Supporting Information-1

Theoretical and experimental studies on visible light driven metal free regioselective functionalization of 1, 4-quinones with diazo esters

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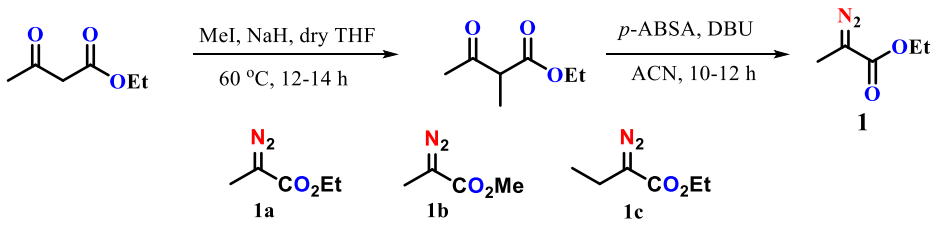
1. General Experimental Procedure:

All blue light reactions were carried out under air as specified unless otherwise mentioned. Photochemical Reactor Aldrich® Penn PhD Photoreactor m2, blue LED lights. LED light is IP68 double density 12V DC waterproof blue light with spectral range of 450 nm with wall plug power supply 85-264 V AC, 50/60 Hz, 120 VA (Figure S1). The irradiation vessel material is borosilicate glass. Reactions were monitored through TLC by visualising in UV detector. All purifications were done in silica gel (100-200 mesh size) column chromatography. All ^{1}H and ^{13}C NMR spectra were recorded taking tetramethylsilane (TMS) as an internal standard at ambient temperature unless otherwise indicated with Bruker 400 MHz instruments at 400 MHz for ^{1}H and 100 MHz for ^{13}C NMR, 376 MHz for ^{19}F spectroscopy. Splitting patterns are designated as singlet (s), broad singlet (br s), doublet (d), triplet (t), quartet (q), quintet (quin) doublet of doublets (dd) and triplet of doublets (td). Splitting patterns that could not be interpreted or easily visualized are designated as multiplet (m). Ultra-performance liquid chromatography (UPLC) was carried out using an Agilent 6540 accurate–mass Q-TOF LC/MS (Agilent Technologies, U.S.A.). Liquid chromatographic separations ware performed at room temperature of 25 °C, using a UPLC C18 analytical column. MS analyses were performed under the following operation parameters: dry gas temperature 350 °C, dry gas (N_2) flow rate 10 L/min, nebulizer pressure 30 psi, Vcap 4000 and fragmentor voltage 100 V. Mass spectra were acquired in the positive ion mode by scanning from 100 to 1500 in the mass to charge ratio (m/z). The mobile phase composition used for UHPLC–QTOF MS comprised of H_2O (A) and ACN (B), with optimized linear gradient elution. The injection volume was 5 µL. The flow rate was set at 0.3 mL/min. Accurate mass analysis calibration was carried out by ESI-low concentration tuning mix solution provided by Agilent technologies, U.S.A. The accuracy error threshold was set at 5 ppm. Steady state UV-vis(visible) absorption was measured by Shimadzu UV-26001 UV-Vis Spectrophotometer in a conventional quartz cell cuvette. Fourier transform infrared spectroscopy was performed on Thermo Scientific Nicolet iS20 equipped with iD5-ATR accessory, in the range of 4000 to 400cm^{-1} with a resolution of 4cm^{-1}. All reagents used in this work were purchased from Sigma-Aldrich, Alfa-Aesar, TCI Chemicals, Spectrochem and were used without any further purification.

Figure S1: *The Blue LED Photoreactor set-up used.*

2. Synthetic Procedure:

2.1: General procedure for the preparation of α-Alkyl-α-Diazoester (1a - 1c)



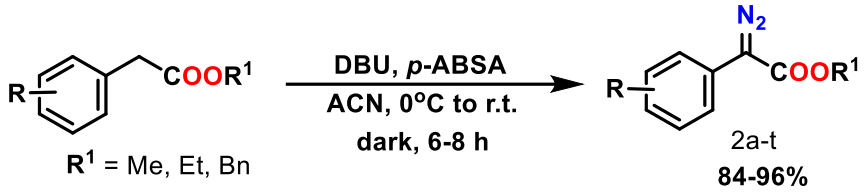
Scheme S1. Synthesis of α-alkyl-α-diazo ester

Step-1: An oven dried 100 mL double neck round bottom flask equipped with a magnetic stir bar was evacuated and made inert with argon. Then 25 mL dry THF was added into the flask. Flask was charged with NaH (60% dispersion in mineral oil, 0.42 g, 10.53 mmol, 1.2 equiv.) at 0°C. The suspension was stirred at 0°C for 10 minutes. A solution of ethyl acetoacetate (2.00 g, 15.36 mmol, 1.75 equiv.) in 5 mL THF was added dropwise by using syringe over 10 minutes of time. Then the reaction mixture was stirred at room temperature for 30 minutes. Then methyl iodide (1.25 g, 8.78 mmol, 1 equiv.) was added and then again stirred at 60°C for 12-14 h. After 12-14 h the flask was cooled and 20 mL saturated NH_4Cl was added. Then the product was extracted with DCM (3×30 mL). Then the combined organic layer was washed with 50 mL brine solution and dried with Na_2SO_4. The organic layer was concentrated under reduced pressure. The crude was further purified by column chromatography using 25% ethyl acetate/ hexane to afford ethyl 2-methyl-3-oxobutanoate as a colorless oil (1.17 g, 53%). Spectroscopic data are matched with the previous literature. [1]

Step-2: To an oven dried 100 mL round bottom flask equipped with a stir bar, ethyl 2-methyl-3-oxobutanoate (1.17 g, 8.12 mmol, 1 equiv) and *p*-acetamidobenzenesulfonyl azide (*p*-ABSA, 2.92 g, 12.18 mmol, 1.5 equiv.) was dissolved in 25 mL dry acetonitrile and kept it in ice bath. The flask was then cooled for 15 minutes. DBU (1.45 mL,9.74 mmol, 1.2 equiv.) was added dropwise while stirring. The flask was then allowed to warm at room temperature in a dark place and stirred for 10-12 h. Saturated aqueous NH_4Cl (30 mL) was added to the reaction mixture and extracted with DCM (3×20 mL). The combined organic layer was washed with brine solution (50 mL) and dried over Na_2SO_4. Organic layer was concentrated under reduced pressure and further purified by column chromatography using 10% ethyl acetate/ hexane. The compound **1a** (520.2 mg, 50%) was appeared as a yellow oil. Spectroscopic data were matched with previous literature. [1]

2.2: Synthesis of Donor-Acceptor diazoesters:

All aryl alkyl diazo acetates **2** were prepared by the reported procedure.[2] Aryl alkyl acetates (1 equiv, 5 mmol) were dissolved in ACN (10 mL) in a clean oven-dried round bottom flask. 1,8-diazabicyclo[5.4.0]undec-7-ene (1.2 equiv, 6 mmol) was added and stirred for 10 min. p-ABSA (4-acetamidobenzenesulfonyl azide) (1.2 equiv, 6 mmol) was added and stirred for 6 h in the dark and room temperature (r.t.); after completion, ACN was removed under vacuum, diluted with ethyl acetate (25 mL), washed with water, and the organic layer was dried with brine and sodium sulfate, and purified with flash column chromatography in silica gel (100−200 mesh size) with 5% ethyl acetate in hexane to yield 84-96%.



Scheme S2: Synthesis of aryl diazoesters

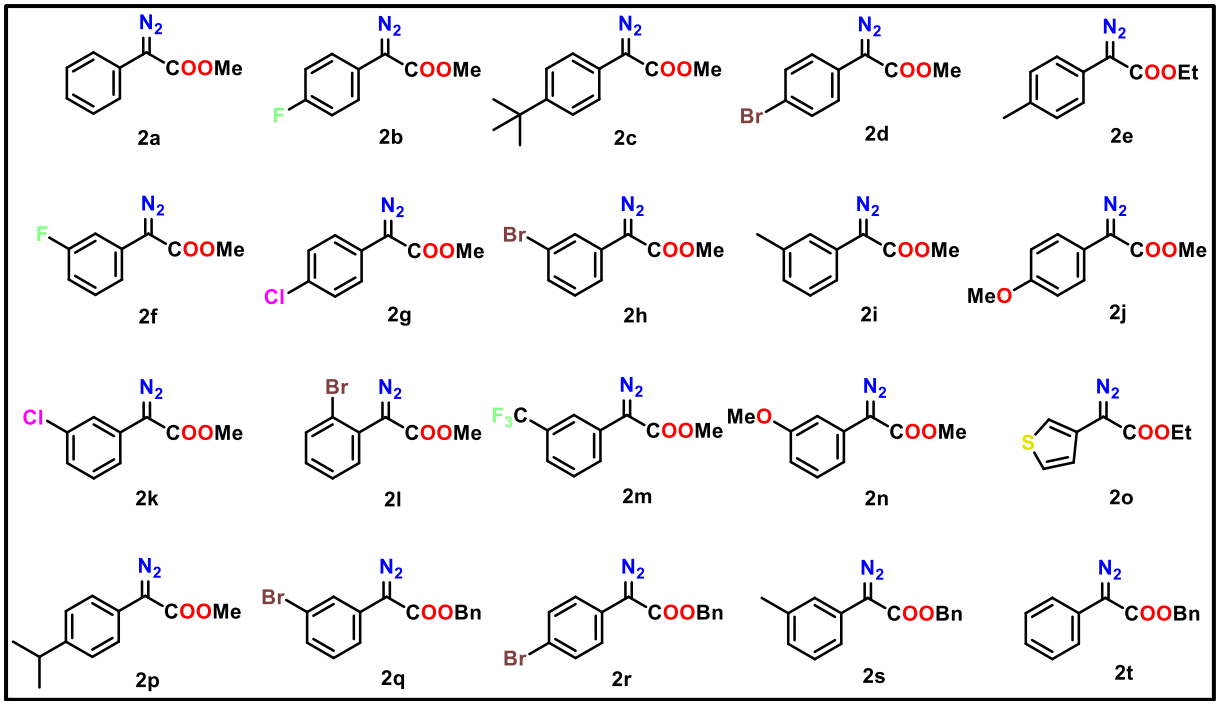
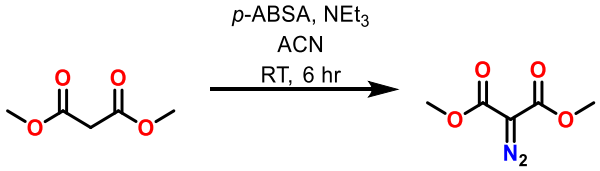


***Figure S2**. Structures of Donor-Acceptor diazoesters **2** used in our study*

2.3: Synthesis of Acceptor-Acceptor diazoesters:



Scheme S3. Synthesis of dimethyl-2-diazomalonate

Dimethyl malonate (1 equiv, 5mmol) was dissolved in ACN (10 mL) in a clean oven-dried round bottom flask. Triethylamine (1.2 equiv, 6 mmol) was added and stirred for 10 min. Next, *p*-ABSA (4-acetamidobenzenesulfonyl azide) (1.2 equiv, 6 mmol) was added and stirred for 6 h in the dark and room temperature (r.t.); after completion, ACN was removed under vacuum, diluted with ethyl acetate (25 mL), washed with water, and the organic layer was dried with brine and sodium sulfate, and purified with flash column chromatography in silica gel (100–200 mesh size) with 15% ethyl acetate in hexane to yield 96%.[3]

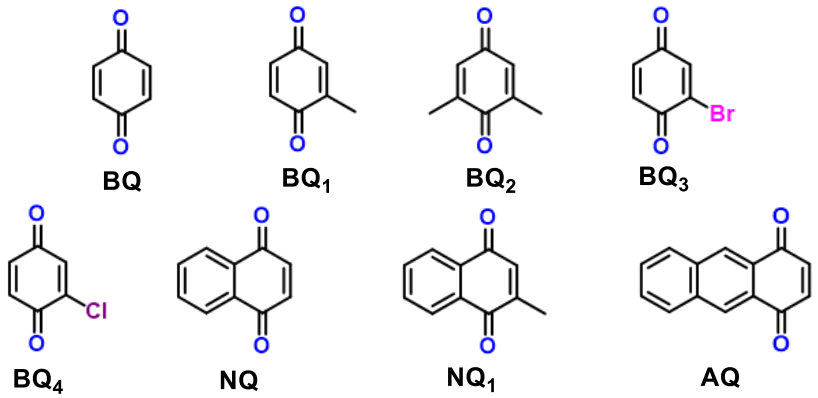


Figure S4. Numerous 1, 4-quinones that are used for this study

2.4: General procedure for the preparation of aryloxy vinyl ether:

Various substituted 1,4-quinones (**BQ, BQ_{1-4}**) (0.6 mmol, 1 equiv.) and α-alkyl-α-diazoesters (**1a-c**) (1.32 mmol, 2.2 equiv.) were taken in a 15 mL borosilicate glass vial and dissolved in DCM (5 mL). The reaction mixture was stirred under the irradiation of blue LED in inert atmosphere for 2-2.5 h. Reaction was monitored by TLC. After completion of reaction, solvent was removed under reduced pressure, purification was carried out by column chromatography using silica gel (100-200 mesh size) in 5-20 % ethyl acetate in hexane to afford respective aryloxy vinyl ethers (**5a-i**).

2.5: General procedure for the preparation of *p*-spiro epoxide quinones:

Various substituted 1,4-quinones (**NQ, NQ_1, AQ**) (0.6 mmol, 1 equiv.) and α-alkyl-α-diazoester (**1a** and **1c**) (1.32 mmol, 2.2 equiv.) were taken in a 15 mL borosilicate glass vial and dissolved in DCM (5 mL). The reaction mixture was stirred under the irradiation of blue LED in inert atmosphere for 2-2.5 h. Reaction was monitored by TLC. After completion of reaction, solvent was removed under reduced pressure, and purification was carried out by column chromatography using silica gel (100-200 mesh size) in 5-20 % ethyl acetate in hexane to afford respective *p*-spiro epoxide quinone products **6a-c** and **7a**.

2.6: General procedure for the preparation of C-H alkylation and cyclopropanation of quinones:

Numerous substituted aryl diazo esters (**2a** - **t**) (1.4 equiv, 0.84 mmol.) and **BQ, NQ** and **AQ** (1 equiv., 0.6 mmol.) were taken in a 15 mL borosilicate glass vial and dissolved in DCM (5 mL). The reaction mixtures were stirred under the irradiation of blue LED in oxygen atmosphere for 12-14 h. The solvent was removed under reduced pressure, and purifications were carried out by column chromatography using silica gel (100-200 mesh size) in 20% ethyl acetate in hexane to afford corresponding C-H alkylated products, **10a-t** with NQ and cyclopropanated products **8a-f** with BQ and **9a-b** with AQ.

2.7: Synthesis of *p*-spiro epoxide quinones:

Methyl diazoacetate, **3** / dimethyl 2-diazomalonate, **4** (1.4 equiv., 0.84 mmol.) and various 1, 4-quinones (BQ, MBQ, NQ) (1 equiv., 0.6 mmol.) were taken in a 15 mL borosilicate glass vial and dissolved in DCM (5 mL). The reaction mixtures were stirred at room temperature under the irradiation of blue LED for 6-8 h. After completion of the reaction (monitored by TLC), the solvent was

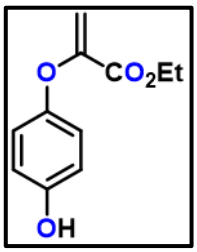
removed under reduced pressure, and purifications were carried out by column chromatography using silica gel (100-200 mesh size) in 20% ethyl acetate in hexane to afford p-spiro epoxide quinones **11a-f.**

2.8: Scale up Synthesis:

For scale-up syntheses **2a** (1.4 equiv., 9.20 mmol, 1.6 g) and **3** (1.4 equiv., 9.20 mmol, 0.921 g) were added to two 100 mL flasks, **NQ** (1 equiv., 6.57 mmol, 1g) were added and the reaction was stirred under blue LED and oxygen atmosphere for 16 h, monitored with TLC. After completion (monitored by TLC) the products were purified by flash chromatography to yield **10a (**1.44 g, 75%) and **11c (**1.08g, 72%) respectively.

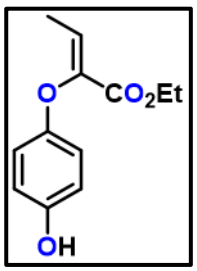
2.9: Characterization Data:

ethyl 2-(4-hydroxyphenoxy)acrylate, 5a:



5a was prepared according to the general procedure **2.4** using **BQ** (0.6 mmol, 64.8 mg) and **1a** (1.32 mmol, 169.1 mg). After column chromatography using silica gel [SiO_2, Hexane/EtOAc (95:5 to 80:20)], the expected product **5a** was obtained as a yellow liquid (111.1 mg, 89% yield). ***^{1}H* NMR** ($CDCl_3$, 400 MHz) δ_H: 6.92 (d, *J* = 8.0 Hz, 2H), 6.81 (d, *J* = 8.0 Hz, 2H), 5.56 (d, *J* = 2.1 Hz, 1H), 5.20 (s, 1H), 4.71 (d, *J* = 2.1 Hz,1H), 4.31 (q, *J* = 8.0 Hz, 2H), 1.33 (t, *J* = 6.0 Hz, 3H) ppm. ***^{13}C* {*^{1}H*} NMR** ($CDCl_3$, 100 MHz) δ_c:163.1, 152.6, 152.1, 148.5, 121.4, 116.4, 101.2, 61.8, 14.2 ppm. FT-IR (Neat) ν_{max} (cm^{-1}) = 3889.44, 2974.78, 1716.21, 1625.22, 1504.85, 1450.50, 1372.85, 1316.81, 1179.88, 1090.01, 1022.08, 963.88, 836.29, 785.79, 708.30. **HRMS (ESI) m/z**: $[M+H]^+$ calcd for $C_{11}H_{13}O_4$ 209.0808 found 209.0810.

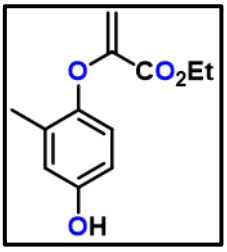
ethyl (Z)-2-(4-hydroxyphenoxy)but-2-enoate, 5b:



5b was prepared according to the general procedure **2.4** using **BQ** (0.6 mmol, 64.8 mg) and **1c** (1.32 mmol, 187.6 mg). After column chromatography on silica gel [SiO_2, Hexane/EtOAc (95:5 to 80:20)], the expected product **5b** was obtained as a yellow liquid (84.0 mg, 63% yield). ***^{1}H* NMR** ($CDCl_3$, 400 MHz) δ_H: 6.80-6.76 (m, 2H), 6.74-6.71 (m,2H), 6.64 (q, *J* =8.0 Hz, 1H), 4.92 (s, 1H), 4.16 (q, *J* = 6.7 Hz, 2H), 1.79 (d, *J* = 8.0 Hz, 3H), 1.20 (t, *J* = 6.0 Hz, 3H) ppm. ***^{13}C* {*^{1}H*} NMR** ($CDCl_3$, 100 MHz) δ_c: 163.4, 151.4, 150.7, 142.7, 130.6, 126.7, 116.2, 116.1, 115.4, 61.2, 14.2, 11.5 ppm. **HRMS (ESI) m/z**: $[M+H]^+$ calcd for $C_{12}H_{14}O_4$ 223.0965 found 223.0971. FT-IR (Neat) ν_{max} (cm^{-1}) = 3296.39, 3171.94, 2975.61,

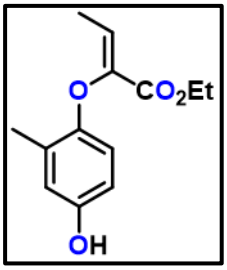
1740.73, 1658.10, 1555.03, 1504.63, 1456.85, 1375.25, 1229.04, 1109.68, 1013.75, 958.78, 847.90, 760.14, 648.79, 587.91, 513.59.

ethyl -2-(4-hydroxy-3-methylphenoxy)acrylate, 5c:



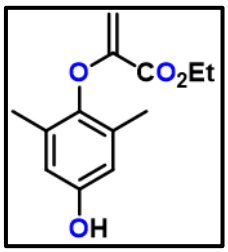
5c was prepared according to the general procedure **2.4** using **BQ_1** (0.6 mmol, 73.2 mg) and **1a** (1.32 mmol, 169.1 mg). After column chromatography on silica gel [SiO_2, Hexane/EtOAc (95:5 to 80:20)], the expected product **5c** was obtained as a dark yellow liquid (86.6 mg, 65% yield). ***^{1}H* NMR** ($CDCl_3$, 400 MHz) δ_H: 6.83 (d, *J* = 2.4 Hz, 1H), 6.78-6.72 (m, 2H), 5.55 (d, *J* = 2.1 Hz, 1H), 4.74 (s, 1H), 4.71 (d, *J* = 4.0 Hz, 1H), 4.31 (q, *J* = 6.7 Hz, 2H), 2.22 (s, 3H), 1.33 (t, *J* = 6.0 Hz, 3H) ppm. ***^{13}C* {*^{1}H*} NMR** ($CDCl_3$, 100 MHz) δ_c: 163.1, 152.1, 150.7, 148.4, 125.4, 122.7, 118.6, 115.8, 101.2, 61.7, 16.0, 14.3 ppm. **HRMS (ESI) m/z**: $[M+H]^+$ calcd for $C_{12}H_{15}O_4$ 223.0965 found 223.0968. **FT-IR (Neat) ν_{max} (cm^{-1}) =** 3423.05, 2927.73, 2123.27, 1715.66, 1624.74, 1501.36, 1374.31, 1316.58, 1176.13, 1100.31, 1011.05, 866.19, 791.13, 702.89, 448.68.

ethyl (Z)-2-(4-hydroxy-3-methylphenoxy)but-2-enoate, 5d:



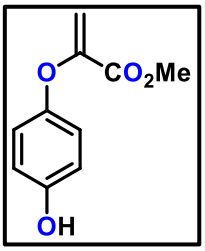
5d was prepared according to the general procedure **2.4** using using **BQ_1** (0.6 mmol, 73.2 mg) and **1c** (1.32 mmol, 187.6 mg). After column chromatography on silica gel [SiO_2, Hexane/EtOAc (95:5 to 80:20)], the expected product **5d** was obtained as a black liquid (100.6 mg, 71% yield). ***^{1}H* NMR** ($CDCl_3$, 400 MHz) δ_H: 6.73-6.65 (m, 3H), 5.87 (q, *J* = 8.0 Hz, 1H), 4.66 (s, 1H), 4.20 (q, *J* = 6.7 Hz, 2H), 2.20 (s, 3H), 2.05 (d, *J* = 8.0 Hz, 3H), 1.21 (t, *J* = 8.0 Hz, 3H) ppm. ***^{13}C* {*^{1}H*} NMR** ($CDCl_3$, 100 MHz) δ_c: 163.6, 151.1, 149.4, 143.4, 125.1, 124.4, 119.6, 115.6, 115.3, 61.0, 16.1, 14.2, 12.8 ppm. **HRMS (ESI) m/z**: $[M+H]^+$ calcd for $C_{13}H_{17}O_4$ 237.1121 found 237.1129. **FT-IR (Neat) ν_{max} (cm^{-1})** = 3416.17, 2928.22, 1706.61, 1497.41, 1341.56, 1235.46, 1160.33, 1092.01, 1019.58, 854.16, 793.92, 567.00, 441.31.

ethyl 2-(4-hydroxy-3,5-dimethylphenoxy)acrylate, 5e:



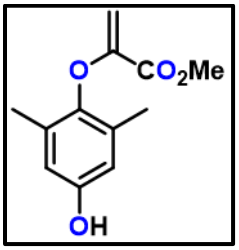
5e was prepared according to the general procedure **2.4** using **BQ_2** (0.6 mmol, 81.69 mg) and **1a** (1.32 mmol, 169.1 mg). After column chromatography on silica gel [SiO_2, Hexane/EtOAc (95:5 to 80:20)], the expected product **5e** was obtained as a yellow liquid (96.3 mg, 68% yield). ***^{1}H* NMR** ($CDCl_3$, 400 MHz) δ_H: 6.68 (s, 2H), 5.53 (d, *J* = 4.0 Hz, 1H), 4.71 (d, *J* = 2.0 Hz, 1H), 4.57 (s, 1H), 4.30 (q, *J* = 6.7 Hz, 2H), 2.22 (s, 6H), 1.33 (t, *J* = 8.0 Hz, 3H) ppm. ***^{13}C* {*^{1}H*} NMR** ($CDCl_3$, 100 MHz) δ_c: 163.1, 152.1, 149.0, 147.8, 124.4, 120.0, 101.1, 61.7, 16.2, 14.3 ppm. **HRMS (ESI) m/z**: $[M+H]^+$ calcd for $C_{13}H_{17}O_4$ 237.1121 found 237.1133. **FT-IR (Neat) ν_{max} (cm^{-1})** = 3492.59, 2930.70, 2121.70, 1722.12, 1624.11, 1477.59, 1375.04, 1313.77, 1171.77, 1018.97, 861.48, 784.82.

methyl -2-(4-hydroxyphenoxy)acrylate, 5f:



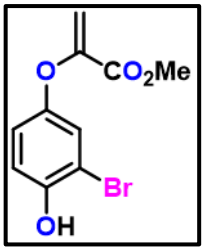
5f was prepared according to the general procedure **2.4** using **BQ** (0.6 mmol, 64.8 mg) and **1b** (1.32 mmol, 150.6 mg). After column chromatography on silica gel [SiO_2, Hexane/EtOAc (95:5 to 80:20)], the expected product **5f** was obtained as a brown viscus liquid (92.0 mg, 79% yield). ***^{1}H* NMR** ($CDCl_3$, 400 MHz) δ_H: 6.90 (d, *J* = 12.0 Hz, 2H), 6.81 (d, *J* = 8.0 Hz, 2H), 5.56 (d, *J* = 4.0 Hz, 1H), 5.45 (s, 1H), 4.70 (d, *J* = 4.0 Hz, 1H), 3.86 (s, 3H) ppm. ***^{13}C* {*^{1}H*} NMR** ($CDCl_3$, 100 MHz) δ_c: 163.7, 152.8, 151.8, 148.2, 121.4, 116.5, 101.3, 52.8 ppm. **HRMS (ESI) m/z**: $[M+H]^+$ calcd for $C_{10}H_{11}O_4$ 195.0652 found 195.0658. **FT-IR (Neat) ν_{max} (cm^{-1})** = 3847.62, 3742.11, 3398.63, 2357.04, 1720.08, 1625.83, 1504.02, 1444.72, 1325.61, 1196.50, 1157.78, 965.44, 836.77, 779.78, 707.06, 517.60.

methyl -2-(4-hydroxy-3,5-dimethylphenoxy)acrylate, 5g:



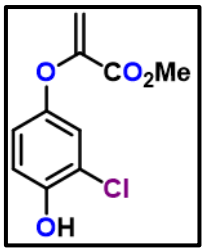
5g was prepared according to the general procedure **2.4** using **BQ_2** (0.6 mmol,81.6 mg) and **1b** (1.32 mmol, 150.6 mg). After column chromatography on silica gel [SiO_2, Hexane/EtOAc (95:5 to 80:20)], the expected product **5g** was obtained as a brown solid (82.4 mg, 62% yield). ***^{1}H* NMR** ($CDCl_3$, 400 MHz) δ_H: 6.68 (s, 2H), 5.55 (d, *J* = 4.0 Hz, 1H), 4.72 (d, *J* = 2.1 Hz, 1H), 4.50 (s, 1H), 3.85 (s, 3H), 2.22 (s, 6H) ppm. ***^{13}C* {*^{1}H*} NMR** ($CDCl_3$, 100 MHz) δ_c: 163.6, 151.9, 149.1, 147.7, 124.5, 120.0, 101.3, 52.6, 16.2 ppm. **HRMS (ESI) m/z**: $[M+H]^+$ calcd for $C_{12}H_{15}O_4$ 223.0965 found 223.0972. **FT-IR (Neat) ν_{max} (cm^{-1})** = 3450.24, 2924.67, 2115.15, 1719.68, 1619.48, 1480.18, 1444.16, 1330.08, 1168.52, 1024.64, 936.09, 871.38, 782.47, 725.04, 590.75.

methyl -2-(3-bromo-4-hydroxyphenoxy)acrylate, 5h:



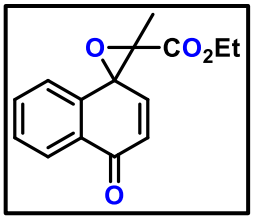
5h was prepared according to the general procedure **2.4** using **BQ_3** (0.6 mmol,112.1mg) and **1b** (1.32 mmol, 150.6 mg). After column chromatography on silica gel [SiO_2, Hexane/EtOAc (95:5 to 80:20)], the expected product **5h** was obtained as a brown viscus liquid (132.3 mg, 73% yield). ***^{1}H* NMR** ($CDCl_3$, 400 MHz) δ_H: 7.19 (d, *J* = 4.0 Hz, 1H), 7.01 (d, *J* = 8.0 Hz, 1H), 6.95 (dd, ^1J = 8 Hz, ^2J = 4 Hz, 1H), 5.66 (d, *J* = 4.0 Hz, 1H), 5.40 (s, 1H), 4.82 (d, *J* = 2.4 Hz, 1H), 3.85 (s, 3H) ppm. ***^{13}C* {*^{1}H*} NMR** ($CDCl_3$, 100 MHz) δ_c: 163.1, 151.3, 149.5, 148.6, 123.4, 120.9, 116.6, 103.0, 52.8 ppm. **HRMS (ESI) m/z**: $[M+H]^+$ calcd for $C_{10}H_{10}BrO_4$ 272.9757 found 272.9758. **FT-IR (Neat) ν_{max} (cm^{-1})** = 3392.21, 2940.06, 1722.69, 1626.88, 1489.83, 1434.23, 1322.61, 1157.79, 1033.47, 969.55, 869.42, 788.39.

methyl-2-(3-chloro-4-hydroxyphenoxy)acrylate, 5i:



5i was prepared according to the general procedure **2.4** using **BQ_4** (0.6 mmol, 85.5 mg) and **1b** (1.32 mmol, 150.6 mg). After column chromatography on silica gel [SiO_2, Hexane/EtOAc (95:5 to 80:20)], the expected product **5i** was obtained as a black liquid (96.0 mg, 70% yield). ***^{1}H* NMR** ($CDCl_3$, 400 MHz) δ_H: 7.05 (d, *J* = 4.0 Hz, 1H), 7.00 (d, *J* = 8.0 Hz, 1H), 6.90 (dd, ^1J = 10 Hz, ^2J = 2Hz, 1H), 5.65 (d, *J* = 4 Hz, 1H), 5.45 (s, 1H), 4.82 (d, *J* = 4 Hz, 1H), 3.85 (s, 3H) ppm. ***^{13}C* {*^{1}H*} NMR** ($CDCl_3$, 100 MHz) δ_c: 163.1, 151.2, 148.5, 148.4, 120.6, 120.2, 116.9, 103.0, 52.80 ppm. **HRMS (ESI) m/z**: $[M+H]^+$calcd for $C_{10}H_{10}ClO_4$ 229.0262 found 229.0258. . **FT-IR (Neat) ν_{max} (cm^{-1})** = 3405.63, 2949.39, 1722.96, 1627.04, 1493.52, 1433.40, 1323.73, 1156.64, 1047.59, 971.22, 871.50, 788.64, 727.51, 515.28.

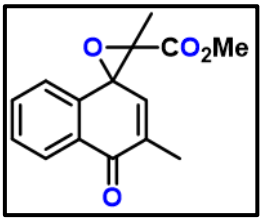
ethyl 3'-methyl-4-oxo-4H-spiro[naphthalene-1,2'-oxirane]-3'-carboxylate, 6a:



6a was prepared according to the general procedure **2.5** using using **NQ** (0.6 mmol, 94.8 mg) and **1a** (1.32 mmol, 169.1 mg). After column chromatography on silica gel [SiO_2, Hexane/EtOAc (95:5 to 80:20)], the expected product **6a** was obtained as a black solid (125.5 mg, 81% yield). ***^{1}H* NMR** ($CDCl_3$, 400 MHz) δ_H: 8.15-8.12 (m, 1H), 7.54- 7.42 (m, 3H), 6.91 (d, *J* = 8 Hz, 1H), 6.70 (d, *J* = 12 Hz, 1H), 4.04-3.94 (m, 2H), 1.77 (s, 3H), 0.94 (t, *J* = 6 Hz, 3H) ppm. ***^{13}C* {*^{1}H*} NMR** ($CDCl_3$, 100 MHz) δ_c: 184.0, 167.7, 144.6, 137.2, 134.4, 133.0, 132.3, 128.9, 127.3, 124.2, 70.4, 61.7, 61.6, 18.1, 13.9 ppm. **HRMS (ESI) m/z**: $[M+H]^+$ calcd for $C_{15}H_{15}O_4$ 259.0965 found 259.0954. **FT-IR (Neat) ν_{max} (cm^{-1})** = 3403.29, 2922.20,

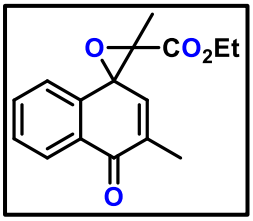
1732.91, 1662.64, 1594.33, 1454.80, 1372.42, 1261.61, 1121.33, 1009.33, 854.80, 762.36, 535.33, 456.29.

methyl 3,3'-dimethyl-4-oxo-4H-spiro[naphthalene-1,2'-oxirane]-3'-carboxylate, 6b:



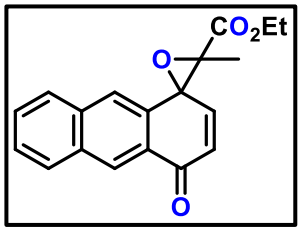
6b was prepared according to the general procedure **2.5** using **NQ1** (0.6 mmol, 103.3 mg) and **1b** (1.32 mmol, 150.6 mg). After column chromatography on silica gel [SiO_2, Hexane/EtOAc (95:5 to 80:20)], the expected product **6b** was obtained as a yellow liquid (113.1 mg, 73% yield). ***^{1}H* NMR** ($CDCl_3$, 400 MHz) δ_H: 8.11 (dd, ^1J = 7.6 Hz, ^2J =1.6 Hz, 1H), 7.58-7.49 (m, 2H), 7.38- 7.36 (m, 1H), 6.46 (d, J = 1.4 Hz, 1H), 3.79 (s, 3H), 1.93 (d, J = 1.4Hz, 3H), 1.45 (s, 3H) ppm. ***^{13}C* {*^{1}H*} NMR** ($CDCl_3$, 100 MHz) δ_c: 184.3, 169.6, 156.7, 137.1, 134.2, 131.3, 130.9, 128.7, 127.0, 125.7, 66.7, 65.7, 52.8, 18.0, 16.0 ppm. **HRMS (ESI) m/z**: $[M+H]^+$ calcd for $C_{15}H_{15}O_4$ 259.0965 found 259.0971. **FT-IR (Neat) ν_{max} (cm^{-1})** = 2938.55, 1742.25, 1658.06, 1600.21, 1446.16, 1370.92, 1266.86, 1124.24, 1024.49, 970.86, 876.00, 773.46, 655.03, 513.59.

ethyl 3,3'-dimethyl-4-oxo-4H-spiro[naphthalene-1,2'-oxirane]-3'-carboxylate, 6c:



6c was prepared according to the general procedure **2.5** using **NQ_1** (0.6 mmol, 103.3 mg) and **1a** (1.32 mmol, 169.1 mg). After column chromatography on silica gel [SiO_2, Hexane/EtOAc (95:5 to 80:20)], the expected product **6c** was obtained as a yellow liquid (109.4 mg, 67% yield). ***^{1}H* NMR** ($CDCl_3$, 400 MHz) δ_H: 8.12 (dd, ^1J = 8 Hz, ^{2}J = 4 Hz, 1H), 7.58- 7.49 (m, 2H), 7.37 (dd, ^1J = 7.8 Hz, ^2J = 1 Hz, 1H), 6.46 (d, J = 1.5 Hz, 1H), 4.28-4.19 (m, 2H), 1.95 (d, J = 1.5 Hz, 3H), 1.45 (s, 3H), 1.30 (t, J = 8 Hz, 3H) ppm. ***^{13}C* {*^{1}H*} NMR** ($CDCl_3$, 100 MHz) δ_c: 184.4, 169.2, 157.0, 137.2, 134.2, 131.1, 130.9, 128.7, 127.0, 125.7, 66.6, 65.8, 62.0, 18.2, 16.0, 14.1 ppm. **HRMS (ESI) m/z**: $[M+H]^+$ calcd for $C_{16}H_{17}O_4$ 273.1121 found 273.1124. **FT-IR (Neat) ν_{max} (cm^{-1})** = 2927.63, 1737.78, 1658.87, 1599.80, 1453.72, 1374.50, 1262.72, 1123.65, 1015.51, 874.83, 776.53, 656.86, 511.92, 451.49.

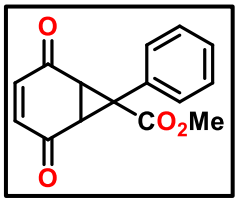
ethyl 3'-methyl-4-oxo-4H-spiro[anthracene-1,2'-oxirane]-3'-carboxylate, 7a:



7a was prepared according to the general procedure **2.5** using **AQ** (0.6 mmol, 124.9 mg) and **1a** (1.32 mmol, 169.1 mg). After column chromatography on silica gel [SiO_2, Hexane/EtOAc (95:5 to 80:20)],

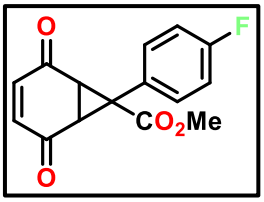
the expected product **7a** was obtained as a black solid (109.1 mg, 59% yield). ***¹H* NMR** ($CDCl_3$, 400 MHz) δ_H: 8.68 (s, 1H), 8.00 (d, *J* = 8 Hz, 1H), 7.92 (s, 1H), 7.86 (d, *J* = 8 Hz, 1H), 7.62-7.53 (m, 2H, 6.97 (d, *J* = 8 Hz, 1H), 6.76 (d, *J* = 12 Hz, 1H), 3.95- 3.86 (m, 2H), 1.80 (s, 3H), 0.80 (t, *J* = 8 Hz, 3H) ppm. ***¹³C* {*¹H*} NMR** ($CDCl_3$, 100 MHz) δ_C: 184.5, 167.8, 145.0, 134.8, 134.4, 132.4, 131.7, 129.9, 129.8, 129.1, 129.1, 128.3, 127.4, 124.1, 71.0, 61.9, 61.7, 17.9, 13.8 ppm. **HRMS (ESI) m/z**: $[M+H]^+$ calcd for $C_{19}H_{17}O_4$ 309.1121 found 309.1118. **FT-IR (Neat) ν_{max} (cm^{-1})** = 2926.10, 1733.89, 1664.19, 1619.76, 1450.13, 1378.22, 1263.77, 1127.12, 1016.77, 857.95, 747.38, 471.47.

methyl 2,5-dioxo-7-phenylbicyclo[4.1.0]hept-3-ene-7-carboxylate, 8a:



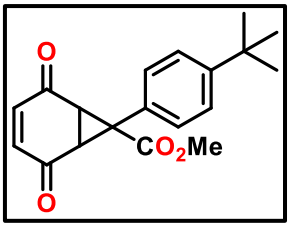
8a was prepared according to the general procedure **2.6** using **BQ** (0.6 mmol, 65 mg) and **1a** (0.84 mmol, 147 mg). After column chromatography on silica gel [SiO_2, Hexane/EtOAc (95:5 to 80:20)], the expected product **8a** was obtained as a Pale-Yellow viscous liquid. (122.1 mg, 80%) ***¹H* NMR** ($CDCl_3$, 400 MHz) δ_H 7.78 (d, *J*=8Hz, 1H), 7.45 (dd, ^1J=7.4Hz, ^2J=1.4Hz, 1H), 7.21-7.16 (m, 3H), 7.10-7.08 (m, 2H), 4.01 (s, 2H), 3.83 (s, 3H) ppm. ***¹³C* {*¹H*} NMR** ($CDCl_3$, 100 MHz) δ_C 190.8, 166.7, 138.4, 134.4, 132.5, 130.6, 123.7, 53.6, 47.6, 36.6 ppm. FT-IR (Neat) ν_{max} (cm^{-1}) = 2916.34, 1727.68, 1666.82, 1456.76, 1377.40, 1227.82, 1083.87, 800.24. HRMS (ESI) m/z calcd for $C_{15}H_{13}O_4$ $[M + H]^+$ 257.0814, found 257.0808.

methyl 7-(4-fluorophenyl)-2,5-dioxobicyclo[4.1.0]hept-3-ene-7-carboxylate, 8b:



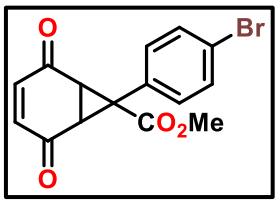
8b was prepared according to the general procedure **2.6** using **BQ** (0.6 mmol, 65 mg) and **2b** (0.84 mmol, 163 mg). After column chromatography on silica gel [SiO_2, Hexane/EtOAc (95:5 to 80:20)], the expected product **8b** was obtained as a Pale-Yellow viscous liquid. (124 mg, 76%). ***¹H* NMR** ($CDCl_3$, 400 MHz) δ_H 7.11-7.07 (m, 2H), 6.99-6.95 (m, 2H), 6.19 (s, 2H), 3.69 (s, 3H), 3.28 (s, 2H) ppm. ***¹³C* {*¹H*} NMR** ($CDCl_3$, 100 MHz) δ_C 191.6, 170.4, 164.0, 139.2, 133.0, 132.9 (d, *J*=Hz), 127.0, 116.2 (d, *J*=2Hz), 53.9, 42.2, 36.7 ppm. ***¹⁹F* NMR** ($CDCl_3$, 376 MHz) δ_F -111.73, -111.75 ppm. FT-IR (Neat) ν_{max} (cm^{-1}) = 3422.28, 2918.29, 1726.12, 1670.33, 1454.76, 1372.36, 1208.90, 1018.71, 810.78, 504.97. HRMS (ESI) m/z calcd for $C_{15}H_{12}FO_4$ $[M + H]^+$ 275.0720, found 275.0708.

methyl 7-(4-(tert-butyl)phenyl)-2,5-dioxobicyclo[4.1.0]hept-3-ene-7-carboxylate, 8c:



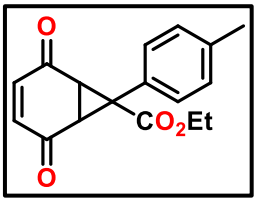
8c was prepared according to the general procedure **2.6** using **BQ** (0.6 mmol, 65 mg) and **2c** (0.84 mmol, 194 mg). After column chromatography on silica gel [SiO_2, Hexane/EtOAc (95:5 to 80:20)], the expected product **8c** was obtained as a Pale-Yellow viscous liquid. (148 mg, 79%). ***^{1}H* NMR** ($CDCl_3$, 400 MHz) δ_H : 7.27-7.26 (m, 1H), 7.26-7.25 (m, 1H), 7.01 (d, *J* = 8 Hz, 2H), 6.13 (s, 2H), 3.68 (s, 3H), 3.26 (s, 2H), 1.27 (s, 9H) ppm. ***^{13}C* {*^{1}H*} NMR** ($CDCl_3$, 100 MHz) δ_C 191.9, 170.8, 151.9, 138.9, 130.9, 127.8, 125.9, 53.8, 42.9, 36.8, 34.8, 31.3 ppm. FT-IR (Neat) ν_{max} (cm^{-1}) = 3229.95, 2914.96, 2851.17, 1728.87, 1667.92, 1463.16, 1389.35, 1241.30, 1175.48, 1100.65, 1050.50, 986.34, 713.89. HRMS (ESI) m/z calcd for $C_{19}H_{21}O_4$ $[M + H]^+$ 313.1434, found 313.1451.

methyl 7-(4-bromophenyl)-2,5-dioxobicyclo[4.1.0]hept-3-ene-7-carboxylate, 8d:



8d was prepared according to the general procedure **2.6** using **BQ** (0.6 mmol, 65 mg) and **2d** (0.84 mmol, 214.3 mg). After column chromatography on silica gel [SiO_2, Hexane/EtOAc (95:5 to 80:20)], the expected product **8d** was obtained as a Pale-Yellow viscous liquid. (139.4 mg, 70%). ***^{1}H* NMR** ($CDCl_3$, 400 MHz) δ_H 7.41 (d, *J* = 8Hz, 2H), 6.98 (d, *J* = 8Hz, 1H), 6.20 (s, 2H), 3.68 (s, 3H), 3.28 (s, 2H) ppm. ***^{13}C* {*^{1}H*} NMR** ($CDCl_3$, 100 MHz) δ_C 191.4, 170.1, 139.2, 132.7, 132.3, 130.2, 123.3, 54.0, 42.3, 36.7 ppm. FT-IR (Neat) ν_{max} (cm^{-1}) = 3224.67, 2946.10, 1725.87, 1652.54, 1581.23, 1426.74, 1294.89, 1146.11, 1078.46, 1013.23, 760.31, 667.91, 533.66, 451.23. HRMS (ESI) m/z calcdfor $C_{15}H_{11}BrO_4$ $[M + H]^+$ 334.9913, found 334.9917.

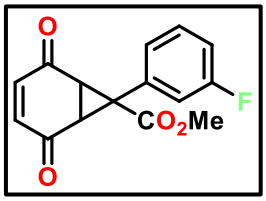
ethyl 2,5-dioxo-7-(p-tolyl)bicyclo[4.1.0]hept-3-ene-7-carboxylate, 8e:



8e was prepared according to the general procedure **2.6** using **BQ** (0.6 mmol, 65 mg) and **2e** (0.84 mmol, 171.5 mg). After column chromatography on silica gel [SiO_2, Hexane/EtOAc (95:5 to 80:20)], the expected product **8e** was obtained as a Pale-Yellow viscous liquid. (111.7 mg, 66%). ***^{1}H* NMR** ($CDCl_3$, 400 MHz) δ_H 7.40 (d, *J*= 8Hz, 2H), 7.18 (d, *J*= 8Hz, 2H), 6.54 (s, 2H), 4.06 (q, *J* = 8Hz, 2H), 2.88(s, 2H), 2.34 (s, 3H), 1.16 (t, *J*= 6Hz, 3H) ppm. ***^{13}C* {*^{1}H*} NMR** ($CDCl_3$, 100 MHz) δ_C 191.9, 190.6, 149.0, 134.5, 131.0, 130.9, 116.4, 116.2, 53.5, 37.4, 36.2, 16.5 ppm. FT-IR (Neat) ν_{max} (cm^{-1}) = 3237.49, 2916.93,

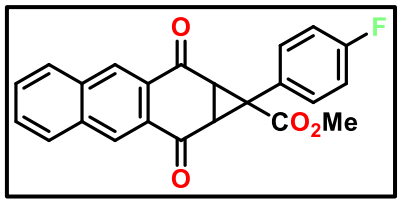
1707.28, 1455.55, 1380.74, 1253.27, 1180.04, 1083.84, 1028.69, 801.83, 749.92, 689.24, 620.96, 478.11. HRMS (ESI) m/z calcd for $C_{17}H_{17}O_4$ $[M + H]^+$ 285.1121, found 285.1118.

methyl 7-(3-fluorophenyl)-2,5-dioxobicyclo[4.1.0]hept-3-ene-7-carboxylate, 8f:



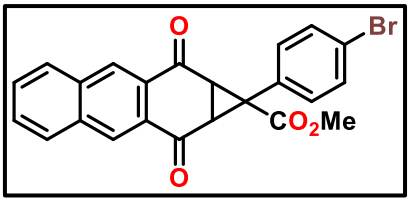
8f was prepared according to the general procedure **2.6** using **BQ** (0.6 mmol, 65 mg) and **2f** (0.84 mmol, 163 mg). After column chromatography on silica gel [SiO_2, Hexane/EtOAc (95:5 to 80:20)], the expected product **8f** was obtained as a Pale-Yellow viscous liquid. (102.7 mg, 63%). ***^{1}H* NMR** ($CDCl_3$, 400 MHz) δ_H 7.35-7.33 (m, 1H), 7.30 (dt, ^1J= 8Hz, ^2J=2 Hz, 1H), 7.23 (dt, ^1J= 10.7Hz, ^2J=2 Hz, 1H), 7.09-7.05 (m, 1H), 6.57 (s, 2H), 3.64 (s, 3H), 2.90 (s, 2H) ppm. ***^{13}C* {*^{1}H*} NMR** ($CDCl_3$, 100 MHz) δ_C 190.8, 138.4, 130.9 (J = 7 Hz), 124.5 (J = 3 Hz), 116.6 (J = 21 Hz), 116.2(J = 23 Hz), 53.7, 36.7 ppm. ***^{19}F* NMR** ($CDCl_3$, 376 MHz) δ_F -111.00, -111.01 ppm. FT-IR (Neat) ν_{max} (cm^{-1}) = 3297.00, 2916.67, 2853.05, 1723.44, 1680.95, 1589.55, 1440.87, 1373.68, 1253.73, 1159.59, 931.60, 870.39, 794.22, 684.77, 517.08. HRMS (ESI) m/z calcd for $C_{15}H_{12}FO_4$ $[M + H]^+$ 275.0714, found 275.0611.

methyl 1-(4-fluorophenyl)-2,9-dioxo-1a,2,9,9a-tetrahydro-1H-cyclopropa[b]anthracene-1-carboxylate, 9a:



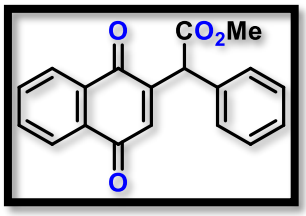
9a was prepared according to the general procedure **2.6** using **AQ** (0.6 mmol, 124.9 mg) and **2b** (0.84 mmol, 163 mg). After column chromatography on silica gel [SiO_2, Hexane/EtOAc (95:5 to 80:20)], the expected product **9a** was obtained as a Dull Yellow solid. (149.4 mg, 67%) ***^{1}H* NMR** ($CDCl_3$, 400 MHz) δ_H 8.34 (s, 2H), 7.89 (dd, ^1J = 6.7Hz, ^2J =3Hz, 2H), 7.61 (dd, ^1J =8Hz, ^2J = 4Hz, 2H), 7.14 (q, J = 4Hz, 2H), 6.63 (t, J = 8Hz, 2H), 3.70 (s, 3H), 3.57 (s, 2H) ppm. ***^{13}C* {*^{1}H*} NMR** ($CDCl_3$, 100 MHz) δ_C 190.4, 174.1, 134.8, 132.9, 132.9 130.0, 129.7, 129.7, 128.6, 128.5, 128.4, 115.8, 115.6, 115.6, 115.4, 72.3, 53.8, 53.3, 38.5 ppm. ***^{19}F* NMR** ($CDCl_3$, 376 MHz) δ_F -112.17, -112.18, -112.19, ppm. FT-IR (Neat) ν_{max} (cm^{-1}) = 2947.70, 1731.90, 1674.60, 1609.35, 1506.45, 1446.51, 1394.83, 1284.25, 1208.53, 1087.13, 894.37, 825.06, 753.85, 535.08, 476.38. HRMS (ESI) m/z calcd for $C_{23}H_{16}FO_4$ $[M + H]^+$ 375.1027, found 375.1006.

methyl 1-(4-bromophenyl)-2,9-dioxo-1a,2,9,9a-tetrahydro-1H-cyclopropa[b]anthracene-1-carboxylate, 9b:



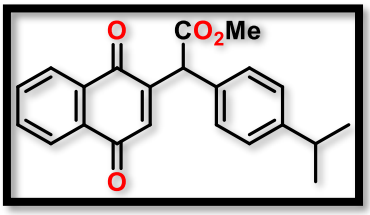
9b was prepared according to the general procedure **2.6** using **AQ** (0.6 mmol, 124.9 mg) and **2d** (0.84 mmol, 214.3 mg). After column chromatography on silica gel [SiO_2, Hexane/EtOAc (95:5 to 80:20)], the expected product **9b** was obtained as a Dull Yellow solid. Dull Yellow solid. (157.9 mg, 61%) ***¹H* NMR** ($CDCl_3$, 400 MHz) δ_H 8.36 (s, 2H), 7.92 (dd, ^1J = 8Hz, ^2J =4Hz, 2H), 7.61 (dd, ^1J =4Hz, ^2J = 4Hz, 2H), 7.10-7.02 (m, 4H), 3.70 (s, 3H), 3.57 (s, 2H) ppm. ***¹³C* {*¹H*} NMR** ($CDCl_3$, 100 MHz) δ_C 134.9, 132.7, 131.9, 131.6, 130.2, 129.8, 128.8, 128.4, 38.4 ppm. FT-IR (Neat) ν_{max} (cm^{-1}) = 3225.67, 2924.54, 1679.07, 1451.66, 1053.32, 796.18, 442.90. HRMS (ESI) m/z calcd for $C_{23}H_{16}BrO_4$ $[M + H]^+$ 435.0154, found 435.0147.

methyl 2-(1,4-dioxo-1,4-dihydronaphthalen-2-yl)-2-phenylacetate, 10a:



10a was prepared according to the general procedure **2.6** using **NQ** (0.6 mmol, 91 mg) and **2a** (0.84 mmol, 147 mg). After column chromatography on silica gel [SiO_2, Hexane/EtOAc (95:5 to 80:20)], the expected product **10a** was obtained as a Yellow semi-solid. (213.2 mg, 79%) ***¹H* NMR** ($CDCl_3$, 400 MHz) δ_H 8.12-8.10 (m, 1H), 8.06-8.04 (m, 1H), 7.75-7.73 (m, 2H), 7.42-7.36 (m, 3H), 7.32-7.30 (m, 2H), 6.57-6.56 (d, J=4Hz, 1H), 5.18 (s, 1H),3.76 (s, 3H) ppm. ***¹³C* {*¹H*} NMR** ($CDCl_3$, 100 MHz) δ_C 185.1, 184.6, 171.4, 148.8, 136.9, 134.4, 134.2, 134.1, 132.1, 132.0, 129.8, 129.4, 129.2, 128.5, 128.3, 127.0, 126.4, 52.9, 51.3 ppm. FT-IR (Neat) ν_{max} (cm^{-1}) = 3230.83, 2950.75, 1674.79, 1441.18, 1055.04, 798.66, 446.38. HRMS (ESI) m/z calcd for $C_{19}H_{15}O_4$ $[M + H]^+$ 307.0965, found 307.0970.

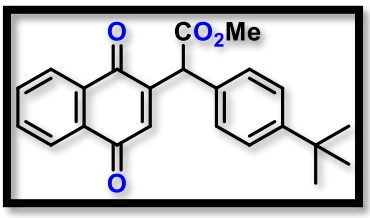
methyl 2-(1,4-dioxo-1,4-dihydronaphthalen-2-yl)-2-(4-isopropylphenyl)acetate, 10b:



10b was prepared according to the general procedure **2.6** using **NQ** (0.6 mmol, 91 mg) and **2p** (0.84 mmol, 194 mg). After column chromatography on silica gel [SiO_2, Hexane/EtOAc (95:5 to 80:20)], the expected product **10c** was obtained as a Yellow semi-solid. (160 mg, 74%). ***¹H* NMR** ($CDCl_3$, 400 MHz)

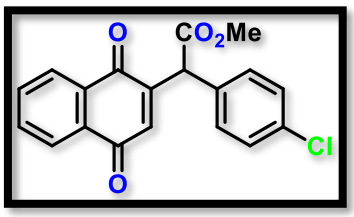
δ_H 8.12-8.10 (m, 1H), 8.05 (dd, ^1J=8Hz, ^2J=4Hz, 1H), 7.75-7.73 (m, 2H), 7.23 (q, J=8Hz, 4H), 6.58 (s, 1H), 5.14 (s, 1H), 2.92 (q, J= 8 Hz, 1H), 3.75 (s, 3H), 1.27 (s, 3H), 1.25 (s, 3H) ppm. ***^{13}C*** {***^{1}H***} **NMR** ($CDCl_3$, 100 MHz) δ_C 185.2, 184.7, 171.6, 149.2, 149.0, 136.8, 134.1, 134.0, 132.2, 132.1, 131.5, 129.1, 127.5, 127.0, 126.4, 52.9, 50.9, 33.9, 24.0 ppm. FT-IR (Neat) ν_{max} (cm^{-1}) = 2920.63, 1680.03, 1615.01, 1448.69, 1383.62, 1240.84, 1147.40, 1012.69, 904.58, 811.21, 738.89, 566.18, 473.70. HRMS (ESI) m/z calcd for $C_{22}H_{21}O_4$ $[M + H]^+$ 349.1434, found 349.1441.

methyl 2-(4-(tert-butyl)phenyl)-2-(1,4-dioxo-1,4-dihydronaphthalen-2-yl)acetate, 10c:



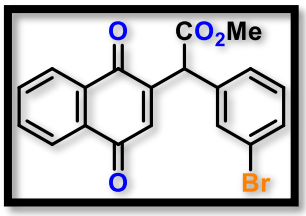
10c was prepared according to the general procedure **2.6** using **NQ** (0.6 mmol, 91 mg) and **2c** (0.84 mmol, 194 mg). After column chromatography on silica gel [SiO_2, Hexane/EtOAc (95:5 to 80:20)], the expected product **10c** was obtained as a Yellow semi-solid. (160 mg, 74%). ***^{1}H*** **NMR** ($CDCl_3$, 400 MHz) δ_H 8.13-8.10 (m, 1H), 8.06-8.04 (m, 1H), 7.75-7.73 (m, 2H), 7.41 (d, J=8Hz, 2H), 7.22 (d, J=8Hz, 2H), 6.59 (s, 1H), 5.15 (s, 1H), 3.76 (s, 3H), 1.33 (s, 9H) ppm. ***^{13}C*** {***^{1}H***} **NMR** ($CDCl_3$, 100 MHz) δ_C 151.4, 136.9, 134.1, 134.0, 128.8, 127.0, 126.4, 52.9, 50.9, 34.8, 31.4 ppm. FT-IR (Neat) ν_{max} (cm^{-1}) = 3227.81, 2917.31, 2853.59, 1723.69, 1600.00, 1456.99, 1257.11, 1172.29, 1089.69, 795.40, 721.00, 660.78, 441.81. HRMS (ESI) m/z calcd for $C_{23}H_{23}O_4$ $[M + H]^+$ 363.1591, found 363.1588.

methyl 2-(4-chlorophenyl)-2-(1,4-dioxo-1,4-dihydronaphthalen-2-yl)acetate, 10d:



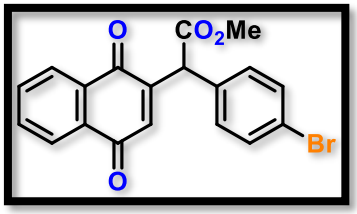
10d was prepared according to the general procedure **2.6** using **NQ** (0.6 mmol, 91 mg) and **2g** (0.84 mmol, 176.9 mg). After column chromatography on silica gel [SiO_2, Hexane/EtOAc (95:5 to 80:20)], the expected product **10d** was obtained as a Yellow semi-solid. (179.8 mg, 88%). ***^{1}H*** **NMR** ($CDCl_3$, 400 MHz) δ_H 8.12-8.07 (m, 1H), 8.06-8.05 (m, 1H), 7.75 (dd, ^1J=6Hz, ^2J=2Hz, 2H), 7.38 (d, J=8Hz, 2H), 7.28-7.26 (m, 2 H), 6.59 (s, 1H), 5.15 (s, 1H), 3.77 (s, 3H) ppm. ***^{13}C*** {***^{1}H***} **NMR** ($CDCl_3$, 100 MHz) δ_C 184.9, 184.3, 171.0, 148.2, 136.7, 134.6, 134.3, 134.1, 133.0, 132.1, 131.9, 130.6, 129.6, 127.0, 126.5, 53.1, 50.6 ppm. HRMS (ESI) m/z calcd for $C_{19}H_{14}ClO_4$ $[M + H]^+$ 341.0575, found 341.0577.

methyl 2-(3-bromophenyl)-2-(1,4-dioxo-1,4-dihydronaphthalen-2-yl)acetate, 10e:



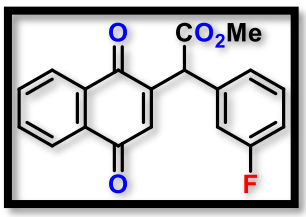
10e was prepared according to the general procedure **2.6** using **NQ** (0.6 mmol, 91 mg) and **2h** (0.84 mmol, 214.3 mg). After column chromatography on silica gel [SiO_2, Hexane/EtOAc (95:5 to 80:20)], the expected product **10e** was obtained as a Yellow semi-solid. (180.2 mg, 78%). ***¹H* NMR** ($CDCl_3$, 400 MHz) δ_H 8.12-8.07 (m, 1H), 8.06 (dd, ^1J=4Hz, ^2J=4Hz, 1H), 7.76 (dd, ^1J=8Hz, ^2J=4Hz, 2H), 7.51-7.49 (m, 2H), 7.28-7.27 (m, 2H), 6.61 (s, 1H), 5.15 (s, 1H), 3.77 (s, 3H) ppm. ***¹³C* {*¹H*} NMR** ($CDCl_3$, 100 MHz) 167.5, 138.3, 136.8, 136.0, 134.3, 134.2, 132.4, 132.4, 132.2, 131.9, 131.7, 130.9, 129.9, 128.4, 127.8, 127.1, 126.5, 122.4, 53.1, 50.7 ppm. FT-IR (Neat) ν_{max} (cm^{-1}) = 2916.61, 1727.73, 1591.98, 1455.57, 1375.72, 1204.29, 1071.99, 1018.47, 789.98, 685.00, 433.36. HRMS (ESI) m/z calcd for $C_{19}H_{14}BrO_4$ [M + H]$^+$ 385.0070, found 385.0074.

methyl 2-(4-bromophenyl)-2-(1,4-dioxo-1,4-dihydronaphthalen-2-yl)acetate, 10f:



10f was prepared according to the general procedure **2.6** using **NQ** (0.6 mmol, 91 mg) and **2d** (0.84 mmol, 214.3 mg). After column chromatography on silica gel [SiO_2, Hexane/EtOAc (95:5 to 80:20)], the expected product **10f** was obtained as a Yellow semi-solid. (195.4 mg, 85%). ***¹H* NMR** ($CDCl_3$, 400 MHz) δ_H 8.11-8.04 (m, 2H), 7.76-7.74 (m, 2H), 7.53 (d, J=8Hz, 2H), 7.21 (d, J=8Hz, 2H), 6.59 (s, 1H), 5.14 (d, J=4Hz, 1H), 3.76 (s, 3H) ppm. ***¹³C* {*¹H*} NMR** ($CDCl_3$, 100 MHz) δ_C 184.8, 184.3, 170.9, 148.1, 136.7, 134.3, 134.1, 133.5, 132.6, 132.1, 131.9, 130.9, 127.0, 126.4, 122.7, 53.1, 50.6 ppm. HRMS (ESI) m/z calcd for $C_{19}H_{14}BrO_4$ [M + H]$^+$ 385.0070, found 385.0077.

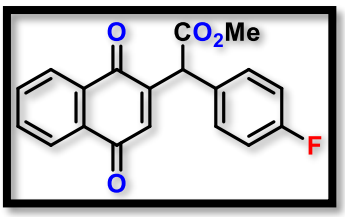
methyl 2-(1,4-dioxo-1,4-dihydronaphthalen-2-yl)-2-(3-fluorophenyl)acetate, 10g:



10g was prepared according to the general procedure **2.6** using **NQ** (0.6 mmol, 91 mg) and **2f** (0.84 mmol, 163 mg). After column chromatography on silica gel [SiO_2, Hexane/EtOAc (95:5 to 80:20)], the expected product **10g** was obtained as a Yellow semi-solid. (149 mg, 77%). ***¹H* NMR** ($CDCl_3$, 400 MHz) δ_H 8.12-8.10 (m, 1H), 8.07-8.04 (m, 1H), 7.75 (dd, ^1J=6Hz, ^2J=6Hz, 2H), 7.40-7.37 (m, 1H), 7.12-7.08 (m,

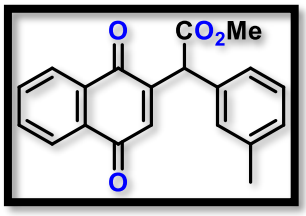
1H), 7.07-7.04 (m, 2H), 6.59 (s, 1H), 5.18 (s, 1H), 3.77 (s, 3H) ppm. ***^{13}C*** {***^{1}H***} **NMR** ($CDCl_3$, 100 MHz) δ_C 184.88, 184.32, 170.9, 164.5, 162.0, 148.1, 136.8, 136.7, 134.3, 134.1, 132.1, 131.9, 131.0 130.9, 127.1, 126.5, 124.9 (J = 3 Hz), 116.3 (J = 22 Hz), 115.6 (J = 20 Hz), 53.1, 50.9 (J = 1 Hz) ppm. ***^{19}F*** **NMR** ($CDCl_3$, 376 MHz) δ_F -111.39, -111.41, -111.41, ppm. HRMS (ESI) m/z calcd for $C_{19}H_{14}FO_4$ $[M + H]^+$ 325.0871, found 325.0878.

methyl 2-(1,4-dioxo-1,4-dihydronaphthalen-2-yl)-2-(4-fluorophenyl)acetate, 10h:



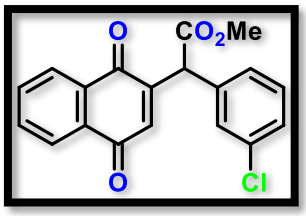
10h was prepared according to the general procedure **2.6** using **NQ** (0.6 mmol, 91 mg) and **2b** (0.84 mmol, 163 mg). After column chromatography on silica gel [SiO_2, Hexane/EtOAc (95:5 to 80:20)], the expected product **10h** was obtained as a Yellow semi-solid. (159.2 mg, 82%). ***^{1}H*** **NMR** ($CDCl_3$, 400 MHz) δ_H 8.12-8.10 (m, 1H), 8.07-8.04 (m, 1H), 7.75 (dd, ^1J=6Hz, ^2J J=6Hz, 2H), 7.32-7.29 (m, 2H), 7.09 (t, J=10Hz, 2H), 6.59 (d, J=4Hz, 1H), 5.16 (s, 1H), 3.76 (s, 3H) ppm. ***^{13}C*** {***^{1}H***} **NMR** ($CDCl_3$, 100 MHz) δ_C 184.9, 184.4, 171.3, 161.5, 148.5, 136.7, 134.2 (J = 15 Hz), 130.9 (J = 8 Hz), 127.0, 126.4, 116.4 (J = 21 Hz), 53.0, 50.5 ppm. ***^{19}F*** **NMR** ($CDCl_3$, 376 MHz) δ_F -113.45 ppm. FT-IR (Neat) ν_{max} (cm^{-1}) = 3234.53, 2915.54, 1730.99, 1657.44, 1591.82, 1455.16, 1300.30, 1257.67, 1149.63, 1086.89, 1020.96, 799.67, 668.95, 578.47, 502.89. HRMS (ESI) m/z calcd for $C_{19}H_{14}FO_4$ $[M + H]^+$ 325.0871, found 325.0880.

methyl 2-(1,4-dioxo-1,4-dihydronaphthalen-2-yl)-2-(m-tolyl)acetate, 10i:



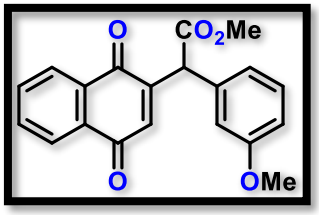
10i was prepared according to the general procedure **2.6** using **NQ** (0.6 mmol, 91 mg) and **2i** (0.84 mmol, 159.7 mg). After column chromatography on silica gel [SiO_2, Hexane/EtOAc (95:5 to 80:20)], the expected product **10i** was obtained as a Yellow semi-solid. (134.7 mg, 71%). ***^{1}H*** **NMR** ($CDCl_3$, 400 MHz) δ_H 8.12-8.09 (m, 1H), 8.05-8.03 (m, 1H), 7.74-7.72 (m, 2H), 7.30-7.26 (m,1H), 7.16 (d, J=8Hz 1H), 7.10 (d, J=8Hz 2H), 6.57(s, 1H), 5.14 (s, 1H), 3.76 (s, 3H), 2.36 (s, 3H) ppm. ***^{13}C*** {***^{1}H***} **NMR** ($CDCl_3$, 100 MHz) δ_C 185.1, 184.6, 171.5, 166.0, 162.5, 148.8, 139.2, 138.7, 136.9, 134.2, 134.2, 134.0, 133.1, 132.1, 132.0, 129.8, 129.3, 129.3, 128.9, 128.6, 128.1, 127.0, 126.4, 126.2, 125.3, 52.9, 52.8, 52.3, 51.2, 21.6 ppm. FT-IR (Neat) ν_{max} (cm^{-1}) = 2922.04, 1723.71, 1652.19, 1590.13, 1432.99, 1295.17, 1228.86, 1148.67, 1014.17, 928.68, 766.64, 692.94, 536.29, 446.39. HRMS (ESI) m/z calcd for $C_{20}H_{17}O_4$ $[M + H]^+$ 321.1049, found 321.1074.

methyl 2-(3-chlorophenyl)-2-(1,4-dioxo-1,4-dihydronaphthalen-2-yl)acetate, 10j:



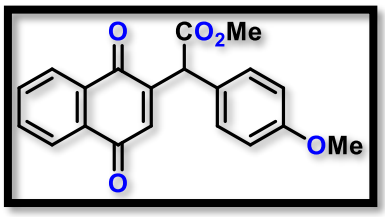
10j was prepared according to the general procedure **2.6** using **NQ** (0.6 mmol, 91 mg) and **2k** (0.84 mmol, 176.9 mg). After column chromatography on silica gel [SiO_2, Hexane/EtOAc (95:5 to 80:20)], the expected product **10j** was obtained as a Yellow semi-solid. (149.2 mg, 73%). ***^{1}H* NMR** ($CDCl_3$, 400 MHz) δ_H 8.11-8.09 (m, 1H), 8.07-8.05 (m, 1H), 7.76 (dd, ^1J=8Hz, ^2J=4Hz, 2H), 7.34 (dd, ^1J=6Hz, ^2J=2Hz, 3H), 7.22-7.20 (m,1 H), 6.60 (s, 1H), 5.15 (s, 1H), 3.77 (s, 3H) ppm. ***^{13}C* {*^{1}H*} NMR** ($CDCl_3$, 100 MHz) δ_C 184.9, 184.3, 170.8, 148.0, 136.8, 136.4, 135.2, 134.3, 134.1, 132.1, 131.9, 130.6, 129.3, 128.8, 127.4, 127.0, 126.5, 53.1, 50.8 ppm. FT-IR (Neat) ν_{max} (cm^{-1}) = 2950.06, 1727.93, 1651.88, 1582.62, 1430.51, 1296.89, 1200.38, 1145.45, 1009.37, 959.91, 759.40, 672.54, 532.65, 451.10. HRMS (ESI) m/z calcd for $C_{19}H_{14}ClO_4$ $[M + H]^+$ 341.0575, found 341.0574.

methyl 2-(1,4-dioxo-1,4-dihydronaphthalen-2-yl)-2-(3-methoxyphenyl)acetate, 10k:



10k was prepared according to the general procedure **2.6** using **NQ** (0.6 mmol, 91 mg) and **2n** (0.84 mmol, 173.2 mg). After column chromatography on silica gel [SiO_2, Hexane/EtOAc (95:5 to 80:20)], the expected product **10k** was obtained as a Yellow semi-solid. (153 mg, 76%). ***^{1}H* NMR** ($CDCl_3$, 400 MHz) δ_H 8.12-8.10 (m, 1H), 8.06-8.04 (m, 1H), 7.75-7.73 (m, 2H), 7.30 (d, J=8Hz, 1H), 6.91-6.89 (m, 2H), 6.88-6.84 (m, 1H), 6.58 (s, 1H), 5.14 (s, 1H), 3.81 (s, 3H), 3.76 (s, 3H) ppm. ***^{13}C* {*^{1}H*} NMR** ($CDCl_3$, 100 MHz) δ_C 185.1, 184.6, 171.3, 160.3, 148.6, 136.9, 135.7, 134.2, 134.1, 132.2, 132.0, 130.4, 129.7, 127.0, 126.4, 121.4, 120.5, 115.0, 113.8, 113.3, 55.4, 53.0, 51.3 ppm. FT-IR (Neat) ν_{max} (cm^{-1}) = 2918.98, 2848.53, 1730.13, 1661.94, 1591.94, 14442.98, 1245.19, 1163.60, 1034.38, 746.33, 540.55, 456.79. HRMS (ESI) m/z calcd for $C_{20}H_{17}O_5$ $[M + H]^+$ 337.1071, found 337.1074.

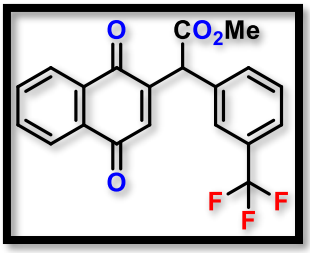
methyl 2-(1,4-dioxo-1,4-dihydronaphthalen-2-yl)-2-(4-methoxyphenyl)acetate, 10l:



10l was prepared according to the general procedure **2.6** using **NQ** (0.6 mmol, 91 mg) and **2j** (0.84 mmol, 173.2 mg). After column chromatography on silica gel [SiO_2, Hexane/EtOAc (95:5 to 80:20)],

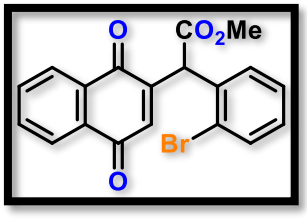
the expected product **10l** was obtained as a Yellow semi-solid. (169.2 mg, 84%). ***^{1}H* NMR** ($CDCl_3$, 400 MHz) δ_H 8.12-8.09 (m, 1H), 8.06-8.03 (m, 1H), 7.74 (dd, ^{1}J=4Hz, ^{2}J=4Hz, 2H), 7.23 (d, J=8Hz, 2H), 6.93 (d, J=12Hz, 2H), 6.58 (s, 1H), 5.11 (s, 1H), 3.82 (s, 3H), 3.75 (s, 3H) ppm. ***^{13}C* {*^{1}H*} NMR** ($CDCl_3$, 100 MHz) δ_C 185.1, 184.7, 171.6, 159.7, 149.1, 136.7, 134.2, 134.0, 132.2, 132.1, 130.3, 127.0, 126.4, 126.2, 114.8, 55.5, 52.9, 50.5 ppm. FT-IR (Neat) ν_{max} (cm^{-1}) = 2918.65, 1725.59, 1657.16, 1593.27, 1509.93, 1441.33, 1299.20, 1244.51, 1151.34, 1021.35, 757.11, 663.13, 580.83, 526.72, 437.05. HRMS (ESI) m/z calcd for $C_{20}H_{17}O_5$ $[M + H]^+$ 337.1071, found 337.1079.

methyl 2-(1,4-dioxo-1,4-dihydronaphthalen-2-yl)-2-(3-(trifluoromethyl)phenyl)acetate, 10m:



10m was prepared according to the general procedure **2.6** using **NQ** (0.6 mmol, 91 mg) and **2m** (0.84 mmol, 205.1 mg). After column chromatography on silica gel [SiO_2, Hexane/EtOAc (95:5 to 80:20)], the expected product **10m** was obtained as a Yellow semi-solid. (157 mg, 70%). ***^{1}H* NMR** ($CDCl_3$, 400 MHz) δ_H 8.13-8.10 (m, 1H), 8.07-8.05 (m, 1H), 7.76 (dd, ^{1}J=8Hz, ^{2}J=4Hz, 2H), 7.40-7.35(m, 1H), 7.12-7.04(m, 3H), 6.60 (s, 1H), 5.18 (s, 1H), 3.78 (s, 3H) ppm. ***^{13}C* {*^{1}H*} NMR** ($CDCl_3$, 100 MHz) δ_C 193.6, 192.3, 167.5, 167.0, 149.1, 138.4, 137.5, 135.0, 134.9, 134.5, 130.9, 130.8, 125.3, 125.2, 124.5, 116.9, 116.6, 116.4, 116.3, 116.1, 53.6, 41.7, 39.5, 37.2, 36.1, 16.5, 15.7 ppm. ***^{19}F* NMR** ($CDCl_3$, 376 MHz) δ_F -111.39, -111.41, -111.43, -111.48, -111.49 ppm. FT-IR (Neat) ν_{max} (cm^{-1}) = 2917.14, 1731.48, 1664.00, 1590.74, 1448.99, 1236.46, 1167.36, 1079.08, 966.56, 756.92, 437.08. HRMS (ESI) m/z calcd for $C_{20}H_{14}F_3O_4$ $[M + H]^+$ 375.0766, found 375.0745.

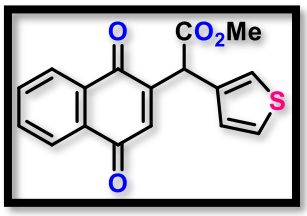
methyl 2-(2-bromophenyl)-2-(1,4-dioxo-1,4-dihydronaphthalen-2-yl)acetate, 10n:



10n was prepared according to the general procedure **2.6** using **NQ** (0.6 mmol, 91 mg) and **2l** (0.84 mmol, 214.3 mg). After column chromatography on silica gel [SiO_2, Hexane/EtOAc (95:5 to 80:20)], the expected product **10n** was obtained as a Yellow semi-solid. (168.1 mg, 73%). ***^{1}H* NMR** ($CDCl_3$, 400 MHz) δ_H 8.15-8.13 (m, 1H), 8.07-8.05 (m, 1H), 7.77-7.75 (m, 2H), 7.65 (dd, ^{1}J =8Hz, ^{2}J =4Hz, 1H), 7.40-7.36(m, 1H), 7.32 (dd, ^{1}J =8Hz, ^{2}J =0Hz, 1H), 7.25-7.22 (m, 1H), 6.36 (s, 1H), 5.68 (s, 1H), 3.79 (s, 3H) ppm. ***^{13}C* {*^{1}H*} NMR** ($CDCl_3$, 100 MHz) δ_C 184.9, 184.2, 171.0, 147.5, 136.8, 134.5, 134.2, 134.1, 133.9, 132.2, 132.0, 130.0, 128.3, 127.1, 126.5, 125.4, 53.1, 51.1 ppm. FT-IR (Neat) ν_{max} (cm^{-1}) = 3300.89,

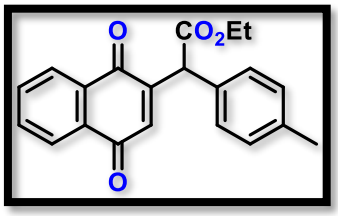
2915.66, 1730.60, 1661.67, 1597.15, 1457.59, 1376.40, 1257.78, 1174.77, 1085.96, 1024.81, 802.33, 696.51, 582.95, 496.58. HRMS (ESI) m/z calcd for $C_{19}H_{14}BrO_4$ $[M + H]^+$ 385.0070, found 385.0081.

methyl 2-(1,4-dioxo-1,4-dihydronaphthalen-2-yl)-2-(thiophen-3-yl)acetate, 10o:



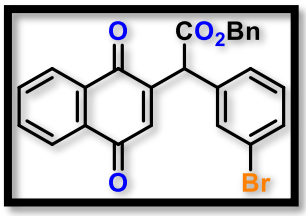
10o was prepared according to the general procedure **2.6** using **NQ** (0.6 mmol, 91 mg) and **2o** (0.84 mmol, 164.8 mg). After column chromatography on silica gel [SiO_2, Hexane/EtOAc (95:5 to 80:20)], the expected product **10o** was obtained as a Yellow semi-solid. (133 mg, 68%). ***¹H* NMR** ($CDCl_3$, 400 MHz) δ_H 8.13-8.10 (m,1H), 8.07-8.04 (m, 1H), 7.76 (m, 2H), 7.38(dd, ^1J=4Hz, ^2J=4Hz, 1H), 7.26-7.25 (m, 1H), 7.05-7.03(m, 1H), 6.61 (s, 1H), 5.26 (s, 1H), 4.23 (q, J=8Hz, 2H), 1.27(t, J=8Hz, 3H) ppm. ***¹³C* {*¹H*} NMR** ($CDCl_3$, 100 MHz) δ_C 185.1, 184.5, 170.6, 148.5, 136.6, 134.3, 134.2, 134.1, 132.2, 132.0, 127.9, 127.0, 127.0, 126.4, 124.4, 62.0, 46.9, 14.2 ppm. FT-IR (Neat) ν_{max} (cm^{-1}) = 3295.42, 2914.60, 2850.52, 1728.01, 1463.07, 1387.22, 1173.72, 1100.82, 1049.33, 986.58, 716.46, 655.02. HRMS (ESI) m/z calcd for $C_{17}H_{13}SO_4$ $[M + H]^+$ 313.0456, found 313.0445.

ethyl 2-(1,4-dioxo-1,4-dihydronaphthalen-2-yl)-2-(p-tolyl)acetate, 10p:



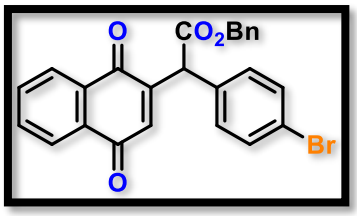
10p was prepared according to the general procedure **2.6** using **NQ** (0.6 mmol, 91 mg) and **2e** (0.84 mmol, 171.5 mg). After column chromatography on silica gel [SiO_2, Hexane/EtOAc (95:5 to 80:20)], the expected product **10p** was obtained as a Yellow semi-solid. (126 mg, 63%). ***¹H* NMR** ($CDCl_3$, 400 MHz) δ_H 8.12-8.10 (m, 1H), 8.06-8.03 (m, 1H), 7.75-7.73 (m, 2H), 7.20 (s, 3H), 6.98 (s, 1H), 6.55 (s, 1H), 5.11 (s, 1H), 4.29-4.18 (m, 2H), 2.36 (s, 3H), 1.29 (t, J=6Hz, 3H) ppm. ***¹³C* {*¹H*} NMR** ($CDCl_3$, 100 MHz) δ_C 185.2, 171.0, 149.2, 138.2, 136.8, 134.1, 134.0, 132.2, 132.1, 131.5, 130.1, 129.7, 129.0, 128.0, 127.0, 126.4, 61.8, 51.1, 21.3, 14.2 ppm. FT-IR (Neat) ν_{max} (cm^{-1}) = 2915.97, 1724.16, 1655.57, 1587.50, 1457.12, 1369.57, 1287.44, 1148.27, 1023.86, 967.73, 769.86, 575.79, 497.14. HRMS (ESI) m/z calcd for $C_{21}H_{19}O_4$ $[M + H]^+$ 335.1278, found 335.1274.

benzyl 2-(3-bromophenyl)-2-(1,4-dioxo-1,4-dihydronaphthalen-2-yl)acetate, 10q:



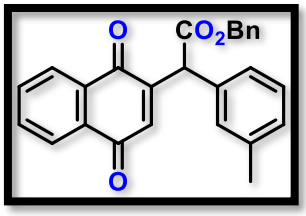
10q was prepared according to the general procedure **2.6** using **NQ** (0.6 mmol, 91 mg) and **2q** (0.84 mmol, 278 mg). After column chromatography on silica gel [SiO_2, Hexane/EtOAc (95:5 to 80:20)], the expected product **10q** was obtained as a Yellow semi-solid. (189.2 mg, 69%). ***^{1}H* NMR** ($CDCl_3$, 400 MHz) δ_H 8.11-8.09 (m, 1H), 8.06-8.04 (m, 1H), 7.75 (dd, ^1J=4Hz, ^2J=4Hz, 2H), 7.48 (dt, ^1J=8Hz, ^2J=4Hz, 1H), 7.44 (d, J=8Hz, 1H), 7.33-7.28(m, 5H), 7.24-7.22 (m, 2H), 6.58 (s, 1H), 5.22 (s, 1H), 5.19 (s, 2H) ppm. ***^{13}C {^{1}H}* NMR** ($CDCl_3$, 100 MHz) δ_C 184.8, 184.2, 170.1, 148.0, 136.8, 136.6, 135.3, 134.3, 134.1, 132.2, 132.1, 131.9, 131.7, 130.8, 128.7, 128.6, 128.4, 127.9, 127.1, 126.5, 123.3, 67.8, 50.8 ppm. FT-IR (Neat) ν_{max} (cm^{-1}) = 3061.68, 2937.60, 1727.58, 1657.93, 1582.85, 1443.93, 1300.77, 1194.11, 1145.82, 1080.54, 1018.01, 795.95, 741.74, 687.03, 592.04, 531.29, 451.77. HRMS (ESI) m/z calcd for $C_{25}H_{18}BrO_4$ $[M + H]^+$ 461.0383, found 461.0386.

benzyl 2-(4-bromophenyl)-2-(1,4-dioxo-1,4-dihydronaphthalen-2-yl)acetate, 10r:



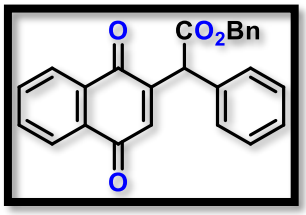
10r was prepared according to the general procedure **2.6** using **NQ** (0.6 mmol, 124.9 mg) and **2r** (0.84 mmol, 278 mg). After column chromatography on silica gel [SiO_2, Hexane/EtOAc (95:5 to 80:20)], the expected product **10r** was obtained as a Yellow semi-solid. (182.6 mg, 66%). ***^{1}H* NMR** ($CDCl_3$, 400 MHz) δ_H 8.10-8.09 (m, 1H), 8.05-8.04 (m, 1H), 7.75 (dd, ^1J = 4Hz, ^2J = 4Hz, 2H), 7.50 (d, J = 8Hz, 2H), 7.33-7.32 (m, 3H), 7.29-7.28(d, J=4Hz, 2H), 7.16 (d, J = 8Hz, 2H), 6.57 (s, 1H), 5.21 (s, 1H), 5.18 (s, 2H) ppm. ***^{13}C {^{1}H}* NMR** ($CDCl_3$, 100 MHz) δ_C 184.8, 184.3, 170.3, 148.1, 136.6, 135.3, 134.3, 134.1, 133.4, 132.5, 132.1, 131.9, 131.7, 131.4, 130.9, 128.8, 128.7, 128.6, 128.5, 128.4, 127.0, 126.4, 122.7, 67.7, 50.7 ppm. FT-IR (Neat) ν_{max} (cm^{-1}) = 2915.92, 1724.57, 1658.00, 1586.03, 1458.72, 1373.87, 1282.62, 1144.21, 1082.47, 1019.68, 799.70, 561.75, 503.38. HRMS (ESI) m/z calcd for $C_{25}H_{18}BrO_4$ $[M + H]^+$ 461.0383, found 461.0386.

benzyl 2-(1,4-dioxo-1,4-dihydronaphthalen-2-yl)-2-(m-tolyl)acetate, 10s:



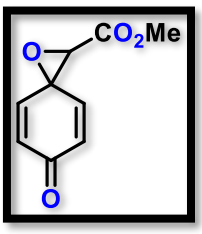
10s was prepared according to the general procedure **2.6** using **NQ** (0.6 mmol, 91 mg) and **2s** (0.84 mmol, 223.7 mg). After column chromatography on silica gel [SiO_2, Hexane/EtOAc (95:5 to 80:20)], the expected product **10s** was obtained as a Yellow semi-solid. (144.8 mg, 61%). ***^{1}H* NMR** ($CDCl_3$, 400 MHz) δ_H 8.10-8.07 (m, 1H), 8.03-8.01 (m, 1H), 7.73 -7.70 (m, 2H), 7.44-7.40 (m, 1H), 7.30-7.27 (m, 5H), 7.12 (d, *J*=8Hz, 1H), 7.04-7.02 (m, 2H), 6.53 (d, *J*=4Hz, 1H),5.23 (s, 1H), 5.20-5.16 (m, 2H), 2.29 (s, 3H) ppm. ***^{13}C {^{1}H}* NMR** ($CDCl_3$, 100 MHz) δ_C 185.1, 184.6, 170.8, 148.9, 139.1, 136.9, 135.6, 134.1, 134.0, 132.2, 129.8, 129.2, 129.2, 128.8, 128.8, 128.7, 128.6, 128.4, 128.3, 127.0, 126.4, 126.3, 67.5, 51.3, 21.6 ppm. FT-IR (Neat) ν_{max} (cm^{-1}) = 2930.74, 1730.97, 1662.22, 1594.74, 1452.39, 1292.16, 1223.22, 1156.06, 1020.16, 908.12, 733.87, 588.25, 452.00. HRMS (ESI) m/z calcd for $C_{26}H_{21}O_4$ $[M + H]^+$ 397.1434, found 397.1444.

benzyl 2-(1,4-dioxo-1,4-dihydronaphthalen-2-yl)-2-phenylacetate, 10t:



10t was prepared according to the general procedure **2.6** using **NQ** (0.6 mmol, 91mg) and **2t** (0.84 mmol, 211.9 mg). After column chromatography on silica gel [SiO_2, Hexane/EtOAc (95:5 to 80:20)], the expected product **10t** was obtained as a Yellow semi-solid. (146.3 mg, 64%). ***^{1}H* NMR** ($CDCl_3$, 400 MHz) δ_H 8.12-8.10 (m, 1H), 8.06-8.03 (m, 1H), 7.75-7.73 (m, 2H), 7.59 (^1J=8.2 Hz, ^2J=1.4 Hz, 2H)7.47-7.45 (m, 2H), 7.36-7.34(m, 3H), 7.30-7.29 (m, 2H), 7.27-7.26 (m, 1H), 6.56 (s, 1H), 5.24-5.22 (m, 2H), 5.19 (s, 1H) ppm. ***^{13}C* {^{1}H}* NMR** ($CDCl_3$, 100 MHz) δ_C 185.1, 184.5, 170.7, 148.7, 136.8, 135.5, 134.3, 134.2, 134.0, 132.1, 132.0, 129.4, 129.2, 128.9, 128.7, 128.6, 128.4, 128.4, 128.3, 128.2, 127.0, 126.4, 67.5, 51.4 ppm. FT-IR (Neat) ν_{max} (cm^{-1}) = 2919.61, 1731.12, 1661.08, 1594.18, 1452.15, 1290.90, 1154.94, 992.84, 694.15, 585.36, 537.28, 492.36. HRMS (ESI) m/z calcd for $C_{25}H_{19}O_4$ $[M + H]^+$ 383.1278, found 383.1282.

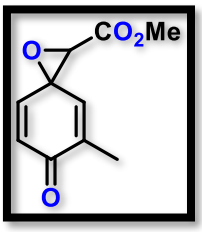
methyl 6-oxo-1-oxaspiro[2.5]octa-4,7-diene-2-carboxylate, 11a:



11a was prepared according to the general procedure **2.7** using **BQ** (0.6 mmol, 65 mg) and **3** (0.84 mmol, 84 mg). After column chromatography on silica gel [SiO_2, Hexane/EtOAc (95:5 to 80:20)], the expected product **11a** was obtained as a Grayish viscous liquid (90.1 mg, 84%). ***^{1}H* NMR** ($CDCl_3$, 400 MHz) δ_H 6.88 (dd, ^1J =10Hz, ^2J =2Hz, 1H), 6.56-6.52 (m, 2H), 6.44 (dd, ^1J=10Hz, ^2J =2Hz, 1H), 3.99 (s, 1H), 3.86 (s, 3H) ppm. ***^{13}C* {^{1}H}* NMR** ($CDCl_3$, 100 MHz) δ_C 184.9, 166.5, 144.4, 140.9, 135.5, 134.6, 60.3, 57.9, 53.3 ppm. FT-IR (Neat) ν_{max} (cm^{-1}) = 3272.79, 2916.01, 2853.18, 1706.45, 1598.48, 1448.27,

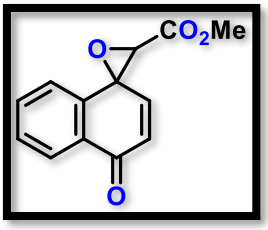
1367.82, 1189.58, 1073.31, 969.03, 810.55, 713.84, 500.96. HRMS (ESI) m/z calcd for $C_9H_9O_4$ $[M + H]^+$ 181.0423, found 181.0444.

methyl 5-methyl-6-oxo-1-oxaspiro[2.5]octa-4,7-diene-2-carboxylate, 11b:



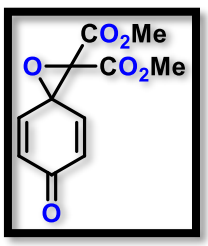
11b was prepared according to the general procedure **2.7** using **MBQ** (0.6 mmol, 73 mg) and **3** (0.84 mmol, 84 mg). After column chromatography on silica gel [SiO_2, Hexane/EtOAc (95:5 to 80:20)], the expected product **11b** was obtained as a Grayish viscous liquid (77.3 mg, 67%). ***¹H* NMR** ($CDCl_3$, 400 MHz) δ_H 6.63-6.61 (m, 1H), 6.52 (d, *J* =12Hz, 1H), 6.41 (dd, ^1J =10Hz, ^2J =2Hz, 1H), 3.96 (s, 1H), 3.87 (s, 3H), 1.97 (s, 3H) ppm. ***¹³C* {*¹H*} NMR** ($CDCl_3$, 100 MHz) δ_C 144.4, 135.5, 134.3, 60.2, 29.9 ppm. FT-IR (Neat) ν_{max} (cm^{-1}) = 3298.40, 2916.28, 2854.03, 1728.66, 1459.29, 1382.58, 1256.89, 1176.51, 1032.25, 800.84, 654.63. HRMS (ESI) m/z calcd for $C_{10}H_{11}O_4$ $[M + H]^+$ 195.0579, found 195.0574.

methyl 4-oxo-4H-spiro[naphthalene-1,2'-oxirane]-3'-carboxylate, 11c:



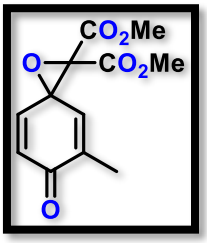
11c was prepared according to the general procedure **2.7** using **NQ** (0.6 mmol, 91 mg) and **3** (0.84 mmol, 84 mg). After column chromatography on silica gel [SiO_2, Hexane/EtOAc (95:5 to 80:20)], the expected product **11c** was obtained as a Grayish viscous liquid (109.1 mg, 79%). ***¹H* NMR** ($CDCl_3$, 400 MHz) δ_H 8.18 (dd, ^1J =8Hz, 2^1J =4Hz, 1H), 6.55-6.61 (m, 1H), 6.56-6.52 (m, 1H), 7.28-7.26 (m, 1H), 7.06-7.03 (d, *J* =12Hz, 1H), 6.71 (d, *J* =12Hz, 1H), 4.07 (s, 1H), 3.86 (s, 3H) ppm. ***¹³C* {*¹H*} NMR** ($CDCl_3$, 100 MHz) δ_C 183.5, 166.5, 142.2 137.5, 135.3, 133.4, 133.0, 129.5, 127.3, 123.1, 63.7, 57.6, 53.2 ppm. FT-IR (Neat) ν_{max} (cm^{-1}) = 3293.79, 2915.40, 2850.67, 1728.90, 1668.60, 1585.16, 1464.60, 1396.36, 1256.77, 1177.34, 1045.40, 794.28, 713.83, 574.63. HRMS (ESI) m/z calcd for $C_{13}H_{11}O_4$ $[M + H]^+$ 231.0579, found 231.0574.

dimethyl 6-oxo-1-oxaspiro[2.5]octa-4,7-diene-2,2-dicarboxylate, 11d:



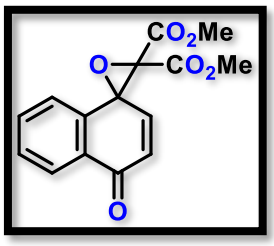
11d was prepared according to the general procedure **2.7** using **BQ** (0.6 mmol, 65 mg) and **3** (0.84 mmol, 132.8 mg). After column chromatography on silica gel [SiO_2, Hexane/EtOAc (95:5 to 80:20)], the expected product **11d** was obtained as a Grayish viscous liquid (125.5 mg, 88%). ***^{1}H* NMR** ($CDCl_3$, 400 MHz) δ_H 6.63 (d, *J* =12Hz, 2H), 6.54(d, *J* =12Hz, 2H), 3.89 (s, 3H) ppm. ***^{13}C* {*^{1}H*} NMR** ($CDCl_3$, 100 MHz) δ_C 184.4, 163.9, 140.4, 135.5, 67.6, 61.3, 54.0 ppm. HRMS (ESI) m/z calcd for $C_{11}H_{11}O_6$ $[M + H]^+$ 239.0477, found 239.0468.

dimethyl 5-methyl-6-oxo-1-oxaspiro[2.5]octa-4,7-diene-2,2-dicarboxylate, 11e:



11e was prepared according to the general procedure **2.7** using **MBQ** (0.6 mmol, 73 mg) and **3** (0.84 mmol, 132.8 mg). After column chromatography on silica gel [SiO_2, Hexane/EtOAc (95:5 to 80:20)], the expected product **11e** was obtained as a Grayish viscous liquid (109.4 mg, 73%). ***^{1}H* NMR** ($CDCl_3$, 400 MHz) δ_H 6.60 (dd, ^1J =12Hz, ^2J =4Hz, 1H), 6.54 (d, *J* =12Hz, 1H), 6.38-6.36 (m,1H), 3.91 (s, 3H), 3.90 (s, 3H), 1.97 (s, 3H) ppm. ***^{13}C* {*^{1}H*} NMR** ($CDCl_3$, 100 MHz) δ_C 185.1, 143.3, 140.3, 135.3, 135.0, 61.7, 53.9, 34.3, 22.5, 16.4, 14.2 ppm. FT-IR (Neat) ν_{max} (cm^{-1}) = 3291.34, 2915.71, 2851.25, 1727.67, 1458.84, 1251.35, 1177.62, 1050.46, 802.85, 712.15. HRMS (ESI) m/z calcd for $C_{12}H_{13}O_6$ $[M + H]^+$ 253.0634, found 253.0646.

dimethyl 4-oxo-4H-spiro[naphthalene-1,2'-oxirane]-3',3'-dicarboxylate, 11f:



11f was prepared according to the general procedure **2.7** using **NQ** (0.6 mmol, 91 mg) and **3** (0.84 mmol, 132.8 mg). After column chromatography on silica gel [SiO_2, Hexane/EtOAc (95:5 to 80:20)], the expected product **11f** was obtained as a Grayish viscous liquid (140.7 mg, 81%). ***^{1}H* NMR** ($CDCl_3$, 400 MHz) δ_H 8.17-8.15 (m, 1H), 7.56-7.54 (m, 2H), 7.29-7.27 (m, 1H), 7.12 (d, *J* =12Hz, 1H), 6.68 (d, *J* =12Hz, 1H), 3.89 (s, 3H), 3.58 (s, 3H) ppm. ***^{13}C* {*^{1}H*} NMR** ($CDCl_3$, 100 MHz) δ_C 183.5, 164.2, 163.6, 141.7, 135.3, 135.3, 133.2, 132.5, 129.9, 127.6, 123.7, 69.4, 62.7 ,54.1, 53.2 ppm. FT-IR (Neat) ν_{max} (cm^{-1}) = 3298.06, 2917.03, 2853.38, 1733.19, 1662.41, 1598.06, 1444.31, 1251.91, 1058.72, 772.64, 714.17, 527.93. HRMS (ESI) m/z calcd for $C_{15}H_{13}O_6$ $[M + H]^+$ 289.0634, found 289.0651.

3. Computational details

All the calculations are done by using hybrid DFT functional, B3LYP as implemented in the Gaussian 09 suite of package, with 6-311+G(d,p) basis set.[4-11] The D3 version of Grimme's dispersion with Becke-Johnson damping has been added to account for the weak interactions between the reactants.[12] The ground state geometry of the reactants, products and the intermediates are determined by geometry optimizations. Four varieties of X-groups such as Ph, CO_2Me, H and CH_3 in the carbene X-C(CO_2R) are taken into consideration for the calculations. Solvent interactions are included using the polarizable continuum model (PCM).[13] In case of Ph, CO_2Me and H carbene, continuum dichloromethane solvent is taken, whereas with CH_3-carbene the calculations are performed with dichloroethane continuum solvent. The R-group at the CO_2R moiety of the carbene corresponds to methyl group for the calculations with Ph, CO_2Me and H carbene, while R-group corresponds to Et group for CH_3-carbene.

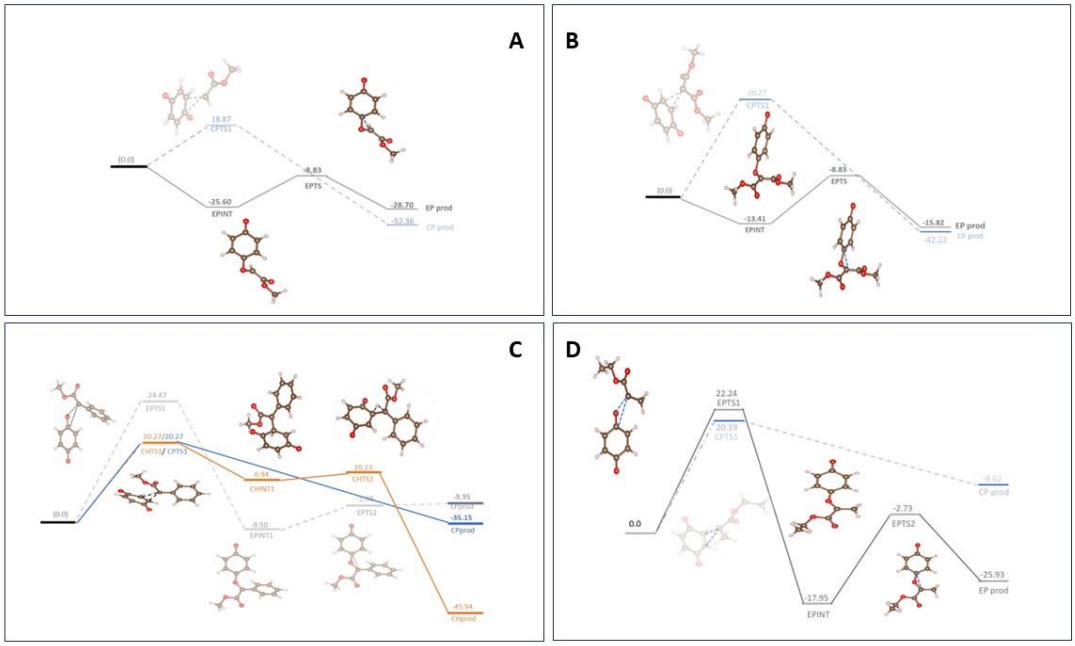
Prior to the transition state calculations bond/angle scans are performed following the potential energy surfaces from the reactants to the product formation. Starting the highest point geometries obtained during the potential energy scanning, transition states are calculated using Berny's optimisation algorithm.[14-16] Hessian calculations and intrinsic reaction coordinate searches are done based upon the obtained transition states to verify the transition states. All the reaction energies are calculated in reference with that of reactants.

Potential energy diagrams of the quinones with the different carbenes.

The potential energy diagrams for the reaction of BQ (Figure 1), MBQ (Figure 2), NQ (Figure 3) and AQ (Figure 4) with the different carbenes are shown in the following figures. The reaction energies are shown with respect to the reactants in kcal/mol. The reaction path leading to the formation of epoxide product (EP path) is shown in grey, the blue path shows the reaction path for cyclopropane product (CP path) and the orange path corresponds to the formation of C-H inserted products. The most favourable pathway is highlighted in darker colours, whereas the less favourable pathways are denoted in faded colours.

The structures of the reactants, products, intermediates and the transition states have been denoted using the ball and stick model. The bonds between the atoms are denoted by the solid lines between the atoms for all the structures except for the transition states. To denote the bond making and the breaking process, we have used dotted lines to indicate the bonds that will be formed in the products or to be broken in the reactants while moving towards the transition barrier. The vibrational frequency associated with the displacement of the corresponding atoms connected through the dotted lines corresponds to the imaginary modes and contributes to the non-restorative force leading to the increase of the energy along the potential energy surface.

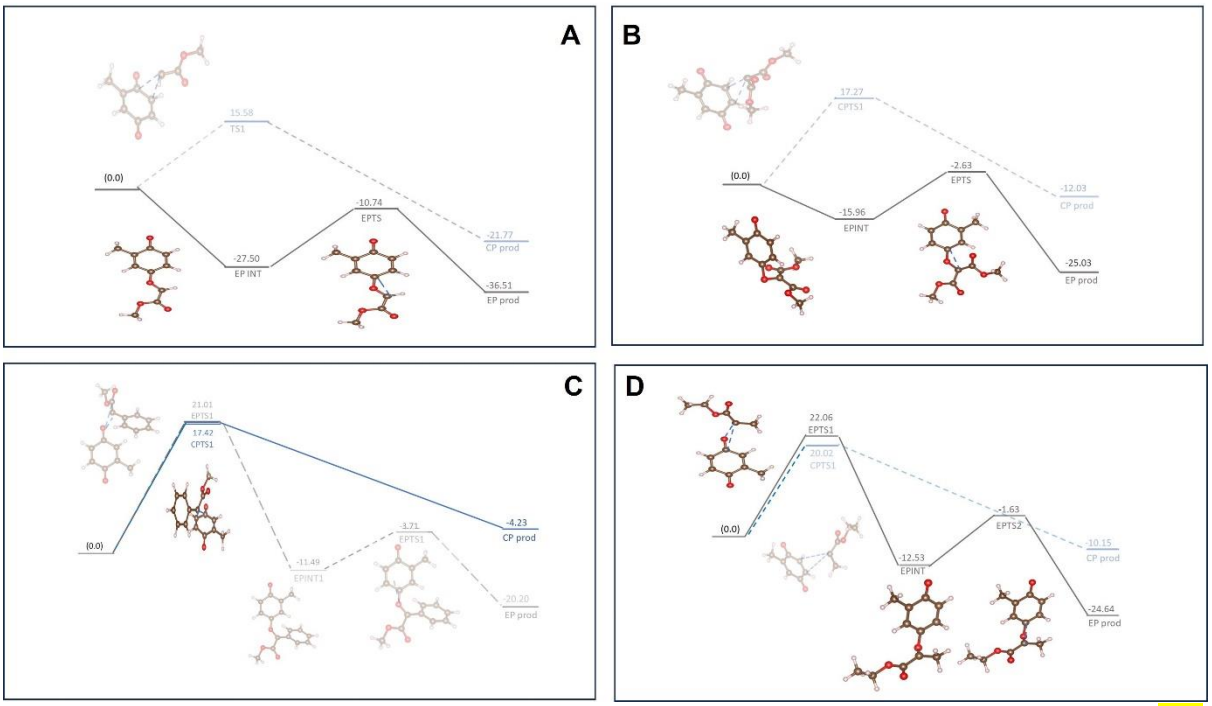
All the reaction energies are calculated in reference with that of reactants. We have added the zero-point energy corrections and the entropic corrections at room temperature to the electronic energies. These corrections are done using the harmonic approximations, by determining the vibrational frequencies of all the reactants, products, intermediates and transition states.



689

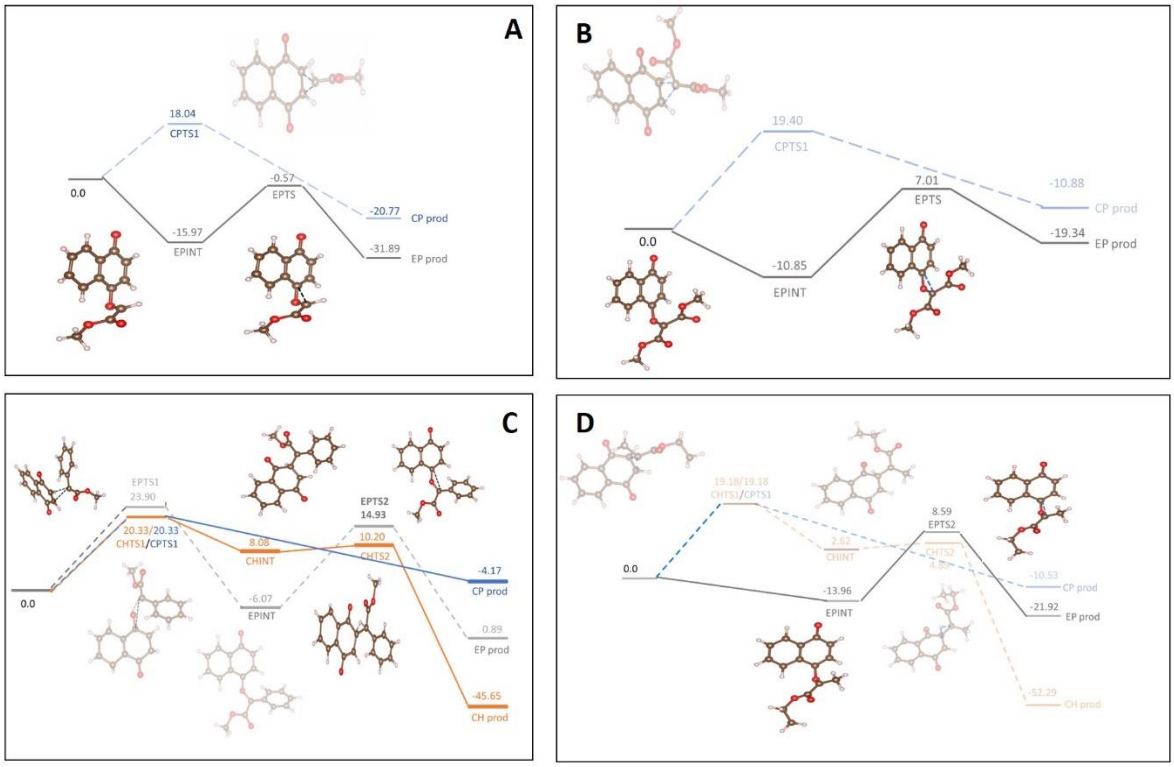
690 **Figure S5**: Potential energy diagram for BQ with H (A), CO_2Me(B), Ph(C) and CH_3 (D) carbene. The
691 energy values correspond to the reaction Gibbs free energies and denoted in kcal/mol.

692

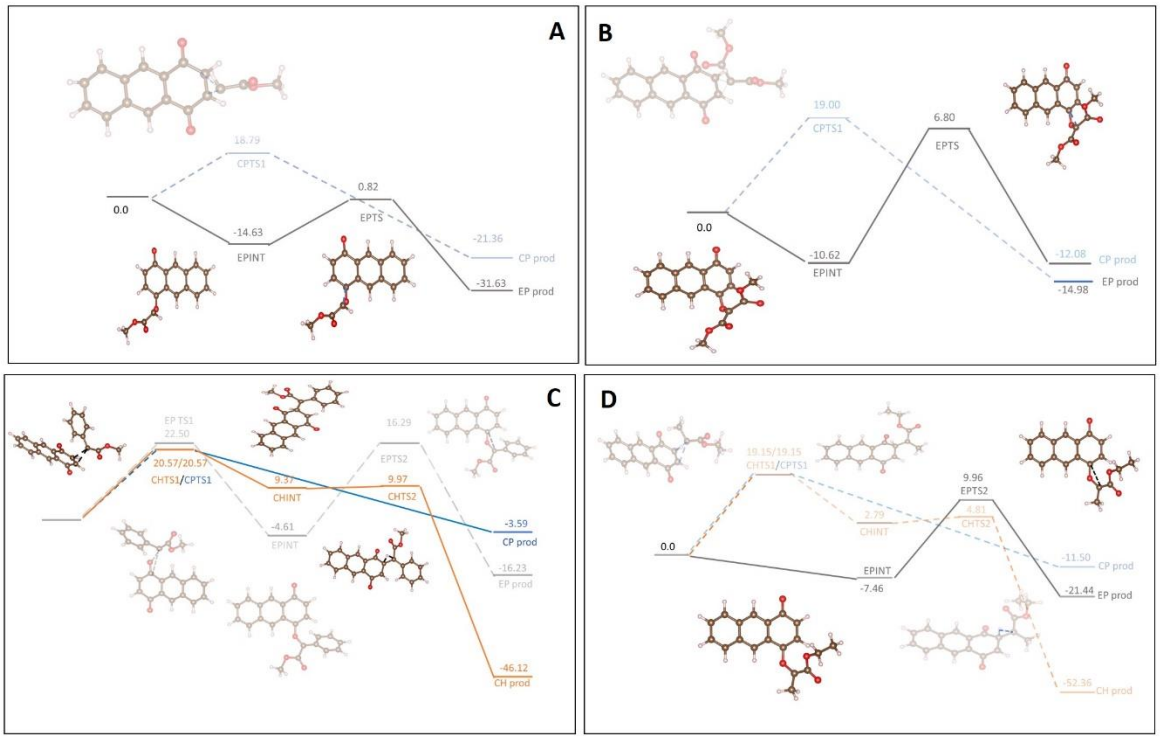


693 **Figure S6**: Potential energy diagram for MBQ with H (A), CO_2Me(B), Ph(C) and CH_3 (D) carbene. The
694 energy values correspond to the reaction Gibbs free energies and denoted in kcal/mol.

695



696 **Figure S7**: Potential energy diagram for NQ with H (A), CO_2Me(B), Ph(C) and CH_3 (D) carbene. The
697 energy values correspond to the reaction Gibbs free energies and denoted in kcal/mol.



698

699 **Figure S8**: Potential energy diagram for AQ with H (A), CO_2Me(B), Ph(C) and CH_3 (D) carbene. The
700 energy values correspond to the reaction Gibbs free energies and denoted in kcal/mol.

Table S1. The reaction free energies of the different quinone -carbene combinations. The reaction free energy values are given in kcal/mol, calculated with respect to the reactants. The thermal corrections and the entropic corrections are done using the harmonic approximation of the molecular vibrations to calculate the reaction Gibbs free energies from the electronic energies.

QUINONE	X GROUPS	ΔG (KCAL/MOL) FOR REACTANTS, TRANSITION STATES, INTERMEDIATES AND PRODUCT FORMATION									
		Epoxide formation				Cyclopropanation		CH insertion			
		EPTS1	EPINT1	EPTS2	EPprod	CPTS1	CPprod	CHTS1	CHTS2	CHINT1	CHprod
BQ	Ph	24.47	-9.50	-1.08	-9.94	20.27	-35.15	20.27	10.23	6.94	-45.94
	H	-	-25.60	-8.83	-28.70	18.87	-52.36	-	-	-	-
	CO_2Me	-	-13.41	-0.12	-15.82	20.93	-42.22	-	-	-	-
	CH_3	22.24	-17.95	-2.73	-25.93	20.19	-9.62	-	-	-	-
MBQ	Ph	21.01	-11.49	-3.71	-20.20	17.42	-4.23	-	-	-	-
	H	-	-27.50	-10.74	-36.51	15.58	-21.77	-	-	-	-
	CO_2Me	-	-15.96	-2.63	-25.03	17.27	-12.03	-	-	-	-
	CH_3	22.06	-12.53	-1.63	-24.64	20.02	-10.15	-	-	-	--
NQ	Ph	23.90	-6.07	14.93	0.89	20.33	-4.17	20.33	10.20	8.08	-45.65
	H	-	-15.97	-0.57	-31.89	18.04	-20.77	-	-	-	-
	CO_2Me	-	-10.85	7.01	-19.34	19.04	-10.88	-	-	-	-
	CH_3	-	-13.96	8.59	-21.92	19.18	-10.53	19.18	4.89	2.62	-52.29
AQ	Ph	21.78	-4.61	16.29	-16.23	20.57	-3.59	20.57	9.97	9.37	-46.12
	H	-	-14.63	-0.82	-31.63	18.79	-21.36	-	-	-	-
	CO_2Me	-	-10.62	6,80	-14.98	19.00	-12.08	-	-	-	-
	CH_3	-	-7.46	9.96	-21.44	19.15	-11.50	19.15	4.81	2.79	-52.36

Table S2. The imaginary frequencies obtained for the transition states of the different quinone -carbene combinations. The frequencies are given in cm^{-1}, calculated following harmonic approximations.

BQ	
H carbene	
Transition state	Frequency(cm-1)
CPTS1	-98.87
EPTS	-142.62
CO2Me carbene	
Transition state	Frequency(cm-1)
TS1	-141.68
EPTS	-93.39
Ph carbene	
Transition state	Frequency(cm-1)
CHTS1	-226.07
CHTS2	-728.85
EPTS1	-160.45
EPTS2	-64.88
Me carbene	
Transition state	Frequency(cm-1)

CHTS1	-140.34
CHTS2	-477.99
EPTS2	-63.07

MBQ

H carbene

Transition state	Frequency(cm-1)
TS1	-149.73
EPTS	-98.38

CO2Me carbene

Transition state	Frequency(cm-1)
TS1	-80.8
EPTS	-139.77

Ph carbene

Transition state	Frequency(cm-1)
CHTS1	-228.11
CHTS2	-725.41
EPTS1	-152.72
EPTS2	-55.55

Me carbene

Transition state	Frequency(cm-1)
CHTS1	-138.43
CHTS2	-487.42
EPTS2	-104.88

NQ

H carbene

Transition state	Frequency(cm-1)
TS1	-98.02
EPTS	-141.46

CO2Me carbene

Transition state	Frequency(cm-1)
TS1	-135.49
EPTS	-75.02

Ph carbene

Transition state	Frequency(cm-1)
CHTS1	-190.19
CHTS2	-655.65
EPTS1	-138.72
EPTS2	-50.66

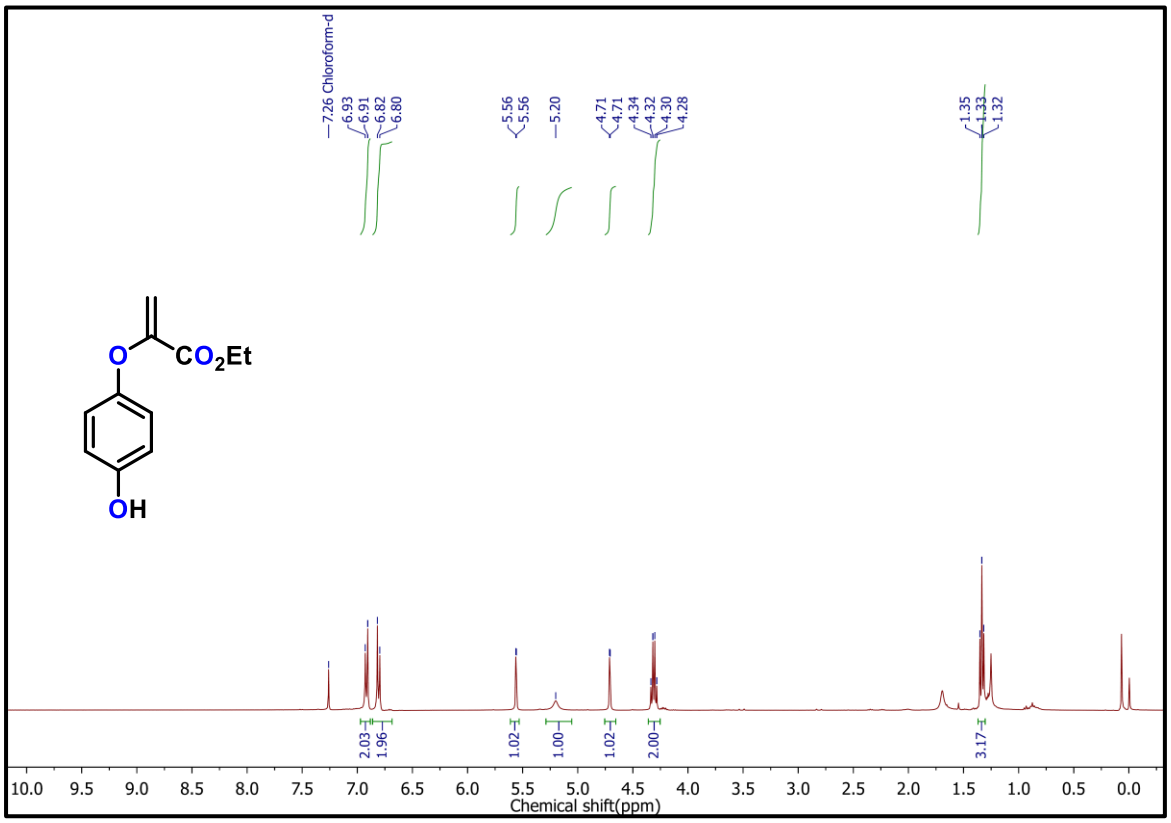
Me carbene

Transition state	Frequency(cm-1)
CHTS1	-81.93
CHTS2	-376.67
EPTS2	-107.21

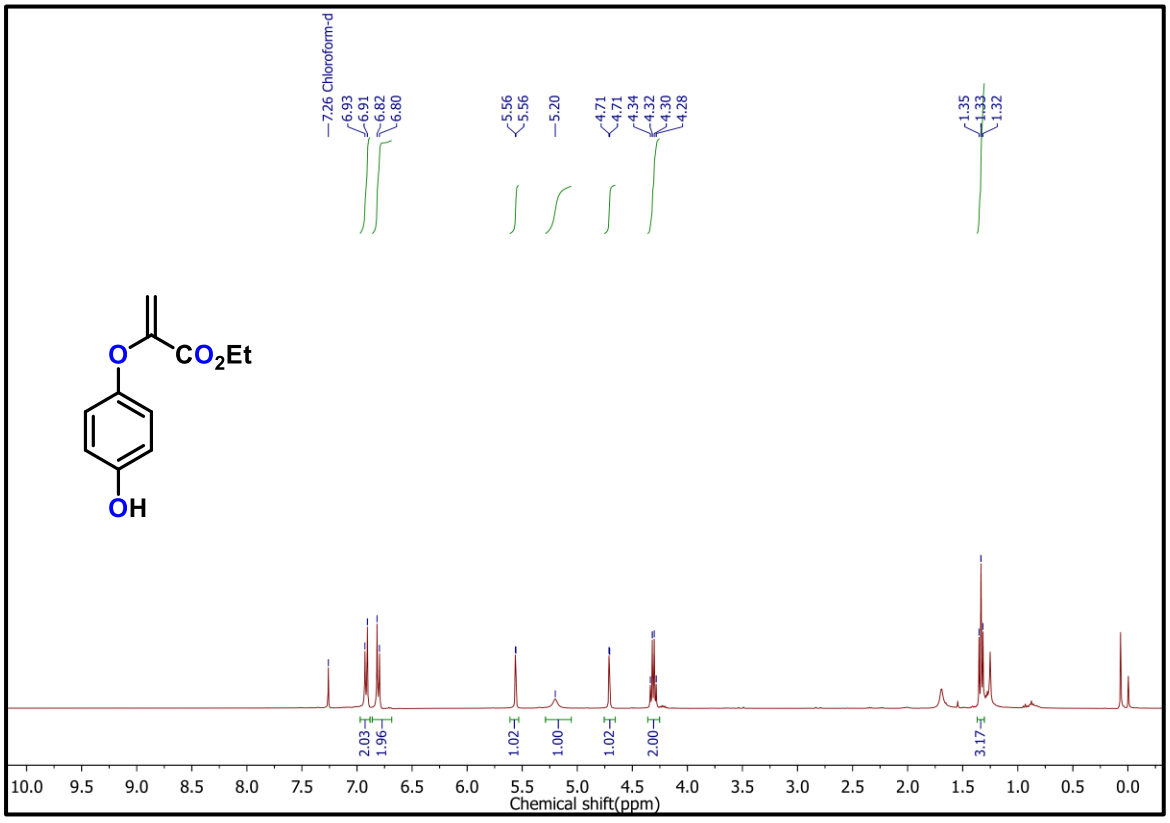
AQ	
H carbene	
Transition state	Frequency(cm-1)
TS1	-91.85
EPTS	-128.2
CO2Me carbene	
Transition state	Frequency(cm-1)
TS1	-69.35
EPTS	-134.27
Ph carbene	
Transition state	Frequency(cm-1)
CHTS1	-189.34
CHTS2	-631.19
EPTS1	-121.6
EPTS2	-42.47
Me carbene	
Transition state	Frequency(cm-1)
CHTS1	-80.1
CHTS2	-359.21
EPTS2	-100.7

4. NMR Spectra

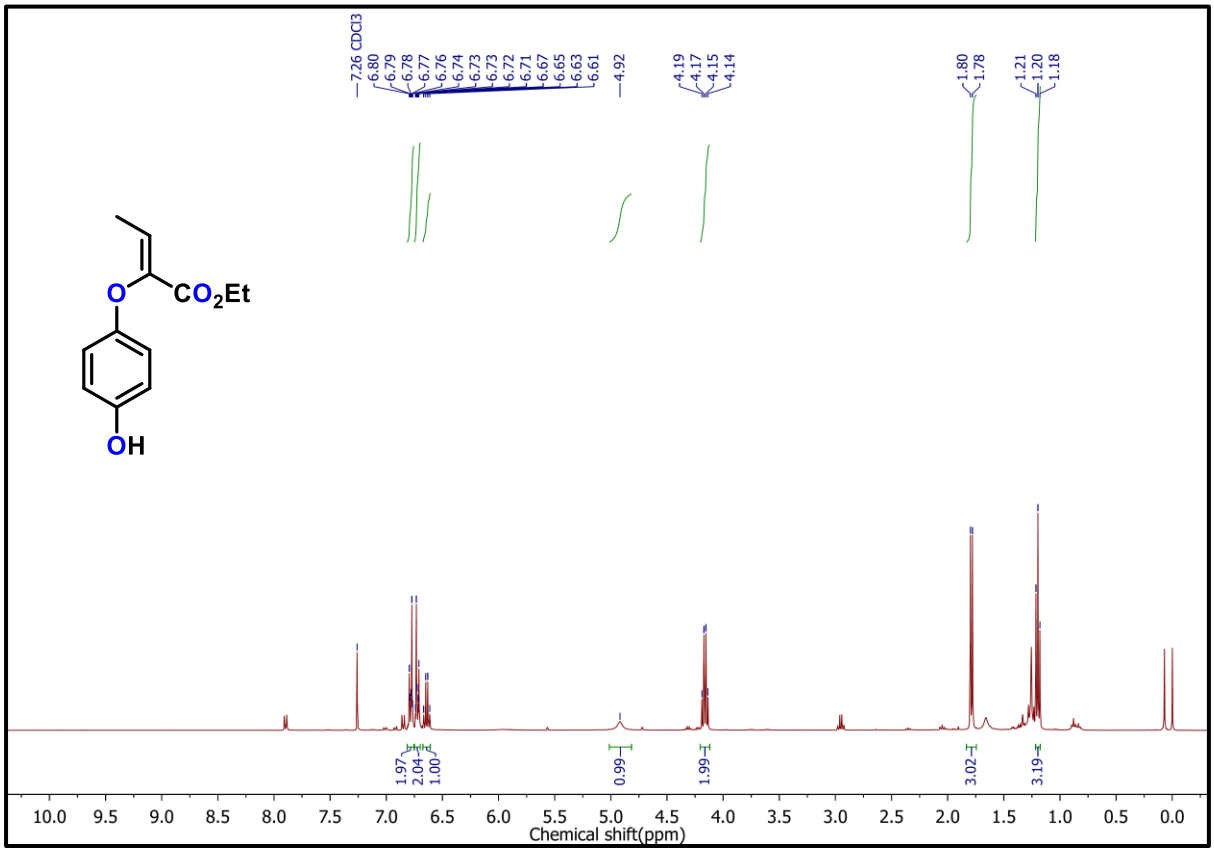
^{1}H NMR (400 MHz) of **5a** in $CDCl_3$



^{13}C NMR (100 MHz) of **5a** in $CDCl_3$

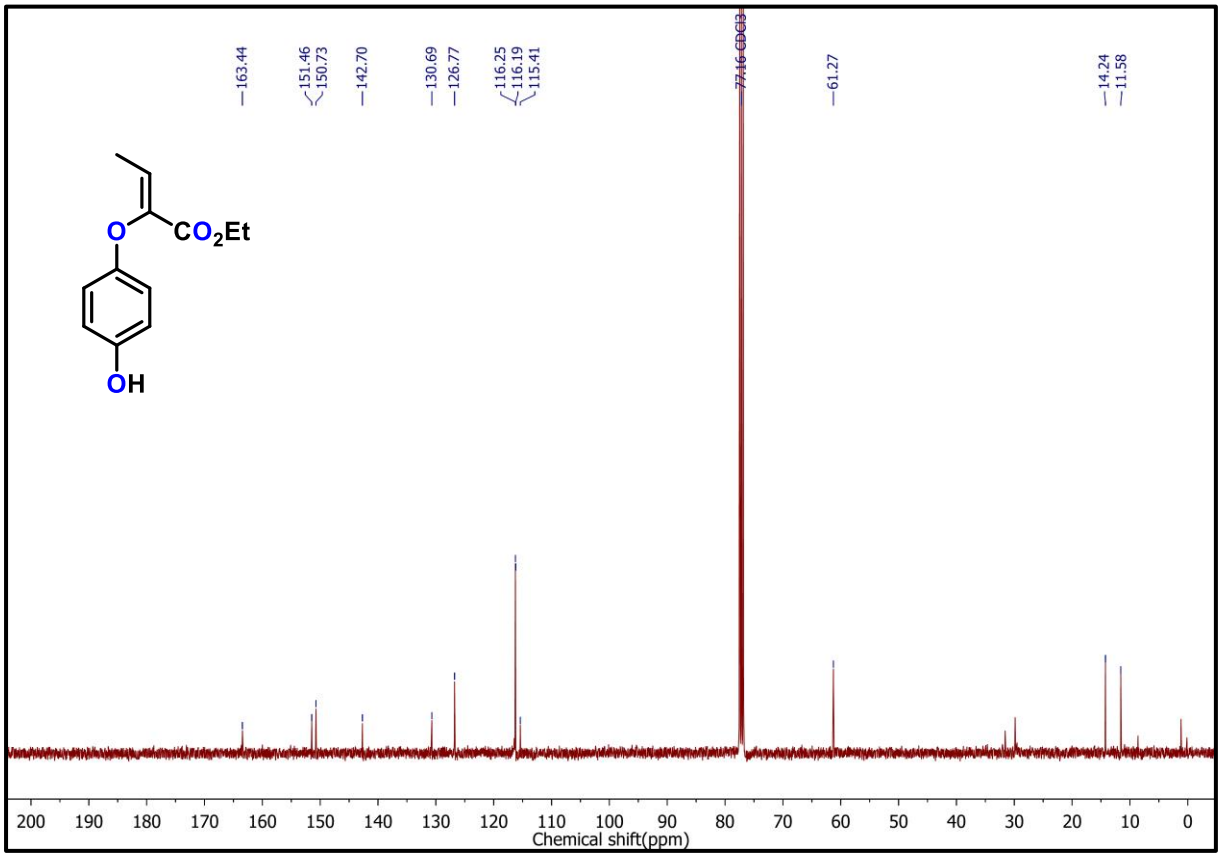


734 ^{1}H NMR (400 MHz) of **5b** in $CDCl_3$



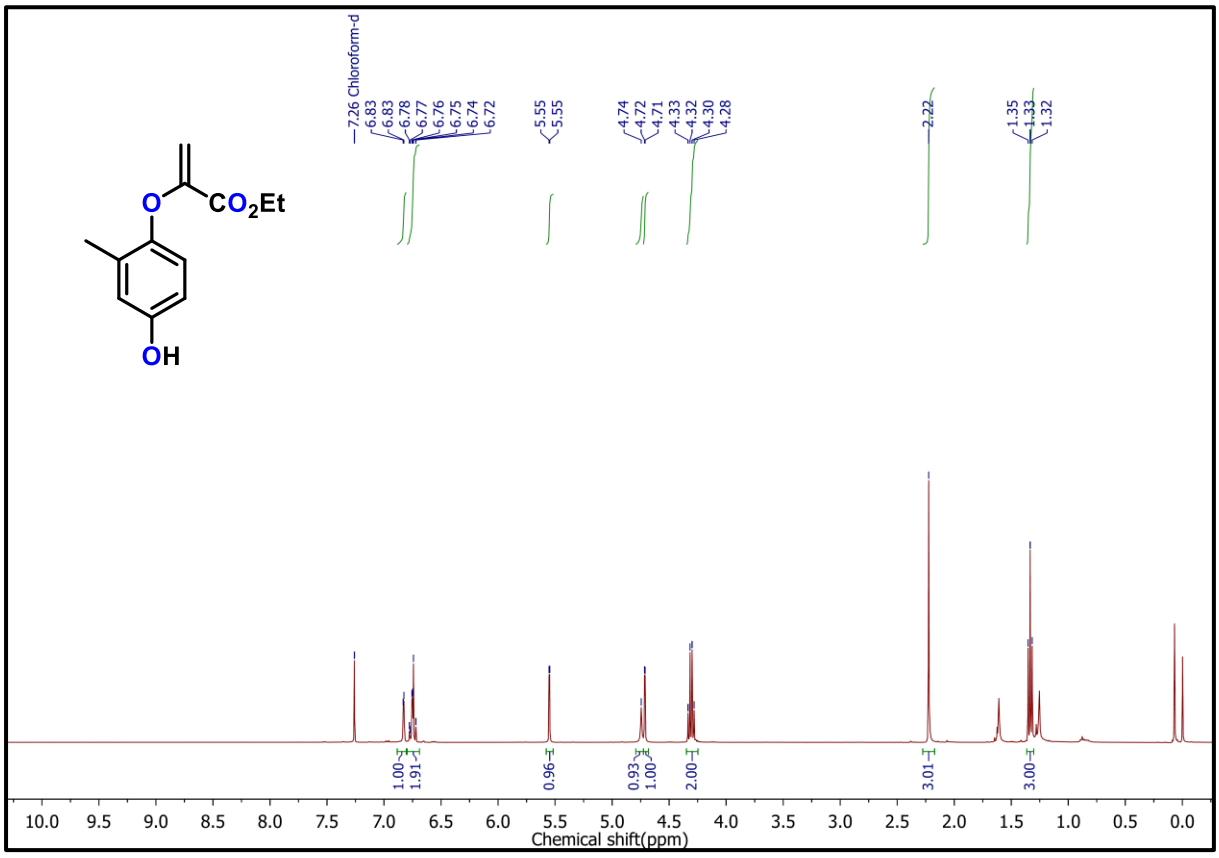
735

736 ^{13}C NMR (100 MHz) of **5b** in $CDCl_3$



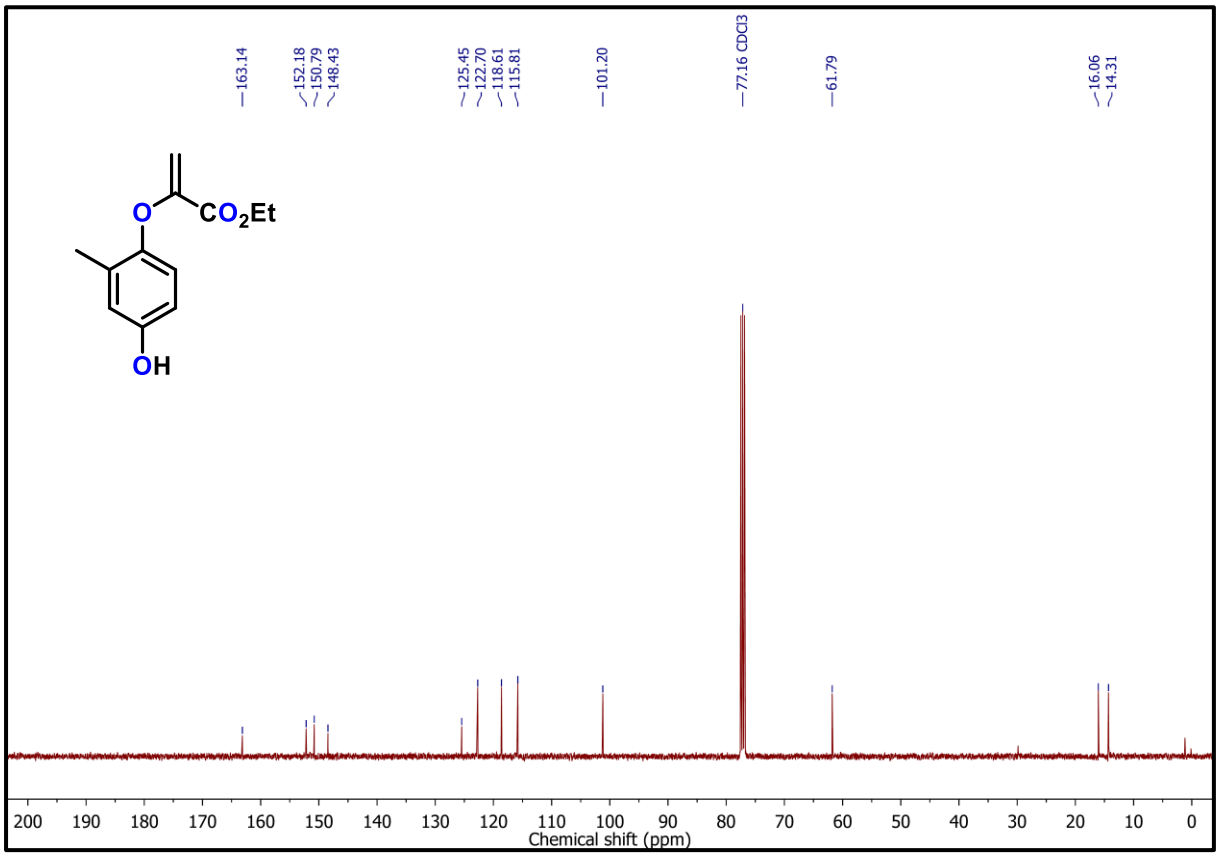
737

738 ^{1}H NMR (400 MHz) of **5c** in $CDCl_3$



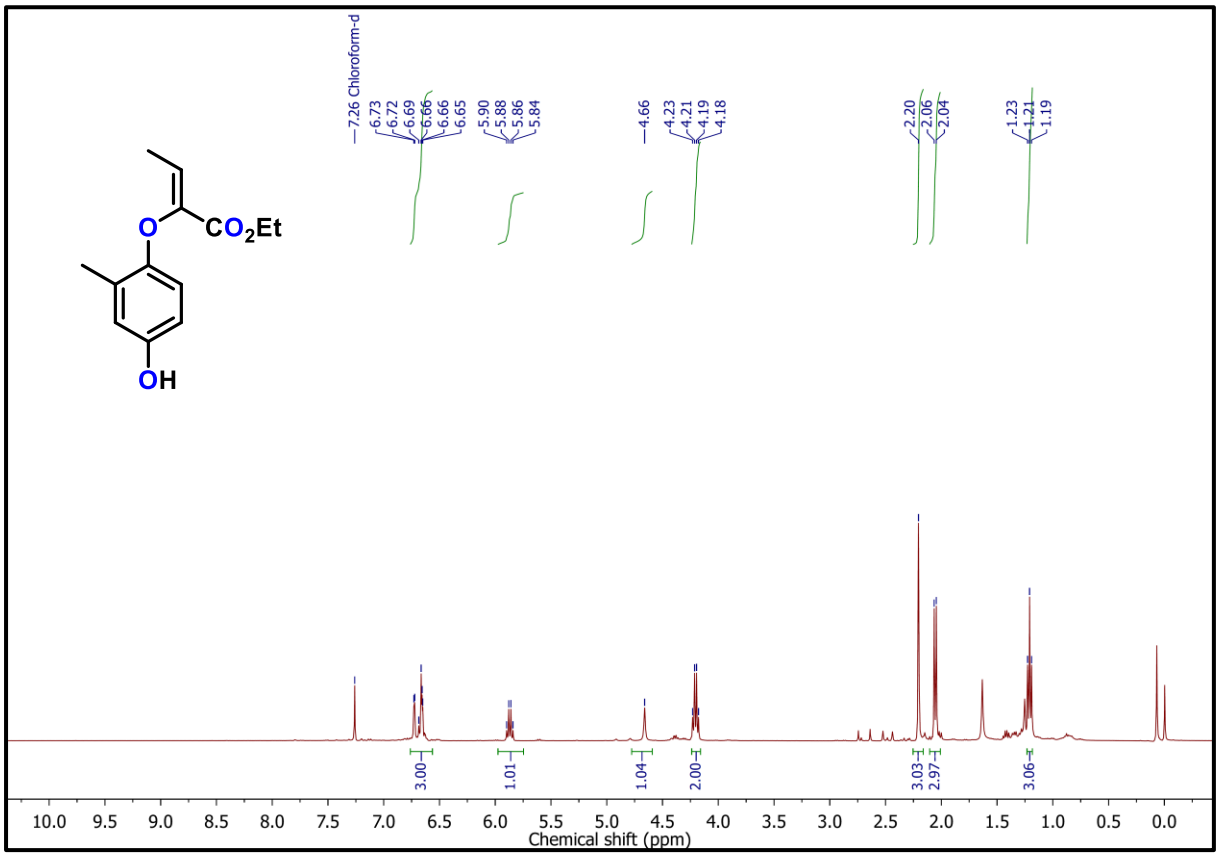
739

740 ^{13}C NMR (100 MHz) of **5c** in $CDCl_3$



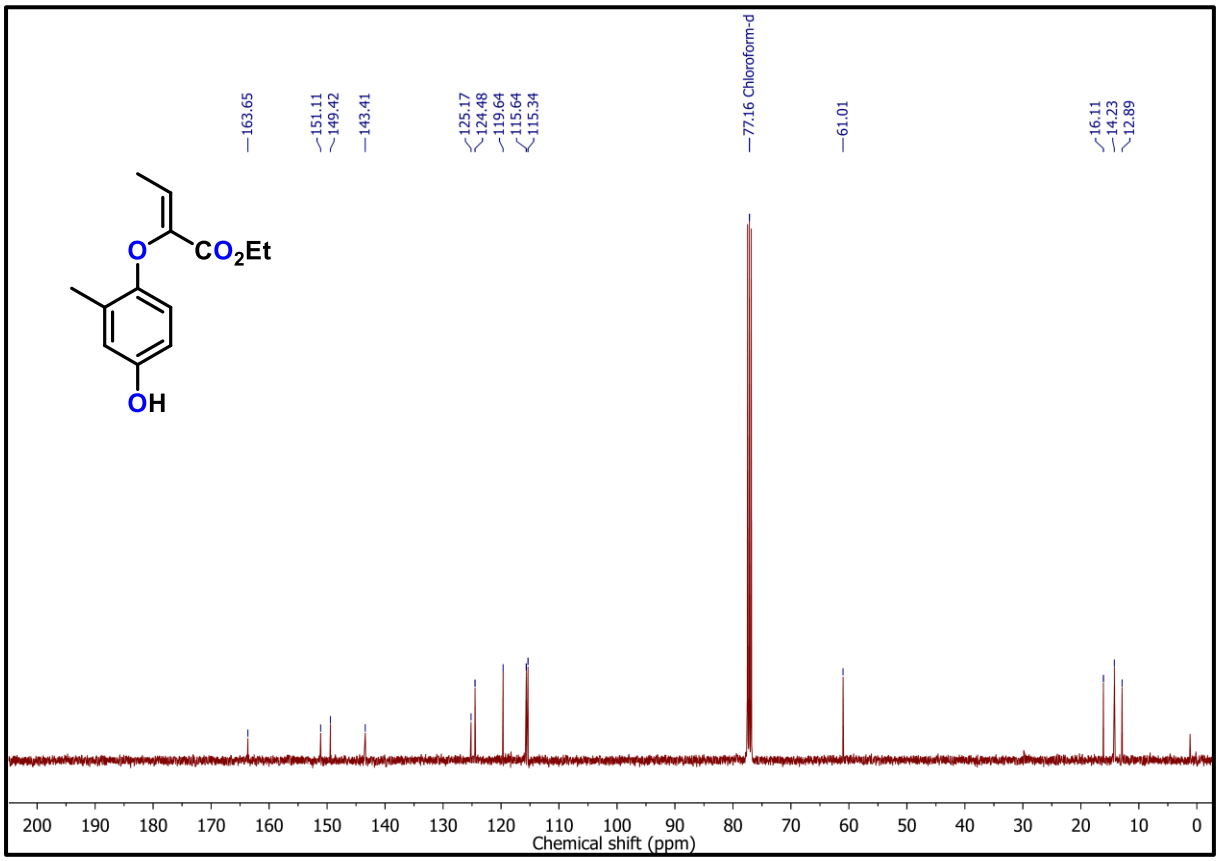
741

742 *[1]H* NMR (400 MHz) of **5d** in $CDCl_3$



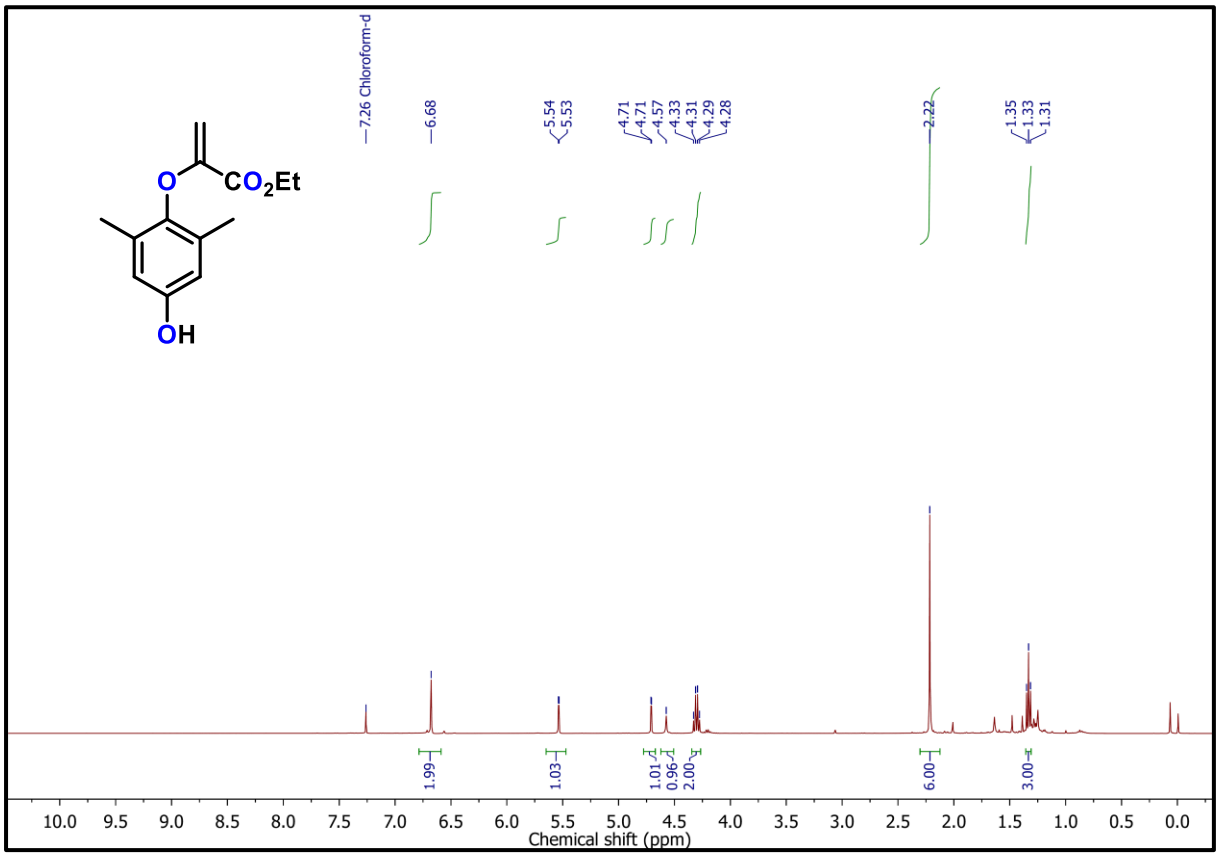
743

744 *[13]C* NMR (100 MHz) of **5d** in $CDCl_3$



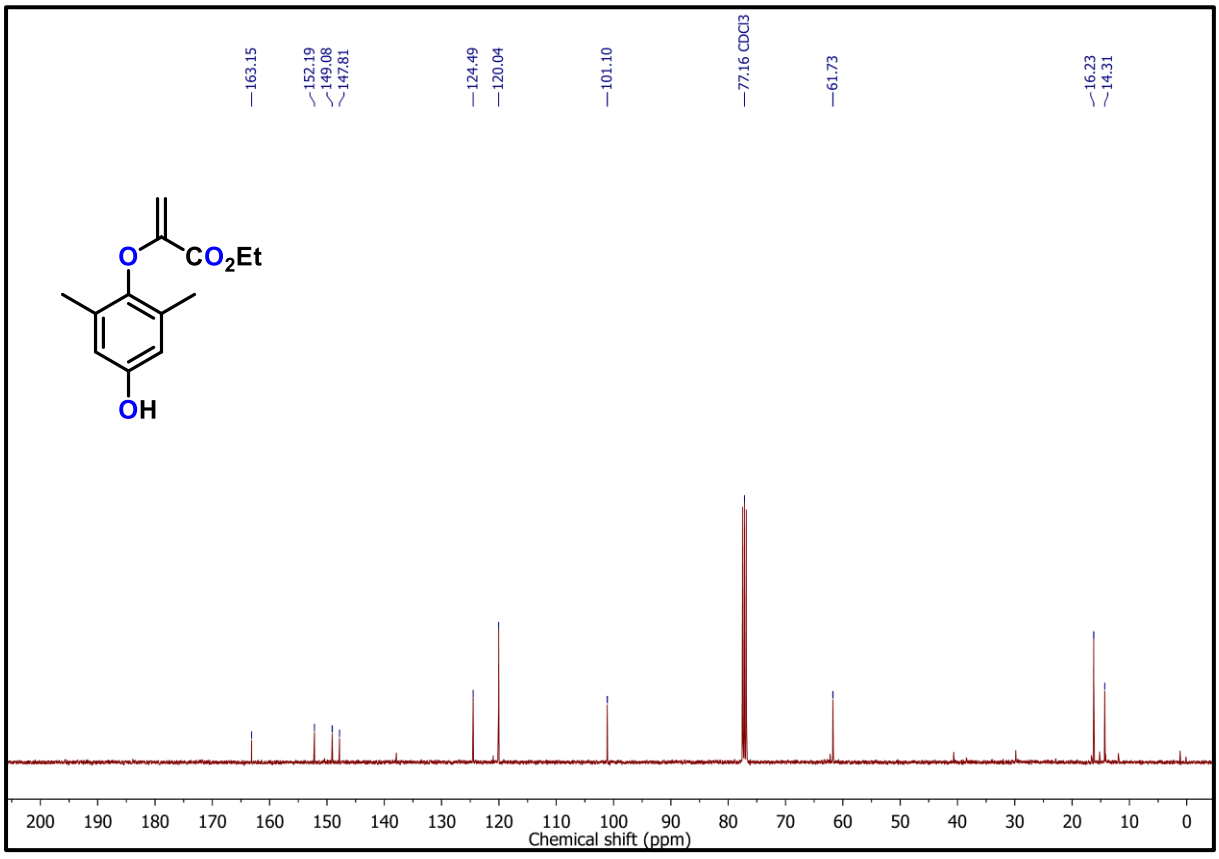
745

746 *[1]H* NMR (400 MHz) of **5e** in $CDCl_3$



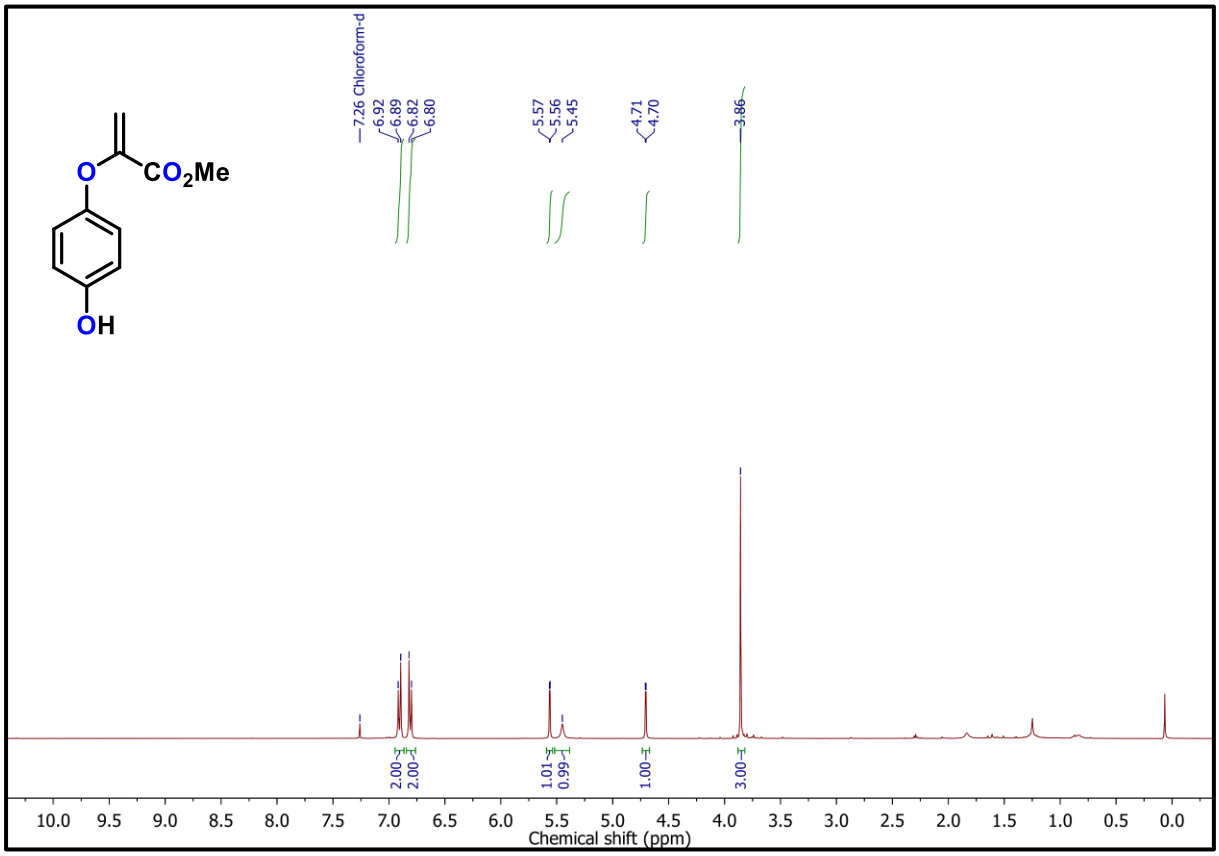
747

748 *[13]C* NMR (100 MHz) of **5e** in $CDCl_3$



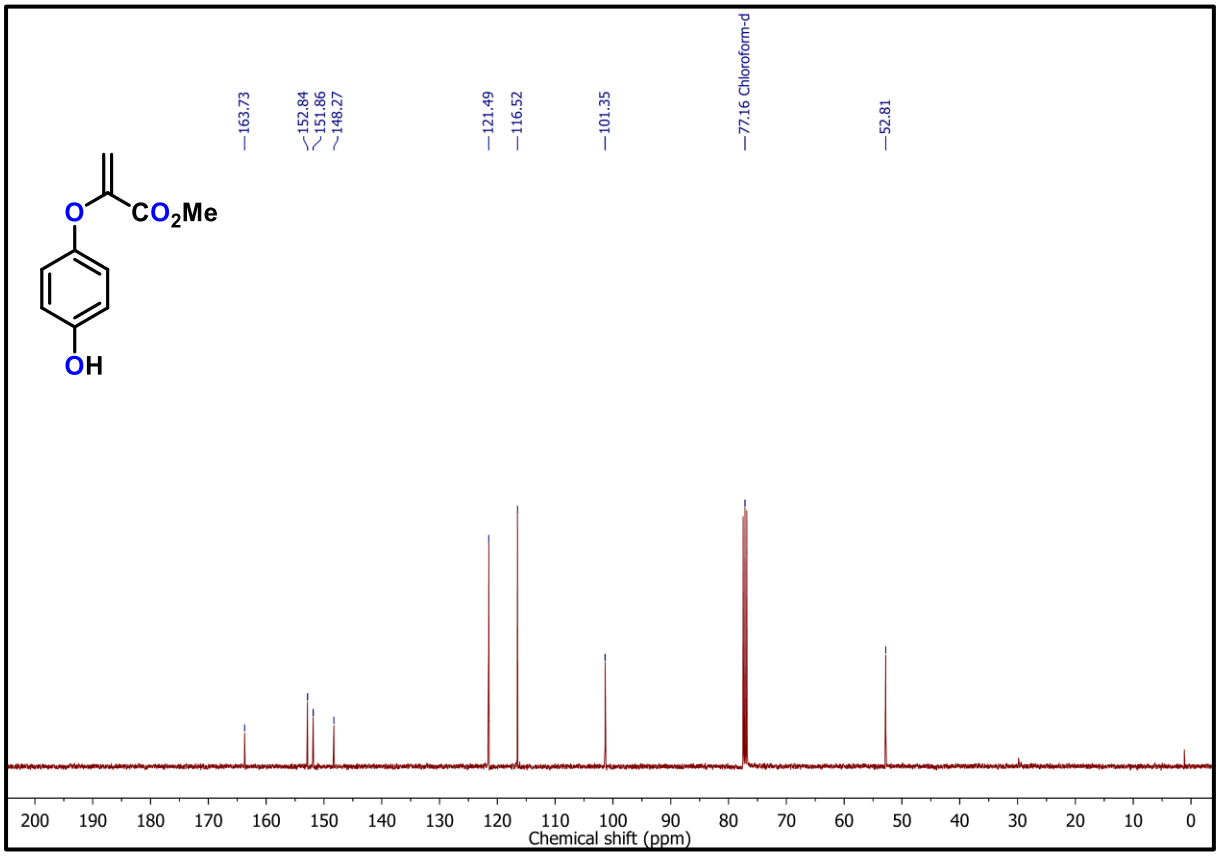
749

750 ^{1}H NMR (400 MHz) of **5f** in $CDCl_3$



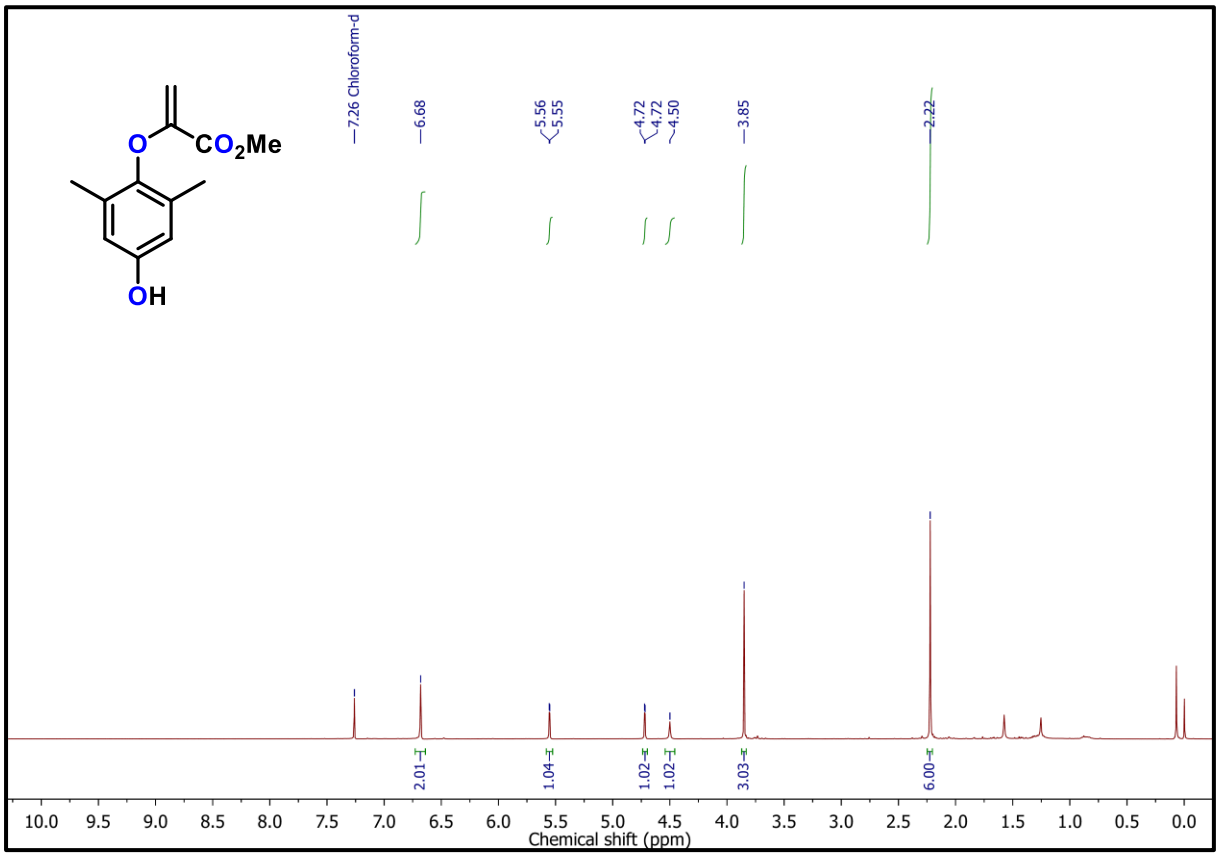
751

752 ^{13}C NMR (100 MHz) of **5f** in $CDCl_3$

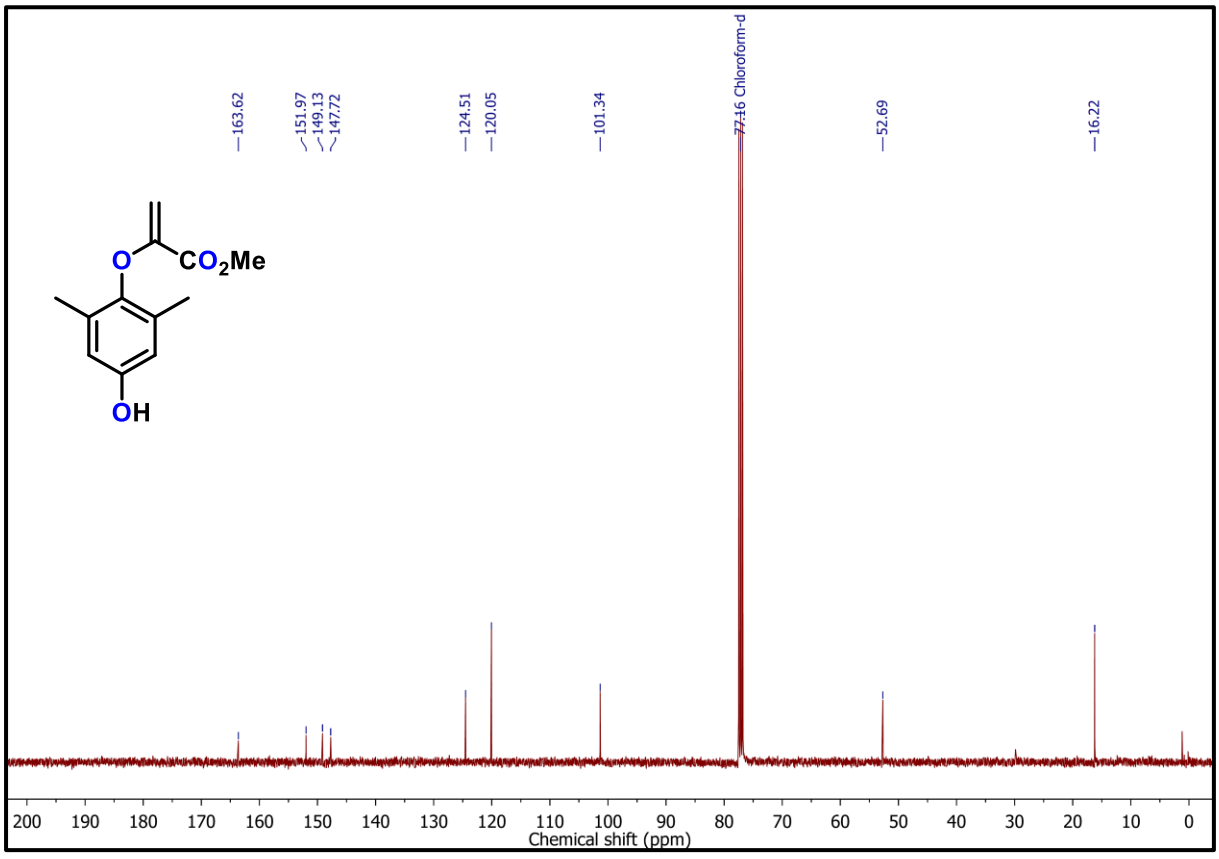


753

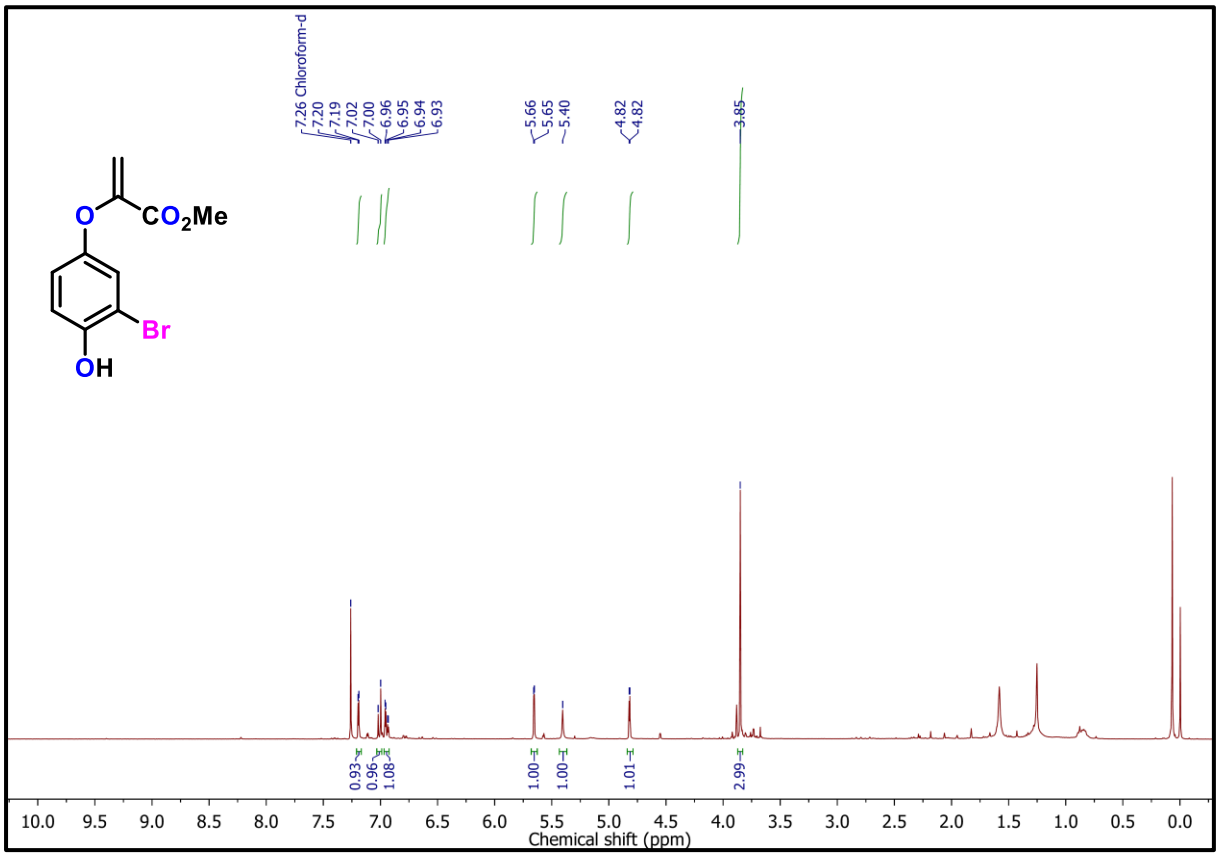
^{1}H NMR (400 MHz) of **5g** in $CDCl_3$



^{13}C NMR (100 MHz) of **5g** in $CDCl_3$

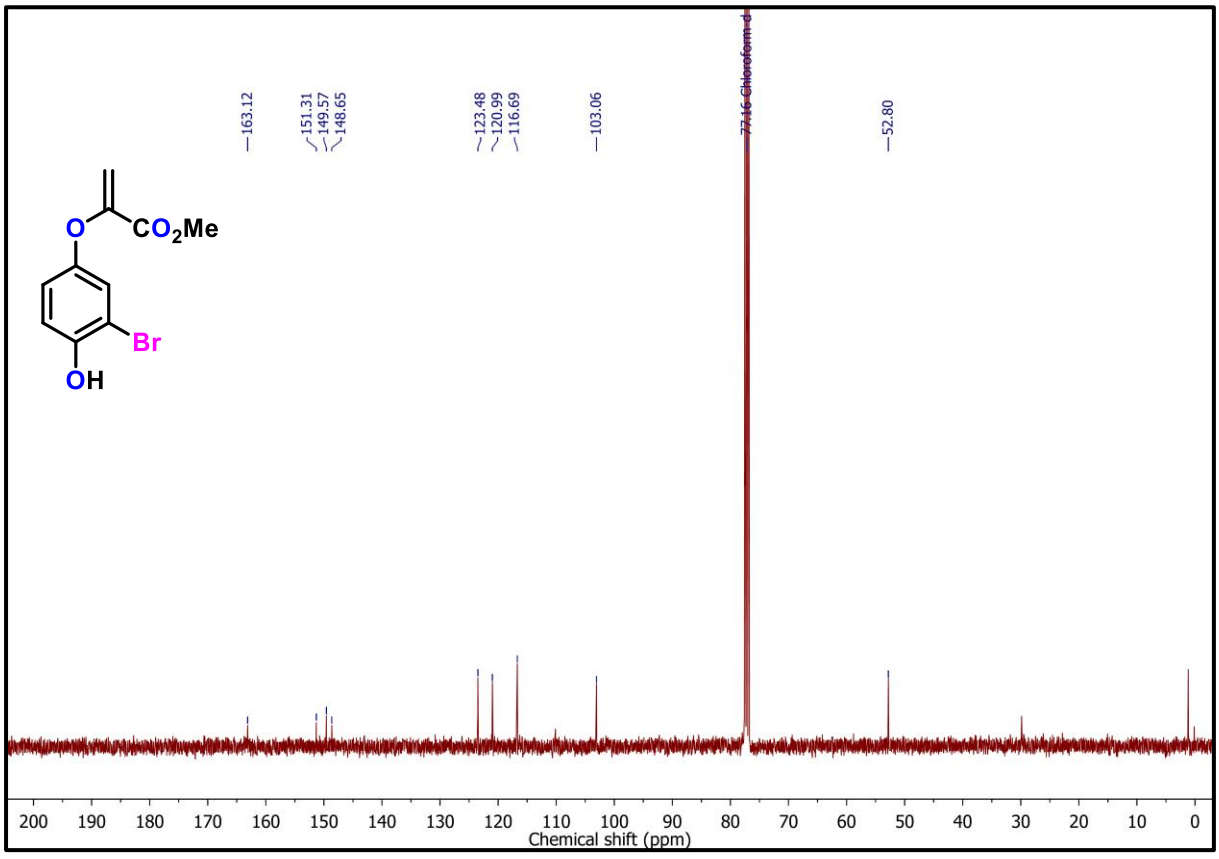


758 ^{1}H NMR (400 MHz) of **5h** in $CDCl_3$



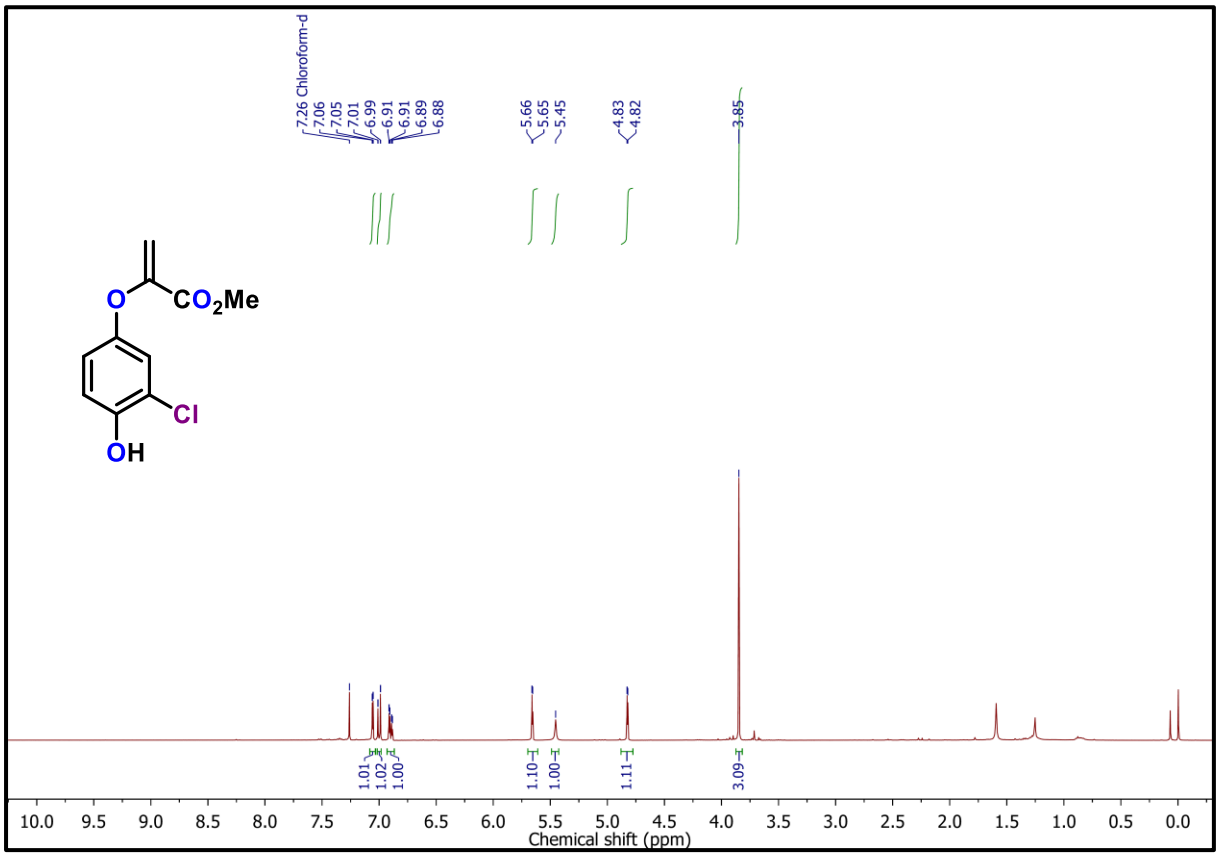
759

760 ^{13}C NMR (100 MHz) of **5h** in $CDCl_3$



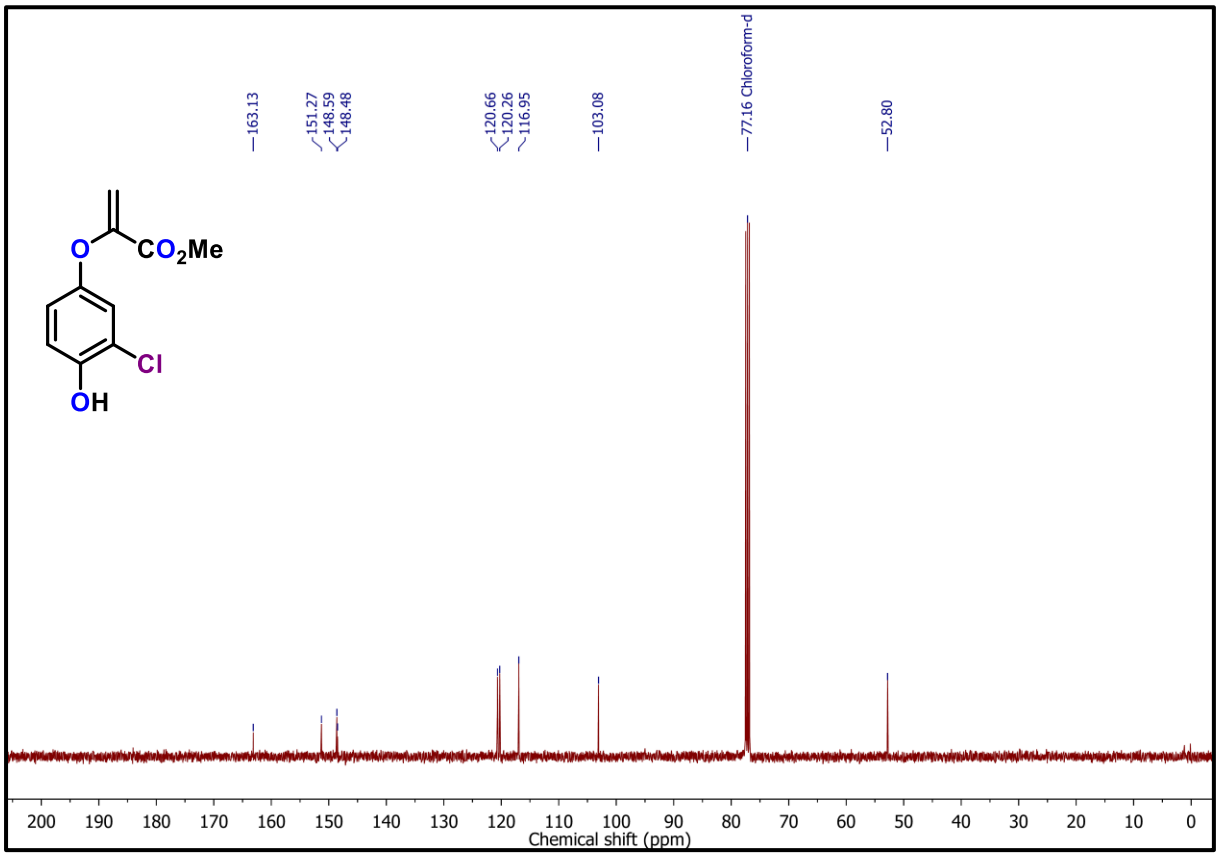
761

762 *[1]H* NMR (400 MHz) of **5i** in $CDCl_3$



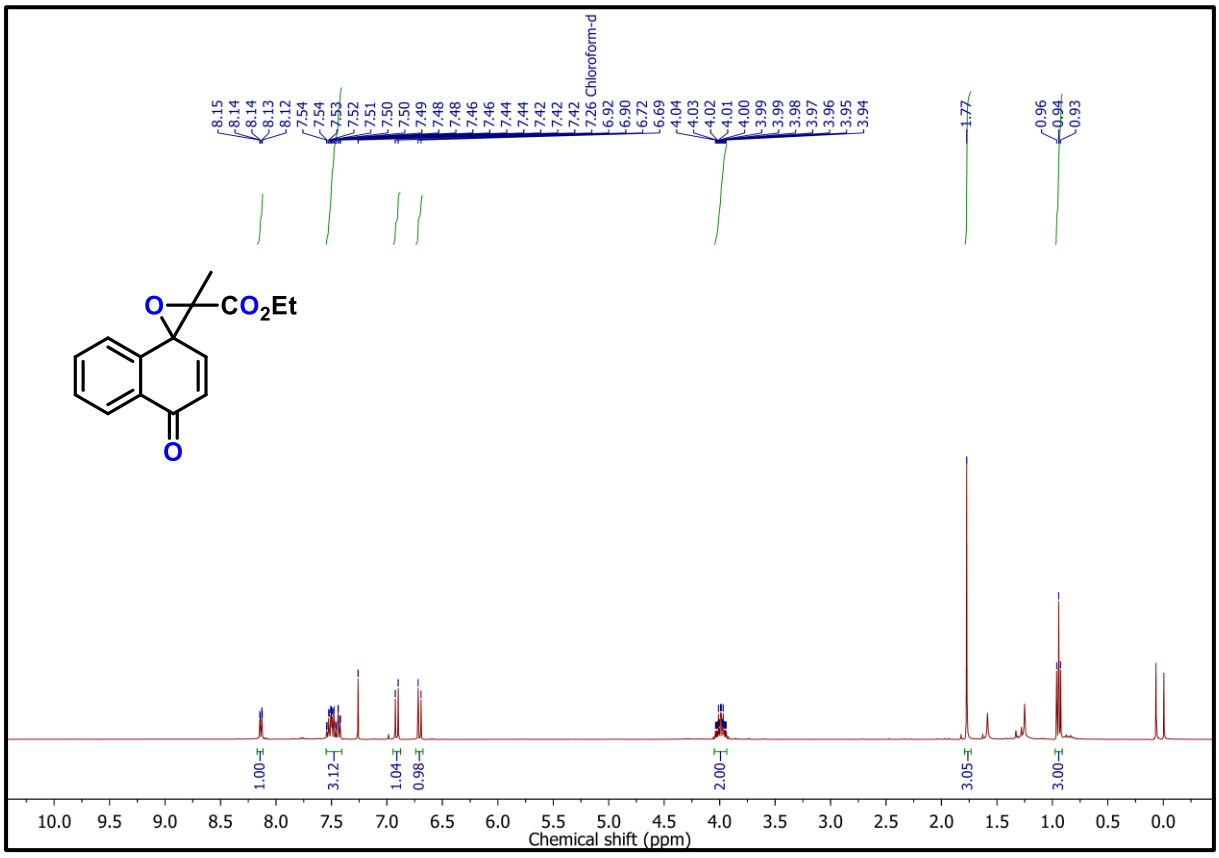
763

764 *[13]C* NMR (100 MHz) of **5i** in $CDCl_3$



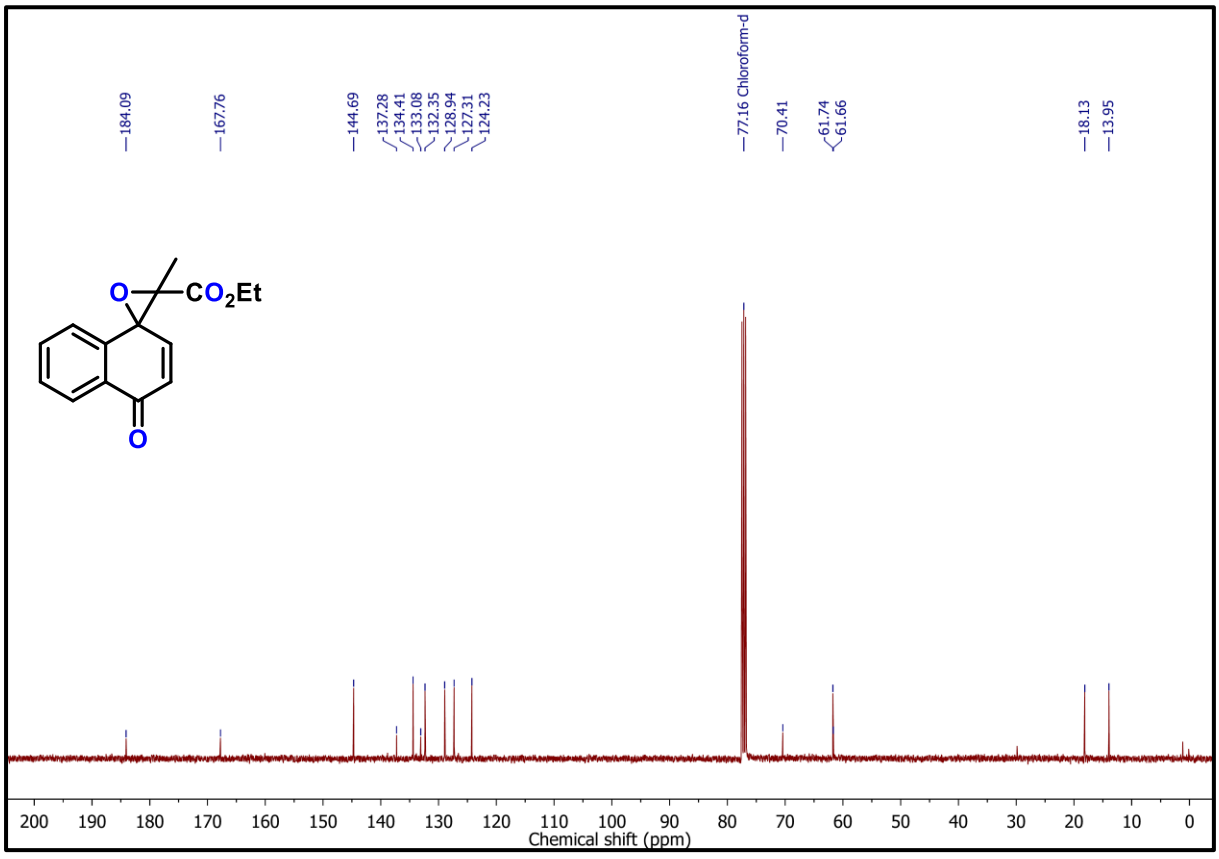
765

766 *[1]H* NMR (400 MHz) of **6a** in $CDCl_3$



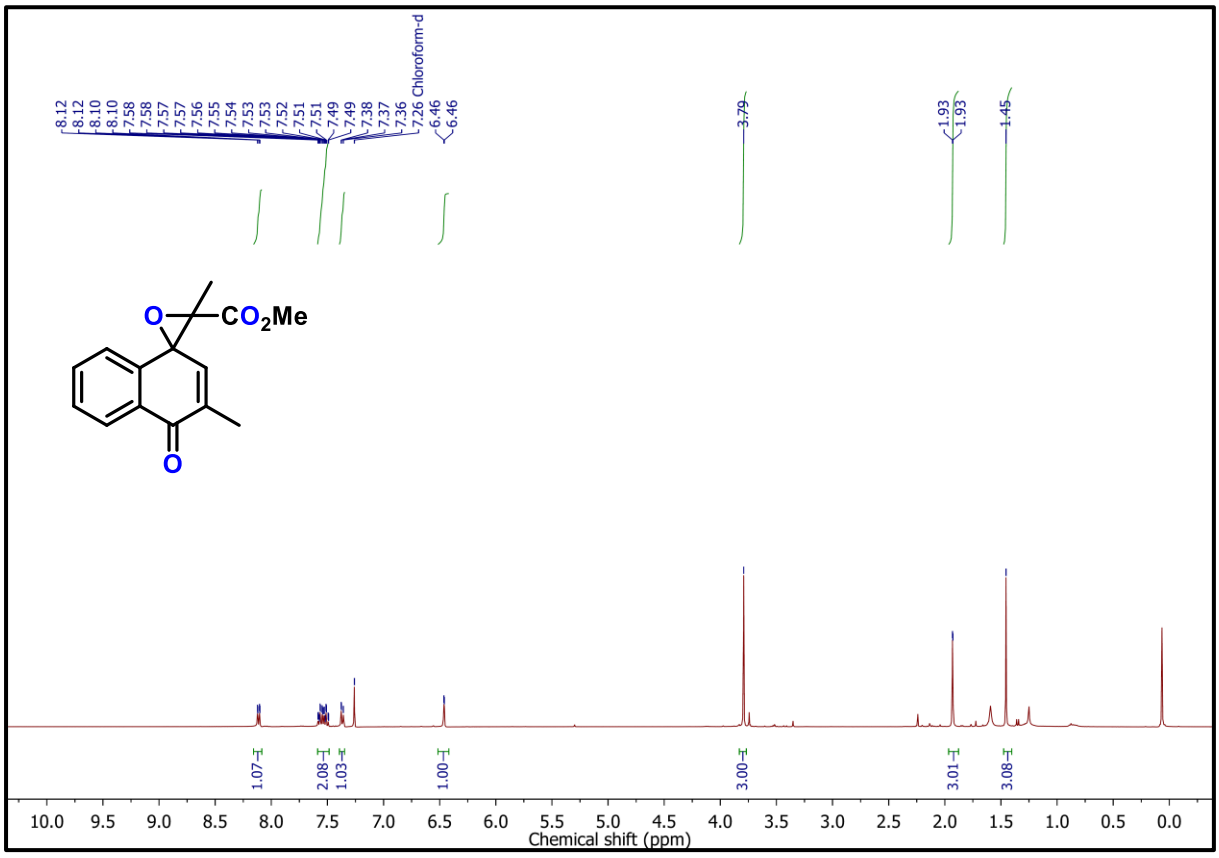
767

768 *[13]C* NMR (100 MHz) of **6a** in $CDCl_3$



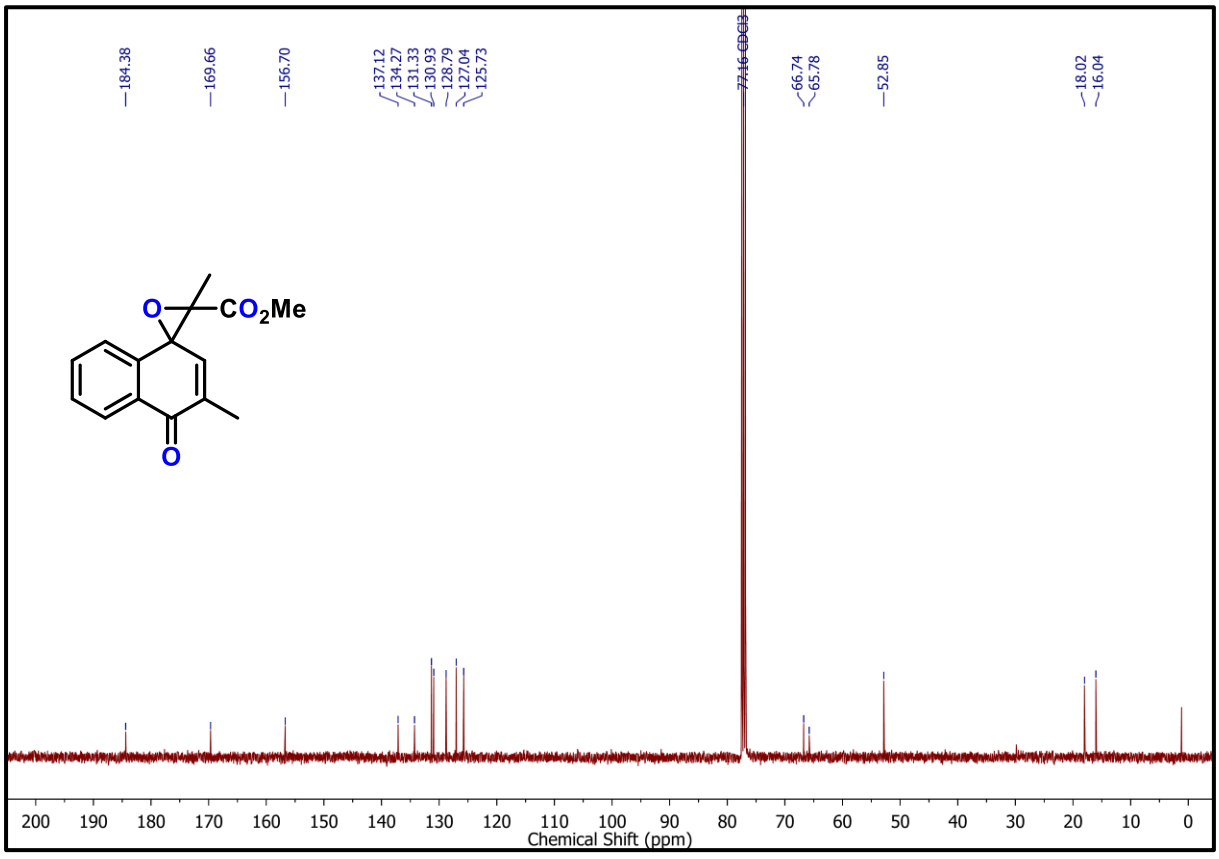
769

770 *[1]H* NMR (400 MHz) of **6b** in $CDCl_3$



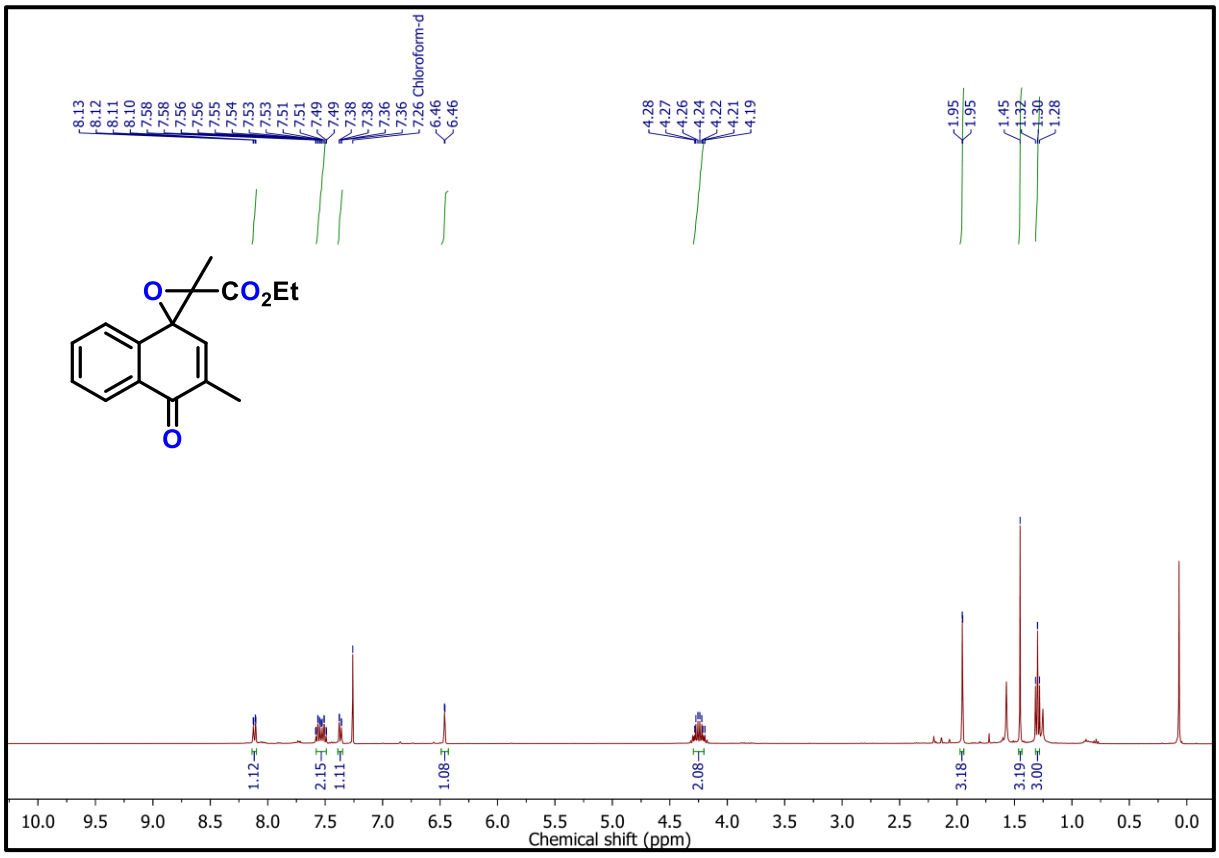
771

772 *[13]C* NMR (100 MHz) of **6b** in $CDCl_3$



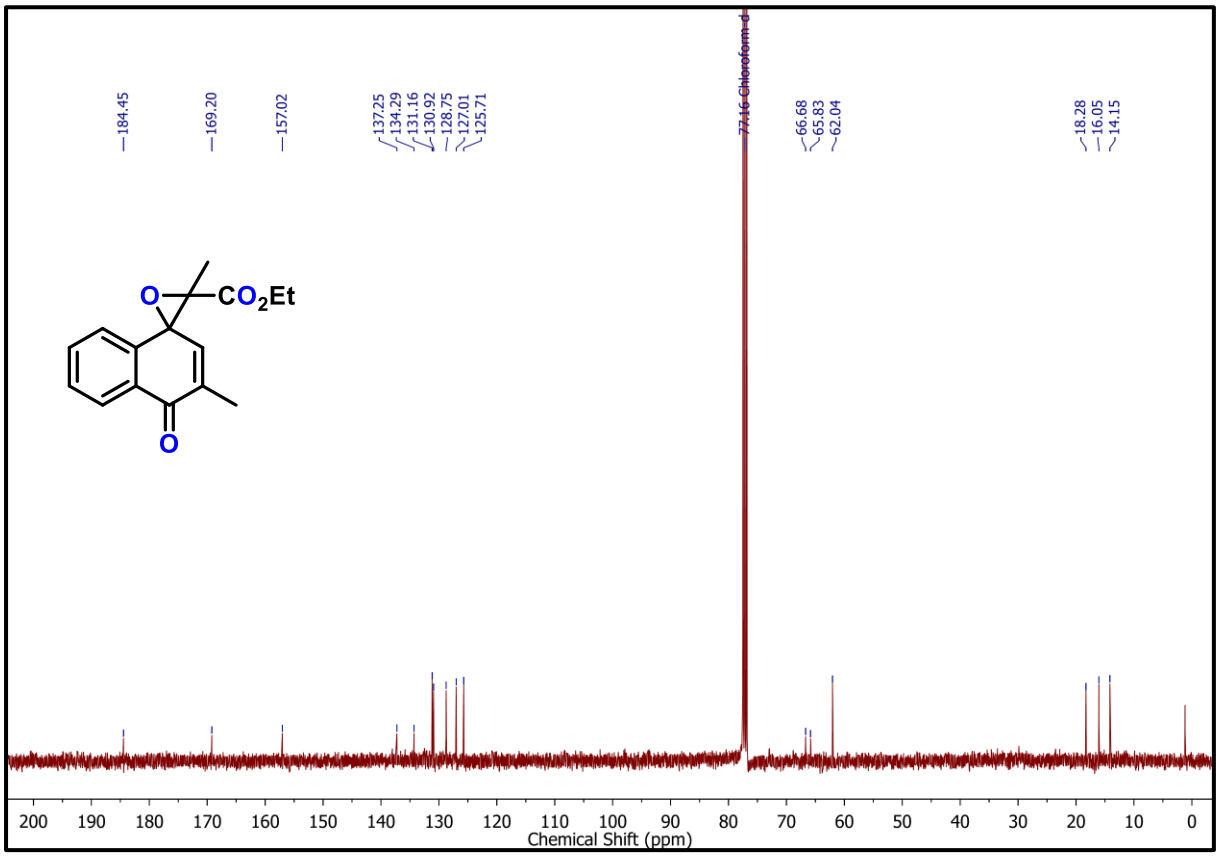
773

774 ^{1}H NMR (400 MHz) of **6c** in $CDCl_3$



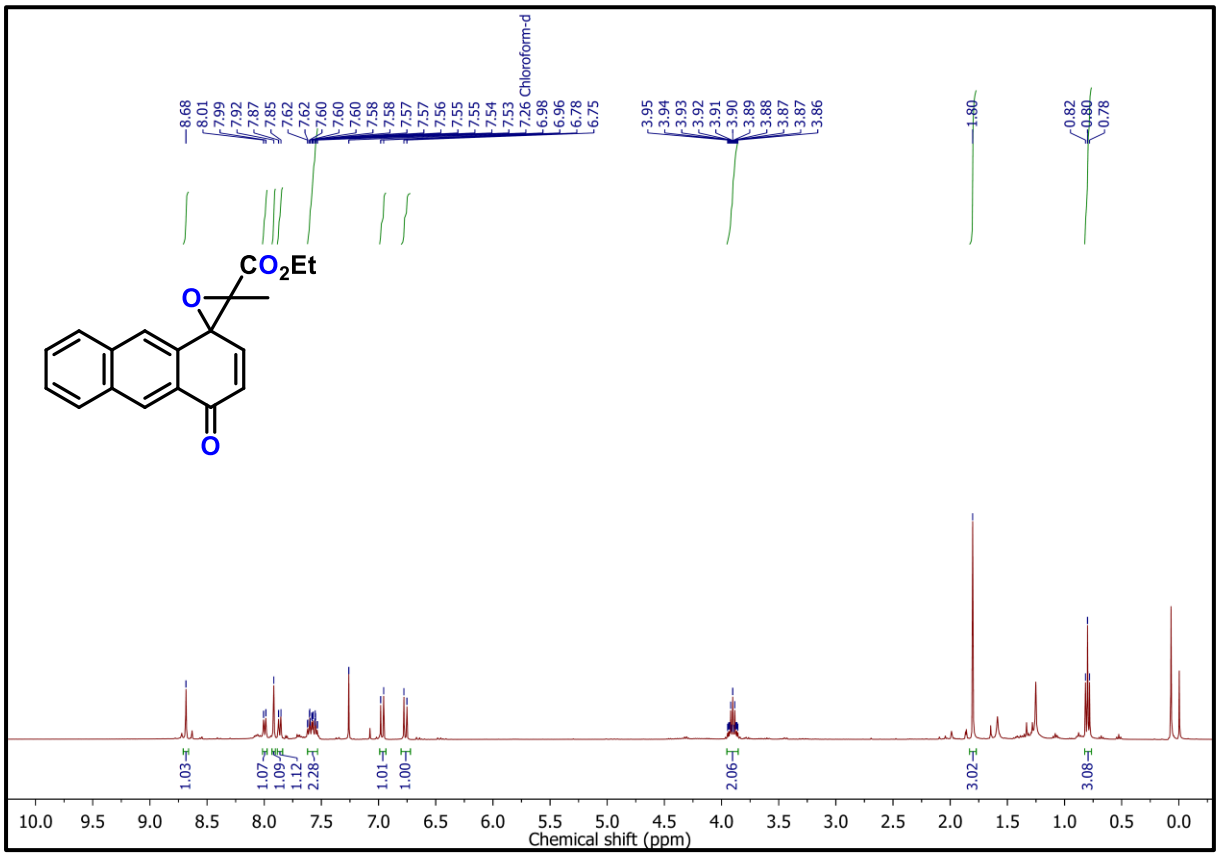
775

776 ^{13}C NMR (100 MHz) of **6c** in $CDCl_3$



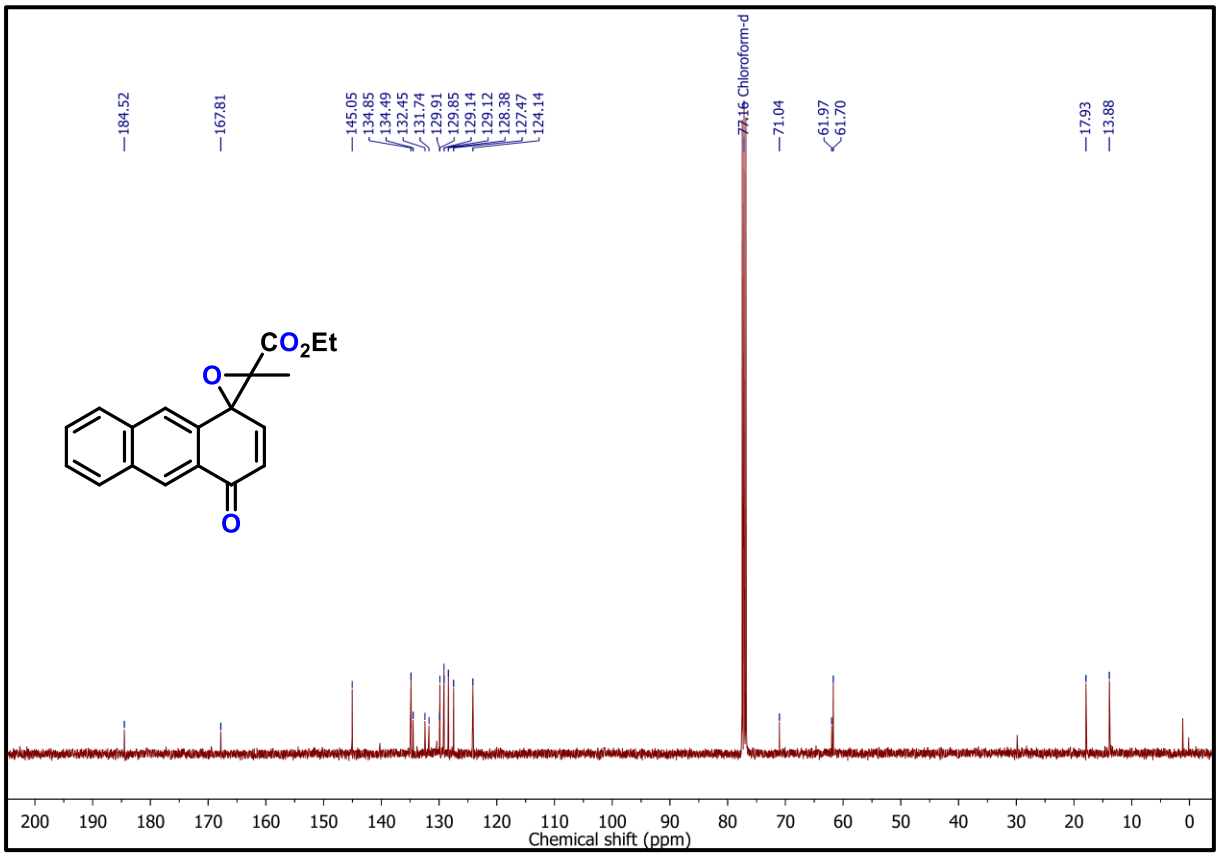
777

778 *[1]H* NMR (400 MHz) of **7a** in $CDCl_3$



779

780 *[13]C* NMR (100 MHz) of **7a** in $CDCl_3$



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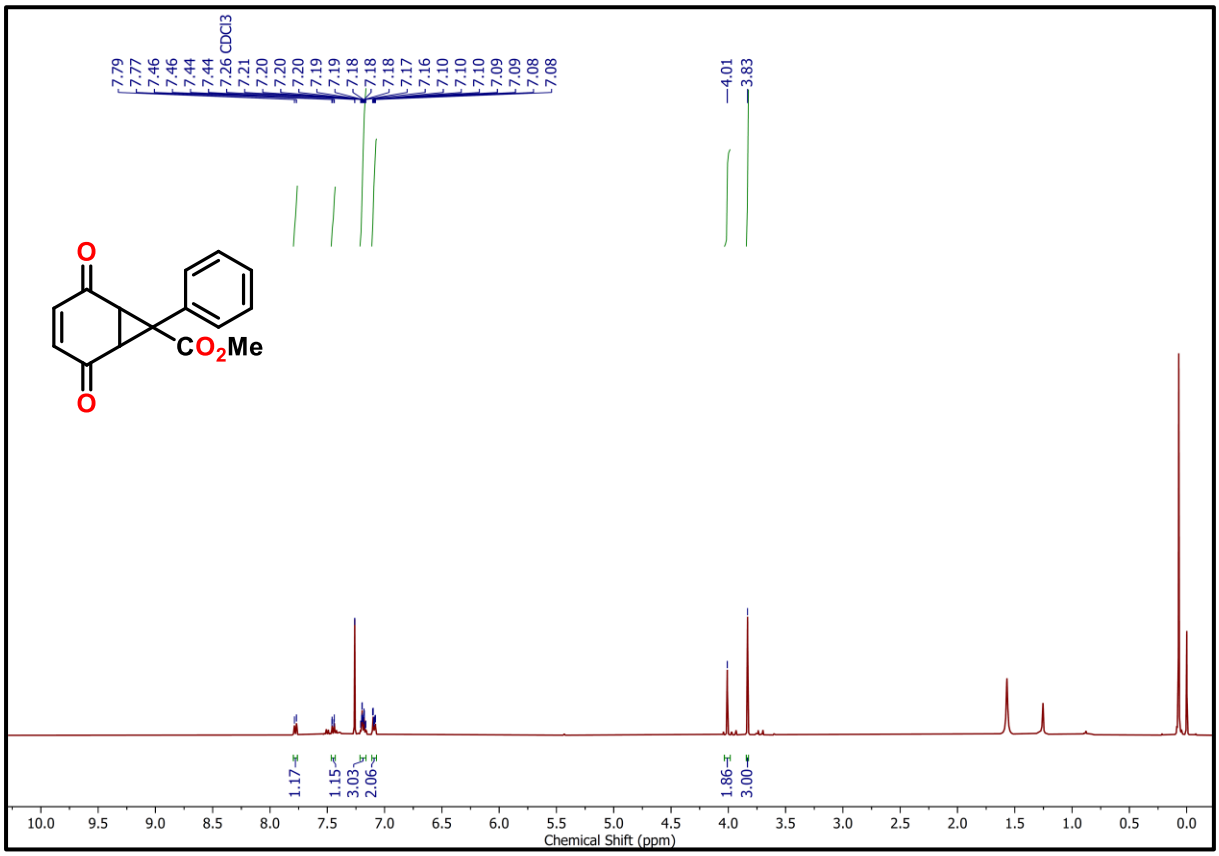
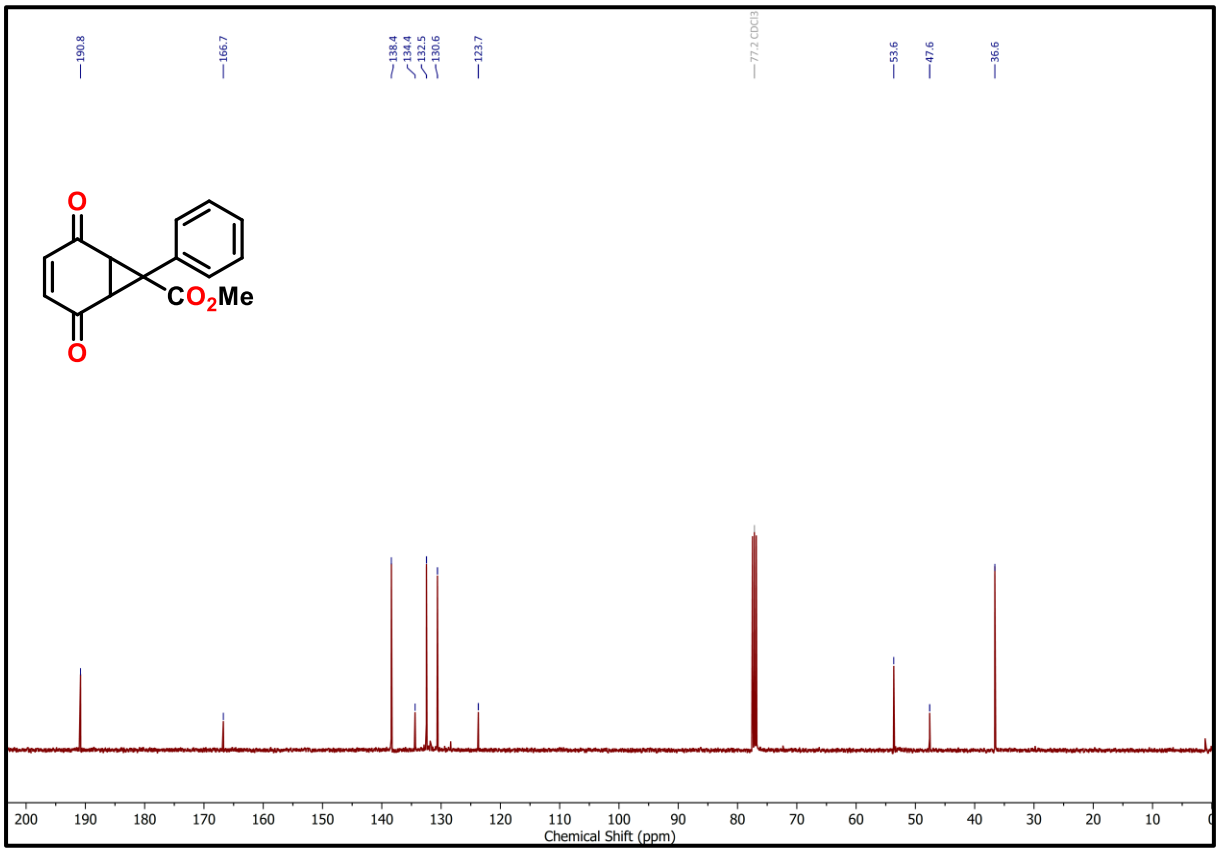
782 *[1]H* NMR (400 MHz) of **8a** in $CDCl_3$



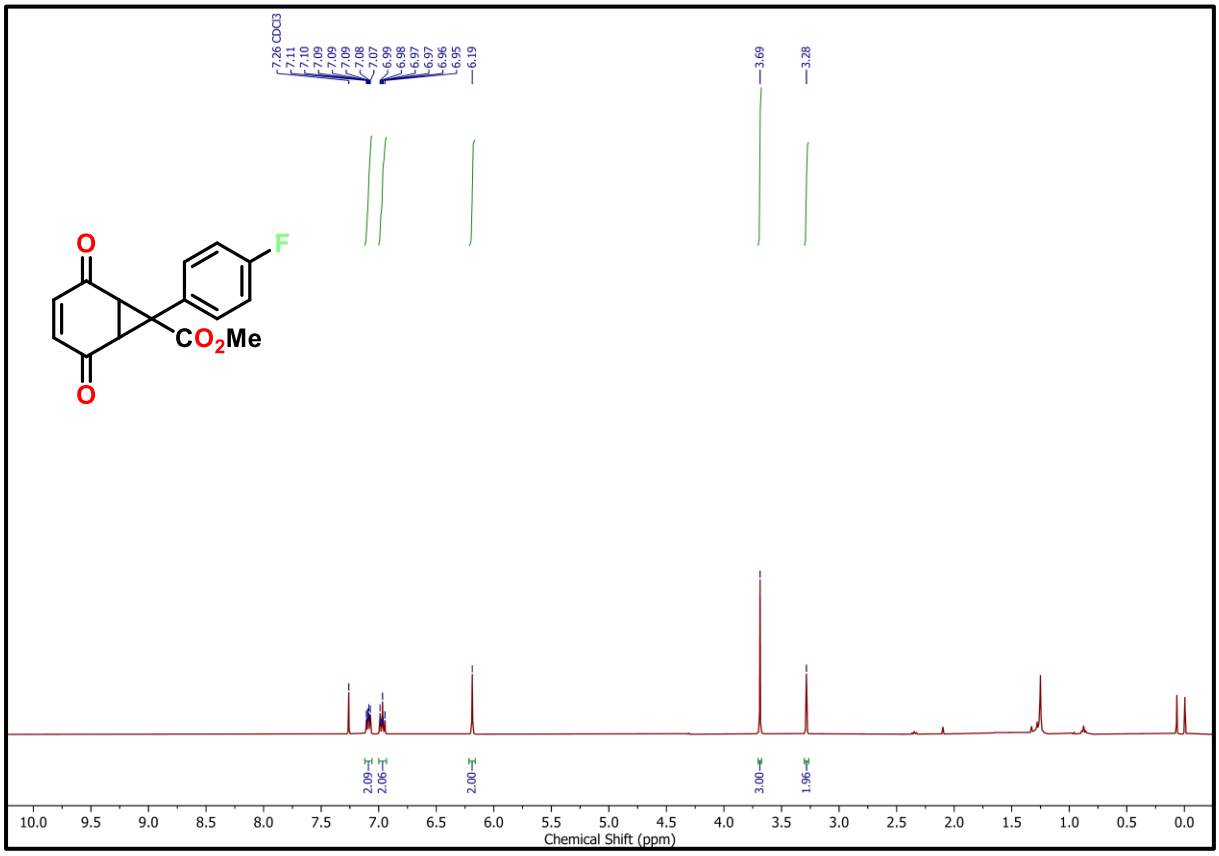
783

784 *[13]C* NMR (100 MHz) of **8a** in $CDCl_3$



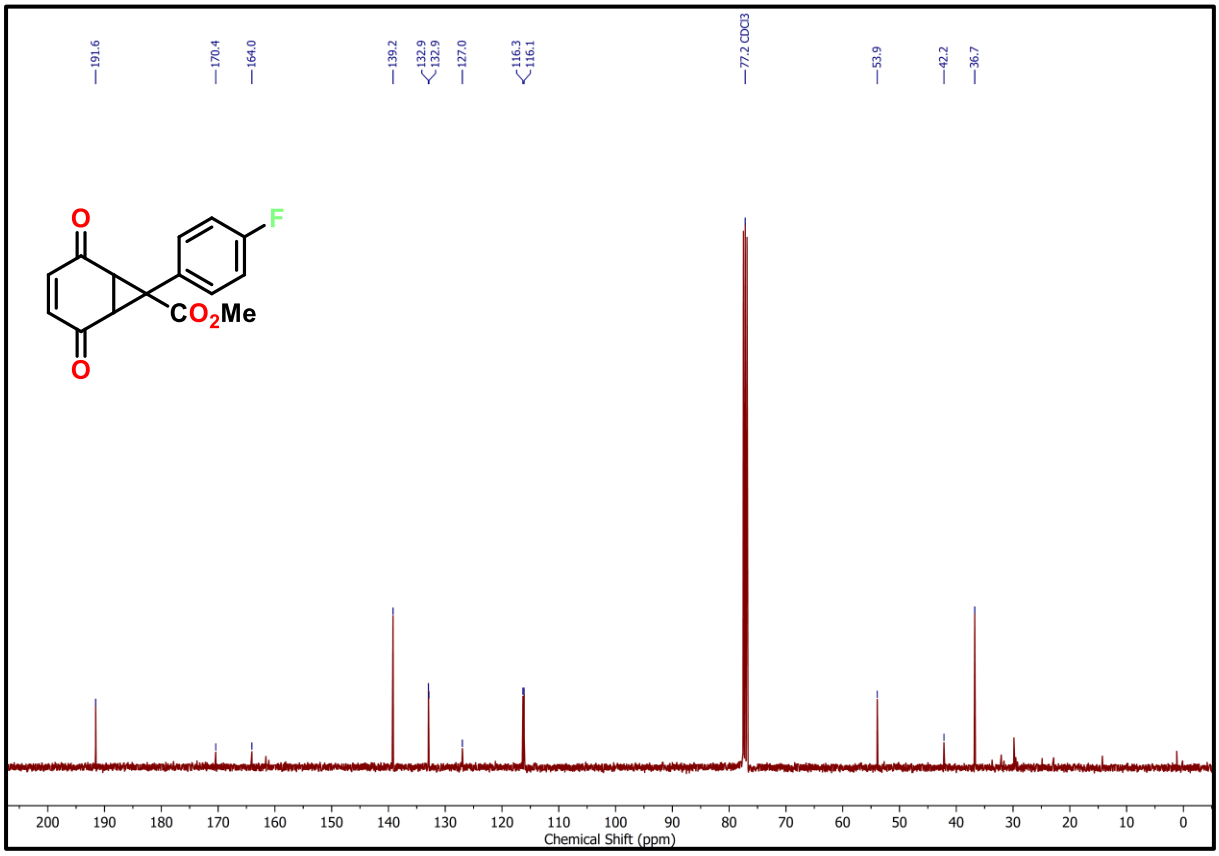
785

786 ^{1}H NMR (400 MHz) of **8b** in $CDCl_3$



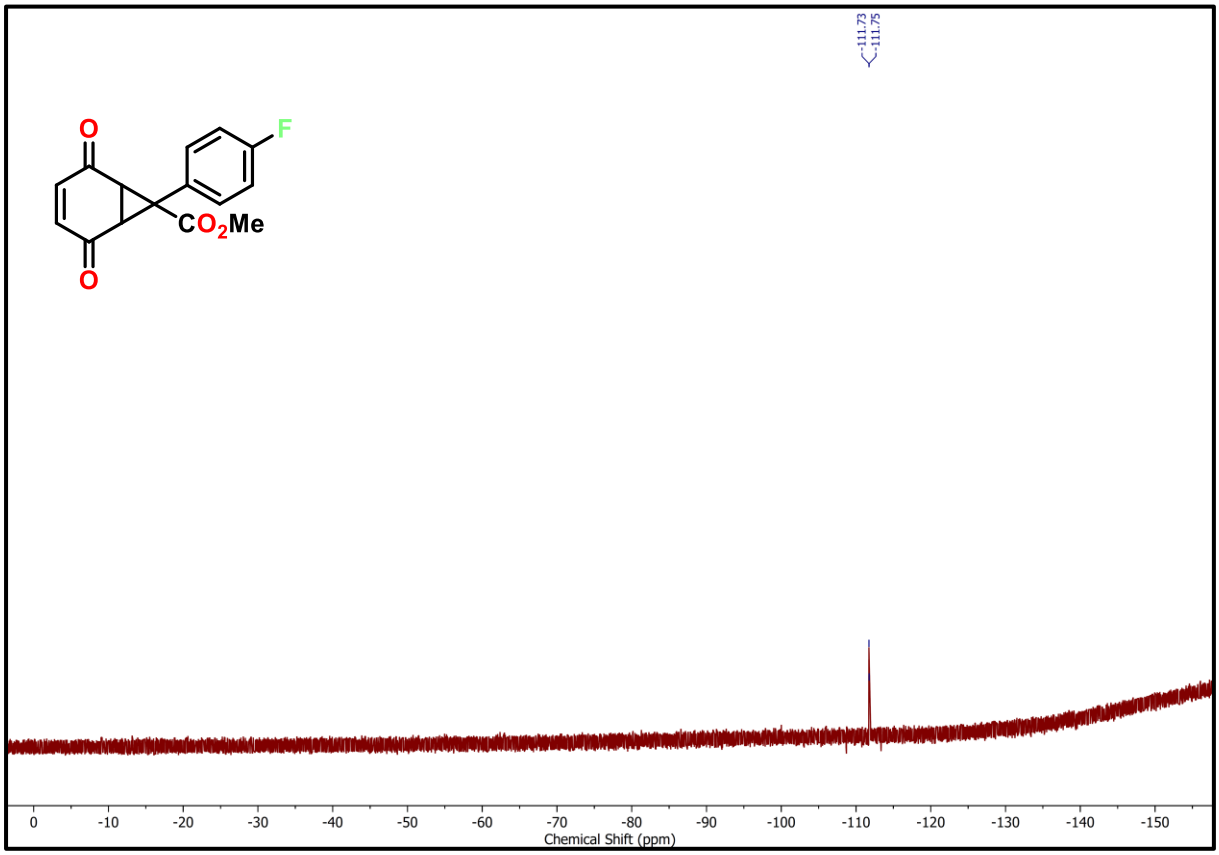
787

788 ^{13}C NMR (100 MHz) of **8b** in $CDCl_3$

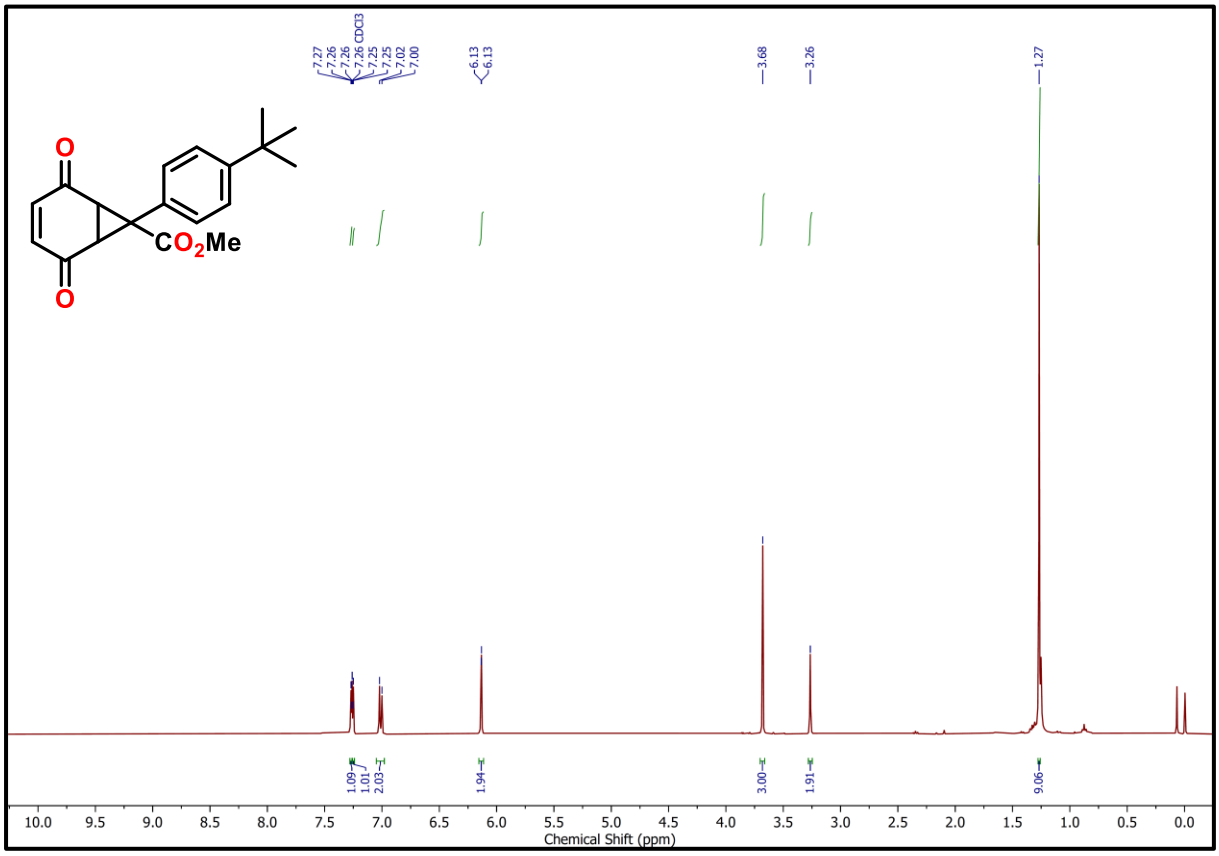


789

^{19}F NMR (376 MHz) of **8b** in $CDCl_3$

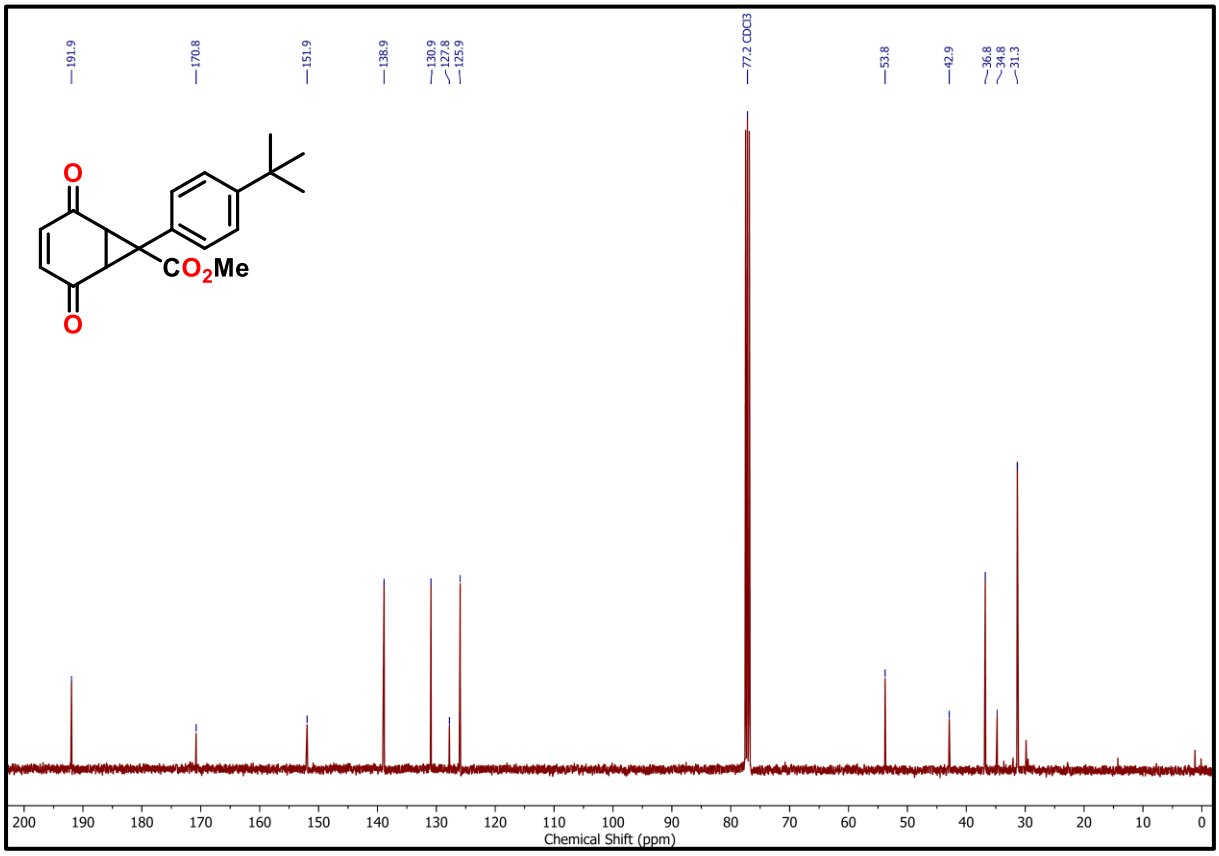


807 ^{1}H NMR (400 MHz) of **8c** in $CDCl_3$



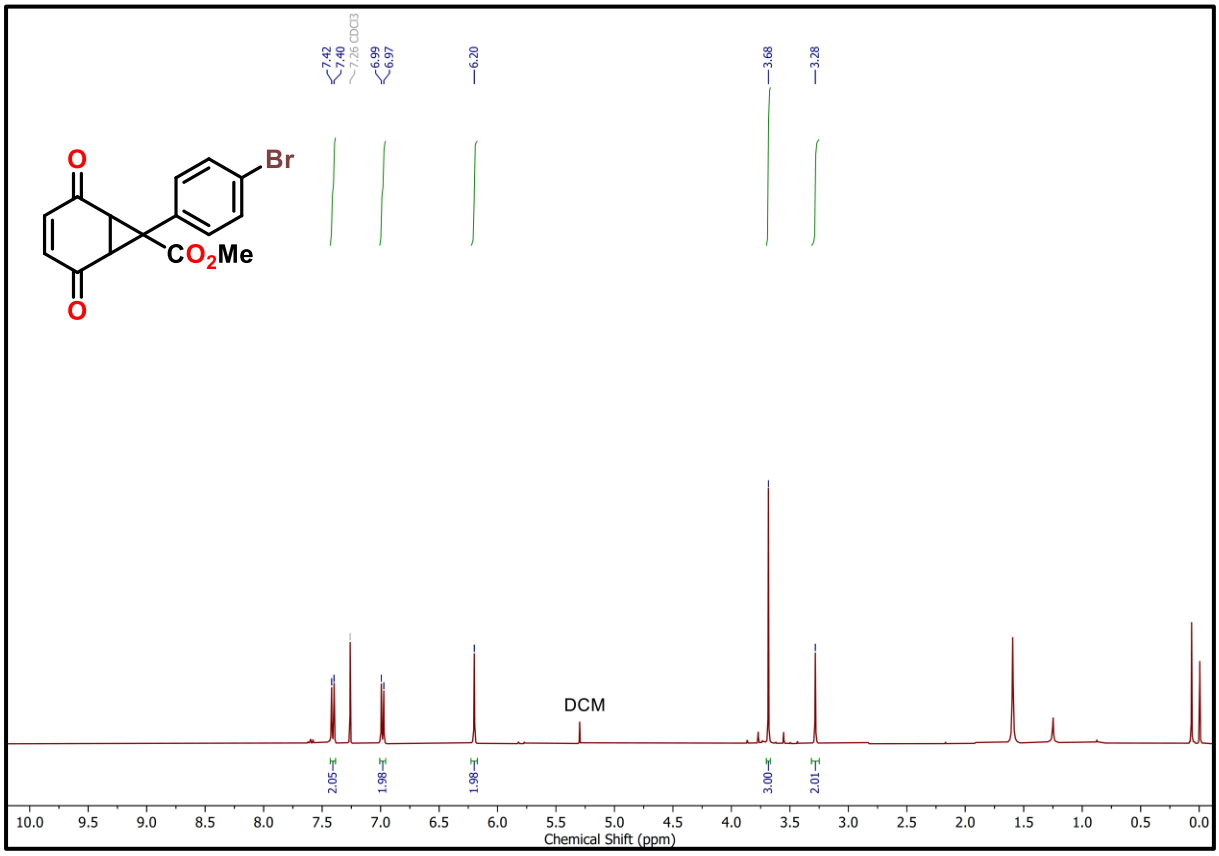
808

809 ^{13}C NMR (100 MHz) of **8c** in $CDCl_3$



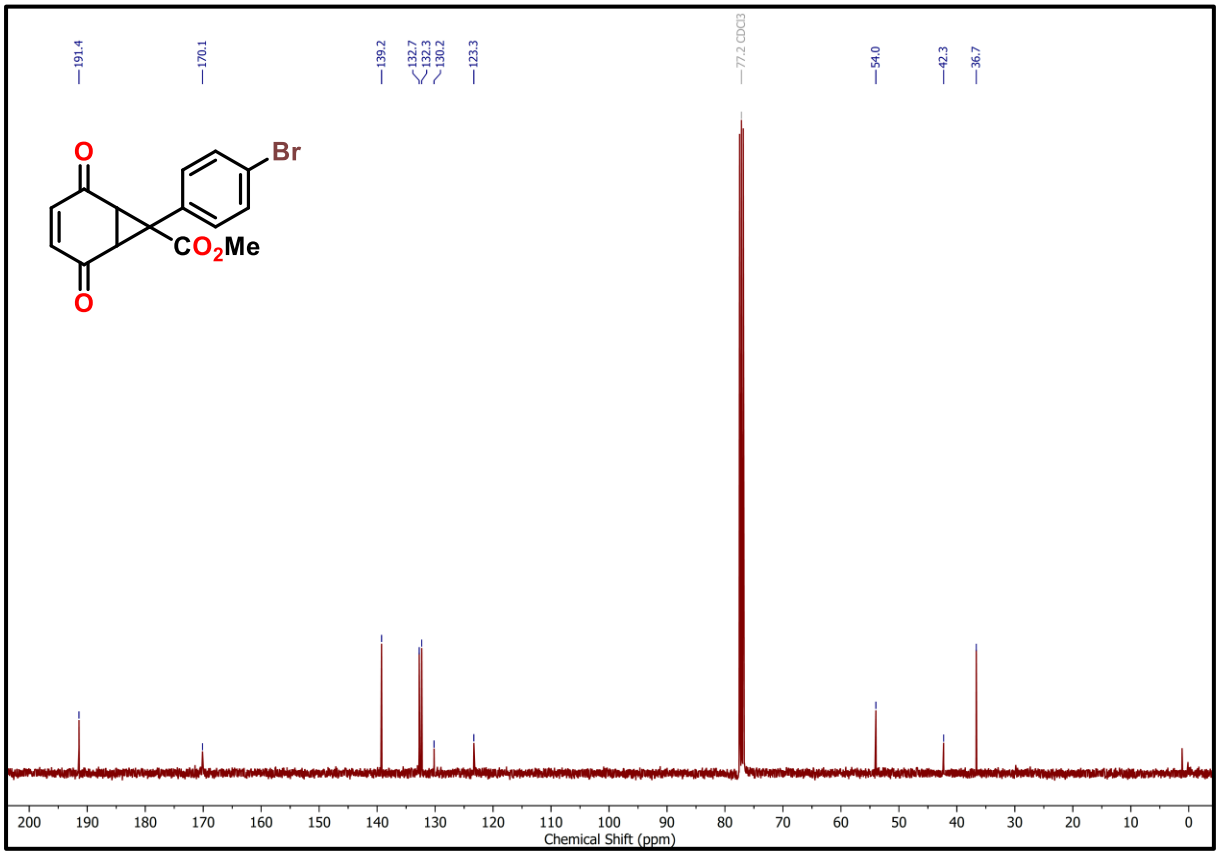
810

811 ^{1}H NMR (400 MHz) of **8d** in $CDCl_3$



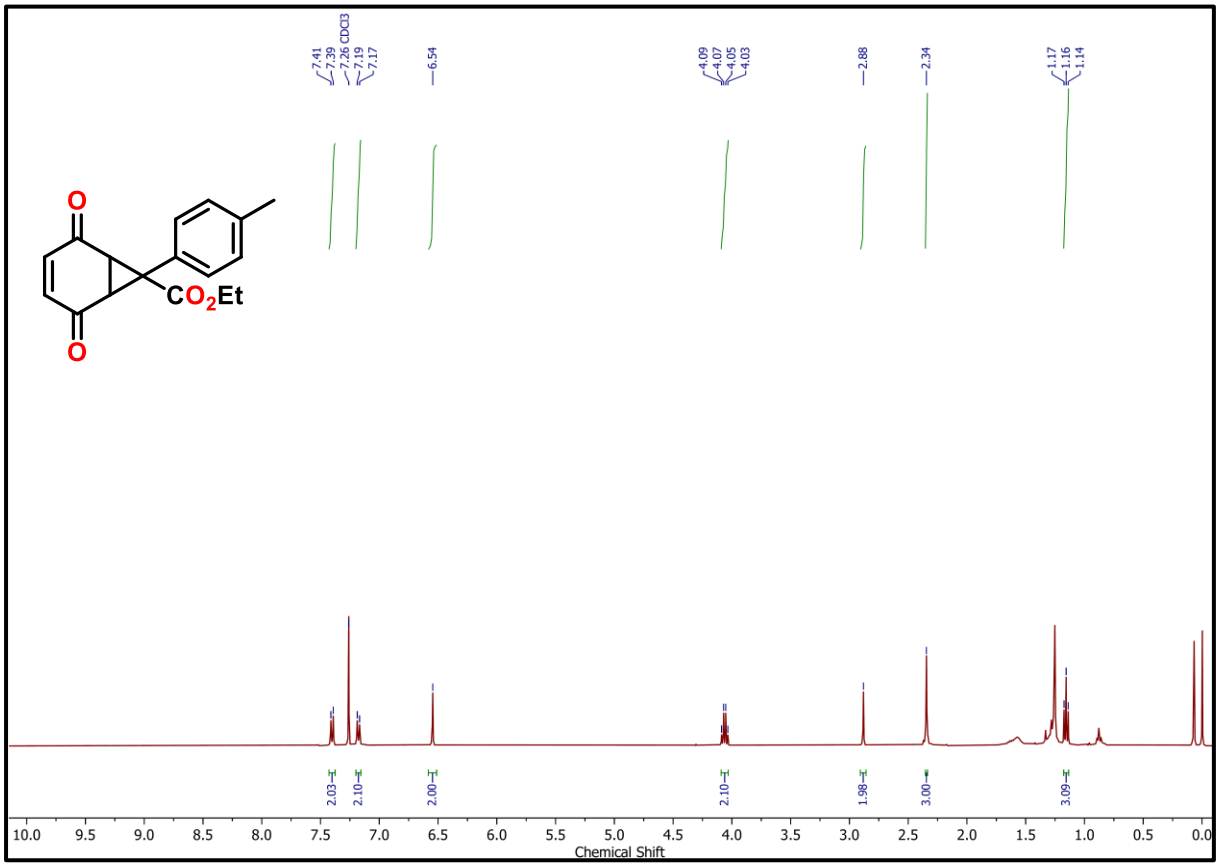
812

813 ^{13}C NMR (100 MHz) of **8d** in $CDCl_3$



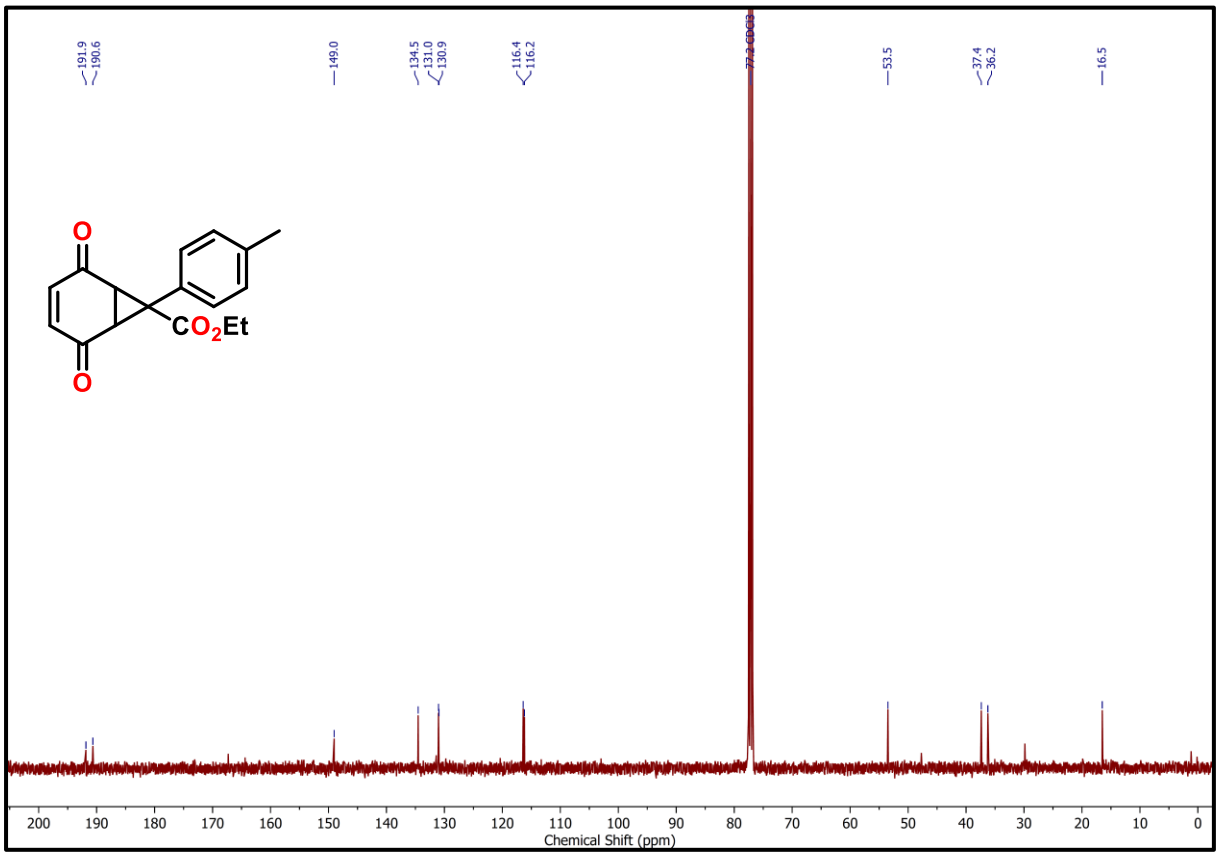
814

815 ^{1}H NMR (400 MHz) of **8e** in $CDCl_3$



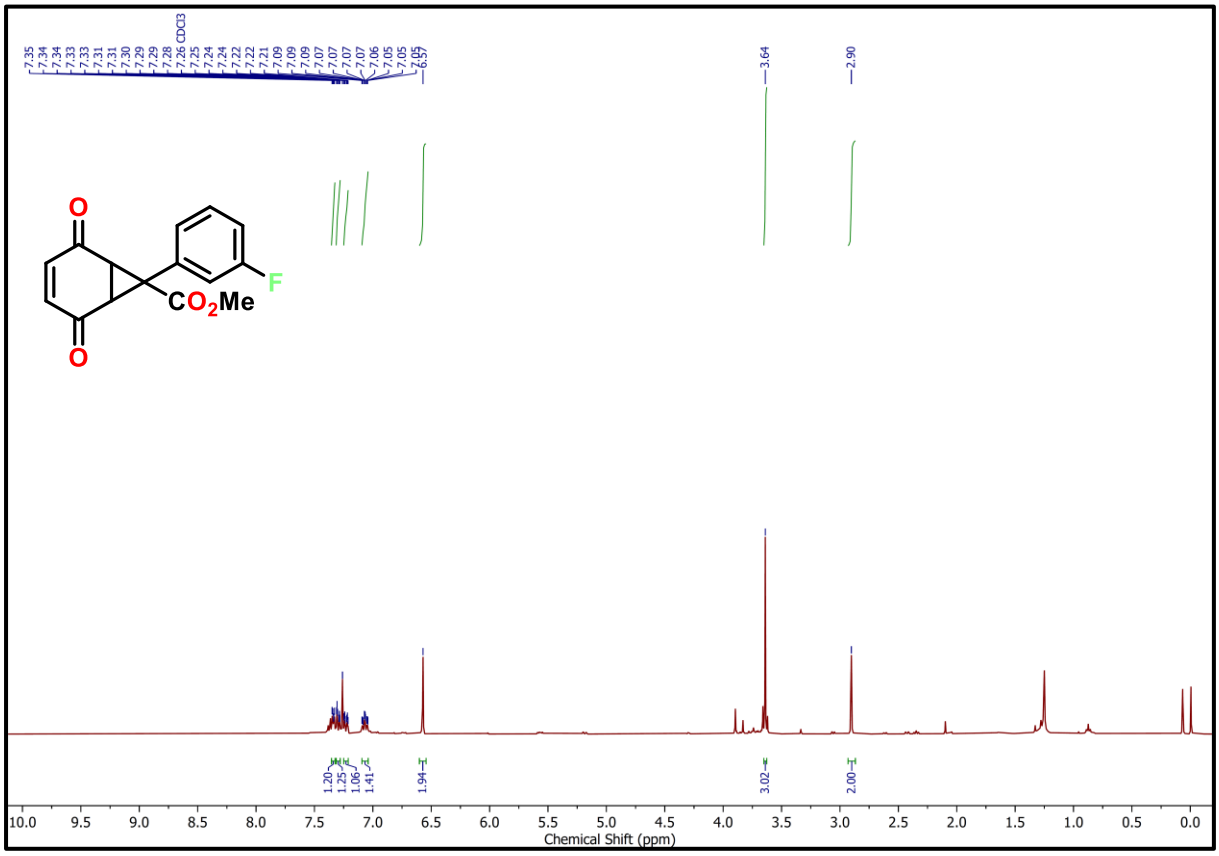
816

817 ^{13}C NMR (100 MHz) of **8e** in $CDCl_3$



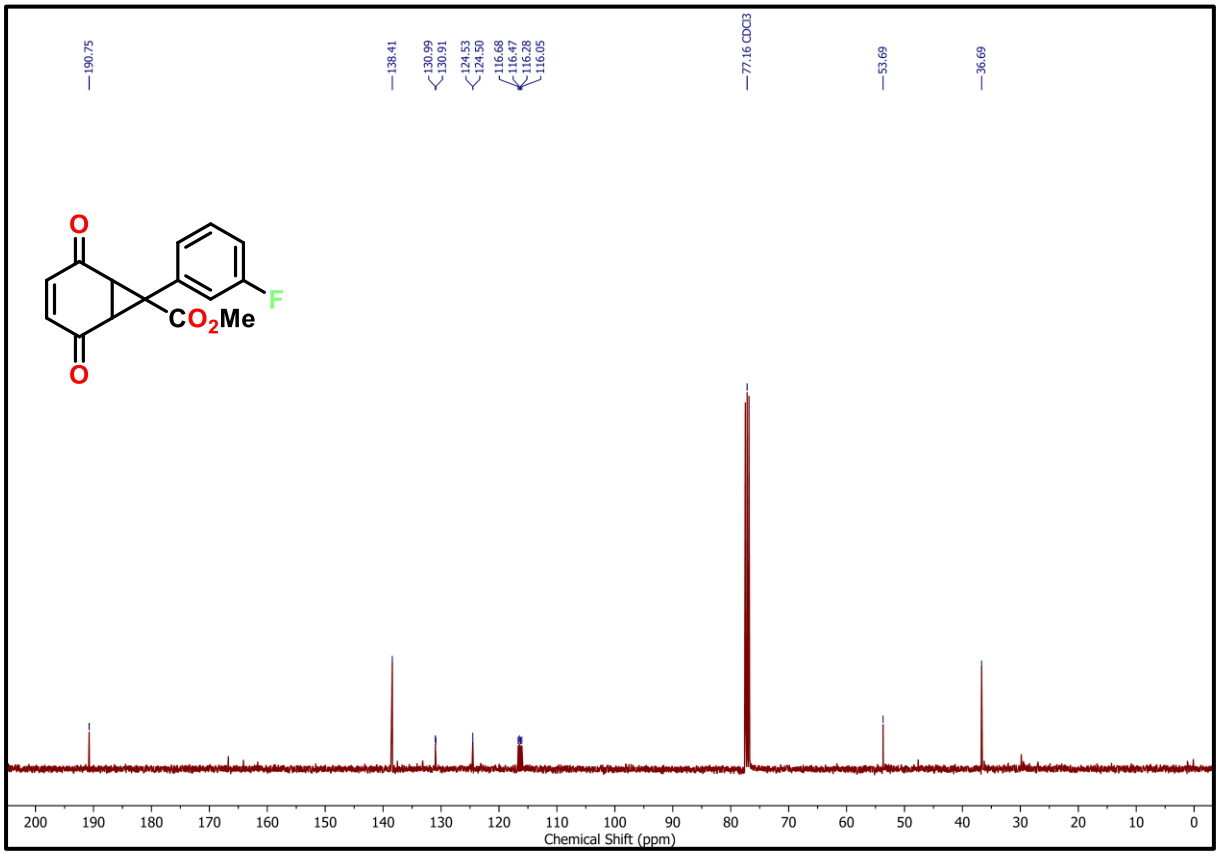
818

819 ^{1}H NMR (400 MHz) of **8f** in $CDCl_3$



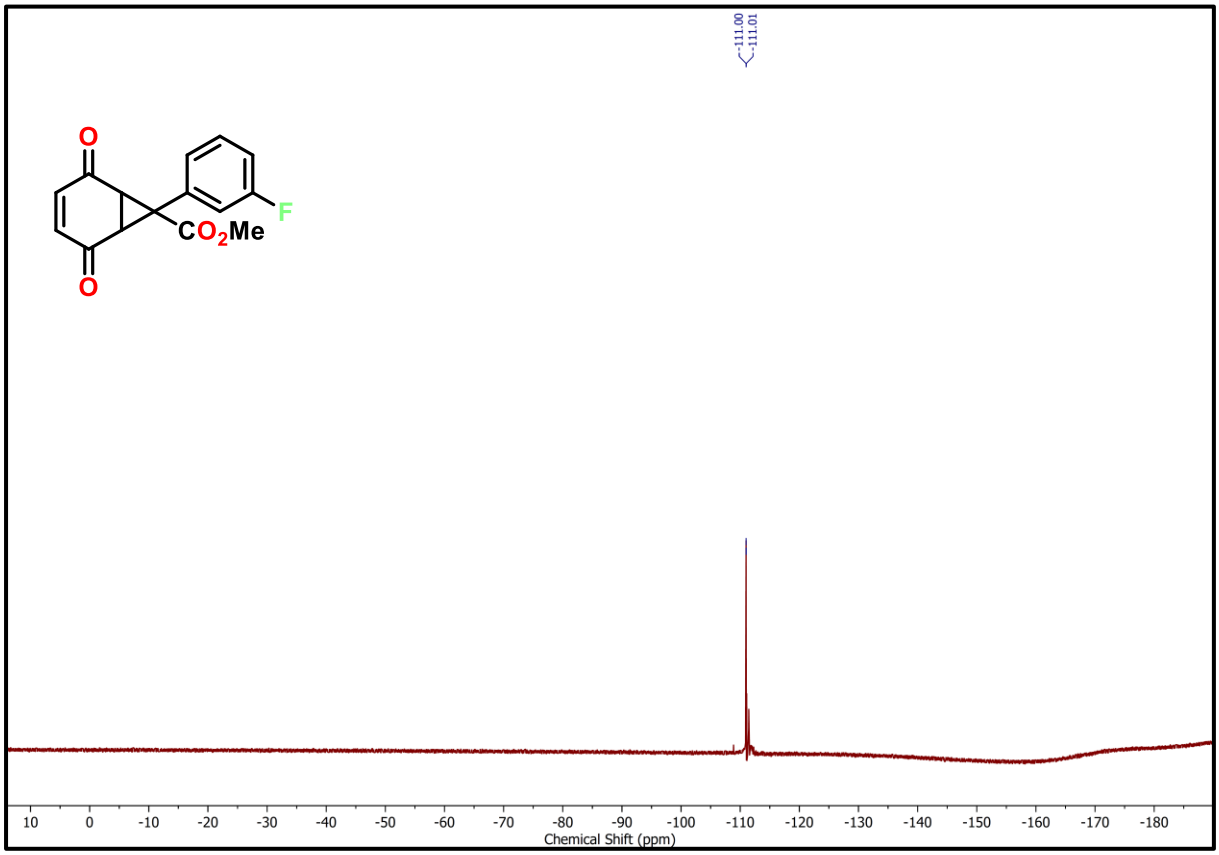
820

821 ^{13}C NMR (100 MHz) of **8f** in $CDCl_3$

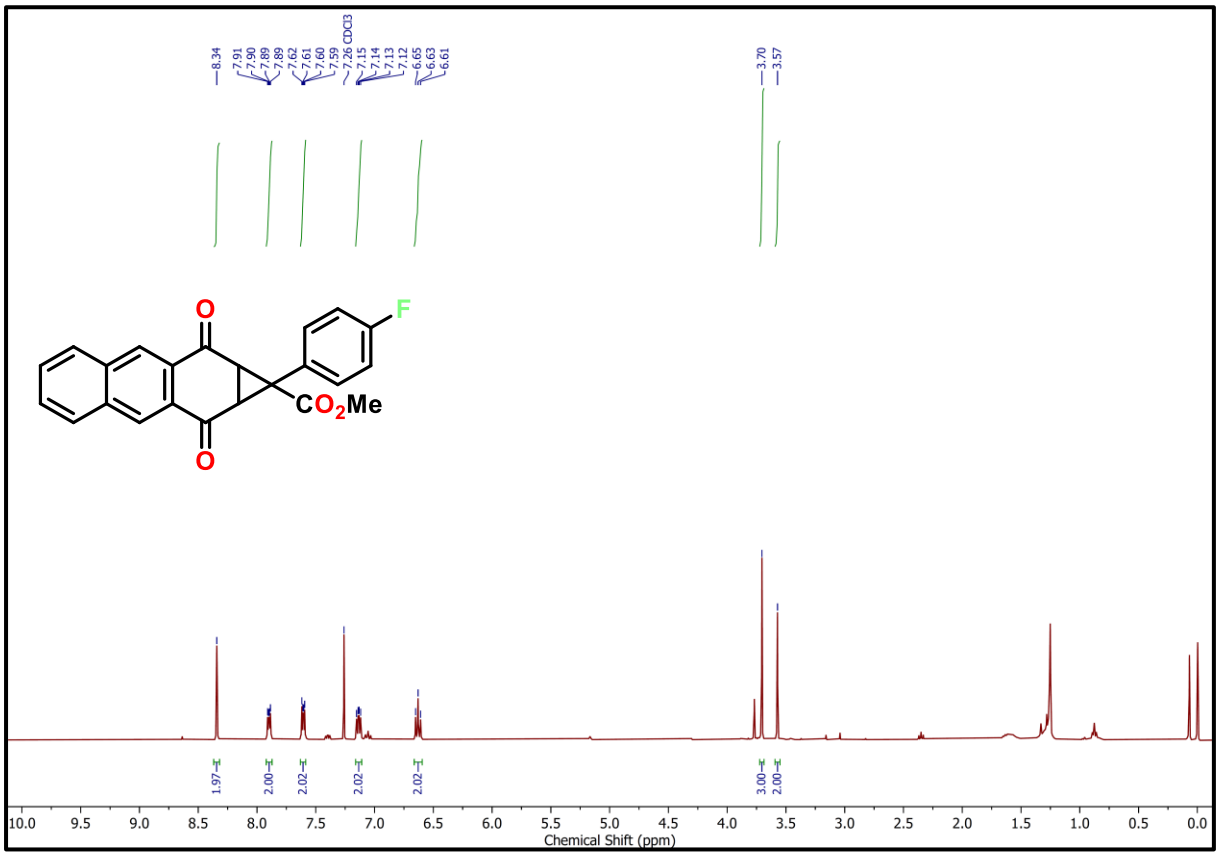


822

^{19}F NMR (376 MHz) of **8f** in $CDCl_3$



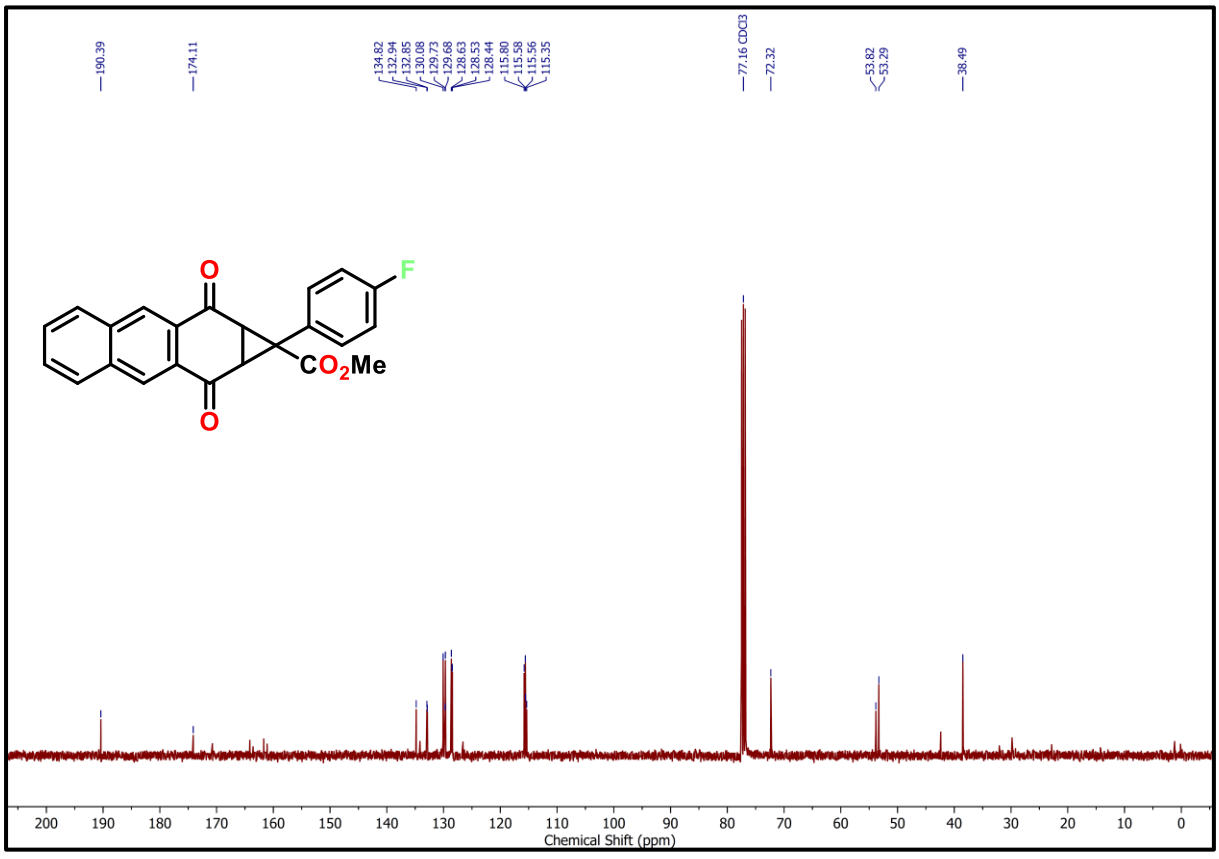
840 ^{1}H NMR (400 MHz) of **9a** in $CDCl_3$



841

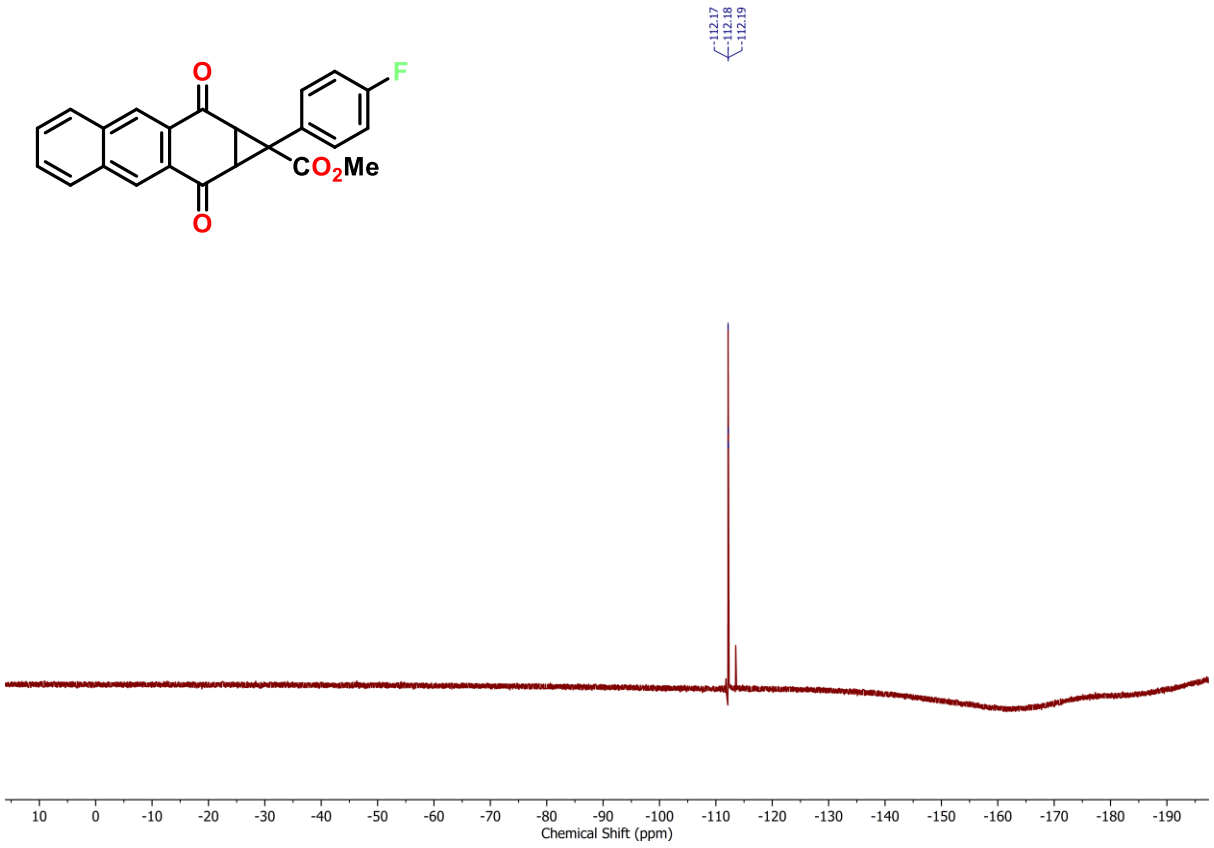
842

843 ^{13}C NMR (100 MHz) of **9a** in $CDCl_3$

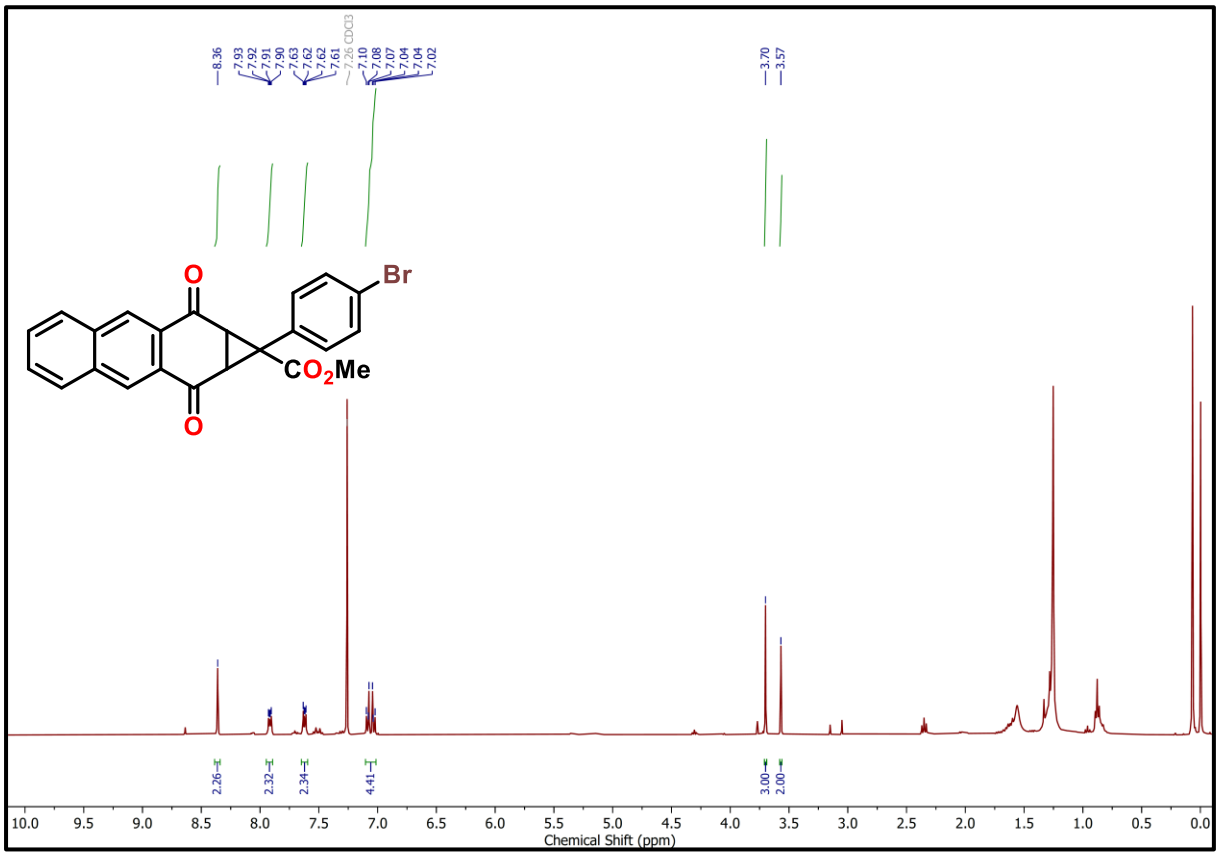


844

^{19}F NMR (376 MHz) of **9a** in $CDCl_3$



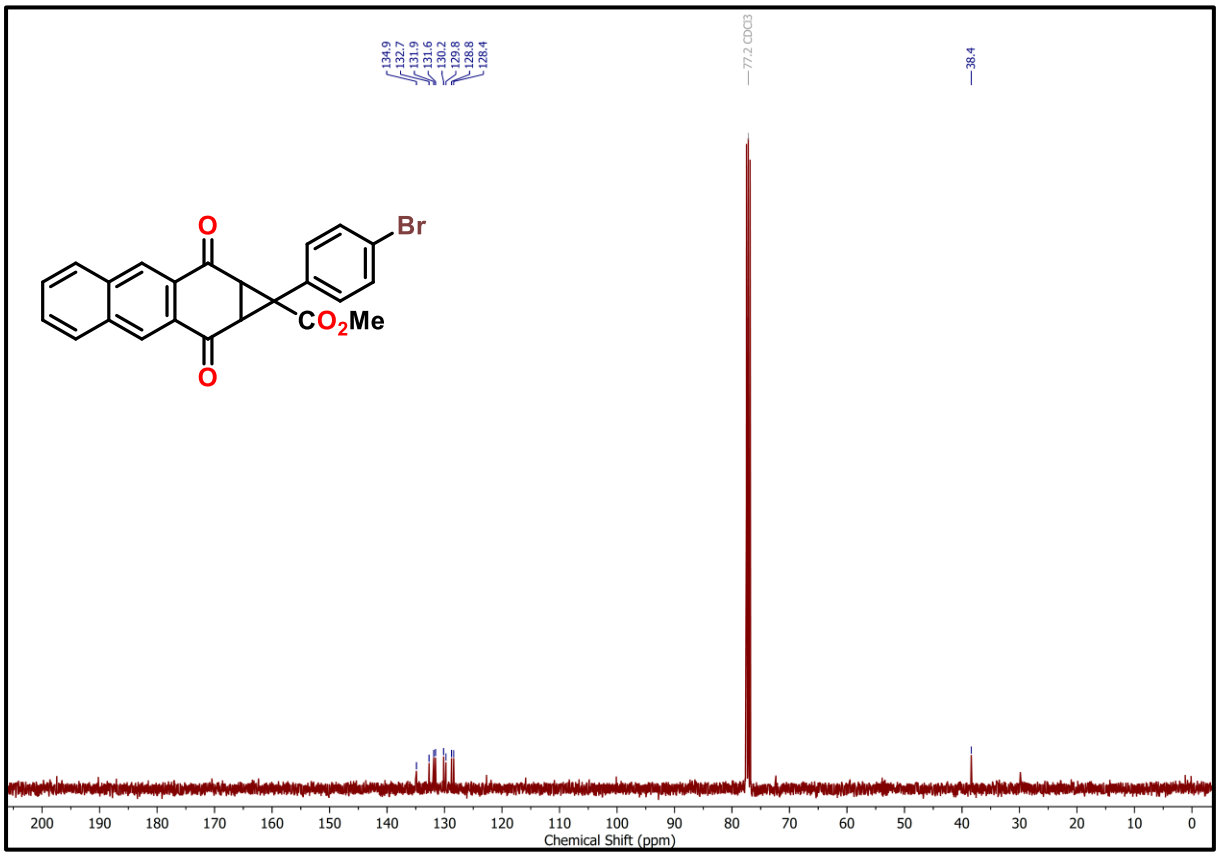
862 ^{1}H NMR (400 MHz) of **9b** in $CDCl_3$



863

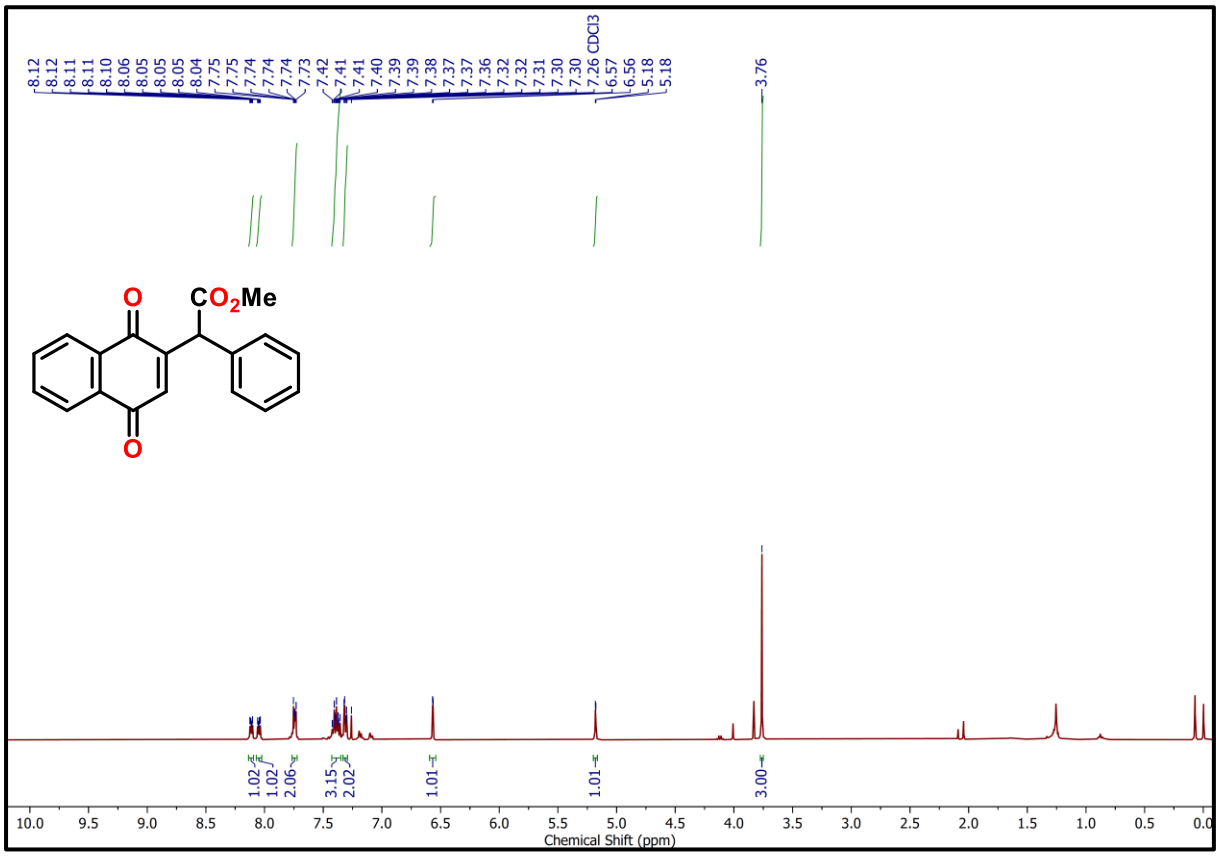
864

865 ^{13}C NMR (100 MHz) of **9b** in $CDCl_3$



866

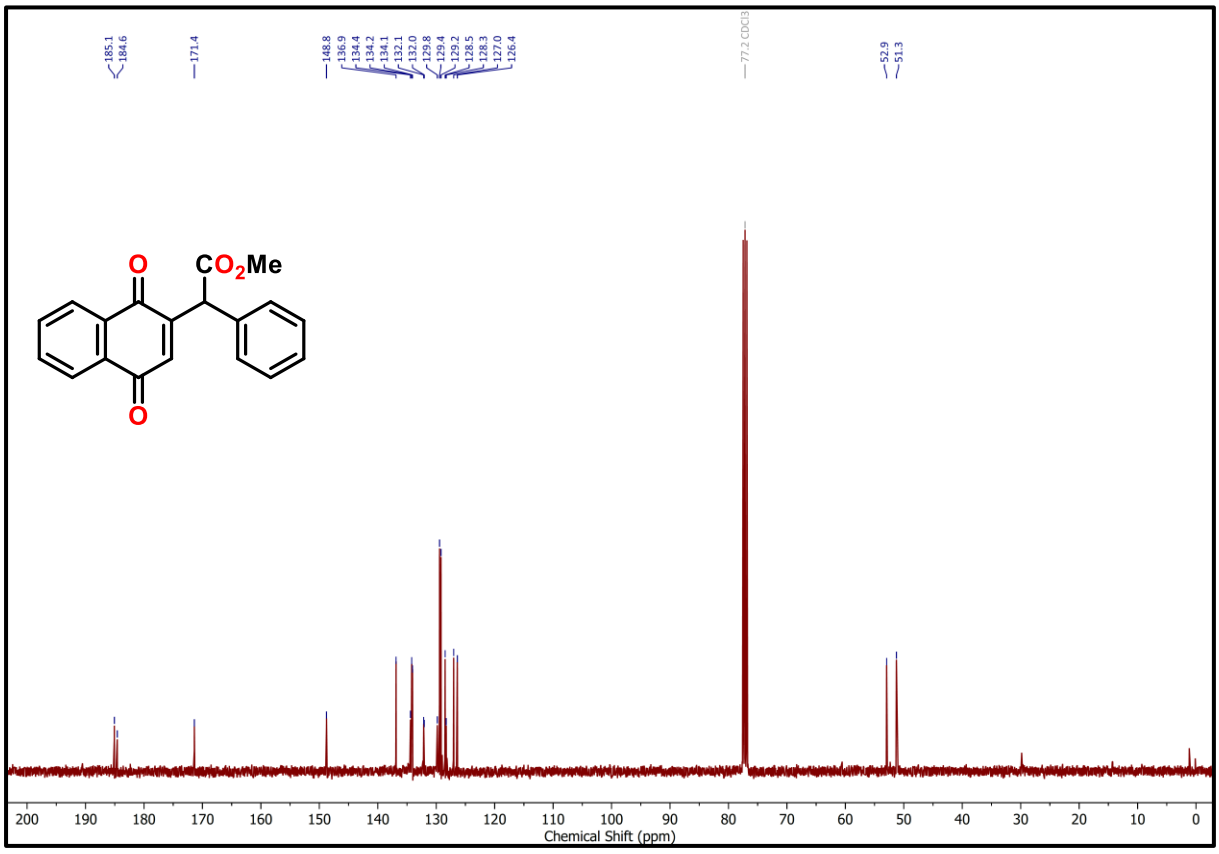
867 ^{1}H NMR (400 MHz) of **10a** in $CDCl_3$



868

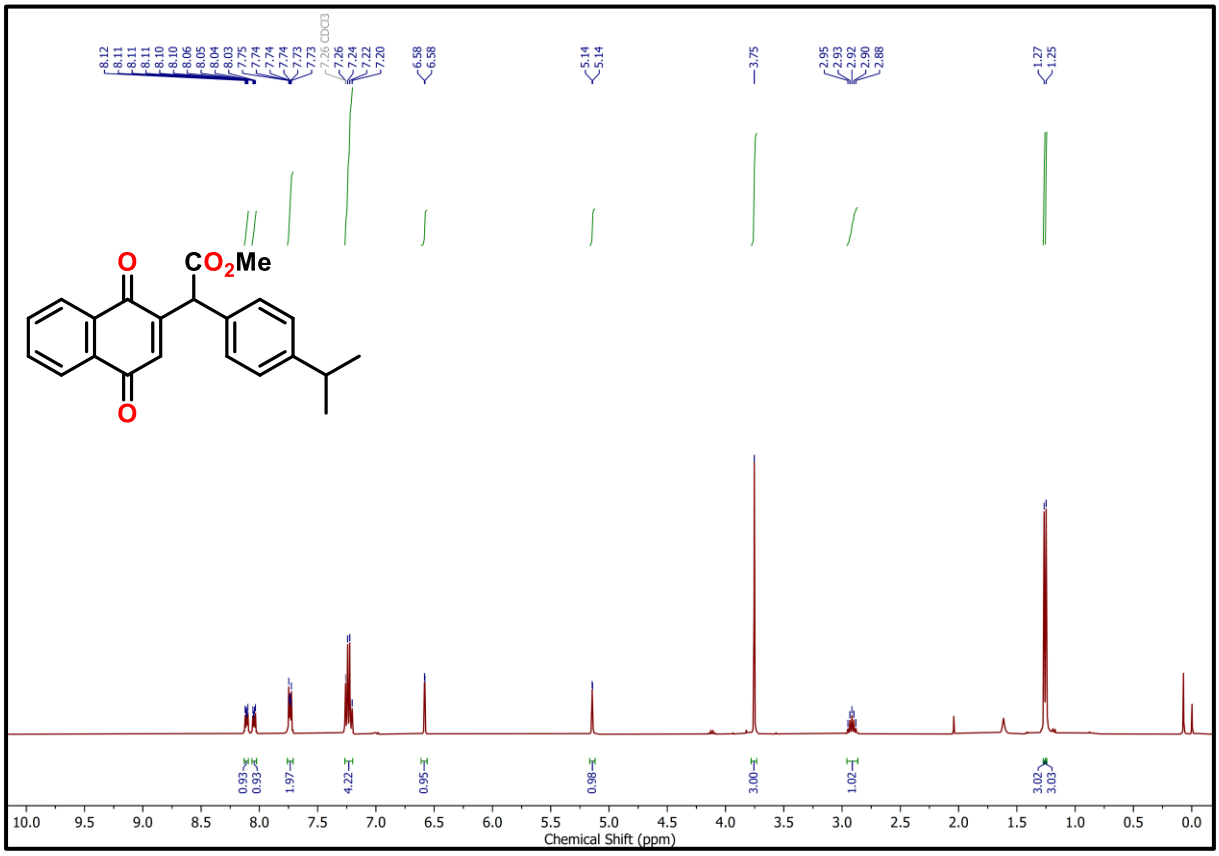
869

870 ^{13}C NMR (100 MHz) of **10a** in $CDCl_3$



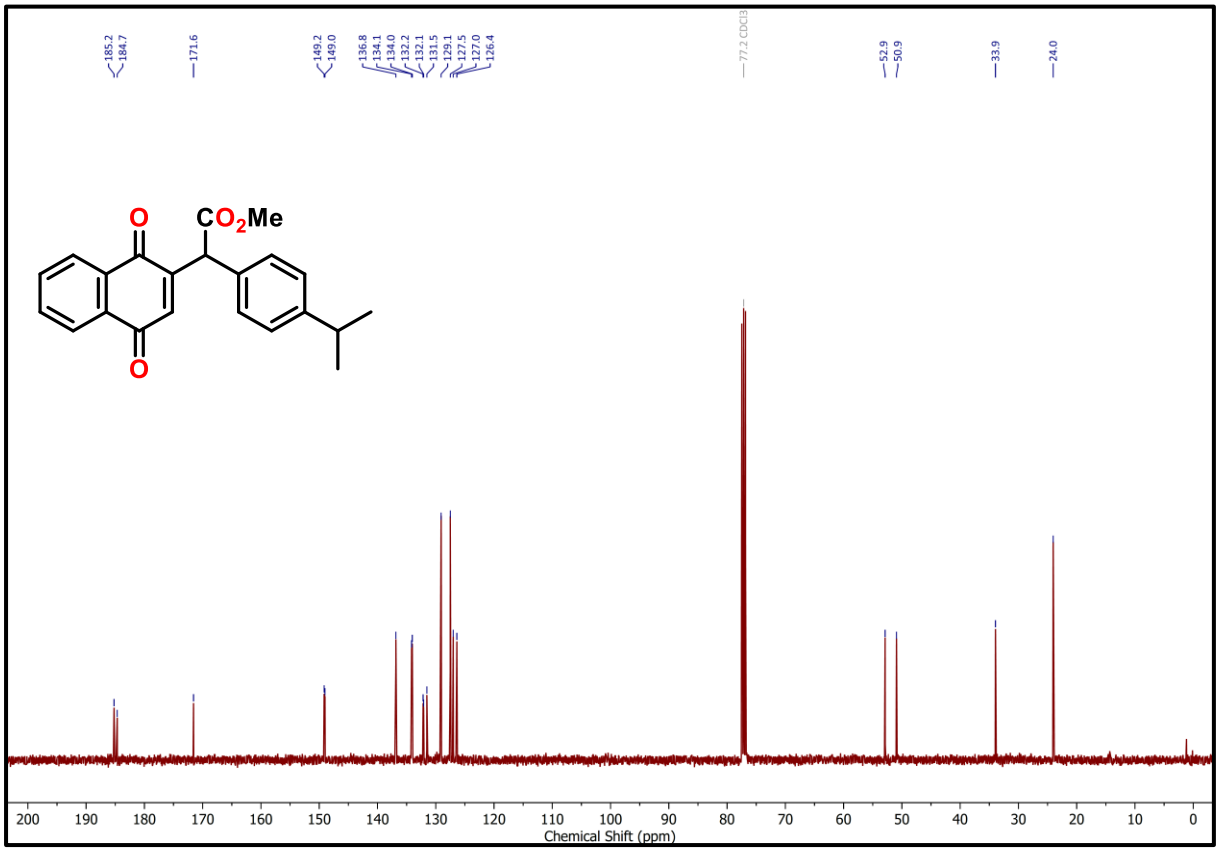
871

872 ^{1}H NMR (400 MHz) of **10b** in $CDCl_3$



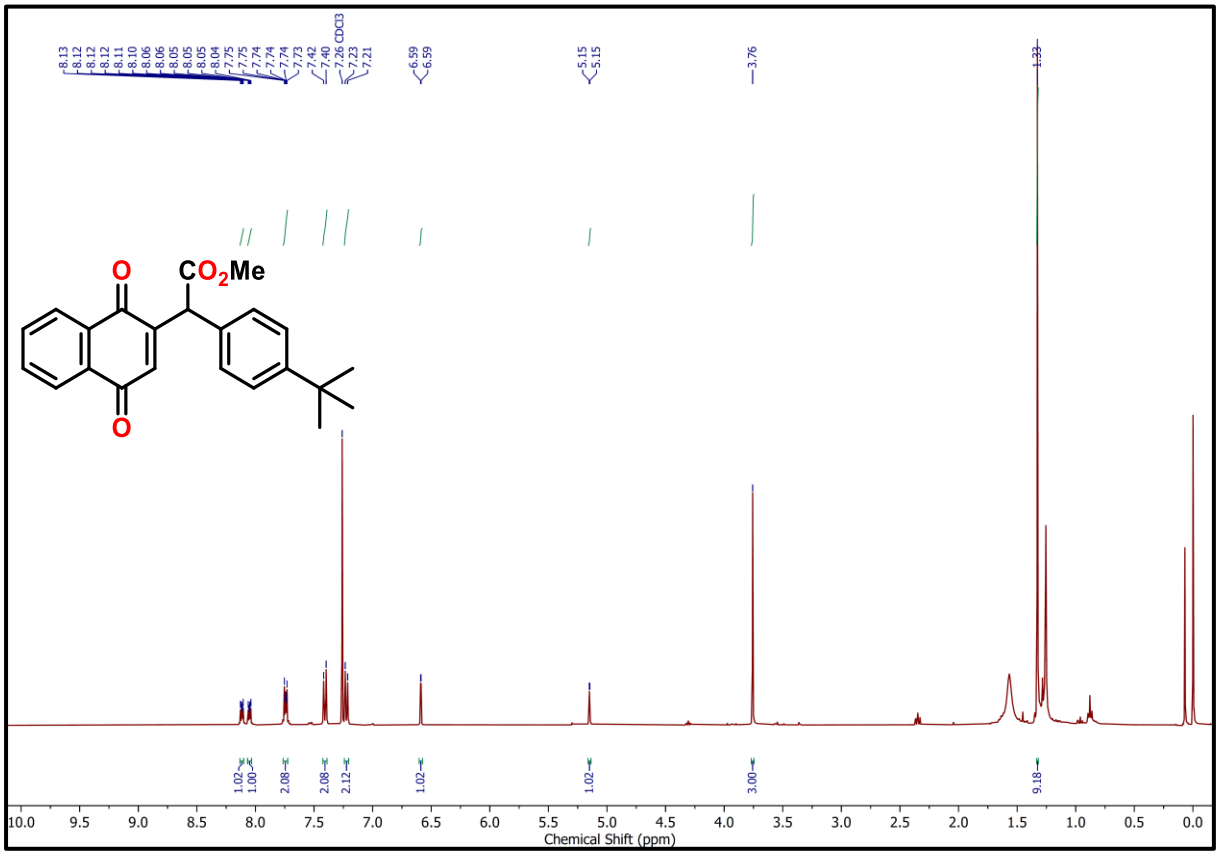
873

874 ^{13}C NMR (100 MHz) of **10b** in $CDCl_3$



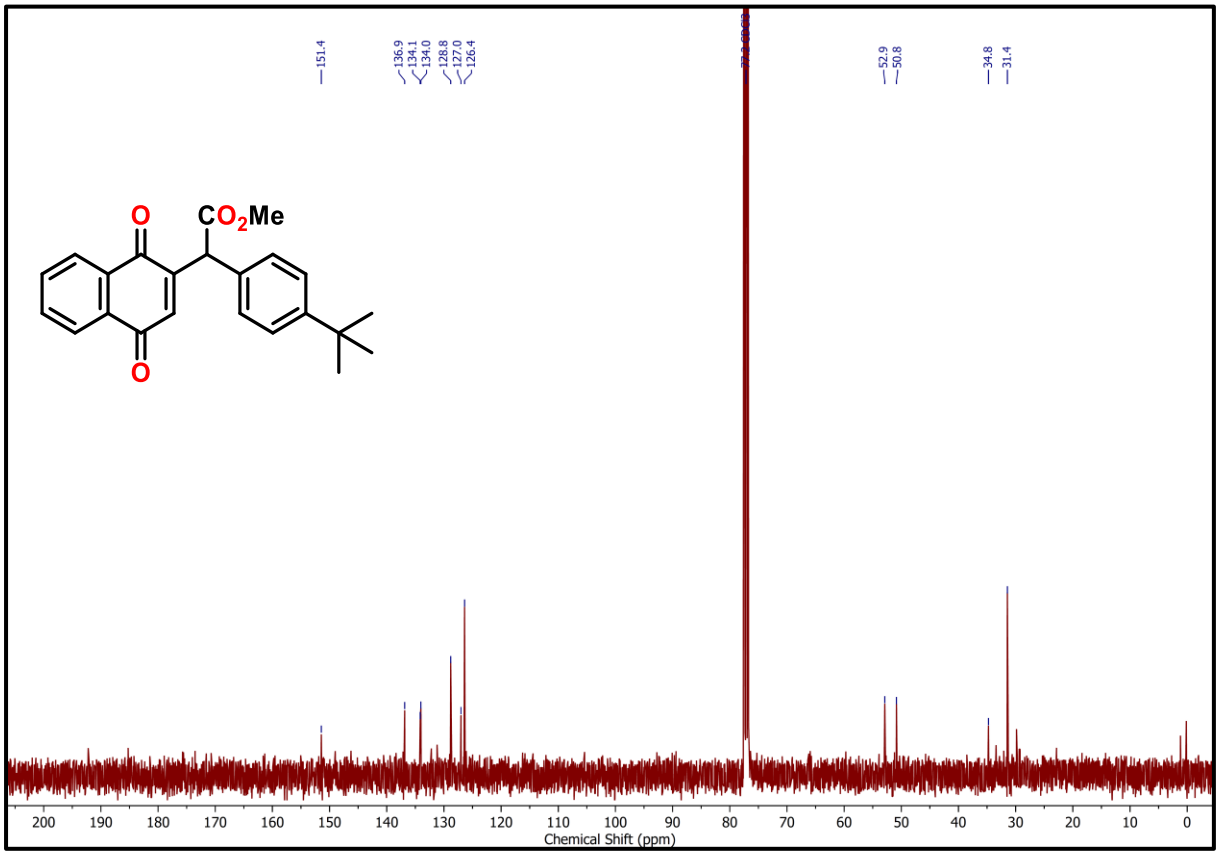
875

876 *[1]H* NMR (400 MHz) of **10c** in $CDCl_3$



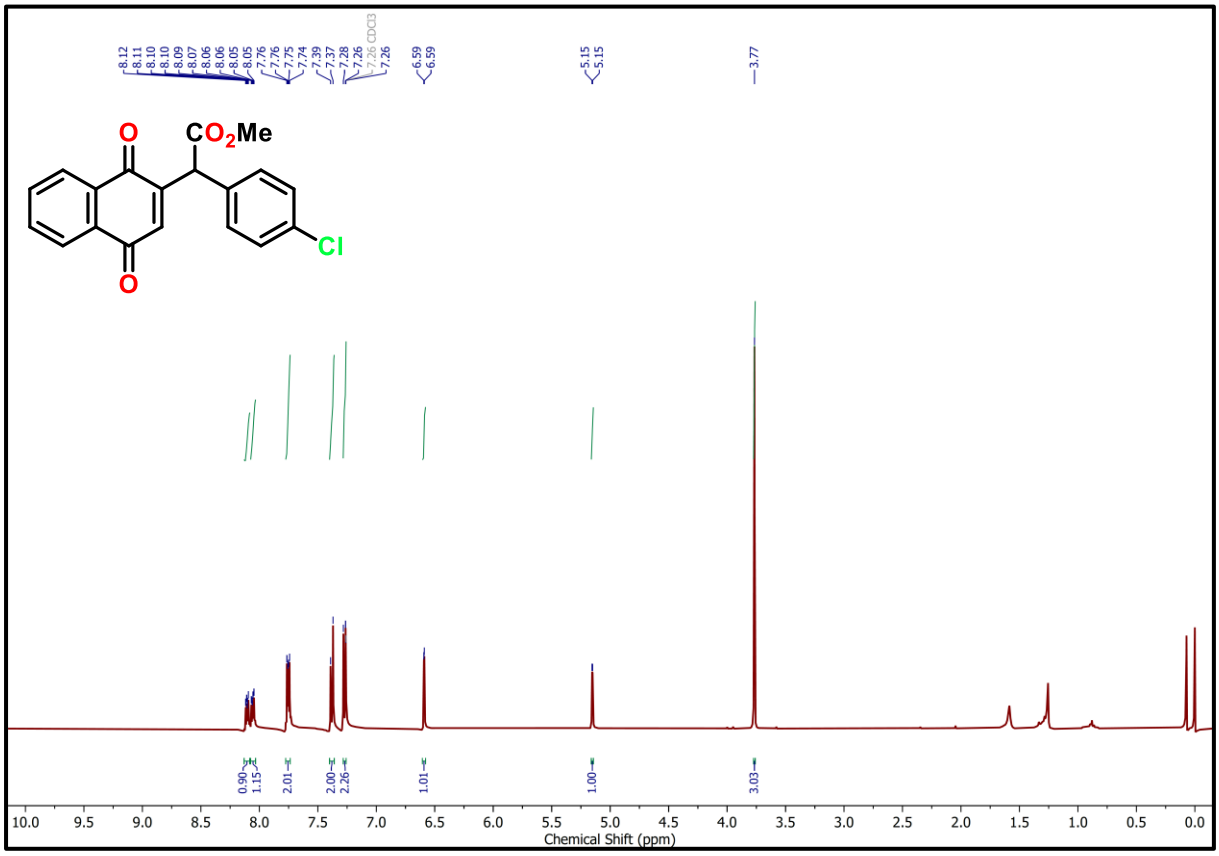
877

878 *[13]C* NMR (100 MHz) of **10c** in $CDCl_3$



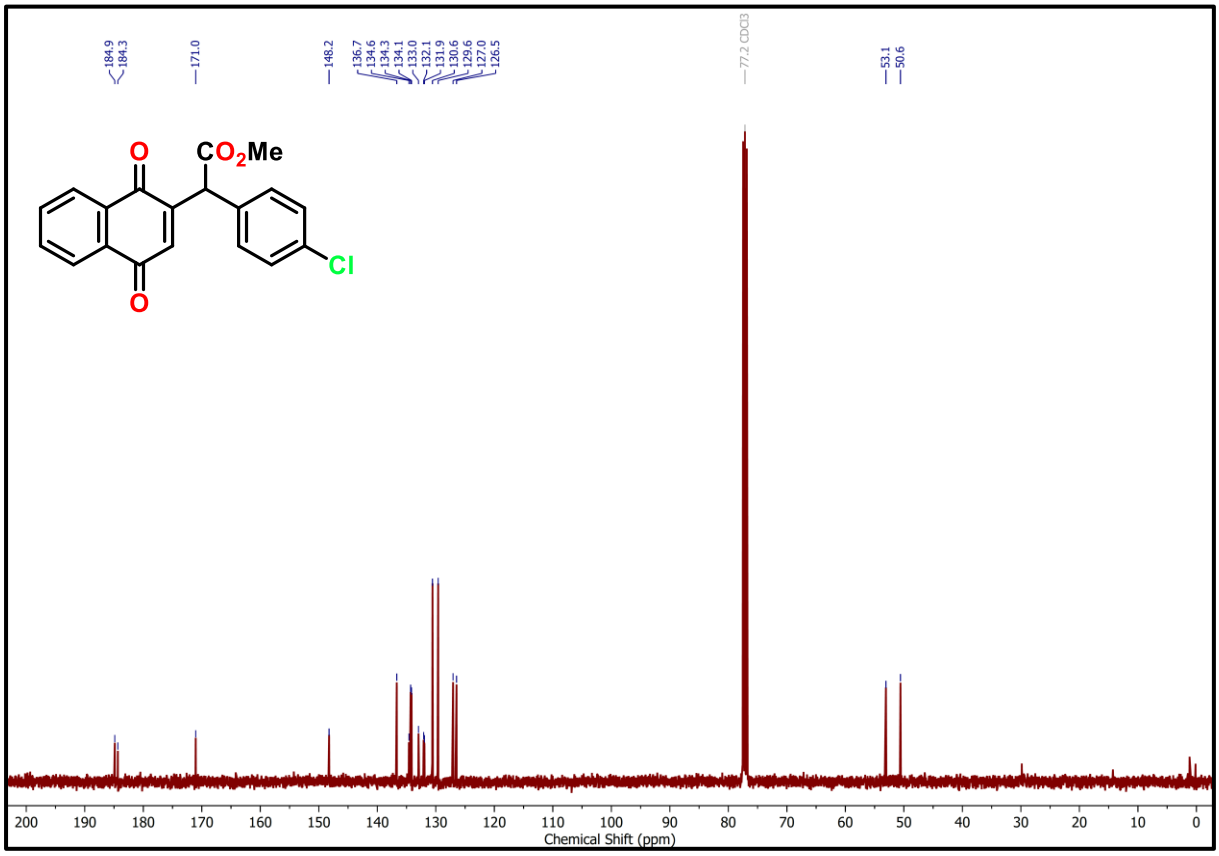
879

880 ^{1}H NMR (400 MHz) of **10d** in $CDCl_3$



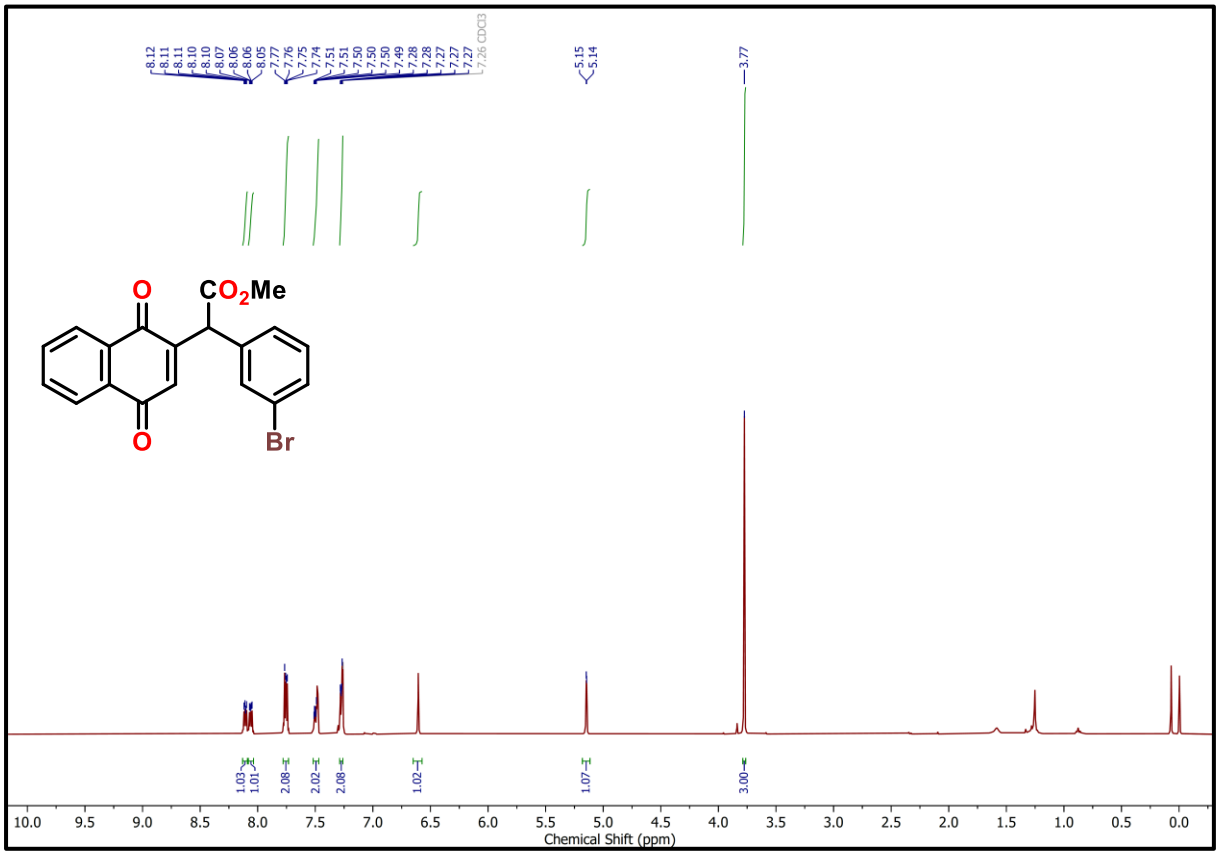
881

882 ^{13}C NMR (100 MHz) of **10d** in $CDCl_3$



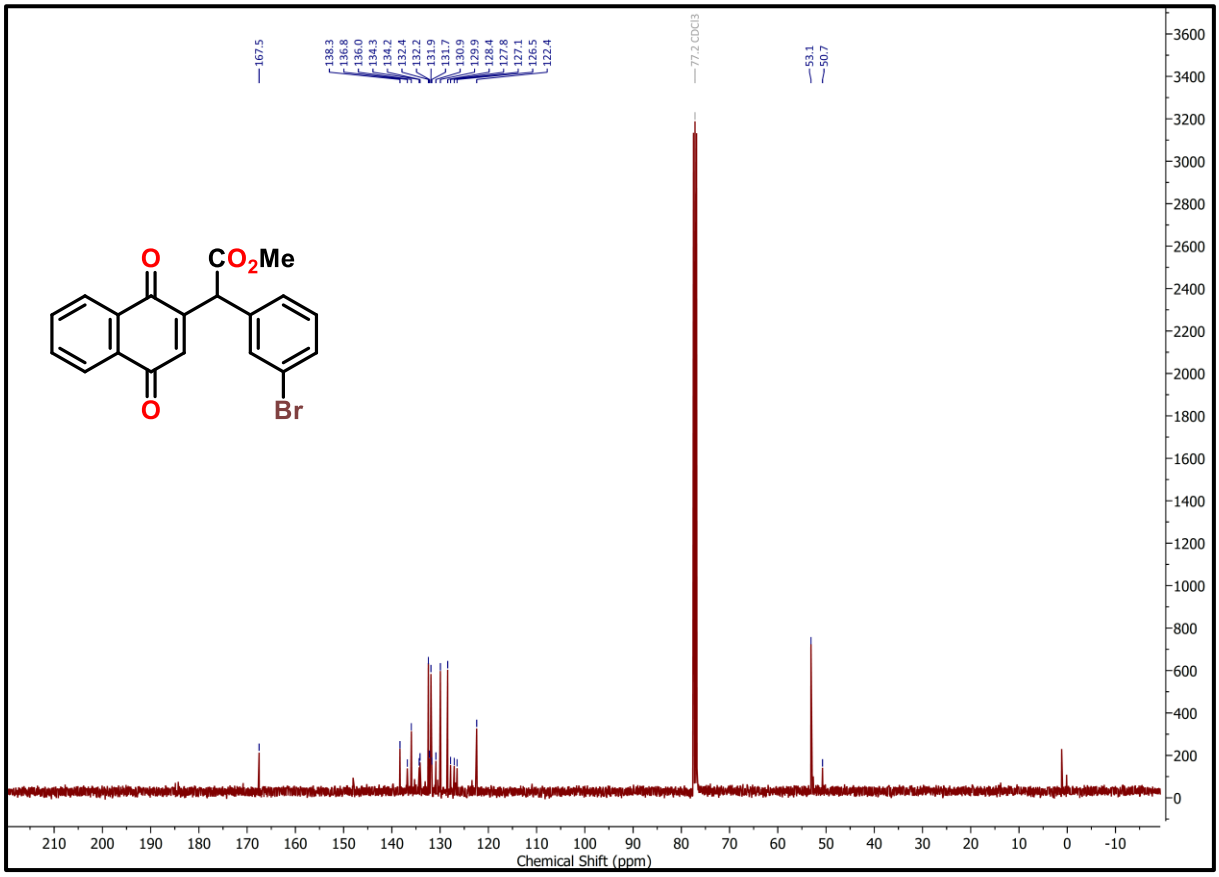
883

884 ^{1}H NMR (400 MHz) of **10e** in $CDCl_3$



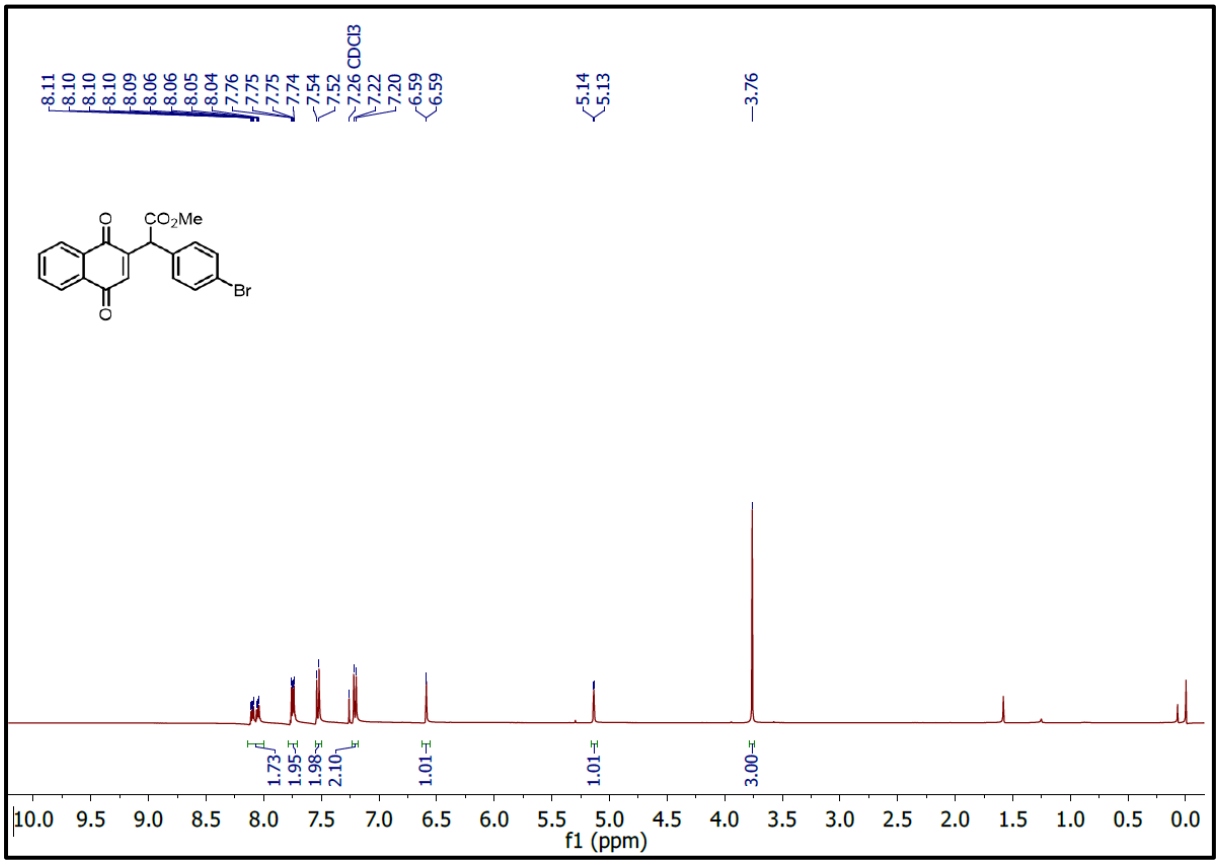
885

886 ^{13}C NMR (100 MHz) of **10e** in $CDCl_3$



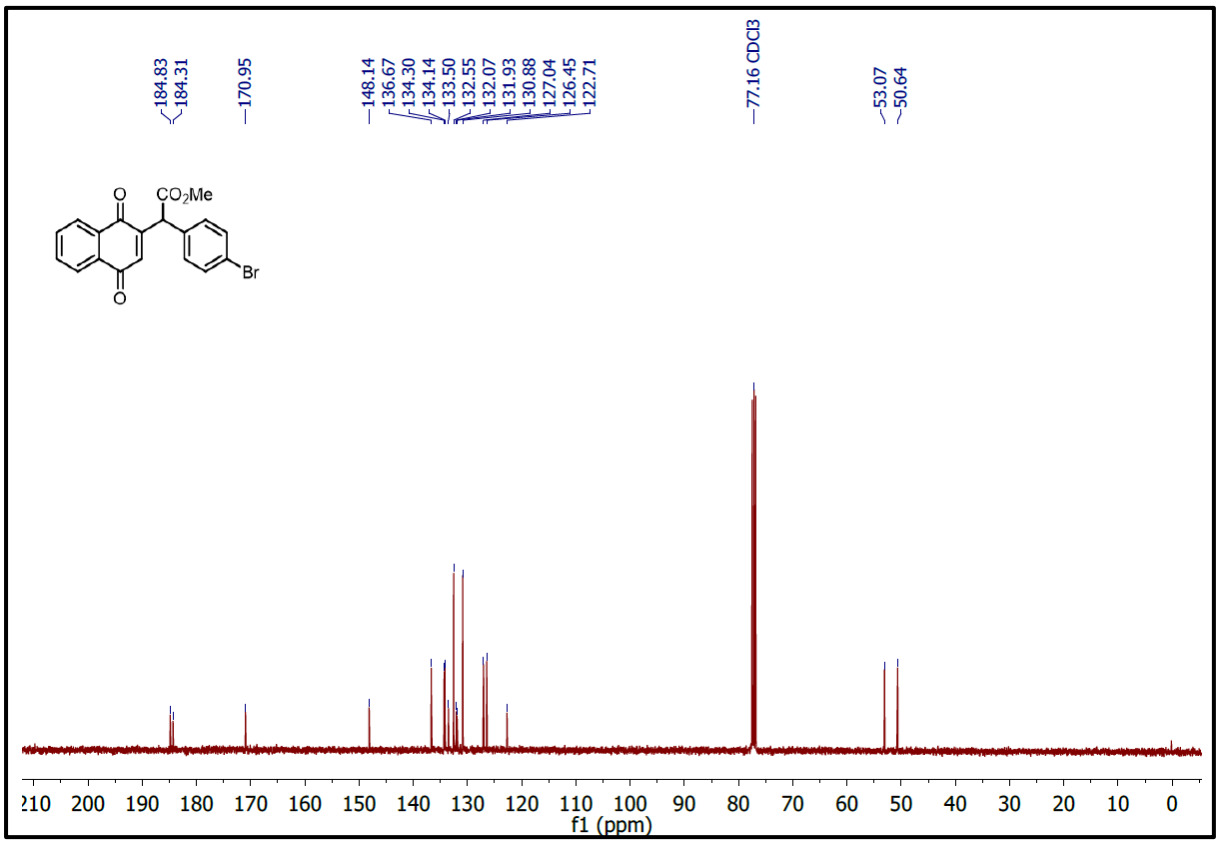
887

888 *[1]H* NMR (400 MHz) of **10f** in $CDCl_3$



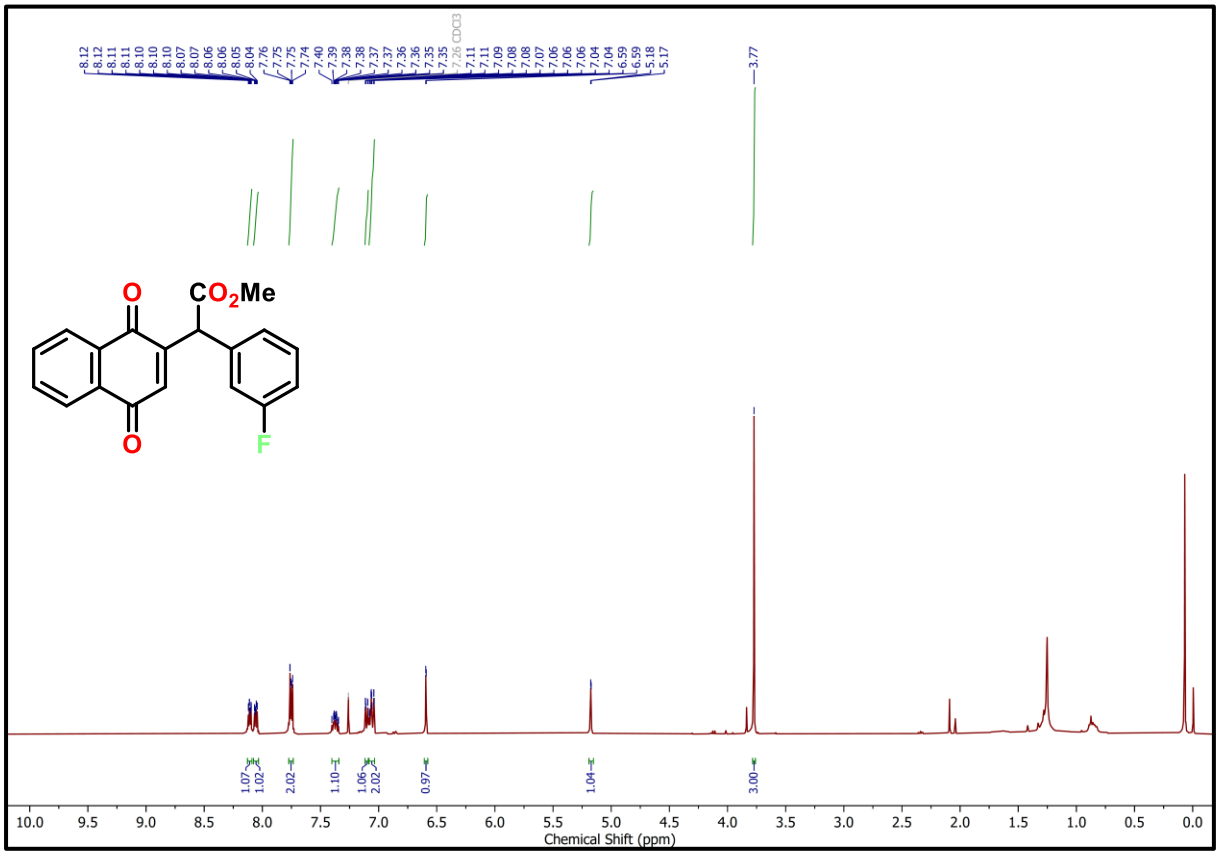
889

890 *[13]C* NMR (100 MHz) of **10f** in $CDCl_3$



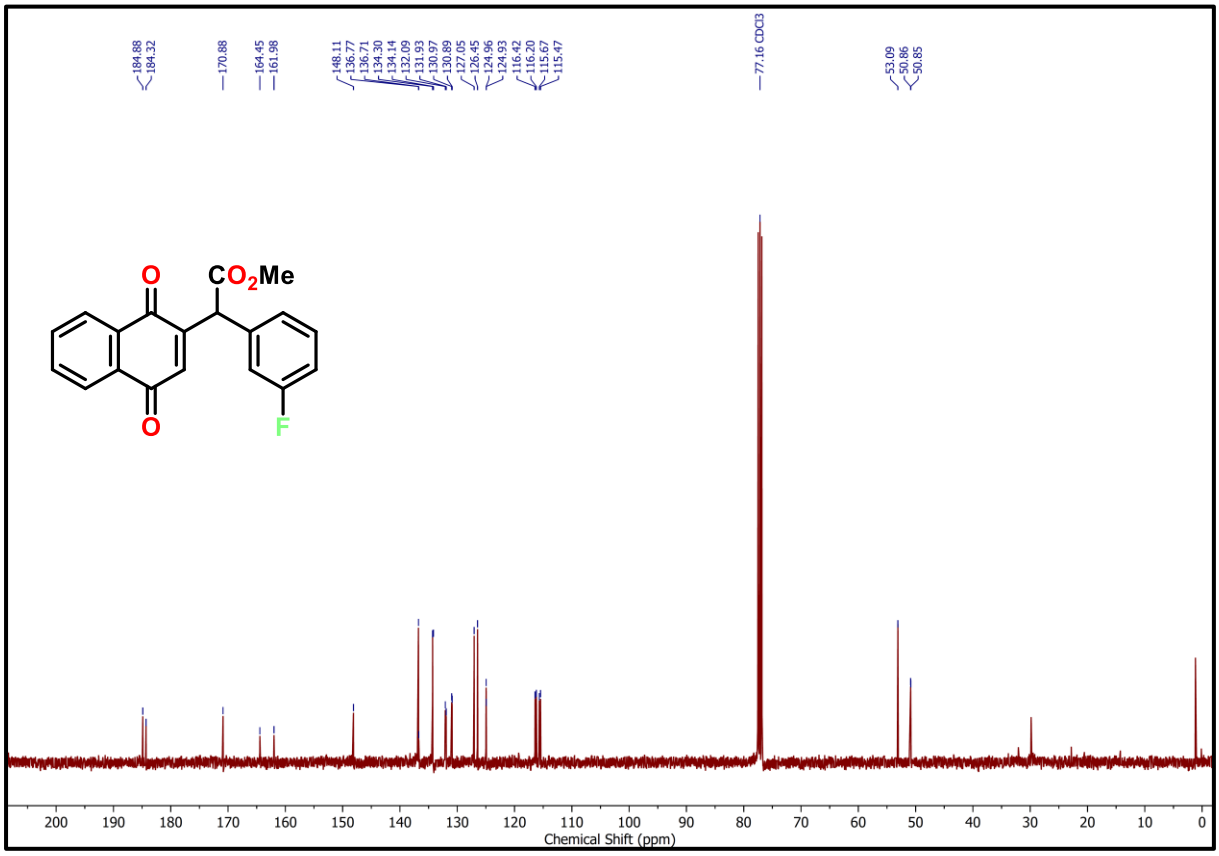
891

892 ^{1}H NMR (400 MHz) of **10g** in $CDCl_3$



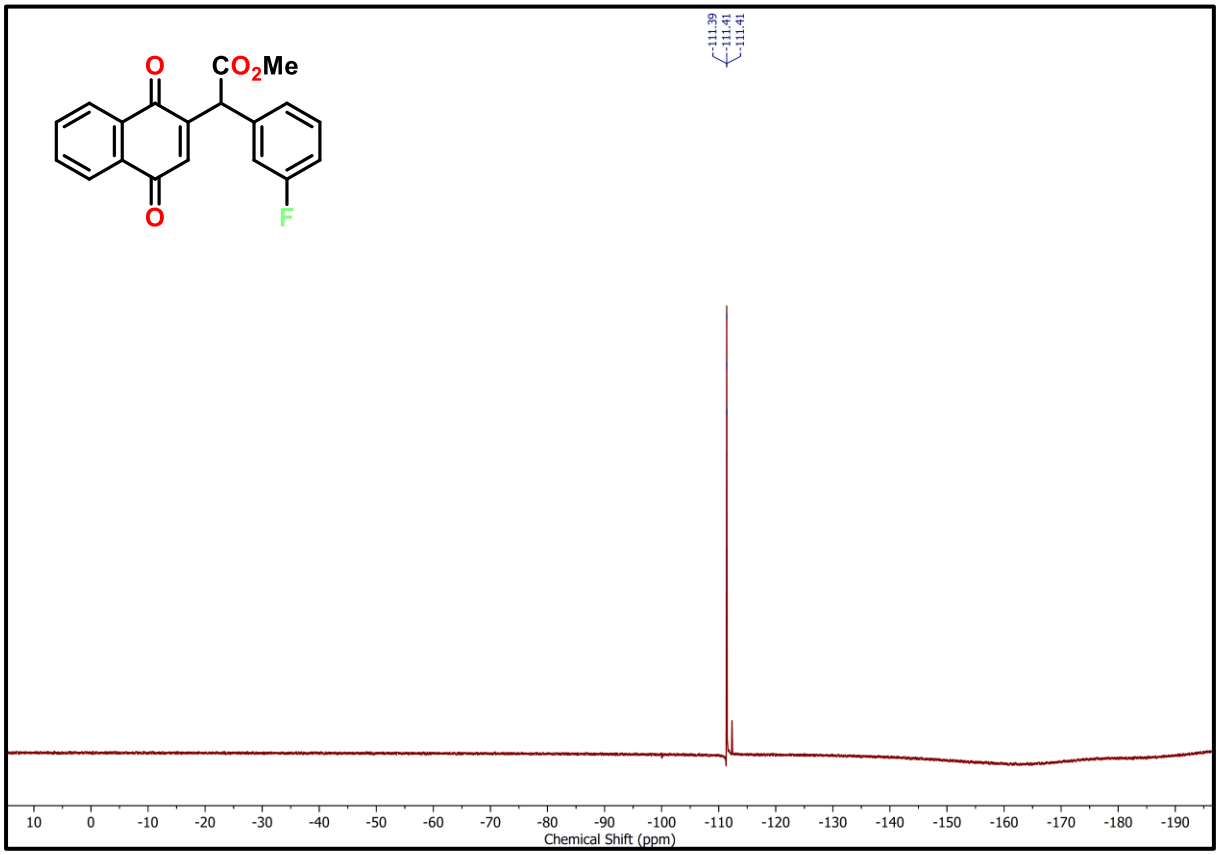
893

894 ^{13}C NMR (100 MHz) of **10g** in $CDCl_3$

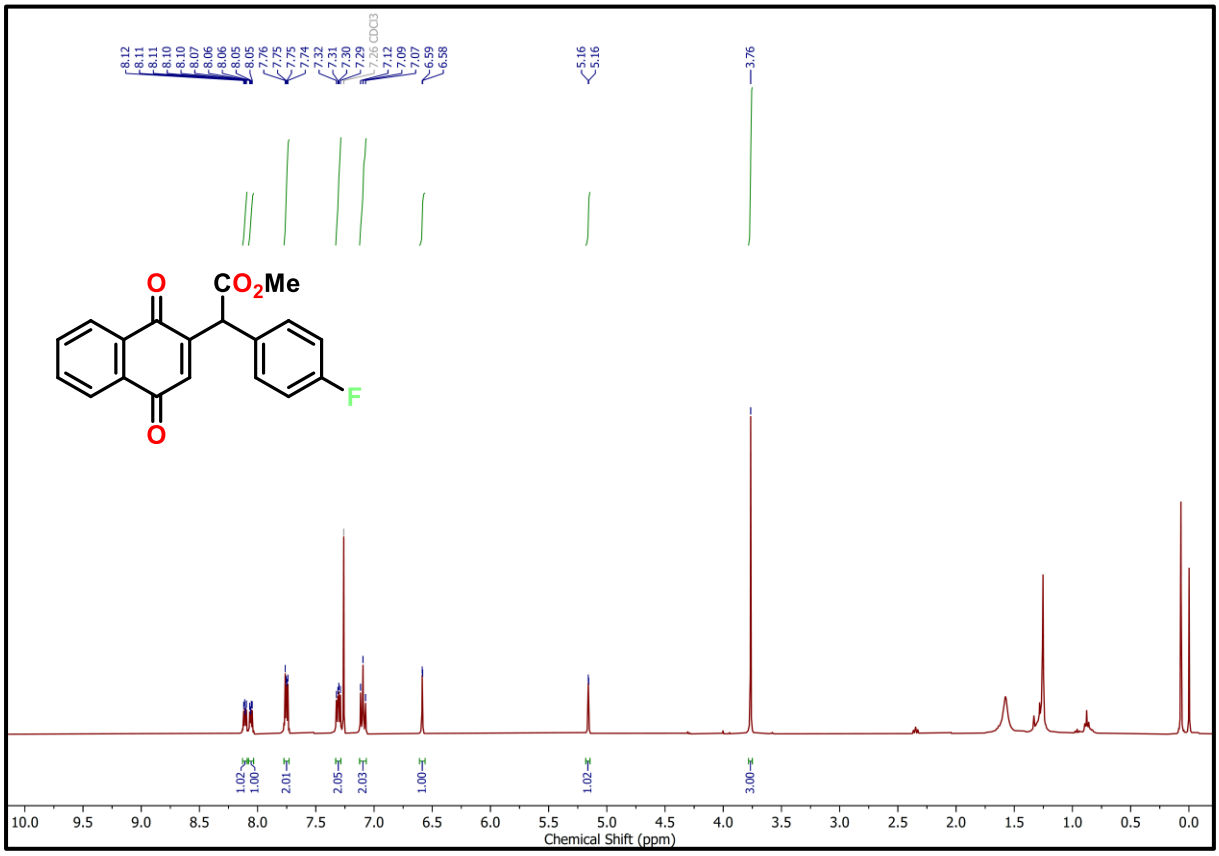


895

^{19}F NMR (376 MHz) of **10g** in $CDCl_3$

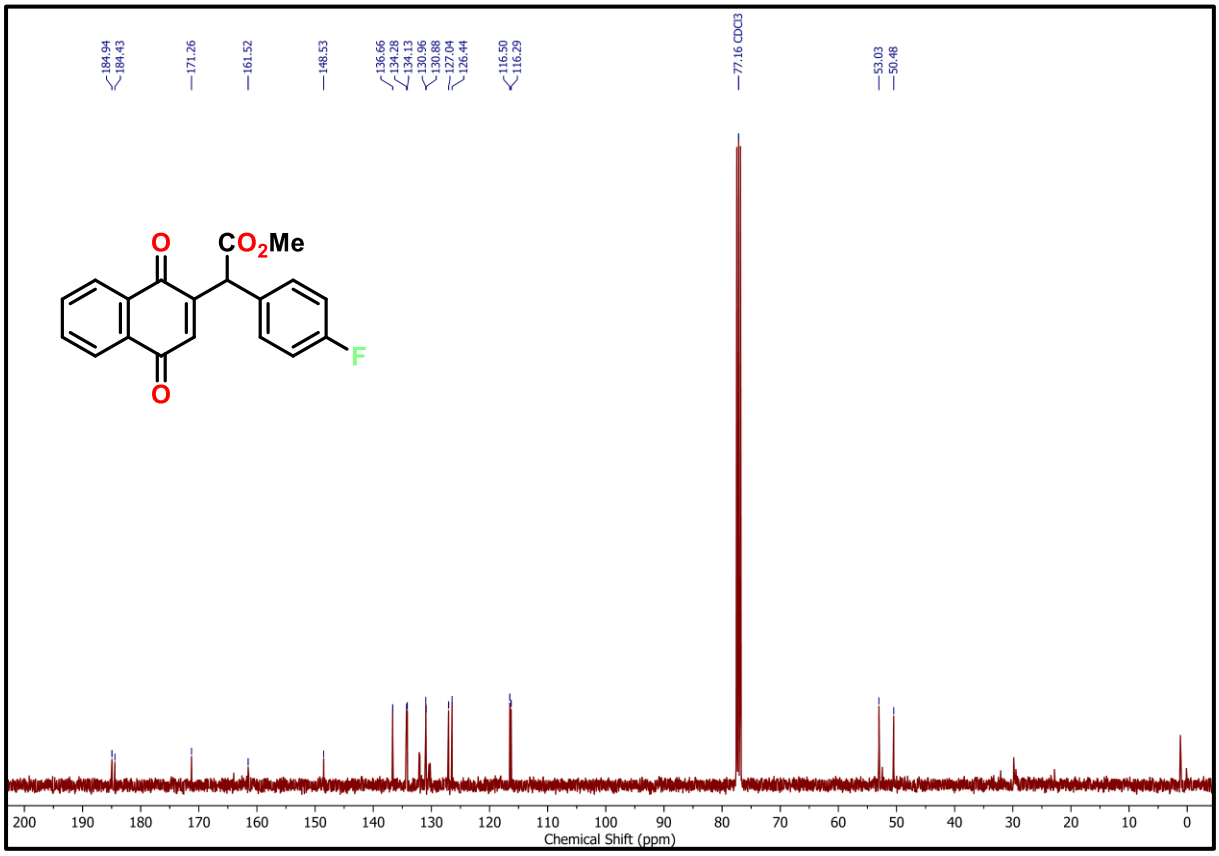


913 ^{1}H NMR (400 MHz) of **10h** in $CDCl_3$



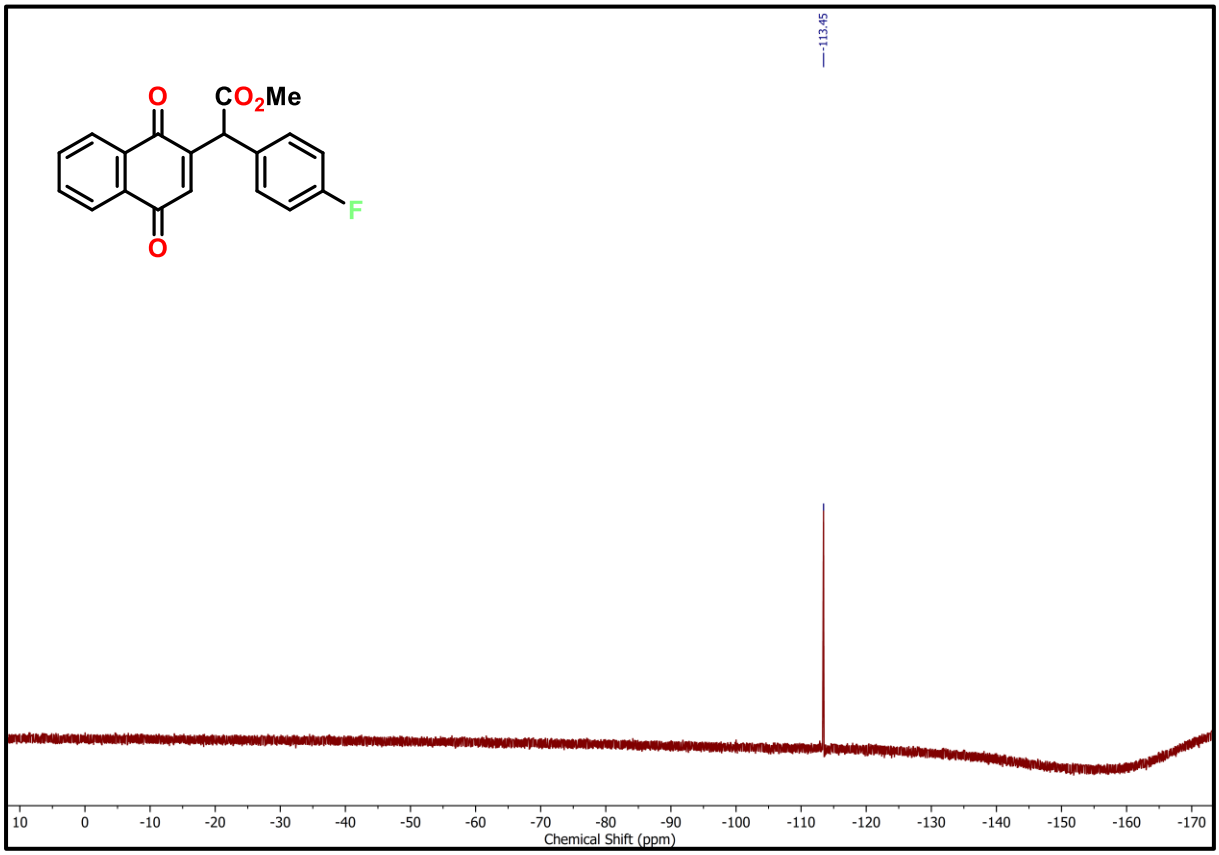
914

915 ^{13}C NMR (100 MHz) of **10h** in $CDCl_3$

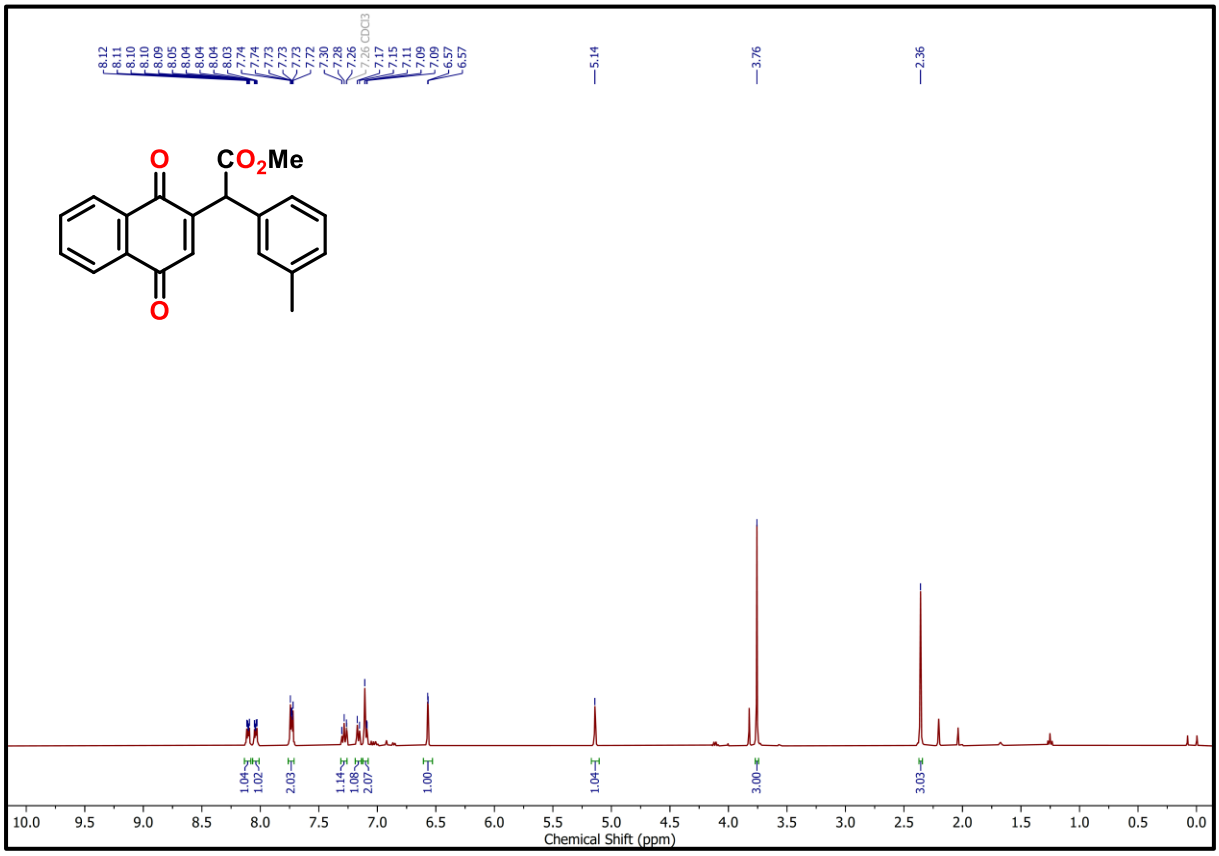


916

^{19}F NMR (376 MHz) of **10h** in $CDCl_3$

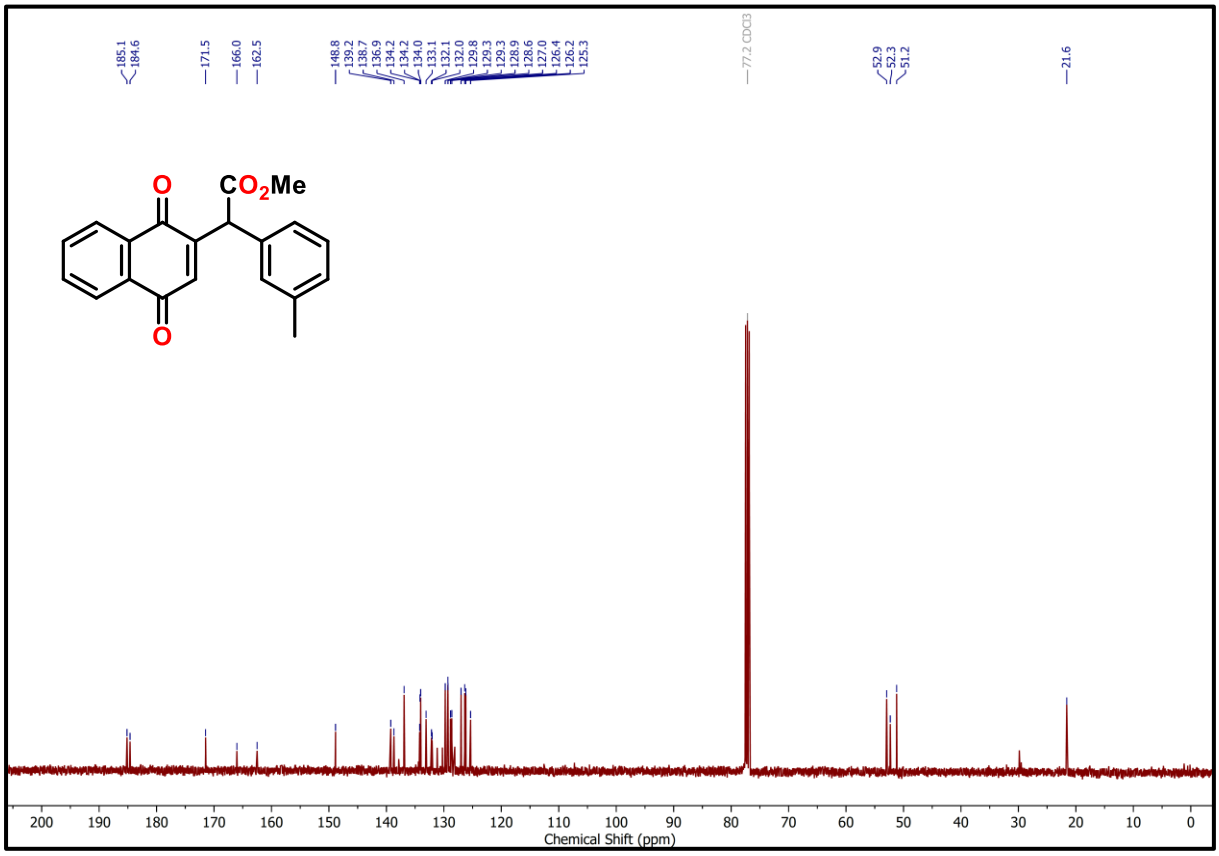


934 ^{1}H NMR (400 MHz) of **10i** in $CDCl_3$



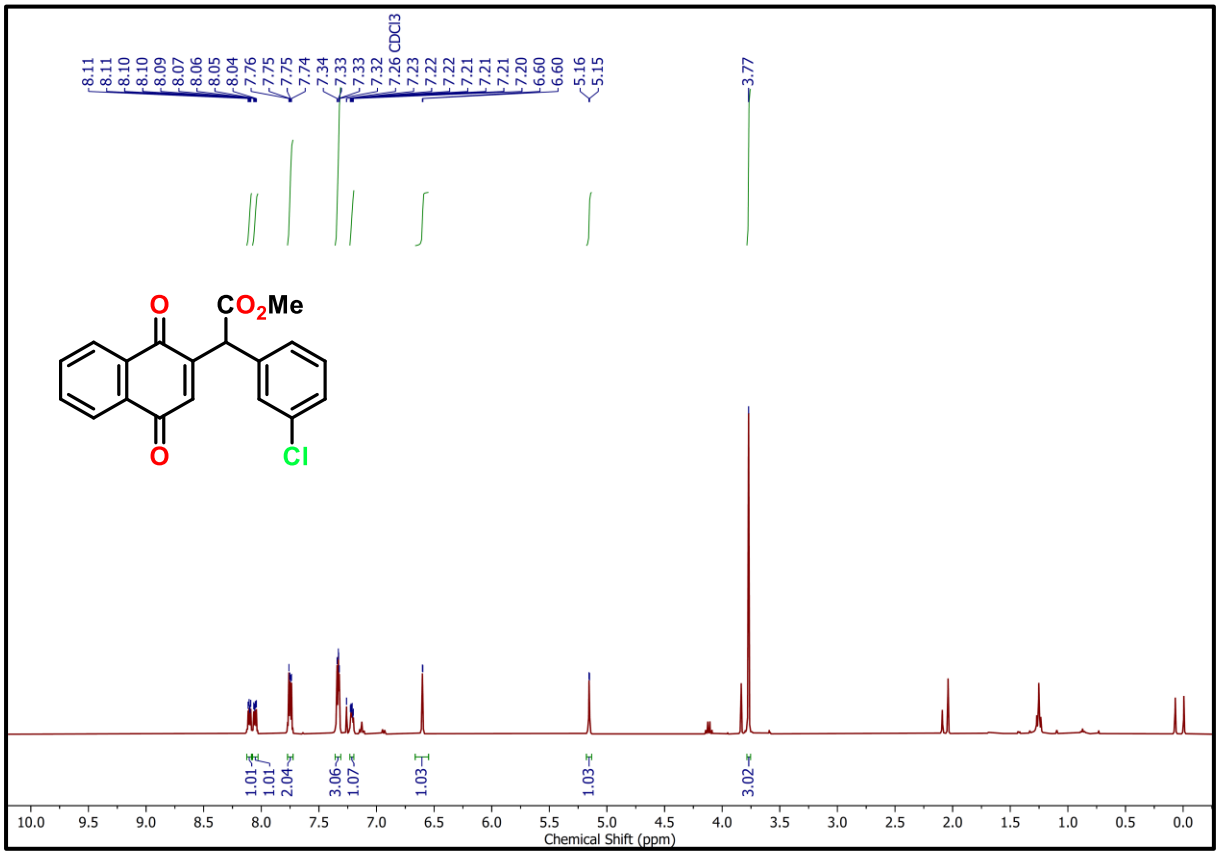
935

936 ^{13}C NMR (100 MHz) of **10i** in $CDCl_3$



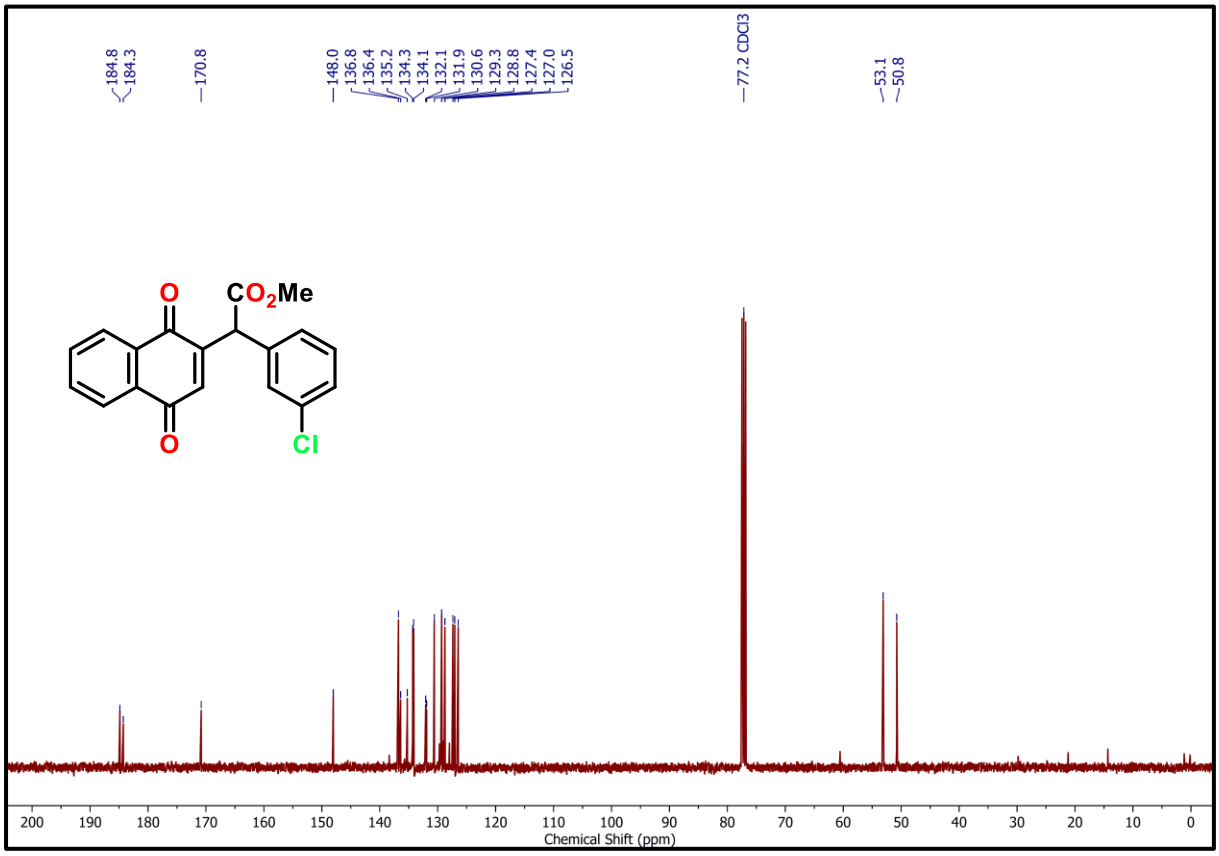
937

938 *[1]H* NMR (400 MHz) of **10j** in $CDCl_3$



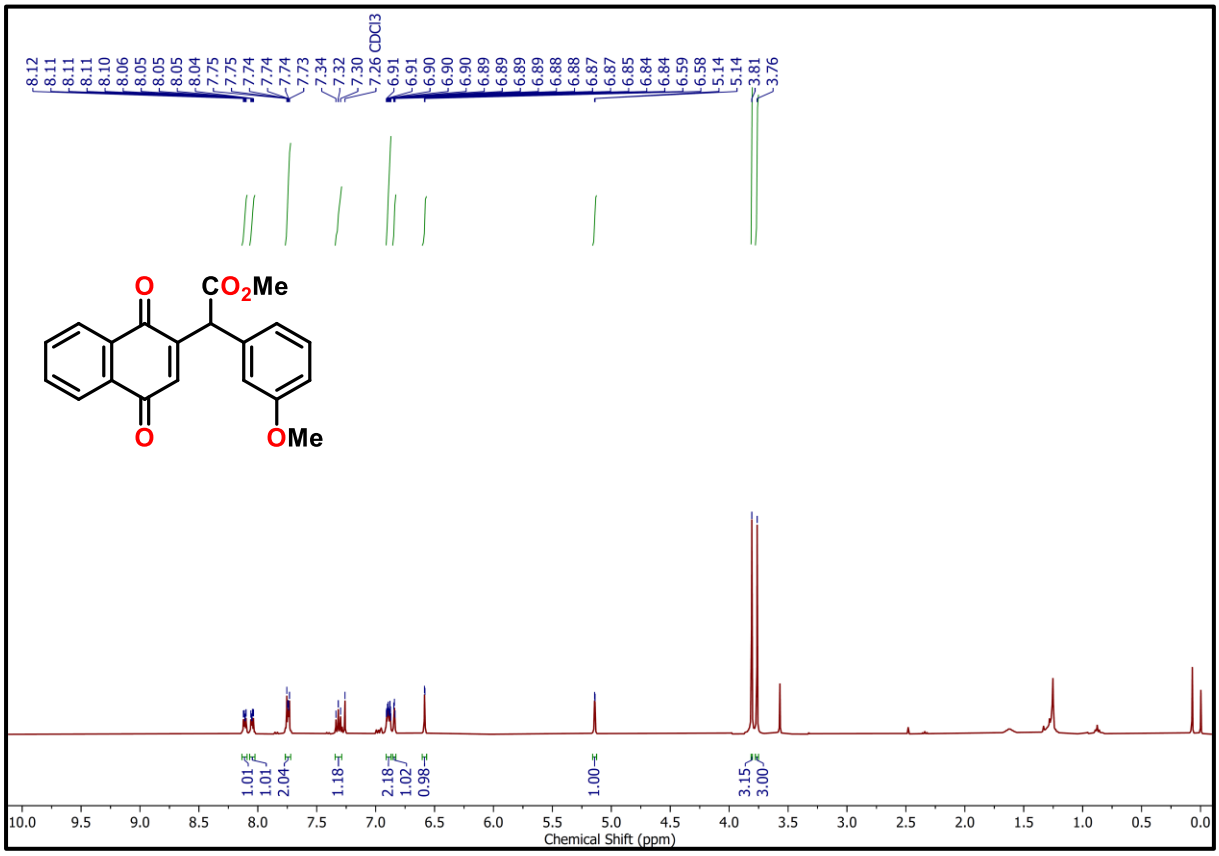
939

940 *[13]C* NMR (100 MHz) of **10j** in $CDCl_3$



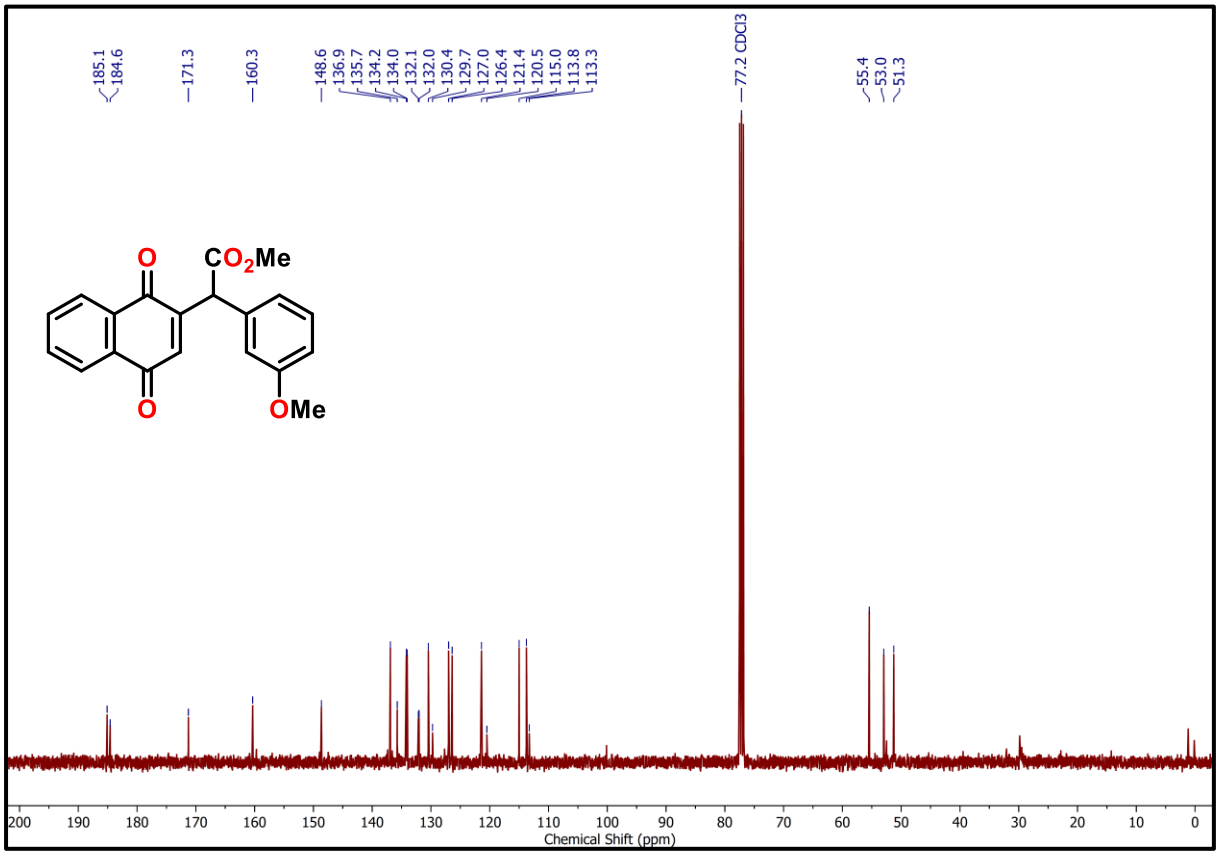
941

942 *[1]H* NMR (400 MHz) of **10k** in $CDCl_3$



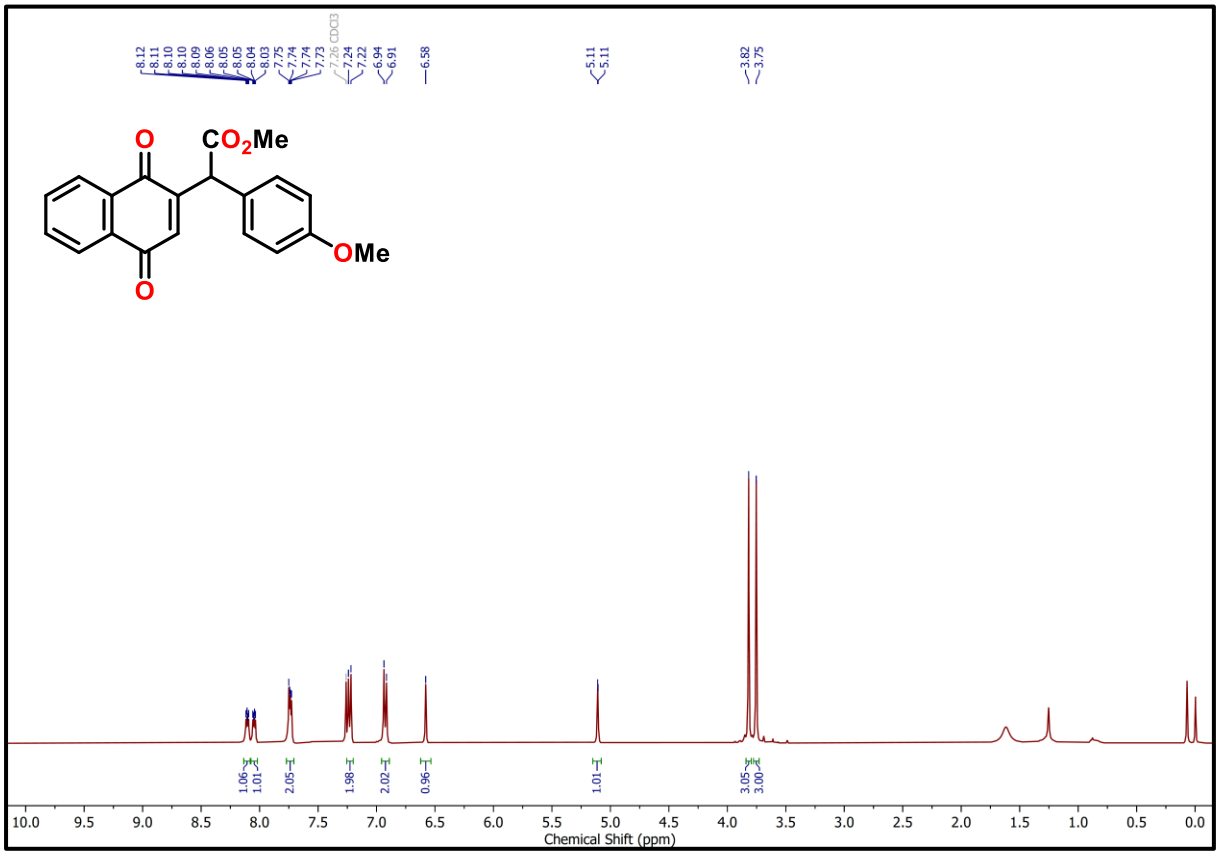
943

944 *[13]C* NMR (100 MHz) of **10k** in $CDCl_3$



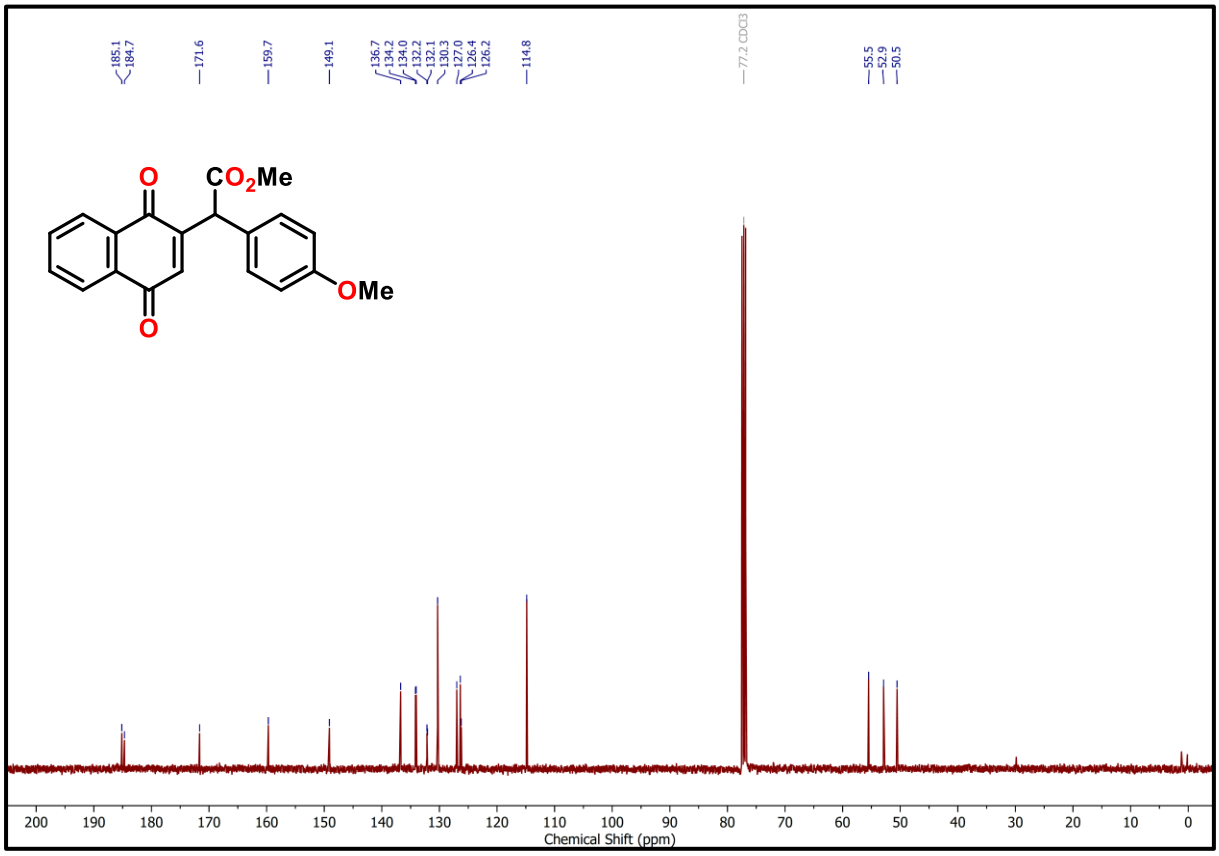
945

946 ^{1}H NMR (400 MHz) of **10l** in $CDCl_3$



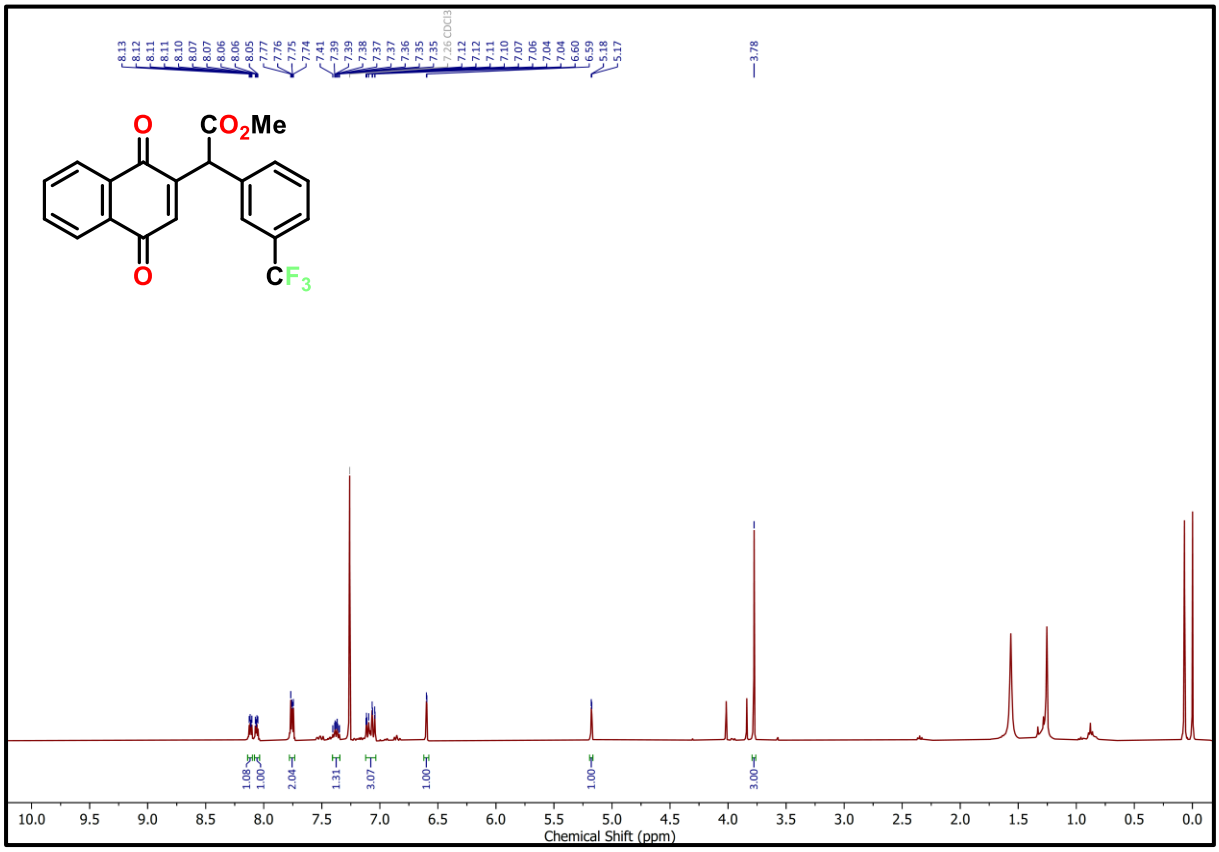
947

948 ^{13}C NMR (100 MHz) of **10l** in $CDCl_3$



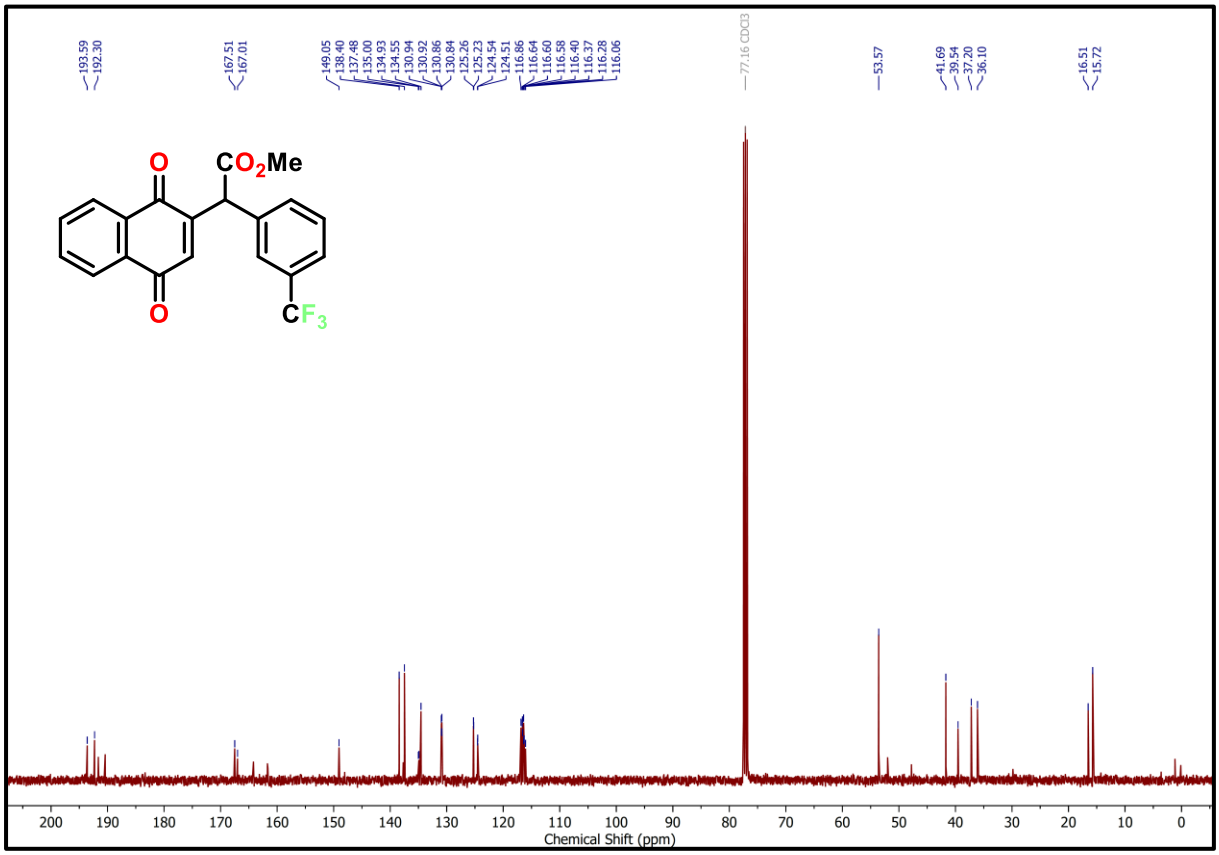
949

950 ^{1}H NMR (400 MHz) of **10m** in $CDCl_3$



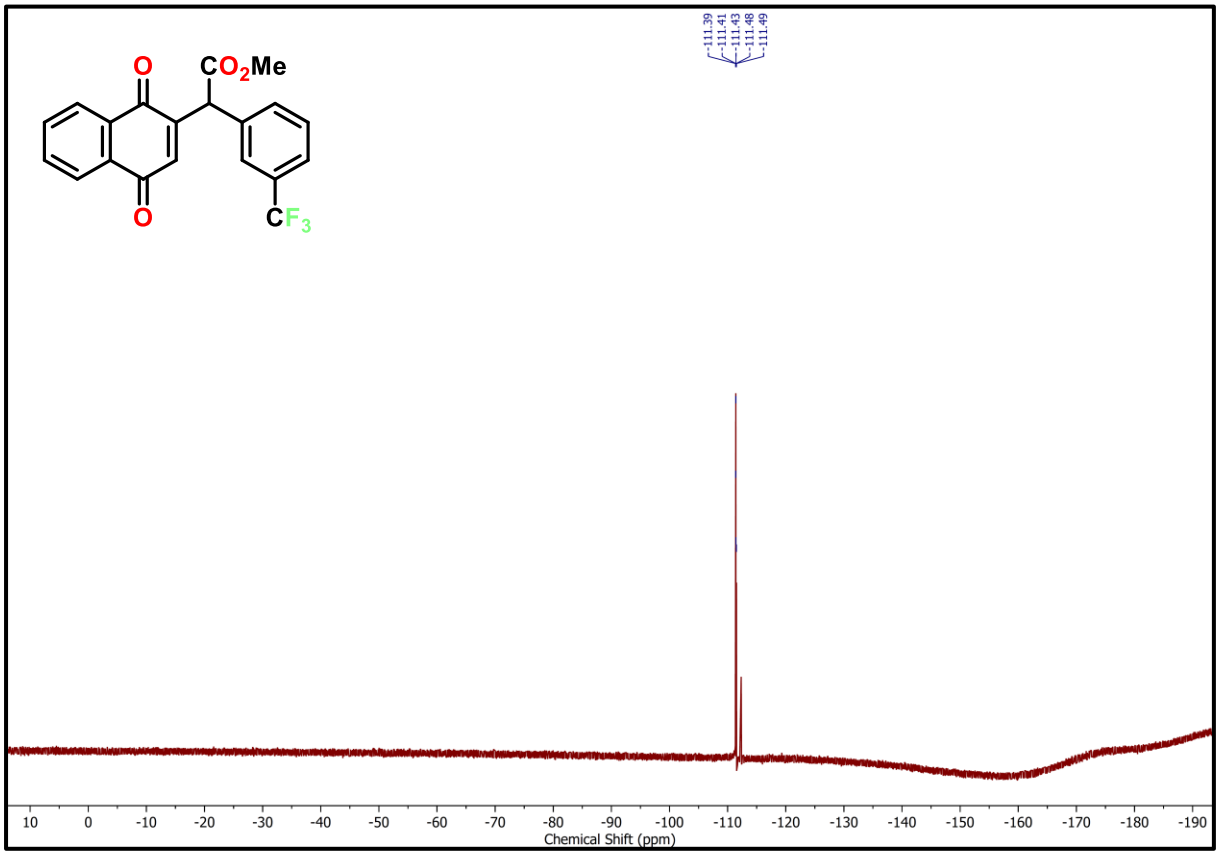
951

952 ^{13}C NMR (100 MHz) of **10m** in $CDCl_3$

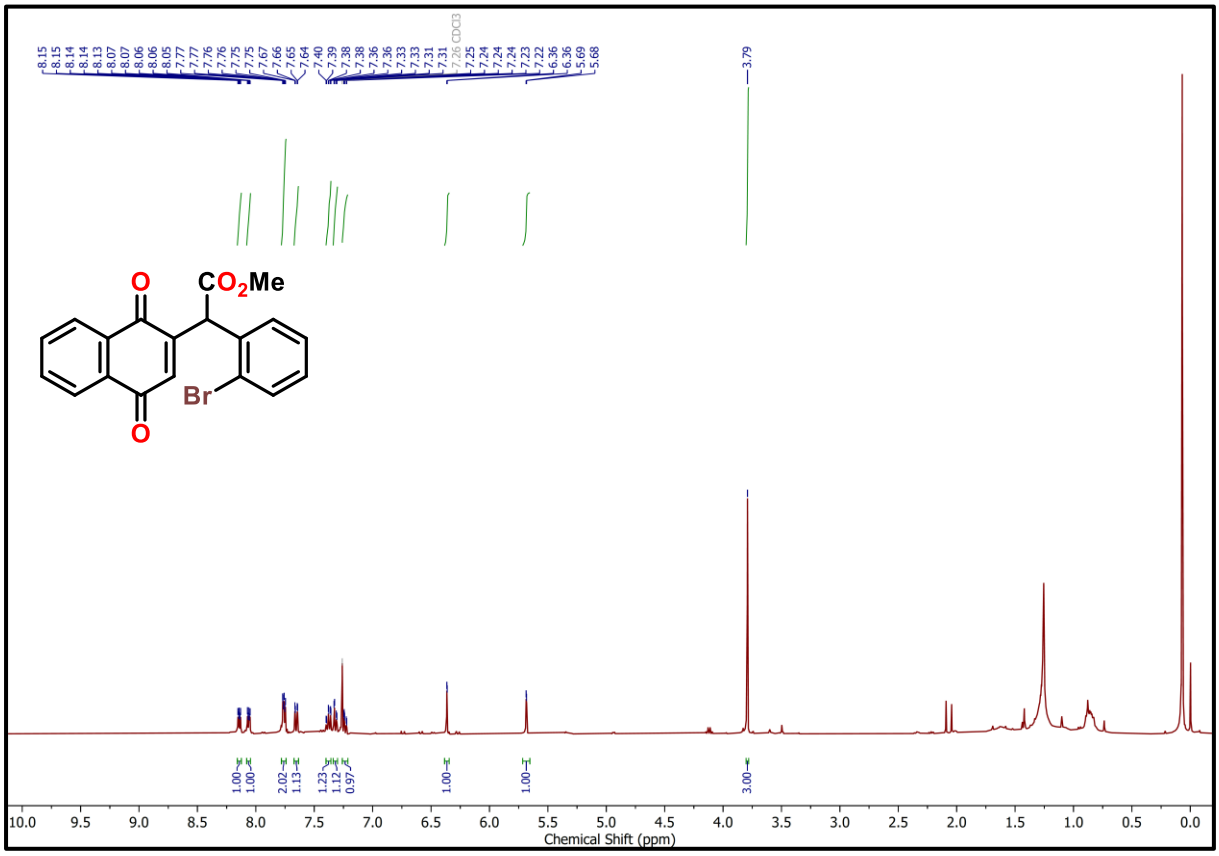


953

^{19}F NMR (376 MHz) of **10m** in $CDCl_3$

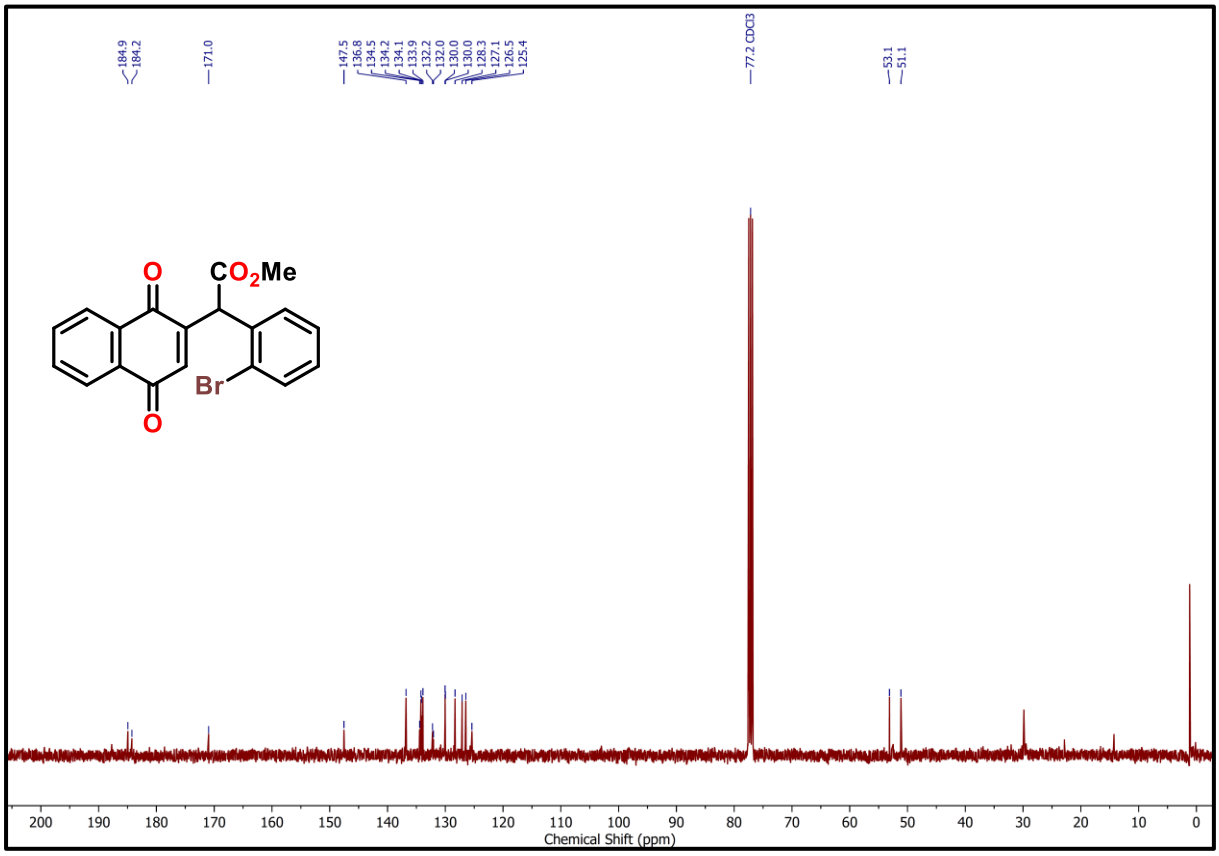


971 ^{1}H NMR (400 MHz) of **10n** in $CDCl_3$



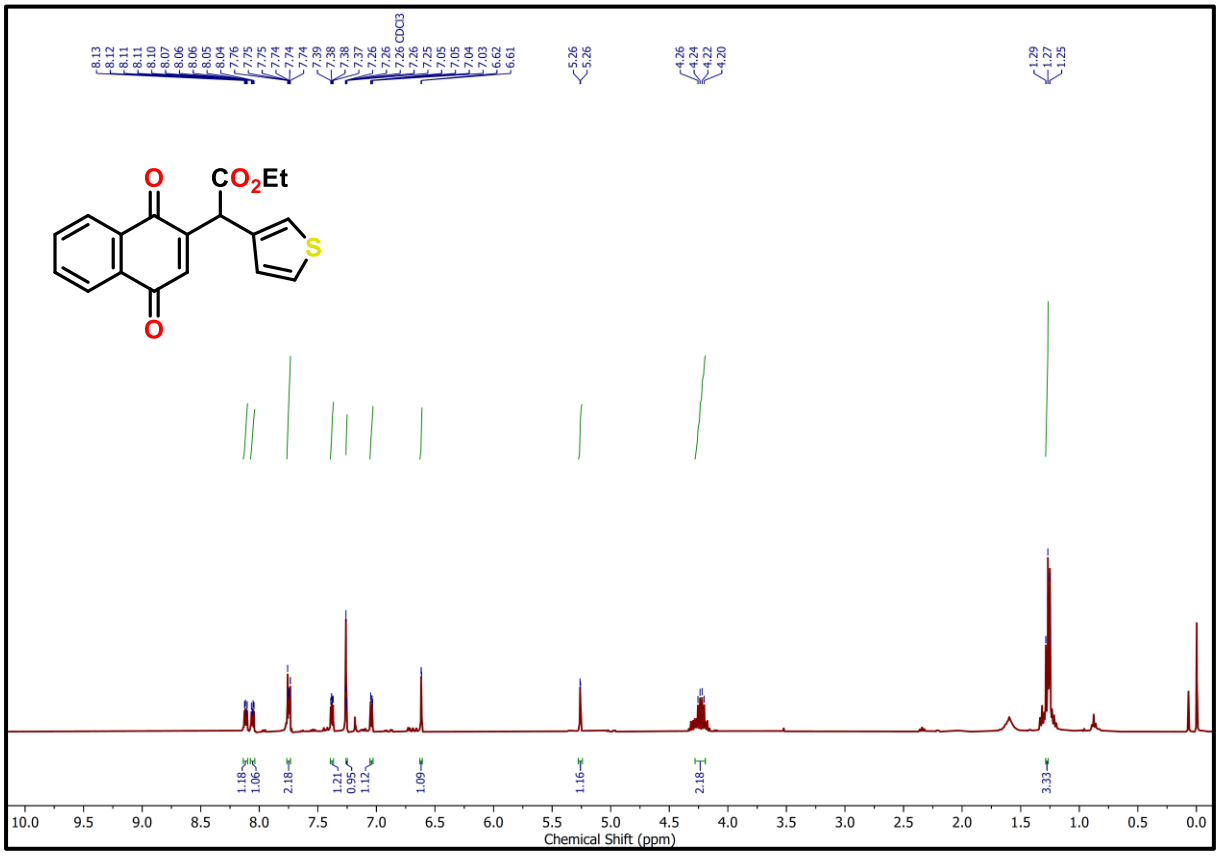
972

973 ^{13}C NMR (100 MHz) of **10n** in $CDCl_3$



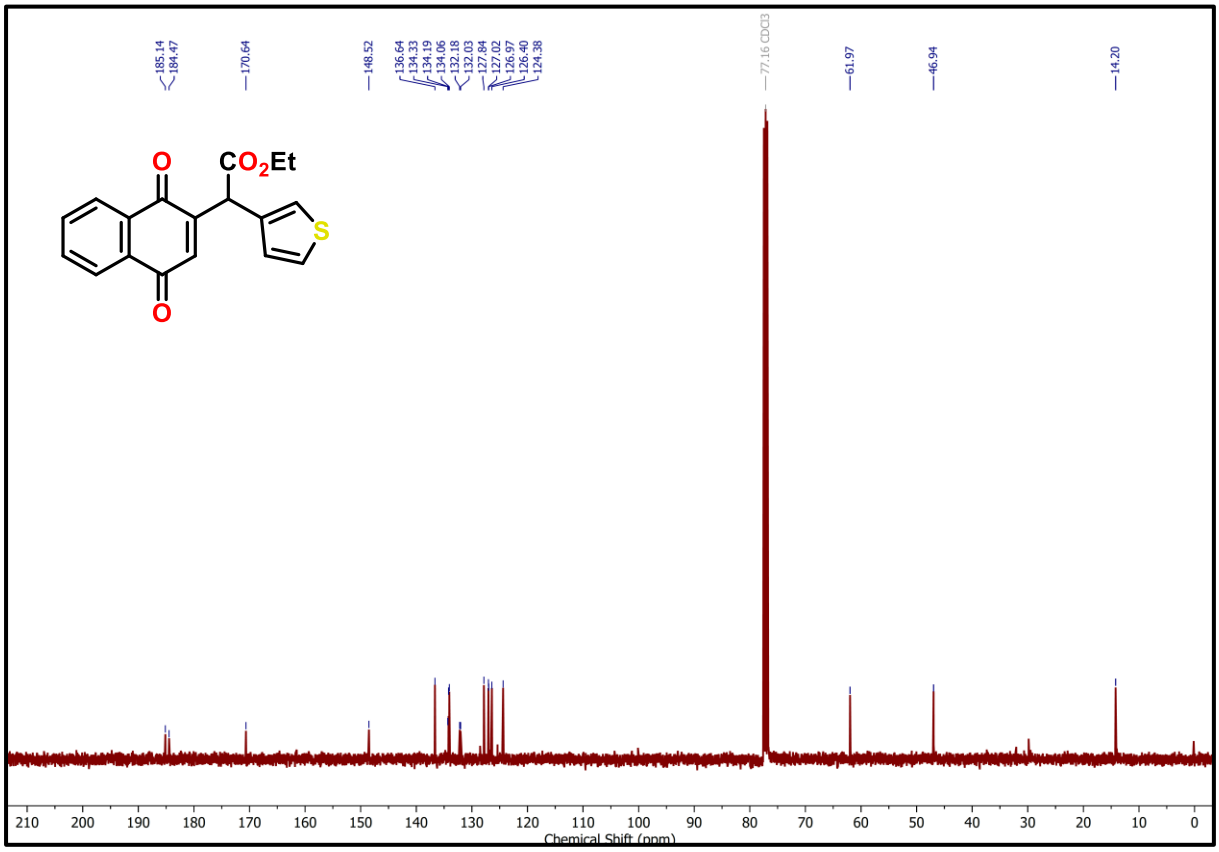
974

975 ^{1}H NMR (400 MHz) of **10o** in $CDCl_3$



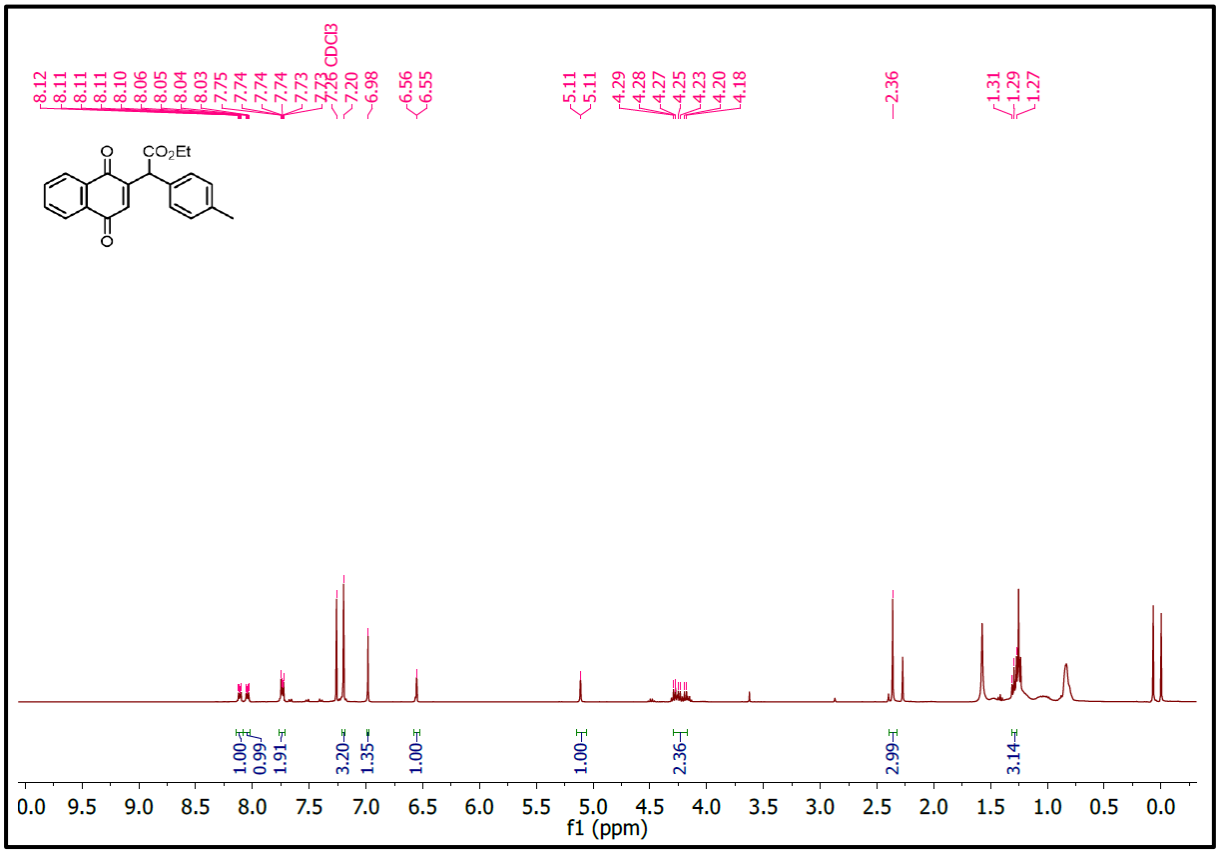
976

977 ^{13}C NMR (100 MHz) of **10o** in $CDCl_3$



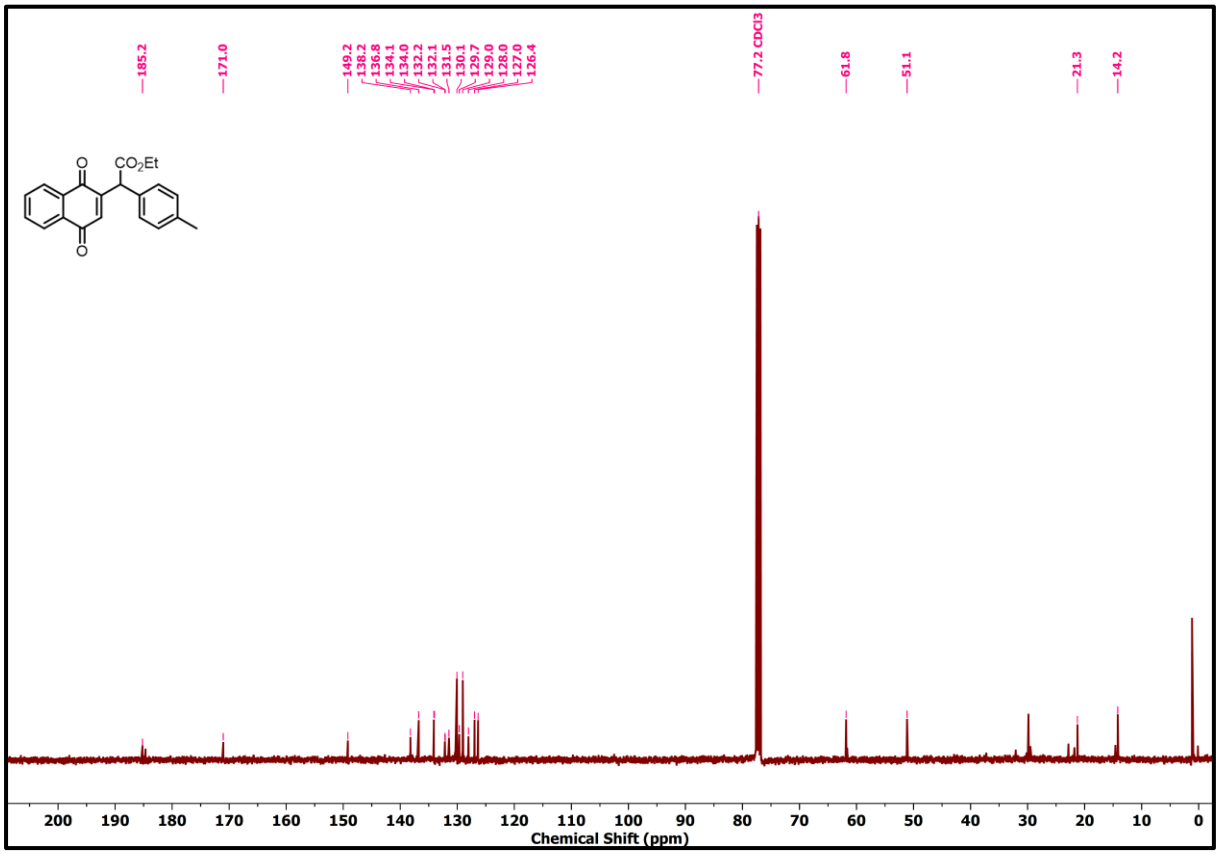
978

979 *[1]H* NMR (400 MHz) of **10p** in $CDCl_3$



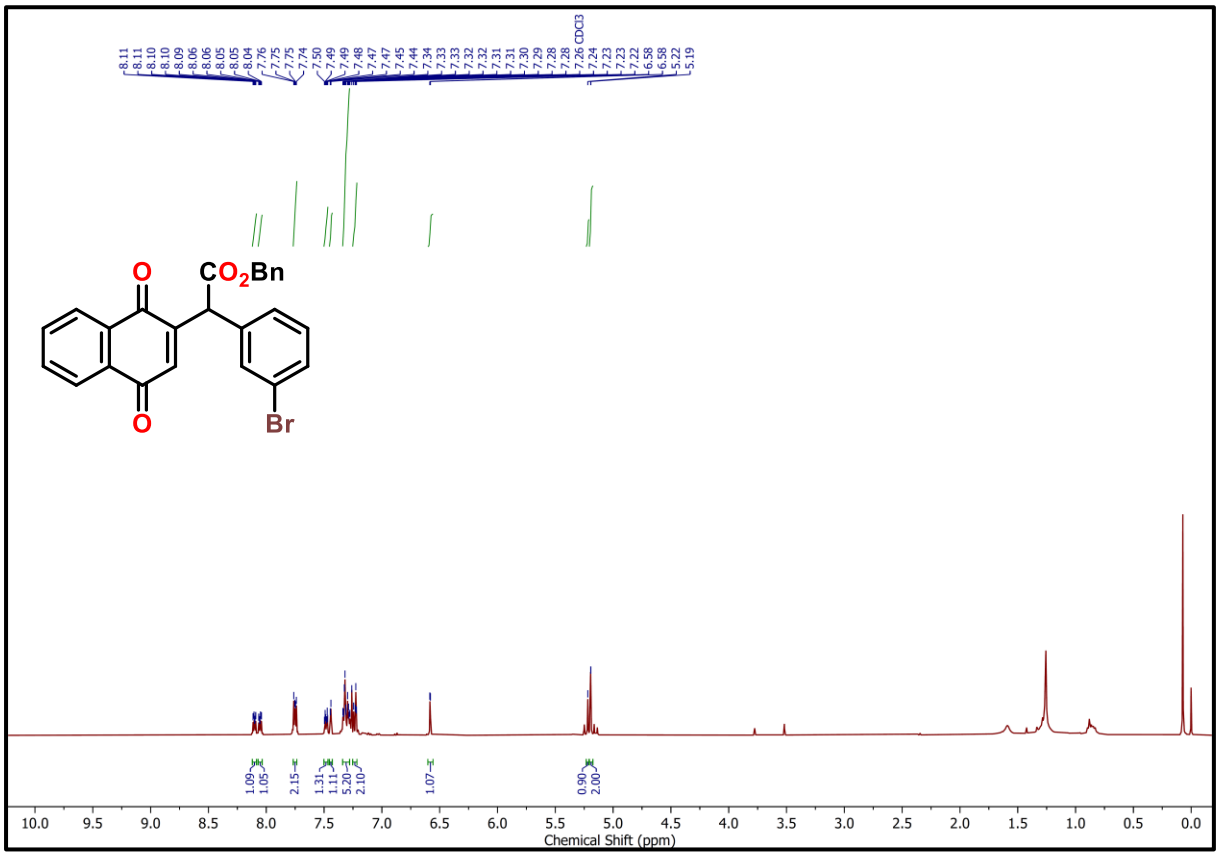
980

981 *[13]C* NMR (100 MHz) of **10p** in $CDCl_3$



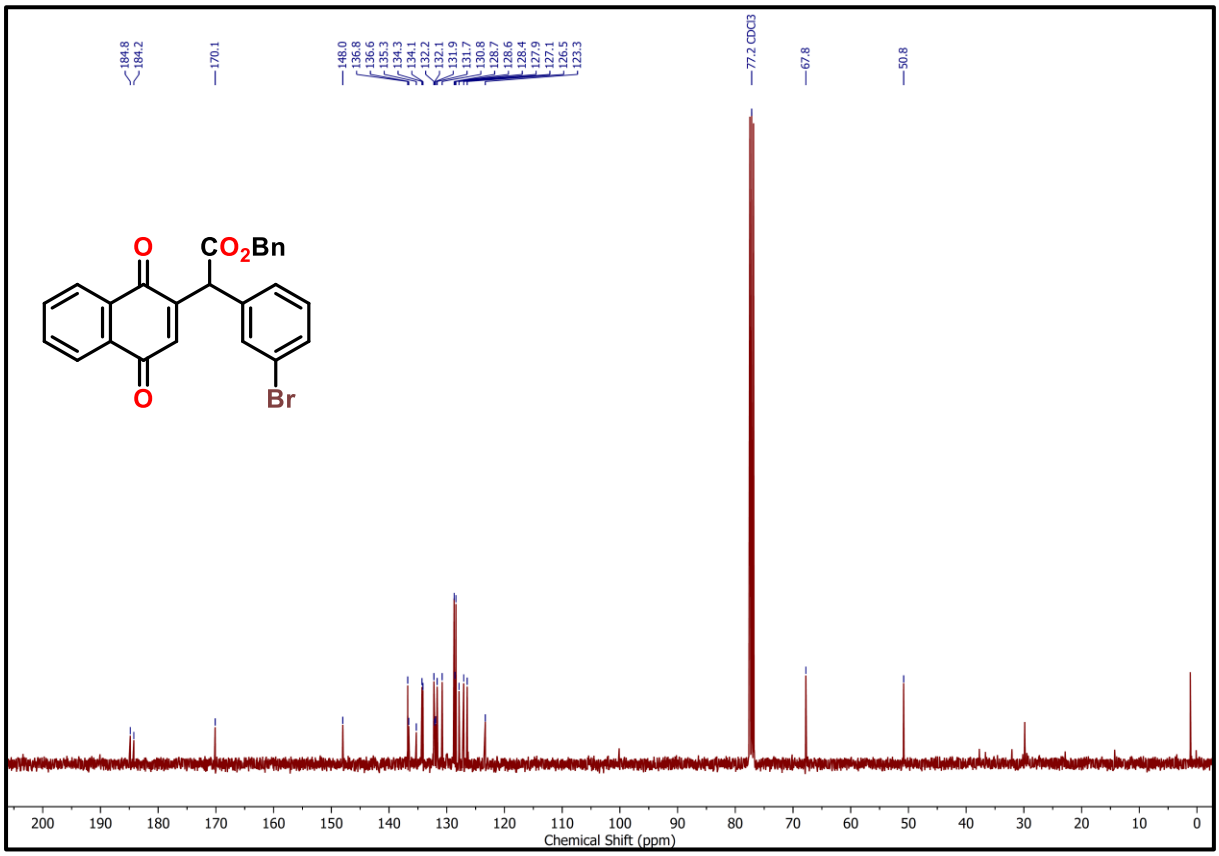
982

983 ^{1}H NMR (400 MHz) of **10q** in $CDCl_3$



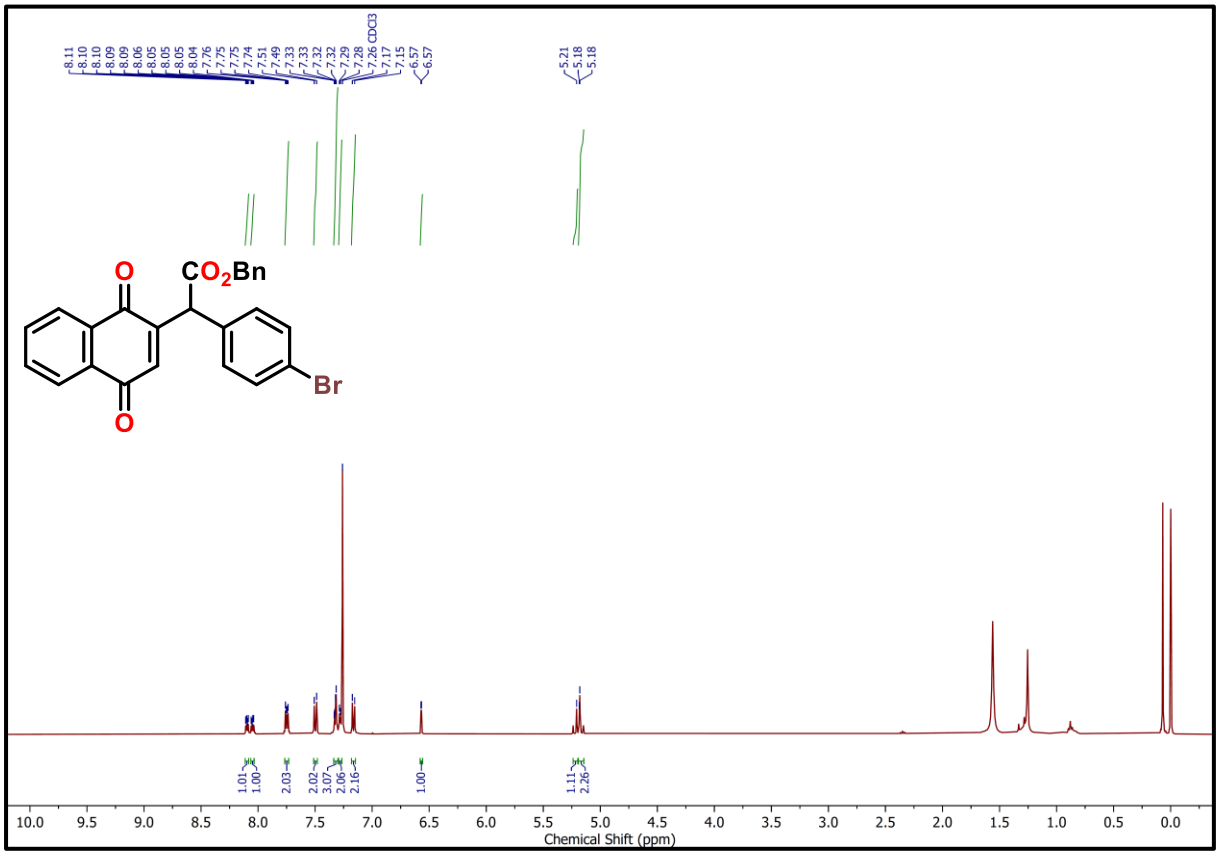
984

985 ^{13}C NMR (100 MHz) of **10q** in $CDCl_3$



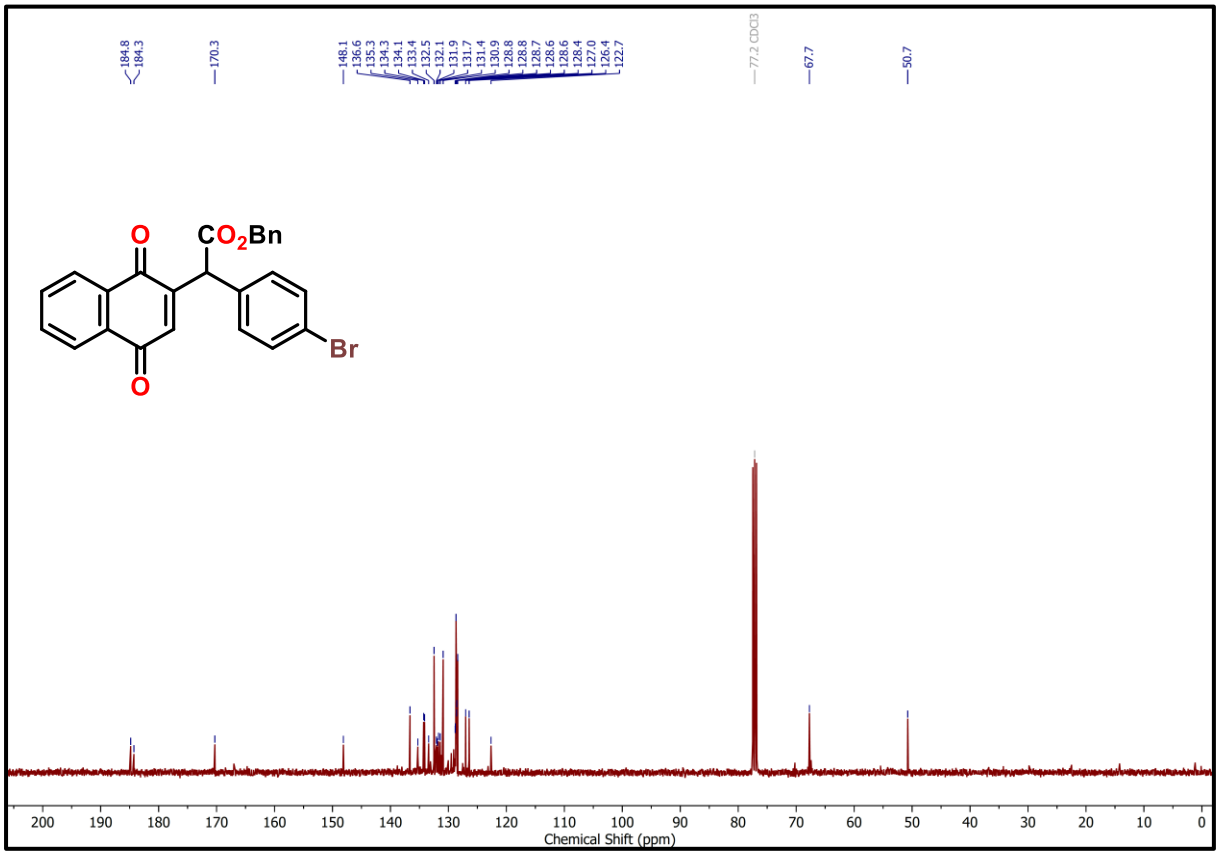
986

987 *[1]H* NMR (400 MHz) of **10r** in $CDCl_3$



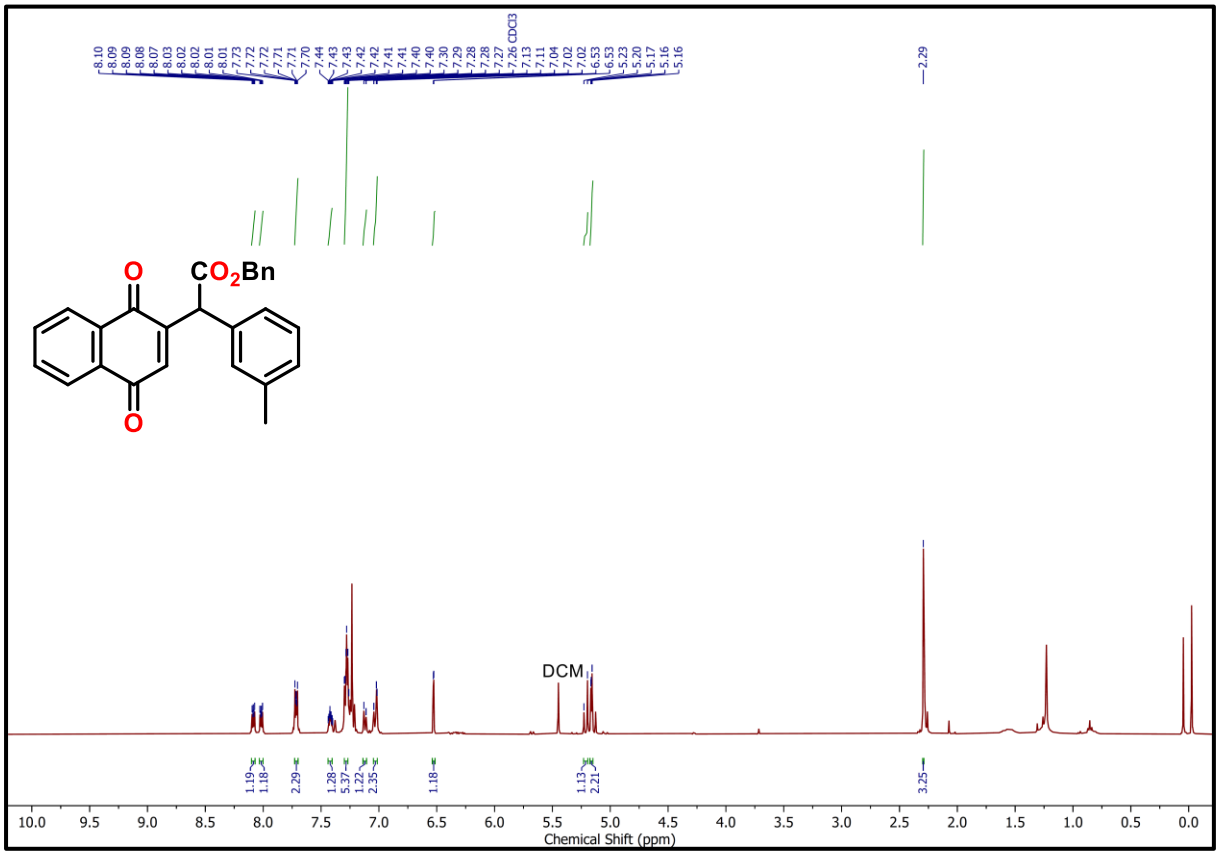
988

989 *[13]C* NMR (100 MHz) of **10r** in $CDCl_3$



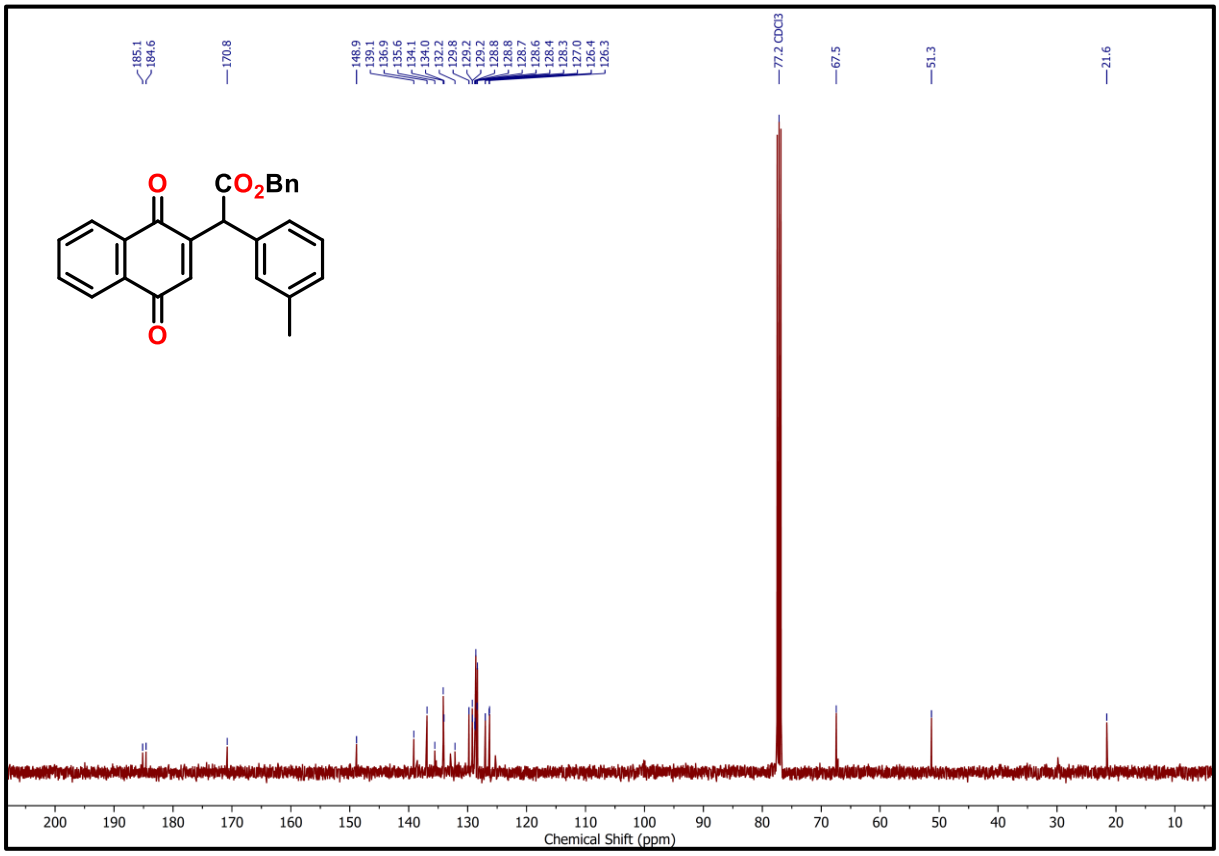
990

991 ^{1}H NMR (400 MHz) of **10s** in $CDCl_3$



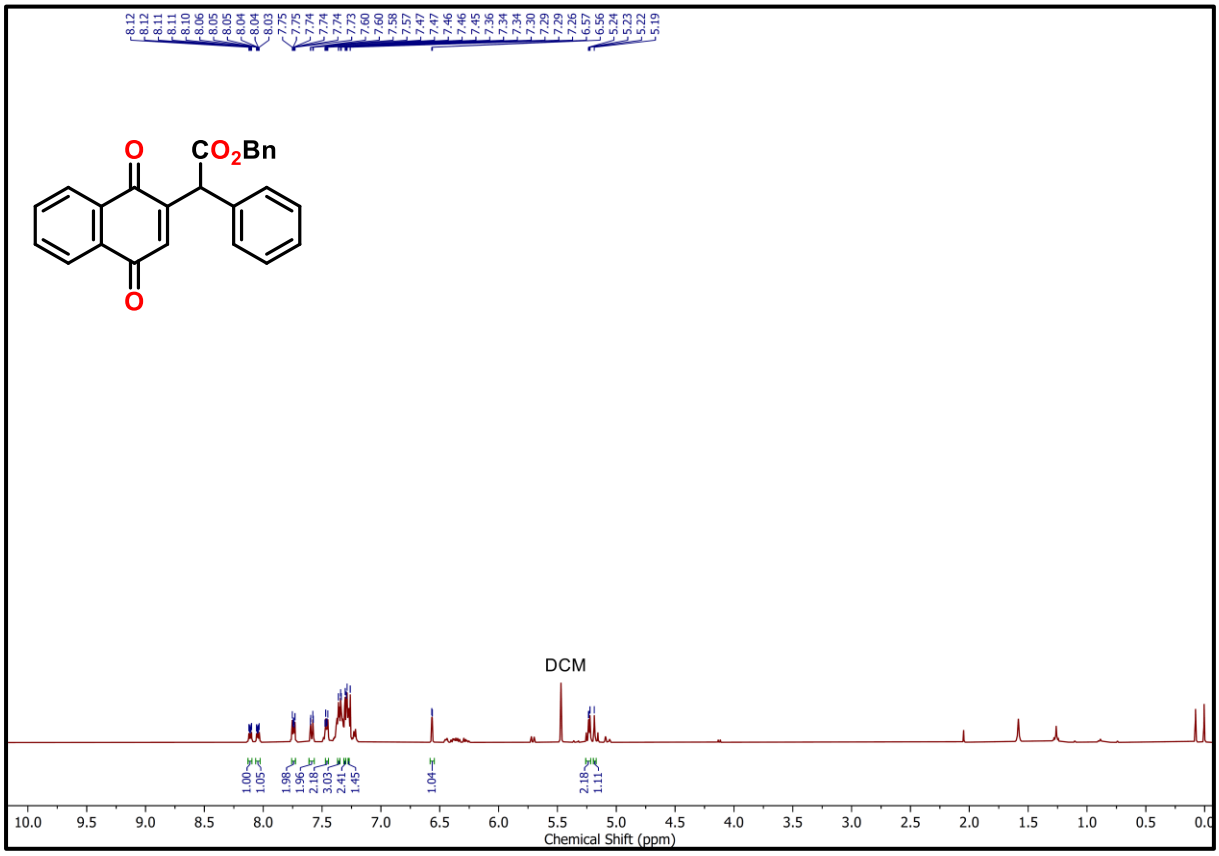
992

993 ^{13}C NMR (100 MHz) of **10s** in $CDCl_3$



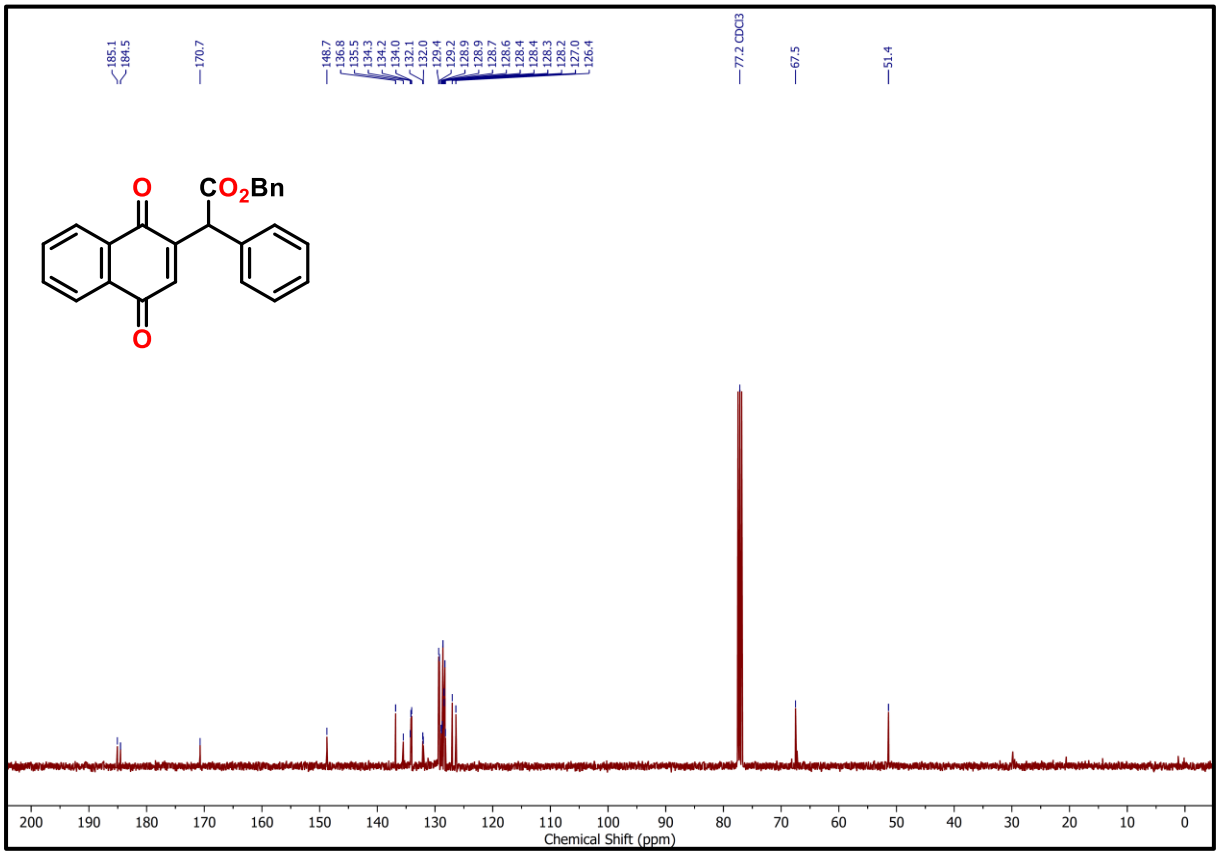
994

995 ^{1}H NMR (400 MHz) of **10t** in $CDCl_3$



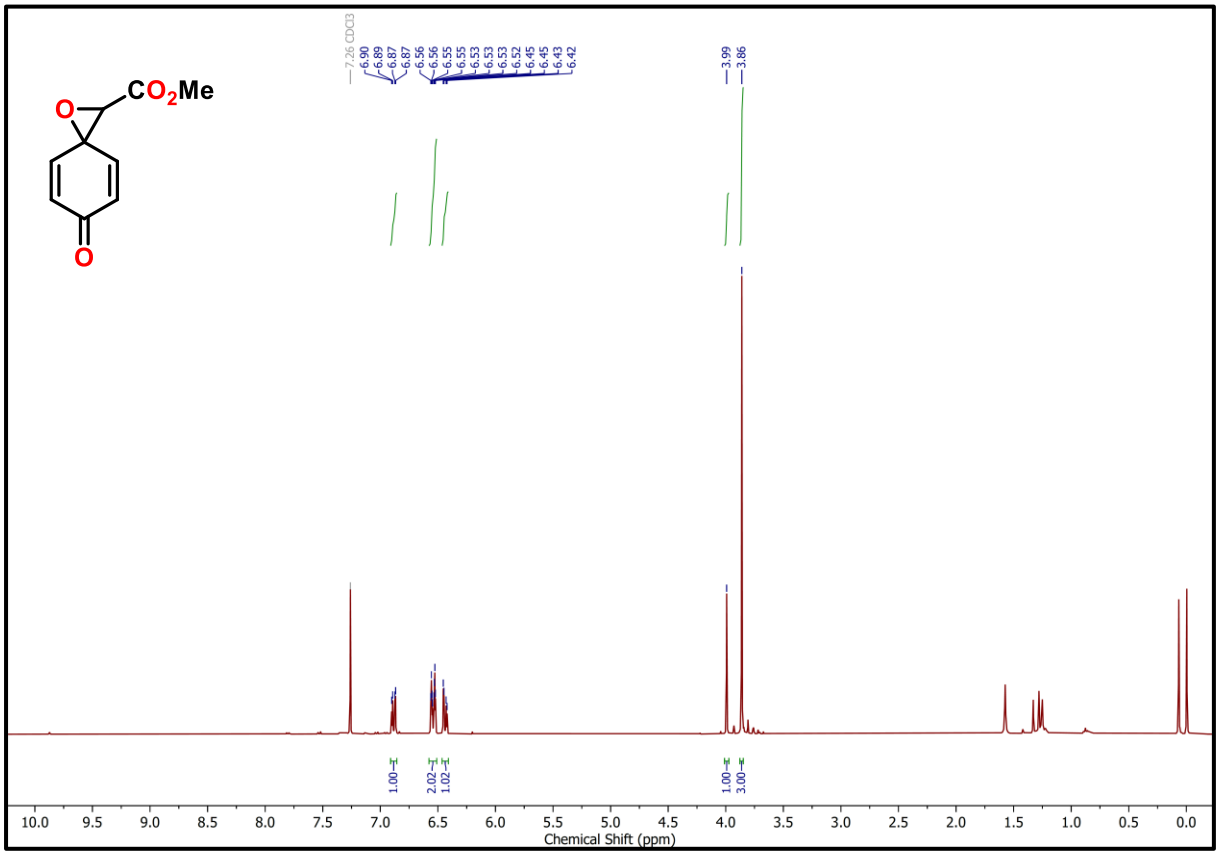
996

997 ^{13}C NMR (100 MHz) of **10t** in $CDCl_3$



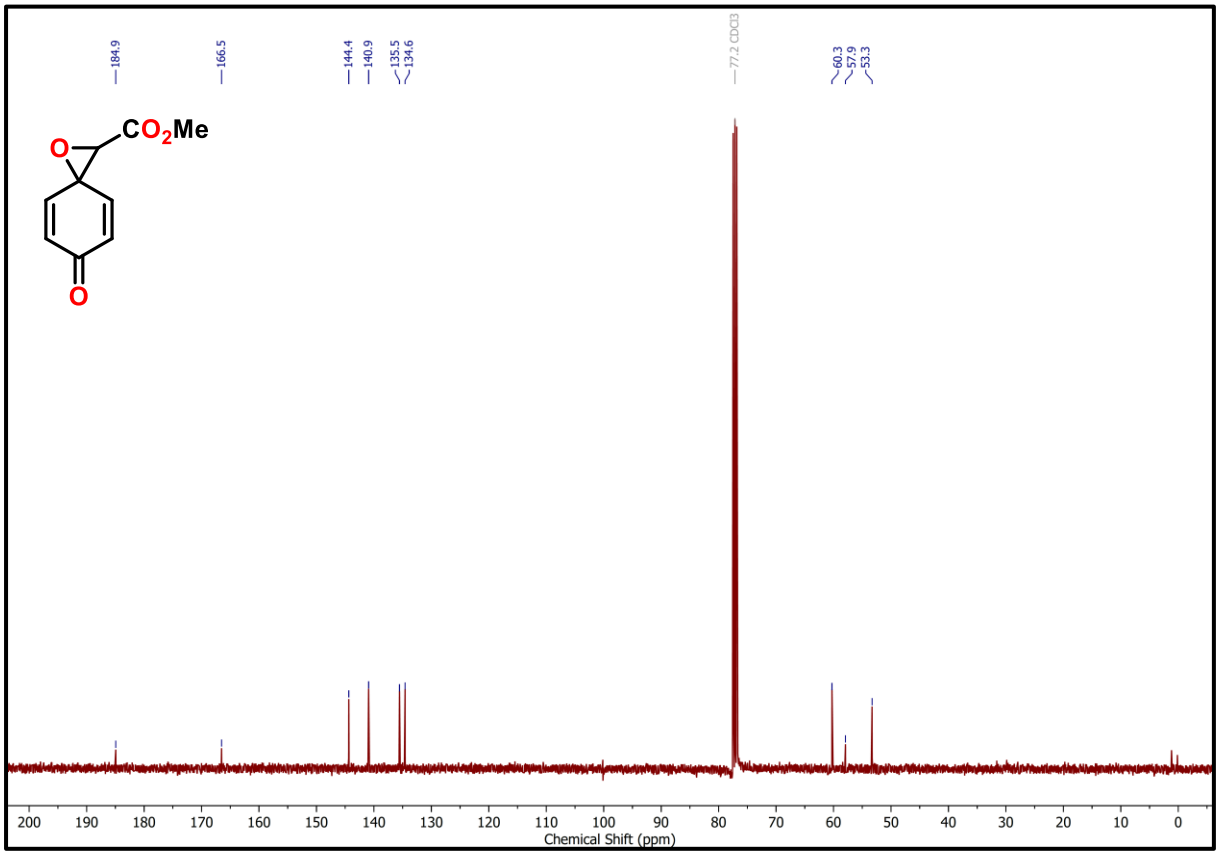
998

999 ^{1}H NMR (400 MHz) of **11a** in $CDCl_3$



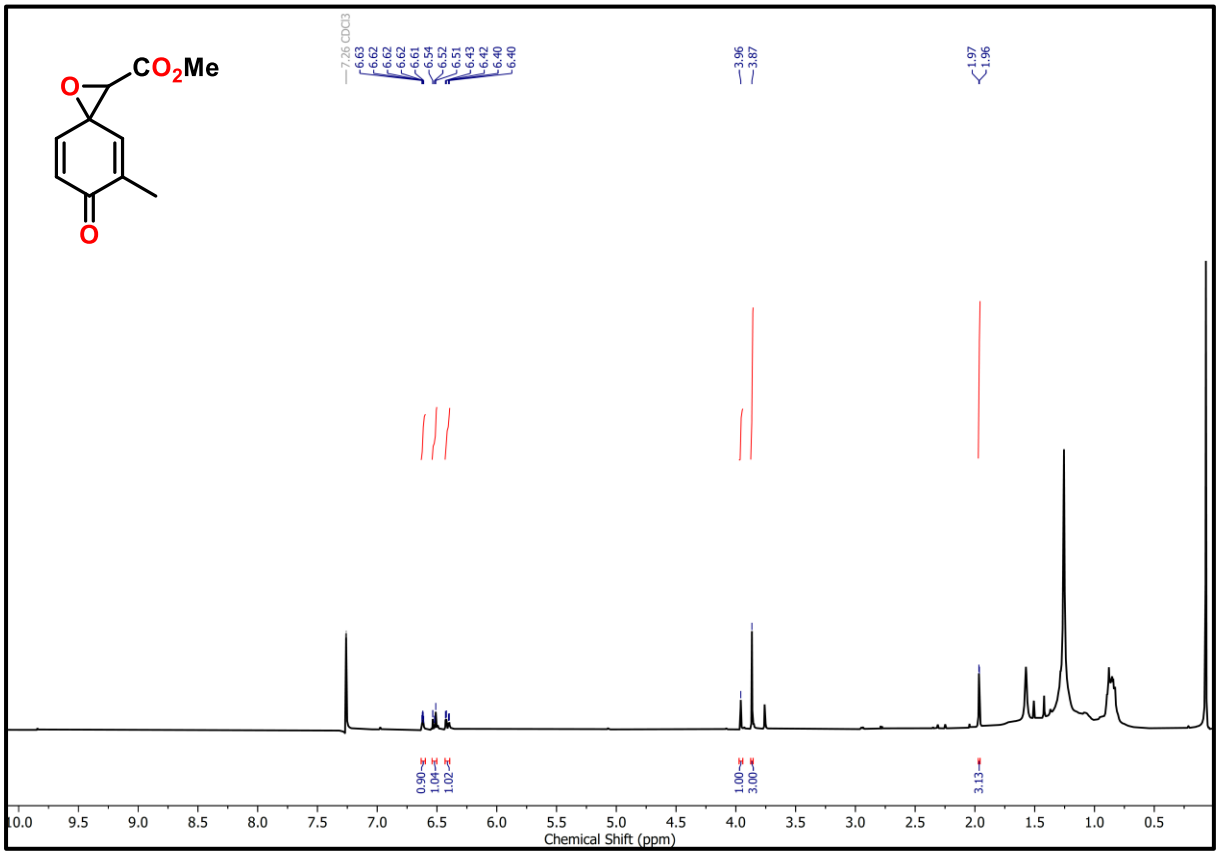
1000

1001 ^{13}C NMR (100 MHz) of **11a** in $CDCl_3$



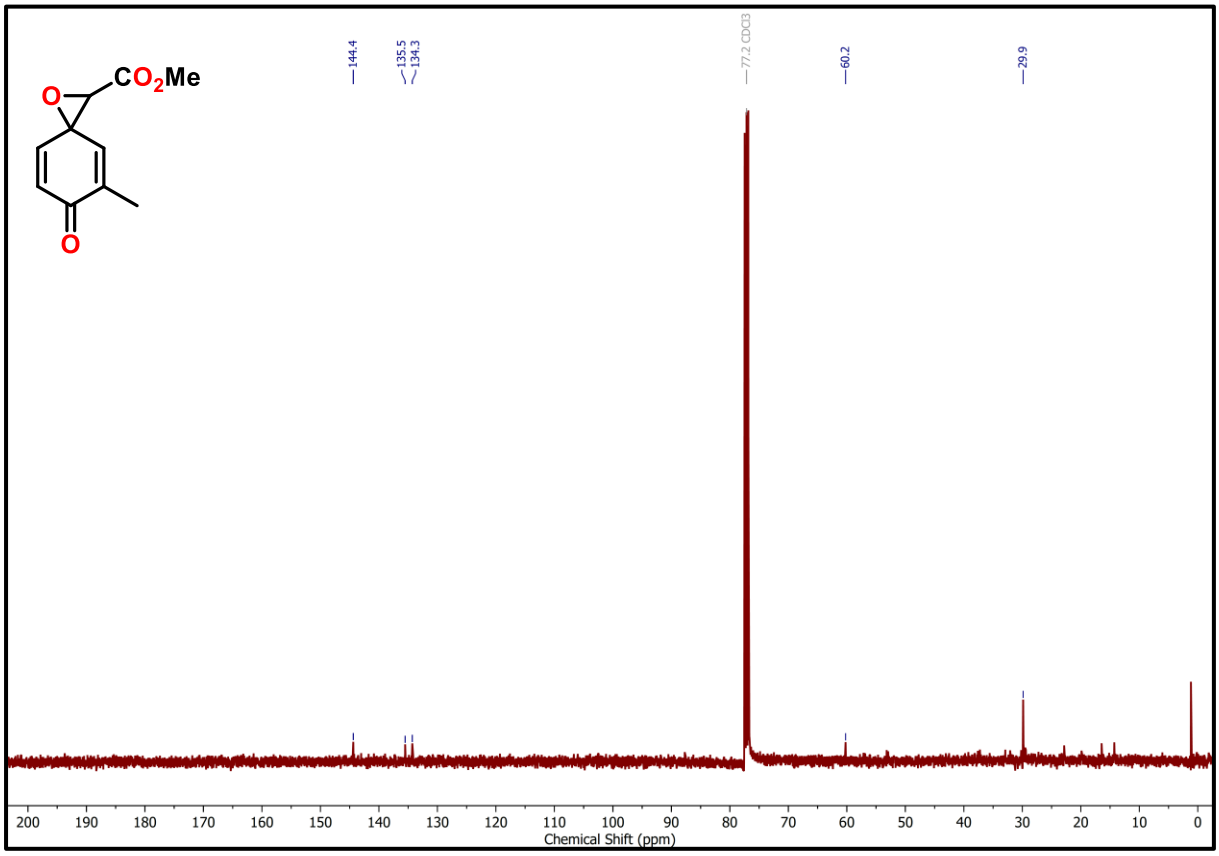
1002

1003 *[1]H* NMR (400 MHz) of **11b** in $CDCl_3$



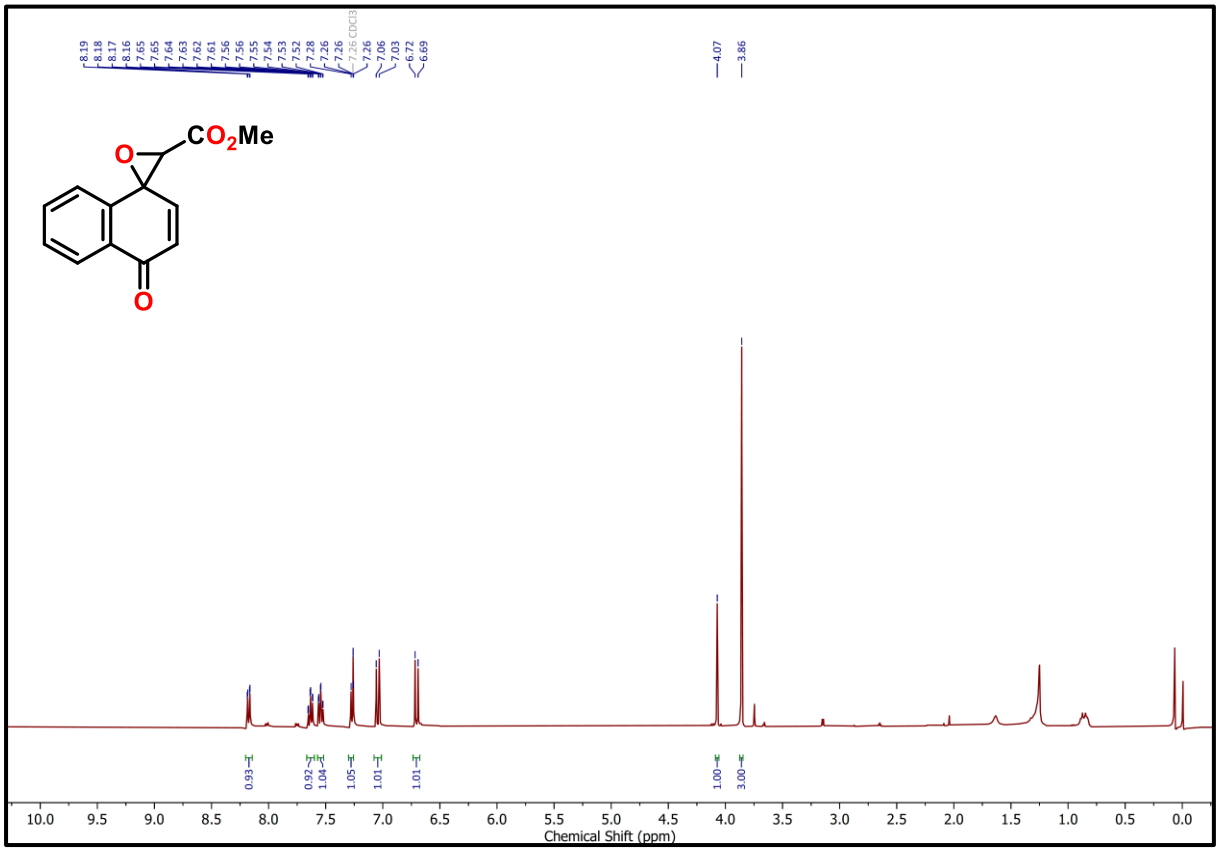
1004

1005 *[13]C* NMR (100 MHz) of **11b** in $CDCl_3$

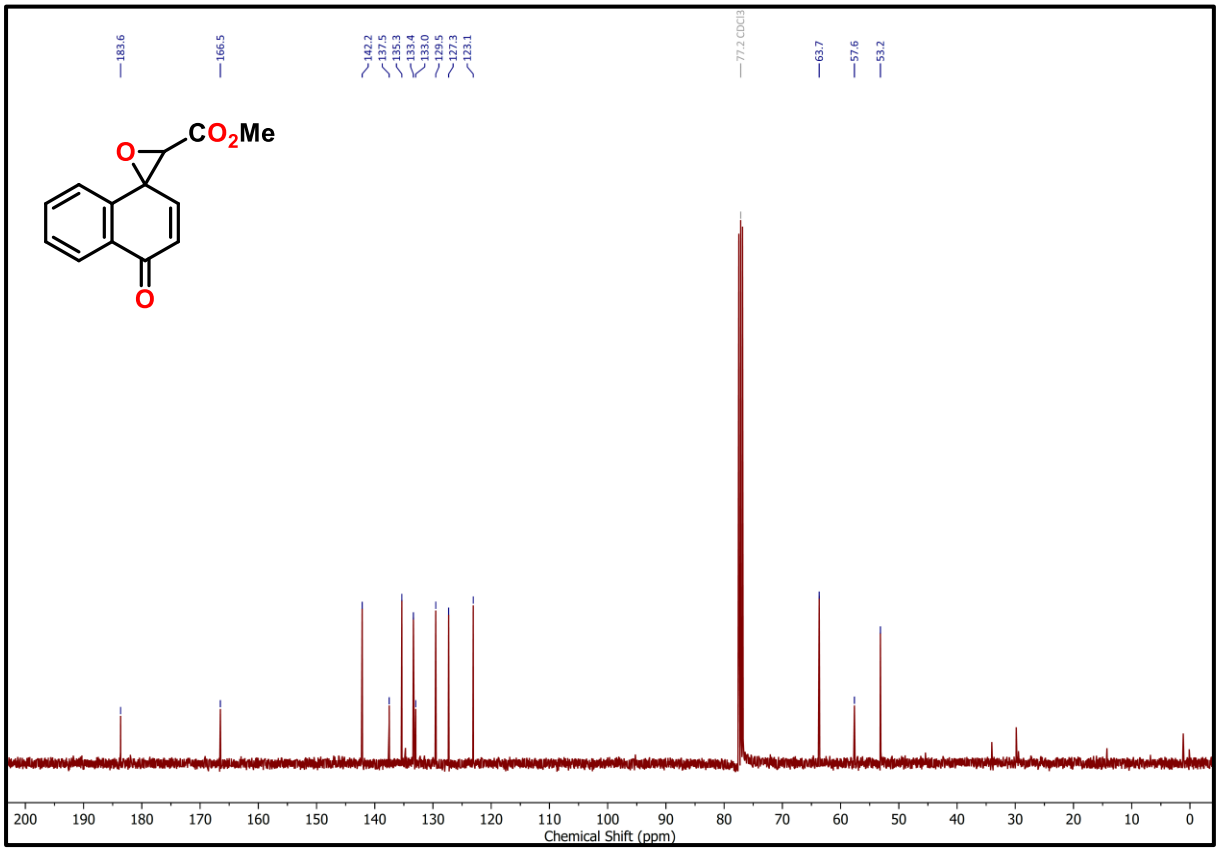


1006

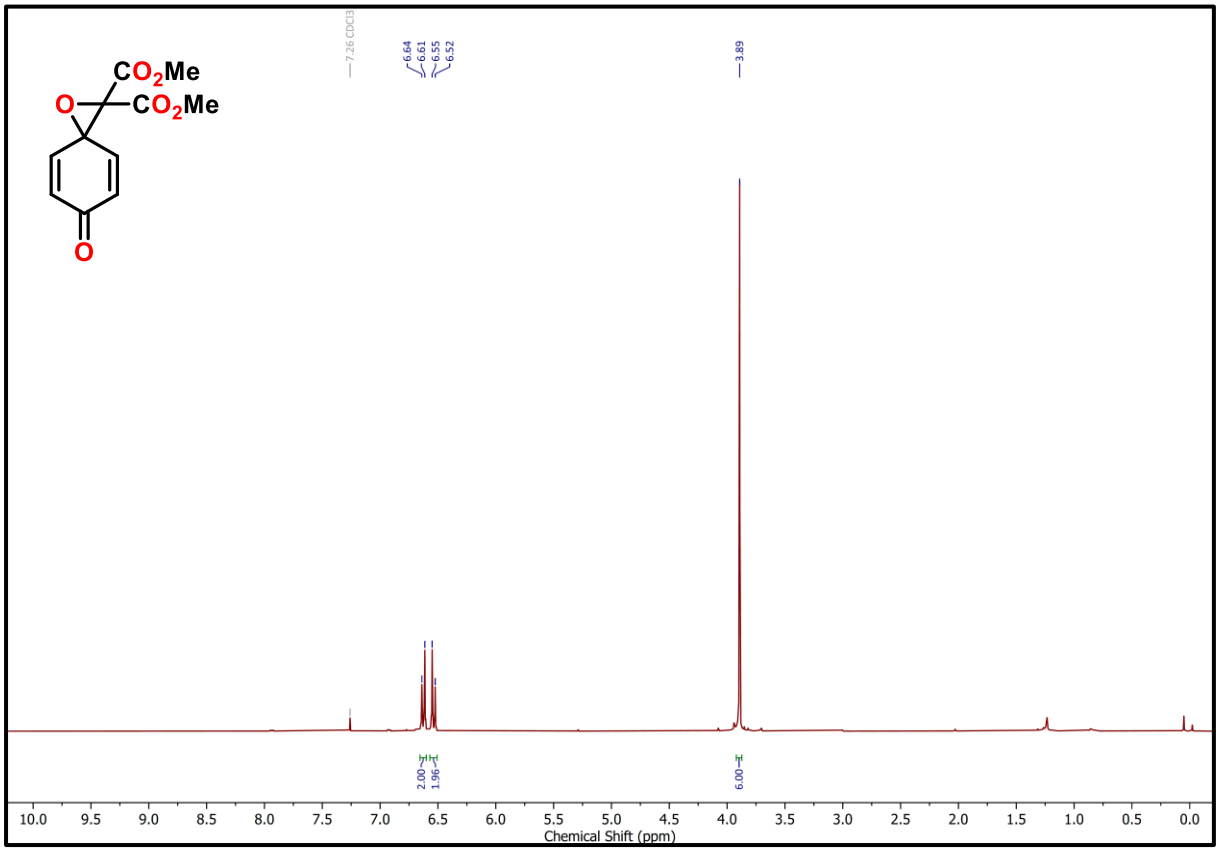
^{1}H NMR (400 MHz) of **11c** in $CDCl_3$



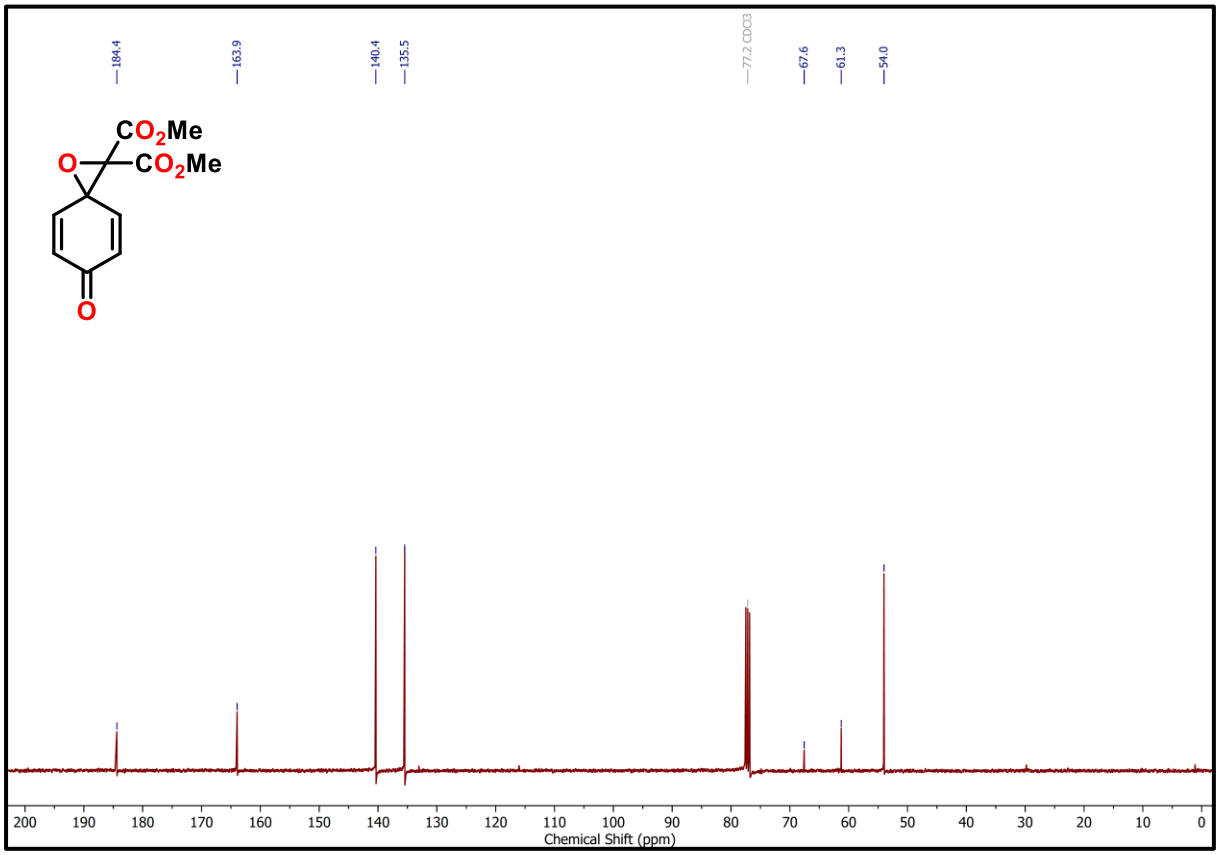
^{13}C NMR (100 MHz) of **11c** in $CDCl_3$



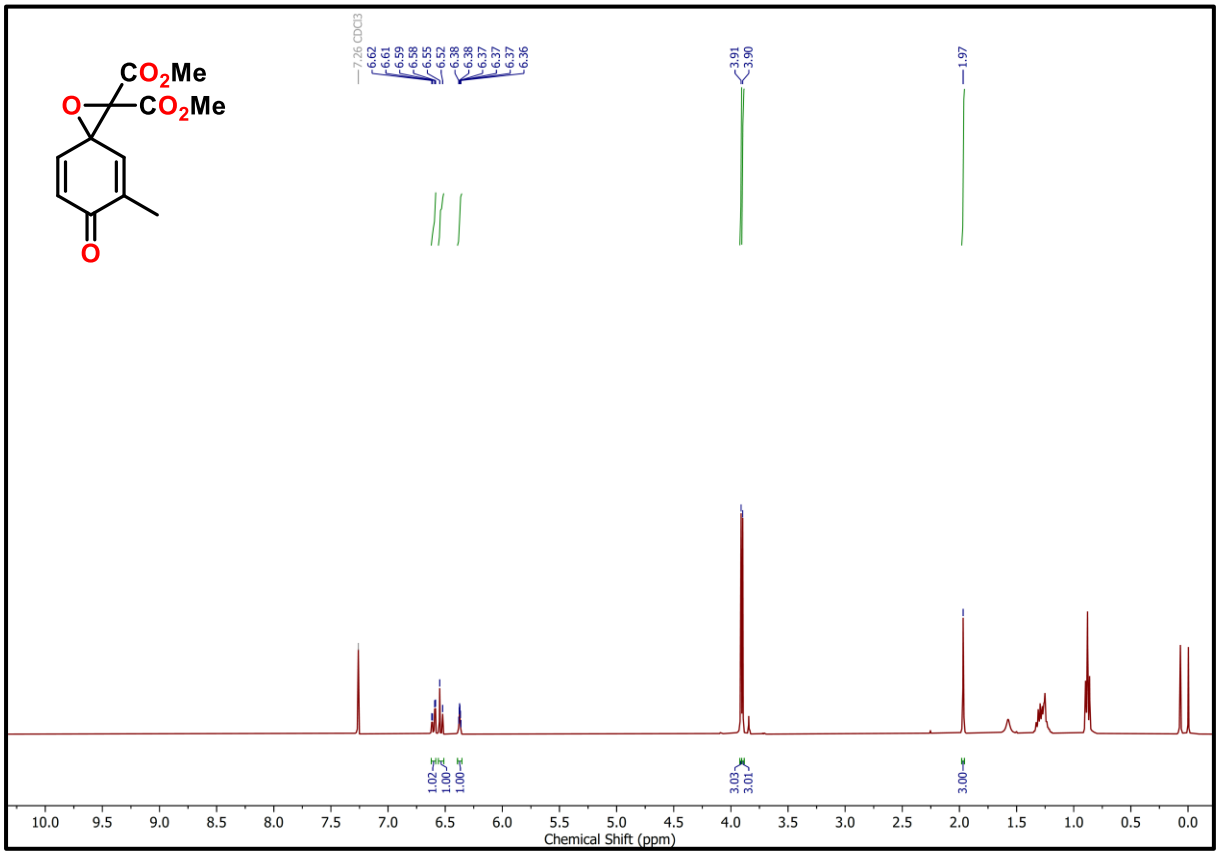
^{1}H NMR (400 MHz) of **11d** in $CDCl_3$



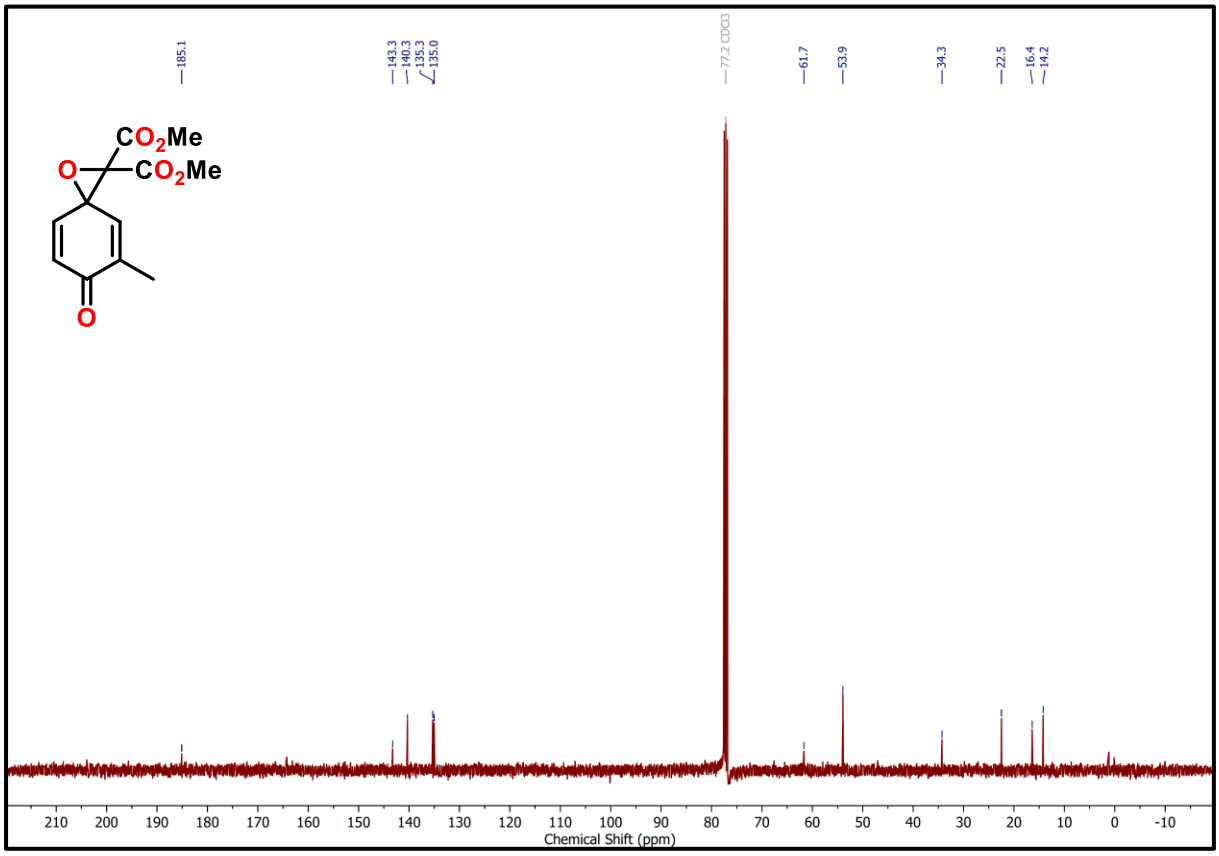
^{13}C NMR (100 MHz) of **11d** in $CDCl_3$



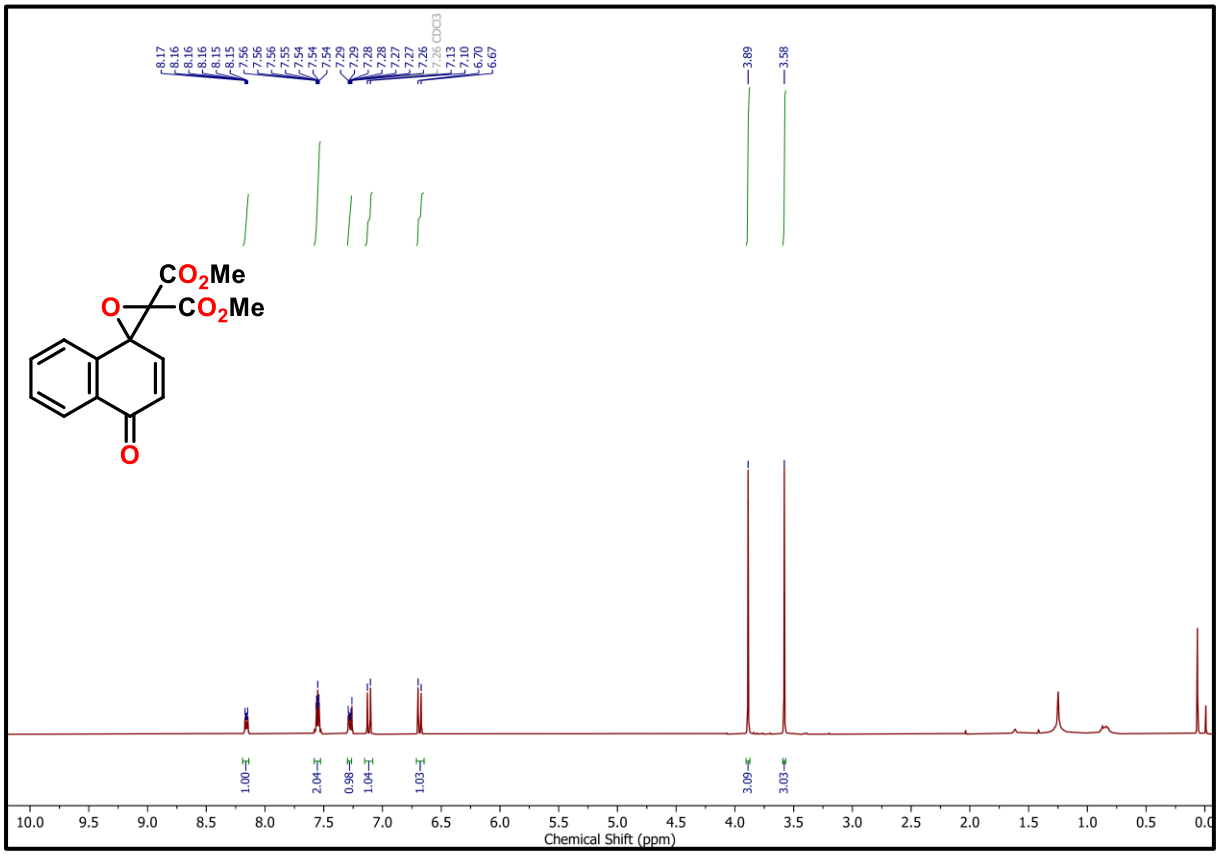
^{1}H NMR (400 MHz) of **11e** in $CDCl_3$



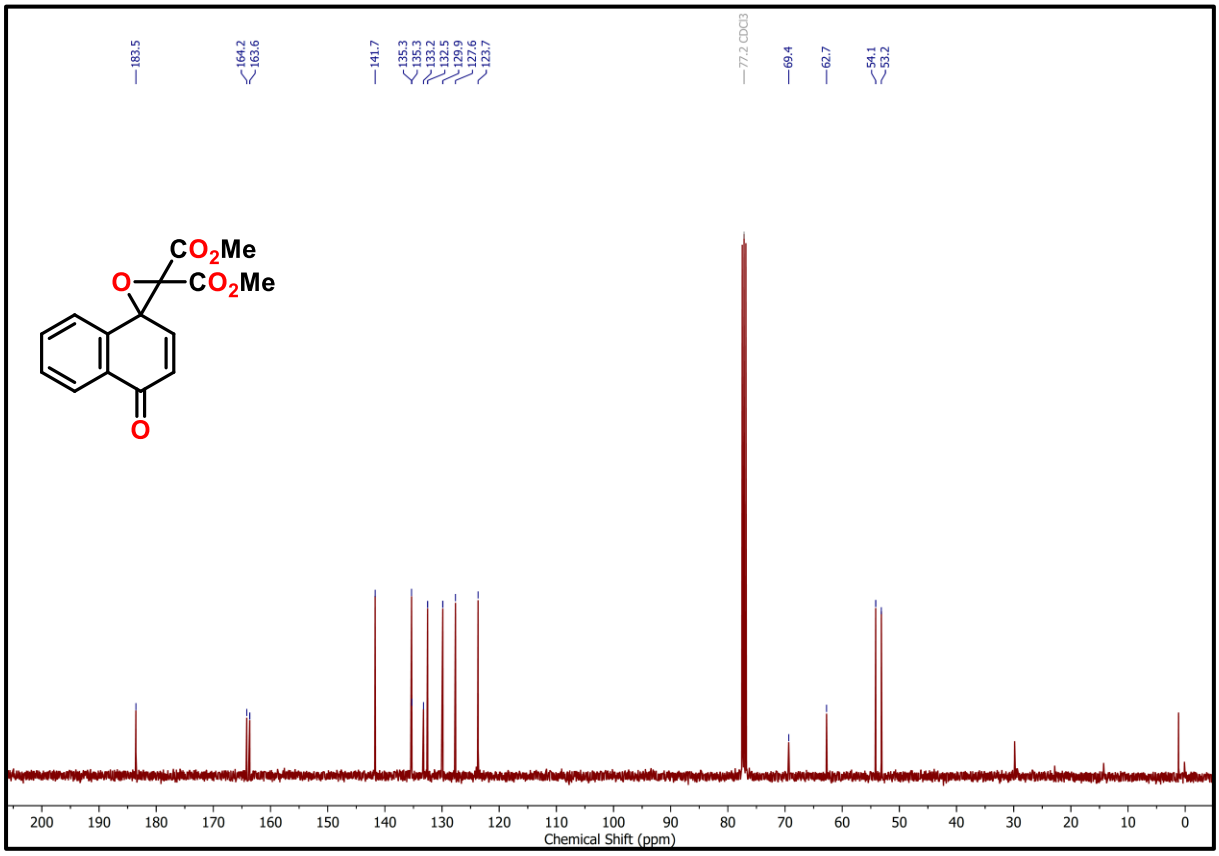
^{13}C NMR (100 MHz) of **11e** in $CDCl_3$



^{1}H NMR (400 MHz) of **11f** in $CDCl_3$



^{13}C NMR (100 MHz) of **11f** in $CDCl_3$



2-D NMR of Compound 5d

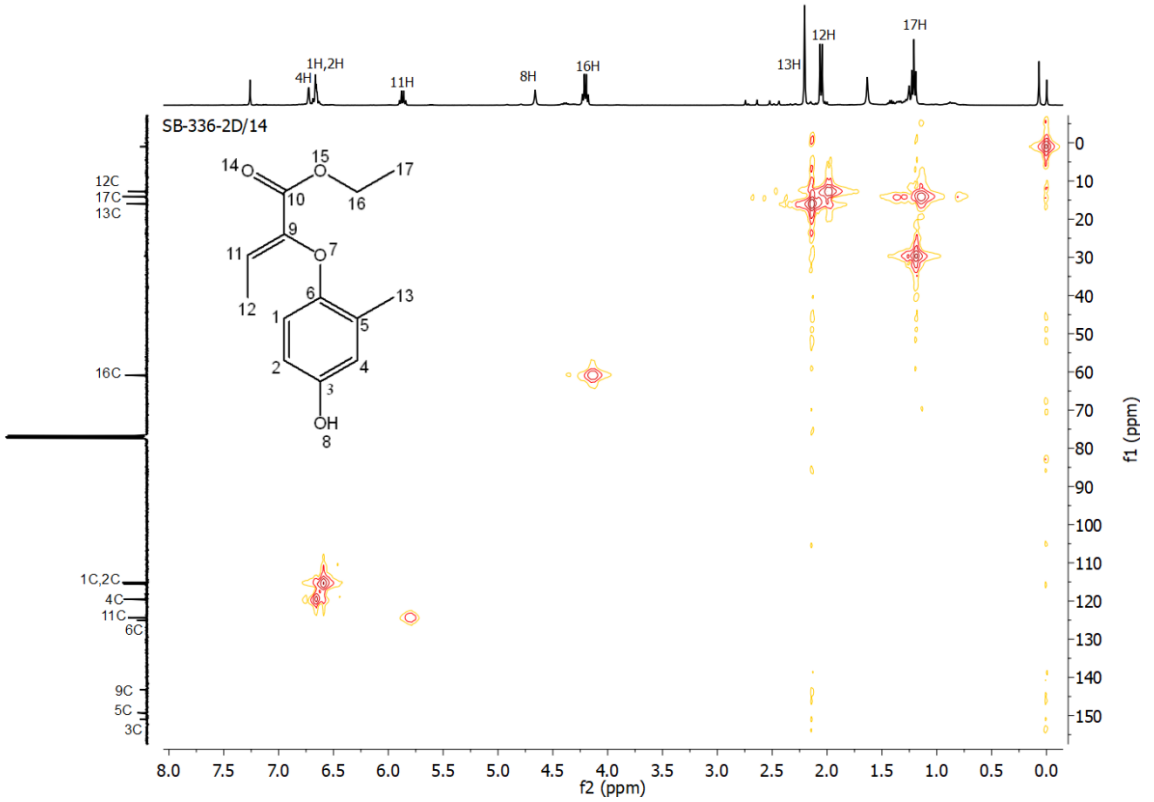


Figure S8. HSQC: for assigning carbon and proton peaks

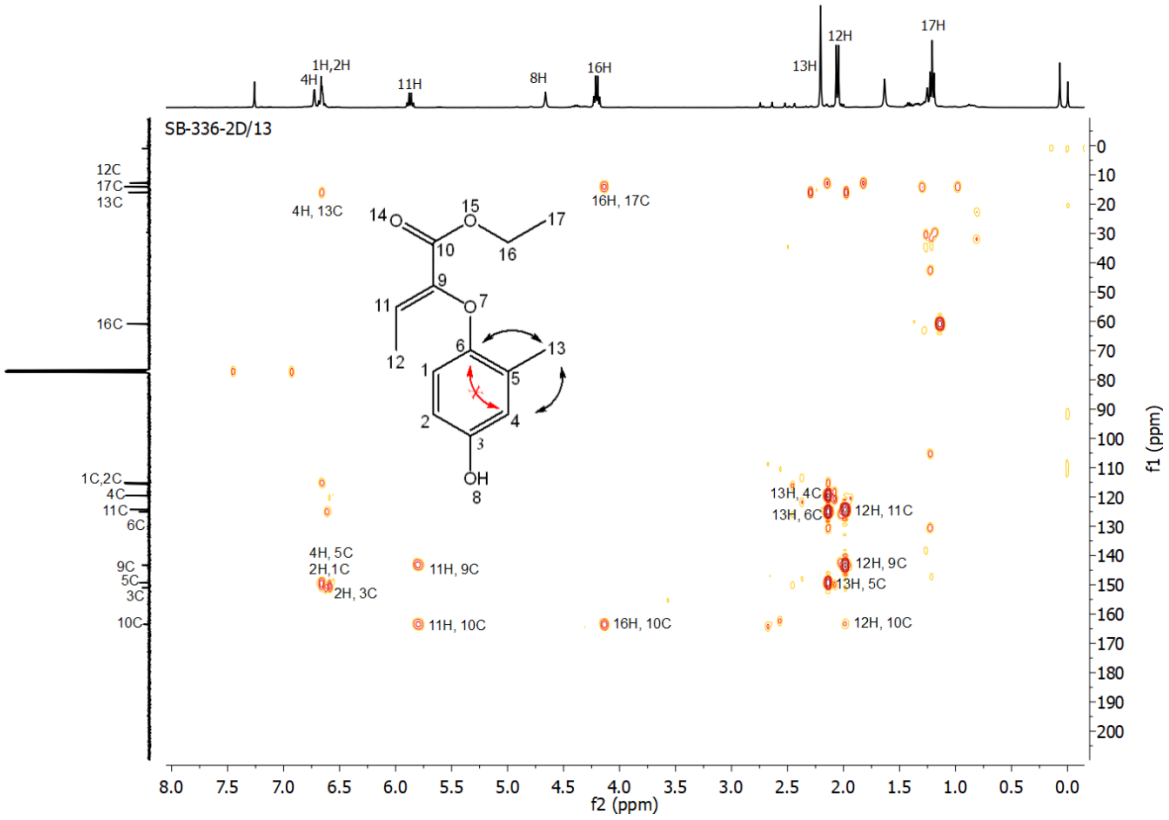


Figure S9. HMBC: for confirmation of regiomer

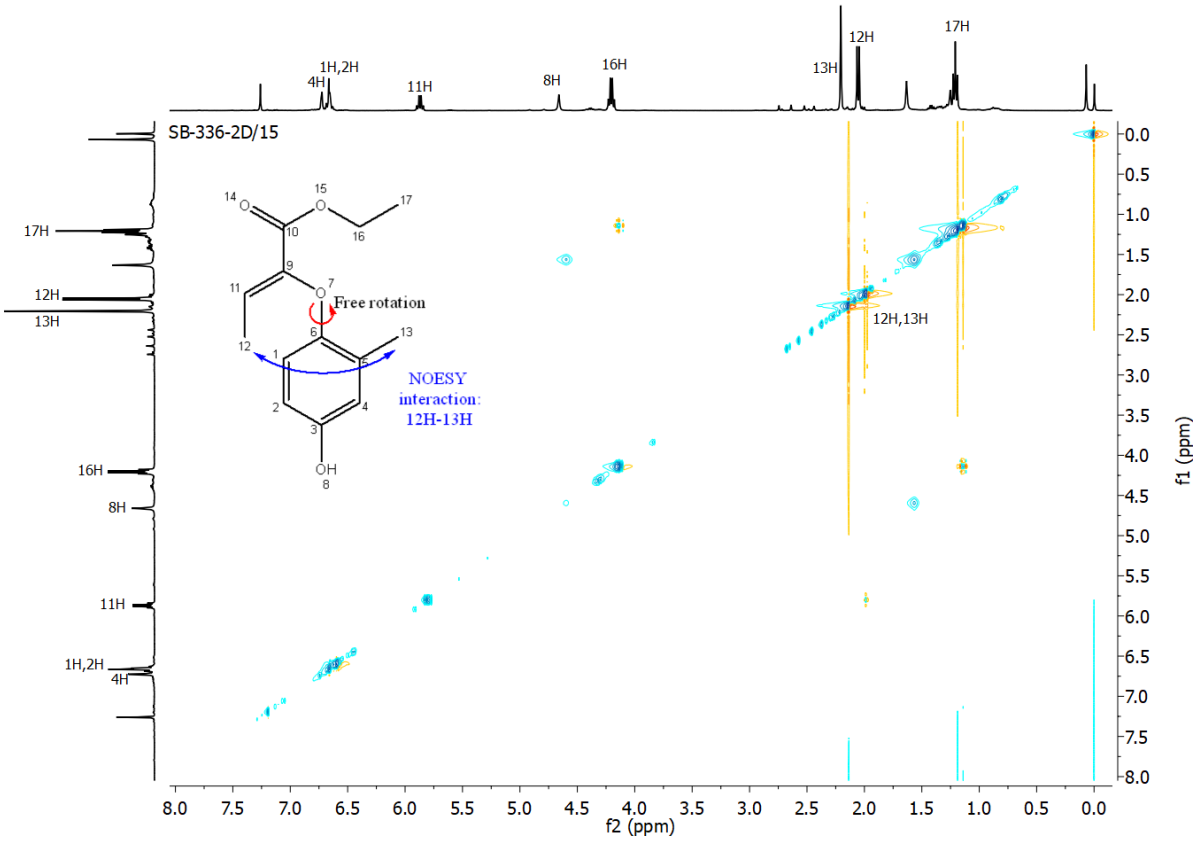


Figure S10. NOESY: for confirmation of Z-isomer

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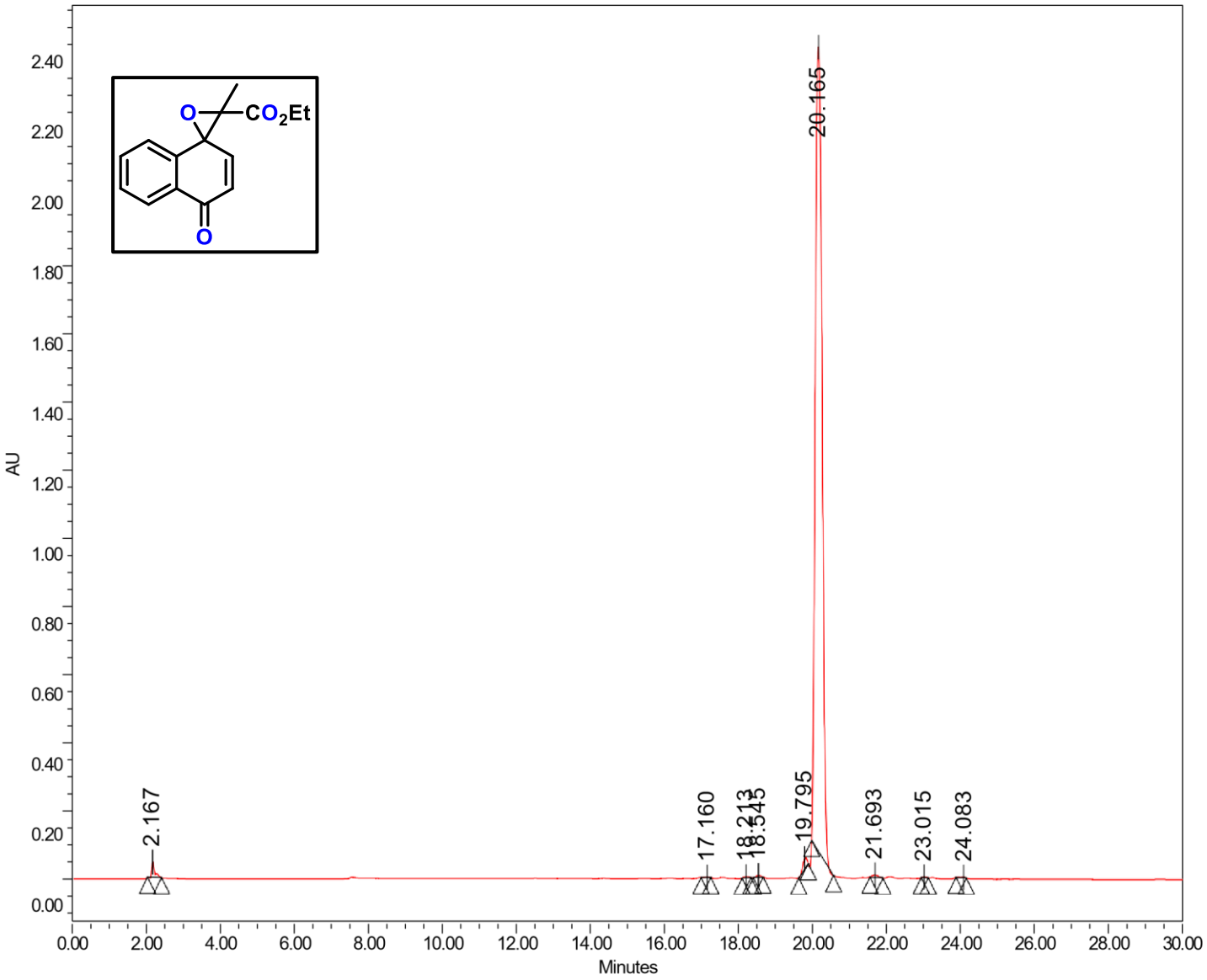

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Peak Summary with Statistics Name:

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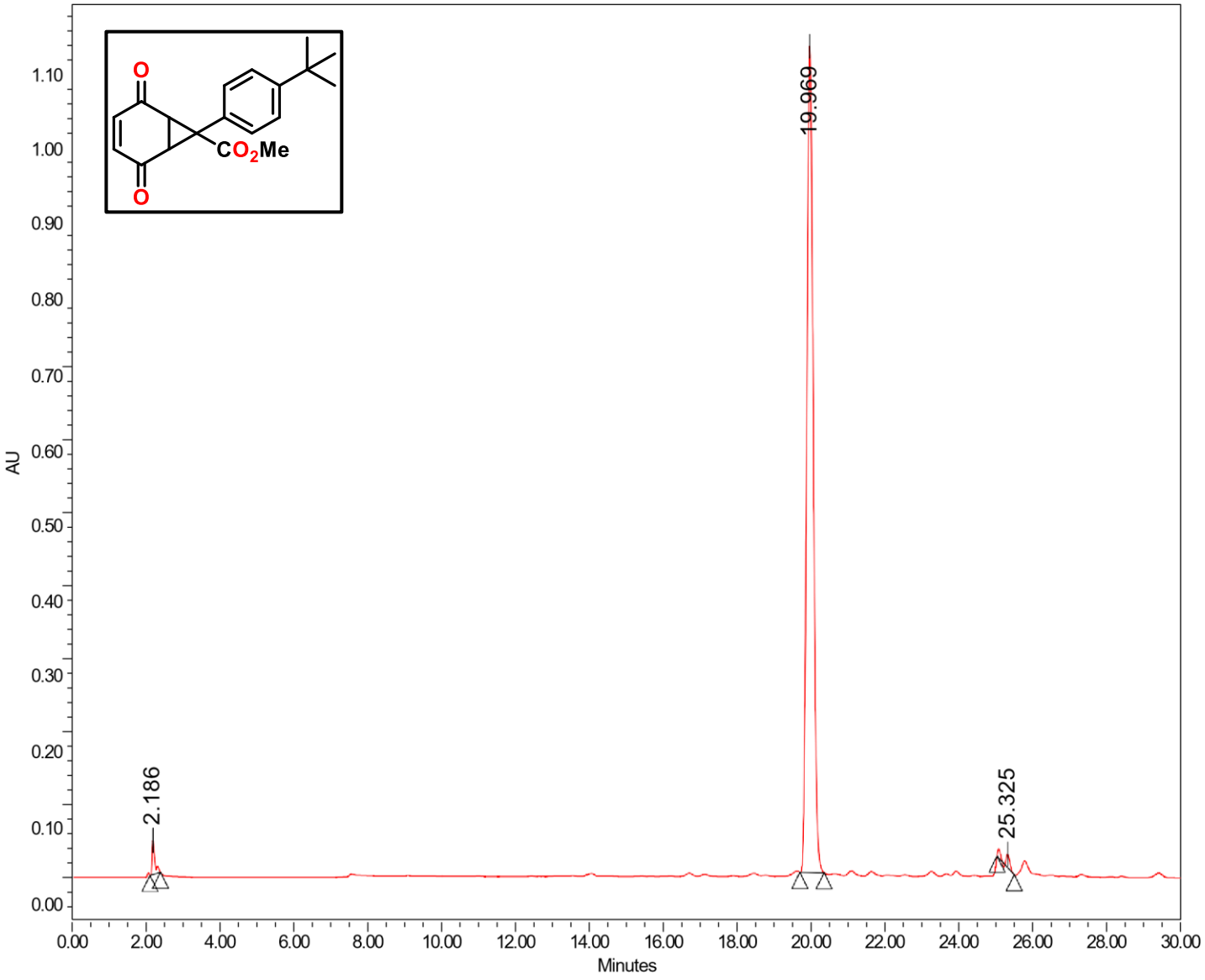
2	TP-22	99	1	17.160	10455	0.03	1271
3	TP-22	99	1	18.213	32091	0.10	3674
4	TP-22	99	1	18.545	51658	0.17	5644
5	TP-22	99	1	24.083	16808	0.05	2016
6	TP-22	99	1	20.165	30043871	97.73	2361249
7	TP-22	99	1	21.693	83388	0.27	7745
8	TP-22	99	1	23.015	17252	0.06	2701

Project Name: SSEN Group/Quinone

Date Printed: 4/17/2022



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Peak Summary with Statistics

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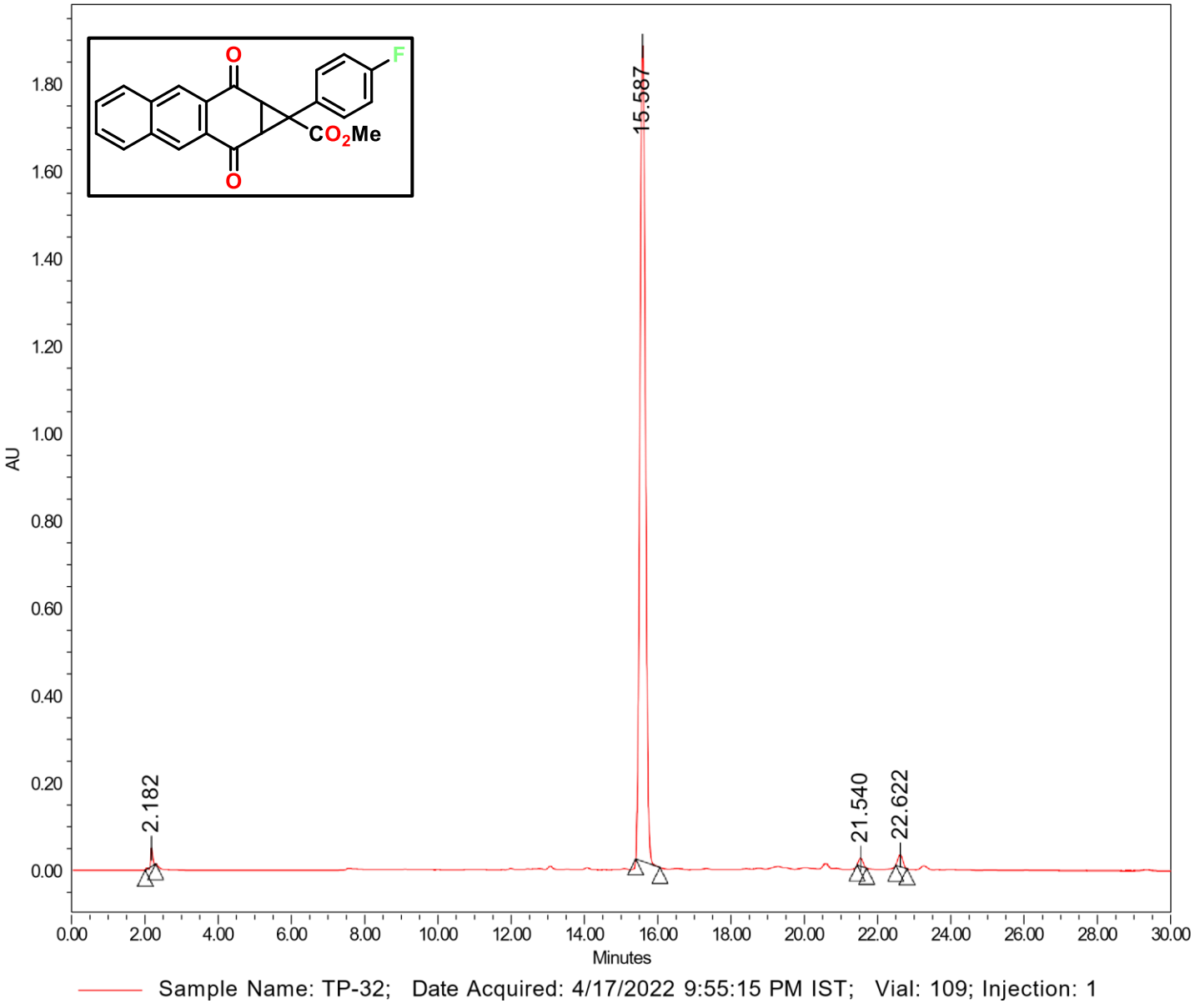
3	TP-31	108	1	19.969	13608281	96.85	1132380
Mean				15.827			
Std. Dev.				12.113			
% RSD				76.54			

Project Name: SSEN Group/Quinone

Date Printed:



Peak Summary with Statistics

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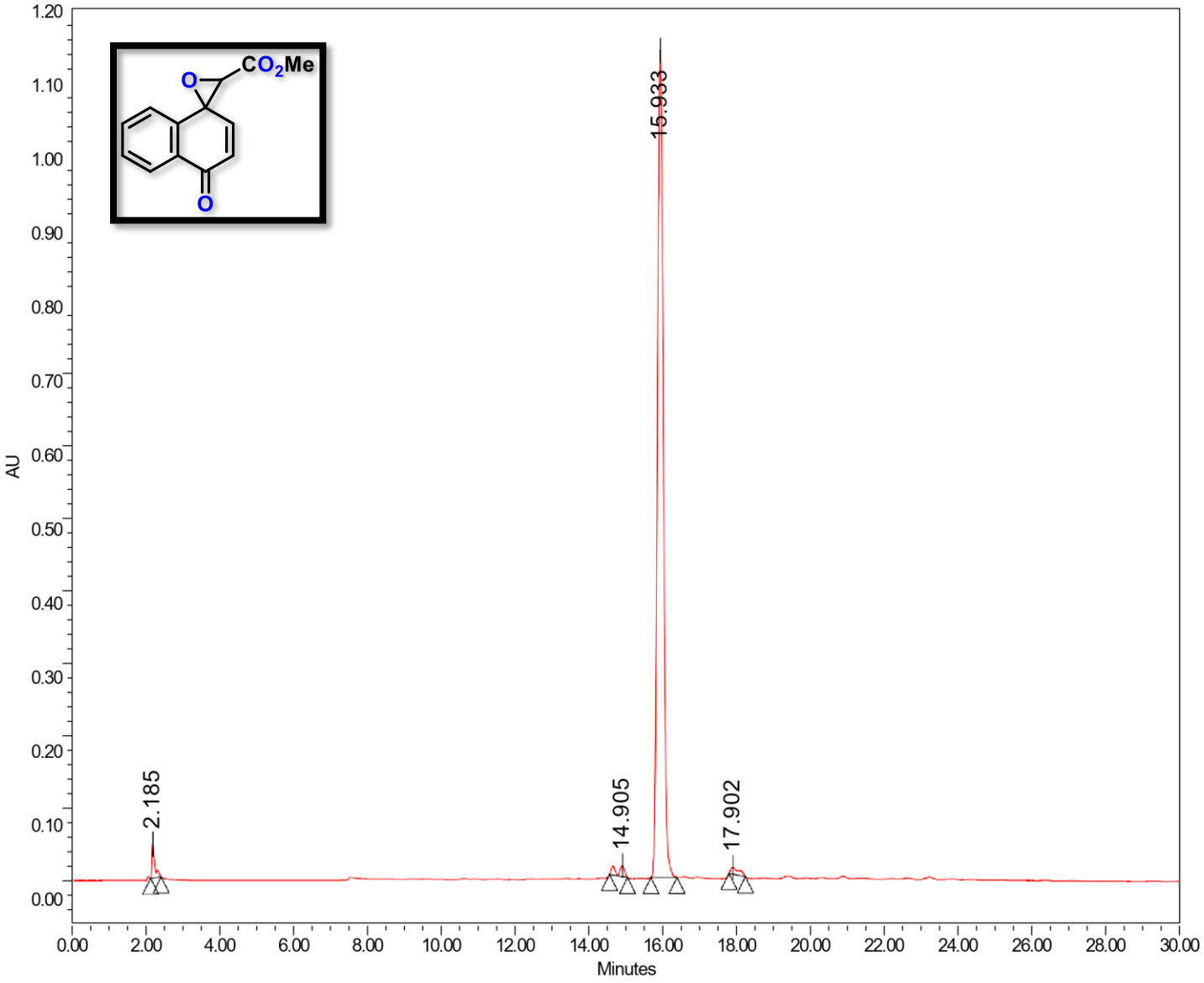
3	TP-32	109	1	2.182	167880	0.84	41623
4	TP-32	109	1	22.622	247381	1.23	27125
Mean				15.483			
Std. Dev.				9.391			
% RSD				60.65			



Peak Summary with Statistics

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3	TP-29	106	1	15.933	12569254	95.28	1141824
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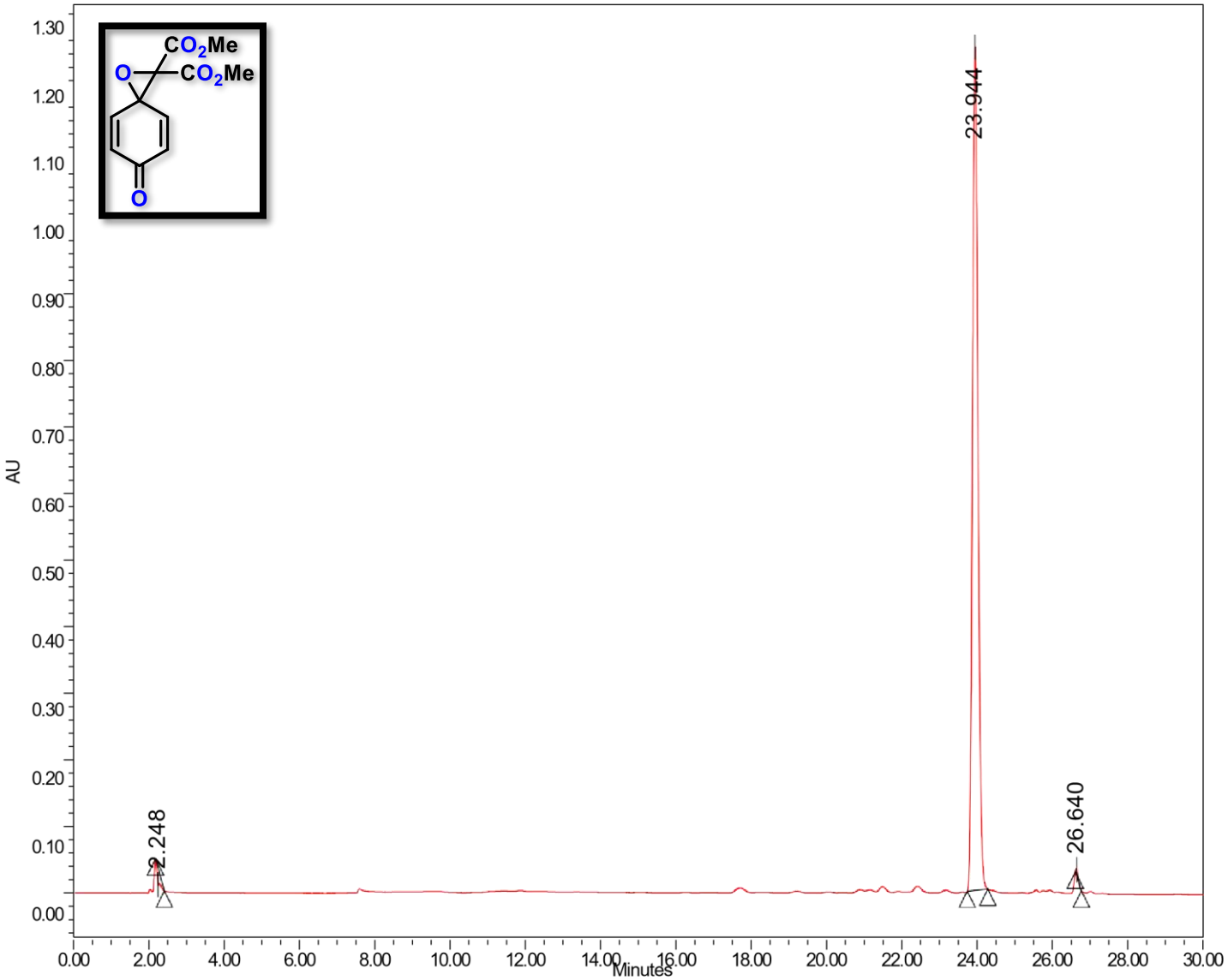
Mean				12.731			
Std. Dev.				7.140			
% RSD				56.08			



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Peak Summary with Statistics

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3	TP-21	97	1	23.944	12993884	98.44	1266789
Mean				17.611			
Std. Dev.				13.372			
% RSD				75.93			

Project Name: SSEN Group/Quinone

Date Printed: