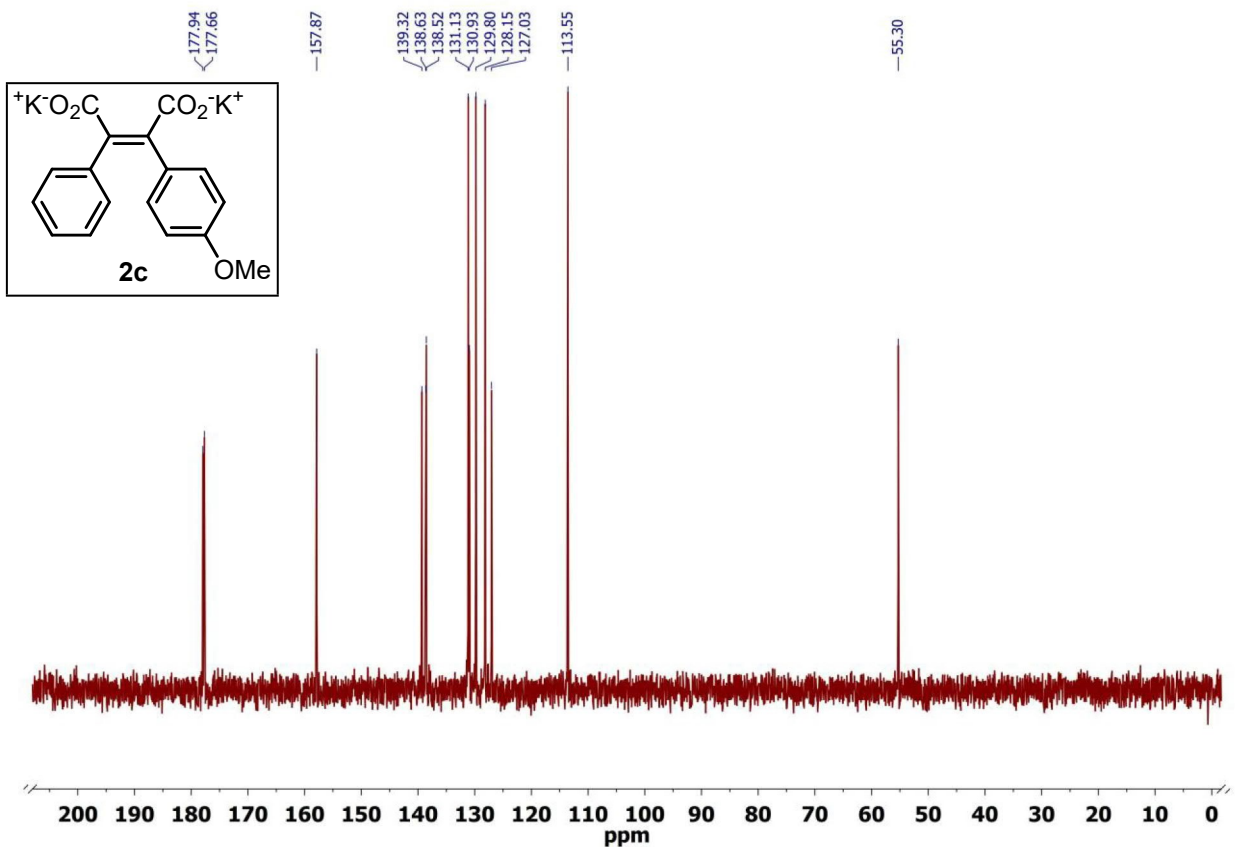
^{13}C NMR spectrum of **2b** in D_2O



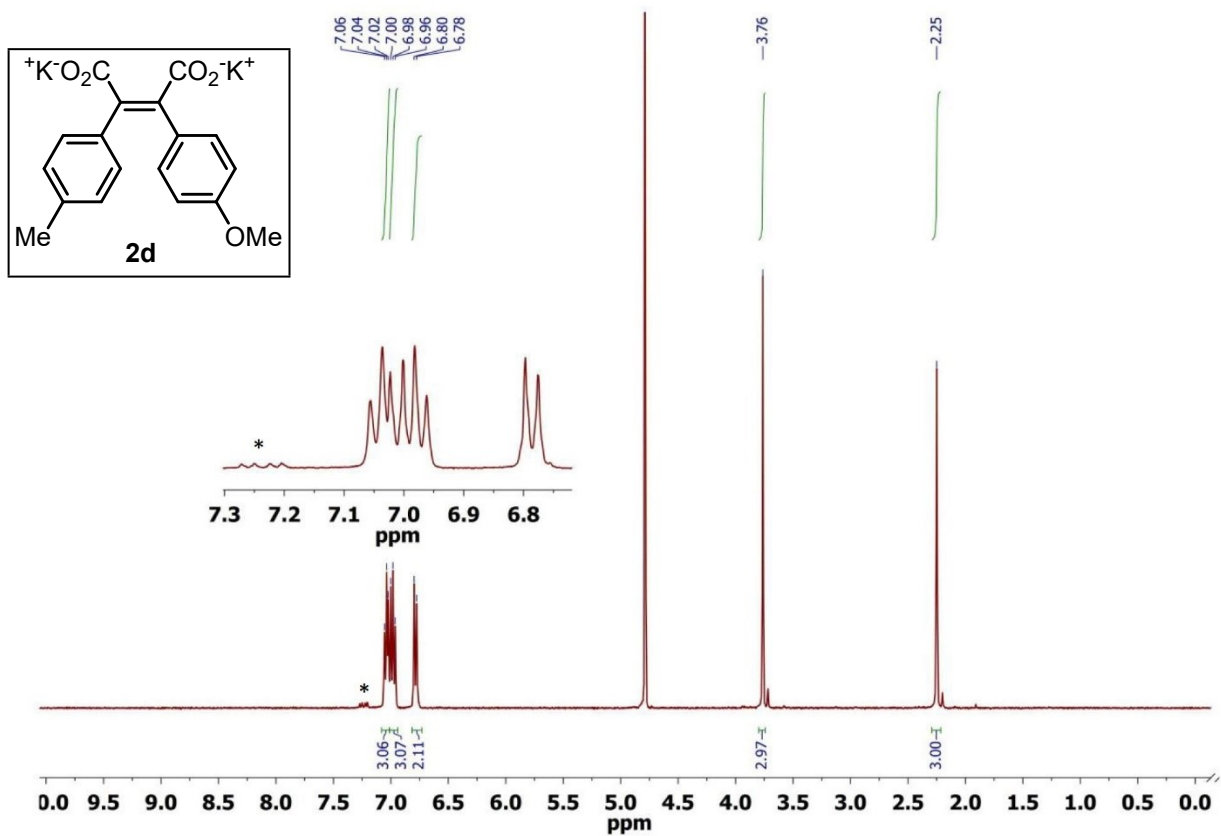
^1H NMR spectrum of **2c** in D_2O



^{13}C NMR spectrum of **2c** in D_2O

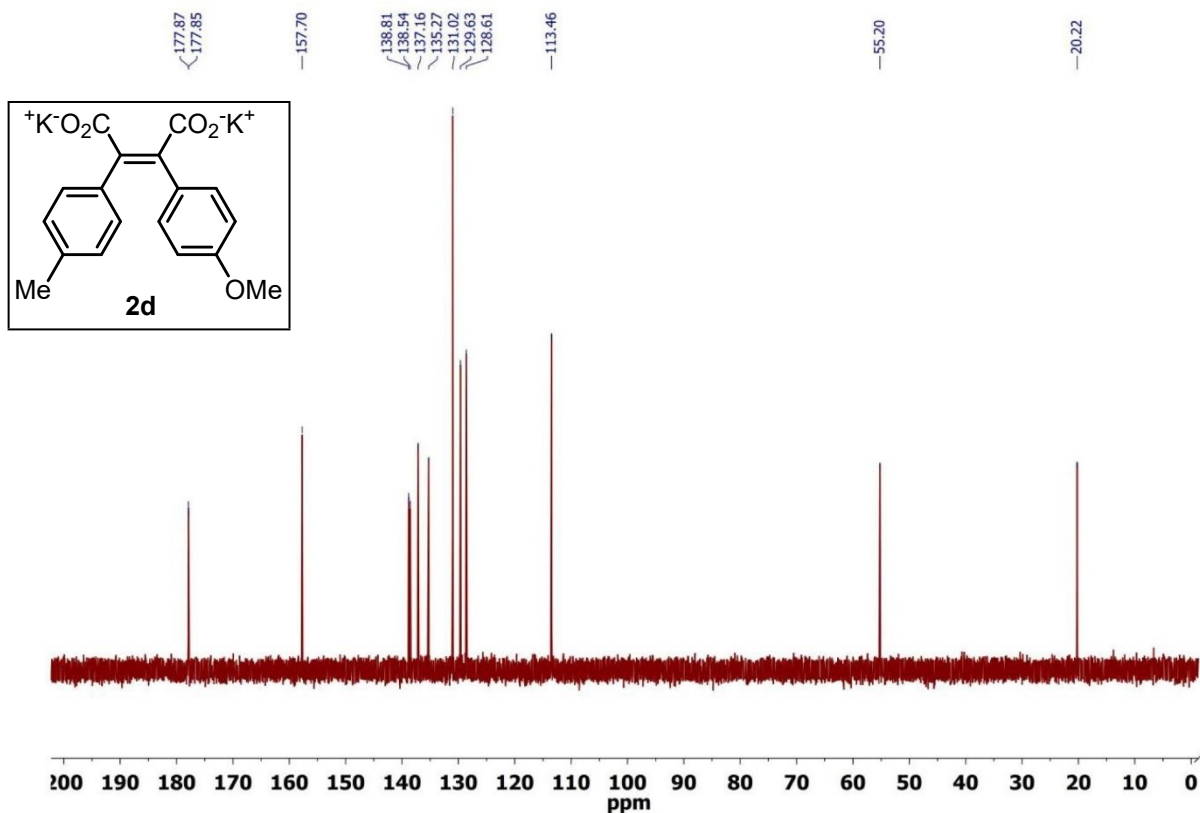


^1H NMR spectrum of **2d** in D_2O

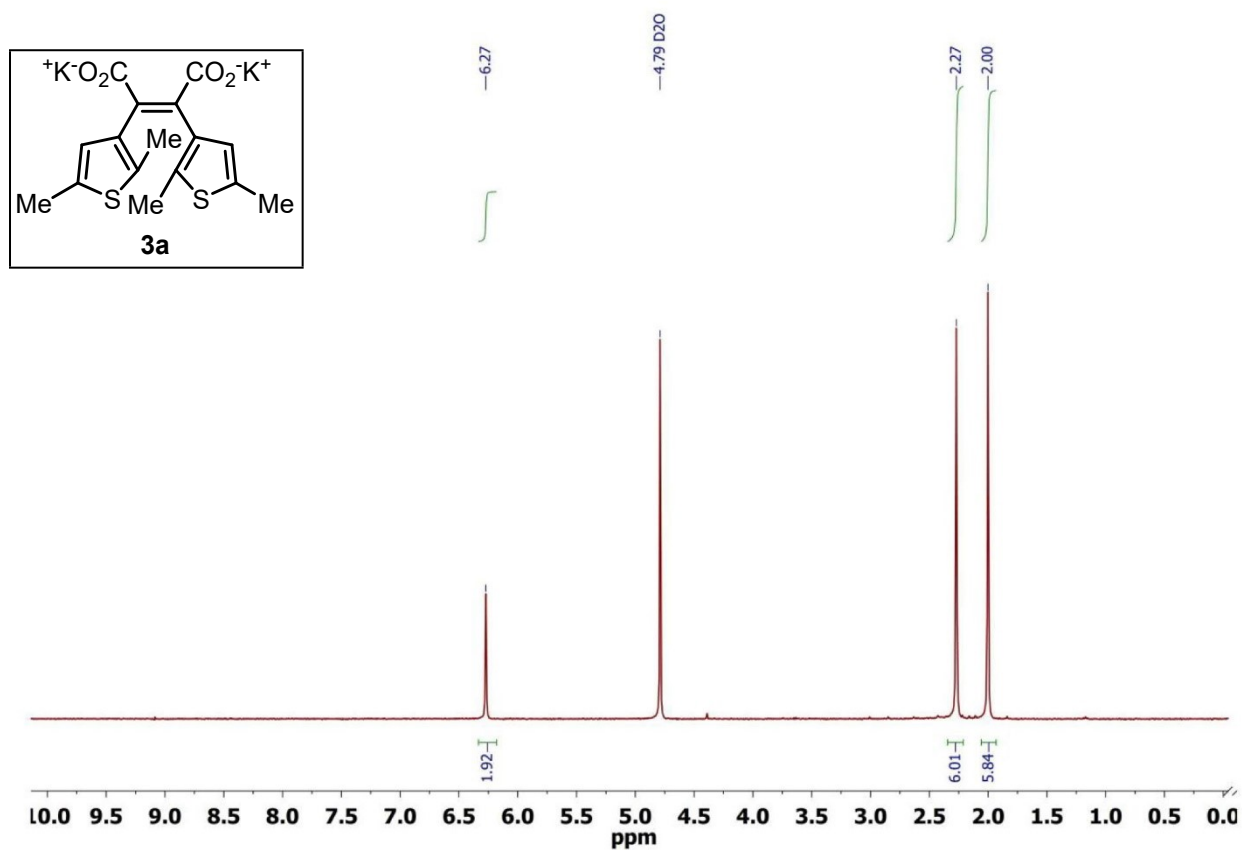


* The sample contains impurities of *E*-isomer of **2d**.

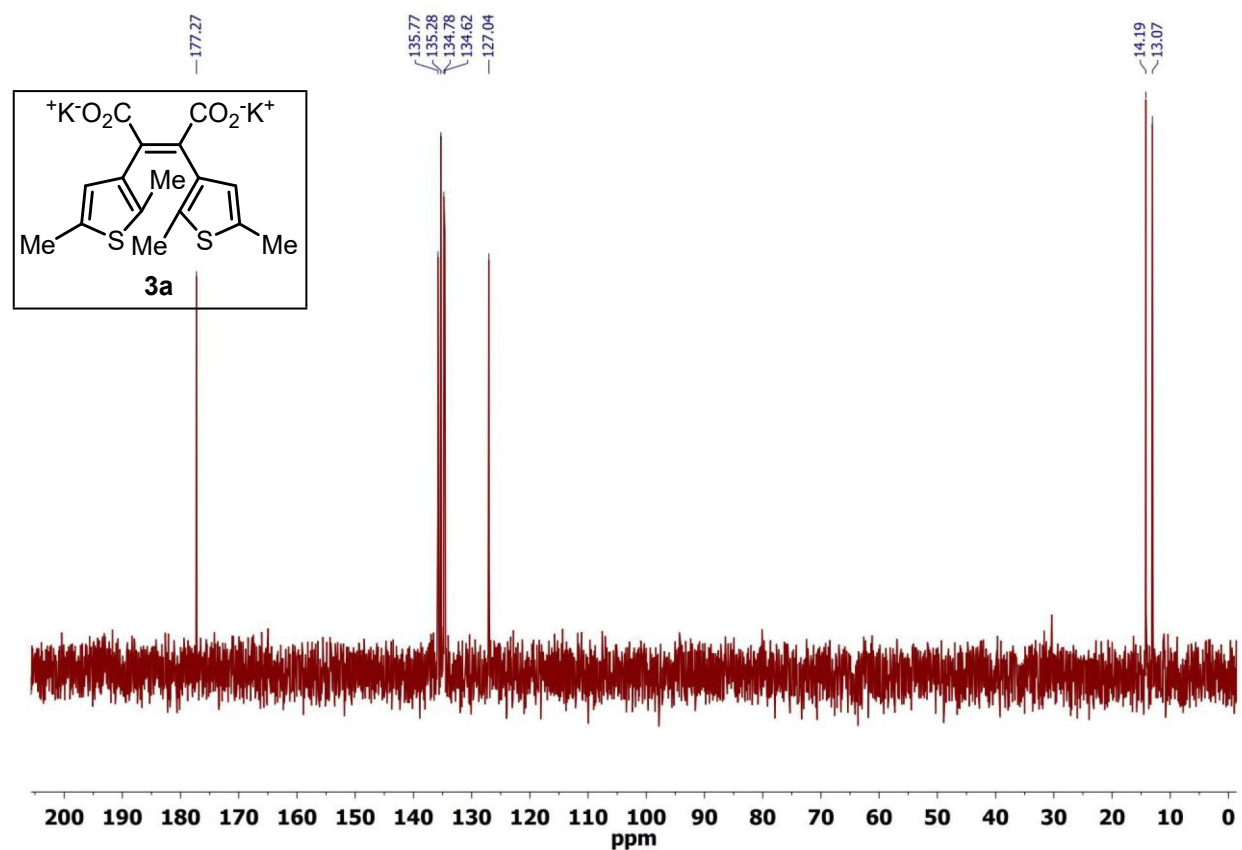
^{13}C NMR spectrum of **2d** in D_2O



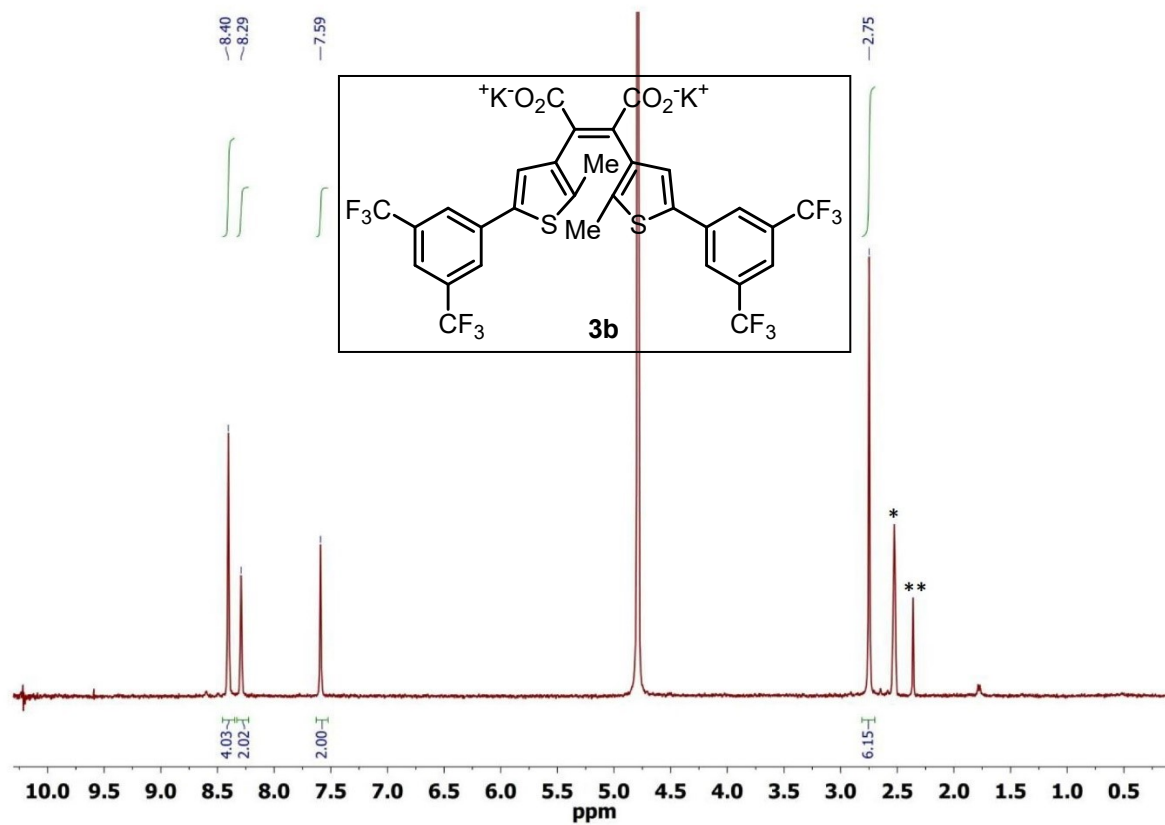
^1H NMR spectrum of **3a** in D_2O



^{13}C NMR spectrum of **3a** in D_2O

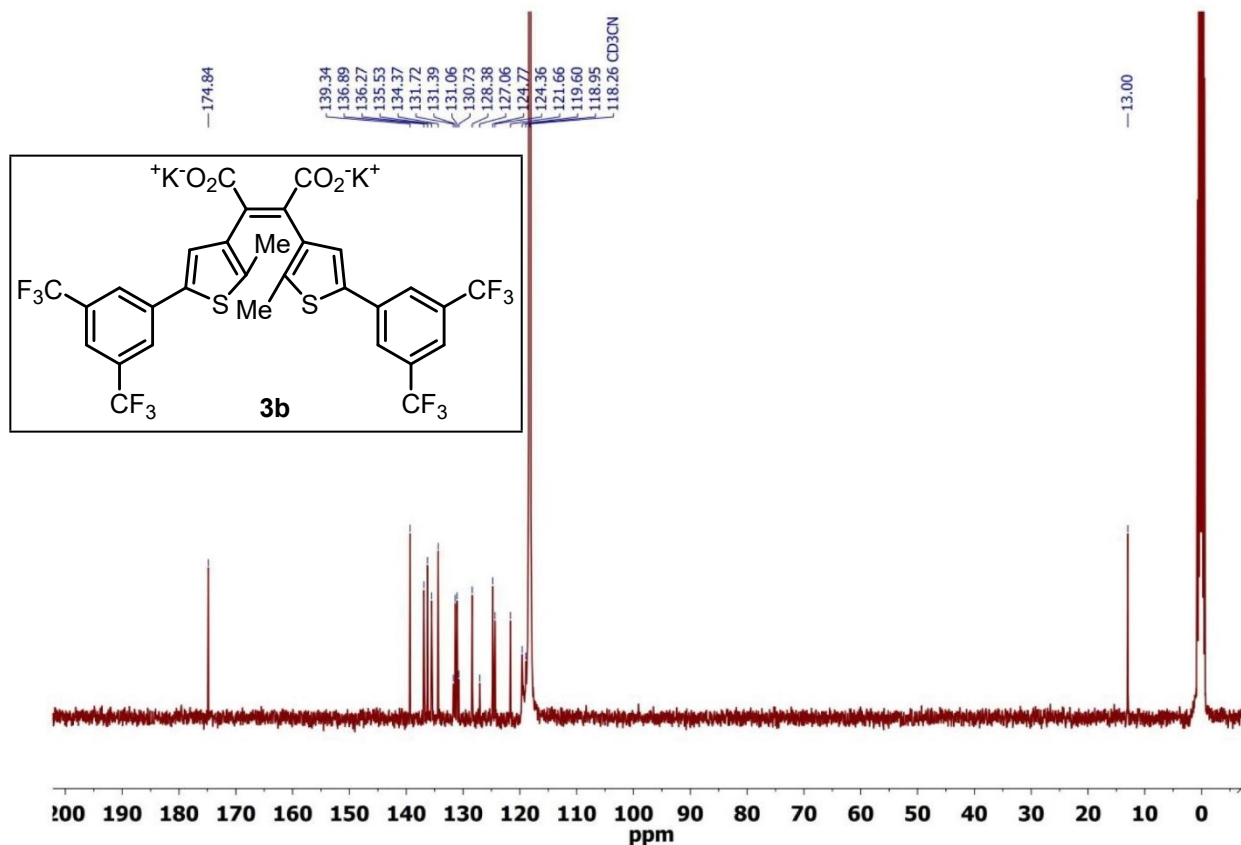


^1H NMR spectrum of **3b** in D_2O and CD_3CN (1:1)

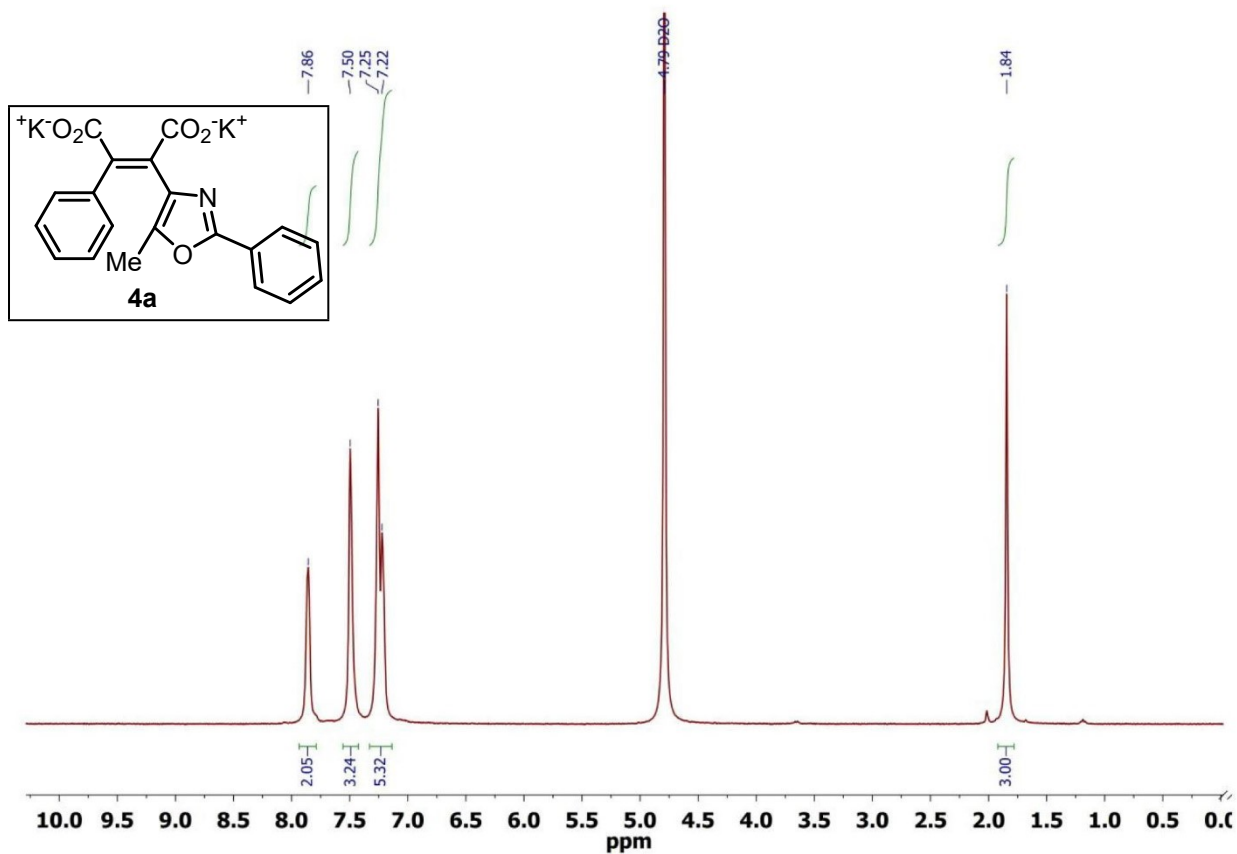


* - MeCN ($\delta = 2.53$); ** - acetone ($\delta = 2.36$)

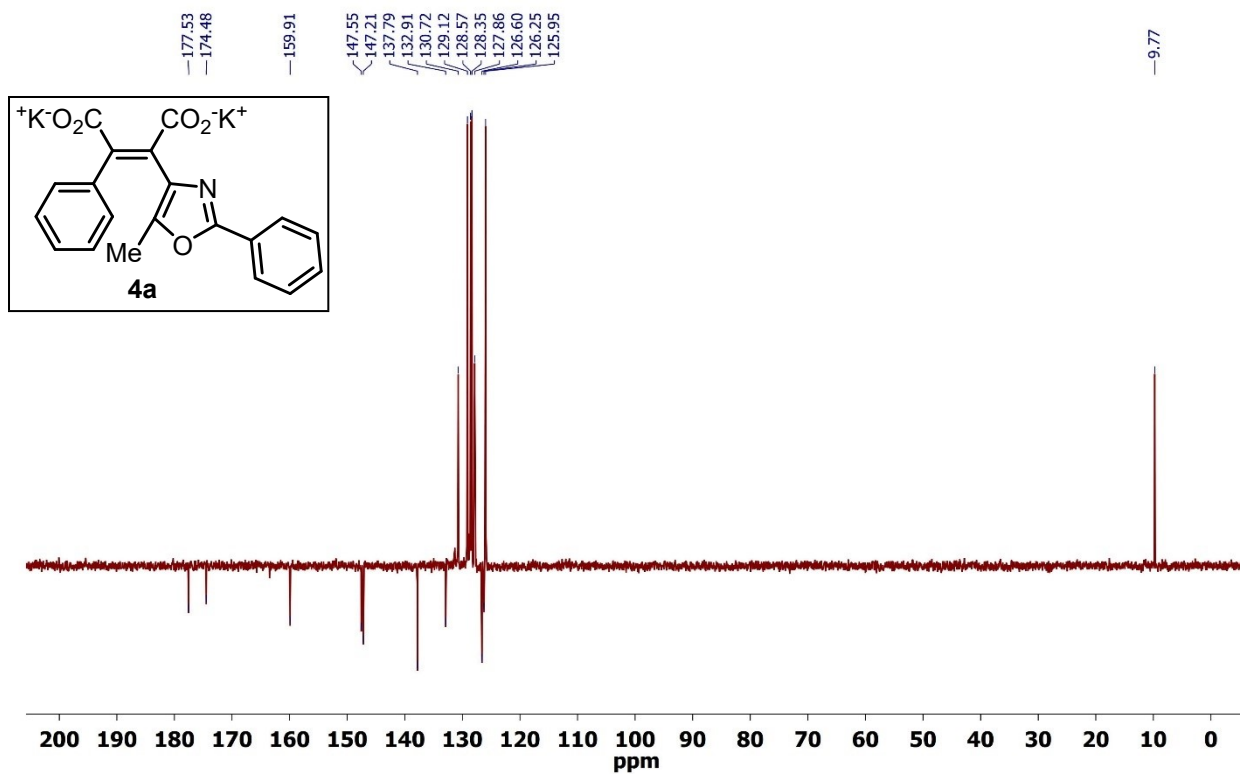
^{13}C NMR spectrum of **3b** in D_2O and CD_3CN (1:1)



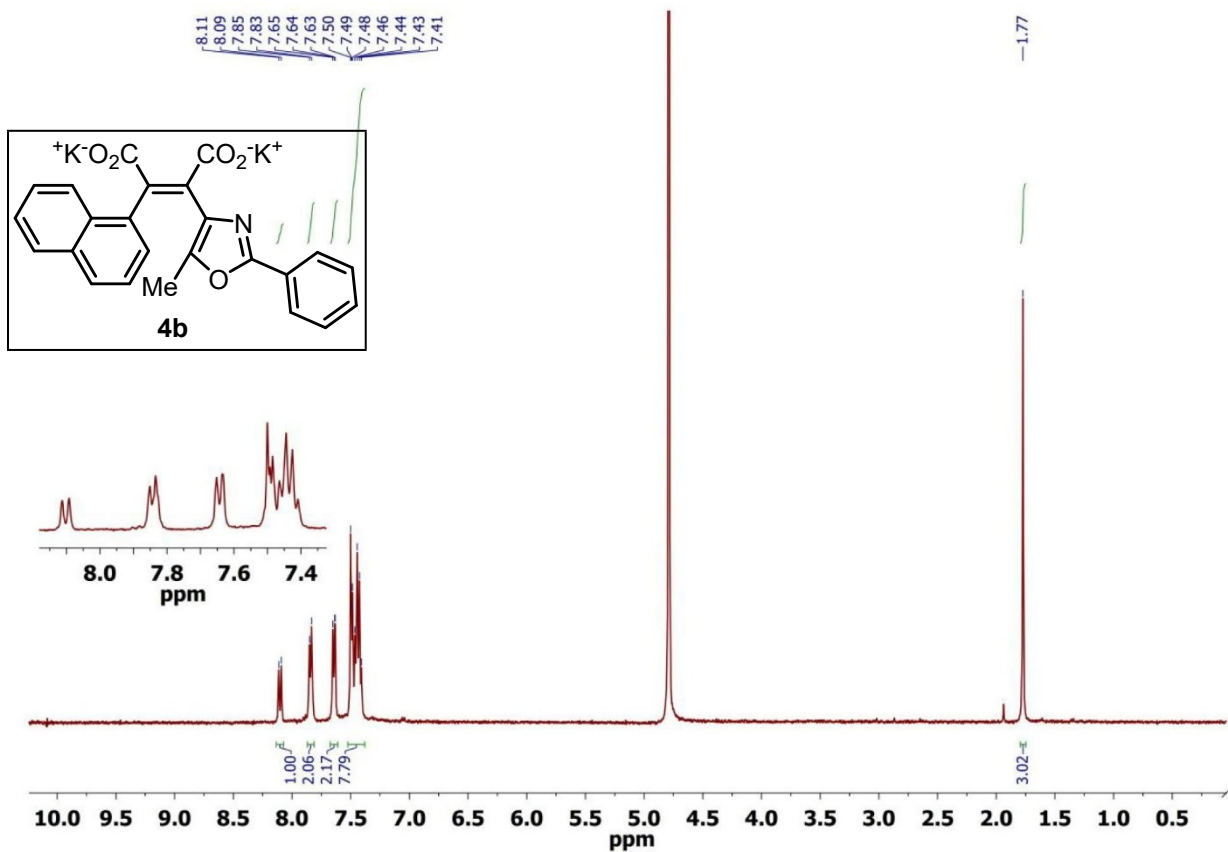
^1H NMR spectrum of **4a** in D_2O



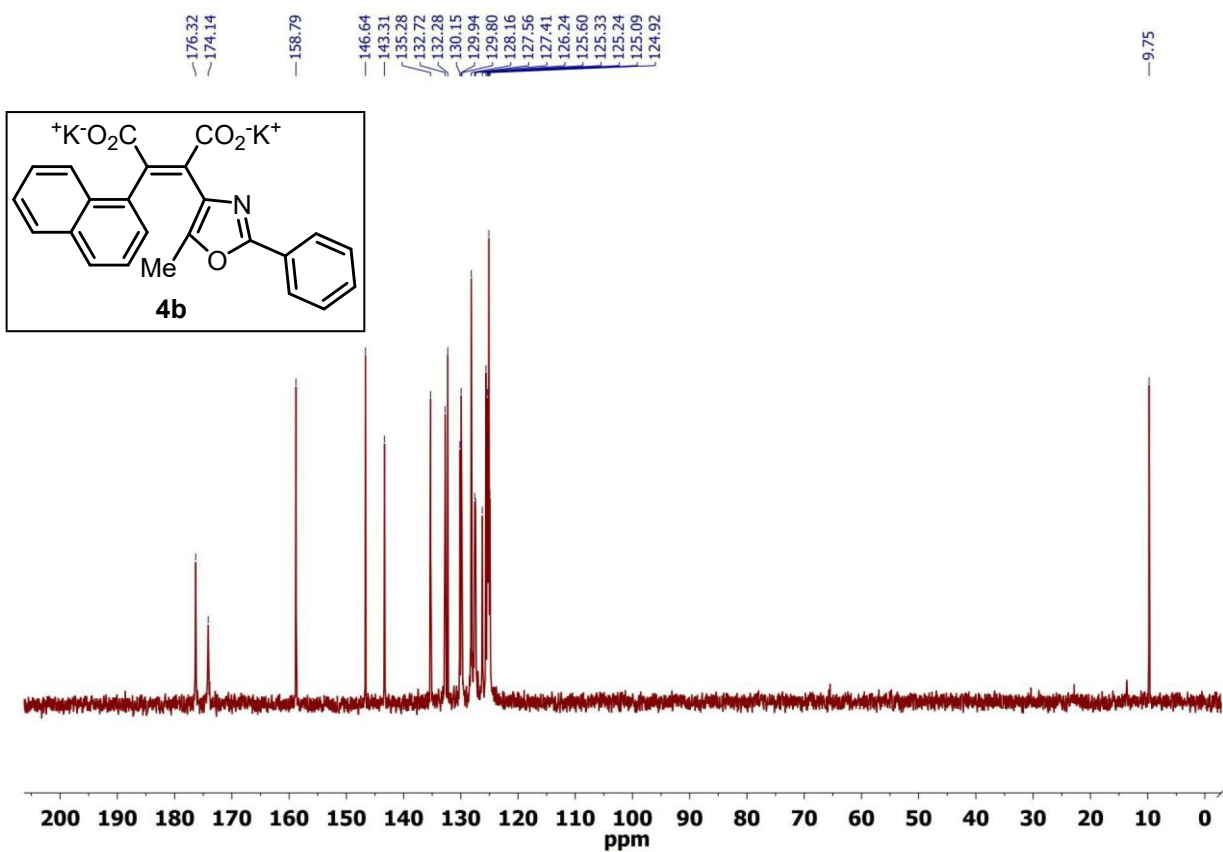
^{13}C NMR spectrum of **4a** in D_2O



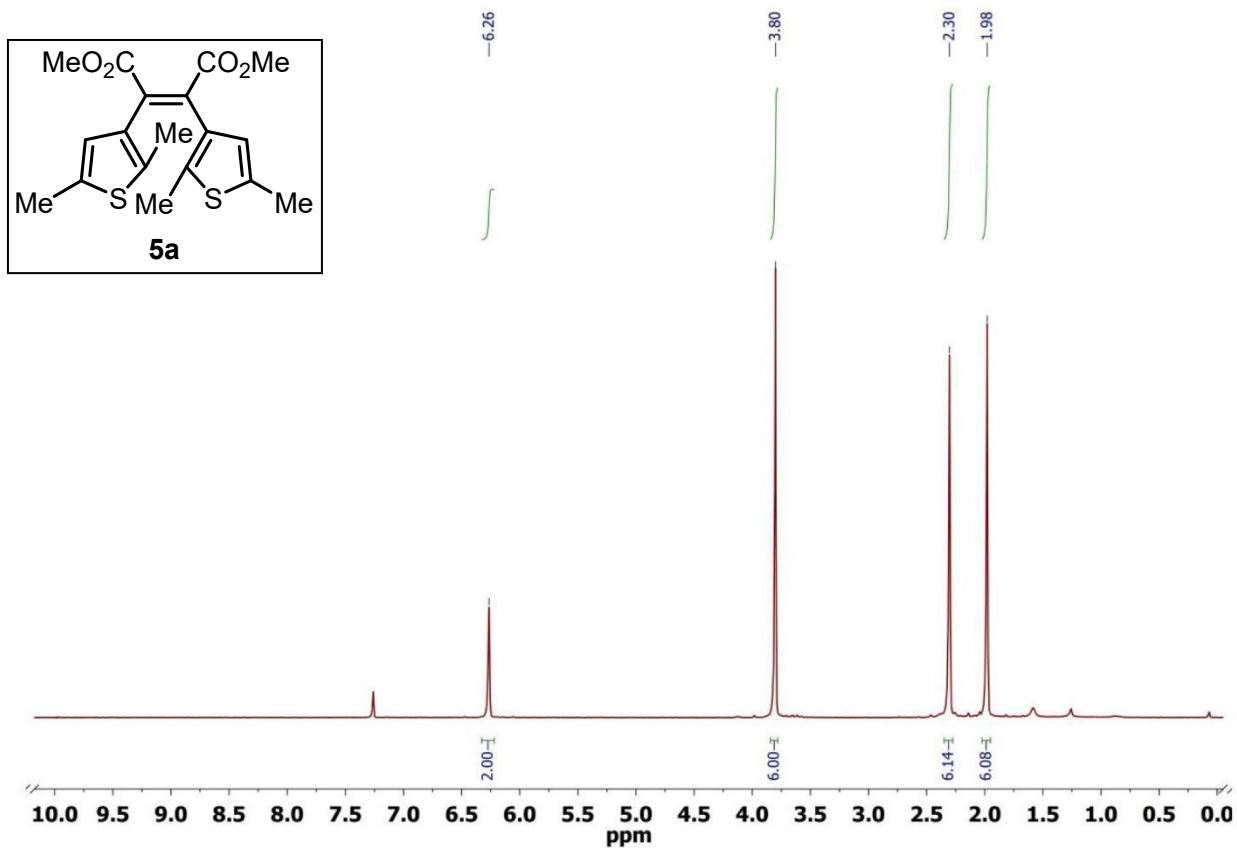
^1H NMR spectrum of **4b** in D_2O



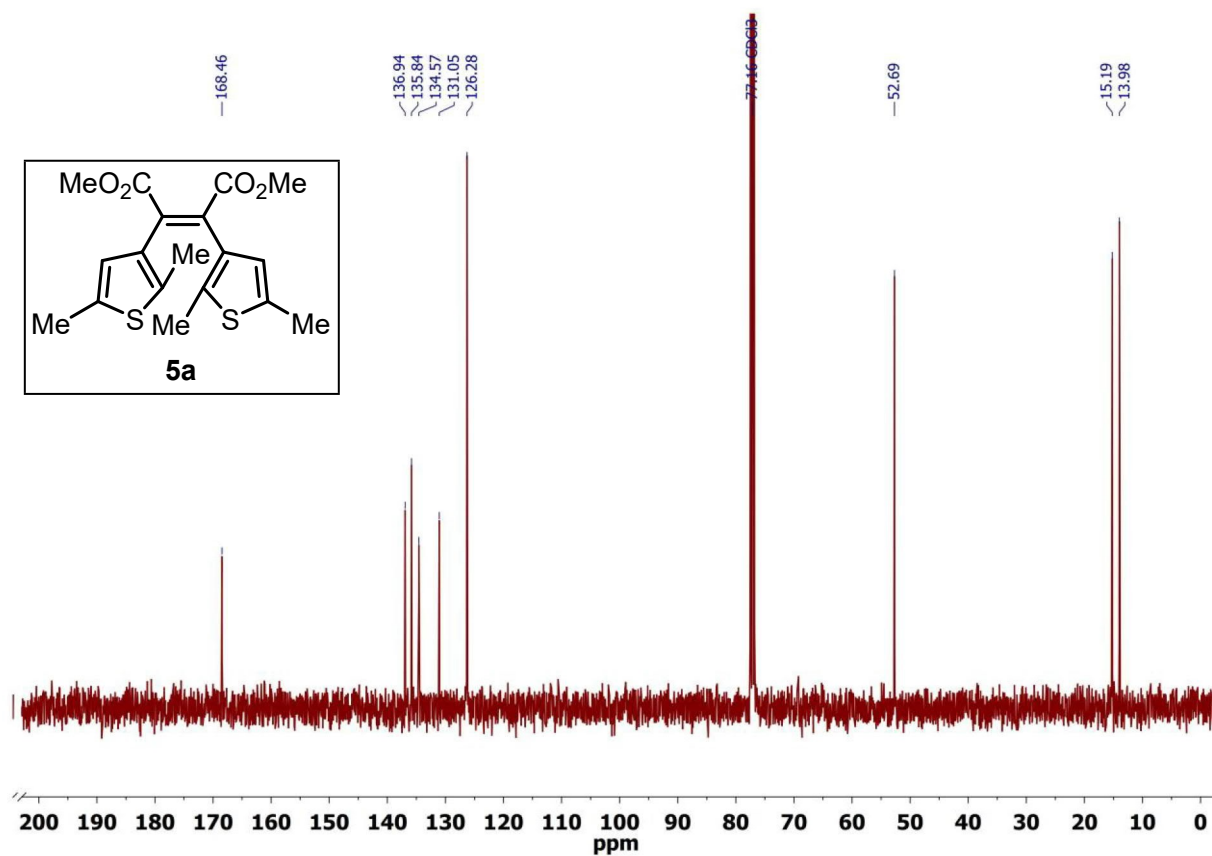
^{13}C NMR spectrum of **4b** in D_2O



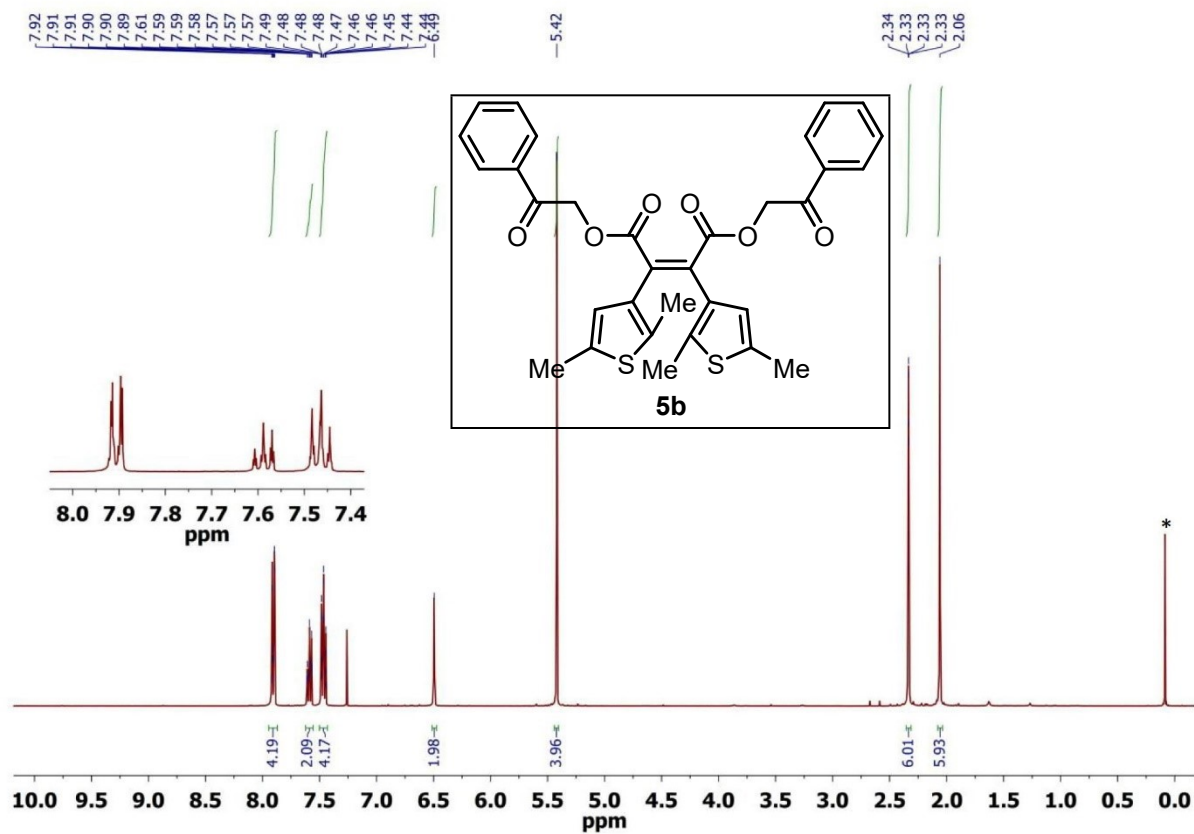
^1H NMR spectrum of **Z-5a** in CDCl_3



^{13}C NMR spectrum of **Z-5a** in CDCl_3

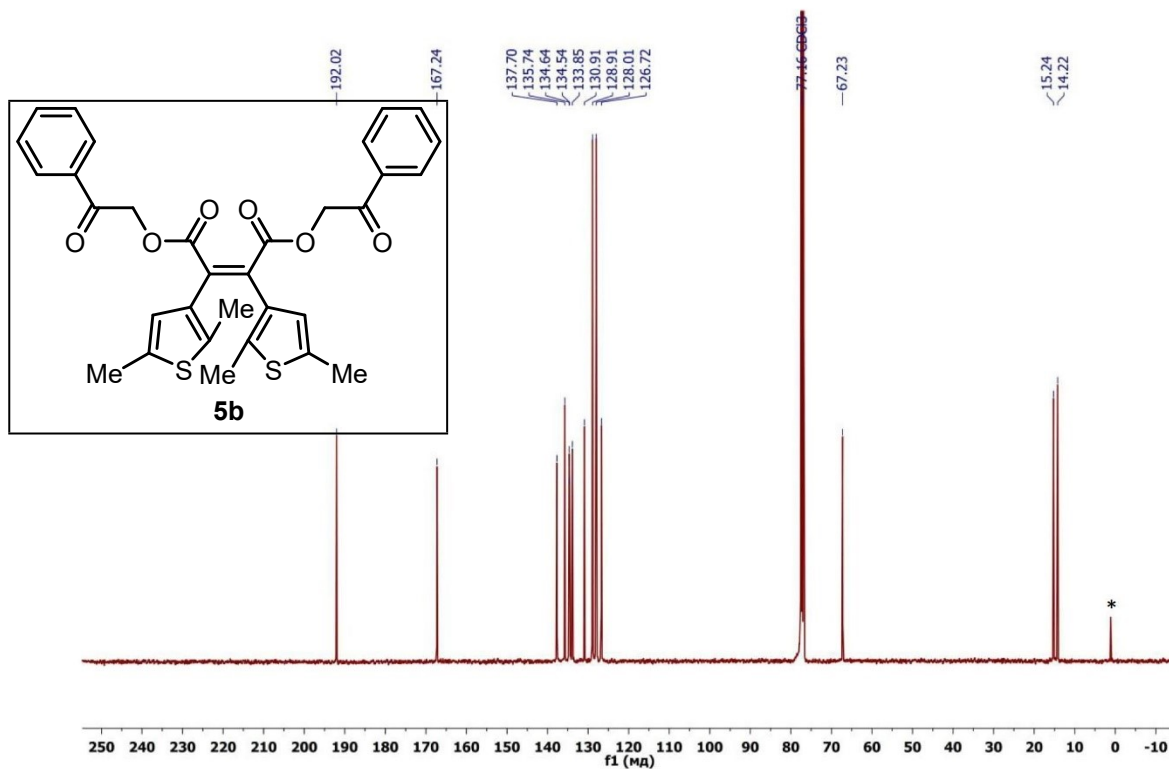


¹H NMR spectrum of **5b** in CDCl₃



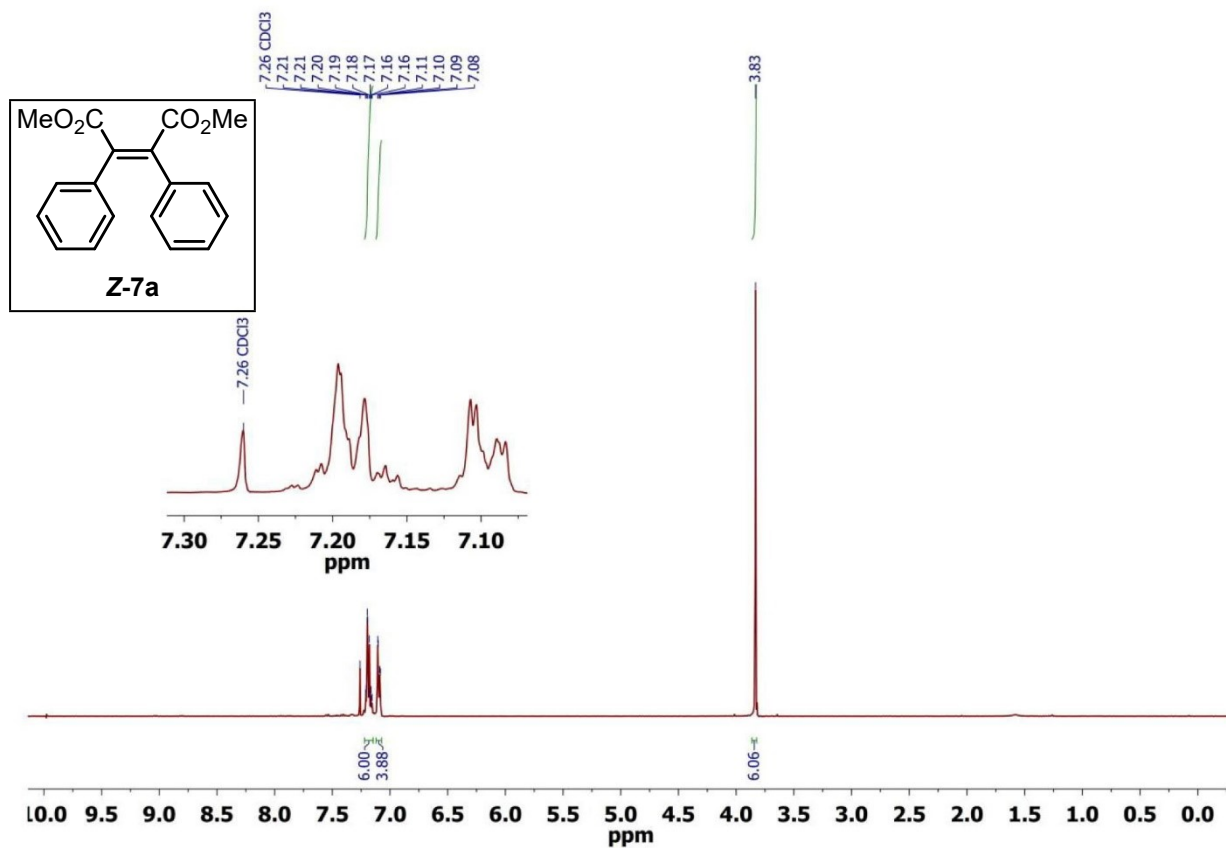
* - grease ($\delta = 0.09$)

¹³C NMR spectrum of **5b** in CDCl₃

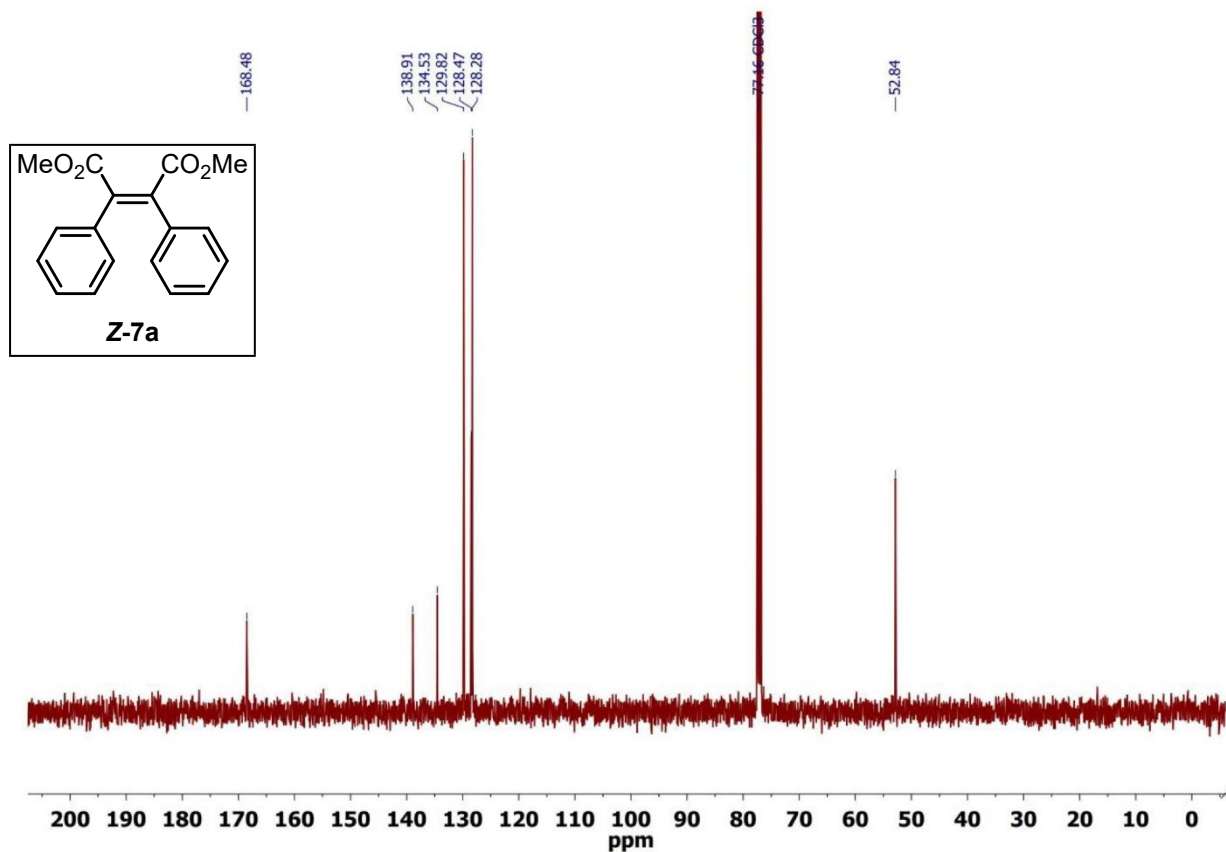


* - silicone grease ($\delta = 1.13$)

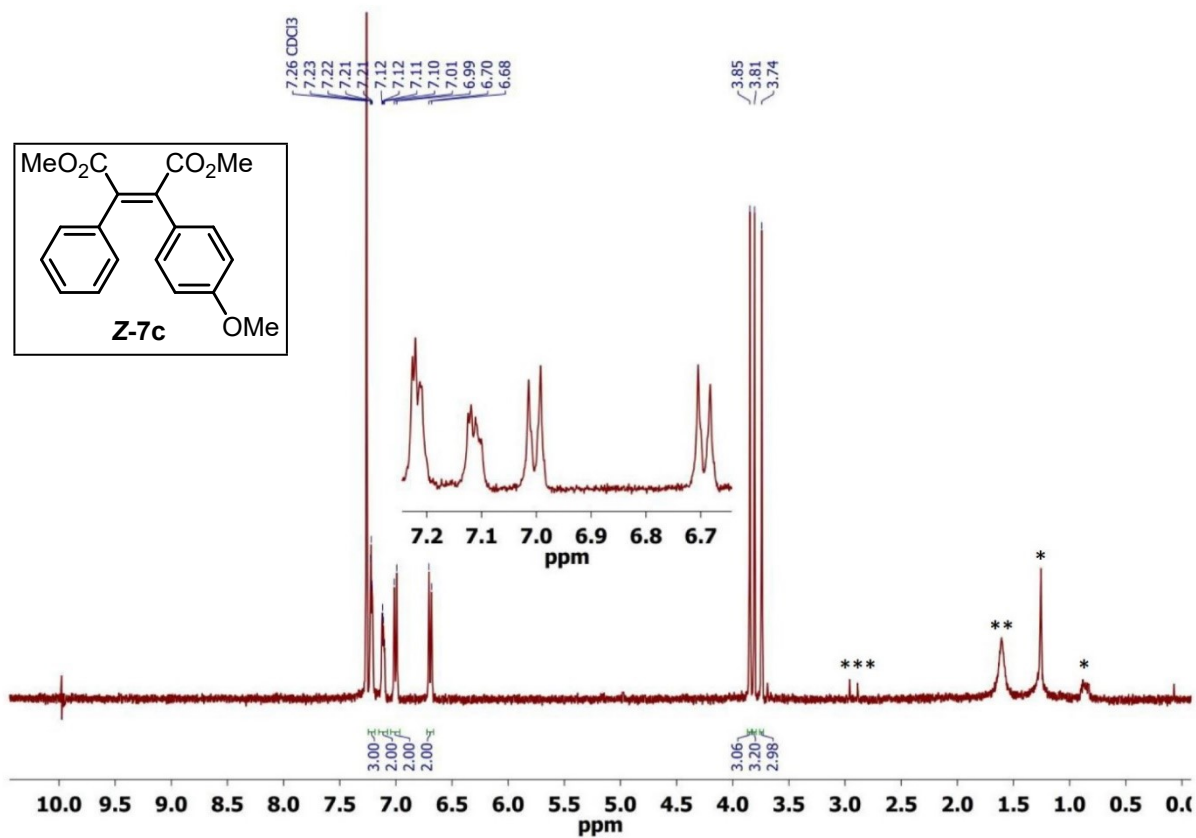
^1H NMR spectrum of **Z-7a** in CDCl_3



^{13}C NMR spectrum of **Z-7a** in CDCl_3

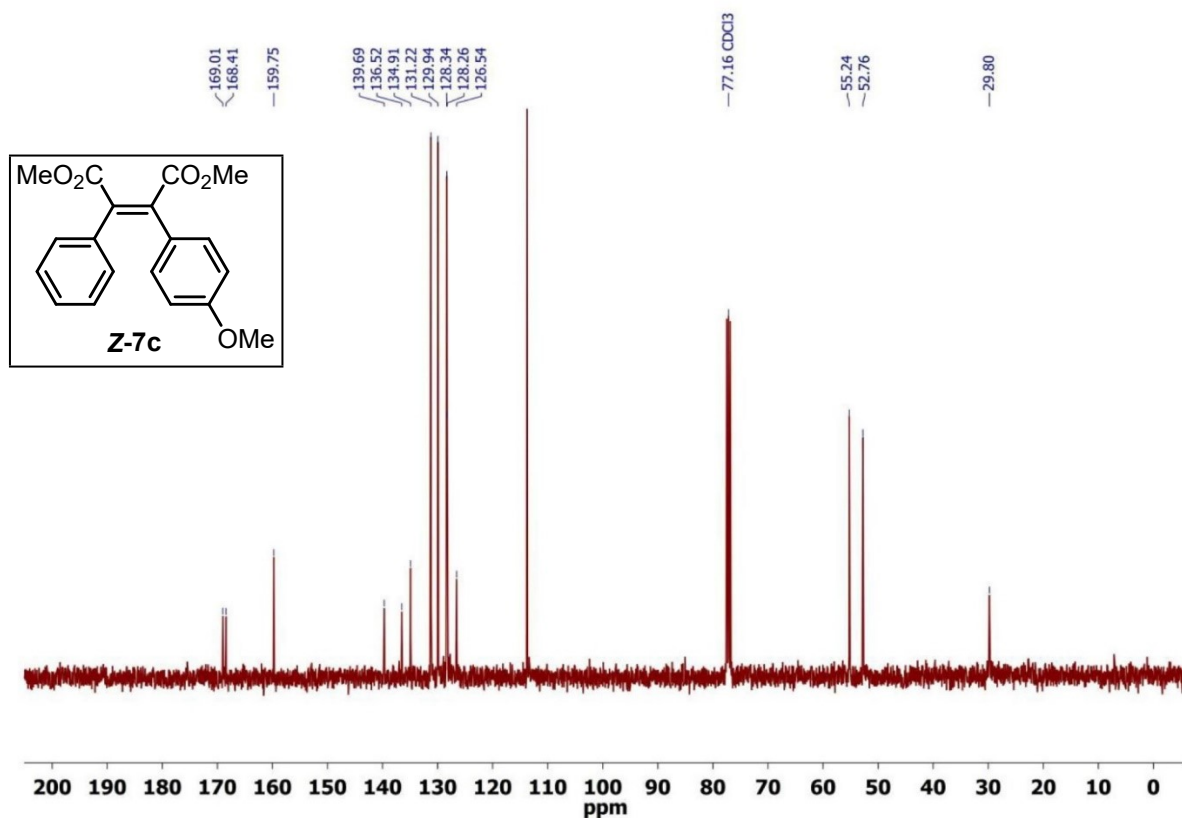


^1H NMR spectrum of **Z-7c** in CDCl_3

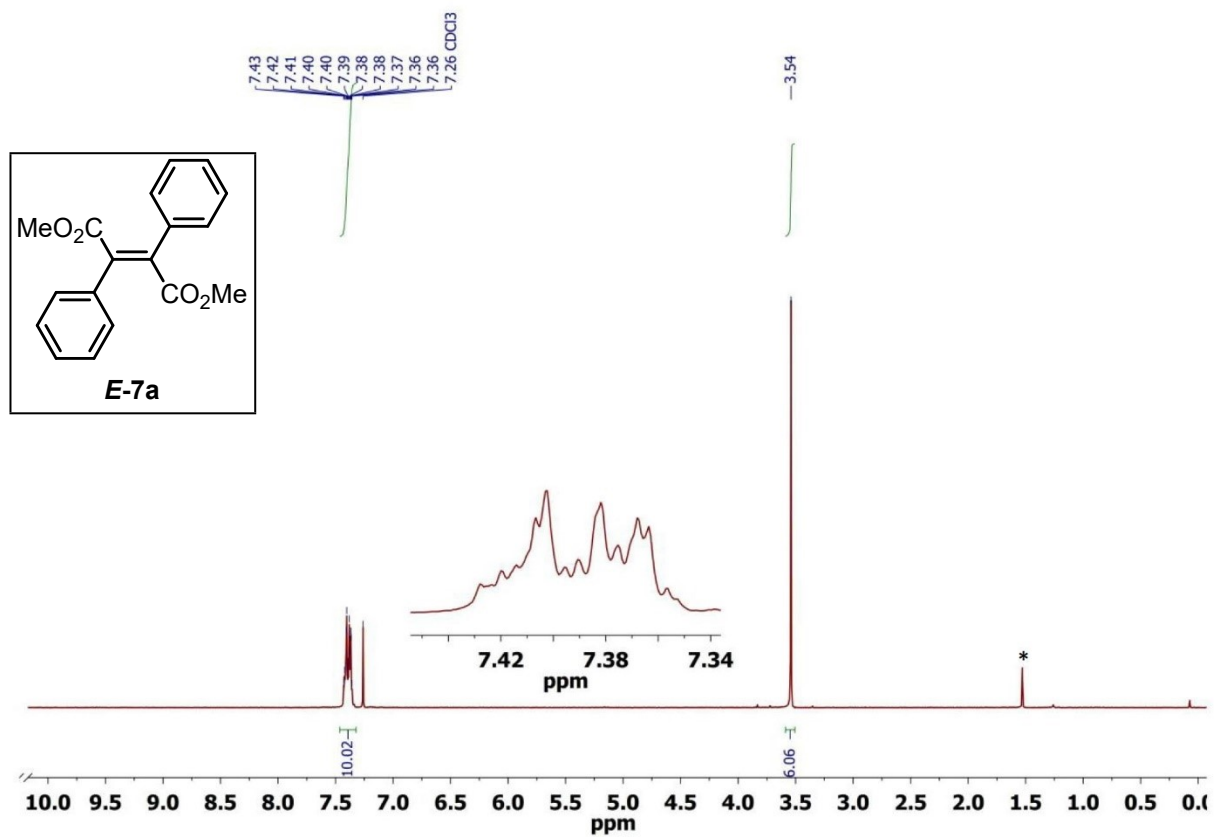


* - grease ($\delta = 0.88, 1.26$); ** - water ($\delta = 1.61$); *** - DMF ($\delta = 2.86, 2.96$)

^{13}C NMR spectrum of **Z-7c** in CDCl_3

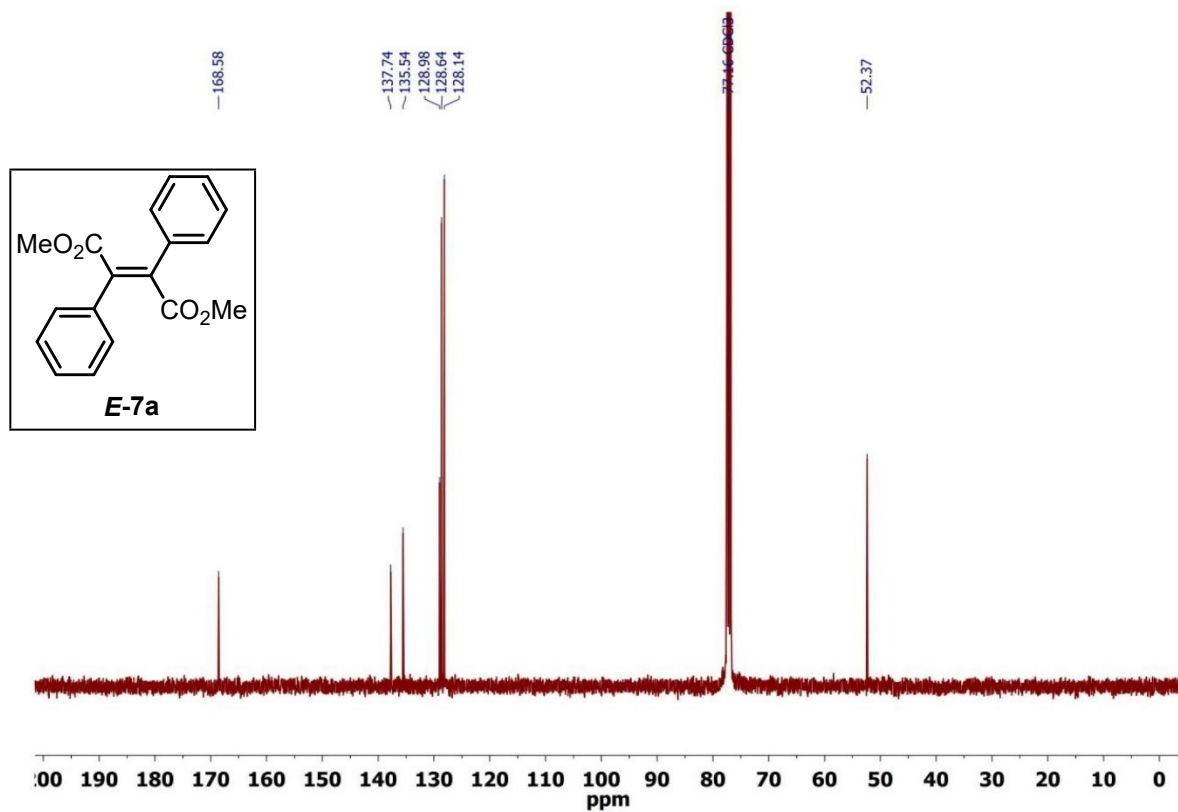


^1H NMR spectrum of *E-7a* in CDCl_3

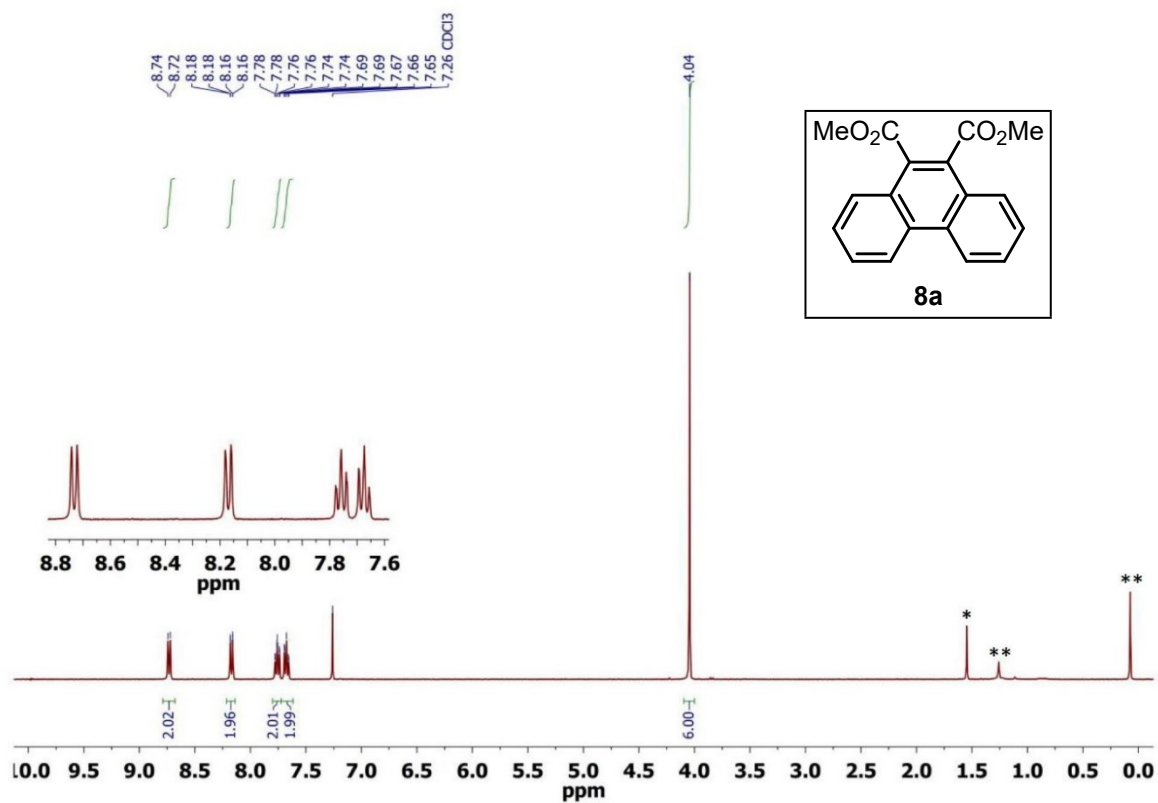


* - water ($\delta = 1.53$)

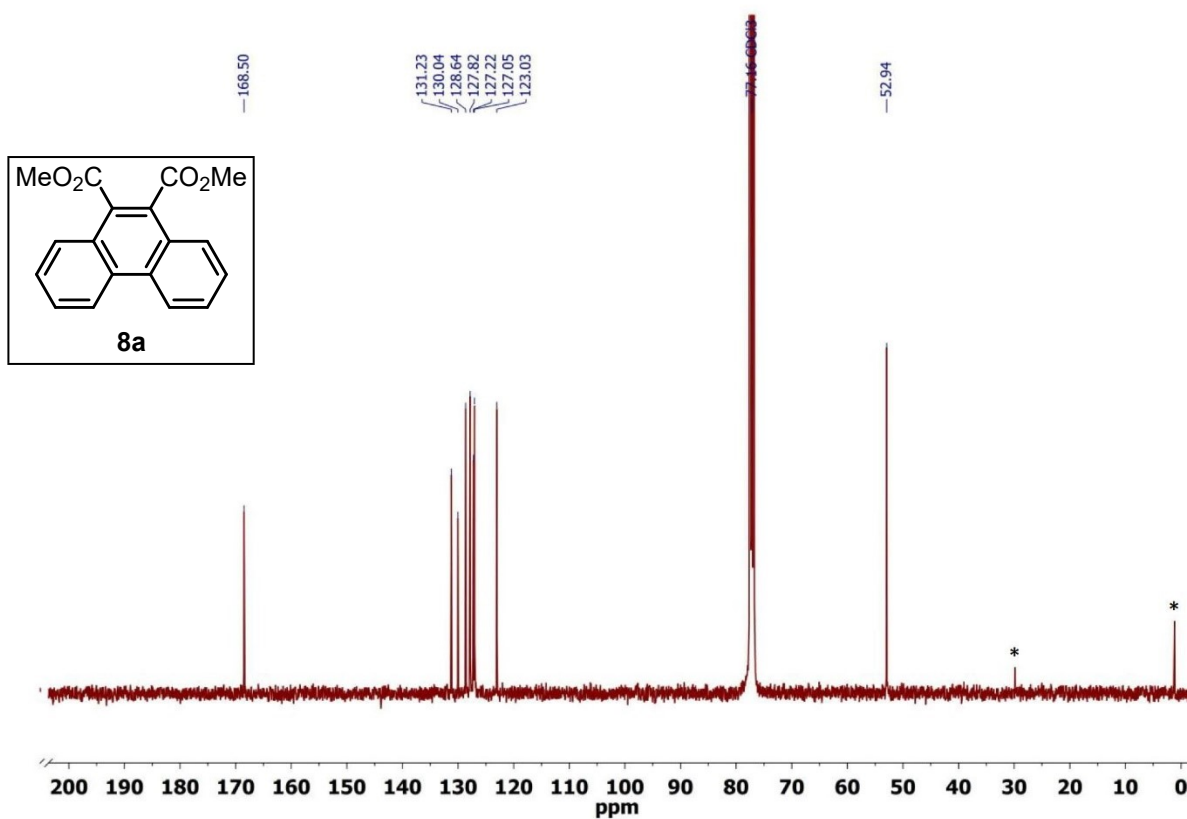
^{13}C NMR spectrum of *E-7a* in CDCl_3



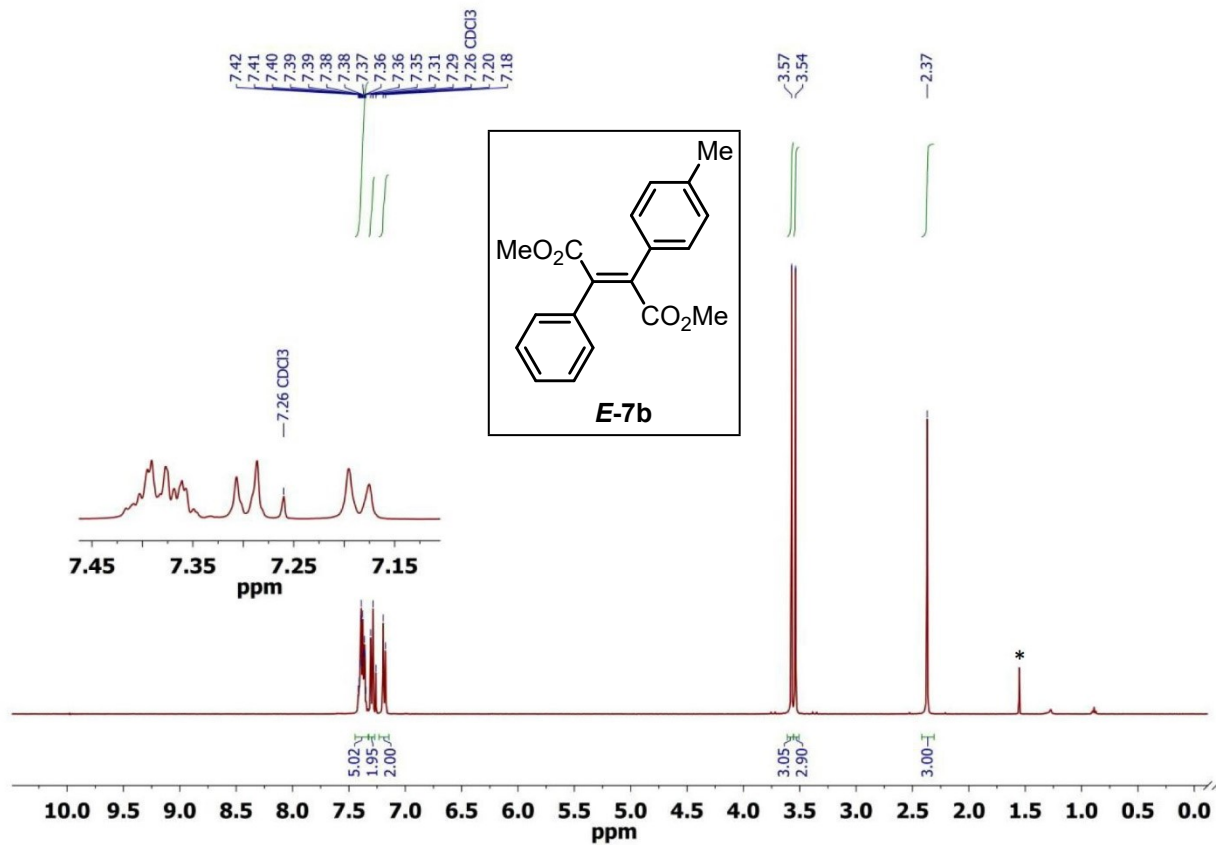
^1H NMR spectrum of **8a** in CDCl_3



^{13}C NMR spectrum of **8a** in CDCl_3

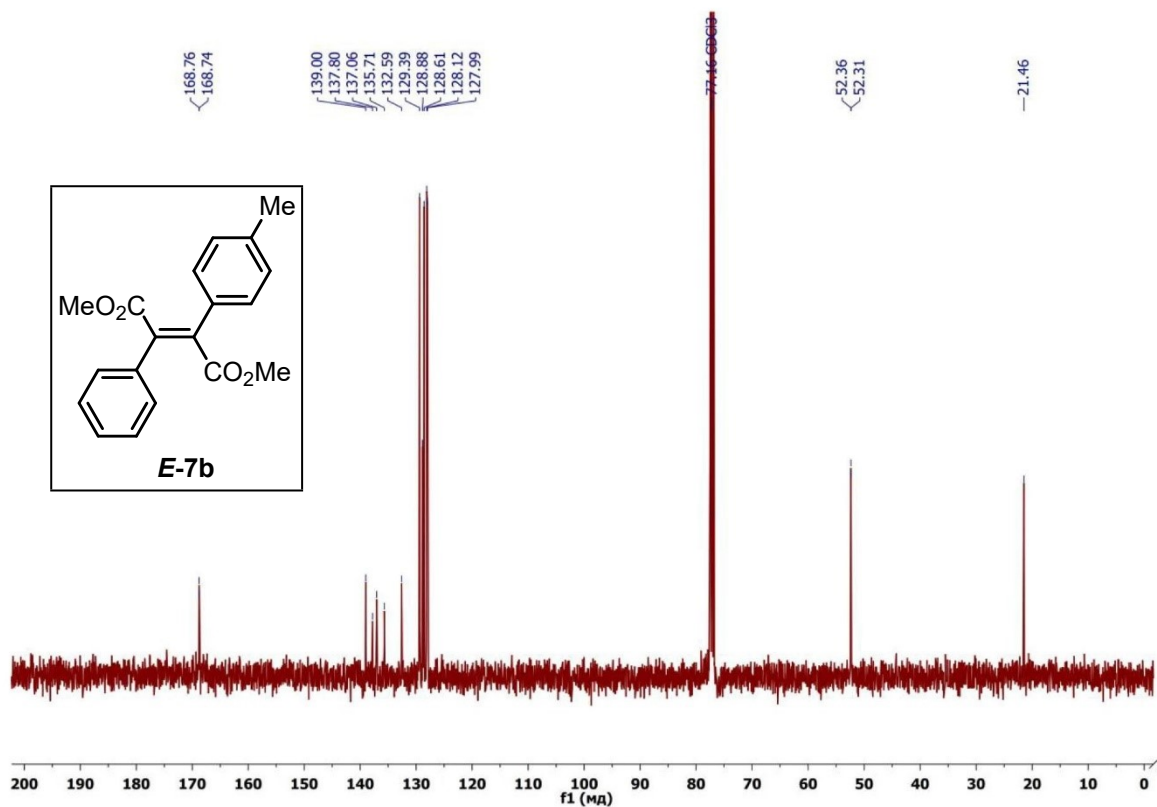


^1H NMR spectrum of *E-7b* in CDCl_3

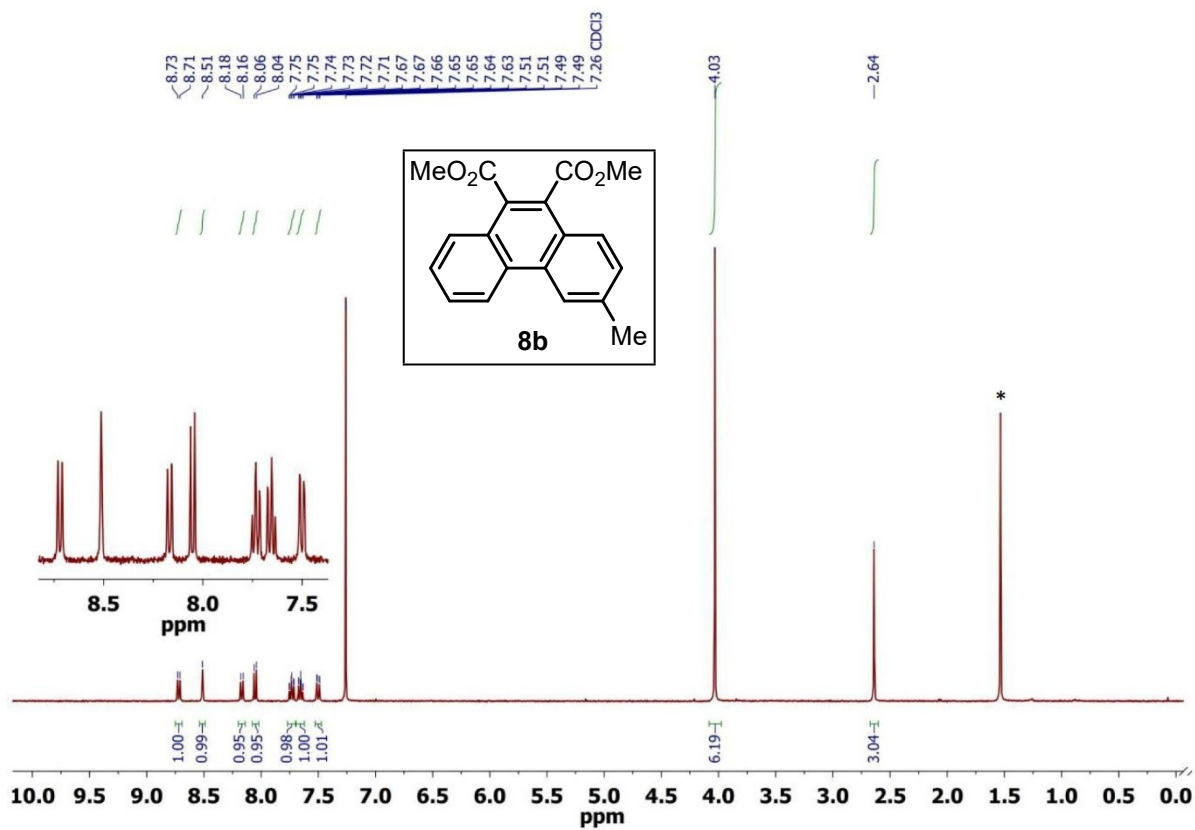


* - water ($\delta = 1.55$)

^{13}C NMR spectrum of *E-7b* in CDCl_3

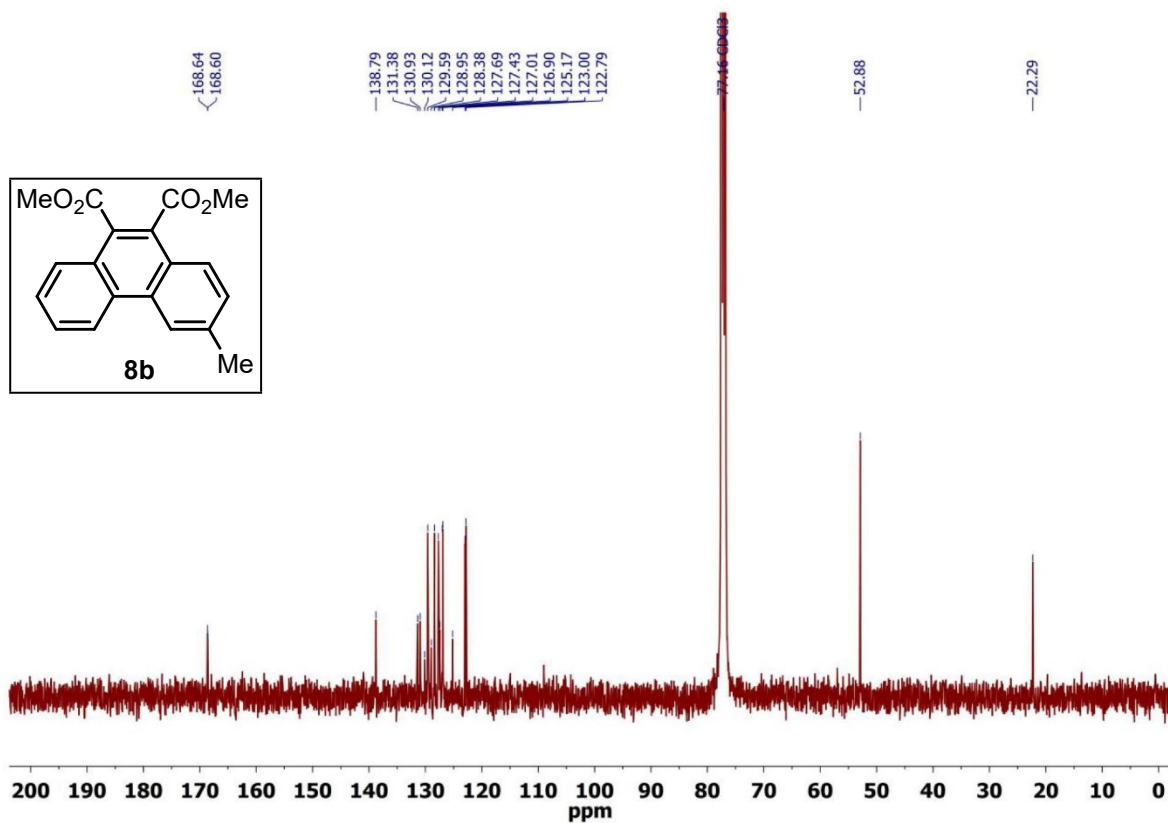


^1H NMR spectrum of **8b** in CDCl_3

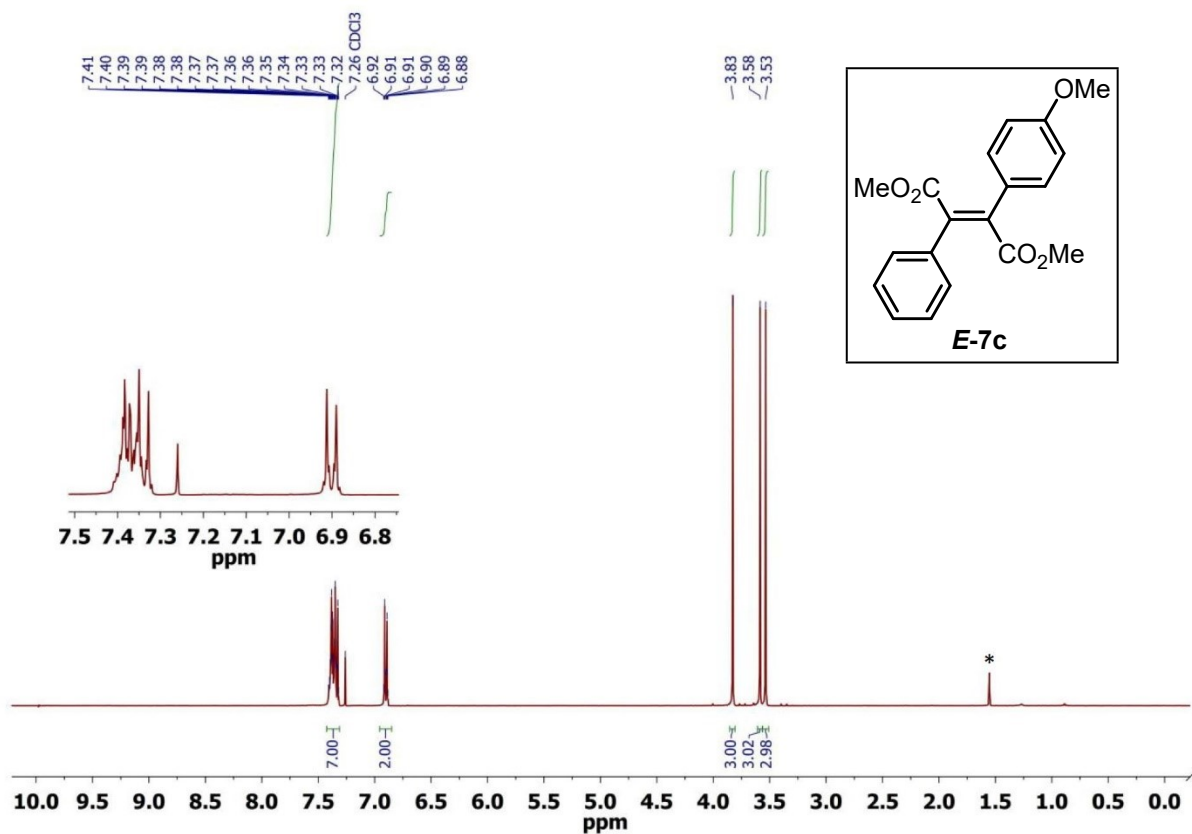


* - water ($\delta = 1.53$)

^{13}C NMR spectrum of **8b** in CDCl_3

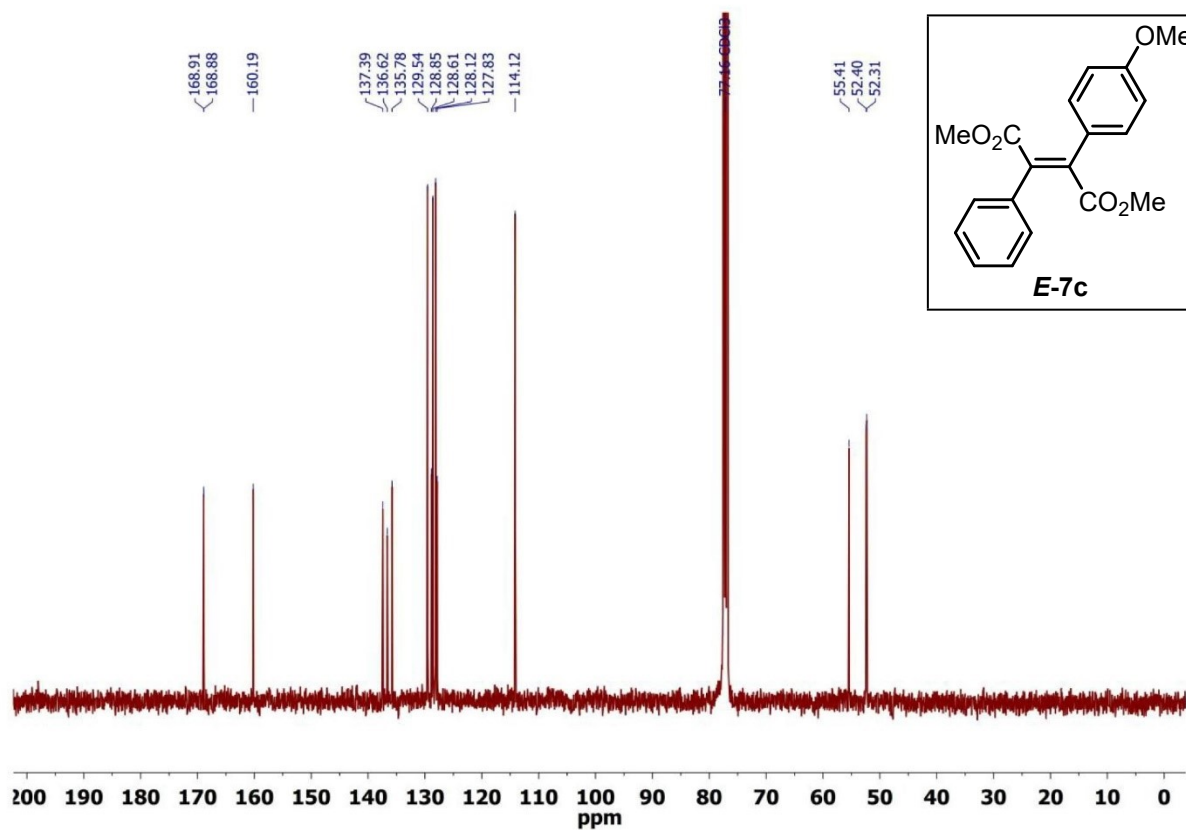


^1H NMR spectrum of *E-7c* in CDCl_3

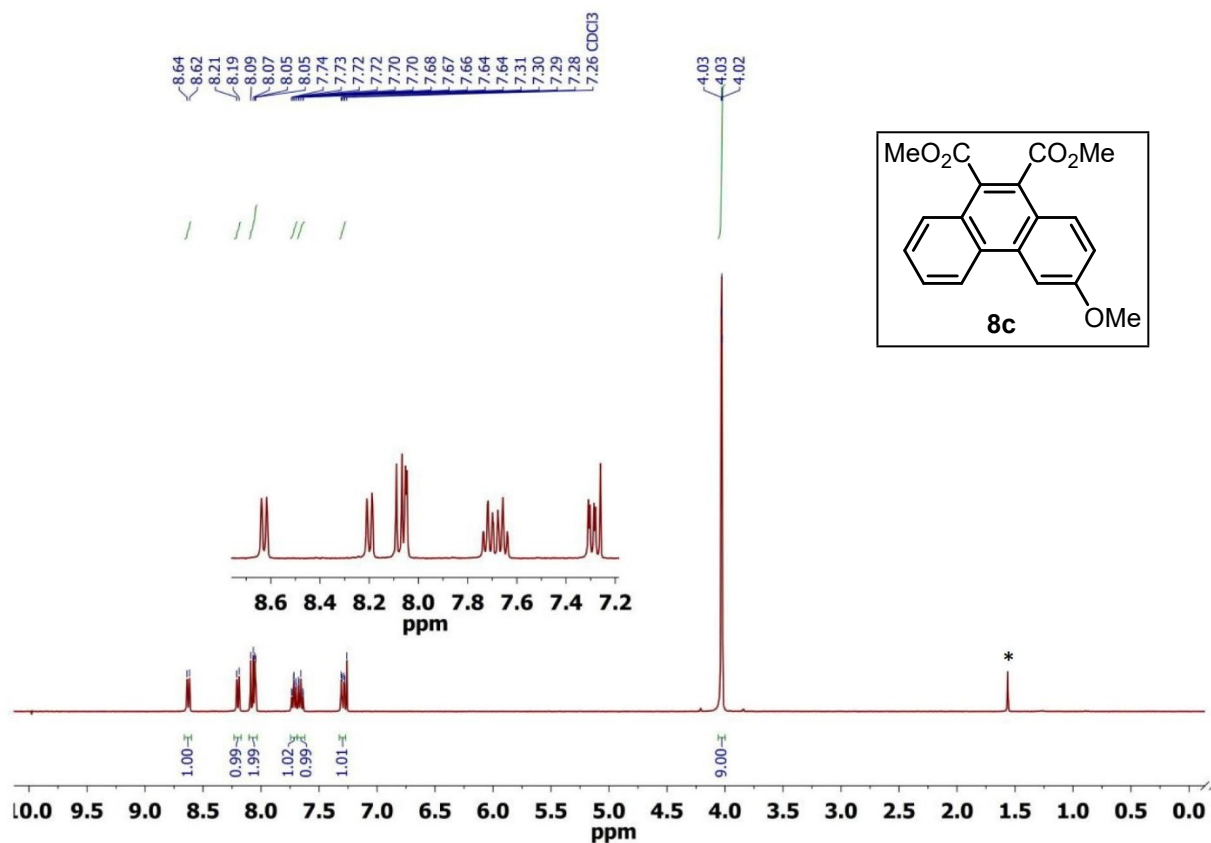


* - water ($\delta = 1.55$)

^{13}C NMR spectrum of *E-7c* in CDCl_3

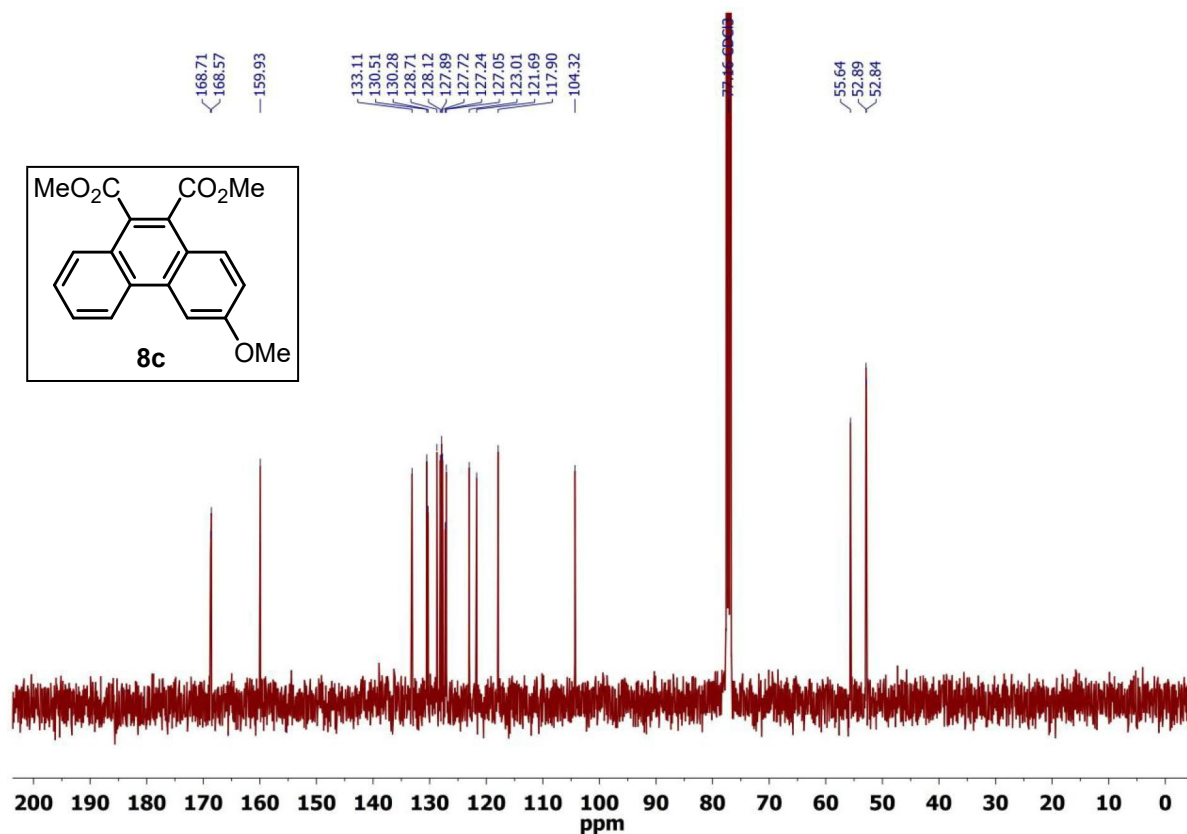


^1H NMR spectrum of **8c** in CDCl_3

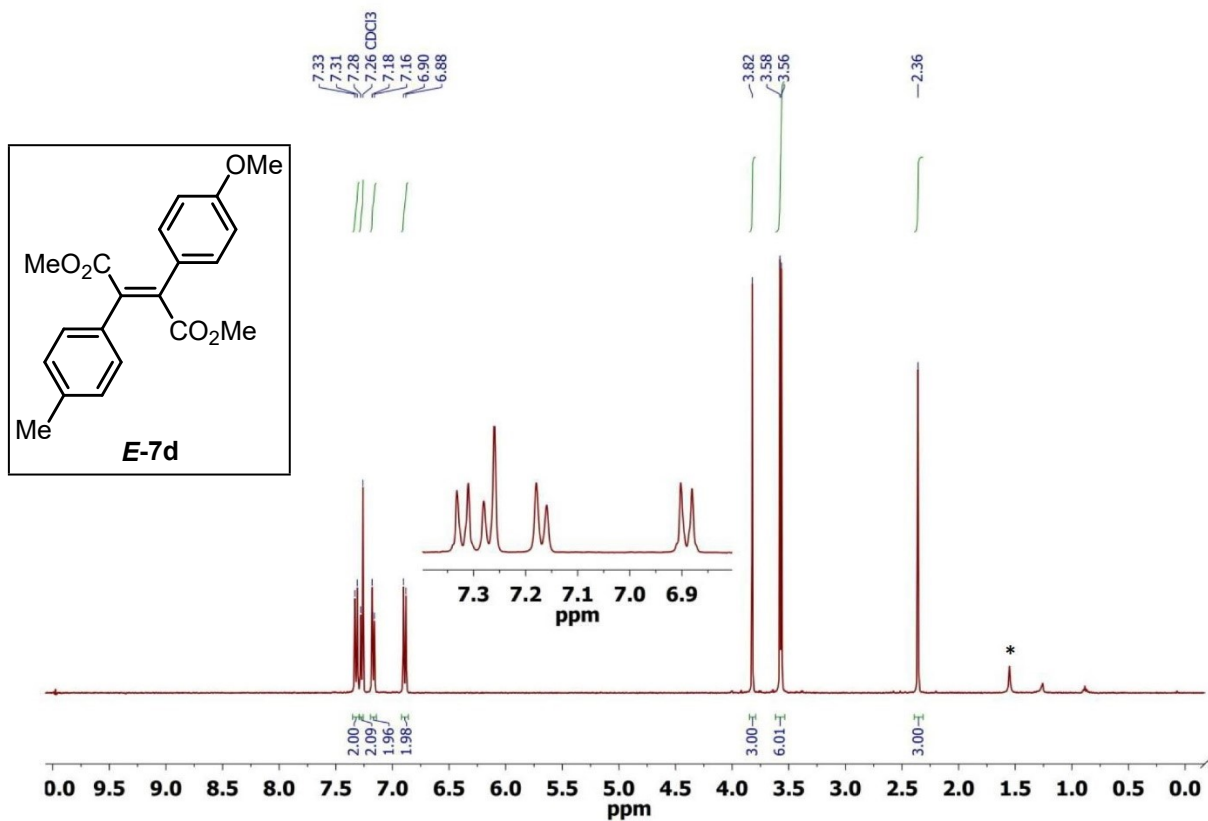


* - water ($\delta = 1.56$)

^{13}C NMR spectrum of **8c** in CDCl_3

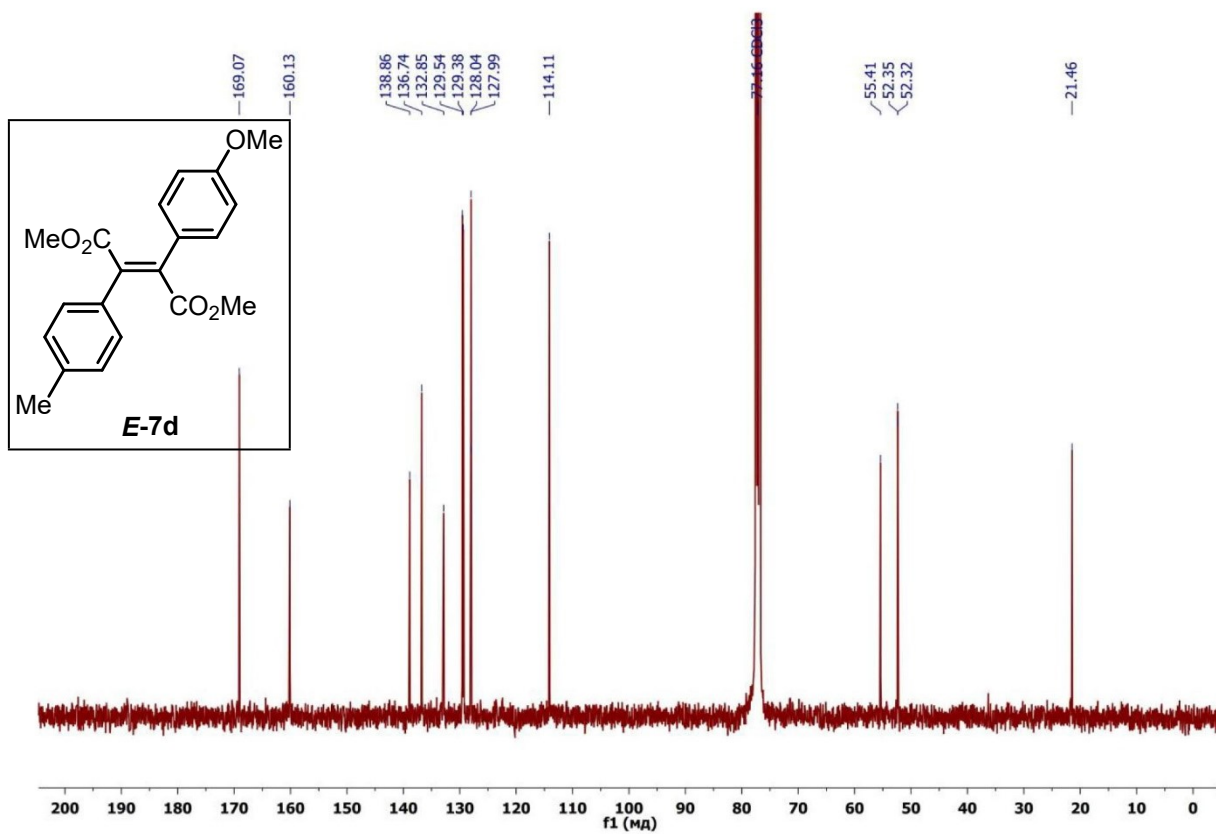


^1H NMR spectrum of *E-7d* in CDCl_3

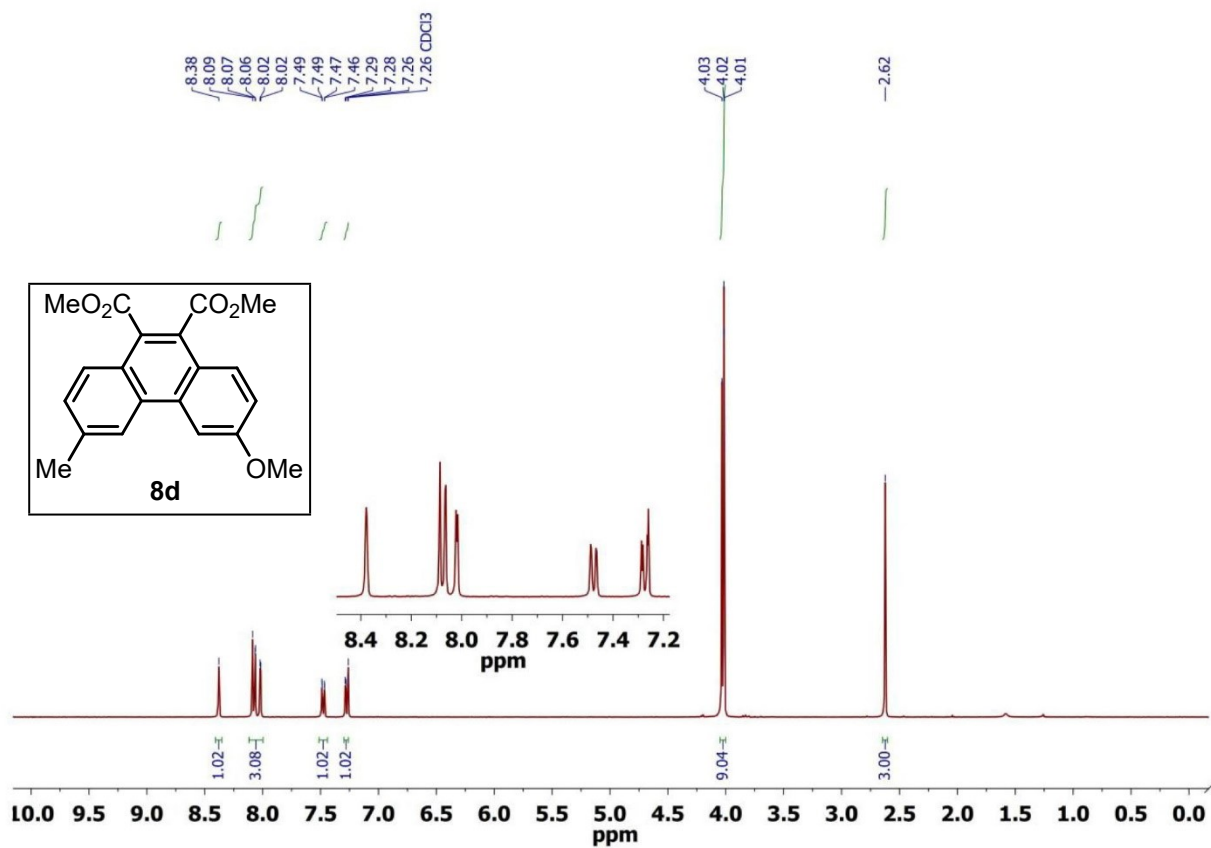


* - water ($\delta = 1.55$)

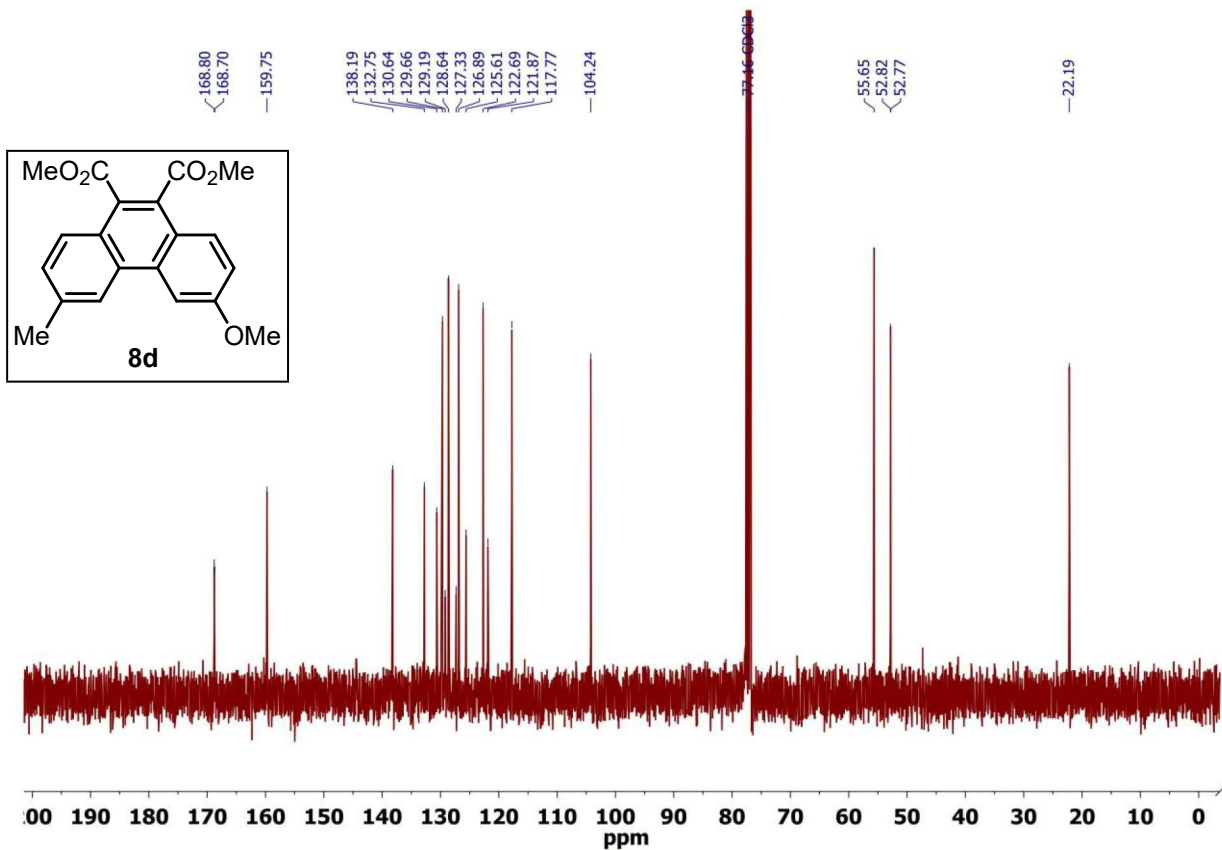
^{13}C NMR spectrum of *E-7d* in CDCl_3



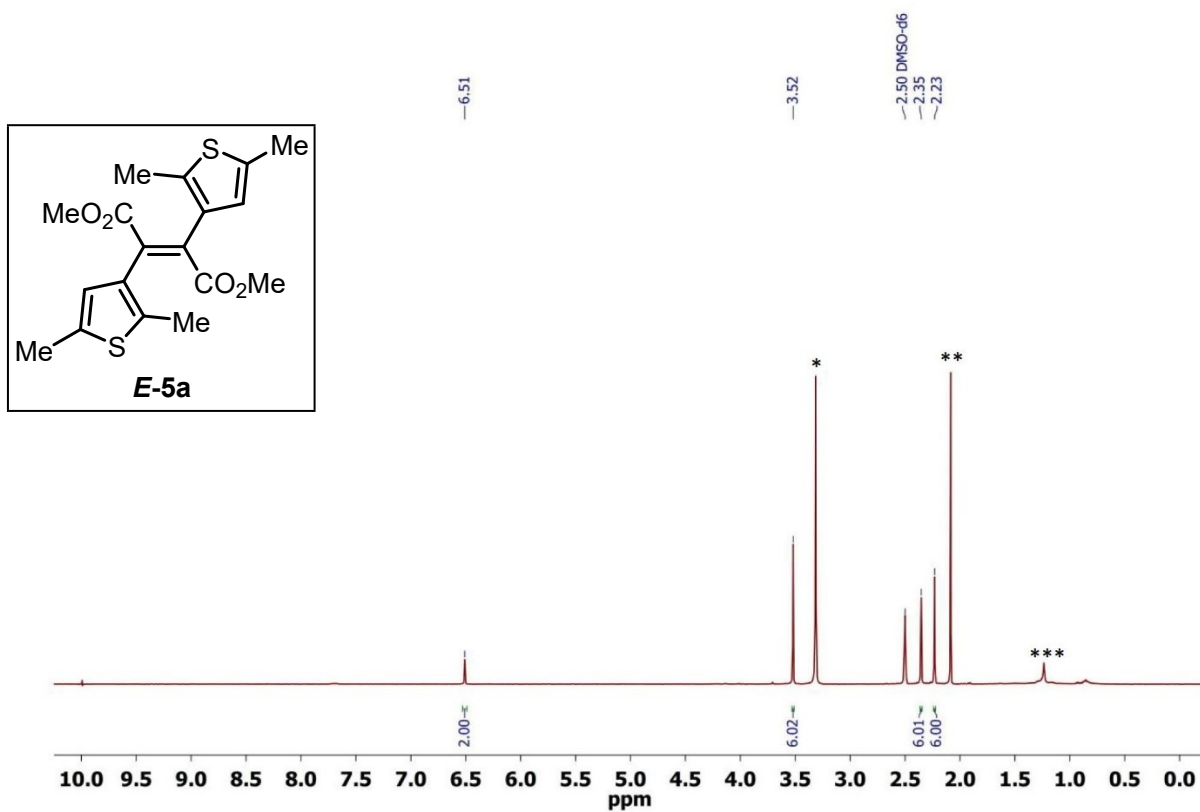
^1H NMR spectrum of **8d** in CDCl_3



^{13}C NMR spectrum of **8d** in CDCl_3

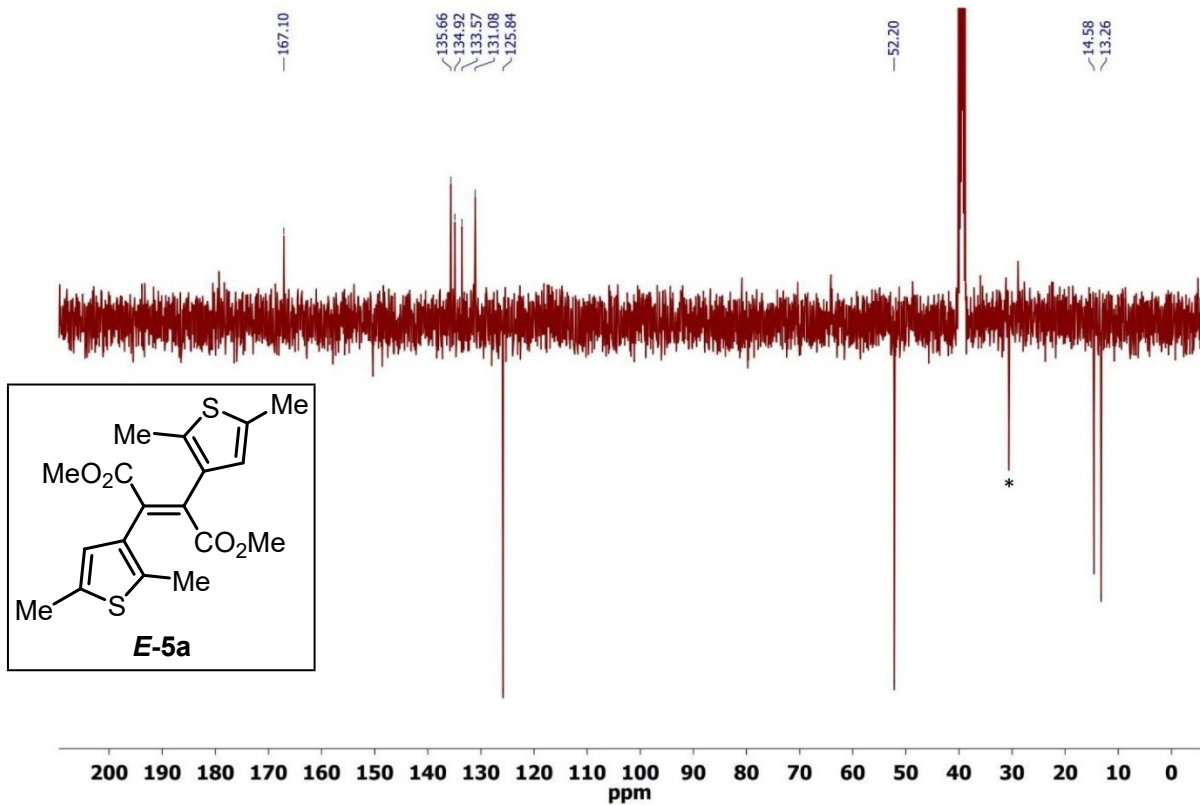


^1H NMR spectrum of *E-5a* in $(\text{CD}_3)_2\text{SO}$



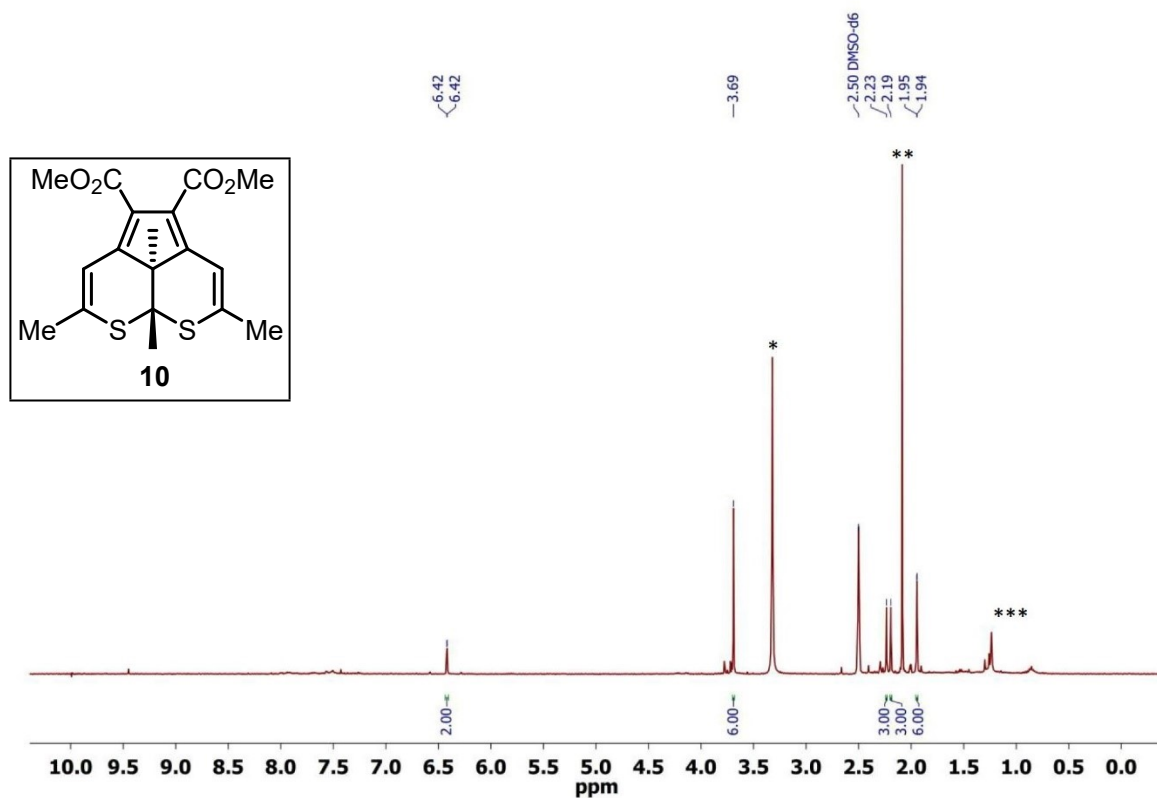
* - water ($\delta = 3.31$); ** - acetone ($\delta = 2.08$); *** - grease ($\delta = 1.24$)

^{13}C NMR spectrum of *E-5a* in $(\text{CD}_3)_2\text{SO}$



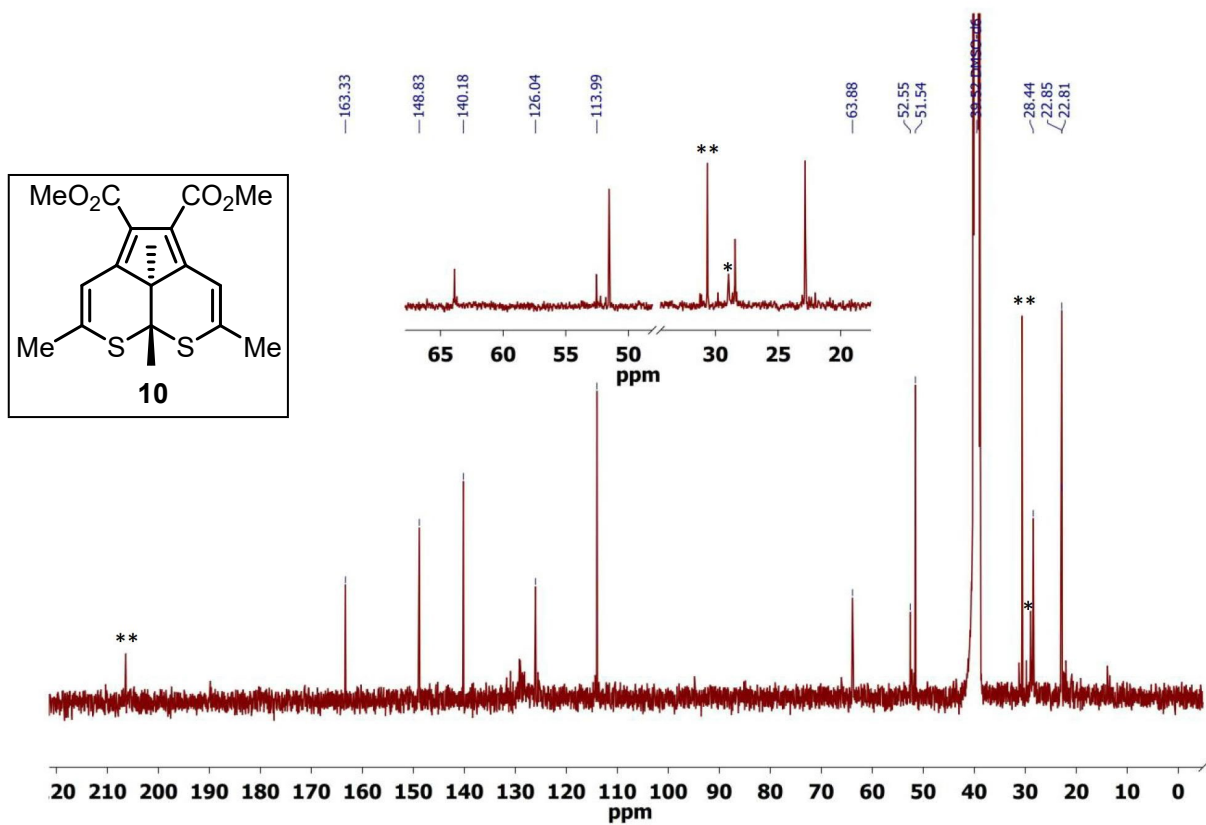
* - acetone ($\delta = 30.61$)

^1H NMR spectrum of **10** in $(\text{CD}_3)_2\text{SO}$



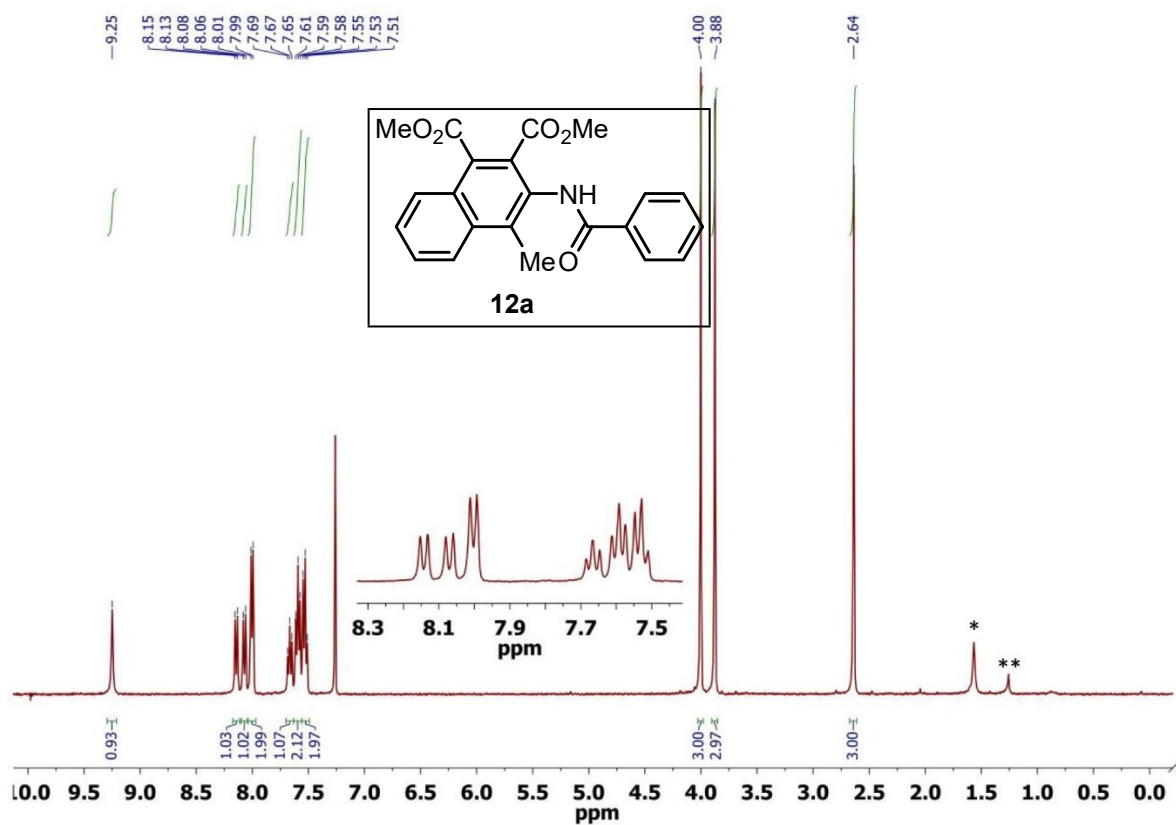
* - water ($\delta = 3.32$); ** - acetone ($\delta = 2.08$); *** - grease ($\delta = 1.24$)

^{13}C NMR spectrum of **10** in $(\text{CD}_3)_2\text{SO}$



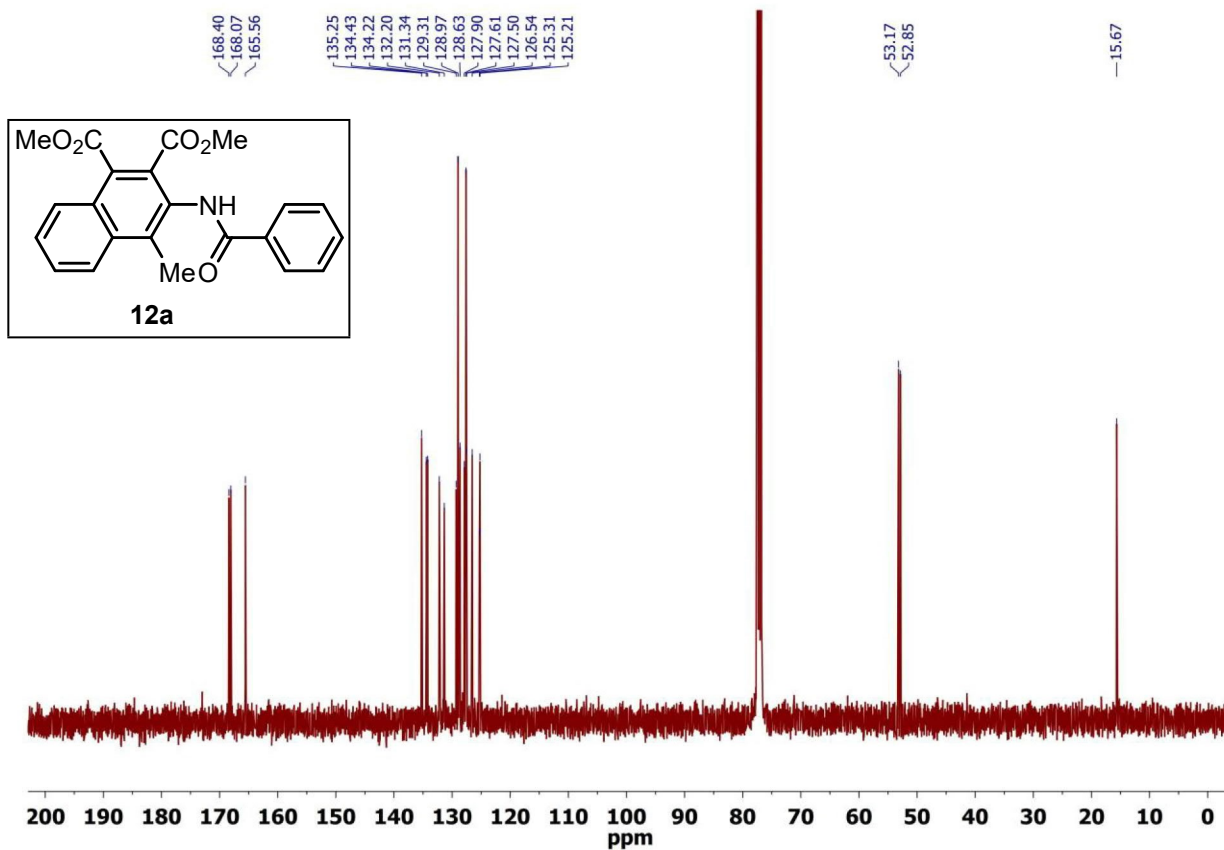
* - grease ($\delta = 28.95$); ** - acetone ($\delta = 30.64, 206.41$)

¹H NMR spectrum of **12a** in CDCl₃

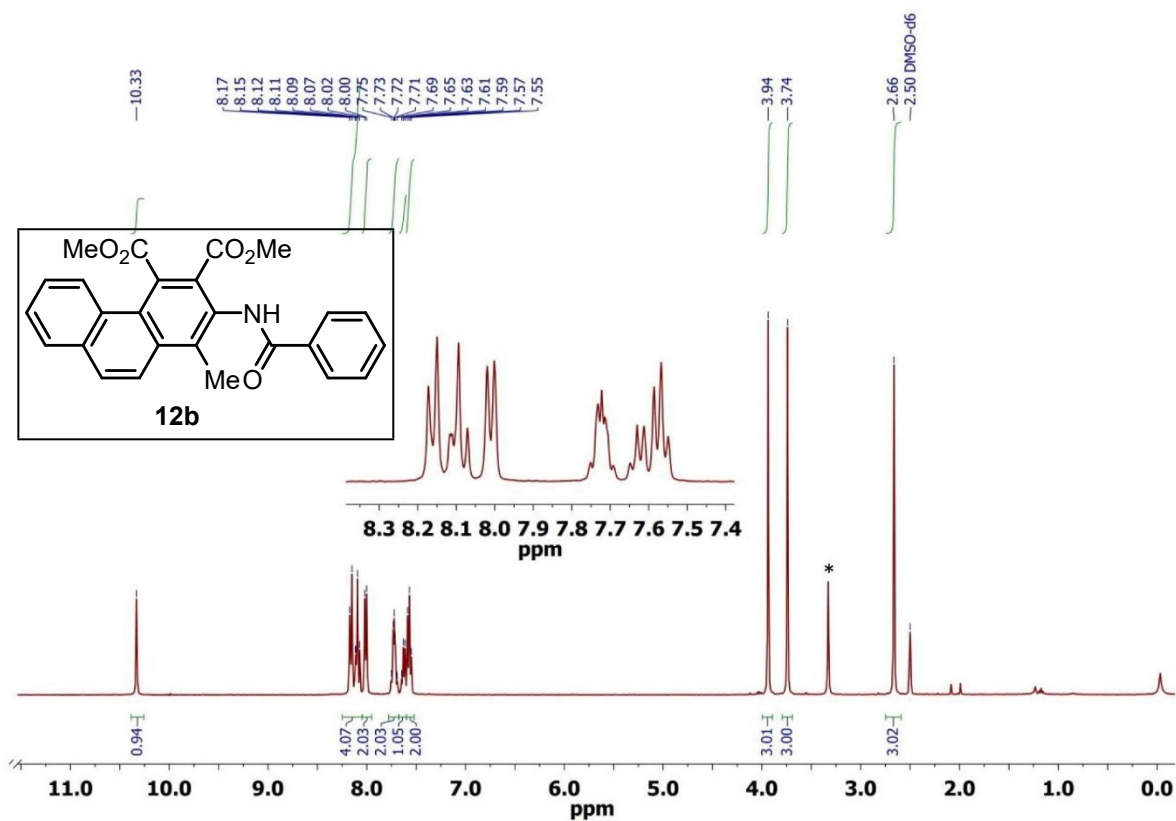


* - water ($\delta = 1.57$); ** - grease ($\delta = 1.26$)

¹³C NMR spectrum of **12a** in CDCl₃

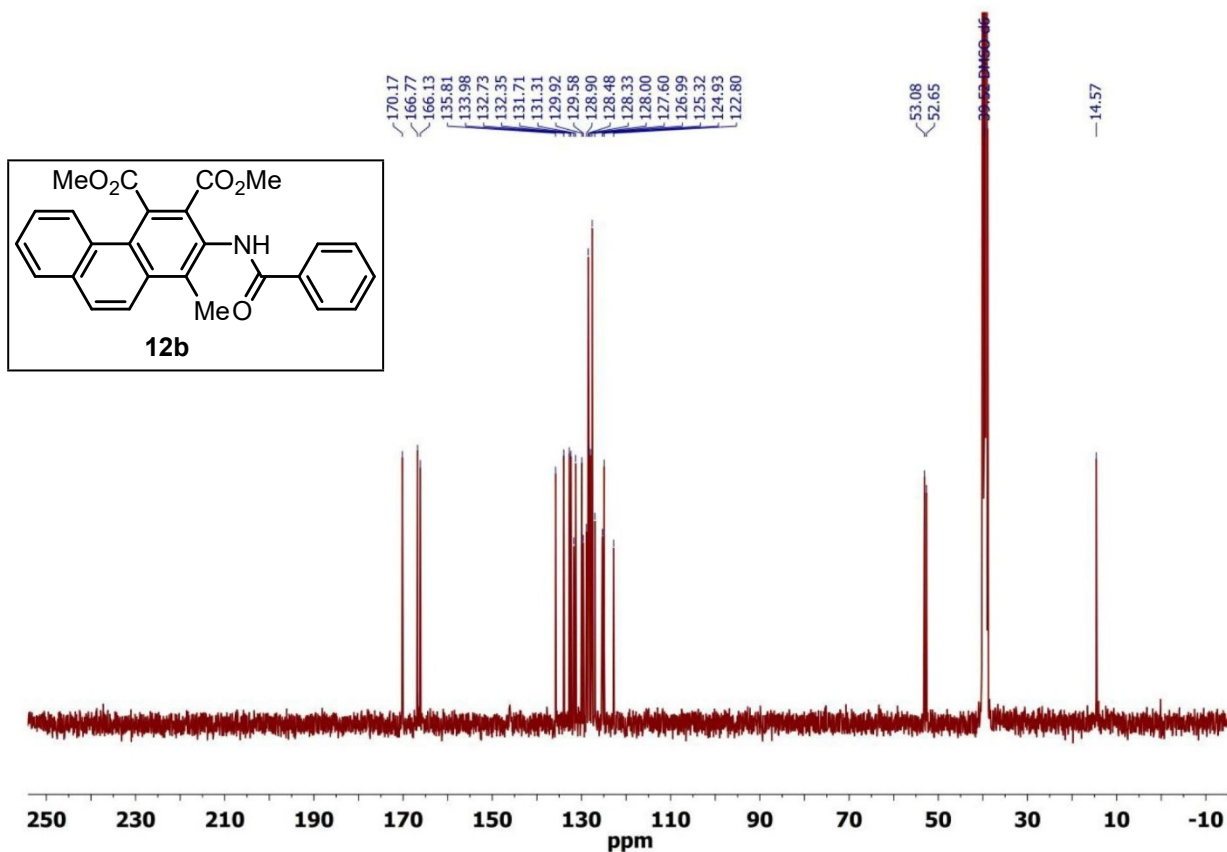


^1H NMR spectrum of **12b** in $(\text{CD}_3)_2\text{SO}$



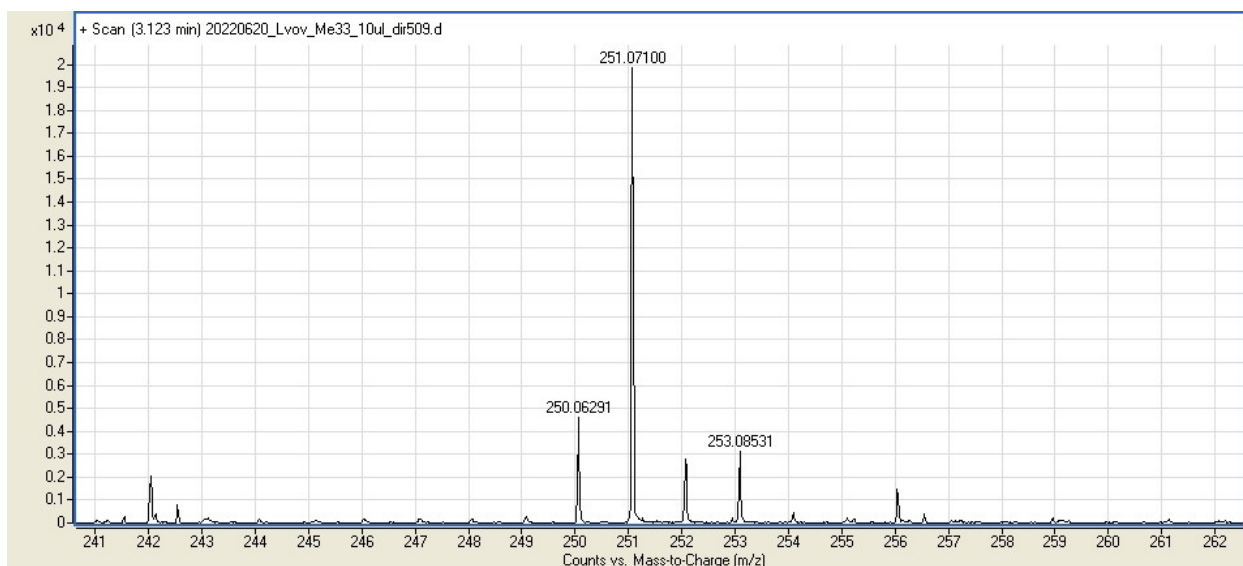
* - water ($\delta = 3.33$)

^{13}C NMR spectrum of **12b** in $(\text{CD}_3)_2\text{SO}$

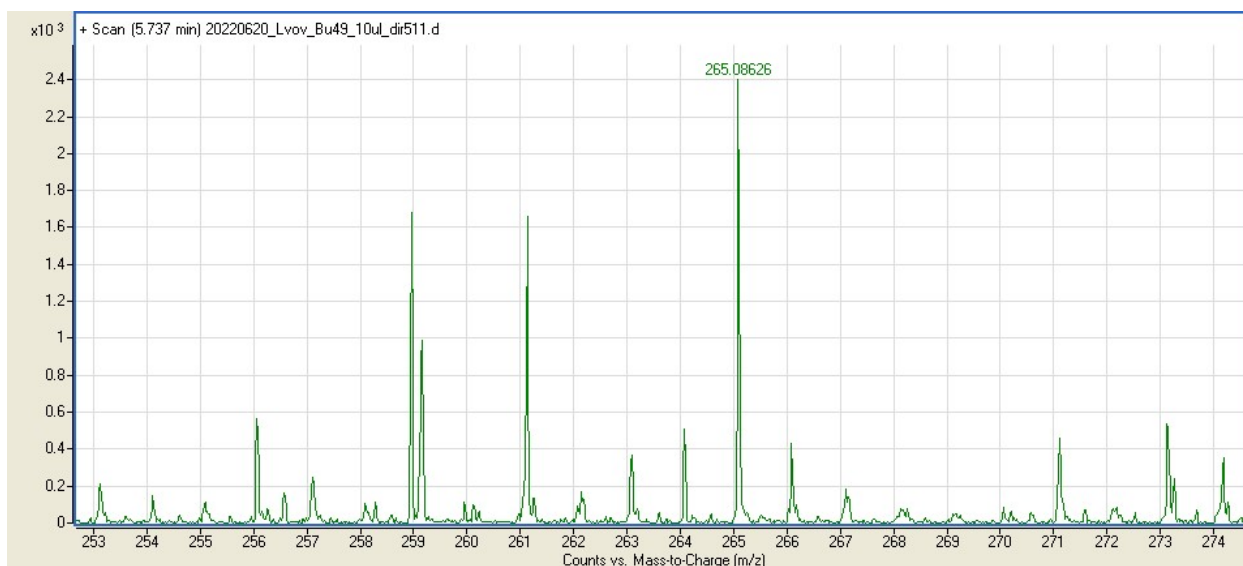


VIII. Copies of HRMS spectra

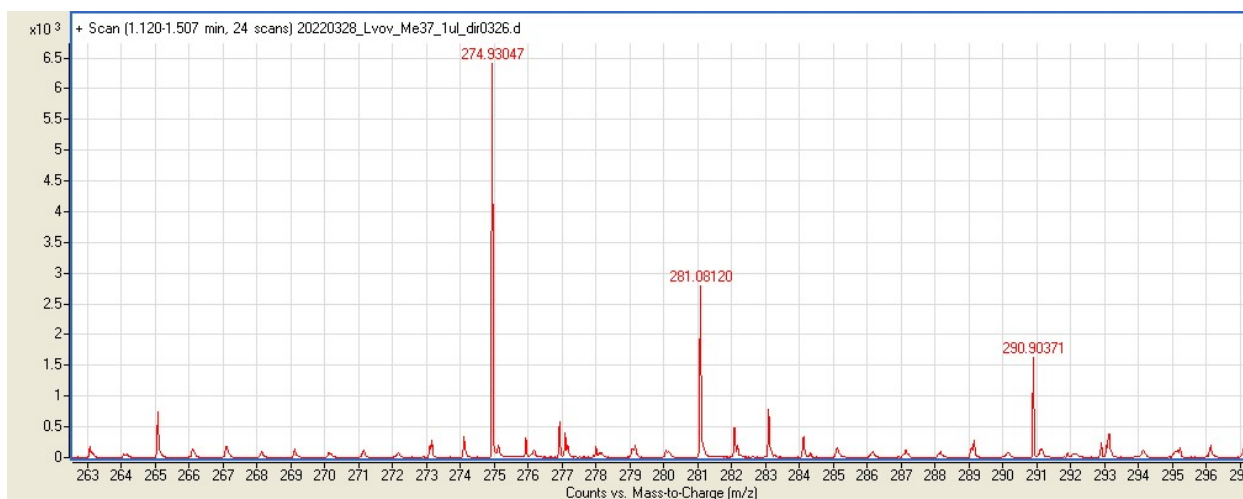
HRMS spectrum of **1a**



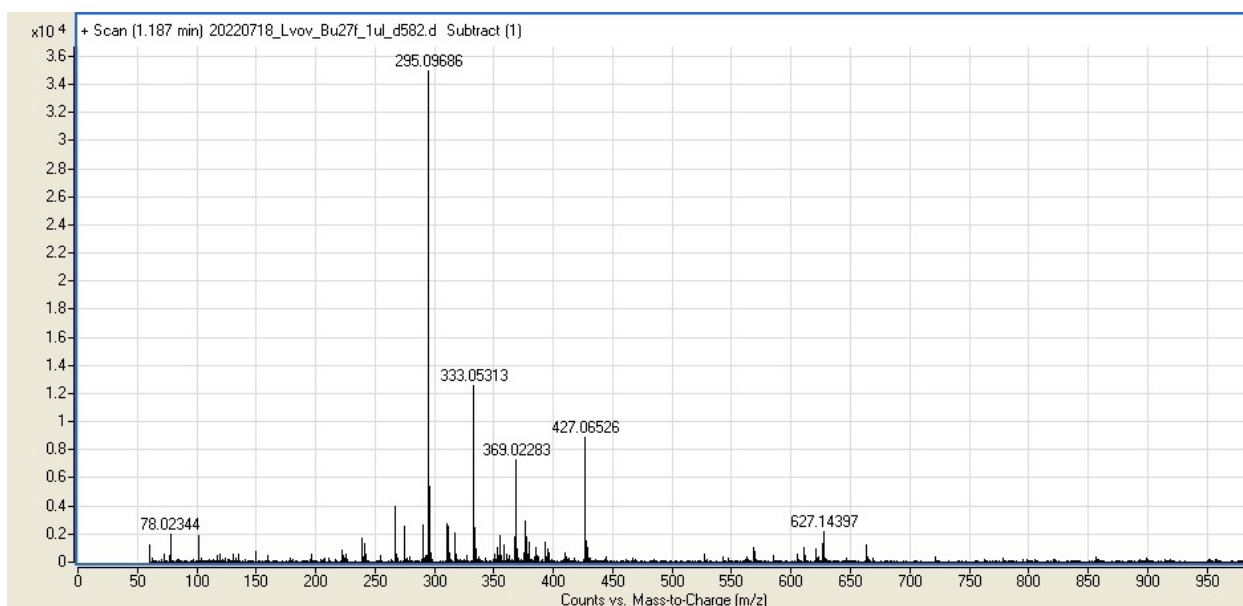
HRMS spectrum of **1b**



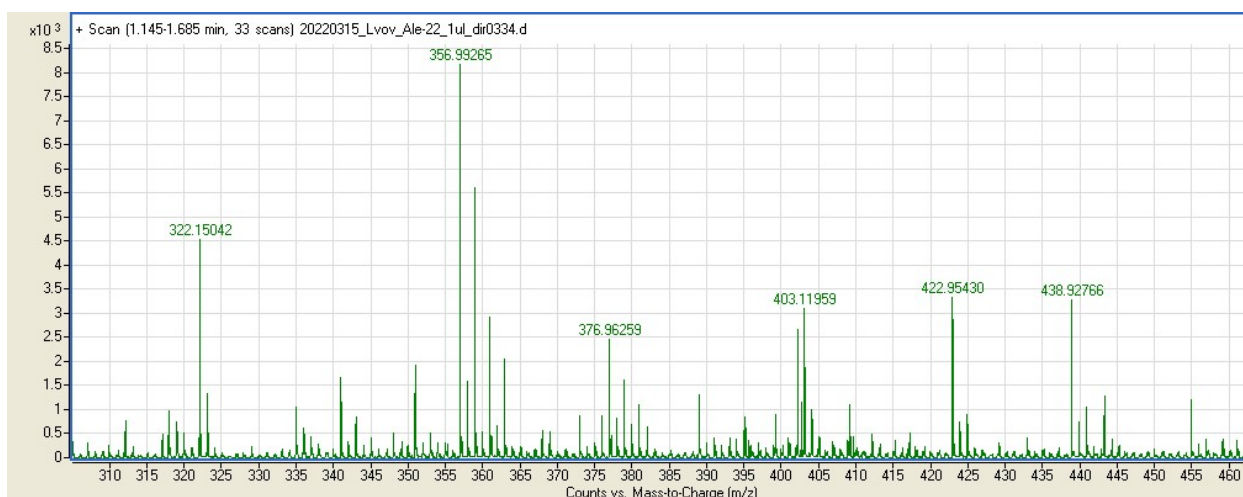
HRMS spectrum of **1c**



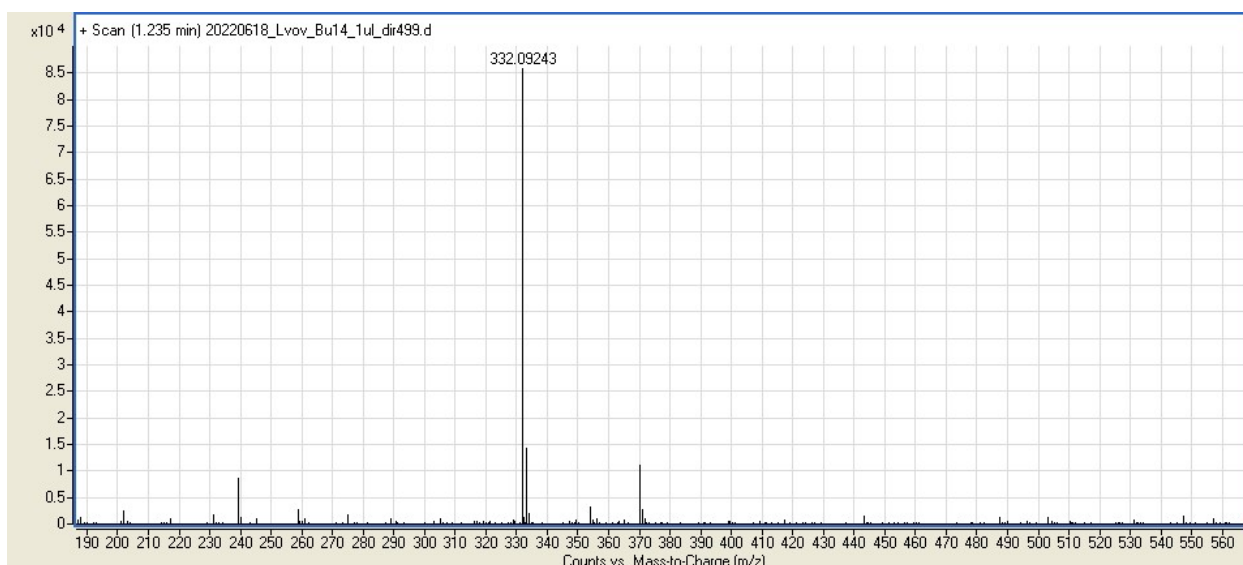
HRMS spectrum of **1d**



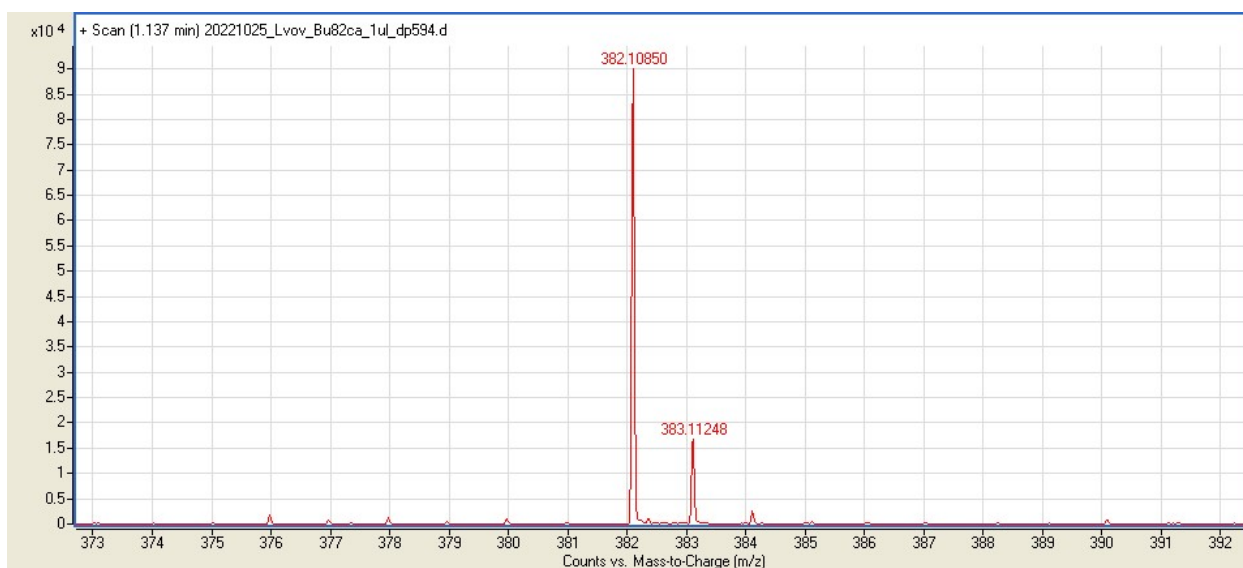
HRMS spectrum of **1e**



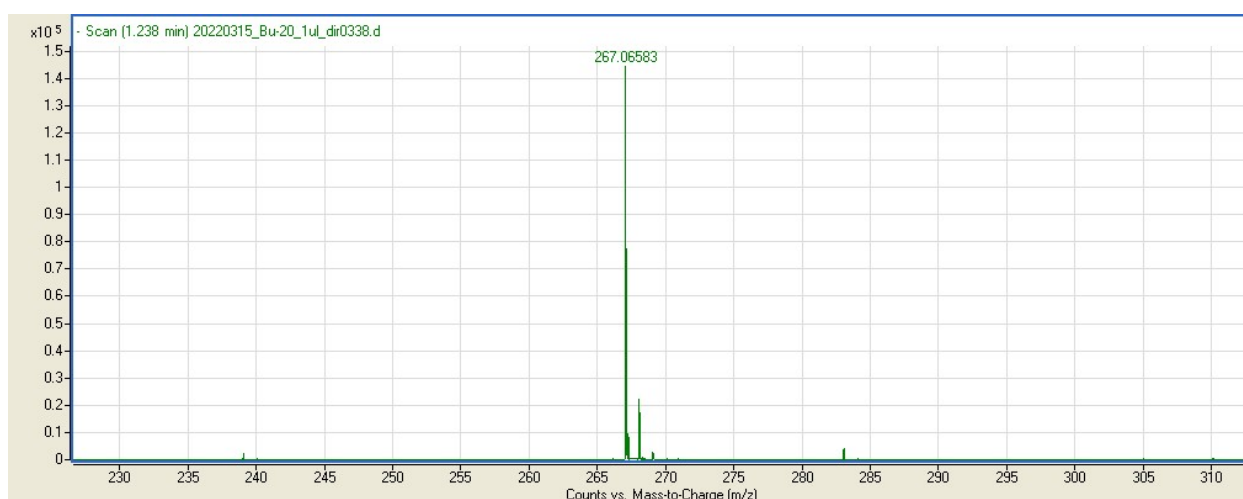
HRMS spectrum of **1g**



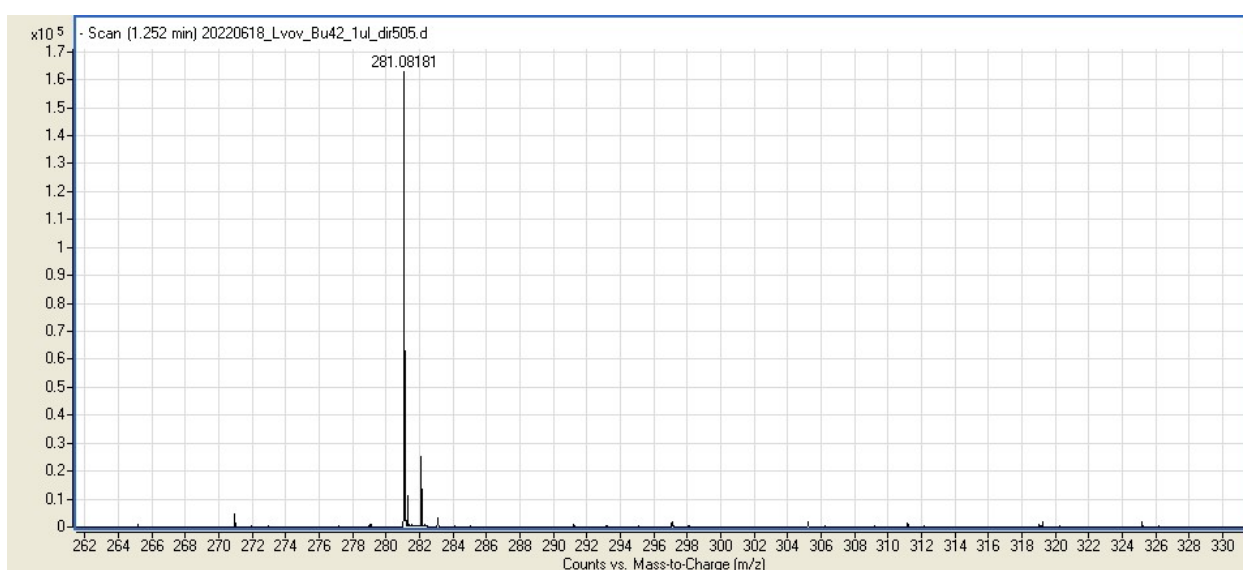
HRMS spectrum of **1h**



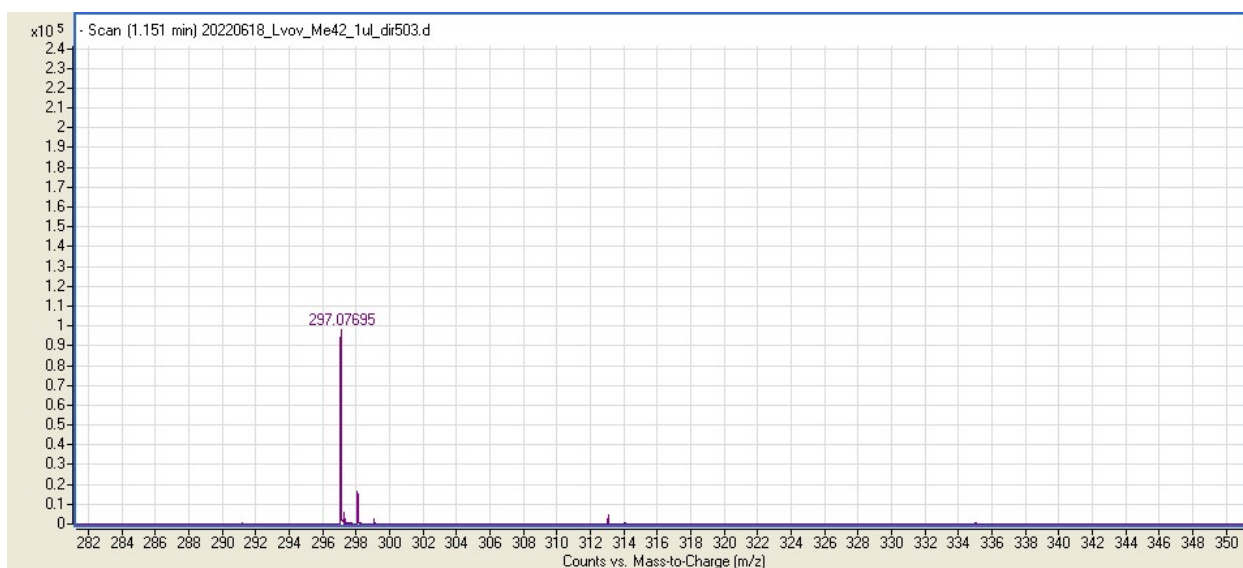
HRMS spectrum of **2a**



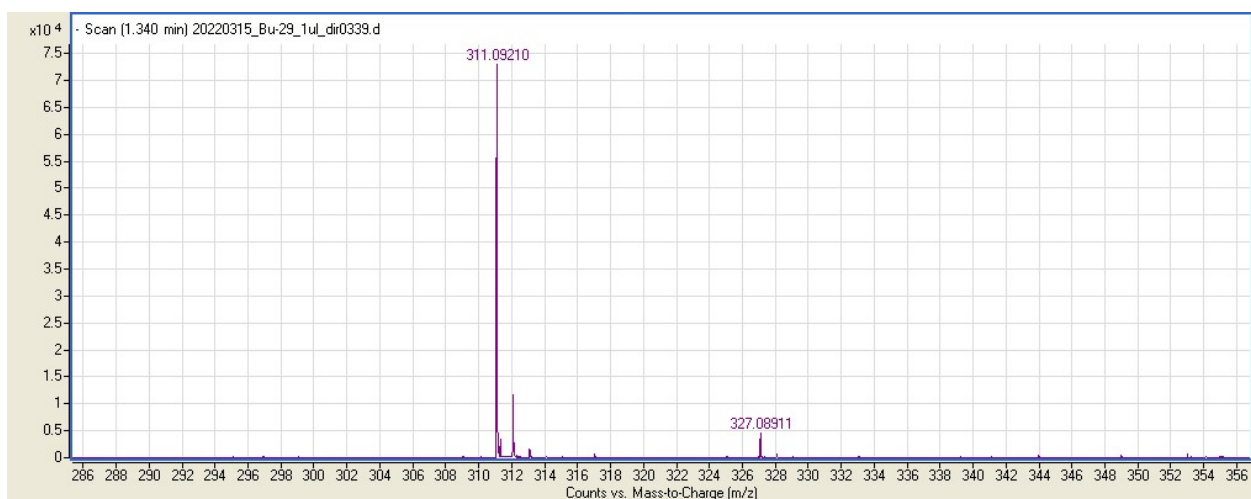
HRMS spectrum of **2b**



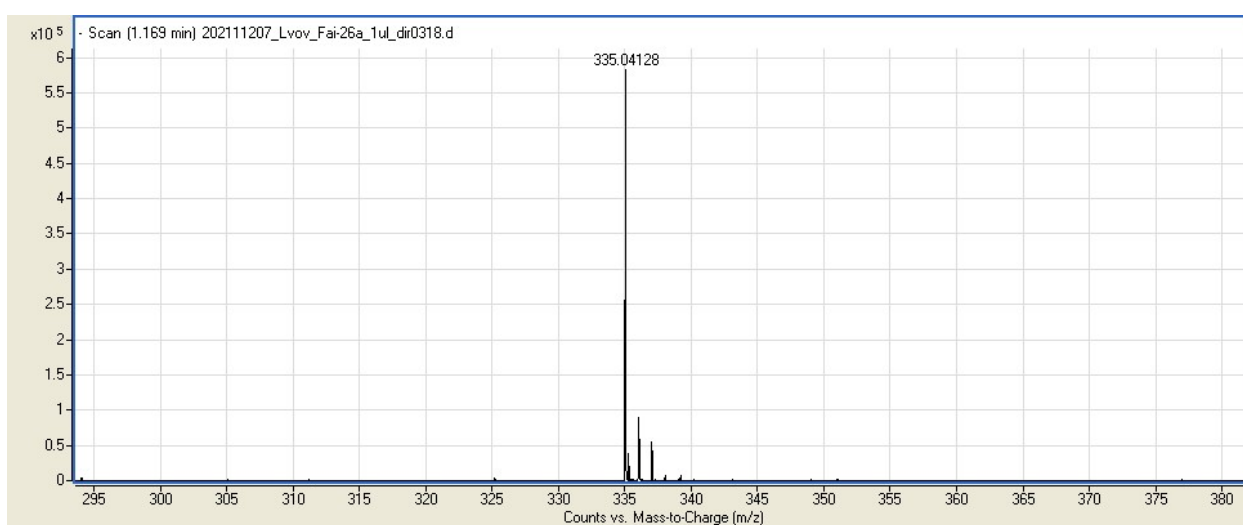
HRMS spectrum of 2c



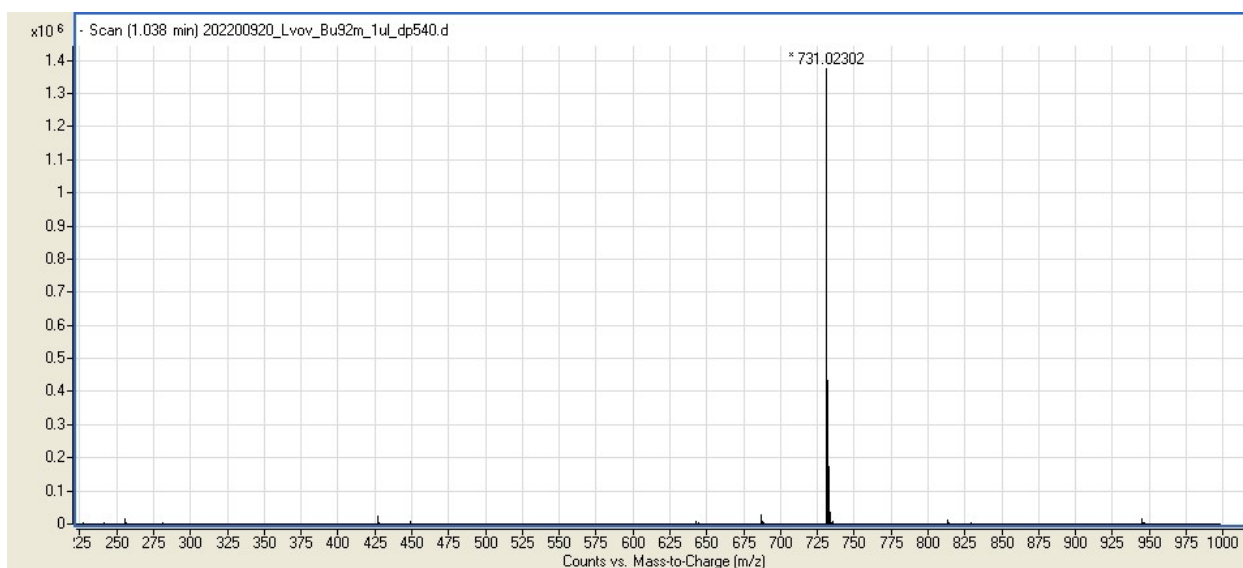
HRMS spectrum of 2d



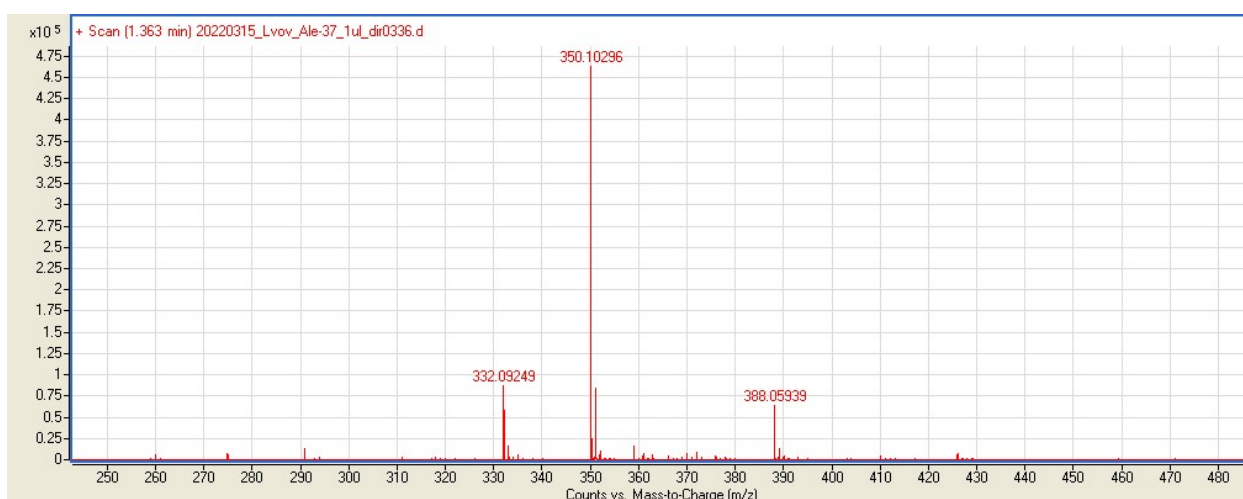
HRMS spectrum of 3a



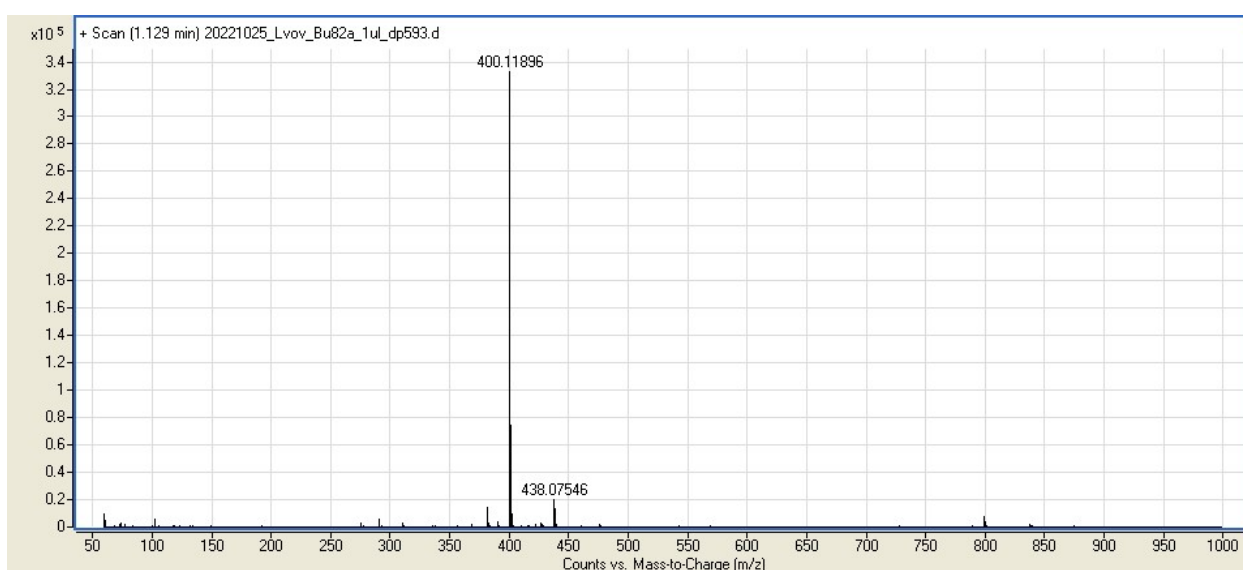
HRMS spectrum of **3b**



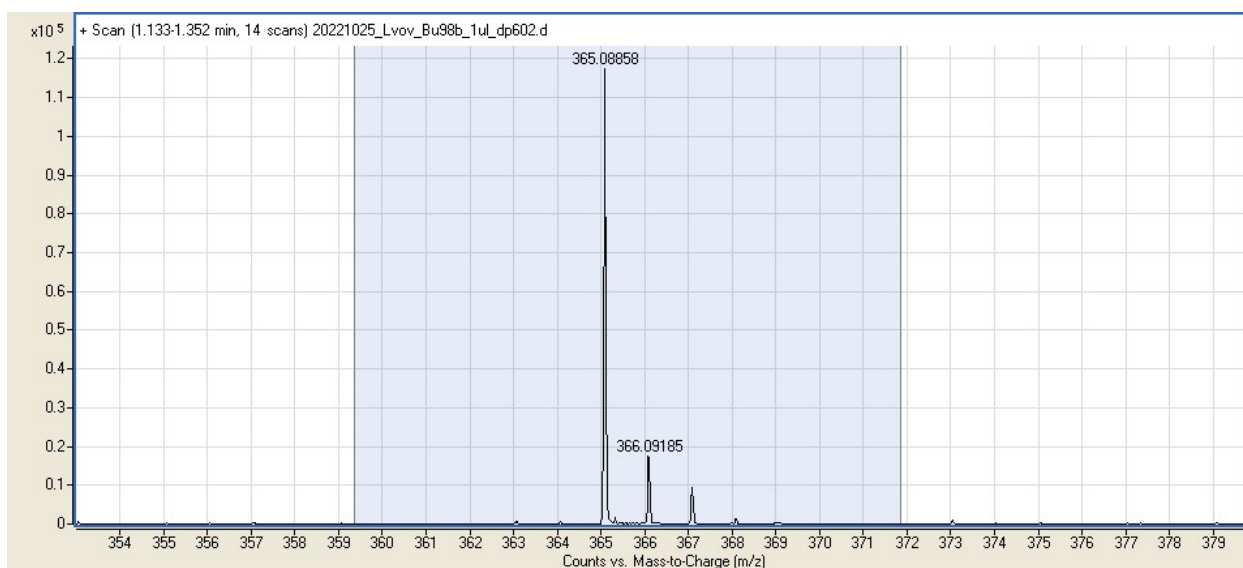
HRMS spectrum of **4a**



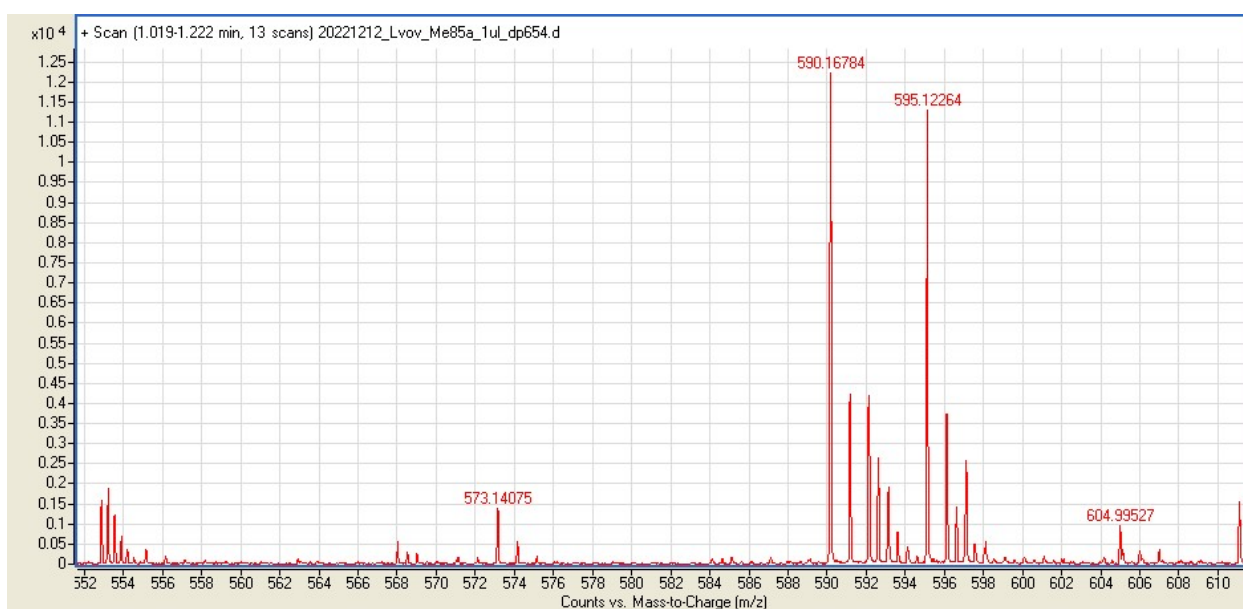
HRMS spectrum of **4b**



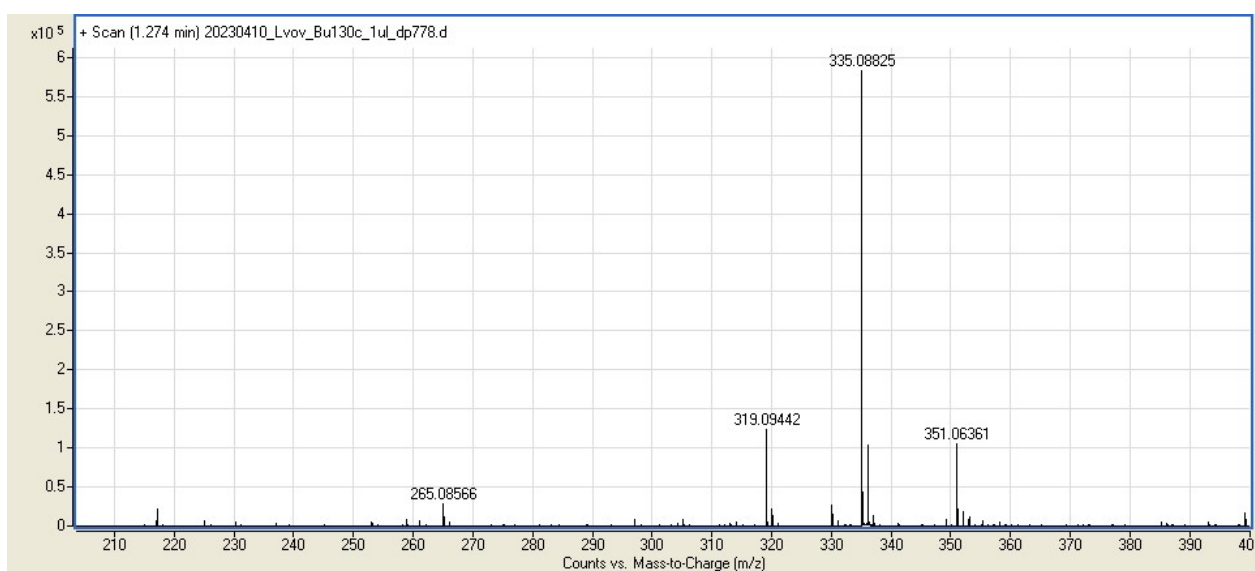
HRMS spectrum of **Z-5a**



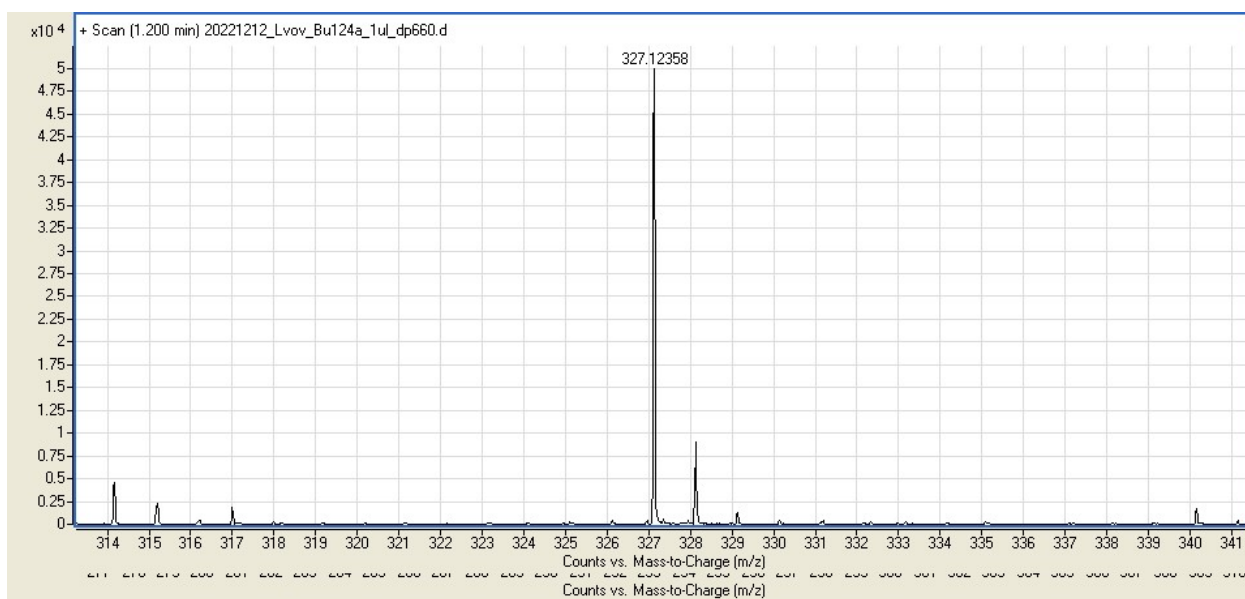
HRMS spectrum of **5b**



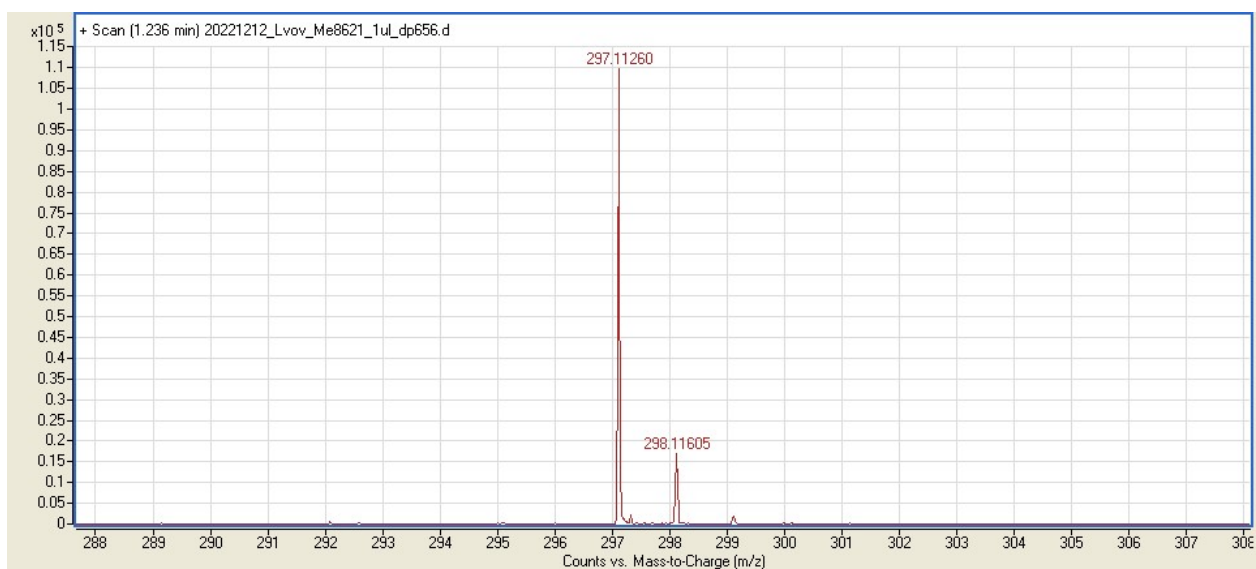
HRMS spectrum of **Z-7a**



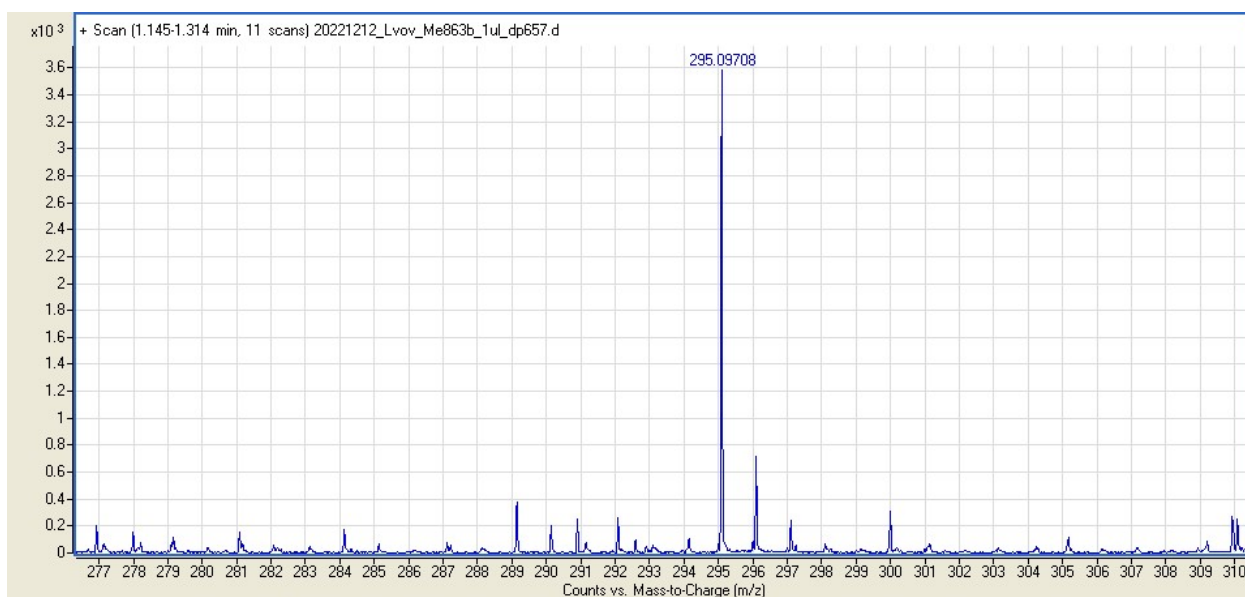
HRMS spectrum of *Z*-7c



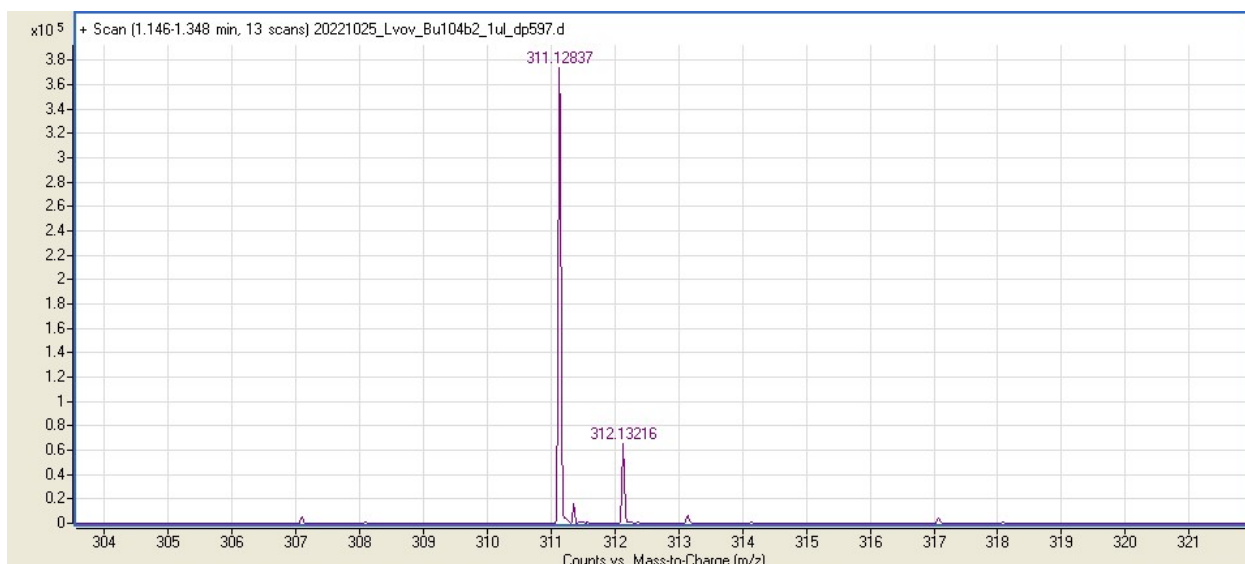
HRMS spectrum of *E*-7a



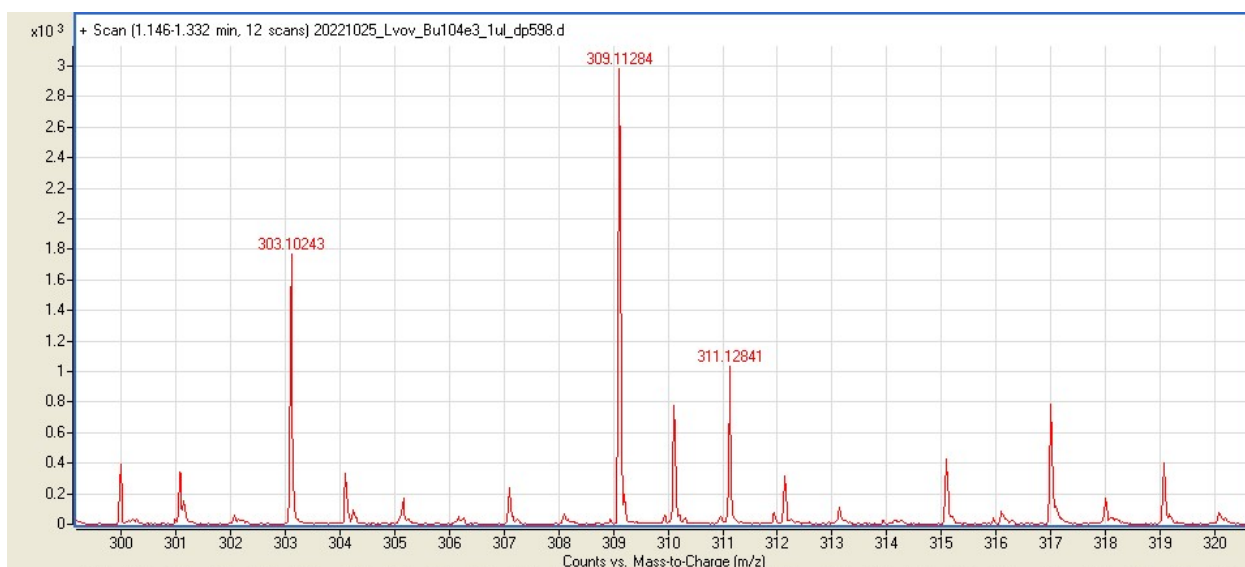
HRMS spectrum of **8a**



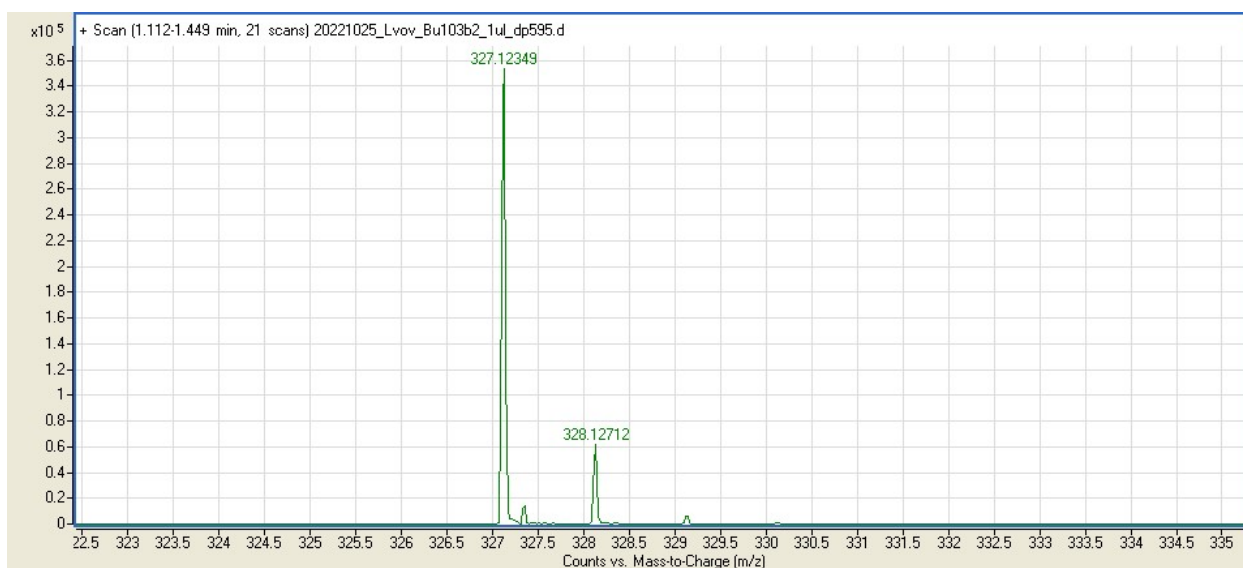
HRMS spectrum of **E-7b**



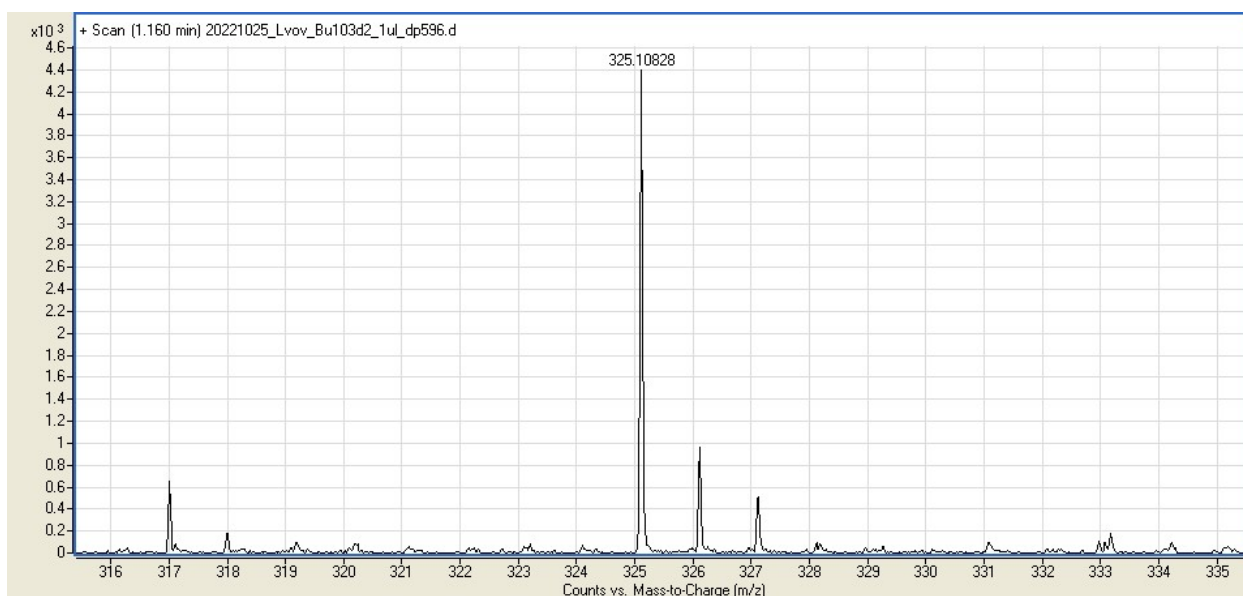
HRMS spectrum of **8b**



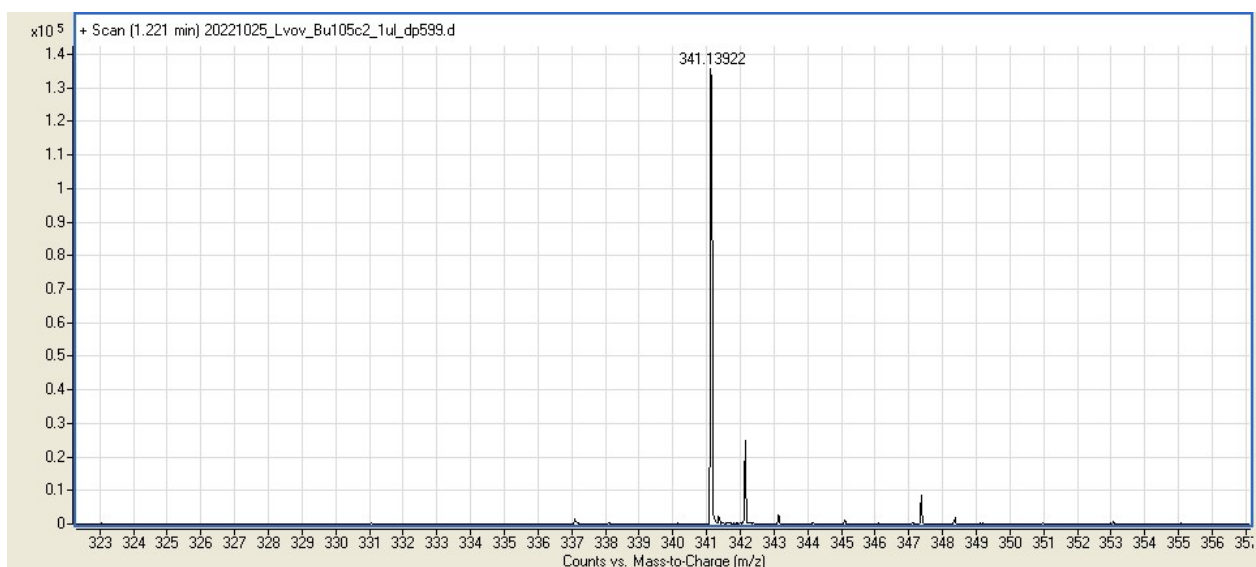
HRMS spectrum of *E-7c*



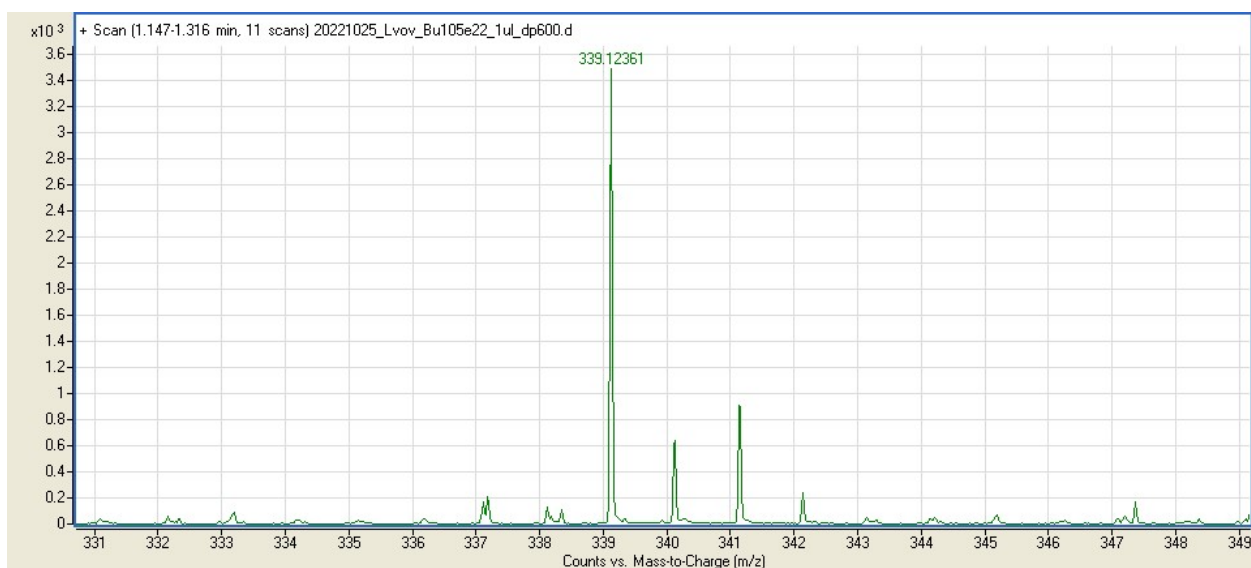
HRMS spectrum of *8c*



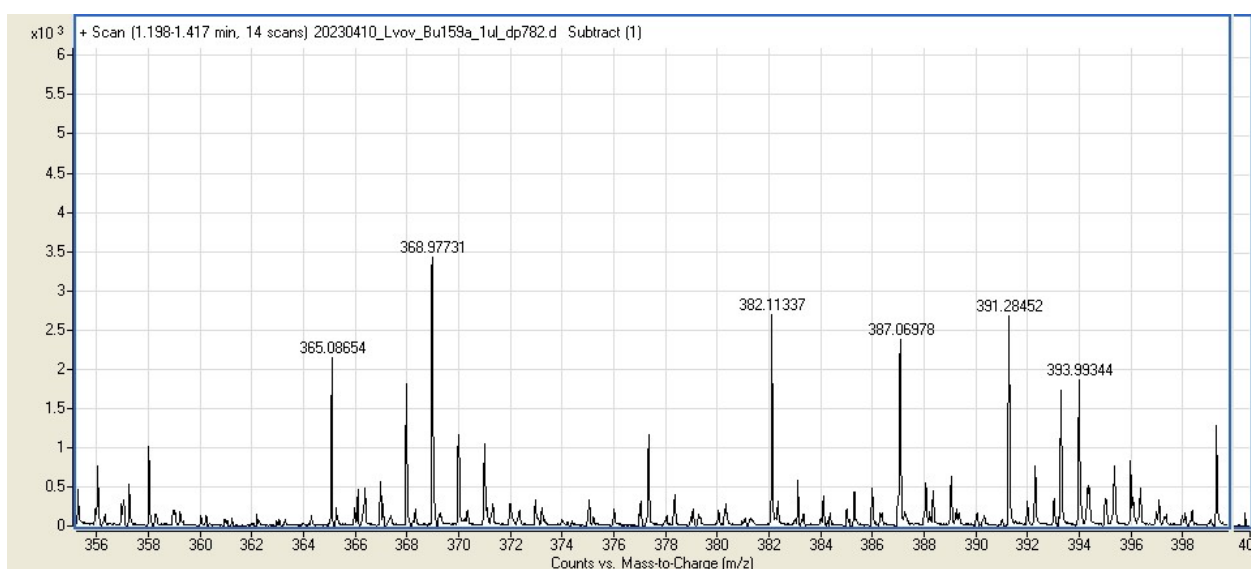
HRMS spectrum of *E-7d*



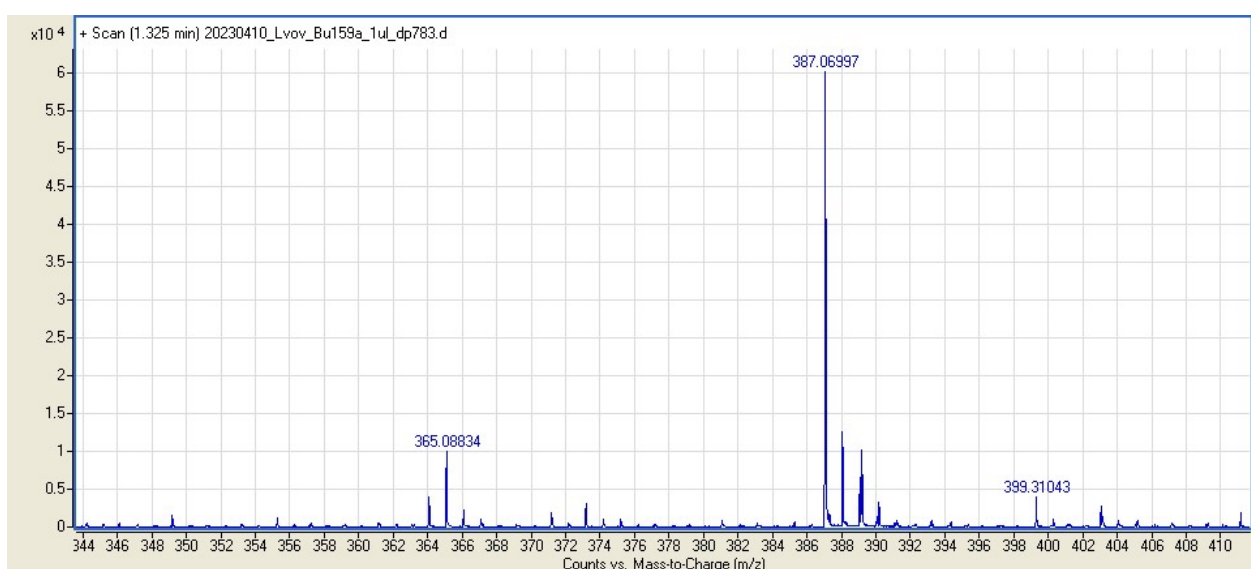
HRMS spectrum of **8d**



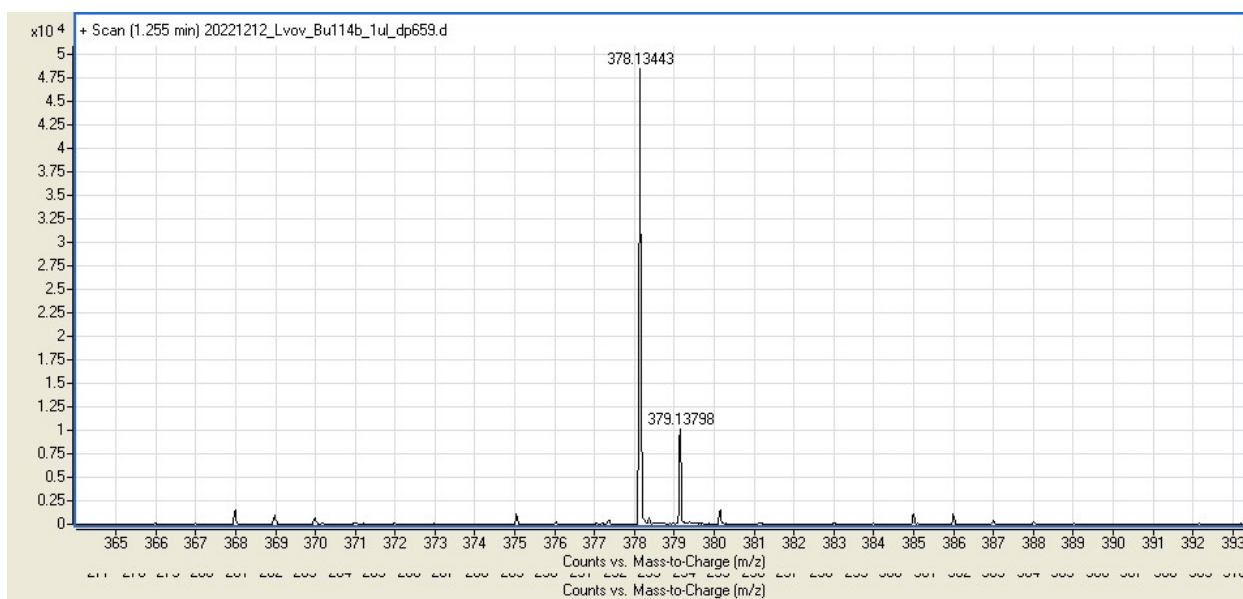
HRMS spectrum of **E-5a**



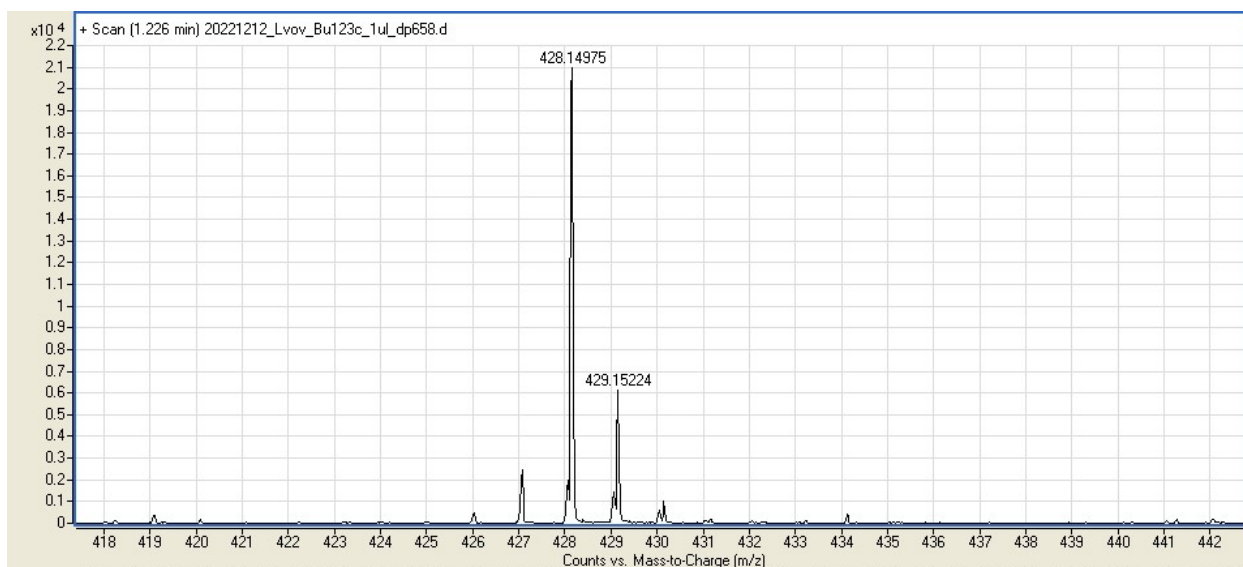
HRMS spectrum of **10**



HRMS spectrum of 12a



HRMS spectrum of 12b



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